The Impact of Commercially Treated Oil and Gas Produced Water Discharges on Bromide Concentrations and Modeled Brominated Trihalomethane Disinfection Byproducts at two Downstream Municipal Drinking Water Plants in the Upper Allegheny River, Pennsylvania, USA

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Abstract

In 2010, a dramatic increase in the levels of total trihalomethane (THM) and the relative proportion of brominated species was observed in finished water at several Pennsylvania water utilities (PDW) using the Alleghenv River as their raw water supply. An increase in bromide (Br-) concentrations in the Allegheny River was implicated to be the cause of the elevated water disinfection byproducts. This study focused on quantifying the contribution of Br⁻ from a commercial wastewater treatment facility (CWTF) that solely treats wastes from oil and gas producers and discharges into the upper reaches of the Allegheny River, and impacts on two downstream PDWs. In 2012, automated daily integrated samples were collected on the Allegheny River at six sites during three seasonal two-week sampling campaigns to characterize Br⁻ concentrations and river dispersion characteristics during periods of high and low river discharge. The CWTF discharges resulted in significant increases in Br⁻ compared to upstream baseline values in PDW raw drinking water intakes during periods of low river discharge. During high river discharge, the assimilative dilution capacity of the river resulted in lower absolute halide concentrations, but significant elevations Br⁻ concentrations were still observed at the nearest downstream PDW intake over baseline river levels. On days with active CWTF effluent discharge the magnitude of bromide impact increased by 39 ppb (53%) and 7 ppb (22%) for low and high river discharge campaigns, respectively. Despite a declining trend in Allegheny River Br⁻ (2009-2014), significant impacts from CWTF and coal-fired power plant discharges to Br⁻ concentrations during the low river discharge regime at downstream PDW intakes was observed, resulting in small modeled increases in total THM (3%), and estimated positive shifts (41-47%)

to more toxic brominated THM analogs. The lack of available coincident measurements of THM, precursors, and physical parameters limited the interpretation of historical trends.

Keywords: Specific Conductivity, Source Attribution.

Introduction

Elevated bromide (Br⁻) levels in source water can lead to the formation of higher levels of brominated disinfection byproducts (DBP) in finished drinking water; currently, conventional drinking water treatment processes do not effectively remove Br from source water (States et al., 2013). In 2010 the Pittsburgh Water and Sewer Authority (PWSA) observed significantly increased concentrations of total trihalomethanes (THM; a group of regulated DBPs) in their water distribution system that were near the regulatory limit of 80 ppb (U.S. EPA, 1998), and found the proportion of brominated THM species to be substantially higher than normal (States et al., 2013). Six additional drinking water companies relying on the Allegheny River as their source of raw water had their finished water tested and elevated levels of total and brominated THM concentrations were also found, suggesting that the concentration and chemical makeup of the THMs were changing in response to increased Br⁻ concentrations in the river source water (States et al., 2013). Brominated DBPs are of particular concern to public health authorities since they are more carcinogenic, cytotoxic, and genotoxic than their chlorinated DBP analogs (WHO, 2000; Plewa et al., 2002; Richardson et al., 2007), from consumption, inhalation during showering, and dermal exposure (Cantor et al., 2010; Font-Ribera et al., 2010; Kogevinas et al., 2010; Richardson et al., 2010). Discharges of treated oil and gas well produced wastewater and commercial coal-fired power plants have been implicated as the primary sources of excess Br⁻ in both the Allegheny and Monongahela rivers in Western Pennsylvania (States et al., 2013; Warner et al., 2013; Wilson and VanBriesen, 2013). Naturally occurring brine in the hydrocarbon rich formations in the Appalachian Plateau in Western Pennsylvania leads to elevated Br⁻ and chloride (Cl⁻) concentrations in the oil and gas produced wastewater (Dresel and Rose, 2010; Haluszczak et al., 2013). These elevated levels of Br⁻ and Cl⁻ being discharged into the Allegheny River have raised concerns of many Western Pennsylvania water suppliers over their ability to comply with the U.S. Environmental Protection Agency (EPA) Stage 2 Disinfectant/Disinfection Byproduct Rule (2006) amending the sampling and quarterly DBP calculation methodologies with compliance beginning in 2012 for the largest systems.

The large national increase in exploration, drilling, and production of oil and gas from nonconventional shale resources has generated large volumes of additional wastewater that ultimately needs to be reused/recycled or disposed (Kargbo et al., 2010; Gregory et al., 2011; Vidic et al., 2013). Most oil and gas well wastewater is disposed through deep well injection in many parts of the U.S. (Gregory et al., 2011). However, in Pennsylvania, there is currently a limited capacity for deep well injection with only eight EPA approved Class IID brine disposal wells, and the development of the Marcellus Shale has increased the total wastewater generated in the region by ~570% since 2004 (Lutz et al., 2013). The majority of oil and gas well wastewater that is not reused is either trucked out of state for deep brine disposal well injection or disposed of using alternative methods (Veil, 2010; Wilson and VanBriesen, 2013).

In Pennsylvania, the first Marcellus Shale gas well was drilled in 2004 (PA DCNR, 2014). Through March 9, 2012 the Pennsylvania Department of Conservation and Natural Resources issued 11,772 permits for non-conventional wells in the Marcellus Shale, of which 1,456 well completion reports were received (PA DCNR, 2014). Overall, the number of gas producing wells increased in Pennsylvania from 46,654 in 2005 to 55,136 in 2012 (U.S. EIA, 2014). Historically, Pennsylvania has allowed oil and gas produced wastewater to be discharged into publicly owned sewage treatment works (POTWs) where it was diluted, or treated by commercial wastewater treatment facilities (CWTF) that solely treat wastes from oil and gas producers with subsequent discharge to surface waters (Veil, 2010; Lutz et al., 2013). Most CWTFs are designed to chemically precipitate, flocculate, and filter solids; but are not designed nor successful in removing dissolved monovalent halides like Br⁻ and Cl⁻ (Ferrar et al., 2013; Warner et al., 2013). In 2011 the Pennsylvania Department of Environmental Protection (PADEP) issued a letter to oil and gas producers requesting that they voluntarily discontinue using POTWs and CWTFs to dispose of Marcellus formation wastewaters (PA DEP, 2011), which accounted for 79% of gas-related wastewater in Pennsylvania that year (Vidic et al., 2013). All indications suggest that the producers have complied and diverted Marcellus derived wastewater to other reuse or disposal options (Wilson and VanBriesen, 2013). However, other non-Marcellus Devonian unit oil and gas wastewaters continue to be sent to both POTWs and CWTFs that ultimately discharge to surface waters (Vengosh et al., 2014; U.S. EPA 2015). The concentrations of Br⁻ and Cl⁻ in the upper Devonian well brines have been reported to be as high or higher than the Marcellus wastewater (Dresel and Rose, 2010; Warner et al., 2013).

The Allegheny River is a vital natural resource to residents of Western Pennsylvania. Among its provisioning services are accepting waste discharge and supplying drinking water. There is a delicate balance between these services, especially during low river discharge periods when the

river's assimilative capacity to dilute contaminant concentrations down to safe levels is diminished (Ferrar et al., 2013). The Allegheny watershed is vulnerable to impairment due to current discharges from POTWs, CWTFs, coal-fired power plants, iron and steel production, manufacturing, urban runoff, roadway deicing materials, ongoing coal mining activities, legacy mine discharges, and acid rain (Schofield 1982; PA DEP 2002; Wilson and VanBriesen, 2013). The water quality at the intakes for public drinking water systems (PDW) is degraded by these upstream discharge sources, and concern over this balance is heightened due to perceived impacts from increased oil and gas drilling activities (States et al., 2013). Many of the sources of impairment to river water quality have distinctive chemical characteristics, discharge at different spatial locations, and are variable in time (U.S. EPA 2015). To manage these valuable watershed services, investigative tools and strategies that exploit these unique discharge properties are needed that track and quantitatively apportion discharge source impacts on surface water quality.

This study's goals were to (i) establish an approach whereby the impact of a surface water discharge from a single CWTF in the upper reaches of the Allegheny river on the raw water halide concentrations at the nearest downstream PDW could be quantitatively evaluated, and (ii) to estimate the impact of CWTF discharges on total THM concentrations and the relative abundance of brominated DBPs in finished drinking water at two PDWs on the Allegheny River using empirical EPA models.

