

CHALLENGES FOR DRINKING WATER PLANTS FROM ENERGY EXTRACTION ACTIVITIES

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ABSTRACT

Fossil-fuel associated wastewaters have the potential to affect drinking water quality through surface water disposal. These wastewaters are elevated in certain components, such as bromide, which can affect drinking water quality for consumers. In Pennsylvania, the recent expansion of drilling in the Marcellus Shale has significantly increased the volume of produced water that must be managed. It is essential to determine the potential of this produced water to affect surface water. Assessment of the characteristics of this produced water, as well as other fossil-fuel associated wastewaters, will enable evaluation of the effects of surface water disposal practices on drinking water.

The objective of this work is to identify the challenges for drinking water plants from management of wastewaters associated with energy extraction activities. Focusing on regional activity in Pennsylvania, a state with significant energy and water resources, this work has reached three conclusions. First, increases in the volume of oil and gas produced water disposed of to surface water from 2008 to 2010 increased the total dissolved solids and bromide loads in Pennsylvania, which affected concentrations of those constituents at the drinking water intakes. Changes to the management of this produced water in 2011 significantly decreased the total dissolved solids and bromide loads, and thus the concentrations at the drinking water intakes. Second, regional fossil-fuel wastewaters can be differentiated by their anion ratios, and the use of anion ratios in conjunction with concentration data enables evaluation of the extent of mixing between oil and gas produced waters and freshwater. This method can be used to track water quality changes in areas experiencing fossil fuel activity and provide insight into causes of

observed changes. Finally, high bromide concentrations at drinking water intakes in 2010 were not attributed solely to low flow conditions in the river. River conditions were similar in 2010 and 2012, but significant load reductions improved water quality in 2012. The decrease in bromide loading is likely associated with a voluntary ban on the use of surface-discharging treatment plants for shale gas produced water disposal in the region.

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ABBREVIATIONS AND NOTATIONS

TDS	Total dissolved solids
DBPs	Disinfection by-products
EPA	Environmental Protection Agency
PaDEP/PADEP	Pennsylvania Department of Environmental Protection
NPDES	National Pollutant Discharge Elimination System
THMs	4 Trihalomethanes
HAAs	9 Haloacetic acids
POTWS	Publicly owned treatment works
CWTs	Centralized waste treatment/brine treatment plants
MCL	Maximum contaminant level
UIC	Underground injection control/underground disposal well
AMD	Abandoned mine drainage

Chapter 1

INTRODUCTION, PROBLEM IDENTIFICATION, AND RESEARCH OBJECTIVES

1.1 Introduction

Pennsylvania is a state with significant fossil fuel-based energy resources. Energy extraction activities require water, and produce significant volumes of wastewater. Coal-mining and coal-associated wastewaters have significantly affected water quality in Pennsylvania for more than 100 years (PaDEP 2002). Conventional oil and gas production has a long history in Pennsylvania as well (Dresel and Rose 2010), but the recent expansion of unconventional natural gas development in the Marcellus Shale gas reservoir has significantly expanded the industry. The management and disposal of energy-related wastewaters from coal, oil, and natural gas has the potential to affect water resources, and specifically drinking water sources.

Potential groundwater impacts of shale gas development have been researched (Osborn et al. 2011; Warner et al.), and studies have begun to explore the disposal of oil and gas produced water on surface water quality (Ferrar et al. 2013). Recent research has demonstrated that shale gas wastewater treatment raises chloride concentrations in surface water downstream of discharge points (Olmstead et al. 2013). Rozell and Reaven (2012) conclude that the greatest risk to water pollution from shale gas extraction in the Marcellus Shale is through hydraulic

fracturing wastewater disposal (Rozell and Reaven 2012). However, the effect of wastewater disposal to surface waters on downstream drinking water sources has not been evaluated.

Fossil-fuel associated wastewaters are often brines containing a variety of salts, and drinking water treatment plants are especially concerned if that salt water is high in chloride, sulfate, and bromide. In Pennsylvania, there are many different potential sources of TDS and constituent ions, and control of drinking water concentrations is difficult without knowing the characteristics of the wastewaters and how much is discharged to surface waters.

Energy-extraction related wastewaters that have the potential to affect surface water sources in Pennsylvania are oil and gas produced waters (conventional and unconventional natural gas produced water, oil produced water, and brine treatment plant effluent) and coal-related wastewaters (coal-fired power plant effluent, coal-mine discharge, and abandoned mine drainage). Changes in water quality associated with mining activities that do not directly produce wastewater (e.g., strip mining) are not included in the present analysis.

1.2 Problem Identification

The composition and management of wastewaters from energy development activities is important in assessing their potential for water quality impacts. From a drinking water perspective, energy-related wastewaters high in total dissolved solids (TDS), chloride, sulfate, and bromide can have significant effects on drinking water quality if they are released to surface waters. Although drinking water treatment plants using this water as a source water treat the water, they do not remove TDS. Drinking water treatment plants disinfect the water, which is

necessary to kill or inactivate pathogenic microorganisms and to oxidize toxic contaminants. Although disinfectants have made water safer to drink by decreasing microbial contamination and risk, they also react with natural organic matter in source water to form disinfection by-products (DBPs) in consumers' tap water. DBPs are carcinogenic and are regulated by the Environmental Protection Agency (EPA) (Singer 1994; USEPA 1998) to protect human health. In particular, elevated bromide in water used as a source for drinking water plants has the potential to significantly increase the concentration of brominated disinfection by-products (DBPs) and research has shown that brominated DBPs are more cytotoxic and genotoxic than their chlorinated counterparts (Richardson et al. 2007; Richardson et al. 2003). Bromide concentrations in surface waters in the United States have typically been low, with average inland surface water values ranging from 0.014 to 0.20 mg/L (Stanley 2009; Stanley et al. 2010). However, increasing concentrations of bromide in inland surface waters used as drinking water sources have been reported associated with extraction and utilization of fossil fuels, including shale gas and coal (USEPA 2009; Wilson and VanBriesen 2012).

Recently, disinfection by-product formation in Southwestern Pennsylvania has shown significant shifts at multiple plants, potentially related to changes in coal mine discharges, dilution of produced waters from gas mining, or changes in the characteristics of wastewater from coal-burning power plants. In 2008, a study was conducted by the Pennsylvania Department of Environmental Protection (PaDEP), the Allegheny County Health Department (ACHD), and the U.S. Environmental Protection Agency (EPA) to determine the speciation of disinfection by-products at surface water treatment facilities on the Monongahela, Allegheny, and Ohio Rivers.

Results of that report showed that the percentage of brominated THMs was higher than expected, likely due to increasing source water bromide concentrations. For the months of October 2008 to December 2008, brominated DBPs accounted for 85% to 94% of the total THMs. A source water sample was tested and a bromide concentration of 0.17 mg/L was found (Handke 2008), a value considered moderate for drinking water sources (Weinberg et al. 2002). To decrease risk to consumers, drinking water providers need to know how changes in fossil fuel extraction activities are affecting their source water quality.

The composition of energy-extraction-associated produced waters, and their potential to affect surface water supplies, must be understood to properly manage and dispose of these wastewaters while minimizing any human health effects. Specifically, in Southwestern Pennsylvania, the Monongahela River provides fresh water for energy extraction activities, treatment plants for disposal of many different wastewaters (including those associated with fossil fuel extraction), and is also a drinking water source for over a million people. The potential of increases in energy-related wastewaters to affect surface and drinking water must be understood for this region and for other areas that may see significantly expanded development of unconventional oil and gas reserves.

1.3 Research Objectives

The objective of this research is to identify the source water and drinking water quality impacts associated with energy extraction activities in Pennsylvania. To accomplish this, this dissertation explores:

1. Oil and gas produced water management disposal options used in Pennsylvania, and changes in management choices associated with recent increases in produced water quantities associated with shale gas development;
2. The characteristics of high total dissolved solids fossil-fuel associated wastewaters and analysis of how these characteristics can be used to evaluate potential impacts; and
3. Water quality changes that affected drinking water sources in the Monongahela Basin, Pennsylvania from Fall 2009 to Fall 2012.

1.4 Structure of the Dissertation

This dissertation is structured as separate but unified chapters under the research objective. Chapter 1 is this introductory chapter, while Chapters 2 through 4 discusses the key component analyses developed to address the research objective. Chapter 5 briefly discusses current and future work related to the objective of this research.

In this chapter, the potential challenges associated with energy extraction activities in Pennsylvania have been summarized. Chapter 2 focuses on the management of oil and gas produced water during the past decade in Pennsylvania, and the potential for recent changes to affect drinking water sources in Pennsylvania. Chapter 3 evaluates the relevant constituents in fossil-fuel associated wastewaters and proposes a method to track water quality changes using

easily measured constituent and anion ratios. Chapter 3 also introduces application of this method to tributary data from a 3-year field study conducted in the Monongahela Basin. Chapter 4 is focused on the analysis of data collected during the 3-year field study. In Chapter 5, the potential for future research in this area is discussed, for both source water and drinking water.

Chapter 2

OIL AND GAS PRODUCED WATER MANAGEMENT AND SURFACE DRINKING WATER SOURCES IN PENNSYLVANIA¹

2.1 *Abstract*

Produced water from oil and gas development requires management to avoid negative public health effects, particularly those associated with dissolved solids and bromide in drinking water. Rapidly expanding drilling in the Marcellus Shale in Pennsylvania has significantly increased the volume of produced water that must be managed. Produced water management may include treatment followed by surface water discharge, such as at publically owned wastewater treatment plants (POTWs) or centralized brine treatment plants (CWTs). The use of POTWs and CWTs that discharge partially treated produced water has the potential to increase salt loads to surface waters significantly. These loads may cause unacceptably high concentrations of dissolved solids or bromide in source waters, particularly when rivers are at low-flow conditions. The present study evaluates produced water management in Pennsylvania from 2006 through 2011 to determine whether surface water discharges were sufficient to cause salt or bromide loads that would negatively affect drinking water sources. The increase in produced water that occurred in 2008 in Pennsylvania was accompanied by an increase in use of CWTs and POTWs that were exempt from discharge limits on dissolved solids. Estimates of salt loads associated with produced water and with discharges from CWTs and POTWs in 2008 and 2009 indicate that

¹ The contents of this chapter have been published as: Wilson, J.M. and J.M. VanBriesen. "Oil and gas produced water and surface water sources in Pennsylvania." *Environmental Practice*, 2012, 14, 288-300.

more than 50% of the total dissolved solids in the produced water generated in those years were released to surface water systems. Especially during the low-flow conditions of 2008 and 2009, these loads would be expected to affect drinking water.

2.2. *Introduction*

Pennsylvania has been a gas-producing state for 180 years (Harper 2008), and there have been multiple gas booms (Tarr 2009). Unconventional gas has long been known to exist in shale of the Marcellus and Utica formations. However, economic recovery of unconventional gas has only recently been enabled by directional drilling, which optimizes gas production from thin formations, and hydraulic fracturing, which improves formation permeability. These techniques were first applied together in the Barnett Shale formation in Oklahoma and Texas in the 1990s, and were first used in the Marcellus shale formation in Pennsylvania in 2003. Drilling in the Marcellus formation began in Pennsylvania slowly, with only a few wells in 2003–5, after which the rate of drilling increased exponentially ($R^2 = 0.97$) before leveling out in 2011 (PaDEP 2012b), likely due to the declining price of natural gas.

All types of fossil fuel extraction require water and generate wastewater, including drilling wastewaters and production wastewaters. Oil production has long generated significant amounts of water during the production phase, with volumes increasing over the life of the well. Produced water associated with gas extraction has varied based on the water present in the formation with the gas. Typically, shale formations do not contain much water and thus would not be expected to liberate significant amounts of produced water. However, hydraulic fracturing introduces water to the formation (millions of gallons per well) in order to increase permeability through

fracture generation, and thus this water has the potential to return to the surface with the gas. In general, for hydraulically fractured wells, during the initial flowback period (approximately the first 10–14 days after well completion), 10%–25% of the load water returns to the surface (Hayes 2009). Lower volumes during flowback have been reported for wells in the Marcellus formation (Hoffman 2010; Mantell 2011); however, significantly higher initial water use is required for horizontally drilled wells (such as those in the Marcellus). Thus, while the percentage of water returning to the surface is lower during flowback, the overall volume of water from Marcellus wells is typically much higher than conventional wells in Pennsylvania. After gas production begins, produced water volumes decrease at all types of gas wells, and the volume of production water shows significant variability. The Marcellus Shale formation is a *low* long-term water-producing shale, with estimates at less than 200 gallons per million cubic feet (MMCF) of gas. By contrast, the Barnett Shale is a *high* produced water shale, with estimates at more than 1,000 gallons per MMCF of gas (Mantell 2011).

Like other industrial or mining-generated wastewaters, produced water must be managed to protect environmental resources and human health. Produced waters vary in their chemical makeup, but they generally contain naturally occurring inorganic and organic chemicals, including naturally occurring radioactive materials (NORMs); salts (e.g., sodium, calcium, magnesium, chlorine, bromine), typically measured as dissolved solids; and hydrocarbons (e.g., benzene). When hydraulic fracturing is used, produced water also contains residual chemicals from the fracturing fluid. Produced water management can include reuse within operations, disposal through underground injection, and various types of wastewater treatment. Treatment

focuses on removal of constituents in the water; however, few methods remove the naturally occurring salts. When salts are released to surface waters, the resultant changes in water quality can affect aquatic life and alter the ecology of the surface water systems (Hart et al. 1991; Kaushal et al. 2005; Nielsen et al. 2003). These environmental effects can be significant; however, they are not the focus of the present work, which considers potential human health effects. Salts released to surface waters that are used as sources for drinking water treatment plants can cause direct and indirect problems with finished drinking water, with the potential to affect consumers negatively.

The present work examines produced water management in Pennsylvania, particularly in the past several years when volumes have increased during development of shale gas. Analysis of wastewater treatment options and their use for conventional and Marcellus-associated produced water provides insight into challenges faced by drinking water treatment plants using affected source waters.

2.3 Background

Produced water varies in its constituents, its production volumes, and the management options available for its reuse, treatment, or disposal. Characteristics of the water and the different ways in which it is managed interact to control the possible effects of produced water on surface waters used as drinking water sources.

Produced water from oil and gas wells in Pennsylvania is generally salty, with reported total dissolved solids (TDS) ranging from 68,000 to 354,000, with a median of 215, 000 mg/liter; oil-associated produced water is slightly less salty than gas produced water (Dresel and Rose 2010). Produced water from the Marcellus formation is similarly high in dissolved solids or salts, with reported TDS ranging from 3,010 to 261,000 mg/liter, with a median value of 157,000 mg/liter (Hayes 2009). Core analysis from the Marcellus Shale shows that it contains sodium, calcium, magnesium, potassium, iron, strontium, and barium (Blauch et al. 2009). Nearby formations, the Oriskany and Medina, are also high in halites, and brines from other Devonian and Ordovician horizons (including the Utica Shale) are also quite high in TDS, sodium, and chloride. These salts are of particular concern for drinking water systems since the salts are unlikely to be removed through conventional treatment of produced water or within the drinking water plant. Table 1 provides a summary of the characteristics of produced water quality that are of particular interest for drinking water plants, and their associated secondary standard maximum contaminant levels (MCLs) (USEPA 2009).

Table 2.1. Chemical constituents of total dissolved solids (TDS) in produced water relevant for drinking water treatment plants.

Chemical constituent	Range reported in produced water from Marcellus shale at 14–90 days after hydraulic fracturing (mg/liter)^a	Range reported in produced water from conventional oil and gas production (mg/liter)^b	Range reported in effluent from brine treatment plants in Southwestern Pennsylvania^c	Drinking water maximum contaminant level (MCL) secondary standards (mg/liter)^d
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	Range	Median	Range	Median	Range	Median	
TDS	3,010– 345,000	157,000	68,000– 354,000	215,000	16,600–201,100	130,100	500
Chloride	1,670– 196,000	98,300	5,760– 207,000	116,500	1,752–96,909	57,250	250
Sulfate	0.2–89.3	0.8	1–850	140	5–1,500	667	250
Bromide	15.8– 1,990	849	94–2,240	1,010	76.2–8,290	1,105	—

^a Adapted from Hayes (2009). 16 gas wells in Pennsylvania and 3 in West Virginia. TDS, n = 29; chloride, n = 29; sulfate, n = 29; bromide, n = 29

^b Adapted from Dresel and Rose (2010). 24 gas wells and 15 oil wells in Western Pennsylvania. TDS, n = 16; chloride, n = 39; sulfate, n = 36; bromide, n = 38

^c Adapted from US EPA (2012a). TDS, n = 22; chloride, n = 28; sulfate, n = 26; bromide, n = 30. Data are from laboratory analysis submitted by three brine treatment plants in Southwestern Pennsylvania at the request of the US EPA located in the Allegheny River Basin

^d Secondary standards deal with aesthetic issues rather than human health issues (US EPA, 2009)

The overall salt content of produced water is the first issue of concern. Freshwater (less than 1,500 mg/liter TDS) is used extensively as a source for agriculture, industry, and potable water consumption. Waters that contain more salt are unsuitable for human consumption but may be used for industrial activities, including cleaning, firefighting, and some types of irrigation. The drinking water standard for TDS is 500 mg/liter, a level set to avoid poor taste for consumers and to reduce the corrosive effects of the salt on industrial and household plumbing fixtures. Similarly, the secondary drinking water standards for chloride and sulfate are set to 250 mg/liter each because these levels are associated with objectionable taste, odor, or corrosivity. Ideally, source waters would be below these levels to meet consumer requirements for water usability.

The presence of elevated concentrations of bromide in produced waters raises an additional concern, although it is not regulated in drinking water (DiCosmo 2012). Bromide is a trace element found often at very low concentrations in freshwater systems. At concentrations that are unlikely to be observed in drinking waters, it is toxic to humans (Flury and Paprtiz 1993; WHO

2009). However, even low concentrations of bromide in waters subject to disinfection at drinking water treatment plants lead to increases in the formation of disinfection by-products (DBPs) that are carcinogenic and potentially teratogenic (Chang et al. 2001; Cowman and Singer 1996; NCI 1976). When source water bromide increases, disinfection by-product formation increases, and the DBPs become more brominated (Hellergrossman et al. 1993; Krasner et al. 1989). More brominated DBPs are associated with increased human health risk compared with less brominated forms (Plewa et al. 2004; Richardson 2003; Richardson et al. 2008; Richardson et al. 2007). Like TDS, bromide is not removed at drinking water treatment plants. Thus, produced water management that leads to increased concentrations of bromide in source waters for drinking water treatment plants can lead to increased concentrations of brominated DBPs in drinking water.

2.4 Data Sources and Analysis Methods

The present work focuses on evaluation of changes in produced water management in Pennsylvania in 2006–11, a period during which Marcellus drilling expanded rapidly. Produced water management options and their utilization by drillers changed frequently during this period in response to significant increases in volumes requiring management and in response to concerns from regulatory agencies and citizen groups. The objective of this work is to evaluate the potential for the increase in produced water and the changes in how it was managed during this time to affect source water quality for drinking water plants. Little direct source water data are available for the critical time period, especially 2008–9. And it is difficult to generalize about the concentrations of various constituents in produced water, given the high variability of

produced water quality (see Table 1) and the rapid changes to water management over the past seven years. Nevertheless, the current analysis will provide insights into the potential for source water effects associated with different management options for produced water in Pennsylvania.

Publicly available data were acquired from various sources, predominately from data published to websites by the PA DEP. Data for wells drilled in the Marcellus and in other formations are available on the oil and gas portal (PADEP 2012c).

Produced water management data was acquired from the PA DEP (PaDEP 2012a). From 2001 through 2009, data are for all wells in the state and do not distinguish those targeting the Marcellus formation. In 2010 and 2011, Marcellus wells are reported separately. The present analysis is based on these data (downloaded originally on May 4 and then again on July 27, 2012). Changes were made in the DEP data between the original and final downloads, including corrections to volumes of wastewater and changes to labels for different types of disposal options. The quantitative data provided here are as reported in the later download; however, the classifications reflect data from the prior years for consistency.

Produced water management data from the PA DEP were organized by treatment or disposal type into the following categories for this analysis:

- Reuse other than road spreading
- Injection disposal well [underground injection control (UIC)]
- Brine or industrial waste treatment plant [centralized waste treatment (CWT)]
- Municipal sewage treatment plant [a publicly owned treatment works (POTW)]
- Road spreading

- Other, not determined, unknown

In addition to classification into these broad categories, the DEP data include information on the waste management provider (e.g., name of treatment plant or disposal well and sometimes its permit number). The classifications are important in order to understand the different ways produced water has been managed during the recent expanded natural gas development, especially in order to understand how treated water that might have been released to surface waters have been changing. Despite the importance of these classifications, the DEP data sheets contain significant misclassification of treatment providers. Our analysis included reclassifying based on permit number (and when that was not specified, based on facility name) to ensure produced water was correctly assigned to the broad groupings. Errors were particularly common in classifications of treatment plants as either POTWs or CWTs, with many facilities listed in both categories at different times in the data sheets.

Another critical issue is that the DEP does not distinguish between CWTs that discharge to waterways and those that treat water for reuse.¹ Further, no distinction is made between CWTs that are required to meet the recently passed more stringent discharge standards (500 mg/liter) and those that are exempt. Clearly, exempt facilities have the potential for significantly more loading of TDS and bromide (see Table 1).

In the present analysis, the eight CWT facilities *currently* permitted to accept produced water under their exemption from TDS discharge limits (see Table 2) were considered separately from other CWT facilities. Although there were many additional exempt CWTs discharging *prior to*

2011, we considered only the same eight CWTs in our analysis of 2006–11 data. All other CWTs, some of which may have been discharging to the rivers in earlier years or may be currently discharging at no more than 500 mg/liter, are reported together as “other CWTs.” This classification also includes plants that do not discharge treated water at all but rather return it to producers for reuse. The decision not to consider possible discharges from *any facility other than those currently exempt* may underestimate the loads introduced to the major rivers associated with produced water management at CWTs, especially during 2008 and 2009 prior to the more stringent discharge limits implemented by Pennsylvania (PaDEP 2010). However, this assumption ensures that no plant is misclassified as discharging when it is actually treating for reuse. Potential impacts on surface waters of the TDS and bromide associated with water sent to CWTs may therefore be underestimated in this analysis.

Table 2.2. Centralized waste facilities accepting oil and gas produced water in 2011 with discharge limit exemptions.

Name	Permit number	Receiving stream
PA Brine Josephine	PA0095273	Blacklick Creek
PA Brine Franklin	PA0101508	Allegheny River
Hart Resource Technologies	PA0095443	McKee Run
Tunnelton Liquids ^a	PA0091472	Conemaugh River
Advanced Waste Services (AWS) of Pa [formerly Castle Environmental (CE) Inc.]	PAR00051 as AWS	N/A. Discharges to New Castle City POTW
McCutcheon Enterprises ^b	PAR00002 as CE PAD013826847	N/A. Discharges to Kiski Valley Sanitary Authority
Waste Treatment Corporation	PA0102784	Allegheny River
Sunbury Generation Wastewater Treatment System ^c	PA0008451	Susquehanna River

^a Tunnelton Liquids closed by EPA action on May 12, 2011 (US EPA, 2012b).

^b McCutcheon Enterprises. On May 19, 2011, Kiski Valley requested McCutcheon to cease discharges to the plant (US EPA, 2012b).

^c Suspended accepting Marcellus produced water in April 2011.

Finally, one other distinction was made for data associated with CWTs. In 2011, the DEP suspended the licenses of Tri-County Waste Water Management and Allan's Waste Water Services after the firms' owner was indicted for allegedly illegally disposing of millions of gallons of wastewater in southwestern Pennsylvania. In March 2012, the owner pled guilty to illegal dumping from 2003 through 2009. In addition to charges stemming from the pollution, the owner pled guilty to falsifying records of total volumes of waste transported and disposed of in order to defraud clients (Pattera 2011). Since the volumes of wastewater reported and their ultimate management remain unknown, data associated with these two firms were separated from the rest of the CWT data. The data on the former are included in the group designated "other" in the analyses. Although it is plausible that some of this produced water made its way into surface waters through the described illegal dumping to drains and wastewater plants, it is impossible to conduct a meaningful evaluation of this. Further, since quantities remain in doubt, the volume of water managed by these companies is not used in estimates of potential impact to surface waters. Following his conviction in 2012, the former owner divested his interests in these companies (Ove 2012).

The POTW data from the DEP required additional analysis, particularly because many facilities were misclassified in the available spreadsheets. As with the CWTs, the number of POTWs accepting oil and gas produced water in 2008 was greater than the number currently accepting produced water. The analysis here includes all POTWs that accepted produced water during 2006–11, because these could be identified (by name), and all of these facilities would have

discharged the produced water to surface waters after treatment. Thus, POTWs always represent loading potential for TDS and bromide to the basin.

Finally, the PA DEP data for 2010 required some additional manipulation. Published by the DEP are a file for total produced water in 2010 and a file for Marcellus produced water from July 2009 through December 2010 (18 months). The Marcellus July 2009–December 2010 data sheet was analyzed for overlap with the total produced water (including Marcellus) for 2009. Duplicates between these two files were considered to represent Marcellus produced water in 2009. These were removed from the Marcellus July 2009–December 2010 total. The balance then represents Marcellus produced water for January 2010–December 2010, and these data were used in subsequent annual analyses.

2.5 *Results and Discussion*

Pennsylvania has long required oil and gas producers to report on how their produced water is managed annually. Data are readily available for the last decade, including volumes and the produced water management method used. Beginning in mid-2009, Marcellus Shale–associated produced water was separately tabulated in six-month periods by Pennsylvania. The balance of oil and gas produced water is still reported annually. Figure 1 shows total produced water for 2001–11, with Marcellus and conventional wells shown separately in 2010–11. It is clear that the expansion of unconventional gas development in 2008 coincided with significantly increased volumes of produced water requiring management. The average produced water for 2001–6 was

6.3 million barrels a year, whereas the average for 2008–11 was 26 million barrels (a fourfold increase).² Despite the larger number of conventional wells in Pennsylvania, Marcellus wells are responsible for much more produced water in 2011 than are conventional wells. For example, at the end of 2010, Pennsylvania had 22,491 oil and condensate wells in production and 67,049 gas-producing wells. Through the end of 2010, there were 1,575 wells drilled in the Marcellus; not all of these are producing gas and wastewater. If all Marcellus wells were producing, they would represent less than 3% of all gas-producing wells and less than 2% of total oil and gas wells. Despite this small fraction of the well inventory for the state, the produced water from these wells is significant. Produced water data indicate significant increases in water requiring management in 2008 and 2009 (Figure 1), coinciding with an increase in wells drilled overall (4,127 in 2008 and 2,520 in 2009) and an increase, particularly in 2009, in wells drilled in the Marcellus formation (324 in 2008 and 807 in 2009). Further, although overall produced water volumes declined in 2010 before climbing again in 2011, the contribution of Marcellus wells to produced water is significant. In 2010 and 2011, produced water associated with Marcellus development accounted for 68% and 79%, respectively, of the total produced water requiring management.

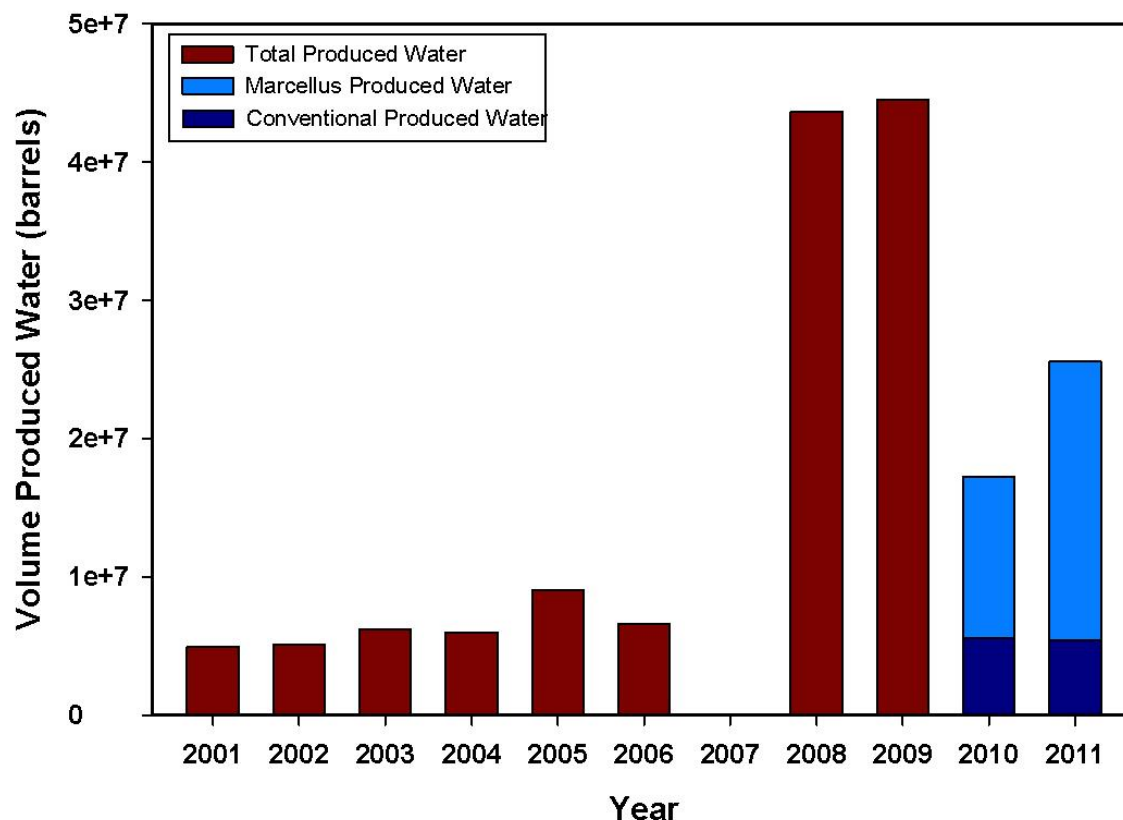


Figure 2.1. Produced water volumes in Pennsylvania, 2001 - 11. (PaDEP 2012a)

Produced water management may include storage, recycling, and reuse on site for additional operations, treatment off site with return of treated water for reuse, treatment off site with discharge of partially treated water, and disposal into underground injection wells. In the US, most onshore produced water is injected underground for disposal or to maintain formation pressures and increase the output of oil production wells (Clark, Bonura, and Voorhees, 2006; Clark and Veil, 2009). Alternatives such as recycling and reuse are typically used when injection wells are not plentiful, such as in Pennsylvania, or when high-quality produced water can be reused beneficially, such as in some coal-bed methane regions in the western US.

Treatment followed by surface water discharge is not a common management strategy for produced waters in the US but has been widely practiced in Pennsylvania because of the paucity of underground injection wells. Two types of facilities have historically been involved in produced water treatment in Pennsylvania: Municipal wastewater treatment plants (POTWs) and dedicated brine treatment facilities (CWTs). Historically, POTWs and CWTs have discharged partially treated wastewater to surface water systems, where dilution reduced concentrations of TDS. Existing CWTs are exempt from the regulations passed in 2008 that included increased restrictions to TDS discharges (PaDEP 2010). New CWTs built in the region in response to increasing produced water volumes must meet stringent discharge limits for TDS. Many of the new CWTs treat water and return it to the drilling sites for reuse rather than discharging it to surface waters.

While produced water volumes clearly increased significantly over the past few years in Pennsylvania, this may not have directly affected drinking water plants unless the increased produced water was being treated in ways that resulted in release to the surface water that is the source for drinking water (through exempt CWTs and POTWs). Thus, we considered not just the total volumes of produced water and how these have changed but also the management options employed for these increasing volumes.

Analysis of the DEP data (shown in Figure 2) indicates significant changes over the past few years. Shown as a representative pre-Marcellus development year is 2006, when 48% of produced water was sent to the eight identified exempt brine treatment plants (3.2 million

barrels) and 5% was sent to POTWs (346,000 barrels). From 2006 to 2008, produced water increased more than sixfold, from 6.6 million barrels to 43.6 million barrels; increases were seen across all management options. Use of injection wells increased fourfold (from 390,000 to 1.5 million barrels). Exempt brine treatment plant use increased fourfold (from 3.1 million to 13.5 million barrels). POTW use increased by 32 times (from 346,000 to 11.2 million barrels). CWTs not on the exempt list increased by 136 times (from 41,000 to 5.6 million barrels). As noted previously, prior to the revision to PA TDS standards (PA DEP, 2010), some of these CWTs might have been discharging to surface waters, but this is not easily determined, and the analysis of impacts will not include these plants as potential surface dischargers. Total management that included surface discharge of treated or diluted wastewater (exempt CWTs and POTWs) increased sevenfold (from 3.5 million to 24.6 million barrels).

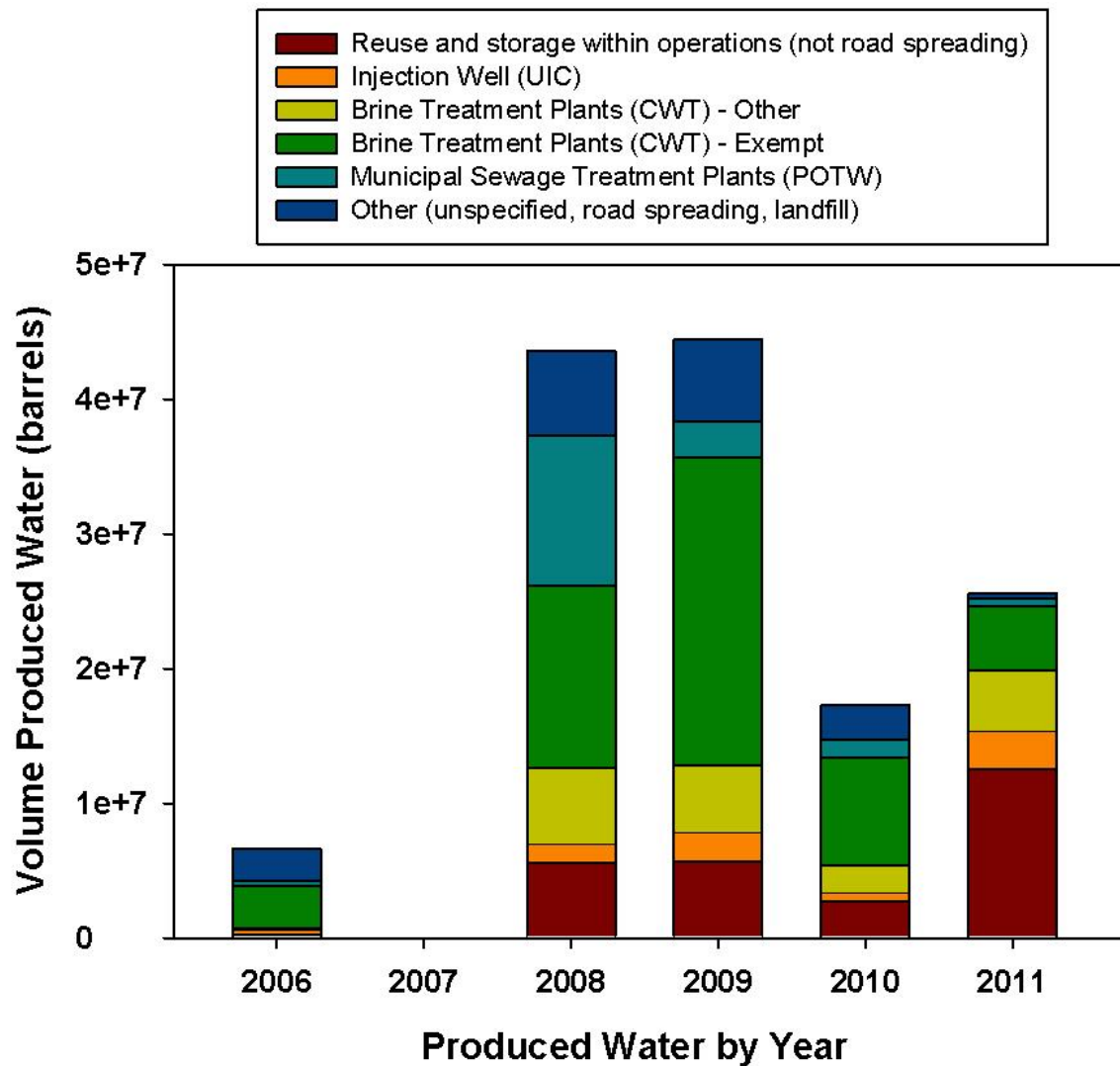


Figure 2.2. Produced water by management option, 2006 - 11. CWT, centralized waste treatment; POTW, a publicly owned treatment works; UIC, underground injection control. (PaDEP 2012a).

