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

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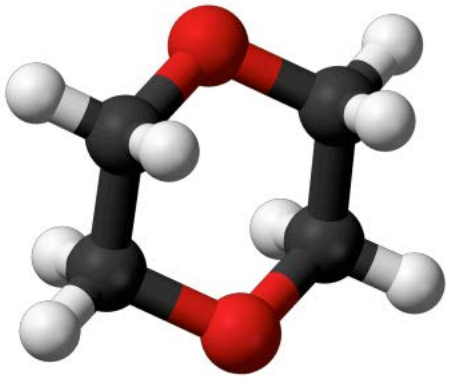
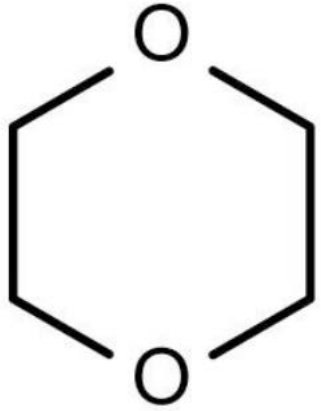




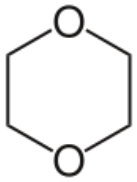
Fayetteville, NC, May 24, 2017

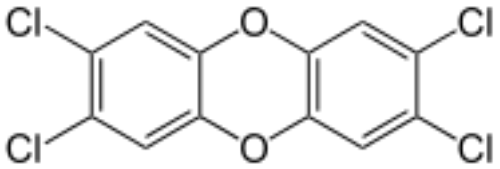
Presentation Overview

- 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

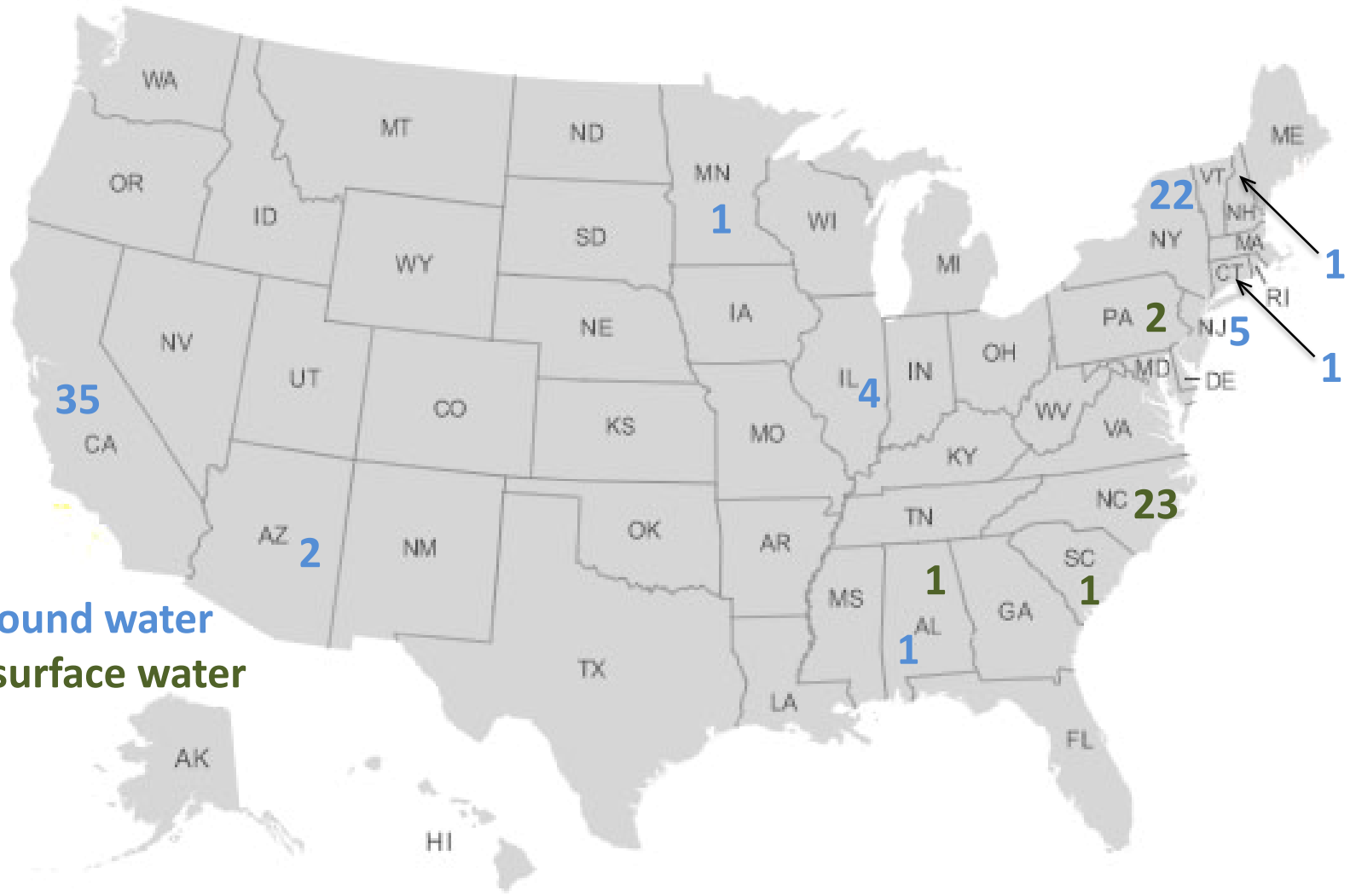
Occurrence - EPA's Third Unregulated Contaminant Monitoring Rule (UCMR3)

		Samples*	Public Water Systems+
≥0.35 μg/L	US	3.0%	7.0%
	NC	6.0%	15.9%

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

- Drinking water samples ≥0.35 μg/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)

