BioDNAPL Treatment: Fact or Fantasy?

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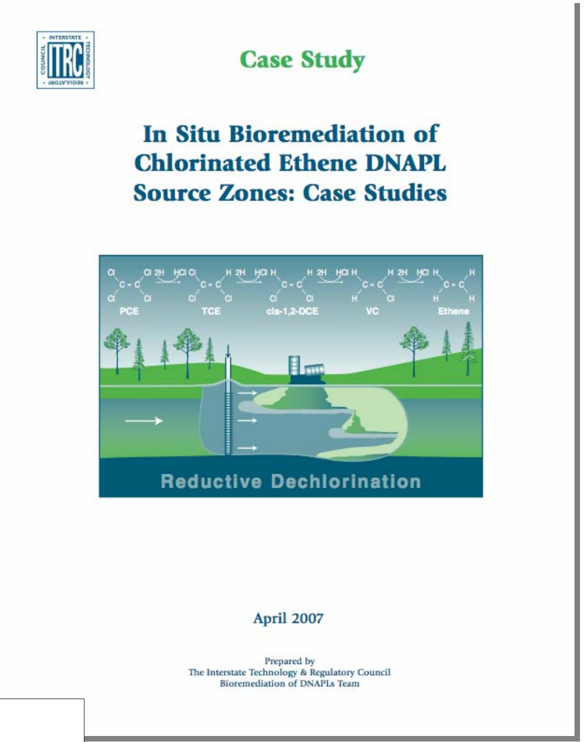
General Meeting of the
Federal Remediation Technologies Roundtable

Arlington, VA 22202
Wednesday, May 2, 2007

Something is Afoot!

- Remediation of DNAPL Through Sequential In-Situ Chemical Oxidation and Bioaugmentation (ER-0116)
- Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation (ER-0424)
- Reductions in DNAPL Longevity Through Biological Flux Enhancement (ER-0438)
- Biodegradation of Dense Non-Aqueous Phase Liquids (DNAPL) Through Bioaugmentation of Source Areas (ER-0008)
- In Situ Bioremediation of Chlorinated Solvent Source Areas with Enhanced Mass Transfer (ER-0218)



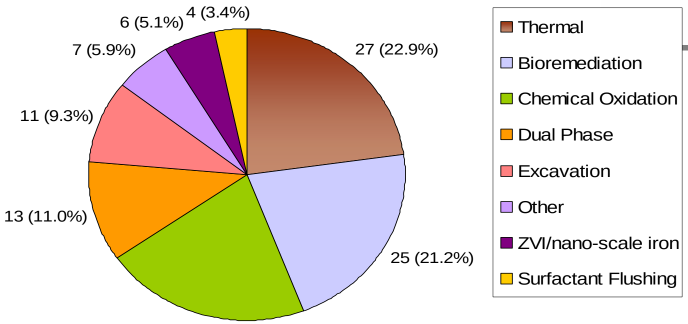
Case Study

In Situ Bioremediation of Chlorinated Ethene DNAPL Source Zones: Case Studies

April 2007

Prepared by
The Interstate Technology & Regulatory Council
Bioremediation of DNAPLs Team

Lebron, C.A., et al. 2003



Number of Sites with Specified Technology Data = 118

Something is Afoot!

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- Carr, C.S., S.Garg, and J.B. Hughes, 2000. Effect of dechlorinating bacteria on the longevity and composition of PCE-containing non-aqueous phase liquids under equilibrium dissolution conditions, Environmental Science and Technology, 34(6):1088-1094.
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- Christ, J.A, C.A. Ramsburg, L.M. Abriola, K.D Pennell and F.E. Loffler, 2005. Coupling aggressive mass removal with microbial reductive dechlorination for remediation of DNAPL source zones: a review and assessment, Environmental Health Perspectives, 133(4):465-477.
- Cope, N., and J.B. Hughes, 2001. Biologically-enhanced removal of PCE from NAPL source zones, Environmental Science and Technology, 34(10):2014-2021.
- Isalou, M., B.E. Sleep, and S.N. Liss, 1998. Biodegradation of high-concentrations of tetrachloroethene in a continuous-flow column system. Environmental Science and Technology, 32:3579-3585.
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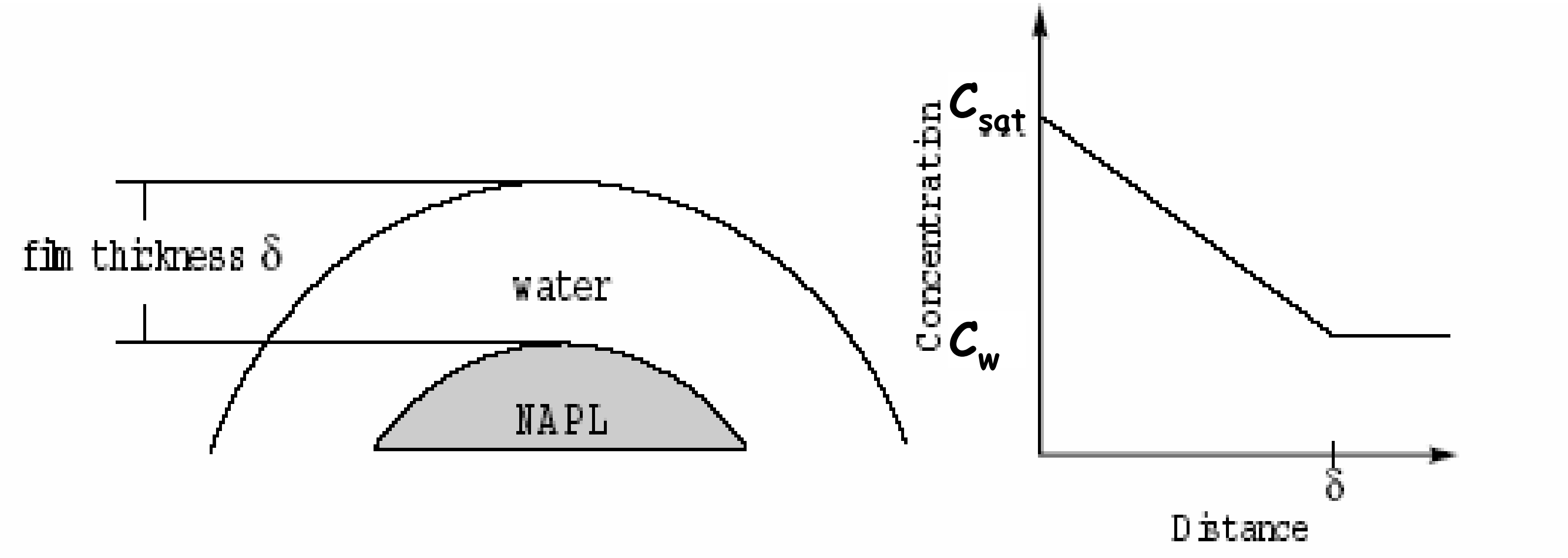
- Nielsen, R.B. and J.D. Keasling, 1999. Reductive dechlorination of chlorinated ethene DNAPLs by a culture enriched from contaminated groundwater, Biotechnology and. Bioengineering 62:160-165.
- Seagren, E.A., B.E. Rittman, and A.J. Valocchi, 1993. Quantitative evaluation of flushing and biodegradation for enhancing in situ dissolution of nonaqueous-phase liquids, Journal of Contaminant Hydrology, 12:103-132.
- Seagren, E.A., B.E. Rittmann and A.J. Valocchi, 1994. Quantitative evaluation of the enhancement of NAPL-pool dissolution by flushing and biodegradation, 28(5):853-839.
- Seagren, E.A., B.E. Rittman, and A.J. Valocchi, 2002. Bioenhancement of NAPL pool dissolution: experimental evaluation, Journal of Contaminant Hydrology, 55:57-85.
- Yang, Y., and P.L. McCarty, 2000. Biologically enhanced dissolution of tetrachloroethene DNAPL, Environmental Science and Technology, 34(14):2979-2984.
- Yang, Y., and P.L. McCarty, 2002. Comparison between donor substrates for biologically enhanced tetrachloroethene DNAPL dissolution, Environmental Science and Technology, 36(15):3400-3404.

