Emerging Contaminants: A Case Study for the Cape Fear River Basin

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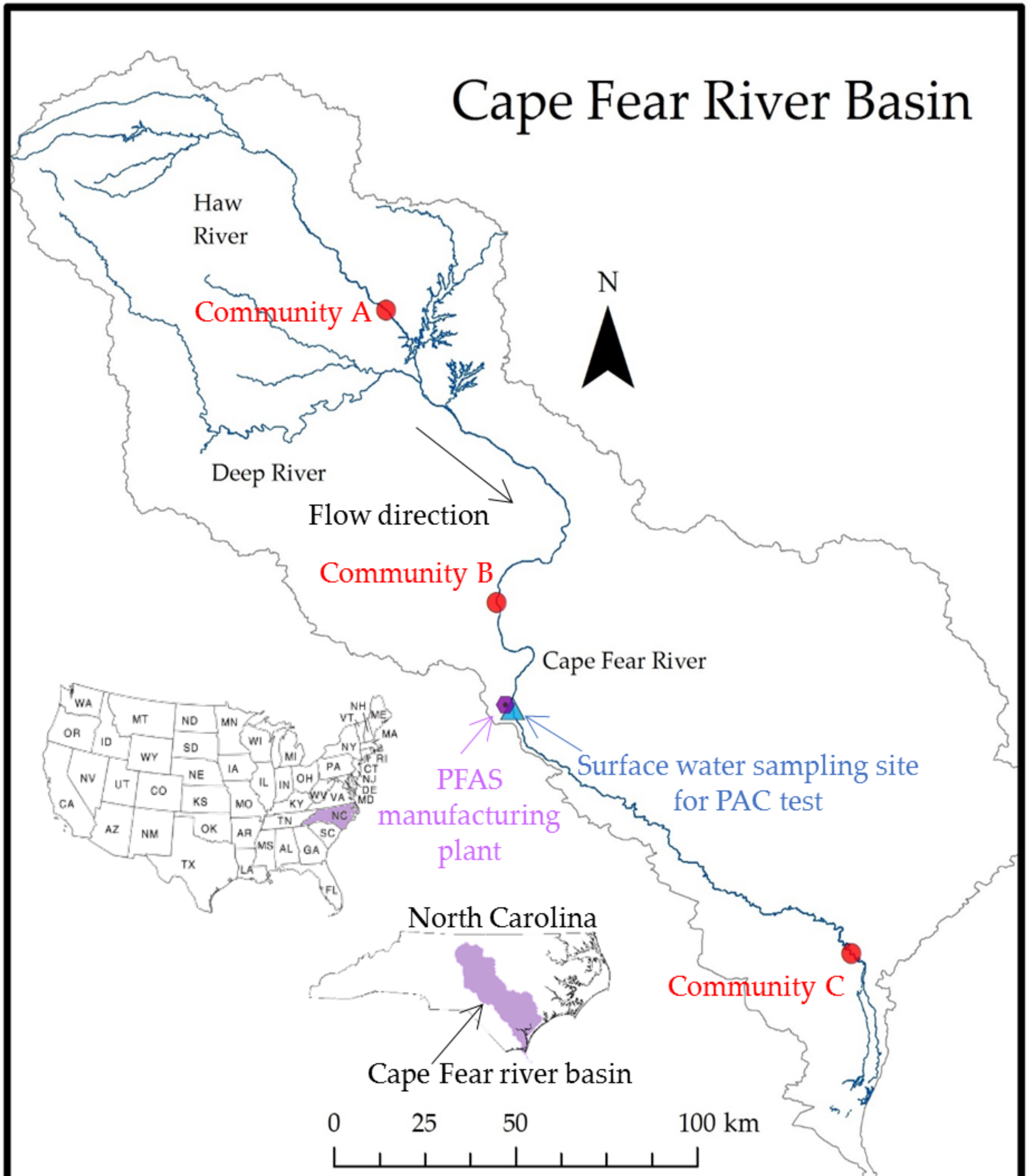
Presentation Overview

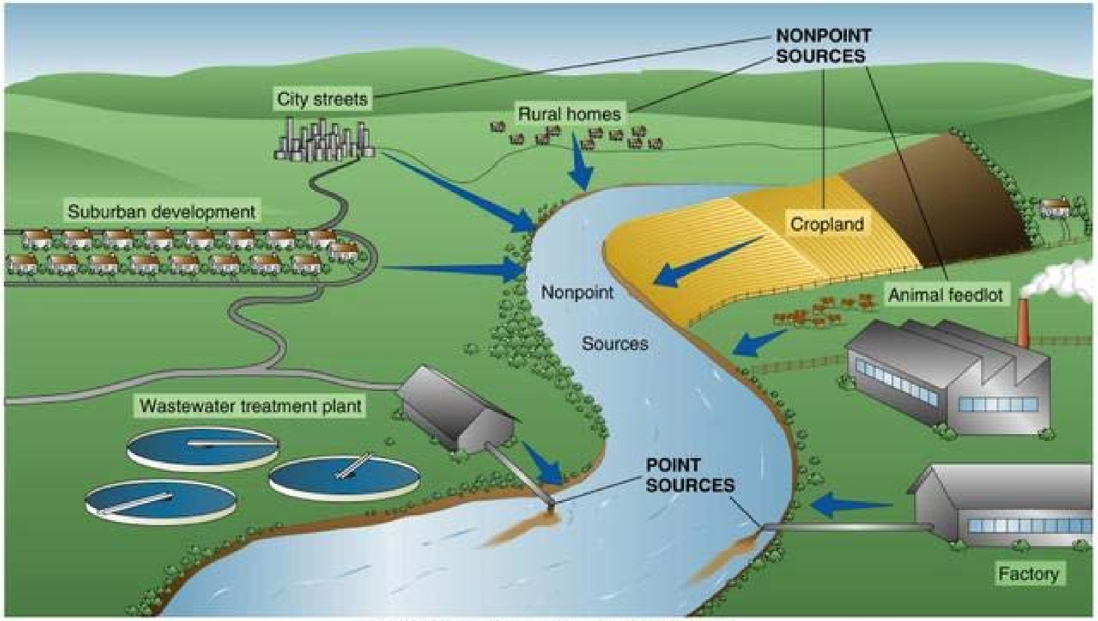
- Cape Fear River basin case study
  - We all live downstream/unplanned potable reuse
  - The Universe of Chemicals
  - Example contaminants of concern
    - Bromide
    - 1,4-Dioxane
    - Perfluoroalkyl substances
- Targeted and non-targeted analysis



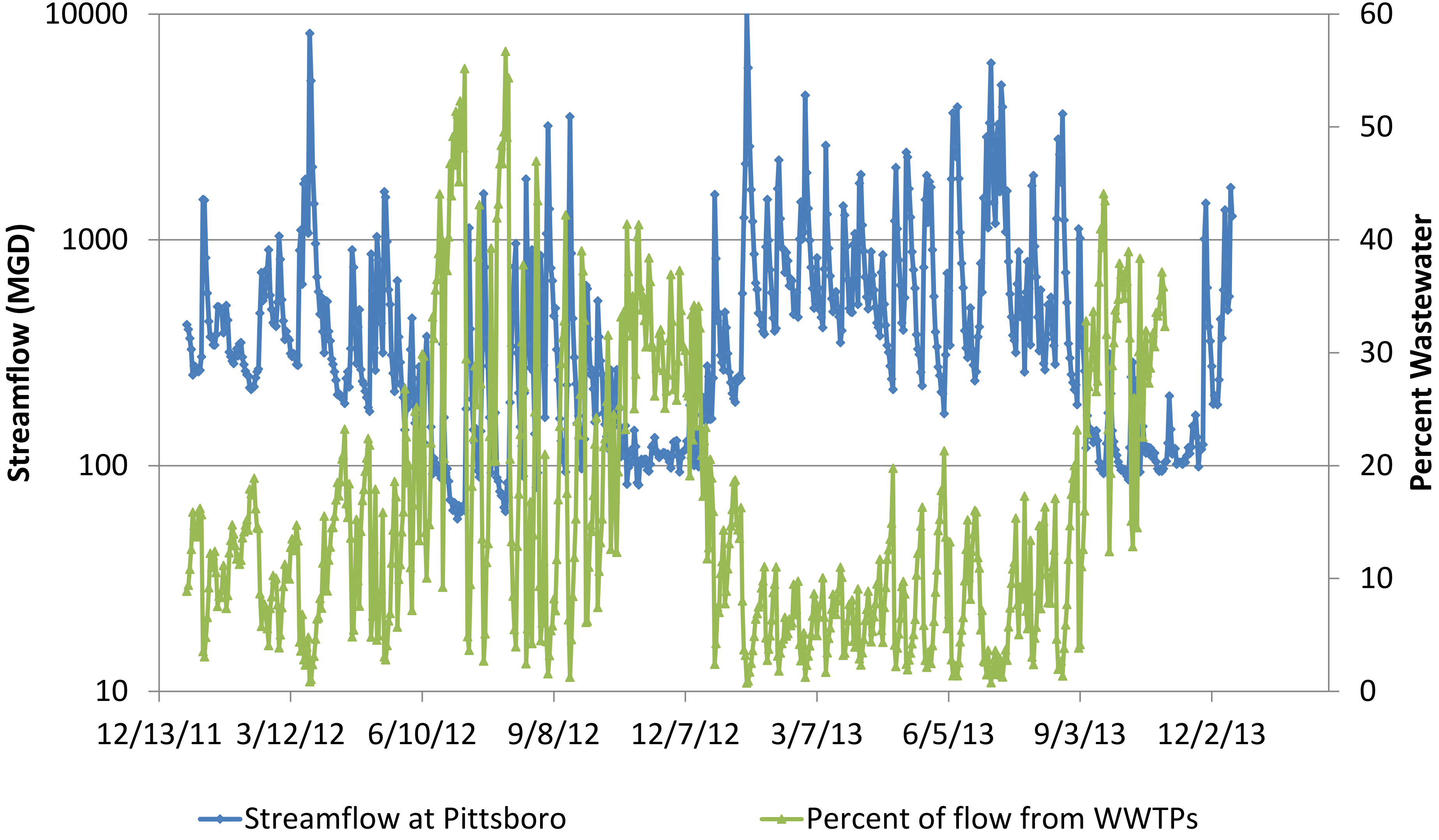
- Largest watershed in NC
- Supplies ~1.5M people with drinking water
- About 1M people affected by wastewater discharges containing high levels of industrial contaminants

We all live downstream

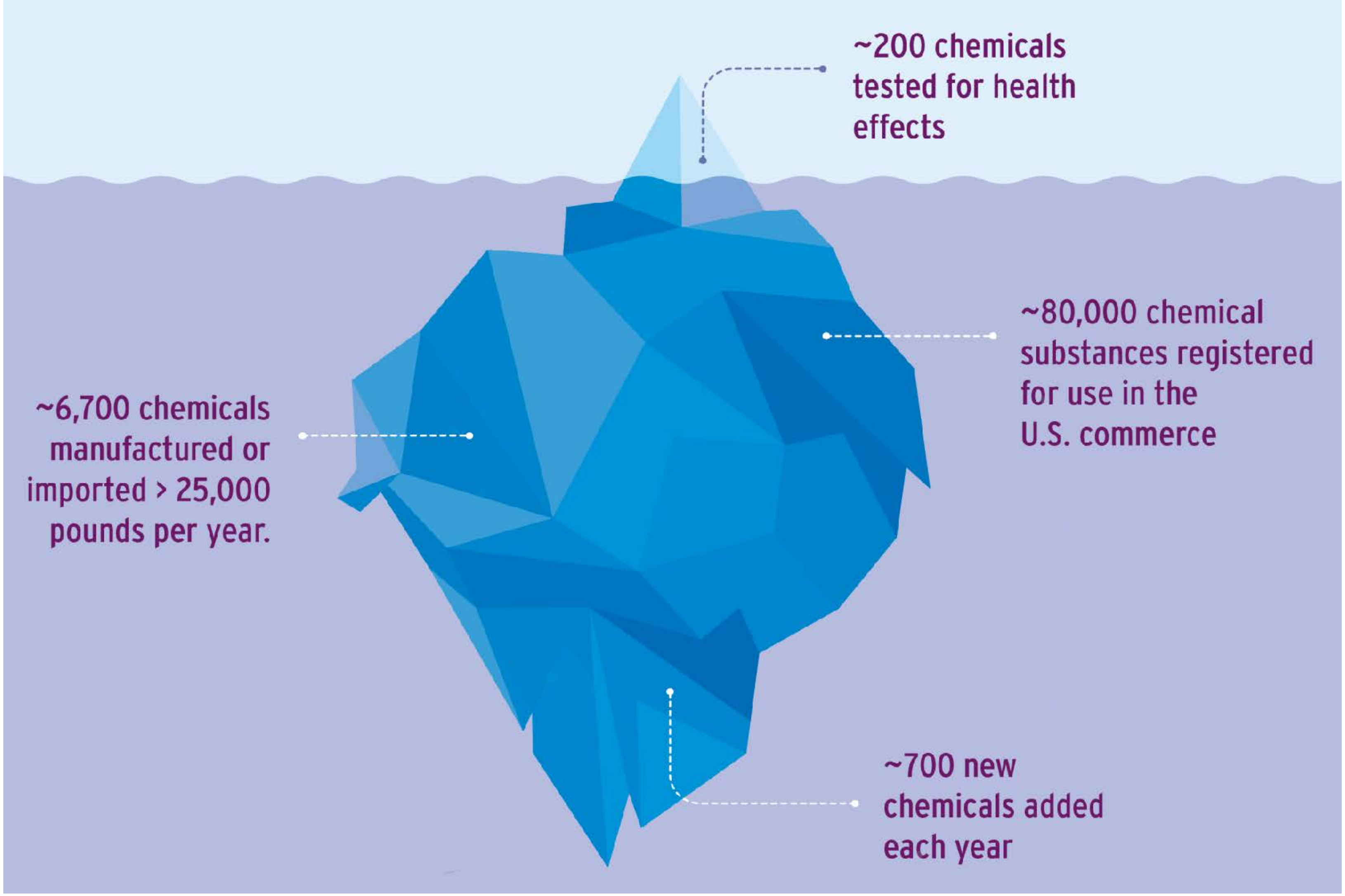
- Point sources
  - Municipal wastewater treatment plants
    - Industrial wastewater inputs
    - Landfill leachate
    - Coal ash leachate
  - Industrial wastewater treatment plants
  - (Coal-fired) power plants
- Non-point sources
  - Urban stormwater
  - Agricultural runoff
  - Land application sites for wastewater treatment plant biosolids
  - Contaminated groundwater discharge
  - Dry and wet deposition of air pollutants