In 2008 and 2009, with similar totals for produced water, similar amounts of produced water were reused and classified as other (including road spreading, landfill, and unspecified disposal methods). Produced water to injection wells increased (from 1.4 million to 2.2 million barrels), but this represents less than 5% of the produced water overall. Differences are seen in the management of produced water by POTWs and CWTs between 2008 and 2009. In 2008, similar

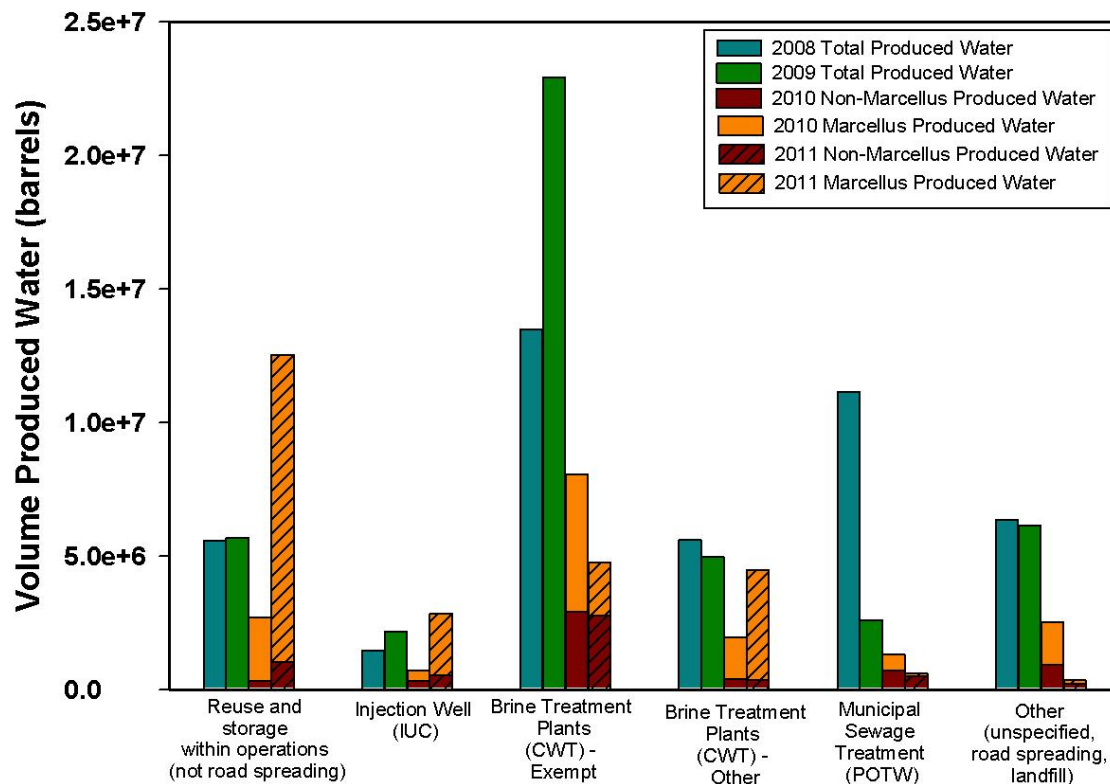
amounts were sent to POTWs [11.2 million barrels (26%)] and the eight identified exempt CWTs [13.5 million barrels (31%)]. A smaller amount was sent to other CWTs [5.6 million barrels (13%)]. However, this changed in 2009, with the volume going to POTWs declining significantly [to 2.6 million barrels (6%)], a decline of 80%. The volume going to the eight identified exempt CWTs increased 70% [to 22.9 million barrels (52%)]. The other CWTs did not see significant increases [4.9 million barrels (11%)] from 2008 to 2009.

The significant decline in overall produced water requiring management from 2009 to 2010 resulted in decreases in all categories. POTWs treated only 1.3 million barrels, half of what they treated in 2009 and a tenth of what they treated in 2008, although still more than threefold as much as in 2006. Exempt CWTs treated 8.0 million barrels, less than a third of what they treated in 2009 and less than half of what they treated in 2008, although still 2½ times more than in 2006. Other CWTs treated even less (just under 2 million barrels).

In 2011, the total produced water requiring management was 25.5 million barrels, an increase from 2010 but still lower than levels reported in 2008 and 2009 and more than threefold more than in 2006. Very significant shifts in management choices can be seen, with much more reuse [12 million barrels (48%)] and an increase in water delivered to CWTs that are *not* exempt from discharge limits [4.7 million barrels (19%)]. With the opening of several facilities specifically targeting the treat-for-reuse market, some of this produced water would be more appropriately classified in the reuse category. Disposal to injection wells increased to slightly above the 2009 level [2.8 million barrels (11%)]. Treatment at POTWs declined even further [to 588,000 barrels

(2%)] and treatment at exempt CWTs also declined [to 4.5 million barrels (17%)]. Comparison with 2006 (pre-Marcellus days) shows all of these levels are still higher than in the pre-Marcellus days, with exempt CWTs remaining 50% higher and POTWs remaining 70% higher overall.

A specific analysis for 2010 and 2011 by type of water (Marcellus vs. conventional) provides further insights (Figure 3). The previously described shift from 2008 to 2009 in treatment away from POTWs and toward exempt CWTs is clearly seen, as well as the significant increase in use of other CWTs in 2011. The exempt CWTs received about equal amounts of water from non-Marcellus wells in 2010 and 2011, but over 3 million barrels more of Marcellus produced water in 2010 than 2011. Further dividing the Marcellus data into the six-month periods before and after the request from the DEP for Marcellus drillers to eliminate all use of exempt facilities (PA DEP, 2011) tells a different story. From January through June in 2011, exempt CWTs received 1.97 million barrels of Marcellus produced water. From July through December, they received only 33,000 barrels, a 98% decline. The *total* produced water delivered to the exempt facilities declined approximately 40% from 2010 through 2011 (from 8.0 million to 4.8 million barrels). This is predominately due to the reduction in Marcellus water as the conventional produced water to the exempt facilities showed little change (2.9 million to 2.7 million barrels from 2010 through 2011).



Produced Water Management Option

Figure 2.3. Produced water management options, 2008 - 11, including Marcellus and non-Marcellus produced water for 2010 - 11. CWT, centralized wastewater treatment; POTW, a publicly owned treatment works; IUC, underground injection control. (PaDEP 2012a).

Similarly, POTWs received 102,000 barrels of Marcellus produced water from January through June 2011 and only 408 barrels from July through December 2011, a decline of more than 99%. Non-Marcellus produced water is not tracked in six-month periods, so it is unclear whether there was an increase in use of POTWs for conventional produced water disposal over this period; however, annual totals for 2010 and 2011 for non-Marcellus produced water show a slight decrease (from 695,000 to 485,000 barrels) in the use of POTWs. Comparison with 2006 shows more conventional produced water going to POTWs in 2010 and 2011 than before the Marcellus drilling boom. With the produced water divided by type, it is also clear that significantly more

Marcellus produced water is reused within operation or treated at nonexempt CWTs (again, some of this is also reuse) than is conventional oil and gas produced water. This likely reflects a concerted effort on the part of companies working in the Marcellus, many of which have declared their intention to reuse or recycle 100% of water produced during flowback and nearly 100% of water produced during the life of the well (Miller and Svarczkopf, 2011).

2.6 Potential Role of Produced Water Discharges on Source Water TDS and Bromide Levels

Nationally, most large drinking water plants are on surface water sources (e.g., rivers or large lakes), and these sources have significant dilution capacity for salts. However, in Pennsylvania many surface waters already receive high salt loads from legacy resource extraction, as well as from current resource extraction and industrial activities. During low-flow conditions, many Appalachian surface waters have little assimilative capacity (Bodkin et al. 2007; Green and Passmore 2000; Wozniak 2011).

The potential effect of treated produced water discharges from CWTs and POTWs on TDS concentrations in source water is a direct concern for drinking water providers. This concern was highlighted when high TDS was observed in the fall of 2008 in the Monongahela River (Hopey 2008; PADEP 2008). The Monongahela has a long history of salty discharges from mine drainage and industrial use, and it has little capacity for diluting additional salt, especially when flows are low. In the fall of 2008, during low flows, the Monongahela River exceeded the secondary drinking water standard for TDS (500 mg/liter) and for sulfate (250 mg/liter). The exceedances in the source water led to exceedances in the finished drinking water supplied to the

one million people who rely on the Monongahela River as their drinking water source. The significant increase in produced water requiring management in 2008 (shown in Figure 1) and the fact that produced waters contain significant TDS suggest that surface discharges from POTWs and CWTs could play a role in higher TDS levels in surface waters.

Using the total produced water volume and the average TDS concentration in oil and gas produced waters from Pennsylvania [200,000 mg/liter (Dresel and Rose 2010; Hayes 2009)] a TDS load requiring management can be estimated for Pennsylvania. Further, by using the volumes of produced water being treated through exempt CWTs and POTWs, where TDS removal is not expected (see data in Table 1), we can estimate the *TDS loads* that might be reaching the waterways used as sources for drinking water. Figure 4 shows these results.

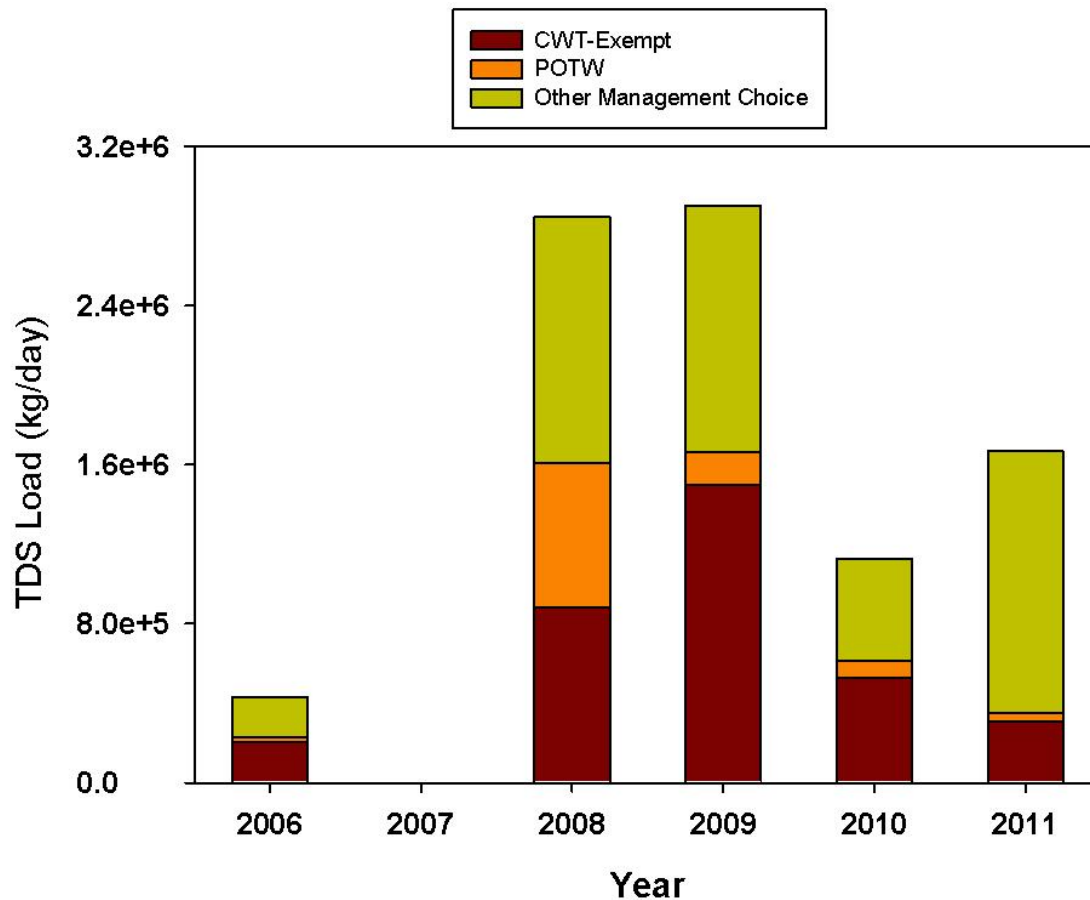


Figure 2.4. Total dissolved solids (TDS) load (kg/day) for produced water by year and by management option. CWT, centralized waste treatment; POTW, a publicly owned treatment works.

Although these results are statewide, not specific to any particular river system, they suggest a significant increase in loading of TDS to surface waters in Pennsylvania, especially in 2008 and 2009. The total TDS loads liberated in the produced water being managed rose from 431,000 kg/day in 2006 to 2.8 million and 2.9 million kg/day in 2008 and 2009, respectively, and then fell to 1.2 million and 1.7 million kg/day in 2010 and 2011, respectively. The differences in loads managed at exempt CWTs and POTWs reflect the changes in management choices for produced water over the past few years. This analysis suggests that in 2008 and 2009 the extensive use of these surface-discharging produced water disposal options led to release to the environment of a

significant fraction of the total TDS being liberated from the subsurface during gas production (56% in 2008 and 57% in 2009). In 2010, with less overall produced water, the loads are lower; however, a similar fraction of the produced water was managed at exempt CWTs and POTW (54% of TDS released). Only in 2011, when produced water management shifted to increased recycling, reuse, and use of CWTs that were not exempt from discharge limits, did the estimated fraction of TDS load released to surface waters decline significantly (21%). Compared with 2006, however, the TDS load to surface waters from produced water remains elevated (230,000 kg/day in 2006 and 350,000 kg/day in 2011). The shift to non-discharging management options has significantly reduced TDS loading to surface waters in Pennsylvania over the past four years; however, loads had not returned to pre-Marcellus development levels by 2011.

Similarly, the increasing produced water volumes lead to an increase in the amount of bromide that is being brought to the surface and potentially released to waterways. By using the total produced water volume and the average bromide concentration in that water, a bromide load requiring management can be estimated for Pennsylvania for 2006–11. Further, by using the volumes of produced water being treated through exempt CWTs and POTWs, where bromide removal is not expected (see data in Table 1), we can estimate the *bromide loads* that might be reaching the waterways used as sources for drinking water.

Figure 5 presents the results of this analysis. A bromide concentration of 1,000 mg/liter was used based on average bromide concentrations in Marcellus produced water, conventional oil and gas produced water, and effluent from brine treatment plants. The total bromide load associated with

produced waters was calculated by multiplying this concentration by the total volume of produced water. Bromide loads for CWTs and POTWs were calculated similarly from this concentration and the volumes reported for these treatment options.

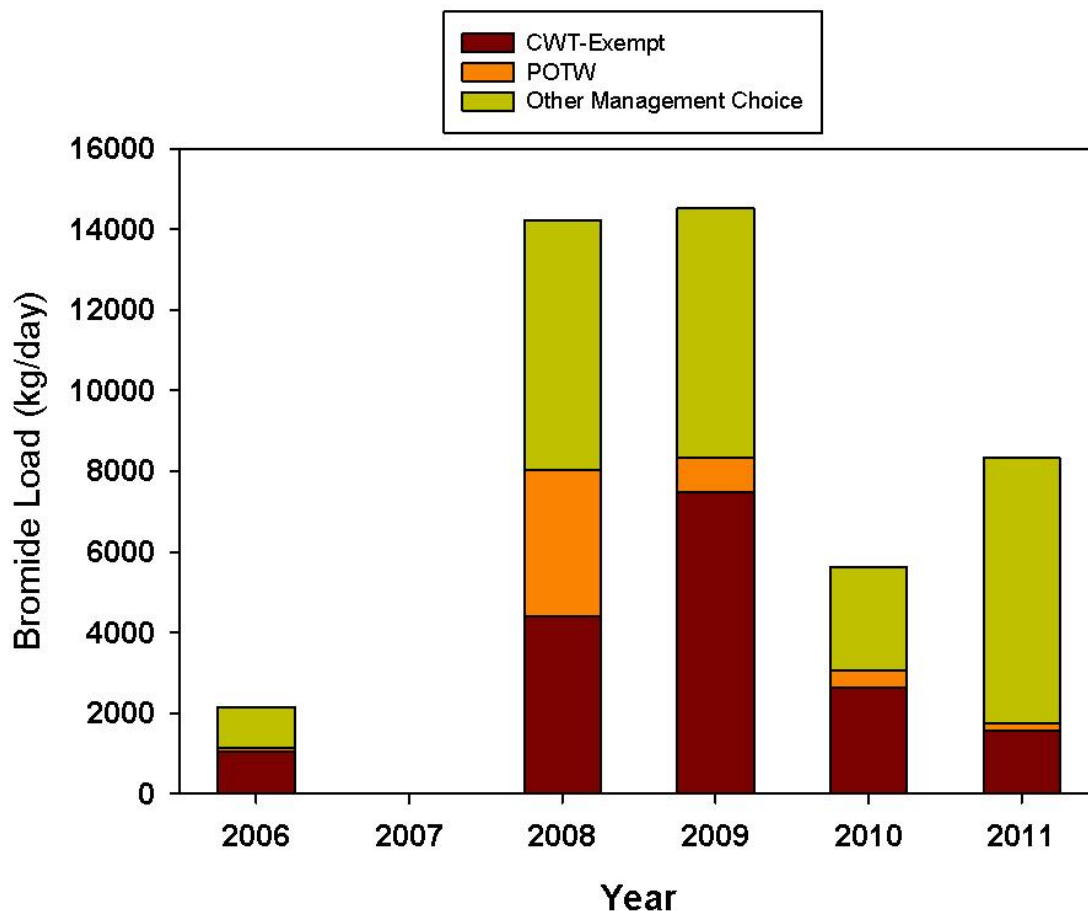


Figure 2.5. Bromide load (kg/day) for produced water by year and by treatment method. CWT, centralized waste treatment; POTW, a publicly owned treatment works.

The total loads (highest in 2008 and 2009 and significantly lower in 2010 and 2011) reflect the differences in total reported produced water for the years. The differences in predicted loads from exempt CWTs and POTWs reflect the changes in management choices. As with TDS, in 2006–10, more than 50% of the bromide in the produced water was being released to the

environment, whereas this declined to 20% in 2011. In 2011, bromide loads from produced water being discharged to surface waters remained 50% higher than in 2006, but were 42% lower than in 2010 and 80% lower than in 2008 and 2009. The selection of non-discharging treatment options reduced the potential for surface water bromide concentrations to affect drinking water in Pennsylvania.

The analysis of bromide loads to the basin can also be used to evaluate how these loads could affect bromide concentrations in the surface waters used by drinking water plants as their source. The Pennsylvania rivers are large and have significant flow during most of the year; however, low-flow conditions are common in late summer and early fall in many locations.

As an example, in the Allegheny River Basin, where seven of the eight exempt CWTs discharge, and where the Pittsburgh Water and Sewer Authority (PWSA) extracts water for Pittsburgh's drinking water supply, in-stream concentrations for TDS and bromide can be estimated. By using volumes of produced water managed by each of the facilities and average concentrations of TDS and bromide in produced water, loads from CWT discharging facilities were computed. Any POTW loads in the Allegheny River Basin were neglected in this calculation. Flow data for the river were obtained from US Geological Survey (USGS 2012) to determine dilution, and concentrations were estimated for 2006–11. Based on the load and the flow, the Allegheny River would be expected to have had a TDS concentration below 500 mg/liter for the entire period. The river would be expected to have had bromide concentrations in excess of 0.50 mg/liter for brief periods during low flow in 2008 and 2009. Reduced loading to the basin associated with

reductions in produced waters being sent to exempt CWTs would predict lower TDS and bromide concentrations for 2010–11, if flows were similar. However, 2010 was an unusually dry year, and 2011 was wetter than usual. The drop in bromide load from 2009 to 2010 might have been masked by low flows, while the additional drop from 2010 to 2011 would be expected to be diluted further by the high flows. Using reported flows (USGS 2012), bromide concentrations were predicted to be between 9.89×10^{-3} mg/liter and 0.31 mg/liter, with a mean concentration of 0.15 mg/liter.

Samples of Allegheny River water taken at the PWSA intake from September 2010 through December 2011 are reported to be 25–299 µg/liter (0.025–0.299 mg/liter), with a mean value of 100 µg/liter (0.100 mg/liter) (CUAHSI 2012; States et al. 2011). States et al. (2011) provide a more thorough analysis of the sources of bromide to the Allegheny River, but the present analysis suggests that surface discharges of produced water upstream of the intake were sufficient to account for the concentrations of bromide observed by the drinking water plant. The bromide level in source waters that leads to acceptable treatment at surface water plants has not been determined, but lower loads and resultant lower concentrations reduce the potential to form brominated disinfection by-products that are of human health concern.

2.7 *Conclusions*

Produced water associated with hydrocarbon extraction in Pennsylvania contains high levels of TDS and elevated bromide compared with other waters and wastewaters. Expanded development of shale gas resources significantly increased the volume of produced water, beginning in 2008.

Historical methods of managing this produced water included treatment at dedicated brine facilities and sewage treatment plants. These treatment methods remove some constituents, but not salts, leading to surface water discharges of significant loads of TDS and bromide.

Analysis of produced water management in Pennsylvania from 2006 through 2011 indicates a significant increase in the use of surface-discharging facilities from 2006 to 2008, with a significant decline from 2009 through 2010. The recent changes in management reduce the TDS and bromide load that is entering surface waters compared with the high loads in 2008 and 2009 but still represent increases from the pre-shale development (2006). Decreasing releases of treated brine to surface waters reduces the concentration of TDS and bromide reaching drinking water treatment plants. Going forward, produced water management decisions should be informed by the potential contribution of this wastewater to the formation of disinfection by-products in downstream drinking water treatment plants. Produced waters containing elevated bromide levels should be managed in ways that do not lead to increasing bromide loads delivered to surface waters.

Chapter 3

SOURCES OF HIGH TOTAL DISSOLVED SOLIDS TO DRINKING WATER SUPPLY IN SOUTHWESTERN PENNSYLVANIA²

3.1 *Abstract*

Fossil fuel extraction activities generate wastewaters that are often high in total dissolved solids (TDS) and specific constituents that can affect drinking water, if these wastewaters enter surface waters. Control of TDS in source waters is difficult without identification of the potential sources of high TDS wastewater associated with fossil fuel activities. Characteristics of natural waters, oil and gas produced waters, and coal-related wastewaters were analyzed to extract information about constituent concentrations and anion ratios. Statistical analysis of the anion ratios indicates the SO_4/Cl ratio is higher in coal-related wastewaters than in oil and gas produced waters, suggesting that wastewaters can be distinguished based on this ratio. An approach that compared the SO_4/Cl ratio to bromide concentration for the wastewaters can serve to separate oil and gas produced waters from brine treatment plant discharges, as well as from the various coal-related wastewaters. This method was applied to surface water quality data collected from two tributaries in Southwestern Pennsylvania from September 2009 to September 2012. Results show that this constituent and ratio method, combined with mixing curve calculations, can be used to identify water quality changes in these two tributaries. This analysis

² This work was submitted in November 2012 to the *ASCE Journal of Environmental Engineering* and resubmitted after revision in February 2013. It is under review. The Supplemental Information referred to in the text can be found in Appendix C.

method, when applied to regionally relevant high TDS wastewater data, can be used in other areas experiencing similar water quality changes due to fossil fuel activities.

3.2 Introduction

Total dissolved solids (TDS) is a measure of the inorganic and organic constituents dissolved in water. Inorganic ions found in natural waters may include carbonate, calcium, sulfate, chloride, sodium, and other, often minor constituents, such as iron, copper, bromide, or manganese. Waters are classified by the concentration of dissolved solids they contain: *freshwater* has a TDS less than 1,500 mg/L, while *brackish* water ranges from 1,500 to 5,000 mg/L, and *saline* water has a TDS greater than 5,000 mg/L (Hem 1985). *Seawater* is between 34,000 to 38,000 mg/L TDS (Hem 1985), and *potable* water supplies in the United States (US) are desired to be below 500 mg/L TDS (the secondary drinking water standard). In engineered systems, high TDS waters are corrosive, leading to decreased efficiency in boilers and scaling in pipes. For drinking water consumers, water with elevated TDS is often reported to have a poor taste (salty or metallic) and poor mouthfeel. Drinking water treatment plants that treat freshwater sources do not include desalination operations to remove TDS. Therefore, when source water (untreated water from streams, rivers, lakes or underground aquifers that is used as supply for public drinking water and private wells (USEPA 1999)), is elevated in TDS, finished drinking water that leaves the treatment plant and travels through pipes to consumers will remain elevated in TDS.

Drinking water treatment facilities are particularly interested in three components of TDS: chloride, sulfate, and bromide. High chloride and sulfate in drinking water can lead to increased pipe corrosion, or increased scaling or sedimentation, which can decrease efficiency of boilers

and heat exchangers, as well as cause taste and odor problems in drinking water. Chloride and sulfate are not specifically targeted for removal from water supplies during conventional drinking water treatment; like other components of TDS, levels in the source water persist in the finished water after treatment.

Bromide is a component of TDS that is of concern to drinking water providers, but not due to taste or odor issues. Bromide is found in all fresh water, generally at very low concentrations (0.014-0.2 mg/L, (Bowen 1966; Bowen 1979). Bromide concentrations in freshwater depend on the geochemistry of the materials that come into contact with the water, for example, aquifer formations that contain natural salts, runoff from road salt applications (Kjensmo 1997), or localized addition of the fumigant methyl bromide (Wegman et al. 1983). Bromide is not regulated in drinking water with either a primary or secondary standard as it is toxic to humans at concentrations that are unlikely to be observed in drinking waters (drinking water value of concern for a 60 kg adult consuming 2 liters/day is 6 mg/L, (Flury and Papritz 1993; WHO 2009). However, the presence of even very low concentrations of bromide increases the formation of disinfection by-products (DBPs) in drinking water plants and creates more brominated DBPs (Hellergrossman et al. 1993; Richardson et al. 2007). DBPs are carcinogenic and teratogenic (NCI 1976; USEPA 1998), and brominated DBPs are associated with increased human health risk compared with chlorinated DBPs (Plewa et al. 2004; Richardson et al. 2008; Richardson et al. 2007; Richardson et al. 2003). Bromide is not removed at drinking water treatment plants, thus increased concentrations of bromide in source waters generally leads to increased concentrations of brominated DBPs in drinking water delivered to consumers (Cowman and Singer 1996).

Recently, in Southwestern Pennsylvania, concerns have arisen regarding TDS and sulfate concentrations in surface waters. In 2008, the Pennsylvania Department of Environmental Protection (PaDEP) found levels of sulfate and TDS that exceeded the drinking water secondary maximum contaminant levels in the Monongahela River (Handke 2008). Finished water from treatment plants using this TDS-impacted water showed higher levels of brominated DBPs, suggesting increasing changes in bromide concentrations in the source water (Handke 2008). In 2009, a large fishkill occurred in Dunkard Creek, a tributary to the Monongahela River. This event was attributed to a bloom of golden algae triggered by high TDS in the creek (PADEP 2011a; Soraghan 2011). Increasing TDS concentrations have also been reported in Dunkard Creek in 2012, associated with discharges from mine pools and lower rainfall levels leading to less dilution (Renner 2009).

A dominant source of the three components of TDS discussed above (chloride, sulfate, and bromide) in Southwestern Pennsylvania is the extraction and utilization of fossil fuels. Historically, coal mine discharges and abandoned mine drainage (AMD) have significantly contributed to anion concentrations in surface waters; these wastewaters are typically high in sulfate and some may be high in chloride (Cravotta 2008a; Cravotta 2008b; Schwartz 2010a; Schwartz 2010b). Oil and gas development in Pennsylvania also produces water that is typically high in salts, particularly chloride (Dresel and Rose 2010), and coal-bed methane (CBM) extraction wastewaters may also be high in chloride (Veil et al. 2004). Recently, expanded development in unconventional gas in the Marcellus shale formation has significantly altered the volumes of saline produced water requiring management in Pennsylvania (Wilson and

VanBriesen 2012), while regional power plant wastewater has changed with the addition of flue-gas desulfurization units (PADEP 2006; PADEP 2008a).

Produced water from Marcellus shale natural gas extraction, typically high in TDS, chloride, and bromide concentrations (Blauch et al. 2009; Hayes 2009), as well as other oil and gas brines, can be treated through a variety of methods. Direct discharge at well pads is precluded by federal statute (Copeland 2010), and deep well injection is a common disposal method throughout the US (Clark et al. 2006). However, in Pennsylvania, limited sites for injection led to the use of surface-water discharging centralized wastewater treatment plants (CWTs) and dilution in publically-owned treatment works (POTWs) as common management choices. Centralized brine treatment plants are industrial wastewater treatment facilities that provide partial treatment of oil and gas brines, typically removing solids by settling and coagulation and divalent ions through chemical precipitation reactions. Effluent from CWTs can contain elevated TDS, chloride, bromide, and, at times, sulfate, due to sulfate addition at the plant to remove barium (USEPA 2012). CWTs can return this water to developers for reuse or, if their permits do not restrict TDS, they can discharge effluent to surface water. In Pennsylvania, from 2001 to 2009, approximately 50% of oil and gas wastewaters were treated in plants that resulted in surface discharge of high TDS waters (Wilson and VanBriesen 2012). The significant increase in the volumetric production of brines in 2008 and 2009, concomitant with increased development in the Marcellus formation, led to a seven-fold increase in the total volume of produced waters sent to surface-discharging treatment plants. While in 2006, 3.4 million barrels were treated in discharging plants, in 2008, 24.7 million barrels were managed in this way. In 2011, this practice was significantly curtailed by request of PaDEP (PaDEP 2011b), and volumes to

surface-water-discharging plants fell to 5.1 million barrels. Thus, changes, particularly in the management of shale gas produced water, but also in power plant operations, are implicated in increased bromide concentrations in source waters to drinking water plants (States et al. 2011; Wilson and VanBriesen 2012).

With the many different potential sources of TDS and constituent ions, control of source water concentrations to reduce problems at drinking water plants is difficult. Following the 2008 TDS increases reported in the Monongahela River, many possible causes were suggested (Handke 2008; PADEP 2008b; TetraTech 2009), but limited information in identifying the role of different wastewaters in the TDS issue has hindered the planning to avoid future elevated TDS events. Recently, geochemical and strontium isotope characterization has been used to characterize produced waters from Marcellus Shale natural gas extraction (Chapman et al. 2012); however, this method requires analysis rarely undertaken at drinking water plants. Previously, simple anion ratios have been used to study brine contamination of groundwater (Davis et al. 1998; Freeman 2007), ground water systems containing potable water (Davis et al. 2001; Davis et al. 2004), and saline intrusion into aquifers (Andreasen and Fleck 1997). Bromide and bromide to chloride ratios have also been used to identify pollution sources from agriculture applications (Wegman et al. 1981; Wegman et al. 1983) or waste from cooling towers at power plants (USEPA 2009). Attempts to identify shale gas produced water contamination to shallow groundwaters and characterization of Marcellus produced waters using bromide and bromide to chloride ratios has also been reported (Siegel and Kight 2011; Wolford 2011).

Understanding the contributions of different wastewaters to the concentrations *at the drinking water plant* is critical to assess how to reduce TDS constituents that increase drinking water risks. In this work we focus on the characteristics of legacy and emerging wastewaters in the region and how these characteristics can be used to identify causes of changing source water quality. We then present a method for identifying these wastewaters based on anions that are routinely monitored by drinking water treatment plants. We use this method to characterize water quality in two tributaries, Ten Mile Creek and Redstone Creek, located in the Monongahela River Basin in Southwestern Pennsylvania. These creeks feed into the Monongahela River, which serves as a source for downstream drinking water treatment plants. Ten Mile Creek is a basin that, over the past 5 years, has been experiencing a significant increase in Marcellus Shale drilling activity (Kimmel and Argent 2011), and also contained a facility receiving produced water for treatment. It has historically had significant mine discharges as well (Kimmel and Argent 2009). Redstone Creek has not seen a significant change in fossil-fuel related activities or wastewater discharges. It is a generally low TDS stream with some mine discharges; our sampling location is near its discharge to the Monongahela, far from any direct impacts of fossil fuel extraction. Thus, we expect to be able to identify and compare water quality in the two creeks.

3.3 *Data Sources and Methods*

Natural water has been extensively studied in the US and many constituents, such as the total content of dissolved solids or salts, have been monitored. Other constituents have only recently been considered of interest (e.g., bromide), and fewer data exist.

Sources for information on characterization of relevant types of waters are summarized in Table S1. Natural water data collected include data for seawater (Bather and Riley 1954; Fukai and Shiokawa 1955; Haslam and Gibson 1950; Hem 1985; Matida 1954; Matida and Yamauchi 1951; Miyake 1939; Riley and Skirrow 1965; Thompson and Korpi 1942); inland surface water (Stanley 2009; Stanley et al. 2010); potable groundwater (Davis et al. 2004); saline groundwater (Nordstrom et al. 1989; Vengosh et al. 2005); and US source water (USEPA 2000). Oil and gas produced water data include data for produced water from the Marcellus Shale (Hayes 2009); conventional oil and gas produced water (Dresel and Rose 2010); and wastewater from brine treatment plants (USEPA 2012). Brine treatment plants treat both conventional oil and gas produced water as well as Marcellus shale produced water, with a focus on chemically removing the dissolved metals from brines (Wincek et al. 2002). Coal-related wastewater data include data from coal-fired power plant wastewater (EPRI 2007; Frank 2011); mine pool discharge (Schwartz 2010a; Schwartz 2010b); and abandoned mine drainage (Cravotta 2008a). Although coal-bed methane wastewater can also contribute to high TDS in Southwestern Pennsylvania, regional data were not available and were thus excluded from the analysis. Statistical analyses on these data (mean, median, standard deviation) were performed using Sigmaplot (Systat Software, San Jose, CA). The Mann-Whitney rank sum test was used on the medians of the data for determining statistical significance in Sigmaplot. Table 1 includes statistical descriptors for TDS, chloride, sulfate, bromide, Br/Cl (by mass) and SO₄/Cl (by mass) for the data sources. In addition to analysis of the distinct types of water and wastewaters described in Table 1, specific groupings were also analyzed. For example, a test of significance was performed on a comparison between Marcellus produced water and conventional oil and gas water. At an even

higher level, the group including all oil and gas produced water (both Marcellus and conventional) was compared to the group including all post-treatment oil and gas brines. Ratio based analysis was employed to provide insights, to overcome the limitations of single ion analysis, and to enable the use of multiple parameters together for source differentiation. Ratio analysis is also independent of flow conditions, which is particularly useful in large river systems where changes in flow regimes cause concentrations to show strong dependence on dilution effects. Further, where wastewaters increase in TDS concentration with time, as is typical for oil and gas produced water, the use of ratios can identify stable relationships despite concentration changes.