Mass Transfer and Implication of Biological Treatment of DNAPL Sources

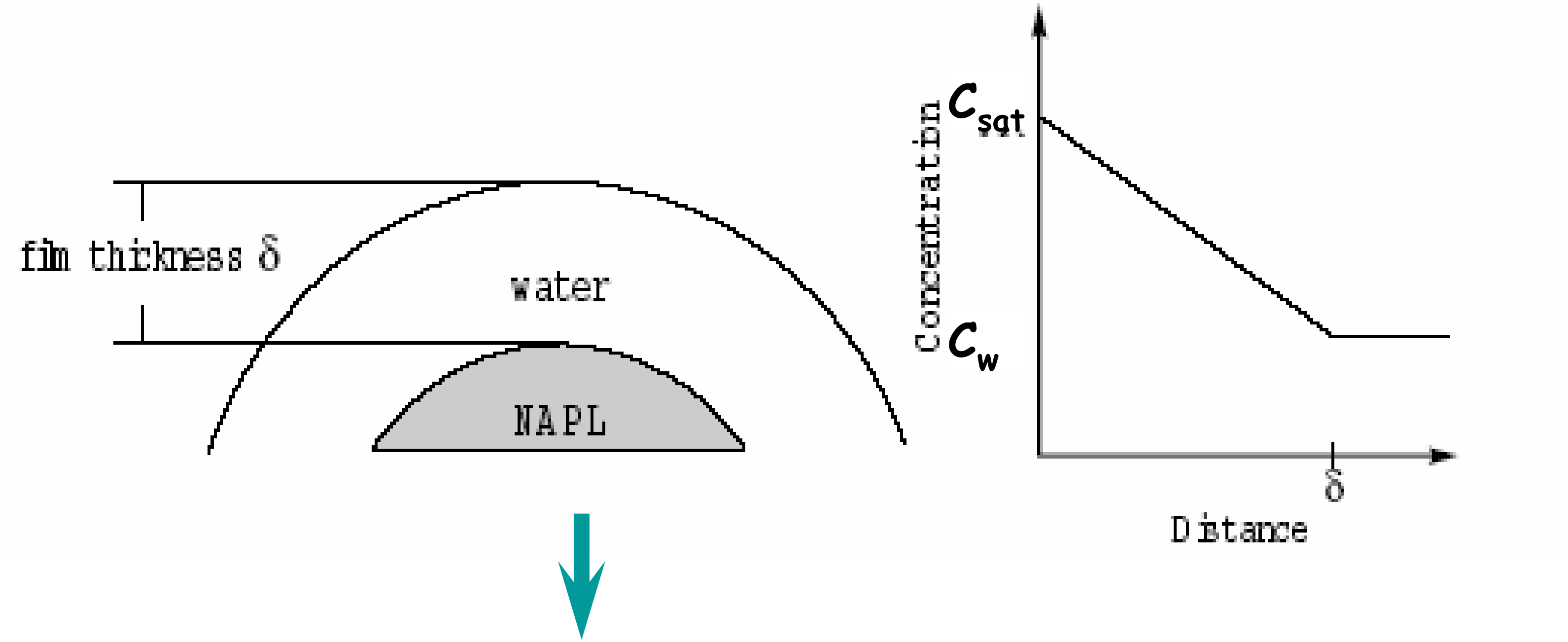
How to Affect the Mass Transfer Rate



$$J = \lambda(C_{sat} - C_w)$$

$$\lambda = f(surface\ area, velocity)$$

How to Affect the Mass Transfer Rate



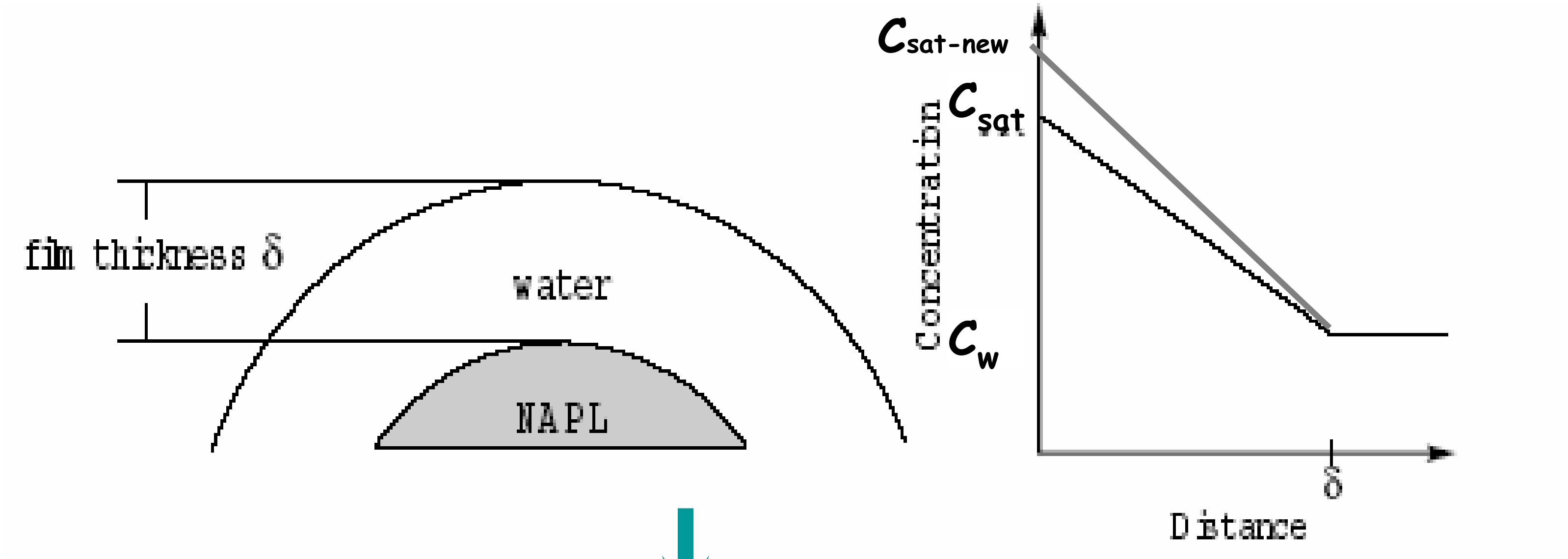
$$J = \lambda(C_{sat} - C_w)$$

Engineered Processes

e.g., flushing (increase *v*)

$$\lambda = f(surface\ area, velocity)$$

How to Affect the Mass Transfer Rate



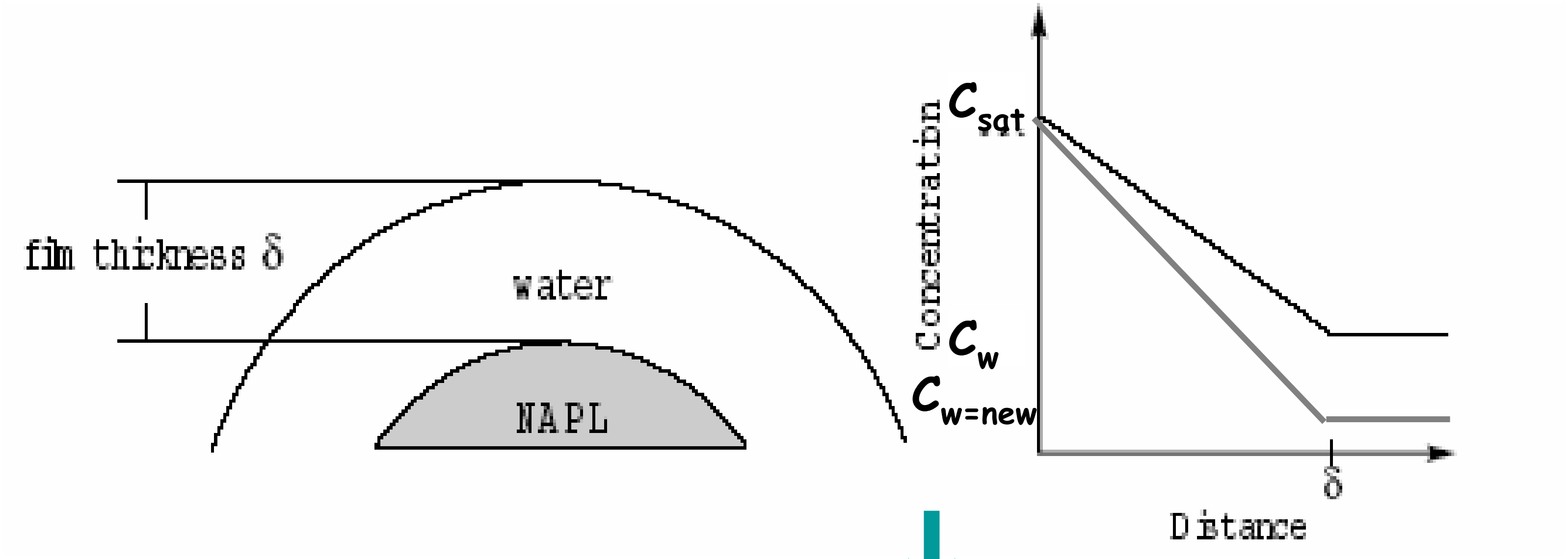
$$J = \lambda(C_{sat} - C_w)$$

Engineered Processes

e.g., surfactant, cosolvent or heat

$$\lambda = f(\mathit{surface\ area}, \mathit{velocity})$$

How to Affect the Mass Transfer Rate



$$J = \lambda(C_{sat} - C_w)$$

Engineered Processes

e.g., biodegradation or oxidation

$$\lambda = f(surface\ area, velocity)$$

Calculation of Dissolution Rate

$$M_a = C_{sat}\, \eta \sqrt{\frac{4 D_v\, \nu}{\pi L_p}}$$

M_a = Surface-area-averaged mass-transfer rate (g/m^2/d)

C_{sat} = Aqueous saturation (g/m^3)

