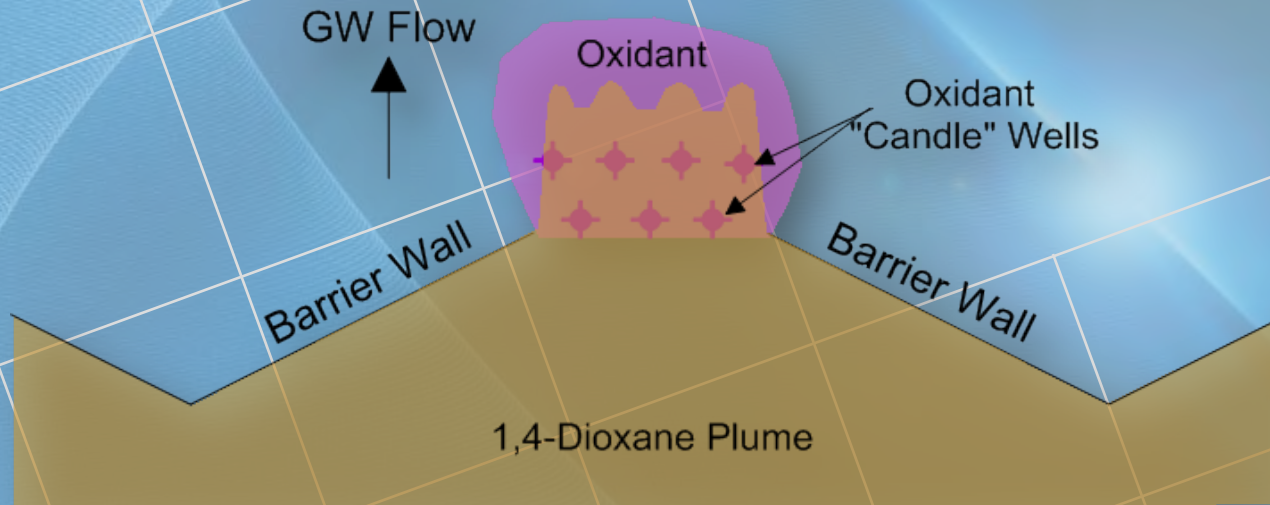


# *In Situ* Chemical Oxidation of Dioxane Using Slow-Release Chemical Oxidant Candles

*GRA Emerging Contaminants Symposium*

Patrick Evans (CDM Smith)  
Pamela Dugan (Carus)  
Michelle Crimi (Clarkson University)

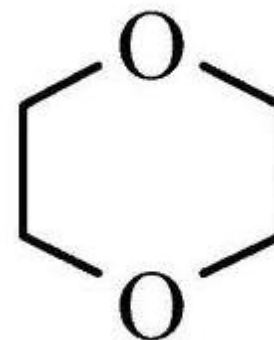
February 5, 2014



**CDM  
Smith**

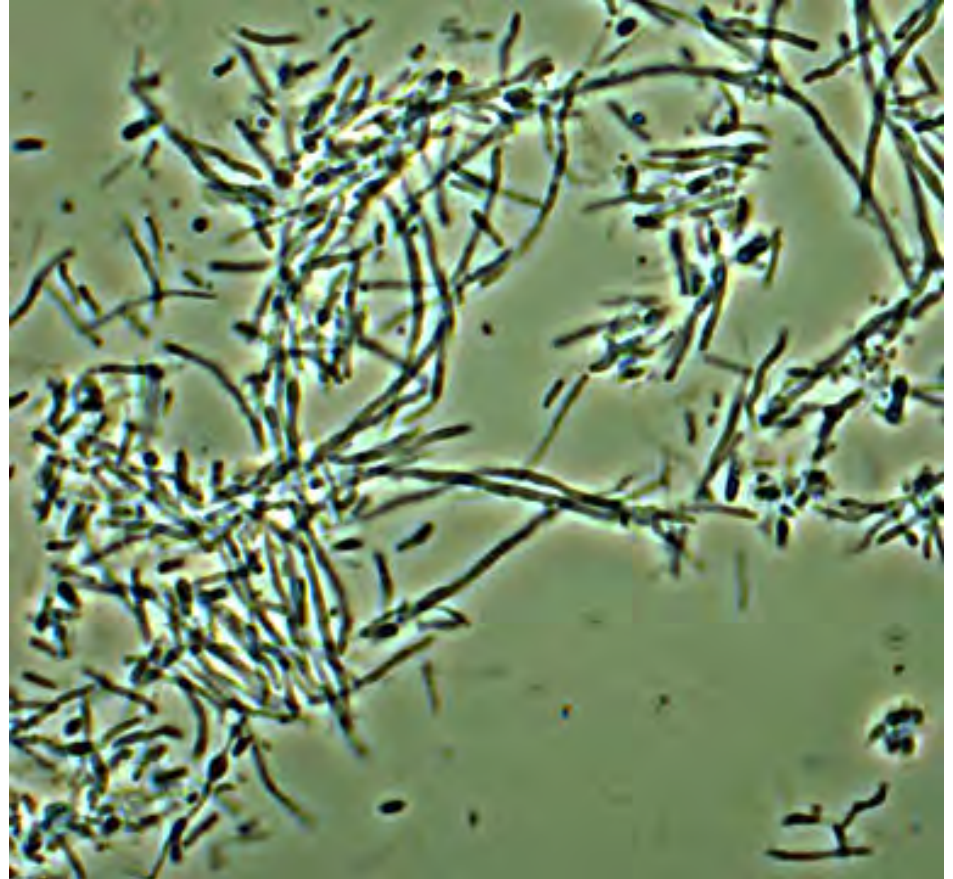
# Problem Statement

- Dioxane is a challenging contaminant:
  - More widespread than previously thought
  - Large and dilute plumes
  - Increased cancer slope factor published in 2010
- Current approaches don't work well or are expensive:
  - Pump and treat / advanced oxidation processes
  - Biodegradation (Evans, Paraless, & Paraless 2007)



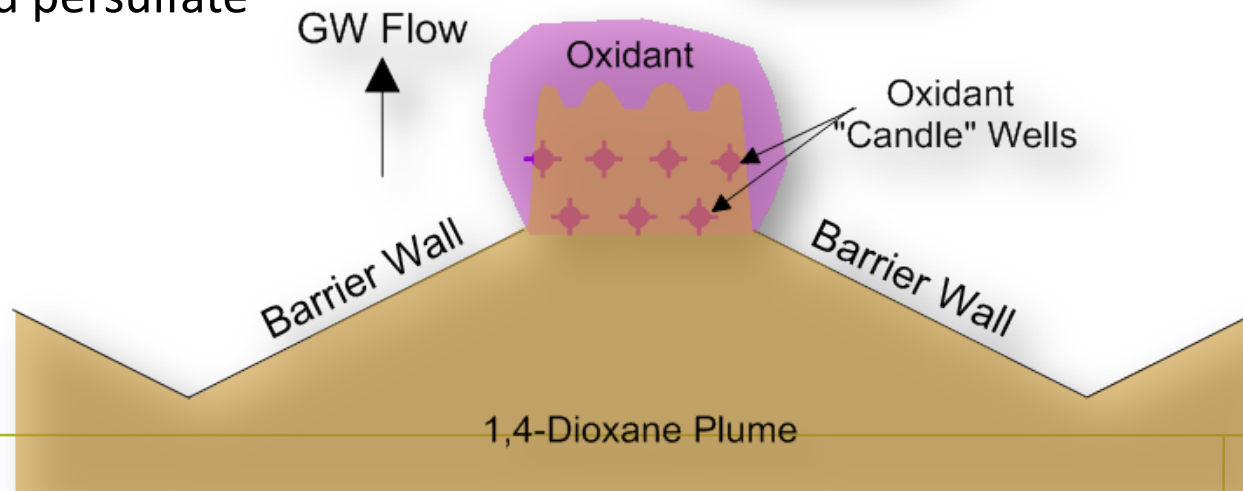
## CB1190

- *Pseudonocardia dioxanivorans* – an actinomycete
- First isolate capable of growth on dioxane (Parales et al., 1994)
- > 50% dioxane converted to CO<sub>2</sub>
- Specific activity 0.33 µg/mg/min
- Doubling time 30 hours
- Also grows on tetrahydrofuran



