NC STATE UNIVERSITY

Considerations for large and small utilities for addressing emerging contaminants from upstream sources

Detlef Knappe
Professor of Civil, Construction, and Environmental Engineering
North Carolina State University
(knappe@ncsu.edu)

Students and post-doc: Elisa Arevalo, Amber Greune, Catalina Lopez-Velandia, Mei Sun

Funding: National Science Foundation, NC Water Resources Research Institute, NC Urban Water Consortium

Freshwater in the North Carolina Coastal Plain, New Bern, NC, February 16, 2016

Presentation Overview

- Upstream sources
- The Universe of Chemicals
- Example contaminants of concern
  - Bromide
  - 1,4-Dioxane
  - Perfluoroalkyl substances
- Implications

Increasing Reliance on Surface Water and Associated Water Quality and Treatment Challenges

Central Coastal Plain Capacity Use Area Trends	2007	2014
Population	198,362	219,966
Surface Water Sources (mgd)	13.4	21.8
Groundwater Source (mgd)	12.1	4.0
Drinking Water Derived from Surface Water (%)	52.5	84.6

Shift to surface water also occurring outside of the CCPCUA. For example, Lower Cape Fear River Water and Sewer Authority provides water to:

- Pender County Utilities
- Brunswick County
- Cape Fear Public Utility Authority

Shift to surface water introduces new drinking water quality and treatment challenges:

- Disinfection (pathogens in surface water)
- Disinfection by-product formation (higher total organic carbon concentration, bromide discharges from power plants and industries)
- Unregulated contaminants

Upstream Sources

- Point sources
  - Municipal wastewater treatment plants
    - Industrial wastewater inputs
    - Landfill leachate
    - Coal ash leachate
    - Coal/oil/gas extraction wastewater
  - 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

Bromide (Br^-)

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

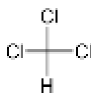
http://www.epa.gov/eg/steam-electric-power-generating-effluent-guidelines-2015-final-rule

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

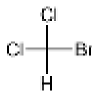
- $Cl_2 + H_2O \longleftrightarrow HOCl + H^+ + Cl^-$
- $HOCl + Br^- \longleftrightarrow HOBr + Cl^-$
- DOM + HOCl + HOBr ⟷ trihalomethanes (THMs) + haloacetic acids (HAAs) + …

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

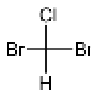
Trihalomethanes (THMs)



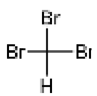
- Chloroform
  Molecular weight = 119.4 g/mol
  One-in-a-million cancer risk: -



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



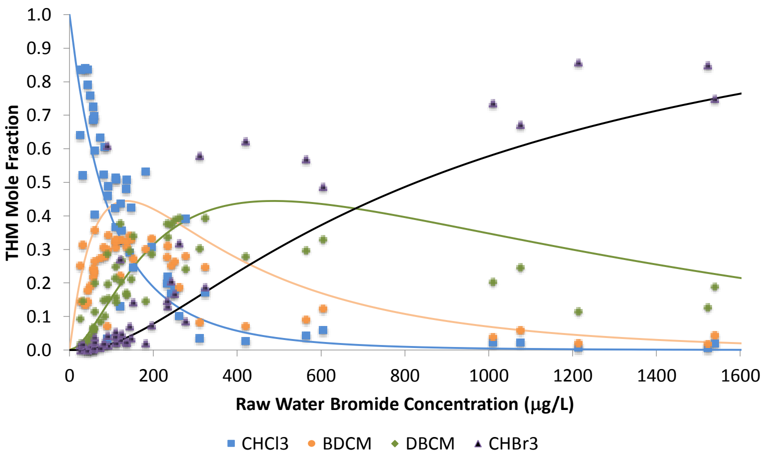
- Dibromochloromethane
  Molecular weight = 208.3 g/mol
  One-in-a-million cancer risk: 0.4 μg/L



