

# Iodide, Bromide, and Ammonium in Hydraulic Fracturing and Oil and Gas Wastewaters: Environmental Implications

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## S Supporting Information

**ABSTRACT:** The expansion of unconventional shale gas and hydraulic fracturing has increased the volume of the oil and gas wastewater (OGW) generated in the U.S. Here we demonstrate that OGW from Marcellus and Fayetteville hydraulic fracturing flowback fluids and Appalachian conventional produced waters is characterized by high chloride, bromide, iodide (up to 56 mg/L), and ammonium (up to 420 mg/L). Br/Cl ratios were consistent for all Appalachian brines, which reflect an origin from a common parent brine, while the I/Cl and NH<sub>4</sub>/Cl ratios varied among brines from different geological formations, reflecting geogenic processes. There were no differences in halides and ammonium concentrations between OGW originating from hydraulic fracturing and conventional oil and gas operations. Analysis of discharged effluents from three brine treatment sites in Pennsylvania and a spill site in West Virginia show elevated levels of halides (iodide up to 28 mg/L) and ammonium (12 to 106 mg/L) that mimic the composition of OGW and mix conservatively in downstream surface waters. Bromide, iodide, and ammonium in surface waters can impact stream ecosystems and promote the formation of toxic brominated-, iodinated-, and nitrogen disinfection byproducts during chlorination at downstream drinking water treatment plants. Our findings indicate that discharge and accidental spills of OGW to waterways pose risks to both human health and the environment.



## INTRODUCTION

The exploration and production of oil and gas resources has generated large volumes of oil and gas wastewater (OGW) from thousands of wells in the U.S. The estimated volume of produced water generated annually in the U.S. varies between 3.18 billion m<sup>3</sup> and 3.97 billion m<sup>3</sup>.<sup>1,2</sup> This volume has further increased due to the rapid development of unconventional oil and gas production (e.g., shale gas and tight sand oil). The wastewater produced from hydraulic fracturing includes flowback fluid, fluids that return to the surface immediately following hydraulic fracturing, and produced waters, which are brought to the surface at slower rates but over longer time-scales during gas and oil production. Each unconventional shale gas well is estimated to generate between 3500 and 7200 m<sup>3</sup> of wastewater during its lifetime.<sup>3,4</sup> In Pennsylvania, where the Marcellus shale has been extensively exploited, the total volume of OGW was estimated as 3000–5000 million liter (ML) per year in 2011 and 2012.<sup>5</sup> Given the accelerated rate of shale gas drilling, the overall OGW generated in the U.S. is expected to rise.

In most states, OGW is injected to deep saline aquifers. However, an estimated 22 000 ML of produced water is annually discharged to surface water in the U.S., mostly (56%) in

Alabama.<sup>5</sup> In other areas where deep injection is not available (e.g., Pennsylvania, New York) or restricted because of proximity to fault systems, wastewater is recycled and reused for hydraulic fracturing,<sup>6</sup> or treated and then discharged to surface water.<sup>7</sup> Elsewhere, (e.g., New York, West Virginia) operators occasionally spread wastewater on roads for dust suppression or deicing. Unfortunately, illegal disposal, leaking from surface impoundments, and accidental spills of OGW often occur in areas of extensive shale gas development.<sup>3</sup>

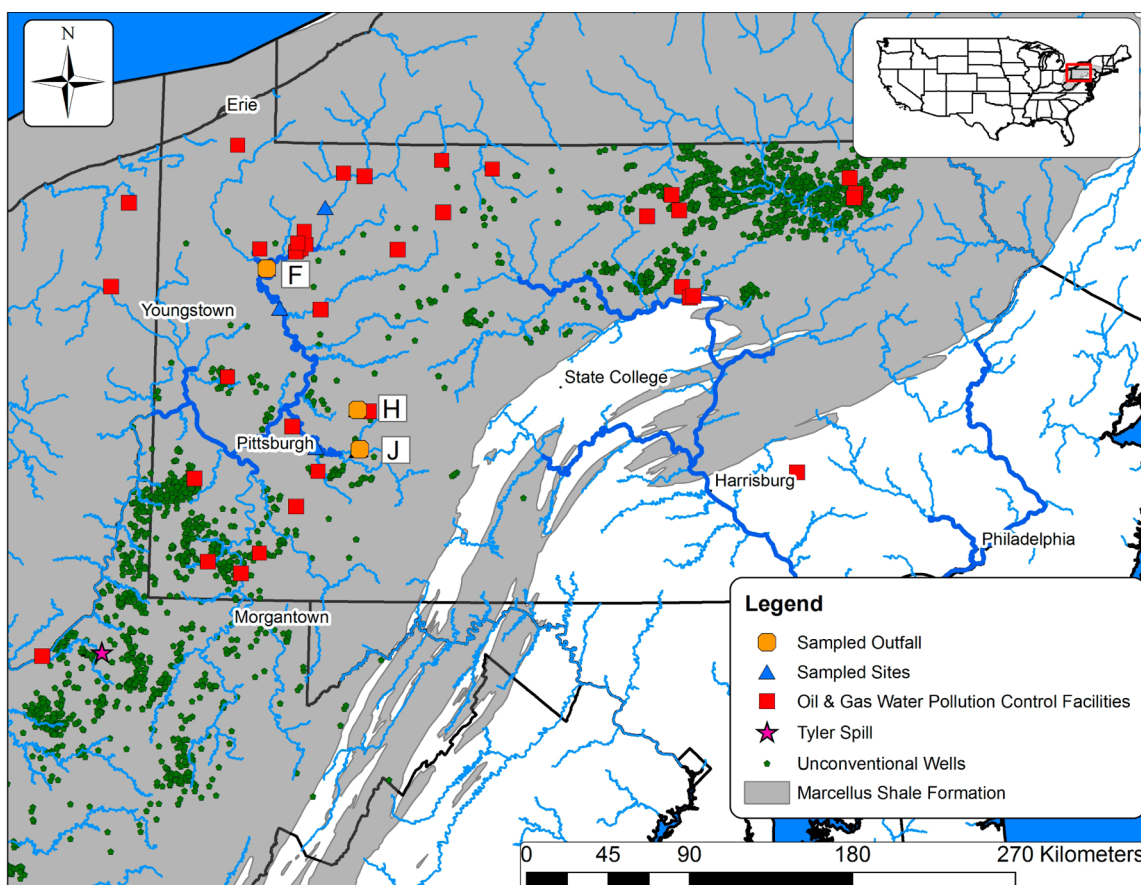
Since the beginning of shale gas exploration and hydraulic fracturing, OGW from unconventional oil and gas operations in Pennsylvania has been treated at publicly owned treatment works (POTWs), municipal wastewater treatment plants (WWTP), or commercially operated industrial brine treatment plants.<sup>8</sup> Maloney and Yoxheimer (2012)<sup>9</sup> reported disposal of 390 ML during 2011, and Lutz et al. (2013)<sup>5</sup> reported ~1750 ML and ~1200 ML in 2010 and 2011, respectively. Since 2011, OGW

