Development and Evaluation of Methods to Remove Contaminants of Emerging Concern from Drinking Water

Arjun K. Venkatesan, *Research Scientist*

Yuyin Tang, *Graduate Student*

Cheng-Shiuan Lee, *Research Technician*

Xinwei Mao, *Faculty Collaborator*

Harold Walker & Chris Gobler, *Co-Directors*

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Drinking Water Initiative

- In September 2016 Governor Cuomo awarded $5 million dollars to CCWT to leverage innovation and promote advances in clean water technology
- Initial-phase prioritizes research and advancement of 1,4-dioxane treatment technologies
- Funding: NYS Environmental Facilities Corporation (EFC); Managed by NYS Department of Health (NYSDOH)

State-of-the-art emerging contaminant treatment systems for drinking water :

The primary objectives of this initiative are:

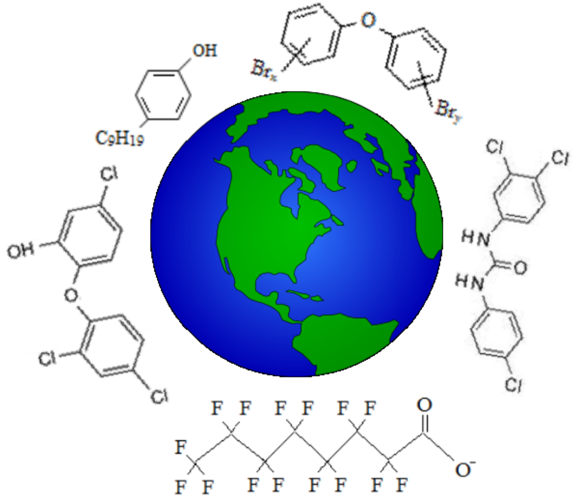
1. Provide grants to support the pilot testing of treatment technologies by water suppliers,
2. Evaluate the efficacy of pilot treatment technologies, and
3. Research and develop novel or refined treatment technologies to remove targeted contaminants from drinking water

Timeline

April 1, 2017:	Execution of MOU
July 12, 2017:	Contract approved
April – August, 2017:	Hiring of essential staff; Identification of lab and office space
September, 2017:	Pilot grant program and research work initiated

Contaminants of Emerging Concern (CEC)

- Chemicals not regulated, but occur in the environment
- Unknowns
    - Risk to human and environmental health
    - Frequency of occurrence
    - Source



http://www.dreamstime.com/

- >40,000 CEC identified
- Endocrine disruption, cancer, birth defects, etc.
- Untreated urban wastewaters and effluents from wastewater treatment plants (WWTPs)

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In Long Island almost all drinking water is from groundwater

Sole source aquifer

"There are no reasonably available alternative drinking water sources should the aquifer become contaminated" (U.S. EPA)

http://www.euwfd.com/assets/images/Groundwater-pollution02.jpg

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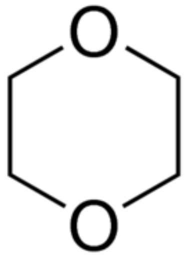
Initial Focus: 1,4-Dioxane



- Industrial solvent: stabilizer; purifying agent; byproduct in processes

Reporting Year	2012	2013	2014	2015
Total Aggregate Production Volume (lbs)	894,505	1,043,627	474,331	1,059,980

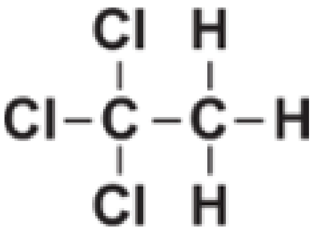
- Likely human carcinogen
- No federal MCL; 0.35 ug/L = 1 in a million cancer risk

This means that no more than one in 1 million exposed persons is expected to develop cancer from life-long exposure at the indicated level

Assumption – 70 kg adult; 2 L d^{-1} water; 70 years

Sources of 1,4-Dioxane

- Co-occur with chlorinated solvents at many contaminated sites
  - Particular 1,1,1-trichloroethane, due to its historic use as a stabilizer
- Used in paint strippers, dyes, greases, varnishes, and waxes
- Impurity in antifreeze and aircraft deicing fluids
- Consumer products: deodorants, shampoos, and cosmetics
- By-product in the manufacture of polyethylene terephthalate (PET) plastic
- Purifying agent in the manufacture of pharmaceuticals



