A Cooperative Study on 1,4-Dioxane

October 2014 - August 2015

North Carolina
Division of Water Resources
Overview

• What is 1,4-Dioxane?
• Potential sources
• Treatment and removal
• Background
• UCMR3
• Current studies/monitoring
• Hot spots
• The future
What Exactly are we Talking About?

- **Chemical Name:** Dioxane (1,4-dioxane)
- **CAS#:** 123-91-1
- **Chemical Formula:** $\text{C}_4\text{H}_8\text{O}_2$
- **Department:** Organics
- Fully miscible in water
What is 1,4-Dioxane?

- Probable human carcinogen
- Industrial solvent stabilizer
- Found in paint strippers, varnishes, soaps, make-up, antifreeze, etc.
- By-product of process used to make/recycle polyethylene terephthalate (PET) plastic and polyester products

(Mohr, 2001; Zenker et al., 2003)
Potential Sources

- **Industrial wastewater streams**
  - Solvent
  - Stabilizing agent
  - By-product

- **Wastewater treatment facilities**
  - Point of entry

- **Groundwater**
  - Landfill leachate
  - Active/inactive hazardous sites – TCA plumes
Treatment and Removal

• Removal via conventional water and wastewater treatment processes are generally ineffective.

• Advanced oxidation processes can achieve substantial removal
  ▫ Hydrogen peroxide
  ▫ Ozone
  ▫ UV photooxidation

(Mohr, 2001; Zenker et al., 2003)
Background

- DWR Alerted of potential contamination in Cape Fear River – March 2014
  - NCSU Professor Dr. Detlef Knappe
  - Unregulated Contaminant Monitoring Rule (UCMR3) data

- No current Federal or State regulation
Unregulated Contaminant

- No EPA established maximum contaminant level for drinking water
  - 2012 Drinking Water Standards and Health Advisory
    - 1 in 1,000,000 estimated lifetime cancer risk at 0.3 μg/L
    - 1 in 10,000 estimated lifetime cancer risk at 35 μg/L
  - EPA currently in process of collecting and evaluating unregulated contaminant monitoring rule (UCMR) data.
What is UCMR3?

*The third Unregulated Contaminant Monitoring Rule*

- Per 1996 SDWA - EPA, States, Laboratories and PWSs are required to monitor for ≤30 unregulated contaminants using EPA methods

- 2013 – 2015
  - 28 chemicals + 2 viruses (includes dioxane)

- All PWSs serving more than 10,000 people and 800 representative PWSs serving 10,000 or fewer people will monitor
UCMR3 Data Continued...

- UCMR3 data set is one of the primary sources of occurrence and exposure information EPA uses to develop regulatory decisions for emerging contaminants

- Data reported quarterly

http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/ucmr3/
NC Regulatory Framework

• NC groundwater standard = 3.0 μg/L (outdated)

• NC calculated surface water criteria to protect human health (15A NCAC 02B.0208) based on 1 in 1 million cancer risk.
  ▫ 0.35 μg/L in water supply waters (except WS-V, Jordan)
  ▫ 80 μg/L in non-water supply waters
What’s the Issue?

• As of August 2015, North Carolina has ~ 70 PWSs with detectable levels of 1,4-dioxane
  ▫ ~17 PWSs with levels in excess of the NC calculated surface water criteria to protect human health (0.35 ug/L)

• Health effects of long-term exposure
• Public perception
• Water treatment facilities are receiving 1,4-dioxane contaminated water
• Removal is difficult/expensive
• EPA may regulate 1,4-dioxane
  ▫ Regulations would likely fall on water treatment facilities
DWR Studies

• 1-year study initiated in October 2014
  ▫ Screen surface waters at 12 sites monthly – 2 of which are WTP intakes
    • 9 current ambient stations
    • 3 study-specific stations

• Source ID study initiated in June 2015
  ▫ Anticipated completion date of May 2016
  ▫ Screen 7 additional sites monthly

• Solid waste method 8270 SIM (3.0 μg/L PQL)
Other Special Studies

- Fayetteville PWC
  - 4 stations at/near WTP intake
  - WWTP process samples

- Dr. Detlef Knappe - NCSU
  - Monthly collection at all DWR sites + ~43 other stations
*Median 1,4-dioxane concentration range: <0.1 – 227 µg/L

*Mean 1,4-dioxane concentration range: <0.1 – 384 µg/L
Hot Spots

- Haw River
- South Buffalo Creek
- Haskett Creek
- Reedy Fork Creek near Ossipee
Confluence with Reedy Fork

Jordan Lake

B2100000 near Pittsboro WTP Intake
Haw River

EL = 0.35 µg/L

1,4-dioxane EL = 80 µg/L

EL = 0.35 µg/L

- Reidsville WWTP
- NPS?
- NPS?
- Burlington Eastside WWTP
- Median load = 33 lb/day
- Pittsboro WTP Intake
- Median load = 32 lb/day
- Jordan Lake

Flow Direction

Month:
- October
- November
- December
- January
- February
- March
- April
- May
- June
- July
- August

Mean
Median
Reidsville

• Upstream Reidsville WWTP (NCSU44)
  ▫ Class WS-IV, NSW (0.35 µg/L)
    • Average 1,4-dioxane concentration = 0.9 µg/L
• Downstream Reidsville WWTP (NCSU43)
  ▫ Class WS-IV, NSW (0.35 µg/L)
    • Average 1,4-dioxane concentration = 88.5 µg/L
• Downstream Reidsville WWTP (B4, June-Aug)
  ▫ Class WS-IV, NSW (0.35 µg/L)
    • Average 1,4-dioxane concentration = 124.1 µg/L
• Downstream Reidsville WWTP (B1)
  ▫ Class WS-V, NSW (80 µg/L)
    • Average 1,4-dioxane concentration = 48.6 µg/L
Haw River near Reidsville