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**Figure 1.** Map of the location of the outfalls from the Franklin (marked as F), Hart (H), and Josephine (J) facilities in Pennsylvania, associated surface water sampling sites, and the spill site in Tyler County, West Virginia investigated in this study. The map also presents the location of other oil and gas water pollution facilities (red squares), unconventional wells, and major waterways in the study area. Data for the locations of oil and gas treatment facilities were originally available from the Pennsylvania Department of Environmental Protection (PADEP),<sup>60</sup> and also from the Pennsylvania spatial data clearinghouse.<sup>61</sup>

management in Pennsylvania has changed substantially.<sup>8</sup> In May 2011, OGW disposal through POTWs and WWTP was terminated, but brine treatment facilities continue to receive OGW and are exempt from the salinity and water quality restrictions (e.g., TDS < 500 mg/L) for discharged effluents. In addition, the volume of flowback and hydraulic fracturing fluids from unconventional shale gas wells sent to brine treatment sites has decreased and several of the brine treatment sites reported accepting only produced waters from conventional oil and gas operations. Data from 2013 indicate that 1206 ML of OGW was reused for hydraulic fracturing operations, which consists of 67% of the total OGW volume (1788 ML) generated in PA during 2013 (Supporting Information (SI) Table S1). About 582 ML of OGW was distributed to brine treatment facilities, including three facilities that are investigated in this study (Figure 1). Traditionally, brine treatment included lime and Na<sub>2</sub>SO<sub>4</sub> addition,<sup>10</sup> which removes metals such as barium and radium, but not halides such as chloride and bromide.<sup>3,11</sup> In contrast, thermal evaporation/distillation treatment can remove all dissolved salts, but as of 2014 was implemented at only one site in PA.<sup>3</sup> At all of the brine treatment sites (Figure 1), treated effluents are released to adjacent streams or rivers.

OGW management is an engineering challenge because it is typically characterized by elevated levels of salinity (e.g., Williston Basin, North Dakota with TDS up to 400 000 mg/L<sup>12</sup>), anthropogenic (chemicals injected during drilling or

fracturing) and naturally occurring organic compounds, heavy metals, and naturally occurring radioactive materials (NORMs),<sup>3,13–15</sup> which all pose environmental and human health risks upon release to the environment. As observed near the Josephine treatment plant site in PA, NORMs from OGW have accumulated in stream sediments.<sup>7,11</sup> An additional risk following the release of high salinity OGW to surface water is the increase in halide concentrations downstream of discharge sites. When impacted surface waters are used as source waters by downstream drinking water treatment plants, reactions of disinfectants with halides can form carcinogenic *disinfection byproducts* (DBPs).<sup>16,17</sup> Previous studies have addressed the environmental implications of high Br<sup>−</sup> in OGW. For example, elevated Br<sup>−</sup> concentrations resulting from OGW discharges along the Monongahela River<sup>18</sup> and Clarion River<sup>19</sup> increased DBP concentrations, especially brominated species, in municipal drinking water in Pittsburgh, PA.<sup>19</sup> Brominated DBPs tend to be more cyto- and genotoxic than their chlorinated analogues.<sup>16,20,21</sup>

While several studies have reported elevated iodide (I<sup>−</sup>)<sup>14,20–26</sup> and ammonium (NH<sub>4</sub><sup>+</sup>)<sup>15,21,27–31</sup> concentrations in produced waters from conventional oil and gas wells, their concentrations in fluids from unconventional oil and gas exploration (i.e., shale gas) have not been previously reported. In addition, the environmental implications of disposal of iodide- and ammonium-rich effluents to surface waters have not been

systematically evaluated. Disposal or release of ammonium-rich OGW effluents to the environment can have direct negative impacts on aquatic organisms,<sup>32–34</sup> while the addition of iodide- and bromide-rich effluents would increase the risk of forming toxic DBPs in drinking water utilities downstream from disposal or accidental spill sites.<sup>17,35,36</sup>

Iodinated DBPs are often more cyto- and genotoxic than their chlorinated or brominated analogues,<sup>16</sup> but are not typically monitored or regulated.<sup>36,37</sup> When present at high concentrations in source waters of drinking water utilities practicing chlorine disinfection,  $\text{NH}_4^+$  could convert chlorine to chloramines, altering the efficacy of disinfection and the array of DBPs produced.<sup>38–41</sup> In addition to impacts of ammonium on the disinfection process, haloacetamides are an emerging class of unregulated nitrogen-containing DBPs that can form when ammonium-rich waters are introduced during disinfection and have been shown to be toxic.<sup>42–44</sup> Chlorine disinfection treatment simulations using blends of natural surface water with hydraulic fracturing flowback fluids have shown that OGW contribution as low as 0.01% by volume would increase the total concentrations of trihalomethanes (THMs) and haloacetamides (HANs), and would shift speciation toward the more toxic brominated or iodinated species.<sup>36</sup> Similarly, small contributions of hydraulic fracturing fluids promoted the formation of bromate during ozonation and of *N*-nitrosodimethylamine during chloramination.<sup>36</sup> The results from these experiments show that even small contributions of  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{NH}_4^+$  can alter the total concentrations and speciation of DBPs in drinking water.

Here we present, for the first time, a systematic evaluation of  $\text{I}^-$  and  $\text{NH}_4^+$  concentrations in unconventional hydraulic fracturing flowback fluids from both the Marcellus and Fayetteville shale formations, combined with data from produced waters from conventional oil and gas wells from the Appalachian Basin. We also evaluate halides and  $\text{NH}_4^+$  in effluents from three OGW treatment sites in PA, surface waters downstream from the disposal sites, and flowback from an accidental spill site in WV (Figure 1). The objectives of this study are to evaluate the sources of halides and  $\text{NH}_4^+$  in OGW from both conventional and unconventional oil and gas exploration and to quantify the contribution of these contaminants to the environment from direct and accidental release of OGW.

