Methods to Assess Anthropogenic Bromide Loads from Coal-fired Power Plants and Their Potential Effect on Downstream Drinking Water Utilities

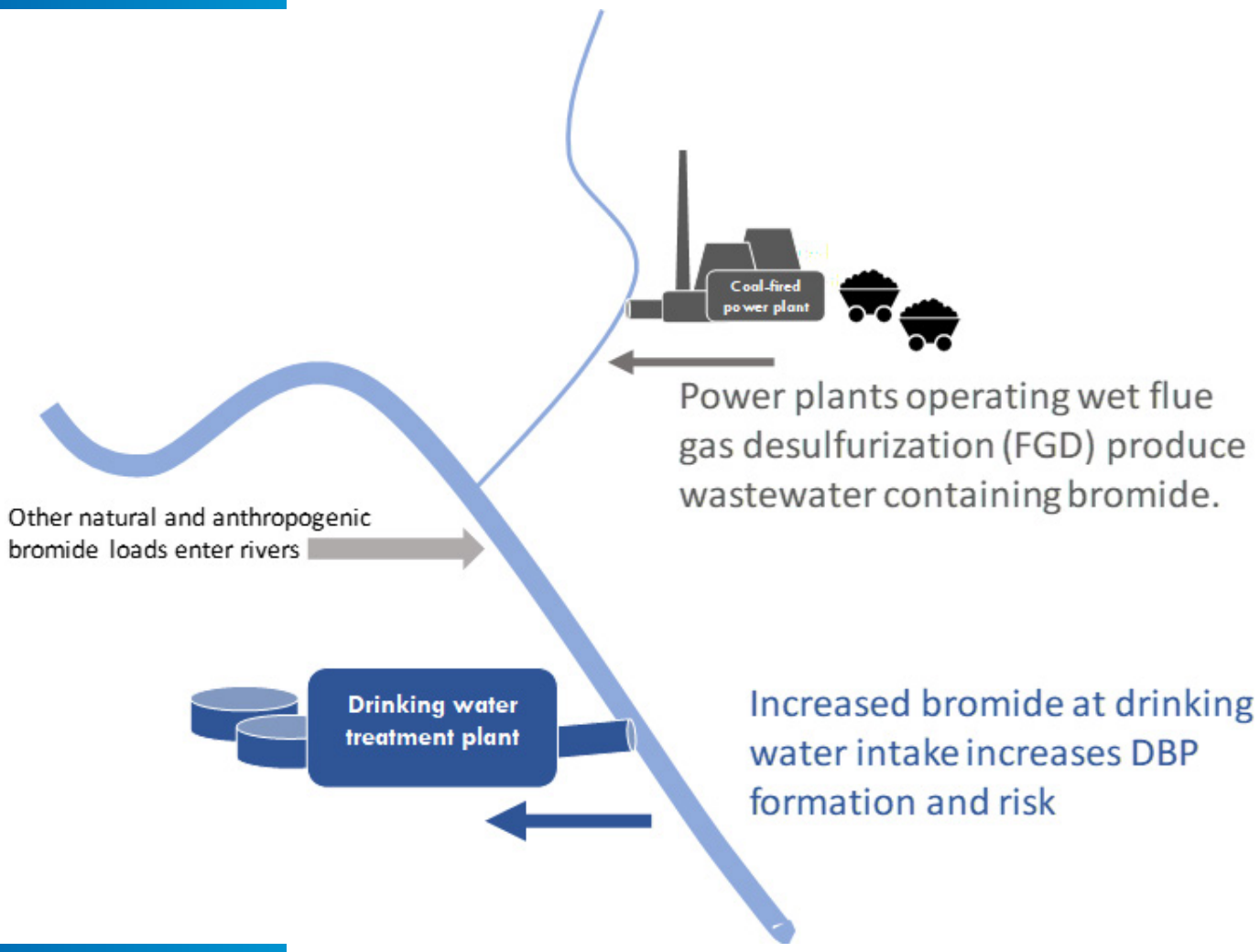
Prepared by:
Jeanne M. VanBriesen, Ph.D., P.E.

December 2019

Project Funding: This project was funded by the American Water Works Association, utilizing the Water Industry Technical Action Fund (WITAF), project #024 and managed by Adam T. Carpenter.

American Water Works Association

Dedicated to the World's Most Important Resource®



Disclaimer:

The authors, contributors, editors, and publisher do not assume responsibility for the validity of the content or any consequences of its use. In no event will AWWA or its contractors be liable for direct, indirect, special, incidental or consequential damages arising out of the use of information presented herein. In particular, AWWA and its contractors will not be responsible for any costs, including, but not limited to, those incurred as a result of lost revenue.

AWWA does not claim copyright on any material used in this report which is owned by others and used with permission (e.g., figures with the notation "courtesy of…") or used with attribution through a Creative Commons license.

Executive Summary

Anthropogenic bromide loads discharged to surface waters increase the concentration of bromide in rivers and lakes that are used as source waters for drinking water treatment plants. Elevated bromide in these source waters increases the formation of disinfection by products (DBPs), including trihalomethanes (THMs), which pose health risks to consumers of drinking water.

Coal naturally contains bromide, and bromide can be added to coal to increase control of mercury and other air pollutants. Bromide that enters the coal-fired power plant can partition into flue-gas desulfurization (FGD) wastewaters, which may be discharged to surface waters. Wastewater associated with coal-fired power plant discharges is regulated through the Effluent Limitation Guidelines for Steam-Electric Power Plants (ELGs); however, the ELGs did not set numerical limits for bromide concentrations or loads in power plant discharges. Rather, the EPA recommended that permitting authorities consider regulation of bromide discharges on a case-by-case basis, considering the potential of individual power plants to affect downstream drinking water plants.

Figure ES-1 summarizes the context for the issue. Bromide enters rivers from multiple sources, including coal-fired power plants. Power plant bromide loads depend on the type and amount of coal being used as well as any added bromide (upper right Figure ES-1). These loads are diluted in river flows, which often show strong seasonal variability (upper left Figure ES-1). Bromide concentrations at drinking water intakes are controlled by the upstream loads and the flow conditions at the intake (lower right Figure ES-1). Once the water enters the treatment plant, the bromide reacts with the applied disinfectant to increase DBP formation and its associated risk (lower left Figure ES-1). In any watershed there may be multiple drinking water plants and multiple power plants, so cumulative effects must be considered.

© Copyright 2019 American Water Works Association

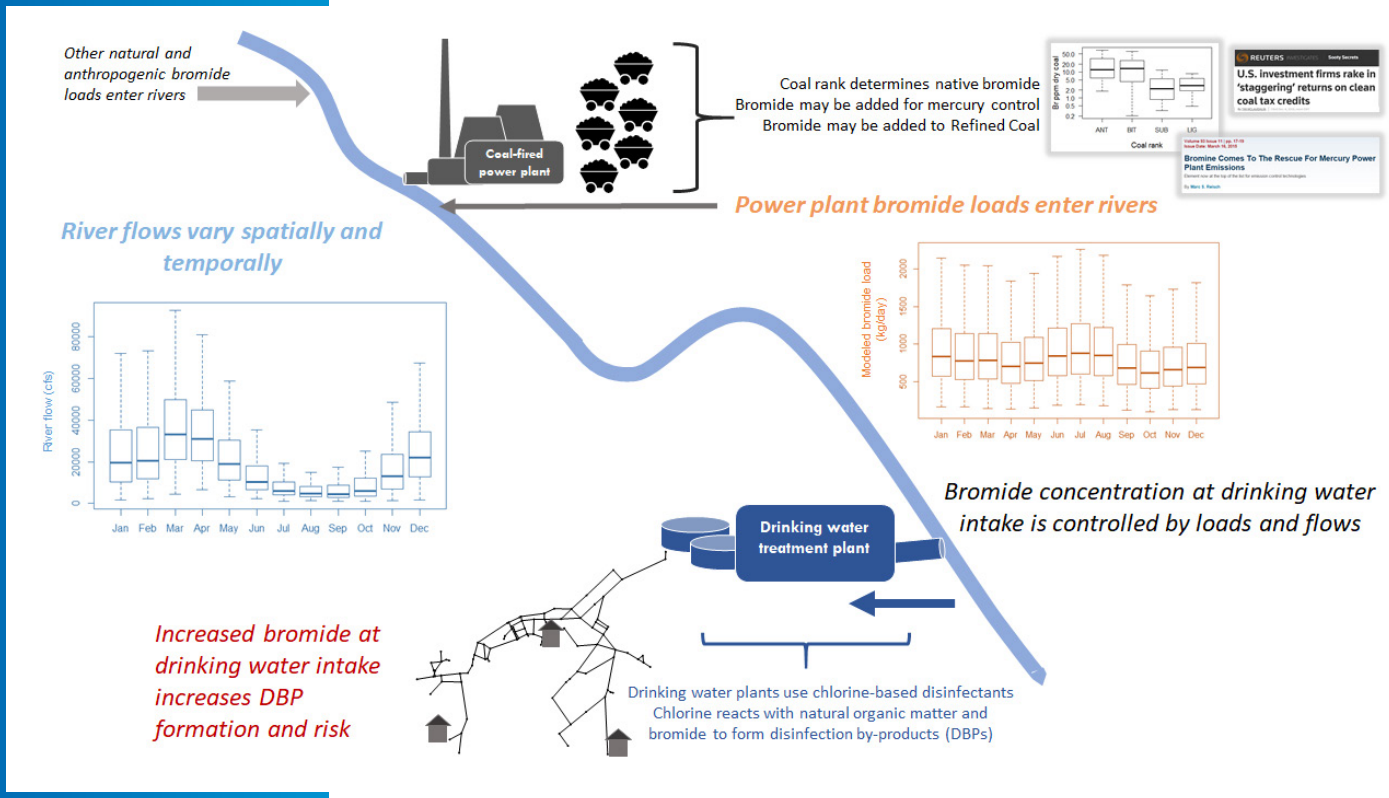


Figure ES-1. *Schematic for anthropogenic bromide loads from coal-fired power plants and their potential effect on downstream drinking water utilities*

The purpose of this study was to summarize methods that can be used to enable case-by-case assessment of individual power plants and associated bromide discharges. The report provides details on methods (1) to identify power plants that may be discharging bromide upstream of drinking water utilities (section 2); (2) to estimate bromide loads from power plants when monitoring data are not available (section 3); (3) to estimate the contribution of power plant bromide loads to in-stream bromide concentrations at drinking water intakes (section 3); and (4) to estimate the effect of contributed bromide on downstream drinking water total THM and associated risk (section 4). Each component is summarized below (see **Figure 2** for a schematic of how the methods can be linked).

Relevant power plants can be identified by review of data from the Energy Information Administration (EIA), which provides the capacity and the monthly coal usage for each plant operating in the United States. EIA also provides information on pollution control units at each power plant, and thus, utilities using wet flue-gas desulfurization (FGD) can be identified. Power plants operating wet FGD and burning refined coal or adding bromide for compliance with the Mercury and Air Toxics Standards (MATS) should be prioritized for permit review as these facilities are expected to have the highest potential bromide loads. Good and VanBriesen (2018) analyzed the power plant fleet using 2016 EIA data; 140 coal fired power plants operating wet FGD were identified, with 23 of these using refined coal. Since receiving waters can be affected by multiple power plants, another way to prioritize permits for review is a watershed-level analysis of coal consumption. At the regional level (HUC2), wet FGD coal consumption was highest in the Ohio River Basin (HUC-05) and the South Atlantic-Gulf Region (HUC-03) in 2016, suggesting these areas should be prioritized for power plant permit review (See Report **Figure 5**). Sub-watershed (HUC4) analysis can provide greater resolution to the prioritization (see Report **Figure 6**). As an alternative, watersheds for early prioritization

could be selected based on current bromide conditions. Regions with existing elevated bromide concentrations could be more at risk from bromide loads. Historical bromide data are often sparse, but the EPA ICR includes 18 months of data for bromide at large drinking water utilities in the U.S. from 1997-1998. These data can be used to identify regions that already experience higher bromide concentrations (and associated drinking water risk), and when combined with more recent bromide sampling data can be used to evaluate whether bromide concentrations in a region have been increasing. Drinking water utility data for DBPs, measured and reported for compliance, can also be used to identify regions where bromide concentrations are already affecting TTHM and to prioritize evaluation of power plant loads in those areas.

As shown in **Figure ES-1**, determining the relationship between a power plant bromide discharge and a drinking water utility DBP concentration requires multiple steps. First, a geospatial analysis is needed to identify the flow paths for water between the power plant discharge and the drinking water intake. All power plants upstream of a particular drinking water utility should be considered to determine the total bromide reaching the drinking water system. In parallel, all drinking water plants downstream of a specific power plant should be identified in order to determine the cumulative effect of each power plant discharge on drinking water consumers. This can be done using an EPA tool called Drinking Water Mapping Application to Protect Source Waters (DWMAPS), which includes drinking water source information from the Safe Drinking Water Information System (SDWIS) at 12-digit HUC level. A recently completed analysis by Good and VanBriesen (2018) joined information from DWMAPs to National Hydrography Dataset (NHD) Flowlines in ArcGIS to enable identification of flow paths downstream of wet FGD receiving waters that intersect watersheds containing source waters for drinking water systems. For the contiguous U.S., the dataset included 9,134 surface water facilities (intakes, reservoirs, springs, infiltration) for 6,802 systems serving 134 million people in 5,177 watersheds. **Figure 15** provides a visualization of this result.

Bromide concentrations in power plant wastewaters are rarely measured, and thus, loads may need to be estimated. These estimates can be based on the quantity of coal being burned and its type. For any power plant, a load can be estimated using a general bromide concentration distribution for coal type or using specific bromide concentrations associated with the source coal (e.g., bromide values reported for each coal mine delivering coal to a given power plant). Both estimates will result in a range of values for the estimated loads since there is uncertainty in all of these measurements. To predict a point value for bromide load, the analyst will have to decide if use of the median (most likely) estimate is preferred or if a range of values will be considered for multiple parameters.

Since bromide is conservative and will not be removed through any biogeochemical process in the river, the effect of a discharge on the downstream drinking water plant is controlled only by the bromide load and the river flow conditions at the intake. Streamflow often shows strong seasonal variability, and this variability can be incorporated into models to predict bromide concentration contributions to the intakes. With daily streamflow data for a river (from the USGS), daily bromide concentration estimates can be developed, and a distribution of predicted bromide concentration contributions can be used to assess exceedance frequencies for any selected concentration. To predict a point value for bromide concentration contribution from upstream power plant discharges, the analyst will have to decide if use of the median flow or some specific low flow condition (e.g., 7Q10 or lowest monthly median) is more appropriate for assessment of the effects of the discharges on the drinking water intakes. **Figure 19** in the report demonstrates how bromide concentration can be estimated for any flow condition at a river location.

The relationship between bromide concentration in the source water and DBP concentrations in finished water is complex. DBP formation is affected by additional source water characteristics (e.g., type and amount of organic carbon), physical conditions (e.g., temperature), and operational choices (e.g., disinfectant dose and type). DBP prediction models are generally most accurate when they are developed for individual drinking water plants. However, generalized models are available and have been used to estimate effects from changing bromide concentrations. Total THM (TTHM) concentration associated with bromide contributed from power plant discharges can be estimated using these models, and TTHM concentration can then be used to predict risk, following methods used by the EPA in the D/DBP rule. As in prior steps, the analyst will need to decide if median predicted TTHM values are used for risk estimates or if a range of TTHM values will be assessed to predict a range of risk outcomes.

Once the effect of bromide discharges on TTHM formation at downstream drinking water plants has been assessed, the analyst must then select an acceptable level of risk, or an acceptable TTHM concentration contribution, in order to determine if bromide discharges should be controlled in the source water for the drinking water plant. These target values are then considered in selection of a total maximum daily load (TMDL) that can be used to set Waste Load Allocations (WLAs) for bromide discharges in the basin.

Determining the acceptable risk or TTHM or bromide concentration in the river is complicated by the lack of any regulatory standards specific to bromide. EPA has suggested that the acceptable bromide concentration in the source water is that which would not cause a violation of the Maximum Contaminant Level (MCL) for TTHM at any downstream drinking water facility. Since the TTHM MCL is a running annual average based on a mass sum of four THM (3 of which contain bromide), it is very difficult to determine *a priori* a value of bromide that would ensure TTHM was always under the MCL on an annual basis. As an alternative, analysts could assess historical bromide levels in affected basins or consider reported bromide concentrations associated with regions that are experiencing bromide-induced DBP compliance problems. The high degree of temporal and spatial variability in bromide concentrations in river systems complicates this approach.

A significant challenge in preparing methods to assess bromide contributions from power plants was the limited data on bromide concentrations in specific flue-gas desulfurization wastewater discharges. Bromide is rarely monitored in power plant wastewater, and FGD wastewater is often mixed with other wastewaters at the power plant. Improved monitoring by power plants, would provide additional insight and reduce the uncertainty associated with estimates currently available. Since bromide can vary significantly depending upon the type of coal, chemical additions, and treatment processes, it is important to use flow-weighted sampling to ensure loads can be estimated from sample data. Coal-fired power plant permits in NC and PA have begun to require bromide sampling in discharges, and these provide key guidance on the frequency and type of sampling that could be required.

 © Copyright 2019 American Water Works Association

Table of Contents

Executive Summary 3

Section 1. Introduction 15

Report Structure 21

Section 2. Prioritize power plants or watersheds for analysis 25

Approach 1. Identify power plants likely to discharge significant bromide. 25

Approach 2. Identify watersheds at elevated risk of bromide loads of concern due to coal consumption at power plants operating wet FGD 31

Approach 3. Identify watersheds or source waters with existing elevated bromide and thus less capacity to accept additional bromide loads 35

Regional historical bromide levels 35

Watershed-specific bromide concentration changes 38

Utility-specific bromide concentration data 40

Approach 4. Identify watersheds where drinking water plants are already experiencing increased bromine incorporation in DBPs. 42

Bromine incorporation metrics 42

Watershed-specific DBP Data 43

Section 2 Data Sources. 46

Section 3. Evaluate bromide concentration contributions from each upstream power plant at each downstream drinking water plant 48

Step 1. Linking each NPDES-permitted power plant with potentially affected drinking water utilities 49

Step 2. Estimate power plant bromide loads. 52

Step 3. Extract and analyze river flow information. 54

Step 4. Predict river bromide concentration contributions from load and flow estimates 57

Step 5. Consider load and flow effects to narrow selection of power plants likely to affect downstream drinking water plants 59

Step 6. Integrate the effects on multiple drinking water plants from a single power plant discharge 62

Step 7. Integrate the effects of multiple power plants on a single drinking water plant. 64

Section 3 Data Sources 65

Section 4. DBP formation and associated risk at downstream drinking water plants. . . 67

Modeling DBP Formation 74

Linking changes in DBP concentrations to changes in risk 80

Section 4 Data Sources. 83

Section 5. Methods to assist permit writers 84
Water quality criteria and bromide 86
Bromide concentrations and variability in receiving waters 89
Bromide concentrations and variability in FGD associated wastewaters 92
Flow, concentration and load management for FGD-associated wastewaters 96
Review of power plant permits requiring bromide monitoring 100
Permit application requirements 108
Monitoring requirements for bromide in NPDES permits 109
Consideration of Technology-Based Effluent Limitations (TBELs) and Best Professional Judgment (BPJ) technology effluent limitations 110
Section Five Data Sources 111

Section 6. Acknowledgements 112

References 114

 © Copyright 2019 American Water Works Association

List of Figures

Figure 1. Schematic of watershed containing multiple drinking water plants and multiple coal-fired power plants 20

Figure 2. Schematic of components of analysis presented in report 23

Figure 3. Application of major steps to develop and issue NPDES individual permits to power plant FGD Wastewater Discharges containing bromide. 24

Figure 4. United States coal-fired power plants as of 2016. Symbols are sized by capacity (MW) and colored according to FGD type. Hydrologic regions are outlined and labeled by two-digit hydrologic unit codes (HUC)(Good and VanBriesen 2018) 29

Figure 5. Coal consumption (by type) associated with power plants utilizing different FGD treatment technologies. FGD status from EIA Form 860 (EIA 2017) and consumption data from EIA Form 923 (EIA 2018)(following (Good and VanBriesen 2018)). Figure courtesy Dr. Kelly Good. 32

Figure 6. Coal consumption (in tons) associated with power plants using wet FGD treatment; HUC4 watershed scale. FGD status from EIA Form 860 (EIA 2017)and consumption data from EIA Form 923 (EIA 2018). Red outline indicates watersheds with refined coal consumption reported in 2016. Adapted from (Good and VanBriesen 2018). Figure courtesy Dr. Kelly Good. 33

Figure 7. Influent bromide concentration measured at drinking water utilities during the ICR by HUC2, plotted on a log scale. The red horizontal dashed line represents the detection limit for the data set (20 µg/L); values reported as below detection were imputed using Regression on Order Statistics (ROS) (Helsel 1990). The box plot for each subregion (HUC2) includes a solid line for its median and a blue diamond for the mean value. The box extends to the interquartile range (IQR), and the whiskers extend to 1.5 times the IQR. Black dots indicate values outside this range. The number of plants reporting data within each HUC2 is provided at the top of the plot. Each plant provided monthly values for July 1997 to December 1998. Adapted from (Kolb 2018); Figure courtesy Dr. Chelsea Kolb. 36

Figure 8. Influent bromide concentration measured at drinking water utilities during the ICR by HUC4 for the Central U.S. region (HUC05 to HUC11). The red horizontal dashed line represents the detection limit for the data set; values reported as below detection were imputed using Regression on Order Statistics (ROS) (Helsel 1990). The box plot for each subregion (HUC4) includes a solid line for its median and a blue diamond for the mean value. The box extends to the interquartile range (IQR), and the whiskers extend to 1.5 times the IQR. Black dots indicate values outside this range. The number of plants reporting data within each HUC4 is provided at the top of the plot. Each plant provided monthly values for July 1997 to December 1998. Adapted from(Kolb 2018); Figure courtesy Dr. Chelsea Kolb. 37

Figure 9. Bromide concentrations reported in the Susquehanna River for the EPA ICR (1997-1998) and from WQN201 near Marietta, PA (2015-2016) in ppb (µg/L). Daily mean flows from USGS gage 01576000 at Marietta, PA (in m^3/s). Below detection limit results are shown as open squares and plotted at zero for visualization purposes only; the detection limit in the ICR was 20 µg/L while the detection limit for the WQN data was 8 µg/L. The median for each period is shown horizontal dashed line (below the detection limit of 20µg/L for the ICR and thus shown at zero, and 22µg/L for the more recent data). Figure courtesy Dr. Adam Cadwallader. 39

Figure 10. Bromide concentrations at a public drinking water utility reported during the ICR (WY1998) as well as during a more recent time period (WY 2013-2017); 12 samples per water year. Median is solid dark line and mean is the blue diamond. The box extends to the interquartile range (IQR), and the whiskers extend to 1.5 times the IQR. Black dots indicate values outside this range. Below detection data were imputed using Regression on Order Statistics (ROS) (Helsel 1990). Data from (Kolb, Good et al. 2019). Figure Courtesy Dr. Chelsea Kolb. 40

Figure 11. Empirical cumulative probability distribution of observed bromide concentration (µg/L) at a drinking water plant on the Allegheny River. Shown for water year 2011 (October 2010 through September 2011); data as published in States et al. 2013, includes two values below 25 µg/L detection limit shown at half this value) and water year 2013 (October 2012 through September 2013; data also shown in Good 2018). Data courtesy Pittsburgh Water and Sewer Authority; Figure courtesy Dr. Kelly Good. . 41

Figure 12. Total trihalomethanes (average at sampling locations) (top) and Percent Bromine incorporation (by mass) in Trihalomethanes (bottom) from quarterly compliance data at Steelton (green) and Wrightsville (blue) (2012-2015). Dotted lines are calculated running annual averages (RAA). Data from (PADEP 2018). 44

Figure 13. Bromine Substitution Factor (BSF) in THM for water utilities using different source waters in Pennsylvania (based on 2016-2017 compliance data). The center line represents the median, shown with its 95th percentile confidence interval (internal box). The larger box shows the extent of the 25th and 75th percentiles, while the whiskers extend to 1.5 times this interquartile range. The stars indicate values outside that range. Data from (PADEP 2018). Figure courtesy Dr. Adam Cadwallader. 45

Figure 14. Schematic of model components to predict bromide concentration contributions from power plants (Good and VanBriesen 2017). 48

Figure 15. Identified power plants with wet FGD (blue triangles) upstream of HUC12 watersheds that contain drinking water intakes (pink). Figure adapted from Good and VanBriesen (2018)and courtesy Dr. Kelly Good. 51

Figure 16. Bromide load estimate calculation method and data sources. Following Good and VanBriesen (2016, 2017, 2018) corrected. Data references: (Meij 1994, Peng, Li et al. 2013, Palmer, Oman et al. 2015, EIA 2018). Figure courtesy Dr. Kelly Good. 53

Figure 17. Cumulative distribution functions for flow in four Pennsylvania Rivers. Values for water years within the ICR and more recent periods are identified. (Cadwallader and VanBriesen 2019). 55

 © Copyright 2019 American Water Works Association

Figure 18. Monthly mean daily flow data using USGS gaging station 03049500 (Allegheny River at Natrona, PA) for Water years 1939-2014. Solid line in the median for each month, boxes extend to the interquartile range (IQR) and whiskers extend to 1.5 times the IQR; open circles are values beyond this range. (Good and VanBriesen 2016) 56

Figure 19. Prediction of bromide concentration contribution at the drinking water intake at Good and VanBriesen (2017) site 16 from the discharge of wet FGD wastewater at the Montour power plant (based on 2015-2016 coal usage). (Adapted from (Good and VanBriesen 2017)). 58

Figure 20. Identified power plants with wet FGD (blue triangles) potentially affecting downstream drinking water intakes in identified HUC12 watersheds (orange), based on 2016 coal consumption data and NHD+ mean annual flow in receiving waters. Figure adapted from Good and VanBriesen (2018) and courtesy Dr. Kelly Good. 61

Figure 21. Wet FGD load contributions (kg/day) for each drinking water intake site in Pennsylvania, based on median predicted August bromide loads. (Good and VanBriesen 2017). 64

Figure 22. THM species concentration for different surface water source bromide concentrations. The box plot for each species includes a solid line for its median value. The box extends to the interquartile range (IQR), and the whiskers extend to 1.5 times the IQR. Open circles indicate values outside this range. Figure courtesy Dr. Chelsea Kolb. Data analysis from (Kolb, Francis et al. 2017). 69

Figure 23. Measured surface water intake bromide concentration (top; µg/L) and THM species in finished water (bottom, left axis) and mass-based bromine-incorporation (bottom, right axis). Data from Wang et al (2016). Figure courtesy Dr. Jessica Wilson. . 71

Figure 24. Relationship between measured surface water intake bromide concentration and TTHM in finished water (top) and bromine incorporation (bottom) from field study in the Monongahela River (2009-2011). Data from Wang et al (2016). Figure courtesy Dr. Jessica Wilson. 72

Figure 25. Probability of meeting TTHM standard (blue), 80% of standard (orange) and risk threshold (purple) for source waters with different concentrations of bromide (Wang, Small et al. 2016). 73

Figure 26. Quarterly predicted TTHM for observed bromide data based on three TTHM models as well as observed TTHM concentrations at a drinking water utility on the Monongahela River. Models include: Malcolm-Pirnie (blue), Montgomery Watson (red) and Cornwell (green). Observed data are grey. Plots show the median (horizontal line), 25th to 75th percentile (box), and 1.5 times the interquartile range (whiskers), while dots are values outside that range. Figure Courtesy Dr. Chelsea Kolb. 78

Figure 27. Exceedance probability plot for bromide concentration contributions (panel a) and TTHM (panel b) for two water years by quarter and annually. The horizontal dashed lines on the top panel indicate bromide concentration contributions of 30 and 100 µg/L. The horizontal dashed line on the bottom panel indicate TTHM concentration contribution of 20 µg/L. Figure Courtesy Dr. Chelsea Kolb. 79

Figure 28. Odds ratio risk simulation associated with simulated TTHM concentration increases. Plots show the median (horizontal line), 25th to 75th percentile (box), and 1.5 times the interquartile range (whiskers), while dots are values outside that range. Figure Courtesy Dr. Chelsea Kolb. 82

Figure 29. Method and data support for steps in developing Water Quality Based Effluent Limitations (WQBELs) for bromide discharges from power plants 85

Figure 30. Bromide concentration at the Pittsburgh Water and Sewer Authority Intake and flow at the closest river gage for 2013. Bromide data courtesy PWSA; flow data from USGS gage 03049500. Reprinted with Permission from (Good 2018). 90

Figure 31. Bromide concentration in the Susquehanna River at Marietta and flow at the closest river gage for 2013 through 2016. Bromide data from PADEP WQN0201; flow data from USGS gage 01576000. Figure courtesy Dr. Kelly Good. 91

Figure 32. Bromide concentration in the Monongahela River for 2009 to 2012, measured at multiple drinking water intakes. Data from (Wilson and VanBriesen 2014). Figure courtesy Dr. Jessica Wilson. 92

Figure 33. Reported bromide concentrations in FGD wastewaters (as summarized in (VanBriesen 2013). Data from (USEPA 2009a, Frank 2011, EPRI 2014). 93

Figure 34. Contributions of FGD wastewater to outfall flows as estimated in the 2009 steam electric survey ELG questionnaire (USEPA 2010b). Values less than 100 percent indicate commingling with other waste streams. Reprinted with Permission from (Good 2018). 95

Figure 35. Discharge monitoring report (DMR) bromide concentrations (mg/L) for outfall 003 at the Belews Creek Plant. Reprinted with Permission from (Good 2018). 97

Figure 36. Reported bromide concentration in outfall at 003 at Belews Creek plant. Letters indicate significant differences across medians and distributions. Reprinted with Permission from (Good 2018). 98

Figure 37. Bromide load in discharge from Belews Creek power plant, computed from reported flow and concentration data; letters indicate significant differences across medians and distributions. Reprinted with Permission from (Good 2018). 99

Section 1. Introduction

In the United States, surface waters (e.g., rivers and lakes) are the source for potable water supply for 260 million people (USEPA 2005, USEPA 2006a). These source waters are chemically disinfected to kill pathogens and reduce waterborne illnesses (e.g., cholera, typhoid, dysentery). Chemical disinfection results in the formation of disinfection byproducts (DBPs), which are toxic and carcinogenic (Richardson, Plewa et al. 2007, Yang, Komaki et al. 2014). Consumption of chemically treated water is associated with increased risk of cancer in epidemiological studies (Villanueva, Cordier et al. 2015). Bromide is a precursor to formation of disinfection by-products (DBPs) in drinking water, and its presence increases the rate of DBP formation as well as increasing the incorporation of bromine into the formed DBPs (Pourmoghaddas, Stevens et al. 1993, Symons, Krasner et al. 1996, Westerhoff, Chao et al. 2004, Hua, Reckhow et al. 2006, Krasner, Weinberg et al. 2006, Heeb, Criquet et al. 2014). Bromine-containing DBPs have higher molar masses than chlorinated DBPs, thus, they contribute more to mass-based concentrations, which are regulated as class sums (USEPA 1998, USEPA 2006b). Further, brominated DBPs are more toxic than chlorinated DBPs (Richardson, Plewa et al. 2007, Yang, Komaki et al. 2014, Sawade, Fabris et al. 2016, Cortes and Marcos 2018), and brominated DBPs are associated with negative human health outcomes in epidemiological studies at lower concentrations than their chlorinated analogs (Villanueva, Cantor et al. 2007, Chisholm, Cook et al. 2008, Nieuwenhuijsen, Grellier et al. 2009, Kogevinas and Villanueva 2011, Salas, Cantor et al. 2013, Villanueva, Cordier et al. 2015). Thus, source water bromide concentrations are a concern with respect to DBP-associated risk in drinking water (Regli, Chen et al. 2015, Wang, Small et al. 2016). DBP regulatory surrogates (e.g., total trihalomethanes, TTHM), may be inadequate to represent drinking water risk when DBPs become more brominated (Francis, Small et al. 2009, Francis, VanBriesen et al. 2010). Due to this role of bromide in DBP formation, drinking water utilities are concerned about increasing concentrations of bromide in source waters (Wilson, Wang et al. 2013, McTigue, Cornwell et al. 2014, USEPA 2015b). Recognizing changing bromide concentrations as a concern for drinking water utilities, the U.S. Environmental Protection Agency (EPA) included bromide in the Safe Drinking Water Act (SDWA) fourth Unregulated Contaminant Monitoring Rule (UCMR 4) (USEPA 2016b).

Naturally-occurring surface water bromide concentrations are typically low (Bowen 1966, Bowen 1979) except where saltwater intrusion affects coastal aquifers or estuaries (Krasner, Sclimenti et al. 1994, Holm, Harader et al. 2007, Chen, Haunschild et al. 2010, Ged and Boyer 2014). However, anthropogenic loads can cause significant concentration increases (Soltermann, Abegglen et al. 2016). Fossil fuel-associated wastewaters are elevated in salts, including bromide (Wilson and VanBriesen 2012, Ferrar, Michanowicz et al. 2013), and the discharge of these wastewaters has been reported to increase bromide at drinking water intakes (States, Cyprych et al. 2013, Wilson and VanBriesen 2013, McTigue, Cornwell et al. 2014, USEPA 2015d, Landis, Kamal et al. 2016) especially when river flow conditions result in insufficient dilution (Wilson, Wang et al. 2013, Weaver, Xu et al. 2016).

Since bromide is unreactive under typical environmental conditions, it is not removed in natural water systems, nor does it accumulate in any environmental compartment. Due to its relatively high human and ecotoxicity thresholds (Flury and Papritz 1993, WHO 2009), bromide has not generally been regulated with in-stream or discharge standards (DiCosmo 2012). Routine in-stream monitoring is uncommon, and measurements in anthropogenic discharges has only recently been included in permits (e.g. (NCDENR 2012)). Bromide is also not removed in conventional drinking water treatment processes (Amy and Siddiqui 1999, Watson, Farre et al. 2012, States, Cyprych et al. 2013). Thus,

prevention of bromide effects at drinking water plants requires control of bromide discharges to the environment.

The focus of the present work is on bromide discharges from coal-fired power plants. Coal contains bromide in trace amounts (Finkelman 1993, Vassilev, Eskenazy et al. 2000) with the concentration dependent on the coal type (Kolker and Quick 2015). During combustion at the power plant, bromide is converted to bromine and hydrogen bromide, which are typically released in stack gasses (Clarke 1993, Meij 1994, Xu, Yan et al. 2004, Vejahati, Xu et al. 2010, Peng, Li et al. 2013). However, when power plants install wet flue gas desulfurization systems, halogen species are incidentally captured in the wet FGD wastewater (Meij 1994, Srivastava, Hutson et al. 2006). FGD wastewater has been reported to contain 10-100 mg/L bromide (EPRI 2004, EPRI 2007a, USEPA 2009a, USEPA 2009b, Frank 2011); however, individual FGD discharges are rarely monitored for bromide concentration. Further, FGD wastewater may be managed in multiple ways at power plants, including discharge to coal ash ponds, mixing with other waste streams prior to discharge, or treatment prior to discharge (USEPA 2015e). These management choices may alter the bromide concentration in the discharged wastewater. However, with the exception of zero liquid discharge treatment, FGD wastewater treatment does not alter the bromide load.

In addition to naturally-occurring bromide in coal, bromide may be added to coal to increase capture of mercury (Kolker, Quick et al. 2012, Meier, Keiser et al. 2015); this technology may be deployed to improve compliance with the Mercury and Air Toxics Standards (MATS) (EPRI 2006, USEPA 2011, USEPA 2012, Werkheiser 2016). Also, bromide may be added in the generation of Refined Coal (EPRI 2014), which is a product defined through the U.S. Tax Code in Section 45 (IRS 2010).

Wastewater associated with coal-fired power plant discharges is regulated through the 2015 Effluent Limitation Guidelines for Steam-Electric Power Plants (USEPA 2015b). This regulation is designed to control release of toxicants in power plant wastewaters. While EPA acknowledged the potential effects of bromide discharges from wet FGD systems on drinking water DBP formation (USEPA 2013a, USEPA 2015e), no numerical limits were set for bromide concentrations or loads. Rather, the EPA recommended that permitting authorities consider regulation of bromide discharges on a case-by-case basis, considering the potential of individual power plants to affect downstream drinking water plants (USEPA 2015b). Figure 1 shows the challenge associated with this approach. Multiple power plants discharge into receiving waters that are also source waters for multiple drinking water plants. Some drinking water plants have no upstream power plants, while others have multiple power plant discharges at different upstream locations. Each power plant has the potential to affect multiple downstream drinking water plants, with discharged bromide loads diluted in receiving water flows.

FGD wastewater discharges have been implicated in elevated bromide in source waters in several locations in the United States. States et al (2013) identified upstream power plant contributions as a source affecting the Pittsburgh Water system, and Good and VanBriesen (2016) determined this source contributed approximately 1/3 of the observed bromide concentration at the drinking water plant. McTigue et al (2014) identified fifty-seven coal fired power plants operating wet FGD nationally that contributed bromide to 96 downstream drinking water plants. Recently, Good and VanBriesen (2018) completed a national analysis, linking each power plant to potentially affected downstream drinking water utilities and estimating the bromide contributed by each power plant to each drinking water plant's intake. However, there has been no further guidance from EPA regarding the methods to assess and regulate bromide discharges on a permit-by-permit basis as recommended in the ELGs.

