Distinguishing sites where MNA has a reasonable chance of success from sites where MNA will be disappointing

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Evaluation of Monitored Natural Attenuation (MNA) of Organic Contaminants in Ground Water

National Association of Remedial Project Managers (NARPM) Annual Training Conference
Portland, Oregon, July 9, 2008.

U.S. EPA Policy On Use of Monitored Natural Attenuation For Site Remediation

EPA's Office of Solid Waste and Emergency Response (OSWER) Policy Directive:

Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites, Directive 9200.4-17, December 1, 1997.

EPA Definition

. . . the use of natural attenuation processes within the context of a carefully controlled and monitored site cleanup approach that will reduce contaminant concentrations to levels that are protective of human health and the environment within a reasonable time frame.

MNA Processes

- Physical, chemical, or biological processes that act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants.
- Includes biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization or destruction of contaminants.

Sites Where MNA May Be Appropriate

In RCRA enforcements, MNA has been used as a risk management tool for a plume that has not left the property boundary, and is stable or shrinking.

In CERCLA, MNA is generally considered a remedy like any other remedy. The concentrations of contaminants must reach a clean up goal.

Sites Where MNA May Be Appropriate

- MNA is appropriate as remedial approach only where it:
  - Can be demonstrated to achieve remedial objectives <u>within a reasonable time frame</u>, and
  - Meets the applicable remedy selection criteria for the particular OSWER program.

Resist any pressure to select MNA based on a feeling that MNA 'appears' to be appropriate, with the intention that the data necessary to actually demonstrate that MNA is occurring will be collected after the ROD is in place.

Certain data must be collected and evaluated to document that MNA is occurring at the site and will likely meet the ARARs to even consider choosing MNA as the remedial alternative.

Demonstrating the Efficacy of MNA

Three types of site-specific information may be required:

1. Historical ground water and/or soil chemistry data demonstrates trend of declining contaminant concentration.
2. Hydrogeologic and geochemical data that demonstrate NA processes and rates.

Demonstrating the Efficacy of MNA

Three types of site-specific information may be required:

3. Field or microcosm studies.

Unless #1 is of sufficient quality and duration, #2 is generally required (regulatory decision).

What sort of historical ground water and/or soil chemistry data can be used needed to demonstrate a trend of declining contaminant concentration?

There are two rates of decline, the rate of decline in a single well over time, and the rate of decline along a flow path in ground water.

The rate of decline in a well over time determines how long a plume will last.

The rate of decline in a well along the flow path will determine how far the plume will extend.

How much historical ground water and/or soil chemistry data is needed to demonstrate a trend of declining contaminant concentration over time in well?

This question is considered in detail in the second hour of this course.

Quick rule of thumb:

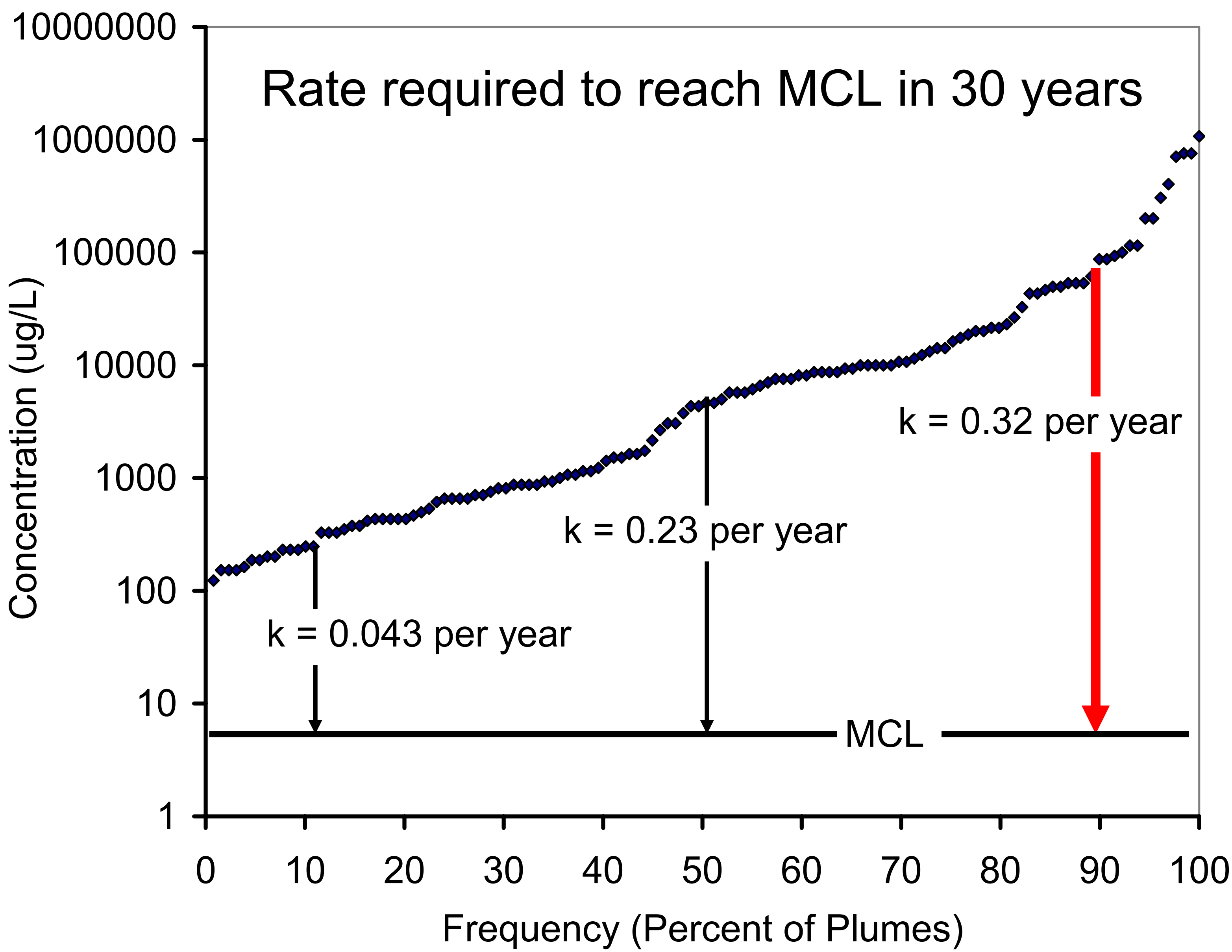
Sites with at least ten years of monitoring data showing at least a ten fold reduction in concentration of the contaminants have a reasonable chance to demonstrate a declining trend.

Which sites *can be demonstrated to achieve remedial objectives within a reasonable time frame*?

Depends on the attenuation required to reach the goal, and how long you are willing to wait.

McNab, W.W., D.W. Rice, and C. Tuckfield. 2000. Evaluating chlorinated hydrocarbon plume behavior using historical case population analyses.

Bioremediation Journal 4(4):311-335.


Rate required to reach MCL in 30 years
k = 0.043 per year
k = 0.23 per year
k = 0.32 per year
MCL
Concentration (ug/L)
10000000
1000000
100000
10000
1000
100
10
1
0
10
20
30
40
50
60
70
80
90
100
Frequency (Percent of Plumes)

$$R = \frac{\ln\left({Cg}/{Co} \right)}{t}$$

Co = Current concentration of contaminant

Cg = concentration goal for cleanup

t = time allowed to reach cleanup goal

R = first order rate of attenuation required to meet clean up goal.

What if the current concentration of TCE were 1,000 µg/L, and you wanted to close the site at the MCL in 20 years?

$$R = \frac{\ln\left(5/1000\right)}{20}$$

The required rate of change is -0.265 per year, or the rate of attenuation is + 0.265 per year.

What *hydrogeologic and geochemical data* are useful *that can demonstrate NA processes and rates*?

Data on the consumption of contaminants along with consumption of soluble electron acceptors can explain the processes that destroy petroleum hydrocarbons and similar contaminants.

What *hydrogeologic and geochemical data* are useful *that can demonstrate NA processes and rates*?

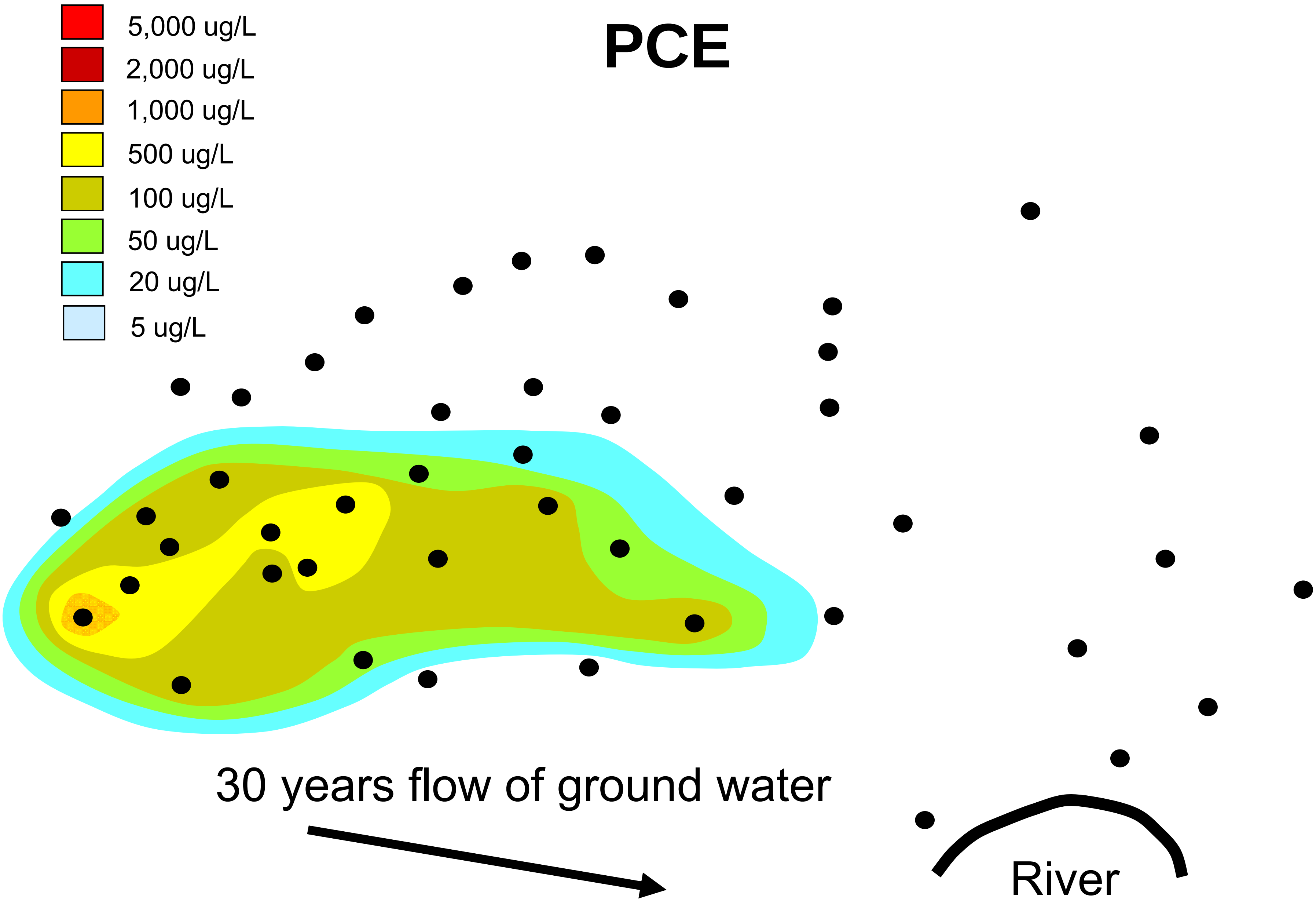
What about chlorinated solvent plumes?