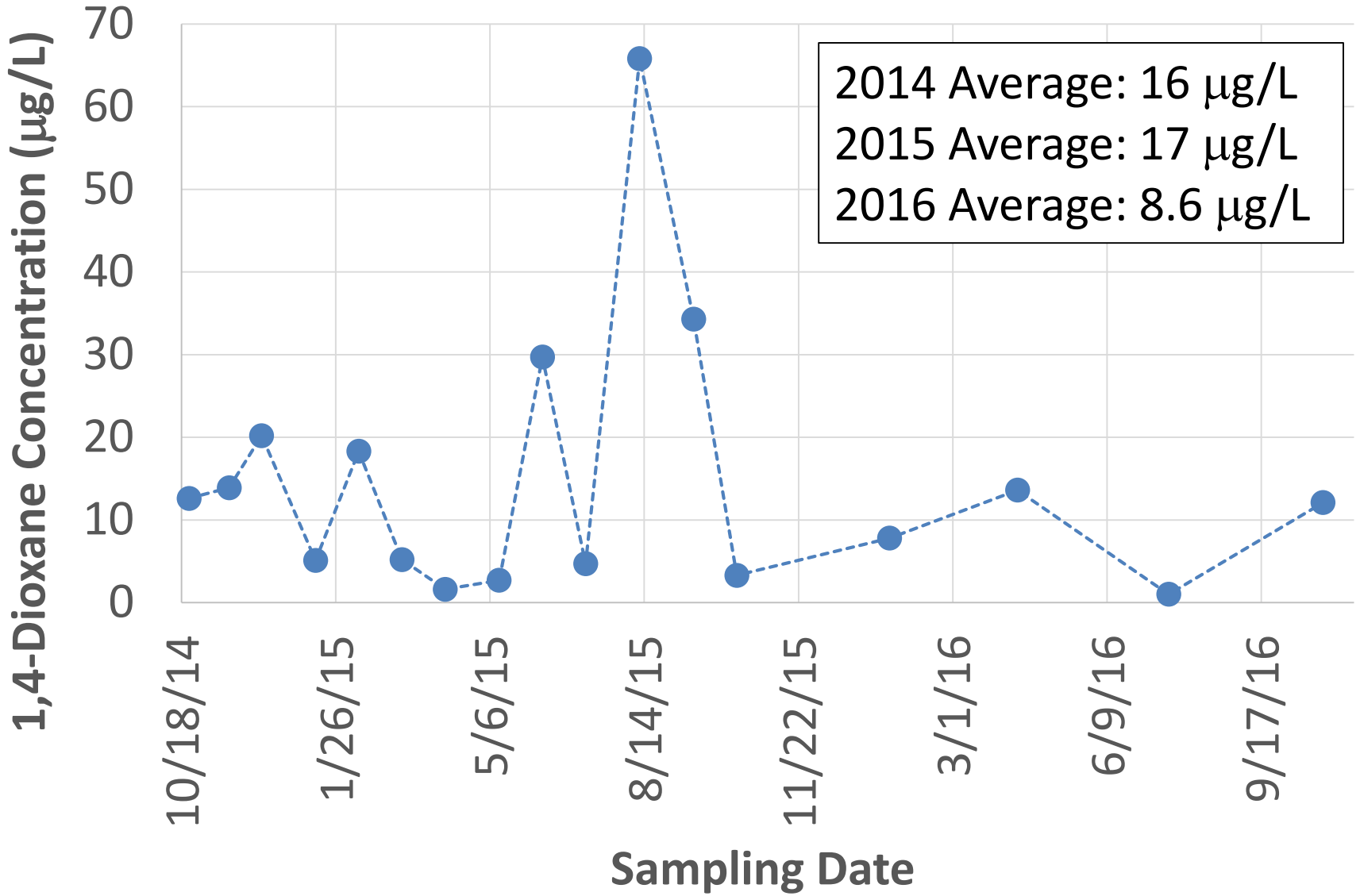


Field Sample Collection

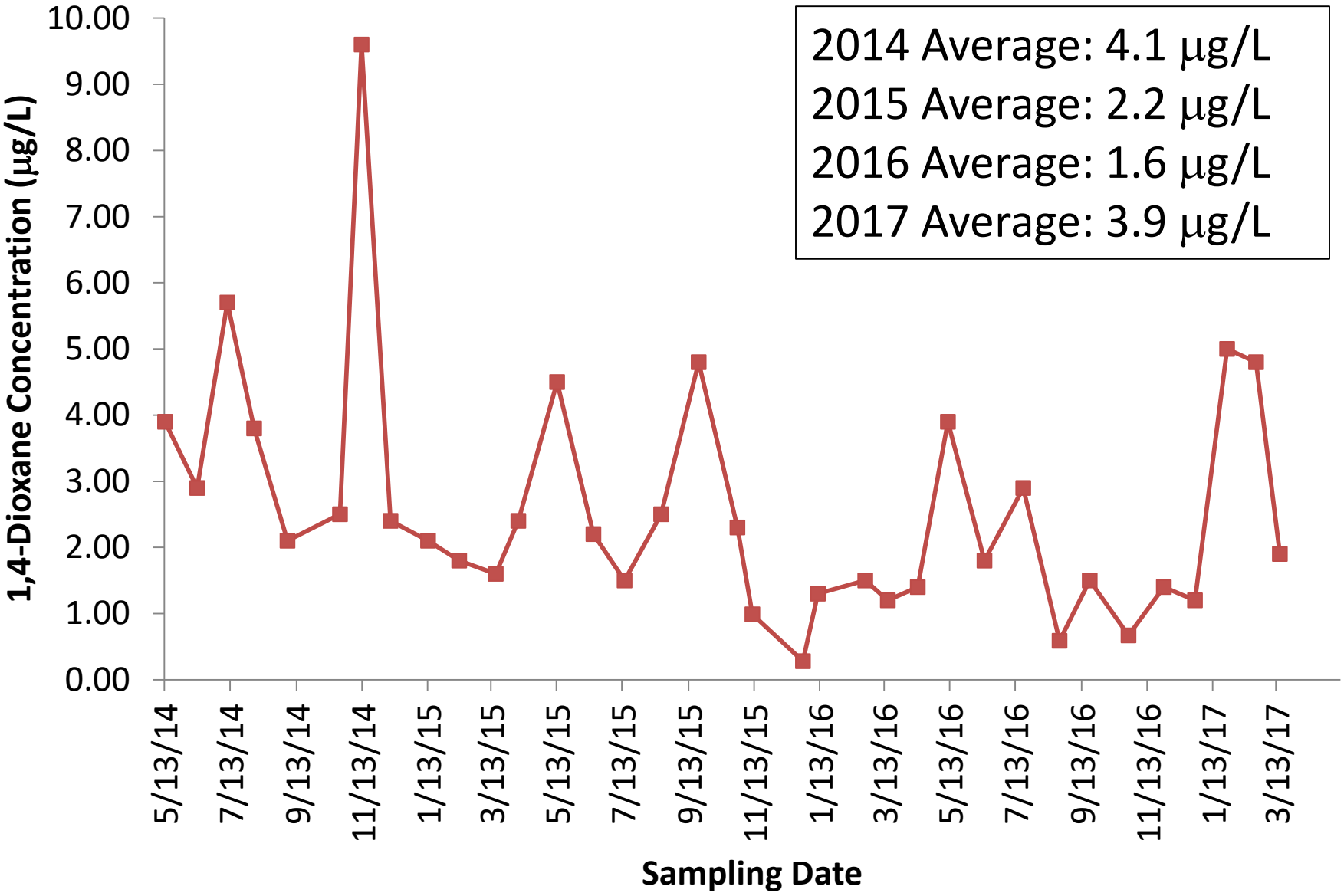
Brown glass bottles 500 mL with PTFE Caps

Preservatives:
50 mg/L sodium sulfite
1 g/L sodium bisulfate
Added sequentially in the field

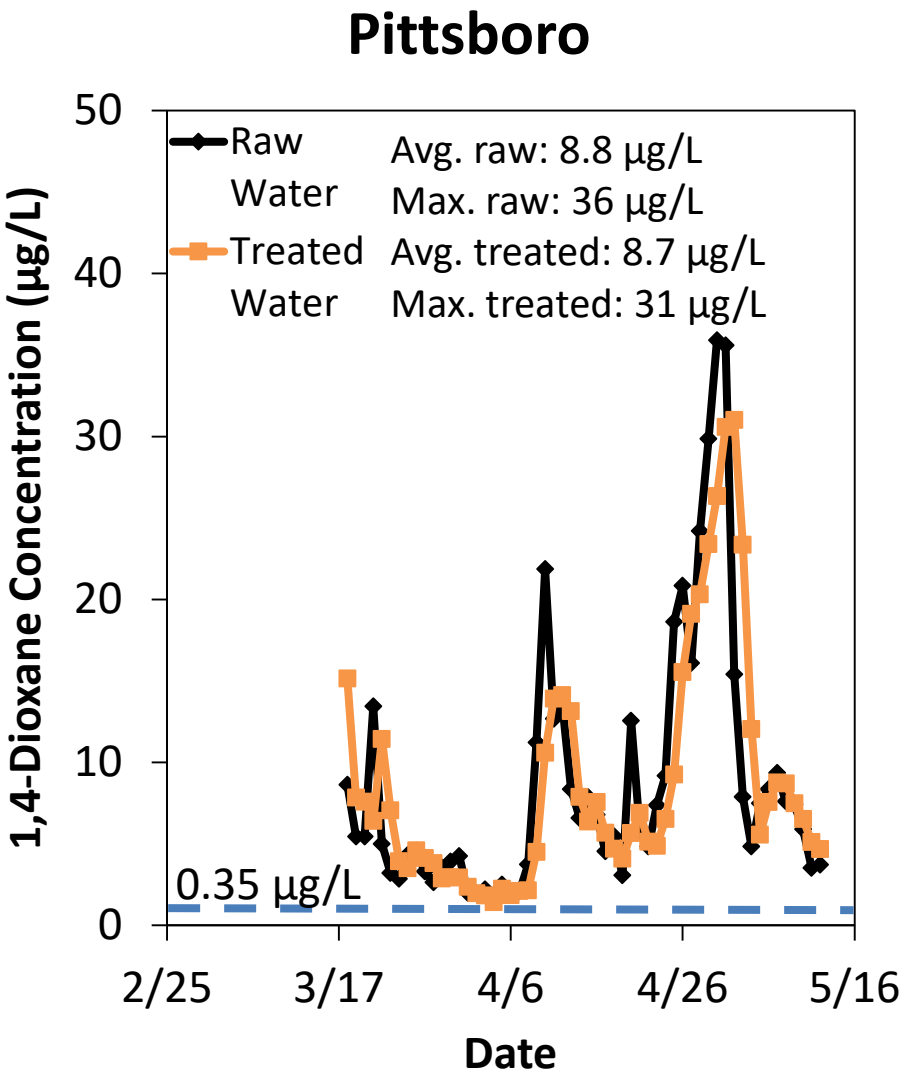
1,4-Dioxane Concentrations in Haw River at Bynum

