

Abiotic Degradation Can Account for Rate Constants for Natural Attenuation of TCE and cDCE in Groundwater

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Photo by Wes McCall of
Geoprobe Systems®

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Denver, CO, June 5, 2024



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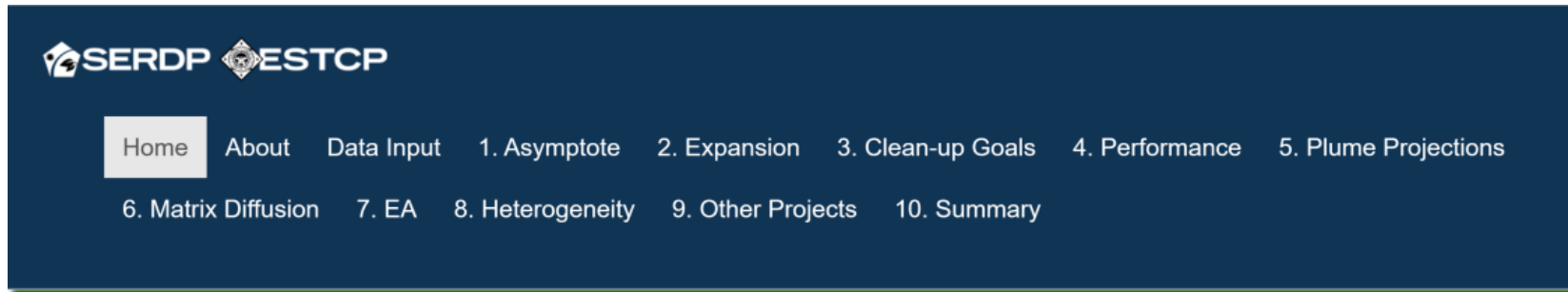
Clemson University

The rate constants for abiotic degradation of *c*DCE or TCE in sediment samples were determined in laboratory of David Freedman at Clemson University. The data are not yet published, they are provisional, and are to be considered personal communication from David Freedman

SERDP project ER20-1368.

Development of Protocols
to Quantify Abiotic
Transformation Rates and
Mechanisms for
Chlorinated Ethenes in
Water Supply Aquifers

**David Adamson
Charles Newell
Shahla Farhat
and
Horiko Hort
Brian Strasert**



TA²: THE SERDP *TRANSITION ASSESSMENT ASSISTANT*

The data analysis and evaluation of attenuation with distance along a flow path was done using draft versions of tools developed for TA².

**SERDP project
ER20-1429.**

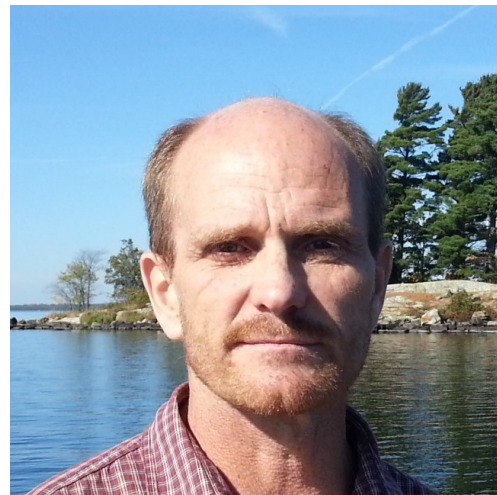
**Transitioning from
Active Remedies to
Monitored Natural
Attenuation**

Ramona Iery



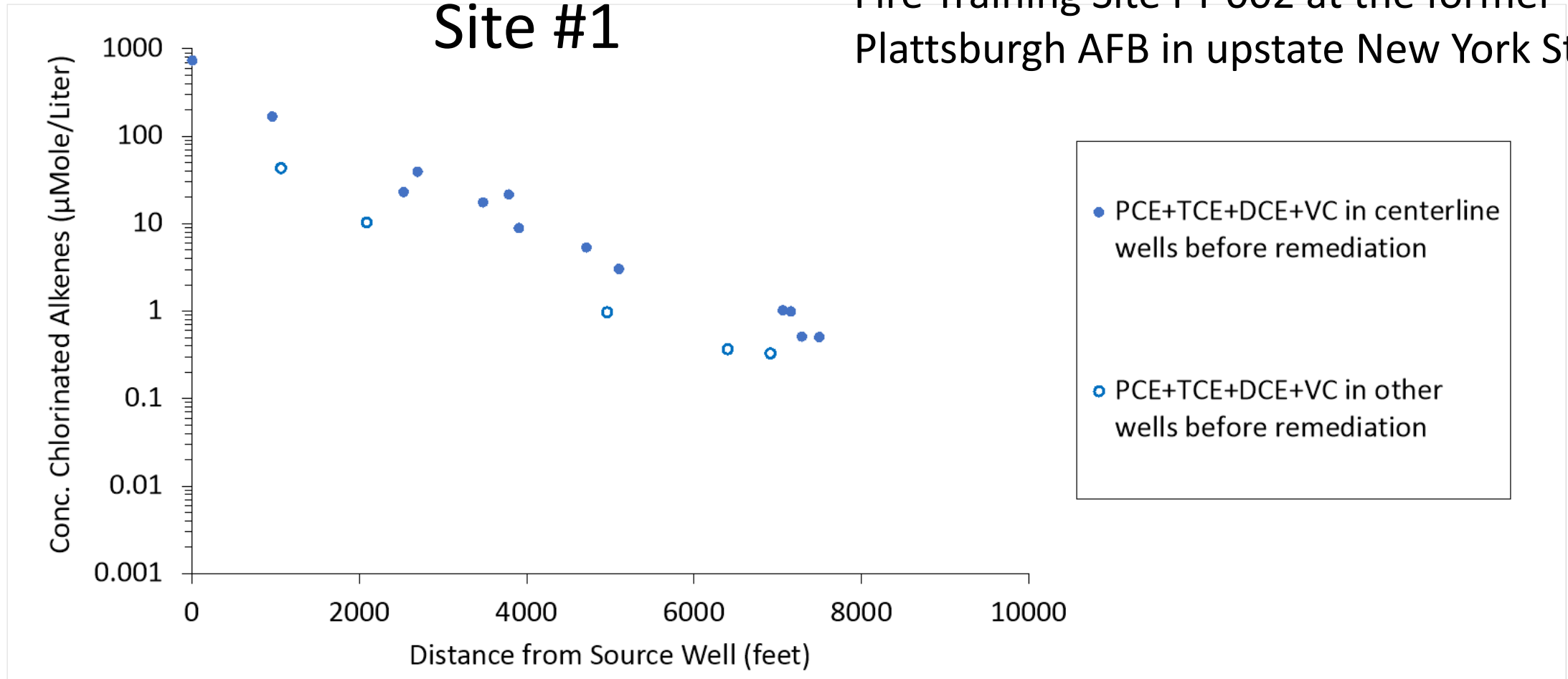
**Naval Facilities
Engineering and
Expeditionary
Warfare Center**

Mark Ferrey



**Minnesota Pollution
Control Agency**

Fire Training Site FT-002 at the former
Plattsburgh AFB in upstate New York State.



Distribution of cVOC contamination with distance from the source

Site #1

Rate constants from Clemson microcosm study

	Plattsburgh	Clemson Microcosm	Water Control
	cDCE		
		per year	
Anoxic	Rate Constant	0.32	0.0077
Anoxic	95% Confidence	0.06	0.0031
Aerobic	Rate Constant	0.083	0.0077
Aerobic	95% Confidence	0.021	0.0031

