

# *Investigating Treatment Effects on Targeted Endocrine Disrupting Compounds and Pharmaceuticals in Drinking Water*



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Protection

**Partners: EarthTech & 13 Utilities**

# EDCs and PPCPs

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- Why study these?
  - Direct impacts on ecological health
    - Well documented: feminization of fish, etc.
  - Direct impacts on human health
    - Maybe not? Sub therapeutic doses
  - Indicators & promoters of antibiotic resistance
  - Precursors to more Hazardous DBPs
  - Tracers of wastewater contamination
  - Public perception
    - Becoming a very sensitive issue

# Antibiotic Resistance

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- One of the most critical human health challenges of the 21<sup>st</sup> century (WHO report)
  - >1,000,000 Americans infected each year
  - 14,000 deaths annually
- Cause: antibiotics are everywhere
  - Up to 95% of antibiotics in US are excreted in an unaltered state
  - Over prescription in humans
  - Heavy use in agriculture
- Result: Antibiotic resistant genes (ARGs) are ubiquitous in the aquatic environment
  - e.g., Pruden et al., 2006 [ES&T]

# UMass Research Study

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- Purpose
- Process
- Any utility can participate
- Outputs
- Schedule

# Scope

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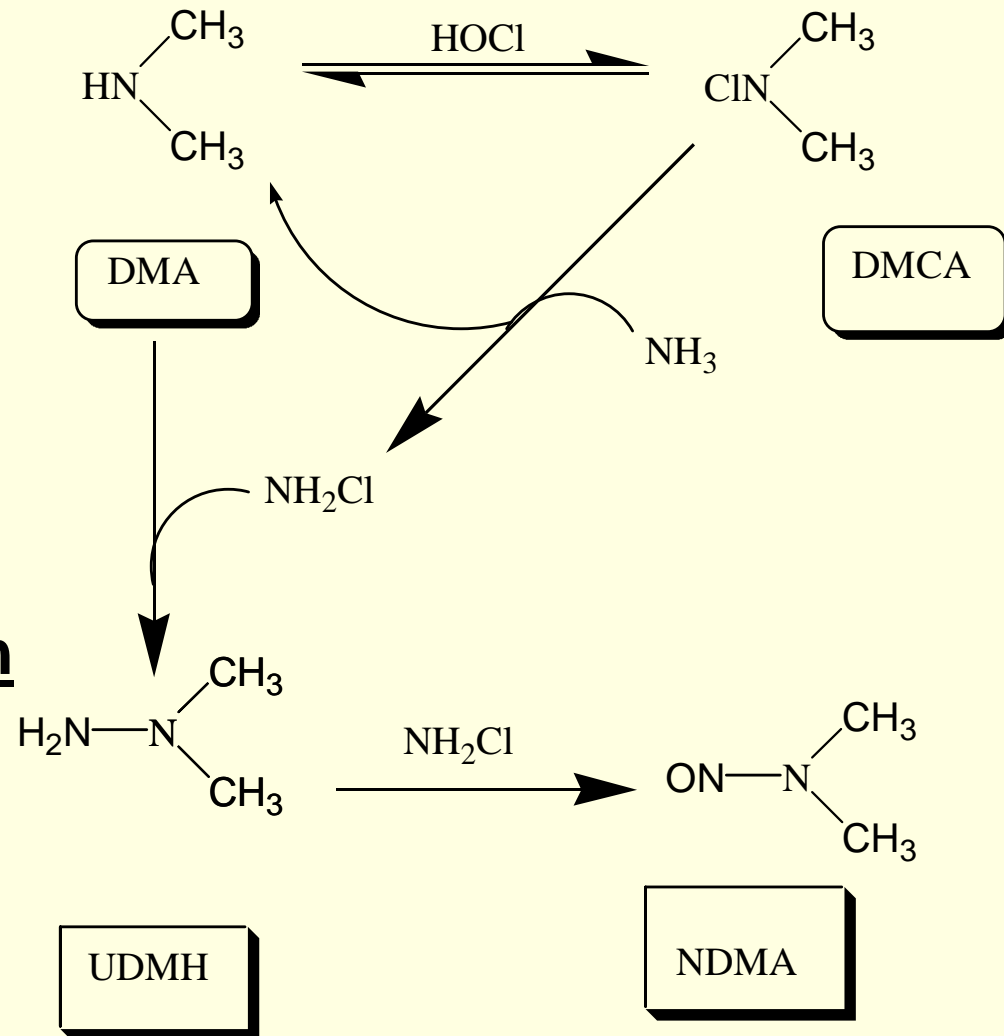
- Task 1: literature update
- Task 2: Raw Water Occurrence Survey
  - Anonymous: Double Blind design
- Task 3: Site-specific Removal
  - On spiked raw water
    - 3a: Existing treatment
    - 3b: Oxidation: O<sub>3</sub>, HOCl, NH<sub>2</sub>Cl
- Task 4: O<sub>3</sub>/Biofiltration
  - Lab pilot (next slide)