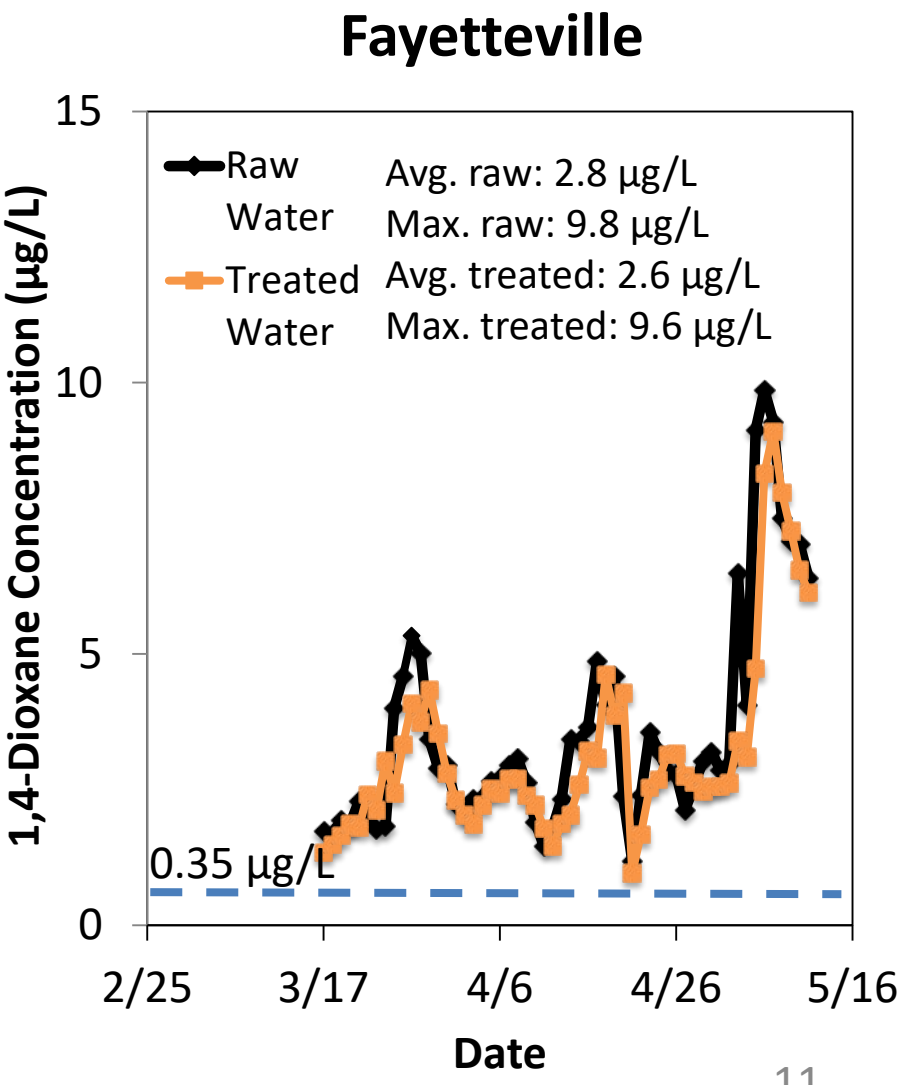


Fayetteville Intake (P.O. Hoffer)

