Source Longevity:

Data Mining and Models

C. J. Newell, T. M. McGuire, I. C. Cowie, J. M. McDade, and D. T. Adamson Groundwater Services, Inc.

Tom Sale Colorado State University

Walt McNab, Jr.
Lawrence Livermore National Lab



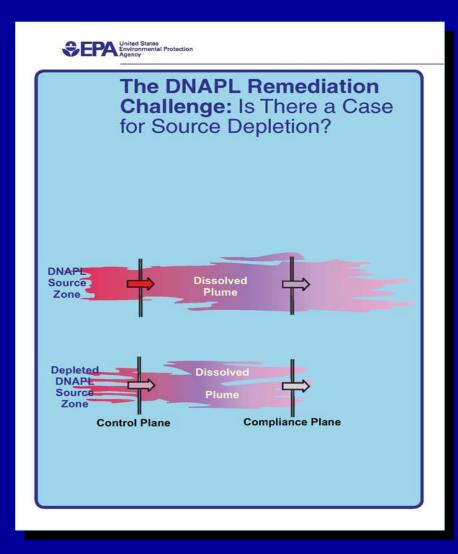




This Talk.....

- 1. Longevity Data Mining Studies SERDP Project
 - Performance & Cost Database
 - Untreated Site Database
- 2.) Simple Longevity Models
 - SourceDK
 - SERDP Equations
- 3. Qualitative Decision Chart from "DNAPL Remediation Challenge"

Motivation...



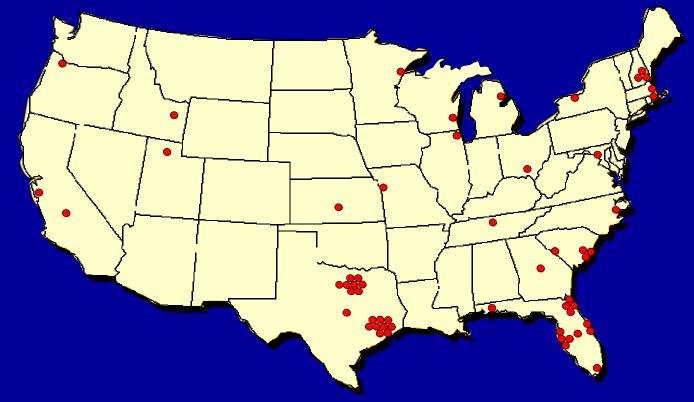
Primary Research Need:

"...a thorough and independent review of a selected number of DNAPL sites where sufficient documentation is available to assess the performance of source depletion..."

TEMPORAL CONCENTRATION DATA FROM 59 CHLORINATED SOLVENT SITES

FOUR SOURCE DEPLETION TECHNOLOGIES:

- Enhanced Biodeg.
- Chem. Oxidation
- Surfactants/Cosolv.
- Thermal Treatment
- Median Treatment
 Volume = 3,800 yd³
- ~70% Full-Scale
 Projects

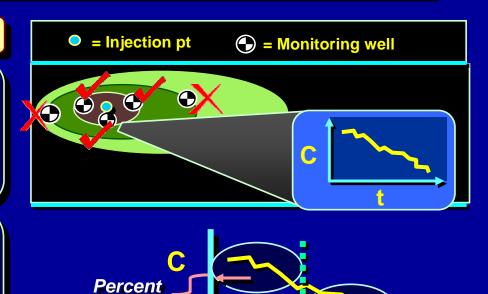


Source: McGuire et al., 2006, Ground Water Monitoring and Remediation

DATA ANALYSIS METHODS

PERFORMANCE:

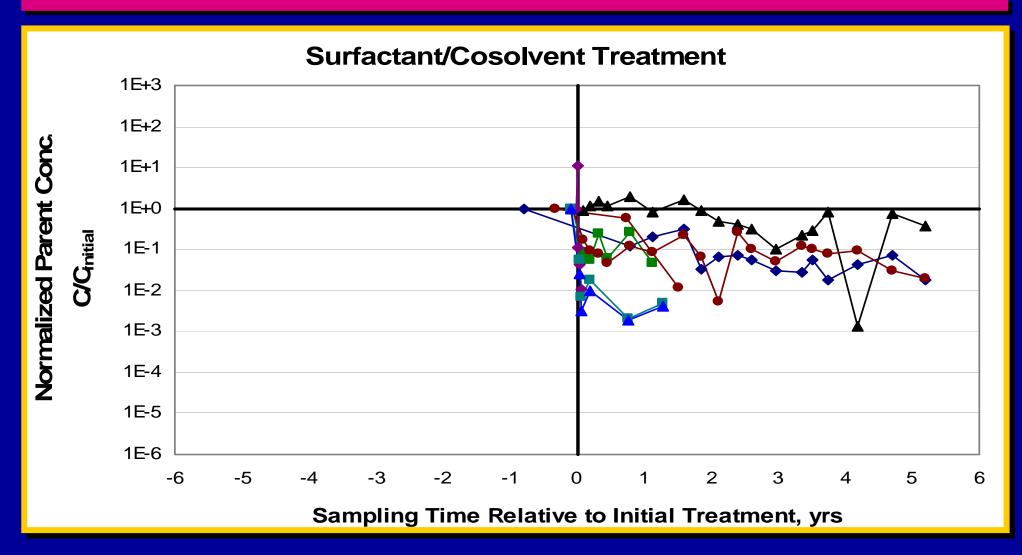
- Compiled conc. vs. time data (before and after treatment) for up to 4 wells within treatment zone
- Calculated geometric mean conc. of before treatment data and after treatment data;
- Then calculated percent reduction for each well
- Median percent reduction of all treatment zone wells as final performance metric



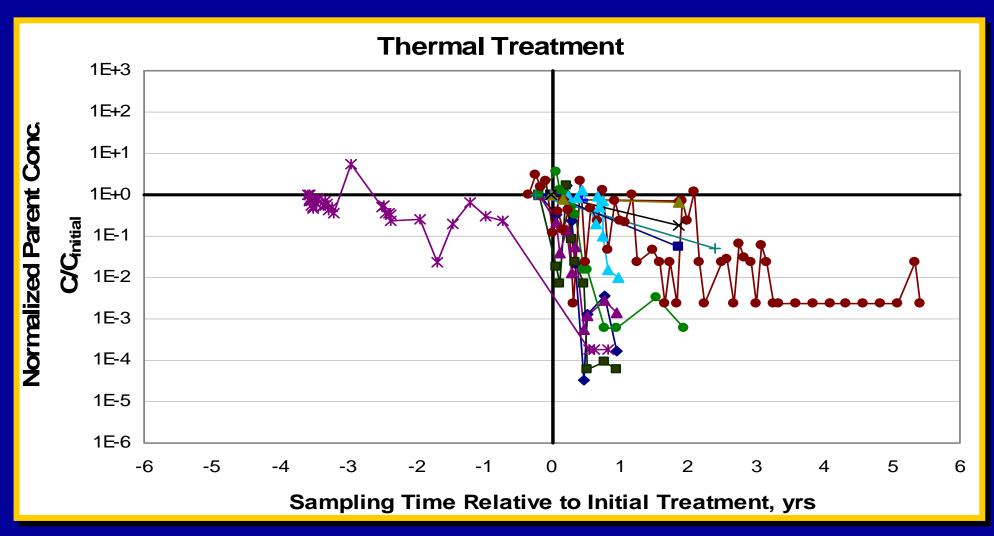
reduction

| | <u>% Red'n</u> | Site % Red'n |
|----------|----------------|--------------|
| Well # 1 | 99.9 | 90.0 |
| Well #2 | 91.0 | |
| Well #3 | <i>89.0</i> | |
| Well #4 | + 10.0 | |

