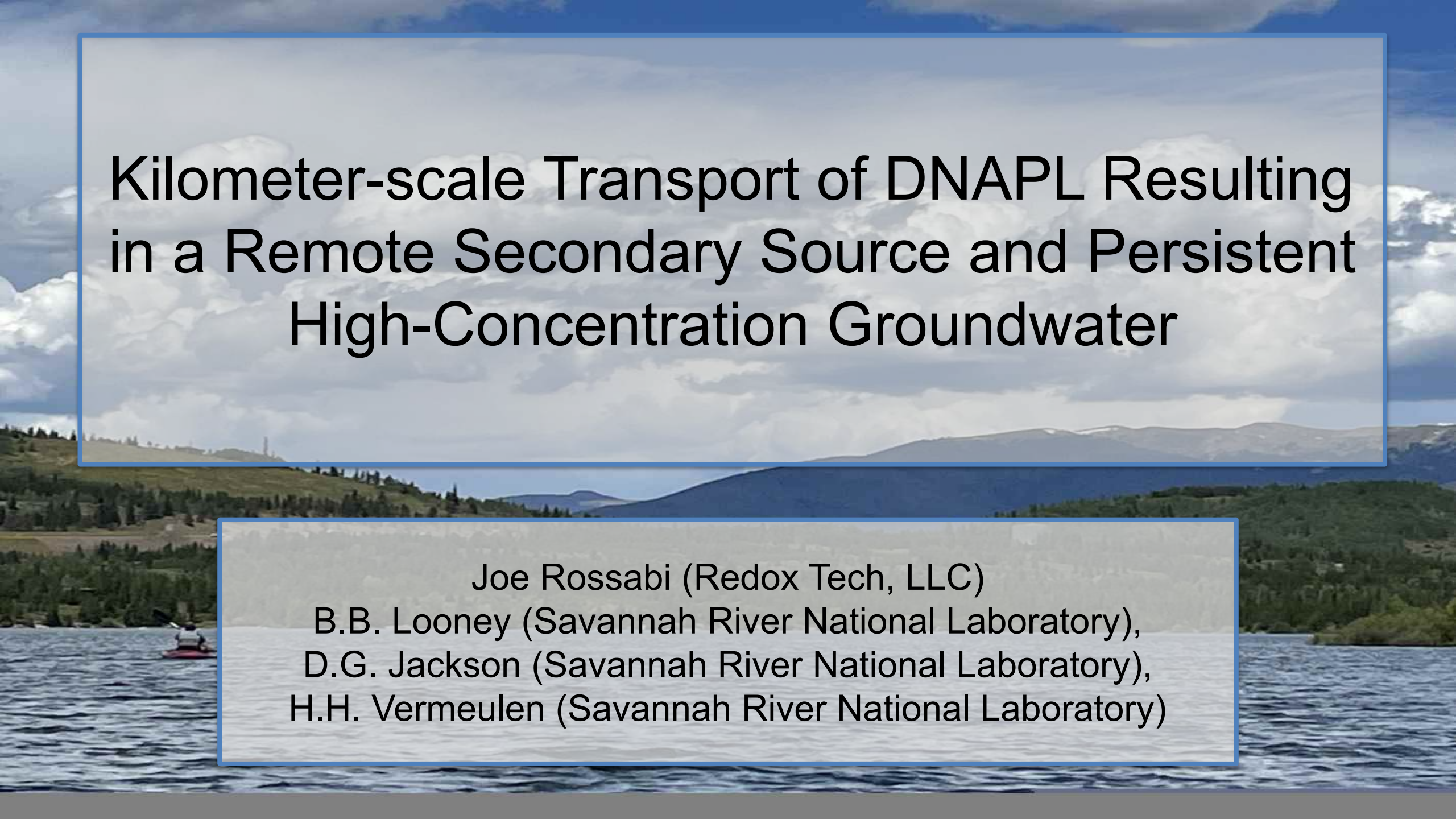


Kilometer-scale Transport of DNAPL Resulting in a Remote Secondary Source and Persistent High-Concentration Groundwater

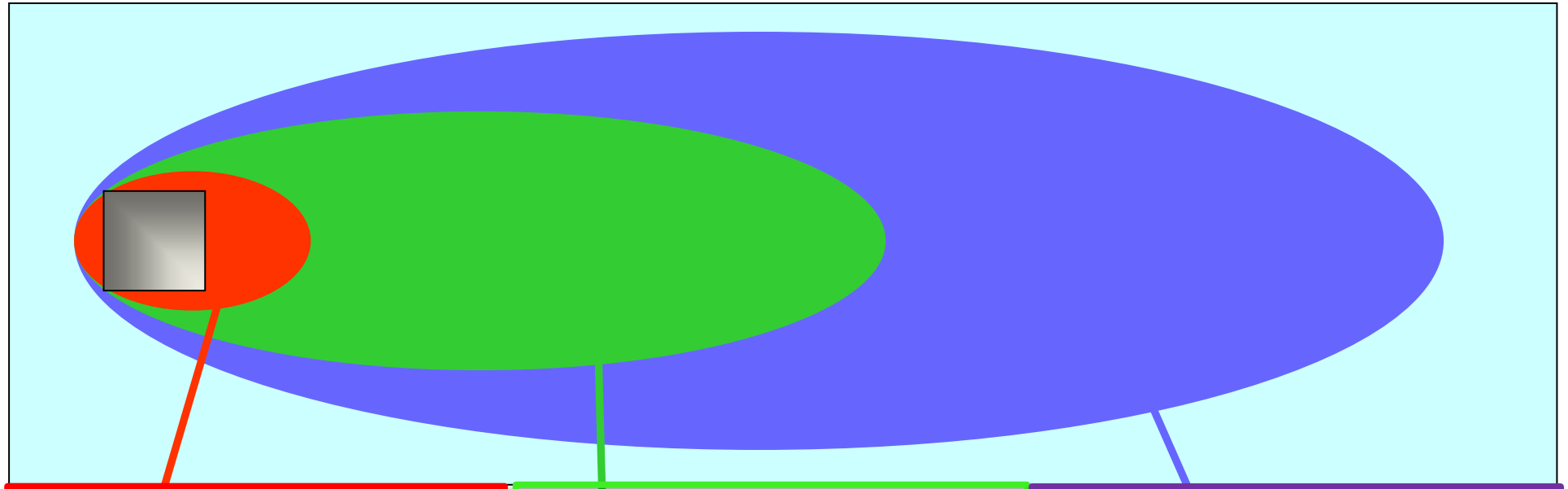
Joe Rossabi (Redox Tech, LLC)
B.B. Looney (Savannah River National Laboratory),
D.G. Jackson (Savannah River National Laboratory),
H.H. Vermeulen (Savannah River National Laboratory)

Basic Overview: DNAPL is confirmed far from source release area

- Conceptual Models of DNAPL and Persistent Contamination
- Non Unique Solutions
- ISCO testing in Western Sector
- Positive Identification of Remote DNAPL
- Apparent Oxidant Threshold for Destruction
- Conclusions

Environmental Contamination Conceptual Model

ca. 1992



Source Zone

Characteristics:

High Conc./NAPL;

Significantly perturbed

Need:

Aggressive technologies to limit long term damage

Primary GW/Vadose Zone Plume

Characteristics:

Moderate to high aqueous/vapor phase concentrations

Need:

Presumptive baseline or moderately aggressive alternatives

Dilute Plume/Fringe

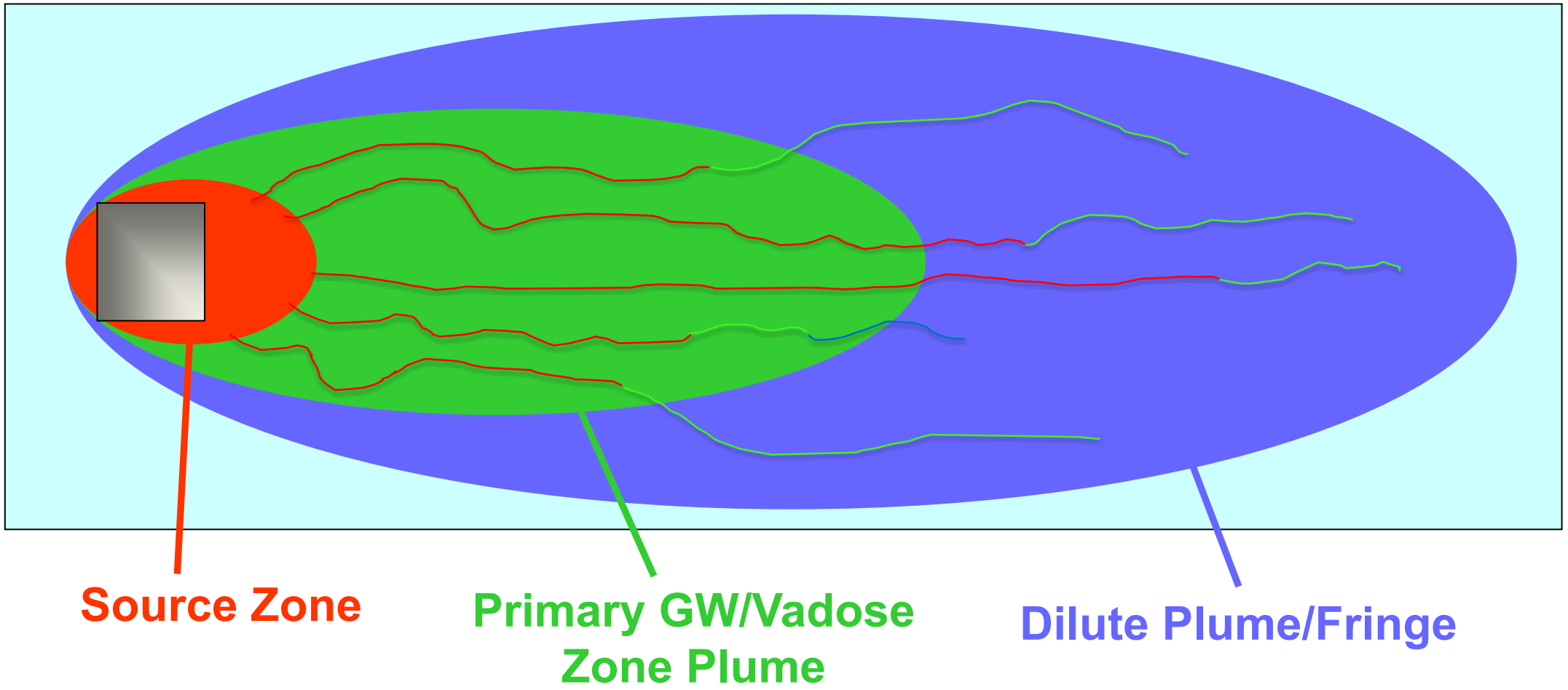
Characteristics:

Low aqueous/vapor phase concentrations

Need:

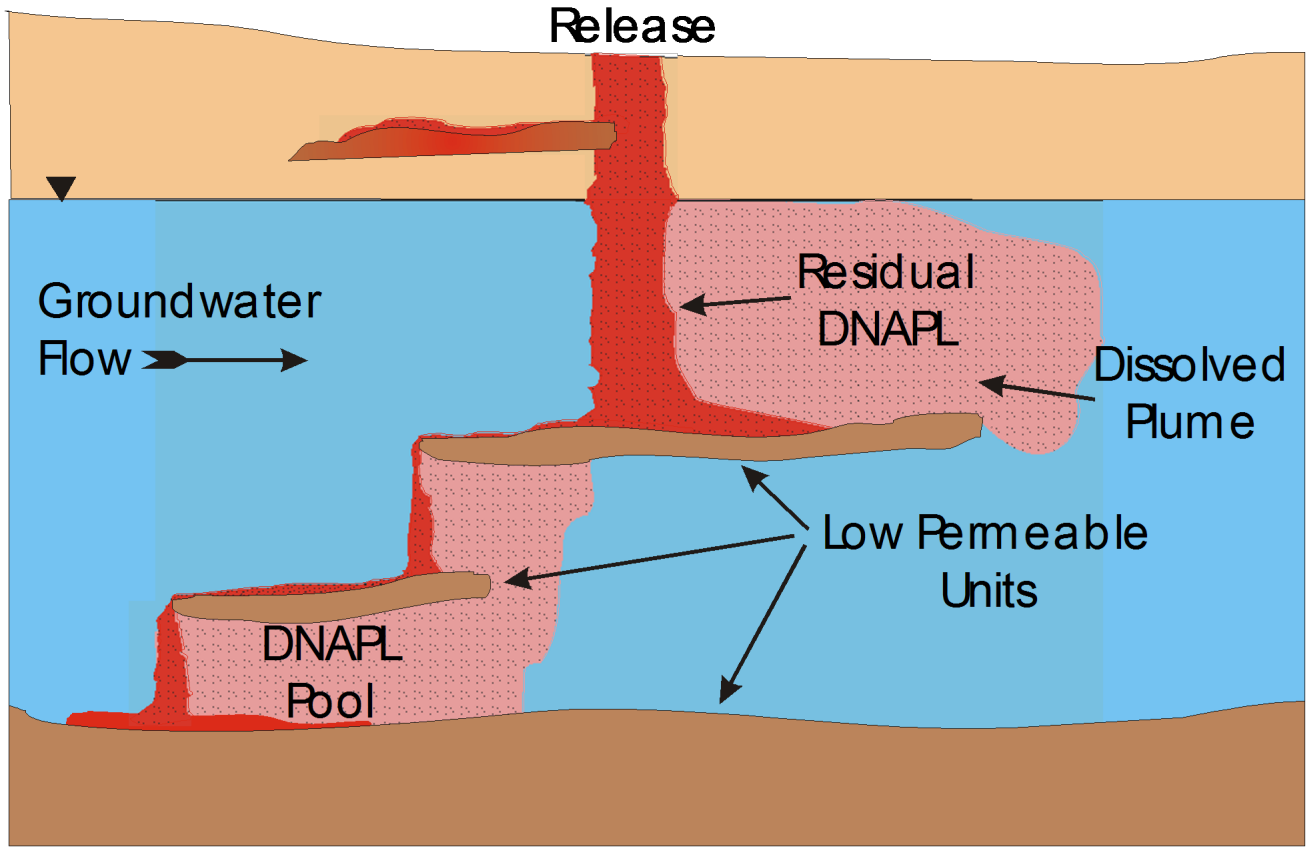
Innovative technologies - sustainable low energy concepts

