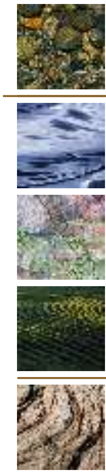


Site Characterization for DNAPLs

Presented by:
Seth Pitkin, Stone Environmental, Inc.

NEWMOA DNAPL Investigation & Remediation:
The Evolving State-of-Practice Workshop
September 2014

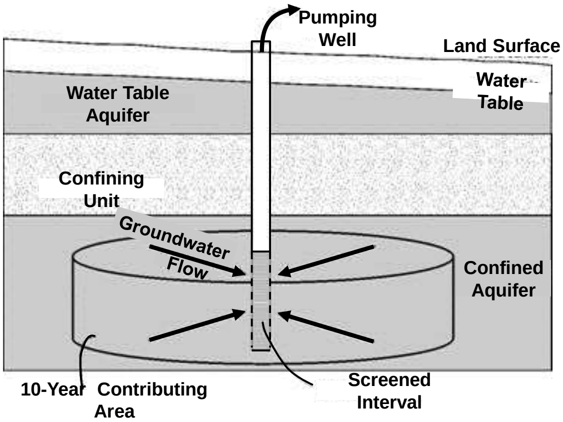
STONE ENVIRONMENTAL INC

Presentation Overview

- **Introduction**
  - What is High Resolution Site Characterization (HRSC)?
  - Scientific Basis for HRSC
  - Matrix Diffusion
  - Implementation of HRSC
  - HRSC Tools and Approaches
  - Mass Flux and Mass Discharge
  - Wrap Up

History and Development of Contaminant Hydrogeology

Historical Perspective – Water Supply



- Aquifers are:
  - Homogeneous
  - Isotropic
  - Infinite extent
- Treated as a single bulk entity
  - T
  - S
  - How much water can we get out of it?

Introduction

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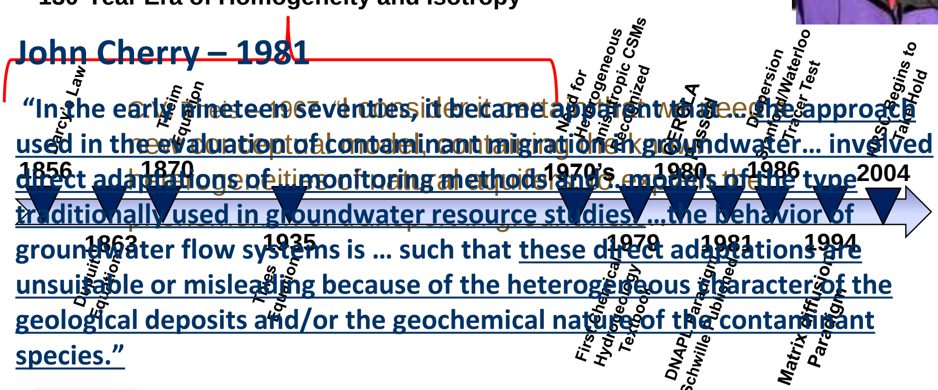
Development of (Contaminant) Hydrogeology

~130-Year Era of Homogeneity and Isotropy



John Cherry – 1981

"In the early nineteen seventies, it became apparent that … the approach used in the evaluation of contaminant migration in groundwater… involved direct adaptations of … monitoring methods and … models of the type traditionally used in groundwater resource studies. …the behavior of groundwater flow systems is … such that these direct adaptations are unsuitable or misleading because of the heterogeneous character of the geological deposits and/or the geochemical nature of the contaminant species."

Key Point

Our science is a young one. Our thinking on solute transport is powerfully and inappropriately influenced by the first 150 years of the development of hydrogeology.

Introduction

Data Needs: What you need to know at a "DNAPL Site"

- What phases are the contaminants in? (DNAPL, aqueous, sorbed, gas)
- What is the source? (DNAPL, sorbed mass, solute mass in low K zones)
- Where is the source located in 3 dimensions
- Where is the source located w.r.t. permeability? (in high K zones or low K zones)
- Where are the primary transport pathways?
- Where are the receptors?
- What attenuation mechanisms are active? (sorption/retardation, biodegradation, abiotic degradation, dispersion, diffusion into low K zones

For most DNAPL sites these questions can only be answered using High Resolution Site Characterization (HRSC)

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What is HRSC ?

Subsurface investigation <u>appropriate to the scale of heterogeneities</u> in the subsurface which control contaminant distribution, transport, and fate, at the required <u>degree of detail</u>

- Spatial structure of hydrogeologic variables controlling contamination distribution, transport, and fate is on the centimeter scale
- Remedies involving injection/extraction of fluids are controlled by the same variables at the same scales

What is HRSC?

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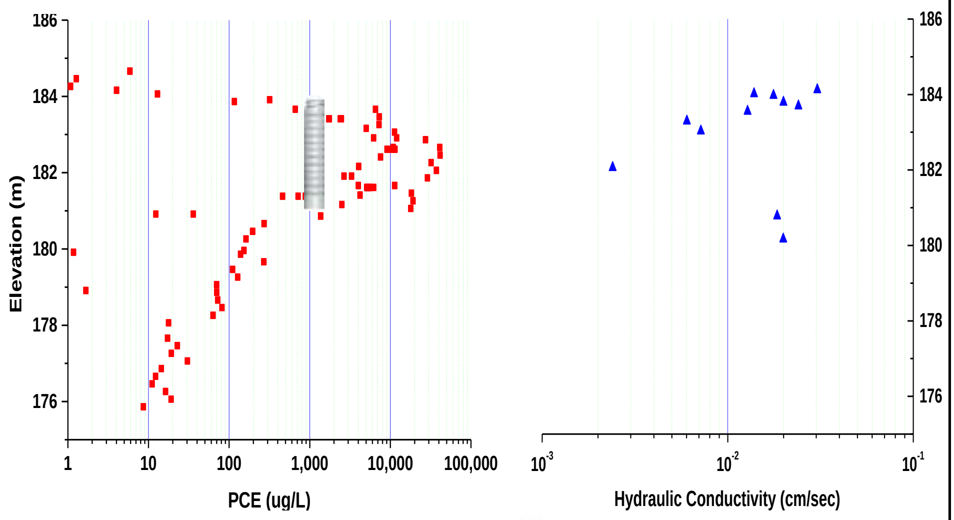
Depth-Integrated, Flow Weighted Averaging



What is HRSC?

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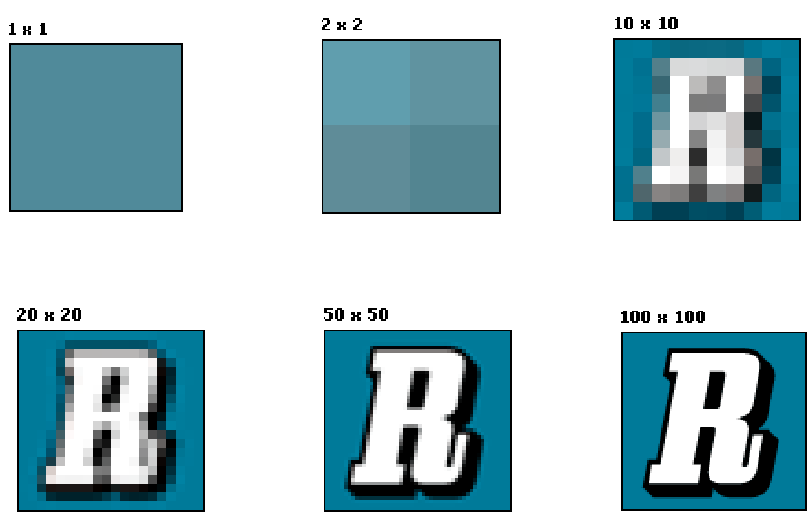
HRSC Addresses Two Critical Issues

- Sampling Scale and Data Averaging
  - Measurements must be made at a scale that is meaningful with respect to the variability of the quantity being measured
- Coverage
  - Profiles and Transects
  - Horizontal spacing
  - Vertical spacing

High Resolution (more pixels): Sampling Scale and Averaging



How Much Data Do You Need?:
HRSC Wisdom Through the Ages

Pitkin

Cherry

Blake

"You never know what is enough, unless you know what is more than enough"

William Blake

Key Point **The only way to know what degree of resolution you need is to look at a high level of resolution.**

What is HRSC?

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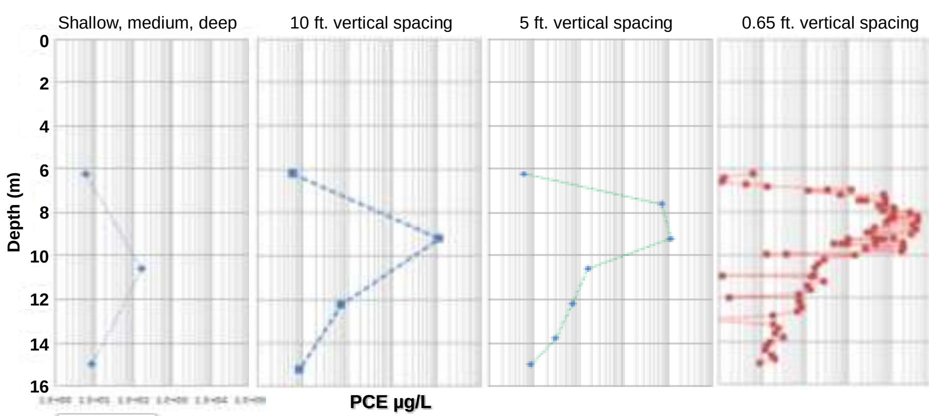
What is Right Vertical Spacing?

A Profile Through PCE Plume in Sandy Aquifer



Key Point **The vertical spacing you use determines whether you understand the nature of the plume or not.**

What is HRSC?

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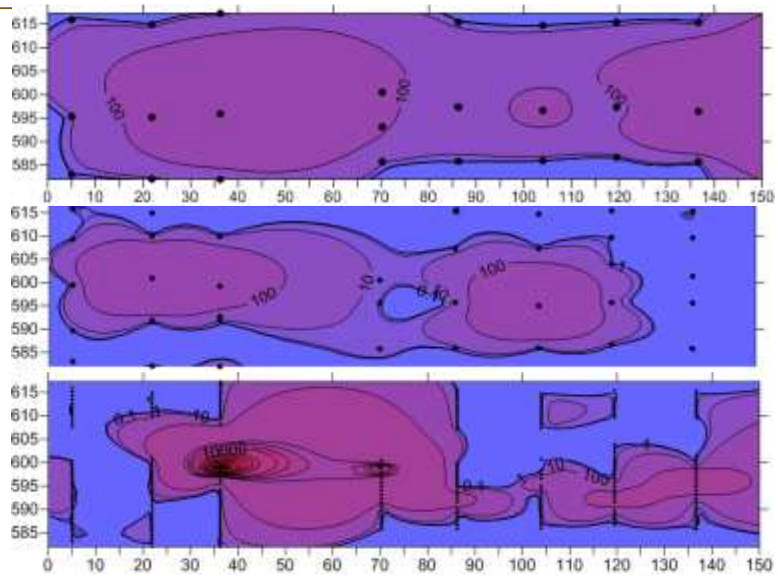
Multi-Level Sampling Transect

PCE in a Sandy Aquifer

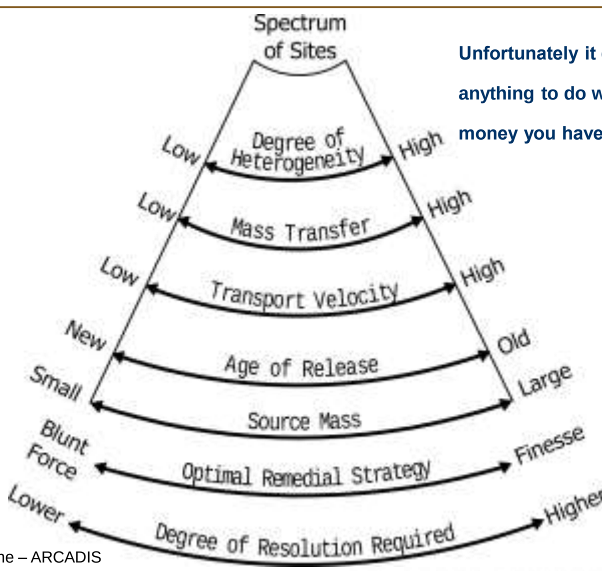
Shallow, medium, deep

10-ft vertical spacing

0.8-ft vertical spacing



Influence of Site Conditions on Required Degree of Resolution and Remedial Strategy