MNA has a better chance when the plume of important reduction daughter products is contained within the plume of the parent compounds.

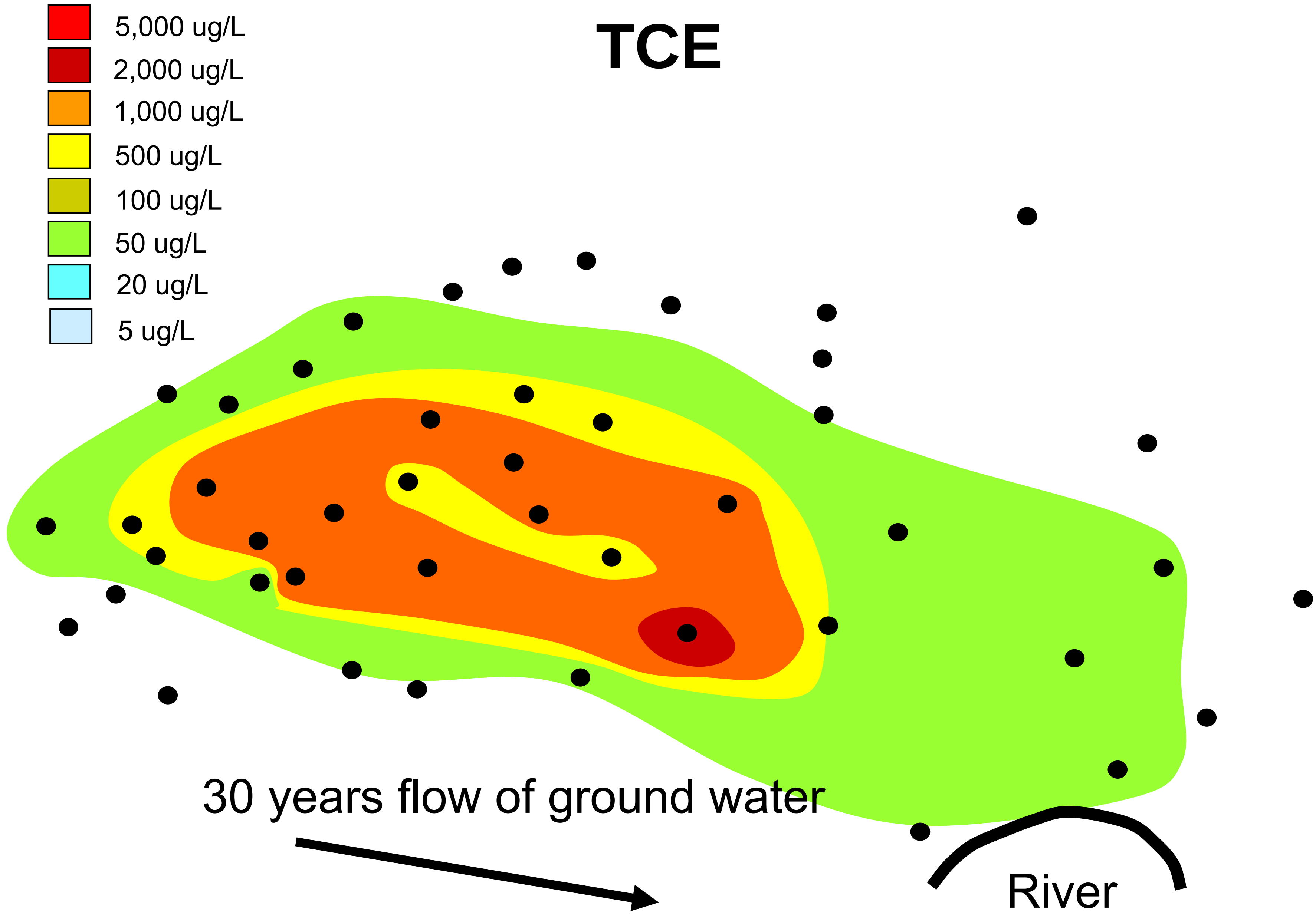
Stable carbon isotope evidence for intrinsic bioremediation of tetrachloroethene and trichloroethene at area 6, Dover Air Force Base.

Sherwood Lollar, B., G. F. Slater, B. Sleep, M. Witt, G. M. Klecka, M. Harkness and J. Spivack. Environmental Science & Technology 35: 261-269 (2001).

PCE


5,000 ug/L
2,000 ug/L
1,000 ug/L
500 ug/L
100 ug/L
50 ug/L
20 ug/L
5 ug/L
30 years flow of ground water
River

TCE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2,000 ug/L
1,000 ug/L
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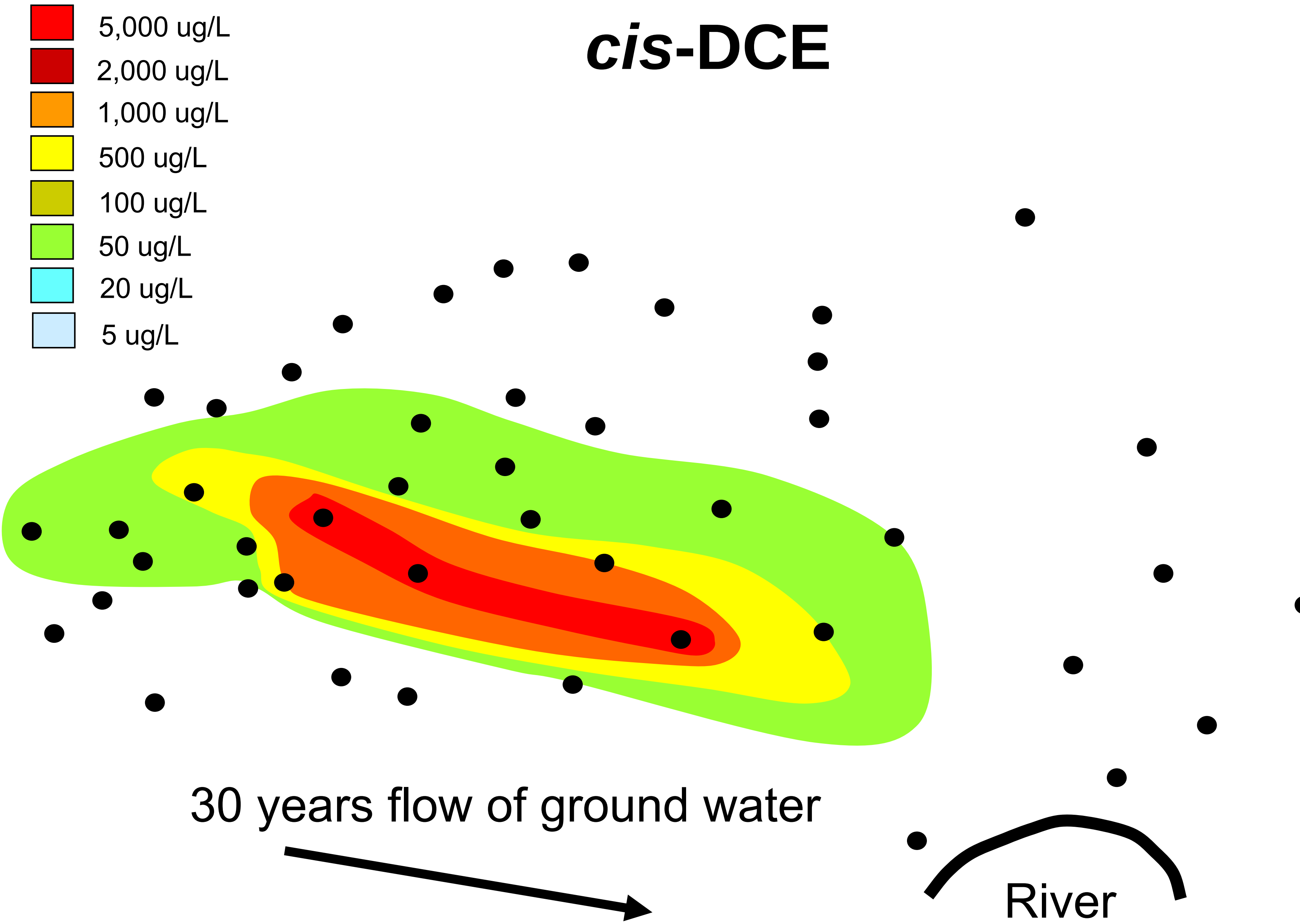
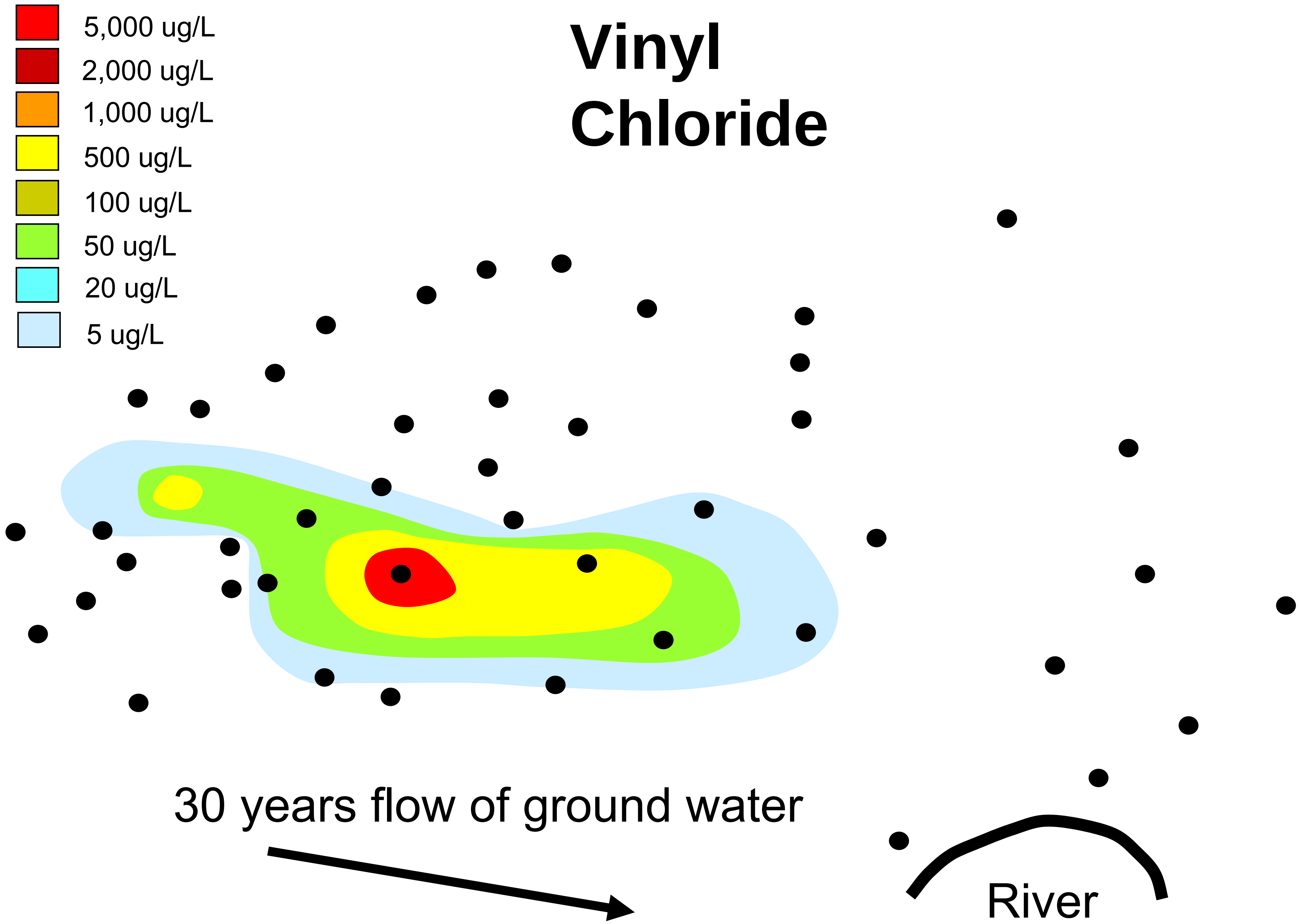
100 ug/L
50 ug/L
20 ug/L
5 ug/L
30 years flow of ground water
River

