



Discharges of produced waters from oil and gas extraction via wastewater treatment plants are sources of disinfection by-products to receiving streams



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HIGHLIGHTS

- CWTs can discharge dibromochloronitromethane (DBCNM) at concentrations in the $\mu\text{g L}^{-1}$ range.
- CWTs can have high levels of DBP precursors (bromide and phenols at $\mu\text{g L}^{-1}$ concentrations).
- POTWs that accept produced waters have elevated levels of brominated and iodinated DBPs.

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ABSTRACT

Fluids co-produced with oil and gas production (produced waters) are often brines that contain elevated concentrations of bromide. Bromide is an important precursor of several toxic disinfection by-products (DBPs) and the treatment of produced water may lead to more brominated DBPs. To determine if wastewater treatment plants that accept produced waters discharge greater amounts of brominated DBPs, water samples were collected in Pennsylvania from four sites along a large river including an upstream site, a site below a publicly owned wastewater treatment plant (POTW) outfall (does not accept produced water), a site below an oil and gas commercial wastewater treatment plant (CWT) outfall, and downstream of the POTW and CWT. Of 29 DBPs analyzed, the site at the POTW outfall had the highest number detected (six) ranging in concentration from 0.01 to 0.09 $\mu\text{g L}^{-1}$ with a similar mixture of DBPs that have been detected at POTW outfalls elsewhere in the United States. The DBP profile at the CWT outfall was much different, although only two DBPs, dibromochloronitromethane (DBCNM) and chloroform, were detected, DBCNM was found at relatively high concentrations (up to 8.5 $\mu\text{g L}^{-1}$). The water at the CWT outfall also had a mixture of inorganic and organic precursors including elevated concentrations of bromide (75 mg L^{-1}) and other organic DBP precursors (phenol at 15 $\mu\text{g L}^{-1}$). To corroborate these DBP results, samples were collected in Pennsylvania from additional POTW and CWT outfalls that accept produced waters. The additional CWT also had high concentrations of DBCNM (3.1 $\mu\text{g L}^{-1}$) while the POTWs that accept produced waters had elevated numbers (up to 15) and concentrations of DBPs, especially brominated and iodinated THMs (up to 12 $\mu\text{g L}^{-1}$ total THM concentration). Therefore, produced water brines that have been disinfected are potential sources of DBPs along with DBP precursors to streams wherever these wastewaters are discharged.

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1. Introduction

Water disinfection is critical for maintaining public health. The disinfection, especially chlorination, of drinking water has played the largest role in reducing the number of waterborne disease outbreaks (USEPA,

2000). In addition, chemical disinfection of municipal wastewaters also minimizes pathogen risk in receiving water bodies. However, disinfection can also create disinfection by-products (DBPs) that are undesirable and have adverse effects on human health (Richardson et al., 2007). Understandably most DBP research has focused on drinking water, however these compounds are also formed when water other than drinking water is disinfected; these ancillary water sources include a variety of wastewaters from municipal, animal agriculture, and energy extraction sources, as well as public baths and swimming pools. Additionally these other sources (besides drinking water) of DBPs could

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enter the environment where they could have deleterious effects on aquatic organisms, but their toxicity in these settings is understudied.

The mixtures and types of DBPs formed from these various sources can be quite different in chemical composition from those found in drinking water due to a range of different precursors, residual disinfectant levels, and other operational factors. Krasner et al. (2009) showed a range of DBPs including trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloacetaldehydes and *N*-nitrosodimethylamine (NDMA) in wastewater effluent sources across the United States and documented the potential risk to water quality of downstream potable water supplies. In particular, bromine incorporation was consistently documented due to the relatively high levels of bromide found in treated wastewater effluents. Bromine incorporation is of particular importance because brominated-DBPs (Br-DBPs) are among the more toxic DBPs (Richardson et al., 2007). Although some of the DBPs documented in wastewater effluent are regulated in finished drinking water (bromo-chloro THMs and HAAs; USEPA, 2013), others are not and are therefore analyzed less frequently even though they may have a greater toxicity (Richardson et al., 2007).

“Produced water” is water that is a by-product of the extraction of oil and gas from the ground; wastewater effluents associated with produced water from both conventional and unconventional oil and gas extraction activities in Pennsylvania can be a source of high bromide concentrations because their origin is from highly evaporated paleoseawater (Dresel and Rose, 2010; Ferrar et al., 2013; Wilson and VanBriesen, 2012) and are often referred to as brines. Recognizing the potential for high bromide concentrations in waters associated with oil and gas extraction (specifically hydraulic fracturing) to impact sources of raw drinking water, the United States Environmental Protection Agency (USEPA) has identified Br-DBPs in future drinking water research needs (USEPA, 2011a). These Br-DBPs may not only be formed in drinking water that has source water influenced by oil and gas production brines but can also be formed when the produced water is disposed of at a wastewater treatment facility; these include publicly owned wastewater treatment plants (POTWs) and oil and gas commercial wastewater treatment plants (CWTs; these can accept other industrial waste) (Wilson and VanBriesen, 2012).

While over 90% of the water produced during oil and gas operations (produced water) is managed through underground injection practices (water flooding or disposal in underground injection control wells), in some regions produced fluids are discharged to surface water, stored in surface impoundments, reused for irrigation, spread on roads, or reused for hydraulic fracturing (ANL, 2009; Wilson and VanBriesen, 2012). Typically brines are not disinfected at the CWT before discharge to surface waters (CWT discharges do need to meet total dissolved solid limits) but they can be treated at other points in their lifecycle; in some instances produced waters are disinfected or mixed with disinfected waters before arrival at the CWT (Bergdale, 2013) which could lead to the formation of DBPs. In other cases the produced water may be sent to a POTW where it can undergo disinfection, including chlorination (Ferrar et al., 2013; Krasner et al., 2008). Because of the unique chemical composition of inorganic and organic precursors in produced water brines there could be many different types/kinds of DBPs formed than those typically measured in treated drinking water or wastewater.

This study was designed to determine if treated produced water brines can be a source of DBPs, especially Br-DBPs, to the environment (and not just a human health/drinking water risk). Further, the study characterizes DBPs formed in several POTWs (including those that do and do not accept produced waters) and CWTs for comparison and to identify DBPs that may be unique to waste streams that include treated produced waters. The target analytes are 29 DBPs (Table 1) that include THMs (four bromo/chloro species are regulated in U.S. drinking water at 80 µg L⁻¹; USEPA, 2013), halonitromethanes (HNMs) and HANs that have been shown or hypothesized to occur in disinfected waters and could be more toxic than those DBPs already regulated (Krasner et al., 2006; Richardson et al., 2007).