Table 3.1. Statistical descriptors of data. Dashed lines represent data not available. Data sources provided in Supplemental Information.

Water Type	Water Quality Parameter						Associated Ratios					
	Total Dissolved Solids (mg/L)		Chloride (mg/L)		Sulfate (mg/L)		Bromide (mg/L)		Br/Cl		SO ₄ /Cl	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean (x 10 ⁻³)	Std. Dev. (x 10 ⁻³)	Mean	Std. Dev.
Seawater (n = 12)	35,000	-----	19,352	154	2,707	4.61	67.2	0.56	3.48	0.0242	0.14	9.05 x 10 ⁻⁴
Inland Surface Water (n = 79)	-----	-----	264	148	198	59	0.33	0.11	1.51	0.521	0.94	0.55
Potable Groundwater (n = 32)	-----	-----	2.36	1.87	-----	-----	0.020	0.013	10.6	5.94	-----	-----
Saline Groundwater (n = 82)	2545	1234	917	635	310	264	4.01	3.85	7.42	23.5	0.38	0.36
Rain (n = 60)	-----	-----	3.33	5.28	1.83	1.80	0.10	0.12	34.9	56.9	0.80	1.02
U.S. Source Waters, 7/97 – 12/98, (n = 5873)	----	----	----	----	----	----	0.095	0.132	----	----	----	----
Produced Water Marcellus Shale (n = 11)	220,667	71,437	133,733	44,005	63	25	1,179	558	9.17	3.37	5.14 10 ⁻⁴	x 2.40 x 10 ⁻⁴
Produced Water Conventional Gas Wells (n = 24)	238,400	62,947	136,540	34,172	124	135	1,287	425	9.63	2.50	9.07 10 ⁻⁴	x 1.01 x 10 ⁻⁴

Water Type	Water Quality Parameter								Associated Ratios			
	Total Dissolved Solids (mg/L)		Chloride (mg/L)		Sulfate	(mg/L)	Bromide (mg/L)		Br/Cl		SO ₄ /Cl	
	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean	Std. Dev.	Mean (x 10 ⁻³)	Std. Dev. (x 10 ⁻³)	Mean	Std. Dev.
Produced Water Oil Wells (n = 15)	97,667	26,417	51,216	23,698	241	250	53	250	11.0	2.16	3.84 x 10 ⁻³	3.65 x 10 ⁻³
Brine Treatment Plants (n = 29)	129,717	48,729	57,977	25,990	671	425	1,602	1,781	59	186	2.44 x 10 ⁻²	5.41 x 10 ⁻²
Coal-fired power plant wastewater (n = 8)	53,518	58,130	12,296	4,385	2,478	116.9	109	7.34	10.6	1.30	1.15	1.58
Mine pool discharge (n = 13)	16,662	8,981	3,637	3,567	6,833	3,389	25	24	6.97	0.711	18.53	37.79
Abandoned mine discharge (n = 42)	----	----	45.9	79.2	689	380.8	0.108	0.137	4.17	3.32	78.72	161.86

Weekly water samples from two tributaries in the Monongahela River Basin located in Southwestern Pennsylvania were collected from September 2009 to September 2012. 500 mL of river water were collected in polypropylene bottles and stored in a cooler with ice during transport and in a refrigerator at 4°C prior to analysis. Sulfate, chloride, and bromide concentrations were determined using an ion chromatograph (Dionex) with an IonPac anion column (4 x 250 mm) and 100 µl sample loop with an eluent of 8 mM Na₂CO₃ and 1 mM NaHCO₃ (Fisher Scientific) following a modification of EPA Method 300.1 (USEPA 1997).

3.4 Results and Discussion

3.4.1 Constituent Analysis

Fig. 1 shows a box plot of TDS for natural waters, oil and gas produced waters, and coal-related wastewaters; data are in mg/L and the y-axis is a log scale. The summary statistics of TDS for the different waters and relevant p-values can be found in Table 2. All summary statistics (for TDS, chloride, sulfate, and bromide) can be found in Tables S2-S3 in the Supplemental Information. In general, oil and gas produced waters are significantly higher in TDS than natural waters, exceeding seawater by up to one order of magnitude. Coal-fired power plant wastewater is more similar to oil and gas produced water than mine pool discharge. There is no statistically significant difference between median TDS for Marcellus Shale gas well produced water and conventional gas well produced water in Pennsylvania, which confirms work by Haluszczak et al. (Haluszczak et al. 2013). The average for all gas produced waters is higher in TDS than the average of oil produced waters. Brine treatment plant discharges for three plants in southwestern

Pennsylvania are statistically significantly lower in TDS than the oil and gas produced waters they treat.

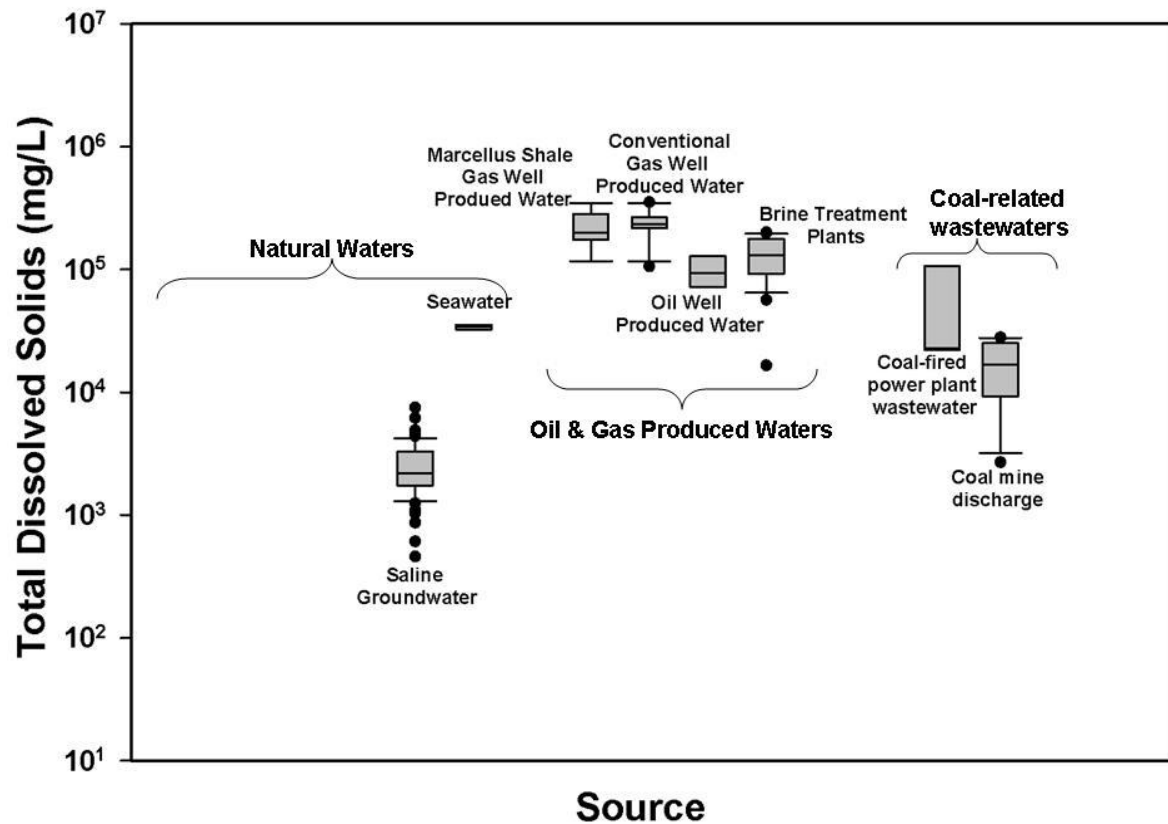


Figure 3.1. Box plot of total dissolved solids (mg/L) for natural waters, oil and gas produced waters, and coal-related wastewaters. Solid line in box is median, box edges are 25% and 75% while whiskers extend to 5% and 95%. Solid dots are outliers beyond the 5-95% range.

Table 3.2. Median TDS concentrations and associated p-values (one-tailed Mann-Whitney Rank Sum Test). Shaded boxes are non-significant p-values.

Water Type		Produced Water Conventional Gas Wells	Produced Water Oil Wells	Brine Treatment Plants	All Oil and Gas Produced Water	All Oil and Gas Produced Water and Brine Treatment Plants	Coal-fired Power Plant Wastewater	Mine-Pool Discharge	All Coal-related Wastewaters	All Natural Waters
		Median TDS (mg/L)								
		234,000	94,000	149,700	200,000	161,300	22,900	16,772	22,300	724
	Median TDS (mg/L)	p-value, $\alpha = 0.05$								
Produced Water Marcellus Shale	200,000	p = 0.205	p = 0.003	p = 0.002	p = 0.842	p = 0.020	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Conventional Gas Wells	234,000		p = 0.015	p = 0.002	p = 0.095	p = 0.003	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Oil Wells	94,000			p = 0.002	p = 0.005	p = 0.020	p = 0.142	p < 0.001	p < 0.001	p < 0.001
Brine Treatment Plants	149,700				p = 0.001	p = 0.071	p = 0.004	p < 0.001	p < 0.001	p < 0.001
Coal-fired Power Plant Wastewater	22,900				p < 0.001	p < 0.001		p = 0.138	p < 0.001	p < 0.001
Mine-Pool Discharge	16,772				p < 0.001	p < 0.001			p = 0.467	p < 0.001

There is no statistically significant difference in median TDS between coal-fired power plant wastewater and coal mine discharge. Overall, coal-related wastewaters are lower in TDS than oil and gas produced waters.

Similarly structured box plots of chloride concentrations for natural waters, oil and gas wastewaters, and coal-related wastewaters are given as Fig. S1 in the Supplemental Information. The Marcellus Shale gas well produced water and conventional gas well produced water are an order of magnitude higher in chloride than seawater and coal-related wastewaters, and these differences are statistically significant, while differences between Marcellus and conventional oil and gas wells are not significant. Coal-related wastewaters show higher variability; no statistically significant differences are found from natural waters, while they are statistically significantly lower in chloride than oil and gas produced waters.

Coal in southwestern Pennsylvania is high in sulfur content (Milici and Dennen 2009); therefore, coal-related wastewaters in the region would be expected to contain significant sulfate. Historical acid mine drainage in the region has been reported to contain high concentrations of sulfate (Cravotta 1993; Cravotta 2008a). Fig. S2 in the Supplemental Information shows the box plots of available data for sulfate ranges in natural waters, oil and gas produced waters, and coal-related wastewaters. As expected, coal associated wastewaters are enriched in sulfate compared with natural waters, and statistically significantly different from oil and gas wastewaters. Conventional and Marcellus produced waters are similar in sulfate, except for waters treated through brine plants, which are higher in sulfate as expected due to additions to remove barium.

As noted above, bromide in source waters is a significant concern for drinking water providers due to the potential for increased formation of brominated DBPs. Oil and gas produced waters are all significantly enriched in bromide compared with natural waters (see Fig. 2). The summary statistics of bromide for the different waters and relevant p-values can be found in Table 3. Coal-related wastewaters are uniformly lower in bromide concentration than oil and gas produced waters. Coal-fired power plant wastewater is significantly higher in bromide than AMD while coal-mine discharges are highly variable in bromide concentration. Power plant effluent bromide concentrations are generally controlled by the bromide content in the feed coal, which can be highly variable (<1-25 mg/L) (Bragg et al. 1998). However, bromide-containing products can also be used within power plants in cooling tower disinfectants and as additives to enhance mercury removal.

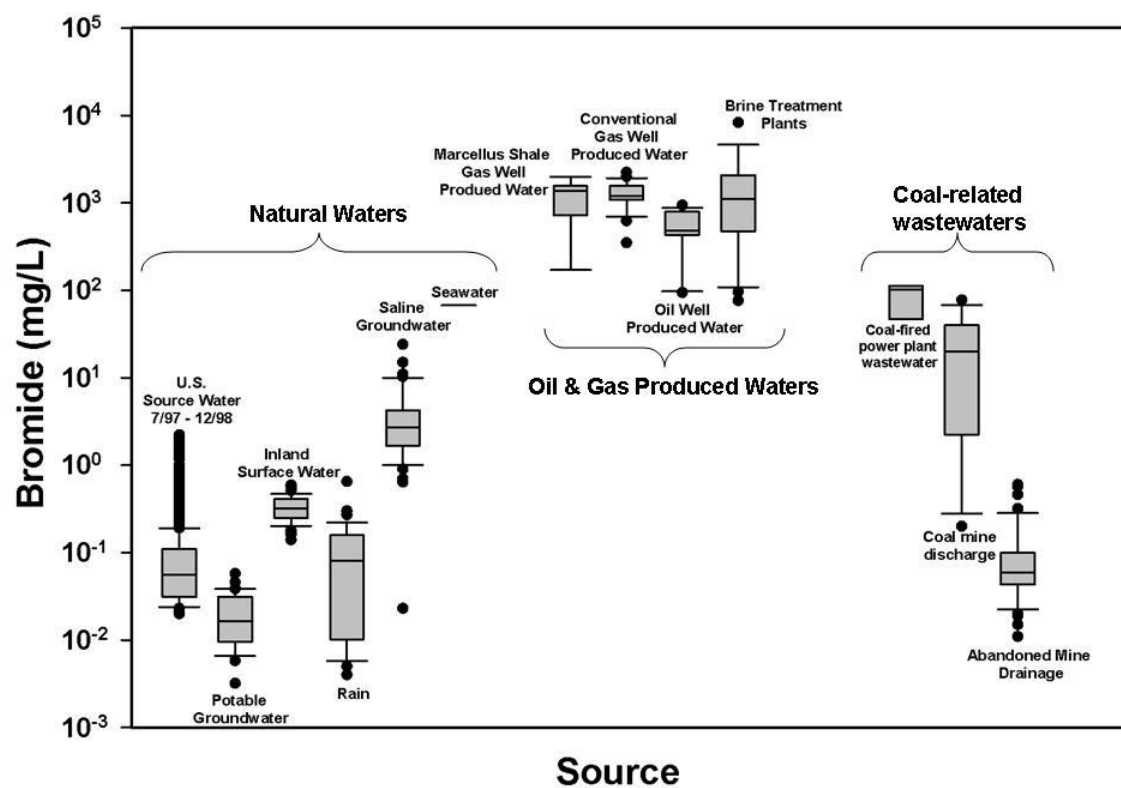


Figure 3.2. Box plot of bromide (mg/L) for natural waters, oil and gas produced waters, and coal-related wastewaters. Solid line in box is median, box edges are 25% and 75% while whiskers extend to 5% and 95%. Solid dots are outliers beyond the 5-95% range.

Table 3.3. Median bromide concentrations and associated p-values (one-tailed Mann-Whitney Rank Sum Test). Shaded boxes are non-significant p-values.

Water Type		Produced Water Conventional Gas Wells	Produced Water Oil Wells	Brine Treatment Plants	All Oil and Gas Produced Water	All Oil and Gas Produced Water and Brine Treatment Plants	Coal-fired Power Plant Waste-water	Mine-Pool Discharge	Abandoned Mine Discharge	All Coal-related Waste - waters	All Natural Waters
		Median Bromide (mg/L)									
		1,200	478	2,240	1,080	1,085	102.7	19.9	5.90×10^{-2}	9.95×10^{-2}	1.95×10^{-2}
	Median Bromide (mg/L)	p-value, $\alpha = 0.05$									
Produced Water Marcellus Shale	1,380	p = 0.475	p < 0.001	p = 0.003	p = 0.428	p = 0.428	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Conventional Gas Wells	1,200		p < 0.001	p = 0.002	p = 0.777	p = 0.105	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Oil Wells	478			p = 0.002	p < 0.001	p = 0.002	p = 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Brine Treatment Plants	2,240				p = 0.600	p = 0.729	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001

		Produced Water Conventional Gas Wells	Produced Water Oil Wells	Brine Treatment Plants	All Oil and Gas Produced Water	All Oil and Gas Produced Water and Brine Treatment Plants	Coal- fired Power Plant Waste- water	Mine- Pool Discharge	Abandoned Mine Discharge	All Coal- related Waste - waters	All Natural Waters
		Median Bromide (mg/L)									
		1,200	478	2,240	1,080	1,085	102.7	19.9	5.90×10^{-2}	9.95×10^{-2}	1.95×10^{-2}
		p-value, $\alpha = 0.05$									
Coal-fired Power Plant Waste- water	102.7				$p < 0.001$	$p < 0.001$		$p < 0.001$	$p < 0.001$	$p < 0.001$	$p < 0.001$
Mine- Pool Discharge	19.9				$p < 0.001$	$p < 0.001$			$p < 0.001$	$p < 0.001$	$p < 0.001$
Abandoned Mine Discharge	5.90×10^{-2}				$p < 0.001$	$p < 0.001$				$p = 0.005$	$p < 0.001$

Within oil and gas produced waters, there is no statistically significant difference in median bromide for Marcellus Shale gas well produced water and conventional gas well produced water; however, gas produced water is higher than oil produced water. There is no statistically significant difference in median bromide concentration between produced waters from oil and gas and treated effluent from brine treatment plants, suggesting treatment at these facilities does not remove bromide, as expected.

The analysis above indicates oil and gas produced waters are enriched in TDS, chloride and bromide compared with natural waters. Coal-related wastewaters are more variable, but are generally enriched in TDS and sulfate. Brine treatment plants do not significantly change the TDS, chloride or bromide in wastewaters; however, they can increase sulfate. The overlap seen in the distribution of values for the different wastewaters (especially for bromide) and the modification of brines that takes place at treatment plants (especially for sulfate) makes the use of simple ion analysis for source identification or apportionment difficult. Despite this challenge, bromide and chloride (among other constituents) have been used to characterize the TDS found in produced water from the Marcellus Shale natural gas reserves (Blauch et al. 2009) and bromide in particular has been suggested as indicative of produced water (States et al. 2011; Wilson and VanBriesen 2012). This concept is supported by the analysis above indicating that all oil and gas produced water sources (including brine plant discharges) are statistically significantly higher in bromide than coal-fired power plant discharges. However, some overlap exists in the data sets for Southwestern Pennsylvania waters; power plant wastewater contains 84 ± 36 mg/L of bromide while oil and gas produced water contains 1246 ± 1182 mg/L of bromide.

While oil and gas produced water is typically much higher in bromide concentration, the reported lower values in *some* produced water and the reported higher values in *some* power plant discharges make differentiation based on this single parameter difficult.

3.4.2 Ratio Analysis

The importance of bromide to drinking water treatment plants, and the relative differences in bromide seen in Fig. 2 and in chloride in Fig S1, suggests the bromide to chloride ratio may enable distinctions between different wastewaters. However, as shown in Fig. 3, the bromide to chloride ratio for natural waters as well as oil and gas produced waters and coal-related wastewaters show overlap across the ranges of values. When considering all oil and gas produced water and all coal-related wastewaters, a statistically significant difference in *median* values is observed. This suggests the Br/Cl ratio can be used to distinguish between oil and gas produced waters from coal-related wastewaters. However, there is no statistically significant difference was observed for oil and gas produced waters and the effluent from brine treatment plants, confirming these plants do not preferentially remove either of these ions. For coal-related wastewaters, there is no statistically significant difference in coal-fired power plant wastewater and mine-pool discharge. Including natural waters that would receive discharges of fossil-fuel related wastewaters further complicates the picture. Although the potable groundwater data is from a national dataset, there is no statistically significant difference median Br/Cl for potable groundwater compared with Marcellus Shale produced water, conventional gas well produced water, or oil well produced water. Overall these results indicate that the Br/Cl ratio cannot be

used to differentiate high TDS wastewaters in the region due to dilution with natural waters that are indistinguishable from fossil-fuel associated waters in this dimension.

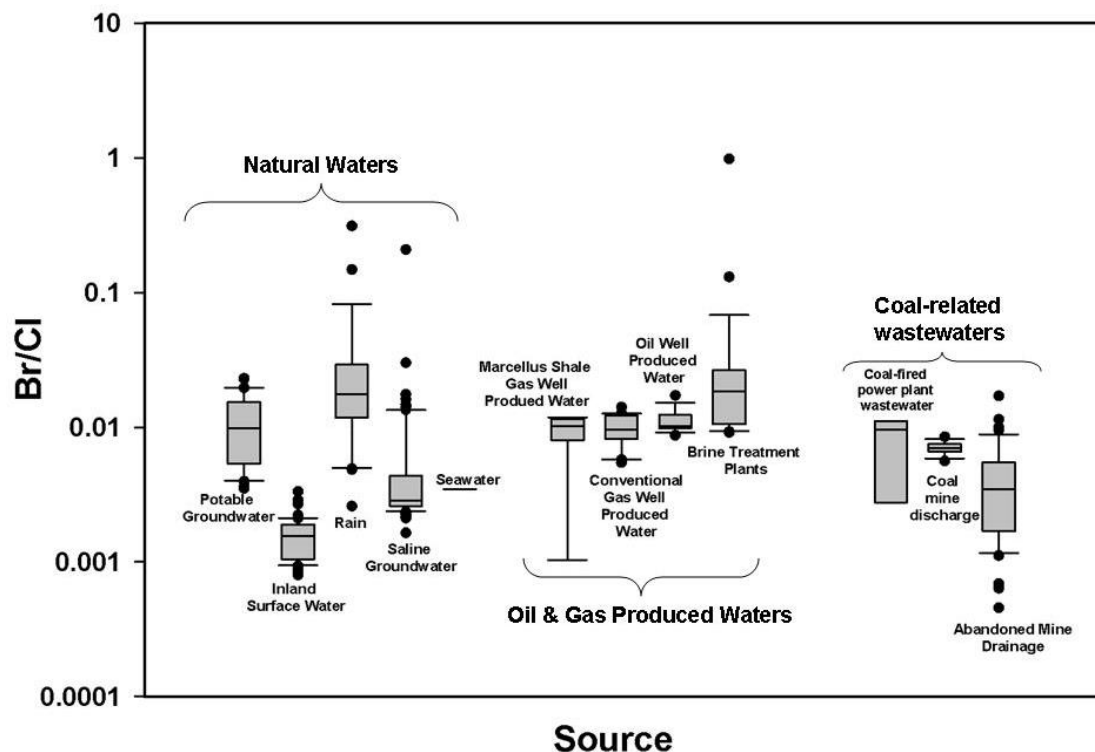


Figure 3.3. Box plot of Br/Cl mass ratios for natural waters, oil and gas produced waters, and coal-related wastewaters. Solid line in box is median, box edges are 25% and 75% while whiskers extend to 5% and 95%. Solid dots are outliers beyond the 5-95% range.

The distinct differences in chloride and sulfate concentrations (Figs. S1 and S2) among the different wastewaters suggests an alternative ratio may provide the desired distinction. Table 4 shows the median SO_4/Cl and associated p-values. Considering the SO_4/Cl for natural waters, oil and gas produced waters, and coal-related wastewaters (Fig. 4), confirms coal-related wastewaters are enriched in sulfate relative to chloride, and oil and gas produced waters are enriched in chloride relative to sulfate. Not surprisingly, coal-related wastewaters have a

statistically significant higher median SO_4/Cl than oil and gas produced waters, *and* natural waters. Similarly, oil and gas produced waters are significantly different from coal-related wastewaters and natural waters. However, there is no statistically significant difference in median SO_4/Cl for Marcellus shale gas well produced water and conventional gas well produced water or between all gas well produced water and oil well produced water. This suggests that SO_4/Cl cannot be used to distinguish *among* gas and oil well produced waters, but it can be used to distinguish between coal-related wastewaters and oil and gas associated wastewaters. Further, the distinctions with natural waters give this metric more power to isolate inputs to natural systems from these two distinct wastewaters.

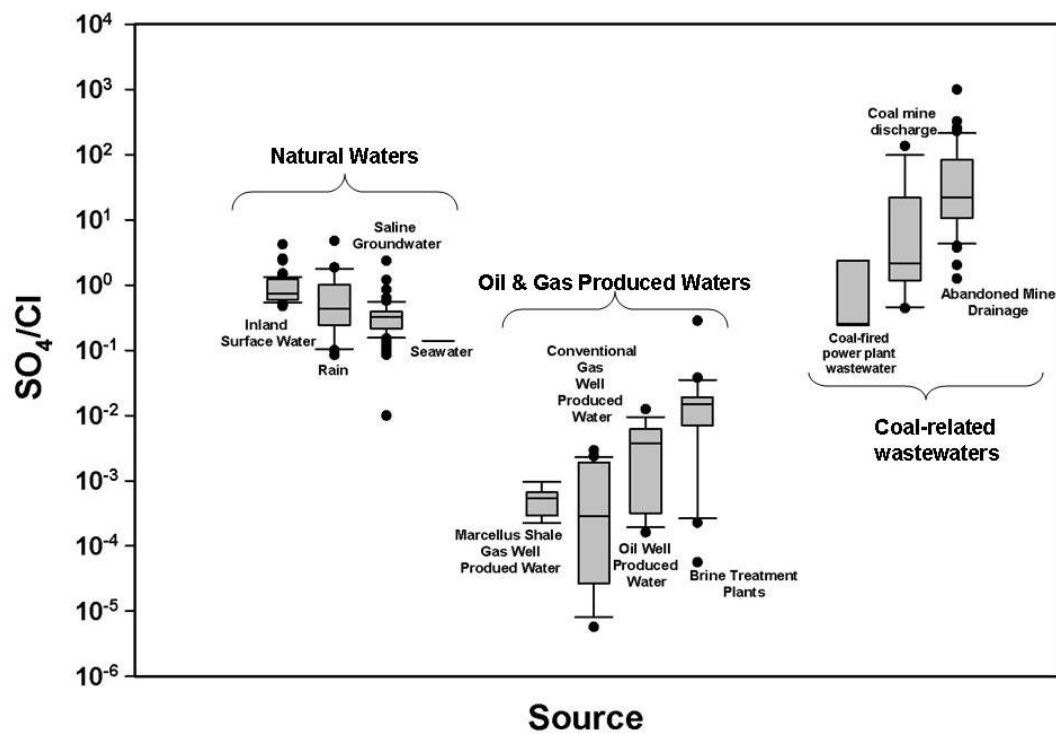


Figure 3.4. Box plot of SO_4/Cl mass ratios for natural waters, oil and gas produced waters, and coal-related wastewaters. Solid line in box is median, box edges are 25% and 75% while whiskers extend to 5% and 95%. Solid dots are outliers beyond the 5-95% range.

Table 3.4. Median SO₄/Cl and associated p-values (one-tailed Mann-Whitney Rank Sum Test). Shaded boxes are non-significant p-values.

Water Type		Produced Water Conventional Gas Wells	Produced Water Oil Wells	Brine Treatment Plants	All Oil and Gas Produced Water	All Oil and Gas Produced Water and Brine Treatment Plants	Coal-fired Power Plant Waste-water	Mine-Pool Discharge	Abandoned Mine Discharge	All Coal-related Waste-waters	All Natural Waters
		Median SO ₄ /Cl (x 10 ⁻⁴)									
		2.88	37.5	100.2	6.20	21.2	2,550	21,800	220,800	167,300	3,070
	Median SO ₄ /Cl (x 10 ⁻⁴)	p-value, $\alpha = 0.05$									
Produced Water Marcellus Shale	5.41	p = 0.645	p = 0.233	p = 0.013	p = 0.498	p = 0.868	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Conventional Gas Wells	2.88		p = 0.002	p < 0.001	p = 0.997	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Oil Wells	37.5			p = 0.002	p = 0.461	p = 0.480	p = 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001

		Produced Water Conventional Gas Wells	Produced Water Oil Wells	Brine Treatment Plants	All Oil and Gas Produced Water	All Oil and Gas Produced Water and Brine Treatment Plants	Coal- fired Power Plant Waste- water	Mine- Pool Discharge	Abandoned Mine Discharge	All Coal- related Waste- waters	All Natural Waters
		Median SO ₄ /Cl (x 10 ⁻⁴)									
		2.88	37.5	100.2	6.20	21.2	2,550	21,800	220,800	167,300	3,070
		p-value, $\alpha = 0.05$									
Brine Treatment Plants	100.2				p < 0.001	p < 0.001	p = 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Coal- fired Power Plant Waste- water	2,550				p < 0.001	p < 0.001		p < 0.001	p < 0.001	p < 0.001	p = 0.542
Mine- Pool Discharge	21,800				p < 0.001	p < 0.001			p = 0.002	p = 0.082	p < 0.001
Abandoned Mine Discharge	220,800				p < 0.001	p < 0.001				p = 0.037	p < 0.001

3.4.3 *Ratio Analysis in Conjunction with Concentration Data*

While the ratio analysis shown above provided insight into the classes of wastewaters and their relative ionic constituents, it fell short in differentiating among all the sources. What is needed is a method to incorporate the differences observed in actual concentrations and those observed in the ratios. For example, the SO_4/Cl ratios (Fig. 4) may provide even more information when combined with the very different total bromide concentrations (Fig. 2).

A common way to visualize this type of analysis is a plot that compares an anion ratio to a single constituent (e.g., SO_4/Cl versus bromide). Fig. 5 shows the data presented in this format. This plot shows the Marcellus shale gas well produced water, traditional gas well produced water, and traditional oil well produced water clustering at the high end of the bromide concentration, but at a low SO_4/Cl . Brine treatment plants show a similar bromide concentration, but a higher SO_4/Cl than the other oil and gas produced waters. AMD is much higher in SO_4/Cl than the oil and gas produced waters, and shows some variability in SO_4/Cl , but the data cluster at the low end of the bromide range. Coal-fired power plant wastewaters and mine pool drainage are moderate in bromide and less variable in SO_4/Cl . Thus, the combination of SO_4/Cl with bromide concentrations enables differentiation among these complex sources.

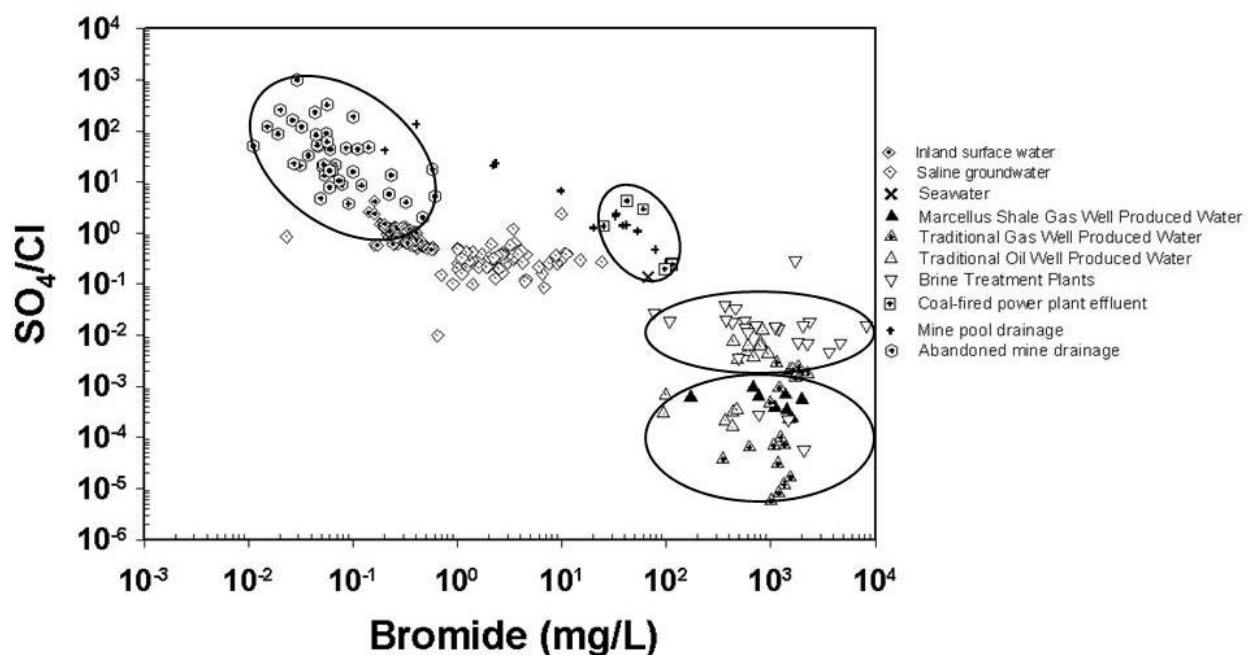


Figure 3.5. SO_4/Cl by mass versus bromide (mg/L) for natural waters, oil and gas wastewaters, and coal-related wastewaters. Circles added manually to highlight clusters.

This method was used to identify water quality changes in samples collected from two tributaries (Redstone Creek and Ten Mile Creek) in the Monongahela River Basin, located in Southwestern Pennsylvania. Fig. 6 shows a plot of SO_4/Cl versus bromide including the water quality data from the two tributaries. Also included on the plot are conservative mixing lines connecting two end member waters ($\pm 10\%$ for the possible SO_4/Cl range). The end members are the average SO_4/Cl and average bromide for oil and gas produced waters and the average SO_4/Cl and average bromide for Redstone Creek. The mixing lines were developed following Whittemore (Whittemore 1995). Redstone Creek was chosen as a representative freshwater endpoint, as it has not been impacted by fossil fuel activity and thus represents typical, unimpacted inland surface water values for the region. The data for seawater, saline groundwater, and inland surface water have been excluded, as they are not specific to Southwestern Pennsylvania. Water samples from Redstone Creek, shown as black circles, have a low bromide concentration and a higher SO_4/Cl .

Water samples from Ten Mile Creek are divided into 2 time periods: Sept. 2009 to June 2011 (grey circles) and July 2011 to Sept. 2012 (open dotted circles). Ten Mile Creek has legacy AMD discharges (Kimmel and Argent 2011), and received produced water discharge through the Franklin Township wastewater treatment plant during the time period of the study (Sept. 2009 to June 2011, corresponding to the samples shown in grey circles). Several samples from Ten Mile Creek during that time period fall within the mixing zone of oil and gas produced water and regional freshwater. After June 2011, the data for Ten Mile Creek show lower bromide concentrations, and less overlap with the mixing zone (open dotted circles). Thus, the application of SO_4/Cl and bromide concentration data combined with mixing curve analyses can be used to identify water quality changes due to the mixing of oil and gas produced water with regional freshwater. Additionally, this analysis can differentiate between two regional waters, as Ten Mile Creek and Redstone Creek, located in the same basin, but having significantly different water quality signatures. In other areas experiencing similar water changes due to fossil fuel extraction and high TDS wastewater disposal, collecting and analyzing regionally specific data and using this following the ratio and mixing curve integrated method would enable determination of the relative impacts of different activities on source water quality.

