# State of the Practice versus State of the Art in Chemical Oxidation / Reduction Technologies.


**Presented by:**

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Principal and Founder


Advances in Oxidation and Reduction Technologies for Remediation of DNAPL, LNAPL and Other Organic and Inorganic Contaminants (AORT), *Atlanta, Georgia, USA, November 13-17, 2016.*

# Who am I?

- B.S. and M.S. Civil / Environmental Engineering; ABD - PhD studies Environmental Engineering – late 70’s – mid 80’s
- Have been focused on development, design and implementation of remediation technologies since early 1980’s

# Discussion on State of the Art vs. State of the Practice

**(primarily molded by pricing pressures)**

- For majority of technologies developed the state of the practice diverged from the state of the art
- Pressure in the industry for low cost solutions is a major driver in the state of the practice
  - With the low cost driver, uncertainty in reaching the desired remedial goals can be high
  - This approach ultimately can result in higher cost to meet the remedial goals due to multiple remedy applications, failures and reevaluations
- For soil vapor extraction and air sparging, initial success is evident; however, it can take years of operation before system failure to meet remedial goals or system design limitations come to light
- For chemical oxidation and reduction, the failures and limitations are more likely to present themselves in the near-term

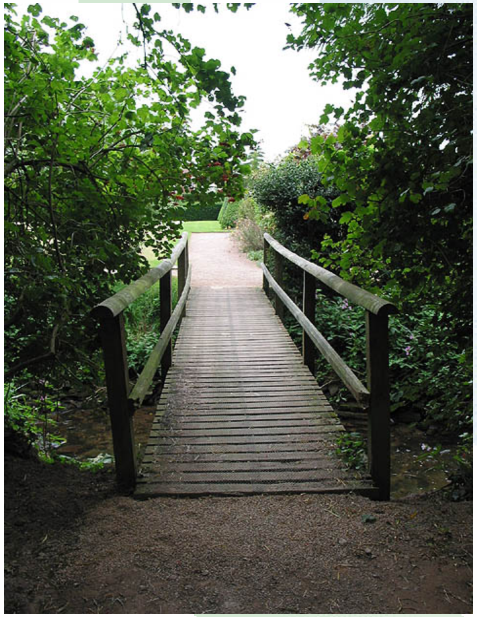
# So the Question I Pose:
# Do we use the right balance of Engineering and Certainty of Success ?

*Choose any Technology*

- State of the Practice

- Initial low cost
- Limited or "rule of thumb" design
- Lower certainty of success
- Ultimately highest cost?

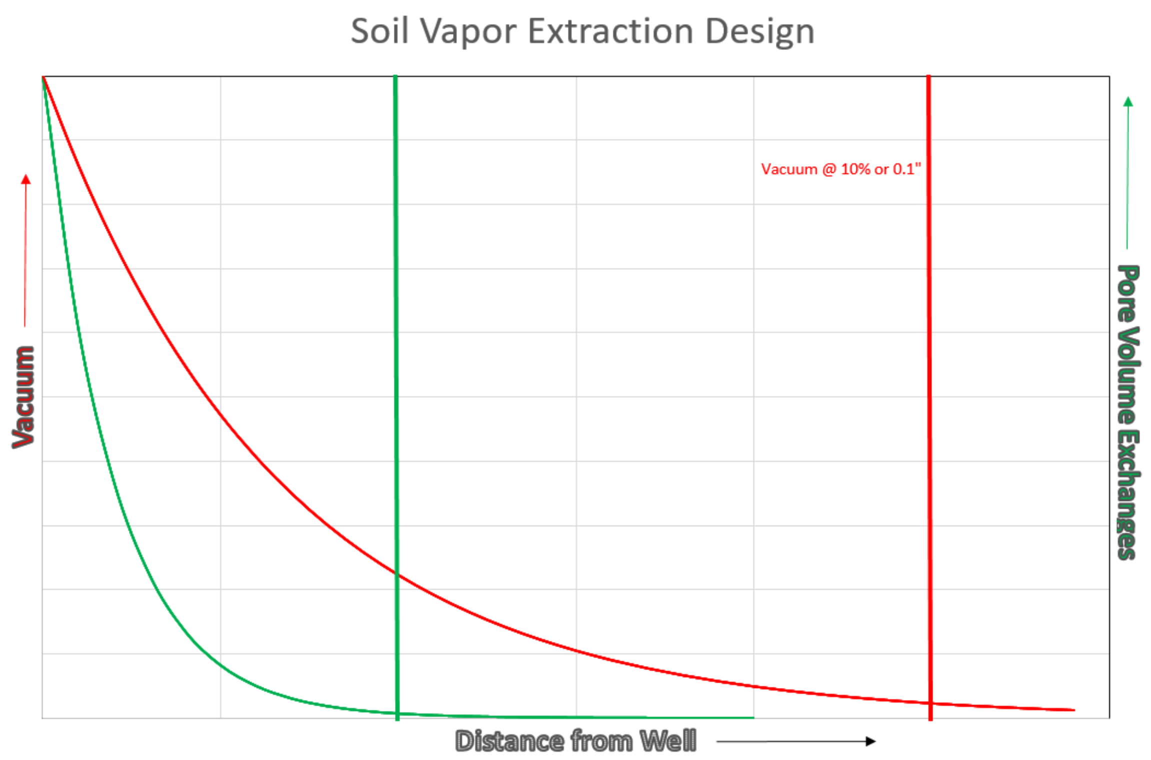
- State of the Art



- Potentially an initial higher cost
- Appropriate testing and design
- Higher certainty of success

