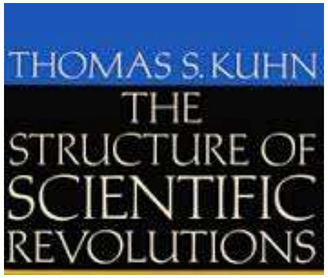
MONITORED NATURAL ATTENUATION (MNA) FOR SITE CLEANUP: APPROPRIATE TOOL OR EASY WAY OUT?

GSI ENVIRONMENTAL



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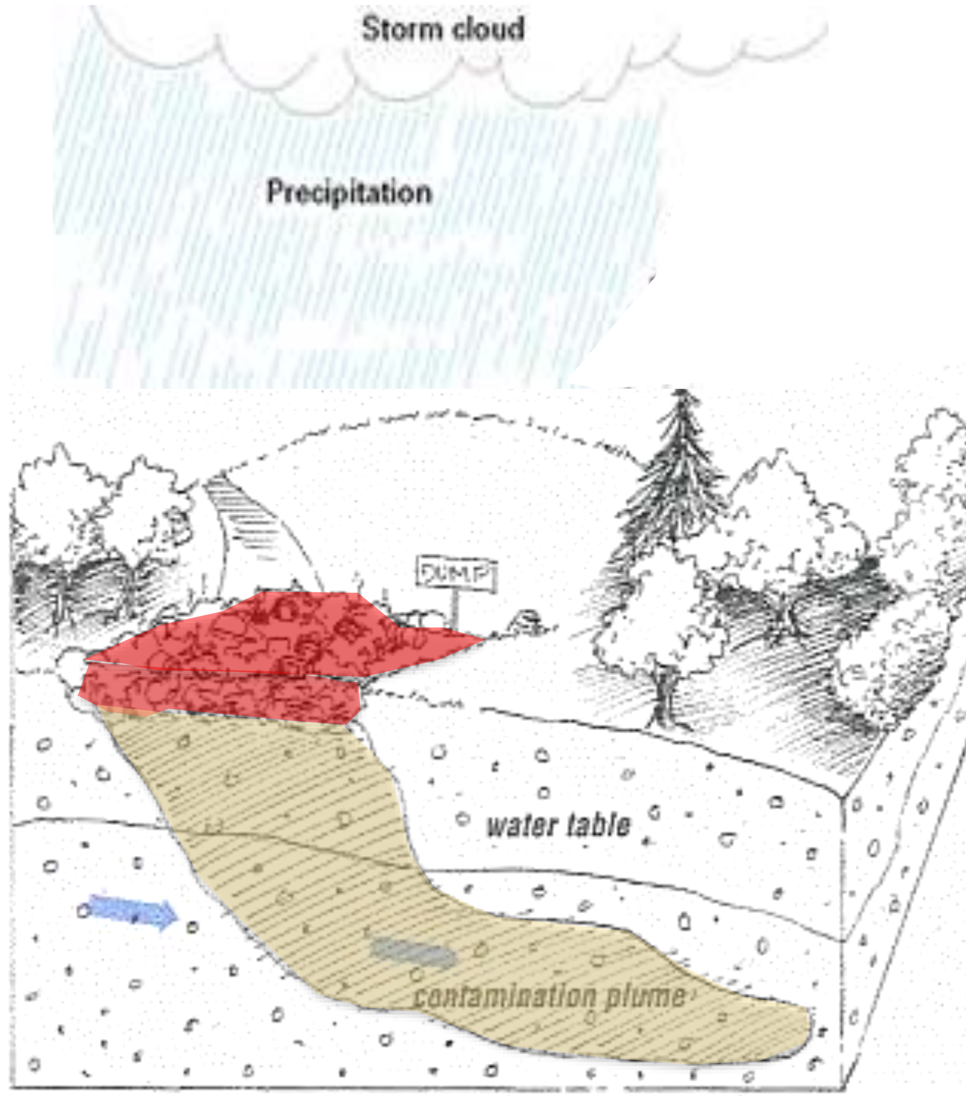
ROAD MAP

- Intro: Changing Paradigms and MNA Principles
- **Key Attenuation Processes**
  - *Biodegradation*
  - *Abiotic Processes*
  - *LNAPL source zone degradation processes*
  - *Other processes (immobilization, storage, dilution)*
- **Field Techniques and Technologies**
  - *Groundwater sampling and analytical methods*
  - *Compound Specific Isotopes Analysis (CSIA)*
  - *Molecular Biological Tools (MBTs)*
  - *Natural Source Zone Depletion (NSZD)*
- **Should MNA be Used? Data Analysis and Monitoring Tools**
  - *Data requirements, LTM, and statistics to understand MNA rates*
  - *Common Graphics and Calculations*
  - *Remediation Timeframe Calculations*
  - *Computer Models*
- **Implementation Topics**

SOURCE
PARADIGM

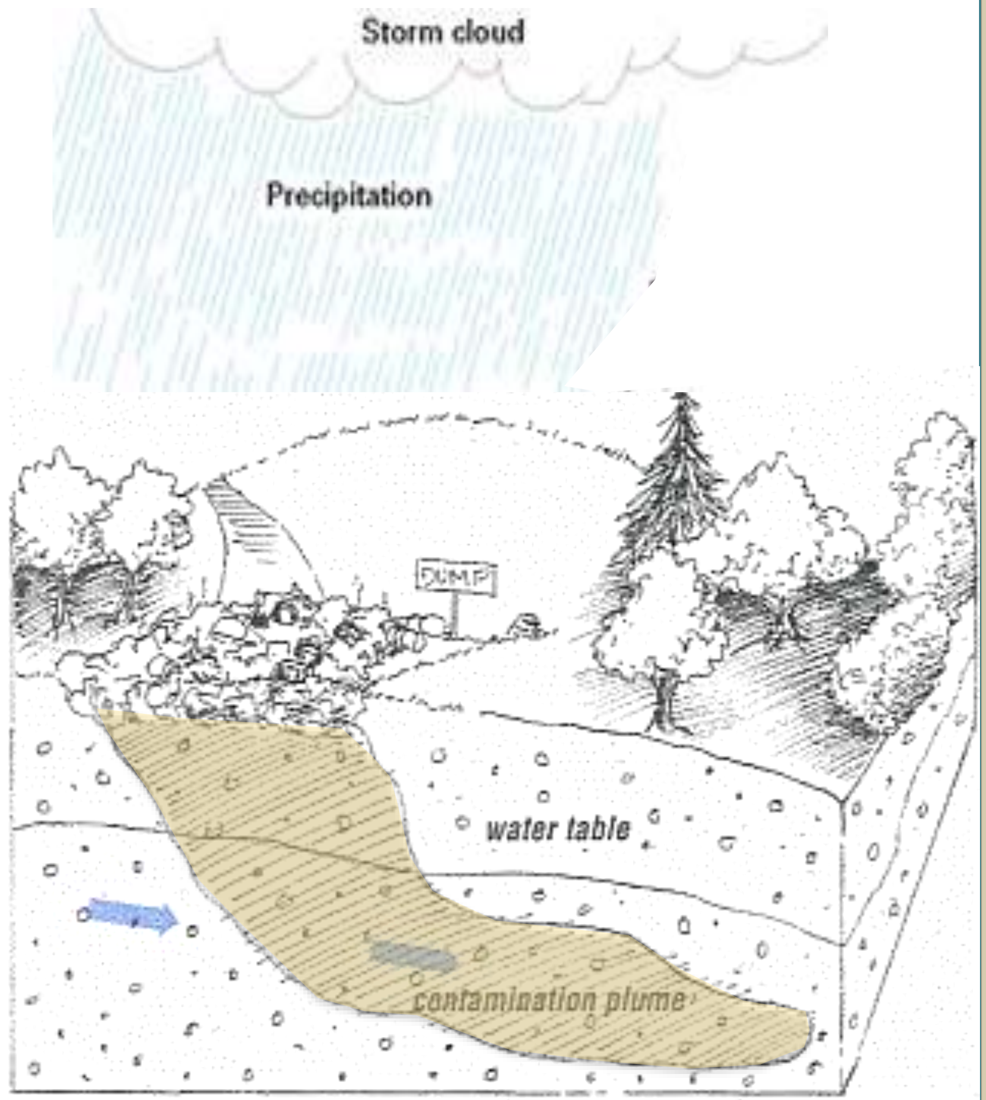
1970s – early 1990s



Contaminants in the ground form a plume

SOURCE
PARADIGM

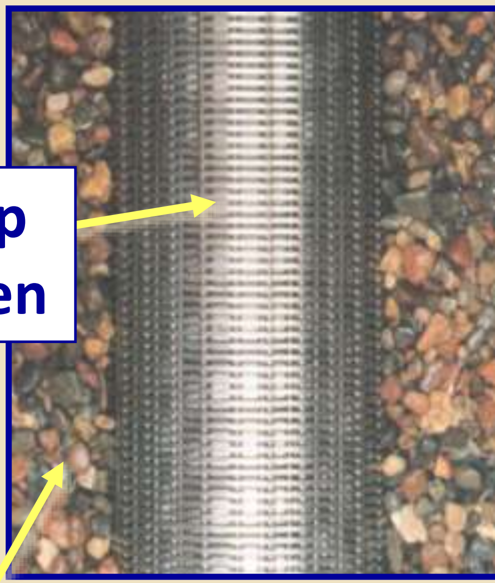
1970s – early 1990s



Contaminants in the ground form a plume

PUMP AND TREAT THE PLUME

Recovery Well Installation



Wire-Wrap Well Screen

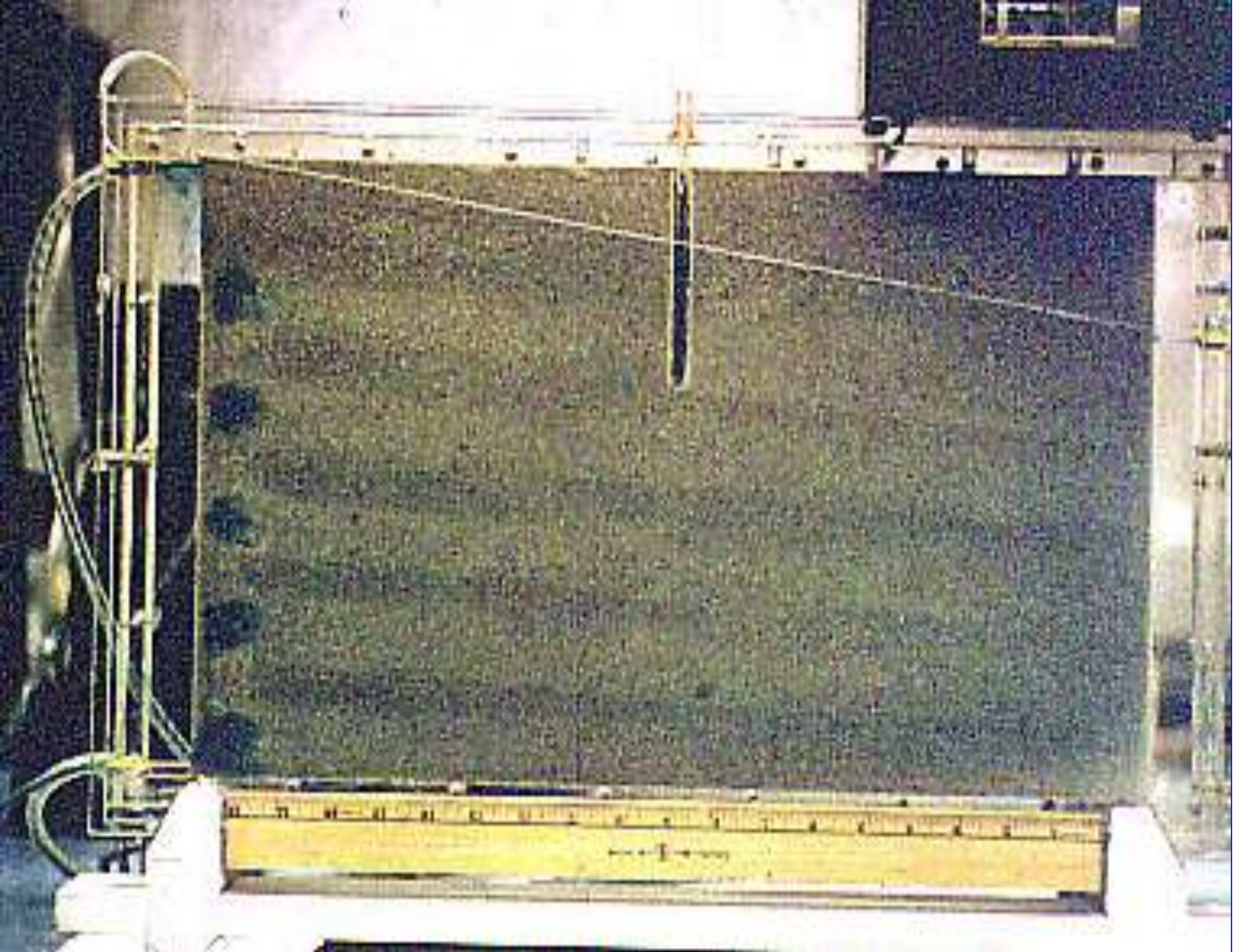
Sand-Gravel Filter Pack

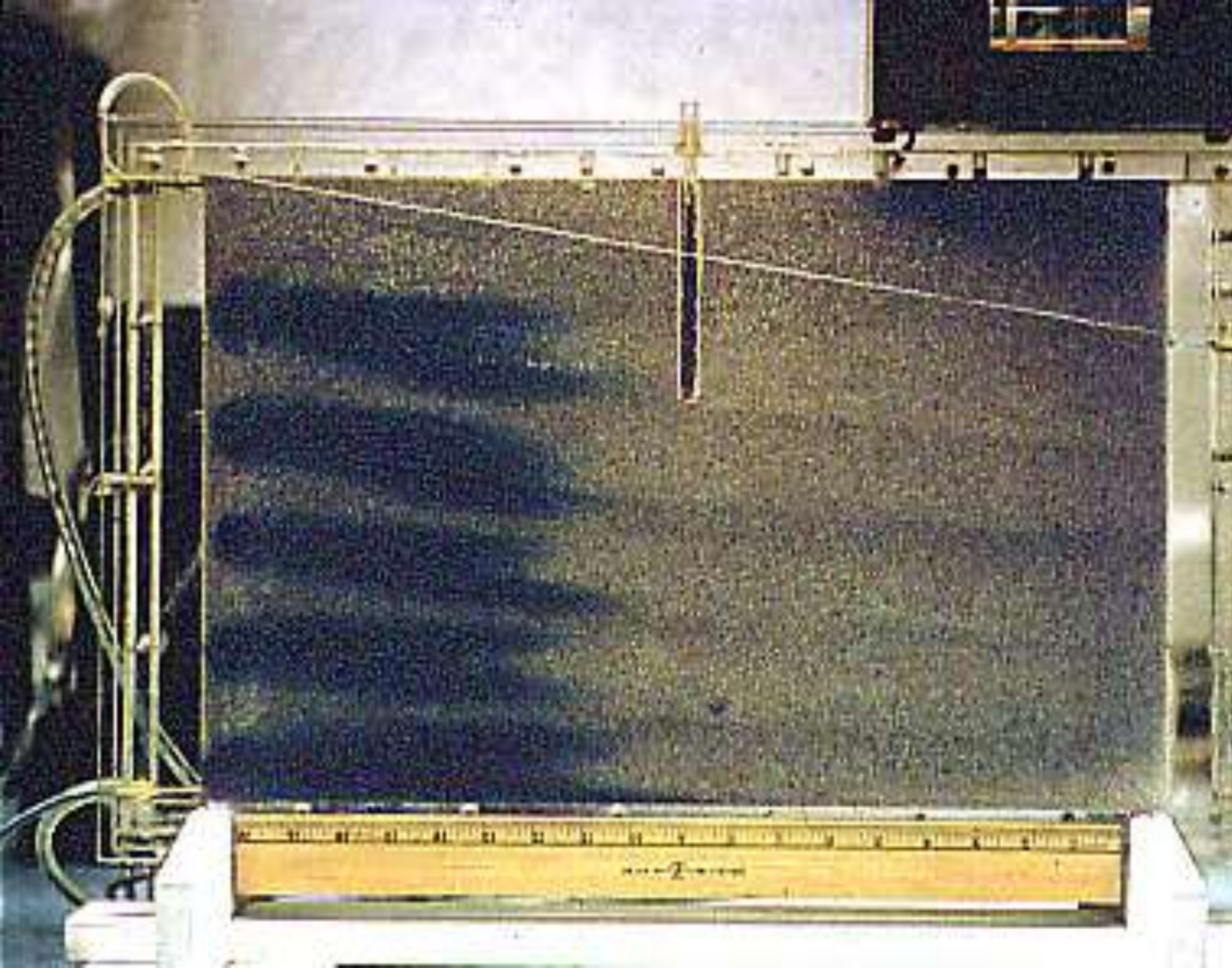
Well Screen

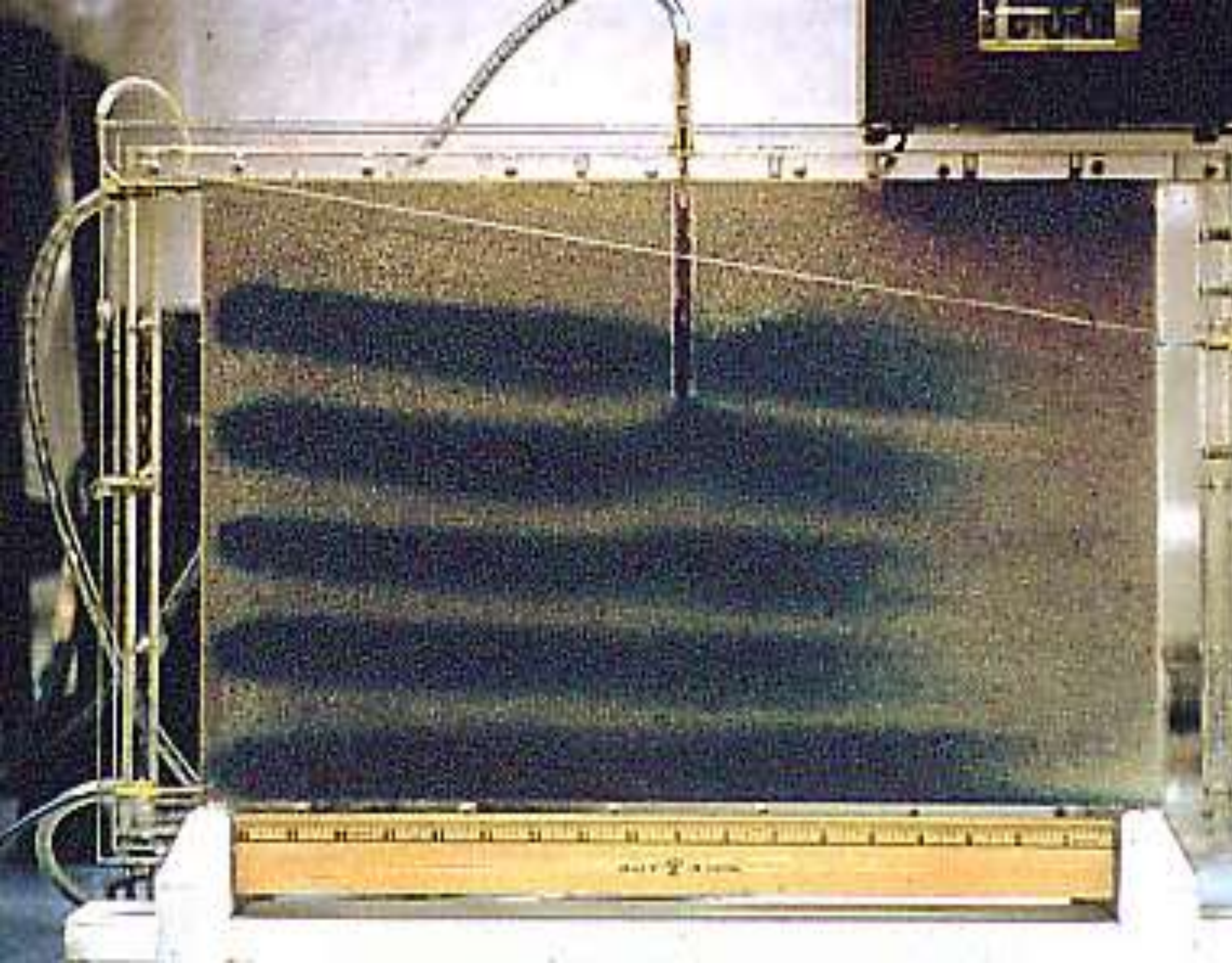
Centralizer

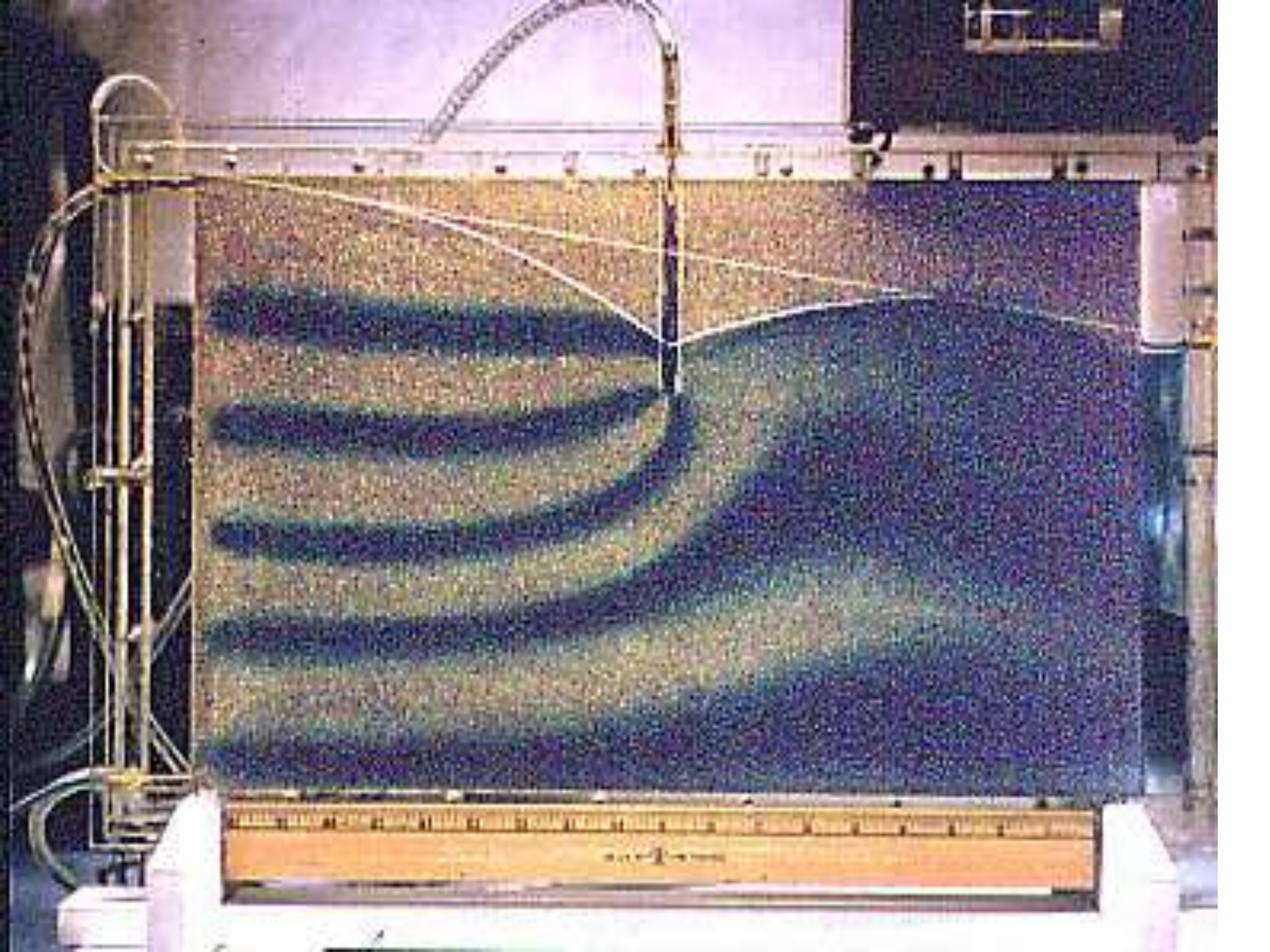
Driller's knee

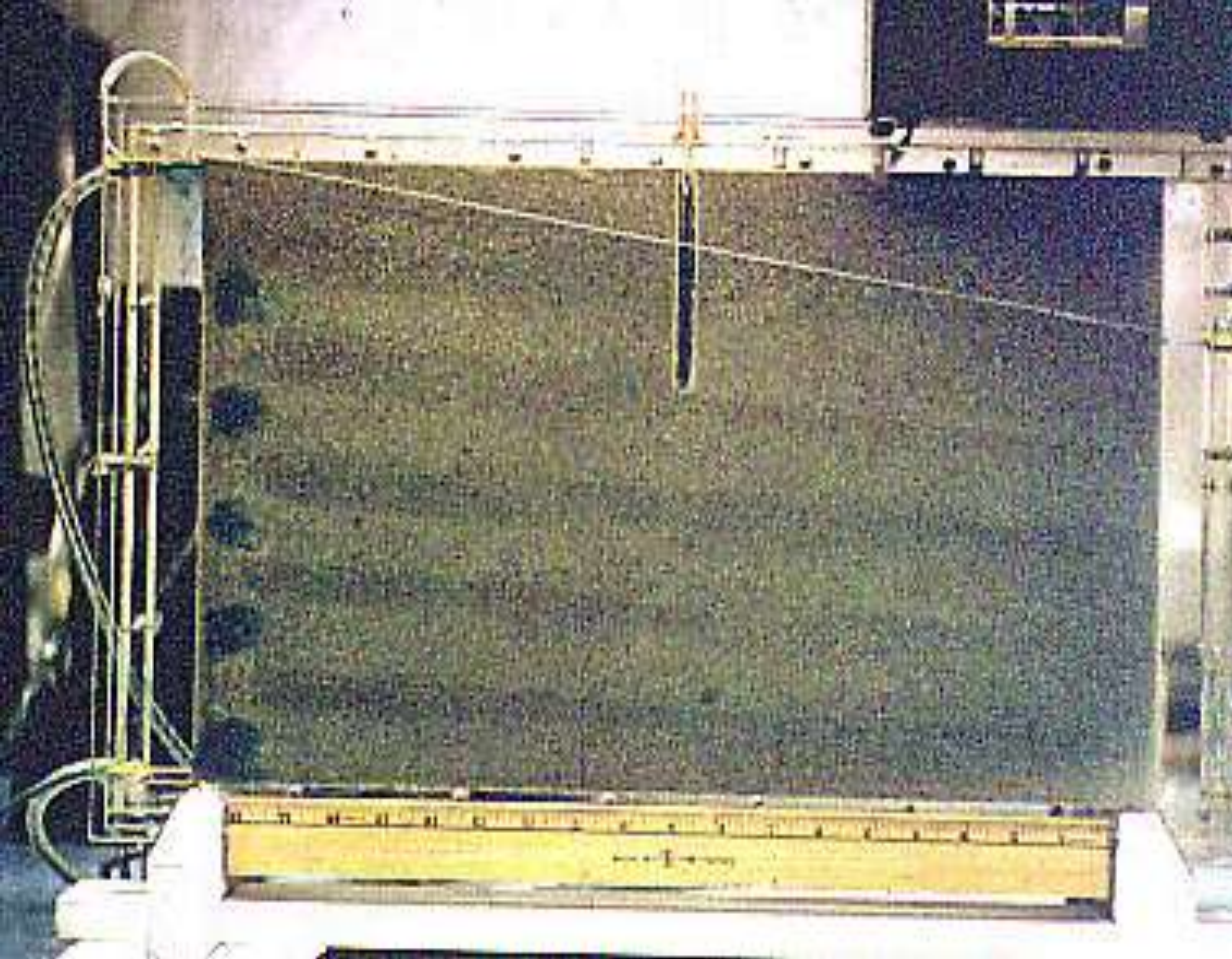
Driller's helper



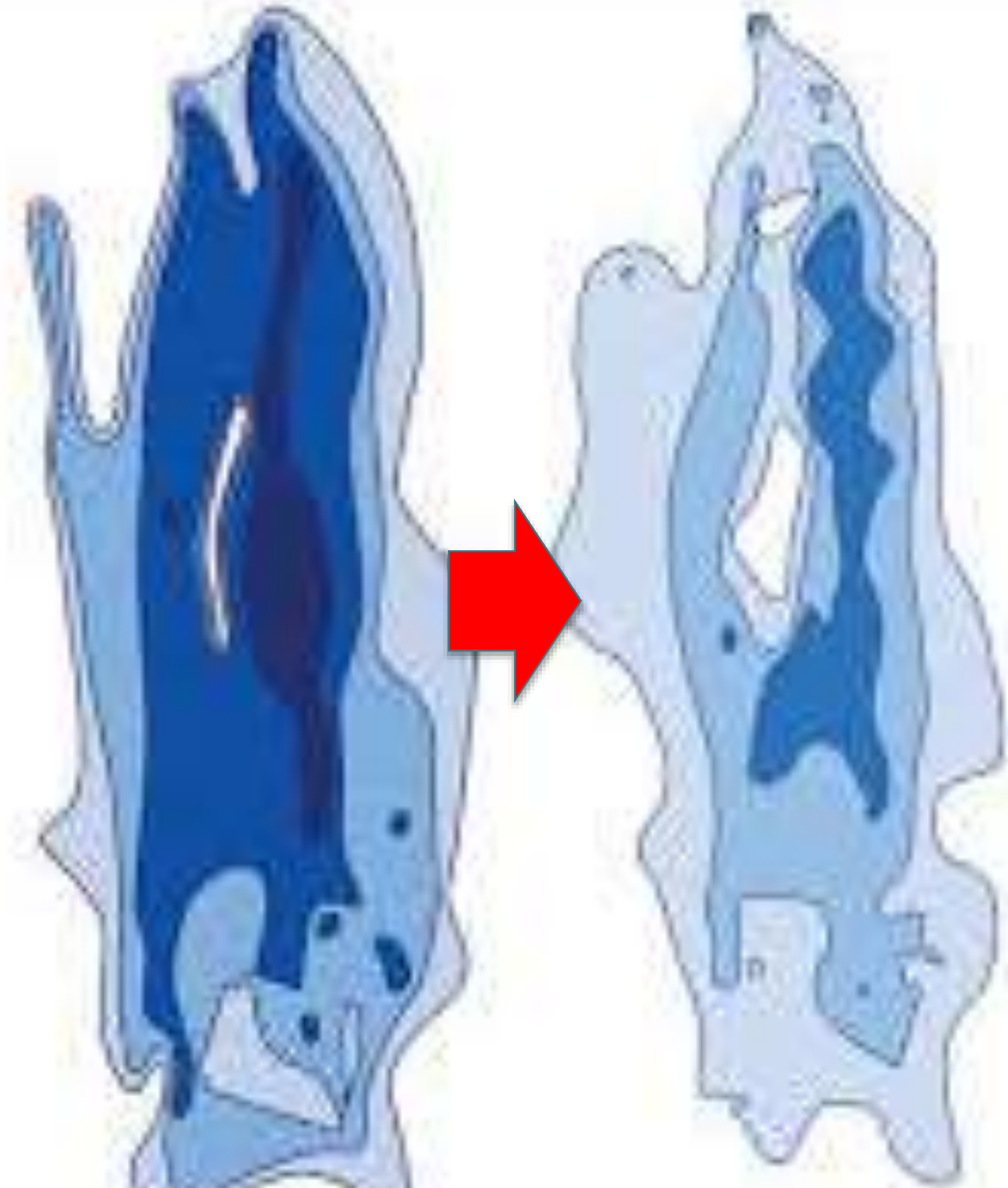








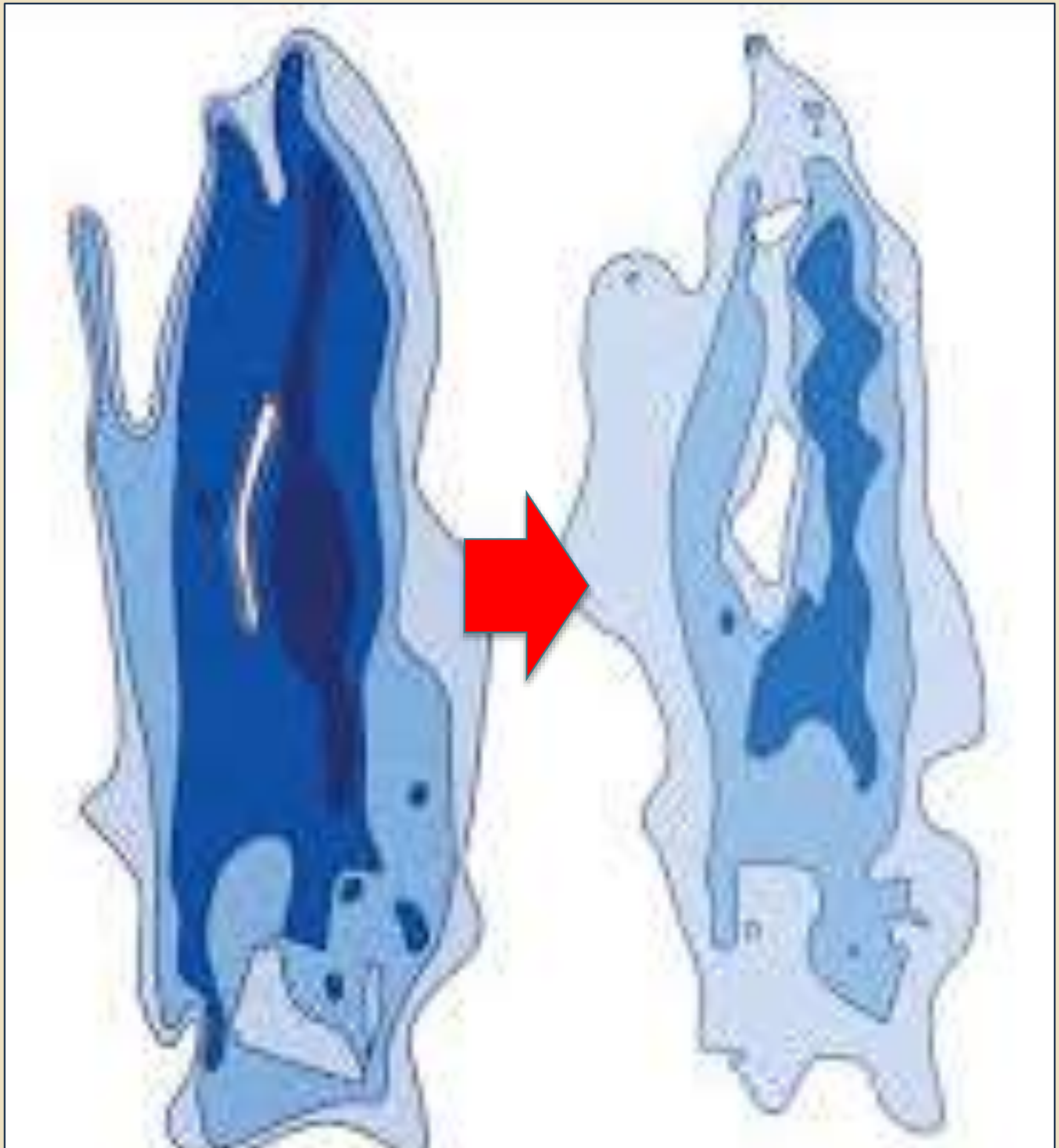
What Happened?



NRC, 2012

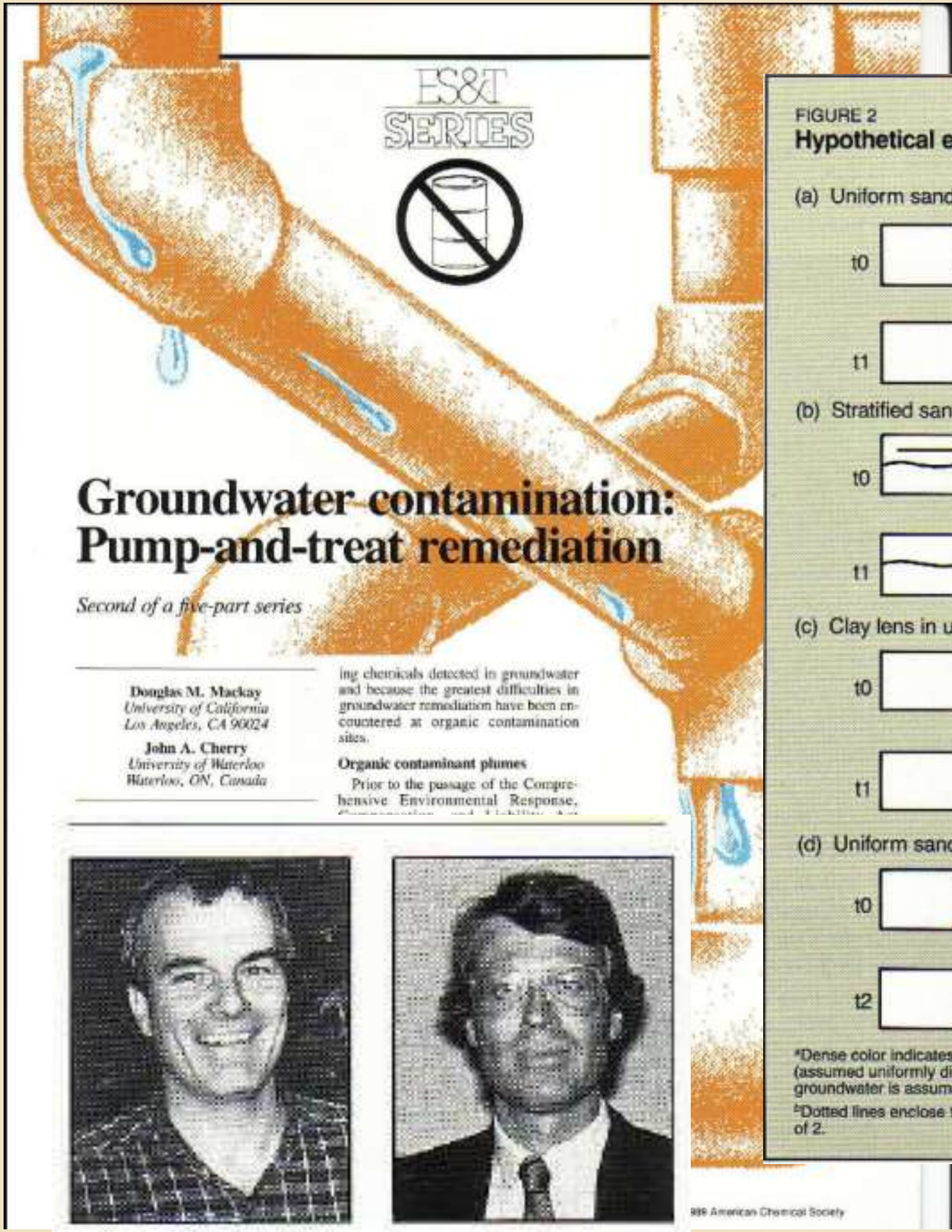
What Happened?

The Good
The Bad
The Ugly



NRC, 2012

1989



ES&T SERIES

Groundwater contamination: Pump-and-treat remediation

Second of a five-part series

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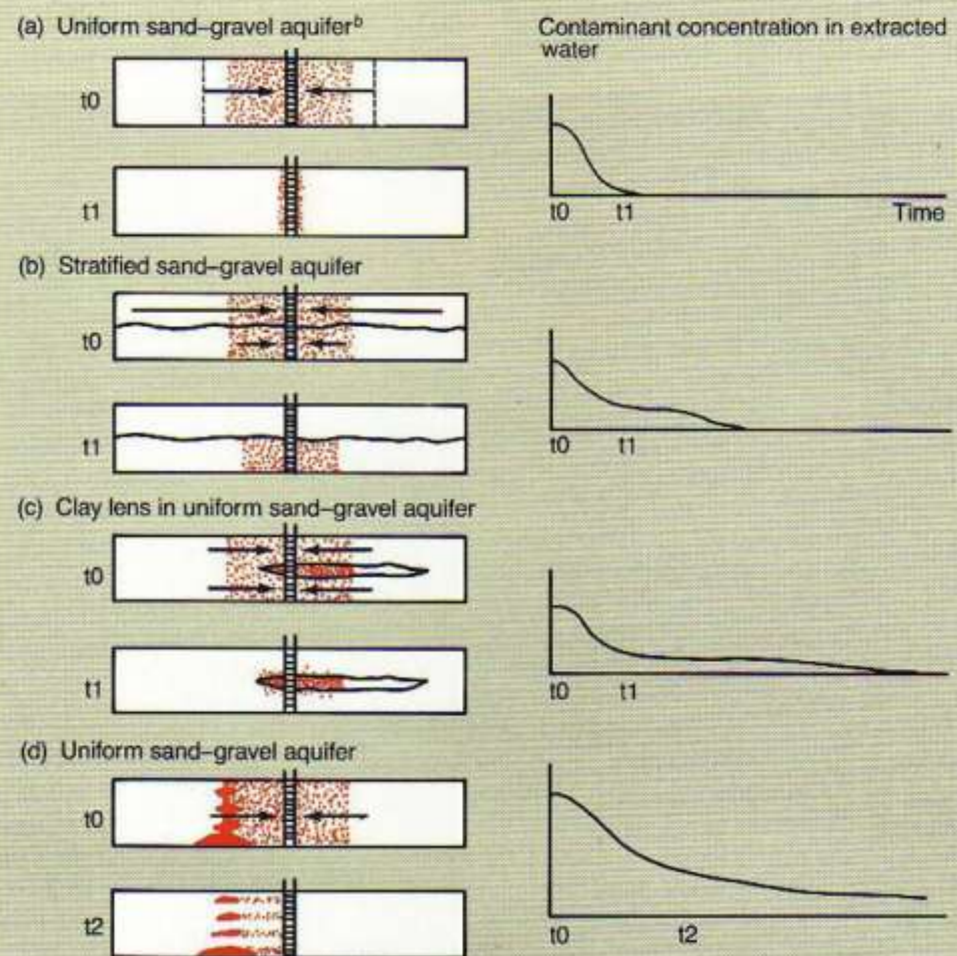
Waterloo, ON, Canada

ing chemicals detected in groundwater and because the greatest difficulties in groundwater remediation have been encountered at organic contamination sites.

Organic contaminant plumes

Prior to the passage of the Comprehensive Environmental Response,

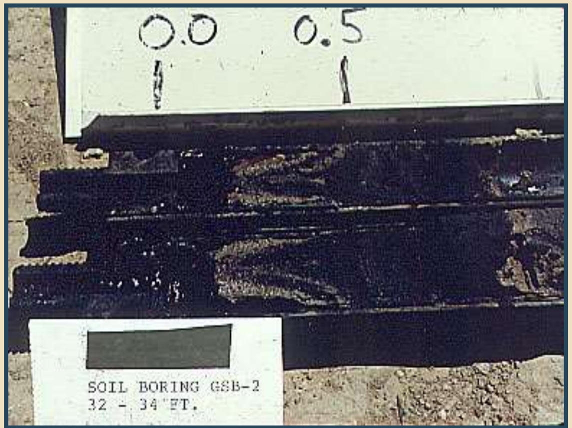
FIGURE 2
Hypothetical examples of contaminant removal from aquifers[a]

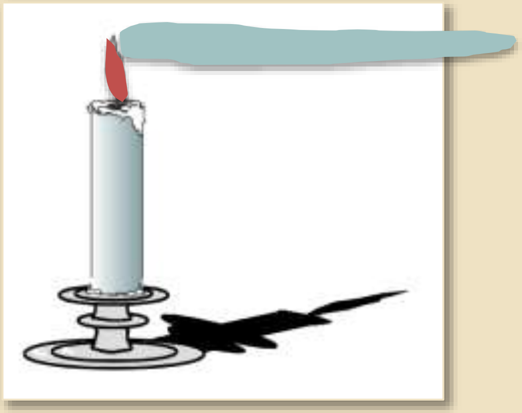


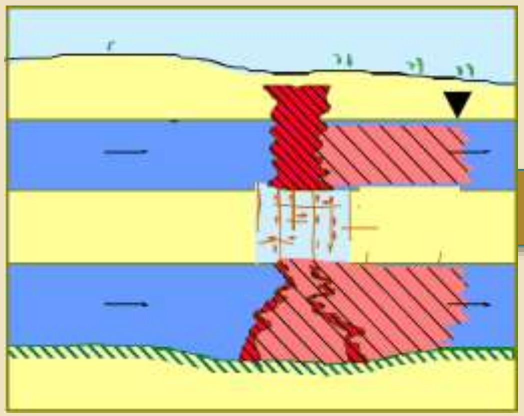
[a]Dense color indicates NAPL contaminant, stippling indicates contaminant in dissolved and sorbed phases (assumed uniformly distributed initially), and arrows indicate relative velocity of groundwater flow. The groundwater is assumed to be extracted from the well at the same rate in the four cases.

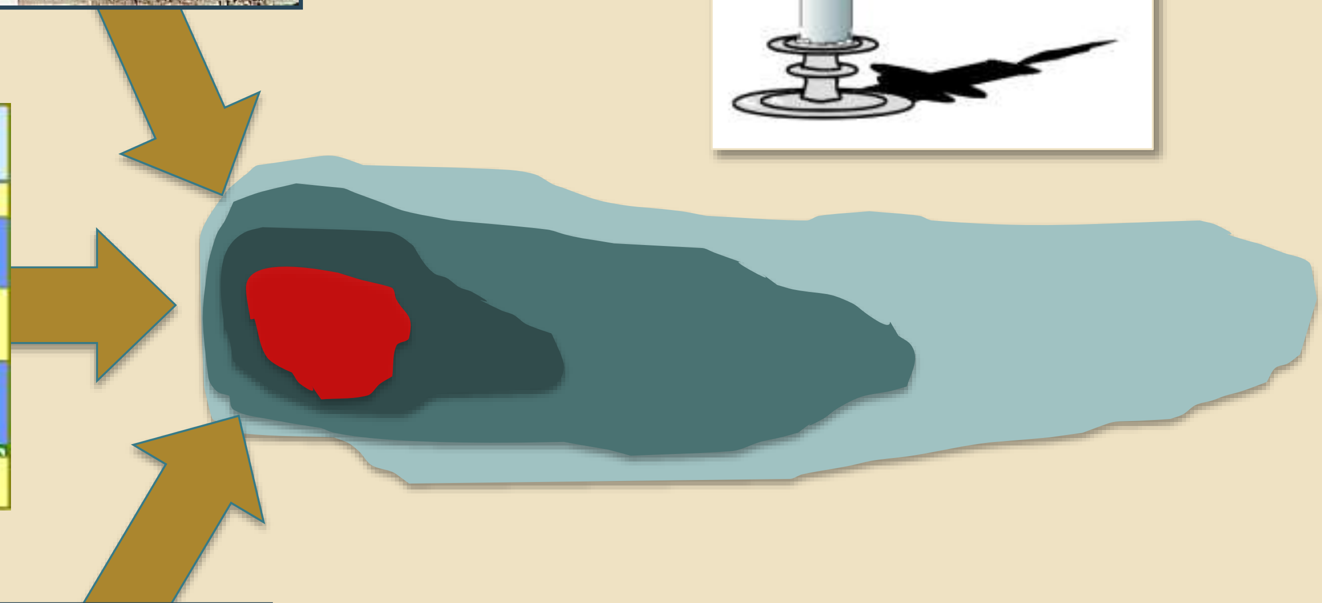
[b]Dotted lines enclose total volume of water that would be pumped to remove contaminant with retardation factor of 2.

DNAPL *PARADIGM*

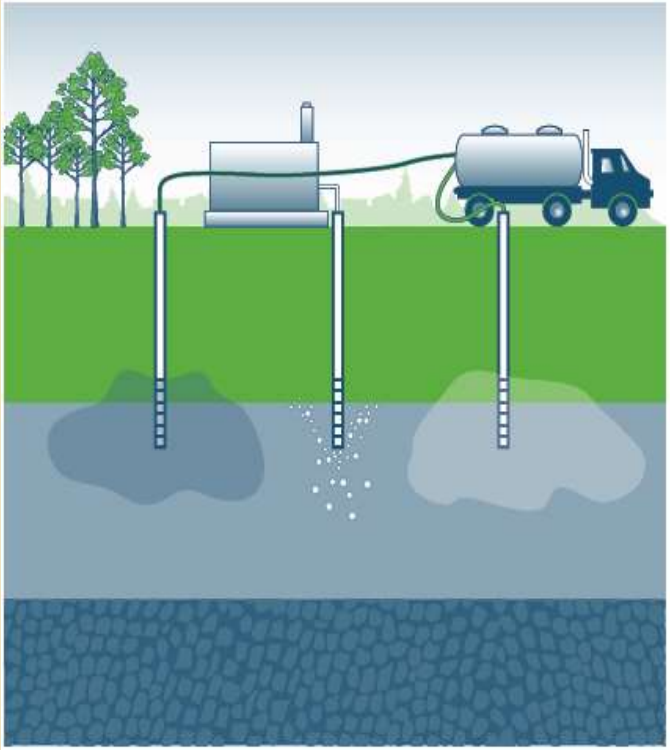




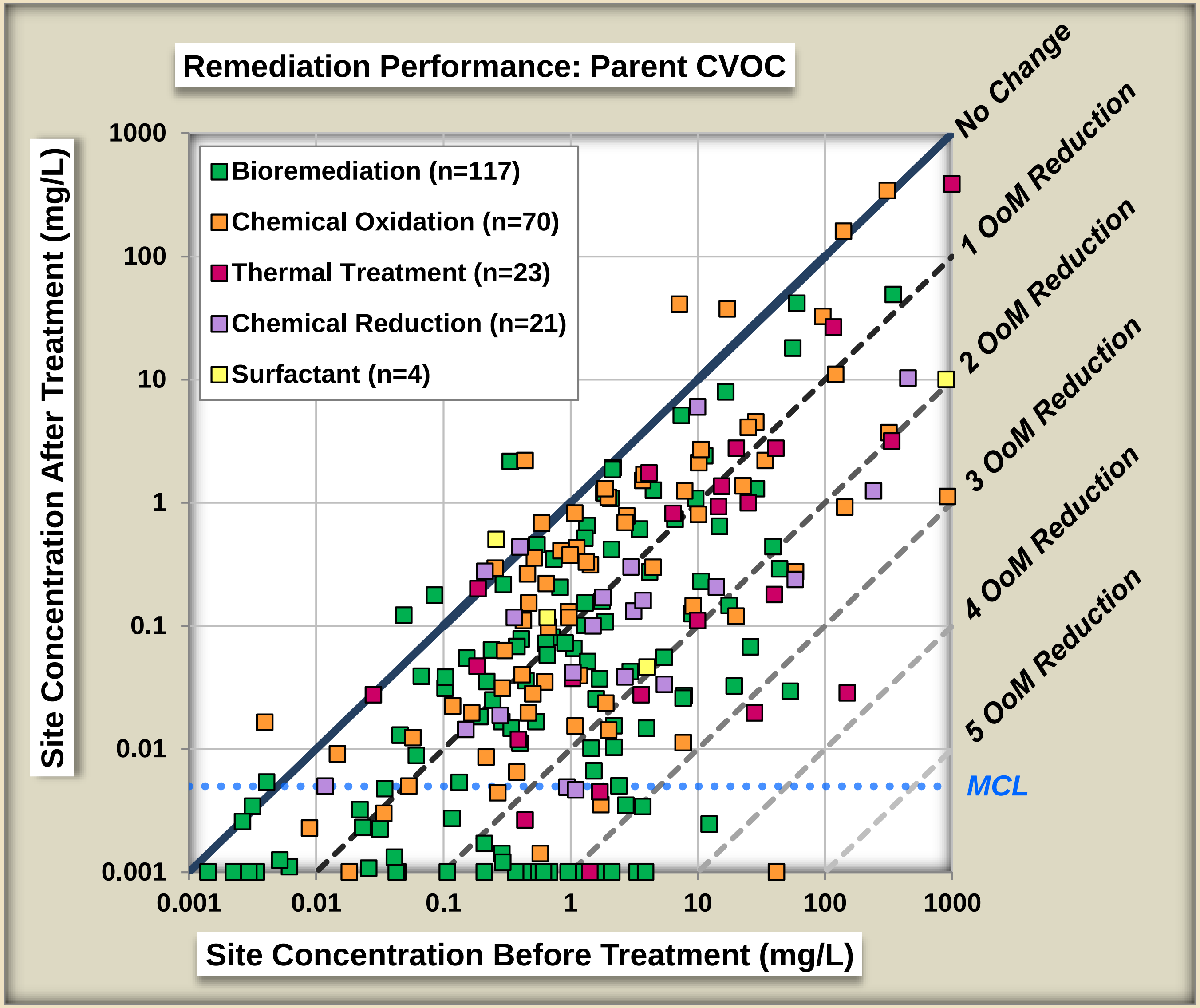




Era of In-Situ Innovation



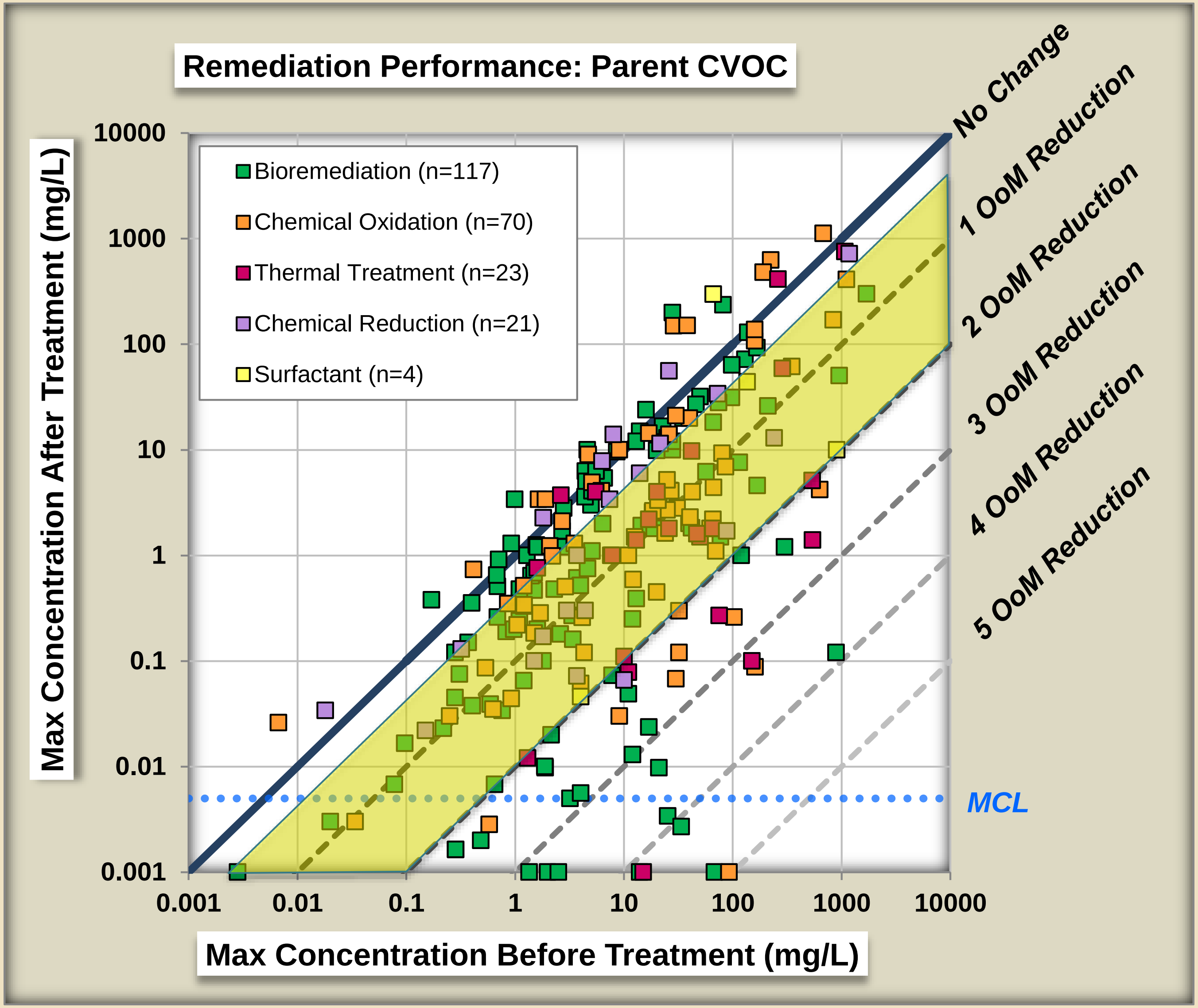
PERFORMANCE:
Geomean Concentration by Site



PERFORMANCE: *Rule of Thumb*

Max. Concs. (Regulatory Drivers)

Middle 50% of Sites Achieved ~ 0.4 to 2 OoM Reduction



A CARTOON HISTORY OF MICROBIOLOGY, COYNE 1996

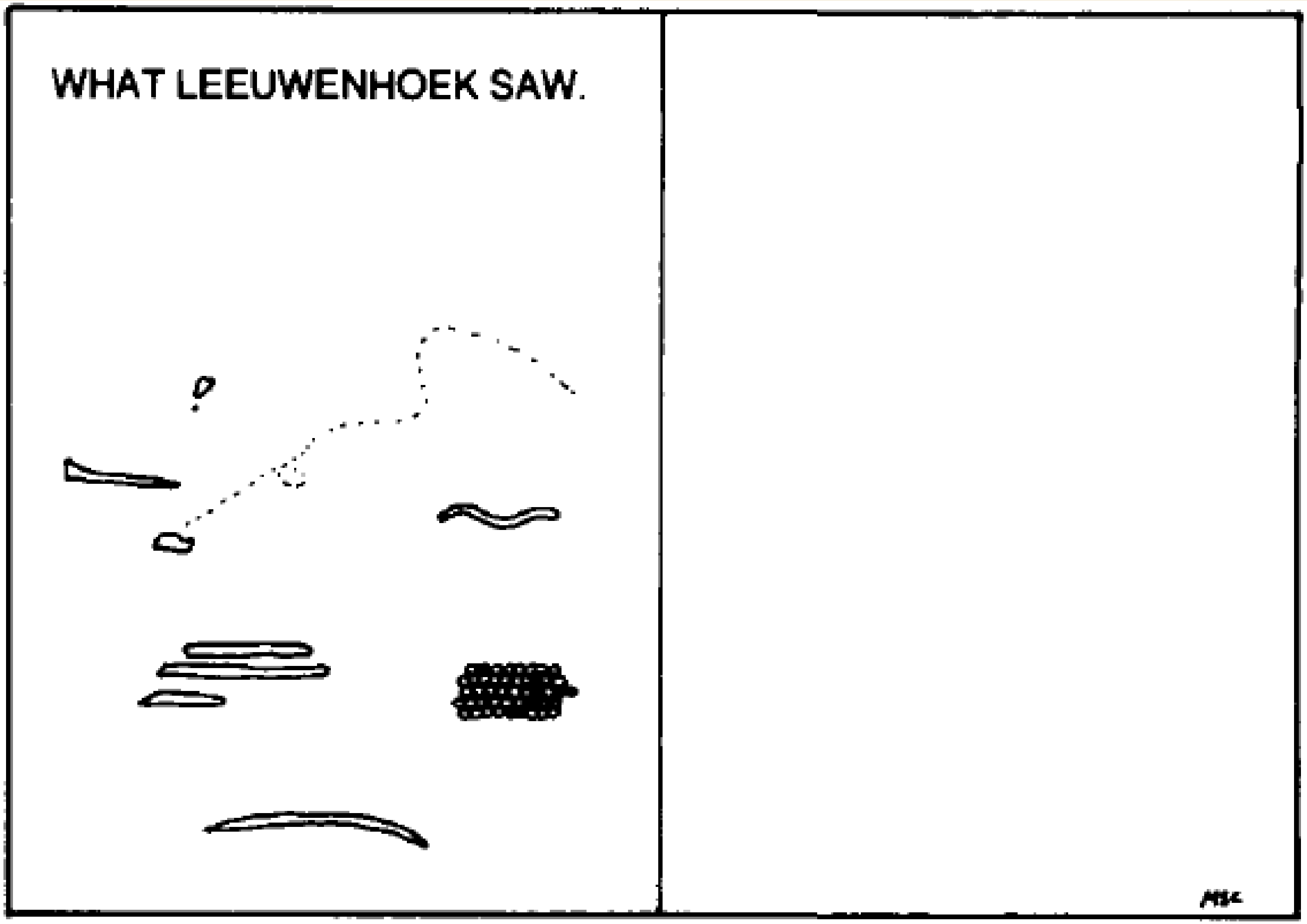


Fig. 3. Leeuwenhoek discovers microbes.

A CARTOON HISTORY OF MICROBIOLOGY, COYNE 1996

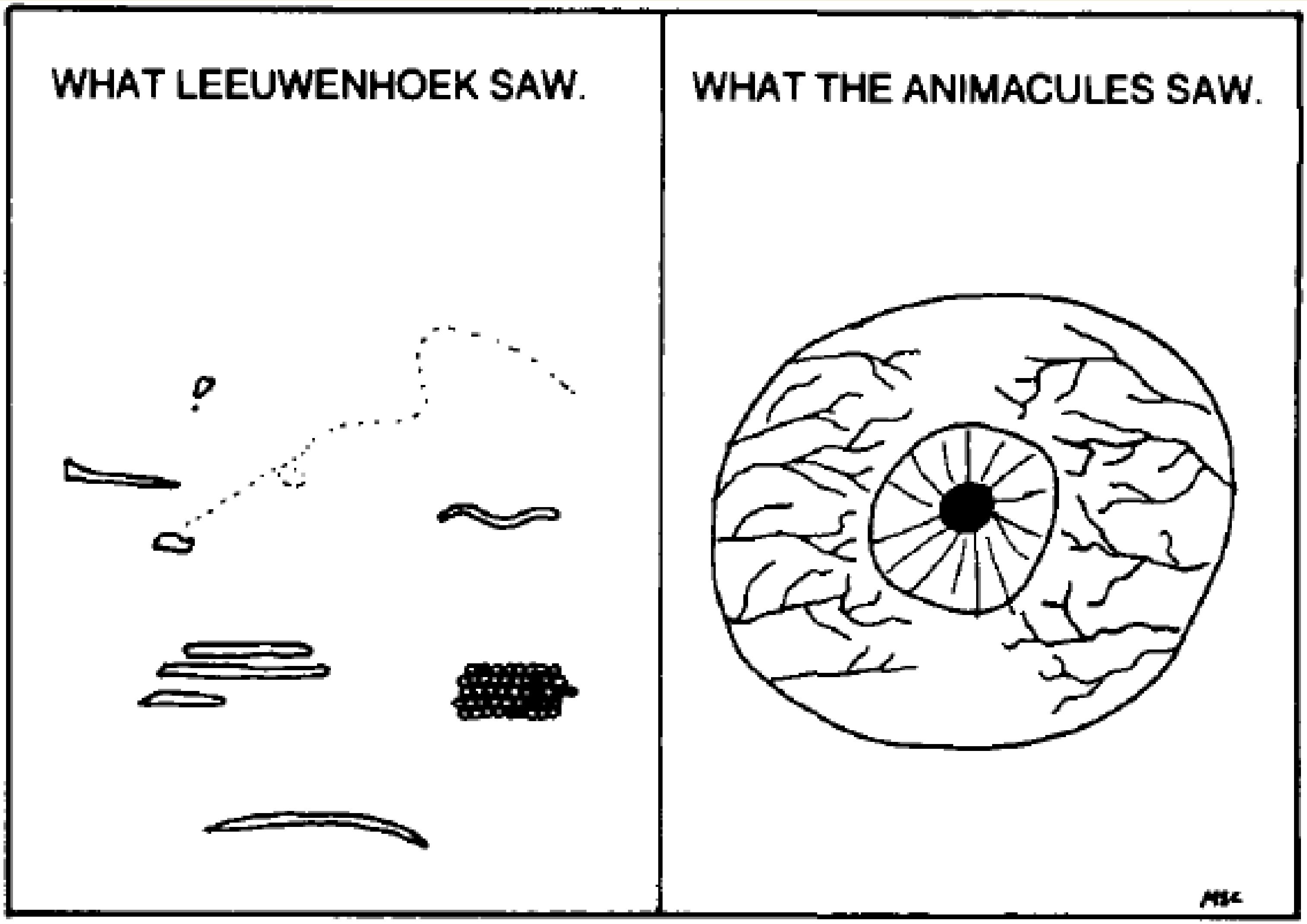


Fig. 3. Leeuwenhoek discovers microbes.

