

# Enhanced Formation of Disinfection Byproducts in Shale Gas Wastewater-Impacted Drinking Water Supplies

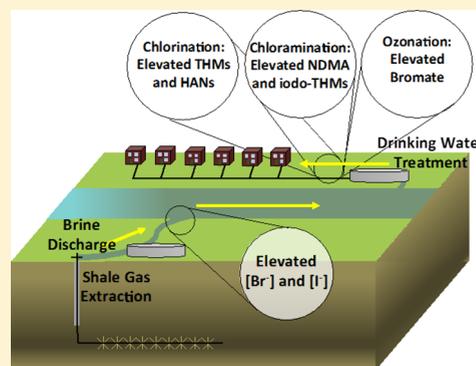
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**S** Supporting Information

**ABSTRACT:** The disposal and leaks of hydraulic fracturing wastewater (HFW) to the environment pose human health risks. Since HFW is typically characterized by elevated salinity, concerns have been raised whether the high bromide and iodide in HFW may promote the formation of disinfection byproducts (DBPs) and alter their speciation to more toxic brominated and iodinated analogues. This study evaluated the minimum volume percentage of two Marcellus Shale and one Fayetteville Shale HFWs diluted by fresh water collected from the Ohio and Allegheny Rivers that would generate and/or alter the formation and speciation of DBPs following chlorination, chloramination, and ozonation treatments of the blended solutions. During chlorination, dilutions as low as 0.01% HFW altered the speciation toward formation of brominated and iodinated trihalomethanes (THMs) and brominated haloacetonitriles (HANs), and dilutions as low as 0.03% increased the overall formation of both compound classes. The increase in bromide concentration associated with 0.01–0.03% contribution of Marcellus HFW (a range of 70–200  $\mu\text{g/L}$  for HFW with bromide = 600  $\text{mg/L}$ ) mimics the increased bromide levels observed in western Pennsylvanian surface waters following the Marcellus Shale gas production boom. Chloramination reduced HAN and regulated THM formation; however, iodinated trihalomethane formation was observed at lower pH. For municipal wastewater-impacted river water, the presence of 0.1% HFW increased the formation of *N*-nitrosodimethylamine (NDMA) during chloramination, particularly for the high iodide (54 ppm) Fayetteville Shale HFW. Finally, ozonation of 0.01–0.03% HFW-impacted river water resulted in significant increases in bromate formation. The results suggest that total elimination of HFW discharge and/or installation of halide-specific removal techniques in centralized brine treatment facilities may be a better strategy to mitigate impacts on downstream drinking water treatment plants than altering disinfection strategies. The potential formation of multiple DBPs in drinking water utilities in areas of shale gas development requires comprehensive monitoring plans beyond the common regulated DBPs.



## INTRODUCTION

Hydraulic fracturing and horizontal drilling have significantly expanded the production of natural gas from low permeability fossil fuel reservoirs in the US over the past decade. With production from such unconventional natural gas production facilities anticipated to provide nearly 50% of total US natural gas production over the coming decades, hydraulic fracturing could yield economic benefits, but there are significant concerns regarding the potential adverse impacts on the environment.<sup>1</sup> Four categories of concerns have been raised: (1) contamination of overlying drinking water aquifers by leakage of natural gas or saline waters from the production formations through well casings, (2) the quantity of freshwater consumed by hydraulic fracturing operations, (3) long-term contamination of sediments resulting from the binding of radioactive cations in wastewaters to sediments adjacent to wastewater discharge locations, and (4) impacts to downstream drinking water treatment plants resulting from discharges of saline wastewaters to surface waters.<sup>1</sup> Wastewaters associated

with hydraulic fracturing, including drilling fluids, flowback waters, and produced waters, frequently contain high levels of halides, heavy metals, and radioactivity.<sup>2</sup> After Marcellus Shale development began, a fraction of hydraulic fracturing wastewaters (HFWs) in Pennsylvania were sent to either publically owned treatment works (POTWs) for municipal wastewater treatment or commercial wastewater treatment (CWT) plants for oil and gas wastewaters and subsequently discharged to surface waters.<sup>3</sup>

Flowback and produced waters typically exhibit elevated chloride and bromide concentrations.<sup>4–8</sup> Halides are poorly removed from both POTWs and CWT treatment plants.<sup>2</sup> As a result of large volume disposal of HFW from disposal sites in PA (until recently), several studies have reported an increase in

Received: June 9, 2014

Revised: August 30, 2014

Accepted: September 9, 2014

Table 1. Water Quality Parameters

source	Ohio River water	Allegheny River water	HFW 1 (Marcellus)	HFW 2 (Marcellus)	HFW 3 (Fayetteville)	municipal wastewater
DOC (mg-C/L)	3.13	1.60	19.7	177	2.09	9.5
pH	7.4	6.7	6.6	6.5	8.8	8.0
SUVA <sub>254</sub> (L mg-C <sup>-1</sup> m <sup>-1</sup> )	3.98	3.12	0.35	3.34	6.31	1.98
Cl <sup>-</sup> (mg/L)	29	23	51 288	34 780	12 000	3600
Br <sup>-</sup> (mg/L)	0.027	0.042	693	310	105	1.4
I <sup>-</sup> (mg/L)	0.0034	0.0033	3.0	5.6	54	NM <sup>a</sup>
NH <sub>4</sub> <sup>+</sup> (mg-N/L)	0.28	<0.05	66.28	65.01	1.31	22
NO <sub>2</sub> <sup>-</sup> (mg-N/L)	<0.02	<0.02	<0.02	<0.02	25.50	0.037
NO <sub>3</sub> <sup>-</sup> (mg-N/L)	1.36	0.69	3.8	3.76	10.05	<0.1

<sup>a</sup>NM = not measured.