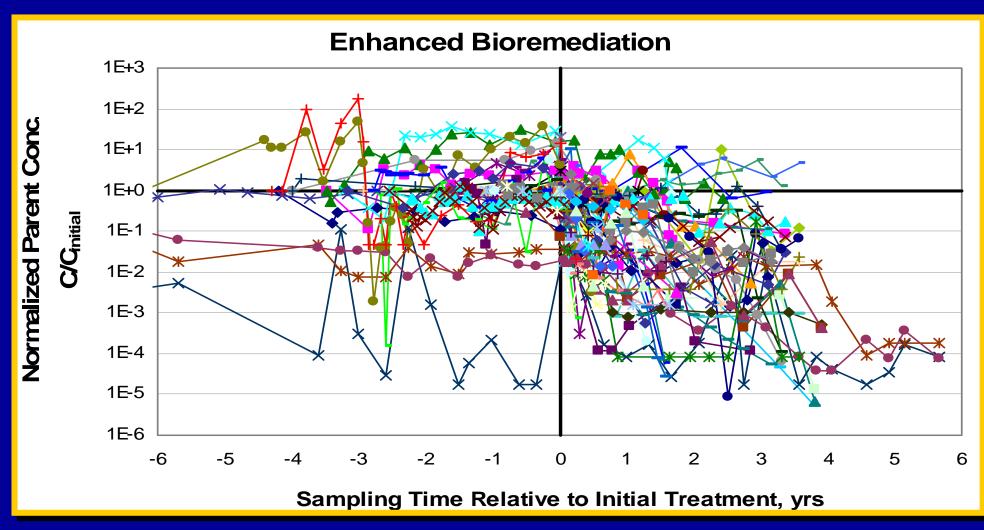
Temporal Records for Surfactant/Cosolvent Wells (4 Sites, 8 Wells)



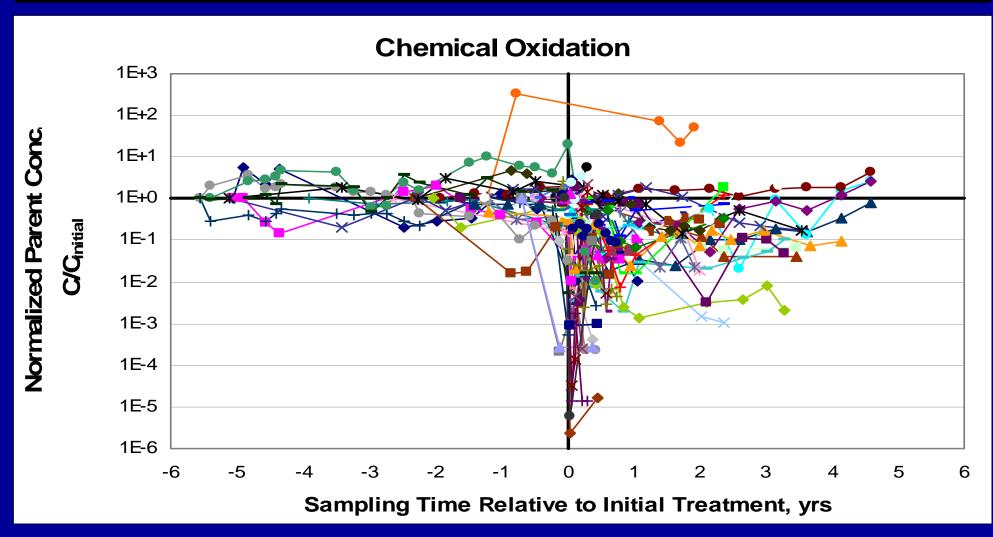
Temporal Records for Thermal Treatment Wells (6 Sites, 13 Wells)



Temporal Records for Enhanced Biodegradation (26 Sites, 68 Wells)

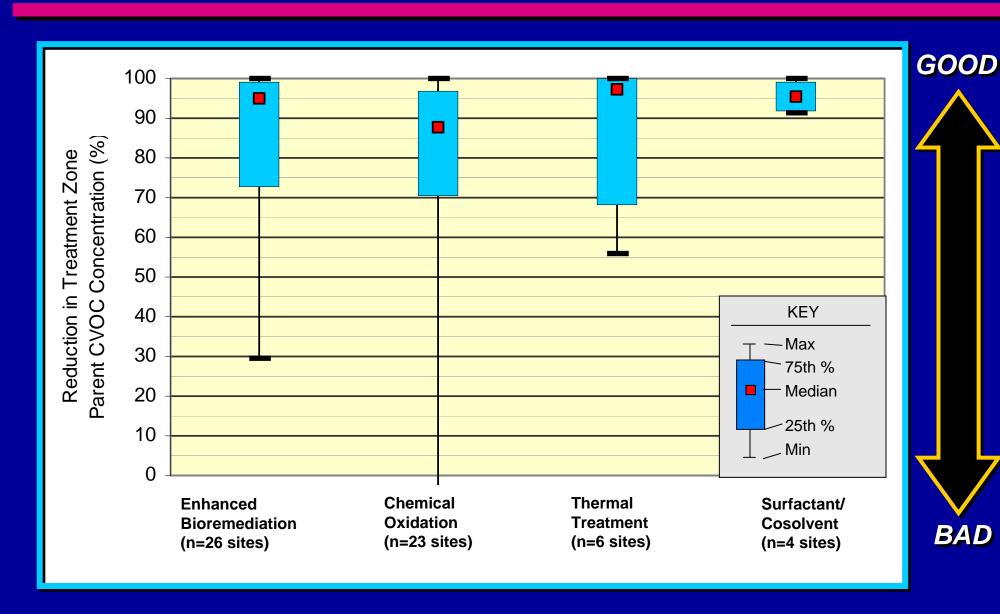


Temporal Records for Chemical Oxidation (23 Sites, 58 Wells)