Methods

Study Design

In 2012, U.S. EPA conducted three seasonal two-week sampling campaigns: spring (April 30-May 14), summer (July 5-19), and fall (September 19-October 4) on the upper Allegheny River in Pennsylvania. Samples were simultaneously collected from an upstream location (S01-Upstream), a CWTF discharge (S02-CWTF), two downstream locations (S03-Downstream1 & S04-Downstream2), and two downstream PDW raw water intakes (S05-PDW1 & S06-PDW2; Figure 1) using automated samplers. The CWTF was accepting, treating, and discharging non-Marcellus Appalachian Plateau Devonian strata oil and gas produced wastewater during all sampling campaigns. The upstream sampling location was to establish "baseline" conditions into the study domain, and the multiple downstream sampling locations were to evaluate transport and dispersion of inorganic species discharged by the CWTF to the closest downstream PDW. The Allegheny River km of each site and their relative distance from the CWTF discharge is presented in Appendix A.1. The first sampler downstream of the CWTF discharge was located ~12 km downstream to allow for adequate initial mixing of the effluent and river water. The second downstream sampler was located between the first downstream sampling location and the closest PDW intake, and was located ~15 km downstream of an 85 megawatt bituminous waste coal-fired power plant discharge. The second PDW plant was included to investigate the general trend of increasing Br⁻ concentrations in the Allegheny as it traverses from the upper into the lower reaches of river.

Allegheny River

The Allegheny River drains a catchment area of approximately 30,300 km² in the Pennsylvania and New York region of the northwestern Appalachian Plateau (PA Fish and Boat Commission, 2011). Most reaches of the upper Allegheny flow over locally-derived river sediment overlying thick layers of glacial outwash (sand and gravel). The Allegheny headwaters flow into the Allegheny Reservoir and leaves via the Kinzua Dam. Approximately 203 km of the Allegheny River downstream of the Kinzua Dam, including the entire upper Allegheny study domain (S01-Upstream to S05-PDW1), remains free-flowing; and is confined within a narrow, severely meandering valley with precipitous side slopes (PA FBC, 2011).

Further downstream, the Allegheny is impounded and regulated by the U.S. Army Corp of Engineers (USACE). The USACE manages the water level of the Allegheny in the study domain by controlling water discharge volumes from the Kinzua, Tionesta, Union City, and Woodcock reservoirs (USACE, 2014). This active management provides for flood control, water quality management, and downstream navigation requirements. The water levels in the upper reaches of the Allegheny River below the Kinzua Dam 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). Due to the resulting annual bimodal nature of Allegheny River water discharge rates, our data analysis is categorized into "high" ($\geq 8500 \text{ m}^3 \text{ min}^{-1}$) and "low" discharge (<8500 m³ min⁻¹) regimes (USGS, 1993).

Sample Collection

Teledyne Isco (Lincoln, NE) Model 6712 computer-controlled automatic sequential water samplers were utilized to simultaneously collect daily 800 ml composite river, CWTF, and PDW samples along the Allegheny River study domain. Acid-cleaned (Landis and Keeler, 1997) polypropylene bottles and Teflon sampling line were used to minimize contamination from the sampler. The samplers were programmed to collect 400 ml twice a day at 09:00 and 12:00 EST, after automatically rinsing the sampling line three times. The river sampler inlets were positioned as far away as possible from vegetation and eddy currents near the river banks, and ~15 cm off the river bed. Isco sampler inlet distance from the river banks ranged from 3.1-4.1 m during the high river discharge campaign, and 4.6-15.3 m during the low river discharge campaigns. Isco sampler inlet depths from the surface ranged from 46-71 cm during the high river discharge campaign, and 15-66 cm during the low river discharge campaigns. Sample bottles were retrieved every 2-4 days. Grab samples were also collected from the POTW and coal-fired power plant (CFPP) in the study domain using acid-cleaned polypropylene dippers and poured into sample bottles. Ultra-clean handling methods for sample deployment and collection were employed to avoid contamination of the collected samples (Landis et al., 2002). All collected samples were packed in ice and shipped overnight to the laboratory.

Conductivity

Onset (Cape Cod, MA) HOBO Model U24-01 in-river sondes were deployed to measure water temperature and electrical conductivity at each of the Isco sampling sites at 5 min intervals. A YSI (Yellow Springs, OH) Model 556 multi-parameter instrument was utilized to collect traceable temperature compensated specific conductivity (SC) readings to scale each Onset in-river sonde using manufacturer provided HOBOware[®] Conductivity Assistant software (Appendix A.2). The YSI instrument was calibrated each morning using YSI-3161 1000 μ S cm⁻¹ standard solution, checked again each night, and checked weekly using YSI-3165 100000 μ S cm⁻¹ standard solution. Daily calibration check precision (n=42) was 98 ± 2% (mean ± standard deviation), and the weekly high range linearity check precision (n=9) was 95 ± 4%. A collocated Onset in-river sonde was deployed at S03-Downstream1 and the collocated precision (n=16685) was 98 ± 3%.

Specific conductivity of Isco samples was determined in an EPA Class 100 clean room using a

Mettler Toledo (Columbus, OH) Model S47-K meter equipped with an InLab[®]731 probe. A two point calibration curve was generated each day using certified Mettler Toledo 1413 μ S cm⁻¹ and 12.88 mS cm⁻¹ conductivity standards. Accuracy checks were conducted using a Ricca Chemical (Arlington, TX) 1, 50, 100, and 200 mS cm⁻¹ certified secondary standards to ensure linearity. Replicate analysis was performed on a minimum of 10% of samples and the observed precision (n=54) was 99 ± 1%, and collocated sample precision (n=123) was 98 ± 5%. The mean of the two five-min Onset in-river conductivity data points corresponding to the two daily Isco sampling times were compared to the Isco sample conductivity and the relative precision was found to be 93 ± 10% (Appendix B.1).

Major Anions

Anions were quantified using a Dionex (Sunnyvale, CA) Model ICS-2000 ion chromatography instrument following an optimized U.S. EPA Method 300.1 (US EPA, 1997) technique as described below. Each sample was injected twice to evaluate analytical precision. Anion separations were performed with a 200 µL sample loop injection onto a Dionex IonPac[©] AG18 (4x50mm guard) and AS18 (4x250mm analytical) ion-exchange column, utilizing an isocratic potassium hydroxide eluent method. The analytical columns used met performance criteria specified in U.S. EPA Method 300.0 (1993). The ICS-2000 instrument was externally calibrated using a six point curve generated from a mixed Dionex seven anion standard (#057590). Initial calibration verification was performed with secondary source standards (High Purity Standards, Charleston, SC) and NIST (Gaithersburg, MD) Standard Reference Materials for Cl⁻ (#3182) and Br⁻ (#3184). Calibration stabilities were verified daily by mid-level continuing calibration verification samples. Linear calibration curve statistics were verified with minimum acceptance criteria of a coefficient of determination $(r^2) > 0.999$. In order to increase the linear dynamic range, two analytes (sulfate (SO_4^{2-}) , Br⁻) were processed with a quadratic regression, utilizing seven calibration points with minimum acceptance criteria of $r^2 > 0.99$. Prior to injection, all field samples were filtered using Millipore (Billerica, MA) IC-Millex syringe filters (25mm, 0.45µm PTFE). Each chromatogram was visually verified for peak shape, retention and identification. CWTF samples were all diluted 1000x with ASTM Type I ultra-pure water (18.2 M Ω ·cm) prior to analysis. Replicate analysis was performed on ~10% of all samples and the resulting analytical precision ranged from 99 $\pm 2\%$ (Br⁻) to 100 $\pm 1\%$ (Cl⁻, SO₄²⁻). Collocated

samples were collected and analyzed for ~30% of all observations and the resulting precision ranged from 96 \pm 10% (SO₄²⁻) to 99 \pm 2% (Cl⁻). A summary of all analyte specific instrument detection limits, method detection limits, and analytical/collocated precision are presented in Appendix A.3.

USGS River Gage Data

River water discharge volumes for the sampling domain were obtained from the U.S. Geological Survey (USGS). Hourly discharge data is available from October 1, 2007 through 2014 (USGS, 2015) for gage station #03025500 (Franklin, PA) located 1.5 km upstream of site S01-Upstream on the Allegheny River, and gage station #03031500 (Parker, PA) located 11 km downstream of S05-PDW1. The Parker gage station is located 1.8 km downstream of the Clarion River confluence. The water discharge contribution from the Clarion River as measured by gage #03030500 (Piney, PA) was subtracted from the gage value downstream of S05-PDW1 to estimate river discharge closure within the upper Allegheny River sampling domain (Appendix B.2).

