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Sources Contributing Inorganic Species to Drinking Water Intakes During Low Flow Conditions on the Allegheny River in Western Pennsylvania

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DISCLAIMER

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PREFACE

The U.S. Environmental Protection Agency (EPA) is conducting a study of the potential impacts of hydraulic fracturing for oil and gas on drinking water resources. This study was initiated in Fiscal Year 2010 when Congress urged the EPA to examine the relationship between hydraulic fracturing and drinking water resources in the United States. In response, EPA developed a research plan (*Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources*) that was reviewed by the Agency's Science Advisory Board (SAB) and issued in 2011. A progress report on the study (*Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources: Progress Report)*, detailing the EPA's research approaches and next steps, was released in late 2012 and was followed by a consultation with individual experts convened under the auspices of the SAB.

The EPA's study includes the development of several research projects, extensive review of the literature and technical input from state, industry, and non-governmental organizations as well as the public and other stakeholders. A series of technical roundtables and in-depth technical workshops were held to help address specific research questions and to inform the work of the study. The study is designed to address research questions posed for each stage of the hydraulic fracturing water cycle:

- Water Acquisition: What are the possible impacts of large volume water withdrawals from ground and surface waters on drinking water resources?
- Chemical Mixing: What are the possible impacts of surface spills of hydraulic fracturing fluid on or near well pads on drinking water resources?
- Well Injection: What are the possible impacts of the injection and fracturing process on drinking water resources?
- Flowback and Produced Water: What are the possible impacts of surface spills of flowback and produced water on or near well pads on drinking water resources?
- Wastewater Treatment and Waste Disposal: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?

This report, Sources Contributing Inorganic Species to Drinking Water Intakes during Low Flow Conditions on the Allegheny River in Western Pennsylvania, is the product of one of the research projects conducted as part of the EPA's study. It has undergone independent, external peer review in accordance with Agency policy and all of the peer review comments received were considered in the report's development.

The EPA's study will contribute to the understanding of the potential impacts of hydraulic fracturing activities for oil and gas on drinking water resources and the factors that may influence those impacts. The study will help facilitate and inform dialogue among interested stakeholders, including Congress, other Federal agencies, states, tribal government, the international community, industry, non-governmental organizations, academia, and the general public.

ABBREVIATIONS

ADQ	audit of data quality
AMD	acid mine drainage
CBM	coal bed methane
cfs	cubic feet per second
CWTF	centralized waste treatment facility
EST	Eastern Standard Time
EPA	(U.S.) Environmental Protection Agency
FGD	flue gas desulfurization
GPD	gallons per day
HF	hydraulic fracturing
HR-ICPMS	high resolution magnetic sector field – inductively coupled plasma mass spectrometry
IC	ion chromatography
ICP-OES	inductively coupled plasma – optical emission spectrometry
km	Kilometers
MDL	method detection limits
MGD	million gallons per day
mg/L	milligrams per liter
mL	Milliliters
MPS	multi-probe system
MW	Megawatt
NPDES	National Pollutant Discharge Elimination System
PDWS	public drinking water system

PDW	public drinking water
PMF	Positive Matrix Factorization
POTW	publicly owned treatment works
QA	quality assurance
QAPP	Quality Assurance Project Plan
QC	quality control
TDS	total dissolved solids
TSA	technical systems audit
USACE	U.S. Army Corps of Engineers
USGS	U.S. Geological Survey
v/v	volume per volume
w/v	weight per volume
µS/cm	microsiemens per centimeter
µg/L	micrograms per liter

AUTHORS

Gary A. Norris,[1] Kasey D. Kovalcik,[1] Matthew S. Landis,[1] Amy Bergdale, [2] Carry Croghan,[1]
Ali S. Kamal[+]

[1] U.S. EPA Office of Research and Development, Research Triangle Park, NC 27711
[2] U.S. EPA Region 3, Office of Monitoring and Assessment, Wheeling, WV 26003
[+] Current Affiliation: Oak Ridge Institute for Science and Education, Oak Ridge, TN 37831-0117

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E. EXECUTIVE SUMMARY

E.1 Background

This study is a component of the U.S. Environmental Protection Agency's (EPA) study of hydraulic fracturing for oil and gas and its potential impact on drinking water resources, and addresses the research question, "Wastewater Treatment and Waste Disposal: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewater on drinking water resources?" (U.S. EPA 2014b). The Allegheny River and its tributaries in western Pennsylvania are affected by many different types of contaminant sources including centralized waste treatment facilities for oil and gas wastewater, coal-fired electric power generating stations, acid mine drainage from historic mining wastes, current mining operations, natural oil seepage, industrial manufacturing facilities, publicly owned treatment plants that treat municipal sewage, and industrial facility sewage treatment plants. These sources discharge a mixture of contaminants into surface waters, some examples of which are the anions bromide, chloride, sulfate, and nitrate. The Allegheny River is the source of raw water for thirteen (13) public drinking water systems serving over half a million people in western Pennsylvania. Understanding sources of contaminants in drinking water is critical due to their potential impacts on drinking water quality (States *et al.*2013).

Centralized waste treatment facilities for oil and gas wastewater that discharged treated wastewater to surface wasters in western Pennsylvania during this study primarily but not exclusively treat conventional oil and gas wastewater, and most conventional wells in Pennsylvania are stimulated or hydraulically fractured (PA DEP 2012). The centralized waste treatment facilities for oil and gas wastewater have treatment processes to remove solids, but do not effectively remove bromide and chloride (Ferrar *et al.* 2013). Discharged bromide can lead to increased levels of brominated disinfection byproducts in downstream drinking water treatment plants (Richardson *et al.* 2007, States *et al.* 2013, Parker *et al.* 2014) which may pose human health risks. Discharge of treated (centralized waste treatment facilities for oil and gas wastewater) and untreated (via publicly owned treatment plants) wastewater from oil and gas production in the Marcellus region was substantially reduced in May 2011 due to a request by the Commonwealth of Pennsylvania asking companies to voluntarily stop sending their Marcellus wastewater to these facilities (PADEP 2011a, 2011b; Wilson and Van Briesen 2012). The request was based on concerns over increased bromide levels at public drinking water system intakes and associated increases in disinfection byproducts within public drinking water system finished water in Pittsburgh (PADEP 2011a). Previous studies have focused on characterizing centralized waste treatment facilities for oil and gas wastewater discharges since they are known sources of bromide (Ferrar *et al.* 2013). However, these studies did not consider other critical sources of contaminants for the Allegheny River; or assess the impact of the discharges on downstream public drinking water systems.

E.2 Objectives

The objectives of this study were to quantify the cumulative contribution of treated oil and gas wastewater from centralized waste treatment facilities for oil and gas wastewater that primarily treat hydraulic fracturing wastewater, and to distinguish that contribution from other potential sources on bromide concentrations at two public drinking water system intakes located on the Allegheny River.

E.3 Approach

Centralized waste treatment facilities for oil and gas wastewater discharges are a known major source of chloride, bromide, and other anions. The contribution of these contaminants from centralized waste treatment facilities for oil and gas wastewater as well as other sources to public drinking water system intakes was evaluated by taking the following approach: (1) development of chemical source profiles, or fingerprints, for all sources upstream of two public drinking water system intakes on the Allegheny River by collecting outfall samples from specific sources within facilities and combined river outfalls, (2) collection and chemical characterization of river samples from multiple sites upstream and downstream of centralized waste treatment facilities for oil and gas wastewater, electric generating stations, industrial facilities, and at the public drinking water system intakes, and (3) analysis of the river sample data with the EPA Positive Matrix Factorization receptor model to quantify the contribution of sources to anion levels at the public drinking water system intakes.

E.4 Results

Daily samples were collected from six river sampling sites, two public drinking water system intakes, and the discharge tanks at two centralized waste treatment facilities for oil and gas wastewater for two weeks in summer and fall 2012 during low river flow conditions. Chemical species profiles were collected for centralized waste treatment facilities for oil and gas wastewater, coal fired power plants (cooling tower, flue gas desulfurization scrubber, demineralizer, coal pile runoff, coal ash), industrial manufacturing processes, publicly owned treatment plants, coal bed methane, acid mine drainage, oil seep, and coal mine runoff. Based on the Positive Matrix Factorization multiple sampling site analysis, the predominant sources of bromide at the public drinking water system intakes were treated wastewater discharged from centralized waste treatment facilities for oil and gas wastewater and flue gas desulfurization, while publicly owned treatment plants and acid mine drainage were sources of nitrate and sulfate.

E.5 Conclusions

This research applied a technique referred to as “source apportionment” to quantify source contributions for a number of common discharge sources. Source measurements were collected to provide reference information for apportioning contaminant sources in the Alleghany watershed, including from centralized wastewater treatment facilities that treat wastes including oil and gas wastewater; coal-fired power plants with and without flue gas desulfurization; industrial manufacturing facilities; municipal and industrial wastewater treatment plants; active coal mine runoff; and acid mine drainage. During the study period, which was focused on low flow conditions, we found that centralized wastewater treatment facilities and

KEY FINDINGS

- The results demonstrate that the 2 public drinking water intakes studied are impacted by multiple sources contributing various inorganic species, including centralized wastewater treatment facilities, power generating stations, and acid mine drainage.
- Source measurements provide a signature or profile for numerous bromide sources.
- The predominate sources of bromide at the 2 public drinking water intakes studied were wastewaters discharged from including centralized wastewater treatment facilities and coal-fired power plants with flue gas desulfurization . CWTFs contributed nearly all the bromide at 1 intake, while both centralized wastewater treatment facilities and coal fired power plants with flue gas desulfurization contributed to bromide levels at the second intake.

coal fired power plants with flue gas desulfurization are contributing bromide to two Allegheny River public drinking water system intakes. Acid mine drainage from historical mining activities also contributes bromide, however, the magnitude of the contribution was 9% at one of the intakes. This study collected a large amount of data and had five key findings:

- Source measurements demonstrated a range of Br/Cl ratios for bromide sources, suggesting the ratio can assist in differentiating the contributions from these sources.
- Centralized waste treatment facilities for oil and gas wastewater, which are known to treat hydraulic fracturing wastewaters, are a major source of bromide at the two public drinking water system intakes in this study with a contribution of 89% and 37%, respectively.
- Flue gas desulfurization wastewater is another source of bromide at public drinking water system intakes. Flue gas desulfurization median percent contributions ranged from 50 to 59% at one of the public drinking water system intakes, which varies daily due to changes in discharges. The coal-fired electrical generating stations in this study domain burned upper Pennsylvanian and Monongahela formation bituminous coal (e.g., Pittsburgh #8), which contains naturally high levels of bromine.
- The combination of bromide transported from centralized waste treatment facilities for oil and gas wastewater, FGDs, and acid mine drainage explains 88–89% of the bromide at one of the intakes, and 96% of the bromide at a second intake.
- This research study demonstrates the efficacy of source apportionment techniques to quantify contaminant impacts in complex river systems with multiple source discharges.
- Understanding the sources will guide efforts to control exposures to drinking water contaminants of concern such as brominated disinfection byproducts.

E.6 Limitations

There are important limitations and uncertainties in the information included in this report:

- In Pennsylvania, hydraulic fracturing is commonly used in conventional and unconventional oil and gas production using both vertical and horizontal wells. Although most of the wastewater from oil and gas operations in western Pennsylvania is associated with hydraulic fracturing, it was not possible to determine with certainty the exact mix of hydraulic fracturing and non-hydraulic fracturing oil and gas wastewater treated by the commercial wastewater treatment facilities during each sampling event since reporting on accepted waste streams is submitted on an annual basis rather than for each daily delivery received by the plant. During the study period, both centralized waste treatment facilities for oil and gas wastewater accumulated the oil and gas wastewater from individual deliveries into large on-site storage tanks prior to batch treatment. As a result, the wastewater from numerous individual wells was combined prior to treatment and discharge.
- Samples were collected from one large river system and one small river system, with different source contributions, chemistry, and flow rates. Data from these two river systems were combined in a Positive Matrix Factorization receptor modeling analysis. The ability of the Positive Matrix Factorization model to resolve flue gas desulfurization as a source varies depending on the sampling sites included in the analysis. The results reported above reflect the combined analysis of both river system contributions. A sensitivity analysis provides results from alternate site inclusion (see section 4.4, Table 23). Regardless of the site combinations, Positive

Matrix Factorization was able to distinguish a centralized waste treatment facility source, either as a single source (subset of sites) or a combined flue gas desulfurization and centralized waste treatment facility source (all sites).

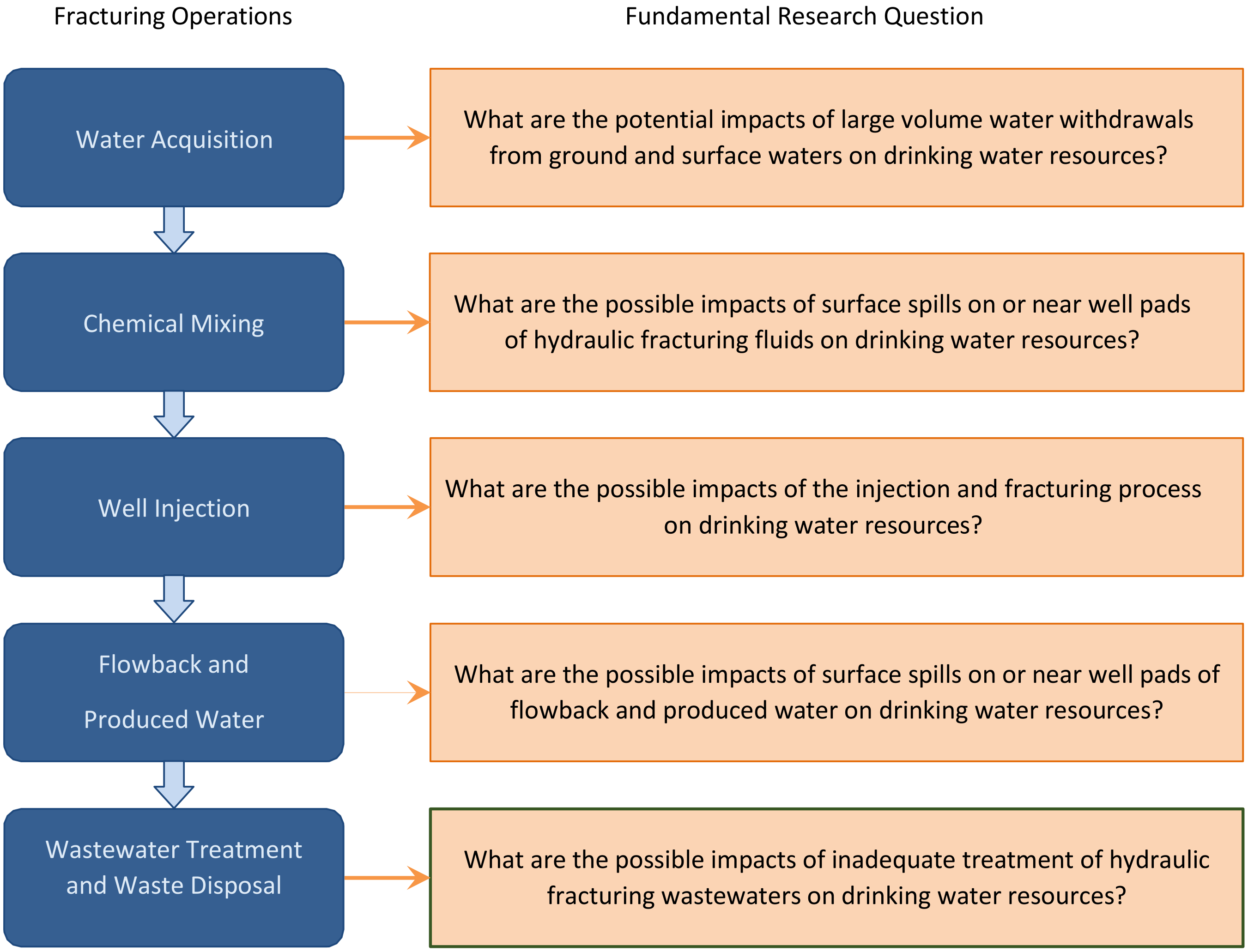
- Ground water contributions were not identified as a significant source of bromide in the source apportionment analysis. However, any hydrologic contribution from ground water may be accounted for in one of the background sources (e.g., acid mine drainage, suspended sediments).
- This report is based on two sampling campaigns in summer and fall 2012 and is not intended to quantify bromide source contributions from all centralized waste treatment facilities or other sources on all the public drinking water system intakes along the Allegheny River during other time periods.

1. INTRODUCTION AND PURPOSE OF STUDY

Hydraulic fracturing is an important means of accessing one of the nation's most vital energy resources, oil and natural gas. Advances in technology, along with economic and energy policy developments, have spurred a dramatic growth in the use of hydraulic fracturing across a wide range of geographic regions and geologic formations in the United States for both oil and gas production. As the use of hydraulic fracturing has increased, so have interests about its potential impact on human health and the environment, including possible effects on drinking water resources. Based on the increasing prevalence of hydraulic fracturing in facilitating increased domestic production of natural gas, the U.S. Environmental Protection Agency's (EPA) study of hydraulic fracturing for oil and gas and its potential impact on drinking water resources emphasizes the impact of hydraulic fracturing operations in shale formations containing natural gas. Portions of the research, however, may provide information on hydraulic fracturing in other types of oil and gas reservoirs, such as coal beds and tight sands.

The purpose of the EPA's study is to assess the potential impacts of hydraulic fracturing on drinking water resources, if any, and to identify the driving factors that may affect the severity and frequency of such impacts. To answer these questions, EPA identified a set of research activities associated with each stage of the hydraulic fracturing water lifecycle (Figure 1), from water acquisition through the mixing of chemicals and actual fracturing to post-fracturing production, including the management of hydraulic fracturing wastewaters (commonly referred to as "flowback" and "produced water") and ultimate treatment and disposal. This report focuses on research activities developed to investigate the last stage of water use in hydraulic fracturing operations (Wastewater Treatment and Waste Disposal) and the associated research question: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources (Figure 1).

In 2012, EPA identified two centralized waste treatment facilities for oil and gas wastewater (CWTFs) that were treating and discharging hydraulic fracturing wastewaters into the Allegheny River or its tributaries in Western Pennsylvania. EPA then conducted three (3) seasonal two-week sampling campaigns to collect CWTF discharge, river water, and downstream public drinking water system (PDWS) raw water intakes. The goal of this effort was to identify if hydraulic fracturing wastewaters were contributing to anion concentrations (e.g., bromide) at PDWS intakes. EPA then undertook a source apportionment modeling study to quantitatively determine the impact of CWTF discharges on contaminants measured at downstream PDWS (Figure 2) during low flow river discharge periods (summer and fall 2012). This analysis improved EPA's understanding of how contaminants in the treated hydraulic fracturing effluent disperse when discharged to surface waters and impact downstream PDWS. EPA also assessed how other sources of contamination (e.g., coal-fired power plants, acid mine drainage) impact contaminant concentrations in the river. In addition, the sampling, analysis, and source apportionment modeling developed and presented in this report provide an approach that can be applied to other river systems. Ultimately, the results of this study and the future application of the research tools presented will provide communities, states, tribes, and industry with sound scientific knowledge on understanding potential impacts of hydraulic fracturing on drinking water resources, and the protection of those resources for the future.



Fracturing Operations	Fundamental Research Question
Water Acquisition	What are the potential impacts of large volume water withdrawals from ground and surface waters on drinking water resources?
Chemical Mixing	What are the possible impacts of surface spills on or near well pads of hydraulic fracturing fluids on drinking water resources?
Well Injection	What are the possible impacts of the injection and fracturing process on drinking water resources?
Flowback and Produced Water	What are the possible impacts of surface spills on or near well pads of flowback and produced water on drinking water resources?
Wastewater Treatment and Waste Disposal	What are the possible impacts of inadequate treatment of hydraulic fracturing wastewaters on drinking water resources?

Figure 1. Fundamental research questions posed for each identified stage.

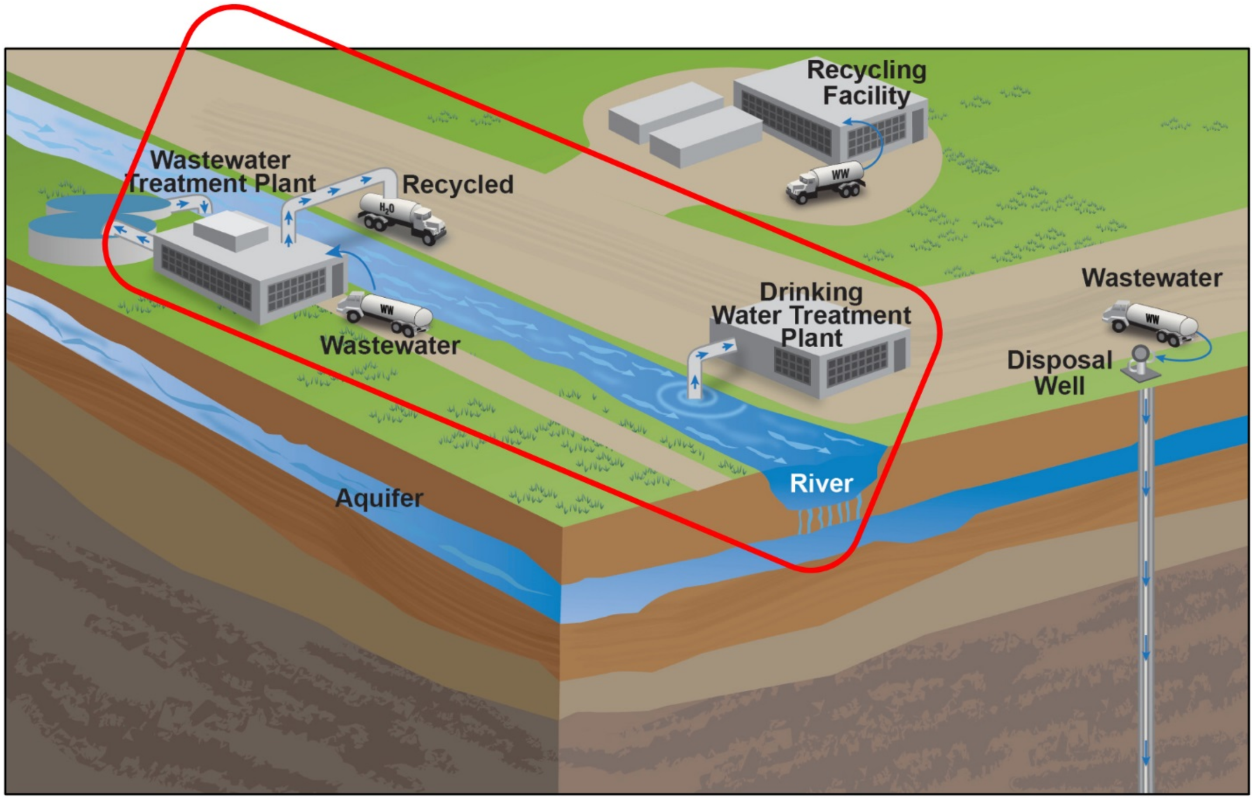


Figure 2. Schematic representation of commercial wastewater treatment, discharge to surface waters, and impact on downstream public drinking water plants (focus area of this project is circled in red).

1.1 Need for Research

Oil and gas wastewater may contain inorganic salts, radioactive substances, heavy metals, and volatile organic substances originating from the producing formation (Vengosh *et al*., 2014; Balaba and Smart, 2012). Oil and gas CWTFs, including those that treat hydraulically fractured wastewater, have processes to remove solids but do not effectively remove monovalent ions such as bromide and chloride (Ferrar *et al.* 2013), which pass through the treatment process and can be discharged into surface waters. Previously published studies have focused on characterizing a single CWTF discharge, since these discharges are known sources of bromide (Ferrar *et al.* 2013; Hladik *et al*. 2014; Warner *et al*. 2013). However, these approaches have been limited to investigating near field downstream enhancement, did not distinguish the contribution of CWTFs relative to other sources of the same contaminant(s), and did not directly evaluate the impact of the discharges on downstream PDWS.

Discharge of treated (CWTF) and untreated (via publicly owned treatment plants (POTWs)) wastewater from oil and gas production in the Marcellus region was substantially reduced in May 2011 due to a request by the Commonwealth of Pennsylvania asking companies to voluntarily stop sending their Marcellus wastewater to these facilities (PADEP 2011a, 2011b; Wilson and Van Briesen 2012). The request was based on concerns over increased bromide levels at PDWS intakes and associated increases in disinfection byproducts within PDWS finished water in Pittsburgh (PADEP 2011a). However, treatment and discharge of wastewater from other oil and gas production (conventional and unconventional) continues (Vengosh *et al.* 2014). Most conventional wells in Pennsylvania require hydraulic fracturing stimulation due to reservoir characteristics (PA DEP 2014c). In 2012, a total of 992,137 barrels of conventional oil and gas wastewater were treated by the two CWTFs evaluated in this study (PA DEP 2014a). The CWTFs also treated basic sediment, drilling fluid, fracking fluid, and servicing fluid wastewater. Conventional oil and gas wastewater has similar composition to Marcellus shale wastewater and both have highly variable compositions (Haluszczak *et al.* 2013; Lutz *et al.* 2013; Wilson and Van Briesen 2012; Wilson *et al.* 2013).