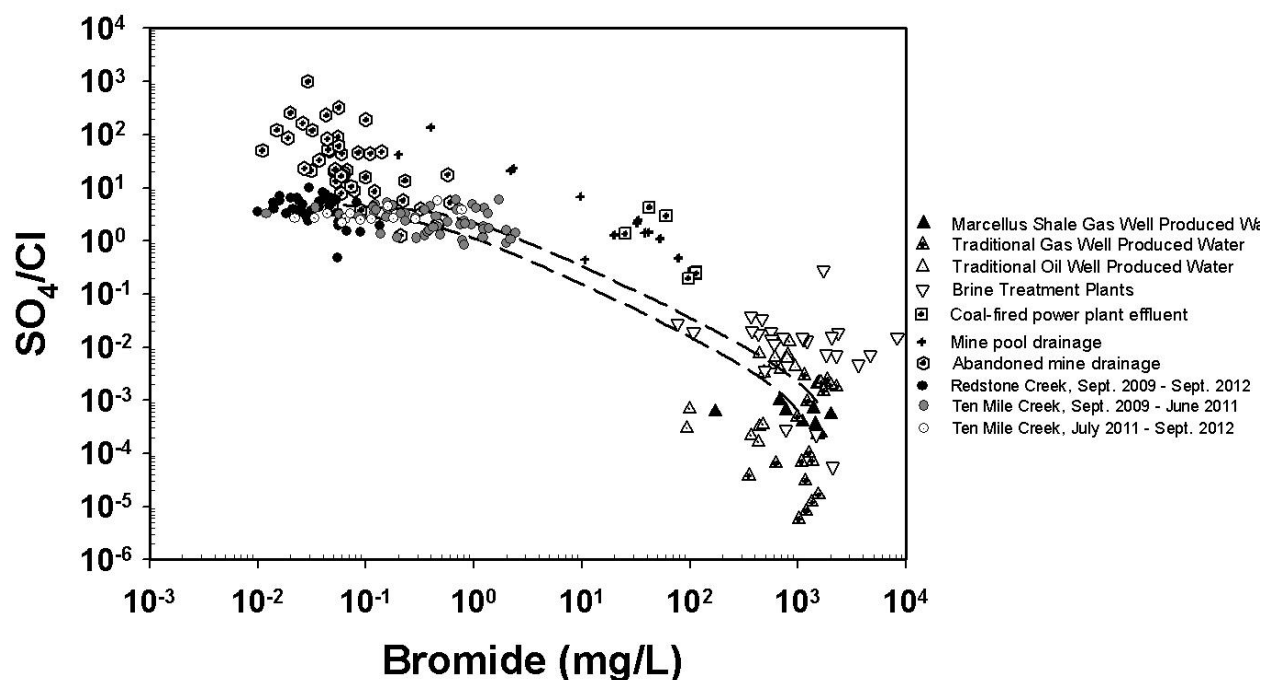


Figure 3.6. SO_4/Cl by mass versus bromide (mg/L) for oil and gas wastewaters and coal-related wastewaters. The dashed curves are mixing lines for oil and gas produced water and Redstone Creek (representing background regional conditions). Also shown are data from field sampling in two creeks in Southwestern Pennsylvania, Ten Mile Creek (shown as grey circles from data from Sept. 2009 to June 2011 and as open dotted circles from July 2011 to September 2012) and Redstone Creek (black circles for Sept. 2009 to Sept. 2012). Each circle represents one water quality sample taken over the period of September 2009 to September 2012.

3.5 Conclusion

The characterization of high total dissolved wastewaters in areas experiencing water quality changes from fossil fuel extraction and associated produced waters disposal can enable source identification and improve remediation decisions. Two commonly measured ions (chloride and sulfate) combined with the infrequently measured bromide concentration enable distinctions among fossil fuel associated inputs to source waters. Drinking water plants in areas experiencing expanded fossil fuel activities should incorporate bromide monitoring to improve information about potential sources of this ion to their watersheds and to inform decisions about control of formation of disinfection by-products in finished water. The presented method of collection and

analysis of anion relationships for regionally-relevant high TDS wastewater data can be used in other areas experiencing similar water quality changes.

Chapter 4

ENERGY EXTRACTION ACTIVITIES AND WATER QUALITY CHANGES IN THE MONONGAHELA RIVER BASIN, PENNSYLVANIA³

4.1 *Abstract*

Fossil fuel wastewaters disposed of to surface waters have the potential to affect drinking water quality. In Southwestern Pennsylvania, legacy coal mining and abandoned mine drainage have significantly impacted water quality, and the recent increases in unconventional extraction of natural gas from the Marcellus shale have the potential to alter water quality as well. Fossil fuel wastewaters contain high concentrations of constituents that are of concern to drinking water providers (including dissolved solids, sulfate, chloride and bromide). Finished drinking water from the Monongahela River Basin contained elevated concentrations of disinfection by-products in 2008, focusing attention on bromide concentrations in the river. A 3-year field study in the Monongahela River Basin was conducted to determine how bromide concentrations and associated loads were changing in the river basin, and whether these changes were caused by changes in fossil fuel wastewater management practices. Although low flow in the summer of 2010 contributed to increases in bromide concentrations at drinking water treatment plants, similar low flows that were observed in summer of 2012 did not, indicating bromide loads decreased from 2010 to 2012. While the cause of higher bromide loads in 2010 and 2011 is not clear, decreases between 2011 and 2012 are likely associated with a voluntary decrease in the use of surface-discharging treatment plants for shale gas produced water disposal. An investigation into Br/Cl at the drinking water plants showed significant increases in Br/Cl over the first year of

³ The Supplemental Information referred to in the text can be found in Appendix D.

the study, and similar increases in Br/Cl were observed at two of the tributaries in the region. Elevated Br/Cl ratios are associated with several forms of fossil fuel wastewater, including oil and gas produced water. The ratio of Br to Cl fell in the final years of the study, again consistent with decreased loading of shale-gas associated wastewaters to the basin. This work demonstrates that measurement of common ions at drinking water intakes can provide warnings of changes in loads in a large basin that signal likely increases of constituents of concern to drinking water utilities.

4.2 Introduction

In Southwestern Pennsylvania, Monongahela River Basin has historically experienced significant water quality challenges due to fossil fuel extraction and wastewater disposal. (PaDEP 2002; USEPA 2009). Unconventional natural gas extraction from the Marcellus shale gas reserves has increased over the past five years, generating additional wastewater with the potential to affect surface water quality (Olmstead et al. 2013; Rozell and Reaven 2012).

The Monongahela River spans 128 miles from West Virginia to Pennsylvania, where it meets the Allegheny River to form the Ohio River. The river is navigationally controlled over its full length through a series of lock/dam structures that maintain a series of pools to allow river traffic and sustain adequate water levels for withdrawals for industrial and public water supply. Several major tributaries to the Monongahela River have been affected by fossil fuel extraction activities for many years. Dunkard Creek, a tributary to the Monongahela River, has historically experienced abandoned mine drainage (AMD), as well as direct discharges from active coal mines. In 1998, Dunkard Creeks suffered a major fish kill attributed to AMD that contained high

concentrations of aluminum (DCNR 2000). In 2009, another large fishkill occurred that was attributed to a bloom of golden algae triggered by high TDS in the creek (PADEP 2011a; Soraghan 2011). Whiteley Creek is another tributary to the Monongahela River that experiences high total dissolved solids loadings from AMD and has an active AMD treatment site (Ziemkiewicz et al. 2011). Ten Mile Creek also has historically had numerous mine discharges (Kimmel and Argent 2009). Over the past 5 years, Ten Mile Creek has experienced a significant increase in Marcellus Shale drilling activity (Kimmel and Argent 2011; Wilson et al. 2013, under review), and also contained a facility receiving oil and gas produced water for treatment. Two other tributaries, Redstone Creek and the Youghiogheny River, have not experienced any significant changes in fossil-fuel activity. Redstone Creek is a generally low TDS stream with some mine discharges, and likely represents typical surface water conditions in the region. The Youghiogheny River is also a generally low TDS tributary. These creeks feed into the Monongahela River, which is a drinking water source for over a million people, and has 17 surface-water-fed drinking water treatment plants. Therefore, there is significant potential for fossil fuel wastewater treatment and disposal practices to affect drinking water quality in this basin.

Concerns regarding source water changes affecting drinking water were highlighted in this basin in 2008 when the Pennsylvania Department of Environmental Protection (PaDEP) found levels of sulfate and TDS that exceeded the secondary drinking water maximum contaminant levels in the Monongahela River (Handke 2008). When TDS and sulfate are elevated in the river (source water), they are not removed during drinking water treatment and remain elevated in the finished water. During this time, the treatment plants that were utilizing the Monongahela River as

source water also showed higher levels of brominated disinfection by-products (DBPs), which form during drinking water disinfection. Brominated DBPs form when the source water contains bromide, suggesting that during this time of high TDS and sulfate, bromide was also higher in the water than previously observed; however, no bromide data were collected at the time. DBPs are carcinogenic and their concentrations in drinking water are regulated by the Environmental Protection Agency. Recent research indicates that brominated DBPs are more cytotoxic and genotoxic than chlorinated DBPs (Plewa et al. 2002; Richardson et al. 2008); thus, increasing bromide concentrations in source waters raise human health concerns.

Drinking water treatment plants are concerned with the *concentration* of TDS and its components in their source waters. TDS, sulfate, and chloride are considered secondary contaminants by the Environmental Protection Agency due to their aesthetic impacts to drinking water (USEPA 2009). Bromide is not secondary regulated contaminant, but as noted above, even low concentrations of bromide result in increased formation of carcinogenic by-products in drinking water (Cowman and Singer 1996; Liang and Singer 2003). As in all systems with variable flow conditions, in the Monongahela River, TDS constituent concentrations are affected by dilution from natural flows. Under low flow conditions, constituent concentrations typically become elevated, and when rainfall-driven runoff keeps flows high, even high constituent loads may not lead to high concentrations. Determining whether an increase in constituent concentration of concern is due to flow conditions can be difficult as both flow and contaminant loads can vary seasonally. Further determining the meaning of year to year changes can be difficult as inter-year flow variation is common. Researchers often consider constituent load (concentration times flow) in a system to provide a flow-independent assessment (Ziemkiewicz

et al. 2011). Similarly, anion ratios can be used for flow independent analysis, and for source tracking (Andreasen and Fleck 1997; Davis et al. 1998; Whittemore 2007).

The present work summarizes the results of a 3 year monitoring study focused on source waters in the Monongahela River Basin (Sept. 2009 to Sept. 2012) for changes in TDS, chloride, sulfate, and bromide. There was significant variability in flow in the Monongahela River during this time period, as well as changes in the management of shale gas produced water, making data interpretation challenging. The present work demonstrates flow alone was not sufficient to explain observed changes, and provides context for evaluating the cause of the concentration changes as well as evaluating the potential impact of these changes on drinking water treatment.

4.2 Experimental Methods

4.2.1 Sampling Locations and Sample Collection

For this study, water samples were collected from the intakes at 6 drinking water treatment plants on the Monongahela River from September 2009 through September 2012. Additionally, samples were collected from four tributaries in the basin that feed into the Monongahela River. Samples were collected at regular intervals during this time period with specific frequencies as noted in Table 1. Figure 1 shows a map of the sampling locations, the navigational lock/dam (L/D) locations, and the drinking water treatment plants. Our sampling locations are within 6 different pools of the Monongahela River formed by the L/Ds; river miles 57 and 46 are within the same pool. Table 1 also lists the locations by river mile (RM), with the confluence of the Allegheny and Monongahela Rivers considered river mile 1; also shown in the pool name for each sample location. Tributaries are identified in Table 1 by name and latitude and longitude of

sampling locations are provided. For all sampling locations, Table 1 lists the number of samples collected over the study period. The latitude and longitude of the drinking water treatment plants is not provided at the request of the plants for security reasons.

Table 4.1. Sampling locations, number of samples taken (including percent below bromide detection limits) and sampling frequency.

Sample Location (latitude; longitude)	N ^a	Percent of samples below bromide detection limit ^b	Sampling frequency
RM 88	86	47	Weekly: Sept. 2009 – Jan. 2010; May 2010 – Oct. 2010; April 2011 – Oct. 2011
RM 71	84	27	
RM 57	84	30	
RM 46	82	29	
RM 25 ^c	84	35	Bi-weekly: Feb.2010 – Apr. 2010; May 2012 – Sept. 2012
RM 4	62	35	
Dunkard Creek (39.7416; -80.0631)	80	11	Weekly: Sept. 2009 – Jan. 2010; May 2010 – Oct. 2010; April 2011 – Oct. 2011 Bi-weekly: Feb.2010 – Apr. 2010 Monthly: Nov. 2010 – Mar. 2011; Nov. 2011 – Sept. 2012
Whiteley Creek (39.81597; -79.95517)	78	1	
Ten Mile Creek (39.98012; -80.03333)	80	10	
Redstone Creek (40.01608; -79.83083)	79	53	
Youghiogheny River (40.33868; -79.86013)	87	76	

^aNumber of samples collected during time period.

^bBromide detection limit is 0.01 mg/L.

^cSampling period for RM 25 is from May 2010 to Sept. 2012.

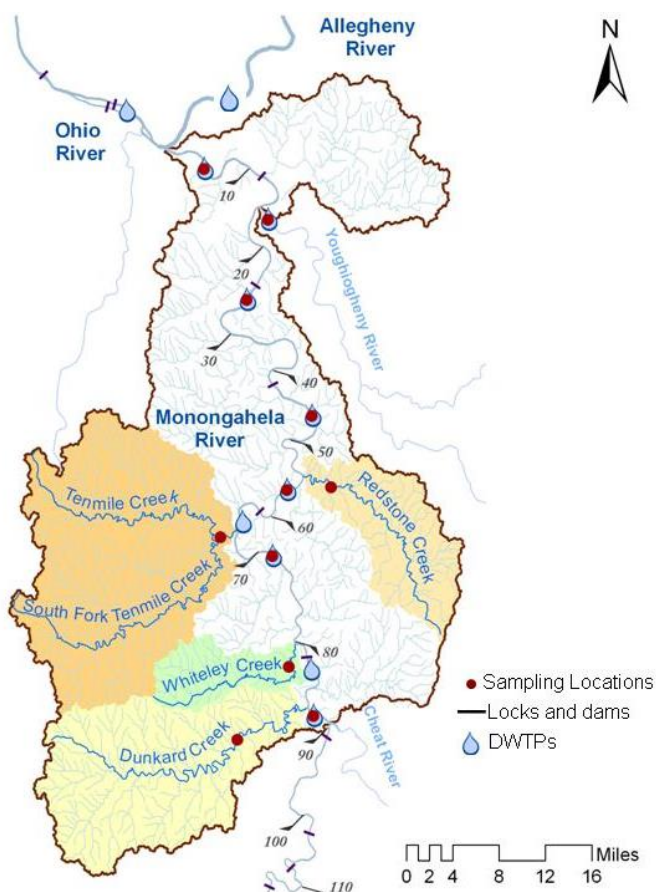


Figure 4.1. Map of the Monongahela River Basin. Sampling locations are shown as red dots.

500 mL samples were collected in clean polypropylene bottles at the river or water intake in the drinking water treatment plant and analyzed for total dissolved solids, pH, sulfate, chloride, and bromide concentrations. Samples were stored in a cooler with ice during transport and in a refrigerator at 4°C prior to analysis. All samples were analyzed within two weeks of collection.

4.2.2. Analytical Methods and Data Treatment

Total dissolved solids (TDS) concentrations were determined for a 50 mL sample using Standard Method 2540C for solids dried at 180°C (Standard Methods 1999). One blank sample (distilled, deionized water, DDW, Milli-Q), one standard TDS/conductivity solution (Ricca Chem Company), and one duplicate sample were completed for every ten environmental samples. The

sample pH was determined through the use of a Fisher Scientific Accumet XL60, which was calibrated with pH standard solutions prior to each use. Sulfate, chloride, and bromide concentrations were determined using an ion chromatograph (IC; Dionex) with an IonPac anion column (4 x 250 mm) and 100 µl sample loop with an eluent of 8 mM Na₂CO₃ and 1 mM NaHCO₃ (Fisher Scientific). Detection limits were determined as the minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (USEPA 1997) and were 0.02 mg SO₄/L, 0.01 mg Cl/L and 0.01 mg Br/L. Calibration standards were prepared by dilution of a multicomponent certified anion standard mix (Fisher Scientific) that provides traceability to NIST standards. Standards and eluent were made in deionized water with a resistivity of 18 MΩ. A standard curve was prepared and analyzed on the IC prior to each batch of samples. At least 10 % of all samples were analyzed in duplicate. A blank and calibration check standard were run every 10 samples. The relative percent difference (RPD) formula was used for quality control of the duplicate samples and the calibration check standard. For quality control, duplicate samples must have an RPD less than 5%, and calibration check standards must have an RPD less than 10%. If samples did not meet these requirements, they were re-analyzed (USEPA 1997).

All samples had detectable concentrations of chloride, sulfate and TDS at all times. However, some samples were quite low in bromide, with concentrations below the detection limit, as noted in Table 1. Data below the detection limit was considered using a robust method that combined observed data above the reporting limit with below-limit values that are extrapolated, assuming a lognormal distribution. A distribution was fit to the data using probability plotting procedures (Travis and Land 1990), and that distribution was used to extrapolate the values that were below

the detection limit (0.01 mg Br/L). These extrapolated values were used in calculating the summary statistics for the data (Helsel 1990), but were not used in any statistical analyses (see explanation in text). For visualization, values below detection limit were plotted as half of the bromide detection limit, and a different symbol is used to distinguish these values (0.005 mg Br/L) (Croghan and Egeghy 2003).

Statistical analyses (min, max, mean, median, standard deviation) were performed using Sigmaplot (Systat Software, San Jose, CA). The Mann-Whitney rank sum test was applied to the medians of the data for determining statistical significance in Sigmaplot. Statistical significance was determined at $\alpha = 0.05$, $p = 0.05$.

4.3 Discussion and Results

4.3.1 Drinking water intakes

The summary statistics for the drinking water intakes for TDS, chloride, sulfate, and bromide are shown in Table 2. Given the significant basin-wide changes in surface water disposal of oil and gas produced water over the three year study period, temporal trends for each constituent of TDS were assessed at each river mile. The flow of the Monongahela River was also included in this analysis. Although there are several flow gages along the Monongahela River that are operated by the United States Geological Survey (USGS), only two gages report daily discharge and are located in the same pools as the sampling locations, and those are located at RMs 71 and 25 (USGS 2012). Although the gages are significantly correlated ($r^2 = 0.98$, $p\text{-value} = 0.001$), suggesting that the flow in the river is stable, analysis of loads was only performed on the two sites located in the same pools as the sampling locations.

Table 4.2. Summary of water quality data for the 6 drinking water intakes. The intakes are identified by river mile (RM).

Sample Location	Parameter	Min ^a	Max	Median	Mean	Std. Dev
RM 87	TDS (mg/L)	46.0	490	210	232	101
	Chloride (mg/L)	4.00	54.5	12.4	14.8	9.79
	Sulfate (mg/L)	46.9	289	103	121	59.9
	Bromide (mg/L)	0.011	0.223	0.036	0.054	0.046
	Br/Cl	4.34×10^{-4}	2.86×10^{-2}	2.38×10^{-3}	3.57×10^{-3}	4.46×10^{-3}
	SO ₄ /Cl	1.39	23.8	9.56	9.70	4.36
	SO ₄ /Br	8.19×10^{-5}	2.49×10^{-3}	2.92×10^{-4}	4.21×10^{-4}	4.25×10^{-4}
RM 71	TDS (mg/L)	80.0	582	240	260	110
	Chloride (mg/L)	5.00	38.8	15.0	15.9	7.17
	Sulfate (mg/L)	34.0	304	125	137	65.3
	Bromide (mg/L)	0.010	0.225	0.038	0.054	0.040
	Br/Cl	9.62×10^{-4}	1.03×10^{-2}	2.69×10^{-3}	3.01×10^{-3}	1.73×10^{-3}
	SO ₄ /Cl	3.22	17.6	9.00	9.04	2.97
	SO ₄ /Br	7.51×10^{-5}	2.59×10^{-3}	3.49×10^{-4}	3.87×10^{-4}	3.33×10^{-4}
RM 57	TDS (mg/L)	88.0	596	302	297	124
	Chloride (mg/L)	4.00	65.4	20.0	19.7	10.3
	Sulfate (mg/L)	27.0	457	150	156	86.1
	Bromide (mg/L)	0.013	0.274	0.059	0.075	0.057
	Br/Cl	8.72×10^{-4}	2.54×10^{-2}	3.23×10^{-3}	3.67×10^{-3}	3.33×10^{-3}
	SO ₄ /Cl	2.89	21.4	7.89	8.25	2.72
	SO ₄ /Br	1.27×10^{-4}	1.98×10^{-3}	4.20×10^{-4}	4.67×10^{-4}	2.97×10^{-4}
RM 46	TDS (mg/L)	58.0	588	317	308	113
	Chloride (mg/L)	8.78	45.5	21.5	21.3	8.37
	Sulfate (mg/L)	43.0	407	147	160	75.7
	Bromide (mg/L)	0.011	0.599	0.064	0.093	0.092
	Br/Cl	7.50×10^{-4}	2.72×10^{-2}	2.90×10^{-3}	4.15×10^{-3}	4.12×10^{-3}
	SO ₄ /Cl	2.56	12.5	7.53	7.57	2.11
	SO ₄ /Br	6.14×10^{-5}	3.16×10^{-3}	4.20×10^{-4}	5.77×10^{-4}	5.20×10^{-4}
RM 25	TDS (mg/L)	130	582	320	332	105
	Chloride (mg/L)	7.00	60.0	23.7	24.2	10.9
	Sulfate (mg/L)	46.0	288	160	159	66.8
	Bromide (mg/L)	0.019	0.187	0.064	0.078	0.046
	Br/Cl	9.58×10^{-4}	5.57×10^{-3}	2.66×10^{-3}	2.77×10^{-3}	1.10×10^{-3}
	SO ₄ /Cl	1.45	12.1	6.93	6.92	2.15
	SO ₄ /Br	1.59×10^{-4}	7.60×10^{-4}	3.94×10^{-4}	4.22×10^{-4}	1.63×10^{-4}
RM 4	TDS (mg/L)	87.0	608	312	308	111
	Chloride (mg/L)	7.00	109.3	33.3	36.1	17.9
	Sulfate (mg/L)	23.0	368	122	134	64.2
	Bromide (mg/L)	0.014	0.310	0.069	0.079	0.062
	Br/Cl	5.00×10^{-4}	5.68×10^{-3}	1.61×10^{-3}	1.89×10^{-3}	1.21×10^{-3}
	SO ₄ /Cl	1.16	10.3	3.79	3.92	1.55
	SO ₄ /Br	1.13×10^{-4}	2.12×10^{-3}	4.64×10^{-4}	5.21×10^{-4}	3.48×10^{-4}

^aFor all sites, the minimum bromide was below detection limit. The minimum value seen here is the minimum bromide concentration found above detection limit.

Figure 2 shows data for the (a) river flow (m³/day), and the concentrations of (b) sulfate, (c) chloride, and (d) bromide in mg/L from Sept. 2009 to Sept. 2012. The flow at this location is

seasonal, with higher flows in the winter and spring than in the fall and summer. The median flow in summer of 2010 (June – Sept.) is statistically significantly lower than in summer 2011 ($p < 0.001$), but shows no statistically significant difference when compared to summer 2012 ($p = 0.582$). The median flow in summer 2011 is also statistically significantly higher than in summer 2012 ($p < 0.001$). These trends are also observed at the gage located at RM 25 (not shown). Summary data for the gage is provided in Table 3. Summer 2010 was relatively dry (50 % of average 74 year flow for summer, June – Sept.) while summer 2011 was wetter (108 % of average 74 year flow for summer, June – Sept.) and summer 2012 was again relatively dry (43 % of average 74 year flow for summer, June – Sept.).

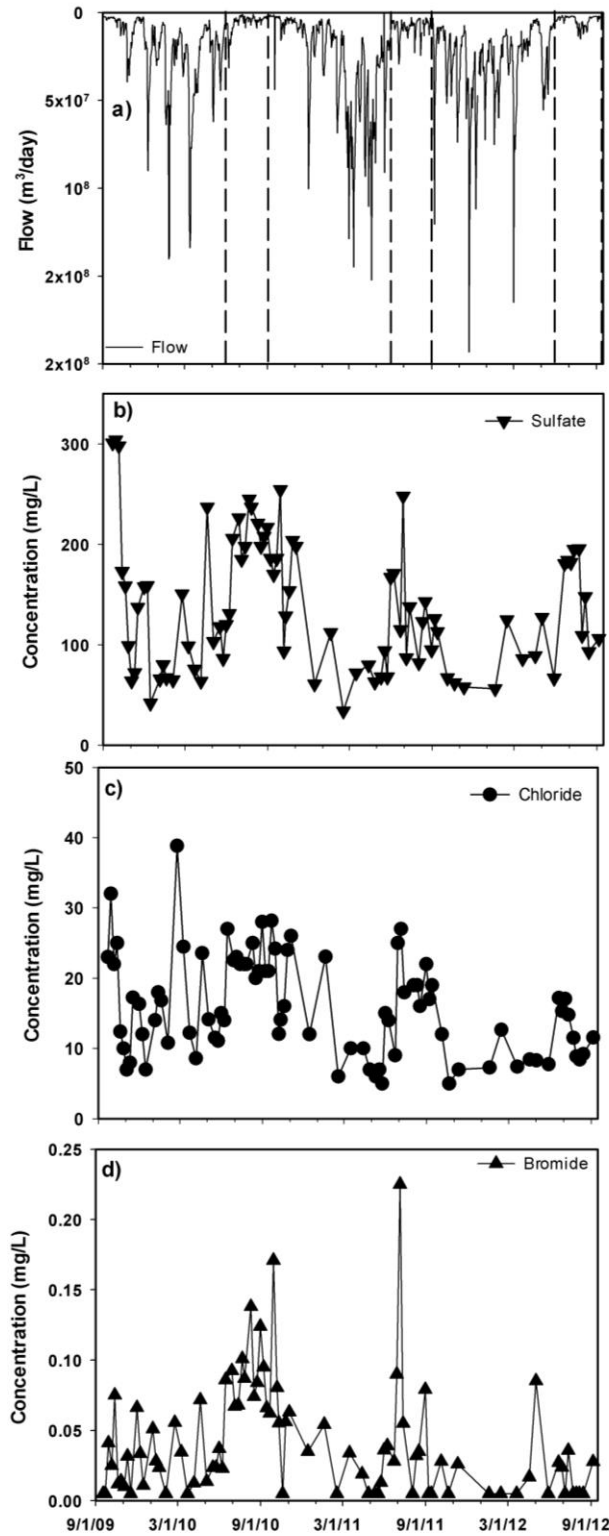


Figure 4.2. Flow (a) (in m³/day) and concentration of constituents (in mg/L) versus time for RM 71 for: b) sulfate; c) chloride; and d) bromide, from Sept. 2009 to Sept. 2012. Shown on panel a are dashed lines representing the low flow, ‘summer’ season each year (June – Sept.)

Table 4.3. Summary statistics for flow for RM 71.

RM 71 Flow (m ³ /day)	Min	Max	Median	Mean	Std. Dev.
Year 1, Sept. 2009 – Aug. 2010	9.90x10 ⁵	1.40x10 ⁸	1.03x10 ⁷	1.75x10 ⁷	2.10x10 ⁷
Year 2, Sept. 2010 – Aug. 2011	1.25x10 ⁶	1.52x10 ⁸	1.17x10 ⁷	2.31x10 ⁷	2.63x10 ⁷
Year 3, Sept. 2011 – Aug. 2012	1.46x10 ⁶	1.93x10 ⁸	1.47x10 ⁷	2.15x10 ⁷	2.28x10 ⁷
Summer 2010 (June – Sept.)	9.90x10 ⁵	4.37x10 ⁷	3.45x10 ⁶	5.11x10 ⁶	5.62x10 ⁶
Summer 2011 (June – Sept.)	2.78x10 ⁶	1.20x10 ⁸	8.12x10 ⁶	1.11x10 ⁷	1.34x10 ⁷
Summer 2012 (June – Sept.)	1.46x10 ⁶	1.50x10 ⁷	2.78x10 ⁶	4.36x10 ⁶	3.02x10 ⁶

It is expected that flow will have an important effect on consistent concentrations, as higher flows lead to more dilution, and thus lower constituent concentrations. From Figure 2, constituent concentrations are the highest during the summer months (June – September) for each year of the study, as expected. Bromide, in particular, shows a concentration increase in summer 2010, and a similar (although not as prolonged) increase in summer 2011. Bromide concentrations are lower in summer 2012 than in summer 2010 or 2011, with many samples below the bromide detection limit. It is expected that at low flow (summer 2010 and 2012), the concentration of bromide should be high, and at higher flow (summer 2011), the concentration of bromide should be lower (due to dilution). Despite similar low flows in summers 2010 and 2012, concentrations were much higher in 2010 than 2012, indicating that flow changes alone cannot explain the concentration changes observed.

Comparisons that either incorporate flow (such as mass loadings) or are independent of flow (such as ratio analyses) may provide more insights into the temporal variability of bromide in this system, and to determine the cause of observed bromide concentration changes.

Estimated chloride and bromide loads (in kg/day) in the river were calculated at RM 71 using the average daily flow data and the measured bromide concentrations in the source water (Figure 3). There is significant variability in the loads for both chloride and bromide. The highest bromide loads are observed in March and June 2011, which is expected as the flow was significantly higher during that time period than 2010 or 2012. However, the bromide load is also statistically significantly higher in Year 1 (Sept. 2009 – Aug. 2010) than in Year 3 (Sept. 2011 – Sept. 2012), ($p = 0.003$ and 0.002 , respectively). Despite having similar flows in summer 2010 and summer 2012, the bromide loadings are significantly different, indicating that there has been a change to bromide load in this system from 2010 to 2012.

In contrast, chloride loading is highest during the late winter and early spring (Feb. – April), likely due to increased runoff to the river from road salt applied in the winter for road deicing; this is a common observation in river systems (Corsi et al. 2010; Trowbridge et al. 2010). However, when bromide load is high during the summer 2010 and 2011 the chloride load is generally low. These differences suggest that the sources of bromide and chloride loads to the basin are different.

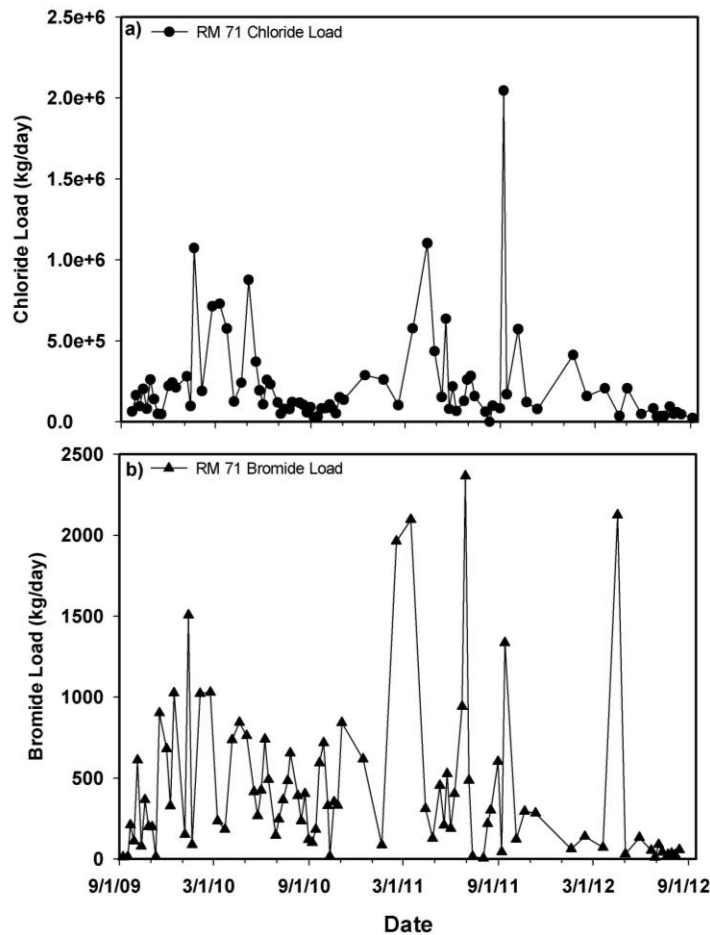


Figure 4.3. RM 71: a) Chloride load in kg/day; b) Bromide load in kg/day.

Although chloride and bromide loads give us insight into the overall trends in the river, there are limitations to computing such loads in a large river system. First, as mentioned previously, there are only two flow gages on the river, limiting the loading estimations that could be determined. Second, water quality sampling is not done at the flow gage location, but rather at the drinking water intakes. Incomplete mixing in the river pool could lead to differences in concentrations at different locations, and this variability introduces uncertainty in the estimation of load (Fulton 2010).

An alternative approach is to consider constituent ratios. These are based on analyses of a single sample, and by creating a ratio any effects of dilution or concentration associated with flow are

eliminated. Bromide/chloride (Br/Cl), sulfate/chloride (SO₄/Cl), and bromide/sulfate (Br/SO₄) (all by mass) were calculated for each river mile using the collected concentration data. A temporal plot of Br/Cl (log-scale) is shown in Figure 4 for RM 71. There were several data points that were below the detection limit for bromide; these are shown as open circles (with bromide concentration assumed to be half the detection limit) so as not to misrepresent the number of samples taken. From Figure 4, the Br/Cl increases from fall 2009 to summer 2010, and then increases again in summer 2011. However, there are more non-detect bromide points in 2011 than 2010, and even more in 2012, making comparisons difficult. A nonparametric rank sum test was performed on various subsets of the data to determine the statistical significance of the changes in Br/Cl. This test was chosen in favor of the maximum likelihood estimation (MLE) because MLE methods generally do not work well for small data sets (< 50 detected values) (Helsel 2006; Shumway et al. 2002), which is a concern when the data set is sub divided for this study. The available data were split into 6 equal time-periods during the three years for comparison. Results from all statistical analyses can be found in the Supporting Information. For RM 71, the median Br/Cl is statistically significantly higher in the second half of Year 1 (Mar. 2010 – Aug. 2010) than the first half of Year 1 (Sept. 2009 – Feb. 2010, $p = 0.010$). The Br/Cl remains higher throughout 2011, showing a statistically significant increase in median Br/Cl from the first half of Year 1 to the first half of Year 2 (Sept. 2009 – Mar. 2010 and Sept. 2010 – Mar. 2011, $p = 0.009$). This time period also showed elevated bromide load while the chloride load was low and stable (see Figure 3), indicating that the increase in Br/Cl was due to an increase in overall bromide load in the system rather than a change in chloride.

