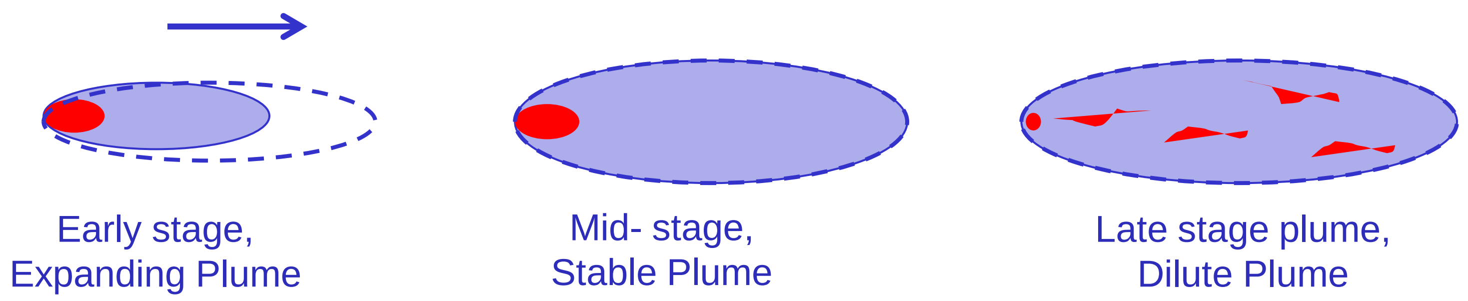
OER2 Webinar
Dealing with Dilute Plumes

Arun Gavaskar (NAVFAC EXWC)
Chuck Newell (GSI Environmental)

Dealing with Dilute Plumes - Topics Covered

- What are dilute plumes?
- What is matrix diffusion and what role does it play in sustaining dilute plumes?
- How do we deal with dilute plumes?
  - MNA?
  - Low-threat closure?
  - Aggressive treatment?
- Summary

What is a dilute plume?
- Low concentrations, weak or undiscernible source



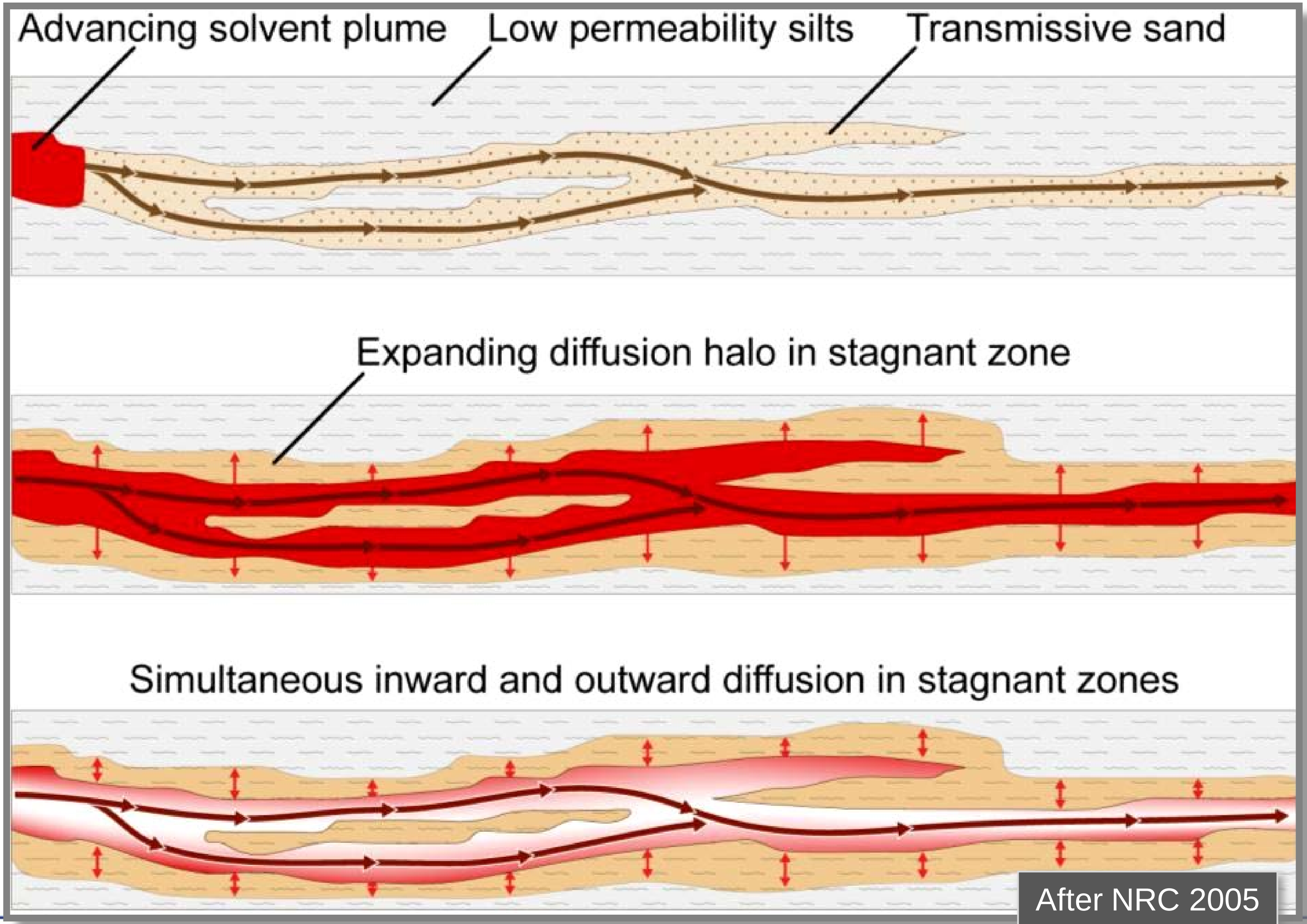
- At many sites, late stage plumes may not recede much, although concentrations may decline
  - Often causing a "Dilute Plume" to linger on
- Often, the cause is matrix diffusion or back diffusion from low-permeability lenses or layers
  - Clay lenses
  - Silt lenses
  - Fine sand stringers in an otherwise medium sand aquifer
  - Rock matrix in fractured bedrock

Most Important Cause of Dilute Plumes: Matrix Diffusion

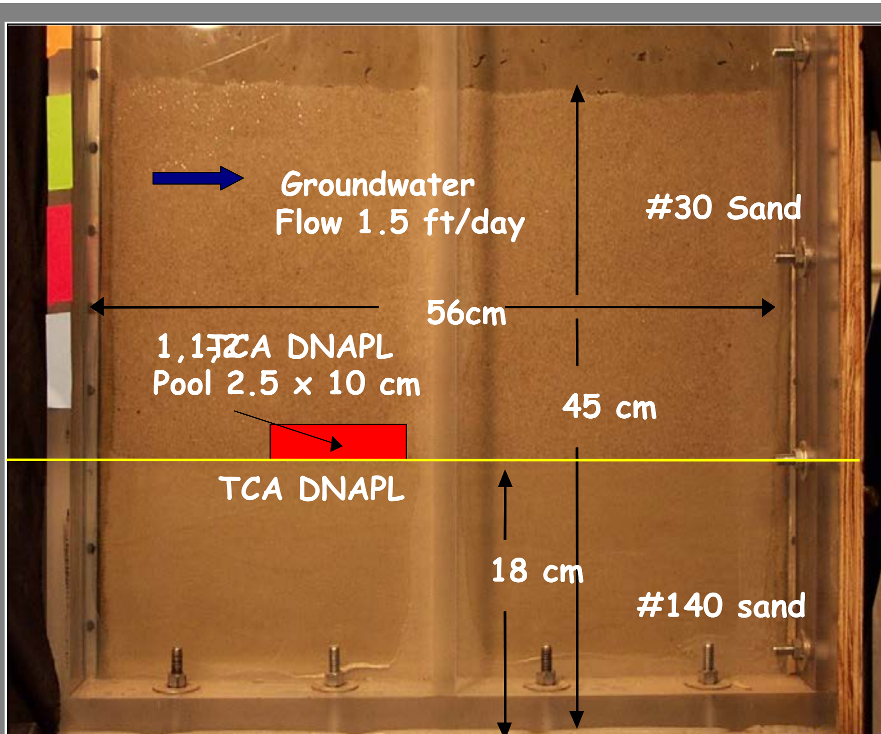
Initial Release

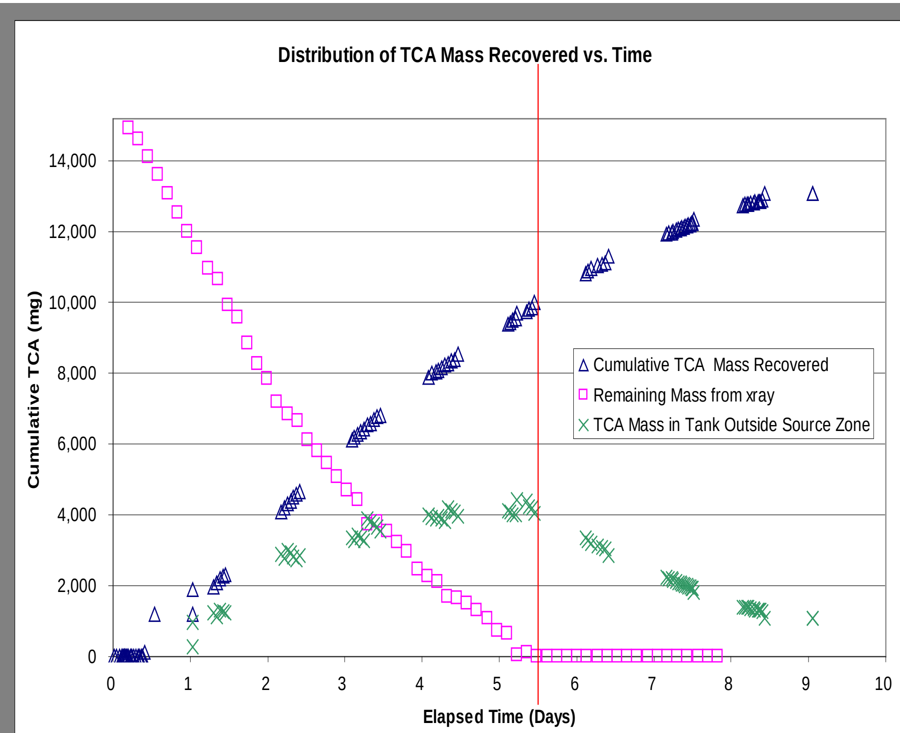
Loading Stage

Back Diffusion Stage



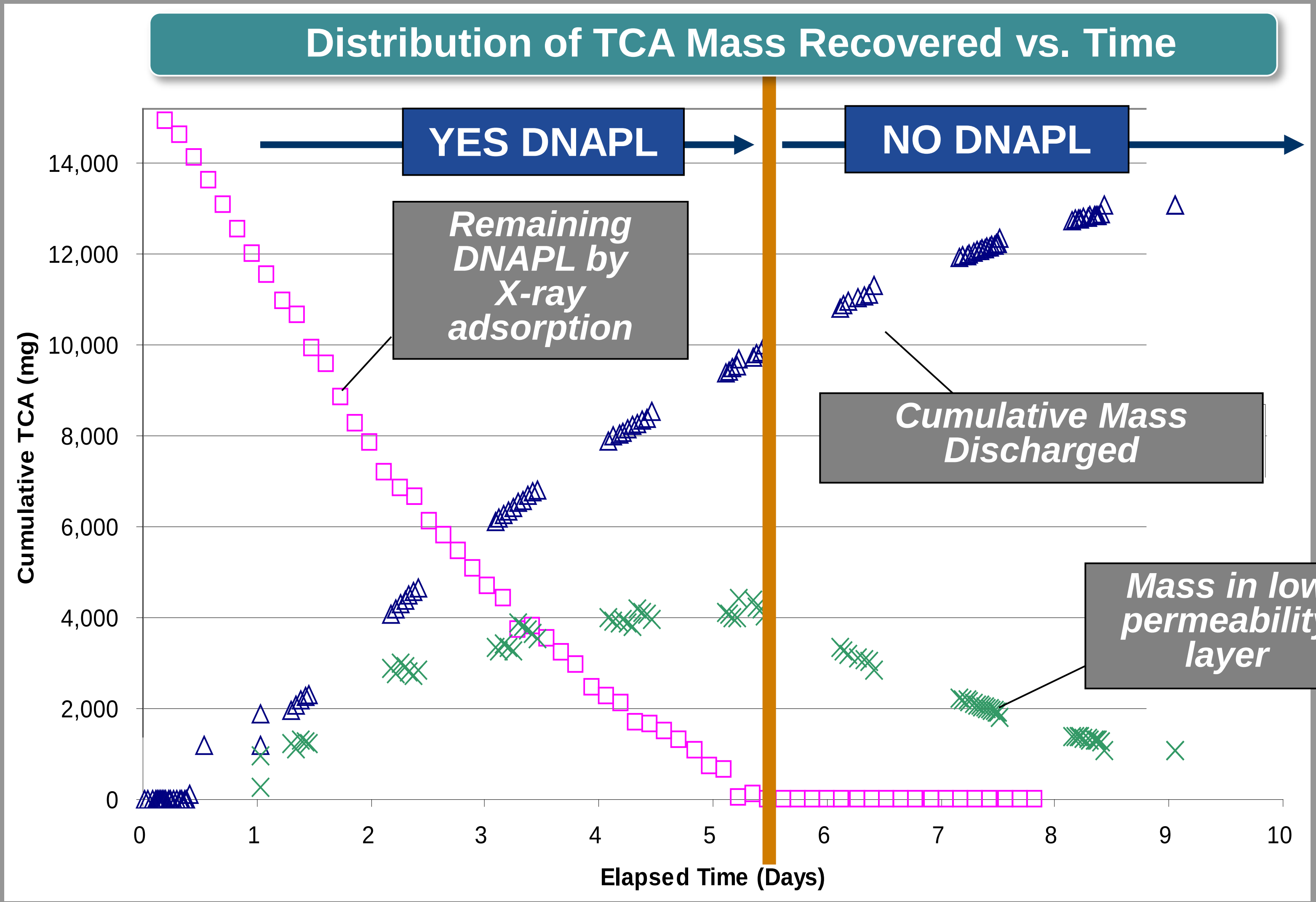
Two layer sand tank study
Colorado School of Mines
(Tissa Illangasekare and Bart Wilkins)