Wastewater percentage in Haw River at Bynum (Pittsboro Drinking Water Source)



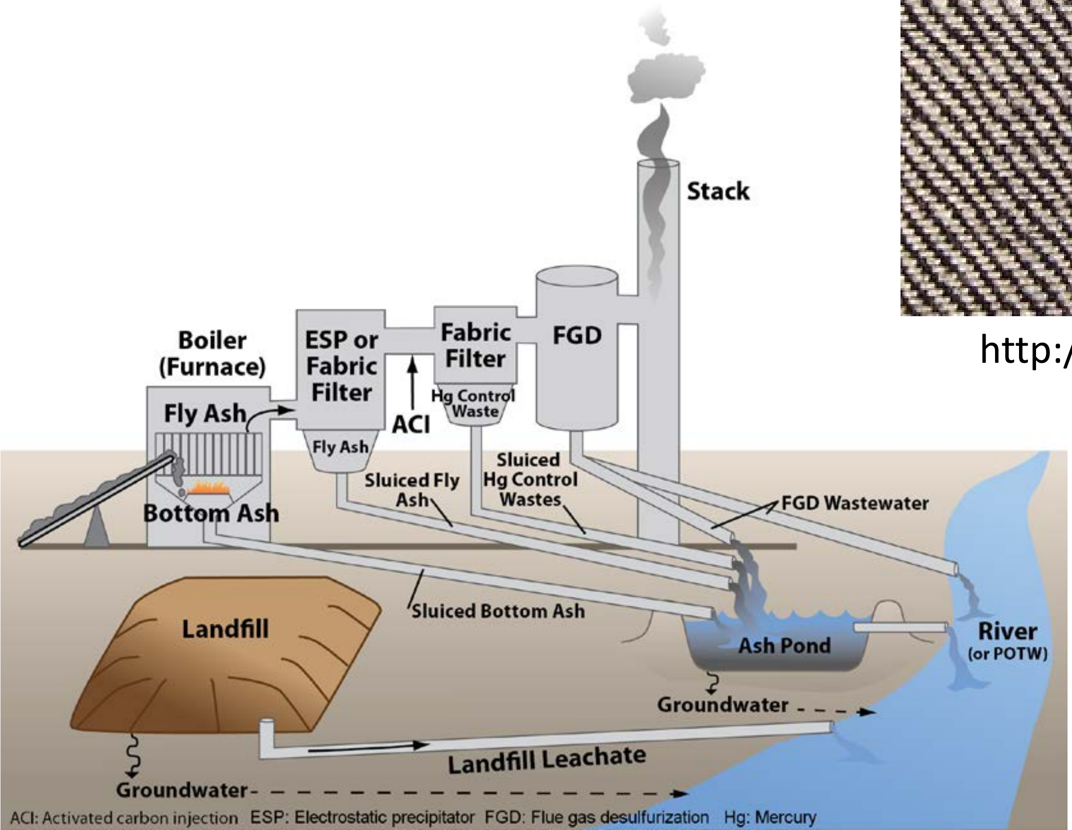
The Universe of Chemicals



Woodruff, T. Identifying Cumulative Exposures to Chemicals in Pregnant Women – Non-targeted Screening of Environmental Chemicals. PPTOX IV, Boston, MA, Oct. 26-29, 2014.

Bromide (Br^-)

http://www.heddels.com/dictionary/sulphur/



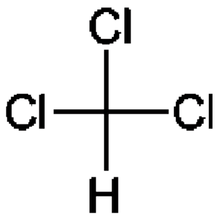
http://www.epa.gov/eg/steam-electric-power-generating-effluent-guidelines-2015-final-rule

Bromide (Br-) is relatively non-toxic, but it reacts with drinking water disinfectants to form disinfection by-products

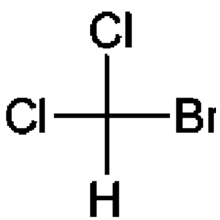
- Organic matter + chlorine + bromide ⟷ trihalomethanes (THMs) + haloacetic acids (HAAs) + …

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

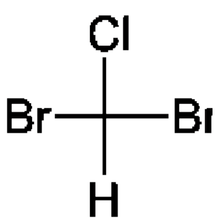
Trihalomethanes (THMs)



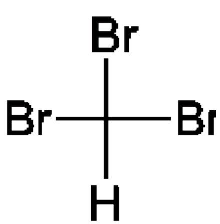
- Chloroform
  Molecular weight = 119.4 g/mol
  One-in-a-million cancer risk: -



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



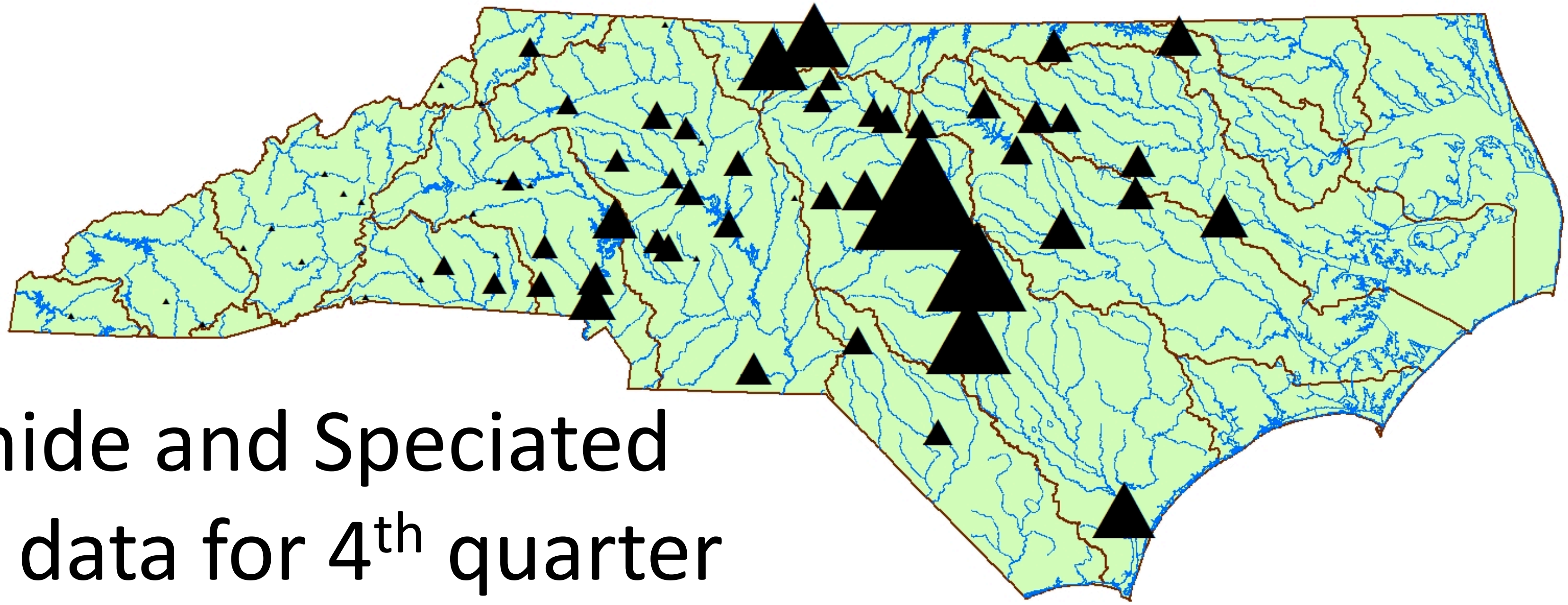
- Dibromochloromethane
  Molecular weight = 208.3 g/mol
  One-in-a-million cancer risk: 0.4 µg/L

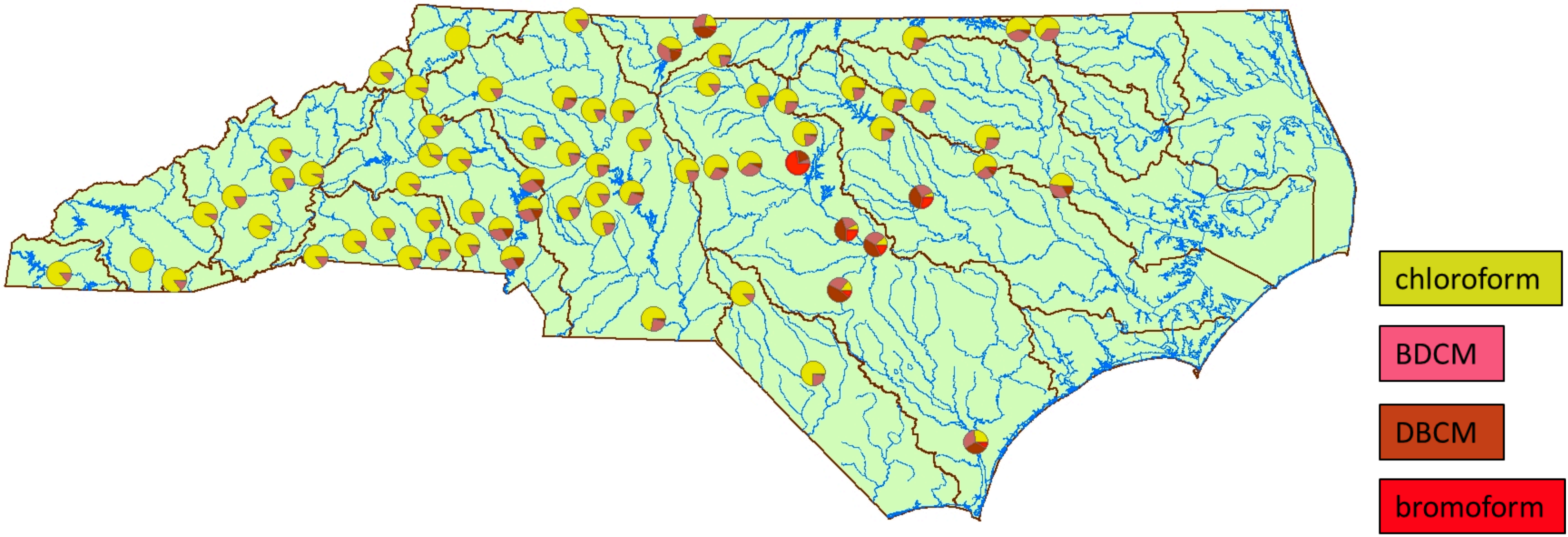


- Bromoform
  Molecular weight = 252.7 g/mol
  One-in-a-million cancer risk: 4 µg/L

