

Groundwater Remediation Program

Madison-Kipp Corporation

June 26, 2013



Imagine the result



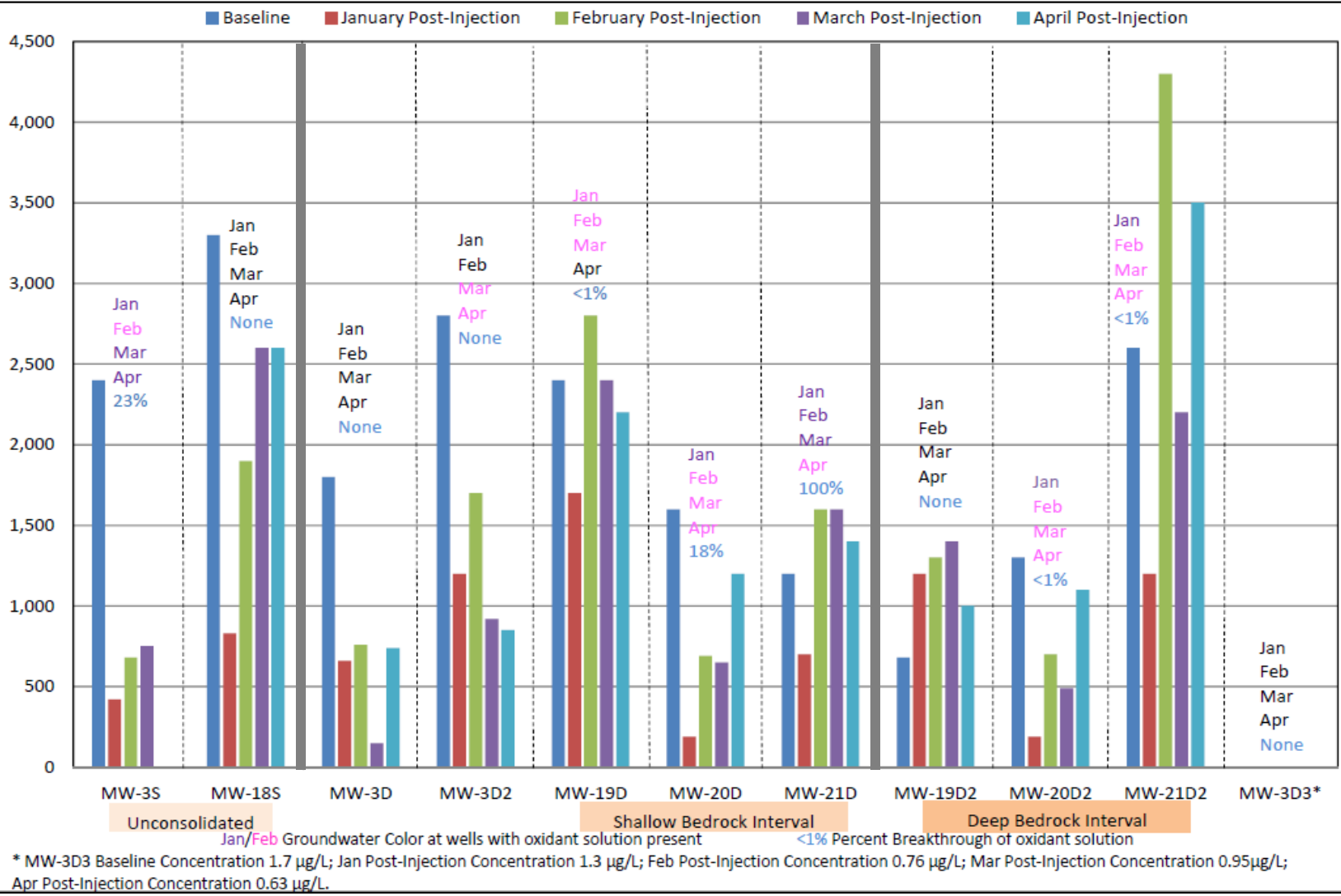
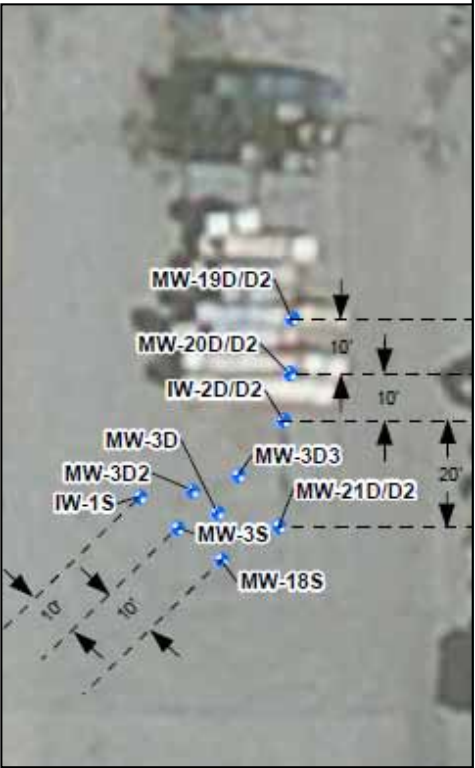
Presentation Outline

- ISCO pilot test conclusions
- Bedrock remediation overview
 - Dual-porosity diffusion review
- Groundwater fate and transport modeling
- Groundwater trends at MKC
- Proposed groundwater remedy



ISCO Pilot Test Conclusions

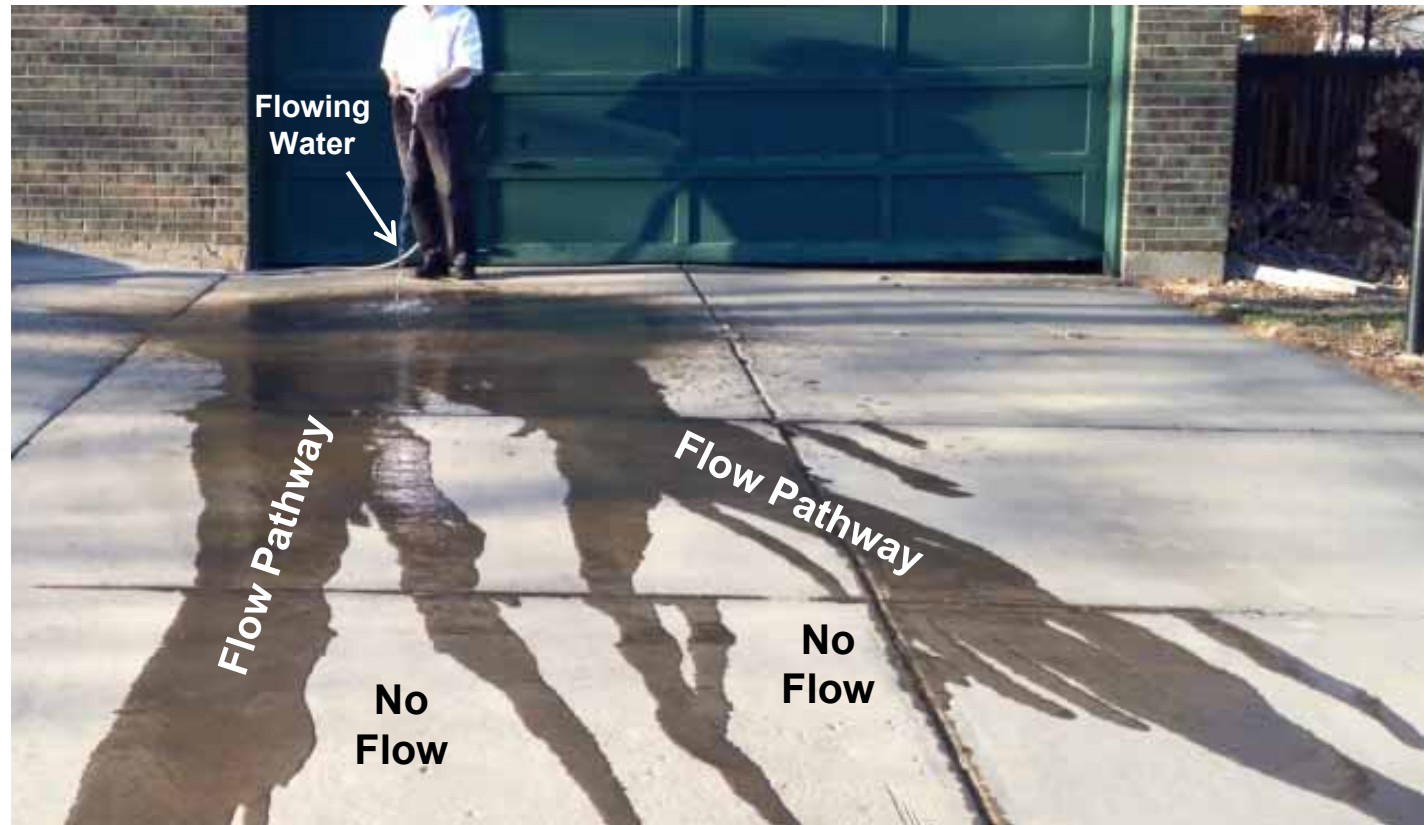
ISCO PCE Reduction



ISCO Effectiveness

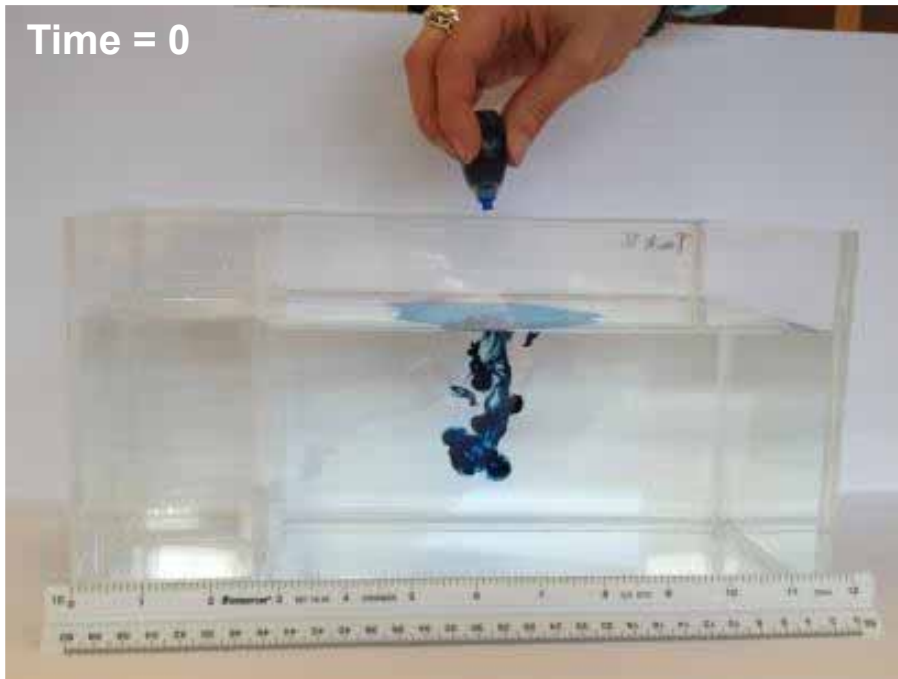
- PCE treatment
 - Unconsolidated (20 – 30 feet in depth)
 - Highly effective in reducing PCE (99% within design zone)
 - Bedrock
 - Complete rebound observed at most bedrock well locations due to back-diffusion between matrix and apertures
- Matrix diffusion impedes active bedrock source treatment

Chemical Transport in Groundwater: Advection



- Occurs primarily in bedrock fractures
- Chemical migration due to flowing groundwater
- Flowing groundwater creates flow pathways for chemical migration
- Controlled by pressure gradients (i.e., groundwater flows from high to low head)

Chemical Transport in Groundwater: Diffusion



- Occurs primarily in bedrock matrix
- Chemical migration due to Brownian motion
- Can occur in the absence of groundwater flow (i.e., in stagnant zones)
- Controlled by direction and magnitude of chemical concentration gradients

Dual-Porosity Conceptual Model

Bedrock Matrix

- Primary porosity, also known as immobile porosity
- Porosity within the bedrock matrix
- Predominant location for storage of groundwater and chemicals