cis-DCE

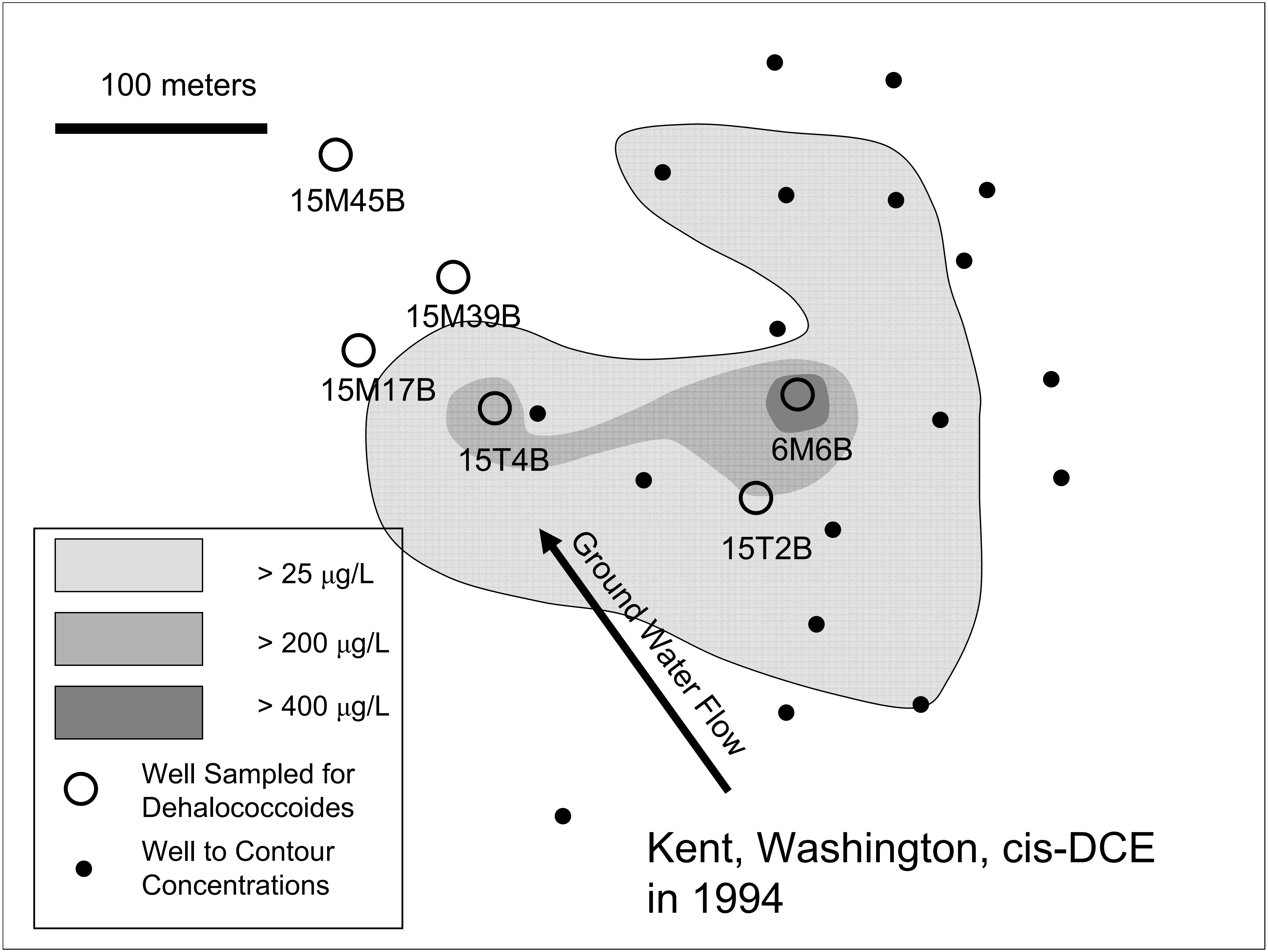

5,000 ug/L
2,000 ug/L
1,000 ug/L
500 ug/L
100 ug/L
50 ug/L
20 ug/L
5 ug/L
30 years flow of ground water
River

Vinyl Chloride



What *hydrogeologic and geochemical data* are useful *that can demonstrate NA processes and rates*?

The values for parameters used for calibration of site specific predictive models can be compared to “reasonable” values to see if expected process can explain the distribution of contamination in a plume.


100 meters
15M45B
15M39B
15M17B
15T4B
6M6B
15T2B
Ground Water Flow
> 25 μg/L
> 200 μg/L
> 400 μg/L
Well Sampled for Dehalococcoides
Well to Contour Concentrations
Kent, Washington, cis-DCE in 1994

BIOCHLOR Natural Attenuation Decision Support System

Version 1.1

Western Processing

Well 6M 6B run 1

Run Name

Data Input Instructions:

115 → 1. Enter value directly....or
or
0.02 ↗ 2. Calculate by filling in gray cells. Press Enter, then
(To restore formulas, hit "Restore Formulas" button)
Variable* → Data used directly in model.

Test if Biotransformation is Occurring → Natural Attenuation Screening Protocol

TYPE OF CHLORINATED SOLVENT: Ethenes (selected) / Ethanes

1. ADVECTION

Seepage Velocity*	Vs	64.0	(ft/yr)
or			
Hydraulic Conductivity	K	2.8E-02	(cm/sec)
Hydraulic Gradient	i	0.0007	(ft/ft)
Effective Porosity	n	0.2	(-)

2. DISPERSION

Alpha x Calc. Method	8	(ft)
(Alpha y) / (Alpha x)	0.2	(-)
(Alpha z) / (Alpha x)	2 E-01	(-)

Change Alpha x Calc. Method

3. ADSORPTION

Retardation Factor* → R

or

Soil Bulk Density, rho	1.52	(kg/L)
FractionOrganicCarbon, foc	7.2E-3	(-)

Partition Coefficient

	Koc		R	
PCE	1	(L/kg)	1.1	(-)
TCE	1	(L/kg)	1.1	(-)
DCE	125	(L/kg)	7.8	(-)
VC	30	(L/kg)	2.6	(-)
ETH	1	(L/kg)	1.1	(-)

Common R (used in model)* = 1.1

4. BIOTRANSFORMATION

-1st Order Decay Coef*

Zone 1	λ (1/yr)	half-life (yrs)	Yield*
PCE → TCE	0.000		0.79
TCE → DCE	0.000		0.74
DCE → VC	0.300		0.64
VC → ETH	3.000		0.45

Zone 2	λ (1/yr)	half-life (yrs)
PCE → TCE	0.000	
TCE → DCE	0.000	
DCE → VC	0.000	
VC → ETH	0.000	
ETH → Ethane	0.000	

5. GENERAL

Simulation Time*	30	(yr)
Modeled Area Width*	400	(ft)
Modeled Area Length*	800	(ft)
Zone 1 Length*	800	(ft)
Zone 2 Length*	0	(ft)

Zone 2= L - Zone 1

6. SOURCE DATA

Source Options

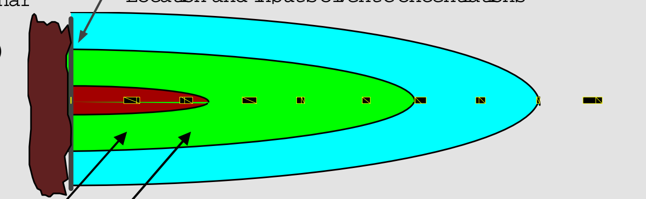
TYPE: Single Planar

Source Thickness in Sat. Zone* 30 (ft)

Width* (ft) 200

Conc. (mg/L)*	C1
PCE	.0
TCE	.0
DCE	3.0
VC	.5
ETH	.0

Vertical Plane Source: Determine Source Well Location and Input Solvent Concentrations



View of Plume Looking Down

Observed Centerline Conc. at Monitoring Wells

7. FIELD DATA FOR COMPARISON

PCE Conc. (mg/L)											
TCE Conc. (mg/L)											
DCE Conc. (mg/L)	3.0	1.6	2.0	.5	.16	.07					
VC Conc. (mg/L)	0.5	.42	.4	.04	.01	.01					
ETH Conc. (mg/L)											
Dist. from Source (ft)	0	153	233	376	694	706					

8. CHOOSE TYPE OF OUTPUT TO SEE:

RUN CENTERLINE | RUN ARRAY | Help | Restore Formulas | RESET | SEE OUTPUT | Paste Example

4. BIOTRANSFORMATION

-1st Order Decay Coef*

Zone 1

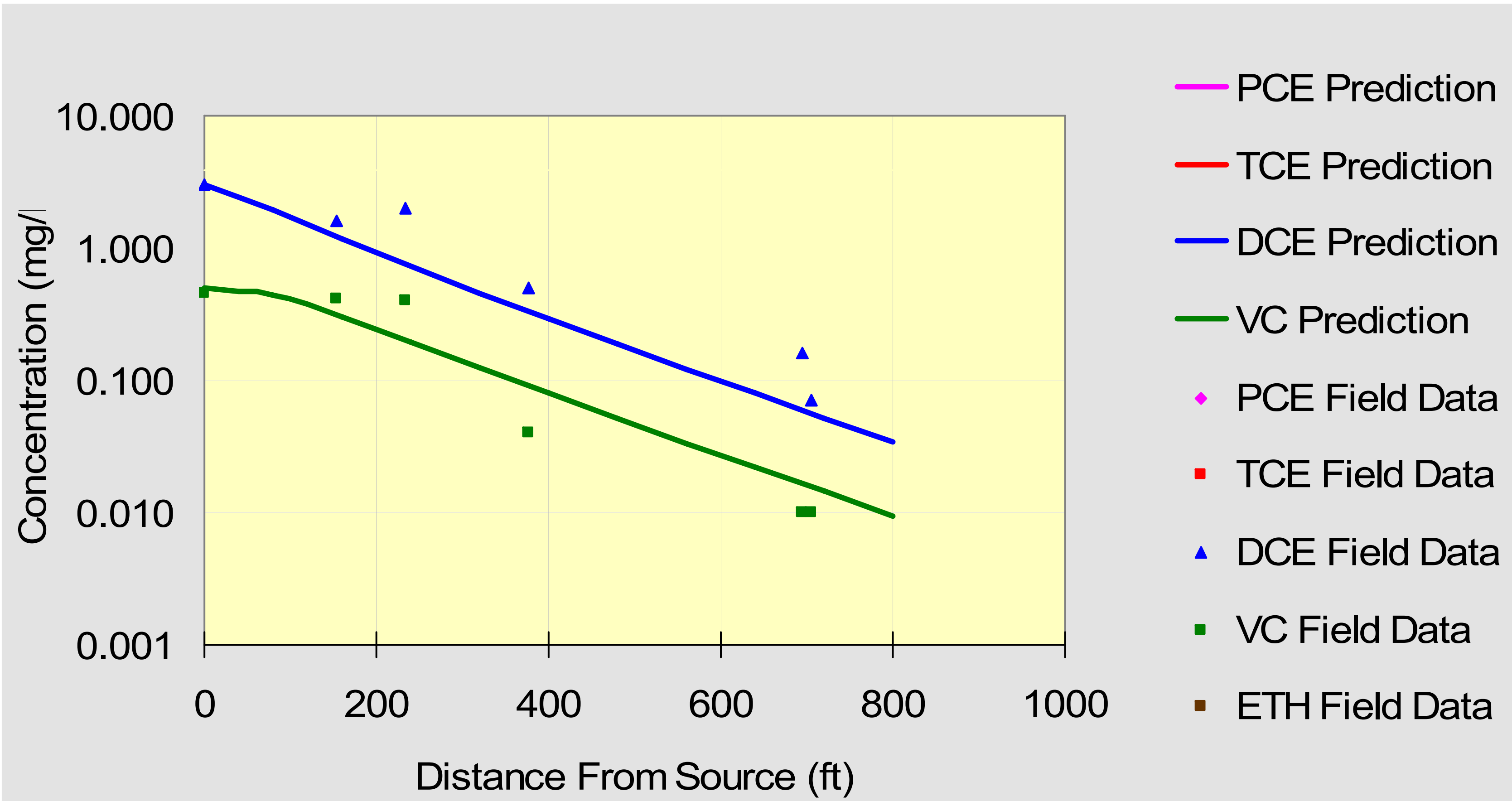
Reaction	λ (1/yr)	half-life (yrs)	Yield*
PCE → TCE	0.000		0.79
TCE → DCE	0.000		0.74
DCE → VC	0.300		0.64
VC → ETH	1.000		0.45