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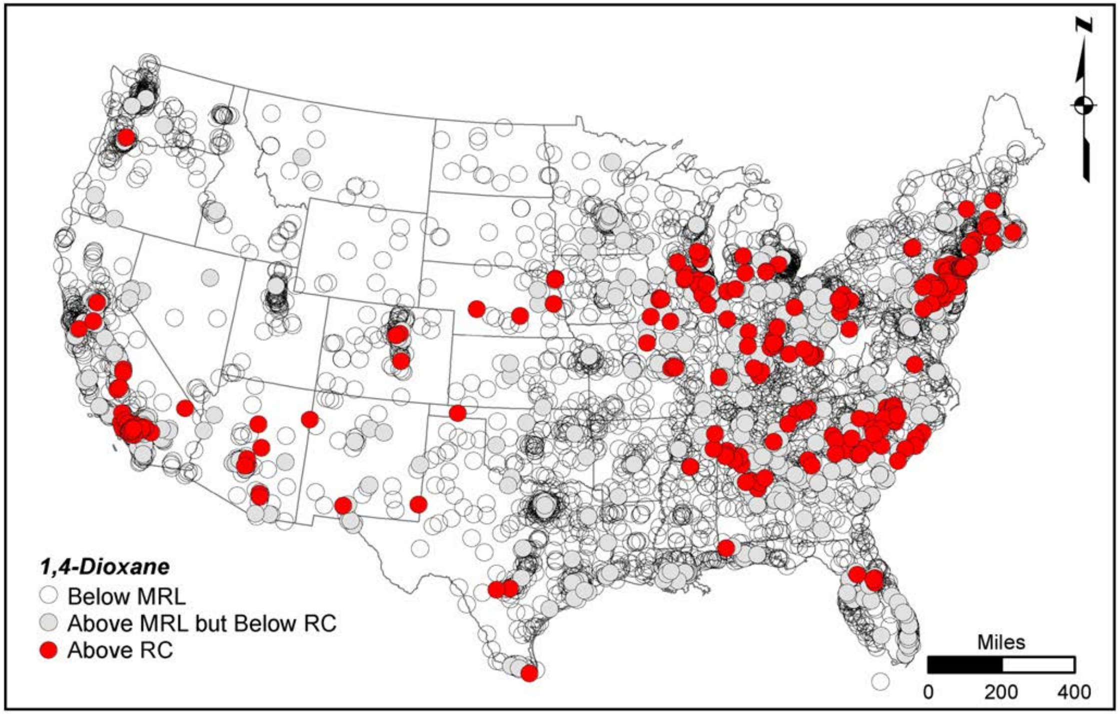
1,4-Dioxane Detection Nationwide

Formal monitoring program: Unregulated Contaminant Monitoring Rule (UCMR) 3 was completed in December 2015: included 1,4-dioxane

>18,000 results nationwide
>2,000 results over MRL (0.07 ppb)
>600 results over RC (0.35 ppb)

174 from NYS
164 from Suffolk and Nassau Counties



Adamson et al., 2017. STOTEN 596-597

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1,4-Dioxane Detection in Long Island, NY

Red: > 0.35 ug/L　　Green: < 0.35 ug/L　　Yellow: Not Tested

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https://www.citizenscampaign.org/campaigns/dioxane.asp

Regulatory Guidelines for 1,4-Dioxane

State	Guideline	Concentration (µg/L)
California	Notification Level	1
Colorado	Drinking Water Standard	3.2
Connecticut	Action Level	3
Maine	Maximum Exposure Guideline	4
Massachusetts	Guideline	0.3
New Hampshire	Proposed Risk-Based Remediation Value	3
South Carolina	Drinking Water Health Advisory	70
New Jersey	Ground Water Quality Standard	0.4
Florida	Drinking water guideline	0.35
New York	Drinking Water Standard	50

New York:
91/205 (44.39%) samples above MRL
Long Island: 33.0 µg/L was found in one of the wells in Hicksville

New State 1,4-Dioxane Drinking Water Standard-New York Threatens to Take Action if U.S. EPA Doesn't

