



# Optimizing In-situ Chemical Oxidation of Residual DNAPL: Geochemical Controls and Sediment Oxidant Demand

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# Towards effective source zone remediation

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# Borden DNAPL Infiltration (BDI) Site



50L DNAPL infiltration

8 April 1999  
DNAPL Day: 1



# 3D “Homogeneous” Aquifer

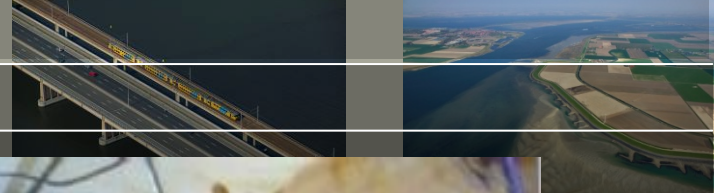
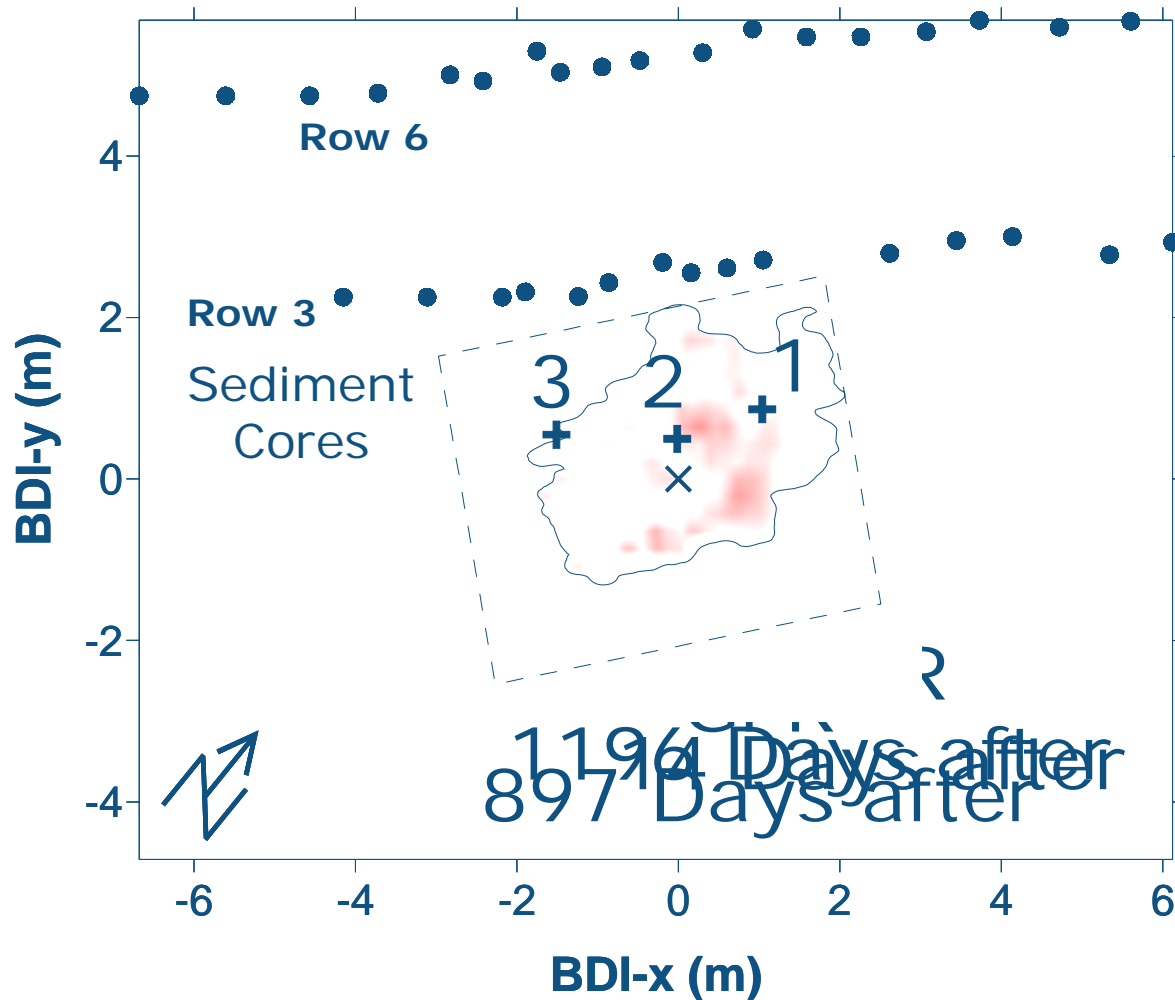


Figure 17: Photograph of the completed excavation showing the southeast, south, and west walls. A meter stick is resting vertically on the aquitard for scale. A 3.5" diameter outer steel core barrel is shown slightly left of the center of the photo.