bromide concentrations in surface waters receiving discharges from hydraulic fracturing operations concurrent with increased drilling.<sup>9,10</sup> After 2009, bromide concentrations measured in surface waters near CWTs were up to 300  $\mu\text{g/L}$ , compared to pre-2003 concentrations of 72 ( $\pm 81$ )  $\mu\text{g/L}$  in Pennsylvania surface waters that were impacted by shale-gas development.<sup>10</sup> For the HFWs used in this work, and in a forthcoming more comprehensive survey, we demonstrate that some hydraulic fracturing wastewaters also exhibit elevated concentrations of iodide and high iodide/chloride ratios. After 2008, the fraction of oil and gas-associated wastewaters sent to POTWs declined; however, routing of wastewaters to CWTs continued to increase.<sup>11</sup> The 2011 voluntary request by the Pennsylvania Department of Environmental Protection (PA-DEP) to halt the disposal of oil and gas-associated wastewaters to treatment plants discharging to surface water decreased the bromide loads to some wastewater treatment plants and diverted oil and gas-associated wastewaters to Ohio for deep well injection, although this disposal option is subject to growing constraints due to concerns regarding earthquakes.<sup>12</sup> Furthermore, while Ferrar et al. observed a significant decrease in bromide concentrations at two of the three wastewater treatment plants studied after May 29, 2011, bromide concentrations from the CWT in the study remained high.<sup>13</sup> On a volume basis, estimates suggest that 30% of Marcellus-associated wastewater is disposed to CWTs, while about 10% is injected underground and 60% is recycled.<sup>11</sup> Given the lack of halide removal from CWTs,<sup>2,11–15</sup> PA-DEP is planning to modify their operation to eliminate contaminant discharge. Regardless, discharge of saline wastewaters from hydraulic fracturing operations may be important in other regions.

The elevated concentrations of bromide and iodide in surface waters resulting from discharges of HFW may increase the formation of disinfection byproducts (DBPs) and alter their speciation during chlorination,<sup>16–18</sup> chloramination,<sup>19,20</sup> and ozonation<sup>21,22</sup> in downstream drinking water treatment plants.<sup>23,24</sup> Hypochlorous acid/hypochlorite (HOCl/OCl<sup>-</sup>,  $\text{p}K_{\text{a}} 7.5^{25}$ ) can oxidize bromide and iodide to hypobromous acid/hypobromite (HOBr/OBr<sup>-</sup>,  $\text{p}K_{\text{a}} 8.7^{25}$ ) and hypoiodous acid/hypoiodite (HOI/OI<sup>-</sup>,  $\text{p}K_{\text{a}} 10.6^{25}$ ), respectively. These species can react with dissolved organic matter (DOM) to form an array of chloro-, bromo-, and iodo-DBPs, including trihalomethanes (THMs) and haloacetonitriles (HANs). However, iodinated DBP formation has been associated with chloramination rather than chlorination,<sup>17,19,20,26–28</sup> because, unlike chloramines, free chlorine rapidly oxidizes HOI to iodate (IO<sub>3</sub><sup>-</sup>),<sup>26</sup> which is harmlessly reduced to iodide in the body.<sup>29</sup> Brominated DBPs typically are more geno- and cytotoxic than

their chlorinated counterparts.<sup>30</sup> Iodo-DBPs have been found to be even more geno- and cytotoxic than chloro/bromo-DBPs<sup>19,31</sup> and are potentially tumorigenic.<sup>32</sup> High bromide concentrations have also been noted to promote the formation of the potent carcinogen,<sup>33</sup> *N*-nitrosodimethylamine (NDMA), during chloramination.<sup>34–36</sup> Finally, ozonation of waters containing elevated bromide concentrations forms the carcinogen,<sup>33</sup> bromate,<sup>22</sup> while ozonation of iodide forms relatively harmless iodate.<sup>26</sup> These alterations potentially could increase the toxicity of the disinfected drinking water and inhibit the ability of utilities to comply with the U.S. Environmental Protection Agency (EPA) Stage 2 Disinfection Byproduct (DBP) Rules.<sup>37</sup> Current EPA regulations limit the total concentration of four THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) to 80  $\mu\text{g/L}$  and bromate to 10  $\mu\text{g/L}$ .<sup>37</sup> California has a 10 ng/L Notification Level for NDMA in drinking water,<sup>38</sup> and the EPA is considering federal regulations on NDMA concentrations.<sup>39</sup>

The purpose of this study was to obtain an initial estimate of the minimum contribution of HFW to river waters that would result in significant alterations to DBP formation upon chlorination, chloramination, or ozonation. Three HFWs from the Marcellus and Fayetteville Shale formations were diluted with fresh water samples collected from the Ohio and Allegheny Rivers to constitute blends with different final volume percentages of HFWs. These dilution series were treated with typical doses of chlorine, chloramines, or ozone in the lab, and the samples were analyzed for THMs, HANs, NDMA, and bromate to determine the lowest volume percentage at which the HFWs enhanced DBP formation or altered the speciation of THMs and HANs toward brominated or iodinated analogues.

## ■ MATERIALS AND METHODS

**Reagents.** Fisher sodium sulfate anhydrous (99.6%), magnesium sulfate heptahydrate (>99.0%), ammonium chloride (99.9%), and sodium hypochlorite (6% solution, laboratory grade), Sigma-Aldrich boric acid (99.5%), and Acros potassium iodide (>99%) were used as received. A complete list of DBP standards, as well as their origins and purities, is provided in the Supporting Information.

**Sample Collection.** Grab samples were collected from the Ohio River in Cincinnati (OH) and from the Allegheny River in Pittsburgh (PA). Three grab samples of HFWs were obtained; two flowback waters associated with the Marcellus Shale formation (PA) were provided by Consol Energy, Inc.,<sup>40</sup> and one produced water associated with the Fayetteville Shale

formation (AR) was provided by the Arkansas Oil and Gas Commission.<sup>41</sup> In addition to the basic water quality analyses provided in Table 1, more analytical results for the two Marcellus flowback waters are provided in Table SI-1, Supporting Information.<sup>40,41</sup> A sample of non-nitrified secondary municipal wastewater effluent was collected upstream of disinfection from the Southeast wastewater treatment plant in San Francisco (CA). Samples were filtered through prebaked 0.7  $\mu\text{m}$  nominal pore size glass-fiber filters to remove particulate matter and stored at 4 °C.