Table 1

List of disinfection by-products measured, their percent recovery and standard deviation along with their method detection limits in surface water.

Compound name	% Recovery (standard deviation)	Method detection limit (µg L ⁻¹)
<i>Trihalomethanes (THM)</i>		
Bromochloriodomethane	73 (8)	0.02
Bromodichloromethane	73 (2)	0.10
Bromodiodomethane	72 (4)	0.02
Bromoform (tribromomethane)	80 (5)	0.02
Chlorodiodomethane	71 (1)	0.02
Chloroform (trichloromethane)	75 (5)	0.02
Dibromochloromethane	103 (2)	0.02
Dibromodiodomethane	75 (5)	0.02
Dichlorodiodomethane	82 (3)	0.04
Triiodomethane (iodoform)	73 (6)	0.02
<i>Halonitromethanes (HNM)</i>		
Bromochloronitromethane	87 (6)	0.02
Bromodichloronitromethane ^a	71 (5)	0.02
Bromonitromethane	73 (5)	0.10
Dibromochloronitromethane ^a	73 (4)	0.10
Dibromonitromethane	74 (2)	0.02
Dichloronitromethane	74 (3)	0.10
Tribromonitromethane (bromopicrin) ^a	71 (3)	0.10
Trichloronitromethane (chloropicrin)	71 (3)	0.10
<i>Haloacetonitriles (HAN)</i>		
Bromoacetonitrile	72 (5)	0.20
Bromochloroacetonitrile	70 (3)	0.20
Bromodichloroacetonitrile ^a	76 (8)	0.04
Dibromoacetonitrile	72 (5)	0.02
Dibromochloroacetonitrile ^a	78 (6)	0.02
Dichloroacetonitrile	74 (6)	0.10
Tribromoacetonitrile ^a	73 (5)	0.02
Trichloroacetonitrile	74 (5)	0.02
<i>Haloacetaldehydes</i>		
Tribromoacetaldehyde	74 (4)	0.02
Trichloroacetaldehyde (chloral hydrate)	71 (1)	0.20
<i>Propanones</i>		
1,1,1-Trichloro-2-propanone	65 (5)	0.04

^a Notes that ammonium chloride was used as a preservative rather than ascorbic acid.

2. Methods

2.1. Field methods and site information

Sampling at Pennsylvania location 1 was along a stretch of river and included four sites: site 1, a location upstream of the treated waters; site 2, at a POTW outfall (does not accept produced water); site 3, one just below a CWT outfall (accepts produced water); and site 4, downstream of both the POTW and CWT (Fig. 1; Table 2). Additional samples were collected below another CWT outfall (accepts produced water) in Pennsylvania (location 2), below two POTW outfalls in Pennsylvania that accept produced waters (POTW-PW; Pennsylvania locations 3 and 4) and three POTW outfalls that do not accept produced waters in three other states (Colorado, Maryland, Virginia) for a comparison of DBPs detected at POTWs (Table 2). The sites in Pennsylvania that had produced water inputs were known to accept water from conventional and unconventional oil and gas production (PADEP, 2013); the amounts ranged from 8.7 to 11 ML at the POTWs and 21 to 170 ML at CWTs in 2012.

Grab water samples were collected on two different dates for the Pennsylvania location 1, one each during normal (August 20, 2012) and low flow (November 28, 2012) conditions. Stream flow information data were taken from a USGS gage approximately 0.8 km upstream of sampling sites. The daily mean discharge on August 20, 2012 was 54 cubic meters per second (cms) and the long term daily mean discharge is 59 cms for that date. This indicates near normal

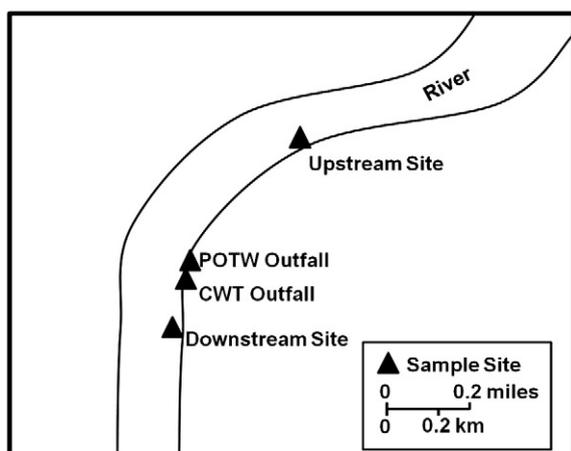


Fig. 1. Schematic showing relative distances between sampling locations for Pennsylvania location 1. Site 1, an upstream river sample; site 2, a POTW = publicly owned treatment plant that does not accept produced waters; site 3, a CWT = oil and gas commercial wastewater treatment plant and site 4, a downstream site.

flow conditions during the 2012 August sampling. The daily mean discharge on November 28, 2012 was 120 cms and the long term daily mean discharge is 240 cms for that date. This indicates lower than typical flow conditions during the November sampling. The gage height remained steady during both sampling events indicating no significant inflow or loss of streamflow on either date. The POTW and CWT outfall grab samples from additional Pennsylvania locations were collected on April, 17, 2013 (locations 2 through 4) and the samples from outside of Pennsylvania were collected between April and October, 2012 (locations 5 through 7).

2.2. Disinfection by-product analysis

Twenty nine disinfection by-products were measured in the water samples. These include both regulated (USEPA, 2013) and non-regulated DBPs.

2.2.1. Chemicals

Target analytes were purchased from either Orchid Cellmark (Westminster, British Columbia, Canada) or Sigma-Aldrich (St. Louis, Missouri, USA). Surrogates, 1-bromo-4-fluorobenzene and d_4 -1,2-dichlorobenzene, and the internal standard 1-chlorooctane were also purchased from Sigma Aldrich. DBPs were dissolved individually in acetone or methyl tert-butyl ether (MTBE) for an initial concentration of the target analyte of 1 mg mL^{-1} . Standard calibration curves were made with concentrations ranging from 0.02 to $5 \text{ ng } \mu\text{L}^{-1}$ in MTBE and stored in a freezer at $-20 \text{ }^\circ\text{C}$. All solvents and other reagents used were of ACS grade or better (Fisher Scientific, Pittsburgh, PA).

Table 2

Description of areas and sites sampled for disinfection by-products. Sites included wastewater treatment plant outfalls that were publicly owned wastewater treatment plants (POTWs) and oil and gas commercial wastewater treatment plants (CWTs). Some of the POTWs accepted produced waters while others did not.

