Identifying and Delineating Hidden Sources Within a Larger Chlorinated Solvent Plume

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REMTEC & EMERGING CONTAMINANTS SUMMIT

OCTOBER 15-17, 2024

Outline

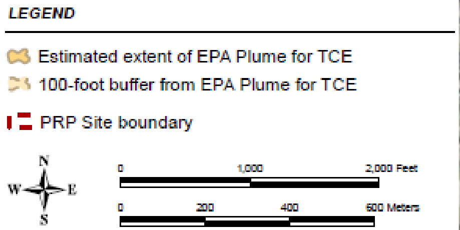
- Commingled plume problem at site
- Methodology
- Results and suggestions for implementation

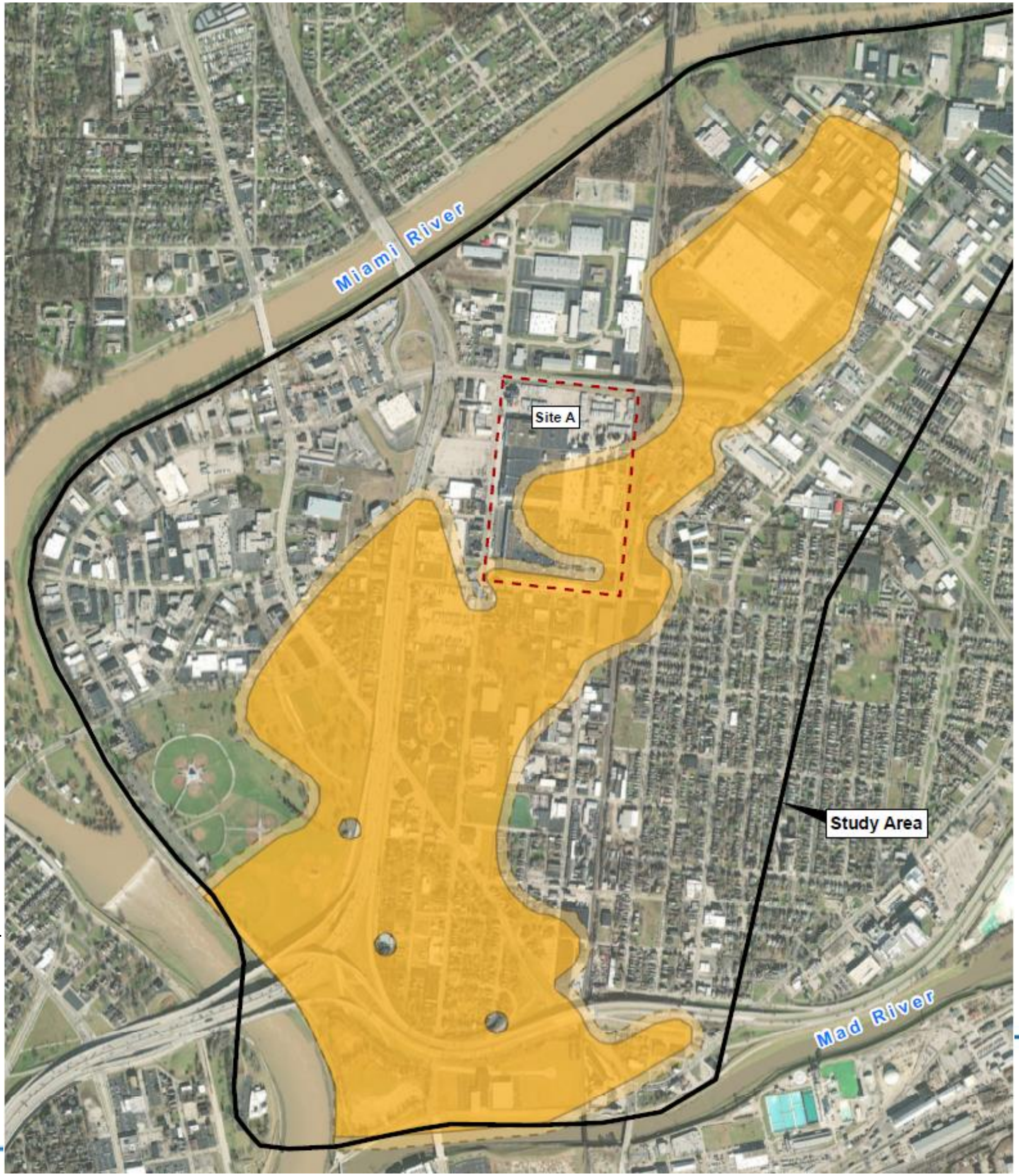
Commingled Plume Problem

- TCE, PCE, and other chlorinated solvents are commonly commingled at contaminated sites and in groundwater at industrial urban areas
- How to distinguish and delineate where one plume ends and another begins?
- Particularly difficult when different sites have released the same chemical

Is all this ours?

- Site A being blamed for all TCE in plume
- Objectives:
  - Is all this TCE from Site A?
  - If not, what are the other sources?
  - Can we delineate the extent of Site A TCE?

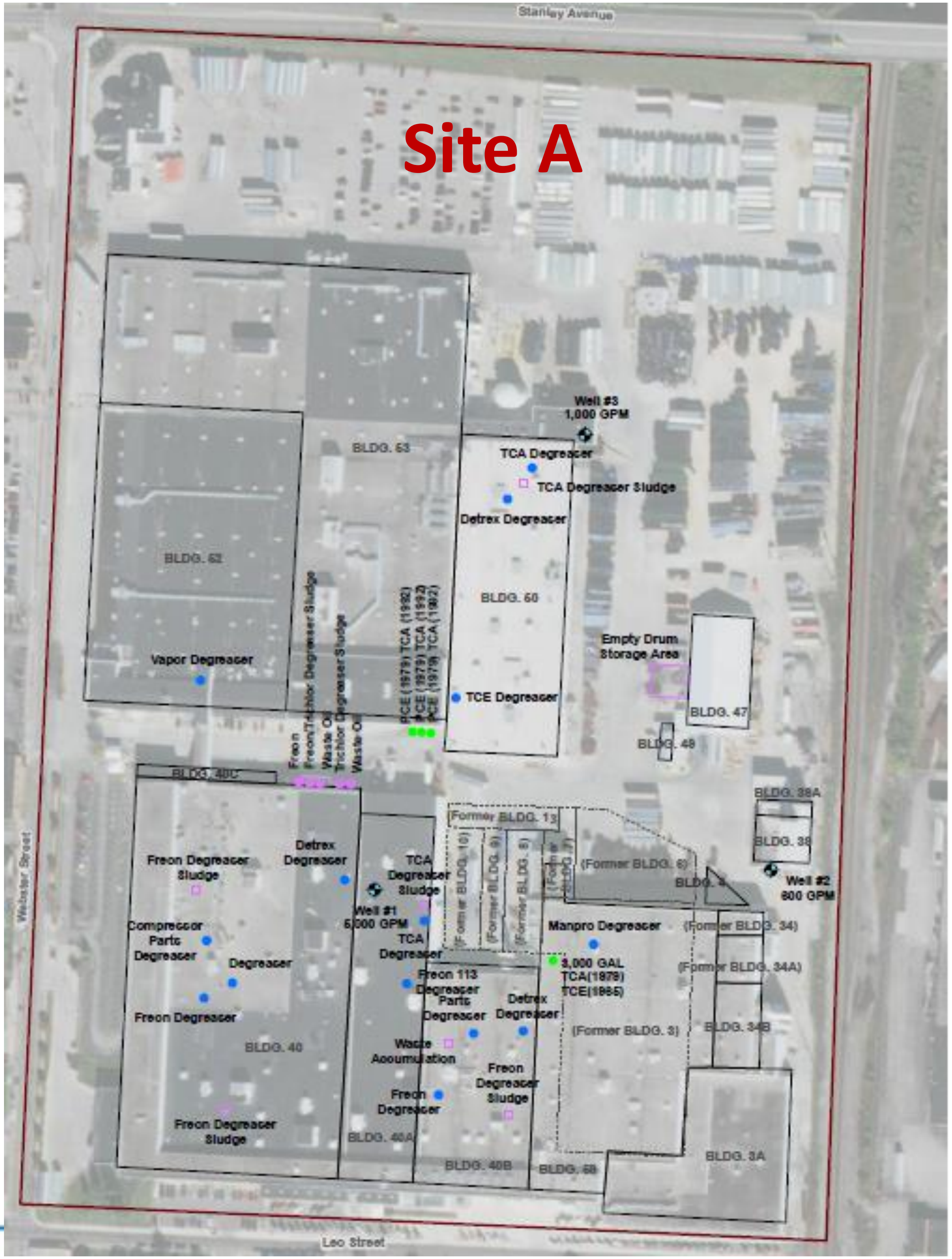




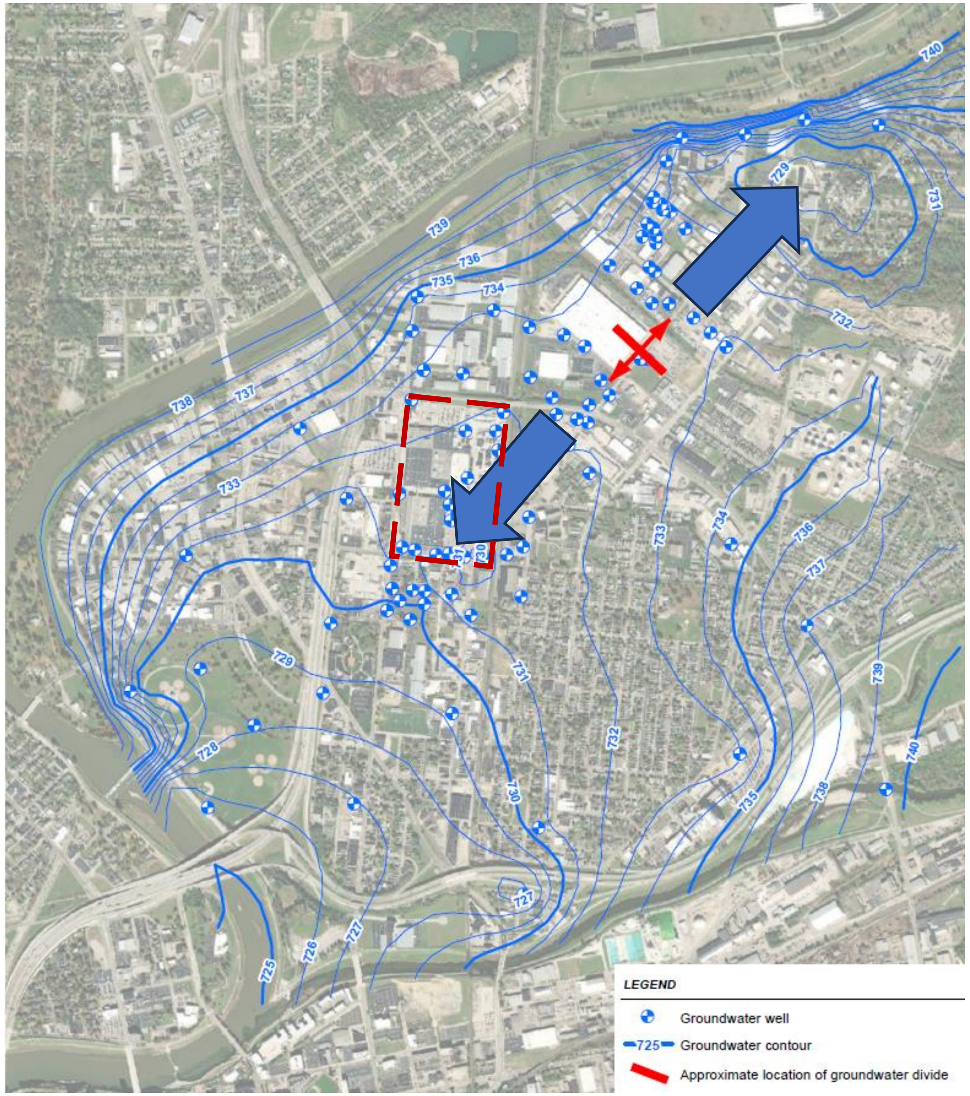
Complicated site with multiple on-site sources

- Site operated 1907 – present
- Multiple vapor degreasers
- Degreasers moved locations over time
- Multiple different solvents over time

LEGEND
- Waste chemical storage
- Virgin chemical storage
- Chemical usage area
- Industrial water supply wells
- Site boundary



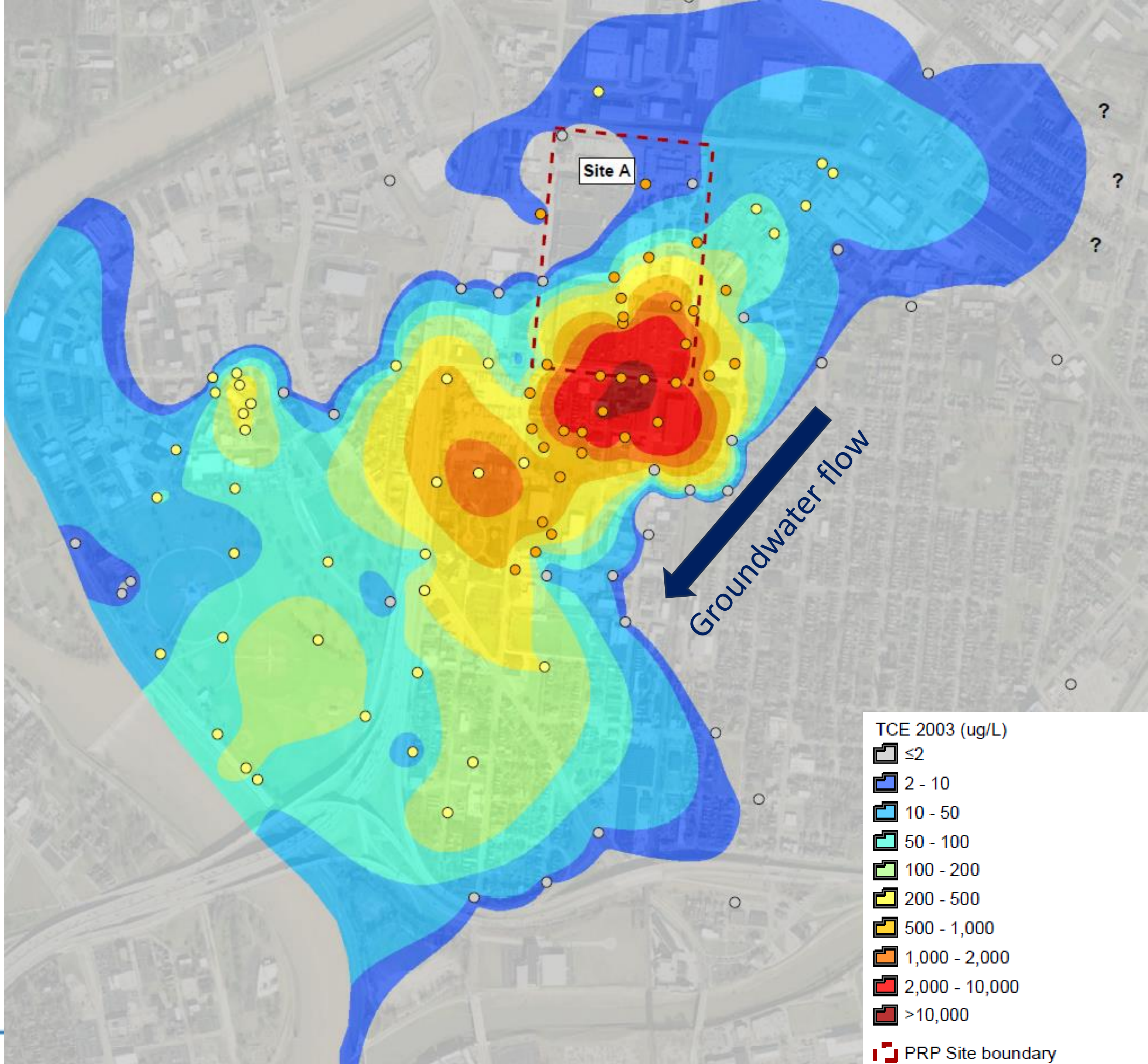
Groundwater flow complicated by hydraulic divide

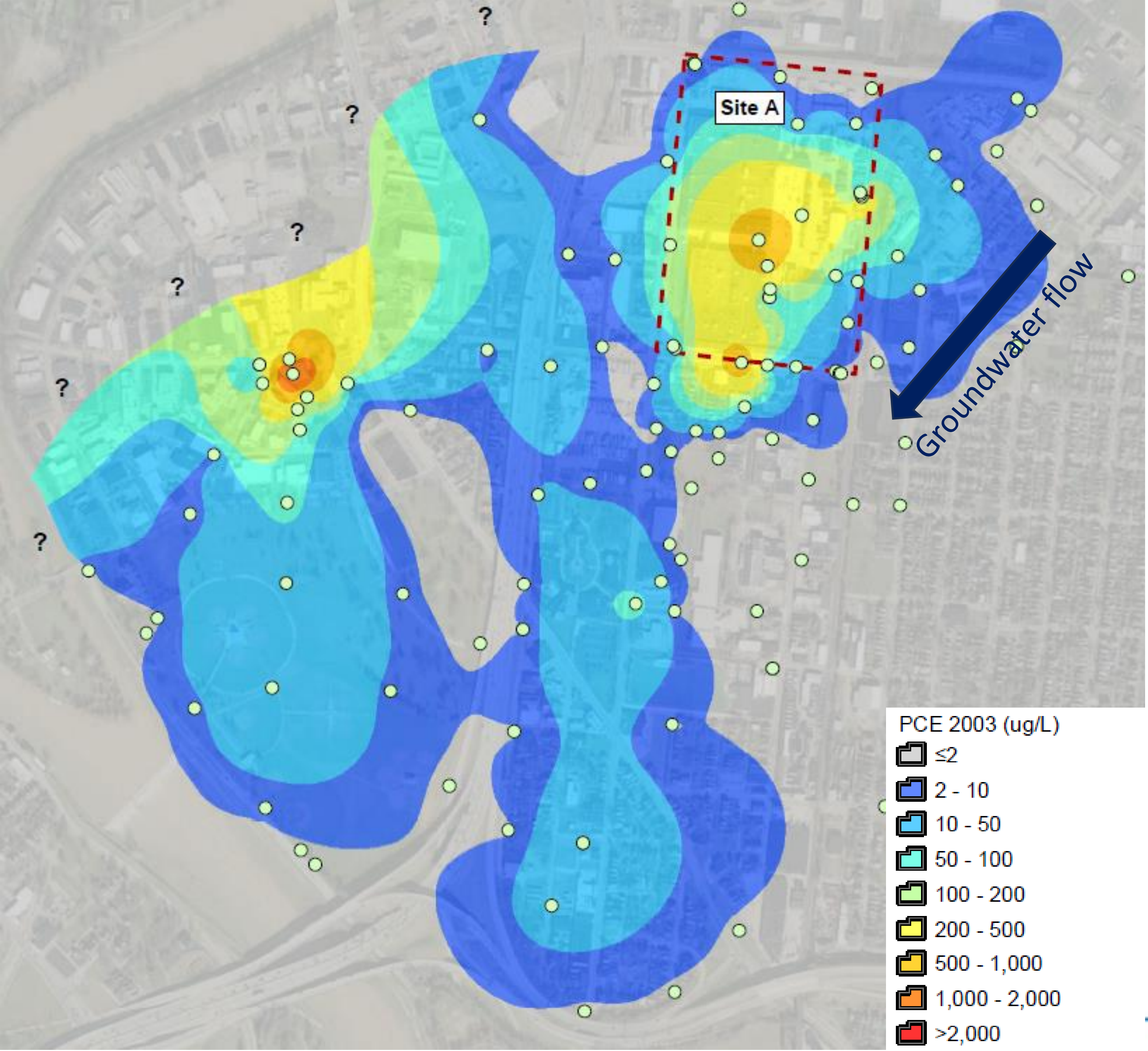


- Groundwater divide due to pumping
  - Divide appeared ~ 1970
- On-site pumping wells impacted groundwater flow locally

TCE contours suggest other contributors to the plume

- TCE contours show hot spots and anomalies inconsistent with the direction of groundwater flow
- TCE flowing onto Site from upgradient source(s)

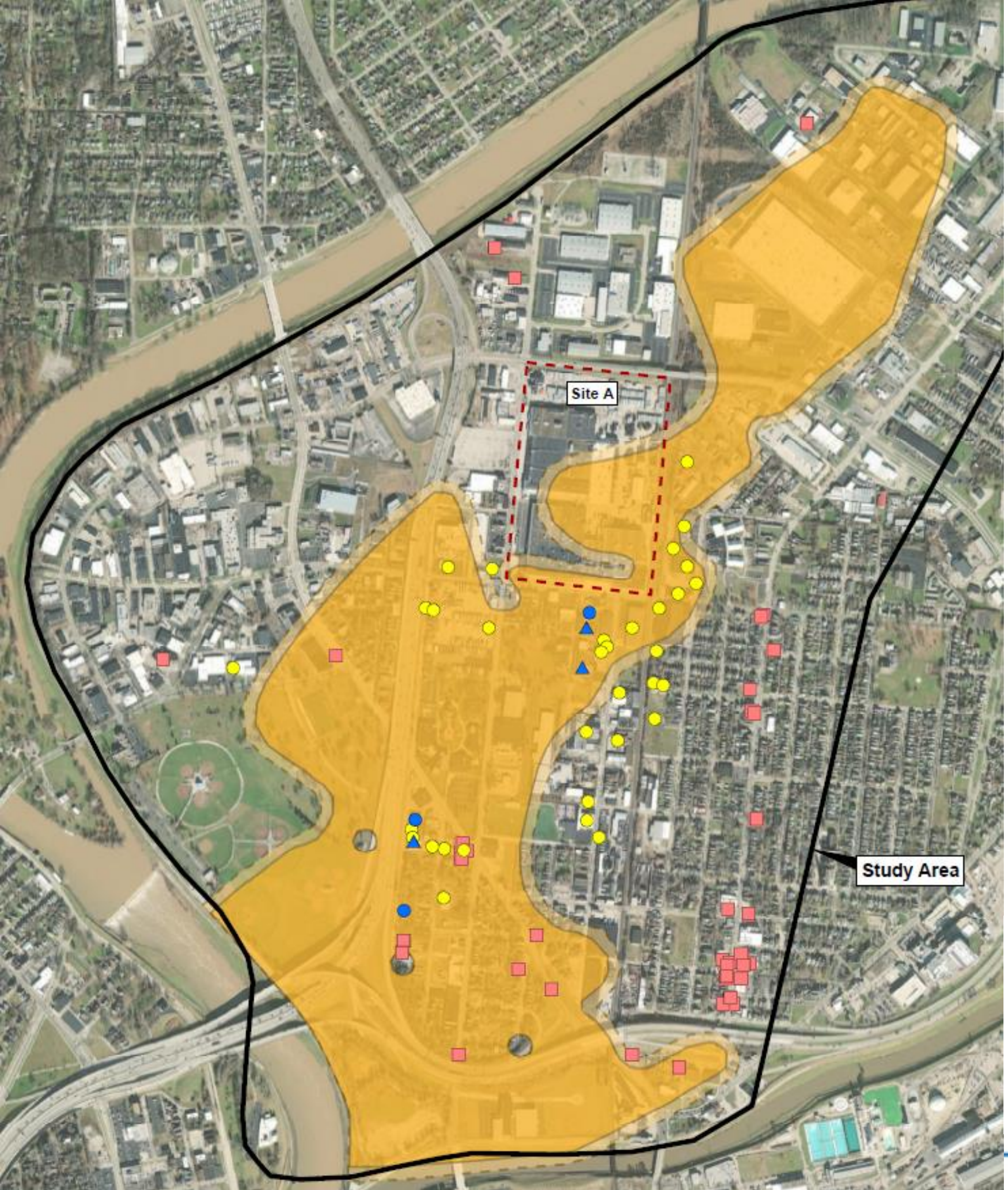




PCE plume looks very different from TCE

- PCE plume ends shortly downgradient of Site A
- Similar short plumes for other solvents, like 1,1,1-TCA
- Therefore, there must be other sources of TCE

