

# Occurrence and consequences of increased bromide in drinking water sources

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Elevated concentrations of brominated disinfection by-products (DBPs) have been reported recently by some drinking water utilities. Some of these occurrences have been correlated with upstream discharges of bromide-containing wastes from coal-fired power utilities, discharges of hydraulic fracturing wastewater, and other industrial sources. This article discusses this problem in terms

of the chemistry of DBP formation when bromide is present, regulatory changes that have resulted in the increased use of bromide by industries, and the number of water utilities potentially affected by these discharges. The authors investigated this problem through a review of published and unpublished sources and through interviews with utility personnel and state regulators.

**Keywords:** *bromide, brominated disinfection by-products, brominated species, power plant effluent*

The formation of unwanted and possibly carcinogenic by-products as a result of the disinfection of drinking water was first recognized by researchers in the 1970s. The first regulations to limit the concentrations of these disinfection by-products (DBPs), a collective term used to describe the suite of compounds resulting from reactions of free chlorine and other oxidants with natural organic matter and other substances in the water, were promulgated by the US Environmental Protection Agency (USEPA) in 1979. Since then, regulations have become more stringent as knowledge of the presence, formation, and health implications of DBPs has increased. More than 500 DBPs have been identified, although only a few have been regulated.

Disinfection of drinking water has contributed significantly to the reduction of waterborne disease. In spite of disinfection's benefits, DBPs have been shown to have adverse health effects after prolonged (i.e., lifetime) exposures (USEPA, 2006; AWWA, 2004). The DBPs most commonly associated with these observed adverse health effects have been halogen-substituted organics, typically DBPs containing chlorine or bromine. Although a large variety of complicated halogen-substituted DBP compounds are believed to result from the chlorination of drinking water, the only currently regulated DBPs are total trihalomethanes (TTHMs), five of the haloacetic acids (HAA5), bromate, and chlorite. TTHMs are the sum of chloroform, bromodichloromethane, dibromochloromethane, and bromoform. HAA5 is the sum of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, and dibromoacetic acid.

Chlorine added to drinking water reacts quickly with reduced substances (e.g., reduced iron), plus it also reacts quickly with ammonia, total organic carbon, organic compounds containing nitrogen, and the bromide ion. Any chlorine not consumed by these reactions can achieve disinfection but can also produce DBPs if enough DBP precursor material is present and if the

unreacted free chlorine residual remains in the water long enough for the DBP formation reactions to occur.

Most chlorine in drinking water is consumed in oxidation reactions, including the oxidation of organics (Jolley, 1975). However, some added chlorine substitutes into organic compounds to produce a chlorine-substituted DBP, and some of the added chlorine can transfer its oxidative or disinfecting power to another compound. In the latter case, chlorine can react with ammonia to produce chloramine (typically monochloramine or  $\text{NH}_2\text{Cl}$ ), react with nitrogen-containing organics to produce organic chloramine, and oxidize bromide to bromine.

## EFFECT OF BROMIDE ON DBP FORMATION

If bromide is present, it affects the formation of DBPs in a number of ways. Free chlorine reacts with bromide to produce free bromine in water, and the bromine reacts analogously to free chlorine during oxidation of any reduced metals still present, disinfection, reaction with ammonia to produce bromamines (typically dibromamine), and formation of bromine-substituted DBPs if DBP precursor material is present.

Therefore, in water, chlorine can react directly with organic DBP precursors but can also react first with bromide, and then the resulting bromine can react with organic DBP precursors to produce brominated organic DBPs. This is important for three reasons described in the following paragraphs.

**Greater health risks are reportedly attributed to brominated DBPs than to chlorinated DBPs.** The risks of cancer and other adverse human health effects are generally thought to be greater from bromine-substituted DBPs than from analogous DBPs containing chlorine instead of bromine (Cantor et al, 2010.) For example, the cancer slope factor for dibromochloromethane is 0.094 mg/kg/d versus 0.031 mg/kg/day for chloroform. Because the molecular weights of the two compounds are also different (119.4  $\mu\text{g}/\mu\text{mol}$  for chloroform and 208.3  $\mu\text{g}/\mu\text{mol}$  for dibromochloromethane),

on a molar basis dibromochloromethane is about five times more potent a carcinogen than chloroform (OEHA, 2009).

**The regulatory limits for drinking water compliance are mass-based, not molar-based.** Drinking water facilities are currently faced with two regulatory limits for halogen-substituted DBPs: TTHMs  $\leq 80$   $\mu\text{g/L}$  and HAA5  $\leq 60$   $\mu\text{g/L}$ . The regulatory limit is simply based on taking the mass concentration of each compound, without correcting for molar weight, and adding each numerical value for the four or five compounds involved. Therefore, a water system with no bromide in the background source water will be in compliance with the TTHM limit if it has 60  $\mu\text{g/L}$  of chloroform and no detectable brominated THMs. In this case, about 0.5  $\mu\text{mol/L}$  TTHMs would be produced. However, if nothing else changes but enough bromide is added to produce bromodichloromethane instead of chloroform, then 0.5  $\mu\text{mol/L}$  TTHM will produce  $\sim 82$   $\mu\text{g/L}$  TTHMs, which could create compliance difficulties. Therefore, a water system currently in compliance with DBP requirements may no longer be in compliance if bromide is added to the drinking water source in amounts sufficient to increase the amount of brominated DBPs produced.

**The formation of brominated DBPs increases as a result of the greater reactivity of bromide.** The preceding information suggests that the presence of bromide during chlorination can increase the numerical value of the regulatory compliance value, even if the same amount of organic precursor material is present and even if the same molar concentration of DBP is produced. However, because free bromine in drinking water reacts more quickly than free chlorine, more DBPs (on a molar basis) will be produced because the increased reactivity of bromine will mean more oxidation of organics by bromine, as well as bromine substitution reactions.

A number of factors determine the formation and ultimate composition of TTHMs—water quality parameters, residence time, amount of disinfectant, temperature, and type and amount of precursor material. At any given utility, the relative amount of each of the four THMs can vary during the year because of changes in these factors. Until recently, however, except in coastal locations where bromide can be introduced by saltwater influences, US utilities have generally seen more chlorinated than brominated species in the TTHMs in their distribution systems. TTHM data collected from 500 water plants under the Information Collection Rule (1997–1998) showed that, in general, chloroform dominated the other three species and was present at the highest mean concentration (McGuire et al, 2002). The mean concentrations of DBP species in all distribution system samples were 23.5  $\mu\text{g/L}$  chloroform, 8.4  $\mu\text{g/L}$  bromodichloromethane, 4.3  $\mu\text{g/L}$  dibromochloromethane, and 1.4  $\mu\text{g/L}$  bromoform.

## BROMIDE OCCURRENCE IN SOURCE WATER

Bromide is a common element in seawater but rarely occurs naturally at high concentrations in fresh surface water sources in the United States (Bowen, 1979). Bromide from seawater can influence drinking water sources either through intrusion or through connate seawater (seawater trapped in geological formations.) Typical seawater concentrations are about 65,000  $\mu\text{g/L}$ , and some coastal drinking water supplies have elevated bromide concentrations as a result of seawater intrusion.

Although bromide in source water can come from seawater, it can also come from a number of anthropogenic sources. In the past, before leaded gasoline was banned in the United States, gasoline emissions were a contributing factor because leaded gasoline contained additives of brominated compounds. Road salt and some fertilizers can also contribute bromide to water sources. Recently, however, there have been reports of increased bromide in source water as a result of natural gas production with hydraulic fracturing, air pollution control methods in coal-fired power plants, and textile production.

Effluent from coal-fired power plants may contribute to bromide in source water because some plants must use wet scrubbers to produce clean air effluent. The scrubbers can introduce bromide into the waste stream, which is then discharged to a surface body of water. Another possible contributor is natural gas production. The development of this fuel requires a significant amount of water, and the wastewater produced typically contains high bromide concentrations. Although most unconventionally produced oil and natural gas wastewater is disposed of through deep underground injection, wastewater that is returned to surface water and processed through surface water treatment plants (WTPs) may contain substantially increased bromide concentrations caused by the increased brominated fraction. Another possible bromide source is textile mill processes that use brominated compounds to flameproof fabrics.

Although these sources have been studied to some extent, their full impact on the populations served by water utilities is not yet well understood because utilities are just beginning to see the effect of bromide on their DBPs. Some water utility personnel have recently noticed an increase in the brominated fraction of their DBPs. A number of utilities with no previous violations have experienced violations of DBP maximum contaminant levels (MCLs) as a result of this brominated fraction. Because bromide is unregulated and has no known health effects at concentrations normally found in source water, bromide has not historically been monitored in source water, except in research studies.

## SOURCE WATER BROMIDE CONCENTRATIONS AND THEIR EFFECT ON DBP SPECIATION

As reported by Amy and colleagues in 1995, a source water bromide survey conducted with 100 utilities during an 18-month period showed that bromide concentrations at large and small randomly selected utilities ranged from  $< 5$  to 429  $\mu\text{g/L}$ . At targeted utilities where the researchers suspected that high concentrations of bromide existed, the average bromide concentration was 210  $\mu\text{g/L}$ . When all data from the 100 utilities were considered, the overall average was about 100  $\mu\text{g/L}$ . The median (50%) value for river and groundwater sources was approximately 60  $\mu\text{g/L}$ , whereas the median for lakes was approximately 30  $\mu\text{g/L}$ . The 90% values for river and groundwater sources were approximately 300  $\mu\text{g/L}$  (Amy et al, 1995).

Under the Information Collection Rule, all large utilities serving more than 100,000 customers were required to measure a number of water quality parameters, including source water bromide and distribution system THMs and HAAs. Samples from 500 WTPs were analyzed during an 18-month period in

1997–1998. The water systems were grouped into five categories for analysis on the basis of bromide concentrations in their source water. The categories were < 20 µg/L, 20–30 µg/L, 30–50 µg/L, 50–100 µg/L, and > 100 µg/L of bromide. About 80% of the samples analyzed for bromide in source water contained < 100 µg/L of bromide. In the highest category (> 100 µg/L of bromide), more than half of the TTHMs were bromine-substituted. When all of the data from the 500 plants were analyzed, systems that used source water with elevated bromide concentrations tended to have elevated concentrations of brominated DBPs in their distribution systems. However, the range of speciation within each category of bromide concentration was quite large (McGuire et al, 2002).

USEPA reported on the results of an extensive nationwide survey of DBP occurrence in drinking water. In this survey, source water bromide concentrations > 400 µg/L were associated with increased concentrations of DBPs in the finished water (Weinberg et al, 2002).

Preliminary data from an extensive monitoring effort taking place in North Carolina indicate that bromide concentrations in some watersheds are elevated, especially during periods of low stream flow. In one river, bromide concentrations as high as 1 mg/L were measured (Greune, 2013). The percentage of chloroform in the TTHMs in the distribution system of a drinking water utility on that river decreased significantly with increased bromide concentrations. At the highest bromide concentration in source water, nearly all of the TTHMs were composed of brominated species. Other recent studies have reported the same trend.

## POTENTIAL EFFECT OF COAL-FIRED POWER PLANT DISCHARGES ON WATER QUALITY

Recently finalized regulations for power plant emissions into the air may result in the use of more air pollution-control technology, including brominated compounds, and ultimately more bromide wastes being discharged to receiving streams. In December 2011, USEPA approved strict, new air-emission limits, referred to as the Mercury and Air Toxics Standards (MATS), targeting oil- and coal-fired electrical power-generating facilities. These requirements are scheduled to take effect in 2015 (USEPA, 2012). MATS will target reductions in emissions of metals (mercury, arsenic, chromium, nickel), acid gases (hydrochloric and hydrofluoric), particulate matter, sulfur dioxide (SO<sub>2</sub>), and nitrous oxides. Figure 1 shows a USEPA-prepared map of US power plants with coal, oil, or both coal and oil units and their relative capacities in megawatts (MW) (USEPA, 2011).