Area	Sites	Type	Accepts produced water
Pennsylvania location 1	1	Upstream river sample	–
	2	POTW outfall	No
	3	CWT outfall	Yes
	4	Downstream river sample	–
Pennsylvania location 2	1	CWT outfall	Yes
Pennsylvania location 3	1	POTW outfall	Yes
Pennsylvania location 4	1	POTW outfall	Yes
Virginia location 5	1	POTW outfall	No
Maryland location 6	1	POTW outfall	No
Colorado location 7	1	POTW outfall	No

2.2.2. Water collection and preservation

For each sample 2 1-L bottles of water were collected as a grab sample; for the WWTP outfalls, the sample was collected in the river where the effluent entered. For sample preservation the bottle contained either 35 mg L^{-1} ascorbic acid or 100 mg L^{-1} ammonium chloride (sample adjusted to pH 3 to 4 with sulfuric acid); two preservation techniques were necessary as the trichloro HNMs and HANs were not stable with the ascorbic acid preservative and ammonium chloride was used instead (Weinberg et al., 2002 and Table 1). Samples were collected with no headspace to minimize volatilization. All water samples were filtered through a pre-baked $0.7 \text{ } \mu\text{m}$ GF/F filter (Whatman; Florham Park, NJ). Each sample was spiked with surrogates (1-bromo-4-fluorobenzene and d_4 -1,2-dichlorobenzene) prior to extraction. Samples were extracted within 48 h of collection.

2.2.3. Sample extraction

An Oasis HLB solid-phase extraction (SPE) cartridge (6 cm^3 , 500 mg; Waters Corporation, Milford, MA) was pre-cleaned with 10 mL of MTBE, 10 mL of methanol and 10 mL of water. The 1-L sample was loaded onto SPE cartridge at 5 mL min^{-1} . The cartridge was then dried under nitrogen for about 15 min. The sample was eluted with 10 mL of MTBE, the MTBE was blown down under a gentle stream of nitrogen (N-evap; Organomation Associates, Berlin, MA) to $400 \text{ } \mu\text{L}$ at which time internal standard (1-chlorooctane) was added. The final sample was placed in a vial with no headspace.

2.2.4. Instrumental analysis

Extracts were analyzed on an Agilent 7890A gas chromatograph (GC) coupled to an Agilent 5975C mass spectrometer (MS) (Santa Clara, CA). The injector was held at $90 \text{ }^\circ\text{C}$, $1 \text{ } \mu\text{L}$ injections were made in a splitless mode. The flow of He through a GC column was constant and set at 1.2 mL min^{-1} . The oven program was $33 \text{ }^\circ\text{C}$, hold for 14 min, ramp at $4 \text{ }^\circ\text{C min}^{-1}$ to $60 \text{ }^\circ\text{C}$, ramp at $10 \text{ }^\circ\text{C min}^{-1}$ to $200 \text{ }^\circ\text{C}$, and ramp at $20 \text{ }^\circ\text{C min}^{-1}$ to $300 \text{ }^\circ\text{C}$. An HP-1MS ultra inert (Agilent, Santa Clara, CA) $30 \text{ m length} \times 0.25 \text{ mm ID} \times 1 \text{ } \mu\text{m}$ phase thickness column was used. The transfer line from the GC to the MS was set at $250 \text{ }^\circ\text{C}$ and the source of the MS was set to $220 \text{ }^\circ\text{C}$. The MS was operated in electron ionization (EI) mode. Data were collected in the selected ion monitoring (SIM) mode.

2.2.5. Quality assurance/quality control

DBP concentrations were validated against a comprehensive set of quality control parameters including: laboratory and field blanks, matrix spikes, replicate samples, and surrogate recovery. No DBPs were detected in any of the blanks. Replicate samples (making up 20% of the total number of samples) were within 20% agreement for all DBPs detected above the analytical method detection limit. Matrix spikes were analyzed as part of the described method validation, with recoveries ranging from 70 to 130% (except for 1,1,1-trichloro-2-propanone where recoveries ranged from 60% to 90%). Recovery of surrogates was used to monitor the efficiency of each extraction and was greater than 70% for all samples. Method detection limits MDLs were determined according to the procedure outlined by the USEPA in 40 CFR 136, Appendix B for 1-L water samples. Following the USEPA procedure, seven replicate water samples (taken from a local surface water) were fortified with compounds at concentrations two to five times the estimated MDL (0.1 to $0.5 \text{ } \mu\text{g L}^{-1}$). The method detection limits and average recovery for each compound in water are listed in Table 1. Analytes identified at concentrations less than the MDL have lower confidence in the actual value and are reported as estimated values.

2.3. Bromide/chloride and precursor measurements

Additional analyses were performed on the collected water for the August 20, 2012 samples at the USGS National Water Quality Laboratory

Table 3
Concentrations ($\mu\text{g L}^{-1}$) of disinfection by-products detected in surface water samples in Pennsylvania from sites below wastewater treatment plant outfalls. Concentrations in parentheses are estimated (below the MDL). The wastewater treatment plants are divided into publicly owned wastewater treatment plants (POTWs) that do not accept produced waters, publicly owned wastewater treatment plants that accept produced waters (POTW-PW), and oil and gas commercial wastewater treatment plants (CWTs).

Site name	Date	Regulated trihalomethanes (THM4)				Iodinated trihalomethanes (iodo-THM)		
		Chloroform	Bromodichloro-methane	Dibromo-chloro-methane	Bromoform	Dichloriodomethane	Bromochloriodomethane	Dibromiodomethane
<i>Pennsylvania location 1</i>								
Upstream	08/20/2012	0.69	ND ^a	ND	ND	ND	ND	ND
(location 1-1)	11/28/2012	ND	ND	ND	ND	ND	ND	ND
POTW outfall	8/20/2012	0.02	0.09	0.05	0.03	ND	ND	ND
(location1-2)	11/28/2012	0.05	ND	0.05	0.04	ND	ND	ND
CWT outfall	8/20/2012	0.46	ND	ND	ND	ND	ND	ND
(location 1-3)	11/28/2012	0.26	ND	ND	ND	ND	ND	ND
Downstream	11/28/2012	0.12	ND	ND	(0.01)	ND	ND	ND
(location 1-4)								
<i>Additional Pennsylvania sites</i>								
CWT outfall (location 2-1)	4/17/2013	0.08	ND	0.10	0.63	ND	ND	ND
POTW-PW outfall (location 3-1)	4/17/2013	0.20	0.03	0.83	10.1	(0.01)	0.10	0.98
POTW-PW outfall (location 4-1)	4/17/2013	0.13	0.03	0.51	9.2	0.02	0.12	1.3

^a ND = not detected.