Many suspicious industrial sites in the area



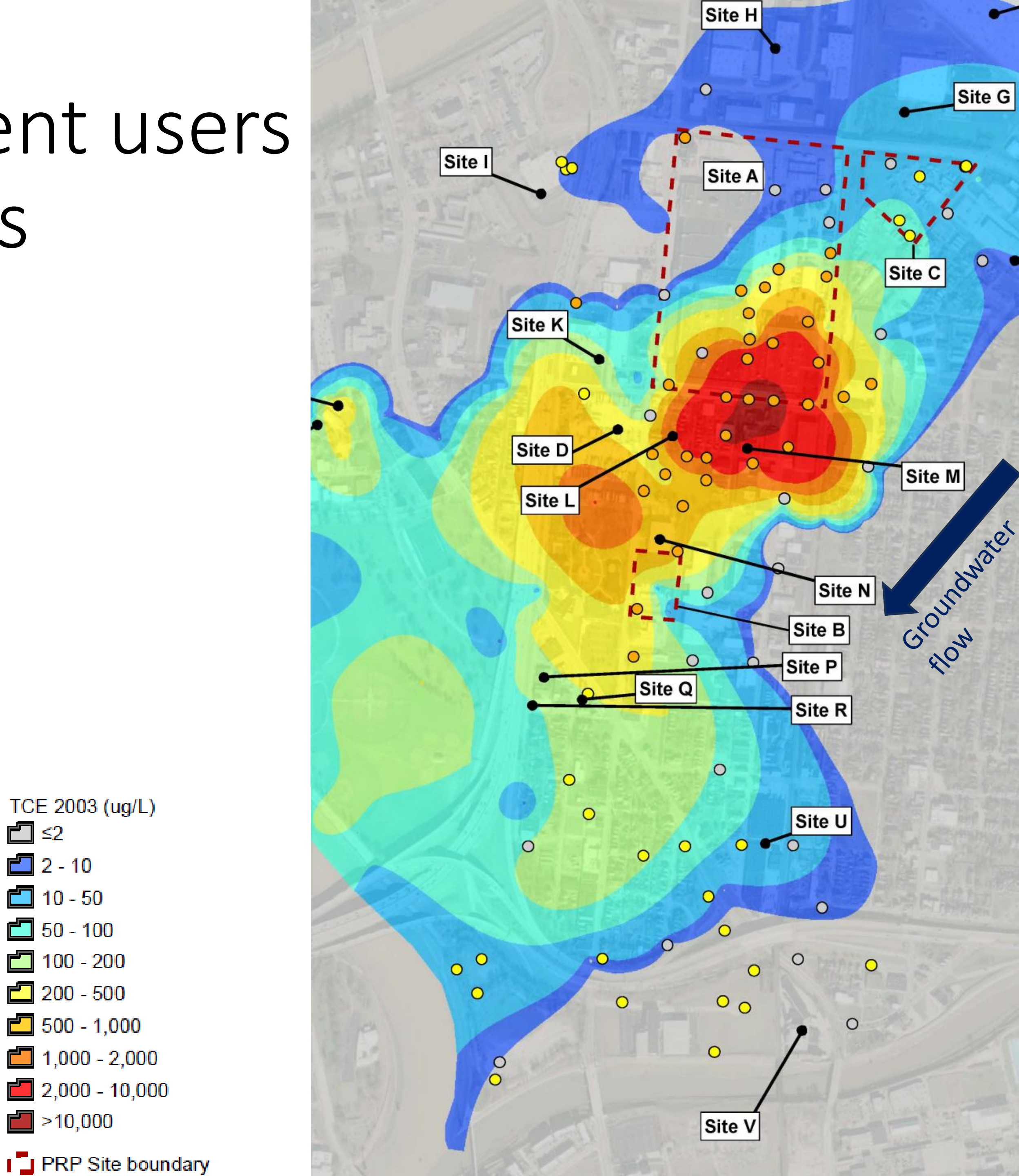
- Site in an urban industrial area
- Many historical metal plating facilities, machine shops, dry cleaners, and other industrial sites with the potential to have used and released chlorinated solvents

LEGEND

Industrial Facility
- Dry Cleaners
- City Directory
- Sanborn - Machine Shop
- Sanborn - Metal/Plating

Potential chlorinated solvent users may explain TCE anomalies

- TCE hotspots located adjacent to documented chlorinated solvent users and some potential users
- Some sites have soil data indicating TCE releases (Sites C, I, and K)
- No soil data for many other sites (Sites D, G, L, M, N, P, R, Q)



How to identify other sources to this plume?
How to separate Site A’s TCE plume from others?
Where does Site A’s TCE plume end?

Methodology involves 3 steps

1. Fingerprinting

1. Prepare "fingerprints" consisting of "pie-charts" of PCE and its daughter products
a. Identify fingerprints that match the site and those that don't

2. Centerline plot

2. Plot contaminant concentrations along the centerline of a plume
a. Identify data points with fingerprints matching the site and those that don't

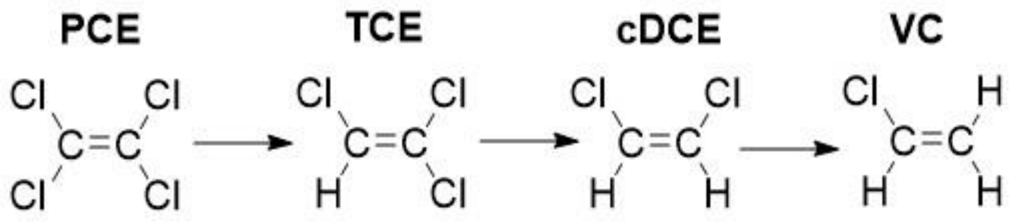
3. First-order decay extrapolation

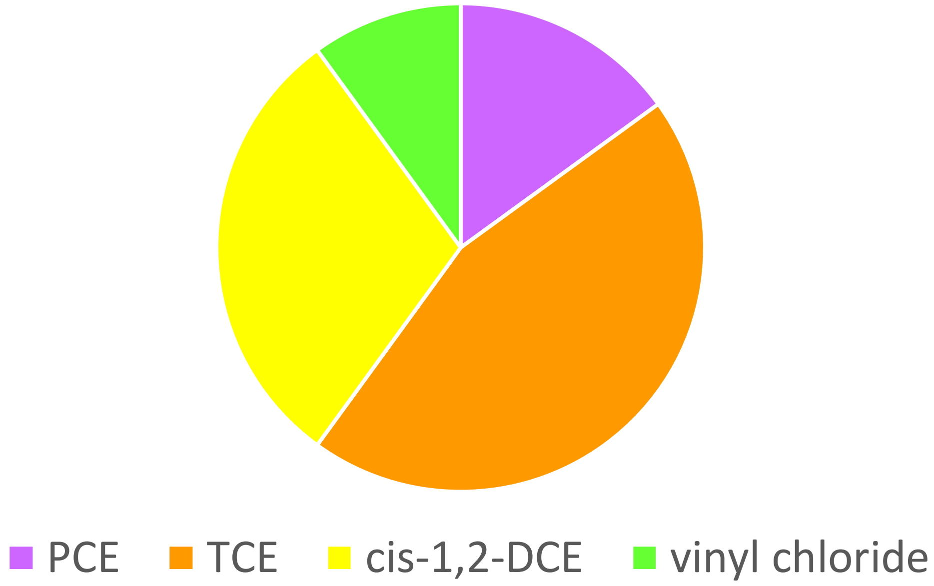
3. Fit a first-order decay curve to observed data with fingerprints matching the site
a. Extrapolate the distance to meet the desired concentration

Sources:

- Dai Q, and Chau T. 2008. "Mass separation and risk assessment of commingled contamination in soil and ground water." GeoEdmonton 2008: 61st Canadian Geotechnical Conference and 9th Joint CGS/IAH-CNC Groundwater Conference, September 21-24, 2008, Edmonton, Canada.
- Robrock K, and Mesard P. 2018. "Distinguishing between multiple dry cleaner sources in a comingled chlorinated solvent plume." Battelle 11th International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Palm Springs, CA, April 2018.
- U.S. EPA. 2002. Ground Water Issue - Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies. Washington, DC: U.S. EPA

Step 1: Molar Pie Chart Fingerprints

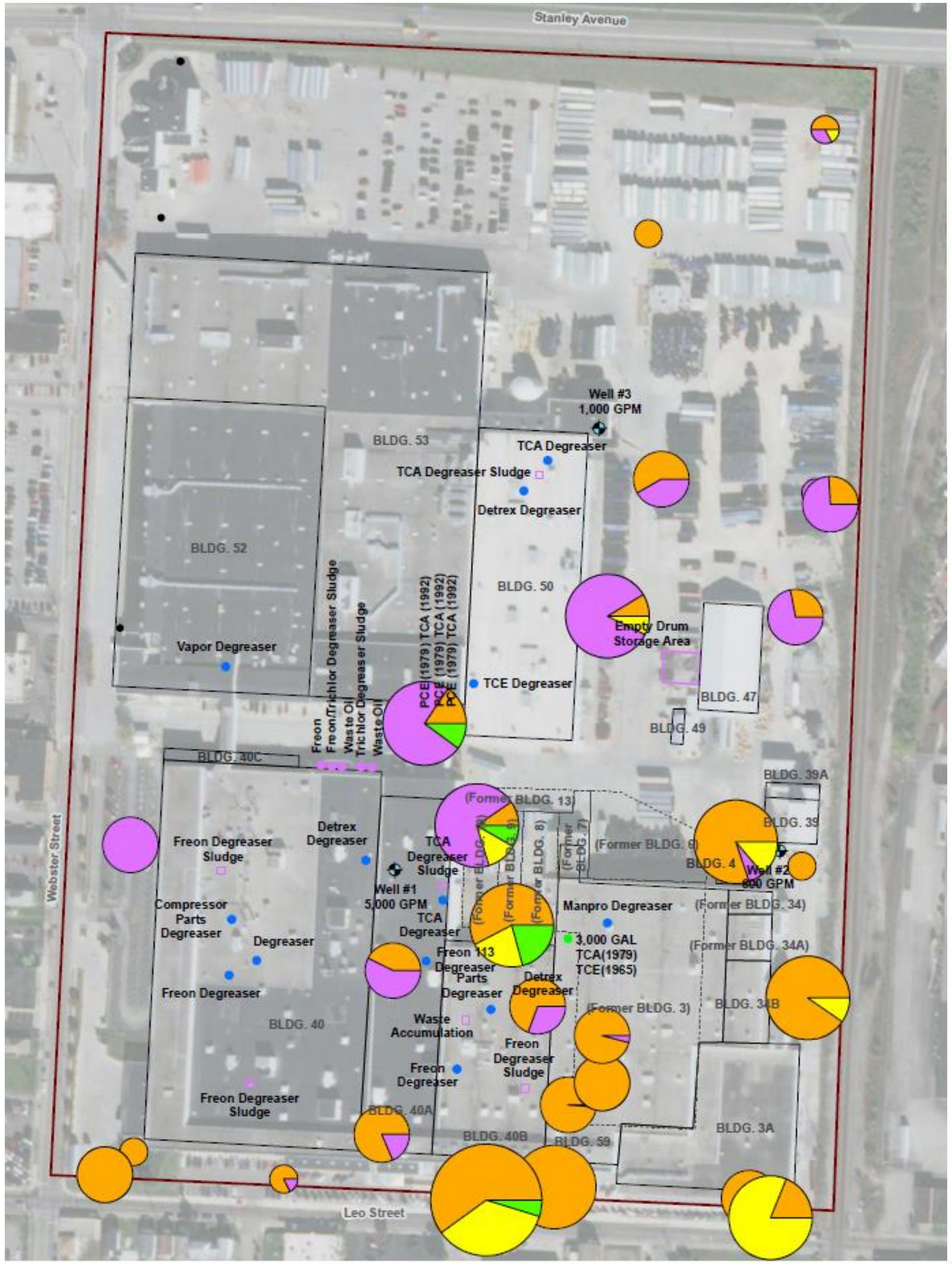




- Increase in size of pie suggests additional release
- Increase in proportion of parent product suggests additional release

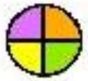
Site A Fingerprints

- Site fingerprints show mixed PCE, TCE and DCE
- Predominantly TCE with some DCE leaving the site



LEGEND

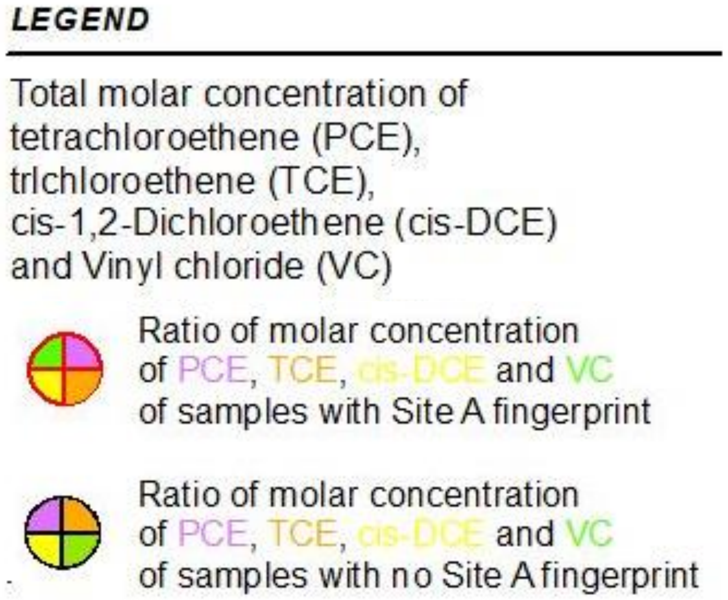
Total molar concentration of tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-Dichloroethene (cis-DCE) and Vinyl chloride (VC)

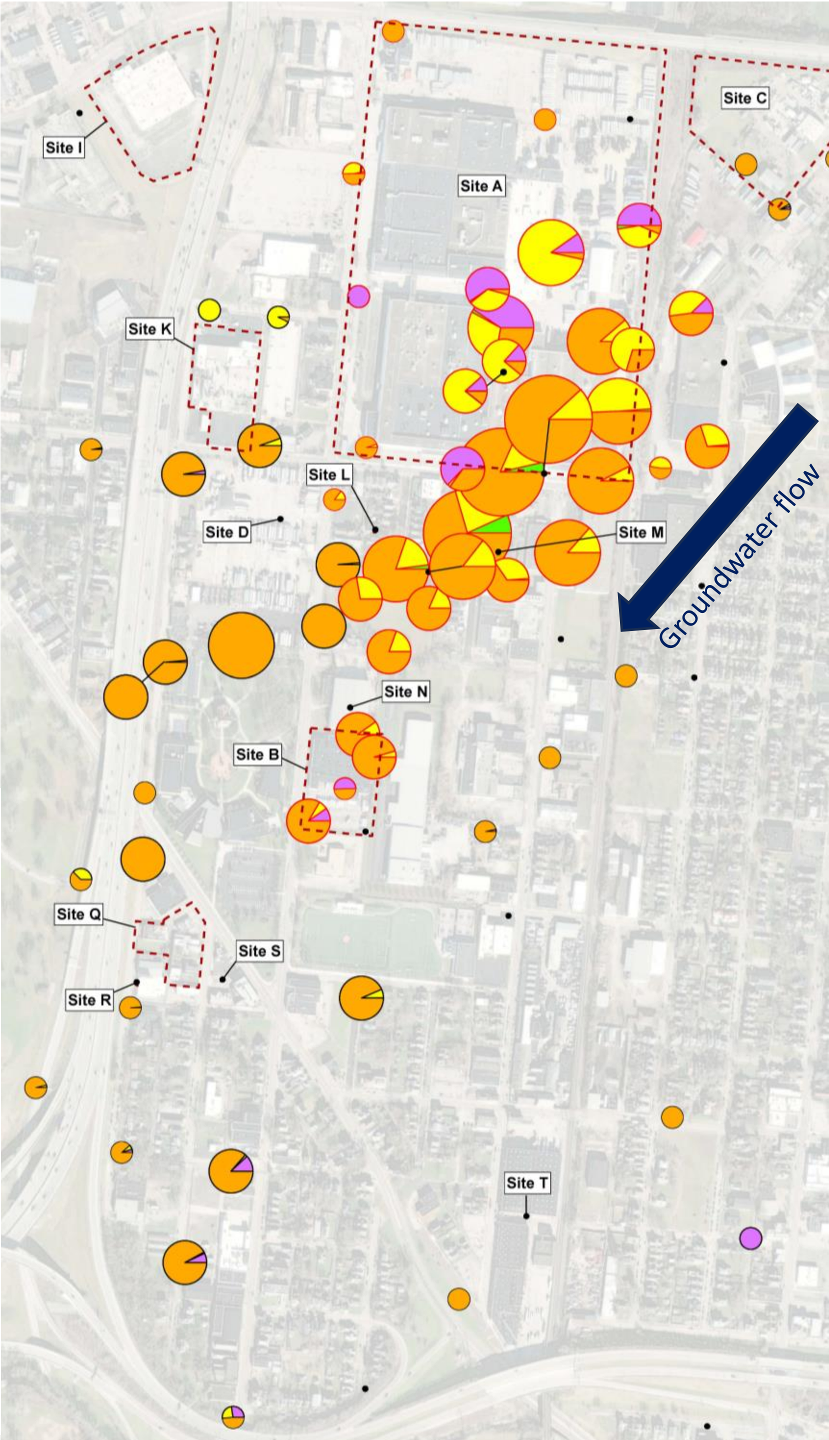


Ratio of molar concentration of PCE, TCE, cis-DCE and VC

Fingerprints suggest other contributors to the plume

- Loss of degradation products and increase in TCE downgradient indicate another TCE source
- PCE source at Site B