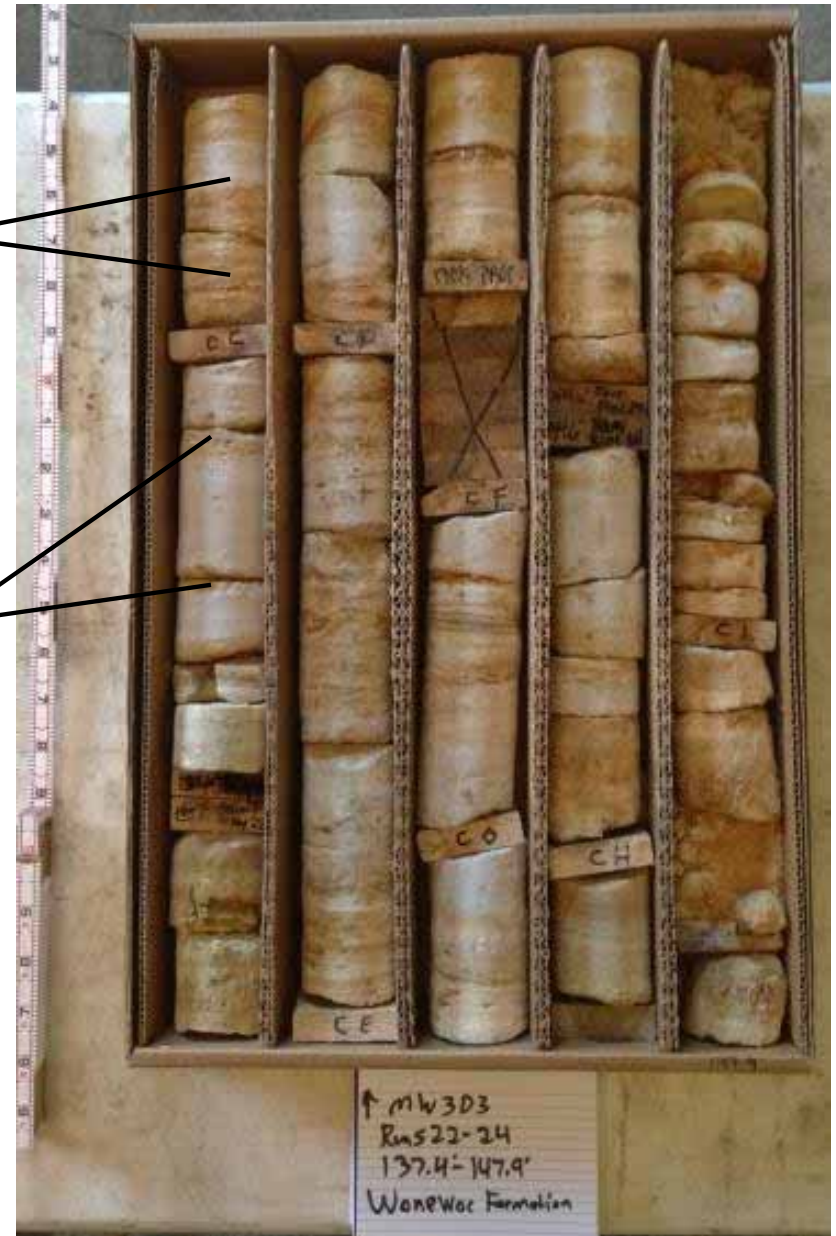
Bedrock Fractures

- Secondary porosity, also known as mobile porosity
- Porosity within bedrock fractures
- Predominant location for transport of groundwater and chemicals

Site Information

- Immobile porosity (bedrock matrix flow): 25%*
- Mobile porosity (bedrock fracture flow): 0.03%*
- Implication: the bedrock matrix can store more than 800 times the groundwater and chemicals than the bedrock fractures.

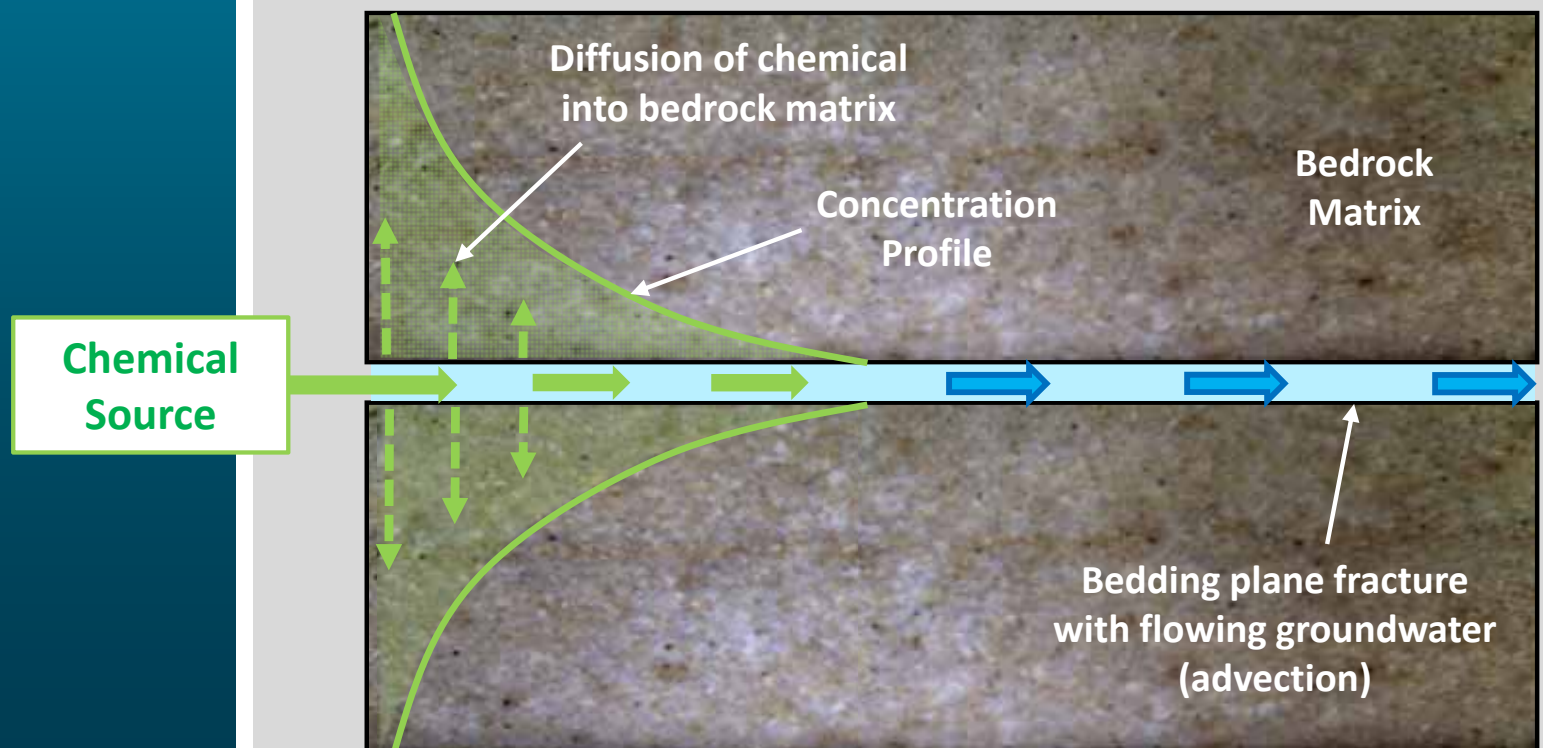
* *Laboratory results from SI investigation*



Dual-Porosity Conceptual Model

When a chemical source is introduced at an open, flowing bedrock fracture:

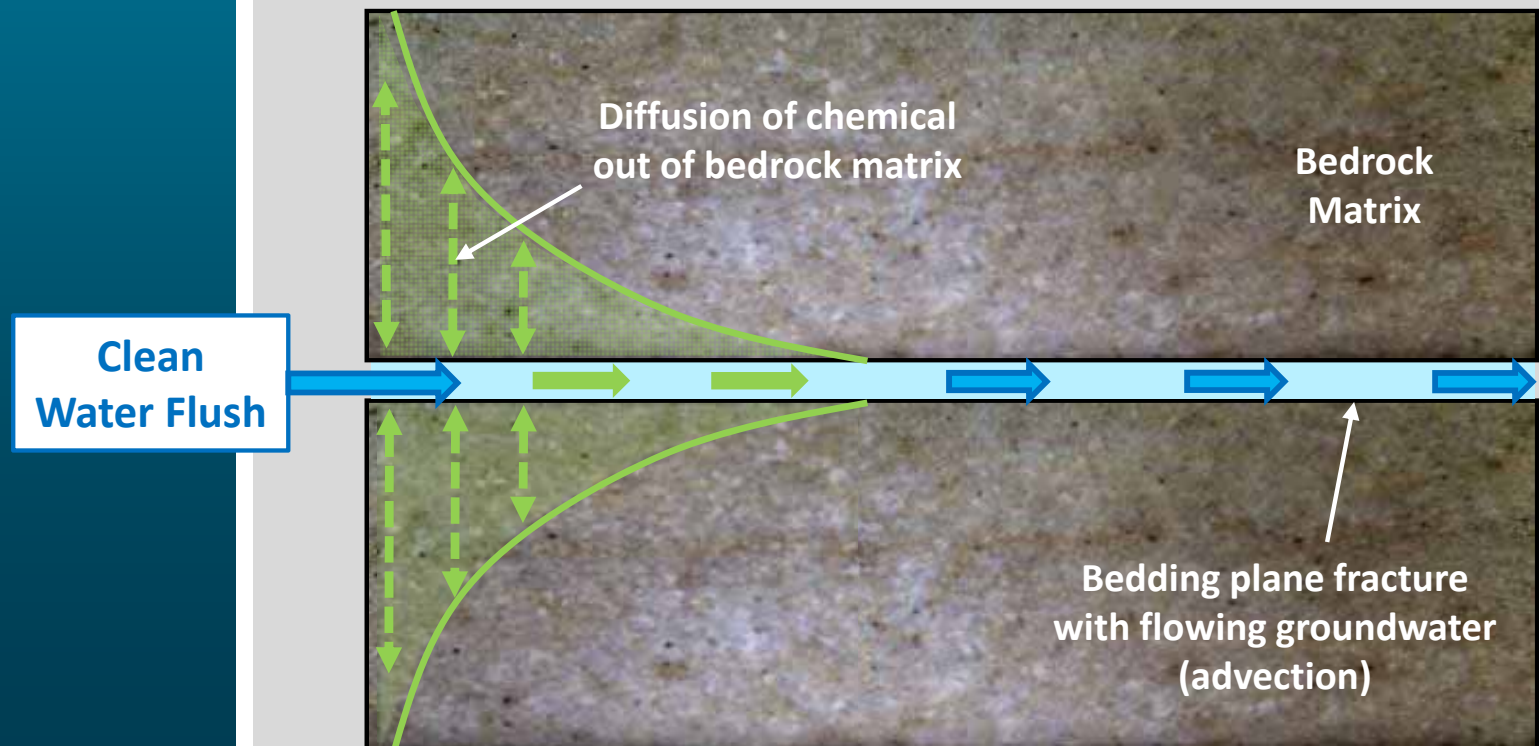
- Chemical is transported along the fracture via advection
- A concentration gradient is created up between the fracture and the bedrock matrix
- Chemical is transported into the bedrock matrix via diffusion
- The matrix diffusion process results in slower plume velocity (i.e., retardation)



Dual-Porosity Conceptual Model

When a clean water flush (i.e. remediation) is attempted in a bedrock fracture:

- Clean water is transported along the fracture via advection
- A chemical concentration gradient develops from the bedrock matrix to the fracture
- Chemical is transported via diffusion from the bedrock matrix into the fracture (i.e., “reverse diffusion”)
- The reverse diffusion process can cause rebound during remediation efforts



Dual-Porosity Mathematical Modeling

- Multiple mathematical models can explicitly simulate fate and transport of chemicals in fractured rock based on advection, matrix diffusion, and other processes (e.g., hydrophobic sorption, chemical transformations).
- We have used these mathematical models to evaluate risk and remediation at numerous fractured rock sites throughout the US. Results of these models have been accepted by USEPA and state regulatory agencies and at several superfund sites.
- Sufficient fracture and bedrock matrix data has been collected at the site to support the development and calibration of a preliminary dual-porosity fate and transport model.
- This model has been completed to understand the fate and transport of PCE within the Lower Lone Rock and Wonewoc formation to provide a greater understanding of both current and future PCE transport.