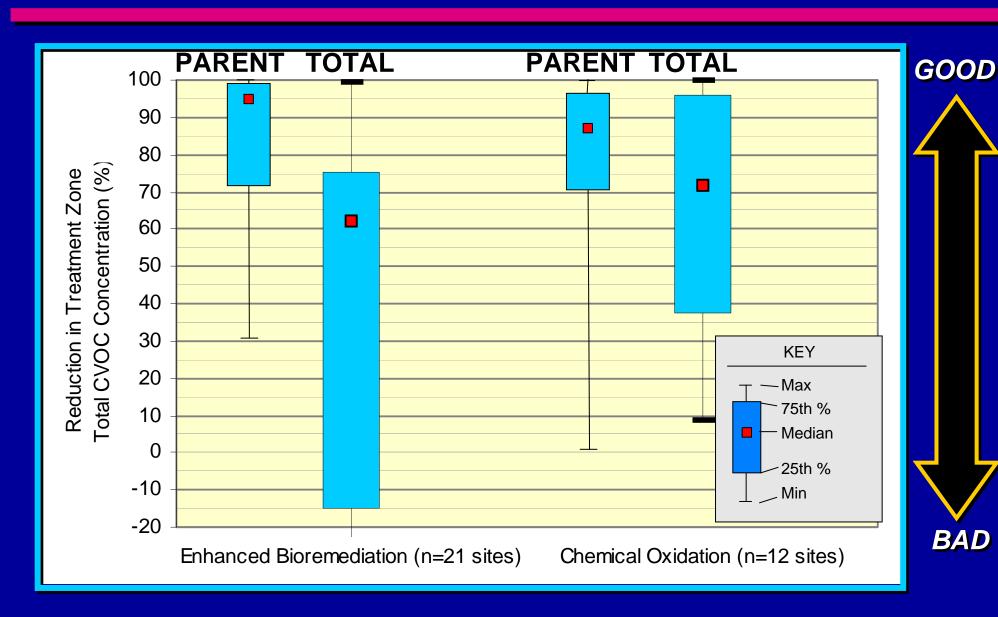


Any site achieve MCLs everywhere? No

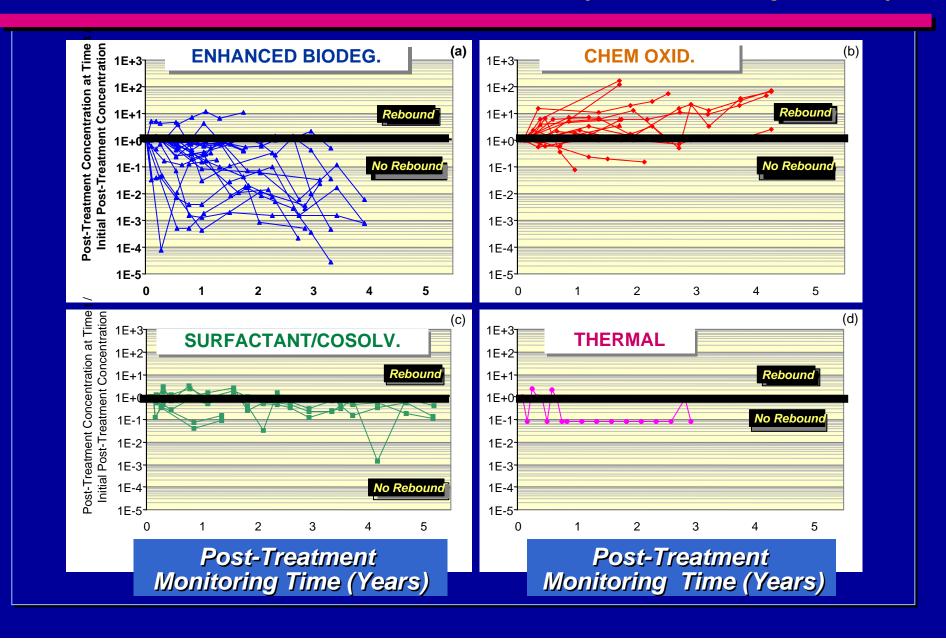
% REDUCTION IN PARENT DUE TO SOURCE DEPLETION



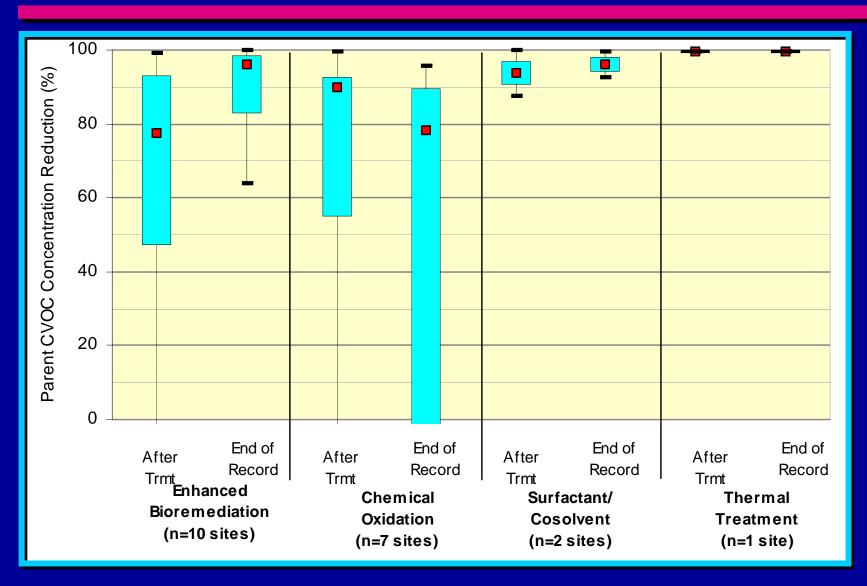
% REDUCTION IN PARENT vs. TOTAL CVOC CONCENTRATION



WHAT ABOUT REBOUND? (Parent Compounds)



WHAT ABOUT REBOUND? (PERCENT REDUCTION)





Cost Study: Data Sources

Peer-Reviewed Literature

- ES&T
- Groundwater
- Groundwater Mon. & Rem.
- J of Contaminant Hydrology
- Surfactants and Cosolvents for NAPL Remediation
- Battelle Conf. Proceedings



Agencies

- FRTR
- Florida DEP
- ITRC
- Lawrence Livermore
- TCEQ
- U.S. EPA
- U.S. DOD
- U.S. DOE

Survey/Web Sites

- SERDP Survey
- CLU-IN Website; www.clu-in.org

Source: McDade et al. 2005. Remediation



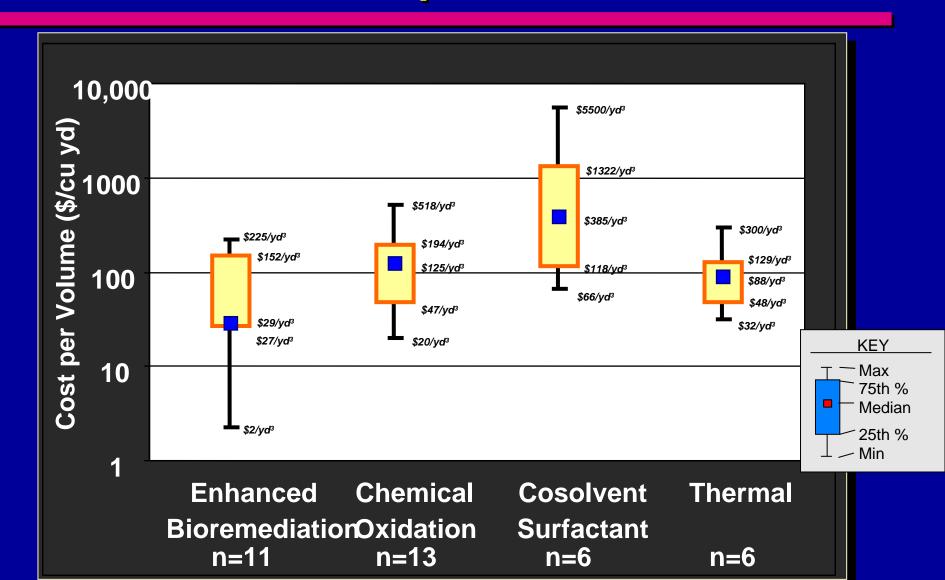




- Lowest MedianTotal Costs =Chemical Oxidation
- Highest MedianTotal CostsThermal
- Highest Total Cost Variation =Enhanced Bioremediation

| | Total Project Costs | | |
|----------------------------|---------------------|-------------|--------------|
| Technology | Minimum | Median | Maximum |
| Enhanced Bioremediation | \$20,000 | \$354,000 | \$35,410,000 |
| Chemical Oxidation | \$73,000 | \$230,000 | \$1,270,000 |
| Surfactant/ Cosolvent | \$222,000 | \$500,000 | \$2,662,000 |
| Thermal | \$138,000 | \$1,065,322 | \$20,000,000 |
| Total | \$20,000 | \$440,000 | \$35,410,000 |

Cost Evaluation – Cost per Volume Breakdown

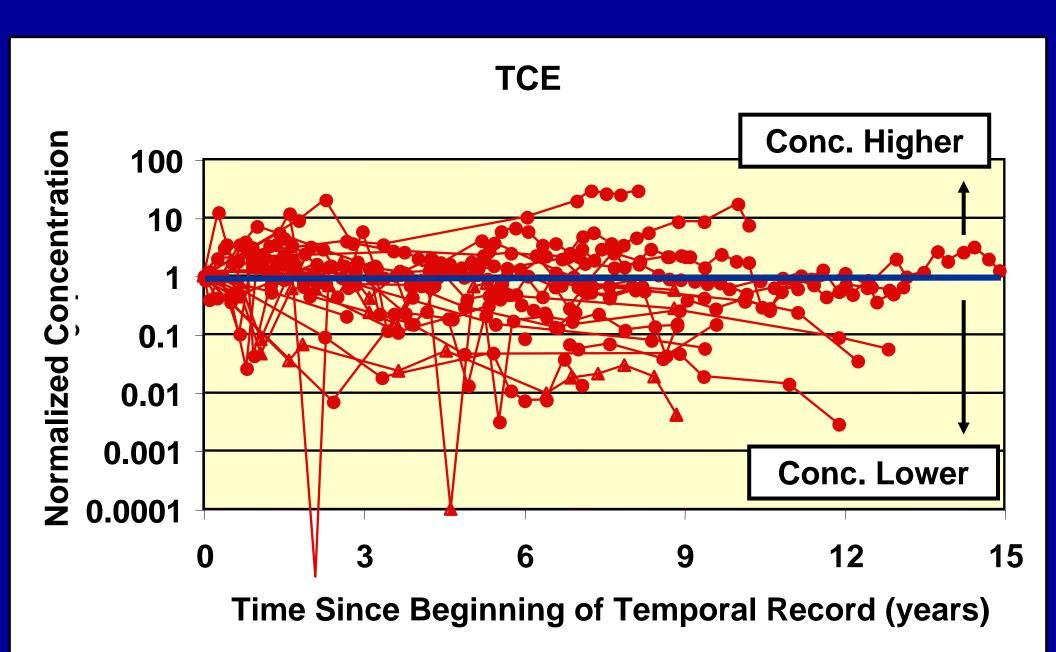




Source: McDade et al. 2005. Remediation

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Change in TCE Over Time

Number: 13 sites, 21 wells

Median Duration: 10 years

Median % Change: -81%

Concentration Trend (MAROS Software)