AFCEE Source Zone Initiative (2007)

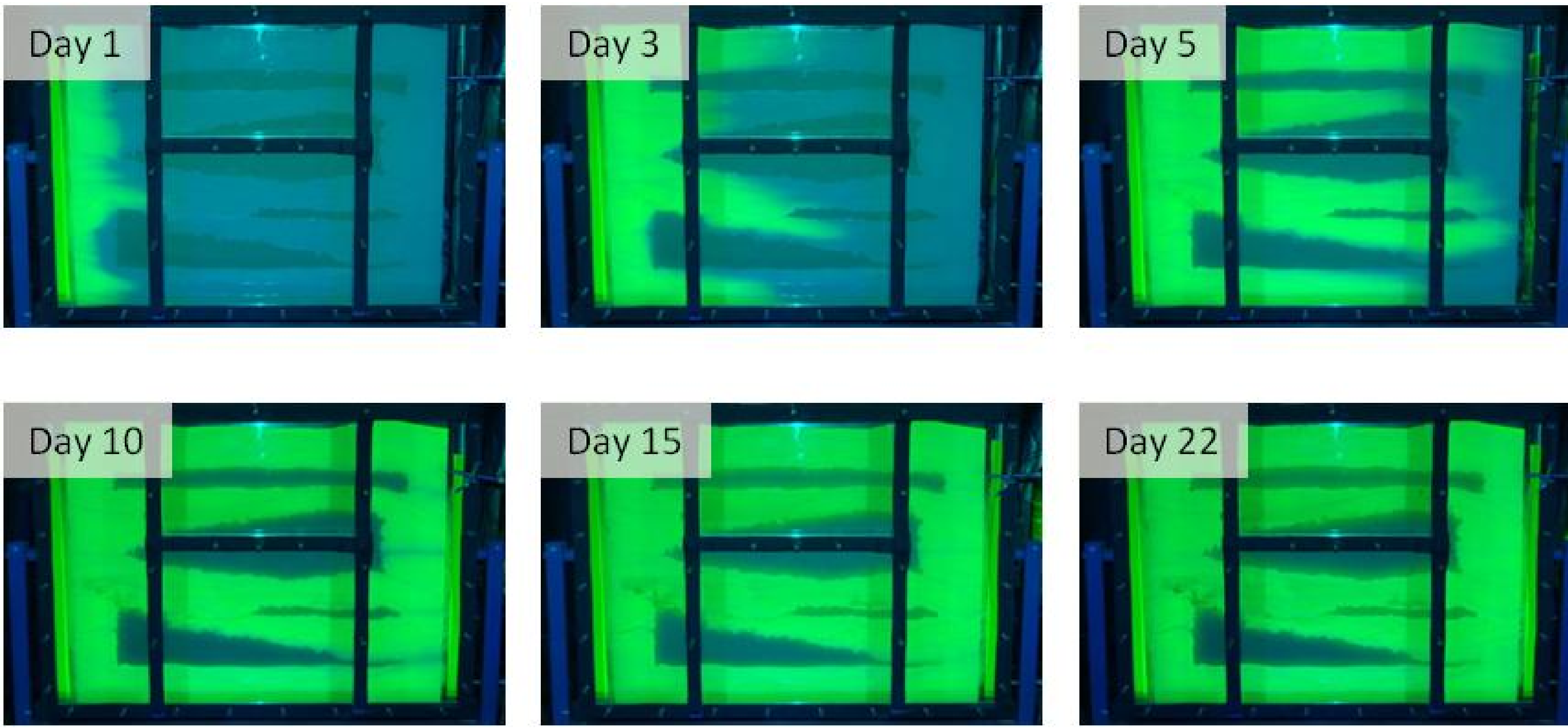
Distribution of TCA Mass Recovered vs. Time



AFCEE Source Zone Initiative (2007)

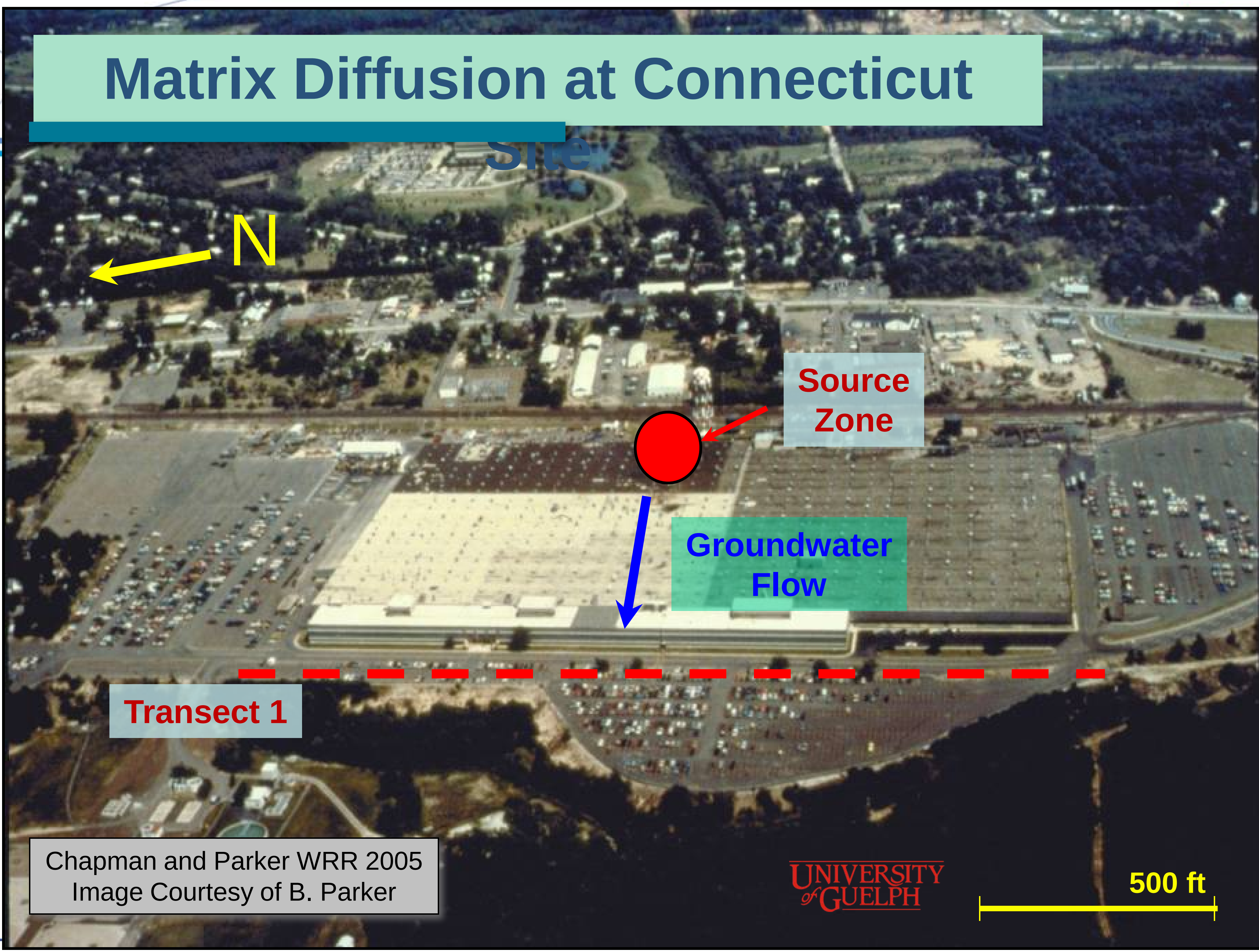
Matrix Diffusion Movie
Doner and Sale, Colorado State