Table 3 (continued)

Site name	Iodinated trihalomethanes (iodo-THM)		Haloacetonitriles (HAN)			Halonitromethanes (HNMs)			
	Bromodiiodomethane	Iodoform	Dichloroacetonitrile	Bromochloroacetonitrile	Dibromoacetonitrile	Dibromonitromethane	Dibromochloronitro-methane	Tribromoacetaldehyde	1,1,1-trichloro-2-propanone
<i>Pennsylvania location 1</i>									
Upstream	ND	ND	ND	ND	ND	ND	ND	ND	ND
(location 1-1)	ND	ND	ND	ND	ND	ND	ND	ND	ND
POTW outfall	ND	ND	(0.04)	ND	ND	ND	ND	ND	(0.03)
(location1-2)	ND	ND	(0.06)	ND	ND	ND	ND	ND	0.07
CWT outfall	ND	ND	ND	ND	ND	ND	5.7	ND	ND
(location 1-3)	ND	ND	ND	ND	ND	ND	8.7	ND	ND
Downstream	ND	ND	ND	ND	ND	ND	1.2	ND	ND
(location 1-4)									
<i>Additional Pennsylvania sites</i>									
CWT outfall (location 2-1)	ND	ND	ND	ND	0.05	ND	3.1	ND	ND
POTW-PW outfall (location 3-1)	0.09	ND	ND	(0.07)	0.82	ND	0.26	0.07	ND
POTW-PW outfall (location 4-1)	0.20	0.06	(0.01)	(0.05)	0.73	0.06	0.59	1.0	ND

(NWQL) in Denver, CO. Chloride and bromide were measured via ion chromatograph (Fishman and Friedman, 1989). Wastewater indicator compounds were measured using an SPE and GC/MS method (Zaugg et al., 2002).

3. Results

3.1. DBPs detected at Pennsylvania location 1

No DBPs were detected at the most upstream sample (location 1-1; Fig. 1) at either date. In contrast, DBPs were detected in the water at the POTW outfall and CWT outfall (Table 3; Fig. 2). A greater number of DBPs were found below the POTW outfall (location 1-2); at each sampling date six DBPs were detected with concentrations ranging from 0.02 to 0.09 $\mu\text{g L}^{-1}$. At the POTW outfall the four regulated THMs were detected (chloroform, bromodichloromethane, dibromochloromethane and bromoform) along with two other DBPs. At the CWT outfall (location 1-3) two DBPs were detected, chloroform and dibromochloronitromethane (DBCNM). The concentrations of DBCNM at the CWT outfall were higher than all other sites, 5.7 and 8.5 $\mu\text{g L}^{-1}$ at the August and November sampling dates, respectively. At location 1-4 (downstream of both the POTW and CWT; Fig. 1) two THMs were detected (chloroform and bromoform) along with DBCNM (Fig. 2). The downstream concentration of DBCNM (1.2 $\mu\text{g L}^{-1}$) was lower than the brine treatment facility but still higher than any other DBP measured in at the POTW outfall; this lower concentration is due to dilution of the CWT effluent with the upstream river water (assuming there was no loss of the DBCNM, the CWT flow accounted for 14% of the river flow at the downstream site).

3.2. DBPs detected below additional Pennsylvania locations that accept produced waters

DBPs were measured at Pennsylvania locations 2 through 4; another CWT and two POTW-PWs (POTWs that accept produced waters; see Table 2 for site description). The additional CWT (location 2-1) had 5

DBPs detected, most notably 3.1 $\mu\text{g L}^{-1}$ of DBCNM (Table 3; Fig. 3). The POTW-PWs had up to 15 DBPs detected in a single sample (Table 3). The POTW-PWs (locations 3-1 and 4-1) had detections of HNMs (DBCNM and dibromonitromethane) up to 0.6 $\mu\text{g L}^{-1}$. Three HANs were detected (dichloroacetonitrile, bromochloroacetonitrile and dibromoacetonitrile) with dibromoacetonitrile detected at the highest concentration (0.8 $\mu\text{g L}^{-1}$). Both regulated and unregulated THMs were detected; from the bromo/chloro regulated THMs (chloroform, bromodichloromethane, dibromochloromethane, bromoform) the more brominated compounds dominated with concentrations of bromoform up to 10 $\mu\text{g L}^{-1}$. The iodinated THMs were also detected; a total of five were detected with the highest concentration of 1.3 $\mu\text{g L}^{-1}$ for dibromiodomethane (Table 3; Fig. 3).

3.3. DBPs detected below POTWs not accepting produced waters

DBPs were also measured at the outfall of three other POTWs (Fig. 3) that do not receive produced waters (locations 5 through 7, see Table 2 for description). Three of the four sites had total THM concentrations up to 0.25 $\mu\text{g L}^{-1}$, the Maryland outfall (location 6-1) did not have detectable concentrations of THMs. HANs were detected at all four sites; dichloroacetonitrile was the most frequently detected HAN and was found at the highest concentrations (up to 1.9 $\mu\text{g L}^{-1}$). The HNMs were detected at two of the POTW outfalls at concentrations of 0.09 to 0.18 $\mu\text{g L}^{-1}$.

3.4. Potential DBP precursors

Bromide and chloride concentrations were measured in August, 2012 at Pennsylvania location 1; sites 1–3 (Fig. 4; Table 4). Bromide and chloride were substantially higher in the CWT outfall (75 and 8200 mg L^{-1} , respectively) than in either the upstream water (<0.03 and 14 mg L^{-1}) or at the POTW outfall (0.05 and 44 mg L^{-1}). Two additional organics, phenol and p-cresol were at higher concentrations in the brine effluent (15 and 4.9 $\mu\text{g L}^{-1}$, respectively; Fig. 4 and Table 4) than the upstream samples (<0.72 $\mu\text{g L}^{-1}$).