Predictive Modeling Approaches



Matrix Diffusion–Derived Plume Attenuation in Fractured Bedrock

by David S. Lipson¹, Bernard H. Kueper², and Michael J. Gefell³

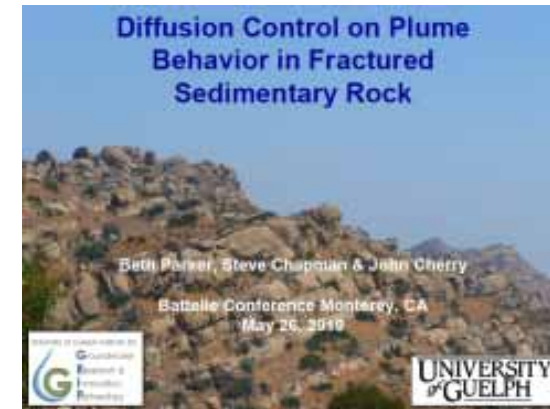
Abstract

Matrix diffusion can attenuate the rate of plume migration in fractured bedrock relative to the rate of ground water flow for both conservative and nonconservative solutes of interest. In a system of parallel, equally spaced constant aperture fractures subject to steady-state ground water flow and an infinite source width, the degree of plume attenuation increases with time and travel distance, eventually reaching an asymptotic level. The asymptotic degree of plume attenuation in the absence of degradation can be predicted by a plume attenuation factor, β , which is readily estimated as $R'(\phi_m/\phi_f)$, where R' is the retardation factor in the matrix, ϕ_m is the matrix porosity, and ϕ_f is the

(*Ground Water*, Vol. 43(1) p. 30-39)

- Simulate contaminant transport in bedrock using DFM and EPM models
- For DFM model, use fracture aperture (b) as fitting parameter
- For EPM model, use dispersivity and retardation factor for fitting
- Perform predictive simulations to address risk-assessment and engineering questions

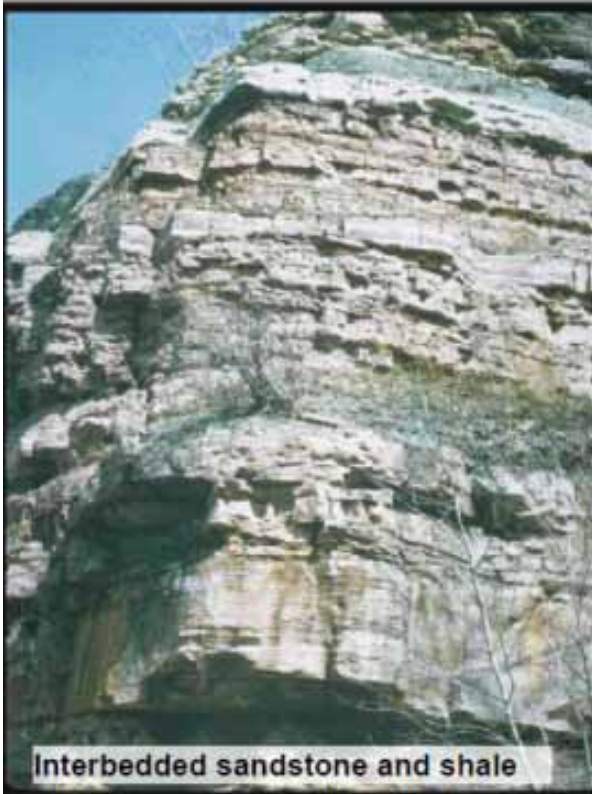
Predictive Modeling Approaches (cont'd)



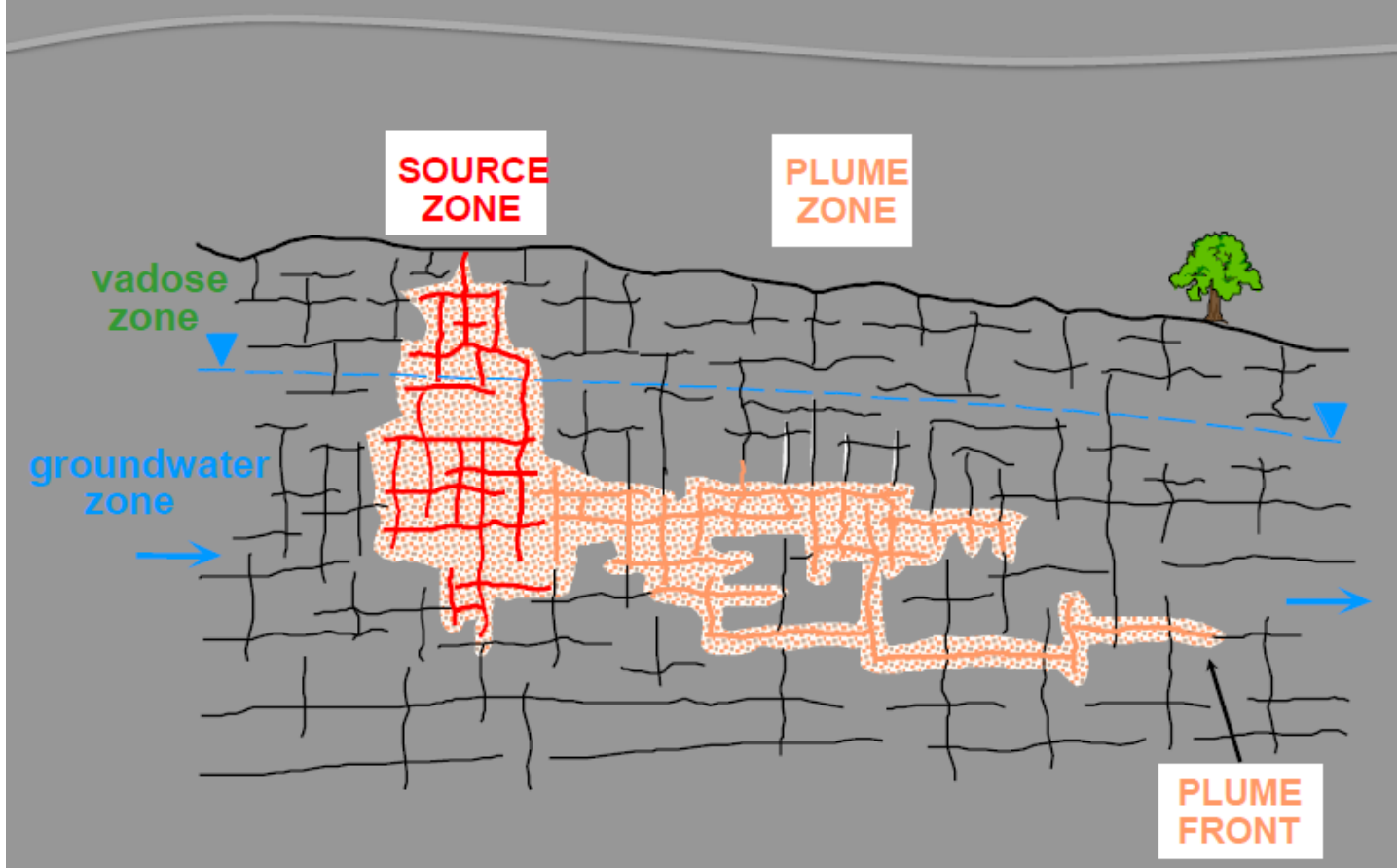
(Parker et al. 2010)

(Parker et al. 2010)

Fractured Porous Media

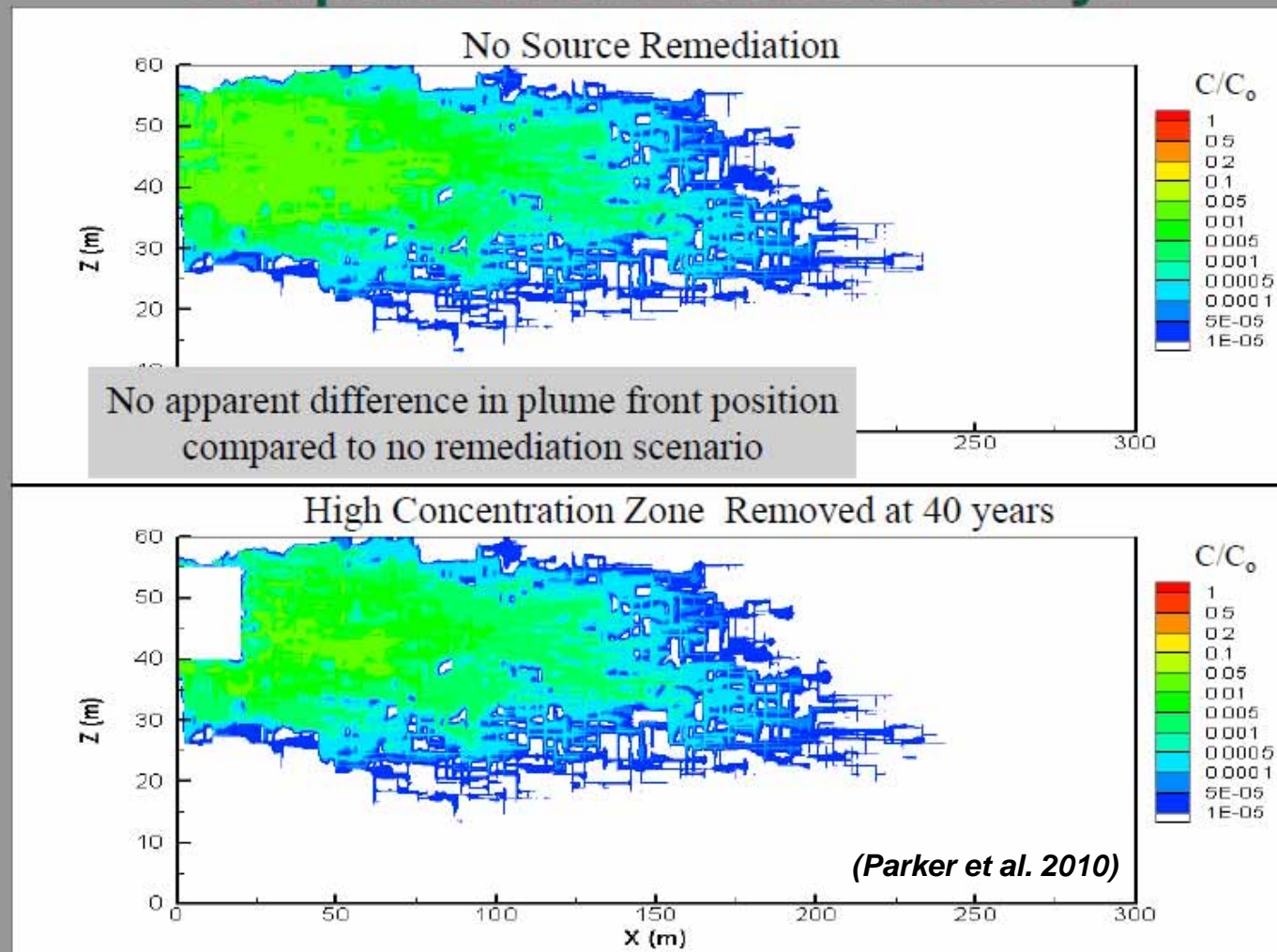


Prediction of Plume Behavior in Fractured Sedimentary Rock Requires a Different Approach



Predictive Modeling Approaches (cont'd)

Comparison of Plumes at 200 yr



- Fate and transport model used to contrast plume transport with and without source treatment (year 40)
- Plume is in equilibrium with bedrock matrix and fracture system
- Diffusion based attenuation requires long duration

