# Developing Targeted Treatment Strategies for Pharmaceuticals and Wastewater-Derived Micropollutants

**Timothy J. Strathmann**
**Department of Civil & Environmental Engineering**
**Center of Advanced Materials for Purification of Water with Systems**
**University of Illinois, Urbana-Champaign, IL**

NSF waterCAMPWS

This research is funded by
U.S. EPA - Science To Achieve Results (STAR) Program
Grant # 90683701-0

Awwa Research Foundation

# Outline

I. Pharmaceuticals and Wastewater-Derived Micropollutants

II. Research Questions

III. Current Projects

A. Conventional: Oxidation by $MnO_4^-$

B. Future: Oxidation by visible light photocatalysis

C. Future: Reduction by $H_2$-activated metal catalysts

IV. Challenges to Treating Pharmaceuticals

# Strathmann Group Research Questions

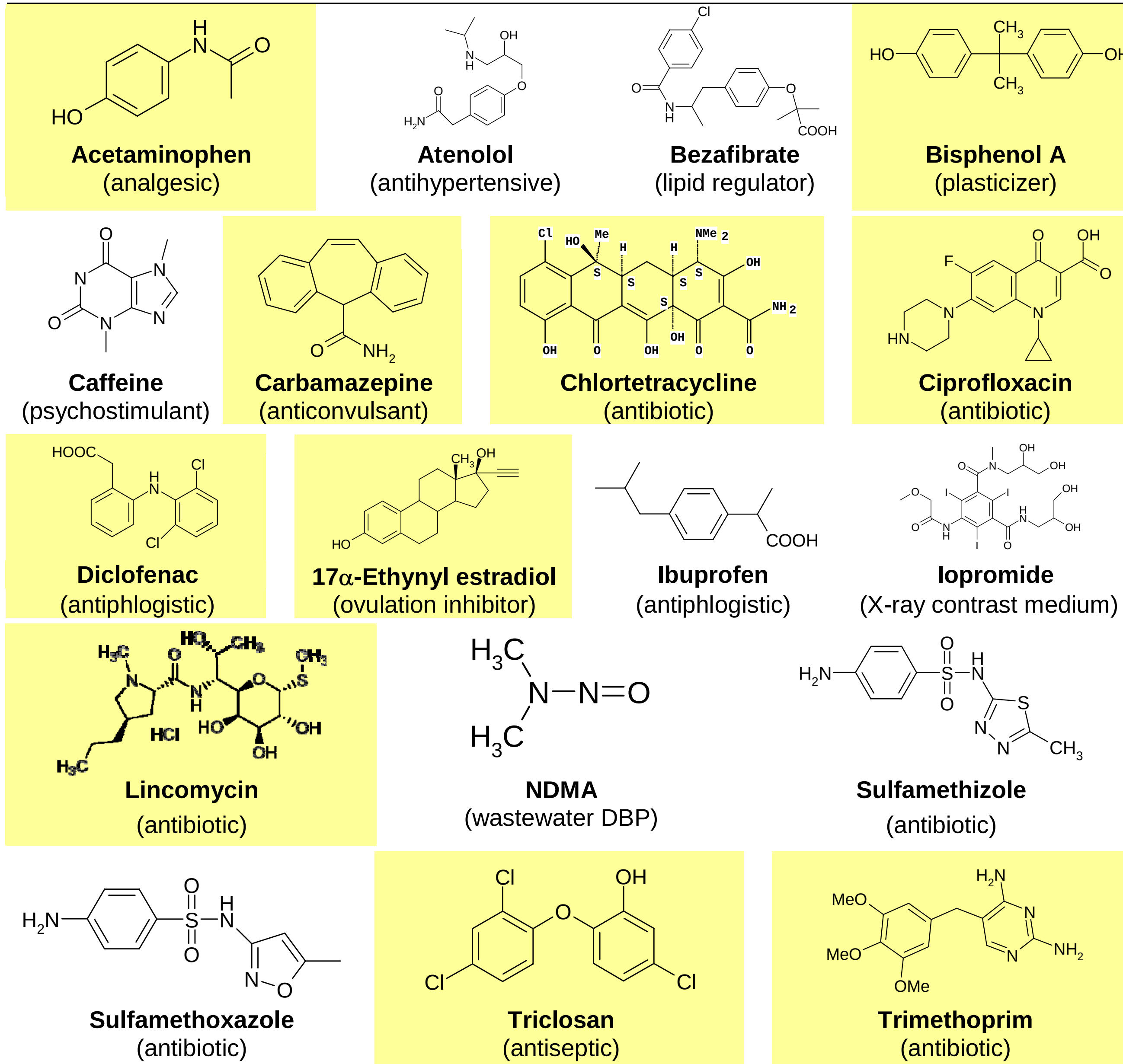
- Can we identify improved strategies for treating Pharmaceuticals & WW-derived micropollutants?
  - *Redox transformation to inactive byproducts*
  - *Selective*
  - *Sustainable*

