



# NEWEA Annual Conference 2015

## Session 2

### Ozonation of Tris-2-Chloroethyl Phosphate (TCEP) in Water

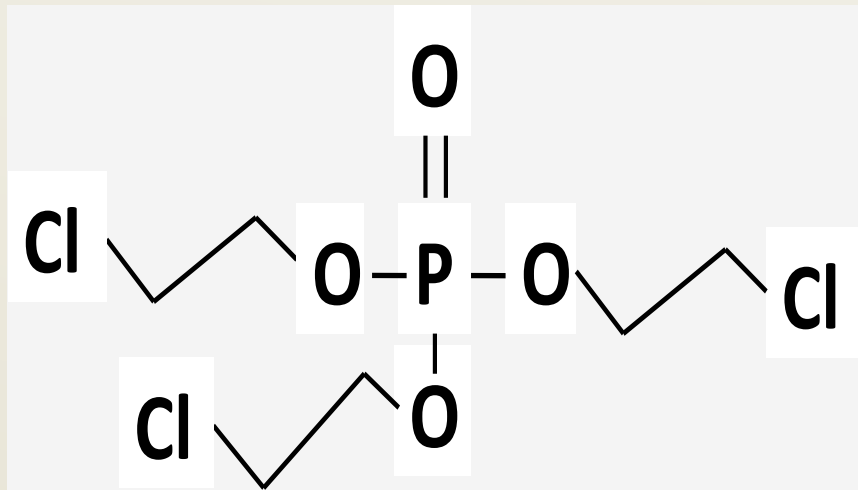
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January 26, 2015

- **Introduction**
- **Objectives**
- **Background**
  - **TCEP**
  - **Ozone Oxidation**
- **Methodology**
- **Results**
- **Conclusions and Future Work**

- Organophosphorus Compounds (OPCs)
  - Used as pesticides, flame retardants, antifoam agents
  - Released to the environment from industrial sources
  - Not chemically bonded to host materials
  - Produced in high quantities: 10-100 thousand tons annually worldwide
  - Chlorinated OPCs have a high mobility in water and are resistant to biological treatment
  - OPCs found in natural waters and wastewater effluents
  - Health concerns: some evidence that OPCs are toxic and carcinogenic



- **Tris-2-Chloroethyl Phosphate (TCEP)**
  - Shown to be genotoxic, neurotoxic, and mutagenic
  - Shown to be damaging to the liver, kidneys, and reproductive system
  - Used as a flame retardant in polyurethane foams
  - Has been found in natural and treated waters

- Processes that use hydroxyl radicals to remove contaminants by destruction
- Free Radicals are formed that aggressively breakdown organic contaminants
- Effective for the removal of several bio-recalcitrant compounds including pharmaceuticals and organophosphates
- $\text{H}_2\text{O}_2/\text{UV}$ ,  $\text{O}_3/\text{H}_2\text{O}_2$ , Fenton's Reagent, and others

- Determine the effect of ozone dose on the removal of TCEP
- Determine the effect of hydrogen peroxide addition on the removal of TCEP
- Study the effect of pH on the removal of TCEP using ozone and ozone/hydrogen peroxide oxidation
- Investigate the removal of TCEP in waters with other contaminants that may competitively react
- Examine the kinetics of TCEP destruction in its reaction with ozone and ozone/hydrogen peroxide

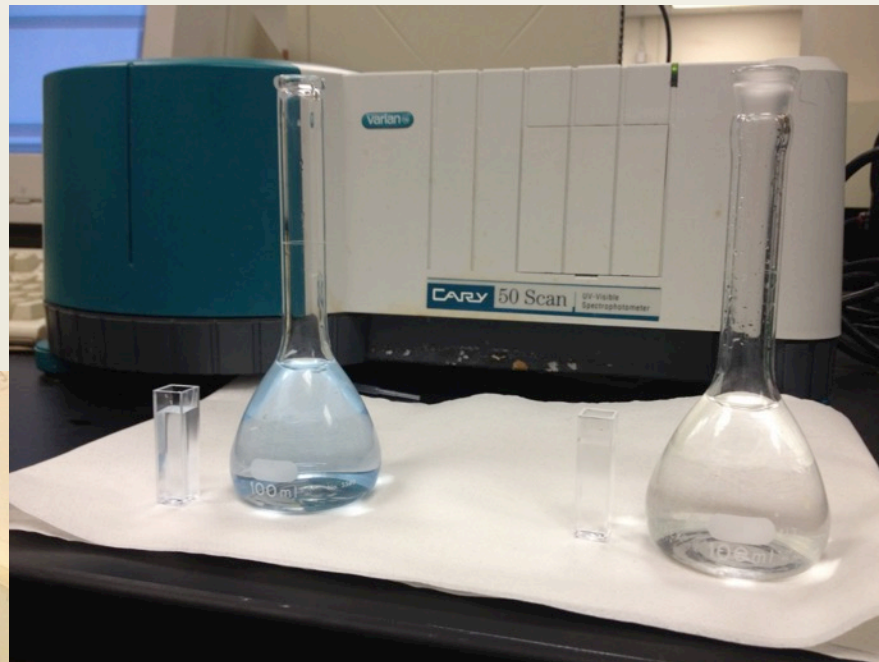
## Previous Research On TCEP Removal Using Advanced Oxidation