 © Copyright 2019 American Water Works Association

Despite the lack of specific guidance, under the authority of the Clean Water Act (40 C.F.R. § 122.21), National Pollutant Discharge Elimination System (NPDES) permit applications are required to indicate whether the wastewater contains specific pollutants, including bromide. The application must provide either quantitative data or a description of the reason the pollutant is expected in the wastewater. Further, 40 C.F.R. § 125.3(c)(3) provides for imposition of technology limitations on a case by case basis where promulgated effluent limitations guidelines only apply to certain aspects of the discharger's operation, or to certain pollutants. Since the Steam Electric ELGs do not include limits on bromide, and bromide is expected to be present in the discharges from FGD scrubber systems, site-specific technology limitations may be set within NPDES permits. Site-specific TBELs reflect the Best Professional Judgement (BPJ) of the permit writer, taking into account the same statutory factors EPA would use in promulgating a national effluent guideline regulation, but they are applied to the circumstances relating to the applicant."(USEPA 2010a). These limitations should ensure that bromide concentrations in receiving waters that are source waters for drinking water utilities do not exceed the level at which negative effects are observed in the drinking water plant. One challenge for selecting bromide limits for discharges is the lack of a numerical water quality standard that must be met to ensure water bodies meet the designated use of drinking water supply. In the absence of such a value, a narrative water quality criteria may be applied to set Water Quality Based Effluent Limitations (WQBELs). "Narrative criteria are statements that describe the desired water quality goal for a waterbody. Narrative criteria can be the basis for limiting specific pollutants for which the state does not have a numeric criteria." (USEPA 2010a) In the ELGs, the EPA recommended the narrative criteria be used to develop water quality based effluent limitations for bromide on a site-by-site basis. "The narrative criteria may be used to develop water quality-based effluent limitations on a site-specific basis for the discharge of pollutants that impact drinking water sources, such as bromide." (USEPA 2015e) Setting such a criteria based on the effect of bromide on DBP formation is challenging due to the high variability in data available for multiple steps needed to assess the effect of bromide concentration changes on DBP formation and associated risk.

This report addresses these challenges and provides technical guidance to regulatory agencies and permit writers on approaches to overcome data limitations in assessment of power plant bromide discharges.

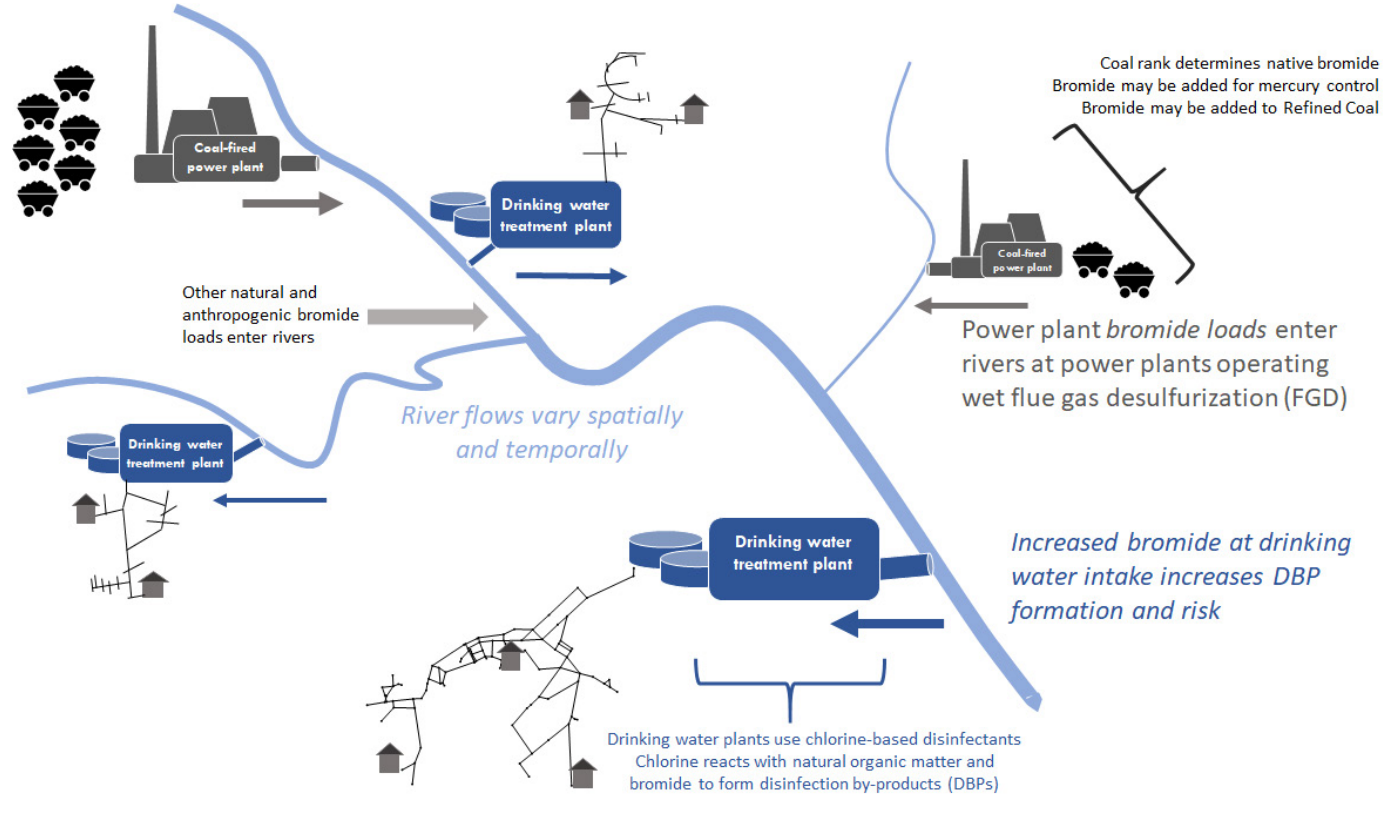


Figure 1. *Schematic of watershed containing multiple drinking water plants and multiple coal-fired power plants*

Report Structure

The purpose of this work was to prepare technical method documents to enable regulators to assess the current or potential impact of specific power plant bromide discharges on downstream drinking water utility disinfection by product (DBP) formation and related human health risk. These technical documents are intended to support National Pollutant Discharge Elimination System (NPDES) permit writers in selecting steam-electric power generating plant permits to review and in setting monitoring, reporting, and control requirements related to bromide in discharges. A secondary objective was to provide information for downstream drinking water utilities to assess conditions that may elevate bromide in their source water and to assess the effect of these changes in bromide on DBP formation and associated drinking water risk.

Figure 2 shows the overall components of the analyses that are described in this report. First, power plants or watersheds must be selected (and prioritized) for review; methods for this selection are described in Section 2. Then, a multi-step process is used to evaluate bromide concentration contributions from the power plants. This requires linking power plants and drinking water plants spatially through a flow path analysis, estimating loads of bromide associated with coal consumption at each power plant, and using river flow data to assess the effect of bromide loads on in stream concentrations. Methods for each of these components are described in Section 3. Then, the effect of the power plant associated bromide discharges on DBP formation and associated risk must be assessed; this is described in Section 4.

The estimation and analysis methods described in section 3 and 4 support a critical component of permit writing associated with water quality based effluent limitations.

 © Copyright 2019 American Water Works Association

Figure 3 shows the major steps in NPDES permit development (USEPA 2010a). On the left are the general steps, and on the right are details of application for consideration of FGD wastewaters containing bromide discharged from facilities upstream of drinking water intakes that might be affected. A key component of these steps is the development of site-specific water quality based effluent limitation guidelines.

Finally, section 5 of the report provides additional insights into spatial and temporal concentration variability expected in receiving waters as well as in bromide-containing power plant wastewaters. This section also summarizes available information on power plant permits that contain bromide monitoring requirements.

In each section of the report, details of the technical method are described, and where relevant, examples of analyses and modeling are provided for select regions or utilities. These examples are provided for demonstration purposes only. Each section ends with details on how to locate the data necessary to undertake the analysis for any specific power plant, river system, or regional watershed.

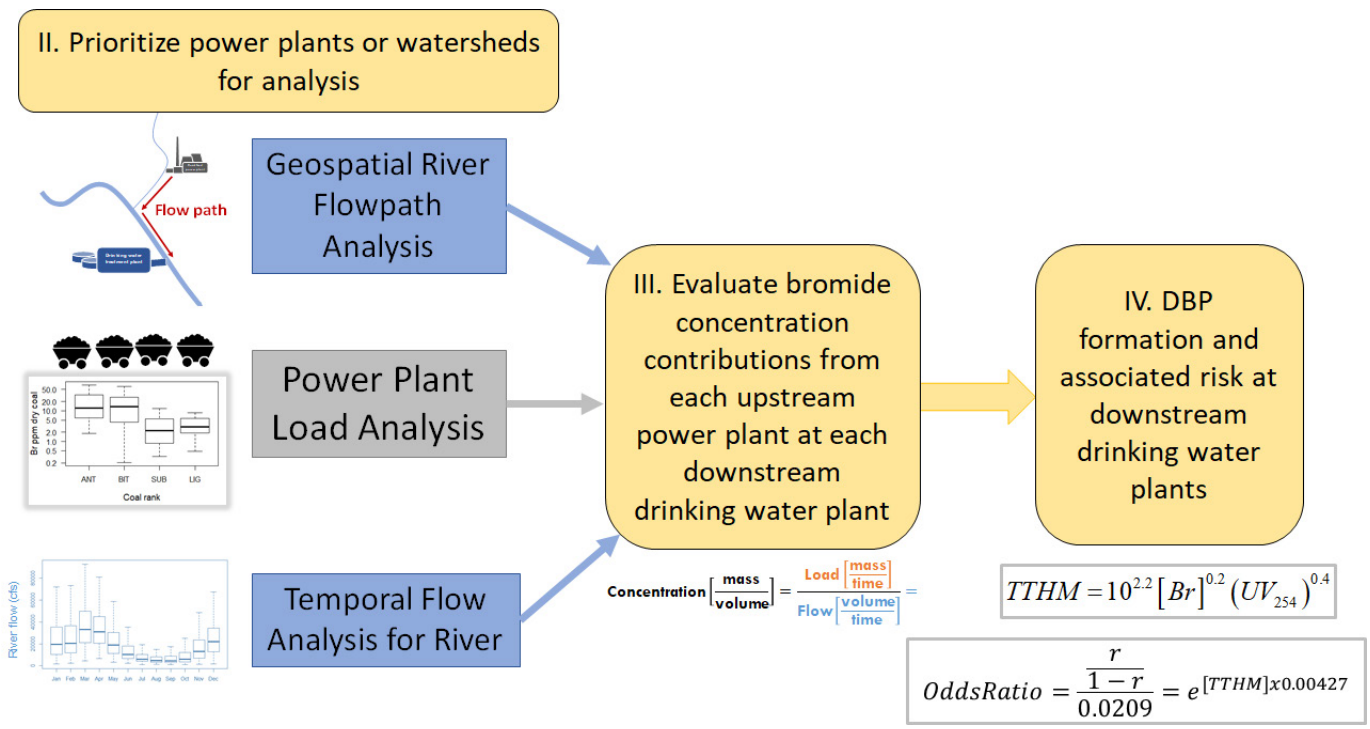


Figure 2. *Schematic of components of analysis presented in report*

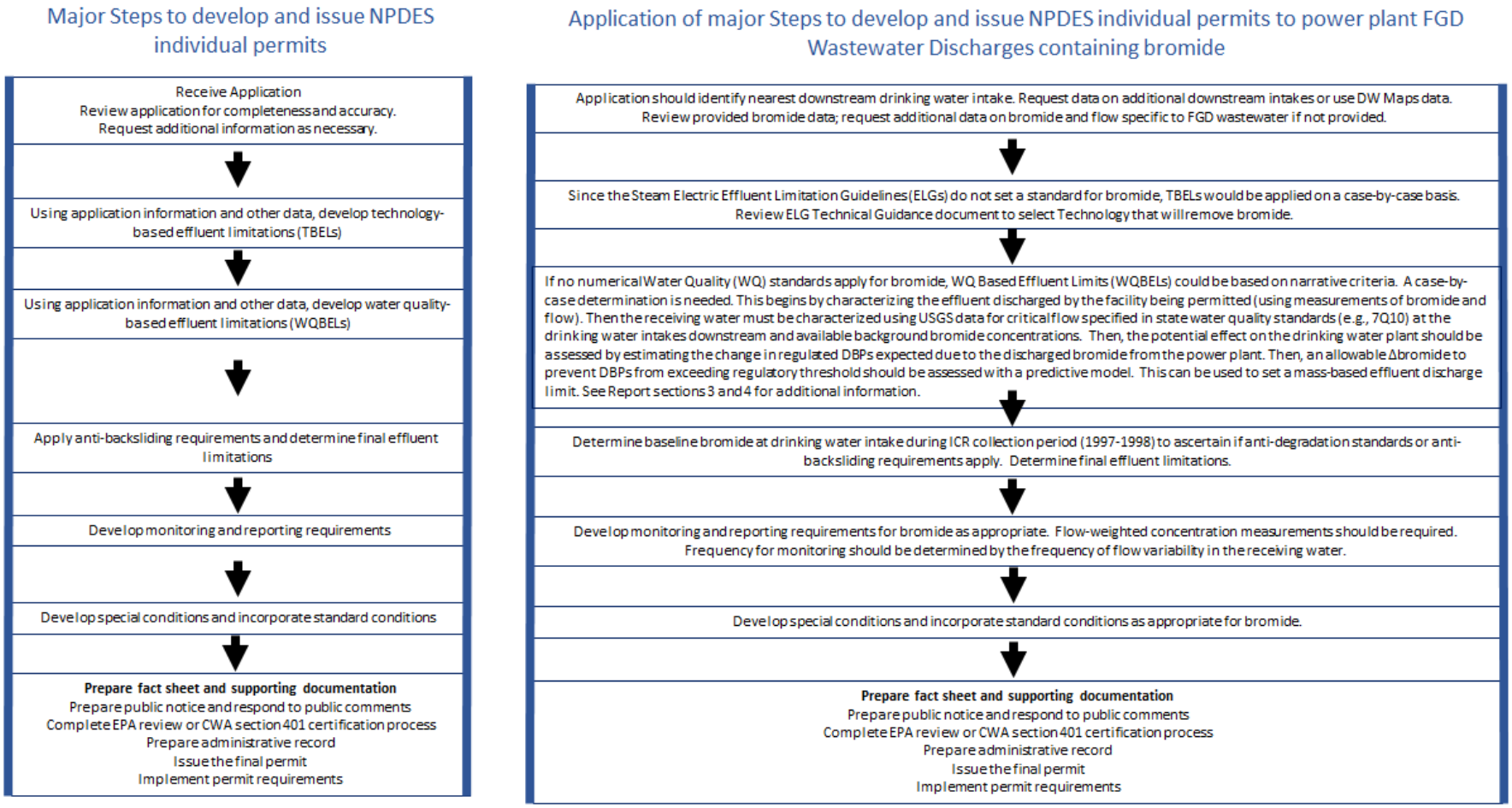


Figure 3. *Application of major steps to develop and issue NPDES individual permits to power plant FGD Wastewater Discharges containing bromide*

Section 2. Prioritize power plants or watersheds for analysis

There are multiple approaches that could be used to select or prioritize NPDES permits for coal-fired power plants that warrant evaluation for potential bromide impacts to downstream drinking water utilities. Four screening methods are summarized here, including specific results where available in the literature. These methods do not include estimating bromide loads or concentration contributions affecting downstream drinking water utilities; those aspects are covered in Section 3.

Approach 1. Identify power plants likely to discharge significant bromide.

Bromide discharges from power plants are predominately associated with wet flue-gas desulfurization (FGD) processes and to a lesser extent with cooling tower biocide additions or coal-ash pond discharges (EPRI 2007a, EPRI 2007b, EPRI 2007c). Wet FGD wastewater contains bromide originally present in the coal and bromide (or iodide) added to the coal. The bromide load expected in the FGD wastewater discharge is directly related to the amount (and type) of coal being used and the amount of bromide being added during coal refining (for section 45 tax credit) or added at the power plant for mercury control (for compliance the Mercury and Air Toxics Standards (MATS)). Thus, as a first screening, Energy Information Administration (EIA) data for power plants can be used to determine the size of the power plant, the amount (and type) of coal being burned in any given month or year, and the type of pollution control systems in place (e.g., wet vs dry FGD). These data can be organized by state or watershed to allow permit writers to screen all power plants within their jurisdiction concurrently.

McTigue et al (2014) used EIA data from 2011, and identified 96 drinking water plants in 22 states downstream of 118 coal-fired power plants operating wet FGD systems. Cornwell et al (2016) revised this analysis using EIA data from 2013 and identified 257 downstream drinking water plants in 24 states associated with 225 coal-fired power plants that have or are likely to add wet FGD systems. Cornwell et al (2016) also assessed the potential for additional wet FGD deployments across the fleet and determined that an additional 316 drinking water plants (in an additional 9 states) would be affected if all power plants not currently operating any FGD systems elected to add wet FGD treatment. Thus, the total number of coal plants was determined to be 407 and the total potentially affected drinking water plants was 573 (Cornwell, Roth et al. 2016).

As this prospective analysis predicted, additional wet FGD systems were deployed at power plants between 2011 and 2016. In addition, some coal-fired power plants ceased operations during this time frame. Good and VanBriesen (2018) used EIA data from 2016 to evaluate all operable coal-fired power plants (325) and determine their status with respect to installed flue-gas desulfurization treatment technology. They identified 140 coal-fired power plants operating wet FGD systems in 35 states in the continental U.S. These wet FGD power plants are all potential sites for bromide discharge.

Comparisons across years (with EIA data beginning in 1991) indicate FGD treatment expanded significantly between 2006 and 2011, likely in response to mercury regulation since FGD (particularly FGD with activated carbon injection, ACI) provides a co-benefit of mercury removal, especially when coals contain or are amended with bromide. Additional FGD was added between 2011 and 2016, with total FGD capacity in the fleet increasing by 20% over those five years (from 202 GW to 243 GW) despite an overall

decline of 16% in total coal generating capacity in the U.S. (from 344 GW to 290 GW). The 2016 fleet includes 47 GW with no FGD treatment (16%), suggesting some potential for additional wet FGD deployment in the future (Good and VanBriesen 2018). The 2016 EIA also lists planned retirements, and 26 GW has a planned retirement by 2025; 15 GW of this was operating with wet FGD and thus, any bromide discharges from these plants would be expected to end by 2025.

Good and VanBriesen (2018) assessed all coal fired power plants operating wet FGD in the 2016 EIA data and identified receiving waters for these plants using information in an EPA survey deployed during the Effluent Limitations Guidelines Rulemaking (USEPA 2015e). **Figure 4** identifies all 325 coal-fired power plants operating in the U.S. in 2016. Blue coloring denotes the 140 operating wet FGD systems, and the size of the circle represents the plant's capacity.

In addition to assessing which plants are producing wet FGD wastewater, it is also important to consider plants that may already have treatment to reduce discharges of wet FGD wastewater. At the national level, this can be challenging, since facility-level reporting for water treatment systems is far less complete than for air treatment systems (which are reported to EIA regularly). The Technical Development Document (TDD) for the Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category (ELGs) refers to a 2009 survey that asked power plants to describe current and future plans related to zero liquid discharge (ZLD) for FGD wastewater. This survey identified 51 plants (37% of the plants that then had wet FGD treatment) as having or *intending* to deploy ZLD by 2014 (USEPA 2015e). The specific plants with current ZLD treatment were not described in the TDD as the survey was considered 'confidential business information.' A separate spreadsheet, titled Current and Future Industry Profile, was available within the Docket (DCN SE00444) (USEPA 2015a); this identified by name 33 power plants with a technology basis called "zero discharge." These plants are identified in the supplemental information provided in Good and VanBriesen (2018).

Unfortunately, this information is not updated regularly through any EIA or EPA data request. For screening purposes, all power plants with wet FGD systems should be assumed to be discharging the associated wastewater within the watershed where they are located. Further refinement and exclusion of power plants with ZLD can take place after screening by reviewing current permits that describe active waste streams and their discharge through permitted outfalls.

Assessment of the power plant fleet (using EIA 860 data) can identify high capacity plants using wet FGD treatment; however, bromide loads from these plants will vary based on quantity and type of coal burned in any given year (data available on a monthly basis in EIA 923). For example, bituminous coal, especially low and medium volatile bituminous coal, is significantly enriched in natural bromide compared with other coals (Kolker and Quick 2015). Plants burning bituminous coal are expected to be discharging more bromide in FGD wastewater than those burning lower bromide coals. Additionally, due to significant uncertainties related to the addition of bromide during production of refined coal (EPRI 2014), permits for all plants burning refined coal (regardless of the bromide in the source coal) should be reviewed. Similarly, addition of bromide for MATS compliance is not a declared technology within any EIA or EPA survey or form, making it difficult to evaluate how extensive bromide addition is currently or will be in the future across the United States. However, an EPA Air Markets Program Database did ask about power plants intentions related to MATS compliance (USEPA 2018a). One choice was "additives to enhance PAC and existing equipment performance," which may indicate plans to add halogens for enhanced mercury removal. Plants selecting this choice, regardless of the type of coal being burned, should be considered for

 © Copyright 2019 American Water Works Association

review. A list of these plants was provided in the supplemental information in Good and VanBriesen (2018).

The results of an analysis following this method will identify all power plants with the *potential* to discharge bromide to the aquatic environment. As an example, and based on EIA data for 2016, plants with capacity greater than 2000 MW are listed in **Table 1**[1]; shading shows plants burning bituminous and refined coal (forms that are elevated in bromide)(EIA 2018). The power plant permits and receiving waters shown were extracted from ECHO(USEPA 2018c). This capacity-based screening method should not be interpreted to mean that plants with lower wet FGD capacity would have no impact on the environment. As noted in prior published work, even plants with anticipated small bromide loads can have significant effects on in-stream bromide concentrations if they discharge to small water bodies or during low flow events (McTigue, Cornwell et al. 2014, Good and VanBriesen 2016, Good and VanBriesen 2017). The identification of power plants through this screening tool should be viewed as a potential prioritization for aligning resources with timing for permit review, not as an indication of impact (or lack of impact).

Once a power plant has been identified as potentially discharging bromide to the aquatic environment, further analysis is needed. The effect of the wet FGD power plant discharges on bromide concentrations in drinking water sources will vary depending upon the bromide load from the power plant and the receiving water flow characteristics between the discharge and the downstream drinking water intake. The effect on DBP formation at downstream drinking water utilities will also depend on other precursor concentrations in the region (e.g., other sources of bromide, iodide, and organic carbon) as well as treatment technologies used within the drinking water plant. These aspects are discussed in Sections 2 and 3 in this report.

1 This table is presented as an example of available data ONLY. The cut off at 2000 MW of wet FGD capacity was selected solely to limit the visual to a single page.

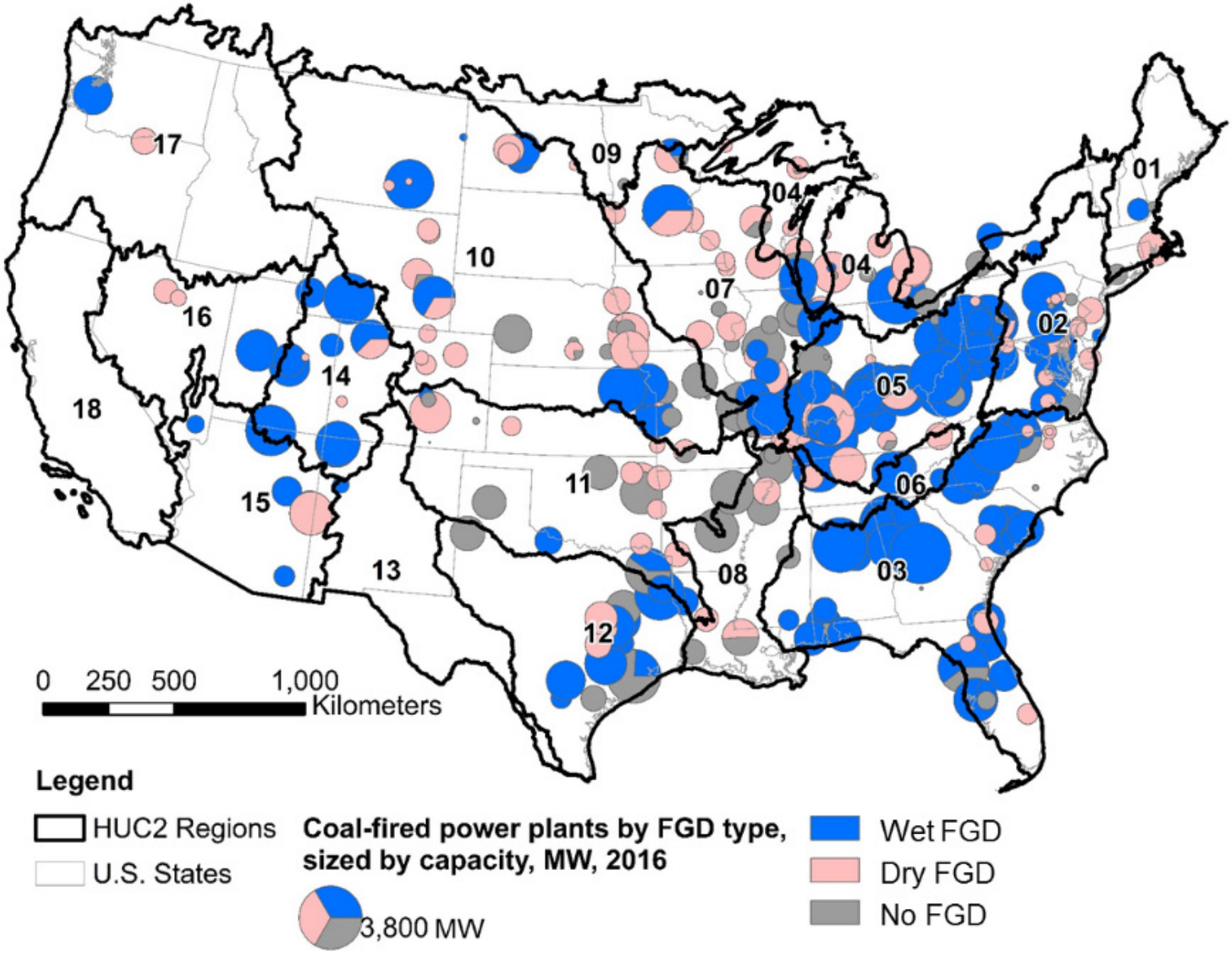


Figure 4. *United States coal-fired power plants as of 2016. Symbols are sized by capacity (MW) and colored according to FGD type. Hydrologic regions are outlined and labeled by two-digit hydrologic unit codes (HUC)(Good and VanBriesen 2018)*

Table 1. *2016 U.S. Coal-fired power plants with wet FGD capacity over 2000 MW, listed in descending order. Dark shading for refined coal consumption; light shading for bituminous coal consumption. Following (Good and VanBriesen 2018).*

Plant information										Coal consumption (million tons) for Wet FGD5					
HUC4	ID	Name	State	ZLD ELG1	MATS additives to PAC2	Plant Capacity (MW)3	NPDES Permit4	HUC12 for discharge4	HUC12 Watershed4	Total	Wet BIT	Wet LIG	Wet RC	Wet SUB	Wet WC
0307	6257	Scherer	GA			3564	GA0035564	030701031307	Berry Creek – Ocmulgee River	10.40	0	0	0	10.40	0
0315	703	Bowen	GA		YES	3498.6	GA0001449	031501041304	Richland Creek – Etowah River	6.41	**6.41**	0	0	0	0
0512	6113	Gibson	IN	YES		3339.5	INRM00341	051201130302	McCarty Ditch – Coffee Bayou	7.59	**7.59**	0	0	0	0
0410	1733	Monroe (MI)	MI			3279.6	MI0037028	041000010104	Swan Creek	7.11	0	0	**7.11**	0	0
0505	3935	John E Amos	WV			2932.6	WV0001074	050500080304	Scary Creek – Kanawha River	5.79	**5.79**	0	0	0	0
0316	6002	James H Miller Jr	AL			2822	AL0027146	031601110412	Fish Trap Branch	10.14	0	0	0	10.14	0
0503	6094	Bruce Mansfield	PA			2741.1	PA0027481	050301011101	Mill Creek	4.72	0	0	**4.72**	0	0
0503	8102	James M Gavin	OH	YES		2600	OH0028762	050302020901	Kyger Creek	5.48	0	0	**5.48**	0	0
0513	3399	Cumberland (TN)	TN			2600	TN0005789	051302050403	Big Elk Creek – Cumberland River	5.33	**1.59**	0	**3.74**	0	0
0511	1378	Paradise	KY			2558.2	KY0004201	05110030503	Jacobs Creek – Green River	4.57	0	0	**4.57**	0	0
0301	8042	Belews Creek	NC			2491.2	NC0024406	030101030306	Reed Creek – Dan River	3.97	**3.97**	0	0	0	0
0503	2866	W H Sammis	OH			2455.6	OH0011525	050301011106	Hardin Run – Ohio River	3.64	**3.41**	0	0	0.24	0
1404	8066	Jim Bridger	WY		YES	2441.9	WYR000342	*Not reported in ECHO*		6.71	0	0	0	6.71	0
0509	2850	J M Stuart	OH			2440.8	OH0004316	050902010605	Lawrence Creek – Ohio River	4.89	**4.89**	0	0	0	0
1407	4941	Navajo	AZ	YES		2409.3	AZR051306	150200180400	Not reported in ECHO	5.83	**5.83**	0	0	0	0
0305	130	Cross	SC			2390.1	SC0037401	030502010101	Lake Moultrie	4.15	0	0	**4.15**	0	0
1201	6146	Martin Lake	TX	YES	YES	2379.6	TX0054500	120100020803	Martin Lake	9.10	0	6.57	0	2.52	0
1010	6076	Colstrip	MT	YES	YES	2272	MTR000058	101000011003	Corral Creek	8.55	0	0	0	8.55	0
0509	1356	Ghent	KY		YES	2225.9	KY0002038	050902031010	McCools Creek – Ohio River	5.53	**5.53**	0	0	0	0
1027	6068	Jeffrey Energy Center	KS			2160	KS0100552	102701020902	Lake Shawnee Shunganunga Ck	6.47	0	0	0	6.47	0
0512	994	AES Petersburg	IN		YES	2146.7	IN0002887	051202021001	Lick Creek – White River	4.33	**4.33**	0	0	0	0
0305	2727	Marshall (NC)	NC			2119	NC0004987	030501011202	Little Creek –Lake Norman	3.64	3.64	0	0	0	0
0502	3944	Harrison Power Station	WV	YES		2052	WV0005339	050200020602	Limestone Run-West Fork River	5.24	5.24	0	0	0	0

1EPA FGD ZLD List from 2009 (EPA, 2015a); 2 EPA Air Markets data for 2016 (EPA, 2018a); 3 EIA Form 860 (EIA, 2017); 4EPA ECHO (2018c); 5 EIA Form 923 (EIA, 2018)

© Copyright 2019 American Water Works Association

Approach 2. Identify watersheds at elevated risk of bromide loads of concern due to coal consumption at power plants operating wet FGD

As **Figure 4** shows, many watersheds contain numerous power plants with wet FGD. Cumulative effects should be considered in evaluating which watersheds are likely to see downstream drinking water plant effects. Power plants within these higher load watersheds could then be evaluated for their contributions. Bromide discharge limits would need to be set by considering the *cumulative* effects of multiple discharges on downstream drinking water plants.

The most direct way to assess watersheds or regions of the country at increased risk of bromide elevated above background is to consider coal consumption levels at all power plants with wet FGD systems within a given geographic area, which could be selected using a Hydrologic Unit Code (HUC). HUC *regions* are defined with a two-digit code and are called HUC2s. *Sub-regions* are defined with a four-digit code and are called HUC4s. Looking at cumulative coal consumption in a hydrologic unit allows identification of watersheds that may be experiencing elevated bromide loading under current conditions. **Figure 5** shows watershed-level coal-consumption associated with FGD treatment type for each HUC2 (outlined and identified by their two-digit code). The circles are sized by coal consumption (tons in 2016) and the colors indicate the FGD treatment type and coal type. The highest 2016 consumption subject to wet FGD treatment was in the Ohio River Basin (HUC-05) and the South Atlantic-Gulf Region (HUC-03), suggesting these two regions should receive additional attention with respect to power plant permits. Several regions show elevated use of refined coal in 2016 (HUCs -02, -04, -05, and -07). **Figure 6** provides greater spatial resolution (HUC4; subregions), with wet FGD coal consumption in blue and refined coal use indicated by red outline. **Table 2** summarizes these data by HUC2.

 © Copyright 2019 American Water Works Association

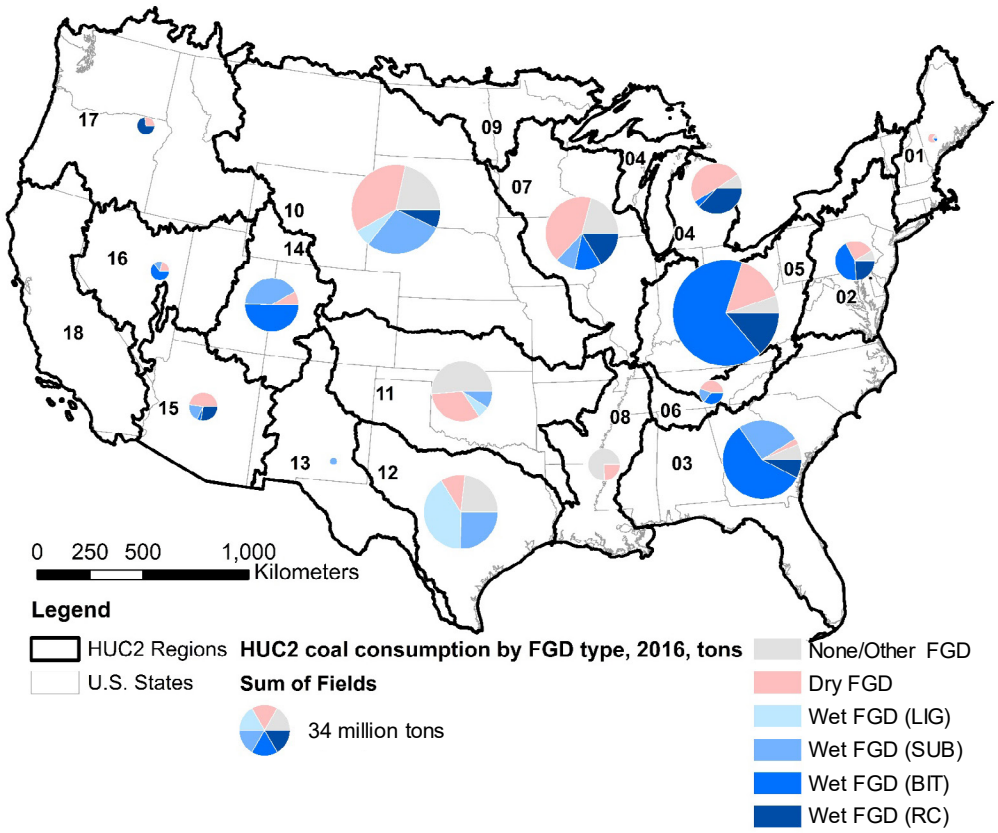


Figure 5. *Coal consumption (by type) associated with power plants utilizing different FGD treatment technologies. FGD status from EIA Form 860 (EIA 2017) and consumption data from EIA Form 923 (EIA 2018)(following (Good and VanBriesen 2018)). Figure courtesy Dr. Kelly Good.*

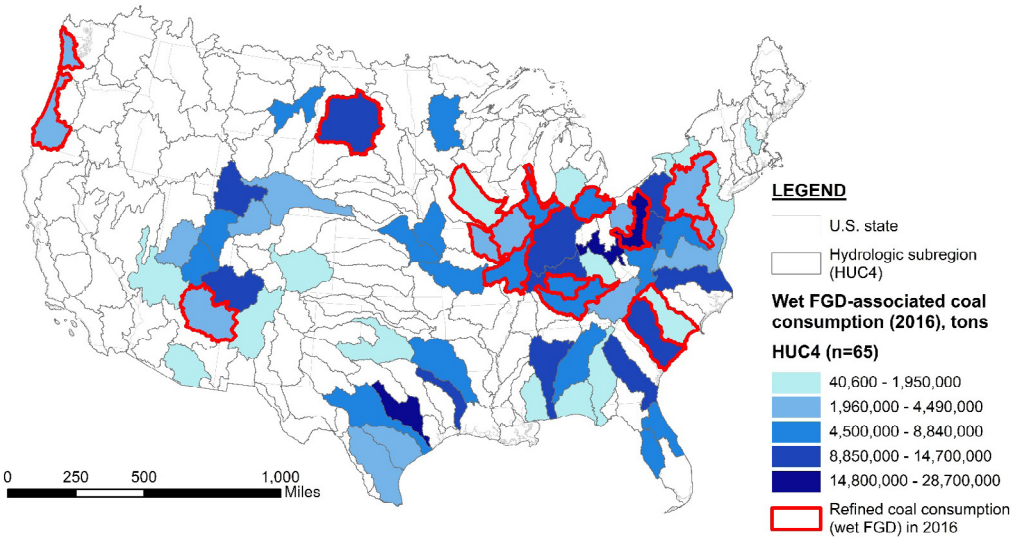


Figure 6. *Coal consumption (in tons) associated with power plants using wet FGD treatment; HUC4 watershed scale. FGD status from EIA Form 860 (EIA 2017)and consumption data from EIA Form 923 (EIA 2018). Red outline indicates watersheds with refined coal consumption reported in 2016. Adapted from (Good and VanBriesen 2018). Figure courtesy Dr. Kelly Good.*

Table 2. *2016 Coal-fired power plant wet FGD-associated capacity and coal consumption by type at the HUC2 region (Good and VanBriesen 2018). Dark shading indicates refined coal consumption; light shading indicates bituminous coal consumption.*

Hydrologic region		Capacity (MW) 2016		Coal consumption (million metric tons)						
HUC2	Name	Total	Wet FGD	Total	Wet Subtotal	Wet BIT	Wet SUB	Wet LIG	Wet RC	Wet WC
01	New England	2,084	459	1.12	0	0	0	0	0	0
02	Mid-Atlantic	14,841	10,508	19.1	12.8	**8.22**	0	0	**4.55**	0
03	South Atlantic-Gulf	47,368	42,037	75.0	68.3	**43.3**	19.3	0	**5.74**	0
04	Great Lakes	18,461	7,583	31.4	13.1	**1.35**	0	0	**11.7**	0
05	Ohio	73,364	59,143	136	109	**89.7**	0.677	0	**18.8**	0
06	Tennessee	4,232	3,064	7.0	3.86	**2.50**	1.35	0	0	0
07	Upper Mississippi	28,933	10,177	64.6	23.9	**7.72**	5.69	0	**10.4**	0
08	Lower Mississippi	5,163	0	12.5	0	0	0	0	0	0
09	Souris-Red-Rainy	129	0	0	0	0	0	0	0	0
10	Missouri	30,385	11,957	96.2	40.3	0	27.6	5.87	**6.60**	0
11	Arkansas-White-Red	19,439	2,441	44.7	6.94	0	4.08	2.86	0	0
12	Texas-Gulf	19,966	11,988	66.8	44.1	0	16.8	27.3	0	0
13	Rio Grande	257	257	0.713	0.713	0	0.713	0	0	0
14	Upper Colorado	14,346	13,174	35.0	32.1	**18**	14.4	0	0	0
15	Lower Colorado	4,130	2,365	10.0	5.19	0	1.99	0	**2.75**	0
16	Great Basin	2,449	1,640	4.4	3.47	**2.81**	0.650	0	0	0
17	Pacific Northwest	2,102	1,460	3.8	2.79	0	0	0	**2.76**	0.0334
18	California	0	0	0	0	0	0	0	0	0
	TOTAL	287,650	178,252	608	366	**174**	93.3	36.0	**63.3**	0.0334

Approach 3. Identify watersheds or source waters with existing elevated bromide and thus less capacity to accept additional bromide loads

The presence of bromide loads from power plants is particularly of concern in watersheds where bromide is already elevated (due to natural or anthropogenic sources). A review of observational data on bromide in U.S. surface waters may identify watersheds where power plant bromide loads will add to existing bromide levels and contribute to downstream drinking water utility problems.