It is estimated that 1,100 coal-fired units and 300 oil-fired units at 600 power plants will be affected by the MATS requirements (USEPA, 2011). Power plants that use coal as a fuel are most likely to install wet scrubbers and are the focus of this article.

The Flue Gas Desulfurization (FGD) process, also known as air scrubbers, is the preferred air pollution-control technology for controlling SO<sub>2</sub> and sometimes mercury. The new MATS requirements for SO<sub>2</sub> and mercury could result in the installation of more wet or dry scrubbers. Economic analysis will dictate which technology is selected, but wet scrubbers are generally favored when coal with higher sulfur content is used, as is the case in much of the eastern United States.

Mercury is present in flue gas in varying percentages, depending on the origin of the coal, in three basic forms (Kellie et al, 2005): particulate-bound mercury, elemental mercury (Hg<sup>0</sup>), and oxidized mercury in gas form (Hg<sup>2+</sup>). Particulate-bound mercury can be removed easily by electrostatic precipitators (ESP) or fabric filters (Bustard et al, 2003). The oxidized mercury tends to stick to particulate matter and is water soluble (Blythe et al, 2002). Consequently, it can be captured by ESPs, fabric filters, or wet or dry scrubbers. However, Hg<sup>0</sup> is highly volatile and insoluble in water and is thus not readily removed by typical air pollution-control devices. The relative concentration of chloride and bromide that naturally occurs in the coal dictates the form of mercury that is present. In general, bromide is lower in lignite and sub-bituminous coal—3 mg/L and 1–2 mg/L, respectively—than in bituminous coal—20 mg/L (Buschmann, et al, 2005). Therefore, the addition of bromide-containing salts (usually calcium bromide) to the coal combustion unit can convert the mercury into the more water-soluble Hg<sup>2+</sup> form. This soluble mercury is better removed by the wet scrubbers used to clean flue gases.

Although mercury in the wastewater can be removed prior to discharge into a receiving stream, the added bromide is not typically removed and ends up being discharged. A US Department of Energy (USDOE) National Energy Technology Laboratory (NETL) report (Benson et al, 2007) documented the correlation between bromide in or added to the coal and the concentration of bromide in the FGD wastewater, referred to as “liquor” in their study. The NETL results (Figure 2) show that after a couple of weeks, the bromide concentration in the FGD liquor was equal to the concentration added to the coal.

In tests of 14 full-scale, coal-fired power plants using calcium bromide to oxidize elemental mercury, more than 90% of the mercury was oxidized with the addition of 25–300 mg/L bromide by weight of coal (Chang et al, 2008). This range is wide because of the coal’s natural abundance of chlorine and bromine, giving the coal varied natural performance for oxidizing mercury. Using this information, it is possible to calculate the amount of bromide that could be discharged as a function of the amount of energy produced by the power plant, as described in the calculations shown in the following paragraph.

A power plant with a 1-MW capacity operated 24 hours a day, 365 days a year would produce 8,760,000 KW·h/year. According to the US Energy Information Administration (USEIA, 2013a), it takes 1.07 lb of coal to produce 1 KW·h of electricity. This means that for each MW of electrical power plant capacity, a coal-fired power plant would require 9,373,200 lb coal/year, or 25,680 lb/d. Using the range of 25–300 mg/L for bromide noted in Chang et al (2008), the amount of bromide added to the system each day per MW of power is estimated as follows:

For coal with 25 mg/L bromide

$$25,680 \frac{\text{lb coal}}{\text{day} \times \text{MW}} \times \frac{25 \text{ lb CaBr}_2}{10^6 \text{ lb coal}} \times \frac{2 \text{ mol Br}}{1 \text{ mol CaBr}_2} \times \frac{1 \text{ mol CaBr}_2}{199.9 \text{ g}} \\ \times \frac{79.9 \text{ g}}{1 \text{ mol Br}} = 0.51 \frac{\text{lb Br}}{\text{day} \times \text{MW}}$$

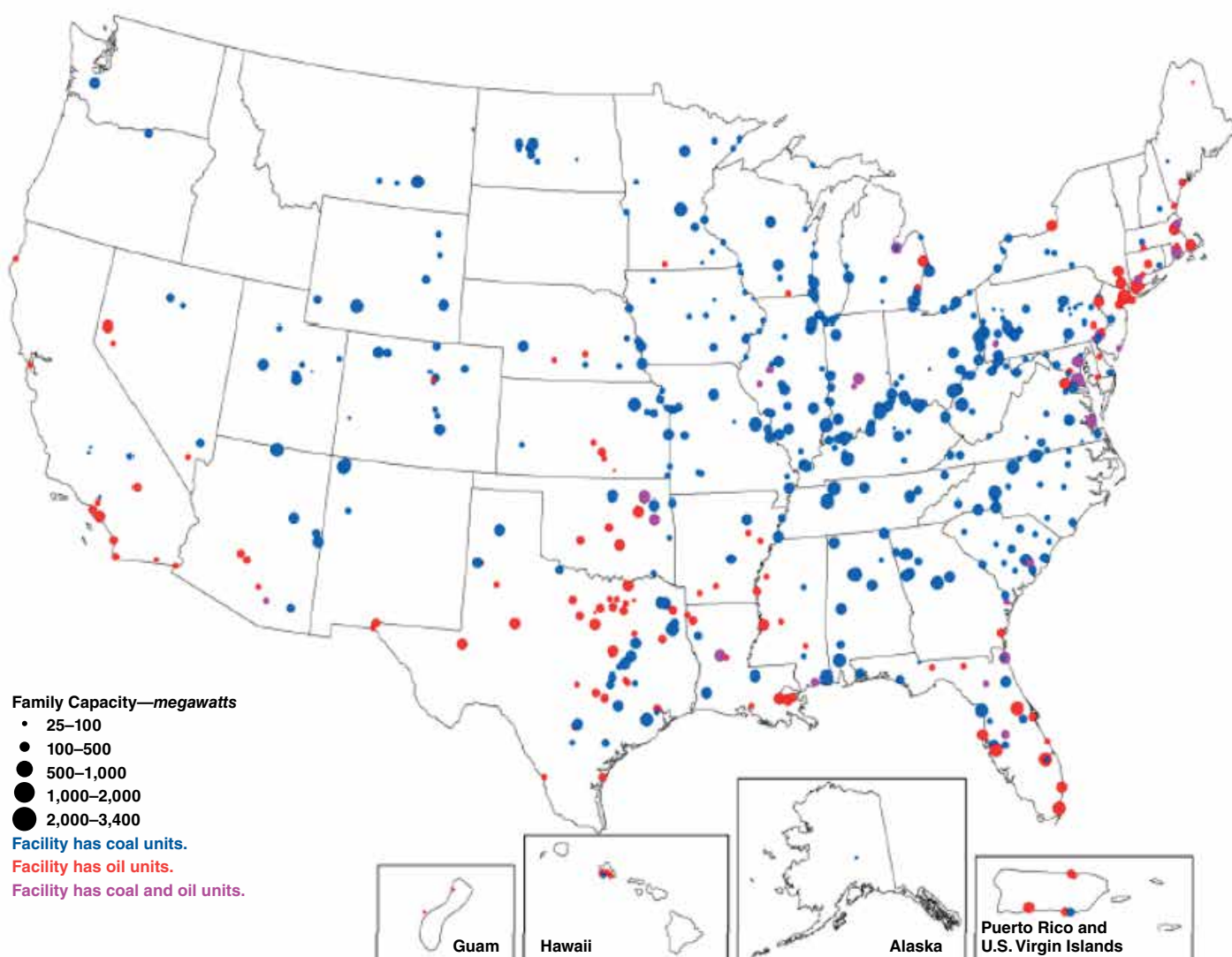
For coal with 300 mg/L bromide

$$25,680 \frac{\text{lb coal}}{\text{day} \times \text{MW}} \times \frac{300 \text{ lb CaBr}_2}{10^6 \text{ lb coal}} \times \frac{2 \text{ mol Br}}{1 \text{ mol CaBr}_2} \times \frac{1 \text{ mol CaBr}_2}{199.9 \text{ g}} \\ \times \frac{79.9 \text{ g}}{1 \text{ mol Br}} = 6.2 \frac{\text{lb Br}}{\text{day} \times \text{MW}}$$

Therefore, depending on the amount of bromide present in or added to the coal, the production of 1 MW of power would result in the addition of 0.51–6.2 lb/d of bromide. Further, according to the NETL report (Benson et al, 2007), all of the bromide added at the power plant is discharged into receiving streams. These calculations indicate that 0.51–6.2 lb/d of bromide per MW of power produced will be discharged into receiving streams.

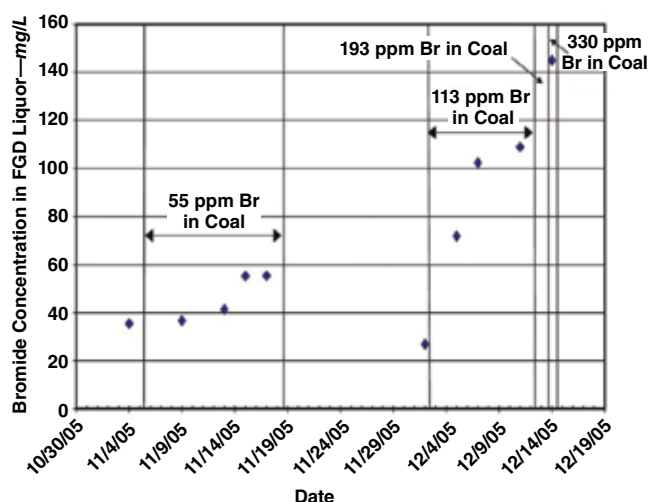
Currently, there are no national standards for bromide. However, the new MATS requirements may increase bromide discharges from coal-fired power plants in a couple of ways. First, coal-fired power plants have already added or will be adding wet scrubbers in response to the MATS requirements for removing SO<sub>2</sub>. Even if a plant uses a coal source with a low bromide content, the increased use of wet scrubbers to remove SO<sub>2</sub> will result in more bromide releases, even in situations in which bromide is not added to improve mercury removal. If the coal source has a high bromide content, these wet scrubber discharges will include even greater amounts of bromide. Furthermore, the increased need to remove mercury in coal-fired power plants may cause bromide to be added, unless the coal already contains naturally high amounts of bromide. In either case, the amount of bromide a power plant releases to receiving water will be greater than before the wet scrubber was installed.