Calculation of the rate constant expected
under conditions in the aquifer

$$k_{\text{expected aquifer}} = k_{\text{microcosms}} * \frac{\text{Water in microcosm}}{\text{Sediment in microcosm}} * \frac{\text{Sediment in aquifer}}{\text{Water in aquifer}}$$

$$k_{\text{expected aquifer}} = 0.31 \text{ per year} * \frac{52.7 \text{ mL}}{100 \text{ g}} * \frac{2.68(1-0.26) \text{ g}}{0.25 \text{ mL}}$$

$$k_{\text{expected aquifer}} = 1.33 \text{ per year}$$

Correction of rate constants to the average
magnetic susceptibility of aquifer

$$k_{corrected\ aquifer} = k_{expected\ aquifer} * \frac{\text{Magnetic Susceptibility of aquifer sediment}}{\text{Magnetic Susceptibiliy of microcosm sediment}}$$

$$k_{corrected\ aquifer} = 1.33\ per\ year * \frac{1.10E-06\ m^3/kg}{1.70E-06\ m^3/kg}$$

$$k_{corrected\ aquifer} = 0.86\ per\ year$$

Site #1

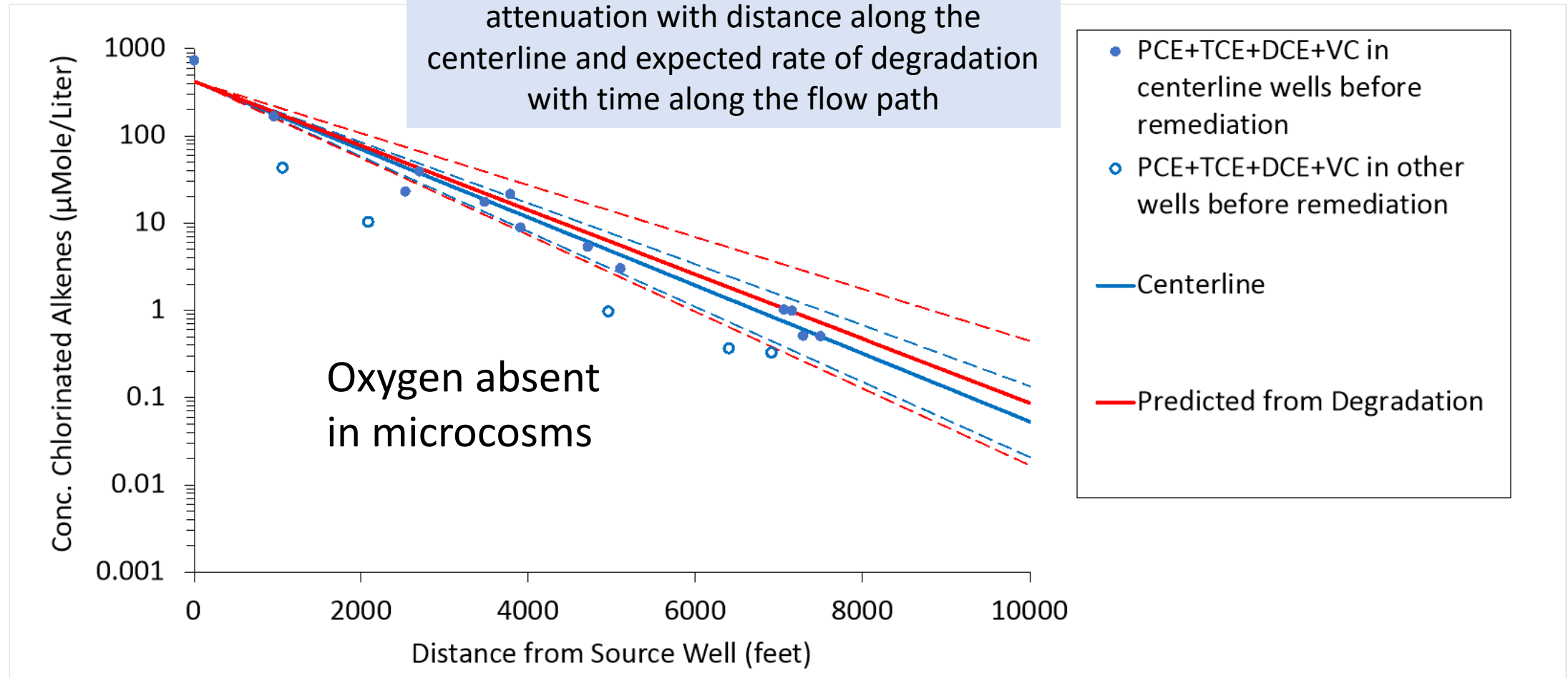
Rate constant to be used to evaluate the contribution of abiotic degradation.

The flow path at the time of sampling was anoxic.

	Plattsburgh	Clemson Microcosm	Minus Control	Expected in Aquifer	Corrected M.S.* of Aquifer
	cDCE				
		per year	per year	per year	per year
Anoxic	Rate Constant	0.32	0.31	1.33	0.86
Anoxic	95% Confidence	0.06	0.06	0.26	0.16
Aerobic	Rate Constant	0.083	0.074	0.32	0.20
Aerobic	95% Confidence	0.021	0.021	0.090	0.58

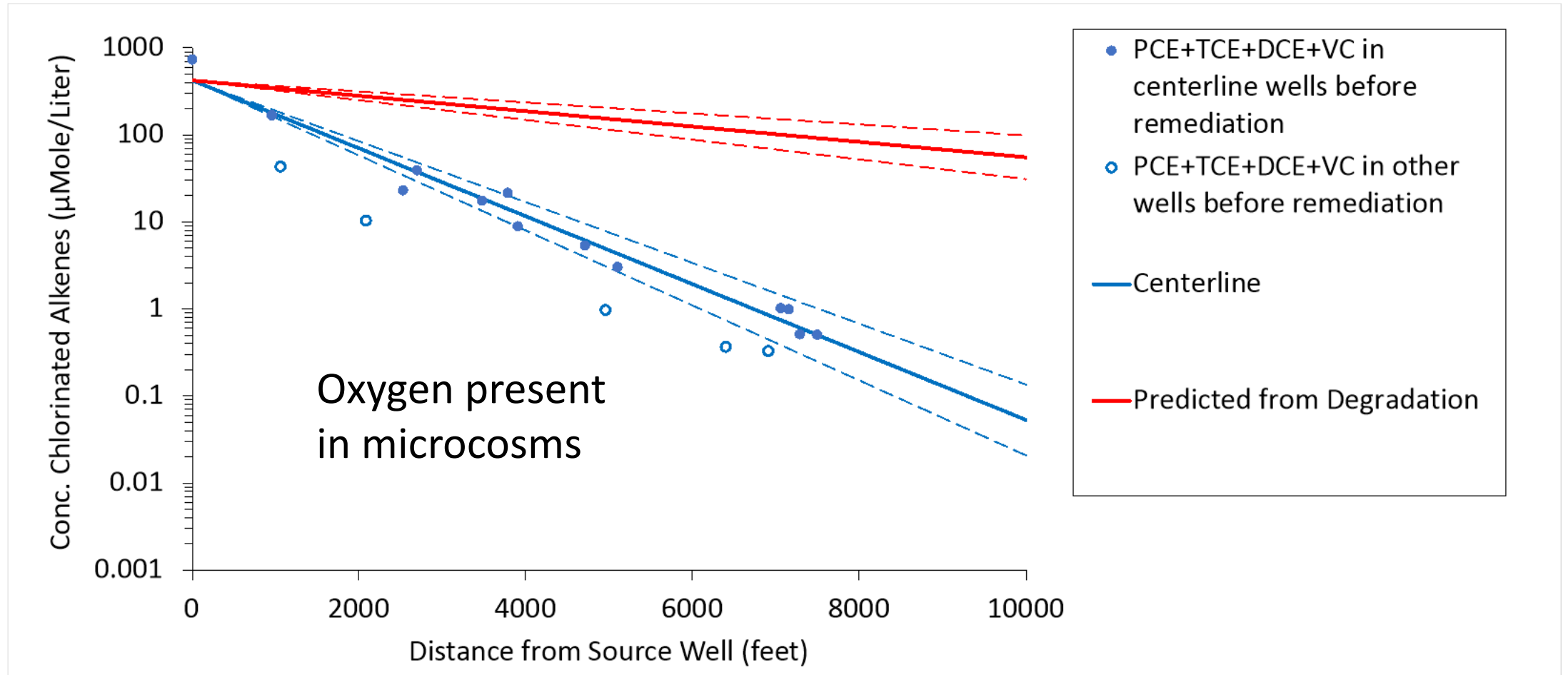
* Mass magnetic susceptibility

Site #1



Degradation of cDCE in anoxic microcosms can account for the attenuation of cVOC contamination along the flow path at the Plattsburgh Site before remediation.

