Toluene Transport and Attenuation in a shallow bedrock aquifer with phytoremediation in an urban setting: Insights from multiple techniques

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Acknowledgments

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Collaborative Project Objectives

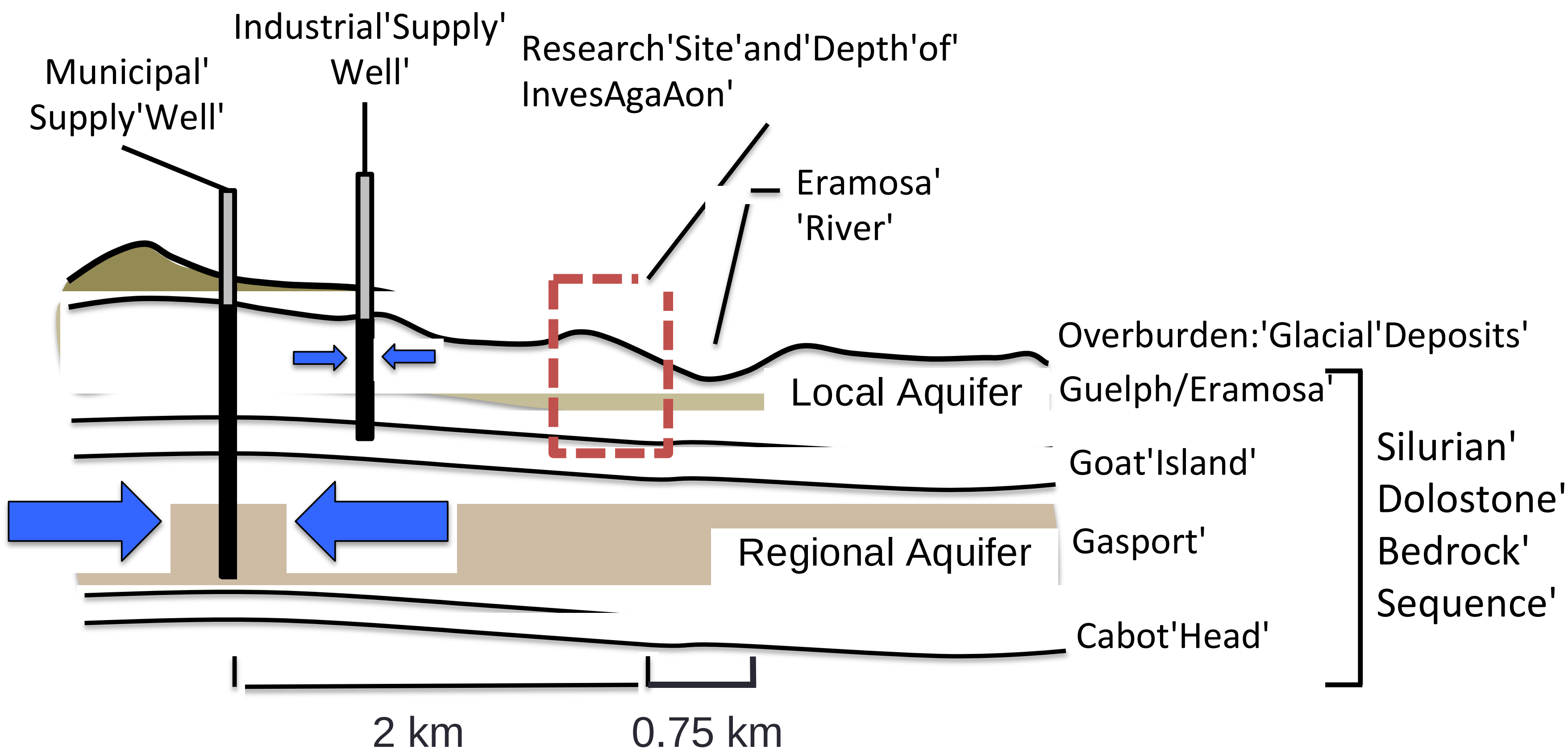
Contaminant Hydrogeology

- 3-D Mass and Phase distribution of toluene in **dual porosity system** using high resolution systems
- Plume transport and fate in fractured porous rock **including matrix diffusion processes**
- Hydrochemistry characterization
- Assessment of biodegradation:
  - Redox
  - CSIA: $\delta^{13}C$ & $\delta^{2}H$ in Toluene, $\delta^{13}C$ in DIC, $\delta^{34}S$ in Sulfate

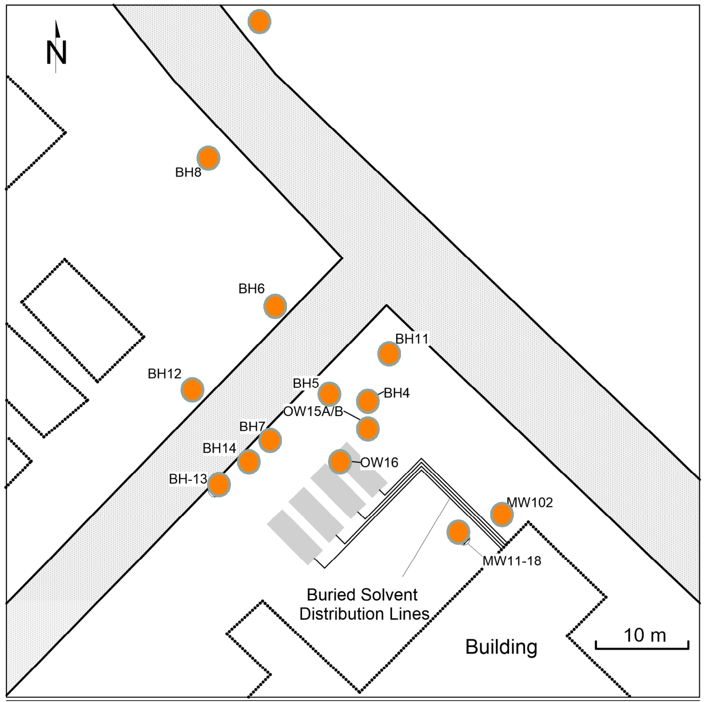
Microbiological Aspects of Phytoremediation

- Toluene Degrading Microbial Activity

Regional Geology and Groundwater Supply Wells



Site History



Pump & treat system operating in shallow bedrock boreholes.

Hybrid poplar cuttings planted: tree-phytoremediation

1952

1991

1991-1999

~2003

2007

2014 - Present

Site Operations:

Metallurgy / Forging

1989

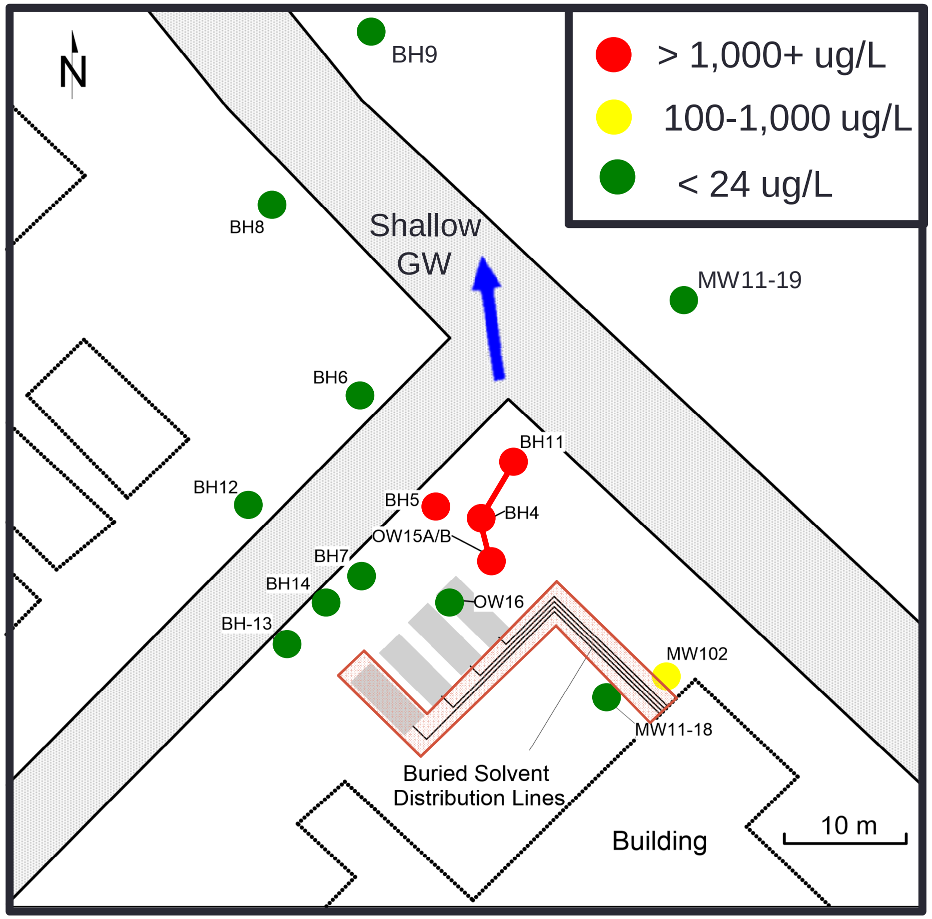
Toluene release discovered

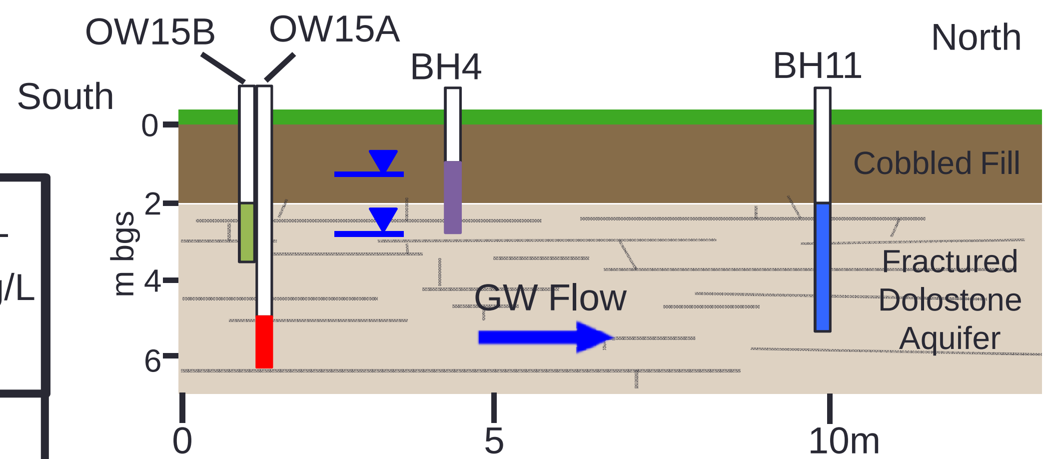
- *Leakage from buried pipeline*
- *Decommission / Remove Tanks*
- *Soil Excavation*

