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Marcellus Shale drilling and brominated THMs in Pittsburgh, Pa., drinking water

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In 2010 the Pittsburgh (Pa.) Water and Sewer Authority (PWSA) observed a significant increase in the concentration of total trihalomethanes (TTHMs), especially brominated THM species, in its finished water. In an effort to explain these changes, PWSA and the University of Pittsburgh's Swanson School of Engineering investigated bromide concentrations in the Allegheny River (PWSA's source water) and THM formation in PWSA's drinking water. Results of the investigation indicated that elevated bromide concentrations in the source water were associated with increased concentrations of TTHMs, especially brominated THMs, in the drinking water. Additionally, a survey of the river system suggested that industrial wastewater treatment plants (brine plants) treating Marcellus Shale wastewater, as well as other wastewaters, were major contributors of bromide in the raw water. The study results also indicated that PWSA's conventional treatment process, which includes enhanced coagulation and secondary sedimentation, was ineffective at removing bromide from the source water. The increase in bromide concentrations in the Allegheny River system could affect the ability of conventional drinking water plants drawing water from this source to comply with the Stage 2 Disinfectants/Disinfection Byproducts Rule.

Keywords: *bromide, Disinfectants/Disinfection Byproducts Rule, disinfection by-products, Marcellus Shale, source water protection, trihalomethanes*

A number of US drinking water utilities have struggled to comply with the US Environmental Protection Agency's (USEPA's) Stage 1 Disinfectant/Disinfection Byproducts Rule (D/DBPR). Even more utilities anticipate difficulty meeting the more stringent requirements of the Stage 2 D/DBPR, which went into effect in 2012. Water companies are using a number of approaches to ensure compliance, including optimizing the treatment process to more effectively remove DBP precursors; optimizing the distribution system to minimize the age of treated water delivered to customers; replacing free chlorine with disinfectants like chloramines, ozone, or ultraviolet light, which form fewer trihalomethanes (THMs); and air stripping in distribution system storage tanks to remove volatile THMs from finished water.

DBPs are formed when source water containing DBP precursors (i.e., natural organic matter such as humic and fulvic acids) and bromide come into contact with chlorine in a drinking water treatment plant or distribution system. If low concentrations of bromide are present in the source water, the THMs that are formed consist primarily of chlorinated species (e.g., chloroform). However, if the source water contains elevated concentrations of bromide, a greater proportion of brominated THMs are formed (e.g., bromoform, dibromochloromethane, and bromodichloromethane). During the water treatment process, chlorine oxidizes bromide to form hypobromous acid. Hypobromous acid behaves as a stronger, more rapidly reacting substituting agent than hypochlorous acid, resulting in the formation of greater amounts of brominated DBPs (Singer & Reckhow, 2011). Additionally, the final concentration of total THMs (TTHMs), expressed on a weight-to-volume basis as micrograms per litre, is greater at equal molarity if excess bromide is present in the source water because bromide is heavier than chloride. The formation of high concentrations of TTHMs, especially brominated THMs, in drinking water derived from source water containing elevated bromide concentrations has been well documented (Luong et al, 1982; Minear & Bird, 1980; Oliver, 1980).

In September 2010, the Pittsburgh (Pa.) Water and Sewer Authority (PWSA) observed significantly increased TTHM concentrations in tap water samples routinely collected from its distribution system. Not only were the TTHMs elevated, but the percentage concentration of brominated species was also substantially higher than typically observed. In an attempt to determine whether this phenomenon was unique to the Pittsburgh utility, PWSA, with the assistance of the Pennsylvania Department of Environmental Protection (PADEP), arranged to analyze

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finished water samples collected from six other drinking water companies located upstream of the PWSA intake on the Allegheny River. As was the case with the Pittsburgh water system, the concentrations of TTHMs, as well as the percentages of brominated THMs, were unusually high in the samples from other utilities. This suggested that the changes in the quantity and chemical nature of DBPs might be associated with a change in the chemical characteristics of the source water, specifically in the concentration of bromide.

A similar increase in TTHM concentrations, along with an increase in brominated species apparently associated with elevated bromide concentrations in source water, had been observed in the nearby Monongahela River two years earlier (Handke, 2009). Although bromide had not previously been analyzed in samples from the Monongahela River, samples collected at that time seemed to contain elevated bromide concentrations, ranging as high as 241 µg/L.

The observation of elevated TTHMs in finished drinking water, along with apparent elevated bromide concentrations in the Allegheny River, raised these questions:

- What is the natural background level of bromide in the Allegheny River, how much does it vary (geographically and temporally), and what are the sources of excess bromide? Specifically, is bromide contributed by industrial sources such as coal-fired power plants, steel mills, municipal sewage treatment plants and industrial wastewater treatment plants (brine plants) that are treating Marcellus Shale wastewater (as well as other wastewaters), or discharges of treated and untreated drainage from coal mines?
- How do changes in source water bromide concentrations affect TTHM formation in conventional water treatment plants located along the river?

To address these questions, PWSA, in conjunction with the University of Pittsburgh's Swanson School of Engineering, conducted a comprehensive research project.

MATERIALS AND METHODS

Effect of source water bromide concentrations on THM formation. To address the question concerning the effect of elevated bromide concentrations on the production of TTHMs—specifically brominated THMs—both a treatment plant survey and a series of laboratory experiments were conducted.

In the treatment plant survey, daily samples of Allegheny River water collected from the PWSA treatment plant's intake were analyzed for bromide content, and the values for Sunday and Monday of each week were averaged during a period of one year. Finished water samples leaving the treatment plant were collected each Wednesday, and gas chromatography was used to measure the concentrations of four THMs—chloroform, bromoform, dibromochloromethane, and bromodichloromethane. The percentage of brominated THM species was then correlated with bromide concentrations in the river, allowing evaluation of the effect of bromide in source water on the speciation of THMs leaving the treatment plant. Sunday and Monday bromide concentrations in the river were correlated with Wednesday THM concentrations in the finished water because average detention time in PWSA's treatment plant is two to three days. Bromide concentrations in the river were not compared with TTHM concentrations because of concern that the effect of varying source water temperatures over the seasons would mask the relationship between river bromide concentrations and TTHM production.

Laboratory experiments were conducted to allow evaluation of the influence of source water supplemented with various concentrations of bromide on THM formation. Aliquots of water collected from the Allegheny River were supplemented with various bromide concentrations ranging from 20 to 300 µg/L, and chlorine was added to the spiked subsamples to produce a concentration of approximately 1.5 mg/L free chlorine. The subsamples were subsequently placed in a water bath with the temperature maintained at 30°C for 14 days. Following the incubation period, THM formation was stopped by the addition of sodium thiosulfate, and the subsamples were analyzed for THM content. The purpose of these trials was to evaluate the effect of increasing concentrations of bromide in the source water on subsequent THM formation in river water disinfected with free chlorine. A temperature of 30°C and an incubation period of 14 days were used to simulate THM formation conditions during the summer months at the most distant reaches of PWSA's finished water distribution network.

Bromide removal from source water with conventional treatment. To investigate the effectiveness of conventional drinking water treatment plants at removing bromide from source water, a series of water samples was collected from various locations in PWSA's treatment plant, beginning at the river intake and ending at the finished water's point of entry into the distribution system. Samples, collected over a period of several days at intervals designed to correspond with the plug-flow movement of water through the plant, were analyzed for bromide content.

Bromide in Allegheny River water. To determine background concentrations of bromide in Allegheny River water, as well as temporal and geographic variations and sources of excess bromide, a comprehensive survey of bromide concentrations in the river and its tributaries was conducted on a regular basis for one year. Bromide in water samples collected from PWSA's treatment plant intake was measured daily. Additionally, monthly samples were collected from 42 locations along the main stem of the Allegheny River and several of its tributaries. Sampling sites were selected to allow the analysis of bromide concentrations upstream and downstream of industrial facilities that might potentially be contributing bromide to the river system. These facilities included six coal-fired power plants, one steel mill, four municipal sewage treatment plants known to have processed wastewater from Marcellus Shale drilling operations, and four industrial wastewater treatment plants (brine plants) known to have treated Marcellus Shale wastewater in addition to other wastewaters. Sampling sites also included two locations where treated and untreated drainage from coal mines is discharged into the river.

Coal-fired power plants and steel mills are potential candidates for bromide discharge because some of them use brominated compounds to help control biological growth in cooling towers. Coal-fired power plants are also a potential source of bromide because some use brominated compounds to help control mer-

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cury in air emissions. Mine drainage is a potential source of bromide because of the possible presence of bromide in coal beds.

Municipal sewage treatment plants and industrial wastewater treatment plants treating Marcellus Shale wastewater were also considered potential sources of bromide in the river system. Although a number of shale deposits throughout the United States contain abundant natural gas resources, the Marcellus Shale layer is the most expansive in play. The Middle Devonian Marcellus Shale formation underlies a large portion of the Appalachian Basin that includes Pennsylvania and parts of West Virginia, New York, Ohio, and Maryland (Chapman et al, 2012; Kargbo et al, 2010). To extract natural gas from geologic deposits like the Marcellus Shale layer, a process called high-volume, horizontal hydraulic fracturing is used. This process involves injection of 2–15 mil gal of water, under high pressure, as deep as 1 mi into each well. It also involves continued lateral injections, configured like the spokes of a wheel, for distances up to 1 mi from the wellbore to create fissures in the deep rock layer and allow the release of gas (Kerr, 2010). A variety of chemicals (e.g., acids, surfactants, scale inhibitors, and biocides) along with sand are injected along with the water to facilitate the extraction of natural gas. Typically, 20–30% of the water injected into the well eventually returns to the surface either as flowback water, which returns to the surface within a short time after hydraulic fracturing, or as produced water, which comes to the surface over time with the gas. These wastewaters typically have total dissolved solids (TDS) concentrations exceeding 200,000 mg/L, with elevated concentrations of strontium, bromide, sodium, calcium, barium, and chloride—most likely resulting from interaction with water and salts in the producing formation (Blauch et al, 2009).