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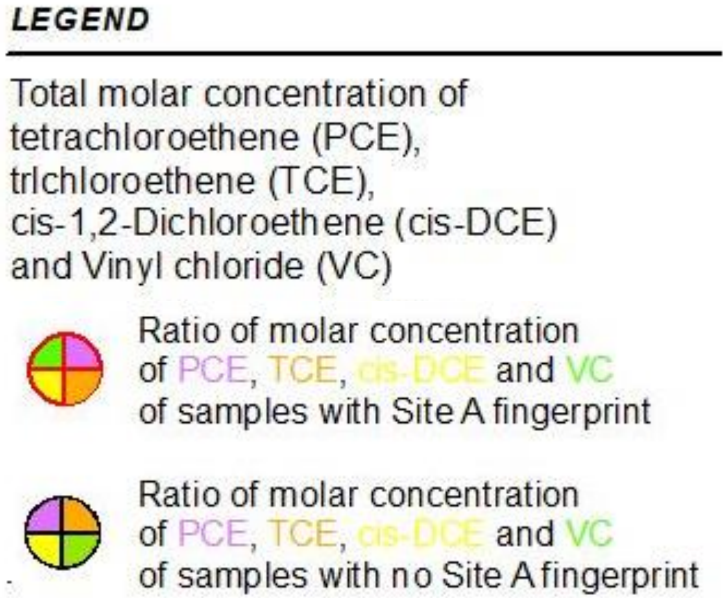
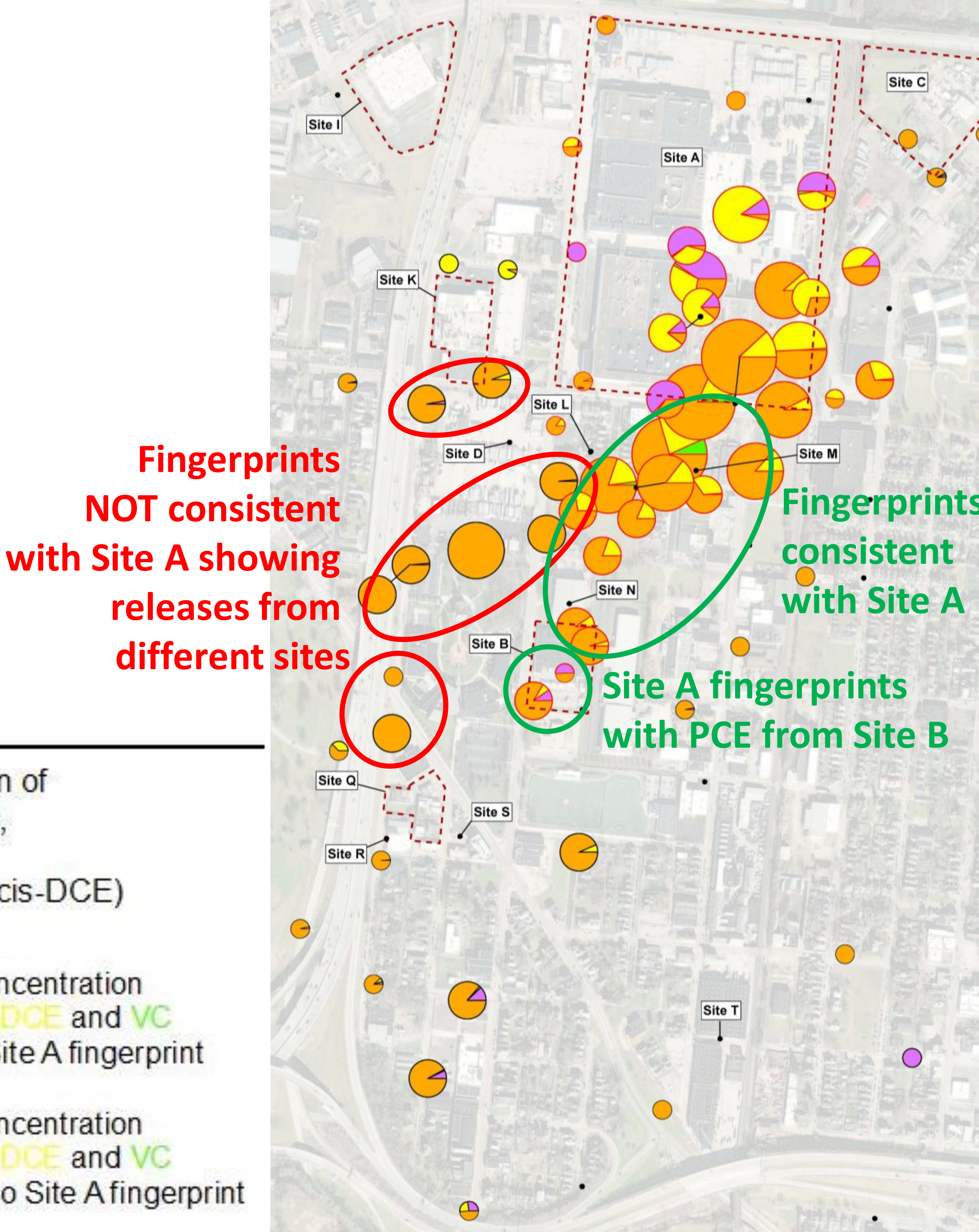
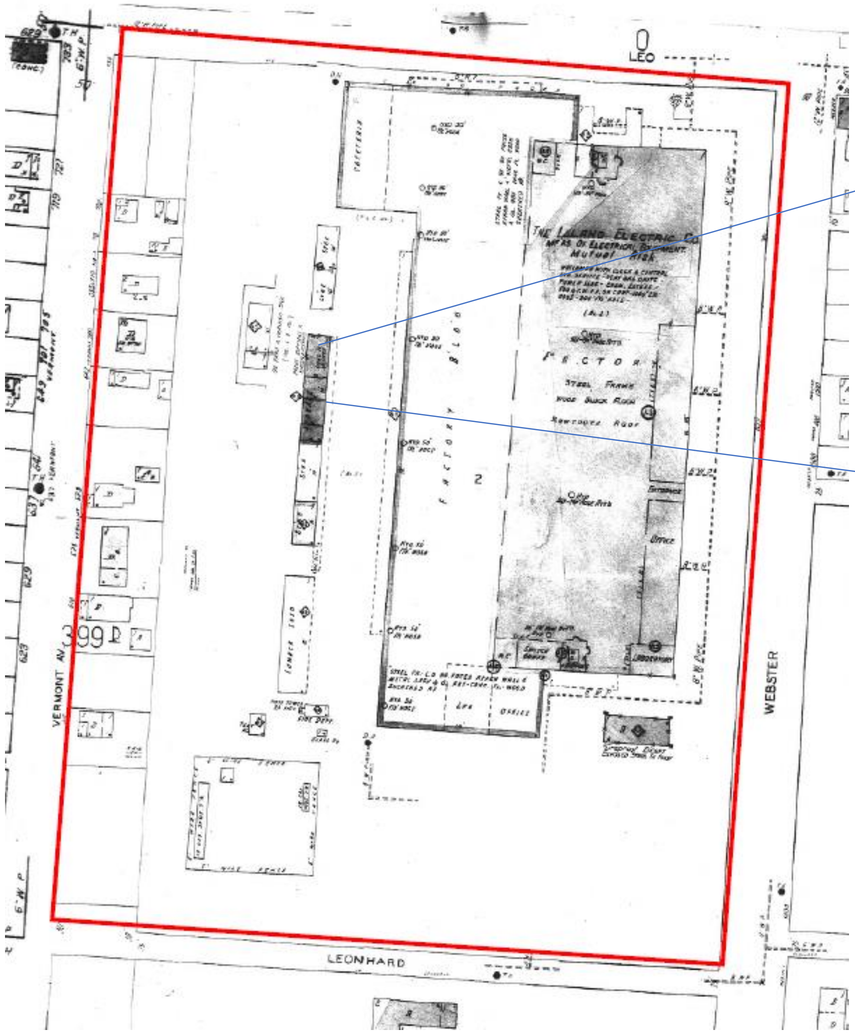
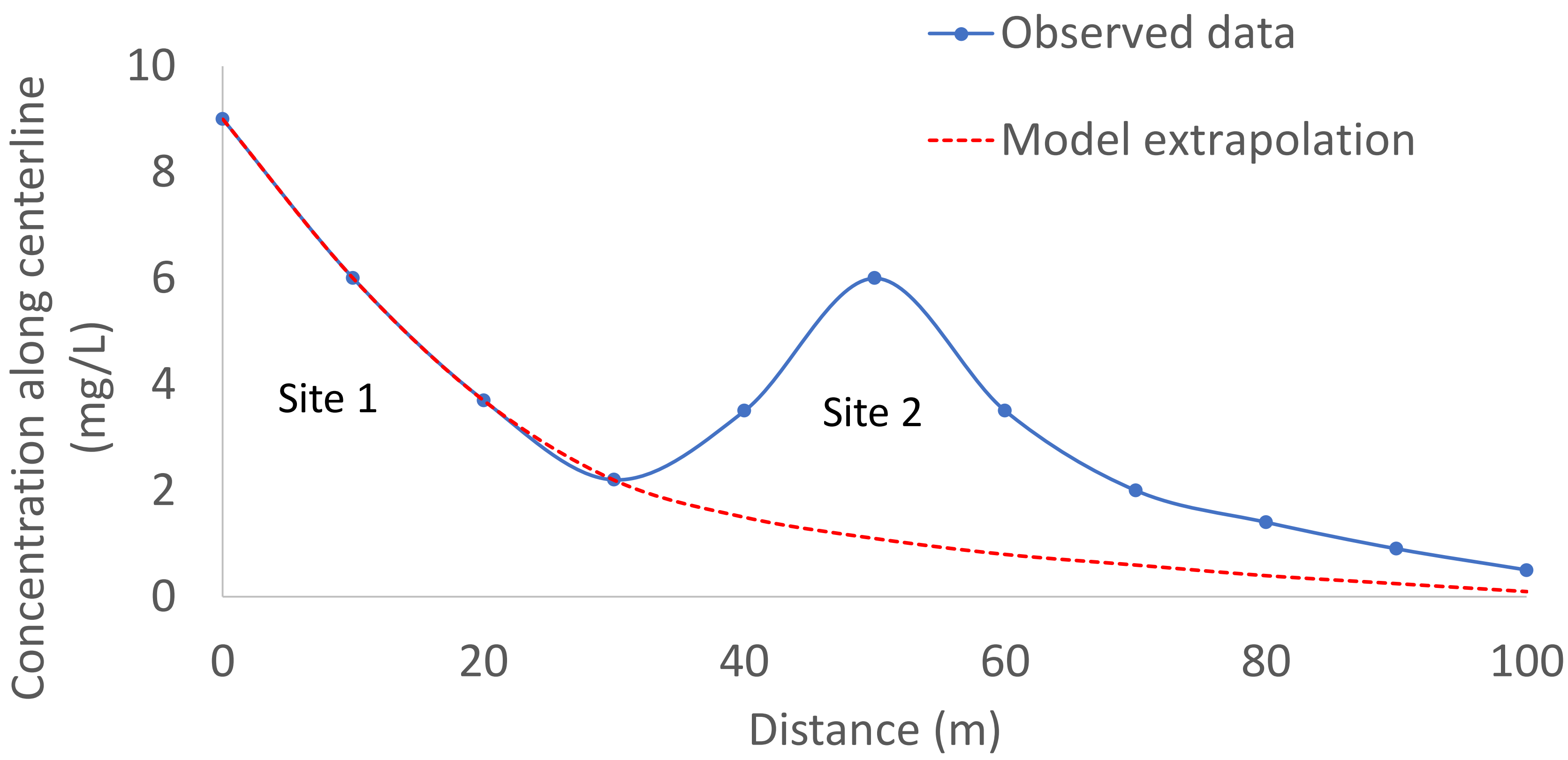




Site D Sanborn

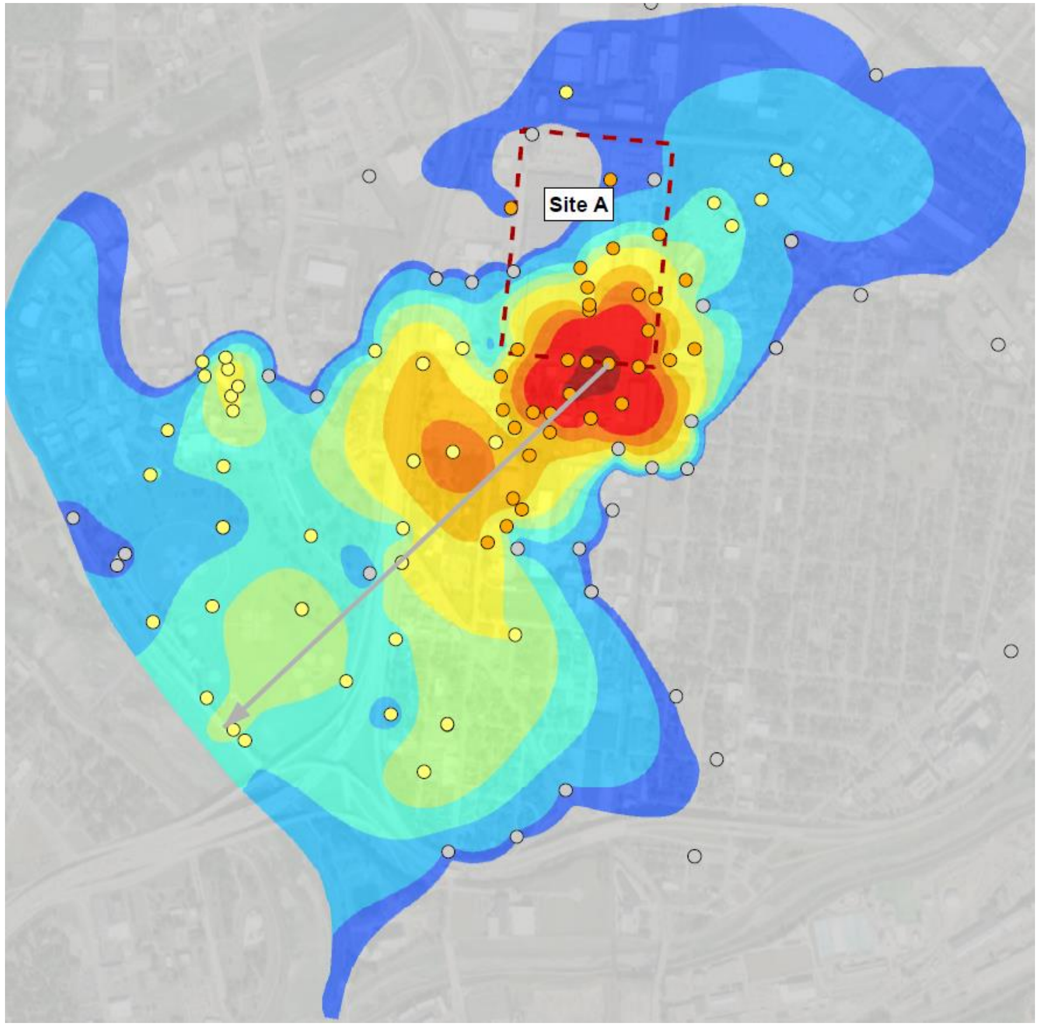


Step 2: Centerline plot



Dai Q, and Chau T. 2008. "Mass separation and risk assessment of commingled contamination in soil and ground water." GeoEdmonton 2008: 61st Canadian Geotechnical Conference and 9th Joint CGS/IAH-CNC Groundwater Conference, September 21-24, 2008, Edmonton, Canada.

Centerline

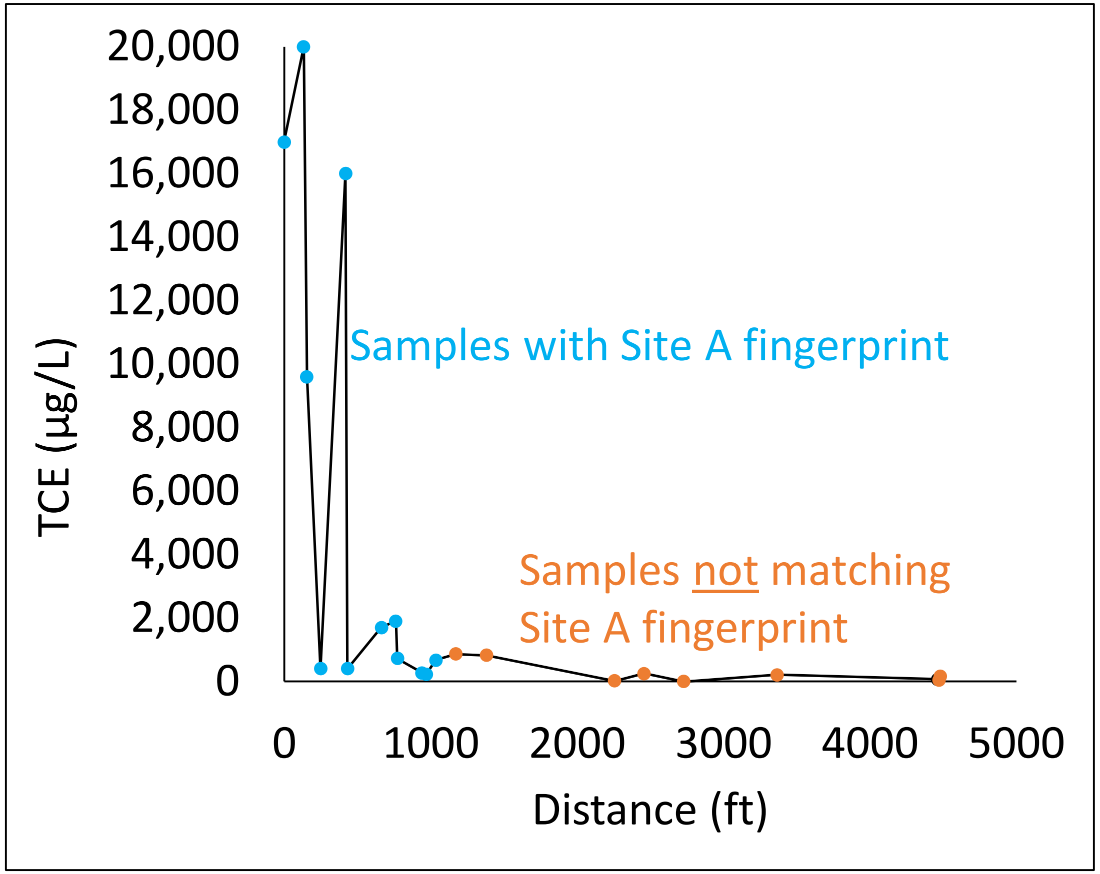


- Plot data along or close to the centerline
- In this case, within 350 ft based on the horizontal dispersion of the plume

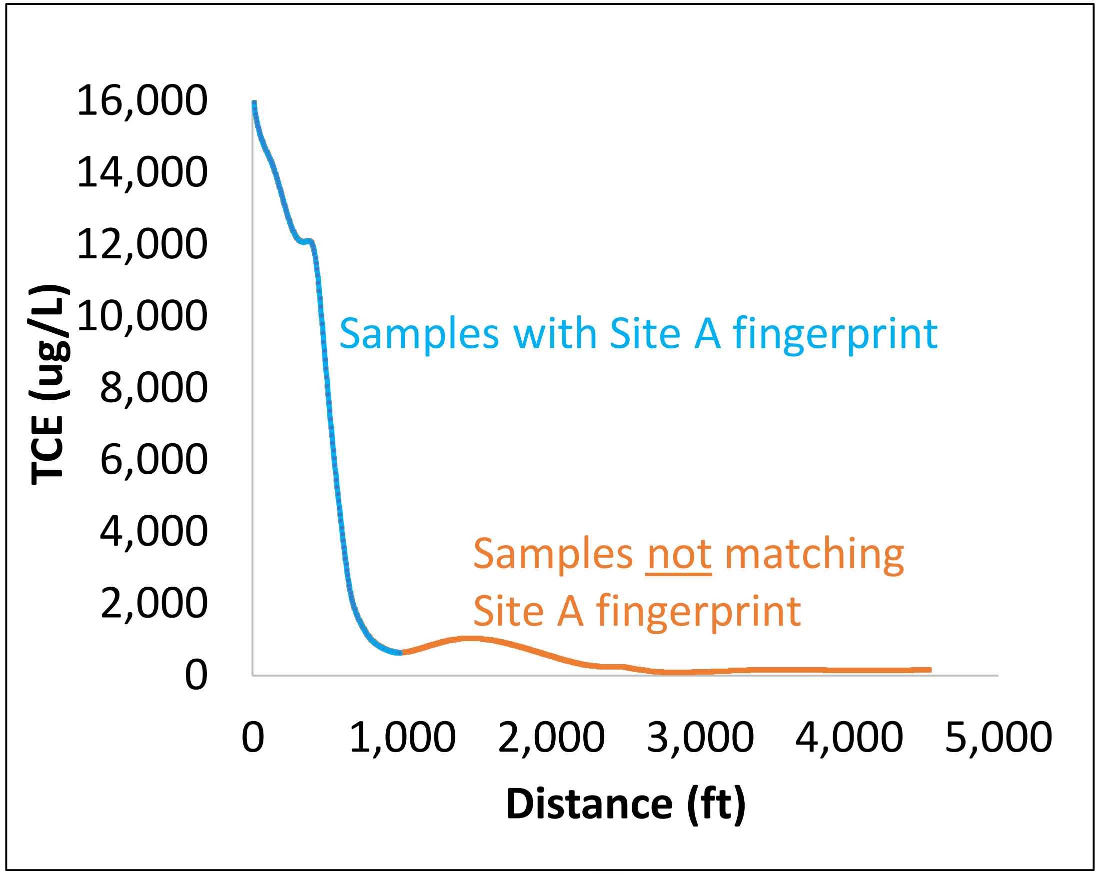
Source: Xu, M. and Y. Eckstein. 1995. "Use of weighted least-squares method in evaluation of the relationship between dispersivity and field scale." Groundwater 33(6): 905-908

TCE concentrations along centerline

Discrete measured data



Interpolated data points from contouring



Step 3: First-order decay extrapolation

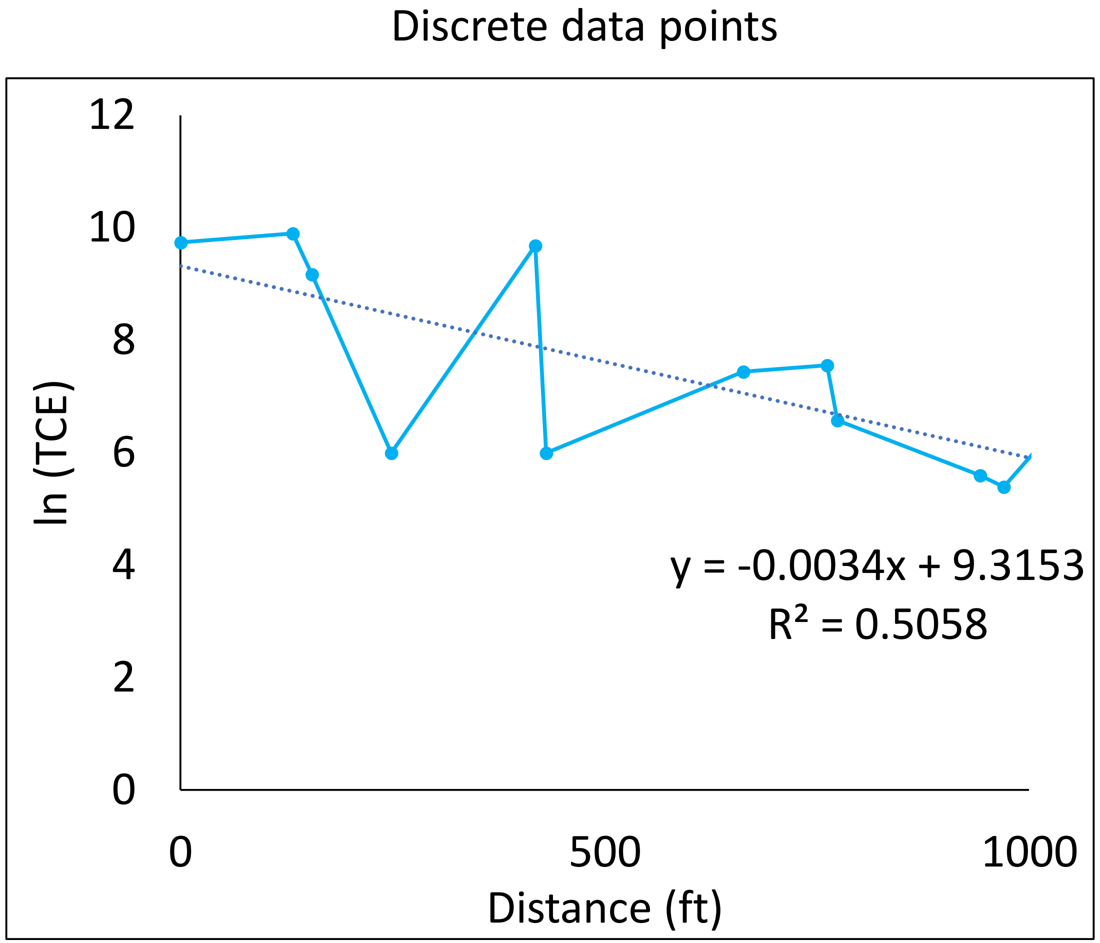
- Plume attenuation follows first-order decay
- Extrapolate hidden plume using first-order decay curve

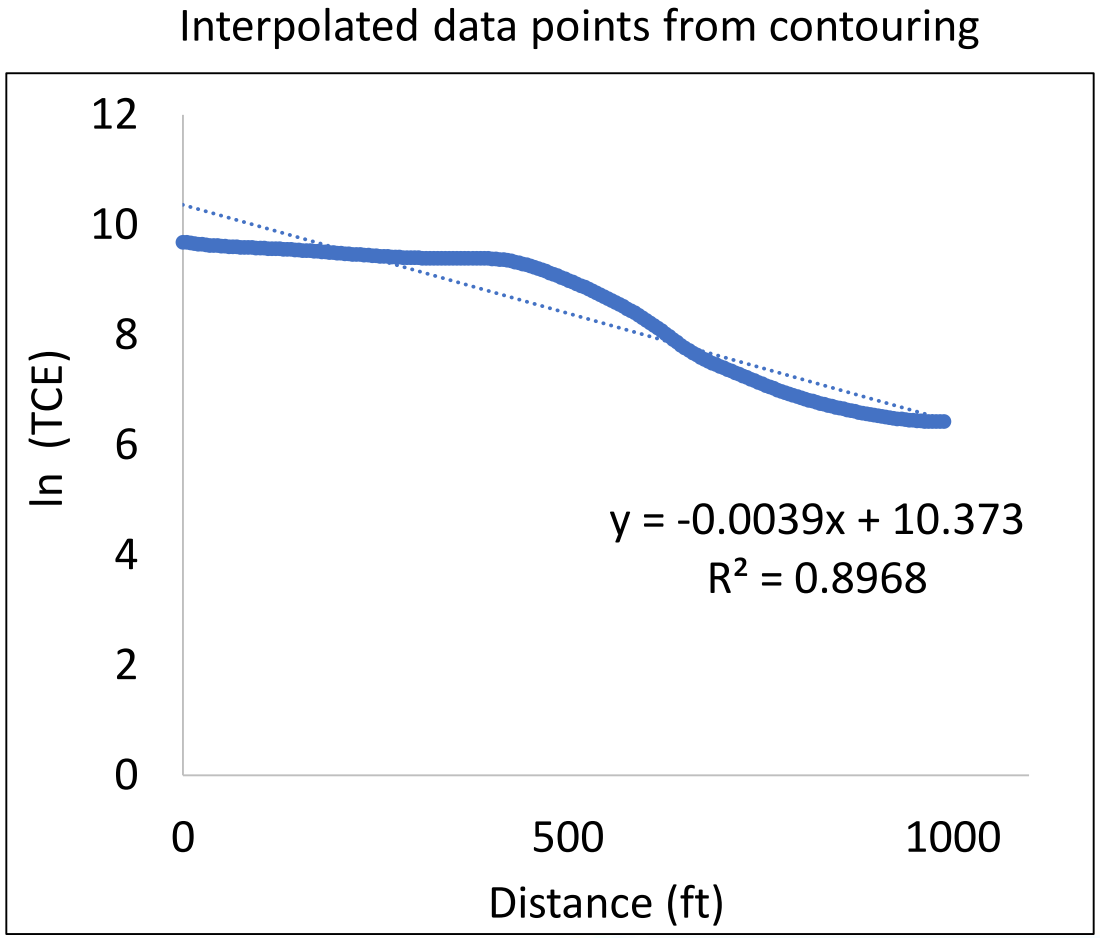
$$k = \frac{\ln\big(C(x)\big) - \ln(C_o)}{x}$$