# Possible Solution

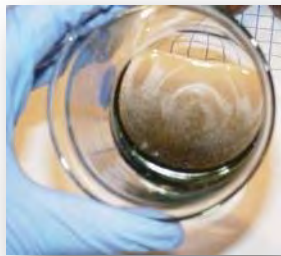
- Slow release oxidants are a solution
- Possible configurations
  - Permeable reactive barrier (PRB)
  - Funnel and gate (F&G)
  - Grid
- Oxidants
  - Permanganate
  - Unactivated persulfate
  - Activated persulfate



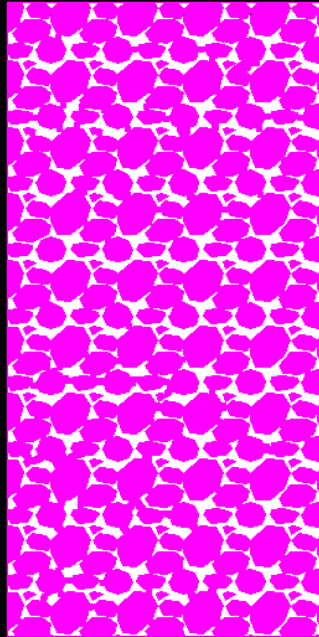


# Technology Description

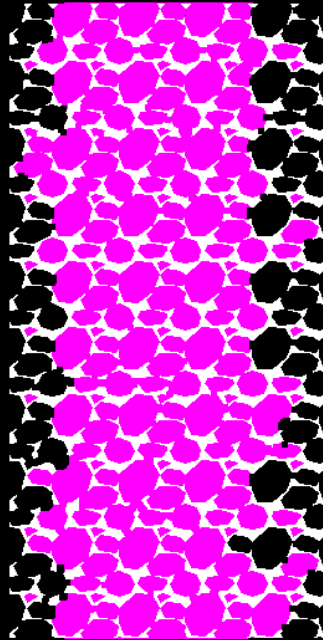
- Solid product formed as candle, chipped for barrier applications, or further processed for hydrofracturing into low permeability media/fractured bedrock
  - 1.35- or 2.5-inch diameter
  - 18 inches long