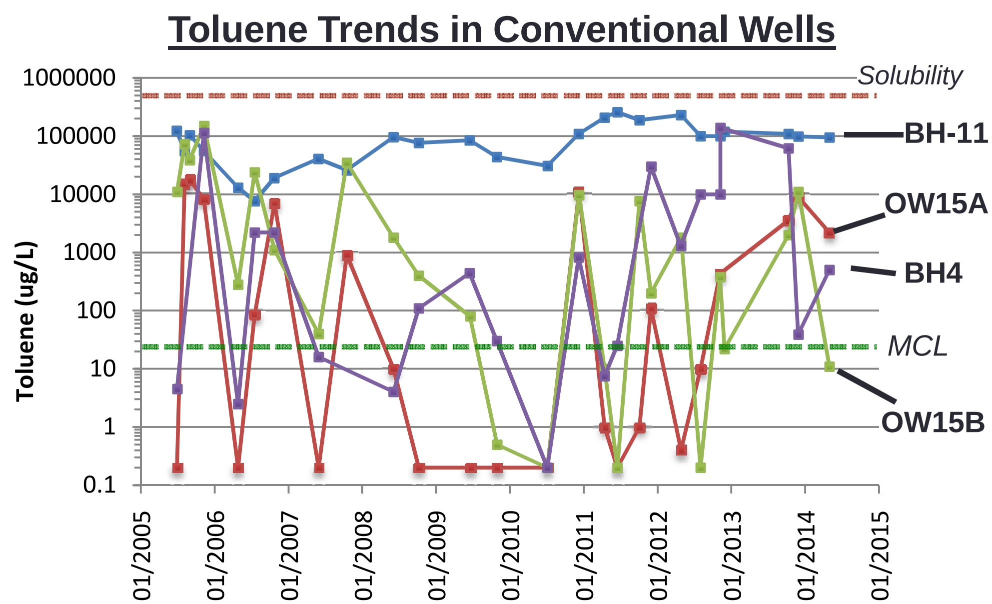
Pilot scale ISCO trial

Initiation as Collaborative Research Site

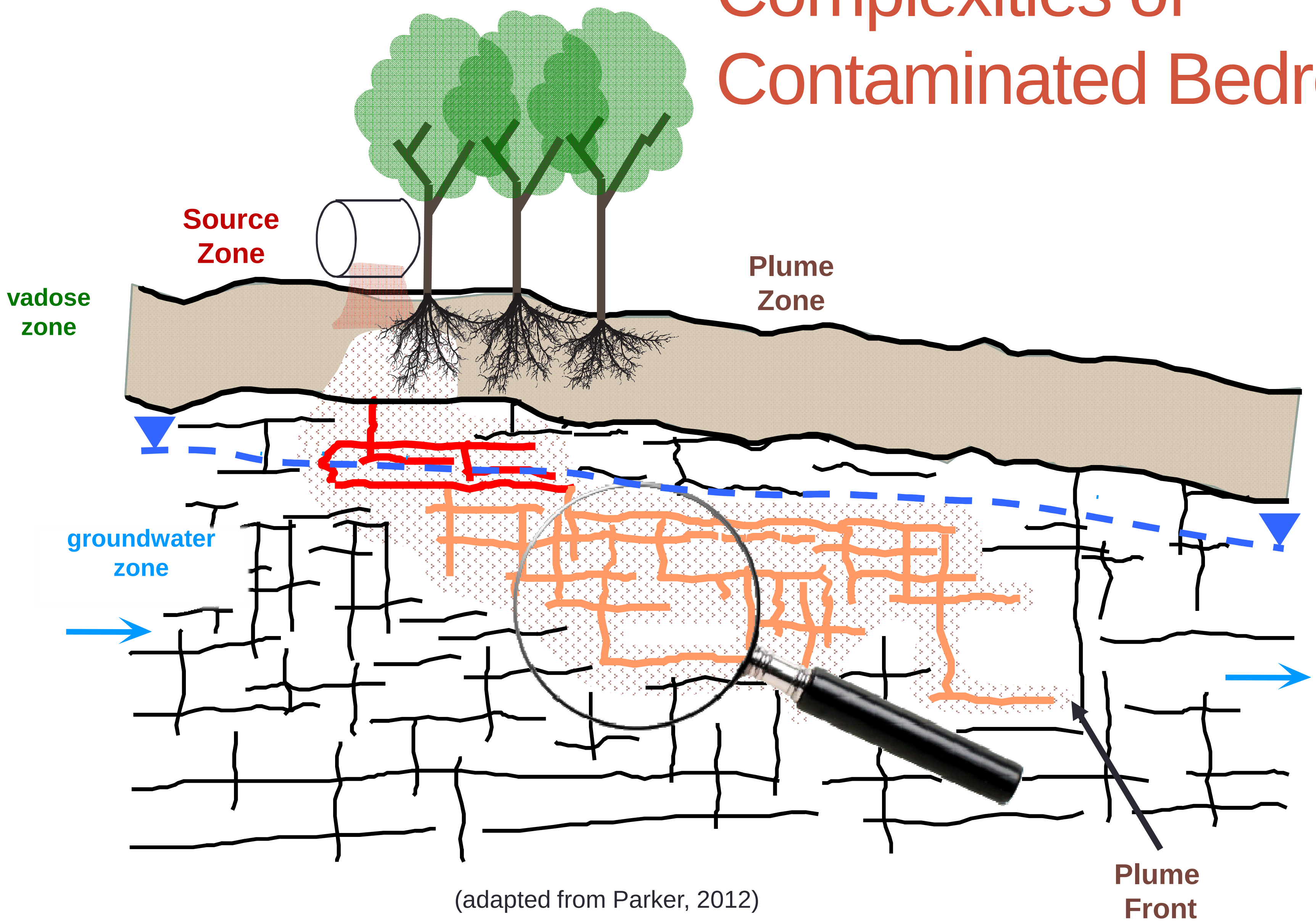
Conventional Monitoring Well Network (1989 – 2014)