# Example: Soil Vapor Extraction Design

- SVE Designs:
  - Vacuum propagation? – State of the Practice
  - Clean air sweeps / pore volume exchanges? – State of the Art



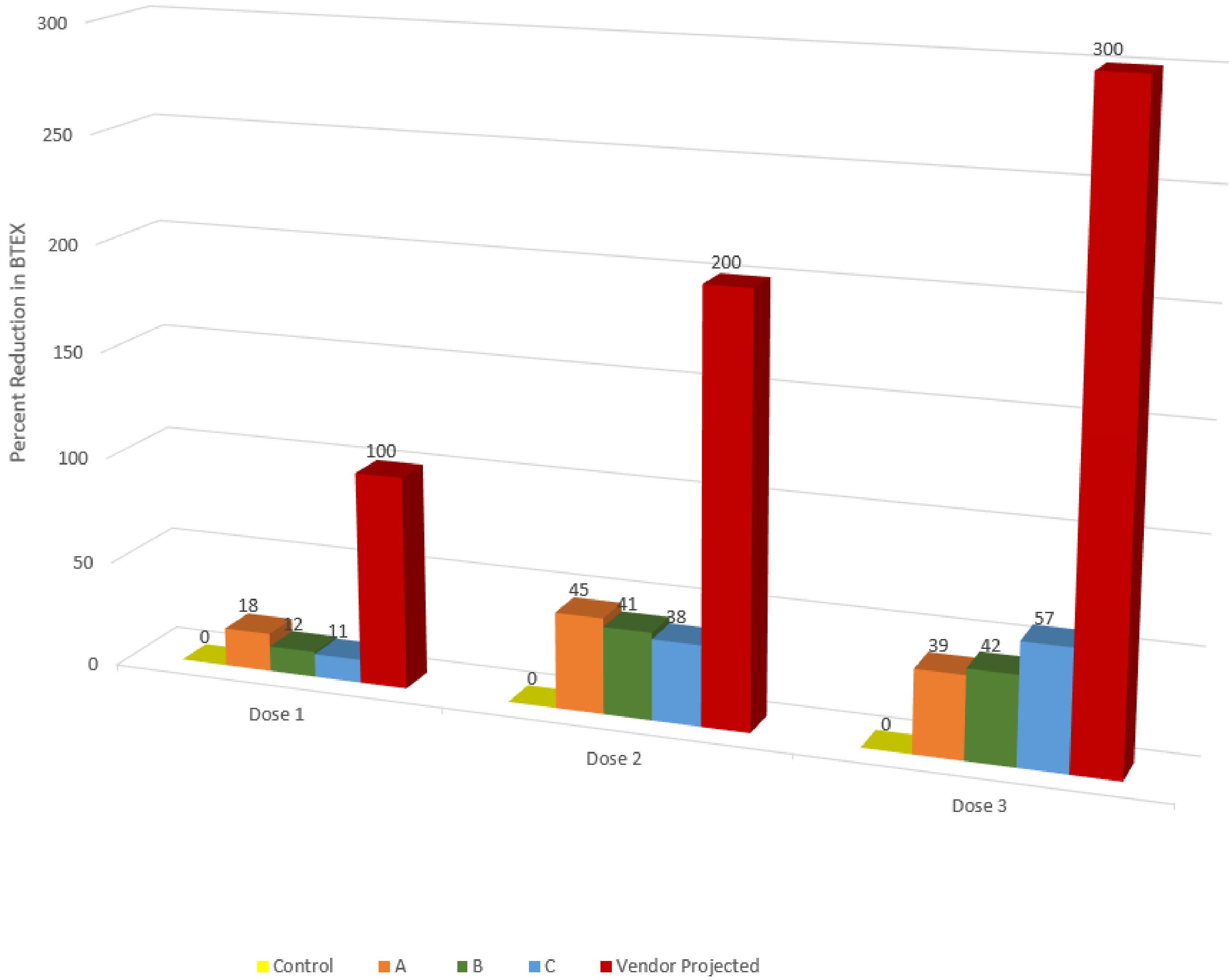

- Recent examples:
  - Example 1 – Large Site in West
    - Inches of water vacuum throughout domain
    - 11 years of operation
    - Essentially ineffective

# Example: Biostimulation with Oxygen Release Compounds

- Superfund Site: Mixed source / plume with chlorinated solvents and petroleum hydrocarbons
- Comparison of oxygen release products
  - Evaluated several oxygen release compounds on the market
  - Provided product vendors with site specific data and requested recommended dosing of product
  - Based on responses – tested all products at MAXIMUM dosage recommended*

    * = some vendors recommended treatability testing to validate dosage assumption
- **Not a product issue but an engineering design issue**

# Example: Oxygen Release Compounds



# Chemical Oxidation

- There are many ISCO technologies / products available – most common are:
  - Peroxide, Persulfate, Permanganate, Ozone
  - Many hybrids and packaged products

- Primary drivers for technology failure - rebound
  - Mass and architecture of target and non-target contaminants
    - Many sites have limited data to determine / estimate mass
    - ISCO is an oxidant mass to contaminant mass reaction technology
    - Characterization is key to estimate the mass with adequate certainty
  - <u>Oxidant demand / stability with site-specific soils</u>
  - <u>Oxidant solution injection volume</u>
  - <u>Geology / soil permeability variability</u>
    - Diffusion from impacted low permeability lenses