## ANALYTICAL TECHNIQUES

**Sample Collection.** Five types of water samples were used in this study: (1) 44 produced waters from conventional oil and gas wells in the Appalachian Basin (31 from the Silurian and 13 from Upper Devonian; SI Figure S2); (2) hydraulic fracturing flowback and produced waters from the Marcellus Formation in Pennsylvania ( $n = 25$ ) and the Fayetteville Formation in Arkansas ( $n = 6$ ); (3) effluents of treated oil and gas wastewater discharged to surface waters from the Josephine, Hart, and Franklin brine treatment facilities in western PA (Figure 1 and SI Figures S3–S6), including effluents collected repeatedly from Josephine site between 2010 and 2014 ( $n = 12$ ); (4) surface waters collected downstream from the Josephine, Hart and Franklin brine disposal sites ( $n = 13$ ); and (5) fluids from an accidental spill site in Tyler County, West Virginia ( $n = 5$ ). On January 2, 2014 a tank from an unconventional well pad, located in Tyler County, WV (Figure 1), burst and released fluids. The fluids migrated beyond the well pad containment and into the adjacent stream, Big Run Creek. A sample was collected on January 3, 2014 from a pool of water adjacent to the well pad. Further samples from the pool and downstream surface water

from Big Run Creek and Middle Island Creek were collected on January 6, 2014 and February 23, 2014.

**Chemical Analysis.** Chloride and bromide (detection limits = 0.1 and 0.02 mg/L, precision =  $\pm 0.5\%$ , and  $\pm 0.6\%$ , respectively) were analyzed by ion chromatography on a ThermoFischer Dionex IC at Duke University. Total iodine in brines was measured using isotope dilution-inductively coupled-mass spectrometry (ID-ICP-MS) on a VG PlasmaQuad-3 ICP-MS. For low salinity samples, iodine was measured directly by ICP-MS. For high salinity waters, samples were spiked with a  $\sim 20$  ppm iodine spike solution with an enriched  $^{129}\text{I}/^{127}\text{I}$  ratio of  $6.2 \pm 0.1$  (compared to the natural abundance ratio of  $10^{-12}$ ). The concentration of iodide in the spike was determined by ID-ICP-MS at Duke University using a 1000 ppb SCA iodide standard diluted to 25 ppm as the ID spike. The  $^{129}\text{I}/^{127}\text{I}$  ratio in the spike was measured at Duke University by ICP-MS. Seronorm Trace Elements Serum L-1 was used as an independent iodide standard. Serum L-1 was spiked, left to equilibrate for 24 h and included in the ID-ICP-MS runs. Samples were diluted in an ammonium solution, but the use of a basic matrix solution limited the effectiveness of the trace element internal standard. Additionally, the high salinity of flowback and produced waters is problematic for direct iodine analysis by regular ICP-MS due to signal enhancement from the high sodium matrix. The use of the isotope dilution technique allowed  $^{129}\text{I}$  to act as an internal standard and any influence from the sodium signal was removed by normalization to the internal standard. Further information on the isotope dilution technique is provided in the SI text. The detection limit of the ICP-MS measurement was determined by dividing three times the standard deviation of repeated blank measurements by the slope of the external standard. The ICP-MS detection limit for iodine was 0.3 ppb. Analytical precision was calculated as the relative percent difference (RPD) of the results of duplicate sample measurements. The analytical precision of iodine was  $\pm 5\%$ . IC analysis was also performed on a subset of 12 OGWs to determine whether the iodine measured by ID-ICP-MS was present as iodide (which affects DBP formation) or iodate (which does not affect DBP formation). Although iodate could not be quantified due to coelution with chloride, the iodine concentrations measured by IC agreed with those measured by ID-ICP-MS (average and maximum percentage differences were 2.1% and 10.1%), indicating that iodide was the predominant form of iodine.

Total ammonium nitrogen (TAN) was measured by Flow Injection Analysis (FIA) on a Hach Lachat, at the Duke University River Center. Samples were diluted to a chloride concentration less than 5 ppt. TAN was analyzed via QuickChem Method 10-107-06-1-J: Ammonia (Phenolate) in Potable and Surface Waters. Nitrate was analyzed via QuickChem Method 10-107-04-2-D: Nitrate/Nitrite in Waters by Hydrazine Reduction. Ammonia was calculated from the combined  $\text{NH}_4^+ + \text{NH}_3$  given by FIA using the partition coefficient and pH measured at the time of sample collection.<sup>45</sup> The detection limit for QuickChem Method 10-107-06-1-J was 0.01 mg/L. The analytical precision was  $\pm 0.8\%$ .

## RESULTS AND DISCUSSION

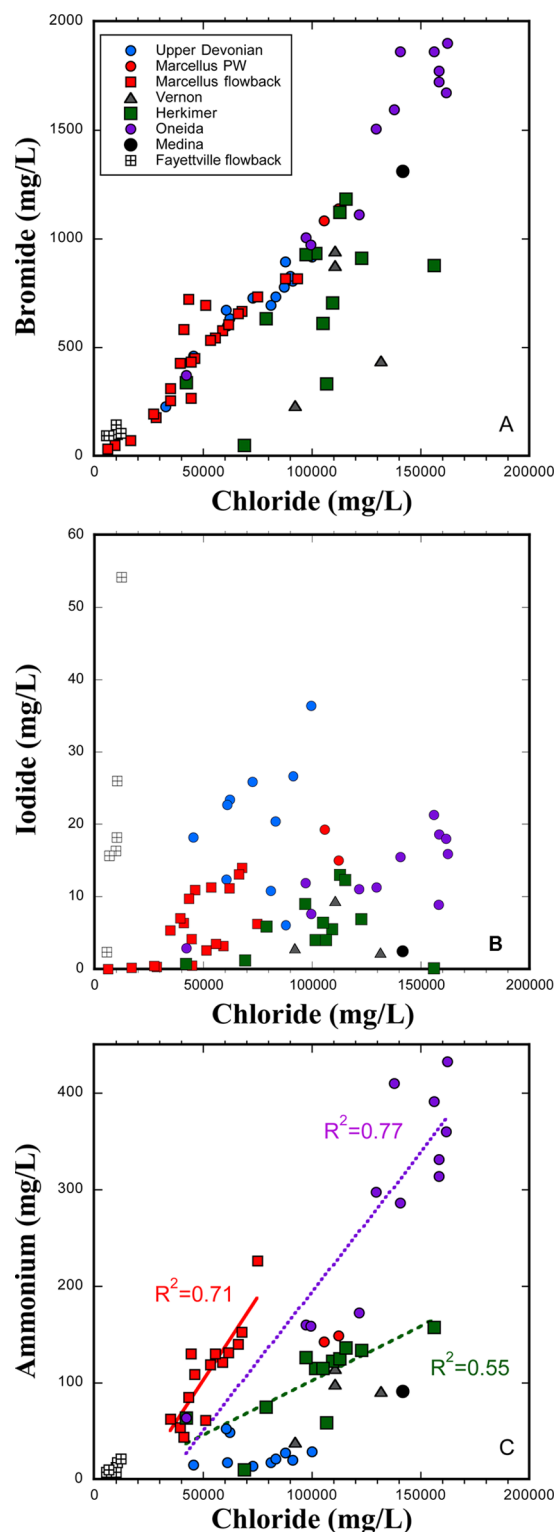
**Occurrence of Bromide, Iodide and Ammonium in Flowback and Produced Waters.** Measurements of chloride ( $\text{Cl}^-$ ), bromide ( $\text{Br}^-$ ), and iodide ( $\text{I}^-$ ) concentrations in hydraulic fracturing flowback waters from the Marcellus Shale ( $n = 23$ ) and Fayetteville Shale ( $n = 5$ ), produced waters from the