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

Drinking water standard: Σ THMs $\leq$ 80 μg/L

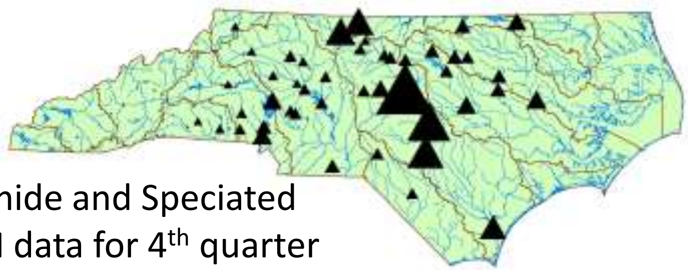
Effect of bromide concentration on THM speciation



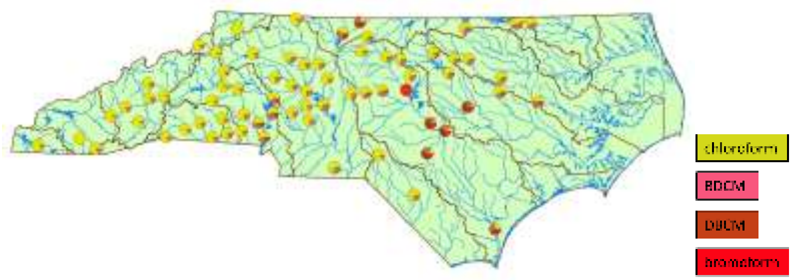
Bromide Impact on THM Compliance

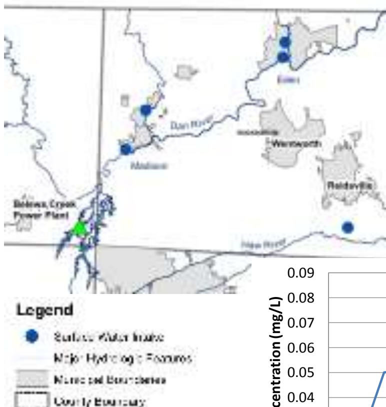
- Bromide reacts with HOCl to form HOBr
- HOBr shifts speciation to brominated DBPs
- Bromine weighs 2.25x chlorine….so shift towards brominated DBPs leads to higher DBP mass concentrations

	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%**



Bromide and Speciated THM data for 4th quarter of 2013

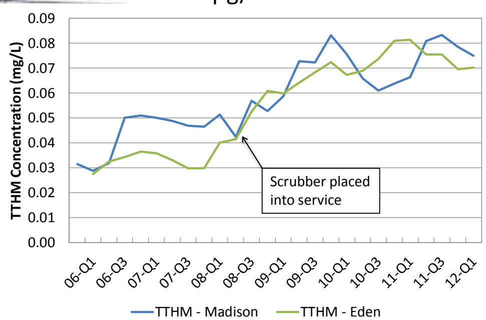




Dan River, NC

- 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

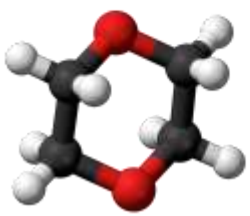
Eden, NC:
- <20% brominated THMs in 2006
- >95% brominated THMs in 2011

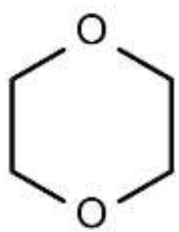


Bromide Management Considerations

- Advocate for discharge limits on bromide (e.g. work with AWWA, contact DEQ)
- Manage hydraulic residence time in clearwell
  - Sufficient contact for disinfection
  - Limit excessive contact to control DBP formation
- Install tank aeration systems to strip out THMs in clearwell and/or storage tanks
- Chloramination can help with compliance of existing DBP regulations, but need to carefully manage
  - Nitrification in distribution system
  - Potential lead corrosion problems
  - Formation of nitrosamines and other N-DBPs