- 95% TCEP removal using  $\text{H}_2\text{O}_2/\text{UV}$  (Watts and Linden)
- 100% TCEP removal using Fenton's Reagent,  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  (Nguyen)
- <50% reduction of TCEP Using  $\text{O}_3$  and  $\text{O}_3/\text{H}_2\text{O}_2$  (Pisarenko et al.)
- <17% reduction of TCEP Using  $\text{O}_3$  and  $\text{O}_3/\text{H}_2\text{O}_2$  (Snyder et al.)
- <5% reduction of TCEP Using  $\text{O}_3$  and  $\text{O}_3/\text{H}_2\text{O}_2$  (Westerhoff et al.)

- Oxidation potential of 2.08 volts (V)
- Non-selective, highly reactive oxidant
- Spontaneous Decomposition and the formation of hydroxyl radicals ( $\text{HO}\cdot$ ), oxidation potential of 2.8 V
  - Can be initiated by hydroxide ions, or by the addition of hydrogen peroxide
- Created on site by an ozone generator



- Batch Experiments
- Ozonation of pH adjusted water



- Indigo Method

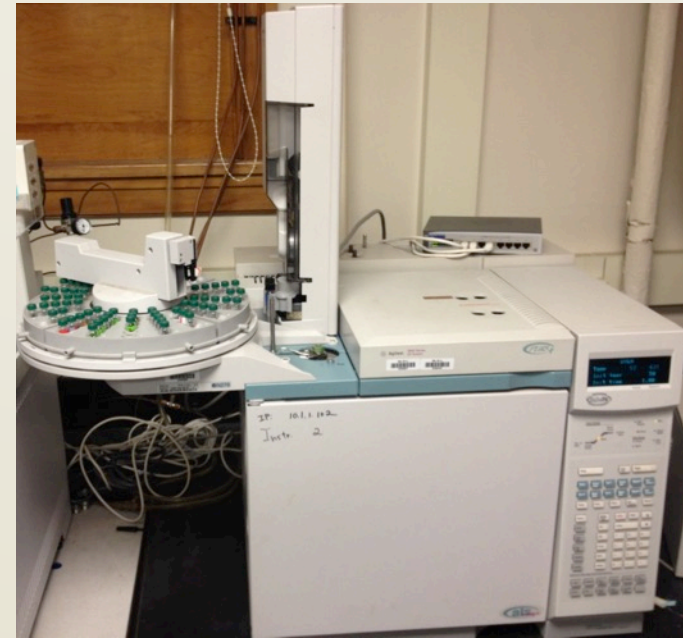
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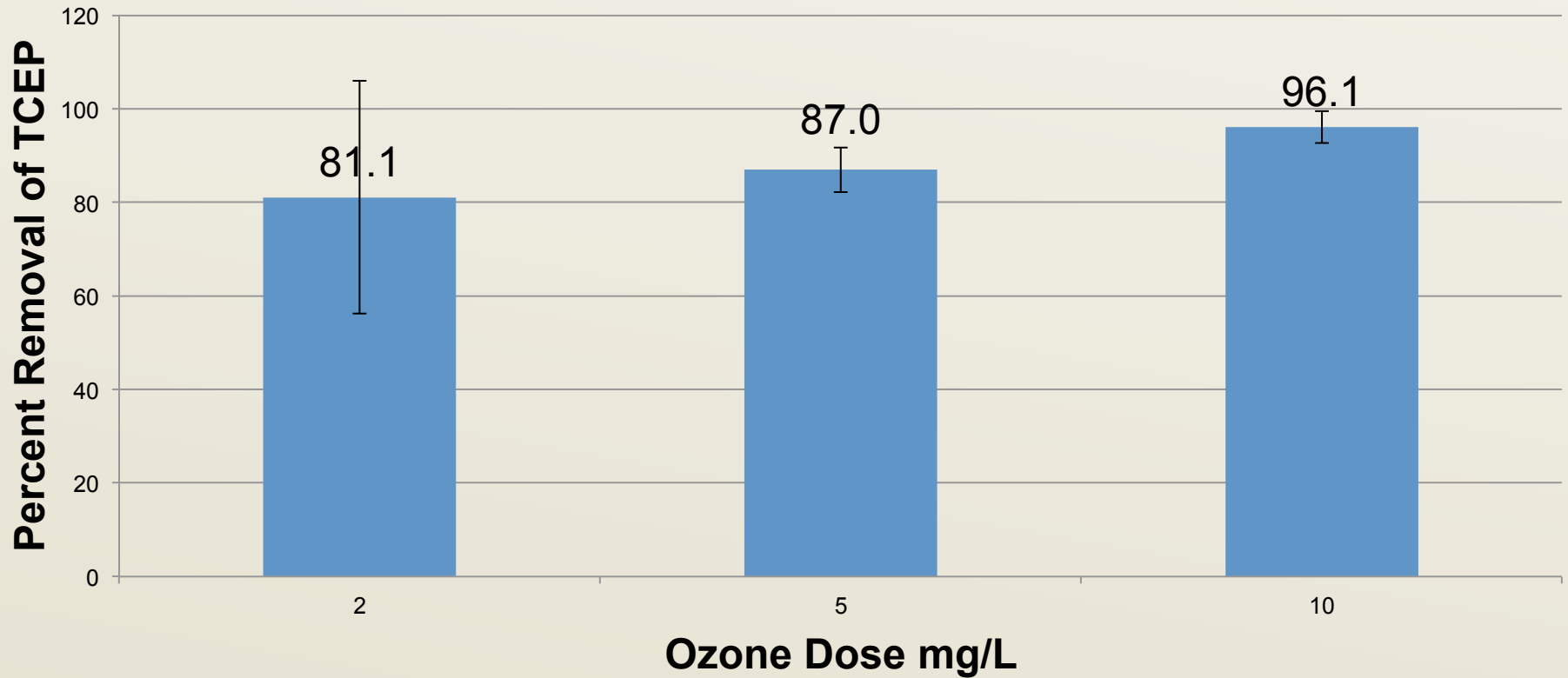
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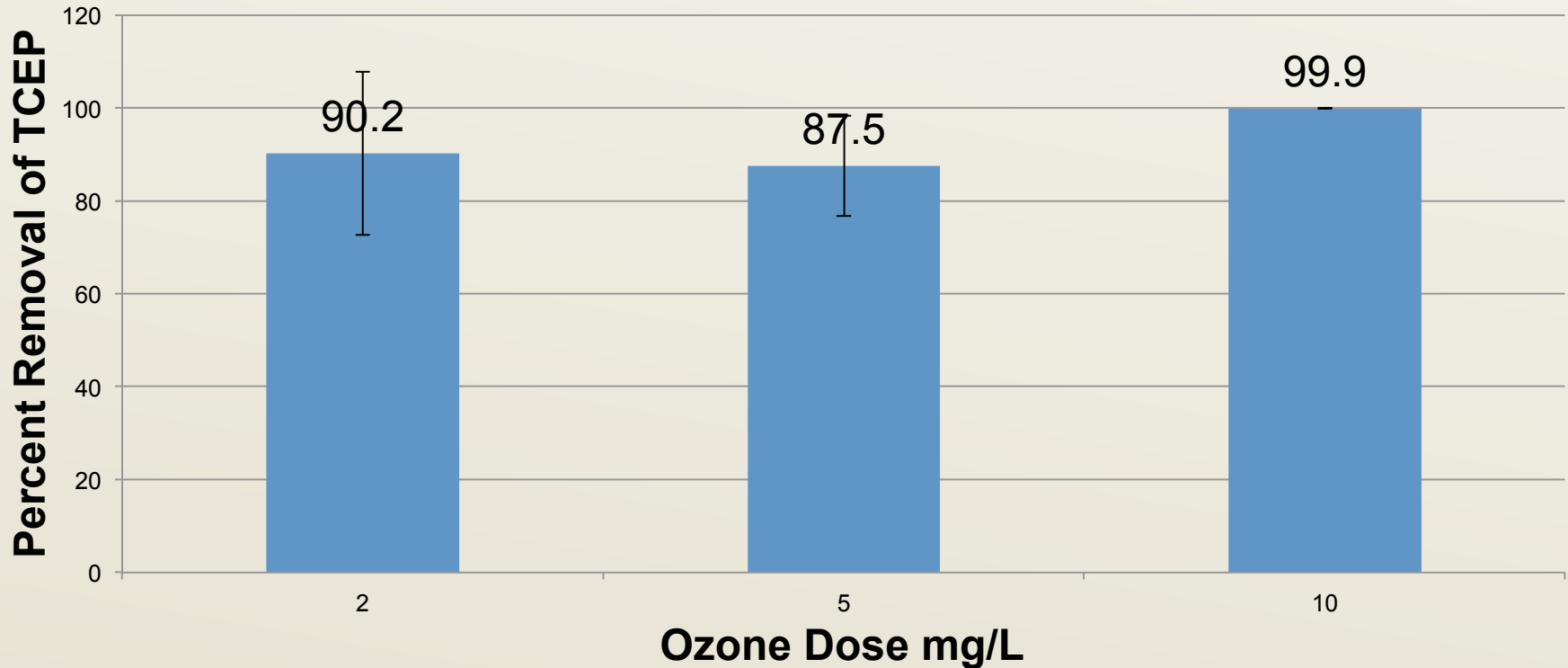


# Results: Variation In Ozone Dose



Effect of Ozone Dose on Ozone Oxidation of TCEP at pH 7.  
Initial TCEP Concentration = 2 mg/L  
24 Hour Reaction Time