Regional historical bromide levels

The Information Collection Rule (ICR) sampled source waters for bromide in 1997-1998 (USEPA 2000), and regional assessments of this dataset suggest certain watersheds were elevated in source water bromide at that time. **Figure 7** is a box-plot of the observed bromide concentrations *in surface water* for each HUC2 watershed, separated by geographic regions (western, mid-west, and eastern). Regional trends are clear, with the Eastern region showing low bromide concentrations (median values in µg/L of 10, 31, 29, and 29 respectively), and the mid-west showing higher levels, with the median always above detection (median values in µg/L are 35, 34, 44, 36, 57, and 36 respectively). The western region shows more variability, with elevated bromide in HUC regions 12 and 13 (median values in µg/L of 150 and 110), which are Texas and parts of New Mexico. Much lower levels of bromide were observed in the Northwest (HUC regions 16 and 17 with medians below detection), while California (HUC 18) and the Southwest (HUC 15) reported values similar to the Midwest region (medians in µg/L of 51 and 82 respectively). **Figure 8** provides greater specificity with median bromide concentrations for drinking water utilities reporting during the ICR shown at the HUC4 level for the mid-west only[2]. Geographic variability is less pronounced, but there are subwatersheds with median bromide concentrations below detection (e.g., 0513, 1019, 1102, 1111) and subwatersheds with median values over 100 µg/L (e.g., 1020, 1105, 1109, 1110 1114).

2 *A comprehensive analysis at HUC4 level was completed; the results for the Midwest are shown as an example*

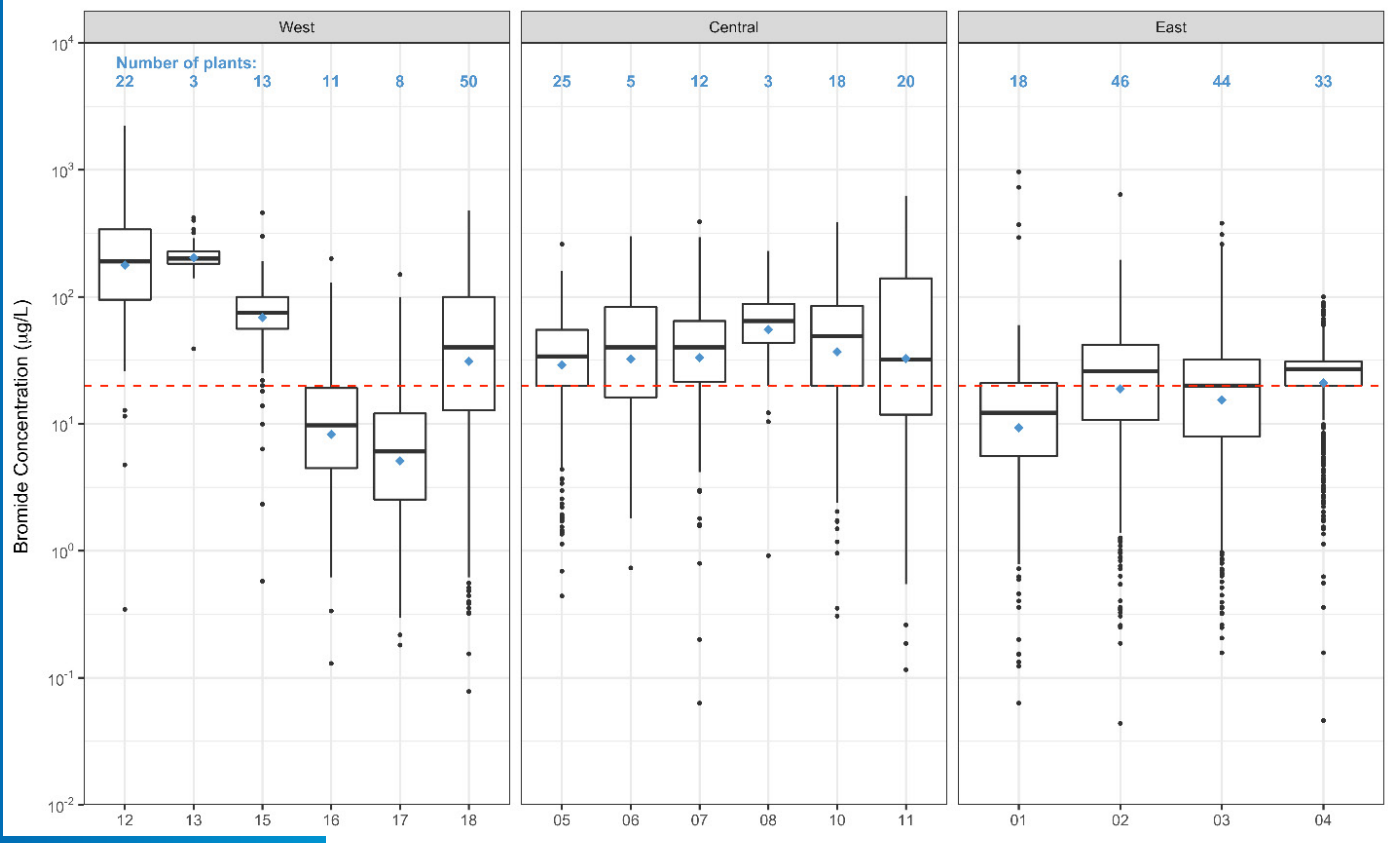


Figure 7. *Influent bromide concentration measured at drinking water utilities during the ICR by HUC2, plotted on a log scale. The red horizontal dashed line represents the detection limit for the data set (20 µg/L); values reported as below detection were imputed using Regression on Order Statistics (ROS) (Helsel 1990). The box plot for each subregion (HUC2) includes a solid line for its median and a blue diamond for the mean value. The box extends to the interquartile range (IQR), and the whiskers extend to 1.5 times the IQR. Black dots indicate values outside this range. The number of plants reporting data within each HUC2 is provided at the top of the plot. Each plant provided monthly values for July 1997 to December 1998. Adapted from (Kolb 2018); Figure courtesy Dr. Chelsea Kolb.*

© Copyright 2019 American Water Works Association

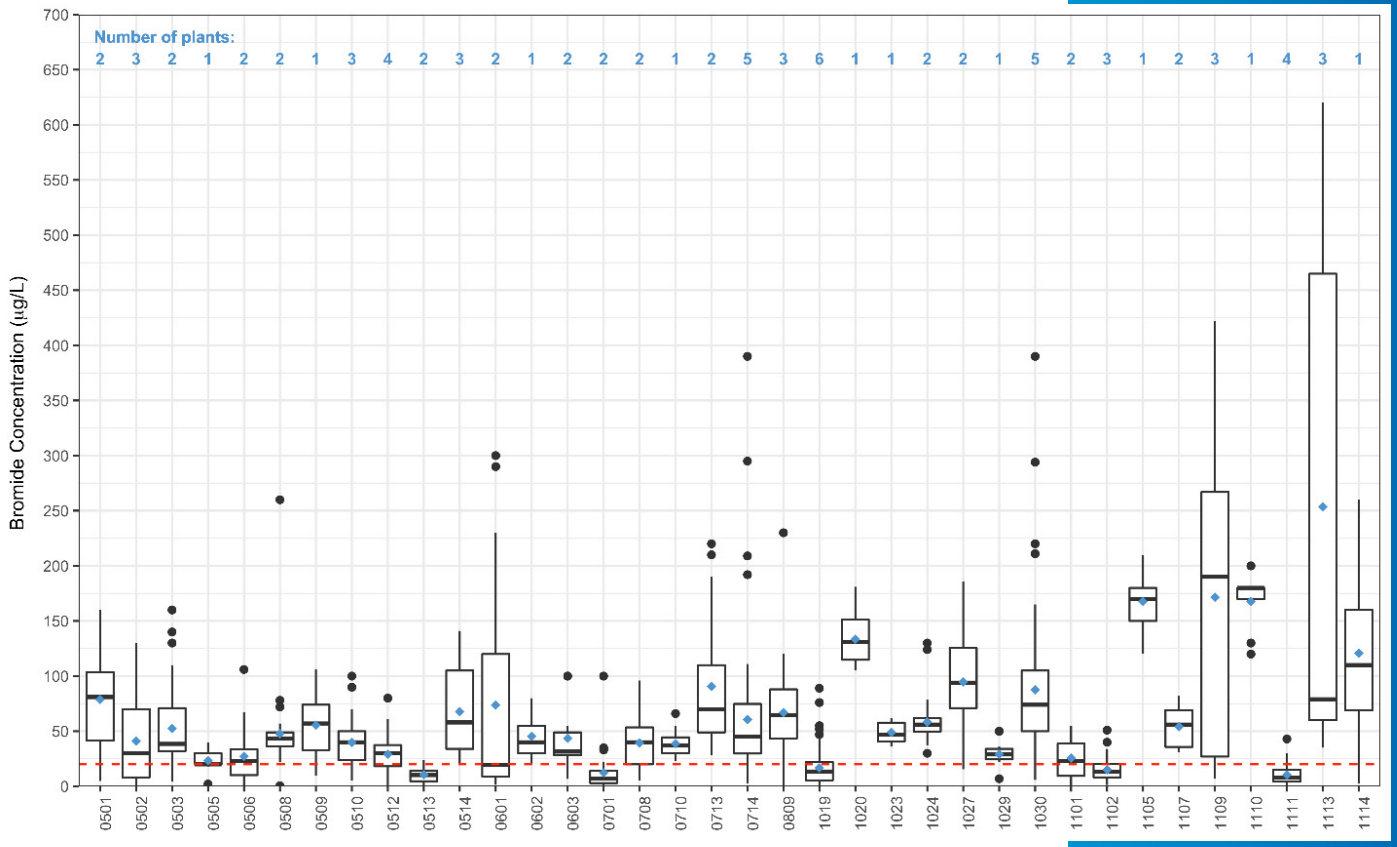


Figure 8. *Influent bromide concentration measured at drinking water utilities during the ICR by HUC4 for the Central U.S. region (HUC05 to HUC11). The red horizontal dashed line represents the detection limit for the data set; values reported as below detection were imputed using Regression on Order Statistics (ROS) (Helsel 1990). The box plot for each subregion (HUC4) includes a solid line for its median and a blue diamond for the mean value. The box extends to the interquartile range (IQR), and the whiskers extend to 1.5 times the IQR. Black dots indicate values outside this range. The number of plants reporting data within each HUC4 is provided at the top of the plot. Each plant provided monthly values for July 1997 to December 1998. Adapted from (Kolb 2018); Figure courtesy Dr. Chelsea Kolb.*

Watershed-specific bromide concentration changes

In addition to the 20-year-old bromide data set from the ICR, more recent bromide monitoring (e.g., in Pennsylvania at the Water Quality Network sites) could be used to identify regions that are experiencing elevated source water bromide compared to the past. As an example, WQN data from site 201 on the Susquehanna River (at the USGS gage 01576000 near Marietta, PA) was assessed by comparing data from the ICR for this region of the river (collected from July 1997 to December 1998) with data collected more recently (from July 2015 to December 2016).

Figure 9 shows these data with the ICR bromide data as red squares and the more recent data as blue squares. Below detection limit results are shown as open squares and plotted at zero for visualization purposes only; the detection limit in the ICR was 20 µg/L while the detection limit for the WQN data was 8 µg/L. The median for each period is shown as a horizontal dashed line (below the detection limit of 20µg/L for the ICR and thus shown at zero, and 22µg/L for the more recent data). Since concentration is strongly influenced by flow conditions that dilute bromide loads, the flow in the river for each relevant period is plotted on the right vertical axis (inverted); sharp spikes downward represent high flow events. The median river flow for the ICR time period was 320 m^3/sec, while the median for the more recent period was 600 m^3/s. Overall, the flow characteristics are not significantly different for these years despite the difference in the median flow. However, this similarity masks a major dry period in Fall 2016 that contributed to the elevated bromide concentrations seen at this time (blue squares after July on the right). While long term stable bromide concentrations suggest Susquehanna River drinking water plants are not exceptionally vulnerable with respect to bromide loads, the recent bromide concentration spikes (to above 140 µg/L after years of values not exceeding 55 µg/L) indicate review of potential bromide discharges into this basin is warranted.

To complete the type of analysis shown in **Figure 9** for a given region or state, bromide data from the ICR must be extracted and joined to geographic information related to more recent bromide data. Unfortunately, more recent bromide data can be difficult to acquire. The Water Research Foundation recently funded a nation-wide occurrence survey of bromide and iodide in water supplies (Westerhoff 2018), which may provide additional information to enable a national review of at-risk watersheds.

 © Copyright 2019 American Water Works Association

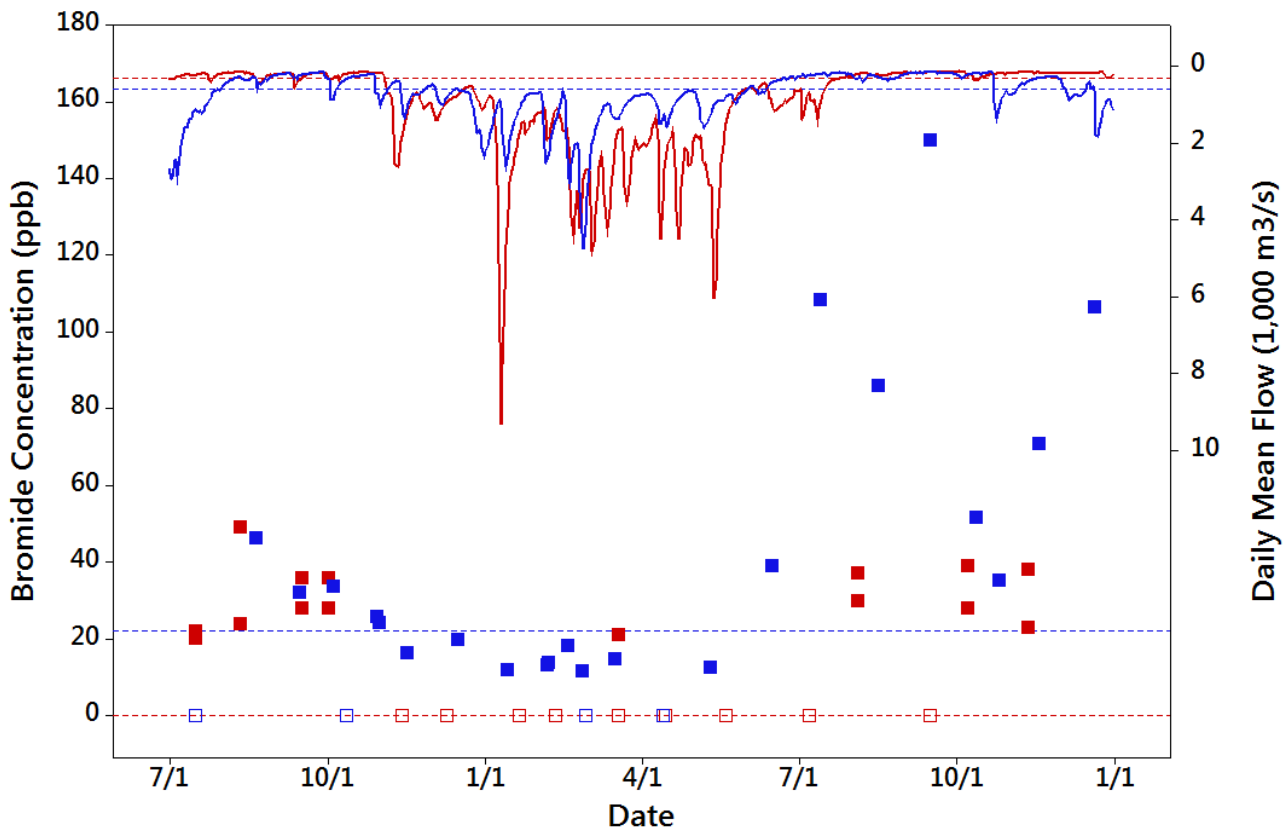


Figure 9. *Bromide concentrations reported in the Susquehanna River for the EPA ICR (1997-1998) and from WQN201 near Marietta, PA (2015-2016) in ppb (µg/L). Daily mean flows from USGS gage 01576000 at Marietta, PA (in m^3/s). Below detection limit results are shown as open squares and plotted at zero for visualization purposes only; the detection limit in the ICR was 20 µg/L while the detection limit for the WQN data was 8 µg/L. The median for each period is shown horizontal dashed line (below the detection limit of 20µg/L for the ICR and thus shown at zero, and 22µg/L for the more recent data). Figure courtesy Dr. Adam Cadwallader.*

Utility-specific bromide concentration data

At the local level, individual drinking water utilities that are measuring bromide concentrations in their intake could provide insights into bromide levels within source watersheds, allowing identification of watersheds at risk from current or future anthropogenic discharges. For example, **Figure 10** shows bromide concentrations collected at a drinking water utility intake on the Monongahela River in southwestern Pennsylvania during the ICR period (WY1998[3]) and during a more recent period (WY2013-WY2017). The median bromide concentration at this utility from 2013 to 2016 was just above 50 µg/L, which could suggest this watershed is at increased risk of bromide effects on DBPs if discharge loads increase. Reductions in anthropogenic loads may be able to mitigate this risk.

3 WY refers to Water Year, a period defined by USGS from October 1 of the previous year through September 30 of the noted year. Thus, WY1998 is October 1, 1997 to September 30, 1998, a period that was within the 18 months collected during the DBP ICR survey.

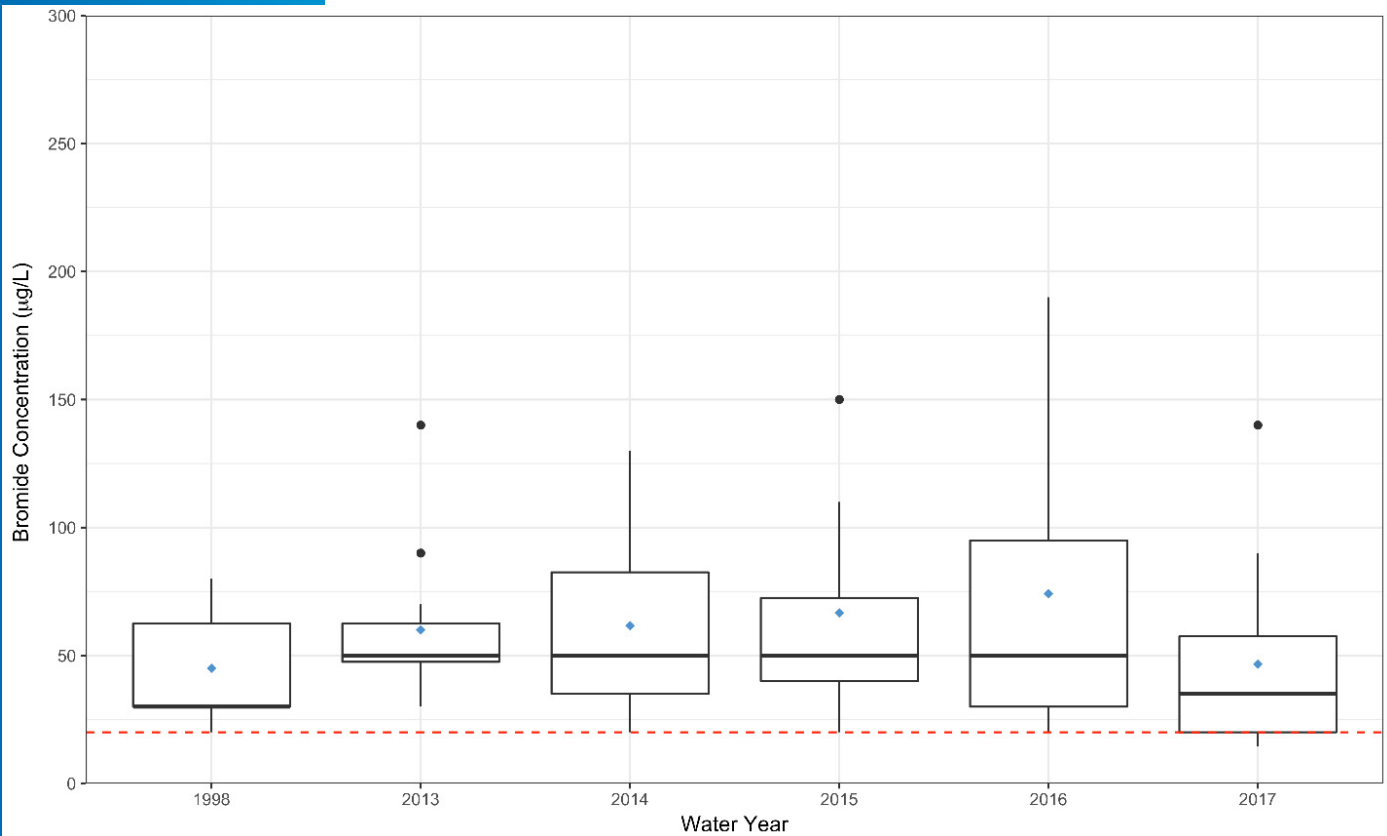


Figure 10. *Bromide concentrations at a public drinking water utility reported during the ICR (WY1998) as well as during a more recent time period (WY 2013-2017); 12 samples per water year. Median is solid dark line and mean is the blue diamond. The box extends to the interquartile range (IQR), and the whiskers extend to 1.5 times the IQR. Black dots indicate values outside this range. Below detection data were imputed using Regression on Order Statistics (ROS) (Helsel 1990). Data from (Kolb, Good et al. 2019). Figure Courtesy Dr. Chelsea Kolb.*

© Copyright 2019 American Water Works Association

When more extensive data are available, cumulative distribution plots can provide additional insight. **Figure 11** is based on approximately daily bromide concentration measurements from a drinking water intake on the Allegheny River for water years 2011 and 2013. The median (50% exceedance) was 98 µg/L in 2011 and 73 µg/L in 2013. The value of 50 µg/L was exceeded 71% of the time in 2011 and 81% of the time in 2013, while 100 µg/L was exceeded 49% of the time in 2011 and only 22% of the time in 2013. Multi-year analyses of this type can be used to assess whether a watershed consistently has elevated bromide concentrations. Since concentration is significantly affected by flow conditions (which can vary year-to-year), these analyses should not be used to determine if a watershed is improving. Rather, load assessments (concentration times flow) could be compared to determine whether anthropogenic loads are increasing or decreasing in a region.

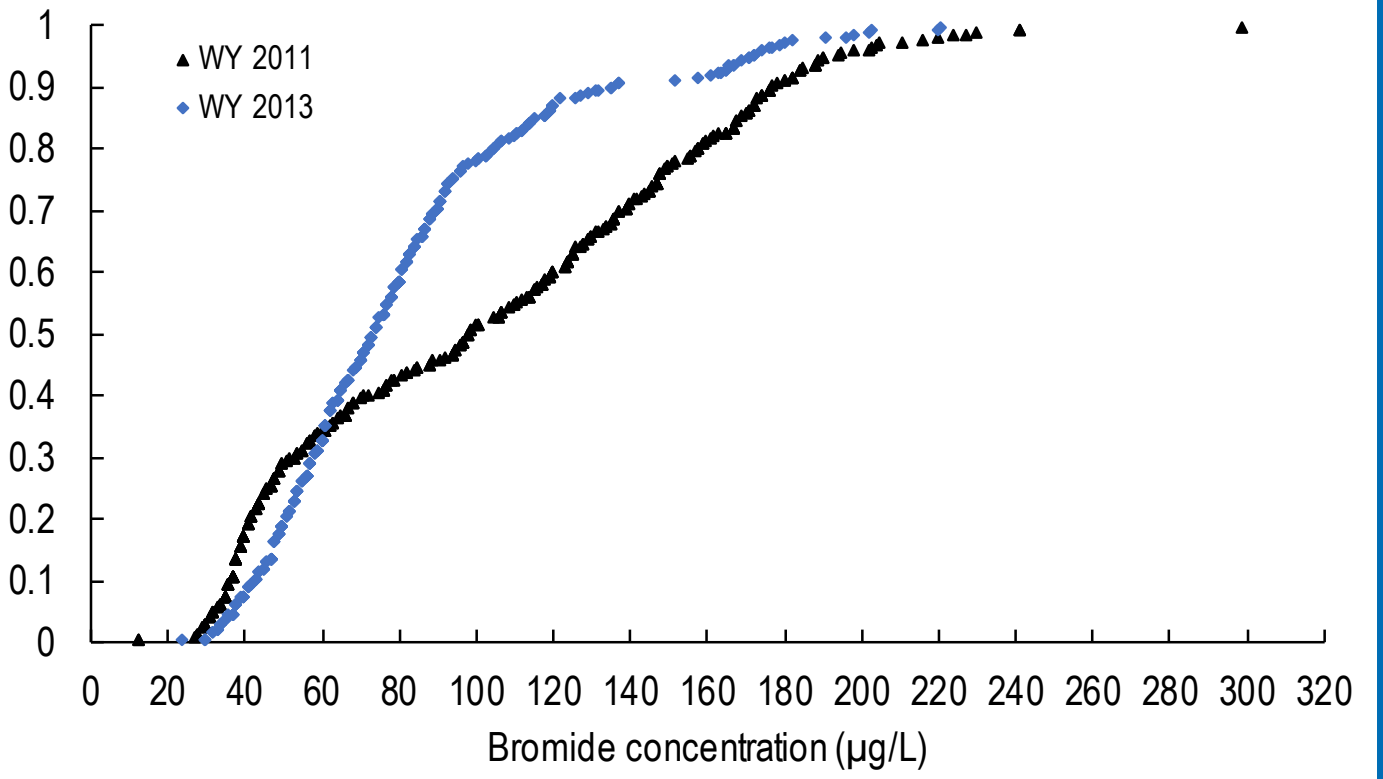


Figure 11. *Empirical cumulative probability distribution of observed bromide concentration (µg/L) at a drinking water plant on the Allegheny River. Shown for water year 2011 (October 2010 through September 2011); data as published in States et al. 2013, includes two values below 25 µg/L detection limit shown at half this value) and water year 2013 (October 2012 through September 2013; data also shown in Good 2018). Data courtesy Pittsburgh Water and Sewer Authority; Figure courtesy Dr. Kelly Good.*

Approach 4. Identify watersheds where drinking water plants are already experiencing increased bromine incorporation in DBPs.

Approach 3 was dependent on recent bromide concentration data, which may be unavailable in many regions. Drinking water utilities do not routinely analyze source waters for bromide unless they suspect a problem. However, some compliance data for disinfection by-products may provide an adequate surrogate. When DBP compliance data include individual species concentrations, these data may identify regions of concern since bromine incorporation is only possible when source waters contain bromide.

Bromine incorporation metrics

Bromine incorporation can be assessed using several different calculated indicators. The bromine incorporation factor (BIF) enables assessment of the rate and extent of formation of brominated THM (Gould, Fitchhorn et al. 1983); the value ranges from 0 (for THM4 at 100% chloroform) to 3 (for THM4 at 100% bromoform). BIF for HAAs can be similarly computed when all species measurements are available; BIF for groups of HAAs have also been reported (e.g., BIF for the trihaloacetic acids, TXAAs) (Hwang, Krasner et al. 2002, Krasner, Lee et al. 2008). The Bromine Substitution Factor (BSF) is an alternative that is normalized (from 0 to 1) (Hua, Reckhow et al. 2006), allowing comparisons across DBP classes (Hua and Reckhow 2012). In addition to molar-based fractions (BIF, BSF), the mass percentage of DBPs containing bromide can be computed. This is not a widely reported unit for bromine incorporation; however, it can provide insights related to regulatory compliance values, which are mass-based, allowing assessment of the extent to which bromine-incorporation is contributing to THM4 and HAA_5 values that are approaching regulatory compliance limits. PaDEP reports that drinking water compliance data showing mass based bromine-incorporation above 34% indicates moderately impacted source waters, and levels above 80% indicate significant impact (Handke 2009). Based on any of these metrics, utilities with elevated bromine incorporation in regulated DBPs (trihalomethanes and haloacetic acids) could be identified and used to identify watersheds associated with elevated bromide (where measured bromide data are unavailable), which could then be evaluated for the presence of power plants with wet FGD discharges that could be contributing bromide.

Watershed-specific DBP Data

Watersheds or water systems that currently have elevated bromide or are at risk of negative drinking water effects of increasing bromide may be identified through analysis of existing drinking water disinfection by-product compliance data reported by utilities.

As an example of this approach, **Figure 12** shows total trihalomethanes (TTHM) in the top panel and mass-based bromine incorporation into TTHM in the bottom panel for two utilities on the Susquehanna River, based on submitted quarterly compliance sampling from 2012 to 2015 (PADEP 2018). Steelton is a small plant (serving 6,300 people) near Harrisburg, PA, upstream of a large power plant. Wrightsville is a small plant (serving 5,500 people) near Marietta, PA, downstream of the same power plant. In the top panel, it is clear that THM values for individual quarters (solid lines) and the running annual average (dotted lines) are very similar for the two plants, with Steelton reporting a RAA of 64 µg/L over the six-year period and Wrightsville reporting a RAA of 54 µg/L. However, the bromine incorporation (bottom panel), is clearly higher at Wrightsville (average 39% by mass) than at Steelton (average 21% by mass). Of particular note is the spike in bromine incorporation at Wrightsville in late 2016; this corresponds to an increase in bromide in the river at this time (see previous **Figure 9**). The top plot in **Figure 12** shows

 © Copyright 2019 American Water Works Association

a fourth quarter TTHM value above 80 µg/L at this time as well, significantly higher than the 3rd quarter value in 2016. All other years (2012-2015 and 2017) show a more typical pattern with 3rd quarter TTHM higher than 4th quarter TTHM. These differences suggest a bromide source between the two drinking water utilities that may be a concern for this downstream drinking water utility as well as other utilities using this river. The effect is most pronounced in 2016 when low flow conditions were observed in the Susquehanna River. Additional analysis would be needed to determine if any load changes also occurred in 2016 (e.g., the power plant increasing use of refined coal or adding bromide for mercury control).

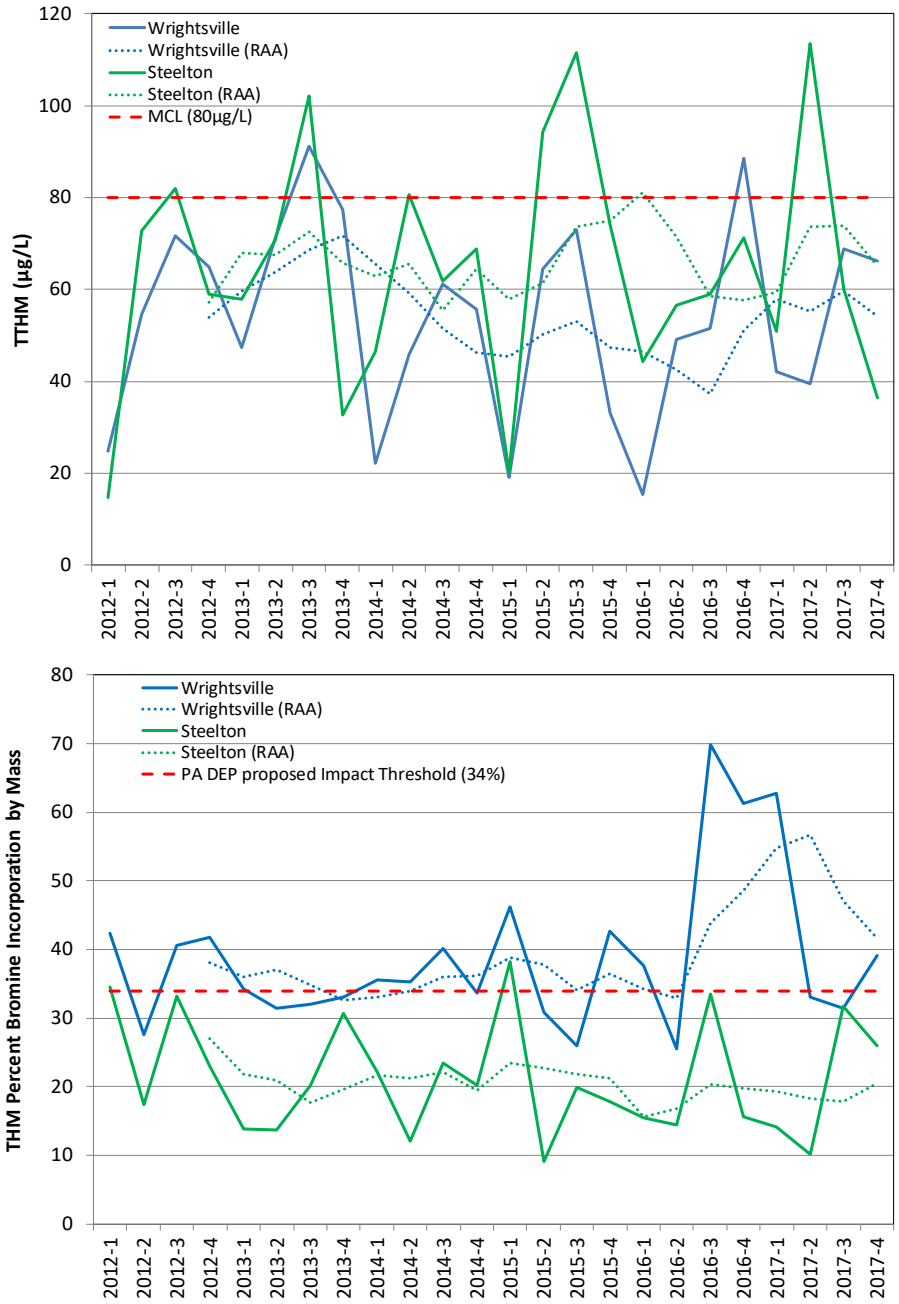


Figure 12. *Total trihalomethanes (average at sampling locations) (top) and Percent Bromine incorporation (by mass) in Trihalomethanes (bottom) from quarterly compliance data at Steelton (green) and Wrightsville (blue) (2012-2015). Dotted lines are calculated running annual averages (RAA). Data from (PADEP 2018).*

Considering reported DBPs for multiple utilities in river basins can assist with prioritization of source-water assessment. For example, **Figure 13** shows a river-based assessment of bromine incorporation in THM based on 2016-2017 compliance data from Pennsylvania water utilities (using BSF as the molar metric). The Allegheny, Monongahela and Ohio Rivers are in Western Pennsylvania while the Delaware and Susquehanna Rivers are in Eastern Pennsylvania. Elevated bromine incorporation within DBPs in the Allegheny and Ohio Rivers suggests these utilities are already struggling with the effects of bromide on DBP formation. Power plants within these basins should be prioritized for review to ascertain whether significant bromide loads are causing elevated bromide that leads to the bromine incorporation of DBPs at downstream drinking water utilities on these rivers.

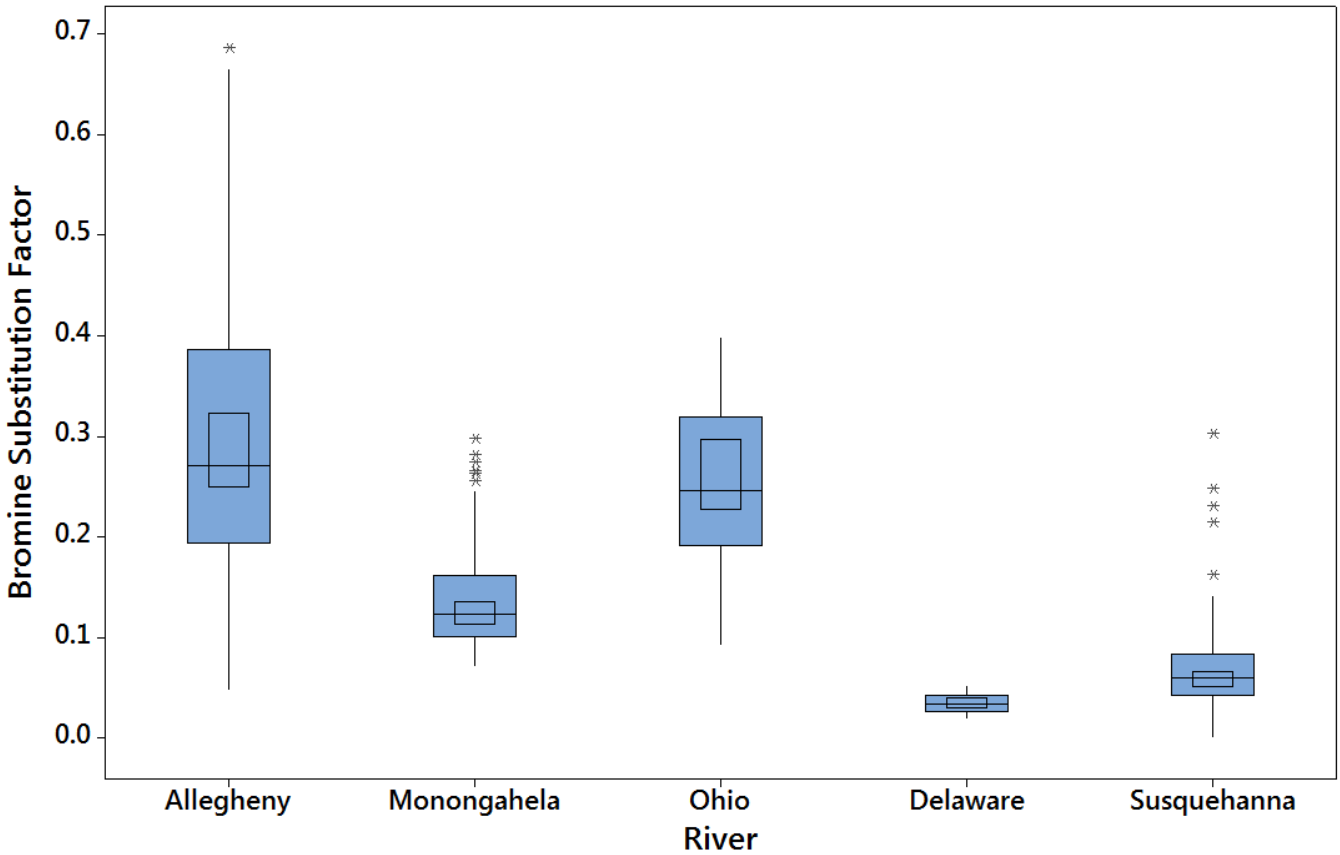


Figure 13. *Bromine Substitution Factor (BSF) in THM for water utilities using different source waters in Pennsylvania (based on 2016-2017 compliance data). The center line represents the median, shown with its 95th percentile confidence interval (internal box). The larger box shows the extent of the 25th and 75th percentiles, while the whiskers extend to 1.5 times this interquartile range. The stars indicate values outside that range. Data from (PADEP 2018). Figure courtesy Dr. Adam Cadwallader.*

 © Copyright 2019 American Water Works Association

Section 2 Data Sources.