- What are the mechanisms controlling micropollutant redox transformations?
  - *kinetics*
  - *transformation products*
  - *effects of water quality & non-target constituents*

# A. Oxidation by $MnO_4^-$

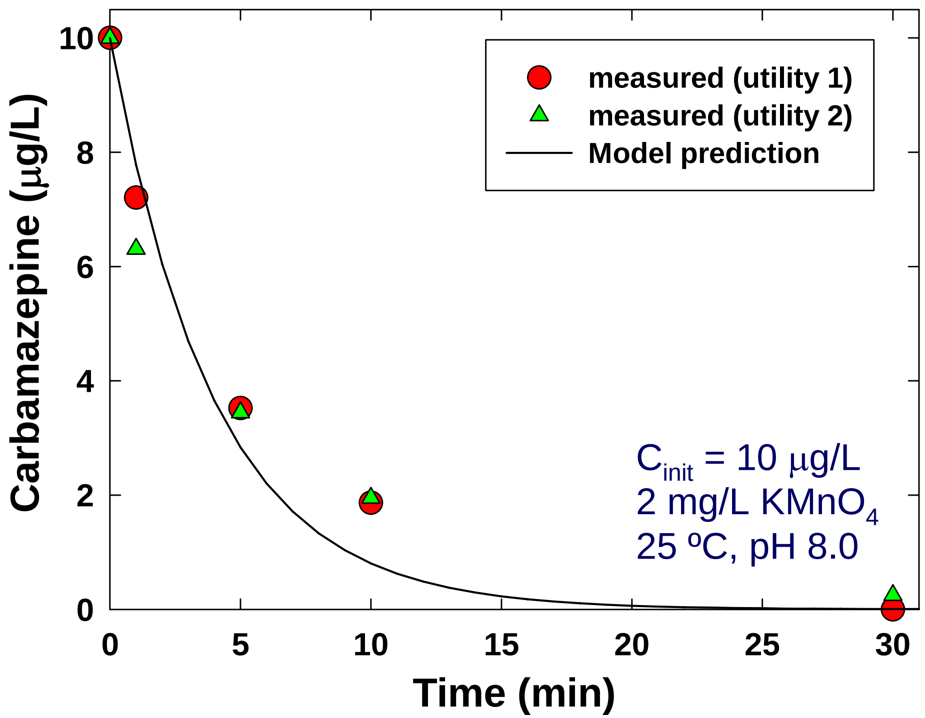
- **Goal:** Assess pharmaceutical fate during existing treatment processes
- Previous work examined reactions with other water treatment oxidants ($Cl_2$, $O_3$), but little known about reactions with $MnO_4^-$

Table 1. List of Target Pharmaceuticals Examined in Study[a]



# A. Oxidation by $MnO_4^-$

- Kinetic model developed from lab experiments accurately predicts extent of carbamazepine removal from utility source waters
- LC-MS$^2$ and NMR methods combined to identify products and elucidate reaction mechanism