Zone 2

Reaction	λ (1/yr)	half-life (yrs)
PCE → TCE	0.000	
TCE → DCE	0.000	
DCE → VC	0.000	
VC → ETH	0.000	
ETH → Ethane	0.000	

7. FIELD DATA FOR COMPARISON

PCE Conc. (mg/L)						
TCE Conc. (mg/L)						
DCE Conc. (mg/L)	3.0	1.6	2.0	.5	.16	.07
VC Conc. (mg/L)	0.5	.42	.4	.04	.01	.01
ETH Conc. (mg/L)						
Dist. from Source (ft)	0	153	233	376	694	706



Concentration (mg/l
10.000
1.000
0.100
0.010
0.001
0
200
400
600
800
1000
Distance From Source (ft)
PCE Prediction
TCE Prediction
DCE Prediction
VC Prediction
PCE Field Data
TCE Field Data
DCE Field Data
VC Field Data
ETH Field Data

Literature Values for Natural Attenuation in Ground Water

Anaerobic Biodegradation of Organic Chemicals in Groundwater: A Summary of Field and Laboratory Studies (SRC TR-97-0223F)

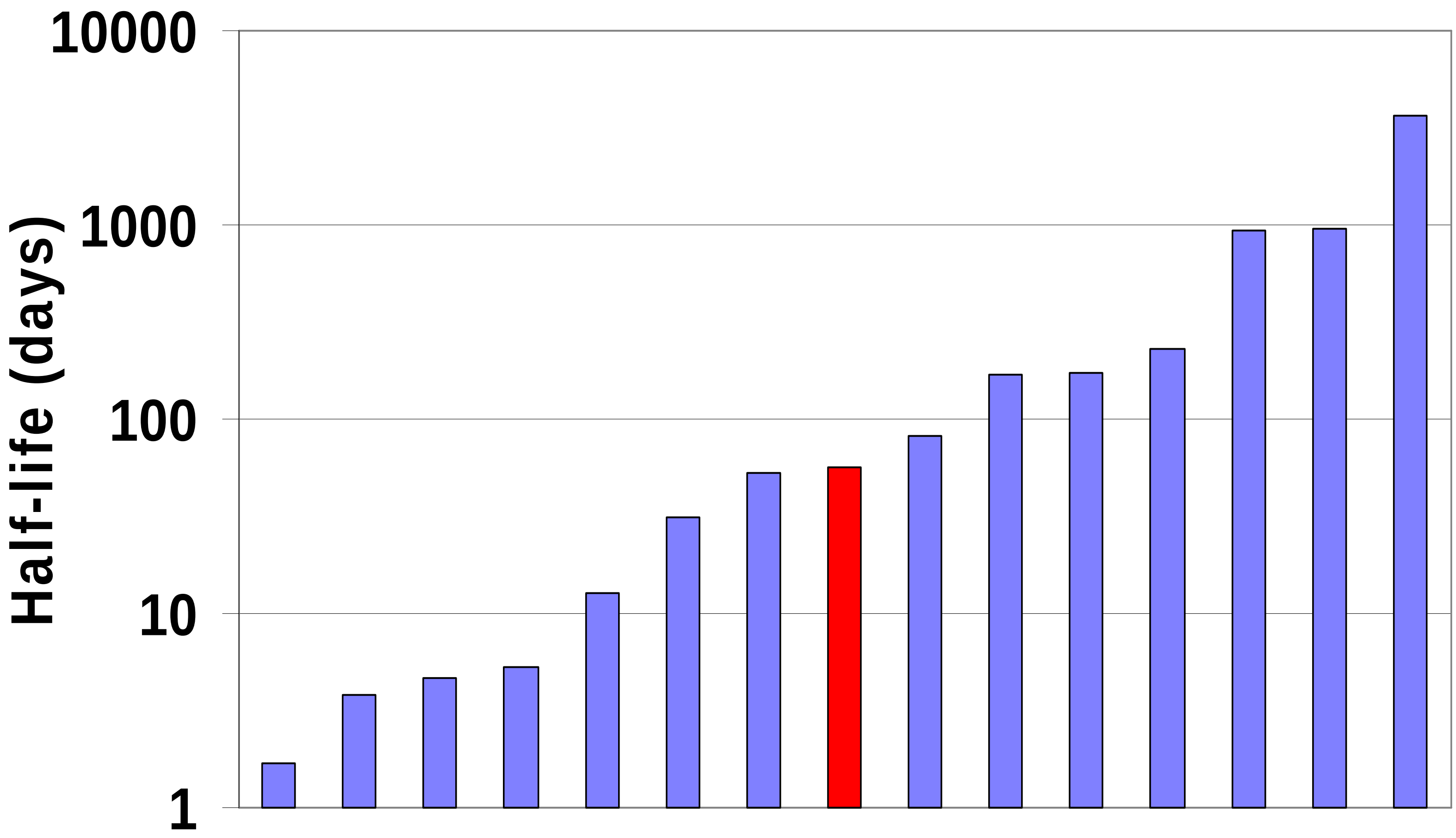
Dallas Aronson

Philip Howard

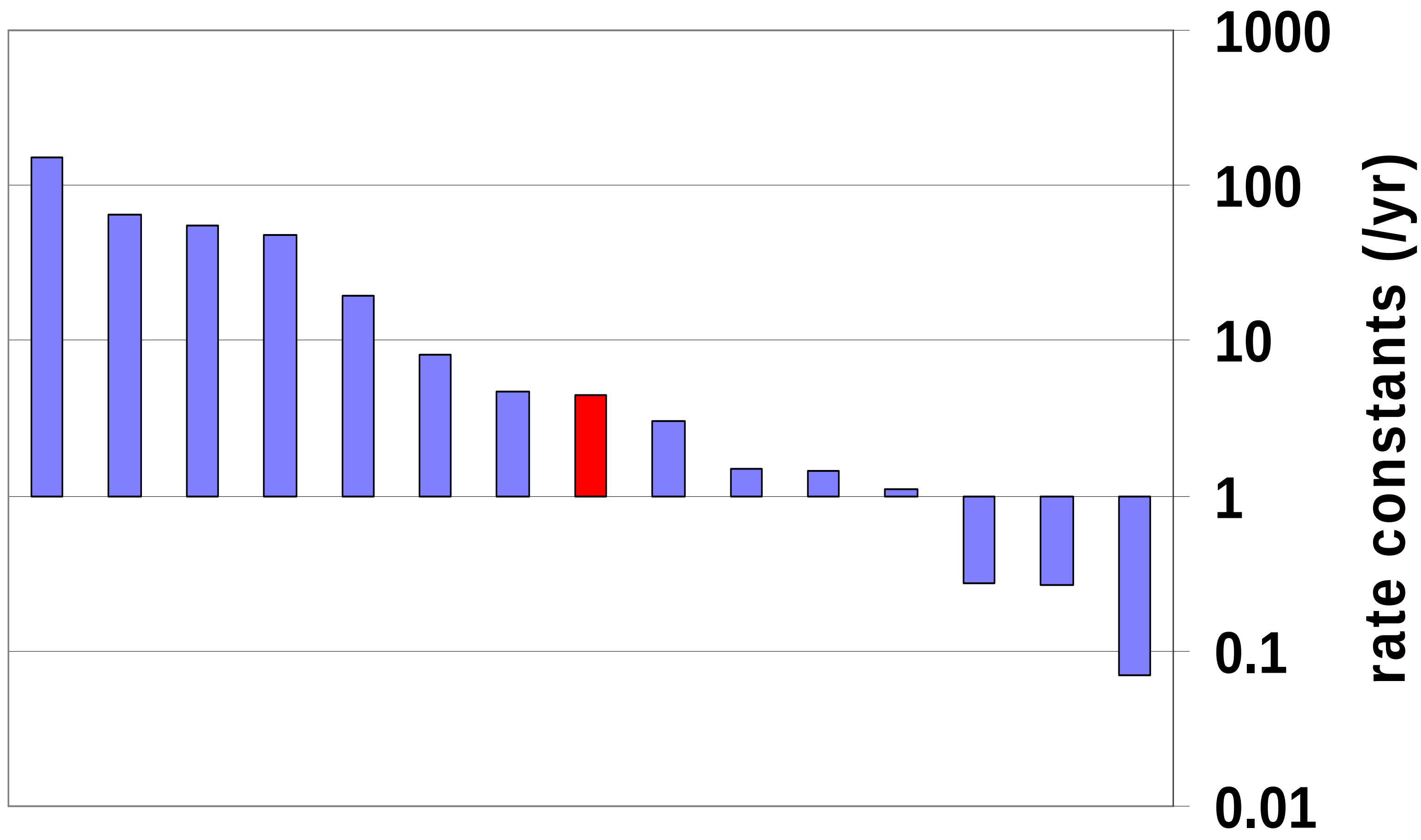
Environmental Science Center, Syracuse Research Corporation, 6225 Running Ridge Road, North Syracuse, NY 13212-2509