Marcellus Shale ( $n = 2$ ) and the Fayetteville Shale ( $n = 1$ ), and conventional oil and gas produced waters from the Silurian formations (Medina, Oneida, Herkimer, and Vernon formations;  $n = 31$ ) and Upper Devonian formations ( $n = 13$ ) of the Appalachian Basin (SI Figure S2) resulted in a wide range of  $\text{Br}^-$  and  $\text{I}^-$  concentrations (Figure 2; SI Table S2). While  $\text{Br}^-$  in the Appalachian brines was highly correlated with  $\text{Cl}^-$  ( $R^2 = 0.8$ ,  $p < 0.05$ ; Figure 2A),  $\text{I}^-$  had no correlation with  $\text{Cl}^-$  ( $R^2 = 0.09$ ;  $p = 0.61$ ; Figure 2B).  $\text{I}^-$  varied between geological formations within the Appalachian Basin; the highest concentrations (18–36 mg/L) were in produced waters from the Upper Devonian formations, while Herkimer and Vernon formations had the lowest  $\text{I}^-$  contents (0.1 to 12 mg/L; SI Figure S7). Selective measurements of iodide species (by IC) show comparable results to the total measured iodine (by ICP-MS) in the formation waters, indicating that the iodide is the predominant species.

The  $\text{Br}^-$  and  $\text{I}^-$  concentrations in the unconventional flowback and produced waters from the Marcellus Formation were similar to levels found in conventional Upper Devonian produced waters, but higher than those in the Silurian formations (SI Table S1, Figure 2). Flowback and produced waters from the Fayetteville Shale in Arkansas had higher  $\text{I}^-$  (2.4–54 mg/L), but lower  $\text{Br}^-$  (95–144 mg/L) and  $\text{Cl}^-$  (5000–12 000 mg/L) relative to flowback waters from the Marcellus Formation (0–19 mg/L, 31–1000 mg/L and 6000–100 000 mg/L, respectively).<sup>46</sup> The relatively high  $\text{I}^-$  in flowback waters from the Fayetteville Shale is consistent with high  $\text{I}^-$  contents (70–1400 mg/L) reported for conventional brines from the Mississippian and Pennsylvanian age formations of the Anadarko Basin in northern Oklahoma,<sup>20</sup> which is associated with the Fayetteville Shale. The similarity in  $\text{I}^-$  concentrations between Marcellus flowback fluids and conventional Appalachian produced waters (Figure 2) indicate that the hydraulic fracturing process does not introduce an additional source of  $\text{I}^-$ . Instead,  $\text{I}^-$  variations are likely related to natural geogenic variations within the host formations. The lower values of  $\text{Br}^-$  and  $\text{I}^-$  in Marcellus flowback waters compared to produced waters from the same region are likely a result of dilution with low-bromide and -iodide freshwater injected during the hydraulic fracturing process.

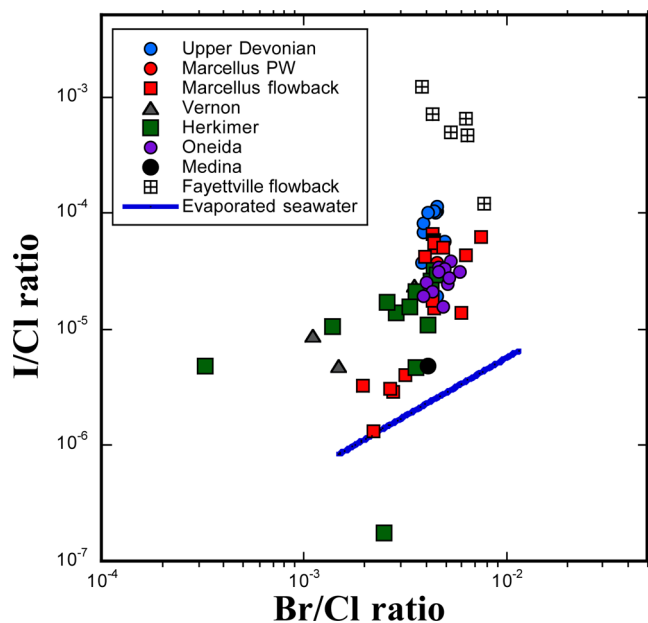
Similar to  $\text{I}^-$ ,  $\text{NH}_4^+$  concentrations in both unconventional Marcellus flowback fluids and Appalachian conventional produced waters (Figure 2) vary between geologic formations and are not related to the extraction process, conventional or unconventional. The highest  $\text{NH}_4^+$  concentrations were found in produced waters from the Lower Silurian Oneida Formation (63 to 432 mg/L), while the lowest concentrations were in the Upper Devonian Formations (12 to 28 mg/L; SI Figure S7). Data from the Fayetteville flowback show relatively low  $\text{NH}_4^+$  contents (7–22 mg/L). Unlike  $\text{I}^-$ ,  $\text{NH}_4^+$  correlated linearly to  $\text{Cl}^-$  within each formation (e.g., Oneida Formation,  $R^2 = 0.77$ ,  $p < 0.05$ ; Herkimer Formation,  $R^2 = 0.55$ ,  $p = 0.03$ ; and Marcellus flowback fluid,  $R^2 = 0.71$ ,  $p < 0.05$ ; Figure 2C). Produced waters from both basins were elevated in  $\text{NH}_4^+$  compared to flowback waters, most likely a result of dilution of formation waters with low  $\text{NH}_4^+$  freshwater during the hydraulic fracturing. Consequently, our data indicate that  $\text{NH}_4^+$  occurrence in both unconventional and conventional OGW is geogenic in nature and has no association with nitrogen chemicals that could be added to the hydraulic fracturing fluids. The preservation of  $\text{NH}_4^+$  in the brines is likely related to the highly reducing conditions, high salinity, and acidity of the formation waters. In addition, we found that elevated  $\text{I}^-$  in oil and gas wastewater is not directly associated with elevated  $\text{NH}_4^+$ . This is demonstrated