$$k_{2,T} = k_{2,298K} \exp\left( \frac{E_a (T - 298)}{298RT} \right)$$

$$k_{2,298K} = 310\ M^{-1}\ s^{-1}$$

$$E_a = 21\ kJ\ mol^{-1}$$

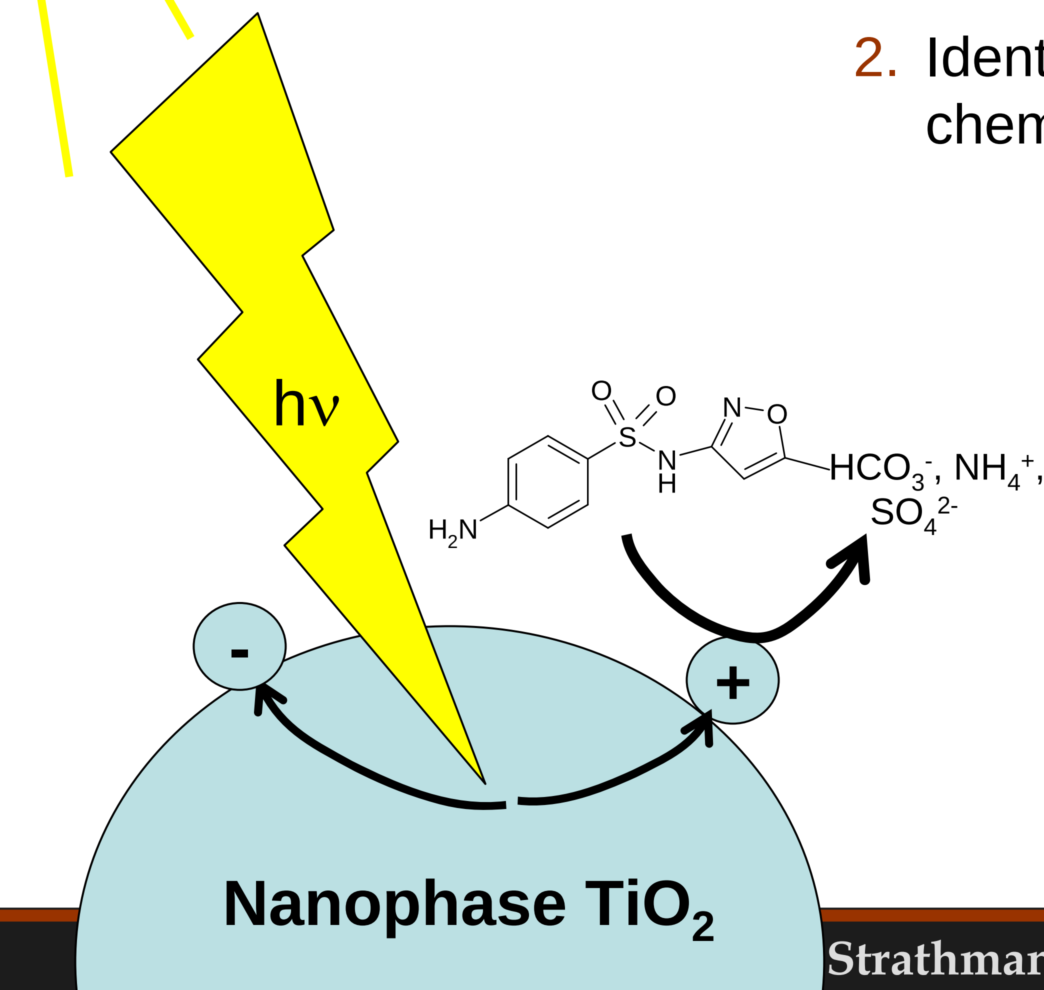
Rate pH independent

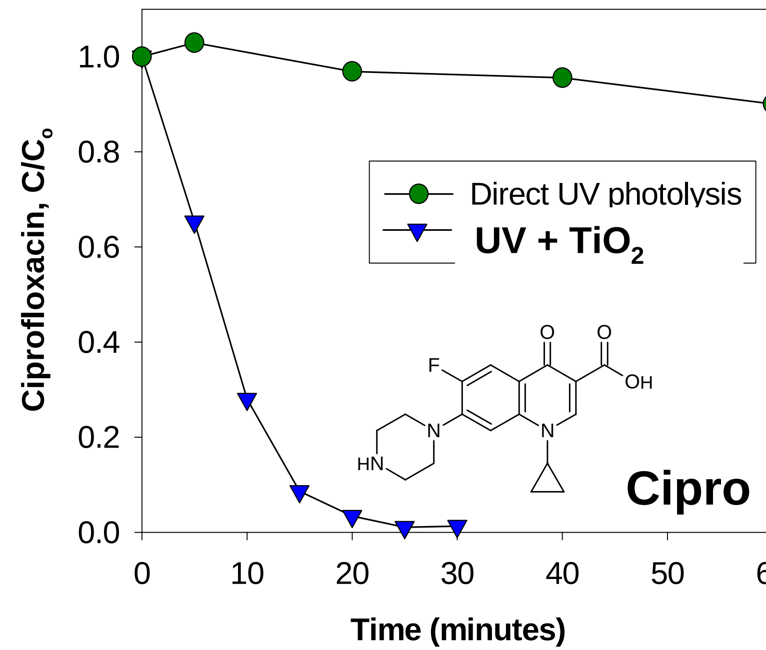
Hu et al., manuscript in prep

# B. Oxidation by $TiO_2$ Photocatalysis

## Goals:

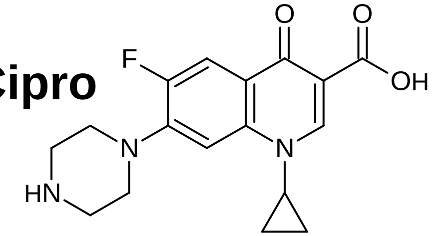
1. Characterize kinetics and mechanism of antibiotic oxidation
2. Identify strategies for improving chemical selectivity