Wastewater from Marcellus Shale operations may be disposed of in several ways. It may be recycled and used for additional hydraulic fracturing operations, it can be returned underground into permitted deep-well injection sites, or it can be discharged to surface water following treatment. Except for ion exchange or reverse osmosis, municipal sewage treatment processes and industrial wastewater treatment processes are relatively ineffective at removing bromide from wastewater. The commercial wastewater treatment plants along the Allegheny River system were built years ago to treat wastewater from conventional gas wells, oil wells, and mines and to discharge the treated wastewater to the river. More recently, these commercial plants have been treating wastewater from unconventional deep-well gas drilling sites and discharging the treated wastewater into nearby surface water. Because these plants were not designed to remove the high concentrations of TDS contained in wastewater from deep-well drilling, the treated effluents discharged into these rivers contain high concentrations of bromide.

Bromide was also measured in two Allegheny River water samples collected quarterly from locations on the main stem of the river believed to be upstream of most industrial contamination. These sites (Tionesta Bridge, at river mile point 152, and Warren Bridge, at mile point 188) are situated far upstream of the PWSA intake, which is located at mile point 8.4. These sampling locations are important because they are believed to provide baseline data on naturally occurring, background bromide concentrations in the Allegheny River system.

In addition, river samples collected on a daily, monthly, or quarterly basis were analyzed for a number of other chemical parameters, including TDS. TDS was measured because it has been used by various regulatory agencies as a primary regulatory parameter and as a surrogate for industrial wastewater discharges in general.

Marcellus Shale wastewater has been shown to contain elevated concentrations of naturally occurring radioactive materials (Hill et al, 2004). The New York State Department of Health analyzed three samples from Marcellus Shale production brine and found elevated levels of radium-226 and gross alpha and gross beta activity (NYSDOH, 2009). In February 2011, an article in a national newspaper suggested that Marcellus Shale wastewater being discharged to rivers after treatment might contain elevated levels of radioactivity (*New York Times*, 2011). In response to concerns expressed by PWSA customers following these news reports, the river survey was expanded to include radiological analysis of monthly river water samples collected from PWSA's treatment plant intake and finished water samples collected from the entry point to the distribution system. In addition, quarterly samples from a number of upstream sites were analyzed for radiological contaminants. The radiological parameters measured included combined radium-226 and -228, uranium, gross alpha activity, and gross beta activity.

THM analyses were conducted by gas chromatography (method 502.2; USEPA, 1989). Bromide was analyzed by ion chromatography (method 300.1; USEPA, 1997). TDS was measured by gravimetric analysis (method 2540 C; *Standard Methods*, 2005).

RESULTS AND DISCUSSION

Effect of source water bromide concentrations on THM formation. To allow evaluation of the effect of bromide concentrations at PWSA's treatment plant intake on THM formation, samples of finished water leaving the treatment plant were analyzed two to three days after the intake samples were analyzed. Figure 1 illustrates the direct relationship between source water bromide concentrations and the percentage of brominated species among the finished water THMs. The correlation coefficient is statistically significant at the 0.001 level. With a source water bromide concentration of 50 µg/L, approximately 62% of the finished water THMs consisted of bromoform, dibromochloromethane, and bromodichloromethane. However, with a source water bromide concentration of 150 µg/L, approximately 83% of the finished water THMs consisted of brominated species. This is a significant increase because brominated DBPs are associated with increased human health risk compared with chlorinated DBPs (Richardson et al, 2007). It is also significant because brominated THMs have a lower Henry's constant than nonbrominated THMs and are therefore more difficult to remove from distribution system storage tanks by air stripping.

Laboratory trials were conducted to assess the effect of untreated source water artificially supplemented with increasing concentrations of bromide on TTHM formation. As Figure 2 shows, the concentration of TTHMs increased from 105 µg/L

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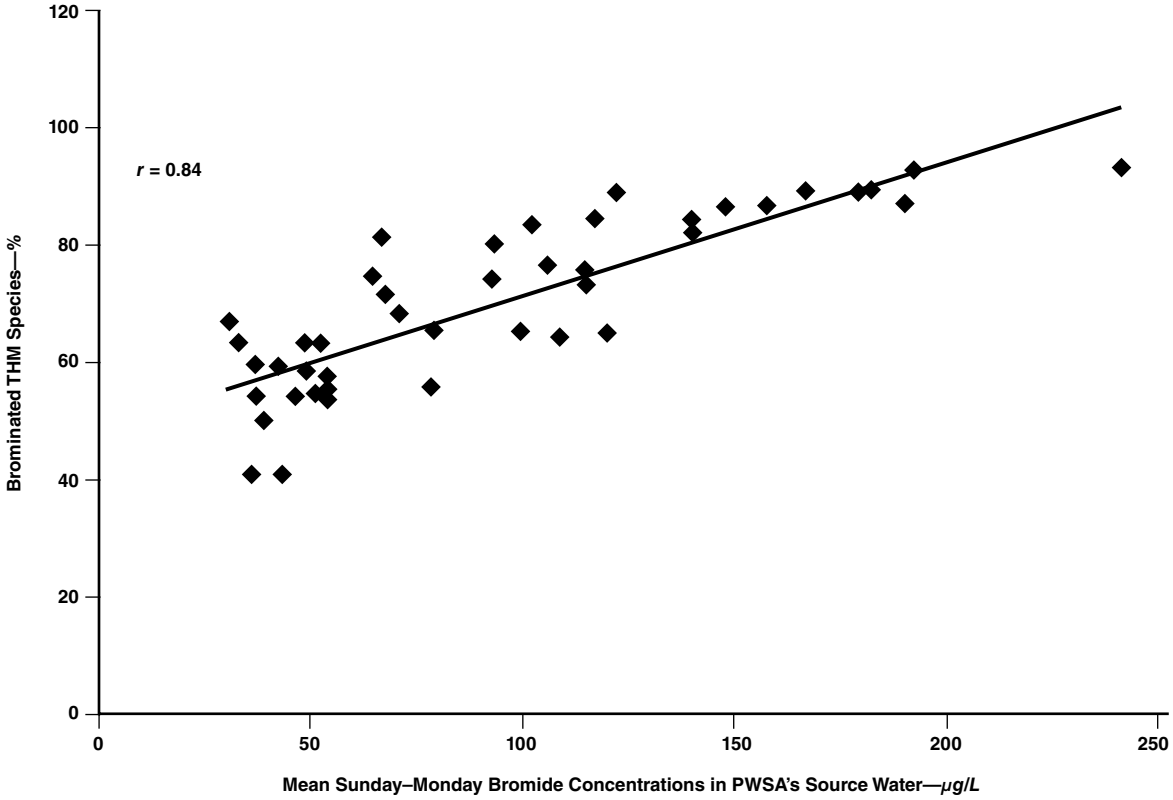
FIGURE 1 Correlation between the percentage of brominated THMs in PWSA's finished water and bromide concentrations in the Allegheny River



PWSA—Pittsburgh Water and Sewer Authority, THMs—trihalomethanes

with a source water bromide concentration of 50 µg/L to 120 µg/L with a bromide concentration of 200 µg/L. The percentage concentration of brominated THMs increased from approximately 25% with a bromide concentration of 50µg/L to 70% with a bromide concentration of 200 µg/L.

Bromide removal from source water with conventional treatment. The current study included an assessment of the effectiveness of conventional drinking water treatment processes, such as those used at PWSA, for removing bromide from source water. The question posed was: do the processes of nonchlorine preoxidation, carbon adsorption, clarification, and filtration make bromide unavailable for DBP formation before the chlorine disinfection step is reached in the treatment chain?

The treatment process at Pittsburgh's water treatment plant is similar to that used in many treatment plants around the world. Approximately 70 mil gal of Allegheny River water is pumped into the plant each day. As the water passes through the intake, potassium permanganate is fed to oxidize dissolved iron and manganese. About 15 min later, ferric chloride (25 mg/L) and a cationic polymer (1 mg/L) are added for coagulation, and lime is added to adjust the pH to 6.7. This coagulant concentration and this particular pH are used to optimize the removal of THM precursors through enhanced coagulation. Powdered activated carbon (1 mg/L) is added for adsorption of DBP precursors. The water then passes through a three-stage flocculation process and is allowed to settle in the clarifier for 2 h. To complete the clarification step, the water then settles for an additional 24 h in a 117–mil gal secondary sedimentation basin. A small amount of sodium hypochlorite is added to the water just prior to rapid sand filtration to oxidize any remaining dissolved manganese and ensure removal during the filtration process. Rapid sand filtration involves passage of the water through 18 in. of coal, 12 in. of sand, and 12 in. of support gravel. Sodium hypochlorite is then added for disinfection, hydrofluorosilic acid for fluoridation, and sodium carbonate for final pH adjustment. The water subsequently passes through a clearwell with a capacity of 44 mil gal, allowing plenty of time for disinfection before it leaves the treatment plant and enters the distribution system. The entire treatment process occurs during a three-day period.