This study was a component of the U.S. EPA study of hydraulic fracturing for oil and gas and its potential impact on drinking water resources, and addresses the research question, "Wastewater Treatment and Waste Disposal: What are the possible impacts of inadequate treatment of hydraulic fracturing wastewater on drinking water resources?" (U.S. EPA 2014b). Monovalent ions such as bromide and chloride, are present in high concentrations in oil and gas wastewater (mean bromide range of 602 to 973 mg/L and mean chloride range of 68,375 to 99,800 mg/L; Ferrar *et al.* 2013). They are not effectively removed in CWTFs, and the treated wastewater is discharged to the Allegheny River and its tributaries (Ferrar *et al.* 2013). Depending on a complex array of factors, the resulting elevated bromide concentrations in the Allegheny River can lead to the formation of brominated disinfection byproduct analogs during the drinking water treatment process.

Other sources also discharge substantial quantities of bromide to the Allegheny River and contribute to the overall river bromide burden. Samples were collected from National Pollutant Discharge Elimination System (NPDES) facility outfalls at coal fired generating stations, POTWs, coal bed methane, and industrial facilities. This study identified and quantified the individual contributions from the source types identified in the study domain (e.g., CWTF, flue gas desulfurization (FGD), acid mine drainage (AMD)) to the elevated bromide concentrations observed in two downstream PDWS raw water intakes in order to quantify and provide context for the contribution from oil and gas wastewater relative to other sources.

The current study is responsive to the research question since most conventional wells in Pennsylvania are hydraulically fractured. However, this study was not able to specifically classify the amount of hydraulically fractured and non-hydraulically fractured oil and gas wastewater treated by the CWTFs for summer and fall 2012 two week sampling campaigns.

1.2 Research Objectives

The objectives of this study were to quantify the cumulative contribution of treated oil and gas wastewater from multiple CWTFs that treat hydraulic fracturing wastewater, and to distinguish that contribution from other potential sources on bromide concentrations at two PDWS intakes located on the Allegheny River.

1.3 Source Apportionment and River Transport Modeling

Source apportionment techniques such as receptor modeling can be used to quantify the sources contributing to water quality degradation (or contamination) based on mathematical modeling that uses a combination of measured water sample species concentrations and discharge source profiles to quantify the contribution of specific source types to observed contaminants. A few previous surface water source apportionment studies have been conducted in the U.S. which focused on quantifying the contribution of contaminants from application of roadway deicing materials and POTWs, and have used a combination of source and river measurements to evaluate relative source contributions using bromide to chloride ratios (Kelly *et al.* 2010). Soonthornnonda and Christensen (2008) utilized Positive Matrix Factorization (PMF) to both identify and quantify water contaminant sources in Milwaukee, Wisconsin. Henry and Christensen (2010) compared results obtained with Unmix and PMF for (i) an artificial air pollution data set and (ii) an actual sediment polychlorinated biphenyls (PCB) data set from a heavily contaminated freshwater estuary (Sheboygan, WI). PMF has been widely used for air pollution source apportionment, as well as to evaluate sediment data (Assefa *et al.* 2013; Norris *et al*. 2014; Praipipat *et al.* 2013; Zou *et al*. 2013). This is the first source apportionment study in the Allegheny River in western Pennsylvania, to quantify contributions from multiple potential sources of halides at public drinking water system (PDWS) raw water intakes. The complex mixture of current and historical energy extraction and production, as well as industrial manufacturing sources, represented a significant challenge.

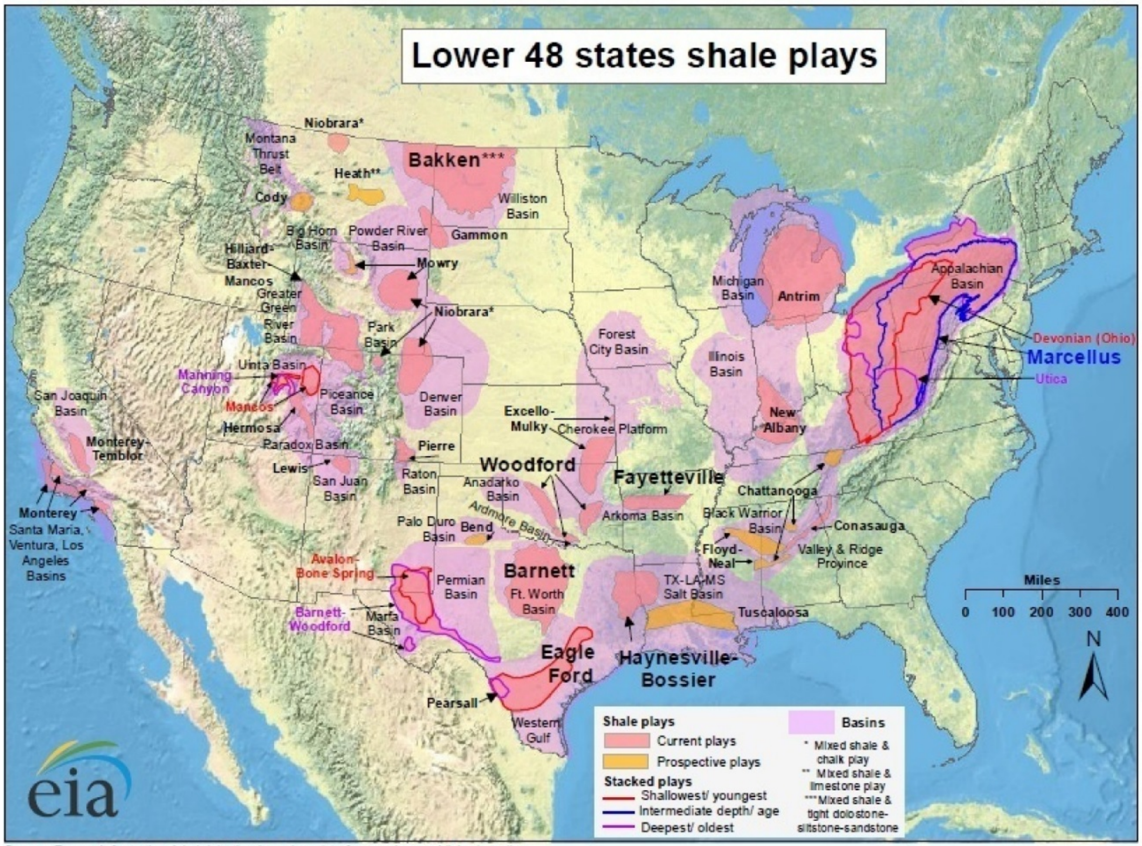
Traditionally, river transport modeling is used to estimate river contaminant concentrations downstream of a discharge location based on mathematical simulations of contaminant movement, attenuation of contaminants downstream of a discharge, and river transport time (Jobson 1996). While many excellent water dispersion models are available, they cannot readily be applied to a specific river system like the Allegheny River without calibration and validation. Detailed information on channel geometry and dispersion coefficients required for accurate modeling are not commonly accessible nor can they be calculated using readily available hydraulic information. Receptor based source apportionment modeling requires no a priori knowledge of river system dynamics or discharge sources. Receptor models identify the source factors and quantify their contributions based solely on contaminant measurement data without specifying numerous model input parameters (Bielski 2012), mass discharge rates, or conducting tracer studies (Jobson 1996) needed for traditional river transport modeling. The input data requirements and outputs for these two modeling approaches are shown in Appendix Figure A1. Two main differences between these modeling approaches make them complementary: (i) source apportionment results are based on actual samples collected at specific river locations and time periods while transport modeling provides estimated concentrations at specified locations for a range of river flow and discharge conditions, and (ii) source apportionment quantifies the combined contribution of a source type (e.g., CWTFs) whereas a transport model simulates the transport and dispersion of discharges from each individual source or facility. Together, the two modeling approaches can be used to identify missing sources, incorrect discharge rates, or the need to adjust modeling parameters.

2. METHODS

Successful application of source apportionment on surface water domains requires a combination of river and source discharge sampling, comprehensive chemical analysis of samples, and application of receptor modeling to identify and quantify sources impacting a sampling location. Knowledge of source discharge chemical characteristics (fingerprints) and their discharge locations are also critical for interpreting and evaluating the source apportionment results.

2.1 Sampling Domain

Western Pennsylvania was chosen as the region to focus our research efforts because (i) the Marcellus is one of the largest shale plays in the U.S. (Figure 3), (ii) development and production in the Marcellus was increasing, (iii) Pennsylvania has a limited capacity for deep well injection of oil and gas waste water with only eight EPA approved Class IID brine disposal wells, (iv) Pennsylvania allows hydraulic fracturing oil and gas wastewater to be discharged into POTWs where it is diluted or treated by CWTFs with subsequent discharge to surface waters, (v) thirteen (13) PDWSs downstream of POTW and CWTF discharges utilize the Allegheny river as their source of raw drinking water, and (vi) PDWSs along the Allegheny River have reported elevated levels of total trihalomethanes (THM; States *et al.*, 2013).



Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

Figure 3. Shale gas plays in the contiguous U.S.

The Allegheny River drains a catchment area of approximately 30,300 km^2 in the Pennsylvania and New York region of the northwestern Appalachian Plateau (Pennsylvania Fish and Boat Commission, 2011). Most reaches of the Northern Allegheny flow over locally-derived river sediment overlying thick layers of glacial outwash (sand and gravel). The Allegheny headwaters flow in a northwesterly direction for approximately 90 km and cross the New York southern border, where the headwaters begin to flow almost due west for another 77 km before cutting south into the head of the Allegheny Reservoir and back into Pennsylvania. The flow leaves the reservoir via the Kinzua Dam, and meanders to the southwest for 319 km. Approximately 203 km of the Allegheny River downstream of the Kinzua Dam remains free-flowing. Further downstream, 116 km of the Allegheny River are impounded and regulated by eight navigatin dams, and, like the upstream Allegheny Reservoir, they are controlled and maintained by the U.S. Army Corp of Engineers (USACE). When the Allegheny River reaches its confluence with the Monongahela River in Pittsburgh, it is classified as a low-gradient seventh-order system (White *et al.*, 2005) and classified by EPA as a large river (Flotemersch *et al*., 2006). Between the sampling sites in this study, the Allegheny River is confined within a narrow, severely meandering valley with precipitous side slopes.

The Allegheny River and its tributaries in western Pennsylvania can be affected by many different types of contaminant sources including CWTFs, coal-fired electric power generating stations, AMD from historic mining wastes, current mining operations, natural oil seepage, industrial manufacturing facilities, POTWs, and industrial facility sewage treatment plants. These various sources discharge a mixture of contaminants into surface waters including anions such as bromide, chloride, sulfate, and nitrate. The Allegheny River is the source of drinking water for 13 water systems serving over half a million people in western Pennsylvania. Understanding the sources of contaminants to water is critical due to their potential impacts on drinking water quality (States *et al.* 2013). In many parts of the U.S. most of the oil and gas well produced wastewater is disposed through deep well injection (Gregory *et al.*, 2011). In Pennsylvania, the majority of oil and gas well wastewater is either trucked out of state for deep well injection or disposed of using alternative methods (Wilson and Van Briesen 2013; Veil 2010). In addition, 1 percent of the conventional wastewater was used for roadway deicing and dust control in 2012 (Skalak *et al*. 2014).

2.2 River Sampling and Discharge Source Location

The EPA Office of Research and Development (ORD) worked with EPA Region 3 personnel to identify two CWTFs in the study domain treating hydraulic fracturing wastewater, discharging to surface waters, with downstream PDWS intakes. The study plan included one CWTF discharging into a large river system, and one discharging into a small river system. Other suggested selection criteria included: (i) a minimum total discharge from a CWTF of 40,000 GPD, (ii) presence of a PDWS intake downstream (<65-85 km), and (iii) no substantial tributary inputs between the CWTF discharge and the PDWS intake. Details concerning the CWTF facilities that meet these criteria are detailed below in Table 1.

Table 1. Waste water treatment facility and receiving stream information.

	CWTF_A	CWTF_B
Approximate Discharge Volume (GPD)	50,000	67,000
Receiving Stream	Allegheny River	Blacklick Creek
Receiving Stream 2010 Mean Daily Flow (cubic feet sec-1 (cfs))	1640	327
Nearest Downstream Drinking Water Intake (km)	51	90

Samples were collected along the two river systems to evaluate the transport and dispersion of bromide and other inorganic species to the closest downstream PDWS intake. All sampling sites and sources were located along the Allegheny River and the Blacklick Creek to the Kiskiminetas River (Blacklick Creek, Two Lick Creek, Conemaugh River, Loyalhanna Creek, and Kiskiminetas River) as shown in Figure 4. Sites were selected due to their proximity to CWTFs, PDWS intakes, as well as other known sources. Allegheny and Blacklick sites are identified with an “A” and “B”, respectively. Samples were collected at five (5) sites on each river system: upstream of the CWTF (S01), the CWTF treated wastewater (S02), downstream of the CWTF outfall (S03), an intermediate location (S04), and finally the closest downstream PDWS intake (S05). River, CWTF, and PDWS samples were collected using automated water samplers (Teledyne Isco Model 6712, Lincoln, Nebraska) to simultaneously collect daily samples at all of the Allegheny and Blacklick study domain sites. An 800 mL daily composite sample was collected in acid cleaned polypropylene bottles at each site by sampling two 400 mL aliquots, one at 09:00 and one at 12:00 Eastern Standard Time (EST). In order to determine the sampling precision of the sampler, collocated sequential samples (e.g., bottle 1 and bottle 2) were collected at the two PDWS intakes and a river site using the Isco sampler.

All of the Allegheny study domain sites were on the Allegheny River with S01_A upstream of the sampled CWTF to provide the chemical composition of the river before it is impacted by the CWTF discharge, and S03_A at a distance downstream of the CWTF where it could be considered initially well mixed. S04_A was downstream of a coal-fired electric generating station (no FGD) and S05_A was at the PDWS intake. An additional CWTF was also located 105 km upstream of S01_A on the Allegheny River (CWTF_C).

The Blacklick study domain sampling sites start on the Blacklick Creek and end at the confluence of the Kiskiminetas and Allegheny Rivers. The Blacklick upstream sampling site (S01_B) and the site downstream of the CWTF (S03_B) are both on the Blacklick Creek prior to its confluence with the Two Lick Creek. The next downstream site (S04_B) is after the confluence of the Conemaugh River with the Blacklick Creek, and a flood control reservoir with a dam. After S04_B, the Conemaugh joins with Loyalhanna Creek to form the Kiskiminetas River. The PDWS intake S05_B is on the Allegheny River after the confluence with the Kiskiminetas River. Site S05_B is 97.8 kilometers downstream of S05_A.

The USACE manages the water discharge rate of the Allegheny River in the study domain by controlling water discharge volumes directly into the river from the Kinzua reservoir, and into tributaries from the Tionesta, Union City, and Woodcock reservoirs (USACE, 2014). This active management provides for flood control, power generation cooling water requirements, water quality management, and downstream navigation requirements. The water levels in the Upper Allegheny have historically been (i) highest in the late fall and winter during reservoir drawdown in preparation for snow melt and spring precipitation, resulting in a relatively high assimilative capacity from source discharges, and (ii) lowest in the summer resulting in elevated concentrations of contaminants (USGS, 1993; USGS, 2013). As a result, the Allegheny River summer and fall low flow periods are typically characterized by water discharge rates that are less than 5000 cfs (Figure 5).

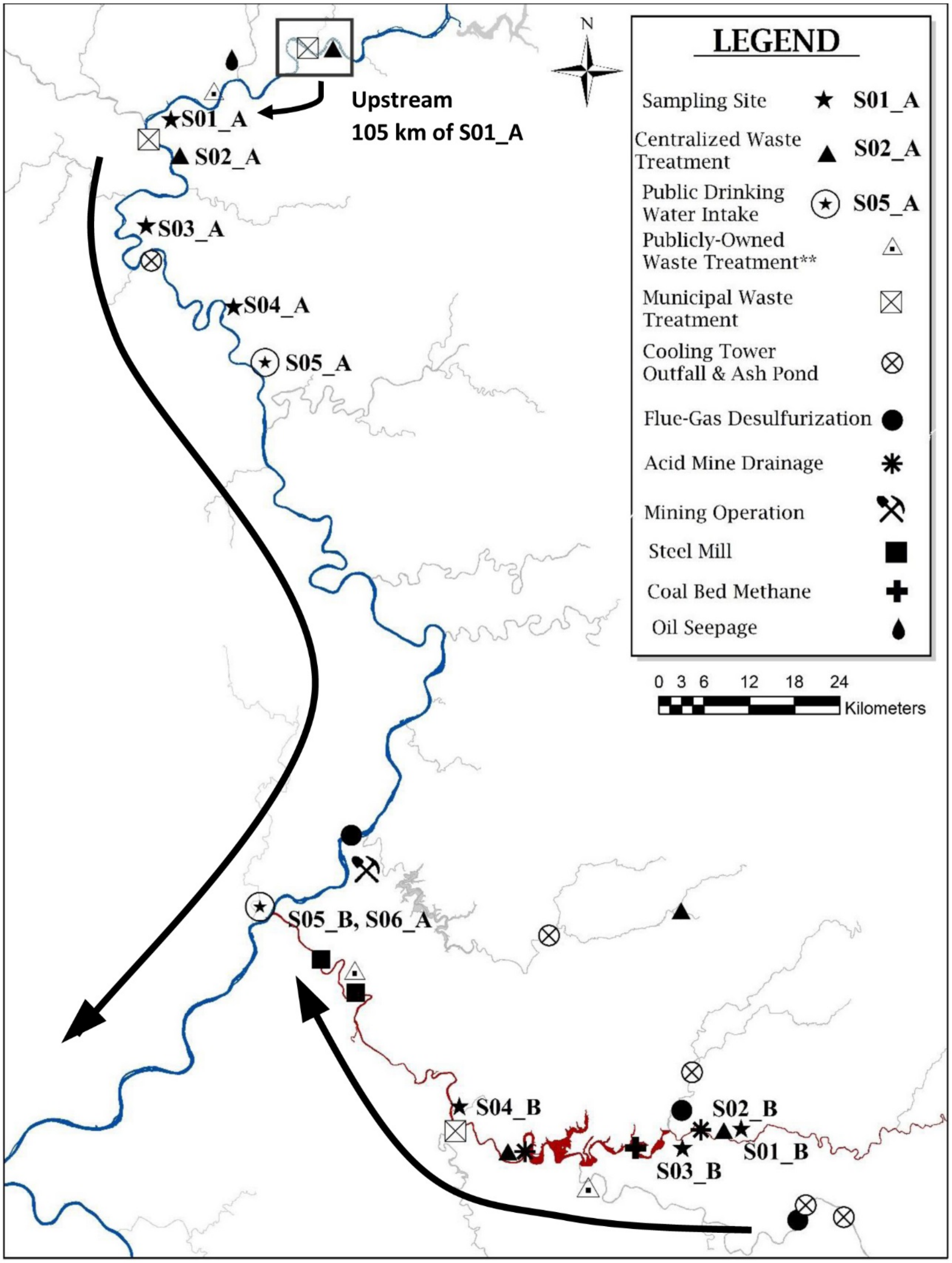


Figure 4. Allegheny River (blue) and Blacklick Creek to Kiskiminetas River (red) sampling sites, and location of major surface water discharges. The arrows show the direction of river flow.

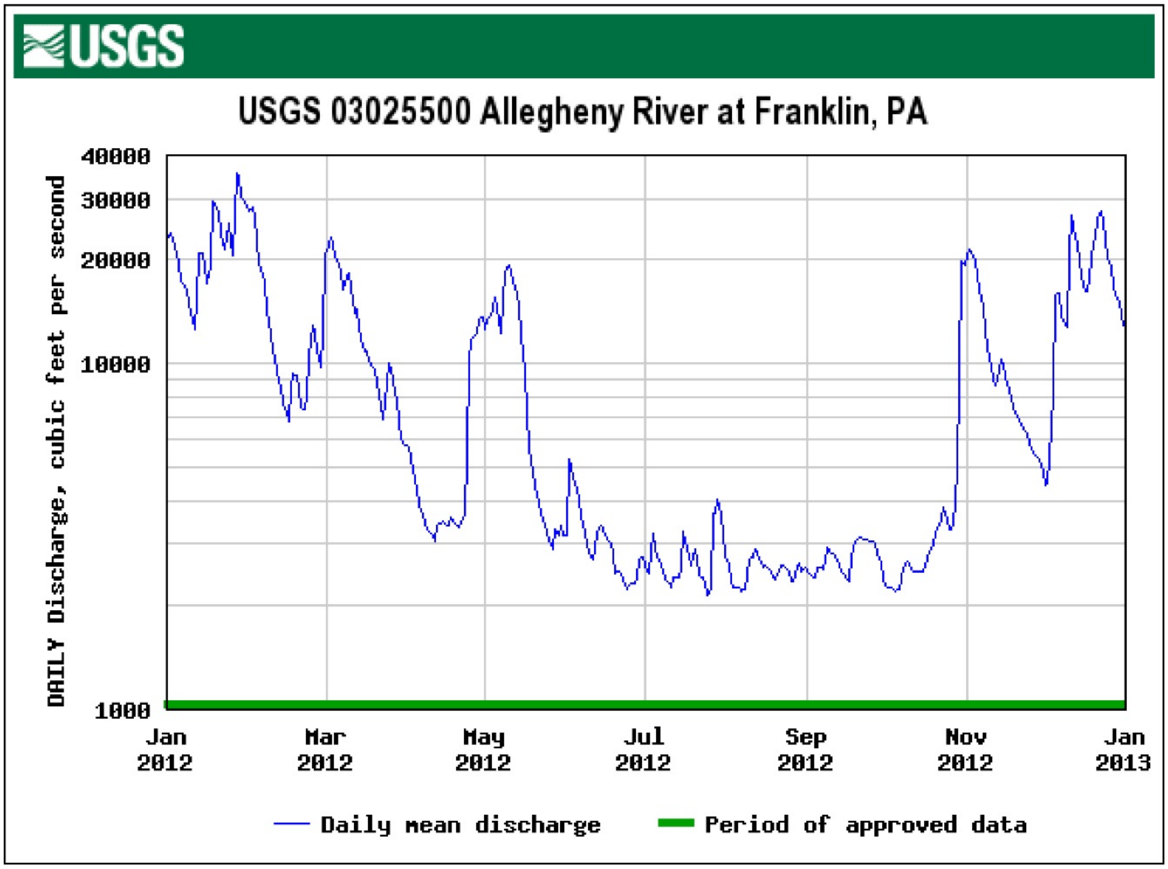


Figure 5. USGS Gauge Station Data for 2012 showing the lower daily mean discharge levels during summer and fall.

Mean discharge rates for low flow conditions are shown in Figure 6 along with U.S. Geological Survey (USGS) gage station ID numbers (USGS 2014). USGS mean discharge data were used to evaluate the differences in river flow between sites since it directly impacts the dilution of the facility discharges. The CWTF_A discharged into the Allegheny River, which had a river flow rate of 2702 cubic feet per second (cfs), and the river flow increased to 3734 cfs at the PDWS intake (S05_A). The CWTF_B discharged into Blacklick Creek, which had a river flow rate of 68 cfs and increased to 886 cfs before the confluence of the Kiskiminetas and Allegheny River. Figure 6 also shows that the contribution from tributaries is very different between the Blacklick and Allegheny sites. River discharge (volumetric flow rate) is also impacted by smaller tributaries without USGS gage data, direct storm water runoff, and hydrologic ground water interactions.

The discharges into the Allegheny are diluted by a large river flow in comparison to the Blacklick sampling sites. Blacklick sampling sites S01_B (upstream) and S03_B (downstream CWTF) are on the Blacklick Creek which has a mean flow rate of 68 cfs. This is approximately three percent of the mean flow in the Allegheny (2702 cfs upstream of CWTF_A), and therefore provides much lower dilution capacity. The Conemaugh Reservoir has contributions from the Conemaugh River (443 cfs), Two Lick Creek (74 cfs), and Blacklick Creek (68 cfs), which provides greater dilution of the discharges.

Numerous wastewater source discharges are found along the Allegheny River and its tributaries that impact the study domain. A simplified diagram of the rivers, creeks, and discharges is depicted in Figure 7. The volumes of wastewater treated by the CWTF_A and CWTF_B are listed in Table 1. The AMD treatment facility on the Conemaugh River is also a CWTF, and it treated 5% of the wastewater treated by CWTF_B (21,607 barrels). In addition, a CWTF discharged to Crooked Creek, and it treated 34% of the volume treated by CWTF_A (193,872 barrels). The river segment with the largest number of source contributions is between S03_B and S04_B (two coal-fired generating stations with FGD, one coal-fired generating station without FGD, and a CWTF). Also, AMD contributes to all of the sites as noted in Sams and Beer (2000). The flow rates and sources on Two Lick Creek, Blacklick Creek, and Conemaugh River create a complex source mixture. The Conemaugh Dam (Figure 6, Figure 7) holds back and integrates the flow from these rivers.

