1,4-Dioxane and Other Emerging Contaminants in the Cape Fear River Basin

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Presentation Overview

• What is 1,4-dioxane?
• 1,4-dioxane occurrence in
  – Haw and Cape Fear River
  – Drinking water
    • Pittsboro
    • Fayetteville
    • Wilmington
• 1,4-dioxane sources
• Other contaminants of concern
  – Per- and polyfluorinated alkyl substances (PFASs)
  – Bromide
What is 1,4-dioxane?

• 1,4-dioxane ≠ dioxin

• Uses and potential sources of 1,4-dioxane
  – Solvent stabilizer (phased out)
  – Industrial solvent (textile, paper, specialty chemicals)
  – By-product of manufacturing processes involving ethylene oxide (polyester, PET, detergents, cosmetics)
1,4-Dioxane – Background Information

- Miscible in water
- Very difficult to remove from water
- Monitored nationwide in drinking water as part of EPA’s 3rd Unregulated Contaminant Monitoring Rule (UCMR3)
  - Finished drinking water samples only
  - Public water systems serving >10,000 people
1,4-dioxane cancer risk

• Likely human carcinogen (EPA IRIS database)
• Lifetime consumption of drinking water containing
  – 0.35 µg/L = 1:1,000,000 excess cancer risk
  – 3.5 µg/L = 1:100,000 excess cancer risk
  – 35 µg/L = 1:10,000 excess cancer risk
• Comparison with disinfection by-products
  – Bromodichloromethane: 0.6 µg/L = 1:1,000,000 risk
  – Dibromochloromethane: 0.4 µg/L = 1:1,000,000 risk
Occurrence - EPA’s Third Unregulated Contaminant Monitoring Rule (UCMR3)

<table>
<thead>
<tr>
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<th>Samples*</th>
<th>Public Water Systems*</th>
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<td>(\geq 0.35 \mu g/L)</td>
<td>US</td>
<td>3.0%</td>
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<td></td>
<td>NC</td>
<td>6.0%</td>
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<td></td>
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<td>7.0%</td>
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<tr>
<td></td>
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<td>15.9%</td>
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</table>

* n = 36,479 (US); 1,325 (NC) + n = 4,905 (US); 151 (NC)

- Drinking water samples \(\geq 0.35 \mu g/L\) derived from surface water:
  - US: 23%
  - NC: 96%

- 7 of the 20 highest 1,4-dioxane concentrations occurred in NC (all derived from Cape Fear River water)
Drinking water samples with 1,4-dioxane ≥3.5 µg/L (UCMR3 data as of July 2016)

Blue: ground water
Green: surface water
Field Sample Collection

Preservatives:
- 50 mg/L sodium sulfite
- 1 g/L sodium bisulfate

Added sequentially in the field

Brown glass bottles 500 mL with PTFE Caps
1,4-Dioxane Concentrations in Haw River at Bynum

2014 Average: 16 µg/L
2015 Average: 17 µg/L
2016 Average: 8.6 µg/L
Fayetteville Intake (P.O. Hoffer)

1,4-Dioxane Concentration (µg/L)

Sampling Date

2014 Average: 4.1 µg/L
2015 Average: 2.2 µg/L
2016 Average: 1.6 µg/L
2017 Average: 3.9 µg/L
1,4-Dioxane is not Removed in Conventional Water Treatment Plants

**Pittsboro**

- Avg. raw: 8.8 µg/L
- Max. raw: 36 µg/L
- Avg. treated: 8.7 µg/L
- Max. treated: 31 µg/L

**Fayetteville**

- Avg. raw: 2.8 µg/L
- Max. raw: 9.8 µg/L
- Avg. treated: 2.6 µg/L
- Max. treated: 9.6 µg/L

**1,4-Dioxane Concentration (µg/L)**

**Date**

- Avg. raw: 0.35 µg/L
- Max. raw: 0.35 µg/L
1,4-Dioxane is Partially Oxidized by Ozone

- Avg. raw: 3.8 µg/L
- Max. raw: 7.7 µg/L
- Avg. treated: 1.2 µg/L
- Max. treated: 2.1 µg/L

Ozone oxidized 67% of influent 1,4-dioxane
Source Identification: Haw River

<table>
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<th>Date</th>
<th>Upstream Concentration (µg/L)</th>
<th>Downstream Concentration (µg/L)</th>
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<td>Feb-15</td>
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<tr>
<td>Mar-15</td>
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<td>&lt;2</td>
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△ WWTP Discharge
● Sampling Point
## Source Identification: S. Buffalo Creek

![Map of S. Buffalo Creek with sampling points and WWTP discharge](image)