Two surveys were conducted to measure bromide removal as water passed through the various steps of the treatment process. In one survey, the initial river water concentration of bromide was quite high (188 µg/L), whereas in the second survey the initial concentration was much lower (44 µg/L). A small amount of bromide was removed in both trials during primary clarification (Table 1). This was likely the result of bromide oxidation by

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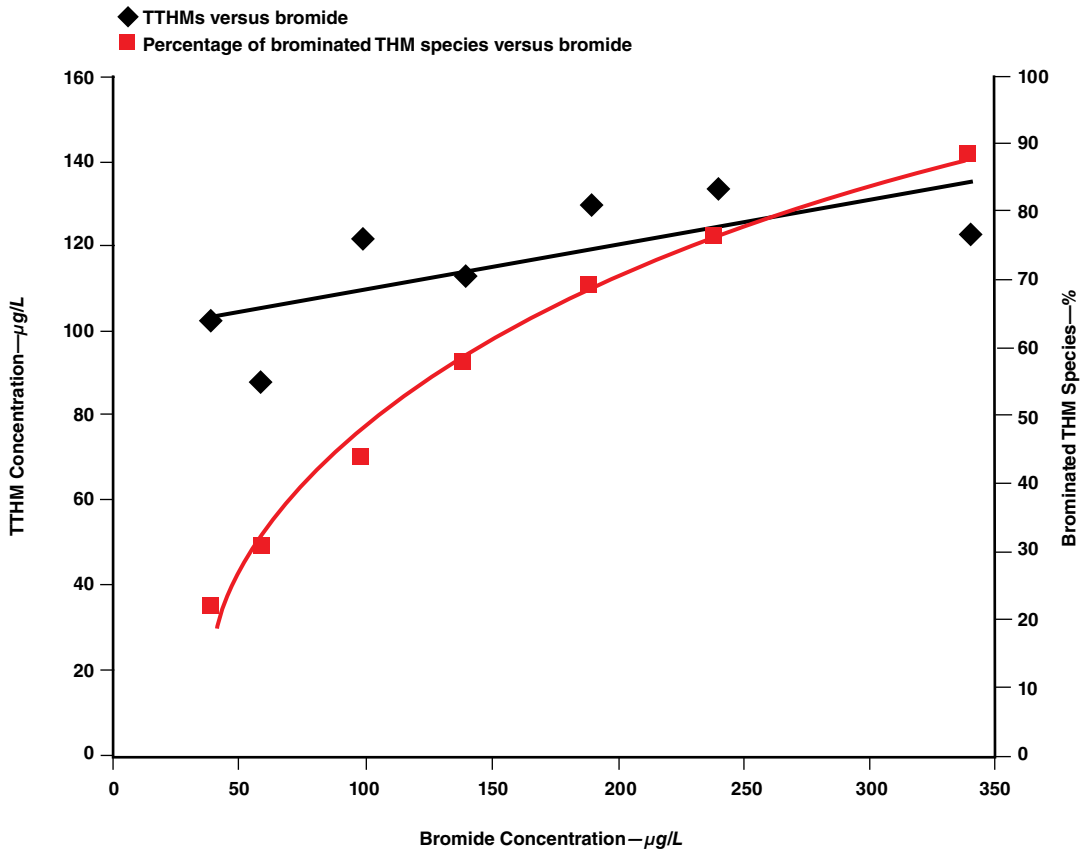
FIGURE 2 TTHM formation potential study—effect of experimental addition of bromide



TTHMs—total trihalomethanes

potassium permanganate. Potassium permanganate oxidizes bromide to hypobromous acid, which is quite reactive and is probably consumed by oxidation of reduced chemical substances in the source water.

Following the initial, partial removal of bromide, the next reduction in concentration occurs when the prefiltered water passes through the rapid sand filters and when the filtered water passes through the clearwell and becomes finished water. It is in these steps that the major doses of free chlorine are added at the PWSA plant. As Table 1 shows, during these final treatment stages, bromide was removed to concentrations lower than the limits detectable by ion chromatography. At this point, free chlorine oxidizes bromide to hypobromous acid, which then reacts with THM precursors to form brominated THMs.

As these trials indicate, the only significant removal of bromide that occurred during conventional water treatment was through the oxidation of bromide by free chlorine, which led to the formation of brominated THMs. Therefore, conventional water treatment processes appear to be generally ineffective at removing bromide and preventing it from being available for DBP formation.

Bromide in Allegheny River water. Other questions addressed by the current study included: how much bromide is in the Allegheny River (especially at the PWSA treatment plant intake); how and why do bromide concentrations in the river vary geographically and temporally; and which natural or industrial processes along the Allegheny and its tributaries contribute bromide to the river system?

Table 2 summarizes daily concentrations of bromide in PWSA's raw water intake on the Allegheny River during late 2010 and 2011. Daily bromide concentrations varied significantly from a low of < 25 µg/L to a high of 299 µg/L. The data shown in this table have been color-coded, with values < 100 µg/L appearing in a white background, values between 100 and 200 µg/L in a yellow background, and values > 200 µg/L shaded in red. If bromide contributions to the river system from natural or industrial sources are assumed to be relatively constant throughout the year, one explanation for the wide fluctuation in bromide values at PWSA's raw water intake may be the volume of water in the river. Figure 3 compares daily river flow (measured at the US Geological Survey stream gauging station at Natrona, Pa., which is closest to the PWSA plant) with bromide concentrations at the

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TABLE 1 Removal of bromide by the PWSA drinking water treatment plant

Sampling Site	2010 *Date, Time*	Bromide Concentration *µg/L*	2011 *Date, Time*	Bromide Concentration *µg/L*
River intake	October 25, 0730	188	March 21, 0720	44
Flume	October 25, 1200	158	March 21,1230	40
Settled water	October 26, 1210	171	March 22, 1300	45
Prefiltered water	October 26, 1515	192	March 22, 1600	< 25
Postfiltered water	October 26, 1505	134	March 22, 1605	< 25
Finished water	October 27, 0800	< 50	March 23, 0800	< 25

PWSA—Pittsburgh Water and Sewer Authority

TABLE 2 Bromide concentrations at the PWSA treatment plant intake—September 2010–December 2011

Day of the Month	Sept. 2010 *µg/L*	Oct. 2010 *µg/L*	Nov. 2010 *µg/L*	Dec. 2010 *µg/L*	Jan. 2011 *µg/L*	Feb. 2011 *µg/L*	March 2011 *µg/L*	April 2011 *µg/L*	May 2011 *µg/L*	June 2011 *µg/L*	July 2011 *µg/L*	Aug. 2011 *µg/L*	Sept. 2011 *µg/L*	Oct. 2011 *µg/L*	Nov. 2011 *µg/L*	Dec. 2011 *µg/L*
1			136	37	85	182	58	48	37	35	114	184	176	140	67	35
2			241	42	81	147	28	62	35	37	98	189	182	119	59	42
3			227	39	123	165	36	68	30		105	172	174	110	38	54
4			195	38	97	145	35	67	39	44	107	161	167	112	38	47
5			216	59	56	135	38	78	46	48	119	144	148	98	38	61
6			172	44	66	136	43	76	43	48	116	148		76	63	46
7			230	48	71	117	28	49	41	53	119	147	168	84	66	53
8			170	49	84	114	< 25	50	45	66	127	134	188	72	86	46
9			194	53	85	125	29	38	54	63	125	140	174	57	74	48
10			124	58	101	126	30		51	72	117	148	172	50	77	92
11			168	64	97	130	32	33	47	70	113	152	129	64	70	50
12		205	160	68	94	118	30	34	44	68	112	139	111	96	101	34
13		203		49	82	123	27	36	52	77	133	158	120	122	92	57
14		188		57	106	110	32	41	55	75	134	174	91	112	94	48
15		151	170	65	95	141	34	36	54	88	136	185	66	88	102	41
16			155	57	125	150	37	37	49	92	137	176	63	110	107	46
17			165	76	82	147	28	44	38	96		167	41	130	77	40
18			143	35	100	136		55		97	190	172	55	87	72	72
19			146	67	147	139	39	36	37	107	157	178	37	91	79	56
20			158		156	95	28	45	41	110	163	169	36	98	79	59
21			176	88	123	62	44	40	31	94	173	167	60	78	90	52
22			140		115	77	31	39	37	99	156	167	76	69	63	45
23			224		124	42	30	40	38	109	128		96	82	88	64
24	220		204	79	120	38	29	40	40	114	129	147	94	75	66	24
25		188	180	66	128	43	50	35	35	137	145	135	101	71	51	34
26		142	139	106	162	61	61	32	37	131	150	171	98	64	54	30
27		156	145	89	130	46	34	33	40	124	159	171	99	76	52	28
28		190	117	101	165	56	44	38	42	119	177	184	107	66	54	32
29		241	97		159		< 25	35	47	124	172	180	132	64	39	25
30		211	79	198	182		42	39	40	115	147	158	120	75	46	29
31		220		98	202		47		40		299	149		67		25

PWSA—Pittsburgh Water and Sewer Authority

White background indicates daily bromide values < 100 µg/L, yellow background indicates daily bromide values between 100 and 200 µg/L, red background indicates daily bromide values > 200 µg/L