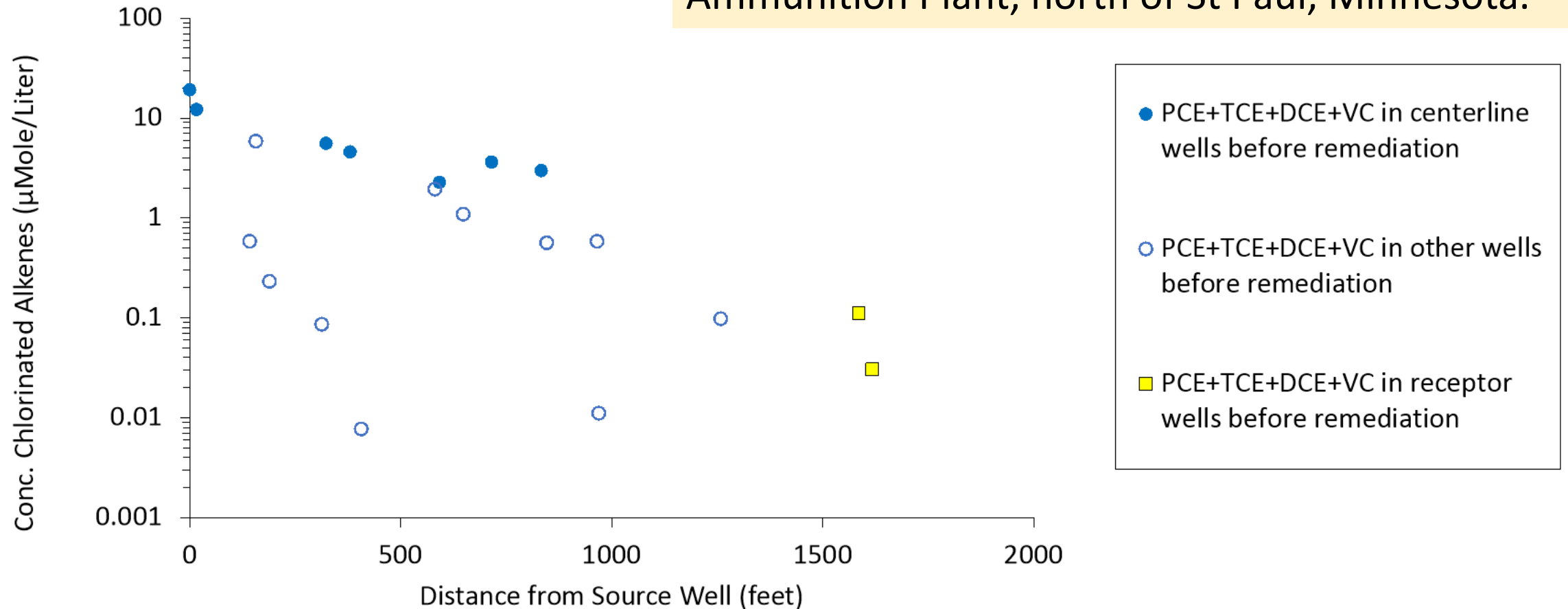
Site #1



Degradation of TCE in aerobic microcosms **does not** account for the distribution of cVOC contamination at the Plattsburgh Site before remediation.

Site #2

Site A at the former Twin Cities Army Ammunition Plant, north of St Paul, Minnesota.



Distribution of cVOCs in wells at the site before remediation

Site #2

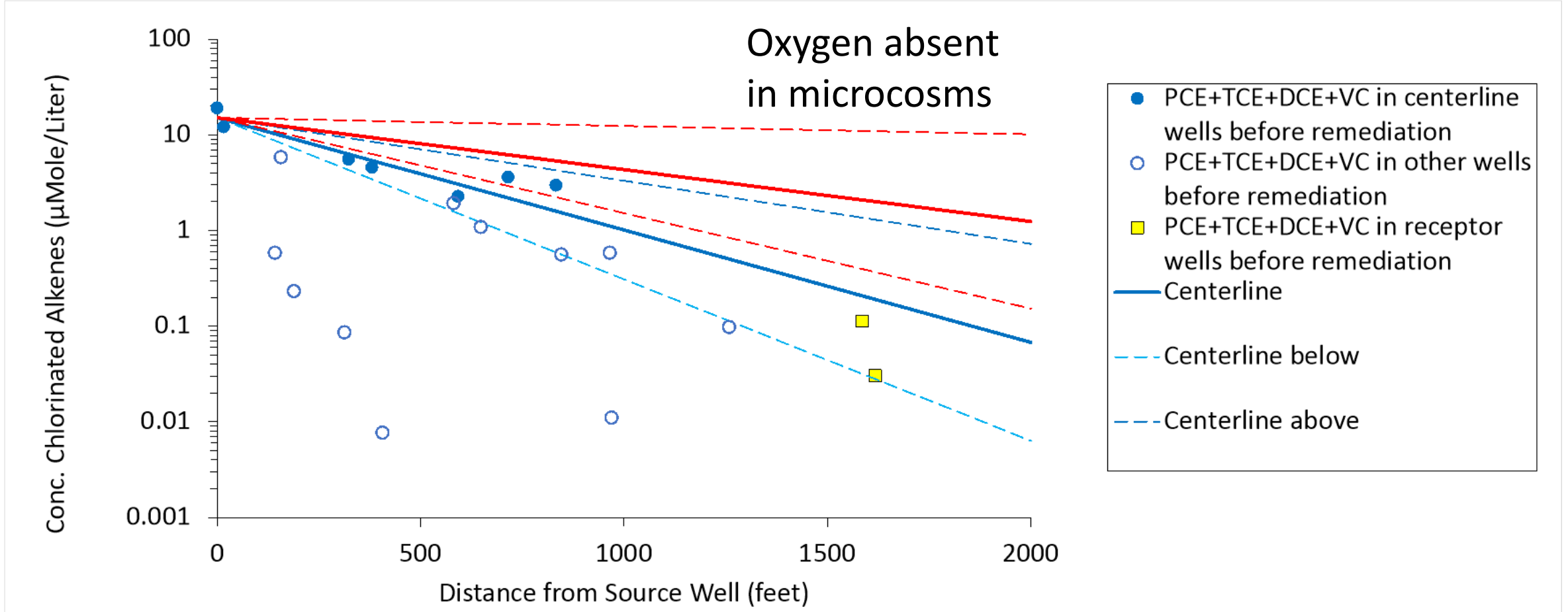
Rate constant to be used to evaluate the contribution of abiotic degradation.

The flow path at the time of sampling was anoxic.

	TCAAP Site A	Clemson Microcosm	Minus Control	Expected in Aquifer	Corrected M.S.* of Aquifer
	TCE				
		per year	per year	per year	per year
Anoxic	Rate Constant	0.0936	0.0663	0.42	0.27
Anoxic	95% Confidence	0.0557	0.0557	0.35	0.22
Aerobic	Rate Constant	0.191	0.138	0.86	0.55
Aerobic	95% Confidence	0.0758	0.0758	0.47	0.30

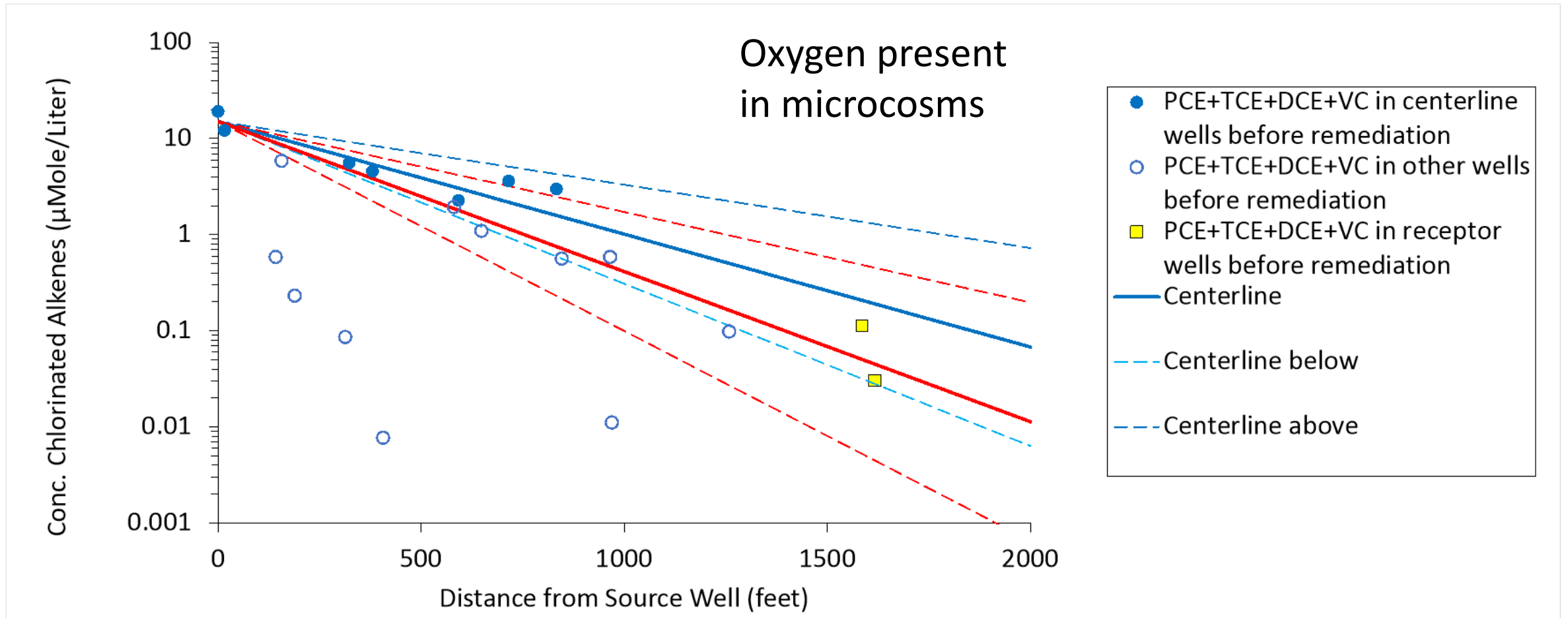
* Mass magnetic susceptibility

Site #2



Degradation of TCE in anoxic microcosms **does not** account for the attenuation of cVOCs along the centerline flow path at the TCAAP site before remediation