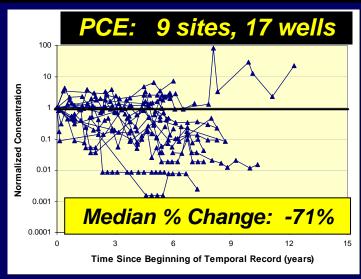
• Increasing: 3 sites

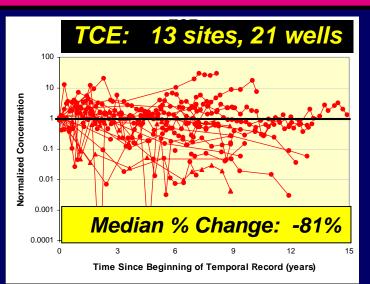
• Stable: 3 sites

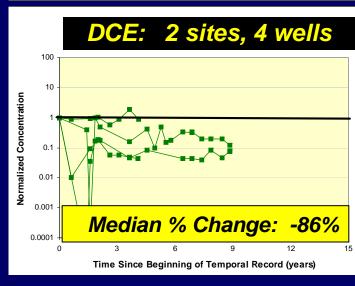
Decreasing: 7 sites

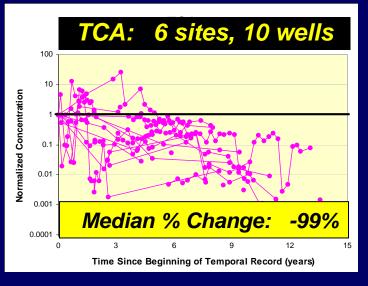


TEMPORAL TRENDS IN UNTREATED PLUME SOURCE ZONES









Two Different Types of Rate Constants



Lambda represents how quickly dissolved organics are biodegraded (half-life months or years)





*k*_{point or} *k*_s represents how quickly <u>source</u> is being dissolved (half-life in years)



Reference: EPA 540/S-02/500 Nov. 2002



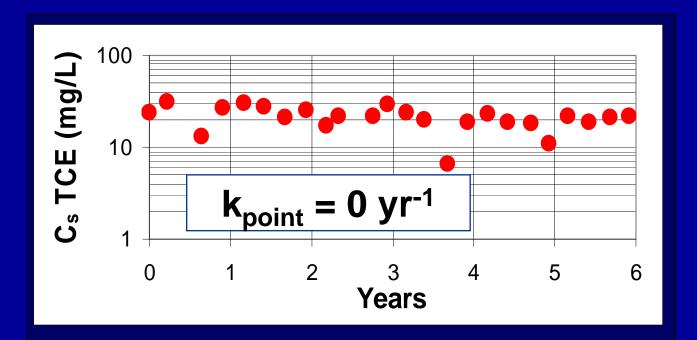
Ground Water Issue

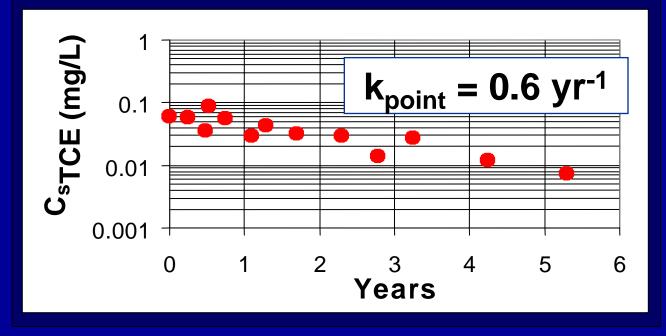
Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies

Charles J. Newell¹, Hanadi S. Rifai², John T. Wilson³, John A. Connor¹, Julia A. Aziz¹, and Monica P. Suarez²

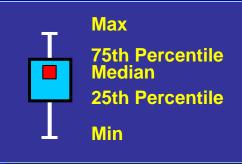
EXAMPLE C_{point} vs. Time Curves

k_{point} = source decay rate constant





POINT DECAY RATES FOR CVOCS BY SITE



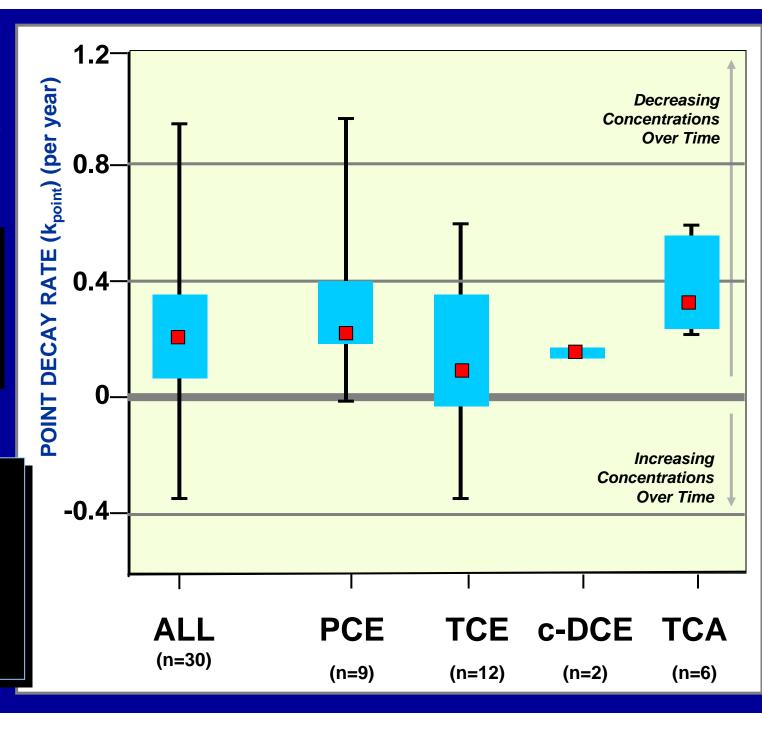
Median Half-life

PCE: 3.0 years

TCE: 6.1 years

DCE: 4.3 years

TCA: 2.0 years



Implication

Benefits of partial source depletion is reduced if source is decaying naturally. For example:

If source depletion gives 88% reduction in concentration....

That is equal to 3 source decay half-lives.....

These <u>untreated</u> source zones need < 20 years to achieve same result (?)

(median decay values from 23 site database)

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What Tools Do What

BIOSCREEN

BIOCHLOR

MAROS

SourceDK

• SERDP Eqns.

HOW FAR DOES PLUME GO?





HOW LONG DOES MNA TAKE?







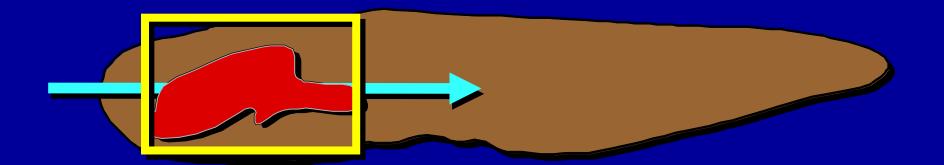




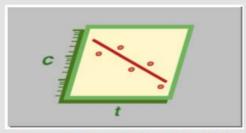
SourceDK

How long will the source be there?

