Impact of Increased Bromide in Water Sources on Drinking Water DBPs

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Reports of increased DBPs could be tied to Bromide in source waters
Bromine has twice the atomic mass of chlorine; thus, brominated DBPs have higher MW compared to their chlorinated counterparts (e.g., bromoform versus chloroform). Bromine can also react with more precursors.

- Because the TTHM MCL is mass based, not molar based, the same amount of precursor will result in a higher concentration of TTHM with bromine than with chlorine.
- Generally brominated DBPs form faster than chlorinated DBPs

Brominated DBPs have reportedly greater health risks than chlorinated DBPs.
Bromide in Source Water

Naturally occurring at background levels.

- ICR database (1998) 80% of samples less than 100 µg/L
- Amy et al. (1994) reported range of <5 to 429 µg/L
Bromide in Source Water

Potential point sources for bromide:

- Coal-fired power plant effluent
- Other possible sources
  - Unconventional gas development wastewater
  - Biocides for cooling tower disinfection
  - Other industries

Bromide levels as high as 1 mg/L were measured in a NC river (Greune 2013).
Bromide Sources: Hydraulic Fracturing
Hydraulic Fracturing Wastewater

- Introduces water (millions of gallons per well) to increase permeability through fracture generation
- Wastewater includes
  - Flowback water quickly returns to the surface
  - Produced water takes longer to return
- Both contain bromide from the shale deposit, produced water has a higher concentration due to the longer time available for the bromide to leach from the deposit
- Flow back water is usually managed onsite through recycling and minimization
- Produced water is injected into the ground or sent to a centralized brine treatment plant (CWT) or publicly owned treatment plant (POTW) followed by surface water discharge.
Many Published and Ongoing Work Looking at Correlation Between Process and Bromide


Greune, A., Knappe, D. (2013.) Bromide Occurrence in North Carolina Surface Waters. NC State University
# Hydraulic Fracturing Wastewater

## Bromide Concentrations of Treatment Plant Effluents that are Treating Fracking Wastewater

<table>
<thead>
<tr>
<th>Name</th>
<th>Treatment Facility Type</th>
<th>Br Concentration (mg/L)</th>
<th>Receiving Watershed</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA Brine Josephine Facility</td>
<td>CWT</td>
<td>601 - 8290</td>
<td>Allegheny</td>
</tr>
<tr>
<td>PA Brine Franklin Facility</td>
<td>CWT</td>
<td>364 - 770</td>
<td>Allegheny</td>
</tr>
<tr>
<td>Minard Oil Dent Treatment Facility</td>
<td>CWT</td>
<td>606 - 657</td>
<td>Monongahela</td>
</tr>
<tr>
<td>Brockway Sewer Authority</td>
<td>POTW</td>
<td>2.32 - 19.2</td>
<td>Allegheny</td>
</tr>
<tr>
<td>Ridgway Borough</td>
<td>POTW</td>
<td>2.88 - 11.5</td>
<td>Allegheny</td>
</tr>
<tr>
<td>City of McKeeport</td>
<td>POTW</td>
<td>0.119 - 0.6</td>
<td>Monongahela</td>
</tr>
<tr>
<td>Franklin TWP of Greene County</td>
<td>POTW</td>
<td>&lt;0.016 - 20.91</td>
<td>Monongahela</td>
</tr>
</tbody>
</table>

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a Laboratory data analysis submissions to EPA at http://www.epa.gov/region03/marcellus_shale
Bromide Sources: Power Plants
Three Sources of Bromide from Coal-Fired Power Plants

- Natural bromide in the coal-continuous discharge
- Bromide added for mercury control-continuous
- Bromide added as biocide-slug discharge
- Discharges associated with wet scrubbers
MATS: Mercury and Air Toxic Standards

- To lower metals (including mercury), acid gases, particulates, NOx, and SO2 emissions
- Power plants must comply by 2015
- Resulting in more treatment, modifications of treatment or installations of wet scrubbers
Increase in Wet Scrubber Use

- With new mercury control requirements scrubber technology will be utilized more frequently
  - Wastewater volumes and bromide concentrations could increase from
    - Oxidant use increase
    - Scrubber use increase
- Scrubber use may also increase if power plants switch to a coal with higher sulfur content
  - Coal with high sulfur content may have higher BTU value and is less expensive
  - Wet Scrubber technology is ideal for coal with sulfur content of >2% (by weight)
Coal-Fired Power Plants: Wet Scrubbers