Loading Phase



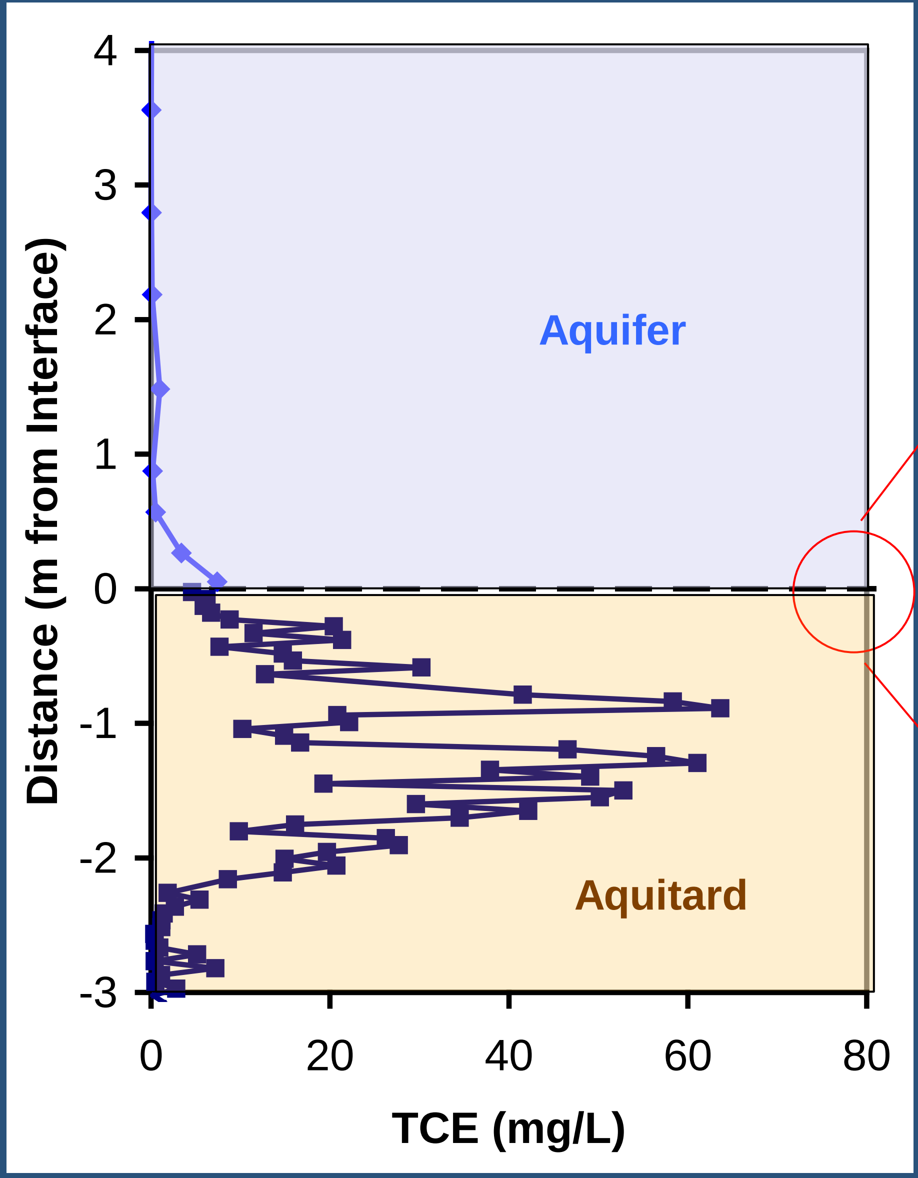
To Download: www.gsi-net.com

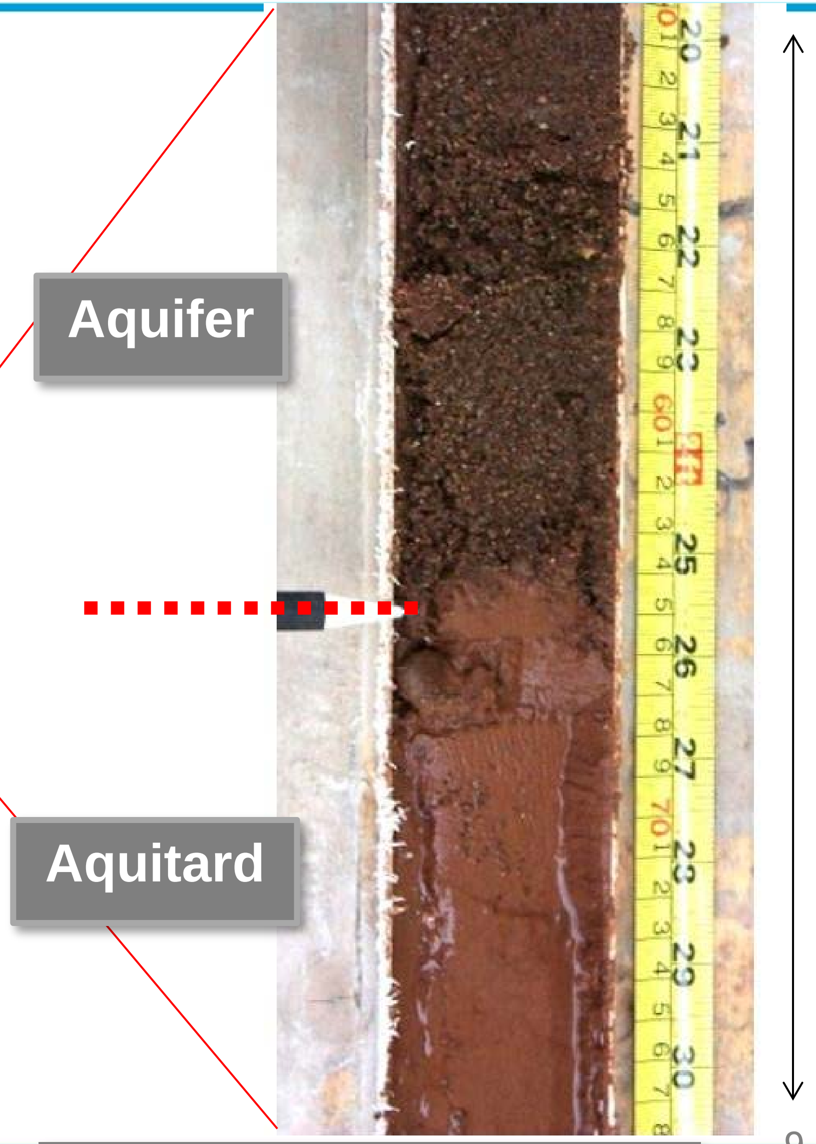
Matrix Diffusion at Connecticut Site



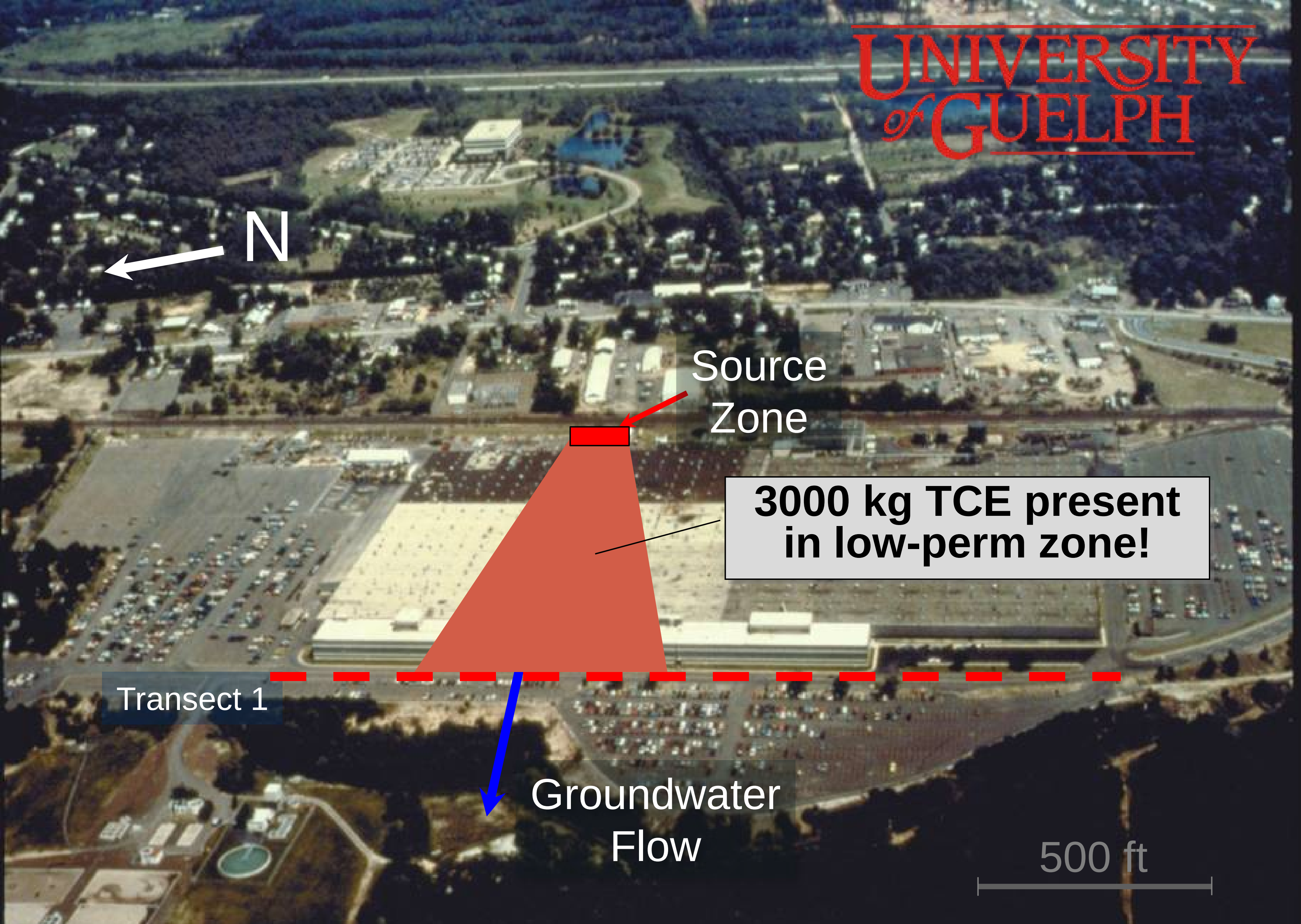
Chapman and Parker WRR 2005
Image Courtesy of B. Parker

High-Resolution Data from Core



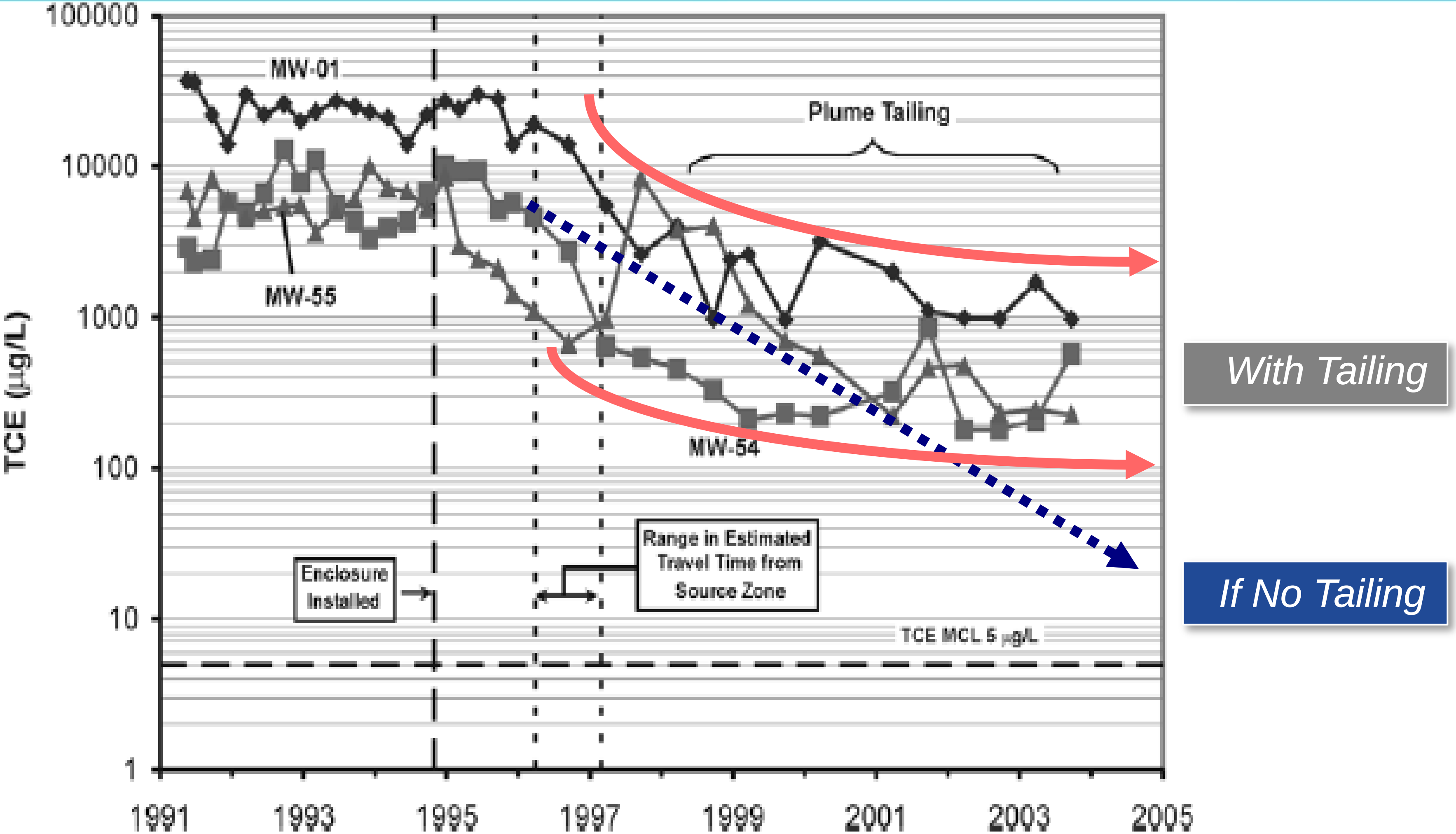


Chapman and Parker 2005



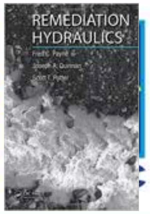
Modified from figure provided by B. Parker. Source of Data: Chapman and Parker, 2005.

Impact of Matrix Diffusion: "Long Tail"



Source: Chapman and Parker

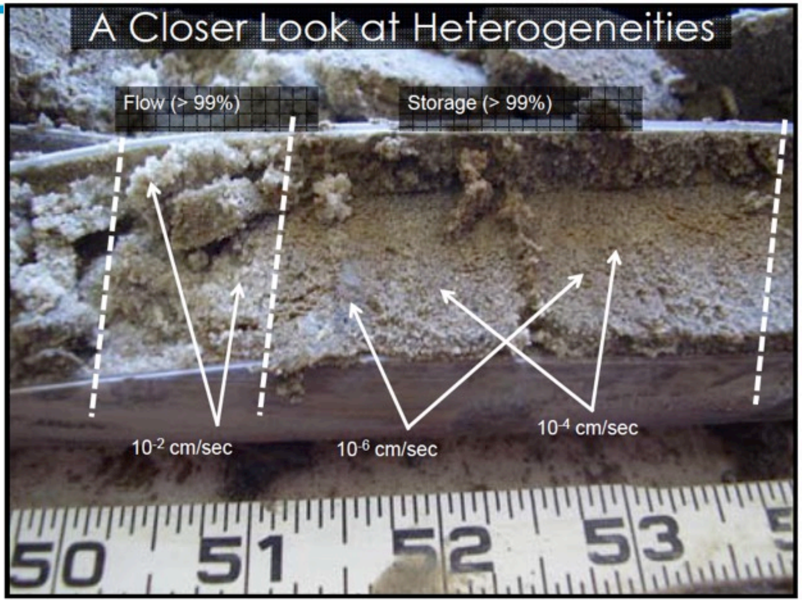
Is There Matrix Diffusion in Sandy Aquifers?
Yes, Some Heterogeneities Can't Be Seen

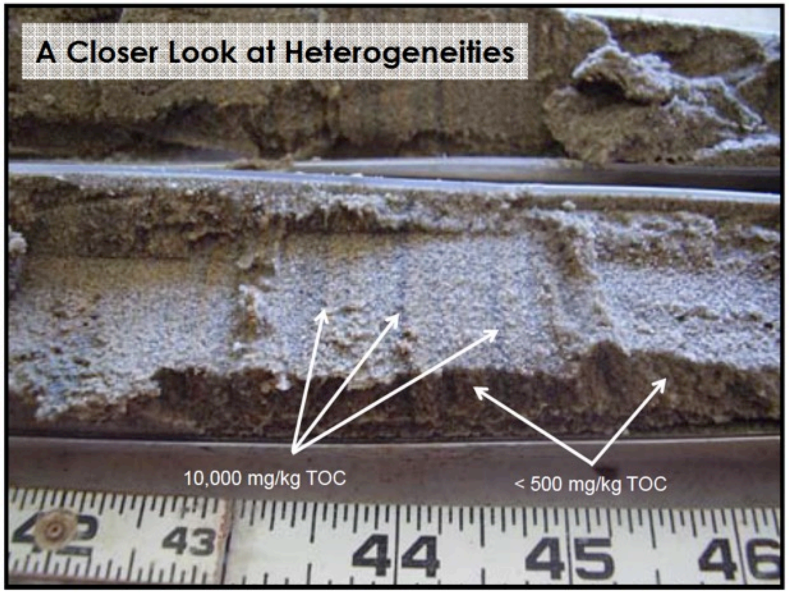


Even sites that are considered archetypically homogeneous have 1,000- to 10,000-fold variation in hydraulic conductivity at scales of 1 to 10 cm.

This leads to a conceptual split of the aquifer matrix, between a small fraction that is transport-active and a much larger fraction that is effectively stagnant and serves as a reservoir of persistent contaminant storage.