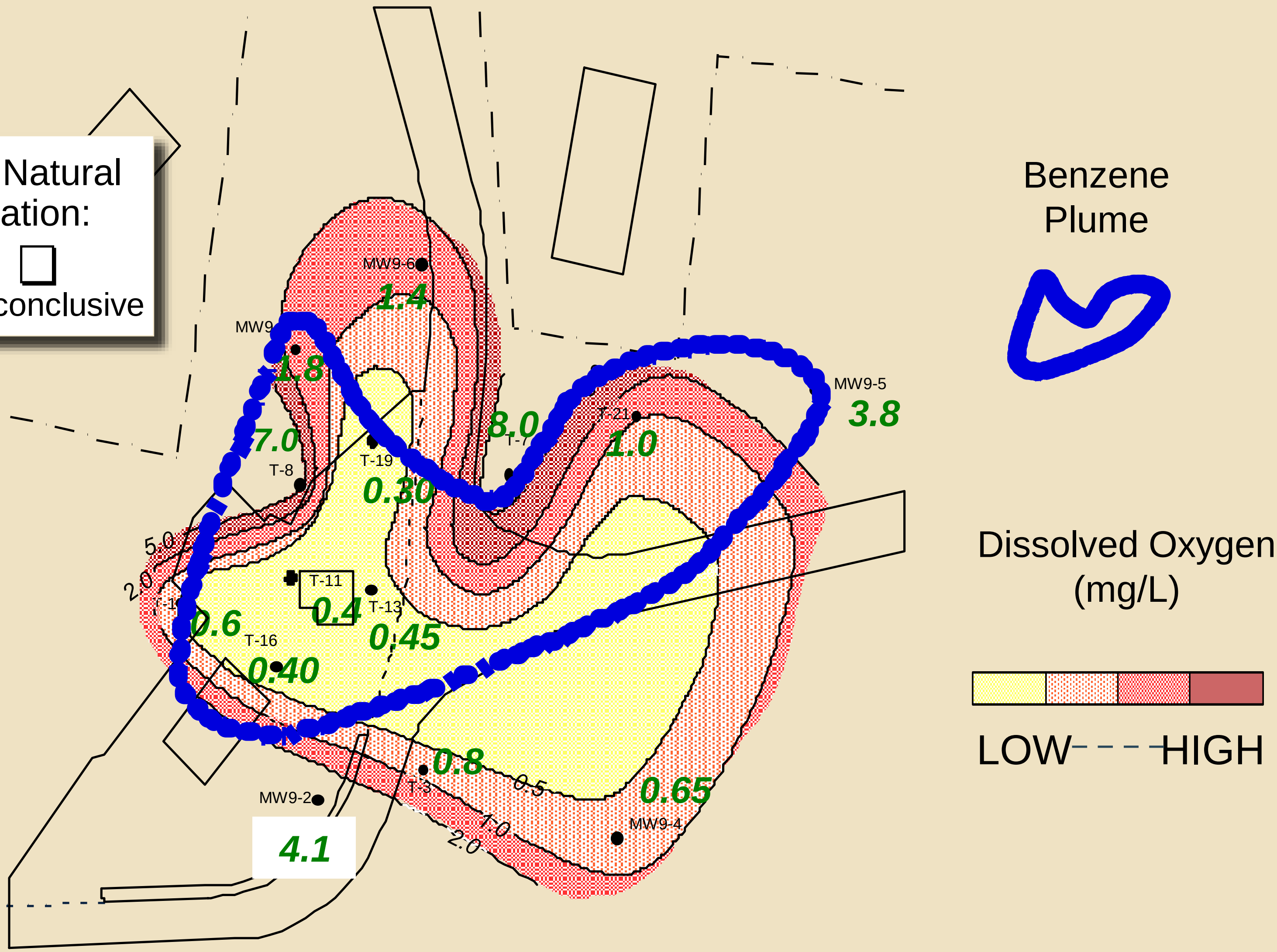
KESSLER AIR FORCE BASE

SWMU 66

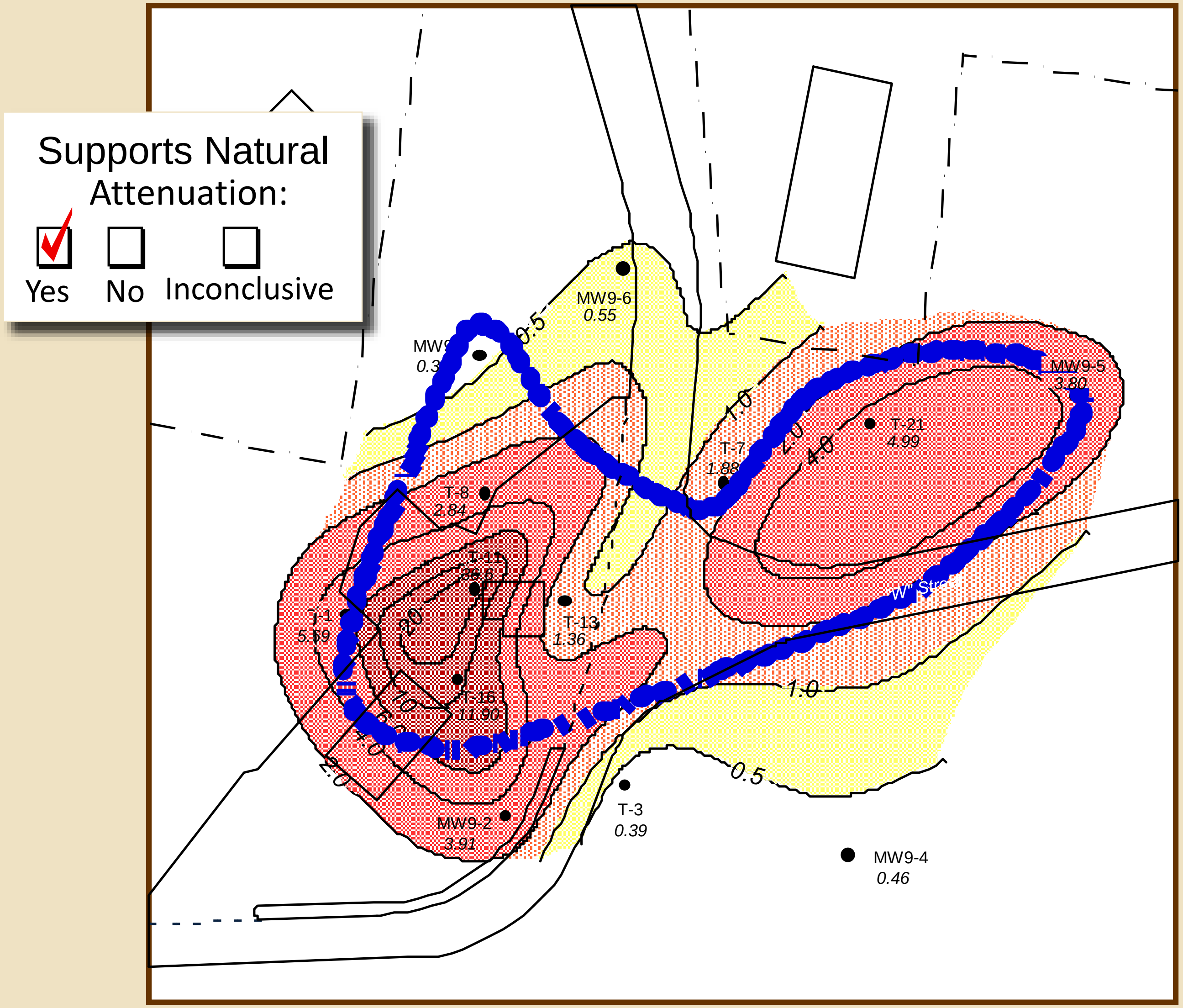
DISSOLVED OXYGEN IN GROUNDWATER

Supports Natural Attenuation:

☑ Yes ☐ No ☐ Inconclusive



FERROUS IRON IN GROUNDWATER



Benzene Plume

Ferrous Iron (mg/L)

LOW ---- HIGH

SULFATE IN GROUNDWATER

Supports Natural Attenuation:

☑ Yes ☐ No ☐ Inconclusive

Benzene Plume

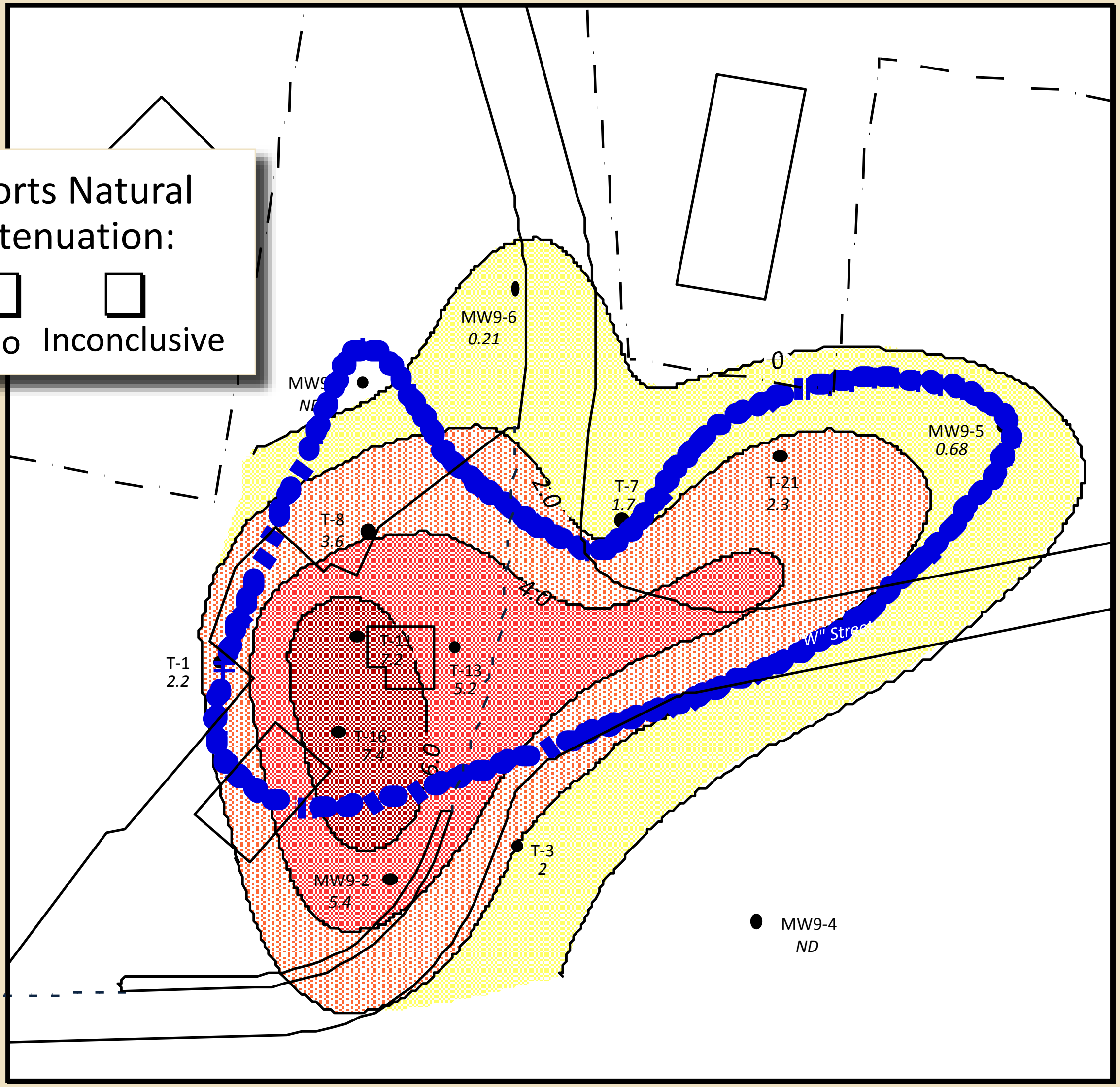
Sulfate (mg/L)

LOW - - - - HIGH

METHANE IN GROUNDWATER

Supports Natural Attenuation:

- [x] Yes
- [ ] No
- [ ] Inconclusive



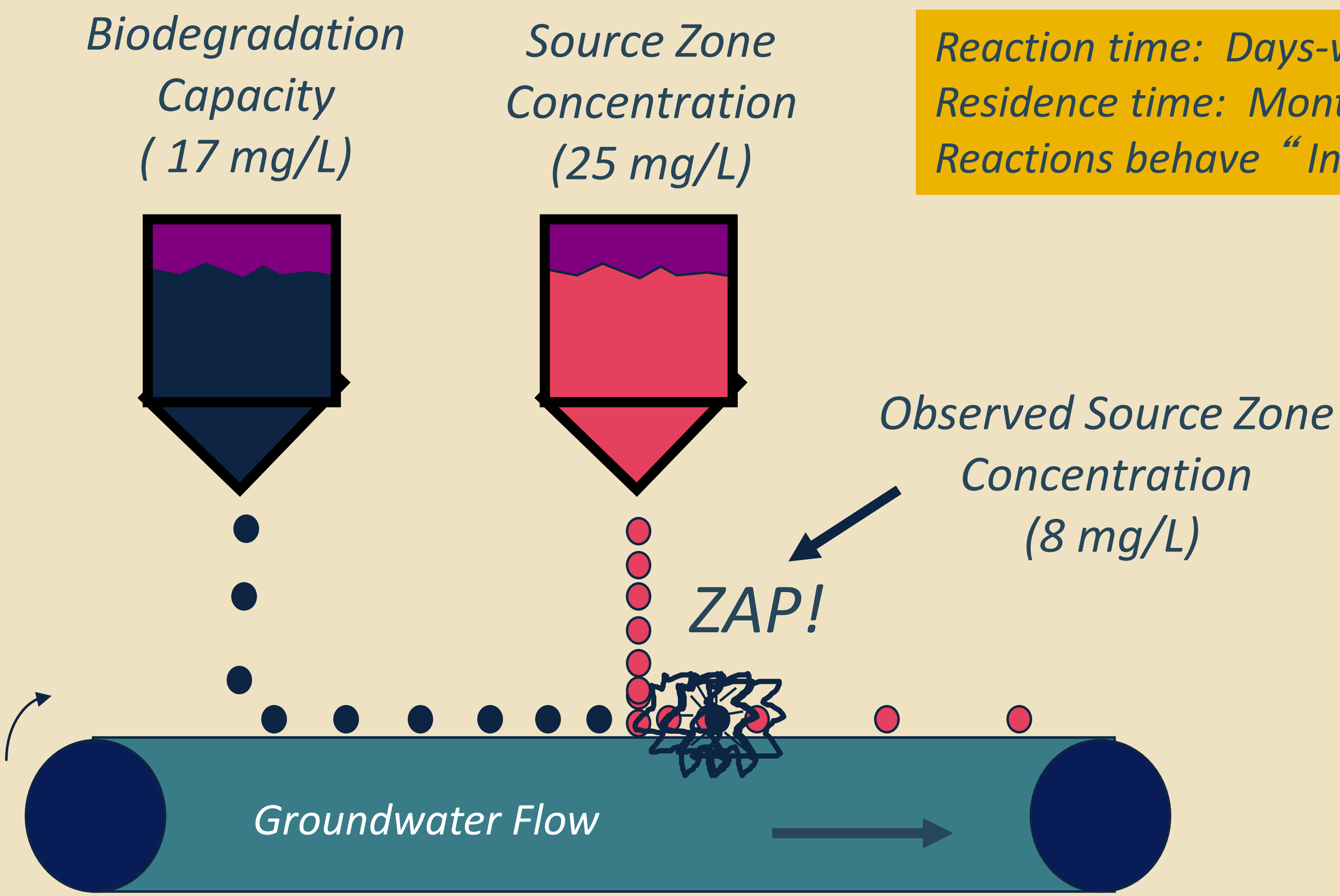
Benzene Plume

Methane (mg/L)

LOW - - - - HIGH

EVALUTING MNA IN PLUMES:
Electron Acceptor Limited Degradation

Reaction time: Days-weeks
Residence time: Months/years
Reactions behave "Instantaneous"



MNA Protocol for Dissolved Contaminant from Fuels

Draft: 1994

Final: 1999

Revision 0
03/08/99

TECHNICAL PROTOCOL FOR IMPLEMENTING INTRINSIC REMEDIATION WITH LONG-TERM MONITORING FOR NATURAL ATTENUATION OF FUEL CONTAMINATION DISSOLVED IN GROUNDWATER

VOLUME I

by

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National Risk Management Research Laboratory
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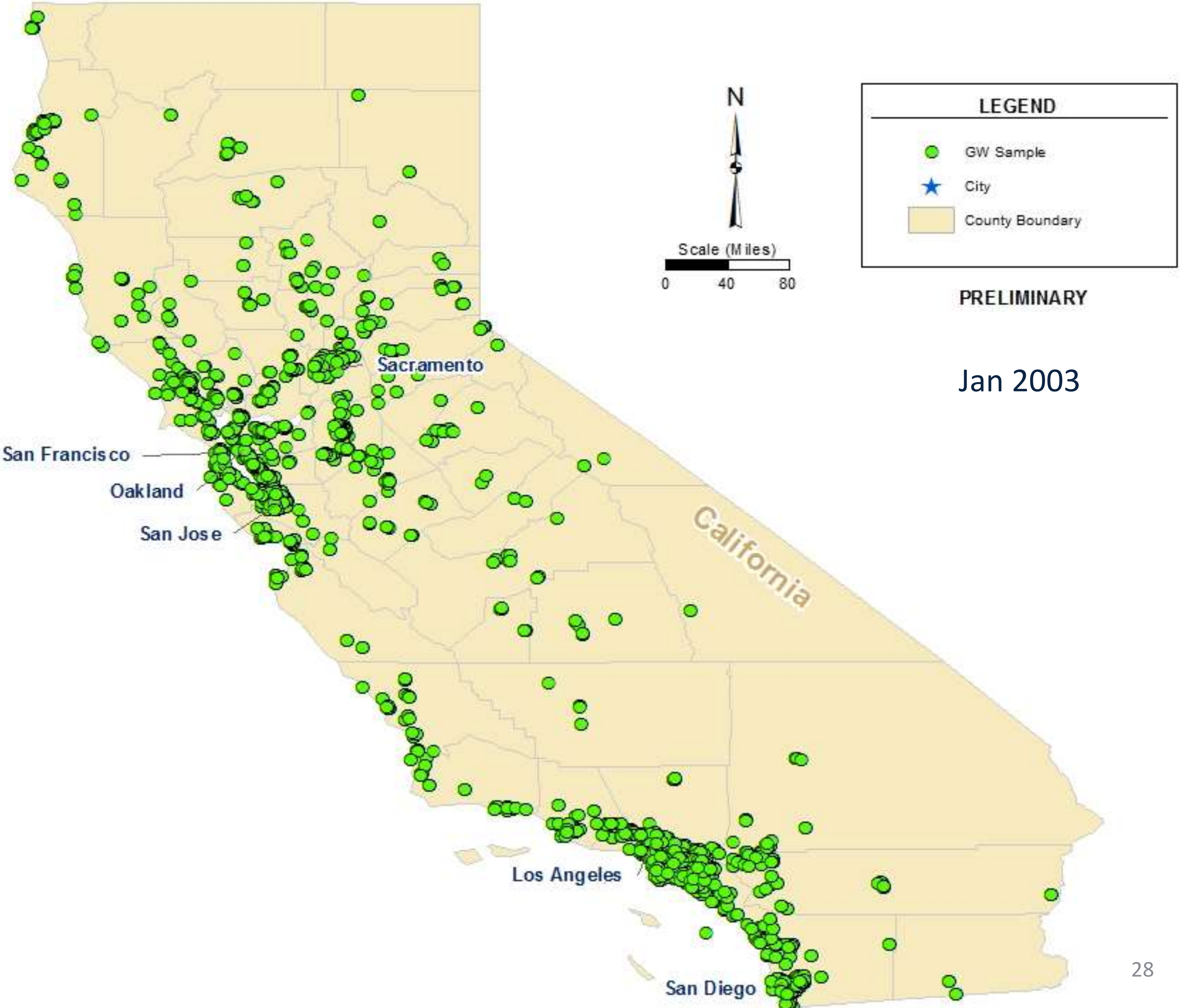
Technology Transfer Division
Brooks Air Force Base, Texas

for

Air Force Center for Environmental Excellence
Technology Transfer Division
Brooks Air Force Base
San Antonio, Texas

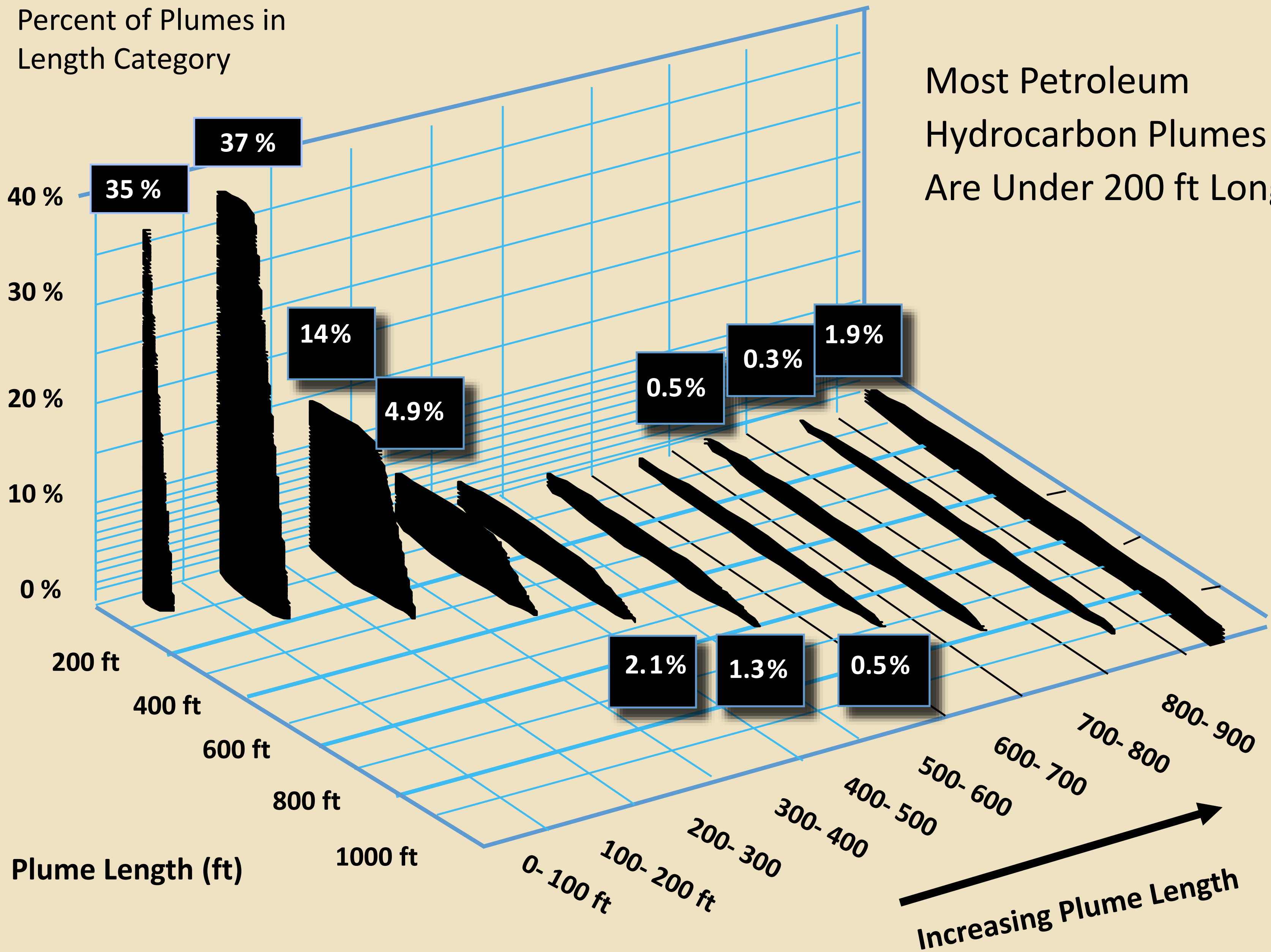
*This United States Air Force guidance was developed in cooperation with United States Environmental Protection Agency (USEPA) researchers but was not issued by the USEPA and does not represent USEPA guidance.


LEGEND
GW Sample
City
County Boundary
PRELIMINARY
N
Scale (Miles)
0
40
80
Sacramento
San Francisco
Oakland
San Jose
California
Los Angeles
San Diego

Jan 2003

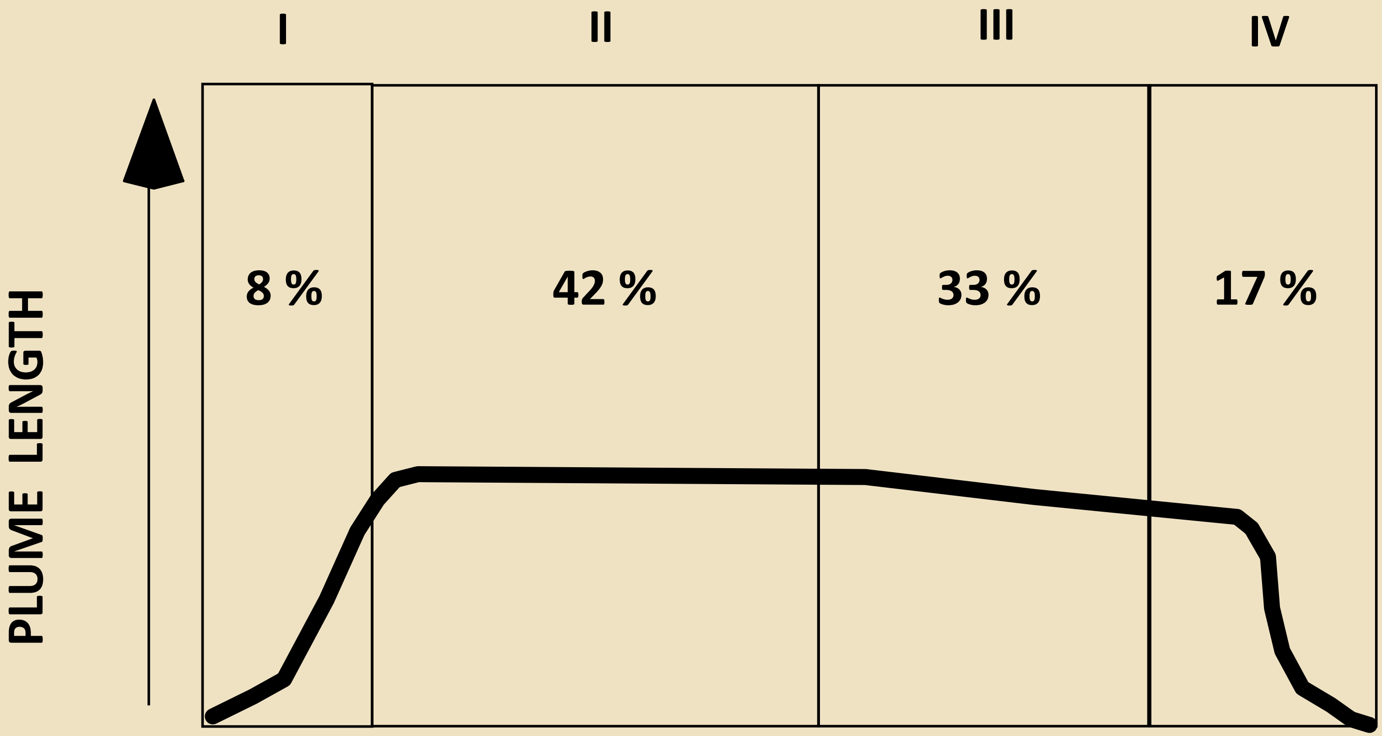
Length of Dissolved BTEX Plumes

Most Petroleum Hydrocarbon Plumes Are Under 200 ft Long

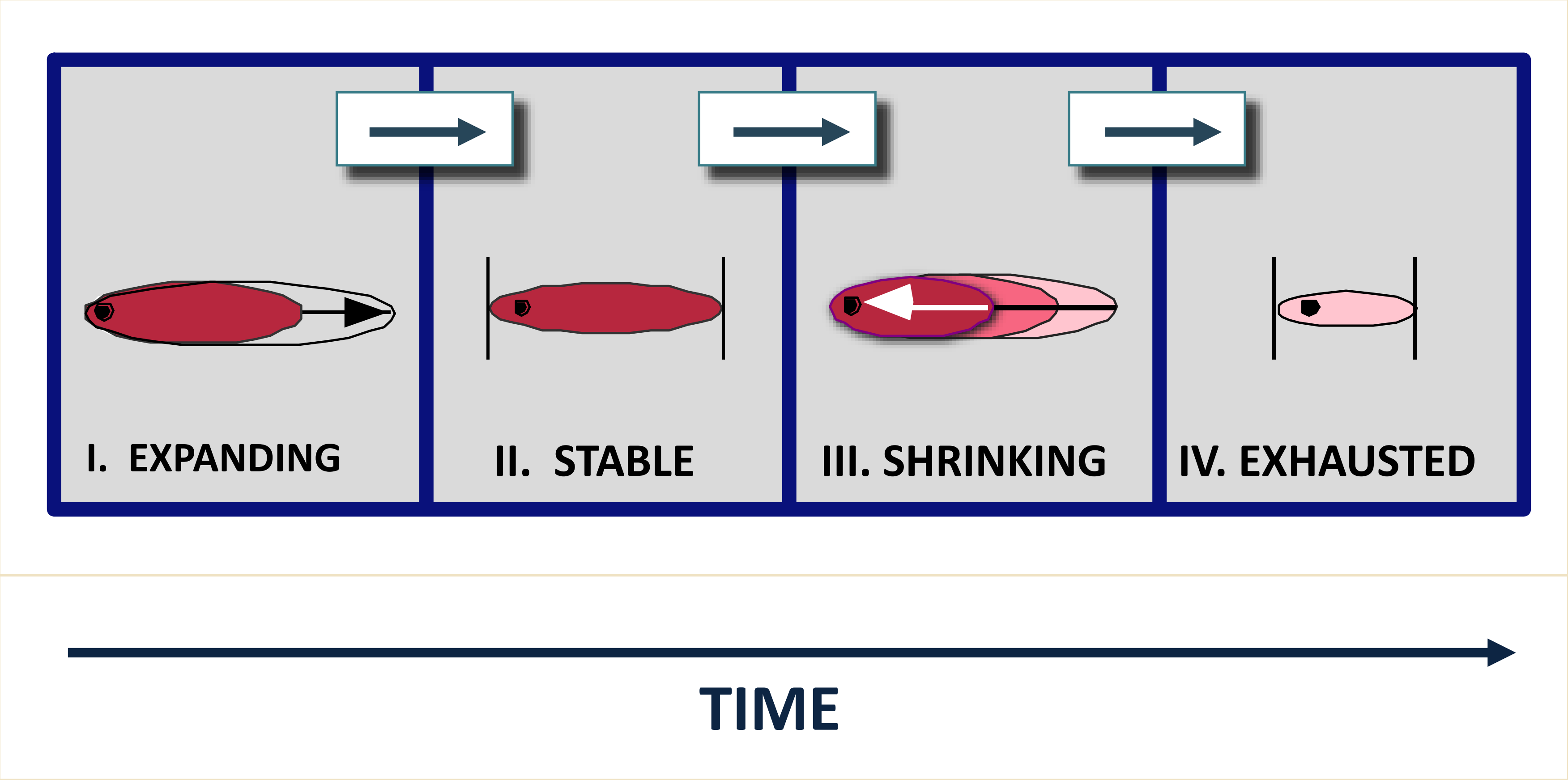


Percent of Plumes in California That Are:

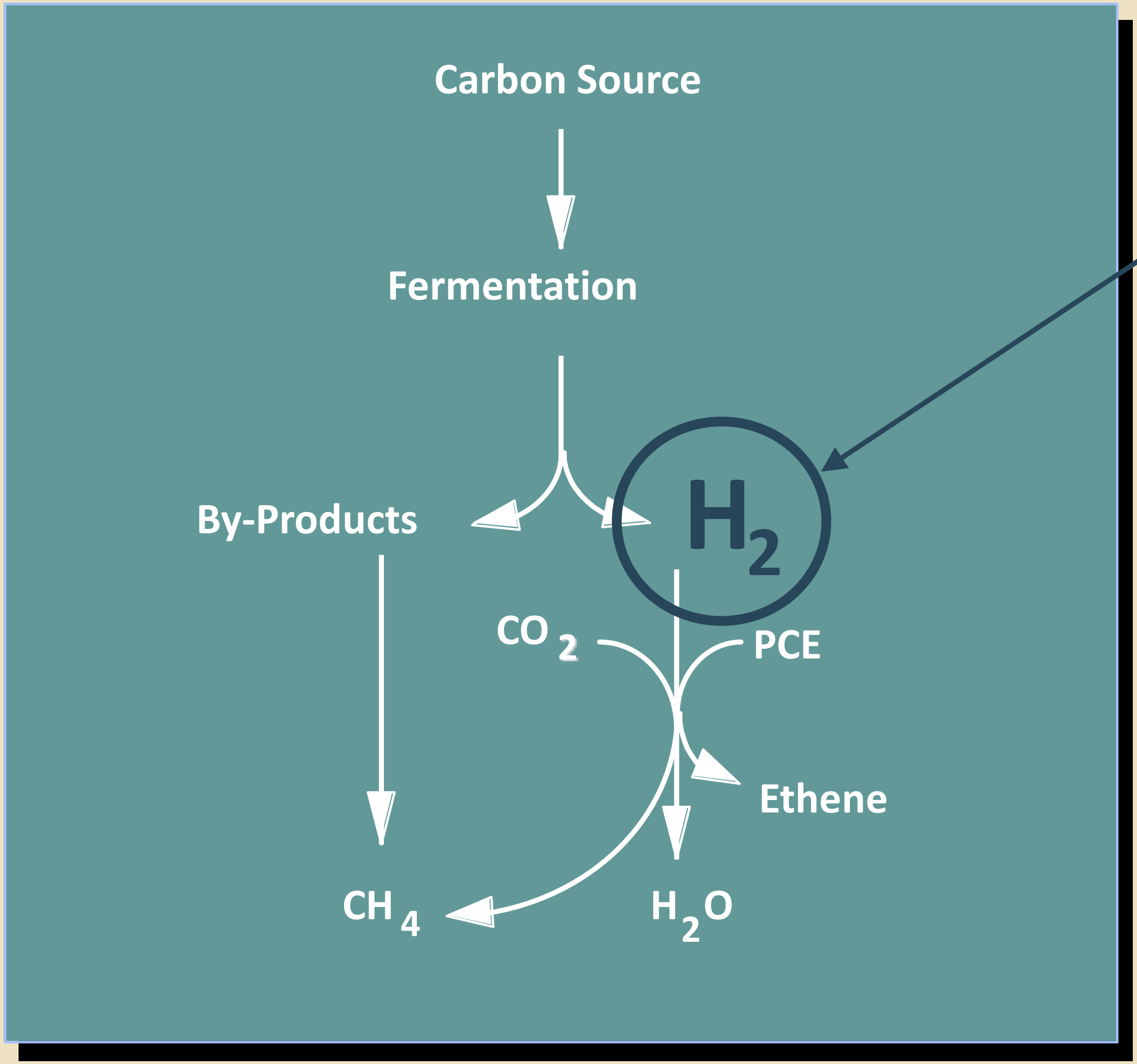
Expanding (I)	Stable (II)	Shrinking (III)	Exhausted (IV)



SCHEMATIC OF PLUME LIFECYCLE



CHLORINATED SOLVENT REDUCTIVE DECHLORINATION

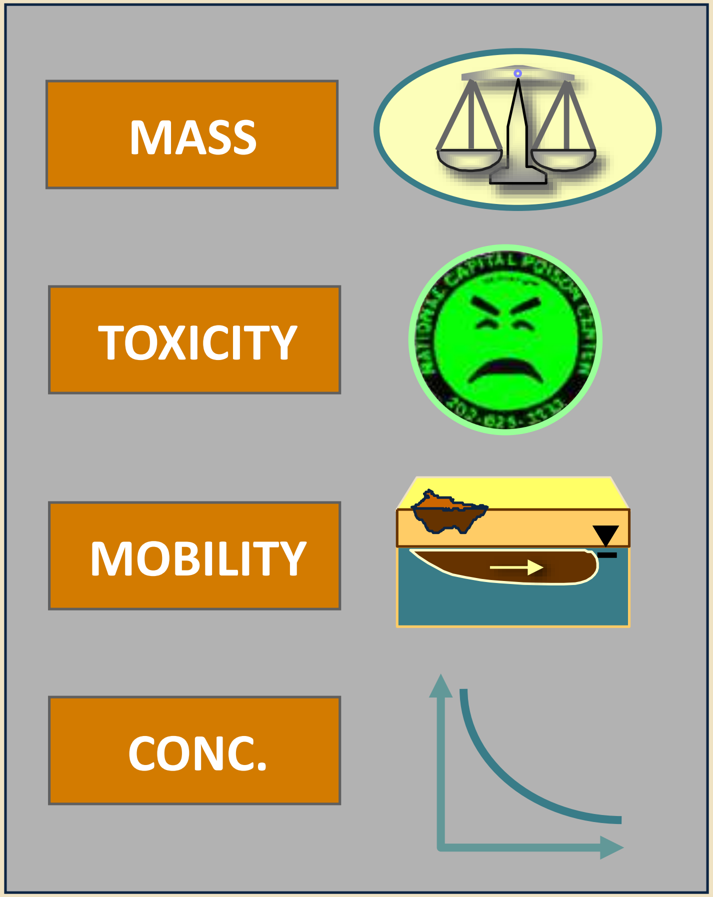


Dissolved Hydrogen Is Key Electron Donor For Reductive Dechlorination of Chlorinated Solvents

WHAT ARE NATURAL ATTENUATION PROCESSES?

US Environmental Protection Agency MNA Directive (1999)

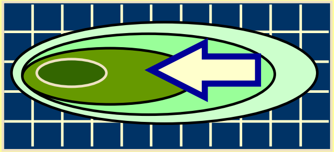
"A variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, or concentration of contaminants in soil and groundwater."



WHAT ARE NATURAL ATTENUATION PROCESSES?

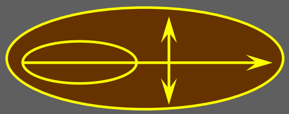
Reduction in contaminant mass or concentration in groundwater over time or distance due to natural processes:

Natural Shrinking of GW Plume Over Time



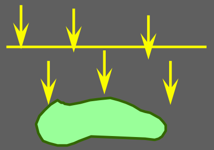
NON-DESTRUCTIVE PROCESSES

Dispersion



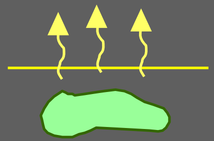
Sorption

$k_d = (K_{oc})*(foc)$



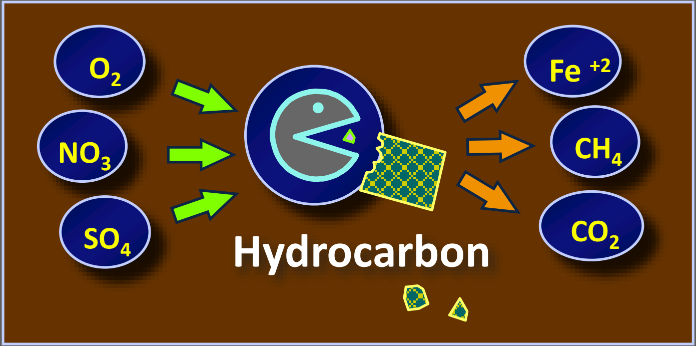
Dilution

Volatilization



DESTRUCTIVE PROCESSES

Biodegradation



Abiotic Reactions (hydrolysis)

WHAT IS THE PHILOSOPHY BEHIND MNA?

Nature can help!

It is harder and more expensive to clean these sites up than first thought.

Nature is amazing and seems to be degrading or sequestering some of these chemicals.

Let's let nature do the job.

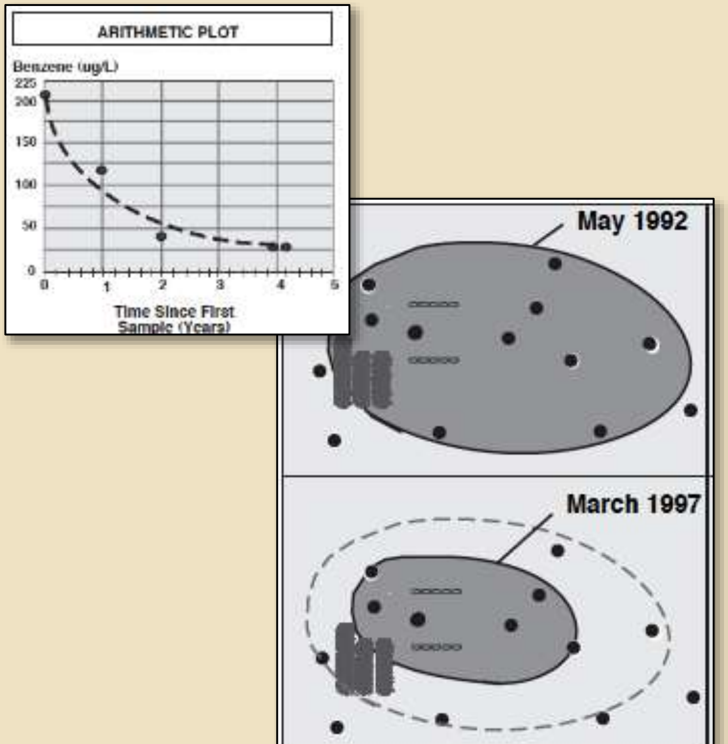
But you have to do three things:

Protect

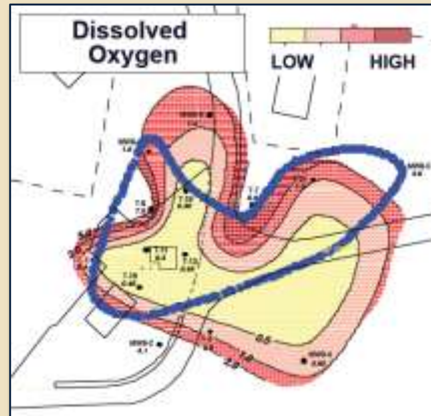
Understand

Watch

WHAT EVIDENCE IS NEEDED FOR MNA?
New Trends in LOEs



***LOE 1:* Historical contaminant mass reduction**

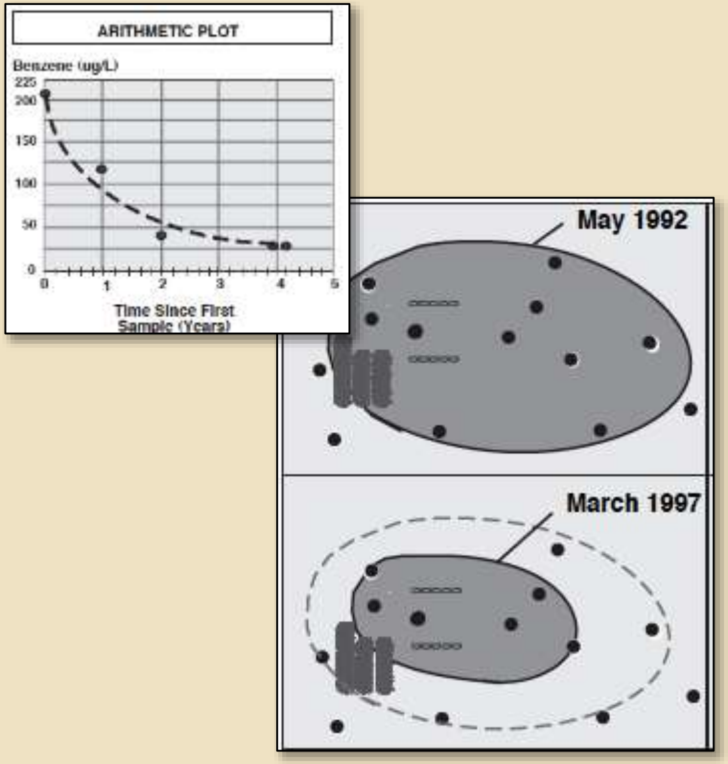


***LOE 2:* Hydrogeologic or geochemical data**

***LOE 3:* Microcosm or Field data**

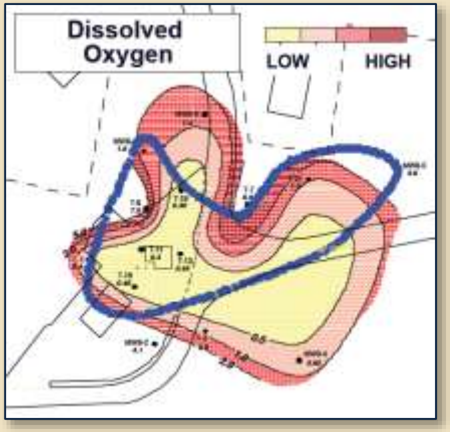
LOE: "Lines of Evidence"

WHAT EVIDENCE IS NEEDED FOR MNA?
New Trends in LOEs



LOE 1: Historical contaminant mass reduction

"I Shrink Therefore I Am"



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WHAT EVIDENCE IS NEEDED FOR MNA?

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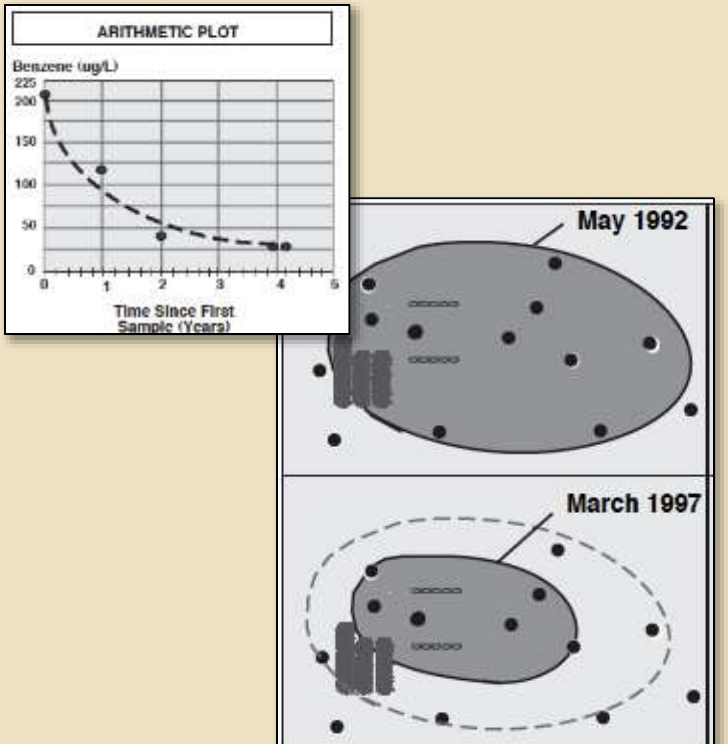

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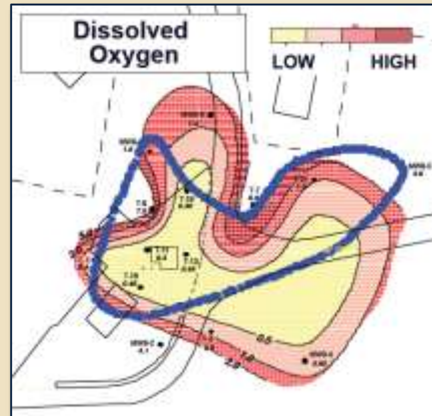

LOE 2: Hydrogeologic or geochemical data

"Am I Swampy"

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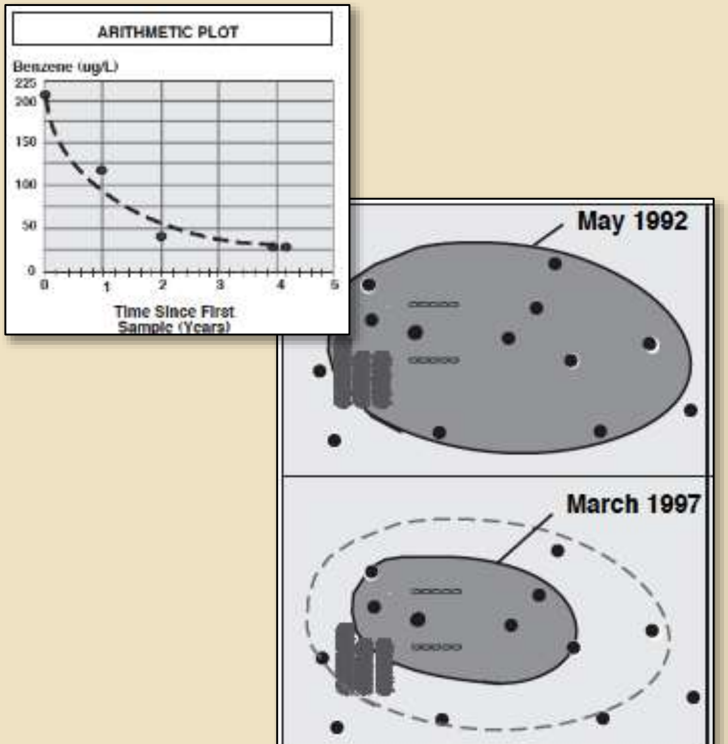
WHAT EVIDENCE IS NEEDED FOR MNA?

New Trends in LOEs



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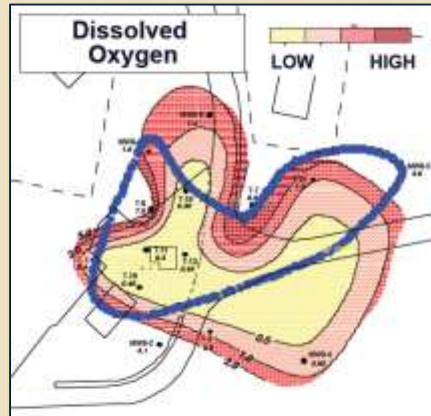


***LOE 2:* Hydrogeologic or geochemical data**

"Am I Swampy"

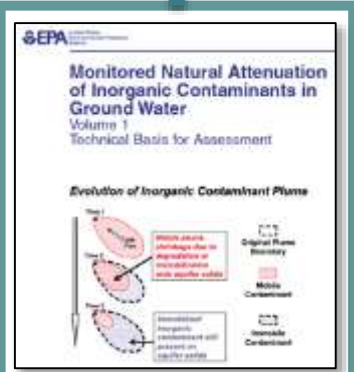
***LOE 3:* Microcosm or Field data**

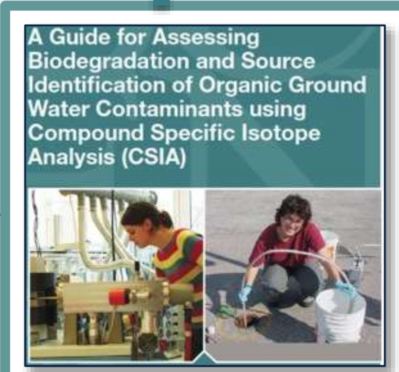
"Put on the Lab Coat"

LOE: "Lines of Evidence"

WHAT ARE THE MOST IMPORTANT NEW MNA DEVELOPMENTS?

Year	*New Contaminant*	*New Measurement*	*New Process*	*New Tools*
2000-2005	MTBE-TBA	Two types of rates	Source attenuation of hydrocarbon sites	BIOChlor MAROS NAS SourceDK
2005-2010	Metals-Rads	Compound-Specific Isotopes Molecular Biological Tools	Biogeochemical/abiotic trans. of chlor. solvents Matrix diffusion Oxidation of chlor. solvents at low DO	REMChlor Mass flux toolkit BIOBALANCE Scenarios for chlor. solvents MNA Sustainability

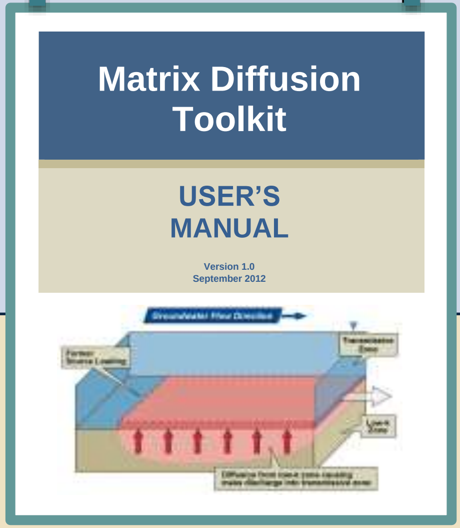




Probably the most important "recent" development?

WHAT ARE THE MOST IMPORTANT NEW MNA DEVELOPMENTS?