Categorization of CWTF Discharge Impacted Samples

The non-continuous operation schedule of the CWTF resulted in periods with and without discharge. High time resolution (5 min) in-river sonde conductivity data from each of the sampling sites clearly elucidated defined CWTF conductivity discharge plume tracer events as they were transported and hydrologically dispersed downstream through the upper Allegheny River sampling domain. Transit time analysis was performed independently between the CWTF-P45 (45 m downstream of the discharge pipe) and each downstream site, similar to conducting a dye or tracer study in the river (Smart and Laidlaw, 1977; Kunkel and Radke, 2011). An example site-to-site transit time analysis of the CWTF discharge conductivity plumes to the 12.2 km downstream site S03-Downstream1 from September 24-29, 2012 is presented in Figure 2. The example transit times (Δ t) defined as the CWTF median discharge time to the maximum downstream conductivity value were ~16 hours during this period, and are depicted as dropdown lines in Figure 2. Figure 3 depicts the CWTF-P45 and S03-Downstream1 site conductivity data example after the Δ t = 16 hour plume transit time adjustment, showing the conductivity peaks observed at site S03-Downstream1 align with the CWTF discharge times (drop down lines represent the programmed Isco sampling times). Transit times were calculated

independently for each sampling site during each seasonal sampling period.

Based on these empirically derived plume transit times to each of the downstream sites and the duration of the CWTF discharge, all Isco samples were categorized as "discharge impacted" if one or both of the sample collection times (9:00 and 12:00 EST) fell within the conductivity plume impact time for each site. Based on the transit time analysis Isco samples from the example time period: September 24-28 and September 29 were categorized as "impacted" and "non-impacted", respectively. Each Isco sample and its associated time corrected in-river sonde conductivity data was visually evaluated to ensure accurate categorization. S06-PDW2 site was too far down stream to track the CWTF discharge conductivity plumes and was therefore not included in the intra-site analysis.

Disinfection Byproduct Empirical Modeling

Empirical modeling of DBP formation in PDW was conducted to estimate the impact of additional Br⁻ contributed by CWTF discharges on total THM and brominated analogs at two downstream intakes. The EPA empirical models employed (U.S. EPA, 1998; Solarik et al., 2000) are statistically-based and were developed by EPA for predicting DBP formation during water treatment disinfection using chlorine and ozone. Each model was formulated through multiple step-wise regression analysis and takes the form of a multiple regression equation. While the predictive empirical models may not accurately predict the complex conditions at any particular PDW (Brown et al., 2011) they are considered to generally descriptive and useful for the evaluation of water treatment facilities and human risk assessment (Sadiq and Rodriguez, 2004; Chowdhury et al., 2009). Different versions of the model were evaluated based on their ability to predict the reported THM concentrations at PDW1 and PDW2 during our sampling periods. Model input parameters are presented in Appendix Table A.4. Due to the use of prechlorination, the raw water version of the THM prediction model provided the best predictive results for both PDW1 and PDW2, and was utilized for all subsequent analysis. Based on median raw water Br⁻, temperature, and pH measurements made during this study and PADEP organic carbon measurements available for 2012-Quarter 2 (Q2) and 2012-Q3 at a location ~28 km upstream of PDW1 (PADEP, 2014;), the model predicted 2012-Q2 (high river discharge regime) total THM to be 50 ppb versus an actual reported concentration of 68, and the model predicted 2012-Q3 (low river discharge regime) THM to be 107 ppb versus an actual reported

concentration of 110 ppb.

EPA's empirical raw water DBP model was also run for PDW2 using the median raw water Br⁻, temperature, and pH measurements made during this study and PADEP organic carbon measurements available for 2012-Q2 and 2012-Q3 at a location ~25 km upstream (PA DEP, 2014). The model predicted 2012-Q2 (high river discharge regime) THM to be 47 ppb versus an actual reported THM concentration of 53, and the model predicted 2012-Q3 (low river discharge regime) THM to be 99 ppb versus an actual reported THM concentration of 101 ppb. Based on the reasonable results of the raw water model, it was used to estimate the impact of the Br⁻ concentrations attributed to CWTF discharges on PDW THM concentrations.

Statistical Analysis

Data processing and all statistical analyses were performed using SAS v.9.4 (SAS Institute, Cary, NC). Parametric statistics used in this analysis include: a t-test for independent samples, and one-way analysis of variance (ANOVA). The assumptions of the parametric procedures were examined using residual plots, skewness and kurtosis coefficients, Shapiro-Wilk test, and the Brown-Forsythe test. If assumptions of the parametric procedures were violated, then the Wilcoxon and Kruskal-Wallis non-parametric procedures were used, respectively. Analytical and collocated precision were calculated as 1-(absolute percent difference) for replicate and collocated sample analysis, respectively. In order to determine which combination of major anions best predicts conductivity, the results, which were first obtained using stepwise regression glmselect procedure, were verified using the general linear model sums of squares and Spearman correlation matrix. One-sided tests and a level of significance of α =0.05 was used for all statistical procedures unless otherwise stated.

To determine if the CWTF discharge significantly increased halide concentrations at downstream sampling sites, the downstream Isco samples were evaluated by both intra- and paired inter-site statistical hypothesis tests. The downstream inter-site "discharge impacted" Isco samples were paired with their associated transit time corrected S01-Upstream sample. During the spring high river discharge measurement intensive, S03-Downstream1 Isco samples paired with S01-Upstream Isco samples on the same day while S01-Upstream Isco samples paired with S04-Downstream2 and S05-PDW1 Isco samples on the following day. During low river discharge

measurement intensives in the summer and fall, S03-Downstream1 Isco samples were lagged by one day whereas S04-Downstream2 and S05-PDW1 Isco samples were lagged by two days with their paired S01-Upstream sample.

Upper Allegheny Mass Balance Model

A box model detailing daily river baseline and source discharge loading was developed to investigate the dilutive capacity of the river in our study domain and to evaluate the estimated CWTF impact on Br⁻ and Cl⁻ at downstream S05-PDW1 based on the inter- and intra-site comparison method. Daily river baseline loadings were calculated as the product of the river volumetric flow and the S01-Upstream river concentration. Source discharge contributions from S02-CWTF were calculated as the product of the facility reported daily discharge volumes and the daily EPA sample concentrations. Source loading from the POTW and CFPP (without flue gas desulfurization (FGD) scrubbers) in the study domain (Figure 1) were calculated using the mean EPA discharge grab sample concentrations and facility reported monthly discharge volume (adjusted to daily discharge volume). The water volume closure of the box model in the upper Allegheny River study domain was evaluated using the results calculated using Equation 1 (Appendix B.2).

$$Closure (\%) = 100 - \left[\left(\frac{Parker \, Gage - (Franklin \, Gage + Clarion \, River \, Gage)}{Parker \, Gage} \right) * 100 \right]$$
(1)

Results and Discussion

Monitoring Campaign Allegheny River Conditions

The river flow conditions and CWTF wastewater discharge characteristics during the sampling campaigns were evaluated to see if they were generally representative of overall 2012 conditions. A non-parametric Wilcoxon Two-Sample Test, found no significant difference between the 2012 daily mean Allegheny River high discharge period volumes ($25,246 \pm 12,067 \text{ m}^3 \text{ min}^{-1}$; p=0.56) and the discharge volumes during the study campaign sampling period ($25,477 \pm 3,880 \text{ m}^3 \text{ min}^{-1}$; Appendix B.3a). However, the Wilcoxon two-Sample Test did find a significant difference between the 2012 daily mean Allegheny River low discharge period volumes ($5,059 \pm 1082 \text{ m}^3 \text{ min}^{-1}$; p=0.05) and the discharge volumes during the study campaign sampling period ($4,591 \pm 566 \text{ m}^3 \text{ min}^{-1}$; Appendix B.3b). When evaluating the 2012 Allegheny River discharge volumes

to the available daily historical records (2007-2014), we found the 2012 high river discharge period volumes to be consistent with the average values ($25,266 \pm 11,575 \text{ m}^3 \text{ min}^{-1}$; p=0.56; Appendix B.3a) but the low discharge rates were found to be significantly lower than the historical average ($4,977 \pm 1,025 \text{ m}^3 \text{ min}^{-1}$; p<0.001; Appendix B.3b) due to a summer drought.

The median CWTF treated wastewater discharge volumes from April 2 - October 31, 2012 (n=157) was 333,976 liters per operation day with a range of 8,210 - 750,269 liters. The median CWTF discharge volume during the monitoring campaigns was (n=38) 245,696 liters per operation day with a range of 9,017 - 676,075 which was not significantly different from the overall period (Wilcoxon Two-Sample Test p=0.06). The facility indicated its discharge volumes were a function of customer demand for brine treatment services and facility operational conditions.