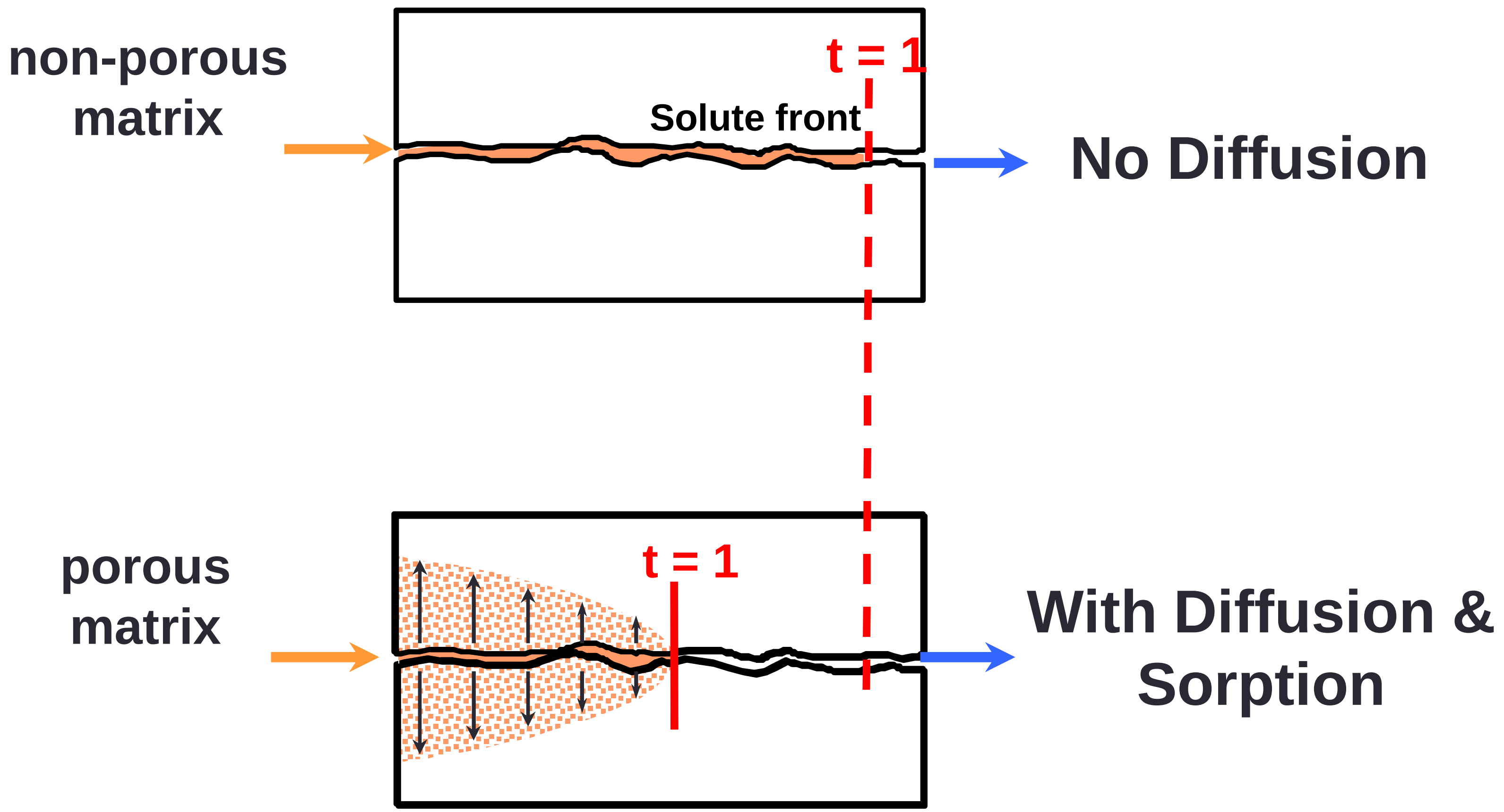


Complexities of Contaminated Bedrock



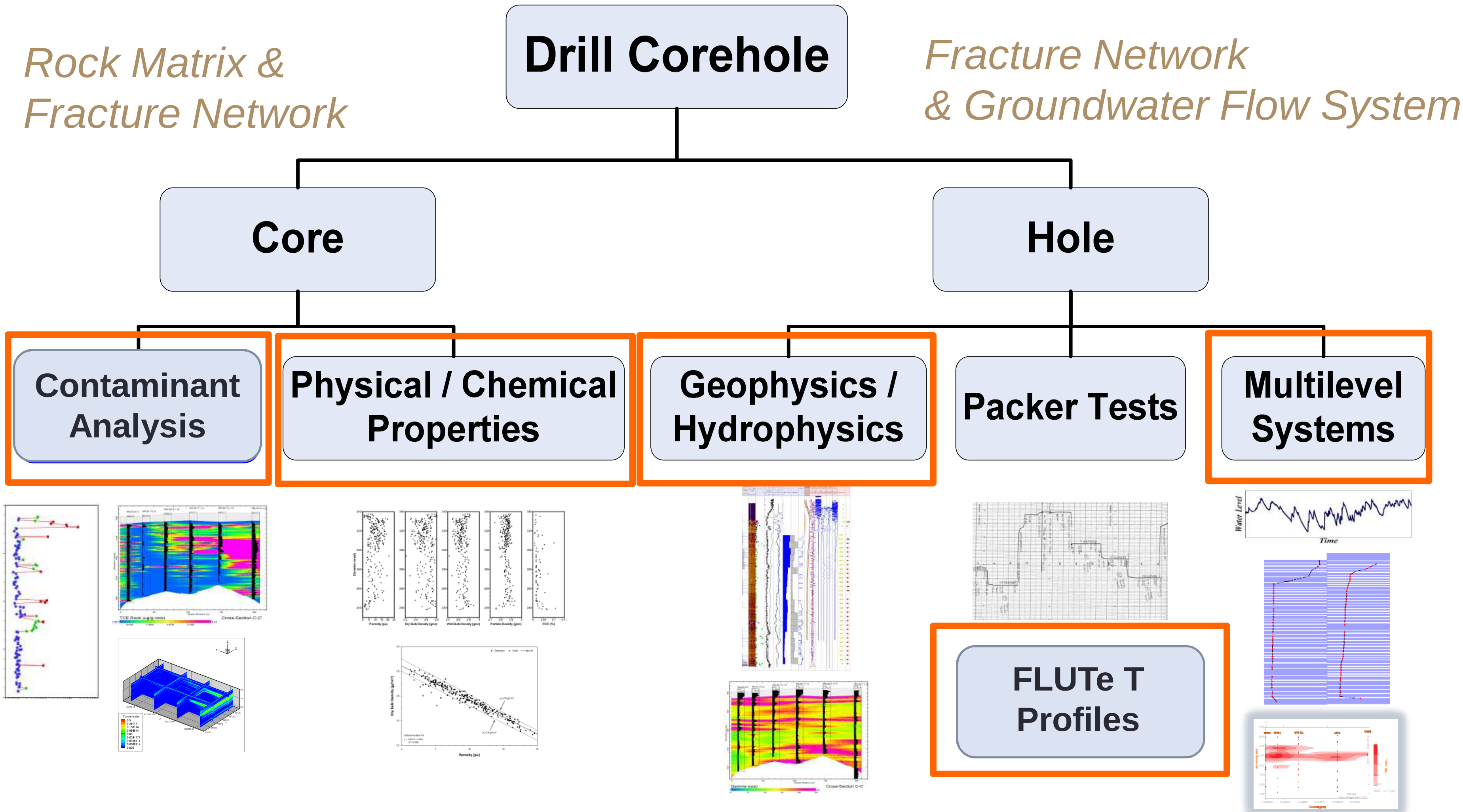
(adapted from Parker, 2012)

Fractured Bedrock Attenuation Mechanisms

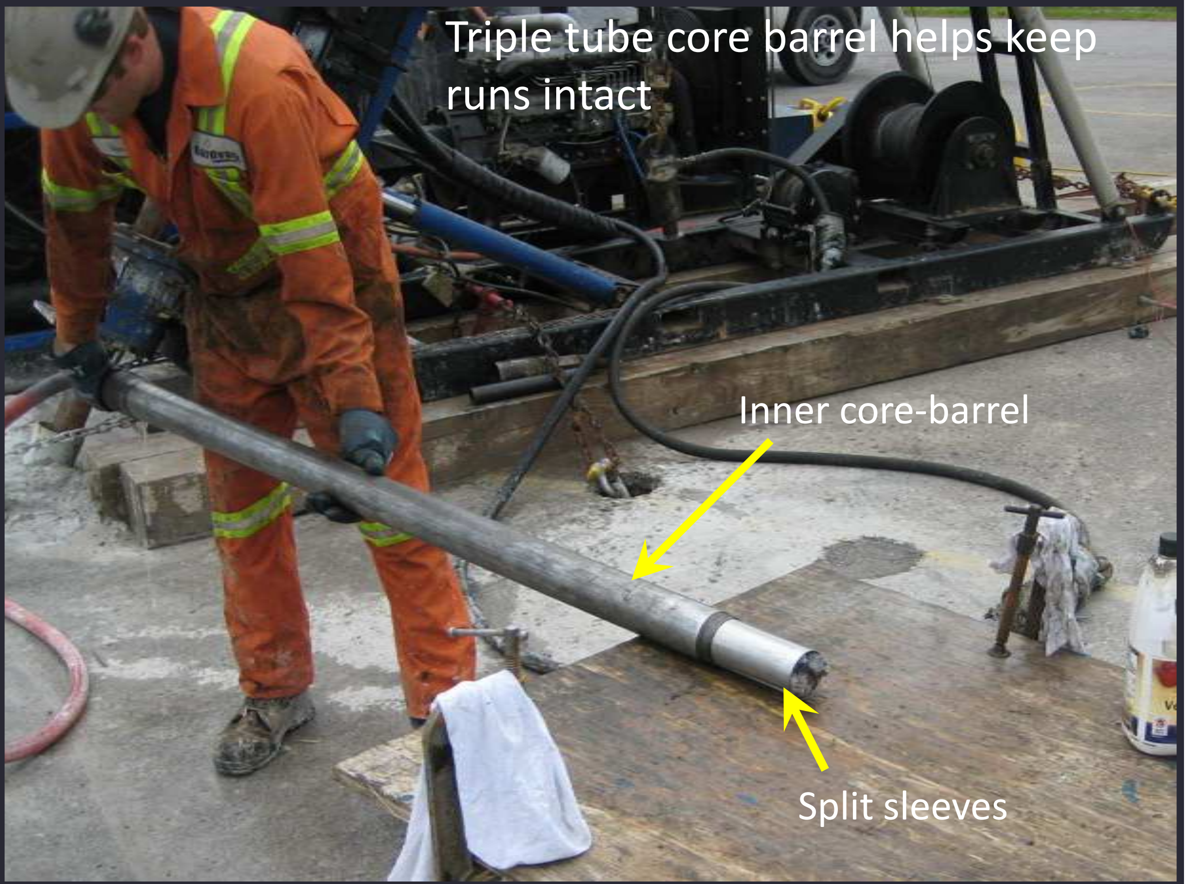


(Adapted from Freeze and Cherry, 1979)

Discrete Fracture Network Framework for Site Characterization (Parker, 2012)