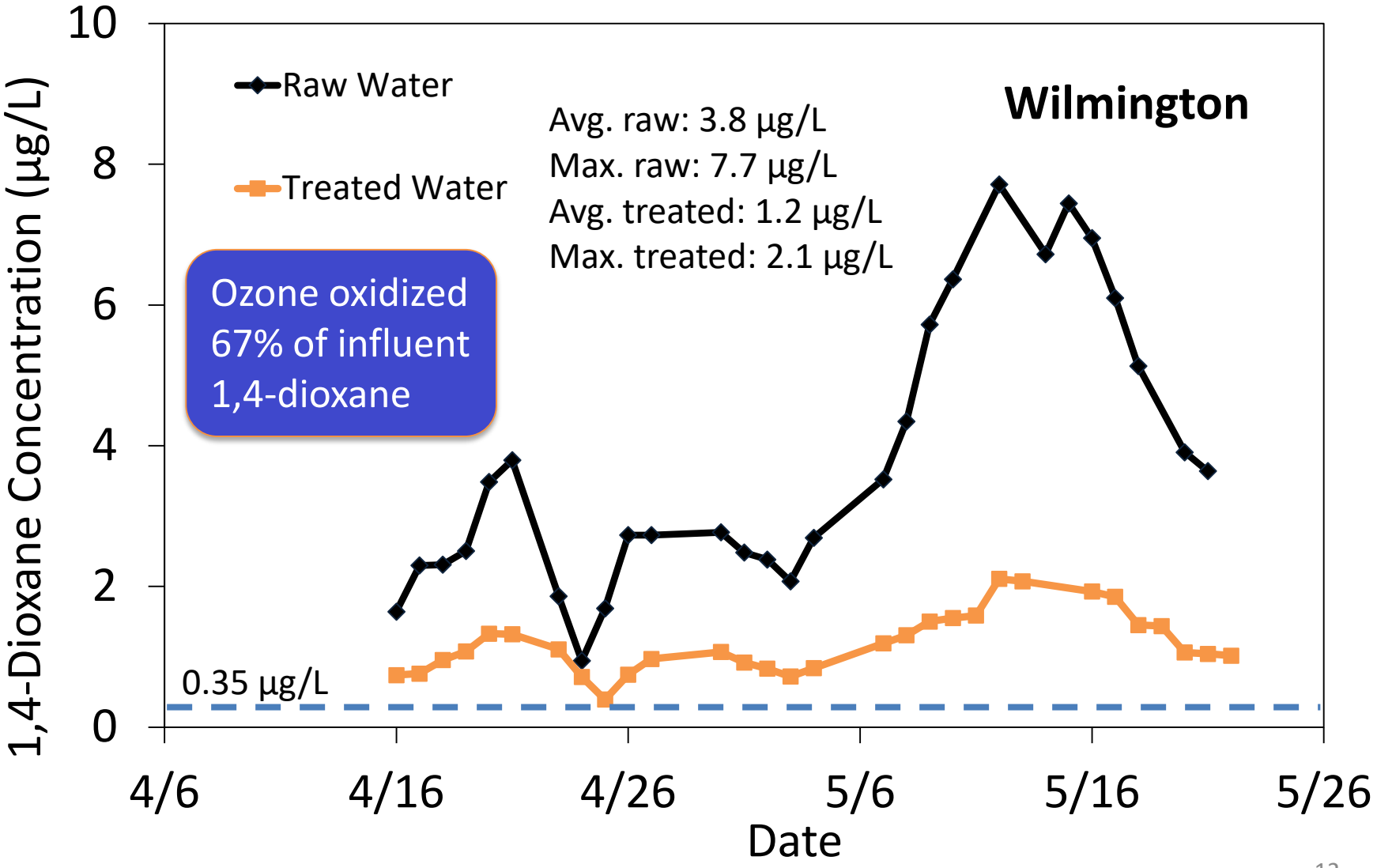


1,4-Dioxane is not Removed in Conventional Water Treatment Plants



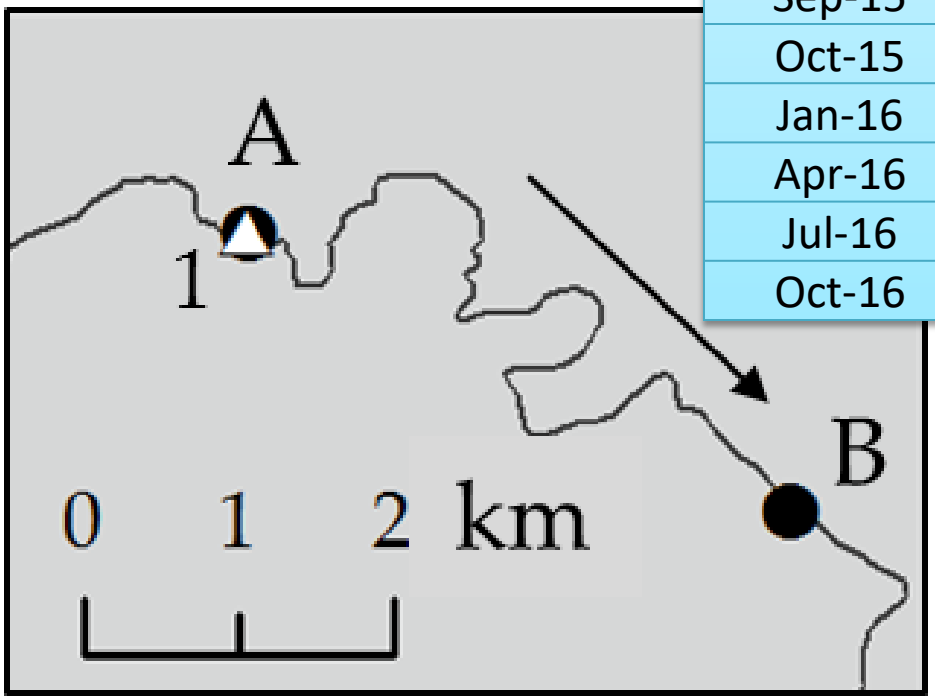


1,4-Dioxane is Partially Oxidized by Ozone



Source Identification: Haw River

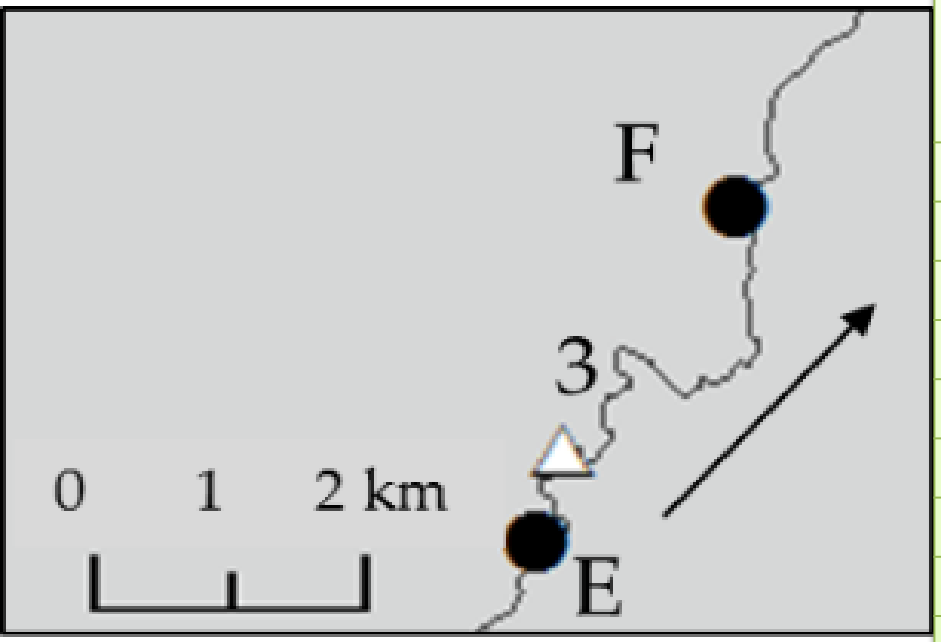
Date	Upstream Concentration (µg/L)	Downstream Concentration (µg/L)
Oct-14	0.60	77
Dec-14	0.16	123
Jan-15	0.20	1.0
Feb-15	0.20	76
Mar-15	<0.15	3.8
Apr-15	0.15	27
May-15	0.20	26
Jun-15	<0.15	40
Jul-15	0.25	270
Aug-15	0.20	86
Sep-15	-	1,030
Oct-15	-	46
Jan-16	-	3.8
Apr-16	-	6.6
Jul-16	-	<2
Oct-16	-	<2



△ WWTP Discharge

● Sampling Point

Source Identification:
S. Buffalo Creek

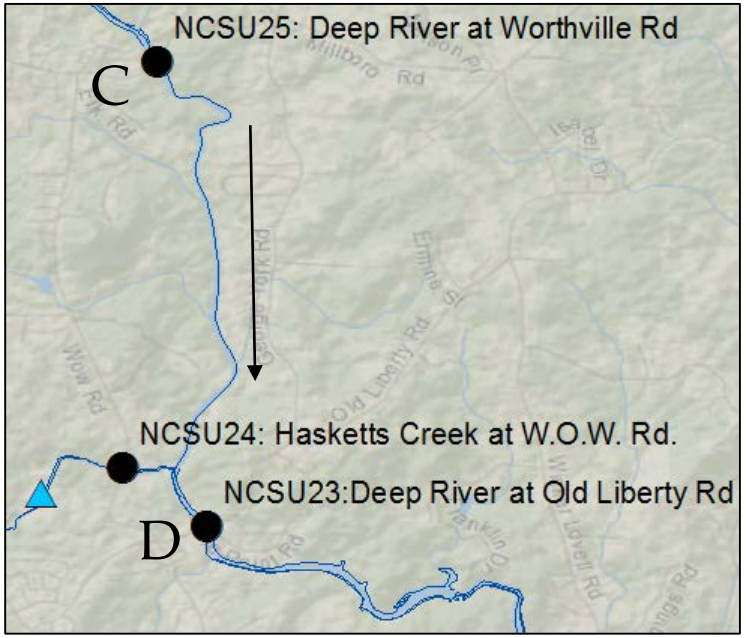


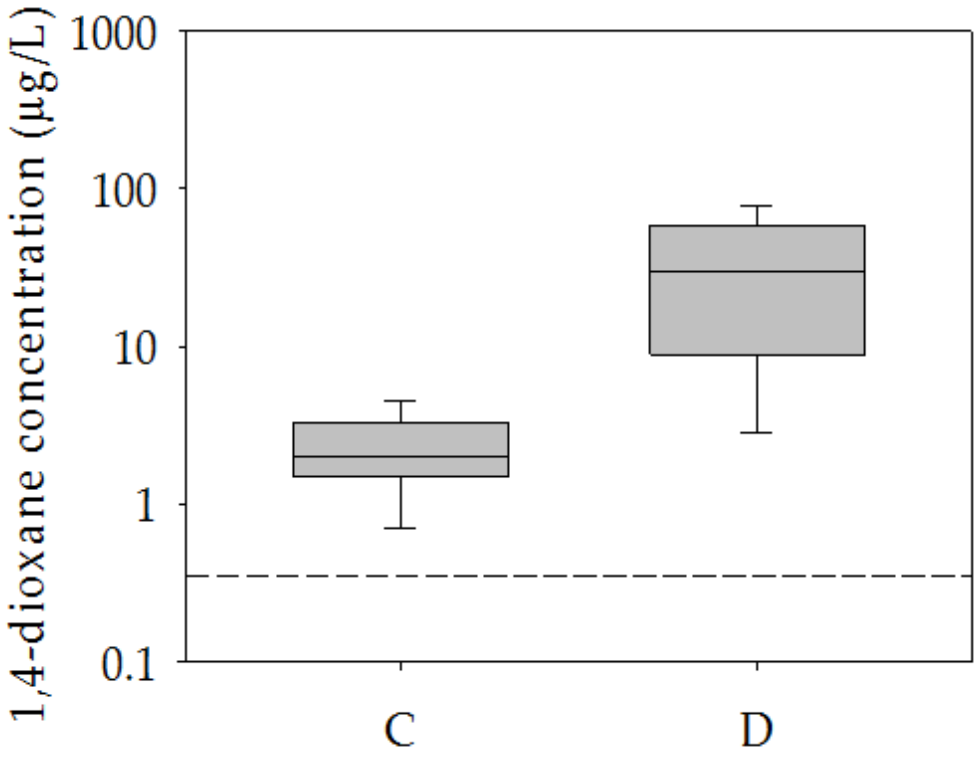
WWTP Discharge

Sampling Point

Date	Upstream Concentration (µg/L)	Downstream Concentration (µg/L)
Oct-14	0.2	4.8
Dec-14	2.0	38
Jan-15	0.9	226
Feb-15	3.7	11
Mar-15	1.8	436
Apr-15	1.9	30
May-15	3.8	20
Jun-15	3.6	62
Jul-15	0.43	22
Aug-15	0.45	14
Sep-15	-	38
Oct-15	-	6.7
Jan-16	-	86
Apr-16	-	15
Jul-16	-	41
Oct-16	-	8.6

Source Identification: Deep River





Regulatory Framework

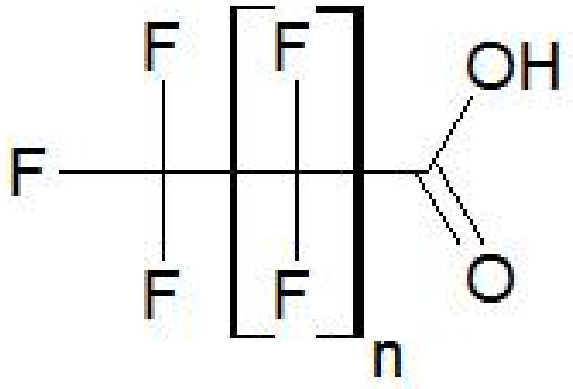
- No federal drinking water standard
- No NC drinking water standard
- NC groundwater standard: 3 μg/L
- Surface water quality (in-stream) standard:
  - 0.35 μg/L for streams classified as water supplies (WS-I through WS-IV)
  - 80 μg/L for other stream classifications

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).