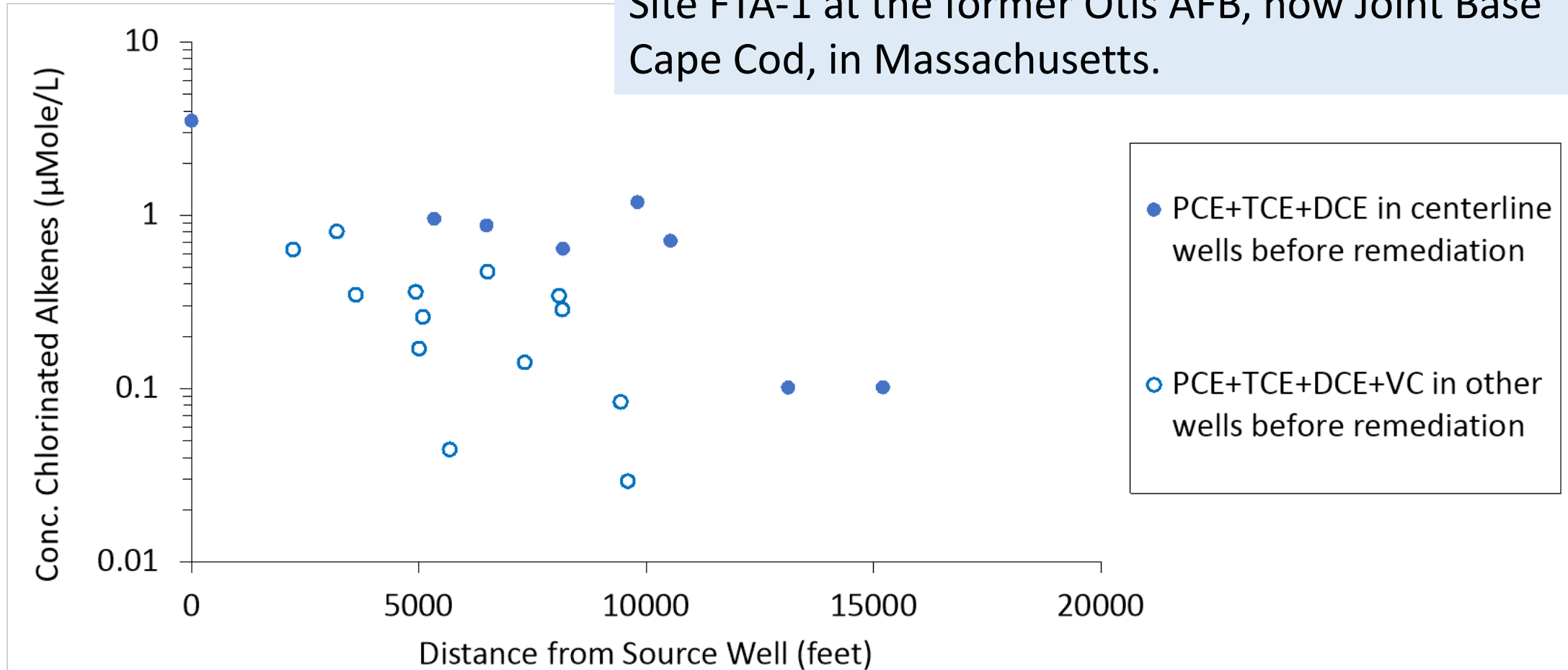
Site #2



Degradation of TCE in aerobic microcosms can account for the attenuation of cVOCs along the centerline flow path at the TCAAP site before remediation

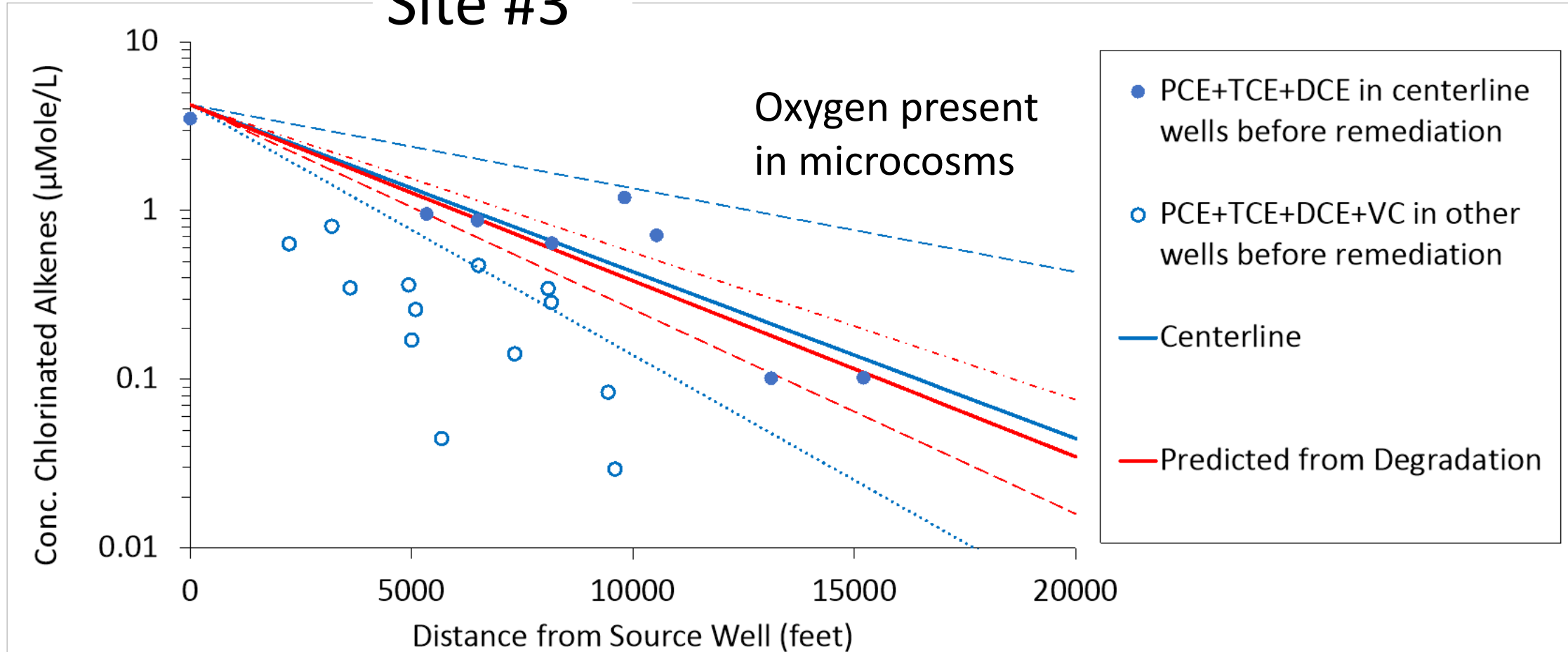
Site #3

Plume in the Ashumet Valley from Fire Training Site FTA-1 at the former Otis AFB, now Joint Base Cape Cod, in Massachusetts.