Blood Shot Ovals



Different zones in actual sites are not neatly separated

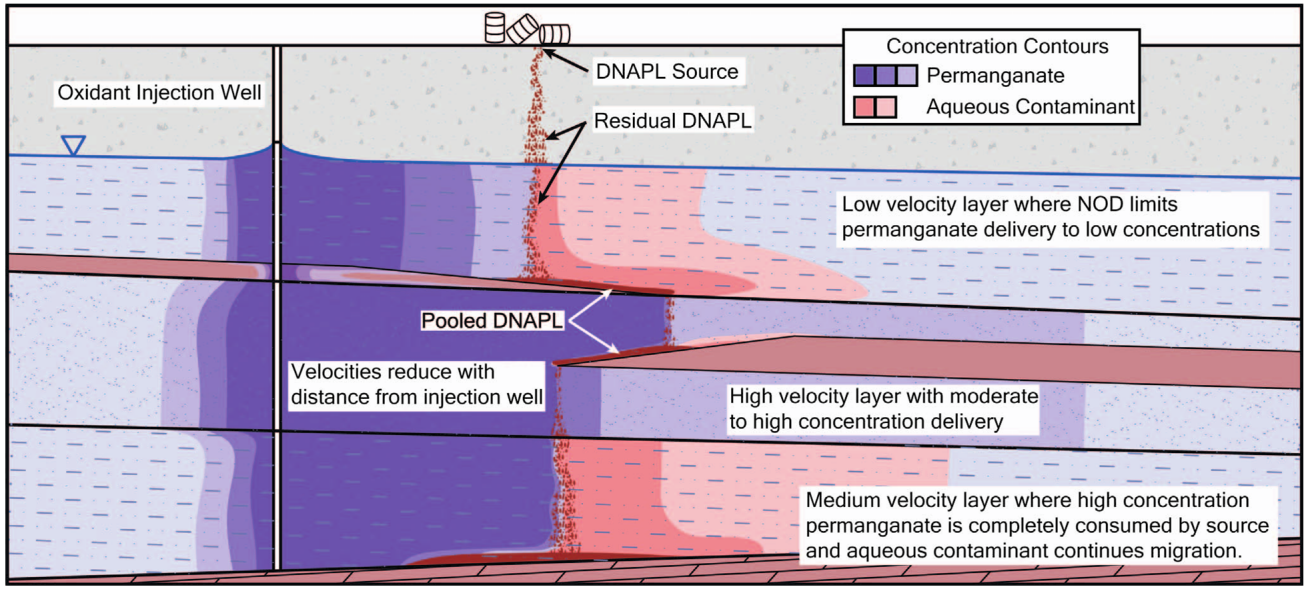
DNAPL Release Scenario

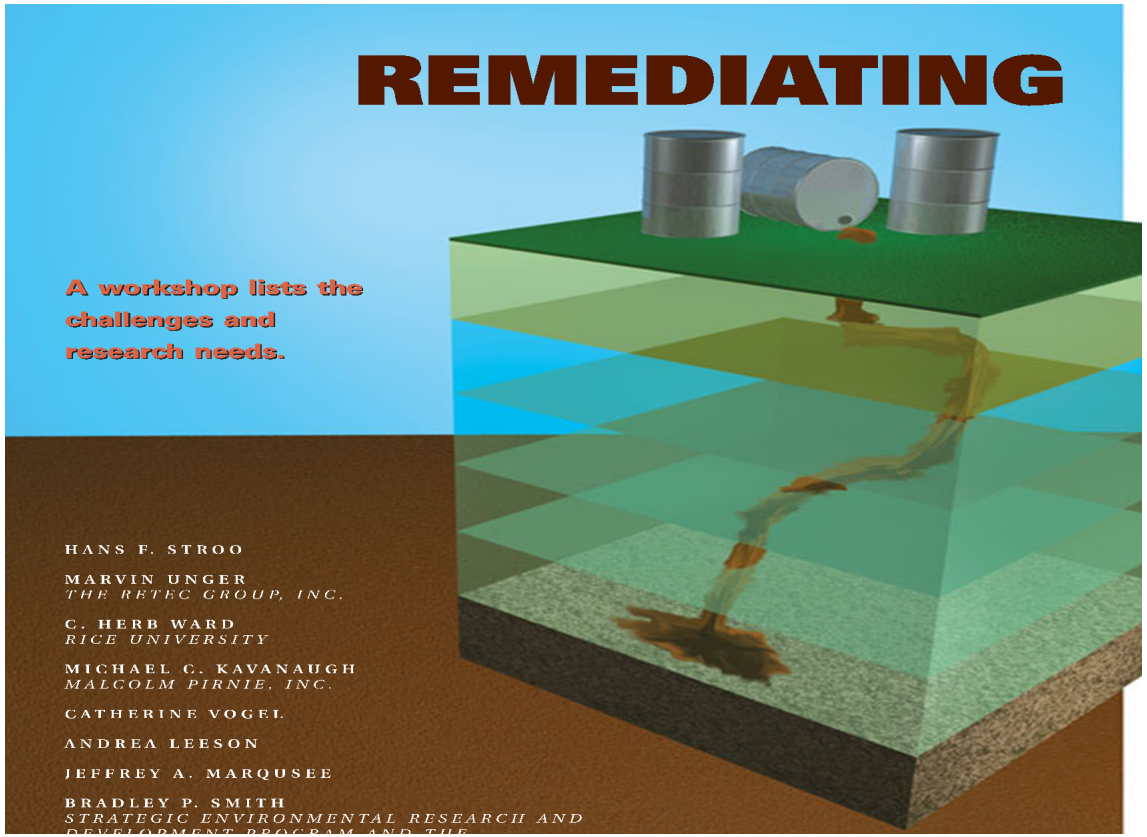


Conceptual Models of Transport

DNAPL mostly descends and pools, then dissolves.

Stays close to the release area!



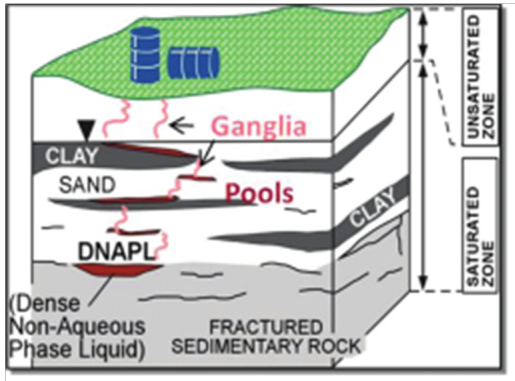


Stroo et al ES&T 2003

Petri et al, JEE 2008

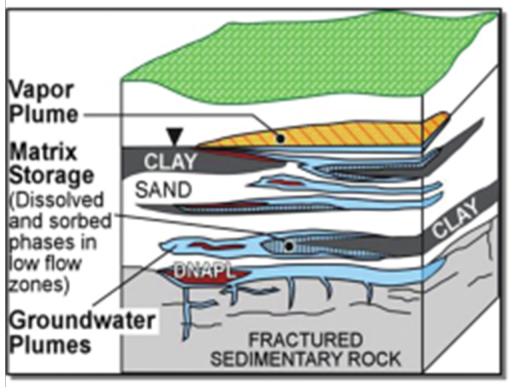
Conceptual Models of Persistence

Back diffusion explains everything?



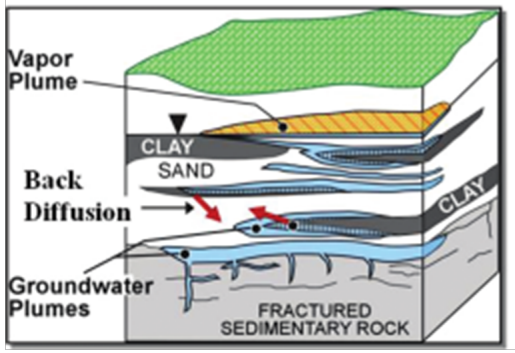
EARLY SOURCES

Relatively low Pool Fraction
Ganglia prevalent, pools at interfaces
Nascent vapor / groundwater plumes
Little matrix diffusion
VOCs in DNAPL and sorbed phases
VOCs primarily in transmissive zones



MATURE SOURCES

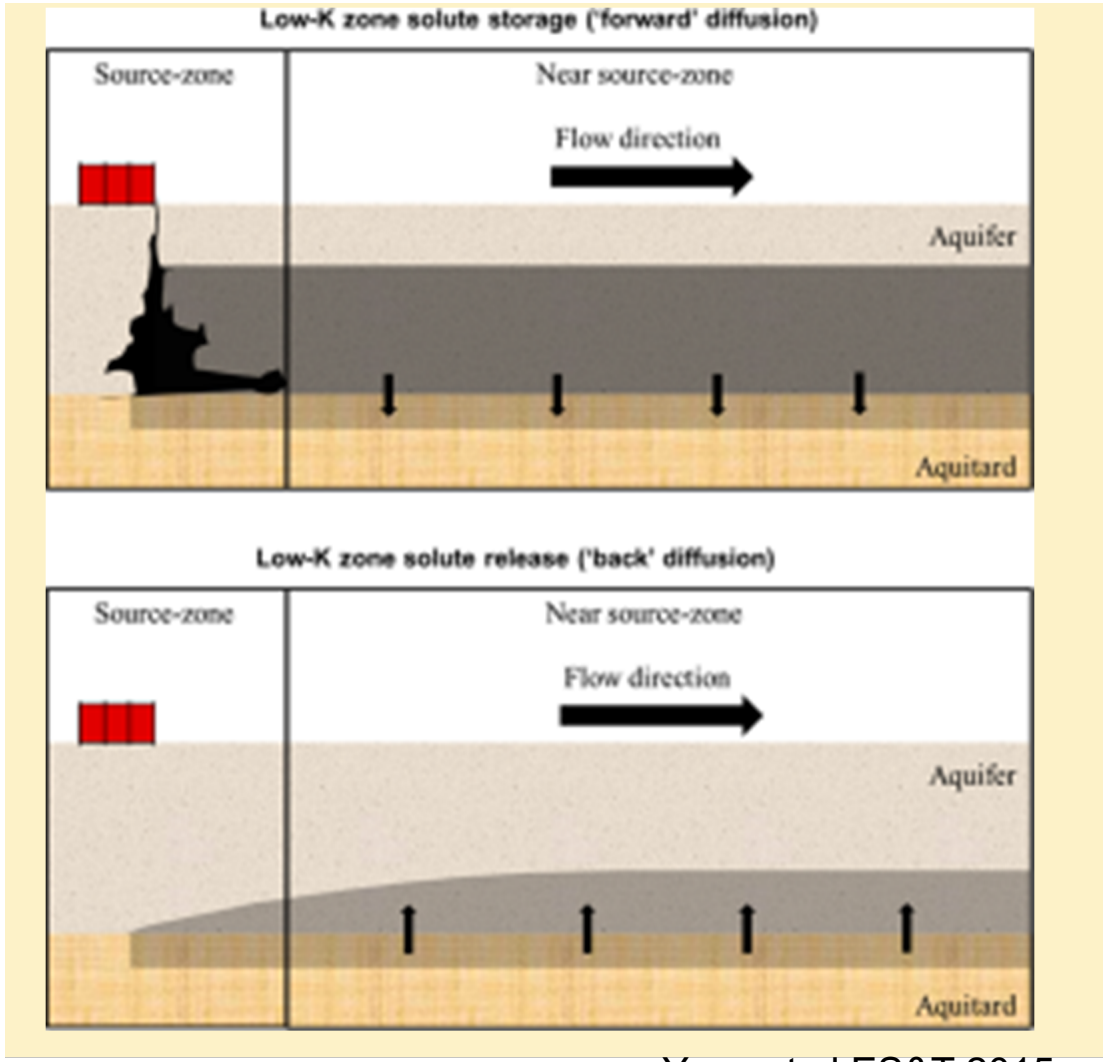
Pool Fraction increases
Ganglia preferentially depleted
Pools partly depleted, leaving ganglia
Mass discharge plateaus
Matrix diffusion in source and plume