Completion of any of the analyses described in this section requires use of publicly-available data from numerous sources. Power plant data are available from the Energy Information Administration (EIA). Form 860 provides generator-level information about existing and planned operation and associated environmental equipment at power plants operating with 1 MW or greater capacity (EIA 2017). *https://www.eia.gov/electricity/data/eia860/*

Form 923 provides monthly and annual data for electricity generation, fuel consumption, fossil fuel stocks and receipts at the power plant level (EIA 2018). At larger utilities (10MW and above) boiler level data are available. Beginning in 2007, environmental data including FGD unit operations was included in the form. *https://www.eia.gov/electricity/data/eia923/*.

Source water bromide data are not widely available. Source water bromide data from the Information Collection Rule for 1997-1998 can be accessed through US EPA (USEPA 2000). Bromide data are also available for a multi-year study in the early 1990s from the American Water Works Association (Amy, Siddiqui et al. 1994). More recent surface water data is available from select organizations and projects. In Pennsylvania, the PA DEP water quality network can be used directly *(http://www.depgis.state.pa.us/WQN/*) or accessed through STORET, where these data and other bromide data are stored by EPA *(https://www.waterqualitydata.us/*). Regional water quality sources are also available, but may be more difficult to locate and access. In Pennsylvania, sources include Susquehanna River Basin Commission (SRBC) *(http://mdw.srbc.net/remotewaterquality/*), Three Rivers Quest *(http://3riversquest.org/*). For the Ohio River Basin, the Ohio River Valley Water Sanitation Commission (ORSANCO) *(http://www.orsanco.org/data/*) has river data. The Water Research Foundation recently funded a nation-wide occurrence survey of bromide and iodide in water supplies (Westerhoff 2018), which may provide additional more recent information to enable a national review of at-risk watersheds. Disinfection by-product data from the Information Collection Rule can be accessed through US EPA (USEPA 2000). Recent data are available from PA Department of Environmental Protection Drinking Water Reporting System. *http://www.drinkingwater.state.pa.us/dwrs/HTM/Welcome.html*.

For other states, species-specific DBP data are available from regulatory agencies through state portals as described by Seidel et al (2017).

Section 3. Evaluate bromide concentration contributions from each upstream power plant at each downstream drinking water plant

For a specific power plant permit (selected using one of the methods described in Section 2 of this report), the effect of its bromide discharges on bromide concentrations at downstream drinking water intakes can be assessed using the methods described in recent work by Good and VanBriesen (2016, 2017, 2018). Briefly, this involves estimating the power plant bromide loads (kg/day) from monthly coal consumption data (type and amount) and estimated bromide concentrations in different types of coal, either using general ranges or using ranges specifically reported for coal mined from the counties identified as delivering to the relevant power plant (Kolb, Good et al. 2019). Following the load estimates, receiving water flow variability must be considered to enable an estimate of bromide concentration at river locations with drinking water intakes. **Figure 14** is a schematic of the necessary models and integration steps; the steps are described in more detail below.

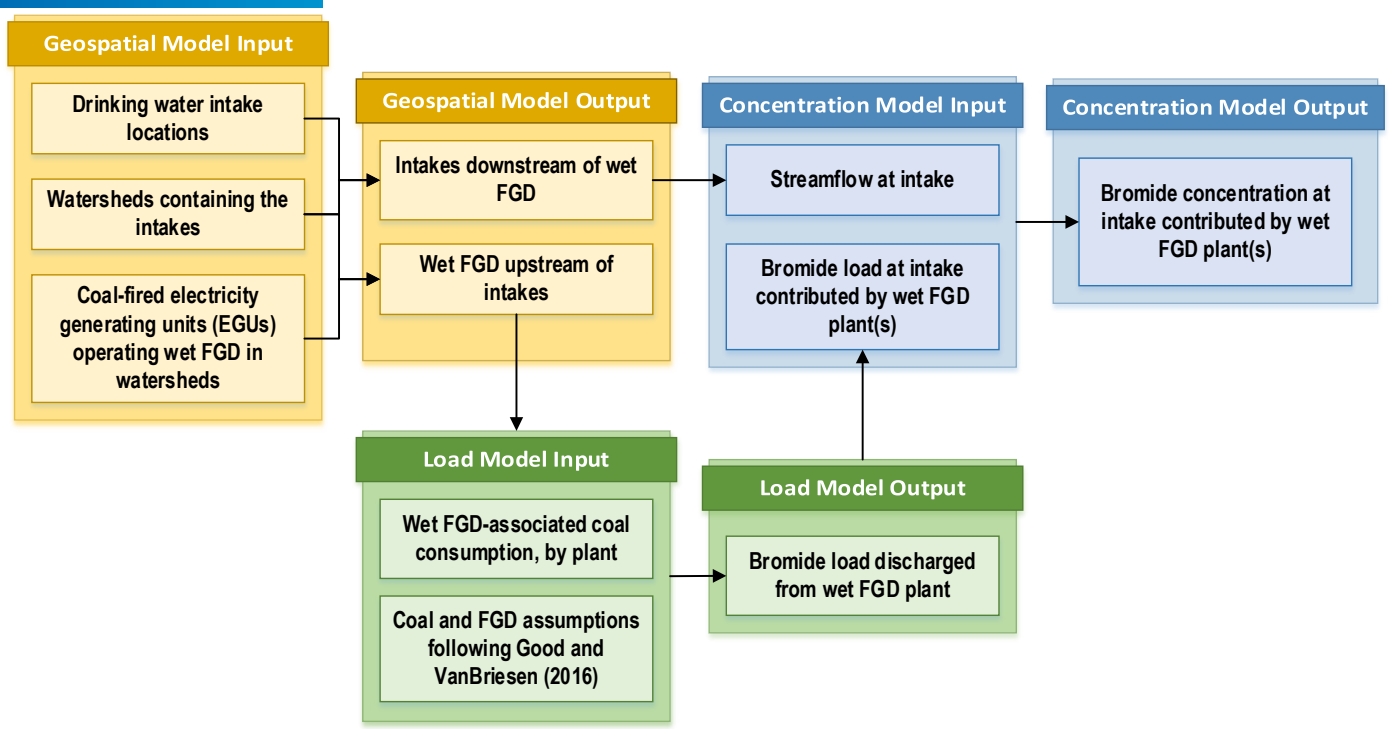


Figure 14. *Schematic of model components to predict bromide concentration contributions from power plants (Good and VanBriesen 2017).*

© Copyright 2019 American Water Works Association

Step 1. Linking each NPDES-permitted power plant with potentially affected drinking water utilities

Bromide is conservative, and thus, once discharged into the environment, it has the potential to affect any drinking water treatment facilities that are downstream of the discharge point. Limited geographic analysis to determine potentially affected drinking water utilities, such as the EPA's five mile buffer described in the Effluent Limitation Guidelines (ELGs) for Steam Electric Power Plants Environmental Assessment[4] (USEPA 2015c), is not supported by either the physical-chemical behavior of bromide in the environment or recent analyses (Good and VanBriesen 2016, Good and VanBriesen 2017, Good and VanBriesen 2018). However, river flow and watershed drainage area between the discharge point and downstream drinking water intakes matters because dilution can reduce concentrations of bromide. Thus, the effect of a particular power plant discharge on a particular drinking water utility depends on the flow conditions between the discharge and the intake. Multiple power plants can affect a single drinking water intake and multiple intakes can be affected by a single power plant (as shown schematically in **Figure 1**).

To consider potential control of bromide discharges, the first step is to locate the drinking water plants downstream of each power plant. This is relatively straight-forward to do using geographic information system software if the locations of drinking water utilities are known. However, exact locations for public drinking water utility intakes are considered sensitive information and are not available to the public. Permit writers and other state and federal government officials should be able to access these data. However, even in the absence of this access, it is possible to use a recently developed EPA tool that provides locations at the watershed scale (12-digit HUC) to provide adequate resolution for initial assessment. The Drinking Water Mapping Application to Protect Source Waters (DWMAPS) includes drinking water source information from the Safe Drinking Water Information System (SDWIS) at 12-digit HUC level (USEPA 2016a, USEPA 2018b). A recently completed analysis joined information from DWMAPs to NHD Flowlines in ArcGIS (ESRI-Inc. 2016) to enable identification of flow paths downstream of wet FGD receiving waters that intersect watersheds containing source waters for drinking water systems (Good and VanBriesen 2018). For the contiguous U.S., the dataset included 9,134 surface water facilities (intakes, reservoirs, springs, infiltration) for 6,802 systems serving 134 million people in 5,177 watersheds. **Figure 15** shows these results.

4 In the Environmental Assessment for the ELGs (EPA 2015), an analysis using a 5-mile range around each power plant suggested that few power plants had drinking water plants downstream that could be affected by bromide discharges.

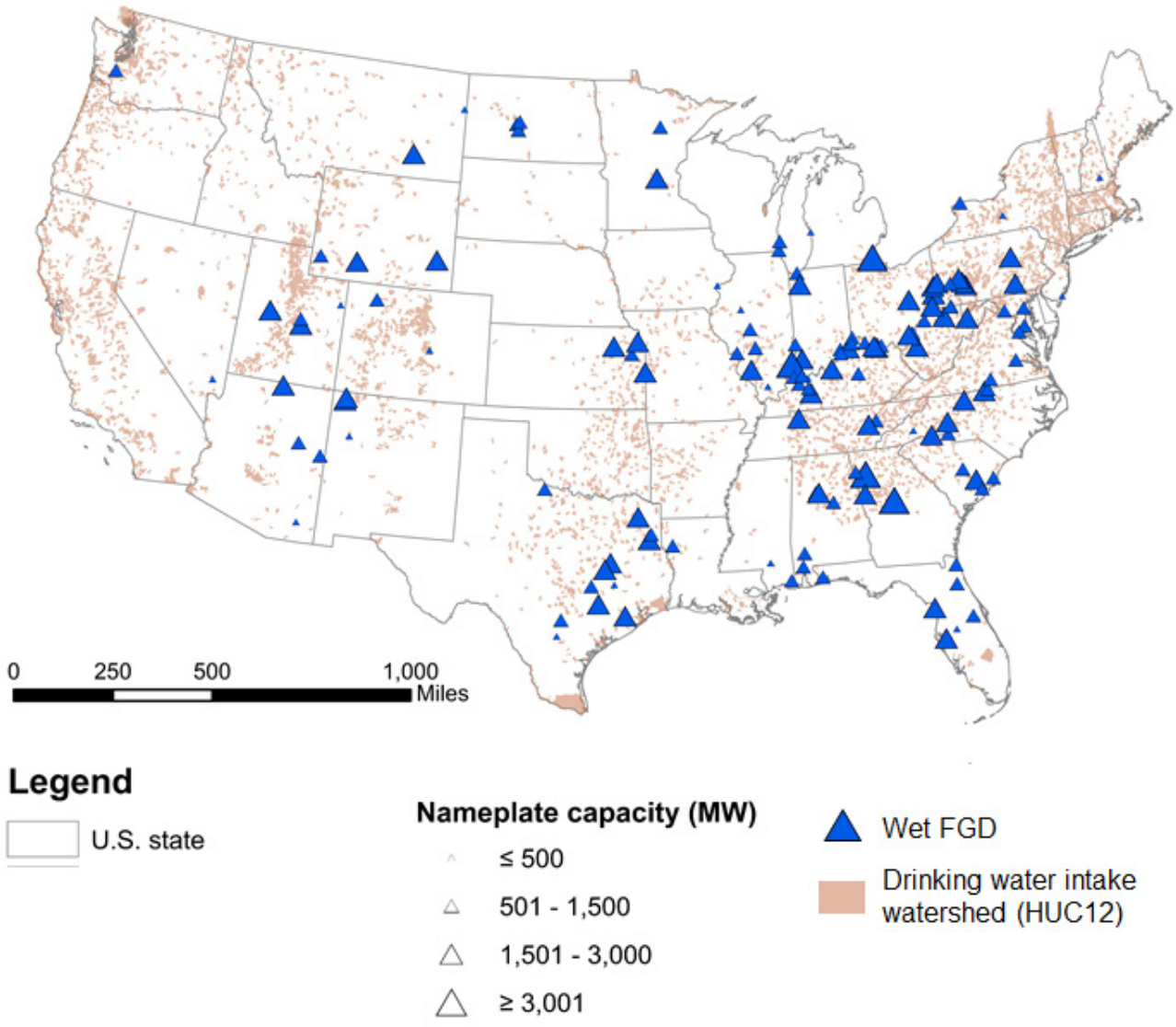


Figure 15. *Identified power plants with wet FGD (blue triangles) upstream of HUC12 watersheds that contain drinking water intakes (pink). Figure adapted from Good and VanBriesen (2018)and courtesy Dr. Kelly Good.*

© Copyright 2019 American Water Works Association

Step 2. Estimate power plant bromide loads.

Power plants discharge multiple waste streams through multiple outfalls, described in their National Pollutant Discharge Elimination System (NPDES) permits. Bromide concentration is not routinely monitored in power plant discharges (or in most other industrial or domestic discharges). Wet FGD wastewater, which is the largest source of bromide, is often mixed with other wastewaters prior to discharge (see **Figure 34** in Section 5). Thus, point bromide measurements from current power plant discharges[5] are unlikely to be useful for estimating bromide loads or predicting downstream effects at drinking water plants.

Power plant FGD bromide discharges can be *predicted* using a load-based assessment, following the work of Good and VanBriesen (2016, 2017, 2018); this is the lower section of **Figure 14** (in green). This method incorporates uncertainty associated with bromide content in coal and operational effects on bromide fate within the power plant. Predicted uncertainty in loads can be reduced by improved information on coal deliveries (e.g., information on the location where the coal was mined; daily coal use data from the power plant) and coal additives (e.g., specific bromide addition amounts at a specific power plant on a daily basis). Bromide loads from cooling towers can also be estimated if information about application rates and intermittent discharge are known for a specific power plant. **Figure 16** shows a corrected version of the equation originally reported in Good and VanBriesen (2016).[6] **Table 3** provides the relevant input parameters for the load estimate.

5 In the future, if flow-weighted bromide measurements are made of FGD wastewater at internal monitoring points as required in the 2016 ELGs, load estimates may be able to be made from discharge monitoring data.

6 Good and VanBriesen (2016) contained an error in this equation. A correction has been submitted to the journal.

$$\text{Estimated wet FGD Br load, kg/day} = \left(\begin{array}{c}\text{Wet FGD–associated}\\ \text{coal consumption,}\\ \text{as received,}\\ \text{million kg/day}\end{array}\right) \times (1 - \textit{moisture content}) \times \left(\begin{array}{c}\text{Br capture in}\\ \text{wet FGD,}\\ \%\end{array}\right) \times \left[\left(\begin{array}{c}\text{Br content,}\\ \text{ppm dry coal}\end{array}\right) + \left(\begin{array}{c}\text{Br added for}\\ \text{Section 45 or MATS,}\\ \text{ppm dry coal}\end{array}\right)\right]$$

Coal consumed (dry basis)

EIA Form 923: Monthly coal consumption by rank, as-received (bituminous, subbituminous, lignite, refined coal, waste coal)

COALQUAL v3 moisture data by rank

Portion of Br captured in wastewater

Estimated as 84% based on median of reported values Peng et al. (2013) Meij (1994)

Br content naturally present in coal *and, if applicable,* Br added for Section 45 tax credit / MATS purposes

COALQUAL v3 Br content data by rank

Values in literature vary widely; Br addition rates are not reported to IRS or EIA; data needed from each utility operator

Figure 16. *Bromide load estimate calculation method and data sources. Following Good and VanBriesen (2016, 2017, 2018) corrected. Data references: (Meij 1994, Peng, Li et al. 2013, Palmer, Oman et al. 2015, EIA 2018). Figure courtesy Dr. Kelly Good.*

Table 3. *Wet FGD bromide load model input parameter ranges. Adapted from (Good and VanBriesen 2018).*

	BITUMINOUS	SUB-BITUMINOUS	LIGNITE	REFINED COAL
Br content ppm dry coal	4.2 to 27.4 (13.8)	0.88 to 5.4 (2.3)	1.9 to 5.5 (3.0)	Depends on source coal
Br added to coal for Hg control, ppm dry coal	25 to 200			
Br added to refined coal, ppm dry coal	0 to >460			
Moisture content of coal	5-10% (6.5%)	10-30% (27%)	30-70% (34%)	9.5-23% (16%)
Br capture in wet FGD	77-100% (84%)			

Table 3 Notes: Coal bromide content ranges listed represent the interquartile range (25th to 75th percentiles) of data reported by coal rank in CoalQual (Palmer, Oman et al. 2015); value in parentheses is the median of reported data. Values for bromide addition are sourced from: (EPRI 2006, Benson, Holmes et al. 2007, EPRI 2008, Dombrowski, Paradis et al. 2010, Dutton, Rosvold et al. 2010, EPRI 2011, Frank 2011, Berry 2012, EPRI 2014, Gadgil, Abbott et al. 2014). Methods for moisture content and capture estimates are described in (Good and VanBriesen 2018).

 © Copyright 2019 American Water Works Association

Step 3. Extract and analyze river flow information.

Bromide concentration is affected by load (step 1) and by the variability in flow characteristics in the receiving water (this step and the blue boxes in **Figure 14**). **Figure 17** shows the period of record mean annual flow for the four largest rivers in Pennsylvania as cumulative distribution functions. The Monongahela regularly has the lowest mean annual flow (blue line at the far left), with a median value of 261 m3/sec, making this river the most susceptible to increasing bromide concentrations in response to anthropogenic discharges. Median values for annual mean flow conditions in the Ohio and the Susquehanna Rivers are similar and much higher (954 and 1067 m3/sec, respectively); however, both show significant inter-annual variability (wide range from top to bottom of curve). Either river could be susceptible to elevated bromide concentrations during years when mean flow was lower than usual (such as 2016 in the Susquehanna River, with a mean flow of 750 m3/sec); however, inter-seasonal variability could also be high during these periods. These annual flow values can be used to estimate bromide concentration contributions from the power plants; however, that approach would lead to over estimations of concentrations during the winter and spring and under estimations in the summer and fall due to significant seasonal flow variability. **Figure 18** shows monthly data for a single river as an example of the effects of seasonality.

As shown in **Figure 17** and **Figure 18**, receiving water flow conditions generally show inter-annual and seasonal variability that can be characterized by reviewing historical flow data. These historical data can be used directly to predict future flow conditions (assuming hydrologic stationarity) or estimates developed from the historical record can be used from the National Hydrography Dataset (NHD)(NHDPlusV2). Both methods have been developed for application to bromide concentration predictions (Good and VanBriesen 2016, Good and VanBriesen 2017). To consider the flow conditions *at each drinking water intake* potentially affected by an upstream power plant, geospatial hydrologic data can be extracted from the Watershed Boundary Dataset (WBD) as part of National Hydrography Dataset Plus Version 2 (NHDPlusV2), including river segments (ComID)(NHDPlusV2). Mean annual flow or minimum monthly flows for each relevant river segment (where there is a drinking water intake) can be used as baseline conditions (again, see (Good and VanBriesen 2017, Good and VanBriesen 2018). Alternatively, bromide concentration predictions could be made based on traditional 7-day 10-year low flow (7Q10) conditions or could be assessed based on flow conditions that are typical in a basin during third quarter, when DBP formation potential is generally highest due to operational changes associated with warmer water.

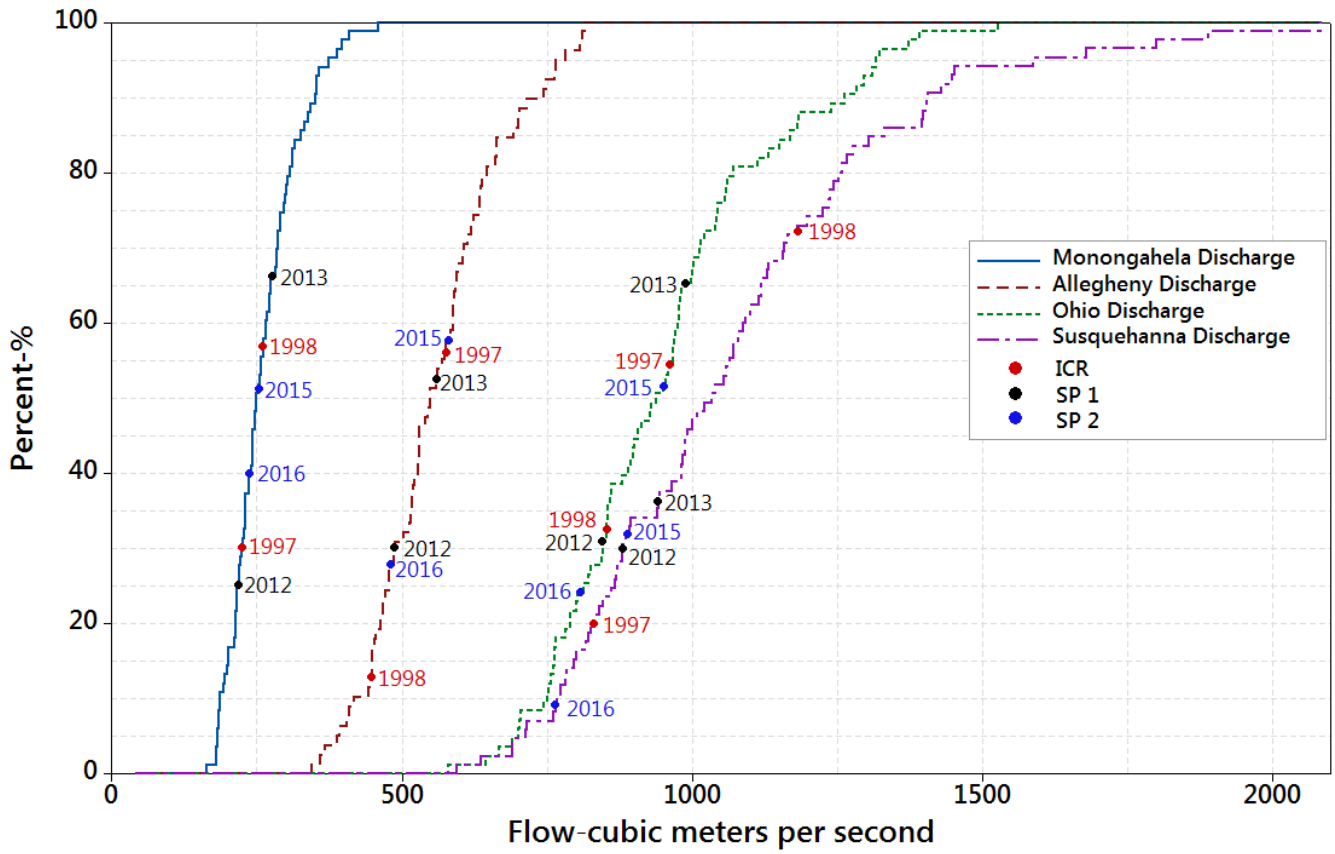


Figure 17. Cumulative distribution functions for flow in four Pennsylvania Rivers. Values for water years within the ICR and more recent periods are identified. (Cadwallader and VanBriesen 2019)

© Copyright 2019 American Water Works Association

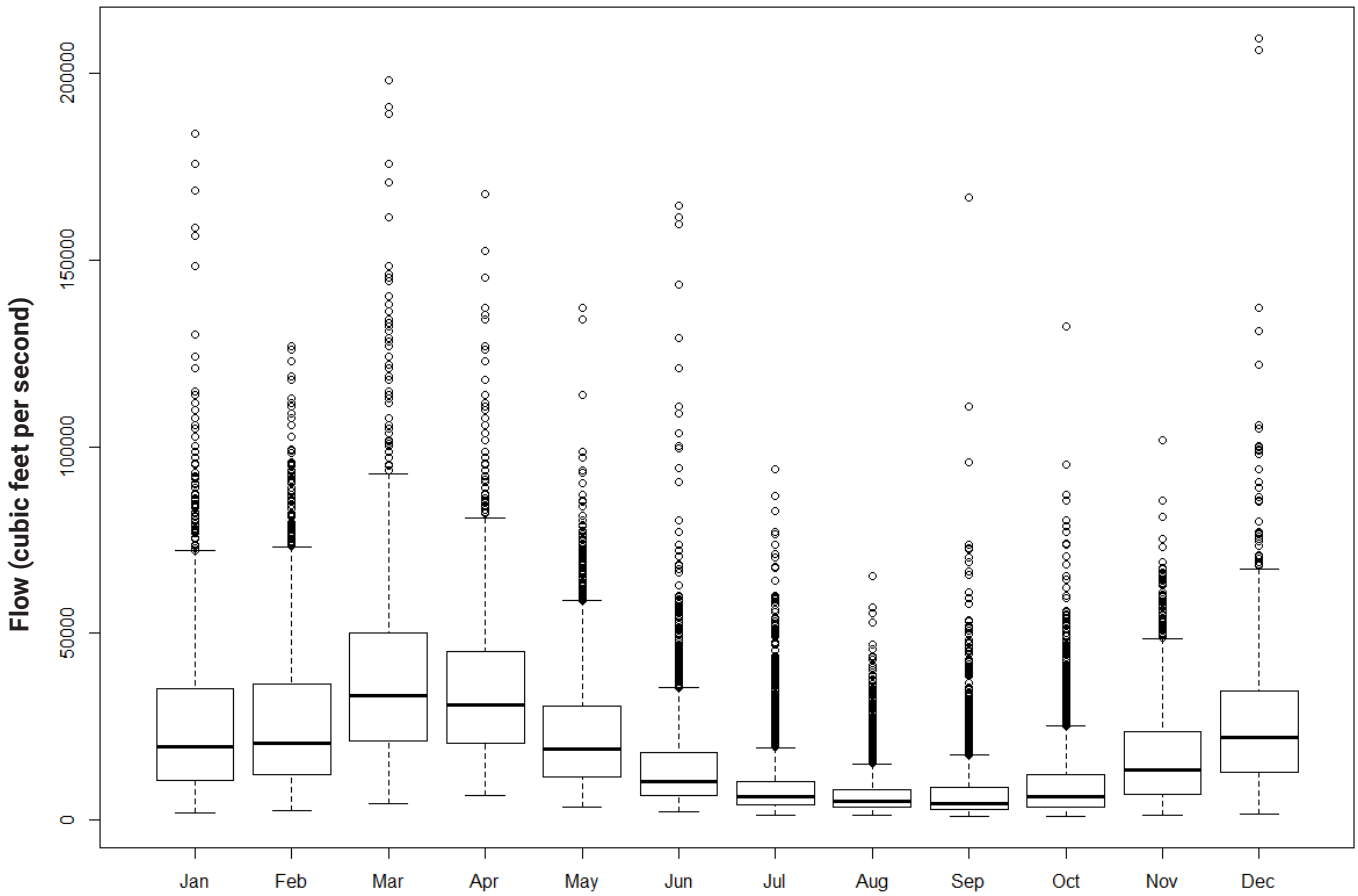


Figure 18. *Monthly mean daily flow data using USGS gaging station 03049500 (Allegheny River at Natrona, PA) for Water years 1939-2014. Solid line in the median for each month, boxes extend to the interquartile range (IQR) and whiskers extend to 1.5 times the IQR; open circles are values beyond this range. (Good and VanBriesen 2016)*

Step 4. Predict river bromide concentration contributions from load and flow estimates

Since bromide loads from power plants will be discharged into rivers that have inter-annual and seasonal flow variation described in **Step 3**, the concentration of bromide that could enter a downstream drinking water plant is likely to show significant variation even if upstream power plant loads are stable, which they may not be. It is the bromide concentration at the intake that affects the rate of DBP formation and the extent of bromine incorporation into DBPs. Thus, the estimated power plant load (**Step 2**) and the selected flow parameter (or range of parameters) (**Step 3**) must be combined to provide an estimate of the bromide concentration at the intakes (identified in **Step 1**). This estimate could be a point estimate based on a particular time of year (3rd quarter) or a particular river flow condition (e.g., 7Q10 or mean annual). The estimate could also be a range representing the expected values across an entire year or across specific flow conditions (e.g., the 5th to 95th percentile of the historic flow record). The calculation involved is simple, following Equation 1.

$$Concentration\left(\frac{mass}{volume}\right) = \frac{Load\left(\frac{mass}{time}\right)}{Flow\left(\frac{volume}{time}\right)} \quad (1)$$

Figure 19 shows the results for a single drinking water plant on the Susquehanna River affected by a single upstream power plant. The bromide load was estimated using 2015-2016 coal use data at the Montour power plant (capacity 1775 MW, all with wet FGD). In 2015, Montour burned 2.5 million short tons of bituminous coal (2.3 metric tons), while in 2016, it burned 1.7 million short tons of refined coal (1.5 metric tons). It is uncertain whether the use of refined coal involved the addition of bromide; however, the analysis presented in **Figure 19** included an estimate of bromide addition based on literature values. Under any flow condition in the river, an estimate of the bromide concentration contribution can be computed from the estimated load for the power plant (for base load or bromide addition load).7 As shown in **Figure 19**, under flow conditions represented by the median (computed from the EROM flow estimates for 1971-2000 for this location (McKay, Bondelid et al. 2018), the base bromide load estimate indicates a concentration contribution of 2.4 µg/L from this power plant to the intake (identified as plant 16 in (Good and VanBriesen 2017). However, under low flow conditions represented by 7Q10 for the Susquehanna River (91 m3/s), the contribution is 17 µg/L for base bromide load, and 50 µg/L under bromide addition conditions.8

7 After correction, in this scenario the base load would be estimated to be 110kg/L and the bromide addition load would be estimated to be 360kg/day

8 After correction, these concentrations would be 14 µg/L under the assume base bromide load and 46 µg/L under the assumed bromide addition scenario.

 © Copyright 2019 American Water Works Association

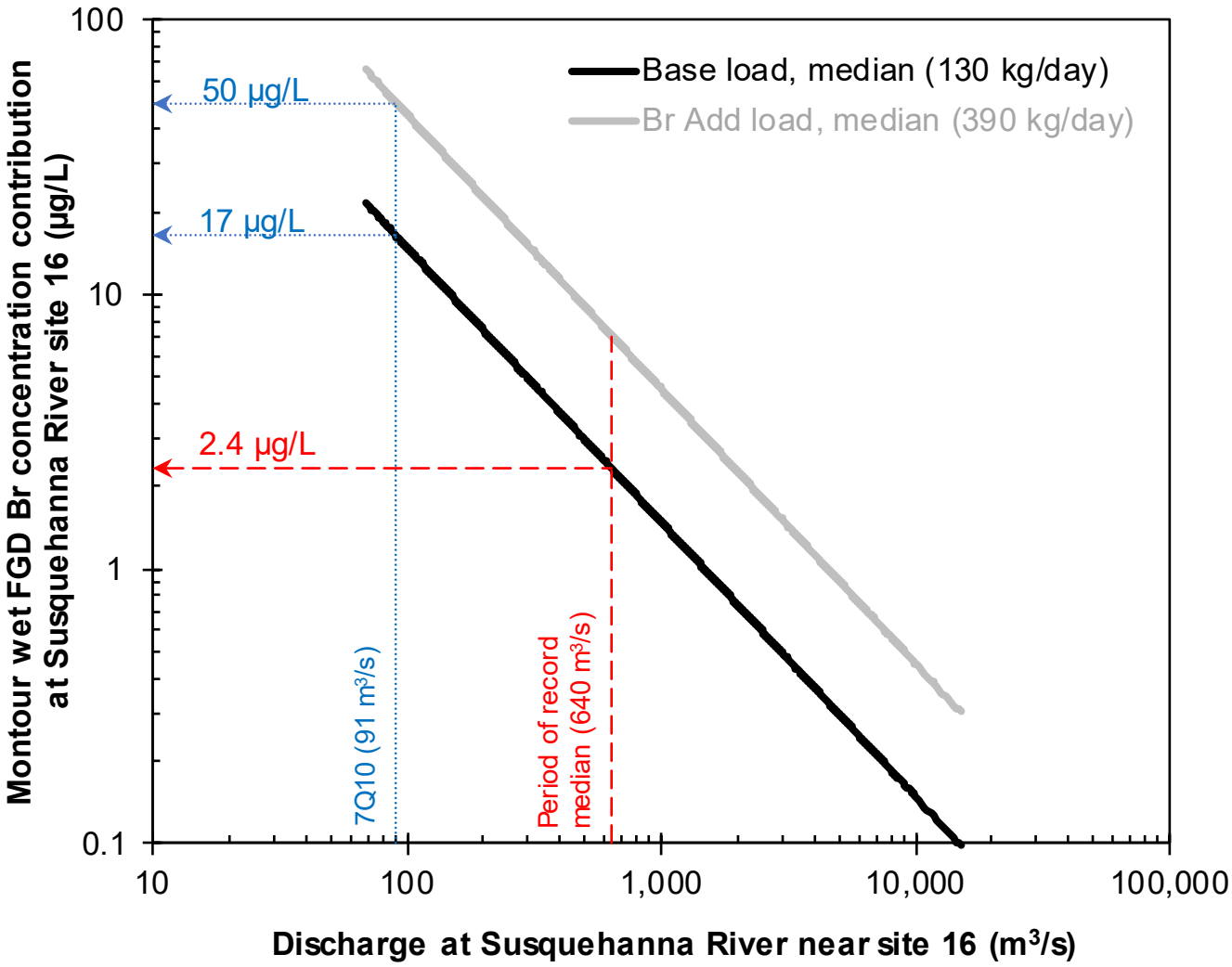


Figure 19. *Prediction of bromide concentration contribution at the drinking water intake at Good and VanBriesen (2017) site 16 from the discharge of wet FGD wastewater at the Montour power plant (based on 2015-2016 coal usage). (Adapted from (Good and VanBriesen 2017)).*

Step 5. Consider load and flow effects to narrow selection of power plants likely to affect downstream drinking water plants

While it is a simple matter to locate power plants and follow flowlines from discharge points downstream to identify all drinking water plants (see **Figure 15**), it is more difficult to assess when dilution will have rendered the bromide load effect too small to warrant consideration. Drinking water plants in close proximity to power plants with small bromide loads or on large rivers may be only minimally affected, while drinking water plants far downstream of large bromide discharges on rivers with smaller dilution capacity may see elevated bromide. These effects cannot be determined without analysis of the cumulative bromide loads from multiple sources and the river flow conditions.

For a single power plant or a small basin, a river-scale hydrologic model can be developed (see, for example, (Cornwell, Sidhu et al. 2018); however, it will have significant dependence on flow conditions that can be predicted only probabilistically and are subject to variability outside the historical record. Further, background or naturally-occurring baseline bromide data are not widely available and thus, model calibration will be difficult.

Good and VanBriesen (2018)assessed all power plants with wet FGD and estimated each power plant's concentration contribution under mean flow conditions to each downstream drinking water plant watershed. This analysis was designed to eliminate from consideration power plants that were unlikely to have significant effects on downstream drinking water plants. Good and VanBriesen (2018) identified 79 power plants operating wet FGD systems that have downstream drinking water utilities where concentration contributions exceeded 1 µg/L bromide under mean flow conditions, based on estimated loads for 2016 coal consumption data[9]. **Figure 20** shows these results.

This should *not* be considered an exhaustive list of potential effects since it does not consider whether the power plants might contribute less than 1µg/L at an individual drinking water plant but have a higher cumulative effect when considering multiple drinking water plants, or whether multiple power plants each contributing less than 1µg/L to a downstream HUC12 might have a cumulative effect of concern at a given drinking water facility. Selection of the conservative 1µg/L value (an order of magnitude below the effect level reported by Regli et al (2015)) was intended to avoid these limitations; however, it cannot account for combinations of effects outside the set of assumptions included in the model.

Further, this analysis does not consider potential changes to coal consumption (amount or type) in the future or changes in bromide addition for mercury control or refined coal tax credit at any facility. It also does not consider power plants that might now or in the future deploy FGD wastewater treatment that could alter bromide discharges. However, the *method* outlined in Good and VanBriesen (2018), after correction, can be used with different threshold levels or even flowline distances if desired to provide alternative impact assessments for specific power plants. Additional information related to bromide loading (from measurements of concentration and flow in discharges) and FGD treatment could also be incorporated into the analysis for individual power plants.

9 After correction for the error identified in the method, six fewer power plants would be identified (73 rather than 79).