**FIGURE 1** Location of US power plants affected by new air quality regulations



Source: USEPA, 2011

**FIGURE 2** Measured bromide concentrations in FGD liquor compared with bromide concentrations in coal



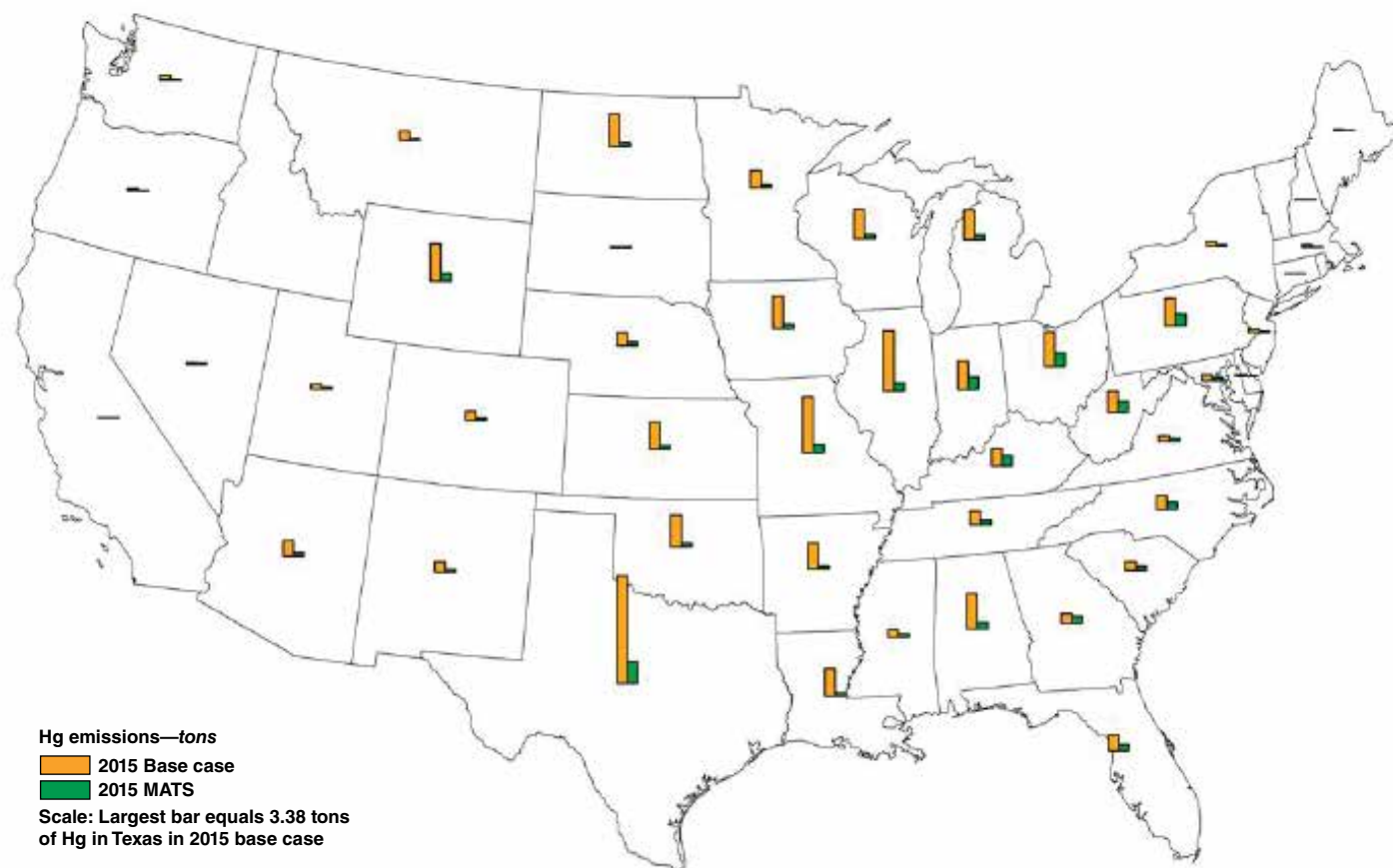
Source: Benson et al, 2007

Br—bromide, FGD—flue gas desulfurization

Figure 3, prepared by USEPA (2011), shows the projected improvement in mercury releases in different states as a consequence of the MATS requirements. A large portion of these improved mercury releases is expected to result from the increased use of bromide, wet scrubber technology, or both. Power plants that have installed scrubbers in response to the MATS may move to a coal source with higher sulfur content because they already have control technology in place. Coal containing higher amounts of sulfur is generally less expensive than low-sulfur coal (USEIA, 2013b) and has a higher British thermal unit (BTU) value (Bowen & Irwin, 2008). Bituminous coal has higher sulfur content and also, as previously discussed, has higher bromide content. The lower cost of bituminous coal alone could increase scrubber use, wastewater volume, and bromide concentrations.

According to USEPA (2013), 85% of the FGD systems installed in the United States are wet systems. Generally, installing a wet scrubber is more cost-effective than installing a dry scrubber for a power plant burning coal with a higher sulfur content—> 2% by weight. Also, dry and spray dry scrubbers are applied to smaller units—those producing < 300 MW (USEPA, 2013). Figure 4 is from a NETL report (Miller et al, 2006) showing that FGD capacity is projected to increase to 231 gigawatts (GW) by 2020.

**FIGURE 3** Projected mercury emissions from coal-fired power plants by state, in response to MATS requirements



Source: USEPA, 2011

Base case—projected mercury emissions if MATS requirements were not in effect, Hg—mercury, MATS—Mercury and Air Toxics Standards



If 90% of the FGD processes installed continue to be wet scrubbers, then 208 GW of the electrical power-generating capacity in 2020 will make use of wet scrubbers. One vendor promoting the use of bromide injection for mercury control claims that a combined total of 8,000 MW of US utility coal-fired boilers use its technology (McIlvaine Company, 2012).

As discussed previously, bromide is present in the coal burned and is often added as calcium bromide in the FGD process. As the use of FGD increases, the amount of bromide that is ultimately released to receiving water may increase dramatically, resulting in adverse effects on downstream drinking water plants.

Consequently, the new air emissions regulation designed to lower mercury emissions may result in increased bromide discharges to drinking water sources as power plants change technology or coal sources in an effort to meet the requirements. Drinking water utilities may, in turn, experience difficulty in meeting regulatory requirements and may see an increase in the production of brominated DBPs, which may pose greater health risks to consumers than analogous chlorinated DBPs.

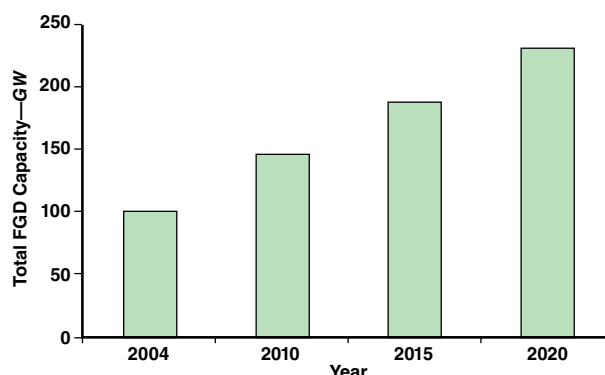
Bromine disinfectants, also referred to as bromine biocides, are also used as an alternative to chlorine for cooling tower disinfection. Regulations have made it particularly difficult to use chlorine to control biological fouling in cooling towers. However, discharges of power plant cooling water containing bromine are controlled by National Pollutant Discharge Elimination System (NPDES) permits, which restrict discharges of bromine compounds to no more than 2 h/d. This could result in a bromide spike and thus a DBP spike in the distribution system of a downstream WTP.

## POTENTIAL EFFECT OF HYDRAULIC FRACTURING ON WATER QUALITY

Unconventional development of natural gas sources, also known as hydraulic fracturing, or “fracking,” made up 23% of US natural gas production in 2010. This percentage is increasing each year and is expected to reach 49% by 2035 (USDOE, 2012). Hydraulic fracturing introduces water (millions of gallons per well) to the shale formation in order to increase permeability, and thus this water has the potential to return to the surface with the gas. From 10 to 80% of the injected water may return to the surface as wastewater. The wastewater from the entire process includes both “flowback” and “produced water.” Flowback is the fracturing fluid that quickly returns to the surface; produced water is the fracturing fluid that takes longer to return to the surface (Robart, 2012).

Both flowback and produced water are enriched with materials from the shale formation—e.g., minerals, brines, hydrocarbons, and naturally occurring radioactive material. The longer the fluid takes to return to the surface, the greater the concentration of formation materials it contains (Hayes, 2009). Management of flowback is usually done as part of on-site operations through minimization, recycling, and reuse. Management of produced water may also include treatment followed by surface water discharges, such as at publicly owned wastewater treatment plants (known as publicly owned treatment works, or POTWs) or centralized waste treatment plants (CWTs). Existing CWTs are exempt from the 2008 regulations that include restrictions on discharges of total

**FIGURE 4** Projected increase in US coal-fired wet FGD capacity



Source: Miller et al, 2006

FGD—flue gas desulfurization

dissolved solids (TDS). This exemption could result in elevated TDS concentrations, including the release of elevated bromide and chloride concentrations found in flowback and produced water.

Table 1 shows the ranges of bromide concentration, the average wastewater flow, and the receiving watershed for a number of Pennsylvania facilities that treat hydraulic fracturing wastewater and discharge it to surface water. Significant quantities of bromide are being introduced to receiving water by these facilities. The West Virginia Department of Environmental Protection also collected 13 produced water samples containing bromide concentrations ranging from 1,290 to 525,000 µg/L, with an average concentration of 185,000 µg/L.

For example, the Josephine brine treatment facility (Table 1), located on the Conemaugh River within the Allegheny watershed, reported discharging 155,000 gpd of treated hydraulic fracturing wastewater containing bromide concentrations of 601,000–8,290,000 µg/L. However, a full understanding of the magnitude of the flow and concentration of this effluent requires knowledge of the flow of the receiving stream. The closest US Geological Survey (USGS) gauge station (USGS 03041500) to the brine facility’s discharge location on the Conemaugh River measured an average flow of 1,629 ft<sup>3</sup>/s. This means that the brine effluent makes up 0.015% of the total river flow, diluting the bromide concentration by the same fraction. With that dilution factor, the bromide concentration added to the river at the discharge location is approximately 88–1,220 µg/L. As discussed previously, the bromide concentrations in US rivers reported by Amy et al in 1995 averaged around 60 µg/L. Because 1995 predates the ongoing boom in shale gas development, those concentrations could be considered the background concentration. This means the lower limit of the Josephine facility’s effluent bromide concentration is more than double the background concentration and the upper limit increased 20-fold.

## POTENTIAL EFFECT OF OTHER INDUSTRIES ON WATER QUALITY

Other industries could also discharge wastewater effluent with elevated bromide concentrations. Any industry with emissions

**TABLE 1** Bromide concentrations at Pennsylvania CWTs and POTWs treating Marcellus Shale wastewater

Name of Facility	Type of Treatment Facility	Bromide Concentration $\mu\text{g/L}$ *†		Date		Plant flow gal/d‡
		Minimum	Maximum	Minimum	Maximum	
Pennsylvania Brine Treatment's Josephine facility	CWT	601,000	8,290,000	5/25/2011	12/21/2011	155,000
Pennsylvania Brine Treatment's Franklin facility	CWT	364,000	770,000	8/2/2011	5/9/2011	300,000
Minard Oil Run Company's Dent treatment facility	CWT	606,000	657,000	10/6/2011	2/9/2012	16,000
Brockway Area Sewage Authority	POTW	2,320	19,200	12/7/2011	11/21/2011	1,500,000
Ridgway Borough	POTW	2,880	11,500	9/8/2011	7/21/2011	2,20,000
City of McKeesport	POTW	119	600	10/20/2010	10/19/2010	11,500,000
Franklin Township of Greene County	POTW	< 0.016	20,910	11/7/2011	11/10/2010	1,250,000

CWT—centralized waste treatment, POTW—publicly owned treatment works (for treating wastewater)

\*USEPA, 2013

†Ferrar et al, 2013

‡Environmental Law Clinic, 2009

containing mercury and sulfur oxides could have or will have wet scrubber installations, and thus their effluent streams could be a new source of bromide in receiving streams.