Rotary Coring



Rock Core VOC Sampling


1. Lith. logging and sample selection

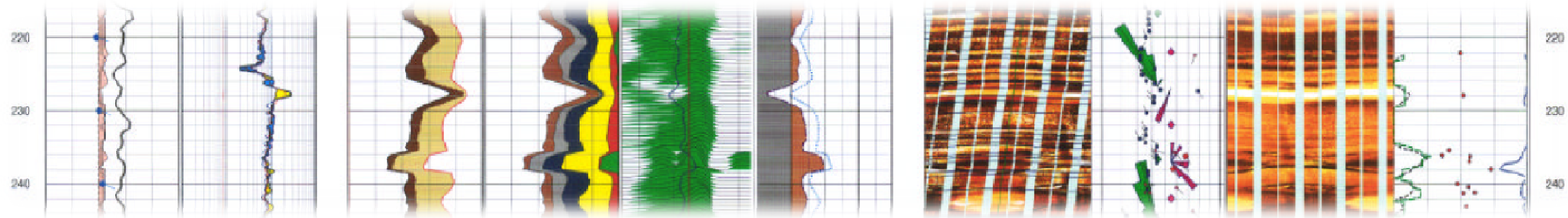

2. Sample Removal


3. Rock Crushing

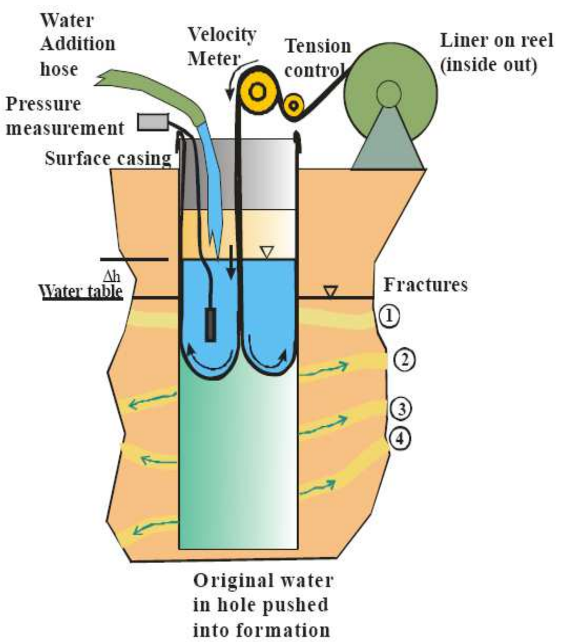

4. Methanol Extraction

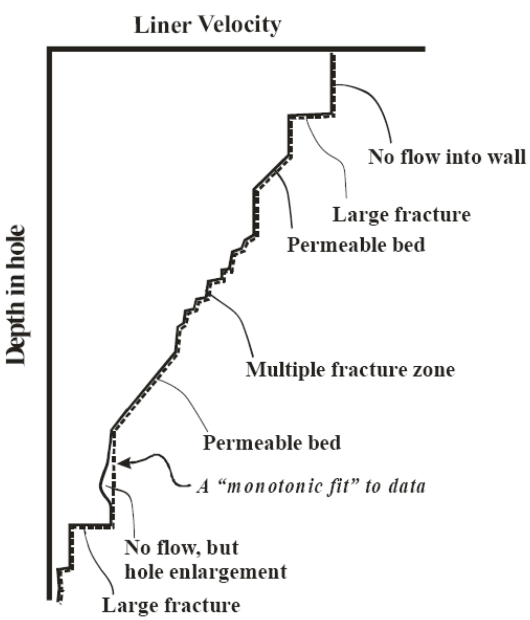
Downhole Geophysical Logging

Natural Gamma, ATV, OTV, Resistivity, FWS, ALS (Pehme et al., 2013)



Flute Transmissivity Profiling *(Keller et al, 2014)*

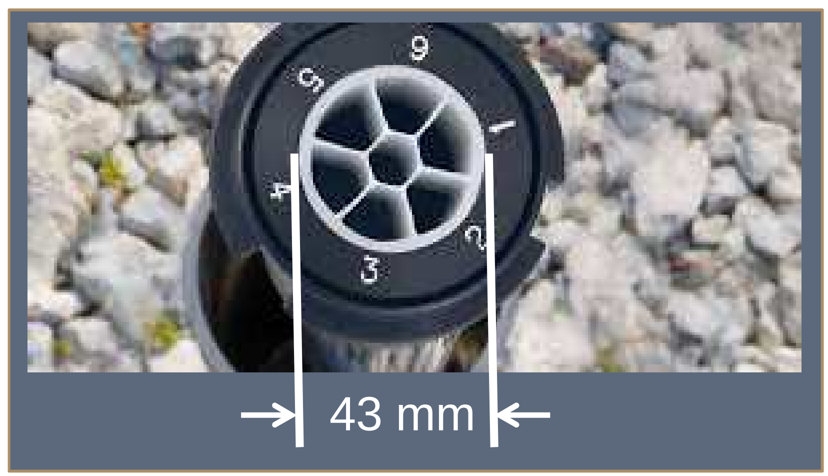




Coring with Portable Drill

- Shaw backpack drill
  www.backpackdrill.com
- Eco-sensitive, small footprint
- ~45cm (1.2 ft) continuous core runs
- Added capability: multi-level monitoring six depth-discrete intervals

Solinst CMT



Hole Diameter = 51 mm / 2-inch

www.solinst.com (Einarson & Cherry, 2002)

Multilevel Monitoring Systems

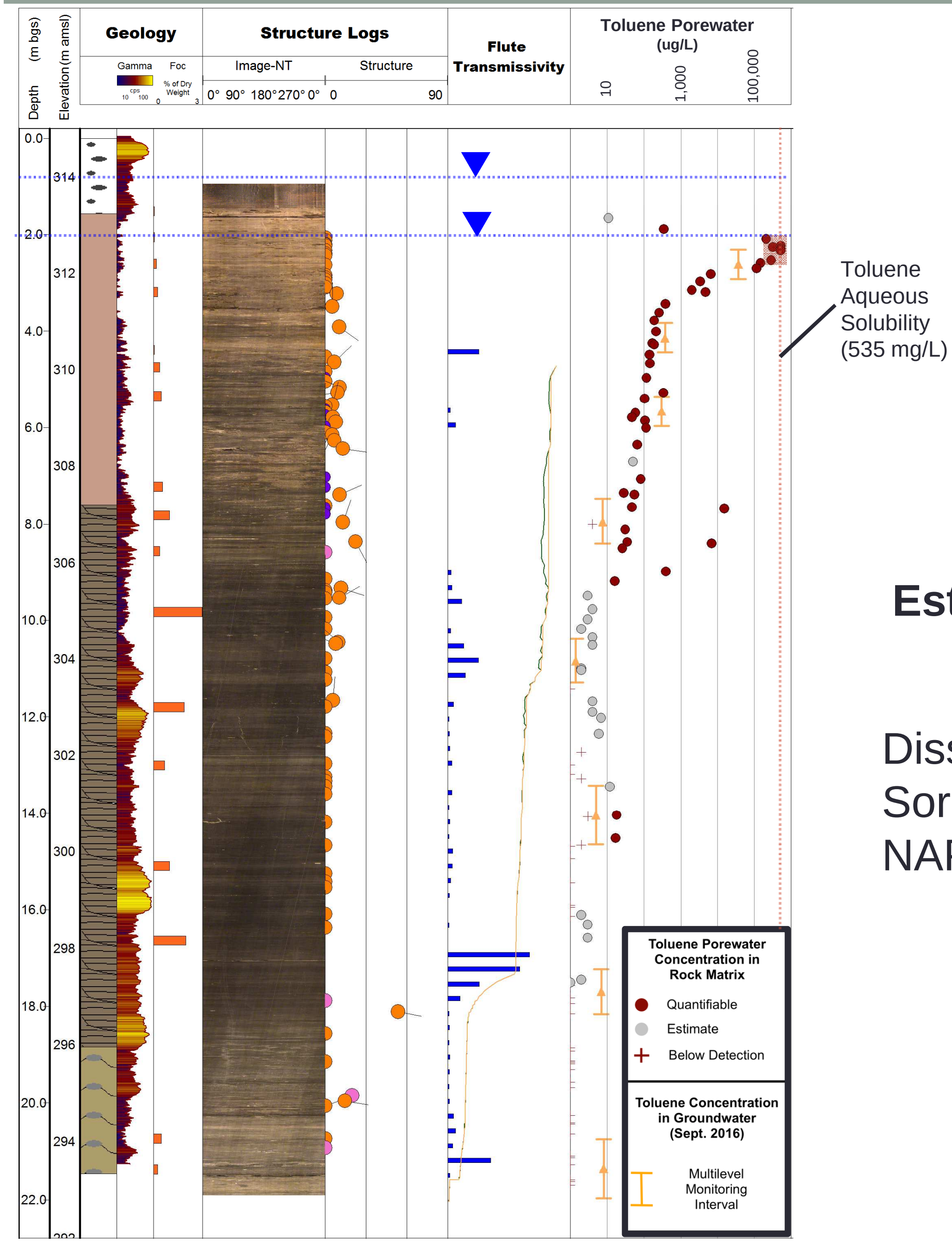
Adapted Solinst CMT® System

Adapted Solinst Waterloo® System (G360 System)

- **Multidepth groundwater sampling**
- **Head measurements in vert. profile**
- **Water inflated, removable**