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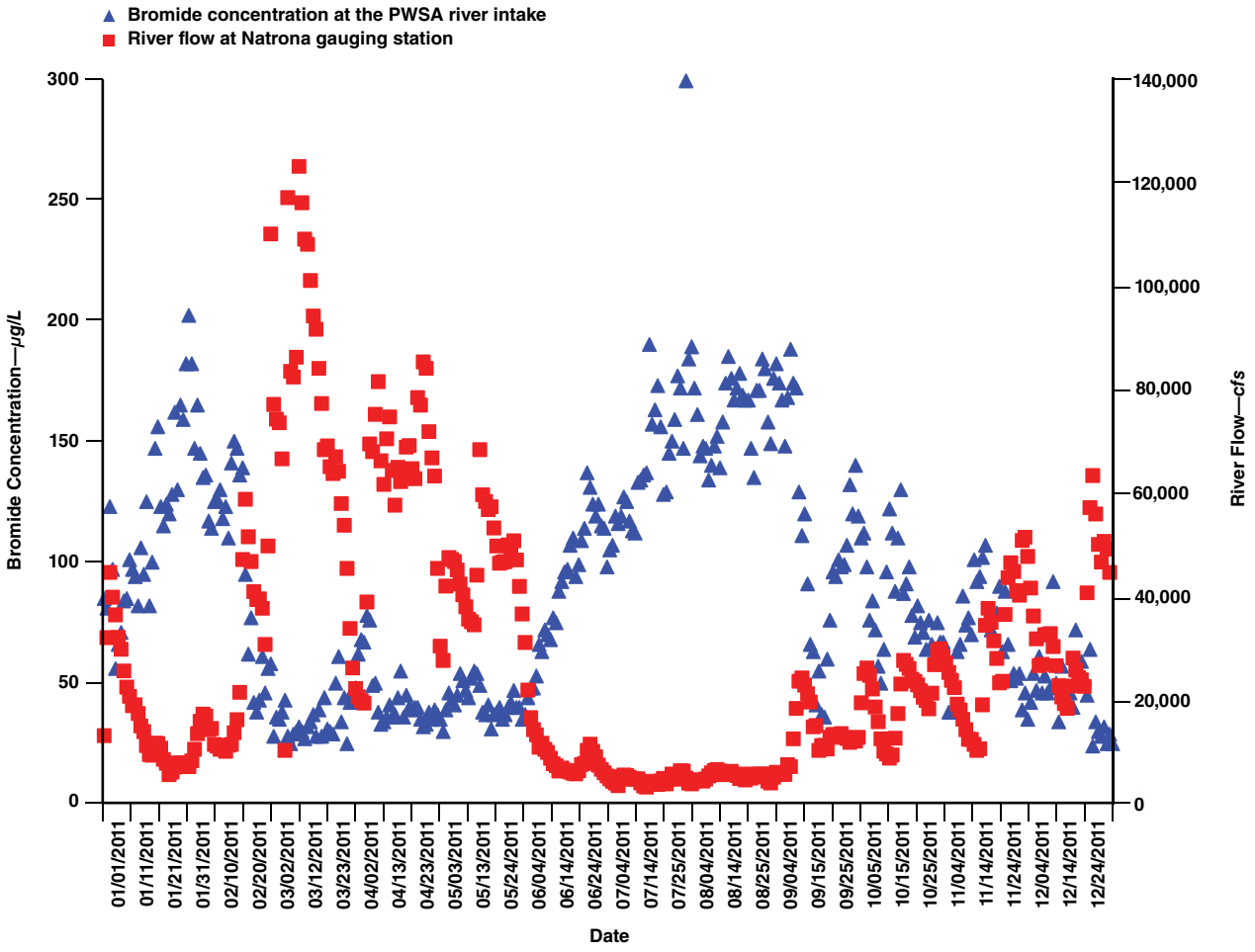
FIGURE 3 Bromide concentration and river flow



PWSA—Pittsburgh Water and Sewer Authority

PWSA intake. As the figure shows, bromide concentrations tend to be greatest when river flow is lowest. This result suggests that regardless of the source of bromide in the Allegheny system, drinking water utilities are exposed to the greatest challenge from bromide during low-flow conditions in the river.

In an attempt to identify potential sources of excess bromide in the Allegheny and its tributaries, an extensive survey of the river system was conducted. Following some initial testing (September–December 2010), a number of locations along the river and its tributaries were sampled monthly throughout 2011 and analyzed for bromide content and TDS. Figure 4 is a map of the entire Allegheny River and its major tributaries. The PWSA intake is located at the base of the river's main stem, just 8.4 mi upstream of the point where the Allegheny converges with the Monongahela River to form the Ohio River. For ease of illustration, the portions of the Allegheny and its tributaries that were intensely investigated in this study have been divided into two sections and are shown in Figures 5 and 6. Special emphasis was placed on analyzing monthly water samples collected from points upstream and downstream of industrial sites suspected of contributing excess bromide to the river. These included six coal-fired power plants, one steel mill, four municipal sewage treatment plants and four industrial wastewater treatment plants that are known to have treated wastewater generated by Marcellus Shale drilling operations, and two areas of the river that are known to contain treated and untreated coal mine drainage.

Figure 5 shows the upper portion of the Allegheny River's main stem, extending from the Warren Bridge to the point where the Kiski (Kiskiminetas) River flows into the Allegheny. Table 3 summarizes bromide data from samples routinely collected along that stretch of the Allegheny's main stem. As the table indicates, bromide concentrations in river water samples collected from the towns of Tionesta and Warren, Pa., were very low, typically < 50 µg/L. These towns are located far upstream (at river mile

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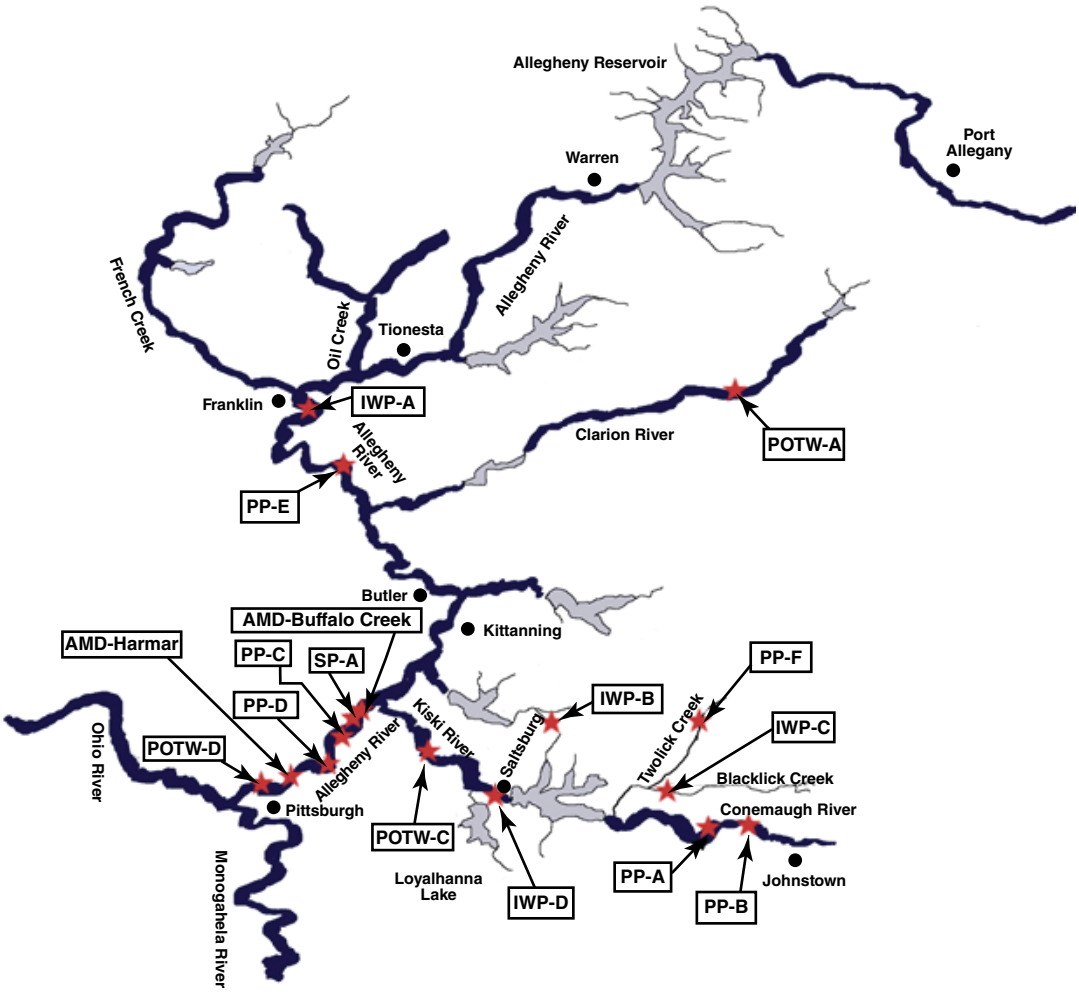
FIGURE 4 The Allegheny River system



AMD—abandoned mine drainage, IWP—industrial waste plant, POTW—public owned treatment works, PP—power plant, SP—steel plant

points 152 and 188, respectively) and consequently were sampled only quarterly during the project. No major industrial discharges of bromide are believed to be occurring upstream of these towns. Therefore, it can be assumed that these low bromide concentrations represent naturally occurring, background levels of bromide in the Allegheny River. A substantial increase in bromide concentrations appeared in the comparison of river water upstream and downstream of industrial waste plant A, which is known to treat wastewater from Marcellus Shale drilling operations. Because this plant discharges effluent directly into the main stem of the Allegheny where the dilution factor is significant, even twofold, threefold, and fourfold increases in bromide concentrations at this location in the river probably represent significant contributions of bromide from this plant. No notable increase in river bromide concentrations appears to be associated with coal-fired power plant E.

Figure 5 also shows the Clarion River, an upstream tributary of the Allegheny, which contains a publicly owned treatment works (POTW) that has been known to treat Marcellus Shale wastewater. As the data in Table 4 indicate, there is no apparent bromide contribution from POTW-A. During most months from May through October, unusually high concentrations of bromide were measured at the Ridgeway Bridge. Because no known waste treatment sites are located upstream of POTW-A, these data suggest the possibility of illegal discharges of untreated wastewater into the upper reaches of the Clarion River. Discharges of this type, involving wastewater from drilling operations, have been reported previously in other parts of the Allegheny River system and have been prosecuted by the PADEP. The upstream increases in bromide coincided with the May 2011 implementation of a voluntary ban, requested by PADEP, on discharges of treated Marcellus Shale wastewater into the state's