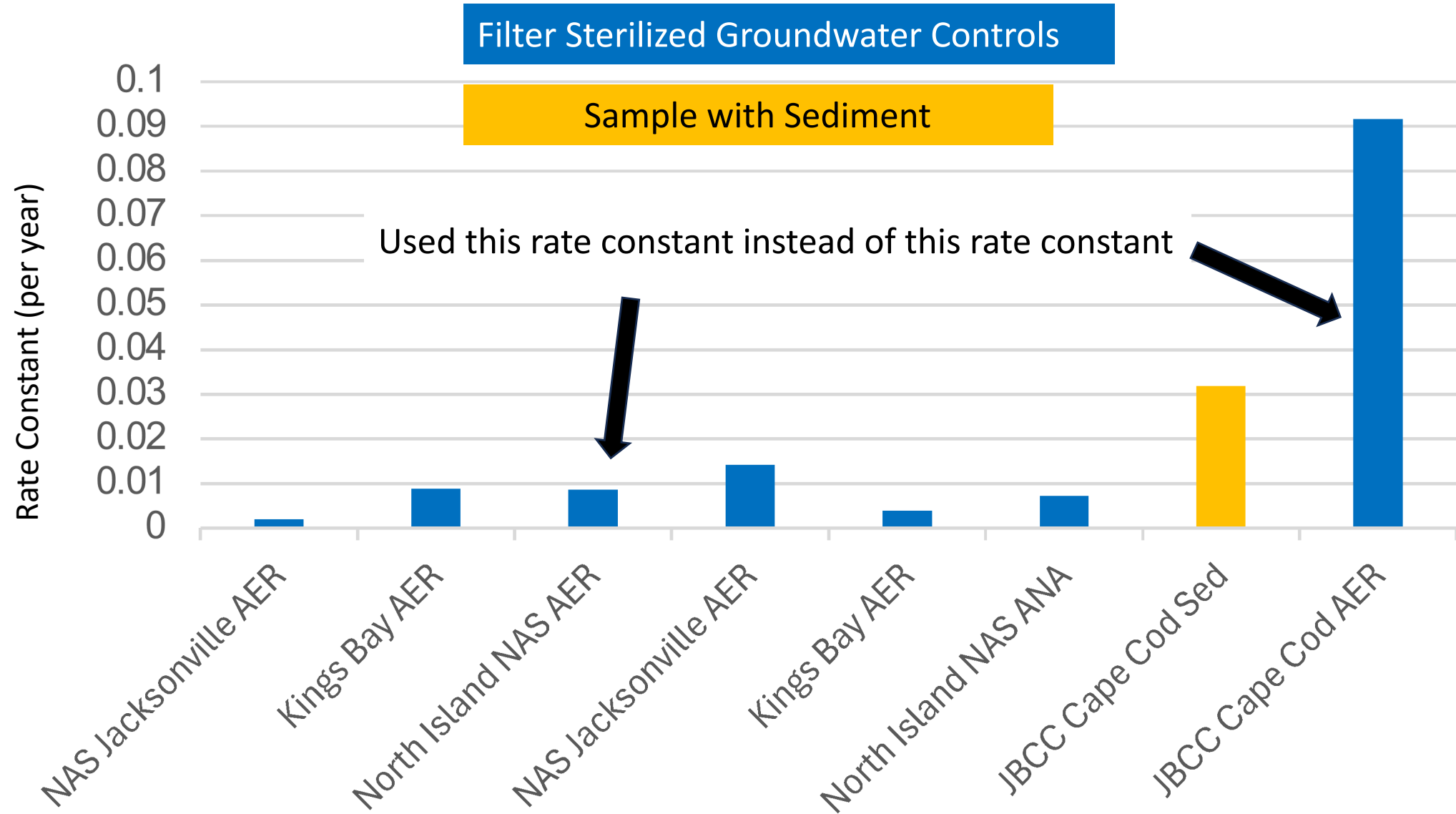


Distribution of cVOCs in wells at the site before remediation

Site #3



Degradation of TCE in aerobic microcosms can account for the attenuation of cVOCs along the centerline flow path at the Ashumete Valley site at Joint Base Cape Cod before remediation. See caveat in next slide.



Site #4

Plume from the Old Camden Road Landfill at the Naval Air Station, Kings Bay, Georgia.

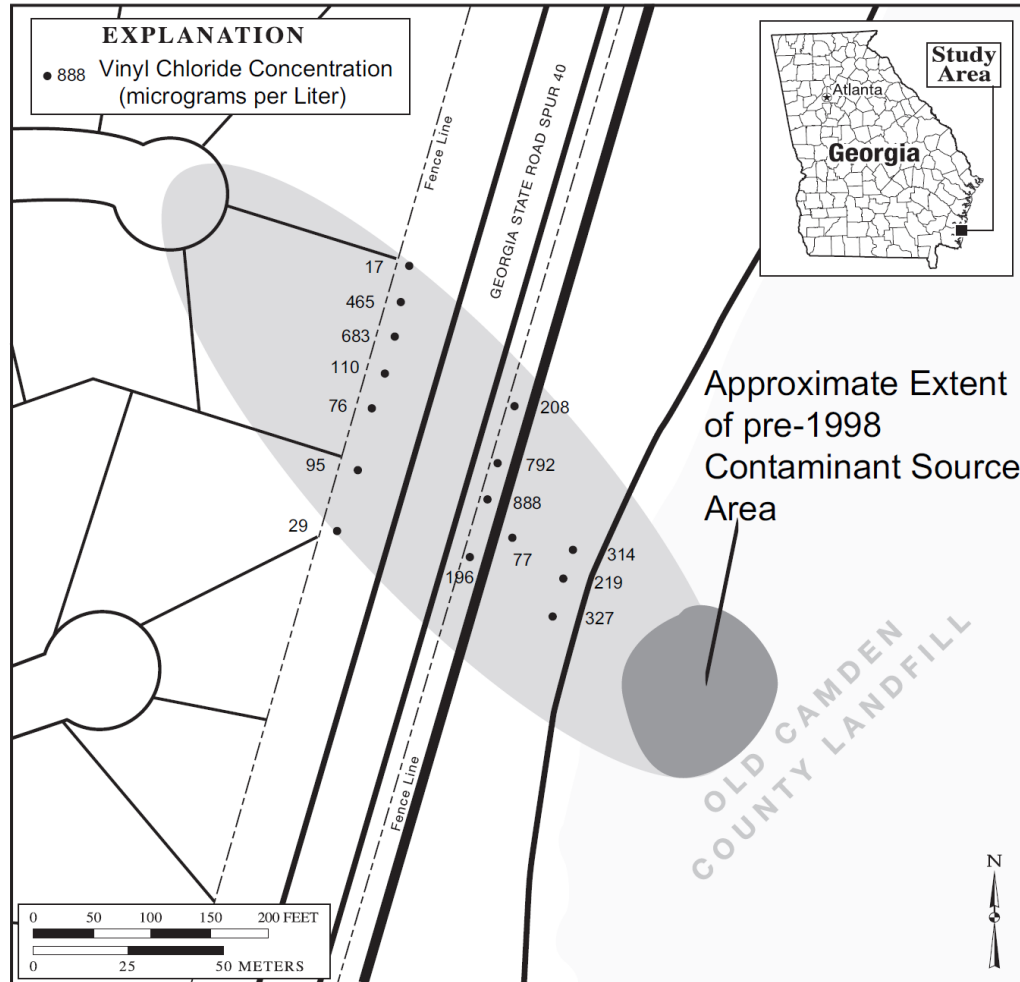


Figure 2. Concentrations of VC in ground water, August 1998.

Figure 4. Francis H. Chapelle, Paul M. Bradley and Clifton Casey (1998) Behavior of a Chlorinated Ethene Plume following Source-Area Treatment with Fenton's Reagent, Ground Water Monitoring & Remediation 25, no. 2/ Spring 2005: pages 131-141.