Unfortunately it doesn't have anything to do with how much money you have available…

Adapted from Fred Payne – ARCADIS

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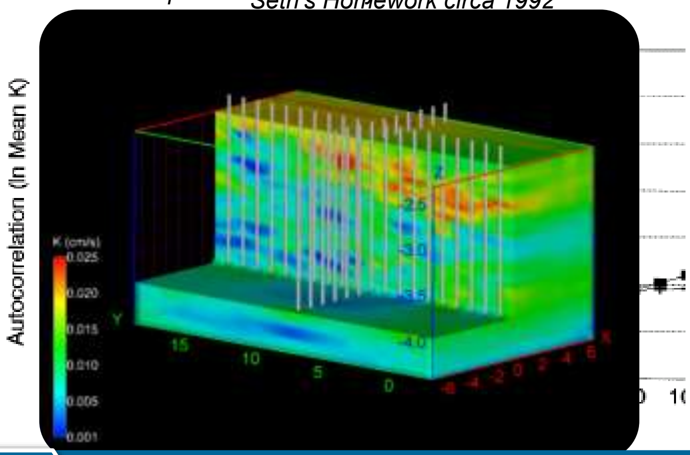
Heterogeneity and Spatial Structure

3D Interpolation of "Sudicky Star" K data – Borden Ontario

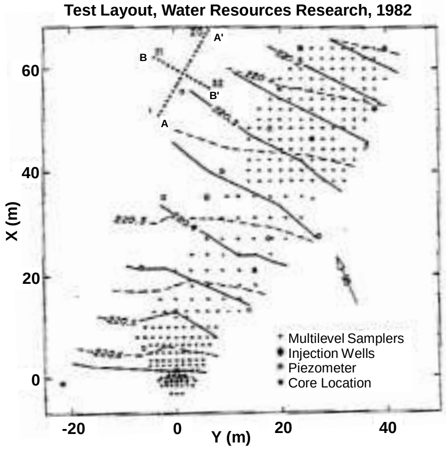
Seth's Homework circa 1992



Key Point **Hydraulic conductivity varies on the scale of tens of centimeters vertically.**

Hydrodynamic Dispersion

Stanford-Waterloo Natural Gradient Tracer Test Layout, Water Resources Research, 1982

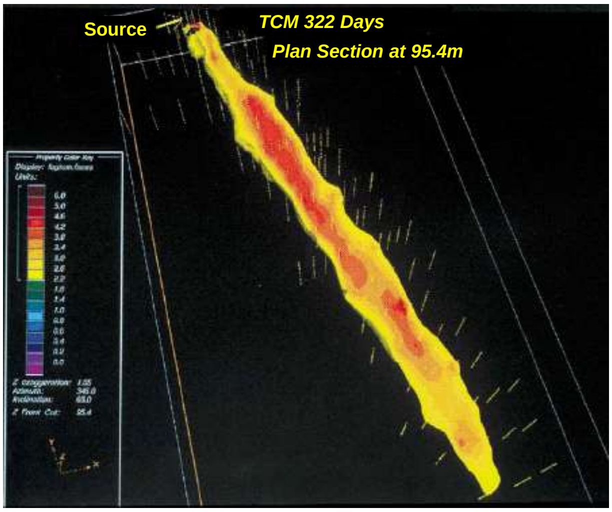


- Natural Gradient Tracer Tests
  - Sudicky – 1979
  - Stanford/Waterloo – 1982
  - USGS Cape Cod – 1986
  - Rivett *et al*. – 1991
- Dispersion is scale- (time/distance) dependent
- Transverse horizontal dispersion is weak
- Transverse vertical dispersion is even weaker
- Longitudinal dispersion is significant

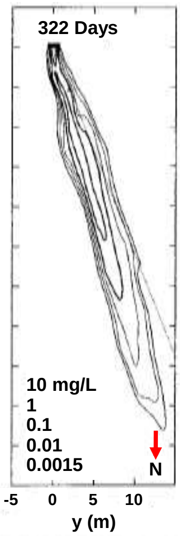
Key Point **Transverse Dispersion is weak – Plumes do not spread out much.**

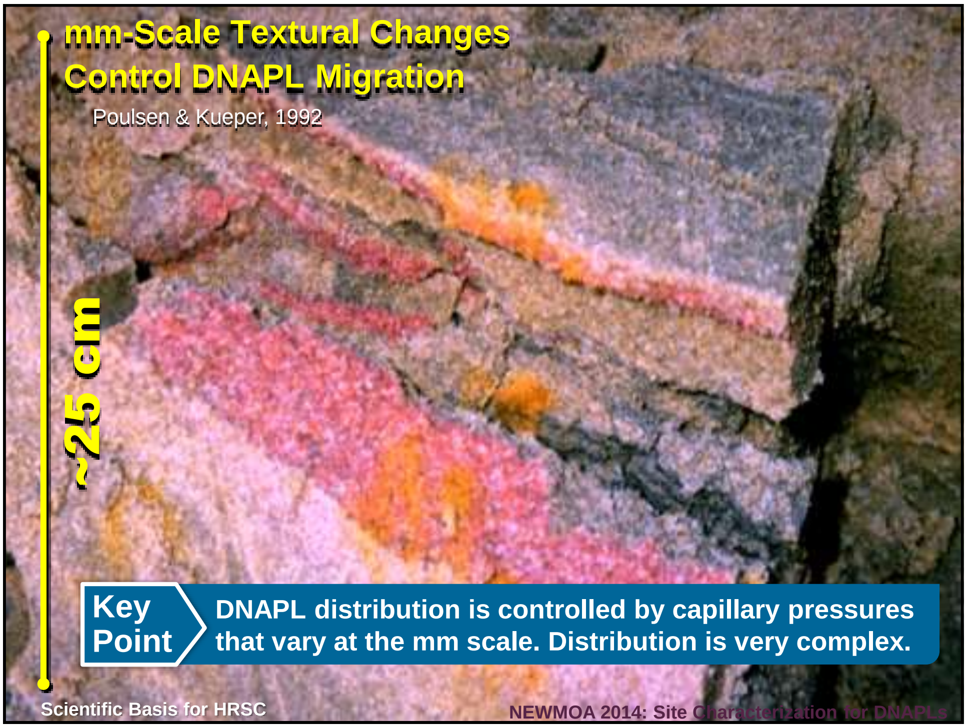
Emplaced Source Site Experiment:

TCM Plume at 322 Days – *Weak Transverse Dispersion*

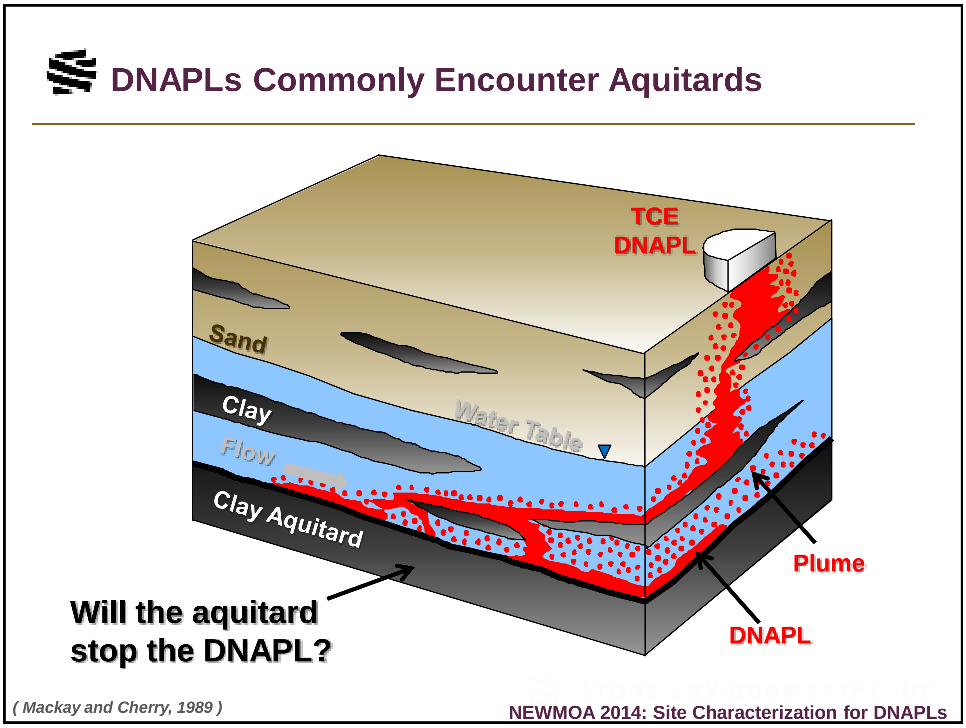


Rivett *et al.*, 2001





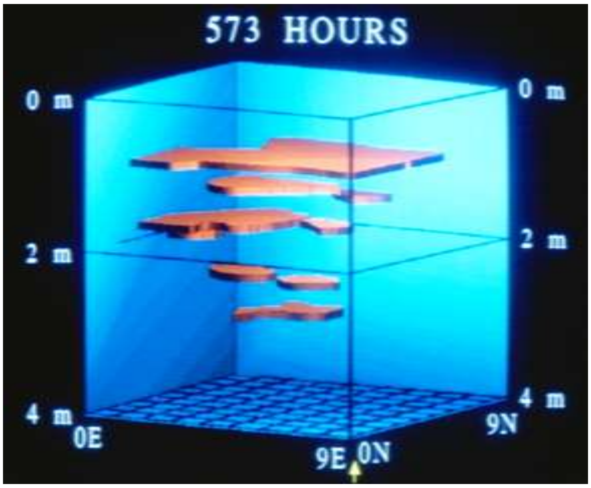
mm-Scale Textural Changes
Control DNAPL Migration
Poulsen & Kueper, 1992
~25 cm
Key Point
DNAPL distribution is controlled by capillary pressures that vary at the mm scale. Distribution is very complex.
Scientific Basis for HRSC
NEWMOA 2014: Site Characterization for DNAPLs



DNAPLs Commonly Encounter Aquitards
TCE
DNAPL
Sand
Clay
Water Table
Flow
Clay Aquitard
Plume
DNAPL
Will the aquitard stop the DNAPL?
(Mackay and Cherry, 1989)
NEWMOA 2014: Site Characterization for DNAPLs

9 x 9 Meter Cell Experiment CFB Borden

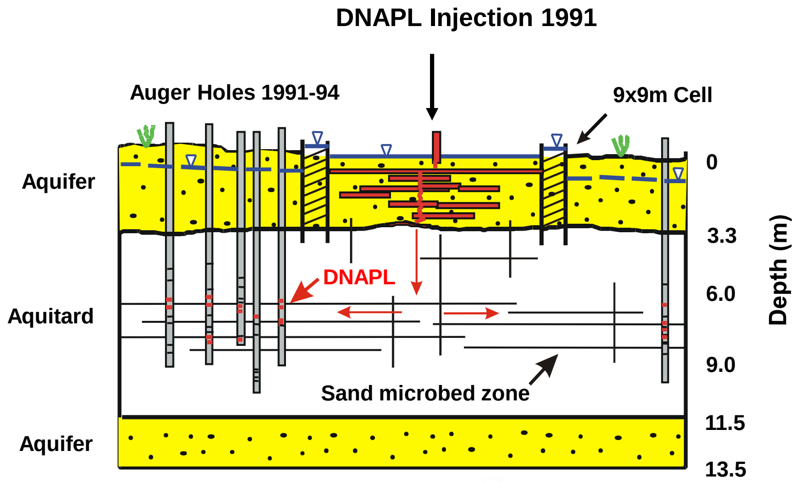
770 Liters DNAPL PCE Injected July 1991



DNAPL Distribution after 573 Hours

Courtesy of Beth Parker

Borden 9x9 m Cell Experiment



Courtesy of Beth Parker

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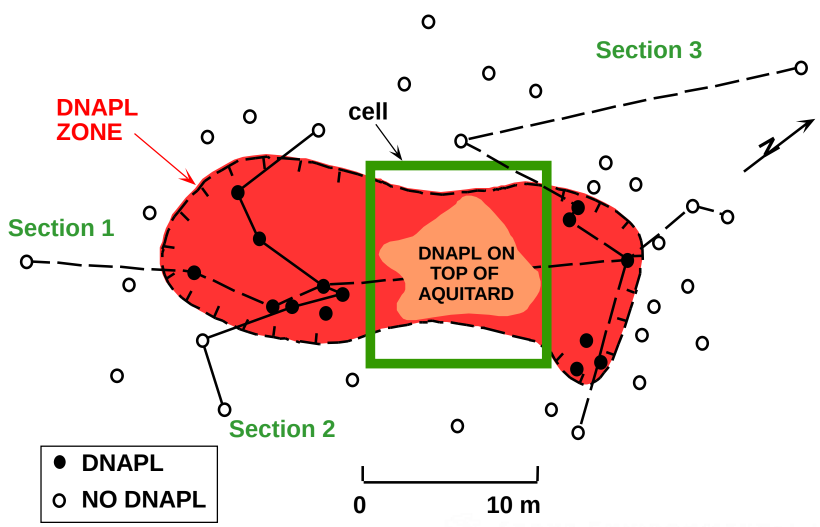
Areal Distribution of DNAPL within Aquitard