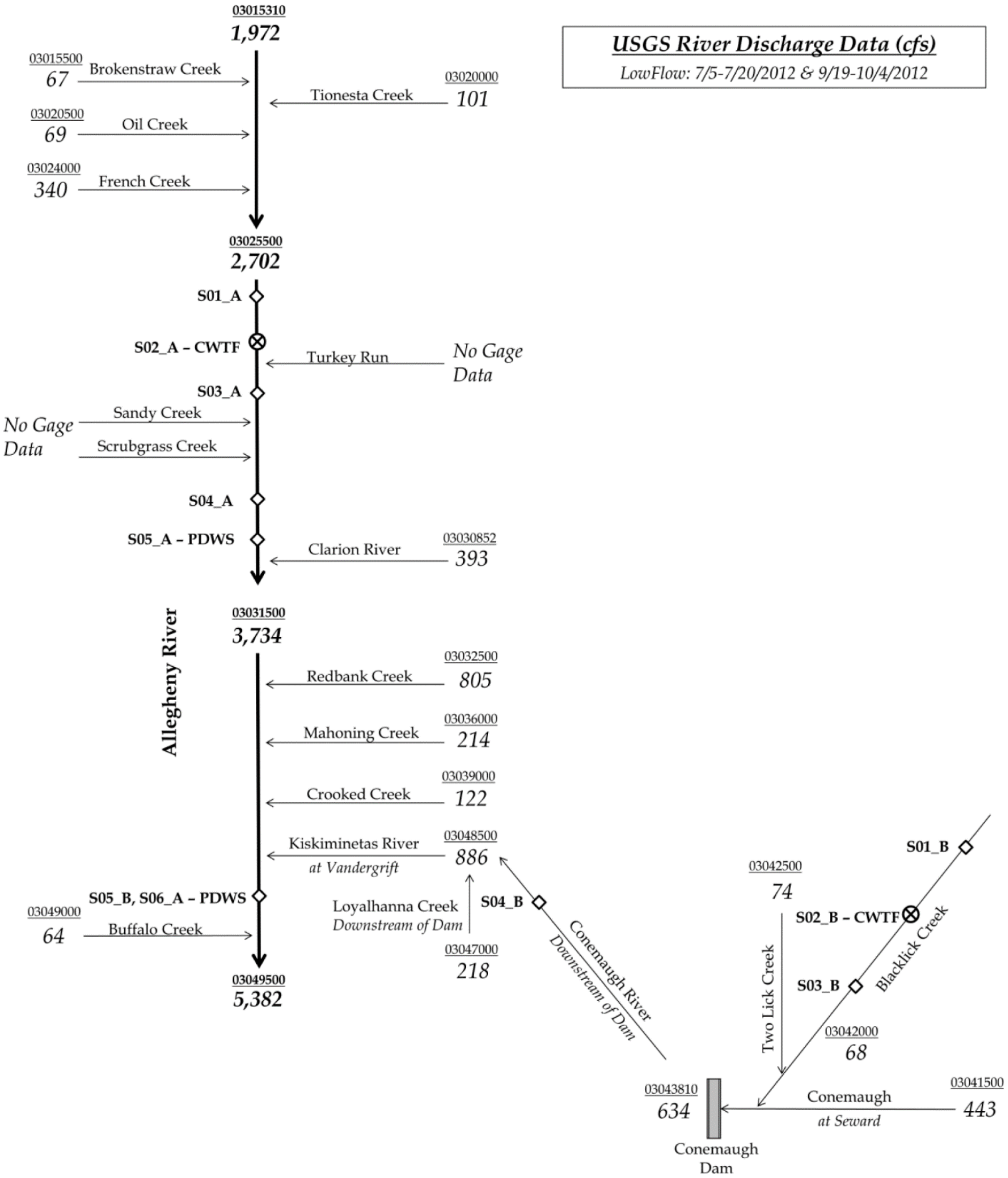


Figure 6. USGS mean discharge rates and gage IDs.

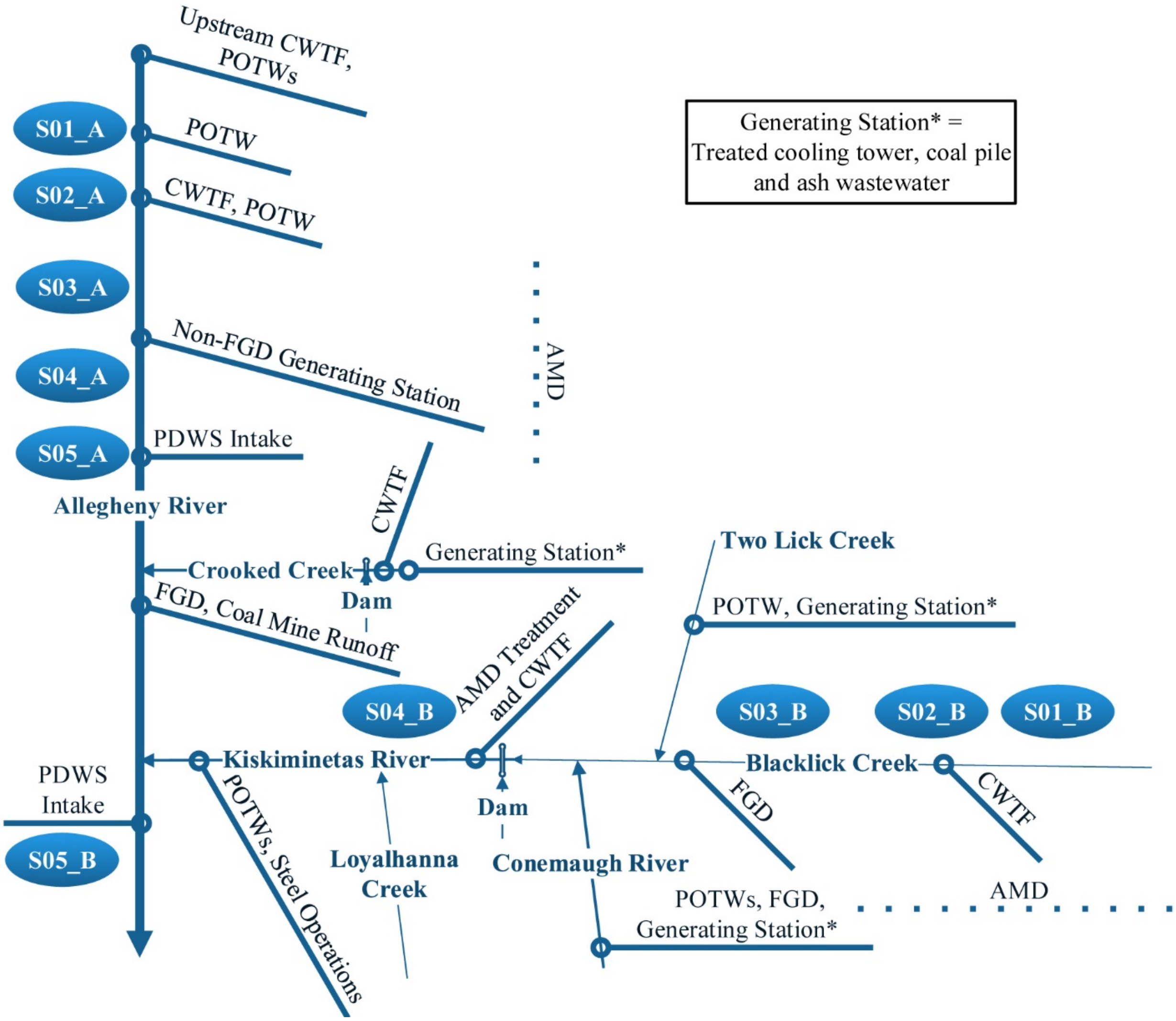


Figure 7. Diagram of sampling sites, rivers, and sources.

2.3 Source Sample Collection

Source discharge grab samples were collected from National Pollutant Discharge Elimination System (NPDES) permitted outfalls that discharged to surface waters in the study domain to generate source profiles (fingerprints). Internal outfall samples were collected in facilities with multiple permitted wastewater sources before they were combined into the river outfalls to allow for chemical characterization associated with each process. Source outfall samples were collected with acid-cleaned polypropylene dippers and transferred into acid-cleaned polypropylene bottles. Source sample bottles were rinsed three times with the wastewater, and two to four replicate samples were collected at each outfall or sampling location. After collection, samples were double bagged with sealed bags, placed in locked coolers with ice, and shipped overnight to EPA laboratories.

The location of sources upstream of the PDWS intakes where source grab samples were collected are shown in Figure 4 and Figure 7. Treated outfall samples were collected from five coal-fired electric power generating stations, three of which had spray lime FGD equipment and did not utilize calcium bromide addition for supplemental mercury emission control (capacity was 1,884 megawatt, or MW, for two and 2,012 MW for the other). Two of the three FGDs discharged scrubber wastewater continuously, while the third had a batch treatment process. Additionally, two of the three FGD outfalls were not located near the generating facilities (3 – 28 km away), as shown in Figure 4. The other two generating stations burn coal and have capacities of 585 and 95 MW. Additional outfall samples (cooling tower, ash and coal pile runoff, and demineralizer) were collected at these facilities to elucidate the composition of other wastewater sources. Four sewage treatment outfall samples were collected, representing a range of discharges (1.3, 2, 0.11, and 0.0004 million gallons per day, or MGD). Samples were collected from three industrial metals operations: specialty steel, specialty metals, and metals coating. Coal bed methane (CBM) samples were collected at one facility with two internal outfalls with wastewater from approximately 268 wells. Samples were also collected to represent untreated AMD, treated AMD, oil seepage (water with visible oil residue), and active coal mine runoff.

The complexity of the source mixtures between the Allegheny and Blacklick sites were substantially different. The sampling domain in the upper reaches of the Allegheny River had a larger volumetric discharge rate and fewer source discharges were present. The Blacklick sampling domain contained more source discharges, including AMD from historical mining activities, and a range of creek and river tributary flow discharge rates.

2.4 Sample Analysis

In the field, a YSI (Yellow Springs, OH) Model 556 hand-held Multi-Probe System (MPS) was used to electronically log instantaneous pH measurements at the river sampling sites and at the CWTFs. A three-point calibration for pH (pH= 4.0, 7.0 and 10.0) was performed each day using calibration standards (Orion™ pH Buffer Bottles, Thermo Scientific, Beverly, MA). An evening drift check was performed. If the difference in pH was not within 0.2 of the calibration standard, data for that day were flagged as being invalid.

Ion chromatography (IC) was used to quantify dissolved inorganic anions, including bromide, chloride, sulfate, and nitrate. Analysis of total extractable elements was performed with both inductively coupled plasma – optical emission spectrometry (ICP-OES) and high-resolution magnetic sector field – inductively coupled plasma mass spectrometry (HR-ICPMS) to cover a wide concentration range of trace and ultratrace species. Prior to the inorganic analyses, the samples were analyzed for specific conductivity using a two point calibration with a Mettler Toledo (Columbus, OH) Model S47-K meter equipped with an InLab Model 731 probe. These data guided volumetric and gravimetric dilution determinations for instrumental analyses. By diluting the dissolved solids in analyzed samples, the potential to cause sample spectral and polyatomic interferences, saturation of the instrument detector, and other analytical issues (e.g., memory effects, internal standard suppression, peak broadening) were minimized. The dilutions can also have the adverse consequence of diluting trace species in the parent sample down to below method detection limit (MDL) in the analytical aliquot.

Major ions were quantified by simultaneous injection on two Dionex (Sunnyvale, CA) Model ICS-2000 instruments following a modified U.S. EPA Method 300.1 (U.S. EPA, 1997). All samples were filtered prior to analysis with IC Millex 0.20 µm PTFE syringe filters (Millipore). Anion separation was achieved using a 200 µL injection loop, AS18 and AG18 analytical and guard columns (Dionex), and an isocratic potassium hydroxide eluent. Cation separation was achieved with a 25 µL injection loop, CS16 and CG16 analytical and guard columns (Dionex), and an isocratic methanesulfonic acid method. Analytical procedures were the same for the river and outfall source samples, except that the outfall and CWTF samples required additional dilutions. The dilution volume was based on the sample conductivity. Samples were acidified and microwave digested using EPA Method SW846 3015A (U.S. EPA 2007) prior to analysis by ICP-OES and HR-ICPMS analysis.

Samples were acidified to 2.0% nitric acid (volume by weight, or v/w) and allowed to leach for 7 days to provide time for the elements to leach from particles (Graney *et al.* 2004; Landis *et al.* 2002). Samples were then acidified to 0.5% hydrochloric acid (volume by volume, or v/v), oxidized with 0.05% hydrogen peroxide (v/v), and immediately microwave digested following EPA Method 3015A (U.S. EPA, 2007a). After microwave extraction the samples were vacuum filtered through 47 mm cellulose nitrate filters. Fifteen (15) mL aliquots were then poured off for ICP-OES and HR-ICPMS analyses. Elemental analysis for major elements was performed with a PerkinElmer (PE) Optima 4300 DV ICP-OES following EPA Method 200.7 (U.S. EPA, 1994). Trace elemental analysis was performed using a ThermoFinnigan (Bremen, Germany) Element2 double focusing HR-ICPMS using EPA Method 6020A (U.S. EPA, 2007b), utilizing all three resolution settings in a multi-element quantitative analysis (U.S. EPA 2014c).

Sample data was considered valid only if analyte concentrations did not exceed the highest concentration calibration standard nor were less than the lowest concentration standard as described in EPA Methods 300.1 and 8000B (U.S. EPA, 1996). For several species, certified reference materials were used to extend the reportable linear range. If a single sample was analyzed at more than one dilution producing multiple valid results within the linear range, specific results were prioritized relative to the analytical method. For IC, the result from the least diluted sample was chosen, because the technique is more robust, which also provided the quantification for the majority of the species. For the ICP methods (ICP-OES and HR-ICPMS), the most diluted sample was chosen due to the trace nature of the technique and the ability of the plasma to be altered due the heavily loaded matrices.

As a matter of instrument performance, MDLs for IC, ICP-OES, and HR-ICPMS are provided in Table 2, Table 3, and Table 4, respectively. IC limits were based upon repeated injections of the lowest calibration standard over multiple sequences (n=3). ICP-OES detection limits were determined from the analysis of repeated reagent blanks and the lowest calibration standard over several calibration sequences. HR-ICPMS detection limits were based upon the analysis of the microwave digested nitric acid blanks that were analyzed over multiple analytical sequences to minimize bias.

Table 2. Ion chromatography method detection limits (MDL).

Species	MDL (mg/L)
Bromide	0.0063
Chloride	0.0258
Fluoride	0.0039
Nitrate	0.0169
Sulfate	0.0129

Table 3. Inductively coupled plasma–optical emission spectrometry method detection limits (MDL).

Species	MDL (mg/L)
Ba	0.000619
Ca	0.00419
Fe	0.00320
K	0.0585
Li	0.00336
Mg	0.00218
Mn	0.000937
Na	0.0122
S	0.0349
Si	0.00445
Sr	0.000792

Table 4. High-resolution–inductively coupled plasma mass spectrometry method detection limits (MDL).

Species	Resolution	MDL (µg/L)	Isotope	Resolution	MDL (µg/L)
Ag	Low	0.0113	U	Low	0.0064
Ba	Low	0.506	W	Low	0.0170
Be	Low	0.0542	Y	Low	0.0323
Bi	Low	0.0126	Al	Medium	1.85
Cd	Low	0.107	Co	Medium	0.178
Ce	Low	0.015	Cr	Medium	0.106
Cs	Low	0.0059	Cu	Medium	0.323
Dy	Low	0.0039	Fe	Medium	1.97
Gd	Low	0.0086	Mn	Medium	0.203
La	Low	0.0290	Ni	Medium	0.473
Mo	Low	0.161	P	Medium	1.16
Nd	Low	0.0286	S	Medium	62.1
Pb	Low	0.0380	Si	Medium	19.0
Pd	Low	0.0231	Sn	Medium	0.111
Rb	Low	0.0776	Ti	Medium	0.0964
Rh	Low	0.0055	V	Medium	0.109
Sb	Low	0.0339	Zn	Medium	0.438
Sm	Low	0.0109	As	High	0.104
Sr	Low	0.283	K	High	6.55
Tb	Low	0.0148	Se	High	0.453
Th	Low	0.0097			
Tl	Low	0.0279			

2.5 PMF Receptor Model

The PMF version 5.0 multivariate receptor model was used to identify sources, quantify contributions, and determine uncertainties (U.S. EPA 2014a). Multivariate receptor models solve the chemical mass balance between measured species concentrations and source profiles by decomposing speciated sample data into two matrices: factor contributions and profiles (Hopke 1991). One of the important receptor modeling assumptions is that species are conserved and not transformed or deposited between the source outfall and the receptor or sampling site.

A speciated data set can be viewed as a data matrix X (entire matrices are denoted by capital boldface letters) of dimensions *n* by *m*, in which *n* samples and m chemical species were measured. Rows and columns of X and of related matrices are indexed by *i* and *j*, respectively. The goal of multivariate receptor modeling, for example with PMF, is to identify the number of factors *p*, the species profile *f* of each factor (mass fraction), and the amount of mass *g* contributed by each factor to each individual sample that solve the chemical mass balance between measured species concentrations and factor profiles. This calculation is show in Equation 1:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} = c_{ij} + e_{ij} \tag{1}$$

Where e_{ij} is the residual for each sample/species and c_{ij} is the modeled solution of x_{ij}. Multivariate receptor models calculate the factor profiles and contributions, which are concentrations, based only on the measured data. In PMF, measured profile information can be used to constrain model results. Additionally, measured source information can also be used as constraints to reduce rotational ambiguity (Amato and Hopke 2012; Norris *et al.* 2009; Paatero 1997; Paatero and Trapper 1994), which represents the range of profiles and contributions that can equivalently reproduce the measured data after implementing non-negativity constraints (Henry 1987; Paatero *et al.* 2002). The PMF solution minimizes the object function Q (Equation 2), based upon the estimated data uncertainties u_{ij}.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{K=1}^{P} g_{ik} f_{kj}}{u_{ij}} \right]^2 \tag{2}$$

The results were evaluated within EPA PMF 5.0 using plots and statistics.

One key component of PMF is the use of user-provided sample species uncertainties to scale the residuals in minimization, which allows for down weighting of more uncertain species or samples. PMF sample uncertainties were developed using the sequential sampling and the precision for each species (see Section 3.1). The uncertainty was calculated as the average percent difference multiplied by the species concentration plus the method detection limit (MDL) for river or outfall samples. Data that were below detection limit were replaced by MDL/√2 and an uncertainty of 3*MDL.

The PMF displacement algorithm was used to evaluate the stability of the solution and to generate factor uncertainties (Paatero *et al.* 2014). Displacement perturbs the individual fitted source profile values until the object function reaches a defined change in Q, and the range of perturbed values is used to determine the upper and lower source profile species interval. The uncertainty or interval range can be high for low concentration species in a PMF factor, and these species were not used to identify the source. PMF provides both factors and their contributions to each species, and each factor was identified to be a source type based on (1) comparison of the PMF source type chemical species ratios to measured profiles and (2) the outfall locations.

2.6 Statistical Analysis

Data processing and all statistical analyses were performed using SAS v.9.4 (SAS Institute). The Kruskal-Wallis non-parametric statistical test was used for comparing species concentrations between the Allegheny and Blacklick sampling sites and the CWTFs. A level of significance of $\alpha=0.001$ was used. Sequential precision was calculated as the absolute percent difference for replicate and sequential sample analysis.

3. QUALITY ASSURANCE AND QUALITY CONTROL

Quality assurance (QA) and quality control (QC) procedures were implemented by following two Quality Assurance Project Plans (QAPPs): Hydraulic Fracturing Wastewater Source Apportionment Study (Revision No. 2, February 2013), and the QAPP for Surface Water Source Apportionment Model Applications (August, 2014). The EPA PMF model was developed under an additional QAPP, EPA Positive Matrix Factorization (EPA PMF) QAPP (approved 9/27/13).

Quality control samples were used where appropriate and available for assessing potential contamination of field sampling materials, and spiked samples were used to assess recovery of inorganic species from the water samples. Sequential Isco samples were collected to determine overall sampling and analytical precision. Data quality reviews were conducted by EPA staff and Alion Science and Technology (EPA contract EP-D-10-070). The QA and QC results described below apply to the methods described in section 2.3 and 2.4.

3.1 Quality Control Results for River and Source Sample Analysis

Conductivity replicate analysis was performed on 10% of the samples, and the observed precision (1 - relative percent difference, n=54) was 99 ± 1%, while the sequential sample precision (n=123) was 98 ± 5%. External IC, ICP-OES, and HR-ICPMS calibrations were verified by regression statistics (r^2), National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM), and secondary source calibration standards (IC in Table 5), ICP-OES in Table 6, and HR-ICPMS in Table 7). Performance verification samples were from the National Institute of Standards and Technology Standard Reference Materials (NIST SRM; Gaithersburg, MD), Environmental Resource Associates (ERA; Golden, CO), High Purity Standards Certified Reference Material (HP CRM; Charleston, SC), and United States Geological Survey. The IC performance evaluation samples (Table 5) were analyzed only once so that no standard deviation is available. Digestion procedures were monitored with digestion blanks, lab control samples, and spiked unknown samples and their recoveries. Instrument analytical sequences were monitored for precision and accuracy by continuing calibration blanks, verification standards, continuing check samples, and duplicate sample analysis.

The analytical sequence precision from laboratory duplicates for the ICP-OES and HR-ICPMS analyses is summarized in Table 8. Only species that were quantified in 50% or more of the laboratory duplicate samples are reported in the table.

For field precision analysis, two sequential samples were collected by the Isco sampler (container 1 and container 2) during defined collection periods: S05_A and S05_B during spring, summer, and fall campaigns; S03_B during spring; SO4_B during summer; and S03_A during fall. Table 9 shows the average sequential sampling precision by analytical method.

Field blanks were collected at all sites (S01, S02, S03, S04, S05) during the field monitoring campaigns. The field blank sample bottles were left uncapped in the Isco samplers in the same manner as the deployed sample collection bottles for two to three days to capture the longest time when a sample would be exposed to potential contamination. The field blank river concentrations for anions and cations were low, as shown in Table 10. The CWTF field blanks for anions and cations are higher, as shown in Table 11 since S02_A was collected inside a treatment facility and S02_B was collected near the top of a large holding tank. Levels found in the field blanks were determined to have no effect on sample values, due to the relatively low concentrations of field blanks with respect to collected samples (river, CWTF, and manually collected samples). As a result, reported sample concentrations were not blank corrected.

Table 5. Ion chromatography recovery of performance evaluation samples.

	ERA 505		ERA 693		ERA 698		ERA 5262	
Species	Target (mg/L)	Recovery %	Target (mg/L)	Recovery %	Target (mg/L)	Recovery %	Target (mg/L)	Recovery %
Fluoride					7.82	85		
Chloride					142	94		
Nitrate (as N)	4.48	102			6.35	108		
Bromide							0.28	90
Sulfate					205	92		
Sodium			19.8	98	236	99		
Potassium					33.8	99		
Magnesium			9.53	98				
Calcium			55.3	103				

Table 6. Inductively coupled plasma–optical emission spectrometry recovery (R) of certified (Cert) materials, reference materials, and sequence calibration accuracy checks.