**Figure 2.** Bromide (A), iodide (B), and ammonium (C) versus chloride concentrations in hydraulic fracturing flowback fluids (Marcellus and Fayetteville) and conventional produced waters from multiple formations in the Appalachian Basin. Note the consistently high  $\text{Br}^-/\text{Cl}^-$  ratios of most of the Appalachian brines, except for produced waters from the Vernon Formation and a few samples from the Herkimer Formation. In contrast, iodide does not correlate with chloride, while the  $\text{NH}_4^+/\text{Cl}^-$  ratios vary between the different geological formations. The data suggest that high  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{NH}_4^+$  concentration in oil and gas produced waters reflect natural variations and sources within the formations and not the method of extraction.

in the Appalachian Upper Devonian produced waters and Fayetteville flowback fluid with the highest  $\text{I}^-$  but with lowest  $\text{NH}_4^+$  contents.

**Geochemical Evaluation.** Both Marcellus unconventional flowback fluids and Appalachian conventional produced waters show high correlations between  $\text{Cl}^-$  and  $\text{Br}^-$ , with  $\text{Br}/\text{Cl}$  ratios higher than the seawater ratio of  $1.5 \times 10^{-3}$  in most of the flowback and produced water samples (Figure 3). This confirms



**Figure 3.**  $\text{I}/\text{Cl}$  versus  $\text{Br}/\text{Cl}$  (molar, log scale) ratios of flowback and produced waters investigated in this study as compared to the projected evaporated seawater curve calculated from Vengosh et al.,<sup>36</sup> assuming iodide is conservative during evaporation of seawater. The  $\text{I}/\text{Cl}$  ratios of most of the flowback and produced waters were several orders of magnitude higher than the projected  $\text{I}/\text{Cl}$  in evaporated seawater for a given  $\text{Br}/\text{Cl}$  ratio, reflecting the net enrichment of iodide in the formation waters due to release of  $\text{I}^-$  from organic matter in the formations. Diluted Marcellus flowback waters had lower  $\text{Br}/\text{Cl}$  and  $\text{I}/\text{Cl}$  ratios, reflecting dilution of the Marcellus brines with  $\text{Br}^-$  and  $\text{I}^-$  free fresh water. Produced waters from the Upper Silurian Vernon and Herkimer formations had also lower  $\text{Br}/\text{Cl}$  and  $\text{I}/\text{Cl}$  ratios that could be derived from contribution of salts originating from dissolution of halite minerals.

previous hypotheses that most of the formation waters in the Appalachian Basin originated from remnants of seawater that were evaporated beyond halite saturation and later diluted by meteoric water.<sup>13,47</sup> Yet some formation waters from the Upper Silurian Vernon and Herkimer formations had lower  $\text{Br}/\text{Cl}$  ratios that were associated with  $\text{Na}/\text{Cl}$  ratios higher than the seawater ratio of 0.86. The combination of  $\text{Na}/\text{Cl}$  ratios close to unity and relatively low  $\text{Br}/\text{Cl}$  ratios indicate that these brines are mixing with formation waters originated from halite dissolution in the Upper Silurian formation.

In contrast to  $\text{Br}^-$ ,  $\text{I}^-$  was not correlated with  $\text{Cl}^-$  (Figure 2B), except in brines from the Oneida Formation ( $r = 0.8$ ). The  $\text{I}/\text{Cl}$  ratios show iodide enrichment, up to 3-fold relative to the  $\text{I}/\text{Cl}$  ratios projected for evaporated seawater (Figure 3). Since  $\text{I}^-$  variation in evaporated seawater has not been reported, we modeled the projected  $\text{I}/\text{Cl}$  variations using enrichment factors calculated for  $\text{Br}^-$  (data from Vengosh et al. (1992)<sup>48</sup> and McCaffrey et al. (1987)<sup>49</sup>) and extrapolated the expected  $\text{I}^-$

concentration relative to the  $\text{I}^-$  content in modern seawater (0.06 mg/L). We assume that  $\text{I}^-$ , like  $\text{Br}^-$ , behaves conservatively during evaporation of seawater and salt precipitation,<sup>48,49</sup> and thus the enrichment determined for  $\text{Br}^-$  can be applied for  $\text{I}^-$ . The  $\text{I}/\text{Cl}$  data reported here for flowback and produced waters from the Marcellus and Fayetteville shale formations show high  $\text{I}/\text{Cl}$  relative to the modeled evaporated seawater (Figure 3). Similar elevated levels of  $\text{I}^-$  and  $\text{I}/\text{Cl}$  were reported for oil and gas brines from Northern Appalachia ( $\text{I}^-$  range of 1.6–110 mg/L),<sup>26</sup> Texas (1–100 mg/L)<sup>23</sup> and Alberta, Canada (40–80 mg/L),<sup>22</sup> as well as formation waters from different basins in the U.S. ( $n = 550$ ) reported by Worden (1987).<sup>25</sup> Thus, it seems that the  $\text{I}^-$  in formation waters is derived from a secondary process rather than a single, primary source. The large  $\text{I}^-$  variations between different formations observed in this and previous studies<sup>25</sup> likely reflect the ranges in  $\text{I}^-$  concentrations in organic matter from the host formations rather the original brine. Iodine is known to accumulate in marine organic matter during early stages of sediment deposition and subsequent diagenesis releases iodine from organic matter to formation water as iodide.<sup>23,25,26</sup> At the same time, our data show that the  $\text{I}/\text{Cl}$  ratios are associated with  $\text{Br}/\text{Cl}$  (Figure 3), which indicates that the original source of the brines (i.e., degree of evaporation of the original brine, or halite dissolution) also plays a role on the abundance of  $\text{I}^-$  in the brines.