**Characterization of Water Samples.** Chloride and bromide was analyzed by a ThermoFisher Dionex ICS-2100 ion chromatograph (IC) at Duke University. The detection limit for bromide on the IC is 16  $\mu\text{g/L}$ . Iodine was measured using isotope dilution methodology in a VG PlasmaQuad-3 inductively coupled-mass spectrometer (ID-ICP-MS) at Duke University. The detection limit for iodine on the ICP-MS is 0.5  $\mu\text{g/L}$ . Samples were spiked with a  $\sim 20$  ppm iodide spike solution with an enhanced  $^{129}\text{I}/^{127}\text{I}$  ratio of  $6.2 \pm 0.2$  (compared to the natural  $^{129}\text{I}/^{127}\text{I}$  abundance ratio of  $10^{-12}$ ). The exact concentration of iodide in the spike solution was determined by ID-ICP-MS using a 1000 mg/L iodide standard diluted to 25 mg/L as the ID spike. Seronom Serum Level-1 for trace elements was used as an independent iodide standard. Serum L-1 was spiked and left to equilibrate for 24 h and included in the ID-ICP-MS runs. To determine whether the iodine in the HFWs measured using ID-ICP-MS was present as iodide rather than iodate, IC analysis was performed. Although the iodate concentration could not be quantified due to coelution with chloride, at least 76% of the iodine in HFW 2 and 94% of the iodine in HFW 3 was confirmed to be iodide using IC; however, greater accuracy could not be achieved due to instrument sensitivity. This evaluation could not be performed for HFW 1 because the total iodine concentration was near the iodide detection limit (3 mg/L, 6000 times higher than the detection limit of ID-ICP-MS).

Dissolved organic carbon (DOC) was measured on a Shimadzu TOC-VCSH total organic carbon analyzer. UV absorbance, for determination of the specific ultraviolet absorbance at 254 nm ( $\text{SUVA}_{254}$ ), was determined using an Agilent Cary 60 UV-vis spectrophotometer. Ammonium, nitrate, and nitrite concentrations were determined using a WestCo SmartChem 200 discrete analyzer for automated spectrophotometric analyses.

**Disinfectant Application.** Prior to the addition of the oxidant, each sample was buffered at pH 8 using 4 mM borate buffer (unless otherwise noted). Free chlorine and chloramine stocks were generated and standardized as described previously.<sup>42</sup> Briefly, for experiments involving application of free chlorine (HOCl), a sodium hypochlorite stock was standardized daily by UV absorbance ( $\epsilon_{292\text{ nm}} = 362\text{ M}^{-1}\text{ cm}^{-1}$ ). Samples were treated with a HOCl dose needed to achieve a 1 mg/L as  $\text{Cl}_2$  residual after 24 h at room temperature (20 °C), as determined in preliminary experiments. Preformed monochloramine ( $\text{NH}_2\text{Cl}$ ) was formed by titrating HOCl into ammonium chloride ( $\text{NH}_4\text{Cl}$ ) to achieve a 1:1.25 Cl/N molar ratio. The  $\text{NH}_2\text{Cl}$  stock was standardized daily by UV absorbance, validating the negligible presence of dichloramine, as described previously.<sup>42</sup> Samples were chloraminated at doses of 2.5 mg/L as  $\text{Cl}_2$ , and the 3-day residual ranged from 1 to 2.3 mg/L as  $\text{Cl}_2$  among the samples analyzed in this study. Initial tests indicated that no significant NDMA formation occurred in chloraminated aliquots of either river water with or without

spiking of the two Marcellus flowback samples, suggesting a lack of NDMA precursors in these river samples. To evaluate the potential impacts of HFWs on NDMA formation, chloraminated samples were supplemented with 10% by volume of the secondary municipal wastewater effluent sample. Samples were held in the dark at room temperature for 24 h (for chlorinated samples) or 72 h (for chloraminated samples). The total chlorine residual after these holding times was measured using the DPD colorimetric method.<sup>43</sup> The chlorine residual was then quenched by addition of 35 mg/L ascorbic acid, and the samples were extracted immediately for analysis as described below.