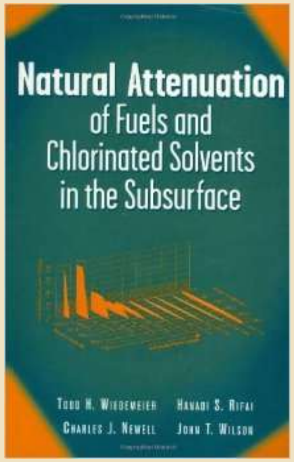
Year	*New Contaminant*	*New Measurement*	*New Process*	*New Tools*
2010-present	"Emerging Contaminants"	CO_2 traps for NSZD	Natural source zone depletion (NSZD) Source attenuation of chlorinated solvent sites Attenuation in low-k zones	PREMChlor Matrix Diffusion Toolkit Scenarios for metals/rads Source History Tool



See Also: ESTCP ER-201129

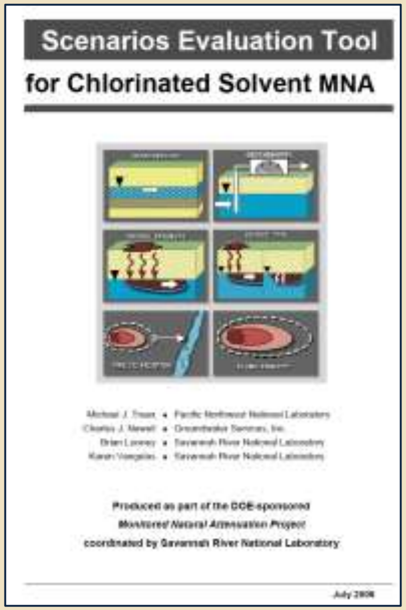
Development and Validation of a Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches (MNA, Biostimulation and/or Bioaugmentation) at Chlorinated Solvent Sites

SOME KEY REFERENCES



1999

www.gsi-net.com



2006

www.gsi-net.com

2011

Google:
ESTCP MNA FAQ

2014

ROAD MAP

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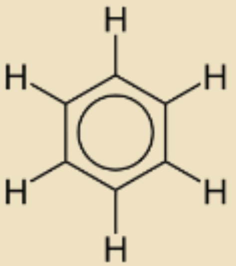
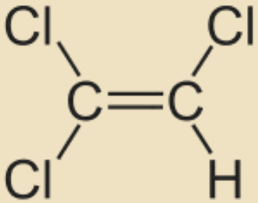
BIODEGRADATION PROCESSES

It's all about the electrons…

- **PETROLEUM HYDROCARBONS: typically serve as electron donors, so you may need more electron acceptor (but not always)**

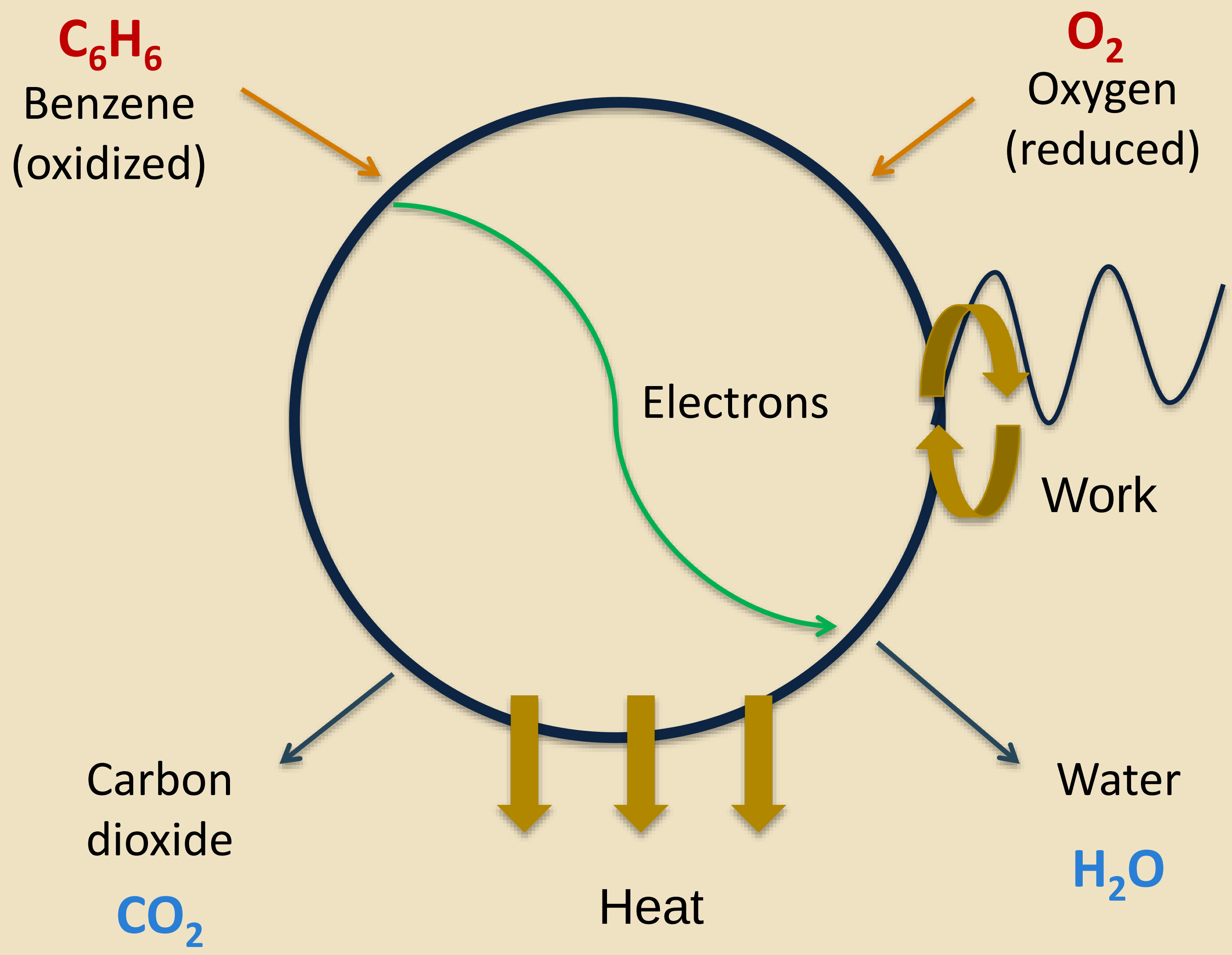


- **CHLORINATED SOLVENTS: typically serve as electron acceptors, so you may need electron donor**



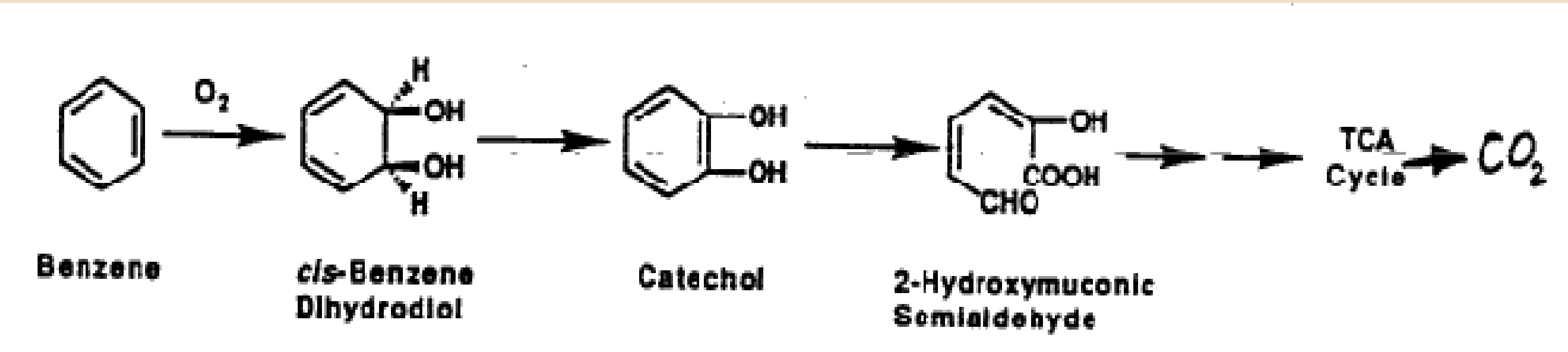
Important Concepts: biodegradation capacity and mass balances

BIODEGRADATION OF PETROLEUM HYDROCARBONS



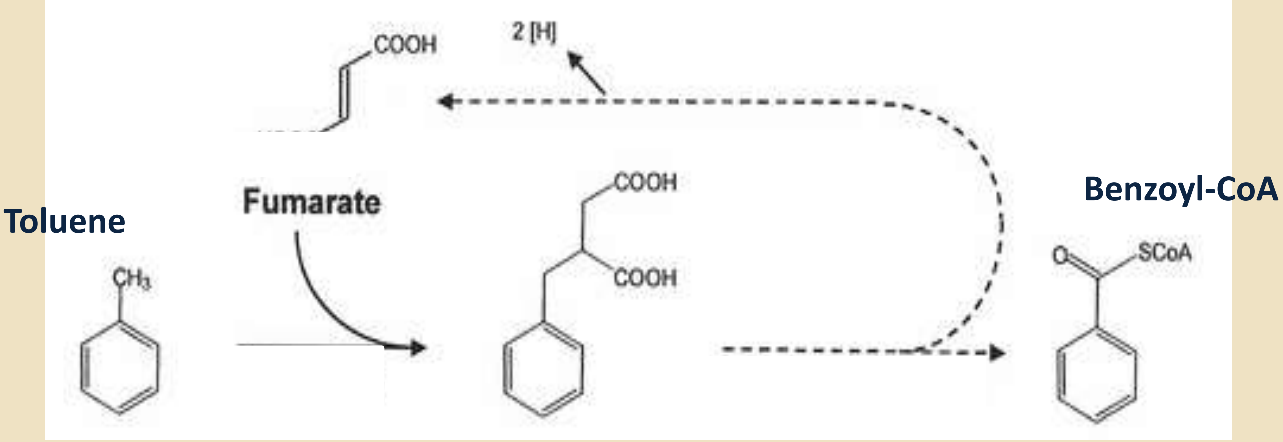
AEROBIC HYDROCARBON BIODEGRADATION

- **Highly thermodynamically feasible (it's a fuel…)**
- **Hydroxylation (i.e., addition of OH) is often the first step**
  - Increases solubility (more susceptible to metabolism)
  - Needs oxygenases (i.e., enzymes that "activate" O_2 and add it to the hydrocarbon molecule.)
  - Needs O_2 whose diffusion may be rate-limiting
- **Aromatic ring must be di-hydroxylated before fission**



ANAEROBIC HYDROCARBON BIODEGRADATION

- **Important natural attenuation mechanism, but tends to occur at slower rates (weaker electron acceptors, NO_3^-, Fe^{+3}, SO_4^{-2}, and CO_2)**
- **Benzene, the most toxic of the BTEX, is relatively recalcitrant under anaerobic conditions (degrades very slowly – after TEX, or not at all)**
- **Benzoyl-CoA is a common intermediate, and it is reduced prior to ring fission by hydrolysis (CO_2 is still the endproduct).**



HYDROCARBON BIODEGRADATION:

Thermodynamic perspective

Electron Acceptor	Type of Reaction	Metabolic By-Product	Redox Potential (pH =7 in volts)	Reaction Preference
Oxygen	Aerobic	CO_2	+ 820	Most Preferred
Nitrate	Anaerobic	N_2, CO_2	+ 740	↓
Ferric Iron (solid)	Anaerobic	Ferrous Iron (dissolved)	- 50	↓
Sulfate	Anaerobic	H_2S	- 220	↓
Carbon Dioxide	Anaerobic	Methane	- 240	Least Preferred

HYDROCARBON BIODEGRADATION: *Use stoichiometry to estimate biodegradation capacity*

Electron Acceptor or By-Product	Utilization Factor * (Mass E. Acceptor / By-Prod. Consumed per Mass Dissolved Hydrocarbon Degraded)
Oxygen	3.14 gm/gm
Nitrate	4.9 gm/gm
Ferrous Iron	21.8 gm/gm
Sulfate	4.6 gm/gm
Methane	0.78 gm/gm

* Based on BTEX

HYDROCARBON BIODEGRADATION: *Use stoichiometry to estimate biodegradation capacity*

EXAMPLE OF HOW TO CALCULATE UTILIZATION FACTOR:

$$C_6H_6 + 7.5\ O_2 \rightarrow 6\ CO_2 + 3\ H_2O$$

Benzene MW = 78 g/mol

Oxygen MW = 32 g/mol

$$\textbf{Mass Ratio} = \frac{\text{Oxygen Mass}}{\text{Benzene Mass}}$$

or "Utilization Factor"

$$= \frac{32\ g\ /\ mol\ \times 7.5\ mol}{78\ g\ /\ mol \times 1\ mol} = \mathbf{3.08}$$

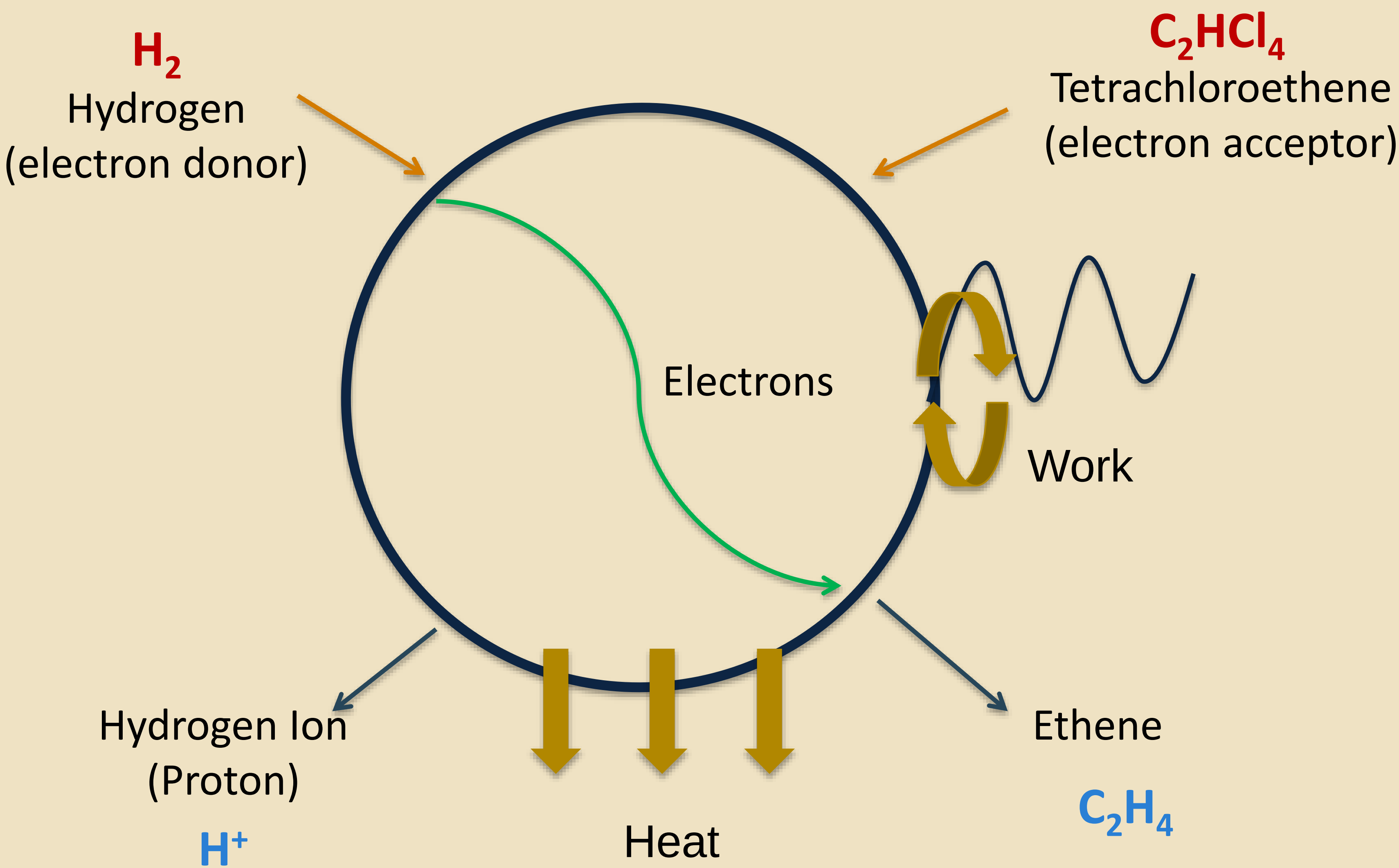
HYDROCARBON BIODEGRADATION:

Biodegradation capacity example

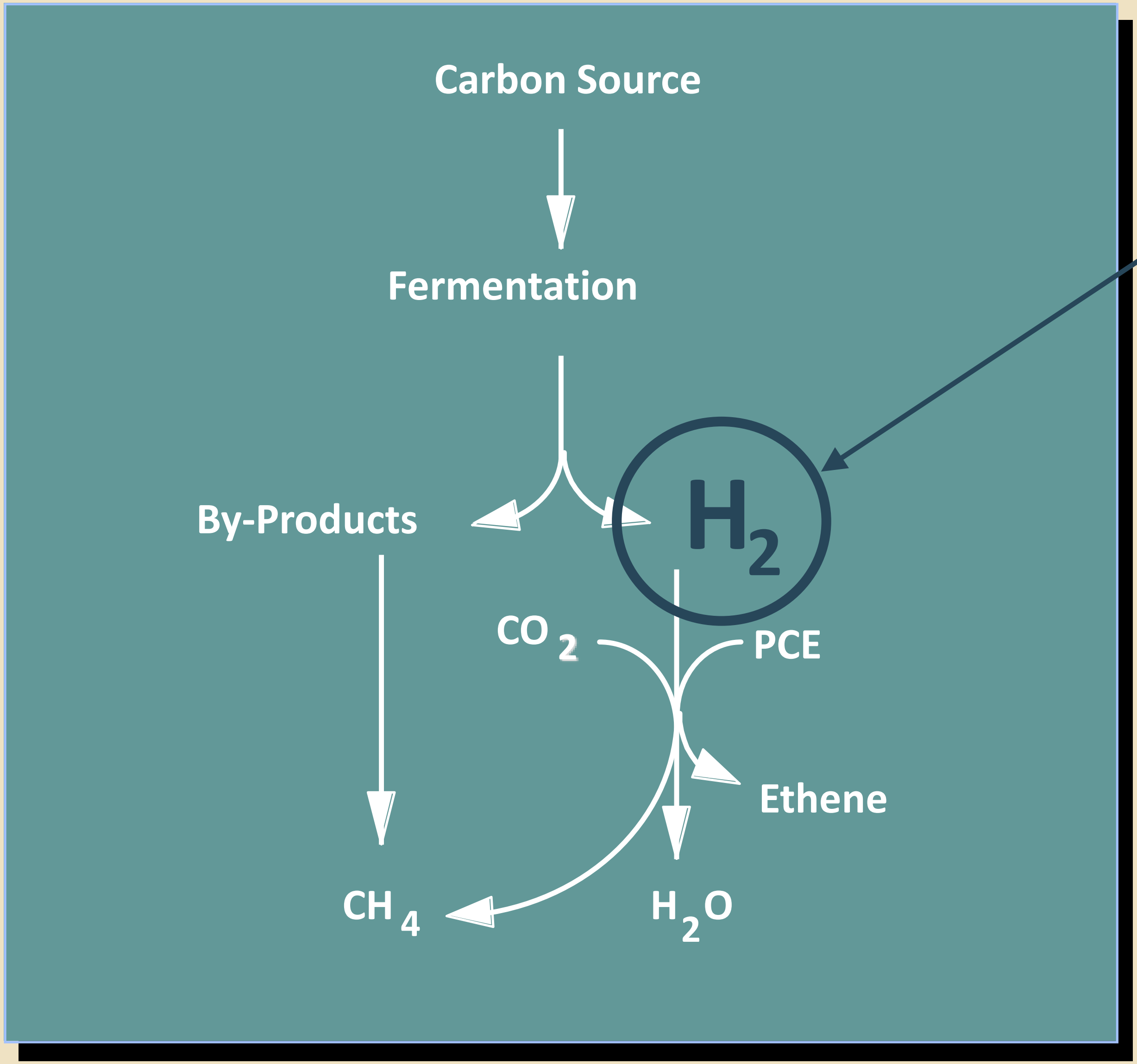
CONCENTRATIONS (mg/L)	D.O.	NO_3	Iron	SO_4	CH_4
Background	2	0.7	0.5	26.2	0
Source	0.4	0	36.6	3.8	7.4
Utilization Factor	*3.14*	*4.9*	*21.8*	*4.6*	*0.78*
BIODEG. CAPAC.	0.5	0.1	1.7	4.9	9.5

Sum to get "Expressed" Biodegradation Capacity = 16.7 mg/L BTEX

BIODEGRADATION OF CHLORINATED SOLVENTS (ANAEROBIC REDUCTIVE DECHLORINATION)



CHLORINATED SOLVENT REDUCTIVE DECHLORINATION: *Electron Donors Are Key*



Dissolved Hydrogen Is Key Electron Donor

Process requires multiple microbial groups and anaerobic conditions

REDUCTIVE DECHLORINATION:
Thermodynamic perspective

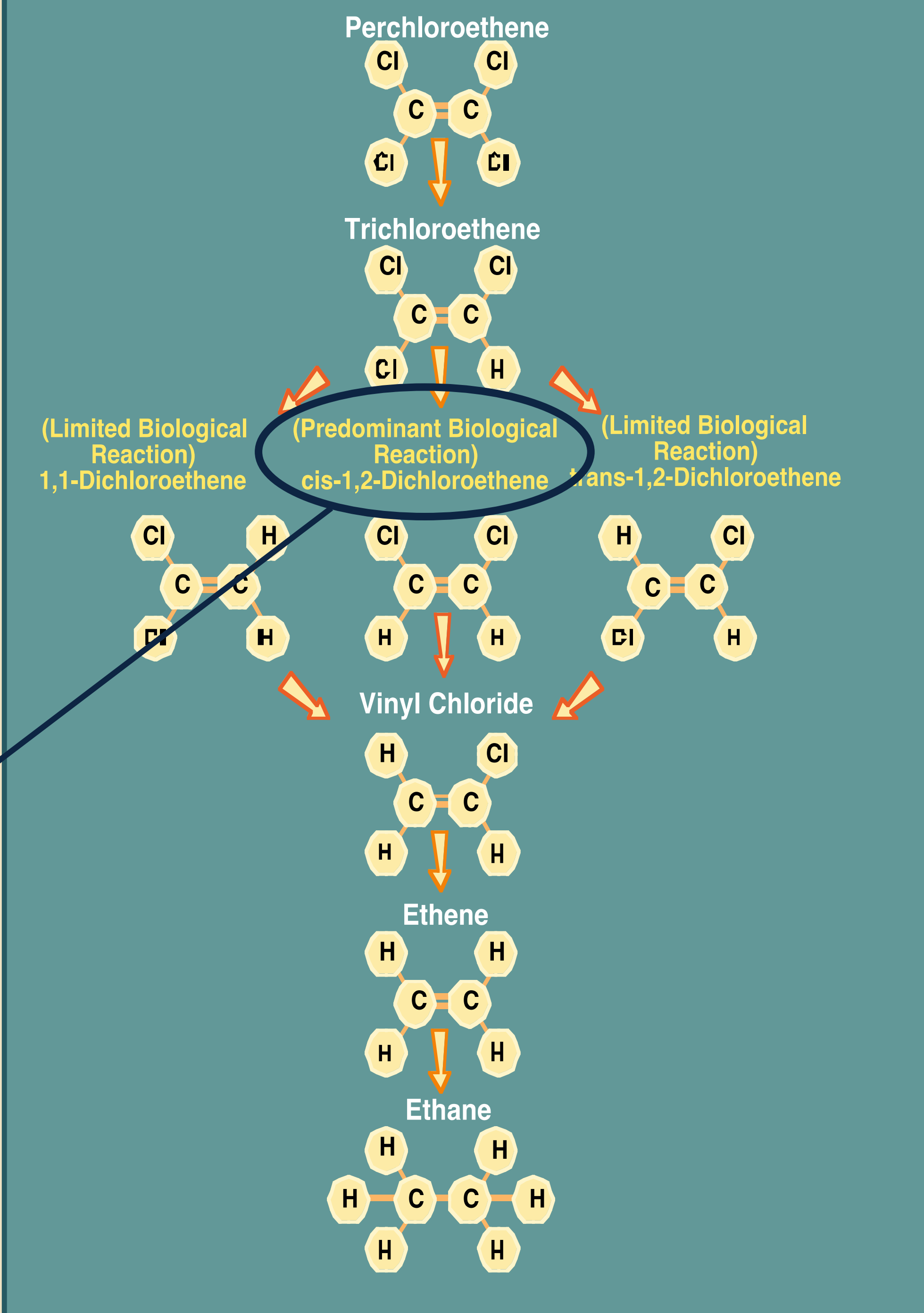
Competing Electron *Acceptors*

Dissolved Oxygen →	H_2O
Nitrate →	N_2
Ferric Iron →	Ferrous Iron
Chlorinated Solvent →	Daughter Product
Sulfate →	H_2S
Methanogens →	Methane

Thermodynamics means that <u>strongly reducing conditions</u> are required

- **High energy reactions are favored**
- **Hydrogen will be used first by aerobes and denitrifying bacteria**

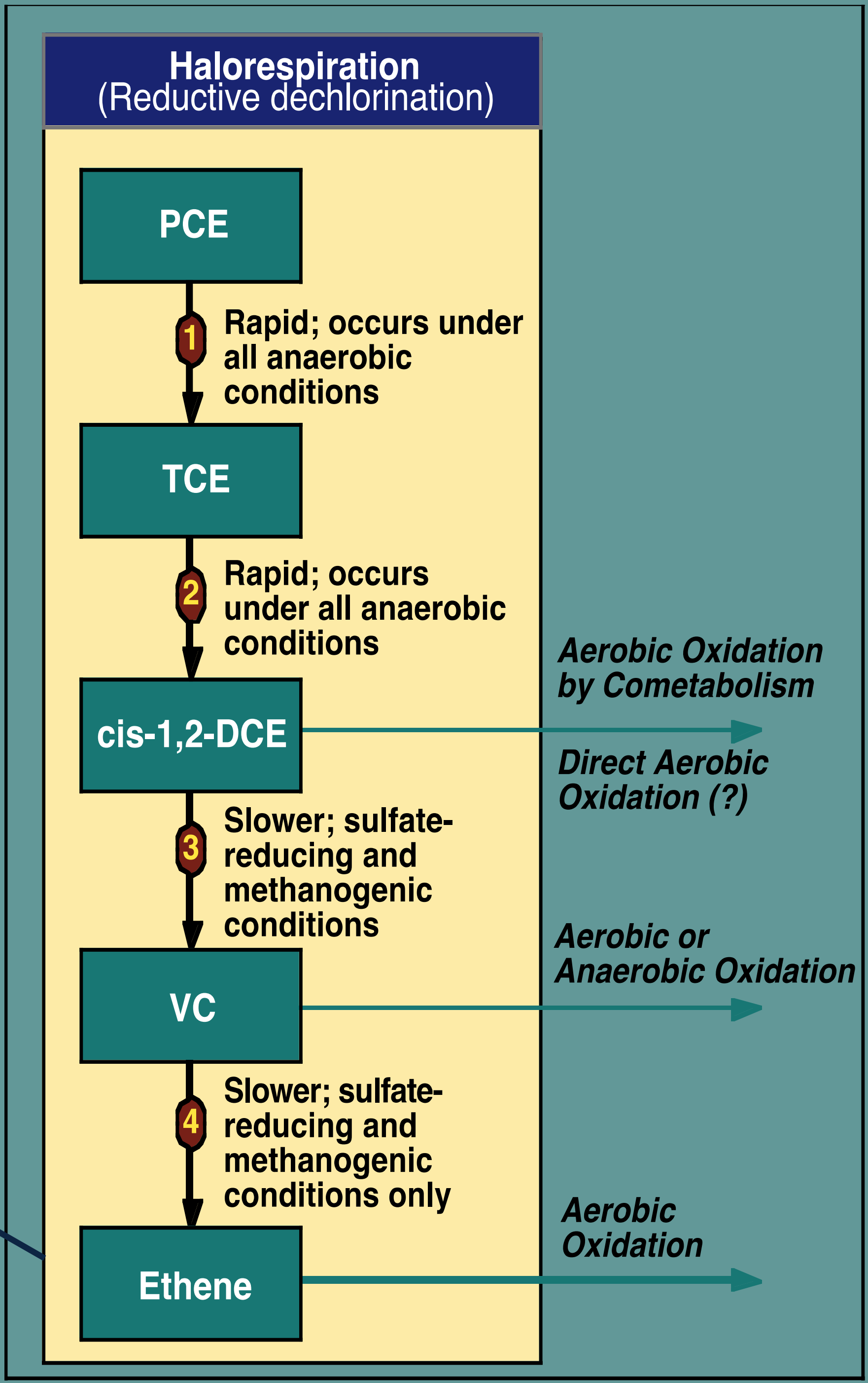
REDUCTIVE DECHLORINATION: *Chlorinated Ethenes*



Key footprint of PCE, TCE biodegradation: presence of cis 1,2-DCE

REDUCTIVE DECHLORINATION: *Pathway for Chlorinated Ethenes*

Key footprint of PCE, TCE, cis-1,2-DCE, VC biodegradation: presence of ethene (or ethane)



(Adapted from RTDF, 1997.)

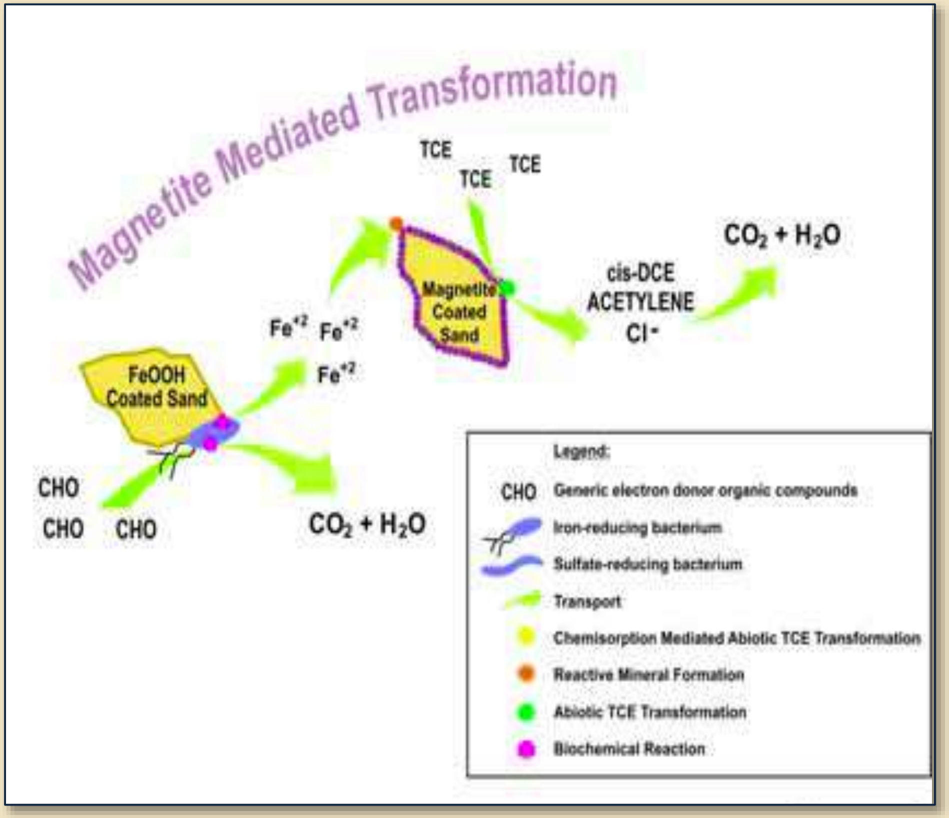
ABIOTIC PROCESSES: *How do reactive mineral species contribute to attenuation?*

Naturally-occurring minerals can degrade contaminants

- **CVOC degradation that is abiotically-mediated by a number of reactive mineral species**

Iron(II) Sulfide (FeS) Mackinawite –($Fe_{1+x}S$) Pyrite (FeS_2) Magnetite (Fe_3O_4) Goethite (α-FeO(OH)) Hematite (Fe_2O_3) Lepidocrocite (γ-FeO(OH)) Green Rust--(Fe^{2+} and Fe^{3+} cations, O^{2-} and OH^- anions, with loosely bound $[CO_3]^{2-}$ groups and H_2O molecules between the layers)

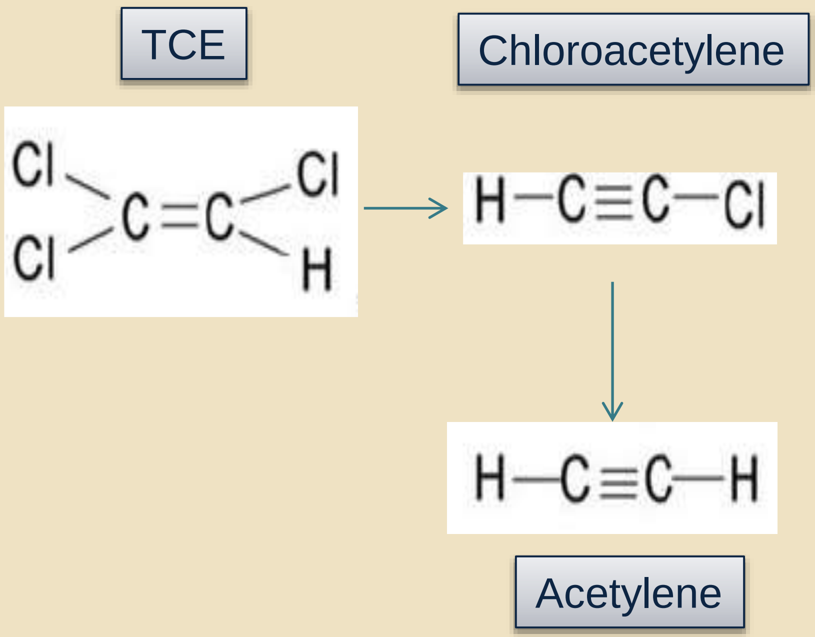
- **Basis for ZVI and other PRB designs, but significant evidence of natural attenuation in anaerobic environments**



Example of abiotic TCE degradation by magnetite (from ESTCP/AFCEE/NAVFAC, 2007)

Note there is biological component to these reactions!

ABIOTIC PROCESSES: *Unique degradation products when reactive minerals are involved*



UNIQUE PRODUCTS:

- If either detected, then this is proof that abiotic attenuation is occurring!

EASIER SAID THAN DONE…

- Products are biodegradable (in situ and following sample collection)
- Highly volatile
- Concentration may be low and hard to quantify

KEY POINT: FALSE NEGATIVES ARE BIG ISSUE

Compounds may be almost gone by the time the sample reaches the lab, and lab may not be able to measure what's left

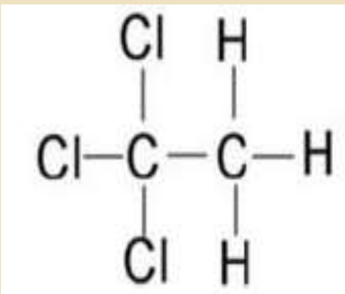
ABIOTIC PROCESSES:
Which contaminants and which minerals?

	Iron sulfides	Magnetite	Green rust
Chlorinated Solvents	YES	YES	YES
Pesticides	YES		
Munitions (RDX)	YES?	YES	
Metals (U, As)	YES		

	Iron sulfides	Magnetite	Green rust
Petroleum hydrocarbons (BTEX, MTBE)			
1,4-dioxane			
1,2,3-trichloropropane	Minor		
PFAS (per- and polyfluorinated alkyl substances)			
N-nitrosodimethylamine (NDMA)	Maybe?		

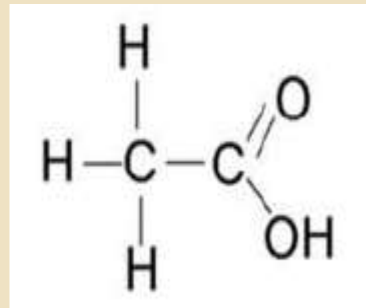
ABIOTIC PROCESSES:
Hydrolysis

1,1,1-TCA



HYDROLYSIS

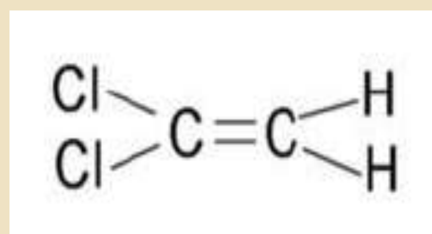
Acetic Acid



Product Yield
= 80%

DEHYDROHALOGENATION

1,1-Dichloroethene



Product Yield
= 20%

TCA half-lives for HYDROLYSIS: ~ 1 – 10 yr

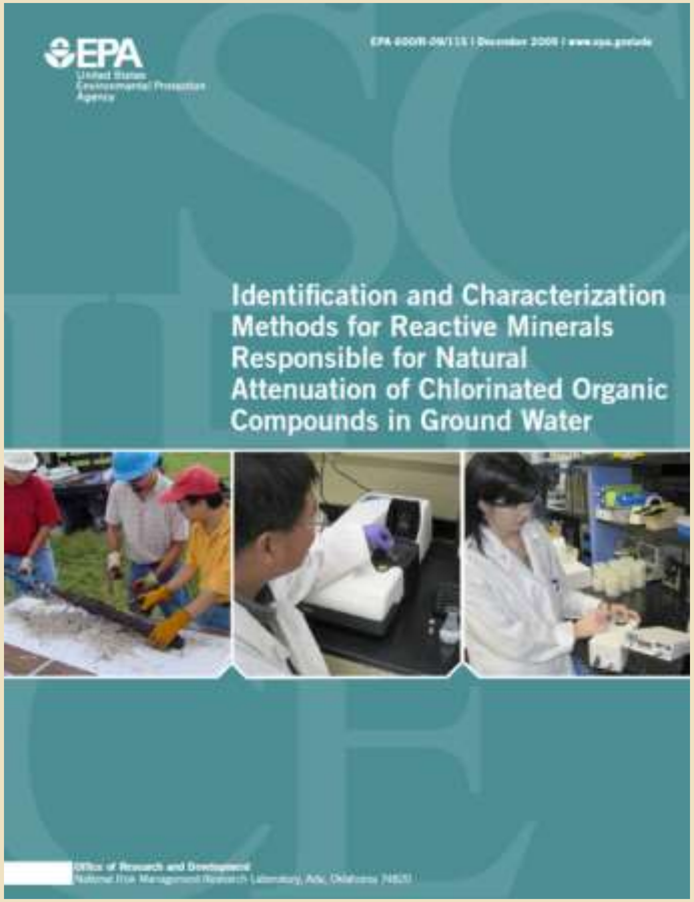
ABIOTIC PROCESSES:
Which contaminants undergo hydrolysis?

Target compound(s)	Undergoes hydrolysis-type reactions?	Product(s)
1,1,1-TCA	YES	Acetic acid, 1,1-DCE
1,1,1,2-TeCA	YES	TCE
1,2-Dichloropropane	YES	1-Chloropropene
Chloroethane	YES	Ethanol, ethene
Carbon Tetrachloride	YES	CO2
1,1-DCA	YES	Chloroethene
1,2-DCA	YES	Chloroethene

ABIOTIC PROCESSES:
How to assess?

- **Methods for assessing abiotic degradation capacity are available and/or being developed**
  - **E.g., magnetite in sediments via magnetic susceptibility testing**

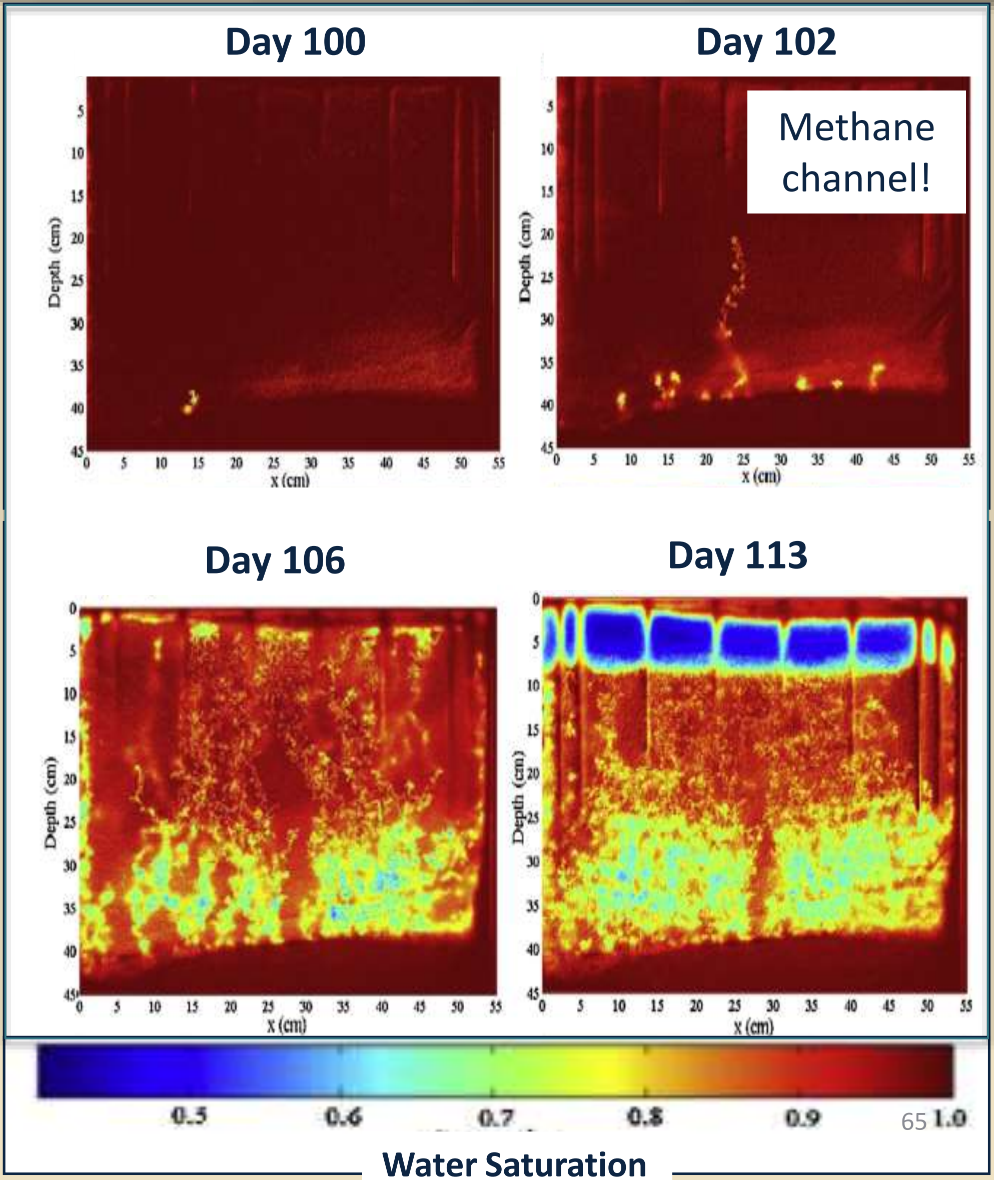
- **Current research suggests slow but sustainable attenuation rates**



EPA, 2009 – detailed descriptions of important methods

LNAPL SOURCE ZONE DEGRADATION:

Methane production results in ebullition



Source: *Ye et al., 2009*

Day 100

Day 102

Methane channel!

Day 106

Water Saturation

Source: CSU

2009

Groundwater Mass Flux vs. Vapor Phase Mass Flux

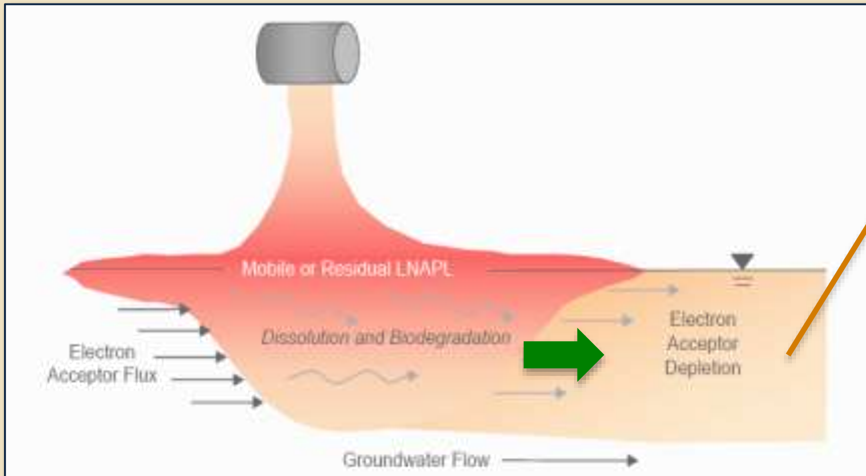


Figure 2-1. Groundwater transport-related NSZD processes.

1-10%

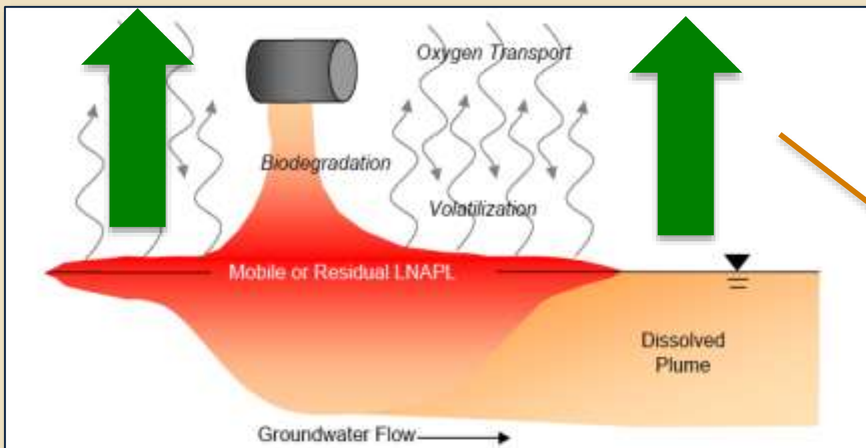


Figure 2-2. Vapor transport-related NSZD processes.

90-99%

Surprising Result: **Vapor transport fluxes much greater than groundwater fluxes!**

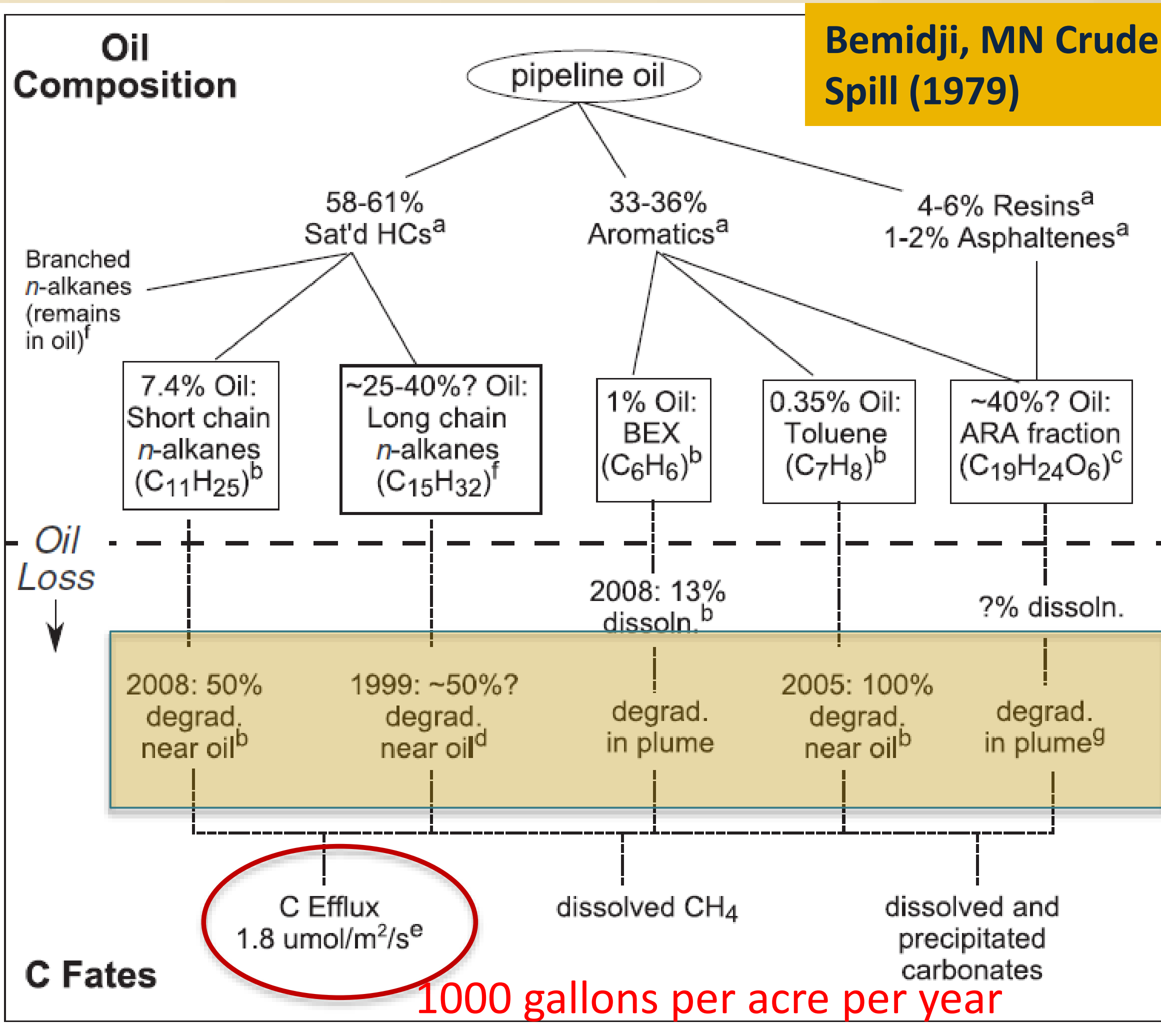
ITRC, 2009; Suthersan 2015

Carbon Eflux Key Process at LNAPL Sites

Journal of Contaminant Hydrology

A mass balance approach to investigating geochemical controls on secondary water quality impacts at a crude oil spill site near Bemidji, MN

Bemidji, MN Crude Oil Spill (1979)

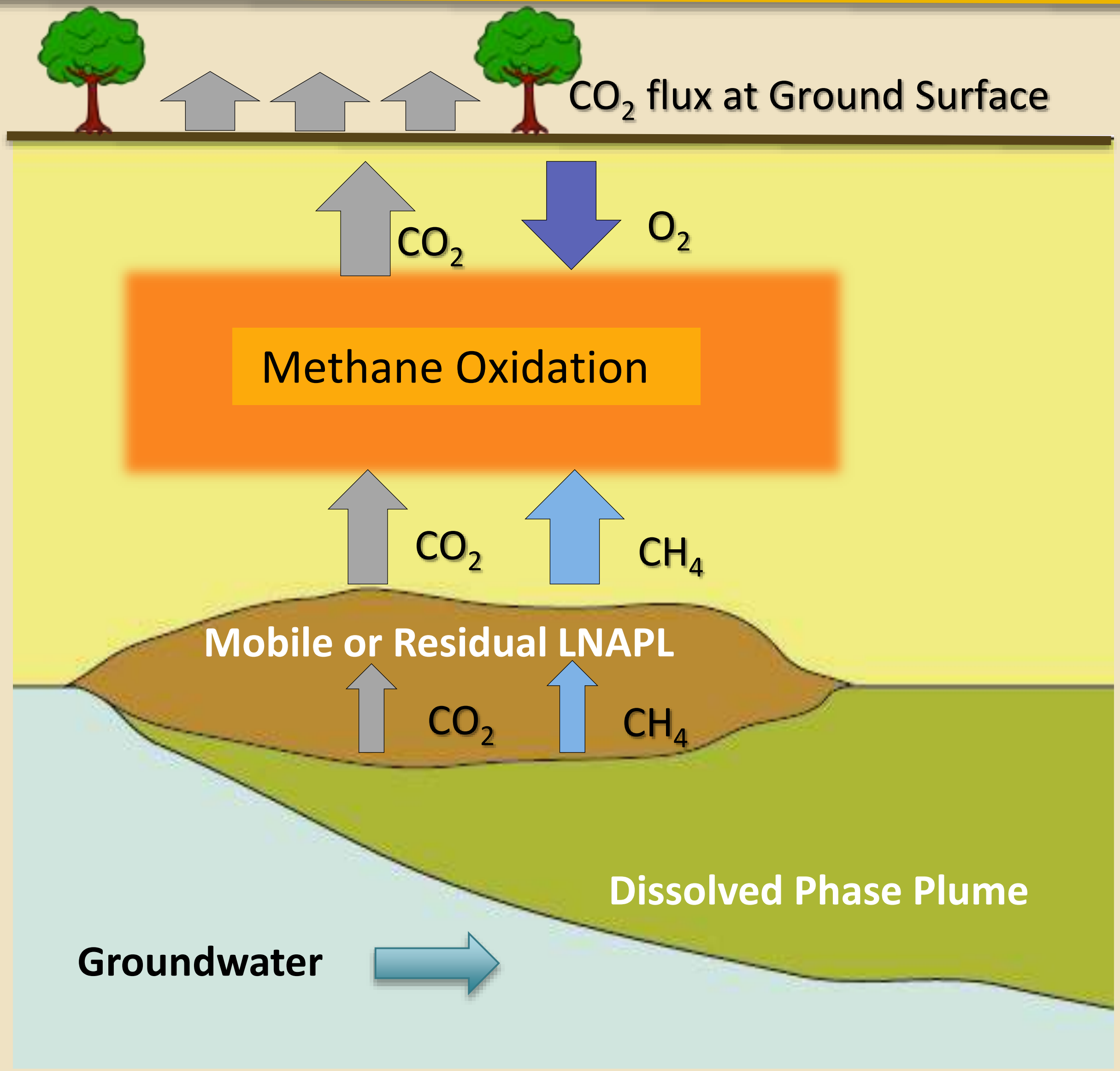


Key Point 1: **Natural Degradation Occurring >30 Years Later**

Key Point 2: **85 - 90% of the carbon biodegradation products outgassed!**

Fig. 2. Original pipeline oil composition (solid lines) and most recently measured fate (dashed lines). Boxed constituents on the level directly above dotted horizontal line provided the basis for oil components used in this study. Entries below dotted horizontal line show oil loss pathways. Note that a significant oil mass remains, and oil phase loss includes some dissolved organic carbon (mostly BEX and NVDOC) that has not fully degraded. Components and pathways lacking data constraining are indicated with (?). Data sources: [a]Eganhouse et al. (1993), [b]Baedecker et al. (2011), [c]Thorn and Aiken (1998), [d]Bekins et al. (2005), [e]Sihota et al. (2011), [f]Hostettler et al. (2007), [g]Amos et al. (2012).

Current NSZD Conceptual Model



Adapted from: CSU, 2016

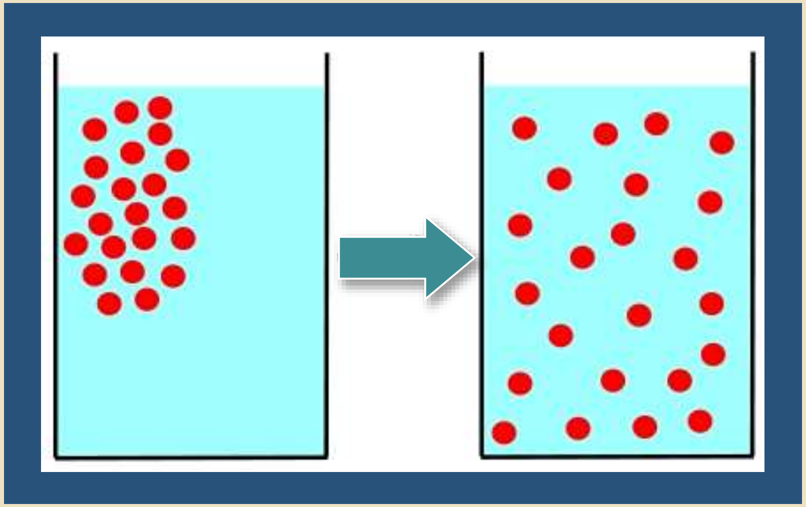
ROAD MAP

- **Intro: Changing Paradigms and MNA Principles**
- **Key Attenuation Processes**
  - *Biodegradation*
  - *Abiotic Processes*
  - *LNAPL source zone degradation processes*
  - *Other processes (immobilization, storage, dilution)*
- **Field Techniques and Technologies**
  - *Groundwater sampling and analytical methods*
  - *Compound Specific Isotopes Analysis (CSIA)*
  - *Molecular Biological Tools (MBTs)*
  - *Natural Source Zone Depletion (NSZD)*
- **Should MNA be Used? Data Analysis and Monitoring Tools**
  - *Data requirements, LTM, and statistics to understand MNA rates*
  - *Common Graphics and Calculations*
  - *Remediation Timeframe Calculations*
  - *Computer Models*
- **Implementation Topics**

CONTAMINANT STORAGE:
WHAT IS DIFFUSION?

Diffusion describes the spread of particles through random motion from regions of higher concentration to regions of lower concentration.

Key people: Fourier (1822), Fick (1855), Einstein (1905), Smoluchowski (1906)



$$J = D \frac{dC}{dx}$$

J = Diffusive flux flowing though a particular cross section (mg/ meter^2 / sec)

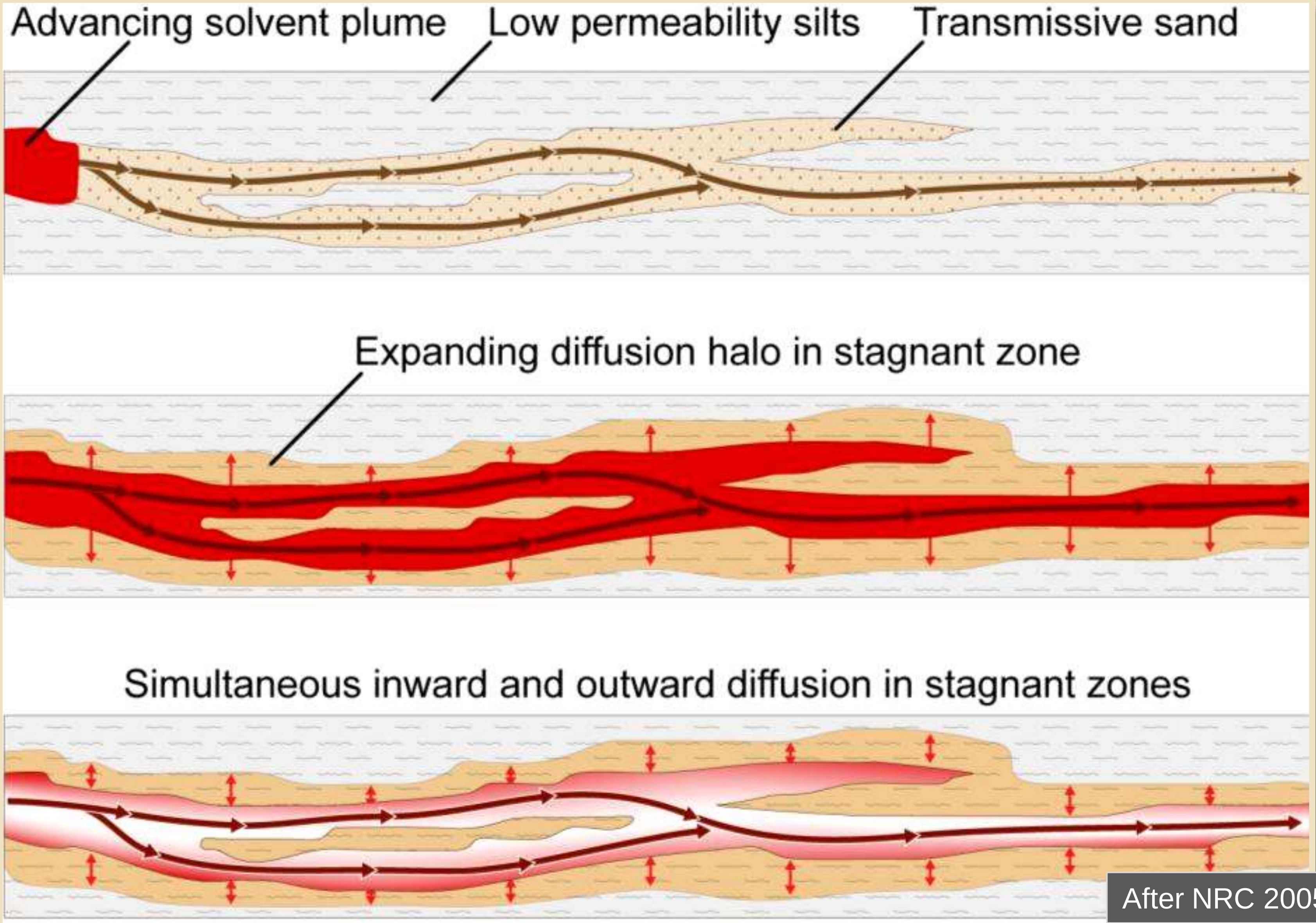
D = Diffusion coefficient (meter^2 / sec)

$\frac{dC}{dx}$ = Concentration gradient (mg / liter / meter)

Coffee Cup: **convection + diffusion**

Laminar Groundwater: **Molecular diffusion - movement of molecules only**

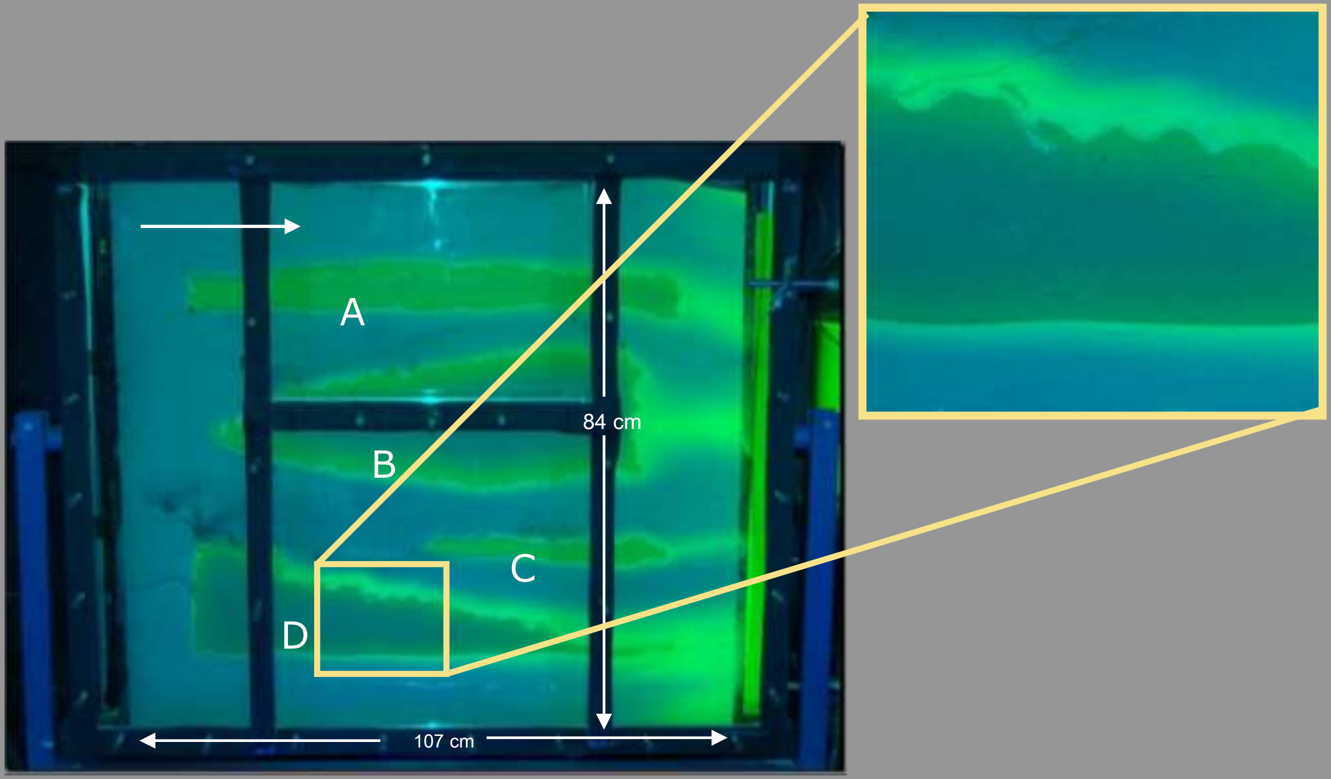
MATRIX DIFFUSION AS CONTAMINANT STORAGE



After NRC 2005

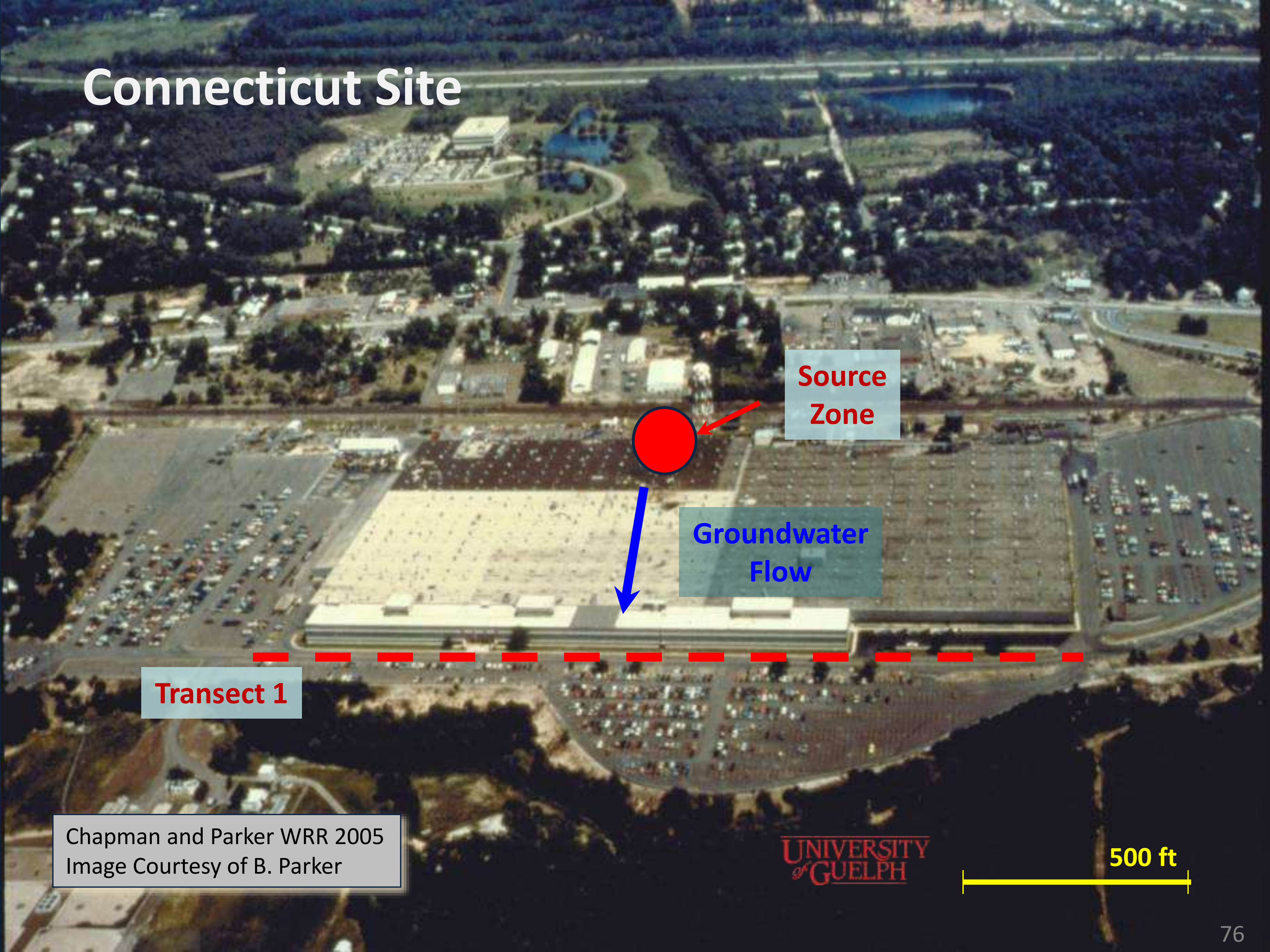
KEY POINT: *Matrix Diffusion is a Small-Scale Phenomena*

Contaminant storage and release processes in low permeability zone is important, but it is governed by concentrations gradients that occur at scales of *centimeters to millimeters.*