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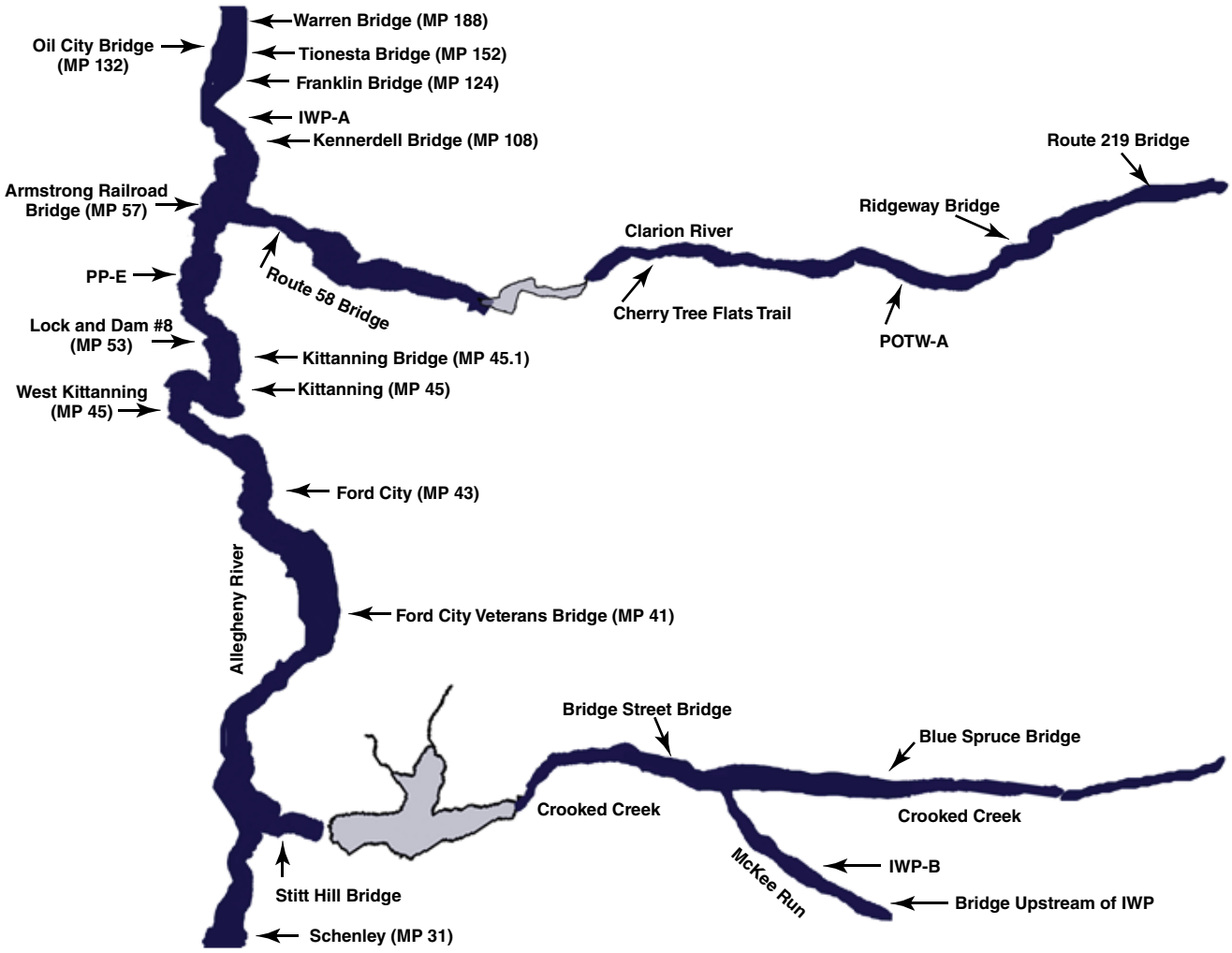
FIGURE 5 The Upper Allegheny River system



IWP—industrial waste plant, MP—mile point, POTW—publicly owned treatment works, PP—power plant

Map not to scale

surface water systems. The ban is discussed in greater detail later in this article.

Figure 5 also shows the Upper Allegheny River's Crooked Creek and McKee Run tributaries, which contain a commercial wastewater treatment plant that treats Marcellus Shale wastewater. Again, the relatively low bromide concentrations measured in samples collected from the bridge upstream of industrial waste plant B and from Blue Spruce Bridge presumably represent the low background levels of bromide in the Allegheny River and its tributaries (Table 4). The increase in bromide concentrations (extending up to a 34-fold increase) in samples collected from Bridge Street Bridge suggests a significant introduction of bromide into the tributary from industrial waste plant B. Downstream bromide concentrations in several of the sampling months (July and August 2011) exceeded 3,000 µg/L, or 3 mg/L. As samples collected from Stitt Hill Road Bridge indicate, bromide concentrations were naturally diluted as they passed through Crooked Creek Lake before entering the main stem of the Allegheny River. However, bromide concentrations in the Stitt Hill Road Bridge samples were still substantially greater than those in samples collected near the upstream ends of the tributaries (i.e., at the bridge upstream of industrial waste plant B and the Blue Spruce Bridge), suggesting a net contribution of bromide to the Allegheny's main stem associated with industrial waste plant B.

Figure 6 shows several Allegheny River tributaries that contain considerable industrial activity. As Table 5 shows, bromide con-

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TABLE 3 Bromide concentrations in the Upper Allegheny River—September 2010–December 2011

Sample Site	Sept. 2010 µg/L	Oct. 2010 µg/L	Nov. 2010 µg/L	Dec. 2010 µg/L	Jan. 2011 µg/L	Feb. 2011 µg/L	March 2011 µg/L	April 2011 µg/L	May 2011 µg/L	June 2011 µg/L	July 2011 µg/L	Aug. 2011 µg/L	Sept. 2011 µg/L	Oct. 2011 µg/L	Nov. 2011 µg/L	Dec. 2011 µg/L
Warren Bridge				< 50			< 25			35			33			29
Tionesta Bridge				52			< 25			29			42			40
Franklin Bridge			85		63	38	< 25	24	21	57	50	94	89	39	38	92
Industrial waste plant A					**2x**	**3x**	**2x**	**1.8x**		**1.6x**	**3x**	**1.1x**		**4x**	**1.2x**	
Kennerdell Bridge			83		125	101	51	43	20	94	134	106	56	141	45	33
Clarion River																
Armstrong Railroad Bridge										87	77	89	107	93	43	24
Coal-fired power plant E																
Lock and Dam #8										84	68	93	111	95	67	40
Kittanning Bridge		104	69	50	68	118	30	31	26	105	82	104	121	85	51	31
Ford City Bridge	150	101		51	57	129	28	39	48	84	82	102	105		59	60
Crooked Creek	**1.1x**	**1.1x**			**1.1x**	**1.2x**	**1.2x**				**1.4x**	**1.1x**	**1.4x**	**1.1x**	**2x**	
Schenley	170	114			64	146	35	28	47	72	114	114	152	94	< 25	62

Gray shading indicates potential point sources of bromide addition to the surface water system; blue shading represents tributaries in the Allegheny River system; yellow shading highlights bromide concentrations ranging between 100 and 200 µg/L.

Increases in concentration appear in bold type; 2x = a twofold increase, and so on.

TABLE 4 Bromide concentrations in Allegheny River tributaries

Crooked Creek and McKee Run

Sampling Site		Oct. 2010 µg/L	Nov. 2010 µg/L	Dec. 2010 µg/L	Jan. 2011 µg/L	Feb. 2011 µg/L	March 2011 µg/L	April 2011 µg/L	May 2011 µg/L	June 2011 µg/L	July 2011 µg/L	Aug. 2011 µg/L	Sept. 2011 µg/L	Oct. 2011 µg/L	Nov. 2011 µg/L	Dec. 2011 µg/L
McKee Run	Bridge upstream of IWP-B		29	79	61	36	27	17	32	66	93	63	26	25	44	36
	IWP-B															
Crooked Creek	Blue Spruce Bridge	57	39	64	87	37	38	13	53	83	116	114	56	25	56	52
	McKee Run	**20x**	**10x**	**9x**	**10x**	**1.1x**	**3x**	**3x**	**8x**	**8x**	**27x**	**34x**	**4x**	**17x**	**4x**	**5x**
Crooked Creek	Bridge Street Bridge	1130	345	639	774	42	111	44	414	640	3100	3900	214	427	244	235
	Stitt Hill Road Bridge		280	467	396	173	74	53	112	258	578	582	426	103	116	167

Clarion River

Sampling Site	March 2011 µg/L	April 2011 µg/L	May 2011 µg/L	June 2011 µg/L	July 2011 µg/L	Aug. 2011 µg/L	Sept. 2011 µg/L	Oct. 2011 µg/L	Nov. 2011 µg/L	Dec. 2011 µg/L
Johnsonburg (Route 219 Bridge)									< 25	25
Ridgeway Bridge	< 25	11	171		121	149	44	261	< 25	24
POTW-A		**1.3x**			**1.1x**		**1.6x**	**1.1x**		**1.9x**
Cherry Tree Flats Trail	27	14	163		132	156	69	279	26	46
State Route 58 Bridge	< 25	23	37		74	115	105	67	33	16

IWP-B—industrial waste plant B, POTW-A—publicly owned treatment works A

Gray shading indicates a potential point source of bromide addition; blue shading represents a tributary in the Allegheny River system; yellow shading highlights bromide concentrations ranging between 100 and 200 µg/L; red shading highlights concentrations > 200 µg/L.

Increases in concentration appear in bold type; 20x = a 20-fold increase, and so on.