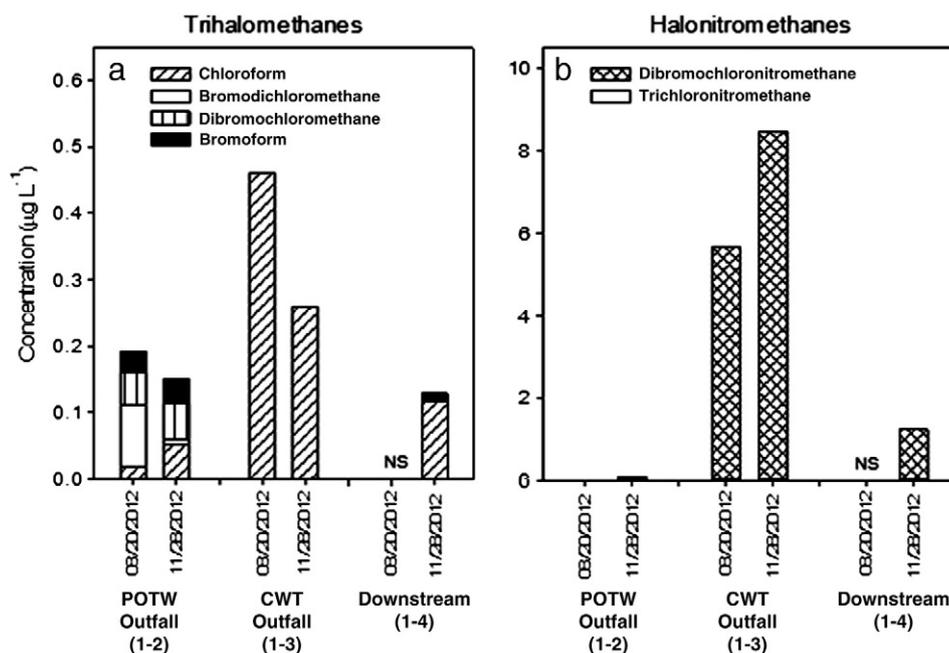


Fig. 2. Concentrations of disinfection by-products at Pennsylvania location 1: (a) trihalomethanes and (b) halonitromethanes measured at two sampling dates (mm/dd/yyyy) in 2012 from a publicly owned treatment plant (POTW) outfall (location 1-2), an oil and gas commercial wastewater treatment plant (CWT) outfall (location 1-3), and a downstream site where mixing has occurred (location 1-4). Note that no DBPs were detected at an upstream site (location 1-1) on either sampling date. NS = not sampled.

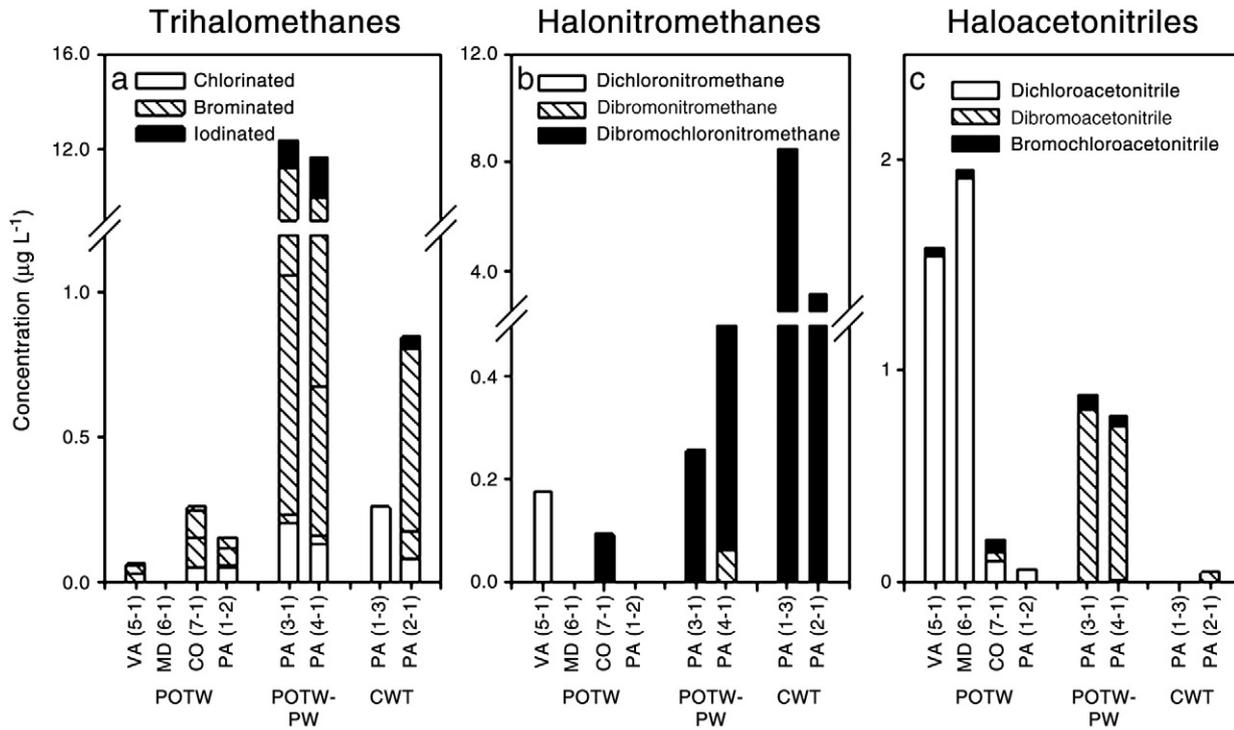


Fig. 3. Comparison of concentrations of: (a) trihalomethanes (divided into those species that are just chlorinate, those that are brominated (also include bromo–chloro compounds) and those that are iodinated (also includes iodo–bromo and iodo–chloro species)), (b) halonitromethanes and (c) haloacetonitriles detected below wastewater treatment plant outfalls. The wastewater treatment plants are divided into publicly owned wastewater treatment plants (POTWs) that do not accept produced waters, publicly owned wastewater treatment plants that accept produced waters (POTW-PW), and oil and gas commercial wastewater treatment plants (CWTs). Their locations, corresponding to Table 2 are in parentheses.

4. Discussion

4.1. Sources of CWT water at Pennsylvania location 1

Molar Cl/Br ratios are extremely useful in the sourcing of waters, particularly brines (Davis et al., 1998). Because bromide preferentially stays in solution when halite forms, brines derived from the dissolution

of halite are bromide poor (Cl/Br > 750), while those consisting of evaporated paleoseawater are bromide rich (Cl/Br < 500). The stream sample collected from location 1-1 (upstream from both POTW and CWT) exhibits a Cl/Br ratio of > 3130, with which a chloride concentration of 14 mg L^{-1} is consistent with a mixture of in-land precipitation with a bromide poor source, such as road salt (Davis et al., 1998). A similarly high Cl/Br ratio of 1980 at location 1-2 (POTW outfall) and a slightly