# Example of Oxidant Stability Issue

## ❑ North East Superfund Site

- Catalyzed hydrogen peroxide (CHP) selected by Army Corp. for treatment of chlorobenzenes in soil and groundwater
- Bench tested CHP and persulfate
  - o CHP with stabilization agents failed due to instability
  - o Iron activated persulfate was appropriate and cost-effective alternate
- Side by side pilots at site confirmed CHP failure (<1-foot ROI) and persulfate success
- Persulfate was applied successfully at pilot and full-scale

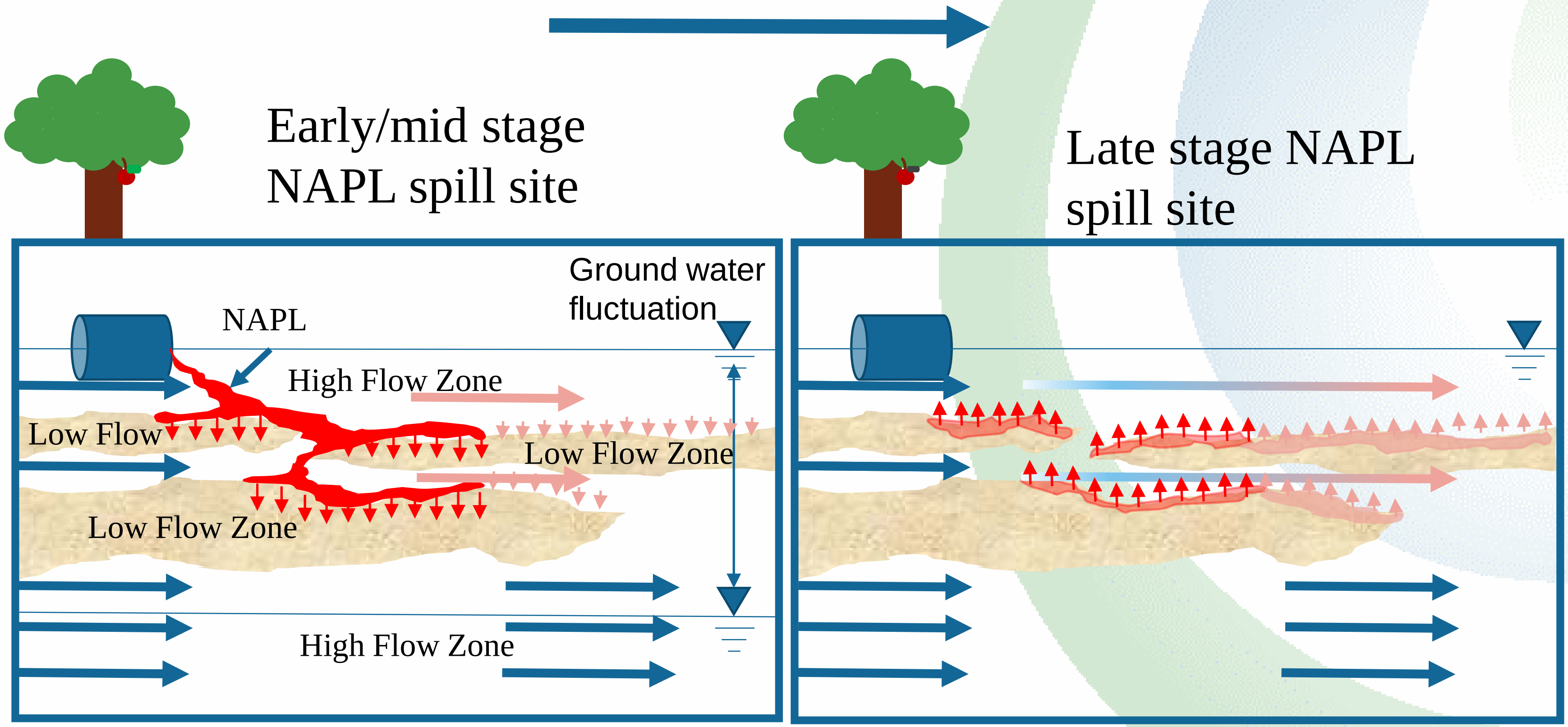
# Oxidant Solution Injection Volume

- Injection Volume vs. Pore Volume
  - Lesser percent pore volume injected
    - Will primarily treat preferential pathways or limited radius from injection point
    - More dependent upon diffusion and groundwater transport
  - Higher percent pore volume injected
    - Greater distribution via advective flow
    - Less dependent upon diffusion and groundwater transport

- EPA Staff paper under review on this issue, expect publication end of 2016, beginning 2017
  - Less volume = less oxidant = less cost - Certainty of success?