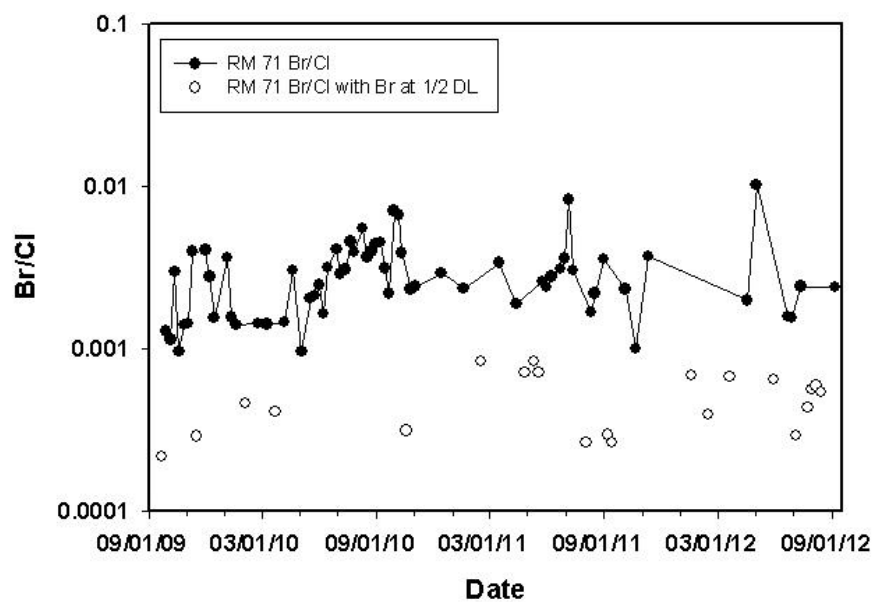


Figure 4.4. Br/Cl versus date for RM 71. Bromide data below the detection limit are plotted as open circles.

This conclusion was further evaluated with consideration of the Br/SO_4 for RM 71 (Figure 5). The Br/SO_4 follows the same trend as Br/Cl , indicating that sulfate, like chloride, is stable in this system, while bromide load is increasing (over Year 1 of the study). All other RMs (except for RM 25, which had insufficient data for analysis) showed a statistically significant increase in median Br/Cl between the first halves of Years 1 and 2. Similar to RM 71, there were no significant changes in Br/SO_4 during the time period while there was a significant increase in Br/Cl . These statistical analyses are provided in the Supporting Information.

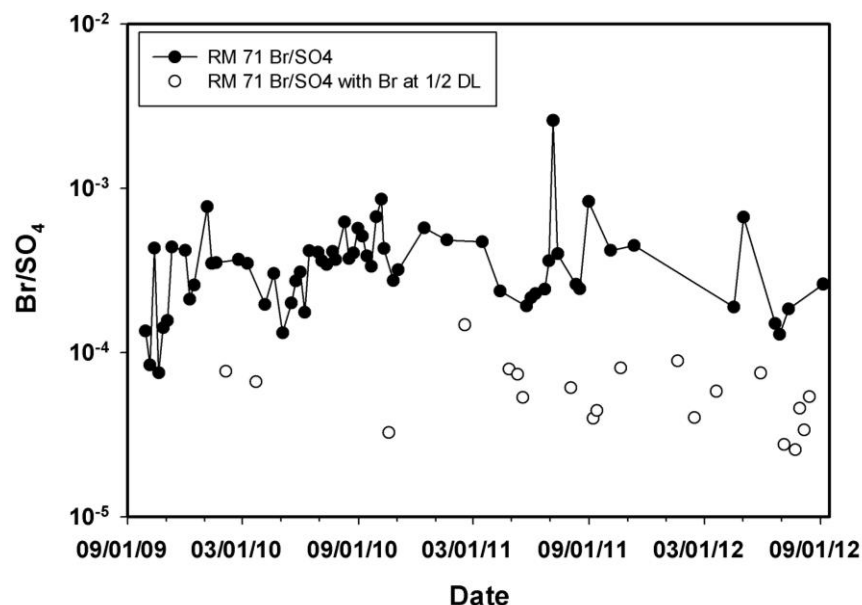


Figure 4.5. Br/SO₄ versus date for RM 71. Bromide data below the detection limit are plotted as open circles.

While the Br/Cl is useful for tracking overall changes at the drinking water intake, it is insufficient in determining the source of these changes in relation to fossil-fuel wastewater disposal. This is because the bromide to chloride ratio for many fossil fuel associated wastewaters is similar (as discussed by Wilson et al, 2013, under review). Figure 6 shows the bromide to chloride ratios as box plots for a number of key fossil fuel wastewaters (right side) as well as for RM 71 and for Redstone Creek, representing typical regional surface water conditions (left side). Redstone Creek has a significantly lower median Br/Cl than the entire dataset from RM 71 ($p < 0.001$). For RM 71, the statistically significant median increases in Br/Cl from Sept. 2009 to August 2010 are shown. It is clear that the median Br/Cl increases through February 2011, and then decreases for the remainder of the sampling period. On the right side of the figure are the Br/Cl ranges for coal-associated wastewaters (AMD, coal-mine discharge, and coal-fired power plant effluent) and for all oil and gas produced water (both conventional and unconventional) in Pennsylvania (Wilson et al. 2013, under review). Oil and gas produced water (both conventional and unconventional) and coal-fired power plant effluent show the

highest median Br/Cl, but there is significant overlap in the Br/Cl for all these fossil fuel wastewaters, making it impossible to unequivocally distinguish them based upon this ratio alone. From Sept. 2009 to Feb. 2010, RM 71 shows a low Br/Cl, within the range of AMD, and consistent with historical causes of water quality impairment in the region. However, in the second half of Year 1 the RM shows a significant increase in median Br/Cl, indicating that a source with elevated Br/Cl (either from coal or oil and gas) may have increased in the region.

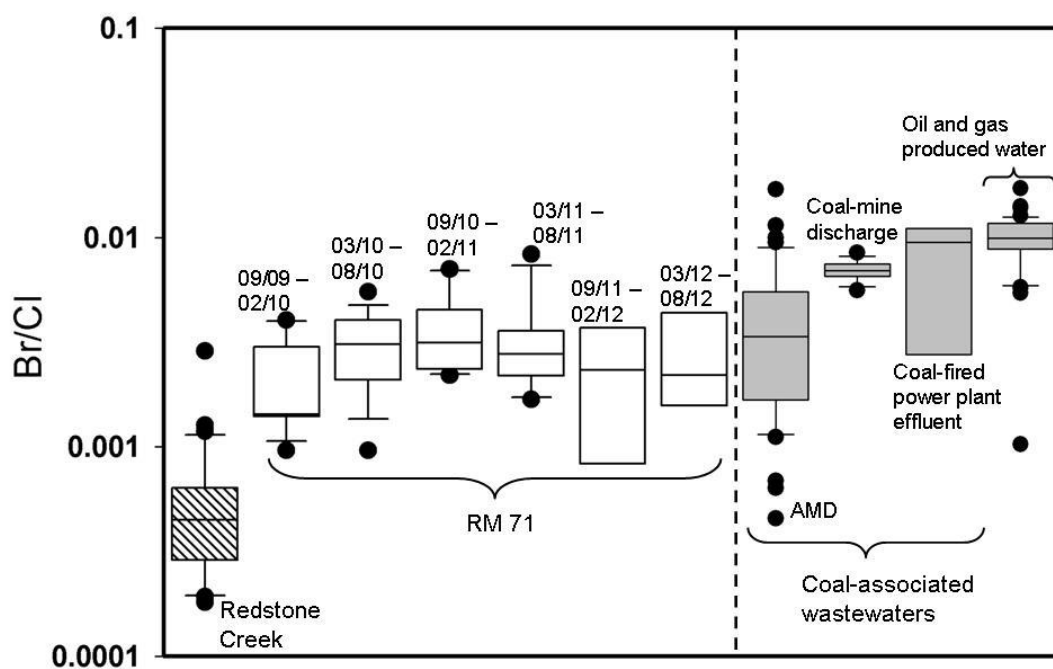


Figure 4.6. Box plot of Br/Cl for RM 71, Redstone Creek, and fossil-fuel associated wastewaters. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% and 95%. Solid dots are outliers beyond the 5-95% range.

4.3.2 Tributaries

As the ratios in the main stem Monongahela River have shown an increase in Br/Cl due to an increase in bromide load to the basin, it is important to evaluate the bromide within the tributaries. As previously discussed, several tributaries in this study have the potential to increase the bromide load to the basin as they are impacted by coal-related wastewaters or oil and gas

produced waters. Dunkard, Whiteley, and Ten Mile Creek all experience legacy mining impacts. Ten Mile Creek also contains a facility that accepted oil and gas produced water until March 2011 (Ferrar et al. 2013). Redstone Creek and the Youghiogheny River have not seen any significant changes in energy extraction activities, and Redstone Creek likely represents background conditions for the region (showing AMD impacts but significant dilution). The summary statistics for all of the tributaries are given in Table 5.

Table 4.4. Summary of water quality data for the five tributaries.

Sample Location	Parameter	Min ^a	Max	Median	Mean	Std. Dev
Dunkard Creek	TDS (mg/L)	156	1.63x10 ³	472	503	274
	Chloride (mg/L)	6.00	252	58.6	70.9	54.7
	Sulfate (mg/L)	28.0	1.05x10 ³	167	218	190
	Bromide (mg/L)	0.011	1.29	0.202	0.270	0.266
	Br/Cl	1.79x10 ⁻⁴	1.22x10 ⁻²	3.32x10 ⁻³	3.57x10 ⁻³	2.32x10 ⁻³
	SO ₄ /Cl	0.670	6.08	3.41	3.29	1.26
	SO ₄ /Br	1.51x10 ⁻⁴	5.83x10 ⁻³	1.08x10 ⁻³	1.20x10 ⁻³	8.76x10 ⁻⁴
Whiteley Creek	TDS (mg/L)	204	4.99x10 ³	2.06x10 ⁴	2.37x10 ³	1.39x10 ³
	Chloride (mg/L)	14.0	1.44x10 ³	140	344	348
	Sulfate (mg/L)	96.0	3.76x10 ³	1217	1316	853
	Bromide (mg/L)	0.010	8.80	1.11	1.88	1.99
	Br/Cl	5.21x10 ⁻⁴	3.88x10 ⁻²	4.52x10 ⁻³	5.67x10 ⁻³	4.88x10 ⁻³
	SO ₄ /Cl	1.65	36.4	4.30	8.09	8.22
	SO ₄ /Br	1.61x10 ⁻⁵	3.96x10 ⁻³	1.13x10 ⁻³	1.19x10 ⁻³	8.57x10 ⁻⁴
Ten Mile Creek	TDS (mg/L)	126	1.74x10 ³	564	658	373
	Chloride (mg/L)	8.00	495	82.9	114	99.8
	Sulfate (mg/L)	26.0	1.36x10 ³	230	281	222
	Bromide (mg/L)	0.012	2.43	0.288	0.520	0.564
	Br/Cl	8.22x10 ⁻⁴	2.32x10 ⁻²	2.76x10 ⁻³	4.14x10 ⁻³	4.26x10 ⁰³
	SO ₄ /Cl	0.831	6.00	2.77	2.98	1.30
	SO ₄ /Br	3.10x10 ⁻⁴	6.34x10 ⁻³	9.63x10 ⁻⁴	1.63x10 ⁻³	1.43x10 ⁻³
Redstone Creek	TDS (mg/L)	204	1.02x10 ³	542	564	208
	Chloride (mg/L)	22.0	285	64.9	69.7	33.7
	Sulfate (mg/L)	58.0	715	256	282	145
	Bromide (mg/L)	0.010	0.135	0.037	0.040	0.025
	Br/Cl	2.03x10 ⁻⁴	2.87x10 ⁻³	4.49x10 ⁻⁴	5.56x10 ⁻⁴	4.93x10 ⁻⁴
	SO ₄ /Cl	0.487	10.1	3.87	4.26	1.95
	SO ₄ /Br	2.64x10 ⁻⁵	1.48x10 ⁻³	9.81x10 ⁻⁵	1.94x10 ⁻⁴	2.68x10 ⁻⁴
Youghiogheny River	TDS (mg/L)	74.0	520	205	210	86.8
	Chloride (mg/L)	4.00	164	29.2	34.8	29.2
	Sulfate (mg/L)	10.0	169	74.7	76.4	30.9
	Bromide (mg/L)	0.012	0.415	0.025	0.061	0.096
	Br/Cl	3.03x10 ⁻⁴	1.40x10 ⁻²	8.57x10 ⁻⁴	2.07x10 ⁻³	3.31x10 ⁻³
	SO ₄ /Cl	0.500	12.1	2.49	2.58	1.40
	SO ₄ /Br	1.12x10 ⁻⁴	7.14x10 ⁻³	3.48x10 ⁻⁴	8.73x10 ⁻⁴	1.59x10 ⁻⁴

^aFor all sites, the minimum bromide was below detection limit. The minimum value seen here is the minimum bromide concentration found above detection limit.

To begin to answer the question of increasing Br/Cl, the bromide loads in the creeks were determined where gages were available. The Youghiogheny River was determined to contribute an insignificant bromide load to the basin (see Supporting Information). The load from Whiteley Creek could not be determined due to a lack of flow data; however, the bromide concentrations

in Whiteley suggest a possible source in that creek (average bromide concentrations are given in Table 5, the high degree of variability from year to year suggests this creek is affected by a specific bromide source although the origin is unknown). Figure 7 shows bromide loads in kg/day for a) Redstone Creek, b) Ten Mile Creek, and c) Dunkard Creek. Flow data for Ten Mile Creek was only available from October 2010 to September 2012 (USGS 2012). Redstone Creek shows significantly lower median bromide loads than either Ten Mile Creek ($p < 0.001$) or Dunkard Creek ($p < 0.001$), suggesting it does not contribute significant bromide load to the basin. For Dunkard Creek and Ten Mile, there was one outlier in bromide load at each of the sites, and these were excluded for plotting purposes, but are noted in the individual panels. For Dunkard Creek, a bromide load of 2,228 kg/day was found on May 4, 2010, and for Ten Mile Creek, a bromide load of 1,043 kg/day was found on May 19, 2011. Dunkard Creek was a significant source of bromide to the Monongahela River in the fall of 2009, but then decreased in summer 2010. There was no statistically significant difference in median bromide loads between Dunkard Creek and Ten Mile Creek from October 2010 to September 2012 ($p = 0.241$). For Ten Mile Creek, the median bromide load was significantly higher when a wastewater treatment plant in that basin was accepting produced water (October 2010 – March 2011) than when it ceased accepting produced water (April 2011 – Sept. 2012, $p = 0.002$ (Ferrar et al. 2013)). As flow data was not available for much of 2010 for Ten Mile Creek, determining the bromide load contribution from Ten Mile Creek during the time period of high Br/Cl at the drinking water intakes on the Monongahela River is not possible. However, anion ratios, which are flow independent, may provide more insight into the trends at Ten Mile Creek.

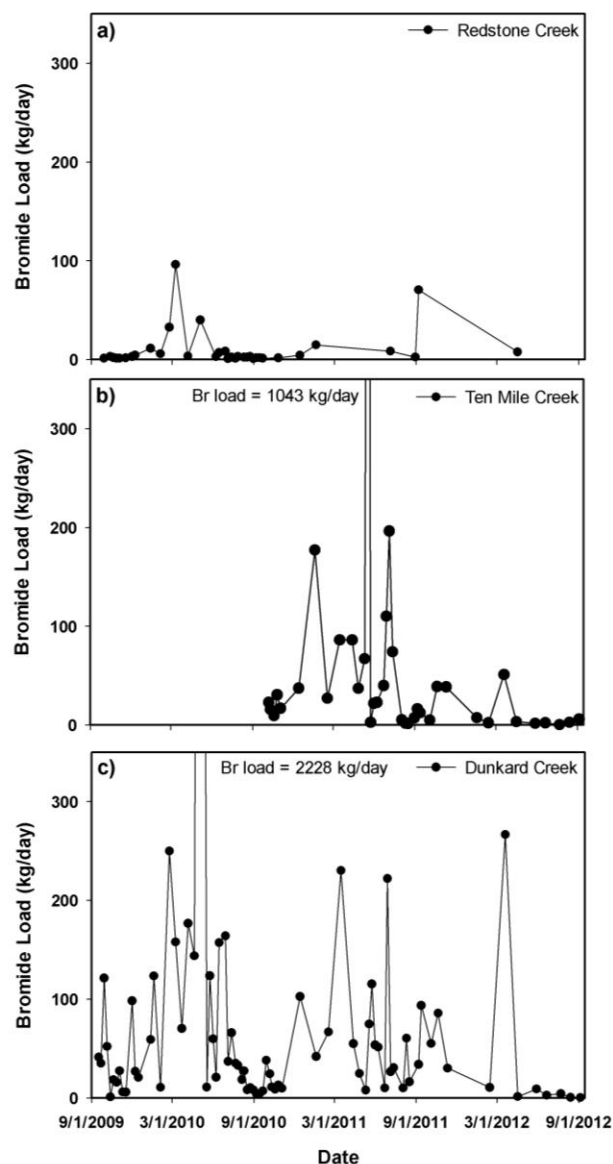


Figure 4.7. Bromide load in kg/day for a) Redstone Creek; b) Ten Mile Creek, and c) Dunkard Creek.

As with the river miles, the anion ratios Br/Cl and SO_4/Cl eliminate the flow-associated concentration effects for the tributaries. These ratios were determined for all 5 tributaries for the same time periods as the river miles. Figure 8 shows the Br/Cl over time for Ten Mile Creek. The median Br/Cl in Year 3 (Sept. 2011 to Sept. 2012) is statistically significantly lower than in Year 1 or Year 2 (Sept. 2009 to Aug. 2010, $p = 0.016$ and Sept. 2010 to Aug 2011, $p = 0.026$). The higher Br/Cl in Years 1 and 2 occurred when the wastewater treatment plant was accepting

produced water, and when they ceased accepting produced water, the median Br/Cl decreased significantly (Ferrar et al. 2013). Dunkard Creek was the only other tributary that showed any significant changes in Br/Cl, which was a statistically significant decrease in Br/Cl between the first half of Year 1 and the second half of Year 1 ($p = 0.006$) (data not shown; see Supporting Information).

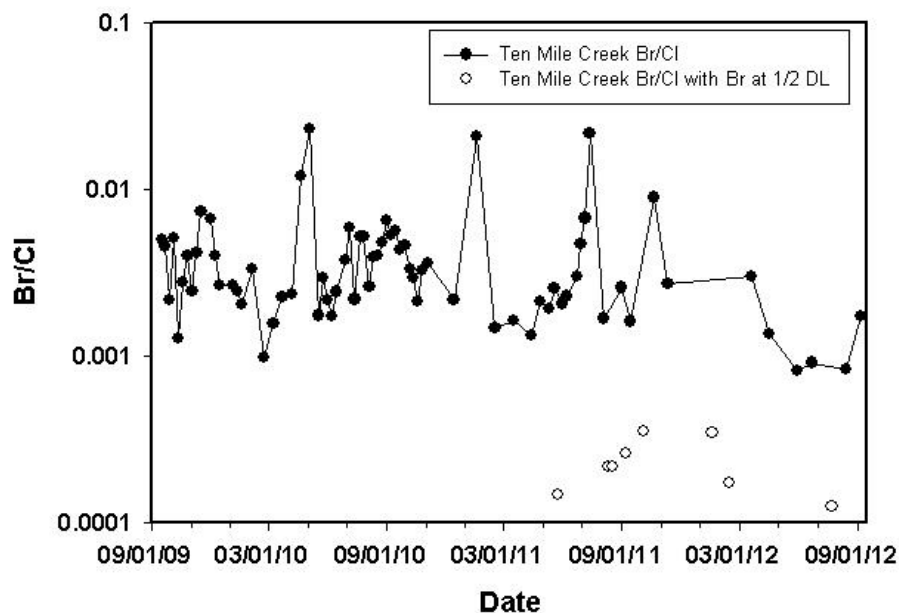


Figure 4.8. Br/Cl versus time for Ten Mile Creek. Bromide data below the detection limit are plotted as open circles.

4.4 Bromide concentrations at drinking water intakes under variable flow conditions

We have demonstrated that bromide loads from tributaries to the Monongahela River Basin can affect bromide concentrations at the drinking water intakes. Especially during periods of low flow, bromide concentrations are expected to be elevated in the tributaries and the main stem Monongahela River. An analysis of bromide loads during our study period can be used to evaluate potential future bromide concentrations in the basin under different flow conditions.

Statistics for flow were determined using USGS data from 74 years (available time period (USGS 2012)): minimum, 25th percentile, mean, 75th percentile, and maximum. Using the calculated loads from this study, bromide concentrations that would be expected at the drinking

water intakes were computed for different flow conditions. The results are shown in Table 5. The minimum, 25th percentile, mean, 75th percentile, and maximum bromide loads were evaluated under different potential flow conditions to determine ranges of expected bromide concentrations. As shown in the table, the minimum bromide load observed in the system was 10.3 kg/day, and under all flow conditions, the bromide concentration would be predicted to fall below the detection limit of 0.01 mg/L. By comparison, for the maximum load observed (2367 kg/day), under all flow conditions, the bromide concentration would be detectable. The worst case condition of high load and low flow would predict a bromide concentration of 0.461, a value considered high by EPA in their evaluation of drinking water sources (Weinberg et al. 2002) and which would be expected to cause significant problems for drinking water utilities.

For 2010, when bromide loading increased, low flow conditions would lead to bromide concentrations in excess of 0.09 mg/L, suggesting that bromide loads at that level cannot be adequately assimilated in this basin to prevent drinking water effects.

For the final year of the study, where bromide load was much lower, even under low flow conditions, bromide concentrations would not exceed 0.01 mg/L, suggesting that the 2012 loads of bromide in the basin produce bromide concentrations that would not affect drinking water.

Table 4.5. Estimated bromide concentrations under various flow conditions. Gray shading indicates a bromide concentration that would fall below our detection limit.

		<i>Flow (m³/day)</i>				
		Minimum	25 th percentile	Mean	75 th percentile	Maximum
		5.14 x 10 ⁶	1.55 x 10 ⁷	3.03 x 10 ⁷	4.26 x 10 ⁷	1.14 x 10 ⁸
<i>Bromide Load (kg/day)</i>		Bromide concentration (mg/L)				
Minimum	10.3	2.01 x 10 ⁻³	6.68 x 10 ⁻⁴	3.41 x 10 ⁻⁴	2.43 x 10 ⁻⁵	9.06 x 10 ⁻⁵
25 th percentile	108	0.021	6.98 x 10 ⁻³	3.56 x 10 ⁻³	2.54 x 10 ⁻³	9.46 x 10 ⁻⁴
Mean	441	0.086	0.029	0.015	0.010	3.86 x 10 ⁻³
75 th percentile	604	0.117	0.039	0.020	0.014	5.28 x 10 ⁻³
Maximum	2367	0.461	0.153	0.078	0.056	0.021

4.5 Mixing curve analyses

To determine if any of these water quality changes were affected by fossil fuel wastewater disposal, we employed a method we previously employed (Wilson et al. 2013, under review). This method uses regional data to develop mixing curves for oil and gas produced water with freshwater. For this method, regional data (for chloride, bromide, and sulfate) was collected for oil and gas produced waters and coal-associated wastewaters, and then the SO₄/Cl is plotted against bromide concentrations. Mixing curves for the mixing of oil and gas produced water with freshwater are added to the plot (Whittemore 1995). For this work, Redstone Creek is chosen as a representative freshwater endpoint, as it has historically been less impacted than other streams in the region, and it represents typical surface water values for the region. Given that Dunkard Creek saw changes in SO₄/Cl over time, an analysis was done to see if those changes were due to fossil fuel disposal. Figure 9 shows data from Dunkard Creek for Year 1 (grey circles) and Year 3 (grey circles). Each circle represents 1 water sample taken during that time

period. As mentioned previously, Dunkard Creek has active mine discharges, however, the water quality signature in Dunkard Creek for Year 1 shows overlap with the mixing curves of oil and gas produced water and freshwater, indicating that it may have been impacted with oil and gas produced water at this time. A significant change in water quality occurred in Dunkard Creek from Year 1 to Year 3 (grey circles), which shows a higher SO_4/Cl and lower bromide, more similar to the water quality signature of abandoned mine drainage (AMD). As previously discussed, there was a fish kill in Dunkard Creek in the fall of 2009, and although the cause has been attributed to a bloom of golden algae triggered by high TDS, the source of the high TDS is still unclear. The Pennsylvania Department of Environmental Protection stated that the high TDS was caused by coal mine discharge, while a U.S. EPA biologist has challenged the statement that coal mine discharge was the sole cause of the fish kill, citing waste disposal brine from the Marcellus Shale (Soraghan 2011).

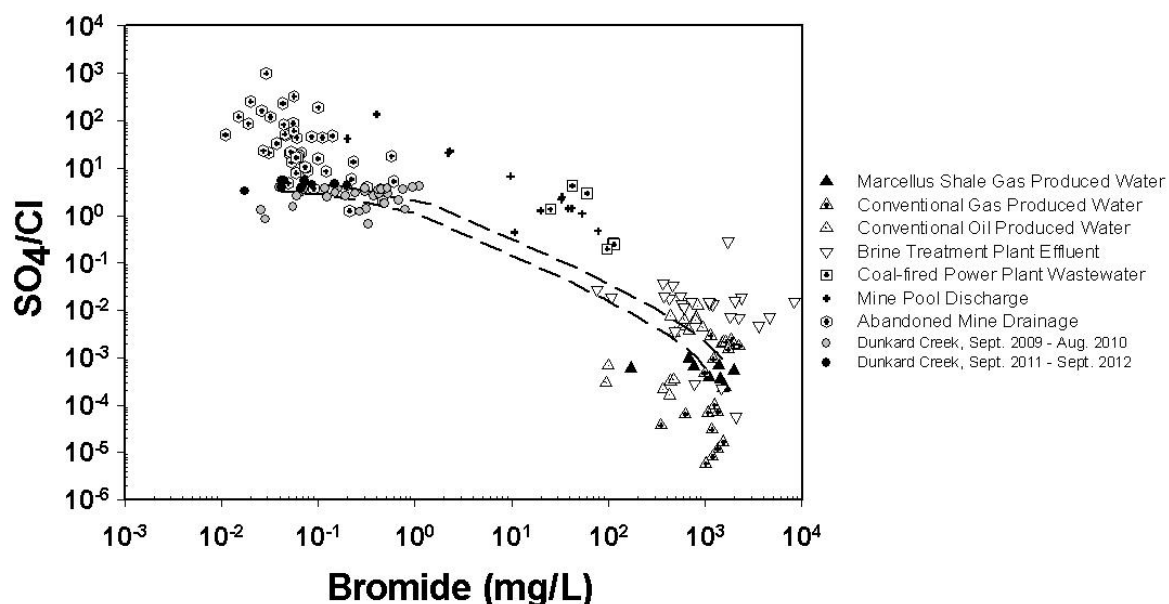


Figure 4.9. SO_4/Cl by mass versus bromide (mg/L) for oil and gas wastewaters and coal-related wastewaters. The dashed curves are mixing lines for oil and gas produced water and freshwater (representing background regional conditions). Also shown are two years of data from field sampling in Dunkard Creek. Year 1 is shown as grey circles and Year 2 is shown as black circles. Each circle represents one water quality sample taken over that time period.

Whiteley Creek also experienced an increase in SO_4/Cl from Year 1 to Year 3. However, the water quality signature is significantly different from that of Dunkard Creek. Figure 11 shows this visualization. In Year 1, Whiteley Creek has higher SO_4/Cl and also higher bromide concentration than Dunkard Creek, but only 3 samples show overlap with the mixing curve of oil and gas produced water with freshwater, and these 3 samples fall at the upper end of the mixing curve, with a similar water quality signature to AMD. In Year 3, SO_4/Cl increased significantly (from both Years 1 and 2), and the bromide concentration decreased, showing a signature indistinguishable from AMD. These results indicate that while Dunkard Creek could have been affected by mixing of oil and gas produced water with freshwater, Whiteley Creek was likely only impacted by AMD.

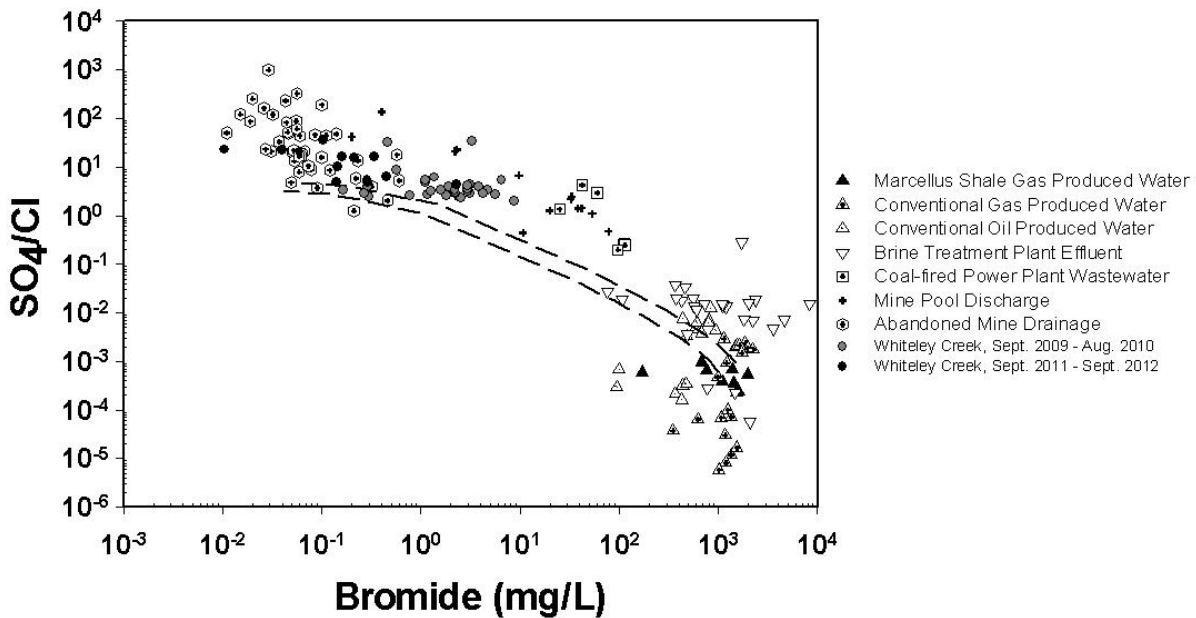


Figure 4.10. SO_4/Cl by mass versus bromide (mg/L) for oil and gas wastewaters and coal-related wastewaters. The dashed curves are mixing lines for oil and gas produced water and freshwater (representing background regional conditions). Also shown are two years of

Similar analyses for Ten Mile Creek and Redstone Creek were previously reported (Wilson et al. 2013, under review). Ten Mile Creek has legacy AMD discharges (Kimmel and Argent 2011),

and received produced water discharge through a publically-owned wastewater treatment plant during part of the time period of the study (Sept. 2009 to March 2011). Several samples from Ten Mile Creek during that time period fell within the mixing zone of oil and gas produced water and regional freshwater. After June 2011, the data for Ten Mile Creek showed lower bromide concentrations, and less overlap with the mixing zone. Redstone Creek showed a water quality signature with low bromide and lower SO_4/Cl than AMD over the entire study period (Sept 2009 to Sept 2012), suggesting no change in wastewater inputs to that basin.

This work shows that surface water disposal of fossil fuel wastewaters that are elevated in bromide have the potential to impact drinking water quality. The increasing concentrations of bromide found at drinking water intakes in the Monongahela River in the summer of 2010, and subsequent decreases in bromide in 2012 were not attributed solely to low flow in the river, and were likely due to changes to the management of produced water. This work demonstrates that measurement of common ions at drinking water intakes can provide warnings of changes in loads in a large basin that signal likely increases of constituents of concern to drinking water utilities.

Chapter 5

CONCLUSIONS

The objective of this work was to identify the source water and drinking water quality impacts associated with the management of fossil fuel wastewaters in Pennsylvania. This dissertation has demonstrated the potential water quality impacts associated with surface water disposal of fossil-fuel associated wastewater.

5.1 Conclusions

In Chapter 2, it was determined that that produced water management decisions for disposal options should be informed by the potential contribution of this wastewater to the formation of disinfection by-products in downstream drinking water treatment plants. Produced waters containing elevated bromide levels should be managed in ways that do not lead to increasing bromide loads delivered to surface waters.

In Chapter 3, the collection and analysis of anion relationships (of interest to drinking water providers) to enable distinctions among fossil-fuel associated inputs to source waters was successfully employed for regional wastewaters. A unique method to assess the mixing of oil and gas produced water with freshwater to assess regional water quality changes was presented. Drinking water treatment plants in areas experiencing expanded fossil fuel activities should incorporate bromide monitoring to improve information about potential sources of this ion to their watersheds and to inform decisions about the control of DBPs in drinking water.

In Chapter 4, increases in bromide concentrations at drinking water treatment plants in the Monongahela River Basin in 2010 were not attributed solely to low flow conditions, and were likely associated with surface water disposal of shale gas produced water. Changes in bromide load in the region affected bromide concentrations at drinking water treatment plants downstream. In summary, the measurement of common ions at drinking water intakes can provide warning of changes in loads in a large basin that signal likely increases in constituents of concern to drinking water providers.

5.2 Research Implications

This work has demonstrated the potential for fossil-fuel wastewater to affect drinking water quality through surface water disposal. This study has important implications for produced water disposal options, and supports bromide monitoring by drinking water treatment plants in areas experiencing fossil-fuel activities.

Findings in this dissertation are important in the future management of oil and gas produced water. It was determined that surface water disposal of produced water has increased bromide concentrations at drinking water treatment plants, which is a major concern for drinking water utilities. Alternatives to surface water disposal of fossil-fuel wastewater that is elevated in bromide should be evaluated and are preferable, especially in areas with downstream drinking water treatment plants.

The anion ratio and concentration method developed in this work to demonstrate the mixing of oil and gas produced water with freshwater can be applied to other areas experiencing similar

changes in surface water quality due to oil and gas produced water disposal. This method is a viable alternative to more advanced characterization methods for oil and gas produced water. This generalized method has important implications for drinking water providers by supporting the addition of source water bromide monitoring in areas experiencing increases in fossil-fuel activity.

This work is important in the management and disposal of produced water in a large river basin with flows that are typically affected by seasonality. In low flow conditions, it is essential that produced water not be disposed of to surface water, as bromide concentrations will be elevated at downstream drinking water treatment plant intakes. Drinking water plants in areas experiencing increases in fossil fuel activity and wastewater disposal should monitor for common ions (chloride, sulfate, and bromide) that can provide warning of changes in loads that could significantly increase constituent concentrations at their intakes.

Chapter 6

FUTURE WORK

6.1 *Summary*

Future work related to this dissertation consists of continued analysis of the extensive dataset collected during the 3-year field study. The proposed work is outlined below.

6.2 *Predictive disinfection by-product modeling from multi-year basin sampling*

As part of the 3-year field study finishing drinking water samples were collected at the same treatment plants where source water was collected. The goal of this work is to deepen understanding of the relationship between source water parameters and disinfection by-product formation in a basin undergoing changes in fossil-fuel extraction produced water management. Although source water effects on DBPs been well studied (e.g. (Cowman and Singer 1996; Liang and Singer 2003)), and multiple models exist in the literature (e.g. (Chowdhury et al. 2009)), the formation of DBPs in systems where source waters have high total organic carbon (TOC) *and* high bromide has not been well studied. Most US source waters are either high in bromide and low in TOC (ground waters predominately) or low in bromide and high in TOC (surface waters predominately) (Francis et al. 2010). High bromide in conjunction with high organic carbon is widely recognized to be a worst-case scenario for drinking water plants as typical dissolved organic carbon (DOC) removal technologies cannot reduce DOC to levels that prevent significant DBP formation in the presence of even moderate bromide levels (Archer and Singer 2006; Babcock and Singer 1979; Liang and Singer 2003).