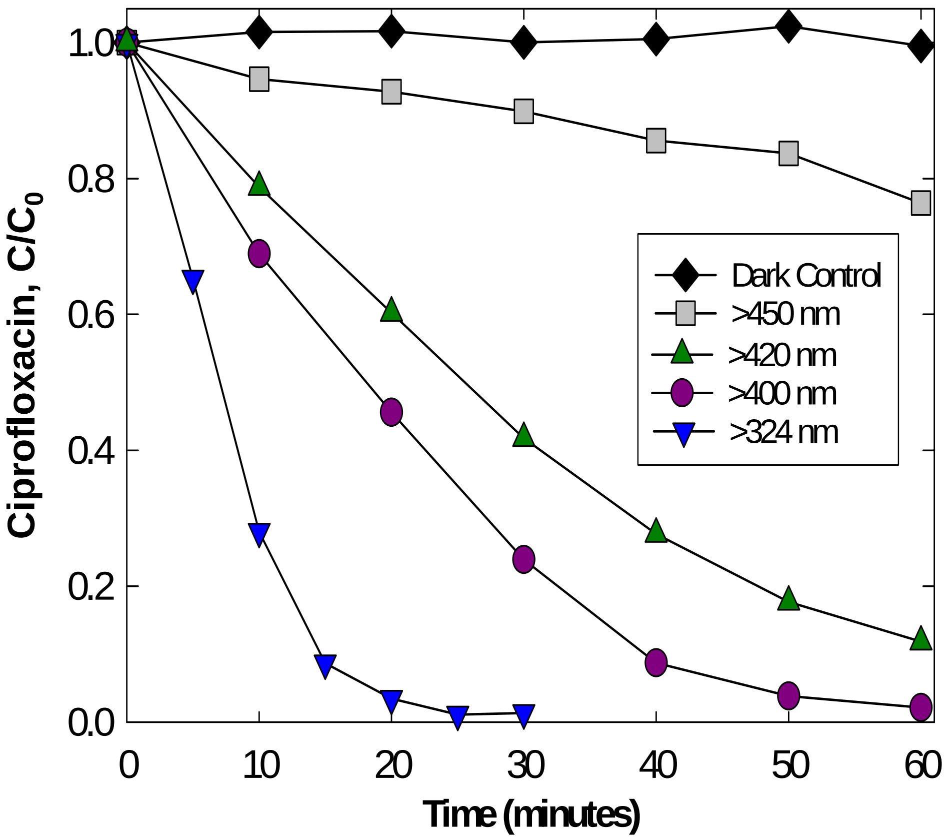


# Photocatalysis Under Visible Light? (λ > 400 nm)

Cipro



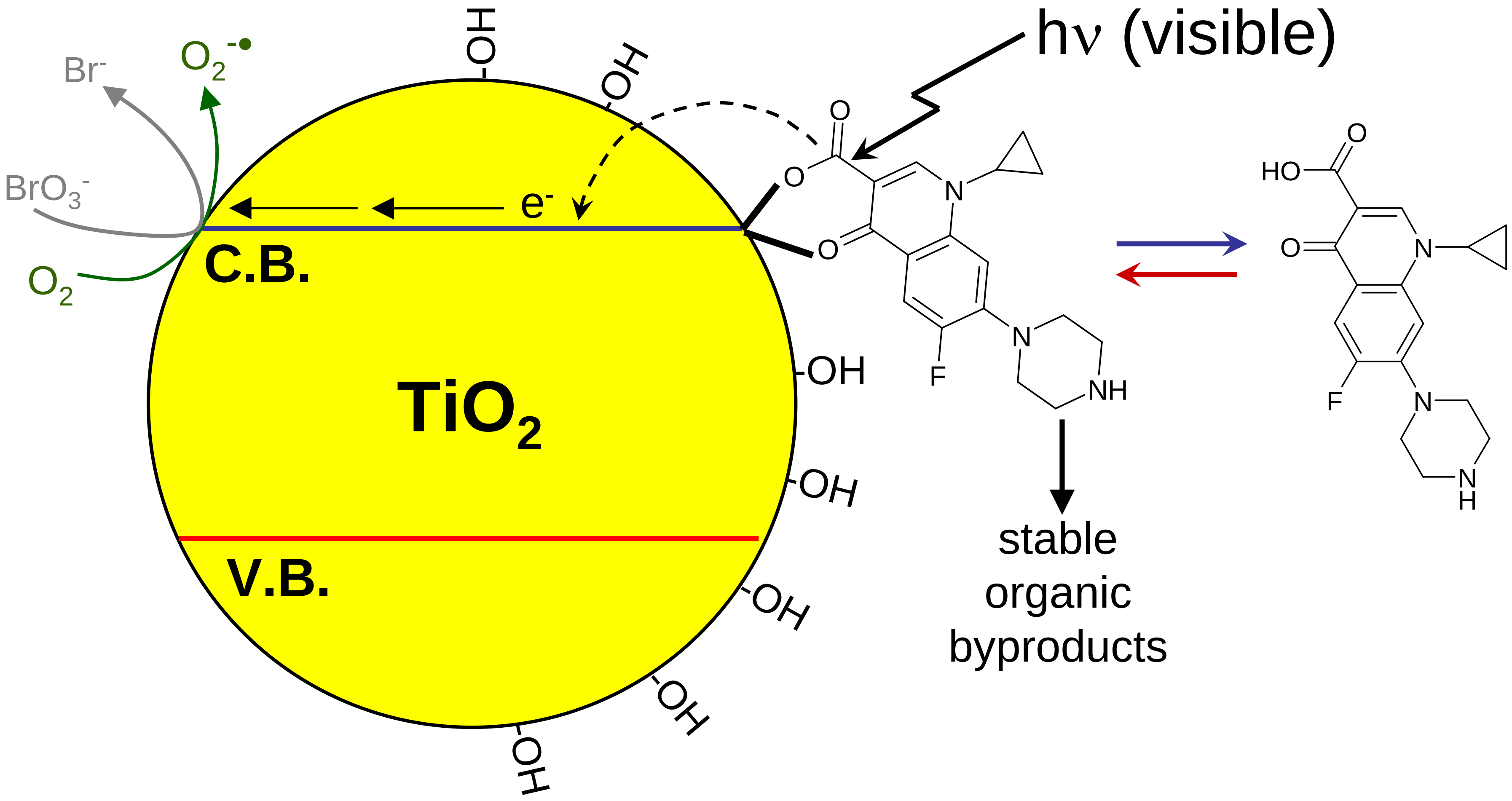




- Photocatalytic degradation under visible light?
- Atypical behavior can be exploited for selective treatment within mixed waste streams

Paul et al., ES&T (2007)

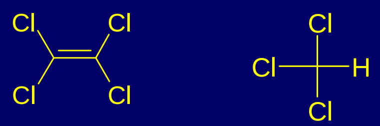
Hu et al., Wat Res(2007)

# Visible Light Photocatalysis Mechanism

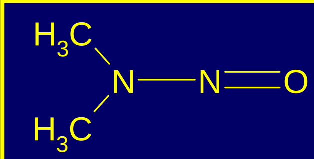


# C. Reduction by $H_2$-activated catalysts

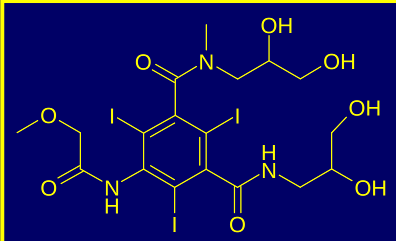
- Reductive processes are functional-group selective