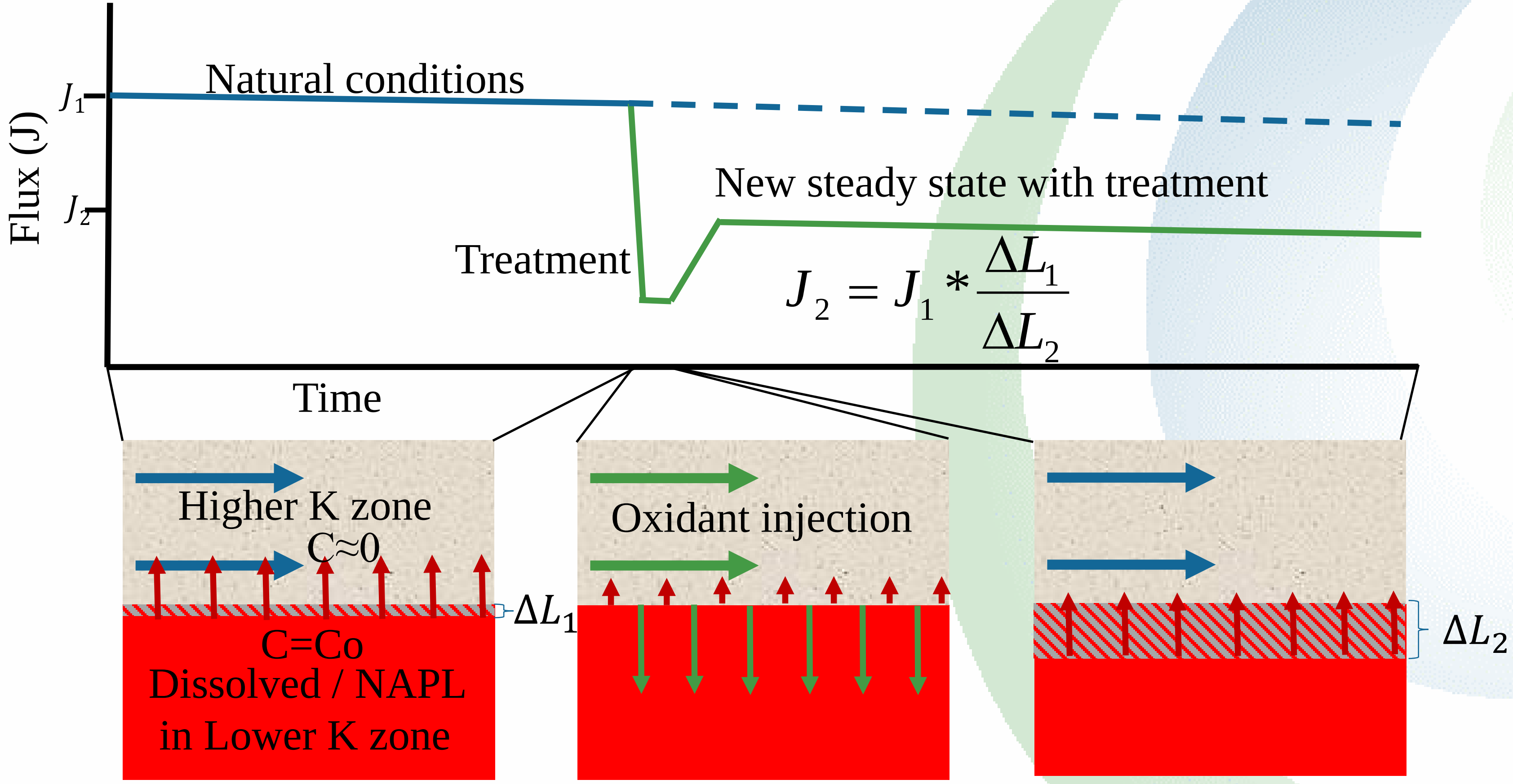
# Geology / Soil Permeability Variability

Natural dissolution or treatment (SVE, P&T, ISCO, etc.)