# Selected Compounds

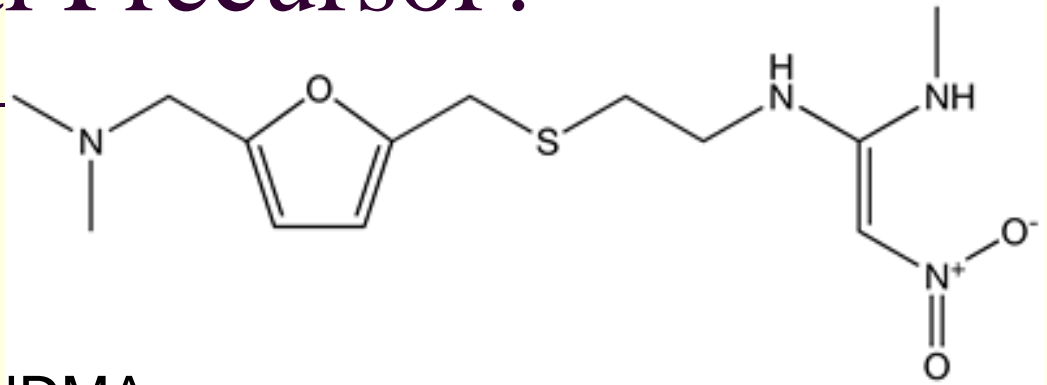
<b>EDC</b>	<b>PhAC</b>	<b>WW associated</b>
17 $\beta$ -estradiol	Atorvastatin or Gemfibrozil	Nitroso- dimethylamine
Estriol	Naproxen	
Estrone	Sulfamethoxazole	
17 $\alpha$ -ethinylestradiol	Trimethoprim	
Perchlorate	Atenolol	
	Ranitidine	
	Primidone?	

# Precursors to NDMA??

- NDMA (nitrosodimethylamine) is a very potent probable human carcinogen
- Formation of NDMA from chloramination of dimethylamine (DMA)
  - Not enough DMA to account for anything much
- NDMA formation is **much** higher in municipal WW than in pristine natural waters
- Major precursor is not natural???



# The Unnatural Precursor?



## ■ Ranitidine (Zantac)

- 63% conversion to NDMA
  - Schmidt et al., 2006 [WQTC]
- Introduced in 1981, largest selling prescription drug by 1988
  - Stomach ulcers and esophageal reflux
- Mean concentration of 3000 ng/L estimated for raw municipal WW (national average)
  - Sedlak 2005 AWWARF report
- 450 ng/L formation in raw WW expected
- Unknowns: how much does this persist in treatment and in the environment?