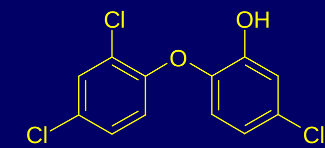

halogenated
DBPs, solvents




N-DBPs



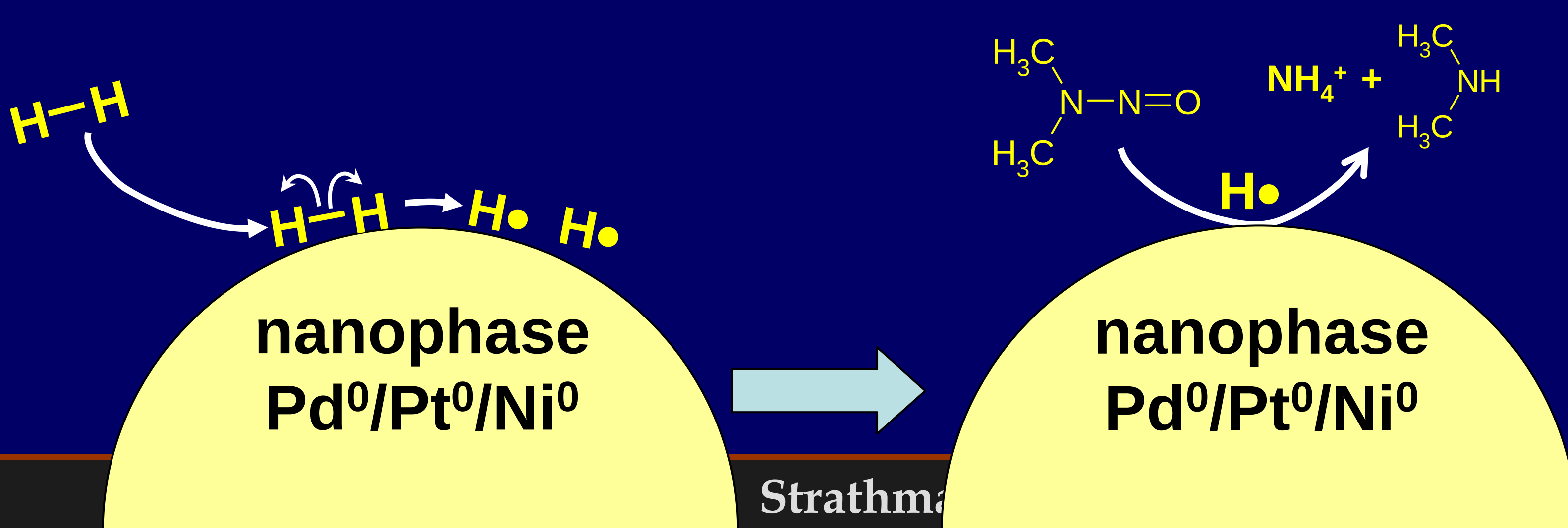

Iodinated
contrast agents




triclosan
(antibacterial soap)

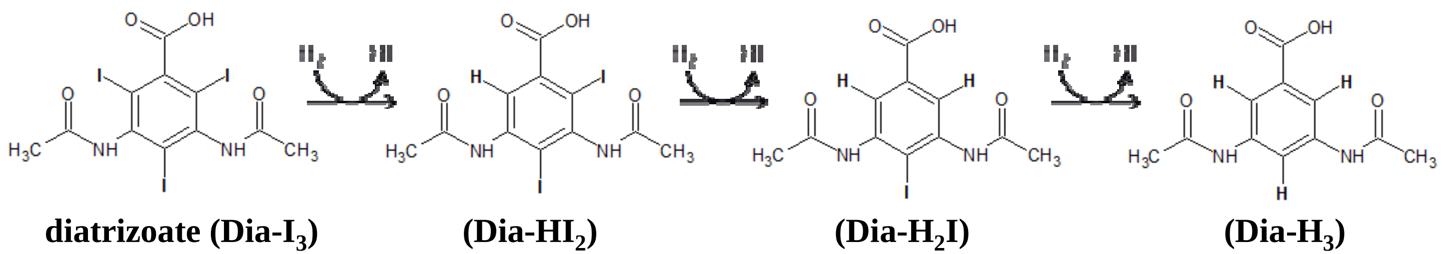
Goals: 1. Characterize kinetics and mechanism