1,4-Dioxane



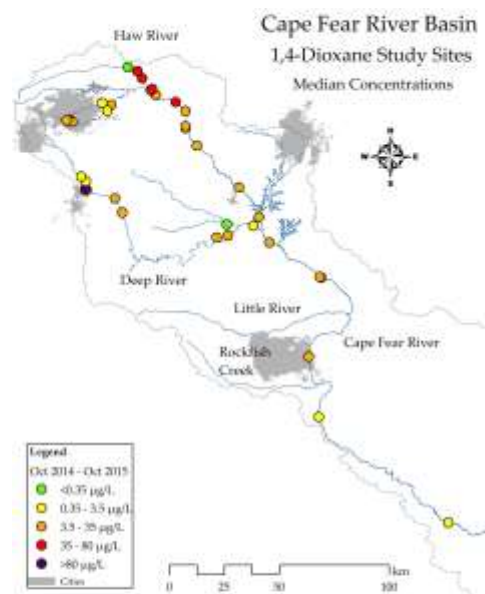


1,4-Dioxane – Background Information

- Sources
  - Solvent stabilizer (declining, mostly GW pollution)
  - Industrial solvent
  - By-product of manufacturing processes involving ethylene oxide
- EPA's Third Unregulated Contaminant Monitoring Rule (UCMR3)
  - Detected nationwide in 11.6% of 32,740 drinking water samples
  - 6 of the 12 highest concentrations occurred in NC (all derived from Cape Fear River water)

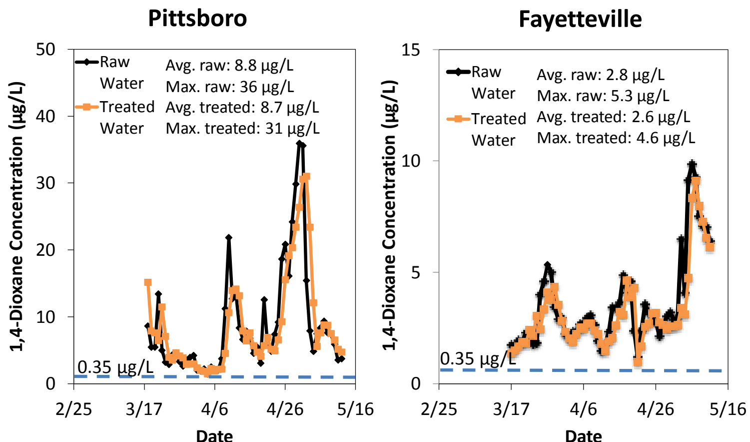
1,4-dioxane cancer risk

- 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



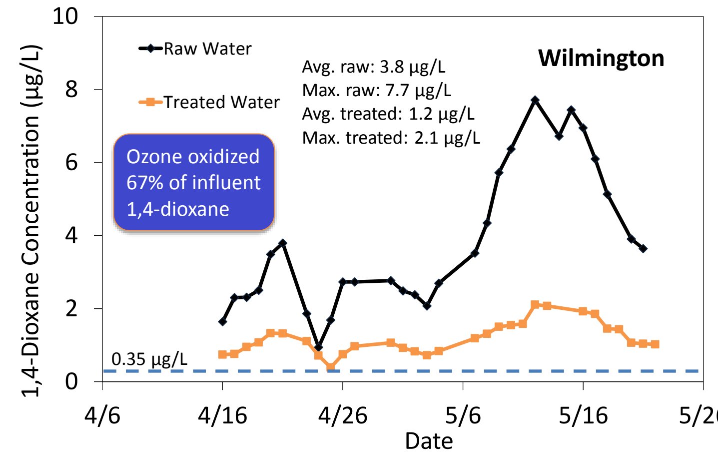
- NC Surface Water Supply Standard (WS I – WS IV): 0.35 μg/L
- Standard violated in vast stretches of the Haw, Deep, and Cape Fear Rivers