Courtesy of Beth Parker

NEWMOA 2014: Site Characterization for DNAPLs

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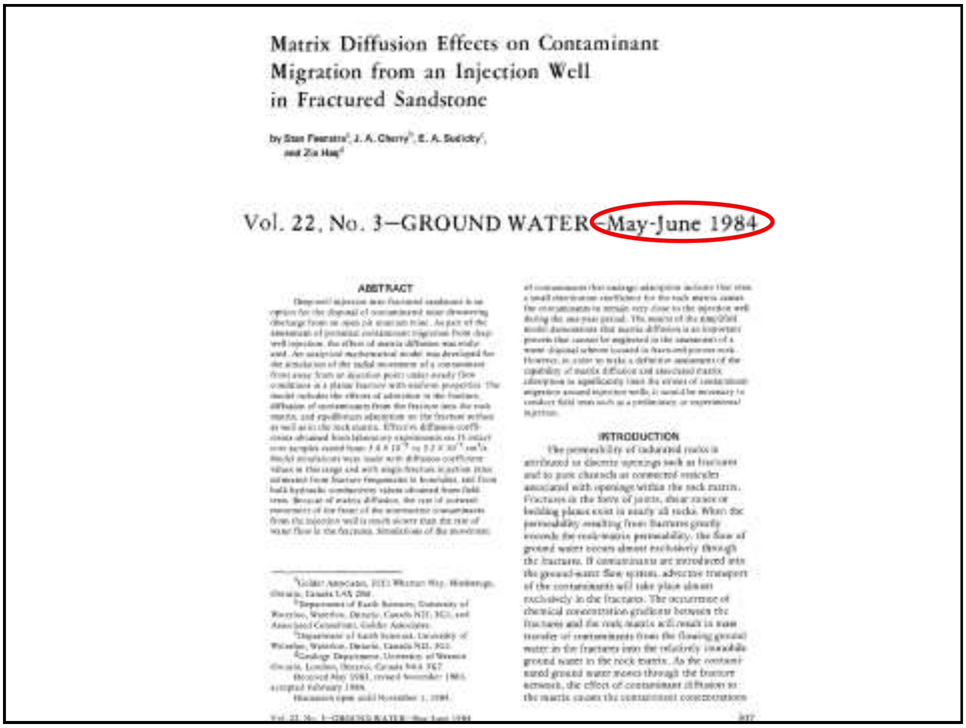
Dual Porosity Systems and Diffusion

- Systems in which there are (relatively) high and low permeability units
- Nearly all advective flow takes place through the pores in the high permeability materials (mobile porosity)
- Water in the saturated pore spaces in the low permeability materials (immobile porosity) is dominated by diffusive, rather than advective flux
- Pore water in the low permeability materials essentially serves as storage for solutes

Matrix Diffusion

NEWMOA 2014: Site Characterization for DNAPLs



Matrix Diffusion Effects on Contaminant Migration from an Injection Well in Fractured Sandstone

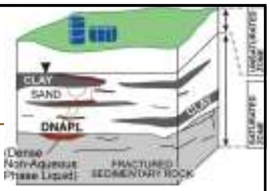
by Stan Feenstra, J. A. Cherry, E. A. Sudicky, and Zia Haq

Vol. 22, No. 3—GROUND WATER—May-June 1984

ABSTRACT

INTRODUCTION

Dual Porosity Systems: 17 Potentially Relevant Fluxes



Phase/Zone	Source Zone: Low Permeability	Source Zone: Transmissive	Plume: Transmissive	Plume: Low Permeability
Vapor				
DNAPL			NA	NA
Aqueous				
Sorbed				

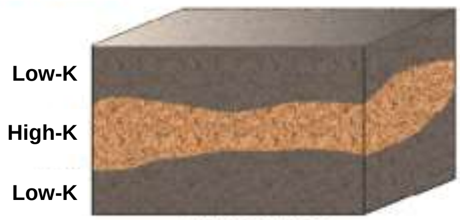
Dual Porosity Systems

Sale *et al.*, 2007

Nature and Challenges of Matrix Diffusion

Aquifer Matrix Challenges

Two aquifer blocks with equal:
- Average hydraulic conductivity
- Mobile porosity
- Groundwater transport velocity



Low Mass Transfer

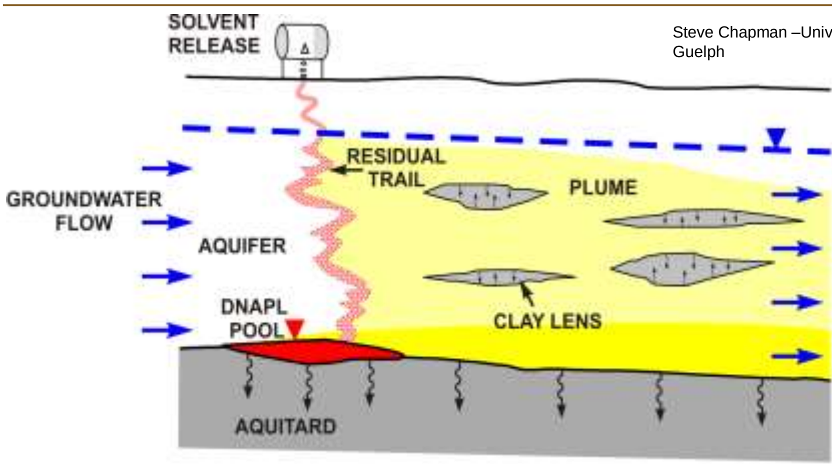
In the high-mass-transfer geometry, the rate of diffusive migration into the low-K zones is approximately 10-fold greater than for the low-mass-transfer case.

High Mass Transfer

Courtesy of Fred Payne – ARCADIS

Sand Aquifer with Clay Lenses and Underlying Aquitard

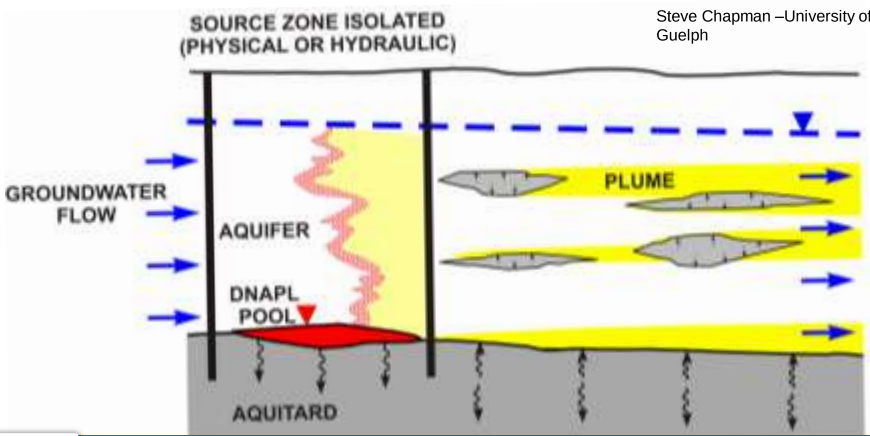
Steve Chapman –University of Guelph



Key Point Solute mass diffuses into low-K zones in the source area and throughout the dissolved plume.

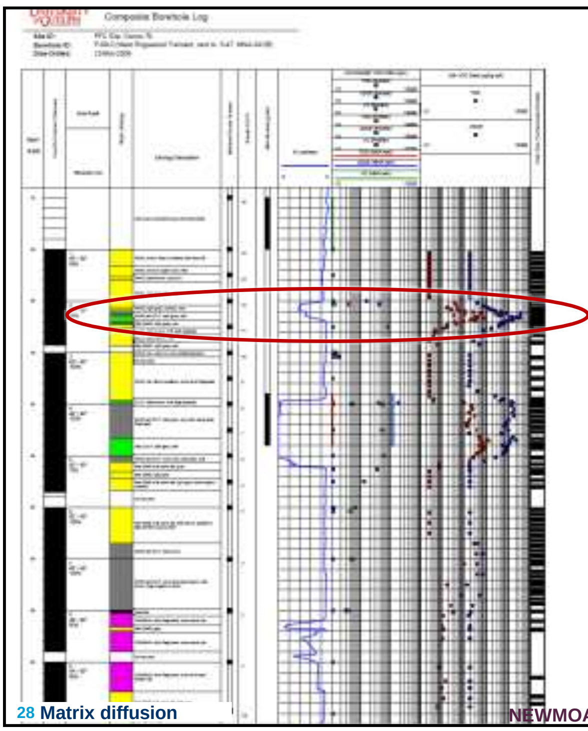
Persistent Plume after Source Isolation due to Back Diffusion

Steve Chapman –University of Guelph



Key Point Solutes diffuse back out of low-K zones following source area isolation/remediation. The whole dissolved plume footprint becomes the source.

Matrix Diffusion



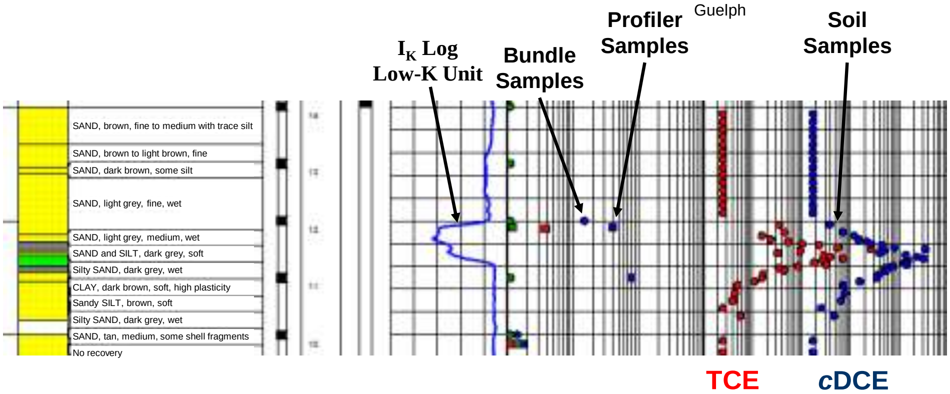
High Resolution Composite Log

Precision Site, Coco Beach, FL

Source: Steve Chapman –University of Guelph

Where the Mass Is
Cocoa, FL

Steve Chapman –University of Guelph



Key Point Contaminant mass mostly in low-K layers creates thin plumes in high-K layers throughout the dissolved plume.