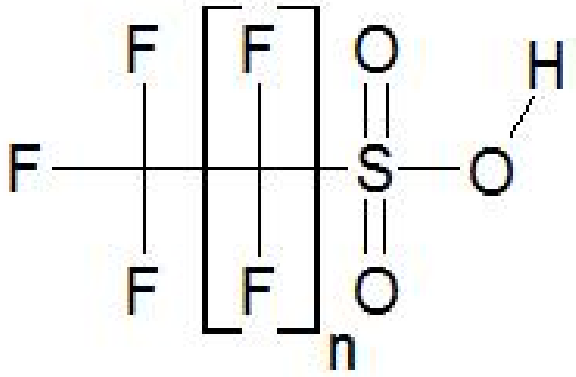
CONCLUSIONS

- 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

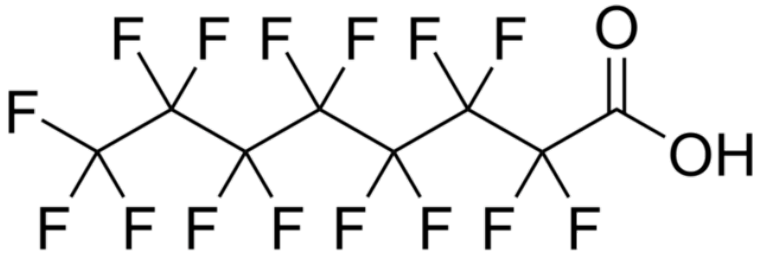
Perfluoroalkyl substances (PFASs) are organic compounds in which all C-H bonds are replaced with C-F bonds.

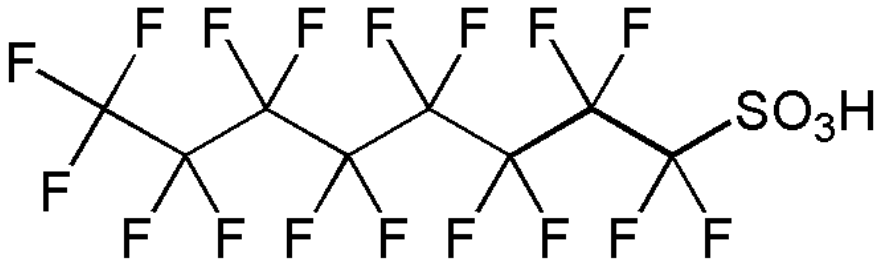


Perfluorocarboxylic acids
(e.g. perfluorooctanoic acid, PFOA or C8)

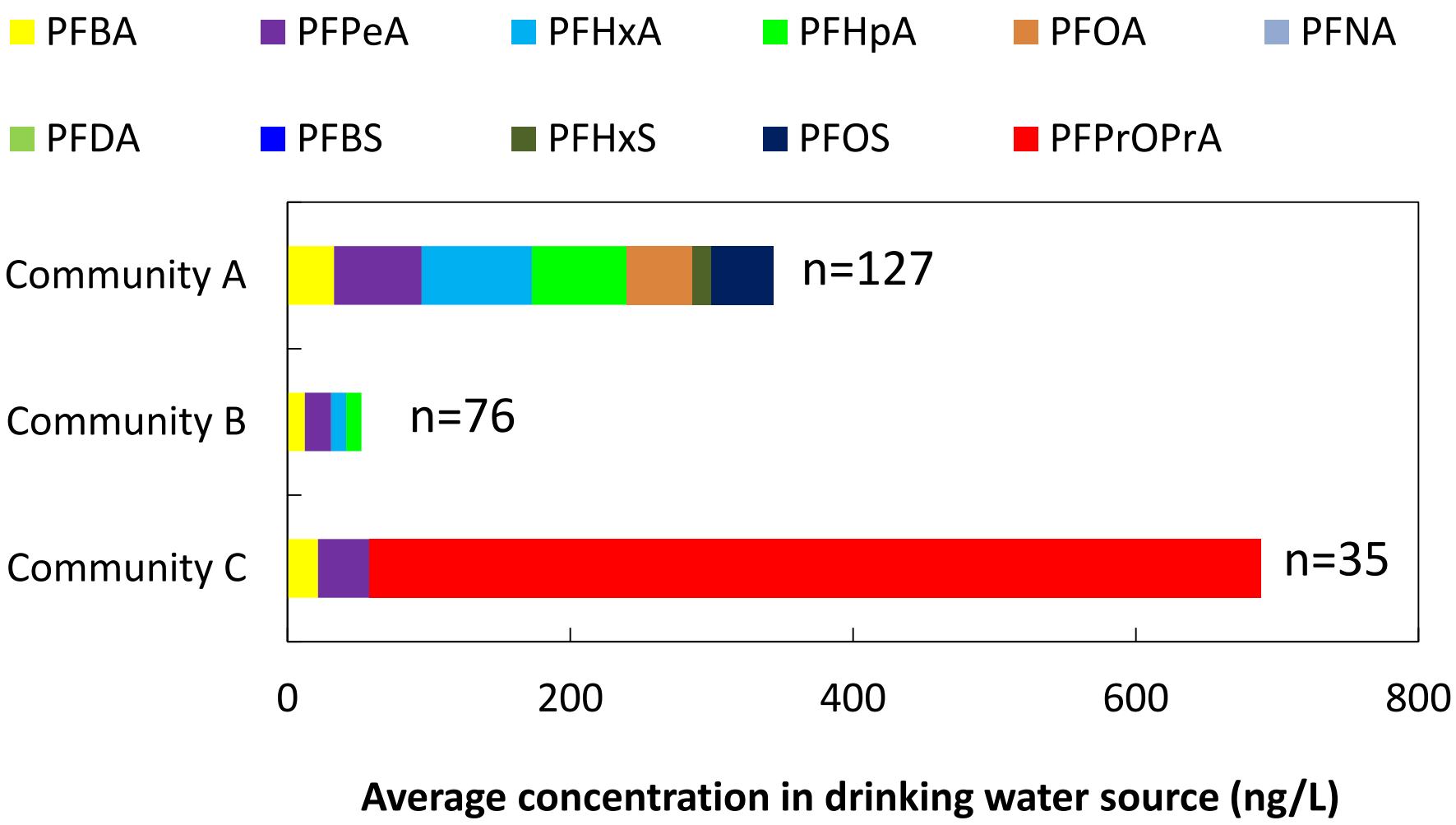


Perfluorosulfonic acids
(e.g. perfluorooctane sulfonate, PFOS)