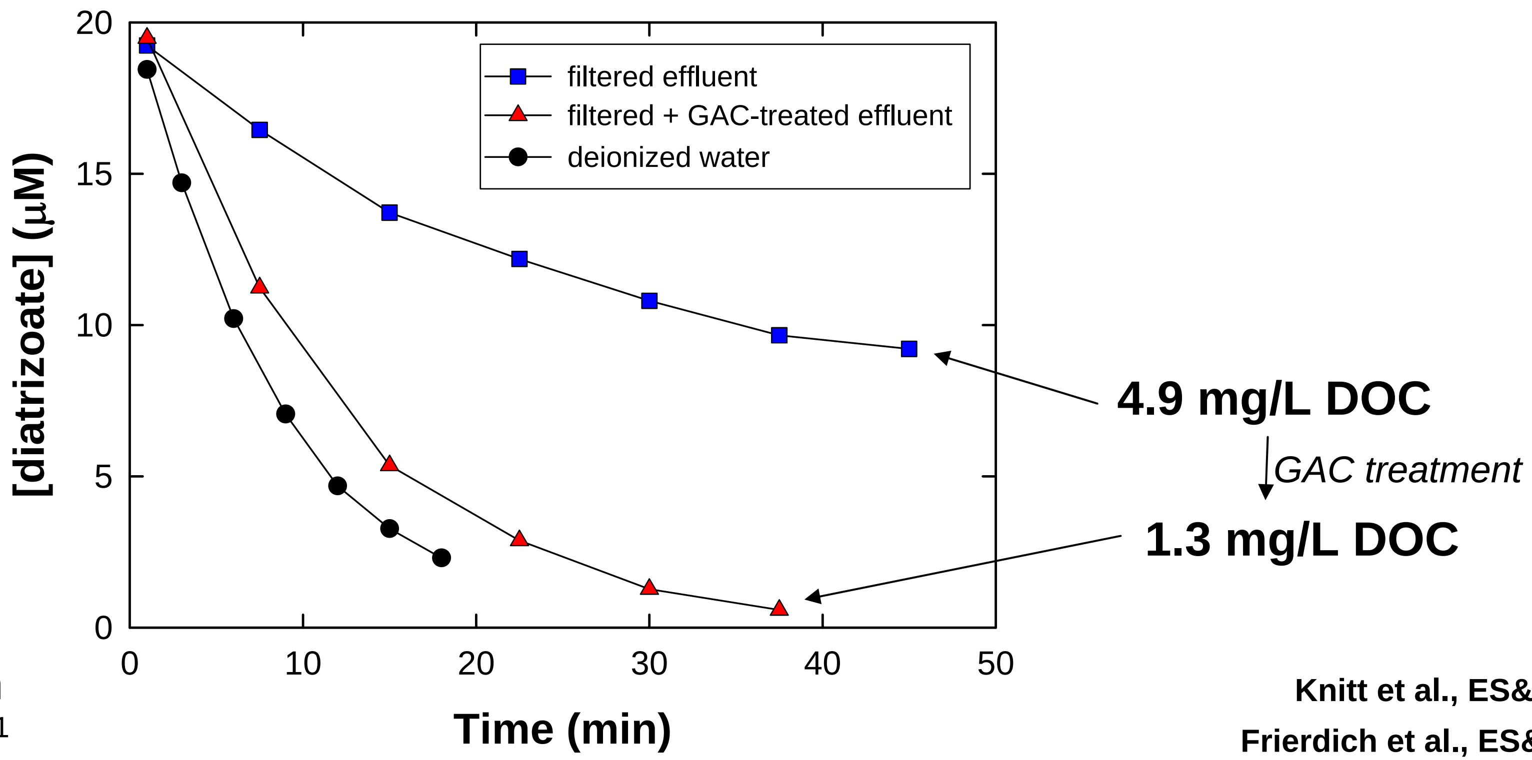
2. Improve process sustainability



# Pd-Catalyzed Reduction of X-ray Contrast Agents

- X-ray contrast agents highly resistant to conventional wastewater treatment
- Rapidly dehalogenated to more biodegradable product