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



17

1,4-Dioxane is Partially Oxidized by Ozone



18

1,4-Dioxane – Treatability

- Miscible in water and essentially non-volatile
- Effectiveness of treatment processes
  - Not removed by conventional treatment
  - Poorly adsorbed by activated carbon
  - Only partially removed by reverse osmosis membranes
  - Permanganate – very slow kinetics
  - Ozone is somewhat effective (via hydroxyl radical generation)
  - Among established treatment processes, advanced oxidation processes (O_3/H_2O_2, UV/H_2O_2) may be the only effective treatment option

1,4-Dioxane Management Considerations

- Advocate for enforcement of existing NC stream water quality standard (0.35 μg/L)
- Advanced oxidation processes may offer a viable treatment option, but expensive
- A biological treatment option is showing promise in the research stage

Non-stick coatings

Grease- and oil- resistant coatings for paper products 

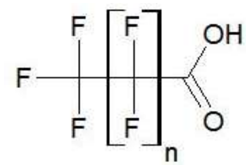
Perfluoroalkyl Substances (PFASs)

Water repellent fabrics

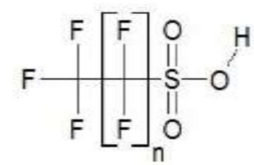
Stain-resistant coatings for fabrics, carpets, and leather

 Aqueous film forming foams

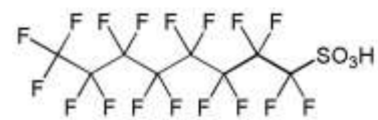
Perfluoroalkyl substances (PFASs) are organic compounds in which all C-H bonds are replaced with C-F bonds.



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



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



PFASs have long half-lives in humans

- Half-lives in humans
  - PFOA: 3.8 years
  - PFOS: 5.4 years
  - PFBS: 4 months
- 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 Provisional Health Advisory (subchronic exposure) → PFOS: 200 ng/L; C8: 400 ng/L

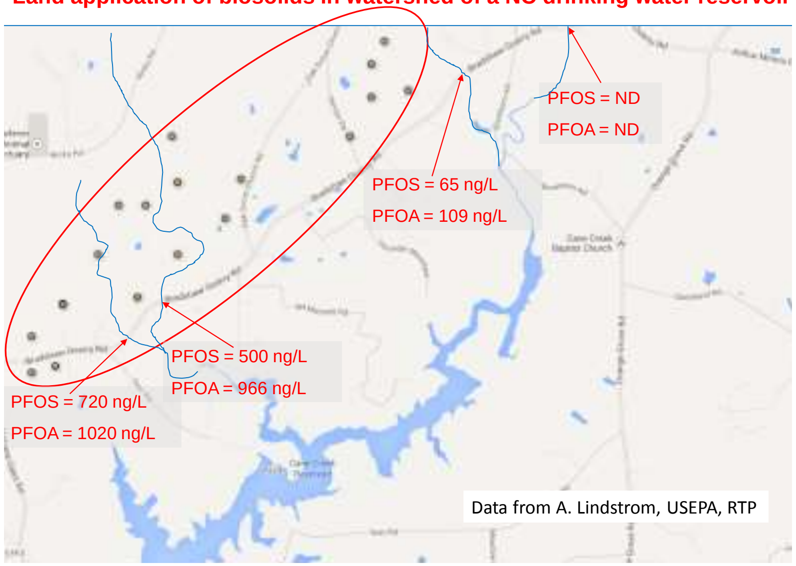
Health-based guidance level, New Jersey (chronic exposure) → C8: 40 ng/L

UCMR3 Data for NC (October 2015 status)