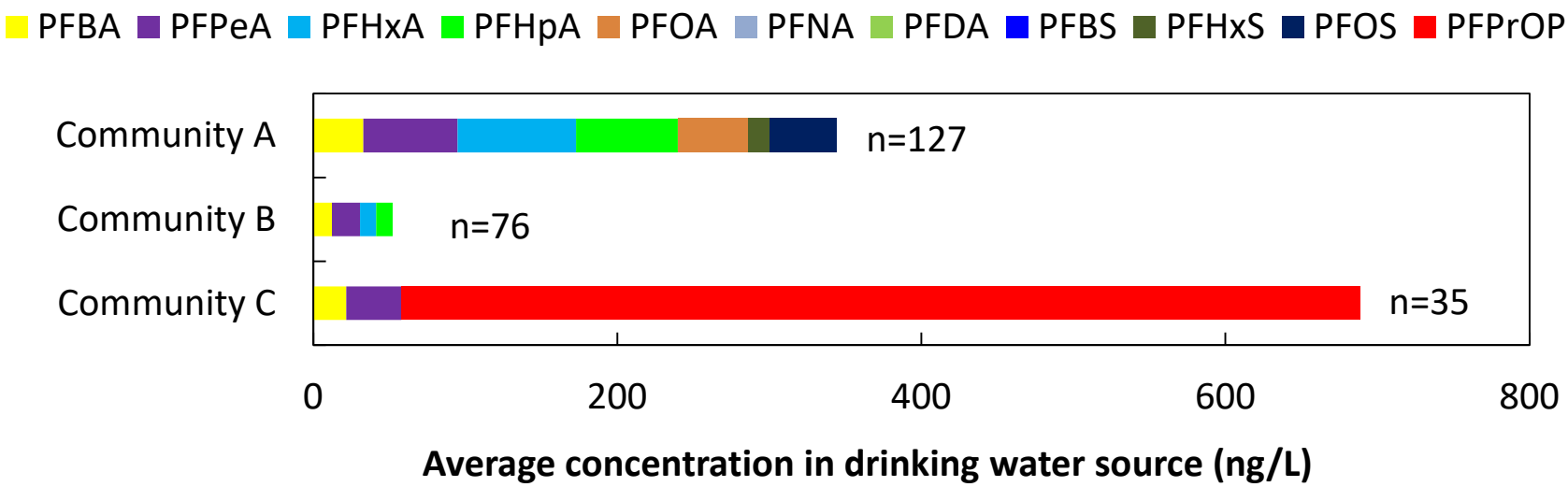


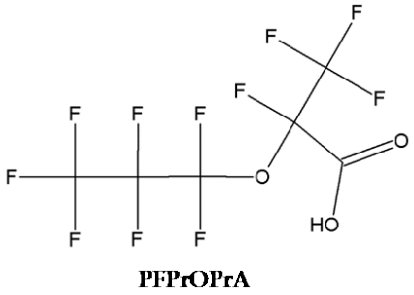


PFAS Occurrence in CFR Watershed



PFAS Concentrations in the Source Water of 3 Communities (June-December 2013)



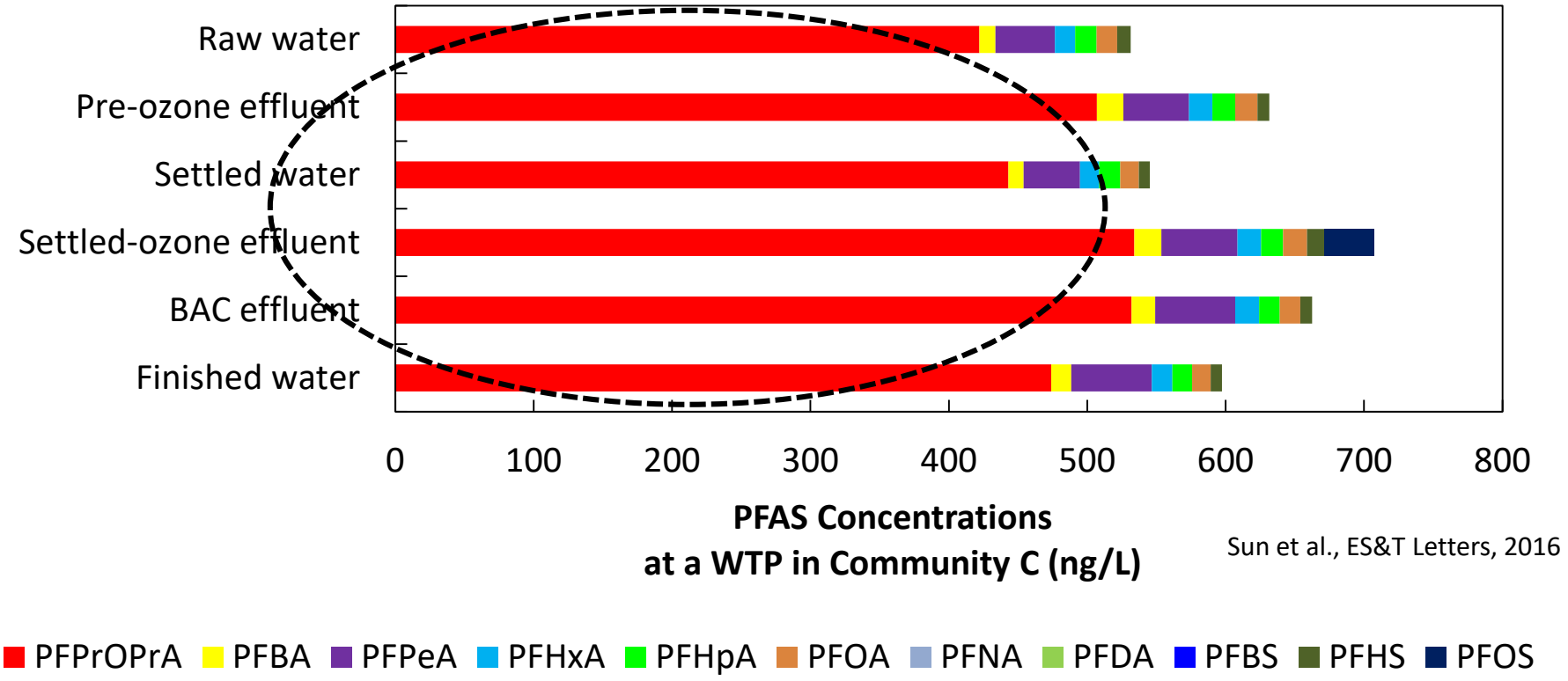


PFPrOPrA

Sun et al., ES&T Letters, 2016

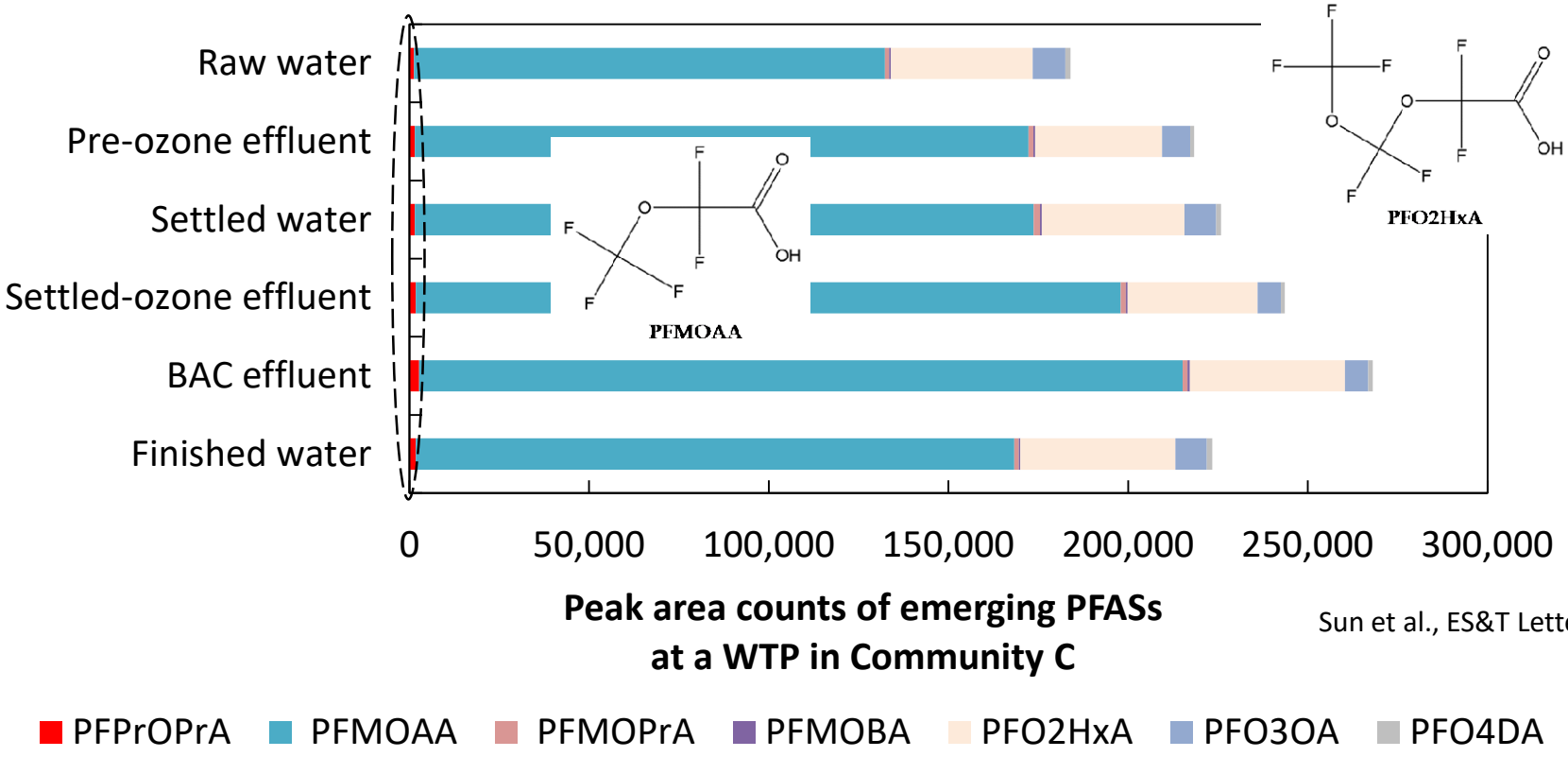
PFPrOPrA = perfluoropropoxypropanoic acid (aka “GenX” – a replacement for PFOA)