This objective of this future work with the field data is to develop regression models for HAA and TTHM (as well as individual DBP species) formation using the data collected at six drinking water treatment plants from the 2009-2012 field study. The focus on multiple plants in a single basin was designed to consider a more uniform source water than has been evaluated previously (e.g., the ICR was a nationwide study). The uniformity of the source water will enable focus on differences in treatment choices and how these affect DBP formation and speciation. The source water was monitored for parameters that affect DBP formation such as bromide, alkalinity, TOC, UV_{254} , and $TSUVA_{254}$, and pH. The finished water was monitored for all four THM and all nine HAA that are formed during chlorine disinfection.

6.3 Natural organic matter characterization in a single basin to improve DBP formation potential prediction

The dominant factor in formation of disinfection by-products is the presence of organic matter in the water that is chlorinated. Naturally occurring organic matter (NOM) in the source water is only partially removed through coagulation, settling and filtration in drinking water treatment and thus, some NOM remains at the point of chlorination. Laboratory work has been extensive on characterization of NOM to better understand DBP precursors and water treatability. The results of these studies have been informative but often complex or contradictory (Croue et al. 2000; Hua and Reckhow David 2008; Kim and Yu 2005; Kim and Yu 2005; Singer 1999). Partly in response to the high variability of results for NOM evaluation in source water, additional methods to characterize NOM as a surrogate for DBP formation potential have been suggested (Krasner et al. 1996), including excitation-emission matrix (EEM) fluorescence spectroscopy (Chen et al. 2003; Coble 1996).

In conjunction the source water anion analysis presented in this dissertation, the natural organic matter in the source water samples has been characterized using fluorescence spectroscopy. Evaluation of this extensive characterization will be combined with the other source water parameters to determine if improved NOM characterization enables improved DBP formation prediction. Other authors have suggested EEM may allow quantitative analysis of THM formation potential (Baghoth 2012; Bell et al. 2012; Ishii and Boyer 2012; Pfifer and Fairey 2013; Wang et al. 2013); however, it is unclear if predictive models will be possible based on source water EEM characterization.

6.4 Natural organic matter characterization within treatment plants after multiple unit operations to predict DBP formation

In conjunction with the 3-year field study at the 6 drinking water treatment plants, a separate 1.5 year in-plant study was undertaken at 3 drinking water treatment plants. Samples were collected after different unit operations to determine if the changes in NOM during the treatment process affected DBP formation and speciation. As discussed previously, some organic matter remains in the water at the point prior to chlorination, and it is unclear if models that just use source water characteristics to predict DBP formation are sufficient. Previous work has shown that natural waters high in total organic carbon contain mostly aquatic humic substances that have a high ultraviolet absorbance and are amenable to removal via coagulation (Archer and Singer 2006). However, this work was conducted using the ICR database, and it is unknown if this relationship is confirmed in field studies. Thus, NOM was characterized by EEM at multiple points within the treatment plant. This will answer the question of whether characterization (by EEM or simpler methods) of water just prior to chlorination will allow prediction of TTHM and

THM speciation in finished water and whether predictions based on this characterization are better than those based on source water characterization. The ability to predict THM formation from the source water characterization has significant operational advantages, as source water characterization would enable process changes in response to detected high precursor surrogates, allowing for reduced TTHM production ‘on demand’ as source waters change. Alternatively, if THM formation is only predictable through analysis of DOM characterization at the point of chlorination, then THM removal technologies deployed in the distribution system will be required as near real-time operational responses to source water changes will not be possible.

APPENDIX A. Sampling. Analysis. Quality Control.

A.1 Sampling locations description

Table A.1 outlines the river miles and sampling locations for the field study and Figure A1 shows a map with the sampling locations. Samples were collected weekly, bi-weekly, or monthly for approximately 3 years. Sampling protocol is outlined in A.2 and A.3.

Table A.1. Sampling locations and river miles with site identifiers, samples taken, sampling period, and analyses included.

Site/River Mile	Site identifier (#)	Samples taken	Sampling period	Analyses included	Site notes
RM 88	14	Source water	09/17/2009 – 09/05/2012	Source water: TDS, Cl, SO ₄ , Br, TOC, UV ₂₅₄ , pH, conductivity, alkalinity	
RM 71	18	Source water	09/22/2009 – 09/05/2012	Source water: TDS, Cl, SO ₄ , Br, TOC, UV ₂₅₄ , pH, conductivity, alkalinity	
RM 57	3	Source water	09/08/2009 – 09/05/2012	Source water: TDS, Cl, SO ₄ , Br, TOC, UV ₂₅₄ , pH, conductivity, alkalinity	
RM 46	1	Source water	09/08/2009 – 09/05/2009	Source water: TDS, Cl, SO ₄ , Br, TOC, UV ₂₅₄ , pH, conductivity, alkalinity	
RM 25	21	Source water	05/04/2010 – 09/05/2012	Source water: TDS, Cl, SO ₄ , Br, TOC, UV ₂₅₄ , pH,	

				conductivity, alkalinity	
RM 4	19	Source water	09/29/2009 – 09/05/2012	Source water: TDS, Cl, SO ₄ , Br, TOC, UV ₂₅₄ , pH, conductivity, alkalinity	
Dunkard Creek	15	Surface water	09/17/2009 – 09/05/2012	TDS, Cl, SO ₄ , Br, TOC, pH, conductivity	Samples taken upstream of WWTP discharge.
Whiteley Creek	10	Surface water	09/17/2009 – 09/05/2012	TDS, Cl, SO ₄ , Br, TOC, pH, conductivity	Samples taken upstream of mine waste treatment discharge.
Ten Mile Creek	11	Surface water	09/17/2009 – 09/05/2012	TDS, Cl, SO ₄ , Br, TOC, pH, conductivity	Samples taken upstream of WWTP discharge.
Redstone Creek	12	Surface water	09/17/2009 – 09/05/2012	TDS, Cl, SO ₄ , Br, TOC, pH, conductivity	Samples taken upstream of WWTP discharge.
Youghiogheny River	5	Source water	09/08/2009 – 09/05/2012	Source water: TDS, Cl, SO ₄ , Br, TOC, UV ₂₅₄ , pH, conductivity, alkalinity	

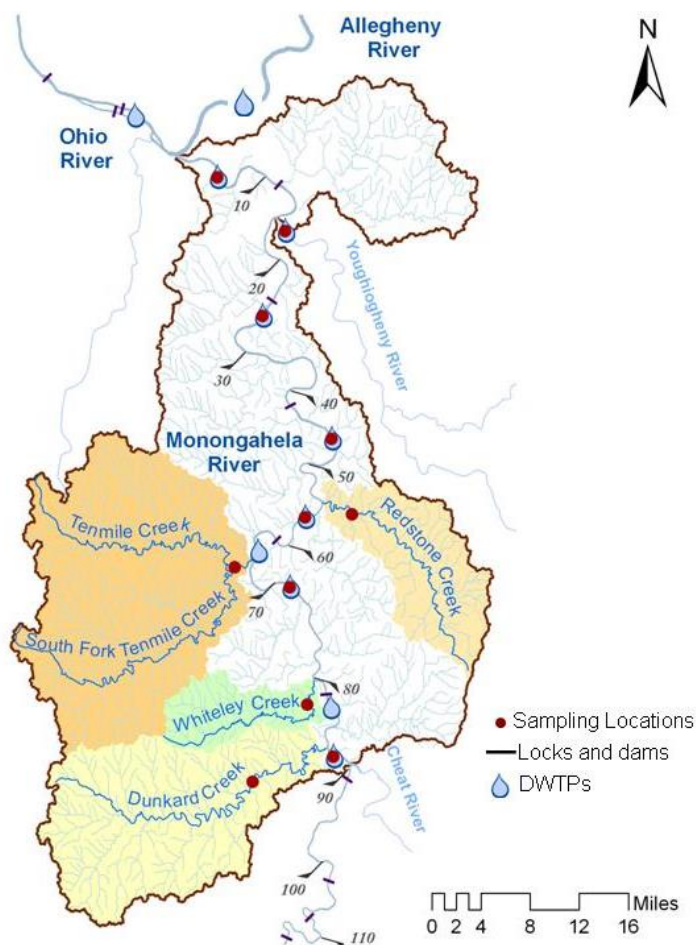


Figure A.1. Map showing sampling locations (red dots) and river miles.

A.2 Source water sample collection

Samples are collected in 500 mL polypropylene bottle (Fisher Scientific). Prior to sample collection, bottles are washed with a laboratory detergent and dried. For sample collection, the date and time of collection is recorded. Each sampling site is given a number for ease of collection (see table above). For collection, either nitrile or latex rubber gloves (Fisher Scientific) are worn by the technician.

At the time of sample collection at the drinking water treatment plants, the conductivity is read directly from the conductivity unit in the plant and recorded. The conductivity is also measured with a hand-held meter. The bottle is rinsed three times with the water being collected and then filled. Samples are stored in a cooler with ice after collection and during transport back to the laboratory.

A.4. Analytical procedure for total dissolved solids analysis

(Following Standard Method 2540C (Standard Methods 1999))

For this method, clean porcelain evaporating dishes (Fisher Scientific) are heated in an oven at 180°C for two hours prior to use. After cooling in a desiccators, the evaporating dishes are weighed on a four decimal balance immediately before use. Whatman glass microfiber filters with a diameter of 47 mm are placed on a membrane filtration apparatus and washed with three portions of distilled, deionized water (DDW) with a resistivity of 18.2 MΩ-cm (Barnstead Nanopure, Thermo Scientific). All traces of water are removed by applying a vacuum to the system after the water has passed. The water is discarded and the filter flask is rinsed with deionized water.

50 mL of sample is filtered through the vacuum filtration apparatus with filter and collected in a clean flask. The filter is washed with three 10 mL portions of DDW, which is added to the filtrate. The total volume of the filtrate including the DDW portions is added to the clean evaporating dishes and the filtration flask is rinsed with 10 mL of DDW. The dish is then placed in the oven at 98°C for evaporation. After evaporation, the dish is heated in the oven at 180°C for at least one hour. The dish is then placed in the desiccators to cool, and weighed. This cycle is repeated until a constant weight is obtained. The total dissolved solids are reported as increase in weight of the dish over total volume, mg/L.

A.4.1 Quality control

Sample volume analyzed must yield 2.5 mg - 200 mg of residue. If <2.5 mg residue, increase sample volume and reanalyze. If >200 mg residue, decrease sample volume and reanalyze. For quality control, one blank sample (DDW), one standard TDS/conductivity solution (Ricca Chem Company), and one duplicate sample are completed for every ten samples.

For sample drying, repeat drying of sample until a constant weight is obtained, or until the weight change is less than 4% of the previous weight or 0.005 g, whichever is less (see Table A2). At least 10% of all samples should be analyzed with duplicates. Duplicate determinations should agree within 5% of their average weight. Standard and blank samples should agree within 10% of their predetermined concentration.

The total dissolved solids standard used in this method is 495 ppm as NaCl. If standards, blanks, and/or duplicates do not meet QC then all samples will be re-analyzed until QC is met. The relative percent difference (RPD) formula is used for quality control of duplicate samples as seen below. The RPD must be less than 5% for duplicate samples. Standard and blank samples should have an RPD less than 10%.

$$RPD = \frac{|Sample1 - Sample2| * 100}{(Sample1 + Sample2) / 2} \quad (1)$$

Check the analytical balance with at least three Class S or equivalent weights each day the analysis is performed. The measured values must adhere to NIST standards or action must be taken. The oven temperature must be measured with a thermometer to ensure accuracy. The

thermometers used to check the temperature of the oven must be checked against an NIST traceable thermometer at least annually.

Table A.2. Total dissolved solids sample lab benchsheet.

Total Dissolved Solids Benchsheet (Standard Method 2540C)							
Date	Sample	Sample #		Crucible Mass (g)	Crucible and Solids Mass 1st Weigh (g)	Crucible and Solids Mass 2nd Weigh (g)	1st - 2nd (<0.0005 g)
11/3/2009							
	Dunkard Creek	15		84.1261	84.1365	84.1361	0.0004
	East Dunkard	14		85.8543	85.8560	85.8561	-0.0001
	Whiteley	10		83.1817	83.3375	83.3371	0.0004
	Southwest PA	18		81.0930	81.0977	81.0980	-0.0003
	Ten Mile	11		80.8210	80.8410	80.8413	-0.0003
	RedStone	12		78.0460	78.0660	78.0664	-0.0004
	Brownsville	3		83.7439	83.7486	83.7490	-0.0004
	Wash Twp	1		84.4813	84.5002	84.5000	0.0002
	McKeesport	5		84.2540	84.2600	84.2596	0.0004
	McKeesport Dup	6		83.6989	83.6964	83.6960	0.0004
	Standard	8		84.4338	84.4418	84.4417	0.0001
	Blank	9		83.7506	83.7708	83.7705	0.0003
	Site B	19		80.7280	80.7105	80.7104	0.0001

A.5 Analytical procedure for anions analysis

(Following Standard Method 4110B (Standard Methods 1999))

Chloride, sulfate, and bromide concentrations were determined using an ion chromatograph (Dionex) with an IonPac anion column (4 x 250 mm) and 100 µl sample loop with an eluent of 8 mM Na₂CO₃ and 1 mM NaHCO₃ (Fisher Scientific). Detection limits of 0.01 mg SO₄/L, 0.005 mg Cl/L and 0.01 mg Br/L have been determined for this method. Calibration standards were prepared by dilution of a multicomponent certified anion standard mix (Fisher Scientific) that provides traceability to NIST standards. A standard curve was prepared and analyzed prior to each batch of samples. A calibration check standard was run every ten samples, and a duplicate sample was run every ten samples. Necessary dilutions (1:10, 1:40, and 1:100, 1:300, 1:500) were also completed for sample analysis.

Standard Calibration Curve (in ppm)

Standard	Chloride	Sulfate	Bromide
1	0.2	0.4	0.4
2	0.5	1	1
3	1.0	2	2
4	2.0	4	4
5	4.0	8	8
6	5.0	10	10

Standard Calibration Curve for samples low in Bromide (in ppm)

Standard	Chloride	Sulfate	Bromide
1	0.005	0.01	0.01
2	0.01	0.02	0.02
3	0.025	0.05	0.05
4	0.04	0.08	0.08
5	0.05	0.10	0.10

A.5.1 Quality control

For anions, at least 10 % of all samples must be analyzed in duplicate. A blank and calibration check standard must be run every 10 samples and the calibration check standard must have an RPD (see Equation 1) less than 10% when compared to the standard concentration. Duplicate

samples must have an RPD less than 5%. For dilutions, samples must have an RPD of less than 5% if run with dilutions.

The calibration check standard (CCS) used in this method is Standard #3, which is 0.1 mg/L chloride, 0.2 mg/L bromide, and 0.2 mg/L sulfate.

A.6 Analytical procedure for pH

pH was analyzed in the laboratory using an Accumet Excel XL60 pH meter (Fisher Scientific).

A.7 Analytical procedure for alkalinity

Alkalinity measurements were performed in the field using Hach Model AL-DT test kits (Hach, Loveland, CO). The range is 10 – 4,000 mg/L alkalinity as CaCO_3 .

APPENDIX B. PaDEP Oil and gas production data compilation.

B.1. Wells drilled in Pennsylvania

Data for oil and gas wells was collected from the PaDEP. Figure C.1. shows the total number of wells and price of gas.

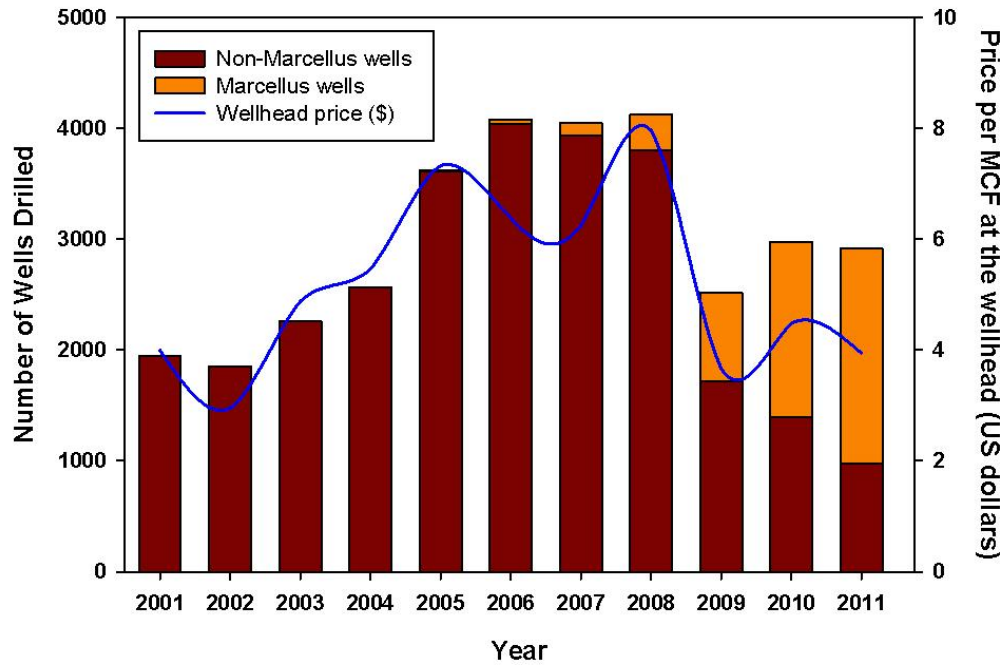


Figure B.1. Number of Marcellus and non-Marcellus wells drilled and price per MCF at the wellhead from 2001 - 11.

B.2. Produced water management volumes

Table C.1 shows the total volume of produced water by each management option. Data is from PaDEP (PaDEP 2012a), with corrections and modifications made as noted in Chapter 2.

Table B.1. Volume of produced water (barrels) by management option from 2008 - 2011, including Marcellus and non-Marcellus for 2010 and 2011.

Produced Water Management Option	2008 Total Produced Water	2009 Total Produced Water	2010 Non Marcellus Produced Water	2010 Marcellus Produced Water	2010 Total Produced Water	2011 Non Marcellus Produced Water	2011 Marcellus Produced Water	2011 Total Produced Water
Reuse and storage within operations (not road spreading)	5,582,079	5,681,465	305,300	2,393,378	2,698,678	1,045,859	11,484,825	12,530,684
Injection Well (UIC)	1,448,874	2,159,019	310,993	395,201	706,194	518,533	2,329,058	2,847,591
Brine Treatment Plants (CWT) - Exempt	13,482,302	22,928,380	2,923,358	5,140,400	8,063,758	2,775,629	1,996,995	4,772,624
Brine Treatment Plants (CWT) - Other	5,603,384	4,954,238	393,033	1,546,443	1,939,475	341,785	4,123,688	4,465,473
Municipal Sewage Treatment Plant (POTW)	11,158,004	2,594,005	694,596	617,693	1,312,289	485,248	102,305	587,554
Other (unspecified, road spreading, landfill)	6,348,383	6,152,450	934,571	1,597,298	2,531,869	208,799	131,994	340,793
TOTAL	43,623,026	44,469,557	5,561,850	11,690,412	17,252,263	5,375,853	20,168,867	25,544,720

APPENDIX C. High TDS data sources and supplemental tables and figures.

Table C.1. Description of data sources.

Data	Number of samples	Description	References
Seawater	12	Data for seawater collected from 1942 - 1985	(Bather and Riley 1954; Fukai and Shiokawa 1955; Haslam and Gibson 1950; Hem 1985; Matida 1954; Matida and Yamauchi 1951; Miyake 1939; Riley and Skirrow 1965; Thompson and Korpi 1942)
Inland Surface Water	79	Data from USGS survey in for Lake Texoma, Texas and Oklahoma in 2009, and from Red River, Texas in 2010.	(Stanley 2009; Stanley et al. 2010)
Potable Groundwater	32	Nationwide survey of potable groundwater in 2004.	(Davis et al. 2004)
Saline Groundwater	82	Data from Mediterranean coastal aquifer, 2005.	(Nordstrom et al. 1989; Vengosh et al. 2005)
Rain	23	Nationwide survey of rainwater in 2004.	(Fuge 1988; Harriss and Williams 1969; Root et al. 2004)
U.S. Source Water	5873	Data from U.S. Source Waters collected by drinking water treatment plants for the Information Collection Rule from 07/97 to 12/98	(USEPA 2000)
Produced Water Marcellus Shale	19	Data collected from hydraulic fracturing wells located in Pennsylvania and West Virginia. Data is for “produced water” which is water sampled 14 or 90 days following hydraulic fracturing. Data collected in 2009.	(Hayes 2009)
Produced Water Conventional Gas Wells	26	Data collected from gas wells in Pennsylvania in 1982.	(Dresel and Rose 2010)
Produced Water Oil Wells	15	Data collected from oil wells in Pennsylvania in 1982.	(Dresel and Rose 2010)
Brine Treatment Plants	29	Effluent data collected from three brine treatment plants in 2011: Josephine Brine Treatment Plant in Black Lick, PA; Franklin Brine in Franklin, PA; and Hart Brine Creekside, PA.	(USEPA 2012)
Coal-fired Power Plant Wastewater	8	Effluent waste data from a power plant in Southwestern PA in 2006 and from Conemaugh Power Plant in Indiana, PA, in 2011.	(EPRI 2007; Frank 2011)
Mine Pool Discharge	13	Unpublished data from the	(Schwartz 2010a; Schwartz 2010b)

		PaDEP from mine pools in Southwestern PA collected in 2010.	
Abandoned Mine Discharge	42	Data from abandoned mine discharges in PA collected in 2008.	(Cravotta 2008)

Table C.2. Median chloride concentrations (mg/L) and associated p-values (one-tailed Mann-Whitney Rank Sum Test). Shaded boxes are non-significant p-values.

Water Type		Produced Water Conventional Gas Wells	Produced Water Oil Wells	Brine Treatment Plants	All Oil and Gas Produced Water	All Oil and Gas Produced Water and Brine Treatment Plants	Coal-fired Power Plant Waste-water	Mine-Pool Discharge	Abandoned Mine Discharge	All Coal-related Waste-waters	All Natural Waters
		Median Chloride (mg/L)									
		133,000	50,000	75,921	121,500	80,135	10,450	2,616	21.00	51.50	724.00
	Median Chloride (mg/L)	p-value, $\alpha = 0.05$									
Produced Water Marcellus Shale	200,000	p = 0.054	p = 0.377	p = 0.006	p = 0.815	p = 0.217	p = 0.148	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Conventional Gas Wells	133,000		p < 0.001	p < 0.001	p = 0.008	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Oil Wells	50,000			p < 0.001	p < 0.001	p = 0.007	p = 0.005	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Brine Treatment Plants	75,921				p < 0.001	p = 0.009	p = 0.002	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Coal-fired Power Plant	10,450				p < 0.001	p < 0.001		p < 0.001	p < 0.001	p < 0.001	p < 0.001

Wastewater											
Mine-Pool Discharge	21.00				$p < 0.001$	$p < 0.001$			$p < 0.001$	$p < 0.001$	$p < 0.001$
Abandoned Mine Discharge	724.00				$p < 0.001$	$p < 0.001$				$p = 0.007$	$p < 0.001$

Table C.3. Median sulfate concentrations (mg/L) and associated p-values (one-tailed Mann-Whitney Rank Sum Test). Shaded boxes are non-significant p-values.

Water Type		Produced Water Conventional Gas Wells	Produced Water Oil Wells	Brine Treatment Plants	All Oil and Gas Produced Water	All Oil and Gas Produced Water and Brine Treatment Plants	Coal-fired Power Plant Waste-water	Mine-Pool Discharge	Abandoned Mine Discharge	All Coal-related Waste-waters	All Natural Waters
		Median Sulfate (mg/L)									
		34	260	667	50	204	2,580	7,946	580	750	1.89
	Median Sulfate (mg/L)	p-value, $\alpha = 0.05$									
Produced Water Marcellus Shale	50	p = 0.803	p = 0.377	p = 0.006	p = 0.842	p = 0.125	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Conventional Gas Wells	34.00		p = 0.080	p < 0.001	p = 0.911	p = 0.013	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Oil Wells	260			p < 0.001	p = 0.232	p = 0.591	p < 0.005	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Brine Treatment Plants	667				p < 0.001	p < 0.001	p < 0.001	p < 0.001	p = 0.625	p < 0.074	p < 0.001
Coal-fired Power Plant Wastewater	2,580				p < 0.001	p < 0.001		p = 0.856	p < 0.001	p < 0.001	p < 0.001
Mine-Pool Discharge	7,946				p < 0.001	p < 0.001			p < 0.001	p < 0.001	p < 0.001

Abandoned Mine Discharge	580				$p < 0.001$	$p < 0.001$				$p = 0.006$	$p < 0.001$
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Table C.4. Median Br/Cl and associated p-values. Shaded boxes are non-significant p-values.

Water Type		Produced Water Conventional Gas Wells	Produced Water Oil Wells	Brine Treatment Plants	All Oil and Gas Produced Water	All Oil and Gas Produced Water and Brine Treatment Plants	Coal-fired Power Plant Wastewater	Mine-Pool Discharge	Abandoned Mine Discharge	All Coal-related Wastewaters	All Natural Waters
		Median Br/Cl ($\times 10^{-3}$)									
		9.59	10.2	18.4	10.1	11.0	9.52	6.98	3.48	4.89	12.6
	Median Br/Cl ($\times 10^{-3}$)	p-value, $\alpha = 0.05$									
Produced Water Marcellus Shale	10.2	p = 0.278	p = 0.640	p = 0.005	p = 0.498	p = 0.992	p = 0.148	p = 0.001	p < 0.001	p < 0.001	p < 0.001
Produced Water Conventional Gas Wells	9.59		p = 0.079	p < 0.001	p = 0.213	p = 0.007	p = 0.286	p = 0.002	p < 0.001	p < 0.001	p < 0.001
Produced Water Oil Wells	10.2			p < 0.001	p = 0.047	p = 0.939	p = 0.016	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Brine Treatment Plants	18.4				p < 0.001	p = 0.004	p < 0.001	p < 0.001	p < 0.001	p < 0.001	p < 0.001
Coal-fired Power Plant Wastewater	9.52				p < 0.001	p < 0.001		p = 0.405	p = 0.027	p = 0.081	p < 0.001
Mine-Pool Discharge	6.98				p < 0.001	p < 0.001			p < 0.001	p = 0.014	p < 0.001
Abandoned Mine Discharge	3.48				p < 0.001	p < 0.001				p = 0.076	p < 0.001

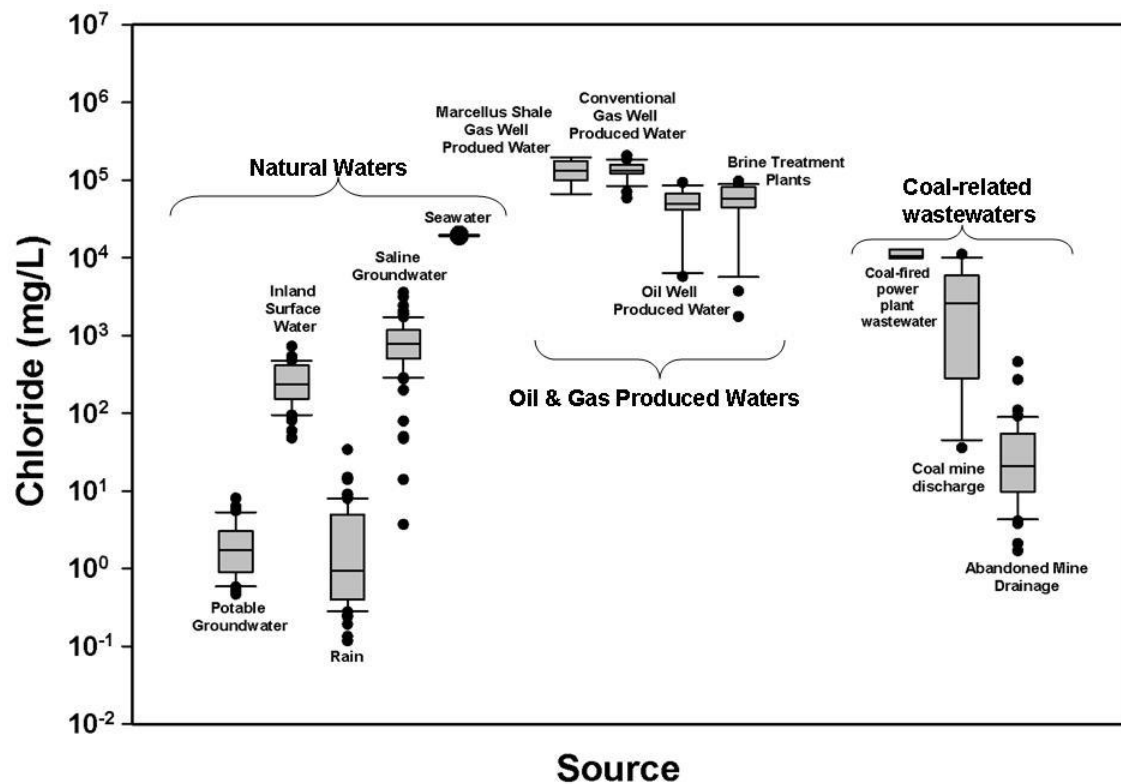


Figure C.1. Box plot of chloride (mg/L) for natural waters, oil and gas produced waters, and coal-related wastewaters. Solid line in box is median, box edges are 25% and 75% while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

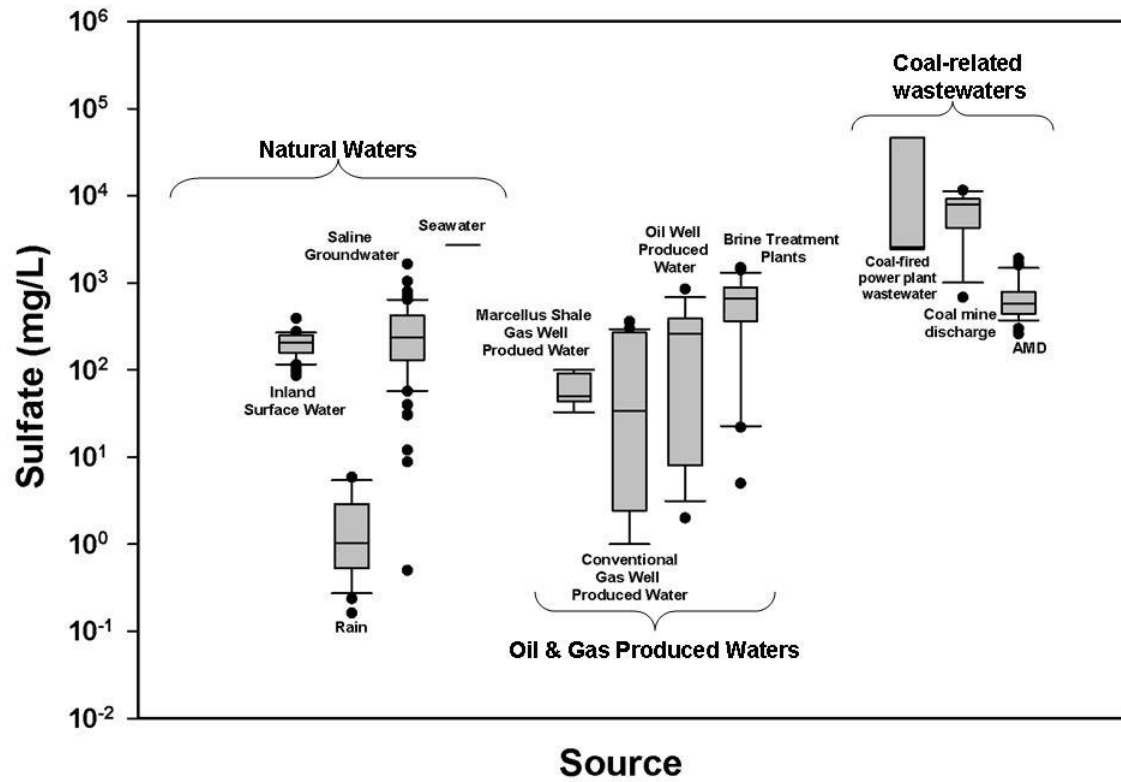


Figure C.2. Box plot of sulfate (mg/L) for natural waters, oil and gas produced waters, and coal-related wastewaters. Solid line in box is median, box edges are 25% and 75% while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

APPENDIX D. All river mile and tributary figures and tables for anion ratios and box plots.

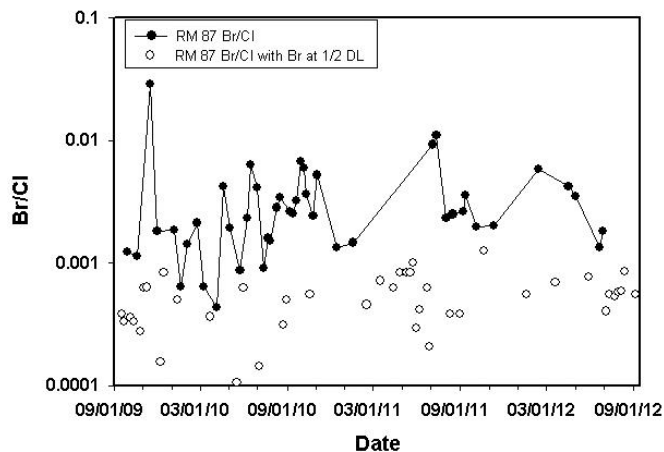


Figure D.1. RM 87 Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

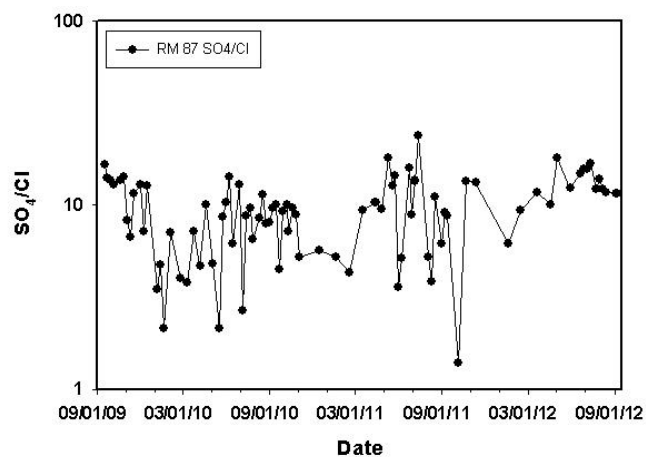


Figure D.2. RM 87 SO_4/Cl versus date.