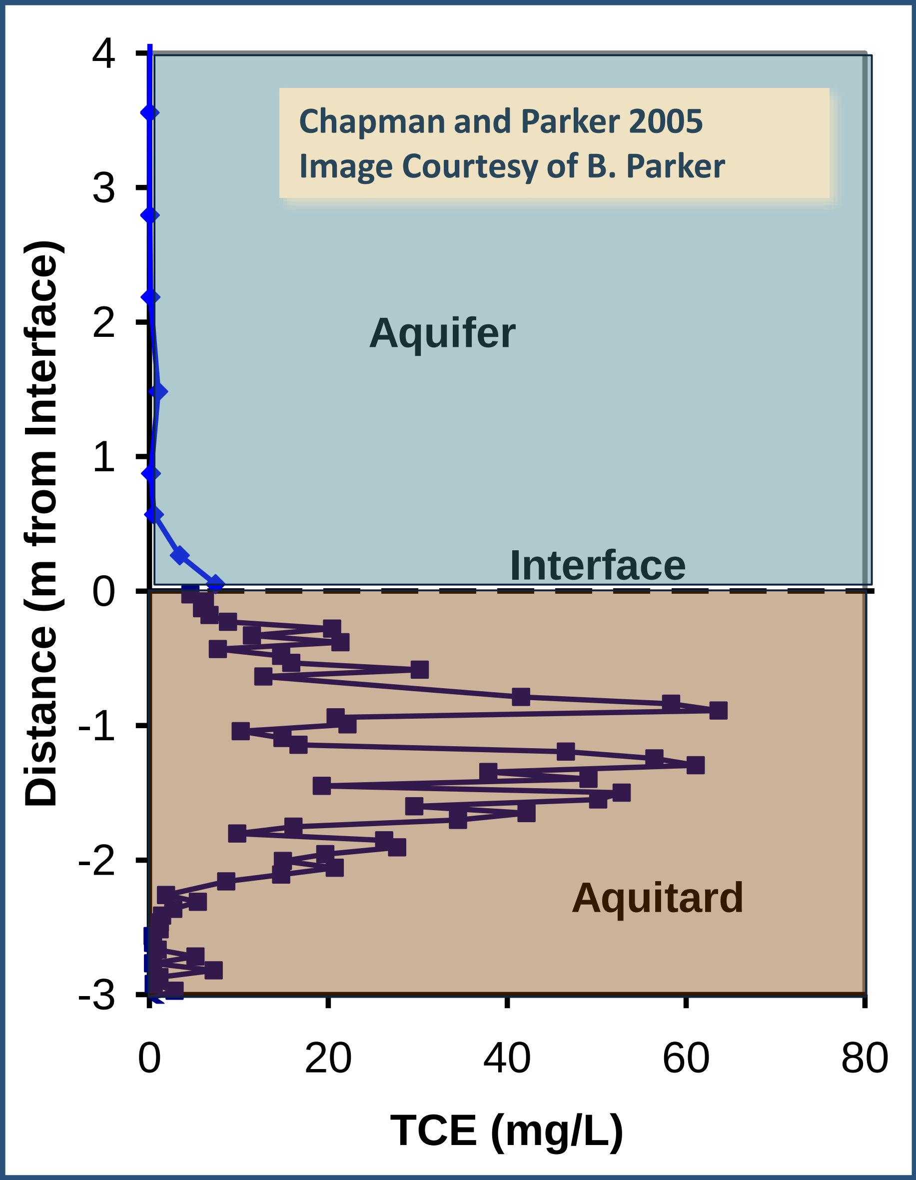


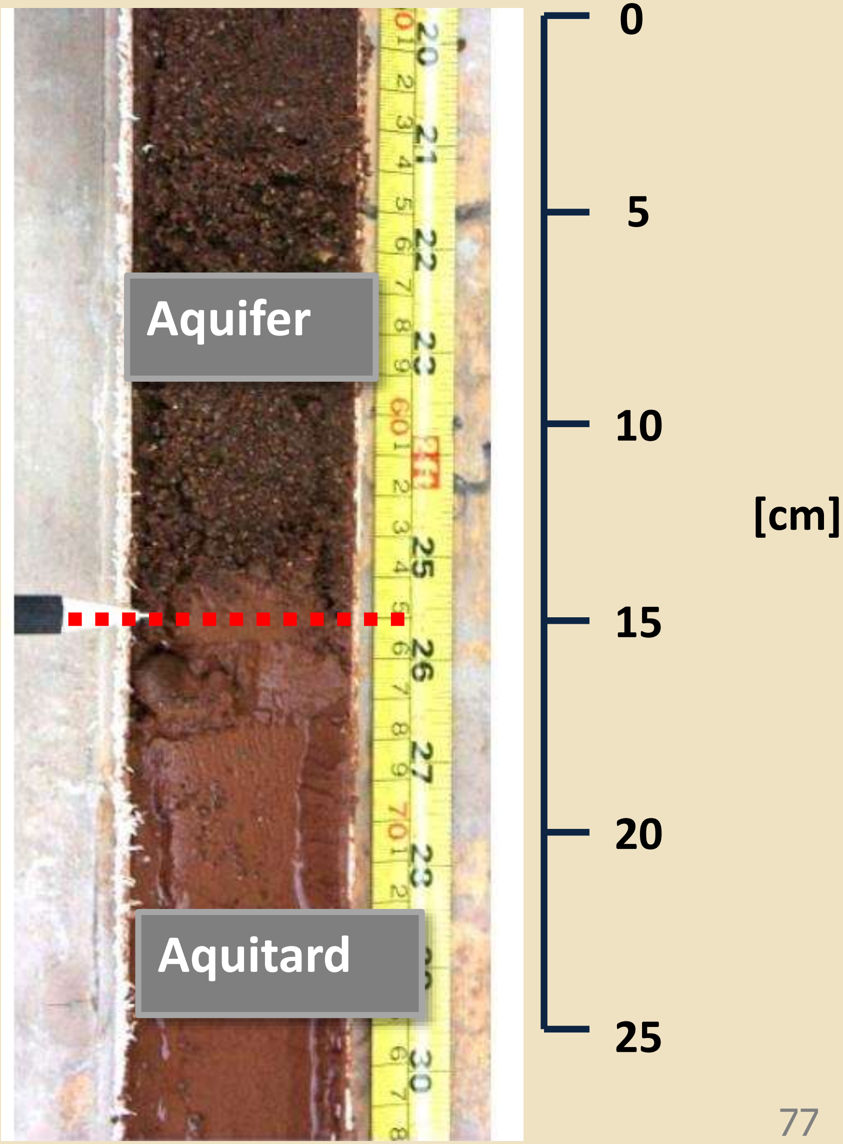
Day 28

Connecticut Site

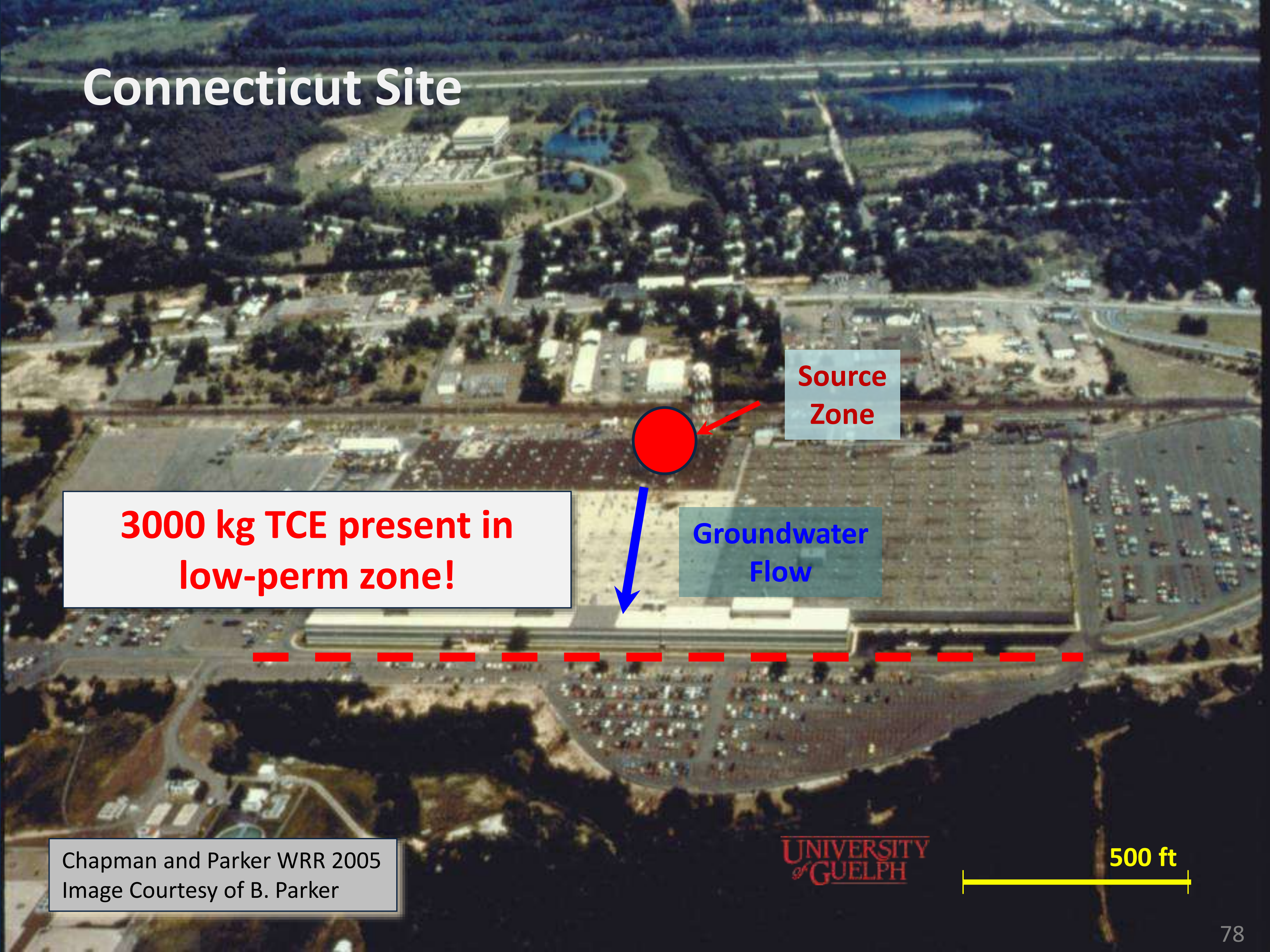


HIGH-RESOLUTION DATA FROM CORE

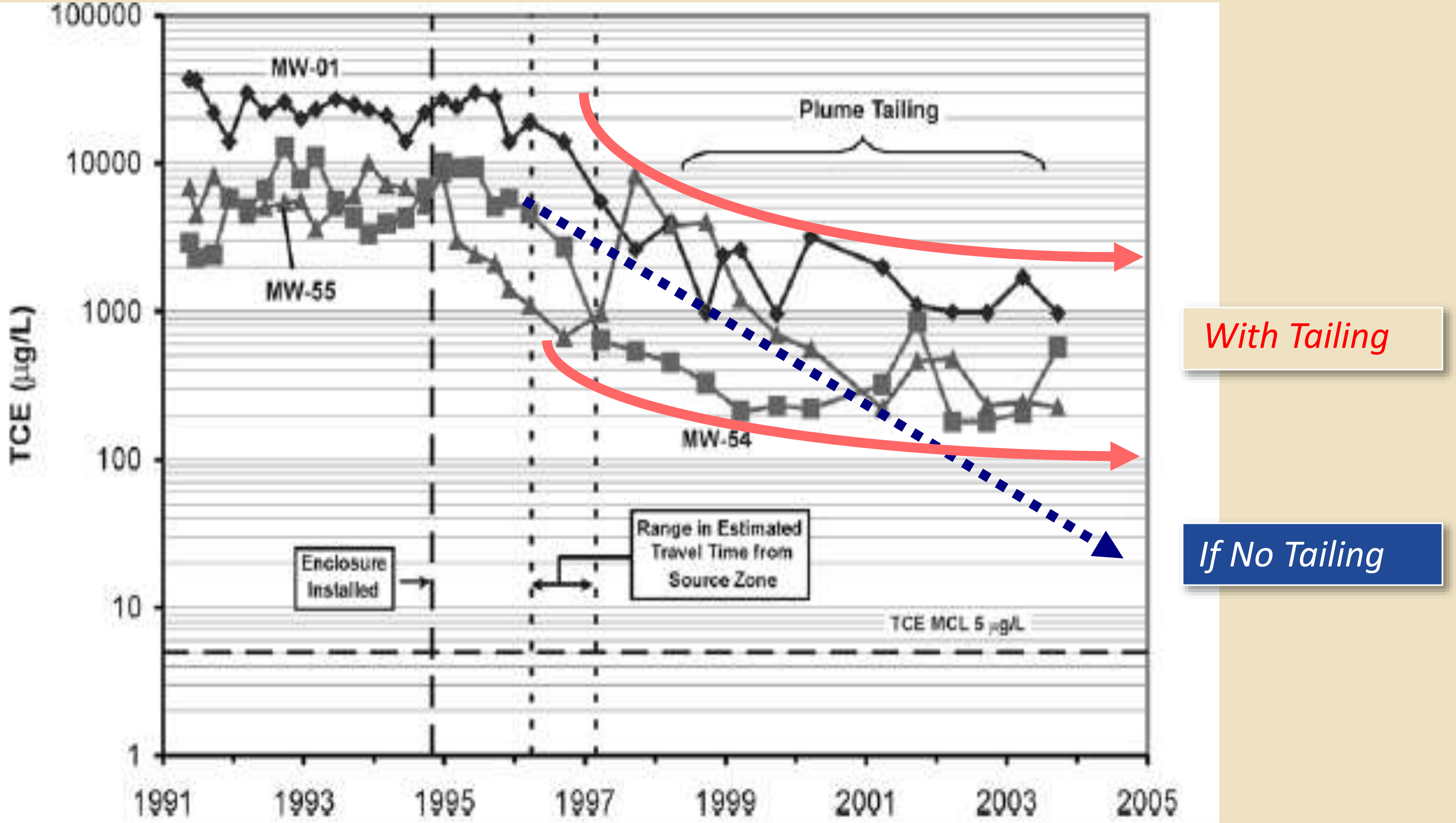




Connecticut Site



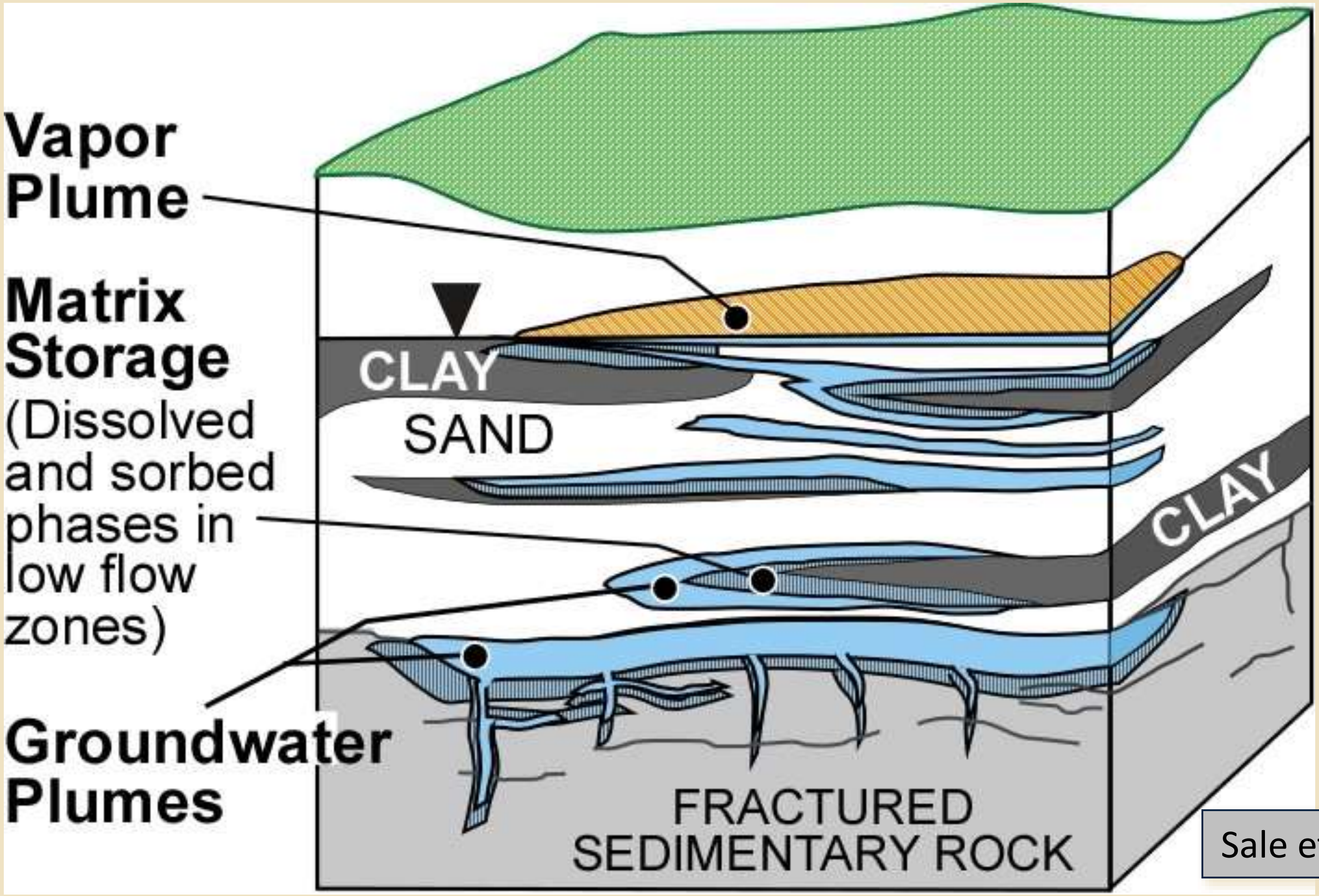
CONCENTRATION VS. TIME FROM MONITORING WELLS



Source: Chapman and Parker, 2005 Copyright 2005 American Geophysical Union. Reproduced/modified by permission of AGU.

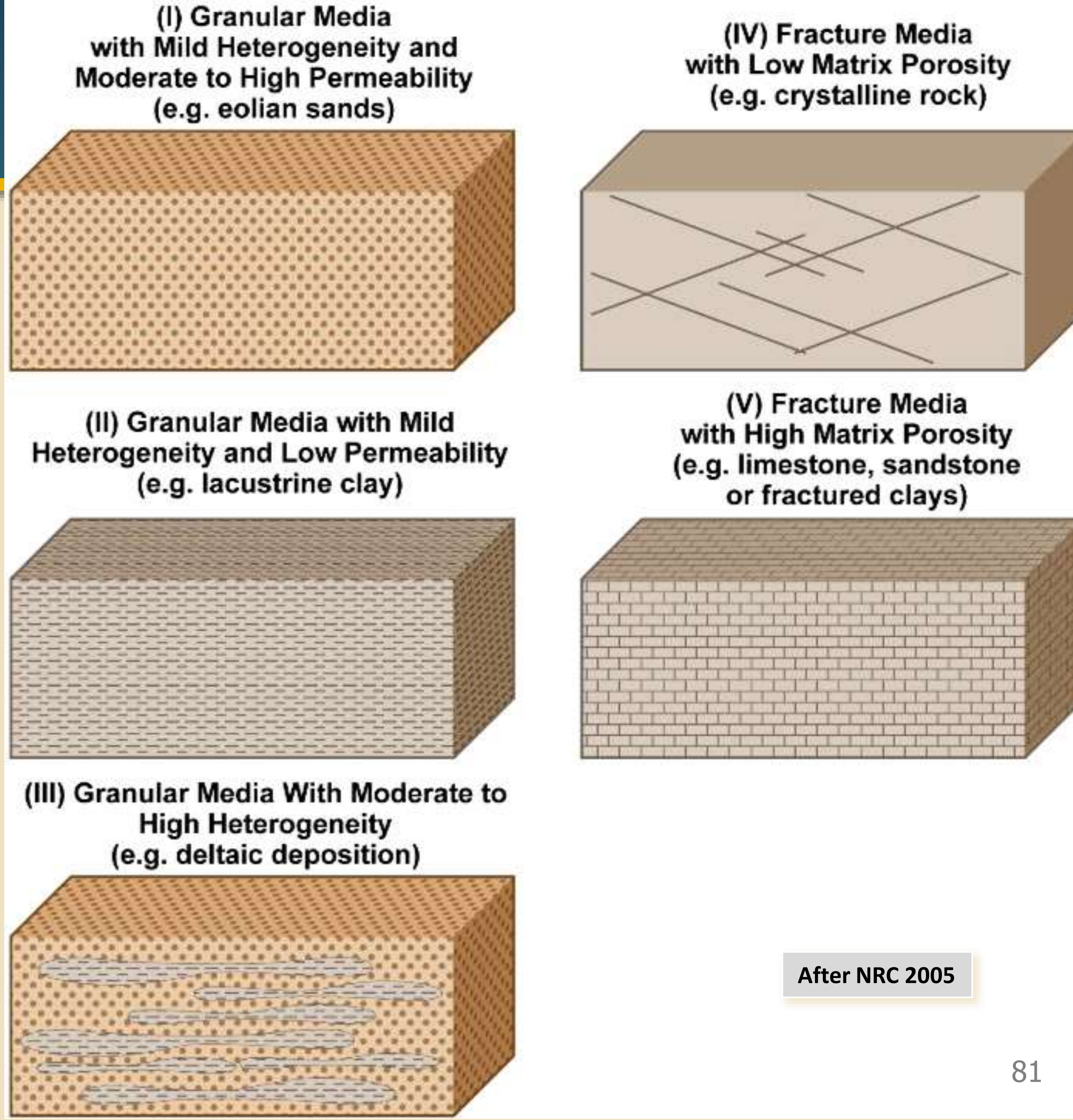
LIFE CYCLE OF A CHLORINATED SOLVENT SITE

Late Stage



Sale et al., 2008

TYPE SETTING

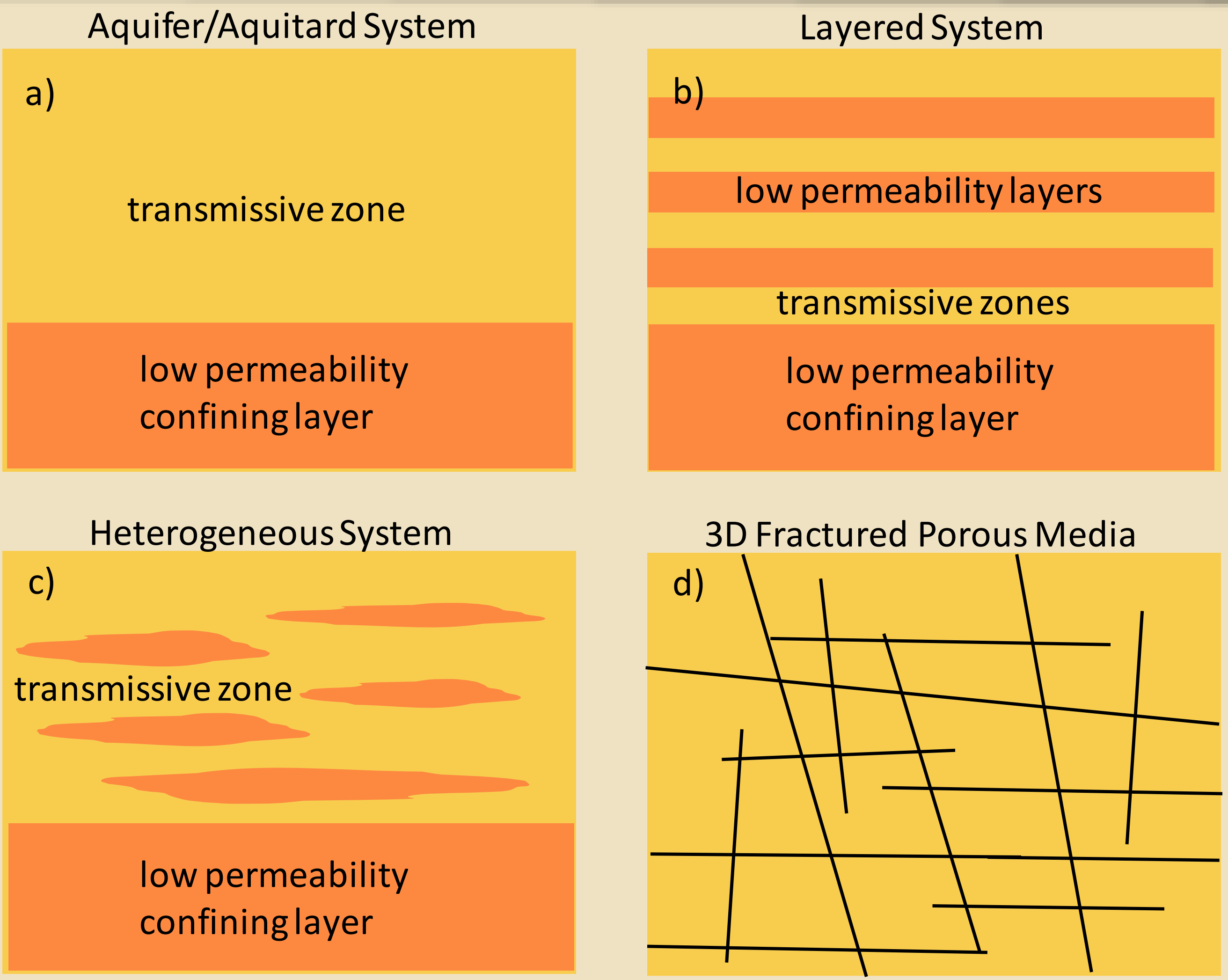


HETEROGENEITY RULES, EVEN IN "SANDY AQUIFERS"

Matrix Diffusion Paradigm:
Remediation Hydraulics (CRC Press)
Fred Payne, Joseph Quinnan, Scott Potter

Image from Fred Payne /ARCADIS

REMCHLOR-MD MATRIX DIFFUSION MODEL:
Game Changer?



For **REMChlor**: google REMChlor USEPA

FOR **REMChlor-MD:** check Jan. 2017 www.gsi-net.com

DILUTION AS AN ATTENUATION PROCESS

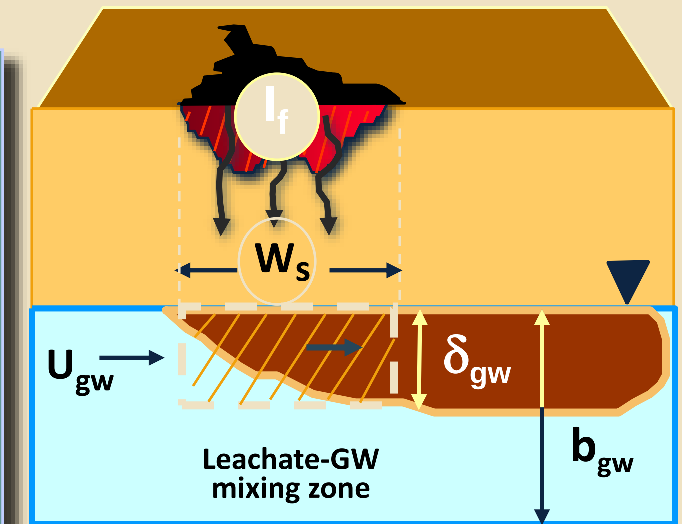
Soil-to-GW Pathway (^{GW}SOIL): *Leachate Dilution Factor (LDF)*

$$LDF = 1 + \frac{U_{gw}\,\delta_{gw}}{I_f\,W_s}$$

- U_{gw}: GW Darcy Velocity
- δ_{gw}: GW mixing zone thickness
- I_f: Net infiltration
- W_s: Width of affected soil in direction of GW flow

$$\delta_{gw} = (2\alpha_v\,W_s)^{0.5} + b_{gw}\left(1-\exp\left(\frac{-I_f\,W_s}{U_{gw}\,b_{gw}}\right)\right)$$

- α_v: Vertical groundwater dispersivity
- b_{gw}: Aquifer thickness



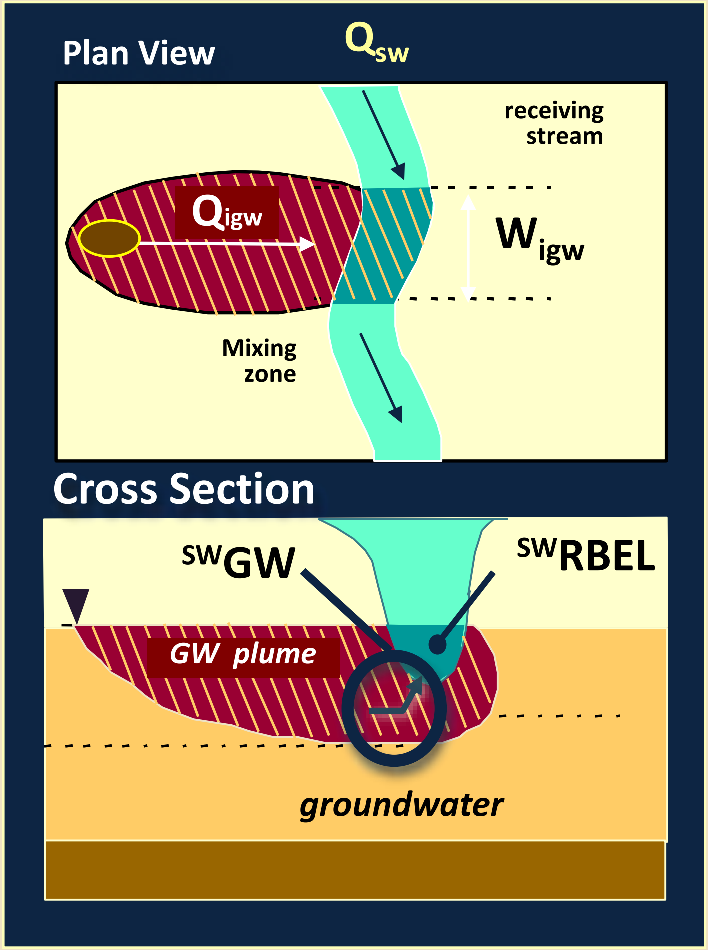
Must use this equation in Tier 2. (Tier 1 PCLs based on default LDF of 10 or 20.)

DILUTION AS AN ATTENUATION PROCESS

Groundwater to Surface Water Pathway (^{SW}GW)

$$^{SW}GW = \frac{^{SW}RBEL}{DF}$$

where DF = Dilution factor for affected GW entering SW.



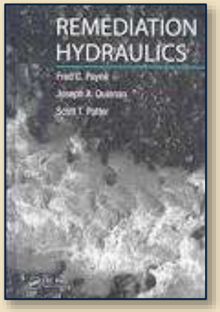
$^{SW}RBEL$ = Lowest applicable value for COC per 350.74 (h).

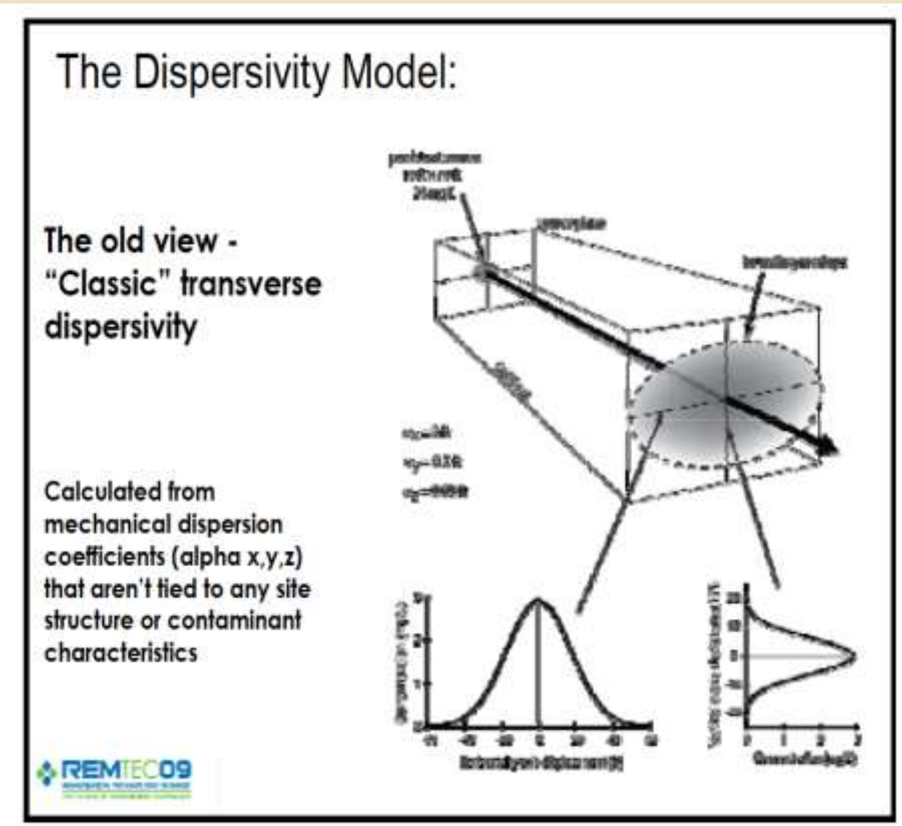
GW = Groundwater

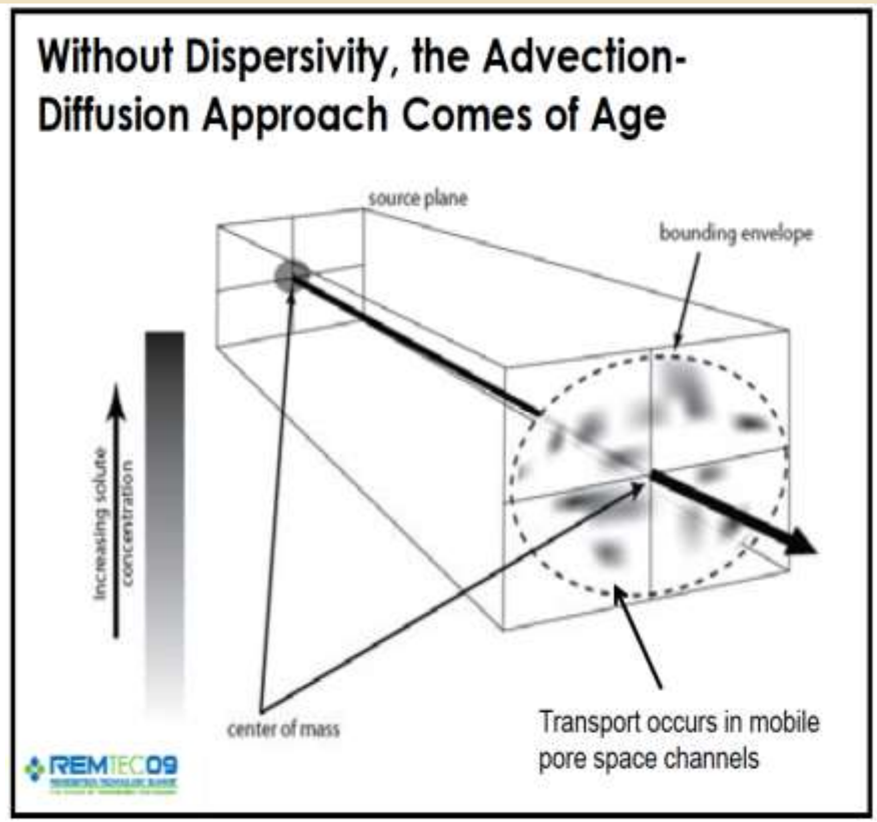
DILUTION VS. *DISPERSION* AS AN ATTENUATION PROCESS

Emerging Conceptual Model:

- Dispersion is very weak process
- Most plumes are long and narrow
- Matrix Diffusion is much more important than dispersion







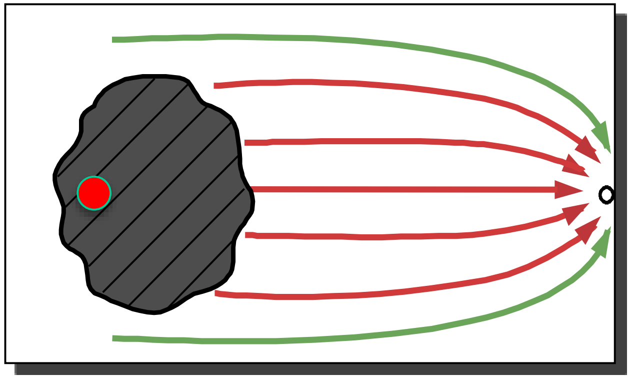
Slides courtesy Fred Payne, Arcadis

Dilution in Mass Flux Calculations Concentration versus Mass Discharge

Site A:

Very wide source

Very fast groundwater

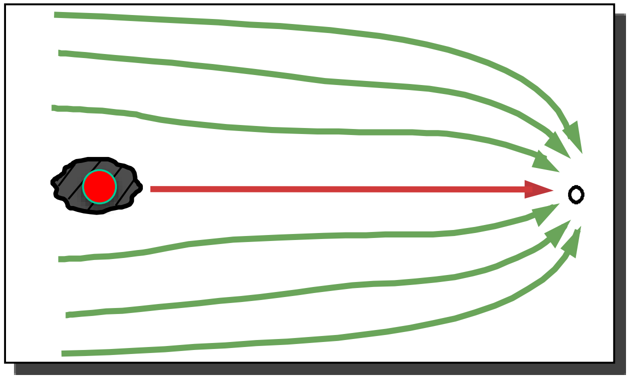


But same maximum groundwater Concentration…

Site B:

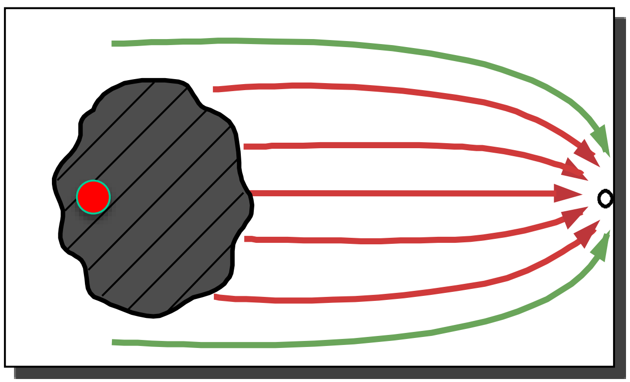
Tiny source

Almost stagnant groundwater

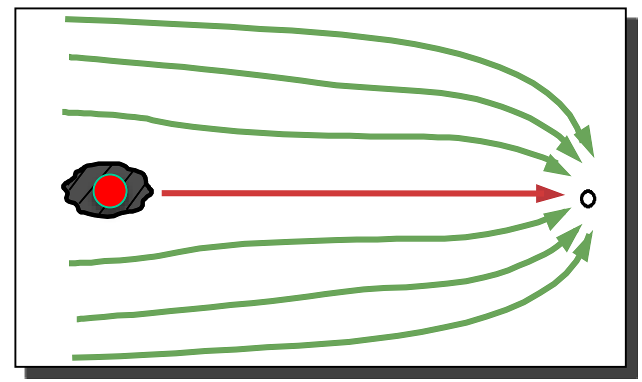


Dilution in Mass Flux Calcuations Concentration versus Mass Discharge

- Concentration-based approach may not account for important site characteristics



But same maximum groundwater Concentration…



Mega Site

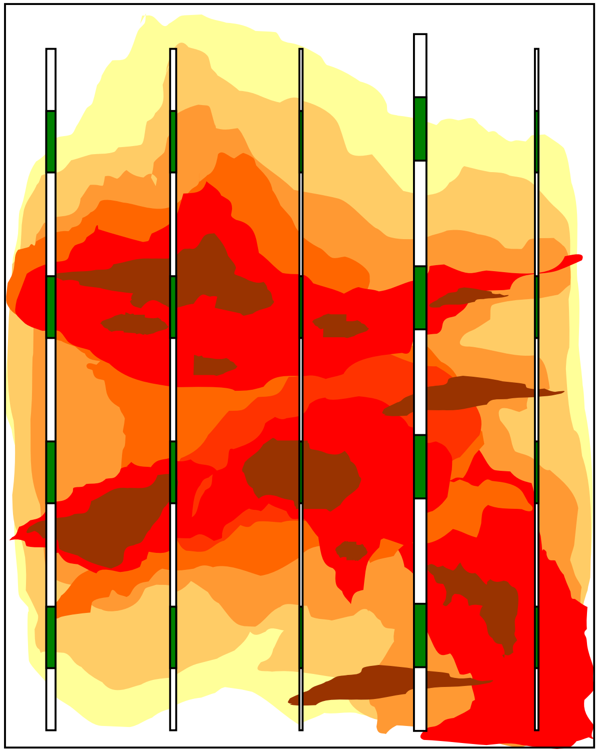
"Piss-Ant" Site

Definitions

Mass flux, J
(mass per area
per time)

Integrate

Mass discharge, M_d
(Mass per time)



$$\int$$

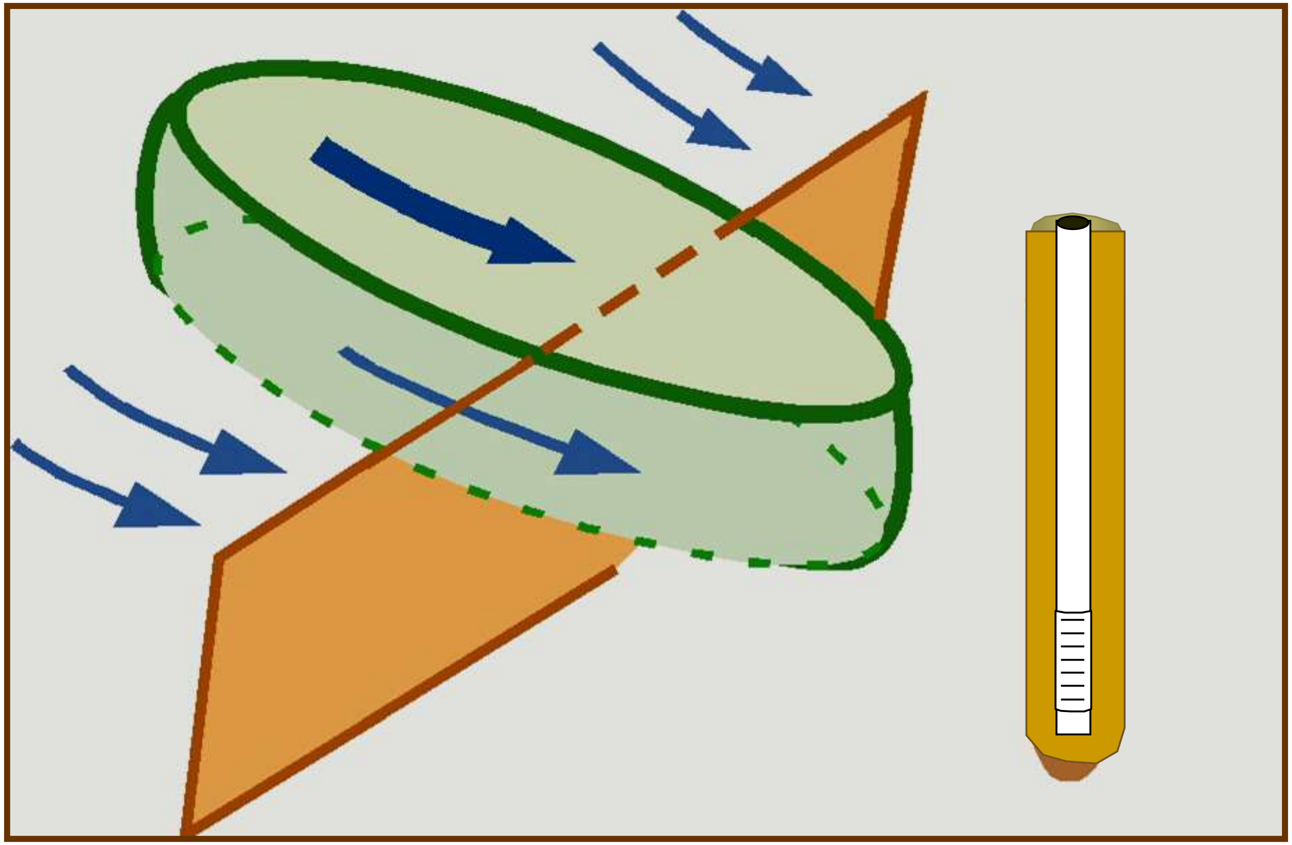
"This plume has a mass discharge of 1.5 grams per day."

Sir Isaac Newton:

"Method of Fluxions"

Mass Flux / Mass Discharge

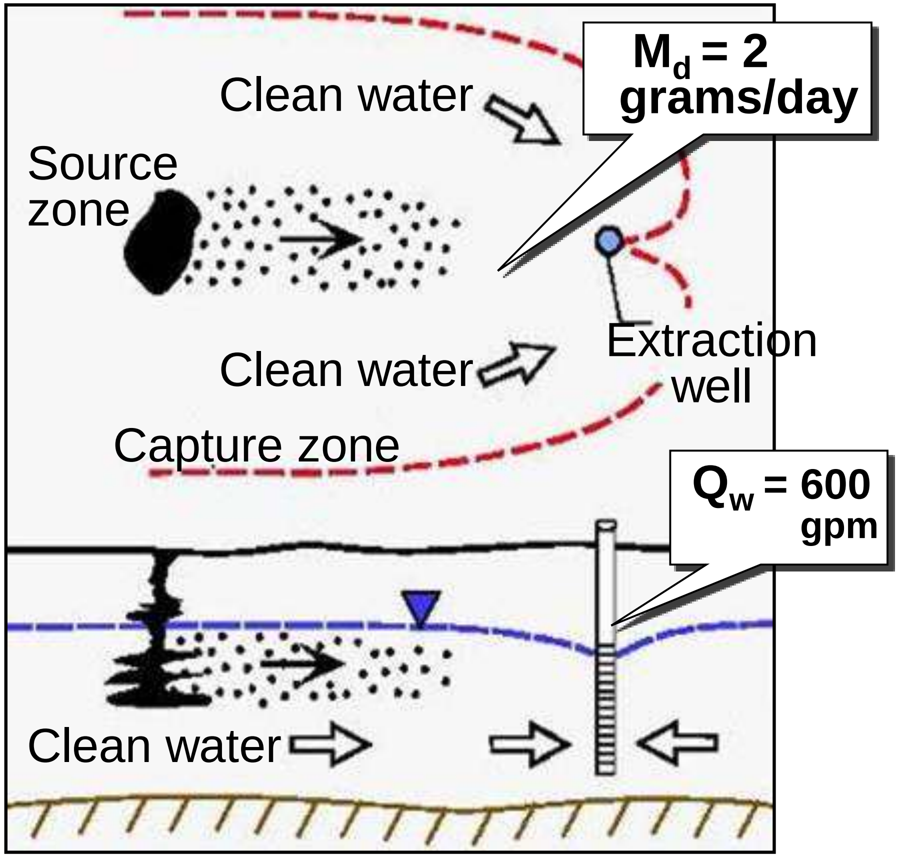
Combine flow, size, concentration to get grams per day (mass discharge)



Using Mass Discharge: Estimating Well Impacts

Einarson and Mackay, 2001

Use mass discharge of plume to predict constituent of concern concentration in downgradient water supply well



$$C_{well} = M_d \div Q_{Well}$$

C_{well} = Concentration in extraction well

Q_{well} = Pumping rate for extraction well

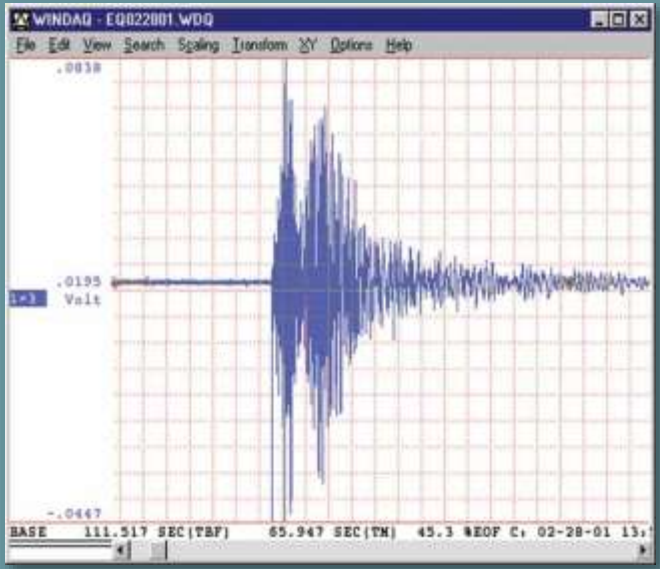
$$\frac{2 \text{ grams}}{\text{day}} \times \frac{1}{600 \text{ gpm}} \div \frac{\text{day}}{1440 \text{ min}} \times \frac{1 \text{ gal}}{3.79 \text{ L}} \times \frac{10^6 \text{ug}}{\text{g}} = < 1 \text{ ug /L}$$

MANAGING SURFACE WATER QUALITY WITH MASS DISCHARGE: *Total Maximum Daily Loads (TMDL)*

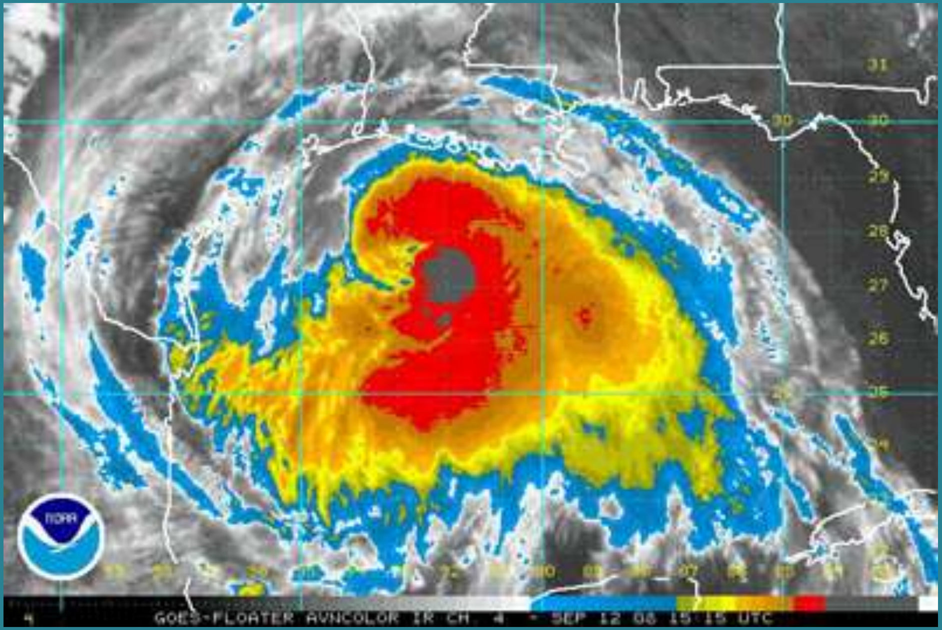
"The maximum amount of a pollutant that a water body or water segment can assimilate without exceeding water quality standards." **(1972 CWA)**

EXAMPLES:

- **PCBs into Susquehanna River (Penn.): 0.64 grams per day *(our Mag 4)***
- **Copper into Eagle River (Alaska): up to 5450 grams per day *(our Mag 8)***
- **Proposed Dioxin into Houston Ship Channel 0.04 grams per day *(our Mag 3)***


WINDAQ - EQ022001.WDQ
File Edit View Search Scaling Transform XY Options Help
.0838
.0195
Volt
-.0447
BASE 111.517 SEC(TBF) 65.947 SEC(TM) 45.3 %EOF C: 02-28-01


MIYAKO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GOES-FLOATER AVNCOLOR IR CH. 4 - SEP 12 08 15:15 UTC


PLUME MAGNITUDE CLASSIFICATION SYSTEM

Mass Discharge (grams/day)	Plume Category
< 0.001	"Mag 1 Plume"
0.001 to 0.01	"Mag 2 Plume"
0.01 to 0.1	"Mag 3 Plume"
0.1 to 1	"Mag 4 Plume"
1 to 10	"Mag 5 Plume"
10 to 100	"Mag 6 Plume"
100 to 1,000	"Mag 7 Plume"
1,000 to 10,000	"Mag 8 Plume"
10,000 to 100,000	"Mag 9 Plume"
>100,000	"Mag 10 Plume"

Newell et al., 2011

ROAD MAP

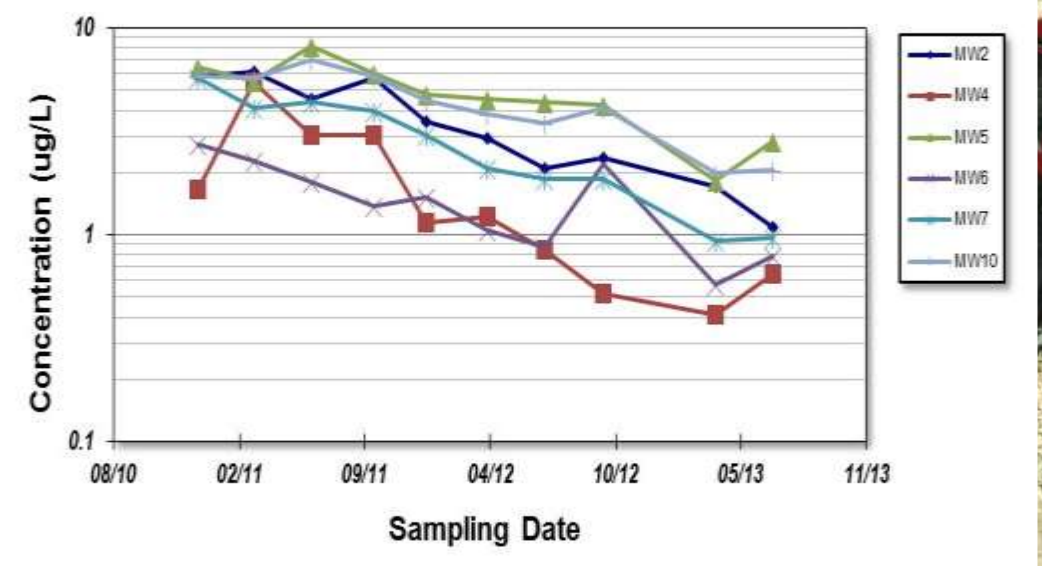
- **Intro: Changing Paradigms and MNA Principles**
- **Key Attenuation Processes**
  - *Biodegradation*
  - *Abiotic Processes*
  - *LNAPL source zone degradation processes*
  - *Other processes (immobilization, storage, dilution)*
- **Field Techniques and Technologies**
  - *Groundwater sampling and analytical methods*
  - *Compound Specific Isotopes Analysis (CSIA)*
  - *Molecular Biological Tools (MBTs)*
  - *Natural Source Zone Depletion (NSZD)*
- **Should MNA be Used? Data Analysis and Monitoring Tools**
  - *Data requirements, LTM, and statistics to understand MNA rates*
  - *Common Graphics and Calculations*
  - *Remediation Timeframe Calculations*
  - *Computer Models*
- **Implementation Topics**

MNA MONITORING

1

Characterization/
Remedy Selection

Line of Evidence 1	Decreasing historical trends in concentration/mass
Line of Evidence 2	Favorable geochemical and daughter product data
Line of Evidence 3	Microcosm or field data showing degradation is occurring (and rate)



CHARACTERIZATION/REMEDY SELECTION:
Gathering Better "Lines of Evidence"

MNA MONITORING

1

Characterization/
Remedy Selection

Increasingly reliant on new techniques:

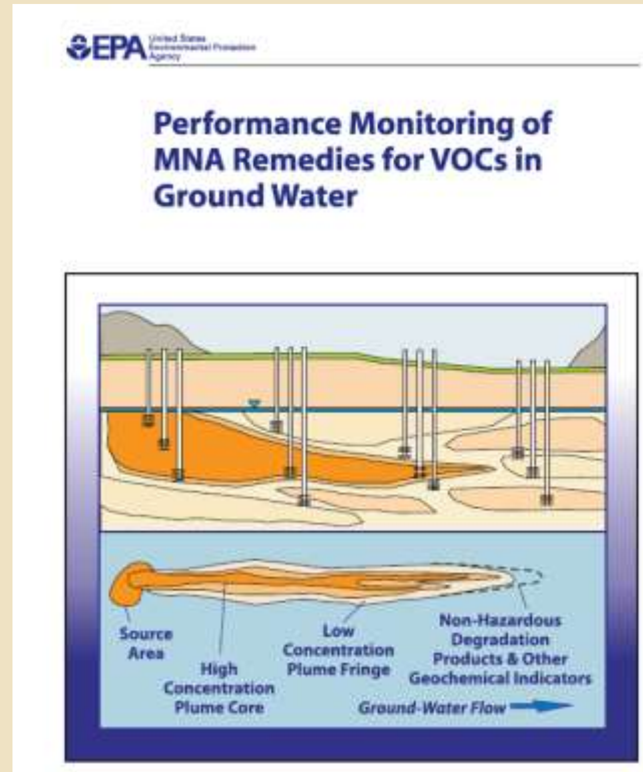
- **Molecular Biological Tools (MBTs)**
- **Compound Specific Isotope Analysis (CSIA)**
- **Natural Source Zone Depletion (NSZD)**
- **Mass discharge**

We'll talk more about these in a minute…

PERFORMANCE MONITORING:
Proving that MNA is working

MNA MONITORING

1. Characterization/ Remedy Selection
2. Performance Monitoring



USEPA, 2004

OBJECTIVES OF LONG-TERM PERFORMANCE MONITORING

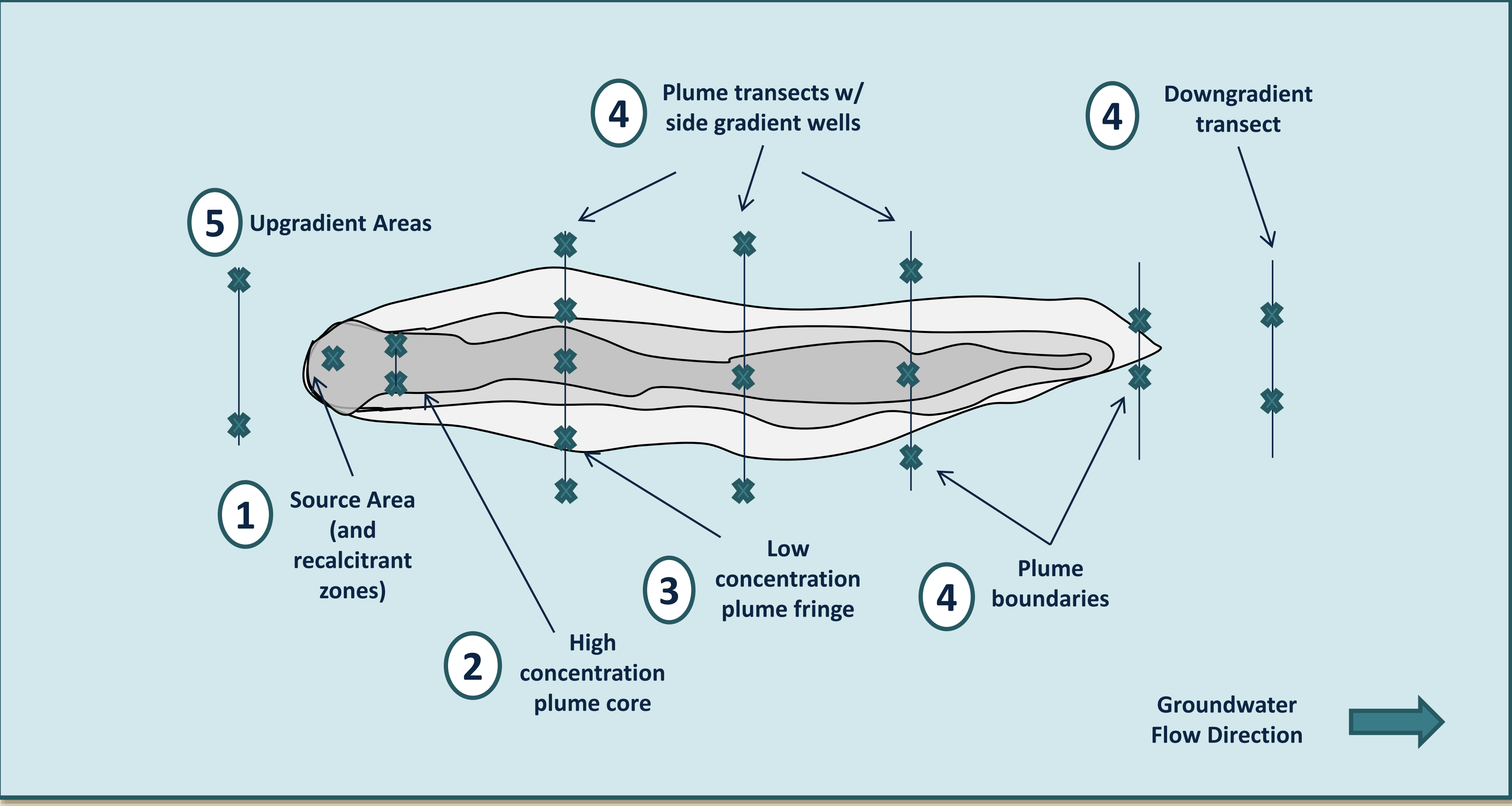
Objectives
Demonstrate that natural attenuation is occurring
Detect changes in conditions that reduce attenuation efficiency
Identify toxic/mobile by-products
Verify that plume is not expanding
Verify no impact to downgradient receptors
Detect new releases
Confirm institutional controls are working
Verify attainment of remedial objectives

Site-specific

REMEDIAL ACTION OBJECTIVES (RAOs)

PRELIMINARY REMEDIATION GOALS (PRGs)

Primarily based on sampling groundwater from monitoring wells



GOALS:

- Assess attenuation rates
- Monitor plume expansion or shrinkage at downgradient locations or transects
- Confirm no risk to receptor(s)
- Establish background, monitor for change in conditions or new releases

TYPICAL ANALYTES FOR LONG-TERM PERFORMANCE MONITORING

Constituents of Concern

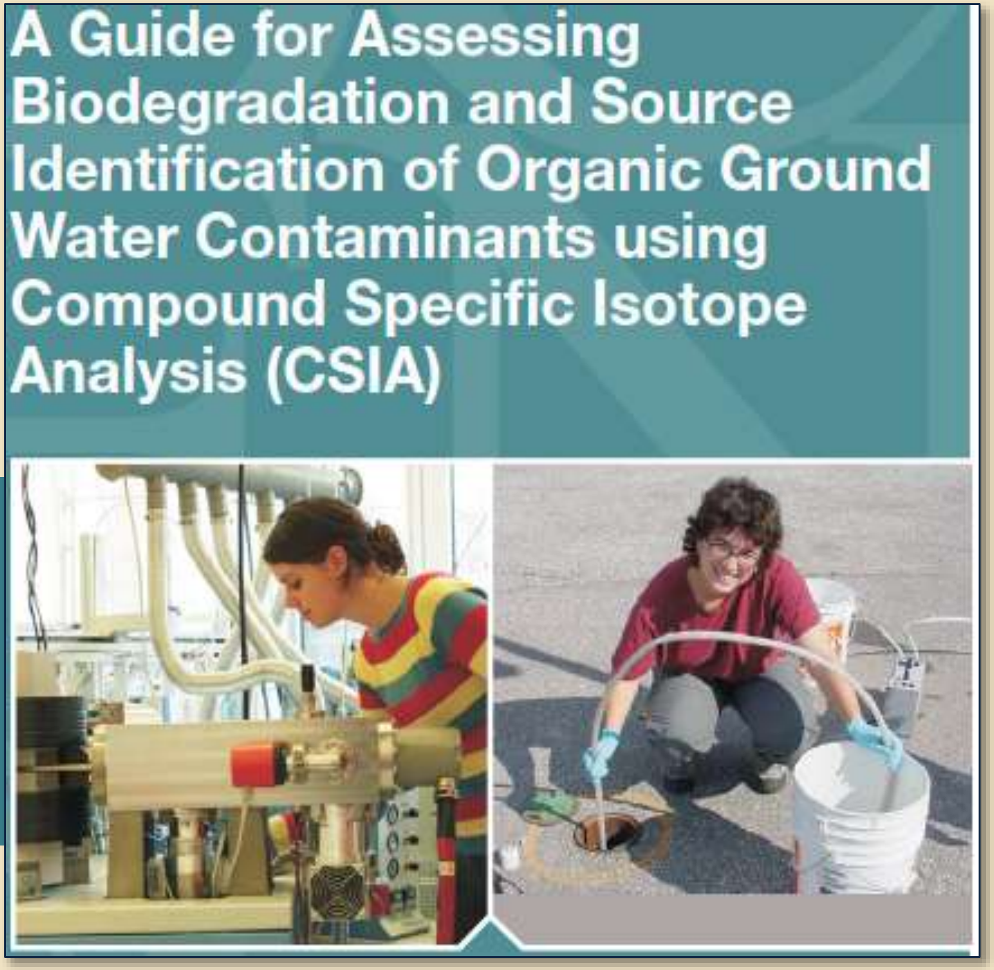
Transformation products: daughters products, metals (e.g., Cr, As)

Geochemical indicators: oxidation-reduction potential, pH, temperature, methane, sulfate, iron, nitrate

Others: water level, isotopes, biomarkers, minerals

ISOTOPE ANALYSIS: *Can they prove contaminants are being destroyed?*

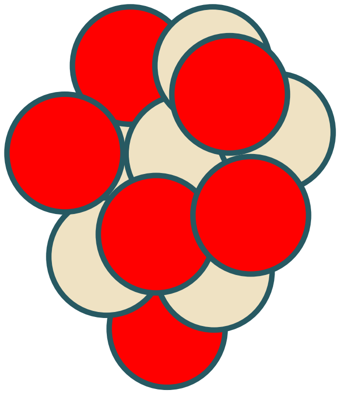
Yes, and more



"Stable isotope analyses can provide unequivocal documentation that biodegradation or abiotic transformation processes actually destroyed the contaminant."
USEPA, 2008

WHAT ARE STABLE ISOTOPES?