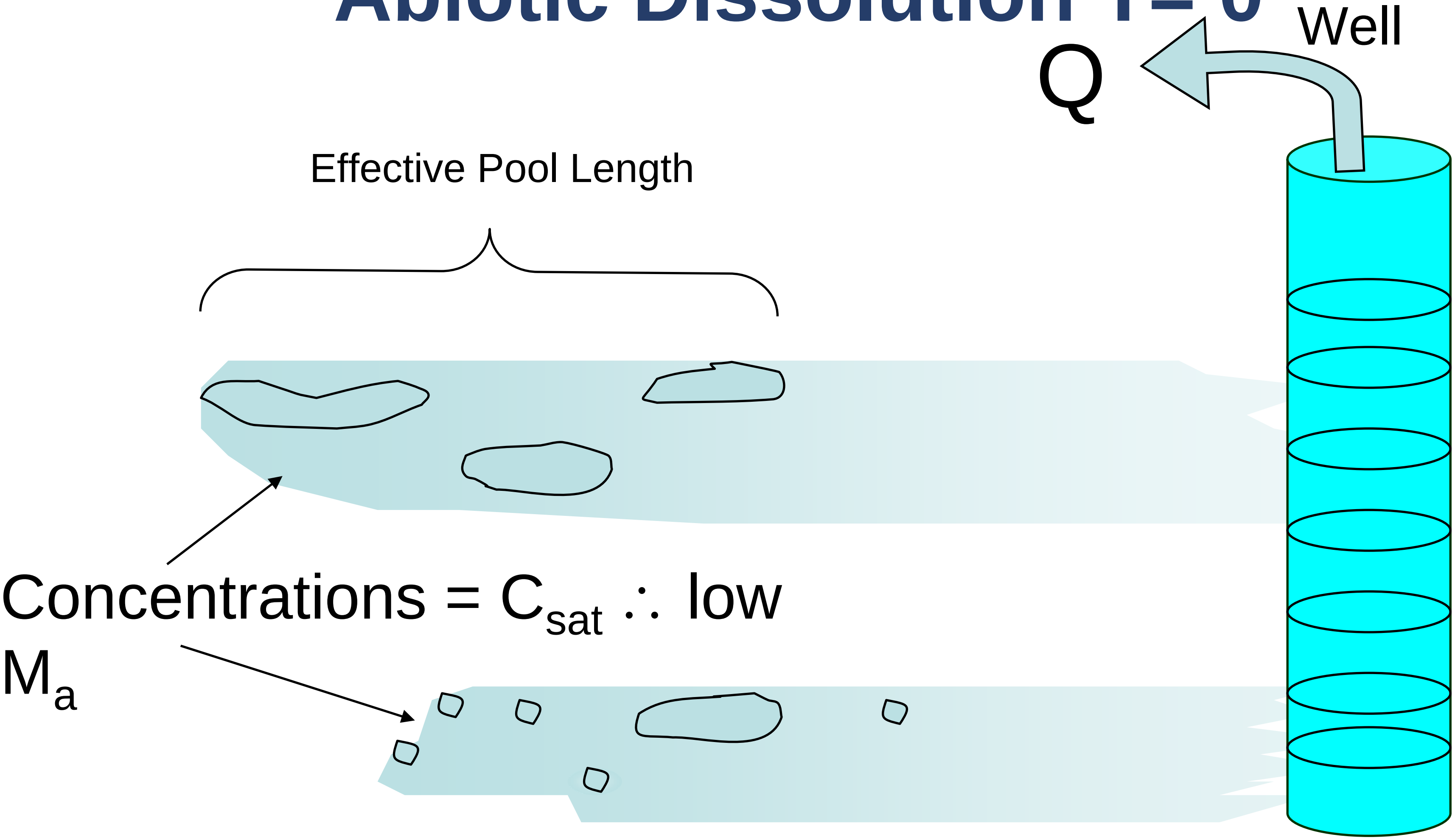
η = Porosity (filled)

D_v = Vertical dispersion coefficient (m)

ν = Average groundwater velocity

L_p = Pool length (m)