- -Based on site data
- -Based on simple model



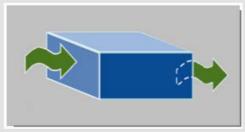




Use Empirical Data (Tier 1)

SourceDK

Remediation Timeframe Decision Support System



Use Box Model (Tier 2)

Version 1.0
Groundwater Services, Inc.

About

System Requirements



Use Process Models (Tier 3)

http://www.afcee.brooks.af.mil/products/techtrans/models.asp

SourceDK

Remediation Timeframe Decision Support System

Air Force Center for Environmental Excellence

Version 1.0 beta

TIER 1
Empirical Data

| ata | Input | instri | ictions: |
|-----|-------|--------|----------|
| | | | |

10.80 - Enter value directly.

10.80 Value calculated by model.
(Don't enter any data).

Site Location and I.D.: LPST

Constituent of Interest: BTEX

| | 1. ENTER CONSTITUENT NAME AND HISTORICAL DATA | | | | | |
|----------------|---|----------------------|---------------|---------------|---------------|---|
| | | Concentration (mg/L) | | | | |
| | Date | Constituent A | Constituent B | Constituent C | Constituent D | |
| | (mm/dd/yy) | Benzene | Toluene | Ethylbenzene | Xylenes | |
| Terror Control | | | | | | |
| 1 | 8/19/86 | 1.8 | 14 | 25 | 3.7 | _ |
| 2 | 7/17/87 | 0.44 | 18 | 2.1 | 14 | |
| 3 | 9/29/87 | 0.37 | 0.25 | 0.34 | 2.3 | |
| 4 | 12/19/87 | 0.32 | 0.081 | 0.065 | 3 | |
| 5 | 6/25/88 | 0.27 | 0.022 | 0.025 | 2.1 | |
| 6 | 9/30/88 | 0.26 | 0.012 | 0.01 | 0.68 | |
| - 7 | 12/21/88 | 0.26 | 0.016 | 0.14 | 3.9 | |
| 8 | 4/25/89 | 0.22 | | 0.155 | 2.17 | |
| 9 | 10/23/89 | 0.11 | | 0.138 | 1.29 | |
| 10 | 7/4/91 | 0.03 | | | | |
| 11 | 11/20/91 | 0.018 | | | | |
| 12 | | | | | | |
| 13 | | | | | | |
| 14 | | | | | | |
| 15 | | | | | | • |

Print Historical Data

2. WHICH CONSTITUENT TO PLOT?

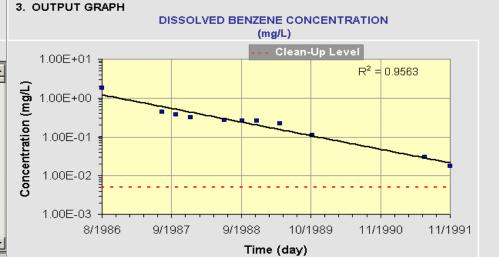
What is the cleanup level?

Benzene 0.005 (mg/L)

♥ Toluene 1 (mg/L)

Ethylbenzene 0.7 (mg/L)

C Xylenes 10 (mg/L)



4. RESULTS

Predicted Date to Achieve Cleanup:

Confidence Interval on Predicted Cleanup Date:

(st least 3 data points needed to calculate confidence interval)

1992

(Lower Limit on Confidence Interval)

(Upper Limit on Confidence Interval)

Return To Main Screen

Number of Years Over Which to Plot Graph

New Site/Clear Screen Paste Example
Data Set

(yr)

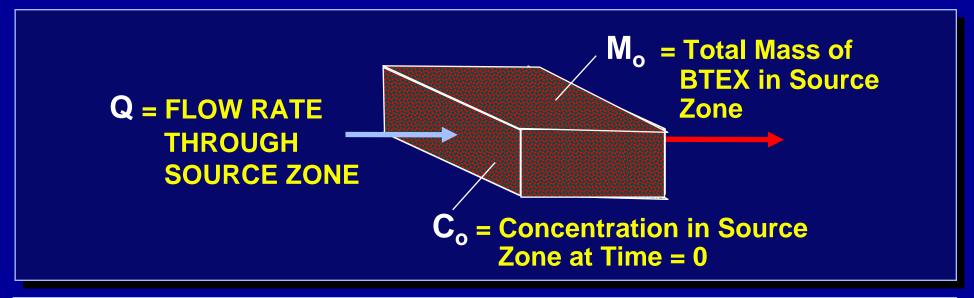
HELP

Update Graph

Tier 2 Approach: Assume Source Zone Is a Box

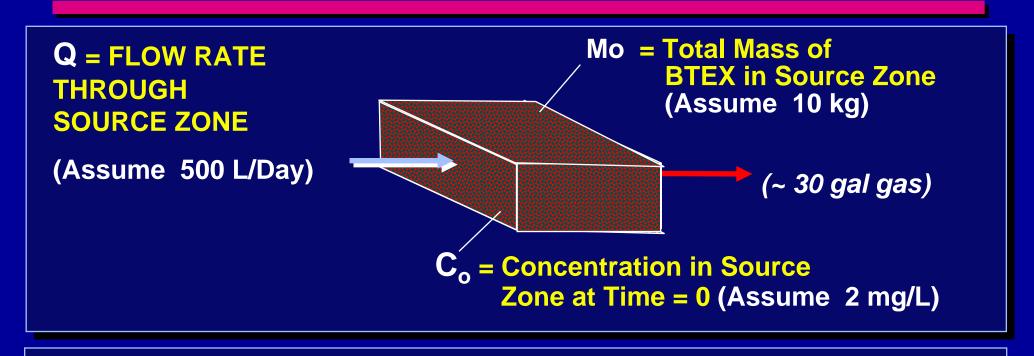
- Simple Box Model
- Estimates source attenuation from:
 - source mass estimate
 - mass flux of contaminants leaving source
 - biodegradation processes in source zone

Approach: Assume Source Zone Is a Box



IF CONSTANT SOURCE CONCENTRATION: C_{o} $t = \frac{M_{o}}{Q}$ C_{o}

Example Assuming Constant Source Conc.



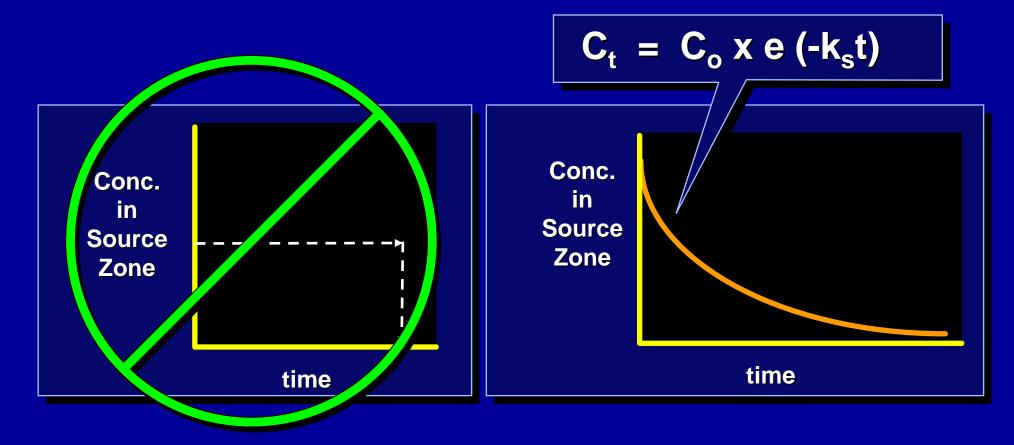
IF CONSTANT SOURCE CONCENTRATION:

$$t = \frac{M_o}{Q C_o} = \frac{10,000,000}{(500)(2)}$$

$$t = 10,000 days (27 yrs)$$

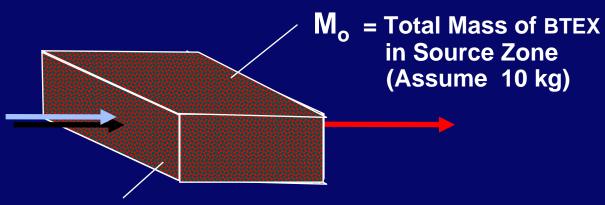
Better Approximation: Conc. Declines With Tail

First Order Decay Model



Example Assuming Declining Source Conc.