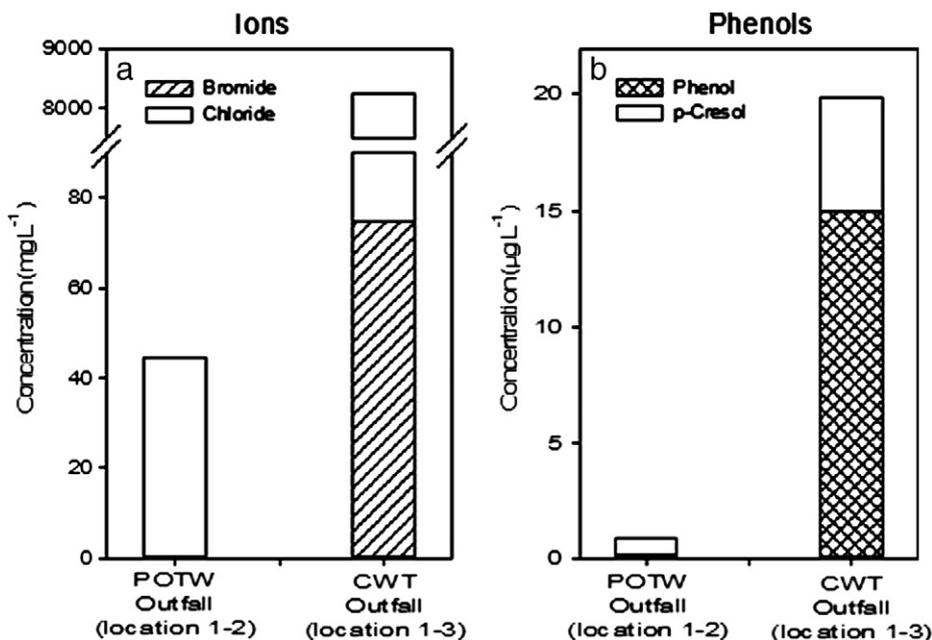


Fig. 4. Concentrations of (a) bromide and chloride ions and (b) two phenols detected below outfalls to a publicly owned wastewater treatment plant (POTW) that does not accept produced waters and an oil and gas commercial wastewater treatment plant (CWT) at Pennsylvania location 1 (August 2012).

higher chloride concentration of 44 mg L^{-1} also suggest a local meteoric source with some possibility of extra chloride from chlorination during water treatment. The sample from location 3-1 (the CWT outfall) contains much more chloride (8200 mg L^{-1}) and a low Cl/Br ratio (250), consistent with being derived from evaporated paleoseawater. For comparison, waters from oil wells produced from the same county as the CWT for this study, exhibit an average molar Cl/Br ratio of 190 ($n = 6$) and chloride concentrations range from 5800 to $68,000 \text{ mg L}^{-1}$ (Dresel and Rose, 2010). These overlaps of Cl/Br molar ratios and chloride concentrations for samples from CWT outfall and of nearby hydrocarbon associated brines indicate, in addition to increased phenol concentrations which are associated with produced water brines (Table 4; ANL, 2004), that the CWT effluent contains an oil and gas production component.

4.2. DBPs in CWT discharges

While few DBPs were below the CWT outfalls (locations 1-3 and 2-1), BDCNM was detected at relatively high concentrations (~ 3 to $9 \mu\text{g L}^{-1}$). These compounds were not coming from upstream as the upstream samples (locations 1-1 and 1-2) had different DBP signatures (Fig. 2). The POTW outfall (location 1-2) contained all four bromo-chloro THMs, which is typical of treated municipal wastewater (Krasner et al., 2009). The CWT sample (location 1-3) had relatively high concentrations of BDCNM (up to $8.5 \mu\text{g L}^{-1}$) and no other DBPs detected besides chloroform; the detection of BDCNM did not seem to be largely influenced by season or flow conditions (summer normal flow versus fall low flow; Table 3) but temporal variation cannot be determined by this dataset. Other researchers have found trihalogenated HNMs could form in POTW effluent (Song et al., 2010) or in drinking water (Hu et al., 2010); those waters that underwent a combination of ozonation and chlorination had the highest concentrations of HNMs, up to $23 \mu\text{g L}^{-1}$ (Song et al., 2010). While the CWT waters in these studies do not have a known treatment scheme, they likely could have undergone chlorination (such as to prevent sulfate reduction from occurring in storage ponds) and thus the brine effluent may create unique DBP signatures. The formation of HNMs does not follow the pattern of THMs (Hu et al., 2010) suggesting different precursors and reaction mechanisms than those typically studied for DBPs.

BDCNM has been found at concentrations as high as $3 \mu\text{g L}^{-1}$ in finished drinking water when source water concentrations of bromide were $150\text{--}330 \mu\text{g L}^{-1}$ (Bond et al., 2011; Krasner et al., 2006). The CWT samples collected from Pennsylvania location 1-3 had bromide concentrations of $75,000 \mu\text{g L}^{-1}$ (over 200 times that of the drinking water studies). Bromine incorporation has been documented where there are relatively high levels of bromide found in the water being treated (Hu et al., 2010; Krasner et al., 2009; Shan et al., 2012; Shi et al., 2013) so Br-DBPs would be expected in these treated produced water brines. Additionally these waters may form high levels of BDCNM upon further treatment.

BDCNM has been shown to be genotoxic while HNMs as a class are mutagenic in *Salmonella* assays and potent genotoxicants in mammalian cells (Kundu et al., 2004; Plewa et al., 2004; Richardson et al., 2007). While HNMs are seen as mutagenic and genotoxic, chronic

toxicity levels have not been determined that would adversely affect either human health or aquatic organisms. The environmental fate of BDCNM is unknown, the downstream sample shows it persists $\sim 0.2 \text{ km}$ after discharge (which includes mixing; Fig. 2). Modeling work on the persistence of DBPs indicates that BDCNM is less volatile than the other DBPs and will probably not sorb or settle out downstream (Jin et al., 2012).

4.3. DBP precursors at Pennsylvania location 1

Previous studies have shown that organic compounds found in oil and gas such as benzene, ethyl benzene, toluene, and phenol typically occur in produced waters from oil and gas production (Benko and Drewes, 2008; Breit and Otton, 2002; Ferrar et al., 2013). The total oil content of produced waters can range from 40 mg L^{-1} to 2000 mg L^{-1} (Benko and Drewes, 2008), indicating the organic compounds in these waters vary in concentration and composition. The water sample collected from at the CWT outfall (location 1-3) for the current study was much higher in phenolic compounds as compared to the upstream sample (location 1-1) and POTW outfall (location 1-2) (Fig. 4). Prior research has shown phenols can undergo nitration with different disinfectants in the presence of nitrate (Choi and Richardson, 2004; Thibaud et al., 1987) to produce HNMs. Chlorination of amino acids, in the presence of nitrite and bromide, can increase trihalogenated HNM occurrence (Shan et al., 2012) such as BDCNM. The nitrogen component of the produced water brine is unknown; compounds such as nitrates can be associated with produced waters (USEPA, 2011a), although ammonia is a more likely component in hydrocarbon influenced waters it could be oxidized to nitrate during the produced water lifecycle. The chlorination of amino acids can also result in the formation of aldehydes and nitriles, with subsequent or concomitant chlorine substitution to form chloral hydrate (trichloroacetaldehyde) and dichloroacetonitrile, respectively (Trehy et al., 1986); these are DBPs that could preferentially form downstream.