Source:

- U.S. EPA. 2002. Ground Water Issue - Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies. Washington, DC: U.S. EPA

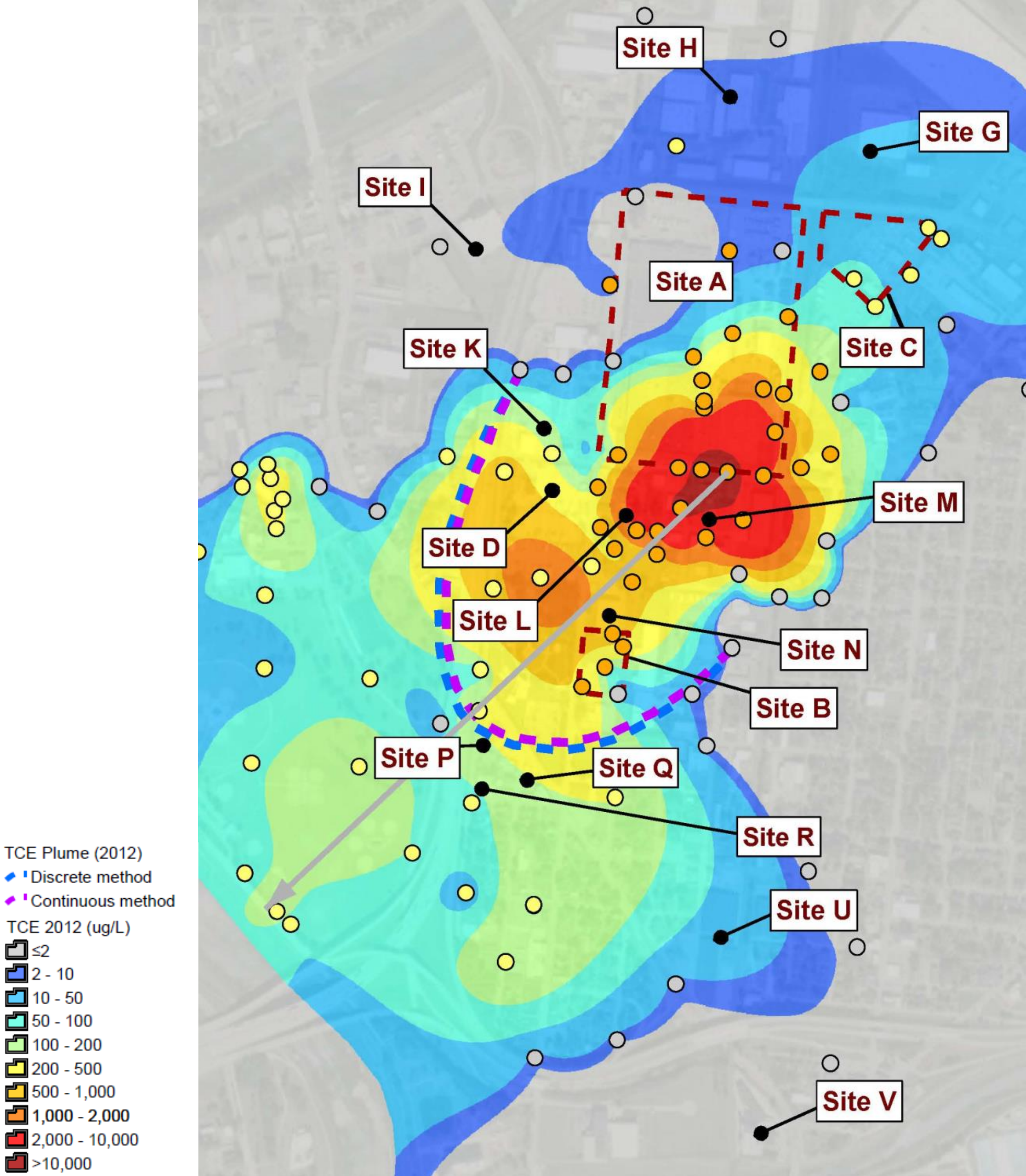
First-order decay curve for Site A TCE



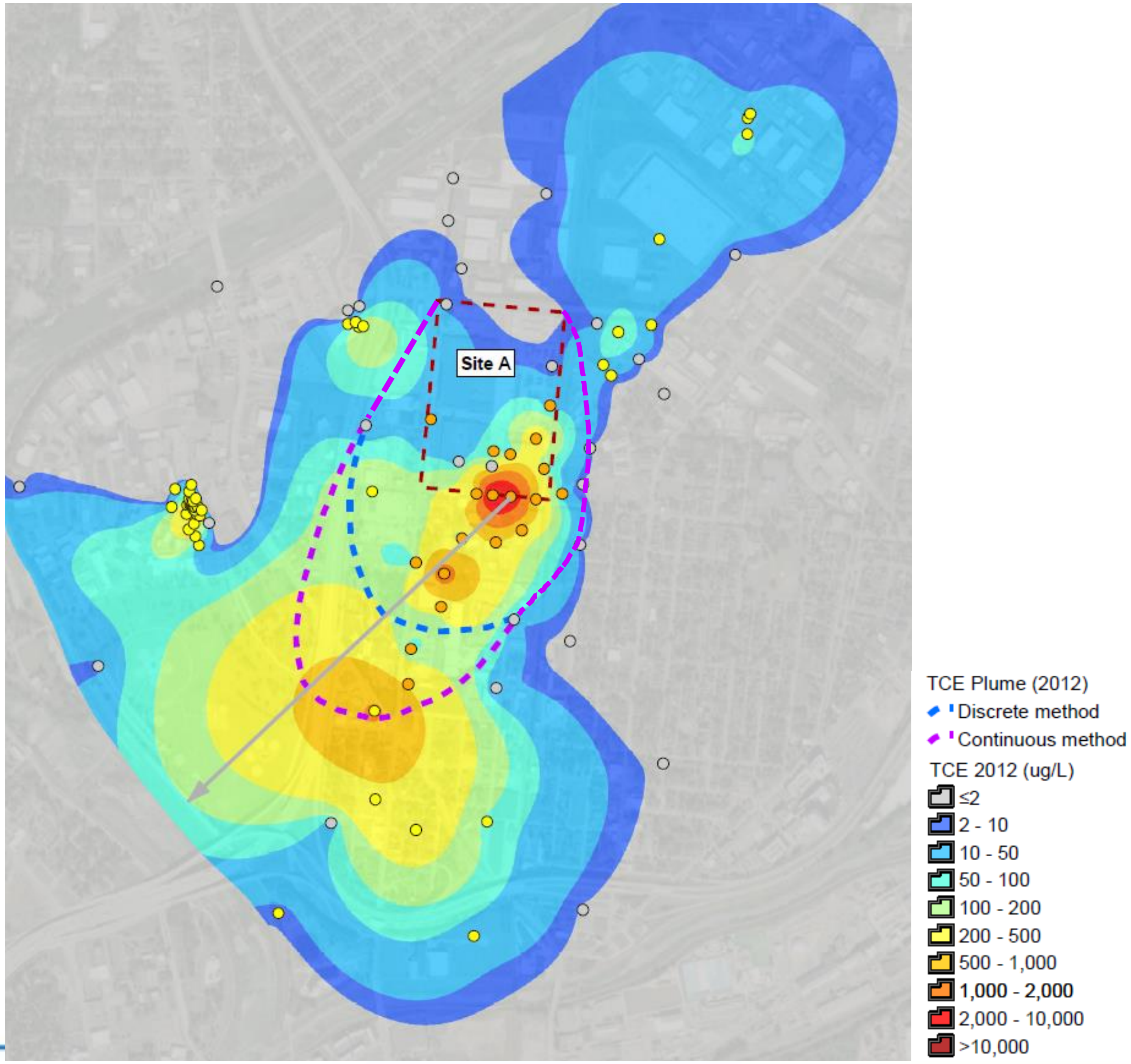


Use decay curve to extrapolate end of TCE plume (2 ppb) from Site A

- Extrapolate to 2 ppb along centerline to find end of Site A TCE plume
- Manually connect centerline to the edges of the plume
- Discrete and continuous extrapolations yielded similar plume lengths



Site A TCE plume delineation for sampling event 10 years later



- Fewer data yielded greater variability between discrete and continuous methods

Conclusions and suggestions for implementing

- Simple, easily implementable forensic method using existing, conventional data
- Works best with:
  - Consistent sampling locations over the years
  - Sampling locations along the centerline of the plume
- Recommend comparing discrete measured data and interpolated data from contouring program for better reliability of results

Thank you!

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REMTEC & EMERGING CONTAMINANTS SUMMIT

OCTOBER 15-17, 2024

Geologic Models Utilizing Environmental Sequence Stratigraphy: *An Essential Tool to More Effectively Remediate Contaminated Groundwater Sites*

Colin Plank, CPG

October 16, 2024

Agenda

1. *The Problem:* Subsurface complexity impacts performance and causes uncertainty.
2. *Addressing The Problem:* Types of geologic models in use
3. *Best Practice*: Environmental Sequence Stratigraphy (ESS)
    1. What it is and how it impacts a model's success.
4. Project Examples
5. Conclusions

The Problem: The Subsurface is Complex

Complexity Consists of:

Lithologic Heterogeneity

- Cumulative impacts of seemingly small features

Stratigraphic Geometry

- Reality vs. Interpreted Hydro stratigraphic unit continuity

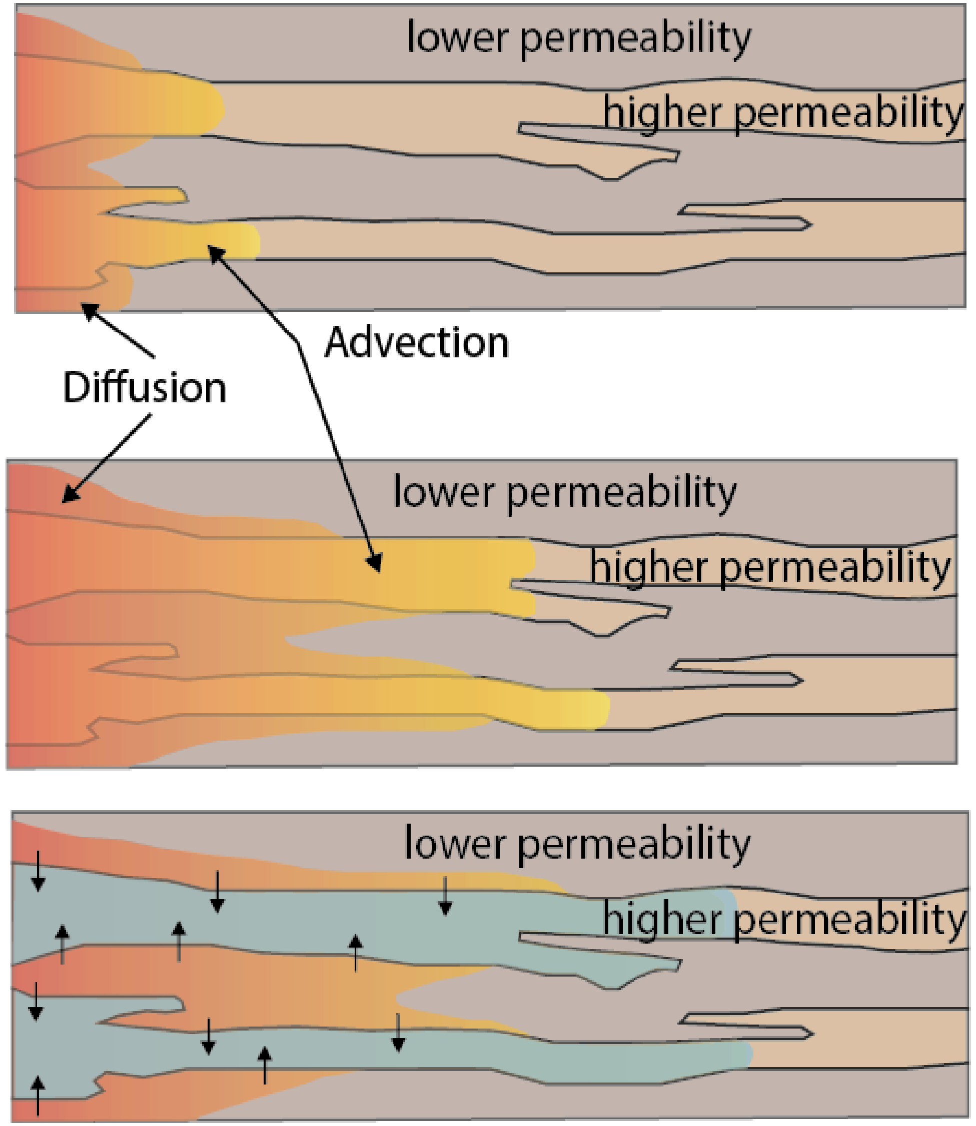
Van Etten Creek, Oscoda, MI

The Subsurface is *NOT* Homogeneous

Significance of Heterogeneity

Prolonged remediation time frames:

- Grainsize and Sorting Controls Hydraulic Conductivity (K)
- Back-diffusion of contaminant mass from fine-grained *storage zones* often occurs

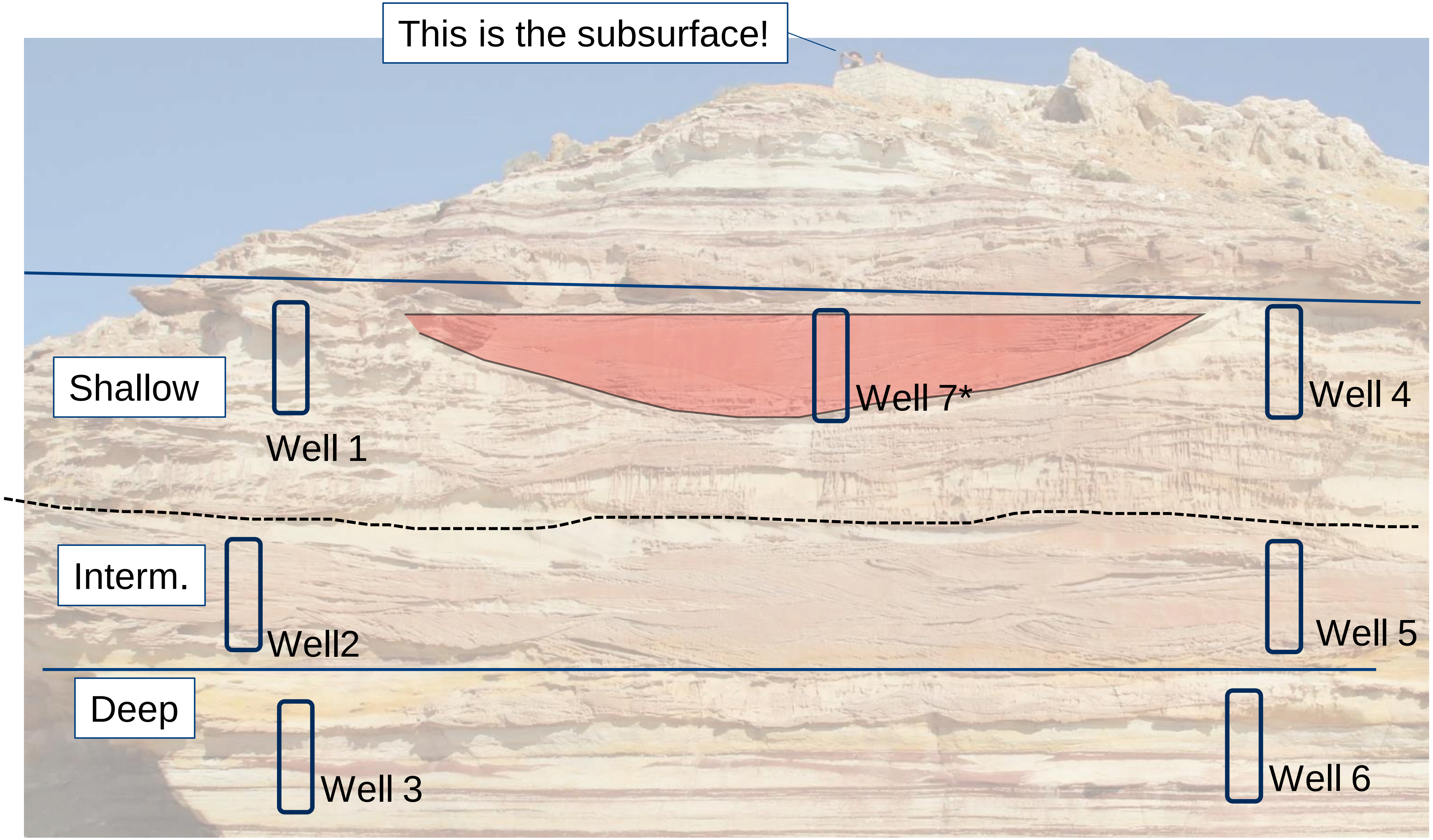


Modified from Gillham and Cherry, 1983, Fig. 10

Significance of Geometry

Impacts hydraulic connectivity, well performance, and/or amendment efficacy

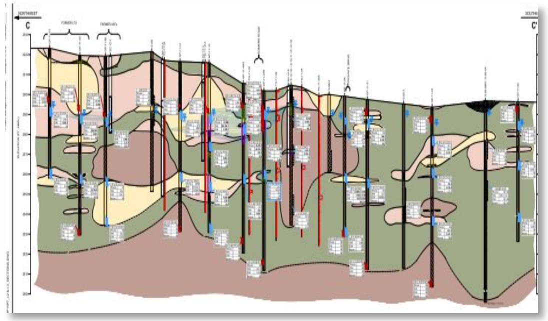
Why is Well 7 Off? Where Else on My Site Might I expect This?

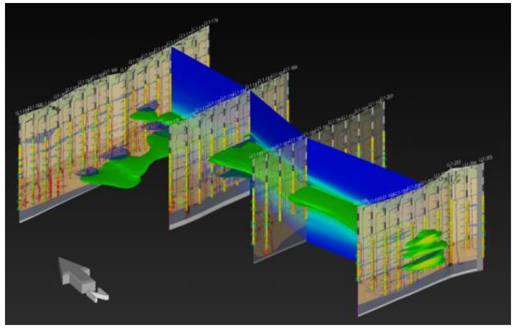


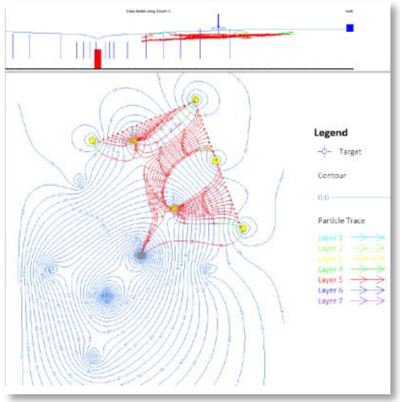
You Need A Better Geologic Model

Geologic Model Types In Use:

- Static Cross Sections and Maps:
  - 2D Conceptual/Lithostratigraphic Representations
- 3D Visualizations:
  - Predominately Lithostratigraphic & Analytical Interpolations
- Numerical Models:
  - Derive Geometry and Parameterization from Above



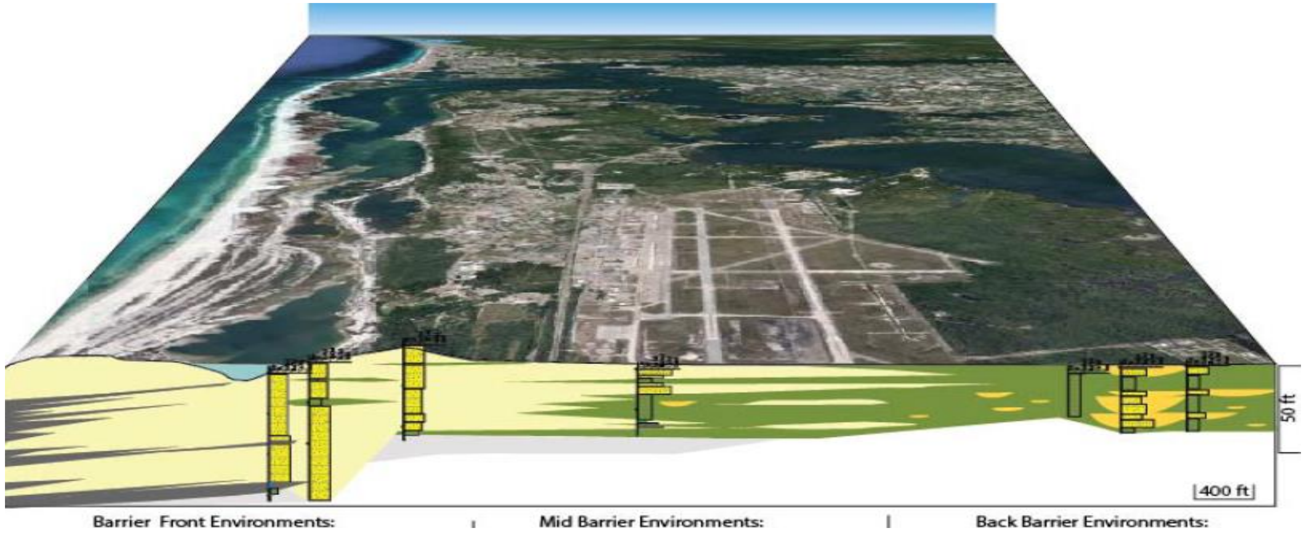


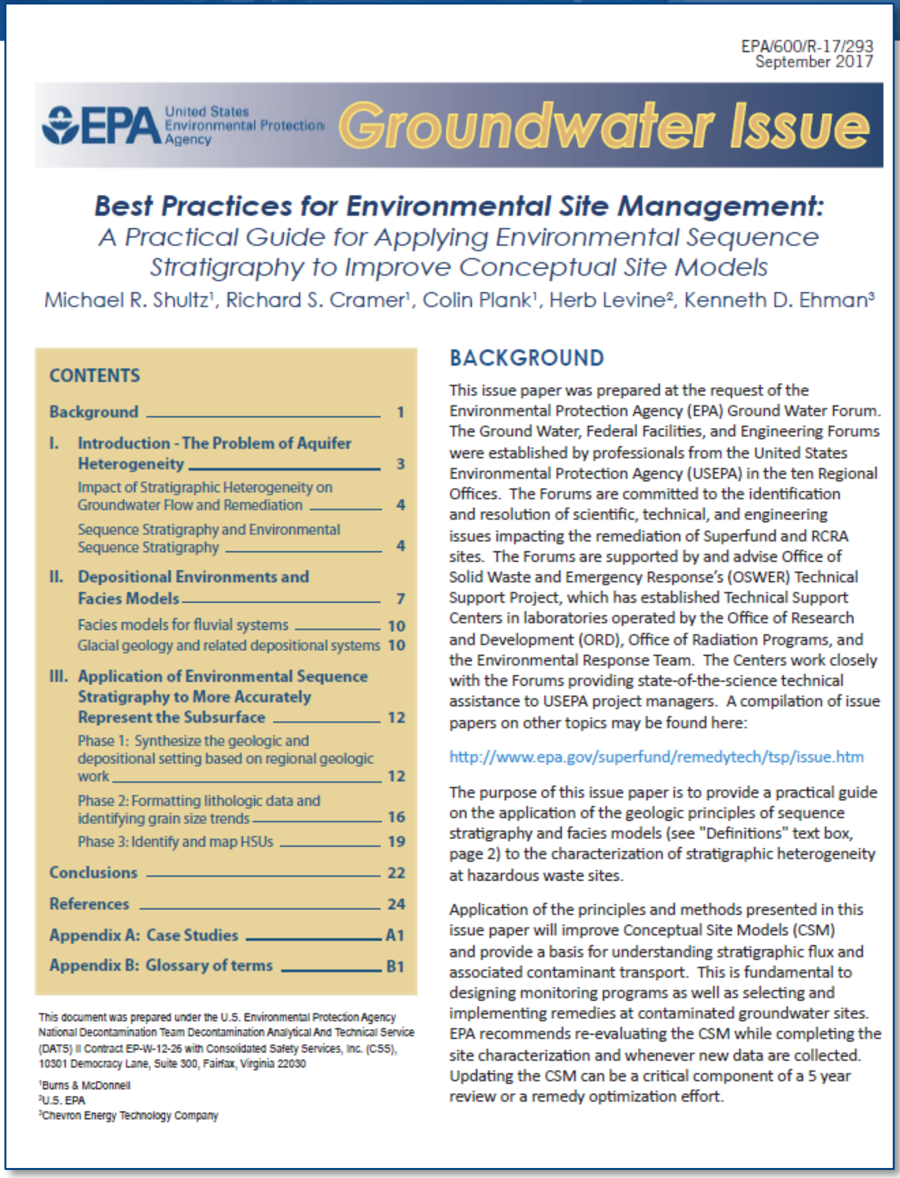


Environmental Sequence Stratigraphy (ESS):