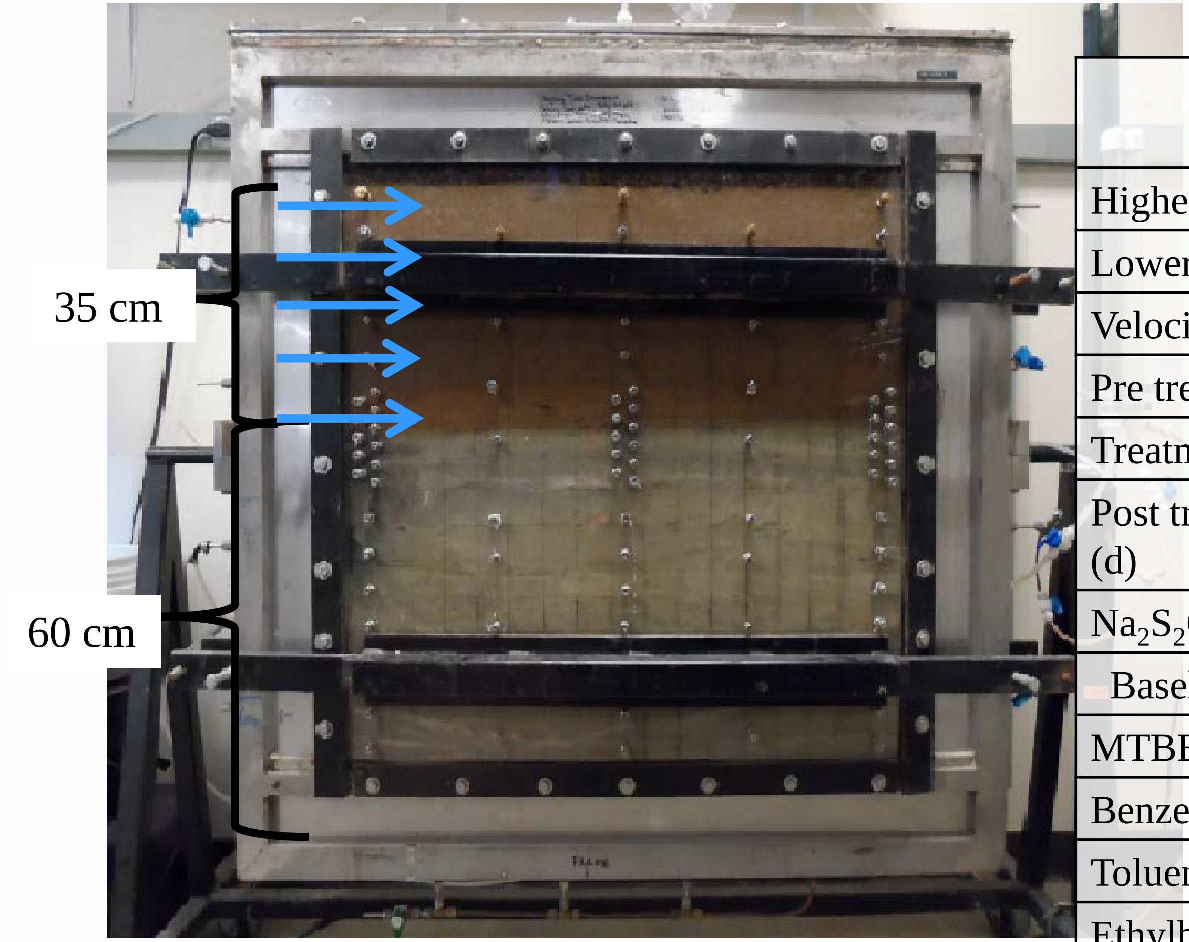

Slides curtesy Bridget Cavanagh, PhD – Doctoral Research 2014,
Environmental Science & Technology, 2014, 48 (24)

# Effects of Treatment on Flux




- Key Oxidant Characteristics Needed
  - Higher concentrations – potassium permanganate problematic / limited solubility
  - Slower reaction kinetics – peroxide and ozone problematic / no diffusion into LKZ

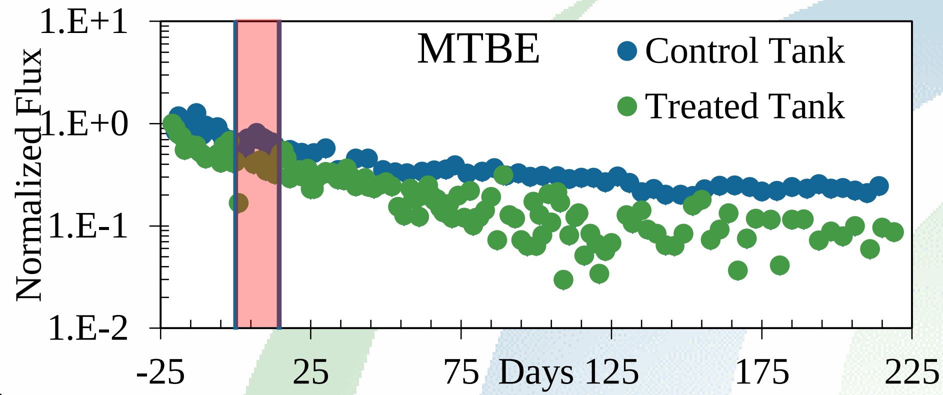
# Persulfate Treated Dissolved Source Tank

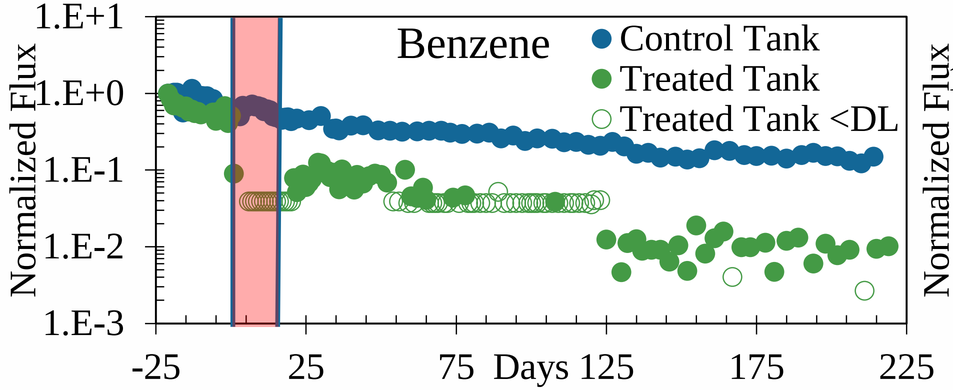


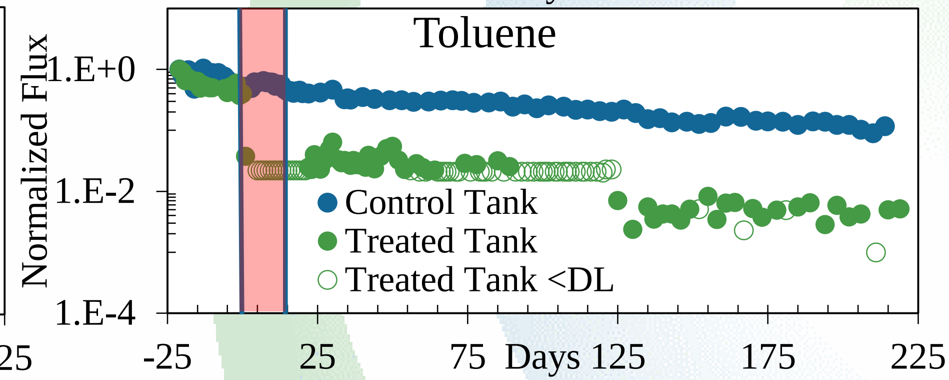

| | Control Tank | Experimental Tank |
|---|---|---|
| Higher K sand (cm/s) | $6x10^{-2}$ | |
| Lower K sand (cm/s) | $8x10^{-5}$ | |
| Velocity (ft./d) | 1.33 | |
| Pre treatment stage (d) | 239 | 26 |
| Treatment stage (d) | 0 | 14 |
| Post treatment stage (d) | 0 | 203 |
| $Na_2S_2O_8$ (g/L) | 0 | 100 |
| Baseline Source Dissolved Condition (mg/L) | | |
| MTBE | 37 | 41 |
| Benzene | 12 | 14 |
| Toluene | 20 | 26 |
| Ethylbenzene | 7 | 11 |
| P-Xylene | 7 | 8 |