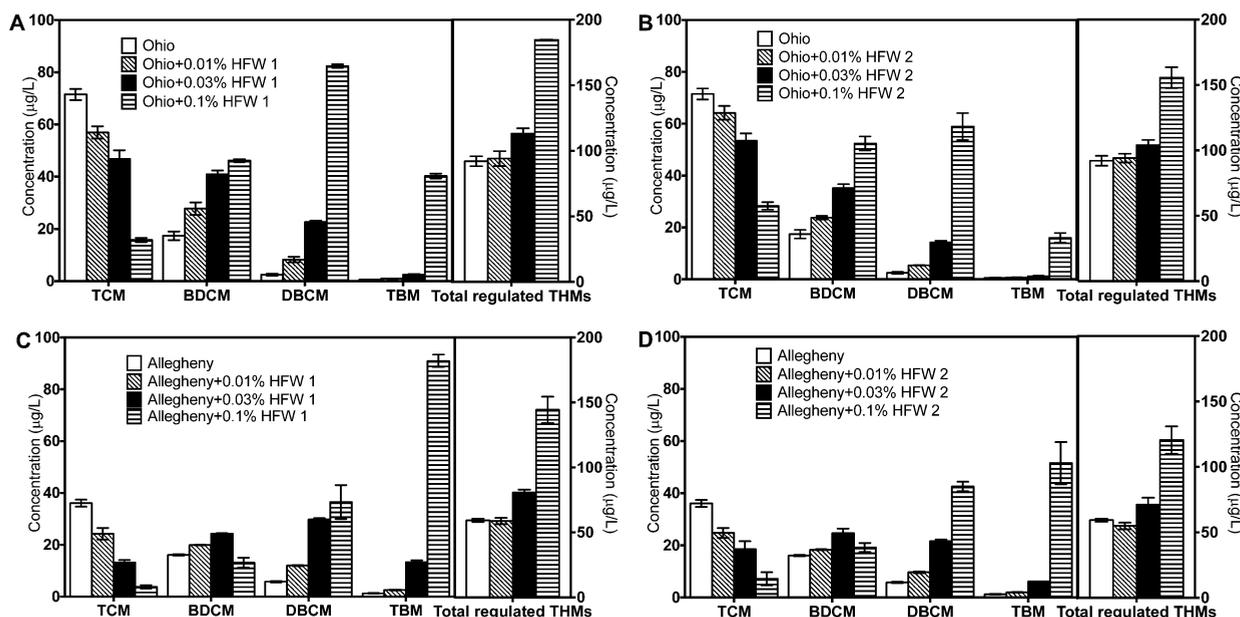
Ozone was applied using an ozone stock solution produced by purging ozone gas from a Triogen LAB2B Ozone generator through deionized water cooled to 4 °C. The stock was standardized by making a 1:2 dilution into 0.5 M phosphoric acid and measuring UV absorbance ( $\epsilon_{258\text{ nm}} = 3000\text{ M}^{-1}\text{ cm}^{-1}$ ). Ozone was added to samples at a 1:1 weight ratio of ozone to DOC, and reactions were held for several hours, permitting complete ozone consumption.

**Analytical Methods.** Halogenated DBPs (primarily THMs and HANs) were analyzed by solid phase extraction (SPE; Varian Bond Elut-PPL, 200 mg, 3 mL) of 40 mL samples spiked with 1,2-dibromopropane as an internal standard based on the method of Chinn et al.<sup>44</sup> Briefly, the cartridges were conditioned with 10 mL of methanol. After passing the sample through the SPE cartridge, the cartridge was eluted with 2 mL of methyl *tert*-butyl ether (MtBE). The MtBE extract was dried with sodium sulfate anhydrous and analyzed using gas chromatography–mass spectroscopy (Agilent 240 GC-MS system). Aliquots (3  $\mu\text{L}$ ) were injected in splitless mode (inlet temperature 90 °C). DBPs were separated using a J&W DB-1701 column (30 m  $\times$  0.250 mm  $\times$  1  $\mu\text{m}$ ). The oven temperature was held at 35 °C for 23 min, then raised to 139 °C at 4 °C/min, and finally raised to 274 °C at 27 °C/min, where it was held for 1 min. Method quantification limits (MQLs), method extraction efficiencies (ME), and response factors (RF) for each analyte are reported in Table SI-2, Supporting Information. To analyze *N*-nitrosamines in chloraminated samples, EPA Method 521 was used.<sup>45</sup> No DBPs were detected in deionized water blanks chlorinated or chloraminated as described above.

Bromate ( $\text{BrO}_3^-$ ) was analyzed using a Dionex DX-500 Ion Chromatograph equipped with an IonPac AS11-HC column. A sodium hydroxide (50 mM) eluent was applied at 5% for 25 min, ramped to 50% for 2 min, and then held at 50% for an additional 20 min. Bromate (retention time, RT = 18 min) was separable from chloride (RT = 21 min). Additional analytical details are provided in Tables SI-3 and SI-4, Supporting Information.

## RESULTS AND DISCUSSION

**Water Quality.** Table 1 presents basic water quality data for the river, HFW, and wastewater samples. The overall chloride (a range of 12 000–51 000 mg/L) and bromide (100–693 mg/L) concentrations in HFW samples investigated in this study are relatively low compared to typical produced waters from both unconventional hydraulic fracturing and conventional oil and gas operations (Table SI-5, Supporting Information). Nonetheless, the halide concentrations measured in the HFW samples were orders of magnitude higher than in the river waters. The chloride/bromide ratios in the river waters (548 and 1074) were higher than in the HFW (range of 74–114).



**Figure 1.** Regulated THM concentrations in dilutions of Marcellus Shale flowback waters into Ohio River (A and B) and Allegheny River (C and D) waters after chlorination for 24 h at pH 8. Total regulated THMs is the sum of TCM, BDCM, DBCM, and TBM. Error bars represent the standard deviation of experimental replicates ( $n \geq 2$ ).

The iodine concentrations in HFW (speciated predominantly as iodide, see above) had a wide range (3–54 mg/L) and did not correlate with bromide (i.e., bromide/iodine ratios of 231 and 55 for Marcellus Shale flowback waters 1 and 2, respectively, and 1.9 for Fayetteville Shale produced water 3). In contrast, the iodine concentrations in the Ohio and the Allegheny River samples were several orders of magnitude lower (3.4 and 3.3 µg/L, respectively), which is consistent with previous data on iodide concentrations in rivers in the eastern US (e.g., Susquehanna River with 2.8 µg/L).<sup>46</sup>