	Standard Reference Material (SRM)1640a (n = 31)				SRM 1643e (n = 31)				High Purity (HP), CRM-TMDW (n = 14)				USGS, M-172 (n = 31)				ERA-500 (n = 3)				ERA custom mix (n = 3)			
Species	Cert., µg/L	R %, Mean	±	SD[1],	Cert., µg/L	R %, Mean	±	SD,	Cert., µg/L	R %, Mean	±	SD,	Cert., µg/L	R %, Mean	±	SD,	Cert., µg/L	R %, Mean	±	SD,	Cert., mg/L	R %, Mean	±	SD,
Al	50.7	96	±	16	138.8	99	±	6	120.0	96	±	5					530.0	102	±	3				
As	4.4 (a)	92	±	24	59.0	95.5	±	4.4	80.0	99	±	3					753.0	101	±	2				
B	318.1	106	±	4	154.0	104.7	±	5.7					97.1	123	±	15	859.0	99	±	1				
Ba	151.4	101	±	4	531.0	99.8	±	3.4	50.0	100	±	2					827.0	101	±	2				
Ca	5542.7	100	±	4	31500.0	96.5	±	3.1	35000.0	100	±	3	8360.0	106	±	5								
Cd	3.9	100	±	15	6.4	103.8	±	12.6	10.0	98	±	8					689.0	91	±	1				
Ce																					45.4	101.5	±	1.8
Co	19.6	98	±	3	26.4	95.1	±	3.1	25.0	97	±	2					215.0	104	±	2				
Cr	39.7	99	±	2	19.9	101.0	±	4.0	20.0	100	±	3					214.0	100	±	1				
Cu	83.7	98	±	4	22.2	115.9	±	17.4									842.0	92	±	1				
Fe	36.4	100	±	8	95.7	101.4	±	8.9	100.0	100	±	3					795.0	102	±	2				
K	562.8	98	±	4	1984.0	96.8	±	3.2	2500.0	99	±	2	3800.0	105	±	4								
Li					17.0	105.8	±	12.0	20.0	98	±	7												
Mg	1031.5	98	±	4	7841.0	97.1	±	2.9	9000.0	99	±	3	4730.0	104	±	5								
Mn	39.4	98	±	3	38.0	99.8	±	3.2	40.0	101	±	2					1850.0	101	±	2				
Mo	42.6	94	±	7	118.5	100.9	±	3.0	100.0	99	±	2					575.0	102	±	1				
Na	3075.7	99	±	4	20230.0	98.0	±	3.0	6000.0	100	±	2	12500.0	104	±	5								
Ni	22.2	89	±	5	1984.0	94.0	±	0.1	60.0	92	±	1					1720.0	97	±	2				
P													1350.0	102	±	3								
Pb	11.7 (a)	97	±	20	19.2	94.7	±	12.3	40.0	97	±	3												

	Standard Reference Material (SRM)1640a (n = 31)				SRM 1643e (n = 31)				High Purity (HP), CRM-TMDW (n = 14)				USGS, M-172 (n = 31)				ERA-500 (n = 3)				ERA custom mix (n = 3)			
Species	Cert., µg/L	R %, Mean	±	SD[1],	Cert., µg/L	R %, Mean	±	SD,	Cert., µg/L	R %, Mean	±	SD,	Cert., µg/L	R %, Mean	±	SD,	Cert., µg/L	R %, Mean	±	SD,	Cert., mg/L	R %, Mean	±	SD,
S													4105.7	109	±	3	460.0	98	±	1				
Sb	4.1 (a)	82	±	33	56.9	94.9	±	4.0	10 (a)	84	±	18					632.0	100	±	1				
Se	18.9 (a)	95	±	17	11.7 (a)	125.9	±	27.0	10.0 (a)	108	±	20					291.0	101	±	2				
Si	5231.1	101	±	3									5697.4	104	±	2								
Sn																								
Sr	124.5	100	±	4	315.2	97.8	±	4.6	250.0	100	±	2	54.0	105	±	5	65.1	99	±	3				
Ti																					56.8	102.0	±	0.6
Tl									10.0 (a)	135	±	37					744.0	101	±	2				
V	14.7	99	±	6	36.9	99.4	±	2.2	30.0	99	±	3	10.3	100	±	9	931.0	100	±	1				
Zn	55.8	101	±	5	76.5	101.7	±	5.5	70.0	101	±	2					1330.0	96	±	2				

[1] standard deviation

Table 7. High-resolution–inductively coupled plasma mass spectrometry recovery (R) of certified reference materials.

	NIST SRM 1640a					NIST SRM 1643e					ERA Mix A[4]		ERA Mix B[4]	
Species	Target (µg/kg)	Digest R % Mean[1] (n=18)	(±) SD[2] %	Daily Accuracy R % Mean[3] (n=31)	(±) SD%	Target (µg/kg)	Digest R % Mean[1] (n=18)	(±) SD %	Daily Accuracy R % Mean[3] (n=31)	(±) SD %	Target (µg/L)	R %	Target (µg/L)	R %
Al	52.6	102	4	104	6	138.33	103	6	108	4	530	105		
As	8.01	94	4	101	6	58.98	87	5	91	4	753	103		
Ba	150.6	101	4	101	3	531.00	105	4	108	4	827	101		
Cu	85.07	96	5	104	5	22.2	88	3	96	4	842	99		
Fe	36.5	100	6	104	5	95.7	100	3	105	4	795	101		
K	575.3	100	4	104	4	1984	98	4	105	5				
Mn	40.07	99	4	105	5	38.02	97	4	105	4	1850	105		
Mo	45.24	105	5	106	6	118.5	106	7	112	6	575	101		
Ni	25.12	96	3	103	5	60.89	92	3	101	4	1720	106		
Pb	12.005	102	8	97	4	19.15	102	4	98	4	460	101		
Rb	1.188	97	5	103	6	13.8	101	3	108	4			65400	116
Sb	5.064	99	3	99	3	56.88	95	4	96	3	632	108		
Sr	125.03	103	4	105	4	315.2	103	5	111	5	65.1	95		
U	25.15	102	8	95	6									
Zn	55.2	94	8	100	6	76.5	80	4	84	4	1330	102		

[1] Microwave Digested Lab Control Sample

[2] Standard deviation

[3] Daily sequence calibration accuracy checks (not microwave digested)

[4] Diluted within Linear Dynamic Range prior to HR-ICPMS analysis

Table 8. Analytical precision for laboratory duplicates.

Species	HR-ICPMS[1] Average Relative Percent Difference (± SD) (n=96)	ICP-OES[2] Average Relative Percent Difference (±SD) (n=120)
Al	3 (±5)	9 (±8)
As	16 (±30)	
Ba	2 (±4)	3 (±4)
Ca		4 (±9)
Cu	3 (±9)	12 (±9)
Fe	7 (±17)	6 (±11)
K	3 (±7)	5 (±8)
Mg		4 (±8)
Mn	4 (±8)	5 (±13)
Mo	16 (±43)	
Na		6 (±15)
Ni	3 (±4)	
P	9 (±35)	
Pb	2 (±5)	
Rb	1 (±1)	
S	5 (±13)	2 (±2)
Sb	17 (±33)	
Si		5 (±12)
Sr	2 (±4)	4 (±6)
U	10 (±29)	
Zn	5 (±10)	

[1] High-resolution–inductively coupled plasma mass spectrometry

[2] Inductively coupled plasma–optical emission spectrometry

Table 9. Average sequential sampling precision (%).

Species	Analysis	Precision[1]
Ba	ICP-OES	96.5
Br	IC	99.3
Ca	ICP-OES	96.4
Cl	IC	99.6
Cu	HR-ICPMS	87.7
F	IC	97.6
Fe	HR-ICPMS	66.4
Fe	ICP-OES	71.6
K	HR-ICPMS	96.4
K	ICP-OES	93.7
Li	ICP-OES	90.9
Mg	ICP-OES	96.3
Mn	HR-ICPMS	92.9
Mn	ICP-OES	76.4
Mo	HR-ICPMS	96.3
Nitrate (NO_3^-)	IC	92.6
Na	ICP-OES	96.0
Ni	HR-ICPMS	88.4
Pb	HR-ICPMS	68.2
S	ICP-OES	96.9
Sulfate (SO_4^{2-})	IC	98.0
Si	ICP-OES	91.5
Sr	HR-ICPMS	97.1
Sr	ICP-OES	96.3
Zn	HR-ICPMS	70.9

[1] Precision = (100 – 100*(absolute value (first sequential sample – second sequential sample)/average))

Table 10. Summary of river and PDWS sampling site field blanks (mg/L).

	N	% detected	Mean	Standard Deviation	Median	Max	min
Fluoride	36	33	0.00600	0.00452	0.00475	0.0268	0.0024
Chloride	102	95	0.0814	0.0582	0.0679	0.334	0.0228
Bromide	0	0				0	0
Sulfate	87	80	0.0114	0.0123	0.0061	0.055	0.0007
Nitrate	95	87	0.0307	0.0325	0.0227	0.186	0.004
Lithium	2	2	0.0027	0	0.0027	0.0027	0.0027
Sodium	104	95	0.0292	0.0309	0.0235	0.168	0.0018
Ammonium	102	94	0.0142	0.0102	0.0120	0.0414	0.0002
Potassium	63	59	0.0281	0.0271	0.0165	0.156	0.0119
Magnesium	66	62	0.0129	0.0140	0.0097	0.0529	0.0045
Calcium	80	76	0.0235	0.0189	0.0226	0.135	0.0003

Table 11. Summary of CWTF sampling site field blanks (mg/L).

	N	% detected	Mean	Standard Deviation	Median	Max	min
Fluoride	16	47.1	0.00476	0.00183	0.00445	0.0075	0.0027
Chloride	30	88.2	1.02	3.21	0.121	12.8	0.0246
Bromide	0	0				0	0
Sulfate	4	11.8	0.0394	0.0423	0.0394	0.0762	0.0026
Nitrate	22	64.7	0.0200	0.0289	0.00445	0.0985	0.0022
Lithium	28	82.4	0.0956	0.226	0.0322	0.892	0.009
Sodium	1	2.94	0.0976		0.0976	0.0976	0.0976
Ammonium	6	17.6	0.00532	0.00421	0.0026	0.0108	0.0026
Potassium	0	0				0	0
Magnesium	30	88.2	0.0393	0.0461	0.0206	0.186	0.0006
Calcium	24	70.6	0.113	0.428	0.0188	2.12	0.0119

3.2 Quality Control Results for PMF Analysis

PMF results were evaluated using observed versus predicted regression and time series plots, and the displacement algorithm was used to evaluate the stability of the results. Known source discharge chemical signatures (fingerprints) were also used to evaluate the results as well as to interpret the measured source profiles. All of the results were numerically stable based on the displacement evaluation (no swaps at dQmax = 4), and the regression results for observed versus predicted had a coefficient of determination greater than 0.9 for the strong or non-down-weighted species.

3.3 Quality Assurance Assessments

QA assessments of field data collection and laboratory analyses were performed at multiple levels. A summary of reviews and outcomes is provided below.

- On-site QA assessment of field sampling procedures and adherence to protocols was performed via a Technical Systems Audit (TSA) on May 3, 2012. Field sampling activities were observed at five individual sites, and two corrective actions were implemented. The first action, implemented immediately, was to ensure that the scribe consistently repeated the sampling result (as called out by the researcher taking the reading) to confirm that correct measurements were being recorded in the field. The second corrective action added the logging of cooler temperatures during sample collection in addition to the logging of cooler temperature during shipment of the samples to Research Triangle Park, NC.
- On-site QA assessment of laboratory sample storage, processing, and analysis processes for IC, ICP-MS, and ICP-OES analysis was performed via a Technical Systems Audit (TSA) on July 16-17, 2012. Using bar codes and scanners to track samples was noted to be best practice. No corrective actions were deemed necessary based on the findings of this audit.
- Surveillance audits were conducted during pH and conductivity measurements (February 22, 2013), IC analysis (March 5, 2013), ICP-OES analysis (May 9, 2013), and HR-ICPMS analysis (February 19, 2014) prior to performance evaluation sample analysis. The assessments found that protocols were being properly implemented, and no corrective actions were deemed necessary.
- Performance evaluation samples were analyzed using blind samples obtained from a third party vendor (ERA) for the conductivity (June 14-15, 2013), IC (June 14-15, 2013), ICP-OES (June 19, June 27, and July 1, 2013), and HR-ICPMS analyses (February 20, 2014). All samples analyzed were within the acceptance limits except for fluoride for the IC analysis, which was approximately 1.5% below the acceptance range. All fluoride concentrations were flagged as being only estimated values.
- The analytical laboratory performed ongoing review of calibration, continuing calibration verification checks, QC recovery and background assessments, and instrumental performance parameters. Any samples identified by QC as being out of range were reanalyzed or flagged as needed.
- Analytical laboratory results were always QA reviewed by the analyst to ensure that the results were complete and accurate. QC results were summarized and examined to ensure overall data quality objectives were met.
- Audits of data quality (ADQs) were performed on the IC pH/conductivity data (July 2013), IC data (August/September 2013), ICP-OES data (February 2014 and March/April 2014), and HR-ICPMS data (April 2014). The ADQs helped to ensure that the measurement data were

accurately transcribed into data analysis files, calculations were correctly performed, and data qualifiers (flags) were appropriately assigned. All findings that may have potentially affected data quality were either addressed immediately during the audit, or prior to use of the data in any report. Any data that did not meet the designated quality criteria were not used, or were qualified accordingly.

4. RESULTS AND DISCUSSION

A total of 117 river and PDWS intake samples were collected during summer (July 5–19, 2012) and 114 samples were collected during fall (September 19–October 4, 2012). In addition, 47 samples were collected from CWTFs, and 71 outfall or source samples were collected with two to four samples for each source type at a facility. River and outfall samples were analyzed using conductivity, IC, ICP-OES, and HR-ICPMS. The concentration data were analyzed with EPA PMF, and the results were compared to measured outfall profile concentrations and Br/Cl ratios, which are indicative of sources (Andreasen and Fleck 1997, Davis *et al.* 1998). Species that were quantifiable in approximately 90% or more of the Allegheny or Blacklick downstream samples (S03, S04, S05) included: bromide (IC), chloride (IC), fluoride (IC), nitrate (IC), sulfate (IC), barium (ICP-OES and HR-ICPMS), calcium (ICP-OES), iron (ICP-OES and HR-ICMPS), potassium (ICP-OES and HR-ICMPS), lithium (ICP-OES), magnesium (ICP-OES), manganese (ICP-OES and HR-ICPMS), sodium (ICP-OES), sulfur (ICP-OES), silicon (ICP-OES), strontium (ICP-OES and HR-ICMPS), aluminum (HR-ICPMS), copper (HR-ICPMS), molybdenum (HR-ICPMS), nickel (HR-ICPMS), lead (HR-ICPMS), rubidium (HR-ICPMS), antimony (HR-ICPMS), and zinc (HR-ICPMS). These species were considered for the PMF analysis except for Ba, which could form barium sulfate ($BaSO_4$), a salt, in the high sulfate concentrations on the Blacklick Creek and would potentially precipitate out of solution and settle into sediments before reaching the downstream sites (Lee *et al.* 2002).

The CWTF contribution as well as other sources were quantified using a comprehensive source apportionment modeling approach including: (i) developing chemical source profiles, or fingerprints, for all sources located upstream of two PDWS intakes on the Allegheny River by collecting outfall samples from specific sources within facilities and combined river outfalls; (ii) collecting and chemically characterizing river samples from multiple sites upstream and downstream of CWTFs, generating stations, industrial facilities, and at the PDWS intakes, and (iii) using the EPA implemented Positive Matrix Factorization (PMF) source apportionment model to quantify the contribution of sources to anion levels at the PDWS intakes. Although the two PDWS intakes in this study were both on the Allegheny River, their relative location with respect to the numerous source discharges warranted a source apportionment approach, since the approach is not reliant on the many unavailable model specifications needed by other modeling approaches such as deterministic dispersion modeling. One PDWS intake is in the upper reaches of the Allegheny River 51 km downstream of a CWTF with few tributaries and other discharges between, while the other is located in the middle reaches of the river 1.3 km downstream from a river confluence with a major tributary (Kiskiminetas River). The Kiskiminetas River drains a catchment area containing a complex mixture of discharge sources and elevated contaminant concentrations. This second PDWS intake was the sampling location with the highest raw water intake bromide concentration, and it was located downstream of several CWTFs. The second PDWS intake represents a challenge for river transport modeling due to the complex nature of the larger catchment basin, numerous source discharges, intermittent discharges, and confluence mixing dynamics.

4.1 River Sample Composition

Upstream and downstream differences in halide concentrations between the Allegheny and Blacklick study domains were evaluated to assess whether the combination of sources and flow rates impacted the observed concentrations. Species concentrations for all upstream and downstream samples are summarized and presented in Table 12. Bromide concentrations upstream of the CWTFs on the

Table 12. Downstream (S03, S04, S05) and upstream (S01) concentrations (mg/L).

		Allegheny Sites		Blacklick Sites	
Species	Statistic	Downstream	Upstream	Downstream	Upstream
Br	mean (std)	0.0925 (0.044)	0.0718 (0.0254)	0.432 (0.71)	0.0696 (0.0175)
(IC[1])	median (IQR)	0.0827 (0.0425)	0.0721 (0.0446)	0.187 (0.307)	0.0726 (0.0287)
	min - max	0.037 - 0.28	0.0329 - 0.117	0.0635 - 4.36	0.0352 - 0.0889
Ca	mean (std)	17.8 (1.72)	15.2 (1.19)	52.8 (26.2)	56.3 (19.7)
(ICP-OES[2])	median (IQR)	17.8 (2.7)	15.3 (1.4)	48.8 (35.3)	53.8 (26.4)
	min - max	13.8 - 21.6	12.4 - 17.6	23.3 – 168	25.6 - 89.9
Cl	mean (std)	23.7 (4.56)	20.8 (2.93)	64.6 (97.5)	19.6 (1.79)
(IC)	median (IQR)	22.8 (4.35)	21 (4.9)	35.7 (29)	19.6 (2.2)
	min - max	16.6 - 41.6	16.2 - 25.8	21.6 – 621	14.1 - 23.2
Fe	mean (std)	0.192 (0.107)	0.176 (0.0903)	0.943 (3.15)	2.6 (4.43)
(HR-ICPMS[3])	median (IQR)	0.146 (0.125)	0.154 (0.097)	0.336 (0.402)	1.33 (1.39)
	min - max	0.0767 - 0.541	0.071 - 0.384	0.0791 – 32	0.479 - 23.7
Mg	mean (std)	3.63 (0.285)	3.09 (0.191)	15 (6.28)	15.7 (5.31)
(ICP-OES)	median (IQR)	3.64 (0.44)	3.11 (0.25)	13.2 (11.8)	16.1 (8.1)
	min - max	3.02 - 4.27	2.56 - 3.44	6.93 - 27.8	6.79 - 24.4
Mn	mean (std)	0.0716 (0.0433)	0.0607 (0.0326)	0.281 (0.303)	0.808 (0.207)
(HR-ICPMS)	median (IQR)	0.0548 (0.0685)	0.0536 (0.059)	0.136 (0.3)	0.913 (0.34)
	min - max	0.0215 - 0.191	0.0181 - 0.123	0.0279 - 1.02	0.417 - 1.06
NO3	mean (std)	0.42 (0.309)	0.59 (0.366)	2.56 (1.05)	1.83 (0.384)
(IC)	median (IQR)	0.335 (0.535)	0.545 (0.558)	2.39 (1.72)	1.8 (0.34)
	min - max	0.0178 - 1.2	0.0188 - 1.26	0.823 - 4.75	1.04 - 2.76
Na	mean (std)	12.6 (1.93)	11.2 (1.45)	38.7 (40.2)	24.3 (8.11)
(ICP-OES)	median (IQR)	12.3 (2)	11.5 (2.3)	28.7 (19.7)	23.3 (10.7)
	min - max	9.27 – 20	8.18 - 13.5	15.2 – 255	13.9 - 40.7
SO4	mean (std)	9.06 (0.783)	7.47 (0.341)	172 (92.7)	244 (87.3)
(IC)	median (IQR)	8.97 (0.94)	7.49 (0.31)	157 (169)	242 (133)

		Allegheny Sites		Blacklick Sites	
Species	Statistic	Downstream	Upstream	Downstream	Upstream
	min - max	7.75 - 11.7	6.78 - 8.6	46.2 – 370	93.9 – 377
Si	mean (std)	0.958 (0.397)	0.961 (0.335)	2.26 (1.29)	4.24 (0.842)
(ICP-OES)	median (IQR)	0.86 (0.631)	1.01 (0.472)	1.91 (1.31)	4.52 (1.56)
	min - max	0.198 - 1.87	0.134 - 1.55	0.531 - 5.47	2.7 - 5.21
Sr	mean (std)	0.0814 (0.0166)	0.0655 (0.00886)	0.677 (1.23)	0.341 (0.118)
(ICP-OES)	median (IQR)	0.077 (0.0167)	0.0641 (0.0136)	0.388 (0.386)	0.341 (0.177)
	min - max	0.0607 - 0.144	0.0483 - 0.0838	0.132 - 7.55	0.151 - 0.531

[1] Ion chromatography; [2] Inductively coupled plasma–optical emission spectrometry; [3] High-resolution–inductively coupled plasma mass spectrometry.

Allegheny River and Blacklick Creek were not significantly different during the low flow sampling campaigns (summer and fall 2012), with median concentrations of 0.072 and 0.073 mg/L, respectively. The overall distributions of downstream concentrations were affected by the intermittent CWTF discharges due to each facility's operation schedule, with CWTF_A discharging on 17 days and CWTF_B discharging on 15 days of the total 25 sampling days. Median bromide concentrations at the downstream sites (S03, S04, S05) were significantly higher on the Blacklick (0.187 mg/L) compared to the Allegheny (0.083 mg/L). The relatively high downstream site bromide impacts in the Blacklick study domain were a function of mean CWTF discharge volumes during the study period from CWTF_A (75,116 gallons/day) and CWTF_B (58,551 gallons/day), discharging into the Allegheny River (2,702 cfs) and Blacklick Creek (68 cfs), respectively, with their large differences in water discharge rate (Figure 6) and resulting dilution capacities. Median chloride concentrations were significantly higher at the Blacklick downstream sites (35.7 mg/L) compared to upstream (19.6 mg/L). Chloride concentrations at the Allegheny downstream sites were also significantly higher but the magnitude of absolute difference (~4 mg/L) was smaller than the Blacklick observations. The aggregate mean chloride concentration of 64.3 mg/L for the Blacklick downstream sites reflects the relatively high chloride concentrations measured at site S03_B during CWTF_B discharge days. The Blacklick sites also had much higher sulfate concentrations (median downstream=157 mg/L) compared to the Allegheny sites (median downstream=8.97 mg/L), indicating higher AMD contributions on the Blacklick. Iron and Mn were highest at the Blacklick upstream site due to AMD, and Si was also elevated at this site due to the influence of runoff and rapid changes in river discharge rate in the creek. Although Ca and Na were elevated in the CWTF and FGD source samples and CWTFs discharge significant levels of Sr (Table 13), these species did not have large differences between Blacklick upstream (median Ca=53.8 mg/L, median Na=23.3 mg/L, median Sr=0.341 mg/L) and downstream sites (median Ca=48.8 mg/L, median Na=28.7 mg/L, median Sr=0.388 mg/L). High peak concentrations relative to the mean were observed for most of the species indicating variability in natural or industrial sources influencing the sites. The maximum bromide concentration for each sampling domain was measured at site S03 closest to each respective CWTF discharge, with 4.36 mg/L and 0.28 mg/L observed on the Blacklick Creek and Allegheny River, respectively.

Twelve target elements were selected for the species summary and PMF analysis (bromide, chloride, nitrate, sulfate, Ca, K, Mg, Na, Si, Sr, Fe, and Mn), because they were valid for almost all of the samples, were present in the high bromide sources, and also captured sediment species. The Appendix Tables A1 and A2 have a summary of these species concentrations for each site as well as the number of valid samples. Sequential samples were included in the summary, which accounts for the increased number of samples at S03_A, S04_B, S05_A, and S05_B.

A summary of the PDWS intake (raw water) bromide, chloride, nitrate, and sulfate concentrations are shown in Table 14 and the median bromide concentration increased 0.0468 mg/L from S05_A to S05_B due to a combination of sources downstream of S05_A and the confluence of the Allegheny and Kiskiminetas Rivers. The largest difference in concentrations between the intakes was found for sulfate which increased from a median of 9.58 mg/L at S05_A to 82.6 mg/L at S05_B.

As expected the low river discharge period bromide concentrations presented in Table 14 are significantly higher than the concentrations measured at the same sites during the spring (high river discharge; April 30 – May 14, 2012) with median concentration of 0.038 and 0.035 mg/L for S05_A and S05_B, respectively.

Table 13. Average Br/Cl ratio and key species concentrations (mg/L) for measured source profiles.

Source	N[1]	Br/Cl Ratio	Br	Ca	Cl	NO_3	Na	SO_4	Sr
CWTF[2]_A	23	0.0111	684	9420	61700	<16.9	23800	218	395
CWTF_B	23	0.0097	808	12100	83200	<16.9	31700	577	1010
CWTF_C	1	0.0100	658	10266	66110	<16.9	21900	487	247
Cooling Towers	5	0.0030	0.651	248	216	28.5	162	809	1.12
Treated FGD[3]	3	0.0146	187	2780	12800	183	844.0	2080	23.7
Demineralizer	1	0.0001	<0.006	27.9	82.6	4.23	2290	2100	0.130
Treated Coal Pile Runoff	2	0.0031	0.169	136	54.0	10.9	225	902	0.533
Treated Coal Ash Wastewater	2	0.0247	2.48	384	101	11.4	126	1190	2.29
Treated Industrial Wastewater	3	0.0010	0.259	396	254	235	245	482	0.374
POTW[4]	4	0.0003	0.0418[5]	34.3	138	98.5	96.2	24.5	0.0999
Treated AMD[6] and Oil and Gas Wastewater	1	0.0063	5.34	684	844	<4.06	629	2420	6.68
CBM[7]	2	0.0077	35.1	284	4560	0.875	2290	358	8.80
AMD	1	0.0058	0.124	92.9	21.4	<0.0169	10.8	469	0.555
Oil Seep	1	0.0119	<0.06	65.7	5.04	<0.169	7.66	7.36	0.312
Coal Mine Runoff	1	0.0055	1.76	75.3	322	15.9	536	787	0.606

[1] for CWTFs, N is the number of samples collected during summer and fall campaigns; for all other source types, N is the number samples collected at different facilities.