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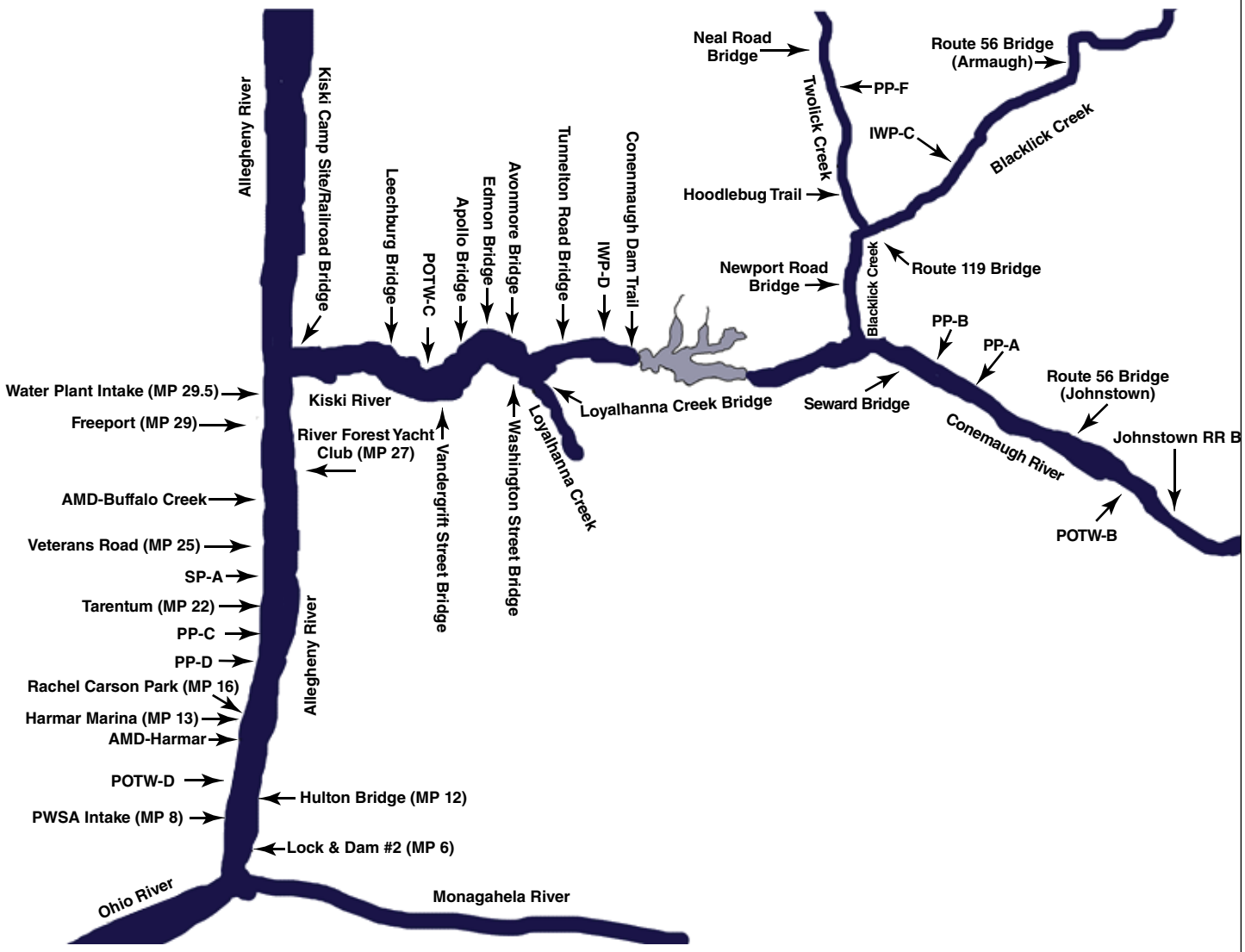
FIGURE 6 The Lower Allegheny River system



AMD—abandoned mine drainage, IWP—industrial waste plant, MP—mile point, POTW—publicly owned treatment works, PP—power plant, PWSA—Pittsburgh Water and Sewer Authority, SP—steel plant

Map not to scale

centrations in water samples collected at sites upstream of known industrial discharges (Neal Road Bridge, Route 56 Bridge in Armaugh, and Johnstown Railroad Bridge) were almost always < 100 µg/L and usually < 50 µg/L. These values typify the low, naturally occurring concentrations of bromide in the river system. Increases in bromide concentration ranging up to 21-fold downstream of industrial waste plant C versus upstream of the plant suggest significant discharges of bromide from this facility. Bromide concentration increases ranging up to sevenfold downstream versus upstream of POTW-B suggest sporadic releases of excess bromide from this municipal sewage treatment plant, which has been known to process Marcellus Shale wastewater. Up to ninefold increases in bromide concentration in downstream versus upstream measurements at coal-fired power plants A and B suggest periodic releases of bromide from these facilities as well. The apparent power plant discharges seem to be greater during the summer months. This could be associated with seasonal use of brominated antifouling compounds in the cooling towers of these plants during the warmer seasons of the year.

Figure 6 also shows the Kiski River, which continues from the Conemaugh River and flows into the Allegheny. The low bromide concentrations (almost always < 50 µg/L) in Loyalhanna Creek,

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TABLE 5 Bromide concentrations in the Conemaugh River and Blacklick Creek—October and December 2010–December 2011

Sampling Site	Oct. 2010 µg/L	Dec. 2010 µg/L	Jan. 2011 µg/L	Feb. 2011 µg/L	March 2011 µg/L	April 2011 µg/L	May 2011 µg/L	June 2011 µg/L	July 2011 µg/L	Aug. 2011 µg/L	Sept. 2011 µg/L	Oct. 2011 µg/L	Nov. 2011 µg/L	Dec. 2011 µg/L
Neal Road Bridge									90	46	33	41	42	29
Coal-fired power plant F									**1.8x**	**1.7x**			**3x**	
Hoodlebug Trail								151	166	77	31	45	114	27
Route 56 Bridge (Armaugh)	46		86	< 25	28	18	45	75	116	50	33	40	38	19
Industrial waste plant C			**11x**	**8x**	**4x**	**5x**	**6x**	**21x**	**21x**	**1.7x**	**4x**		**13x**	**1.3x**
Route 119 Bridge									2400	84	133	39	492	24
Two Lick Creek										**2x**		**4x**		**2x**
Newport Road Bridge			961	203	115	87	252	1600	1910	210	47	144	290	49
Johnstown Railroad Bridge	< 50	94	52	< 25	< 25	13	20	32	43	< 25	27	35	< 25	23
POTW-B						**1.4x**	**1.4x**	**1.2x**	**1.3x**	**7x**				
Route 56 Bridge (Johnstown)	< 50	52	57	< 25	< 25	18	29	39	54	169	< 25	< 25	< 25	14
Coal-fired power plants A and B		**2x**							**4x**	**6x**	**9x**			**2x**
Seward Bridge	< 50	115	60	< 25	< 25	20			234	1,010	230	< 25	< 25	34
Blacklick Creek		**4x**		**3x**	**2x**	**3x**			**3x**			**5x**	**4x**	
Conemaugh Dam Trail				82	48	63	146	282	637	342	80	119	101	80
Industrial waste plant D					**1.2x**	**1.2x**	**1.5x**	**1.2x**	**1.1x**	**1.3x**	**1.2x**	**1.1x**	**1.1x**	
Tunnelton Road Bridge		431	237	77	60	78	219	336	711	442	92	131	107	56

POTW-B—publicly owned treatment works B

Gray shading indicates potential point sources of bromide addition; blue shading represents tributaries in the Allegheny River system; yellow shading highlights bromide concentrations ranging between 100 and 200 µg/L; red shading highlights concentrations > 200 µg/L.

Increases in concentration appear in bold type; 2x = a twofold increase, and so on.

a tributary flowing into the Kiski River, again demonstrate the low background levels of bromide in the Allegheny River system (Table 6). This contrasts sharply with the elevated bromide concentrations in the upper portion of the Kiski River (e.g., the Washington Street Bridge sampling site), which is heavily influenced by industrial discharges of bromide on the Conemaugh River and its tributaries. The absence of an apparent increase in bromide concentrations downstream versus upstream of POTW-C, which had accepted Marcellus wastewater, is typical of most of the POTWs surveyed in this investigation.

Figure 6 also shows the lower Allegheny River from the point where the Kiski River flows into the Allegheny's main stem, to the PWSA intake, and finally to Lock and Dam #2 just before the confluence of the Allegheny and the Monongahela. As Table 6 indicates, discharge sites along this stretch of the river do not suggest significant contributions of bromide. These potential discharge sites include steel plant A, coal-fired power plants C and D, and POTW-D, as well as two locations, labeled Buffalo Creek and Harmar Mine, where there are ongoing discharges of treated and untreated coal mine drainage. The absence of increases in bromide concentrations at the downstream versus the upstream sampling locations at these two sites suggests no apparent bromide contribution from abandoned mine drainage. These observations are consistent with a Cravotta (2008) study that found an average bromide concentration of only 45 µg/L in 99 samples of untreated effluent from abandoned bituminous coal mines in Pennsylvania. A bromide concentration of 45 µg/L is approximately the background level observed in the authors' survey of the upper reaches of the Allegheny River and its tributaries.

Figure 7 illustrates the substantial differences in bromide concentration among various sampling sites along the Allegheny River and its tributaries. Data from July 2011 were chosen for this figure because some of the highest concentrations of bromide in river samples were observed at this time.

Mass balance analysis of bromide in the Allegheny River system. Mass balances were calculated using US Geological Survey stream flow data (Table 7). Stream flow data were available for river or stream locations near several of the industrial facilities shown in the year-long survey to be discharging bromide. These facilities included industrial waste plants A, C, and D, as well as coal-fired power plants A and B. Bromide mass (expressed in pounds per day) was calculated for monthly samples collected upstream and downstream of these apparent discharge sites using measured bromide concentration data and flow data. Because flow data were not available for either McKee Run or Crooked Creek in the vicinity of industrial waste plant B, the bromide mass contribution from this site could not be calculated.

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TABLE 6 Background bromide concentrations in the Kiskiminetas and Lower Allegheny river system

Sampling Site	Sept. 2010 µg/L	Oct. 2010 µg/L	Oct. 2010 µg/L	Nov. 2010 µg/L	Dec. 2010 µg/L	Jan. 2011 µg/L	Feb. 2011 µg/L	March 2011 µg/L	April 2011 µg/L	May 2011 µg/L	June 2011 µg/L	July 2011 µg/L	Aug. 2011 µg/L	Sept. 2011 µg/L	Oct. 2011 µg/L	Nov. 2011 µg/L	Dec. 2011 µg/L
Kiskiminetas River																	
Loyalhanna Creek Br.				33	< 50	51	45	< 25	14	18	35	54	43	< 25	30	26	30
Washington Street Bridge		< 50		460	470	179	141	70	55	159	434	544	312	145	95	135	80
Avonmore Bridge				390	376	147	145	65	54	141	366	315				136	87
Edmon Bridge				380	358	137		62	57	117	366	304	230	128	95	125	84
Apollo Bridge				160	234	144	125	70	52	118	371	267	264	124	96	134	90
Vandergrift Bridge		498		340	317	175	108	73	55	127	368	284	238	149	90	128	83
POTW-C								**1.2x**							**1.1x**		
Leechburg Bridge		489			177	143	108	84	57	126	316	271	191		102	106	83
Kiski Railroad Bridge	850	500		109	181	219				113	300	274	186	146	116	122	
Lower Allegheny River																	
Water plant intake	170	115		72	76		137	30	40	26	90	220	202	124	107	66	64
River Forest Yacht Club		155		96	134			60	47	44	123	203	155	144	110	98	62
Buffalo Creek (AMD)																	
Veterans Road											113	150	142	86	72	96	66
Steel plant A												**1.1x**	**1.6x**	**1.2x**			
Tarentum	220	158		158			62	34	34	43	112	161	231	104	69	70	64
Coal-fired power plants C and D				**1.2x**					**1.2x**			**1.2x**					**1.3x**
Rachel Carson Park							48	34	40	49	116	196	170	79	69	77	85
Harmar Marina	230	149	220	190	65	122		35	55	43	113	183	176	132	111	67	73
Harmar Mine (AMD)																	
POTW D																	
Hulton Bridge	220	139	205	191	51	128		< 25	49	40	101	184	168	126	102	61	70
PWSA intake	220	151	241	204	79	130		< 25	49	38	94	177	172	107	122	63	59
Lock and Dam #2	230	147	263	213	62	141		< 25	52	45	126	180	161	117	109	56	64

AMD—abandoned mine drainage, POTW-C—publicly owned treatment works C, POTW-D—publicly owned treatment works D, PWSA—Pittsburgh Water and Sewer Authority

Gray shading indicates potential point sources of bromide addition; yellow shading highlights bromide concentrations ranging between 100 and 200 µg/L; red shading highlights concentrations > 200 µg/L.