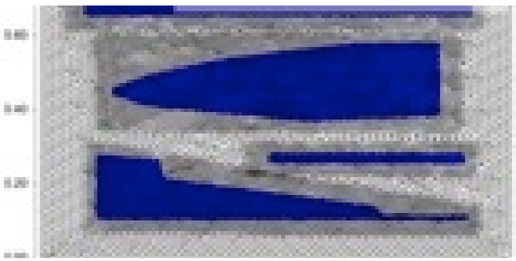
Remediation Hydraulics (Payne et al., 2008)

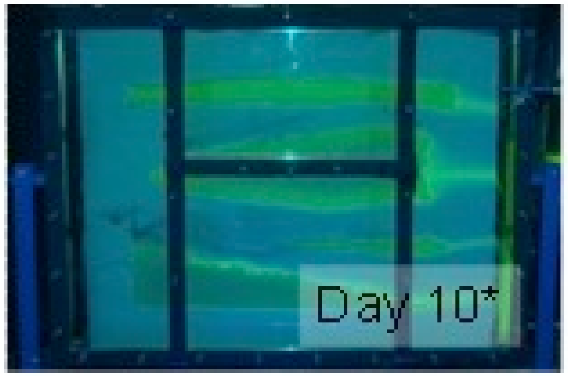


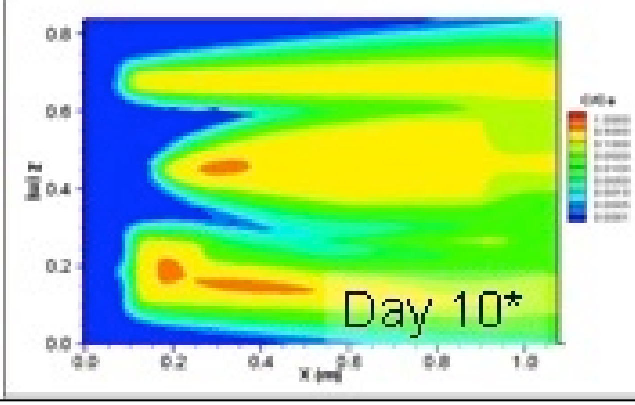


Can Numerical Transport Models Miss the Matrix Diffusion? Yes Unless Lots of Layers

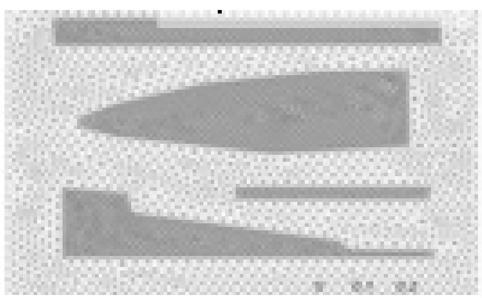
HydroGeoSphere



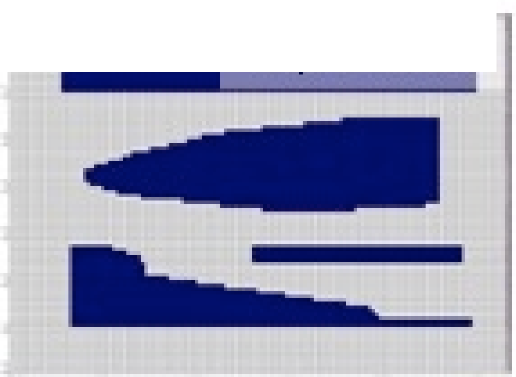


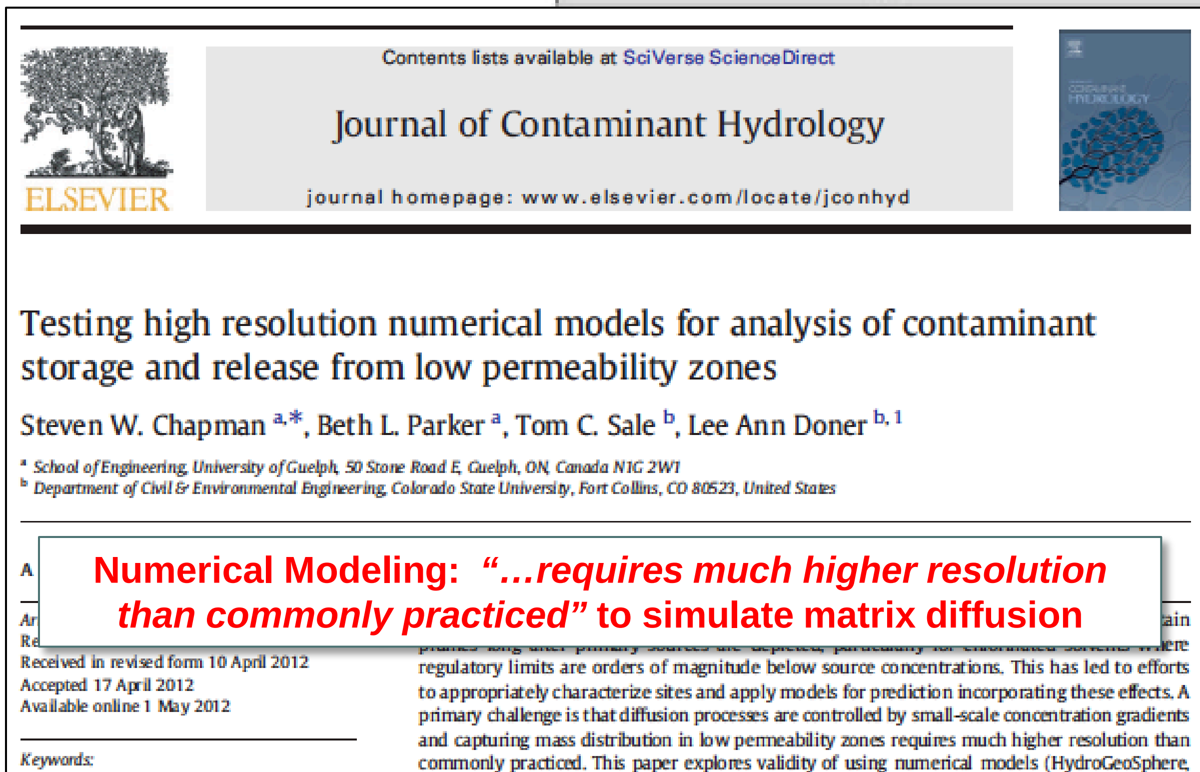


FEFLOW



MODFLOW/MT3DMS





Contents lists available at SciVerse ScienceDirect

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Testing high resolution numerical models for analysis of contaminant storage and release from low permeability zones

Steven W. Chapman [a,*], Beth L. Parker [a], Tom C. Sale [b], Lee Ann Doner [b,1]

[a] School of Engineering, University of Guelph, 50 Stone Road E, Guelph, ON, Canada N1G 2W1
[b] Department of Civil & Environmental Engineering, Colorado State University, Fort Collins, CO 80523, United States

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Keywords:

... regulatory limits are orders of magnitude below source concentrations. This has led to efforts to appropriately characterize sites and apply models for prediction incorporating these effects. A primary challenge is that diffusion processes are controlled by small-scale concentration gradients and capturing mass distribution in low permeability zones requires much higher resolution than commonly practiced. This paper explores validity of using numerical models (HydroGeoSphere,

Numerical Modeling: *"…requires much higher resolution than commonly practiced"* to simulate matrix diffusion

Matrix Diffusion Toolkit (GSI and CSU)
Lead Developer: Shahla Farhat

NAVFAC

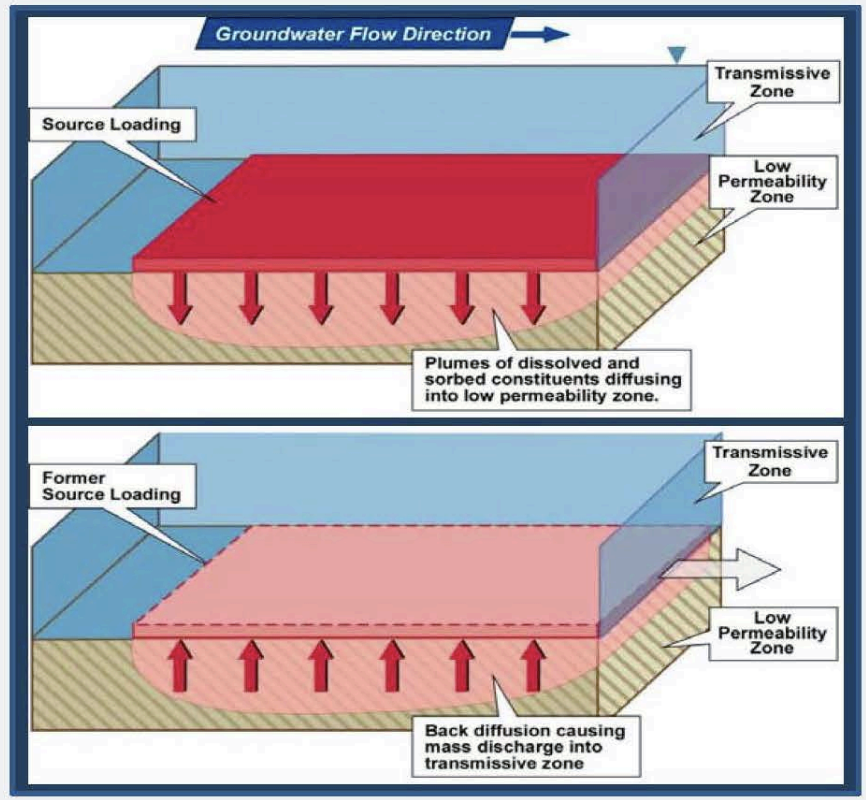
Model Selection Screen

Matrix Diffusion Toolkit — *Vol. 1.0 beta*

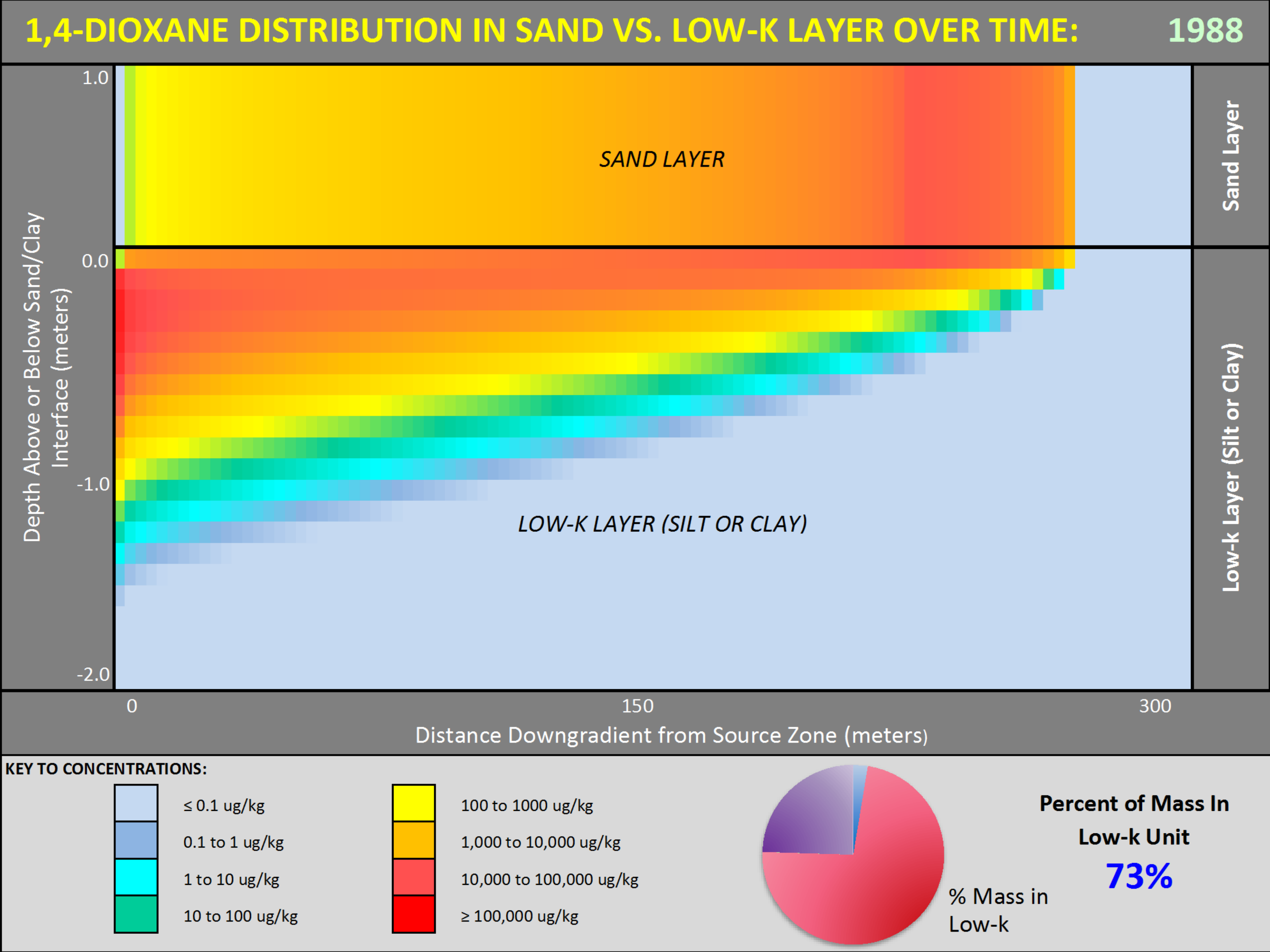
ESTCP

Evaluate Matrix Diffusion

- Use Simple "Square Root Model" (SRM)
- Use More Detailed "Dandy-Sale Model" (DSM)



Return to Main Screen | Apply Related Tools | *Which Model Should I Choose?*



1,4-DIOXANE DISTRIBUTION IN SAND VS. LOW-K LAYER OVER TIME:
1988
1.0
0.0
-1.0
-2.0
Depth Above or Below Sand/Clay Interface (meters)
SAND LAYER
LOW-K LAYER (SILT OR CLAY)
Sand Layer
Low-k Layer (Silt or Clay)
0
150
300
Distance Downgradient from Source Zone (meters)
KEY TO CONCENTRATIONS:
≤ 0.1 ug/kg
0.1 to 1 ug/kg
1 to 10 ug/kg
10 to 100 ug/kg
100 to 1000 ug/kg
1,000 to 10,000 ug/kg
10,000 to 100,000 ug/kg
≥ 100,000 ug/kg
% Mass in Low-k
Percent of Mass In Low-k Unit
73%

Dilute Plume
- Definition

- Large and Dilute (L&D) Plume: *A plume of relatively low concentration that extends over a large spatial area without a clear delineation between the "source(s)" and the "plume(s)"*

- Dilute Plume (for the purposes of this discussion)
  - –Low concentrations of COCs throughout plume, including in "source" area
  - –Upgradient source concentrations are low, but could be slightly higher than in rest of the plume
  - –Plume is stable or receding
  - –Plume may be small or it may be large
  - –Often a residual of past source or plume treatment activities (or just a result of a weak release).