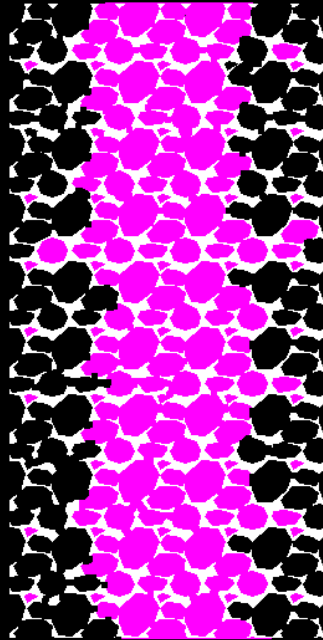
# Permanganate Candle Release from Wax



# Permanganate Candle Release from Wax

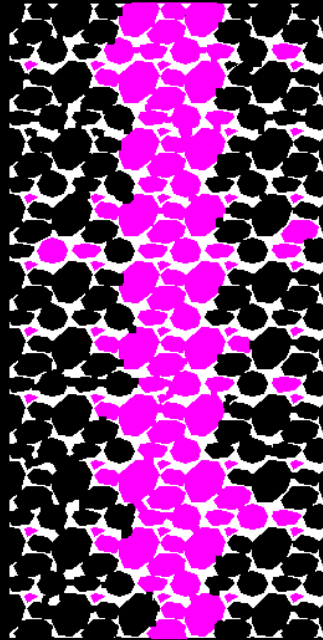


# Permanganate Candle Release from Wax

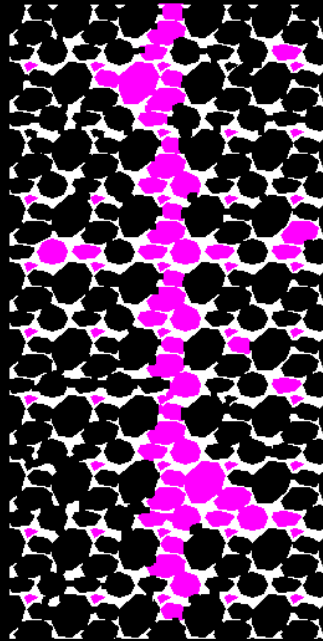




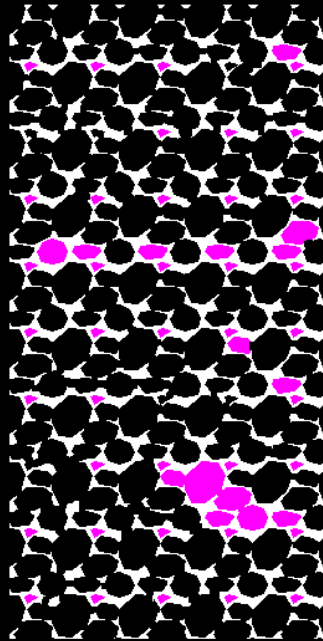
# Permanganate Candle Release from Wax



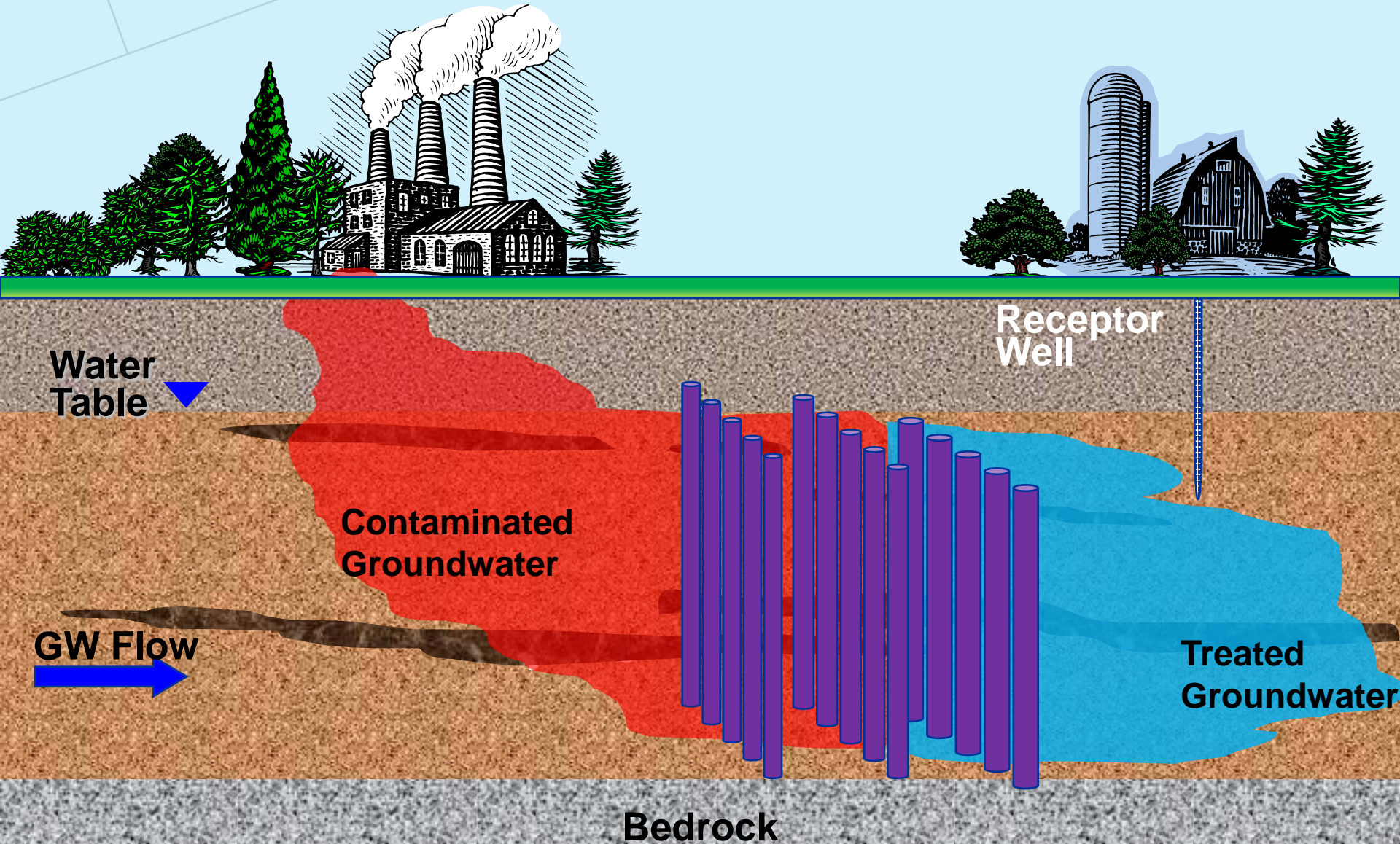