Increases in concentration appear in bold type; 1.2x = a 1.2-fold increase, and so on.

A substantial portion of the increase in bromide as water flowed down the Allegheny River system could be accounted for by the other three industrial wastewater treatment plants and coal-fired power plants A and B. For example, in August 2011, the difference between the single-day bromide mass calculated at Franklin Bridge (1,454 lb/d) and the mean daily bromide mass calculated at the PWSA treatment plant intake (4,632 lb/d) was 3,178 lb/d. The sum of individual contributions of bromide mass from industrial waste plants A, C, and D and from power plants A and B totaled 1,622 lb/d. These data suggest that the industrial wastewater sites account for approximately 51% (1,622 lb/d divided by 3,178 lb/d) of the increase in bromide mass as water flowed downriver. Over 12 months, the mean monthly percentage contribution of the various industrial sites to the increase in bromide mass between the upstream Franklin Bridge sampling location and the downstream PWSA intake was 52%. Although this mass balance approach is only a rough approximation because of the necessity of using a monthly average for bromide mass at the PWSA intake, the estimate suggests that the industrial sites are significant contributors of excess bromide to the Allegheny River system.

Radiological analyses of river samples. A number of samples were analyzed for radiological parameters. Although actual radiological data are not shown because of manuscript length limitations, the results indicate that radioactivity levels in sam-

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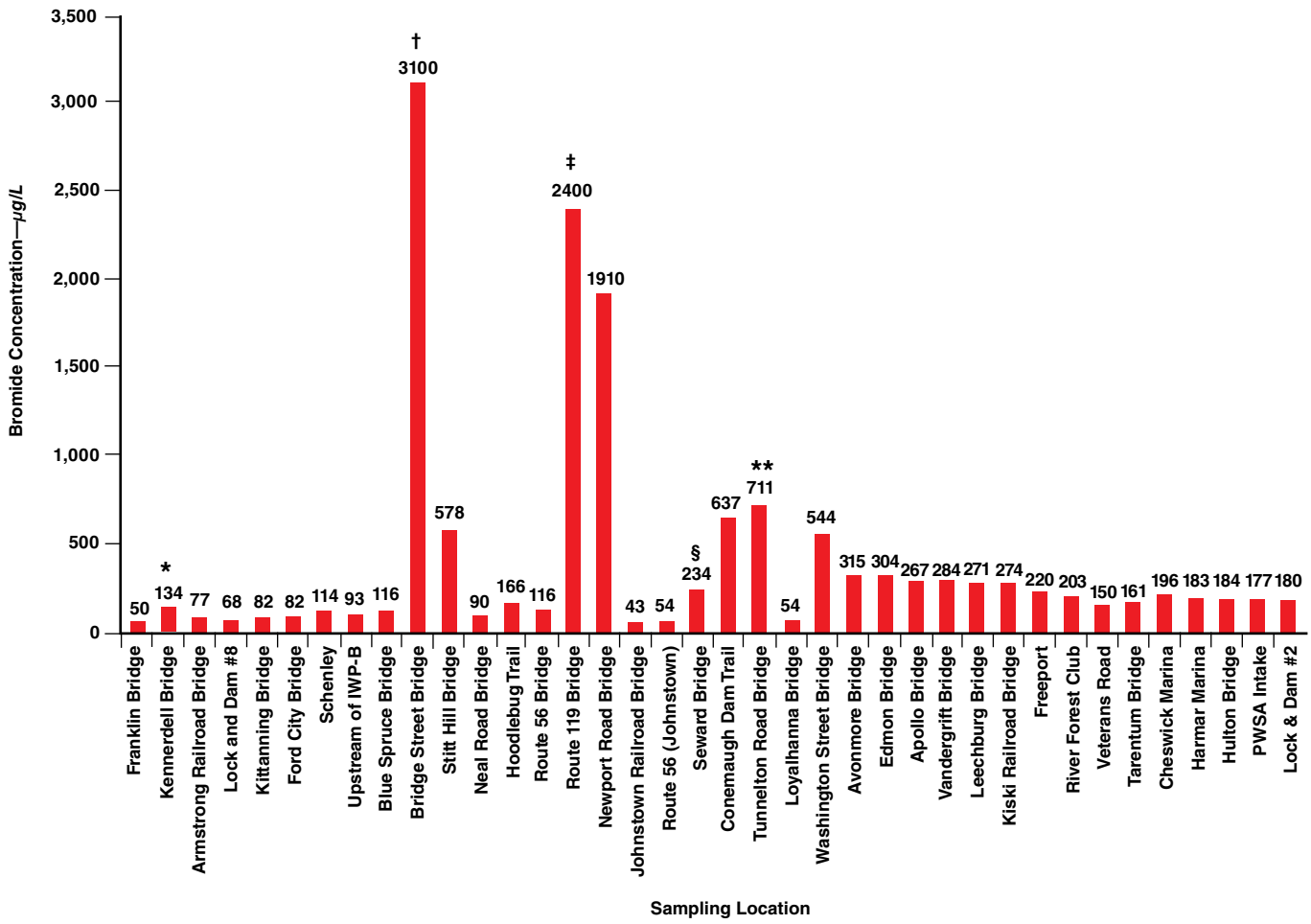
FIGURE 7 Results of PWSA bromide sampling in July 2011



IWP-B—industrial waste plant B, PWSA—Pittsburgh Water and Sewer Authority

* Downstream of industrial waste plant A
† Downstream of industrial waste plant B
‡ Downstream of industrial waste plant C
§ Downstream of power plants A and B
**Downstream of industrial waste plant D

ples collected from the Allegheny River and in finished water samples collected at the PWSA treatment plant were lower than the limits specified for drinking water in the Safe Drinking Water Act (USEPA, 2012). Furthermore, no consistent increases in radionuclides were observed in downstream versus upstream sampling locations for facilities associated with industrial discharges of bromide or for downstream locations compared with samples from Warren, Pa. These data suggest no apparent contribution of radionuclides associated with Marcellus Shale wastewater discharges in the Allegheny River.

Regulatory control of discharges of drilling wastewater into natural bodies of water. In April 2011, the PADEP asked drillers to voluntarily stop using municipal and industrial wastewater treatment plants to treat and ultimately dispose of Marcellus Shale wastewater in surface water systems. However, the current study indicates that discharges of bromide from several industrial locations continued after that request was made. This raises the question of whether hydraulic fracturing wastes are still being processed by these facilities or, alternatively, whether bromides are being released from treatment of other wastewaters (e.g., conventional gas and oil drilling). In either case, downstream drinking water utilities are being exposed to problematic concentrations of bromide in their source water supplies.

In October 2011, USEPA announced plans to develop national standards for the treatment of wastewater discharges produced by natural gas extraction from underground coal bed and shale

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TABLE 7 Bromide mass input to the Allegheny River system

Sampling Locations	Jan. *lb/d*	Feb. *lb/d*	March *lb/d*	April *lb/d*	May *lb/d*	June *lb/d*	July *lb/d*	Aug. *lb/d*	Sept. *lb/d*	Oct. *lb/d*	Nov. *lb/d*	Dec. *lb/d*
Franklin Bridge	2,377	5,018	2,870	5,989	6,927	1,760	1,021	1,454	2,437	917	4,690	2,212
Mass added from industrial waste plant A	**2,339**	**8,319**	**2,985**	**4,742**	**–330**	**1,143**	**1,716**	**186**	**–904**	**2,397**	**864**	–1,418
Kennerdell Bridge	4,716	13,337	5,855	10,731	6,597	2,903	2,737	1,640	1,533	3,314	5,554	793
Route 56 Bridge (Armaugh)	56	75	74	95	89	42	30	46	201	60	90	134
Mass added from industrial waste plant C	**566**	**532**	**229**	**365**	**409**	**847**	**591**	**32**	**609**	**–1**	**1,072**	**35**
Route 119 Bridge(Jan.–June); Newport Road Bridge (July–Dec.)	622	606	303	460	498	888	621	78	810	58	1,162	169
Route 56 Bridge (Johnstown)	180	362	383	417	200	72	14	157	152	194	218	250
Mass added from coal-fired power plants A and B	**9**	**0**	**0**	**46**	**807**	**448**	**47**	**780**	**1,249**	**0**	**0**	357
Seward Bridge	190	362	383	464	1,007	520	61	936	1,401	194	218	607
Conemaugh Dam Trail		2,974	5,148	1,603	2,739	803	2,348	2,138	845	2,777	2,025	2,574
Mass added from industrial waste plant D		**–181**	**1,287**	**382**	**1,369**	**154**	**273**	**625**	**127**	**280**	**120**	**–772**
Tunnelton Road Bridge		2,793	6,436	1,984	4,108	956	2,621	2,764	972	3,057	2,145	1,802
Sum of the measured bromide mass added to the Allegheny River system*	**2,915**	**8,669**	**4,501**	**5,535**	**2,256**	**2,591**	**2,626**	**1,622**	**1,081**	**2,676**	**2,056**	–1,798
Bromide mass at the PWSA intake												
Minimum	3,687	6,640	5,902	5,537	4,317	2,979	2,245	3,309	2,154	3,396	4,608	4,088
Maximum	28,507	34,313	35,013	28,510	18,012	8,049	8,090	6,322	16,409	16,256	19,897	19,731
Mean	8,884	11,708	14,209	14,049	9,970	4,299	3,623	4,632	7,164	9,065	9,705	8,143
Mean bromide mass at the PWSA intake minus bromide mass at Franklin Bridge	**6,507**	**6,690**	**11,339**	**8,060**	**3,043**	**2,539**	**2,601**	**3,178**	**4,728**	**8,148**	**5,015**	**5,931**
Percentage of observed changes in bromide mass measured at industrial sites compared with the difference in bromide mass at Franklin Bridge and the PWSA intake	45	130	40	69	74	102	101	51	23	33	41	–30