AGED/TREATED SOURCES

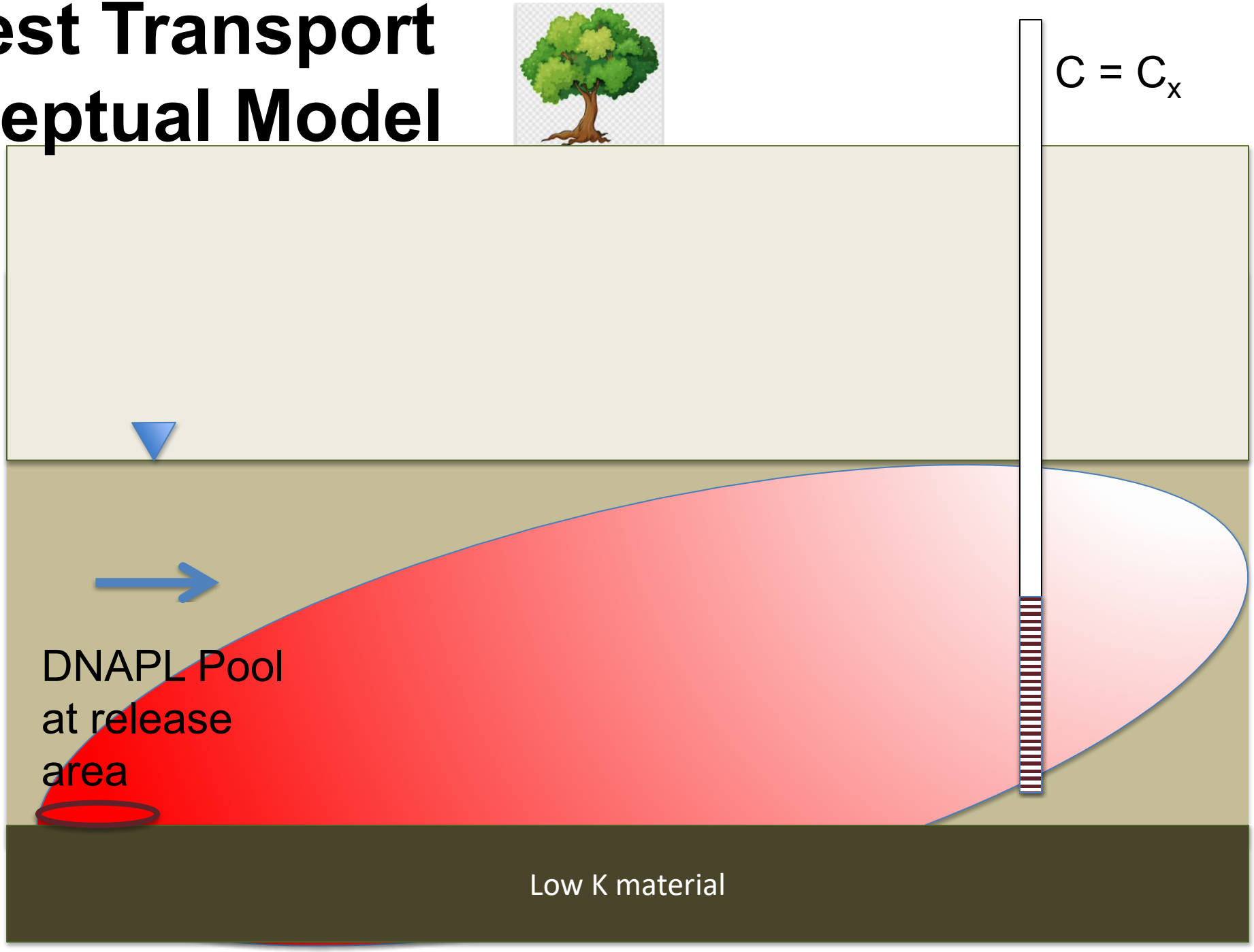
Little to no DNAPL remains
Mass discharge greatly reduced
Low VOCs in transmissive zones
Back diffusion / desorption continue