Foundational Geology For A Stronger Geologic Model

- Use legacy data and understanding of depositional systems to build a predictive understanding of site stratigraphy
- Hypothesis testing guides investigation





EPA/600/R-17/293
September 2017

EPA United States Environmental Protection Agency **Groundwater Issue**

Best Practices for Environmental Site Management:
A Practical Guide for Applying Environmental Sequence Stratigraphy to Improve Conceptual Site Models

Michael R. Shultz[1], Richard S. Cramer[1], Colin Plank[1], Herb Levine[2], Kenneth D. Ehman[3]

CONTENTS

This document was prepared under the U.S. Environmental Protection Agency National Decontamination Team Decontamination Analytical And Technical Service (DATS) II Contract EP-W-12-26 with Consolidated Safety Services, Inc. (CSS), 10301 Democracy Lane, Suite 300, Fairfax, Virginia 22030

[1]Burns & McDonnell
[2]U.S. EPA
[3]Chevron Energy Technology Company

BACKGROUND

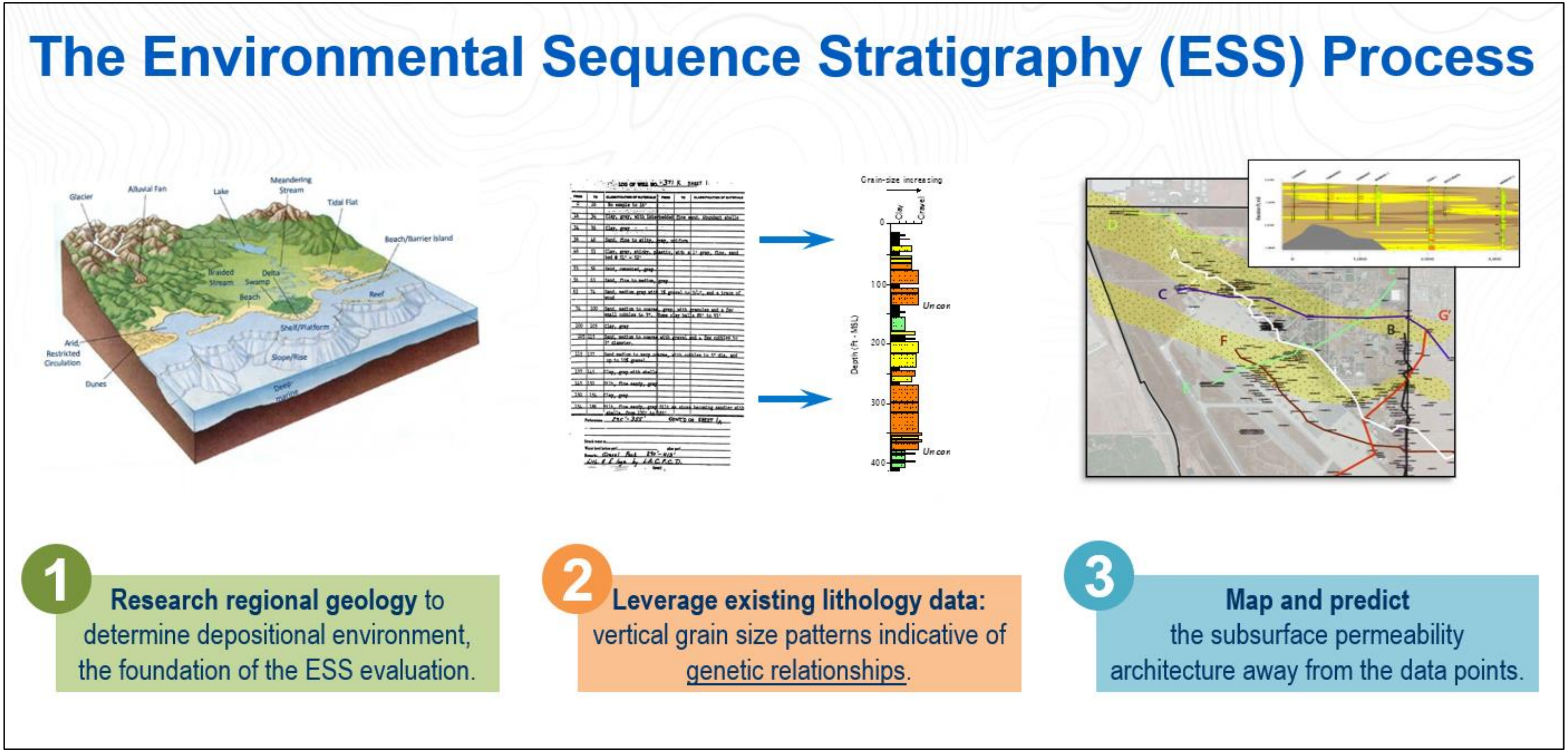
This issue paper was prepared at the request of the Environmental Protection Agency (EPA) Ground Water Forum. The Ground Water, Federal Facilities, and Engineering Forums were established by professionals from the United States Environmental Protection Agency (USEPA) in the ten Regional Offices. The Forums are committed to the identification and resolution of scientific, technical, and engineering issues impacting the remediation of Superfund and RCRA sites. The Forums are supported by and advise Office of Solid Waste and Emergency Response's (OSWER) Technical Support Project, which has established Technical Support Centers in laboratories operated by the Office of Research and Development (ORD), Office of Radiation Programs, and the Environmental Response Team. The Centers work closely with the Forums providing state-of-the-science technical assistance to USEPA project managers. A compilation of issue papers on other topics may be found here:

http://www.epa.gov/superfund/remedytech/tsp/issue.htm

The purpose of this issue paper is to provide a practical guide on the application of the geologic principles of sequence stratigraphy and facies models (see "Definitions" text box, page 2) to the characterization of stratigraphic heterogeneity at hazardous waste sites.

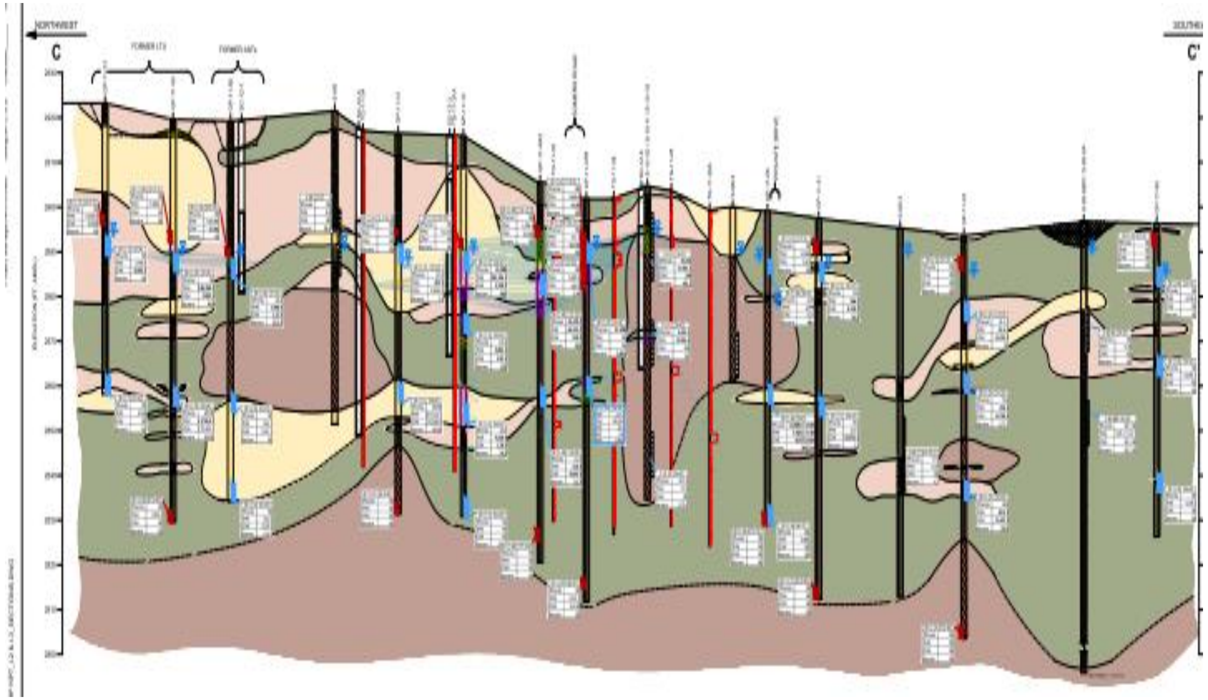
Application of the principles and methods presented in this issue paper will improve Conceptual Site Models (CSM) and provide a basis for understanding stratigraphic flux and associated contaminant transport. This is fundamental to designing monitoring programs as well as selecting and implementing remedies at contaminated groundwater sites. EPA recommends re-evaluating the CSM while completing the site characterization and whenever new data are collected. Updating the CSM can be a critical component of a 5 year review or a remedy optimization effort.

ESS Methodology

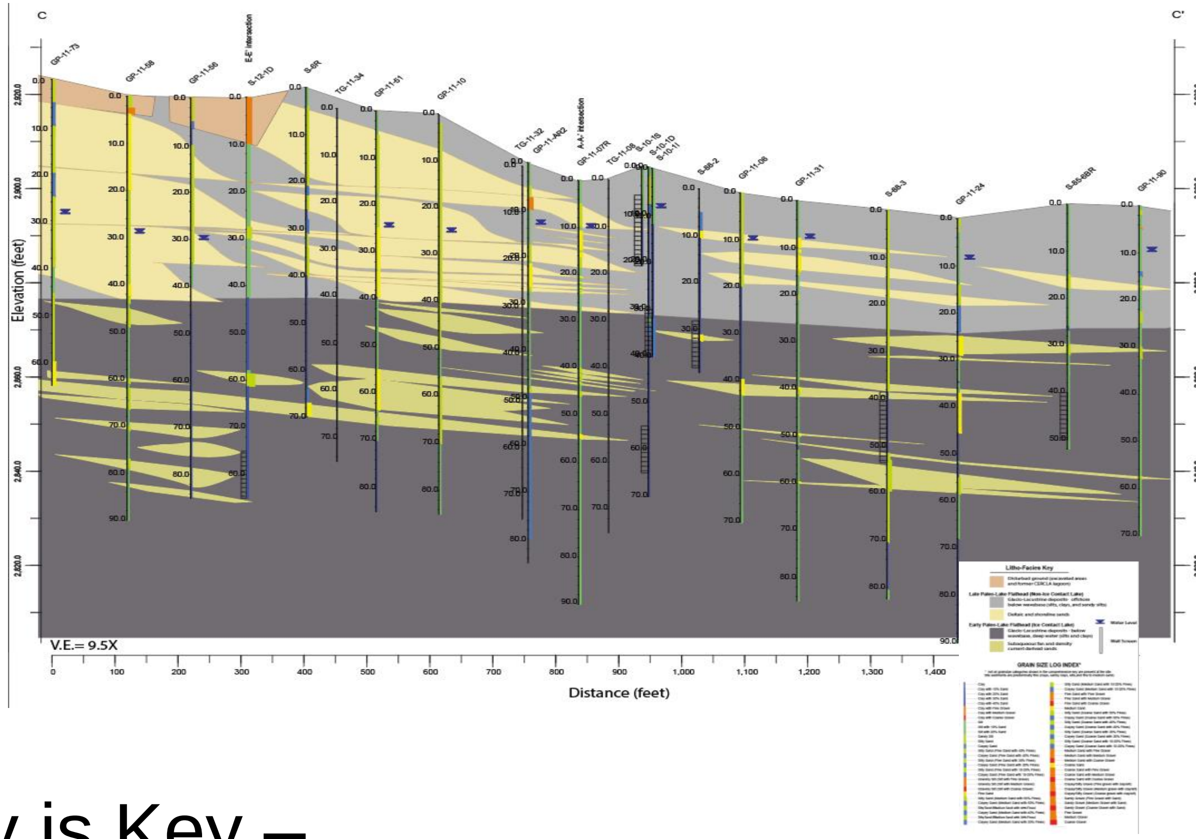


ESS Can Improve All Model Types Because It Impacts Foundational Geologic Interpretation

Before ESS USCS Codes and No Facies Analogue



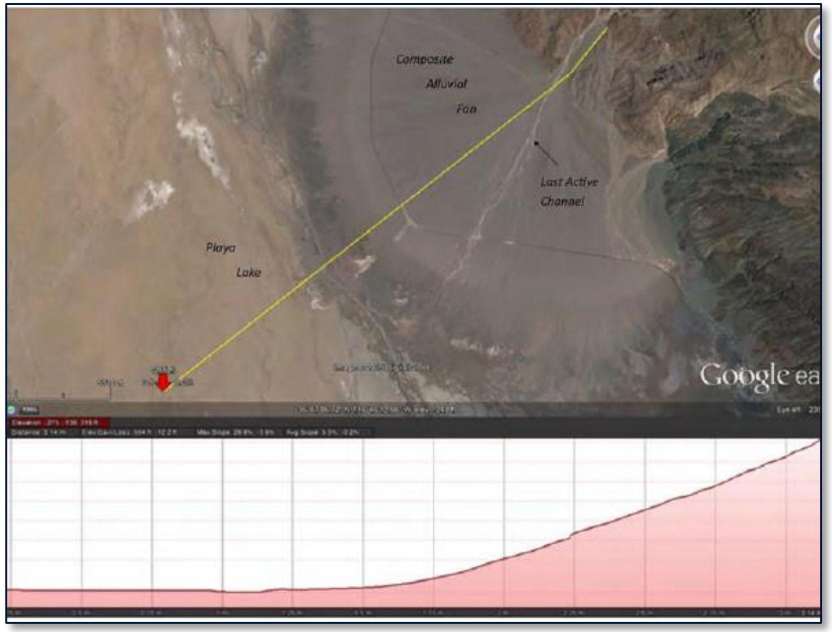
After ESS- Lacustrine/Deltaic Facies Correlations



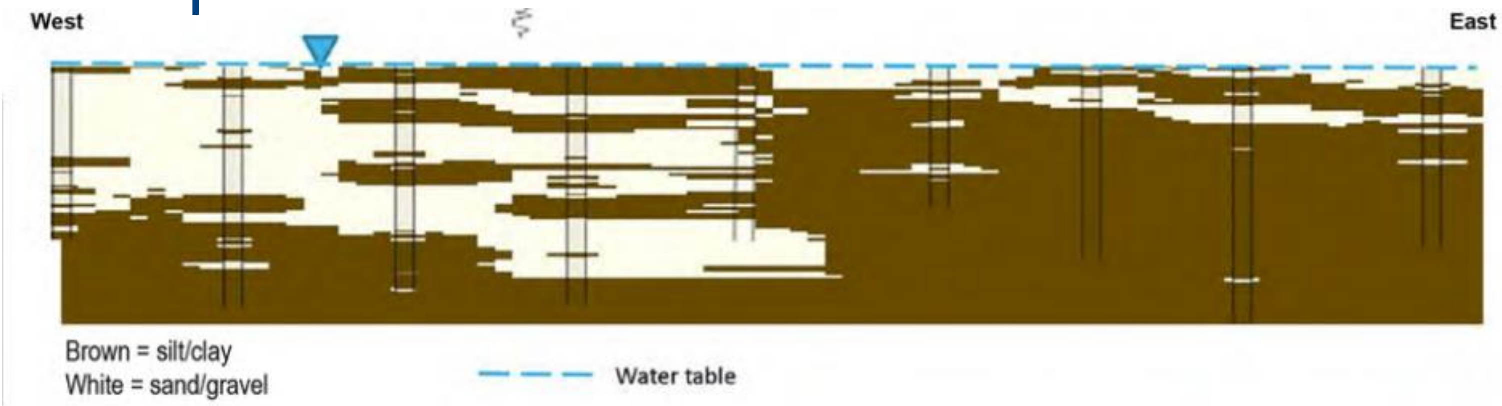
Facies-Based Stratigraphic Geometry is Key – Predictive Value.