Site #4

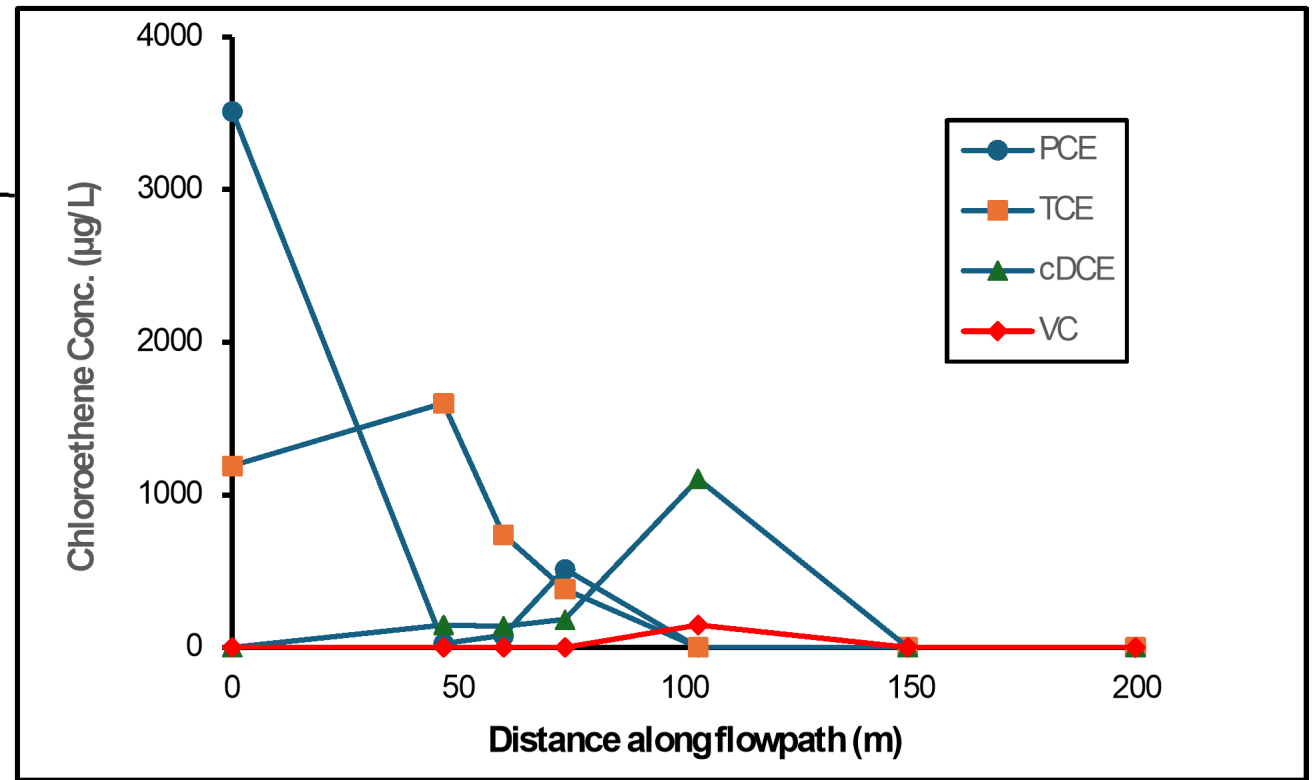
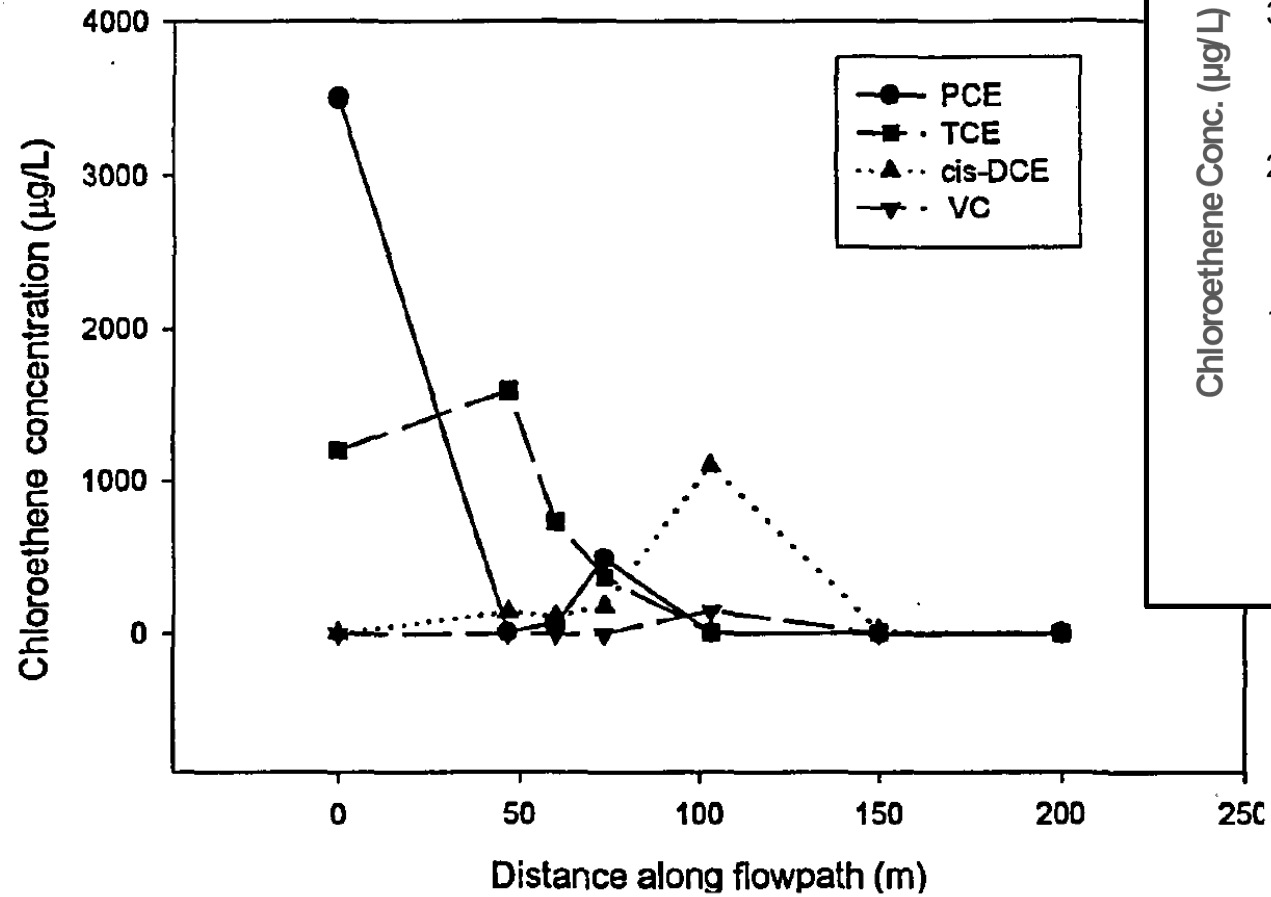
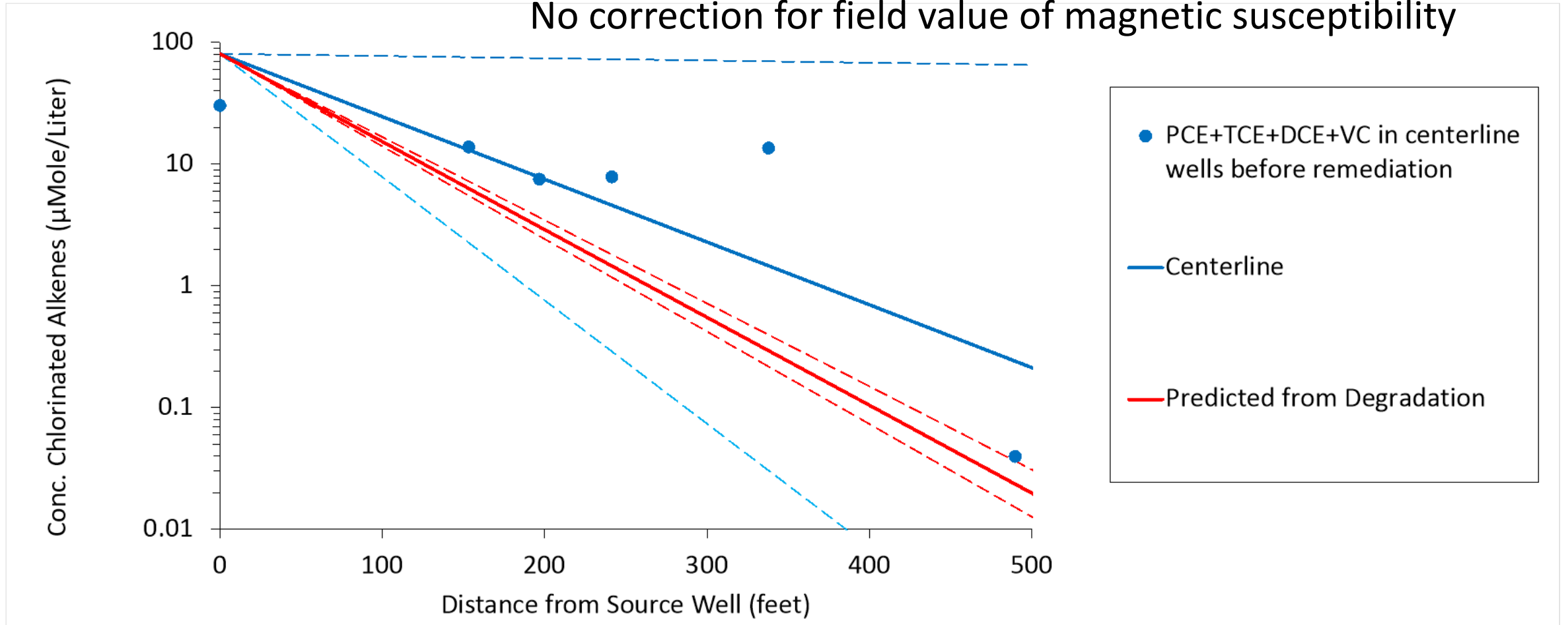


Figure 4. Francis H. Chapelle & Paul M. Bradley (1998) Selecting remediation goals by assessing the natural attenuation capacity of groundwater systems, *Bioremediation Journal*, 2:3-4, 227-238, DOI: 10.1080/10889869809380381.