Stroo et al ES&T 2012



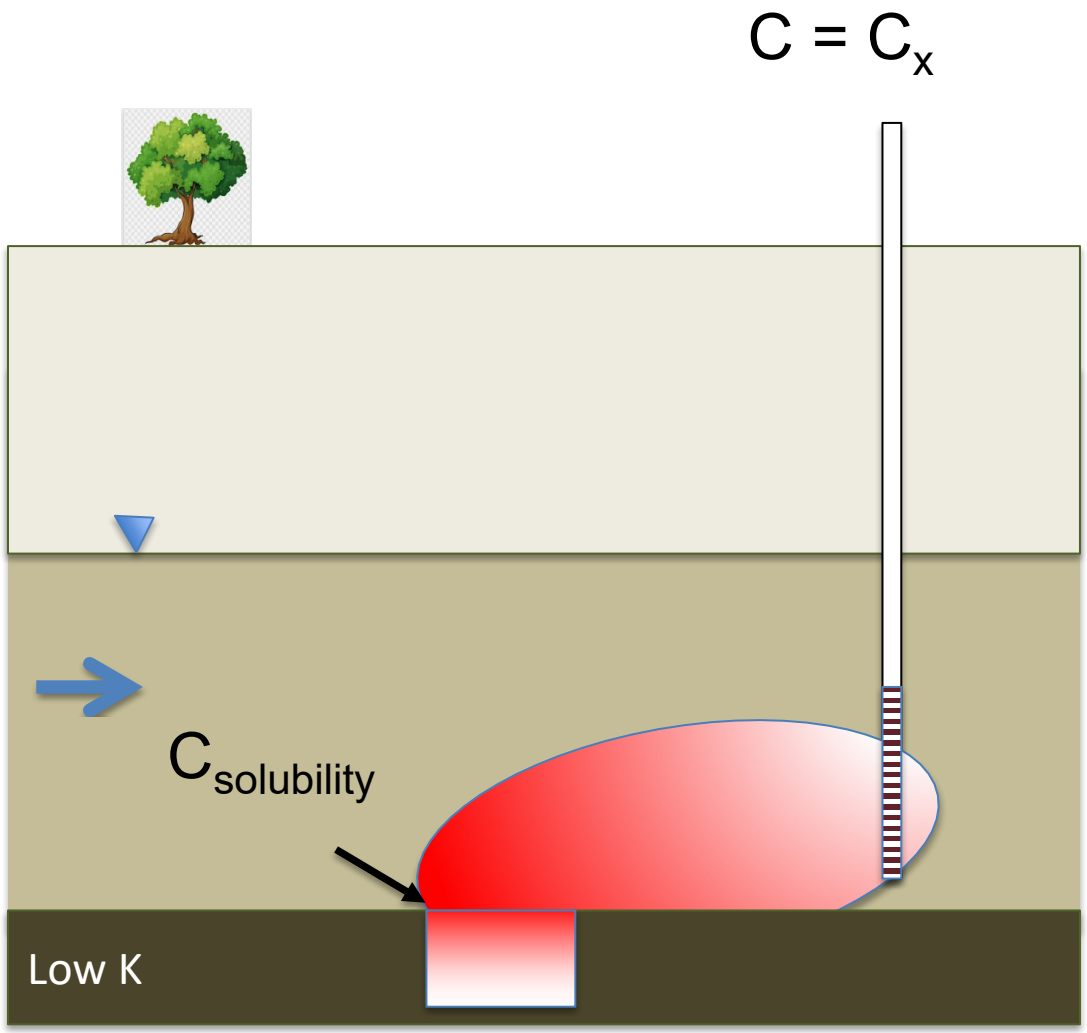
Yang et al ES&T 2015

Earliest Transport Conceptual Model

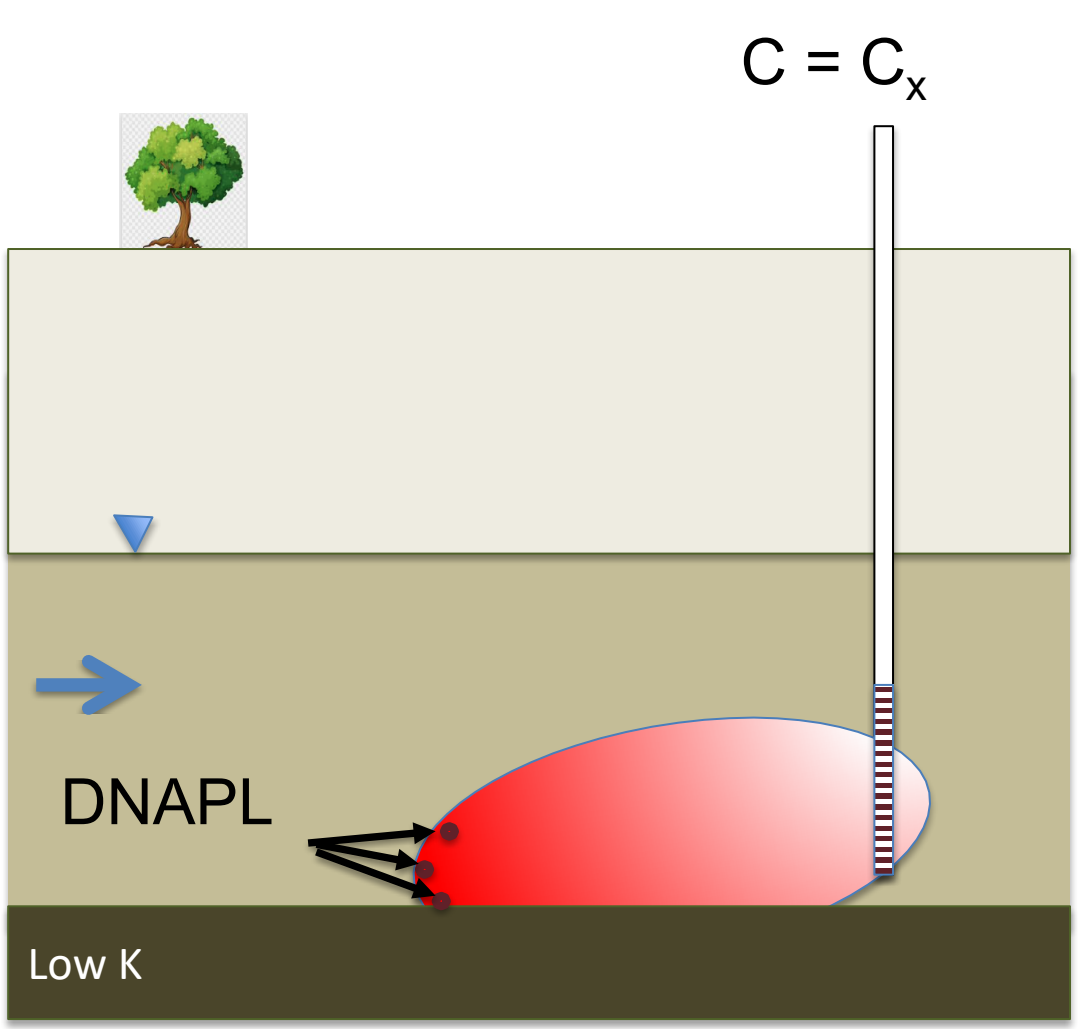


Non-unique

Back Diffusion



DNAPL



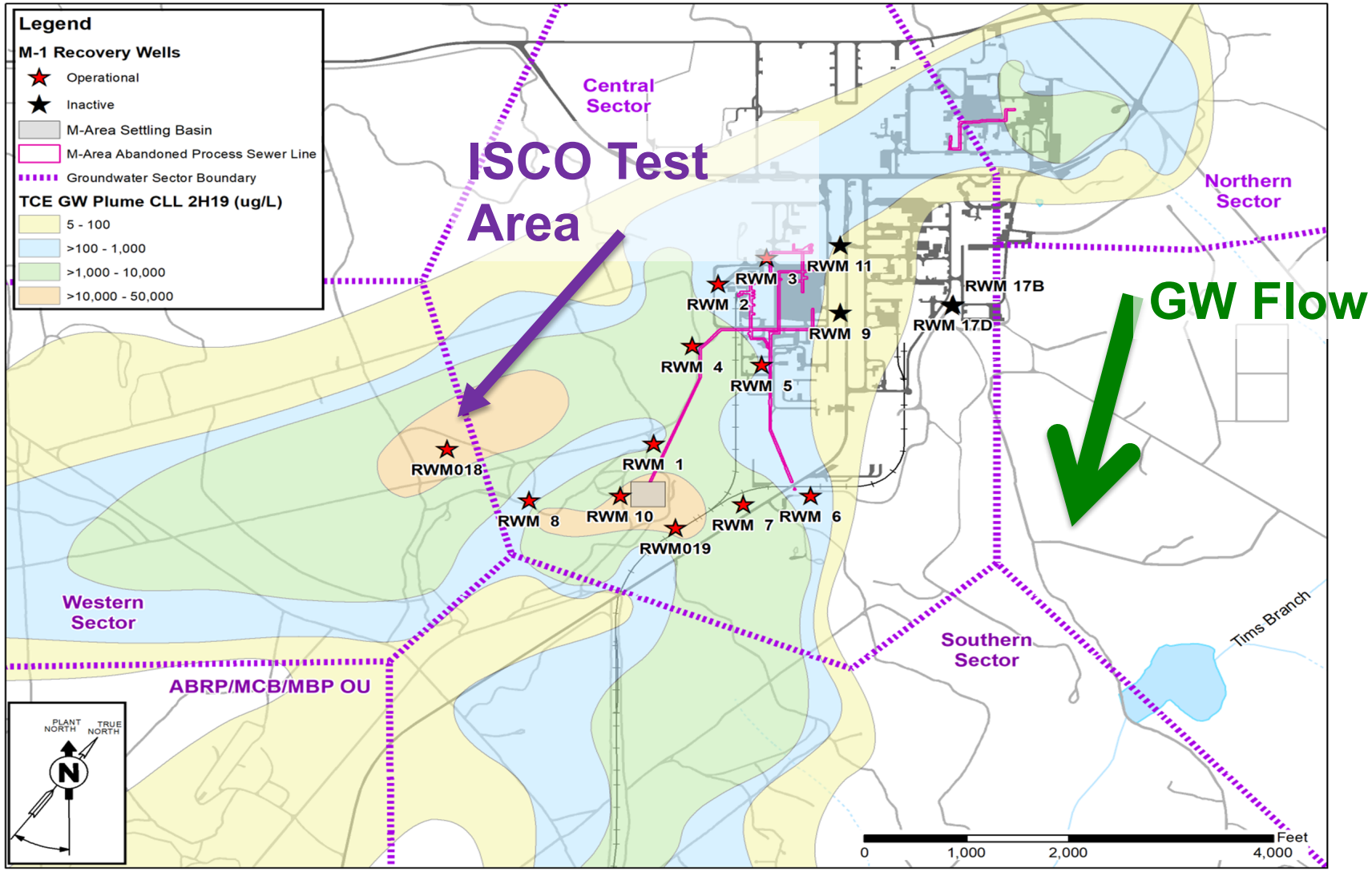
Non-Unique Solutions

- Concentrations in a well can be created by different source scenarios
- Persistence determined by loading of diffusion source or mass of DNAPL
- Architecture of DNAPL source and loading/unloading of diffusion source is complicated
- Groundwater flow and heterogeneity further complicate things