^{12}C

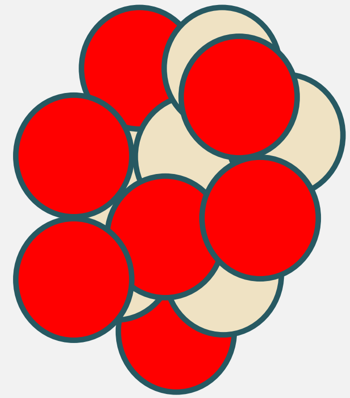


"LIGHT"

6 neutrons + 6 protons

Abundance = 98.9%

^{13}C



"HEAVY"

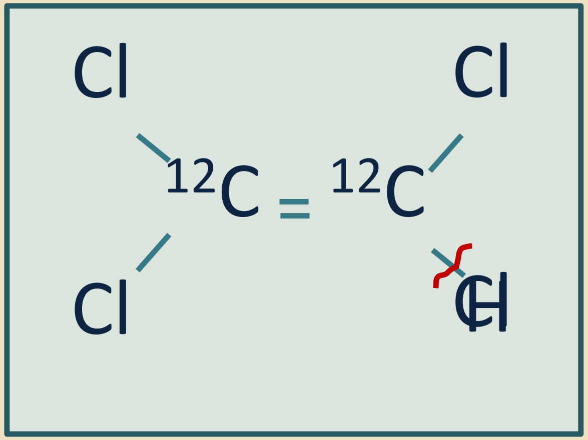
7 neutrons + 6 protons

Abundance = 1.1%

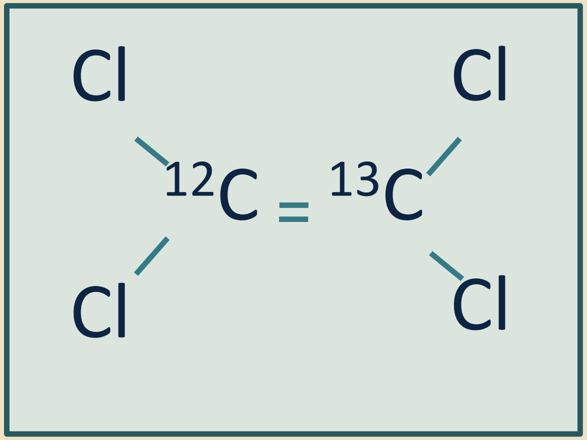
^{14}C is subject to radioactive decay and not considered stable

WHAT ARE "COMPOUND-SPECIFIC" STABLE ISOTOPES?

PCE



Lighter isotopes are degraded preferentially (more rapidly)



Degradation causes remaining PCE to become enriched in heavier isotope

Process is called FRACTIONATION – the isotopic ratio is changing due to degradation

HOW DO YOU EXPRESS ISOTOPIC DATA?

Ratio = R = (“heavy”) / (”light”)

e.g., (^{13}C) measured in TCE

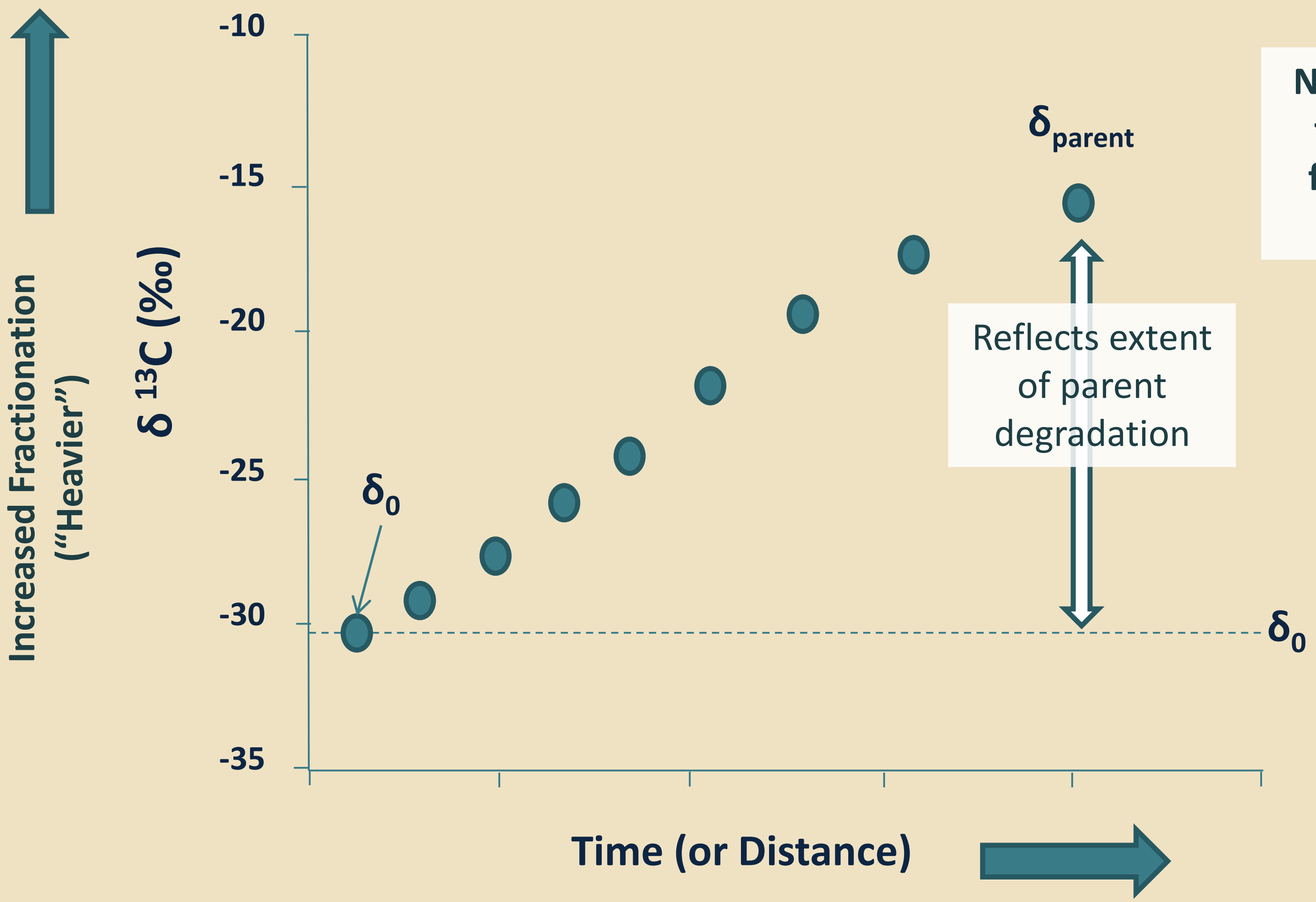
e.g., (^{12}C) measured in TCE

$$\delta_{TCE} = \text{“del”} = (R_{TCE} - R_{std})/(R_{std})*1000$$

Units are “per mil” or ‰

HOW TO USE CSIA:

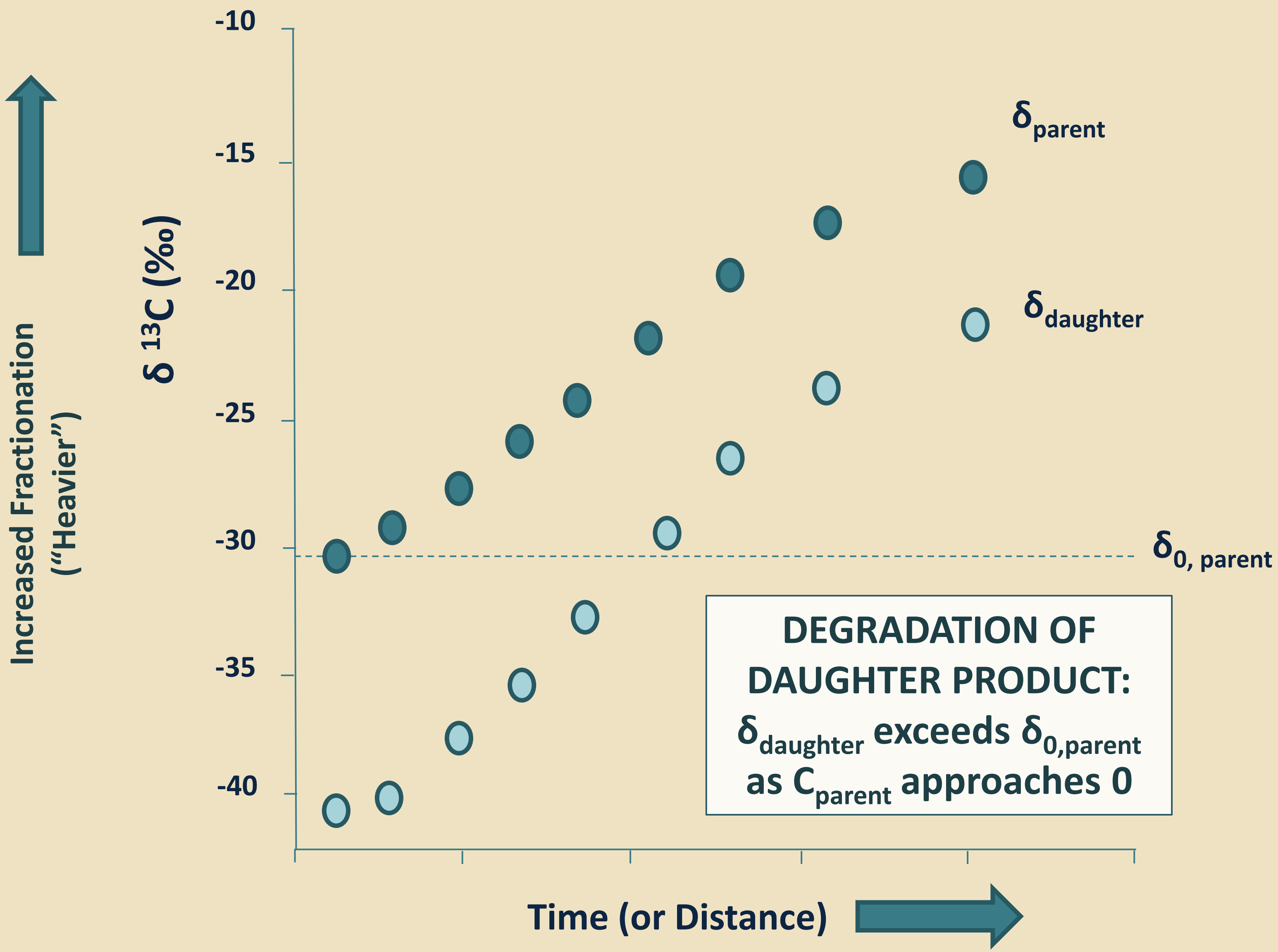
Evidence for degradation of parent compound



Need > 2‰ for to confirm C fractionation (EPA, 2008)

HOW TO USE CSIA:

Evidence for degradation of daughter compound



KEY BENEFITS OF CSIA

- Demonstrating that parent compound is being degraded
- Estimating the extent of degradation
- Differentiating between destructive and non-destructive pathways
- Differentiating between various destructive pathways
- Demonstrating that complete degradation has occurred
- Estimating rate of degradation
- Source identification and differentiation
- Can be incorporated into reactive transport modeling

carbon ($^{13}C/^{12}C$)
oxygen ($^{18}O/^{16}O$)
nitrogen ($^{15}N/^{14}N$)
chlorine ($^{37}Cl/^{35}Cl$)
hydrogen ($^{2}H/^{1}H$)

Easy protocol: collect groundwater from monitoring wells and send to lab

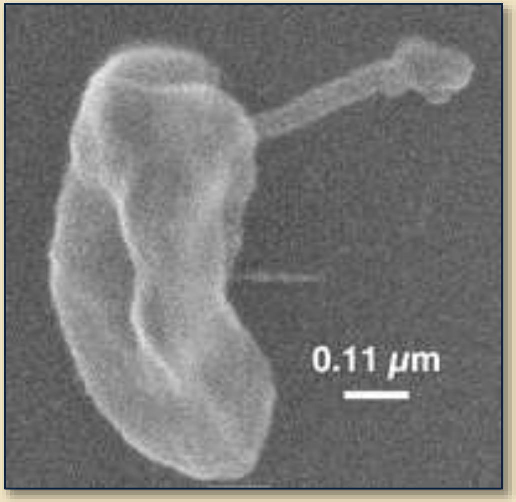
MOLECULAR BIOLOGICAL TOOLS: *Can they prove contaminants are being destroyed?*

MBTs provide strong, but not definitive evidence of MNA

1. **Show that key organisms are present (e.g., *Dehalococcoides*, *Dehalobacter*)**

2. **Show that key enzymes are present (e.g., *vcrA*, oxygenase-encoding genes)**

3. **Establish relative abundance of key microbial populations**



Our friend, Dehalococcoides (Apkarian and Taylor)

KEY ISSUE: **Most tests focus on presence, not activity!**

MOLECULAR BIOLOGICAL TOOLS:
How can they help me with MNA?

MOST POPULAR?

Evaluating chlorinated solvent degradation using PCR-based methods for tracking *Dehalococcoides (Dhc)*

Tools	MNA Application	MNA Limitations
PCR / qPCR	• Identify if key organisms / enzymes • Determine if abundance of key biomarkers is increasing	• Many techniques cannot differentiate between live and inactive cells • Attempts to correlate in situ activity and gene expression still in infancy • Target mostly well-known pathways (others in development)

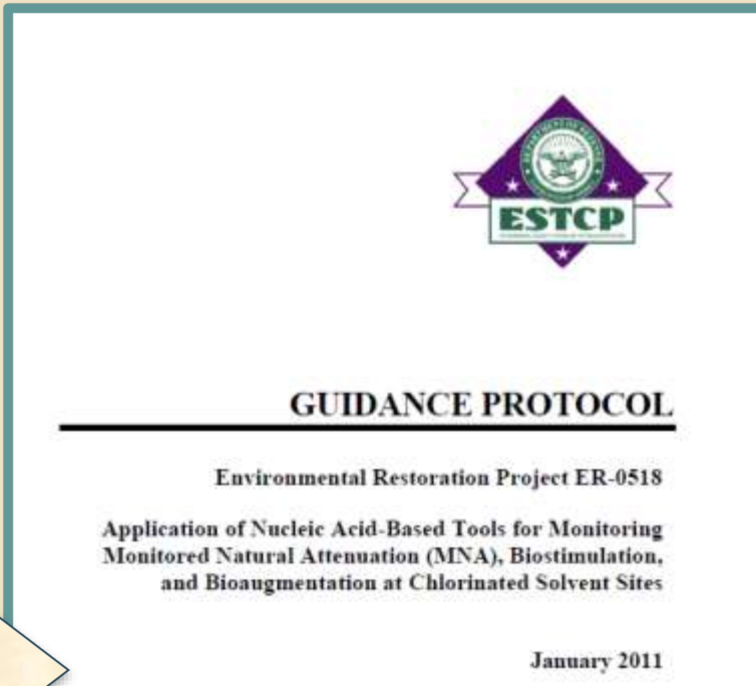
Others:

Stable Isotope Probing (SIP), microbial fingerprinting, microarrays, enzyme activity probes

MOLECULAR BIOLOGICAL TOOLS:
How to collect and use the data?

- **Groundwater or Soil using established procedures**
  - starting at about $200 per sample/target)

- **Quantitative Rules for MNA.**
  - Specific recommendations for MNA
  - Lu et al., 2006: "generally useful" attenuation rates of *cis*-1,2-DCE and VC (> 0.3/yr) were associated with sites where *Dhc* was detected, while no attenuation was observed at sites where it was absent


ESTCP

GUIDANCE PROTOCOL

Environmental Restoration Project ER-0518

Application of Nucleic Acid-Based Tools for Monitoring Monitored Natural Attenuation (MNA), Biostimulation, and Bioaugmentation at Chlorinated Solvent Sites

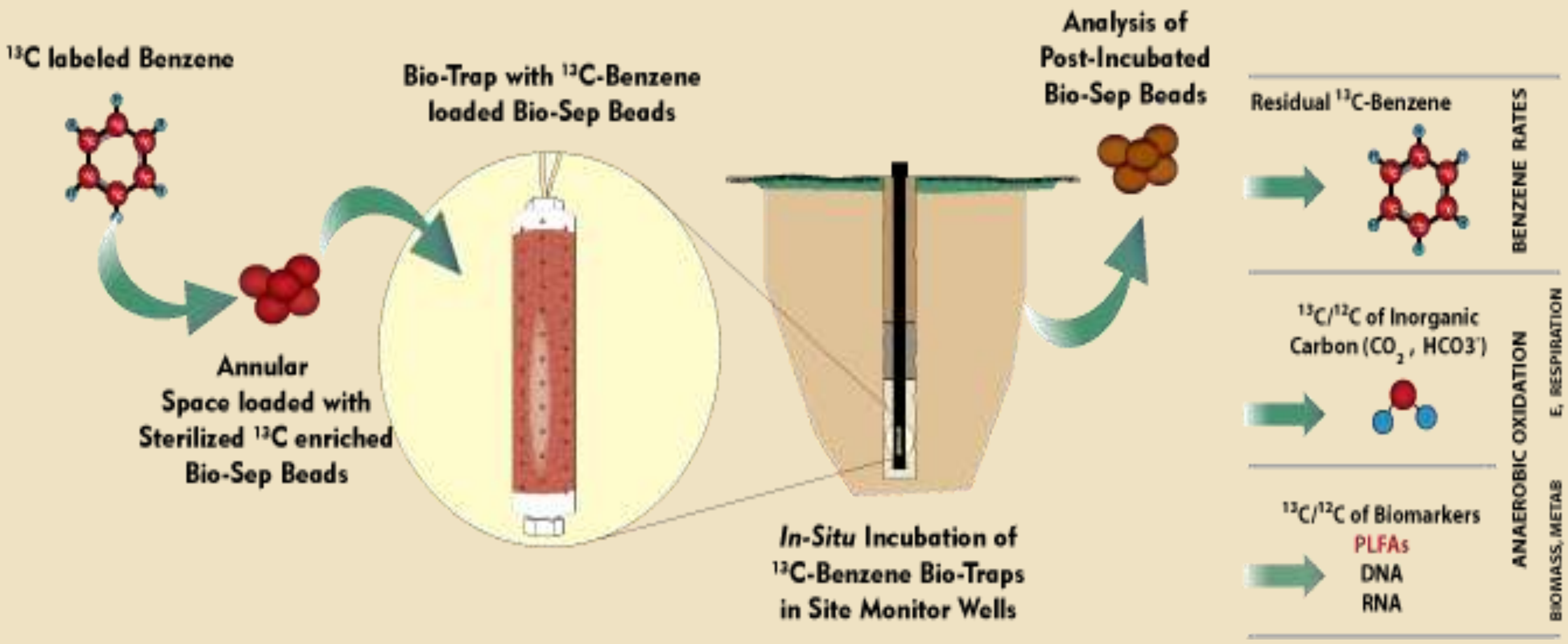
January 2011

- ***Dhc*** **at 10^4 to 10^6 gene copies/L can support MNA**
- ***Dhc*** **at > 10^6 gene copies/L is the target threshold for ensuring ethene production**

Guidance also included in "BioPIC" discussed later in this presentation

STABLE ISOTOPE PROBING: *Combo method that's increasingly being used for MNA*

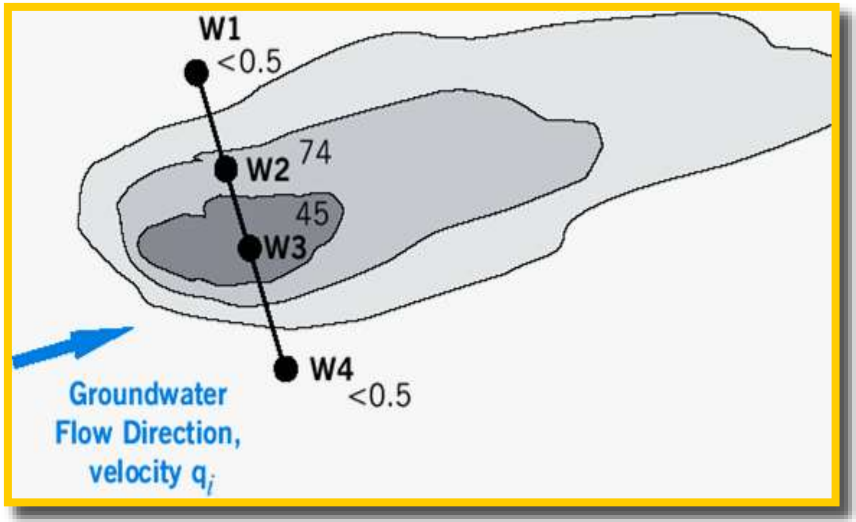
TYPICAL APPLICATION: "Passive microbial sampling devices", e.g., BioTraps, are installed in monitoring well for 30 days or more



Graphic courtesy of Microbial Insights:
http://www.microbe.com/stable-isotope-probing-sip-bio-trap-samplers/

Calculating Mass Discharge: Transect Method Simple Example

Nichols and Roth, 2004



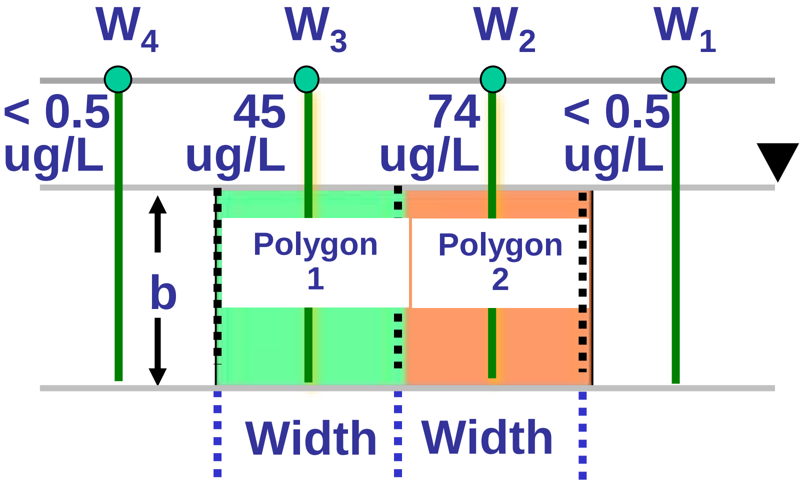
Step-by-step approach assuming uniform groundwater velocity

1. Characterize plume (C)
2. Characterize flow (q)
3. Draw transect: with simple approach, just build cross-sectional polygons ("window panes") for each well across flow
4. Determine area (W • b = A)
5. Multiply and sum together:

$$M_d = \Sigma (C_n \cdot A_n \cdot q)$$

M_d = Mass discharge
C_n = concentration in polygon n
A_n = Area of segment n

CROSS-SECTION



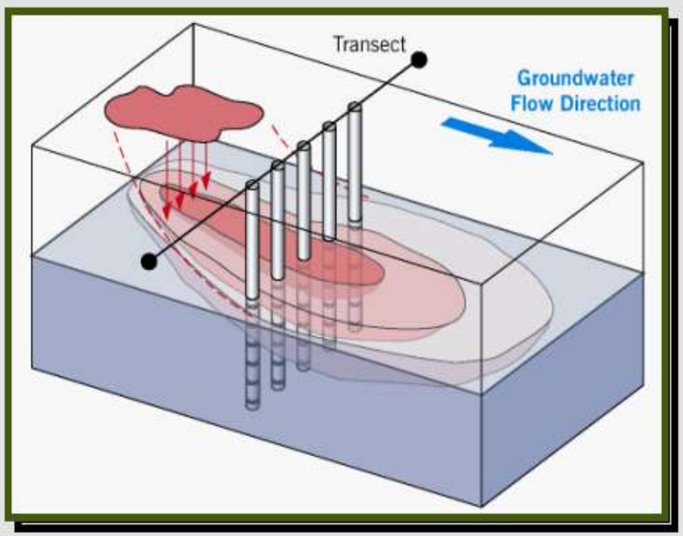
Tools for Transect Method: Calculator

Lead author: Shahla Farhat, Ph.D.
free at www.gsi-net.com
Microsoft Excel-based

ESTCP

Mass Flux Toolkit

To Evaluate Groundwater Impacts, Attenuation, and Remediation Alternatives



Calculate Flux

Impact of Flux

Learn About Flux

About | Help

Version 1.0 Beta

Input Data and Grid

Data Input Instructions:

10.80 → Enter value directly.

10.80 → Value calculated by model.

Site Location and I.D.: Texas

Description: MTBE

4. CHOOSE TRANSECT Transect 1

5. CHOOSE TIME PERIOD 1

6. ENTER TRANSECT DATA

Distance of Transect 1 from Source → 193 (ft)

○ Darcy Velocity ◉ Hydraulic Conductivity

◉ Sampling Interval ○ Mid Point of Sampling Interval

Hydraulic Conductivity Units: cm/sec

Uniform Hydraulic Conductivity? Yes → Hydraulic Conductivity 3.20E-02 (cm/sec)

Uniform Hydraulic Gradient? Yes → Hydraulic Gradient 2.00E-03 (cm/cm)

	Monitoring Point	Distance from Edge of Transect (ft)	Sampling Interval (ft bgs)		Plume Top (ft bgs)	Plume Bottom (ft bgs)	Concentration (mg/L)	
			Top	Bottom			Constituent A	Constituent B
							MTBE	
1	TR1-2	10	5	10	5	15	2.3	
2	TR1-2	10	10	15	5	15	0.47	
3	TR1-4	27.5	5	10	5	20	19.7	
4	TR1-4	27.5	10	15	5	20	7.2	
5	TR1-4	27.5	15	20	5	20	0.34	
6	TR1-6	45	5	10	5	20	87.2	
7	TR1-6	45	10	15	5	20	35.6	
8	TR1-6	45	15	20	5	20	9.5	
9	TR1-8	62.5	5	10	5	20	54.1	
10	TR1-8	62.5	10	15	5	20	15.3	
11	TR1-8	62.5	15	20	5	20	0.67	
12	TR1-12	80	5	10	5	15	4.5	
13	TR1-12	80	10	15	5	15	5.6	
14								
15								

7. CHOOSE GRID

Orig mean cell width (x-axis) (ft) 14.0 → Refine cell width by 1

Orig cell thickness (y-axis) (ft) 1.5 → Refine cell thickness by 1

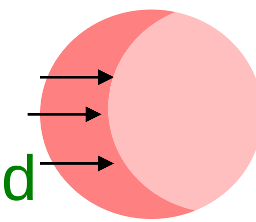
8. SELECT CONSTITUENT FOR CALCULATIONS

◉ MTBE ○ Constituent B

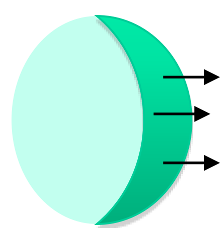
Next Step: Complete Grid | Go Back | Clear Screen | Paste Example | See Saved Grids | Print | HELP

Method 3 – Passive Flux Meter

- Permeable sorbent
  - Accumulates contaminant based on flow and concentration



- Soluble tracers
  - Loses tracer based on groundwater velocity and flux convergence calculations



1. Contaminant adsorbed onto passive flux meter over time to get Concentration

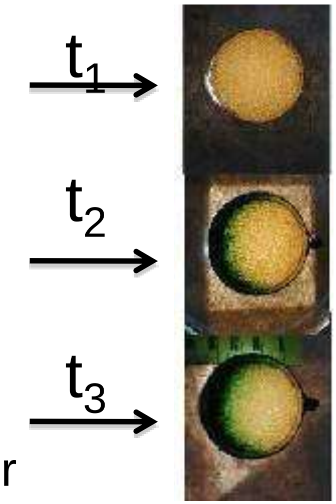
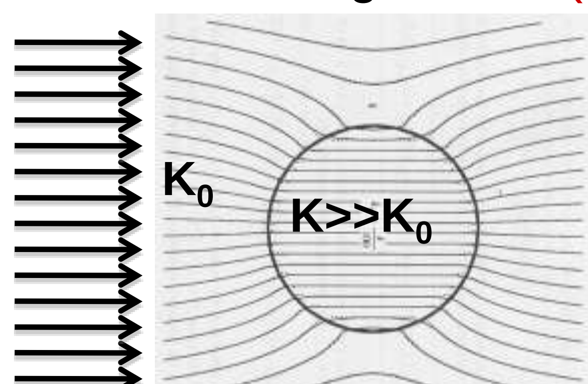


Photo: Dye intercepted in a meter

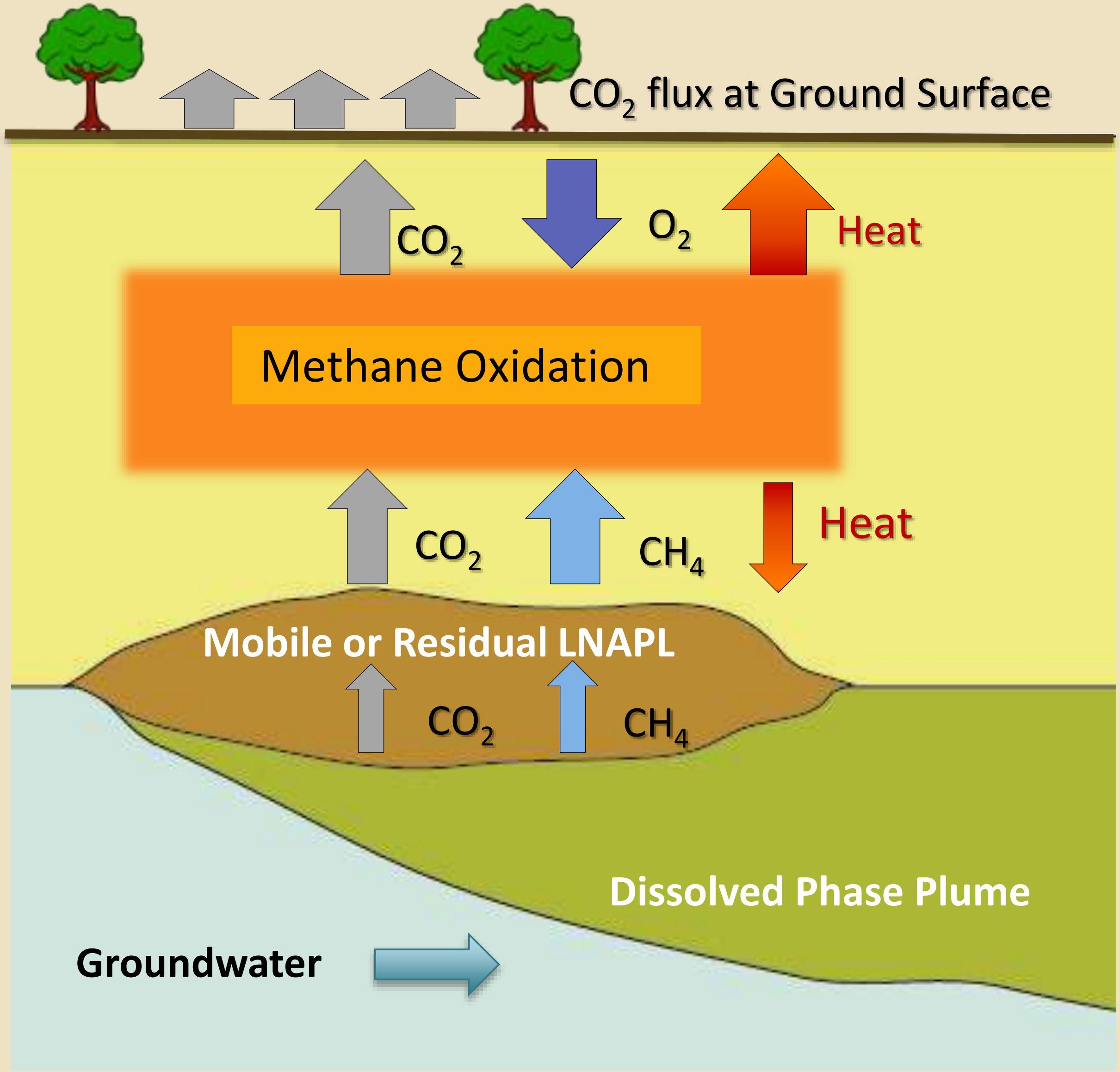
2. Tracer desorbs from passive flux meter over time to get Flow (Q)



Groundwater Flowlines

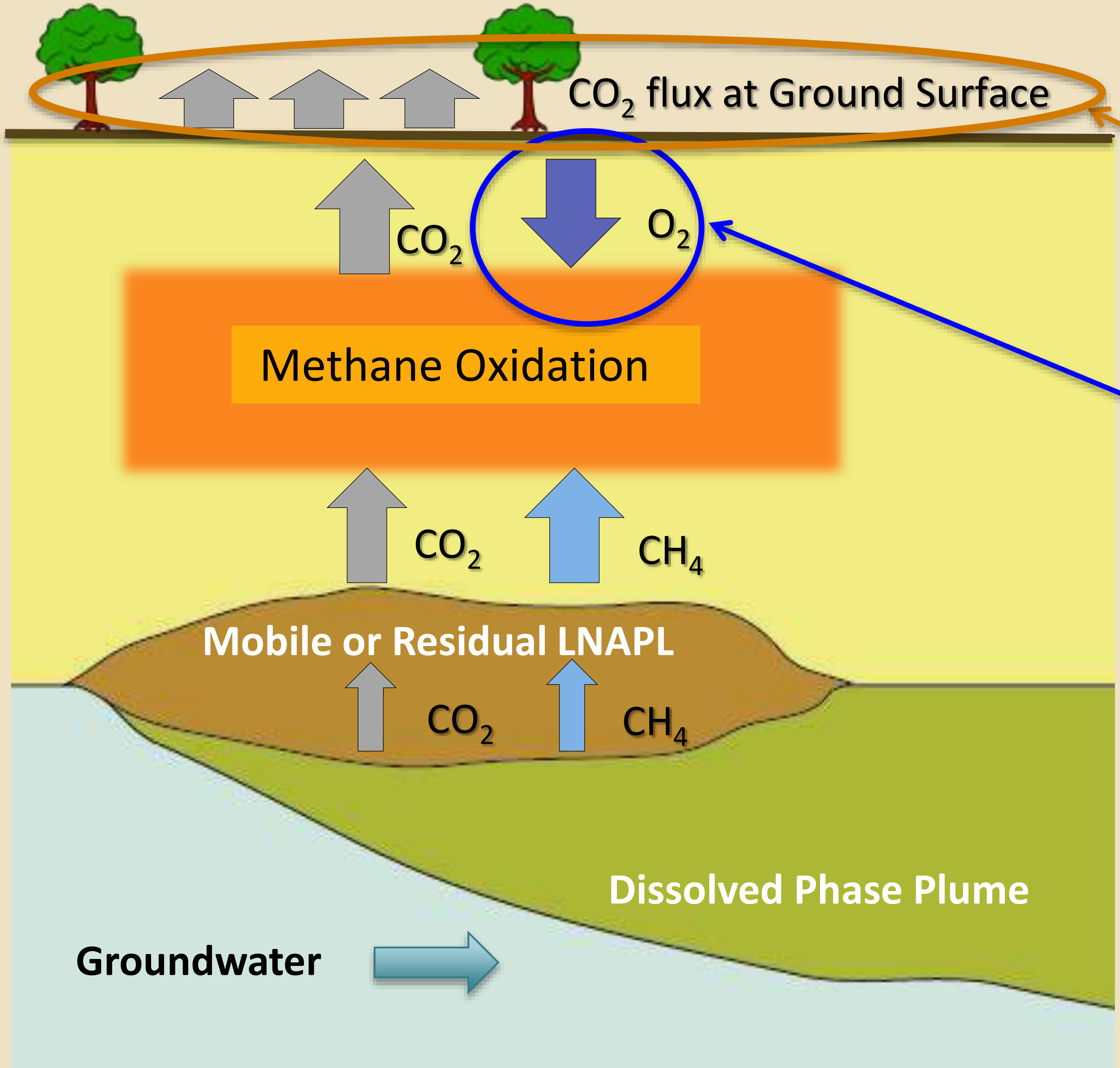
Source: Hatfield and Annable

CURRENT NATURAL SOURCE NSZD CONCEPTUAL MODEL



Adapted from: CSU, 2016

CURRENT NATURAL SOURCE NSZD CONCEPTUAL MODEL

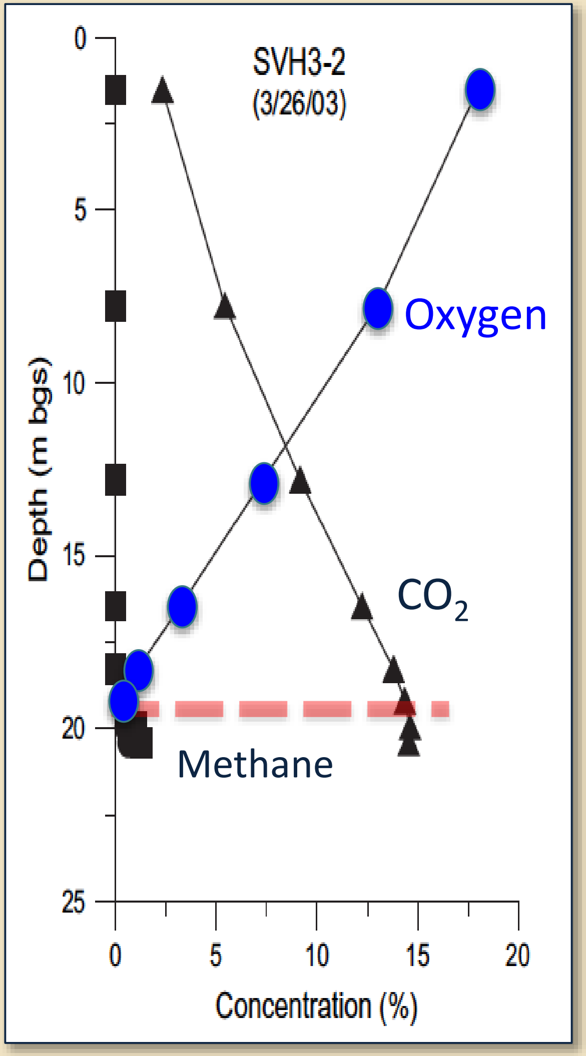


CO_2 Flux Measurement at Surface

Measure Inward Diffusion of Oxygen

Adapted from: CSU, 2016

NSZD STUDIES: *Johnson et al, 2006; Lundegard and Johnson, 2006; Sihota et al., 2011; McCoy et al., 2013*



Lundegard and Johnson, 2006


EFLUX
Easy set-up. Expert results.

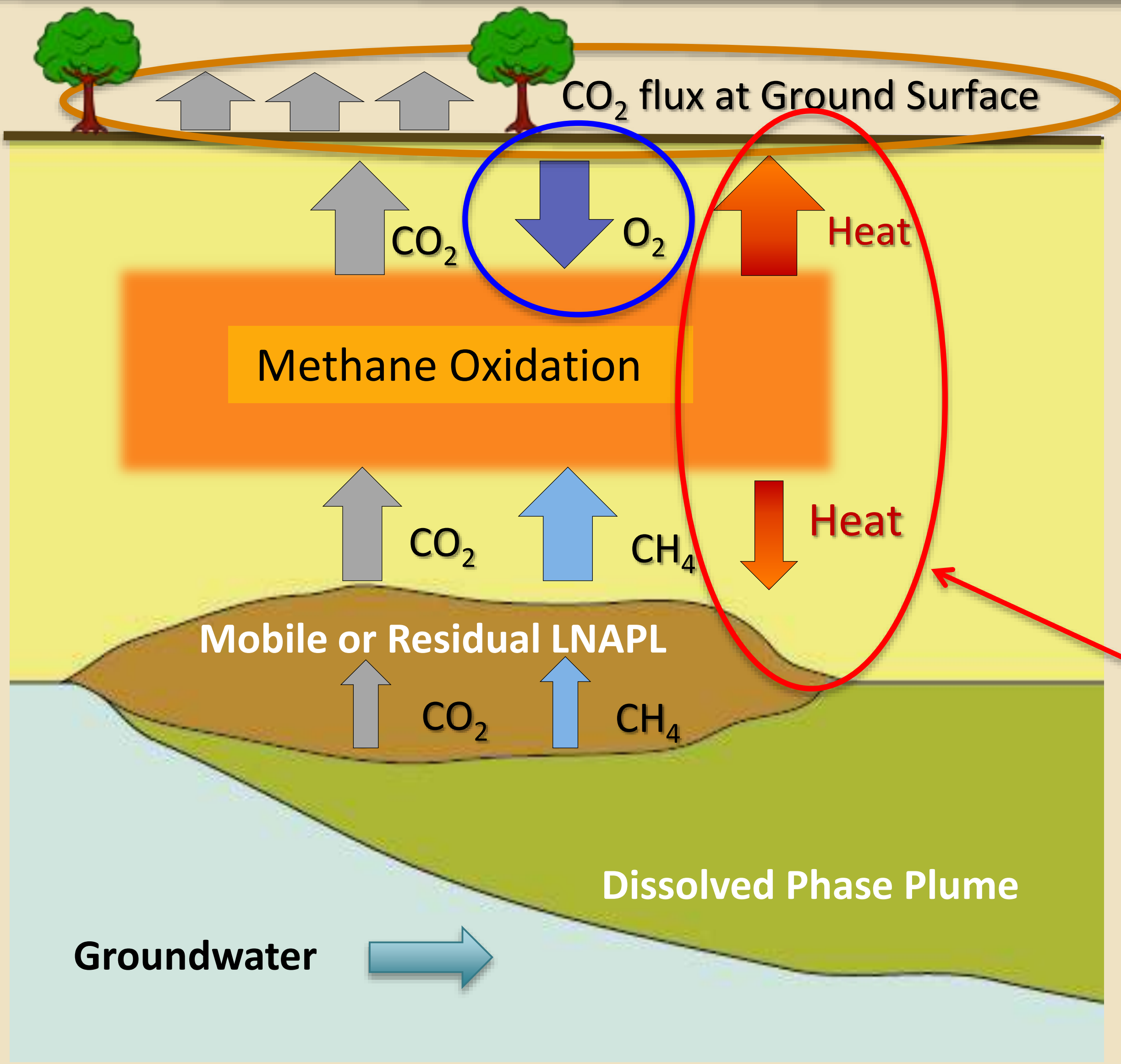
WHAT NSZD RATES ARE BEING OBSERVED?

NSZD Study	Site-wide NSZD Rate (gallons/ acre /year)
Six refinery terminal sites (McCoy et al., 2012)	2,100 – 7,700
1979 Crude Oil Spill (Sihota et al., 2011)	1,600
Refinery/Terminal Sites in Los Angeles (LA LNAPL Wkgrp, 2015)	1,100 – 1,700
Five Fuel/Diesel/Gasoline Sites (Piontek, 2014)	300 - 3,100
Eleven Sites, 550 measurements (Palia, 2016)	300 – 5,600 (median: 700)

Locations across U.S. where carbon traps have been used to measure NSZD rates (E-Flux, 2015).

KEY POINT: **Measured NSZD rates in the 100s to 1000s of gallons per acre per year.**

CURRENT NATURAL SOURCE NSZD CONCEPTUAL MODEL



CO_2 Flux Measurement at Surface

Measure Inward Diffusion of Oxygen

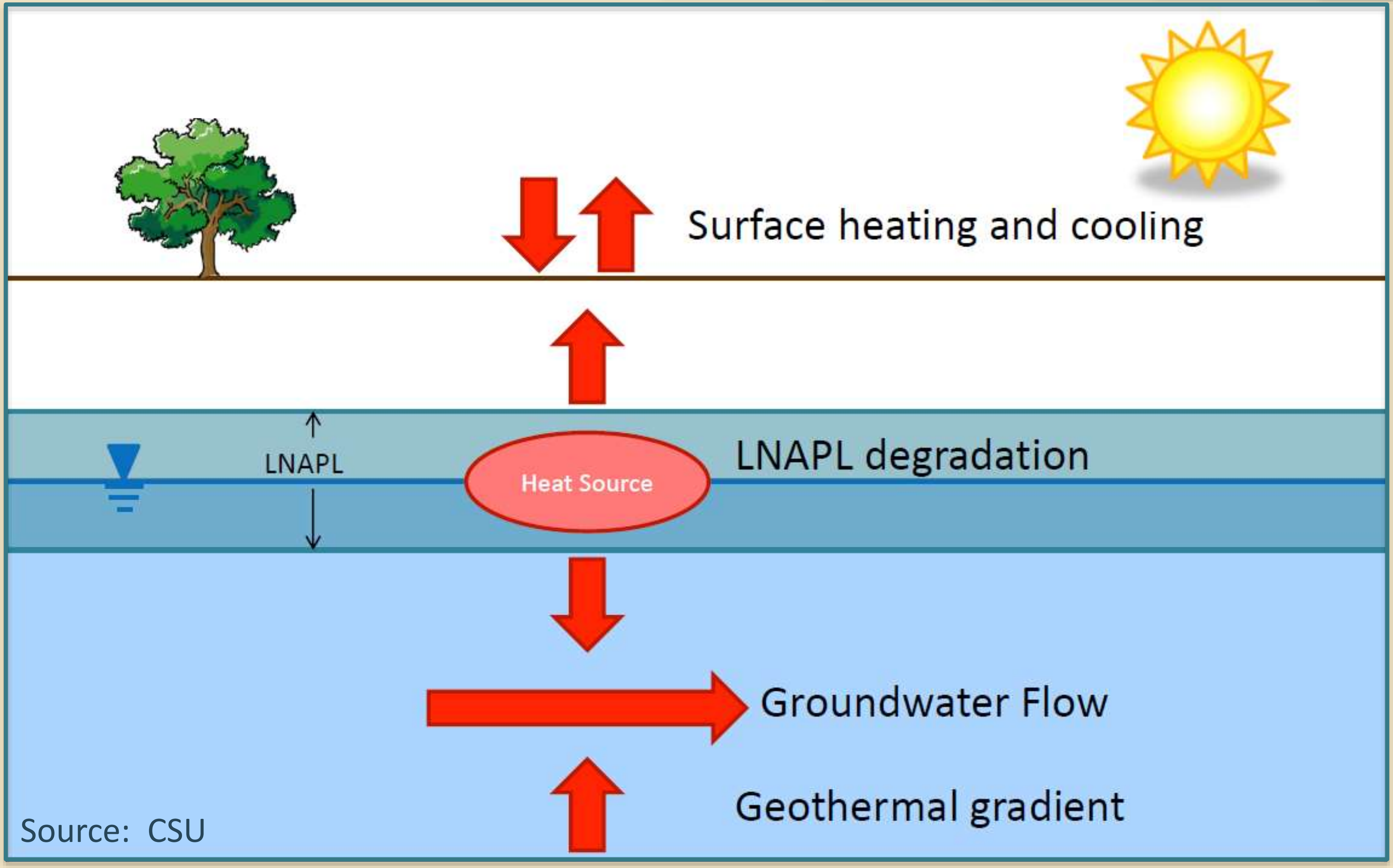
Subsurface Temperature Measurement

Adapted from: CSU, 2016

HEAT RELEASED FROM BIODEGRADATION

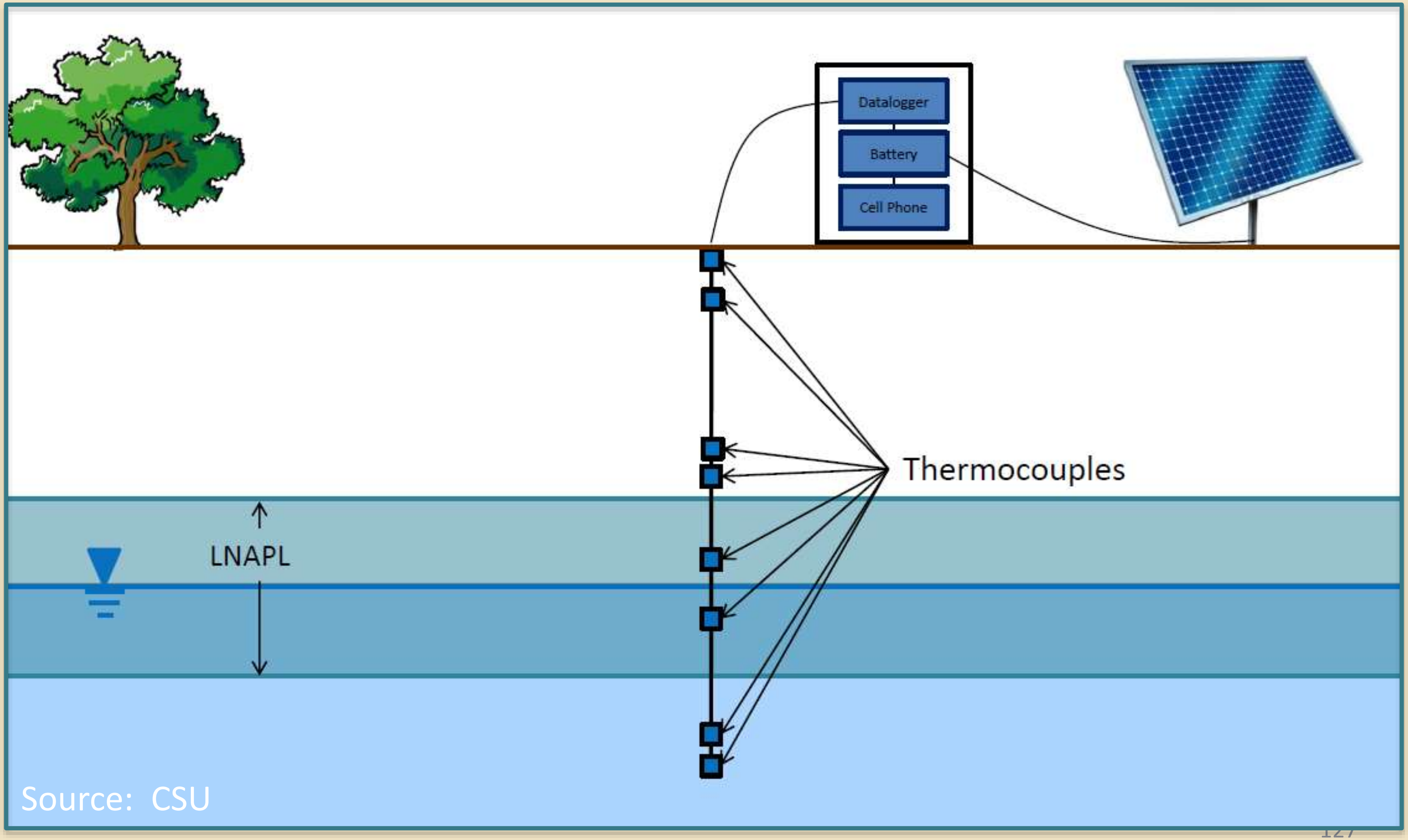
Key Objective: Use heat released from biodegradation to calculate continuous estimates of NSZD rates.

CONCEPTUAL MODEL

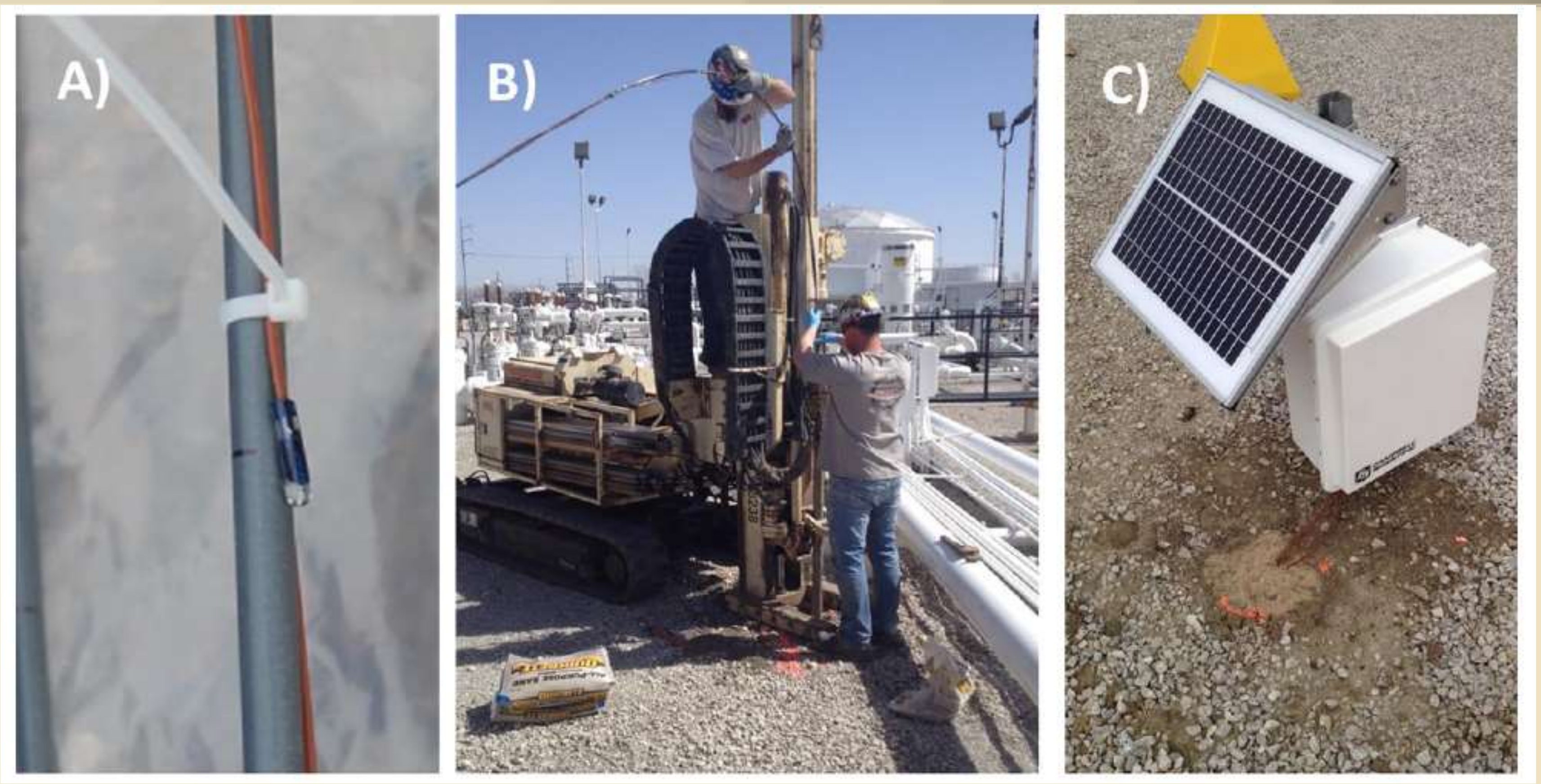


Source: CSU

FIELD INSTALLATION: *Thermal Monitoring System*



FIELD INSTALLATION: *Thermal Monitoring System*



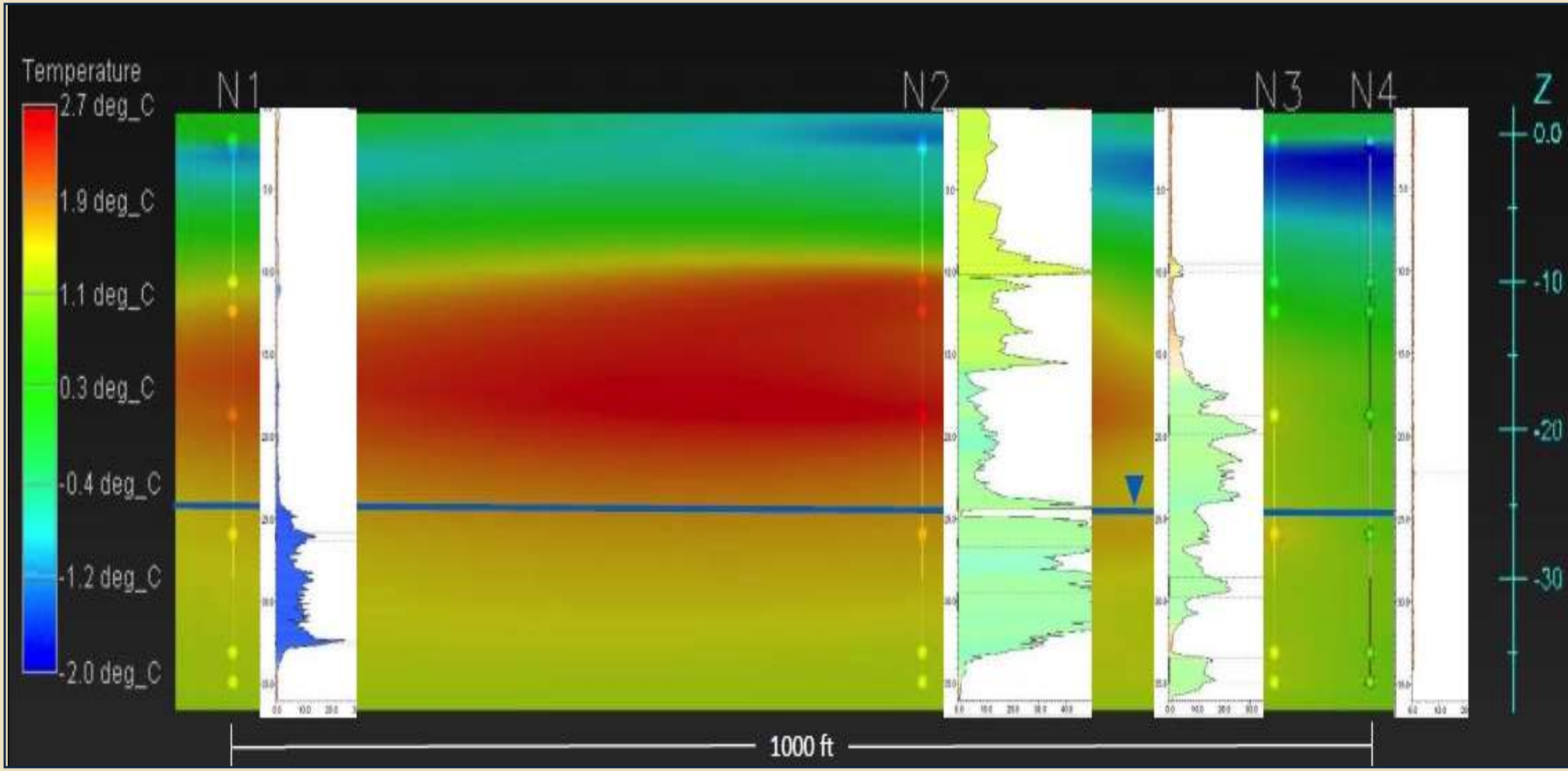
Thermocouple on temperature monitoring "stick"

Installation of stick using direct push rig.

Solar power supply and weatherproof box with data logger and wireless communications system.