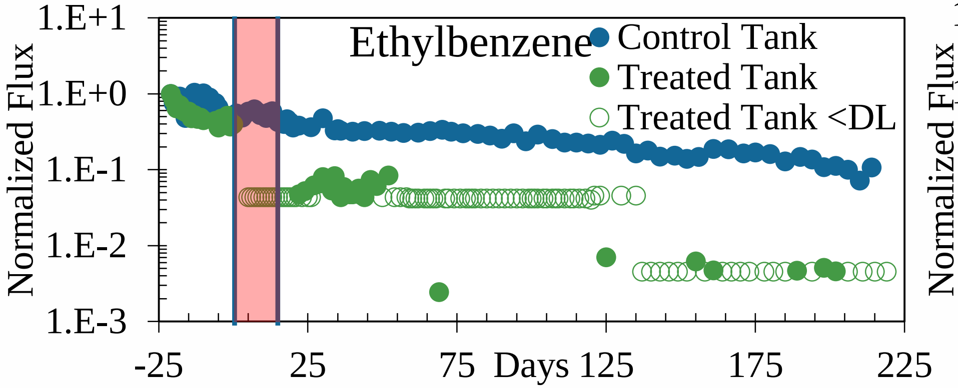
- Dissolved source mass ≈ 0.9 g

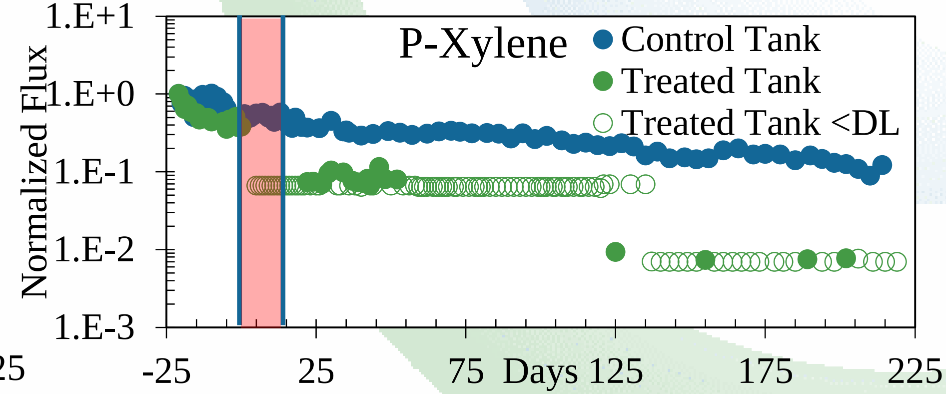
# Flux Reduction: Dissolved Source



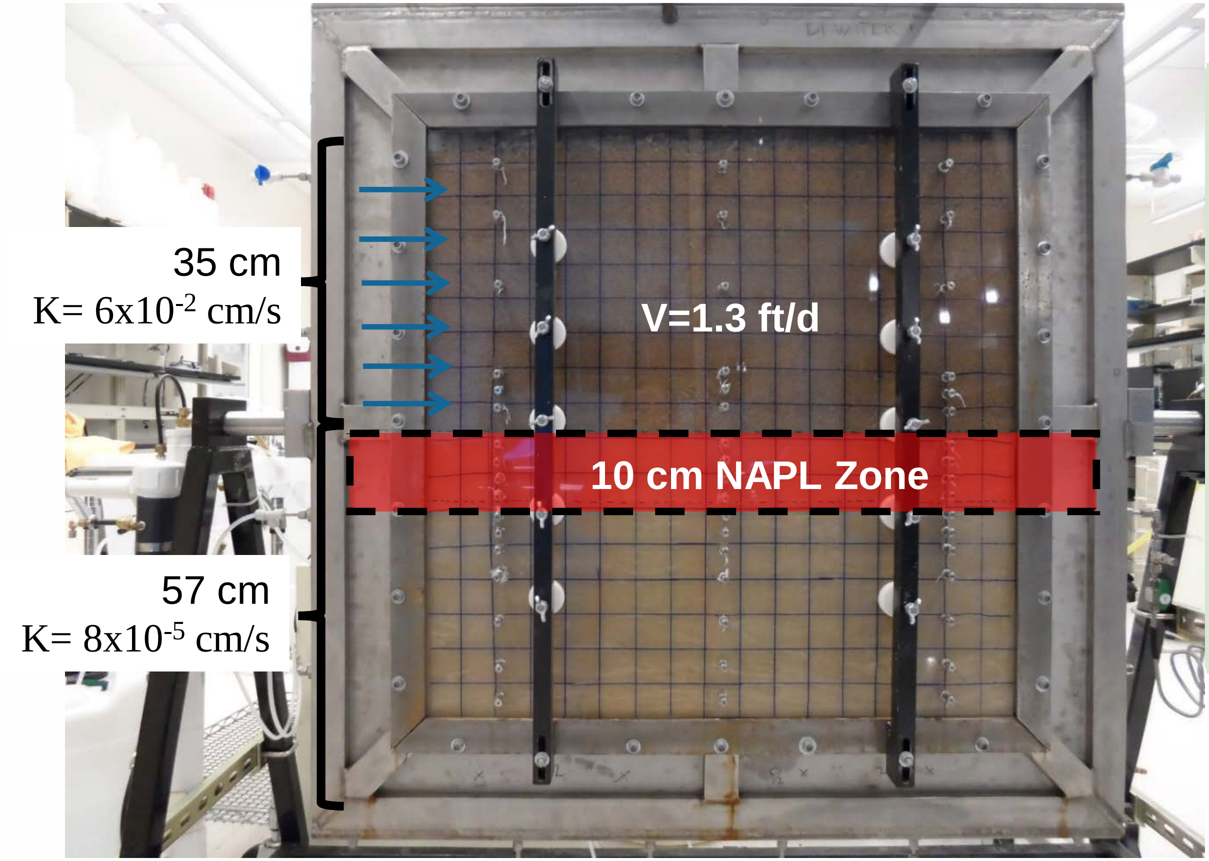




= Active treatment period

Normalized to -21 d (4 days from start of flow)