Wednesday, February 15, 2017

By Steven M. Siros

In a February 11, 2017 letter to U.S. EPA, New York Governor Andrew Cuomo indicated that if U.S. EPA didn't move promptly to establish a federal maximum contaminant level (MCL) for 1,4-dioxane, New York would be forced to set its own MCL for drinking water in the state. Governor Cuomo pointed to a perceived regulatory gap, noting that New York has expended tremendous resources to address unregulated emerging contaminants such as 1,4-dioxane, PFOA and PFOS. The Governor also noted that water systems serving fewer than 10,000 people are not required to test for unregulated contaminants such as 1,4-dioxane but that

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

News Feature | January 18, 2017

New York Struggles With 1,4-Dioxane In Drinking Water

By Peak Johnson

Long Island, NY, has a growing problem with its drinking water. In August, the U.S. EPA released a survey that showed 1,4-dioxane, a manmade chemical, contaminated the island's water and exceeded the national average.

xane emerges in the creation of personal roducts such as "cosmetics, toothpaste, poo, and deodorants through a process as ethoxylation, which is conducted to these products less abrasive and increase foaming." The compound has been classified

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Protect Long Island's Drinking Water from 1,4-Dioxane

Tell NYS that we need a drinking water stand

1,4-Dioxane, also known as dioxane, is an emerging contaminant of concern found in Long Island's groundwater and drinking water. According to an EPA study, Nassau and Suffolk water suppliers have reported some of the highest levels of dioxane contamination in the nation.

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GOVERNOR ANDREW M. CUOMO PRESSROOM SCHEDULE ISSUES LEGISLATION ABOUT CONTACT

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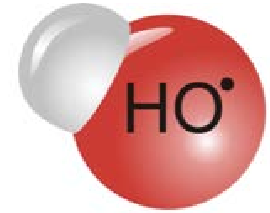
Why is it difficult to remove 1,4-dioxane from drinking water?

Property	Challenges in Treatment
High miscibility in water	High mobility (difficulty in containment)
Low vapor pressure	No to air stripping
High boiling point	No to distillation (economically infeasible)
Low sorption coefficient	No to adsorption
Resistant to biodegradation	No to conventional biological treatment

Advanced Oxidation Processes (AOP)



- Hydroxyl radical (.OH) production
- Various configuration
  - Hydrogen peroxide (H_2O_2)/UV; H_2O_2/ozone; UV/HOCl; Fenton; photocatalytic oxidation with TiO_2
- AOP pretreatment and enhanced biodegradation
- Carbonates, bicarbonates, NOMs: free radical scavengers

+ •OH → Aldehydes + organic acids + esters ($k = 2.5 \times 10^9\ M^{-1}\ s^{-1}$)

Process Evaluation and Other Considerations

- Different configuration and locations => different performance
- Source water quality => hydroxyl radical scavengers/byproducts
- Energy consumption
- Removal of excess chemicals (ozone, peroxide, TiO_2 etc.)
- Corrosion control
- Presence of other contaminants
- Disinfection => byproduct generation?

First full-scale system in NY State: UV/H_2O_2 at SCWA

https://www.scwa.com/14-dioxane_treatment_system_approved/

1. Pilot Grant Program – In Progress

- Issued a Request for Proposals (RFP)
- AOP or any new/alternative treatment for removing 1,4-dioxane from drinking waters
- Pilot scale (60 – 200 gpm); treated waters cannot be discharged into distribution system
- Opportunity for water utilities to perform required pilot testing
- Proposals are being reviewed currently
    - Awards: TBD
- Test multiple AOP configuration and determine effect of different source water quality

Partnership with NYSDOH and TAC

- Partnership with NYSDOH
  - Experience with 1,4-dioxane treatment techniques
  - Oversight of design, construction and operation
- Technical Advisory Committee (TAC)
  - NYSDOH, NYCDEC, Academics, Industry
  - Closing knowledge gaps
  - Identifying best available technologies (BATs)
  - Rapid and widespread implementation of BATs
  - Better understanding of operations and practical compliance monitoring strategies
  - Understanding of potential treatment intermediates