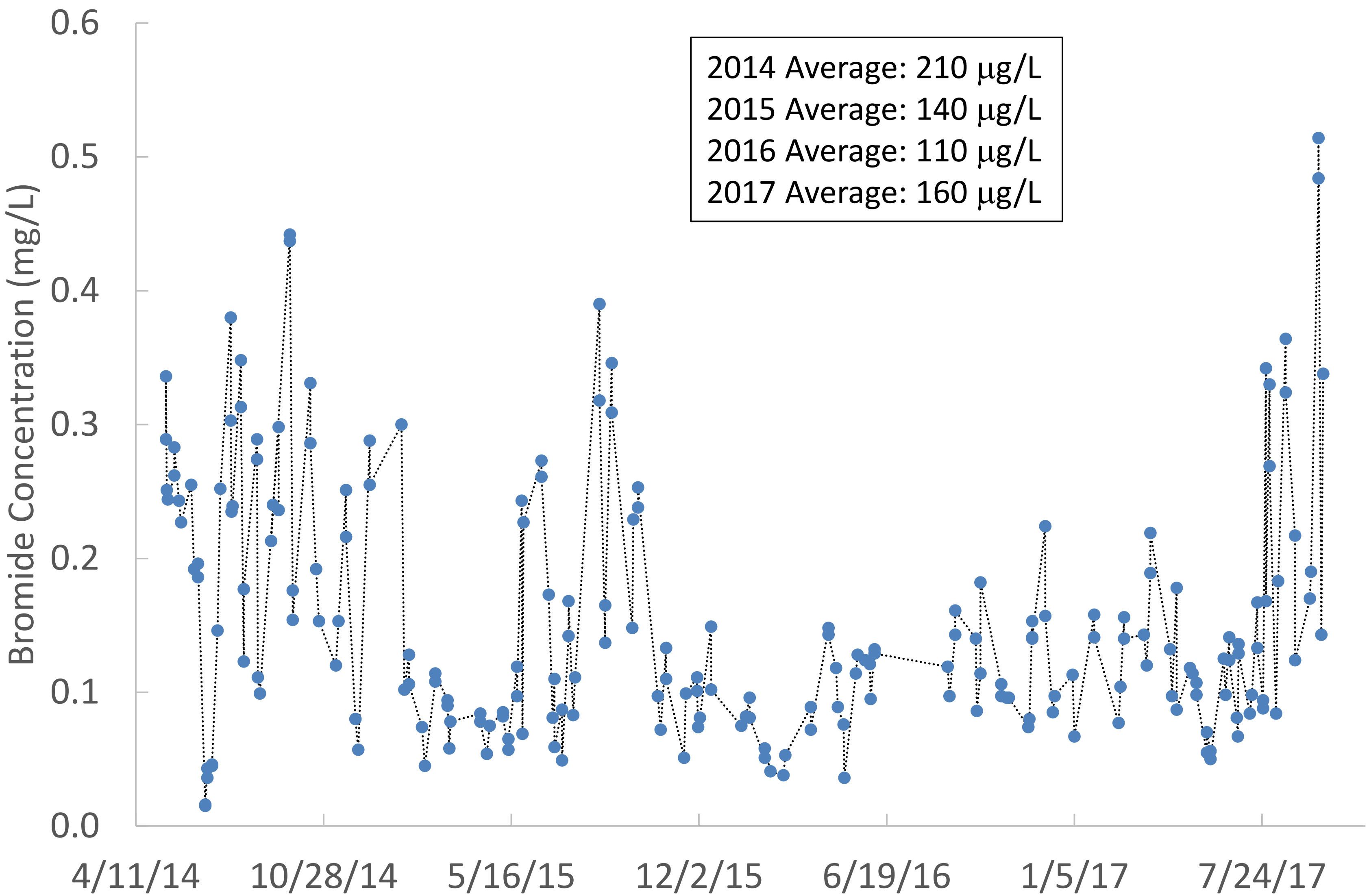
Drinking water standard: Σ THMs = 80 µg/L

Bromide and Speciated THM data for 4th quarter of 2013





Bromide Concentrations at Intake of Community B



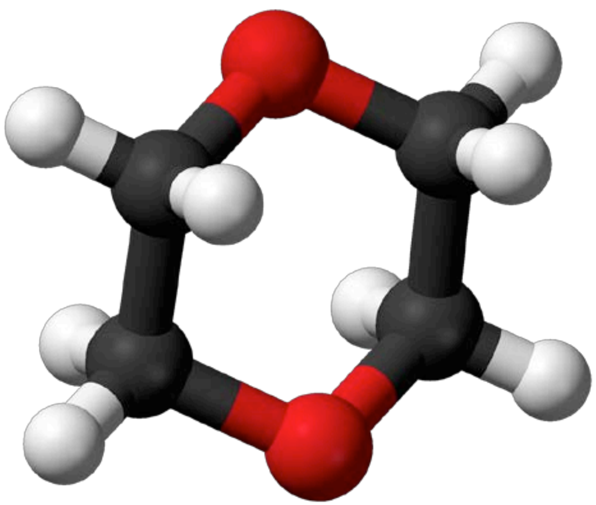
Bromide Impacts

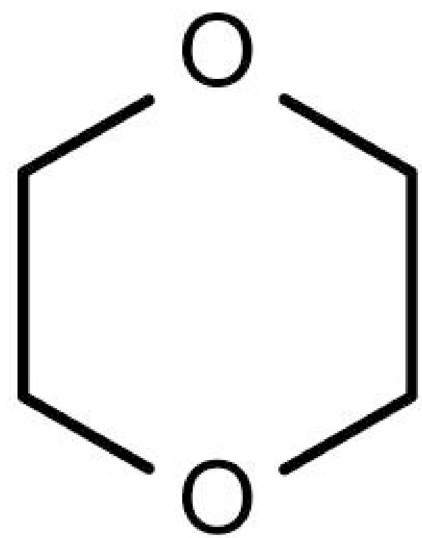
- As bromide levels increase
  - Concentration of disinfection by-products increases
  - Toxicity of disinfection by-products increases
- Upgrades to drinking water treatment plants needed to maintain compliance with drinking water standards
  - Cape Fear River basin
  - Dan River basin
- Bromide discharges a violation of the Clean Water Act?

  "Impact of [wastewater] discharge on public water supplies" (40 CFR 125.62):

  [Such discharge] "must not have the effect of requiring treatment over and above that which would be necessary in the absence of such discharge in order to comply with local and EPA drinking water standards."

1,4-Dioxane



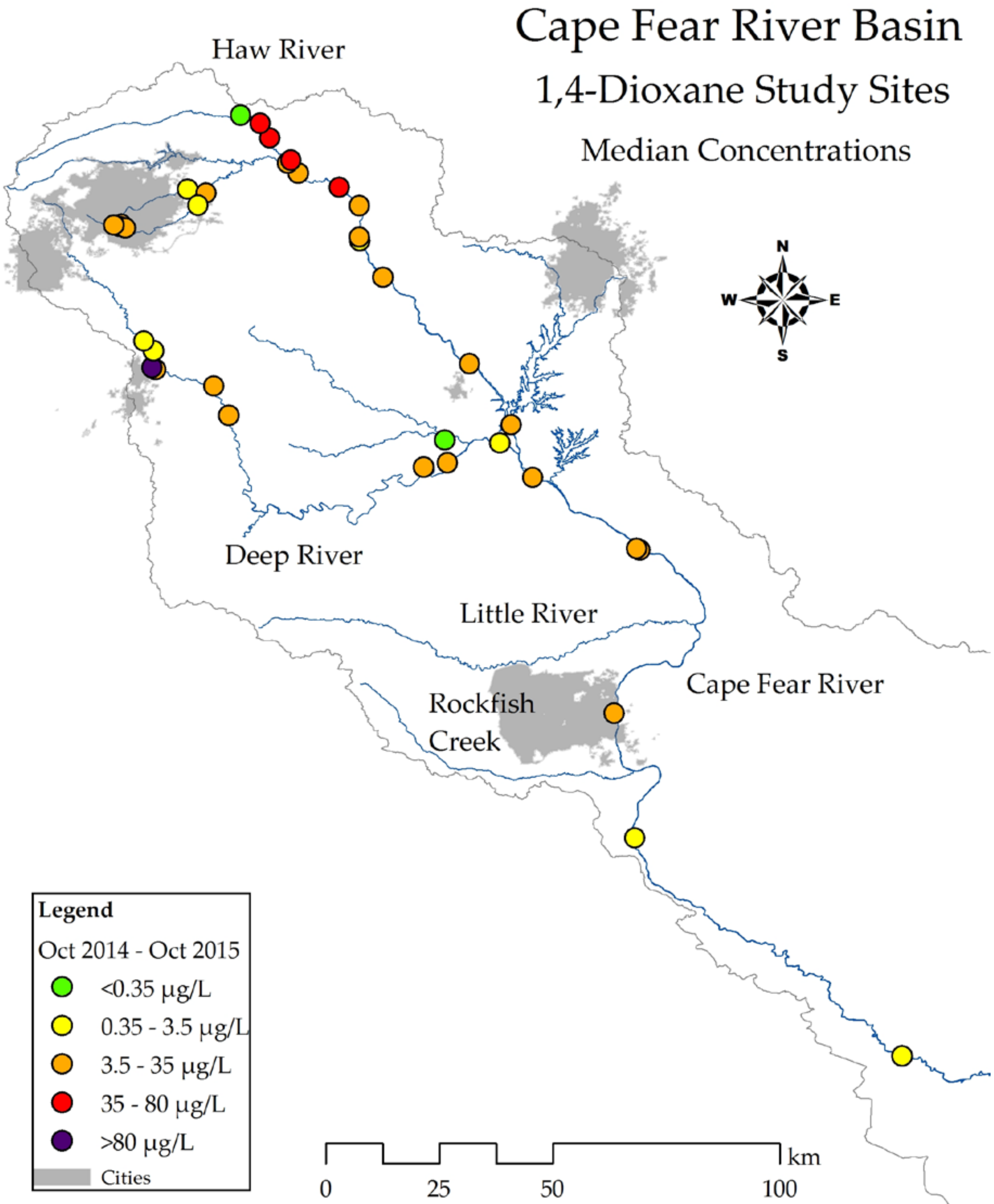


1,4-Dioxane – Background Information

- Sources
  - Solvent stabilizer (declining, mostly GW pollution)
  - Industrial solvent
  - By-product of manufacturing processes involving ethylene oxide (e.g. plastics, detergents)
- EPA's Third Unregulated Contaminant Monitoring Rule (UCMR3)
  - Detected nationwide in 11.5% of 36,479 drinking water samples
  - 7 of the 20 highest concentrations across the US occurred in NC (all derived from Cape Fear River water)