In contrast to  $\text{I}^-$ ,  $\text{NH}_4^+$  contents were highly correlated to  $\text{Cl}^-$  but with different  $\text{NH}_4^+/\text{Cl}$  ratios for different formation waters (Figure 2C). The high  $\text{NH}_4^+$  concentrations and the linear correlations with  $\text{Cl}^-$  shown in this study are consistent with data reported for formation waters from Fordoche Field in the Louisiana Gulf Coast Basin.<sup>29</sup> It has been suggested that  $\text{NH}_4^+$  in oil–brines has evolved from the release of nitrogen during thermal decomposition of organic matter.<sup>29</sup> The high correlation of  $\text{NH}_4^+$  with  $\text{Cl}^-$  within the formation fluids (Figure 2C) suggests that nitrogen mobilization from organic matter occurred during early stages of brine evolution and subsequent changes in both  $\text{Cl}^-$  and  $\text{NH}_4^+$  concentrations were due to dilution by meteoric water. The preservation of  $\text{NH}_4^+$  in the brines is most likely related to the highly reducing conditions, high salinity, and acidity of the formation waters. Most of the brines samples we analyzed had  $\text{pH} < 7.5$  (SI Table S1), in which  $\text{NH}_4^+$  is the predominant nitrogen species. Likewise, high salinity would increase the stability of  $\text{NH}_4^+$  (see speciation discussion below). Our data show that brines from different geological formations have distinctive  $\text{NH}_4^+$  levels, from which the Oneida brines were distinguished by the highest  $\text{NH}_4^+$  concentrations (mean =  $281 \pm 117$  mg/L; SI Figure S7).

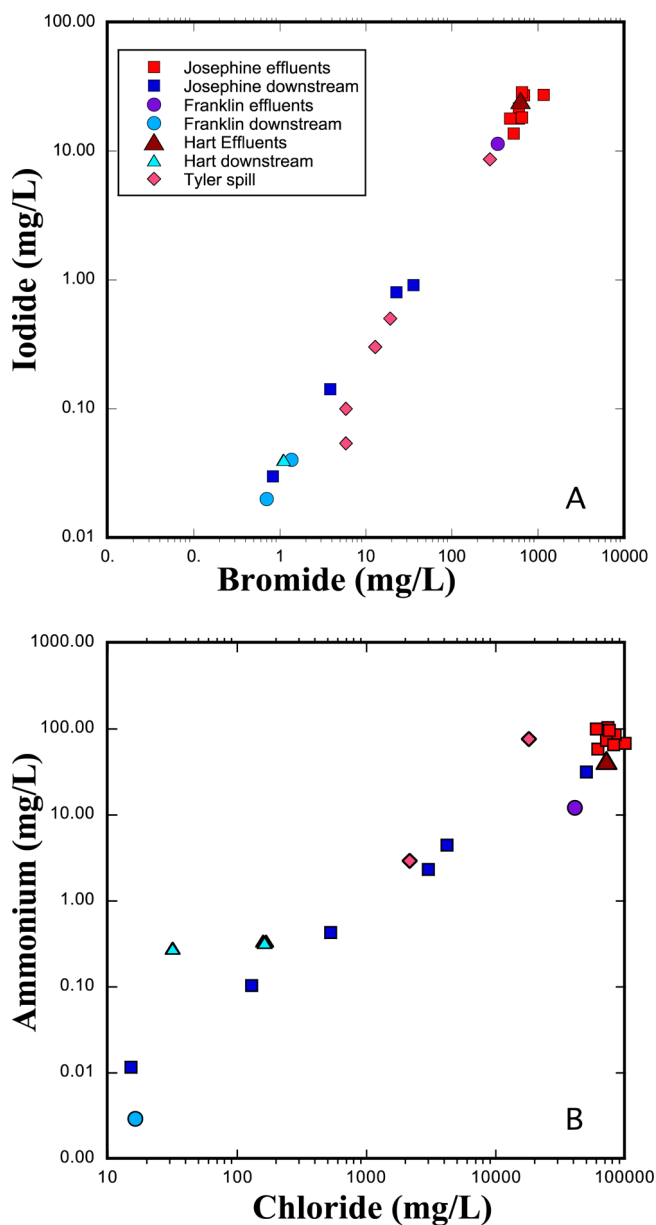
Previous studies have shown that shale rocks have typically high  $\text{NH}_4^+$  content (range of 1031 to 1345 ppm), relative to other rocks types (e.g., sandstone with a range of 30 to 287 ppm).<sup>27</sup> Thus, one would expect also high  $\text{NH}_4^+$  for formation water from shale formations. However, our data do not show differential enrichment of  $\text{NH}_4^+$  in flowback fluids from shale formations relative to conventional oil and gas produced waters. Overall, while the  $\text{Br}/\text{Cl}$  ratio was consistent for all of the Appalachian brines (Figure 1A), which reflects an origin from common parent brine, the  $\text{I}/\text{Cl}$  and  $\text{NH}_4^+/\text{Cl}$  ratios varied among brines from different geological formations in the Appalachian Basin (Figure 2). The variations of  $\text{I}/\text{Br}$  ratios have been used to identify flow of formation waters to overlying drinking aquifers in New York.<sup>50</sup> Our data indicate that the Upper Devonian formation waters have typically high  $\text{I}/\text{Br}$  and low  $\text{NH}_4^+/\text{Cl}$  ratios relative to formation waters from the Middle Devonian (Marcellus) and Silurian (Vernon, Herkimer, Oneida, and

Medina) formations (Figure 1 and SI Figure S8). This distinction could be used to further elucidate the migration of deep formation waters into shallow aquifers in the Appalachian Basin.<sup>47,50</sup>

**Environmental Implications.** In this study, we examined the discharge of OGW effluents from three brine treatment facilities in western Pennsylvania (Josephine, Franklin, and Hart) and flowback water spilled in Tyler County, WV (SI Table S3). The annual volume of treated OGW effluents discharged from the three brine treatment facilities varied from a maximum of 150 ML (Franklin site in 2010 and 2011) to about 50 ML (Franklin and Josephine sites in 2013; SI Figure S9). Treated effluents collected from the outfalls of each facility and downstream surface waters (Figure 1 and SI Figures S3–S6) contained elevated  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{NH}_4^+$  compared to upstream samples, which all had  $\text{I}^-$  and  $\text{NH}_4^+$  concentrations below the detection limits (Figure 4; SI Table S3). The data from the most recent Josephine effluent, collected in June 2014, were consistent with historical data (collected between 2010 and 2013) (Figure 5), indicating a long-term and continuous discharge of OGW effluents with high  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{NH}_4^+$  to surface waters. The latest data available from the Franklin site (SI Figure S4) indicate continued discharge of saline effluents in August 2014 (SI Table S3). Linear relationships for both  $\text{I}^-$  versus  $\text{Br}^-$  and  $\text{NH}_4^+$  versus  $\text{Cl}^-$  were observed in downstream surface waters affected by the discharge of the treated OGW (Figure 4). Surface water downstream from the Josephine site had linear correlations between  $\text{NH}_4^+$  and  $\text{Cl}^-$  ( $R^2 = 0.99$ ;  $p < 0.05$ ) and  $\text{I}^-$  and  $\text{Br}^-$  ( $R^2 = 0.91$ ;  $p < 0.03$ ). While halides are expected to mix conservatively, our data indicate that  $\text{NH}_4^+$  also behaves conservatively without any retardation, oxidation (abiotic or biotic), or outgassing of  $\text{NH}_3$ . This implies that there is no natural apparent attenuation of these contaminants when OGW enters streams, and, unlike radionuclides or heavy metals, halogens and ammonium will be transported downstream from discharge sites. Likewise, fluids collected from an accidental spill of hydraulic fracturing fluids (Tyler spill site in WV) showed similarly elevated concentrations of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{NH}_4^+$  and fit to the same linear relationships (Figure 4).