4.4. Comparison of DBPs at POTWs that do and do not receive produced waters

POTWs were sources of HANs but not BDCNM whereas the CWTs contributed BDCNM but lower amounts of HANs (Table 3; Fig. 3). These results are similar to other studies looking POTWs; a range of DBPs including THMs and HANs were detected in POTW effluents across the United States (Krasner et al., 2009). Previous studies (Krasner et al., 2009) also detected dihalogenated HNMs at concentrations in POTW effluents, up to $0.5 \mu\text{g L}^{-1}$, but did not measure trihalogenated HNMs such as BDCNM.

POTWs that receive produced waters (POTW-PW) had a DBP signature different from both the CWTs and the POTWs that did not receive produced waters (Fig. 3). The POTW-PWs had higher concentrations of both brominated and iodinated THMs. Bromoform is the most toxic of the regulated THMs and both sites had bromoform concentrations of near $10 \mu\text{g L}^{-1}$. The highest iodinated THM concentration was about 10 times less than bromoform and while the iodinated THMs are not regulated they have been proposed to be more toxic than bromo/chloro THMs (Richardson et al., 2008). While iodide is not as well characterized as bromide in produced waters it is known to be a common constituent (Collins and Egleston, 1967; Xu et al., 2008). The POTW-PWs had total HAN concentrations that were in the range of POTWs. However, where the POTW did not accept produced waters dichloroacetonitrile dominated while POTW-PWs had dibromoacetonitrile as the dominant HAN, once again showing the likelihood of more Br-DBPs in areas that receive treated produced waters.

POTW-PWs undergo a higher level of disinfection than CWTs leading to more THMs in the outfall water. Total THM concentrations for the POTW-PWs were around $12 \mu\text{g L}^{-1}$ for all bromo-chloro-iodo species and $10 \mu\text{g L}^{-1}$ for just the bromo-chloro species. Other work

Table 4

Concentrations of two major ions and two phenols in water samples collected on Aug 20, 2012 at Pennsylvania location 1. The treatment plants are divided into publicly owned wastewater treatment plant (POTW) and oil and gas commercial wastewater treatment plant (CWT).

Site name	Bromide (mg L^{-1})	Chloride (mg L^{-1})	Phenol ($\mu\text{g L}^{-1}$)	p-Cresol ($\mu\text{g L}^{-1}$)
Upstream sample (location 1-1)	<0.02	14	0.26	0.05
POTW outfall (location 1-2)	0.05	44	0.15	0.72
CWT outfall (location 1-3)	75	8200	15	4.9

has found concentrations of the four regulated bromo–chloro species (THM4) to be near $100 \mu\text{g L}^{-1}$ after chlorination at a POTW (Krasner et al., 2009), however since individual THM concentrations were not reported (Krasner et al., 2008) the amount that the more highly brominated species (such as bromoform) contributed to these samples could not be calculated. In a sampling of treated drinking water for bromo–chloro–iodo THMs (Krasner et al., 2006), for the THM4 species bromoform typically contributed the smallest portion; this study was the opposite in the more highly brominated species found at higher concentrations and bromoform dominated the THM4 species (Table 3). In the prior drinking water studies for the iodo-THMs, dichloriodomethane has dominated (Krasner et al., 2006; Richardson et al., 2008) but in this study the dibromiodomethane (the most brominated iodo-THM) was detected at concentrations higher than the other iodo-THMs (Table 3).

The bromo–chloro THMs (THM4) have a maximum contaminant level (MCL) of $80 \mu\text{g L}^{-1}$ in drinking water (USEPA, 2013), the outfalls of POTW-PWs were below this level but these concentrations could be a baseline DBP level for downstream drinking water intakes and an indicator of more highly brominated (and iodinated), and therefore more toxic, DBPs (Richardson et al., 2007, 2008) forming after further treatment downstream. In recent years, the amount of produced water disposed of at surface discharge facilities in Pennsylvania has been reduced but in 2011 the amount of produced water sent to POTWs and CWTs was still 93 ML and 750 ML, respectively (Wilson and VanBriesen, 2012). In May of 2011 the Pennsylvania Department of Environmental Protection (PADEP) requested that drillers of Marcellus shale cease in discharging their produced water to POTWs and CWTs (USEPA, 2011b). While this will limit the amount of treated produced water that is discharged to surface water (most waste will be injected via underground wells) this directive does not apply to produced waters from conventional oil and gas production and areas that are near these treated produced water discharges should be aware of potential issues.

5. Conclusions

This study documents a source of unique environmental DBPs associated with the management of treated produced water from oil and gas extraction, mainly from conventional oil and gas extraction. Produced water brines are composed of various inorganic and organic DBP precursors that can react with disinfectants to form DBPs, especially Br-DBPs, which are suspected to be among the more toxic DBPs. These precursors are the reason of concern for drinking water managers wherever they may enter raw-water intakes due to oil and gas extraction and produced water management activities in their watersheds. However, this study has shown that treated produced waters contribute to the formation of DBPs even before they are discharged to these watersheds. The environmental-water samples collected at the outfalls of CWTs and POTWs have indicated that DBPs, including some that are not typically detected in other wastewaters, are associated with treated produced water management activities and result in unique signatures of DBPs in receiving streams.