http://www.syrres.com/pdfs/ratecon.pdf

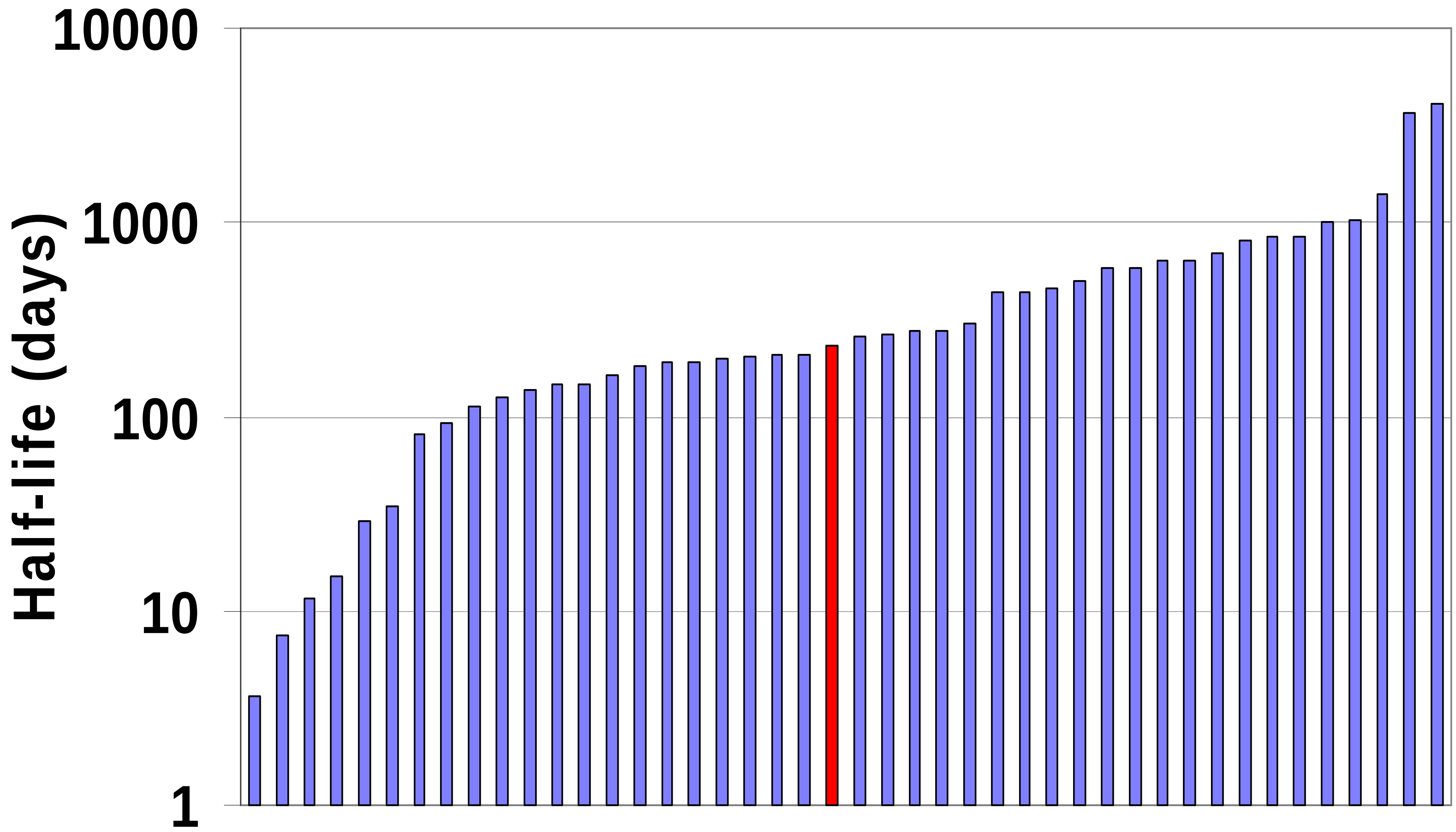
Field Half-Lives for PCE as Reported in Literature



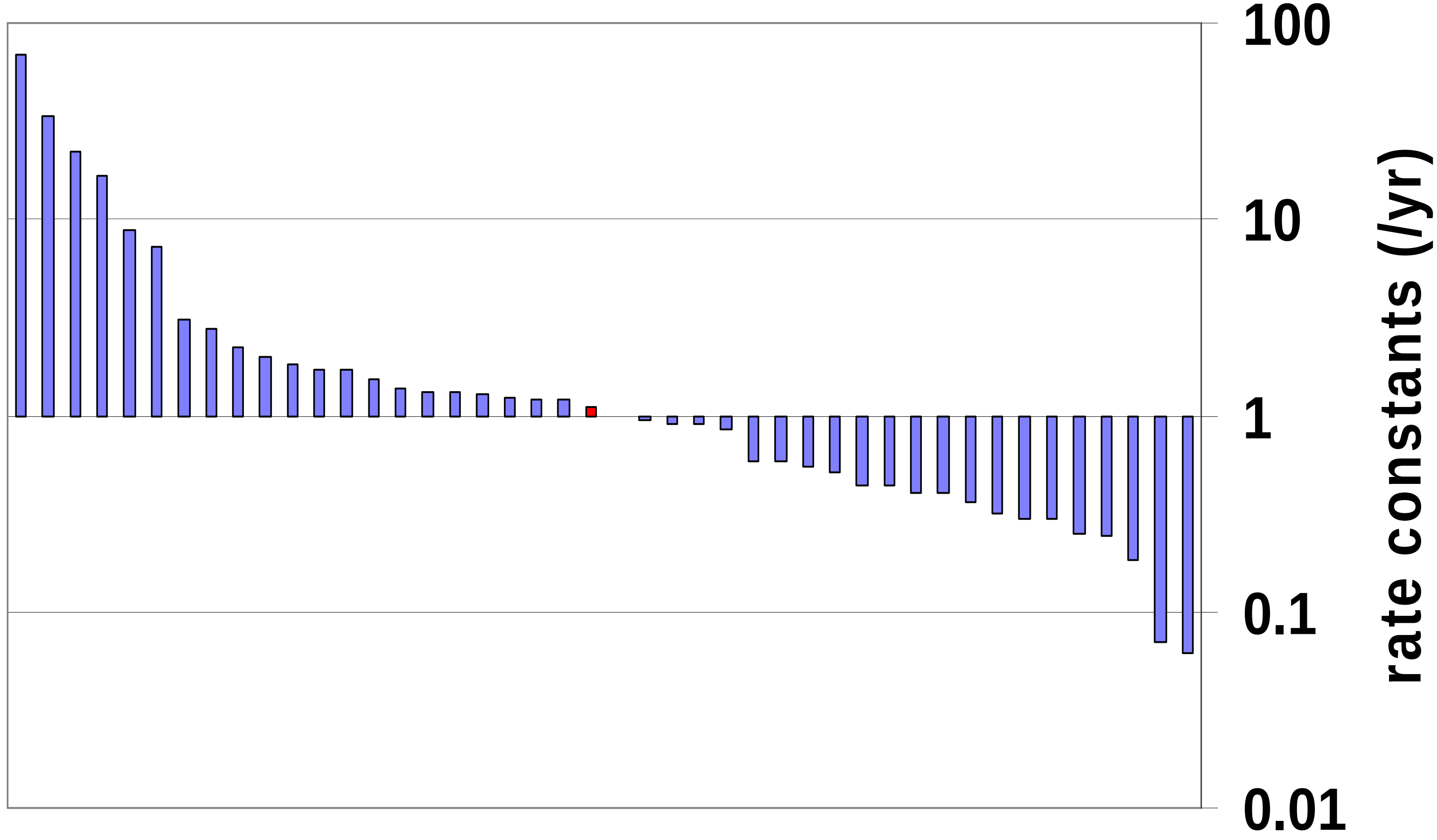
Field Rate Constants for PCE as Reported in Literature



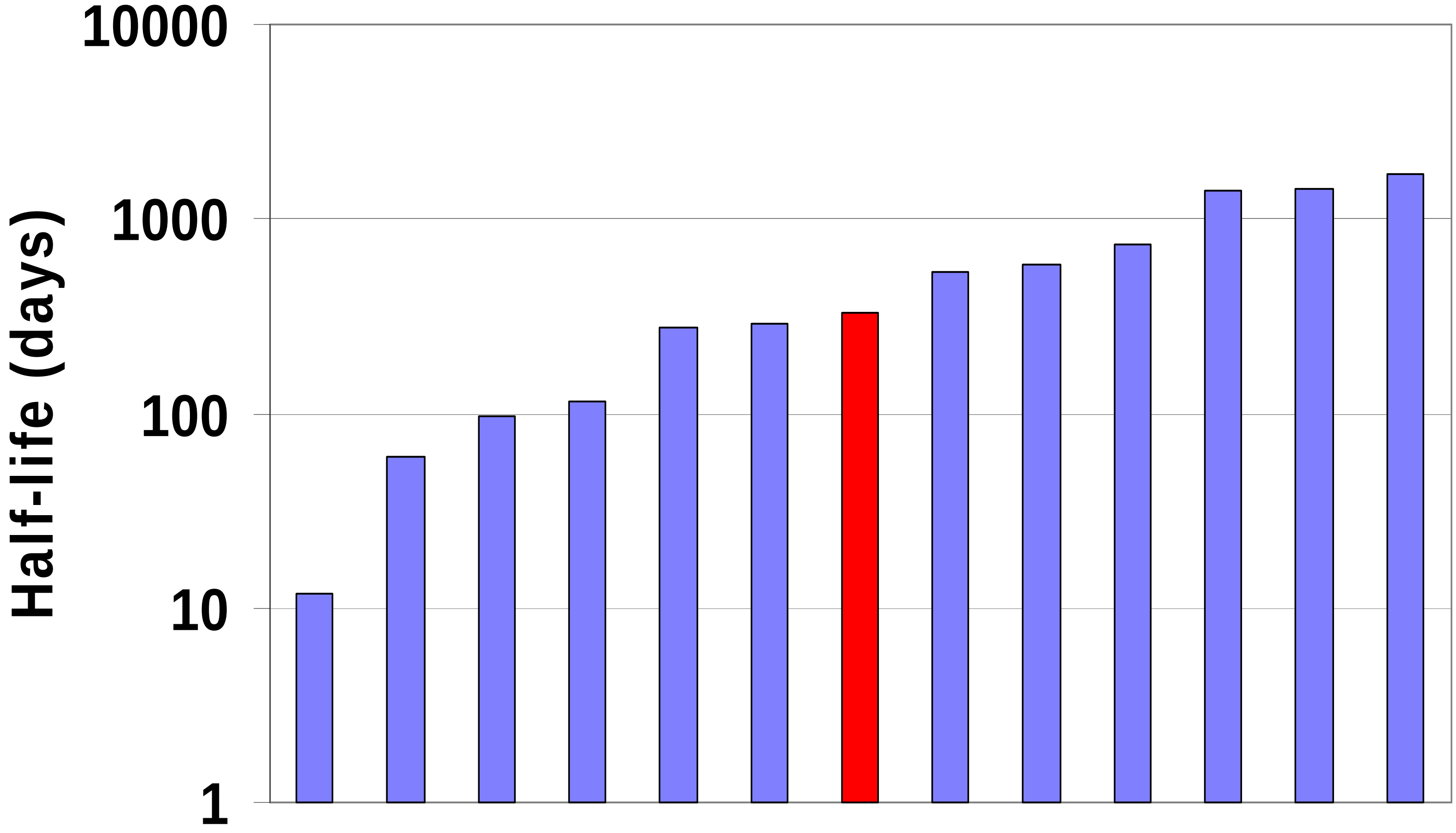
Field Half-Lives for TCE as Reported in Literature