Upper Allegheny River Observations

The overall study conductivity and halide results are generally consistent with previous observations (States et al., 2013), which demonstrate that background levels in the upper Allegheny River are relatively low and significantly increase downstream. When the high and low river discharge regimes are examined independently (Table 1), the assimilative dilution capacity of the river during periods of high discharge is evident for halide species and results in significantly (p<0.001) lower conductivity, Br⁻, and Cl⁻ at each of the sites (S01-Upstream through S05-PDW1). The median domain baseline conductivity (126 μ S cm⁻¹), Br⁻ (25 ppb), and Cl⁻ (13.1 ppm) at S01-Upstream during the spring high river discharge campaign were lower than the corresponding medians of 174 μ S cm⁻¹, 72 ppb and 21.0 ppm during the combined summer/fall low river discharge campaigns. The median S05-PDW1 conductivity (158 μ S cm⁻¹), Br⁻ (38 ppb) and Cl⁻ (17.0 ppm) during the high river discharge campaign increased to 202 μ S cm⁻¹, 85 ppb and 23.5 ppm, respectively, during the low river discharge campaigns. While the overall halide concentrations were lower during the high discharge spring campaign, the S05-PDW1 site downstream of the CWTF discharge in our study domain was significantly higher than S01-Upstream baseline site for conductivity, Br⁻, and Cl⁻.

Lower Allegheny River Observations

While not in the upper Allegheny River study domain, comparing the results observed at S06-

PDW2 ~100 km further downstream from S01-PDW1 is informative to evaluate the integrative impact of additional downstream sources in the watershed on another public drinking water resource (U.S. EPA, 2015; Appendix B.4a-c). Significant increases in conductivity, Br⁻, Cl⁻, and SO₄²⁻ were observed between S05-PDW1 and S06-PDW2 during the low river discharge campaigns, and significant increases in conductivity, and SO_4^{2-} were observed during the high river discharge campaign (Table 1; Appendix B.4a-d). On an integrated basis during the high river discharge campaign, there was a 154% increase in SO_4^{2-} (11.3 to 28.7 ppm), a 16% increase in conductivity (157 to 182 µs cm⁻¹), a 3% decrease in Br (36 to 35 ppb), and an 8% decrease in Cl⁻ (17.3 to 15.9 ppm) from S05-PDW1 to S06-PDW2. During the low discharge campaigns there were significant increases (Table 1; Appendix B.4a-d) in all contaminant concentrations at S06-PDW2 relative to S05-PDW1 including a 754% increase in SO_4^{2-} (9.6 to 82.0 ppm), a 83% increase in conductivity (204 to 374 µs cm⁻¹), a 63% increase in Br⁻ (87 to 142 ppb), and a 29% increase in Cl⁻ (23.6 to 30.4 ppm). A stepwise multi-linear regression analysis found that conductivity at S01-Upstream and S06-PDW2 were best predicted by Cl⁻ and SO₄²⁻ ($R^2 = 0.965$), while conductivity at S03-Downstream1, S04-Downstream2, and S05-PDW1 were best predicted by Cl⁻ and Br⁻ ($R^2 = 0.862$). This finding indicates that in the upper reaches of the Allegheny River (S03-Downstream1 to S05-PDW1) downstream of the CWTF discharge conductivity is halide dominated, whereas in the lower reaches of the Allegheny River (S06-PWD2) it reverts back to a more SO_4^{2-} dominated system.

The distance, tributary inflow (Appendix B.2), and additional anthropogenic discharge sources downstream of S05-PDW1 preclude identification of the source types contributing to the elevated concentrations at S06-PDW2 within the context of this work. One indication that coal-related sources are substantially impacting halide concentrations at S06-PDW2 is the large increase in SO₄²⁻ (Table 1) in combination with a downward shift in the Cl⁻/Br⁻ ratio in relation to the upper Allegheny River study domain (Appendix B.5). During the low river discharge campaigns the median Cl⁻/Br⁻ drops from 278 (S05-PDW1) in the upper Allegheny River study domain to 217 (S06-PDW2) suggesting an impact from a characteristically lower Cl⁻/Br⁻ source such as upper Pennsylvanian Conemaugh and Monongahela formation bituminous coals that are mined regionally (Seere and Lee, 2009; U.S. EPA, 2015).

Impact of CWTF on S05-PDW1 Raw Water

The operation schedule of the CWTF during the study campaigns, nominally 06:00-13:00 EST Monday through Friday, allowed us to investigate downstream river conditions both in the presence and absence of treated oil and gas wastewater discharge. During both the high and low river discharge campaigns, the automated samplers captured a sufficient number of CWTF discharge impacted and non-impacted categorized samples at the S03-Downstream1, S04-Downstream2 river sites, and S05-PDW1 intake for inter- and intra-site statistical analyses. A summary of the high and low river discharge regimes CWTF impacted and non-impacted categorized data and inter-site paired Kruskal-Wallis one-sided test results are presented in Tables 2 and 3, respectively.

Evaluating the impact of the S02-CWTF discharge on downstream sites can be characterized on an inter-site basis by evaluating the S01-Upstream conductivity and anion species means versus the downstream site means for those species that were found to have no significant sources in the study domain other than the CWTF discharge. In this case we define no other significant source impacting the PDW intake as a condition whereby (i) the non-discharge impacted categorized samples at S05-PDW1 and their paired S01-Upstream site samples are not significantly different during both high (Table 2) and low (Table 3) river discharge conditions and (ii) no significant contribution from the POTW and CFPP discharge grab samples, only Br⁻ meets this criterion. During both the high (Table 2) and low (Table 3) river discharge sampling periods the observed Br⁻ concentrations at S03-Downstream1, S04-Downstream2, and S05-PDW1 raw drinking water intake were not significantly different than the paired S01-Upstream Br⁻ concentrations during non-discharge impacted days, but were significantly higher during CWTF discharge impacted days. These relationships for the Allegheny River low discharge regime are clearly depicted in Figure 4a where the stable Br⁻ concentrations throughout the study domain during non-CWTF discharge days are contrasted with the clearly observable downstream enhancement during discharge days, which was initially highest at the S03-Downstream1 site with decreasing concentrations as a result of dilution and hydraulic dispersion downstream to S05-PDW1. This inter-site analysis takes into account the periods of CWTF discharge only and provides a quantitative overall estimate of Br⁻ enhancement through the study domain. The magnitude of the integrated Br⁻ enhancement during low river discharge from the CWTF on downstream sites was 109% (81 ppb) at S03-Downstream1, 45% (33 ppb) at S04-Downstream2, and 51% (38 ppb) at S05-PDW1. During high river discharge the integrated Br⁻ enhancement on downstream sites was 50% (14 ppb) at S03-Downstream1, 31% (8 ppb) at S04-Downstream2, and 50% (13 ppb) at S05-PDW1. At first glance the lower relative impact of the CWTF effluent discharge on observed Br⁻ concentrations at the S03-Downstream1 site during the high river discharge period seemed to suggest that the Allegheny River's assimilative capacity was adequate to dilute CWTF related contaminants down to lower relative levels within the 12 km distance between the discharge and the site. However, when we evaluated the Isco sampling times categorized as CWTF impacted versus the associated in river sonde conductivity plume impact time (e.g., Appendix B.5), it was observed that the automated sampler did not capture the main discharge plume which was still clearly evident and not fully mixed. The systematic mismatch of Isco sampling and CWTF discharge plume impact times encountered at site S03-Downstream1 during the high discharge sampling campaign biased the relative impact down in relation to both the impact observed at the site during the low river discharge campaigns and the S04-Downstream2 and S05-PDW1 sites during the high river discharge campaign. While Cl⁻ presented a similar overall response as Br⁻ (Figure 4b) demonstrating a clear impact from CWTF effluent, the S05-PDW1 site high river discharge sampling period Cl⁻ concentration was significantly higher (p=0.016) than S01-Upsteam during non-discharge days (Table 2); suggesting another contributing source(s) (e.g., CFPP discharge) and precluding its inclusion in the inter-site analysis.