Q = FLOW RATE
THROUGH
SOURCE ZONE
(Assume 500 L/Day)



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

IF DECLINING
SOURCE
CONCENTRATION:

$$k_s = \frac{Q C_o}{M_o} = \frac{(500)(2)}{10,000,000} = 0.0001$$

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

Example: Source Concentration vs. Time

| Time (days) | Time (years) | Source Concentration (mg/L) |
|----------------|-----------------|-----------------------------------|
| 0 | 0 | 2.0 |
| 365 | 10 | 1.4 |
| 7,300 | 20 | 0.96 |
| 18,250 | 50 | 0.32 |
| 36,500 | 100 | 0.052 |
| 54,750 | 150 | 800.0 |
| 73,000 | 200 | 0.001 |

Rearrange eqn. to yield time:

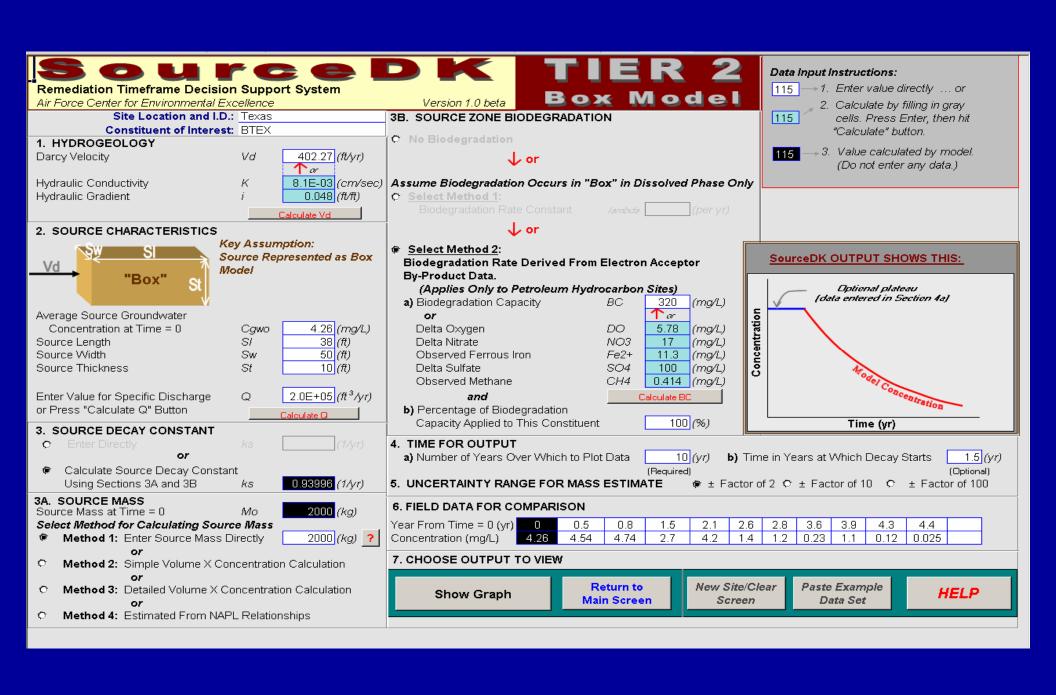
$$C_t = C_o e^{-ks}$$

$$t = \frac{\ln (C_t/C_o)}{-k_s}$$

$$t = \ln (0.005/2)$$

- 0.0001

$$t = 73,000 \text{ days } (200 \text{ yrs})$$



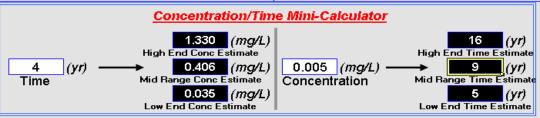
| Time (yr) | | | | | | | | | | | | | | | |
|------------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| TYPE OF MODEL | 0.00 | 0.50 | 0.80 | 1.50 | 2.10 | 2.60 | 2.80 | 3.60 | 3.90 | 4.30 | 4.40 | 5.52 | 6.64 | 7.76 | 10.00 |
| Model Conc. (mg/L) | 4.260 | 4.260 | 4.260 | 4.260 | 2.424 | 1.515 | 1.255 | 0.592 | 0.446 | 0.306 | 0.279 | 0.097 | 0.034 | 0.012 | 0.001 |
| Actual Conc. (mg/L) | 4.260 | 4.540 | 4.740 | 2.700 | 4.200 | 1.400 | 1.200 | 0.230 | 1.100 | 0.120 | 0.025 | | | | |
| Mass Discharge (kg/yr) | 2.4E+01 | 2.4E+01 | 2.4E+01 | 2.4E+01 | 1.4E+01 | 8.6E+00 | 7.1E+00 | 3.4E+00 | 2.5E+00 | 1.7E+00 | 1.6E+00 | 5.5E-01 | 1.9E-01 | 6.7E-02 | 8.2E-03 |



- 1. **●** Display Concentration Vs. Time Chart or
 - Display Source Mass Vs. Time Chart

2. Number of Years Over Which to Plot Graph
(Press "Calculate Current Sheet" button after changing value.)





Return To Input

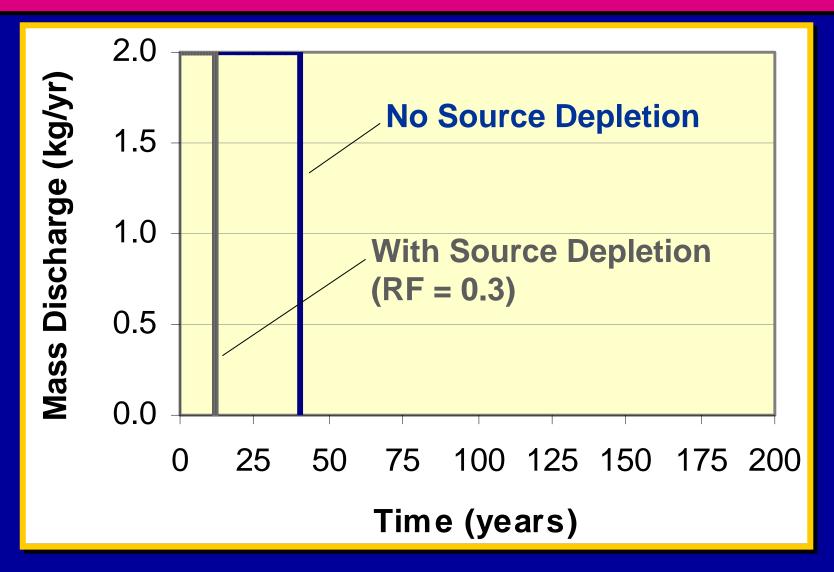
Calculate Current Sheet

HELP

This Talk.....