# Results: Variation In Ozone Dose

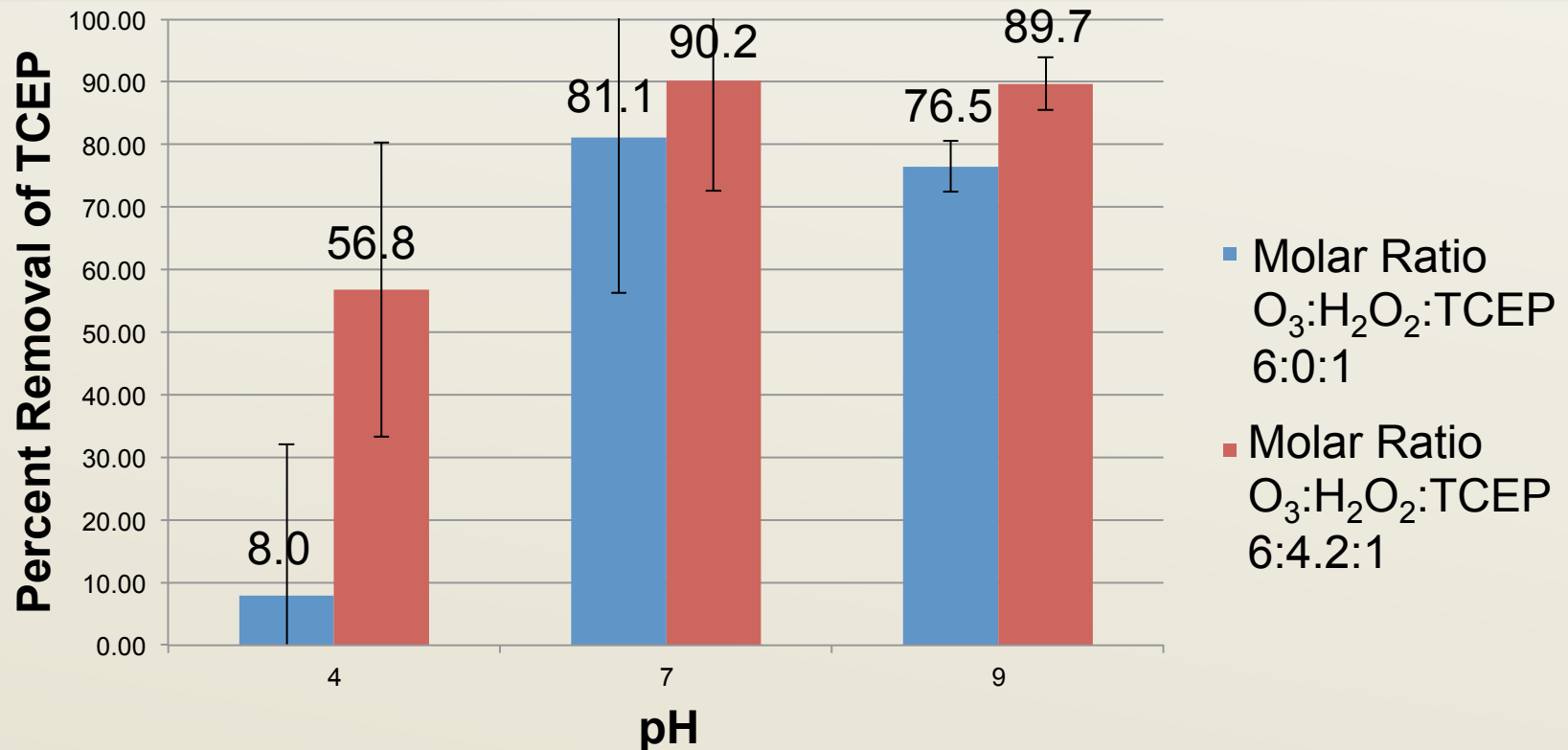


Effect of Ozone Dose on Ozone/Hydrogen Peroxide Oxidation of TCEP  
at pH 7 (Ratio of  $\text{H}_2\text{O}_2:\text{O}_3$  of 0.5:1 by Weight).