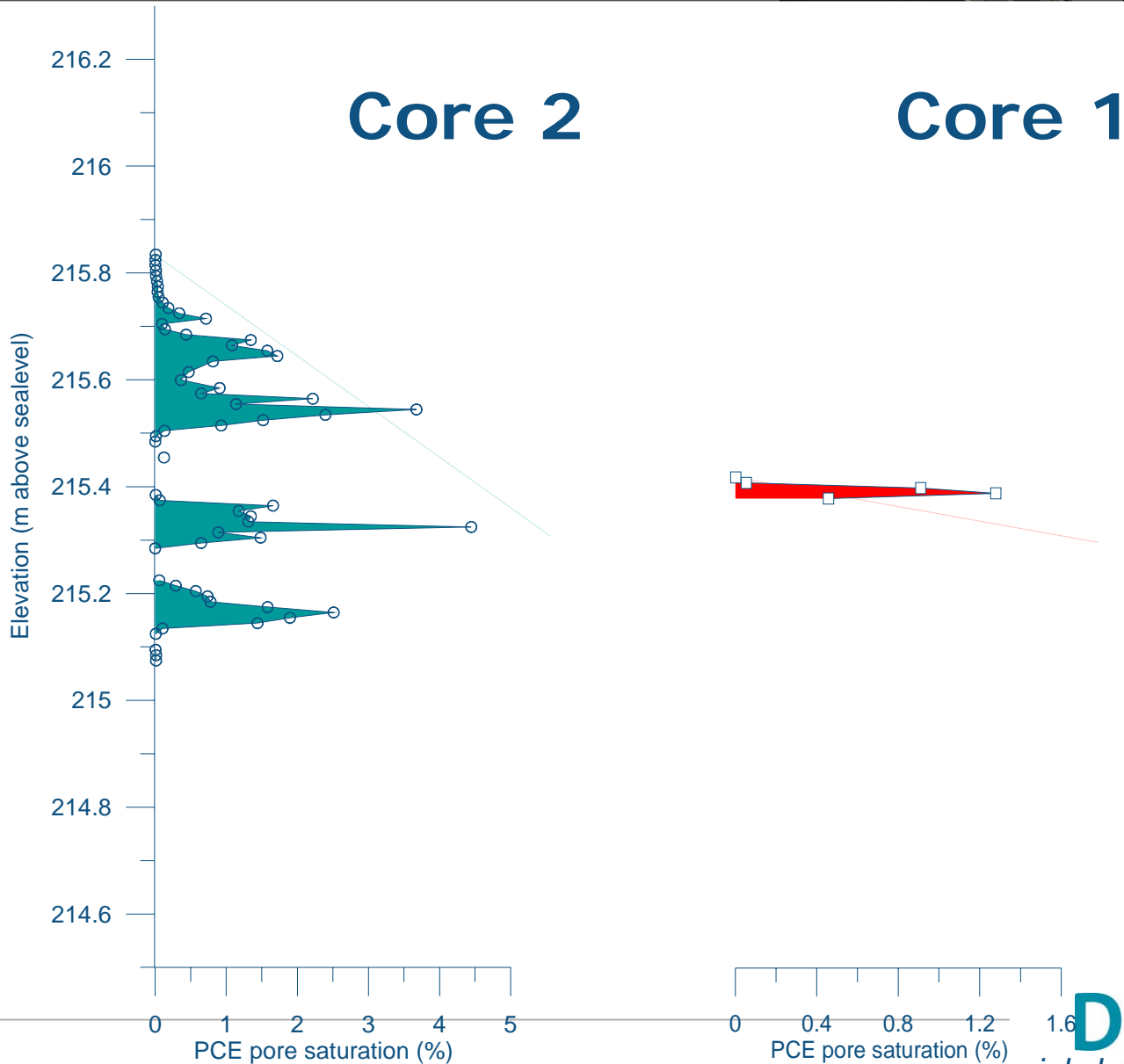
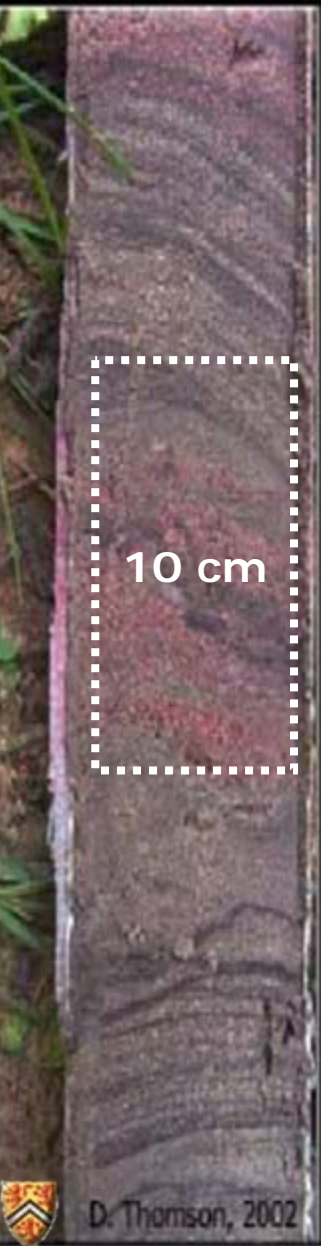
Photograph taken with an 18 mm lens. Photo by Sara Thomson, SWL.