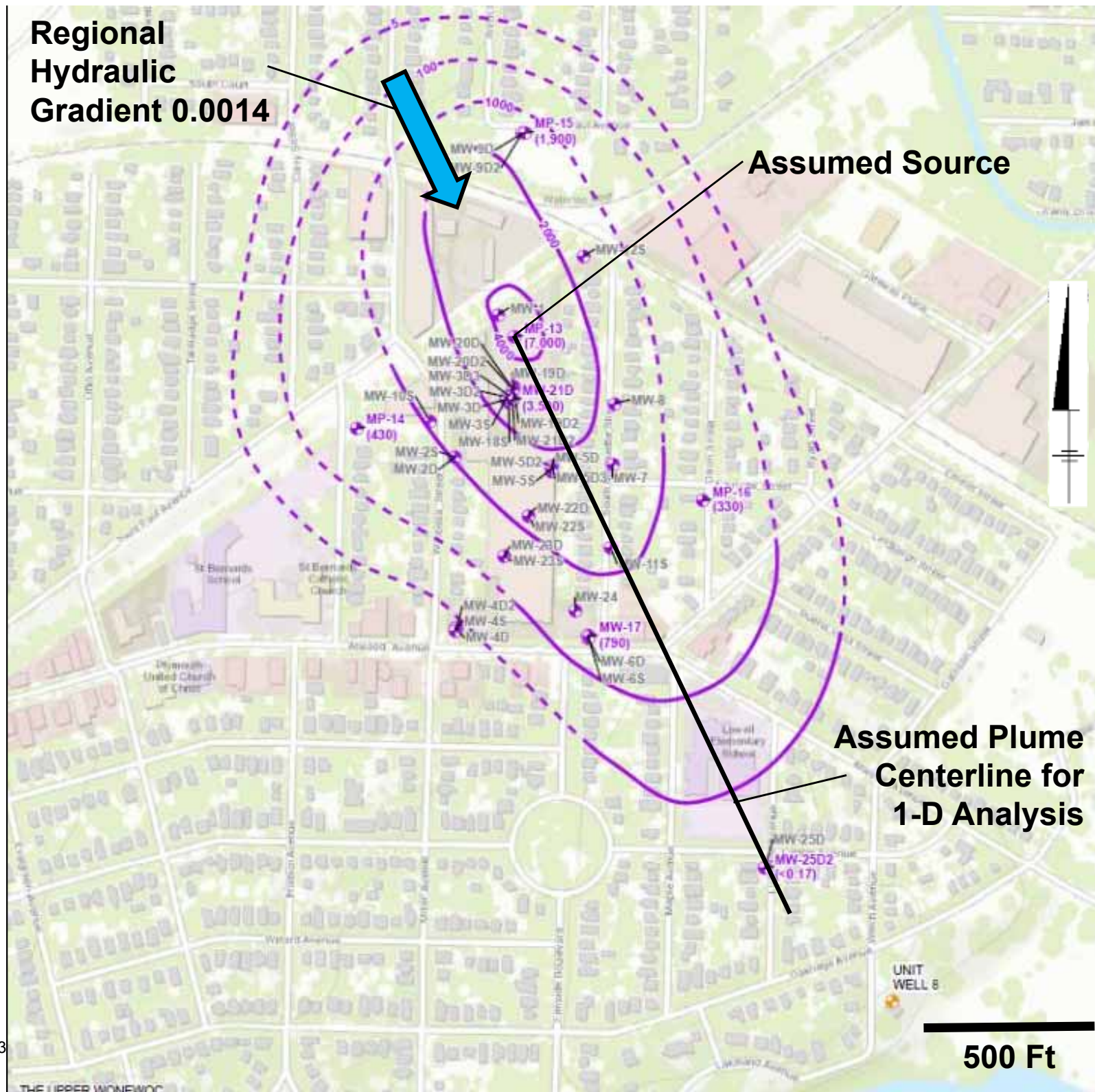
MKC Modeling Objectives

- Validate the dual-porosity conceptual model for bulk plume migration in fractured bedrock at the site.
- Evaluate primary controls on bulk plume migration.
- Perform screening-level feasibility analysis for remedial strategies.

MKC Modeling Approach

- Use a 1-dimensional discrete-fracture, dual-porosity mathematical model to simulate fate and transport of PCE in site groundwater
- Fate and transport processes in bedrock fractures:
 - Advection
 - Dispersion
 - Chemical transformations (abiotic degradation, biodegradation)
- Fate and transport processes in bedrock matrix:
 - Molecular diffusion
 - Hydrophobic-sorption based retardation
 - Chemical transformations (abiotic degradation, biodegradation)
- Diffusive mass transfer between bedrock fractures and bedrock matrix

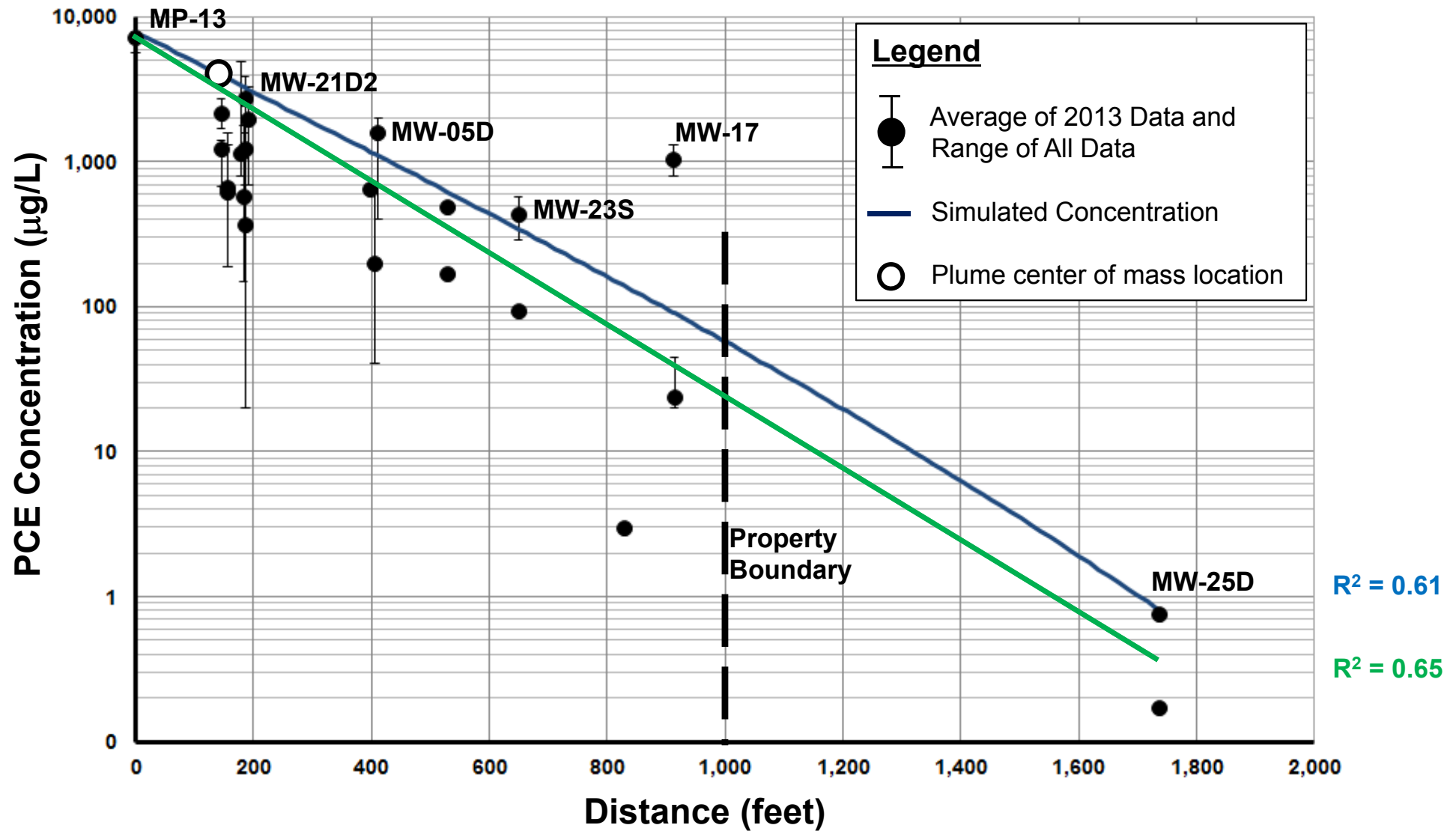
Site Plan and Model Location



Model Parameters

Fractures		
Aperture (hydraulic)	270	microns
Hydraulic gradient	0.0014	--
Average linear groundwater velocity	23.5	ft/day
Dispersivity	1.0	ft
Spacing	2.6	ft
Hydrophobic-sorption based retardation factor	1.0	--
Matrix		
Porosity (immobile porosity)	25	%
Tortuosity	0.15	--
Hydrophobic-sorption based retardation factor	1.4	--
PCE Parameters		
Highest concentration observed	7,900	µg/L
Diffusion coefficient (aqueous)	9.46×10^{-6}	cm/sec
Degradation rate (half-life)	8.3	years
Residence time	47.8	years

Calibrated Model – Current Conditions



Results – Current Conditions

Parameters

- Average linear groundwater velocity = 23.5 ft/day
- Residence time of PCE = 47.8 years

Results

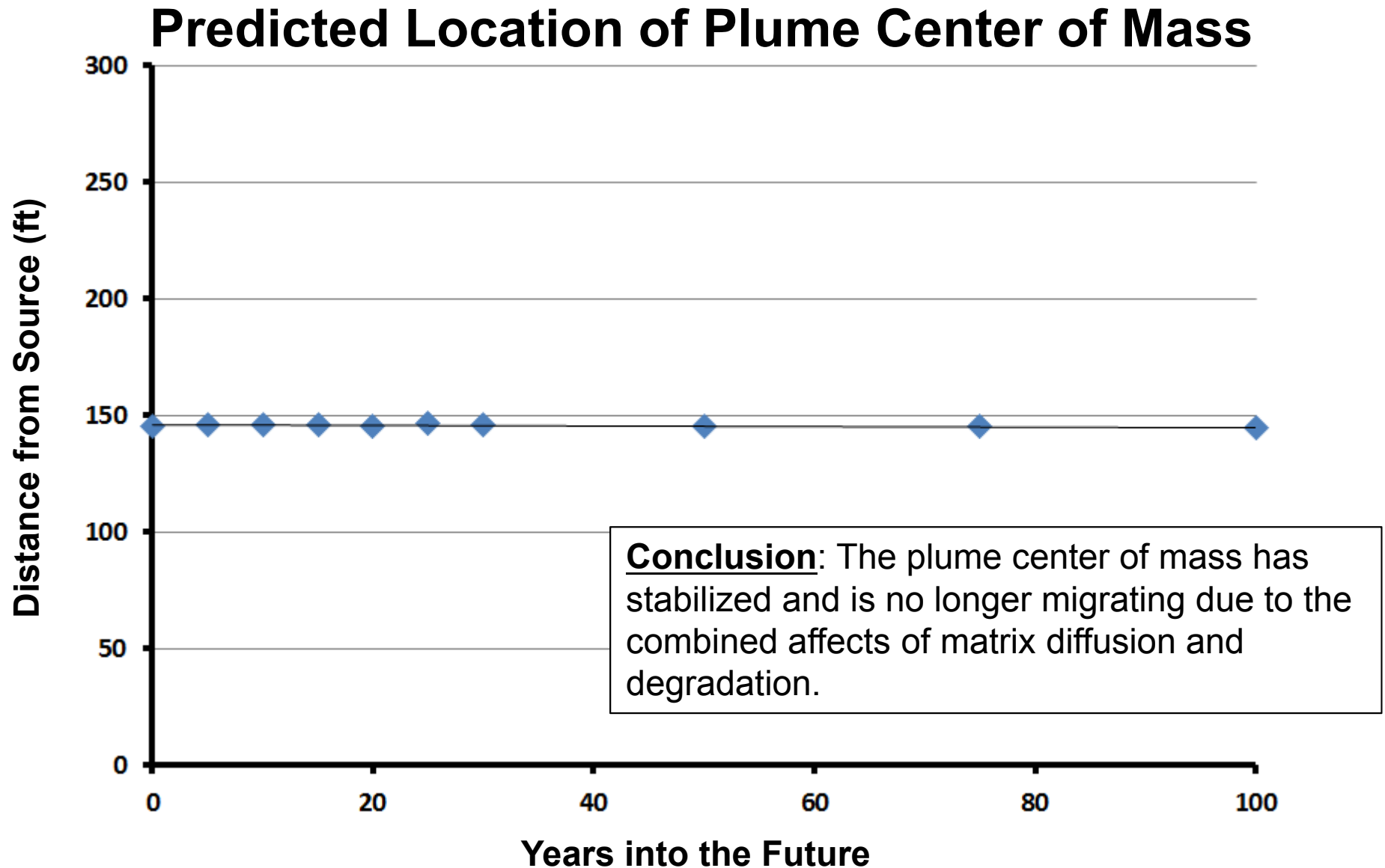
- Actual location of plume center of mass based on data = 145 feet from source
- Matrix-diffusion-derived retardation factor > 2,800
- Current location of 5 ppb contour line = 1,440 feet from source (~800 feet from Unit Well 8)