[2] centralized waste treatment facility

[3] flue gas desulfurization

[4] publicly owned treatment works

[5] one POTW had an average bromide concentration of 0.0418 mg/L, and the three other POTW's had bromide concentrations below the bromide method detection limit of 0.0063 mg/L.

[6] acid mine drainage

[7] coal bed methane

Table 14. PDWS intake low flow intake concentrations (mg/L).

Site	Statistic	Bromide	Chloride	Nitrate	Sulfate
S05_A	mean	0.0867	23.6	0.327	9.62
	median	0.0852	23.5	0.284	9.58
	IQR[1]	0.0436	4.45	0.477	0.960
	maximum	0.166	32.1	1.20	10.9
S05_B	mean	0.143	30.4	2.05	82.2
	median	0.132	29.7	2.07	82.6
	IQR	0.0455	6.20	1.12	40.9
	maximum	0.205	37.6	3.88	129

[1] Interquartile range (75th–25th percentile)

4.2 Source Profiles

Inorganic species compositions of sources must be known in order to identify the PMF factor profiles. Using the same extraction and analysis techniques for both river samples and source samples allowed for direct comparison of PMF-generated profiles and measured profiles. However, only CWTF and AMD source profile information had been previously published (Ferrar *et al.*2013; Warner *et al.* 2013). Multiple source samples from facilities discharging to the surface waters in this study were critical for (1) an evaluation of source variability and (2) calculation of an average profile that was representative of the source contributions at the PDWS intakes.

- In light of the voluntary diversion of the Marcellus waste away from CWTFs discharging to surface waters (PADEP 2011b; Wilson and Van Briesen, 2012), we characterized the 2012 wastewater treated by the CWTF_A and CWTF_B as to whether or not it originated from a hydraulically fractured well. The characterizations were based on our review of the conventional and unconventional wastewater annual reports of treated waste provided to the Pennsylvania Department of Environmental Protection (PA DEP 2014a). The Pennsylvania Department of Environmental Protection well waste classification is based on the formation that produces the oil or gas. Conventional waste is derived from a formation above or below the Elk Sandstone. Unconventional waste results from a geologic shale formation. Both conventional and unconventional wells typically require stimulation by hydraulic fracturing although much greater volumes of fluid are required for unconventional wells (PA DEP 2012). The total volume of unconventional wastewater treated during the course of this study was low and CWTF_A did not have any reported unconventional wastewater while CWTF_B had a total of 1,585 barrels. Conventional wastewater was further classified as stimulated or hydraulically fractured, not fractured, or unknown based on a comprehensive review of over 7,250 well file records in the Pennsylvania Department of Environmental Protection Internet Record Imaging System (PA DEP 2014c). The total volumes of wastewater (drilling fluid waste, fracking fluid waste, produced fluid) treated by the CWTFs during this study were 572,464 barrels and 419,673 from CWTF_A and CWTF_B, respectively (Table 15). Less than 12% of the wastewater was classified as unknown due to missing information in the well completion report. Of the total treated oil and gas wastewater treated, 76% (CWTF_A) and 92% (CWTF_B) were determined to be from hydraulically fractured wells. In 2012, the CWTFs also treated basic sediment (CWTF_A total barrels = 110, CWTF_B total barrels = 5,808), drilling fluid (CWTF_A total barrels = 46,454.40, CWTF_B total barrels = 12,324), and servicing fluid (CWTF_A total barrels = 300, CWTF_B total barrels = 707). During the study period, both CWTFs accumulated the oil and gas wastewater from individual deliveries into large on-site storage tanks prior to batch treatment. As a result, the wastewater from numerous individual wells was combined prior to treatment and discharge. Accordingly, although these data suggest that there is a high probability that hydraulically fractured waste water was being treated during the sampling period, we do not have specific information as to the wastewater being discharged on days of sampling.

Table 15. CWTF wastewater volumes treated in 2012 (barrels).

	CWTF_A		CWTF_B	
Hydraulically Fractured	Total	Percent	Total	Percent
No	69,451	12 %	16,097	4 %
Unknown	68,246	12 %	19,144	5 %
Yes	434,766	76 %	384,431	92 %
All	572,464	100 %	419,673	100 %

Table 13 provides a summary of the source sample concentrations for bromide, chloride, nitrate, sulfate, Na, Ca, Sr, and Br/Cl ratio. The Br/Cl ratio can be used to identify brine or salt sources (Davis *et al.* 1998), and it was used in this study to compare the PMF and measured source profiles. Outfalls typically capture wastewater from multiple processes as described in the NPDES permits, and the wastewater is generally treated prior to discharge to meet discharge limits. Other water contaminant source types include AMD from historic and ongoing mining activities, and natural oil seepage. Road salt has been reported as a significant source of chloride (Kelly *et al.* 2010), but this source was not expected to have a significant contribution, since this report focuses on summer and fall seasons when roadway deicing materials are not typically applied. Furthermore, bromide concentrations in the roadway deicing materials used in this region were extremely low (0.0033% and 0.0063% by weight) for two road salt piles sampled near S04_B. Finally, samples were collected from two ground water-supplied PDWS facilities to characterize the ground water that could contribute to the Allegheny River. One of the water facilities was supplied by three wells, and the other was supplied by four. The mean concentrations were 0.241, 62.7, and 10.4 mg/L for bromide, chloride, and sulfate, respectively. Ground water can hydraulically exchange with surface water, and this potential source of bromide was not identified in the source apportionment analysis. This result was expected since background bromide concentrations in the Allegheny have been reported to be low (States *et al.*, 2013), and the upper and middle reaches of the river flow over locally-derived river sediment overlying thick layers of glacial outwash (sand and gravel).

Separation of sources requires that sources have a difference in relative species compositions and that their contribution varies at the multiple sampling sites. Two key sources of bromide and chloride were CWTFs and FGDs, with FGDs having higher sulfate and nitrate concentrations, and CWTFs having higher Sr concentrations. Both bromide and chloride are conserved in surface waters due to their solubility (Davis *et al.* 1998). Sources with elevated sulfate concentrations included treated and untreated AMD, CBM, treated coal ash and coal pile runoff, active coal mine runoff, and cooling towers. CBM wastewater and untreated AMD also had high Fe concentrations. The oil seepage, however, had elevated

Fe and low sulfate. Treated AMD was low in Fe (0.0464 mg/L) compared to untreated AMD (36.0 mg/L). The industrial metals treated wastewater source had more unique species with elevated F (5.09 mg/L) and Mo (1.45 mg/L), and low Fe (0.06 mg/L) due to the type of industries. POTWs had a nitrate concentration of 98.5 mg/L and only one of the POTWs had measurable bromide concentrations (the facility located upstream of S01_A). The two samples collected from that facility had similar bromide concentrations (0.406 and 0.431 mg/L), which were low compared to a nearby CWTF (657.6 mg/L). These sources combine in the surface water after they are discharged (Figure 7), and the ratios of the measured profiles species along with the known outfall locations were critical for evaluating the PMF results.

The two highest sources of bromide were the CWTF (average of 746 mg/L) and FGD (187 mg/L). The Br/Cl ratios for these two sources were different, with average ratios of 0.0104 and 0.0146 for CWTF (A and B only) and FGD, respectively. Upper Pennsylvanian and Monongahela formation bituminous coal (e.g., Pittsburgh #8) that is currently being burned by coal-fired power plants in this region of the U.S. has naturally high levels of bromine (Seere and Lee, 2009). The FGD had higher concentrations of nitrate and sulfate compared to the CWTF. However, other sources contribute to the Blacklick sampling sites including nitrate from POTWs and sulfate from AMD (Figure 4, Figure 7). The CWTF Br/Cl ratio was similar to the ratio of 0.0080 reported by Warner *et al.* (2013) and the ratio of 0.0091 reported by Hladik *et al.* (2014). Discharge schedules for CWTF_A were between 06:00 and 13:00 EST Monday through Friday, while CWTF_B discharges were more sporadic and ranged from nine to 39 hours based on river conductivity measurements. The FGD discharges were continuous for two of the three generating stations; the other had a batch treatment process.

Comparison of coal-fired generating discharges to other studies was limited due to the lack of published data. Wilson *et al.* (2013) reported that there was no statistically significant difference in total dissolved solids (TDS) between coal-fired power plant wastewater and coal mine discharge. The similar concentrations in the sources indicate either that they were collected at non-FGD power plants, or that the FGD discharge was not captured in the sample. Our study results show that treated coal pile waste had much lower concentrations of bromide and chloride (bromide = 0.169 mg/L, chloride = 136 mg/L) compared to FGD wastewater (bromide = 187 mg/L, chloride = 2,780 mg/L). In addition, a coal mine discharge sample was collected as part of this study, and the conductivity was 8,273 µS/cm, compared to 29,725 µS/cm for one of the FGDs.

4.3 PMF Receptor Modeling Results

River sampling data from multiple sites were used in the PMF analysis to provide a range of source contributions and to take advantage of the study design, which focused on selecting sites that were upstream and downstream of CWTFs and other sources. Species concentration data for all river sampling sites were initially combined together in the PMF analysis; however, the magnitude of the CWTF, POTW, and AMD contributions for the Blacklick sites dominated the source contributions at the Allegheny sites. This was due to the low discharge flow rate of the Blacklick Creek (68 cfs) compared to the Allegheny River (2,702 cfs), and the substantial AMD impairment of the Blacklick Creek (Sams and Beer 2000).

The Allegheny and Blacklick sampling site data were then evaluated separately by PMF to determine the source contributions for each set of sample sites, excluding S05_B, which was on the Allegheny River.

Lastly, in order to understand the source contributions to the PDWS intakes, PMF was used to evaluate the combined Allegheny and Blacklick downstream sites and PDWS samples (S05_A and S05_B). Twelve species were included in all PMF analyses: bromide, chloride, nitrate, sulfate, Ca, K, Mg, Na, Si, Sr, Fe, and Mn. Tables with the PMF settings and Q values for the three analyses are provided in the Appendix Tables B1 to B3.

PMF analysis of species concentrations for the Allegheny sites (S01_A, S03_A, S04_A, and S05_A) found four factors, identified as CWTF, sediments, POTW, and AMD based on the source profiles in Table 13 and Br/Cl ratios. Measured source profiles were also used to determine if any of the PMF factors contained multiple sources. Bromide in the PMF POTW factor exceeded the measured source profile, indicating that PMF was not able to definitively separate the source based only on the measurement data. When this factor was constrained using the Br/Cl ratio in Table 13, the bromide level decreased in the POTW source and Q increased 0.06%, indicating a small change from the optimum PMF solution. This constrained result was used, and the resultant median bromide concentration at the PDWS intake (S05_A) was found to be 0.0553 mg/L from the CWTF, with no contributions from the POTW or sediments. The PMF results also showed downstream transport of bromide from a CWTF that contributed 0.0743 mg/L to S01_A. Additional bromide was contributed by CWTF_A resulting in a combined contribution of 0.0803 mg/L at S03_A. Downstream transport was also observed with nitrate from POTWs. S01_A had a nitrate concentration of 0.538 mg/L from multiple upstream POTWs. Additional nitrate was contributed by a POTW upstream of site S03_A, resulting in 0.454 mg/L at that site. AMD sulfate contributions increased from S01_A (2.19 mg/L) to S05_A (5.20 mg/L,) which follows the increase in bituminous coal mining activity near the downstream sites (PA DCNR 2014).

Three factors were found in the PMF analysis of river sample data for the Blacklick sites (S01_B, S03_B, and S04_B) which were identified as CWTF, POTW, and AMD. The PMF POTW profile had elevated bromide, which was partially removed with the same constraint as used for the Allegheny analysis; however, the bromide remained high in the profile (0.0626 mg/L), and the AMD profile contained bromide (0.0349 mg/L) as well. PMF results demonstrated that the CWTF_B discharge had a large contribution to the bromide source concentrations at the immediate downstream site (S03_B). The median was determined to be 0.231 mg/L with an IQR of 0.817 mg/L and a maximum of 4.55 mg/L. These high and variable concentrations were due to the low flow in the Blacklick Creek which did not significantly dilute the CWTF discharge. An FGD source was not identified in the Blacklick site analysis even though the FGD source had high bromide levels and two generating stations with FGDs were discharging into the Blacklick domain. The PMF results were investigated by comparing discharge rates using the Pennsylvania Department of Environmental Protection Discharge Monitoring Records and the CWTF and FGD profile concentrations in Table 13 (PA DEP 2014b). Average daily discharge of bromide from two FGD discharges (396 kg/day) was higher than CWTF_B (161 kg/day), and the bromide contributed from these discharges and from the AMD treatment and CWTF facility was quantified at the sampling site after the Conemaugh Dam (S04_B). Based on the mass discharge analysis and the CWTF profile contributing the majority of the bromide, the CWTF source was capturing the combined CWTF and FGD sources.

Based on the results from each river, the PMF analysis of the combined Allegheny and Blacklick downstream sites (S03_A, S04_A, S05_A, S04_B, and S05_B, but excluding site S03_B), was used to evaluate the FGD and CWTF contributions on the two PDWS intakes. This combination of sites also provides a focus on the sources contributing to the PDWS intakes, since it only uses the Blacklick sites downstream of the Conemaugh Dam (S04_B and S05_B; Figure 7). The combined analysis was the focus of this report, and the steps used to interpret the PMF are shown below.

1. Select the number of factors based on the number of expected sources and evaluate increasing or decreasing the number of factors.
2. Evaluate the observed vs. predicted concentrations to evaluate if the residual (observed – predicted) is similar across sites and the regression statistics.
3. Evaluate the stability of the solution using the displacement algorithm and reduce or increase the number of factors if the solution is not stable. Assess the minimum to maximum uncertainty range provided by the displacement algorithm.
4. Compare the PMF factors to measured profiles and identify the sources using species ratios.
5. Evaluate the source contributions at each sampling site to determine if the source contributions increase downstream of outfall or are not present at a site, such as the Allegheny sites (S01_A to S05_A) that were not downstream of a FGD.
6. Evaluate different site combinations in a multiple site dataset and evaluate if a PMF profile represents multiple sources.

The observed vs. predicted bromide concentration plot for each site shows excellent agreement, as shown in Figure 8. Data from each of the sampling sites are displayed by site and sorted by date. The observed versus predicted regression statistics for all of the species in Table 16 show good agreement, except for Fe and Mn which were categorized as weak to reduce their influence on the results.

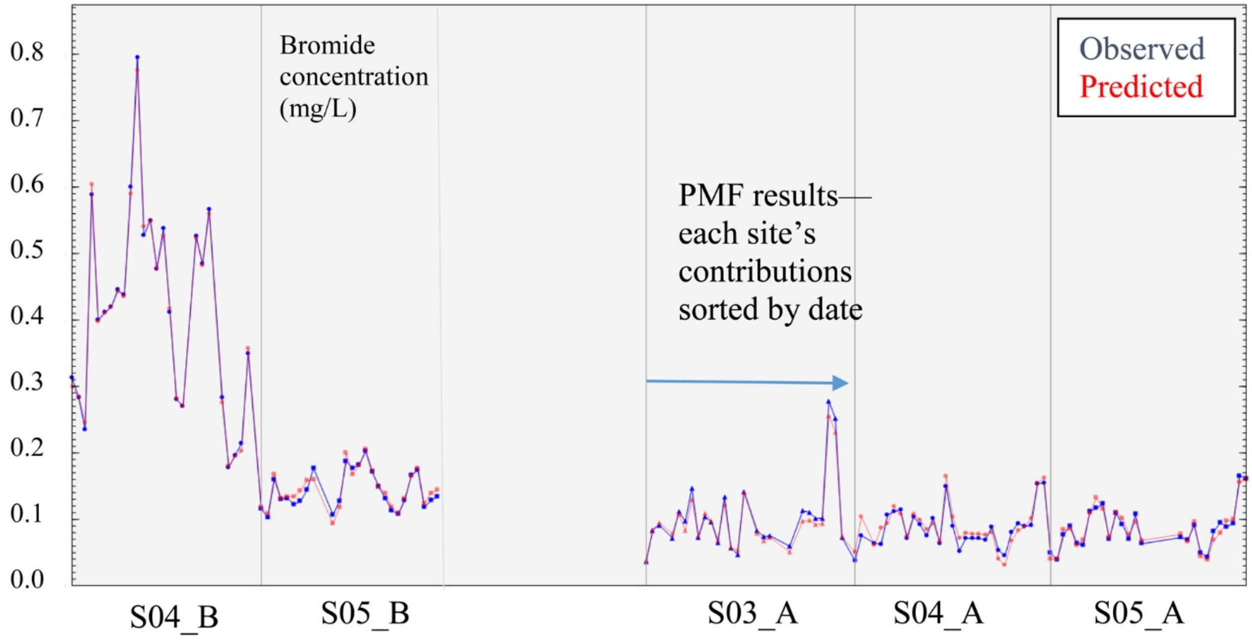


Figure 8. EPA PMF observed (blue) vs. predicted (red) time series plot for bromide by site (mg/L).

Table 16. Positive Matrix Factorization measured versus predicted regression statistics.

Species	Intercept	Slope	Coefficient of Determination
Br_IC[1]	0.002	0.990	1.00
Cl_IC	-0.036	1.001	1.00
NO_3_IC	-0.023	0.925	0.90
SO^4_IC	-0.085	1.002	1.00
Ca_ICP-OES[2]	1.338	0.943	0.99
K_ICP-OES	0.064	0.957	0.98
Mg_ICP-OES	0.112	0.980	1.00
Na_ICP-OES	0.052	0.994	0.99
Si_ICP-OES	0.035	0.956	1.00
Sr_ICP-OES	0.006	0.944	0.98
Fe_HR-ICPMS[3]	0.132	0.193	0.44
Mn_HR-ICPMS	0.042	0.282	0.55

[1] Ion chromatography

[2] Inductively coupled plasma–optical emission spectrometry

[3] High-resolution–inductively coupled plasma mass spectrometry

The stability of the solution was first confirmed by evaluating the displacement output. A stable solution has zero swaps for all of the factors at the lowest displacement level. PMF factors were identified by comparing them to the measured profiles and the Br/Cl ratios. PMF profiles and Br/Cl ratios are shown for high bromide sources in Table 17 and low bromide sources in Table 18. Sources with low bromide concentrations (Table 17) had minimum displacement error estimates of zero, indicating they are not significant bromide sources. The AMD profile in Table 18 is from the Blacklick site PMF analysis since it was able to separate an AMD source. PMF source profiles represent the source fingerprint in the diluted river sample, so the concentrations are lower than the measured profiles. In addition, a sediment source type with Fe, Si, and Mn was found in PMF analyses.

The PMF profiles are displayed in Figure 9. Blue bars show the PMF profile species concentrations (mg/L), and red boxes show the percent of the species associated with the source. Normalized contribution (the average of the normalized contributions for a source = 1) time series by site are shown in Figure 10, and the contributions were evaluated to determine if the increase in the PMF contribution was consistent with known outfall locations. Measured source profiles, PMF profiles, and contribution time series were used to identify the four source types:

1. CWTF factor, characterized by high bromide and chloride and a Br/Cl ratio of 0.0066, compared to the measured profile average of 0.0104. In addition, it had low sulfate and nitrate concentrations. Peak bromide concentrations were observed at S04_B, which is downstream of two CWTFs.
2. FGD + AMD factor, characterized by: high bromide, chloride, sulfate, and nitrate; and a Br/Cl ratio 0.016, which was similar to the FGD measured profile average of 0.0146 but higher than the AMD ratio of 0.0058. This factor may also be impacted by coal ash wastewater, which has a Br/Cl ratio of 0.0247. Generating stations, plus AMD from historic mining and coal mining.

Table 17. Positive Matrix Factorization high-bromide source type profiles and minimum and maximum estimates from the displacement algorithm (mg/L).

	Combined CWTF[1] Br/Cl = 0.007			Combined FGD + AMD [2] Br/Cl = 0.016		
Species	**Profile**	**Min**	**Max**	**Profile**	**Min**	**Max**
Br	0.0894	0.0745	0.135	0.068	0.0303	0.0790
Cl	13.5	11.0	21.1	4.24	0	6.16
NO_3	0	0	0.0330	0.662	0.189	0.887
SO_4	6.23	2.25	9.93	50.8	40.2	64.4
Ca	7.00	5.57	11.8	7.01	1.85	9.20
K	0.450	0.344	0.797	0.293	0	0.419
Mg	1.41	1.16	2.42	3.23	1.94	4.06
Na	6.14	4.99	9.97	4.21	1.34	5.319
Si	0	0	0.306	0.234	0.00489	0.429
Sr	0.0485	0.0392	0.0766	0.0822	0.0605	0.0999
Fe	0.0166	0.00928	0.0613	0.00491	0	0.0246
Mn	0.00226	0.000656	0.0209	0.00991	0	0.0161

[1] Centralized waste treatment facility

[2] Flue gas desulfurization and acid mine drainage

Table 18. Positive Matrix Factorization low-bromide source type profiles and minimum and maximum estimates from the displacement algorithm (mg/L).

	Combined POTW[1] Br/Cl = 0			Combined Sediment Br/Cl = 0			Blacklick AMD[2] Br/Cl = 0.0041		
Species	**Profile**	**Min**	**Max**	**Profile**	**Min**	**Max**	**Profile**	**Min**	**Max**
Br	0	0	27.6	0.00716	0	0.0456	0.0349	0.00	0.0444
Cl	25.6	17.2	52.1	5.82	1.59	13.9	8.45	3.453	9.69
NO_3	46.4	28.0	84.8	0	0	0.139	0.246	0.127	0.607
SO_4	12.8	0	36.3	2.07	0	11.2	110	101	127
Ca	34.7	25.7	53.2	5.12	2.26	10.4	24.2	21.3	27.7
K	40.0	29.2	63.0	0.379	0.148	0.767	1.59	1.43	1.84
Mg	27.9	17.0	43.4	1.14	0.751	2.28	6.14	5.40	7.66
Na	28.6	20.4	46.8	3.46	1.41	7.44	10.4	7.88	11.7
Si	18.3	0	38.7	0.785	0.626	1.16	2.18	2.05	2.27
Sr	15.3	6.91	30.7	0.0219	0.0139	0.0525	0.219	0.139	0.227
Fe	27.7	1.37	39.7	0.112	0.0839	0.174	0.257	0.243	0.262
Mn	9.95	0	26.7	0.0530	0.0423	0.0701	0.481	0.454	0.530

[1] Publicly owned treatment works

[2] Acid mine drainage

runoff contributed to all of the sites on the Blacklick to Kiskiminetas, and the high sulfate on this source may be due to a combination of the FGD and AMD sources.

3. Sediment factor, characterized by high concentrations of Si, Fe, and Mn. The variability in this source is associated with changes in the Allegheny River flow rate after rainfall.
4. POTW factor, characterized by high concentrations of nitrate, low bromide, and a Br/Cl ratio of zero, compared to the measured profile ratio of 0.0003. S04_B and the sites on the Allegheny had POTW contributions.

The PMF normalized contributions are multiplied by the PMF profiles to generate the sample source contributions. The POTW source in Figure 9 has a low bromide contribution with a concentration less than 0.001 mg/L in contrast to the bromide contributions for the CWTF, FGD + AMD, and sediment sources which are shown in Figure 11. The concentration range for each of the time series plots is different with the CWTF and FGD + AMD plots having similar ranges of approximately 0.4 mg/L and the sediment range is less than 0.02 mg/L. The highest combined bromide concentrations were observed at S04_B after the Conemaugh River Dam which is downstream of CWTF and FGD discharges. The CWTF and FGD + AMD bromide source contributions are similar for S05_B, while S05_A only has contributions from the CWTF source. The sediment source contributions are more uniform across all of the sampling sites.

PMF used the river sampling data to solve the chemical mass balance between measured species concentrations and source profiles by decomposing the speciated sample data into two matrices: factor or source contributions and profiles (Hopke 1991). Since the PMF profiles are based on the river samples, and the source concentrations have been diluted by the time they reach the sampling location, ratios are an ideal way to compare the measured profiles and the PMF source type profiles. Comparing the concentration patterns also helps confirm the sources, as shown in Figure 12. For example, the measured CWTF and PMF profiles have higher concentrations of chloride and sodium.