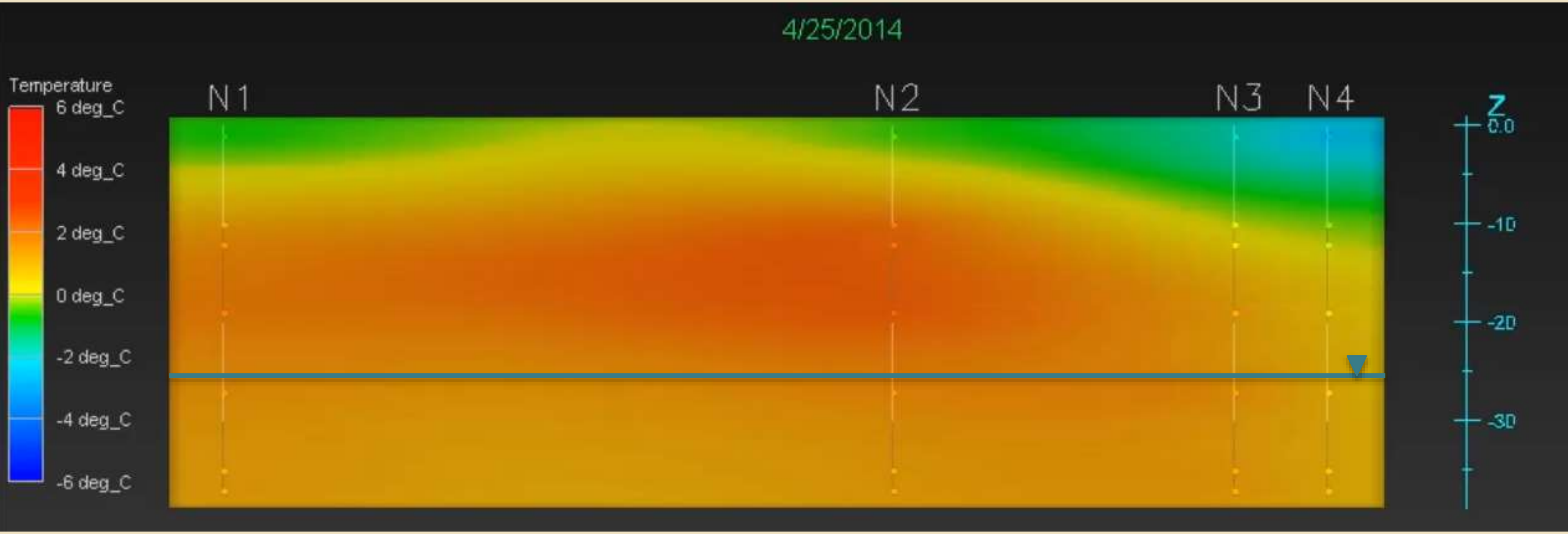
Source: CSU

Background on Corrected Temperature
(Stockwell, 2015 Colorado State)



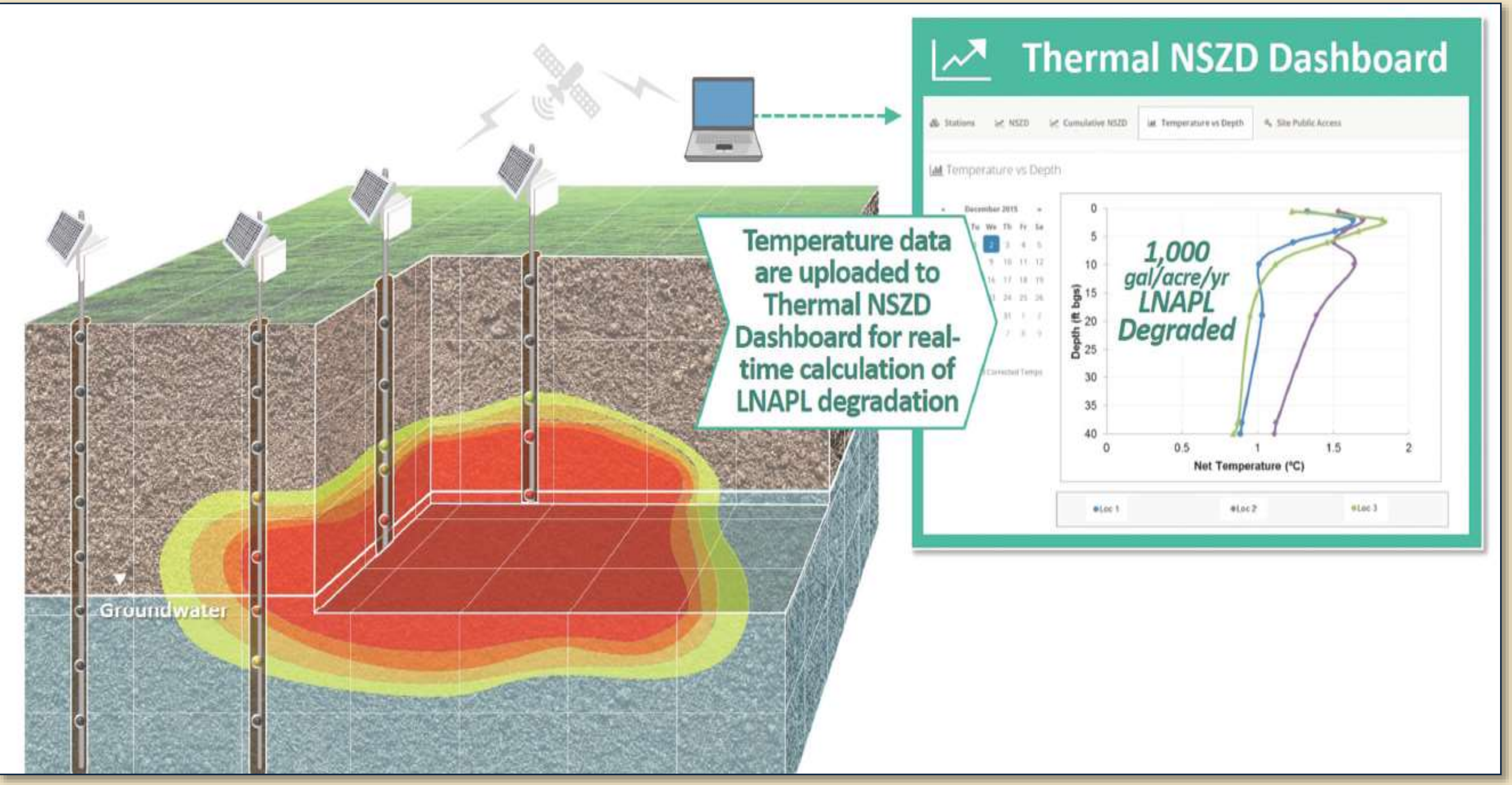
Most of heat released by methane oxidation (conversion to CO_2) in vadose zone, not by the methane generation itself

HEAT SIGNAL OVER TIME: *Kansas Tank Farm*



Source: Stockwell, 2015; Colorado State University

THERMAL NSZD DASHBOARD



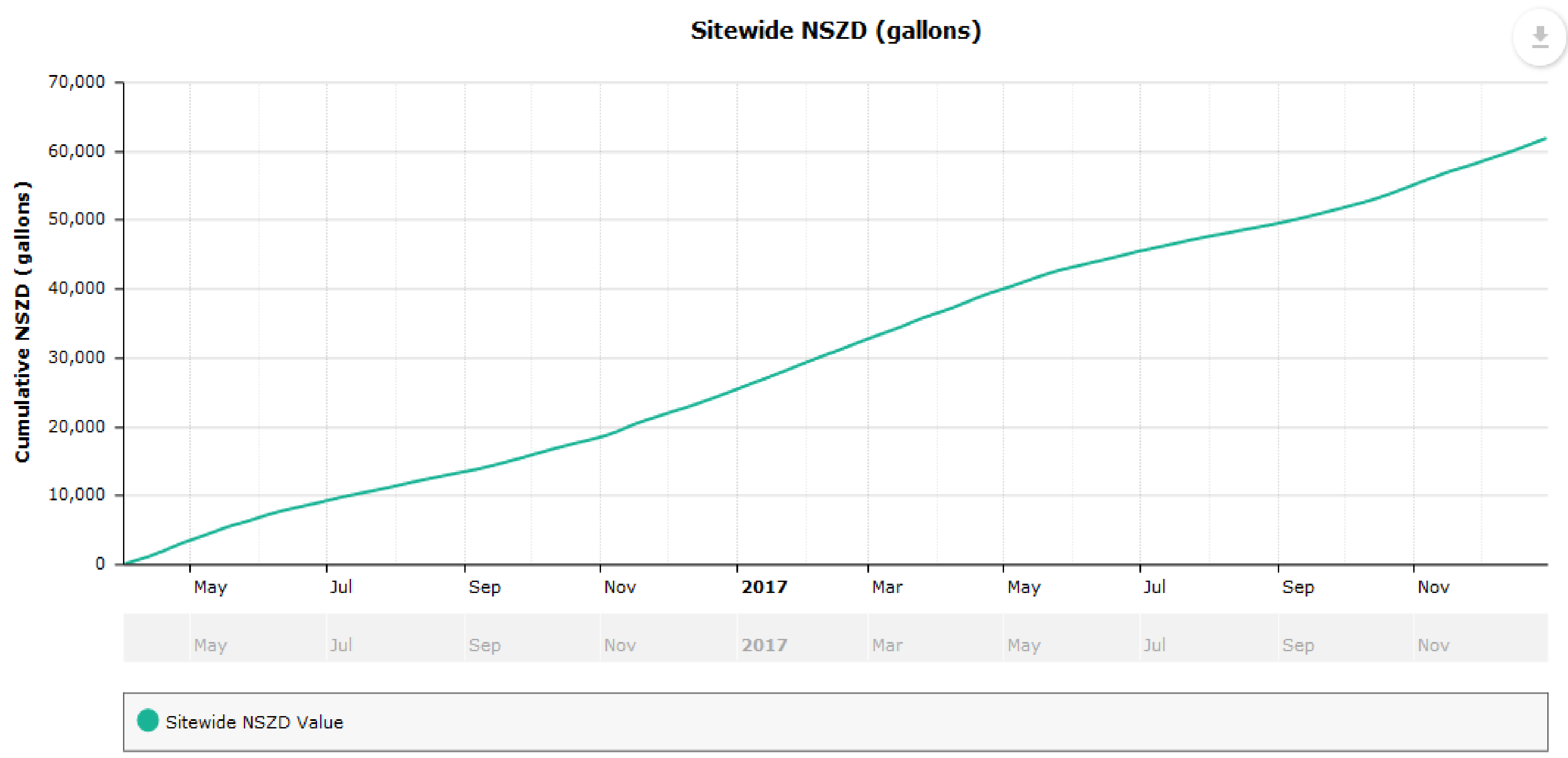
www.ThermalNSZD.com

THERMAL NSZD DASHBOARD:

Cumulative Sitewide NSZD Updated Daily

Amount of LNAPL Degraded Since NSZD Monitoring Began: 61,966 gallons LNAPL

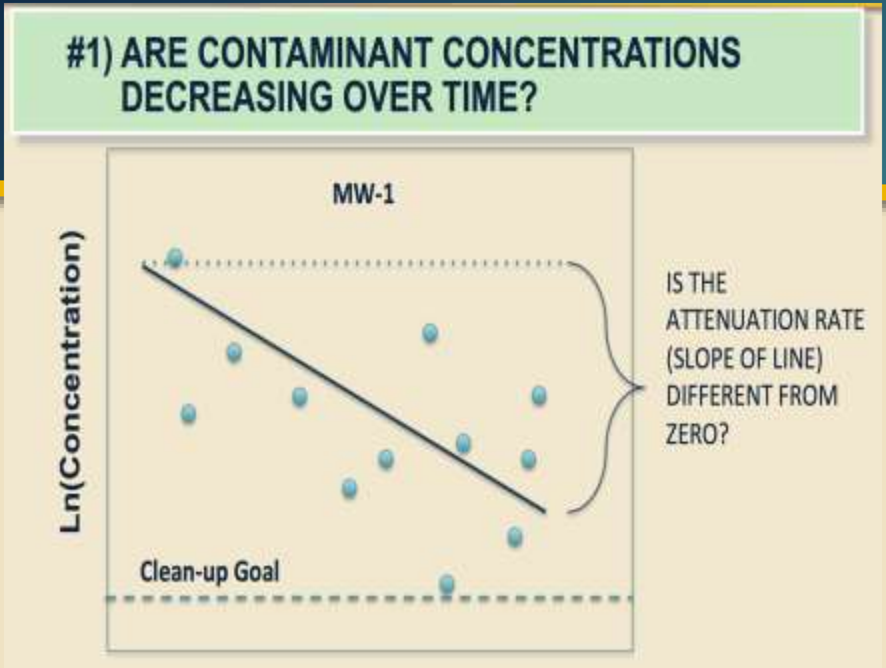
Natural Source Zone Depletion Rate Over Past 30 Days: 518 gallons/acre/year

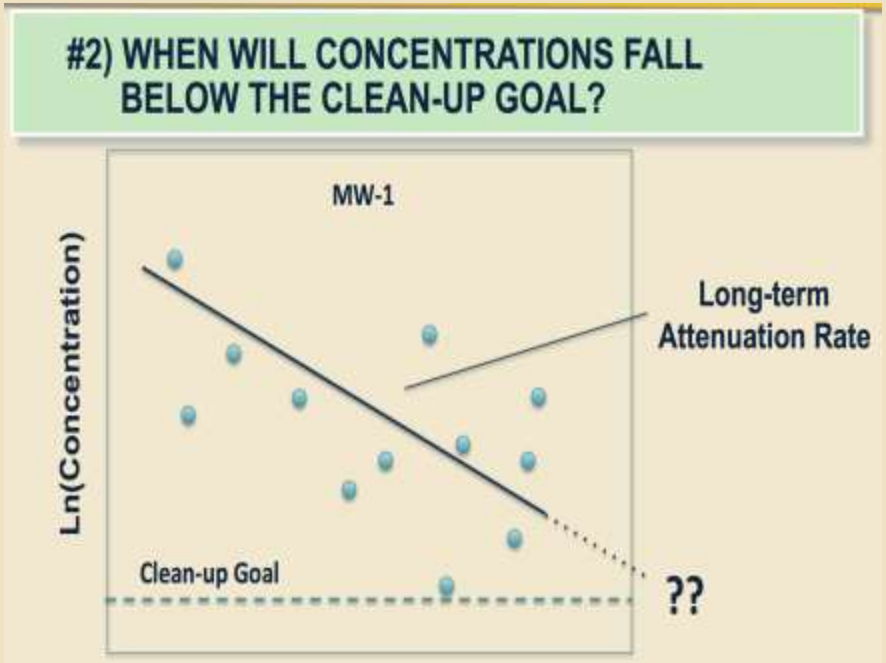


ROAD MAP

- **Intro: Changing Paradigms and MNA Principles**
- **Key Attenuation Processes**
  - *Biodegradation*
  - *Abiotic Processes*
  - *LNAPL source zone degradation processes*
  - *Other processes (immobilization, storage, dilution)*
- **Field Techniques and Technologies**
  - *Groundwater sampling and analytical methods*
  - *Compound Specific Isotopes Analysis (CSIA)*
  - *Molecular Biological Tools (MBTs)*
  - *Natural Source Zone Depletion (NSZD)*
- **Should MNA be Used? Data Analysis and Monitoring Tools**
  - *Data requirements, LTM, and statistics to understand MNA rates*
  - *Common Graphics and Calculations*
  - *Remediation Timeframe Calculations*
  - *Computer Models*
- **Implementation Topics**

WHY DO WE NEED TREND ANALYSIS?

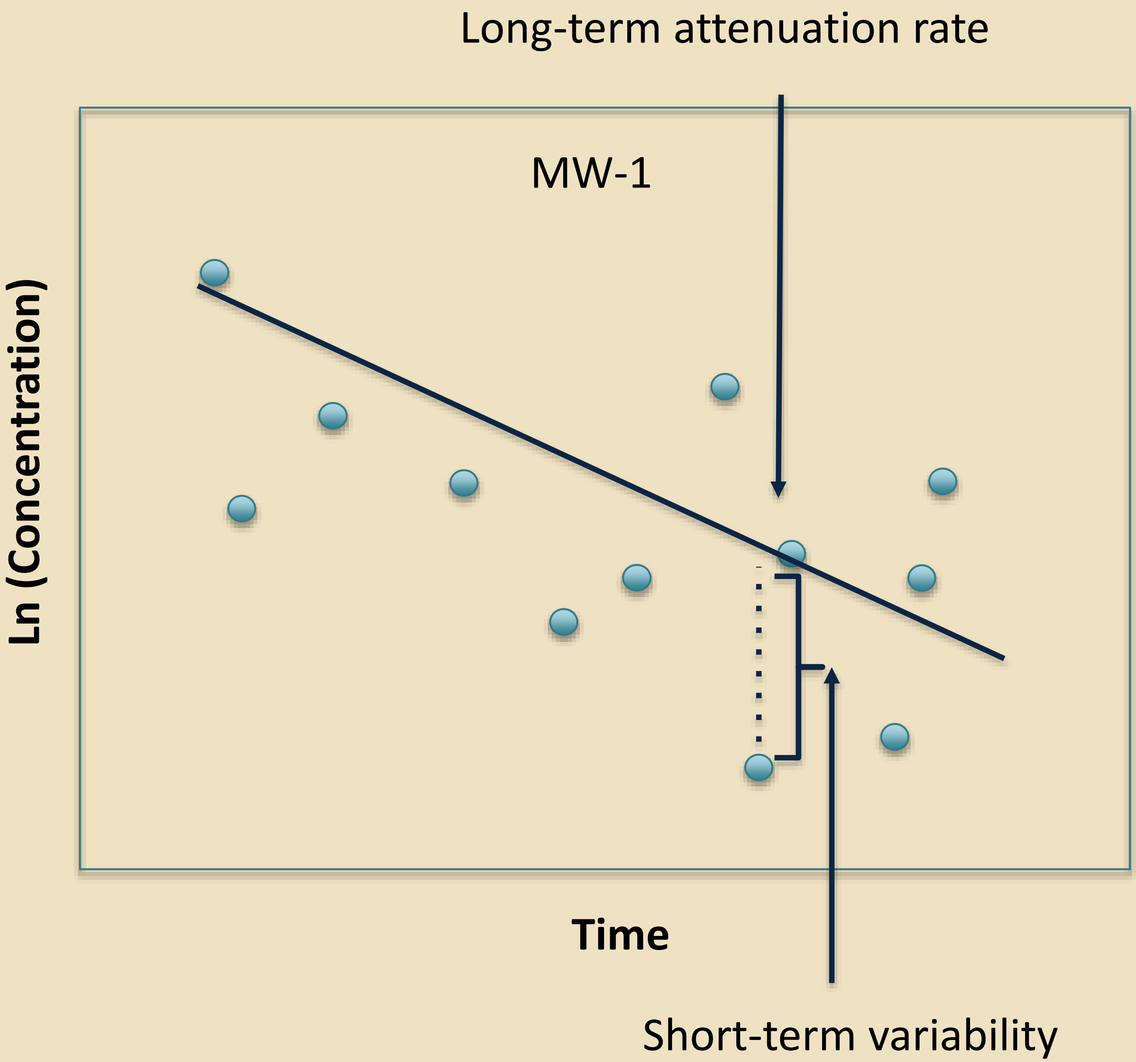




- **Answers important questions!**
- **Short-term variability can make this challenging, so need statistical methods**
- **Linear regression has limitations**

Source: **McHugh et al., 2015**

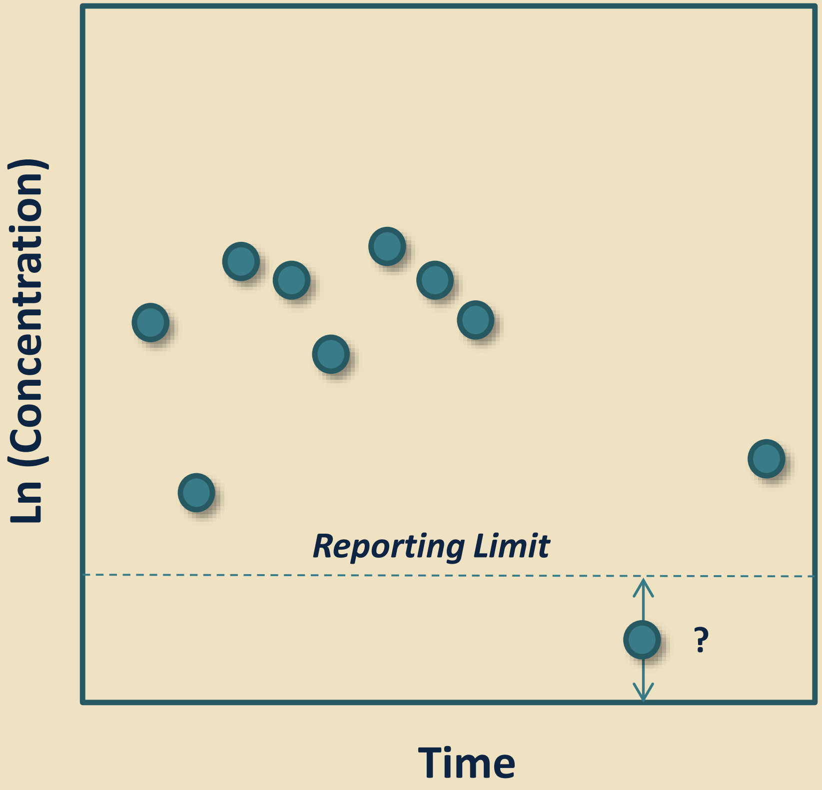
LONG-TERM ATTENUATION RATES VS. SHORT-TERM VARIABILITY



KEY POINTS:

- Short-term variability makes it harder to determine trend and increases the amount of monitoring needed to evaluate progress in remediation
- Long-term trend apparent over longer monitoring period

WHY SHOULD WE USE MANN-KENDALL FOR TREND ANALYSIS?



- Mann-Kendall only cares about relative magnitudes of the concentrations, not the actual concentrations
- Easier to establish trend even with a modest slope
- Non-detects are more easily handled
- Simple method – can use existing software tools

HOW DO YOU PERFORM MANN-KENDALL ANALYSIS?

CALCULATE 3 DIFFERENT METRICS	
S Statistic (S)	Test statistic; indicates if trend is increasing (positive S) or decreasing (negative S)
Confidence Factor (CF)	Reflects degree of confidence in result; equivalent to (1-*p*)
Coefficient of Variation (COV)	Reflects variability in concentration vs. t data; used to distinguish between "stable" and "no trend"

For description of how each are calculated, see User's Guide for Mann-Kendall Toolkit (GSI, 2012): Also see MAROS (www.gsi-net.com/en/software)

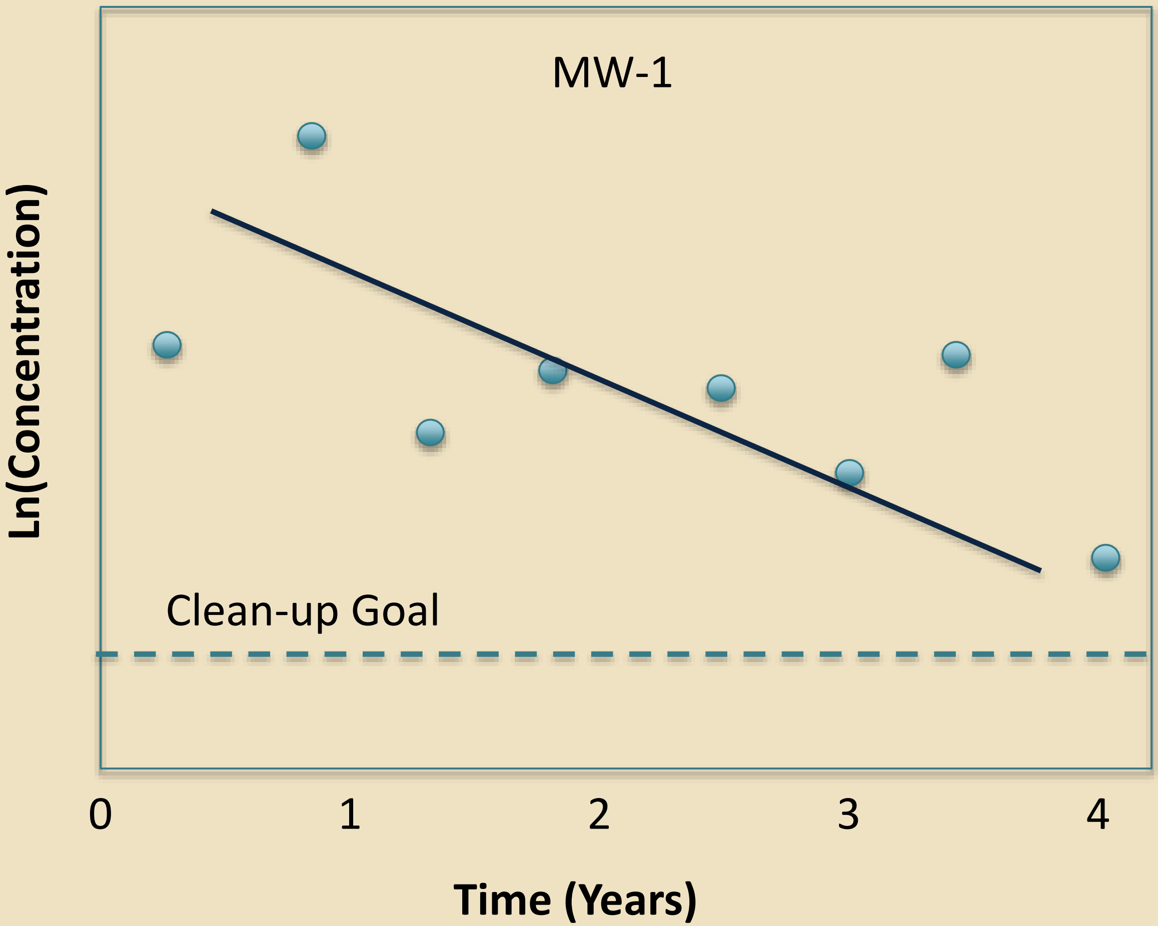
HOW DO YOU PERFORM MANN-KENDALL ANALYSIS?

S Statistic	Confidence in Trend	Trend
S > 0	CF > 95%	Increasing
S > 0	95% ≥ CF ≥ 90%	Probably Increasing
S > 0	CF < 90%	No Trend
S ≤ 0	CF < 90% and COV ≥ 1	No Trend
S ≤ 0	CF < 90% and COV < 1	Stable
S < 0	95% ≥ CF ≥ 90%	Probably Decreasing
S < 0	CF > 95%	Decreasing

2 other options: ND = locations w/ all non-detect values
N/A = locations w/ < 4 datapoints

HOW DOES MONITORING FREQUENCY AFFECT CONFIDENCE AND ACCURACY OF THE RATE?

Eight Semiannual Monitoring Events



Increasing the time between monitoring events will increase the CONFIDENCE and ACCURACY of your long-term attenuation rate…

But by how much?

HOW MUCH DATA IS NEEDED TO DEFINE TREND WITH CONFIDENCE AND ACCURACY?

Accuracy/Confidence Cost
Medium Confidence: Statistically-significant; decreasing concentration trend ($p < .1$) for 80% of monitoring wells
Medium Accuracy: Determine the long-term attenuation rate with an accuracy (i.e., 95% confidence interval) of +/- 50% or +/- 0.1 yr^{-1} (whichever is larger) for 80% of monitoring wells

20 sites were examined to see how much data was needed to meet these thresholds

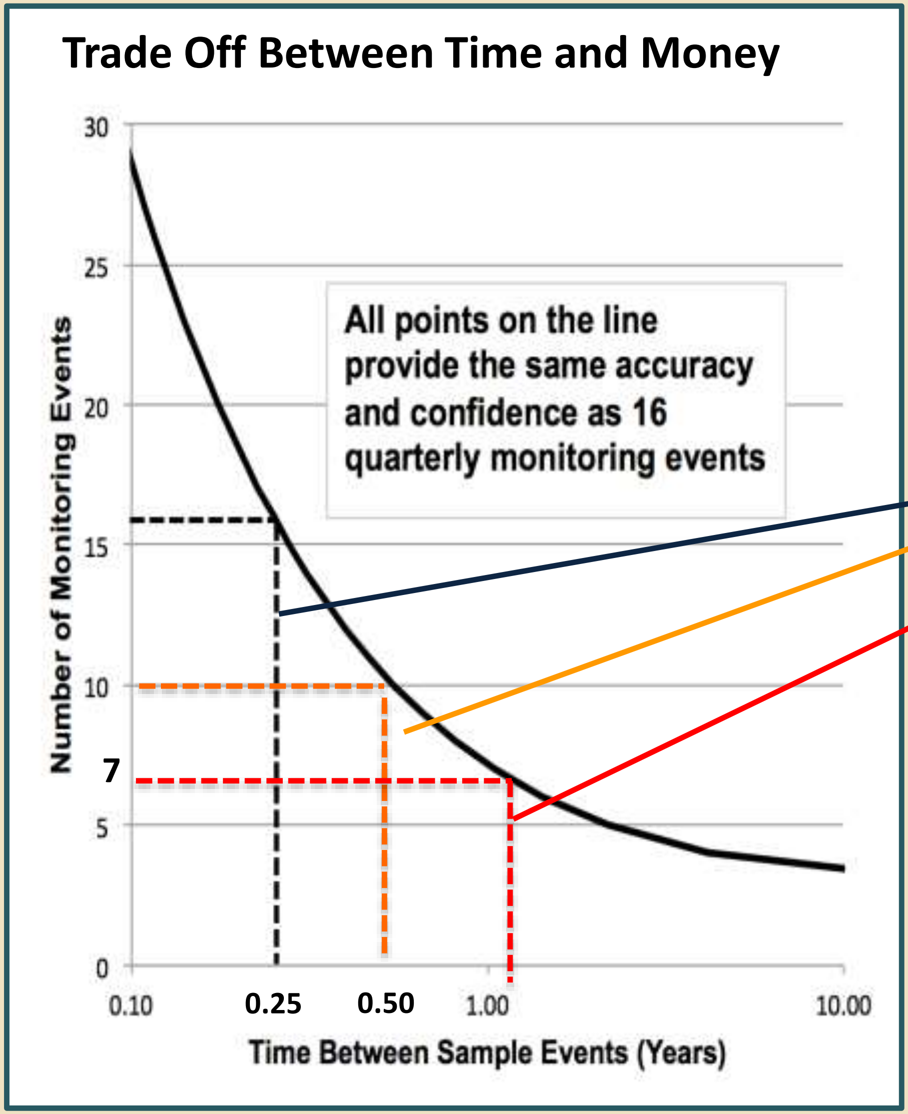
HOW MUCH DATA IS NEEDED TO DEFINE TREND WITH CONFIDENCE AND ACCURACY?

Accuracy/Confidence Cost	Best Site	Median Site	Worst Site
Medium Confidence: Statistically-significant; decreasing concentration trend ($p < .1$) for 80% of monitoring wells	2.8 years	7.3 years	30 years
Medium Accuracy: Determine the long-term attenuation rate with an accuracy (i.e., 95% confidence interval) of +/- 50% or +/- 0.1 yr^{-1} (whichever is larger) for 80% of monitoring wells	4.0 years	7.4 years	14.5 years

HOW MUCH DATA IS NEEDED TO DEFINE TREND WITH CONFIDENCE AND ACCURACY?

1) It commonly takes **seven years or more of quarterly monitoring data** to characterize the attenuation rate with even a medium level of accuracy (i.e., +/- 50%).
2) Making decisions (e.g., remedy effectiveness; remediation timeframe) based on insufficient data can result in incorrect decisions.

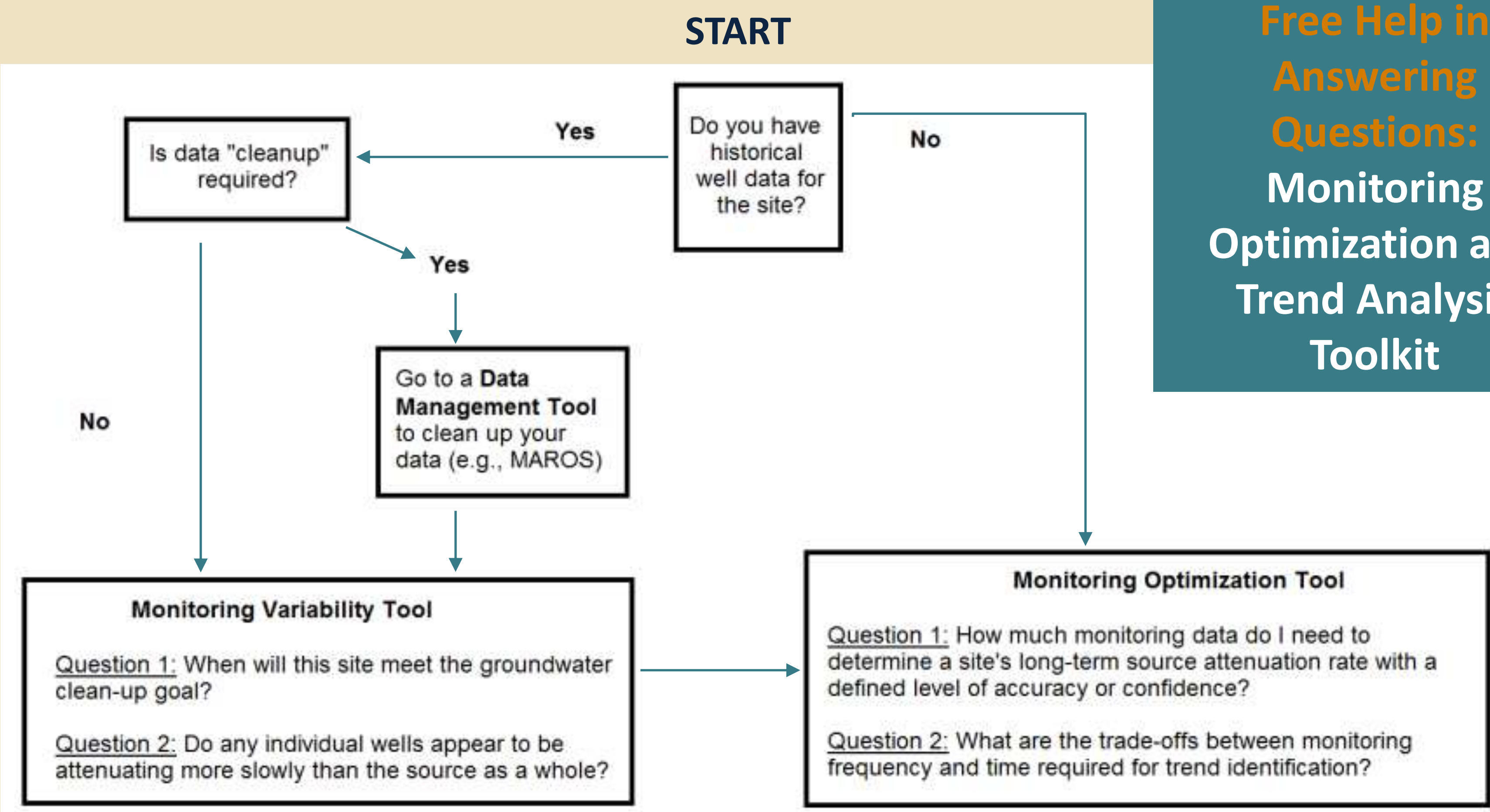
WHAT IS THE TRADE-OFF BETWEEN MONITORING FREQUENCY AND DURATION?



The answer is the same

4 yrs quarterly monitoring
5 yrs semiannual monitoring
7 yrs annual monitoring

WHAT IS THE TRADE-OFF BETWEEN MONITORING FREQUENCY AND DURATION?



Free Help in Answering Questions:
Monitoring Optimization and Trend Analysis Toolkit

EXAMPLE

Monitoring Optimization – Question #2:

What are the trade-offs between monitoring frequency and time required for trend identification

Option	Sample Frequency	Total Sampling Events	Cost Per Well ($K)
Option 1:	Sample weekly for 1.6 years	82	123
Option 2:	Sample monthly for 2.7 years	33	49
Option 3:	Sample quarterly for 4.1 years	16	25
Option 4:	Sample semiannually for 5.0 years	10	15
Option 5:	Sample annually for 6.5 years	7	10
Option 6:	Sample every 2 years for 9.0 years	5	7
Option 7:	Sample every 5 years for 18.4 years	4	6

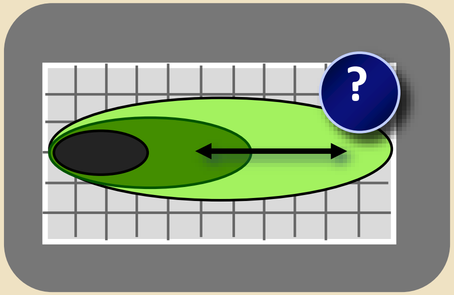
MONITORING REQUIREMENTS: *KEY POINTS*

- Short-term variability makes it harder to determine trend and increases the amount of monitoring needed to evaluate progress in remediation
- It commonly takes seven years or more of quarterly monitoring data to characterize the attenuation rate with even a medium level of accuracy
- Less frequent monitoring over longer periods of time may be more cost appropriate for determining trends during MNA

PRIMARY LINES OF EVIDENCE:
Mass Loss and Plume Stability

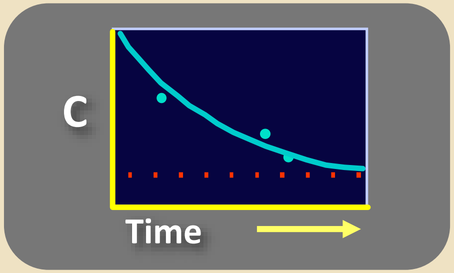
WHAT?

Define groundwater plume status as *stable, shrinking, or expanding.*



HOW?

Evaluate historical concentration measurements in groundwater.



WHEN?

Always apply based on sufficient historical data.

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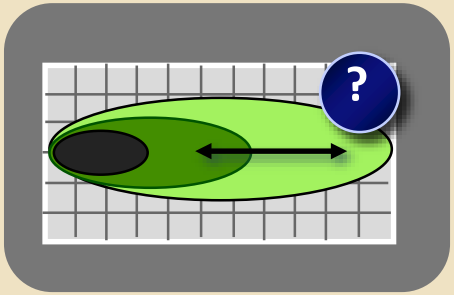

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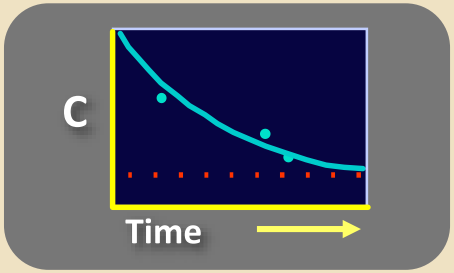

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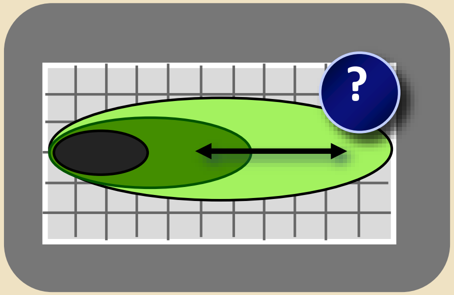

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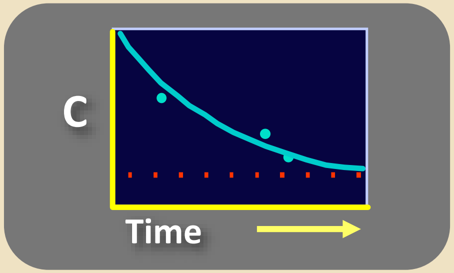
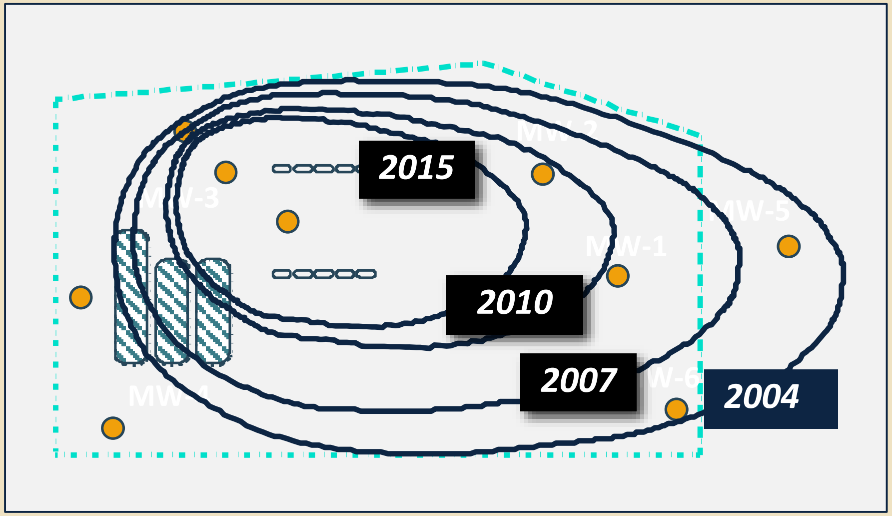


WHEN?

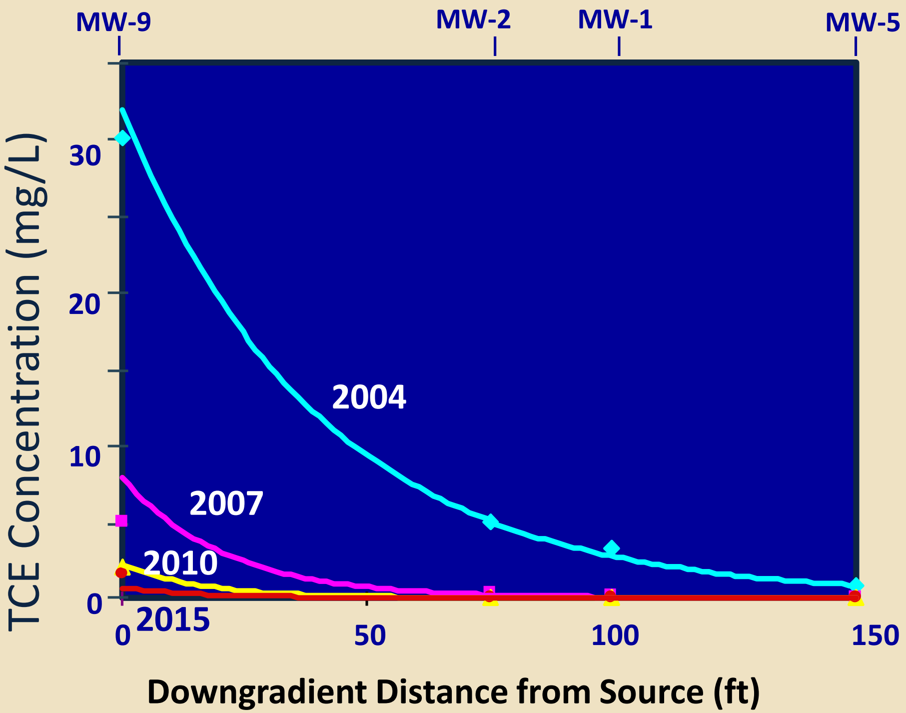
Always apply based on sufficient historical data.

LINE OF EVIDENCE 1: *Demonstrate Mass Loss, Plume Stability With Two Common Graphs*

Plume Outer Contour vs. Time



Concentration vs. Distance at Different Times



DEMONSTRATE MASS LOSS AND PLUME STABILITY:

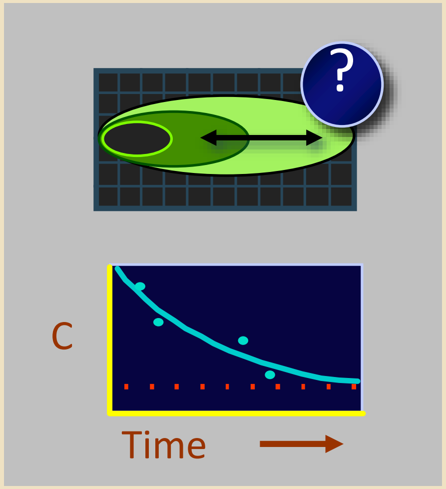
2 Graphical Methods

METHOD 1

Well Concentration vs. Distance

METHOD 2

Well Concentration vs. Time



LINE OF EVIDENCE 2:

Rate Calculations

EPA United States Environmental Protection Agency

Ground Water Issue

Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

Charles J. Newell[1], Hanadi S. Rifai[2], John T. Wilson[3], John A. Connor[1], Julia A. Aziz[1], and Monica P. Suarez[2]

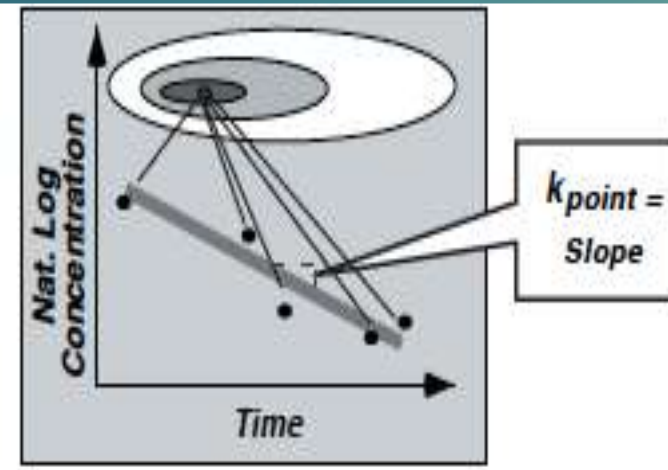


Figure 1. Determining concentration vs. time rate constant (k_{point}).

Rate Constant	Method of Analysis	Significance	Use of Rate Constant		
			Plume Attenuation	Plume Trends?	Plume Duration?
Point Attenuation Rate (Fig. 1) (k_{point}, time per year)	C vs. T Plot	Reduction in contaminant concentration over time at a single point	NO*	NO*	YES
Bulk Attenuation Rate (Fig. 2) (k; time per year)	C vs. D Plot	Reduction in dissolved contaminant concentration with distance from source	YES	NO*	NO

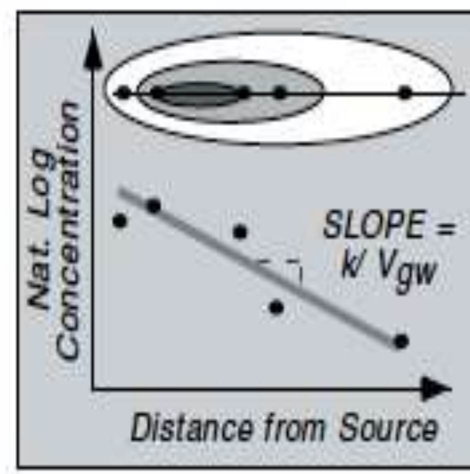
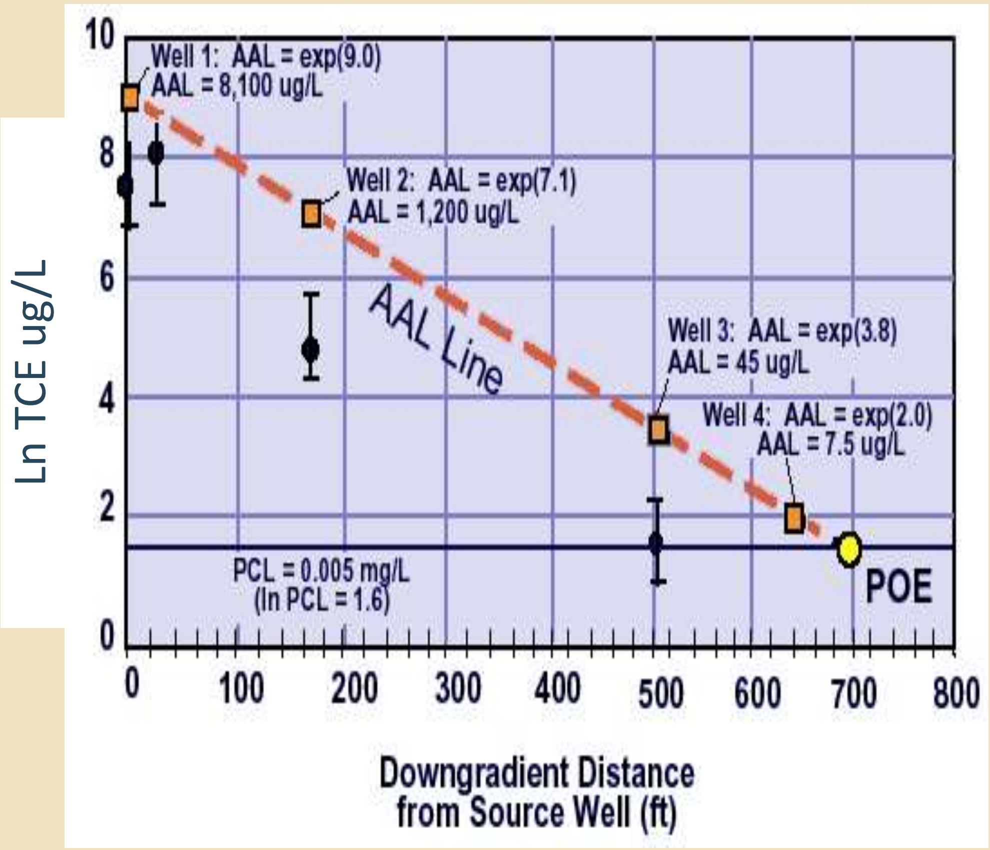


Figure 2. Determining concentration vs. distance rate constant (k).

CONTROL REMEDY: *Deriving Attenuation Action Levels (AALs)*



AAL = Attenuation Action Level

AMP = Attenuation Monitoring Point

POE = Point of Exposure

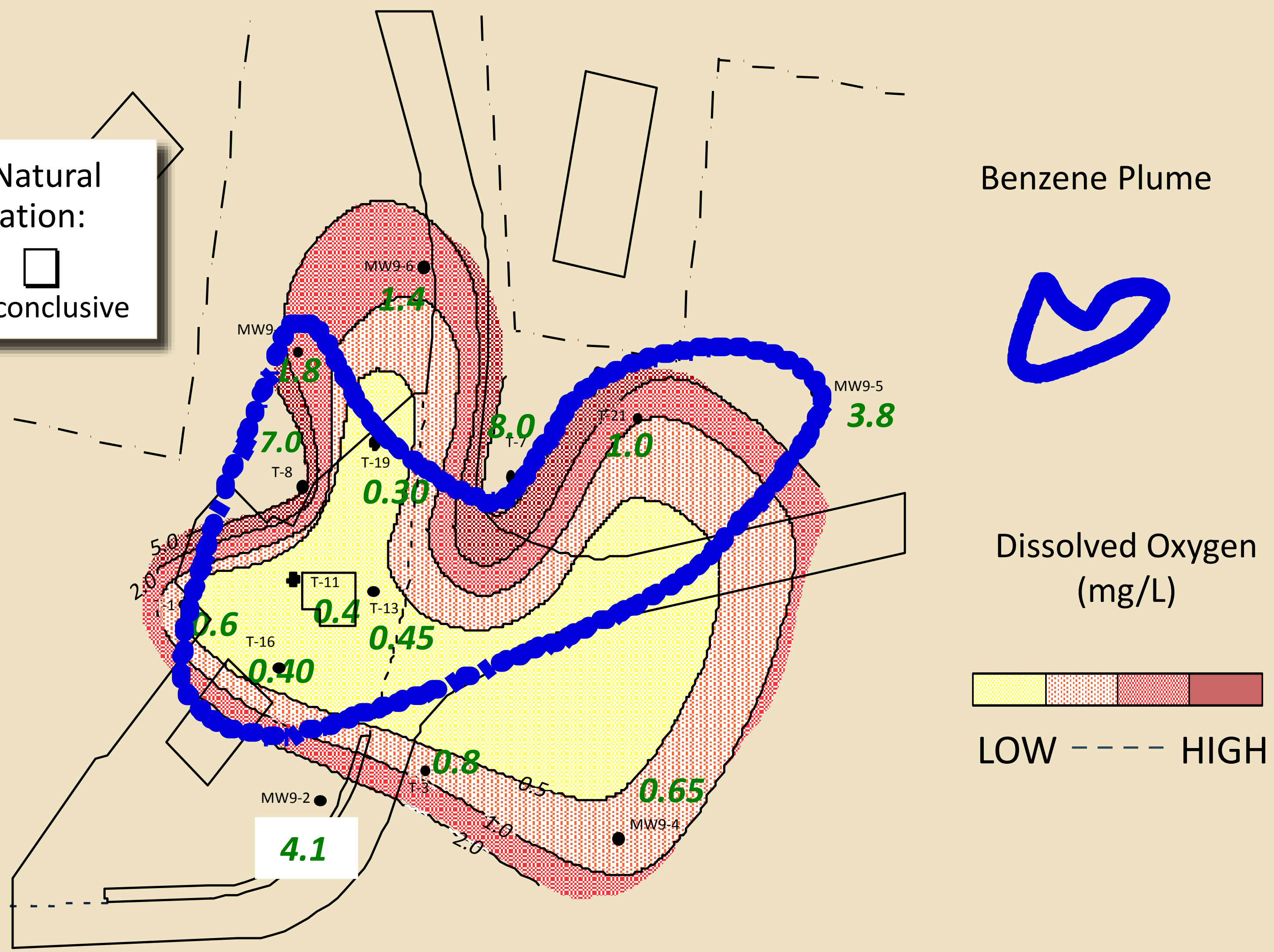
Option 1:
Graphical Method

1. ***Plot C vs. D***
   whisker plot showing range of historical COC concentrations.
2. ***Draw AAL line***
   connecting max conc. at point near source to PCL conc. at POE.
3. ***Determine AAL***
   for each AMP as the intersect of well distance with AAL line.

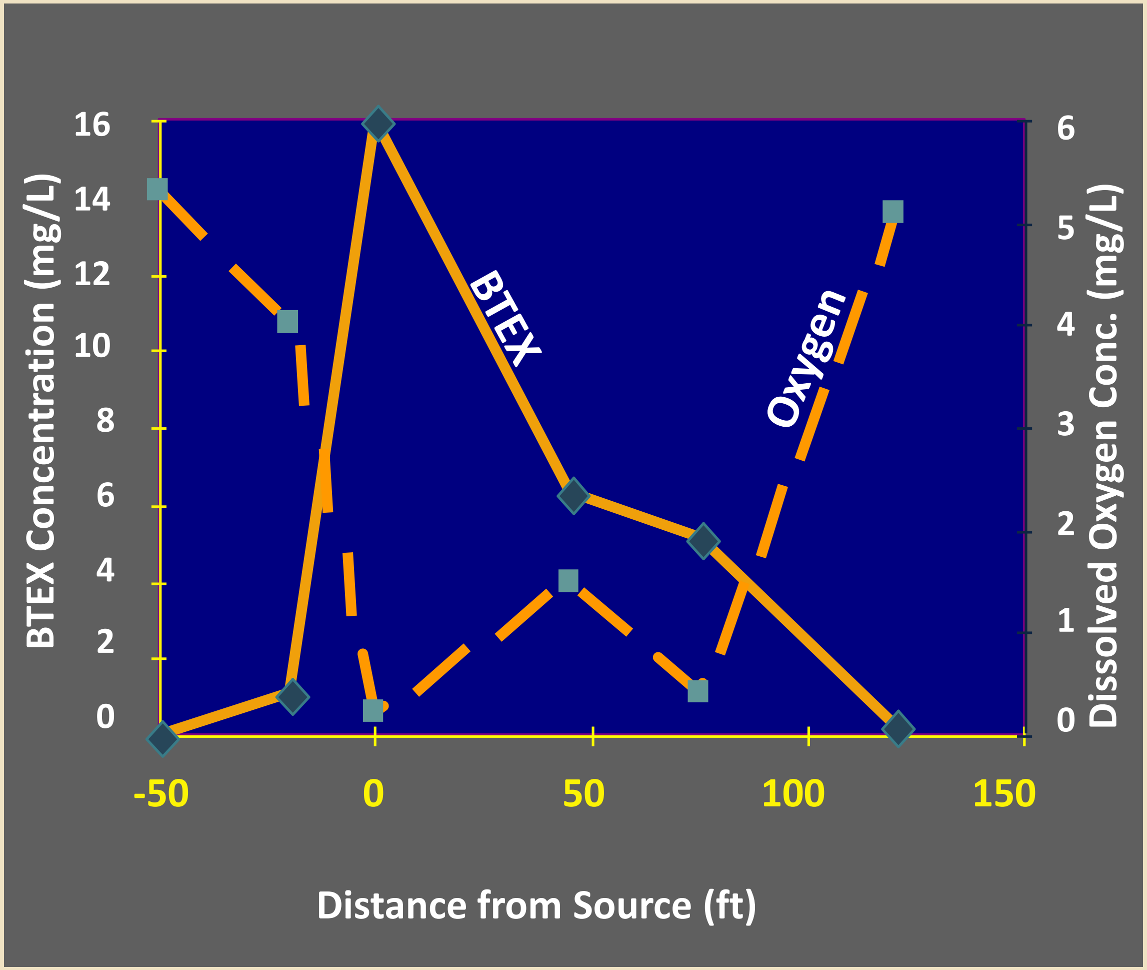
LINE OF EVIDENCE 2: *Appropriate Geochemical Conditions – Dissolved Oxygen Example*

Supports Natural Attenuation:

- [x] Yes
- [ ] No
- [ ] Inconclusive

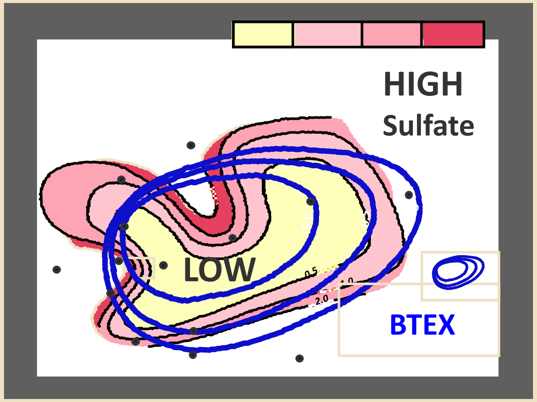


LINE OF EVIDENCE 2: *Appropriate Geochemical Conditions – Dissolved Oxygen Example*



Key Patterns for MNA

- Dissolved oxygen "hole" in BTEX plume location.
- Same for NO_3, SO_4.
- "Mountain" of Fe(II) and methane

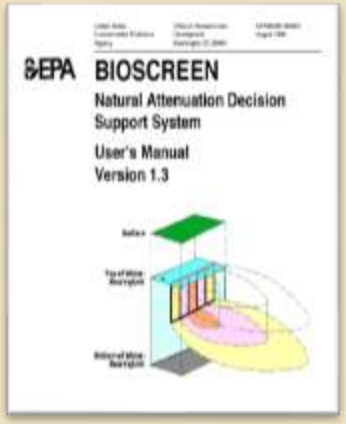


HOW FAR?
HOW LONG?

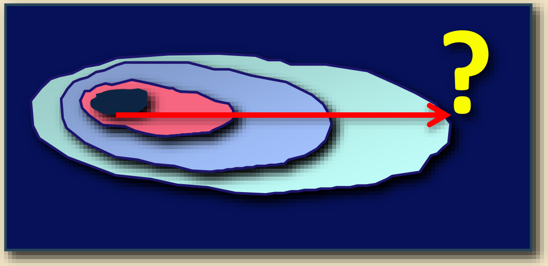
How Far? How Long?
The BIOSCREEN Natural Attenuation Decision Support System

Charles J. Newell, Ph.D., P.E.
R. Kevin McLeod
Groundwater Services, Inc. [1]

James R. Gonzales
Air Force Center for Environmental Excellence [2]



How Far Will Plume Migrate?

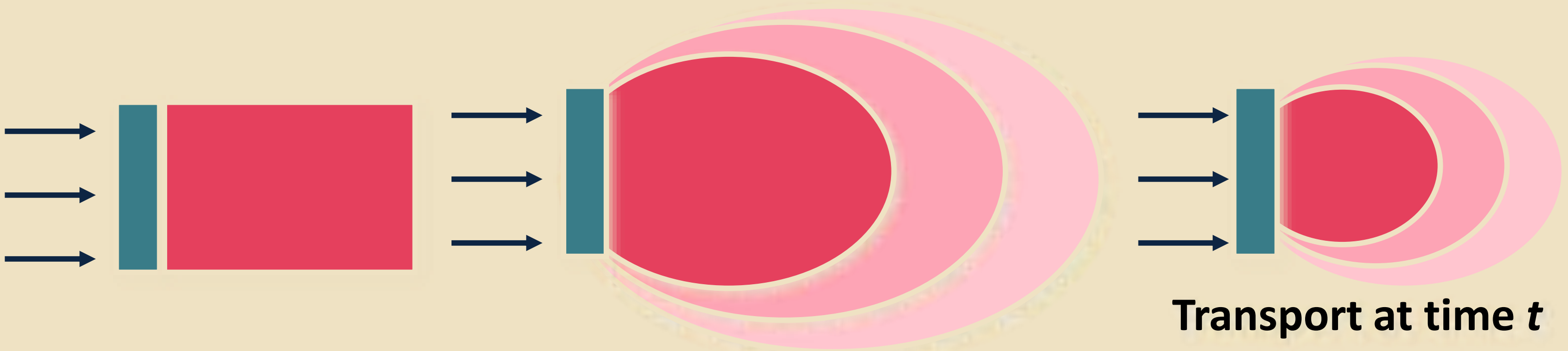


How Long Will Source Be There?

HOW FAR WILL PLUME GO?
Groundwater Transport Modeling

Advective-dispersive-degradation equation:

{ rate of change in conc. at any point } = { net rate of advective transport to that point } + { net rate of dispersive transport to that point } - { net rate of degradation at that point }



Transport at time t advection only

Transport at time t with dispersion

Transport at time *t* with dispersion & degradation

1-DIMENSIONAL ADVECTION DISPERSION EQUATION

$$\text{Conc}(x) = C_o \cdot \exp\left\{ \frac{x}{2\,\alpha_x} \left[1 - \left(1 + \frac{4\,\lambda\,\alpha_x}{V_s/R} \right)^{1/2} \right] \right\} \operatorname{erf}\left[\frac{S_w}{\sqrt{4\,\alpha_y\,x}} \right] \operatorname{erf}\left[\frac{S_d}{\sqrt{4\,\alpha_z\,x}} \right]$$

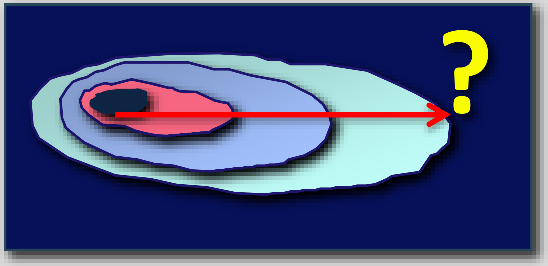
$$V_s = \frac{K\,i}{n_e}$$

- Concentration at Downgradient Location X: $\text{Conc}(x)$
- Source Concentration: C_o
- Longitudinal Dispersivity: α_x
- First-Order Decay Constant: λ
- Retardation Coefficient: R
- Groundwater Seepage Velocity: V_s
- Error Function: erf
- Groundwater Source Width and Depth: S_w, S_d
- Transverse Dispersivity: α_y
- Vertical Dispersivity: α_z
- Hydraulic Conductivity: K
- Hydraulic Gradient: i
- Effective Soil Porosity: n_e

HOW FAR? *Using a Model to Evaluate if MNA Can/Will Stabilize a Plume*

KEY POINT:

Calibrate, then Predict



Step 1

Calibrate model to existing monitoring data.

Step 2

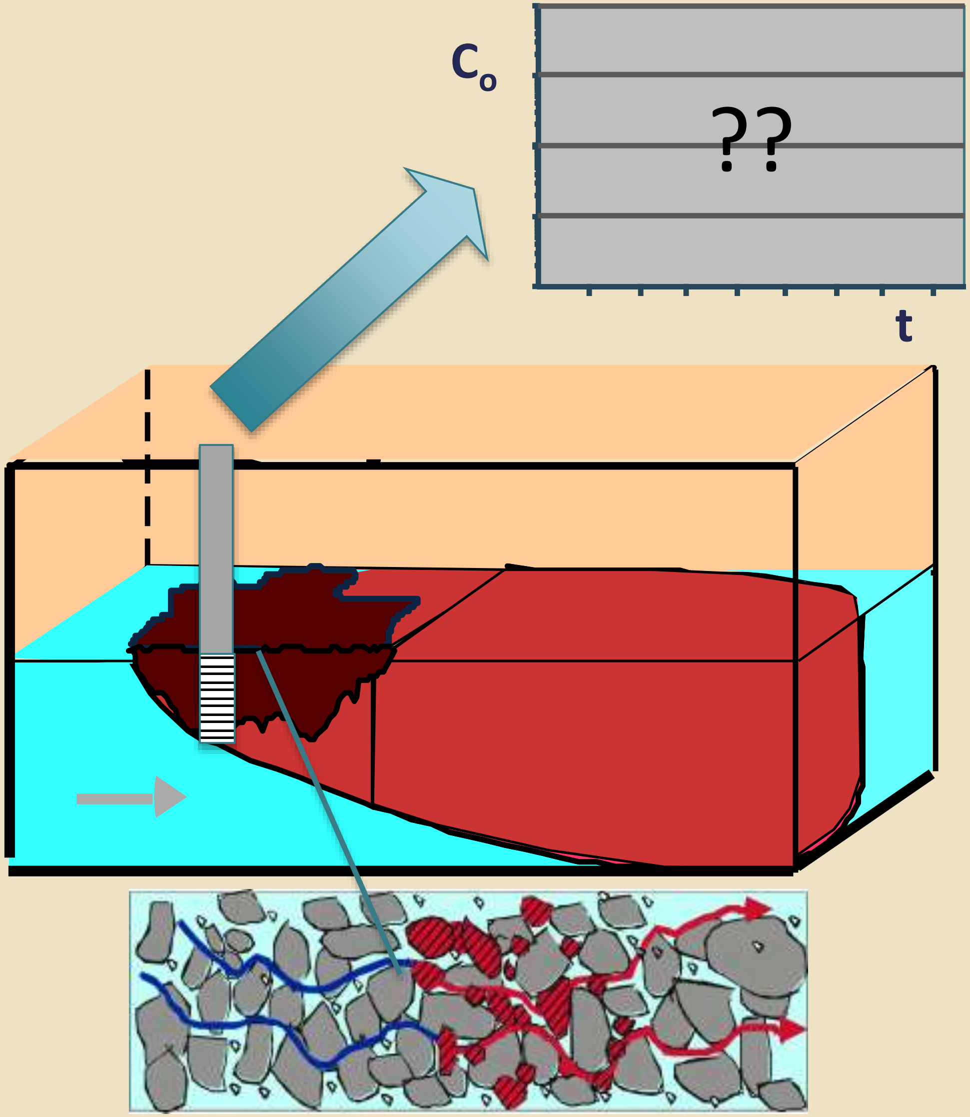
Increase time to some time in the future.