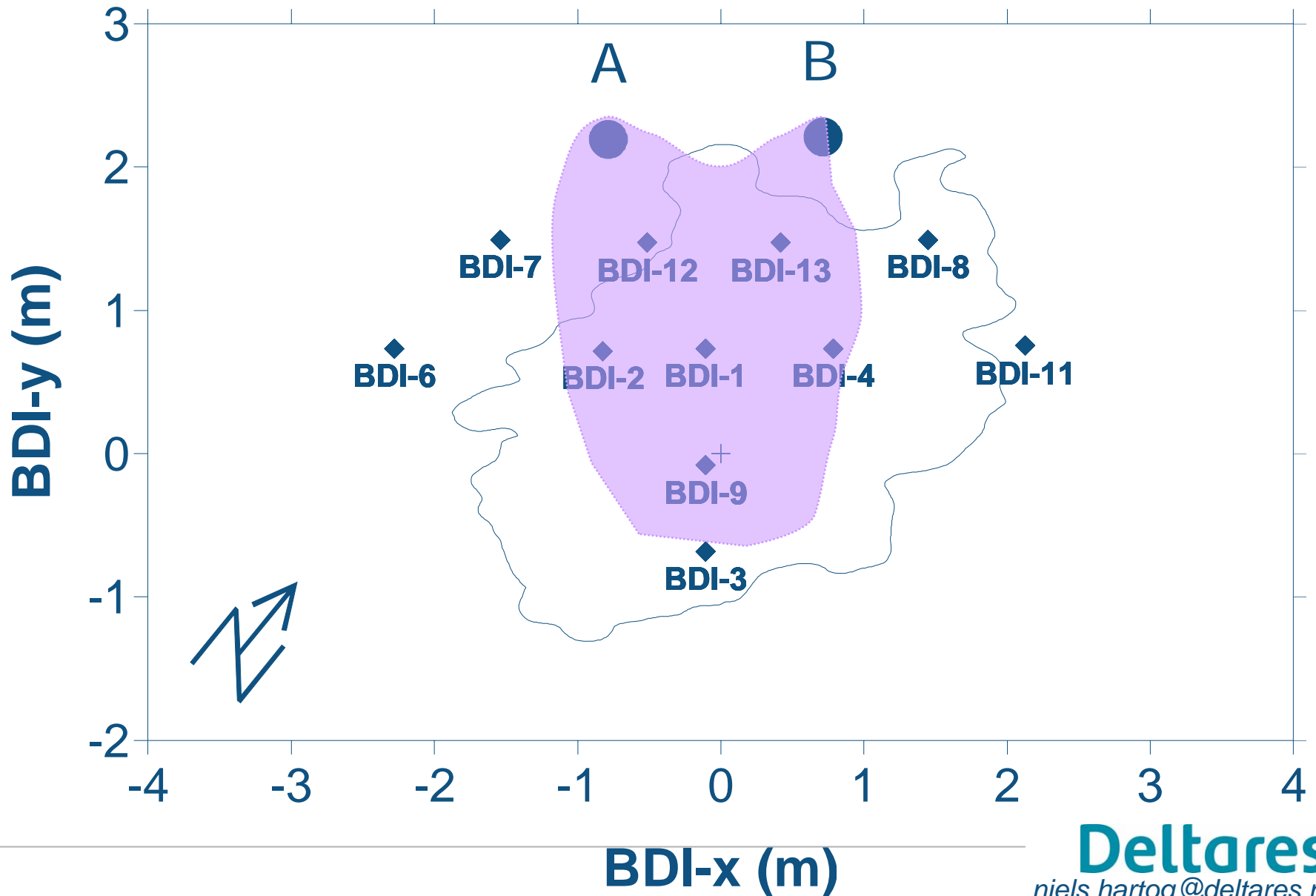
# Remaining Mass in Source Zone



# DNAPL pore saturation variability



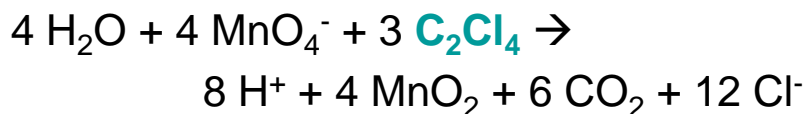
# Permanganate Injection Overview



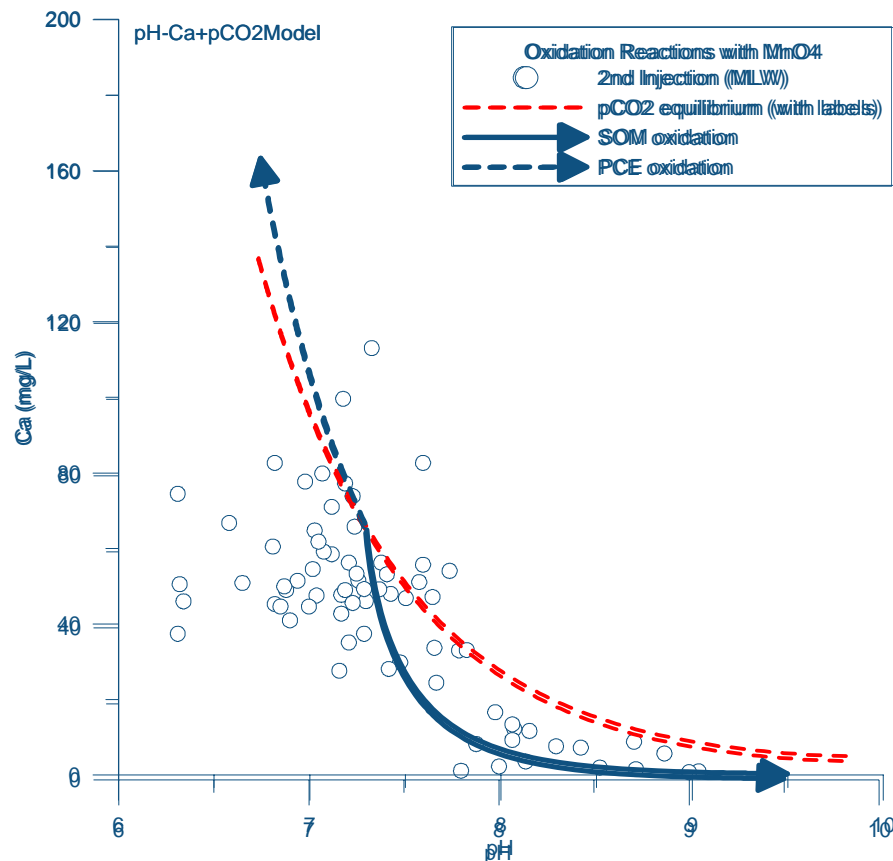
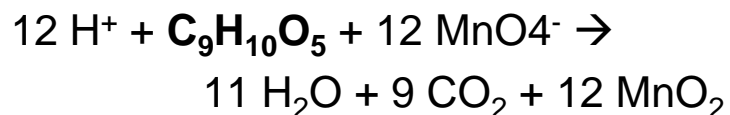
# Modeling Permanganate Oxidation Reactions (PHREEQC)