Using ESS Correlations to Improve or Replace Lithologic Interpolation

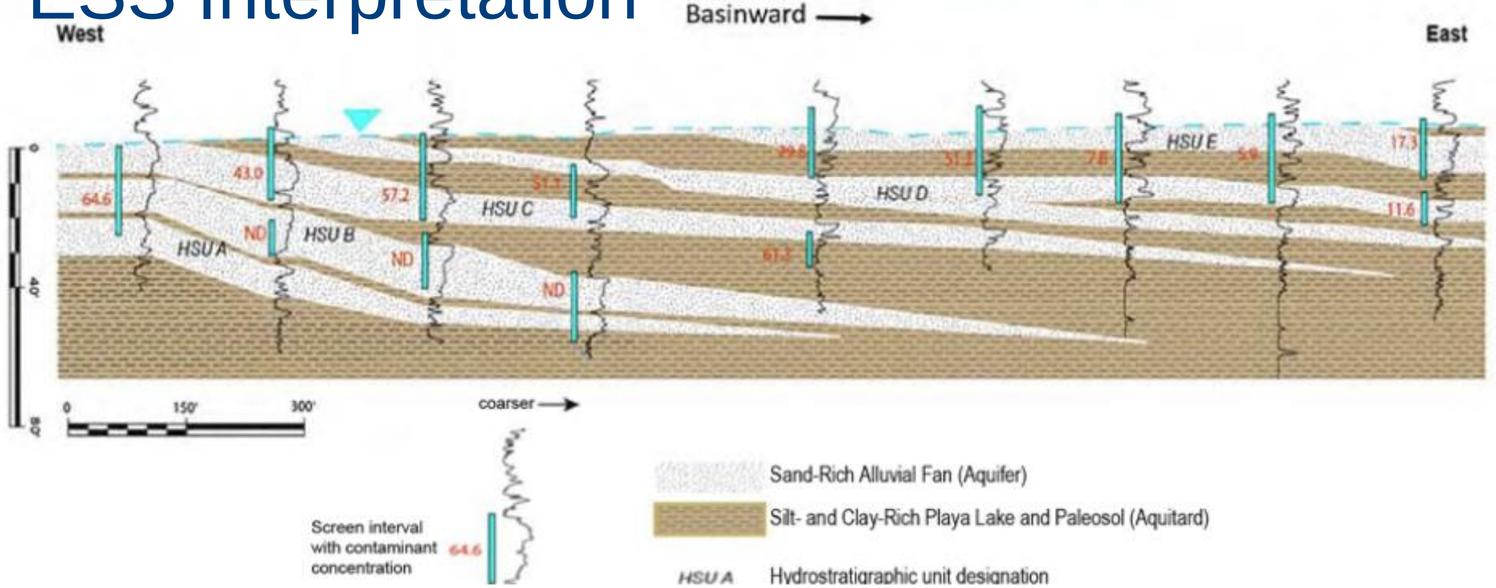
Modern Fan



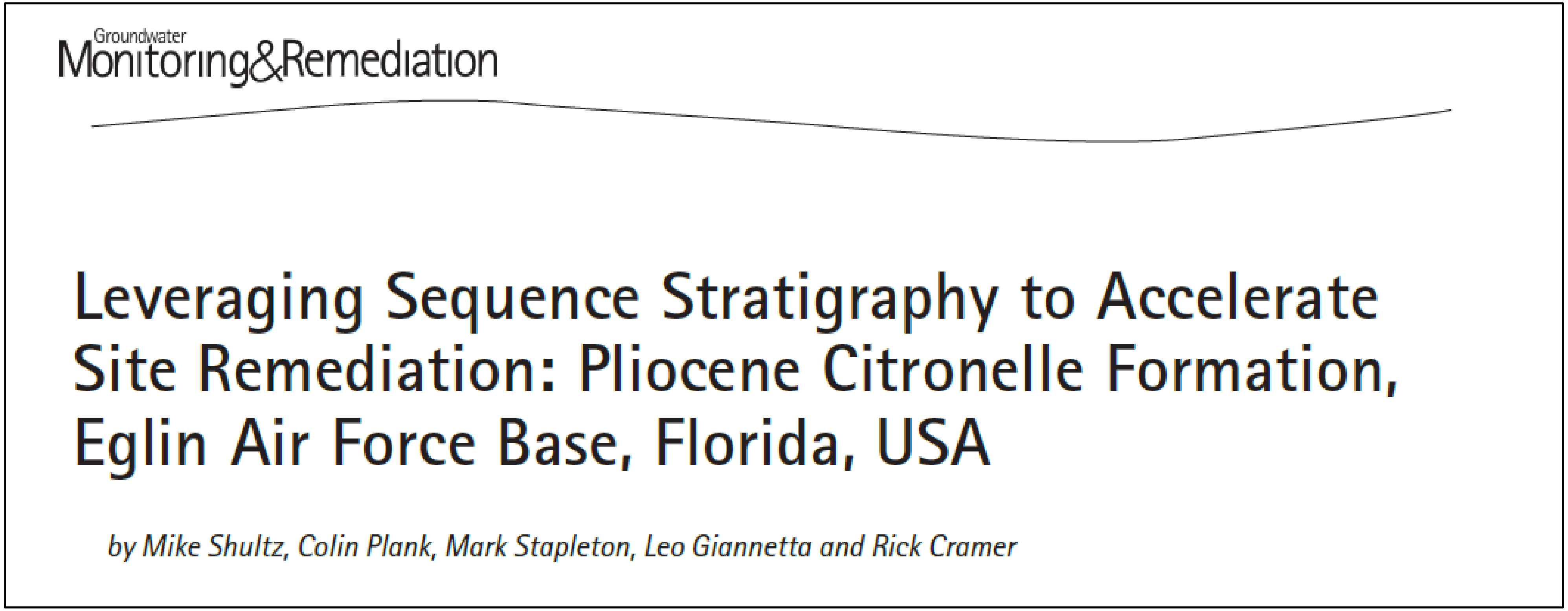
Interpolation



ESS Interpretation



Using ESS to Inform Numerical Modeling and Optimize Remediation

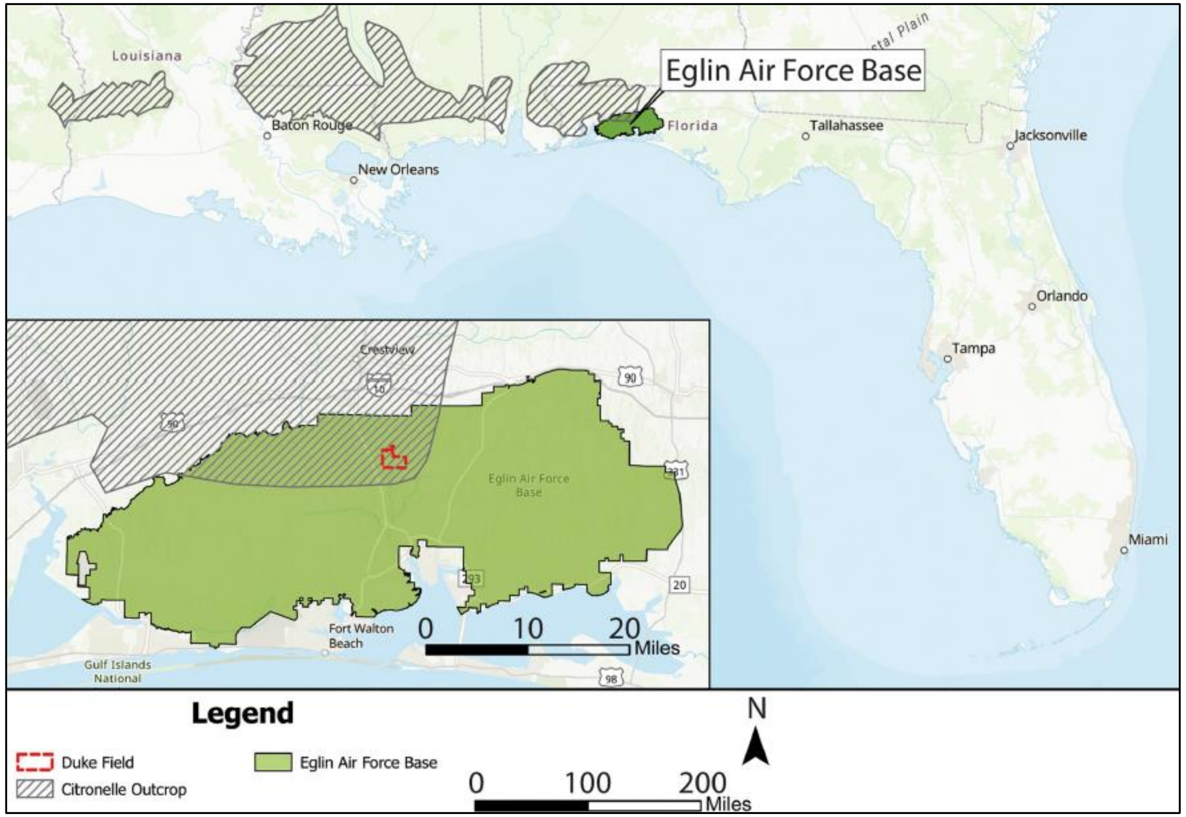

Groundwater Monitoring&Remediation

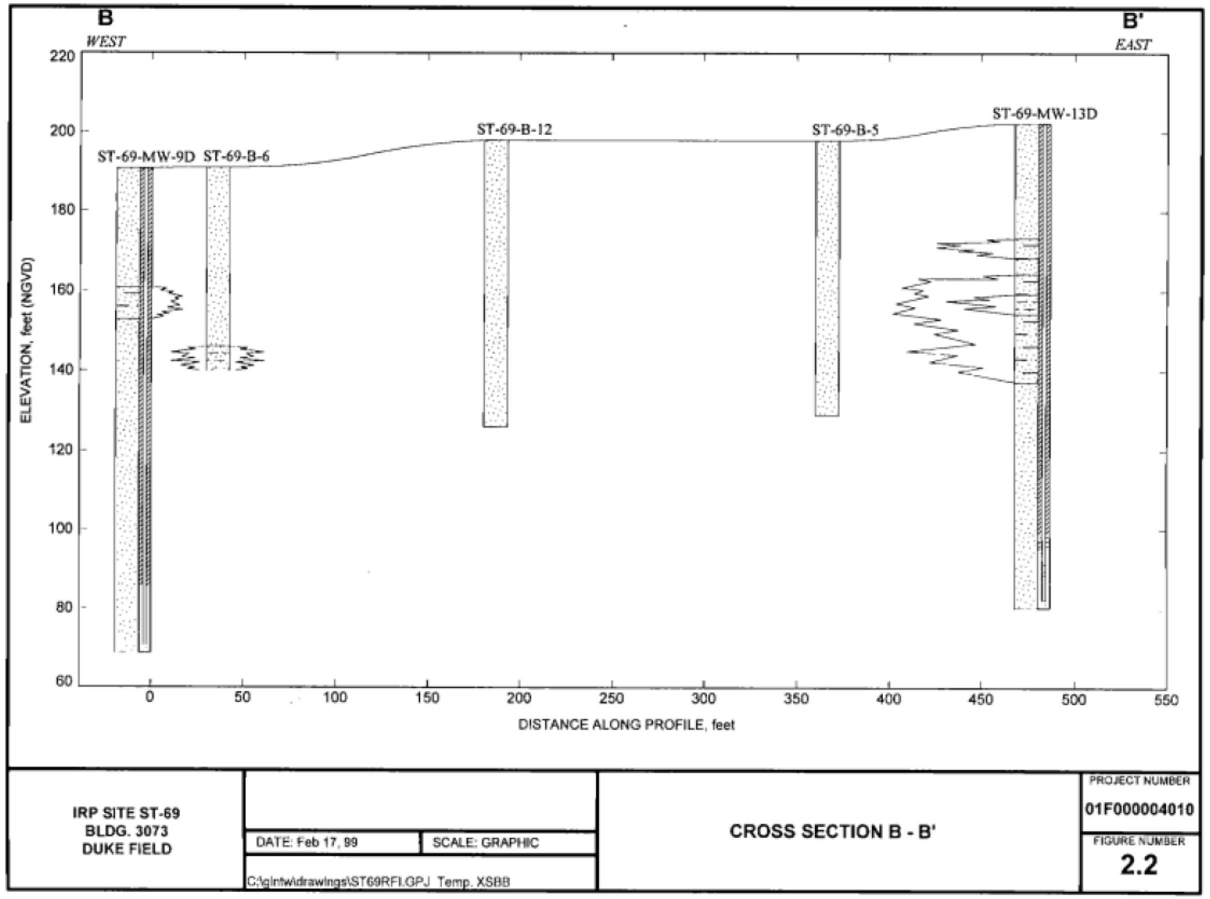
Leveraging Sequence Stratigraphy to Accelerate Site Remediation: Pliocene Citronelle Formation, Eglin Air Force Base, Florida, USA

by Mike Shultz, Colin Plank, Mark Stapleton, Leo Giannetta and Rick Cramer

Groundwater Monitoring & Remediation 43, Summer 2023, pages 79–92

Using ESS to Inform Numerical Modeling and Optimize Remediation

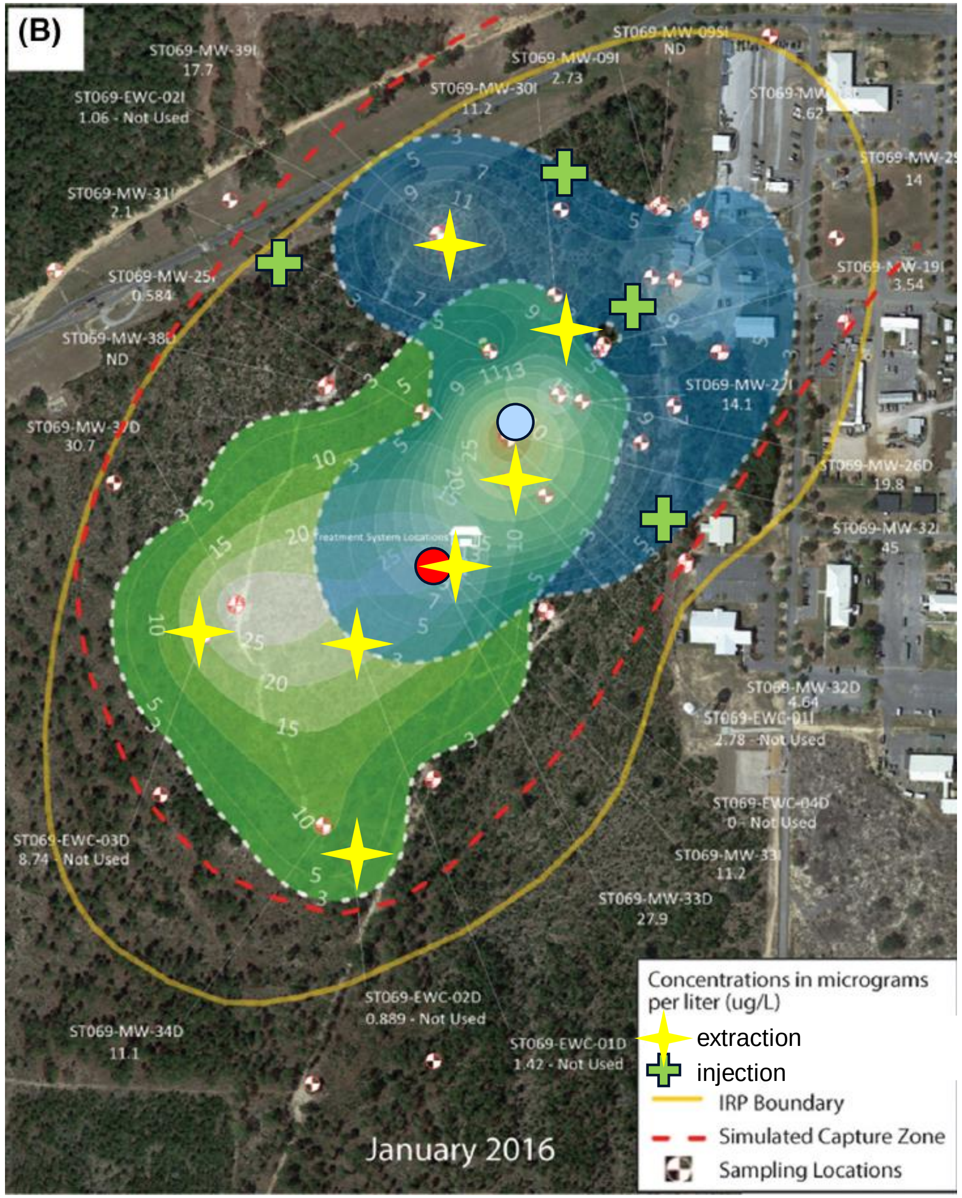


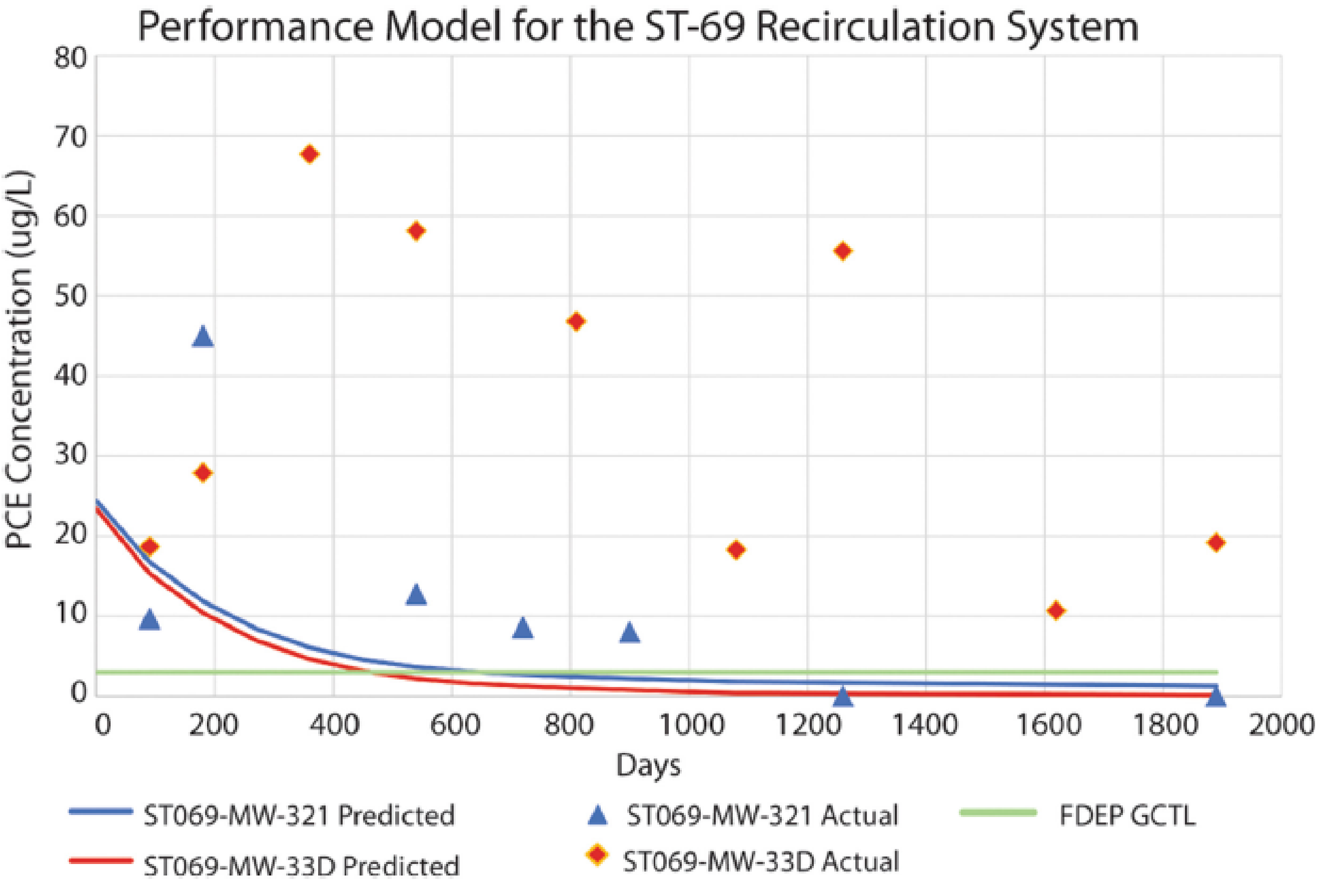


Geologic Model: Site is a sandbox

Numerical Model Assumptions: Homogeneous and Isotropic

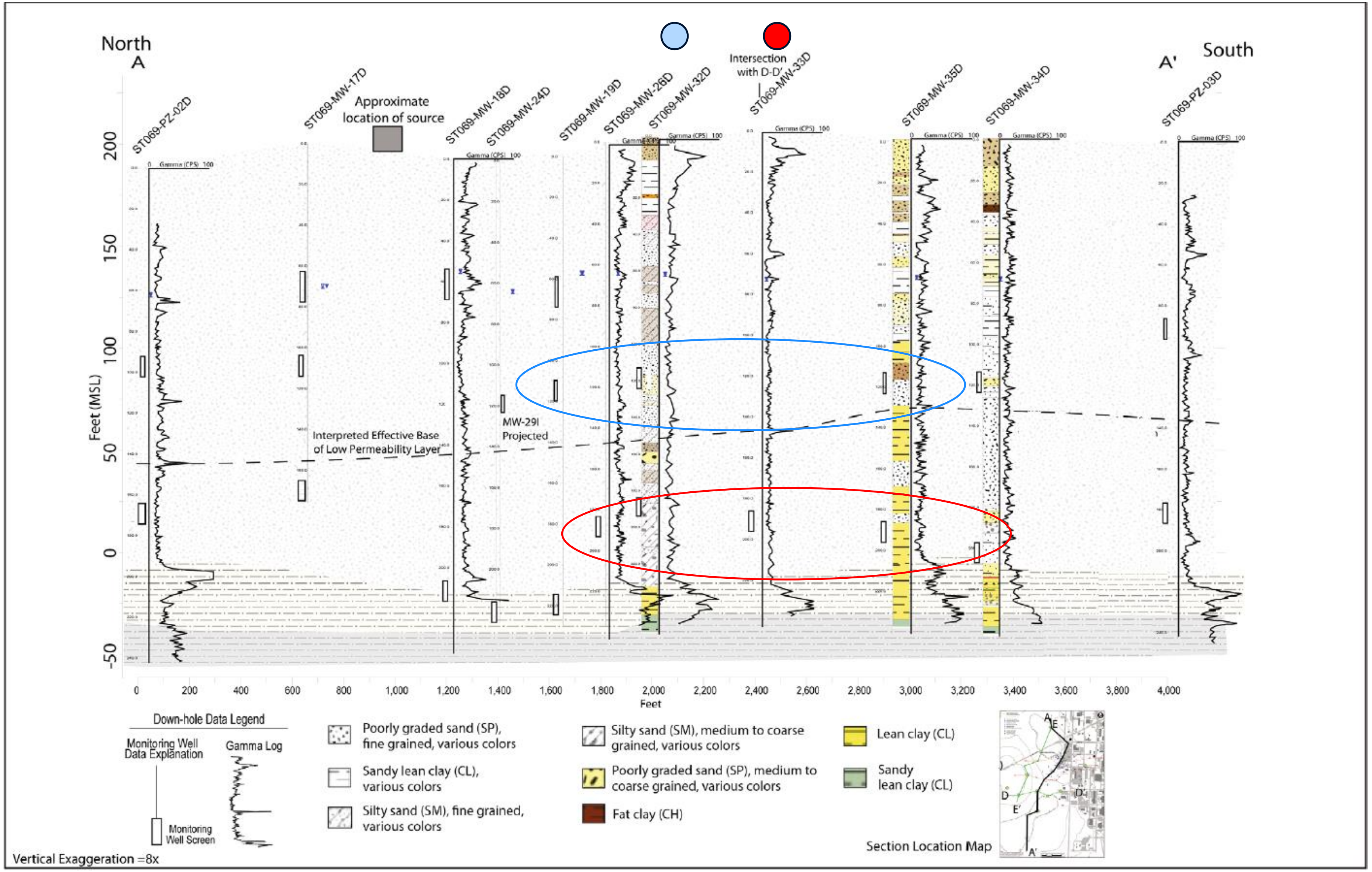
PCE Pump and Treat Remediation System Not Meeting Predicted Performance Goals





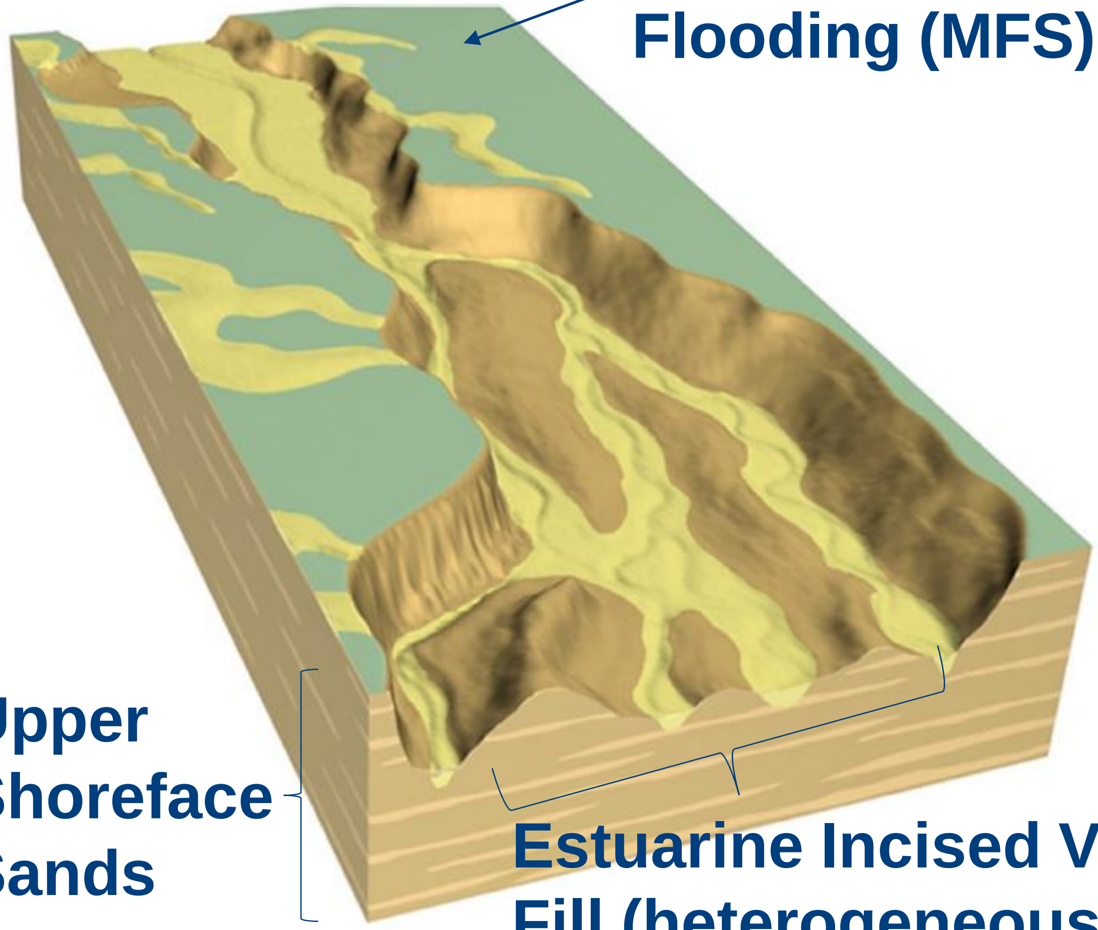
ModFlow and PEST modeling predicted total Plume Capture

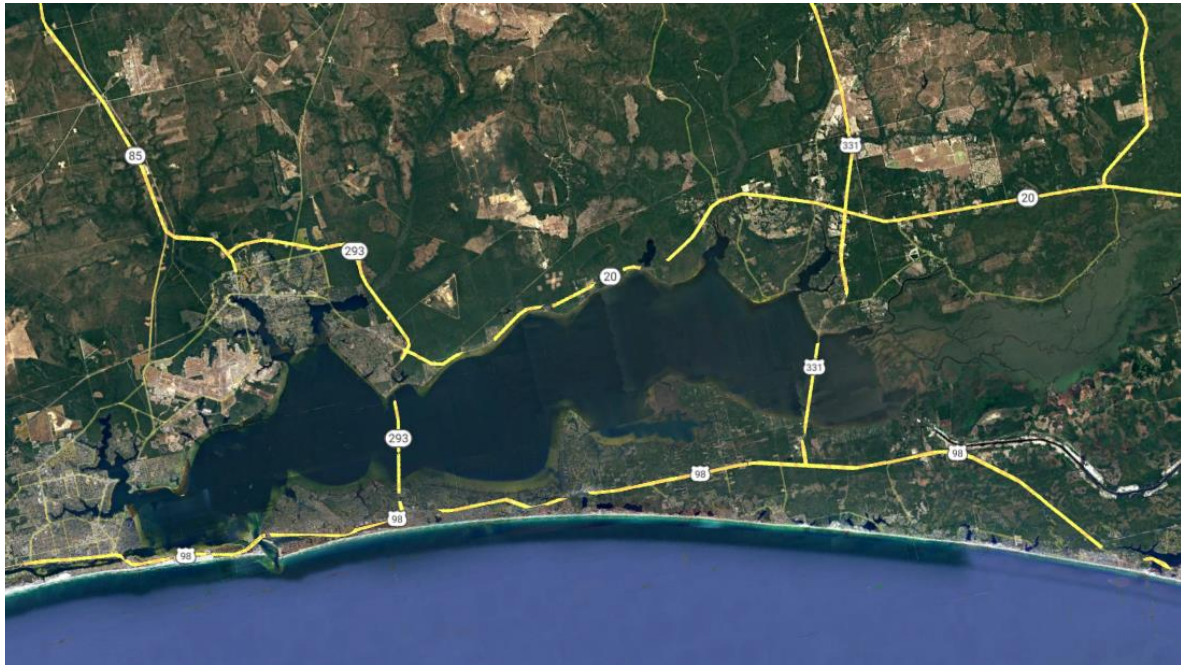
Existing Sections Did Not Effectively Correlate or Communicate Key Features