  - –Note that we could have a dilute plume of one COC, say 1,4 dioxane, within a stronger plume of another COC, say TCE/TCA

Dilute Plumes
- Concentrations

- What are the low and stable concentrations in a dilute plume fed by matrix diffusion?
  - –May vary depending on COCs and site conditions
  - –At many sites in the Navy's portfolio, TCE appeared to be stabilizing at 50 to 75 ppb (or below)
  - –1,4 dioxane at 1 to 10 ppb???

How do we deal with dilute plumes?

- Challenges with aggressive treatment

- Low concentrations in dilute plume may be spread over large portions of the aquifer
  - May make further treatment impractical or uneconomical

- Even when dilute plume is small, treatment may be difficult
  - Pump-and-treat efficiency is limited by slow diffusion of COCs from low-permeability lenses
  - In-situ treatment may not penetrate finer lenses (or rock matrix) where much of the residual COC mass resides

Dilute Plumes
- How do we deal with dilute plumes?

<u>Site with lower risk profile</u>

<u>(*MNA or low-threat closure*)</u>

- Stable or receding plume
- Nearest downgradient receptor is surface water
- Groundwater has high TDS
- Aquifer has low yield

<u>Site with higher risk profile</u>

<u>(*May warrant active measures*)</u>

- Expanding plume
- Nearest downgradient receptor (within, say, a mile) is an existing drinking water well
- Vapor intrusion risk based on groundwater concentrations <u>near the water table</u> or based on sub-slab soil gas concentrations in source areas
    - Mitigation (engineering controls) is an option

Dilute Plumes
- How do we deal with dilute plumes?

- For stable or receding plumes at a low-risk site, most technically practicable and economical solution is:
  - –MNA, or
  - –Low-threat closure

  (Response Complete [RC] with LUCs; or RC with LUCs and LTM]

- Higher cost, more uncertainty of cleanup outcome with aggressive treatment:
  - –Upgradient source treatment
    - Uncertain outcome in source area, especially if MCLs are the goal
    - It may take years for upgradient source treatment to lower downgradient plume concentrations, especially in longer plumes
  - –Plume treatment to target cleanup levels
    - Might be feasible for smaller plumes with little matrix diffusion occurring
    - Difficult if matrix diffusion is occurring throughout the plume

Dilute Plumes
- How do we deal with dilute plumes (in lower risk situations)?

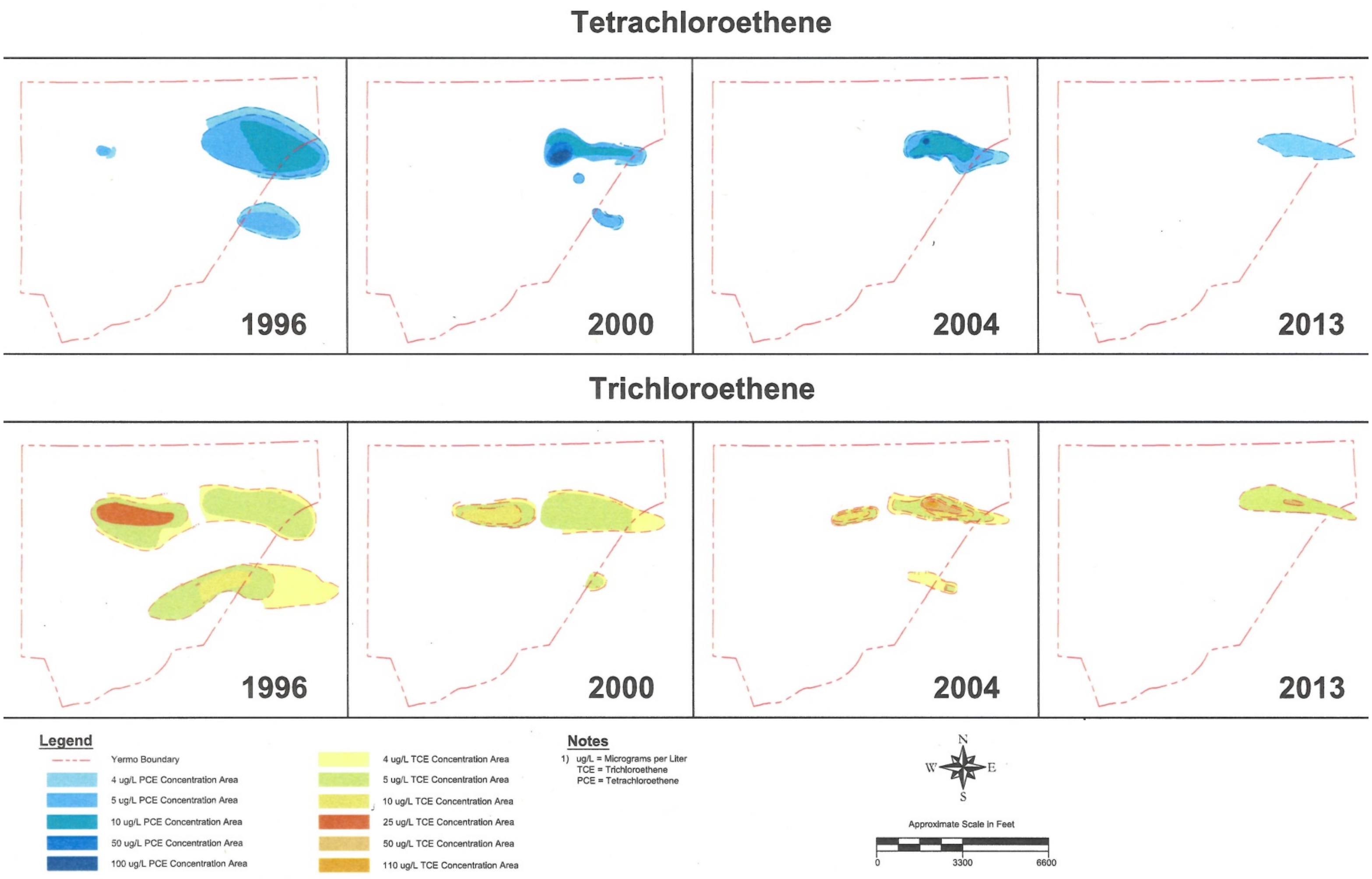
<u>Dilute plume that has reached their naturally stable size</u>

- MNA
- Low-threat closure (Response Complete [RC] with LUCs, RC with LUCs and LTM)

<u>Dilute plume that has stable concentrations but has been constrained from reaching a stable size by containment system</u>

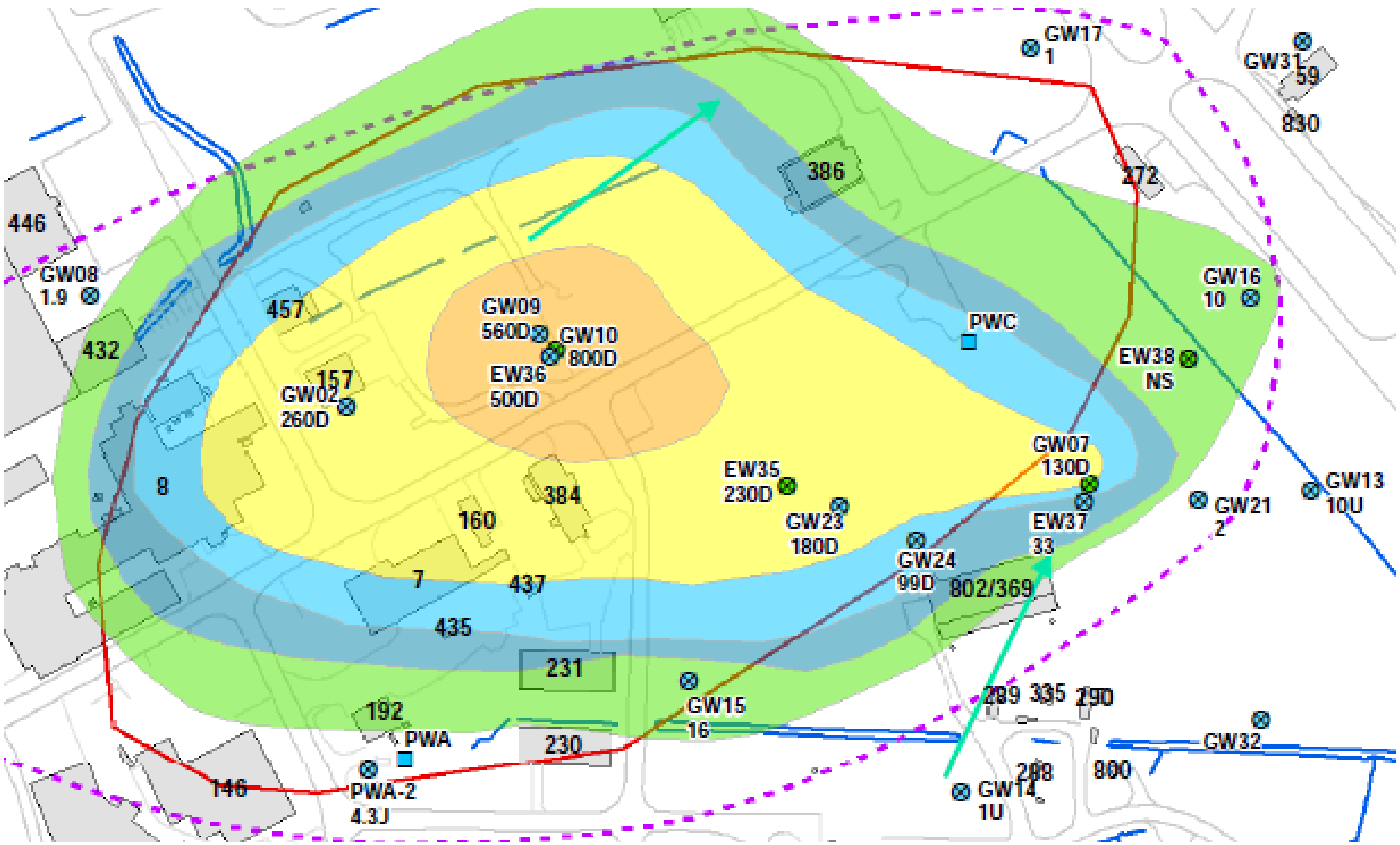
- E.g., Pump-and-treat systems and a <u>weak or weakened source</u>
- If a dilute plume is present in a constrained footprint, chances are that plume will not expand much if constraint is now removed
  - At least, a temporary shutoff of treatment system may be warranted, allowing time to study the development of a new stable footprint that is close to the current footprint

Example Site 1 - Stable or receding or expanding plume? - *Pump-and-treat system may have to continue until this question is answered*



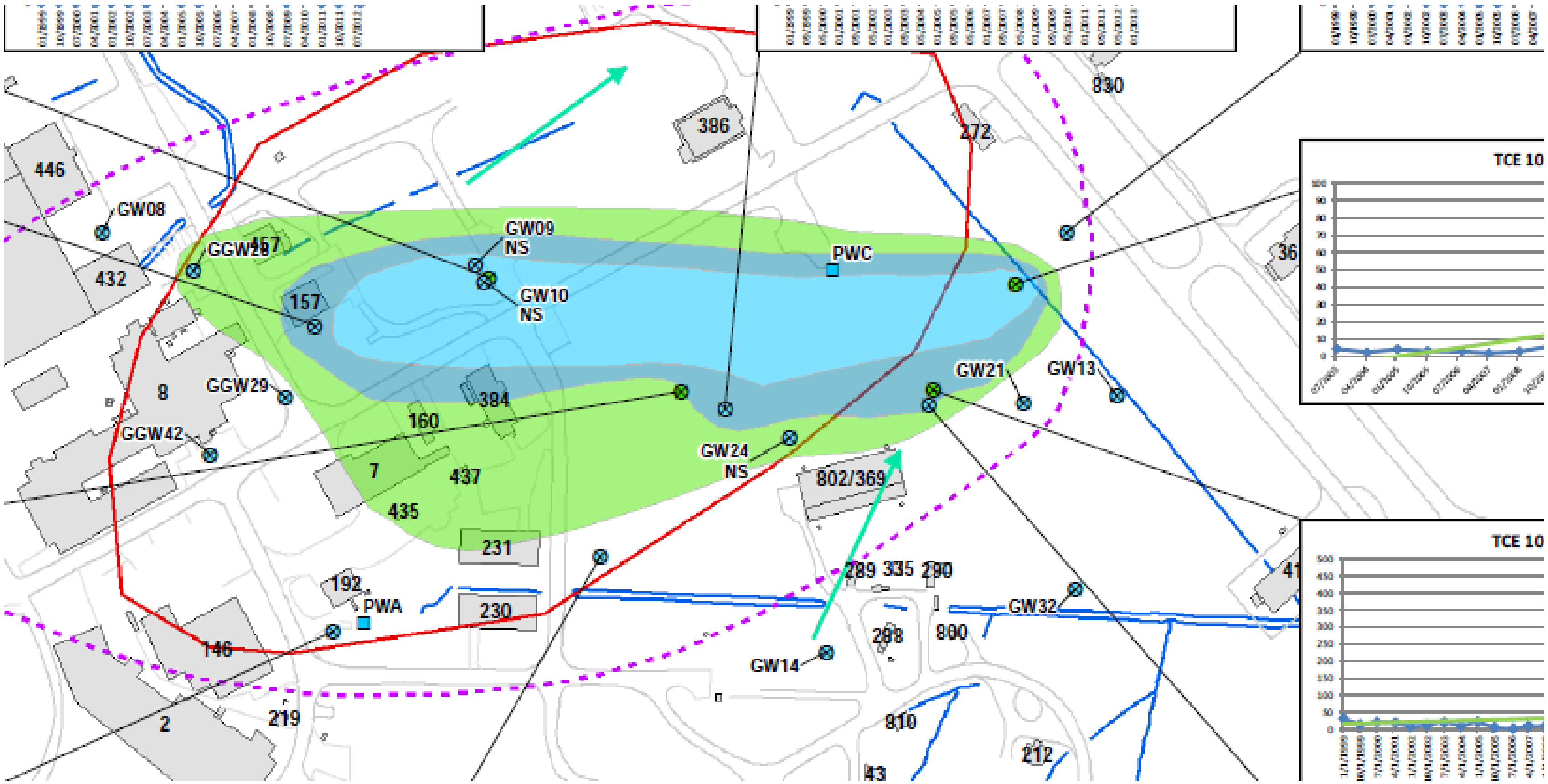
Example Site 2 of a dilute plume (precursor)
- Overburden aquifer