## Oxidation Reactions with MnO4

### PCE



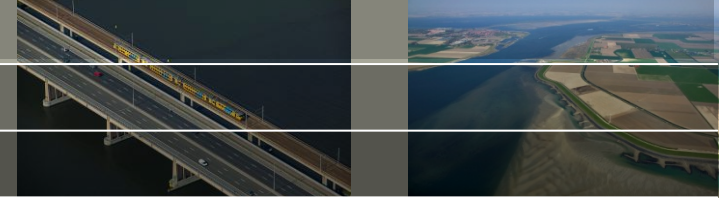
### SOM



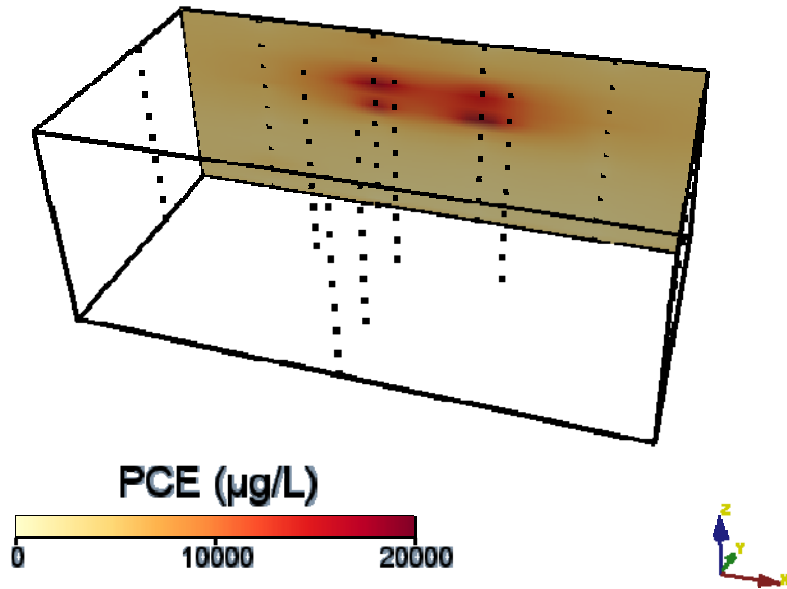
> 95% MnO4 consumed by sediment!