Matrix Diffusion NEWMOA 2014: Site Characterization for DNAPLs

The Matrix Diffusion Challenge

- Low-K zones serve as ongoing sources of contamination separate from the initial source and throughout the plume footprint
- This source persists for long time periods
- Concentrations in permeable zones rebound following remediation of those zones
- Introduction of remedial agents into the low-K zones is controlled by the rate of diffusion and takes a very long time

Matrix Diffusion NEWMOA 2014: Site Characterization for DNAPLs

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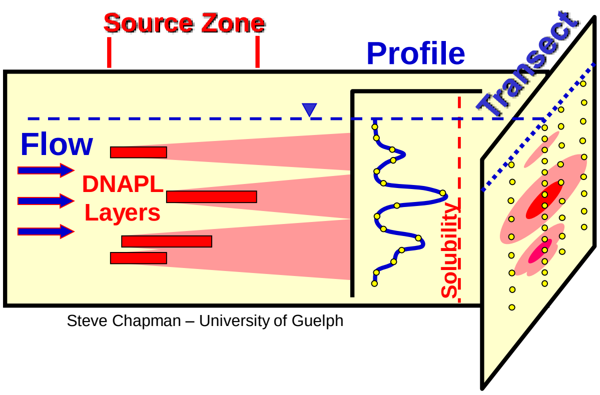
Transect Approach for Groundwater Contaminant Plumes



Steve Chapman – University of Guelph

Outside In Approach

- **Profiles**
  - Close vertical spacing of sampling points/measurements at a single location
  - Small volume of sample/measurement
  - Vertical spacing?
- **Transects**
  - Series of profiles along a line oriented at a right angle to the direction of transport
  - Horizontal spacing?
- Not longitudinal sections

Implementation of HRSC

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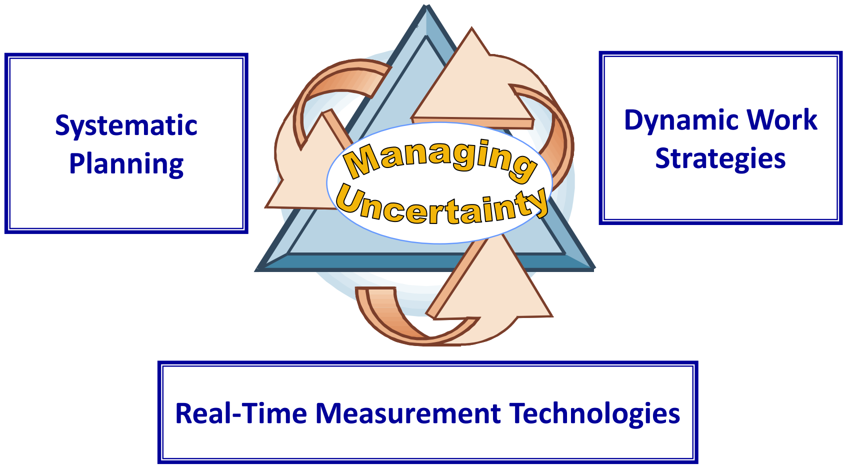
The Triad Approach



www.triadcentral.org

Implementation of HRSC

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Deployment of HRSC Tools

- Vadose zone
  - Soil gas sampling (passive, active, profile, temporal)
  - Screening tools (*e.g.*, MIP)
  - Soil coring and profile sampling
- Saturated zone
  - Screening tools for rapid reconnaissance of source zones, plume cores, hot spots (*e.g.*, MIP, DyeLIF)
  - Groundwater sample profiling of permeable zones (mobile porosity)
  - Soil coring and profile sampling for low-K zones (immobile porosity

HRSC Tools and Approaches

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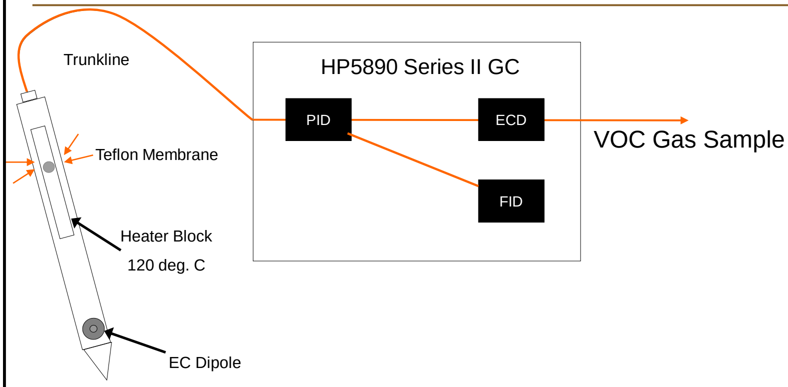
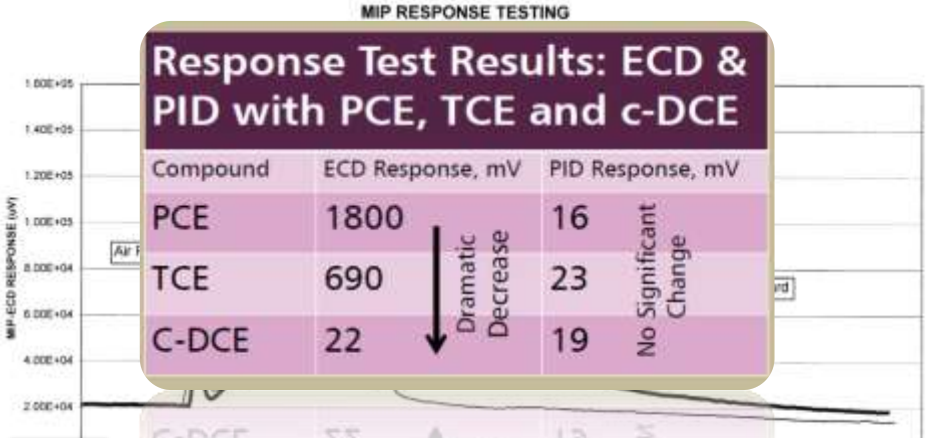
Membrane Interface Probe (MIP) Screening Tool



MIP Screening Tool (cont.)

- Strengths
  - Vertically continuous, real-time data
  - Can typically complete 150 to 250 linear feet of exploration per day
  - Ideal for locating source areas and plume cores
- Limitations
  - Limited depth penetration
  - Units (volts) not the same as with soil or water concentration
  - Correlations with soil/water concentrations problematic
  - Generally does not distinguish between analytes
  - Apparent "dragdown" of contamination
  - No particular NAPL signature
  - Once in NAPL the tool is highly contaminated and needs to be cleaned before continuing

MIP: Variability in Detector Response



Response Test Results: ECD & PID with PCE, TCE and c-DCE

Compound	ECD Response, mV	PID Response, mV
PCE	1800	16
TCE	690	23
C-DCE	22	19

ECD: Dramatic Decrease. PID: No Significant Change.

Key Point ECD is best detector for low level CVOCs but it is very sensitive to the number of chlorine atoms on the contaminant molecules.

HRSC Tools and Approaches – Screening

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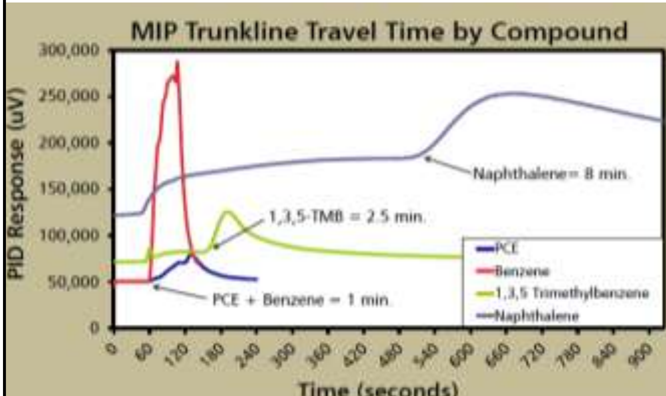
MIP: Variability in Travel Time

Trip Time Disparity



- Different compounds travel at different rates, causing potential inaccuracies in contaminant distribution

Key Point MIP data can be misleading if complex contaminant mixtures are present.

HRSC Tools and Approaches – Screening

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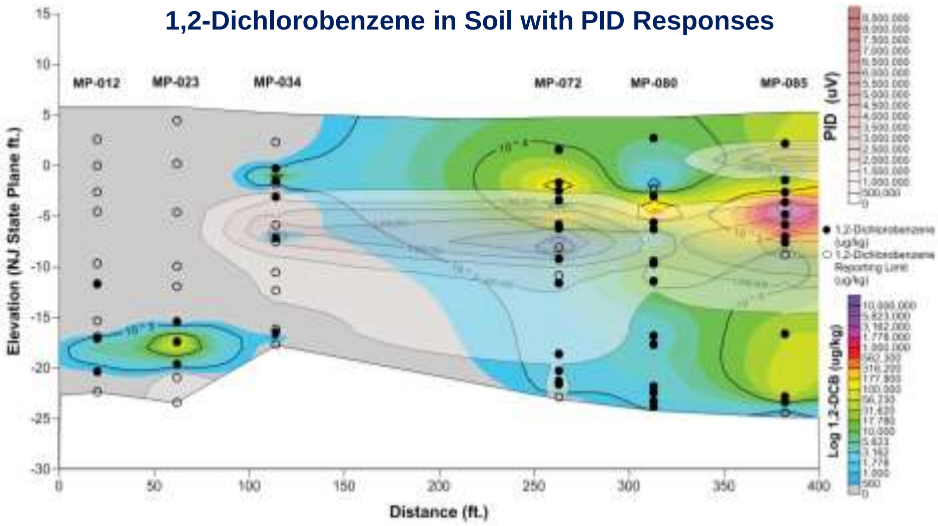
Correlations and Complex Mixtures
Trip Time Disparity

1,2-Dichlorobenzene in Soil with PID Responses



HRSC Tools and Approaches – Screening

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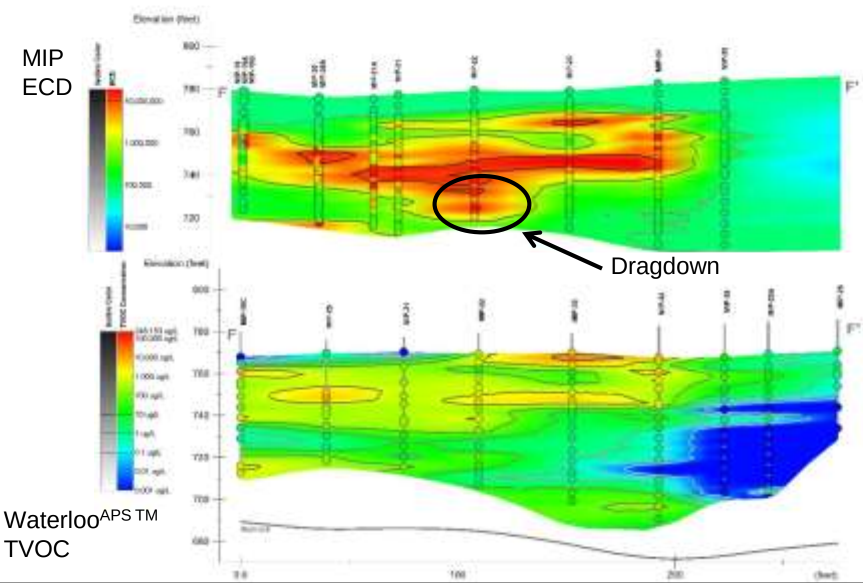
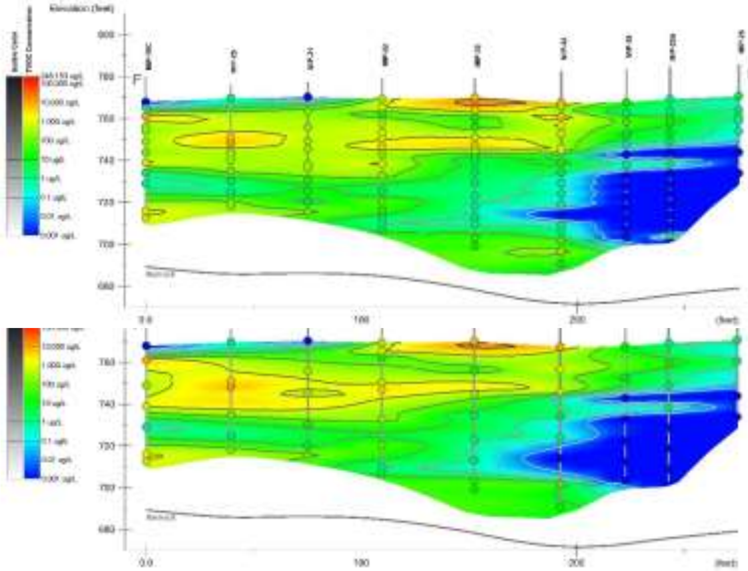
Use of MIP to Reduce Sampling Density and Cost
Transect F MIP/ECD and TVOC