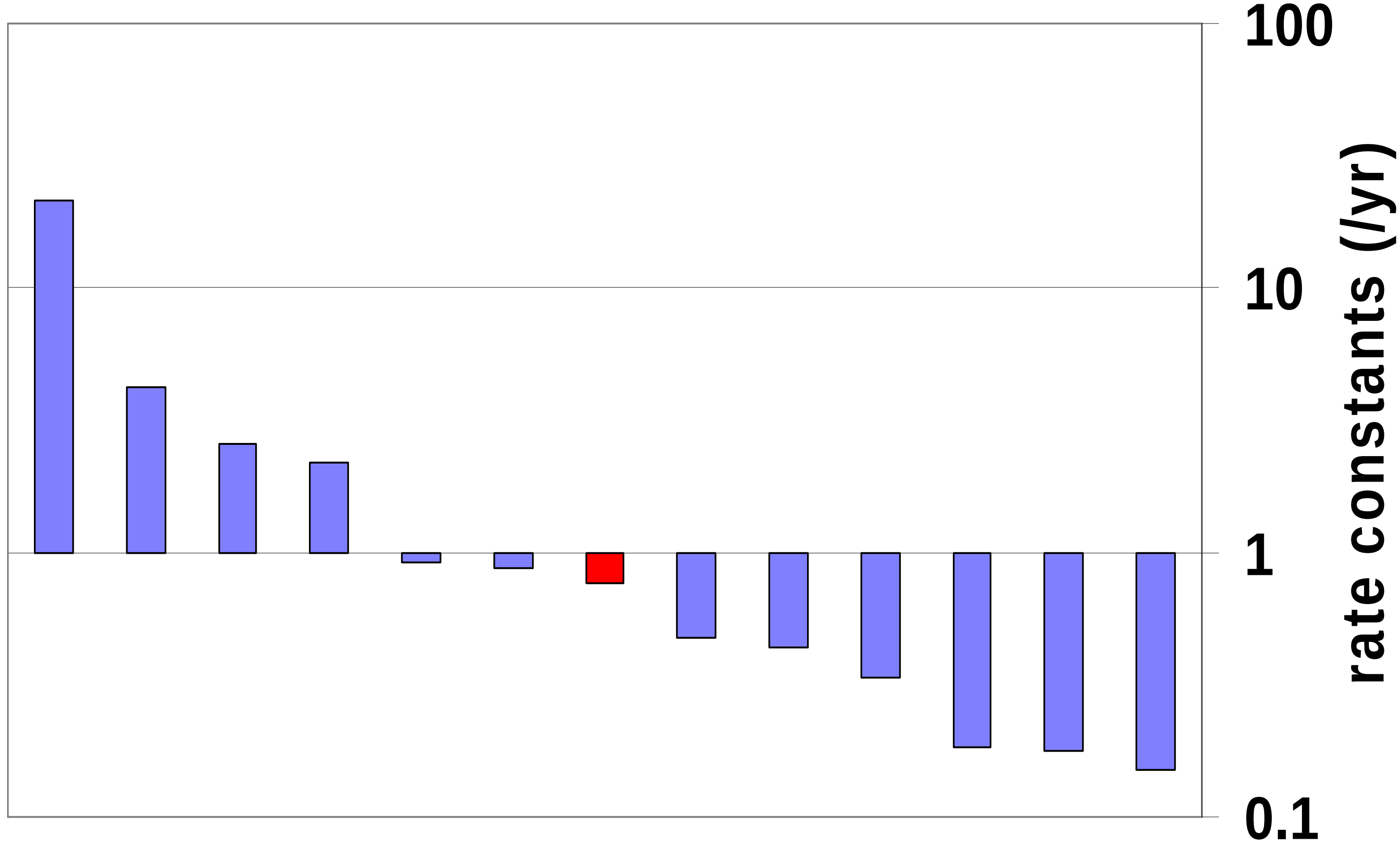
Field Rate Constants for TCE as Reported in Literature



Field Half-Lives for VC as Reported in Literature



Field Rate Constants for VC as Reported in Literature



Field Data

Analyte	Number	Rate (per year)
PCE	4	4.0
TCE	18	1.1
cis-DCE	13	1.6
Vinyl chloride	6	1.3

What *hydrogeologic and geochemical data* are useful *that can demonstrate NA processes and rates*?

Data on the density of active organisms can be used to estimate a rate of natural biodegradation of chlorinated solvents.

The only organisms known to completely dechlorinate PCE, TCE, or cis-DCE to ethylene are members of the *Dehalococcoides* Group.

The DNA from this group is easy to amplify and recognize using the polymerase chain reaction.

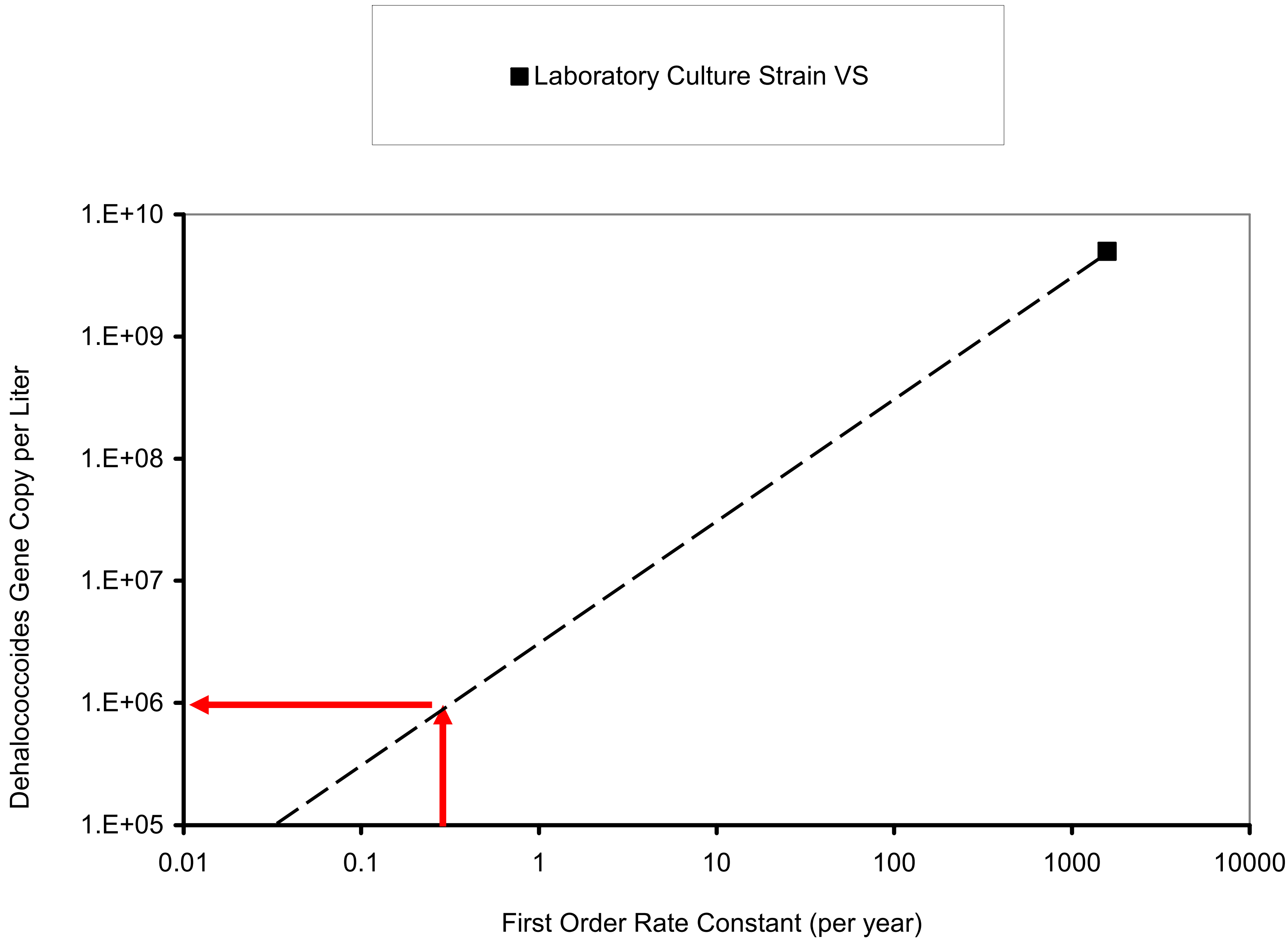
The following figure compares the first order rate of attenuation of cis-DCE in a laboratory culture of *Dehalococcoides*.

Data from:

Cupples A.M., Spormann A.M., and P.L. McCarty. 2004.

Vinyl chloride and *cis*-dichloroethene dechlorination kinetics and microorganism growth under substrate limiting conditions.

Environ Sci. Technol. 38(4):1102-7.


Laboratory Culture Strain VS
1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
Dehalococcoides Gene Copy per Liter
0.01
0.1
1
10
100
1000
10000
First Order Rate Constant (per year)

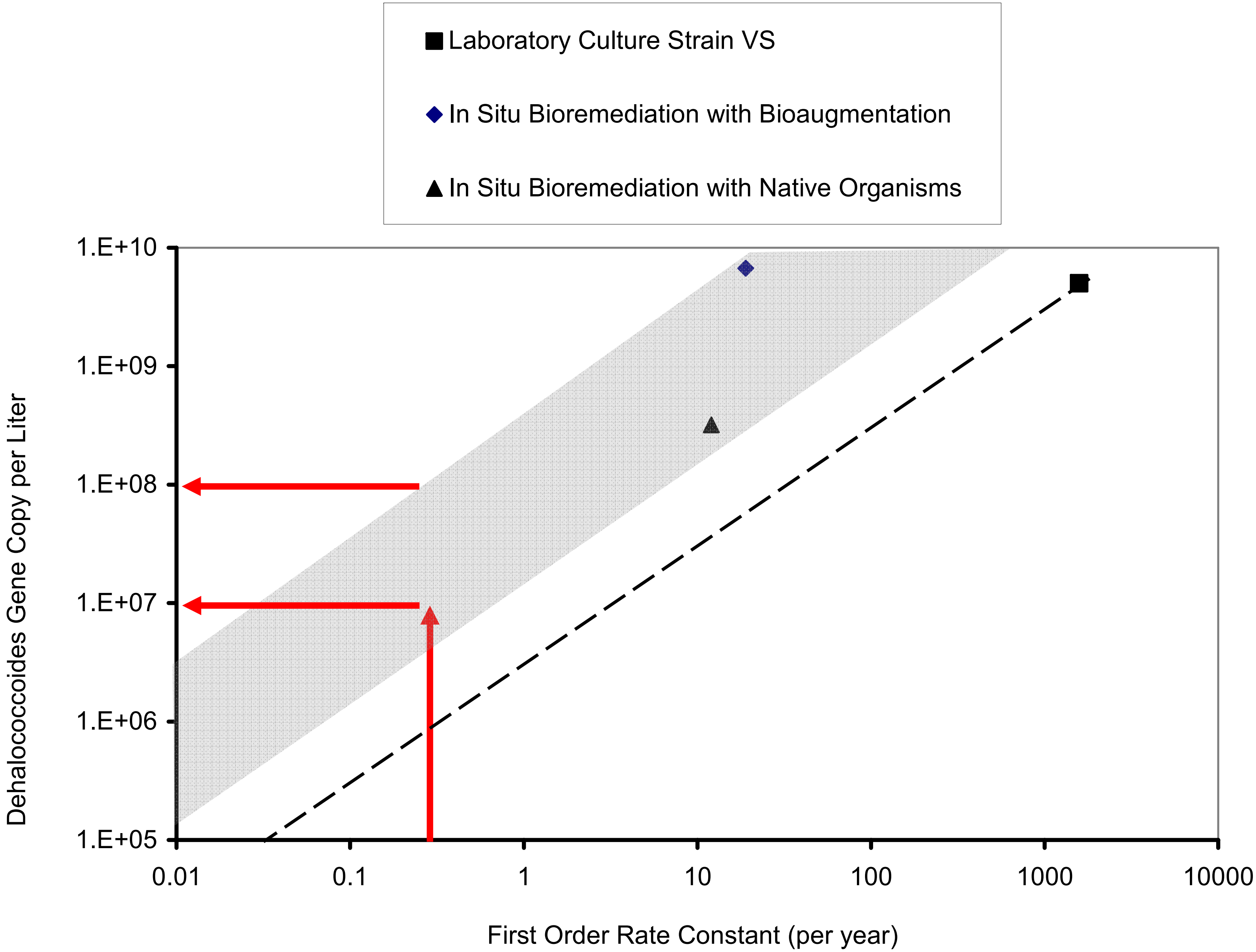
The following figure compares the first order rate of attenuation of cis-DCE in a field study of bioremediation using *Dehalococcoides.*

Data from:

Lendvay, J.M., F.E. Loffler, M. Dollhopf, M.R. Aiello, G. Daniels, B.Z. Fathepure, M. Gebhard, R. Heine, R. Helton, J. Shi, R. Krajmalnik-Brown, C.L. Major, M.J. Barcelona, E. Petrovskis, R. Hickey, J.M. Tiedje, and P. Adriaens. 2003.