<table>
<thead>
<tr>
<th>Date</th>
<th>Upstream Concentration (µg/L)</th>
<th>Downstream Concentration (µg/L)</th>
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<td>Jul-16</td>
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<td>Oct-16</td>
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</table>
Source Identification: Deep River

![Map of Deep River with sampling sites](image)

![Box plots showing 1,4-dioxane concentration (µg/L)](image)
Regulatory Framework

• No federal drinking water standard
• No NC drinking water standard
• NC groundwater standard: 3 μg/L
• Surface water quality (in-stream) standard:
  – 0.35 μg/L for streams classified as water supplies (WS-I through WS-IV)
  – 80 μg/L for other stream classifications

15A NCAC 02B .0208 STANDARDS FOR TOXIC SUBSTANCES AND TEMPERATURE
For carcinogens, the concentrations of toxic substances shall not result in unacceptable health risks and shall be based on a Carcinogenic Potency Factor (CPF). An unacceptable health risk for cancer shall be considered to be more than one case of cancer per one million people exposed (10^-6 risk level).
CONCLUSIONS

• In the Cape Fear River watershed, multiple sources of 1,4-dioxane exist in the uppermost reaches of the watershed
• NC surface water quality standard of 0.35 µg/L continuously exceeded at drinking water intakes in the watershed
• Pretreatment staff at municipalities have identified at least some 1,4-dioxane sources
• At some locations, 1,4-dioxane concentrations exhibit a decreasing trend, possibly as a result of source control efforts
Perfluoroalkyl substances (PFASs) are organic compounds in which all C-H bonds are replaced with C-F bonds.

Perfluorocarboxylic acids
(e.g. perfluorooctanoic acid, PFOA or C8)

Perfluorosulfonic acids
(e.g. perfluorooctane sulfonate, PFOS)
**PFAS Occurrence in CFR Watershed**

![Bar chart showing PFAS occurrence in different communities.]

- **Community A**: n=127
- **Community B**: n=76
- **Community C**: n=35

*Average concentration in drinking water source (ng/L)*

- PFBA
- PFPeA
- PFHxA
- PFHxA
- PFOA
- PFNA
- PFDA
- PFBS
- PFHxS
- PFOS
- PFPrOPrA
PFAS Concentrations in the Source Water of 3 Communities (June-December 2013)

Sun et al., ES&T Letters, 2016

PFPrOPrA = perfluoropropoxypropanoic acid (aka “GenX” – a replacement for PFOA)
PFASs, including “GenX,” were not measurably removed in a full-scale WTP employing ozonation, biofiltration, and UV disinfection (Aug. 20, 2014)

Sun et al., ES&T Letters, 2016
Other PFECAs were present at much higher concentrations and were not measurably removed in a full-scale WTP employing ozonation, biofiltration, and UV disinfection (Aug. 20, 2014)

Sun et al., ES&T Letters, 2016
Bromide is a precursor for disinfection by-products (DBPs)

- $\text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^-$
- $\text{HOCl} + \text{Br}^- \leftrightarrow \text{HOBr} + \text{Cl}^-$
- $\text{DOM} + \text{HOCl} + \text{HOBr} \leftrightarrow \text{trihalomethanes (THMs)} + \text{haloacetic acids (HAAs)} + \ldots$

Trihalomethanes (THMs)

- Chloroform
  Molecular weight = 119.4 g/mol
  One-in-a-million cancer risk: -

- Bromodichloromethane
  Molecular weight = 163.8 g/mol
  One-in-a-million cancer risk: 0.6 µg/L

- Dibromochloromethane
  Molecular weight = 208.3 g/mol
  One-in-a-million cancer risk: 0.4 µg/L

- Bromoform
  Molecular weight = 252.7 g/mol
  One-in-a-million cancer risk: 4 µg/L

Drinking water standard:
Σ THMs = 80 µg/L
Effect of bromide concentration on THM speciation

THM Mole Fraction

Raw Water Bromide Concentration (µg/L)

CHCl3  BDCM  DBCM  CHBr3
Bromide and Speciated THM data for 4th quarter of 2013
Acknowledgments

• Students in the Knappe research group: Zachary Hopkins, Harold Hounwanou, Joshua Kearns, Catalina Lopez, Amie McElroy, Jonathan Moreno Barbosa, Hillary Stoll, Mei Sun, Chuhui Zhang

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  – NSF RAPID;GOALIE (#1449768)

• Utility participants: Fayetteville Public Works Commission, Cape Fear Public Utilities Commission, Town of Pittsboro

• North Carolina Department of Environmental Quality: Carrie Ruhlman, Tammy Hill
### Source Identification: Deep River

#### NCSU24 - Downstream WWTP
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