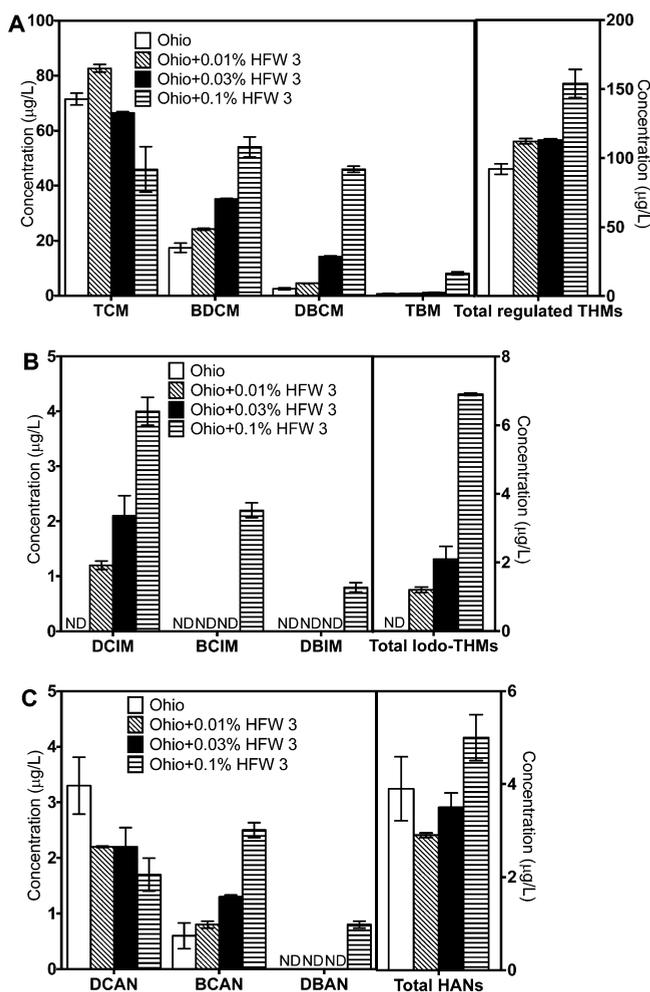
Flowback waters exhibited elevated concentrations of ammonium ( $\text{NH}_4^+$ ) and dissolved organic carbon (DOC) (Table 1), constituents of particular interest for DBP formation. Ammonium concentrations were higher in the Marcellus flowback waters by a factor of up to ~230 compared to the river waters. The high ammonium concentrations may derive from the use of ammonium salts in hydraulic fracturing products<sup>47</sup> or could be naturally occurring. If the ammonium loadings contributed by the flowback waters significantly increase the ammonium concentrations in the flowback/river water mixtures, the application of free chlorine within drinking water plants would result in *de facto* chloramination. The change in disinfectant would reduce pathogen deactivation and alter the array of DBPs formed. For the ~2.5 mg/L as  $\text{Cl}_2$  (37 µM) free chlorine doses evaluated here, relevant to drinking water disinfection, *de facto* chloramination would occur for ammonium concentrations >0.35 mg/L as N (25 µM). At ammonium concentrations below this level, the free chlorine dose would exceed the breakpoint (1.5:1  $\text{Cl}_2/\text{NH}_4^+$  molar ratio or 7.6:1  $\text{Cl}_2/\text{NH}_4^+$  weight ratio) and a free chlorine residual would ensue. For the Marcellus flowback waters in this study, *de facto* chloramination would occur for river waters containing >0.5% flowback waters. Accordingly, chlorination was evaluated only for river waters containing ≤0.1% flowback waters.

The DOC concentrations were significantly higher in the Marcellus flowback water samples than the river samples, particularly for HFW 2 (177 mg-C/L). If HFW 2 constituted

1–2% of a mixture with either river water, it would significantly increase the DOC of the mixture and thereby could potentially contribute organic DBP precursors. The characteristics of the HFWs also appear to be highly variable. Specific UV absorbance at 254 nm ( $\text{SUVA}_{254}$ ) values were an order of magnitude lower in HFW 1 than in either the river waters or HFW 2 or 3, suggesting that the organic matter in HFW 1 has less aromatic character than the other HFW samples.

None of the raw (without treatment) river waters or HFWs contained DBPs above detection limits. The municipal wastewater sample contained 26 ng/L NDMA. Constituting 10% by volume of some of the chloraminated samples described below, the wastewater contributed 2.6 ng/L to the NDMA concentrations measured after chloramination.

**DBP Formation from Chlorination.** When either the Ohio River or Allegheny River samples contained at least 0.03% of Marcellus Shale flowback waters (HFW 1 and 2), the formation of EPA regulated chlorinated and brominated THMs increased by ~10–35% on a mass basis (Figure 1). At 0.03% contribution of the flowback waters, the bromide concentrations in the river samples would have increased by 208 µg/L for HFW 1 and 93 µg/L for HFW 2. At 0.1% flowback water content, the increase in the mass concentration of regulated THMs was 70–140%. At this dilution of flowback water, an increase also was observed in the total molar concentration of regulated THMs (Figure SI-1, Supporting Information). For Fayetteville Shale HFW 3, the concentrations of total regulated THMs increased even for the 0.01% dilution of HFW 3 in the Ohio River sample (Figure 2A). Although the total concentrations of regulated THMs equaled or exceeded the 80 µg/L regulatory level in the Ohio River water without mixing with HFW, it is important to note that conventional drinking water treatment schemes can remove organic DBP precursors but not halides. Accordingly, lower absolute concentrations of DBPs might be expected had these samples received conventional treatment prior to disinfectant application.



**Figure 2.** Concentrations of (A) regulated THMs, (B) iodo-THMs, and (C) HANs in dilutions of Fayetteville Shale HFW 3 into Ohio River water after chlorination for 24 h at pH 8. Error bars represent the standard deviation of experimental replicates ( $n \geq 2$ ).

However, for either river water containing as low as 0.01% of either of the Marcellus flowback waters and for the Ohio River sample containing as low as 0.01% of the Fayetteville HFW 3 sample, the speciation of THMs shifted significantly toward the formation of brominated analogues at the expense of chloroform (Figures 1 and 2A). At 0.01% HFW, the bromide concentrations in the river waters would have increased by 69  $\mu\text{g/L}$  for HFW 1, 31  $\mu\text{g/L}$  for HFW 2, and 11  $\mu\text{g/L}$  for HFW 3. Iodo-THMs were not detected following chlorination of either river water with or without mixing with Marcellus HFW 1 or 2. However, 1  $\mu\text{g/L}$  dichloriodomethane (DCIM) was detected at 0.01% dilution of HFW 3 in the Ohio River sample (Figure 2B). At 0.1% HFW 3, bromochloriodomethane (BCIM) and dibromiodomethane (DBIM) were detected in addition to DCIM, with a total concentration of iodo-THMs of 7  $\mu\text{g/L}$ .