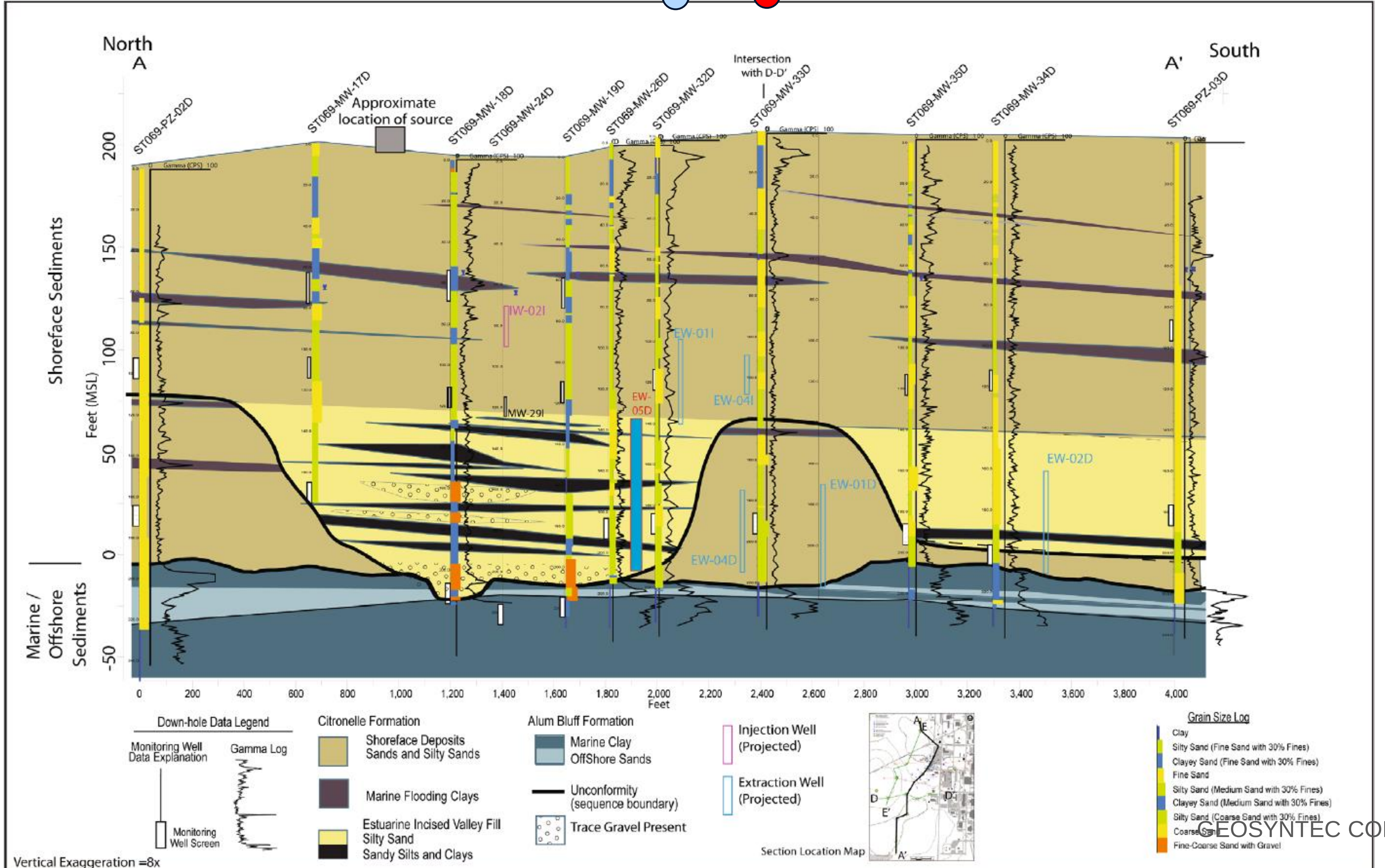
- Lith. logs indicated some heterogeneity
- Gamma indicated some seemingly insignificant clays
- A loose shallow, intermediate, and deep zonation being used

General Facies Model and Two Key Site Features

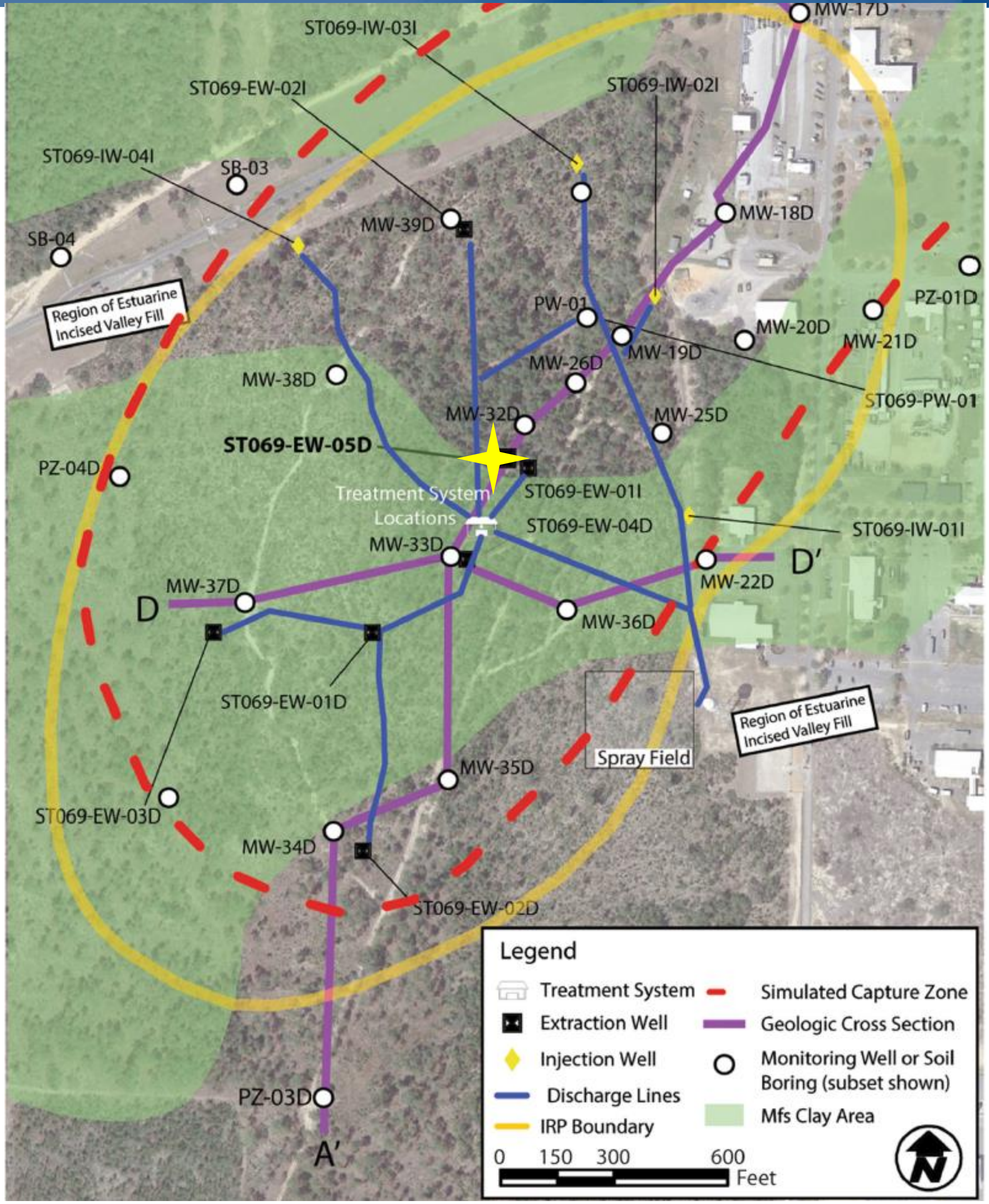


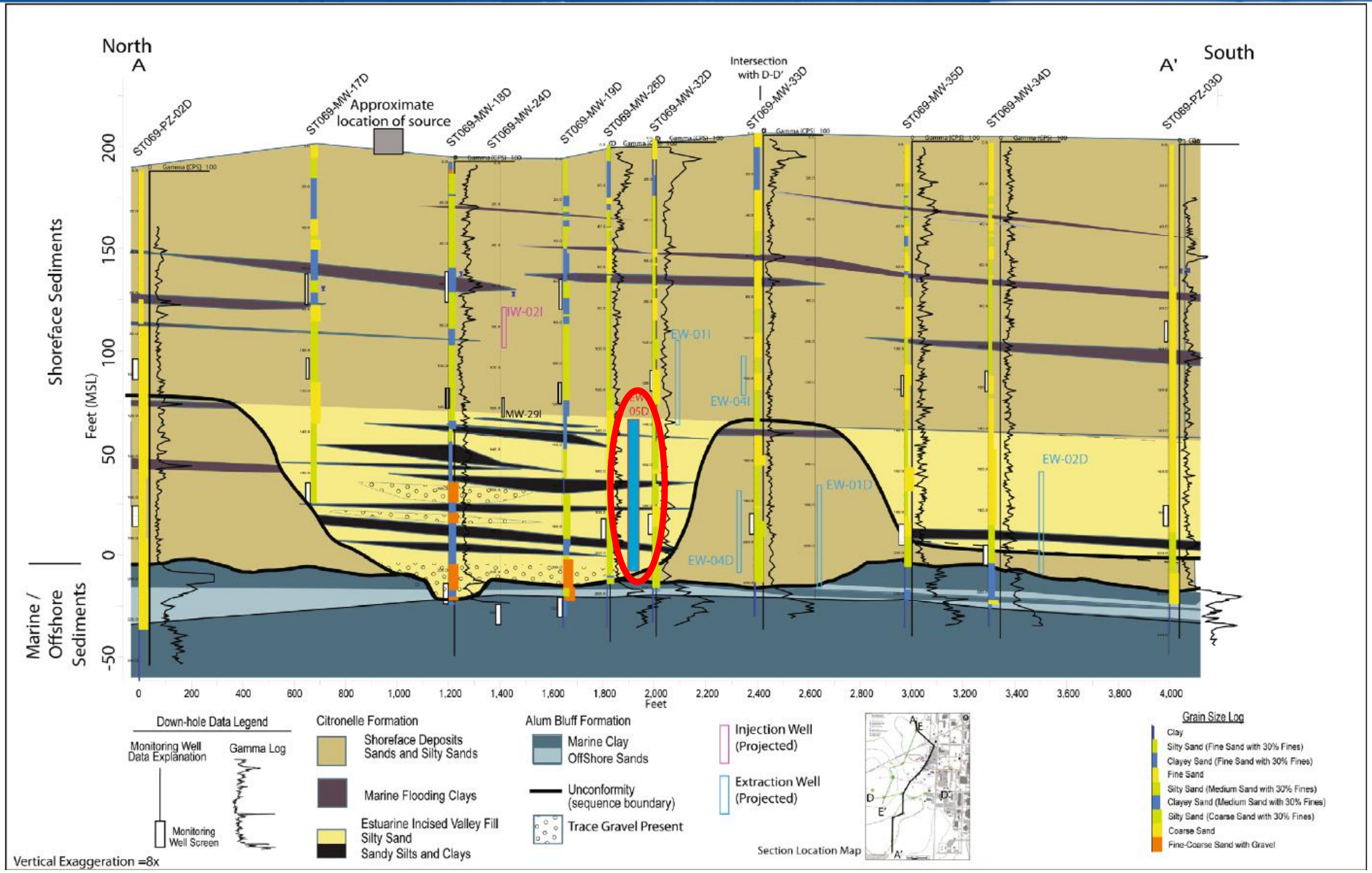


ESS Analysis Reveals and Communicates Key Features

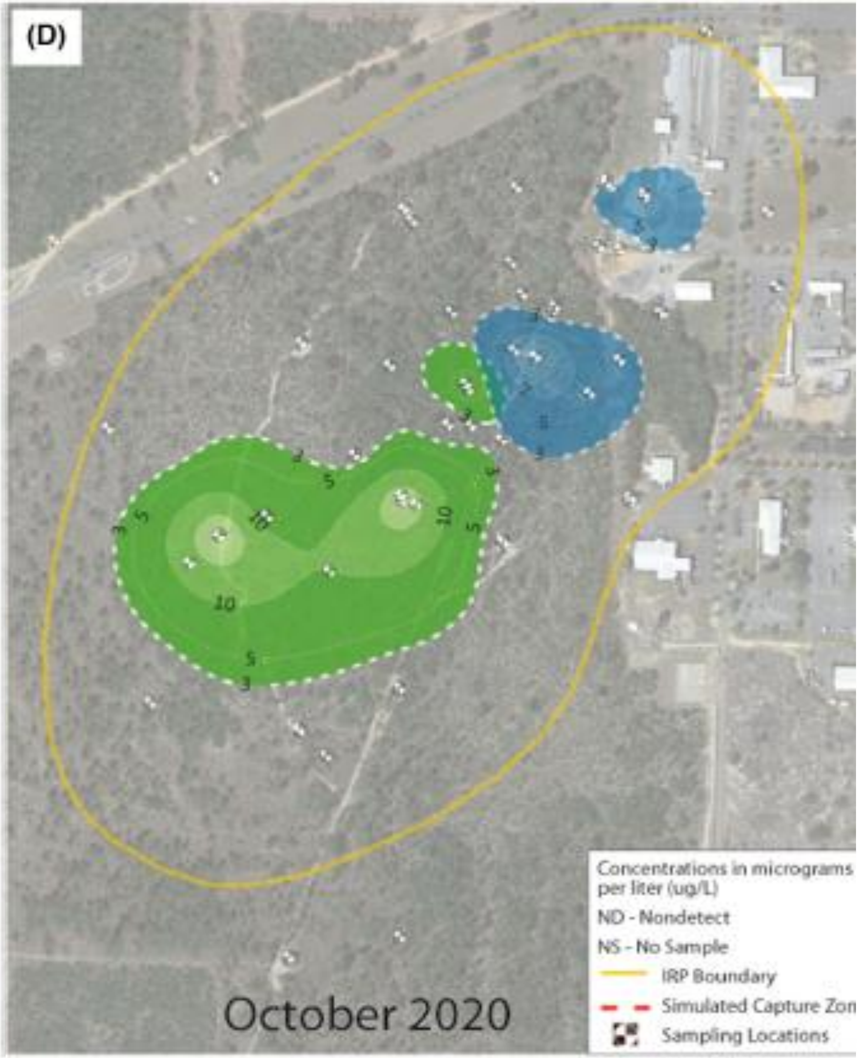


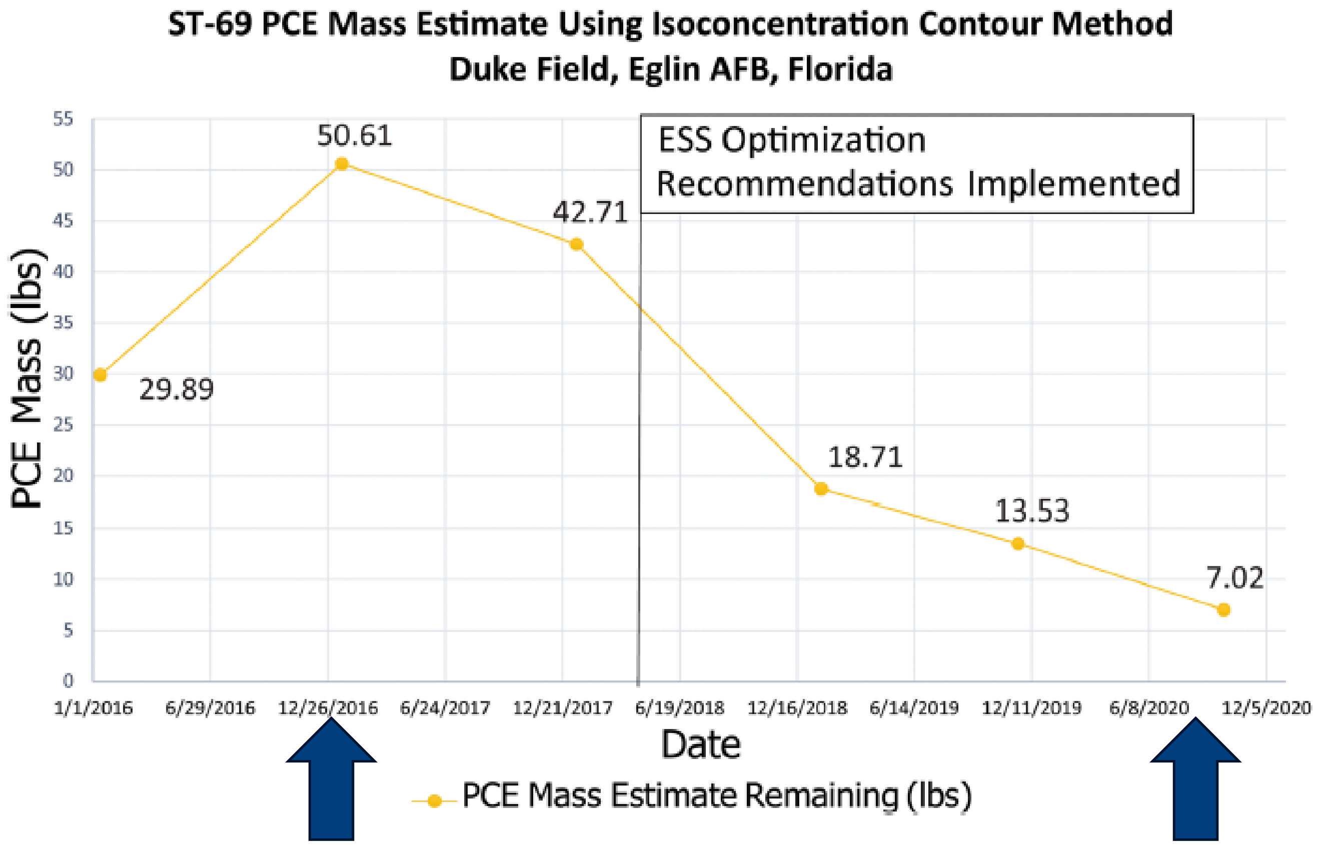
Mapping Leads to Single Targeted Additional Extraction Well





Evolution of PCE Plume Mass Post ESS Optimization





Conclusion : A Robust Geologic Model is Key to Success

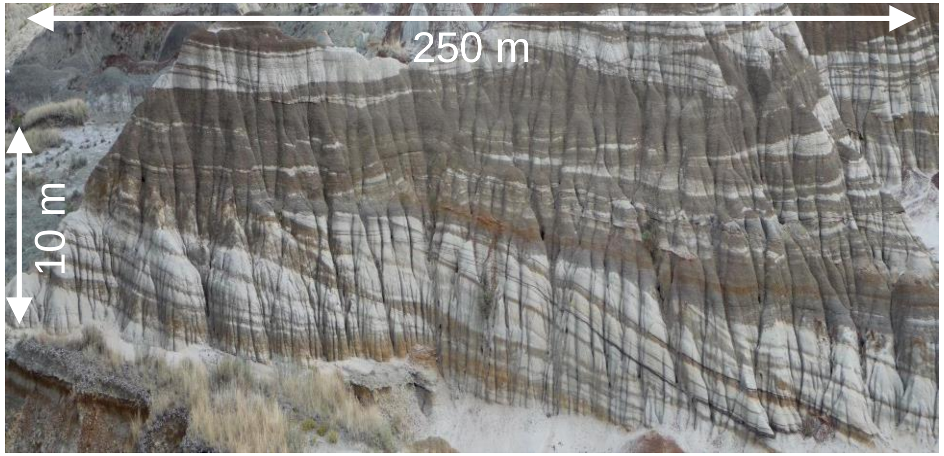
Every site has a conceptual model in use, whether you deliberately created one or not:

- **“The A-Sand, The B-Sand….”**
- **“Shallow, Intermediate, and Deep”**
- **“The Site is a Sandbox…”**

None of these are particularly geologic…

The question is, “Is your model based on…

- **Trial and error learning?**
- **Inherited site lore?**
- **USCS code interpolations? OR**
- **Sound stratigraphic hypotheses and the predictive framework that results?**



Thank You!