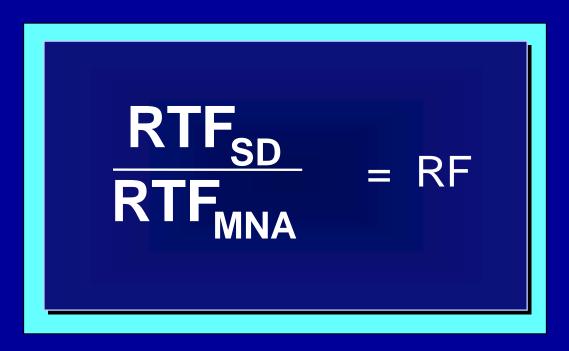
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STEP FUNCTION MODEL - WITH AND WITHOUT SOURCE DEPLETION



RF: Remaining Fraction

REMEDIATION TIMEFRAME EQUATIONS - STEP FUNCTION



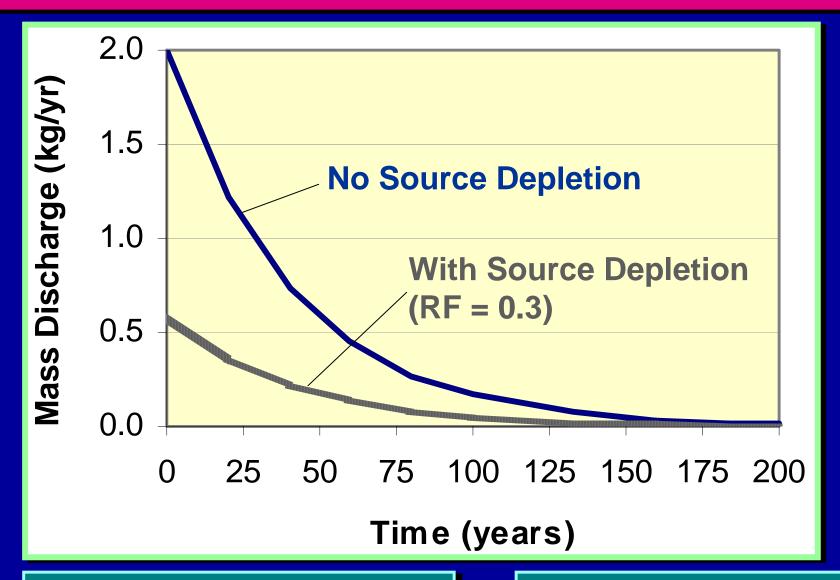
TERMS

RTF_{MNA}: Remediation Timeframe MNA (Untreated Source Zone)

RTF_{SD}: Remediation Timeframe with Source Depletion

RF: Remaining Fraction of Source Mass After Source Depletion

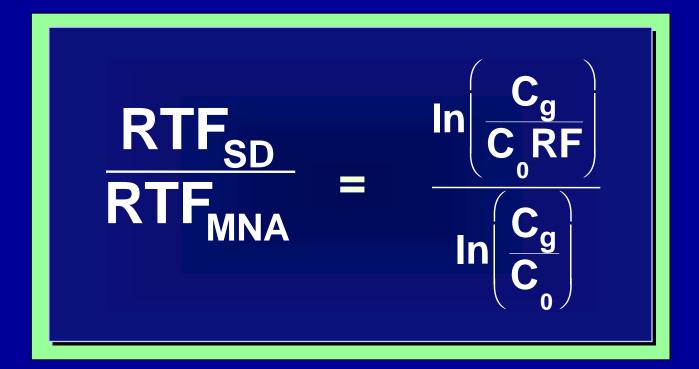
FIRST ORDER DECAY MODEL - WITH AND WITHOUT SOURCE DEPLETION



Assume C_t proportional to M_t

RF: Remaining Fraction

REMEDIATION TIMEFRAME EQUATIONS – FIRST ORDER DECAY



TERMS

 C_g = Concentration Goal (such as MCL)

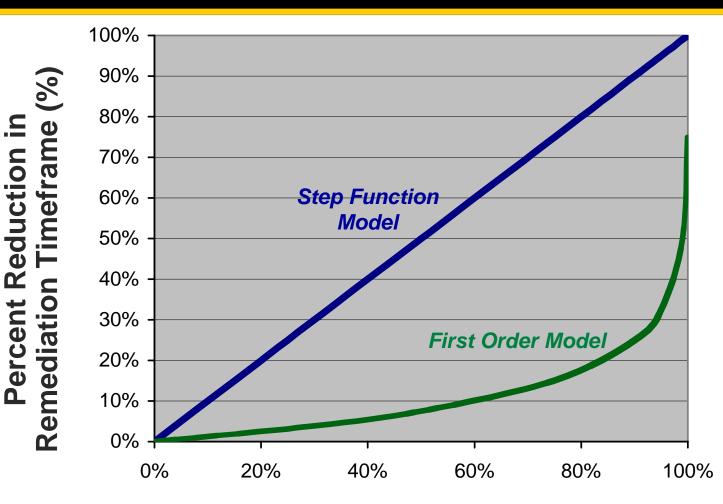
 C_0 = Original Source Concentration

Newell and Adamson, 2005

RF: Remaining Fraction of Source Mass After Source Depletion

SOURCE REDUCTION FACTOR vs. REDUCTION IN REMEDIATION TIMEFRAME



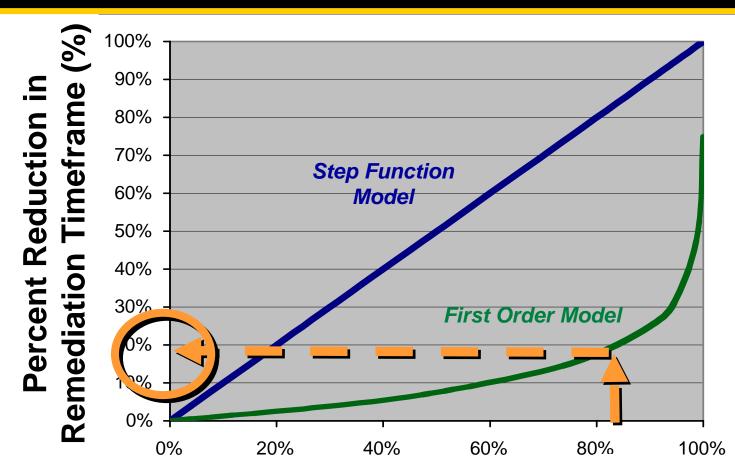


% Reduction in Source Mass (1-RF)

 $C_o/C_o = 0.0001$

FIRST ORDER DECAY MODEL: REMOVE 80% SOURCE MASS REDUCE RTF BY 17%





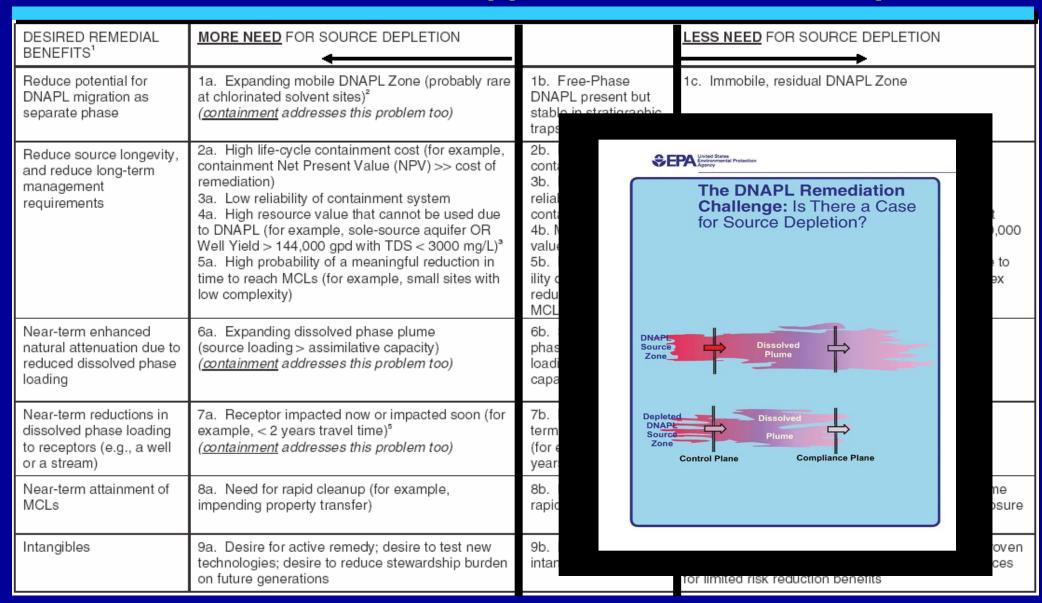
% Reduction in Source Mass (1-RF)

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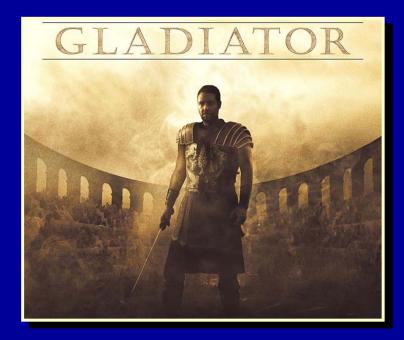
"Benefits from Full-Scale Application of Source Depletion"

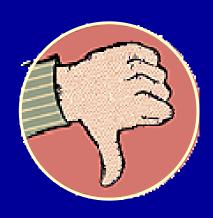


Qualitative Decision Chart: Definition of Thumbs Up



If Thumbs Up, Apply Source Depletion





If Thumbs Down, Contain Source

Reduce Potential for DNAPL Migration as Separate Phase

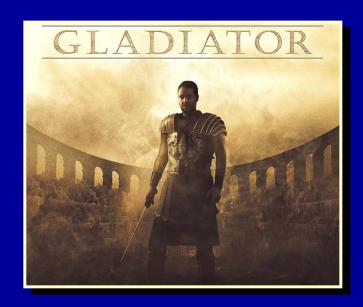
Status of NAPL Zone:

Expanding



Immobile, residual DNAPL





Reduce Source Longevity and Reduce Long-term Management Requirements

Life-cycle containment cost

High



Low



Reliability of containment system

Low



High



Resource value

High



Low



Probability that remediation timeframe can be signif. reduced?