Step 3

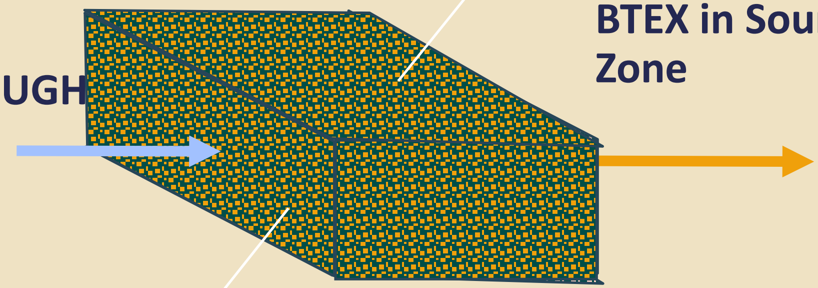
See if plume gets larger or smaller or becomes stable

HOW LONG? HOW LONG WILL SOURCE BE THERE?

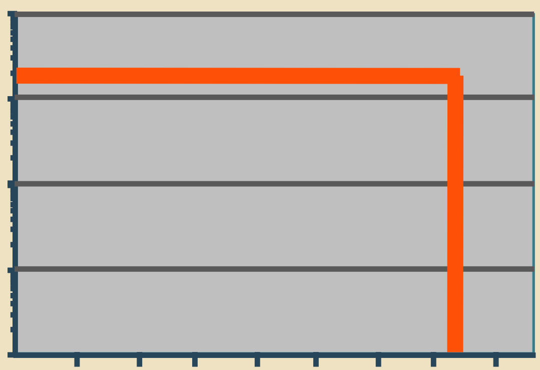
Source Term Mass Balance



APPROACH: *Assume Source Zone is a Box*



IF CONSTANT SOURCE CONCENTRATION:

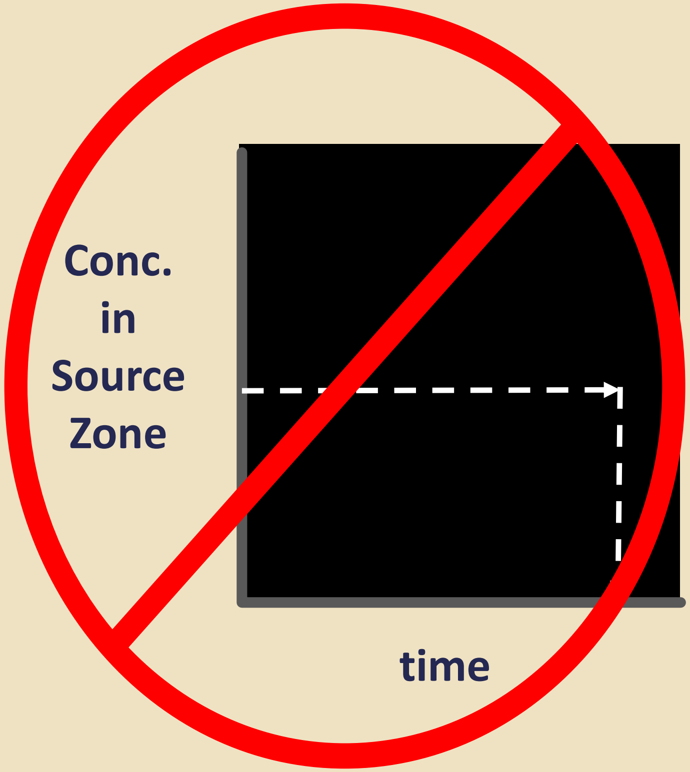


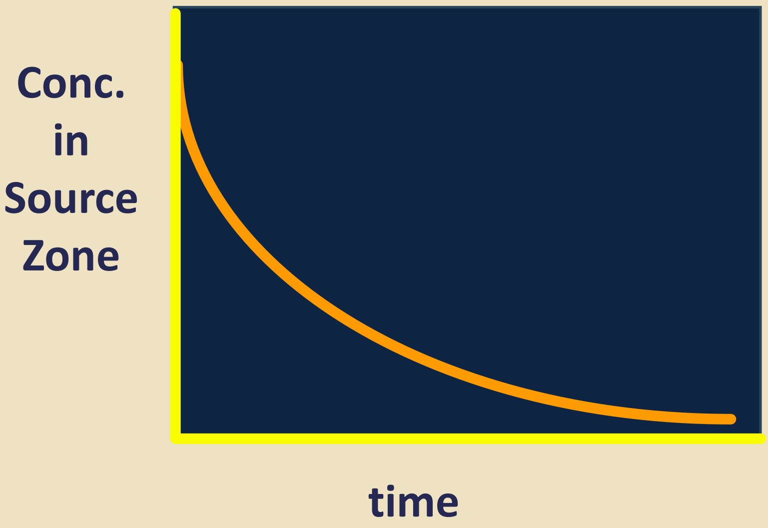
$$t = \frac{M_o}{Q \quad C_o}$$

BETTER SOURCE DECAY MODEL:

Concentration Declines with Tailing Effect

$$C_t = C_o \times \exp^{(-k_s t)}$$

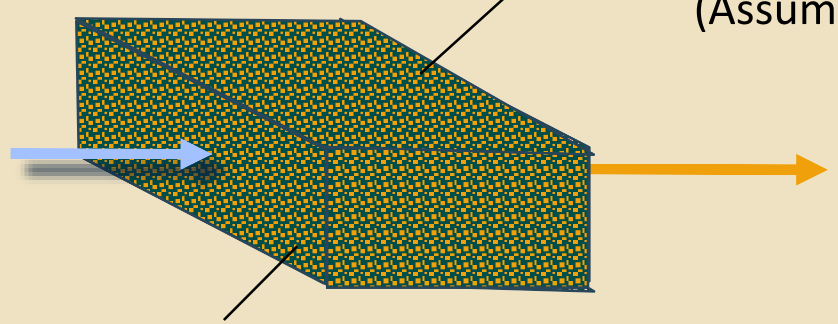




HOW LONG? *Example assuming first-order decay of source*

Q = Flow Rate Through Source

(Assume 500 L/Day)



$\mathbf{M_o}$ = Total Mass in Source (Assume 10 kg)

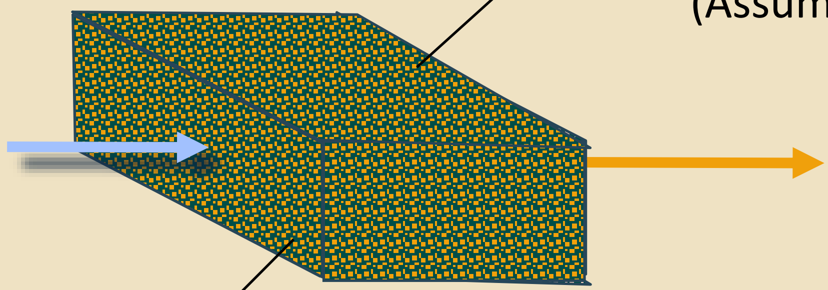
$\mathbf{C_o}$ = Concentration in Source Zone at Time = 0 (Assume 2 mg/L)

HOW LONG? *Example assuming first-order decay of source*

Q = Flow Rate
Through Source

(Assume 500 L/Day)

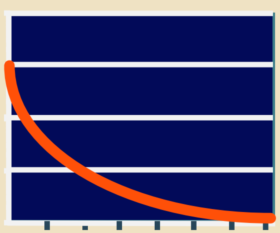
M_o = Total Mass in Source
(Assume 10 kg)



C_o = Concentration in Source
Zone at Time = 0 (Assume 2 mg/L)

IF DECLINING SOURCE CONCENTRATION:

C_o



t

k_s =

HOW LONG? *Example assuming first-order decay of source*

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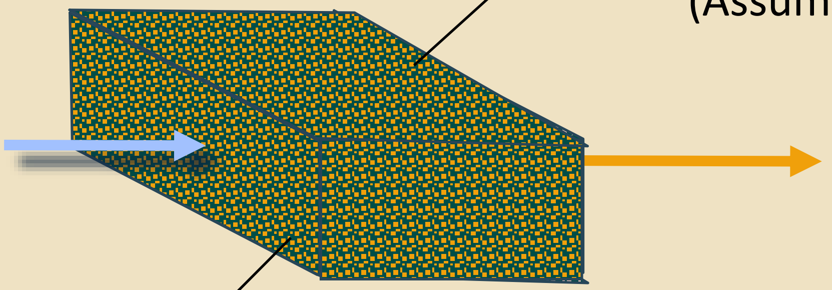

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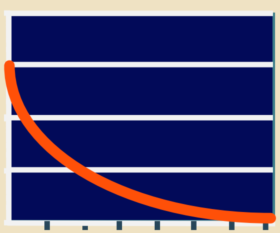


$$k_s = \frac{Q \quad C_o}{M_o} = \frac{(500)\ (2)}{10{,}000{,}000} = 0.0001\ \text{day}^{-1}$$

$$C_t = C_o \times e^{-0.0001\,t}$$

BIOSCREEN Natural Attenuation Decision Support System

Air Force Center for Environmental Excellence — *Version 1.3*

Kessler AFB
SWMU 66
Run Name

Data Input Instructions:

115 → 1. Enter value directly....or
↑ or
0.02 → 2. Calculate by filling in grey cells below. (To restore formulas, hit button below).

Variable* → Data used directly in model.
20 → Value calculated by model. (Don't enter any data).

1. HYDROGEOLOGY

Seepage Velocity*	Vs	113.8	(ft/yr)
or		↑ or	
Hydraulic Conductivity	K	1.1E-02	(cm/sec)
Hydraulic Gradient	i	0.003	(ft/ft)
Porosity	n	0.3	(-)

2. DISPERSION

Longitudinal Dispersivity*	alpha x	32.5	(ft)
Transverse Dispersivity*	alpha y	3.3	(ft)
Vertical Dispersivity*	alpha z	0.0	(ft)
or		↑ or	
Estimated Plume Length	Lp	280	(ft)

3. ADSORPTION

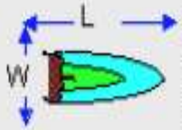
Retardation Factor*	R	1.0	(-)
or		↑ or	
Soil Bulk Density	rho	1.7	(kg/l)
Partition Coefficient	Koc	38	(L/kg)
FractionOrganicCarbon	foc	5.70E-05	(-)

4. BIODEGRADATION

1st Order Decay Coeff*	lambda	4.6E+0	(per yr)
or		↑ or	
Solute Half-Life	t-half	0.15	(year)
or Instantaneous Reaction Model			
Delta Oxygen*	DO	1.65	(mg/L)
Delta Nitrate*	NO3	0.7	(mg/L)
Observed Ferrous Iron*	Fe2+	16.6	(mg/L)
Delta Sulfate*	SO4	22.4	(mg/L)
Observed Methane*	CH4	6.6	(mg/L)

5. GENERAL

Modeled Area Length*	320	(ft)
Modeled Area Width*	200	(ft)
Simulation Time*	6	(yr)



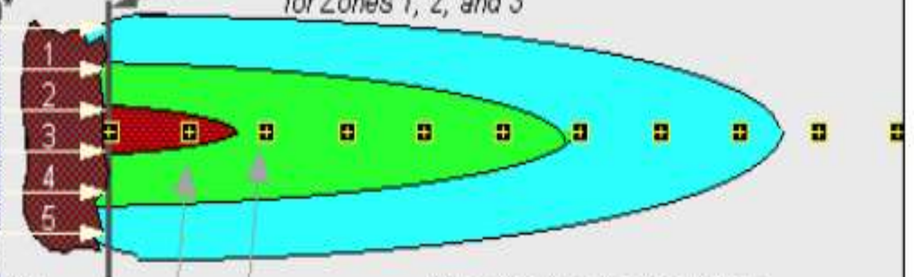
6. SOURCE DATA

Source Thickness in Sat.Zone* 10 (ft)

Source Zones:

Width* (ft)	Conc. (mg/L)*
28	0.057
30	2.508
14	13.68
30	2.508
28	0.057

Vertical Plane Source: Look at Plume Cross-Section and Input Concentrations & Widths for Zones 1, 2, and 3



View of Plume Looking Down

Source Decay (see Help):
SourceHalflife* 60 - 400 (yr)
Soluble Mass ↑ or
In NAPL, Soil 2000 (Kg)

Observed Centerline Concentrations at Monitoring Wells
If No Data Leave Blank or Enter "0"

7. FIELD DATA FOR COMPARISON

Concentration (mg/L)	12.0	5.0	1.0				.5			.001	
Dist. from Source (ft)	0	32	64	96	128	160	192	224	256	288	320

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN CENTERLINE — View Output

RUN ARRAY — View Output

Help

Recalculate This Sheet

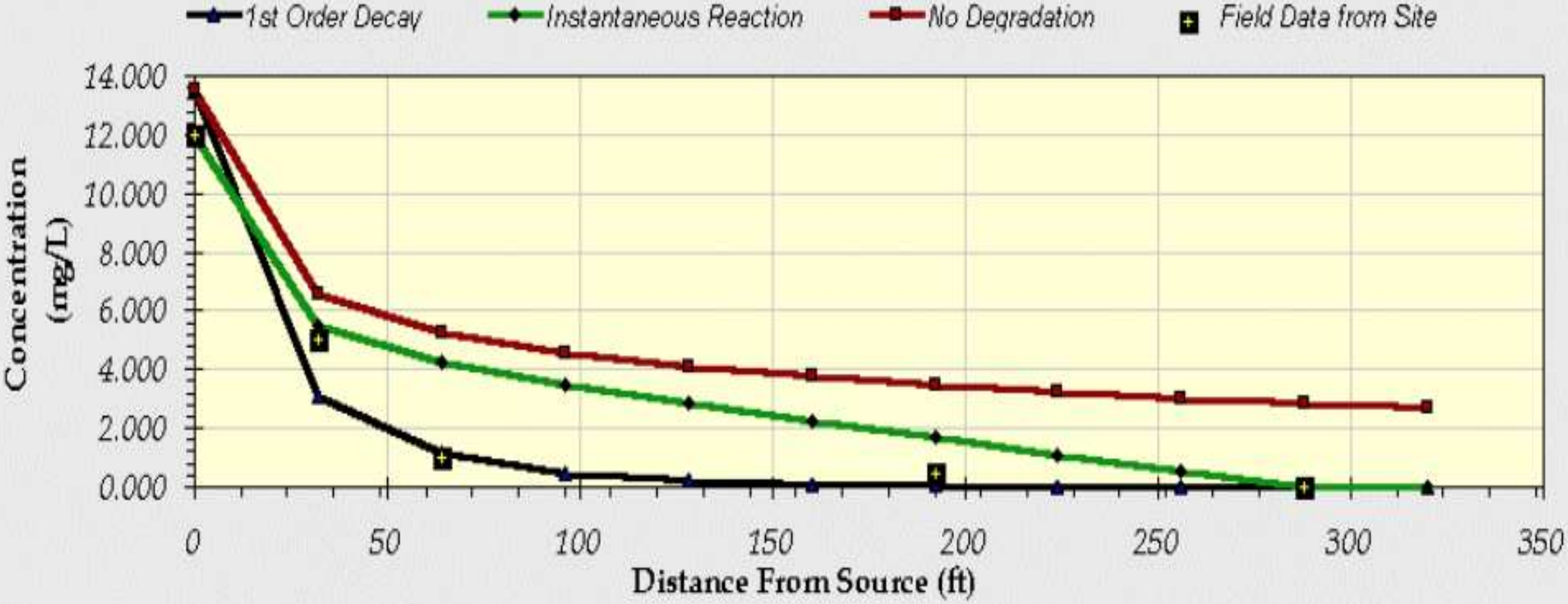
Paste Example Dataset

Restore Formulas for Vs, Dispersivities, R, lambda, other

DISSOLVED HYDROCARBON CONCENTRATION ALONG PLUME CENTERLINE (mg/L at Z=0)

Distance from Source (ft)

TYPE OF MODEL	0	32	64	96	128	160	192	224	256	288	320
No Degradation	13.544	6.575	5.280	4.581	4.107	3.754	3.474	3.241	3.040	2.861	2.697
1st Order Decay	13.544	3.117	1.186	0.488	0.208	0.090	0.040	0.018	0.008	0.004	0.002
Inst. Reaction	12.021	5.463	4.248	3.500	2.860	2.257	1.678	1.114	0.559	0.004	0.000
Field Data from Site	12.000	5.000	1.000				0.500			0.001	



Calculate Animation

Time:

6 Years

Return to Input

Recalculate This Sheet

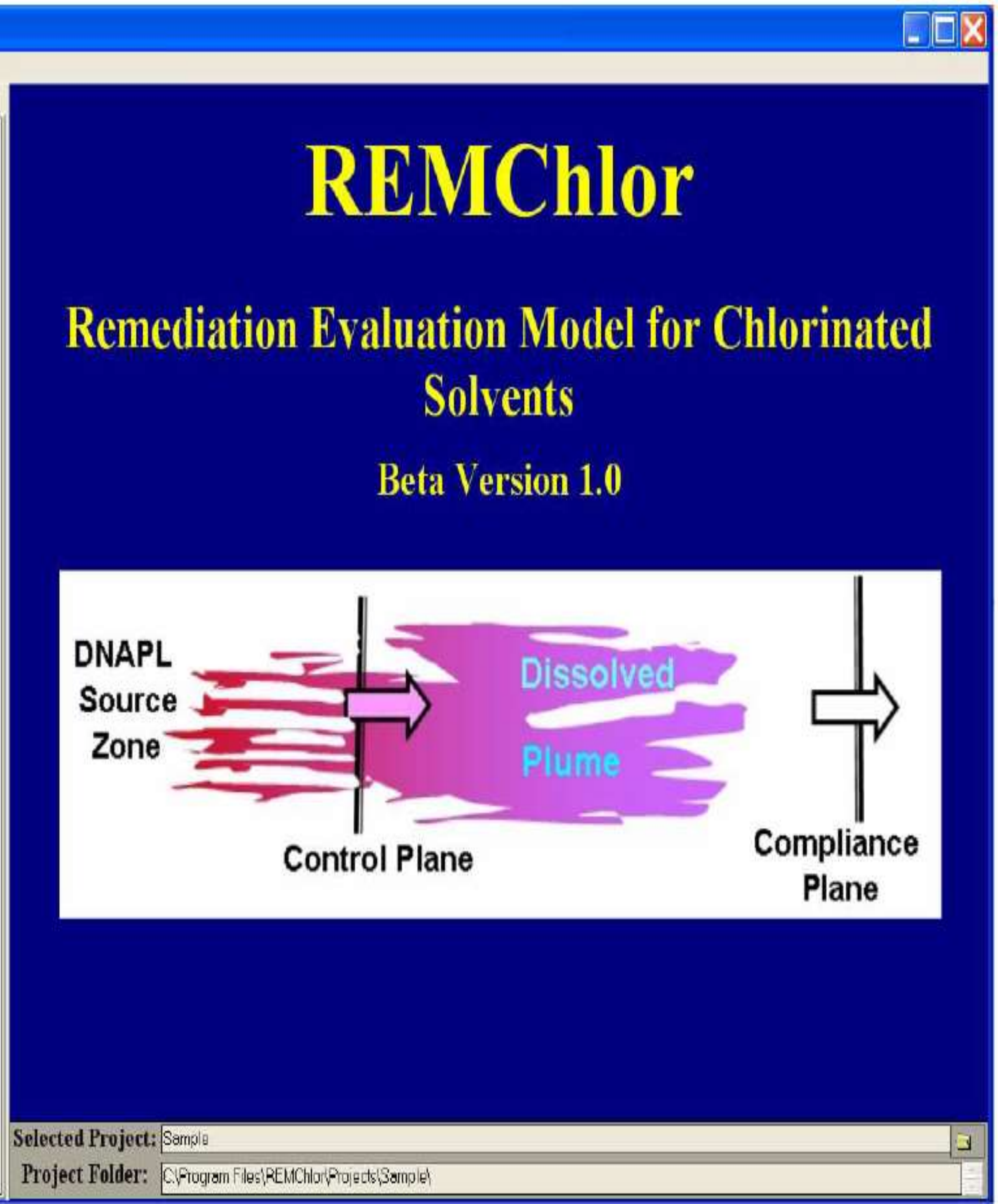
WHY USE MODELS?

- Method for Predicting Something Precisely ? **No**

- System to Organize Site Data . . . . **Yes**
- Tool to Help Understand Site Processes . **Yes**
- Additional Line of Evidence . . . . **Yes**
- Screen for Applicability of MNA . . . . **Yes**

	Contaminant?	Matrix Diffusion?	Analyze Remediation?	Platform
BIOSCREEN	Hydrocarbons	No	No	Excel
BIOCHLOR	Chlorinateds	No	No	Excel
REMChlor	Chlorinateds	Source – yes Plume – no	Yes	Stand alone
REMFuel	Hydrocarbons, MTBE	Source – yes Plume – no	Yes	Stand alone
Matrix Diffusion Toolkit	Any	Yes	Yes*	Excel

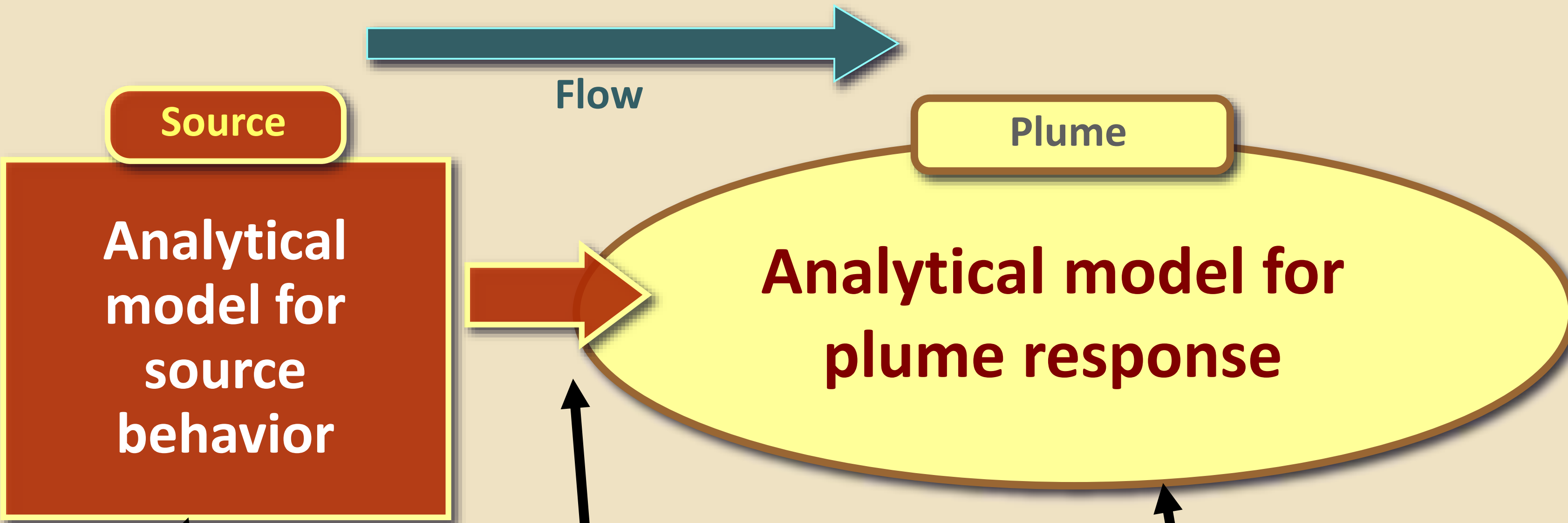
	Contaminant?	Matrix Diffusion?	Analyze Remediation?	Platform
BIOSCREEN	Hydrocarbons	No	No	Excel
BIOCHLOR	Chlorinateds	No	No	Excel
REMChlor	Chlorinateds	Source – yes Plume – no	Yes	Stand alone
REMFuel	Hydrocarbons, MTBE	Source – yes Plume – no	Yes	Stand alone
Matrix Diffusion Toolkit	Any	Yes	Yes*	Excel



Google:
USEPA
Remchlor

Developed by
Dr. Ron
Falta,
Clemson
University

REMCHLOR MODEL: *Source and Plume Terms*

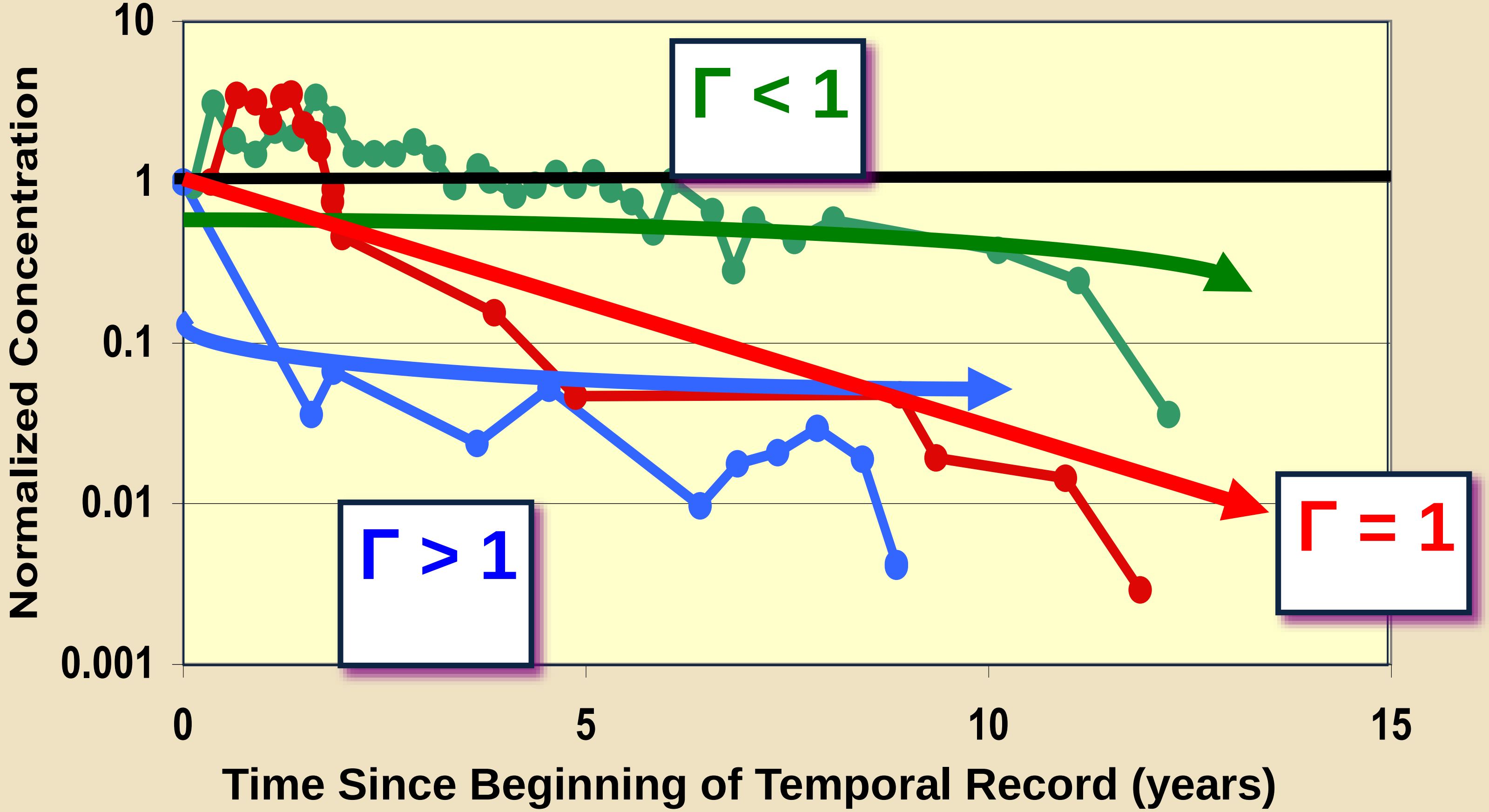


Mass balance model on source zone predicts discharge <u>including effects of remediation</u>

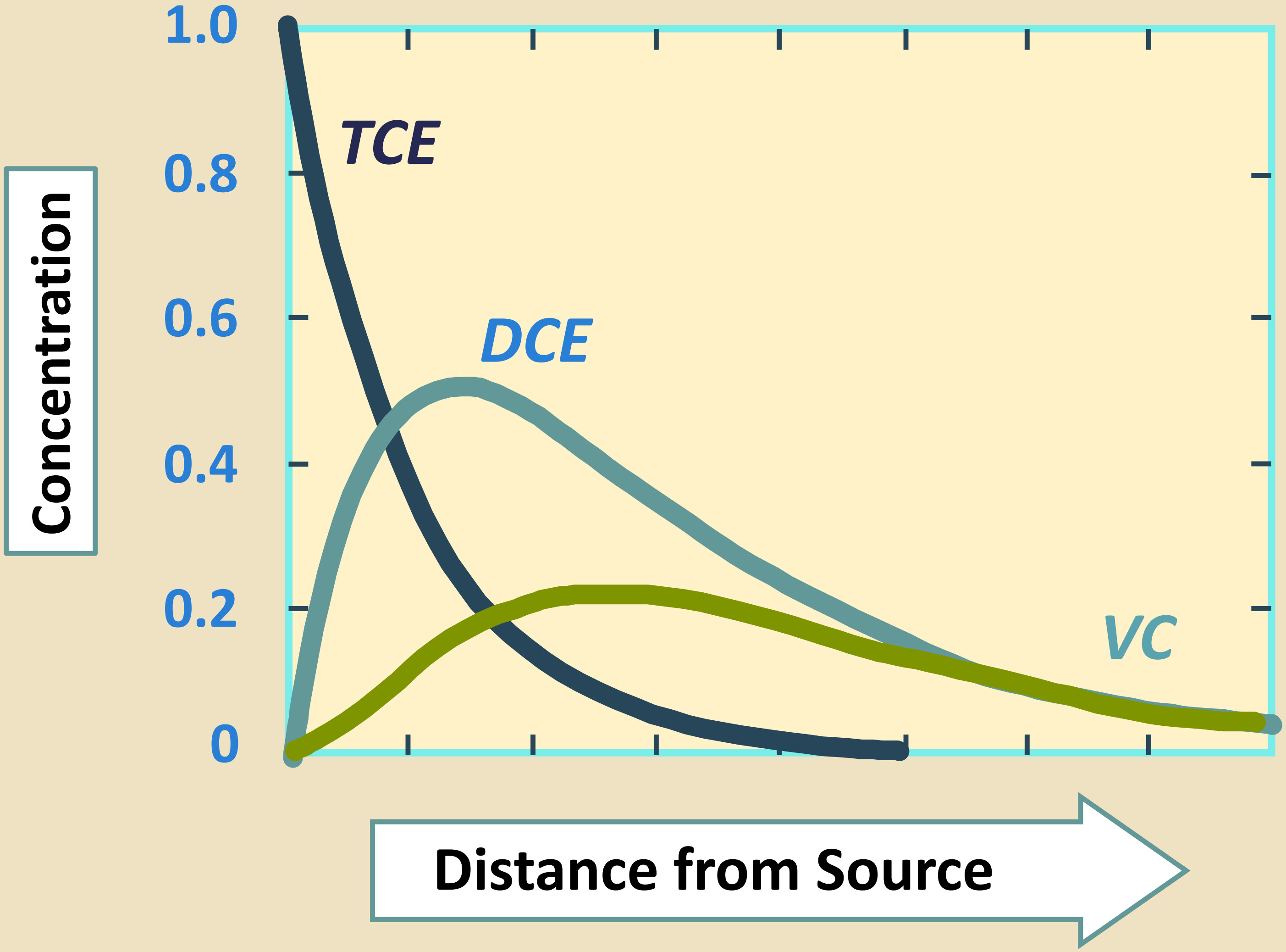
Couple Models At the Edge of the Source Zone to Provide Contaminant Discharge to Plume Model

Plume model simulates mass balance based on advection, dispersion, retardation, and degradation reactions
\+
<u>plume remediation</u>
(but all with simple flow field)

HOW GAMMA (Γ) MIGHT FIT THESE DATA

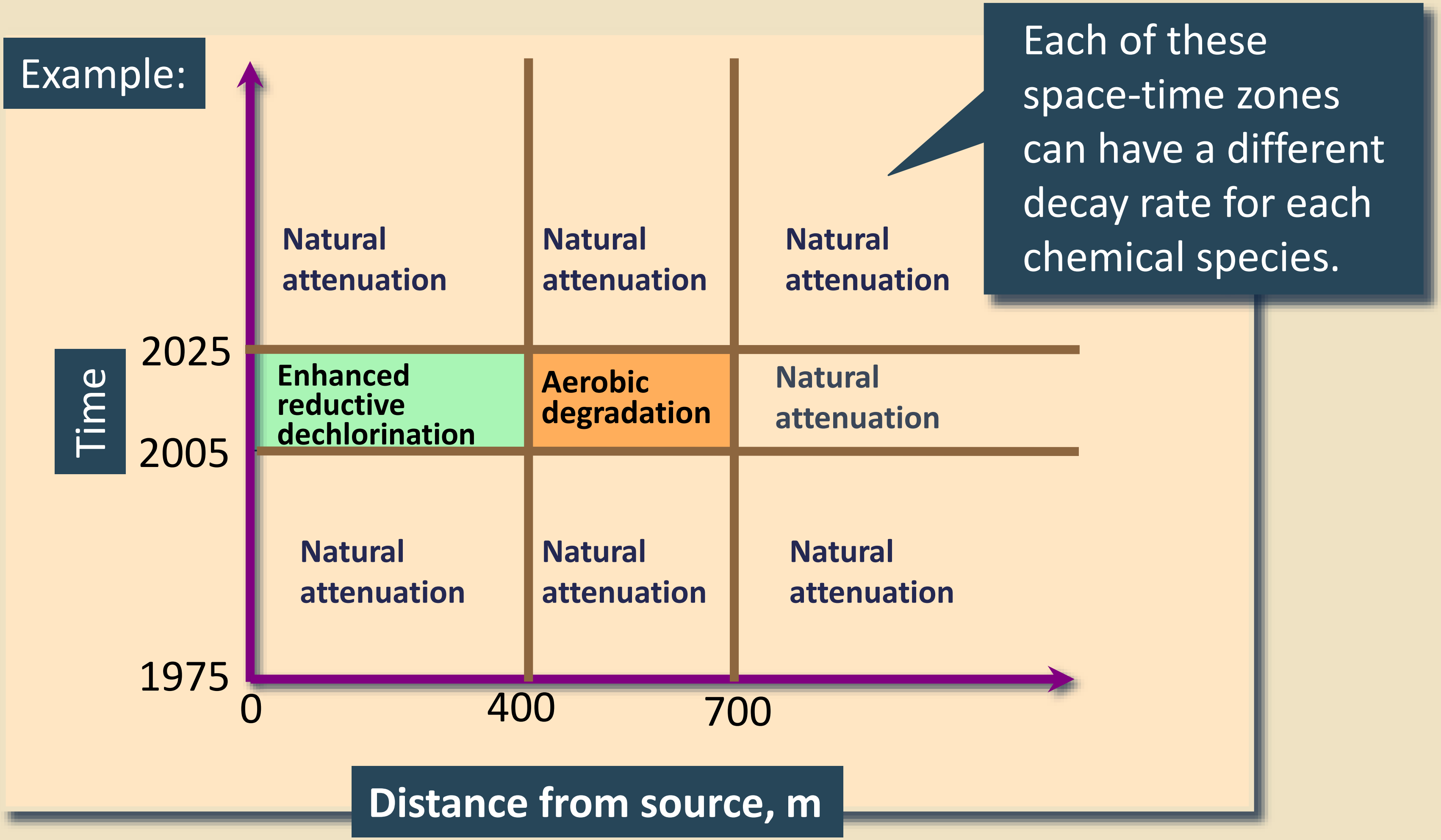


RESULTS OF SEQUENTIAL REACTIONS

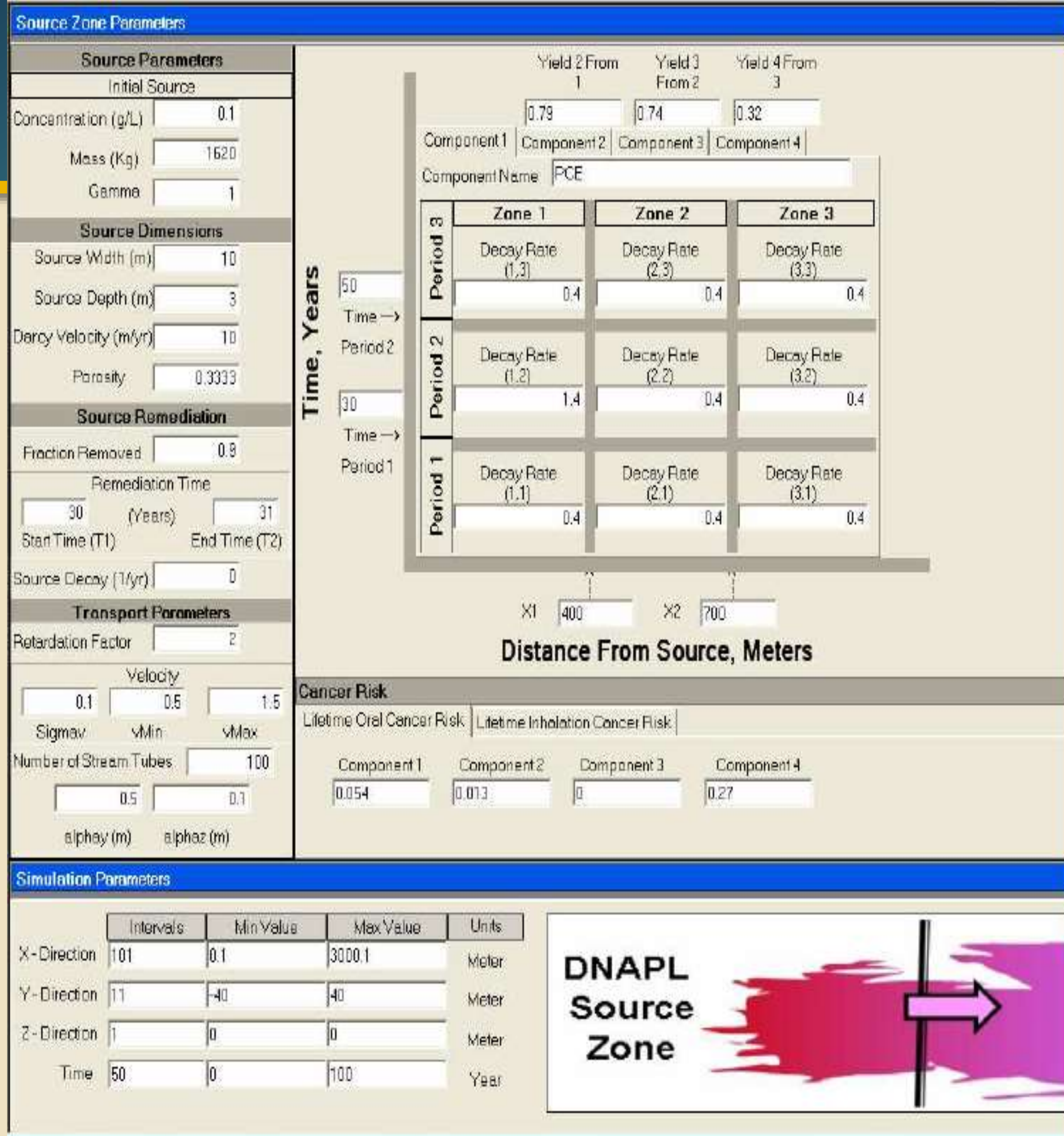


PLUME REMEDIATION MODEL

Divide space and time into "reaction zones", solve the coupled parent-daughter reactions for chlorinated solvent degradation in each zone



REMCHLOR INPUT



ROAD MAP

- **Intro: Changing Paradigms and MNA Principles**
- **Key Attenuation Processes**
  - *Biodegradation*
  - *Abiotic Processes*
  - *LNAPL source zone degradation processes*
  - *Other processes (immobilization, storage, dilution)*
- **Field Techniques and Technologies**
  - *Groundwater sampling and analytical methods*
  - *Compound Specific Isotopes Analysis (CSIA)*
  - *Molecular Biological Tools (MBTs)*
  - *Natural Source Zone Depletion (NSZD)*
- **Should MNA be Used? Data Analysis and Monitoring Tools**
  - *Data requirements, LTM, and statistics to understand MNA rates*
  - *Common Graphics and Calculations*
  - *Remediation Timeframe Calculations*
  - *Computer Models*
- **Implementation Topics**

MOTIVATION FOR BIOPIC:
Obtaining better rate data for MNA

To select MNA, you need lines of evidence (often within several tiers) to demonstrate it will be effective

1. *Historical groundwater…data that demonstrate a clear and meaningful trend of decreasing contaminant…concentration over time at appropriate monitoring locations*
2. *Hydrogeologic and geochemical data that can be used to demonstrate indirectly the types of natural attenuation processes and the **rate** at which such processes will reduce…to required levels*

United States Environmental Protection Agency
Office of Solid Waste and Emergency Response

EPA

DIRECTIVE NUMBER: 9200.4-17P

TITLE: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites

APPROVAL DATE: April 21, 1999

EFFECTIVE DATE: April 21, 1999

ORIGINATING OFFICE: OSWER

☒ FINAL

☐ DRAFT

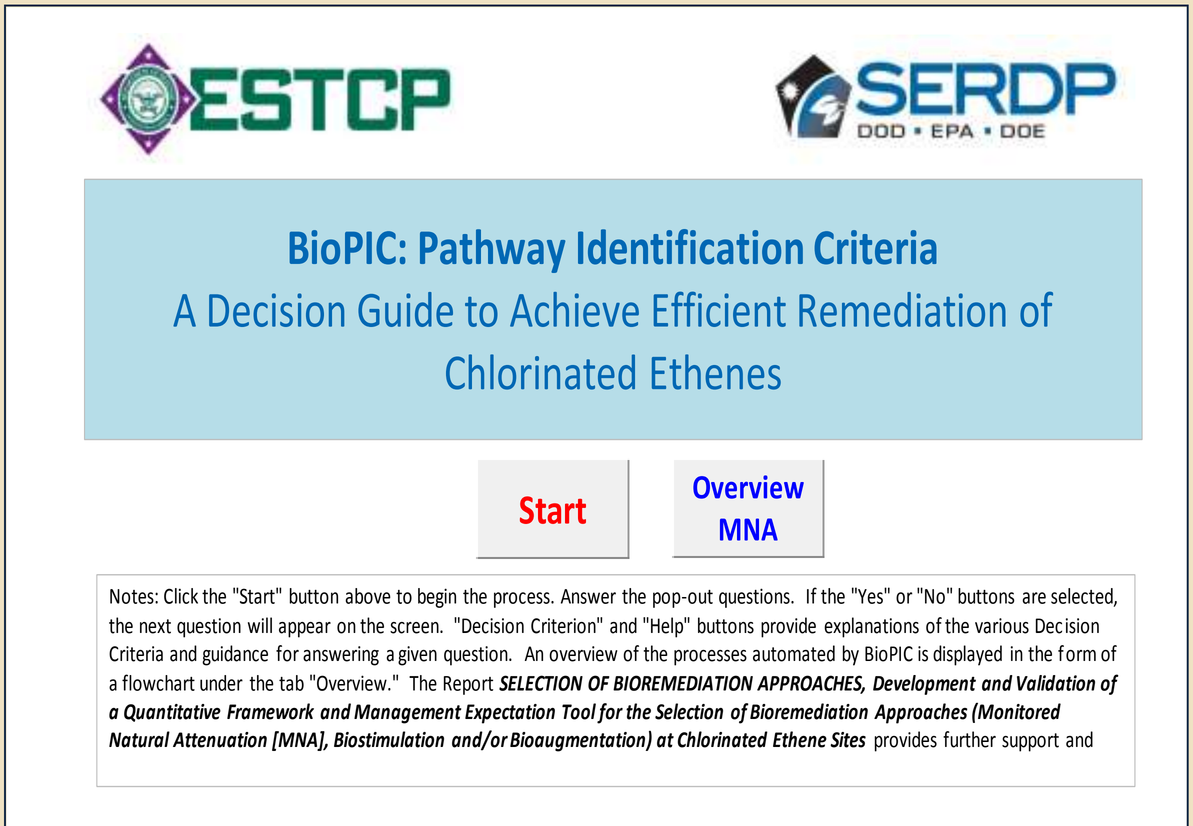
STATUS:

REFERENCE (other documents):

OSWER DIRECTIVE OSWER DIRECTIVE OSWER DIRECTIVE

WHAT IS BIOPIC?

QUANTITATIVE FRAMEWORK: “A systematic approach to evaluate whether MNA is an appropriate remedy based on site-specific conditions”



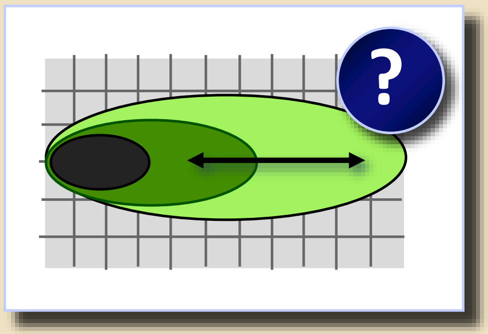
Search “ESTCP ER-201129” for tool download and guidance

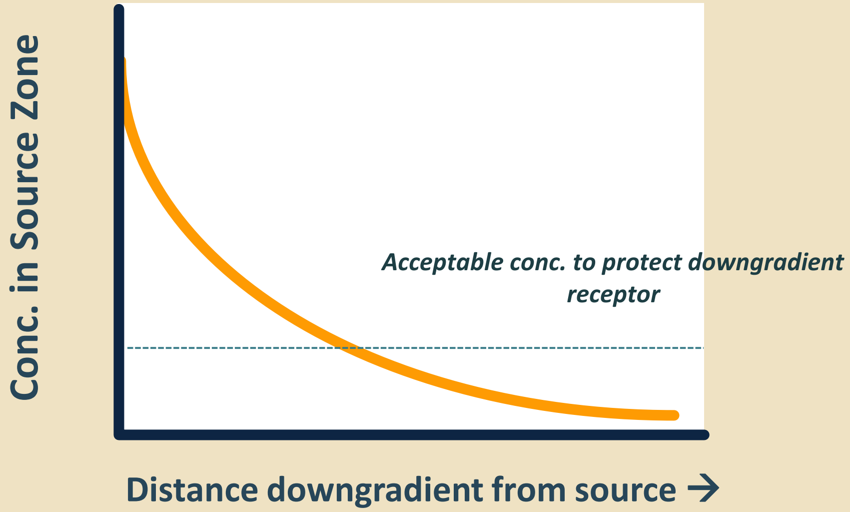
Another way to think about it: basis for choosing between 3 options for chlorinated ethene sites

1. Biostimulation
2. Bioaugmentation
3. MNA

HOW BIOPIC WORKS

Framework is designed to help answer question of:
"Will a plume impact a receptor?"

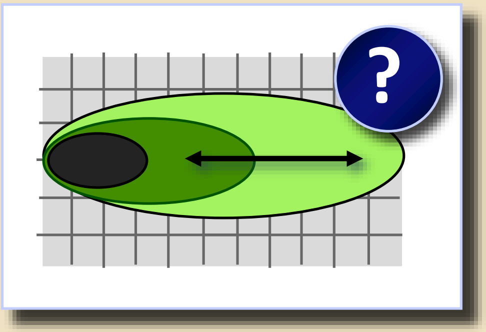


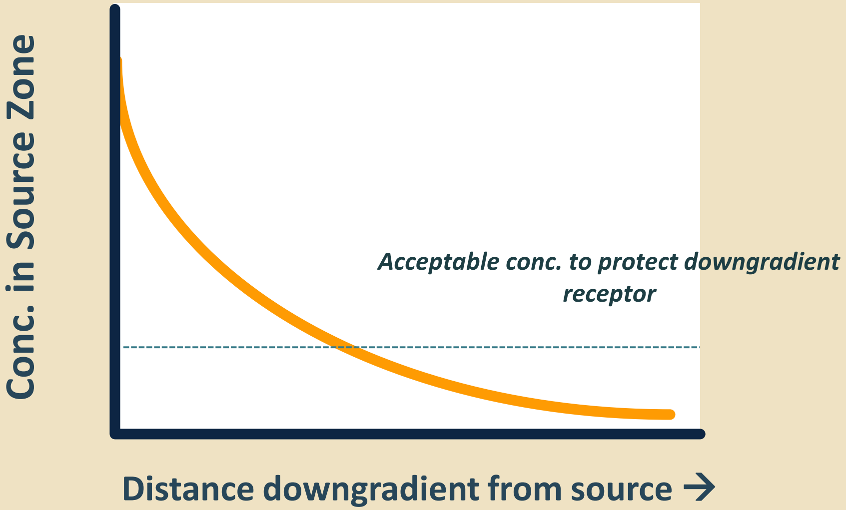


FIRST: Use GW Fate and Transport model to extract rate constants from field data to determine the necessary rate of degradation to achieve goal

HOW BIOPIC WORKS

Framework is designed to help answer question of:
“Will a plume impact a receptor?”





SECOND: Use BioPIC to confirm if that rate is consistent with rates that have been observed in other studies for any potentially-applicable pathways (2nd Line of Evidence)

HOW BIOPIC WORKS

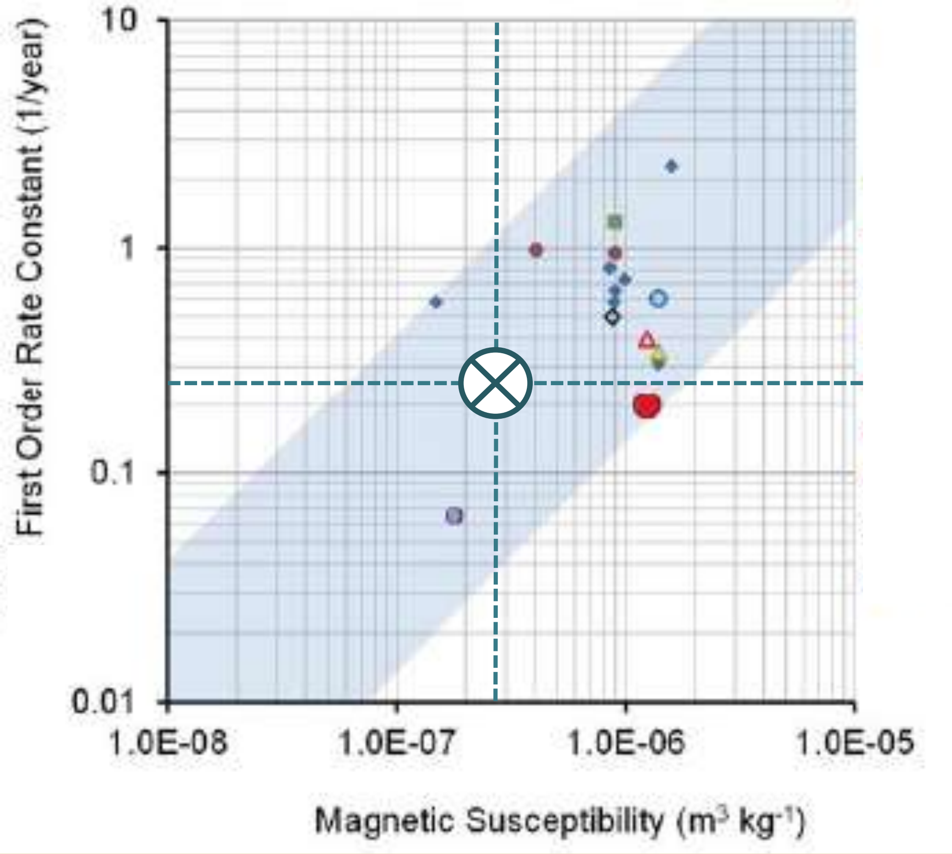
Attenuation Pathways **that are included**
Complete Anaerobic Reductive Dechlorination
Partial Anaerobic Reductive Dechlorination
Aerobic Biological Oxidation
Abiotic Degradation

EPA Directive (1999) only included reductive dechlorination

Parameters **found to have direct** ***correlation*** **on attenuation rate**
Dehalococcoides density (for TCE, cDCE, and VC)
Magnetic susceptibility
Iron sulfide (FeS)
Methane (CH_4)
Ferrous iron (Fe(II))

Lots of other parameters were evaluated but no correlation could be established

HOW BIOPIC WORKS: *Example using abiotic degradation pathway*



Compare your data to data from other sites

- Magnetic susceptibility = $2.6 \times 10^{-7}\ m^3/kg$
- Rate coefficient estimated from field data = 0.25/yr

RESULT:

- Your data fall within blue shaded area of high confidence
- Abiotic degradation explains observed rate
- SERVES AS LINE OF EVIDENCE FOR MNA

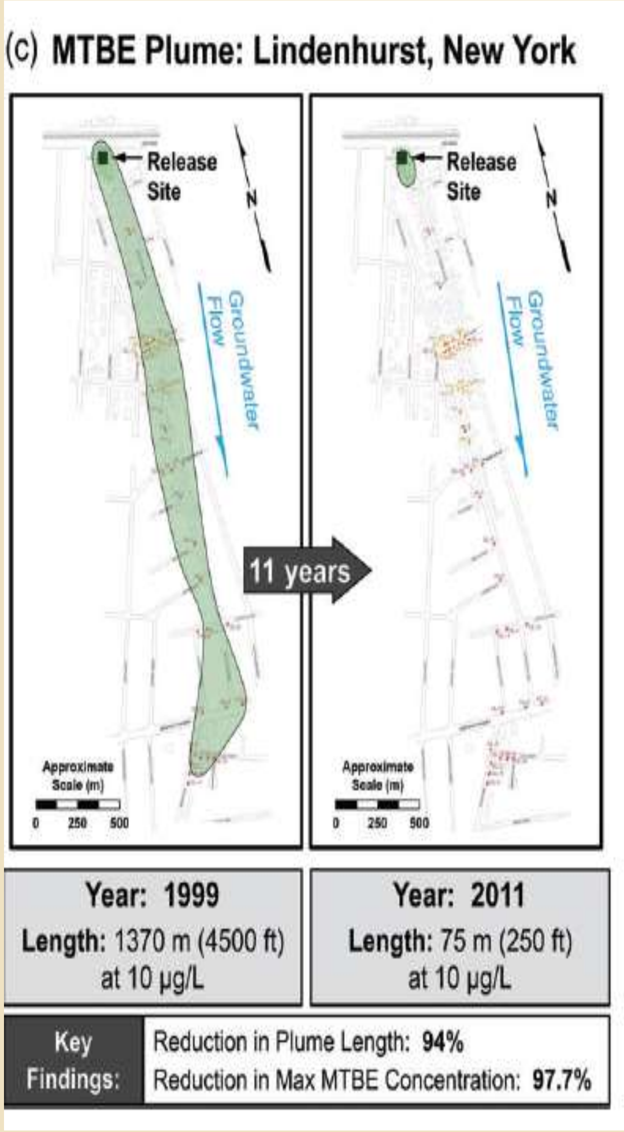
CAN I APPLY MNA TO CONTAMIANTS BESIDES CHLORINATED SOLVENTS AND BTEX?

YES - CONSIDER MTBE AS AN EXAMPLE

- **Not promising in early protocols**

  MTBE had been found to "*…migrate large distances and threaten downgradient water supplies at the same sites where the BTEX component of a plume has either stabilized or diminished due to natural attenuation*" and included MTBE among compounds "*…that tend not to degrade readily in the subsurface*".

- **Lots of research and field work in the following 5-10 years, and we ended up with a completely different story!**

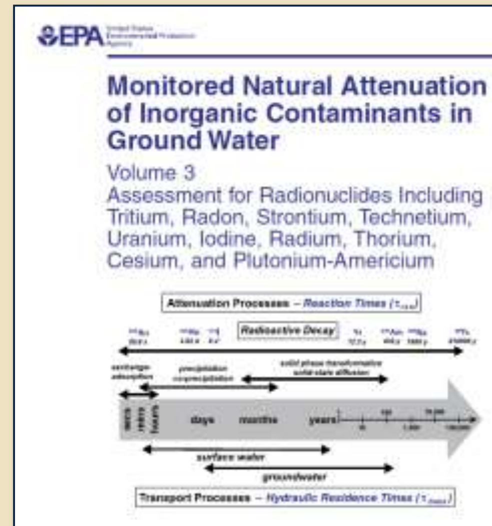


CAN I APPLY MNA TO METALS, INORGANICS, AND RADIONUCLIDES?

YES, says USEPA

2007

2008



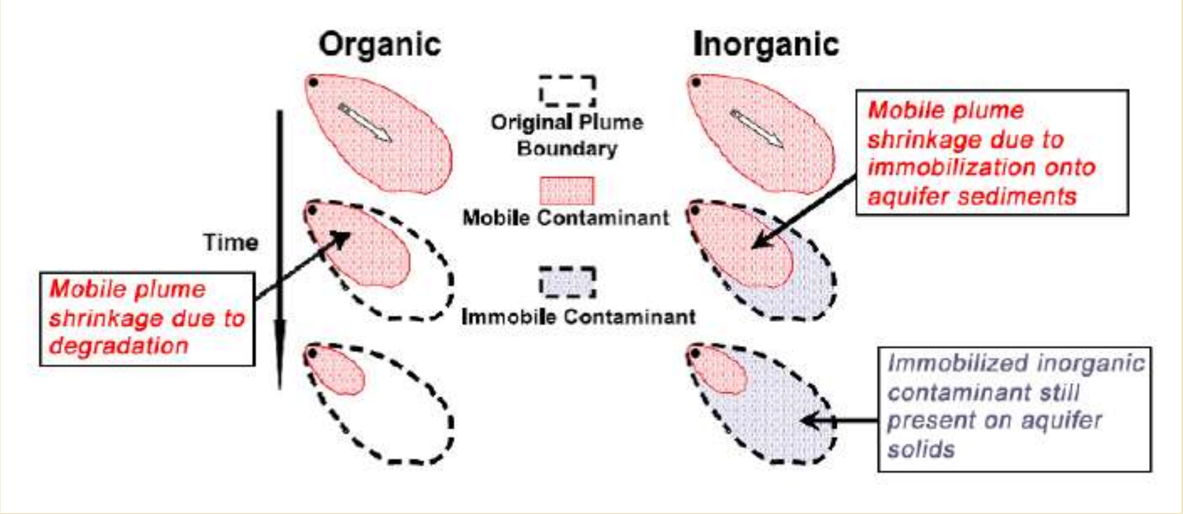
2010

Tiered Lines-of-Evidence Approach
(similar to protocols for organics)

1. Plume is not expanding and sorption is occurring
2. ID the attenuation mechanism and estimate rate
3. Determine capacity and sustainability
4. Develop monitoring and contingency measures

CAN I APPLY MNA TO METALS, INORGANICS, AND RADIONUCLIDES?

- Primary attenuation pathway for many inorganics is transformation to less mobile forms through co-precipitation or sorption
- Reactions are generally more complex and highly influenced by geochemical conditions



USEPA's 2015 policy document

EPA United States Environmental Protection Agency

Directive 9283.1-36
August 2015
Office of Solid Waste and Emergency Response

USE OF MONITORED NATURAL ATTENUATION FOR INORGANIC CONTAMINANTS IN GROUNDWATER AT SUPERFUND SITES

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Directive 9283.1-36

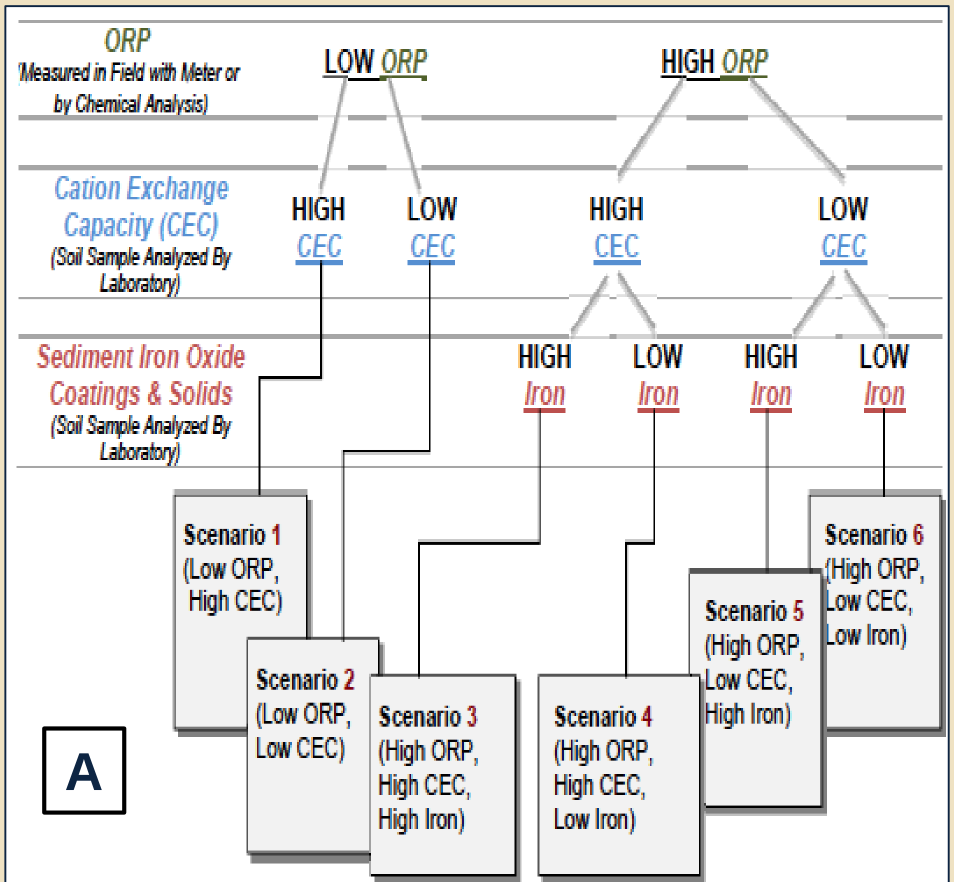
August 2015

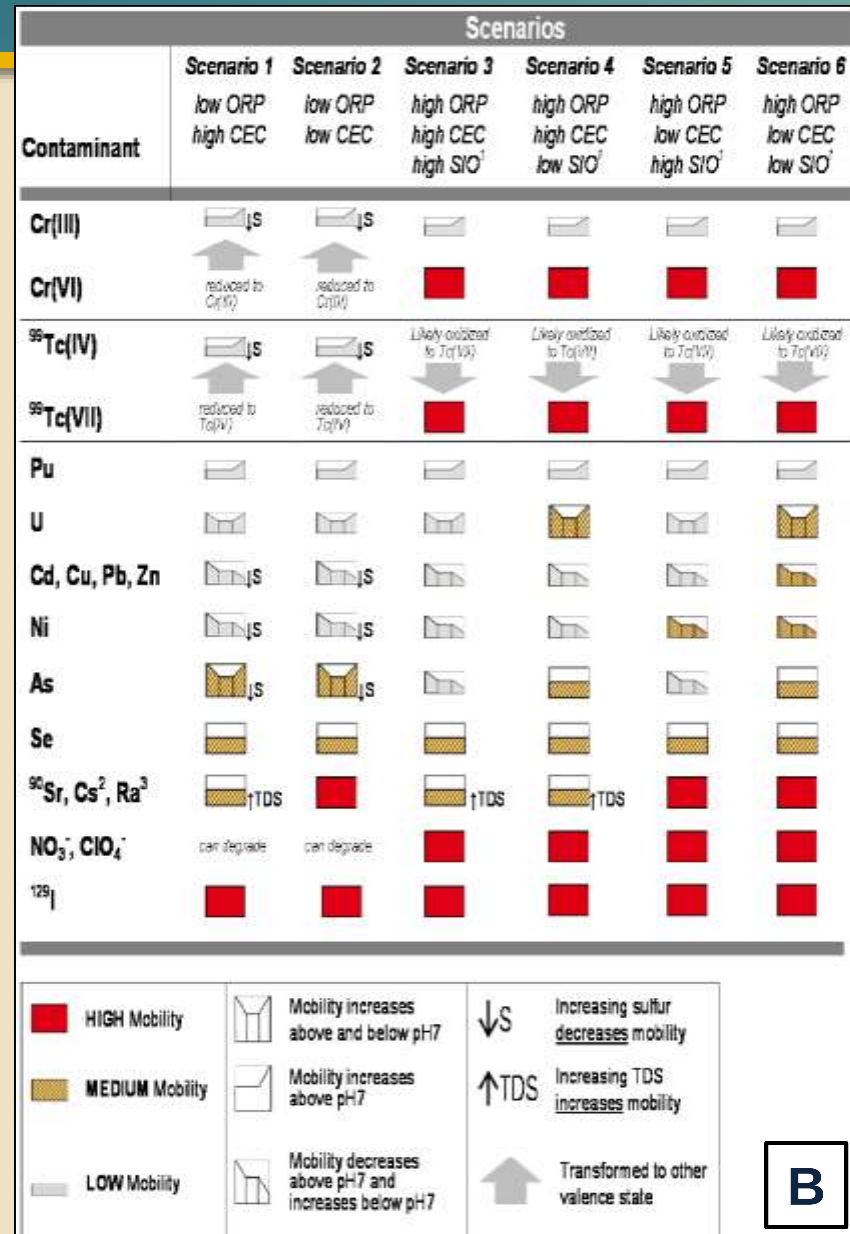
Contaminant	Biological Reaction		Abiotic Reaction	Sequestration
	Anaerobic	Aerobic		
Nitrate	Yes, degradation	No	Yes (reactive iron)	No
Perchlorate	Yes, degradation	No	Conflicting Data	No
Chromium (Cr), Selenium (Se), Copper (Cu), Cadmium (Ca), Lead (Pb), Nickel (Ni), Zinc (Zn), Beryllium (Be), Arsenic (As) (metalloid)	Valence change, generally favorable	Valence change, generally unfavorable	Valence change, generally favorable	Yes (sorption, co-precipitation)
Uranium, Technetium, Strontium, Cesium, Radium, Iodine	Valence change, generally favorable	Valence change, generally unfavorable	Valence change, generally favorable	Yes (sorption, co-precipitation)

CAN I APPLY MNA TO METALS, INORGANICS, AND RADIONUCLIDES?