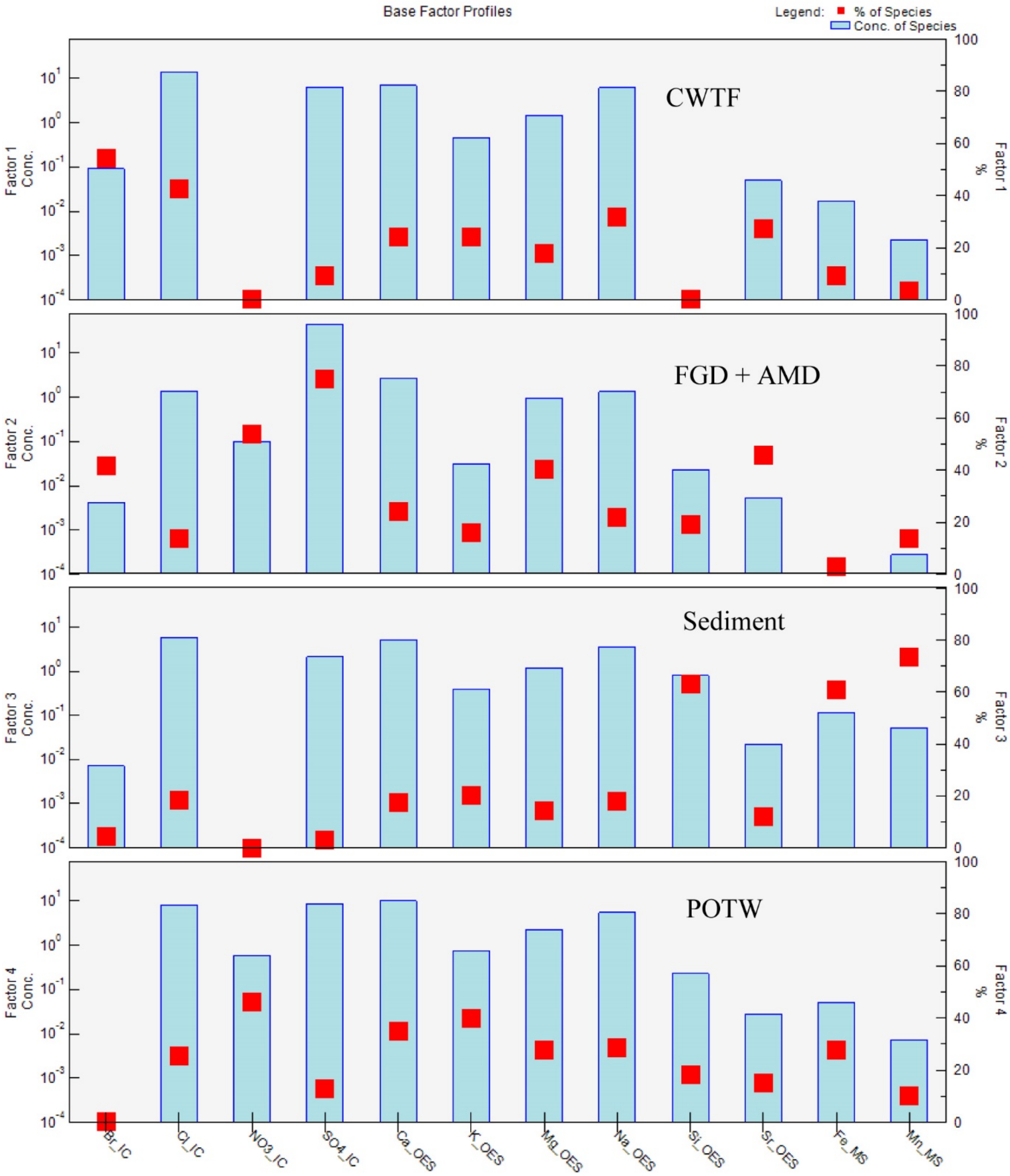


Figure 9. EPA PMF source profile plot showing the species concentration (left axis) and the percentage of species associated with each source (right axis). Blue bars show the PMF profile species concentrations (mg/L), and red boxes show the percent of the species associated with the source. The two PMF sources with significant bromide were CWTF and FGD+AMD sources with each source contributing over 40% of the bromide.

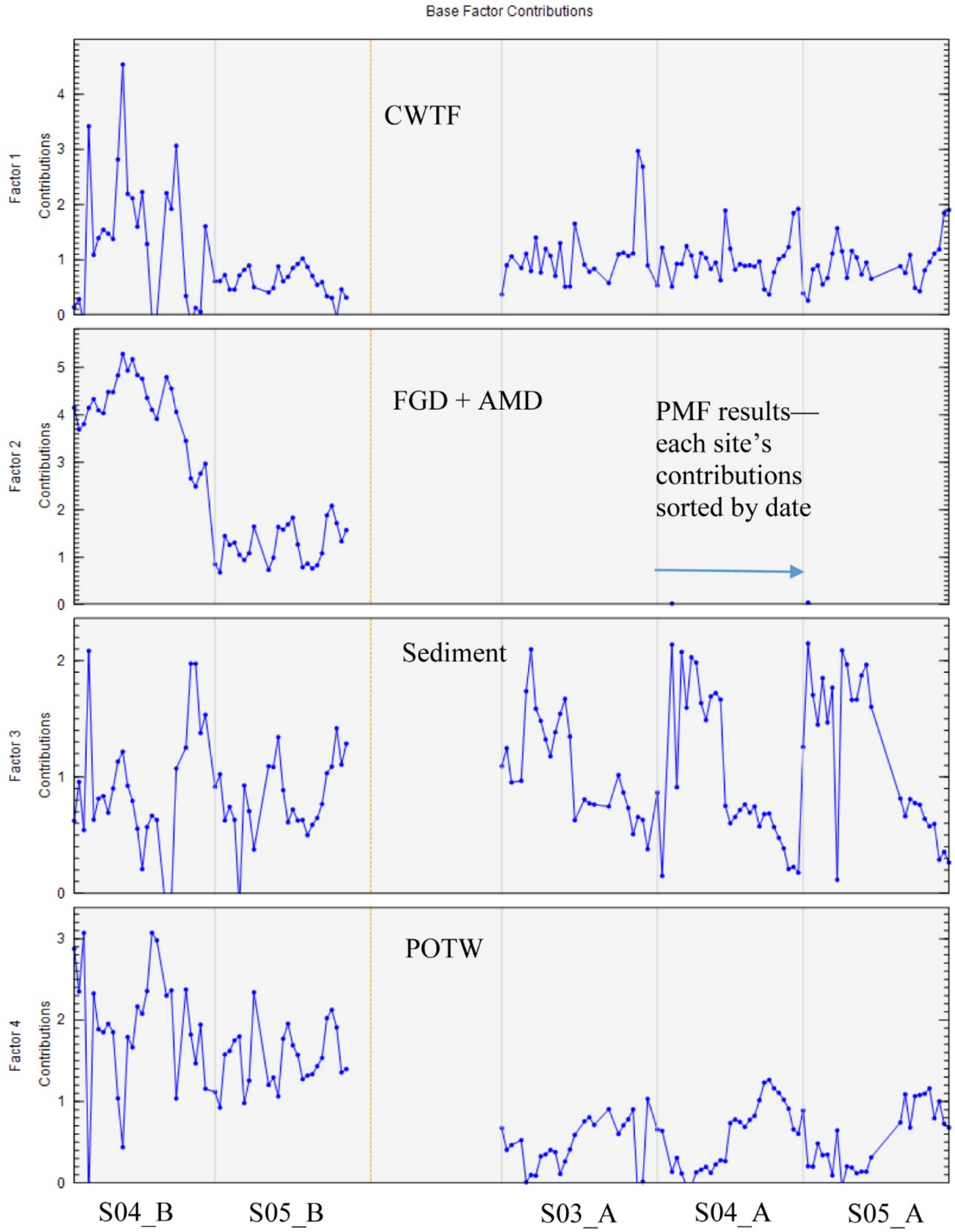


Figure 10. EPA PMF time series plot of normalized factor contributions (average contribution = 1 for each factor) by site and date. The contribution axis scale was set to show the variation in the source contribution and each plot has a different scale.

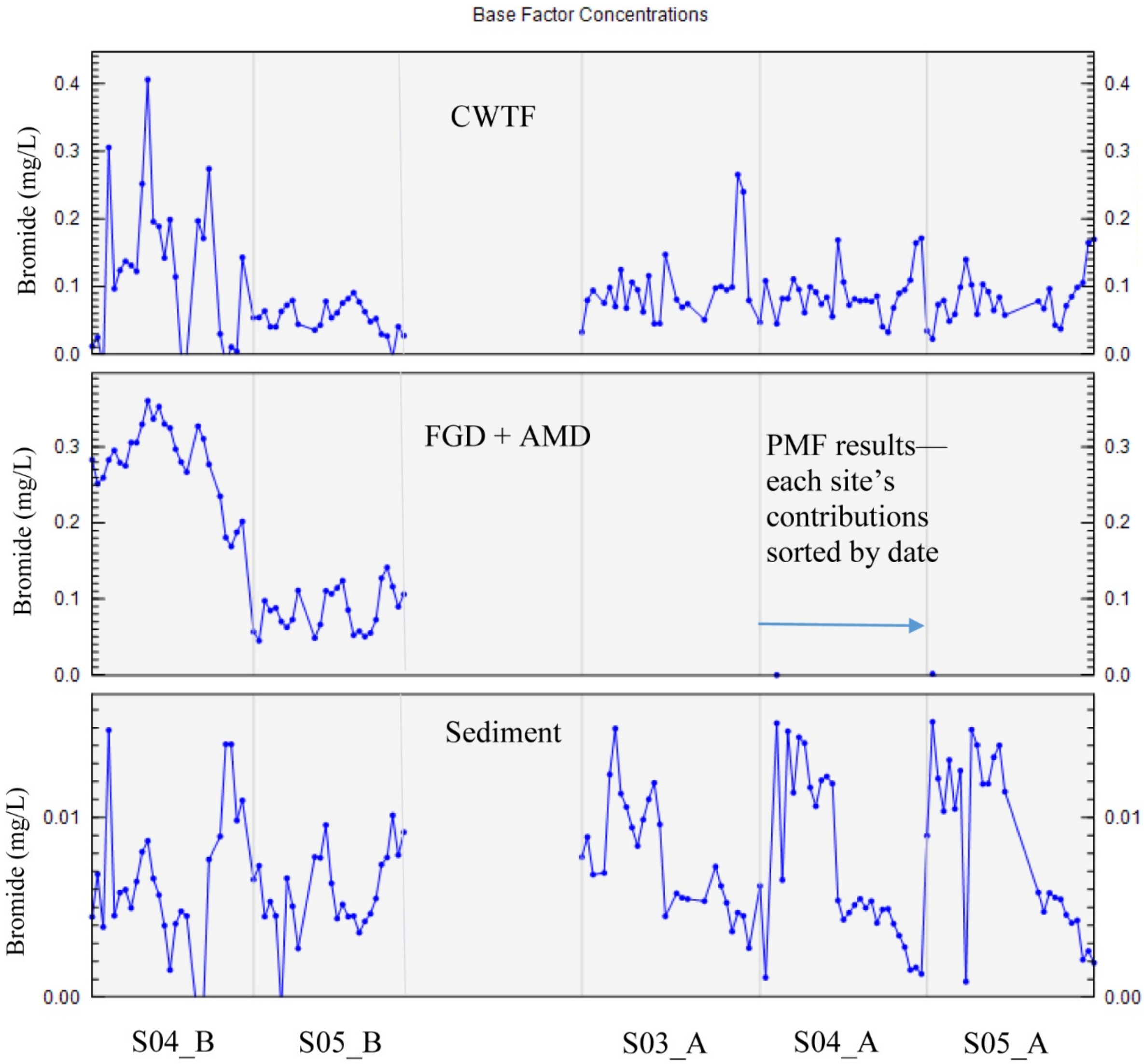


Figure 11. EPA PMF source contribution plot for the 3 sources with elevated bromide concentrations.

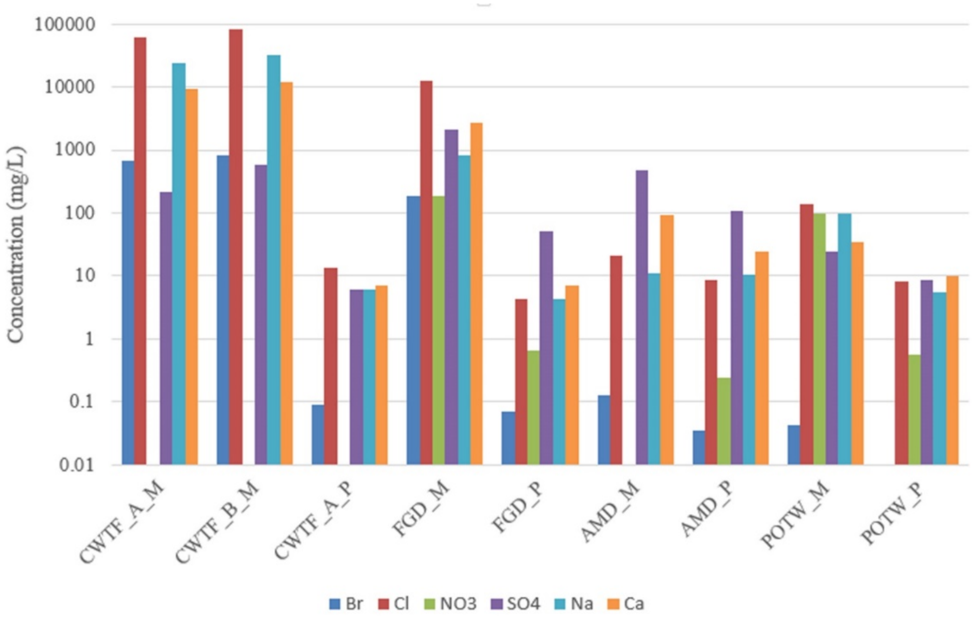


Figure 12. Comparison of the measured (_M) and Positive Matrix Factorization (_P) profiles.

Bromide source contributions for each sampling site are shown in Figure 13 and Table 19. The boxplots show the daily variation in each source contribution. S04_B has the largest range in concentrations because the CWTF_B had variable daily discharge levels. All of the bromide at the S05_A PDWS intake (median = 0.079 mg/L) originated from upstream CWTFs. A combination of discharges from CWTFs and FGD + AMD contributed to the concentrations at the S05_B PDWS intake, resulting in median bromide contributions of 0.054 mg/L from the CWTFs (37%) and 0.086 mg/L from FGDs (59%).

The relative CWTF and FGD+AMD source contributions at S05_A and S05_B were further evaluated by plotting the distribution of the daily sample contribution to the total bromide (Figure 14). The S05_A distributions show that the CWTF contributed over 80% of the bromide in the majority of the samples and the FGD+AMD contribution was 10% or less (only one sample had a 5% contribution and the rest had zero). For site S05_B the distribution shows that majority of daily bromide contributions ranges between 30 - 60% for CWTF, and 40 - 70% for FGD + AMD.

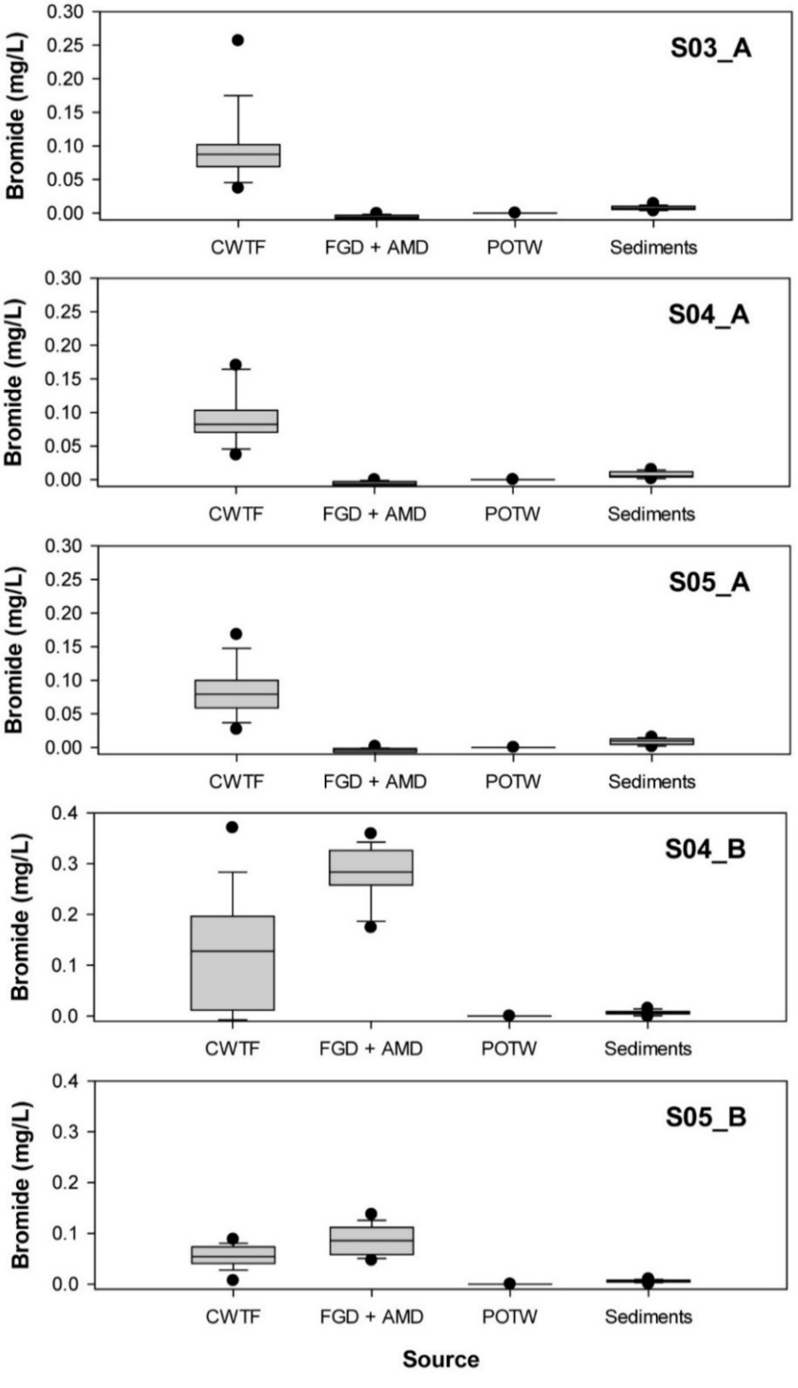


Figure 13. Positive Matrix Factorization (PMF) combined analysis (Allegheny and Blacklick) bromide concentrations (mg/L) for PMF source types by river sampling site. The figure shows the elevated contributions associated with centralized waste treatment facilities (CWTFs) and flue gas desulfurization scrubbers (FGDs). AMD = acid mine drainage. POTW = publicly owned treatment works.

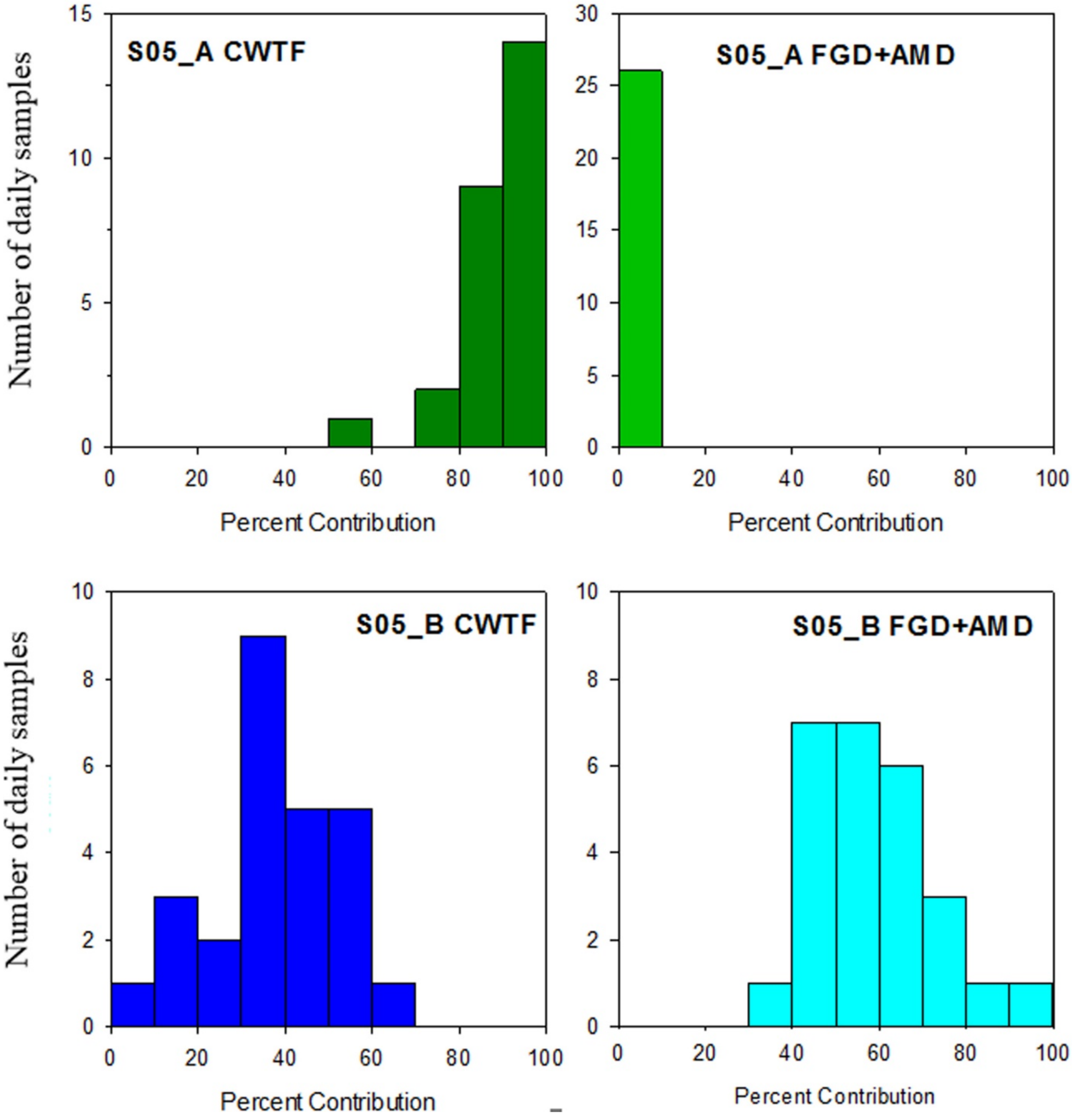


Figure 14. Distribution of CWTF and FGD + AMD bromide source contributions (%) to S05_B.

Median concentrations of bromide, chloride, nitrate, and sulfate contributed by each source type and sampling site are provided for the three PMF analyses in Table 19, Table 20, Table 21, and Table 22, respectively. The bromide concentration for the sediment source was 0.0 mg/L for the Allegheny PMF analysis, and the combined sites had median bromide concentrations that ranged from 0.0054 to 0.0097 mg/L (Table 19). The sediment source most likely represents a background concentration; no sediment samples were collected as part of this study.

Table 19. Positive Matrix Factorization (PMF) bromide concentrations by PMF analysis and sampling site (mg/L).

Allegheny		CWTF[1]		AMD[2]		POTW[3]		Sediments	
Site	N	Median	IQR[4]	Median	IQR	Median	IQR	Median	IQR
S01_A	30	0.074	0.044	0.010	0.0090	0.0	0.0	0.0	0.0
S03_A	26	0.080	0.037	0.012	0.0064	0.0	0.0	0.0	0.0
S04_A	29	0.060	0.037	0.025	0.012	0.0	0.0	0.0	0.0
S05_A	26	0.055	0.041	0.025	0.0075	0.0	0.0	0.0	0.0
Blacklick		**CWTF**		**AMD**		**POTW**			
Site	**N**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**		
S01_B	28	0.0004	0.045	0.060	0.049	0.043	0.0064		
S03_B	29	0.23	0.82	0.043	0.0530	0.033	0.018		
S04_B	26	0.280	0.15	0.0048	0.0050	0.123	0.038		
Combined		**CWTF**		**FGD[5] + AMD**		**POTW**		**Sediments**	
Site	**N**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
S03_A	26	0.088	0.031	0.0	0.0	0.0	0.0	0.0071	0.0046
S04_A	29	0.082	0.027	0.0	0.0	0.0	0.0	0.0053	0.0076
S05_A	26	0.079	0.040	0.0	0.0	0.0	0.0	0.0097	0.0081
S04_B	26	0.13	0.18	0.28	0.065	0.0	0.0	0.0059	0.0042
S05_B	26	0.054	0.0320	0.086	0.053	0.0	0.0	0.0054	0.0033

[1] Centralized waste treatment facility

[2] Acid mine drainage

[3] Publicly owned treatment works

[4] Interquartile range

[5] Flue gas desulfurization

Table 20. Positive Matrix Factorization (PMF) chloride concentrations by PMF analysis and sampling site (mg/L).