Brominated flame retardants are used in a variety of consumer products, and several of those are produced in large quantities. The use of flame retardants has grown dramatically over the past 30 years in response to concerns related to the increasing use of flammable plastics and textiles. Many concerns about these compounds focus on their persistence in the environment and bioaccumulation. Although the flame retardants themselves are unlikely to form DBPs as a result of their inherent environmental persistence, effluent streams from the facilities that produce and use these compounds (i.e., textile mills) could be a possible source of bromide in receiving streams.

## ANALYZING POTENTIAL EFFECTS ON DRINKING WATER SOURCES

There are no current standards for bromide in drinking water or receiving water, because in its unreacted form, bromide has no known health effects associated with ingestion. Drinking water utilities have not traditionally monitored their source water for bromide, and in most cases industries are not required to report concentrations of bromide discharged to receiving water.

In order to determine the potential number of drinking water utilities that could be affected by bromide discharges resulting from wet scrubber installations at coal-fired plants, a number of databases and tools were used.

According to the USEIA, 332 electric utilities used coal during the period 2002–2011 (USEIA, 2011). This number includes electricity production only by public entities and not by independent power producers or the commercial and industrial sectors. These sectors operated an additional 257 coal-fired facilities during 2011, but they are generally much smaller than those owned by electric utilities. Of the 332 public entities identified, 302 have NPDES permits. With the use of the latitude and longitude information provided in the NPDES permits for these plants, a map was created in a software program for

analyzing geospatial data (Figure 5). Along with latitude and longitude, the database for these power plants also contains the plant nameplate capacity (USEIA, 2011), the NPDES permit number (USEPA, 2013), the hydrologic unit code (USEPA, 2013), the FGD type and year of installation (USEIA, 2011), and the current sulfur content of the coal used (USEIA, 2013c). This information was used to identify bodies of water potentially at risk for bromide contamination.

Most of the power plants using coal are east of the Mississippi River (Figure 5). They are typically located on or near a large body of surface water. Also, high densities of coal-fired power plants are located on the borders of Ohio, West Virginia, Kentucky, and Indiana, along the Ohio River.

Of the 302 identified coal-fired electric utility power plants with NPDES permits, 118 had wet scrubber installations (Figure 5, part A), 39 had dry scrubber installations, and eight used coal with a high sulfur content (> 2%), making these plants good candidates for installing a wet scrubber.

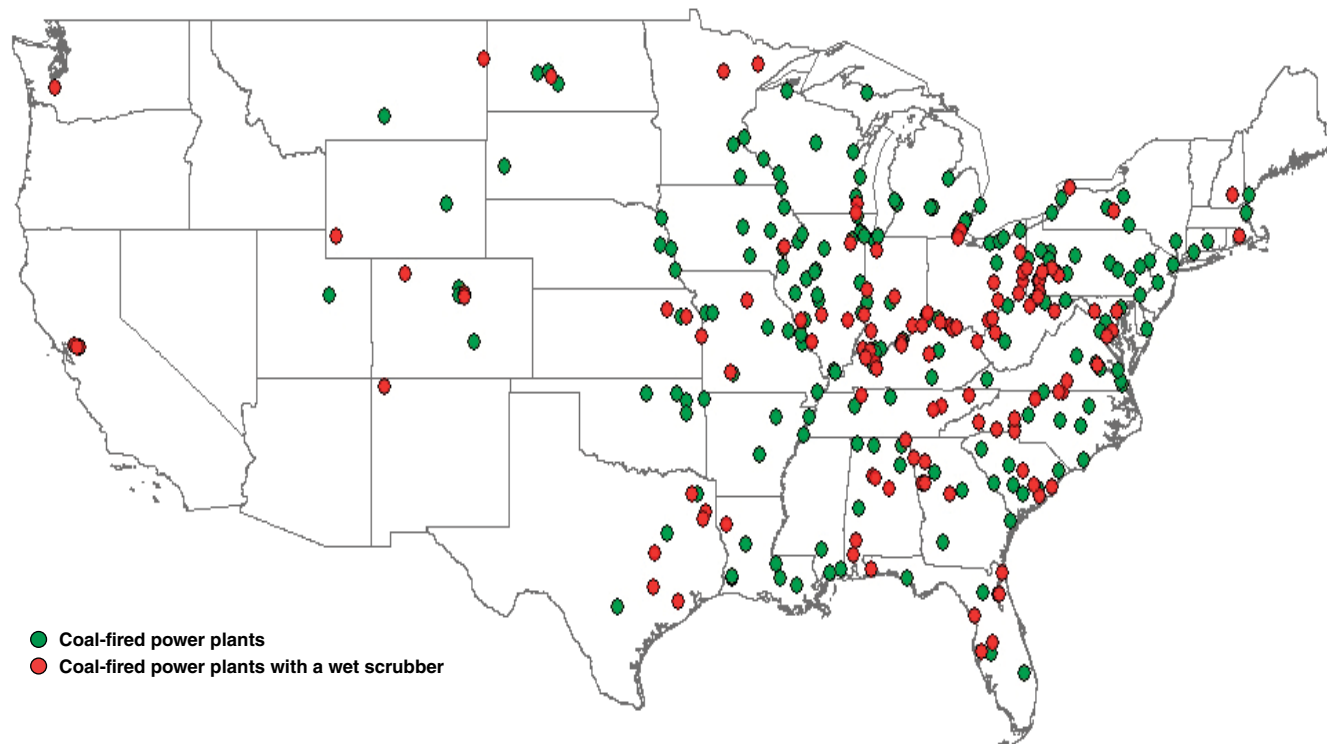
The database of the Safe Drinking Water Information System (SDWIS) was then used to map community water systems that use surface water. The SDWIS database contains information on all community surface drinking WTPs in the United States, including the location, public water system identification number, population served, and contact information. The database included 8,370 surface WTPs serving a population exceeding 500.

The surface WTPs and the 118 coal-fired power plants with wet scrubbers were plotted in the same software program<sup>1</sup> (Figure 5, part B) with layers for streams, canals, rivers, and other bodies of water. This plot was prepared to display power plants whose wastewater effluent could contain bromide. Then with knowledge of stream flow directions, NPDES hydrologic unit codes for the power plants, and visual confirmation of drinking WTP locations, 96 surface WTPs were identified as being downstream from 57 coal-fired power plants with wet scrubbers (Figure 6). The effluent from one power plant could affect multiple WTP intakes.

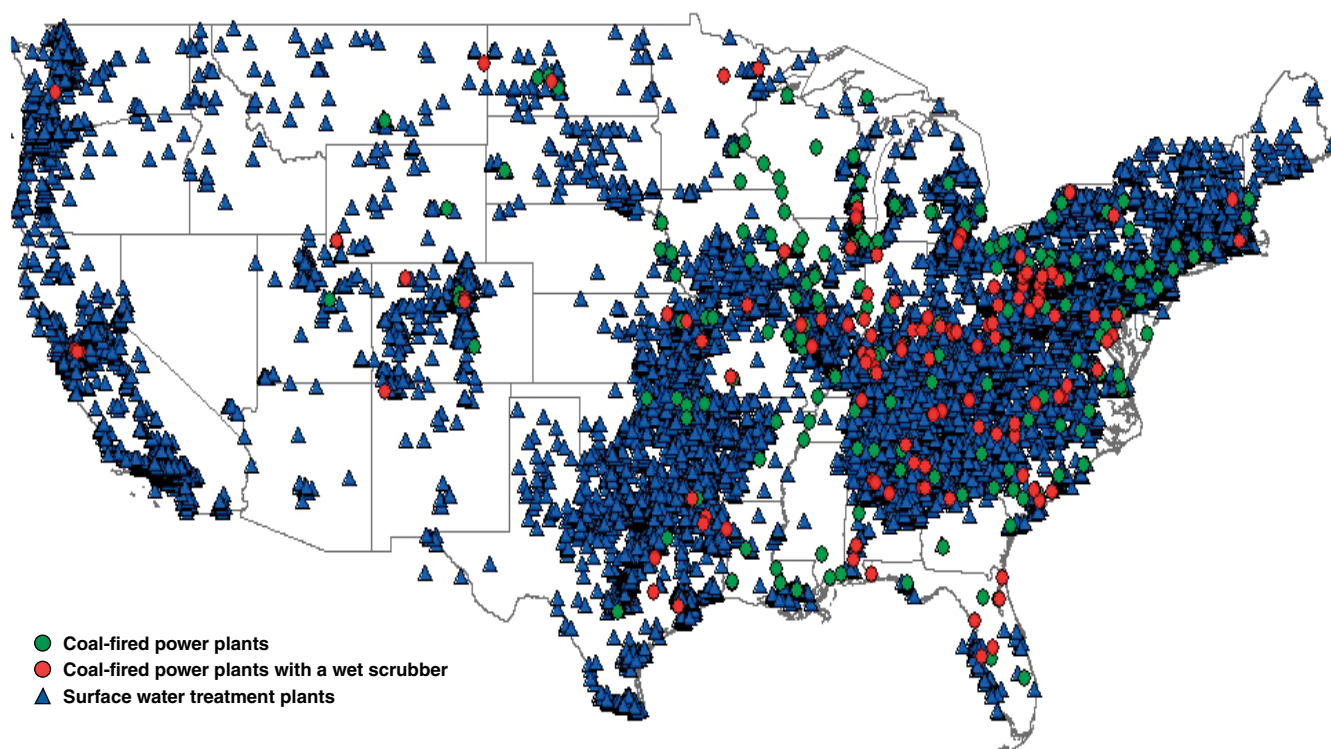
Figure 7 shows how potentially affected facilities were identified with the use of databases of the power plant and WTP locations.

**FIGURE 5** Locations of surface water treatment plants and coal-fired power plants

**A** Location of US coal-fired power plants with NPDES permits (302) and those with wet scrubbers (118)



**B** Location of US surface water treatment plants in relation to coal-fired power plants with and without wet scrubbers