 © Copyright 2019 American Water Works Association

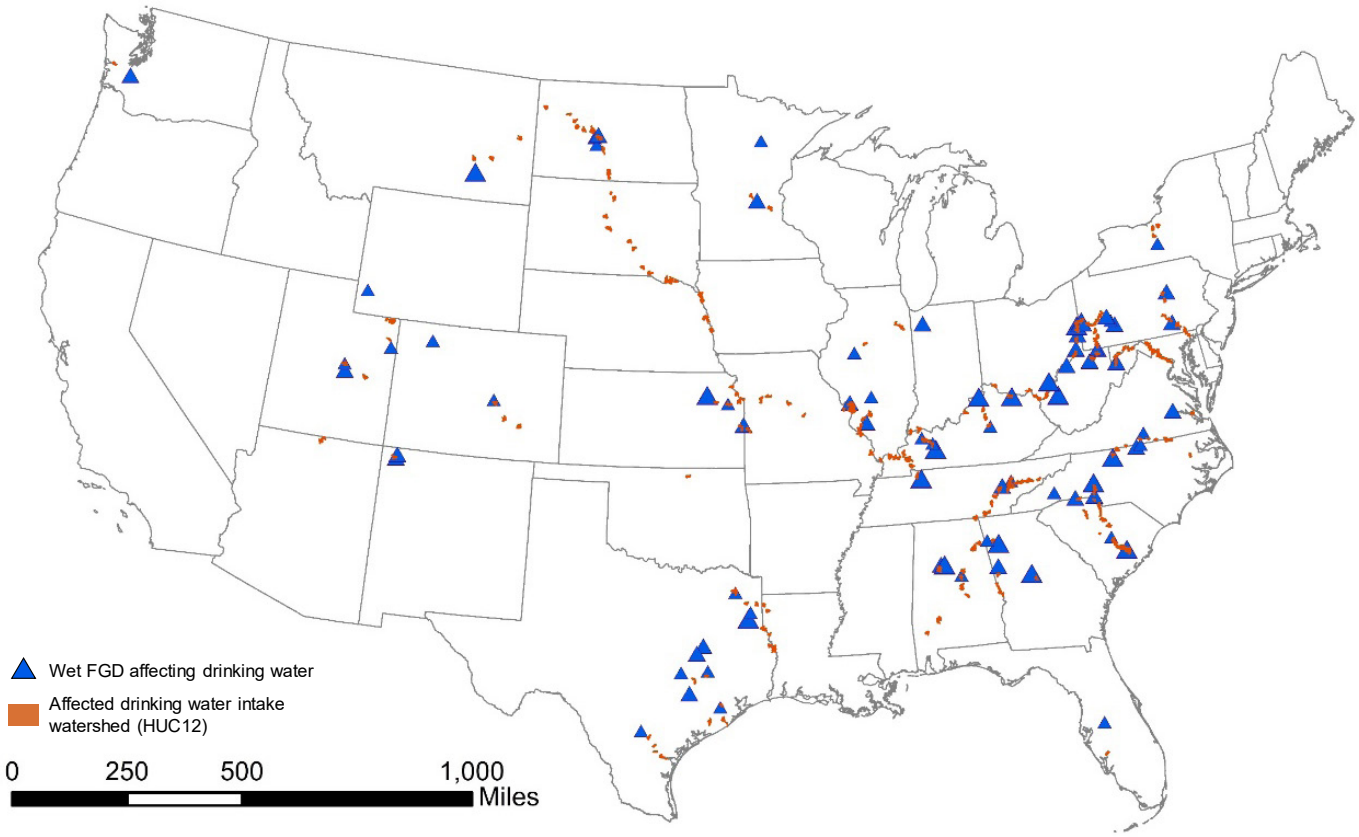


Figure 20. *Identified power plants with wet FGD (blue triangles) potentially affecting downstream drinking water intakes in identified HUC12 watersheds (orange), based on 2016 coal consumption data and NHD+ mean annual flow in receiving waters. Figure adapted from Good and VanBriesen (2018) and courtesy Dr. Kelly Good.*

Step 6. Integrate the effects on multiple drinking water plants from a single power plant discharge

While some power plants will have only one downstream drinking water plant, many will have the potential to affect more than one drinking water plant and these effects will depend on the power plant load and the flow conditions at multiple drinking water plants. In order to inform decisions about appropriate limits to NPDES-permitted bromide discharges at a specific power plant, its potential effect across *all* downstream drinking water utilities must be assessed.

The analysis in Good and VanBriesen (2018) identified 230 HUC12 watersheds containing surface water drinking water facilities with at least one upstream power plant bromide discharge modeled to produce at least 1 µg/L bromide in the watershed under mean flow conditions.[10] Half of these were affected by more than one discharge. These multiple effects will contribute to changing DBPs in the drinking water facilities, which will be discussed more fully in Section 4 below. For the NPDES permit writer, however, the key point is to determine the effects of *each* power plant on *all* the relevant downstream drinking water plants.

This involves integrating the results of the bromide concentration contribution from a single power plant for all the downstream drinking water plants. As an example, potential bromide discharges from the Mt Storm power plant (EIA 3954) in West Virginia (NPDES permit number WV0005525) were simulated. The analysis in Good and VanBriesen (2018) identified 26 active surface water facilities (in SDWIS) downstream of this discharge, serving a total population of 3.1 million. The intakes are in 15 watersheds (HUC12 level) and thus have different dilution factors under mean annual flow conditions. This results in different modeled concentration contributions for each intake. **Table 4** presents these data. An important caveat is that this power plant is listed as having or intending to have zero liquid discharge (ZLD) treatment for its FGD wastewater. Thus, the modeled concentration contributions in **Table 4** may not be representative of observations in this watershed if the bromide is being removed during treatment.

If a downstream concentration threshold were set at 10 µg/L under mean flow conditions, 8 drinking water facilities would be considered affected by this power plant (serving 133,524 people). If a threshold were set at 25 µg/L, only 6 utilities would be considered affected (serving 8,229 people). In this watershed, the largest populations are the furthest downstream, and thus have the potential to be affected only by much lower concentrations of bromide.

10 After correction for the identified methodological error, five fewer watersheds (225 rather than 230) would be identified as having at least one upstream power plant bromide discharge modeled to produce at least 1µg/L bromide in the watershed under mean flow conditions and based on 2016 coal consumption.

 © Copyright 2019 American Water Works Association

Table 4. *Modeled wet FGD bromide concentration contributions to downstream drinking water intakes from Mt Storm Power Plant (3954) under estimated mid-point bromide load and mean annual flow conditions. Adapted from Good and VanBriesen (2018).*

Sub-region (HUC4)	Watershed (HUC12)	SDWIS active surface water facilities, count	SDWIS active surface water facilities, population served	Mean Annual flow, m3/s	Modeled total wet FGD Br concentration contribution, µg/L
0207		**26**	**3,168,231**	**-**	**-**
	020700020202	1	2,072	9	286
	020700020205	1	370	14	186
	020700020207	2	915	22	121
	020700020403	2	3,200	29	90.5
	020700020803	3	1,150	51	51.9
	020700030801	1	522	105	25.3
	020700041103	2	115,335	174	15.3
	020700041106	3	9,960	194	13.7
	020700041108	1	2,122	293	9.10
	020700080202	1	6,394	299	8.92
	020700080401	1	46,769	303	8.80
	020700080403	1	58,500	338	7.88
	020700080904	1	1,074,422	357	7.46
	020700081005	5	1,846,500	363	7.33
	020700100103	1	0	366	7.27

Step 7. Integrate the effects of multiple power plants on a single drinking water plant

While NPDES permit decisions for the power plants will be made based on the role each individual power plant plays in contributing bromide to multiple downstream drinking water plants as described in the previous section, predicting the effect of bromide on drinking water plants (Section 4) requires integrating across multiple upstream sources, which may include multiple power plants and other natural and anthropogenic sources. **Figure 21** shows the results of predicting loads from multiple power plants on 21 drinking water intakes in Pennsylvania11.

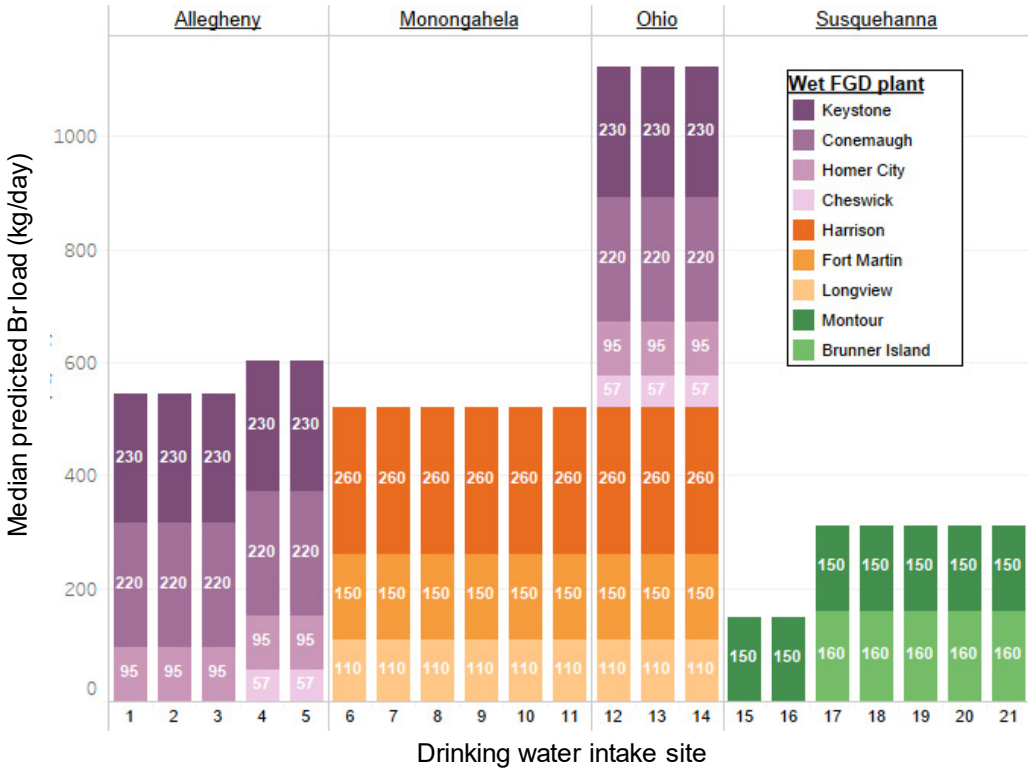


Figure 21. *Wet FGD load contributions (kg/day) for each drinking water intake site in Pennsylvania, based on median predicted August bromide loads. (Good and VanBriesen 2017).*

11 This figure is based on EIA 2016 coal consumption data published in April 2017. Subsequently EIA updated this information to include refined coal usage not originally included. Thus, estimated bromide load values in this figure do not account for refined coal consumption in 2016, which can contain additional bromide.

© Copyright 2019 American Water Works Association

Section 3 Data Sources

Completion of any of the analyses described in this section requires use of publicly-available data from numerous sources.

Power plant data are available from the Energy Information Administration (EIA). Form 860 provides generator-level information about existing and planned operation and associated environmental equipment at power plants operating with 1 MW or greater capacity (EIA 2017). *https://www.eia.gov/electricity/data/eia860/*. Form 923 provides monthly and annual data for electricity generation, fuel consumption, fossil fuel stocks and receipts at the power plant level (EIA 2018). At larger utilities (10MW and above) boiler level data are available. Beginning in 2007, environmental data including FGD unit operations was included in the form. Source information for coal is available at the county-level in Form 923. *https://www.eia.gov/electricity/data/eia923/*.

The United States Geological Survey (USGS) coal quality (COALQUAL) database was revised to include previously collected but not released bromine data in 2015 (Palmer, Oman et al. 2015). Bromine data in coal is available at the county-level, on a dry weight basis, allowing estimated bromide loads for power plants to reflect county-level coal type. *https://ncrdspublic.er.usgs.gov/coalqual/*.

Drinking water facility location data are not readily available; however, state and national regulatory agencies should have access to these data. The Drinking Water Mapping Application to Protect Source Waters (DWMAPS) includes drinking water source information from the Safe Drinking Water Information System (SDWIS) at 12-digit HUC level (USEPA 2016a, USEPA 2018b). *https://www.epa.gov/sourcewaterprotection/drinking-water-mapping-application-protect-source-waters-dwmaps*. Information about the facilities (e.g., population served) is available in SDWIS. *https://www.epa.gov/ground-water-and-drinking-water/safe-drinking-water-information-system-sdwis-federal-reporting*.

Flow data for receiving waters is available from the United States Geological Survey (USGS) at *https://waterdata.usgs.gov/nwis/rt*. The Watershed Boundary Dataset (WBD) as part of National Hydrography Dataset Plus Version 2 (NHDPlusV2), including river segments (ComID) is available for download (NHDPlusV2). *https://www.epa.gov/waterdata/nhdplus-national-data* and a navigator toolbar is available *http://horizon-systems.com/nhdplus/nhdplusv2_tools.php*.

Disinfection by-product data from the Information Collection Rule can be accessed through US EPA (USEPA 2000). Recent data are available from PA Department of Environmental Protection Drinking Water Reporting System. *http://www.drinkingwater.state.pa.us/dwrs/HTM/Welcome.html*.

For other states, species-specific DBP data are available from regulatory agencies through state portals as described by Seidel et al (2017).

Section 4. DBP formation and associated risk at downstream drinking water plants

Perhaps the most challenging component of assessing the potential for power plant bromide discharges to negatively affect drinking water utilities is the difficulty in identifying a stable quantitative relationship between source water bromide *increases* and finished water DBP concentration *increases*, especially for the two class sum regulated values, total trihalomethanes (TTHM) and haloacetic acids 5 (HAA_5).[12] Further, the association between these class sum values and drinking water risk is complicated by the presence of many additional classes of disinfection by-products, including haloacetonitriles, haloketones, halonitromethanes, haloaldehydes, halogenated furanones, haloamides, and nonhalogenated carbonyls (Weinberg, Krasner et al. 2002, Krasner, Weinberg et al. 2006, Hebert, Forestier et al. 2010, Chen, Zhang et al. 2015), which can also be affected by bromide concentrations. TTHM and HAA_5 concentrations may not be adequate to represent drinking water risk (Weinberg, Krasner et al. 2002, Bull, Rice et al. 2009a, Bull, Rice et al. 2009b), particularly when source water bromide is elevated and TTHM and HAA_5 bromine incorporation does not predict other bromine incorporation rates (Francis, VanBriesen et al. 2010).

Despite these challenges, higher bromide source waters are widely reported to cause higher DBP formation and increased bromine incorporation of the DBPs that form (Westerhoff, Chao et al. 2004, Heeb, Criquet et al. 2014). Laboratory experiments have been used to develop relationships between bromide concentrations and DBP concentrations (Hellergrossman, Manka et al. 1993, Pourmoghaddas, Stevens et al. 1993, Symons, Krasner et al. 1993, Krasner, Sclimenti et al. 1996, Wu and Chadik 1998, Diehl, Speitel et al. 2000, Hua, Reckhow et al. 2006, Ates, Yetis et al. 2007, Bond, Huang et al. 2014). Field work confirms these observations (Duong, Berg et al. 2003, Ye, Wang et al. 2009, Chang, Tung et al. 2010, Charisiadis, Andra et al. 2015). Similarly, in surveys of U.S. drinking water utilities, higher source water bromide was associated with higher levels of brominated DBPs in finished water (Amy, Siddiqui et al. 1993, McGuire and Hotaling 2002, Weinberg, Krasner et al. 2002), and source water bromide concentration is a predictor of DBPs species (Obolensky and Singer 2005). Amy et al (1994) found "virtually any level of bromide present in a water source can potentially form brominated chlorination by-products, such as THMs," and Amy et al (1993) suggest that "given the efficient conversion of bromide to DBP-bound bromine (DBP-Br), even trace levels of bromide (e.g., <10µg/L) can be problematic."

Figure 22 shows THM species concentrations for surface water sources with different bromide concentrations from the D/DBP Rule ICR database (USEPA 2000). The data were binned by examination of the bromide concentration distribution in the database (median 30 µg/L). Below detection data were classified as low; the detection limit was 20 µg/L. Values between the detection limit and the 75th percentile were classified

12 The primary trihalomethanes include four regulated species: chloroform; bromodichloromethane, BDCM; chlorodibromomethane, CDBM; and bromoform; three of these contain bromide. The sum of the four regulated THM is referred to as THM4 or sometimes total trihalomethanes (TTHM). While iodated and mixed chloro-bromo-iodo THM exist, and thus THM4 is not equal to TTHM, in the present work these terms will be used interchangeably. The HAAs include five regulated forms (monochloroacetic acid, MCAA; dichloracetic acid, DCAA; trichloroacetic acid, TCAA; monobromoacetic acid, MBAA; dibromoacetic acid, DBAA), which include two bromine-containing compounds; the sum of the five regulated forms is often reported as HAA5. There are also four unregulated but commonly observed HAAs (bromochloroacetic acid, BCAA; dibromochloroacetic acid, DBCAA; bromodichloroacetic acid, BDCAA; tribromoacetic acid, TBAA,), which all include bromide. These four are sometimes referred to as HAA4, and the sum of HAA5 and the four unregulated forms is reported as HAA9.

as moderate (20-36 ug/L); while values between the 75th and 90th percentile were considered high (31-71 ug/L); and values above the 90th percentile were considered very high (>71 ug/L). With low or moderate source water bromide, THM is dominated by chloroform (light blue at the left of each panel). With increasing bromide (moving right), the amount of BDCM (dark blue) increases, and its median value exceeds chloroform for very high bromide concentrations. Similarly, DBCM (light green) is negligible at low bromide concentrations but exceeds chloroform when bromide is very high. Bromoform (dark green) is rarely detected unless the bromide is very high.

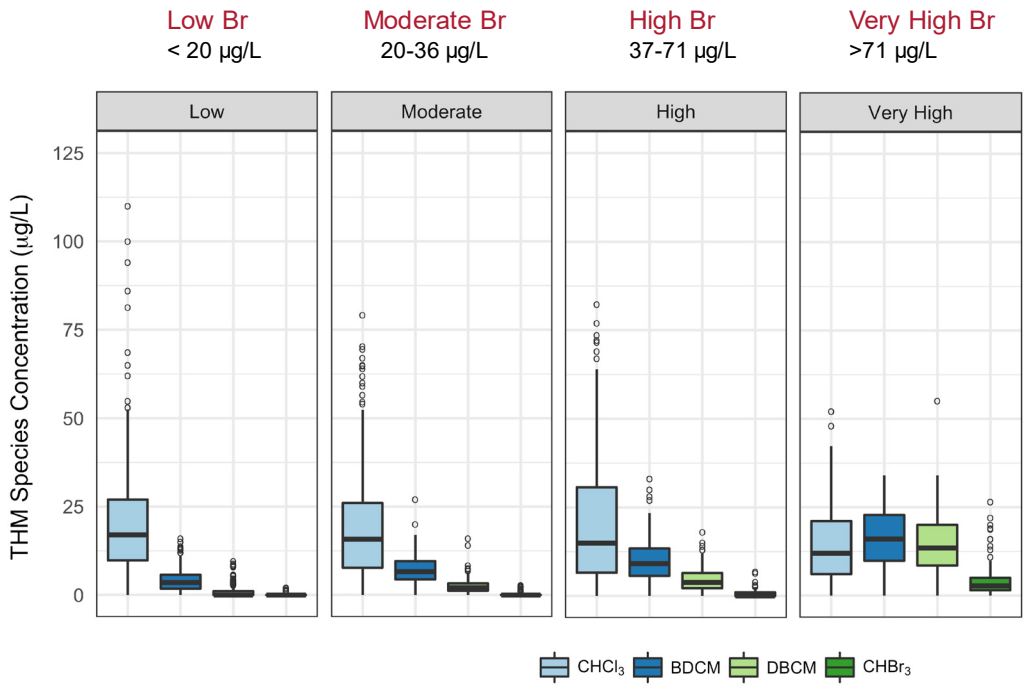


Figure 22. *THM species concentration for different surface water source bromide concentrations. The box plot for each species includes a solid line for its median value. The box extends to the interquartile range (IQR), and the whiskers extend to 1.5 times the IQR. Open circles indicate values outside this range. Figure courtesy Dr. Chelsea Kolb. Data analysis from (Kolb, Francis et al. 2017).*

Figure 23 shows a typical field study result, in this case from the Monongahela River. The top panel is measured bromide in the influent (in µg/L) and the bottom panel is finished water measurements of THM speciation (left axis in µg/L) and bromine incorporation (right axis in percent). Lower bromide levels from Fall 2009 through Spring 2010 correspond with predominately chloroform (red bars) in the finished water. The increase in bromide in the source water, starting mid-2010, corresponds to an increase in bromine-containing THM species, shown as orange, yellow and green bars. The fraction of bromine containing THM (by mass) also increases (blue dots). TTHM (the sum of the species, shown as the top of the stacked bar) follows its typical seasonal pattern, with higher levels in the summer and lower in the winter, consistent with prior observations that TTHM is strongly influenced by source water total organic carbon (TOC), temperature and applied chlorine dose, all of which show seasonal effects. HAA results show similar patterns; however, at elevated source water bromide concentrations, HAA speciation shifts toward the four unregulated forms and the regulated HAA5 concentration may decline. **Figure 24** shows a plot of observed bromide concentrations and finished water TTHM (top) and bromine incorporation by mass in TTHM (bottom) for all sites in the Monongahela River field study. As expected, bromide alone cannot predict TTHM concentrations; however, it is predictive of the incorporation of bromine into TTHM. As an alternative approach to developing a predictive model based solely

© Copyright 2019 American Water Works Association

on bromide, Wang et al (2016) considered the Monongahela River data and created a statistical model using bromide bins. **Figure 24** shows the probability of a utility meeting the TTHM standard (80 µg/L) or the target concentration in finished water (80% of the standard; 64 µg/L) as a function of a range of bromide concentrations. As bromide concentrations increase in the source water, the probability of meeting the standard declines from 90% to 60%, again confirming that bromide increases TTHM, making compliance with the TTHM standard more difficult.

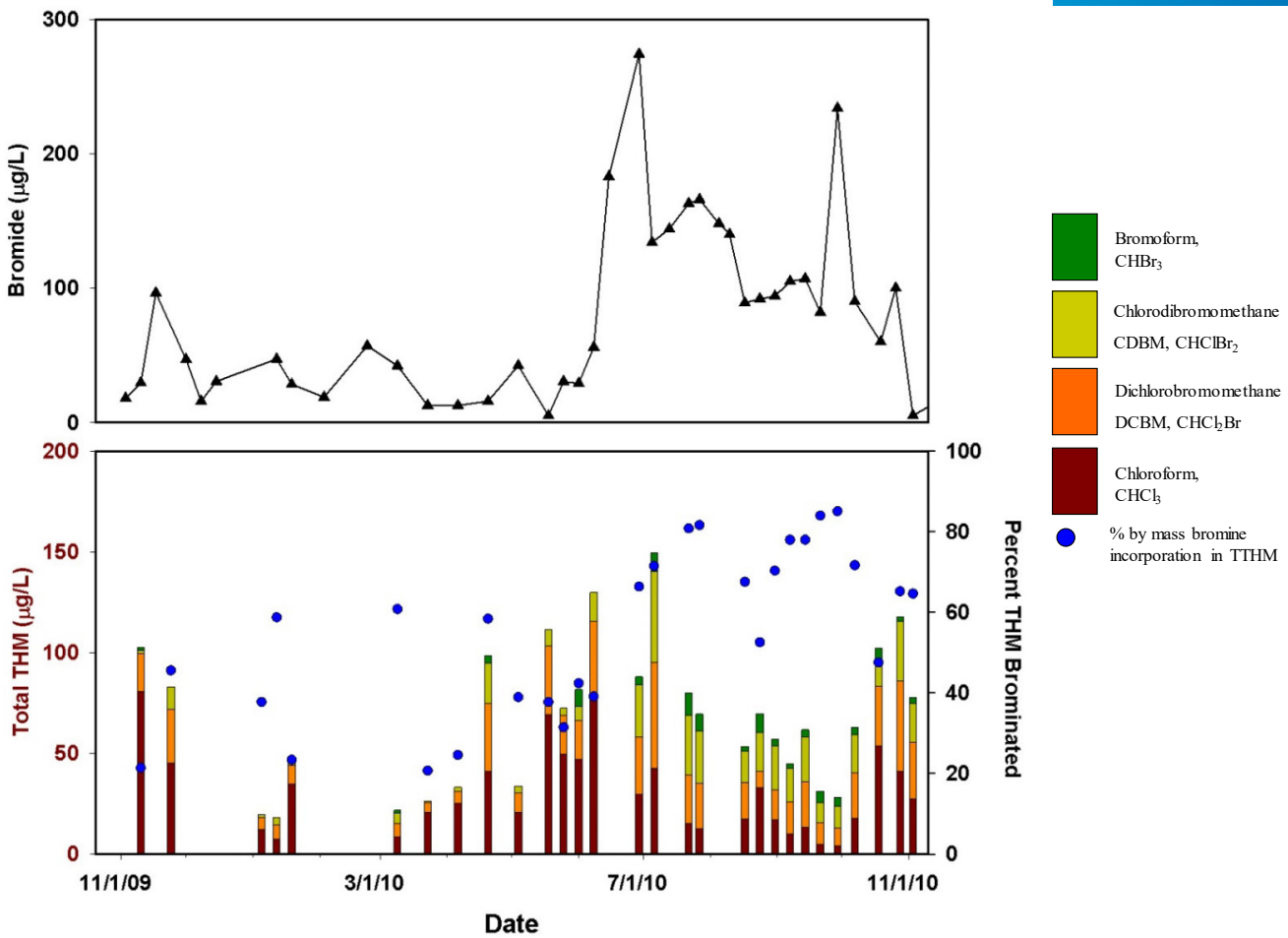


Figure 23. *Measured surface water intake bromide concentration (top; µg/L) and THM species in finished water (bottom, left axis) and mass-based bromine-incorporation (bottom, right axis). Data from Wang et al (2016). Figure courtesy Dr. Jessica Wilson.*

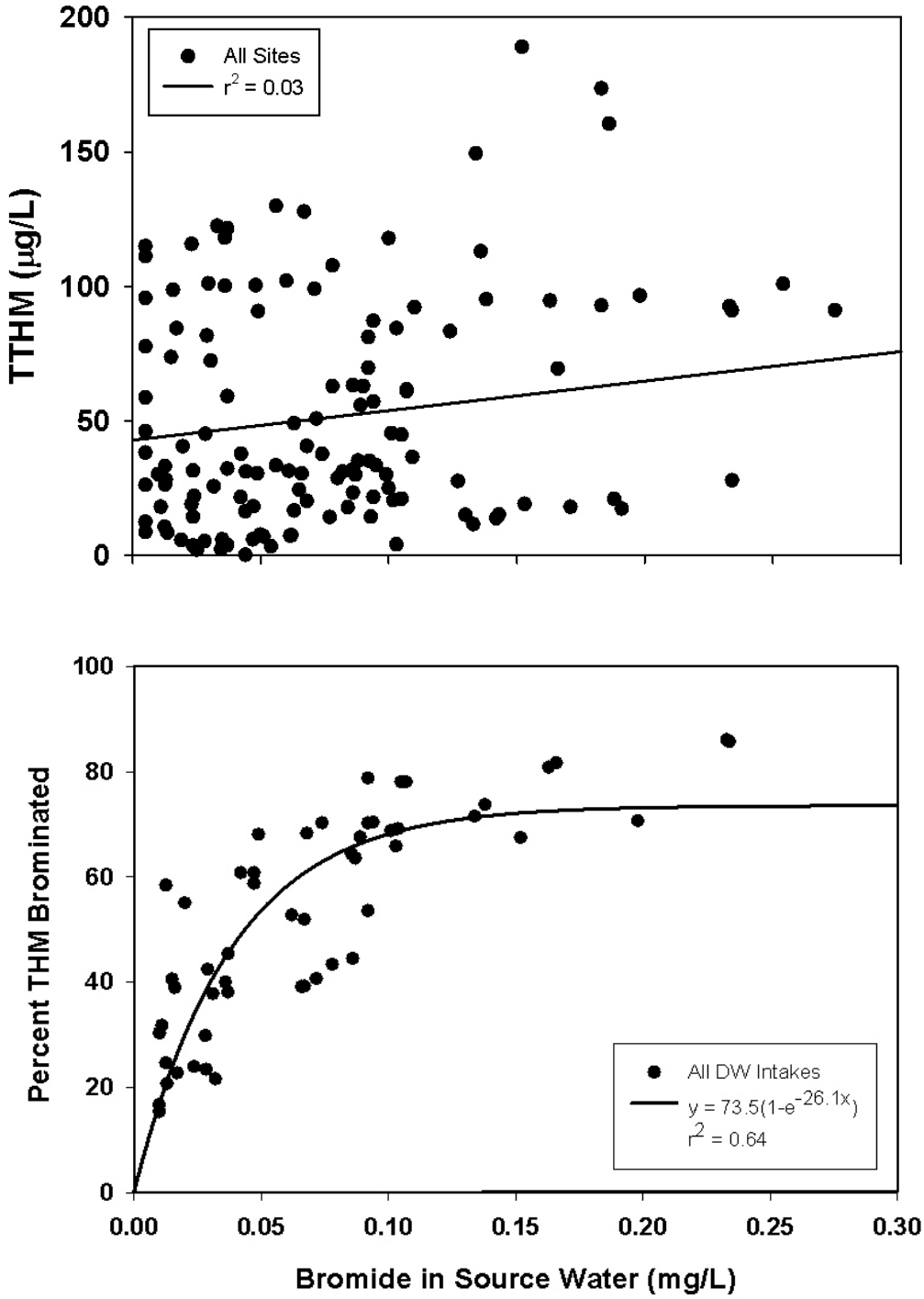


Figure 24. *Relationship between measured surface water intake bromide concentration and TTHM in finished water (top) and bromine incorporation (bottom) from field study in the Monongahela River (2009-2011). Data from Wang et al (2016). Figure courtesy Dr. Jessica Wilson.*

© Copyright 2019 American Water Works Association

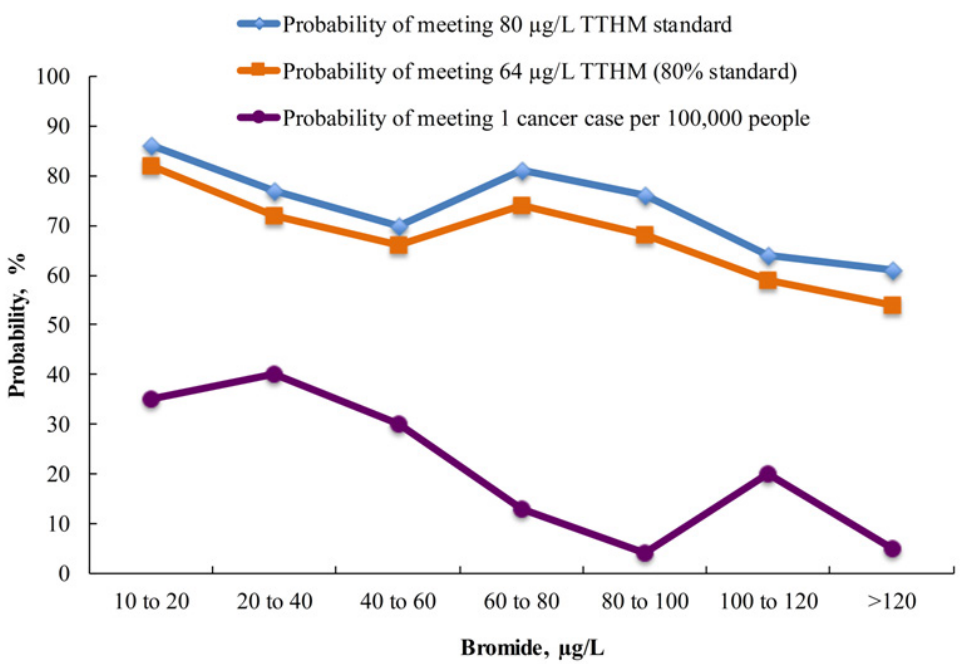


Figure 25. ***Probability of meeting TTHM standard (blue), 80% of standard (orange) and risk threshold (purple) for source waters with different concentrations of bromide (Wang, Small et al. 2016).***

Modeling DBP Formation

Assessing the role of power plant bromide contributions in DBP formation and associated risk will require models that either predict DBP formation (as TTHM, HAA5, or their species) or predict drinking water risk *based on increases in bromide concentrations*. This is a significant challenge since occurrence studies show wide variation in DBP levels associated with different source water bromide levels (Amy, Siddiqui et al. 1994, McLain, Obolensky et al. 2002), and DBP concentrations are generally dependent on multiple factors.

Many models have been developed to predict DBPs in finished water using source water conditions (e.g., bromide, organic carbon concentrations, temperature) and plant operational conditions (e.g., disinfectant dose) (Sadiq and Rodriguez 2004, Chowdhury, Champagne et al. 2009, Ged, Chadik et al. 2015). Many of these models were developed using databases that contain predominately low bromide source waters, and thus, the models do not include bromide as an explanatory variable; Ged et al (2015) report models without bromide are less accurate across a wide range of waters. When models do include bromide, they predict higher brominated THM species with higher source water bromide concentrations; however, the prediction range is quite wide, especially with respect to the TTHM MCL13 (Ged, Chadik et al. 2015). As an example, **Equation 2** is the predictive model for TTHM developed by Malcolm-Pirnie (1993).

$TTHM = 7.21(TOC)^{0.004}(pH-2.6)^{0.719}(TEMP)^{0.480}((Cl_2DOSE)-7.6NH3)^{0.224}(Br+1)^{2.01}(UV-254)^{0.534}(time)^{0.255}$	**(2)**
TTHM is predicted in µg/L; TOC=Total Organic Carbon (mg/L); Br=bromide concentration (mg/L); Cl_2DOSE=chlorine dose (mg/L as Cl_2); UV-254 = ultraviolet absorbance at 254 nm wavelength (cm^{-1}); time=contact time (hours); TEMP=temperature (°C); NH3 = ammonia concentration (mg/L)	

A challenge to use of **Equation 2** (and similarly designed models) is that many source water and operational parameters are required. Using this type of model at each drinking

13 Ged et al (2015) report models are accurate to ±48 µg/L TTHM, which is not very useful since the MCL is 80 µg/L.

water plant potentially affected by bromide discharges from power plants will require working with the utilities to acquire operational data. Alternatively, a modeler could assume no other parameters would change and use the equations to predict the change in DBP species in response to changes in bromide. Regli et al (2015) used this approach by using the EPA Water Treatment Plant (WTP) model and the ICR database. Assuming all conditions other than bromide remained the same for each utility, they used the WTP model equations (Malcolm-Pirnie 1992)

to predict TTHM concentrations for changes in source water bromide levels. They report a 50 µg/L bromide increase caused a TTHM increase of 1 µg/L at 90% of the plants and a TTHM increase of 10 µg/L at 5-30% of plants; the median TTHM increase was 3.7 µg/L. They report a 10 µg/L bromide increase caused a median increase of 1.1 µg/L in TTHM, with 5% of the plants showing a 3.4 µg/L or greater increase. Regli et al (2015) did not include a predictive model based on their results since the underlying analysis was dependent on the WTP model. Use of the WTP model should yield comparable results; however, this requires extensive plant operational data and thus the TTHM contribution from power plant bromide discharges cannot be simulated directly from solely the estimated bromide concentration contributions.

Recently, Cornwell et al. (2018) developed a model to predict TTHM formation under variable source water bromide concentrations (**Equation 3**); the model required only the bromide concentration and the UV-254 value for the source water because the experiment was conducted at constant temperature.

$$[TTHM] = 10^{2.2269}\left[Br^{-}\right]^{0.2149}\left[UV-254\right]^{0.4279}$$	**(3)**
TTHM is predicted in µg/L; Br=bromide concentration (mg/L); UV-254 = ultraviolet absorbance at 254 nm wavelength (cm^{-1}); Temp held constant at 21°C; pH at 7.2	

Each of these generalized models can be used to predict TTHM from bromide concentration contributions from power plants; however, their suitability for any individual drinking water plant remains uncertain. An improved WTP model (under development by EPA (Yang 2017)) may enable better assessment of the potential effect of rising source water bromide concentrations on specific drinking water utilities, but this remains uncertain.

Plant-specific models may be more accurate than generalized models, especially when developed for sites with varying bromide concentrations. As described above, Wang et al (2016) developed a statistical model for prediction of TTHM for drinking water utilities on the Monongahela River that enabled assessment of compliance probability. Bergman et al (2016) created a classification tree model for TTHM based on the field work of Wilson and Wang (Wilson, Wang et al. 2013, Wilson and VanBriesen 2014, Wang, Small et al. 2016); this model requires excitation emission fluorescence spectroscopy information as input, limiting its predictive applicability since this is not a routinely measured value. When available, plant or river-specific models should be used to predict DBP species concentrations under changing bromide concentrations.

Figure 26 shows predicted TTHM using three different models (Malcolm-Pirnie 1993, Montgomery-Watson 1993, Cornwell, Sidhu et al. 2018) for a drinking water intake on the Monongahela River where the utility has monthly bromide measurements as well as operational data (chlorine dose, contact time, temperature, UV-254). The observed finished water TTHM reported as compliance data are shown as well. The models show variable results in predicting TTHM. In general, the Malcolm-Pirnie model is statistically significantly different from the other models and from the observed data. The other models (Montgomery-Watson and Cornwell) are not statistically significantly different

© Copyright 2019 American Water Works Association

from each other or from the observed values when considering the full distribution of values; however, the model simulations show wide ranges for each quarter.

Once an adequate model for TTHM prediction is available for a site, it can be used to estimate the increase in TTHM based on an increase in bromide due to the estimated load from the power plants. Using the bromide concentration contributions estimated following the methods described in Section 3, and the models described in this section, the TTHM increase associated with the bromide concentrations can be estimated. **Figure 27** shows a demonstration of the result of this type of estimation. The top panels show estimated bromide concentration contributions, following the methods described in Section 3, based on median load estimates for upstream power plants and the reported range of flow conditions in the river for each year (WY1998 in blue and WY2016 in red). The bottom panels show the simulated TTHM concentration contributions associated with the bromide concentration contributions. Considering third quarter (July-Sept), in 1998, the bromide concentration contribution estimated to be from the power plants upstream of this intake was 30µg/L or greater 50% of the time. For the same period in 2016, the concentration contributions exceeded 30µg/L 80% of the time and exceeded 60µg/L 50% of the time.