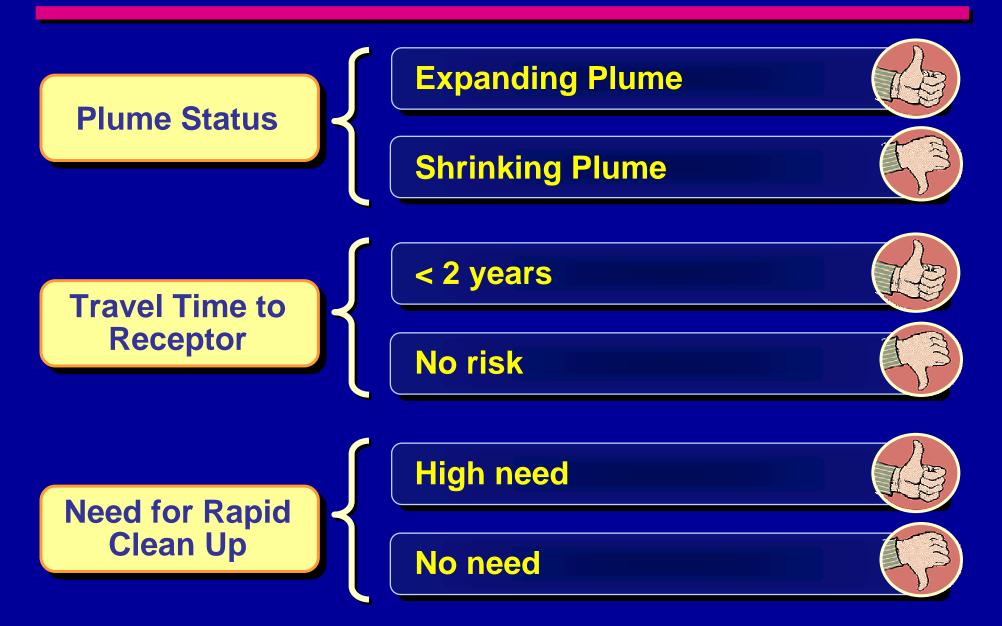
High



Low



Other Categories



Example: Less Likely to Benefit from Source Depletion

| DESIRED REMEDIAL BENEFITS ¹ | MORE NEED FOR SOURCE DEPLETION | LESS NEED FOR SOURCE DEPLETION |
|--|--|--|
| Reduce potential for DNAPL migration as separate phase | 1a. Expanding mobile DNAPL Zone (probably rare at chlorinated solvent sites) ² (containment addresses this problem too) | 1b. Free-Phase 1c. Immobil 3 APL Zone DNAPL present bb. stable in stratigraphic traps |
| Reduce source longevity, and reduce long-term | High life-cycle containment cost (for example, containment Net Present Value (NPV) >> cost of remediation) | 2b. Moderate life-cycle 2c. Low life-cycle tainment cost (for example, containment cost of value (NPV) << cost of |
| management requirements | 3a, Low roli Liliana in the second responsibility of the second responsibi | reliability of containment system 4b. Moderate resource value 5b. Moderate probable ility of a meaning of reach MCLs MCLs 3c. High religion animent system for our proposition of the probable of the pro |
| Near-term enhanced natural attenuation due to reduced dissolved phase loading | 6a. Expanding dissolved phase plume (source loading > assimilative capacity) (containment addresses this problem too) | 6c. Shrinking dissolved phase plume (source loading ~ assimilative capacity) 7b. Potential longer 7c. No risk |
| Near-term reductions in dissolved phase loading to receptors (e.g., a well or a stream) | 7a. Receptor impacted now or impacted soon (for example, < 2 years travel time) ⁵ (containment addresses this problem too) | 7b. Potential longe term risk to receptor (for example, >2 years travel time) |
| Near-term attainment of MCLs | 8a. Need for rapid cleanup (for example, impending property transfer) | 8b. Limited need for sc. No users within expected in frame quifer and no other posure athways lik r migration |
| Intangibles | 9a. Desire for active remedy; desire to test ne technologies; desire to reduce stewardship burk to on future generations | 9b. Neutral on intangible issues 9c. Desire for its past remedy, desire to use proven technologies; desire to not expend financial resources for limited risk reduction benefits |

Example: More Likely to Benefit from Source Depletion

| DESIRED REMEDIAL BENEFITS ¹ | MORE NEED FOR SOURCE DEPLETION | | LESS NEED FOR SOURCE DEPLETION |
|---|--|---|---|
| Reduce potential for DNAPL migration as separate phase | 1a. Expandin at chlorinated a containment a problem too) | 1b. Free-Phase DNAPL present but stable in stratigraphic traps | 1c. Immobile, residual DNAPL Zone |
| Reduce source longevity, and reduce long-term management requirements | 2a. High life-cycle containment cost (for example, containment Net containment Net containment Net containment Net containment Net containment cost (for example, containment Net containment cost (for example, cost of c | 2b. Moderate life-cycle containment cost 3b. Moderate Paiability of containment system 4b. Moderate resource value 5b. Moderate probability of a meaningful reduction in time to MCLs | containment Net Present Value (NPV) << cost of remediation) 3c. High religibility of the cost of remediation and resource value (NPV) << cost of remediation) 3c. Low resource value (NPV) << cost of remediation) 4c. Low resource value (NPV) << cost of remediation) 4d. Low resource not olived Solids > 10,000 mg/L or Well Yield of the cost of reach MCLs (for example, large releases at complex sites) |
| Near-term enhanced natural attenuation due to reduced dissolved phase loading | 6a. Expanding dissolved phase plume (source loading > assimilative capacity) (containment addresses this problem too) | 6b. Stable dissolved phase plume (source loading ~ assimilative sapacity) | 6c. Shrinking dissolved phase plume (source loading < assimilative capacity) |
| Near-term reductions in dissolved phase loading to receptors (e.g., a well or a stream) | 7a. Receptor example, < 2 y or impacted soo. (for e) ⁵ problem too) | 7b. Potential longer- term risk to receptor (for example, >2 years travel time) | 7c. No risk to receptors now or in the future |
| Near-term attainment of MCLs | 8a. Need for reimpending pro | 8b. Limited need for rapid cleanup | 8c. No users of resource within expected time frame needed for restoration of aquifer and no other exposure pathways likely, e.g., vapor migration |
| Intangibles | 9a. Desire for action medy; desire to test ney technologies; desire to reduce stewardship but len on future generations | 9b. Neutral on intangible issues. | 9c. Desire for low-impact remedy; desire to use proven technologies; desire to not expend financial resources for limited risk reduction benefits |

This Talk.....

- 1. Longevity Data Mining Studies SERDP Project
 - Performance & Cost Database
 - Untreated Site Database
- 2. Simple Longevity Models
 - SourceDK
 - SERDP Equations
- 3. Qualitative Decision Chart from "DNAPL Remediation Challenge"