NPDES—National Pollutant Discharge Elimination System



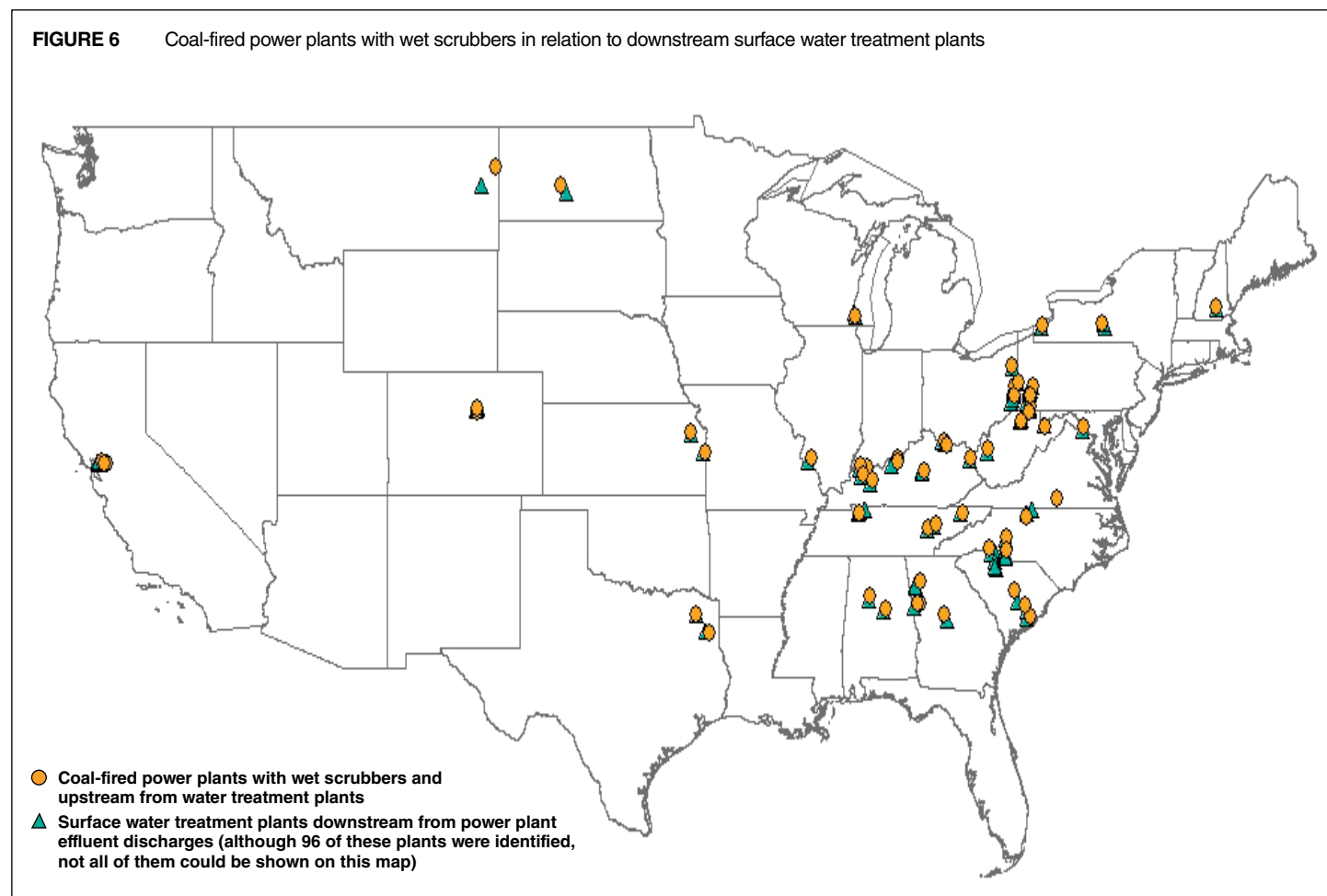
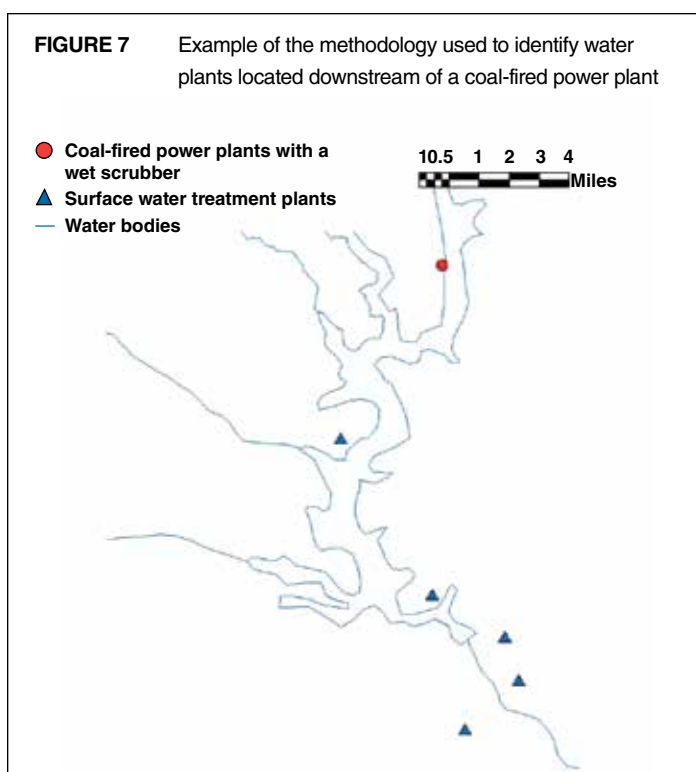


Figure 7 shows the location of a power plant along with downstream rivers, streams, and drinking water treatment facilities using surface water. All of the facilities shown in Figure 7 use the same source whether it is WTP influent or power plant effluent.

The SDWIS database was used to determine whether these 96 downstream utilities had reported MCL violations of TTHMs or HAA5. Of the 96 WTPs identified, 25 had DBP MCL violations, and 17 of those had violations that occurred after wet scrubber installations. Of those 17, six WTPs experienced violations within a year of the installation. These numbers suggest that there may be a correlation between installation of the wet scrubber and increased DBP formation at downstream water plants, although many factors affect the formation of DBPs. To determine if these increases could be caused by power plant effluents, state regulators and utility personnel at these water plants were contacted for further information.

#### UTILITY EFFECTS FROM COAL-FIRED PLANT DISCHARGES

Personnel at 14 utilities and eight state primacy agencies were contacted. Some of these utilities and primacy agencies reported no increase in DBPs. Four drinking water utilities were identified as having documented increases in brominated DBPs, along with increased source water bromide concentrations believed to be from wet scrubber installations at coal-fired power plants (Table 2). All



of these increases followed a wet scrubber installation at an upstream power plant. Data from each of these four WTPs (WTPs A through D) are described in the following paragraphs.

**WTP A.** As shown in Table 2, WTP A has not had a DBP violation. But the plant's THM and HAA data showed increases in brominated DBPs in the same time periods during which elevated bromide concentrations were noted in the source water. The increased bromide in the plant's source water appears to have occurred shortly after the wet scrubber installation at the upstream power plant in 2009.

The TTHM compound most affected by the increase in source water bromide concentrations was bromoform. Bromoform concentrations in the plant's finished water increased by a factor of 10–20. Concentrations of bromodichloromethane and bromochloroacetic acid also increased. Other WTPs in the area made similar observations; however they declined to provide these data.

**WTP B.** Two WTPs—WTP B and WTP C—that were identified in the NPDES permit of a coal-fired power plant that installed a wet scrubber in 2008 were contacted. WTP B shared quarterly compliance data. WTP B did not have a violation, but utility personnel stated that bromide was observed in the plant's source water in 2008 and had not been present before this time. In response to the elevated bromide concentrations, utility staff took samples from the source water and then collected samples several miles upstream at the location of each effluent source. They concluded that the upstream power plant was the source of the bromide.

WTP B uses free chlorine for disinfection but intends to switch to chloramines to avoid exceeding the DBP MCL. Figure 8 shows WTP B's average quarterly TTHM speciation for all sampling locations over time. The black line on part A of the figure represents the TTHM MCL, and the vertical red line shows the year that the upstream power plant installed a wet scrubber. For a TTHM MCL violation to occur, the running annual average must exceed 80 µg/L. Exceeding the MCL for one quarter may not result in a violation if TTHM concentrations for the last three quarters are far enough below the MCL to cause the average concentration for the four quarters to be below the MCL. Prior to 2008, the year of the wet scrubber installation, WTP B had relatively low TTHM concentrations composed mostly of chloroform. After the wet scrubber installation, the plant's TTHMs not only increased but the speciation was dominated by brominated THMs.

The speciation change is better illustrated by a comparison of average TTHM concentrations in two of the same quarters from different years, one preceding the wet scrubber installation and one following it. WTP B's average TTHM concentrations during the second and fourth quarters before and after the wet scrubber installation are shown on part B of Figure 8, where chloroform is shown in blue. Before the wet scrubber was installed in 2008, < 25% of the plant's TTHMs consisted of brominated compounds; after the installation, > 80% of the TTHMs consisted of brominated compounds.

**WTP C.** When WTP B started to monitor bromide, its staff contacted WTP C. In response, WTP C also began to monitor bromide at its intake. WTP C is approximately 8 mi from the power plant discharge location, whereas WTP B is about 20 mi from the source. After the wet scrubber installation (shown by the red line in part A of Figure 9), the speciation changed and the concentrations increased. Bromide monitoring data are also shown in part A of Figure 9. WTP C has experienced three quarters of THM violations. All of these violations—one in 2009 and two in 2011—occurred after the wet scrubber installation in 2008. During the quarter before the scrubber installation, the plant's average TTHM concentration was composed almost entirely of chloroform (part B of Figure 9). During the quarters with violations, > 90% of the TTHMs consisted of brominated compounds. In response to the violations, the utility initiated a flushing program in its distribution system and has installed an aeration system to remove DBPs.

**WTP D.** WTP D is also located downstream from a wet scrubber power plant's discharge location. The upstream power plant installed two wet scrubbers, one in 2006 and one in 2007, indicated by the red lines in part A of Figure 10. Although the change was not as dramatic as that documented at WTP B, the majority of the THMs after the wet scrubber installations were brominated compounds. The change is more easily observed in part B of Figure 10, which shows that brominated species made up < 20% of TTHMs before 2006, when the first wet scrubber was installed, and > 50% after 2007, when the second wet scrubber was installed.

Changes in TTHM speciation are often measured by a bromide incorporation factor (BIF), which is the ratio of THM-associated bromine to TTHMs on a molar basis (McGuire et al, 2002). When BIF = 0, only chloroform is formed, and at the high end, when BIF = 3, only bromoform is formed. Figure 11

**TABLE 2** Water treatment plants affected by bromide sources

Water Treatment Plant	Bromide Source	Population Served	Wet Scrubber Installation year	TTHM Violation year	HAA5 Violation year
A	Power plant	227,000	2006, 2007, 2009		
B	Power plant	16,000	2008		
C	Power plant	3,000	2008	2008, 2009	
D	Power plant	24,000	2006, 2007		2003
E	Shale gas wastewater discharge	22,000		2008, 2009	
F	Textile mill	18,000		2012	

HAA5—five of the haloacetic acids, TTHM—total trihalomethane

shows the BIF for the data discussed for water plants B, C, and D. At these three locations, the BIF increased after the wet scrubber installations. The DBPs not only shifted to more brominated species but, as shown by the bar heights, the mass of DBPs also increased.