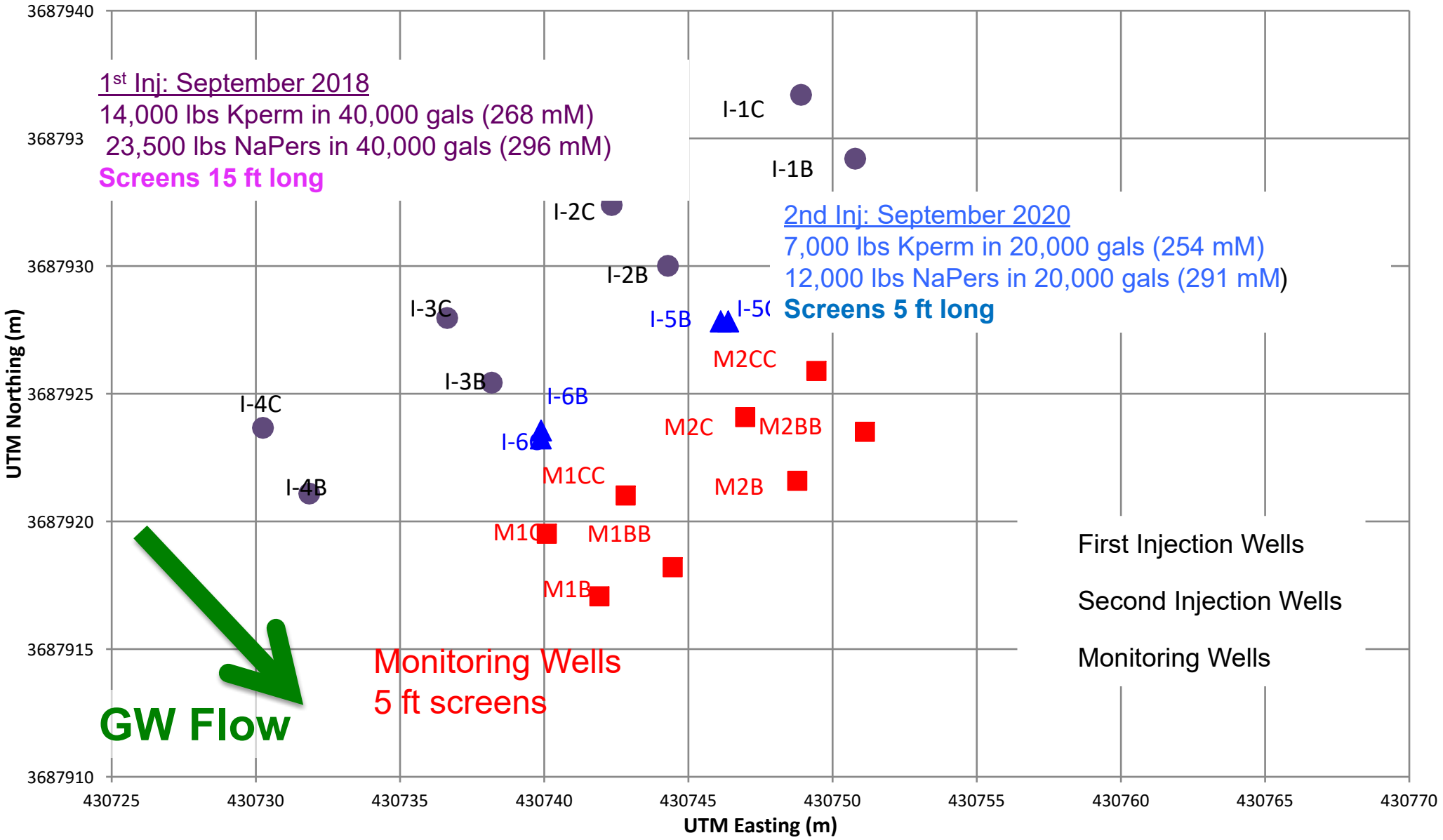
DNAPL vs Diffusion

- Per unit surface area, 1000x more mass.
- Per unit surface area, dissolution is faster.
- Cannot be formed from aqueous phase without distillation
- **Got to those places by advection in different flow conditions, therefore can be accessed by advection**

A/M-Area VOC Plume Map with Recovery Wells



Oxidants injected in 2 ISCO Events

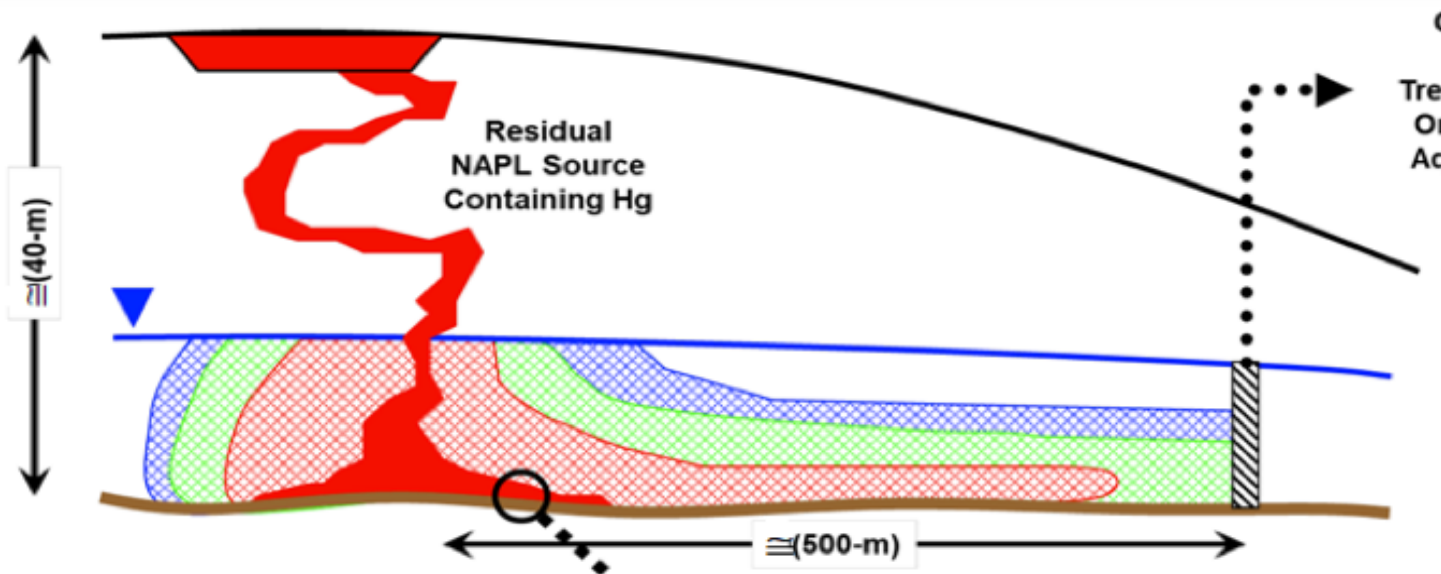


Bailed DNAPL found in one of > 500 wells (3.5 million lbs released in this area)

Notice the rich amber color…

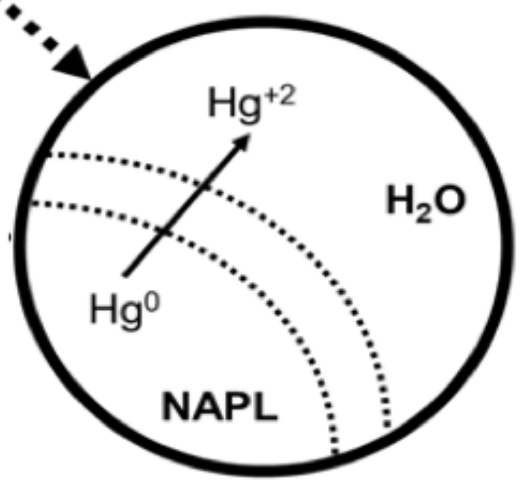
…but aren't PCE and TCE clear?