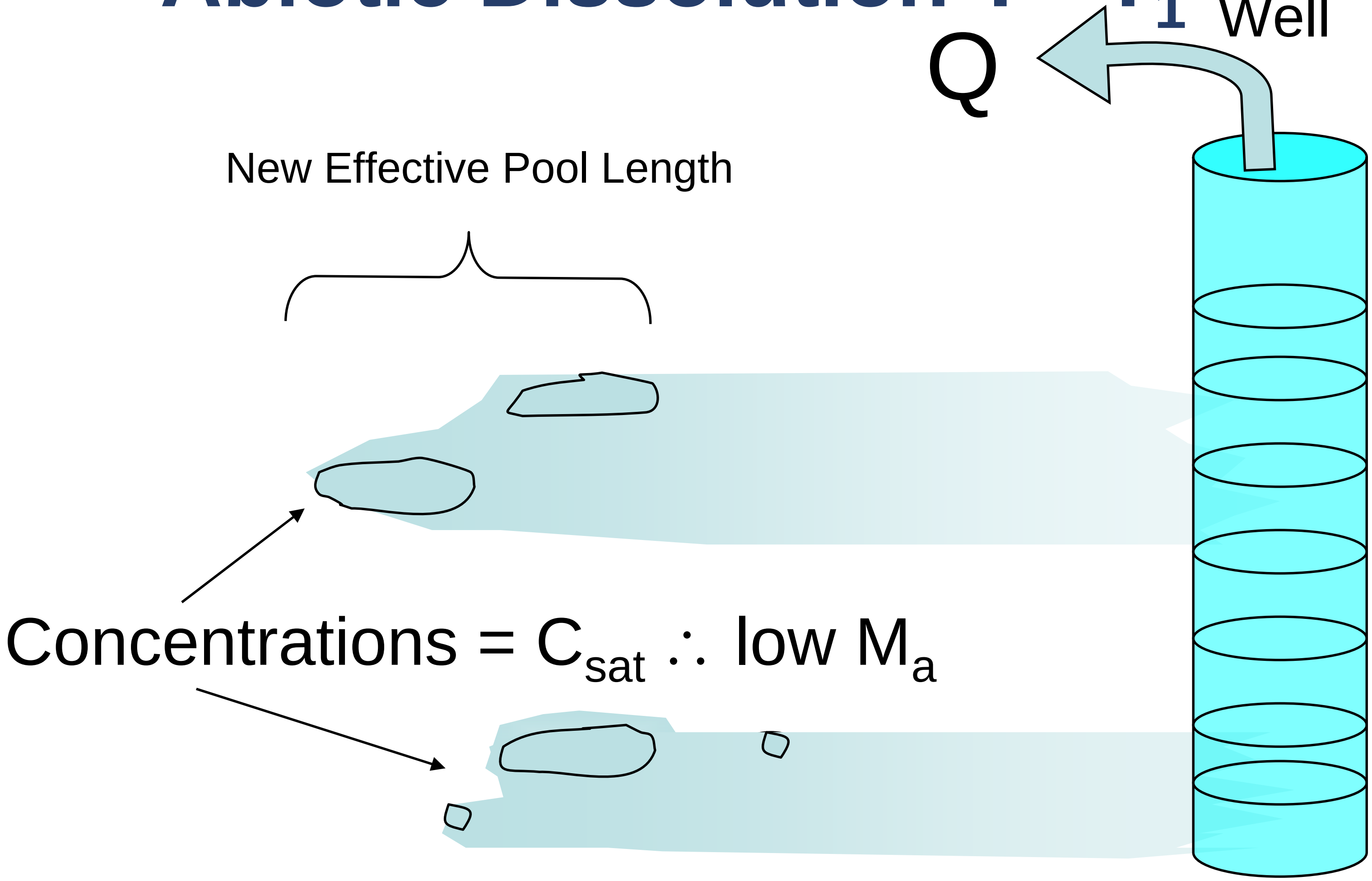
Abiotic Dissolution T= 0



Concentrations = C_{sat} ∴ low M_a

Dissolution only occurs at leading edge of the pool

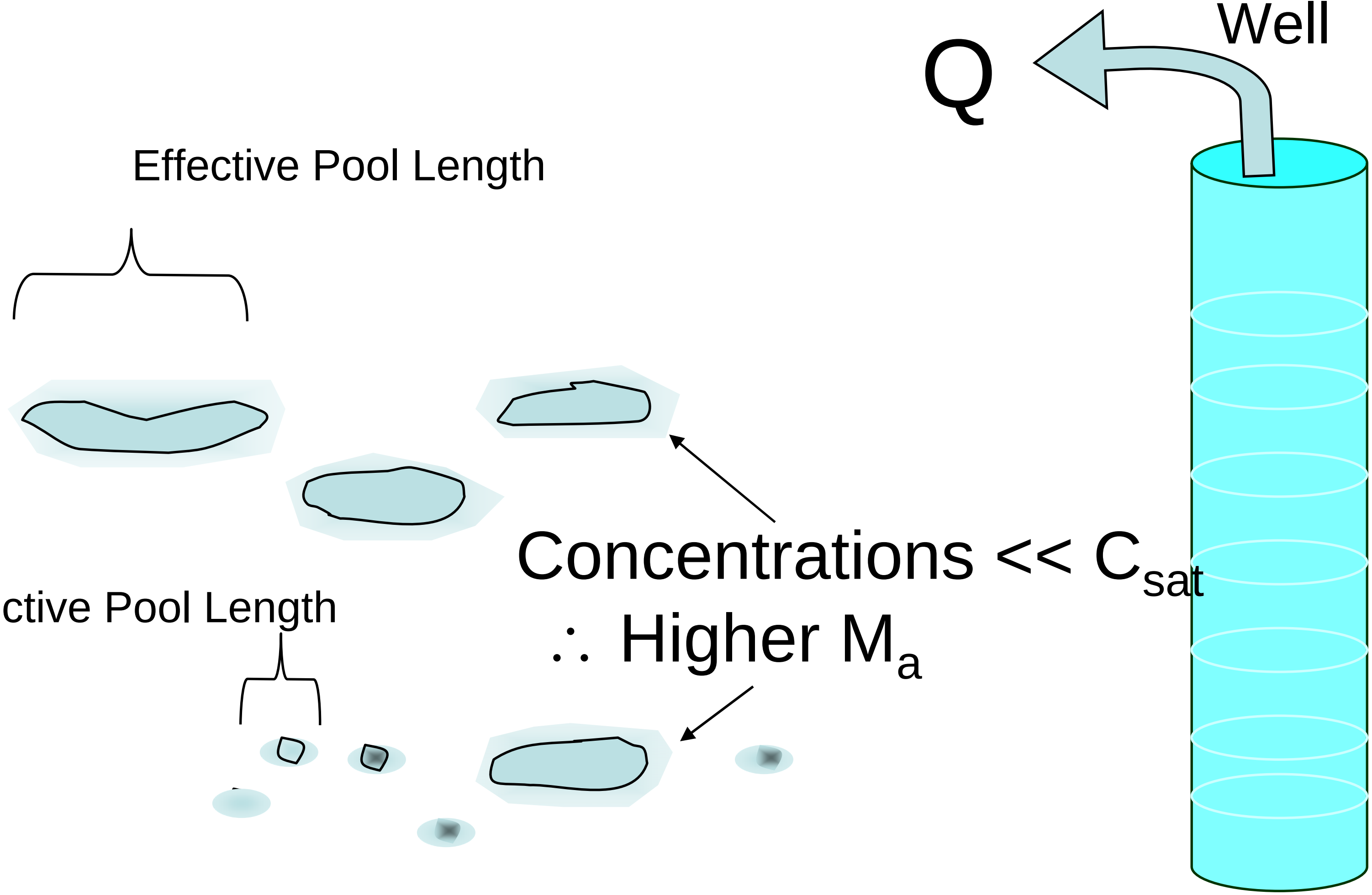
Abiotic Dissolution T= T_1



Concentrations = C_{sat} ∴ low M_a

Rest of pool dissolves only after depletion of leading edge

Impact of Biodegradation



Well

Q

Effective Pool Length

Effective Pool Length

Concentrations << C_{sat}

$\therefore$ Higher M_a

Dissolution occurs over entire surface area, increasing effective Ma

Launch Complex 34, Kennedy Space Center

LC 34 Cape Canaveral Air Force Station History

LC 34 used extensively to develop and test the Gemini and Apollo space missiles

LC 34 History

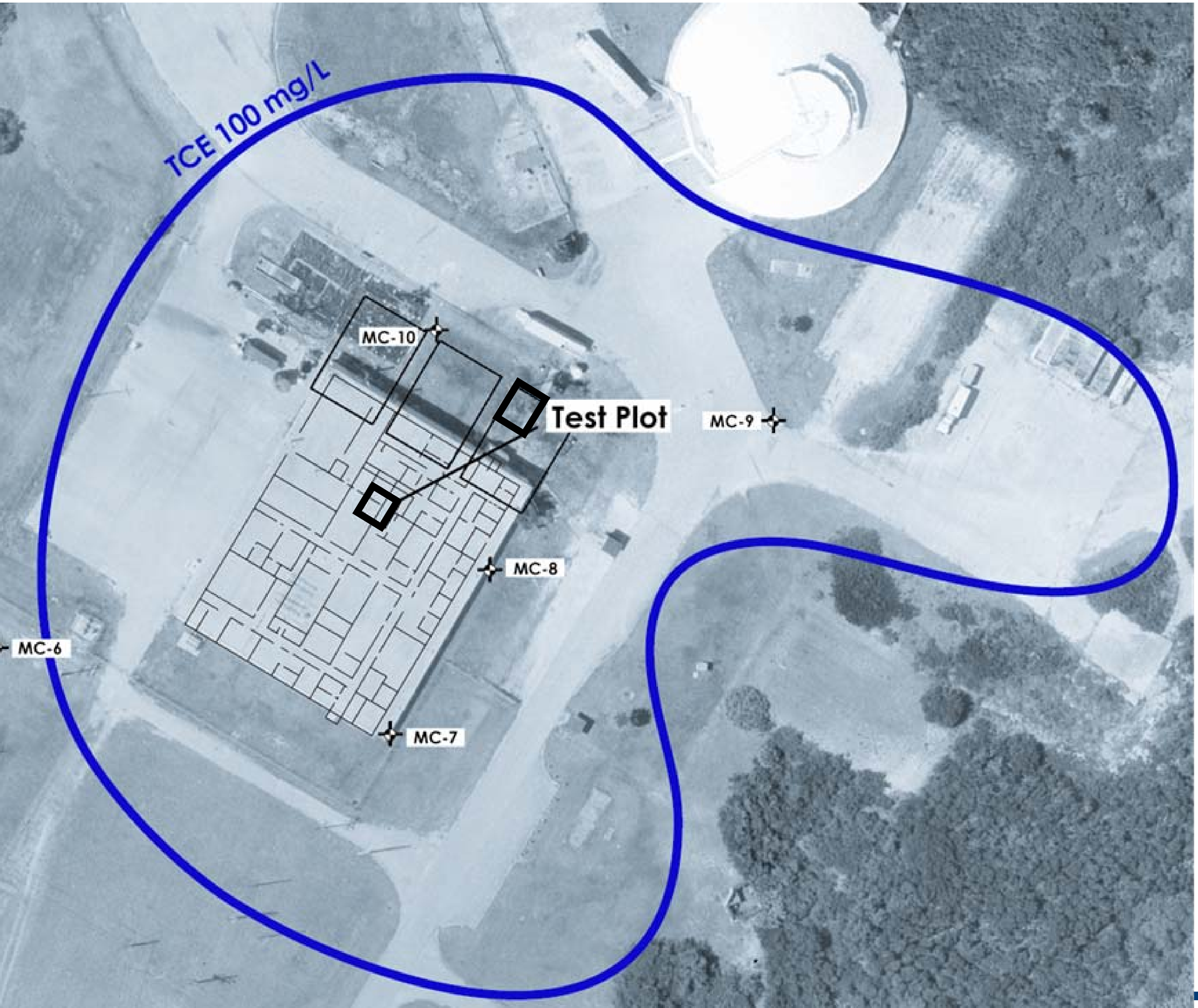
Gus Grissom, Ed White, Roger Chaffee at LC 34 which houses their Saturn 1 Launch vehicle.

All were killed 27 Jan. 1967 when a fire swept through their capsule.

NASA's first fatal tragedy

LC 34 was abandoned "in place" in their honour

Site Characterization



- Active launch facility 1960's
- Unconfined aquifer, fine-to-medium sand
- Shallow water table (<5 ft)
- TCE DNAPL released (up to 40,000 kg)