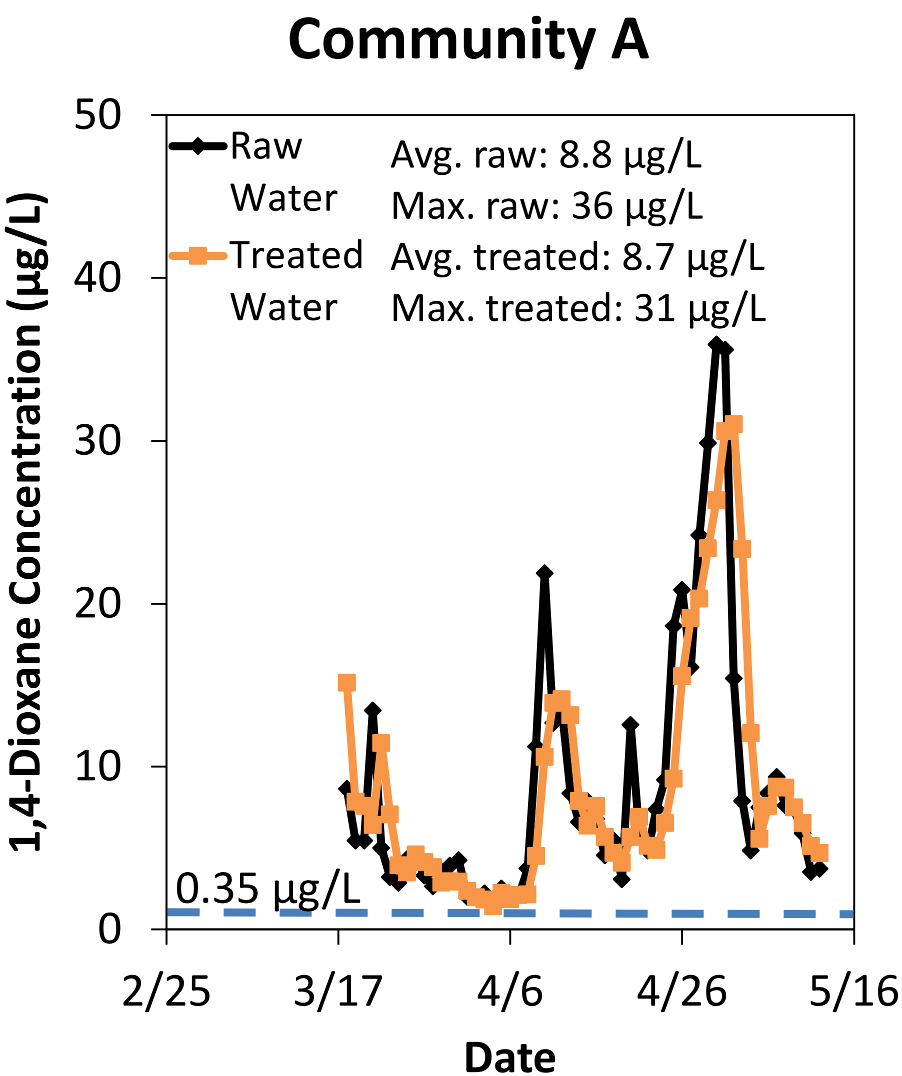
1,4-dioxane cancer risk

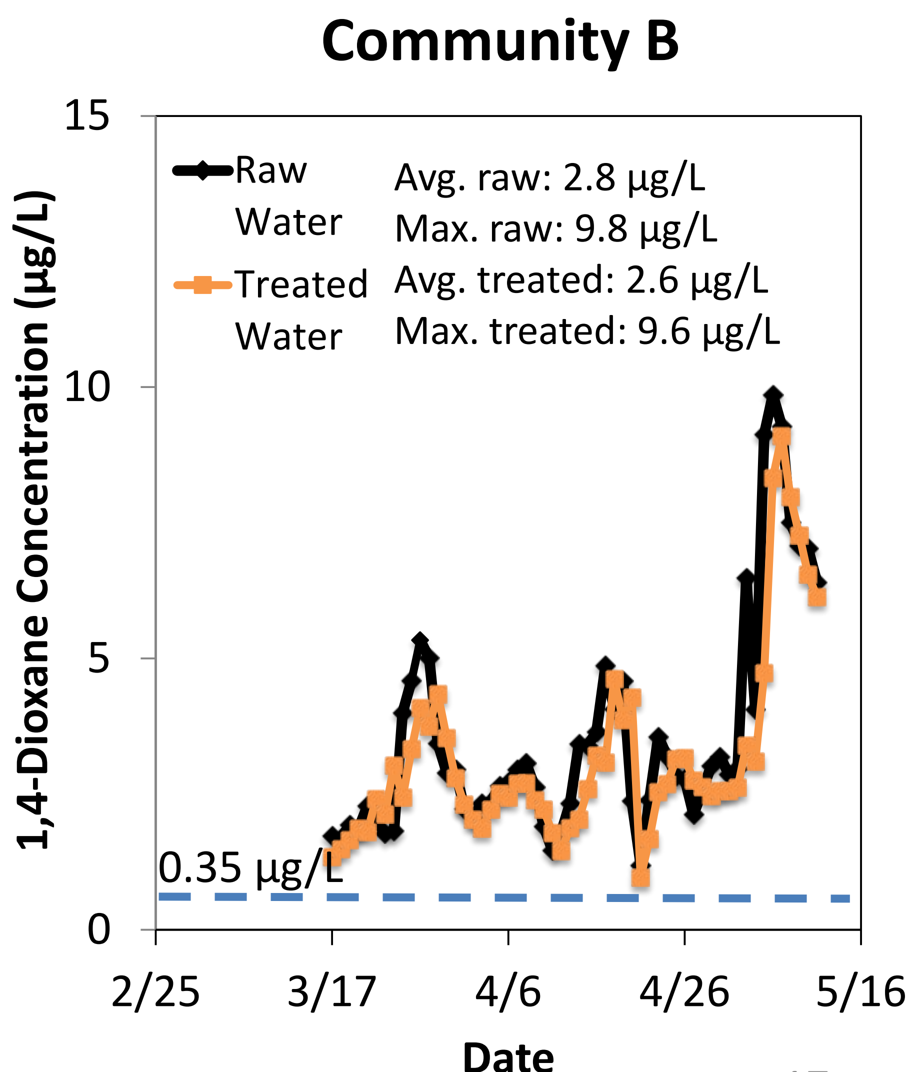
- Likely human carcinogen (EPA IRIS database)
- Lifetime consumption of drinking water containing
  - 0.35 μg/L = 1:1,000,000 excess cancer risk
  - 3.5 μg/L = 1:100,000 excess cancer risk
  - 35 μg/L = 1:10,000 excess cancer risk
- Comparison with disinfection by-products
  - Bromodichloromethane: 0.6 μg/L = 1:1,000,000 risk
  - Dibromochloromethane: 0.4 μg/L = 1:1,000,000 risk



- NC Surface Water Supply Standard (WS I – WS IV): 0.35 µg/L
- Standard violated in vast stretches of the Haw, Deep, and Cape Fear Rivers

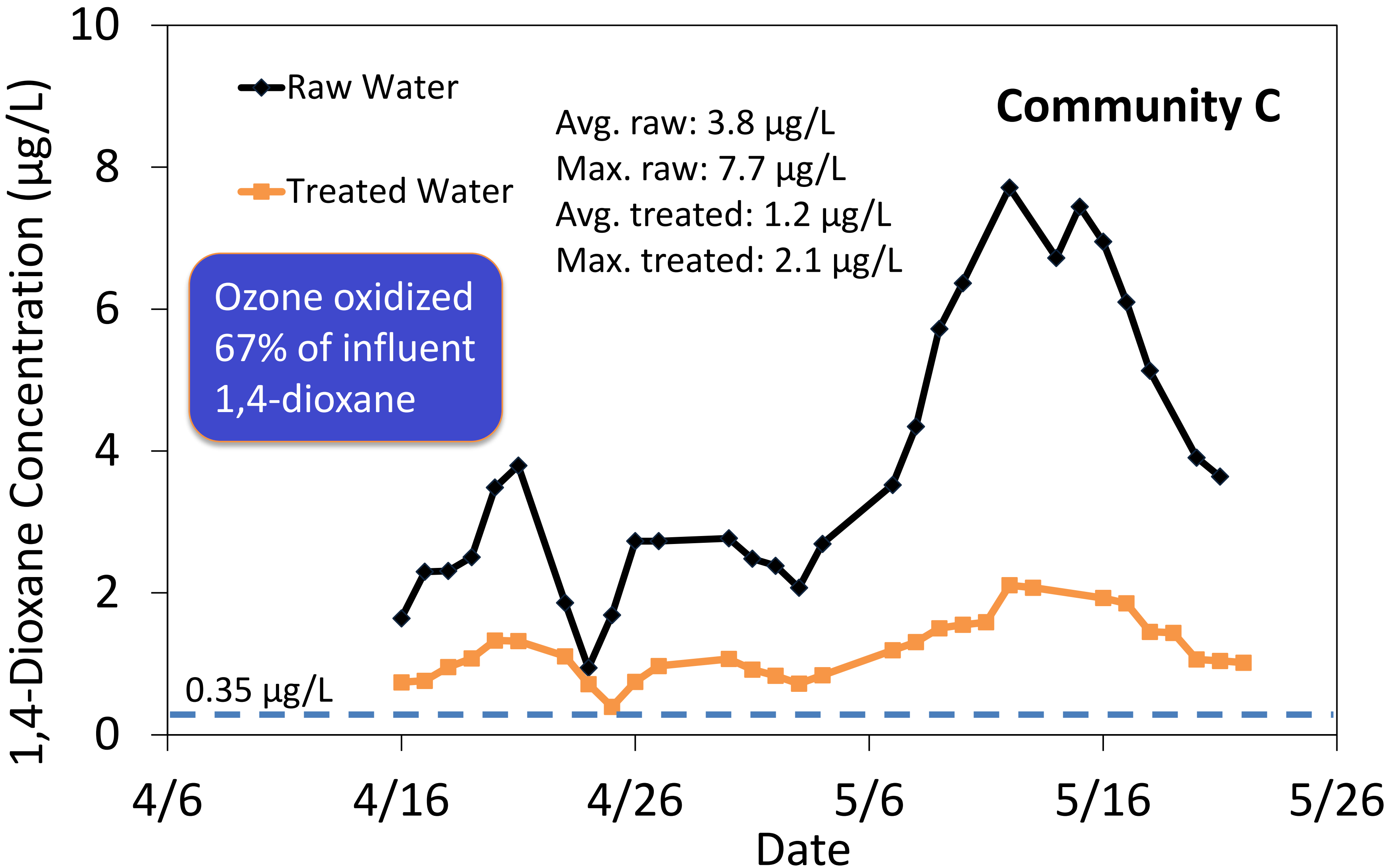
1,4-Dioxane is not Removed in Conventional Water Treatment Plants





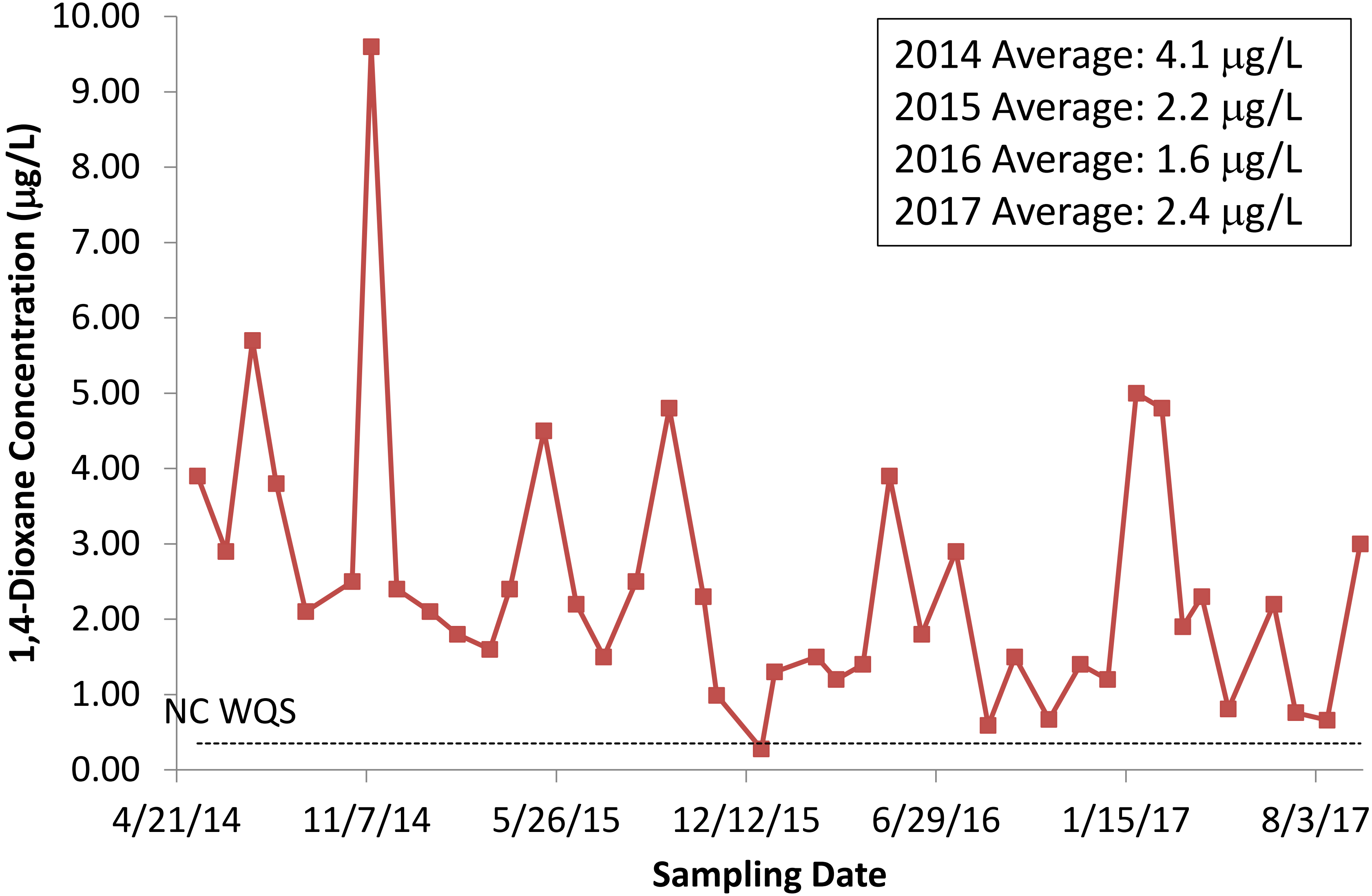
2015 Data

1,4-Dioxane is Partially Oxidized by Ozone



2015 Data

1,4-Dioxane Concentrations at Intake of Community B

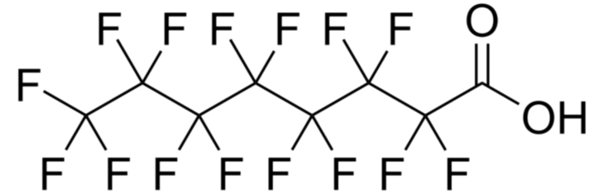


1,4-Dioxane Management Considerations

- Enforce NC surface water quality standard (0.35 $\mu g/L$)
  15A NCAC 02B .0208 states that "for carcinogens, the concentrations … shall not result in unacceptable health risks and shall be based on a Carcinogenic Potency Factor. An unacceptable health risk for cancer shall be considered to be more than one case of cancer per one million people exposed (one-in-a-million risk level)."
- Control of upstream sources
  - Industrial pretreatment programs
  - NPDES discharge permits
  - Treatment technologies exist to remove or oxidize 1,4-dioxane in water
    - Advanced oxidation (UV/H_2O_2)
    - Tailored sorbents (carbonaceous resins)
    - Reverse osmosis
    - Biological methods (in the research stage)