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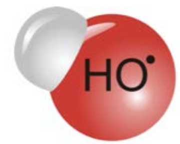
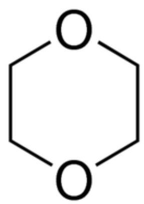
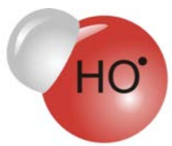
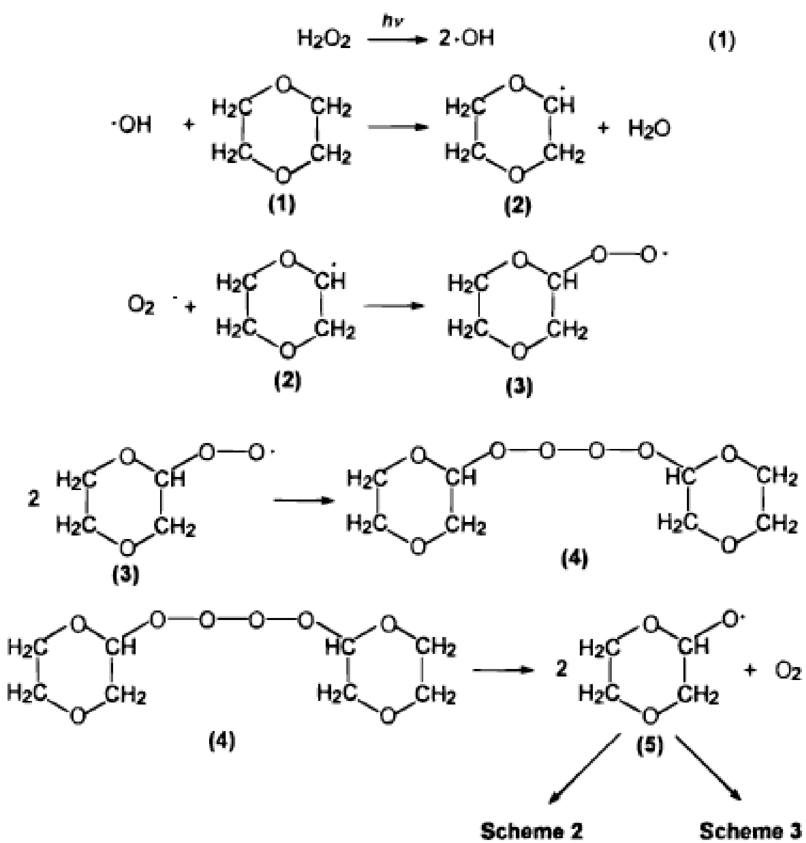
2. Research on Byproducts of 1,4-Dioxane