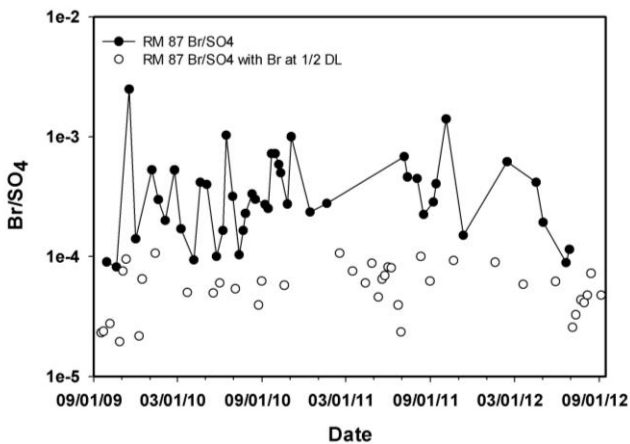


Figure D.3. RM 87 Br/SO_4 versus date. Bromide data below the detection limit are plotted as open circles.

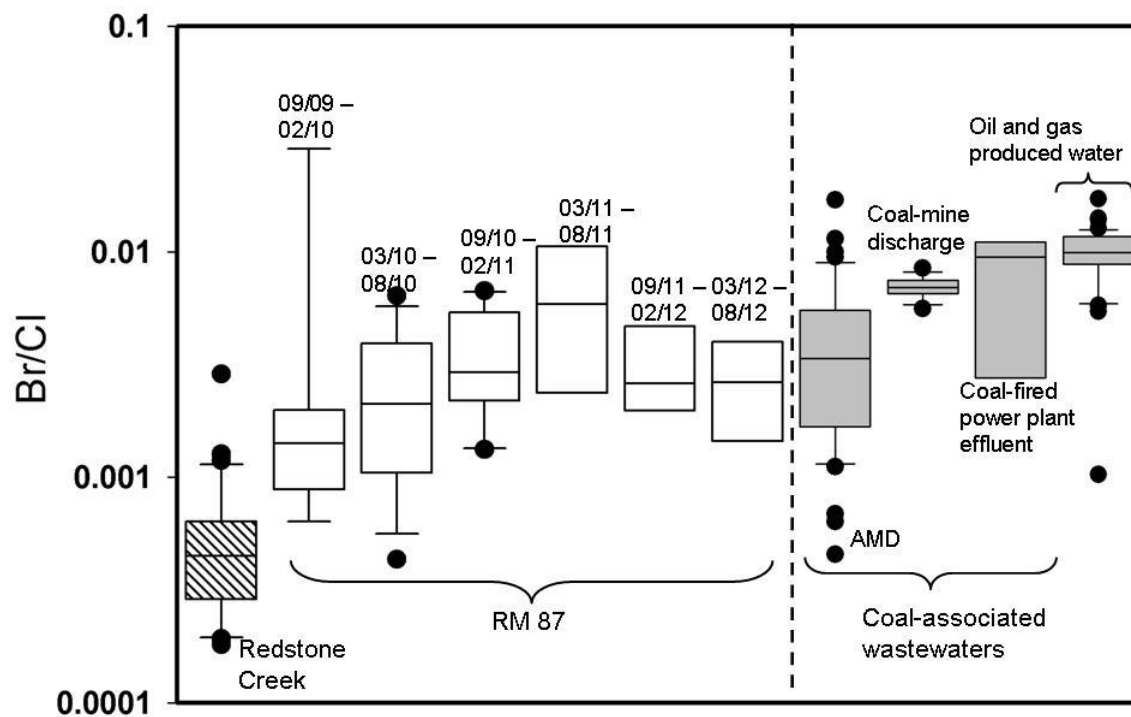


Figure D.4. Box plot of Br/Cl for RM 87 and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

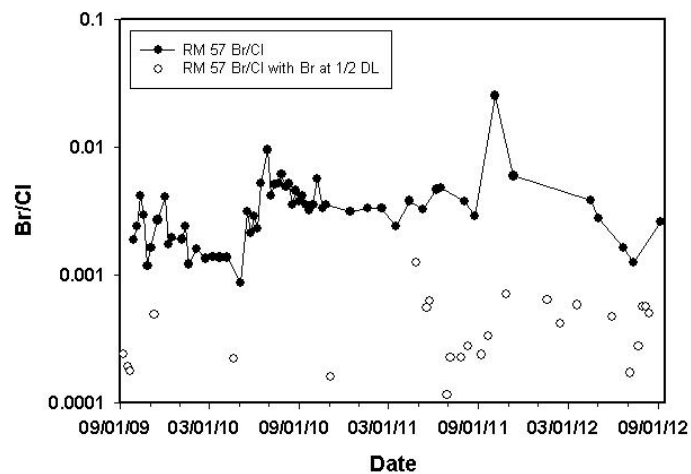


Figure D.5. RM 57 Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

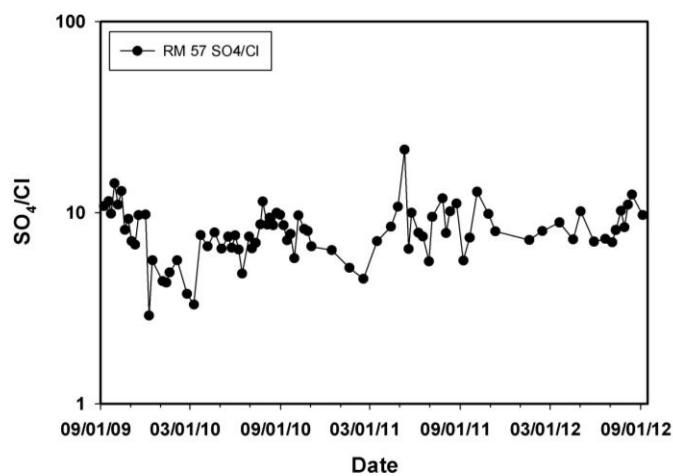


Figure D.6. RM 57 SO_4/Cl versus date.

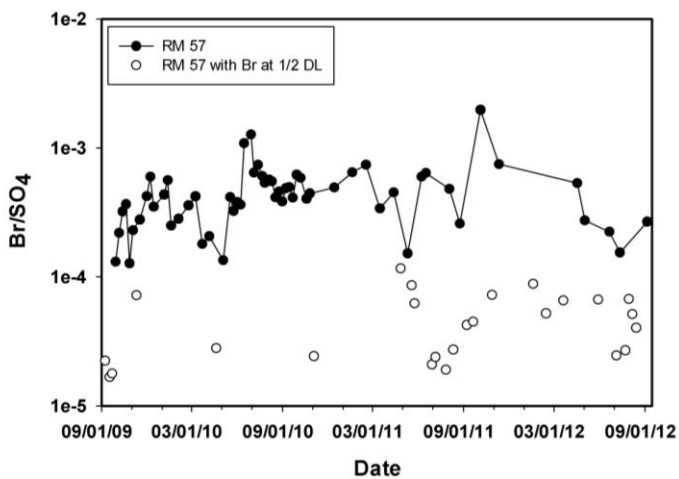


Figure D.7. RM 57 Br/SO_4 versus date. Bromide data below the detection limit are plotted as open circles.

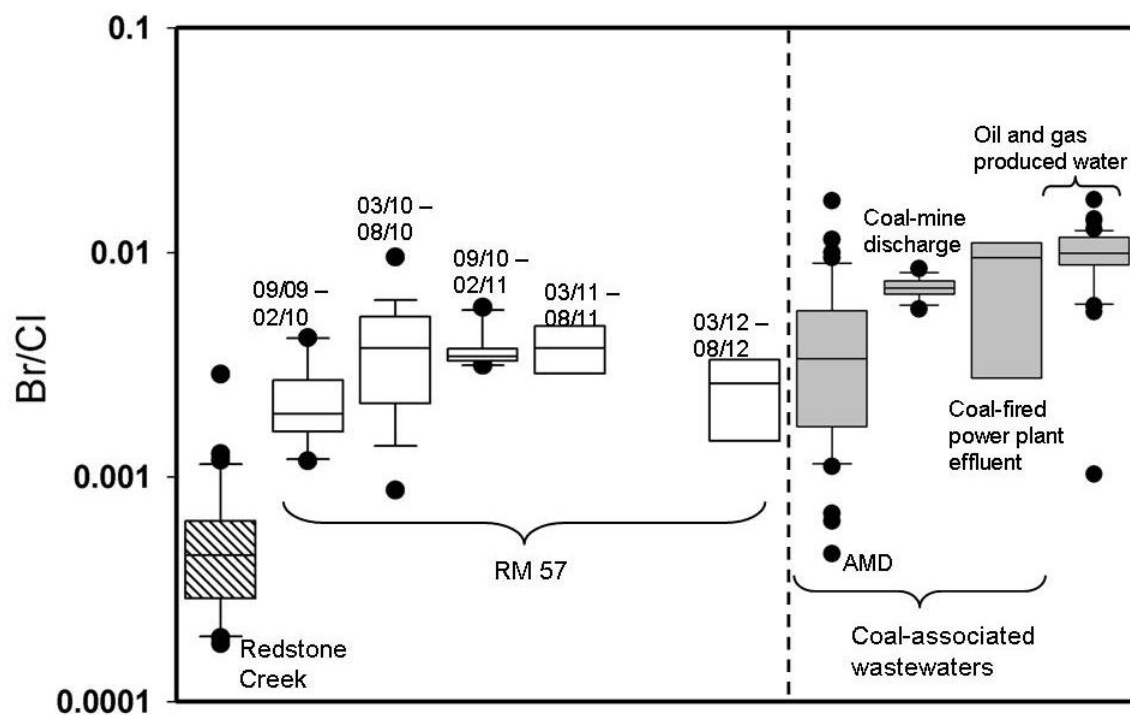


Figure D.8. Box plot of Br/Cl for RM 57 and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

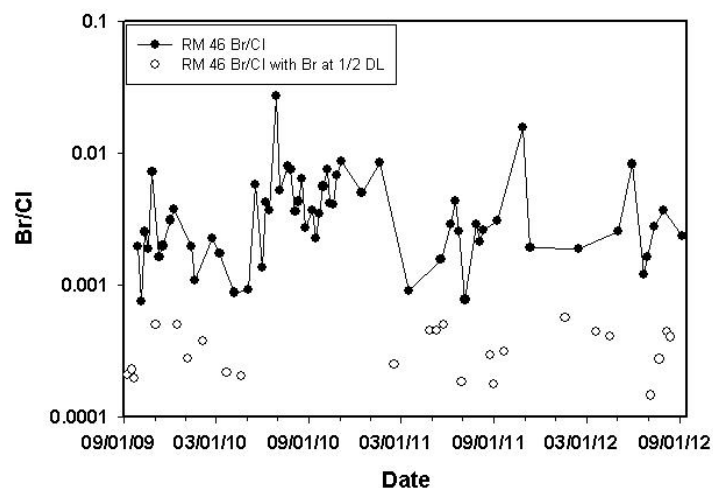


Figure D.9. RM 46 Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

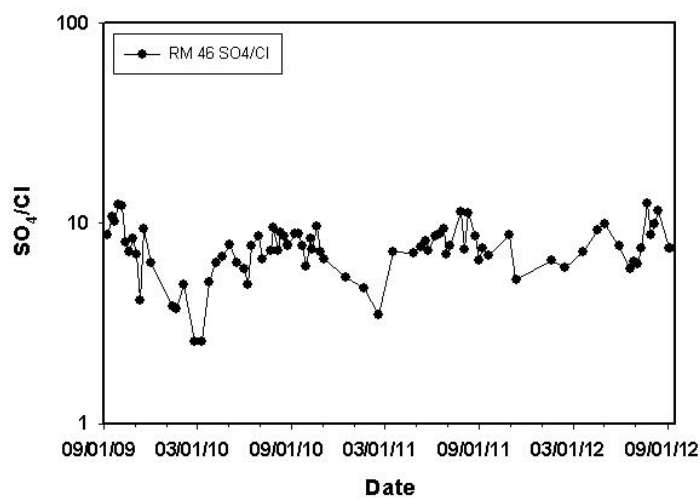


Figure D.10. RM 46 SO₄/Cl versus date.

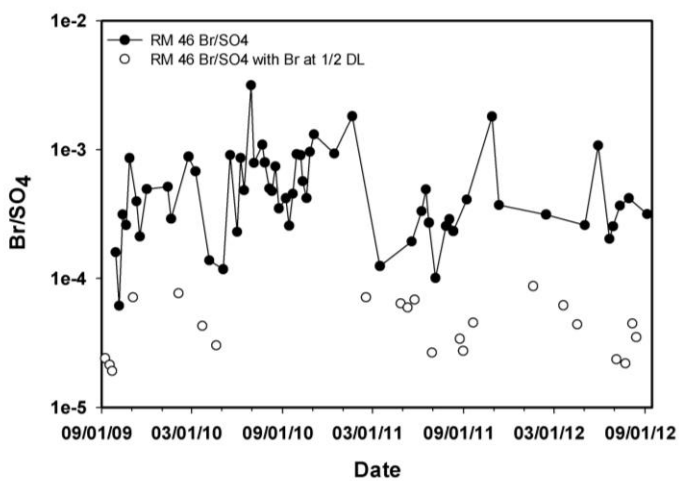


Figure D.11. RM 46 Br/SO₄ versus date. Bromide data below the detection limit are plotted as open circles.

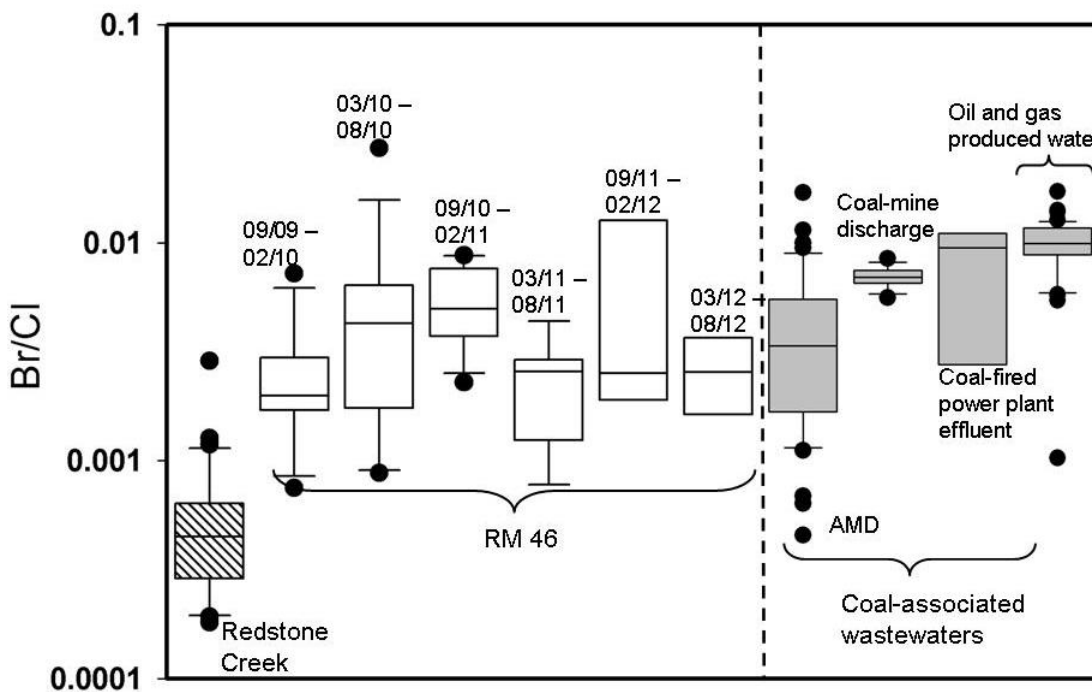


Figure D.12. Box plot of Br/Cl for RM 46 and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

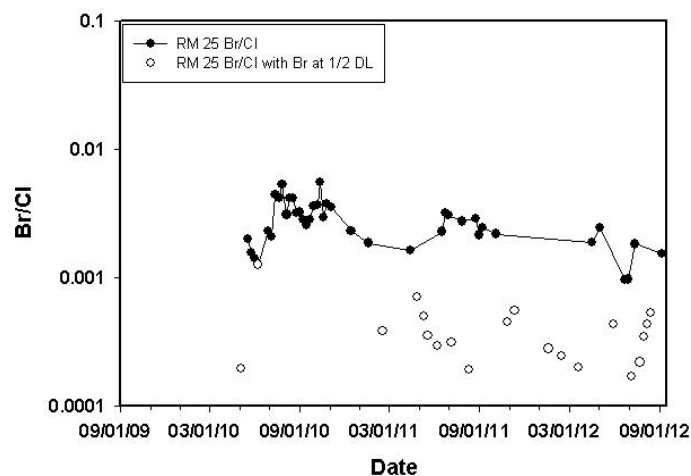


Figure D.13. RM 25 Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

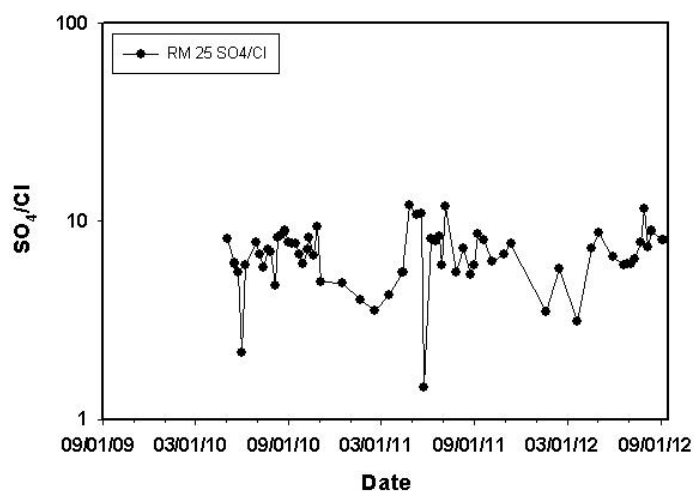


Figure D.14. RM 25 SO₄/Cl versus date.

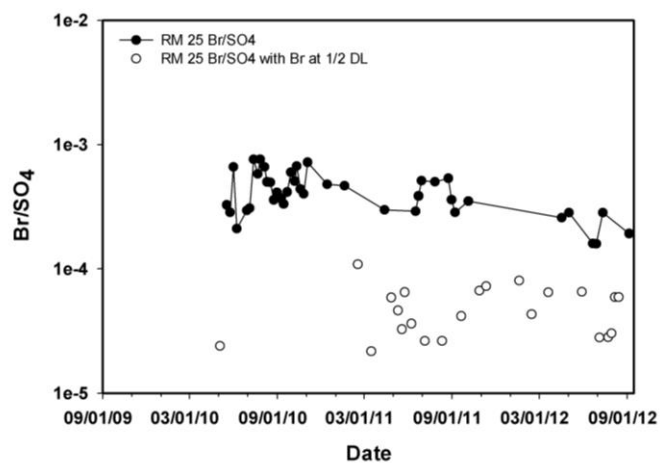


Figure D.15. RM 25 Br/SO₄ versus date. Bromide data below the detection limit are plotted as open circles.

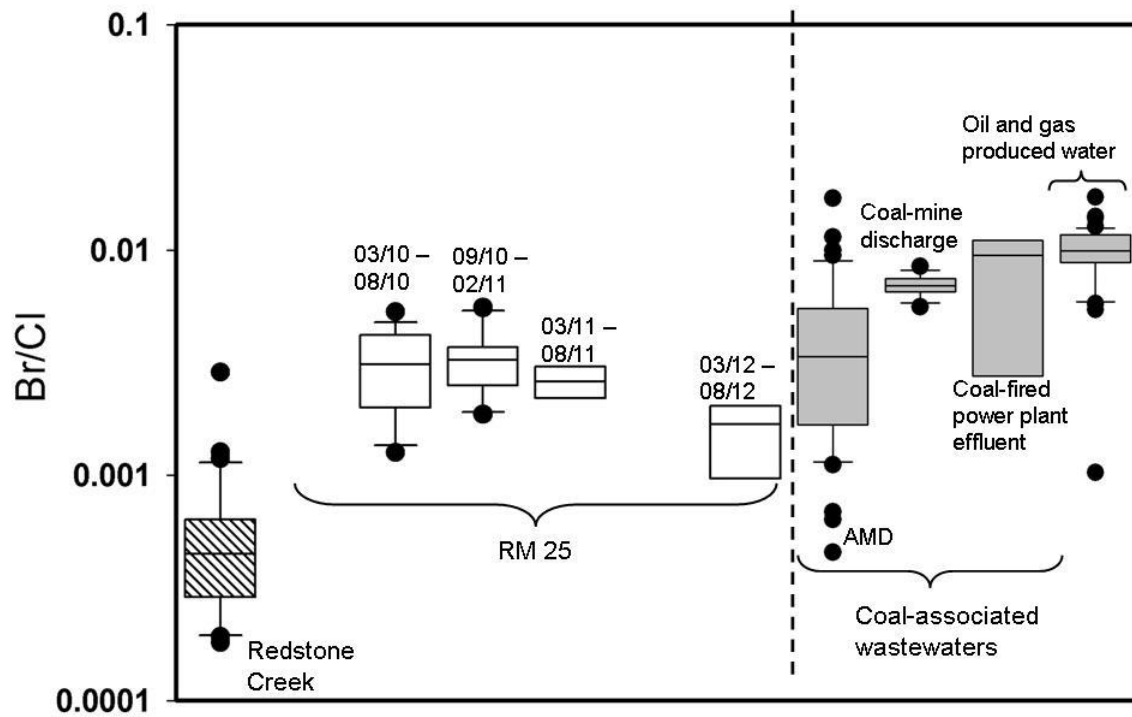


Figure D.16. Box plot of Br/Cl for RM 25 and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

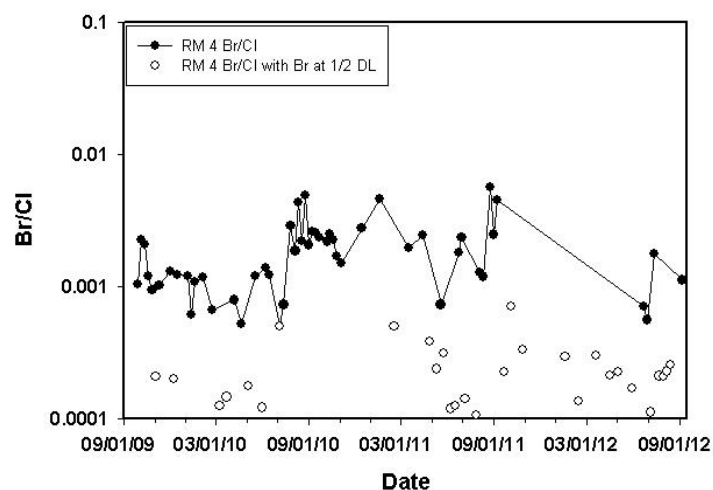


Figure D.17. RM 4 Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

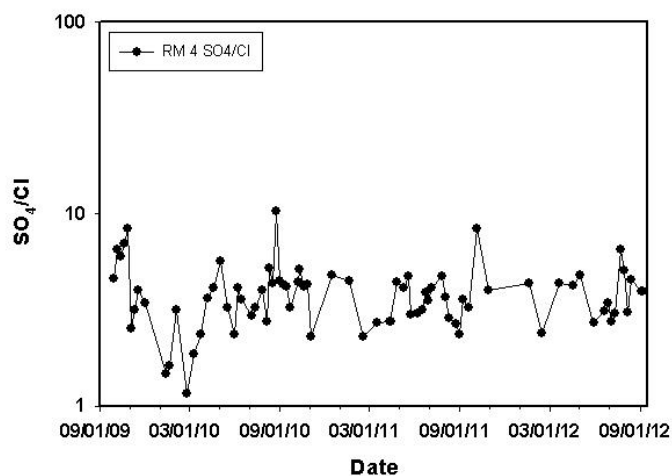


Figure D.18. RM 4 SO₄/Cl versus date.

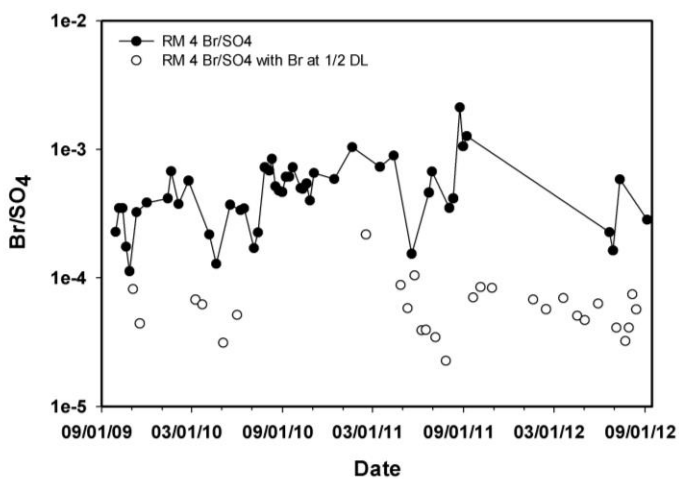


Figure D.19. RM 4 Br/SO₄ versus date. Bromide data below the detection limit are plotted as open circles.

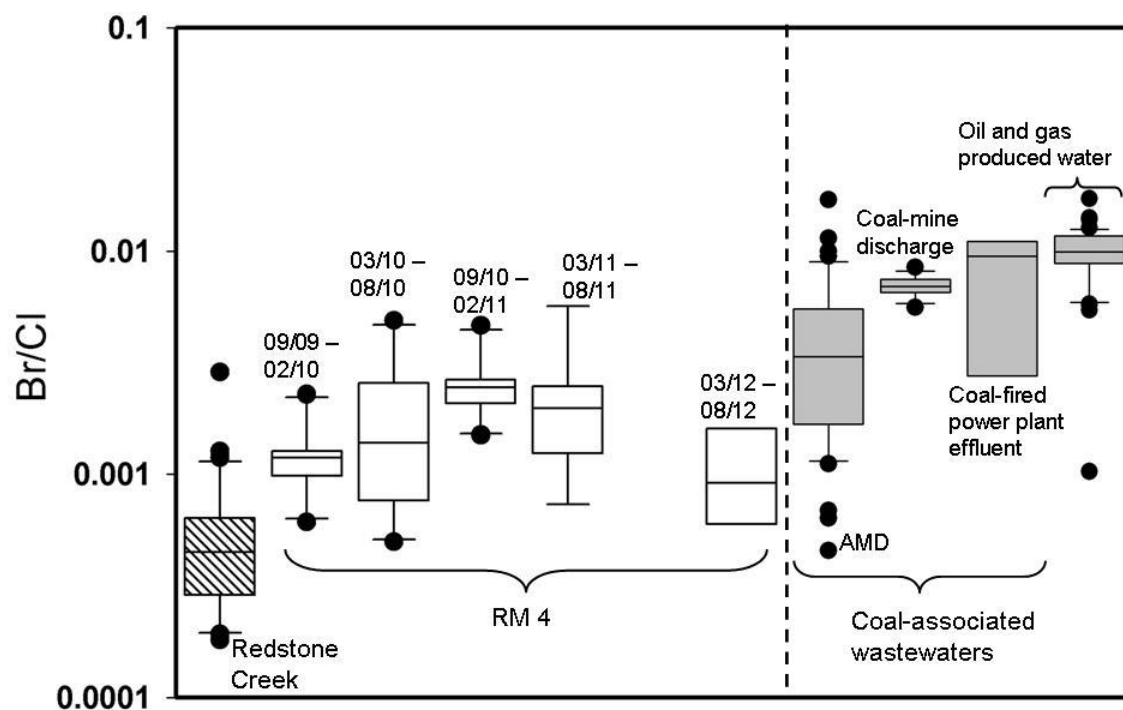


Figure D.20. Box plot of Br/Cl for RM 4 and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

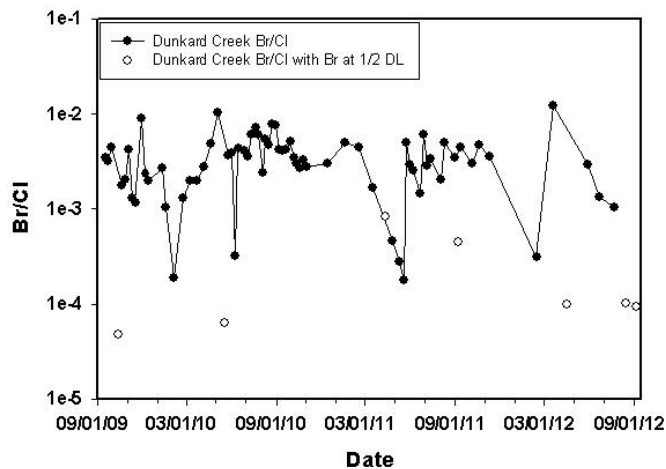


Figure D.21. Dunkard Creek Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

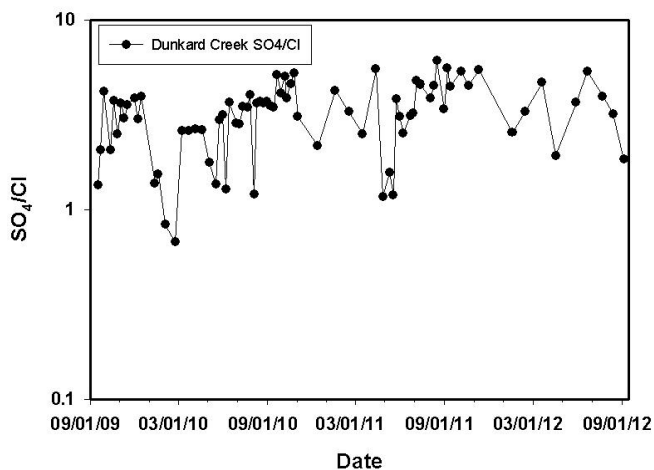


Figure D.22. Dunkard Creek SO₄/Cl versus date.

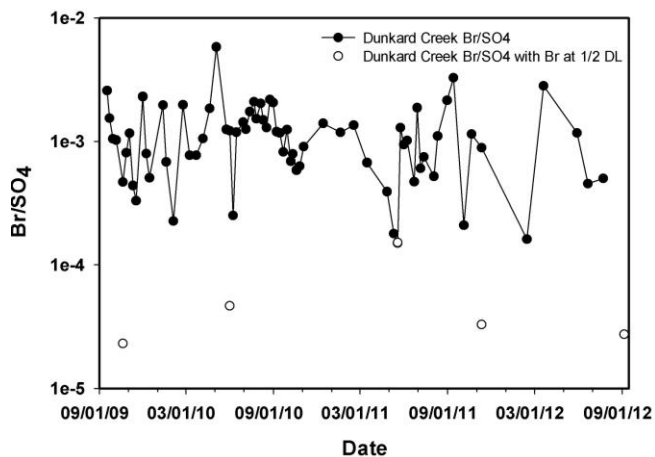


Figure D.23. Dunkard Creek Br/SO₄ versus date. Bromide data below the detection limit are plotted as open circles.

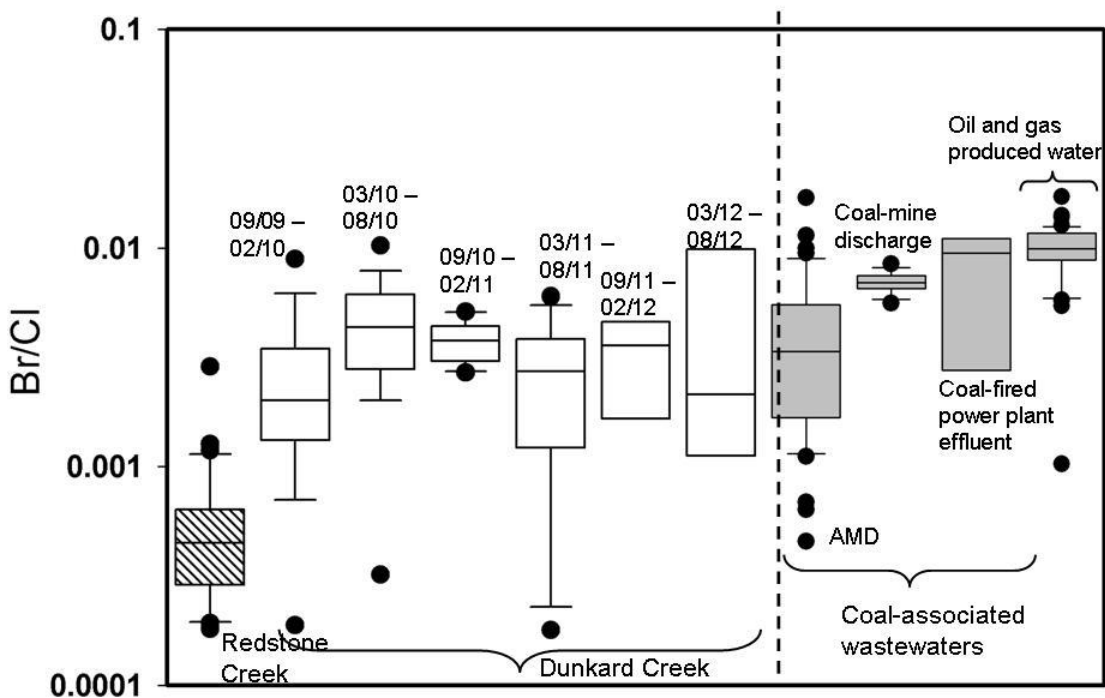


Figure D.24. Box plot of Br/Cl for Dunkard Creek and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

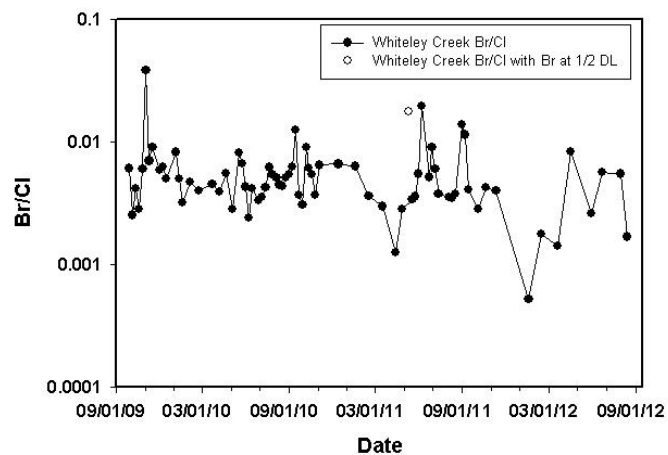


Figure D.25

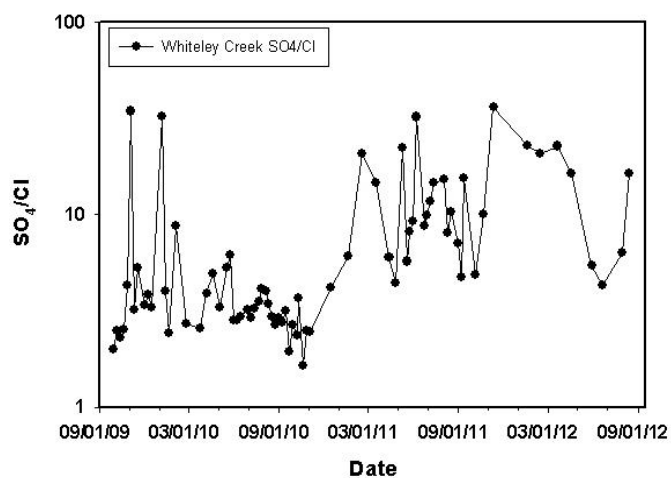


Figure D.26

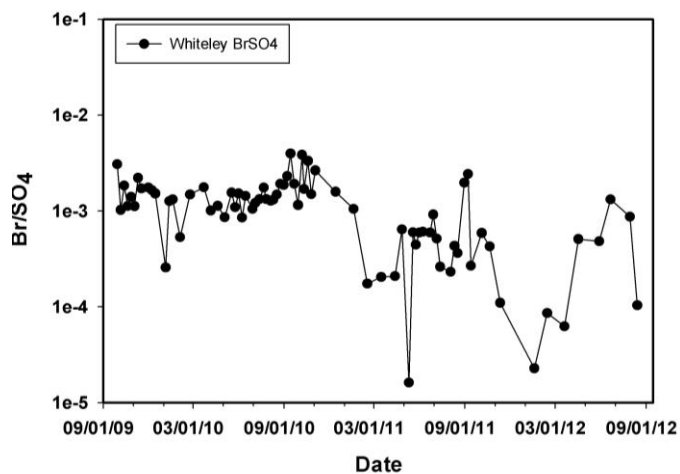


Figure D.27. Whiteley Creek Br/SO₄ versus date. Bromide data below the detection limit are plotted as open circles.