Reduced/Optimized Sampling Scheme

Transect F



Original Data

49% Reduction In Sampling Points

MiHPT – Combined MIP and HPT

FLUTe NAPL Ribbon Sampler

Direct Detection of DNAPL

NAPL FLUTe Deployed in Direct Push Casing

Stains Caused by Reactive Dye Indicate Presence of DNAPL

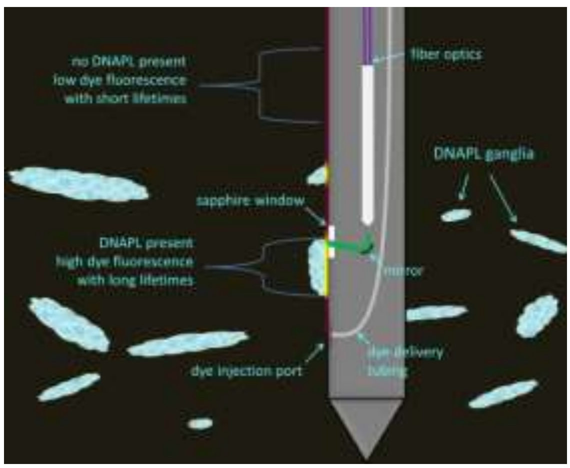
HRSC Tools and Approaches – Screening

NEWMOA 2014: Site Characterization for DNAPLs

Dye LIF from Dakota Technologies

Direct Detection of Cl Solvent DNAPLs

- Laser Induced Fluorescence is a powerful, high resolution, direct sensing tool for locating NAPLs consisting of aromatic compounds (e.g., fuels, coal tar etc)
- However, chlorinated solvents do not fluoresce – so LIF does not work for chlorinated solvent DNAPLS
- Dye LIF developed to overcome this limitation



Courtesy of Dakota Technologies

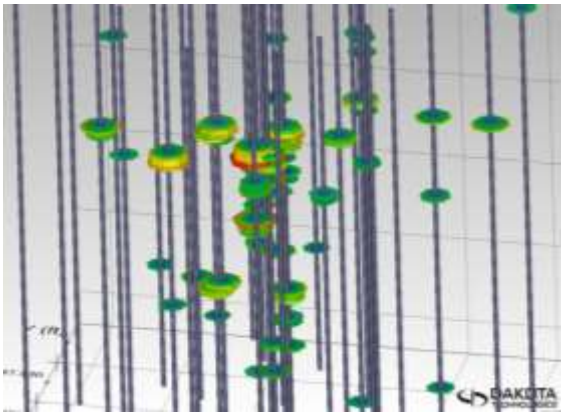
HRSC Tools and Approaches – Screening

NEWMOA 2014: Site Characterization for DNAPLs

Dye LIF Field Trials Successful

Dense Push Array at Highly Characterized DNAPL Source Zone

Post Processed 3D rendering of DNAPL Distribution from Dye-LIF Data



Courtesy of Dakota Technologies

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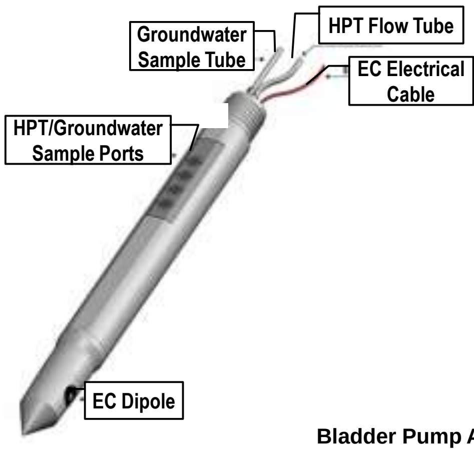
Geoprobe® HPT-GWS

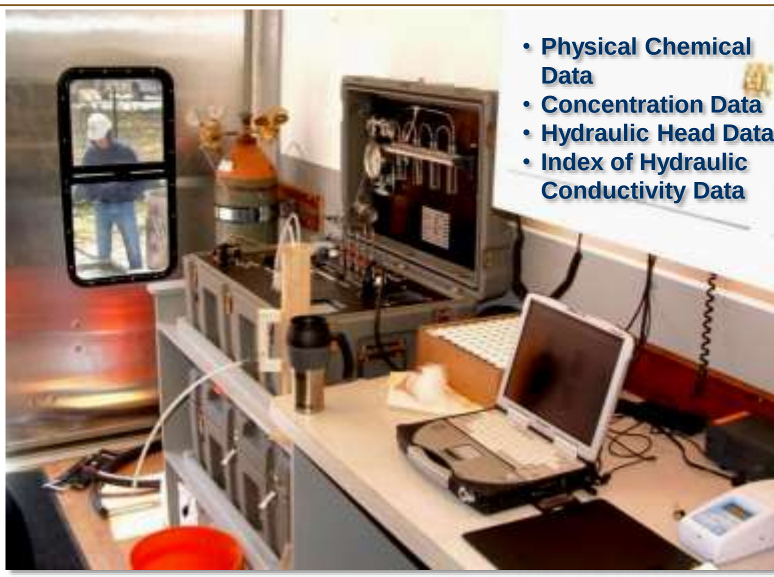


Bladder Pump Actuator, Sample Tubing and Trunkline at the Surface

HRSC Tools and Approaches – Groundwater Profiling

NEWMOA 2014: Site Characterization for DNAPLs

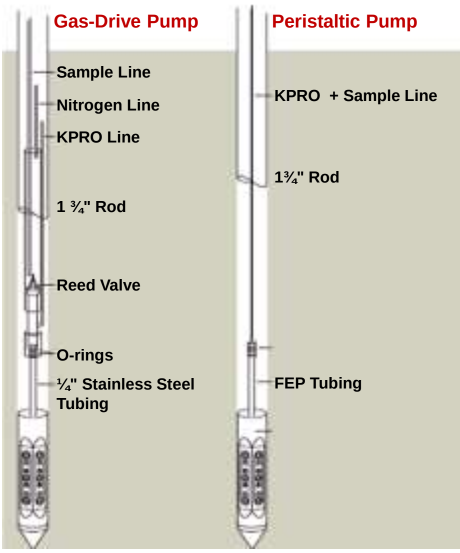
Integrated Data Acquisition – Waterloo^APS™



HRSC Tools and Approaches – Groundwater Profiling

NEWMOA 2014: Site Characterization for DNAPLs

Waterloo$^{APS™}$ Configurations

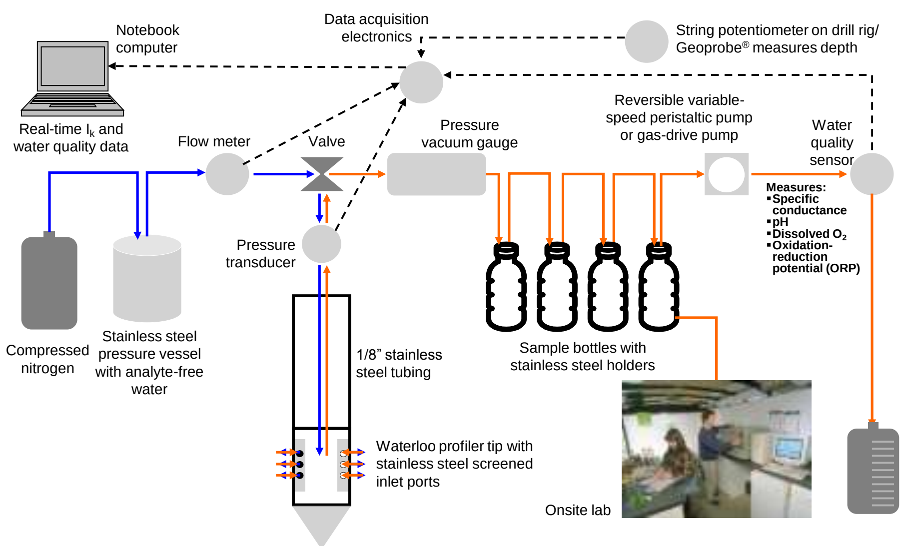


APS 225

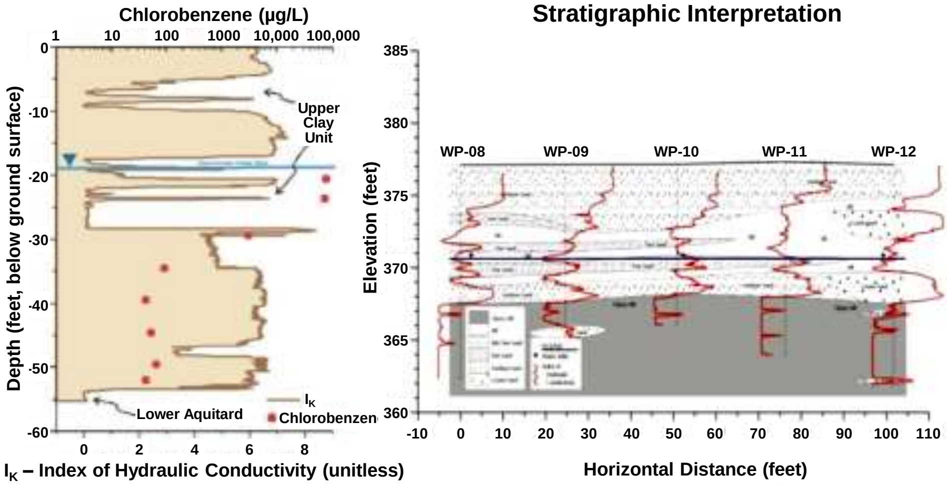
APS 175

APS 150

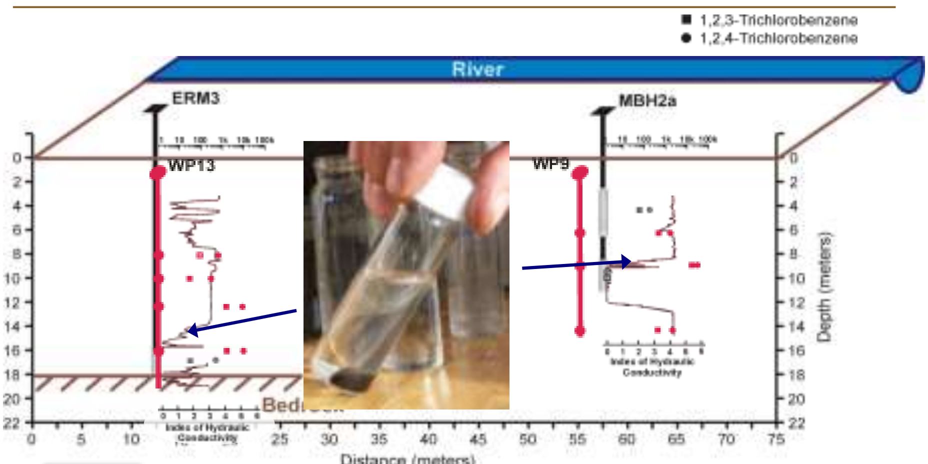
Waterloo$^{APS™}$ Data Acquisition Configuration and Process



Two Uses of I_K Data



Post-Remedy Investigation Northern England



Key Point Use of low resolution (conventional) techniques resulted in remedy failure and need for second remedy.

Presentation Overview

- Introduction
- What is High Resolution Site Characterization (HRSC)?
- Scientific Basis for HRSC
- Why Do HRSC?
- Implementation of HRSC
- **HRSC Tools and Approaches**
  - Screening
  - Groundwater Profiling
  - **Soil Coring**
- Case Study – Naval Air Station Jacksonville
- Wrap Up

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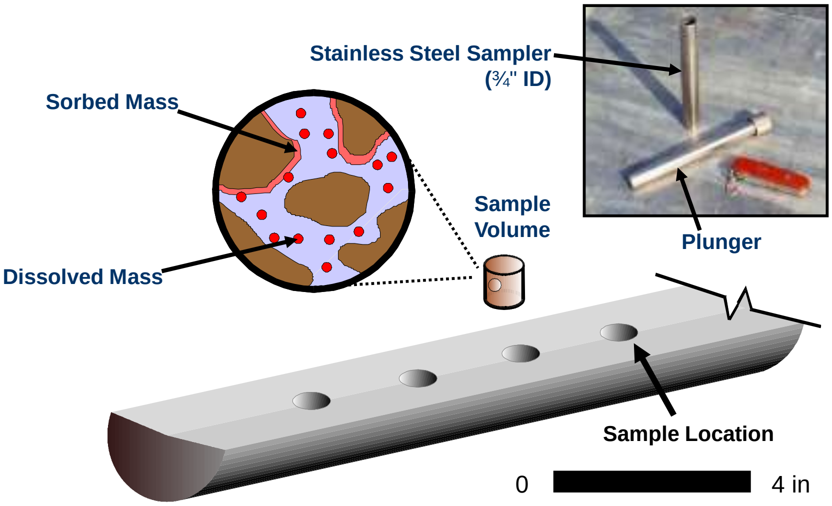
Essential Information from Cores

- Geologic/hydrogeologic features
- Physical, chemical & microbial properties
- Contaminant mass distributions (high- & low-K zones)
- Concentration gradients/diffusive fluxes
- Effectiveness of remedial technologies