# PCE Concentrations in MLWs

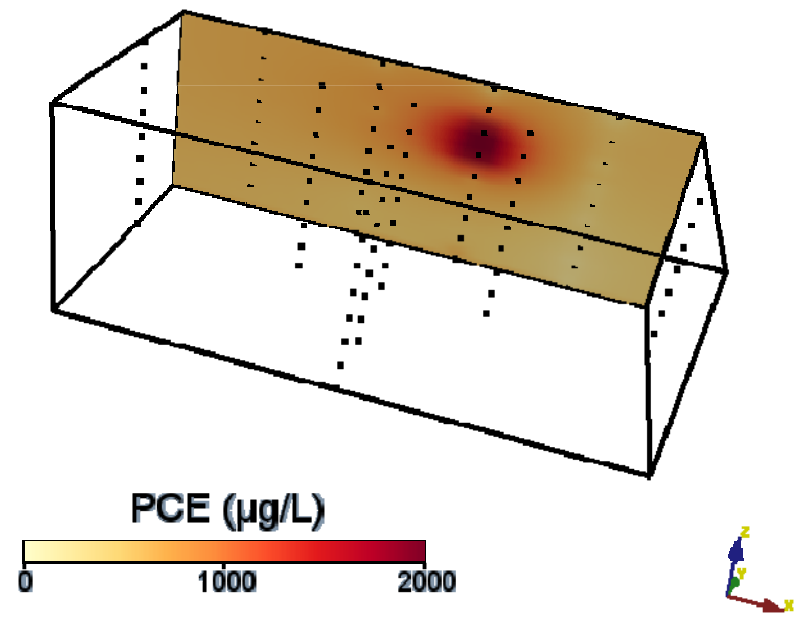


## Before 1<sup>st</sup> Injection



## After 1<sup>st</sup> Injection

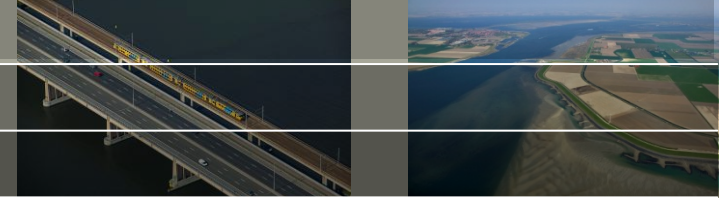
- Plume size reduction



- 10-fold reduction [PCE]
- 100-fold reduction PCE flux



# Canada ↔ The Netherlands



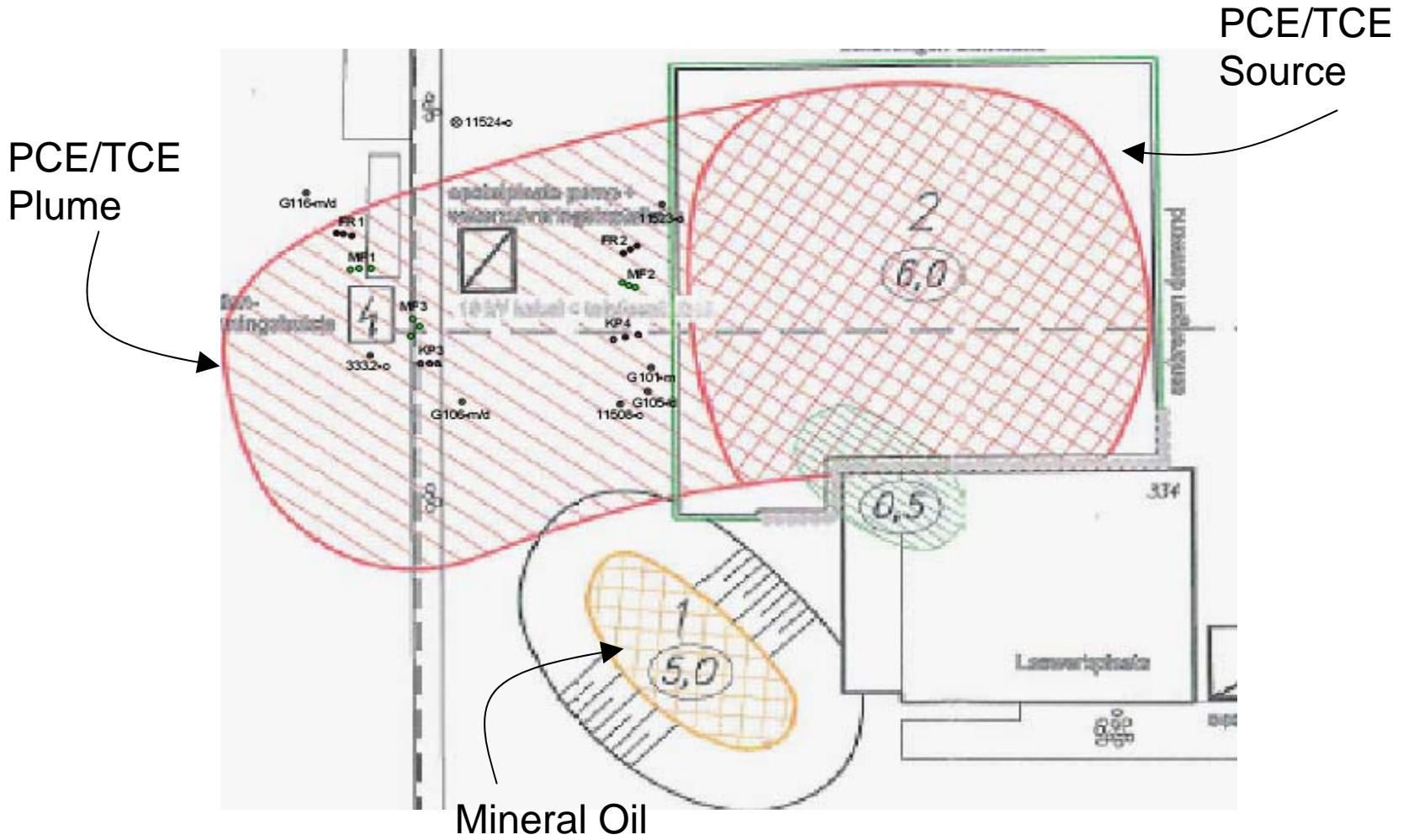
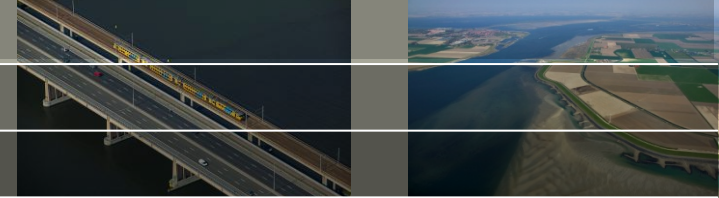
# Overview contaminated Sites in The Netherlands

<b>Site Characteristics</b>		<i>Occurrence (% of total)</i>
15,000 most urgent sites		
<b>Contaminant type (C)</b>	C.1 Chlorinated Hydrocarbons	45
	C.2 Aromatics/Oil/MTBE/Cyanide	45
	C.3 Other	10
<b>Geo-hydrology (G)</b>	G.1 Permeable (sandy)	45
	G.2 Layered, permeable and impermeable layers	45
	G.3 Other	10
<b>Built Environment (B)</b>	B.1 Urban	70
	B.2 Industrial	25
	B.3 Other	5

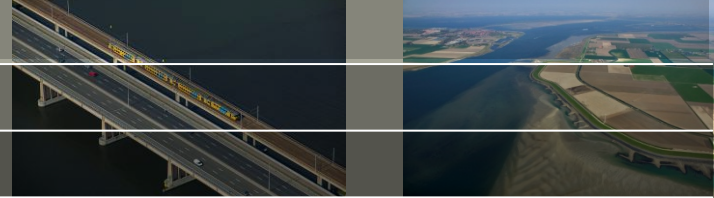
# Optimizing the ISCO remediation of Chlorinated Solvents