Similar results were found for dihalogenated chlorinated and brominated haloacetonitriles (Figures 2C and 3); standards for iodinated dihaloacetonitrile analogues were not available. When the Allegheny River sample contained at least 0.03% of either flowback water, the total concentration of HANs increased slightly. However, at 0.1% of either flowback water, total HANs increased by a factor of 3. For the Ohio River sample, significant increases in total HAN concentrations were recorded

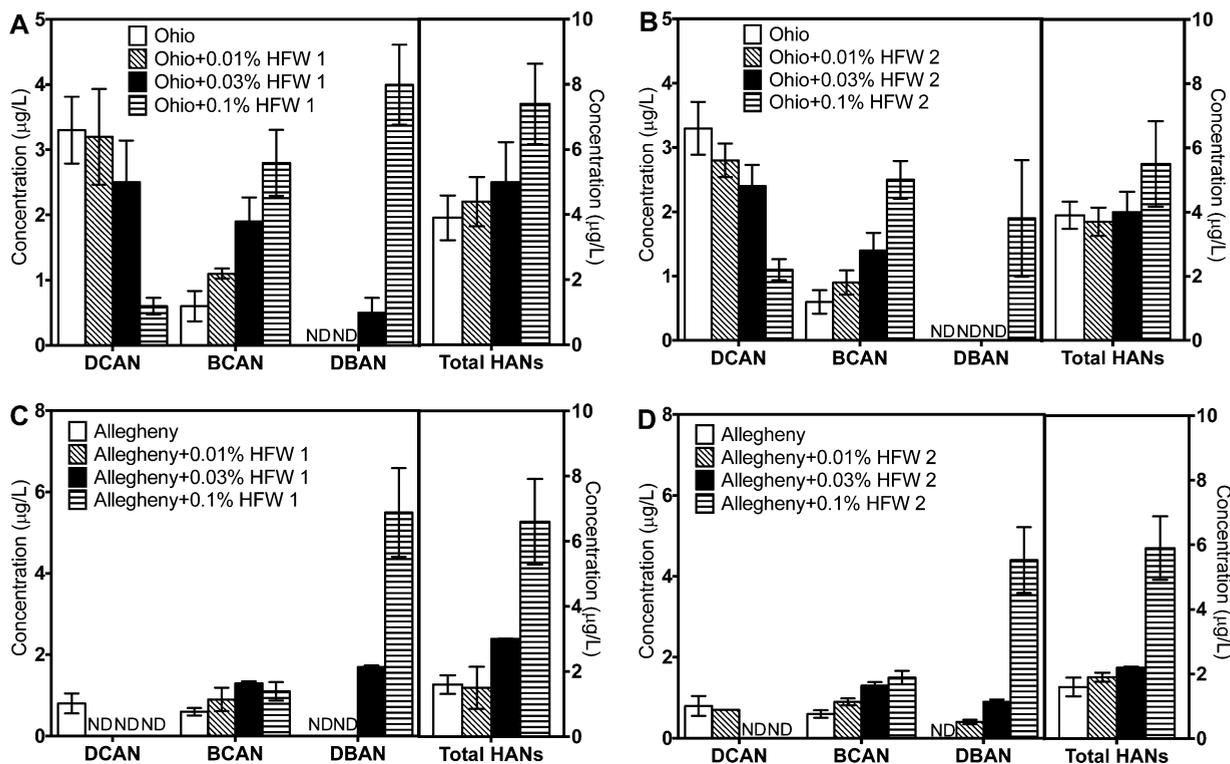
for 0.1% input of any of the three HFWs (Figures 2C and 3), but at this level, the total HAN concentration approximately doubled for HFW 1. The speciation of HANs shifted toward brominated analogues at the expense of dichloroacetonitrile (DCAN) for 0.01% of any of the HFWs diluted into the Ohio River sample (Figure 2C and 3) and for Marcellus HFW 1 or 2 diluted into the Allegheny River sample (Figure 3).

To determine whether the high DOC concentrations in HFW 1 or 2 (Table 1) contributed significantly to the observed DBP formation by providing organic DBP precursors, these waters were spiked into deionized water to constitute 0.01–0.1% by volume. After chlorination, low levels of regulated THMs were detected at 0.1% HFW, but all were  $<2 \mu\text{g/L}$ . At this percentage dilution, the highest contribution of DOC from the HFW to the mixture would be 0.18  $\text{mg-C/L}$  for HFW 2. Accordingly, the impact of the HFWs stemmed from the increase in halide loadings, rather than DBP precursors. Plots of regulated THMs vs the increase in bromide associated with the HFW 1 and 2 waters exhibited strong correlations (0.14  $\mu\text{g}$  THMs per  $\mu\text{g}$  bromide,  $R^2 = 0.93$  for Ohio River water,  $R^2 = 0.91$  for Allegheny River water), with little dependence on the river water or the flowback water. However, an even stronger correlation was observed for the high iodine-containing HFW 3 (0.54  $\mu\text{g}$  THMs per  $\mu\text{g}$  bromide,  $R^2 = 0.94$ ), suggesting other factors than bromide alone may be important.

**DBP Formation from Chloramination.** The application of preformed monochloramine at pH 8 to 0.1% HFW 1 or 2 in Ohio River or Allegheny River waters did not result in the formation of regulated THMs, iodo-THMs, HANs, or EPA Method 521 *N*-nitrosamines above detection limits. Similarly, no significant regulated THM, iodo-THM, or HAN formation was detected for 0.1% HFW 3 in Ohio River water. No DBP formation was observed for chloramination of 0.1% of any of the HFW in DI water.