As discussed earlier, some of the increase would be due to the difference in the molecular weight of bromide compared with that of chloride; substitution causes a higher concentration of DBPs on a mass basis. Some of the increase could also be due to the more reactive properties of bromide, with the precursor materials causing more DBP formation. Data from the three utilities were analyzed to assess these two factors. The results are reported as an increase in the median DBP concentration prior to and after the scrubber

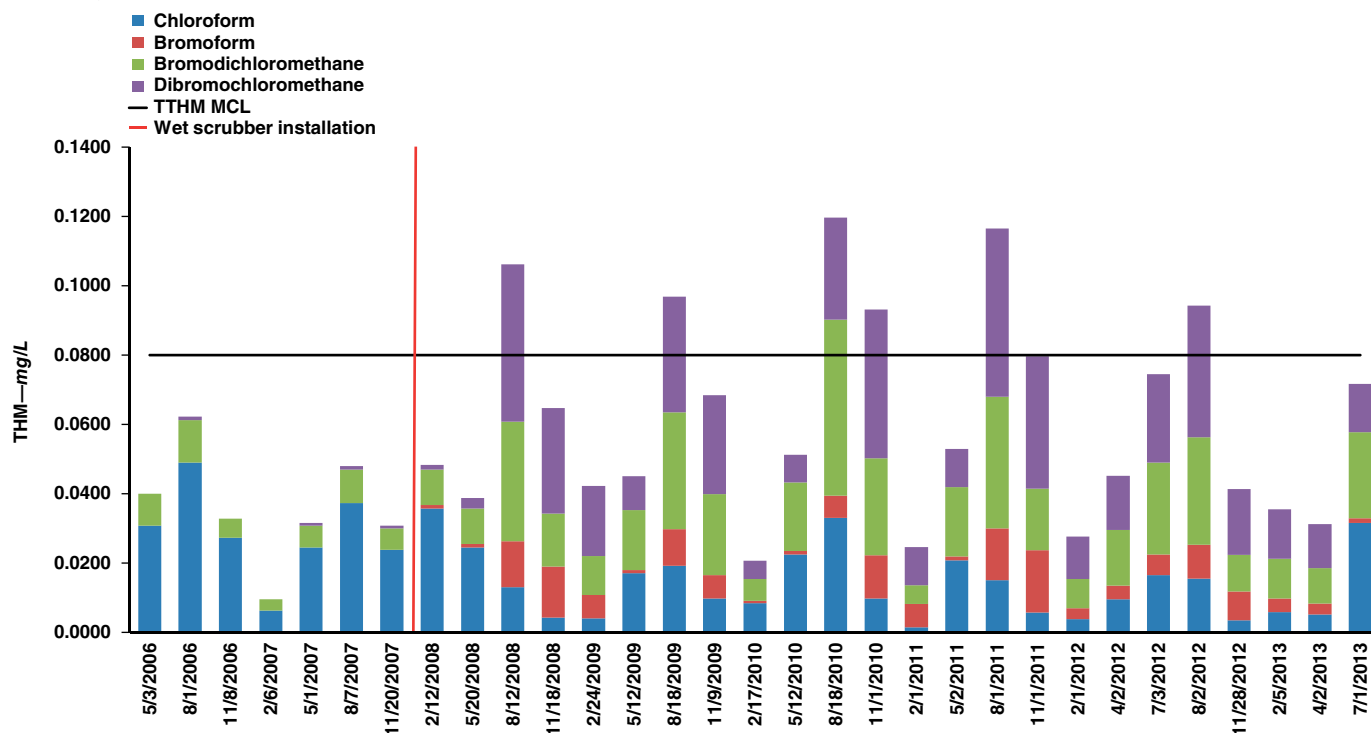
installation. At WTP B, 43% of the mass increase in DBPs was due to bromide substitution, and 57% was due to an actual increase in DBP formation. At WTP C, 70% of the mass increase was due to bromide substitution, and 30% was due to increased DBP formation. At WTP D, 30% of the mass increase was caused by bromide substitution, and 70% was caused by increased DBP formation. Therefore, both factors play a role in increasing DBP formation when source water bromide concentrations rise.

## UTILITY EFFECTS FROM DISCHARGES BY OTHER INDUSTRIES

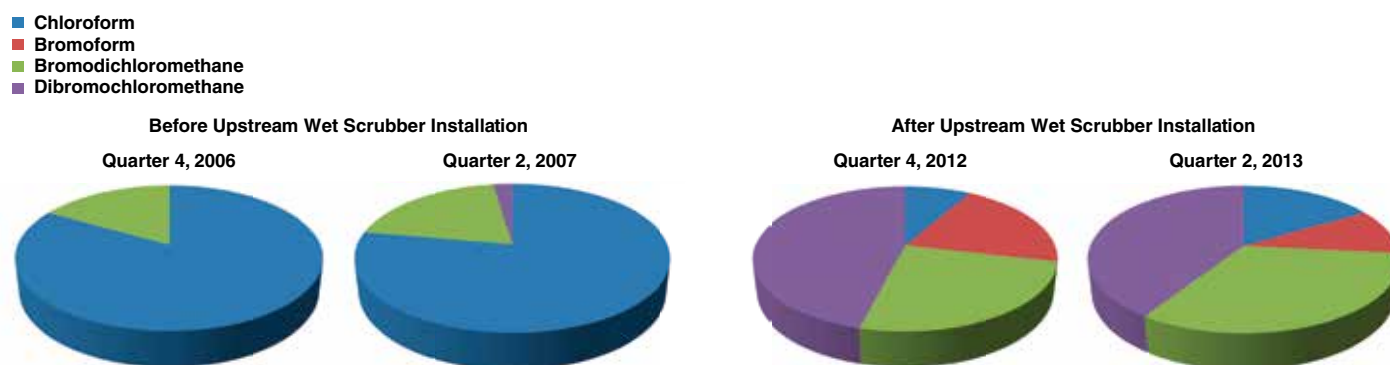
Other potential sources of bromide such as hydraulic fracturing and textile production have been reported. Wilson and VanBriesen (2012) reported bromide concentrations in excess of 500 µg/L during

**FIGURE 8** THM data from water treatment plant B

**A** Average quarterly TTHM concentrations at water treatment plant B from quarter 2 of 2006 to quarter 3 of 2013



**B** THM speciation at water treatment plant B for the same quarters preceding and following 2008, the year the upstream wet scrubber was installed



MCL—maximum contaminant level, THM—trihalomethane, TTHM—total trihalomethane

periods of low stream flow on the Allegheny River in 2008 and 2009. The authors correlated these increases with increased DBP violations. Between 2008 and 2011, 33 Western Pennsylvania drinking water systems exceeded THM MCLs (Frazier & Murray, 2011).

States et al (2012) reported that during 2010, seven WTPs using the Allegheny River as a source had effluent TTHM concentrations of 19–110 µg/L, with 12–55% composed of bromoform.

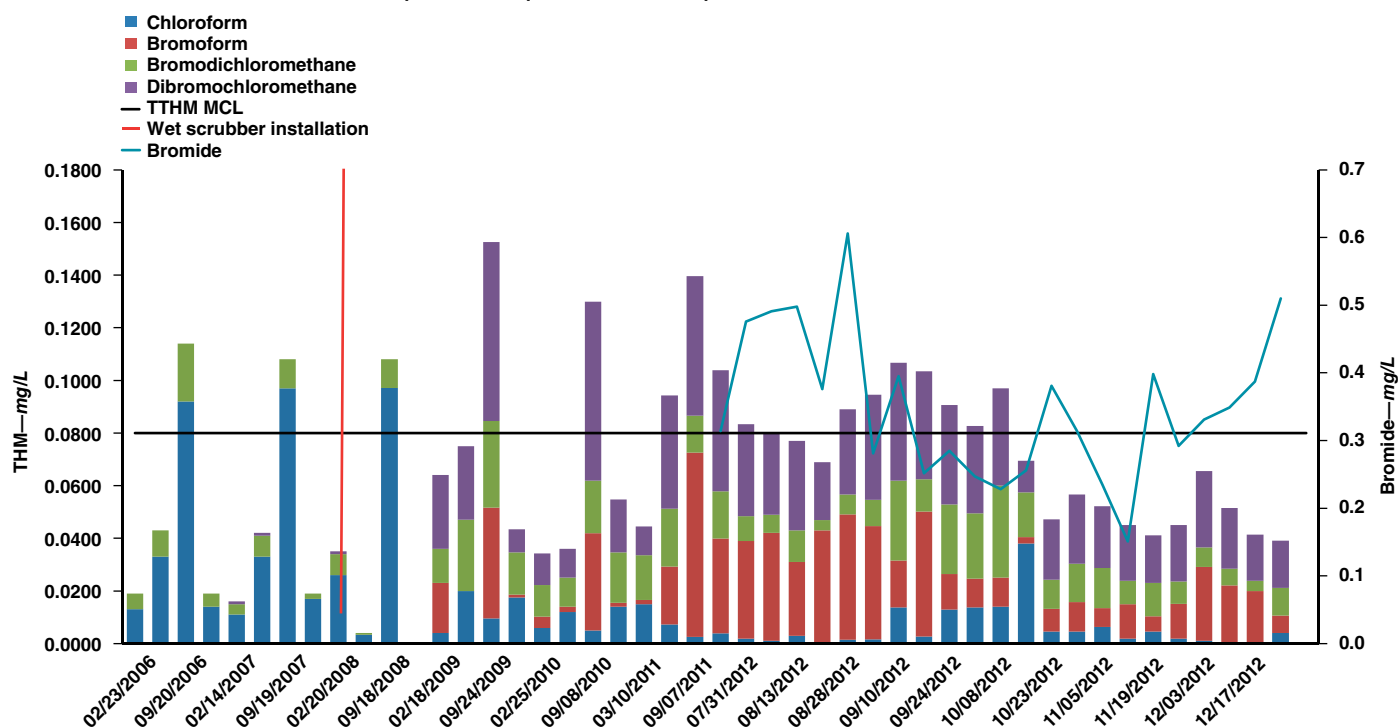
**WTP E.** WTP E was initially identified through use of the databases of coal-fired power plants and surface WTPs. Utility personnel contacted believe that hydraulic fracturing was the main cause of WTP E's increased bromide and subsequent TTHM concentrations. Since 2008, WTP E's source water has contained high TDS concentrations, so the utility has added groundwater

from backup wells for dilution. Utility personnel stated that these increases occurred around the time that hydraulic fracturing began nearby, and they believe fracturing has caused these changes. Nearby WTPs have also violated the TTHM MCL since 2008. Another city that received its water supply from WTP E exceeded the TTHM MCL in May 2013.

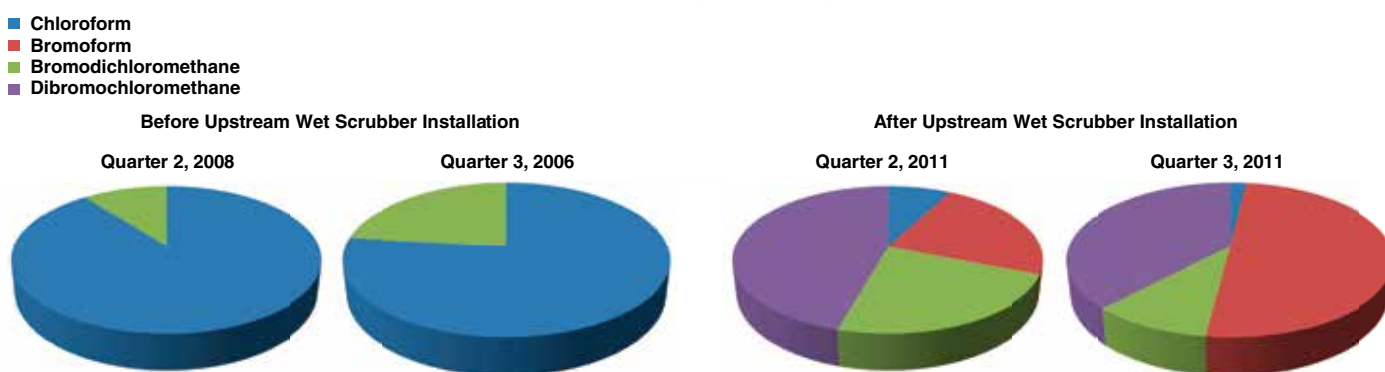
Average quarterly TTHM speciation at all WTP E sampling locations from 1999 to 2013 is shown in part A of Figure 12. According to utility staff, discharges of hydraulic fracturing wastewater in the area started in 2008. It is clear that the chlorinated portion (blue) of the utility's TTHMs decreased after 2008 and that the brominated portion (all other colors) increased. This comparison is better shown in part B of Figure 12, in which

**FIGURE 9** THM data from water treatment plant C

**A** TTHM concentrations at water treatment plant C from quarter 1 of 2006 to quarter 4 of 2012



**B** THM speciation at water treatment plant C for the same quarters preceding and following 2008, the year the upstream wet scrubber was installed



MCL—maximum contaminant level, THM—trihalomethane, TTHM—total trihalomethane

the first column represents samples collected before the effects of hydraulic fracturing and the second column represents samples collected after these effects. Before hydraulic fracturing discharges, brominated compounds made up 50% or less of WTP E's TTHMs; after these discharges, they made up > 80%.