# Persulfate Treated LNAPL Source Tank

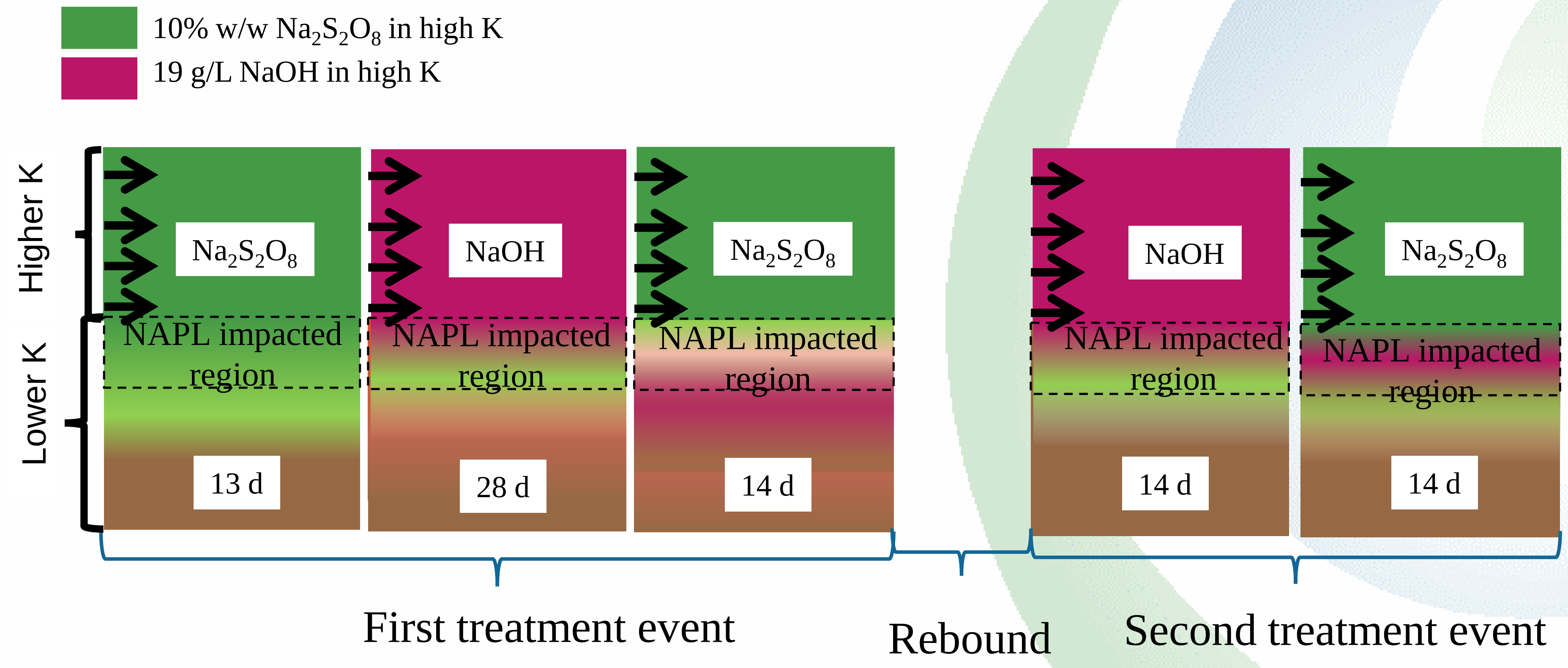



| Compounds | *NAPL Zone mg/kg-soil |
|---|---|
| Benzene | 98 |
| Toluene | 600 |
| Octane | 3800 |
| Ethylbenzene | 620 |
| P-Xylene | 640 |
| O-Xylene | 650 |
| n-Propyl | 570 |
| 1,3,5 TMB | 310 |
| Total | 7400 |