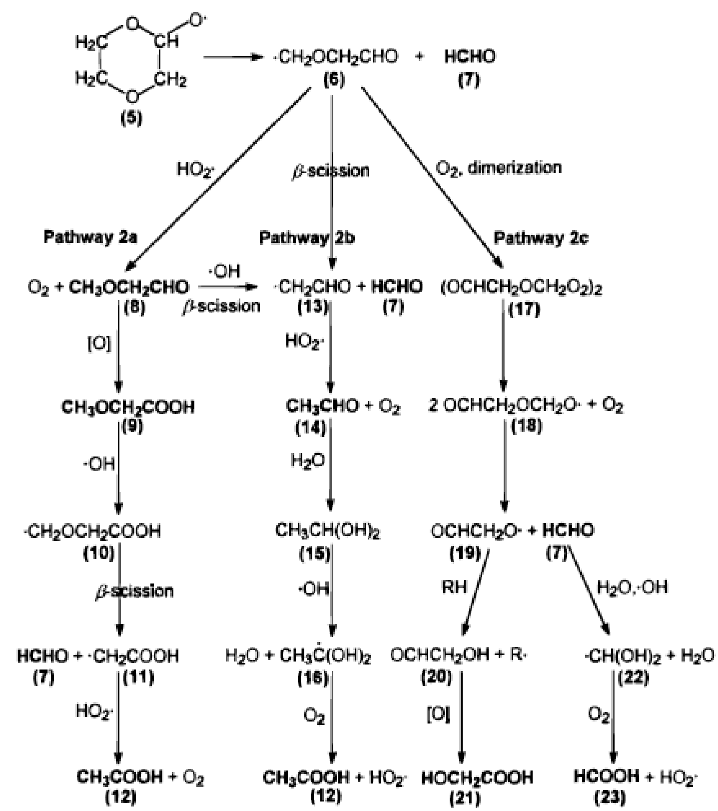
H_2O_2 => 2 



\+ 

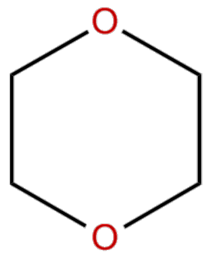
→ Degradation compound(s) + CO_2 + H_2O





Stefan and Bolton, *Env. Sci. Technol.*, 32, 1588-1595, 1998

Degradation By-products of 1,4-Dioxane

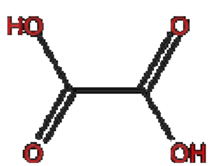


1,4-dioxane

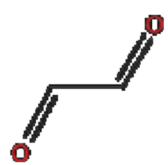
UV/AOP

+ Other Contaminants

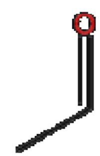
Known Intermediates



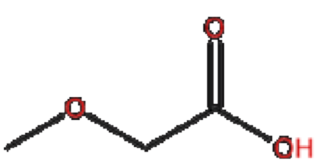
oxalic acid



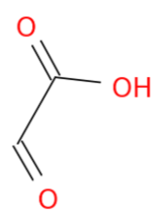