Initial TCEP Concentration = 2 mg/L

24 Hour Reaction Time

# Results: Variation In Solution pH

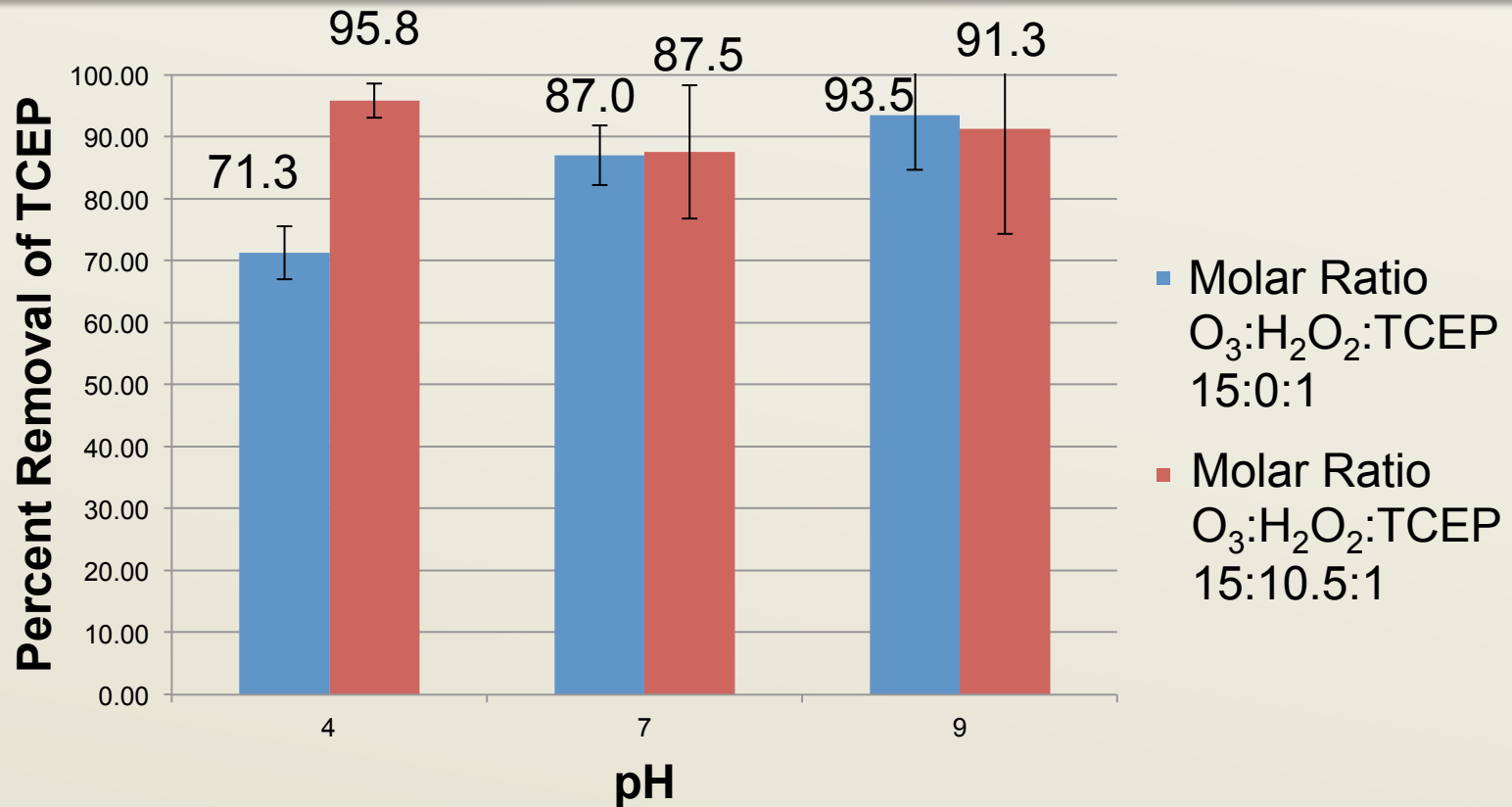


Percent Removal of TCEP for O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> Treatments at Varied pH  
(Ozone Dose of 2 mg/L).