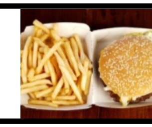
Per- and polyfluoroalkyl Substances (PFASs)

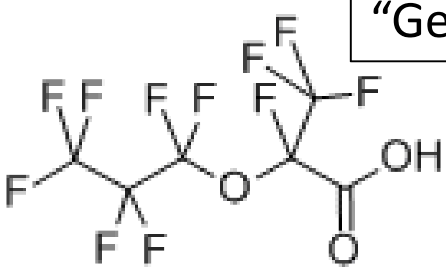
Non-stick coatings



C8 = PFOA

Grease- and oil- resistant coatings for paper products



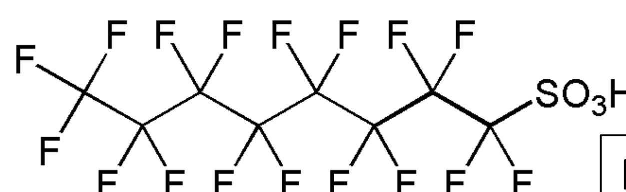


"GenX"

Water repellent fabrics

Stain-resistant coatings for fabrics, carpets, and leather

Aqueous film forming foams



PFOS

PFASs have long half-lives in humans

- Half-lives in humans
  - PFOA: 3.8 years
  - PFOS: 5.4 years
  - GenX: ?

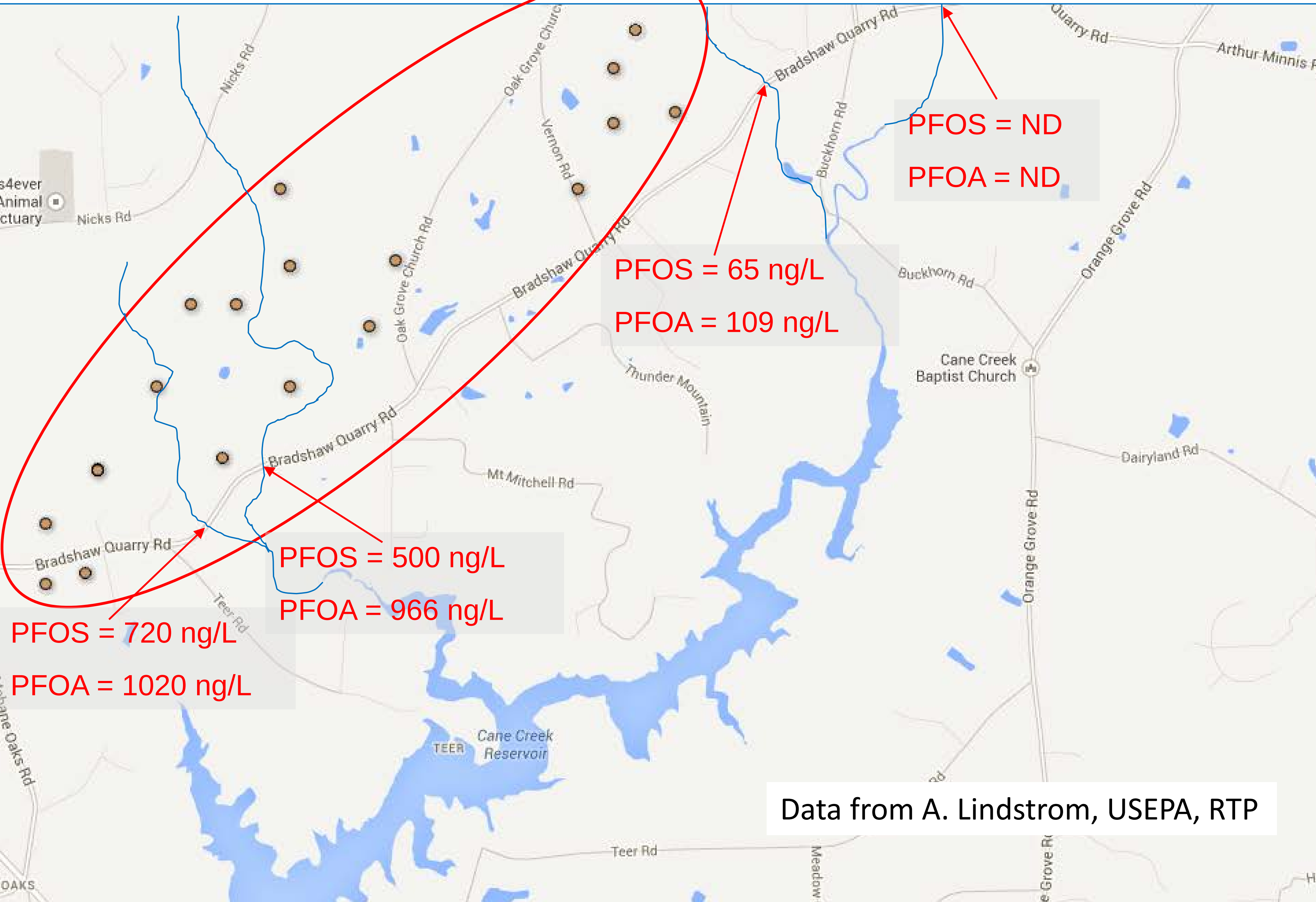
- Toxicokinetic differences for PFOA
  - 17-19 days in mice
  - 4 hours in female rats

To protect the public from adverse health effects, health based guidelines have been established.

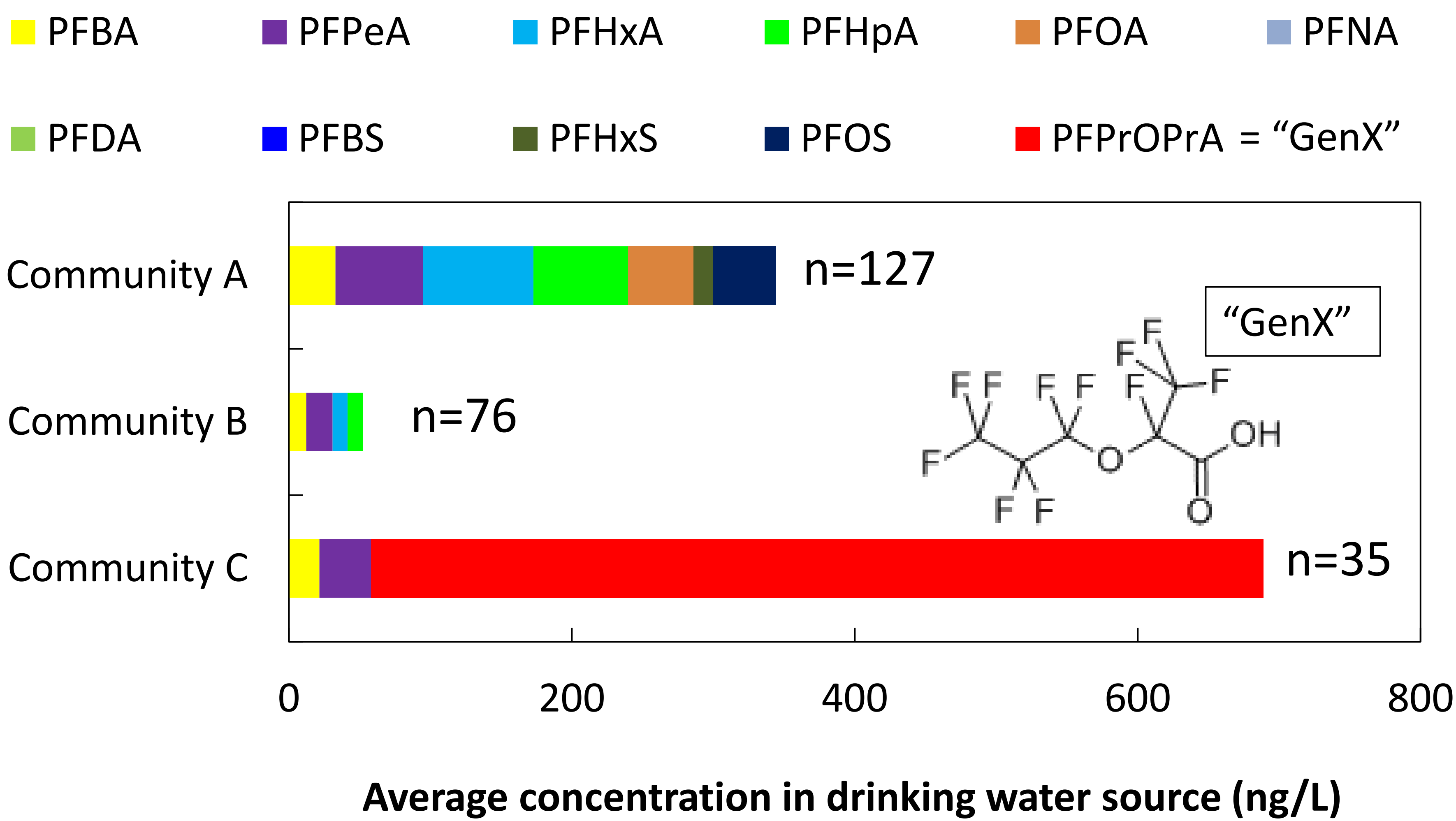
EPA Health Advisory (chronic expoure) →	PFOS + C8: 70 ng/L
New Jersey guidance level (C8) and recommended MCL (C9) →	C8: 40 ng/L C9: 13 ng/L
North Carolina health goal (GenX) →	140 ng/L

PFOS+PFOA Concentrations often exceed EPA's Health Advisory Level in Haw River at Bynum (Pittsboro drinking water source)