# WW Tracers

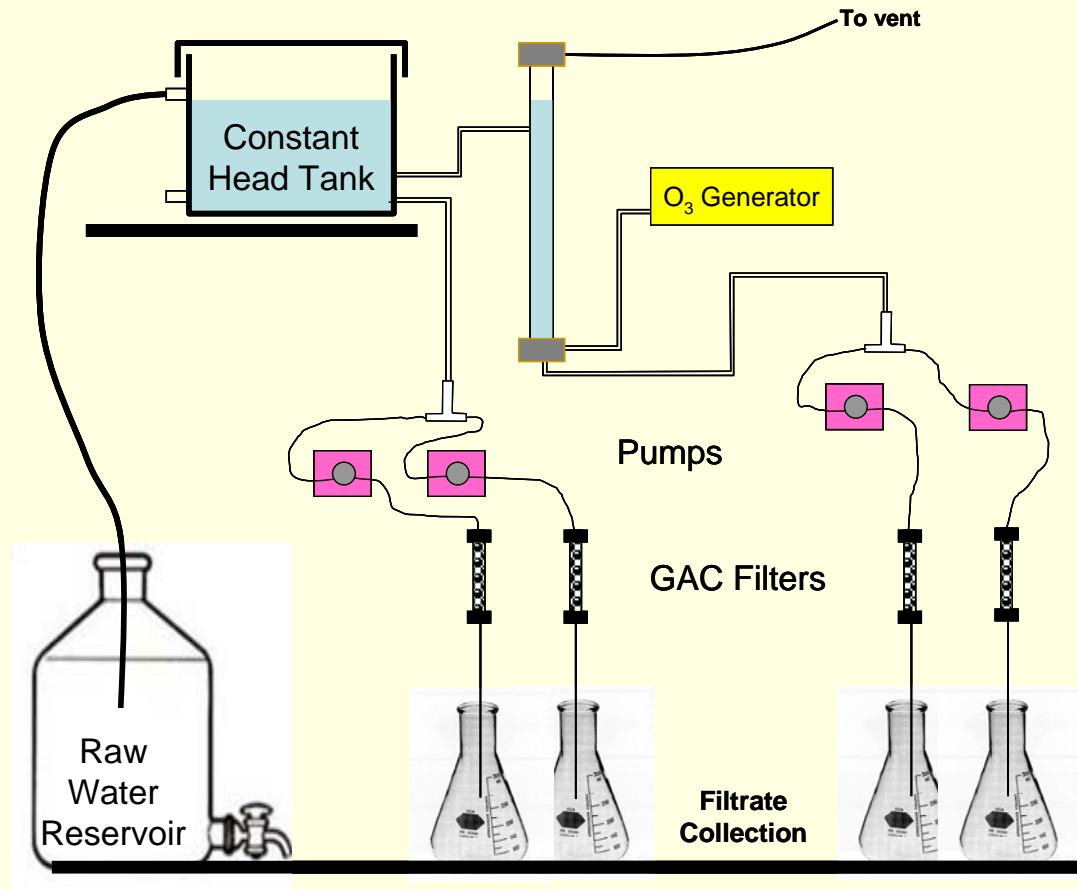
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- WW contributions: use “conservative” PPCP tracers
  - Primidone
  - Others? Carbamazepine, caffeine, etc.
- Raw vs Treated WW: use PPCPs with unique structural geometry
  - Two “sterioisotopes exist of many pharmaceuticals
  - In some cases only one of the two forms is removed in wastewater treatment
  - Ratio of the two forms tells you if the PPCP came from treated or untreated WW contributions
    - Propranolol example: Fono & Sedlak, 2005 [ES&T]

# Experimental Design: Lab Pilot

- Ozone/biofiltration with controls

- No-O<sub>3</sub>
- No bio



# Pilot Operation

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- One year duration
  - 3 months initial acclimation
  - 9 months testing
- Target 10 min EBCT
- Spike raw water with PPCPs
- Run until stable removals under varying conditions
  - Ozone doses
  - Temperatures
  - Others: EBCT, backwash?

# Raw Water

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- Objective
  - 1 year supply for pilot; stable & consistent
  - Representative of WW impacted river
  - Containing organic & inorganic matrix
- Blackstone River
  - Location: Downstream of the Upper Blackstone WPAD wastewater treatment outfall
- Sample treatment
  - 1,100 liters collected
  - Rotary evaporated to 11,000 mL.
  - Brought to dryness in a freeze dryer
  - Homogenized and stored in a freezer

# Lab Analysis

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- Conventional parameters
  - DOC, etc.
- PPCP Analysis
  - LC/MS
    - HPLC or UPLC with triple quadrupole MS; isotope dilution
  - Parent Compound & Daughter Products
- Estrogenic Activity
  - Cell-based reporter assay
    - stably-transfected MCF-7 cell line which produces luciferase
  - Measuring changes in gene expression in the Japanese medaka fish and the fathead minnow

# Utility Participation

Participation Level	Contribution	Testing					
		Source Water		After Oxidation (O <sub>3</sub> , Cl <sub>2</sub> , NH <sub>2</sub> Cl)			Bench-scale treatment
		Chem	Bio	Chem	Daughter	Bio	Chem
Gold	\$12,000	X	X	X	X	X	X
Silver	\$6,000	X		X	X		X
Bronze	\$3,000	X					X

# Cooperative Effort

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- State regulators/University/Private
- Focus on emerging contaminants is challenging

# Regulatory challenges

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- Solicit PWS participation
  - PWS reporting requirements under CCR
- Incentives for water suppliers
  - Sample anonymity
  - New sampling category
- Senior management support
  - Make the case to senior management

# Risk Communication

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## ■ Challenges

- Describing the current state of occurrence
  - Is my water safe?
- What if a chemical is detected without health guidance

## ■ Solutions

- PPCP workgroup
- Prepare outreach strategy
  - Mission statement
  - Website
  - Identify and work with stakeholders

# PIE Risk Reduction Strategy

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- MassDEP will:
  - aggressively pursue the issues of pharmaceuticals in the environment,
  - develop a framework to rank and prioritize PPCPs for further regulations and,
  - Commit to sharing information with all interested parties especially the public
- Pollution Prevention a major component

# Summary

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- Multi-component project
  - Analytical chemistry
  - Toxicity
  - Treatment
- Collaborative
- Encourage PWS participation
- Contacts
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  - Dr. Nicholas Anastas [nicholas.anastas@state.ma.us](mailto:nicholas.anastas@state.ma.us)