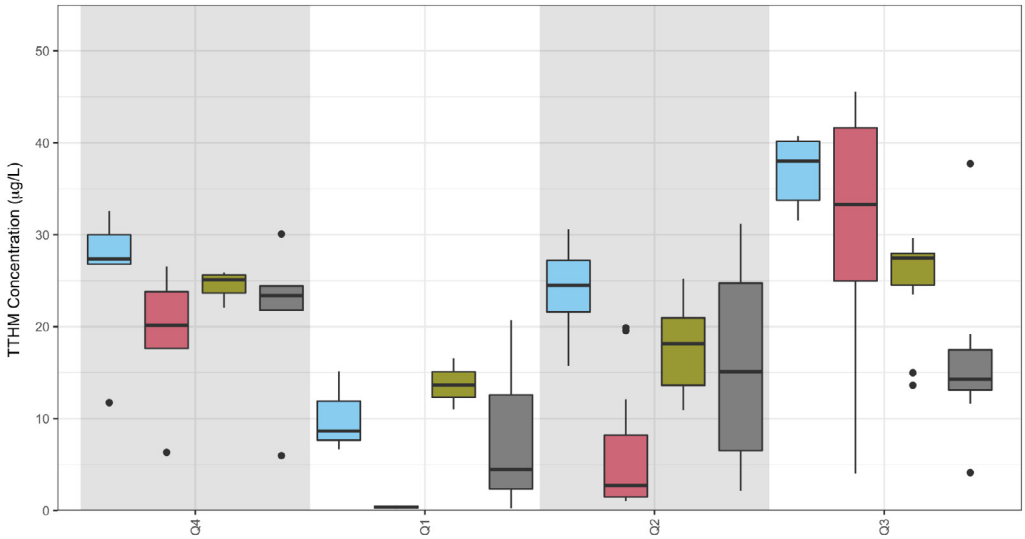


Figure 26. ***Quarterly predicted TTHM for observed bromide data based on three TTHM models as well as observed TTHM concentrations at a drinking water utility on the Monongahela River. Models include: Malcolm-Pirnie (blue), Montgomery Watson (red) and Cornwell (green). Observed data are grey. Plots show the median (horizontal line), 25th to 75th percentile (box), and 1.5 times the interquartile range (whiskers), while dots are values outside that range. Figure Courtesy Dr. Chelsea Kolb.***

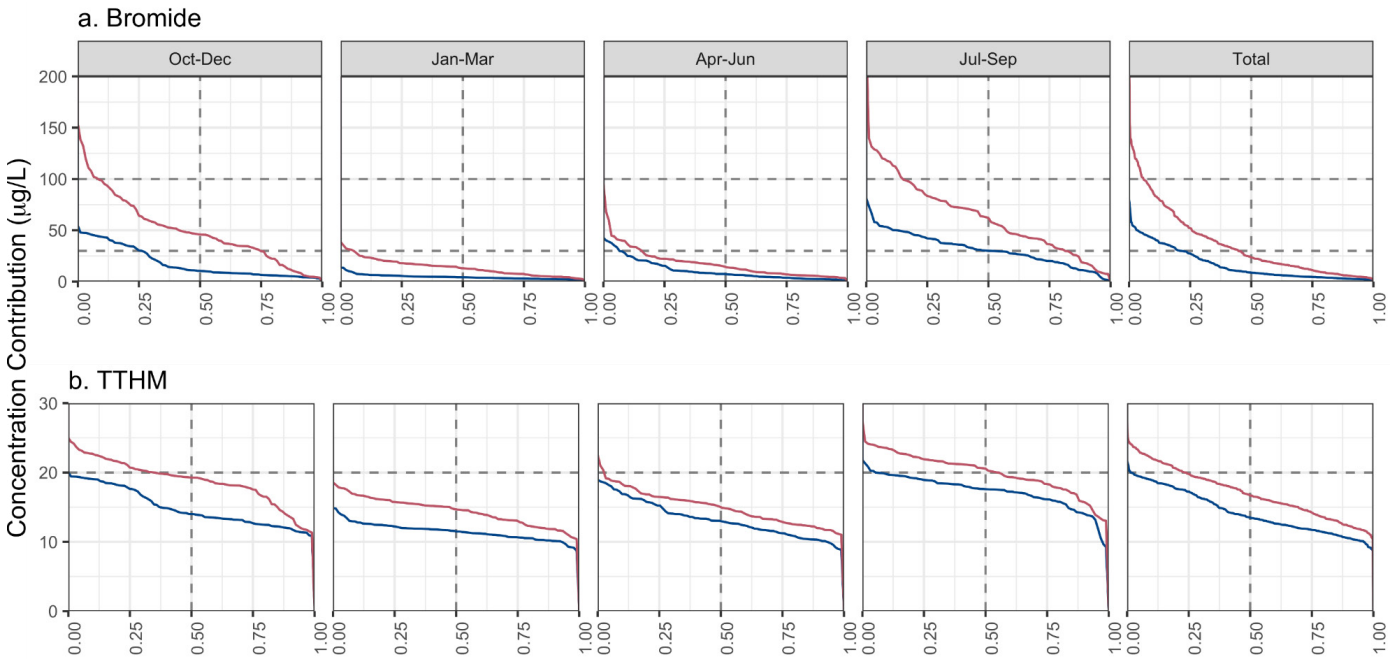


Figure 27. ***Exceedance probability plot for bromide concentration contributions (panel a) and TTHM (panel b) for two water years by quarter and annually. The horizontal dashed lines on the top panel indicate bromide concentration contributions of 30 and 100 µg/L. The horizontal dashed line on the bottom panel indicate TTHM concentration contribution of 20 µg/L. Figure Courtesy Dr. Chelsea Kolb.***

Linking changes in DBP concentrations to changes in risk

Epidemiological studies have established an association between bladder cancer risk and the use of chlorinated drinking water; Villanueva et al. (2015) provides a good summary. Negative reproductive effects have been reported at high concentrations (Nieuwenhuijsen, Grellier et al. 2009, Villanueva, Cordier et al. 2015) and may be associated with bromine incorporation (Chisholm, Cook et al. 2008). Richardson et al. (2007) provides a summary of mutagenicity and toxicity research.

Briefly, all four regulated THM are reported to be carcinogenic; the three brominated forms are also reported to be genotoxic.14 For HAAs, four of the five regulated forms are considered genotoxic (MCAA, MBAA, DCAA, and DBAA); two are reported to be carcinogenic (DCAA and DBAA). For the four unregulated HAAs, one is reported to be genotoxic (TBAA) and three are considered carcinogenic (BCAA, DBCAA, BDCAA). The brominated acetic acids are more cytotoxic, genotoxic and mutagenic than their chlorinated analogues. Toxicological and carcinogenicity data are more limited for unregulated DBPs (Richardson, Plewa et al. 2007).

Hrudey et al (2015) summarized a workshop on the challenges of quantitative risk assessment for DBPs and reported that the strongest epidemiological data are associated with source waters with elevated bromide (e.g., (Villanueva, Cantor et al. 2007, Salas, Cantor et al. 2013)). Across multiple types of DBPs, brominated forms are associated with negative outcomes at lower concentrations than their chlorinated analogs (Echigo, Itoh et al. 2004, Plewa, Wagner et al. 2004, Richardson, Plewa et al. 2007). Thus, increased formation of brominated DBPs, associated with bromide

14 Mutagenicity refers to assays that measure a change in DNA sequence. Genotoxicity refers to mutagenicity as well as DNA damage. Cytotoxicity refers to assays for cell death. Carcinogenicity refers to causing cancer in animal studies.

© Copyright 2019 American Water Works Association

in source waters, increases the risk associated with use of chlorinated drinking water (Hong, Liang et al. 2007, Yang, Komaki et al. 2014, Regli, Chen et al. 2015).

While the relationship between DBP speciation and risk is complex, risk estimates in the D/DBP rule were based on limited epidemiological data using TTHM as an exposure surrogate (USEPA 1998, USEPA 2006b). Thus, models for DBP risk are often based on TTHM. Regli et al. (2015) estimated the effect of source water bromide increases on risk estimates based on odds ratios (ORs), following the method described in the D/DBP rule and summarized in **Equation 4**, where r represents the risk associated with the TTHM concentration of concern. ORs are used to compare the relative odds of negative health outcome for an exposed population compared to a population with little to no exposure.

$$OR = \frac{r}{1-r} = 0.0209 \times e^{TTHM\ Concentration \times 0.00427} \quad (4)$$

Regli et al (2015) determined that a 50µg/L increase in source water bromide would be expected to cause a 10-3 to 10-4 increase in lifetime bladder cancer risk for consumers of treated water from that source. For some plants in their study, a smaller increase (10µg/L) in source water bromide was predicted to cause an increase in risk as well (Regli, Chen et al. 2015). **Equation 4** can be used with TTHM concentration contributions to estimate the risk associated with the additional TTHM exposure resulting from power plant associated bromide discharges relative to zero exposure to TTHM (where risk of zero exposure is defined as r0 = 0.02047, following Regli et al (2015). **Figure 28** shows the results of this type of analysis for a drinking water utility on the Monongahela River for WY1998 (prior to most power plants having wet FGD) and WY2016 (when all power plants had wet FGD systems). These results are based on bromide load estimates (following Section 3 methods) and bromide and TTHM concentration estimates (shown in **Figure 27**). The calculated risk associated with the power plant contributed TTHM is higher in each quarter in 2016 compared with 1998. This is expected as the bromide concentration contributions and associated TTHM were higher in 2016 (see **Figure 27**).

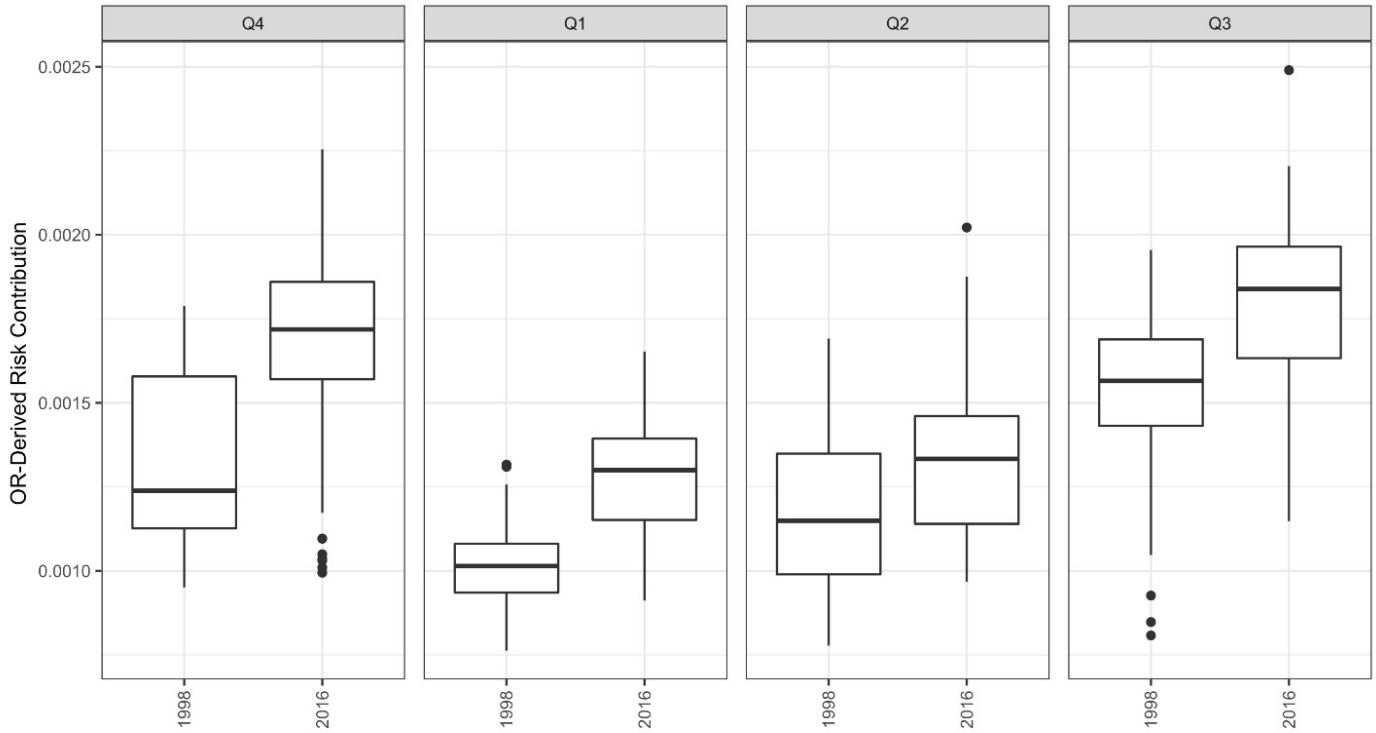


Figure 28. ***Odds ratio risk simulation associated with simulated TTHM concentration increases. Plots show the median (horizontal line), 25th to 75th percentile (box), and 1.5 times the interquartile range (whiskers), while dots are values outside that range. Figure Courtesy Dr. Chelsea Kolb.***

Section 4 Data Sources.

Completion of any of the analyses described in this section requires output from the analyses completed in Sections 2 and 3 as well as models for predicting changes in DBPs associated with changes in bromide.

The predicted concentration component for each power plant (see Section 3) *could* be used in conjunction with observed or estimated bromide contributions from other sources and with a revised water treatment plant model to predict DBP levels in drinking water and thus to estimate effects on compliance with the TTHM standard directly. However, this depends upon the structure and suitability of the DBP prediction model and will require data from each drinking water utility.

Several models were described above, including the Water Treatment Plant Model (WTP). EPA's WTP model was released in the mid-1990s on an early Windows Platform; the user's manual is still available (USEPA 2001). It can still be run within the proper operating system emulator; however, an updated version is expected that may be easier to use (Yang 2017).

© Copyright 2019 American Water Works Association

Section 5. Methods to assist permit writers

This section focuses on development of materials for NPDES permit writers to support monitoring and reporting requirements that protect downstream drinking water utilities. **Figure 3** previously outlined the major steps in developing NPDES permits for power plants discharging bromide upstream of drinking water intakes. Section 2 of the report provided guidance on prioritization or selection of power plants that might require revised NPDES permits related to bromide discharges. Sections 3 and 4 of the report provided guidance on assessing the potential bromide loads from power plants and their potential effect on DBP formation at downstream drinking water plants. These estimation methods support the assessment of whether a water quality based effluent limitation (WQBEL) is needed and how potential impact could be determined in setting that limit.

Once a decision is made to set a WQBEL, key steps are undertaken that require additional data and analysis. **Figure 29** provides more detail on necessary sub-steps and data sources. There are significant challenges in the development of WQBELs for bromide from power plant discharges.

First, in the absence of in-stream water quality criteria, alternative approaches to selection of target concentrations is considered. Second, there is significant variability in bromide concentrations in drinking water source waters (i.e., rivers), which are also the receiving waters for the power plant discharges. This variability means that discharges will have different effects on in-stream concentrations for different rivers at different times of year (under different flow conditions). Third, there is significant variability in bromide concentrations in power plant wastewater, which may lead to differences in the effect of these discharges on receiving waters.

Following discussion of these challenges, a summary of existing permits that contain bromide monitoring requirements is provided. Finally, recommendations for permit language are discussed.

A. Identify ALL downstream drinking water plants that could be affected:

Section 3. Data Sources

1. Permit applications often identify the nearest downstream drinking water utility; however, the conservative nature of bromide means that additional downstream utilities may need to be identified.
2. EPA DW Maps tool may be used to identify downstream drinking water intakes.

B. Assess bromide concentration and load from power plant discharge:

1. Bromide is included in 40CFR122.21 Appendix D. This requires the concentration of bromide in the wastewater that will be discharged under the NPDES permit to be submitted with the application.
2. Bromide concentrations may be reported in DMR data for existing permitted discharges. Chloride may be more typically reported and known. Br:Cl ratios for coal can be used to estimate associated bromide concentrations.
3. Bromide data for FGD wastewater was collected as part of the Steam Electric Power Plant Effluent Limitation Guidelines Review and is also reported in other literature. These values provide a range.
4. If data source are insufficient, the permit writer can request bromide and flow data for FGD wastewater from permittee.

C. Identify background/baseline bromide concentrations in receiving water and dilution capacity of receiving water:

Section 2. Data Sources

1. Bromide data for receiving waters maybe available from EPA STOrage and RETrieval database (STORET)
2. Bromide data are available for drinking water intakes during the ICR collection period (1997-1998); these values may provide insight into background bromide concentrations in the absence of anthropogenic discharges from power plants. This baseline information may also be useful for determining if anti-degradation standards or anti-backsliding requirements apply.
3. USGS flow data is available to assess receiving water dilution capacity.

D. Assess potential effects of bromide concentration contribution from power plants on drinking water DPBs

Section 4 data sources

1. Baseline DBP data is available from the ICR for large utilities.
2. More recent DBP data for utilities is available from state databases.
3. The Water Treatment Plant Model is available and can be used with data from the drinking water plant to assess the effect of changing bromide on DBPs following the work of Regli et al (2015).

Figure 29. ***Method and data support for steps in developing Water Quality Based Effluent Limitations (WQBELs) for bromide discharges from power plants***

Water quality criteria and bromide

A significant challenge for management of bromide at drinking water intakes through NPDES permit limits at power plant wastewater outfalls is the lack of ambient water quality criteria for bromide. Since bromide has a high human and ecotoxicity threshold (Flury and Papritz 1993), it poses little risk to the aquatic environment. However, as noted above, the presence of bromide in waters used as sources for drinking water treatment plants increases the rate and extent of DBP formation, and can lead to higher DBP-associated risk for consumers of the treated water.

Since drinking water supply is a “designated use,” the Clean Water Act requires that the water body so designated must meet the criteria for that use. Water quality standards are established to ensure water bodies meet designated uses. In Pennsylvania, when no ambient in-stream water quality standard exists for a constituent believed to be leading

© Copyright 2019 American Water Works Association

to an impairment, a reference watershed concentration can be used to determine the contaminant reduction necessary to mitigate the impairment.

The challenge with this approach is determining the bromide concentration in a suitable reference watershed. Surface water bromide concentrations in the absence of anthropogenic discharges are infrequently measured, and background bromide concentrations are often below the detection limit of commonly deployed analysis methods (USEPA 1993, USEPA 1999). Further, different watersheds may have different background concentrations from natural and anthropogenic nonpoint sources (e.g., road salt or brine runoff, mine discharges). Good and VanBriesen (2016) used maximum dilution concentrations (values recorded at very high flow) as an estimate of natural background levels in the Allegheny River (22 µg/L). However, for many river systems, maximum dilutions conditions produce concentrations below detection (e.g., for the Susquehanna River (Steffy 2013, Hintz and Steffy 2015)and the Monongahela River (Ziemkiewicz 2013, 3RQ 2015)). In some river systems, historical concentrations reported during the D/DBP rule ICR may be suitable for background estimates, especially when anthropogenic discharges were not present in 1997-1998 (see **Figure 7** and **Figure 8**); however, many utilities reported samples below the detection limit (20 µg/L). Kolb et al (2019)proposed use of the ICR data as a baseline for a utility modeled in their Monongahela River analysis; however, they determined a coal-fired power plant installed wet FGD in 1994, prior to the ICR data collection. Similarly, analysis of the Susquehanna River basin bromide data indicates a mine discharge with elevated bromide concentrations is in the headwaters, complicating baseline assessment (Hintz 2016).

When available, drinking water utility specific bromide concentrations could be used as river-wide targets. For example, the CALFED Drinking Water Quality Program in California has set a target of 50 µg/L (0.05 mg/L) to protect the public from the health effects of brominated disinfection by-products (Holm, Harader et al. 2007); this target reflects knowledge of their source waters and treatment facility capabilities. In the Allegheny River (PA), States et al. (2013) report that laboratory results suggest a bromide concentration of 50µg/L would lead to 25% bromination of finished water THM4, while data collected in the plant showed bromide at or below 50µg/L in the source water led to between 40 and 60% bromination in the finished water THM4 (States, Cyprych et al. 2013). Wilson and VanBriesen (2013)(report bromide concentrations at multiple drinking water intakes along the Monongahela River for 2009-2012, with median values of 63µg/L and 69 µg/L at two sites that also reported during the ICR; values were statistically significantly higher in 2010 when compared with 1998. Wang et al (2015)

report this elevated bromide was associated with elevated TTHM and brominated THM. Thus, for these utilities, the elevated bromide values reported during 2009-2012 were affecting drinking water TTHM and risk, and a target concentration for bromide in this basin should be lower than the observed values in order to mitigate this risk. If regional or utility-specific baseline data for bromide are not available, national historical bromide data may provide a baseline bromide concentration. For example, across the U.S. drinking water systems included in the ICR, the median bromide concentration in surface waters was 30µg/L. This value could be used as a target for bromide concentration at drinking water intakes.

While a value of bromide relevant for meeting the designated use of drinking water supply has not been set by any regulatory authority, a narrative criteria may be applied. In Pennsylvania the narrative criteria reads: “Water may not contain substances attributable to point or nonpoint source discharges in concentrations or amounts sufficient to be inimical or harmful to the water uses to be protected, or to human, animal, plant, or aquatic life.”15 The EPA specifically referred to the use of narrative water

15 §93.6(a) Commonwealth of Pennsylvania Code http://www.pacode/com/secure/data/025/chapter93/s93.6.html

quality criterion for protection drinking water sources in the Technical Development Document (TDD) related to the ELGs, stating "These narrative criteria may be used to develop water quality-based effluent limitations on a site-specific basis for the discharge of pollutants that impact drinking water sources, such as bromide."(USEPA 2015e). Unfortunately, it is not clear how this narrative criteria is to be interpreted with respect to bromide, given its variable effect on DBPs. EPA makes a suggestion in the TDD, stating that: "The maximum level of bromide in source waters at the intake that does not result in an exceedance of the MCL for DBPs is the numeric interpretation of the narrative criterion for protection of human health and may vary depending on the treatment processes employed at the drinking water treatment facility." However, this proposed approach depends on the existence of a simple relationship between bromide and TTHM and HAA5. As noted in Section 4 above, this relationship is complex and different for different utilities. Further, the relationship is strongly dependent on temperature and applied chlorine dose, both of which are seasonally variable. The concentration of bromide in the source water that would not cause an exceedance of TTHM at a utility in February may be quite different from the concentration meeting this goal in July. Reducing bromide concentrations in warm summer months, which may also correspond with lower flow conditions in rivers, may be particularly challenging.

As an alternative to an in-stream bromide criteria determined by a value that would cause an exceedance of the MCL for DBPs, a limit could be set to keep the contributions of bromide from anthropogenic sources from elevating the risk of the drinking water. For example, Regli et al (2015) report that bromide concentration increases at water utilities of 50µg/L would be expected to cause a 10^{-3} to 10^{-4} increase in lifetime bladder cancer risk for consumers of treated water from that source. For some plants in their study, a smaller increase (10µg/L) in source water bromide was predicted to cause an increase in risk as well (Regli, Chen et al. 2015). Thus, bromide concentration contributions from power plants in excess of these levels could be considered to trigger load reduction requirements at power plants.

The methods discussed in Section 3 above enable the assessment of concentration contributions from each power plant to each potentially affected downstream drinking water plant. Thus, power plants causing excess bromide at drinking water intakes can be identified and permit modifications written to prevent bromide discharges that affect DBP formation and risk at downstream drinking water plants. Good and VanBriesen (2018) identified power plants based on 2016 coal consumption data and assuming a target concentration of 1 µg/L under mean flow conditions is the threshold for concern (corresponding to approximately 10 µg/L increase under low flow conditions). Simulations with alternative coal consumption and bromide use patterns as well as under alternative flow scenarios (e.g., 7Q10) can be developed using the same techniques for individual power plants or for specific watersheds to assess the potential for bromide concentration contributions to exceed selected targets.

 © Copyright 2019 American Water Works Association

Bromide concentrations and variability in receiving waters

As noted in Section 3, bromide concentrations are strongly dependent on flow conditions in receiving waters, which show significant variability. Further, large river systems, especially those with navigational control structures, often exhibit significant stratification, leading to poor mixing conditions and spatial variability in measurements. Wang et al (2015) report that mid river sampling (typical of monitoring programs) produced estimates of river concentration that were significantly different from sampling at drinking water intakes. The differences were significant enough to alter decision-making on listing the river for impairment under section 303(d) of the Clean Water Act. Similarly, significant temporal variability in bromide measurements have been reported (States, Cyprych et al. 2013, Wilson and VanBriesen 2014) when considering weekly or daily sampling at drinking water intakes. For example, **Figure 30** shows daily bromide sampling at the Pittsburgh Water and Sewer Authority (black dots) in µg/L (left vertical axis) and flow (blue line) in m^3/sec (inverted on right vertical axis) for 2013. The median bromide concentration was 71 µg/L, while the minimum was 22 µg/L and the maximum was 151 µg/L. River flow is the primary cause of the variable bromide concentration, with high flow winter and spring conditions leading to lower bromide than low flow summer-time conditions. Similarly, **Figure 31** shows bromide concentrations measured by PADEP at the USGS gage on the Susquehanna River near Marietta, PA. The median bromide concentration was 18 µg/L from mid-2013 to mid-2016; however, bromide concentration rose to above 140 µg/L in late 2016, during an unusually low flow period.

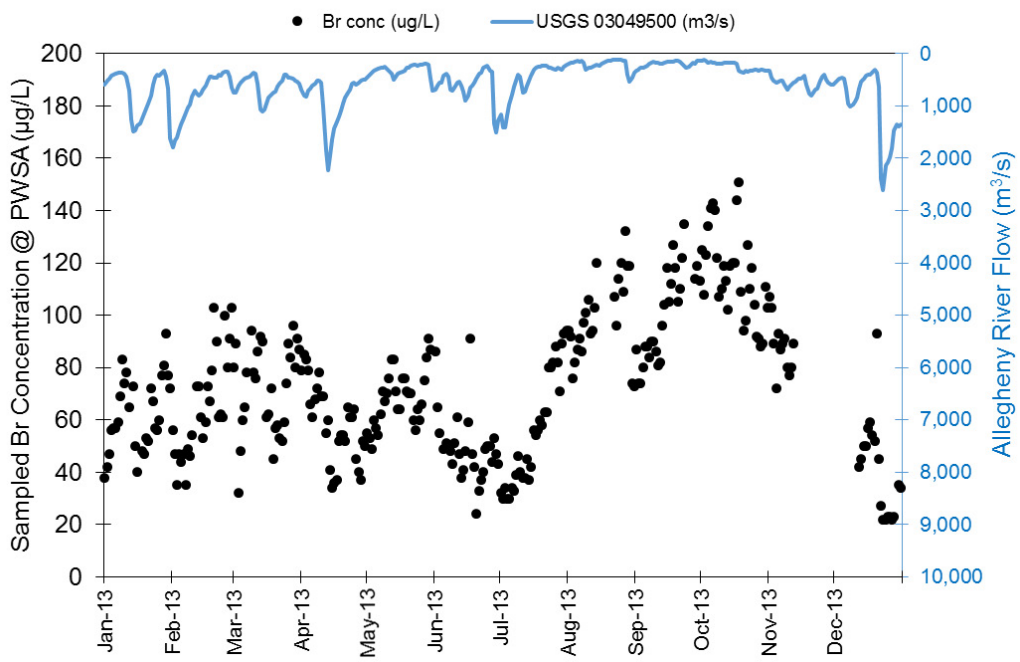


Figure 30. *Bromide concentration at the Pittsburgh Water and Sewer Authority Intake and flow at the closest river gage for 2013. Bromide data courtesy PWSA; flow data from USGS gage 03049500. Reprinted with Permission from (Good 2018).*

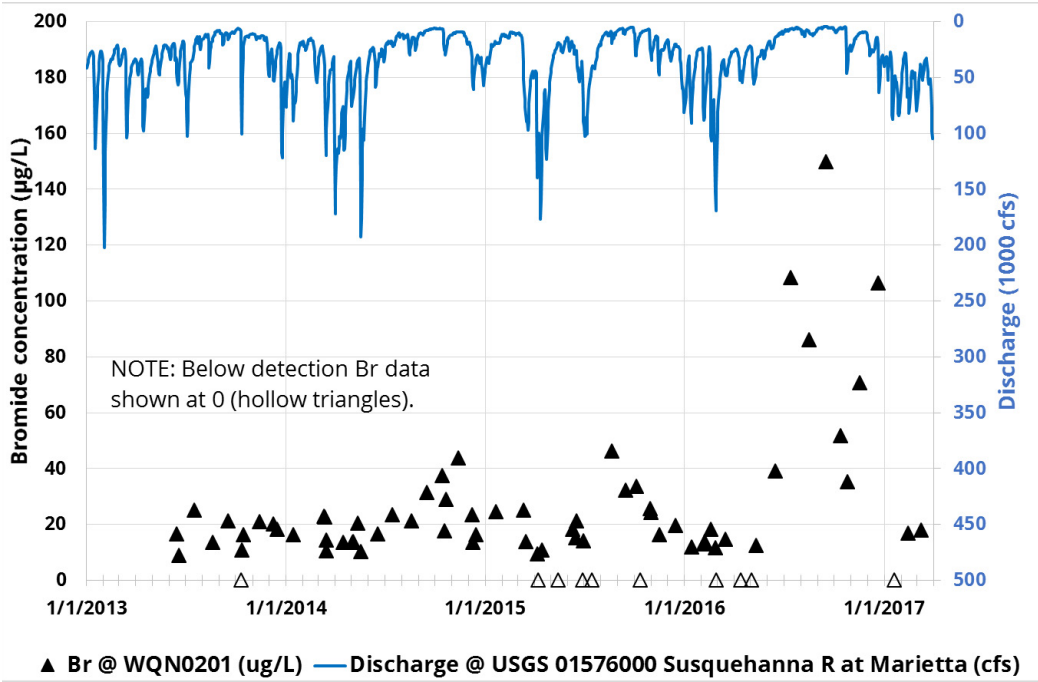


Figure 31. *Bromide concentration in the Susquehanna River at Marietta and flow at the closest river gage for 2013 through 2016. Bromide data from PADEP WQN0201; flow data from USGS gage 01576000. Figure courtesy Dr. Kelly Good.*

Figure 32 shows bromide concentration in the Monongahela River at multiple locations from 2009 to 2012. Significantly lower concentrations throughout 2012 were related to decreased loads rather than flow variability (Wilson, Wang et al. 2013, Wilson and VanBriesen 2014). To enable determination of the effect of increased bromide from power plants on in stream bromide concentrations affecting DBP formation at drinking water plants, permit writers will need to assess bromide concentrations (and variability) at intakes. If drinking water utilities do not have intake monitoring data or states do not have in stream monitoring data for the relevant receiving water, permit writers may need to require river monitoring within NPDES permits for power plants in order to assess the bromide conditions relative to the discharge point. This was required in a permit issued to Duke Energy's Belews Creek plant (see below).

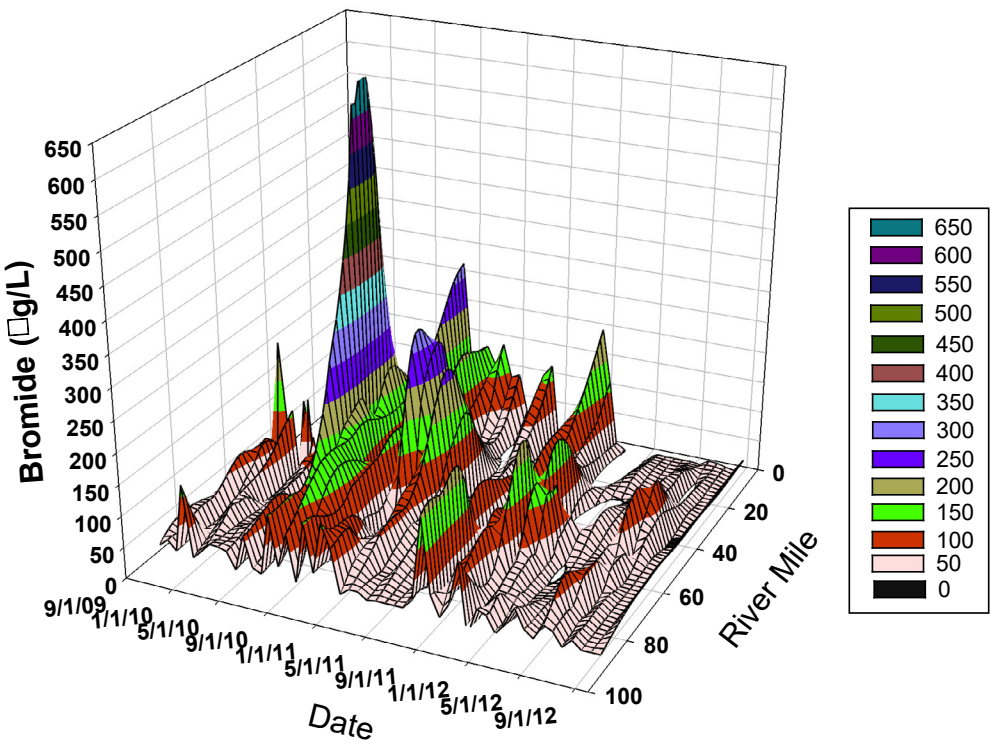


Figure 32. *Bromide concentration in the Monongahela River for 2009 to 2012, measured at multiple drinking water intakes. Data from (Wilson and VanBriesen 2014). Figure courtesy Dr. Jessica Wilson.*

Bromide concentrations and variability in FGD associated wastewaters

FGD wastewaters contain different amount of bromide, based on the coal being burned and the use of bromide-based additives for mercury control or for section 45 tax credit (coal refining). FGD wastewaters are not routinely monitored and thus, assessment of concentrations expected in these discharges is difficult. **Figure 33** presents data from several publicly available studies or data sets. VanBriesen (2013) summarized a set of EPRI reports, concluding that wet FGD discharges contained 69-118 mg/L bromide. Frank (2011) reports on a bromide addition trial at the Conemaugh power plant.[16] Bromide concentration in the FGD wastewater prior to addition was 96-125 mg/L, and it was 243-575 mg/L during the bromide addition trial. EPA requested and received sampling data from two Duke Energy power plants during the ELG revision (USEPA 2009a, USEPA 2013b). From March to July 2009, 68 samples were taken at one plant with bromide concentrations ranging from 2 to 67 mg/L, with a median of 26 mg/L. From December 2008 to December 2009 samples were taken at another plant, and bromide concentrations ranged from 86 to 140 mg/L, with a median of 110 mg/L.

16 The Frank (2011) study is also summarized in EPRI (2014) with slightly different values. EPRI (2014) reports Frank results as 153-173 mg/L (base) and 600-700 mg/L (during bromide addition).

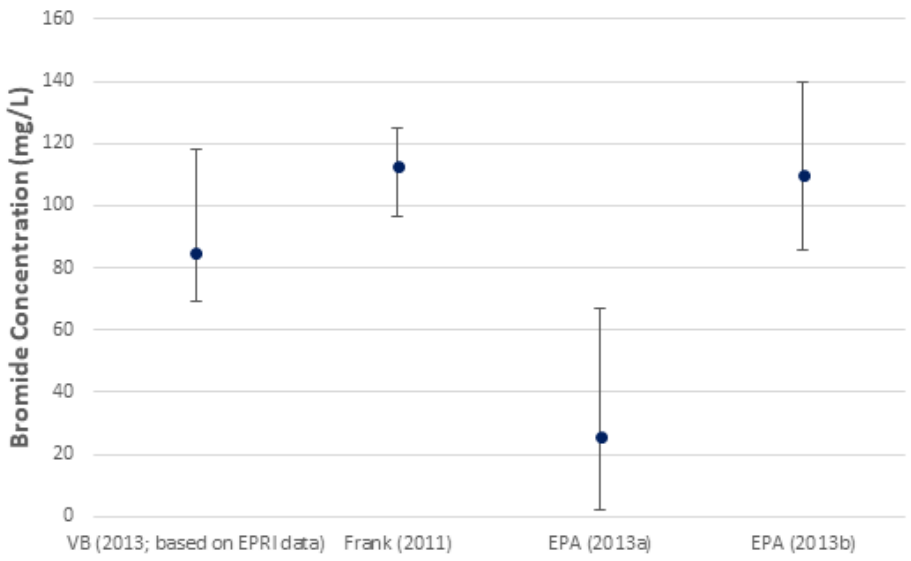


Figure 33. ***Reported bromide concentrations in FGD wastewaters (as summarized in (VanBriesen 2013). Data from (USEPA 2009a, Frank 2011, EPRI 2014).***

The EPA ECHO system identifies facilities with monitoring requirements and effluent limits for bromide (USEPA 2018c). **Table 5** indicates 41 facilities with effluent limitations for bromide; however, only 1 is associated with electricity generation.[17] Of the electricity-generating facilities required to *monitor* for bromide, 18 of the 49 report bromide discharge data for 2018 in ECHO. Reported average bromide concentrations ranged from 0.033 to 849 mg/L, with maximum concentrations from 0.084 to 2357 mg/L. Reported loads varied from 0.07[18] to 7128 kg/day.

Table 5. ***Bromide discharge monitoring requirements for NPDES permits in the United States. (USEPA 2018c)***

	Monitoring Requirements Only	Monitoring Requirements *and* Effluent Limits
All facilities in ECHO	721	41
Industrial Dischargers (not POTW)	375	39
SIC code 4911 (electric services)	48	1

As discussed previously, bromide discharged from power plants is most often associated with wet FGD wastewater; however, under current regulations, this wastewater can be mixed with other process waters or discharged to the ash pond, where it is diluted prior to a discharge monitoring point at the NPDES-permitted ash pond outfall (USEPA 2015e). Using data from the EPA ELG questionnaire (USEPA 2010b), **Figure 34** demonstrates that FGD wastewater contributes less than 5% of total flow at most power plant outfalls.

17 Pittsburg Power Plant in the city of Pittsburg in Contra Costa County in California (permit CA0004880) is listed as having a bromide effluent limit in ECHO; however, no bromide load data are reported for 2018.

18 The reported value for Seward Power Plant (55 lbs/year or 0.07 kg/day) was flagged in ECHO as possibly based on a data error. The next lowest value was 91lbs/year or 0.11 kg/day.