Predictive Analysis

Key Questions

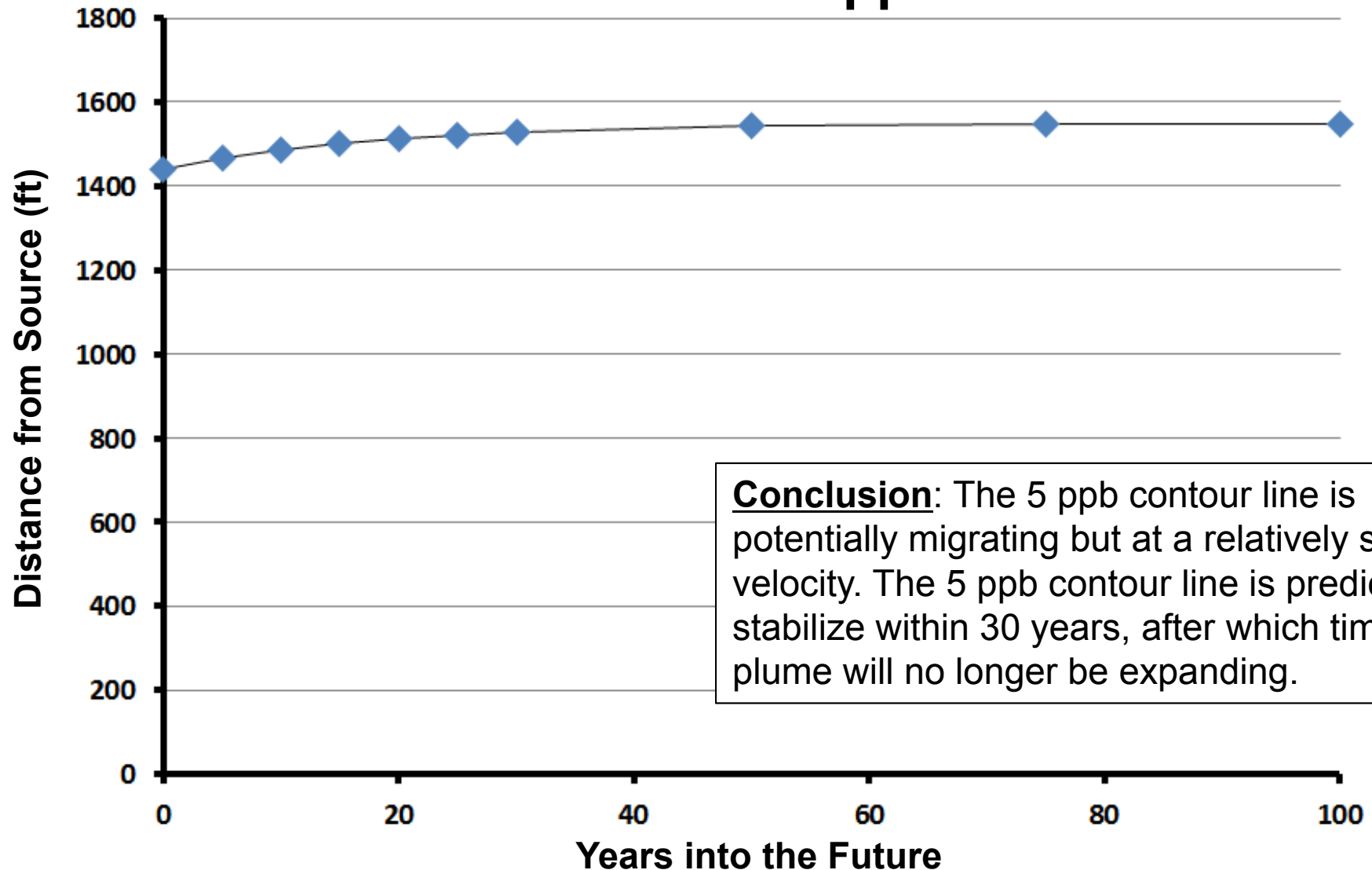
- Is the plume migrating and, if so, at what velocity?
- How far will the plume migrate in the future?

Is the Plume Migrating?



Is the Plume Migrating?

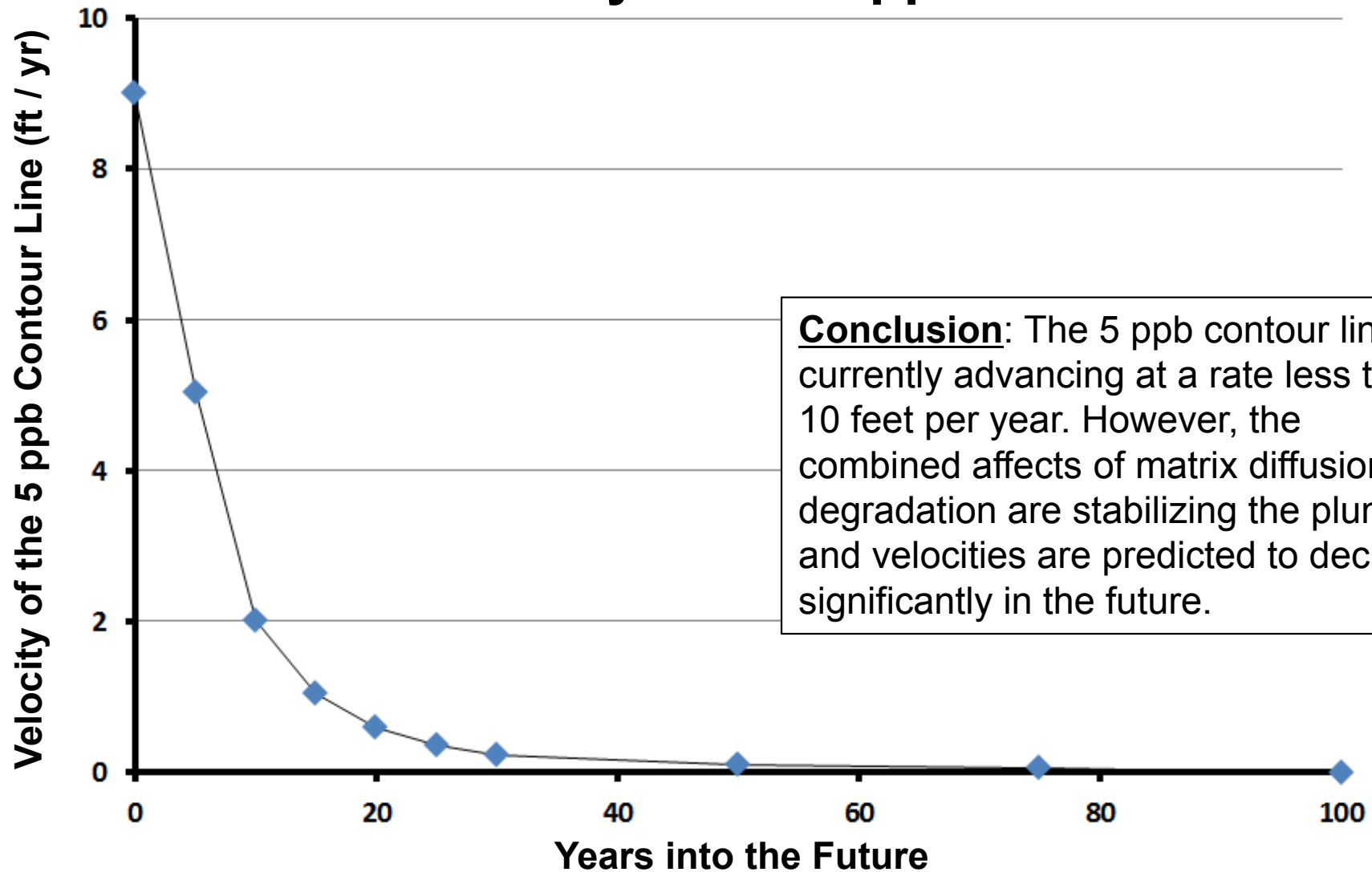
Predicted Location of 5 ppb Contour Line



Conclusion: The 5 ppb contour line is potentially migrating but at a relatively slow velocity. The 5 ppb contour line is predicted to stabilize within 30 years, after which time the plume will no longer be expanding.

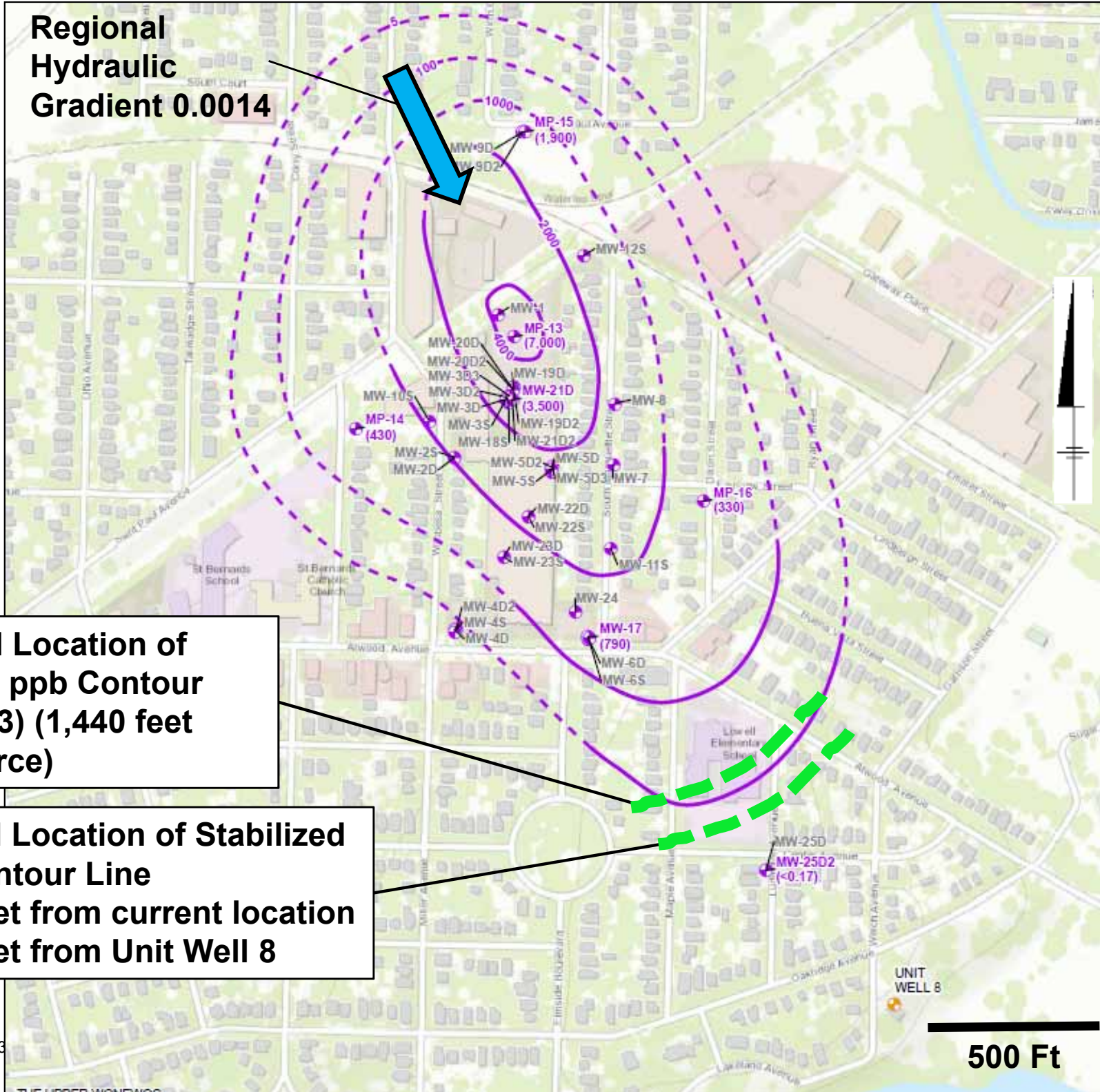
Is the Plume Migrating?