Maximum measured concentration at NCSU44 = 0.6 µg/L
Haw River near Reidsville

1,4-Dioxane Concentration Along Haw River

1,4-dioxane EL = 0.35 µg/L

1,4-dioxane EL = 80 µg/L

Month:
- October
- November
- December
- January
- February
- March
- April
- May
- June
- July
- August

- Red: Mean
- Black: Median

Reidsville WWTP
Greensboro

- **Upstream TZ Osborne (NCSU48)**
  - **Class WS-V (Jordan watershed - 80 µg/L)**
    - Average 1,4-dioxane concentration = 1.8 µg/L

- **Downstream TZ Osborne (B0750000)**
  - **Class WS-V (Jordan watershed - 80 µg/L)**
    - Average 1,4-dioxane concentration = 108 µg/L
Greensboro

- UTs near haz waste sites (NCSU54 & NCSU51)
  - Class WS-V (Jordan watershed - 80 µg/L)
    - NCSU54 Avg 1,4-dioxane concentration = 50.1 µg/L
    - NCSU51 Avg 1,4-dioxane concentration = 21.3 µg/L

- S Buffalo Creek (NCSU55, NCSU52, NCSU53)
  - Class WS-V (Jordan watershed - 80 µg/L)
    - NCSU55 Avg 1,4-dioxane concentration = 10.2 µg/L
    - NCSU52 Avg 1,4-dioxane concentration = 9.2 µg/L
    - NCSU53 Avg 1,4-dioxane concentration = 12.6 µg/L
South Buffalo Creek

* NCSU53 shows possible loading from hazardous waste sites.

* 1,4-dioxane concentration tends to decrease ups T.Z. Osborne (NCSU48), then increase dns of discharge.
South Buffalo Creek

1,4-Dioxane Concentration Along South Buffalo Creek

- **Month**
  - October
  - November
  - December
  - January
  - February
  - March
  - April
  - May
  - June
  - July
  - August
  - September

- **Evaluation Level** = 80 µg/L

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<thead>
<tr>
<th>Location</th>
<th>Median Load</th>
<th>Notes</th>
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<tbody>
<tr>
<td>UT with Haz Waste Site</td>
<td>0.21 lb/day</td>
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<tr>
<td>UT with Haz Waste Site</td>
<td>0.19 lb/day</td>
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<td>T.Z. Osborne WWTP</td>
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Reedy Fork

1,4-dioxane EL = 80 µg/L

Month
- October
- November
- December
- January
- February
- March
- April
- May
- June
- July
- August
- Mean
- Median

Locations:
- Lake Townsend
- Buffalo Creek
- Mobile Home Park
- Used Tire Store
- Inactive Hosiery Mill

Flow Direction
Haw River, from Ossipee to Bynum

1,4-dioxane EL = 80 μg/L at all stations shown

- October
- November
- December
- January
- February
- March
- April
- May
- June
- July
- August
- Mean
- Median

EL = 0.35 μg/L by Pittsboro intake

Flow Direction

Inactive textile mill & haz waste site, school; Added station for source tracking
Reedy Fork (mobile home park, closed hosiery mill, used tire store), school; Added station for source tracking
Mobile home park & haz waste, pre-reg landfill, domestic discharges, brownfield; Need to add station
Stony Creek Reservoir, Burlington Eastside WWTP, inactive industries
Graham WWTP, pre-reg landfills, haz waste (nutrition company)
Big Alamance Creek (Burlington Southside WWTP)

(15 miles downstream) Pittsboro WTP intake
1,4-dioxane:
median = 11 μg/L
mean = 19 μg/L
Deep River
Upstream & Downstream from Hasketts Creek

Monitoring Station
NCSU25 (ups Hasketts Crk)
NCSU23 (dns Hasketts Crk)

Evaluation level = 80 µg/L
Hasketts Creek
Upstream & Downstream from Asheboro WWTP

* B2 sampled beginning in June 2015; Non-detect (<3 µg/L) in June, July and August.

* 4 highest results at NCSU24 were qualified (out of calibration range).
Asheboro

1,4-dioxane EL = 80 ug/L

Month
- October
- December
- January
- February
- March
- April
- May
- June
- July
- August
- Mean
- Median

Asheboro WWTP

Flow Direction
Cape Fear River Stations

- B7480000 near Hoffer Intake
- B8 at Harnett County Intake
- Confluence of Deep & Haw Rivers
1,4-dioxane EL = 0.35 ug/L at all stations

Median load
NCSU07a: 28 lb/day
B8: 30 lb/day
B8370000: Median load 30 lb/day
B7480000: Median load 34 lb/day
B8300000: Median load 30 lb/day

Fayetteville Hoffer WTP Intake

Flow Direction
Downstream on the Cape Fear

• All sites monitored on the Cape Fear River are classified as water supplies

• 77% of data above calculated criteria (0.35 μg/L) for water supply waterbodies
Future Monitoring

- Discontinued monitoring at stations with consistently low ambient concentrations

- Continue with source identification sampling

- Composite sampling on Reedy Fork Creek
  - Cooperative study with NCSU
  - Variations in concentrations over period of time

- Pursue resources to expand monitoring into Neuse and Yadkin River basins
DWR Plans

- Proactively work with industries generating 1,4-dioxane to reduce/eliminate source(s) prior to regulation

- Effluent monitoring requirements to NPDES WWTP permits near hot spots