glyoxal



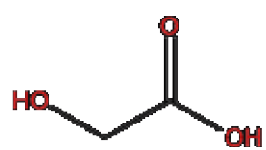
acetaldehyde



methoxyacetic acid



glyoxylic acid



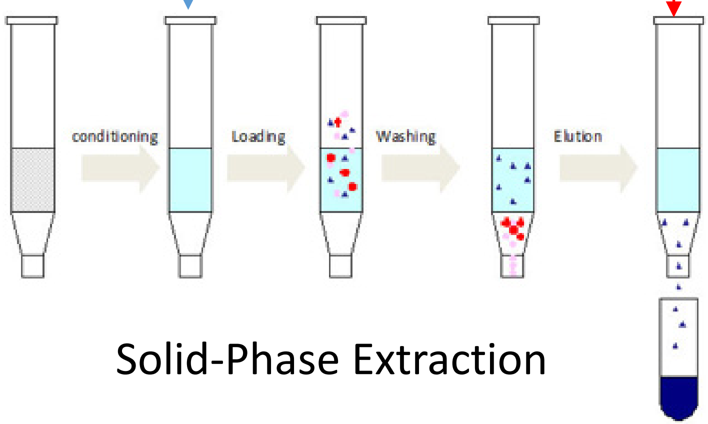
glycolic acid

Unknown Byproducts

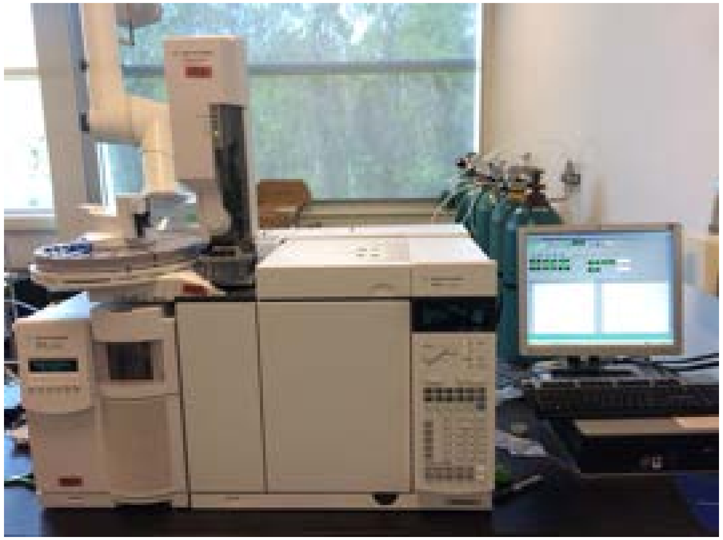
Gas Chromatography-Mass Spectrometry

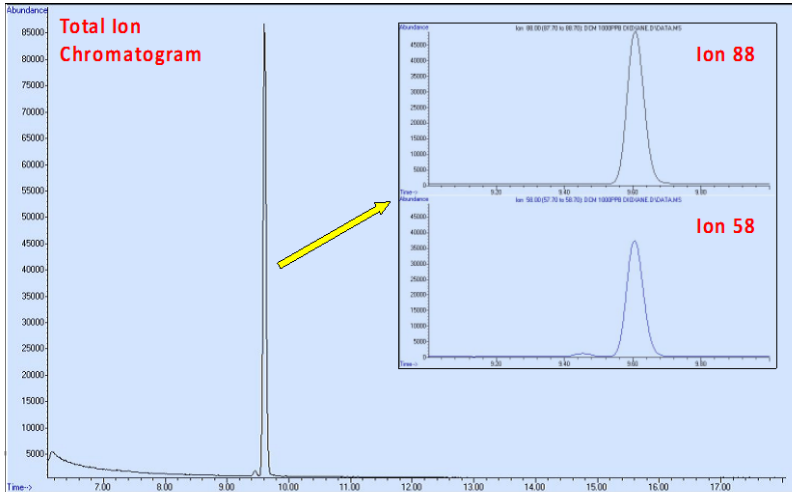
500 mL Water Sample

Solvent



Solid-Phase Extraction





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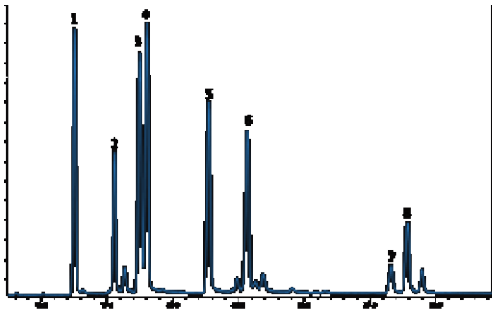
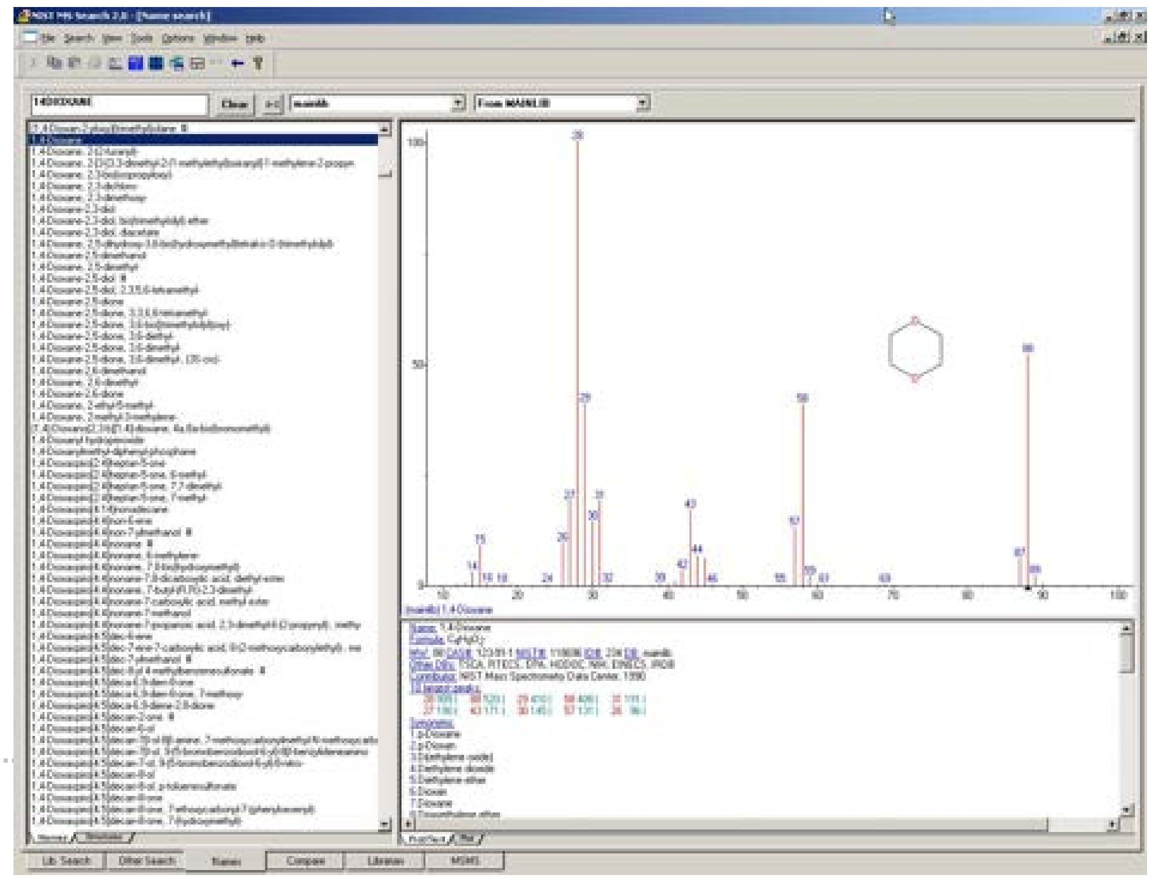
Analyzing and Identifying By-products