Site Characterization

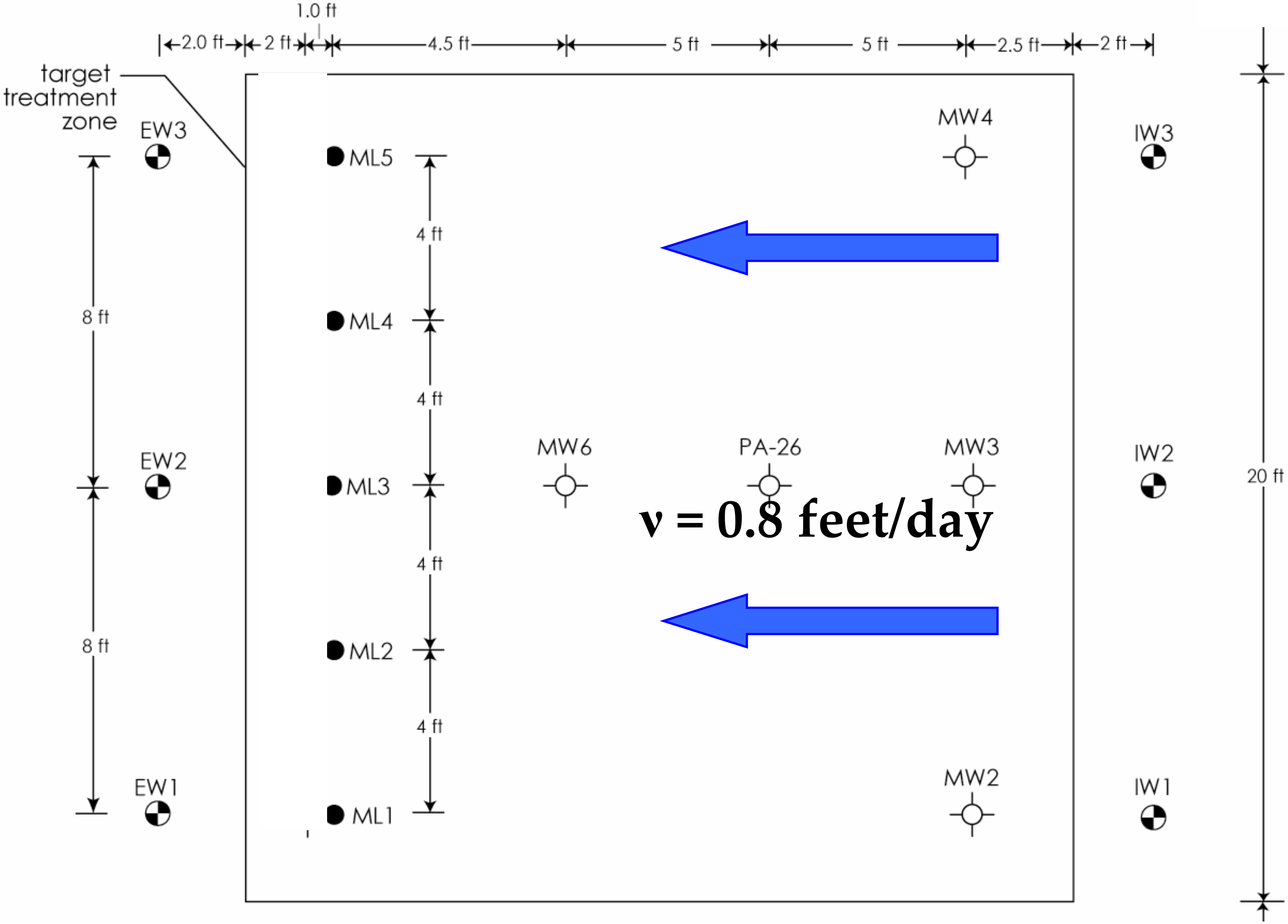
Groundwater Geochemistry

- Geochemical parameters
  - TCE GW up to solubility limit
    Soil up to 8,327 mg/kg
  - Some cis-DCE, minimal VC, trace ethene
  - DO <1 mg/L
  - Sulfate 100-300 mg/L
  - DOC ~20 mg/L
  - Also low concentrations of Fe^{2+} & CH_4
- Anaerobic groundwater with a large plume of TCE- impacted groundwater
- Partial dechlorination to cis-DCE by indigenous microorganisms

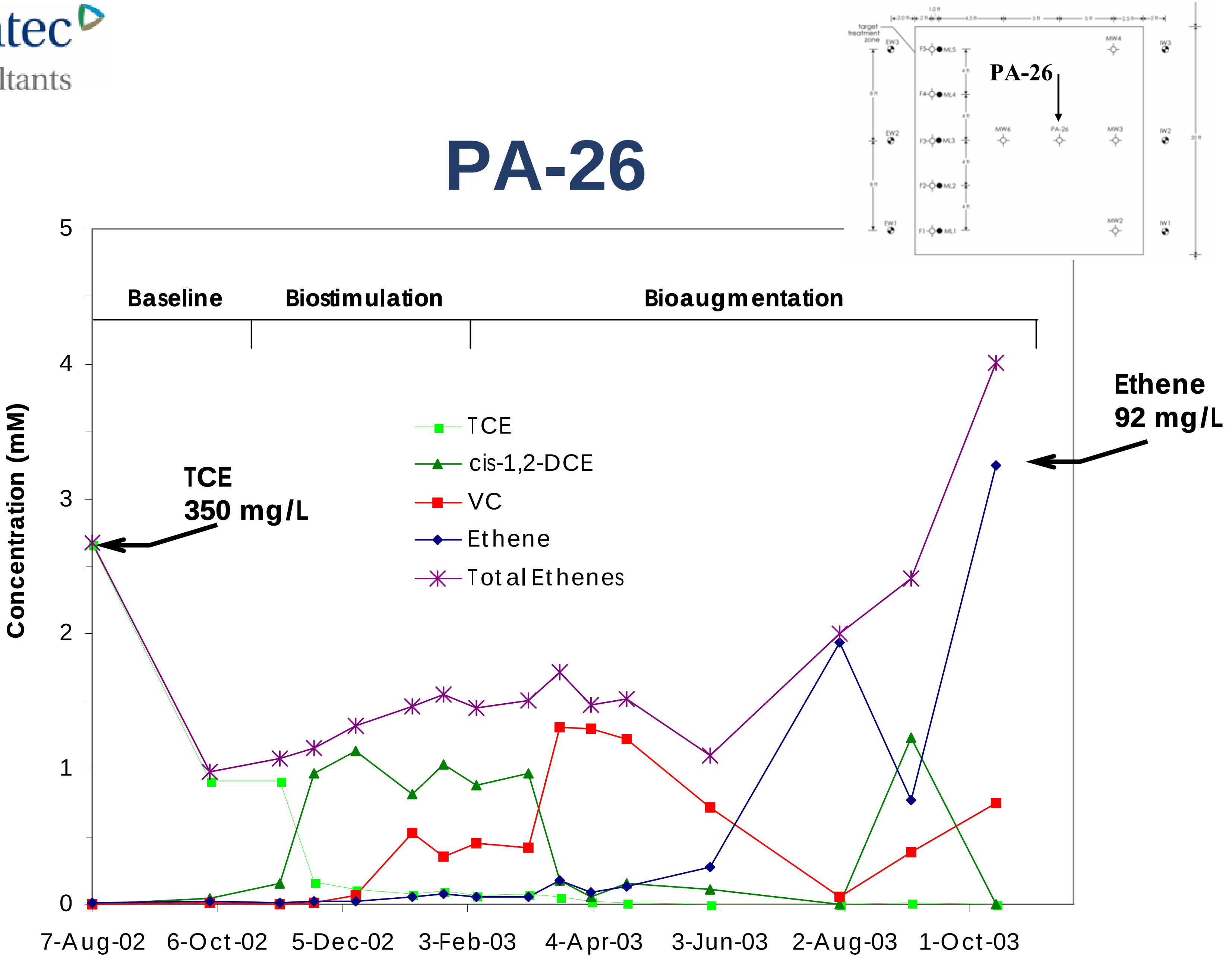
Study Approach

- Provide hydraulic control of Test Plots using groundwater recirculation
- Operate at 1.5 gpm, ~four week residence time (confirmed via tracer testing)
- Operate in three phases
  1. Baseline (no treatment)
  2. Biostimulation (addition of ethanol)
  3. Bioaugmentation (KB-1) with continued ethanol addition
- Monitor chloroethene/ethene concentrations using monitoring wells & a multilevel fence

Site Plan

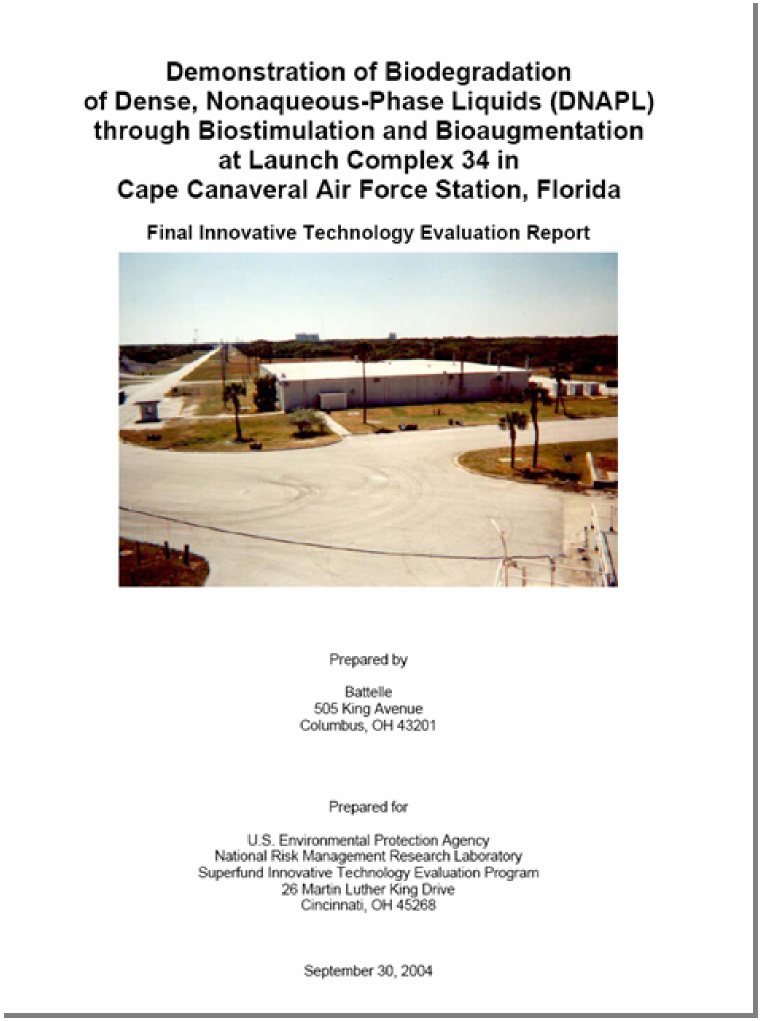

1.0 ft
2.0 ft
2 ft
4.5 ft
5 ft
5 ft
2.5 ft
2 ft
target treatment zone
EW3
EW2
EW1
8 ft
8 ft
ML5
ML4
ML3
ML2
ML1
4 ft
4 ft
4 ft
4 ft
MW4
MW6
PA-26
MW3
MW2
IW3
IW2
IW1
20 ft
v = 0.8 feet/day