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)



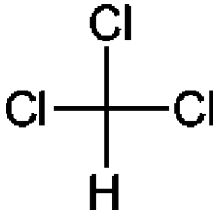
Sun et al., ES&T Letters, 2016

Bromide is a precursor for disinfection by-products (DBPs)

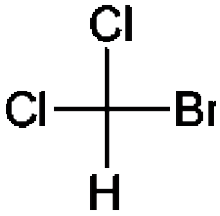
- $Cl_2 + H_2O \longleftrightarrow HOCl + H^+ + Cl^-$
- $HOCl + Br^- \longleftrightarrow HOBr + Cl^-$
- DOM + HOCl + HOBr $\longleftrightarrow$ trihalomethanes (THMs) + haloacetic acids (HAAs) + …

http://water.usgs.gov/edu/pictures/color-tannin-sediment.jpg

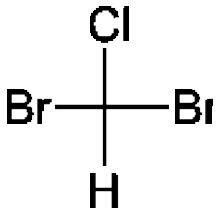
Trihalomethanes (THMs)



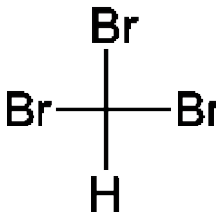
- Chloroform
  Molecular weight = 119.4 g/mol
  One-in-a-million cancer risk: -



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



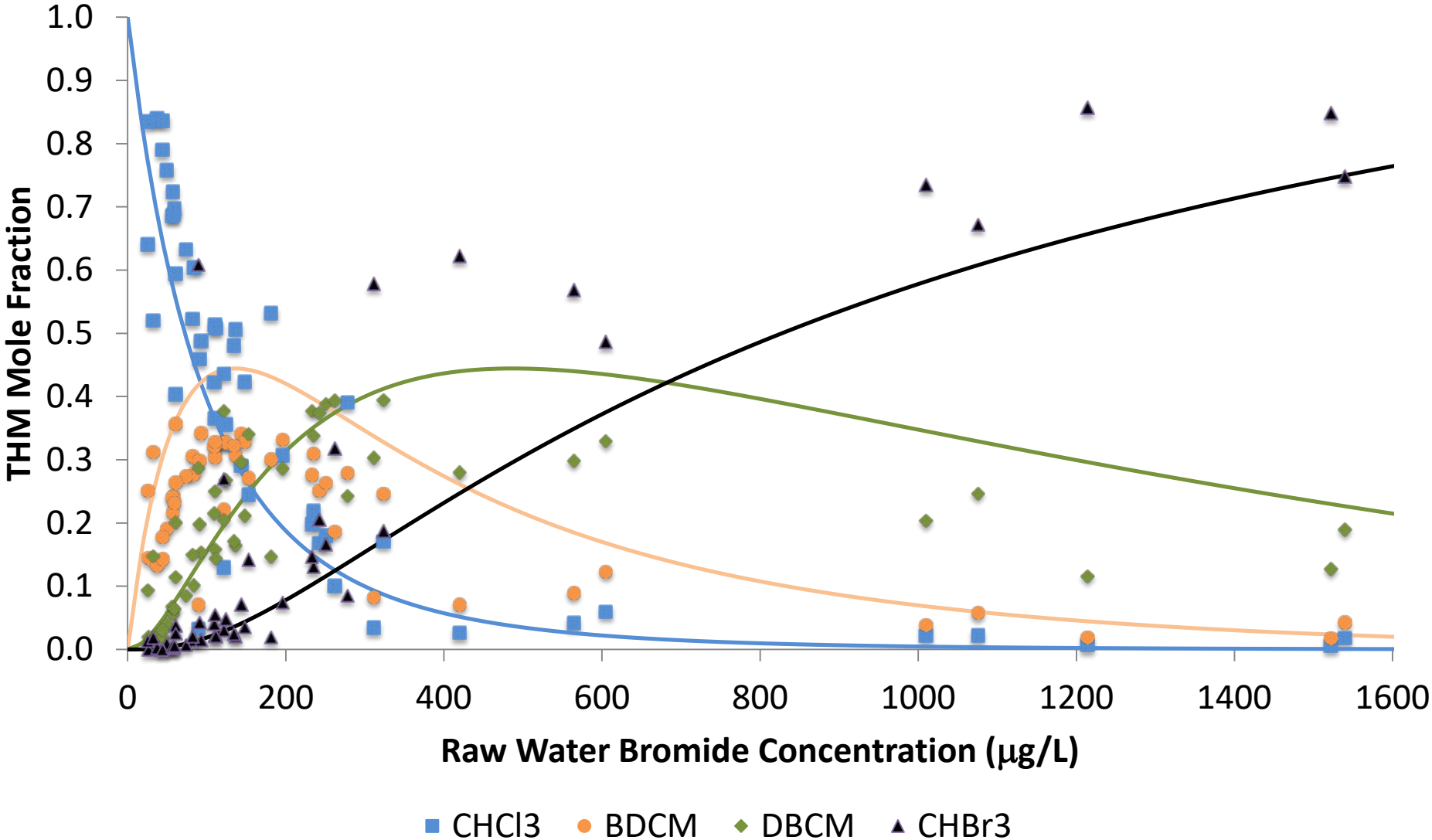
- Dibromochloromethane
  Molecular weight = 208.3 g/mol
  One-in-a-million cancer risk: 0.4 μg/L

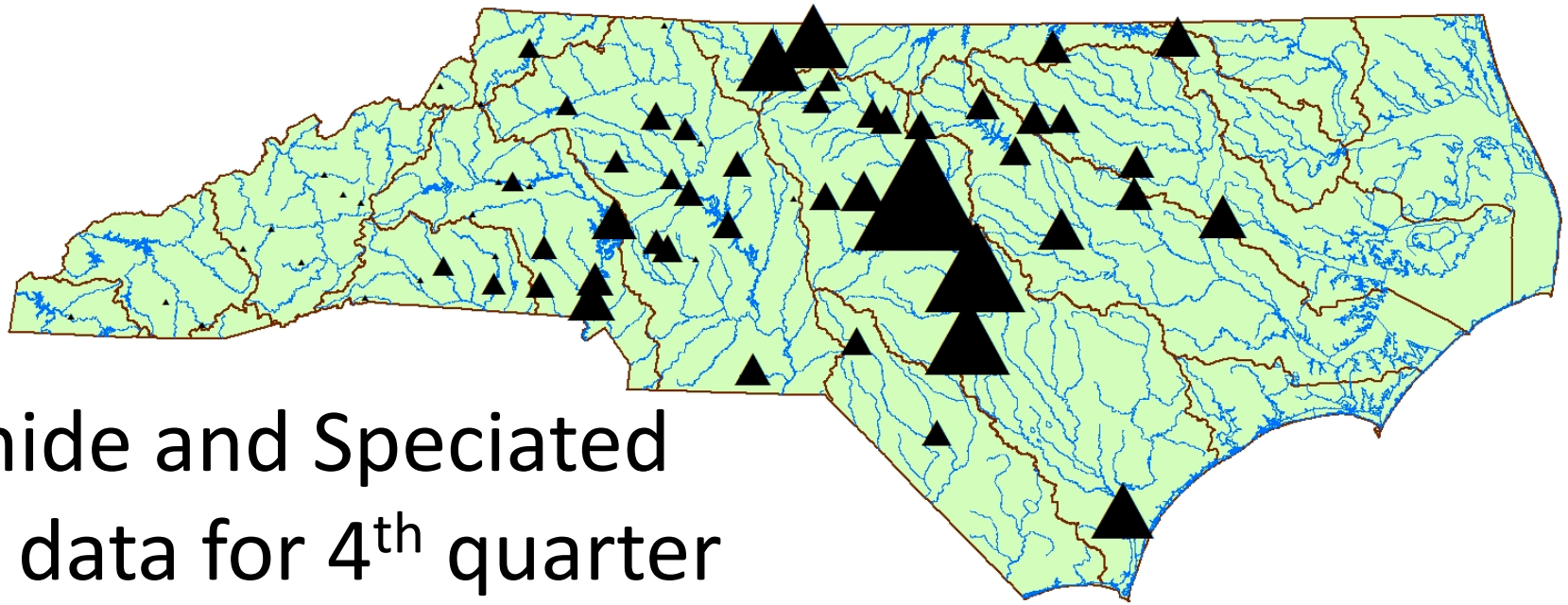


- Bromoform
  Molecular weight = 252.7 g/mol
  One-in-a-million cancer risk: 4 μg/L