Site #4

Rate constant when oxygen is absent

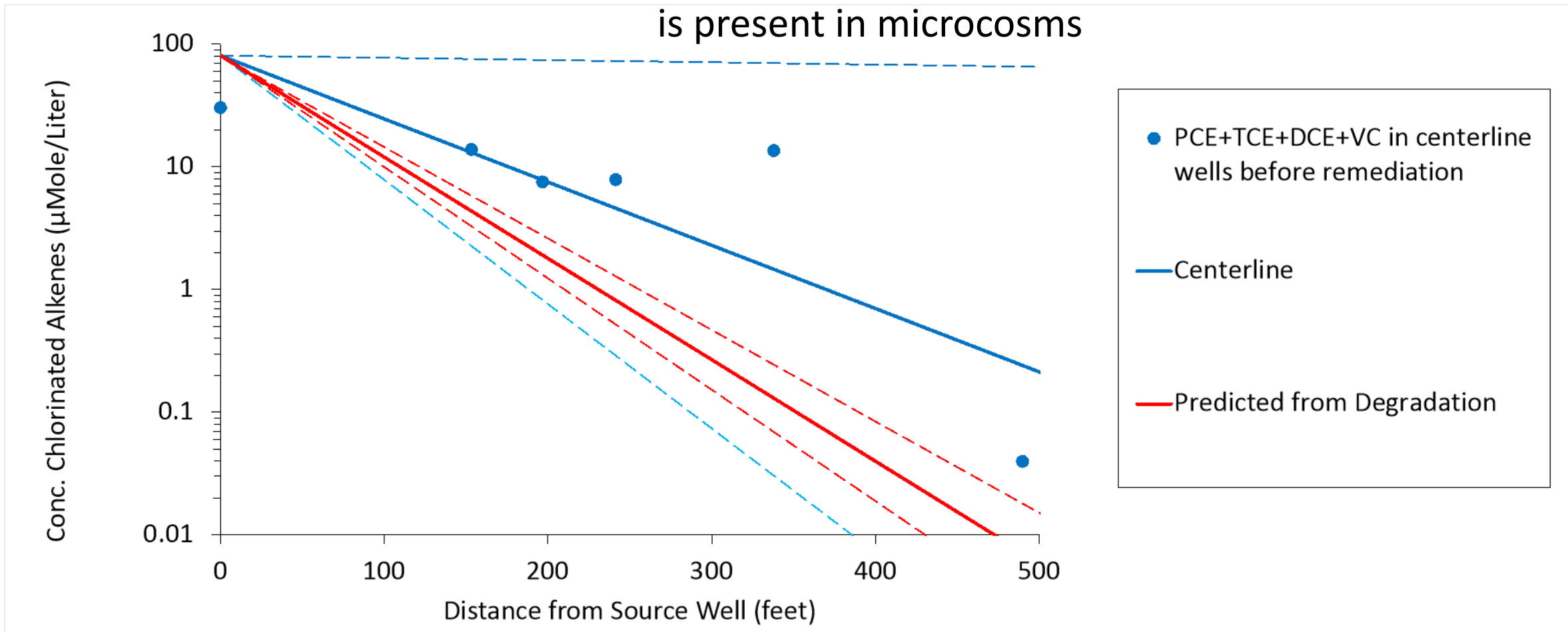
No correction for field value of magnetic susceptibility



Degradation of TCE in the anoxic microcosms can account for the attenuation of cVOCs along the centerline flow path at the Kings Bay site before remediation.

Site #4

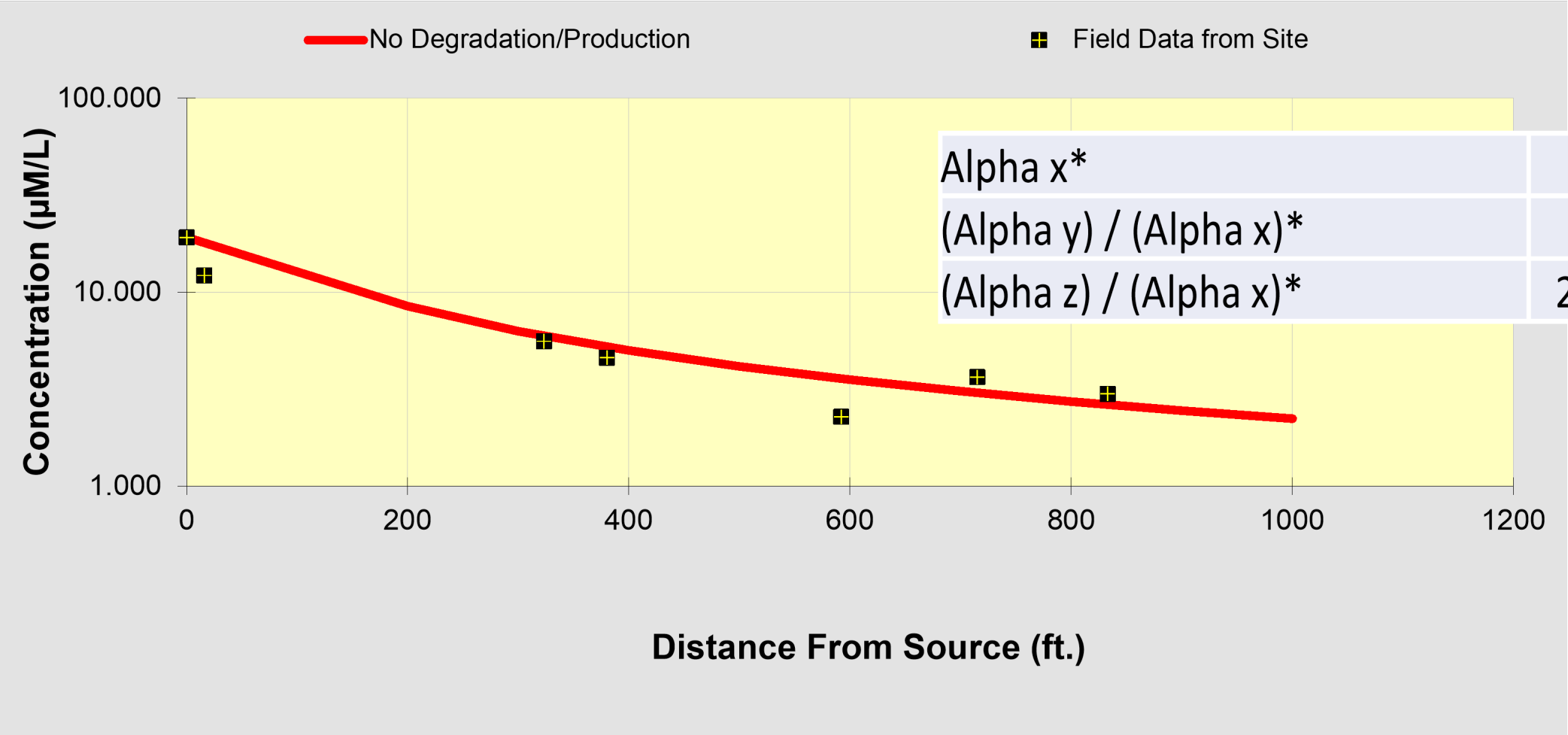
Rate constant when oxygen
is present in microcosms



Degradation of TCE in the anoxic microcosms can also account for the attenuation of cVOCs along the centerline flow path at the Kings Bay site before remediation.

How much longitudinal dispersion would be necessary to account for the extent of attenuation along the centerline in these wells?