The impact of CWTF effluent discharge on downstream sites within the study domain was also evaluated using CWTF discharge categorized intra-site analysis, whereby the CWTF impacted and non-impacted sample subsets at each site were statistically compared (Table 4; Figures 4a-c). Both downstream river sites (S03-Downstream1, S04-Downstream2) and S05-PDW1 were found to have significantly higher conductivity, Br⁻, and Cl⁻ during both high and low river discharge conditions when being impacted by the CWTF effluent discharge plume. The discharge categorized data from the high and low discharge regime campaigns used for intra-site analysis are presented in Table 4 and are depicted in Figures 4a-c. The S01-Upstream conductivity data $174 \pm 13 \ \mu\text{S cm}^{-1}$ has a relatively tight range compared to the CWTF downstream sites and the distribution is not significantly different than normal (Shapiro-Wilk; p=0.166; Figure 4c). The magnitude of the mean conductivity impact from the CWTF on downstream sites during low river discharge, determined by evaluating all the impacted versus non-impacted categorized

samples, was an increase of 15% (28 μ S cm⁻¹) at S03-Downstream1, 12% (23 μ S cm⁻¹) at S04-Downstream2, and 12% (23 μ S cm⁻¹) at S05-PDW1. The CWTF discharge categorized Cl⁻ data from the low discharge regime campaigns are depicted in Figure 4b. Using the same analytical approach described above, the magnitude of the Cl⁻ impact from the CWTF discharge on downstream sites was an increase of 40% (8.4 ppm) at S03-Downstream1, 21% (4.5 ppm) at S04-Downstream2, and 19% (4.3 ppm) at S05-PDW1. The CWTF discharge categorized Br⁻ data from the low discharge regime campaigns are depicted in Figure 4a. The magnitude of the Br⁻ impact during the low discharge regime was an increase of 105% (79 ppb) at S03-Downstream1, 55% (39 ppb) at S04-Downstream2, and 53% (39 ppb) at S05-PDW1. In contrast, the S01-Upstream baseline and non-impacted downstream Br⁻ mean concentrations were indistinguishable (74 ± 2 ppb), which is a strong indication that non-impacted samples were properly categorized and that there were no other significant sources of Br⁻ in the study domain (Figure 4a).

During the high river discharge sampling regime the overall observed concentrations and the magnitude of CWTF impact were lower at all downstream sites due to the river's increased dilution capacity. The CWTF effluent discharge enhancement for (i) conductivity was an increase of 7% (9 μ S cm⁻¹) at S03-Downstream1, 6% (8 μ S cm⁻¹) at S04-Downstream2, and 2% (3 μ S cm⁻¹) at S05-PDW1, (ii) Cl⁻ was an increase of 20% (2.7 ppm) at S03-Downstream1, 11% (1.5 ppm) at S04-Downstream2, and 5% (0.9 ppm) at S05-PDW1, and (iii) Br⁻ was an increase of 75% (18 ppb) at S03-Downstream1, 31% (8 ppb) at S04-Downstream2, and 22% (7 ppb) at S05-PDW1.

Cl⁻/Br⁻ Ratio

Halide ratios (e.g., Cl⁻/Br⁻) are used in hydrogeological studies to elucidate water migration because the species primarily occur as dissolved monovalent ions that typically are conserved during movement through environmental compartments (Davis et al., 1998; Freeman 2007; Alcala and Custodio, 2008). Formation water from Devonian oil- and gas-bearing units such as the Marcellus are enriched in Br⁻ resulting in characteristically lower Cl⁻/Br⁻ ratios (Ferrar et al., 2013; Warner et al., 2013). The Cl⁻/Br⁻ ratio of the S02-CWTF discharge was significantly different (Kruskal-Wallis p<0.0001) during the high (n=13; 110.6 ± 6.2) and low (n=23; 90.4 ± 2.4) discharge regime sampling campaigns. The Cl⁻/Br⁻ ratio of data presented by Warner et al., (2013; and references within) was 127.2 from a similar CWTF discharge in Western Pennsylvania treating a combination of Marcellus and conventional Devonian produced wastewater (2010-2012), 107.8 from raw upper Devonian produced water, 93.4 from raw Marcellus produced water, and 108.5 from raw Lower Devonian produced water. The discharge categorized Cl⁻/Br⁻ ratio data from the low discharge regime campaigns indicate higher values were observed during non-impact conditions compared to impacted conditions (Figure 5). Similar to the Br⁻ results, good agreement between the low discharge regime S01-Upstream (316.0 \pm 80.3) and non-impact categorized downstream Cl⁻/Br⁻ ratios is an indication of no additional significant sources of Br⁻ enriched discharge into the study domain. A significant reduction (p=0.023) of the Cl⁻/Br⁻ ratio is observed at the S03-Downstream1 site when being impacted by the CWTF discharge (205.9 \pm 38.9) and then increases as the halides are diluted by the more Cl⁻ dominated baseline river flow (316.0 \pm 80.3) down to sites S04-Downstream2 (246.2 \pm 33.6) and S05-PDW1 (243.7 \pm 35.5; Figure 5). Within the upper Allegheny study domain (S01-Upstream to S05-PDW1) elevated total Br⁻ and low Cl⁻/Br⁻ sample ratios appear to be a good indicator of CWTF discharge downstream impact.

In the context of S06-PDW2 and other locations in the lower reaches of Allegheny River watershed, interpretation of Cl⁻/Br⁻ ratios becomes more difficult as the number of sources discharging into the river and its tributaries dramatically increase (e.g., public/commercial wastewater treatment facilities, discharges from coal mines, coal bed methane (CBM), CFPP). The mean Cl⁻/Br⁻ ratio observed at S06-PDW2 during the high river discharge regime (460 ± 71) was significantly higher (p<0.0001) than the Cl⁻/Br⁻ ratio during the low river discharge regime (216 ± 17) , suggesting that the elevated halides measured during the low river discharge campaign were the result of discharges of wastewaters containing characteristically lower Cl⁻/Br⁻ ratios into the river. Coal mined in the region from the upper Pennsylvanian Conemaugh and Monongahela formation bituminous coals (e.g., Pittsburgh #8; Kosanke, 1984) have been found to contain high concentrations of Br⁻ (13.4 ppm) and a low Cl⁻/Br⁻ ratio of 72.6 (Seere and Lee, 2009). In addition, contemporaneously collected samples of wastewater discharges from other anthropogenic activities exploiting the same coal formations and discharging into the Allegheny River or its tributaries between sites S05-PDW1 and S06-PDW2 also contain Cl⁻/Br⁻ ratios substantially lower that the upper Allegheny baseline S01-Upstream values (316.0 ± 80.3) including: coal ash (40.7), treated FGD (68.4), CBM (129.9), treated AMD (158.1), AMD seeps

(172.6), and active coal mine runoff (183.0; EPA 2015).

The timeline of increasing PDW THM concentrations along the Allegheny River and its perceived correlation to expanding exploitation of the Marcellus shale in western Pennsylvania for gas and oil production reported by States et al. (2013), was also concurrent with the regional trend of installing air pollution control systems in CFPPs. The development of the EPA 2005 Clean Air Interstate Rule, the 2011 Cross-State Air Pollution Rule, and the 2011 Mercury and Air Toxics Standards have led to the wide spread retrofitting of the US CFPP fleet with FGD scrubbers. Scrubber installations reached 64% of CFPPs by the end of 2012 (US Energy Information Administration). Among other pollutants such as SO₂ and divalent mercury species (e.g., HgCl₂, HgBr₂), scrubbers also efficiently remove halides from the stack gas that originates naturally in the combusted coal. Once FGD scrubbers remove components from the stack exhaust (e.g., halides and sulfur dioxide), CFPPs typically discharge treated scrubber wastewater as well as storm water runoff from coal and residual ash piles enriched in halides and sulfate to surface waters in western Pennsylvania (U.S. EPA 2015).

Upper Allegheny Mass Balance Model

The water volume closure of the box model in the upper Allegheny study domain was evaluated using the results calculated using Equation 1, and the daily mean volume closure was found to be $88 \pm 11\%$. The model on average underestimated the volume of water in the system because of inflows from three ungaged tributaries (Turkey Run, Sandy Creek, Scrubgrass Creek) into the Allegheny River between sites S01-Upstream and S05-PDW1 (Appendix B.2) were not included in the model. Water volume closure during the high river discharge regime (95 ± 12) was on average better than during the low river discharge regime (84 ± 8).

During the low discharge campaigns, the river baseline flow contributed an average of 448 kg of Br⁻ and 133,970 kg of Cl⁻ into the model domain on CWTF discharge days. The daily mean source contribution from S02-CWTF was 202 kg Br⁻ and 18,208 kg Cl⁻, the contribution from the POTW was 0.0 k g Br⁻ and 1,332 Cl⁻, and the contribution from the CFPP was 0.1 kg Br⁻; and 196 kg Cl⁻. Assuming homogeneous steady state conditions with no additional source terms, the box model predicts the S02-CWTF discharge would contribute an average of 44 ± 22% of the Br⁻ and 14 ± 7% of the Cl⁻ into the upper Allegheny River sampling domain (Figure 6a). The box

model results agree well with the 53% Br⁻ (39 ppb) and 19% Cl⁻ (4.3 ppm) contributions from the intra-site analysis, and the 51% Br⁻ (38 ppb) and 26% Cl⁻ (5.4 ppm) contributions from the inter-site analysis at S05-PDW1 (Table 5). The daily box model average estimated total Br⁻ mass (649 kg day⁻¹) contribution into the upper Allegheny River domain was within 8% of the S05-PDW1 measurement based Br⁻ mass estimate (703 kg day⁻¹), indicating the observed impact at PDW1 during low river discharge could be explained through the contributions of the three known discharge sources into the river within the uncertainty of the water volume closure.