HRSC Tools and Approaches – Soil Coring

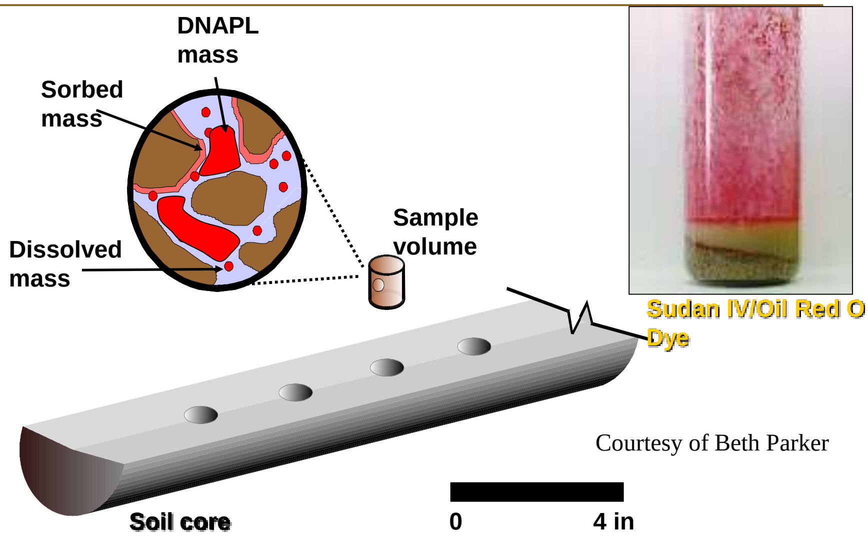
NEWMOA 2014: Site Characterization for DNAPLs

Subsampling (Profile Sampling) for VOCs



Guilbeault, 1999

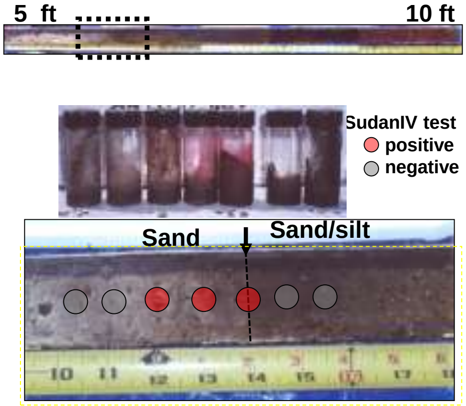
Soil Core Sampling - NAPL Detection



Courtesy of Beth Parker

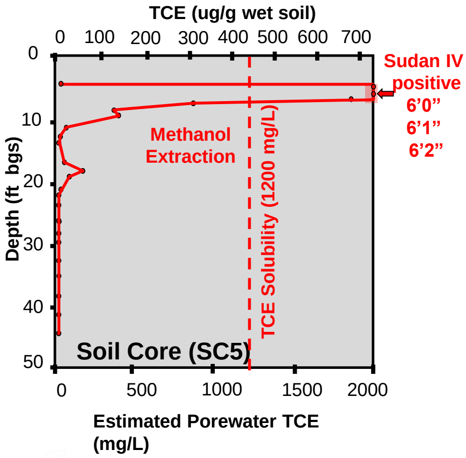
Example of NAPL Detection

Sudan IV Screening



Courtesy of Beth Parker

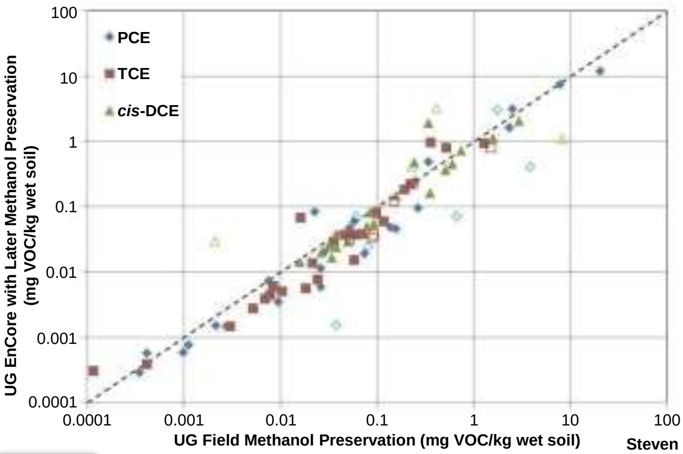
Quantitative TCE Analyses



Soil Coring, Extraction, and Analysis: It Matters How You Do It

- Soil Core Profiling – close vertical spacing
- Soil samples collected into:
  - MeOH in vials
  - EnCore samplers – *24-hr and 72-hr hold time in EnCore*
- Extractions
  - UG Shake Flask (2-week process)
  - Standard EPA 5035 Purge & Trap at Test America (2 week turnaround)
  - Onsite Lab Rapid Disaggregation and Suspension (1 hour)

Field Methanol Preservation vs. EnCore Collection with Later Methanol Shake Flask Extraction



- Solid symbols: placed into methanol within 24 hrs. of collection
- Hollow symbols: placed into methanol within 72 hrs. (evaluate longer hold time in EnCore samplers)

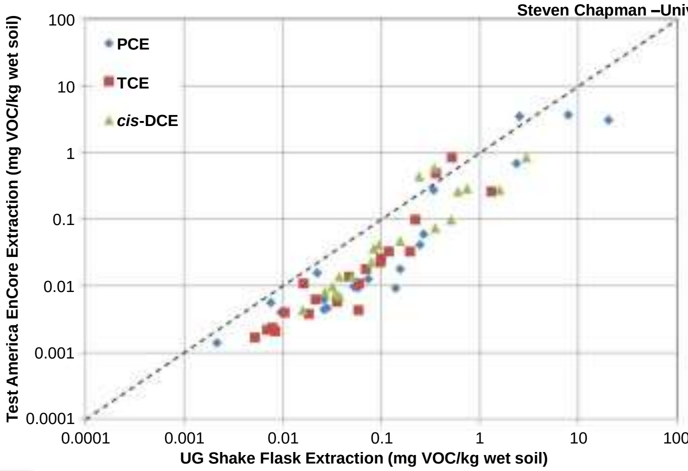
EnCore Sampler

Steven Chapman –University of Guelph

Key Point — **Field methanol preservation results higher for most samples, suggests volatile losses due to storage in EnCore samplers.**

Test America EnCore vs. UG Field Methanol Preservation and Shake Flask Extraction (~6-week extraction period)

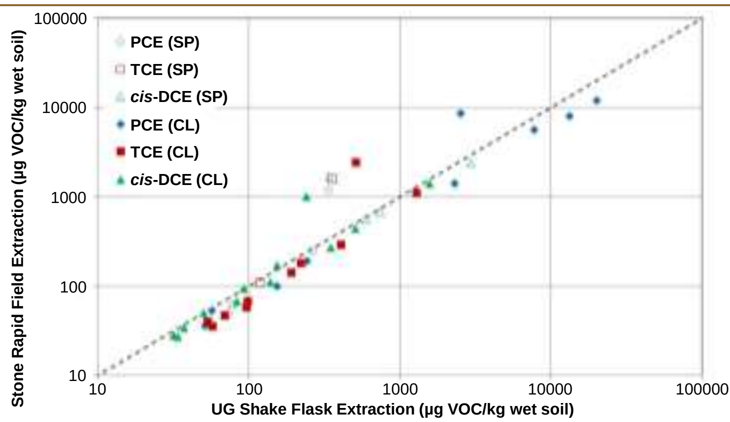
Steven Chapman –University of Guelph



Key Point — **Commercial (*i.e.*, Standard) lab method provides incomplete extraction.**

Rapid Field Extraction vs. Shake Flask Extraction

SP=sands
CL=clays



<u>UG Shake Flask Extraction – 2 weeks</u>

- Intermittent shaking every few days
- Time-series analyses to select optimal extraction period
- 4- to 6-week extraction time used for these samples
  - Constrained by lab schedule (extraction completed sooner)

<u>Field Extraction – 1 Hour</u>

- ~1-hr aggressive shaking on gyratory shaker
- Disaggregation of clay samples into methanol is key

Steven Chapman –University of Guelph

HRSC Tools and Approaches – Soil Coring

NEWMOA 2014: Site Characterization for DNAPLs

Presentation Overview

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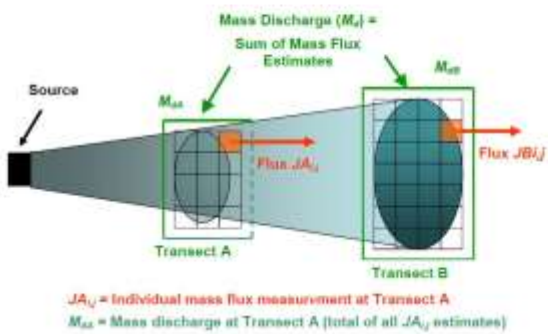
Mass Flux and Mass Discharge

- Mass Flux (J): amount of mass that moves across a unit cross sectional area over a given time (mass/area/time)
- Mass Discharge (M_D) : total solute mass discharging across a transect encompassing the entire plume width in a unit time (mass/time)
  - Mass Discharge is the sum of all of the Mass Flux across the plume
  - $M_D = \sum J_{i...n}$



ITRC August 2010

http://www.itrcweb.org/Guidance/GetDocument?documentID=49

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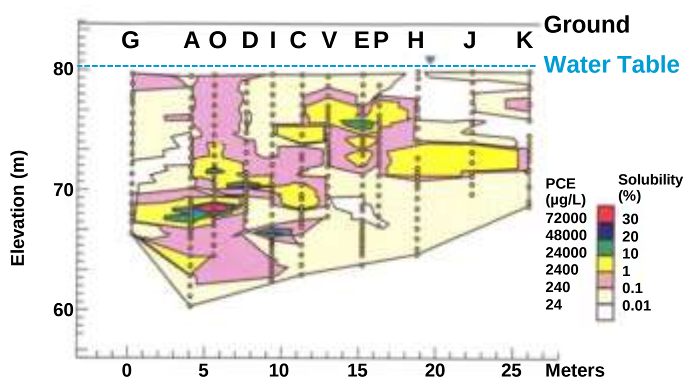
Mass Flux Distribution

New Hampshire PCE Site



Optimal Vertical Sample Spacing is ~0.5 m

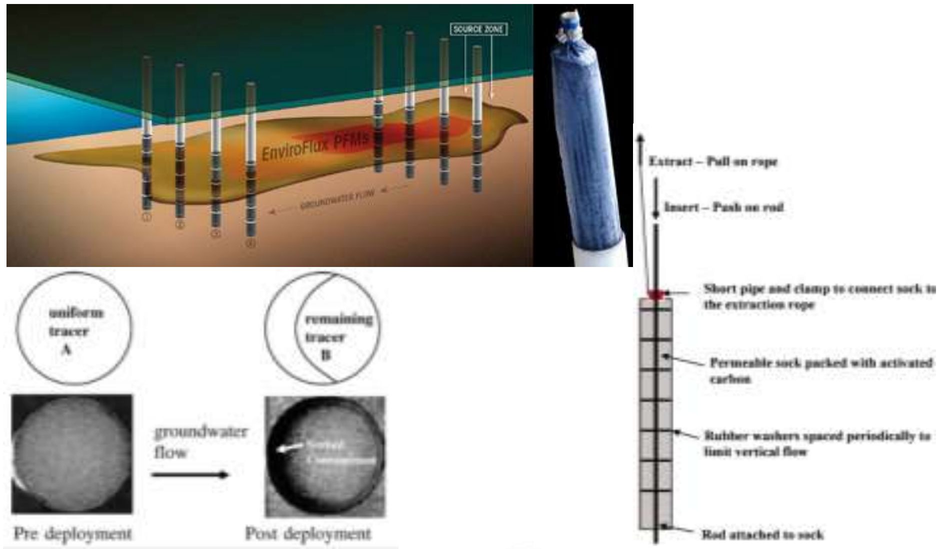
Guilbeault *et al.* 2005

Key Point — **75% of contaminant mass discharge occurs through 5% to 10% of the plume cross sectional area.**

Mass Flux and Mass Discharge

NEWMOA 2014: Site Characterization for DNAPLs

Passive Flux Meter by EnviroFlux



Mass Flux and Mass Discharge

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Waterloo^{APS} Transects at South Municipal Well Superfund Site