- Lignite: 3 ppm, Sub-Bit: 1-2 ppm, Bit: 20 ppm (high S, high BTU/ton)
- Bromide additive (CaBr$_2$) increases mercury removal from effluent air (25 – 300 ppm reduces Hg by 90%)
- ~100% of the bromide from the coal and coal additives is discharged through wet scrubber wastewater
Task: Assess Impact of Power Plant Effluent on Water Plants

Methods

• Review published and unpublished sources to find:
  – Bromide occurrence data
  – Bromide increased occurrence data
  – Requested brominated DBP data through State and AWWA contacts
  – AWWA contacted utilities asking for data

• Map power plants, sources and WTPs to identify at risk facilities

• Interviewed some utility personnel to determine if impacts were noted.
Task: Assess Impact of Power Plant Effluent on Water Plants

Methods

• SDWIS data used to determine if DBP violation had occurred
• Interviews and data review used to determine if the speciation had changed
Power Plants Impacted by New Air Quality Regulations
Surface WTPs and Coal-Fired Plants
DBP Impacts: Power Plant/ Fracking

<table>
<thead>
<tr>
<th>Power Plant Name</th>
<th>Capacity (MW)</th>
<th>Scrubber Installation Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fort Martin Power Station</td>
<td>1152</td>
<td>2013</td>
</tr>
<tr>
<td>Hatfield Power Station</td>
<td>1728</td>
<td>2009</td>
</tr>
<tr>
<td>Mitchell Power Station</td>
<td>300</td>
<td>1982</td>
</tr>
<tr>
<td>Elrama Power Plant</td>
<td>510</td>
<td>1976</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WTP Name</th>
<th>Year of DBP Violation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muni Auth Boro of Carmichaels</td>
<td>2010, 2011</td>
</tr>
<tr>
<td>Tri Cnty JT Muni Auth</td>
<td>2009, 2011</td>
</tr>
<tr>
<td>Century Townhomes Assn</td>
<td>2008, 2009</td>
</tr>
</tbody>
</table>
Bromide Impact Identification: Power Plants

• 332 public electric utilities use coal as an energy source (year 2002-2011)

• 302 of these coal fired power plants have NPDES permits
  – 118 have wet scrubber installations
  – 39 have dry scrubber installations
  – More to come?
WTPs and Coal Plants in Same Watershed

- Coal-Fired Power Plants with Wet Scrubbers and Downstream WTP
- Surface Water Treatment Plants Downstream from Power Plant Effluent
Bromide Impact Identification: At Risk Facilities

- 57 (out of 118 total) coal-fired power plants with wet scrubber installations in WTP watersheds
- 96 downstream surface water treatment plants
  - 25 have had DBP violations
  - 17 could be identified as having DBP violations after wet scrubber installation
Average Quarterly TTHM WTP B 2006 to 2013
THM Speciation for WTP B Quarters Preceding and Following the Wet Scrubber Installation Year, 2008

Before Upstream Wet Scrubber Installation
- Q4 2006
- Q2 2007

After Upstream Wet Scrubber Installation
- Q4 2012
- Q2 2013
THM Data From Water Plant B

Average quarterly TTHM 2006 to 2013

THM Speciation preceding and following wet scrubber installation, 2008
THM Data from Water Plant C

TTHM concentrations 2006 to 2012

TTHM Speciation preceding and following the wet scrubber installation, 2008
THM Data from Water Plant D

Average quarterly TTHM 2005 to 2012

THM speciation preceding and following the wet scrubber installation year, 2006 and 2007
Bromide Incorporation Factor

All Locations for Each System
(BIF = 3 for CHBr$_3$ and BIF = 0 for CHCl$_3$)
Increased DBP due to MW vs Formation

Median Increase in TTHM (µg/L)

- due to substitution of Cl with Br in TTHM
- due to increased number of moles of TTHM produced

<table>
<thead>
<tr>
<th>Water Plant</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median Increase in TTHM (µg/L)</td>
<td>15</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>
Conclusions

• Bromide in source waters had a significant impact on utilities’ DBPs in changing chlorinated to brominated and in increasing DBP concentrations

• Roughly half the DBP increase was due to MW increase and half due to increased formation

• Utilities need to be aware of upstream activities

• Work is continuing on potential impacts from the 332 municipal power plants-looking for utilities