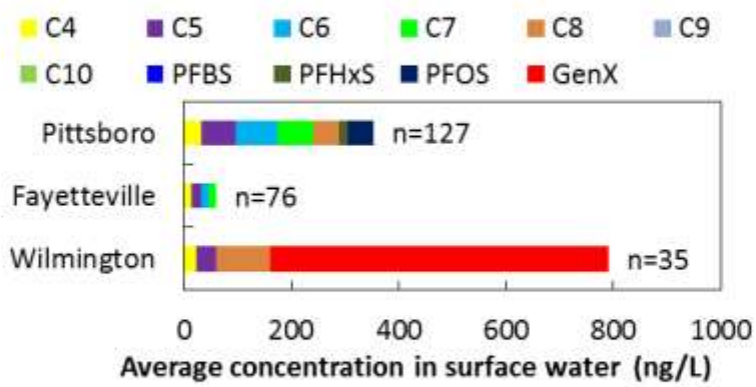
Compound	EPA Method	MRL, μg/L	NC Detects
Perfluorooctanesulfonic acid (PFOS)	537	0.04	7 (max. 90 ng/L)
Perfluorooctanoic acid (PFOA)	537	0.02	9 (max. 30 ng/L)
Perfluorobutanesulfonic acid (PFBS)	537	0.02	0
Perfluorohexanesulfonic acid (PFHxS)	537	0.03	5 (max. 110 ng/L)
Pefluoroheptanoic acid (PFHpA)	537	0.01	26 (max. 50 ng/L)
Perfluorononanoic acid (PFNA)	537	0.09	0

18 out of 145 PWSs that submitted samples had detects (12.4%)

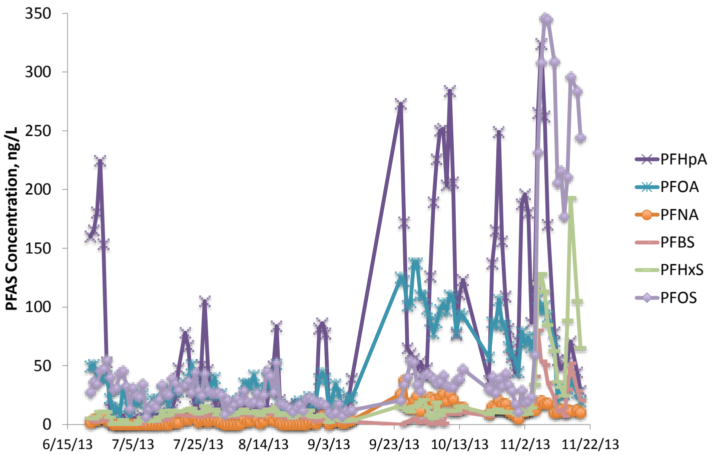
Land application of biosolids in watershed of a NC drinking water reservoir



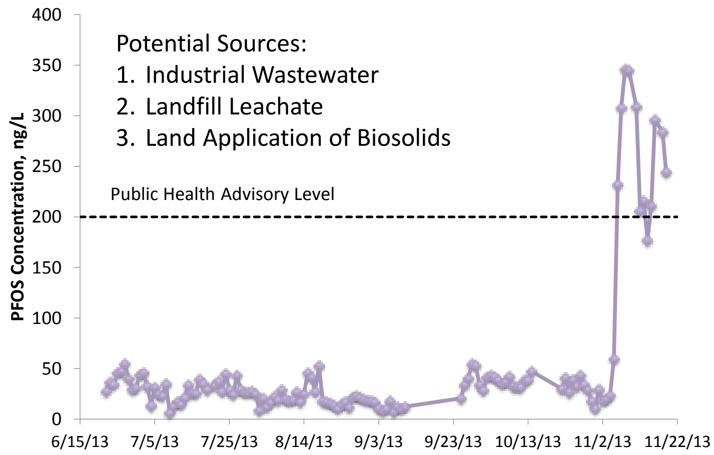
PFAS Occurrence in CFR Watershed



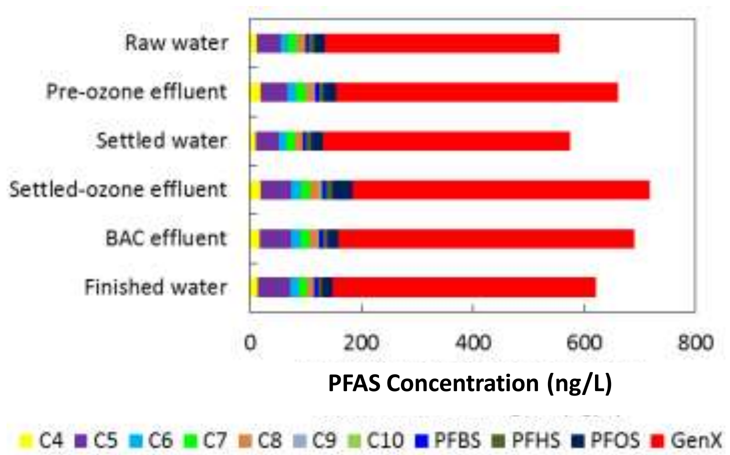
PFAS Concentrations in Haw River at Bynum (Pittsboro source)