Nitrogen dissolved in water is composed of the nonionized form ( $\text{NH}_3$ ) and the ammonium cation ( $\text{NH}_4^+$ ) that, together, comprise Total Ammonia Nitrogen (TAN).<sup>51</sup> Previous data have suggested that the TAN toxicity to aquatic organisms is attributed specifically to the  $\text{NH}_3$  species rather than  $\text{NH}_4^+$ .<sup>45,51</sup> The equilibrium between the two species is controlled by pH, temperature and salinity; higher pH and temperature induce a higher fraction of  $\text{NH}_3$ , while higher salinity would reduce the fraction of  $\text{NH}_3$ .<sup>45,51</sup> The US Environmental Protection Agency (EPA) acute and chronic ambient water quality criteria for protecting freshwater organisms from potential effects of TAN are 17 mg/L and 1.9 mg/L, respectively, at pH = 7.<sup>51</sup> The effluents discharged from the Josephine (TAN = 60 to 100 mg/L), Hart (43 mg/L) and Franklin (12 mg/L) facilities had TAN values far exceeding the chronic EPA water quality standard and even the acute level in effluents from the Josephine and Hart outfalls. The pH of the effluents was typically high, between 8.1 (Franklin) to 9.4 (Josephine), reflecting alkaline conditions that are part of the treatment for NORMs in OGW.<sup>7</sup> The relatively high pH of the  $\text{NH}_4^+$ -rich effluents generates a larger fraction of the un-ionized ammonia ( $\text{NH}_3$ ) species in the solution.

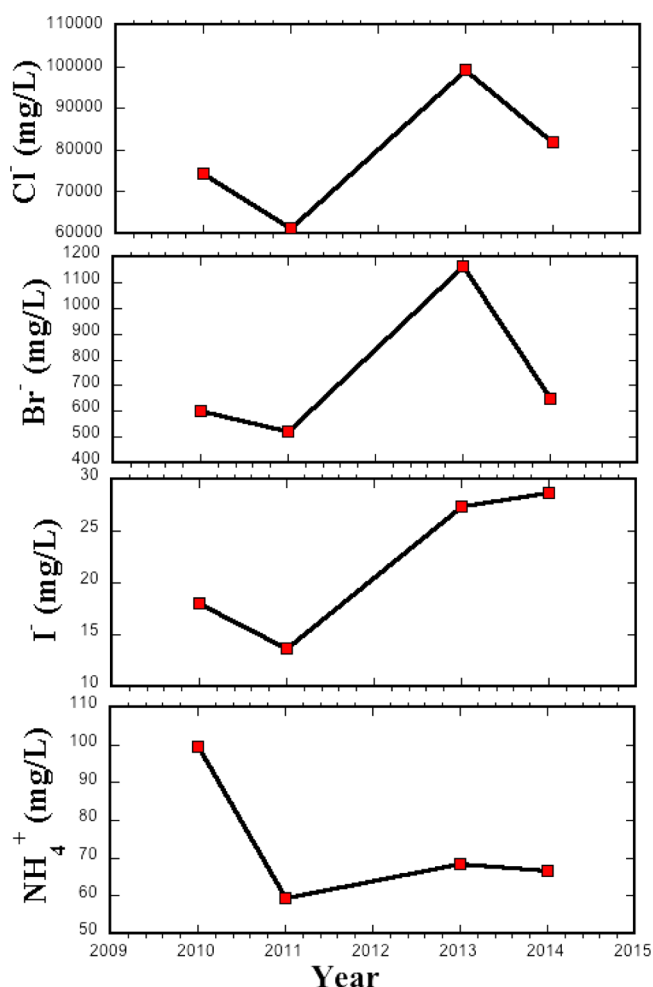
Modeling of the  $\text{NH}_3$  species distribution based on the ammonia dissociation constant (at 25 °C  $\text{p}K_{\text{NH}_4^+} = 9.2448$ ;<sup>45</sup> SI



**Figure 4.** Iodide versus bromide (A) and ammonium versus chloride (B) (log scale) in effluents discharged from three brine treatment sites in PA and effluents from a spill in WV compared to contaminated surface waters from the three disposal sites (see Figure 1 and SI Figure S1 for samples location). Upstream values for bromide, iodide, and ammonium were all below detection limit and therefore not included. Note the linear relationships between  $\text{I}^-$  and  $\text{Br}^-$  and between  $\text{NH}_4^+$  and  $\text{Cl}^-$ , reflecting the conservative behavior of all elements during disposal and mixing with surface waters.

Figure S10) indicates a large  $\text{NH}_3$  fraction at high pH (e.g., 61% at the Josephine site), which yields expected net  $\text{NH}_3$  concentrations of up to 40 mg/L (SI Figure S11). Although the 2013 EPA ambient water quality criteria for ammonia only reports values for waters at pH = 7, previous reports from 2009 and 1999 had lower criteria for pH = 8 (e.g., TAN of 19 mg/L vs 2.9 mg/L for acute exposure and 0.91 mg/L vs 0.26 mg/L for chronic exposure).<sup>51</sup> In addition, mixing of OGW with freshwater would significantly reduce the salinity, and increase the fraction of  $\text{NH}_3$  in the mixed water. Our results can explain a possible cause for widespread and massive death or distress of





**Figure 5.** Time series measurements of Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and NH<sub>4</sub><sup>+</sup> in Josephine effluents since 2010. Data were generated from multiple fieldtrips to Josephine outfall sites between 2010 and 2014. The latest data available are for June 2014.

aquatic species from unauthorized disposal of hydraulic fracturing fluids as observed in Acorn Fork Creek in southeastern Kentucky in 2007.<sup>52</sup> Likewise, severe damage and mortality to ground vegetation was reported from an experimental release of hydraulic fracturing fluids in a forest in WV<sup>53</sup> and may be explained by the elevated concentrations of halogens and ammonium observed in this study. Overall, the direct impact of OGW disposal to the aquatic life in each of the disposal sites (Figure 1) and spill cases depends on the dilution factor and the relationships between the volume of the effluents and the downstream stream and river system. Our data clearly show that both conventional and unconventional OGW release to the environment is associated with significant contributions of I<sup>-</sup> and NH<sub>4</sub><sup>+</sup> to impacted streams.