- Known intermediates – GC, IC, & HPLC
- Unknown products – National Institute of Standards and Technology (NIST) MS search





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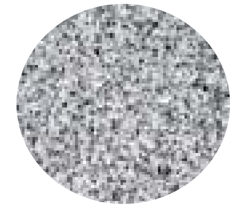
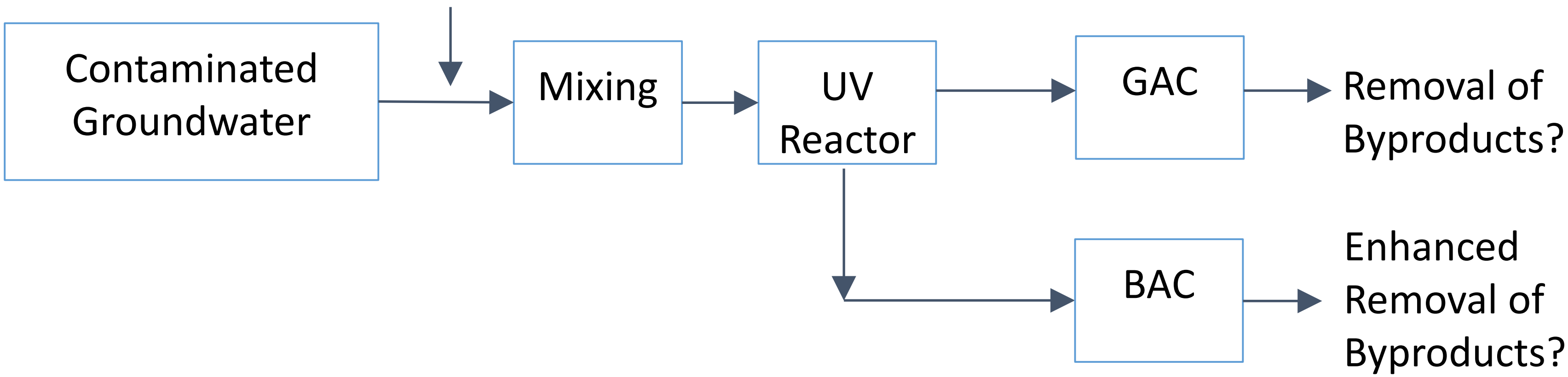
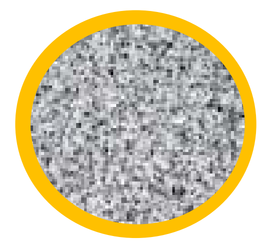
3. Enhanced Treatment: Biological Activated Carbon Filters



Activated Carbon





Activated Carbon Coated with Biofilm

A typical GAC system has a layer of BAC due to bacterial growth

(a) contribute to NOM removal by biodegradation of organic compounds
(b) can plug filter making necessary more frequent backwashing
(c) Affect water quality by the undesirable detachment of microorganisms from BAC