During the high river discharge measurement campaign, the Allegheny River water volume was five times greater than during the low river discharge measurement campaigns. While the high discharge campaign halide concentrations were lower, the river baseline discharge contributed more than double the halide mass (mean of 973 kg of Br⁻ and 490,853 kg of Cl⁻) into the model domain per CWTF discharge day than was observed during the low river discharge periods. The daily mean source contributions from S02-CWTF was 159 kg Br⁻ and 17,323 kg Cl⁻ (Figure 6b). The daily mean source contributions from the POTW and CFPP were 0.0 and 0.1 kg Br; and 1,534 and 147 kg Cl⁻, respectively. During the high discharge regime the box model predicts the S02-CWTF discharge would contribute $16 \pm 6\%$ of the Br⁻ and $4 \pm 1\%$ of the Cl⁻ into the river domain. While the box model results agree relatively well with the 22% Br⁻ (7 ppb) and 5% Cl⁻ (0.9 ppm) contributions from the intra-site analysis (Table 5), overall it under predicts the total average daily loading in the river versus the S05-PDW1 measurement based estimates (Figure 6b). The generally higher CWTF impact estimated by the inter- and intra-site analyses was expected as the Isco sampling times were coincident with the CWTF effluent conductivity impacts measured at S05-PDW1 by the in-river sonde, whereas the box model assumes a homogeneous well mixed system. The observed CWTF effluent discharge impacts at S05-PDW1 suggests the impacts of the elevated halide concentrations on the raw water plant intake could be partially mitigated by conditional pumping based on near-field upstream conductivity measurements.

Implications of CWTF Discharges on PDW THM Concentrations

As reported by States et al. (2013) the PWSA and other water utility operators relying on the Allegheny as their raw water source observed significantly increased total THM concentrations and substantially higher than normal relative abundances in brominated analogs in 2010, and

hypothesized that these observations were a result of increased Br⁻ concentrations in their river source water. A time series analysis of Allegheny River Br⁻ concentration was not possible then as routine Br⁻ measurements by PADEP were not initiated until late 2009 (USEPA, 2014). If Br⁻ is present in PDW raw water it can be oxidized during the chlorination process to form HOBr, which can react with natural organic matter to form a plethora of intermediate brominated disinfection byproducts (Zhai and Zhang, 2011). It has been reported that HOBr is a more efficient substitution agent than HOCl (Symons et al., 1993; Cowman and Singer, 1996), and that HOBr is up to twenty times more reactive than HOCl in the formation of THM and haloacetic acids (Uyak and Toroz, 2007). A current time series of quarterly THM concentrations in finished drinking water and the annual rolling averages are presented in Figure 7a for site S05-PDW1 using all available data contained in the PADEP Drinking Water Reporting System (PADEP, 2014). An upward trend in the annual rolling average of THMs in finished drinking water, and an underlying seasonal variation are observed. A linear regression analysis was completed for quarterly THM rolling concentrations from 2010-Q1 through 2014-Q4 (Figure 7b) and a significant (p<0.0001; $r^2=0.864$) increasing trend of ~6 ppb per year was found. At this rate, S05-PDW1 will exceed the EPA THM standard of 80 ppb by 2016. The Q3 THM concentrations for 2010 through 2014 are significantly higher than the other quarters (p=0.011) reported during this period. The likely contributing factors to elevated Q3 THM concentrations are significantly higher Br⁻ (p=0.015) and organic carbon (p<0.0001) concentrations during the low river discharge regimes, as well as the higher water temperatures in the summer (Appendix A.2).

EPA's empirical raw water DBP treatment model was used to estimate the impact of the CWTF discharge on S05-PDW1 THM formation by comparing discharge impacted and non-discharge impacted intra-site analysis scenarios during the low (2012-Q3) discharge regime when the highest THM concentrations are reported (Figure 7a). The mean low river discharge non-impact categorized Br⁻ concentration from S05-PDW1 (73 ppb; Table 4) and CWTF impacted categorized (112 ppb; Table 4) samples were used to parameterize successive model runs. The predicted total THM concentration for the non-impacted baseline river condition was 105 ppb, and the predicted CWTF discharge impacted river condition yielded an estimated total THM value of 109 ppb (3% increase). While the additional Br⁻ in the S05-PDW1 raw water intake attributed to the CWTF enhancement discharge was not estimated to substantially contribute to

the overall total THM, the model predicted an overall decrease in chlorinated THM analogs and a large 41% increase in the more toxic brominated THM analogs. The model estimated a 37% increase in bromodichloromethane (19.0 to 26.0 μ g L⁻¹), a 113% increase in bromoform (0.2 to 0.4 μ g L⁻¹), and a 117% increase in dibromochloromethane (4.0 to 8.7 μ g L⁻¹).

Since S06-PDW2 samples could not be categorized as impacted and non-impacted by S02-CWTF due to the dissipation of the conductivity plume and additional downstream sources, the relative impact of aggregate CWTF discharges were based on a comprehensive multivariate positive matrix factorization (PMF) statistical receptor modeling analysis reported by U.S. EPA based on measurements made during this same study period at S06-PDW2 and nine other sampling sites located on the Allegheny River and its tributaries (U.S. EPA 2015). During the low river discharge regime, U.S. EPA (2015) attributed 37% and 59% of Br⁻ at S06-PDW2 to CWTF discharges and coal-fired power plants equipped with flue gas desulfurization scrubbers, respectively. EPA's empirical raw water DBP treatment model was used to estimate the impact of the total aggregate of CWTF discharges on S06-PDW2 THM formation by comparing mean observed Br concentration to the mean Br concentrations minus the estimated aggregate CWTF contributions during the low (2012-Q3) discharge regime. The mean low river discharge Brconcentration from S06-PDW2 (142 ppb; Table 1) and the Br⁻ concentration with the estimated 37% CWTF contribution removed (89 ppb) were used to parameterize successive model runs. A predicted total THM contribution at S06-PDW2 from CWTF attributed Br⁻ was 3 ppb, with a 47% increase in brominated THM analogs. The model estimated a 41% increase in bromodichloromethane (18.2 to 25.7 μ g L⁻¹), a 128% increase in bromoform (0.3 to 0.7 μ g L⁻¹), and a 133% increase in dibromochloromethane (5.0 to 11.5 μ g L⁻¹).

The empirical THM modeling results corroborate the States et al. (2013) and Parker et al., (2014) conclusion that increased Br⁻ concentrations in the Allegheny River attributable to CWTF wastewater discharges water can substantially shift PDW total THM from chlorinated to more toxic brominated analogs. However, the empirical THM modeling does not support the contention that Br⁻ attributed to CWTF discharges affects the overall trend of increasing THM concentrations (Figure 7b). From 2010 to 2014, PADEP data shows a significantly (p=0.0045) decreasing Br⁻ trend in the upper reaches of the Allegheny River in the vicinity of S05-PDW1 (Figure 7c) during the concurrent increasing trend in total THM (Figure 7b). The significantly

decreasing Br⁻ trend (p=0.005; Appendix B.7) is also observed in the lower reaches of the Allegheny River in the vicinity of S06-PDW2 during the concurrent (p=0.003) increasing trend in total THM from 2010 to 2013 (Appendix B.6). A sensitivity analysis of the THM formation model parameterized for both S05-PDW1 and S06-PDW2 suggests the increasing trend is more likely due to variability in the Allegheny River dissolved organic carbon (DOC) concentrations. Unfortunately, the majority of the available Allegheny River data reports primarily total organic carbon (TOC) rather than DOC concentrations which are more relevant to THM formation (U.S. EPA, 1998; Solarik et al., 2000). While there are no significant trends observed in the PADEP reported Allegheny River quarterly averaged TOC data in either the upper (p=0.18; Figure 7c) or lower (p=0.15; Appendix B.7) Allegheny River during the time period with available THM data, we did find significantly increasing trends in TOC in the monthly PDW plant reported raw water intake data at both S05-PDW1 and S06-PDW2 (p<0.0001; Figure 8) data from 2003 - 2015. TOC at S05-PDW1 and S06-PDW2 showed virtually identical increasing trends (slopes, intercepts, and coefficients of determination) of 2.4 µg L⁻¹ per year over the 13 year period.