# Permanganate Candle Release from Wax



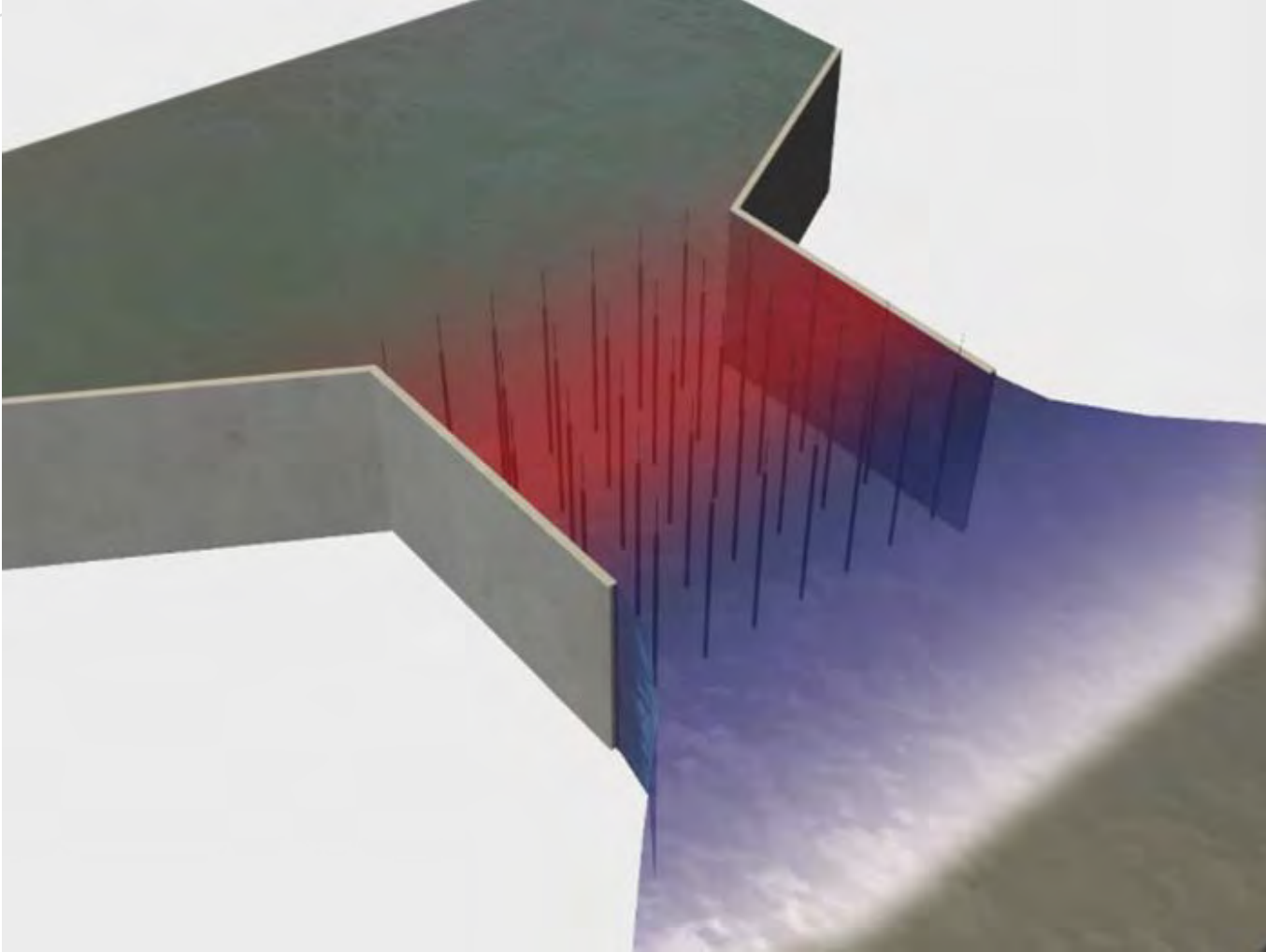
# Permanganate Candle Release from Wax



# Passive Treatment with *In Situ* Reactive Zones / Barriers

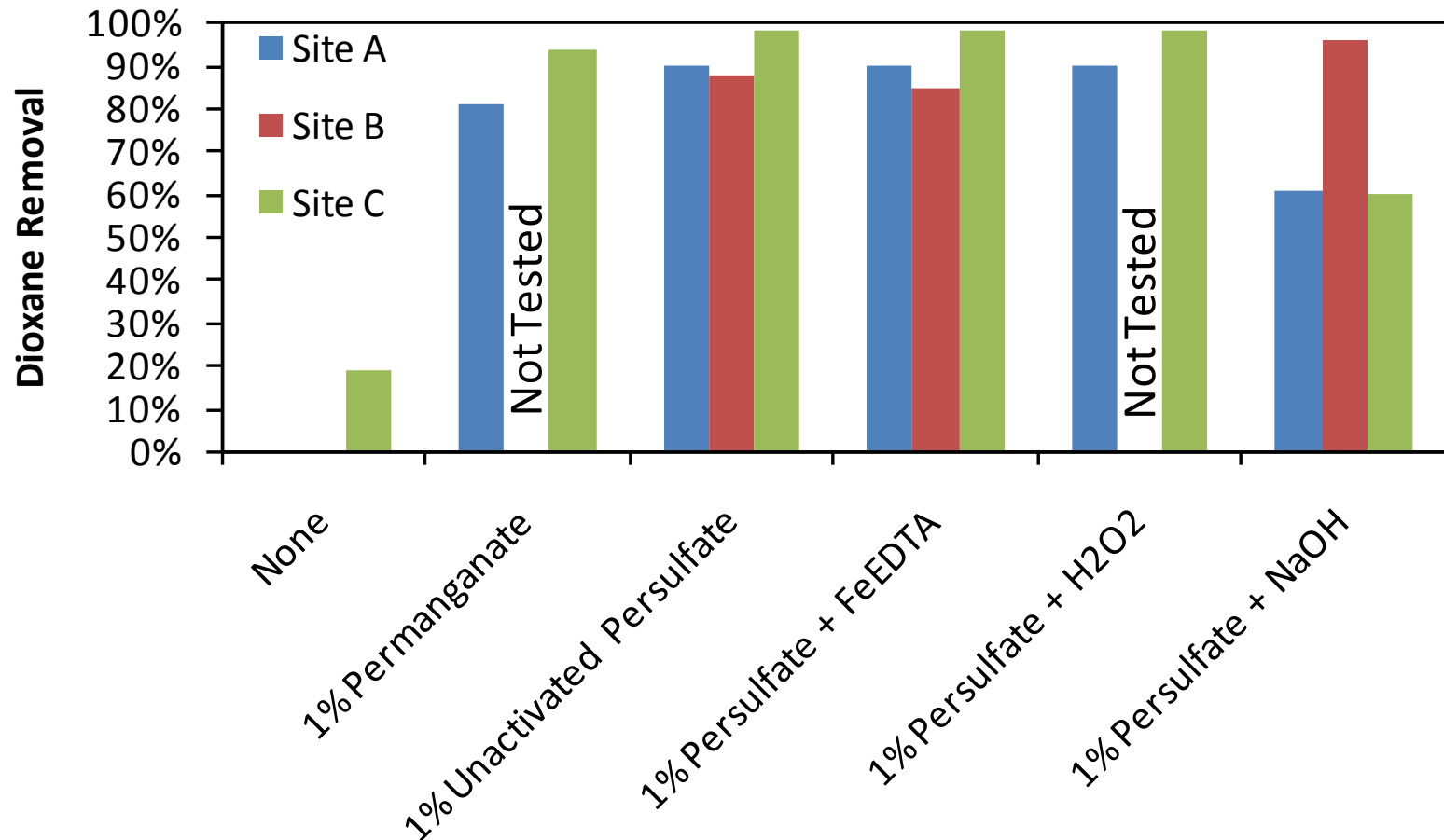


# Technology / Methodology Description



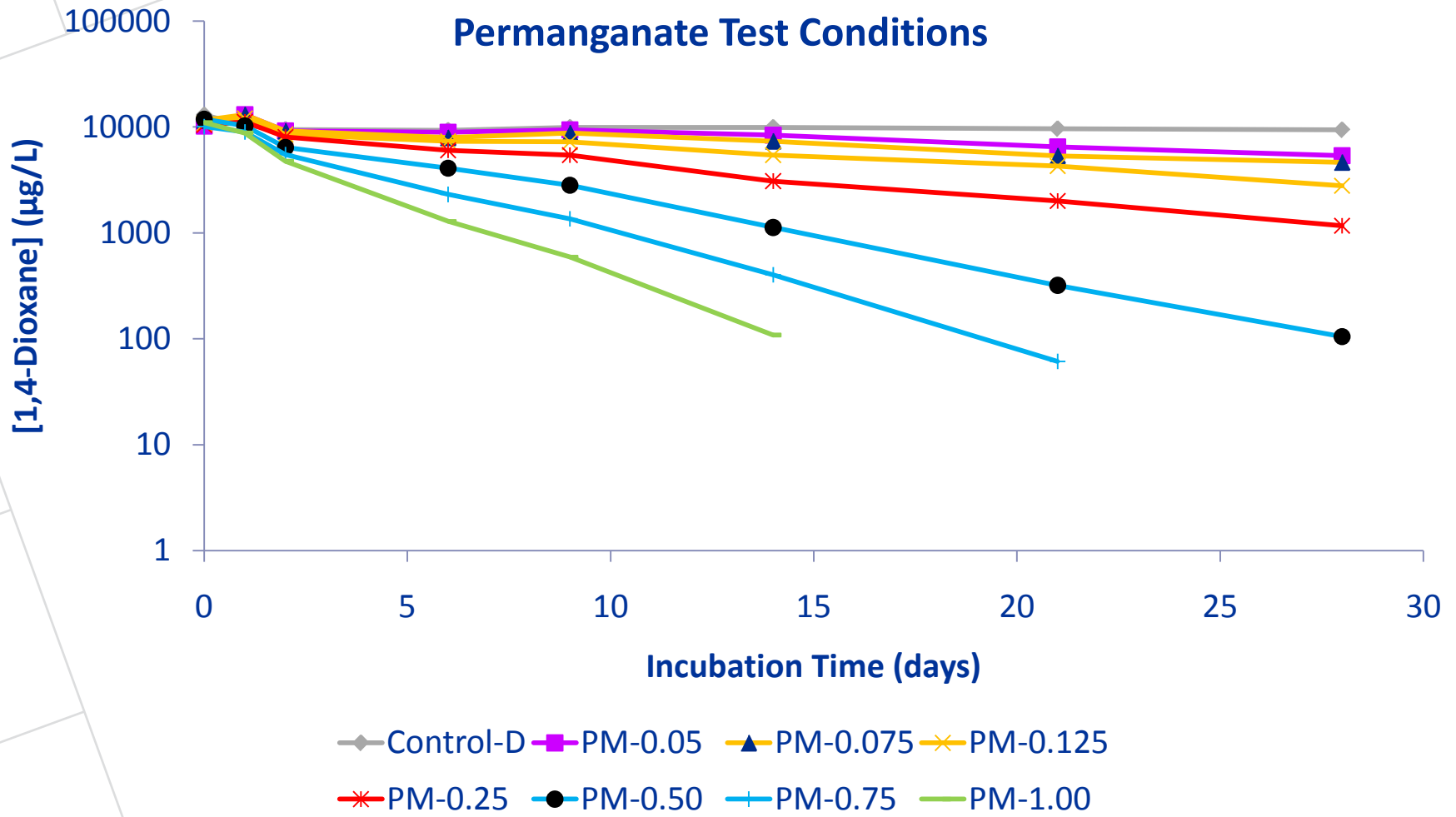


# Dioxane Destruction with Permanganate and Unactivated Persulfate

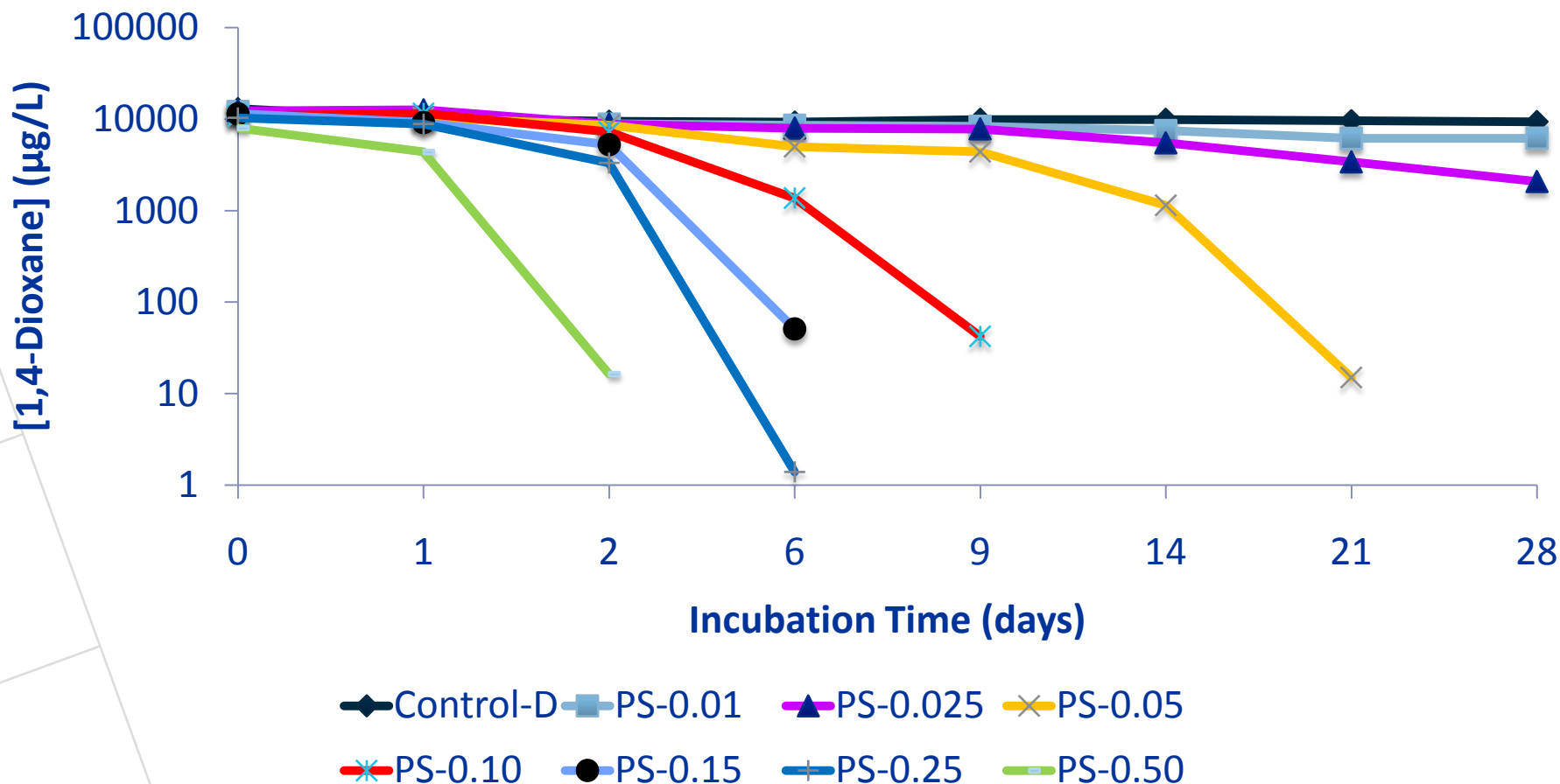