PWSA—Pittsburgh Water and Sewer Authority

*The sum of upstream bromide contributions from industrial waste treatment plants A, C, and D and from coal-fired power plants A and B

Gray shading indicates mass bromide contributions from the sources listed in column 1; boldface numbers are for emphasis.

formations (USEPA, 2011). The agency will consider standards based on demonstrated, economically achievable technologies. After gathering data and consulting with stakeholders, USEPA anticipates soliciting public comment on a proposed rule for coal bed methane in 2013 and for shale gas in 2014. In May 2013, USEPA cited three brine plants upstream of the PWSA intake for violation of their National Pollutant Discharge Elimination System discharge permits.

Future research. This survey of bromide in the Allegheny River and its tributaries suggests several industrial contributors of bromide to the river system (e.g., industrial wastewater treatment plants and certain coal-fired power plants). Because industrial wastewater treatment plants may treat a variety of industrial wastes (including wastewater from Marcellus Shale drilling operations, coal mine drainage, and brine from oil and gas wells in formations shallower than the Marcellus Shale layer), there is some uncertainty as to the ultimate origin of the excess bromide being discharged into the river. The next phase of this research will involve a collaborative effort with the University of Pittsburgh's Department of Geology to identify the sources of bromide-laden TDS in the river system. Chapman et al (2012) described a technique that can be used to differentiate between Marcellus formation wastewater and other potential sources of TDS in groundwater and surface water by analyzing strontium isotope ratios ($^{87}Sr/^{86}Sr$).

SUMMARY AND CONCLUSIONS

In late 2010, PWSA observed a dramatic increase in TTHMs, and in the percentage of brominated THMs in drinking water samples collected from its distribution system. Figure 8 summarizes PWSA's TTHM compliance data during a seven-year period (these data are based on compliance sampling for the Stage 1 D/DBPR). The percentage of brominated THMs observed in 2010 (88%) was significantly higher than in any of the other years. Additionally, despite PWSA's continued efforts to reduce the concentration of TTHMs by optimizing its treatment and distribution processes, the mean concentration of TTHMs in 2010 was the second highest in the seven-year period. Because of concern about these

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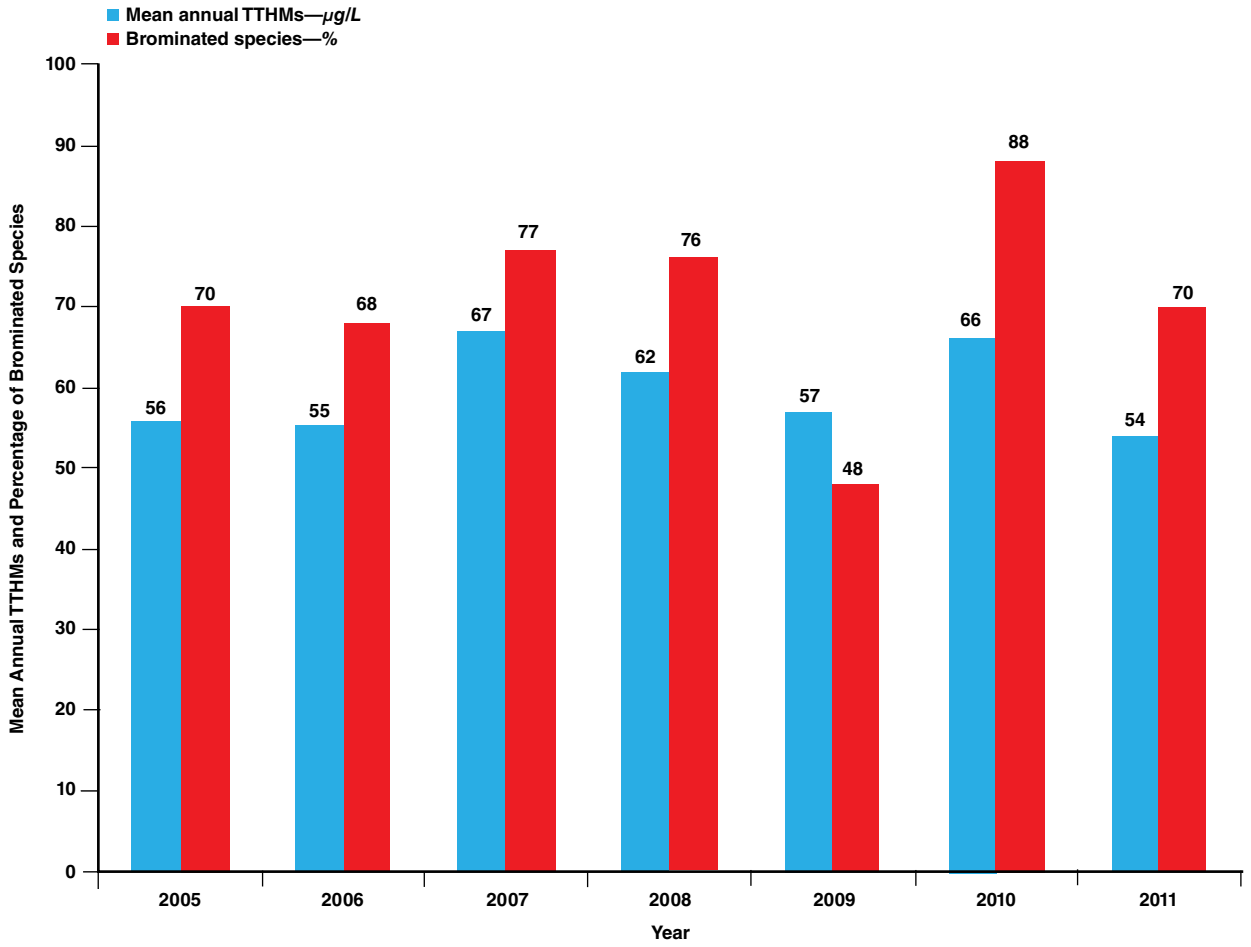
FIGURE 8 Mean annual TTHM concentrations and percentage of brominated species at PWSA



PWSA—Pittsburgh Water and Sewer Authority, TTHM—total trihalomethanes

observations and about PWSA's ability to meet the more stringent requirements of the newly promulgated Stage 2 D/DBPR, PWSA and the University of Pittsburgh's Swanson School of Engineering initiated a comprehensive study of bromide in the Allegheny River and its effect on DBP formation.

The results that were obtained in this study suggest the following conclusions:

- Increased bromide concentrations in PWSA's source water led to elevated TTHM concentrations and an increase in the percentage mass of brominated THMs in the utility's finished drinking water.
- Conventional drinking water treatment processes did not effectively remove bromide from source water.
- Radionuclides did not appear to be elevated in the Allegheny River or its tributaries, despite the apparent discharge into the river system of treated, and possibly untreated, wastewater from Marcellus Shale drilling operations.
- Bromide concentrations in the Allegheny River system appeared to be naturally low, as indicated by the consistently low levels measured in water from upstream sites on the river and its tributaries. Bromide concentrations tended to increase as water moved downstream in the Allegheny system. However, most of the increases appeared to be associated with point discharges of bromide from industrial sites rather than with the accumulation of bromide from the natural environment. Following the introduction of bromide from an industrial site, bromide concentrations tended to decrease naturally with dilution as the water continued to flow downstream.
- Bromide concentrations were significantly affected by the volume of water in the river (e.g., snow melt, heavy rains). Therefore, potential TTHM problems in drinking water associated with excess bromide concentrations in the river would be more acute during low-flow conditions.
- Although TDS has been used as a regulatory parameter for the discharge of industrial wastewater, it was not a reliable indicator or surrogate parameter for bromide in the Allegheny River.
- Bromide concentrations did not appear to increase downstream of most municipal sewage plants treating Marcellus Shale

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wastewater. A likely explanation is that most municipal sewage plants chlorinate their treated effluent for pathogen control before discharging it to surface water. Bromide in the chlorinated effluent is likely oxidized to hypobromous acid, which reacts with organic precursors to produce by-products in the sewage plant effluent. Some brominated organics, including THMs, may be formed at this point, and some of them may be volatilized to the atmosphere or otherwise lost as the river water flows downstream.

- Bromide concentrations increased downstream of industrial wastewater treatment plants (brine plants) treating Marcellus Shale wastewater. This suggests that the treatment processes used in these plants are ineffective at removing bromide.
- Bromide concentrations occasionally increased downstream of some coal-fired power plants. However, these bromide discharges appeared to be smaller than those observed at industrial wastewater treatment plants.
- Bromide concentrations did not appear to increase downstream of the single steel plant or the two acid mine drainage sites surveyed in this study.
- Bromide from industrial wastewater treatment plants and certain coal-fired power plants accounted for approximately 50% of the increase in bromide concentrations as water flowed through the Allegheny River system.

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PEER REVIEW

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