Conclusions

As a result of Marcellus formation wastewater being diverted to other reuse and disposal options (PADEP, 2014), there has been a drastic reduction in the volume of oil and gas wastewater being discharged into the upper Allegheny River and a corresponding decreasing trend in observed Br⁻ surface water concentrations 2009-2014 (Figure 7c; Figure Appendix B.7). But despite the declining Allegheny River Br⁻ concentration, a significant impact of ongoing CWTFs operations to observed Br⁻ concentrations during the high (2012 Q2) and low (2012 Q3) river discharge sampling campaigns were observed at downstream PDW intakes in both the upper and lower reaches of the river. On days with active CWTF effluent discharge the magnitude of Br⁻ enhancement at S05-PDW1 increased by an average of 39 ppb (53%) and 7 ppb (22%) for high and low river discharge campaigns, respectively. The CWTF attributed Br⁻ resulted in small modeled increase in total THM (3%), but a substantial positive shift from chlorinated to more toxic brominated THM analogs at both S05-PDW1 (41%) and S06-PDW2 (47%). The empirical THM modeling results corroborate the States et al. (2013) and Parker et al., (2014) conclusion that increased Br⁻ concentrations in the Allegheny River attributable to CWTF wastewater discharges water can substantially shift PDW total THM from chlorinated to more toxic

brominated analogs. However, the empirical THM modeling does not support the contention that Br⁻ attributed to CWTF discharges affects the overall trend of increasing THM concentrations.

Suggestions for Future THM Monitoring/Modeling

While various sources of surface water and PDW analytical results are available in the public domain (EPA STORET, PADEP DWRS), the fragmented nature both spatially and temporally between open river and PDW sample collection as well as the lack of coincident THM, DOC, water temperature, and pH data prevent a process level understanding behind the underlying mechanisms for THM formation and the causality of the observed historical trends. Due to the multivariate nature of DBP formation, the integration and coordination of the PDW and surface water monitoring programs (e.g., sampling locations, time, analytes, parameters) is necessary to provide a basis for evaluating/modeling THM production mechanisms, underlying system dynamics, and understanding observed trends. For example the PADEP DWRS database contains 141 raw intake and plant water TOC and 40 THM concentrations for the S05-PDW1 facility (January 6, 2004 through August 11, 2015) but only 15 of the THM concentrations have matching TOC data and there are no matching DOC data. Likewise the PADEP DWRS database contains 148 raw intake and plant water TOC and 58 THM concentrations for the S06-PDW2 facility (April 17, 2003 through August 20, 2015) but only 13 of the THM concentrations have matching TOC data and there are no matching DOC data. In addition, there are no water temperature or pH data in the PADEP DWRS database for these facilities. All future studies should directly link THM empirical modeling input water measurement needs (water temperature, pH, DOC, Br⁻), PDW operation conditions (chlorine target, contact time), with actual resulting THM measurements.

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36		



Figure 2.











50 Figure 6.

(a) Low River Discharge Regime

<u>S01-Upstream + POTW + CFPP</u> 448 kg Br day⁻¹ 135,498 kg Cl day⁻¹ <u>S02-CWTF</u> 202 kg Br day⁻¹ 18,208 kg Cl day⁻¹ <u>S05-PDW1 (Actual)</u> 703 kg Br day⁻¹ 167,034 kg Cl day⁻¹



(b) High River Discharge Regime

 S01-Upstream + POTW + CFPP
 S02-CWTF

 973 kg Br day⁻¹
 159 kg Br day⁻¹

 492,534 kg Cl day⁻¹
 17,323 kg Cl day⁻¹

<u>S05-PDW1 (Actual)</u> 1475 kg Br day⁻¹ 671,763 kg Cl day⁻¹









56 Figure 7b.



58 Figure 7c.





Table 1. Summary of Allegheny River High (April 30 - May 14, 2012) and Low (July 5-19 & September 19-October 4, 2012)
 Discharge Isco Sample Results (Kruskal Wallis Tests Indicate all Low Discharge Concentrations are Higher at all Sampling
 Sites p < 0.0001).

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O	.)	

		S01-Upstream		S03-Downstream1		S04-Downstream2		S05-PDW1		S06- PDW2	
		High	Low	High	Low	High	Low	High	Low	High	Low
	n	15	31	14	31	13	30	15	26	15	28
Spec. Cond.	Median	126	174	131	187	142	198	158	202	186	360
$(\mu S \ cm^{-1})$	Mean	126	174	132	193	142	200	157	204	182	374
	Range	116-143	150-194	112-154	154-262	127-157	168-243	144-171	177-250	152-215	271-608
	n	15	31	13	30	13	30	12	26	15	28
Bromide	Median	25	72	28	88	32	78	38	85	35	132
(ppb)	Mean	26	72	34	101	31	85	36	87	35	142
	Range	22-36	33-117	19-56	37-277	20-36	38-154	27-41	39-166	26-44	103-202
	n	15	31	14	31	13	30	15	26	15	28
Chloride	Median	13.1	21.0	13.8	22.5	14.0	22.5	17.0	23.5	15.9	29.6
(ppm)	Mean	13.5	20.8	14.7	23.8	14.3	23.3	17.3	23.6	15.9	30.4
	Range	12.4-16.2	16.2-25.8	12.3-19.2	16.6-41.3	12.8-16.6	17.3-31.3	15.6-18.7	17.6-32	13.1-21.9	24.5-37.3
	n	15	31	14	31	13	30	15	26	15	28
Sulfate	Median	10.3	7.5	11.9	8.3	11.6	8.9	11.1	9.5	27.0	83.2
(ppm)	Mean	10.7	7.5	11.3	8.4	11.5	9.0	11.3	9.6	28.7	82.0
	Range	9.7-13.5	6.8-8.6	3.7-12.8	7.8-9.7	10.2-12.8	8-11.7	10.3-13.1	8.5-10.8	23.3-39.9	47.6-128.8

Table 2. Summary of Spring (April 30 - May 14, 2012) CWTF Discharge Categorized Paired Isco Sample Results for Inter-site
 Analysis, and Kruskal Wallis Non-parametric Hypothesis Test Results (bold are significant).

		CWTF Non-impacted		CWTF Impacted		CWTF Non-impacted		CWTF Impacted		CWTF Non-impacted		CWTF Non-impacted	
	Ì	S01- Upstream	S03- Downstream1	S01- Upstream	S03- Downstream1	S01- Upstream	S04- Downstream2	S01- Upstream	S04- Downstream2	S01- Upstream	S05- PDW1	S01- Upstream	S05- PDW1
	Paired n	Opsiteani	7	Opstream	7	Opsiteani	6	Opsiteani	7	7	1.0.01	Opsiteani	7
	Median	127	130	123	132	125	137	127	148	123	158	127	161
Spec. Cond.	Mean	124	128	128	137	126	137	127	145	125	156	127	159
(µS cm ⁻¹)	Range	116-131	112-137	116-143	122-154	118-138	127-151	116-143	130-157	118-138	144-166	116-143	148-171
	p-Value	0.109		0.016		0	0.031		0.016		16	0.016	
	Paired n	6			7		6		7	4	ł	7	
	Median	24	24	26	41	25	27	25	34	27	34	25	39
Bromide	Mean	25	24	28	42	27	26	26	34	28	34	26	39
(ppo)	Range	22-30	19-28	24-36	26-56	22-36	20-32	23-32	32-36	23-36	28-39	23-32	36-41
	p-Value	0.281		0.016		0.844		C).016	0.2	.50	0.	016
	Paired n	7		7			6		7	7	r		7
	Median	13.3	13.3	13	15.0	13.1	13.1	13.6	15.1	13	16.4	13.6	18
Chloride (ppm)	Mean	13.1	13.3	13.9	16.0	13.5	13.5	13.7	15.0	13.4	16.8	13.7	17.7
(ppm)	Range	12.6-13.6	12.3-13.9	12.4-16.2	13.6-19.2	12.4-16.2	12.8-15.8	12.6-16	13.2-16.6	12.4-16.2	15.6-18.4	12.6-16	16.8-18.7
	. V-l	0.469		0.016		1.000		0.016		0.016		0.016	
	p-value	0	.469	().016	1	.000	L	0.016	0.0	10	•	010
	Paired n	0	7	().016 7	1	6		7	7	,		7
	Paired n Median	10.1	7 11.9	10.3	7 11.9	10.9	6 11.5	9.9	7 11.6	7 10.6	11.1	9.9	7 11
Sulfate	Paired n Median Mean	10.1	7 11.9 10.7	10.3 10.4	7 11.9 11.9	10.9	6 11.5 11.7	9.9	7 11.6 11.4	7 10.6 10.9	11.1 11.3	9.9 10.5	7 11 11.3
Sulfate (ppm)	Paired n Median Mean Range	10.1 10.5 9.8-12.3	7 11.9 10.7 3.7-12.8	10.3 10.4 9.7-12.3	0.016 7 11.9 11.9 11.1-12.4	10.9 11 9.8-12.3	6 11.5 11.7 11.1-12.8	9.9 10.5 9.8-13.5	7 11.6 11.4 10.2-12	7 10.6 10.9 9.8-12.3	11.1 11.3 10.5-13.1	9.9 10.5 9.8-13.5	7 11 11.3 10.3-12.7

Table 3. Summary of Summer and Fall (July 5-19 & September 19-October 4, 2012) CWTF Discharge Categorized Paired IscoSample Results for Inter-site Analysis, and Kruskal Wallis Non-parametric Hypothesis Test Results (bold are significant).