Both permanganate and unactivated persulfate oxidize dioxane at various sites

# Dioxane Oxidation with Permanganate

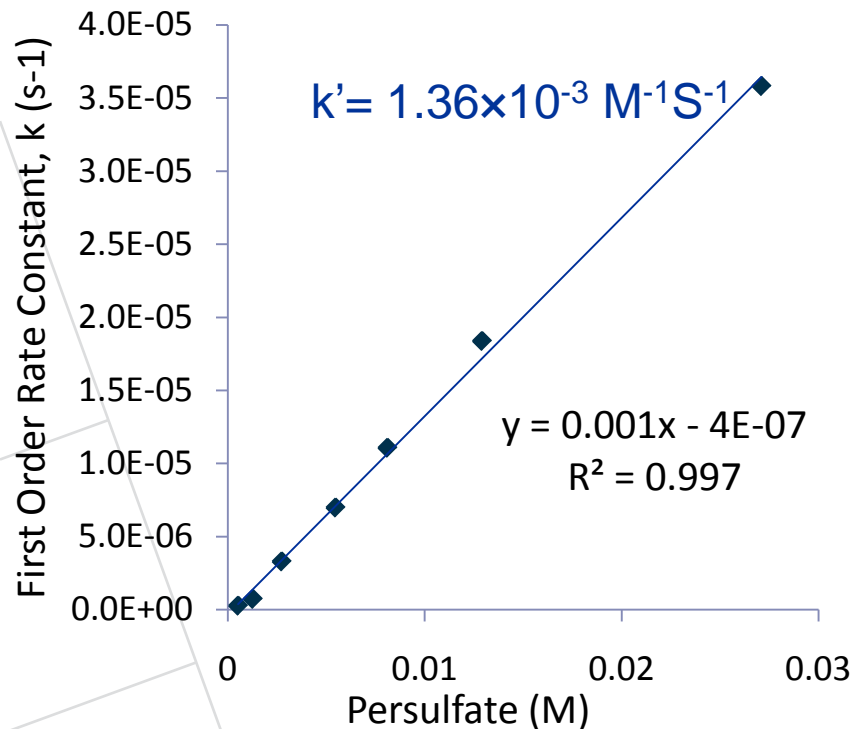


# Dioxane Oxidation with *Unactivated* Persulfate

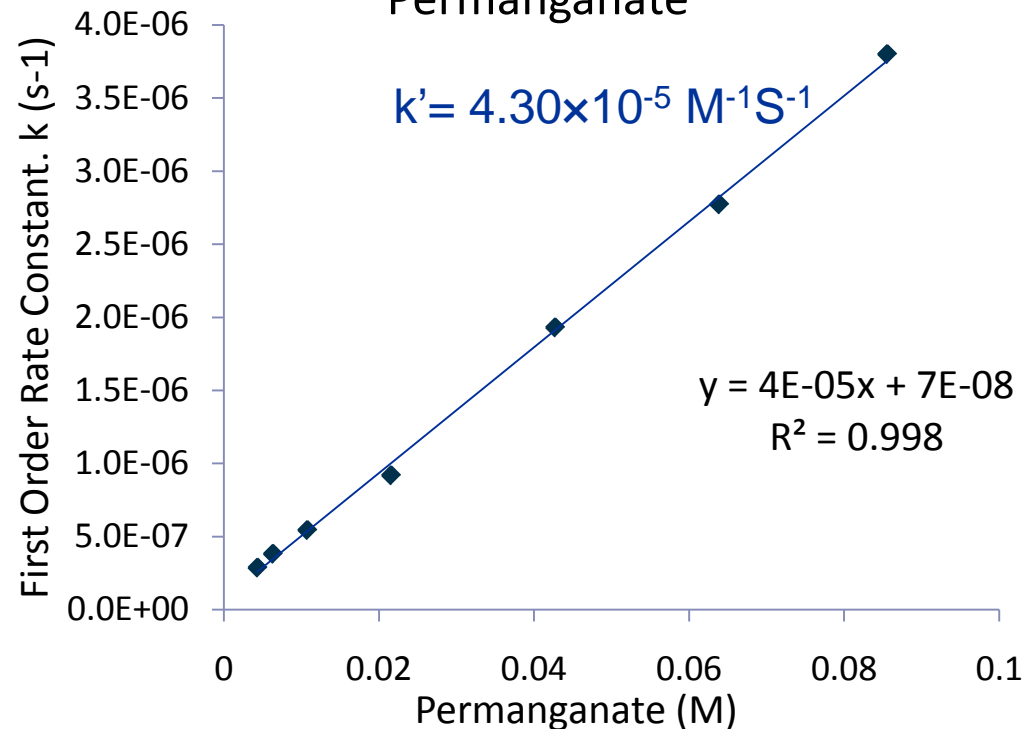


# Laboratory Oxidant Kinetics Results

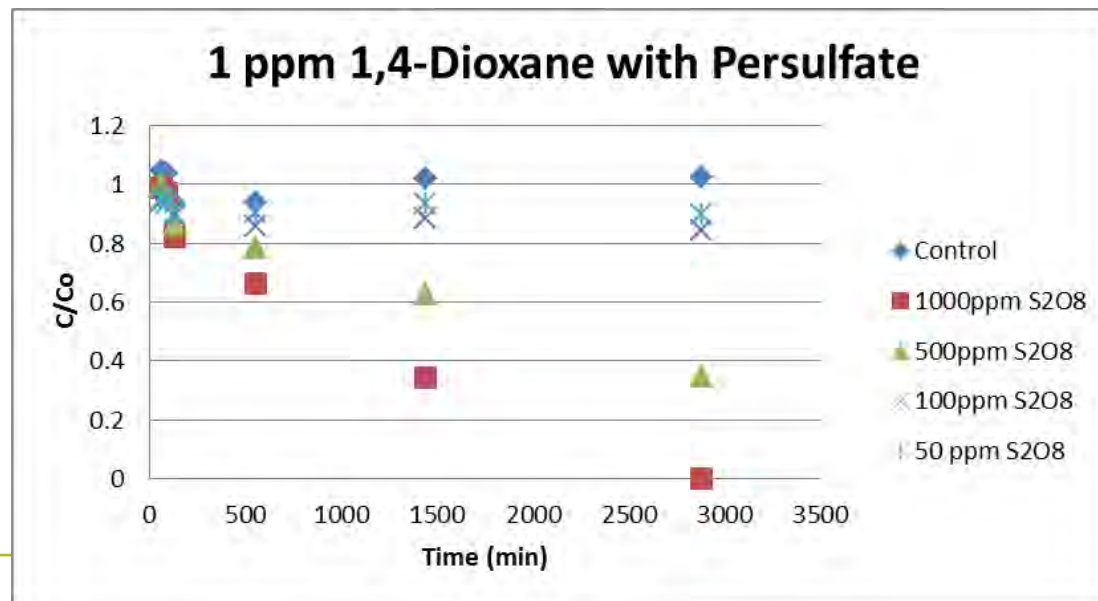
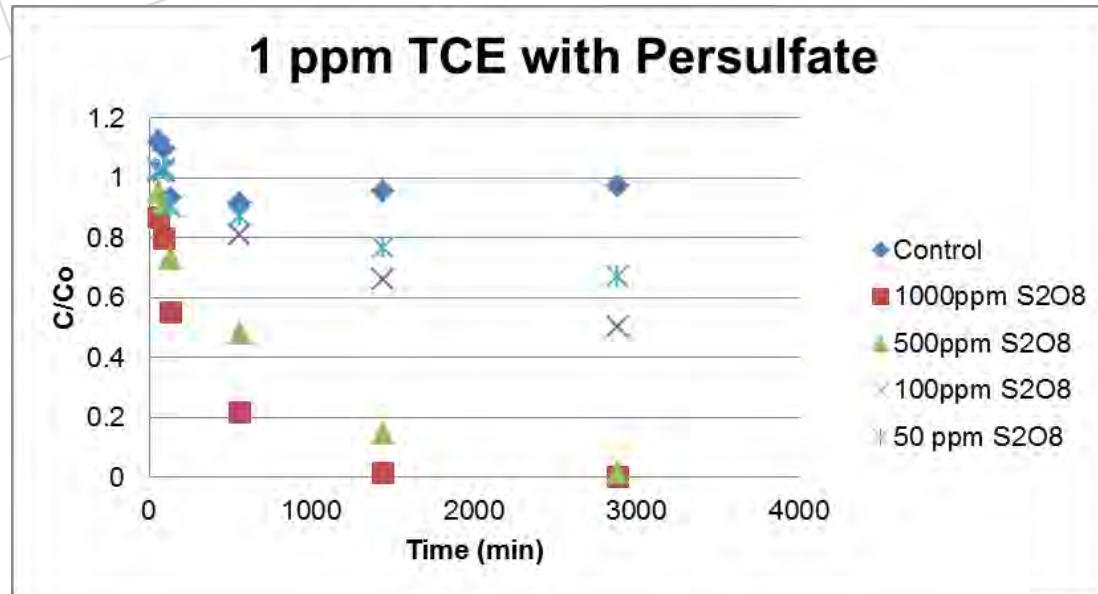
Pseudo-2nd Order Rate Constant for Persulfate