# Overview Contaminated Site



50% : 50%



Fenton's Reagents

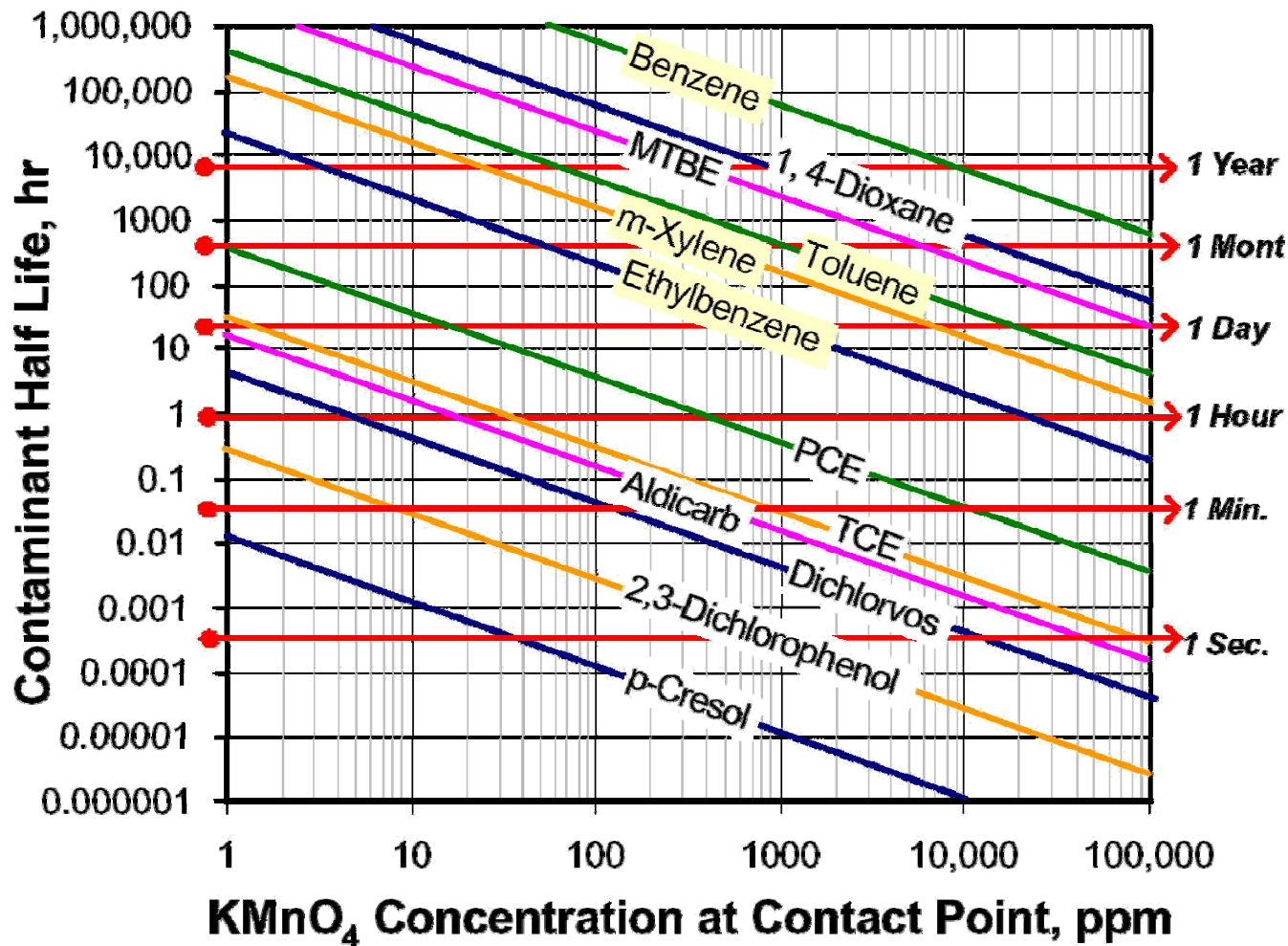


0.001MOL/L

0.1MOL/L

Permanganate

# Rates of contaminant oxidation with MnO<sub>4</sub>



Ref: Waldemer, R., Determination of the Rate of Contaminant Oxidations by Permanganate: Implications for In Situ Chemical Oxidation (ISCO), M.S. Thesis, Oregon

# Natural and Contaminant Oxidant Demand



## Factors:

### Contaminant Oxidant Demand

- Mass, Volume, Distribution

### Sediment Oxidant Demand (SOD, NOD)

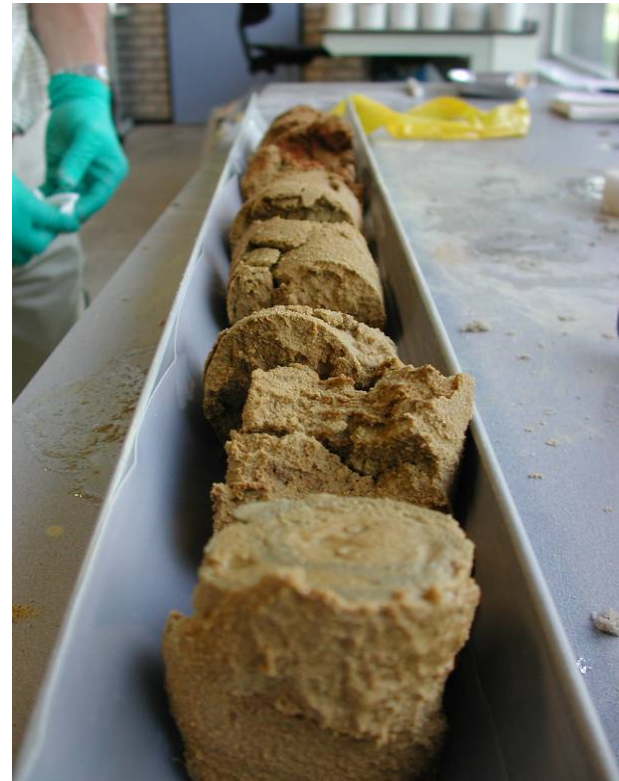
- Geochemistry, Heterogeneity

### Groundwater Oxidant Demand

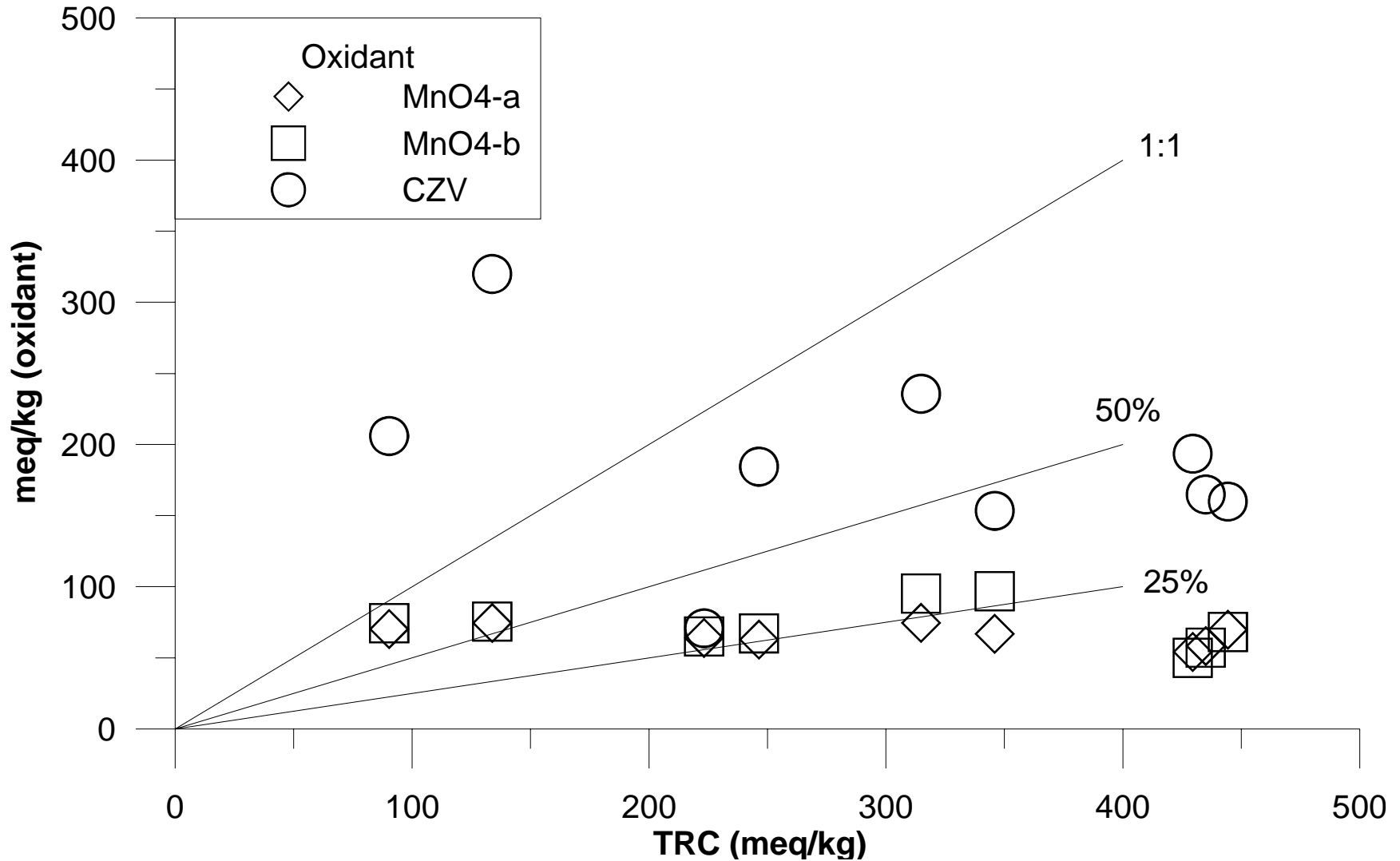
- Groundwater composition, Redox status, Groundwater flow