Bioreactive barriers: a comparison of bioaugmentation and biostimulation for chlorinanted solvent remediation.

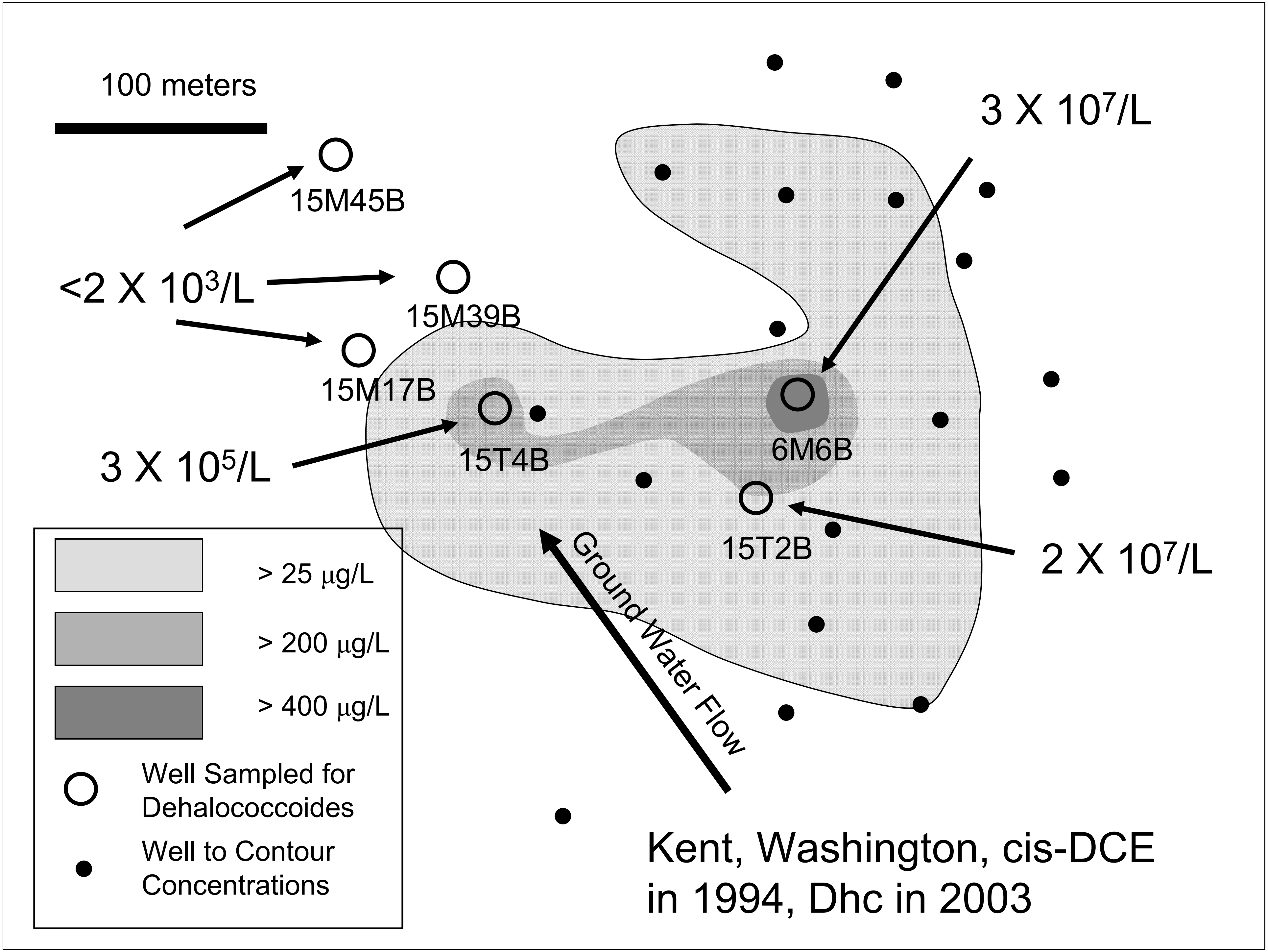
Environ. Sci. Technol. 37(7):1422-1431.



Laboratory Culture Strain VS
In Situ Bioremediation with Bioaugmentation
In Situ Bioremediation with Native Organisms
1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
Dehalococcoides Gene Copy per Liter
0.01
0.1
1
10
100
1000
10000
First Order Rate Constant (per year)

The rate of attenuation per cell in the field-scale pilot study was slower than that in the pure culture.

Based on these studies, a density of *Dehalococcoides* cells near 1 x 10^7 per liter is necessary to produce a rate of cis-DCE dechlorination of 0.3 per year.

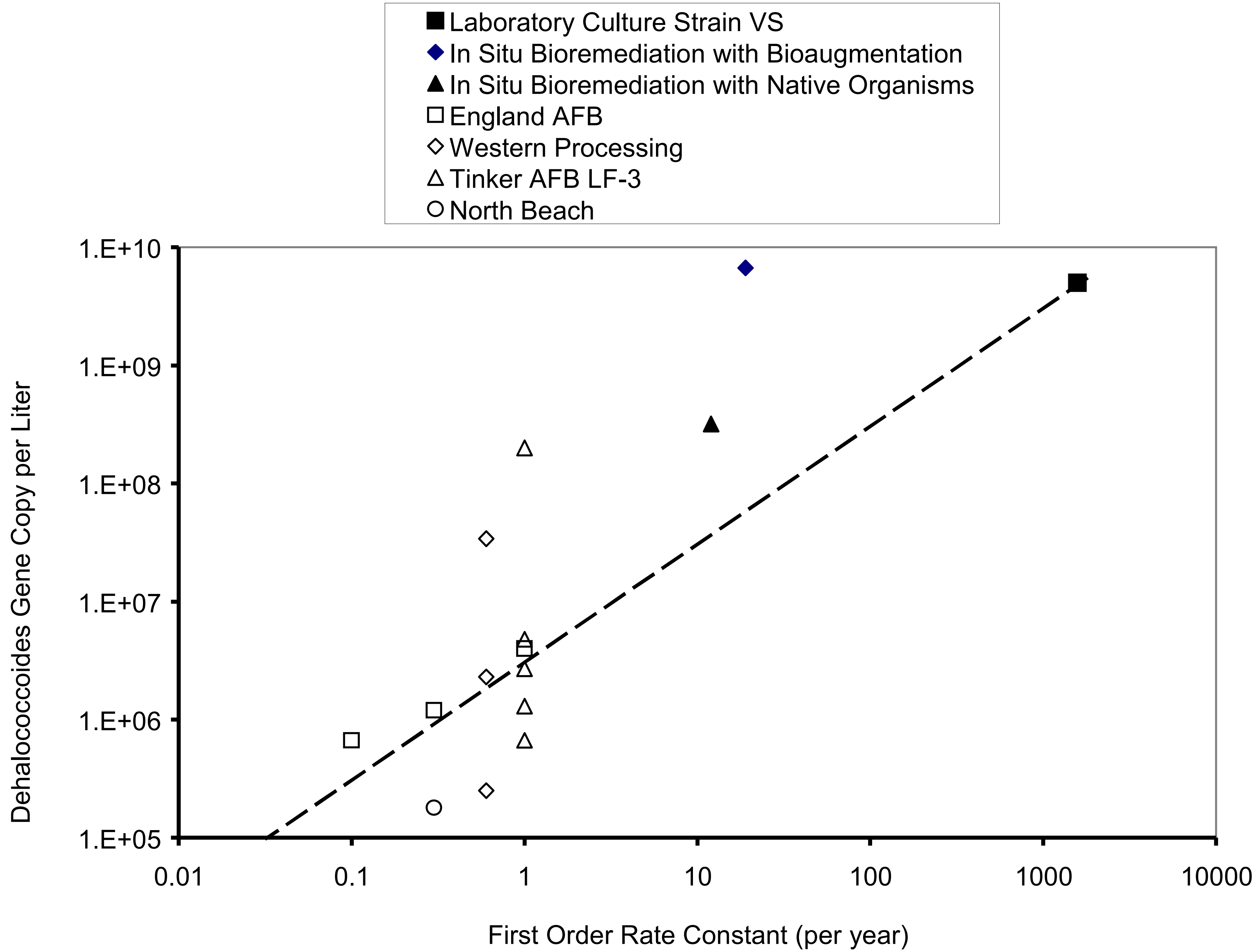

100 meters
3 X 10⁷/L
<2 X 10³/L
15M45B
15M39B
15M17B
3 X 10⁵/L
15T4B
6M6B
15T2B
2 X 10⁷/L
Ground Water Flow
> 25 µg/L
> 200 µg/L
> 400 µg/L
Well Sampled for Dehalococcoides
Well to Contour Concentrations
Kent, Washington, cis-DCE in 1994, Dhc in 2003

The following figure compares the first order rate of attenuation of *cis*-DCE in a survey of natural Attenuation sites.

Taken from:

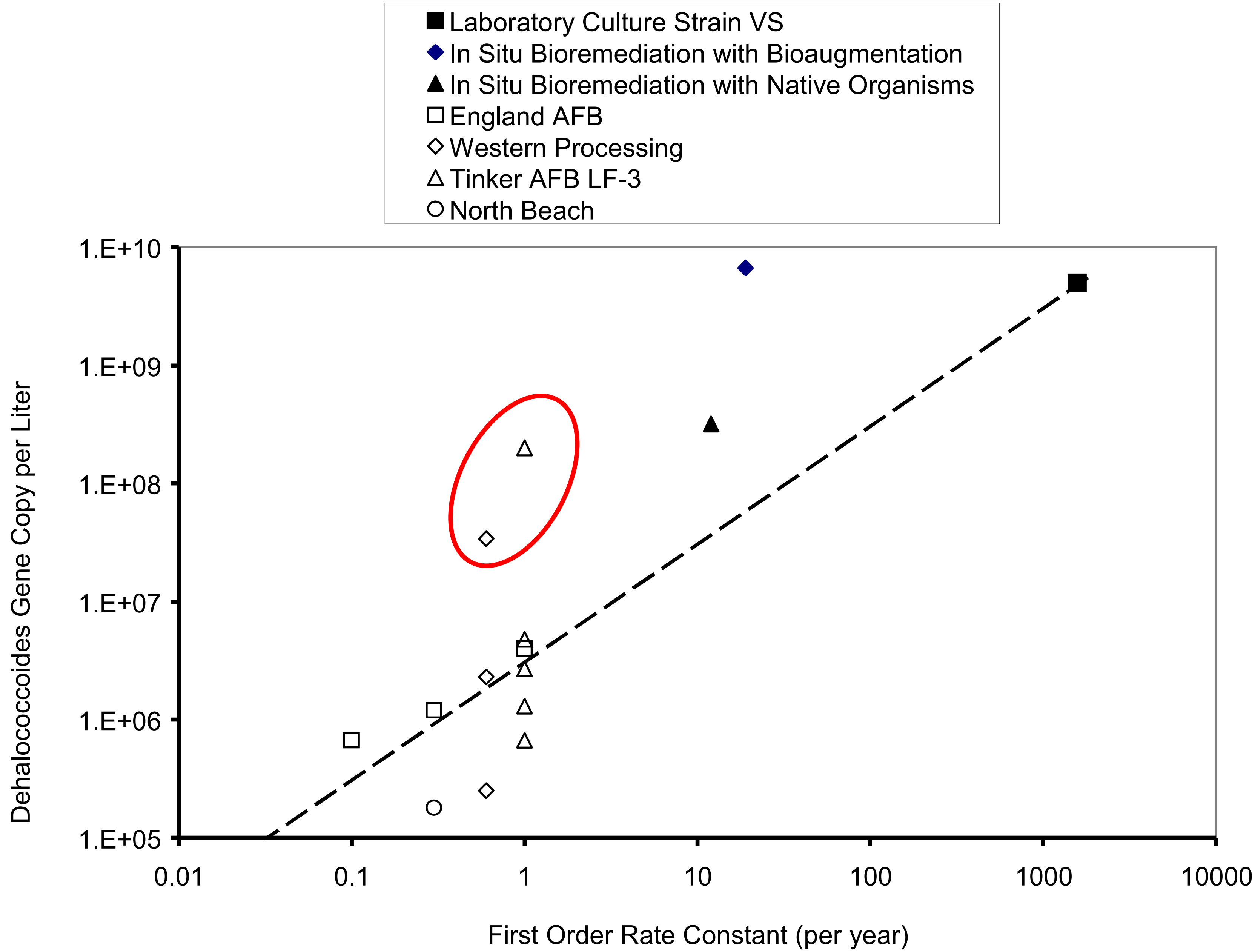
Evaluation of the Role of *Dehalococcoides* Organisms in the Natural Attenuation of Chlorinated Ethylenes in Ground Water. Xiaoxia Lu, Donald H. Kampbell and John T. Wilson. 2006. EPA/600/R-06/029