Approximate direction of transport

2012 Source Area Pre-Design Investigation HRSC Approach

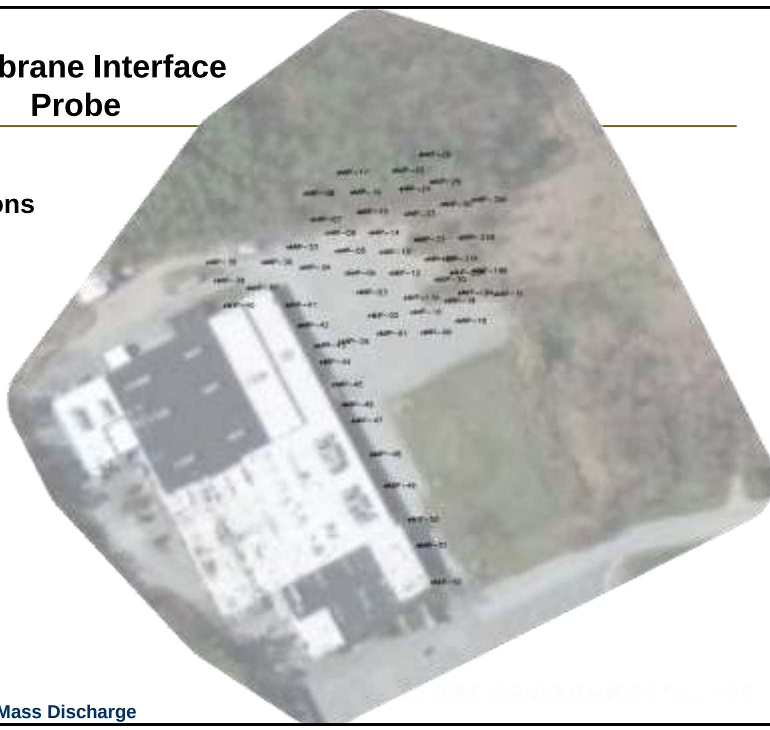
- "Toolbox Approach"
  - Multiple tools provide multiple lines of evidence
- Rapid Screening with Membrane Interface Probe
- Waterloo^APS Profiling to find edges of high concentration zones, DNAPL indications and hydrostratigraphic data
- Soil coring, dye screening and sampling to confirm presence/absence of DNAPL/high mass zones
- On site groundwater and soil analyses by MobiLab (GC/MS)

Mass Flux and Mass Discharge

NEWMOA 2014: Site Characterization for DNAPLs

Membrane Interface Probe

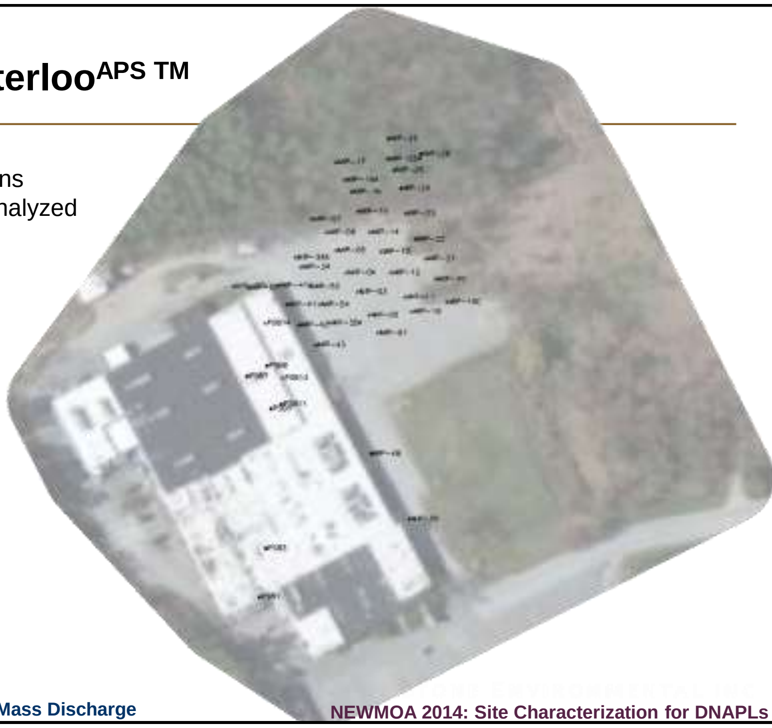
55 Locations



Mass Flux and Mass Discharge

WaterlooAPS TM

47 Locations
755 Samples Analyzed Onsite



Mass Flux and Mass Discharge

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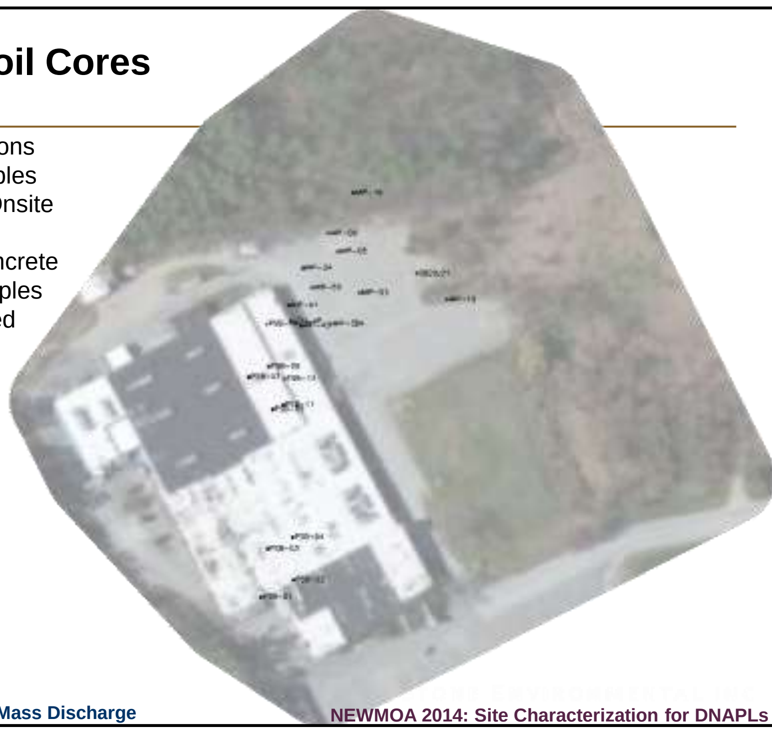
Soil Cores

21 Locations
966 Samples Analyzed Onsite

Plus 17 Concrete Core Samples Analyzed



Mass Flux and Mass Discharge

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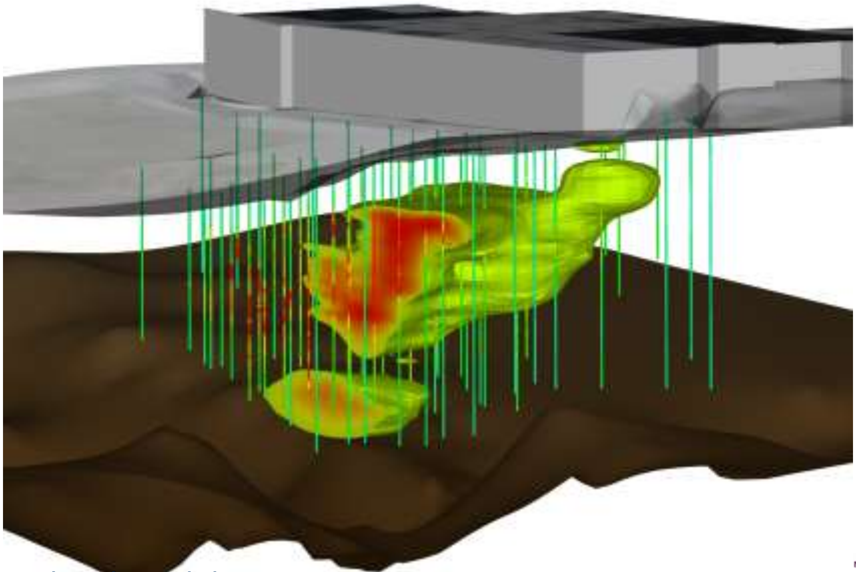
Membrane Interface Probe

Electron Capture Detector Response 12 Volt Isoshell



Mass Flux and Mass Discharge

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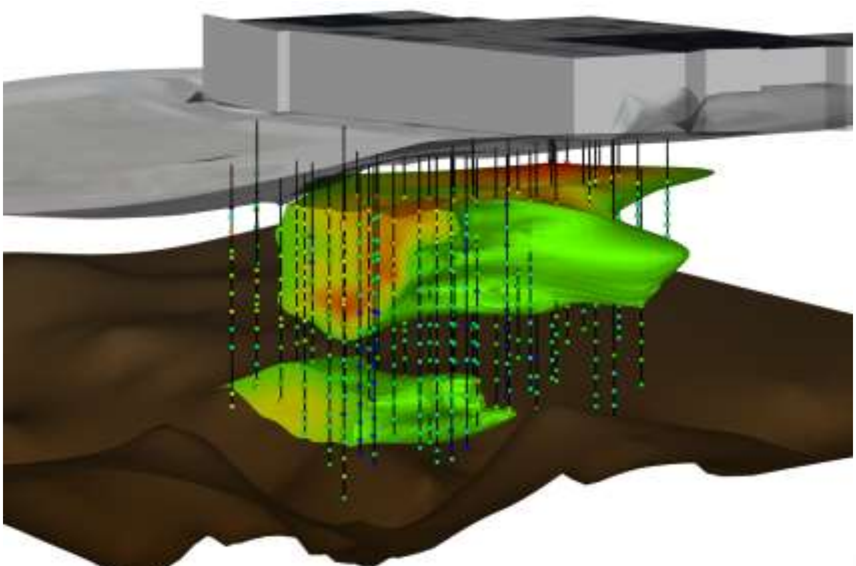
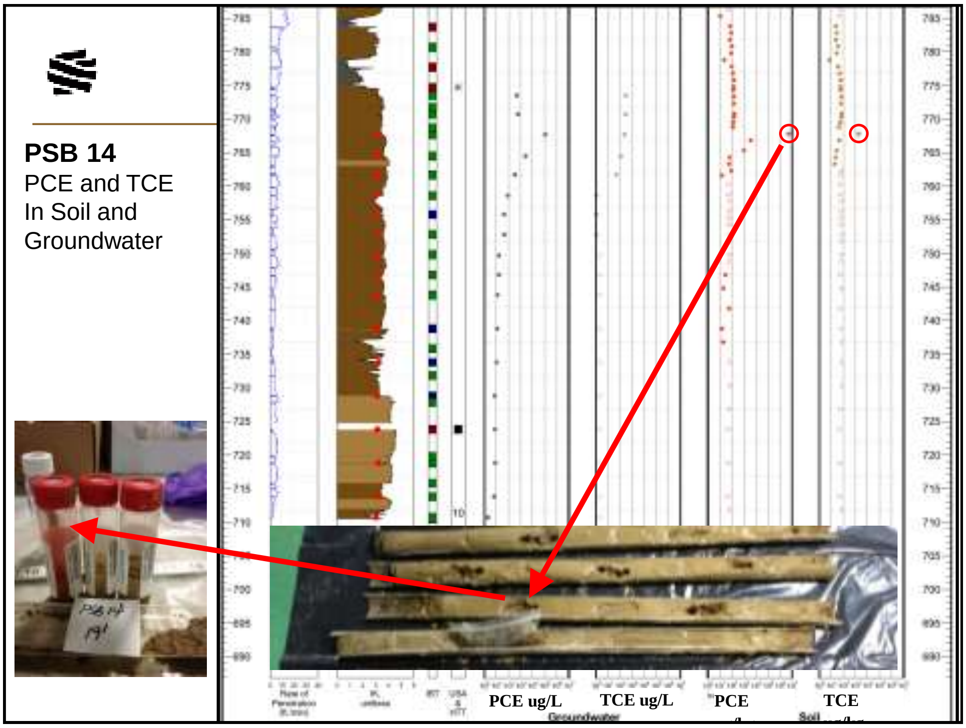
WaterlooAPS Groundwater Profiling