January 1999 (pre-P&T) TCE Concentrations, Alluvial Aquifer
[Orange – 500-800 ug/L, Green 5-25 ug/L]



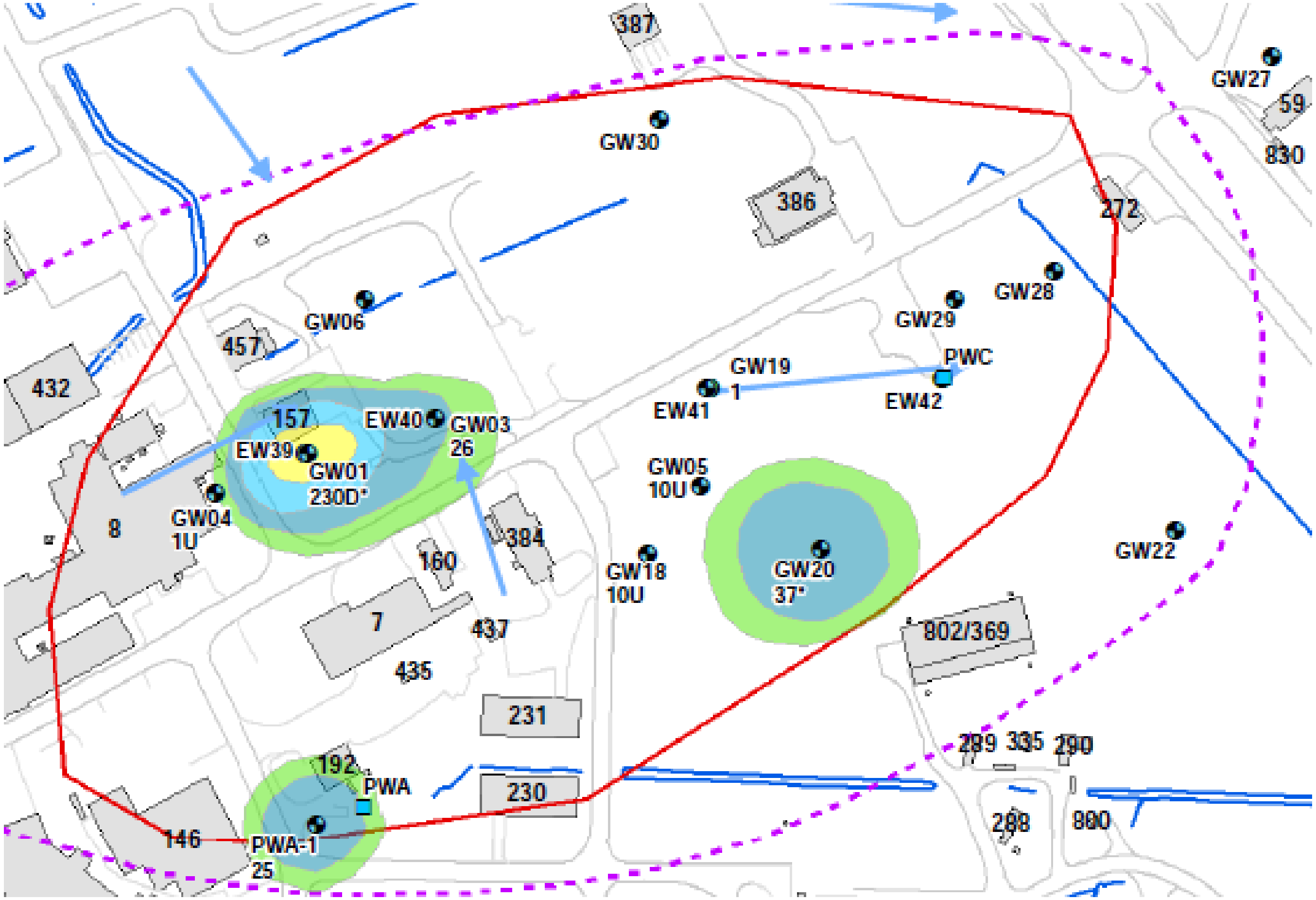
Example Site 2 of a dilute plume (Relatively lower risk)
- Overburden aquifer

September 2012 TCE Concentrations, Alluvial Aquifer
[Light Blue – 50-100 ug/L, Green 5-25 ug/L]



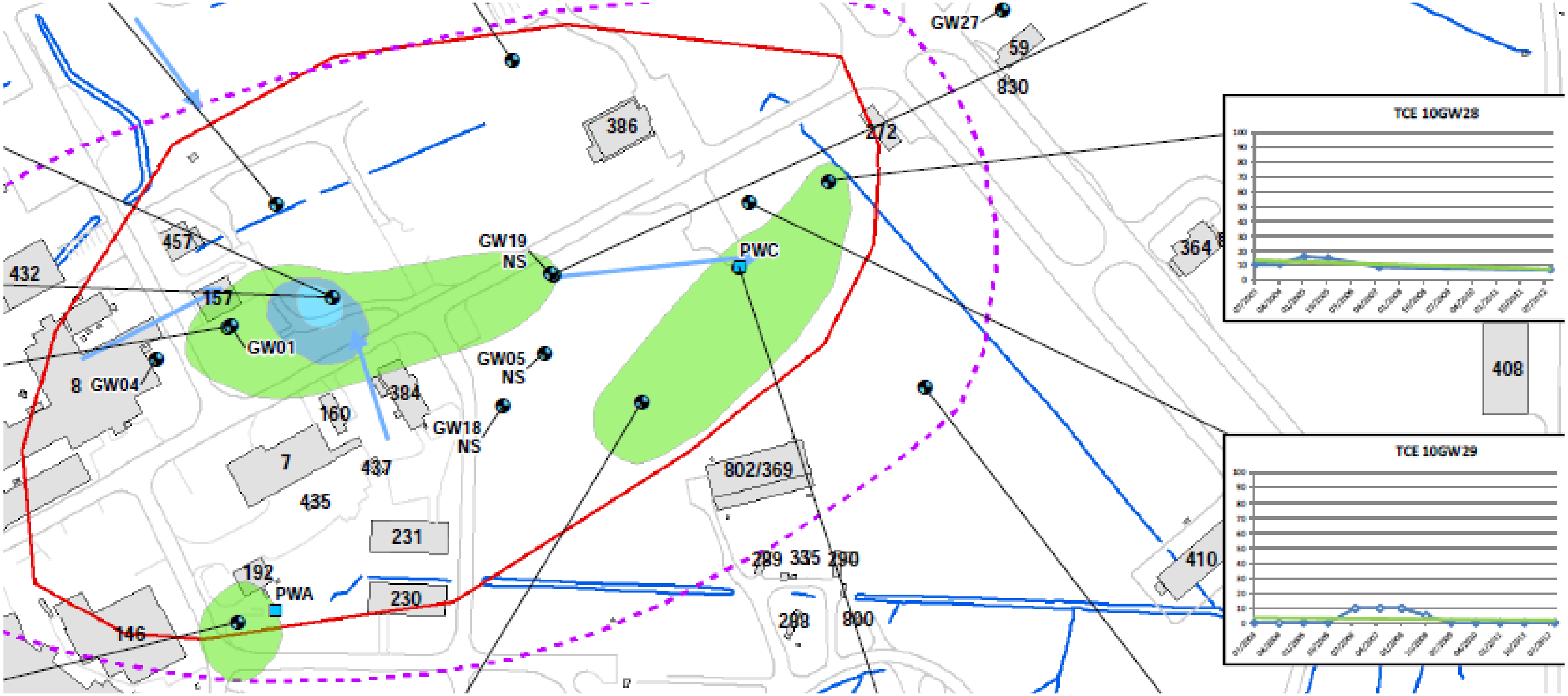
Example Site 2
- Underlying bedrock aquifer

January 1999 (Pre-P&T) TCE Concentrations, Bedrock Aquifer
[Yellow – 100-500 ug/L, Green 5-25 ug/L]

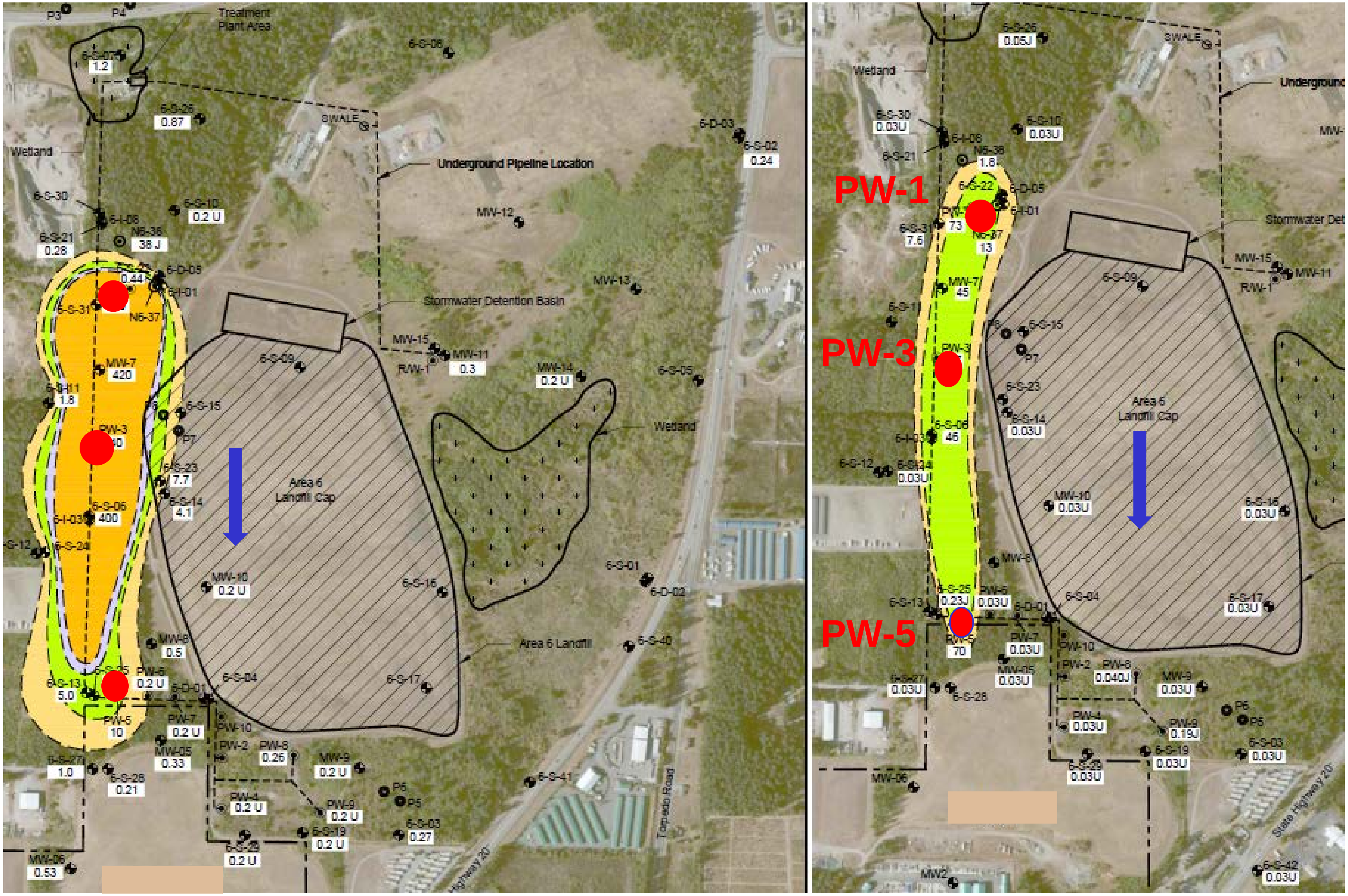


Example 2 of a dilute plume (Relatively lower risk)
- Underlying bedrock aquifer

September 2012, TCE Concentrations, Bedrock Aquifer
[Light Blue – 50-100 ug/L, Green 5-25 ug/L]