**WTP F.** WTP F was identified through contacts made during the project. In August 2012, WTP F had a THM violation that resulted in the utility calling its state primacy agency. The state worked with two point sources, both textile mills located about 100 mi upstream, where bromide was discharged from a chemical manufacturing process. This effect was initially noticed by WTP F's water treatment personnel during the fourth quarter of 2011, which is consistent with the rise in TTHMs above the MCL in the third quarter of 2011, shown in part A of Figure 13. In addition, the speciation depicted in part B of Figure 13

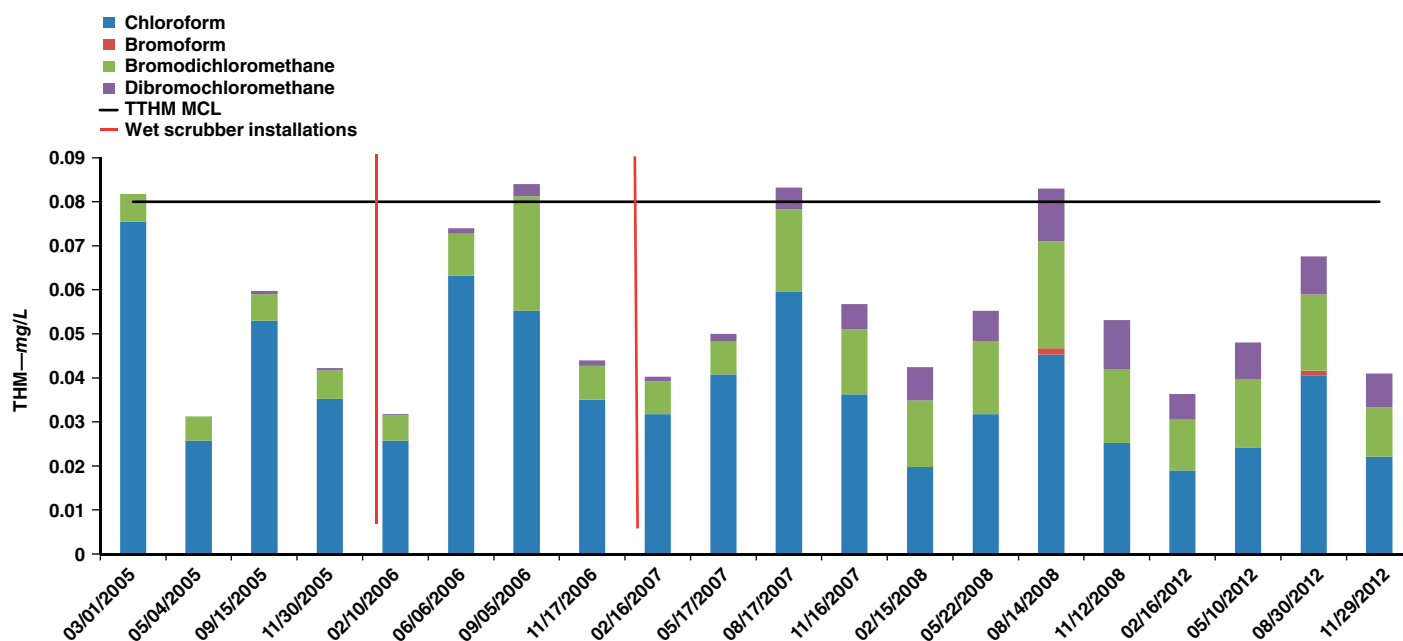
shows a shift from 30% to 80% brominated THMs before and after the textile mill effect, respectively. In response to the elevated bromide concentrations, WTP F changed its treatment process, increasing the permanganate dosage in its reservoir, moving its powdered activated carbon feed to allow for longer contact time, decreasing the chlorine dosage used in prechlorination, and decreasing the chlorine dosage in the distribution system. The state also worked with the textile mills to reduce their discharges.

### POSSIBLE WAYS TO LIMIT BROMIDE IN SOURCE WATER

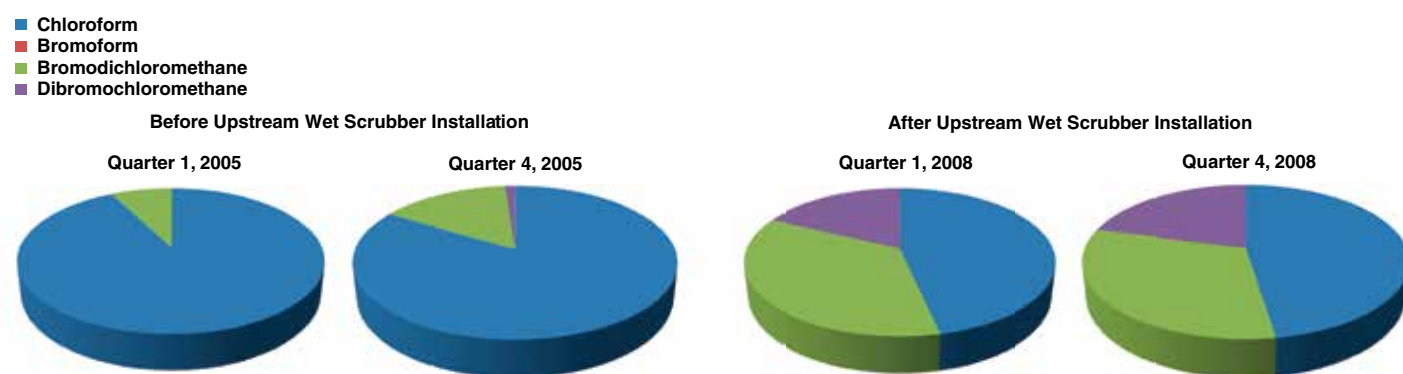
In order to limit the discharge of toxics to a receiving body of water, states must develop water quality standards, as mandated by the Clean Water Act (CWA). Water quality standards, which are provisions of state or federal law, consist of a designated use

**FIGURE 10** THM data from water treatment plant D

**A** Average quarterly TTHM concentrations at water treatment plant D from quarter 2 of 2005 to quarter 4 of 2012



**B** THM speciation at water treatment plant D for the same quarters preceding and following 2006 and 2007, when the upstream wet scrubbers were installed



MCL—maximum contaminant level, THM—trihalomethane, TTHM—total trihalomethane



or uses for the receiving water and water quality criteria for such water on the basis of the designated uses.

The USEPA website—[water.epa.gov/scitech/swguidance/standards/wqsregs.cfm](http://water.epa.gov/scitech/swguidance/standards/wqsregs.cfm)—describes the methods states can use to develop these standards.

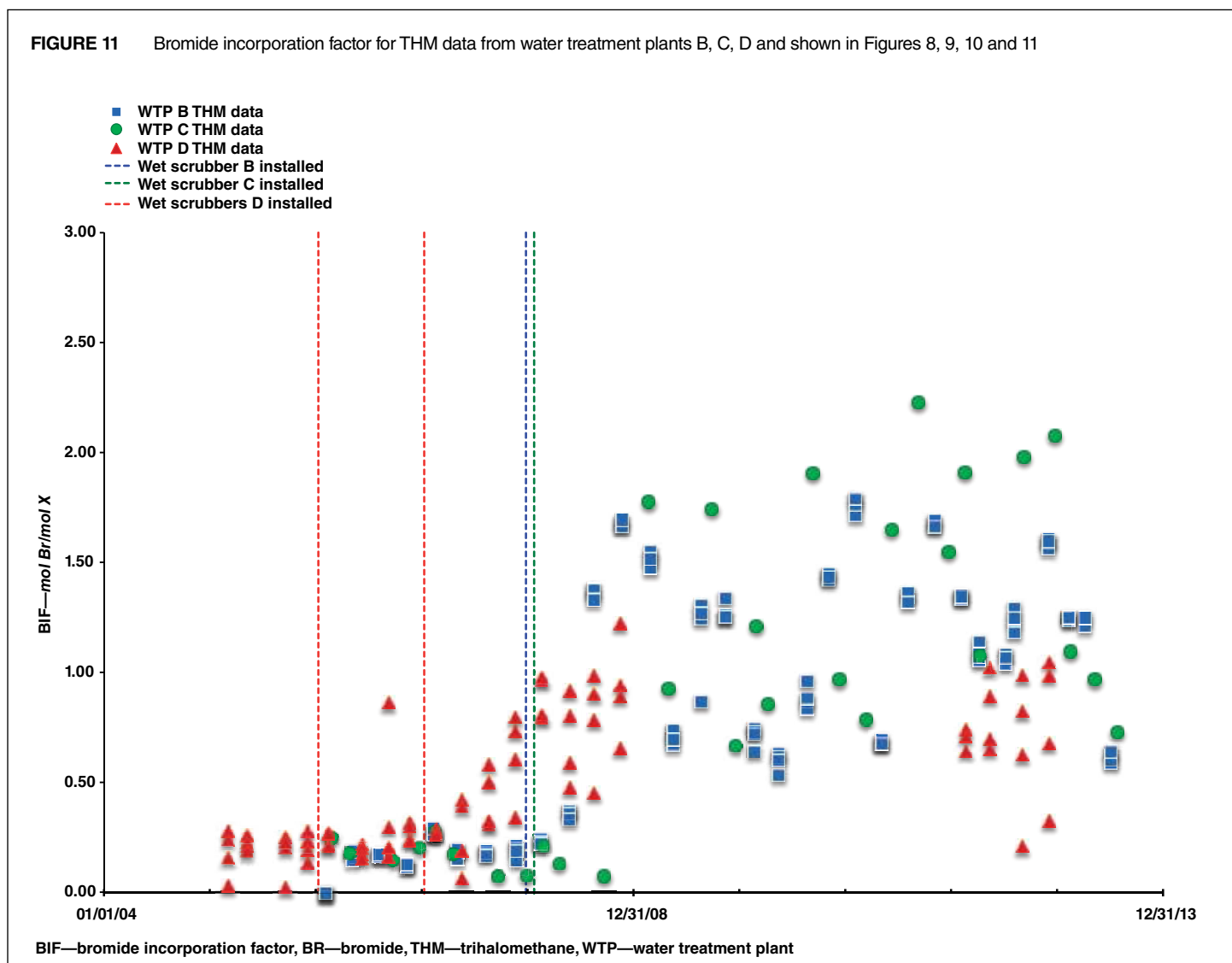
As discussed previously, some states have attempted to limit the discharge of bromide through NPDES permits. Water quality standards can be narrative in nature, and permit writers can establish permit limits for protecting designated uses. But because bromide has not been defined as a “toxic pollutant,” according to the list contained in the CWA (section 307.a), or as a “pollutant,” including bromide limits in discharge permits has been difficult. Nevertheless, because the CWA was designed to “protect the designated use,” states may be able to develop a water quality standard for bromide that recognizes that the transformation of bromide within drinking WTPs into by-products with human health implications justifies limiting its discharge into a receiving body of water.