Land application of biosolids in watershed of a NC drinking water reservoir

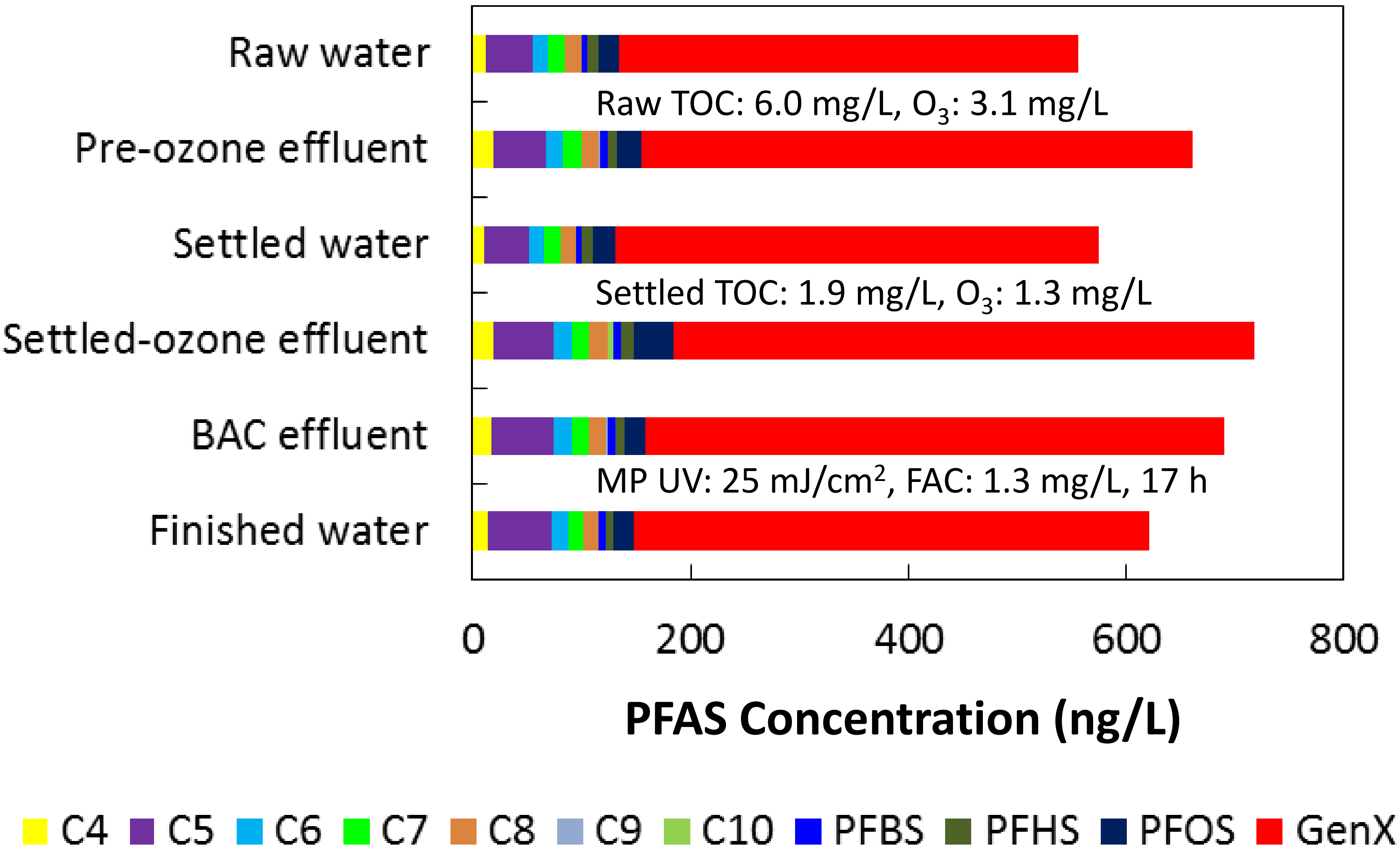


PFAS Occurrence in the Cape Fear River Basin

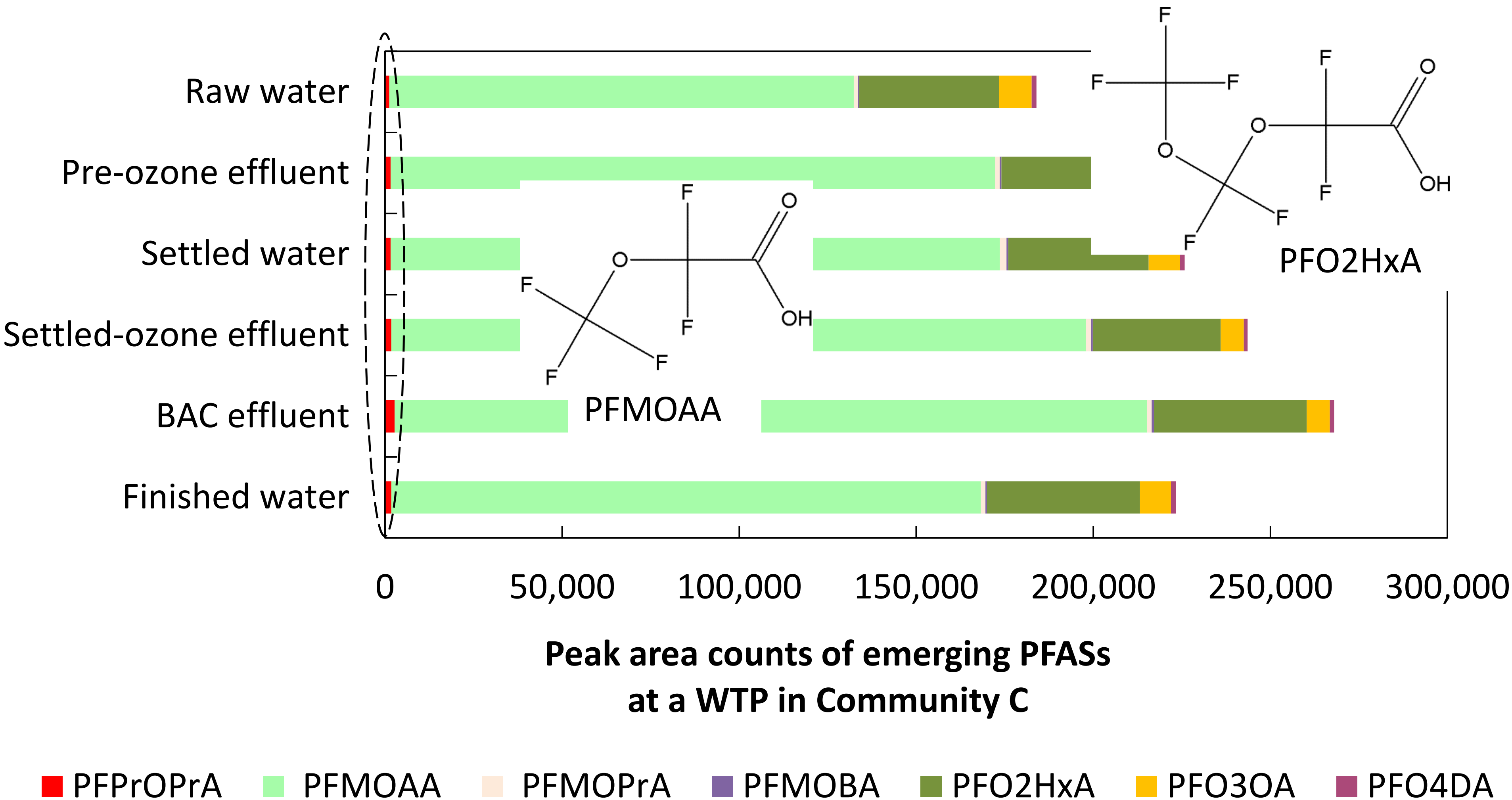


Sun et al. (2016) ES&T Letters

No measurable PFAS removal by conventional and advanced treatment



Recently discovered perfluoroalkyl ether carboxylic acids occur at substantially higher concentrations than traditional PFASs and GenX



Sun et al. (2016) ES&T Letters

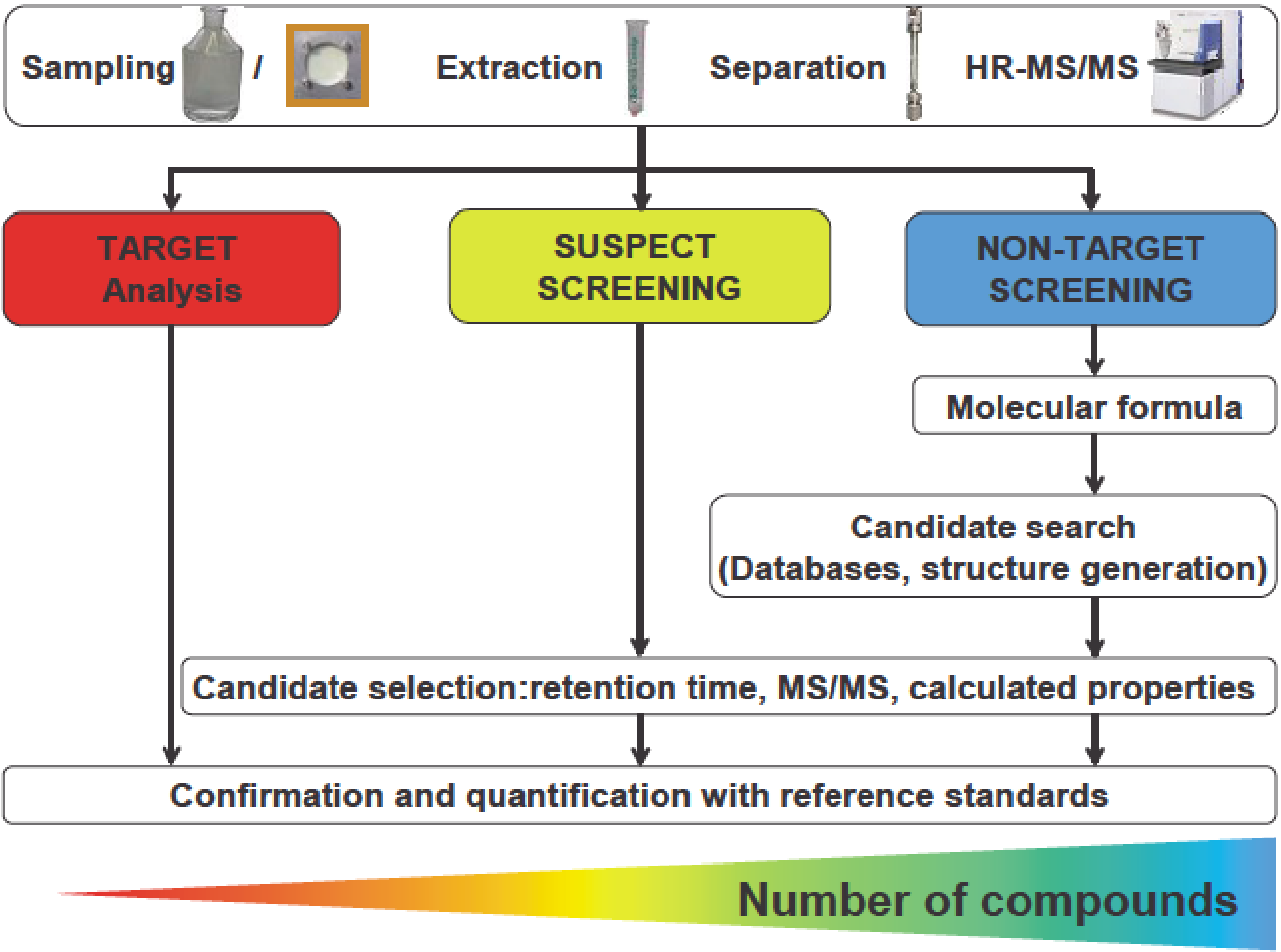
PFAS Management Considerations

- Control of upstream sources
  - NPDES discharges
  - Industrial pretreatment programs
  - Test biosolids prior to land application
  - Manage runoff from fire fighting (training) activities
- Treatment options
  - Activated carbon (effective for some PFASs, but not for others)
  - Anion exchange
  - Reverse osmosis

Take Home Messages

- Many unregulated contaminants are present in Cape Fear River water
- Some “emerging” compounds have been in the river for decades
- Some are by-products of manufacturing processes – lack of analytical standards, toxicity data
- New monitoring and permitting approaches are needed to protect drinking water quality in downstream communities

Work flow for analysis of organic chemicals



Hollender et al. 2014. *Chimia*

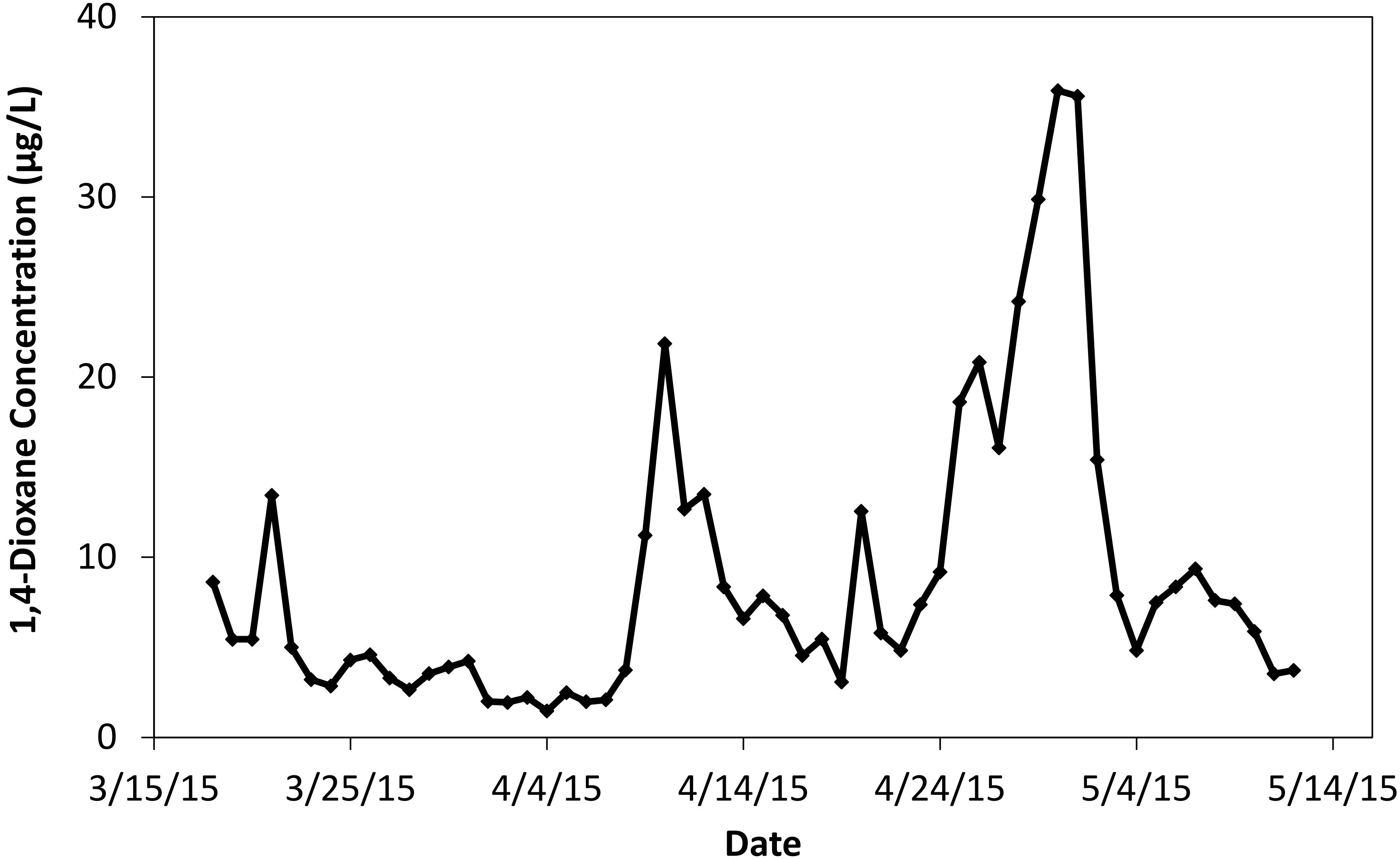
Challenges associated with measuring organic chemicals at low concentrations