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References

- ANL. A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. Argonne National Laboratory; 2004 [<http://www.evsnl.gov/pub/doc/ProducedWatersWP0401.pdf>]. [Accessed March 6, 2013].
- ANL. Produced water volumes and management practices in the United States, ANL/EVS/R-09/1. Argonne National Laboratory; 2009 [http://www.evsnl.gov/pub/doc/ANL_EVS_R09_produced_water_volume_report_2437.pdf]. [Accessed February 15, 2013].
- Benko KL, Drewes JE. Produced water in the western United States: geographical distribution, occurrence, and composition. *Environ Eng Sci* 2008;25:239–46.
- Bergdale A. Personal communication; 2013. United States Environmental Protection Agency Region 3, 1060 Chapline St Suite 303, Wheeling WV 26003. bergdale.amy@epa.gov.
- Bond T, Huang J, Templeton MR, Graham N. Occurrence and control of nitrogenous disinfection by-products in drinking water: a review. *Water Res* 2011;45:4341–54.
- Breit GN, Otton JK. Produced waters database. U.S. Geological Survey; 2002 [<http://energy.cr.usgs.gov/prov/prodwat/contact.htm>]. [Accessed March 29, 2013].
- Choi J, Richardson SD. Formation studies of halonitromethanes in drinking water. Proceedings of the 2004 American Water Works Association Water Quality Technology Conference, San Antonio, TX November 15, 2004: 2004.
- Collins AG, Egleson GC. Iodide abundance in oilfield brines in Oklahoma. *Science* 1967;156:934–5.
- Davis SN, Whittemore DO, Fabryka-Martin J. Uses of chloride/bromide ration in studies of potable water. *Groundwater* 1998;36:338–50.
- Dresel PE, Rose AW. Chemistry and origin of oil and gas well brines in western Pennsylvania. Pennsylvania Geological Survey, 4th series; 2010. [Open-File Oil and Gas Report 10-01.0, 48 pp.].
- Ferrari KJ, Michanowicz DR, Christen CL, Mulcahy N, Malone SL, Sharma RK. Assessment of effluent contaminants from three facilities discharging Marcellus Shale wastewater to surface water in Pennsylvania. *Environ Sci Tech* 2013;47:3472–81.
- Fishman MJ, Friedman LC. Methods for determination of inorganic substances in water and fluvial sediments. U.S. Geological Survey techniques of water-resources investigations; 1989 [book 5, chapter A1, 545 pp.].
- Hu J, Hocheol S, Karanfil T. Comparative analysis of halonitromethane formation and speciation in drinking water: the effects of disinfectants, pH, bromide and nitrate. *Environ Sci Tech* 2010;44:794–9.
- Jin W, Zhou J, Chen B, Zhu X, Cui C. Modeling volatilization and adsorption of disinfection byproducts in natural watersheds. *J Environ Monit* 2012;14:2990–9.
- Krasner SW, Weinberg HS, Richardson SD, Pastor SJ, Chinn R, Scilimenti MJ, et al. The occurrence of a new generation of disinfection by-products. *Environ Sci Tech* 2006;40:7175–85.
- Krasner SW, Westerhoff P, Chen B, Amy G, Nam S-N, Chowdhury ZK, et al. Contribution of wastewater to DBP formation. Denver, CO: AWWA Research Foundation; 2008 [297 pp.].
- Krasner SW, Westerhoff P, Chen B, Rittman BE, Amy G. Occurrence of disinfection byproducts in United States wastewater treatment plant effluents. *Environ Sci Tech* 2009;43:8320–5.
- Kundu B, Richardson SD, Swartz PD, Matthews PP, Richard AM, DeMarini DM. *Mutat Res* 2004;562:39–65.
- PADEP. Pennsylvania Department of Environmental Protection oil and gas reporting website o. <https://www.paoilandgasreporting.state.pa.us/publicreports/Modules/Waste/WasteByWasteFacility.aspx>, 2013. [Accessed May 7, 2013].
- Plewa MJ, Wagner ED, Jazwierska P, Richardson SD, Chen PH, McKague AB. Halonitromethane drinking water disinfection byproducts: chemical characterization and mammalian cell cytotoxicity and genotoxicity. *Environ Sci Tech* 2004;38:62–8.
- Richardson SD, Plewa MJ, Wagner ED, Schoeny R, DeMarini DM. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutat Res* 2007;636:178–242.
- Richardson SD, Fasano F, Ellington JJ, Crumley FG, Buettner KM, Evans JJ, et al. Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. *Environ Sci Tech* 2008;42:8330–8.
- Shan J, Hu J, Kaplan-Bekaroglu SS, Song H, Karanfil T. The effects of pH, bromide and nitrite on halonitromethane and trihalomethane formation from amino acids and amino sugar. *Chemosphere* 2012;86:323–8.
- Shi H, Qiang Z, Adams C. Formation of haloacetic acids, halonitromethanes, bromated and iodate during chlorination and ozonation of seawater and saltwater marine aquaria systems. *Chemosphere* 2013;90:2485–92.
- Song H, Addison JW, Hu J, Karanfil T. Halonitromethanes formation in wastewater treatment plant effluents. *Chemosphere* 2010;79:174–9.
- Thibaud H, Delaet J, Merlet N, Dore M. Chloropicrin formation in aqueous solution – effect of nitrites on precursors formation during the oxidation of organic-compounds. *Water Res* 1987;21:813–21.
- Trehly ML, Yost RA, Miles CJ. Chlorination byproducts of amino acids in natural waters. *Environ Sci Tech* 1986;20:1117–22.
- USEPA. The history of drinking water treatment. United State Environmental Protection Agency; 2000 [<http://www.epa.gov/ogwdw/consumer/pdf/hist.pdf>]. [Accessed February 15, 2013].
- USEPA. Plan to study the potential impacts of hydraulic fracturing on drinking water resources. EPA/600/R-11/122 United State Environmental Protection Agency; 2011a [http://water.epa.gov/type/groundwater/uic/class2/hydraulicfracturing/upload/hf_study_plan_110211_final_508.pdf]. [Accessed March 29, 2013].
- USEPA. Key documents about Mid-Atlantic oil and gas extraction: correspondence between US EPA and PA DEP. United State Environmental Protection Agency; 2011b [http://www.epa.gov/region3/marcellus_shale/]. [Accessed June 12, 2013].
- USEPA. Drinking water contaminants. United State Environmental Protection Agency; 2013 [<http://water.epa.gov/drink/contaminants/index.cfm#List>]. [Accessed March 5, 2013].
- Weinberg HS, Krasner SW, Richardson SD, Thruston AD. The occurrence of disinfection by-products (DBPs) of health concern in drinking water: result of a nationwide

- DBP occurrence study. United States Environmental Protection Agency, National Exposure Research Laboratory; 2002 [EPA/600/R-02/068, 460 pp.].
- Wilson JM, VanBriesen JM. Oil and gas produced water management and surface drinking water sources in Pennsylvania. *Environ Pract* 2012;14:301–7.
- Xu P, Drewes JE, Heil D. Beneficial use of co-produced water through membrane treatment: technical-economic assessment. *Desalination* 2008;225:139–55.
- Zaugg SD, Smith SG, Schroeder MP, Barber LB, Burkhardt MR. Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory. Determination of wastewater compounds by polystyrene-divinylbenzene solid-phase extraction and capillary-column gas chromatography/mass spectrometry: U.S. Geological Survey Water-Resources Investigations Report 01-4186; 2002. [37 pp.].