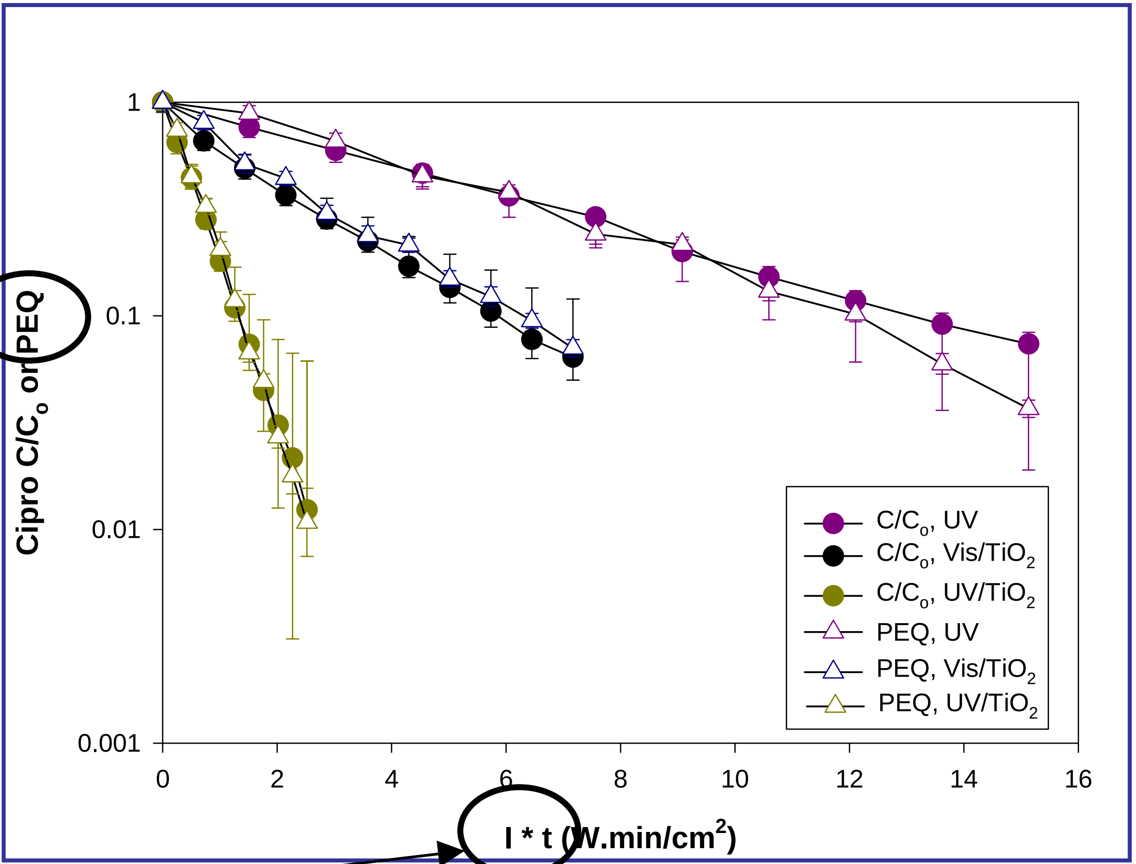

pH 7.0
$P_{H2}$ = 1 atm
1.4 $mg_{Pd}$ $L^{-1}$

Knitt et al., ES&T (2008)
Frierdich et al., ES&T (2008)

# Energy Efficiency and Removal of Pharmaceutical Potency

Photochemical and Photocatalytic Oxidation of Fluoroquinolone Antibiotics

**PEQ =** potency equivalents of product mixture relative to parent pharmaceutical




**I*t =** fluence = photon energy delivered to during treatment

**Dodd et al., in prep**

# Challenges to Treating Pharmaceutical Micropollutants

- Removing the drop of poison in the ocean of water
- How low should we go?
- Which pharmaceuticals/metobolites?
- New solutions should be sustainable
  - Energy efficient
  - Limited chemical inputs
    - Membrane processes
    - Heterogeneous catalytic processes

# Micropollutant Reduction Strategies

Andrew Frierdich

Lindsay Knitt


Claire Joseph

# Micropollutant Oxidation Strategies

Tias Paul

Lanhua Hu

Matt Sugihara

Heather Martin