Allegheny		CWTF[1]		AMD[2]		POTW[3]		Sediments	
Site	N	Median	IQR[4]	Median	IQR	Median	IQR	Median	IQR
S01_A	30	9.03	5.30	4.17	3.63	5.01	4.23	2.84	4.81
S03_A	26	9.75	4.45	4.94	2.58	4.23	4.20	4.10	4.93
S04_A	29	7.27	4.46	9.93	4.77	1.81	2.52	2.37	5.38
S05_A	26	6.72	4.99	9.91	3.04	1.74	3.34	4.92	4.44
Blacklick		**CWTF**		**AMD**		**POTW**			
Site	**N**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**		
S01_B	28	0.0505	6.11	14.6	11.9	6.41	0.957		
S03_B	29	31.2	111	10.4	12.8	5.01	2.63		
S04_B	26	37.8	20.5	1.17	1.22	18.5	5.74		
Combined		**CWTF**		**FGD[5] + AMD**		**POTW**		**Sediments**	
Site	**N**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
S03_A	26	13.2	4.6	0.0	0.0	3.53	3.63	5.77	3.70
S04_A	29	12.4	4.1	0.0	0.0	5.31	5.06	4.34	6.15
S05_A	26	11.9	6.0	0.0	0.0	4.56	5.57	7.87	6.55
S04_B	26	19.2	27.7	17.6	4.1	15.8	5.6	4.80	3.45
S05_B	26	8.14	4.81	5.31	3.3	12.0	4.02	4.39	2.67

[1] Centralized waste treatment facility

[2] Acid mine drainage

[3] Publicly owned treatment works

[4] Interquartile range

[5] Flue gas desulfurization

The highest concentrations of chloride were observed on the Blacklick, with contributions from the CWTF, FGD + AMD, and POTW sources (Table 20). Measured chloride concentrations were higher in both CWTFs and the FGD, and a large increase was found at both S03_B and S04_B. The increase in chloride from the CWTFs on the Allegheny was much smaller due to higher river discharge and resulting increase in dilution capacity.

High concentrations of nitrate were found on the AMD and CWTF sources, indicating that the elevated concentrations measured at S03_B impacted the ability of PMF to separate the nitrate source (Table 21). The combined analysis had nitrate contributions from both the FGD + AMD source and the POTW. The measured FGD profile had significant nitrate, and the generating stations have on-site POTWs which also discharge nitrate. The combination of these sources could be the reason for the nitrate contribution.

PMF sulfate concentrations in Table 22 show that including S03_B in the Blacklick site analysis impacted PMF's ability to apportion sulfate only to the AMD source, since the POTW source had a significant sulfate contribution at S01_B, S03_B and S04_B. The measured profiles had high sulfate concentrations for both the FGD and AMD profiles, and low sulfate for the POTW profile. Furthermore, the discharges from these sources combine at S04_B, and have a large impact on sulfate at the PDWS intake after the confluence of the Kiskiminetas and the Allegheny (S05_B).

Table 21. Positive Matrix Factorization (PMF) nitrate concentrations by PMF analysis and sampling site (mg/L).

Allegheny		CWTF[1]		AMD[2]		POTW[3]		Sediments	
Site	**N**	**Median**	**IQR[4]**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
S01_A	30	0.0008	0.0005	0.0	0.0	0.54	0.45	0.0	0.0
S03_A	26	0.0009	0.0004	0.0	0.0	0.45	0.45	0.0	0.0
S04_A	29	0.0007	0.0004	0.0	0.0	0.19	0.27	0.0	0.0
S05_A	26	0.0006	0.0004	0.0	0.0	0.19	0.36	0.0	0.0
Blacklick		**CWTF**		**AMD**		**POTW**			
Site	**N**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**		
S01_B	28	0.0002	0.022	0.43	0.35	1.3	0.19		
S03_B	29	0.11	0.39	0.30	0.37	1.0	0.53		
S04_B	26	0.13	0.073	0.034	0.036	3.7	1.2		
Combined		**CWTF**		**FGD[5] + AMD**		**POTW**		**Sediments**	
Site	**N**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
S03_A	26	0.0	0.0	0.0	0.0	0.25	0.26	0.0	0.0
S04_A	29	0.0	0.0	0.0	0.0	0.38	0.36	0.0	0.0
S05_A	26	0.0	0.0	0.0	0.0	0.32	0.40	0.0	0.0
S04_B	26	0.0	0.0	2.7	0.63	1.1	0.40	0.0	0.0
S05_B	26	0.0	0.0	0.83	0.51	0.85	0.29	0.0	0.0

[1] Centralized waste treatment facility
[2] Acid mine drainage
[3] Publicly owned treatment works
[4] Interquartile range
[5] Flue gas desulfurization

Table 22. Positive Matrix Factorization (PMF) sulfate concentrations by PMF analysis and sampling site (mg/L).

Allegheny		CWTF[1]		AMD[2]		POTW[3]		Sediments	
Site	**N**	**Median**	**IQR[4]**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
S01_A	30	0.0072	0.0042	2.2	1.9	3.3	2.7	1.8	3.1
S03_A	26	0.0078	0.0036	2.6	1.4	2.7	2.7	2.7	3.2
S04_A	29	0.0058	0.0036	5.2	2.5	1.2	1.6	1.5	3.5
S05_A	26	0.0054	0.0040	5.2	1.6	1.1	2.2	3.2	2.9
Blacklick		**CWTF**		**AMD**		**POTW**			
Site	**N**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**		
S01_B	28	0.024	2.9	190	155	71	11		
S03_B	29	15	53	136	167	55	29		
S04_B	26	18	9.8	15	16	204	63		
Combined		**CWTF**		**FGD[5] + AMD**		**POTW**		**Sediments**	
Site	**N**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**	**Median**	**IQR**
S03_A	26	6.1	2.2	0.0	0.0	3.8	3.9	2.1	1.3
S04_A	29	5.7	1.9	0.0	0.0	5.7	5.4	1.6	2.2
S05_A	26	5.5	2.8	0.0	0.0	4.9	6.0	2.8	2.3
S04_B	26	8.9	13	210	48	17	6.0	1.7	1.2
S05_B	26	3.8	2.2	64	39	13	4.3	1.6	0.95

[1] Centralized waste treatment facility

[2] Acid mine drainage

[3] Publicly owned treatment works

[4] Interquartile range

[5] Flue gas desulfurization

4.4 PMF Bromide Sensitivity and Hybrid Analysis

PMF results are based solely on the measurement data included in the model. Therefore adding or removing data from a sampling site(s) may materially impact the apportionment results. The sensitivity of the numerical receptor modeling results was investigated by including or removing the sampling sites on the Blacklick Creek (S01_B and S03_B). These sites had a high contribution from AMD, and the CWTF source contributions at S03_B were very high due to the low dilution capacity from the creek. The PMF results for S03_B also demonstrated that species were not being conserved due to the reaction of CWTF source with the AMD in the creek. A PMF analysis was conducted with all sites, including S01_B and S03_B, during low river discharge and pH conditions (pH range = 4.42 - 6.83). The analysis extracted both a brine source (bromide, chloride, sodium) and a source composed of Fe and Mn. This additional PMF source was hypothesized to be a precipitate composed of Fe, Mn, and Ba formed when the higher pH CWTF discharge (pH range = 9.47 - 9.78) reacted in the AMD impacted Blacklick Creek (Lee *et al.* 2002). This precipitate would tend to settle in the river/reservoir sediment rather than being transported downstream of the Conemaugh Dam and would change the S01_B creek composition downstream of the CWTF_B discharge. A sensitivity analysis evaluated the impacts of the following combinations of sites included in the PMF analysis:

1. All sites (S01_A, S03_A, S04_A, S05_A, S01_B, S03_B, S04_B, S05_B).
2. All sites except site S03_B which had a high CWTF impact due to the relatively low flow (S01_A, S03_A, S04_A, S05_A, S01_B, S04_B, S05_B).
3. All Blacklick sites downstream from the Conemaugh Dam and Allegheny sites (S01_A, S03_A, S04_A, S05_A, S04_B, S05_B).

The results of the PMF sensitivity analysis are summarized in Table 23 and the results from the combined analysis are shown at the bottom of the table.

Table 23. PMF sensitivity analysis results (mg/L).

	Source			
All Sites	**AMD + Sediments**	**Sediments**	**CWTF +FGD**	**POTW**
PMF Profile Br/Cl ratio	---	0[1]	0.0075	0.0031
S05_A Bromide	0.0023	0	0.076	0.00064
S05_B Bromide	0.0094	0	0.13	0.0091
AMD Estimate (No S03_B)	**CWTF +FGD**	**Sediment**	**POTW**	**AMD**
PMF Profile Br/Cl ratio	0.0066	0	0	0
S05_A Bromide	0.080	0	0	0.0012
S05_B Bromide	0.13	0	0	0.013
No sampling sites on Blacklick Creek (No S03_B, S01_B)	**POTW**	**Sediment**	**CWTF**	**FGD + AMD**
PMF Profile Br/Cl ratio	0	0.0021	0.0062	0.018
S05_A Bromide	0	0.019	0.071	0
S05_B Bromide	0	0.010	0.051	0.085
Combined Analysis (No S03_B, S01_B, S01_A)	**CWTF**	**FGD +AMD**	**Sediment**	**POTW**
PMF Profile Br/Cl ratio	0.0066	0.016	0.0012	0
S05_A Bromide	0.079	0	0.0097	0
S05_B Bromide	0.054	0.086	0.0054	0

The measured profile Br/Cl ratios and known discharge locations were used to evaluate each of the solutions presented in Table 23. CWTF ratios were similar to the measured profiles (0.0097 to 0.011); FGD + AMD ratios were similar to the FGD ratio (0.0146) and not AMD (0.0058). Including or not including Blacklick Creek sampling data provided different results.

Although the mass discharge rates described in Section 4.3 indicated that the FGD discharges contributed a significant bromide contribution, only the third PMF modeling scenario (no sampling sites on Blacklick Creek included) and the combined analysis identified a separate FGD source. A hybrid analysis using results from these two PMF analyses was conducted to discriminate the FGD and AMD contributions, since these two sources were initially combined by PMF. The PMF modeling results for the second scenario presented in Table 23 (excluded site S03_B) were able to separate bromide into a combined CWTF and FGD source and an AMD source (high sulfate). The AMD contribution from this analysis was subtracted off the combined analysis site source contributions to provide estimated FGD and AMD bromide concentrations as shown in Figure 15.

Figure 16 shows the large bromide source contribution difference downstream of the Kiskiminetas River and Allegheny River confluence. The impact of the source discharges clearly increased the Allegheny's mean bromide concentration, from sites S05_A to S05_B, by 0.056 mg/L. After adjusting for the bromide from AMD at S05_B (0.013 mg/L), the FGD contribution decreased from 59% to 50%. These results represent the median percent contribution, which varies on a daily basis due to changes in discharge volumes (e.g., CWTFs only discharging on weekdays).

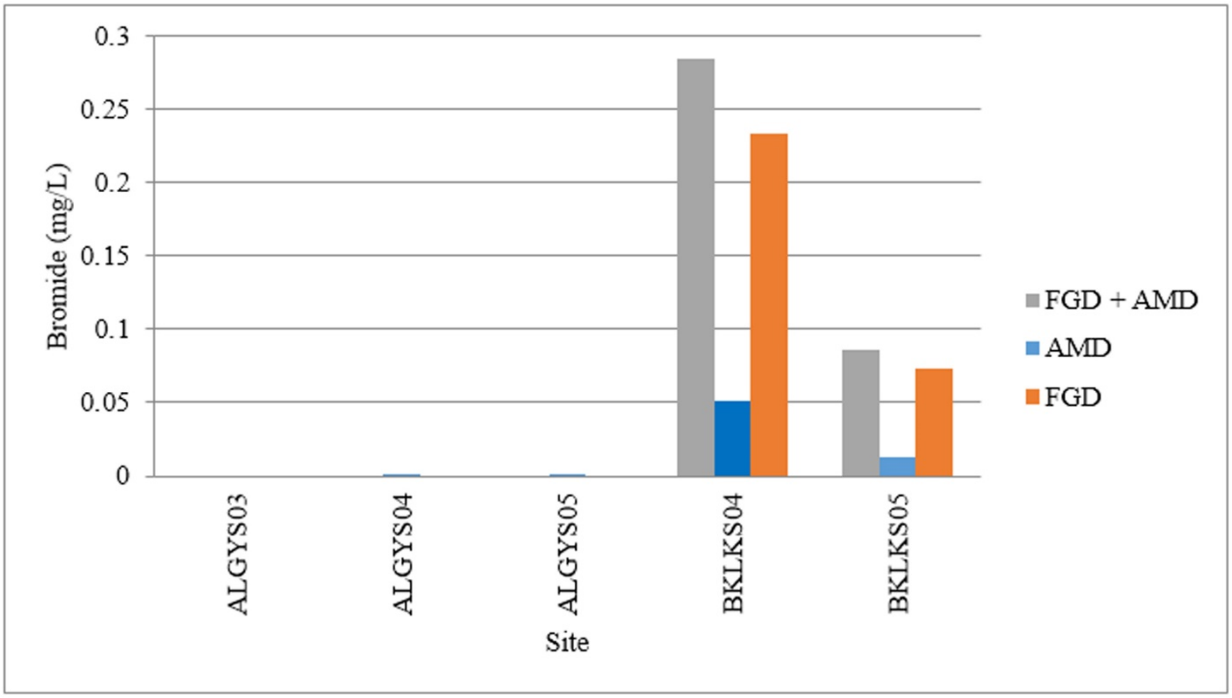


Figure 15. Subtraction of AMD bromide from the FGD + AMD source to provide AMD and FGD estimated source contributions.

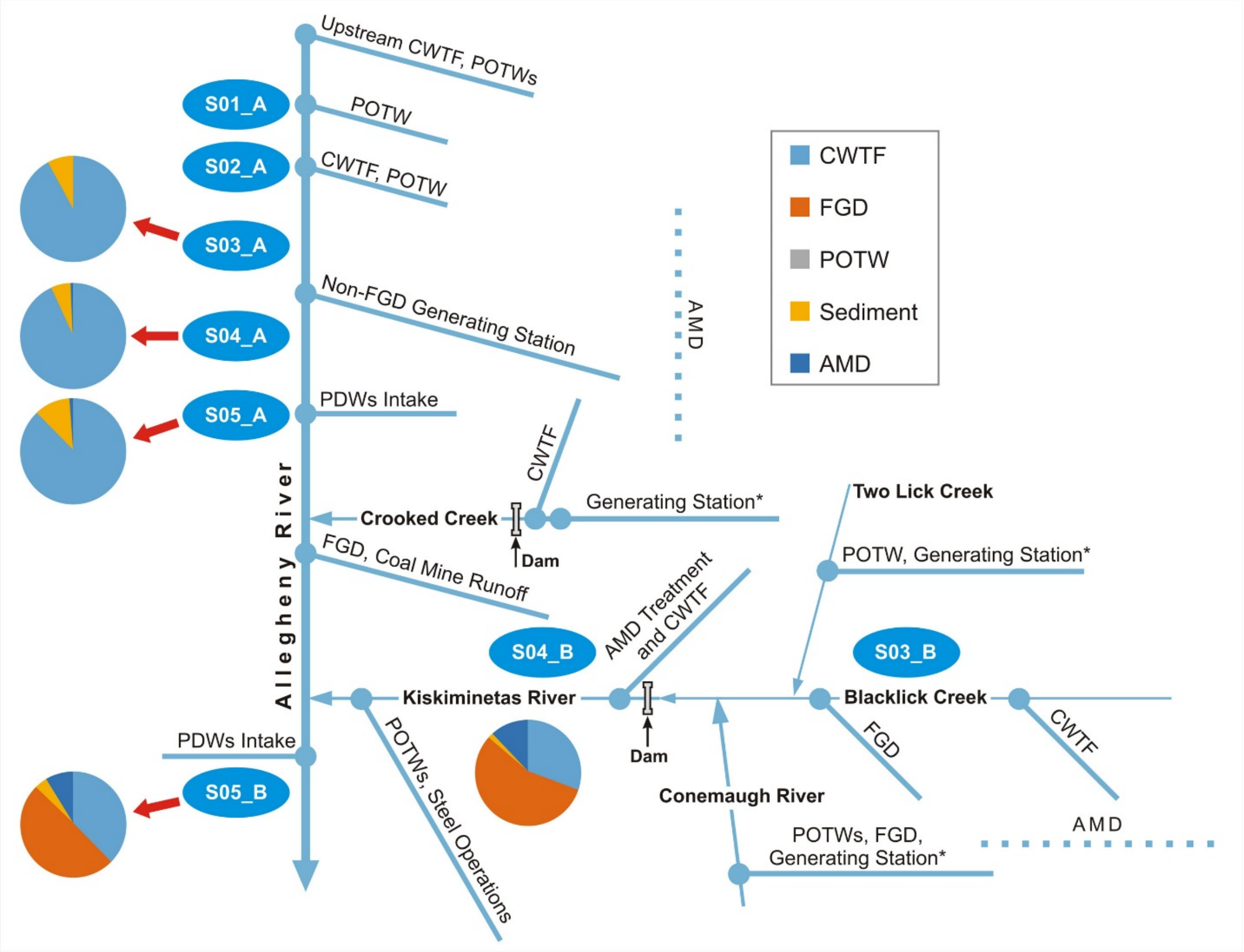


Figure 16. Hybrid PMF source contributions of bromide by sampling site and facility discharges.

5. SUMMARY AND CONCLUSIONS

This research applied a technique referred to as “source apportionment” to quantify source contributions for a number of common discharge sources. Source measurements were collected to provide reference information for apportioning contaminant sources in the Alleghany watershed, including from centralized wastewater treatment facilities (CWTFs) that treat wastes including oil and gas wastewater; coal-fired power plants with and without flue-gas desulfurization (FGD); industrial manufacturing facilities; municipal and industrial wastewater treatment plants; active coal mine runoff; and acid mine drainage (AMD). The study investigated the sources of inorganic species such as bromides and other anions contributing to contaminants at PDWS intakes on the Allegheny River during low river discharge conditions in the summer and fall of 2012. The study included: (i) river sampling from multiple sites and source profile collection; (ii) river and source sample analysis with conductivity, IC, ICP-OES, and HR-ICPMS; and (iii) receptor modeling of measurement data. Results using the study design and methods described in this report showed that during the period of this study, the CWTFs that treated hydraulically fractured oil and gas wastewater, along with other wastes, were a significant source of bromide at both PDWS intakes. Multiple sources contributed chloride, nitrate, and sulfate, including CWTFs, FGDs, AMD, and POTWs to the downstream PDWS intakes.

KEY FINDINGS

- The results demonstrate that the 2 public drinking water intakes (PDWS) studied are impacted by multiple sources contributing various inorganic species, including centralized wastewater treatment facilities (CWTFs), power generating stations, and acid mine drainage (AMD).
- Source measurements provide a signature or profile for numerous bromide sources.
- The predominate sources of bromide at the 2 public drinking water intakes studied were wastewaters discharged from CWTFs and coal-fired power plants with flue-gas desulfurization (FGD). CWTFs contributed nearly all the bromide at 1 intake, while both CWTFs and FGDs contributed to bromide levels at the second intake.
- Publically owned wastewater treatment plants and acid mine drainage were the predominate sources of nitrate and sulfate.

5.1 River Measurements

River contaminant concentrations at the Allegheny and Blacklick sites differed significantly. While the upstream bromide concentrations were similar for the Allegheny and Blacklick sites, downstream concentrations were much higher on the Blacklick. The mean bromide concentration at the PDWS intake located 98 river kilometers upstream from the Allegheny/Kiskiminetas confluence was 0.0867 mg/L (S05_A); while it was 0.143 mg/L (S05_B) just downstream of the confluence. The source apportionment analysis was used to investigate the sources associated with the observed increase in bromide between the two intakes, in particular to understand the possible relative contribution from CWTFs that treat waste from oil and gas operations – the majority of which is hydraulic fracturing wastewater.

5.2 Measured Source Profiles

The measured profiles showed differences in the source Br/Cl ratios (Figure 17). CWTF and FGD sources contributed the highest bromide concentrations. The generating stations had multiple bromide sources, including coal ash and coal pile runoff. The FGD Br/Cl ratio (0.0146) was higher than the ratio for both CWTF (0.0104) and AMD (0.0058) and this suggested that Br/Cl ratios can be used as an indicator to separate the multiple sources contributing bromide to the Allegheny River. This allowed for the identification of a combined FGD and AMD source impacting S04_B, which was downstream from the FGD discharges. Coal ash wastewater from generating stations also had a high Br/Cl ratio (0.0247) compared to CWTF (0.0146); its contribution could not be separated from the FGD source.

5.3 PMF Source Apportionment Results

PMF was used to evaluate the river sample data from multiple sites, and a sensitivity analysis evaluated the impact of including or excluding sites from the analysis. The results were sensitive to the inclusion of the Blacklick Creek site samples (S01_B, S03_B), which were collected from a creek impacted by both a CWTF and AMD from historical mining. The measured profile Br/Cl ratios were used to identify the sources along with the location of the outfalls. In addition, CWTF and FGD mass discharge rates were calculated using the measured profile concentrations. FGDs significantly contributed to anion concentrations in the S04_B samples. As shown in Figure 4 and Figure 7, S04_B was located downstream of the Conemaugh Dam and was impacted by many sources. High sulfate levels on the Blacklick to Kiskiminetas indicated that AMD was a major source. Therefore, despite having a low measured bromide contribution, AMD needed to be accounted for in the PMF analysis.

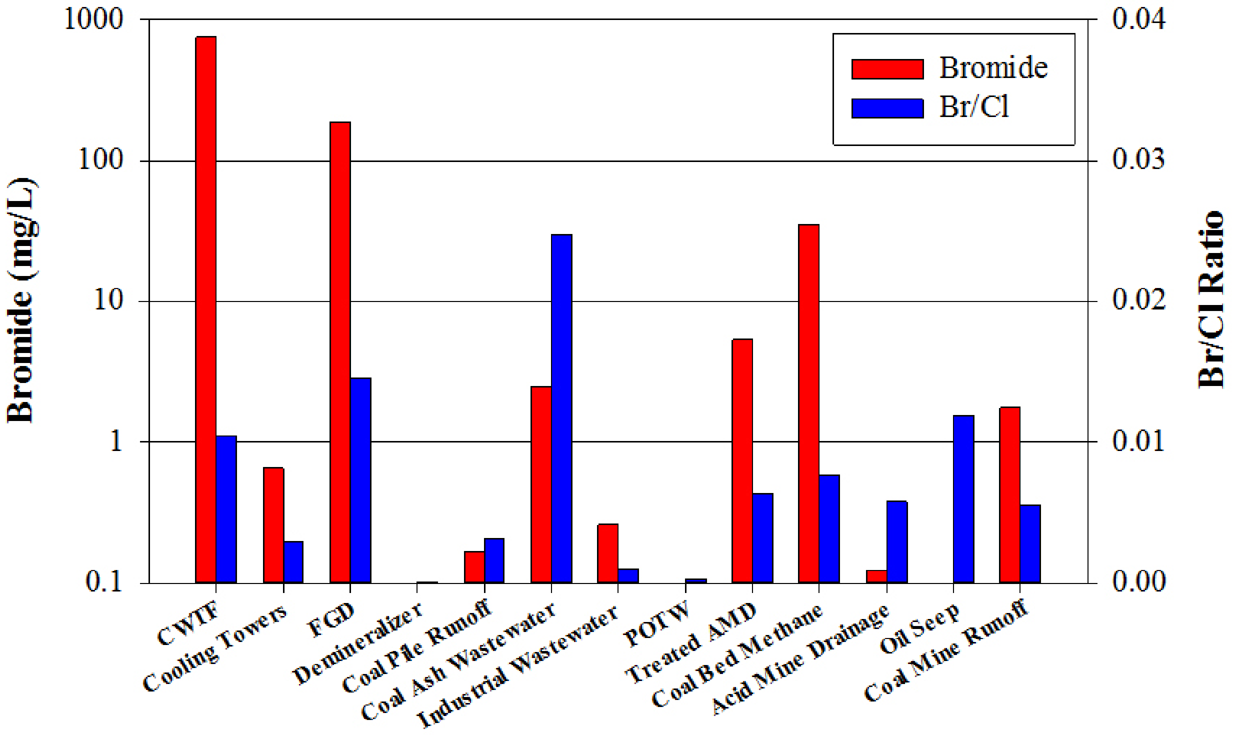


Figure 17. Summary of Br/Cl and bromide mean concentrations for measured sources (Table 13).

A combination of two PMF analyses was used to calculate the bromide sources at the PDWS intakes: (1) downstream combined sites only, and (2) a hybrid using two PMF analyses to separate the AMD/FGD source factor for bromide that could not be resolved in the combined site analysis. Both the combined and hybrid PMF results generated similar overall contributions including all source categories. For example, CWTF contributions at PWDS intake S05_B was 37% for the combined analysis and 37% for the hybrid analysis. The hybrid results are useful because they provided a basis to estimate the FGD bromide contributions (50% at S05_B) in the absence of AMD (9% at S05_B).

Figure 18 presents the bromide source contributions for both PMF analyses of the PDWS intakes and highlights the differences between the two analyses. These results represent the median percent contribution which varies daily due to changes in discharges. The two results provide a range in contributions for the FGD source.