Biodegradation of 1,4-Dioxane

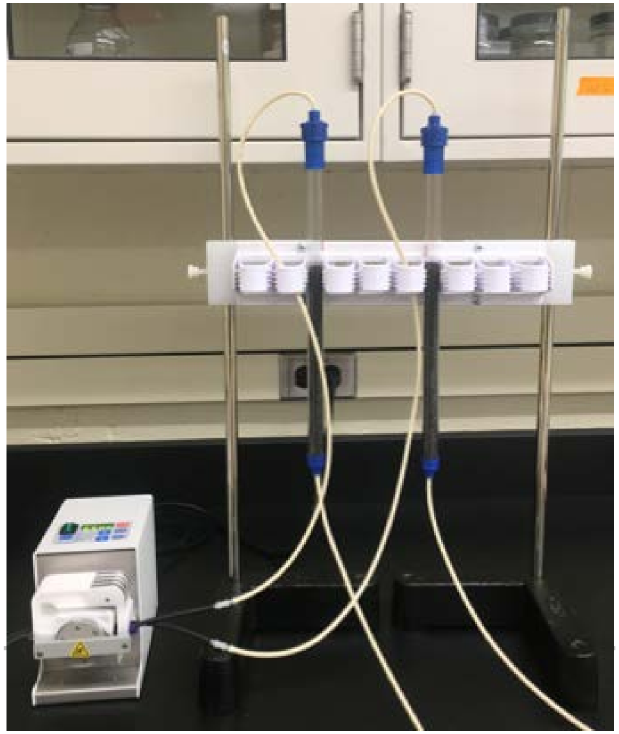
- Co-metabolic reactions (*Mycobacterium austroafricanum* JOB5, *Pseudonocardia* K1, etc.)
- Metabolic reactions (*Pseudonocardia dioxanivorans* CB1190, *Mycobacterium sp.* PH-06, etc.)
- Recent demonstration of natural attenuation of 1,4-dioxane – field studies

Enrichment of microbial communities from various sources that are able to degrade 1,4-dioxane and AOP intermediates

Experimental Set-Up

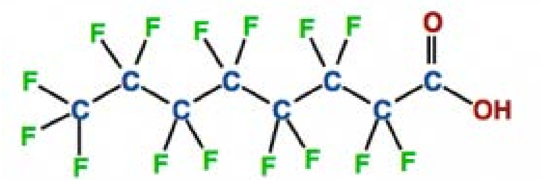
- BAC system in series with AOP/UV system to evaluate removal of 1, 4-dioxane-associated byproducts
- Effect of residual AOP chemicals (H_2O_2, HOCl, etc.) from pretreatment on the performance of BAC/GAC system

Source: TrojanUV

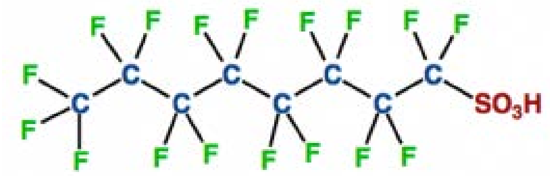


Next Focus: Perfluorinated Compounds

- PFOA and PFOS part of a larger group: perfluoroalkyl substances (PFAS)
- Widely used over the past 60 years
- Water and stain resistant coatings on clothing, carpets, furnishing, non-stick cookware, take-out fast food containers, and in firefighting foam



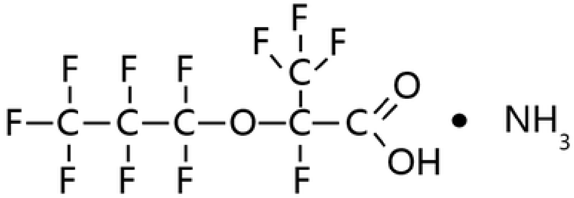
PFOA - perfluorooctanoic acid



PFOS - perfluorooctanesulfonic acid

PFAS Regulation and Treatment

- Between 2000 and 2002: PFOS was voluntarily phased out of production in the U.S.
- 2006: voluntarily phase out of their global production of PFOA and PFOA-related chemicals
- EPA advisory level for PFOA and PFOS to 70 parts per trillion (ppt)
- NJ: PFOA of 14 ppt and for PFOS of 13 ppt
- Available treatment: activated carbon, membrane filtration
  - >90 % removal for PFOS and PFOA
  - What about other short-chained PFAS compounds?
  - Replacement chemicals?



GenX Chemical Structure

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Summary

Research Efforts

- Develop and evaluate novel treatment technologies (Bench-scale –> Pilot-scale ……> Full-scale)
- Identify correlations that may serve as *performance indicators* for removal of CEC
- Explore effects of operating parameters and water quality characteristics on technology performance

Facilities Development

- Existing and shared resources in the form of equipment, space, and supplies within College of Engineering and Applied Sciences, Chemistry Department, and School of Marine and Atmospheric Sciences
- Expanding core analytical capabilities to develop state-of-the-art analytical methods for detection of trace contaminants in waters

Innovation in Water Technology

- Although designed to solve regional problems, the developed solutions are applicable to a broader market, spurring the creation of a new industry in water technology that can serve communities around the state, nation and beyond facing water quality challenges

Questions?