PA-26


PA-26
target treatment zone
EW3
EW2
EW1
F5 ML5
F4 ML4
F3 ML3
F2 ML2
F1 ML1
MW6
PA-26
MW4
MW3
MW2
IW3
IW2
IW1
Concentration (mM)
0
1
2
3
4
5
Baseline
Biostimulation
Bioaugmentation
TCE
cis-1,2-DCE
VC
Ethene
Total Ethenes
TCE 350 mg/L
Ethene 92 mg/L
7-Aug-02
6-Oct-02
5-Dec-02
3-Feb-03
4-Apr-03
3-Jun-03
2-Aug-03
1-Oct-03

Technology Verification USEPA SITE Program

- Superfund Innovative Technology Evaluation, provided independent assessment of technology performance (posted at www.siremlab.com).
- Detailed collection of pre- and post-demonstration soil samples



Demonstration of Biodegradation of Dense, Nonaqueous-Phase Liquids (DNAPL) through Biostimulation and Bioaugmentation at Launch Complex 34 in Cape Canaveral Air Force Station, Florida

Final Innovative Technology Evaluation Report

Prepared by

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Prepared for

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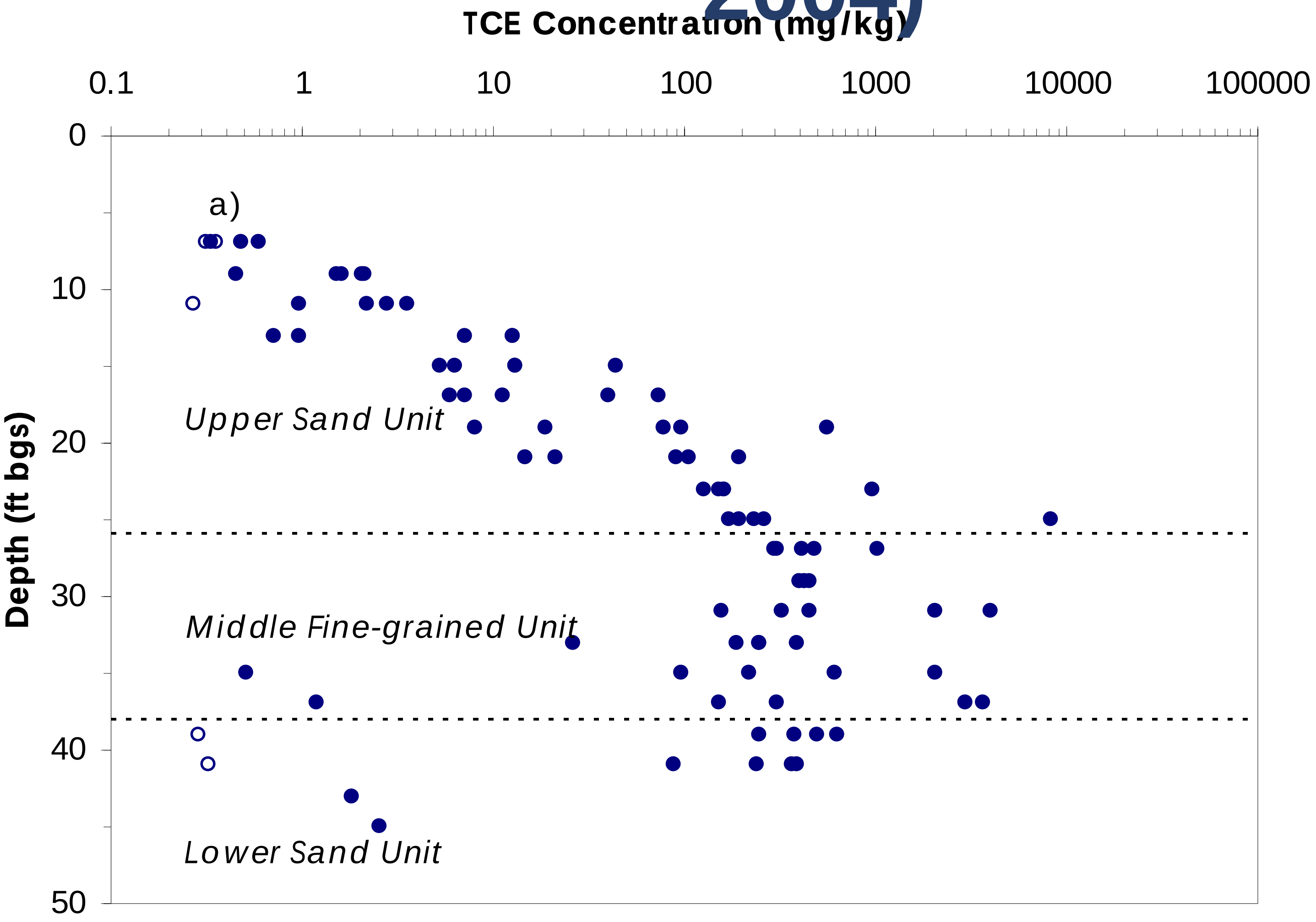
Superfund Innovative Technology Evaluation Program
26 Martin Luther King Drive
Cincinnati, OH 45268

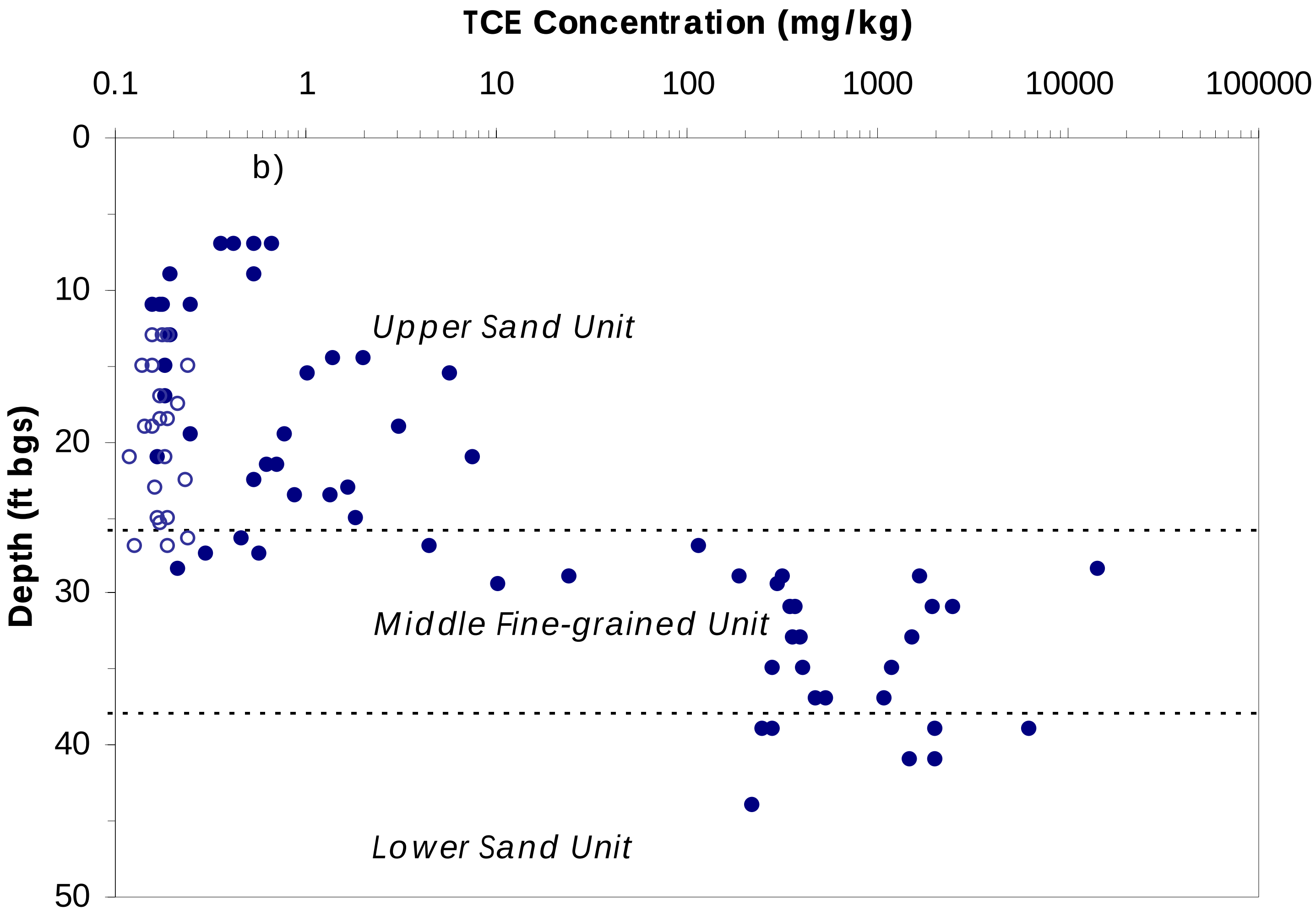
September 30, 2004

TCE Distribution in Soil Pre-demonstration (SITE, 2004)



Open circles = ND

TCE Distribution in Soil Post-demonstration (SITE, 2004)



Open circles = ND

TCE Mass Removal >98.5%

Summary of Results (µM)

Parameter	Baseline	End of Demonstration	Post Demonstration
TCE	1923	2	ND (0.4)
cDCE	27	264	8
Vinyl Chloride	<3	777	19
Ethene	<7	2347	136
Total Ethenes	1965	3390	164
Methane	26	750	709

No rebound 22 months following the end of the demonstration phase

So Why Did It Work?