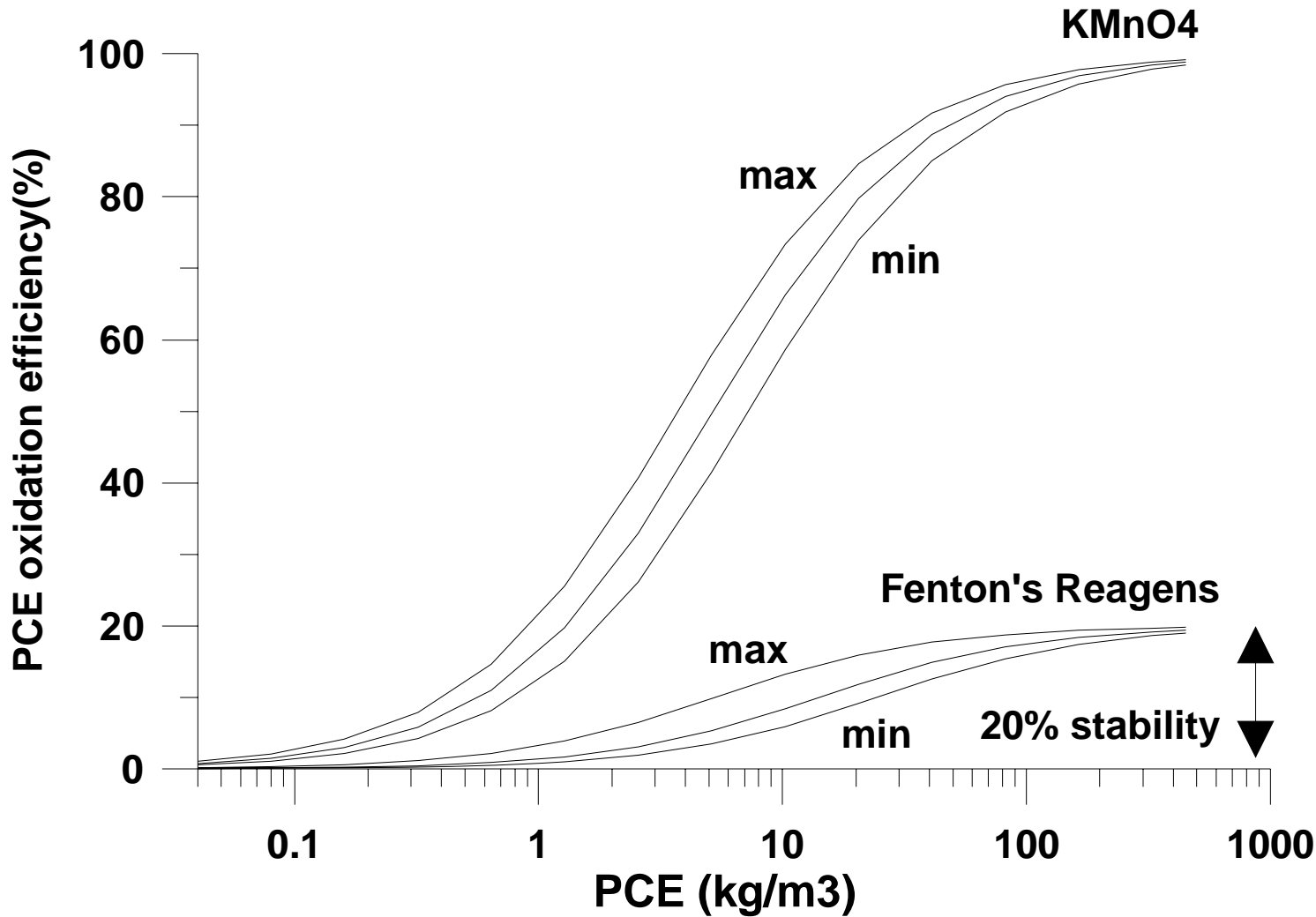
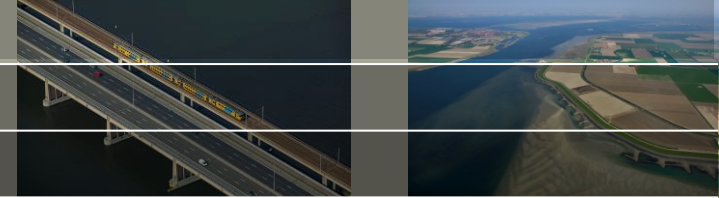
# Soil Samples for Geochemistry and Reactivity