Initial TCEP Concentration = 2 mg/L

24 Hour Reaction Time

# Results: Variation In Solution pH

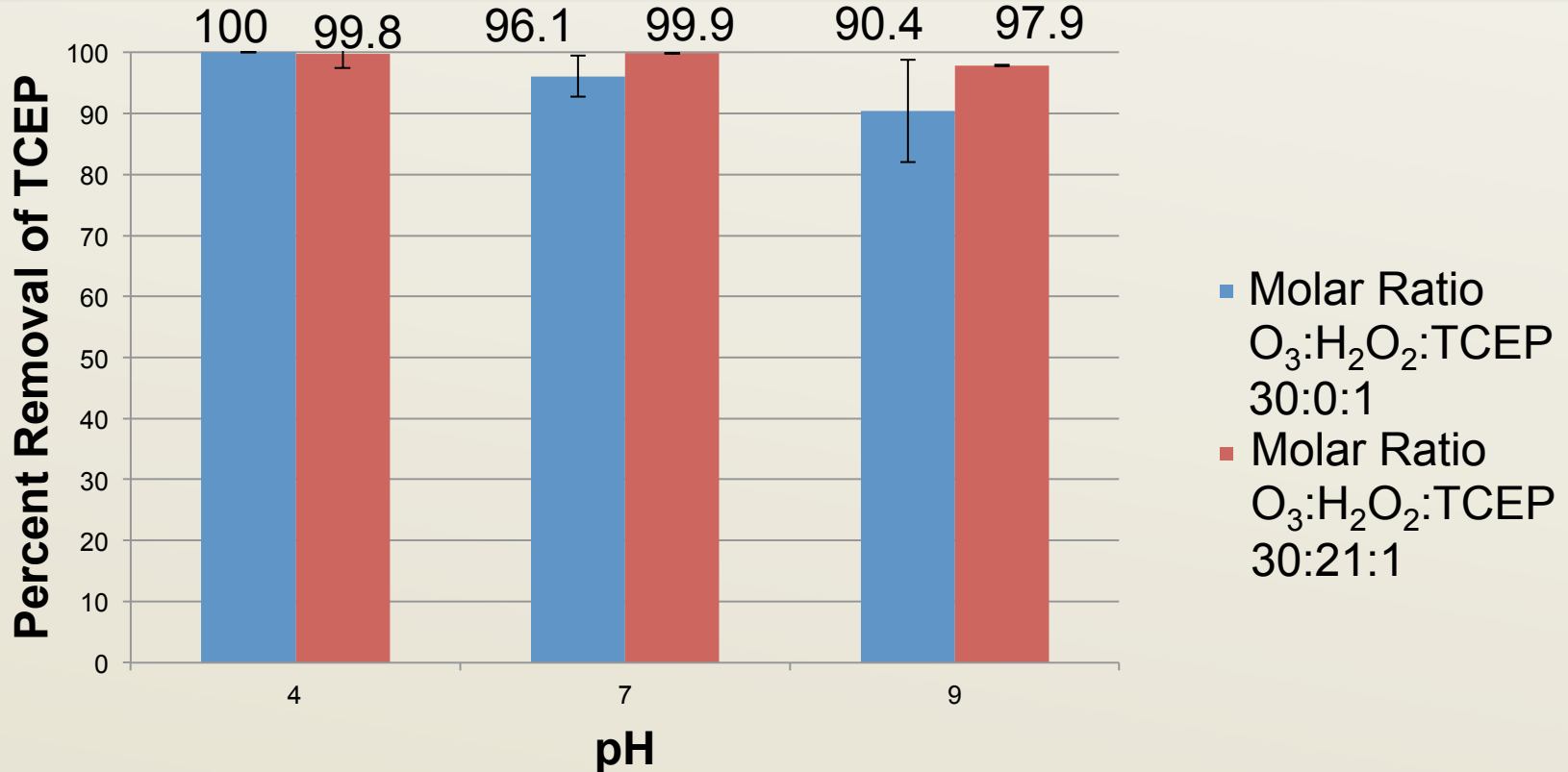


Percent Removal of TCEP for O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> Treatments at Varied pH (Ozone Dose of 5 mg/L).