Results

Toluene storage in Matrix Porewater



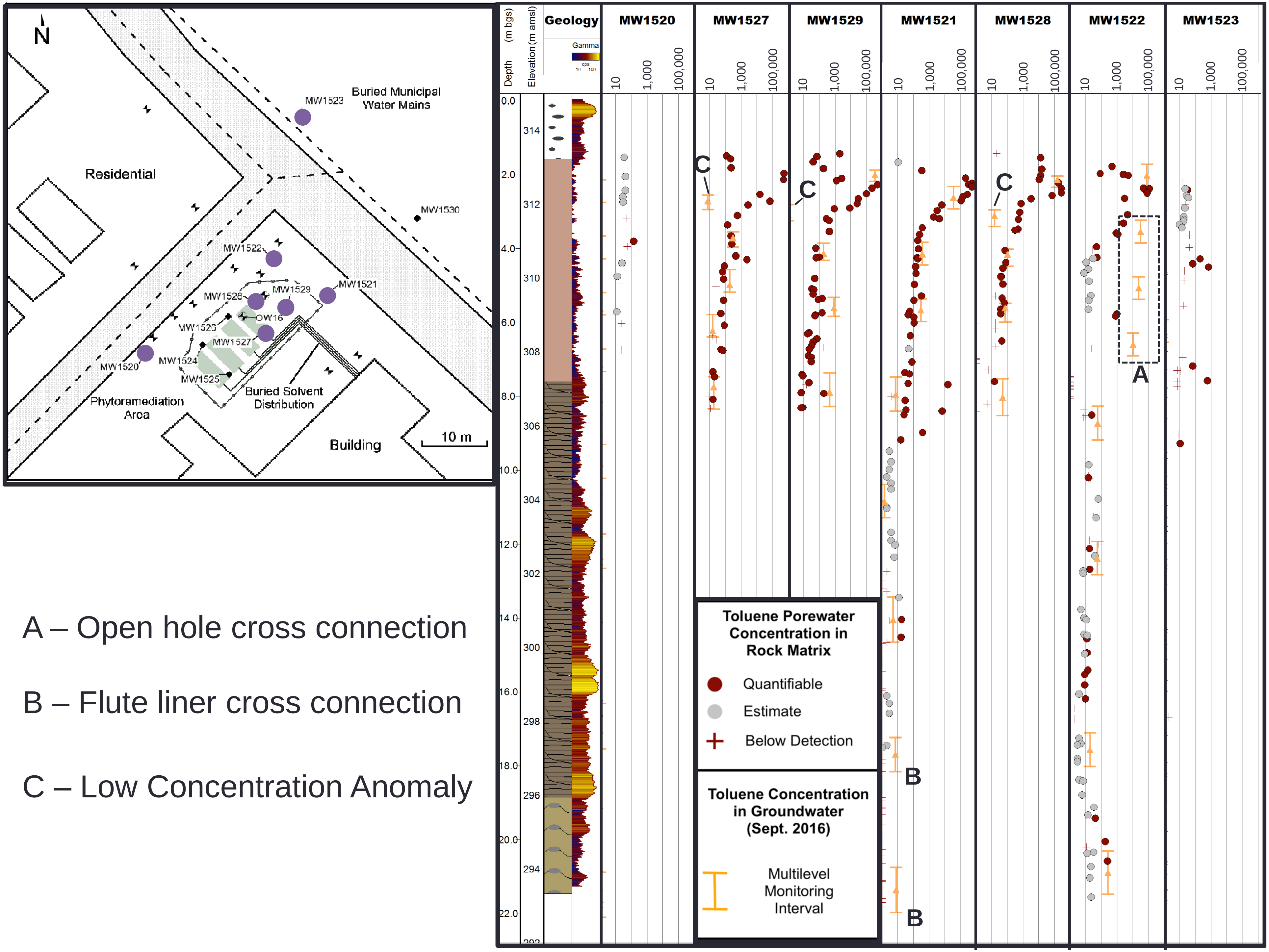
- Thin horizon indicating residual toluene NAPL
- > 95% of mass in 2m depth interval of bedrock matrix

Estimated Phase Distribution in Matrix
(based on 11 cored locations)

Dissolved: ~4%
Sorbed: ~ 95%
NAPL (residual) : ~1%

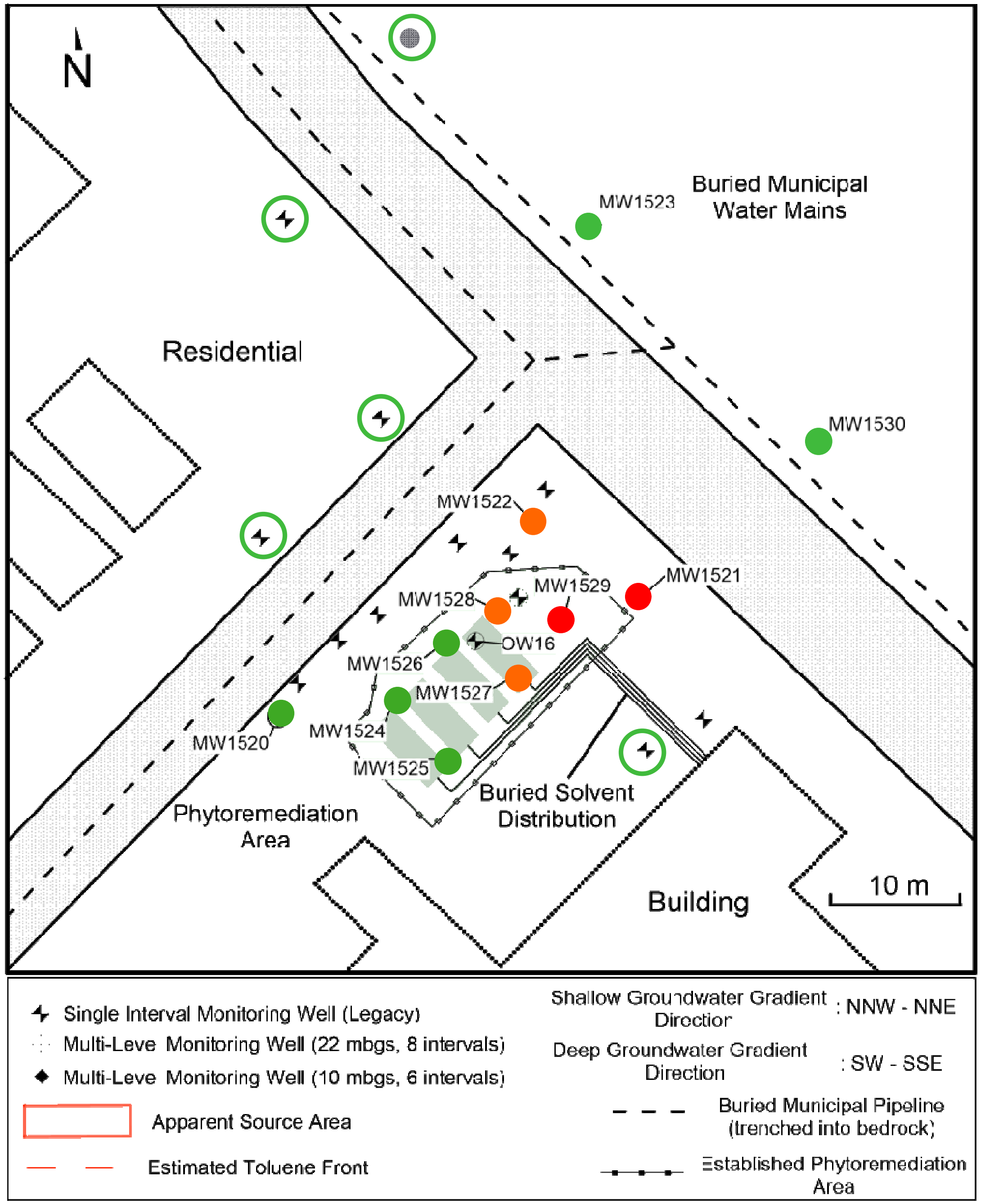
$$C_w = \frac{C_t\ \rho_b}{(K_d \rho_b + \phi_w)}$$

Feenstra et al., 1991



N
Residential
Buried Municipal Water Mains
MW1523
MW1530
MW1522
MW1521
MW1529
MW1528
OW16
MW1526
MW1527
MW1524
MW1520
MW1525
Phytoremediation Area
Buried Solvent Distribution
Building
10 m
Depth (m bgs)
Elevation (m amsl)
Geology
Gamma
MW1520
MW1527
MW1529
MW1521
MW1528
MW1522
MW1523
10
1,000
100,000
A
B
C
Toluene Porewater Concentration in Rock Matrix
Quantifiable
Estimate
Below Detection
Toluene Concentration in Groundwater (Sept. 2016)
Multilevel Monitoring Interval
A – Open hole cross connection
B – Flute liner cross connection
C – Low Concentration Anomaly