 © Copyright 2019 American Water Works Association

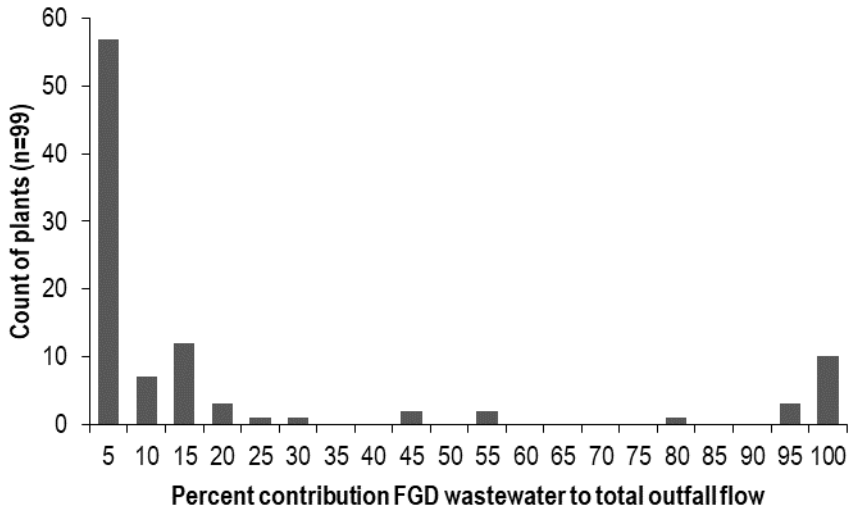


Figure 34. ***Contributions of FGD wastewater to outfall flows as estimated in the 2009 steam electric survey ELG questionnaire (USEPA 2010b). Values less than 100 percent indicate commingling with other waste streams. Reprinted with Permission from (Good 2018).***

The 2016 Effluent Limitation Guidelines for Steam Electric Power Plants (ELGs)(USEPA 2015b) require measurement of the FGD wastewater at an internal monitoring point prior to any mixing, consistent with 40 C.F.R. § 122.45(h), which allows the imposition of effluent limitations on internal waste streams when wastes are mixed prior to discharge. However, until the implementation of that regulatory change, measured bromide concentrations in power plant discharges will be difficult to assess and compare.

Flow, concentration and load management for FGD-associated wastewaters

For power plants identified as warranting permit review for potential bromide effects on downstream drinking water systems, the bromide load must be managed to ensure the concentration of bromide that reaches the downstream drinking water plant is below the value that negatively affects DBP formation and associated risk. Once this value is determined for each drinking water plant (following the methods in Section 4) or for a watershed by considering a reference watershed as described above, conventional TMDL approaches can be used to determine waste allocations for each upstream discharger under selected flow conditions in the receiving water (which could be 7Q10 or 3rd quarter low flow).

Monitoring these loads requires measurement of discharge flow and concentration, which is complicated by the current practice of mixing FGD wastewaters with other wastewater flows prior to discharge (see **Figure 34**). Bromide concentration measurements are significantly affected by dilution effects from mixed wastewaters.

Figure 35 presents data from required sampling at outfall 003 at the Duke Energy ***Belews Creek Steam Station*** (NPDES permit NC0024406). Sampling has been conducted since 2013; these data are submitted to the North Carolina Department of Environmental Quality.

Bromide concentration in the wastewater discharge from outfall 003 shows a downward trend in bromide concentration from high values (7-8 mg/L) to more recent lower

values (4-6 mg/L)[19]. **Figure 36** shows these data as box plots for each year; letters indicate significant differences in means. Again, the pattern is a declining trend, with the median value in 2013 of 7.1 mg/L and a median value in 2017 of 5.5 mg/L. In contrast, **Figure 37** shows the computed *loads* for the discharge, based on the reported bromide concentrations and the reported flow measurements. Loads were not significantly different[20] from 2013 through 2016, with median values of 225, 204, 196 and 182 kg/L. In 2017, the load was significantly lower than previous years (median value 152 kg/day). These results confirm the importance of flow-weighted measurements when assessing bromide concentrations in power plant discharges. Concentrations from grab samples will be variable based on dilution from other wastewaters. Estimates of load can be made with concurrently measured concentration and flow; however, assessment of the meaning of declining concentrations must be made in the context of the flows at the time of sampling. Thus, flow-weighted sampling will improve the value of the concentration measurements by making them directly comparable.

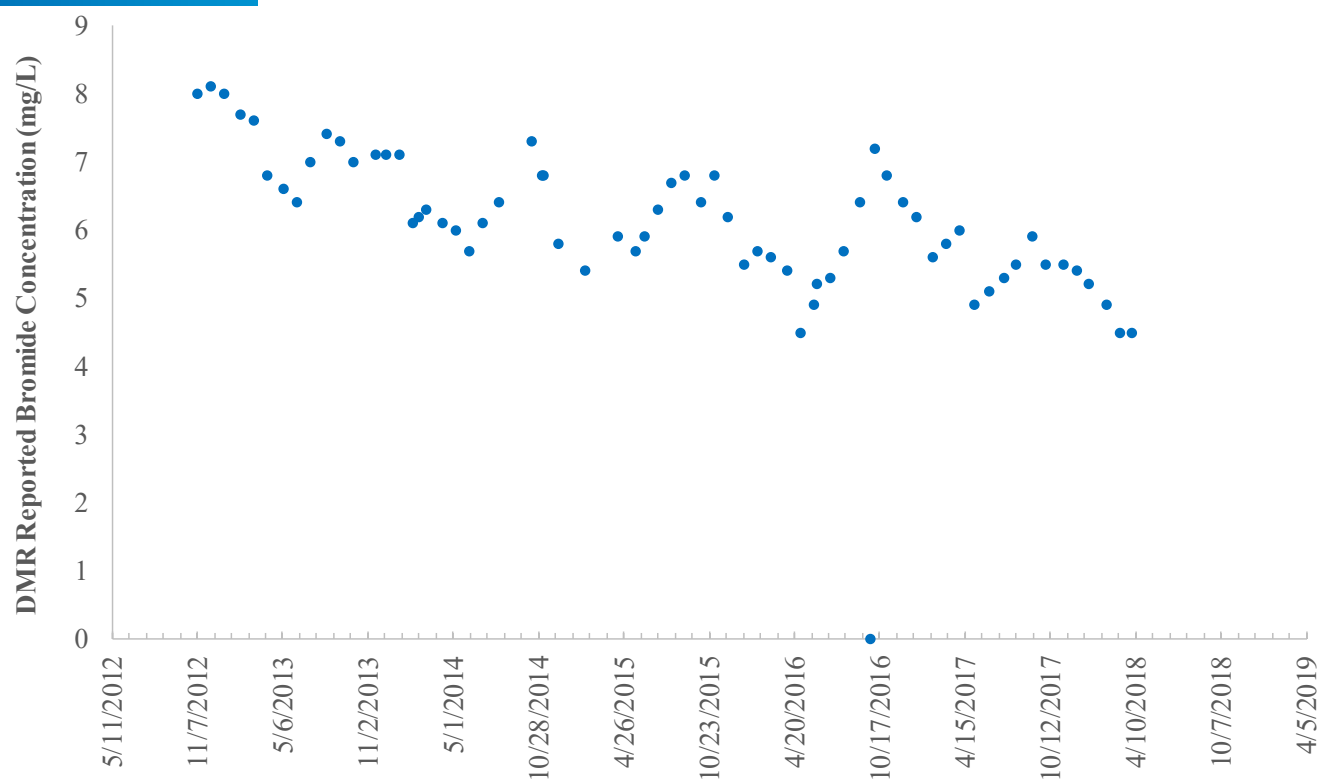


Figure 35. ***Discharge monitoring report (DMR) bromide concentrations (mg/L) for outfall 003 at the Belews Creek Plant. Reprinted with Permission from (Good 2018).***

19 The values plotted at zero for 5/17/2015 represents a missing data point. No bromide concentration was reported on that date although a flow measurement was reported. This value was not used in the distributions of concentrations show in Figure 35 or in the computed loads shown in Figure 36.

20 Difference significance was evaluated using Mann-Whitney test for medians and Kolmogorov-Smirnov test for distributions. See Good (2018) for further details.

© Copyright 2019 American Water Works Association

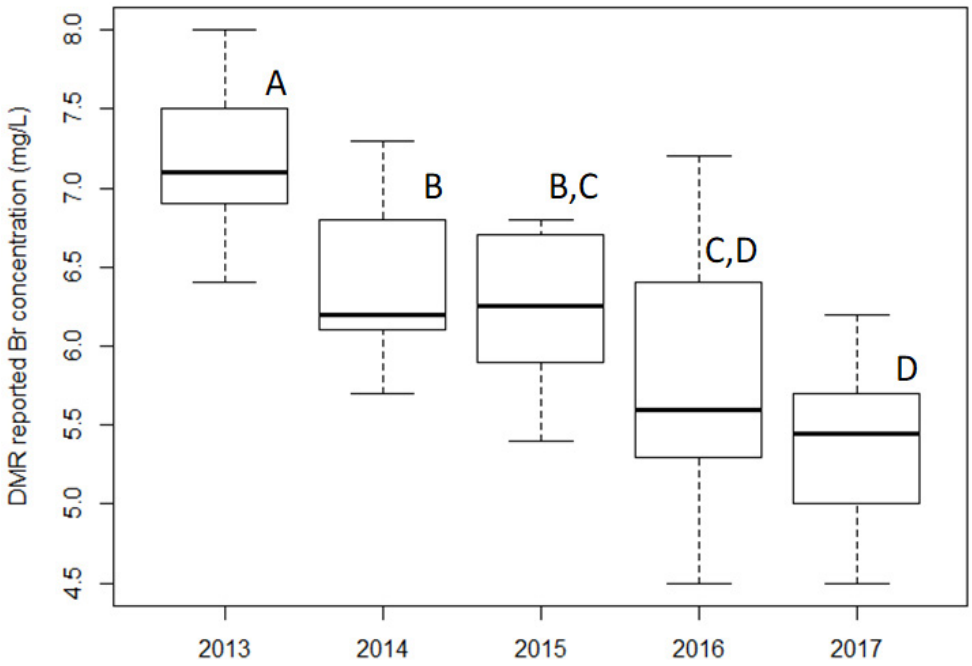


Figure 36. *Reported bromide concentration in outfall at 003 at Belews Creek plant. Letters indicate significant differences across medians and distributions. Reprinted with Permission from (Good 2018).*

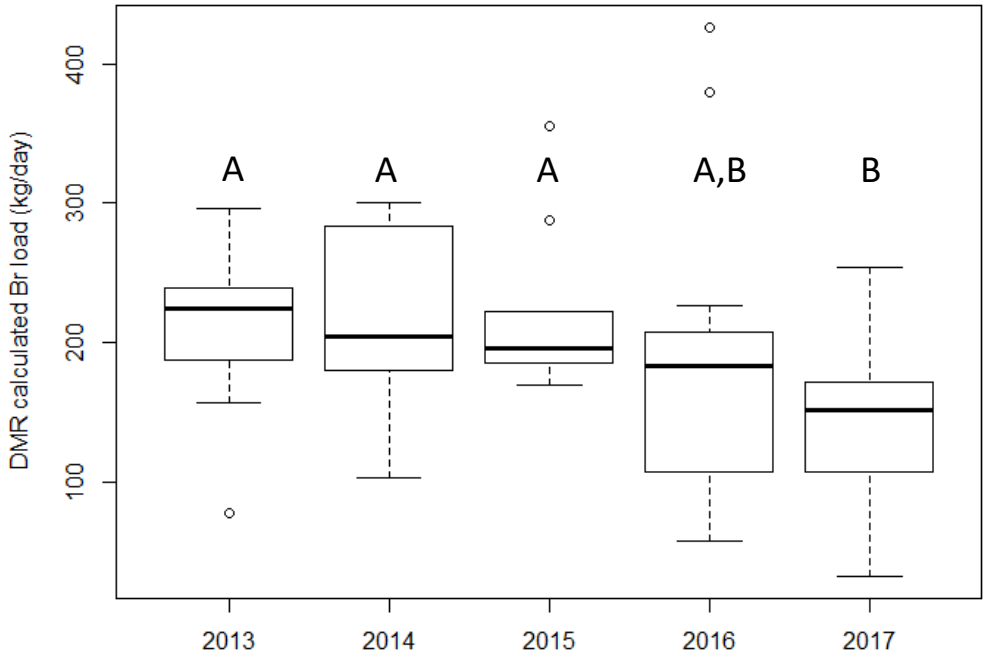


Figure 37. *Bromide load in discharge from Belews Creek power plant, computed from reported flow and concentration data; letters indicate significant differences across medians and distributions. Reprinted with Permission from (Good 2018).*

Review of power plant permits requiring bromide monitoring

Existing power plant permits that require bromide monitoring in Pennsylvania and North Carolina were reviewed to inform development of model language for bromide measurement and control. The North Carolina Division of Water Resources directed Duke Energy to apply for National Pollutant Discharge Elimination System (NPDES) wastewater permit modifications or renewals at the company's 14 coal-fired power plants in 2014.[21] The Pennsylvania Department of Environmental Protection (DEP) has recently focused increased attention on coal-fired power plant permits in response to a settlement with environmental groups.[22] Relevant information related to bromide discharges from available permits for these facilities are summarized here.

Brunner Island Power Plant. NPDES Permit No: PA0008281 authorizes discharge from the Brunner Island Power Plant. The facility operates multiple outfalls, with discharges to Hartman Run, Susquehanna River, and Conewago Creek. The public notice explicitly states: "The discharge is not expected to affect public water supplies." The nearest downstream drinking water intake is not identified in the permit materials. The effluent from the flue gas desulfurization wastewater treatment plant is sent to outfall 007, which discharges to the Susquehanna River via a condenser discharge channel. Outfall 007 is at river mile 54.27 (Lat 40°5'32.00" and Long 76° 41'23.00"). Outfall 007 has a design flow of 0.52 MGD and continuous flow monitoring, which is reported as daily maximum and average monthly. Bromide will be measured once per month as a 24-hour composite and reported as a daily maximum concentration (mg/L) and a daily maximum load (lbs/day). Samples will be taken prior to comingling of wastewaters with stormwater. Brunner Island proposes to install a physical/chemical/biological treatment system to comply with the 2016 ELGs. They also intend to run a pilot program to evaluate an evaporative technology if the physical-chemical-biological method is not selected. In either case, the compliance date is December 31, 2023.

Montour Steam Electric Station. NPDES permit number PA0008443 authorizes discharge from the Montour Power plant. The facility operates 3 outfalls with discharges to Chillisquaque Creek and the West Branch Susquehanna River. For outfalls 050 and 052, the nearest public water supply intake is listed as Sunbury Municipal Water Authority approximately 26 miles downstream on the West Branch of the Susquehanna River. For outfall 053, the nearest public water supply intake is listed as PA American Water Company approximately 4 river miles downstream on the West Branch of the Susquehanna River. FGD wastewater is treated and then mixed with other process waters and sent to outfall 053 (Lat 41°4'5.96" and Long -76°51'18.98"); the NHD Com ID is 66918973. The drainage area at this point is 6,650 mi^2, and the $Q_{7\text{-}10}$ flow is reported to be 798cfs, based on USGS stream gauge 01553500. The FGD treatment system consists of equalization, desaturation, coagulation/precipitation, flocculation, sedimentation, pH control, and sludge thickening and filtration. Sludge cake is deposited in the onsite landfill. The internal monitoring point for the treated FGD wastewater is not specified in the permit.

Outfall 050 requires bromide monitoring 2/month using a 24-hour composite with reporting of the daily maximum and average monthly concentration (mg/L) and average

21 Documents related to this can be accessed at the NC DEQ website: https://deq.nc.gov/about/divisions/water-resources/water-resources-hot-topics/dwr-coal-ash-regulation/duke-energy-npdes-permits-for-facilities-with-coal-ash-ponds/duke-energy-npdes-modifications-renewals

22 The Settlement between Sierra Club et al and the Commonwealth of Pennsylvania Department of Environmental Protection et al. Docket No. 260 M.D. 2017, is available at http://www.pennfuture.org/Files/Admin/DEP-and-Sierra-Club-Settlement-Final—01-10-2018.pdf, and some documents related to PA Power plants can be accessed at the PADEP website: https://www.dep.pa.gov/About/Regional/SouthwestRegion/Community%20Information/Pages/Coal-Power-Plant-NPDES.aspx

© Copyright 2019 American Water Works Association

monthly load (lbs/day). Flow is continuously metered and reported as average weekly and average monthly. Outfall 052 requires bromide monitoring 2/month using a 24-hour composite with reporting of the daily maximum and average monthly concentration (mg/L) and average monthly load (lbs/day). Flow will be monitored once a day and reported as daily maximum and monthly average. Outfall 053 (which is expected to contain the FGD wastewater) requires bromide monitoring 2/month using a 24-hour composite with reporting of the daily maximum and average monthly concentration (mg/L) and average monthly load (lbs/day). Flow is continuously metered and reported as daily maximum and average monthly.

Cheswick Generating Station. NPDES permit PA0001627 authorizes discharge from the Cheswick Generating Station. The facility operates discharges to Little Deer Creek and the Allegheny River. Outfall 003 is at Lat 40°32'12" and Long -79°47'39, and discharges into NHD Com ID 123972852 at river mile 15.75. The drainage area at this point is 11,500 mi^2, and the estimated $Q_{7\text{-}10}$ flow is 2761 cfs. The nearest downstream drinking water intake is Oakmont Borough at Allegheny River mile 13, 2.4 miles downstream of outfall 003. IMP 503 is the FGD wastewater, which is included in outfall 003. Bromide monitoring will be required at both locations with a frequency of 1/week for a 24-hour composite. Bromide to be reported as daily maximum and average monthly concentrations (mg/L) and daily maximum and average monthly load (lbs/day). It is not clear if flow is continuously metered at IMP503 or outfall 003.

Keystone Generating Station. NPDES Permit No: PA0002062 authorizes discharge from the Keystone Generating Station in Armstrong County, PA. The facility operates multiple outfalls, with most discharging to Plum Creek, Crooked Creek, and unnamed tributaries to these creeks. However, the wet flue gas desulfurization wastewater is sent to Outfall 001, which discharges to the Allegheny River at mile point 0.3400 (Lat 40° 44'31.00" and Long -79° 35'11.00"); the NHD Com ID of this location is 123860701. The fact sheet identifies the river at this location as having a $Q_{7\text{-}10}$ of 2,070 cfs, and the relevant drainage area as being 9,023 mi^2. The design flow for the outfall is 0.32 MGD (avg) and 0.4 MGD (max). The permit application identifies the nearest downstream public water intake (for all the outfalls) as the Buffalo Township Municipal Authority in Freeport at river mile 29.4; the flow at the intake is estimated to be 2,250 cfs. The public notice document explicitly states "the discharges are not expected to affect public water supplies." The discharge for outfall 001 will be measured for flow (MGD), and a variety of chemical constituents, including bromide. Measurements will be made only when the discharge incorporates more than one waste stream, which is expected to be twice a year. Flow will be estimated, and bromide will be measured in a grab sample. Measurement of this discharge does not replace measurement of the internal monitoring points (IMPs) for the two waste streams that make up this discharge. IMP 101 represents the treated scrubber blowdown, which will include daily flow measurements and a weekly bromide measurement (as a 24-hour composite). The permit fact sheet indicates the design flow for this location is 0.32 MGD (average) with a 0.4 MGD maximum. The facility reports that the average of reported monthly average flows over the most recent five-year period was 0.256 MGD and the average of the daily maximum flows was 0.32 MGD. Bromide and flow will be measured twice per discharge at internal monitoring point 201, which represents treated wastewater from the pigging wastewater treatment facility. This flow is expected to be variable; the fact sheet indicates it is expected to operate twice per year.

Total Dissolved Solids (TDS) are also required to be monitored. This facility permit pre-dates the changes promulgated in August 2010 (Chapter 95.10) related to treatment requirements for new and expanding mass loadings for TDS. Thus, the new permit is not subject to these changes in chapter 95 discharge limits related to TDS.

Bruce Mansfield Generating Station. NPDES permit number PA0027481 authorizes discharge from the First Energy Generation Bruce Mansfield Plant to multiple tributaries of the Ohio River (Little Blue Run, Mill Creek). The fact sheet summary indicates that flue gas desulfurization wastewaters are only discharged if there is a leak within the FGD system. The nearest public drinking water intake is identified as Midland Borough Municipal Authority (PWSID 5040038), which is less than 2 miles downstream of the outfall on the Ohio River; the flow at the intake is 5,880 cfs. The permit requires grab samples for bromide twice a month from IMP107 (service water filter and backwater water) and once a month from IMPs 307, 407, and 507 (cooling tower blowdown). Bromide monitoring is also required monthly at outfalls 707 and 007, which receive the water from IMP107, 307, 407, and 507 as well as stormwater (IMP 607). Bromide monitoring is also required once a quarter at outfalls 021, 042, and 043, which receive springs and seeps from the lower abutment and springs/seep water affected by the impoundment and discharge into Little Blue Run; once a quarter at each of outfalls 023, 025, 026, 027, 028, 029, 030, 031, 032, 033, 034, 035, 036, 037, 038, and 041 which each receive springs and seeps affected by the impoundment and discharge to Mill Creek; once a quarter at each of outfalls 039 and 040, which each receive springs and seeps affected by the impoundments and discharge to an unnamed tributary to Mill Creek; and twice a month at outfall 022, which receives supernatant from the impoundment as well as seepage and other sources. The Permit Fact Sheet indicates that "no FGD wastewater discharges actively occur or are expected." Only in the event of a line break within the FGD system, outfall 022 might receive FGD wastewater by way of a spill abatement NPDES sump, located in the vicinity of the FGD thickeners.

Cape Fear Steam Electric Power Plant. NPDES Permit NC0003433 authorizes discharge from Duke Energy's Cape Fear Power Plant location; the plant has been decommissioned and is no longer operational. The decommissioned plant site operates three outfalls, with one (007) discharging to an unnamed tributary to the Cape Fear River and two others (008,009) discharging to the Cape Fear River. In stream monitoring monthly for total bromide is required at two locations: 0.9 miles upstream of outfall 008A in the Cape Fear River, and approximately 250 meters downstream of outfall 008A in the Cape Fear River. However, instream monitoring requirements are waived as long as the permittee participates in the Middle Cape Fear River Basin Association, which has agreed to sample for all the required parameters at the specified locations.

Asheville Steam Electric Plant. NPDES Permit NC0000396 authorizes discharge from Duke Energy's Asheville Power Plant. This plant operates outfalls to the French Broad River, an unnamed tributary to the French Broad River, and to Lake Julian, all in the French Broad River Basin. Outfall 001 receives discharges from multiple wastewaters, including FGD wastewater. Internal outfall 005 is the FGD wastewater, which will discharge to the secondary settling basin after the Ash Pond. The internal FGD wastewater monitoring point does not require bromide measurement. FGD wastewater may also be discharged to the local POTW. Monthly instream monitoring for bromide is required 5,500 feet upstream and 2,900 feet downstream of outfall 001. The analysis method and detection limit are not discussed.

Allen Steam Station. NPDES Permit NC0004979 authorizes discharge from Duke Energy's Allen Steam Station to the Catawba River (Lake Wylie), and unnamed tributary to the Catawba River, and the South Fork Catawba River, within the Catawba River Basin. FGD wastewater is treated and discharged through internal monitoring outfall 005 to the ash basin; the ash basin wastewater is treated and then discharged through outfall 002. Upon completion of a new retention basin, FGD wastewater will be sent to the new basin; the basin's wastewater will be treated and discharge through outfall 006. FGD wastewater treatment includes chemical addition (lime, ferric chloride, polymer, hydrochloric acid, nutrients), clarification, heat exchange, bioreactors, sludge treatment.

 © Copyright 2019 American Water Works Association

Bromide is required to be monitored through monthly grab samples at outfall 002, with weekly sampling required during dewatering. Once the retention basin is built, its outfall will have monthly grab sampling for bromide. Weekly flow monitoring or estimation is required.

Marshall Steam Station. NPDES Permit NC0004987 authorizes discharge from Duke Energy's Marshall Steam Station to the Catawba River (Lake Norman) in the Catawabe River Basin. FGD wastewater is discharged through outfall 002 from the ash settling basin. Upon completion of a new retention basin, FGD wastewater will be discharged through the new basin and to outfall 005. Internal monitoring point (outfall 004) contains treated FGD wastewater discharged to the ash settling basin; after modification, IMP (outfall 006) will contain this wastewater prior to discharge to the new basin. Bromide is to be monitored monthly through grab samples of the effluent at the discharge from the ash settling basin. After the modification, bromide will be monitored monthly through grab samples of the effluent at the discharge from the retention basin. Weekly flow monitoring or estimation is required.

Belews Creek Steam Station. NPDES permit NC0024406 authorizes discharge from Duke Energy's Belews Creek Power Plant. This plant operates one outfall to the West Belews Creek / Belews Creek Lake (outfall 001) and one outfall to the Dan River (outfall 003); both in the Roanoke River Basin. Treated FGD wastewater is released through internal outfall 002, and then travels to the ash basin; ash basin discharge is released through outfall 003. A new outfall 003a/006 will receive FGD wastewater after construction of a new lined retention basin; it will discharge to the Dan River. FGD treatment includes chemical addition (lime, ferric chloride, polymer), clarification, filter, two stage bioreactors. Due to residual high selenium, the permit fact sheet indicates a plan to add membrane ultrafiltration treatment to this process. The implications for bromide removal are not clear in the permit or fact sheet; however, ultrafiltration usually refers to a size exclusion membrane that would allow small ions like bromide to pass through. Bromide is required to be measured monthly in grab samples for the effluent from outfall 003. There is no requirement for bromide measurement in the new outfall 003a. No seep discharges have bromide measurement requirements.

The permit contains a section (A 24.) entitled "Bromide Reduction Evaluation." This section is provided here in its entirety:

> A. (24.) BROMIDE REDUCTION EVALUATION
>
> Duke Energy shall investigate technical solutions to reduce bromide in the discharge from Outfall 003. Duke Energy shall submit semi-annual reports on the efforts it undertakes to reduce bromide at the source as well as efforts at downstream water treatment plants to reduce formation of total trihalomethanes (TTHM). Duke Energy shall continue to work with the downstream public water supply systems to find a solution to the issue of the TTHM formation in the distribution system of the downstream water systems. The semi-annual status reports (3 copies) shall be submitted to the Division of Water Resources, Complex NPDES Permitting Unit.
>
> In the event of a Maximum Contaminant Level (MCL) violation for Total Trihalomethanes (THMs) at the Town of Madison, the City of Eden or any wholesale customers of those systems, Duke Energy will within 14 days of the request provide the latest available bromide monitoring data that can be incorporated into required Public Notices issued by the public water system(s).

The permit also contains a section (A.26) entitled "Instream Monitoring." This section is provided here in its entirety:

> A. (26.) INSTREAM MONITORING
>
> The facility shall conduct semiannual instream monitoring (approximately 0.5 mile upstream and approximately 0.5 mile downstream of the ash pond discharge) for total arsenic, total selenium, total mercury (method 1631E), total chromium, dissolved lead, dissolved cadmium, dissolved copper, dissolved zinc, bromide, total hardness, turbidity, and total dissolved solids (TDS). The monitoring results shall be reported in the monthly DMRs and submitted with the NPDES permit renewal application. The monitoring shall be conducted in accordance with the Sampling Plan approved by the Division. Upon approval, the monitoring plan shall become the enforceable part of the permit.

Permit application requirements

Permit applications include extensive information and analyses related to the constituents expected to be in the wastewater and the characteristics of the receiving waters.

The Clean Water Act (40 C.F.R. §122.21) requires a permit applicant to 'indicate whether it knows or has reason to believe that any of the pollutants in Table IV of appendix D of this part (certain conventional and nonconventional pollutants) is discharged from each outfall. If an applicable effluent limitations guideline (ELG) either directly limits the pollutant, or by its express terms, indirectly limits the pollutant through limitations on an indicator, the applicant must report quantitative data. For every pollutant discharged which is not so limited in an effluent limitations guideline, the applicant must either report quantitative data or briefly describe the reasons the pollutant is expected to be discharged." Appendix D includes bromide on the list of Conventional & Non-conventional Pollutants.[23] Thus, permit applications for coal-fired power plants with wet FGD systems that discharge to waterways should indicate bromide as an expected pollutant in the discharge of the outfall that contains the wet FGD wastewater. Quantitative data need not be included since the ELGs for steam-electric power plants do not directly limit bromide.

In addition to national requirements related to bromide, it may also be considered explicitly in state regulations. For example, under the authority of 25 PA Code 92a.61, the Pennsylvania Department of Environmental Protection (PaDEP) has determined that it should implement monitoring in NPDES permits for TDS, chloride, bromide and sulfate.

The monitoring is prompted for discharges that exceed specific thresholds:

a) Where the concentration of TDS in the discharge exceeds 1000 mg/L or the net TDS load from a discharge exceeds 20,000 lbs/day and the discharge flow exceeds 0.1 MGD, Part A of the permit should include monitor and report for TDS, chloride, bromide, and sulfate.

b) Where the concentration of bromide in a discharge exceeds 1 mg/L and the discharge flow exceeds 0.1 MGD, Part A of the permit should include monitor and report for bromide.

These requirements apply to all NPDES permitted discharges in the state of Pennsylvania, and thus, permit applications must include an assessment of whether these thresholds are expected to be exceeded. Similar requirements could be

23 40 C.F.R. §122.21. Table IV-Conventional and Nonconventional Pollutants Required to be Tested by Existing Dischargers if Expected to be Present. In Appendix D to Part 122 NPDES Permit Application Testing Requirements

 © Copyright 2019 American Water Works Association

promulgated by other states to enable identification of facilities that may produce bromide loads with the potential to affect downstream drinking water plants.

Monitoring requirements for bromide in NPDES permits

Based on the significant uncertainty associated with bromide concentrations in wet FGD discharges (due to differences in coal use and bromide addition), as well as the flow variability in receiving waters and the sensitivity of different drinking water utilities to different bromide concentrations, bromide concentration monitoring should be required for all power plants discharging wet FGD wastewater (even if treated to remove other pollutants) upstream of drinking water utility intakes.

At present, FGD wastewaters are routinely mixed with other wastewaters prior to discharge (see **Figure 34** and permit review above) and internal monitoring points (IMPs) are not required. Internal monitoring points for wet FGD wastewaters (as required by the 2016 ELGs) will provide more accurate assessment of the pollutant loads associated with this wastewater. As the compliance dates approach for the ELGs, NPDES permits should require measurement of FGD wastewater flow and bromide concentration at these IMPs.

Grab sampling may not be suitable for wastewaters that have variable flow and concentration conditions. As the analysis in **Figure 36** and **Figure 37** demonstrates, reported concentrations in grab samples in systems with variable flow and mixtures of waste streams can be misleading. *Flow-proportional sampling* should be required to ensure representative load assessments can be made. This is generally achieved by requiring a composite rather than a grab sample. In general, a composite sample means a combination of individual samples (e.g., at least eight for a 24-hour period or four for an 8-hour period) each obtained at spaced time intervals during the compositing period. The size of the sample specified should be sufficient to be representative; a minimum of 100 milliliters (mL) is recommended. The composite must be flow-proportional, with the volume of each sample proportional to discharge flow rate or the sampling interval proportional to the flow rates over the time period used to produce the composite. The reviewed PA permits all include this requirement, while the reviewed NC permits do not.

Sample frequency should be set based on expected variability in the produced wastewater from the FGD system. The reviewed PA permits require weekly sampling (24-hour composite) and the reviewed NC permits require monthly sampling (grab). For continuously operating FGD systems at power plants with stable coal usage (and therefore likely stable bromide loads), monthly sampling is likely adequate; however, as noted above, grab sampling should be avoided.

Consideration of Technology-Based Effluent Limitations (TBELs) and Best Professional Judgment (BPJ) technology effluent limitations.

No permits were reviewed that included bromide limitations on effluents from power plants. However, 40 C.F.R. §125.3(c)(3) provides for imposition of technology limitations on a case by case basis where promulgated effluent limitations guidelines only apply to certain aspects of the discharger's operation, or to certain pollutants. Since the Steam Electric ELGs do not include limits on bromide, and bromide is known to be present in the discharges from FGD scrubber systems (see for example: (EPRI 2007a, EPRI 2007b, EPRI 2007c) case-by-case technology limitations may be set. The methods described in Section 3 and Section 4 could be used to determine the effects of bromide discharges

on downstream drinking water plants in order to set a bromide discharge limit for each power plant on a case-by-case basis.

Section Five Data Sources.

Assessing the potential effects of bromide discharges requires understanding of flow conditions and bromide concentrations in the receiving waters.

Flow data for receiving waters is available from the United States Geological Survey (USGS) at *https://waterdata.usgs.gov/nwis/rt*. Bromide data for receiving waters are not widely available. In Pennsylvania, the PA DEP water quality network can be used directly *(http://www.depgis.state.pa.us/WQN/)* or accessed through STORET, where these data and other bromide data are stored by EPA *(https://www.waterqualitydata.us/)*. Regional water quality sources are also available, but may be more difficult to locate and access. In Pennsylvania, sources include Susquehanna River Basin Commission (SRBC) *(http://mdw.srbc.net/remotewaterquality/)*, Three Rivers Quest *(http://3riversquest.org/)*. For the Ohio River Basin, the Ohio River Valley Water Sanitation Commission (ORSANCO) *(http://www.orsanco.org/data/)* has river data. The Water Research Foundation recently funded a nation-wide occurrence survey of bromide and iodide in water supplies (Westerhoff 2018), which may provide additional more recent information to enable a national review of at-risk watersheds.

Information on the discharge (flow and concentration) is needed. Some information is available in NPDES permit applications or in prior permits. Access to NPDES permits (and related application materials) often requires file review in state offices. Information on facility locations, receiving waters for discharges, and discharge monitoring data (DMR) for certain pollutants can be found in through the Enforcement and Compliance History Online (ECHO) web tool available from the U.S. Environmental Protection Agency(USEPA 2018c). *https://cfpub.epa.gov/dmr/ez_search.cfm*.

Some states also have online systems for DMR reports. For example, PADEP has online DMR reports at *https://www.dep.pa.gov/Business/Water/CleanWater/WastewaterMgmt/eDMR/Pages/default.aspx*.

 © Copyright 2019 American Water Works Association

Section 6. Acknowledgements

Jeanne M. VanBriesen is the Duquesne Light Company Professor in Civil & Environmental Engineering and Engineering & Public Policy at Carnegie Mellon University, where she also directs the Center for Water Quality in Urban Environmental Systems. She is a fellow of the American Society of Civil Engineers (ASCE) and its Environmental Water Resources Institute (EWRI), as well as a fellow of the Association of Environmental Engineering and Science Professors (AEESP). Dr. VanBriesen holds a B.S. in Education and a M.S. and Ph.D. in Civil Engineering from Northwestern University. She is a licensed professional engineer (PE) in the state of Delaware as well as a Board Certified Environmental Engineer (BCEE). Her research is in environmental systems, including: urban water system sustainability, bromine-containing disinfection by-products, and impacts of energy extraction and utilization on water sytems. Dr. VanBriesen has published more than sixty scientific articles and given more than 150 professional presentations. Dr. VanBriesen has served on the U.S.EPA Science Advisory Board as well as the board of AEESP and of EWRI. She is currently the Chair of the Board of the Consortium of Universities for the Advancement of Hydrologic Sciences (CUAHSI).

This report would not have been possible without the extensive work of Dr. Jessica Wilson, Dr. Yuxin Wang, Dr. Adam Cadwallader, Dr. Chelsea Kolb, and Dr. Kelly Good. While doctoral students at Carnegie Mellon University under Dr. VanBriesen's supervision, each of these researchers contributed to expanding understanding of bromide in source waters in Pennsylvania and the role played by coal-fired power plant discharges in the changes observed in regional drinking water disinfection by-products. Their doctoral research was funded by the National Science Foundation, the Heinz Endowments, the Colcom Foundation, and through internal support from the Carnegie Mellon University Center for Water Quality in Urban Environmental Systems (Water Quest) and the Wilton E. Scott Institute for Energy Innovation.

AWWA would like to thank all of those who reviewed drafts of report and contributed their knowledge and expertise, including but not limited to those from state drinking water programs, state NPDES permitting offices, and water utilities. The AWWA staff member managing this project's development was Dr. Adam Carpenter, Manager of Energy and Environmental Policy, with contributions from other staff members through review and production. The project was funded through AWWA's Water Industry Technical Action Fund (WITAF).

References

3RQ. (2015). "Three Rivers Quest Data Management Tool." Retrieved July 15, 2016, from http://3riversquest.org/.

Amy, G. and M. Siddiqui (1999). Strategies to control bromate and bromide. Denver, CO, AWWA Research Foundation and American Water Works Association. https://www.waterrf.org/research/projects/strategies-control-bromate-and-bromide.

Amy, G., M. Siddiqui, W. Zhai, J. DeBroux and W. Odem (1993). *Nation-wide survey of bromide ion concentrations in drinking water sources*. American Water Works Association Annual Conference, San Antonio, TX

Amy, G., M. Siddiqui, W. Zhai, J. DeBroux and W. Odem (1994). Survey of Bromide in Drinking Water and Impacts on DBP Formation. Denver, CO, American Water Works Research Foundation. https://www.waterrf.org/research/projects/survey-bromide-drinking-water-and-impacts-dbp-formation.

Ates, N., U. Yetis and M. Kitis (2007). "Effects of bromide ion and natural organic matter fractions on the formation and speciation of chlorination by-products." *ASCE Journal of Environmental Engineering* 133(10): 947-954. https://doi.org/10.1061/(ASCE)0733-9372(2007)133:10(947).

Benson, S., M. Holmes, D. McCollor, J. Mackenzie, C. Crocker, L. Kong, K. Galbreath, K. Dombrowski and C. Richardson (2007). Large scale mercury control technology testing for lignite-fired utilites - oxidation systems for wet FGD. Morgantown, WV, U.S. Department of Energy National Energy Technology Laboratory. https://www.osti.gov/servlets/purl/925511-jjxLYF/.

Bergman, L., J. Wilson, M. Small and J. VanBriesen (2016). "Application of classification trees for predicting disinfection by-product formation targets from source water characteristics." *Environmental Engineering Science* 33(7): 455-470. https://doi.org/10.1089/ees.2016.0044.

Berry, M. (2012). *Full Scale Calcium bromide injection with subsequent mercury oxidation and removal within wet flue gas desulphurization system: experience at a 700 MW coal-fired power facility*. Ph.D., University of Alabama at Birmingham.