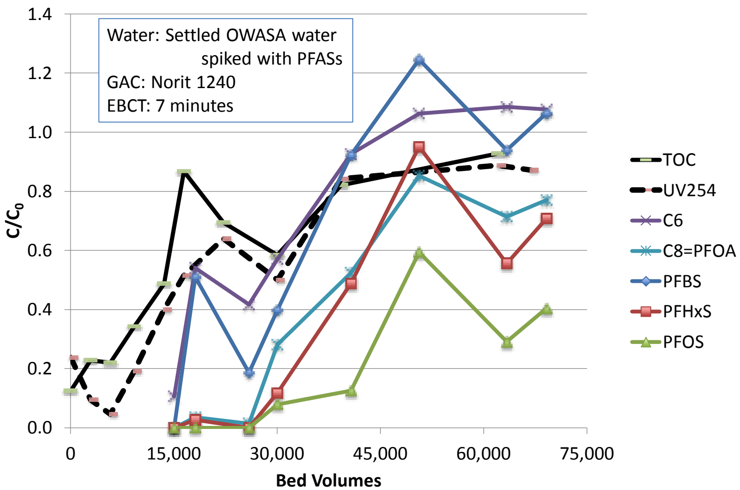
PFOS Concentrations can Exceed EPA's Public Health Advisory Level



No measurable PFAS removal by conventional and advanced treatment



GAC Adsorption Effective for PFAS Control



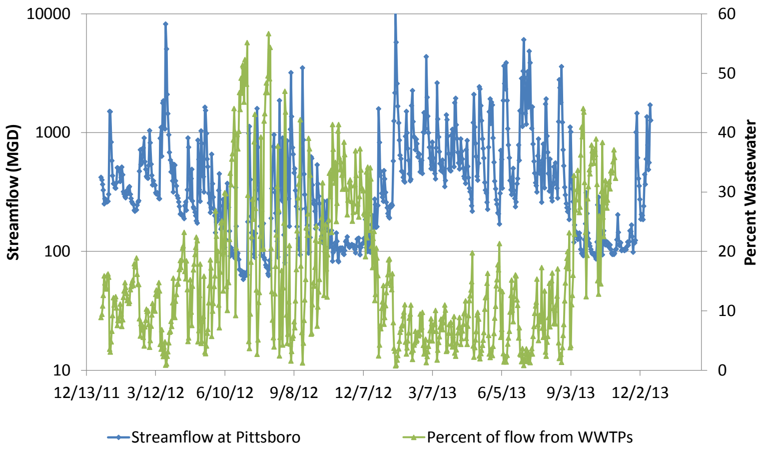
PFAS Management Considerations

- Advocate for control of upstream sources
  - NPDES discharges
  - Test biosolids prior to land application
  - Manage runoff from fire fighting (training) activities
- Install GAC adsorber
  - Monitor TOC removal
  - DBP precursor removal is an added benefit

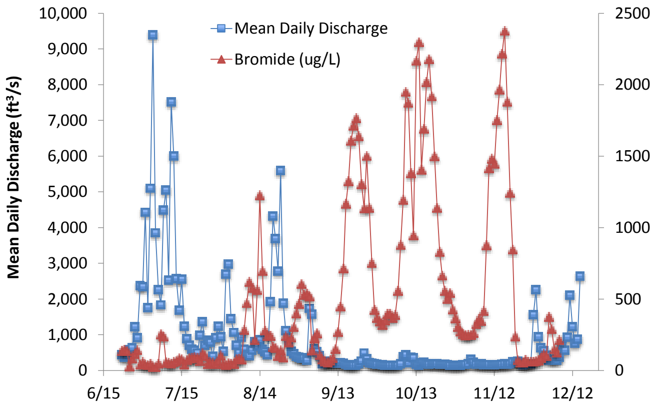
Thank you!