Relationship between *Dehalococcoides* DNA in Ground Water and Rates of Reductive Dechlorination at Field Scale. Xiaoxia Lu, John T. Wilson, and Donald H. Kampbell. 2006. *Water Research* 40(2006):3131-3140


Laboratory Culture Strain VS
In Situ Bioremediation with Bioaugmentation
In Situ Bioremediation with Native Organisms
England AFB
Western Processing
Tinker AFB LF-3
North Beach
1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
Dehalococcoides Gene Copy per Liter
0.01
0.1
1
10
100
1000
10000
First Order Rate Constant (per year)

The first order rate constants from the field sites varied from 0.1 to 1 per year.

For two of the evaluations, the rate attained by *Dehalococcoides* cells in monitoring wells from field sites was equivalent to the performance of the in situ bioremediation studies.



Laboratory Culture Strain VS
In Situ Bioremediation with Bioaugmentation
In Situ Bioremediation with Native Organisms
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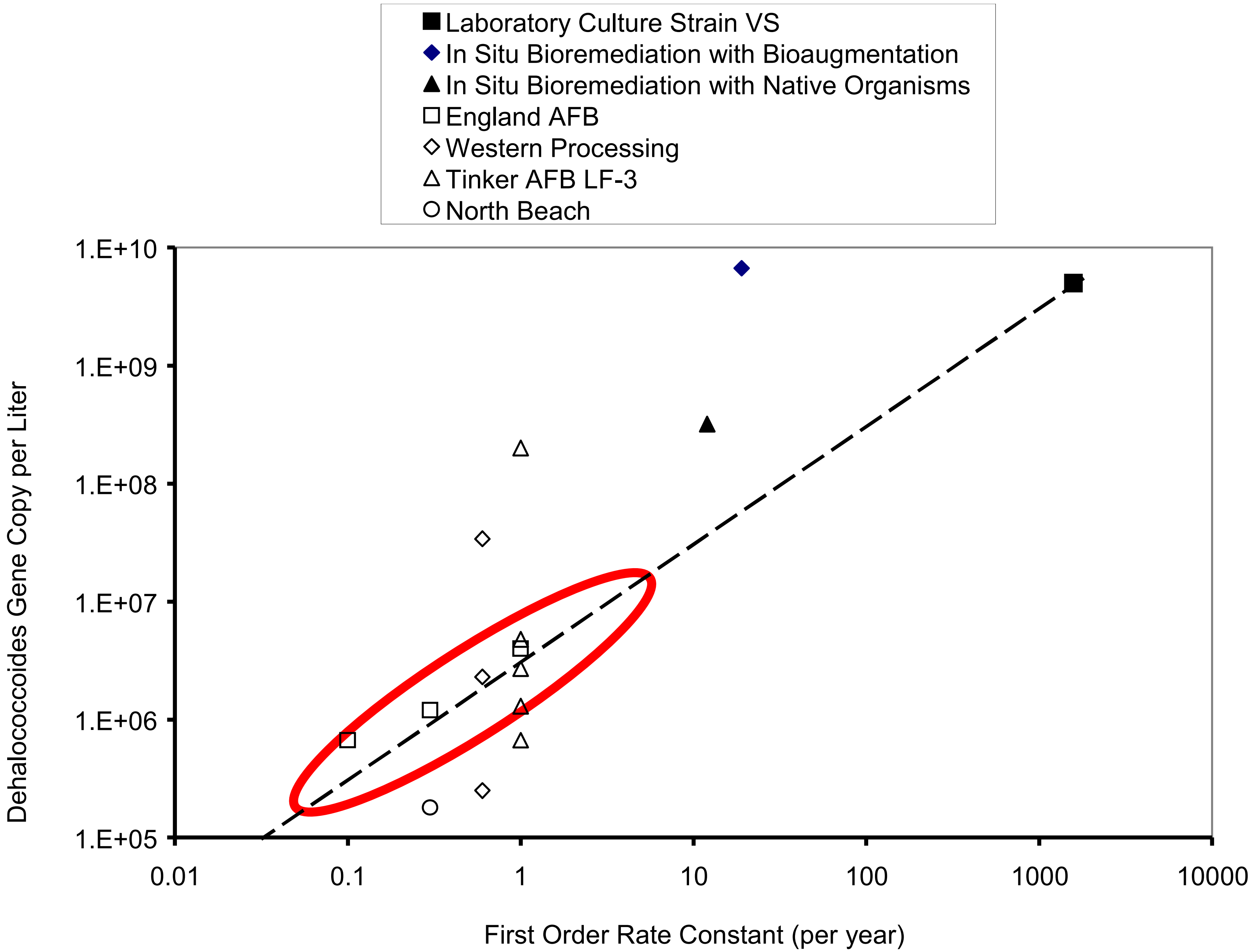
Western Processing
Tinker AFB LF-3
North Beach
Dehalococcoides Gene Copy per Liter
1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
0.01
0.1
1
10
100
1000
10000
First Order Rate Constant (per year)

For most of the evaluations, the rate attained by *Dehalococcoides* cells in monitoring wells from field sites was equivalent to the performance of the pure culture under optimum conditions.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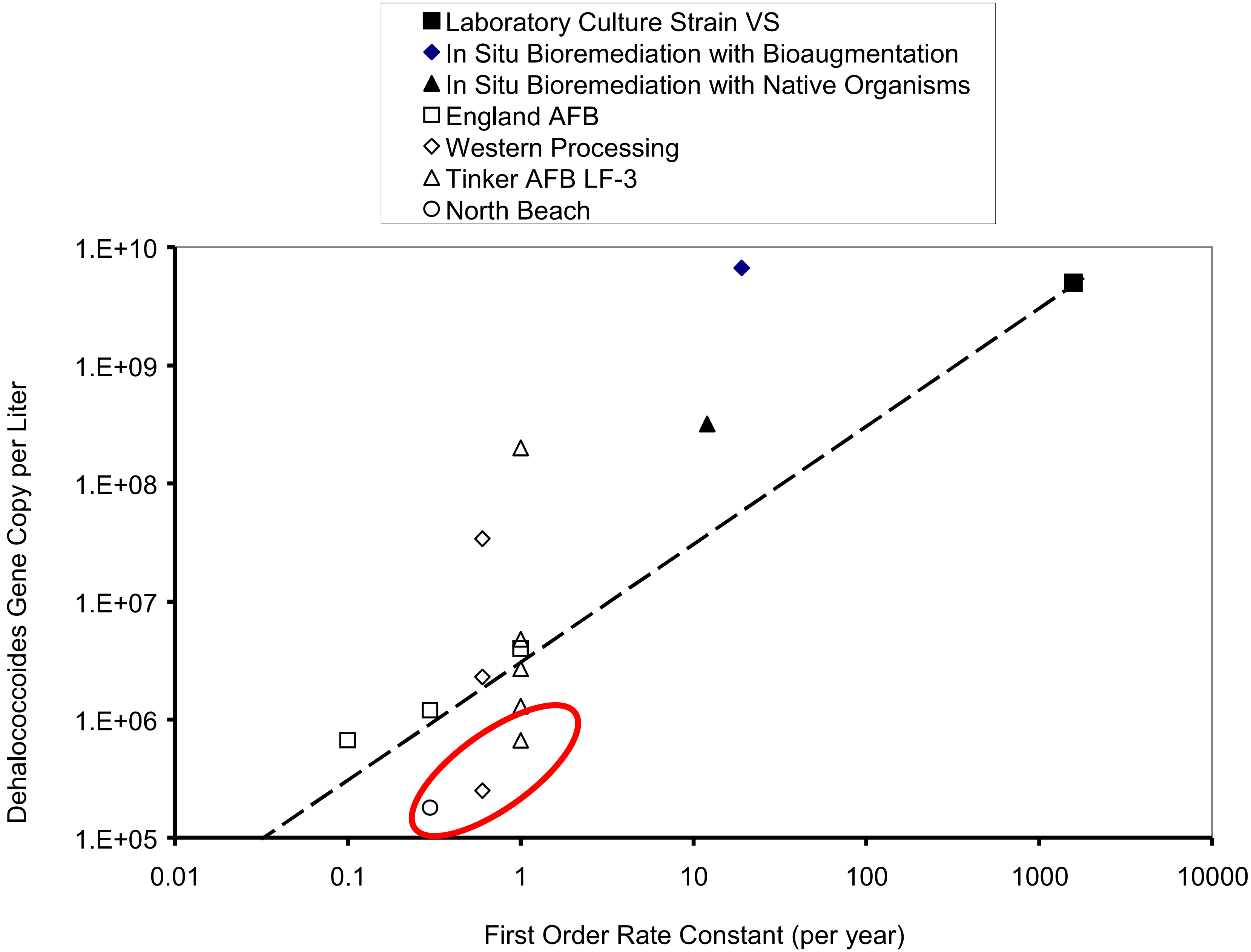
1.E+08
1.E+07
1.E+06
1.E+05
0.01
0.1
1
10
100
1000
10000
Dehalococcoides Gene Copy per Liter
First Order Rate Constant (per year)

For some of the evaluations, the rate attained by *Dehalococcoides* cells in monitoring wells from field sites was better than the performance of the pure culture under optimum conditions.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1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
0.01
0.1
1
10
100
1000
10000
Dehalococcoides Gene Copy per Liter
First Order Rate Constant (per year)

The density of cells in the ground water samples was less than expected based on the rate of reductive dechlorination at field scale, when densities and rates were compared to the behavior of pure cultures.

The monitoring wells were probably not providing a representative sample of density of the *Dehalococcoides* cells in the aquifer. Most of the cells were probably sorbed to aquifer solids and were not planktonic in the ground water.

The estimates of rates from density of *Dehalococcoides* cells in monitoring wells provides at best a semi-quantitative lower boundary on the rate of attenuation.

If the cell numbers are adequate to rationalize the observed rate of attenuation, then the cell numbers can be taken as a second line of evidence.

1×10^7 cells per liter can produce 0.3 per year

3×10^7 cells per liter can produce 1 per year

1×10^8 cells per liter can produce 3 per year

In summary, to distinguishing sites where MNA has a reasonable chance of success from sites where MNA will be disappointing, use the EPA guidance provided in:

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Unless #1 is of sufficient quality and duration, #2 is generally required (regulatory decision).