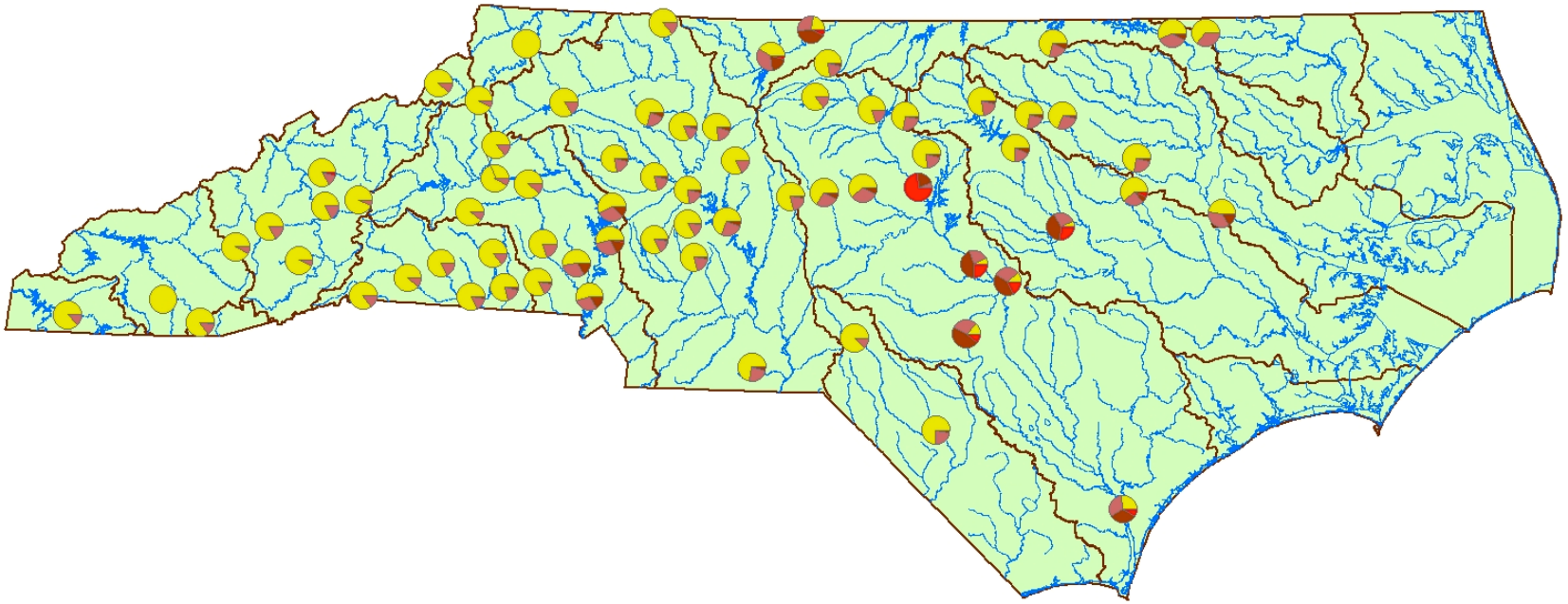
Drinking water standard: Σ THMs = 80 μg/L

Effect of bromide concentration on THM speciation





Bromide and Speciated THM data for 4th quarter of 2013



chloroform

BDCM

DBCM

bromoform

Acknowledgments

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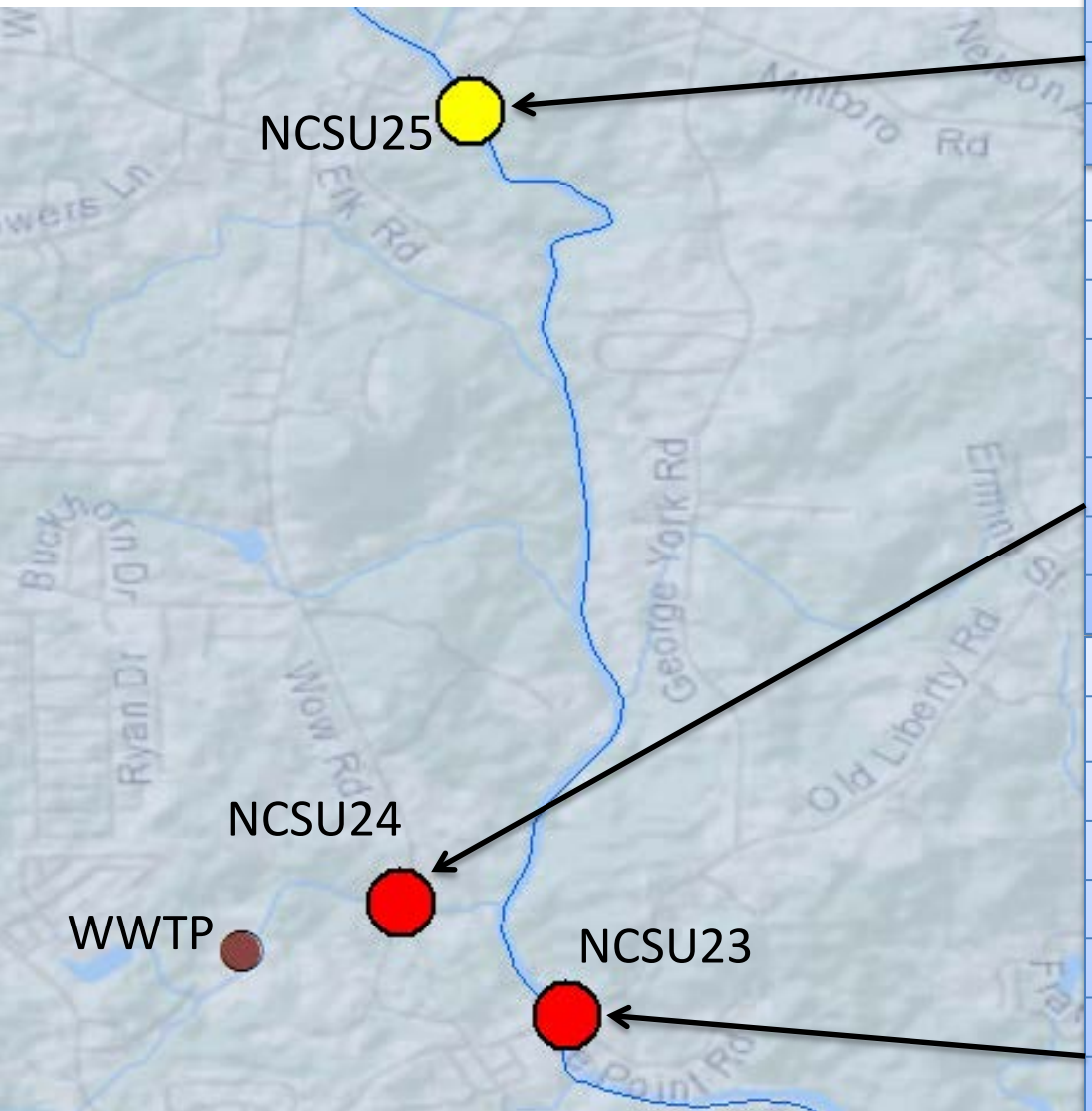
  - NSF RAPID;GOALIE (#1449768)
- Utility participants: Fayetteville Public Works Commission, Cape Fear Public Utilities Commission, Town of Pittsboro
- North Carolina Department of Environmental Quality: Carrie Ruhlman, Tammy Hill

Source Identification: Deep River



NCSU25 - Upstream WWTP	
Date	Concentration (µg/L)
Oct-14	1.5
Dec-14	2.0
Jan-15	0.7
Feb-15	1.7
Mar-15	2.5
Apr-15	4.5

NCSU24-Downstream WWTP	
Date	Concentration (µg/L)
Oct-14	254
Dec-14	1405
Jan-15	177
Feb-15	152
Mar-15	495
Apr-15	844

NCSU23-Downstream WWTP	
Date	Concentration (µg/L)
Oct-14	29
Dec-14	69
Jan-15	47
Feb-15	78
Mar-15	41
Apr-15	8.6