Predicted Velocity of the 5 ppb Contour Line



Conclusion: The 5 ppb contour line is currently advancing at a rate less than 10 feet per year. However, the combined affects of matrix diffusion and degradation are stabilizing the plume, and velocities are predicted to decrease significantly in the future.

Predicted Plume Migration



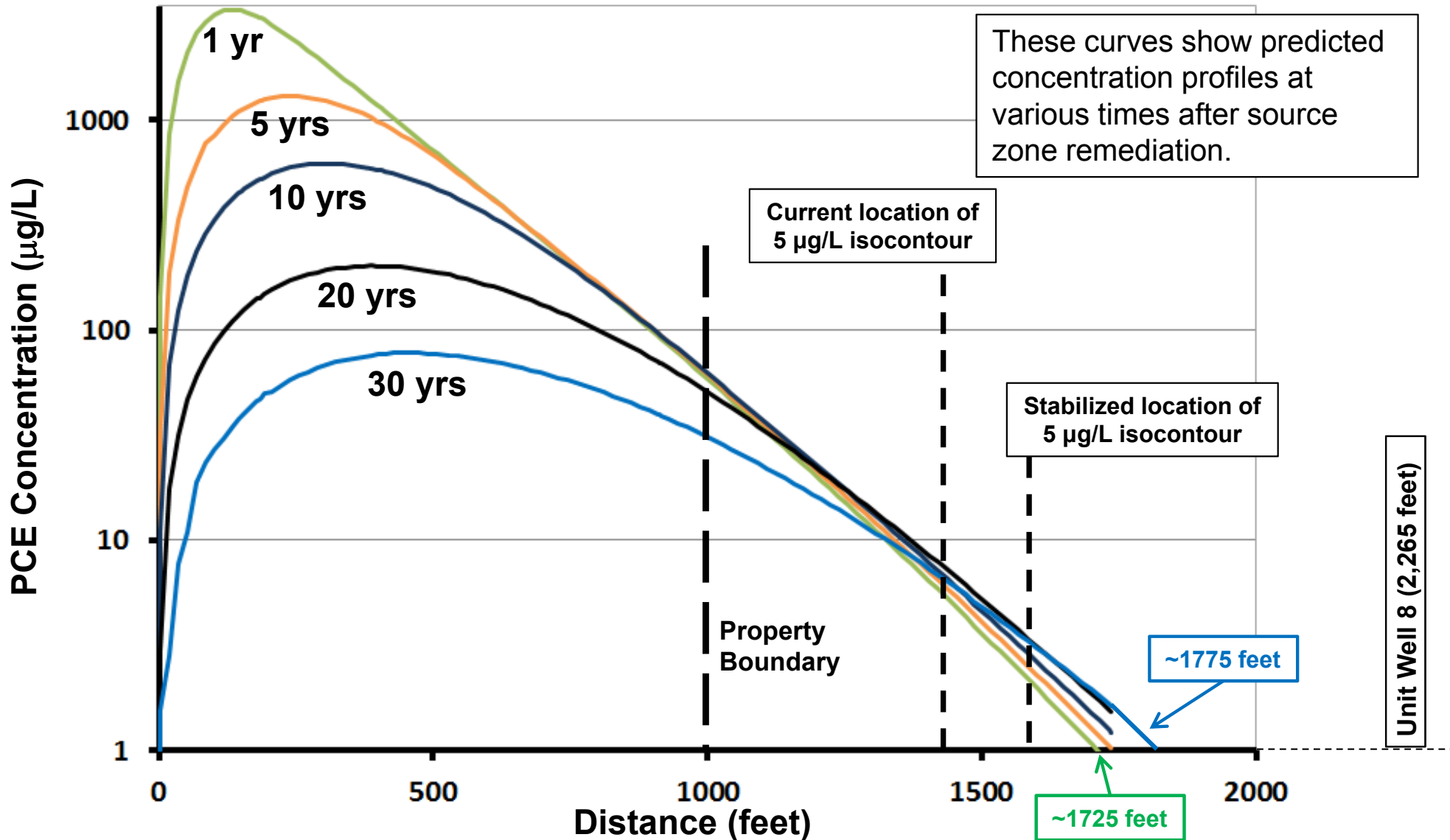
Predictive Analysis

Feasibility Screening of Remedial Strategies

1. Source zone remediation and natural attenuation.
2. Containment at property boundary and natural attenuation off-site.

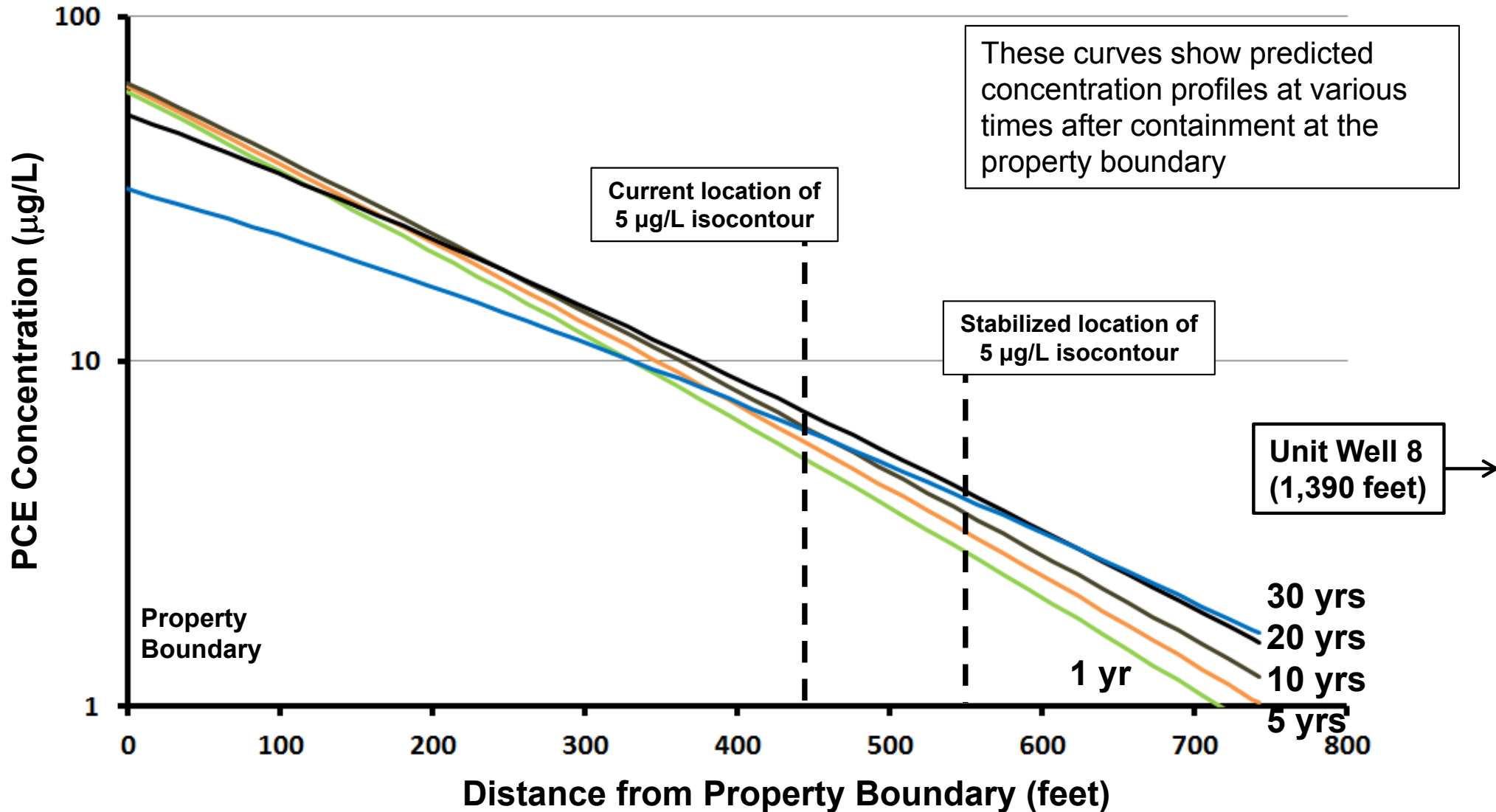
Predictive Analysis

Hypothetical 100% Treatment of Hot Spots



Predictive Analysis

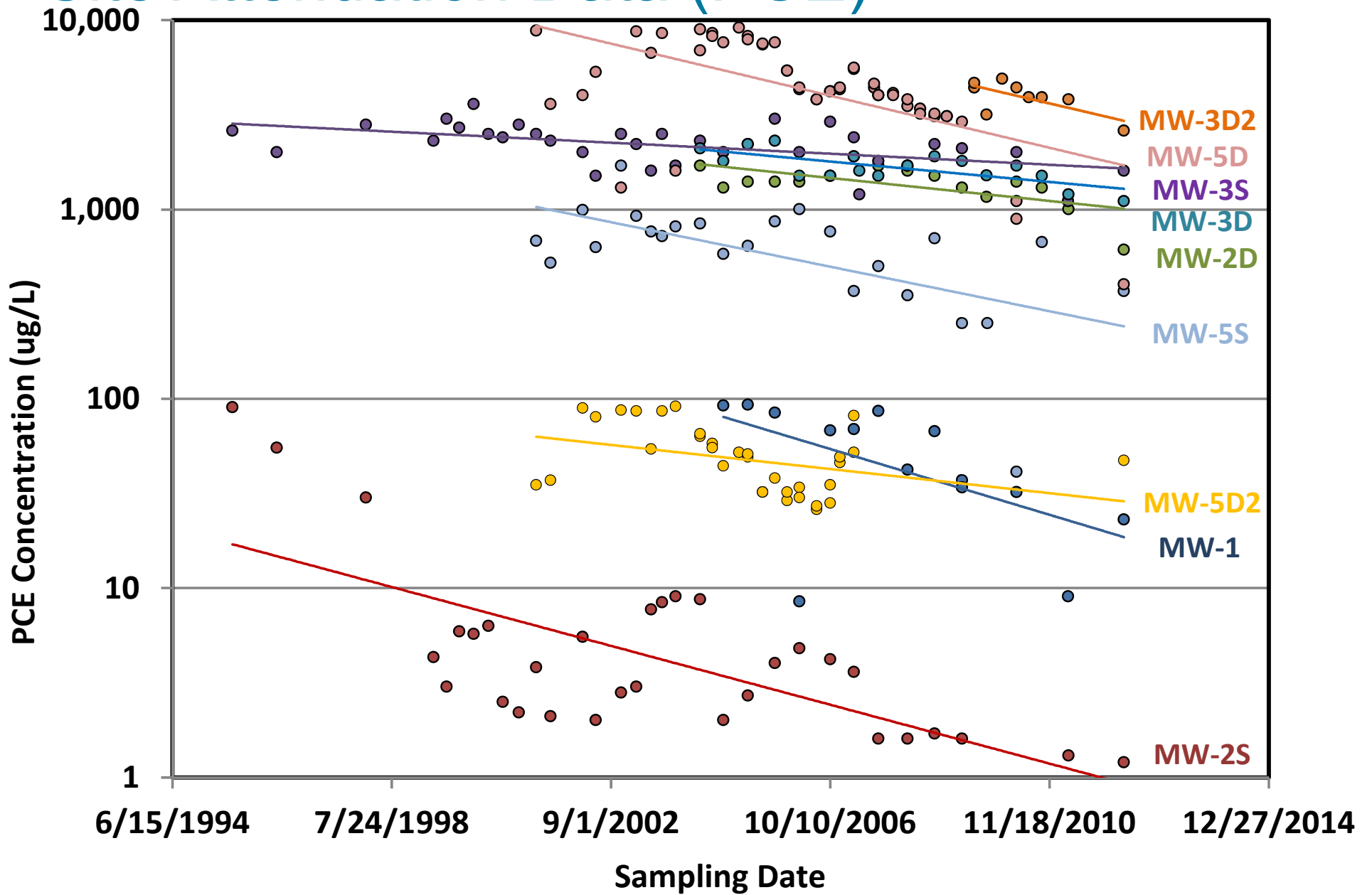
Hypothetical Containment at Property Boundary