Pseudo-2nd Order Rate Constant for Permanganate



# Comparison of TCE and Dioxane Oxidation



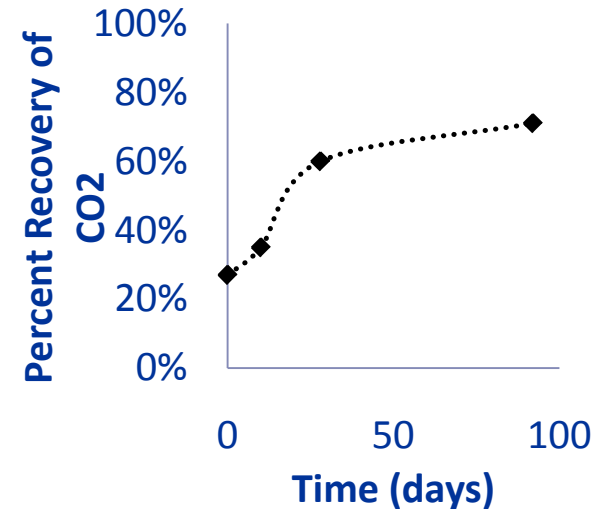
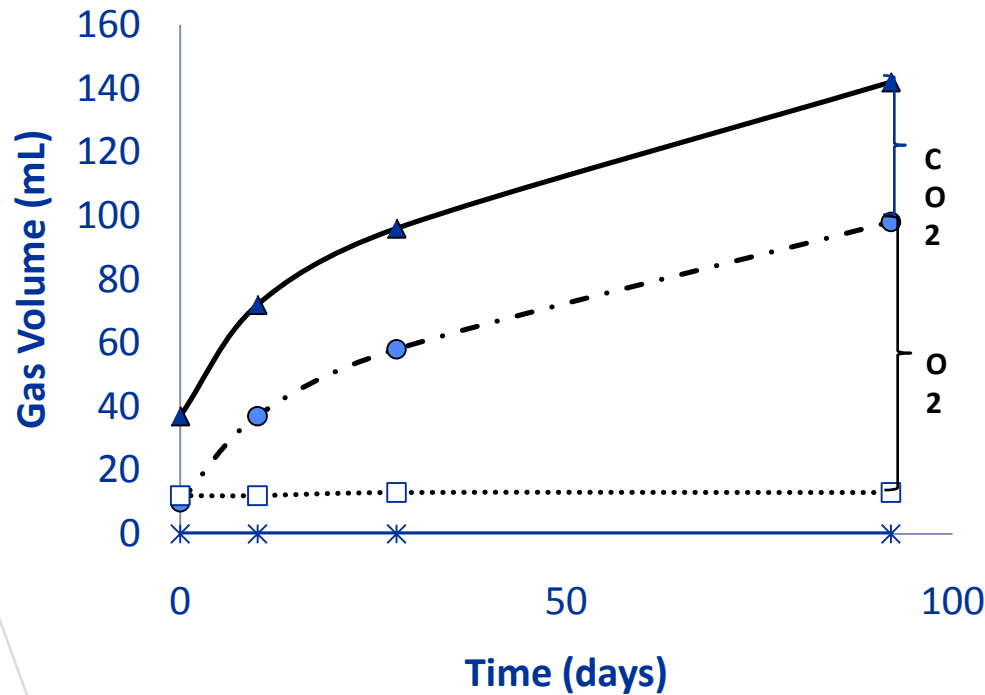


# Kinetic Experiment Summary (Nanopure water, no soil)

<b>Oxidant</b>	<b>Contaminant</b>	<b>Calculated Second Order Rate Constant (M<sup>-1</sup>s<sup>-1</sup>)</b>
Persulfate	Dioxane	1.26 E-03
Persulfate	Dioxane and TCE	1.90E-03
Permanganate	Dioxane	3.25E-05

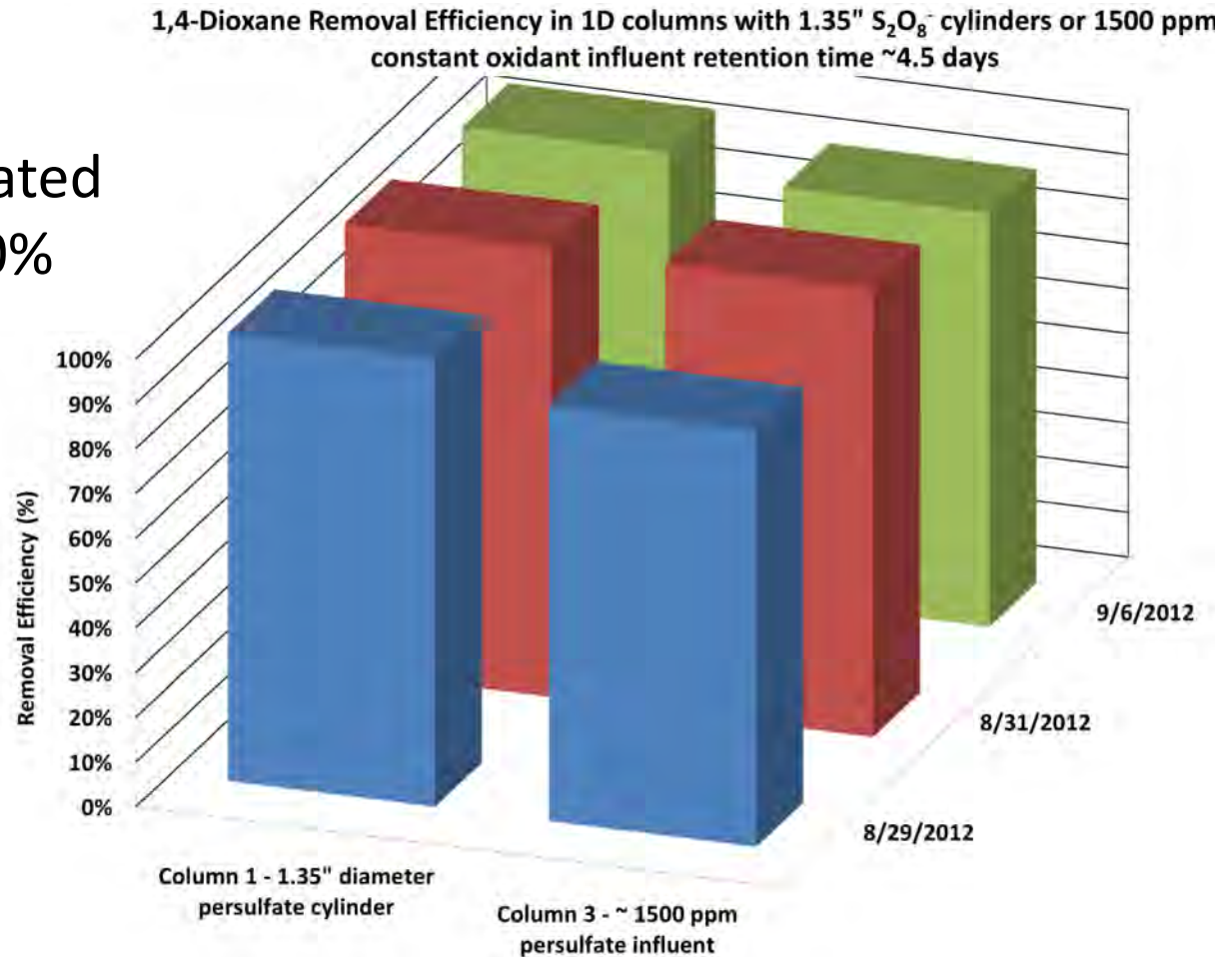
- Oxidation of dioxane with persulfate is about 30X faster than with permanganate.
- Potential enhancement of dioxane oxidation by TCE?
- In progress – Testing with site groundwater and soil