Additional experiments were performed to investigate whether HFW may promote DBP formation during chloramination under conditions previously found to promote the formation of specific DBPs. First, previous research had suggested that iodo-THM formation during chloramination is maximized at pH 6.<sup>48</sup> DBPs were measured after application of preformed monochloramine to 0.3% HFW 1 or 2 in either the Ohio River or Allegheny River waters at pH 6 (Figures SI-3–5, Supporting Information). While regulated THMs, HANs, and iodo-THMs remained at or below the detection limits in either river water without HFW, significant brominated THM and HAN formation was observed for 0.3% HFW 1 or 2 waters in either river water at pH 6. In addition, bromochloriodomethane (BCIM) and dibromiodomethane (DBIM) were detected at pH 6 after chloramination of 0.3% of either flowback water in either river water. For 0.3% HFW 2 mixing with either river water, 2.5–3.5  $\mu\text{g/L}$  dibromiodomethane (DBIM) was formed; HFW 2 exhibited a higher iodide/bromide ratio than HFW 1 (Table 1).

Second, the absence of NDMA formation during application of preformed monochloramine at pH 8 (see above) suggested that the two river water samples lacked NDMA precursors. The Ohio River water was supplemented with a non-nitrified secondary wastewater effluent. At 10% by volume of wastewater effluent, the wastewater effluent contributed 2.2  $\text{mg-N/L}$  (0.16 mM) ammonia (Table 1). With or without the addition of 0.1% by volume of each of the HFW, this water was treated at pH 8 with 5  $\text{mg/L}$  as  $\text{Cl}_2$  (0.07 mM) free chlorine, forming chloramines *in situ*. After 3 days, NDMA concentrations were

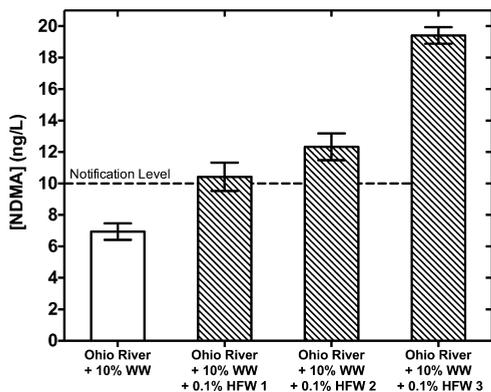


**Figure 3.** Chlorinated and brominated dihalogenated HAN concentrations in dilutions of Marcellus Shale flowback waters into Ohio River (A and B) and Allegheny River (C and D) waters after chlorination for 24 h at pH 8. Total HANs is the sum of DCAN, BCAN, and DBAN at each dilution factor. Error bars represent the standard deviation of experimental replicates ( $n \geq 2$ ).

~50–180% higher in the presence of 0.1% of any of the HFW than in wastewater-impacted Ohio River water without HFW (Figure 4); no other EPA Method 521 *N*-nitrosamines were

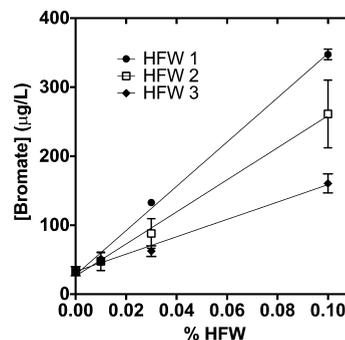
$\mu\text{g/L}$ ). These results agree with previous research suggesting that addition of chlorine to ammonia-containing water promoted the formation of iodinated THMs compared to addition of preformed monochloramine.<sup>48</sup>

**DBP Formation from Ozonation.** Bromate concentrations were recorded after ozonation (3.3 mg/L) at pH 8 of various dilutions of the three HFWs into the Ohio River water sample (Figure 5). The bromate concentrations increased



**Figure 4.** NDMA concentrations in dilutions of HFW into wastewater effluent-impacted (10%) Ohio River water after chloramination for 72 h at pH 8. Error bars represent the standard deviation of experimental replicates ( $n = 2$ ).

detected. Interestingly, the greatest NDMA formation occurred with HFW 3, which contributed the least bromide but the highest iodide. While previous research had suggested that bromide catalyzes NDMA formation,<sup>34,35</sup> the results presented in this study suggest that iodide could be a more potent catalyst. The addition of 0.1% of each of the HFWs, particularly HFW 3, promoted the formation of brominated THMs (Figure SI-6, Supporting Information). In line with its high concentration of iodide, HFW 3 also promoted the formation of iodinated THMs (i.e., dichloriodomethane, [DCIM] = 1



**Figure 5.** Bromate concentrations in dilutions of HFW into Ohio River water after ozonation (dose = 3.3 mg- $\text{O}_3/\text{L}$ ) at pH 8. Error bars represent the standard deviation of experimental replicates ( $n = 2$ ).

linearly with the fraction contribution of the different HFWs ( $R^2 = 0.99$  for HFW 1, 0.95 for HFW 1, 0.97 for HFW 3). Increases in bromate concentrations (40–50%) were observed for HFW volume percentages even as low as 0.01%. For HFW 1, which contained the highest concentration of bromide, bromate concentrations increased by 3-fold and 10-fold at 0.03% (Br = 208  $\mu\text{g/L}$ ) and 0.1% (Br = 693  $\mu\text{g/L}$ ) blending of flowback water, respectively. For each HFW, bromate

concentration increased with the increasing bromide concentration (Figure SI-7, Supporting Information), resulting from the increasing percentage contribution of HFW. However, the slopes of the bromate/( $\Delta$  bromide) relationships varied for the different HFWs, highlighting that bromate formation is influenced by factors other than bromide concentration alone. For example, the slope was the highest for HFW 3, despite the fact that it contained the lowest values of bromide and high levels of iodide and nitrite that would be anticipated to scavenge ozone (Table 1).<sup>22</sup> However, unlike the flowback waters, HFW 3 contained the lowest ammonium, and ammonium addition has been used to minimize bromate formation by sequestering bromide as bromamines.<sup>22</sup> For the Ohio River sample without HFW amendment, the concentration ( $34 \pm 7 \mu\text{g/L}$ ) of bromate formed after ozonation exceeded the  $10 \mu\text{g/L}$  regulatory limit. As for the THMs, it is important to note that treatment processes within a drinking water plant (e.g., lowering the pH during ozonation) could reduce the absolute bromate concentrations observed here.