Conceptual Model Implications

- Matrix diffusion has considerable effect on PCE transport:
 - Significant retardation within hot spot and dilute plume areas
 - Plume stabilization due to physical attenuation
- Stored mass will degrade via biological, abiotic, or physical attenuation
- Unconsolidated source and bedrock concentrations are stable
- Leading edge (5 ppb contour) expected to stabilize within next 30 years
- Combined effects of attenuation and matrix diffusion stabilize the plume and mitigate future risk to Unit Well 8

Site Attenuation Data (PCE)



Data shown are most representative of recent trends observed in selected wells

Potential Receptors – Groundwater

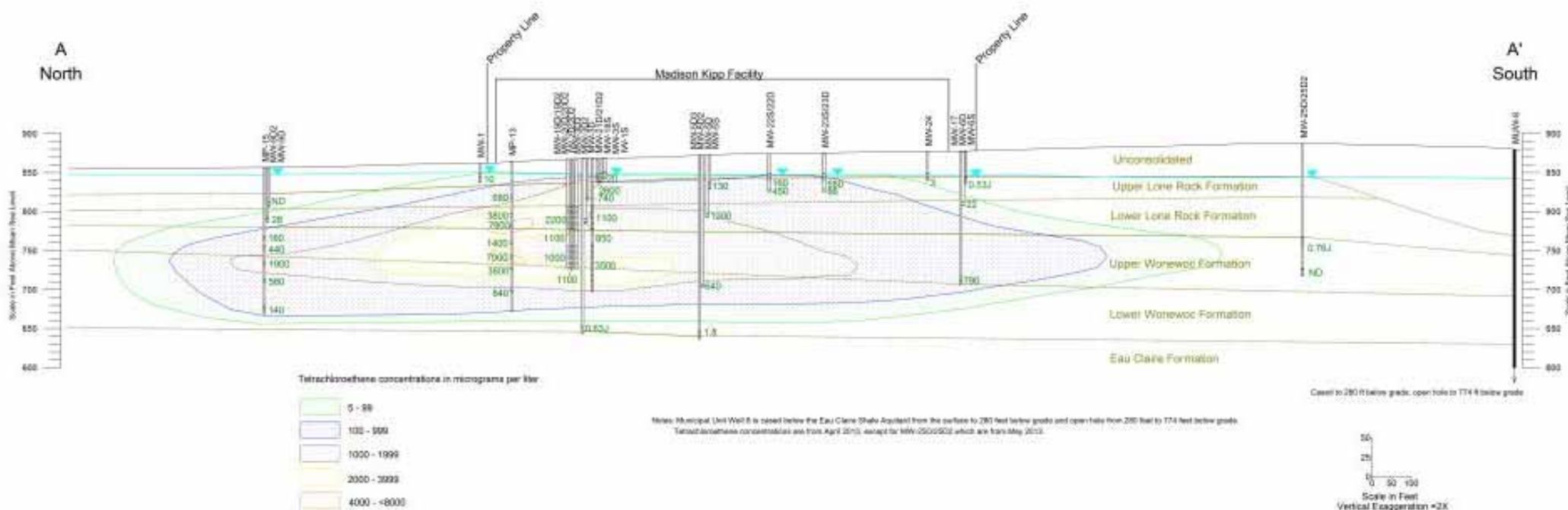
Potential Vapor Intrusion to Off-Site Residences

- Volatilization of PCE from shallow unconsolidated groundwater and potential migration to shallow soil gas

Potential PCE Impacts to Unit Well 8

- Potential transport of PCE via bedrock groundwater to Unit Well 8; subsequent ingestion

Unit Well 8 Evaluation

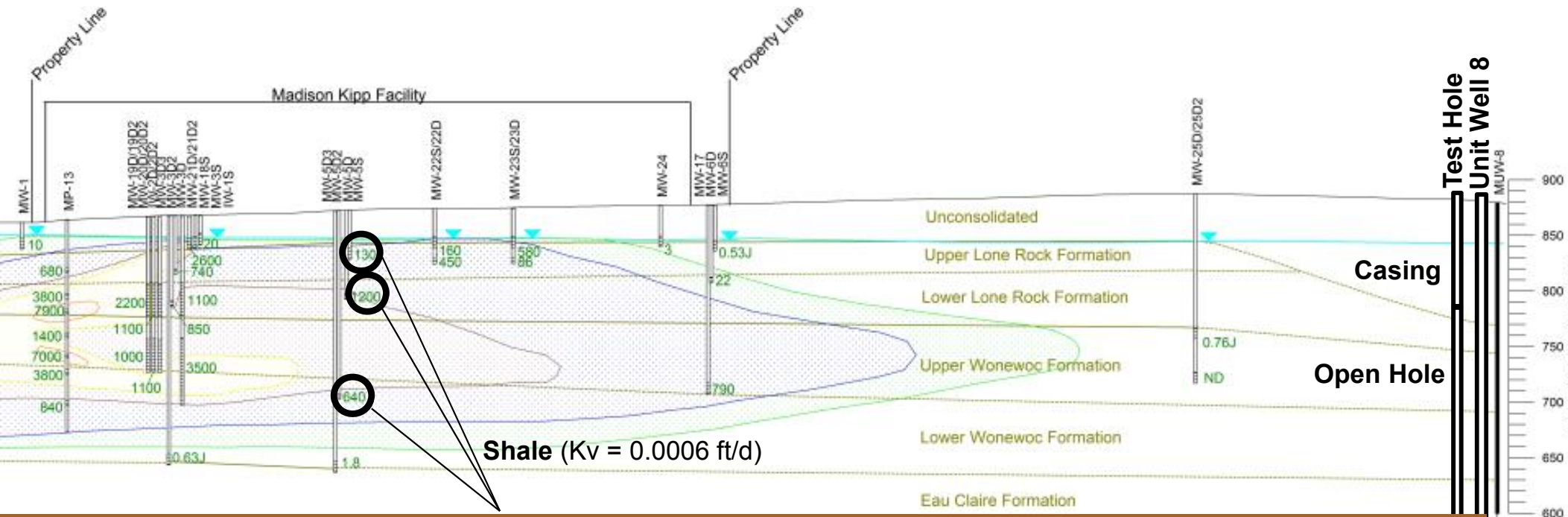


- Modeling shows current plume will stabilize to the north of Unit Well 8
- Eau Claire shale acts as a confining unit between upper paleozoic aquifer and Mount Simon formation
- VOC concentrations within upper bedrock are delineated approximately 50 – 100 feet above the Eau Claire shale in the direction of Unit Well 8
- cis-1,2-DCE is limited on-site, not detected at well MW-25; impacts at Unit Well 8 are not derived from MKC