Possible Reasons

- Flushed it out
    - Not likely, only ~10 pore volumes
    - Mass balance
- Donor (Ethanol) or fermentation products increased the solubility of TCE
- Enhanced mass transfer of free & sorbed phases

Does Donor Concentration Effect TCE Solubility?

Factors Influencing Solubility

- Decreases solubility
  - Ionic strength / salt concentration
  - Non-aqueous phase mixtures (e.g., binary DNAPL)
- Increases solubility
  - Temperature
  - Surface acting agents (surfactants)

Basis for Solubility Enhancement Through Donor Addition

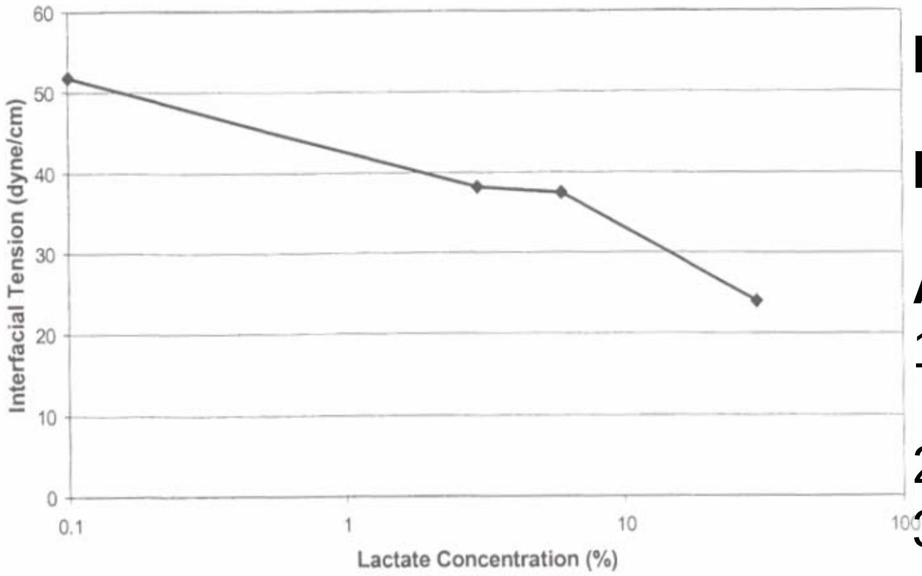


Figure 1. Impact of sodium lactate concentration on DNAPL/water interfacial tension.

Hypothesis: Specific electron donors enhances the solubility of TCE

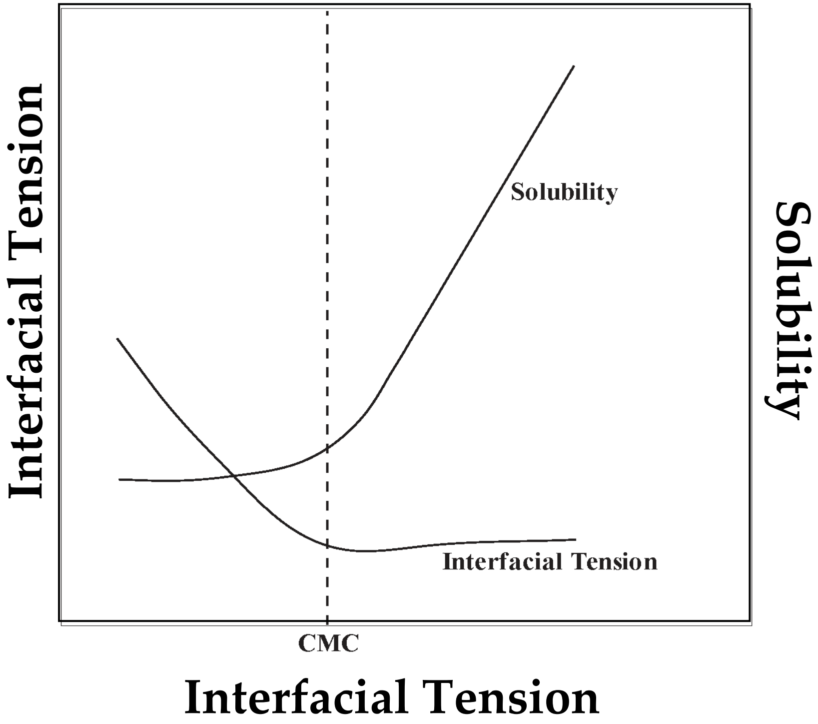
Evidence: Na-lactate decreases NAPL:water interfacial tension

Assumes:

1. Inverse correlation between interfacial tension and solubility
2. Solubility is significantly enhanced
3. Minimal offset of solubility enhancement by competing processes (i.e., increase in the ionic strength of the solution)

Sorenson, K. S., 2002, "Enhanced Bioremediation for Treatment of Chlorinated Solvent Residual Source Areas," *Innovative Strategiesfor the Remediation of Chlorinated Solvents and DNAPLS in the Subsurface*, S. M. Henry ed., ACS Books, Washington, D.C.

Surfactants

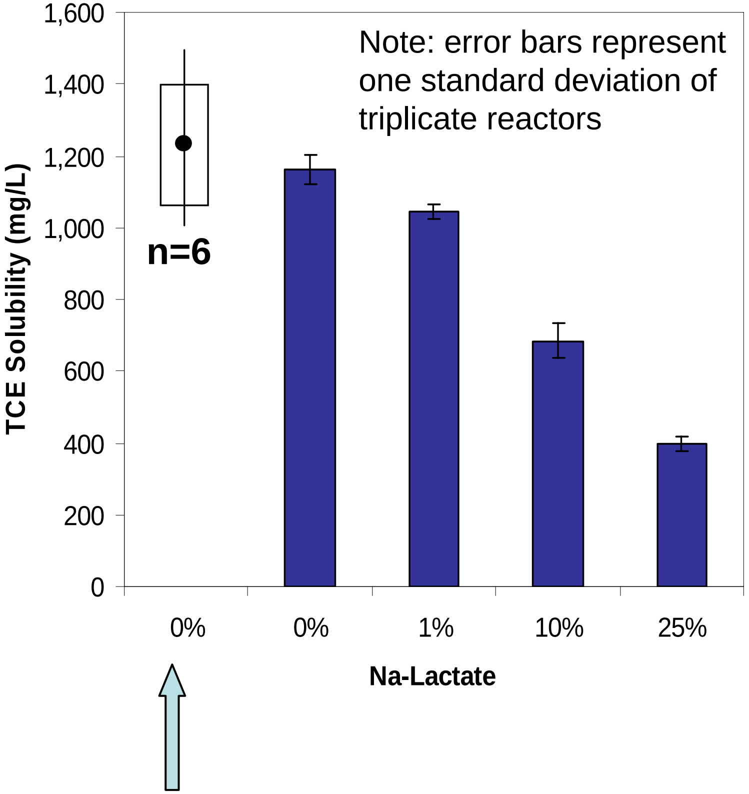


- Initial decrease in interfacial tension resulting from surfactant (well-understood phenomenon)
- Solubility only increases above the critical micelle concentration (typical surfactant concentrations 1-5%
- IFT and solubility not linearly correlated!