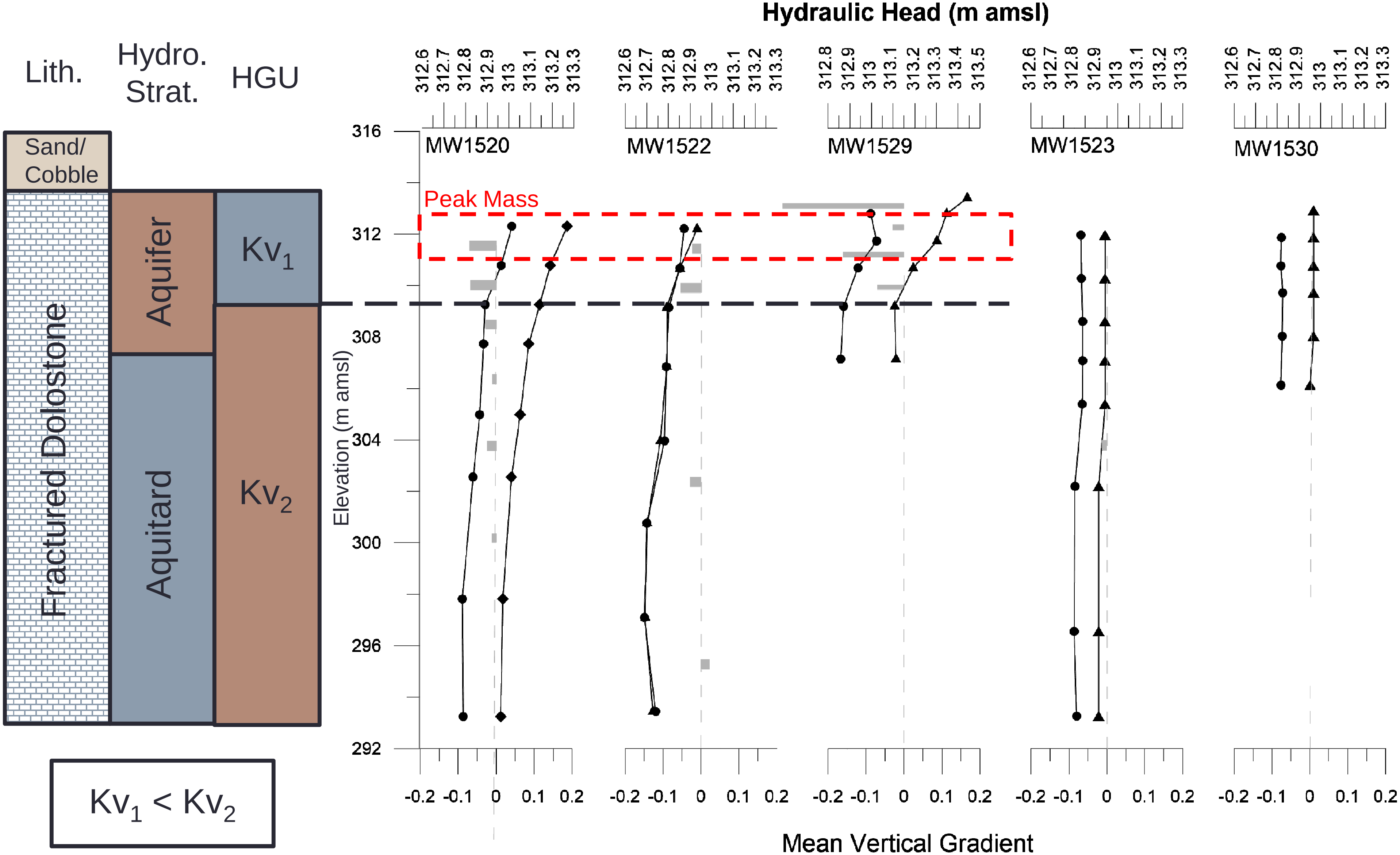
Enhanced Source Zone Delineation



- At or near toluene solubility
- 1,000 - 100,000 ug/L
- < 100 ug/L

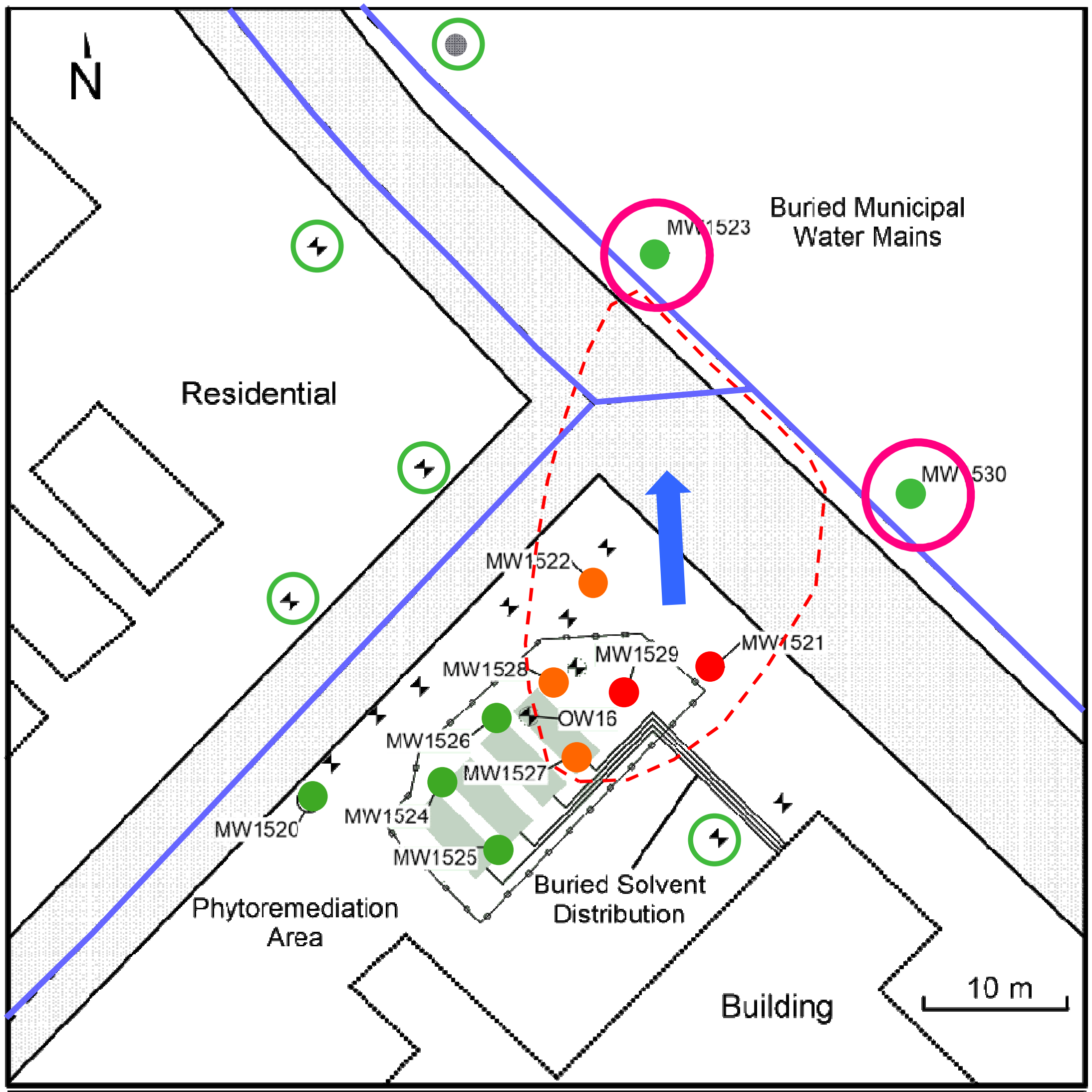
Inferred from rock core and groundwater samples

Flow System Characterization using High Res. Vertical Head Profiles



$Kv_1 < Kv_2$

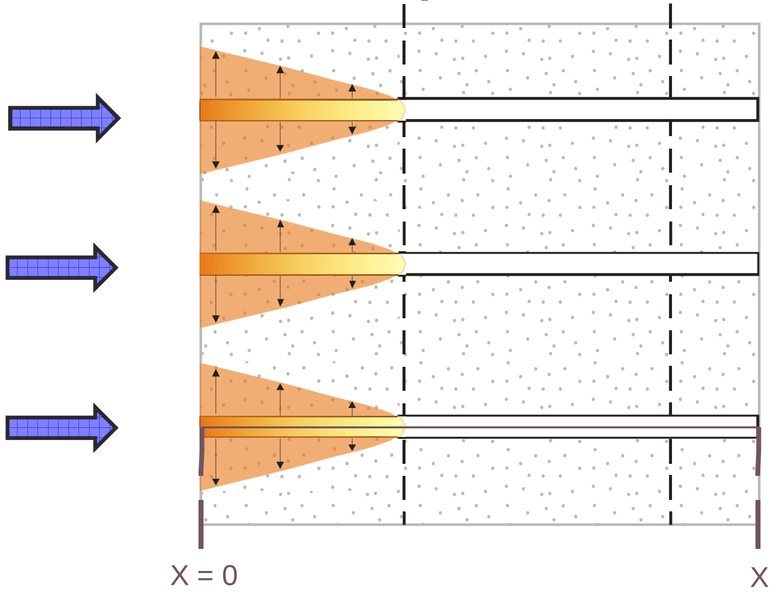
Possible Groundwater Flow System Influences from Infrastructure (Buried Trenches)



1D Discrete Fracture Transport Model

(CRAFLUSH based on Sudicky & Frind, 1982)

- Advection + dispersion in fractures
- Diffusion in matrix
- Sorption
- First order degradation



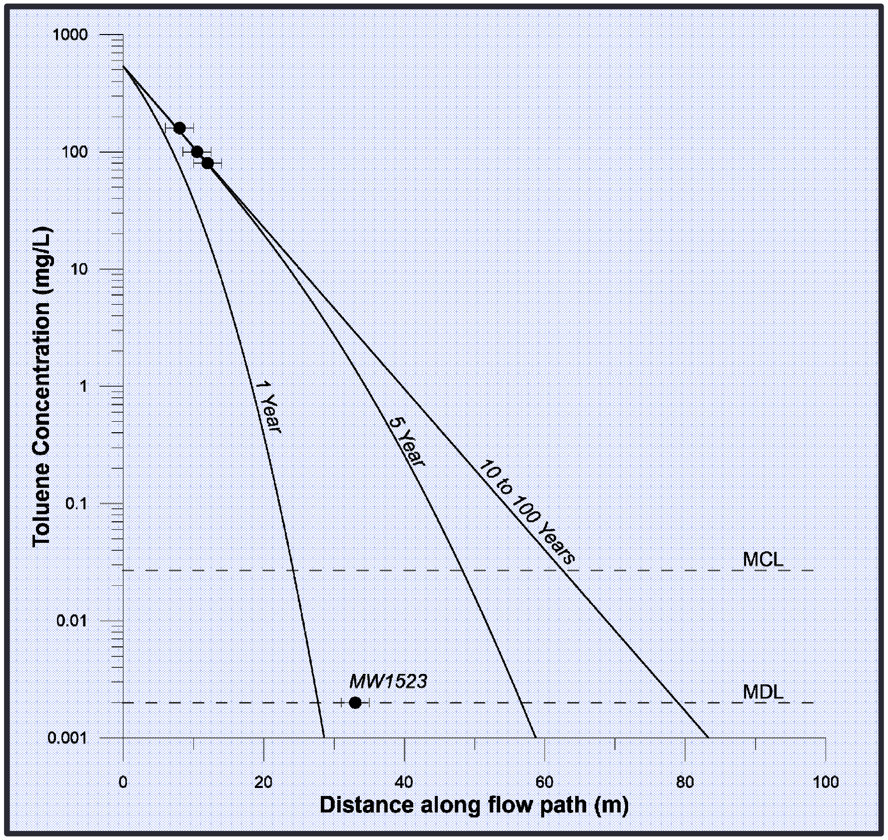
	Model Parameter
R-factor	8
matrix porosity	0.12
fracture porosity	3E-3
Avg. Lin. Vel.	2.7 m/day
Gradient	0.01
1st Order Decay (half-life)	1.0 years *(calibrated)*
Fracture Spacing	0.06m

Aenaerobic Toluene Decay (1/2 Life): 0.04 – 1.5 years (Lawrence, 2006)

1D-Dual Porosity Transport Model: CraFlush

(Sudicky & Frind, 1982)

Simulated Profiles Along Fracture Plane



Plume Front (MDL: 0.2 ug/L)

Predicted: ~80 meters
Actual: < 30 meters

Plug Flow GW Position:
29km

Strong attenuation due to matrix diffusion with sorption and biodegradation

Conclusions

Source Area Delineation

- Enhanced by portable drilled core data and MLS
- Detailed mass / phase delineation of toluene source
- Residual / weathered NAPL inferred from rock matrix sample concentrations
- Diffused source has transitioned from NAPL to multi-phase

Shallow Bedrock Hydrogeology

- Highest impacts in a thin, shallow, bedrock horizon.
- Horizontal fracture flow
- Disconnected fracture network (likely diffusion controlled)
- Transport retarded by sorption, matrix diffusion, biodegradation and *anthropogenic factors (e.g. buried utility trenches)*

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Thank-you

Questions?