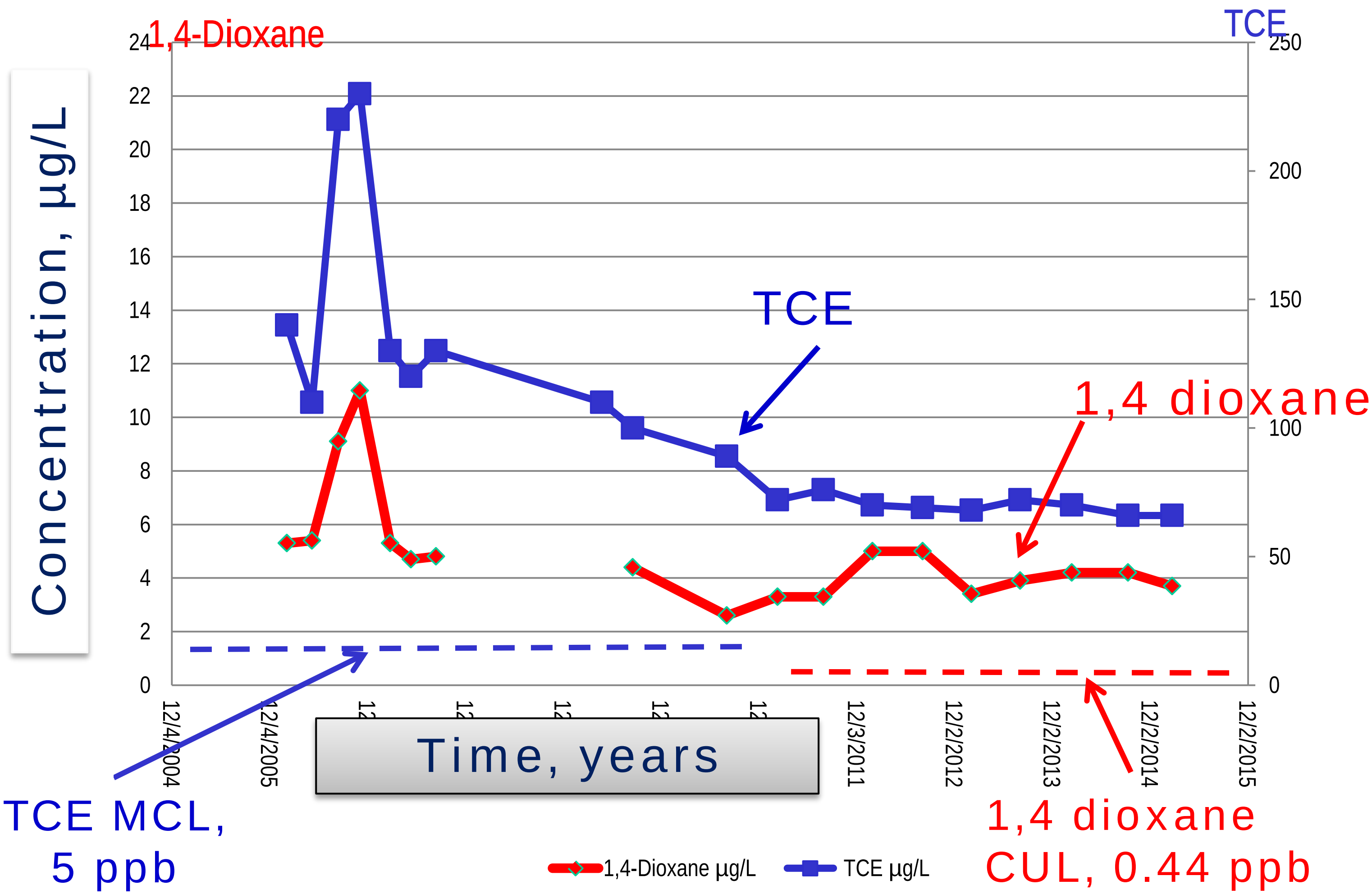
Example Site 3 of a dilute plume (TCE) - Relatively low risk



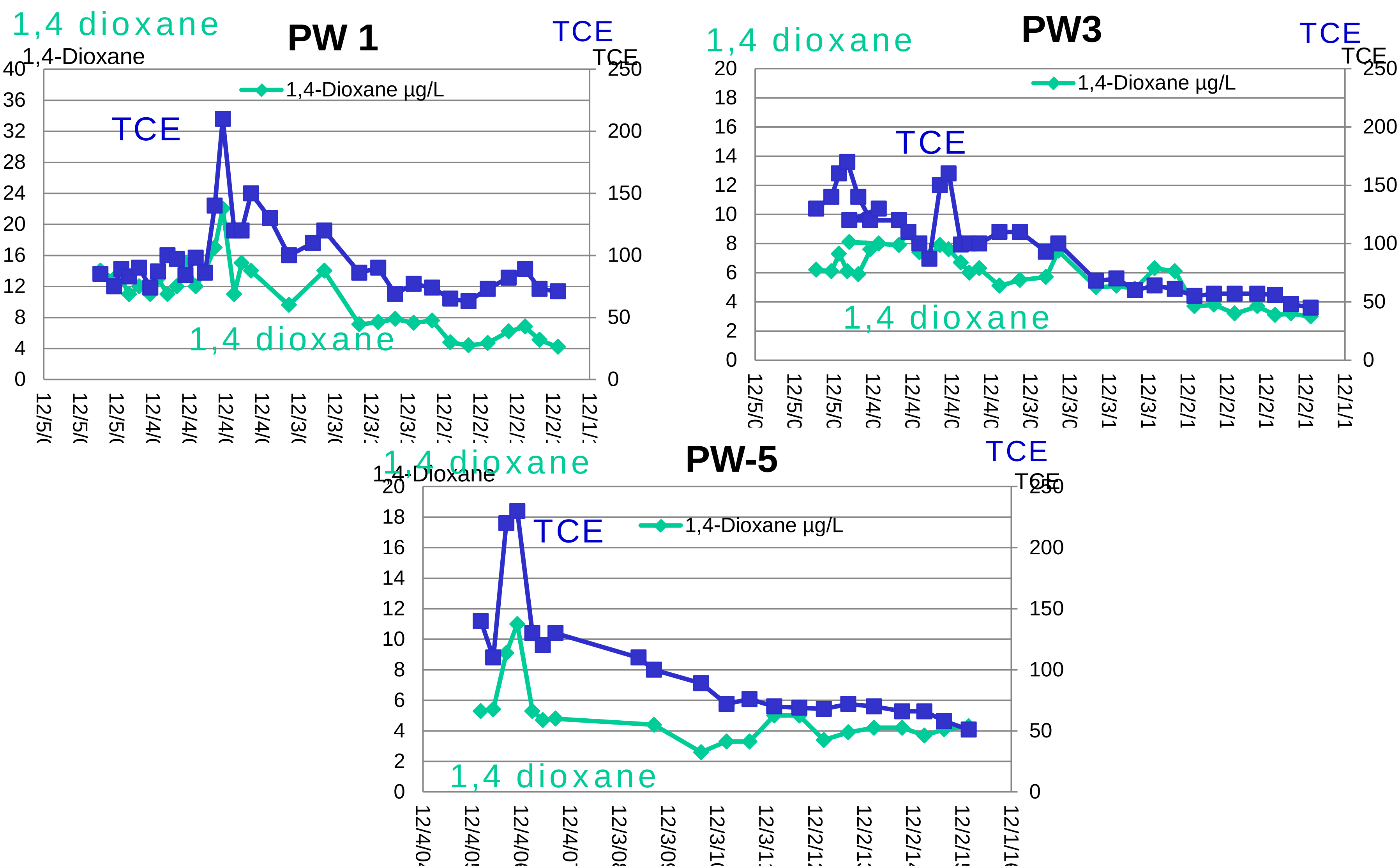
Example Site 3: P&T System, weak or depleted source

– Matrix Diffusion: Concentrations often drop to an asymptote above MCL

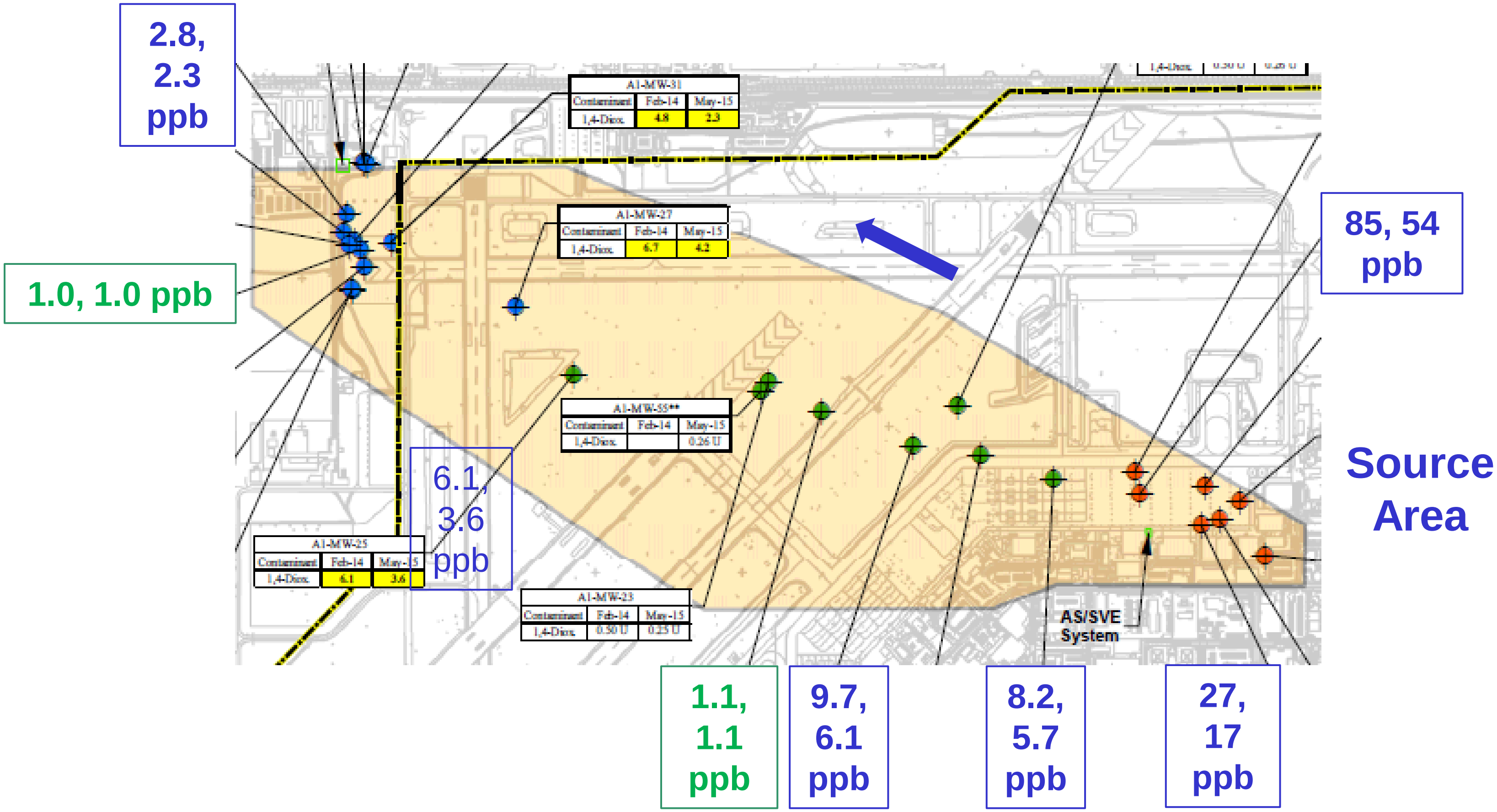
Example Site 2: P&T for TCE – 1997 and 2014



Example 3 dilute plume – Pump-and-treat well date
- Plateaus likely due to matrix diffusion
(TCE, ppb – blue, right scale; 1,4 dioxane, ppb – green, left scale)



Example Site 4: 1,4 dioxane, receding dilute plume? - Concentrations in 2014 and 2015



Nine narrative criteria for low-threat closure

- 1. Develop a complete Conceptual Site Model (CSM)
  - *1a) Pollutant sources are identified and evaluated*
  - *1b) The site is adequately characterized*
  - *1c) Exposure pathways, receptors, and potential risks, threats, and other environmental concerns are identified and assessed*
- 2. Control sources and mitigate risks and threats
  - *2a) Pollutant sources are remediated to the extent feasible*
  - *2b) Unacceptable risks to human health, ecological health, and sensitive receptors, considering current and future land and water uses, are mitigated*
  - *2c) Unacceptable threats to groundwater and surface water resources, considering existing and potential beneficial uses, are mitigated*
- 3. Demonstrate that residual pollution in all media will not adversely affect present and anticipated land and water uses
  - *3a) Groundwater plumes are decreasing*
  - *3b) Cleanup standards can be met within a reasonable timeframe*
  - *3c) Risk management measures are appropriate, documented, and do not require future Water Board oversight*

Assessment Tool for Closure of Low-Threat Chlorinated Solvent Sites, - *California Regional Water Quality Control Board, San Francisco Bay Region, July 2009*

- A groundwater plume is decreasing when pollutant concentrations within the plume are declining over time and the plume's "footprint" is shrinking or remaining stable.