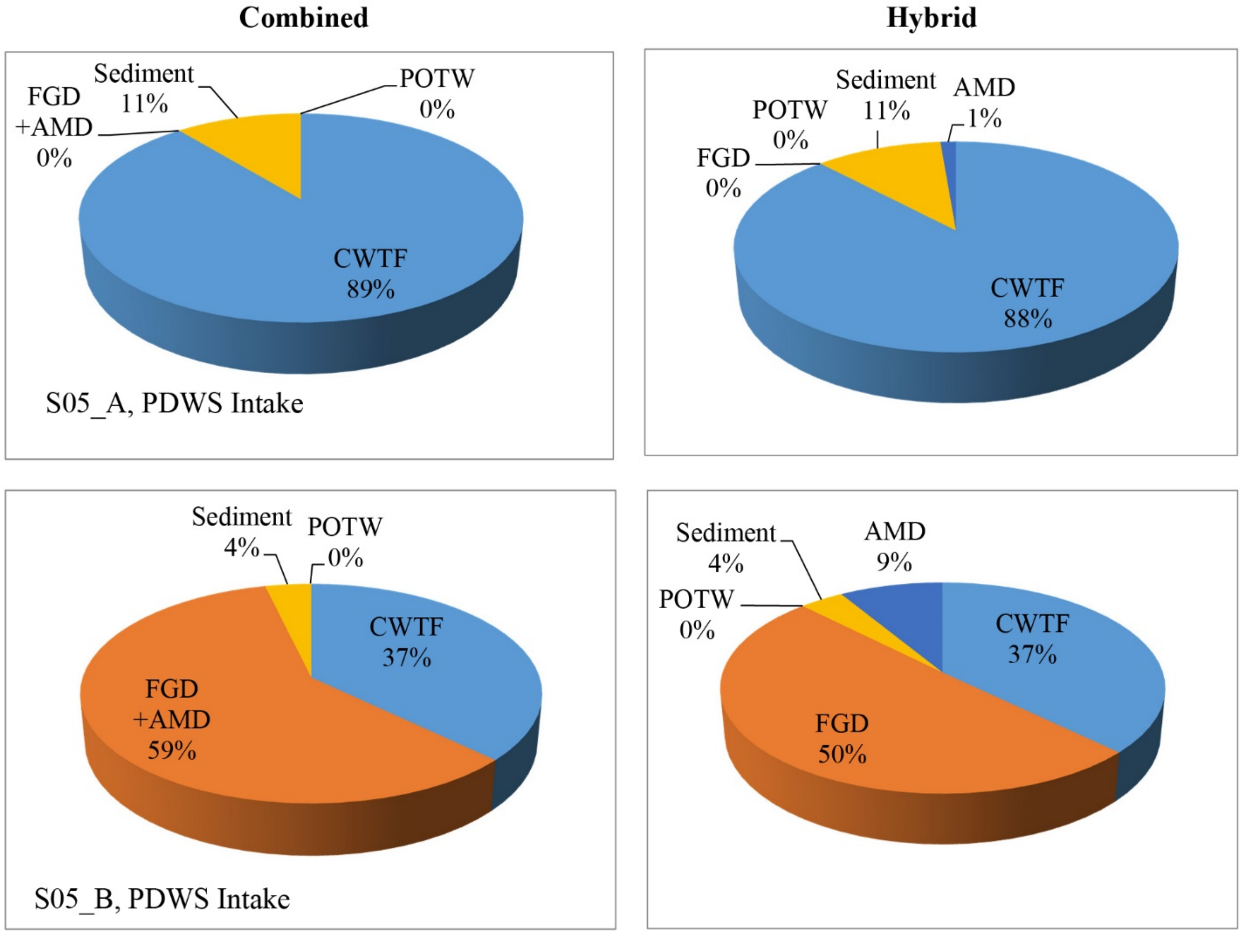


Figure 18. Summary of median PMF bromide source contributions for PDWS intakes.

This source apportionment study also evaluated the sources contributing other inorganic contaminants to the PDWS intakes and the other sampling sites The measured source profiles (Table 13) included chloride, nitrate, and sulfate; and the source contributions for each of these contaminants from CWTF, FGD+AMD, POTW, and Sediment sources are presented in Tables 20, 21, and 22. For the combined PMF analysis, CWTFs contributed the highest amount of chloride to downstream sites (8.14 to 19.2 mg/L), followed by FGD + AMD (5.31 to 17.6 mg/L), and POTWs (3.53 to 15.8 mg/L). Measured source profiles generally supported these receptor model results with CWTFs (CTWT_A, CWTF_B) having an average concentration of 72,450 mg/L, and FGD having concentrations approximately 5 times less (12,800 mg/L). Sources of nitate included both POTWs (0.25 to 1.1 mg/L) and FGD (0.83 to 2.7 mg/L), which is consistent with the measured profiles (FGD = 183 mg/L, POTW =98.5 mg/L). Sulfate sources were CWTF (3.8 to 8.9 mg/L), FGD +AMD (64 to 210 mg/L), and POTW (3.8 to 17 mg/L). Both FGD and AMD had high measured source concentrations of sulfate with 2080 mg/L and 469 mg/L, respectively.

5.4 Application of Source Apportionment Modeling to Surface Water

This study is the first of its kind to demonstrate the application of source apportionment techniques to quantify a complex array of source contributions to measured contaminant concentrations at PDWS raw water intakes. The source apportionment results are based solely on measured sample data and require no *a priori* information on river discharge sources or river dispersion characteristics. Stable PMF results were found when applying a multiple site source apportionment design commonly used for air pollution source apportionment studies to this surface water application. We provide source profiles for a number of common discharge facilities that may be relevant to apportion sources in other locations. We have shown that multiple sources contribute to concentrations of anions at two Allegheny PDWS intakes, including discharges from CWTF, FGD, and AMD sources. Source apportionment can improve our understanding of the magnitude of the impact for the various sources. Understanding the sources will guide efforts to control exposures to drinking water contaminants that are of concern to human health such as brominated disinfection byproducts. These results can inform strategies for source mitigation or treatment optimization using the source contribution summaries. Ultimately, the results of this study and the future application of the research tools presented will provide communities, states, tribes, and industry with sound scientific knowledge on understanding potential impacts of hydraulic fracturing on drinking water resources, and the overall protection of those water resources for the future.

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APPENDIX A

Comparison of Receptor and River Transport Conceptual Models and Summary Statistics for River, CWTF, and PDWS Intake Samples

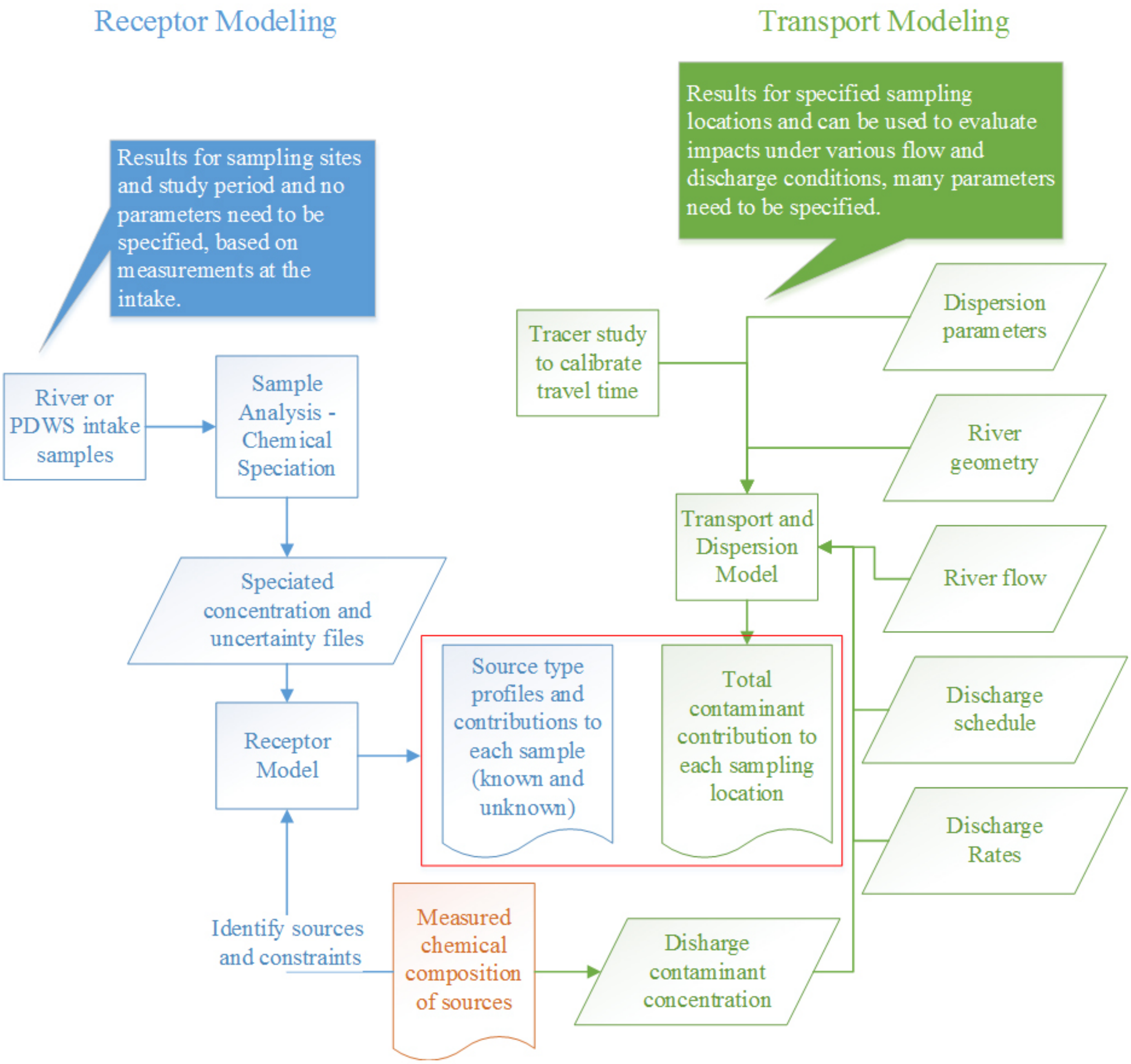

Figure A1. Diagram showing receptor and transport model input requirements and model outputs.

Table A1. Summary of Allegheny River species concentrations (mg/L); n (%) number of valid samples.

Species	Statistic	S01_A	S02_A	S03_A	S04_A	S05_A
Br - IC	**n (%)**	**31 (100%)**	**23 (100%)**	**45 (98%)**	**30 (100%)**	**52 (100%)**
	mean (std)	0.0718 (0.0254)	684 (76.4)	0.104 (0.0596)	0.0851 (0.0302)	0.0867 (0.0317)
	median (IQR)	0.0721 (0.0446)	697 (101)	0.0836 (0.0399)	0.0779 (0.0378)	0.0852 (0.0436)
	min - max	0.0329 - 0.117	536 - 788	0.037 - 0.28	0.0379 - 0.154	0.038 - 0.166
Ca - OES	**n (%)**	**30 (97%)**	**22 (96%)**	**45 (98%)**	**29 (100%)**	**51 (100%)**
	mean (std)	15.2 (1.19)	9420 (1050)	16.8 (1.6)	17.9 (1.78)	18.6 (1.34)
	median (IQR)	15.3 (1.4)	9470 (1560)	16.6 (2.1)	18.2 (3.5)	18.5 (1.8)
	min - max	12.4 - 17.6	7680 - 11500	13.8 - 21.3	14.5 - 20.1	16.3 - 21.6
Cl - IC	**n (%)**	**31 (100%)**	**23 (100%)**	**46 (100%)**	**30 (100%)**	**52 (100%)**
	mean (std)	20.8 (2.93)	61700 (6210)	24.2 (6.04)	23.3 (3.46)	23.6 (3.53)
	median (IQR)	21 (4.9)	61900 (8100)	22.5 (4.2)	22.5 (4.6)	23.5 (4.45)
	min - max	16.2 - 25.8	48800 - 73400	16.6 - 41.6	17.3 - 31.3	17.6 - 32.1
Fe - MS	**n (%)**	**31 (100%)**	**8 (67%)**	**42 (91%)**	**29 (100%)**	**50 (98%)**
	mean (std)	0.176 (0.0903)	0.183 (0.12)	0.202 (0.134)	0.154 (0.0762)	0.206 (0.0931)
	median (IQR)	0.154 (0.097)	0.149 (0.159)	0.145 (0.145)	0.125 (0.045)	0.178 (0.106)
	min - max	0.071 - 0.384	0.0485 - 0.383	0.0767 - 0.541	0.0767 - 0.389	0.0956 - 0.476
Mg - OES	**n (%)**	**30 (97%)**	**23 (100%)**	**45 (98%)**	**29 (100%)**	**51 (100%)**
	mean (std)	3.09 (0.191)	969 (154)	3.41 (0.224)	3.64 (0.272)	3.81 (0.205)
	median (IQR)	3.11 (0.25)	1010 (155)	3.41 (0.33)	3.65 (0.49)	3.79 (0.27)
	min - max	2.56 - 3.44	472 - 1140	3.02 - 4.06	3.09 - 3.98	3.4 - 4.27
Mn - MS	**n (%)**	**31 (100%)**	**10 (83%)**	**42 (91%)**	**29 (100%)**	**51 (100%)**
	mean (std)	0.0607 (0.0326)	0.33 (0.357)	0.0645 (0.0437)	0.0655 (0.0423)	0.081 (0.0428)
	median (IQR)	0.0536 (0.059)	0.144 (0.445)	0.0417 (0.0726)	0.041 (0.055)	0.0686 (0.0732)
	min - max	0.0181 - 0.123	0.0296 - 1.12	0.0215 - 0.183	0.0265 - 0.168	0.0299 - 0.191

Table. A1 (continued) Summary of Allegheny River species concentrations (mg/L); n (%) number of valid samples.

Species	Statistic	S01_B	S02_B	S03_B	S04_B	S05_B
NO3 – IC	**n (%)**	**30 (100%)**		**45 (100%)**	**27 (100%)**	**44 (100%)**
	mean (std)	0.59 (0.366)		0.594 (0.285)	0.283 (0.237)	0.327 (0.292)
	median (IQR)	0.545 (0.558)		0.652 (0.4)	0.243 (0.328)	0.284 (0.477)
	min - max	0.0188 - 1.26		0.0182 - 1.11	0.0284 - 0.807	0.0178 - 1.2
Na - OES	**n (%)**	**30 (97%)**	**22 (100%)**	**45 (98%)**	**29 (100%)**	**51 (100%)**
	mean (std)	11.2 (1.45)	23800 (2560)	12.9 (2.51)	12.2 (1.6)	12.6 (1.45)
	median (IQR)	11.5 (2.3)	24000 (4100)	12.5 (2.3)	11.9 (2.1)	12.5 (1.8)
	min - max	8.18 - 13.5	19100 - 30000	9.27 - 20	9.68 - 16.2	10 - 16.2
SO4 – IC	**n (%)**	**31 (100%)**	**23 (100%)**	**46 (100%)**	**30 (100%)**	**52 (100%)**
	mean (std)	7.47 (0.341)	218 (61.7)	8.44 (0.426)	9.02 (0.72)	9.62 (0.635)
	median (IQR)	7.49 (0.31)	198 (62)	8.35 (0.7)	8.93 (0.67)	9.58 (0.96)
	min - max	6.78 - 8.6	145 - 385	7.75 - 9.69	7.98 - 11.7	8.5 - 10.9
Si - OES	**n (%)**	**30 (97%)**	**23 (100%)**	**45 (98%)**	**29 (100%)**	**51 (100%)**
	mean (std)	0.961 (0.335)	0.738 (0.132)	0.94 (0.332)	0.888 (0.467)	1.01 (0.407)
	median (IQR)	1.01 (0.472)	0.744 (0.236)	0.86 (0.408)	0.697 (0.814)	1.06 (0.548)
	min - max	0.134 - 1.55	0.481 - 0.96	0.446 - 1.64	0.219 - 1.66	0.198 - 1.87
Sr - OES	**n (%)**	**30 (97%)**	**22 (100%)**	**45 (98%)**	**29 (100%)**	**51 (100%)**
	mean (std)	0.0655 (0.00886)	395 (202)	0.085 (0.0227)	0.079 (0.0118)	0.0797 (0.0115)
	median (IQR)	0.0641 (0.0136)	343 (173)	0.0782 (0.016)	0.0746 (0.019)	0.077 (0.0171)
	min - max	0.0483 - 0.0838	218 - 1190	0.0607 - 0.144	0.0627 - 0.105	0.0613 - 0.105

Table A2. Summary of Blacklick Creek species concentrations (mg/L); n (%) number of valid samples.

Species	Statistic	S01_B	S02_B	S03_B	S04_B	S05_B
Br - IC	**n (%)**	**27 (100%)**	**29 (100%)**	**29 (100%)**	**42 (100%)**	**56 (100%)**
	mean (std)	0.0696 (0.0175)	808 (65.9)	0.995 (1.32)	0.428 (0.146)	0.143 (0.0277)
	median (IQR)	0.0726 (0.0287)	812 (80)	0.327 (0.99)	0.419 (0.215)	0.132 (0.0455)
	min - max	0.0352 - 0.0889	713 - 1020	0.0635 - 4.36	0.178 - 0.797	0.102 - 0.205
Ca - OES	**n (%)**	**28 (100%)**	**29 (100%)**	**29 (100%)**	**42 (100%)**	**54 (96%)**
	mean (std)	56.3 (19.7)	12100 (975)	74.1 (34.8)	65.9 (9.76)	31.1 (5.39)
	median (IQR)	53.8 (26.4)	12100 (900)	64 (31.4)	66.4 (12.7)	29.3 (7.6)
	min - max	25.6 - 89.9	8820 - 13600	26.2 - 168	41.6 - 87.1	23.3 - 42.3
Cl - IC	**n (%)**	**28 (100%)**	**29 (100%)**	**29 (100%)**	**42 (100%)**	**56 (100%)**
	mean (std)	19.6 (1.79)	83200 (15900)	140 (185)	58.3 (13.9)	30.4 (3.69)
	median (IQR)	19.6 (2.2)	85800 (6400)	48.7 (107)	57.6 (22)	29.7 (6.2)
	min - max	14.1 - 23.2	7010 - 109000	21.6 - 621	35.2 - 93.7	24.4 - 37.6
Fe - MS	**n (%)**	**28 (100%)**	**14 (93%)**	**29 (100%)**	**40 (95%)**	**56 (100%)**
	mean (std)	2.6 (4.43)	0.213 (0.0692)	2.99 (6.19)	0.36 (0.243)	0.301 (0.152)
	median (IQR)	1.33 (1.39)	0.212 (0.069)	1.05 (1.36)	0.307 (0.218)	0.249 (0.213)
	min - max	0.479 - 23.7	0.0663 - 0.371	0.298 - 32	0.0791 - 0.942	0.137 - 0.8
Mg - OES	**n (%)**	**28 (100%)**	**29 (100%)**	**29 (100%)**	**42 (100%)**	**54 (96%)**
	mean (std)	15.7 (5.31)	749 (94.6)	16.6 (5.4)	21.2 (3.18)	9.22 (1.76)
	median (IQR)	16.1 (8.1)	749 (88)	15.7 (8.7)	21.4 (3.6)	8.64 (2.68)
	min - max	6.79 - 24.4	579 - 979	6.93 - 27.4	13.2 - 27.8	6.94 - 12.9
Mn - MS	**n (%)**	**28 (100%)**	**15 (100%)**	**28 (97%)**	**40 (95%)**	**56 (100%)**
	mean (std)	0.808 (0.207)	0.154 (0.068)	0.797 (0.195)	0.181 (0.103)	0.0945 (0.0314)
	median (IQR)	0.913 (0.34)	0.158 (0.091)	0.853 (0.297)	0.163 (0.103)	0.0909 (0.0513)
	min - max	0.417 - 1.06	0.0399 - 0.269	0.418 - 1.02	0.0279 - 0.438	0.049 - 0.156

Table A2. (continued) Summary of Blacklick Creek species concentrations (mg/L); n (%) number of valid samples.

Species	Statistic	S01_B	S02_B	S03_B	S04_B	S05_B
NO3 – IC	**n (%)**	**30 (100%)**		**45 (100%)**	**27 (100%)**	**44 (100%)**
	mean (std)	0.59 (0.366)		0.594 (0.285)	0.283 (0.237)	0.327 (0.292)
	median (IQR)	0.545 (0.558)		0.652 (0.4)	0.243 (0.328)	0.284 (0.477)
	min - max	0.0188 - 1.26		0.0182 - 1.11	0.0284 - 0.807	0.0178 - 1.2
Na - OES	**n (%)**	**30 (97%)**	**22 (100%)**	**45 (98%)**	**29 (100%)**	**51 (100%)**
	mean (std)	11.2 (1.45)	23800 (2560)	12.9 (2.51)	12.2 (1.6)	12.6 (1.45)
	median (IQR)	11.5 (2.3)	24000 (4100)	12.5 (2.3)	11.9 (2.1)	12.5 (1.8)
	min - max	8.18 - 13.5	19100 - 30000	9.27 - 20	9.68 - 16.2	10 - 16.2
SO4 – IC	**n (%)**	**31 (100%)**	**23 (100%)**	**46 (100%)**	**30 (100%)**	**52 (100%)**
	mean (std)	7.47 (0.341)	218 (61.7)	8.44 (0.426)	9.02 (0.72)	9.62 (0.635)
	median (IQR)	7.49 (0.31)	198 (62)	8.35 (0.7)	8.93 (0.67)	9.58 (0.96)
	min - max	6.78 - 8.6	145 - 385	7.75 - 9.69	7.98 - 11.7	8.5 - 10.9
Si - OES	**n (%)**	**30 (97%)**	**23 (100%)**	**45 (98%)**	**29 (100%)**	**51 (100%)**
	mean (std)	0.961 (0.335)	0.738 (0.132)	0.94 (0.332)	0.888 (0.467)	1.01 (0.407)
	median (IQR)	1.01 (0.472)	0.744 (0.236)	0.86 (0.408)	0.697 (0.814)	1.06 (0.548)
	min - max	0.134 - 1.55	0.481 - 0.96	0.446 - 1.64	0.219 - 1.66	0.198 - 1.87
Sr - OES	**n (%)**	**30 (97%)**	**22 (100%)**	**45 (98%)**	**29 (100%)**	**51 (100%)**
	mean (std)	0.0655 (0.00886)	395 (202)	0.085 (0.0227)	0.079 (0.0118)	0.0797 (0.0115)
	median (IQR)	0.0641 (0.0136)	343 (173)	0.0782 (0.016)	0.0746 (0.019)	0.077 (0.0171)
	min - max	0.0483 - 0.0838	218 - 1190	0.0607 - 0.144	0.0627 - 0.105	0.0613 - 0.105

APPENDIX B

PMF Model Analysis Parameters and Settings

Table B1. Allegheny PMF analysis parameters.[1]

Species	Br_IC, Cl_IC, NO3_IC, SO4_IC, Ca_OES, K_OES, Mg_OES, Na_OES, Si_OES, Sr_OES, Fe_MS, Mn_MS
Number of Samples	124
Number of Sampling Sites	5
Number of Factors	4
Species Categories	Fe_MS (Weak)
Number of Base Runs	50
Random Seed	12
Robust mode	Yes
Non-converged runs	No
Q (Robust)	1330
Q (True)	1350.3
Q (True)/Qexpected	1.85
DISP (dQmax = 4)	0 0 0
Constraints % dQ	0.10
Constraint Equation	[POTW|Br_IC] - 0.0003 * [POTW|Cl_IC] = 0

[1] $Q_{expected} = m \times n - p \times (m+n)$ where $Q_{expected}$ is the degrees of freedom with m chemicals, n samples, and p factors.

Table B2. Blacklick PMF analysis parameters.

Species	Br_IC, Cl_IC, NO3_IC, SO4_IC, Ca_OES, K_OES, Mg_OES, Na_OES, Si_OES, Sr_OES, Fe_MS, Mn_MS
Number of Samples	90
Number of Sampling Sites	3
Number of Factors	3
Species Categories	Fe_MS (Weak)
Number of Base Runs	50
Random Seed	2
Robust Mode	Yes
Non-converged runs	No
Q (Robust)	4355.65
Q (True)	6323.13
Q (True)/Qexpected	10.06868
DISP (dQmax = 4)	0 0 0
Constraints %dQ	0.12
Constraint Equation	[POTW|Br_IC] - 0.0003 * [POTW|Cl_IC] = 0

Table B3. Combined Allegheny and Blacklick PMF analysis parameters.

Species	Br_IC, Cl_IC, NO3_IC, SO4_IC, Ca_OES, K_OES, Mg_OES, Na_OES, Si_OES, Sr_OES, Fe_MS, Mn_MS
Number of Samples	90
Number of Sampling Sites	5
Number of Factors	4
Species Categories	Fe_MS (Weak), Mn_MS (Weak)
Number of Base Runs	50
Random Seed	67
Robust Mode	Yes
Non-converged runs	None
Q (Robust)	2787.78
Q (True)	3283.05
Q (True)/Qexpected	4.3774
DISP (dQmax = 4)	0 0 0 0
Constraints %dQ	NA
Constraint Equation	NA

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