# Dioxane Mineralization with Permanganate

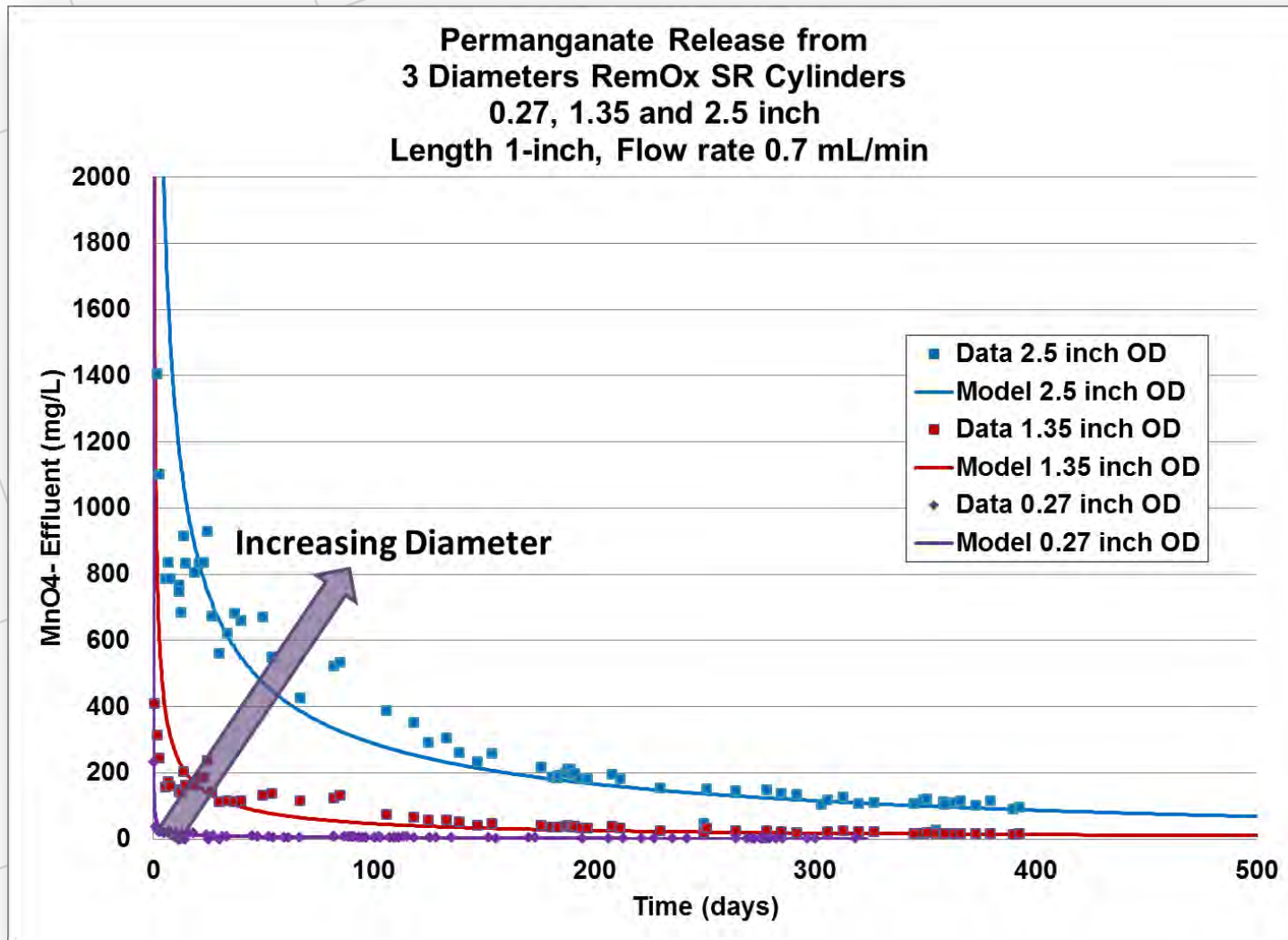


# Column Results for Dioxane Removal

- Persulfate SR cylinder 97%-100%
- 1,500 ppm unactivated persulfate 93%-100%



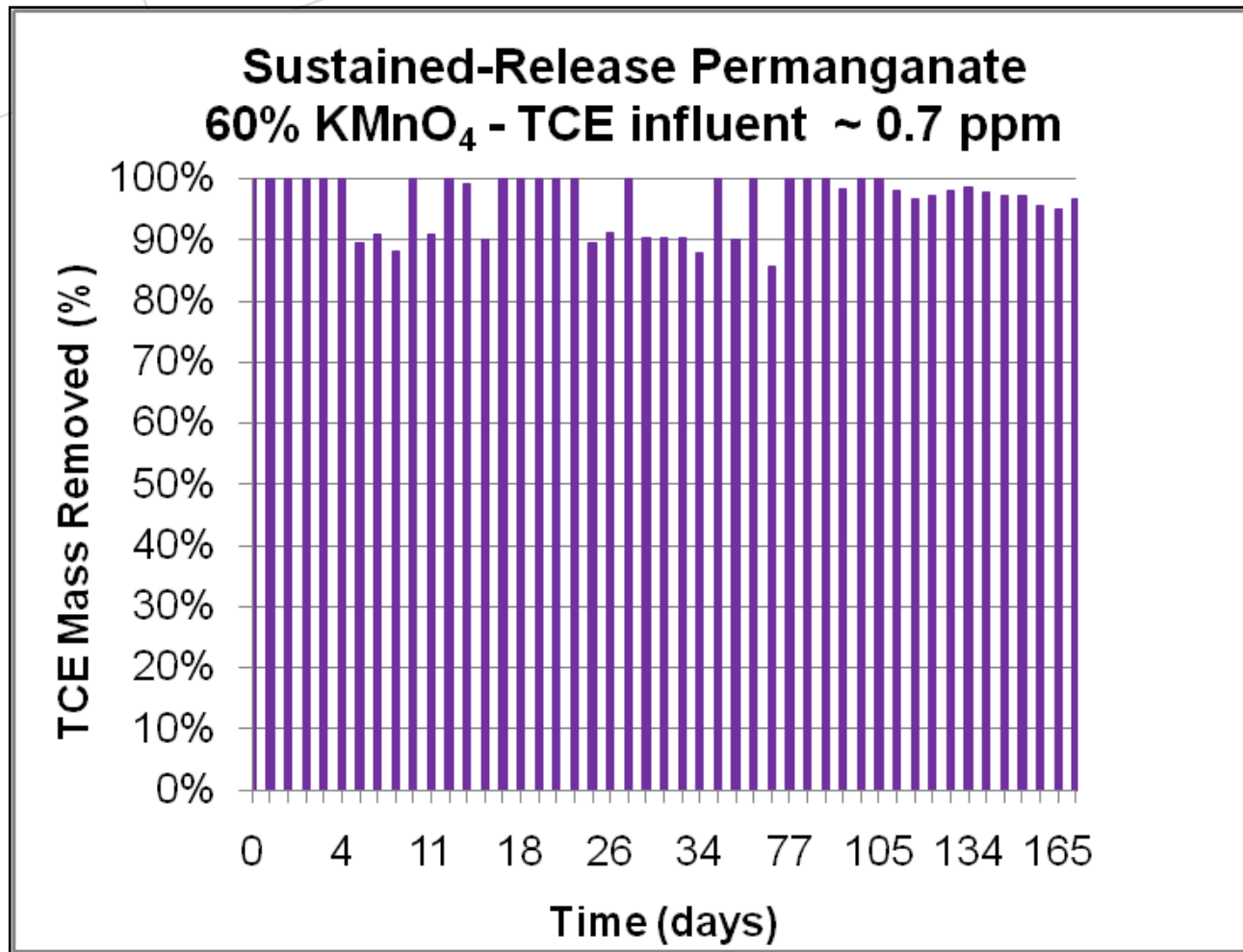
# Oxidant Release Kinetics and Modeling



Permanganate Mini-Cylinder (80% w/w) running for ~6 months



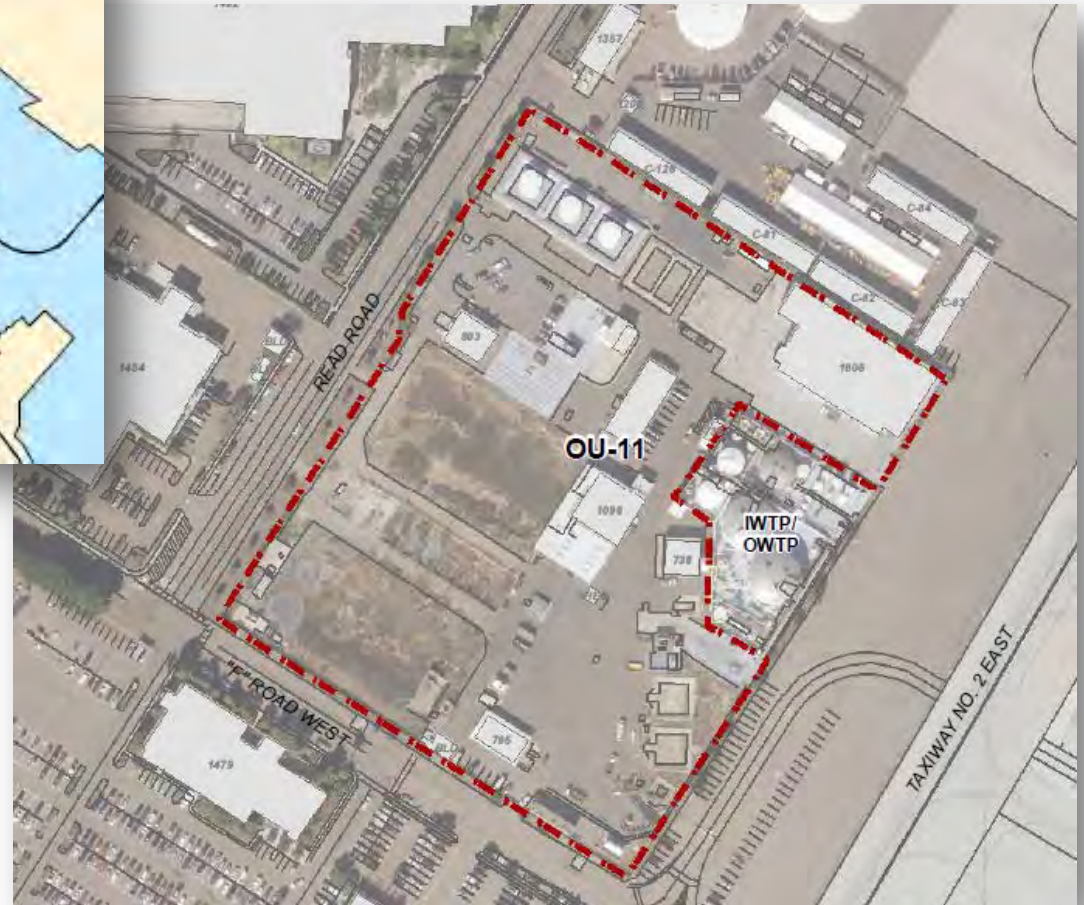
## Results – TCE Removal in 1D Columns



**TCE mass removal 86%-100% over 170 days or > 470 PVs**



# ESTCP Demonstration: Naval Air Station North Island



# Engineering Design Tool

## Slow Release Oxidant - release, reaction, and transport

Project:

Date:

Prepared by:

## Oxidant Release Parameters

Oxidant:

Candle diameter (cm):

Oxidant solubility (mg/l):

Effective diffusion:

Amount of available:

Treatment:

Treatment:

# (per row):

## Site Characteristics\*

Primary contaminant:

Concentration (mg/L):

Secondary contaminant:

Concentration (mg/L):

Longitudinal dispersivity:

Transverse dispersivity:

Vertical dispersivity:

Natural oxidant demand (NOD) (mg/kg):

NOD rate (2nd order;  $M^{-1}s^{-1}$ ):

Hydraulic conductivity (cm/s):

Hydraulic gradient (dh/dl):

Porosity:

\*guidance provided in 'site characteristics guidance' tab