*Samples were collected from remaining sand after tank was packed

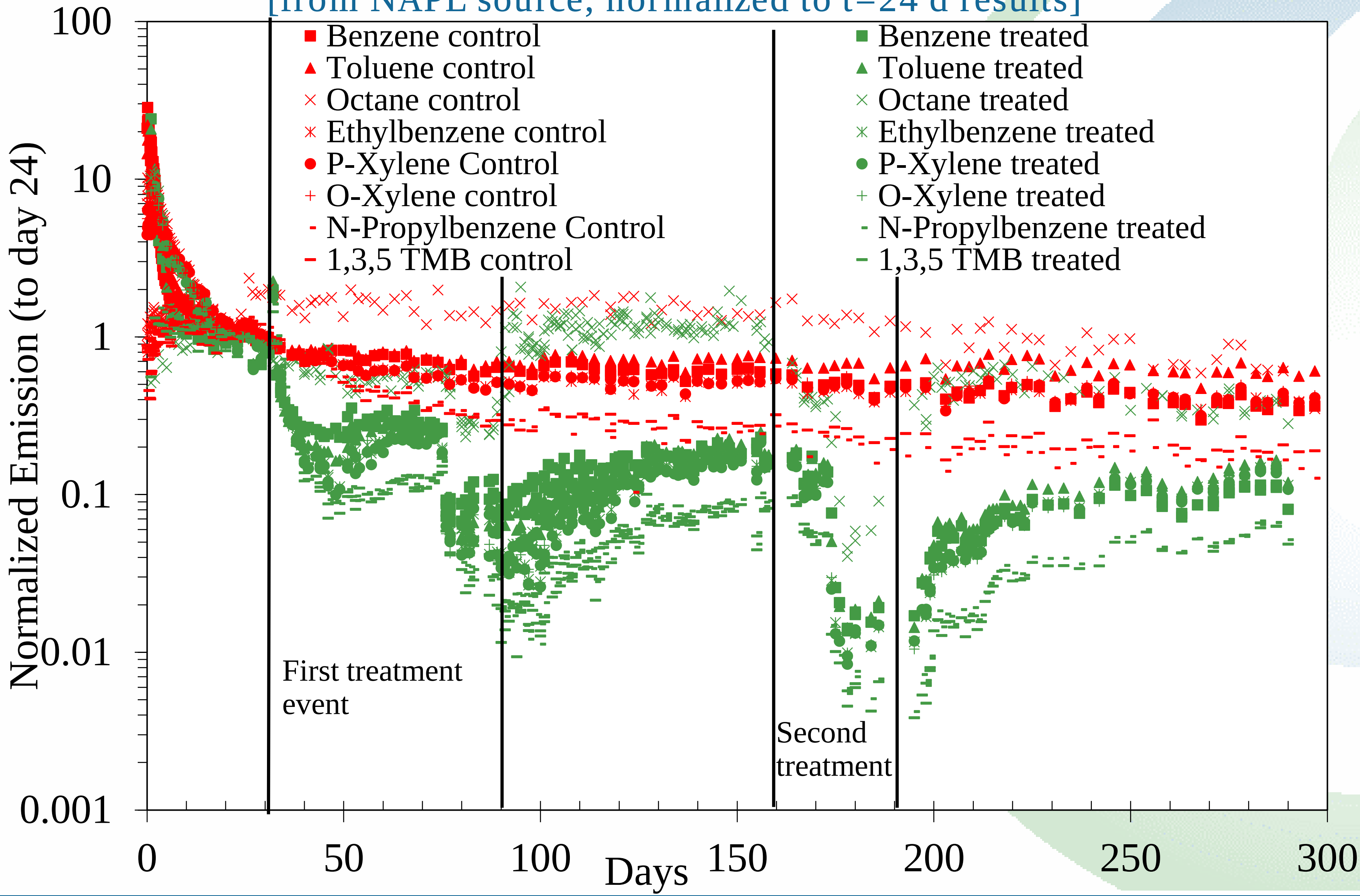
- ❑ LNAPL source mass ≈ 76-82 g

# Treatment Stages



# Normalized Dissolved Emissions

[from NAPL source; normalized to t=24 d results]



# Research Conclusions

## ❑ Dissolved Persulfate

- Long-term emission reduction of 63% for MTBE and 95-99% from a dissolved BTEX source
- Persulfate diffused 10 cm in 14 d (active treatment period) and ≥ 40 cm after 135 d

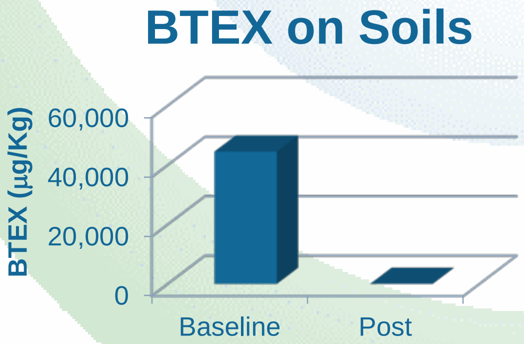
## ❑ NAPL Base Activated Persulfate

- Long-term emission reduction of 60-73% (except octane which was 14%)
- Persulfate diffused 4-18 cm during active treatment period

# Example ISCO Site: In Situ New York, NY

**Petroleum Hydrocarbons Treatment with ISCO**

- **Characterization of target BTEX, additional TPH in silty sands**
- **Treatability Study**
  - Tested multiple oxidants
  - Determined target and non target oxidant demand of soils
  - Alkaline activated persulfate selected
- **Six days of chemical injection**
  - Oxidant loading based on bench testing results
  - Approximately 70% pore space injection volume
- **Site closed by NYSDEC**
  - 92 to 95 % groundwater concentration reduction
  - > 99 % reduction of BTEX, DRO + GRO on soils

# Question:
# Do we use the right balance of Engineering and Certainty of Success ?

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