Questions:
knappe@ncsu.edu

Wastewater percentage in Haw River at Bynum (Pittsboro Intake)

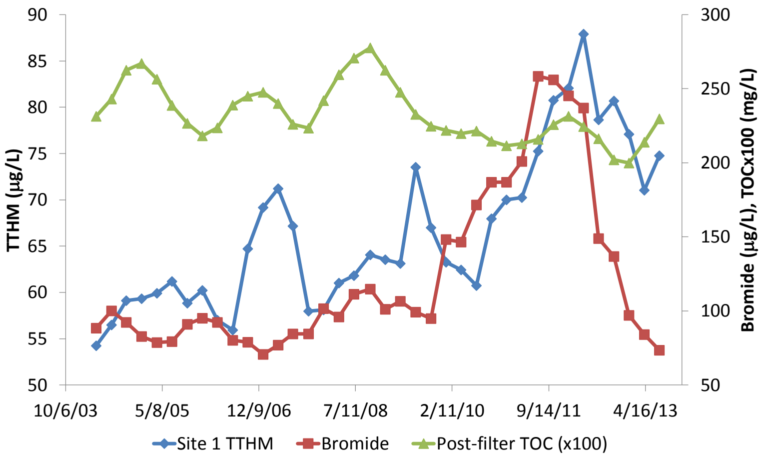


Bromide Concentrations and Streamflow (Haw River at Bynum)

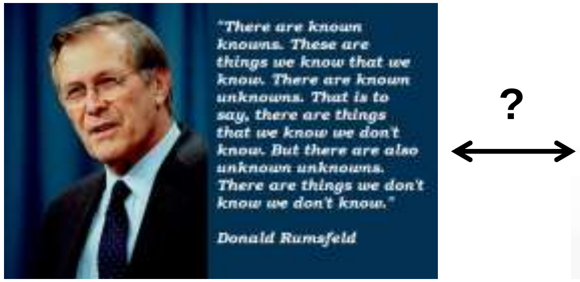


2013 Data

TTHM Levels in Wilmington, NC Trend with Bromide Concentrations in Cape Fear River Source

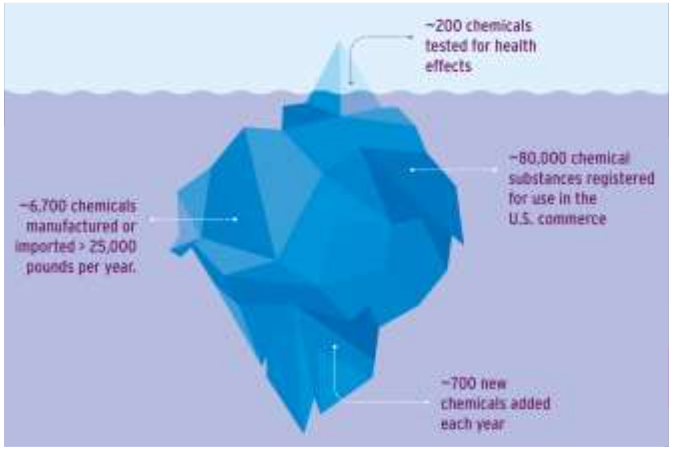


What do we know?



- Regulated contaminants (known knowns)
- Unregulated contaminants on our radar (known unknowns)
- The universe of chemicals (unknown unknowns)

Unknown unknowns



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

How safe are new chemicals?

Precautionary principle:
"When an activity raises threats of harm to human health or the environment, precautionary measures should be taken even if some cause and effect relationships are not fully established scientifically."