Initial TCEP Concentration = 2 mg/L

24 Hour Reaction Time

# Results: Variation in Solution pH

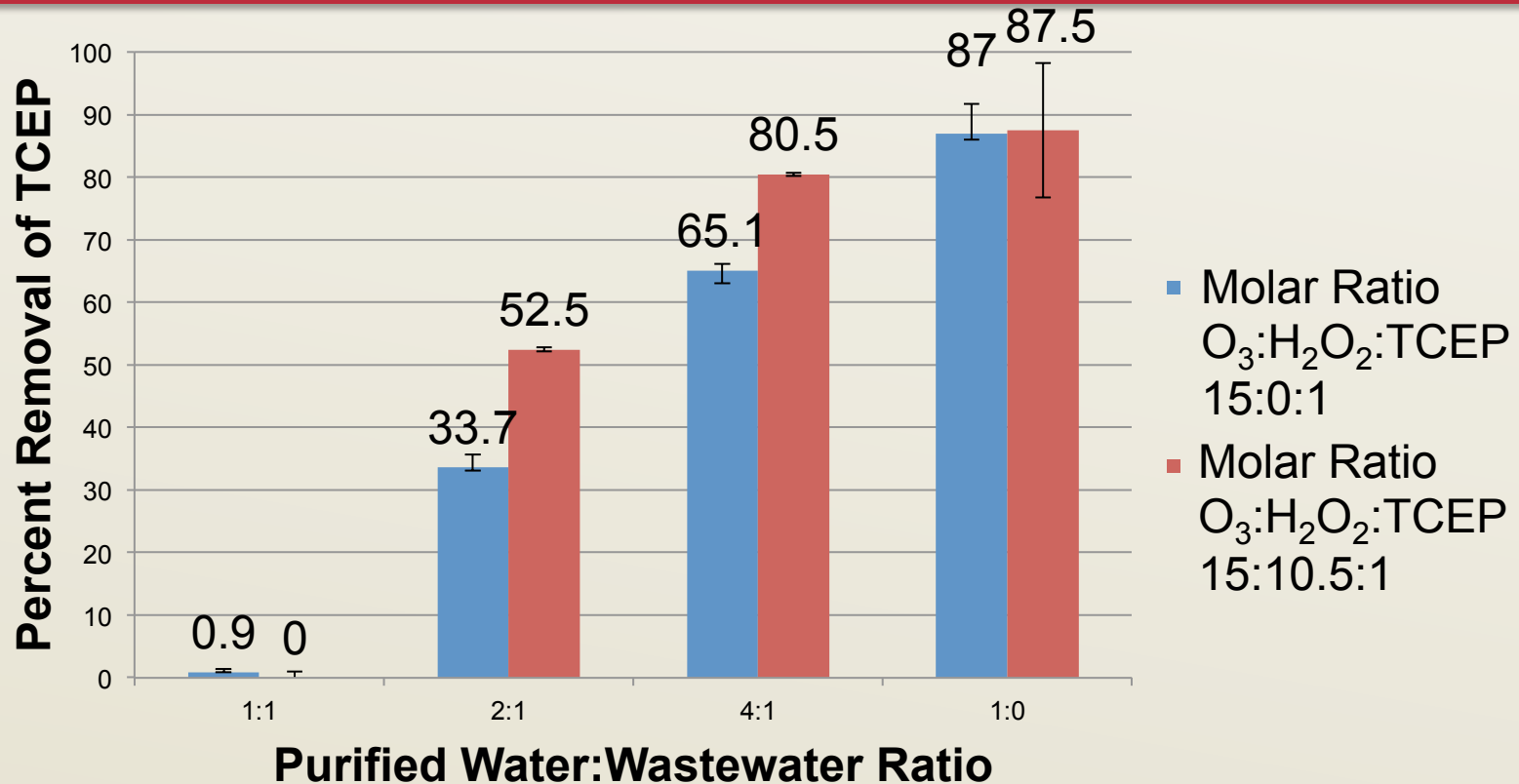


Percent Removal of TCEP for O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> Treatments at Varied pH  
(Ozone Dose of 10 mg/L).