Parker, B. L., Cherry, J. A., & Chapman, S. W. (2012). Discrete fracture network approach for studying contamination in fractured rock. AQUA mundi, 3(2), 101-116.

Einarson, M. D., & Cherry, J. A. (2002). A new multilevel ground water monitoring system using multichannel tubing. *Groundwater Monitoring & Remediation*, *22*(4), 52-65.

Pehme, P. E., Parker, B. L., Cherry, J. A., Molson, J. W., & Greenhouse, J. P. (2013). Enhanced detection of hydraulically active fractures by temperature profiling in lined heated bedrock boreholes. *Journal of hydrology*, *484*, 1-15.

Keller, C. E., Cherry, J. A., & Parker, B. L. (2014). New method for continuous transmissivity profiling in fractured rock. *Groundwater*, *52*(3), 352-367.

Lawrence, S.J., 2006. Description, Properties, and Degradation of Selected Volatile Organic Compounds Detected in Ground Water--A Review of Selected Literature (No. 2006-1338).

Feenstra, S., Mackay, D. M., & Cherry, J. A. (1991). A method for assessing residual NAPL based on organic chemical concentrations in soil samples. *Groundwater Monitoring & Remediation*, *11*(2), 128-136.

Meyer, J. R., Parker, B. L., & Cherry, J. A. (2008). Detailed hydraulic head profiles as essential data for defining hydrogeologic units in layered fractured sedimentary rock. *Environmental Geology*, *56*(1), 27-44.

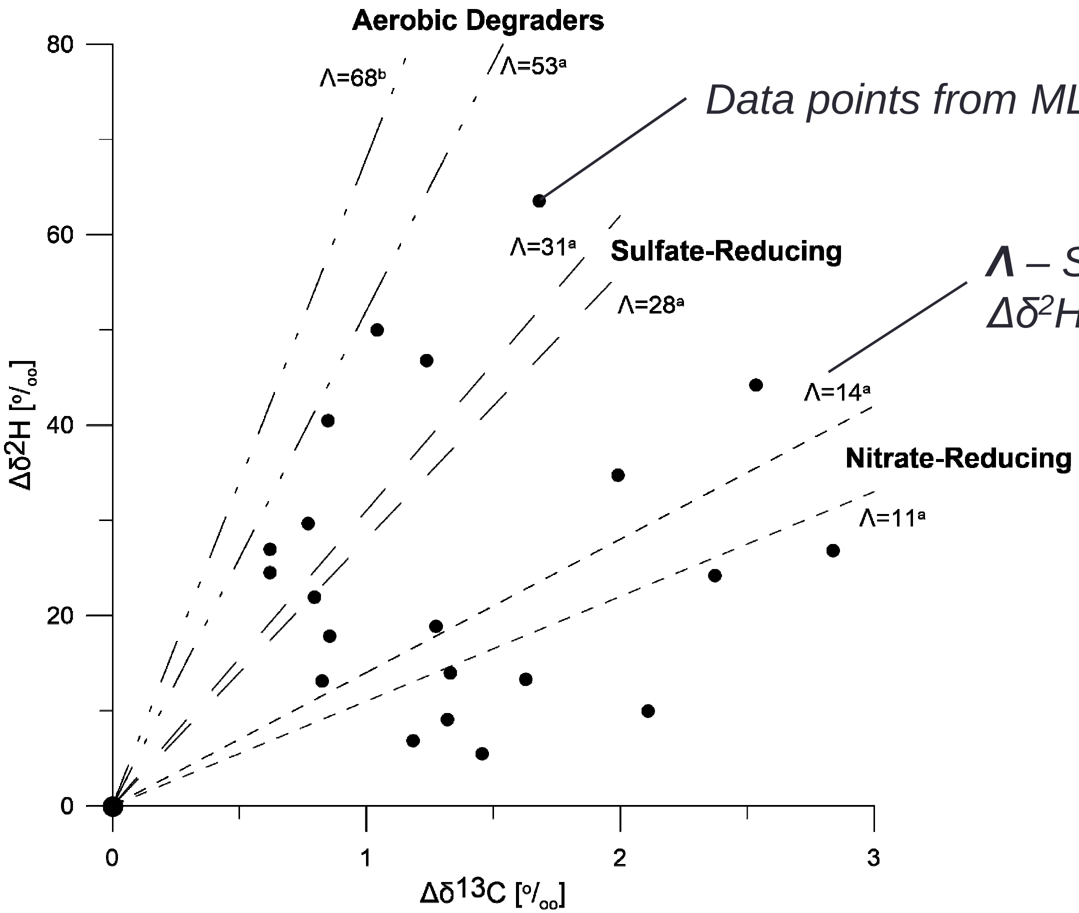
Munn, J. (2013). High-resolution discrete fracture network characterization using inclined coreholes in a Silurian dolostone aquifer in Guelph, Ontario. University of Guelph (Masters Thesis)

Sharp, J. M., Krothe, J. N., Mather, J. D., Gracia-Fresca, B., & Stewart, C. A. (2003). Effects of urbanization on groundwater systems. *Earth science in the city: A reader*, 257-278.

Vogt, C., Cyrus, E., Herklotz, I., Schlosser, D., Bahr, A., Herrmann, S., ... & Fischer, A. (2008). Evaluation of toluene degradation pathways by two-dimensional stable isotope fractionation. *Environmental science & technology*, *42*(21), 7793-7800.

Further evidence: Anaerobic biodegradation occurring along flow path

Dual Isotope Fractionation



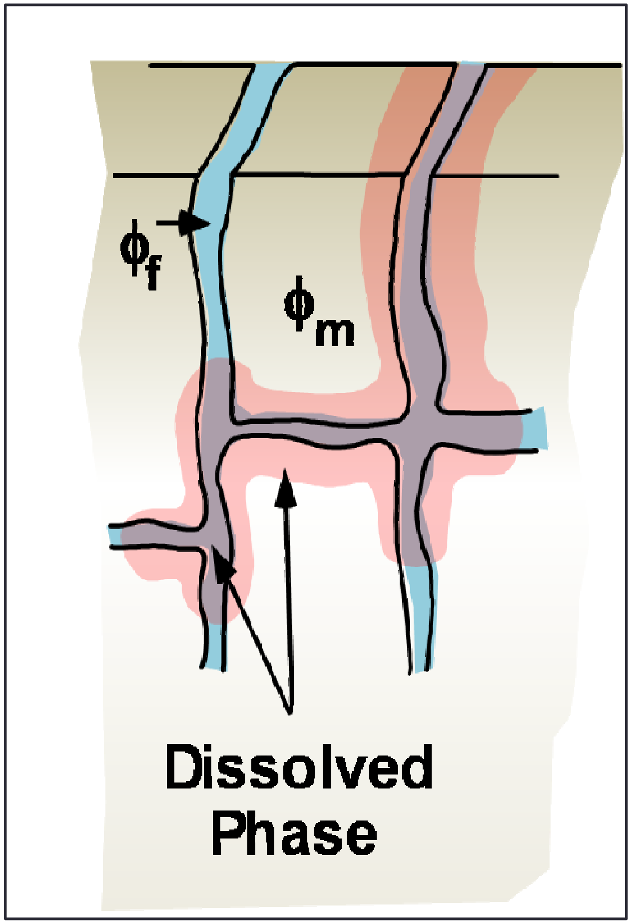
Data points from MLS sampling (this site, 2015 / 2016)

Λ *– Slope of linear regression for $\Delta\delta^2H/\Delta\delta^{13}C$ (Vogt et al., 2008)*

Λ values are specific to individual microbial populations signature enzymatic catalyzed reactions (determined in controlled studies)