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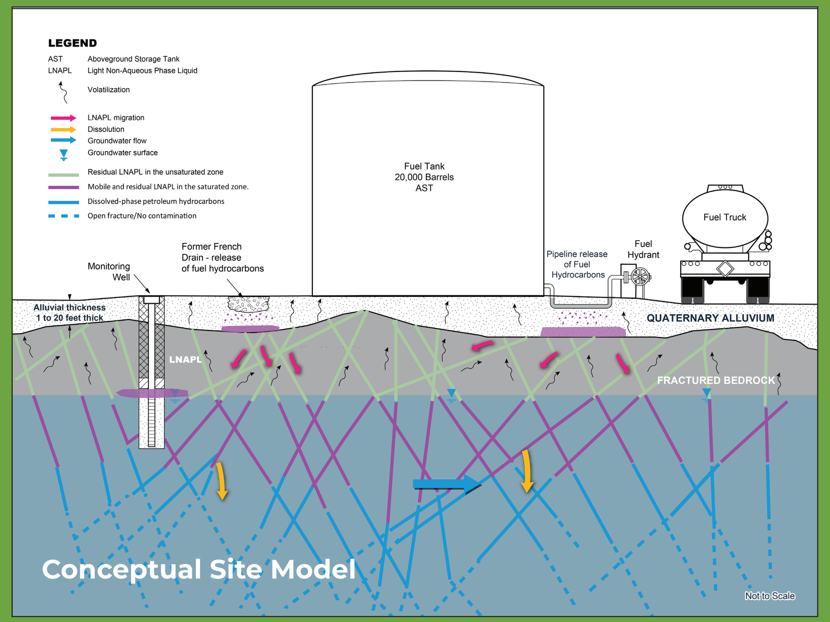
GROUP 1

Natural Source Zone Depletion and the Challenges of Fractured Bedrock Assessments

John Gomez
Staff Engineer
Ventura, CA, USA

ONEIDA ESC Group

LOCATION

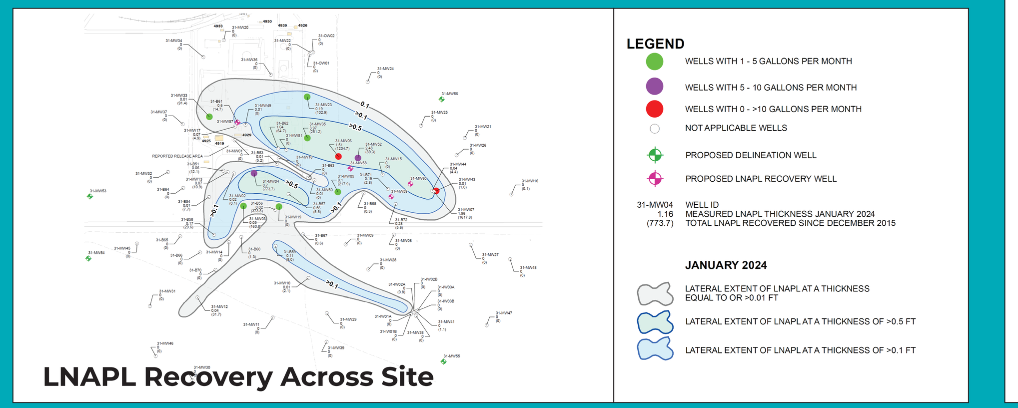


Conceptual Site Model

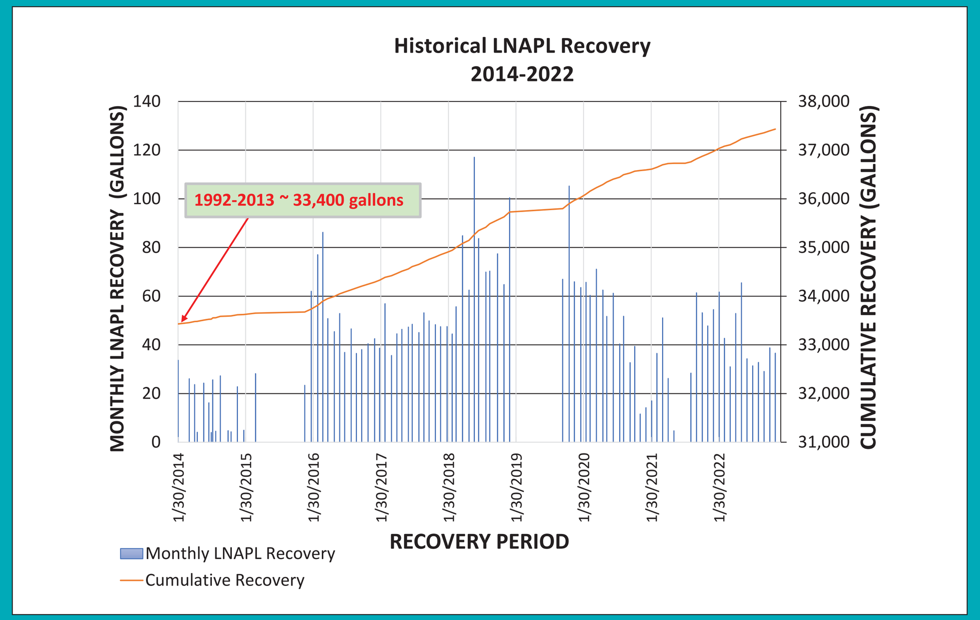
The former fueling facilities at the site were installed in 1956 over approximately 30 acres and comprised of multiple 8,000- and 10,000- to 20,000-barrel aboveground storage tanks (ASTs) associated with fuel stands and hydrants, filter separators and pump houses. The larger ASTs stored JP-4 until 1993 and then stored JP-8; the 8,000-barrel ASTs stored JP-7. The JP-4 fuel line was replaced with the JP-8 line in 1993. Most of the fueling facilities at the site were decommissioned beginning in December 2015 and replaced with new fueling facilities. Both the JP-4 and JP-8 pipelines were abandoned in place and sealed with grout slurry.

GOALS

- Verify LNAPL biodegradation
- Assess the LNAPL plume biodegradation rate
- Update LNAPL conceptual site model
- Evaluation of seasonal changes in the LNAPL biodegradation rate
- Approximate the annual LNAPL biodegradation rate at the Site to compare to mechanical removal methods.

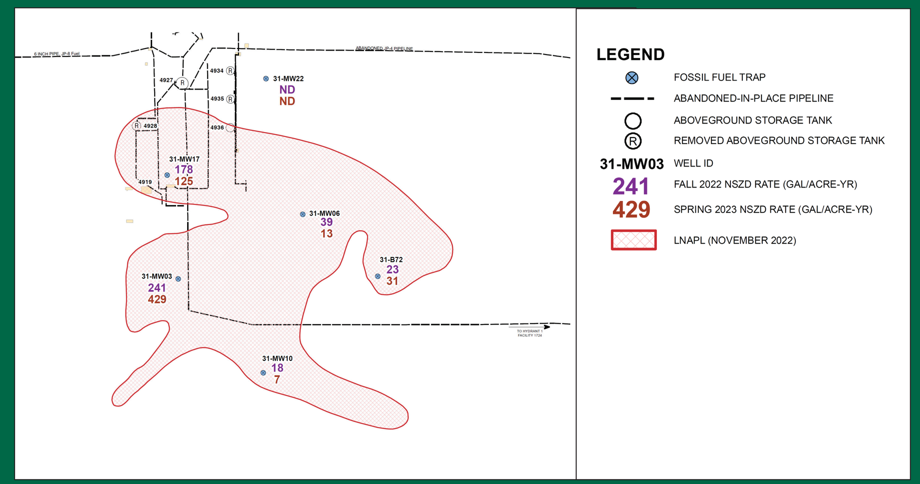


LNAPL Recovery Across Site



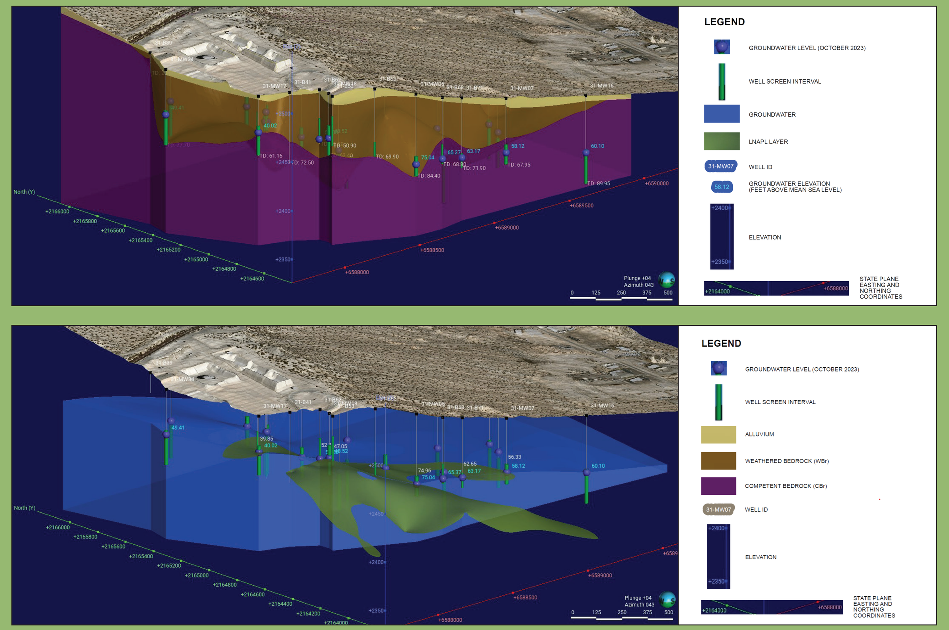
FINAL IMPLEMENTATION

NSZD Trap Locations and Results



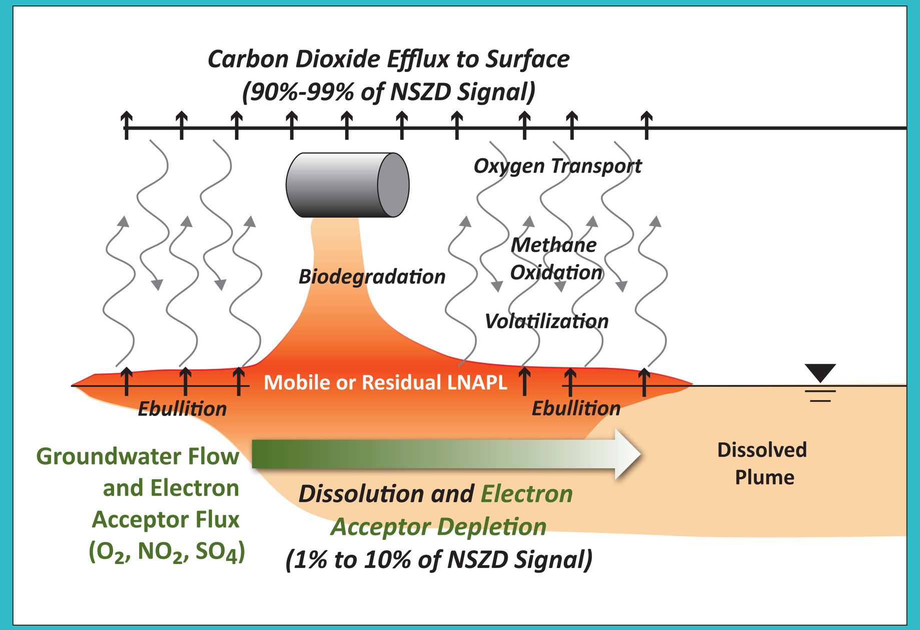
Two locations with high potential for elevated CO_2 flux were selected (31-MW17 and 31-MW06), two locations with medium potential (31-MW03 and 31-MW10), one location with low potential (31-B72), and one location outside of the LNAPL plume closest to 31-MW22 to serve as a background location. To investigate seasonal variation, the same locations were used for the November 2022 (fall) and March/April 2023 (spring) events with a goal for each period of deploying the traps for a period of 14 days.

GEOLOGY



The geology below the site is a complex fractured bedrock environment. The distinction between the weathered and competent bedrock is based on fracture density and weathering observed in the fractures from rock cores and from surface- and downhole-geophysical surveys. Geophysical surveys identified local faulting and a predominant fracture orientation of northeast-southwest (NE-SW) and northwest-southeast (NW-SE). Fractures are in some cases highly weathered and dip at a high angle and can be nearly vertical. Some boring logs have also identified nearly horizontal saprolite zones indicative of low-angle faulting or exfoliation surfaces common in granitic bedrock environments.

NATURAL SOURCE ZONE DEPLETION (NSZD)



NSZD is a three-part process whereby compounds that comprise light non-aqueous phase liquid (LNAPL)are lost from the subsurface due to naturally occurring processes of dissolution, volatilization, and biodegradation. Carbon dioxide (CO_2) is the byproduct of LNAPL biodegradation and/or aerobic degradation of methane formed from LNAPL biodegradation. Subsurface generation of CO_2 above background levels is direct evidence of biodegradation and the verification and quantification of the rate of degradation is the focus of this study. Research has shown that the biodegradation capacity of dissolved-phase petroleum hydrocarbons in the aqueous phase is a small fraction of what potentially can be degraded via methanogenesis of LNAPL.

RESULTS - CHALLENGES OF FRACTURED ROCK

Well ID	NSZD			
	Fall 2022		Spring 2023	
	CO_2 Flux	Equivalent NSZD Rate	CO_2 Flux	Equivalent NSZD Rate
	µmol m^{-2} s^{-1}	gal $acre^{-1}$ $year^{-1}$	µmol m^{-2} s^{-1}	gal $acre^{-1}$ $year^{-1}$
31-B72	0.04	23	0.05	31
31-MW03	0.38	241	0.72	429
31-MW06	0.06	39	0.02	13
31-MW10	0.03	18	0.01	7
31-MW17	0.28	178	0.21	125
31-MW22	ND	ND	ND	ND
Average NSZD Rate Across the Year (gal $acre^{-1}$ $year^{-1}$)	99.8		121	
Estimated LNAPL Plume Area (acres)	32.47			
Estimated Resulting NSZD Flux Rate (gal $year^{-1}$)	3,241		3,929	
Average NSZD Flux Rate Across Fall and Spring Events (gal $year^{-1}$)	3,585			

Definitons
µmol m^{-2} s^{-1} - micromoles per square meter per second
CO_2 - carbon dioxide
DTW - depth to water
ft - feet
gal $acre^{-1}$ $year^{-1}$ - gallon per acre-year
ID- Identification
LNAPL - Light Nonaqueous Phase Liquid
ND- not detected
NSZD- Natural Source Zone Depletion

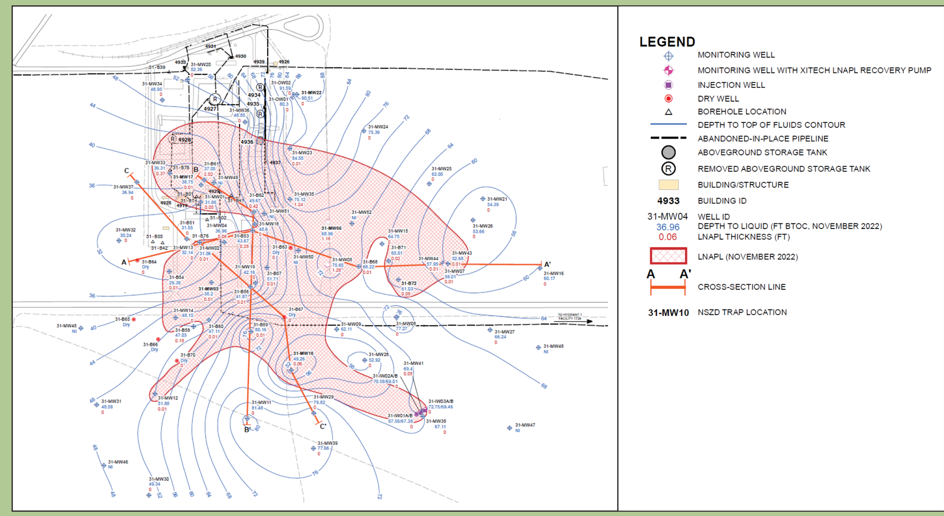
NSZD Results

Higher methane values, in dissolved-phase and well-head vapor, as well as greater LNAPL thickness were anticipated to correlate to higher NSZD rates; however, the survey results do not demonstrate a strong correlation to these relationships. For example, well 31-MW06 had a relatively high dissolved methane value, high well-head vapor methane values, and consistently high LNAPL thickness. However, the fall and spring NSZD flux rates for 31-MW06 were not high compared to those from other locations. One factor that may have contributed to this disparity is the depth to fluids. At locations with the highest calculated NSZD flux rates (wells 31-MW03 and 31-MW17), the depth to LNAPL and water were much less than in the other wells, and thus the CO_2 flux travel path is shorter through the overlying weathered bedrock and alluvium.

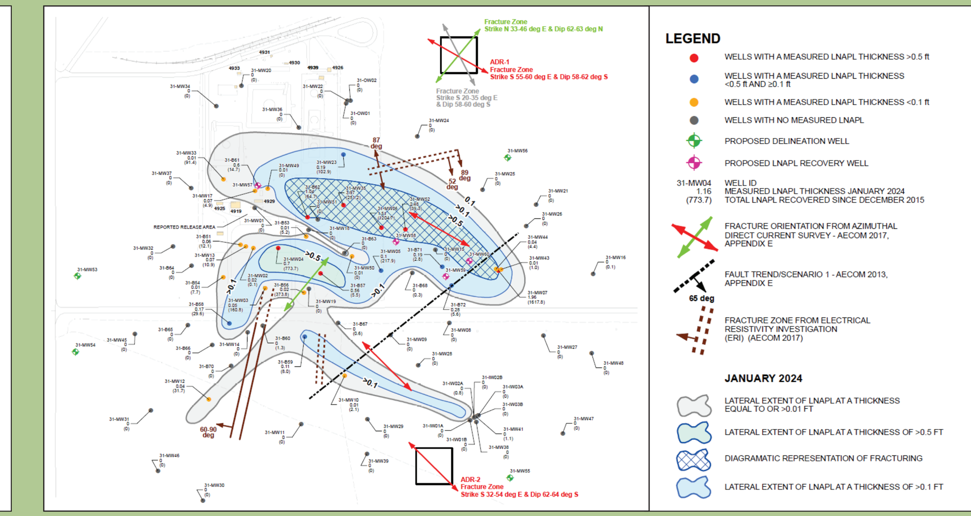
LNAPL EXTENT

The LNAPL plume encompasses approximately 32.5 acres with of the associated dissolved-benzene and MTBE plumes exceeding the maximum plume length allowed by the State of California Low-Threat Underground Storage Tank Case Closure Policy. LNAPL distribution and transport at the Site are functions of the complex fractured bedrock environment and low LNAPL transmissivity of the formation. In 2012, the results of LNAPL transmissivity testing completed at several wells were an order of magnitude lower than the range typically considered practicable for mechanical recoverability using skimming pumps.

Depth to Fluids and LNAPL Extent



LNAPL Thickness Across Site

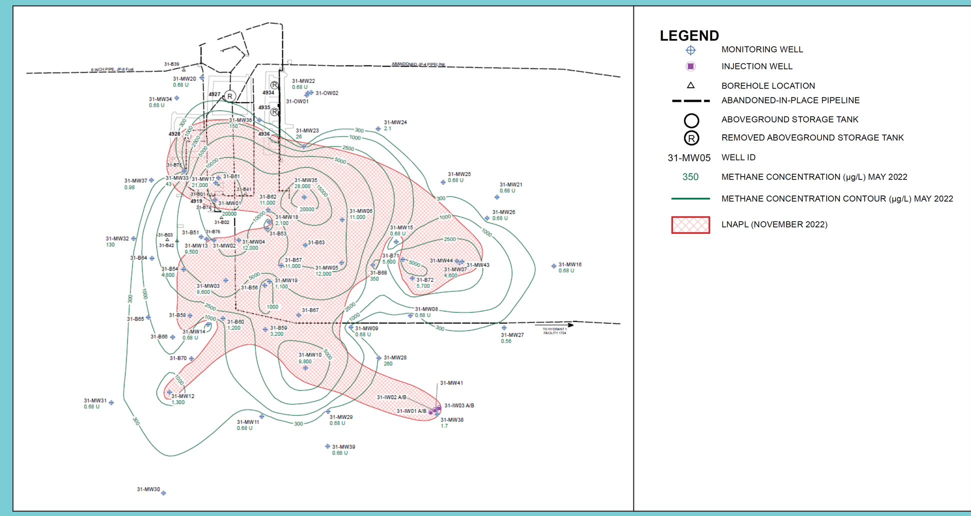


DECISION FACTORS

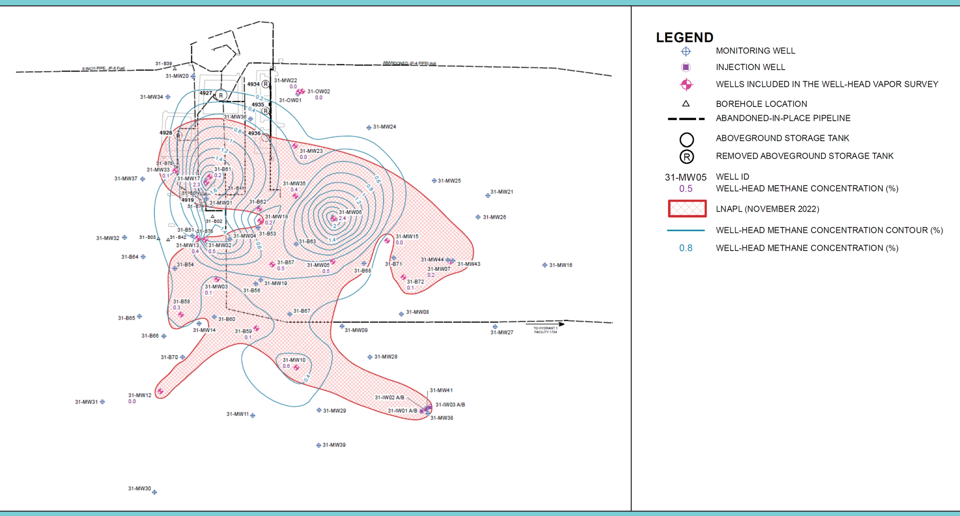
Several factors were considered when determining where to place the five traps within the LNAPL plume:

- LNAPL presence and thickness in monitoring wells, assuming that higher LNAPL thickness would have higher CO_2 flux.
- Dissolved methane, assuming that higher CO_2 flux rates would be associated with areas of higher dissolved-phase methane concentrations.
- Methane vapor concentrations at the wellheads, measured during a well-head vapor survey conducted prior to trap deployment, using a LANDTEC GEM5000 Gas Analyzer was used to monitor wells within the extent of LNAPL at the Site.

Dissolved Methane Concentrations

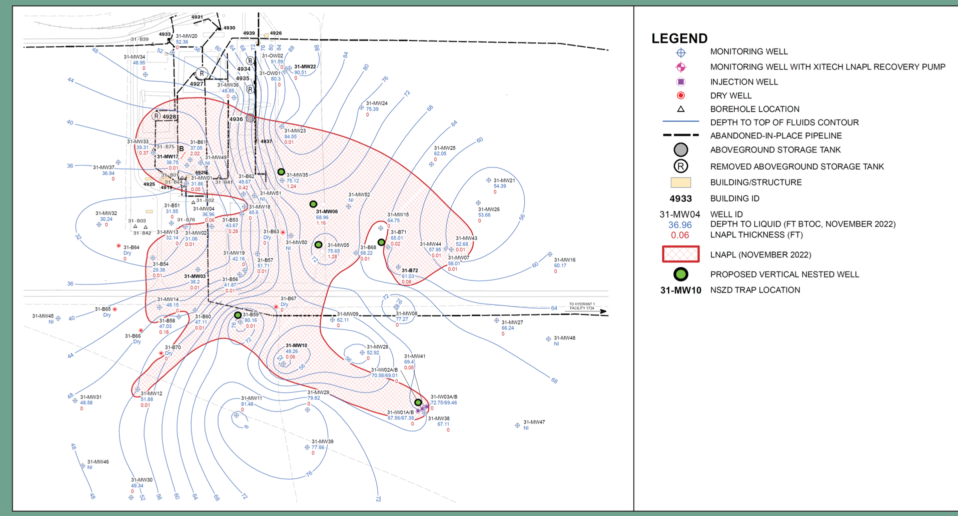


Wellhead Methane Concentrations



RECOMMENDATIONS

Depth to Fluids and Proposed Vertical Nested Wells



Going forward, consideration should be given to incorporate the LNAPL biodegradation rate and alternatives for enhanced biodegradation as part of the final Site remedy. In this regard, the following actions are recommended:

- Implement periodic CO_2 flux sampling to better understand changing flux rates with time, seasonality, and spatial variance of LNAPL degradation.
- The next NSZD evwent should consider using fossil fuel traps at 12 locations within LNAPL extent and one location outside the LNAPL extent for background measurement to better understand the spatial variability in the CO_2 flux rate.
- The fossil fuel traps should be distributed throughout the footprint of the LNAPL plume with consideration given to the depth to groundwater, thickness of weathered bedrock and the nature and permeability of surface soils.
- Nested wells should be installed and sampled to profile vertical changes in the CO_2 concentrations and evaluate dispersion in the deeper parts of the plume.

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1. E-Flux, LLC. 2021. Proposal for Estimation of Natural Source Zone Depletion (NSZD) Rates Measurement of CO2 Fluxes with Fossil Fuel, California. 11 November.
2. Federal Remediation Technologies Roundtable: Technology Screening Matrix – Natural Source Zone Depletion. 2023.
3. Interstate Technology Regulatory Council (ITRC). 2018. LNAPL-3: LNAPL Site Management: LCSM Evolution, Decision Process, and Remedial Technologies. Washington, D.C.: Interstate Technology & Regulatory Council. LNAPL Update Team. March.