ADDITIONAL GUIDANCE:

"SCENARIOS FOR METALS, RADS" (Truex et al., 2011)





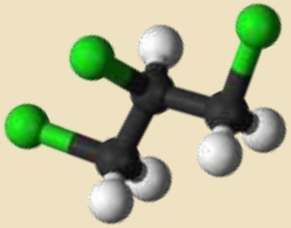
WHICH EMERGING CONTAMINANTS ARE CANDIDATES FOR MNA?

1,4-Dioxane, 1,2,3-TCP, NDMA, Phthalates, and Maybe Others?

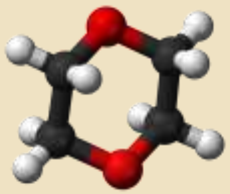
- **DoD general goal for emerging contaminants:**

"Identify chemicals or materials that either lack human health standards or have an evolving science and regulatory status."

- **Other problems**
  - **Prevalence at individual sites is largely unknown**
  - **Absence of well-established treatment technologies**
  - **Absence of tools for establishing MNA (e.g., CSIA, MBTs)**



1,2,3-Trichloropropane



1,4-Dioxane

Emerging Contaminant	Biological Degradation		Abiotic Degradation	Sequestration
	Anaerobic	Aerobic		
1,4-Dioxane	Limited	YES (mostly lab studies; can be cometabolic or used as a carbon source)	Not documented	No (poor sorption)
Per- and polyfluoroalkyl substances (PFAS)	Very limited (incomplete pathway)	Very limited (incomplete pathway)	Limited (a reliable light+Fe(III) reaction has been established)	Moderate (primarily electrostatic sorption to ferric iron minerals; limited organic carbon sorption)
N-Nitrosodimethylamine (NDMA)	YES	YES (cometabolic)	No (several ex situ methods, including UV photolysis)	No (poor sorption)
1,2,3-Trichloropropane	YES (slow, often incomplete pathway)	YES (slow, incomplete pathway)	Very limited (reactive iron, base hydrolysis)	Limited (moderate sorption)

MNA FOR OTHER CONTAMINANTS: *KEY POINTS*

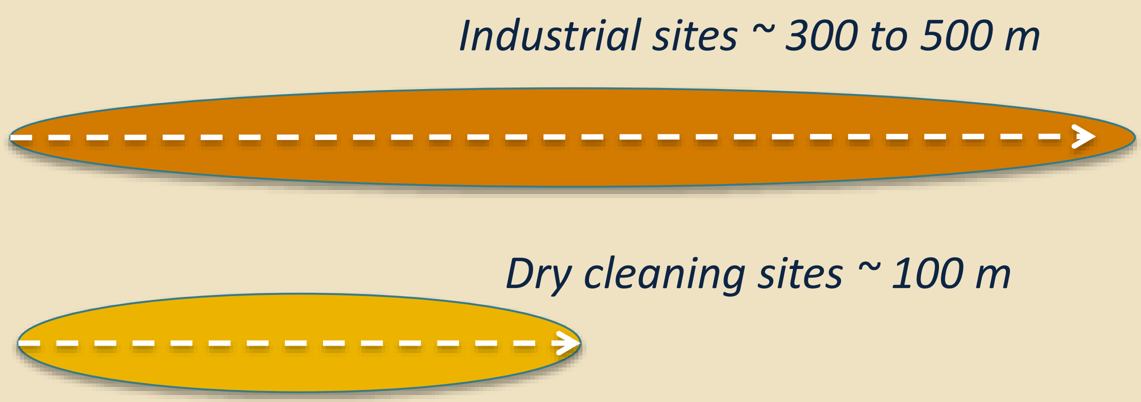
- USEPA has detailed guidance for MNA of inorganics "metals and rads"
- Example of how scientific knowledge advances: MNA of MTBE and other oxygenates
- Lots of research on MNA for emerging contaminants: some contaminants look promising, others not so much

MNA AT DRY CLEANER SITES: *Regulatory Perspective*

- **Most states have guidance on MNA, but don't differentiate between dry cleaners and other sites in their guidance**
- **Many states have dry cleaner cleanup programs, and some specifically discuss MNA**
- **State Coalition for Remediation of Drycleaners has case studies for 36 sites where MNA has been implemented**

MNA AT DRY CLEANER SITES:
Performance

- **Published study of 137 dry cleaner sites in Texas (Suarez et al., 2004)**
  - **Average half lives for PCE = 1 to 3 yr**
  - **Dry cleaner plumes (median = 100 m) were shorter than plumes from industrial sites (median = 300 to 500 m)**




Remediation Journal   Explore this journal >

Natural attenuation of chlorinated solvent plumes at Texas dry cleaners

Monica P. Suarez, Hanadi S. Rifai, Tricia J. Rittaler, Sarah Hausman

First published: 17 June 2004   Full publication history

DOI: 10.1002/rem.20010   View/save citation

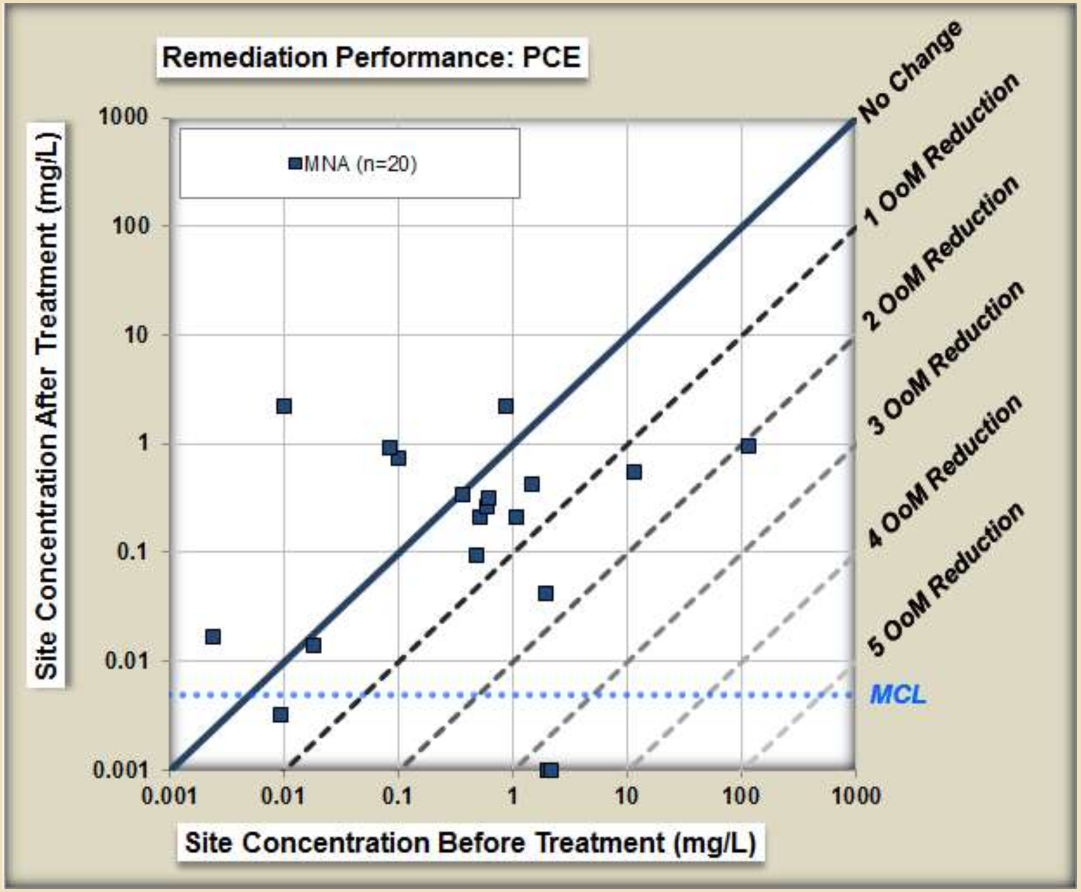
Cited by: 6 articles   Citation tools

REMEDIATION

View issue TOC
Volume 14, Issue 3
Summer 2004
Pages 7-33

MNA AT DRY CLEANER SITES:
Performance

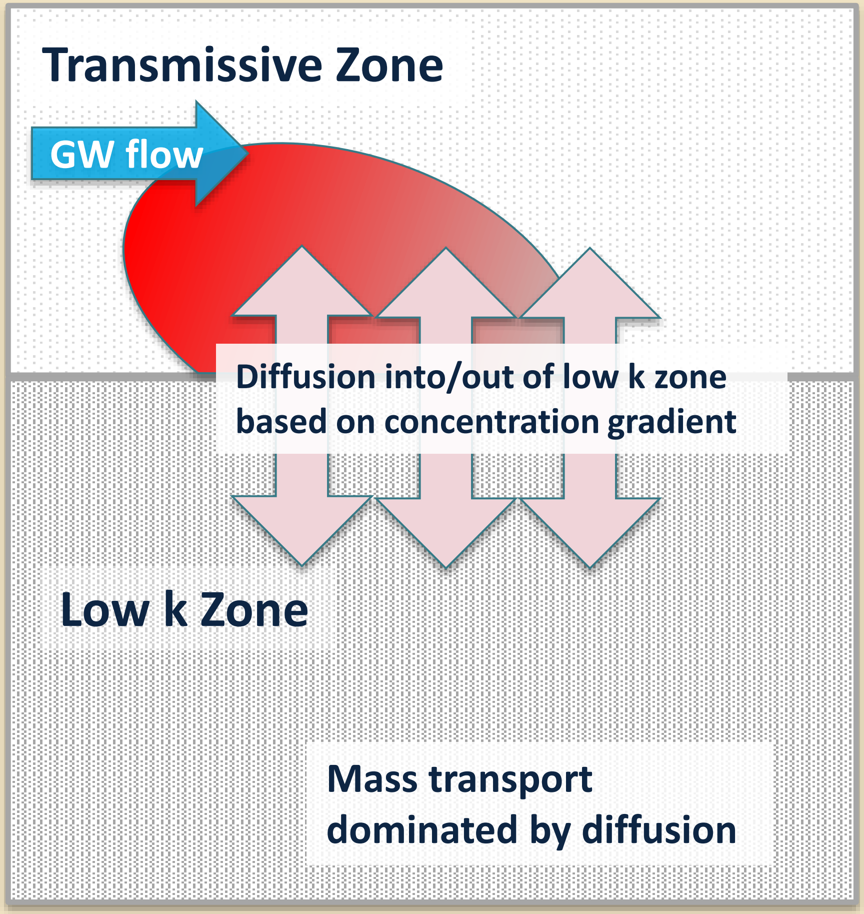
- Remediation performance survey for ESTCP ER-1120 (2016):
  - Similar performance for sites with PCE compared to sites with TCE or other chlorinated solvents
  - MNA performance for PCE was slightly lower than other technologies



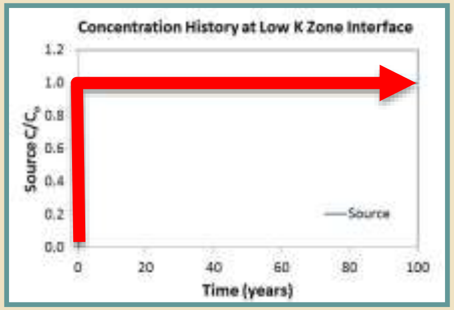
USING MATRIX DIFFUSION TO EVALUATE SOURCE HISTORY: *Comparing a PCE Site vs. a TCE Site*

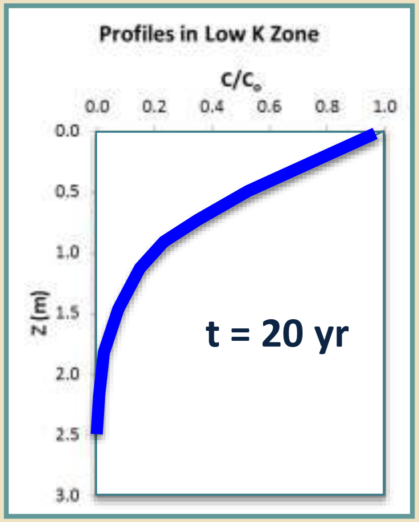
Process:

- Soil profile reflects style of source loading over time

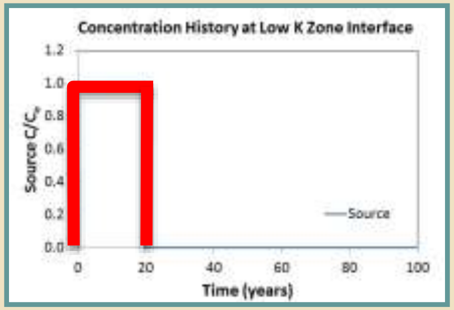


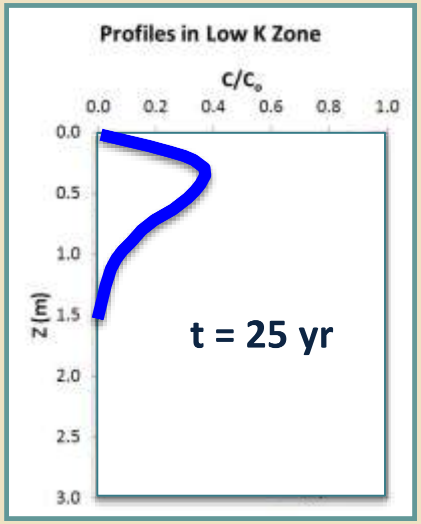
CONSTANT SOURCE





SOURCE REMOVAL





TECHNICAL APPROACH: *Overview*

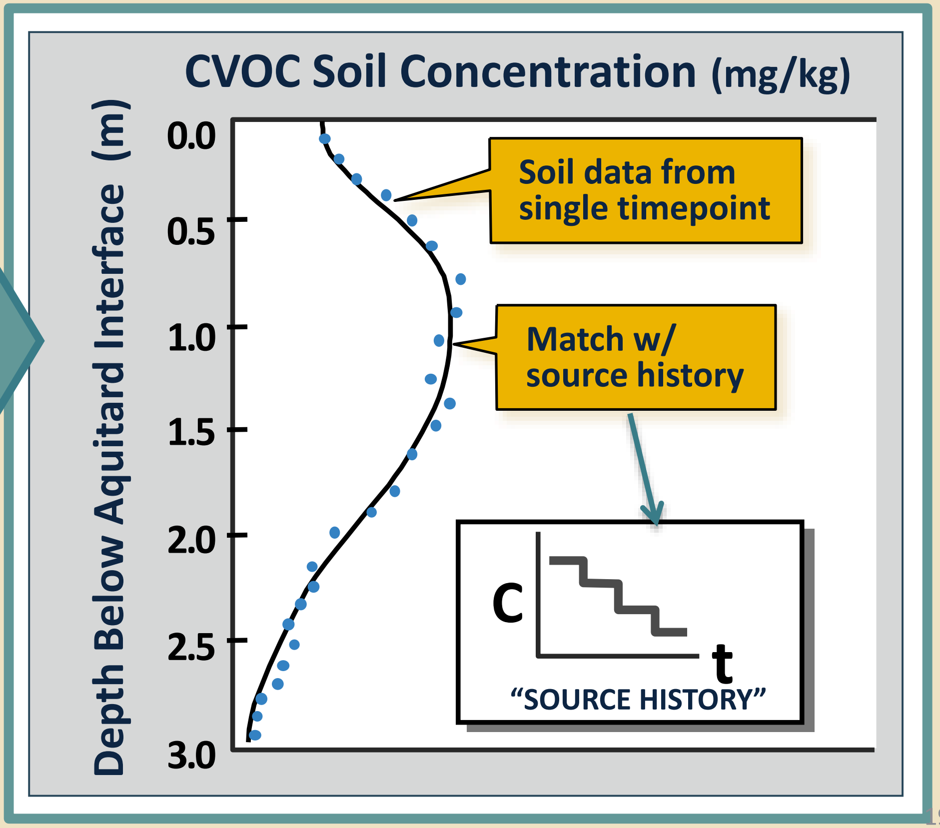
Possible Solution?

- At sites with low-k intervals, high-resolution data from soil cores provides a way to do this

Sampling devices

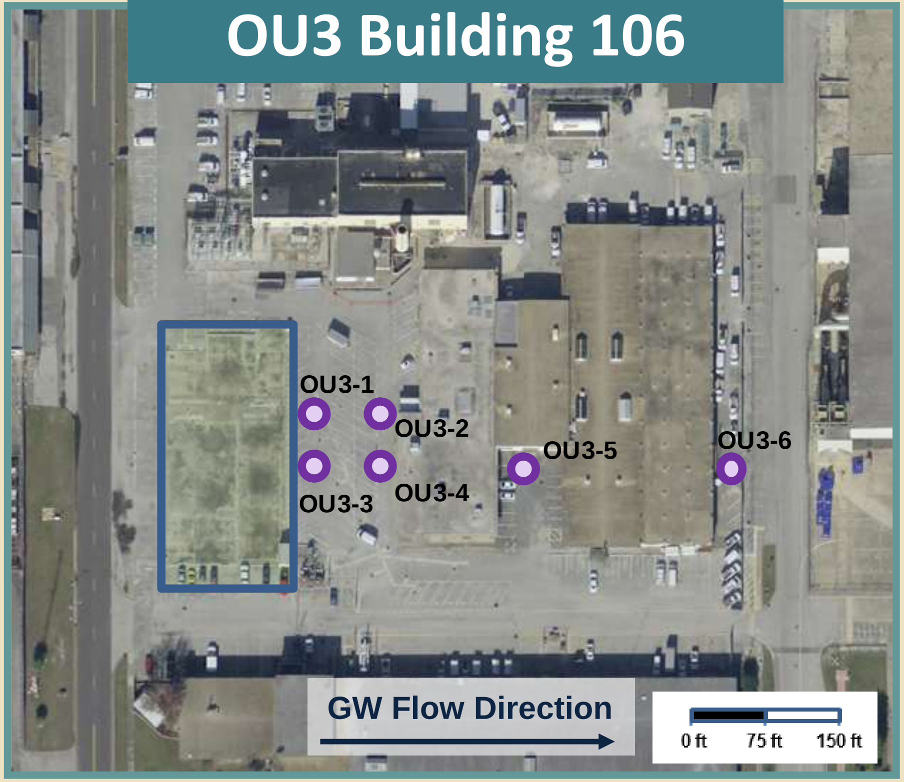
Soil cores

Field methanol preservation



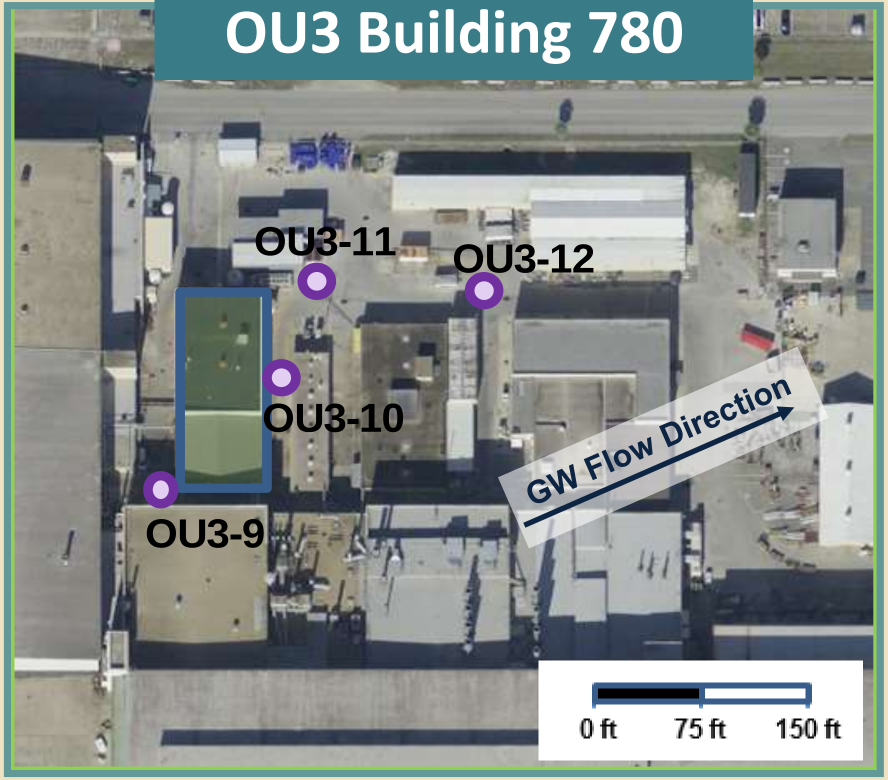
FIELD DEMONSTRATION:
2 Different Source Areas at NAS Jacksonville

Source Area #1: OU3 Building 106



Former dry cleaner (1962 – 1990):
PCE and TCE released to shallow aquifer

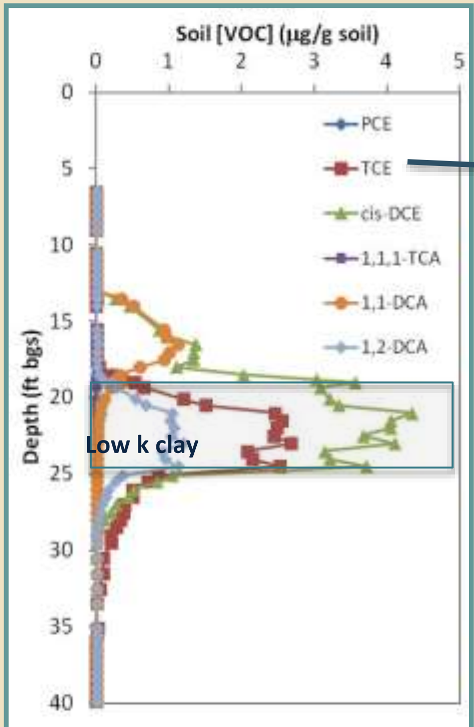
Source Area #2: OU3 Building 780



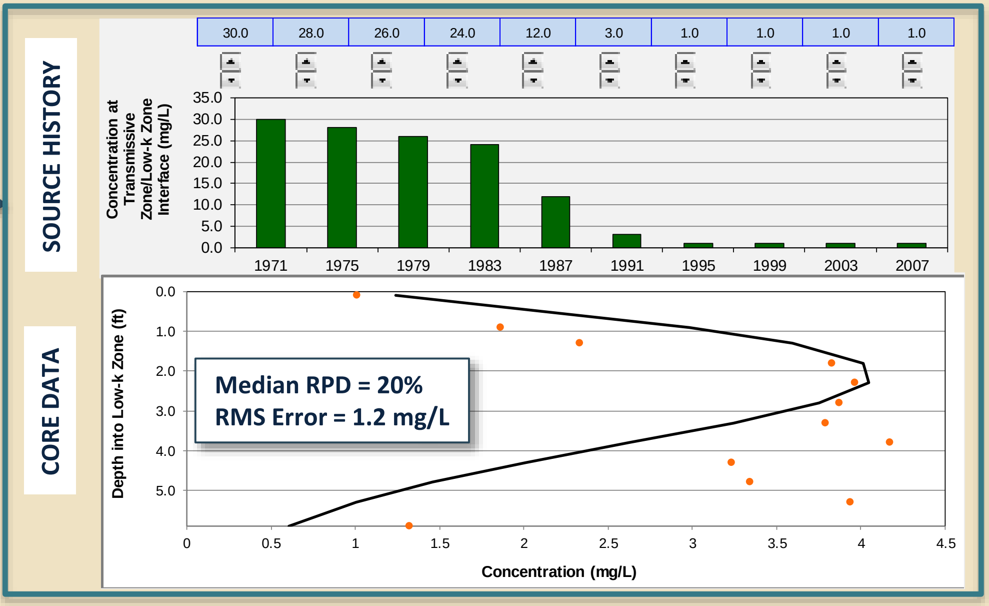
Former paint stripping/solvent recycling facility (1970s – 1980s):
PCE, TCE, and 1,1,1-TCA released to shallow aquifer

MODEL TESTING: *Source Area #2 – Building 780*

EXAMPLE: Soil core VOC profile from OU3-9 shows reasonable match with *declining source*



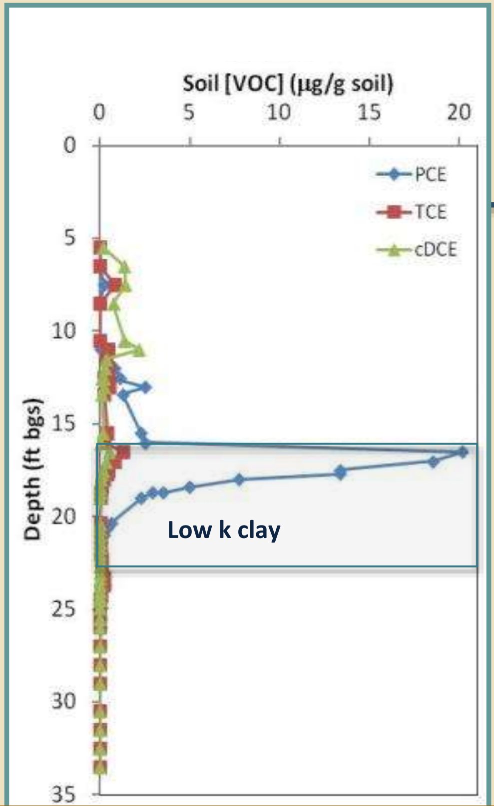
TCE Only



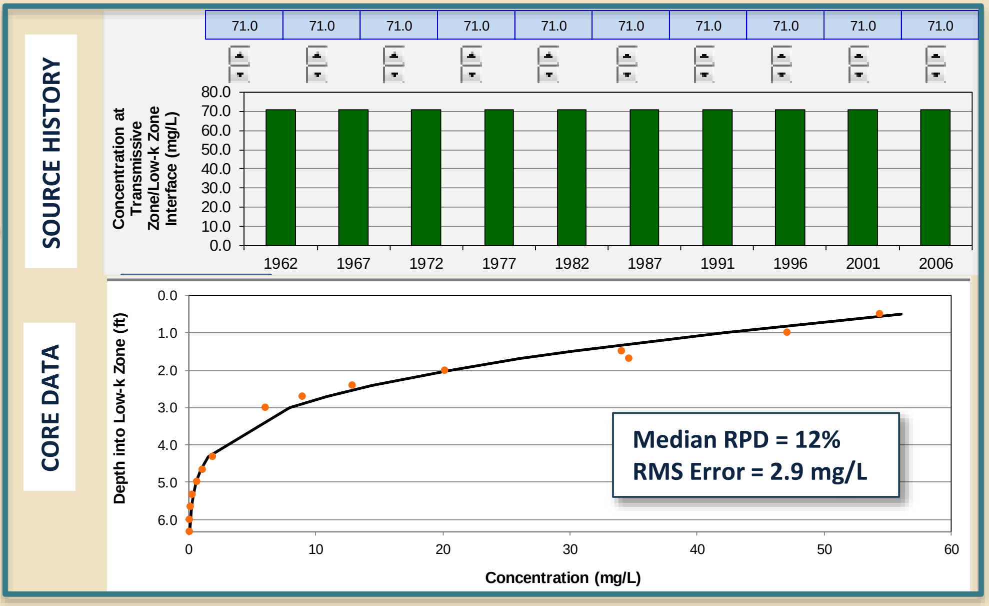
OTHER MODEL RUNS COMPLETED (not shown): **1,1,1-TCA, 1,2-DCA**

MODEL TESTING: *Source Area #1 – Building 106*

EXAMPLE: Soil core VOC profile from OU3-3 shows good match with *constant source*



PCE Only



***NOTE:* GW conc. used to calibrate transmissive zone due to loss of soil mass in sands**

SITES THAT ARE WELL-SUITED FOR MNA

- No receptors impacted
- Decreasing concentration trends w/ reasonable remediation timeframe
- Shrinking or stable plume
- Slow groundwater velocity (or long travel time)
- Attenuation mechanisms have been established
- Geochemical conditions favor continued attenuation
- Weak source

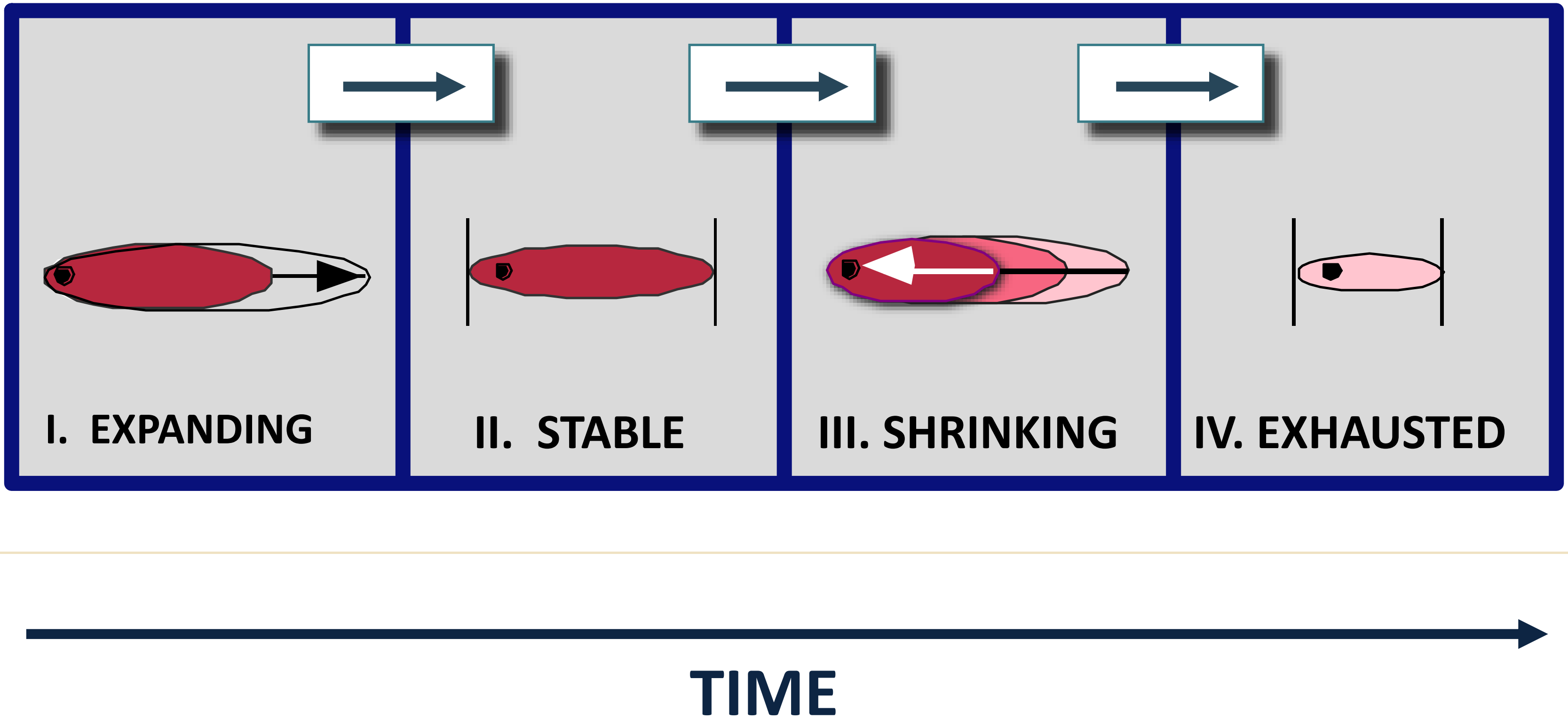
SITES THAT ARE *NOT* WELL-SUITED FOR MNA

- Receptors impacted
- Increasing concentration trends w/ long timeframe
- Expanding plume (or imminent threat)
- Attenuation mechanisms poorly understood
- Geochemical conditions won't sustain attenuation
- Strong or uncontrolled source (some states won't allow free or residual product to remain)
- Monitoring limitations (can't ensure it's protective)

“We are all Keynesians now”

“We are all MNA implementers now”

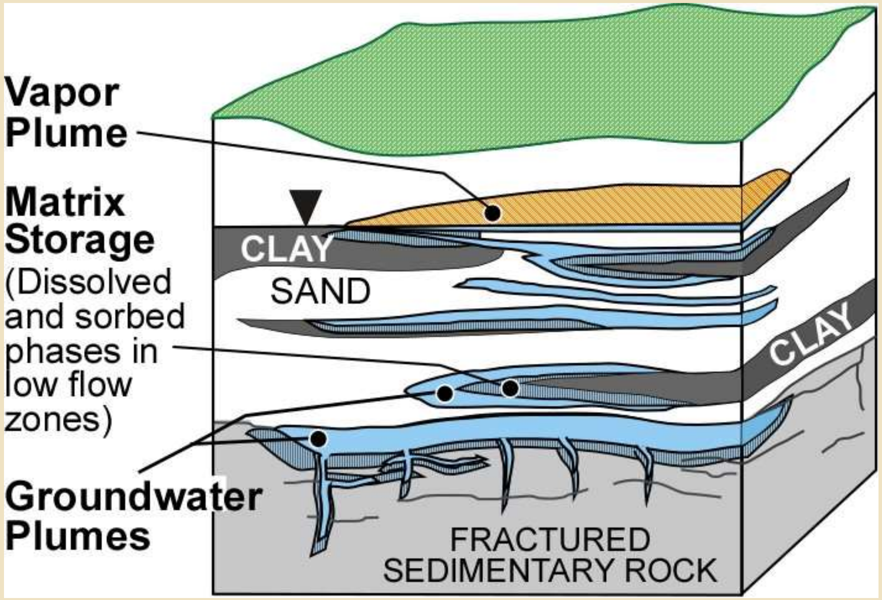
SCHEMATIC OF PLUME LIFECYCLE



LOW RISK SITES AND MATRIX DIFFUSION

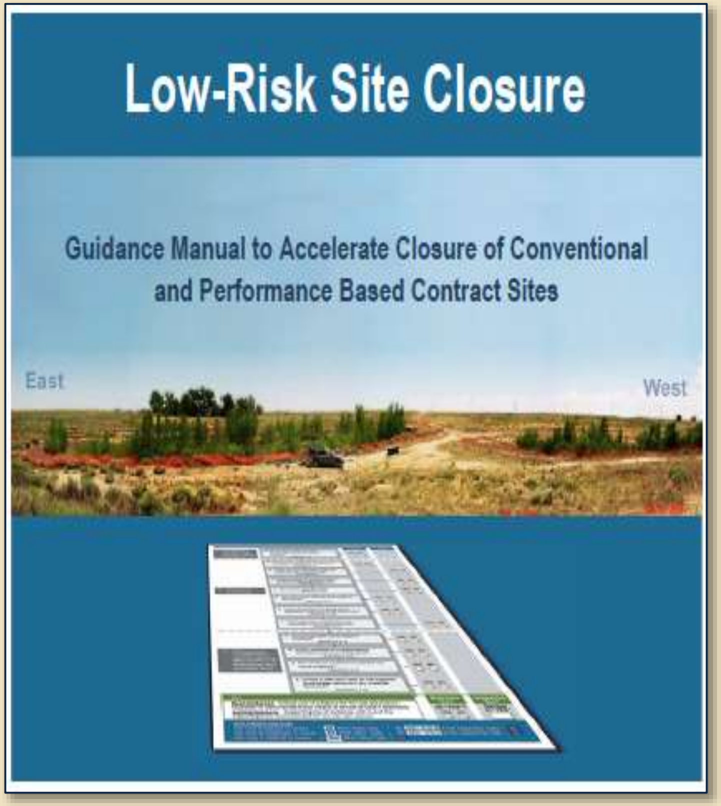
- If site is "Late Stage"
  - Different source process
  - Mass discharge % from NAPL is low
  - Matrix Diffusion % is high
  - Not "Principal Threat Waste"
- Conceptual Model
  - No potential source migration
  - Further source remediation difficult
  - Not practicable to remove mass in low-permeability zones

Late Stage Site (Sale, 2008)



WHAT IS A LOW RISK SITE?

- Low-Risk means MNA the rest of the way
- Recognition that complete closure is difficult/unattainable
- Concentrations low
- Example NOT low risk: mobile NAPL
- Example YES low risk: matrix diffusion



Air Force “LoRSC” Guidance

		ANSWERS FOR "MUST HAVE" QUESTIONS	ANSWERS FOR "SUPPORTING" QUESTIONS
I. Do You Have a Complete CSM that Reflects Key Low-Risk Closure Concepts?	**1.** Have all of the components of the Conceptual Site Model (CSM) been evaluated? (Section 3.1.1)	YES ✓ NO	
II. Are Sources Controlled?	**1.** Are there no significantly mobile source materials? (Section 3.2.1)	YES ✓ NO	
	2. Is the source zone free of any environmentally significant quantity of NAPL? (Section 3.2.2)		YES ✓ NO
	3. Is it possible that any further source zone cleanup will be constrained by matrix diffusion processes? (Section 3.2.3)		YES ✓ NO
	4. Are sources relatively small? (Section 3.2.4)		YES ✓ NO
	5. Are source zone concentrations stable or decreasing? (Section 3.2.5)	YES ✓ NO	
	6. Is there evidence of on-going natural attenuation processes in the source zone? (Section 3.2.6)	YES ✓ NO	
	7. Will future source remediation only marginally improve site conditions? (Section 3.2.7)		YES ✓ NO

III. Will Residual Contamination Have No Adverse Effect on Present and Future Land and Water Uses?

Question	YES	NO
1. Is the groundwater plume stable or shrinking? (Section 3.3.1)	✓	
2. Is there evidence of on-going natural attenuation processes in the plume? (Section 3.3.2)	✓	
3. Are conditions protective of potential and future receptors? (Section 3.3.3)	✓	
4. Is there no near-term need for the impacted groundwater resource or any impacted land uses? (Section 3.3.4)	✓	

KEY:

MUST HAVE DATA: Critical Line of evidence for low-risk site closure - necessary to demonstrate these criteria at almost all sites if applicable.

SUPPORTING DATA: Supporting line of evidence, with 0-4 of the supporting lines recommended for low-risk site closure.

"Must Have" Questions

All "YES"?

YES ✓ NO

"Supporting" Questions

Number of "YES"

4

WHAT IT MEANS

LoRSC **Site Type A** (strongest case for low-risk closure or reduced monitoring)
= **All** "Must Have" Questions = Yes ***AND* 3 or 4** of the "Supporting" Questions = Yes

LoRSC **Site Type B** (Moderately good case for low-risk closure or reduced monitoring)
= **All** "Must Have" Questions = Yes ***AND* 0 to 2** of the "Supporting" Questions = Yes

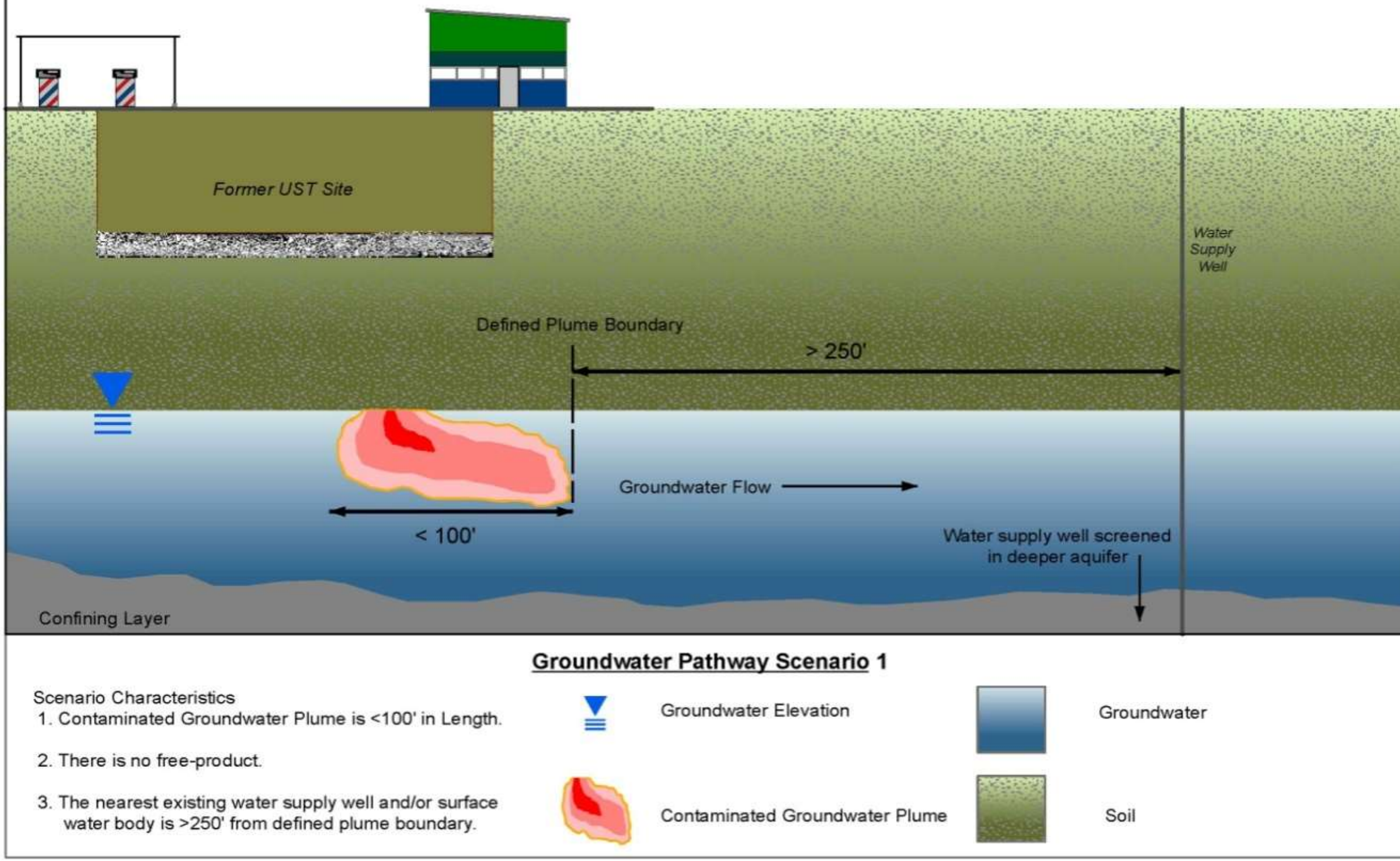
LoRSC **Site Type C** (More difficult for low-risk closure or reduced monitoring)
= ***Any*** "Must Have" Question = No

LOW THREAT SITES

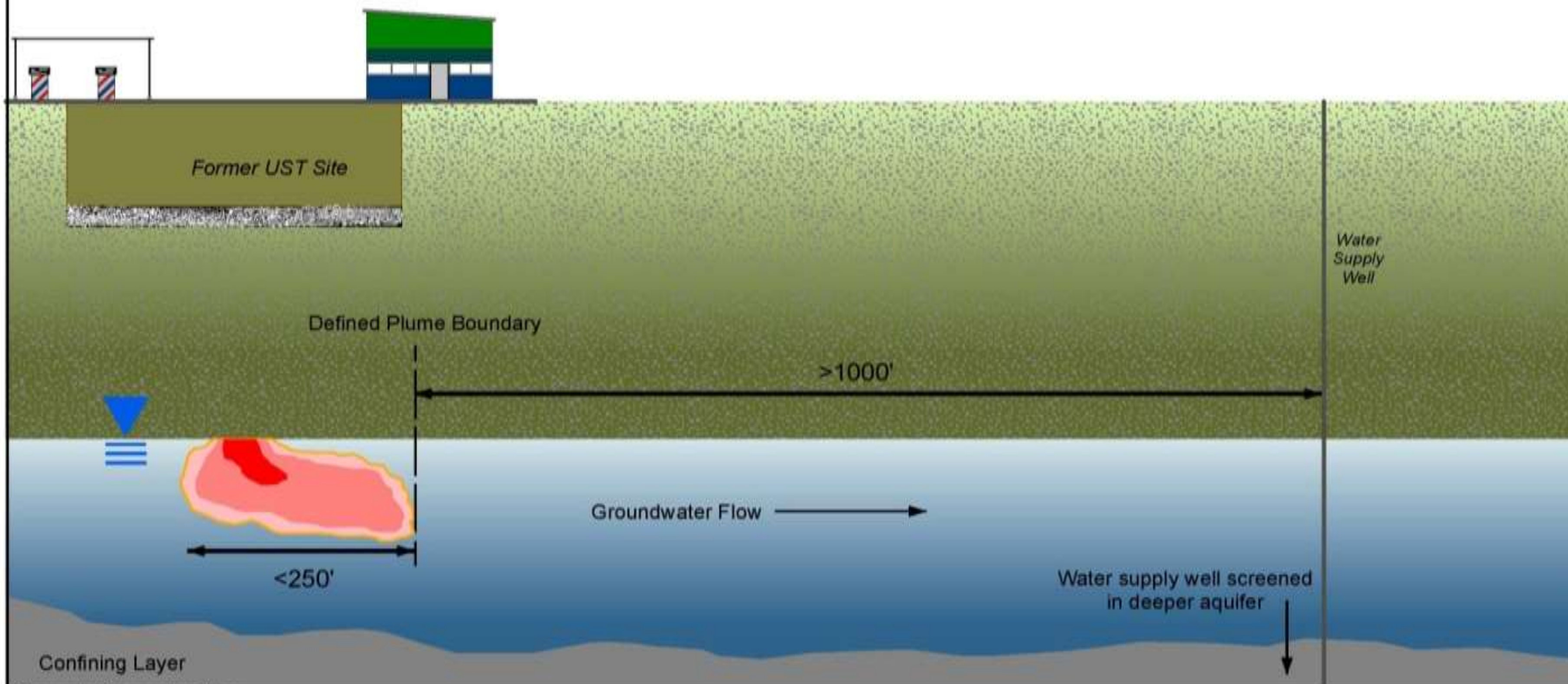
CALIFORNIA'S CRITERIA FOR UNDERGROUND STORAGE TANK LOW-THREAT CLOSURE

1. **Site must be in service area of public water system**
2. **Release must consist of "petroleum"**
3. **Release has been stopped**
4. **Free product removed to the extent practicable**
5. **Conceptual Site Model prepared and validated**
6. **"Secondary Source" removal has been addressed**
7. **MTBE testing requirement**

California Low-Threat Petroleum UST Closure Policy – Scenario 1



California Low-Threat Petroleum UST Closure Policy – Scenario 3



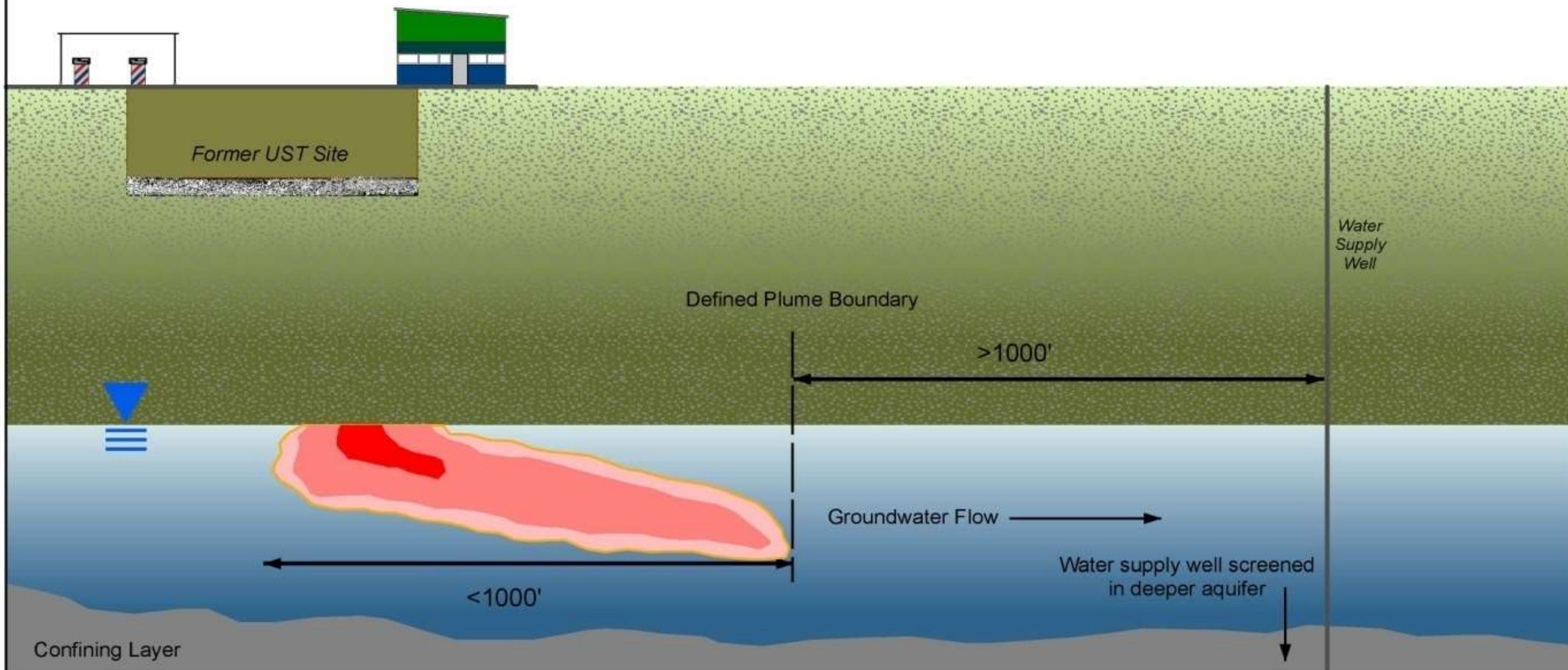
Scenario Characteristics

1. Contaminated Groundwater Plume is <250' in Length.
2. Free-product may be present below the site and not extend off-site.
3. The Plume has been stable or decreasing for a minimum of five years.
4. The nearest existing water supply well and/or surface water body is >1000' from the defined plume boundary.
5. The property owner is willing to accept a deed restriction if the regulatory agency requires a deed restrcition as a condition of closure.

Groundwater Pathway Scenario 3

Groundwater Elevation	Groundwater
Contaminated Groundwater Plume	Soil

California Low-Threat Petroleum UST Closure Policy – Scenario 4



Scenario Characteristics

1. Contaminated Groundwater Plume is <1000' in Length.
2. The nearest existing water supply well and/or surface water body is >1000' from the defined plume boundary.
3. Dissolved concentration of benzene and MTBE are <1 ppm and <1 ppm, respectively.

Groundwater Pathway Scenario 4

- Groundwater Level
- Contaminated Groundwater Plume
- Groundwater
- Soil

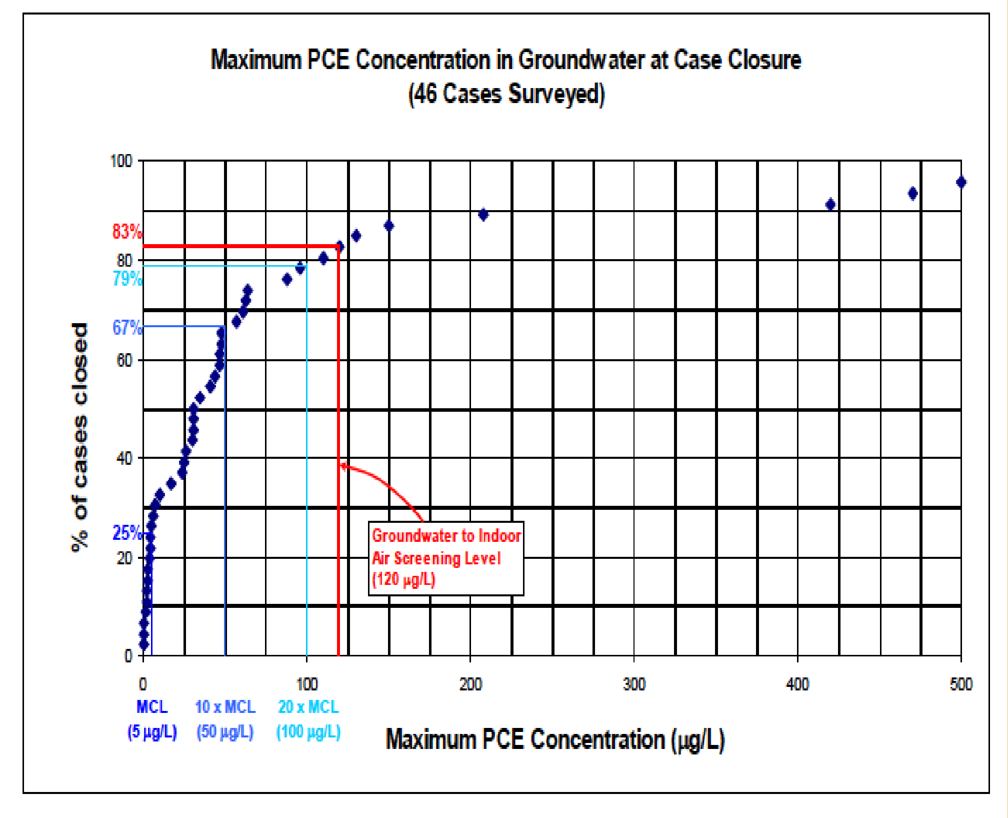
CLOSURE FOR “LOW RISK” SITES: *Key Points*

- MNA is likely to be a component of almost all remedies at some time during the site life cycle
- Examples: California Chlorinated Low Threat Closure, Air Force Low Risk Guidance, National Research Council Transition Assessment
- Not a matter of if, but when MNA is applied

LOW THREAT SITES

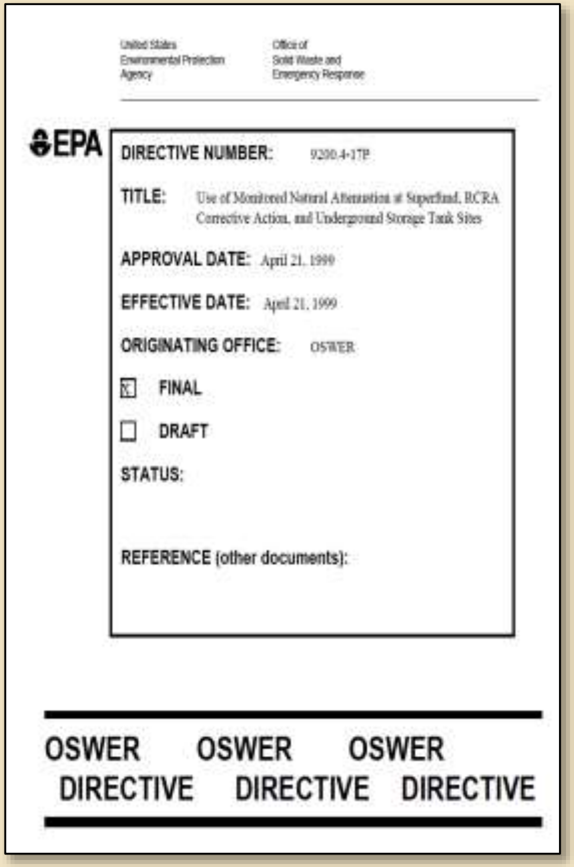
SAN FRANCISCO RWQCB'S LOW-THREAT SITE CLOSURE PROGRAM

- **Regional Water Quality Control Board**
- **9-Point Process**
- **Must demonstrate *residual pollution* will not adversely affect:**
  - **Groundwater plumes**
  - **Cleanup Standards**
  - **Risk Management Measures**



MNA TRANSITION

- 1999 EPA Directive:
  - MNA should not be considered a default or presumptive remedy, and that it should be applied *"very cautiously as the sole remedy"* and that *"source control will be fundamental components of any MNA remedy."*
- MNA being used extensively
  - Sole remedy
  - Sole groundwater remedy
- States have specific criteria


United States Environmental Protection Agency

Office of Solid Waste and Emergency Response

EPA

DIRECTIVE NUMBER: 9200.4-17P

TITLE: Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites

APPROVAL DATE: April 21, 1999

EFFECTIVE DATE: April 21, 1999

ORIGINATING OFFICE: OSWER

☒ FINAL

☐ DRAFT

STATUS:

REFERENCE (other documents):

OSWER DIRECTIVE OSWER DIRECTIVE OSWER DIRECTIVE

ITRC ENHANCED MNA GUIDANCE

Are the risks acceptable?

Is the plume stable or shrinking?

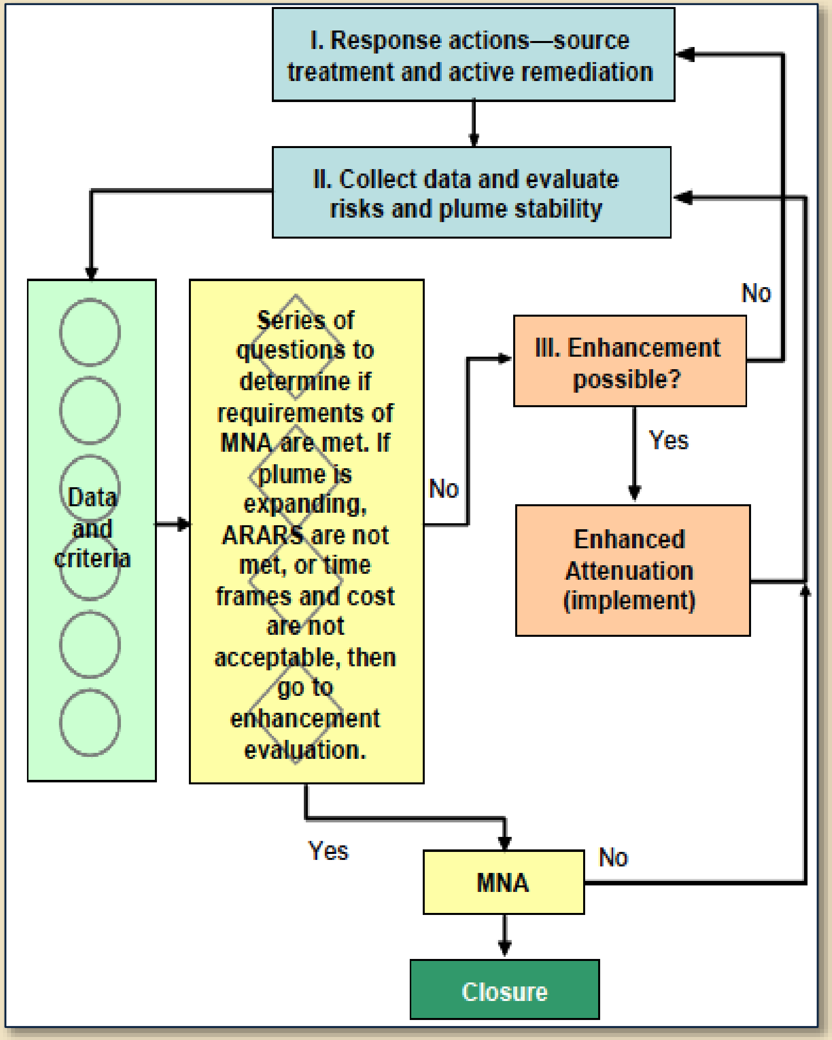
Are conditions sustainable?

Is the remediation timeframe acceptable?

Are the cost-benefits acceptable?

NO?

Enhanced Attenuation (instead of MNA)



TRANSITION ASSESSMENTS

NATIONAL RESEARCH COUNCIL, 2012

"If the effectiveness of site remediation reaches a point of diminishing returns prior to reaching cleanup goals and optimization has been exhausted, the transition to monitored natural attenuation or some other active or passive management should be considered"

ROAD MAP

- **Intro: Changing Paradigms and MNA Principles**
- **Key Attenuation Processes**
  - *Biodegradation*
  - *Abiotic Processes*
  - *LNAPL source zone degradation processes*
  - *Other processes (immobilization, storage, dilution)*
- **Field Techniques and Technologies**
  - *Groundwater sampling and analytical methods*
  - *Compound Specific Isotopes Analysis (CSIA)*
  - *Molecular Biological Tools (MBTs)*
  - *Natural Source Zone Depletion (NSZD)*
- **Should MNA be Used? Data Analysis and Monitoring Tools**
  - *Data requirements, LTM, and statistics to understand MNA rates*
  - *Common Graphics and Calculations*
  - *Remediation Timeframe Calculations*
  - *Computer Models*
- **Implementation Topics**