Mass Storage Capacity

Site Specific Conditions



Total Mass Calulation (Dissolved + Sorbed)

$$M = \phi \times S \times R$$

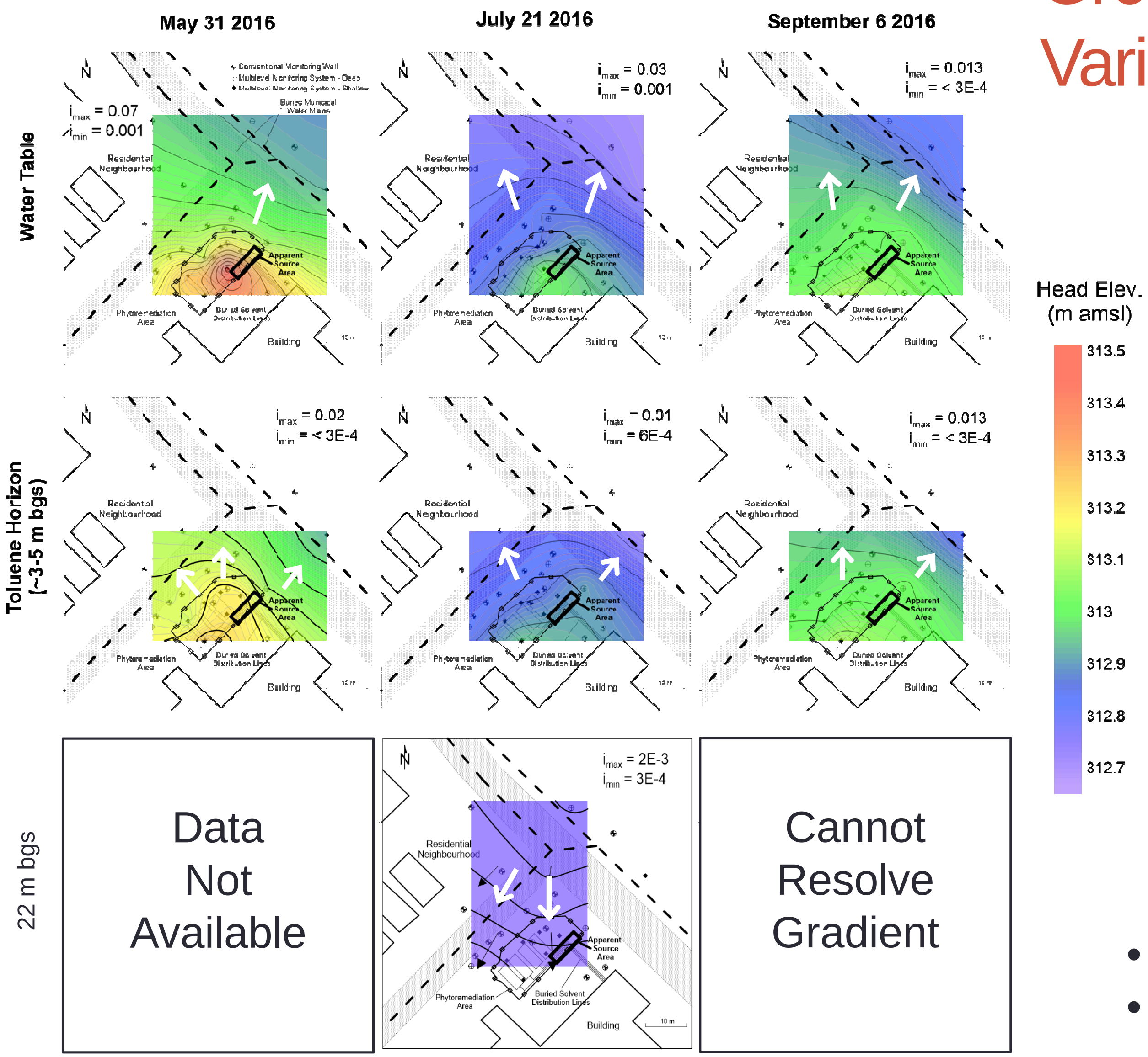
Site Specific Parameters

Aqueous solubility of toluene (S) =	535 mg/L
Retardation Factor (R) =	8
Fracture Porosity ϕ_f =	3E-3
Matrix Porosity ϕ_m=	12%
Density of toluene =	867 kg/m3

$M_f = 0.015\ L/m^3$ $M_m = 0.6\ L/m^3$

>97% of total mass in the matrix

Groundwater Gradient Variability



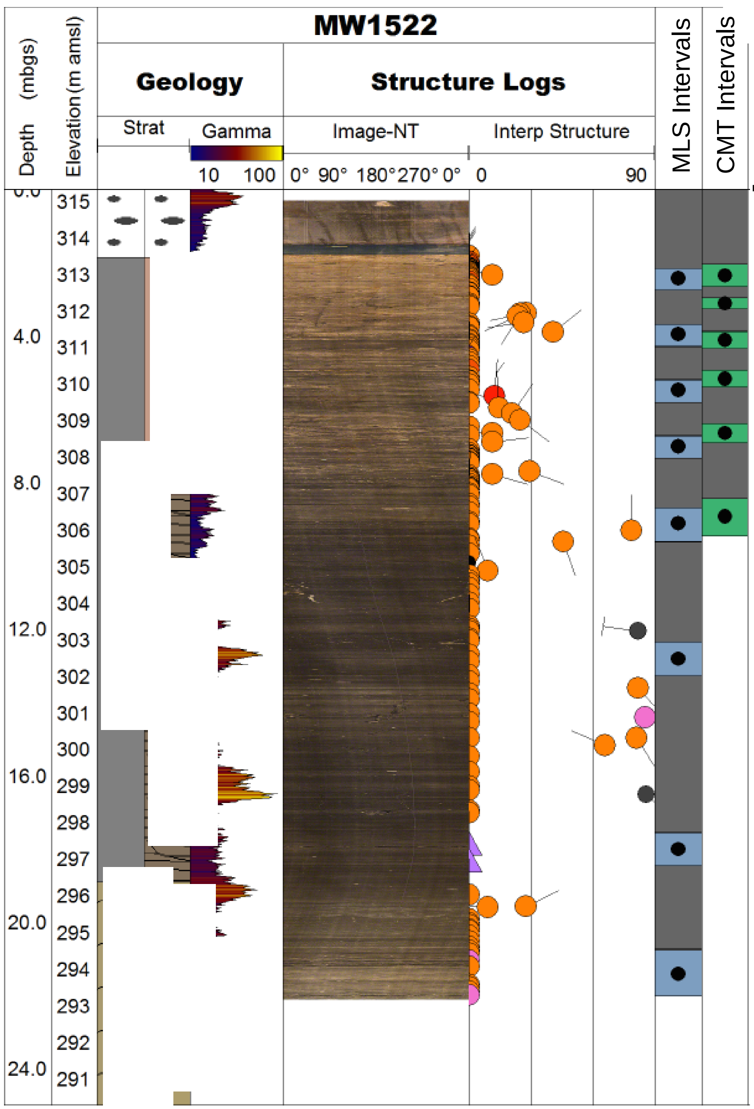
- Temporal & spatial variability in contoured head data

Avg. Linear GW Velocity in Fracture Network

- Shallow = 0.01 – 1.0 m / day
- Deep = 0.1 – 1.0 m/day

Horizontal Fractures Dominate Structure

Site Geology and Fracture Network



Cobbled Silty Sand
Non-native Fill Material
~2 meters deep

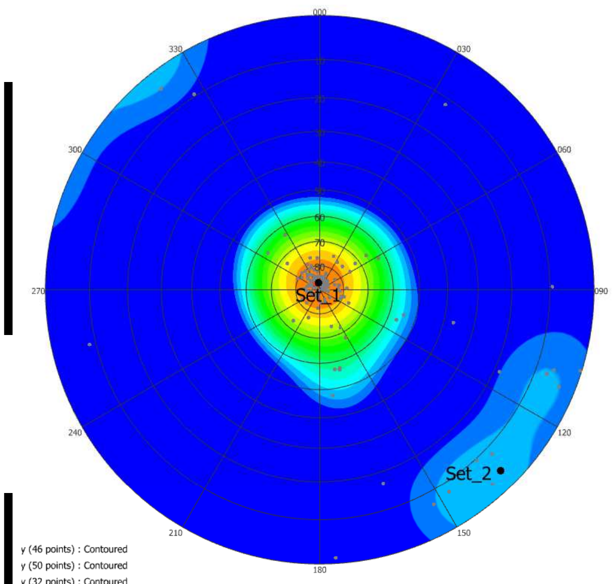
Bedrock Aquifer
Weathered Dolostone
Vuggy/Granular Porosity ~ 10%
Mean Fracture Spacing 0.07m
Primarily Indusial Use

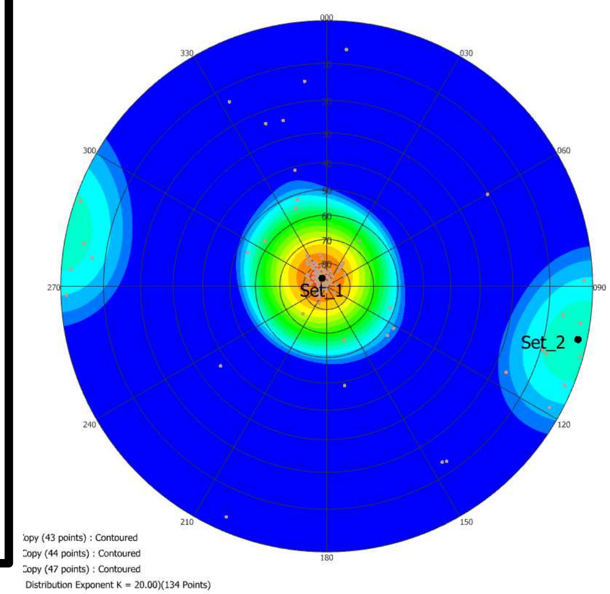
Regionally Discontinuous Aquitard
Shaley/Cemented Dolostone
Porosity 0.3 – 3%
Mean Fracture Spacing 0.20m

Continuous Aquitard
Finely Chrystalline Dolostone

Max Depth of Investigation
22 mbgs (72 ft bgs)

Fracture Pole Orientation





High Angle Fractures in Vertical Core

Top 1.5m / 5 ft of bedock - Evidence of short vertical fractures

15m / 50 ft into bedrock - Vertical fractures run much longer

*Vertical core holes biased (Munn, 2012)