**Environmental Implications.** Although previous studies have speculated that halides from hydraulic fracturing wastewaters could promote DBP formation in downstream drinking water treatment plants,<sup>23,24</sup> this study is the first to systematically investigate the potential impact of diluted HFW on DBP formation. HFW promoted the formation of regulated THMs and nonregulated HANs as well as iodo-THMs during chlorination, of NDMA and iodo-THMs during chloramination, and of bromate during ozonation at volume fractions as low as 0.01–0.1%. For THMs and bromate, the absolute concentrations measured in the different mixtures sometimes exceeded regulatory limits, although lower concentrations might be expected in finished waters due to precursor removal prior to disinfection or alternative operating conditions (e.g., pH). However, a relative increase in DBP formation would be expected compared to baseline concentrations formed prior to impacts from HFW discharges. Moreover, the halide concentrations in our HFW samples were relatively low compared to concentrations reported in previous studies for different types of flowback waters, produced waters, and brine plant effluents (see Table SI-4, Supporting Information).<sup>5,9,12</sup> Therefore, on a volume basis, the impacts associated with HFW may be greater than those observed in our experiments.

During chlorination, the total concentration of regulated THMs increased by 70–140% at 0.1% HFW blending with river water. Because chlorination is the dominant disinfection technique used by drinking water treatment plants withdrawing water from the Allegheny, Monongahela, and Ohio Rivers,<sup>23</sup> the results suggest that discharges of HFW may inhibit the ability of drinking water utilities to meet regulatory limits set by the EPA Stage 2 Disinfection Byproduct Rules.<sup>37</sup> Indeed, at 0.03% HFW contribution, HFW 1, 2, and 3 waters would increase the bromide concentrations in river waters by 208, 93, and  $32 \mu\text{g/L}$ , respectively. This degree of increase is in line with the observation of up to  $300 \mu\text{g/L}$  bromide downstream of CWT discharges after 2009 compared to the average  $\sim 72 \mu\text{g/L}$  measured in the pre-2003 Pennsylvanian surface waters that became impacted by shale-gas development.<sup>10</sup> In 2010, the Pittsburgh Water and Sewer Association noted a shift in the speciation of THMs toward brominated analogues and attributed the shift to the increase in bromide concentrations in the Allegheny River downstream of CWTs.<sup>24</sup> Future work should characterize transects between hydraulic fracturing

discharges and drinking water treatment plants in specific watersheds in areas of shale gas development.

At volume fractions as low as 0.01%, HFWs altered the speciation of HANs toward brominated analogues and of THMs toward brominated and iodinated analogues, in line with previous research on the impact of bromide and iodide on THM speciation.<sup>16–18,20</sup> Brominated and iodinated analogues tend to be orders of magnitude more cyto- or genotoxic than their chlorinated analogues.<sup>19,27,30,31,49,50</sup> Thus, regardless of the potential to violate current DBP regulatory standards, hydraulic fracturing discharges may have the potential to enhance the toxicity of chlorine-disinfected drinking waters in downstream utilities.

Utilities experiencing challenges in meeting the DBP regulatory limits in the EPA Stage 2 Disinfection Byproduct Rules may consider altering their disinfection schemes from chlorination to incorporate chloramination or ozonation. However, our results suggest that this strategy also may be problematic. At 0.1% HFW, the formation of NDMA was significantly enhanced in wastewater-impacted waters. Currently under consideration for federal regulatory action,<sup>39</sup> NDMA has a  $10 \text{ ng/L}$  Notification Level in California,<sup>38</sup> and  $0.7 \text{ ng/L}$  is associated with a  $10^{-6}$  lifetime cancer risk in drinking water.<sup>33</sup> Previous research has associated iodo-THM formation with chloramination, because chlorination rapidly oxidizes iodide to iodate ( $\text{IO}_3^-$ ), minimizing iodo-THM formation from HOI reactions with organic matter.<sup>26</sup> However, iodo-THMs have been identified upon chlorination of high iodide waters.<sup>17</sup> With HFW 3 water, which contained  $54 \text{ mg/L}$  iodine, we observed higher iodo-THM formation during chlorination than during chloramination (Figures 2B and SI-6, Supporting Information). The reason for the elevated iodo-THM formation during chlorination is unclear but may be related to the relatively high iodide concentrations involved. Even at 0.03% by volume, HFW 3 would increase the iodide concentration in a surface water by  $20 \mu\text{g/L}$ .

Ultimately, enforcing zero discharge or establishing halide-specific treatment techniques at centralized brine treatment facilities may be desirable. Adherence to policies regarding appropriate disposal practices varies regionally,<sup>51</sup> leading to elevated halide concentrations in particular regions. In addition, violations and spills can also threaten surface waters.<sup>52,53</sup> For example, as part of the Marcellus Shale exploration, 20% of wells have received a nonadministrative notice of violation, of which 14% are violations associated with disposal of highly saline waters.<sup>53</sup> Direct brine spills to water bodies, comprising approximately 30% of major reported spills, represent another risk.<sup>53</sup>

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Analytical method details and additional figures containing disinfection byproduct formation. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

K.M.P. was supported by the National Science Foundation Graduate Research Fellowship under Grant No. DGE-114747. This research was partially supported by a grant from the National Science Foundation (CBET-1066526). A.V. was supported by the Park Foundation. The authors would like to acknowledge Simone N. Fobi and Nahjan Amer Nordin for assistance with laboratory work; Daniel McCurry for sample collection; Prof. David Sedlak, Doug Turner, and Ning Dai for water quality characterization assistance; and Stuart Krasner and Guangchao Li for help with analytical method development.

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