## Simulation

Simulation time:

Simulation or compliance

distance downgradient:

Basic project information

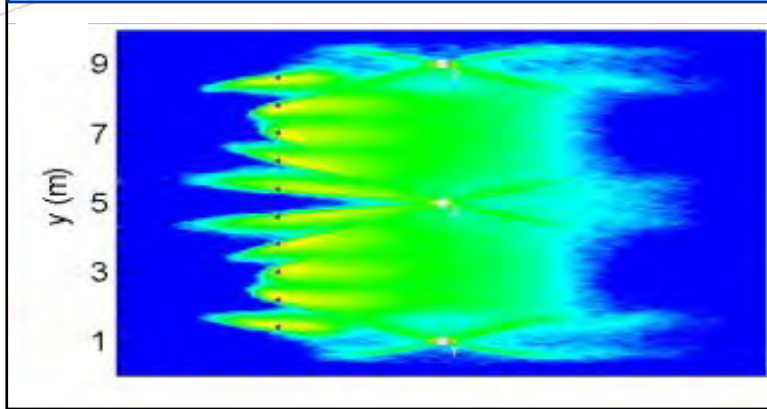
Factors affecting oxidant release rate and resulting concentration

Contaminant characteristics  
Dispersion parameters  
**Oxidant demand – rate and extent**  
**Flow properties**

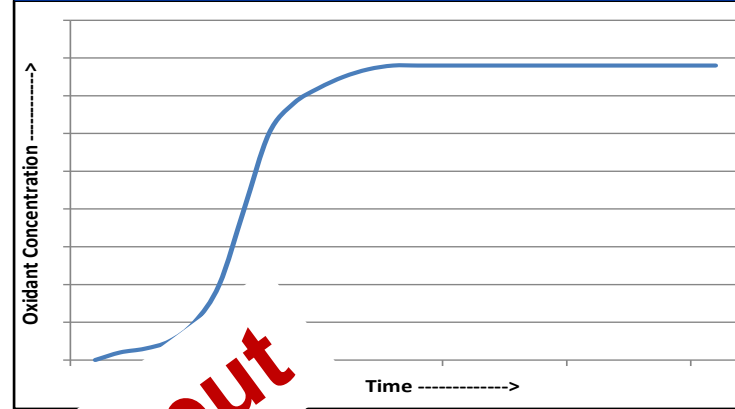
Simulation **time and distance** of interest

# Engineering Design Tool

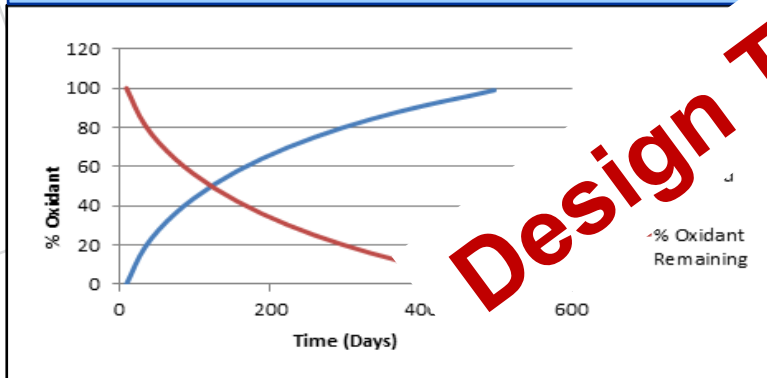
Oxidant concentrations  
vs. distance at a given time



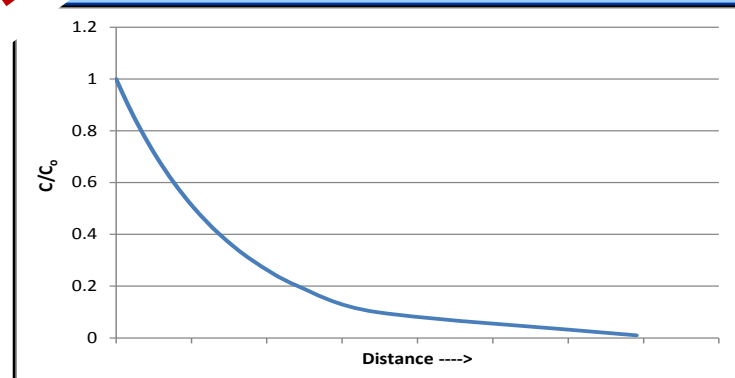
Oxidant concentrations  
at a given point over time



Oxidant release from candles



Contaminant concentrations  
vs. distance at a given time



**Design Tool Output**

# Conclusions

- Dioxane and other contaminants often create large dilute plumes
- Unactivated persulfate and permanganate have potential for treatment
- Slow-release chemical oxidant candles can be used for plume treatment
- Various configurations include permeable reactive barriers, funnel and gate, and grid
- An ESTCP field demonstration will yield practical cost and performance data

# Thank You!

Pat Evans

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