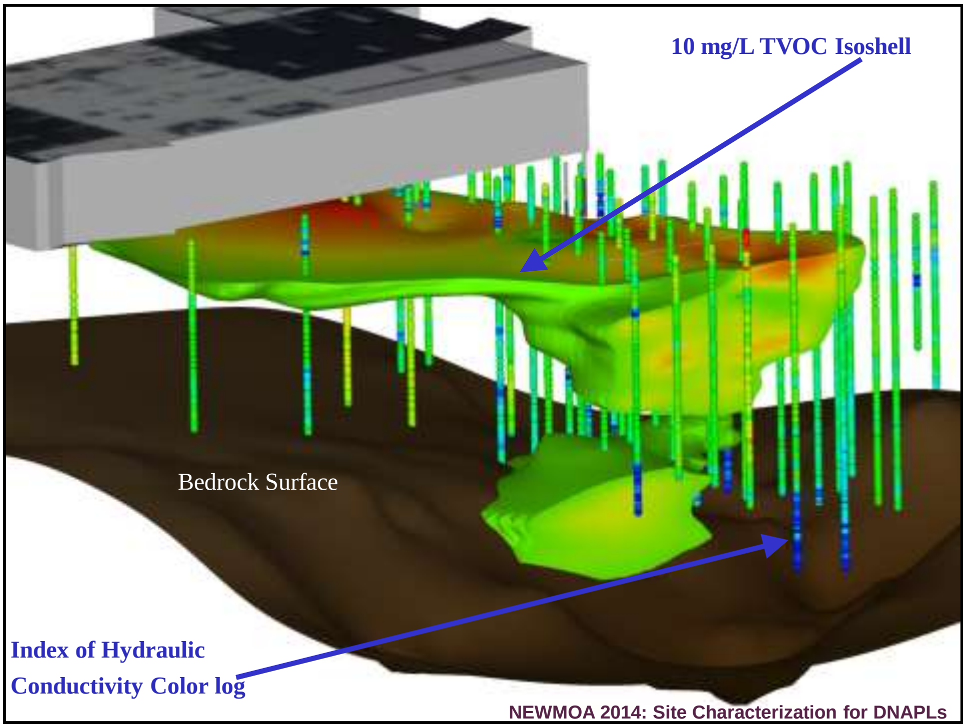
Total VOCs 10 mg/L Isoshell



Mass Flux and Mass Discharge

NEWMOA 2014: Site Characterization for DNAPLs

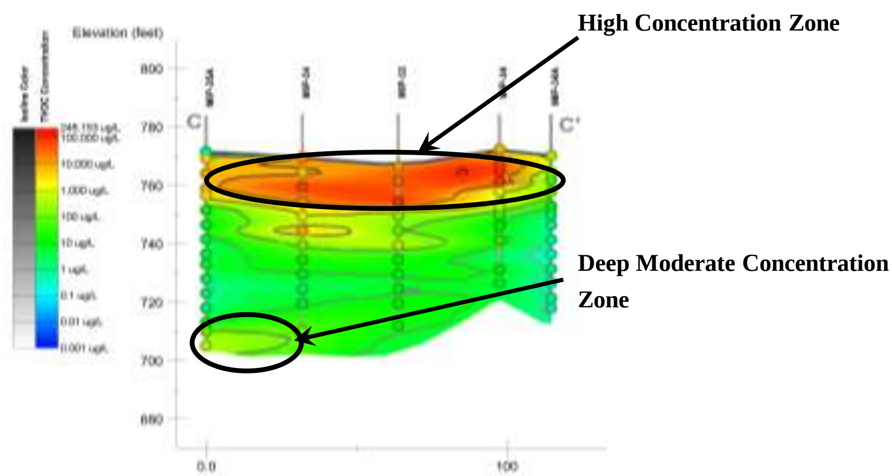

PSB 14
PCE and TCE
In Soil and
Groundwater
PCE ug/L
TCE ug/L
PCE
TCE


10 mg/L TVOC Isoshell
Bedrock Surface
Index of Hydraulic
Conductivity Color log
NEWMOA 2014: Site Characterization for DNAPLs

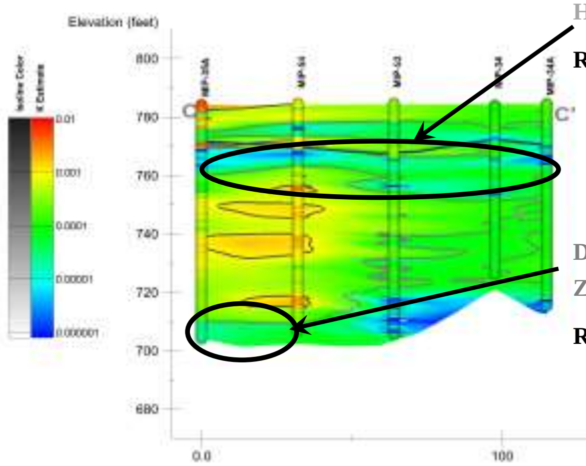
Estimated Relative Mass Flux Distribution on Waterloo$^{APS\ TM}$ Transects

- **Simplified relative flux estimate:**
  - Convert I_K to assumed/estimated K_{est} values
    - In this case - K_{est} (cm/sec) = $8E\text{-}07e^{1.9702\ IK}$
  - Assume variability of i is negligible and assume unit area of 1 cm^2
  - Interpolate K_{est} in 3D and Concentration in 3D; Then multiply the 3D meshes against each other to get 3D flux field in $ug/sec/cm^2$
  - Estimated relative flux values resulting are:
    - Screening Level
    - Relative (as opposed to the absolute values obtained by passive flux meters, integrated pumping tests etc)

Transect C – TVOC Concentration (mg/L)



Transect C – Estimated Hydraulic Conductivity



High Concentration Zone

Relatively Low K

Deep Moderate Concentration Zone

Relatively Low K

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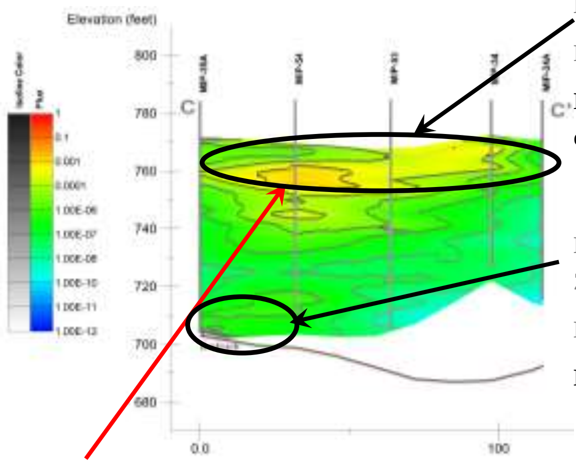
Mass Flux and Mass Discharge

NEWMOA 2014: Site Characterization for DNAPLs

Transect C – Relative Mass Flux Distribution



High Concentration Zone

Relatively Low K

Highest J limited to small area of High C Zone

Deep Moderate Concentration Zone

Low K

Extremely low J

64% of mass discharge across 2% of cross sectional area

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Mass Flux and Mass Discharge

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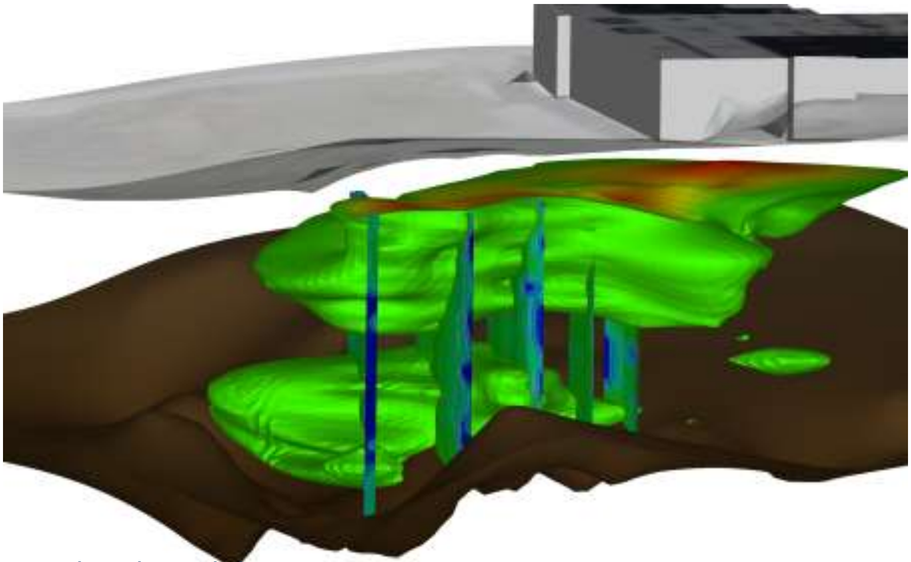
50 ug/L TVOC Isoshell Volume



Mass Flux and Mass Discharge

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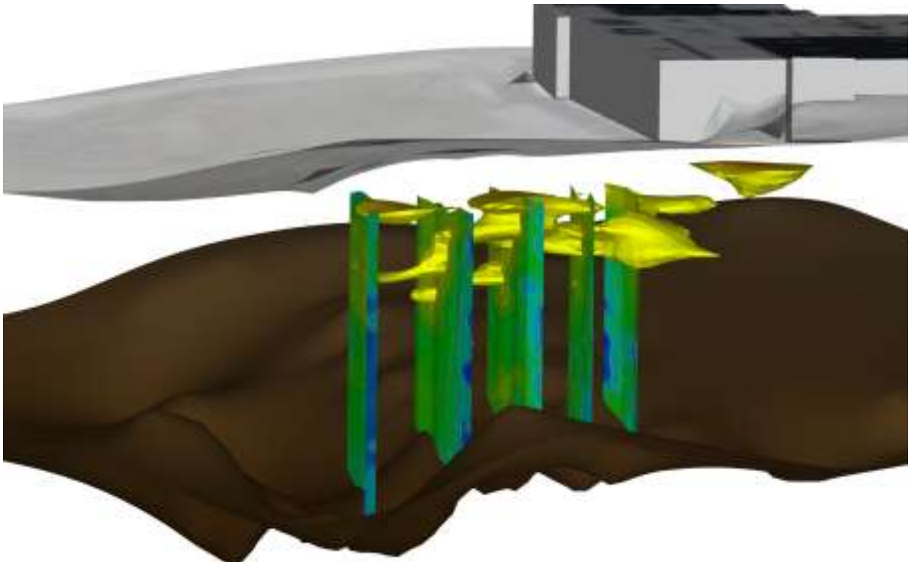
Volumes in which 95% to 99% of the Flux Occurs



Mass Flux and Mass Discharge

NEWMOA 2014: Site Characterization for DNAPLs

Summary

- High degree of heterogeneity (K)
- Multiple "sources"
  - Original DNAPL source zone depleted by remedies and flux over time (approx 29,000 kg to date)
  - "secondary" back diffusion sources located downgradient of original source
- On average 70% of the mass discharge occurs across approximately 6% of the cross sectional area of the plume
- Deep contamination in low K till unit does not contribute significant flux
- Focus future remedies on aquifer volumes providing majority of flux

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Key Points

- Successful remedies require site characterization data collected at a scale consistent with the spatial structure of the controlling variables
- Hydraulic conductivity often varies at the cm scale vertically and the meter scale horizontally
- DNAPL distributions are influenced by capillary pressure distributions that can vary at the mm scale
- Transverse hydrodynamic dispersion is weak (*i.e.*, plumes don't "spread out" much)
- 75% of mass flux occurs through only 5 to 10% of the plume's total cross sectional area

Wrap Up

NEWMOA 2014: Site Characterization for DNAPLs

Key Points (cont.)

- Substantial contaminant mass may be present in low permeability zones due to diffusive flux and cause rebound following remediation
- HRSC is implemented using:
  - Transects (orthogonal to direction of transport) of profiles
  - The Triad Approach principles
- Monitoring wells provide depth-integrated, flow-weighted average data and may obscure important information

Wrap Up

NEWMOA 2014: Site Characterization for DNAPLs

Key Points (cont.)

- Multiple tools and methods are required
  - *Screening tools can save time and money*
  - *Groundwater profiling and analysis in the more permeable zones*
  - *Soil core profiling and analysis in the low permeability zones*
- Methods for low-K soil sample collection, preservation and extraction can have a significant effect on analytical results (purge & trap is not optimal)
- MIP provides high resolution screening data quickly and relatively inexpensively
- MIP data indicate where relatively high concentrations are located but MIP data are not strongly correlative with actual soil and groundwater concentrations

Wrap Up

NEWMOA 2014: Site Characterization for DNAPLs

Questions and Answers

Wrap Up

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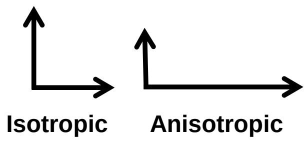
Definitions: Isotropy and Homogeneity



- Isotropic: aquifer properties (*e.g.*, hydraulic conductivity) are the same regardless of the direction of measurement (*e.g.*, horizontal vs. vertical)
- Anisotropic: aquifer properties vary with direction
- Homogeneous: aquifer properties are constant everywhere
- Heterogeneous: aquifer properties vary spatially