A Little Experiment

- Measure TCE solubility using the experimental protocol employed by Broholm and Feenstra (1995)
    - Batch reactors (zero-headspace) containing donor solution (1, 10, and 25%) and neat TCE, agitate for 24 hours and then settle for 72 hours
- Electron Donors
    - Na-lactate: a strong dissociating salt
    - Lactic acid: a strong effect on solution pH
    - Sucrose: non-ionic organic substrate
- Fermentation Products/Effects
    - Fermented sucrose (biosurfactants)
    - Acetic acid
    - pH

Na-Lactate



Note: error bars represent one standard deviation of triplicate reactors

Summary of literature data

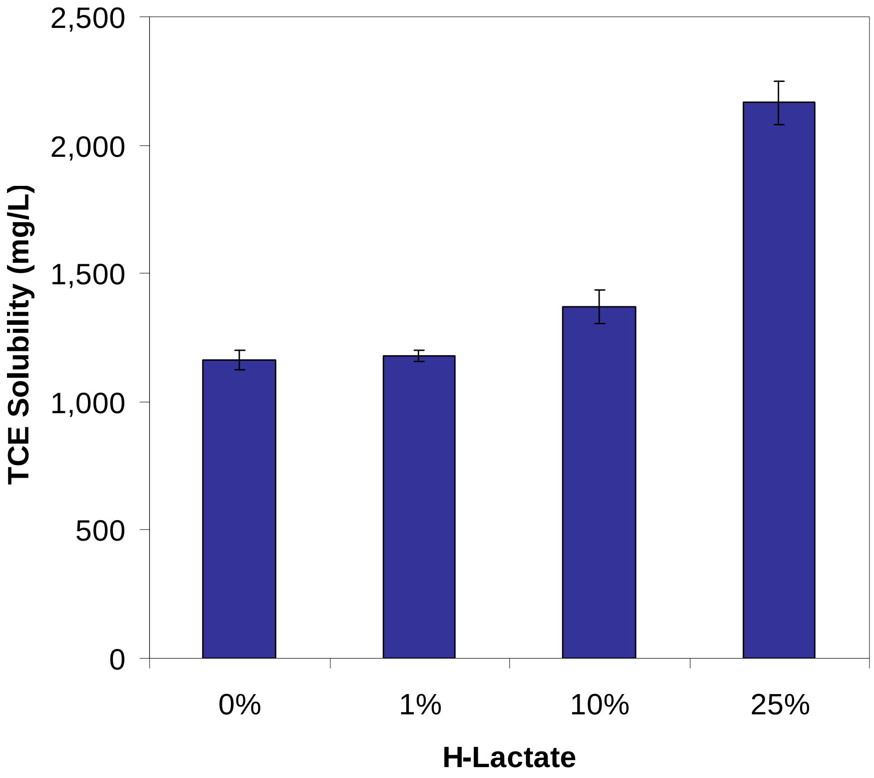
- Good agreement between measured (1,162 mg/L) and literature TCE solubility values
- Reduced TCE solubility by a factor of ~3
- Similar effect with potassium
- “Salting out” effect follows Setschenow equation

$$\log\left(C^{\circ}_{sat} \big/ C_s \right) = K^s \left[salt \right]$$

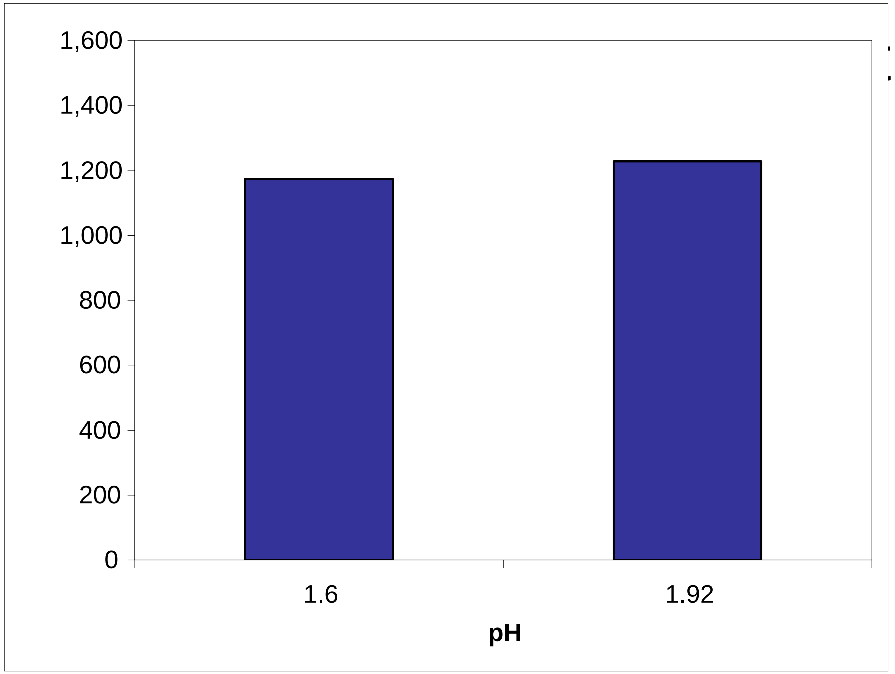
C_s = solubility in salt solution
C°_{sat} = aqueous solubility
K^s = salting constant (typically 01.-0.4 L/mol))
[salt]= salt concentration (mol/L)

- typical K^s (0.1-0.4), minor impact on solubility unless salt concentration>1%
- Salting constant (K^s) of 0.21 L/mol, comparable to K^s for aromatic hydrocarbons in brines (0.12-0.41 L/mol) reported by Schwarzenbach *et al.* (1993)

Lactic Acid

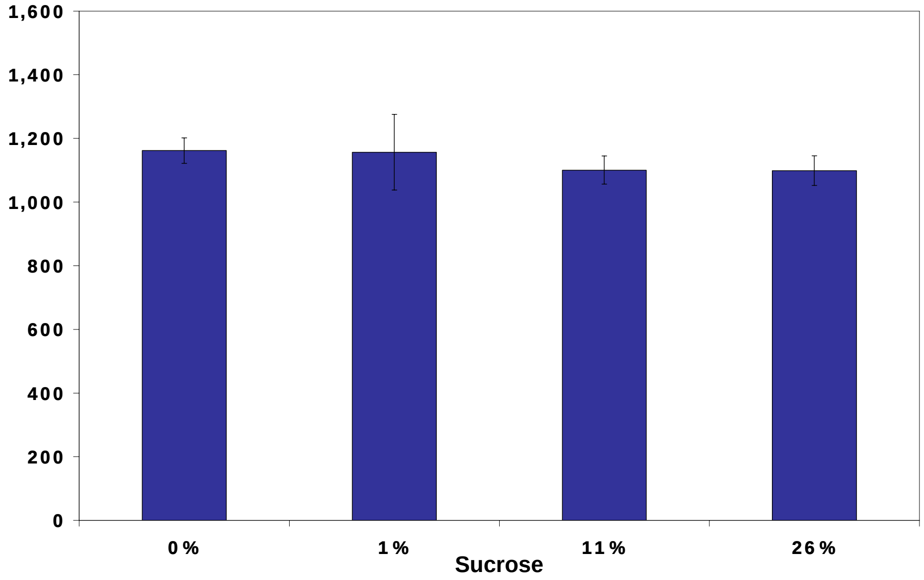


- Lactic acid (pH ~2.1) increased TCE solubility by a factor of ~2

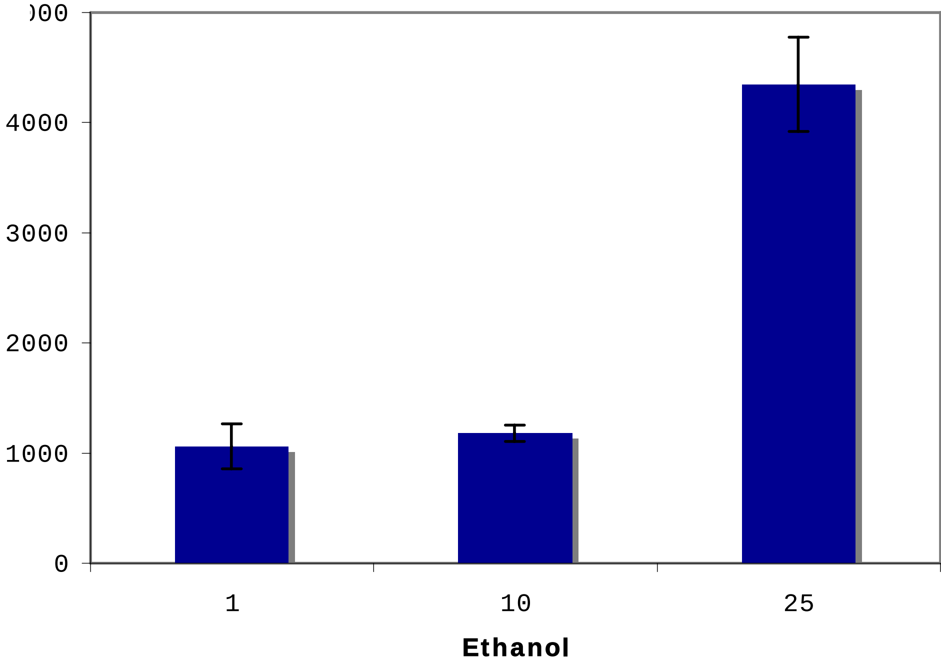


- But TCE solubility is not affected under acidic conditions (adjusted pH<2 with HCl)

Sucrose & Ethanol



- Solubility unaffected by sucrose concentrations
- Fermentation of sucrose (1%, 10% and 25% sucrose) did not affect solubility



- Solubility increased ~4 fold, at ethanol concentrations >10%
- Consistent with co-solvency literature

LC 34 Conclusions

- Clear evidence of reductive dechlorination within a DNAPL source area
- Significant removal residual/sorbed mass in source area
- No rebound of TCE
- Mass removal not from the addition of donor, or fermentation products
- Enhanced mass transfer due to reducing the aqueous concentration of TCE

General Conclusions

- Considerable body of literature supports biologically-enhanced dissolution of DNAPLs
- Field tested, and full-scale applications on-going (some leading to closure or no further action)
- Lab and field data suggests 2 to 10 fold increase in dissolution is achievable
- Most likely suitable for residual or low/highly heterogeneous distribution of pooled DNAPLs
- Can be coupled with other source treatment technologies
- BioDNAPL applications expected to increase