In addition to direct contamination of surface waters and aquatic ecosystems, elevated halides and ammonium in waterways could increase the risk of forming toxic DBPs in drinking water utilities downstream from areas of treated OGW disposal or accidental spills.<sup>17,28,35,36</sup> The I<sup>-</sup> and Br<sup>-</sup> concentrations in all the surface water samples downstream of oil and gas treatment facilities show a linear relationship with an I/Br (molar) ratio of 0.026, which reflects the ratio in OGW from the disposal sites (Figure 4). The I/Br ratio in the OGW would affect the speciation of DBPs formed during chlorine, ozone or chloramine

disinfection.<sup>16</sup> For example, an order of magnitude higher I/Br ratio (mean = 0.2;  $n = 6$ ) was observed in the Fayetteville flowback and produced waters, which would result in a larger ratio in potentially affected natural waters from contamination of Fayetteville OGW. Similarly, high NH<sub>3</sub> in surface water could also affect chlorine disinfection in downstream drinking water treatment plants. If the surface water–ammonia concentration exceeds 0.5 mg-N/L (35  $\mu$ M), then addition of a typical dose of chlorine (2.5 mg/L as Cl<sub>2</sub> or 35  $\mu$ M) would result in de facto chloramination; chloramines tend to be weaker disinfectants than chlorine and alter DBP formation patterns. For produced waters with higher ammonium such as the Lower Silurian Oneida Formation (63–432 mg/L NH<sub>4</sub><sup>+</sup>), these effects would be seen when at a contribution of as little as 0.15–1% OGW.

Likewise, the NH<sub>4</sub>/Cl (weight) ratios of the contaminated waters mimic the NH<sub>4</sub>/Cl ratios in OGW effluents from the treatment sites ( $1-3 \times 10^{-3}$ ; Figure 4). We use these relationships to predict the possible occurrences of Br<sup>-</sup>, I<sup>-</sup>, and NH<sub>4</sub><sup>+</sup> in affected waters. We use the threshold of Cl=250 mg/L, which is the typical upper limit for drinking water. In the case of Josephine treatment site where the average of Cl<sup>-</sup> content of the effluents was 75 000 mg/L, a contaminated water with Cl = 250 mg/L is equivalent to a fraction of 0.003 (0.3%) of OGW mixed with river water (Cl = 30 mg/L). At that chloride level, the Br<sup>-</sup> content would be 2 mg/L, I<sup>-</sup> = 0.06 mg/L, and NH<sub>4</sub><sup>+</sup> = 0.25 mg/L.

The issue of disposal of OGW is not restricted to the Marcellus shale. Elevated levels of halides and ammonium were also recorded in other shale plays in the U.S., such as produced waters from the Bakken formation with Cl<sup>-</sup>, Br<sup>-</sup>, and NH<sub>4</sub><sup>+</sup> mean values of  $154\,320 \pm 72\,000$  mg/L,  $724 \pm 339$  mg/L, and  $2098 \pm 966$  mg/L, respectively.<sup>54,55</sup> In addition, high levels of halides, and possibly ammonium, are expected to occur in many of the highly saline and anoxic formation waters around the world. For example, formation waters from the Sichuan Basin, which consists of about 40% of Chinese shale gas reserves, also contain elevated bromide concentrations, up to 2,460 mg/L.<sup>56</sup> Consequently, the management of OGW, particularly in areas of future shale gas development in different parts of the world (e.g., China, Canada, South Africa, and Australia) should prevent disposal to surface water without adequate treatment and minimize leaking of OGW to the environment. This issue is more urgent in countries such as the EU and China where deep-well injection is not allowed.

In conclusion, this study shows high concentrations of halides (Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>) and NH<sub>4</sub><sup>+</sup> in unconventional flowback and produced waters from the Marcellus and Fayetteville shale plays, as well as conventional oil and gas produced waters from the Appalachian Basin. Our data show that high concentrations of I<sup>-</sup> and NH<sub>4</sub><sup>+</sup> in formation waters reflect geogenic variations within the host geological formations. The occurrence and distribution of these elements in freshwater contaminated by these wastewaters directly mimics the composition of the OGW effluent due to their conservative behavior during the release to natural waters.<sup>52,57</sup> In addition to the direct impacts to aquatic ecosystems, the disposal and/or accidental release of OGW with elevated levels of halides and NH<sub>4</sub><sup>+</sup> can promote the formation of toxic brominated and iodinated DBPs in downstream drinking water utilities. Due to the elevated concentrations in both hydraulic fracturing flowback and produced waters and conventional produced water, halting the disposal of hydraulic fracturing fluids alone will not reduce the risks associated with discharge of OGW to surface waters. The relatively high frequency of spills

associated with the intensity of shale gas development<sup>3</sup> and reports of an overall increase of the salinity in watersheds associated with hydraulic fracturing activities,<sup>58</sup> combined with data presented in this study, suggest that the release of OGW to the environment is one of the major risks associated with the development of hydraulic fracturing.

Finally, it is important to note that oil and gas development in the U.S. is exempted from several federal environmental regulations, including exemptions of hydraulic fracturing from the Safe Drinking Water Act and of oil and gas exploration and production wastes from the hazardous waste portion of the Resource Conservation and Recovery Act. Consequently, state governments are responsible for the operation of OGW and different states have different regulations.<sup>59</sup> In Pennsylvania, OGW is released to the environment from brine treatment sites with limited restriction on the TDS of the effluents. Yet our data indicate that brine treatment for both conventional and unconventional OGW is insufficient to remove halides and ammonium. As far as we are aware, iodide and ammonium are not regulated, nor monitored in any of the OGW operations in the U.S. Consequently, the data presented in this study contribute to the growing body of information that shows there are significant environmental and ecosystem impacts of current OGW disposal practices in the U.S. and that regulatory action is needed to address these concerns.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Further information on the analytical techniques. Eleven figures, and 3 tables. 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.

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