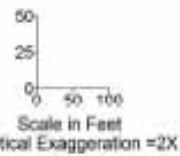
Unit Well 8 Testing – Cross Section

North

South

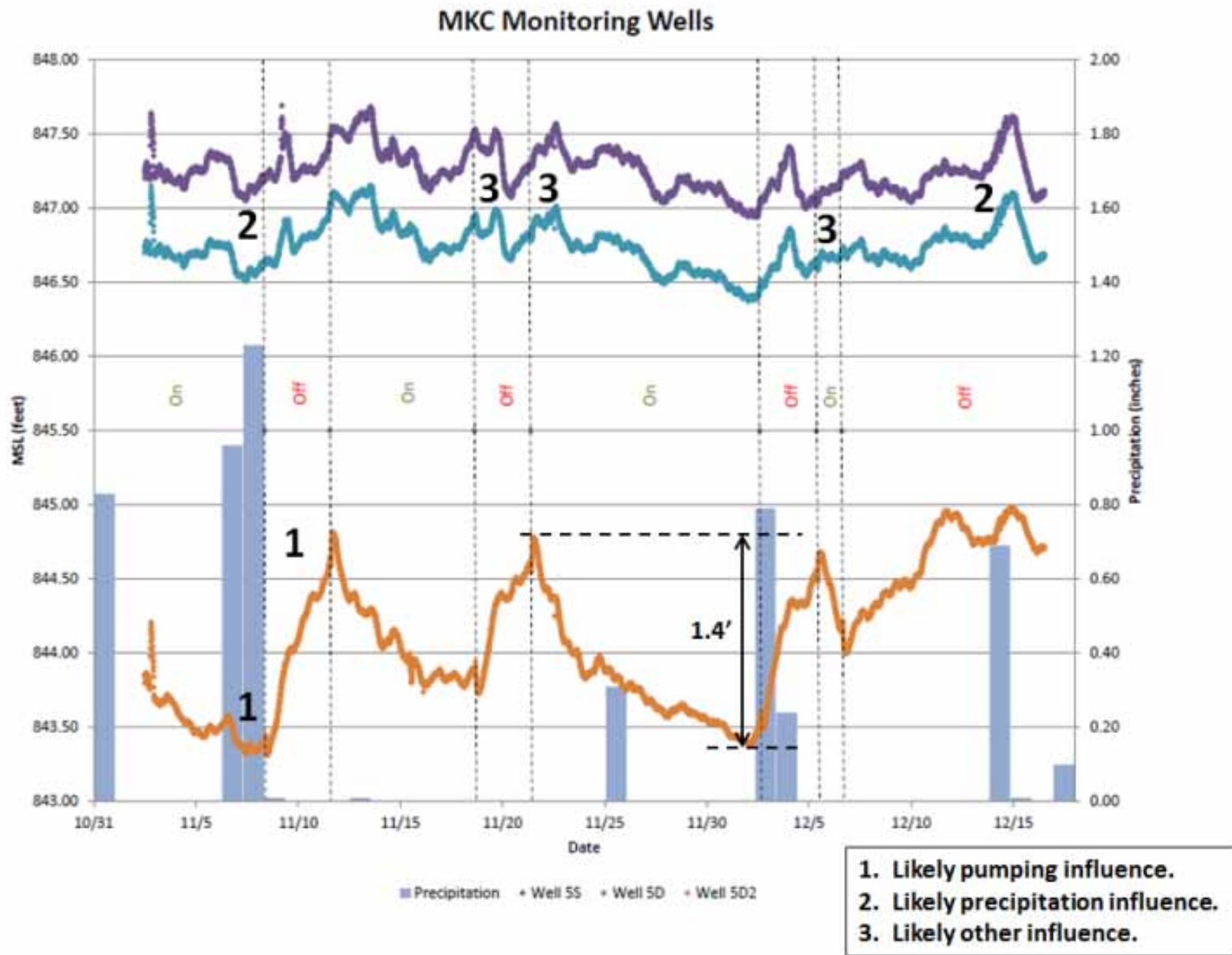


**Wells Monitored During Test Period
MW-5S, MW-5D, MW-5D2**

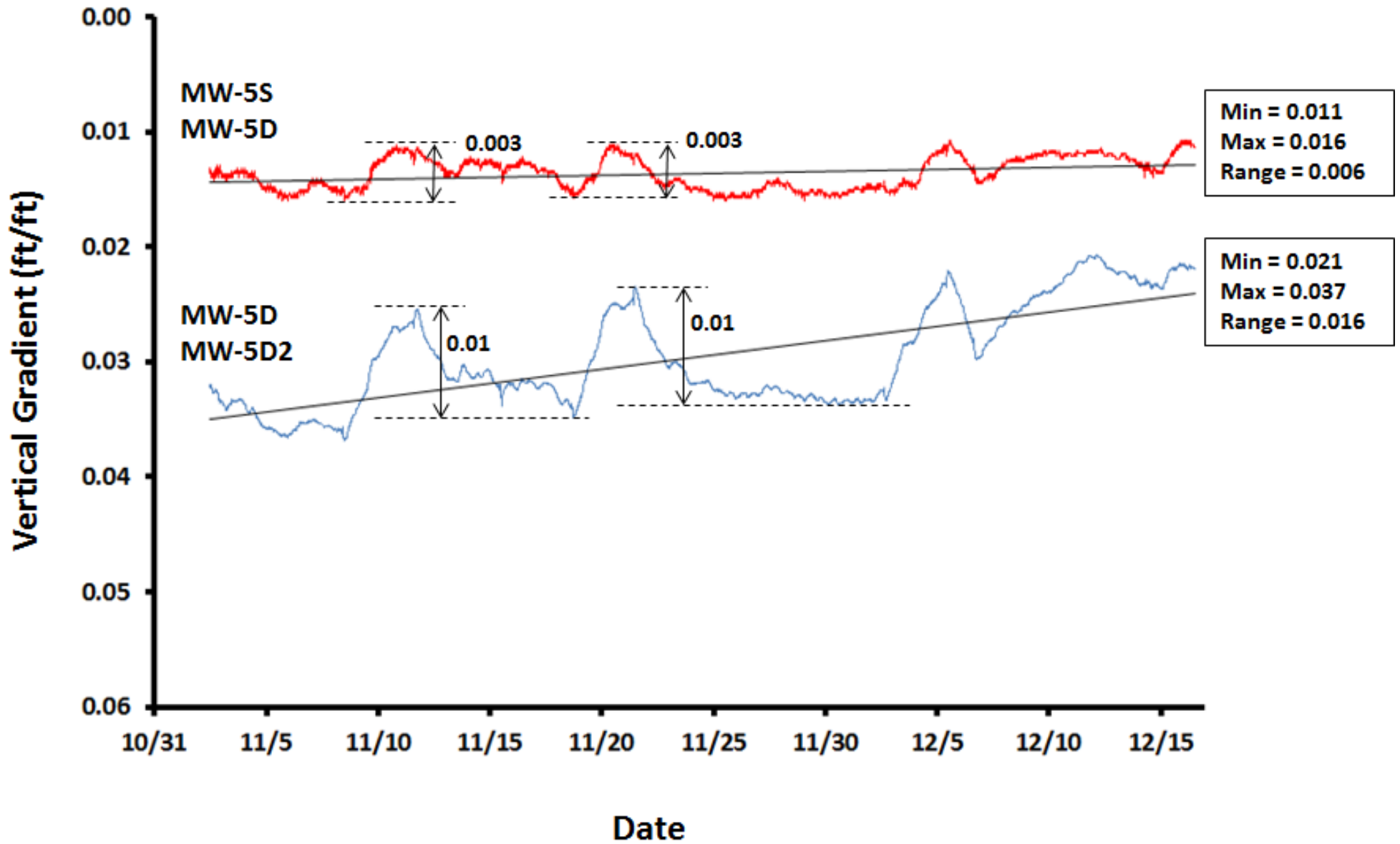


Cased to 380 ft below grade; open hole to 774 ft below grade

Unit Well 8 Testing – Observations at MW-5 well series



Unit Well 8 Testing – Vertical Gradients



Key Observations – Unit Well 8

- The shale layer functions as an aquitard and, where present, severely restricts downward groundwater flow and serves as a protective confining layer
 - Vertical hydraulic conductivity of the shale is 0.0006 ft/d
 - In contrast, hydraulic conductivity of the Wonewoc and Mt. Simon Formations is 5 and 10 ft/d, respectively
- Some groundwater from the Wonewoc Formation drains downward to the Mt. Simon Formation through the Test Well
 - Rate of drainage depends on potentiometric levels in the Wonewoc and Mt. Simon Formations
 - Rate of flow increases when Unit Well 8 is pumping
 - Groundwater flow toward the Test Well is radial and may be subject to impact from alternative chemical sources
- Pumping at Unit Well 8 does not significantly increase the average linear groundwater velocity in the area near the site
- Natural attenuation processes including matrix diffusion and degradation will continue to operate with the same intensity whether or not Unit Well 8 is pumping
 - After over 45 years of subsurface residence time, PCE has not migrated to the base of the Wonewoc Formation or to the location of Unit Well 8 or the Test Well.

Major Conclusions

- Unconsolidated zone ISCO treatment highly effective
- Matrix diffusion has considerable effect on limiting both PCE treatment and fate and transport:
 - Complete rebound observed following bedrock ISCO injections due to reverse diffusion
 - Results in significant PCE retardation within hot spot and dilute plume areas
 - Current 5 µg/L plume edge 1,440 feet from MP-13 and 800 feet from Unit Well 8; will stabilize within 30 years (106 feet further than current extent)
- PCE transport to Unit Well 8 is not occurring and not expected in the future:
 - PCE concentrations delineated at depth, 50 – 100 feet above the shale
 - The shale layer functions as an aquitard and restricts downward groundwater flow
 - Fate and transport model demonstrates plume will never reach Unit Well 8
- Stored mass will degrade via biological, abiotic, or physical attenuation

Proposed Groundwater Remedy

Soil Source Removal

- 300 tons of soil source material (PCE up to 1,800 mg/kg) completed as part of on-site excavation

Unconsolidated Groundwater

- ISCO injections to address unconsolidated PCE source to bedrock
 - Extensive treatment achieved during pilot test
- Addresses primary source of PCE to potential PCE indoor air risk

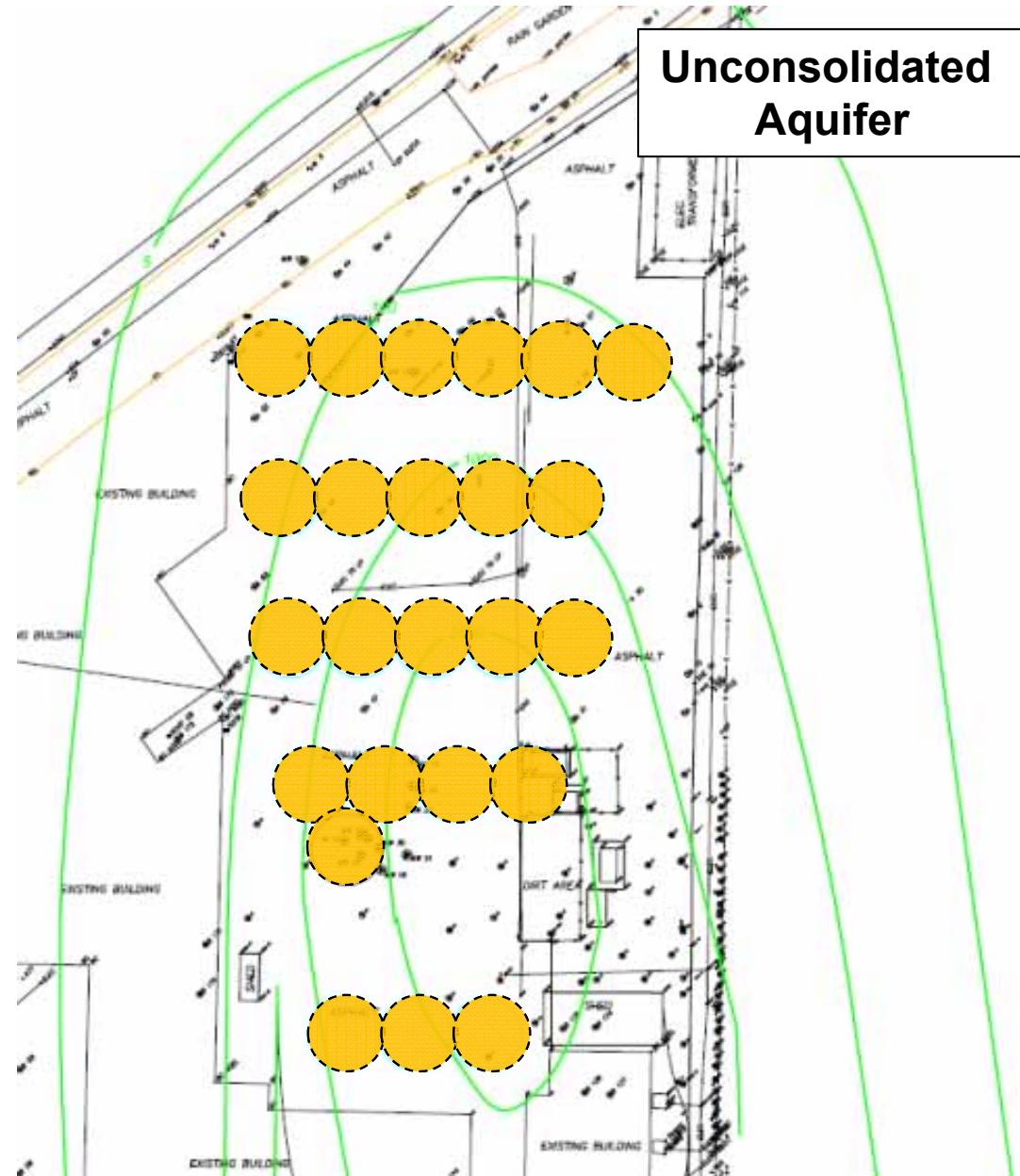
Bedrock Groundwater

- Monitored natural attenuation
 - Active remediation is ineffective
 - Site data demonstrates ongoing decline in PCE in all historic well locations
 - Fate and transport model demonstrates no risk to Unit Well 8
 - Acceptable technology to demonstrate ongoing PCE declines over time
 - MNA monitoring data used to document trends, demonstrate validity of CSM, and MNA applicability for bedrock

Source Area Groundwater Remedy

ISCO Injection Layout

- Multiple injection well transects
 - Located along observed PCE plume flow path
 - Correlated with identified hot spots
- Injection spacing/volumes based on pilot test results
- Injection events timed based on PCE destruction and permanganate longevity



Work Plan Elements – All Due August 1, 2013

MKC will provide one or more work plans to address the following issues:

Background PAH sampling and data analysis.

Additional PCB sampling west of the MKC building.

Sampling for degree and extent of PCB and VOC soil contamination beneath the MKC manufacturing buildings.

Conduct soil sampling in the current rain garden on the north edge of the property to determine potential direct contact concerns during gardening work for PCBs and VOCs.

conduct sub-slab and indoor air testing in the office portions of the MKC building to assess the vapor intrusion pathway in the non-production areas of the plant.

install a water table well between monitoring well MW-1 and monitoring well nest MW9/15.

Install a monitoring well nest north of well nest MW9/15 to describe the extent of contamination in the unconsolidated, Lone Rock and Wonewoc Formations.

Attachment A - MAJOR TASK SUMMARY

Revisions to the SI Report, Including Updating the Conceptual Site Model – All Due September 30, 2013

Expand the conceptual site model to better discuss contaminant source or sources and migration and exposure pathways for soil, soil vapor and groundwater.

Provide more definitive documentation of past material purchases, years of use and handling, storage and disposal practices of all materials containing the detected site contaminants.

Add to the current draft report the tables and maps showing the 2002 to 2011 off-site soil and soil vapor testing locations and results.

Add the off-site sub-slab soil vapor investigation results performed by the Department.

Add to the current report tables and maps that show the pre- and post-remedial soil concentrations from those areas receiving chemical treatments.

Provide a more detailed description of the debris encountered across the site.

Provide water table maps that include maximum and minimum groundwater/piezometric elevation change and flow direction change measured over site history for each identified hydrogeologic unit.

Contact the WGNHS to confirm the groundwater flow descriptions for Lone Rock and Wonewoc Formations

Finalize and provide the on- and off-site soil contamination maps using summer 2012 air photos as the base map to describe the distribution of VOC, PAH and PCB contaminants.

Provide a more complete discussion of the source of on- and off-site detections of the barium, lead, mercury and selenium.

For all groundwater isoconcentration maps, provide contours that range down to and include the enforcement standards for all chlorinated compounds associated with the site.

Provide a map showing the area of influence of each soil vapor extraction well.

SI Report Comments