Initial TCEP Concentration = 2 mg/L

24 Hour Reaction Time

# Results: TCEP Degradation In Wastewater

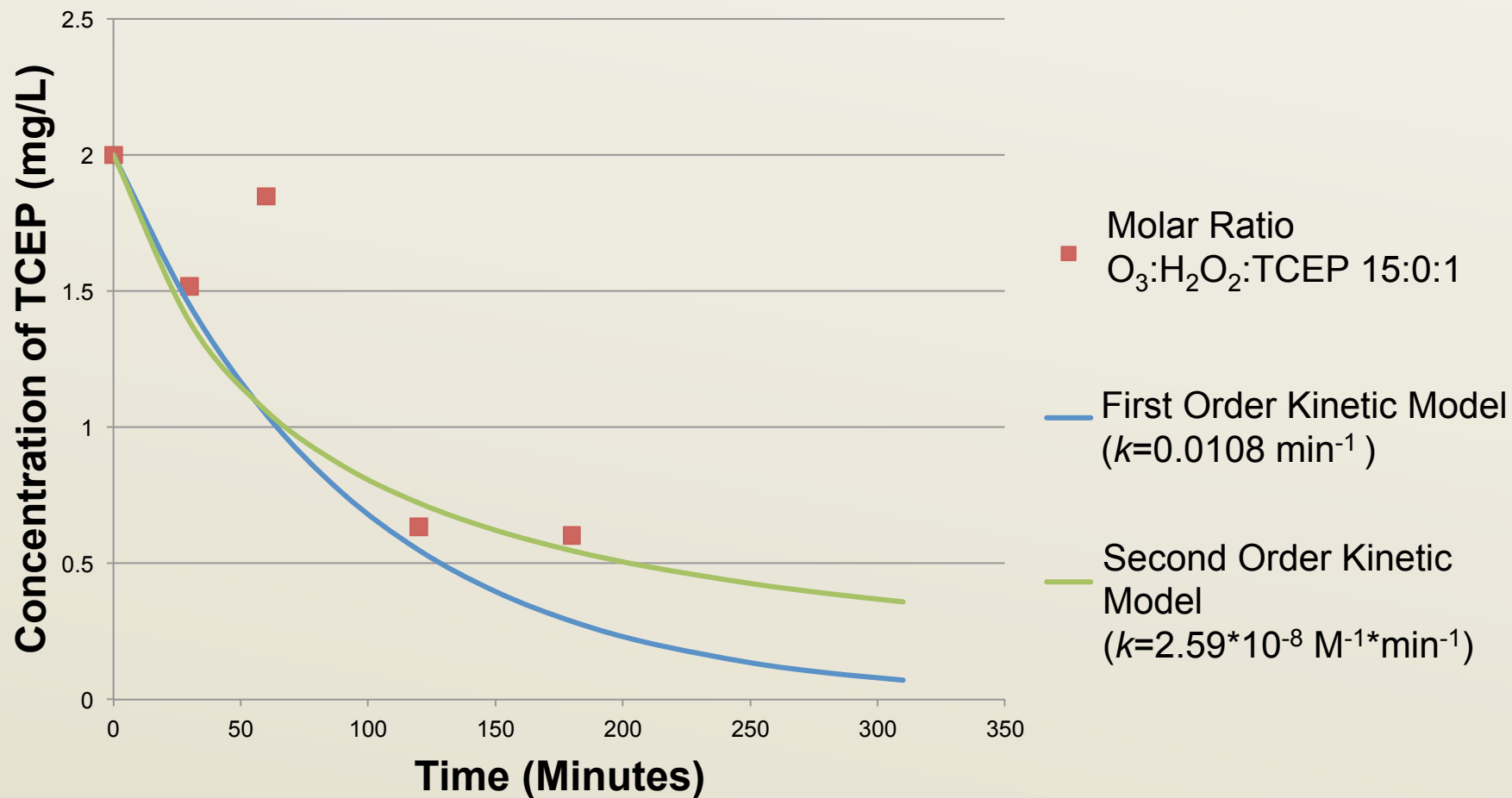


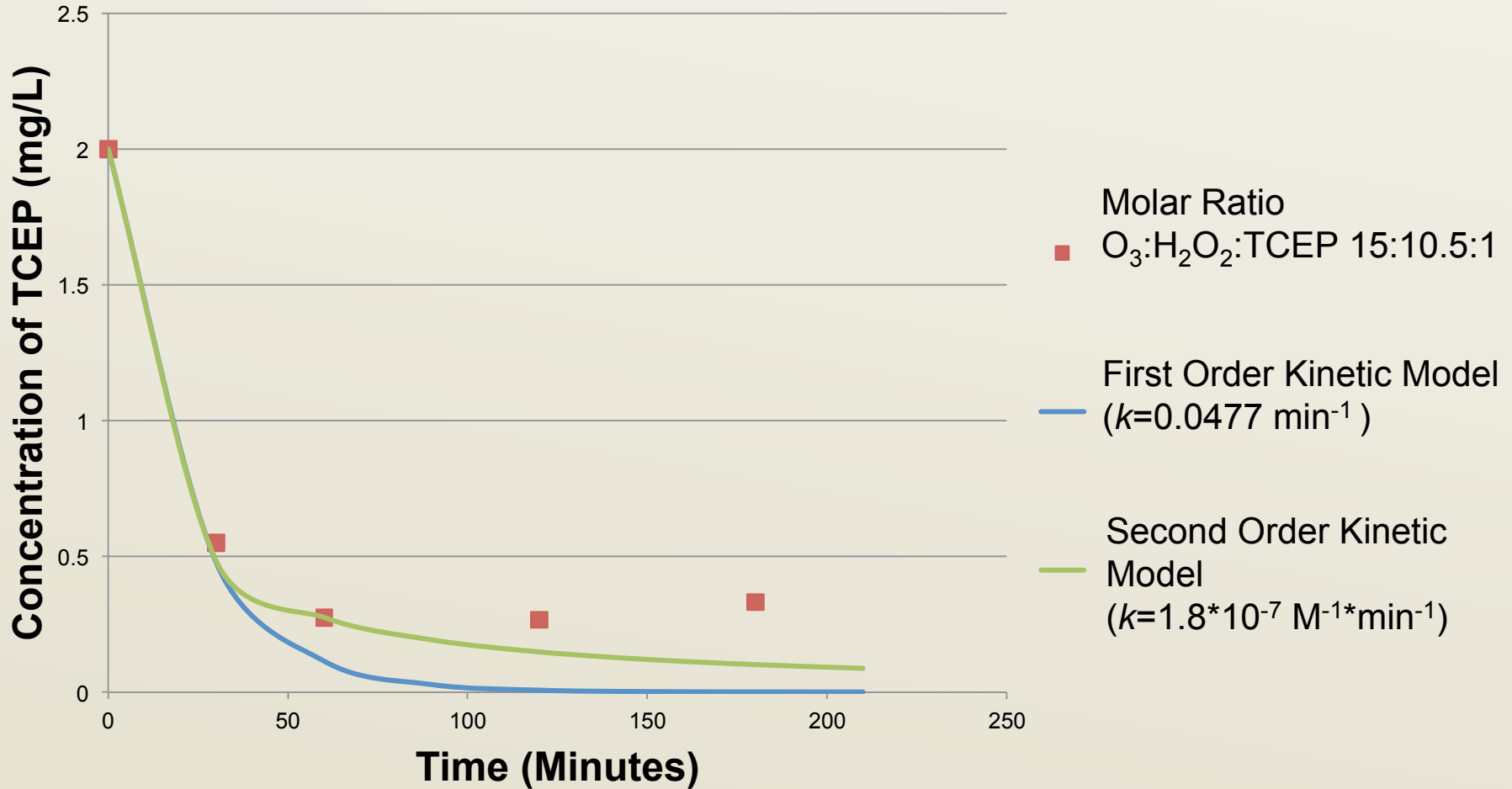
Percent Removal of TCEP for O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub> Treatments in Diluted Wastewater at pH 7 (Ozone Dose of 5 mg/L).

Initial TCEP Concentration = 2 mg/L

24 Hour Reaction Time







## **TCEP removal using ozone or ozone/hydrogen peroxide:**

- **Very effective in pure water (no competition)**
- **Greater ozone dose = greater TCEP removal**
- **Hydrogen peroxide addition achieves greater removal of TCEP in most cases**
- **Effect of pH is more prominent at low ozone doses**
- **Not as effective in wastewater (with other organics present)**
- **Kinetic rate constants found are much lower than those for other contaminants typically found in waters and wastewaters**

- **Determine the products formed from the oxidation of TCEP**
- **Investigate the removal of lower concentrations of TCEP**
- **Evaluate the removal of TCEP in the presence of other organics in wastewater with higher ozone doses.**
- **Examine other forms of advanced oxidation for TCEP removal ( $O_3/UV$ ,  $UV/TiO_2$ )**
- **Assess the feasibility of TCEP removal with the different treatments concerning cost (safety, economic and environmental)**
- **Look at ozone oxidation with other organophosphates as well as other recalcitrant compounds**



# Contact Information

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