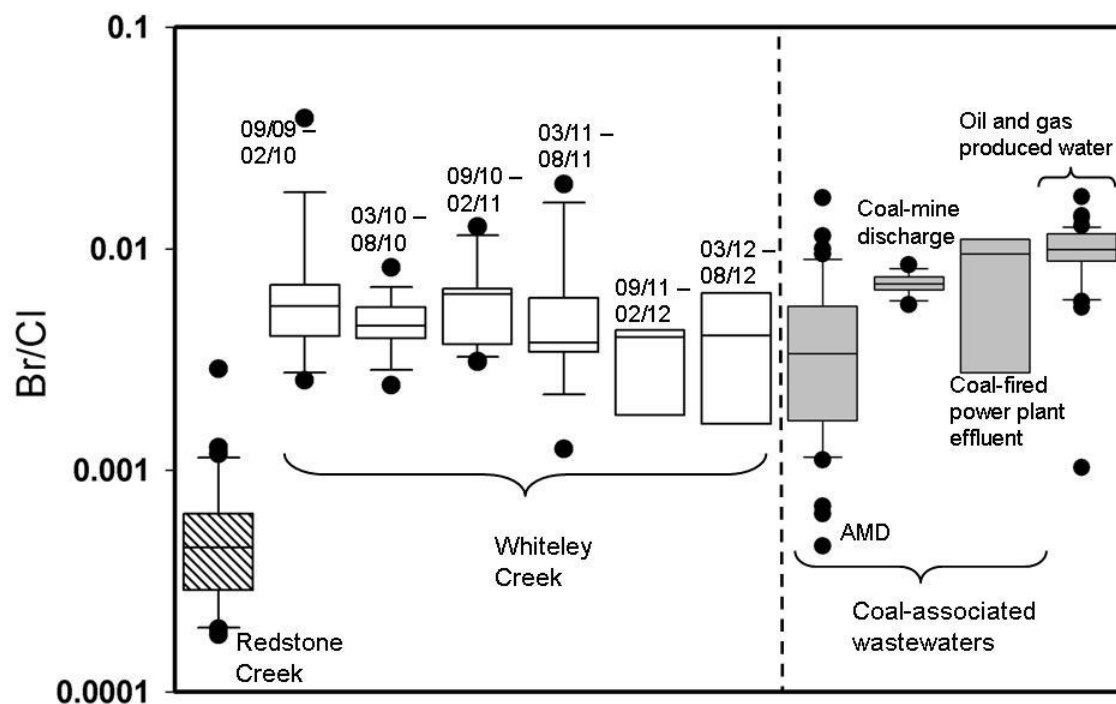


Figure D.28. Box plot of Br/Cl for Whiteley Creek and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

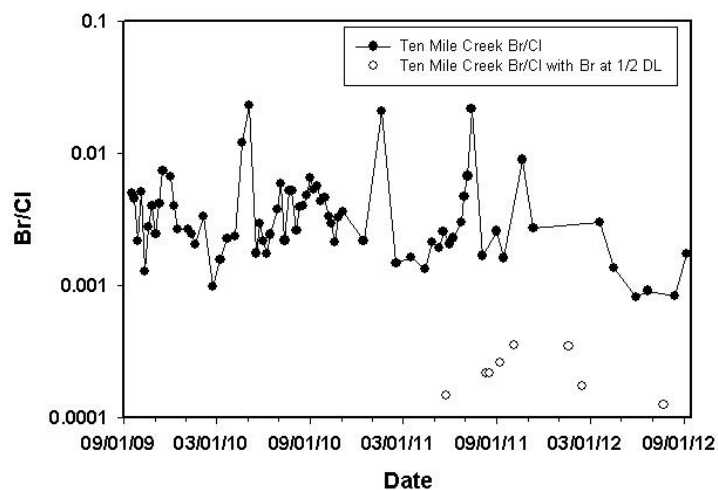


Figure D.29. Ten Mile Creek Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

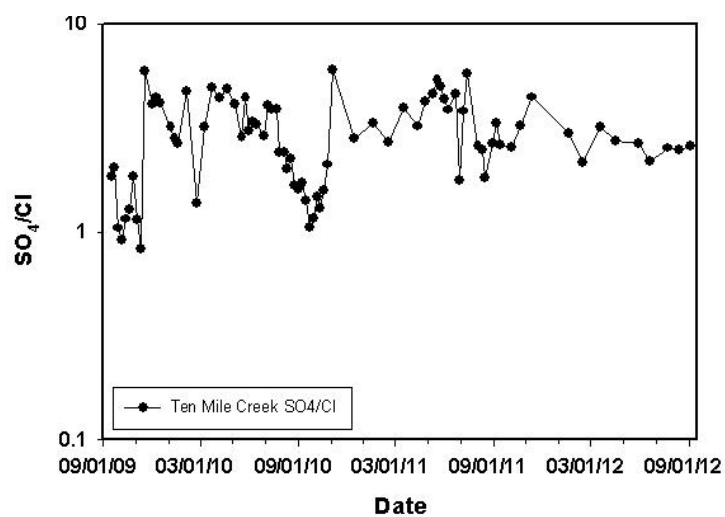


Figure D.30. Ten Mile Creek SO₄/Cl versus date.

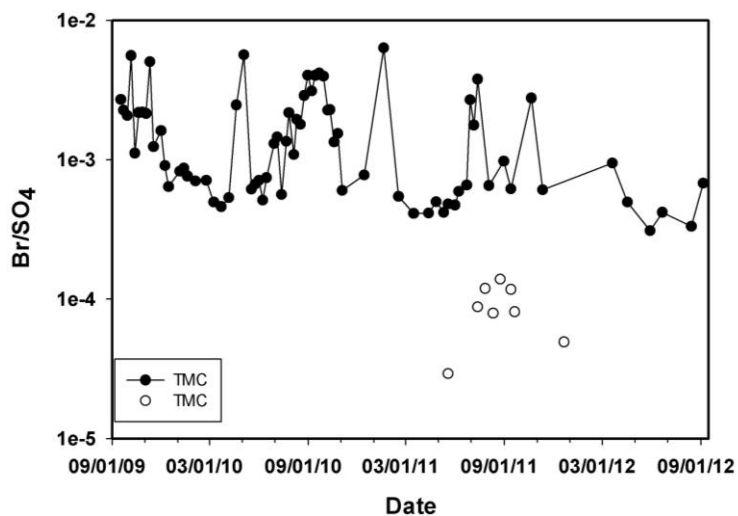


Figure D.31. Ten Mile Creek (TMC) Br/SO₄ versus date. Bromide data below the detection limit are plotted as open circles.

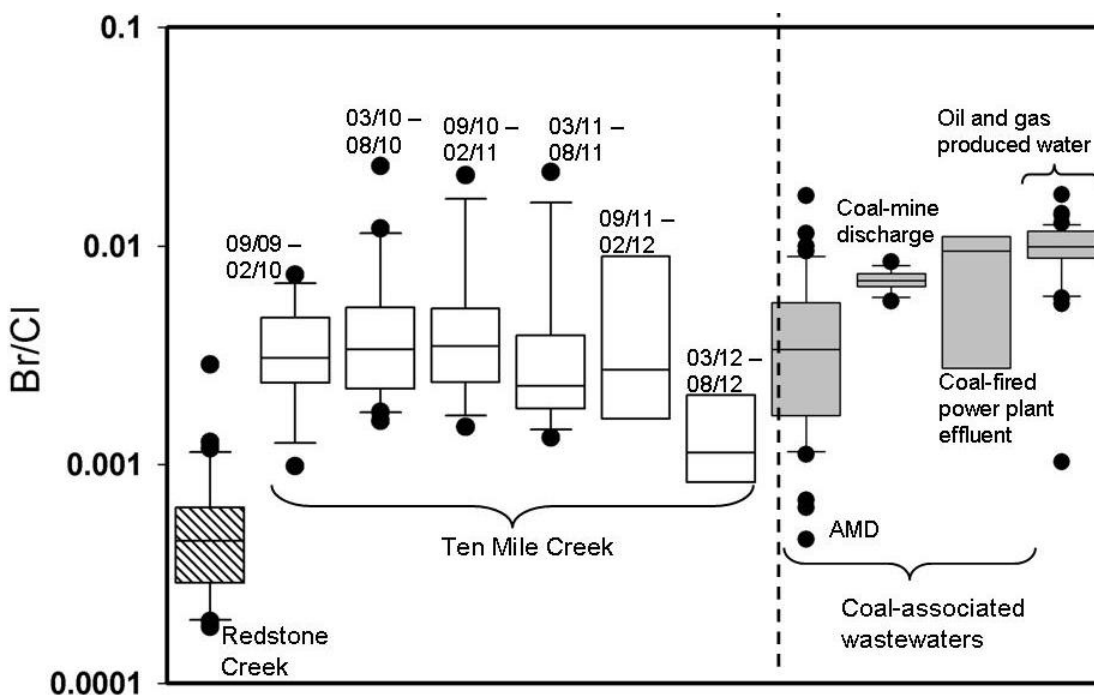


Figure D.32. Box plot of Br/Cl for Ten Mile Creek and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

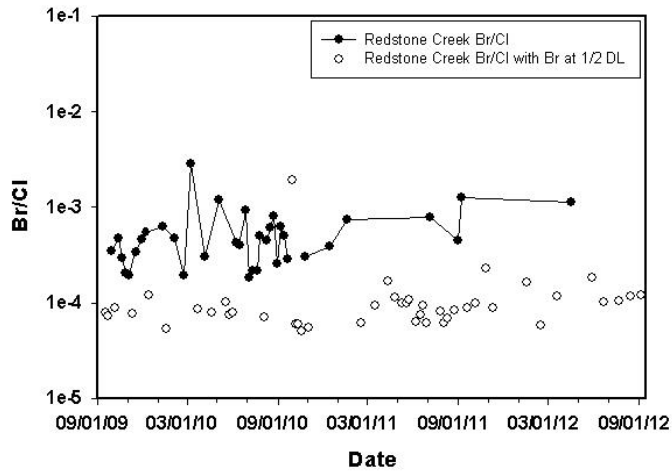


Figure D.33. Redstone Creek Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

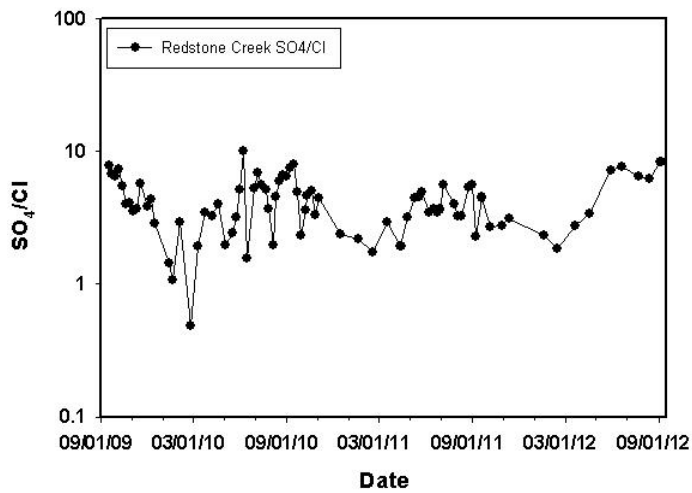


Figure D.34. Redstone Creek SO_4/Cl versus date.

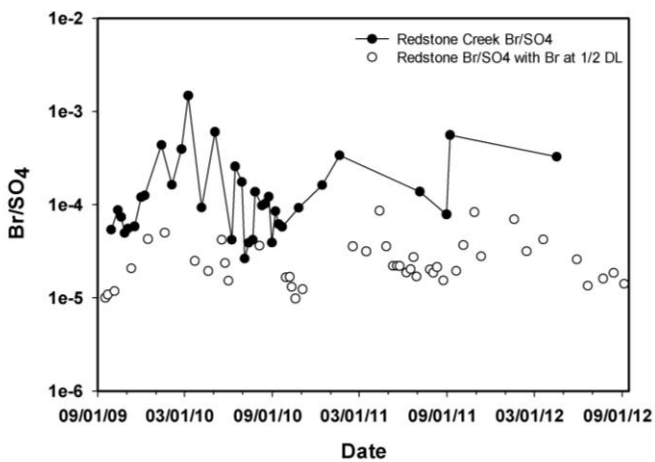


Figure D.35. Redstone Creek Br/ SO_4 versus date. Bromide data below the detection limit are plotted as open circles.

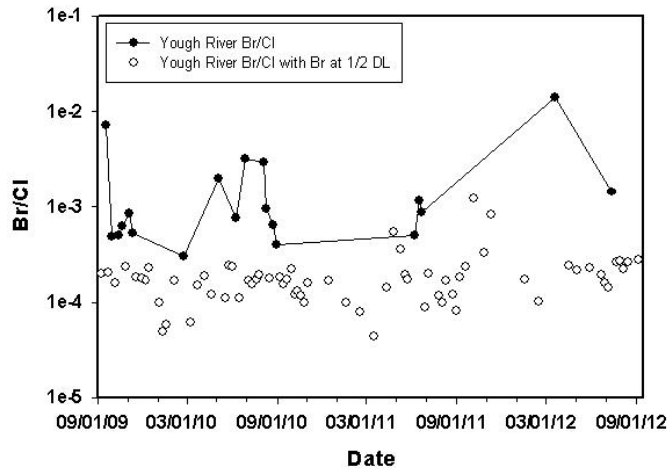


Figure D.36. Youghiogheny River Br/Cl versus date. Bromide data below the detection limit are plotted as open circles.

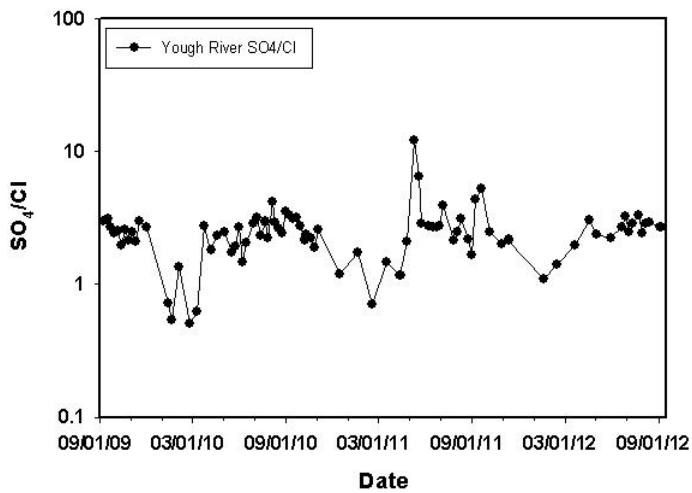


Figure D.37. Youghiogheny River SO_4/Cl versus date.

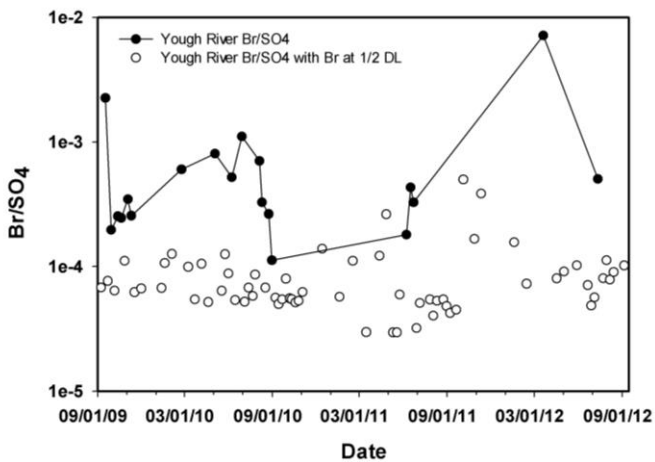


Figure D.38. Youghiogheny River Br/ SO_4 versus date. Bromide data below the detection limit are plotted as open circles.

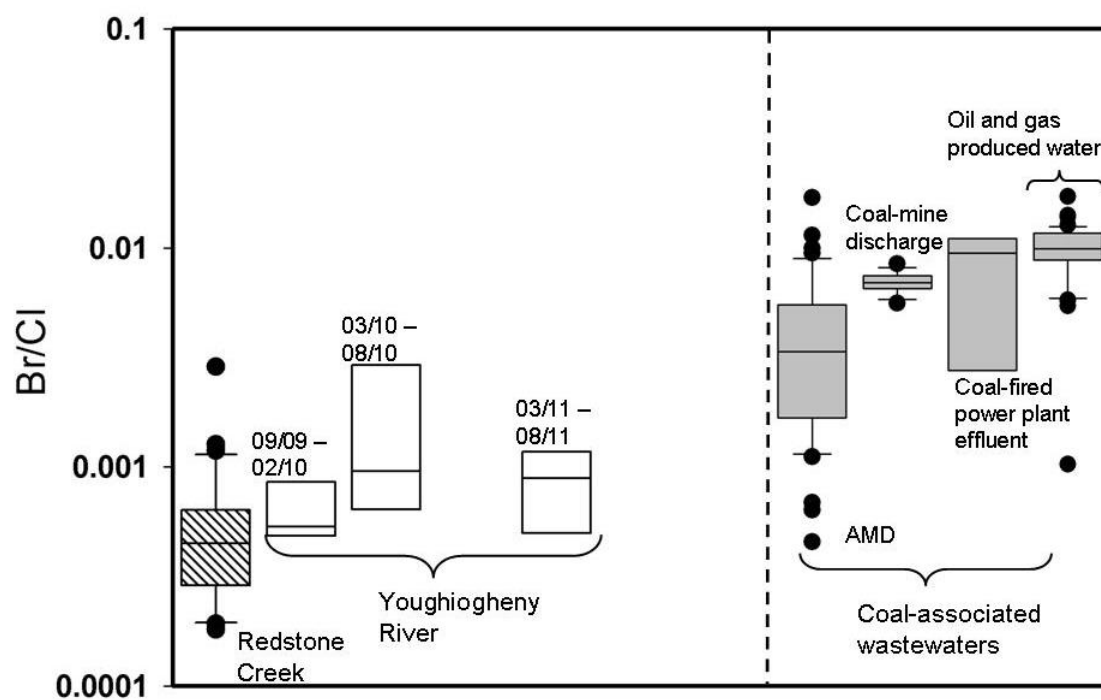


Figure D.39. Box plot of Br/Cl for Youghiogheny River and for fossil-fuel associated wastewaters. Box plot for Redstone Creek (representing background surface water conditions) is also shown. Solid line in box is median, box edges are 25% and 75%, while whiskers extend to 5% to 95%. Solid dots are outliers beyond the 5-95% range.

Table D.1. (a-f). Statistical analysis of median Br/Cl over 3 years for the 6 RMs. p-value for significance = 0.05, $\alpha = 0.05$ (one-tailed Mann-Whitney Rank Sum Test). Blank cell indicates insufficient data and therefore no analysis was performed. Statistically significant p-values are in shaded and in bold.

a)		Sept. 2009 – Aug. 2010 (Year 1)	Sept. 2010 – Aug. 2011 (Year 2)	Sept. 2011 – Sept. 2012 (Year 3)	Sept. 2009 – Feb. 2010 Year 1 (first half)	Mar. 2010 – Aug. 2010 Year 1 (second half)	Sept. 2010 – Feb. 2011 Year 2 (first half)
Sample Location	Br/Cl Median ($\times 10^{-3}$)	1.80	2.93	2.62	1.42	2.12	2.93
RM 87	Sept. 2009 – Aug. 2010		p = 0.014	p = 0.113			
	Sept. 2010 – Aug. 2011			p = 0.361			
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.303	p = 0.025

b)		Sept. 2009 – Aug. 2010 (Year 1)	Sept. 2010 – Aug. 2011 (Year 2)	Sept. 2011 – Sept. 2012 (Year 3)	Sept. 2009 – Feb. 2010 Year 1 (first half)	Mar. 2010 – Aug. 2010 Year 1 (second half)	Sept. 2010 – Feb. 2011 Year 2 (first half)	Mar. 2011 – Aug. 2011 Year 2 (second half)
RM 71	Br/Cl Median (x10 ⁻³)	2.63	2.99	2.36	1.43	3.09	3.14	2.79
	Sept. 2009 – Aug. 2010		p = 0.107	p = 0.774				
	Sept. 2010 – Aug. 2011			p = 0.174				
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.010	p = 0.009	p = 0.038
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.605
	Sept. 2010 – Feb. 2011 Year 2 (first half)							p = 0.358

c)		Sept. 2009 – Aug. 2010 (Year 1)	Sept. 2010 – Aug. 2011 (Year 2)	Sept. 2011 – Sept. 2012 (Year 3)	Sept. 2009 – Feb. 2010 Year 1 (first half)	Mar. 2010 – Aug. 2010 Year 1 (second half)	Sept. 2010 – Feb. 2011 Year 2 (first half)	Mar. 2011 – Aug. 2011 Year 2 (second half)	Sept. 2011 – Feb. 2012 Year 3 (first half)	Mar. 2012 – Sept. 2012 Year 3 (second half)
RM 57	Br/Cl Median ($\times 10^{-3}$)	2.56	3.57	2.80	1.91	3.76	3.45	3.76		2.61
	Sept. 2009 – Aug. 2010		p = 0.062	p = 0.568						
	Sept. 2010 – Aug. 2011			p = 0.525						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.015	p = 0.001	p = 0.961		
	Mar. 2011 – Aug. 2011 Year 2 (second half)									p = 0.106

d)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010 Year 1 (first half)	Mar. 2010 – Aug. 2010 Year 1 (second half)	Sept. 2010 – Feb. 2011 Year 2 (first half)	Mar. 2011 – Aug. 2011 Year 2 (second half)
RM 46	Br/Cl Median ($\times 10^{-3}$)	2.72	3.62	2.56	1.99	4.28	5.00	2.56
	Sept. 2009 – Aug. 2010		p = 0.349	p = 0.949				
	Sept. 2010 – Aug. 2011			p = 0.312				
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.075	p = 0.001	
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.056

e)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010 Year 1 (first half)	Mar. 2010 – Aug. 2010 Year 1 (second half)	Sept. 2010 – Feb. 2011 Year 2 (first half)	Mar. 2011 – Aug. 2011 Year 2 (second half)	Sept. 2011 – Feb. 2012 Year 3 (first half)	Mar. 2012 – Sept. 2012 Year 3 (second half)
RM 25	Br/Cl Median ($\times 10^{-3}$)	3.12	2.86	1.83	---	3.12	3.26	2.61		1.69
	Sept. 2009 – Aug. 2010		p = 0.899	p = 0.020						
	Sept. 2010 – Aug. 2011			p = 0.002						
	Sept. 2009 – Feb. 2010 Year 1 (first half)						p = 0.677	p = 0.458		p = 0.018
	Mar. 2011 – Aug. 2011 Year 2 (second half)									p = 0.020

f)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010 Year 1 (first half)	Mar. 2010 – Aug. 2010 Year 1 (second half)	Sept. 2010 – Feb. 2011 Year 2 (first half)	Mar. 2011 – Aug. 2011 Year 2 (second half)
RM 4	Br/Cl Median ($\times 10^{-3}$)	1.12	1.19	1.38	2.45	1.98	2.37	1.22
	Sept. 2009 – Aug. 2010		p = 0.002	p = 0.786				
	Sept. 2010 – Aug. 2011			p = 0.088				
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.305	p < 0.001	
	Mar. Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.442

Table D.2 (a-f). Statistical analysis of median SO₄/Cl over 3 years for the 6 RMs. p-value for significance = 0.05, α = 0.05 (one-tailed Mann-Whitney Rank Sum Test). Blank cell indicates insufficient data and therefore no analysis was performed. Statistically significant p-values are in shaded and in bold.

a)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010	Mar. 2010 – Aug. 2010	Sept. 2010 – Feb. 2011	Mar. 2011 – Aug. 2011	Sept. 2011 – Feb. 2012	Mar. 2012 – Sept. 2012
RM 87	SO ₄ /Cl Median	8.36	9.36	12.29						
	Sept. 2009 – Aug. 2010		p = 0.750	p = 0.006						
	Sept. 2010 – Aug. 2011			p = 0.016						
	Sept. 2009 – Feb. 2010									
	Mar. 2010 – Aug. 2010.									
	Sept. 2010 – Feb. 2011									
	Mar. 2011 – Aug. 2011									
	Sept. 2011 – Feb. 2012									

b)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010	Mar. 2010 – Aug. 2010	Sept. 2010 – Feb. 2011	Mar. 2011 – Aug. 2011	Sept. 2011 – Feb. 2012	Mar. 2012 – Sept. 2012
RM 71	SO ₄ /Cl Median	9.00	8.29	10.55	7.96	9.00	7.76	9.00	8.00	11.35
	Sept. 2009 – Aug. 2010		p = 0.494	p = 0.037						
	Sept. 2010 – Aug. 2011			p = 0.018						
	Sept. 2009 – Feb. 2010					p = 0.211	p = 0.878		p = 0.770	
	Mar. 2010 – Aug. 2010							p = 0.706		p < 0.001
	Sept. 2010 – Feb. 2011									
	Mar. 2011 – Aug. 2011									
	Sept. 2011 – Feb. 2012									

c)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010	Mar. 2010 – Aug. 2010	Sept. 2010 – Feb. 2011	Mar. 2011 – Aug. 2011	Sept. 2011 – Feb. 2012	Mar. 2012 – Sept. 2012
RM 57	SO ₄ /Cl Median	7.60	7.85	8.120						
	Sept. 2009 – Aug. 2010		p = 0.549	p = 0.159						
	Sept. 2010 – Aug. 2011			p = 0.381						
	Sept. 2009 – Feb. 2010									
	Mar. 2010 – Aug. 2010.									
	Sept. 2010 – Feb. 2011									
	Mar. 2011 – Aug. 2011									
	Sept. 2011 – Feb. 2012									

d)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010	Mar. 2010 – Aug. 2010	Sept. 2010 – Feb. 2011	Mar. 2011 – Aug. 2011	Sept. 2011 – Feb. 2012	Mar. 2012 – Sept. 2012
RM 46	SO ₄ /Cl Median	7.26	7.64	7.55						
	Sept. 2009 – Aug. 2010		p = 0.357	p = 0.372						
	Sept. 2010 – Aug. 2011			p = 1.00						
	Sept. 2009 – Feb. 2010									
	Mar. 2010 – Aug. 2010.									
	Sept. 2010 – Feb. 2011									
	Mar. 2011 – Aug. 2011									
	Sept. 2011 – Feb. 2012									

e)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010	Mar. 2010 – Aug. 2010	Sept. 2010 – Feb. 2011	Mar. 2011 – Aug. 2011	Sept. 2011 – Feb. 2012	Mar. 2012 – Sept. 2012
RM 25	SO ₄ /Cl Median	7.03	6.80	6.81						
	Sept. 2009 – Aug. 2010		p = 0.927	p = 0.862						
	Sept. 2010 – Aug. 2011			p = 0.894						
	Sept. 2009 – Feb. 2010									
	Mar. 2010 – Aug. 2010.									
	Sept. 2010 – Feb. 2011									
	Mar. 2011 – Aug. 2011									
	Sept. 2011 – Feb. 2012									

f)		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010	Mar. 2010 – Aug. 2010	Sept. 2010 – Feb. 2011	Mar. 2011 – Aug. 2011	Sept. 2011 – Feb. 2012	Mar. 2012 – Sept. 2012
RM 4	SO ₄ /Cl Median	3.61	3.90	3.96						
	Sept. 2009 – Aug. 2010		p = 0.994	p = 0.652						
	Sept. 2010 – Aug. 2011			p = 0.518						
	Sept. 2009 – Feb. 2010									
	Mar. 2010 – Aug. 2010.									
	Sept. 2010 – Feb. 2011									
	Mar. 2011 – Aug. 2011									
	Sept. 2011 – Feb. 2012									

Table D.3. Statistical analysis of median Br/Cl over 3 years for the 5 tributaries. p-value for significance = 0.05, $\alpha = 0.05$ (one-tailed Mann Whitney Rank Sum Test).

Sample Location		Sept. 2009 – Aug. 2010 (Year 1)	Sept. 2010 – Aug. 2011 (Year 2)	Sept. 2011 – Sept. 2012 (Year 3)	Sept. 2009 – Feb. 2010 Year 1 (first half)	Mar. 2010 – Aug. 2010 Year 1 (second half)	Sept. 2010 – Feb. 2011 Year 2 (first half)	Mar. 2011 – Aug. 2011 Year 2 (second half)	Sept. 2011 – Feb. 2012 Year 3 (first half)	Mar. 2012 – Sept. 2012 Year 3 (second half)
Dunkard Creek	Br/Cl Median ($\times 10^{-3}$)	3.50	3.19	3.00	2.02	4.34	3.77	2.73	3.60	
	Sept. 2009 – Aug. 2010		p = 0.660	p = 0.709						
	Sept. 2010 – Aug. 2011			p = 0.925						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.006	p = 0.012		p = 0.256	
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.017		
	Sept. 2010 – Feb. 2011 Year 2 (first half)								p = 0.792	
Whiteley Creek	Br/Cl Median ($\times 10^{-3}$)	5.03	5.20	4.00	5.52	4.51	6.26	3.77	4.00	4.08
	Sept. 2009 – Aug. 2010		p = 1.00	p = 0.663						
	Sept. 2010 – Aug. 2011			p = 0.126						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.240	p = 0.626		p = 0.066	
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.555		p = 0.726
	Sept. 2010 – Feb. 2011 Year 2 (first half)								p = 0.118	
	Mar. 2011 – Aug. 2011 Year 2 (second half)									p = 0.508

	2 (second half)									
Ten Mile Creek	Br/Cl Median (x10 ⁻³)	3.15	2.98	1.62	3.08	3.37	3.49	2.30		
	Sept. 2009 – Aug. 2010		p = 0.514	p = 0.016						
	Sept. 2010 – Aug. 2011			p = 0.026						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.849	p = 0.512			
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.179		
Redstone Creek	Br/Cl Median (x10 ⁻³)	0.423	0.447	1.20	0.348	0.437				
	Sept. 2009 – Aug. 2010		p = 0.785	---						
	Sept. 2010 – Aug. 2011			---						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.366				
Youghiogheny River	Br/Cl Median (x10 ⁻³)	0.707	0.889	0.773	0.534	0.962				
	Sept. 2009 – Aug. 2010		p = 0.994	p = 0.131						
	Sept. 2010 – Aug. 2011			p = 0.200						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.209				

Table D.4. Statistical analysis of median SO₄Cl over 3 years for the 5 tributaries. p-value for significance = 0.05, α = 0.05 (one-tailed Mann-Whitney Rank Sum Test).

Sample Location		Sept. 2009 – Aug. 2010	Sept. 2010 – Aug. 2011	Sept. 2011 – Sept. 2012	Sept. 2009 – Feb. 2010 Year 1 (first half)	Mar. 2010 – Aug. 2010 Year 1 (second half)	Sept. 2010 – Feb. 2011 Year 2 (first half)	Mar. 2011 – Aug. 2011 Year 2 (second half)	Sept. 2011 – Feb. 2012 Year 3 (first half)	Mar. 2012 – Sept. 2012 Year 3 (second half)
	SO ₄ /Cl Median	2.90	3.68	4.20	2.74	2.90	3.98	3.29	4.50	3.66
Dunkard Creek	Sept. 2009 – Aug. 2010		p = 0.004	p = 0.003						
	Sept. 2010 – Aug. 2011			p = 0.401						
	Sept. 2009 – Feb. 2010 Year 1 (first half)				p = 0.738	p = 0.07			p = 0.006	
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.272		p = 0.158
	Sept. 2010 – Feb. 2011 Year 2 (first half)									
	Mar. 2011 – Aug. 2011 Year 2 (second half)									
	Sept. 2011 – Feb. 2012 Year 3 (first half)									
Whiteley Creek	SO ₄ /Cl Median	3.30	6.56	15.45	3.35	3.24	2.70	9.57	15.45	11.33
	Sept. 2009 – Aug. 2010		p = 0.016	p < 0.001						
	Sept. 2010 – Aug. 2011			p = 0.032						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.934	p = 0.296		p = 0.008	
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p < 0.001		p < 0.001

	Sept. 2010 – Feb. 2011 Year 2 (first half)								p = 0.004	
	Mar. 2011 – Aug. 2011 Year 2 (second half)									p = 0.971
	Sept. 2011 – Feb. 2012 Year 3 (first half)									
Ten Mile Creek	SO ₄ /Cl Median	2.88	2.76	2.64	1.94	3.23	1.65	3.91	2.97	2.58
	Sept. 2009 – Aug. 2010		p = 0.072	p = 0.959						
	Sept. 2010 – Aug. 2011			p = 0.821						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.068	p = 0.916		p = 0.215	
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.233		p = 0.143
	Sept. 2010 – Feb. 2011 Year 2 (first half)								p = 0.057	
	Mar. 2011 – Aug. 2011 Year 2 (second half)									
	Sept. 2011 – Feb. 2012 Year 3 (first half)									p = 0.959
Redstone Creek	SO ₄ /Cl Median	4.04	3.69	3.28	4.02	4.32	4.04	3.69	2.72	6.53
	Sept. 2009 – Aug. 2010		p = 0.538	p = 0.841						
	Sept. 2010 – Aug. 2011			p = 0.883						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.915	p = 0.947		p = 0.075	
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.535		p = 0.092
	Sept. 2010 – Feb. 2011 Year 2 (first half)								p = 0.163	
	Mar. 2011 – Aug. 2011 Year 2 (second half)									p = 0.049
	Sept. 2011 – Feb.									p =

	2012 Year 3 (first half)									0.004
Youghiogheny River	SO ₄ /Cl Median	2.46	2.53	2.61	2.46	2.44	2.32	2.71	2.17	2.72
	Sept. 2009 – Aug. 2010		p = 0.482	p = 0.203						
	Sept. 2010 – Aug. 2011			p = 0.579						
	Sept. 2009 – Feb. 2010 Year 1 (first half)					p = 0.474	p = 0.693		p = 0.815	
	Mar. 2010 – Aug. 2010 Year 1 (second half)							p = 0.610		p = 0.204
	Sept. 2010 – Feb. 2011 Year 2 (first half)								p = 1.00	
	Mar. 2011 – Aug. 2011 Year 2 (second half)									p = 0.584
	Sept. 2011 – Feb. 2012 Year 3 (first half)									

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