Elemental Hg is transported in DNAPL



Hypothesis:

- Hg^0 from SRS M Area processes partitions into TCE/PCE - total mercury in SRS DNAPL ≅ 656 µg/L
- Co-disposed Hg^0 penetrates to depth with DNAPL as transport vector
- Hg^0 oxidation at DNAPL:water interface under bulk aerobic geochemical conditions
- Relatively mobile complexes of oxidized ionic Hg (e.g., $HgCl_2^0$) are formed
- Mobile complexes are collected in water via monitoring and remediation wells

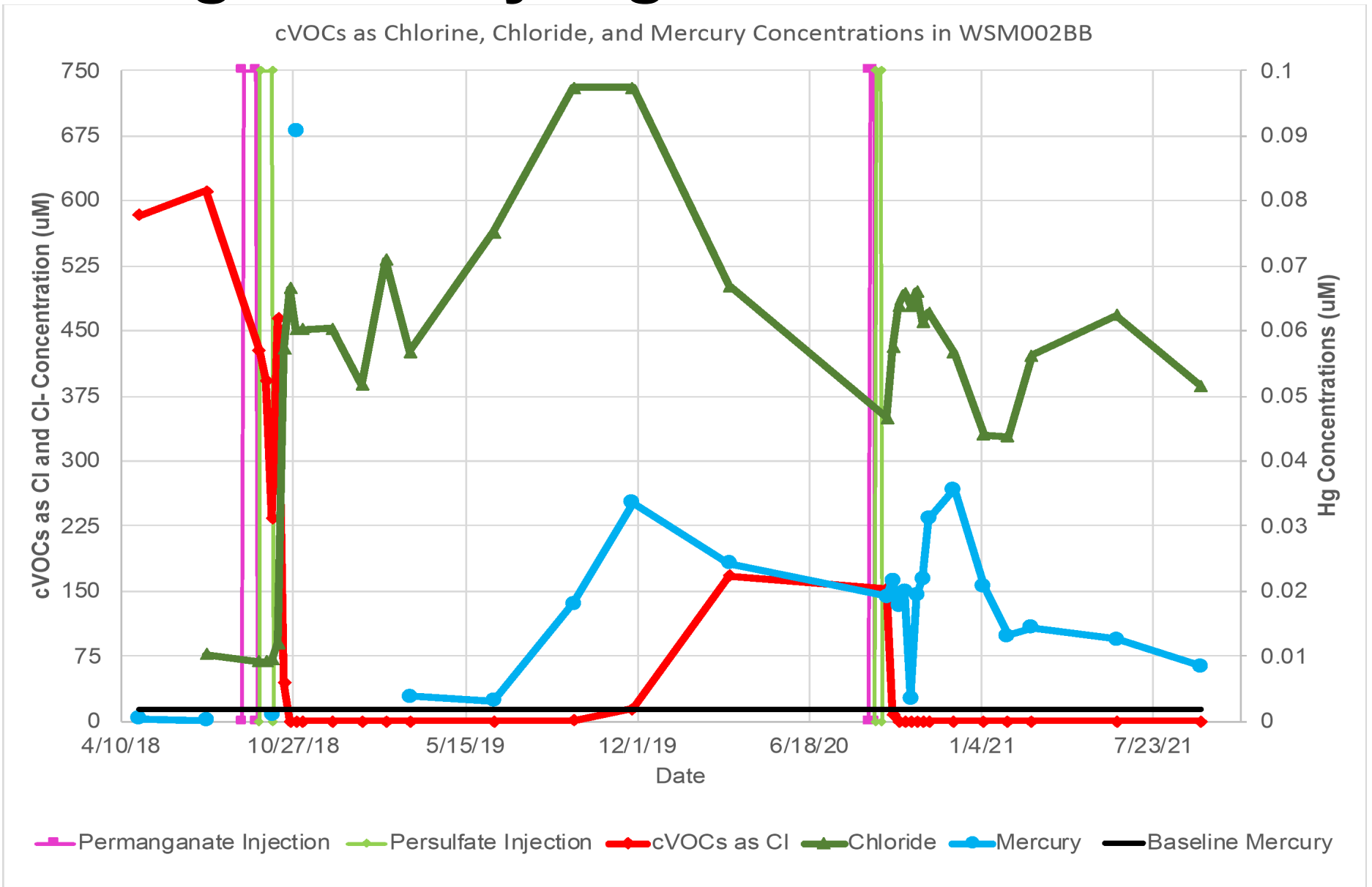


Observations from SRS M Area System:

- Total mercury in water correlates with TCE/PCE
- Hg not methylated (<0.00002 µg/L)
- Hg not elemental (i.e., unaffected by air stripping)
- Hg appears to be ionic and associated mobile Hg complexes
- Total mercury in M Area groundwater ranges from background to ≅ 0.25 µg/L and is <MCL of 2 µg/L

(Jackson, et al., 2006)

Chloride exceeds Cl from CVOC and mercury significantly higher than baseline



Statistically significant increase in Hg found in wells affected by oxidants

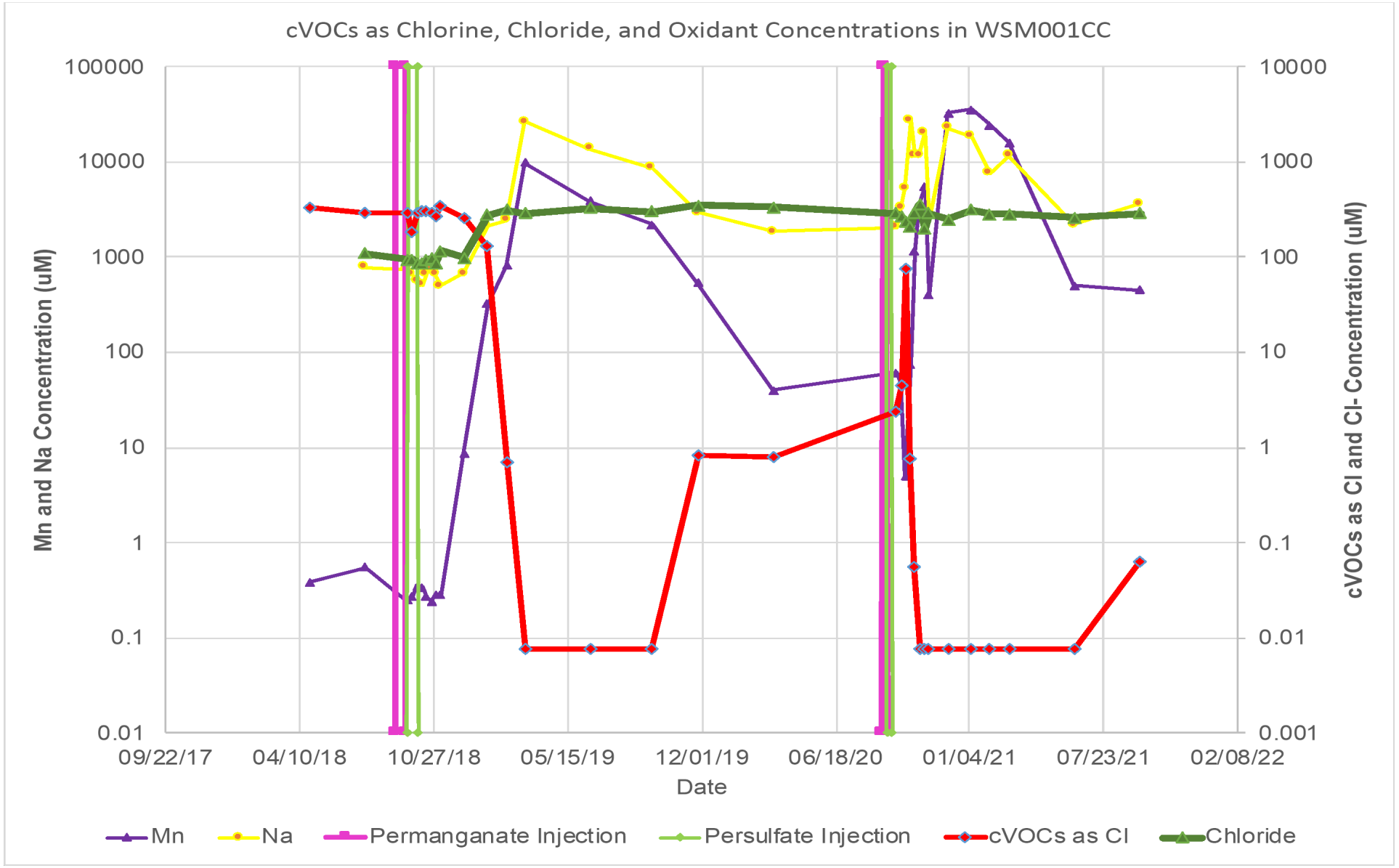
Hg t-Test: Two Tail Assuming Unequal Variances
Hg Baseline n = 61; Mean = 1.789E-03 µM; Variance = 3.47E-06 µM
Tabulated means and variances in units of µM