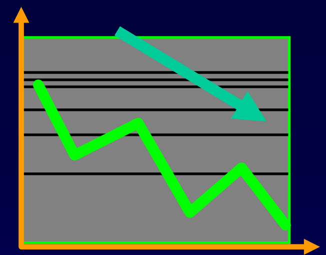
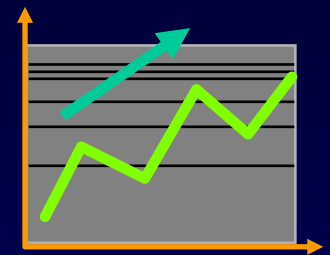
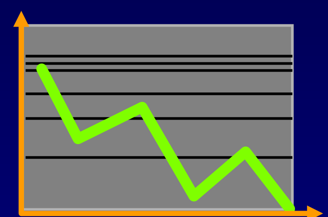
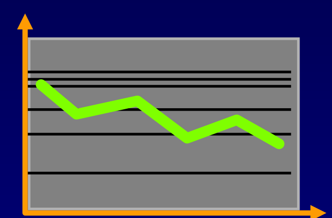
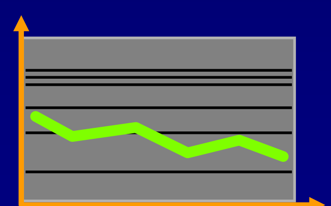
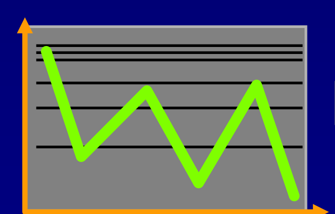
- "For stable plumes that are not decreasing, it may be difficult to estimate a cleanup timeframe. This may indicate that a persistent source remains, that little biological degradation is occurring, and/or that groundwater is essentially stagnant. Under certain limited circumstances a stable but not decreasing plume may be acceptable for low-threat closure, if based on all other factors, there is low potential for future beneficial use, or low potential for adverse affects to future beneficial use.
  - If, for example, it will take 50 years to meet the requisite level of water quality, that may be a reasonable timeframe if neither existing nor anticipated beneficial uses would be impacted during that time."

Navy's groundwater plumes
- Receptors, aquifer characteristics

- Surface water bodies, not drinking water wells, are the closest downgradient receptors for many of the Navy's plumes

- At many of the Navy's coastal sites, high TDS or low-yield may make beneficial use (for drinking) unlikely

Mann-Kendall Method to Determine Plume Stability (Aziz et al., 2003; Connor et al., 2014)

MK Statistic (S)	 MK < 0 — Decreasing Trend	 MK > 0 — Increasing Trend
Confidence Factor (CF)	 CF > 95% — Strong Trend	 CF < 95% — Weak Trend
Coefficient of Variation (COV)	 COV < 1 — Stable Trend	 COV > 1 — Fluctuating Trend

Three Stats Are Used to Put C vs. T Data into One of Six Buckets

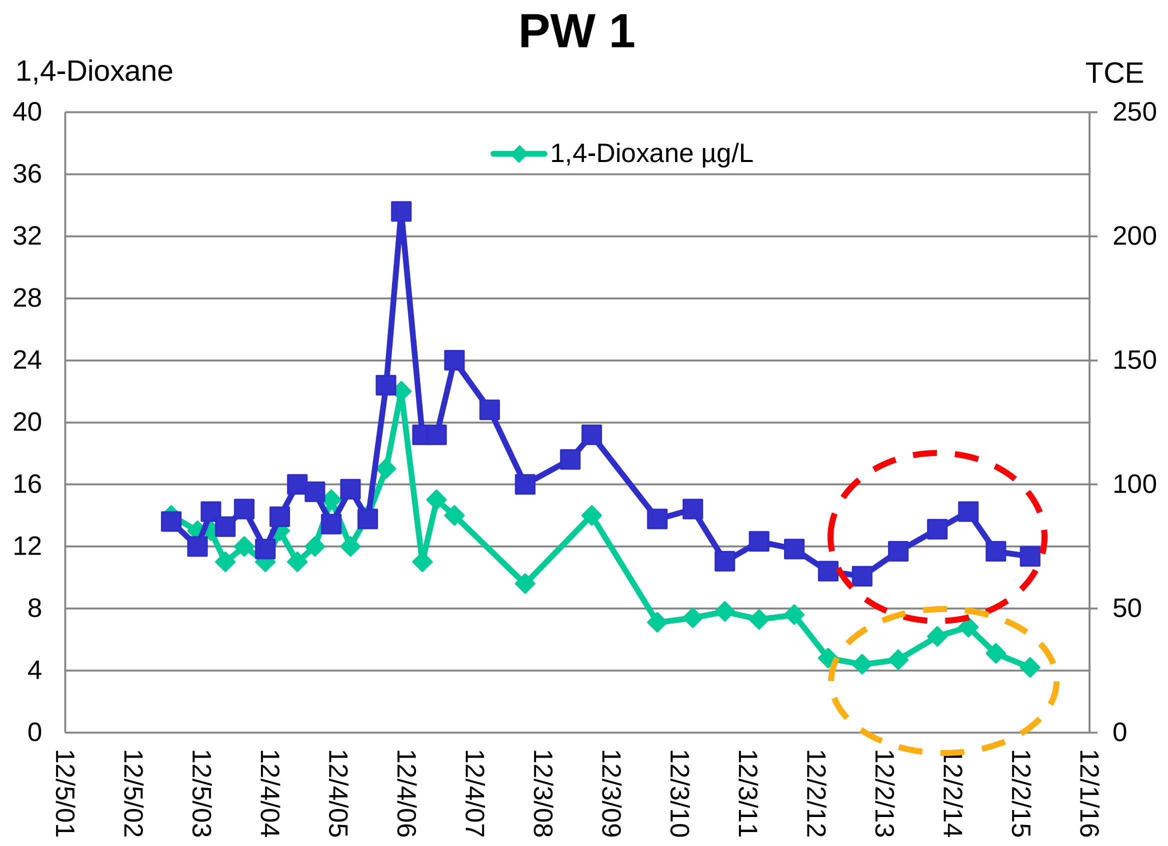
S Statistic	Confidence in Trend
S > 0	CF > 95%
S > 0	95% ≥ CF ≥ 90%
S > 0	CF < 90%
S ≤ 0	CF < 90% and COV ≥ 1
S ≤ 0	CF < 90% and COV < 1
S < 0	95% ≥ CF ≥ 90%
S < 0	CF > 95%

Trend
1. Increasing
2. Probably Increasing
3. No Trend
4. Stable
5. Probably Decreasing
6. Decreasing

Key Tools To Evaluate Plume Stability

Tool	Description/Features	Where
Mann Kendall Toolkit	Spreadsheet tool to evaluate trends	Free www.gsi-net.com
MAROS Tool	Access database platform Data cleanup, aggregation tools Trend analysis, moment analysis Well sufficiency analysis Temporal frequency analyzer	Free www.gsi-net.com
Summit GEMS Tool	Geographic Environmental Mgt. System Database, maps, graphs	http://gems.summite.com/z01/explore/emisMethod.asp
GTS algorithm	Generates plume maps Genetic algorithm to identify redundancy GIS capability Exploratory tools	http://www.itrcweb.org/team/GTS-Optimization-Software
Ricker Method	Trend, moment analysis	Ricker, 2008

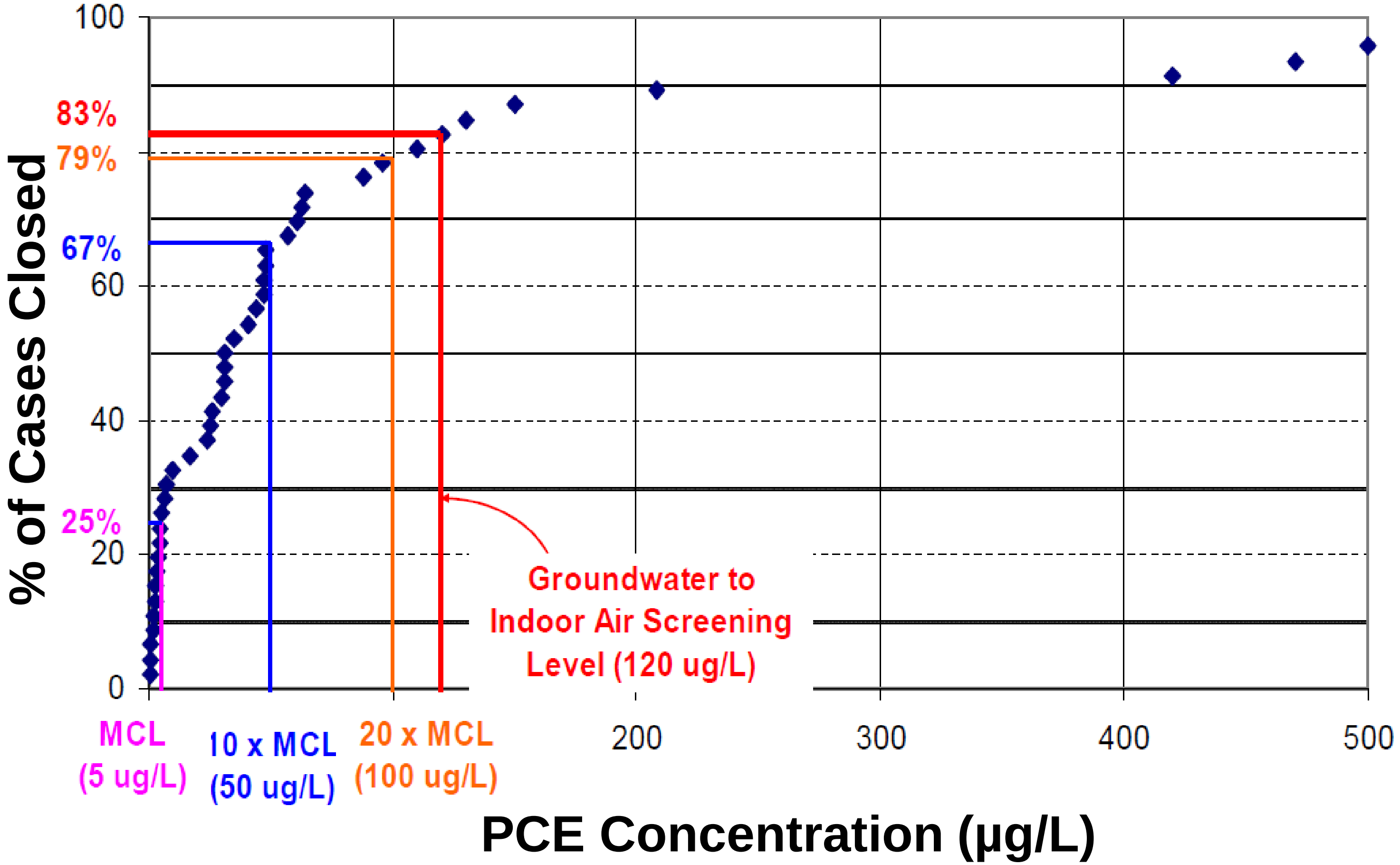
Plume Stability – Increasing concentrations over several events have to be viewed from the overall historical context of the monitoring well



Example Site 3 - TCE and 1,4 dioxane

California's Low-Threat Closure Guidance – PCE Sites Only in Figure Below

Region 2's Practice (over ~last 5 years) Maximum PCE Concentrations at Closure (46 Cases)



Other States

Washington

- Natural attenuation may be appropriate at sites where, prior to relying solely on natural attenuation to achieve cleanup standards, the **ground water plume is** demonstrated to be **stable or shrinking**, thereby shortening the restoration time frame and ensuring that the plume will not continue to migrate and potentially impact other media (surface water, sediments, or air) or receptors (human or ecological).
- If the monitoring well concentrations are determined as **stable** or **shrinking** in 80% or more of the wells within the contaminated plume, then the site plume should be considered stable or shrinking in most circumstances

Hawaii

- If contaminated media is left on site necessitating institutional or engineering controls to prevent potential future exposures, the site is closed with restricted use (i.e., a No Further Action with Restrictions or a Letter of Completion with Restrictions)
- For fuel-impacted sites, monitoring for plume stability is a primary low-risk criterion because fuel plumes are typically limited in size and, once stable, generally begin to retreat in a relatively short timeframe under natural conditions.

Dilute plumes
- The case for MNA

- Declining COC concentrations?
  - Spatial: Matrix diffusion may lead to similar concentrations along plume flow path
  - Temporal: Balance between matrix diffusion and attenuation pathways may not show up as declining trend

- MNA pathways include degradation, sorption, and advection-dispersion, but stakeholders often prefer degradation

- Receding plume, case for MNA is easier

- Case for MNA in a stable plume – a stable plume is not a static situation. It is a dynamic equilibrium between contribution from sources (upgradient sources and/or matrix diffusion) and attenuation that often includes biotic or abiotic degradation

Dilute plumes
- The case for MNA

- Byproducts?
  - –Ethene (CVOCs)
  - –Methane
- Native degraders?
  - –Dehalococcoides, other organisms
  - –Native 1,4 dioxane degraders
  - –Molecular biological tools
- Geochemical indicators
  - –ORP, iron, sulfate
- Abiotic pathways?
  - –Acetylene

- Evaluate MNA separately for each COC
  - –E.g., in an aerobic aquifer, we may have a shrinking plume of VC within a stable plume of, plus possibility of native 1,4 dioxane degraders
  - –Allows us to focus treatment (if required) on other COCs

Dilute Plumes
- Key Points

1. A dilute plume has low concentrations throughout the plume and source area (although source may still be distinguishable from plume)
2. Matrix diffusion is the main factor that prevents dilute plumes from receding quickly, as the original upgradient source depletes
3. Matrix diffusion can occur in “sandy, homogeneous aquifers” too
4. Matrix diffusion may be difficult and costly to overcome through aggressive measures
5. Determining plume stability is a key consideration in path forward
6. Low-threat closure (RC with LUCs, RC with LUCs and LTM) may be an option in some cases
7. A renewed case for MNA can be made, if low-threat closure is not an option