Although some states are not able to get restrictions on effluent bromide concentrations, some have been able to require monitoring

as part of a power plant’s NPDES permits. For example, a power plant in North Carolina that installed a wet scrubber in 2008 is required by its NPDES permit to take monthly grab samples that are analyzed for bromide. The permit also requires the plant to submit a semiannual status report on its effort to reduce bromide at the source of downstream WTPs. In the event of a TTHM MCL violation at either of two named WTPs located downstream or by any wholesale customer, the power plant is required within 14 days of the request to provide the latest available bromide monitoring data for incorporation into required public notices issued by the WTP(s).

## CONCLUSIONS

With new bromide sources being introduced into drinking water sources, it is important that downstream effects be considered. Water utilities need to be made aware of the potential effect of bromide on their distribution system TTHMs and HAAs. This article highlighted a number of instances in which utilities exceeded MCLs because of a shift to brominated DBP species. However, it is suspected that many utilities have experienced elevated DBP concentrations without exceeding MCLs but are unaware of the cause of this change.



Furthermore, state agencies should closely evaluate the discharge permits of industries, such as coal-fired plants, that use bromide in their processes and determine whether monitoring and bromide limits are appropriate. Because it is so difficult for water treatment plants to remove bromide from their sources of supply, the best course of action will be to prevent bromide from entering the influent of any drinking water plant.

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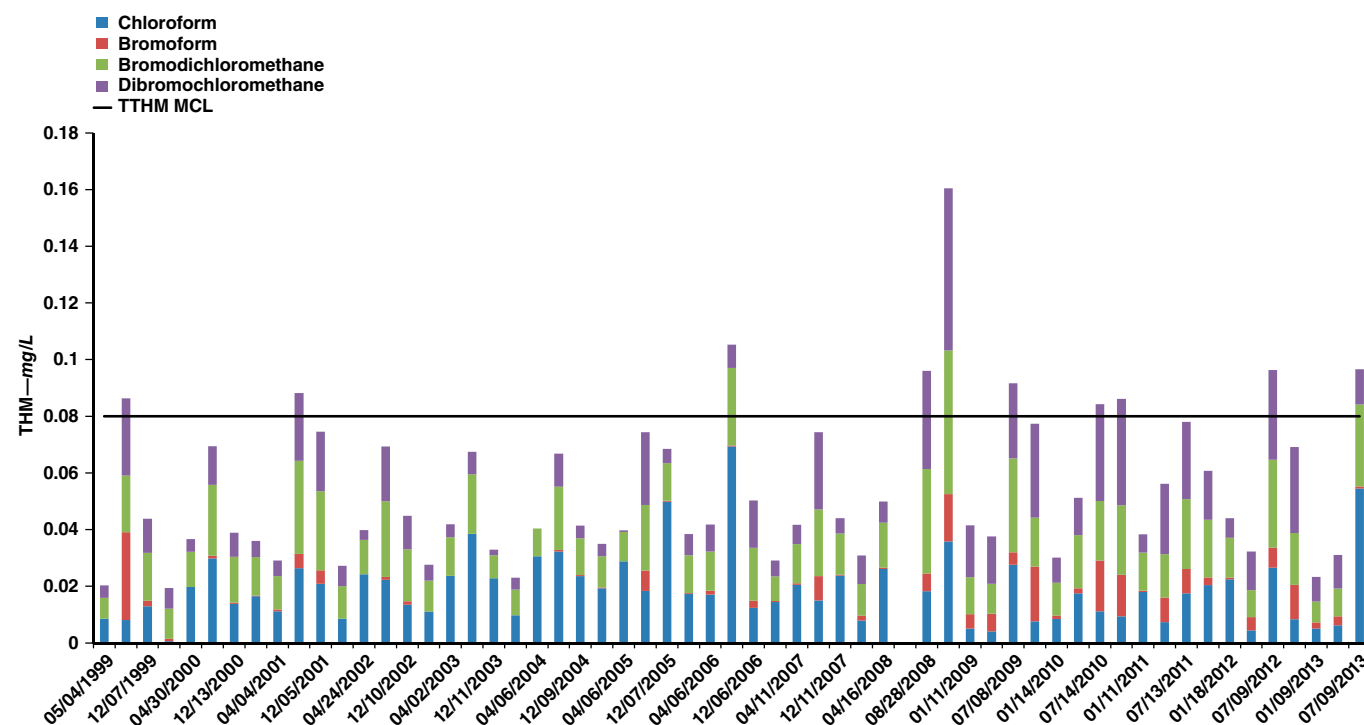
## ABOUT THE AUTHORS



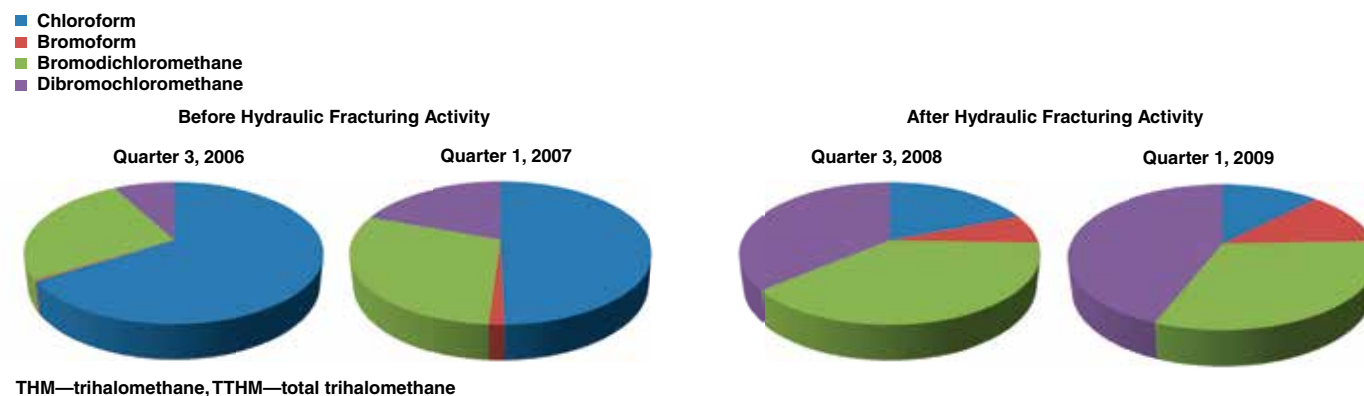
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**FIGURE 12** THM data from water treatment plant E

### A Average quarterly TTHM concentrations at water treatment plant E from quarter 2 of 1999 to quarter 3 of 2013

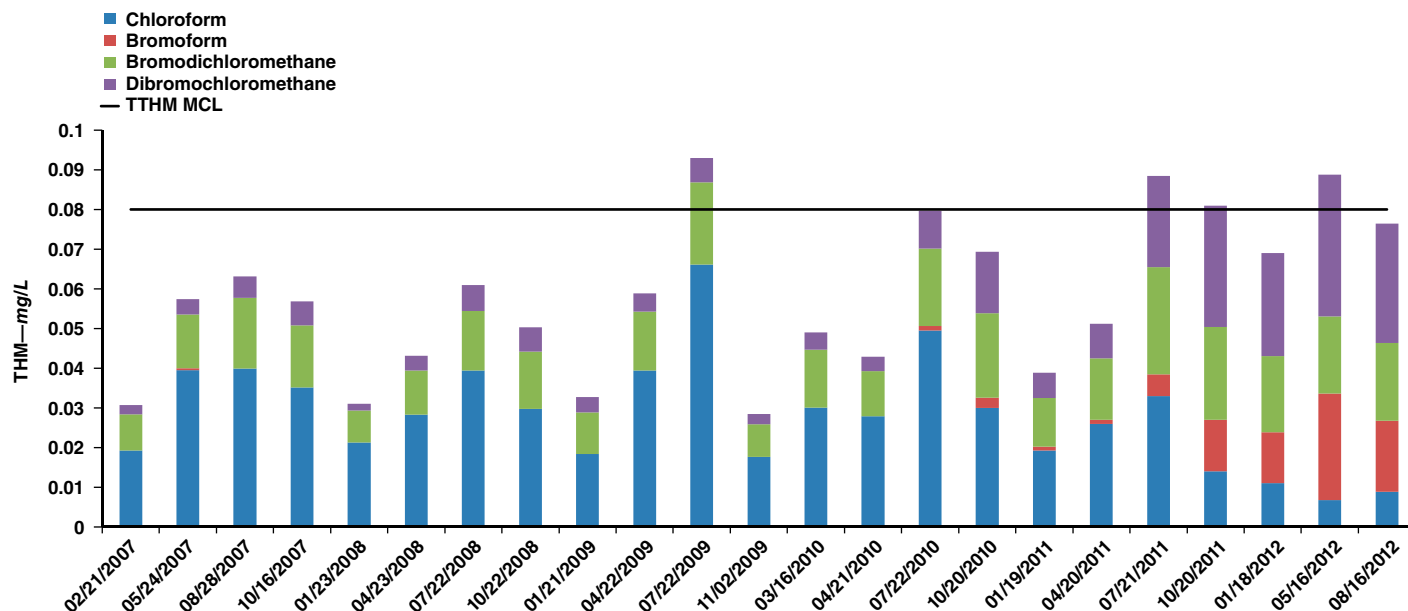


### B THM speciation at water treatment plant E for the same quarters preceding and following the onset of hydraulic fracturing activity

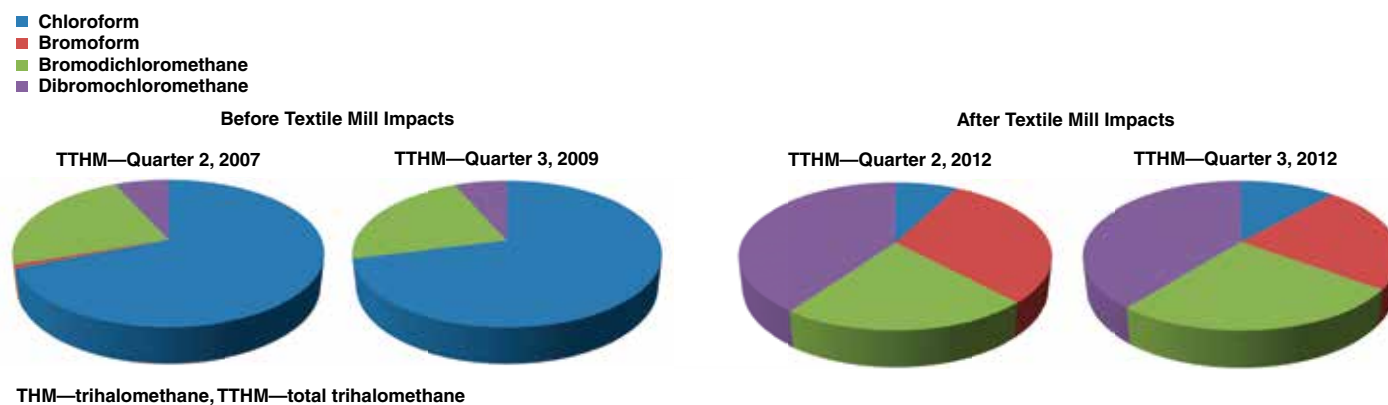


**FIGURE 13** THM data from water treatment plant F

**A** Average quarterly TTHM concentrations at water treatment plant E from quarter 2 of 1999 to quarter 3 of 2013



**B** THM speciation at water treatment plant F for the same quarters preceding and following 2006 and 2007, when the upstream wet scrubbers were installed



president of EE&T, and Katherine Graf is an engineer at EE&T, both in the Newport News office. Richard Brown is manager of water treatment at EE&T's office in Long Beach, Calif.

**FOOTNOTE**

<sup>1</sup>ArcMap, Esri, Redlands, Calif.

**PEER REVIEW**

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