	First Injection (Data from 9/17/18 to 3/16/20)				Second Injection (Data from 9/16/20 to 9/15/21)			
Monitoring Well	**n**	**Mean**	**Variance**	**P Value**	**n**	**Mean**	**Variance**	**P Value**
WSM001B	7	2.91E-03	2.12E-05	0.545	14	1.32E-02	9.05E-04	0.179
WSM001BB	7	8.92E-02	8.48E-03	**0.046**	14	8.51E-02	4.07E-04	**< 0.001**
WSM001C	7	1.63E-03	2.07E-06	0.806	14	6.74E-02	3.60E-04	**<0.001**
WSM001CC	7	9.87E-03	1.17E-04	0.096	14	1.95E-02	2.56E-05	**<0.001**
WSM002B	7	6.79E-03	2.10E-04	0.396	14	6.26E-03	8.26E-05	**0.090**
WSM002BB	7	2.49E-02	9.91E-04	0.100	14	1.85E-02	6.84E-05	**<0.001**
WSM002C	7	1.67E-04*	<1.0E-07	<0.001*	14	3.12E-02	2.84E-04	**<0.001**
WSM002CC	7	3.43E-04*	<1.0E-07	<0.001*	14	4.67E-02	1.78E-04	**<0.001**

Bold = statistical difference at 95% confidence interval. * = measurements below detection limit.

Rossabi, Jackson, Vermeulen, and Looney, *Nature Communications Earth and Environment* 3, 223 (2022)

CVOC destruction correlated to oxidant concentration, threshold apparent



PCE and TCE Destruction Varied with Oxidant Concentration

- PCE and TCE concentrations in wells are variable so normalization needed.
- Advective push from injections enhances variability.
- Contact with oxidants is also variable.
- Sequential oxidation of permanganate then persulfate.

Data Processing

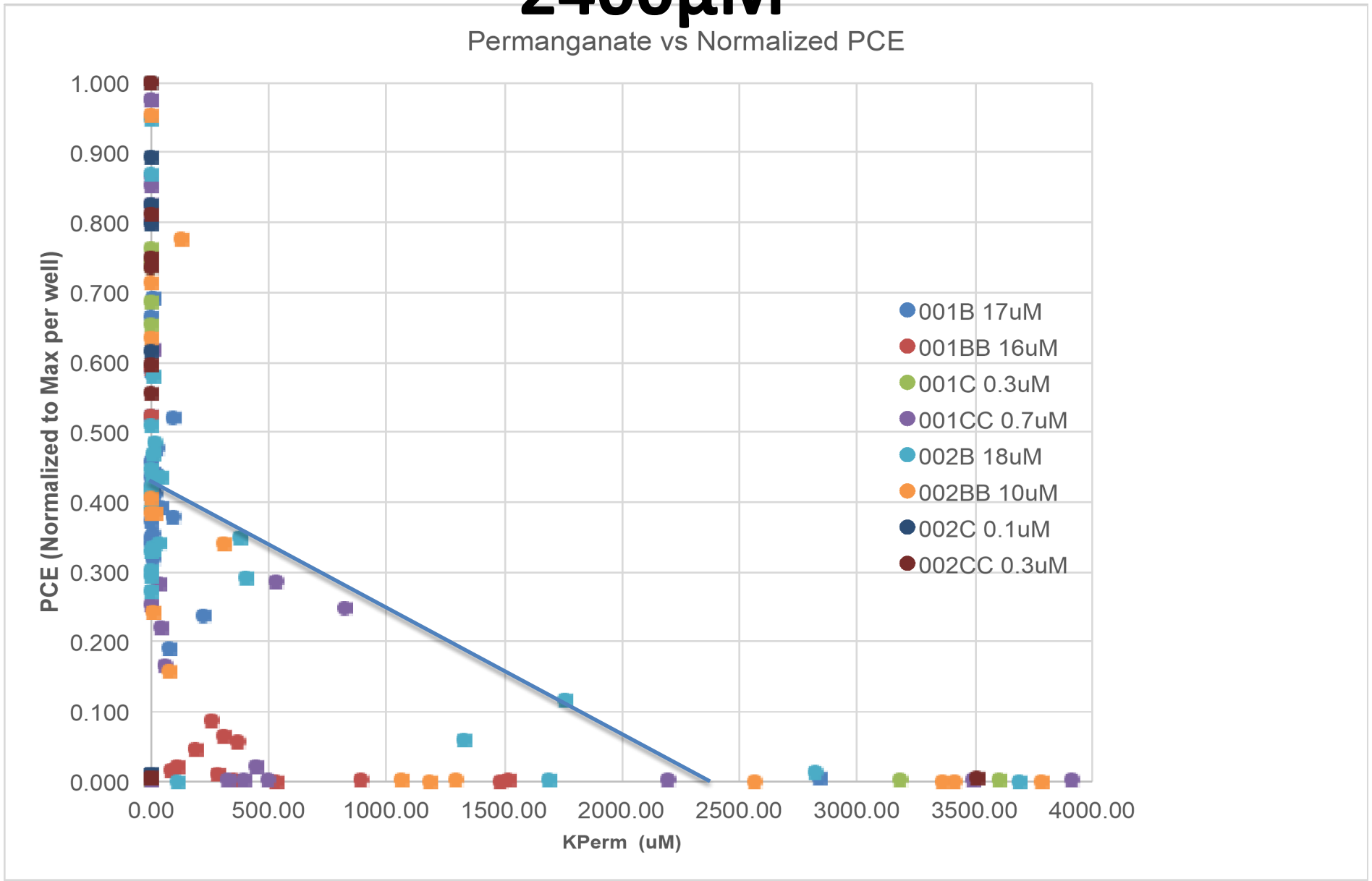
- Normalize individual wells' PCE and TCE concentrations
- Subtract baseline concentrations of K, Mn, Na, SO4, chloride from measurements post injection.
- Use Mn for Kperm, Na (minus sulfate) for persulfate
- Baseline C_0
  - Mn 0.64 uM
  - Na 360 uM
  - SO_4 30 uM

Injectate C_0

$KMnO_4$ ~ 260,500 uM

$Na_2S_2O_8$ ~ 293,700 uM

Permanganate vs PCE Plot shows threshold at ~ 2400µM



Apparent Thresholds Found

- **PCE**
  - **Permanganate ~ 2400 µM = 0.38 g/L**
    - Field Molar Ratio Range from ~ 170:1 to 30,000:1
    - Literature Molar Ratio = 1.3:1 (Schnarr et al, 1998)
  - **Persulfate ~ 7,000 µM = 1.7 g/L**
    - Field Molar Ratio Range from ~ 390:1 to 70,000:1
    - Literature Molar Ratio = 2:1 (FMC)
- **TCE**
  - **Permanganate ~ 700 µM = 0.11 g/L**
    - Field Molar Ratio Range from ~ 3:1 to 13:1
    - Literature Molar Ratio = 1.8:1 (Kim and Gurol, 2005)
  - **Persulfate ~ 3,000 µM = 0.71 g/L**
    - Field Molar Ratio Range from ~ 12:1 to 55:1
    - Literature Molar Ratio = 6:1 (Gu et al, 2017)

Conclusions

- Based on statistically significant rise in mercury concentration after oxidant injections, and excess Cl, **DNAPL must have been present > 650 m from release area.**
- **DNAPL can go a long way and stick around a long time**.
- **Just because we don't have the technology to see it yet, doesn't mean it's not there.**
- Although kinetic destruction should be a function of both oxidant concentration and contaminant concentration, there appears to be a **threshold oxidant concentration** for complete destruction of PCE, TCE
- **Need higher oxidant concentrations than literature stoichiometry**
- **PCE requires higher oxidant concentration than TCE**
- **Persulfate requires higher concentration than permanganate**
- May help explain results of oxidant application and contaminant rebound and guide dosing for remediation
- **The better our conceptual model, the more likely we'll be able to come up with successful solutions.**
- **New opportunities** for analytical and numerical modeling, characterization technologies, remediation strategies, etc.