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CWTF No		on-impacted	CWTF Impacted		CWTF Non-impacted		CWTF Impacted		CWTF Non-impacted		CWTF Impacted			
		S01- Upstream	S03- Downstream1	S01- Upstream	S03- Downstream1	S01- Upstream	S04- Downstream2	S01- Upstream	S04- Downstream2	S01- Upstream	S05- PDW1	S01- Upstream	S05- PDW1	
	Paired n		20		9		17		9	1	5	9)	
Space	Median	174	182	173	199	174	193	173	212	174	202	173	208	
Cond.	Mean	174	185	175	211	175	195	175	213	174	199	175	219	
$(\mu S \text{ cm}^{-1})$	Range	151-194	164-229	150-194	178-262	161-194	181-216	150-194	188-243	161-194	181-222	150-194	197-250	
	p-Value	<.	.001	0	.004	<	.001	0	0.004	<.()01	0.004		
Bromide (ppb)	Paired n		19		9		17		9		5	9)	
	Median	78	74	71	134	77	71	71	102	80	71	71	107	
	Mean	75	77	74	155	75	74	74	107	80	77	74	112	
41.77	Range	37-117	46-112	33-112	84-277	37-117	45-112	33-112	75-154	37-117	43-117	33-112	77-166	
	p-Value	0.731		0.004		0.927		0	0.004	0.454		0.004		
	Paired n	20		9			17		9	1	5	9)	
	Median	21.3	21.3	21	27.1	21.3	21.9	21	24.7	21.9	22.2	21	25	
Chloride (ppm)	Mean	21.1	21.4	21	29.5	21.2	22	21	25.6	21.6	22.6	21	26.4	
41 /	Range	16.3-25.8	17.9-24.9	16.2-25.3	22.4-41.3	16.3-25.8	18.7-25.6	16.2-25.3	22-31.1	16.3-25.8	18.6-26.5	16.2-25.3	22.4-32	
	p-Value	0.	.729	0	.004	0	0.089	0	0.004	0.1	07	0.0	004	
	Paired n		20		9		17		9	1	5	9)	
	Median	7.6	8.2	7.4	8.3	7.6	8.8	7.4	9.1	7.6	9.5	7.4	9.7	
Sulfate (ppm)	Mean	7.6	8.3	7.3	8.6	7.6	8.9	7.3	9.3	7.6	9.7	7.3	9.6	
чт <i>х</i>	Range	7.0-8.6	7.8-8.8	6.8-7.6	7.9-9.7	7.0-8.6	8-10.8	6.8-7.6	8.6-11.7	7.0-8.6	8.5-10.8	6.8-7.6	9.0-10.0	
	p-Value	<.	.001	0	0.004	<	<.001		0.004		<.001		0.004	

Table 4.Summary of all Isco Sample Analysis at Downstream Sites S03-Downstream1 to S05-PDW1 Categorized as either CWTF
Discharge or Non-Discharge Impacted, and Intra-site Analysis Results for those Species found to be Significantly Higher
when being Impacted by the CWTF Discharge. 77

				High River	Discharge		Low F	River Dischar	ge	
Species	Site		CWTF Non-impacted	CWTF Impacted	One-Sided t Approx.	CWTF Contribution	CWTF Non-impacted	CWTF Impacted	One-Sided t Approx.	CWTF Contribution
	002 D (1	Total n	7	7	0.10		21	10	.0.01	
	S03-Downstream1	$Mean \pm SD$	128 ± 8	137 ± 12	0.19		184 ± 16	212 ± 28	<0.01	28 (15%)
Spec. Cond.	004 D / 2	Total n	6	7	0.12		19	11	.0.01	, í
(µS cm ⁻¹)	S04-Downstream2	$Mean \pm SD$	137 ± 9	145 ± 10	0.12		192 ± 12	215 ± 20	<0.01	23 (12%)
	505 DDW1	Total n	8	7	0.17		17	9	0.01	
	505-PDW1	$Mean \pm SD$	156 ± 7	159 ± 9	0.17		196 ± 13	219 ± 23	0.01	23 (12%)
	802 Daamataraan 1	Total n	6	7	0.01		20	10	-0.01	
	S03-Downstream1	$Mean \pm SD$	24 ± 4	42 ± 11	0.01	18 (75%)	75 ± 20	154 ± 64	<0.01	79 (105%)
Bromide	504 Dame traces 2	Total n	6	7	<0.01		19	11	-0.01	
(ppb)	S04-Downstream2	$Mean \pm SD$	26 ± 6	34 ± 1		8 (31%)	71 ± 20	110 ± 30	<0.01	39 (55%)
	S05-PDW1	Total n	5	7	0.05		17	9	-0.01	
		$Mean \pm SD$	32 ± 5	39 ± 2		7 (22%)	73 ± 23	112 ± 32	<0.01	39 (53%)
	602 D 1	Total n	7	7	0.02		21	10	-0.01	
	S03-Downstream1	$Mean \pm SD$	13.3 ± 0.6	16.0 ± 2.4	0.02	2.7 (20%)	21.1 ± 2.4	29.5 ± 6.1	<0.01	8.4 (40%)
Chloride	804 D2	Total n	6	7	0.02		19	11	-0.01	
(ppm)	S04-Downstream2	$Mean \pm SD$	13.5 ± 1.2	15.0 ± 1.2	0.03	1.5 (11%)	21.6 ± 2.3	26.1 ± 3.4	<0.01	4.5 (21%)
	505 DDW1	Total n	8	7	0.04		17	9	-0.01	
	505-PDW1	$Mean \pm SD$	16.8 ± 1.0	17.7 ± 0.7	0.04	0.9 (5%)	22.1 ± 2.6	26.4 ± 3.5	<0.01	4.3 (19%)
	902 D (1	Total n	7	7	0.40		21	10	0.15	
	S03-Downstream1	$Mean \pm SD$	10.7 ± 3.2	11.9 ± 0.5	0.48		8.3 ± 0.4	8.6 ± 0.6	0.15	
Sulfate	004 D / 2	Total n	6	7	0.26		19	11	0.11	
(ppm)	S04-Downstream2	$Mean \pm SD$	11.7 ± 0.6	11.4 ± 0.6	0.36		8.9 ± 0.6	9.2 ± 0.9	0.11	
· · · ·	005 PDW1	Total n	8	7	0.22		17	9	0.20	
	202-PDW1	$Mean \pm SD$	11.3 ± 0.9	11.3 ± 1.0	0.33		9.7 ± 0.7	9.6 ± 0.4	0.39	

78 <u>7</u>80

82 Table 5. Summary of all CWTF Impact Analysis Results at Downstream Sampling Sites S03-Downstream1 to S05-PDW1 on 83 Effluent Discharge Days. 84

- 85
- 86

Species

Site Inter-site Intra-site Box Model Inter-site Intra-site 28 (15%) SO3 Downstroom1

High River Discharge

Low River Discharge

Box Model

Spec Cond	S03-Downstream1	•				28 (15%)	
$(\mu S \text{ cm}^{-1})$	S04-Downstream2					23 (12%)	
	S05-PDW1	•	•	•	•	23 (12%)	
D	S03-Downstream1	14 (50%)	18 (75%)		81	79 (105%)	
bioinide (nnh)	S04-Downstream2	8 (31%)	8 (31%)		33 (45%)	39 (55%)	
(ррб)	S05-PDW1	13 (50%)	7 (22%)	4 (16%)	38 (51%)	39 (53%)	30 (44%)
Chlorida	S03-Downstream1	2.1 (15%)	2.7 (20%)		8.5 (40%)	8.4 (40%)	
	S04-Downstream2	1.3 (9%)	1.5 (11%)		4.6 (22%)	4.5 (21%)	
(ppm)	S05-PDW1		0.9 (5%)	0.5 (4%)	5.4 (26%)	4.3 (19%)	2.8 (14%)

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