# Total Reduction Capacity vs. Oxidant Demand



# Remediation Efficiency



# Assessment of critical parameters: simplified

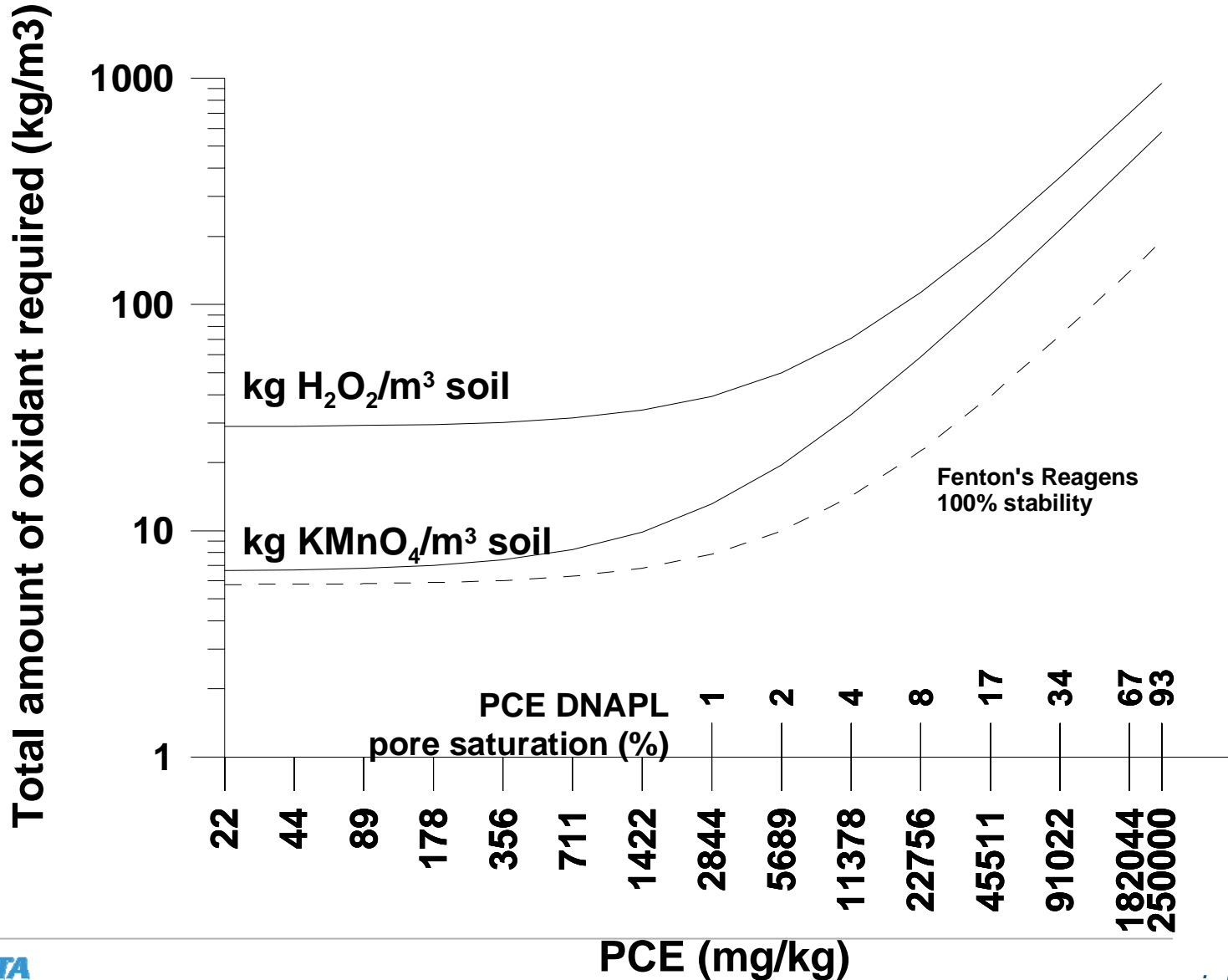
$$Oxidant_{req} = \left( \frac{Oxidant_{cont} + Oxidant_{NOD}}{Oxidant_{stab}} \right)$$

## Main Assumptions:

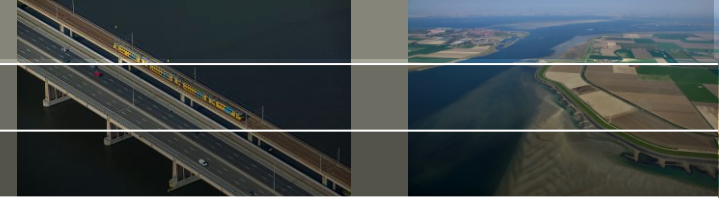
- Direct injection in NAPL zone, no travel
- Oxidant reacts with NOD first, no competition (worst case)
- Constant degree of decomposition

$$Oxidant_{eff} = \frac{Oxidant_{cont}}{\left( \frac{Oxidant_{cont} + Oxidant_{NOD}}{Oxidant_{stab}} \right)}$$

# Cost-effectiveness (kg/m<sup>3</sup> × €/kg)



# Conclusions



- Oxidant specific NOD tests should be performed, due to different reaction mechanisms for different oxidants used in ISCO.
- The influence of NOD on oxidation efficiency is especially important for lower contamination degrees.
- At higher contamination degrees, oxidant stability becomes the dominating factor for ISCO efficiency.
- Remedial ISCO strategies only be based on site-specific cost-effectiveness determinations.
- Source zone characterization crucial for cost-effective optimization of remediation strategy

# Videocone: Take a peak in the black box