Bond, T., J. Huang, N. Graham and M. Templeton (2014). "Examining the interrelationship between DOC, bromide and chlorine dose on DBP formation in drinking water – a case study" *Science for the Total Environment* 470-471: 469-479. https://doi.org/10.1016/j.scitotenv.2013.09.106.

Bowen, H. (1966). *Trace elements in biochemistry*. New York, Academic Press.

Bowen, H. (1979). *Environmental Chemistry of the elements*. London, Academic Press.

Bull, R., G. Rice and L. Teuschler (2009a). "Determinants of whether or not mixtures of disinfection by-products are similar." *J. Toxicol. Environ. Health A* 72: 437-460. https://doi.org/10.1080/15287390802608916.

Bull, R., G. Rice, L. Teuschler and P. Feder (2009b). "Chemical measures of similarity among disinfection by-product mixtures." *J. Toxicol. Environ. Health A* 72: 482-493. https://doi.org/10.1080/15287390802608973.

Cadwallader, A. and J. VanBriesen (2019). "Temporal and spatial variability in bromine incorporation into drinking water disinfection byproducts in Pennsylvania." *ASCE Journal of Environmental Engineering* 145(3). https://doi.org/10.1061/(ASCE)EE.1943-7870.0001499.

Chang, H., H. Tung, C. Chao and G. Wang (2010). "Occurrence of haloacetic acids (HAAs) and trihalomethanes (THMs) in drinking water of Taiwan." *Environ. Monit. Assess.* 162: 237-250. https://doi.org/10.1007/s10661-009-0792-1.

© Copyright 2019 American Water Works Association

Charisiadis, P., S. Andra, K. Makris, C. Christophi, D. Skarlatos, V. Vamvakousis, S. Kargaki and E. Stephanou (2015). "Spatial and seasonal variability of tap water disinfection by products within distribution pipe networks." *Science for the Total Environment* 506-507: 26-35. https://doi.org/10.1016/j.scitotenv.2014.10.071.

Chen, B., T. Zhang, T. Bond and Y. Gan (2015). "Development of quantitative structure activity relationship (QSAR) model for disinfection byproduct (DBP) research: a review of methods and resources." *Journal of Hazardous Materials* 299: 260-279. https://doi.org/10.1016/j.jhazmat.2015.06.054.

Chen, W.-H., K. Haunschild, J. Lund and W. Fleenor (2010). "Current and long-term effects of Delta water quality on drinking water treatment costs from disinfection byproduct formation." *San Fr. Estuary Watershe Sci* 8(3): 1-21. https://doi.org/10.15447/sfews.2010v8iss3art4.

Chisholm, K., A. Cook, C. Bower and P. Weinstein (2008). "Risk of birth defects in Australian communities with high levels of brominated disinfection by-products." *Environ Health Perspect* 116: 1267-1273. https://doi.org/10.1289/ehp.10980.

Chowdhury, S., P. Champagne and P. McLellan (2009). "Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review." *Science of the Total Environment* 407: 4189-4206. https://doi.org/10.1016/j.scitotenv.2009.04.006.

Clarke, L. B. (1993). "The fate of trace elements during coal combustion and gasification: an overview." *Fuel* 89(4): 904-911. https://doi.org/10.1016/0016-2361(93)90072-A

Cornwell, D., D. Roth, R. Brown and T. Boyer (2016). *Impact of increased bromide from industrial sources to water utilities: Bromide relationships in a possible new DBP regulation*. American Water Works Association (AWWA) Annual Conference and Exposition (ACE), Chicago, IL, American Water Works Association.

Cornwell, D., B. Sidhu, R. Brown and N. McTigue (2018). "Modeling bromide river transport and bromide impacts on disinfection byproducts." *Journal of American Water Works Association* 110(11). https://doi.org/10.1002/awwa.1145.

Cortes, C. and R. Marcos (2018). "Genotoxicity of disinfection byproducts and disinfected waters: a review of recent literature." *Mutation Research / Genetic Toxicology and Environmental Mutagenesis* 831(July): 1-12. https://doi.org/10.1016/j.mrgentox.2018.04.005.

DiCosmo, B. (2012). "EPA weighs setting possible first-time water quality criteria for bromide." *Inside EPA*: 1-2. https://insideepa.com/daily-news/epa-weighs-setting-possible-first-time-water-quality-criteria-bromide.

Diehl, A., G. Speitel, Jr., J. Symons, S. Krasner, C. Hwang and S. Barrett (2000). "DBP formation during chloramination." *Journal of American Water Works Association* 92(6): 76-90. https://doi.org/10.1002/j.1551-8833.2000.tb08961.x.

Dombrowski, K., J. Paradis, URSCorporation, G. Looney, A. Sibley and SCServices (2010). Evaluation of Mercury Control Technologies at a Power Plant without SCR Firing Eastern Bituminous Coal. San Francisco, CA, URS Power

Duong, H., M. Berg, M. Hoang, H. Pham, H. Gallard, W. Giger and U. von Gunten (2003). "Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwater in water supplies of Hanoi, Vietnam." *Water Research* 37(13): 3242-3252. https://doi.org/10.1016/S0043-1354(03)00138-6.

Dutton, R., R. Rosvold, J. Conn, S. Morrow, R. Change, J. Paradis, C. Richardson and K. Fisher (2010). Options for High Mercury Removal at PRB-fired Units Equipped with Fabric Filters with Emphasis on Preserving Fly Ash Sales. San Francisco, CA, URS Power.

Echigo, S., S. Itoh, T. Natsui, T. Araki and R. Ando (2004). "Contribution of brominated organic disinfection by-products to the mutagenicity of drinking water." *Water Science and Technology* 50(5): 321-328. https://doi.org/10.2166/wst.2004.0344.

EIA. (2017). "Form EIA-860 year 2016 detailed data." Retrieved November 11, 2017, from https://www.eia.gov/electricity/data/eia860/.

EIA. (2018). "Form EIA-923 detailed data." Retrieved October 27, 2018, from https://www.eia.gov/electricity/data/eia923/.

EPRI (2004). Field evaluation of the comanagement of utility low-volume wastes with high-volume coal combustion by-products: OK Site. Palo Alto, CA, Electric Power Research Institute. https://www.epri.com/#/pages/product/000000000001005268/.

EPRI (2006). Status of Mercury Control Technologies: Activated Carbon Injection and Boiler Chemical Additives. Palo Alto, CA, Electric Power Research Institute. https://www.epri.com/#/pages/product/000000000001010349/.

EPRI (2007a). Field Evaluation of the Comanagement of Utility Low-Volume Wastes with High-Volume Coal Combustion By-Products: LS Site. Palo Alto, CA, Electric Power Research Institute. https://www.epri.com/#/pages/product/000000000001014050/.

EPRI (2007b). Field evaluation of the comanagement of utility low-volume wastes with high-volume coal combustion by-products: PA site. Palo Alto, CA, Electric Power Research Institute. https://www.epri.com/#/pages/product/000000000001012580/.

EPRI (2007c). Sampling and Analytical Plan Guidance for Water Characterization of Coal-Fired Steam Electric Utility Facilities. P. Chu. Palo Alto, CA, Electric Power Research Institute. https://www.epri.com/#/pages/product/1014946/

EPRI (2008). Mercury Control Technology. Palo Alto, CA, Electric Power Research Institute. https://www.epri.com/#/pages/product/000000000001014172/.

EPRI (2011). Mercury Oxidation Behavior of a New Advanced Selective Catalytic Reduction Catalyst Formulation. Palo Alto, CA, Electric Power Research Institute. https://www.epri.com/#/pages/product/000000000001023398/.

EPRI (2014). Program on Technology Innovation: Bromine usage, fate, and potential impacts for fossil fuel-fired power plants. Palo Alto, CA, Electric Power Research Institute. https://www.epri.com/#/pages/product/000000003002002510/.

ESRI-Inc. (2016). ArcGIS Version 10.4.1 for Desktop. Redlands, CA.

Ferrar, K., D. Michanowicz, C. Christen, N. Mulcahy, S. Malone and R. Sharma (2013). "Assessment of Effluents Contaminants from Three Facilities Discharging Marcellus Shale Wastewater to Surface Waters in Pennsylvania." *Environmental Science and Technology* 47(7): 3472-3481. https://doi.org/10.1021/es301411q.

Finkelman, R. (1993). Trace and minor elements in coal. *Organic Geochemistry*. M. Engel and S. Macko. New York, NY, Plenum Press. https://doi.org/10.1007/978-1-4615-2890-6_28.

Flury, M. and A. Papritz (1993). "Bromide in the natural environment: occurrence and toxicity." *Journal of Environmental Quality* 22(4): 747-758. https://doi.org/10.2134/jeq1993.00472425002200040017x.

Francis, R., M. Small and J. VanBriesen (2009). "Multivariate distributions of disinfection by-products in chlorinated drinking water." *Water Research* 43: 3453-3468. https://doi.org/10.1016/j.watres.2009.05.008.

Francis, R., J. VanBriesen and M. Small (2010). "Bayesian Statistical Modeling of Disinfection Byproduct (DBP) Bromine Incorporation in the ICR Database." *Environmental Science and Technology* 44(4): 1232-1239. https://doi.org/10.1021/es9028606.

Frank, S. (2011). Calcium Bromide Chemical Additive Sample Results 2011 Calcium Bromide Performance Trail February 7 to 12, 2011 NPDES Permit No PA0005011 Conemaugh Generating Station. Canonsburg, PA, Letter Report submitted to PA DEP Southwest Region, Pittsburgh PA. March 10, 2011.

Gadgil, M., M. Abbott, S. Batanian, G. Kotch, T. Owens and M. Watson (2014). *Advances in Refined Coal Technology for Emissions Reduction Advances*. Power Plant Pollutant Control "Mega" Symposium, Baltimore, MD.

Ged, E. and T. Boyer (2014). "Effect of seawater intrusion on formation of bromine-containing trihalomethanes and haloacetic acids during chlorination." *Desalination* 345: 85-93. https://doi.org/10.1016/j.desal.2014.04.021.

Ged, E., P. Chadik and T. Boyer (2015). "Predictive capability of chlorination disinfection byproducts models." *Journal of Environmental Management* 149: 253-262. https://doi.org/10.1016/j.jenvman.2014.10.014.

Good, K. (2018). *Coal-fired power plant wastewater contributions to bromide concentrations in drinking water sources*. Ph.D., Carnegie Mellon University.

Good, K. and J. VanBriesen (2017). "Power plant bromide discharges and downstream drinking water systems in Pennsylvania." *Environmental Science and Technology* 51(20): 11829-11838. https://doi.org/10.1021/acs.est.7b03003.

Good, K. and J. M. VanBriesen (2016). "Current and potential future bromide loads from coal-fired power plants in the Allegheny River Basin and their effects on downstream concentrations." *Environmental Science and Technology* 50(17): 9078-9088. https://doi.org/10.1021/acs.est.6b01770.

Good, K. D. and J. M. VanBriesen (2018). "Coal-fired power plant wet flue gas desulfurization bromide discharges to U.S. watersheds and their contributions to drinking water sources." *Environmental Science and Technology* 53(1): 213-223. https://doi.org/10.1021/acs.est.8b03036.

Gould, J., L. Fitchhorn and E. Urheim (1983). Formation of brominated trihalomethanes: extent and kinetics. *Fourth Conference on Water Chlorination: Environmental Impact and Health Effects*. R. Jolley. Ann Arbor, MI, Ann Arbor Science. 4: 297-310.

Handke, P. (2009). Trihalomethane speciation and the relationship to elevated total dissolved solid concentrations affecting drinking water quality at systems utilizing the Monongahela River as a primary source during the 3rd and 4th quarters of 2008. Harrisburg, PA, Pennsylvania Department of Environmental Protection Bureau of Water Standards and Facility Regulation. http://files.dep.state.pa.us/water/Wastewater%20Management/WastewaterPortalFiles/MarcellusShaleWastewaterPartnership/dbp_mon_report__dbp_correlation.pdf.

Hebert, A., D. Forestier, D. Lenes, D. Benanou, S. Jacob, C. Arfi, L. Lambolez and Y. Levi (2010). "Innovative method for prioritizing emerging disinfection by-products (DBPs) in drinking water on the basis of their potential impact on public health." *Water Research* 44: 3147-3165. https://doi.org/10.1016/j.watres.2010.02.004.

Heeb, M., J. Criquet, S. Zimmermann-Steffens and U. vonGunten (2014). "Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds – a critical review." *Water Research* 48: 15-42. https://doi.org/10.1016/j.watres.2013.08.030.

Hellergrossman, L., J. Manka, B. Limonirelis and M. Rebhun (1993). "Formation and distribution of haloacetic acids, THM, and TOX in chlorination of bromide-rich lake water." *Water Research* 27(8): 1323-1331. https://doi.org/10.1016/0043-1354(93)90219-8.

Helsel, D. (1990). "Less than obvious - statistical treatment of data below the detection limit." *Environmental Science and Technology* 24(12): 1766-1774. https://doi.org/10.1021/es00082a001.

Hintz, D. (2016). Email. Topic: Question on publication no 297. J. VanBriesen: 1.

Hintz, D. R. and L. Y. Steffy (2015). Data Report of Baseline Conditions for 2010-2013. *Remote Water Quality Monitoring Network*. Harrisburgh, PA, Susquehanna River Basin Commisssion (SRBC). https://mdw.srbc.net/remotewaterquality/assets/downloads/pdf/RWQMN_datareport_2010-2013.PDF.

Holm, L., S. Harader and P. Fernandez (2007). CALFED Water Quality Program Stage 1 Final Assessment. CALFED, CALFED Bay Delta Program.

Hong, H., Y. Liang, B. Han, A. Mazumder and M. Wong (2007). "Modeling of trihalomethane (THM) formation via chlorination of the water from Dongjiang River (source water for Hong Kong's drinking water)." *Science for the Total Environment* 385: 48-54. https://doi.org/10.1016/j.scitotenv.2007.07.031.

Hrudey, S., L. Backer, A. Humpage, S. Krasner, D. Michaud, L. Moore, P. Singer and B. Stanford (2015). "Evaluating Evidence for Association of Human Bladdar Cancer with Drinking-water Chlorination Disinfection By-Products." *Journal of Toxicology and Environmental Health, Part B* 18(5): 213-241. https://doi.org/10.1080/10937404.2015.1067661.

Hua, G. and D. Reckhow (2012). "Evaluation of bromine substitution factors of DBPs during chlorination and chloramination." *Water Research* 46: 4208-4216. https://doi.org/10.1016/j.watres.2012.05.031.

Hua, G., D. Reckhow and J. Kim (2006). "Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination." *Environmental Science and Technology* 40: 3050-3056. https://doi.org/10.1021/es0519278.

Hwang, C., S. Krasner, M. Sclimenti, G. Amy and E. Dickenson (2002). Polar NOM: Characterization, DBPs, Treatment. Denver, CO, American Water Works Research Foundation. https://www.waterrf.org/research/projects/polar-nom-characterization-dbps-treatment.

IRS (2010). IRS Notice 2010-54: Production Tax Credit for Refined Coal. Washington DC, Internal Revenue Service. https://www.irs.gov/pub/irs-drop/n-10-54.doc.

Kogevinas, M. and C. Villanueva (2011). "Carcinogenicity of Disinfection Byproducts in Humans: Epidemiological Studies." *Encyclopedia of Environmental Health* 2011: 505-515. https://doi.org/10.1016/B978-0-444-52272-6.00100-8.

Kolb, C. (2018). *Drinking Water Quality and Risk Challenges from Increasing Source Water Bromide: Climate and Energy Changes*. Ph.D., Carnegie Mellon University.

Kolb, C., R. Francis and J. M. VanBriesen (2017). "Disinfection by-product regulatory compliance surrogates and bromide-associated risk." *Journal of Environmental Sciences* 58: 191-207. https://doi.org/10.1016/j.jes.2017.05.043.

Kolb, C., K. D. Good and J. M. VanBriesen (2019). "Estimated coal-fired power plant bromide contributions to disinfection byproduct risk in the Monongahela River Basin." *Environmental Science and Technology* submitted.

Kolker, A. and J. Quick (2015). Mercury and Halogens in Coal. *Mercury Control: for Coal-Derived Gas Streams*. E. PGranite, H. Pennline and C. Senior. Weinheim, Germany, Wiley-VCH Verlag GmbH&Co: 13-44.

Kolker, A., J. Quick, C. Senior and H. Belkin (2012). Mercury and Halogens in Coal - their role in determining mercury admissions from coal combustion. *Fact Sheet*. Reston, VA, United States Geological Society. https://pubs.er.usgs.gov/publication/fs20123122

Krasner, S., C. Lee, R. Chinn, S. Hartono, H. Weinberg, S. Richardson, J. Pressman, T. Speth, R. Miltner and J. Simmons (2008). *Bromine incorporation in regulated and emerging DBPs and the relative predominance of mono-, di- and trihalogenated DBPs.* AWWA Water Quality Technology Conference, Cincinnati, OH, American Water Works Association.

Krasner, S., M. Sclimenti, R. Chinn, Z. Chowdhury and D. Owen (1996). The impact of TOC and bromide on chlorination by-product formation. *Disinfection By-Products in Water Treatment: The Chemistry of their formation and control* R. Minear and G. Amy. Boca Raton, FL, CRC Press / Lewis Publishers: 59-90.

Krasner, S., M. Sclimenti and E. Means (1994). "Quality degradation: implications for DBP formation." *Journal of American Water Works Association* 96(6): 34-47. https://doi.org/10.1002/j.1551-8833.1994.tb06208.x.

Krasner, S., H. Weinberg, S. Richardson, S. Pastor, R. Chinn, M. Sclimenti, G. Donstad and A. Thruston, Jr. (2006). "Occurrence of a New Generation of Disinfection Byproducts." *Environmental Science and Technology* 40(23): 7175-7185. https://doi.org/10.1021/es060353j.

Landis, M., A. Kamal, K. Kovalcik, D. Croghan, G. Norris and A. Bergdale (2016). "The impact of commercially treated oil and gas produced water discharges on bromide concentrations and modeled brominated trihalomethane disinfection byproducts at two downstream municipal drinking water plants in the upper Allegheny River, Pennsylvania, USA." *Science of the Total Environment* 542: 505-520. https://doi.org/10.1016/j.scitotenv.2015.10.074.

Malcolm-Pirnie (1992). Water Treatment Plant Simulation Program User's Manual. U. S. E. P. Agency. Washington DC. Version 1.21.

Malcolm-Pirnie (1993). Bay Delta Water Quality Modeling Report #15-041. Los Angeles, CA, Metropolitan Water District of Southern California.

McGuire, M. and M. Hotaling (2002). Relationship between source water quality and choices of primary and secondary disinfectants. *Information Collection Rule Data Analysis*. M. McGuire, J. McLain and A. Obolensky. Denver, CO, American Water Works Research Foundation: 299-315.

McKay, L., T. Bondelid, T. Dewald, J. Johnston, R. Moore and A. Rea (2018). NHDPlus Version 2: User Guide (Data Model Version 2.1).

McLain, J., A. Obolensky and H. Shukairy (2002). Disinfection byproduct speciation. *Information Collection Rule Data Analysis*. M. McGuire, J. McLain and A. Obolensky. Denver, CO, American Water Works Association Research Foundation: 141-168.

McTigue, N., D. Cornwell, K. Graf and R. Brown (2014). "Occurrence and consequences of increased bromide in drinking water sources." *Journal of the American Water Works Association* 106(11): E492-E508. https://doi.org/10.5942/jawwa.2014.106.0141.

Meier, J., B. Keiser and B. S. Higgins (2015). Fuel and Flue-gas additives. *Mercury Control for coal derived gas streams*. E. Granite, H. Pennline and C. Senior. Weinheim, Germany, Wiley-VCH Verlag GmbH & Co: 241-251.

Meij, R. (1994). "Trace-Element Behavior in Coal-Fired Power-Plants." *Fuel Processing Technology* 39(1-3): 199-217. https://doi.org/10.1016/0378-3820(94)90180-5.

Montgomery-Watson (1993). Mathematical modeling of the formation of THMs and HAAs in Chlorinated Natural Waters. Denver, CO, American Water Works Association Research Foundation.

NCDENR (2012). Duke Energy Corporation Belews Creek Steam Station NPDES Permit NC0024406. Raleigh, NC, North Carolina Department of Environmental and Natural Resources.

NHDPlusV2 National Hydrography Dataset Plus Version 2, U.S. Environmental Protection Agency and U.S. Geological Survey. https://www.epa.gov/waterdata/nhdplus-national-hydrography-dataset-plus.

Nieuwenhuijsen, M., J. Grellier, R. Smith, N. Iszatt, J. Bennett, N. Best and M. Toledano (2009). "The epidemiology and possible mechanisms of disinfection by-products in drinking water." *Philosophical Transactions of the Royal Society A* 367: 4043-4076. https://doi.org/10.1098/rsta.2009.0116.

Obolensky, A. and P. Singer (2005). "Halogen substitution patterns among disinfection byproducts in the Information Collection Rule database." *Environmental Science and Technology* 39: 2719-2730. https://doi.org/10.1021/es0489339.

PADEP. (2018). "Drinking Water Reporting System." Retrieved October 27, 2018, from http://www.drinkingwater.state.pa.us/dwrs/HTM/Welcome.html.

Palmer, C., C. Oman, A. Park and J. Luppens (2015). U.S. Geological Survey Coal Quality (COALQUAL) Database Version 3.0. Reston, VA, U.S. Geological Survey Data Series 975. https://ncrdspublic.er.usgs.gov/coalqual/.

Peng, B.-X., L. Li and D.-S. Wu (2013). "Distribution of bromine and iodine in thermal power plant." *J Coal Sci Eng* 19(3): 387-391. https://doi.org/10.1007/s12404-013-0320-3.

Plewa, M., E. Wagner, S. Richardson, A. Thruston, Y. Woo and A. McKague (2004). "Chemical and biological characterization of newly discovered iodoacid drinking water disinfection byproducts." *Environmental Science and Technology* 38(18): 4713-4722. https://doi.org/10.1021/es049971v.

Pourmoghaddas, H., A. Stevens, R. Kinman, R. Dressman, L. Moore and J. Ireland (1993). "Effect of bromide ion on formation of HAA5 during chlorination." *Journal of American Water Works Association* 85(1): 82-87. https://doi.org/10.1002/j.1551-8833.1993.tb05924.x.

Regli, S., J. Chen, M. Messner, M. Elovitz, F. Letkiewicz, R. Pegram, T. Pepping, S. Richardson and J. Wright (2015). "Estimating potential increased bladdar cancer risk due to increased bromide concentrations in sources of disinfected drinking waters." *Environmental Science and Technology* 49(22): 13094-13102. https://doi.org/10.1021/acs.est.5b03547.

Richardson, S., M. Plewa, E. Wagner, R. Schoeny and D. DeMarini (2007). "Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research." *Mutation Research* 636: 178-242. https://doi.org/10.1016/j.mrrev.2007.09.001.

Sadiq, R. and M. Rodriguez (2004). "Disinfection byproducts (DBPs) in drinking water and predictive models for their occurrence: a review." *Science for the Total Environment* 321: 21-46. https://doi.org/10.1016/j.scitotenv.2003.05.001.

Salas, L., K. Cantor, A. Tardon, C. Serra, A. Carrato, R. Garcia-Closas, N. Rothman, N. Malats, D. Silverman, M. Kogevinas and C. Villanueva (2013). "Biological and statistical approaches for modeling exposure to specific trihalomethanes and bladder cancer risk." *American Journal of Epidemiology* 178(4): 652-661. https://doi.org/10.1093/aje/kwt009.

Sawade, E., R. Fabris, A. Humpage and M. Drikas (2016). "Effect of increasing bromide concentration on toxicity in treated drinking water." *Journal of Water and Health* 14(2): 183-191. https://doi.org/10.2166/wh.2015.127.

Seidel, C., C. CSamson, T. Bartrand, A. Ergul and R. Summers (2017). "Disinfection Byproduct Occurrence at Large Water Systems After Stage 2 DBPR." *Journal of American Water Works Association* 109(7): 17-30. https://doi.org/10.5942/jawwa.2017.109.0082.

Soltermann, F., C. Abegglen, C. Gotz and U. vonGunten (2016). "Bromide sources and loads in Swiss surface waters and their relevance for bromate formation during wastewater ozonation." *Environmental Science and Technology* 50(18): 9825-9834. https://doi.org/10.1021/acs.est.6b01142.

Srivastava, R., N. Hutson, B. Martin, F. Princiotta and J. Staudt (2006). "Control of Mercury Emissions from Coal-Fired Electric Utility Boilers." *Environmental Science and Technology*: 1385. https://doi.org/10.1021/es062639u.

States, S., G. Cyprych, M. Stoner, F. Wydra, J. Kuchta, J. Monnell and L. Casson (2013). "Marcellus shale drilling and brominated THMs in Pittsburgh, PA, drinking water." *Journal of the American Water Works Association* 105(8): E432-E448. https://doi.org/10.5942/jawwa.2013.105.0093.

Steffy, L. Y. (2013). Lower Susquehanna River Subbasin Year-2 Focused Watershed Study. Harrisburg, PA, Susquehanna River Basin Commission (SRBC). https://www.srbc.net/our-work/reports-library/technical-reports/288-lower-subbasin-reservoirs-water-quality-assessment/docs/lower-subbasin-reservoirs-survey.pdf.

Symons, J., S. Krasner, M. Sclimenti, L. Simms, H. Sorensen, Jr. , G. Speitel, Jr. and A. Diehl (1996). Influence of bromide ion on trihalomethane and haloacetic acid formation. *Disinfection By-Products in Water Treatment: The chemistry of their formation and control* R. Minear and G. Amy. Boca Raton, FL, CRC PRess / Lewis Publishers: 91-130.

Symons, J., S. Krasner, L. Simms and M. Sclimenti (1993). "Measurement of THM and precursor concentrations revisited - the effect of bromide ion." *Journal of American Water Works Association* 85(1): 51-62. https://doi.org/10.1002/j.1551-8833.1993.tb05921.x.

USEPA (1993). Method 300.0 Determination of inorganic anions by ion chromatography. Washington DC, U.S. Environmental Protection Agency. https://www.epa.gov/sites/production/files/2015-08/documents/method_300-0_rev_2-1_1993.pdf.

USEPA (1998). National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts, Final Rule. *40 C.F.R*, Federal Register. 63:241: 69390-69476. https://www.govinfo.gov/content/pkg/FR-1998-12-16/pdf/98-32887.pdf.

USEPA (1999). Method 300.1 Determination of Inorganic Anions in drinking water by ion chromatography. Washington DC, US Environmental Protection Agency. https://www.epa.gov/sites/production/files/2015-06/documents/epa-300.1.pdf.

USEPA (2000). ICR Auxiliary 1 Database Version 5.0 Query Tool Version 2.0, U.S. Environmental Protection Agency.

USEPA (2001). Water Treatment Plant Model, Version 2.0, User's Manual, U.S. Environmental Protection Agency. https://www.epa.gov/sites/production/files/2017-03/documents/wtp_model_v._2.0_manual_508.pdf.

USEPA (2005). Appendices to the Economic Analysis for the Final Stage 2 Disinfectants and Disinfection Byproducts Rule. I. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100NJFH.TXT.

USEPA (2006a). Economic analysis for the final stage 2 disinfectants and disinfection byproducts rule. Washington DC, U.S. Environmental Protection Agency. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1005OOX.TXT.

USEPA (2006b). National primary drinking water regulations: Stage 2 disinfectant and disinfection byproduct rule. Washington, DC, U.S. Environmental Protection Agency: 388-493. https://www.govinfo.gov/content/pkg/FR-2006-01-04/pdf/06-3.pdf.

USEPA (2009a). Industry Provided Sampling Data from Duke Energy's Allen Steam Station. FGD Purge Analytical Data from 3/3/09 to 5/21/11. Washington,DC, United States Environmental Protection Agency. EPA HQ OW 2009-0819-1227-1.

USEPA (2009b). Steam Electric Power Generating Point Source Category: Final Detailed Study Report. Washington DC, U.S. Environmental Protection Agency. https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1005J8A.TXT.

USEPA (2010a). NPDES Permit Writers' Manual. Washington, DC, United States Environmental Protection Agency. EPA 833 K 10 001. https://www.epa.gov/sites/production/files/2015-09/documents/pwm_2010.pdf.

USEPA. (2010b). "Steam Electric Power Generating Effluent Guidelines Questionnaire Responses. Publically Available Version." Retrieved July 31, 2018, from https://www.epa.gov/eg/steam-electric-power-generating-effluent-guidelines-questionnaire.

USEPA (2011). Regulatory Impact Analysis for the Final Mercury and Air Toxics Standards. Research Triangle Park, NC, U.S. Environmental Protection Agency. https://www3.epa.gov/ttnecas1/regdata/RIAs/matsriafinal.pdf.

USEPA (2012). National Emission Standards for Hazardous Air Pollutants from Coal- and Oil-Fired Electric Utility Steam Generating Units and Standards of Performance for Fossil-Fuel-Fired Electric Utility, Industrial-Commercial-Institutional, and Small Industrial-Commercial-Institutional Steam Generating Units. *Final Rule*. Washington, DC, U.S. Environmental Protection Agency 77: 9304-9513. https://www.govinfo.gov/content/pkg/FR-2012-02-16/pdf/2012-806.pdf

USEPA (2013a). Environmental Assessment for the Proposed Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category. Washington DC, United States Environmental Protection Agency Office of Water.

USEPA (2013b). Industry provided sampling data from Duke Energy's Belews Creek Steam Station. Belews Creek Biochem Effluent Analytical Data from 12/3/08 to 12/7/09. Washington DC, U.S. Environmental Protection Agency. DCN SE01808.

USEPA (2015a). Current and Future Industry Profile. DCN SE00444. Washington, DC, United States Environmental Protection Agency.

USEPA (2015b). Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category (final). *EPA-HQ-OW-2009-0819*. Washington DC, United States Environmental Protection Agency. 40 C.F.R.: 67837-67903. *https://www.govinfo.gov/content/pkg/FR-2015-11-03/pdf/2015-25663.pdf*

USEPA (2015c). Environmental Assessment for the Effluent Limitatiosn Guidelies and Standards for the Steam Electric Power Generating Point Source Category. Washington, DC, United States Environmental Protection Agency. *https://www.epa.gov/sites/production/files/2015-10/documents/steam-electric-envir_10-20-15.pdf*

USEPA (2015d). Sources contributing inorganic species to drinking water intakes during low flow conditions on the Allegheny River in western Pennsylvania. Washington DC, U.S. Environmental Protection Agency. *https://www.epa.gov/sites/production/files/2015-05/documents/epa_source_apportionment_rpt_final_07may2015_508_km.pdf*.

USEPA (2015e). Technical Development Document for the Effluent Limitations Guidelines and Standards for the Steam Electric Power Generating Point Source Category. Washington, DC, United States Environmental Protection Agency. *https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P100NTDT.TXT*.

USEPA (2016a). EPA's Safe Drinking Water Information System. Washington, DC, United States Environmental Protection Agency. *https://www.epa.gov/ground-water-and-drinking-water/safe-drinking-water-information-system-sdwis-federal-reporting*.

USEPA (2016b). Revisions to the Unregulated Contaminant Monitoring Rule (UCMR 4) for Public Water Systems and Announcement of Public Meeting. Washington, DC, U.S. Environmental Protection Agency. 81: 92666-92692. *https://www.govinfo.gov/content/pkg/FR-2016-12-20/pdf/2016-30469.pdf*.

USEPA. (2018a). "Air Markets Program Data." Retrieved July 28, 2018. *https://ampd.epa.gov/ampd/*.

USEPA. (2018b). "Drinking Water Mapping Application to Protect Source Waters (DWMAPS)." Retrieved July 27, 2018, from *https://www.epa.gov/sourcewaterprotection/drinking-water-mapping-application-protect-source-waters-dwmaps*.

USEPA. (2018c). "ECHO (Enforcement and Compliance History Online)." Retrieved December 26, 2018, 2018, from *https://echo.epa.gov/trends/loading-tool/water-pollution-search*.

VanBriesen, J. M. (2013). Potential Drinking Water Effects of Bromide Discharges from Coal-Fired Electric Power Plants (submitted comments for ELGs). Washington DC, U.S. Environmental Protection Agency.

Vassilev, S., G. Eskenazy and C. Vassileva (2000). "Contents, modes of occurrence and origin of chlorine and bromine in coal." *Fuel* 79(8): 903-921. *https://doi.org/10.1016/S0016-2361(99)00236-7*.

Vejahati, F., Z. Xu and R. Gupta (2010). "Trace elements in coal: associations with coal and minerals and their behavior during coal utilization - a review." *Fuel* 89(4): 904-911. *https://doi.org/10.1016/j.fuel.2009.06.013*.

Villanueva, C., K. Cantor, J. Grimalt, N. Malats, D. Silverman, A. Tardon, R. Garcia-Closas, C. Serra, A. Carrato, G. Castano-Vinyals, R. Marcos, N. Rothman, F. Real, M. Dosemeci and M. Kogevinas (2007). "Bladder cancer and exposure to water disinfection by products through ingestion, bathing, showering and swimming in pools." *American Journal of Epidemiology* 165(2): 148-156. *https://doi.org/10.1093/aje/kwj364*.

Villanueva, C., S. Cordier, L. Font-Ribera, L. Salas and P. Levallois (2015). "Overview of Disinfection By-products and Associated Health Effects." *Curr Envir Health Rpt* 2: 107-115. https://doi.org/10.1007/s40572-014-0032-x.

Wang, Y., M. Small and J. M. VanBriesen (2016). "Assessing the risk associated with increasing bromide in drinking water sources in the Monongahela River, Pennsylvania." *ASCE Journal of Environmental Engineering* 143(3). https://doi.org/10.1061/(ASCE)EE.1943-7870.0001175.

Wang, Y., J. Wilson and J. VanBriesen (2015). "The effect of sampling strategies on assessment of water quality criteria attainment." *Journal of Environmental Management* 154: 33-39. https://doi.org/10.1016/j.jenvman.2015.02.019.

Watson, K., M. Farre and N. Knight (2012). "Strategies for the removal of halides from drinking water sources, and their applicability in disinfection by-product minimisation: a critical review." *J Environ Manage* 110: 276-298. https://doi.org/10.1016/j.jenvman.2012.05.023.

Weaver, J., J. Xu and S. Mravik (2016). "Scenario Analysis of the Impact on Drinking Water Intakes from Bromide in the Discharge of Treated Oil and Gas Wastewater." *ASCE Journal of Environmental Engineering* 142(1). https://doi.org/10.1061/(ASCE)EE.1943-7870.0000968.

Weinberg, H., S. Krasner, S. Richardson and A. Thruston, Jr. (2002). The Occurrence of Disinfection By-Products (DBPs) of Health Concern in Drinking Water: Results of a Nationwide DBP Occurrence Study. Washington DC, National Exposure Research Laboratory. Office of Research and Development. EPA/600/R-02/068. https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=525040

Werkheiser, E. J. (2016). Brunner Island, LLC Mercury and Air Toxics Standards (MATS) Initial Compliance Demonstration Report Dated January 22, 2016. Harrisburg, PA, PA Department of Environmental Protection.

Westerhoff, P. (2018). "Occurrence Survey of Bromide and Iodide in Water Supplies." Retrieved 9/28/2018, 2018, from http://www.waterrf.org/Pages/Projects.aspx?PID=4711.

Westerhoff, P., P. Chao and H. Mash (2004). "Reactivity of natural organic matter with aqueous chlorine and bromine." *Water Research* 38(6): 1502-1513. https://doi.org/10.1016/j.watres.2003.12.014.

WHO (2009). Bromide in drinking water: Background document for development of WHO *Guidelines for Drinking-water Quality.* Geneva, Switzerland, World Health Organization. *https://apps.who.int/iris/handle/10665/70169*.

Wilson, J. and J. VanBriesen (2012). "Oil and gas produced water management and surface drinking water sources in Pennsylvania." *Environmental Practice* 14(4): 288-300. https://doi.org/10.1017/S1466046612000427.

Wilson, J. and J. VanBriesen (2013). *Effects of oil and gas produced water management on surface drinking water sources in Pennsylvania*. AEESP Conference, Colorado School of Mines, Goldon, CO.

Wilson, J. and J. VanBriesen (2014). "Source water changes and energy extraction activities in the Monongahela River, 2009-2012." *Environmental Science and Technology* 47(21): 12575-12582. https://doi.org/10.1021/es402437n.

Wilson, J., Y. Wang and J. VanBriesen (2013). "Sources of high total dissolved solids to drinking water supply in Southwestern Pennsylvania." *ASCE Journal of Environmental Engineering* 140(Special Issue on Shale Gas Environmental Impacts): B4014003. https://doi.org/10.1061/(ASCE)EE.1943-7870.0000733.

Wu, W. and P. Chadik (1998). "Effect of bromide ion on haloacetic acid formation during chlorination of Biscayne aquifer water." *ASCE Journal of Environmental Engineering* 124(10): 932-938. https://doi.org/10.1061/(ASCE)0733-9372(1998)124:10(932).

Xu, M., R. Yan, C. Zheng, Y. Qiao, J. Han and C. Sheng (2004). "Status of trace element emissions in a coal combustion process: a review." *Fuel Process. Technol.* 85: 215-237. https://doi.org/10.1016/S0378-3820(03)00174-7.

Yang, J. (2017). *An Update on Modifications to Water Treatment Plant Model*. AWWA Water Quality Technology Confrence, Portland, OR, AWWA.

Yang, Y., Y. Komaki, S. Kimura, H.-Y. Hu, E. Wagner, B. Marinas and M. Plewa (2014). "Toxic impact of bromide and iodide on drinking water disinfected with chlorine and chloramines." *Environmental Science and Technology* 48: 12362-12369. https://doi.org/10.1021/es503621e.

Ye, B., W. Wang, L. Yang, J. Wei and E. Xueli (2009). "Factors influencing disinfection by-products formation in drinking water of six cities in China." *J. Hazard. Mater.* 171: 147-152. https://doi.org/10.1016/j.jhazmat.2009.05.117.

Ziemkiewicz, P. (2013). "Three Rivers Quest. Baseline River Water Quality Data Collection." Retrieved August 11, 2013, from http://3riversquest.org/.

American Water Works Association