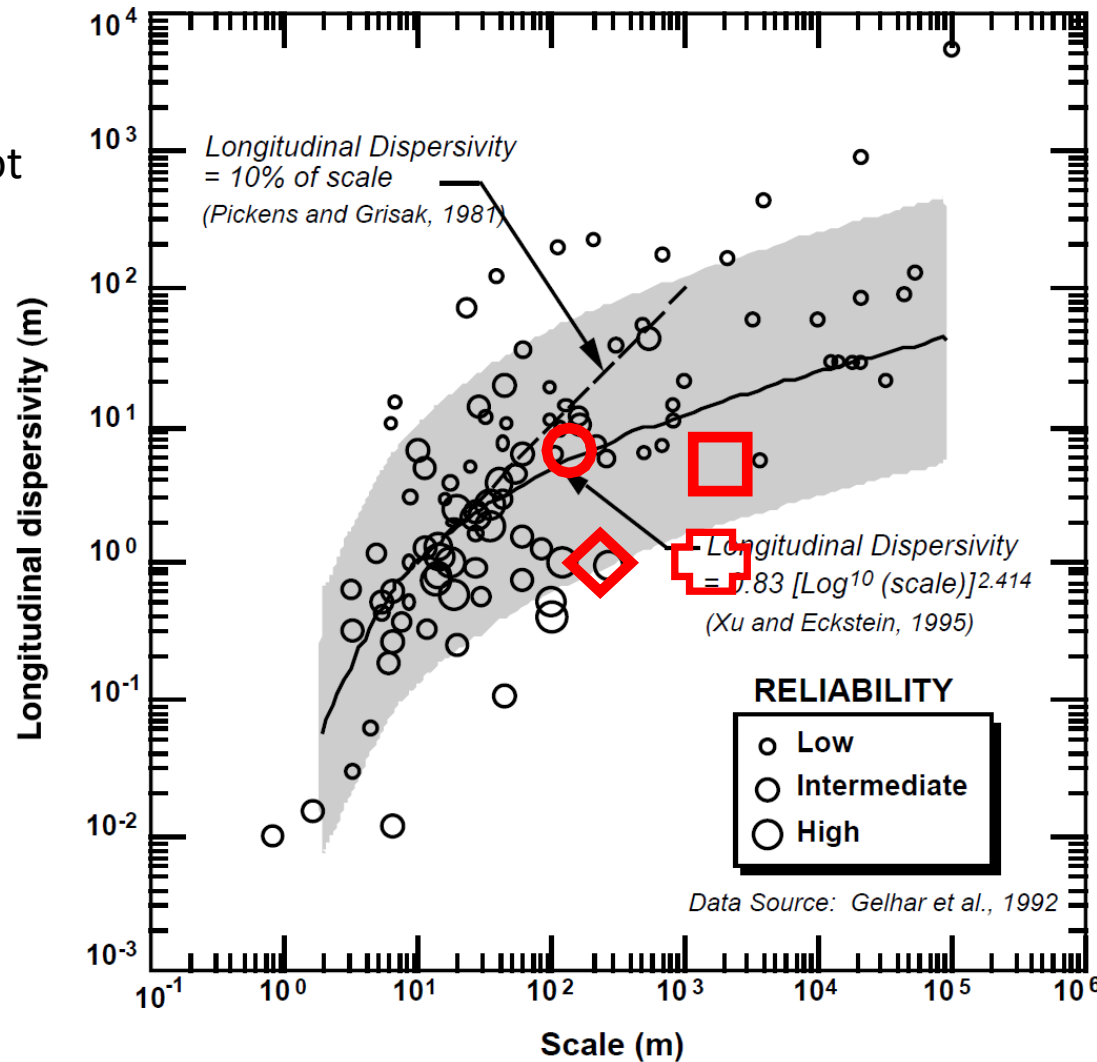
The computer application ***Bioscreen*** was calibrated to the centerline data, assuming no degradation. The common retardation factor was 2.5. Time in the simulation was extended until the calibration came to a steady state.



Alpha x*	3	(ft)
(Alpha y) / (Alpha x)*	0.3	(-)
(Alpha z) / (Alpha x)*	2.E-01	(-)

Example calibration for TCAAP Site A

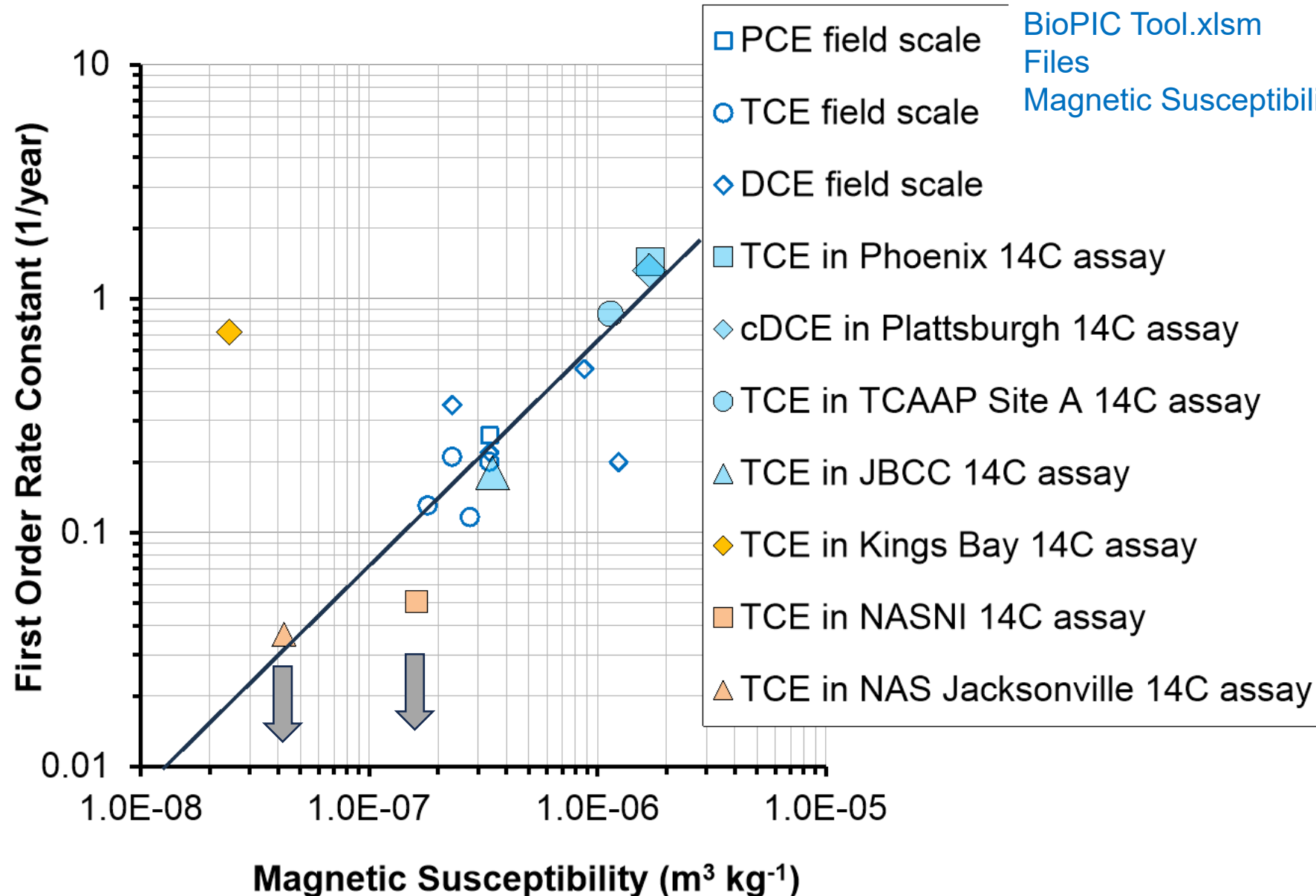
- ⊕ JBCC from hotspot
- Kings Bay
- Plattsburgh
- ◇ TCAAP Site A



The grey shape bounds plausible values for dispersivity provided by the User's Guide for **Bioscreen**.

Have we been using dispersivity to model plumes controlled by degradation?

Figure A.3. Longitudinal dispersivity vs. scale data reported by Gelhar et al. (1992). Data includes Gelhar's reanalysis of several dispersivity studies. Size of circle represents general reliability of dispersivity estimates. Location of 10% of scale linear relation plotted as dashed line (Pickens and Grisak, 1981). Xu and Eckstein's regression shown as solid line. Shaded area defines ± 1 order of magnitude from the Xu and Eckstein regression line and represents general range of acceptable values for dispersivity estimates.



Degradation by magnetite is a plausible explanation for natural attenuation of chloroethenes at **most** of the sites where the Clemson assay provided a rate constant.