- Sample collection
  - Sample containers and cleaning
  - Preservation
  - Representativeness
- Matrix Interference
  - Isotope dilution method
  - Matrix spikes
  - High resolution mass spectrometry

Sample collection

- Containers – QA/QC is important!
  - No leaching (blanks)
  - No sorption (fortified blanks)
  - Detergents can contain interferences (e.g. 1,4-dioxane)
- Preservation
  - Not a critical factor for persistent organic pollutants, but acidification helps control biological growth that interferes with sample filtration
  - Critical for reactive compounds (e.g. hydrolysis, biodegradation)
- Representativeness
  - Spatial (groundwater plume, surface water with multiple point and non-point sources)
  - Temporal (surface water with multiple point and non-point sources, hydrological conditions)

1,4-Dioxane concentrations vary rapidly in surface water – results of daily composite samples

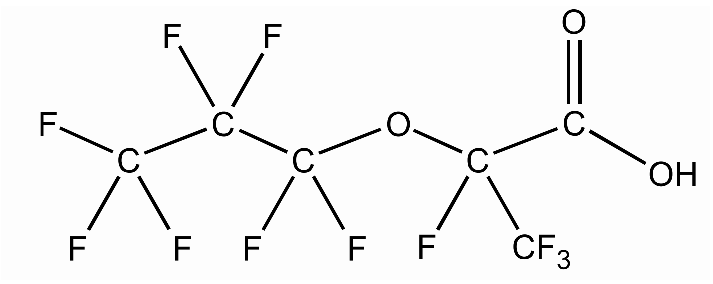


Matrix Interference

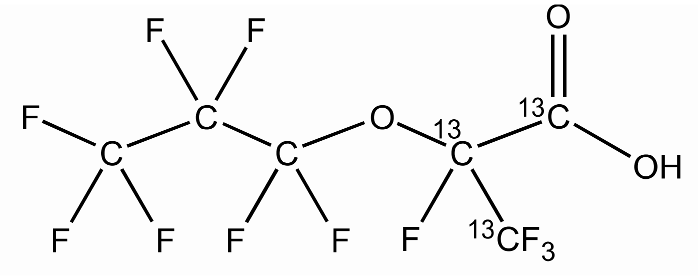
- Matrix interference is a commonly used argument to raise doubt about the accuracy of analytical results
- Proper QA/QC approaches are required:
  - Isotope dilution (spike known quantity of isotopically labeled analog into sample prior to sample extraction and analysis)
  - Matrix spikes
- High resolution mass spectrometry

Isotope Dilution

- Need reference standards
  - Native (^{12}C, ^{1}H) for calibration standard preparation
  - Isotopically labelled (^{13}C, ^{2}H) internal standard added to calibration standards and unknowns



GenX



MW: 330 Da

MW: 333 Da

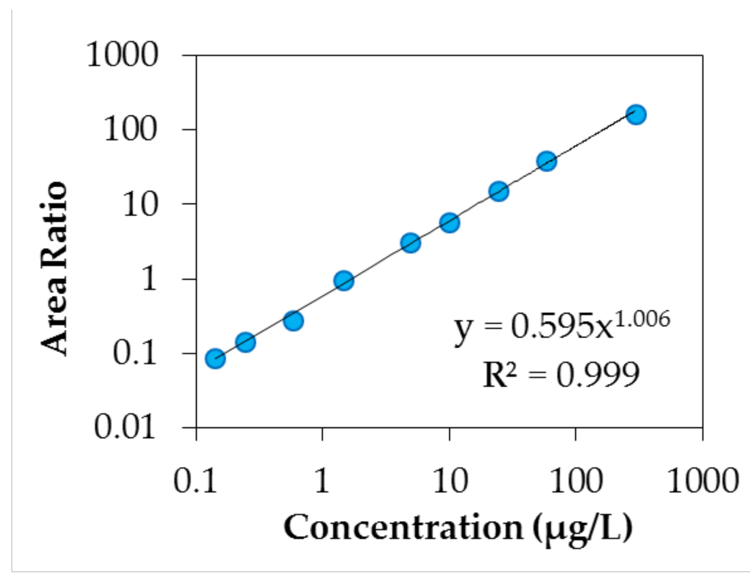
- Add isotopically labeled to sample prior to extraction to account for
  - Extraction efficiency and variability
  - Instrument variability

Isotope dilution

- Base calibration and sample analysis on area ratio:

  Analyte peak area/Internal standard peak area

- If extraction efficiency in a particular matrix is low, it is similarly low for analyte and internal standard
- If instrument response is affected (e.g. ion supression by background matrix), effect is similar for analyte and internal standard



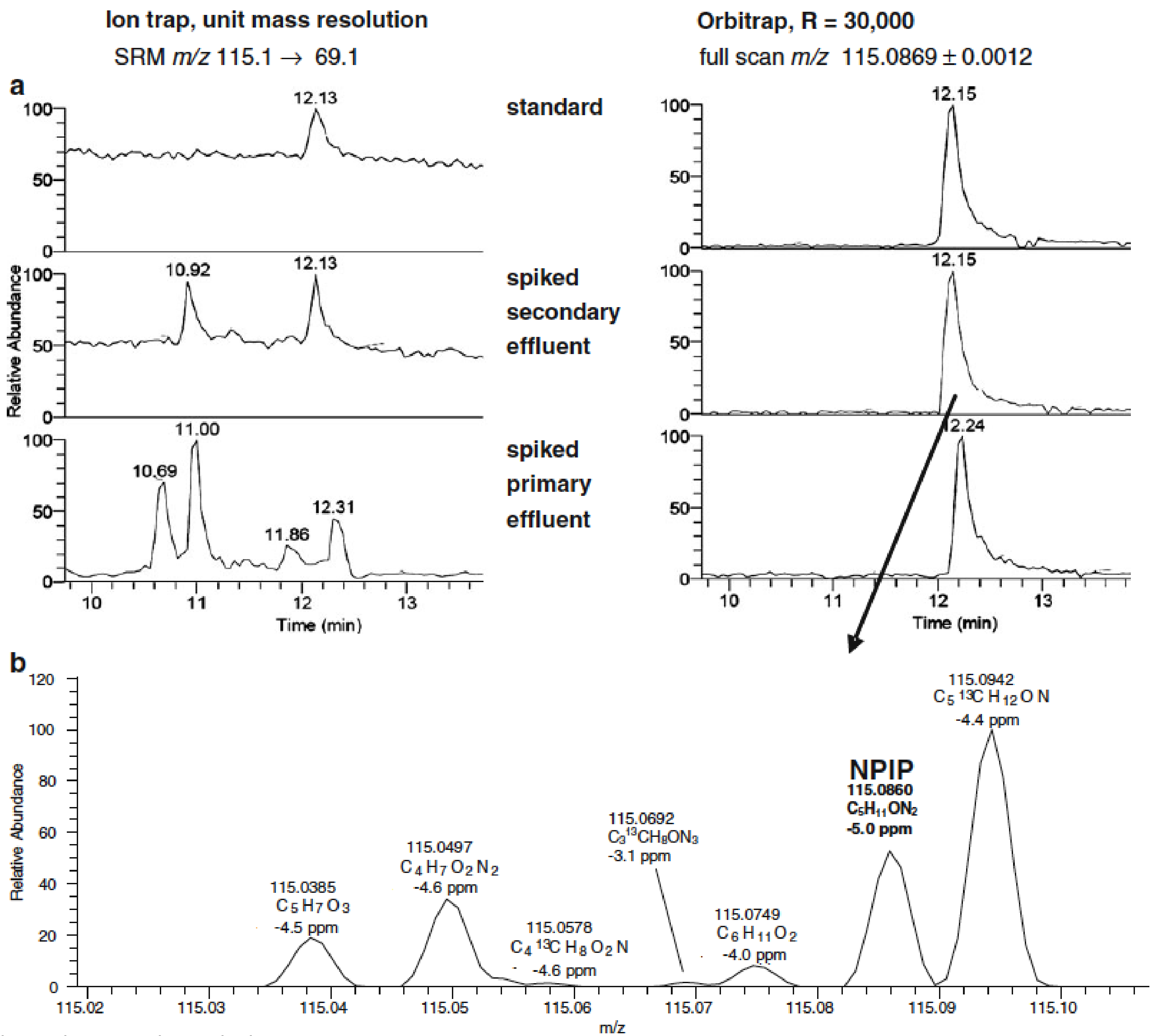
Matrix Spike Experiments: 1,4-Dioxane

Matrix	Background concentration (μg/L)	Recovery of matrix spike	RSD
Drinking Water A	<0.15	95-106%	4-5%
Drinking Water B	8.72	93%	2-5%
Groundwater A	<0.15	95-97%	5-9%
Groundwater B	1.36	86-95%	2-6%
Surface water A	<0.15	104-115%	7-8%
Surface water B	58.08	108-115%	2-3%
Wastewater A	2.15	99%	5-9%
Wastewater B*	118.45	103-113%	2-5%

* After 5 times dilution

Sun et al. 2016. ES&T

Enhanced selectivity with high resolution mass spectrometry



Krauss et al. 2010. *Analytical Bioanalytical Chemistry*

Thank you!

Questions:

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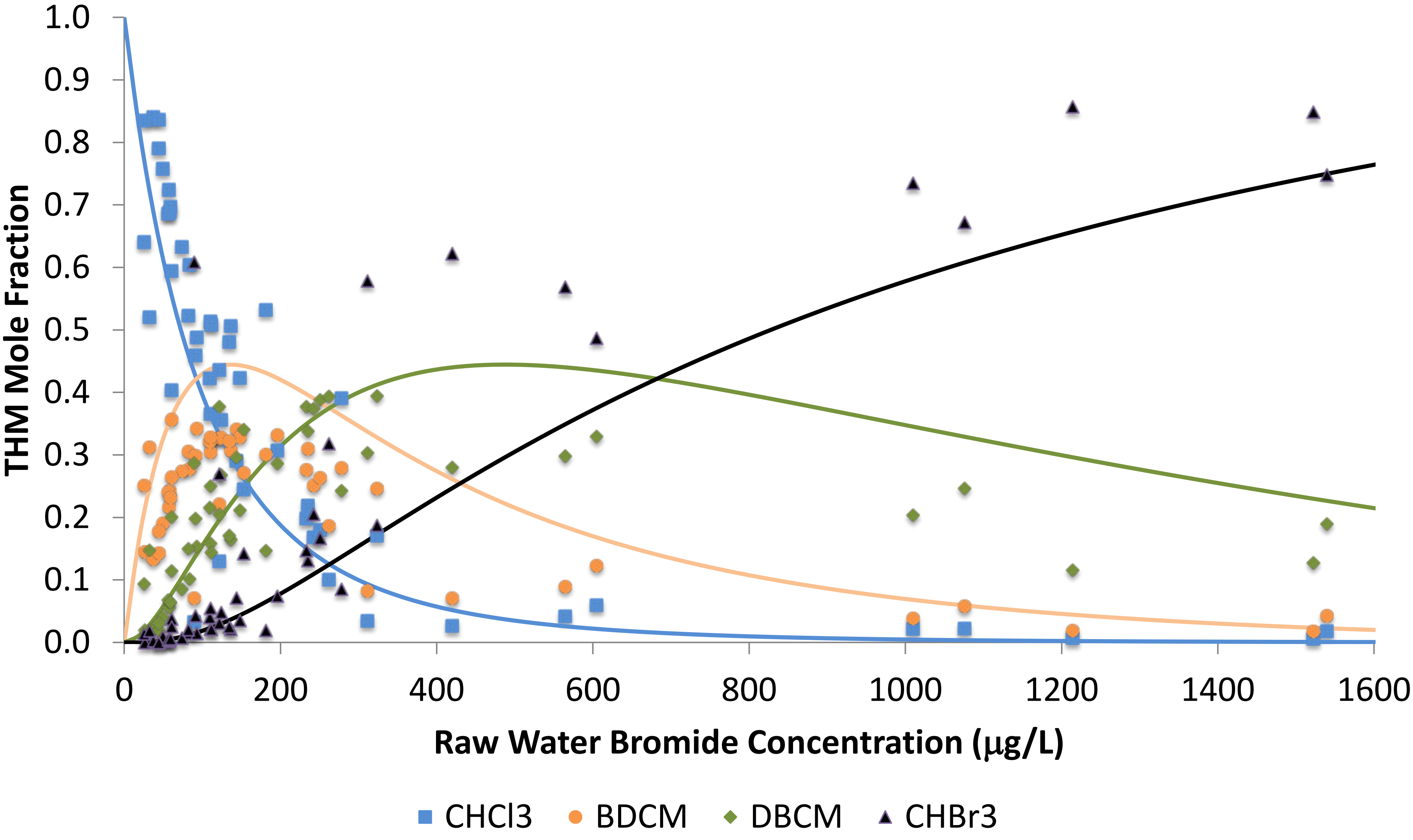
Bromide Impact on THM Compliance

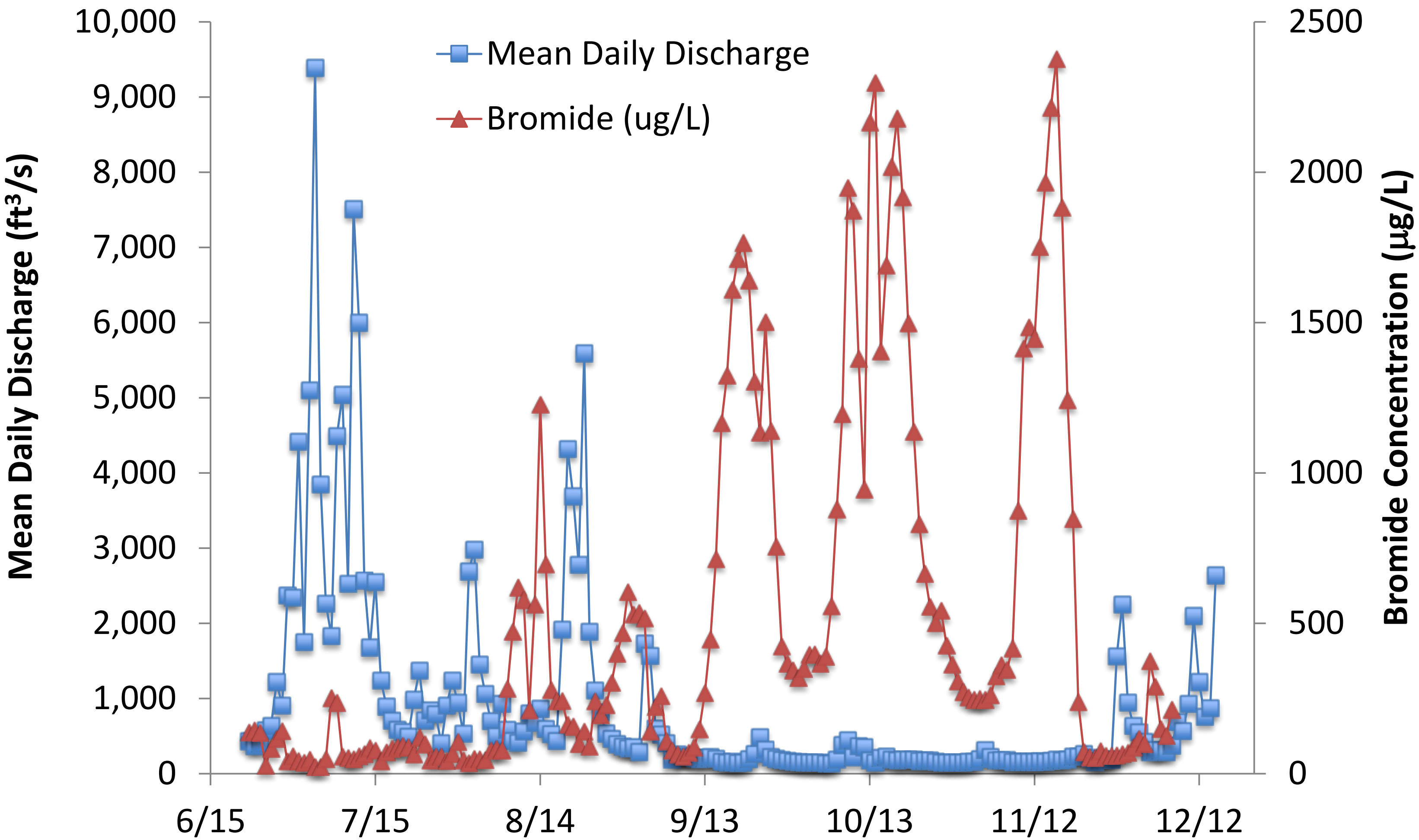
- Bromide reacts with HOCl to form HOBr
- HOBr shifts speciation to brominated DBPs
- Bromine weighs 2.25x chlorine….so shift towards brominated DBPs leads to higher DBP mass concentrations

	Quarter 3, 2003 (Raw Bromide = 50 µg/L)			Quarter 3, 2012 (Raw Bromide = 106 µg/L)		
	µmol/L	µg/L	Percent	µmol/L	µg/L	Percent
Chloroform	0.44	53	68%	0.21	25	27%
Bromodichloromethane	0.11	18	23%	0.20	32	34%
Dibromochloromethane	0.03	7	9%	0.14	29	31%
Bromoform	0	0	0%	0.03	7	8%
TTHM	**0.58**	**78**	**100%**	**0.57**	**93**	**100%**

Effect of bromide concentration on THM speciation

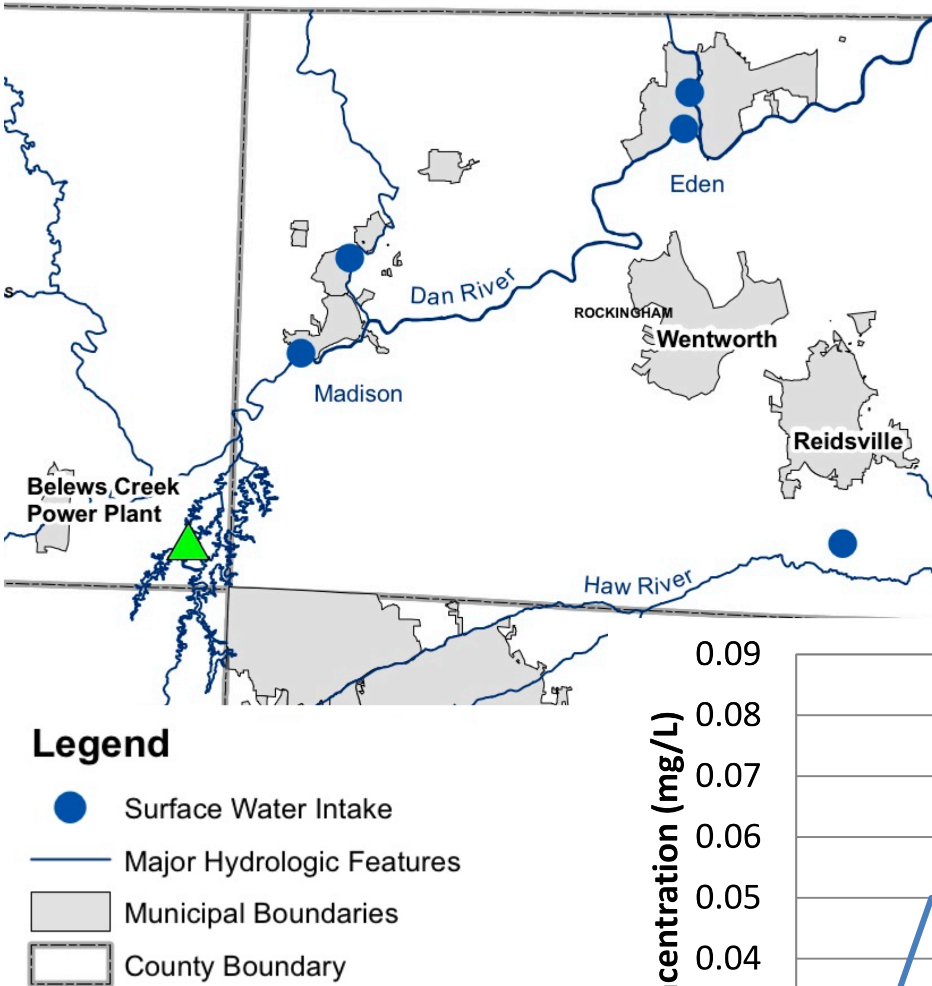


Bromide Concentrations and Streamflow (Community A Intake)



2013 Data

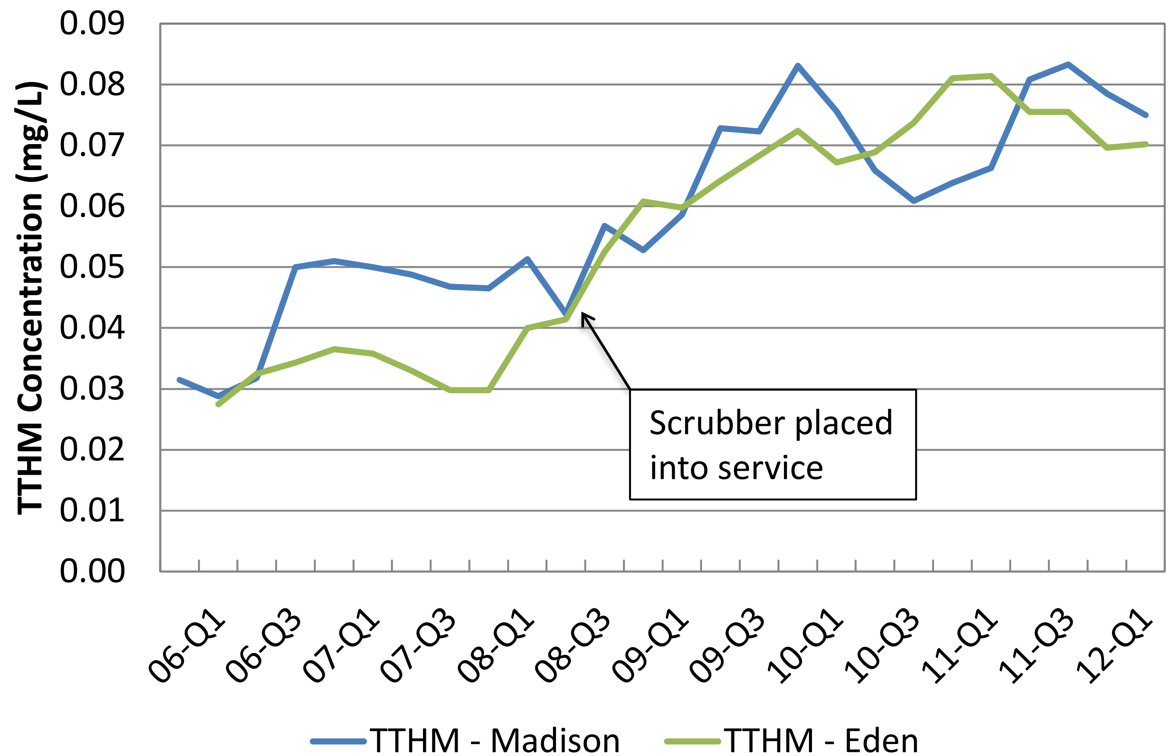
Dan River, NC



- Wet flue gas desulfurization scrubber went online in 2008
- No baseline bromide data
- 2011 bromide levels in Dan River at Eden reached 430 µg/L

Eden, NC:

- <20% brominated THMs in 2006
- >95% brominated THMs in 2011



PFAS Concentrations in Haw River at Bynum (Pittsboro source)