Understanding the Fate of Ground Water Contaminants

Redefining Natural Attenuation

32 years ago

1975:

Jamison, V. W., R. L. Raymond, and J. O. Hudson. Biodegradation of high-octane gasoline in groundwater. Developments in Industrial Microbiology **16**.

1970s

- “Microbiologists reasoned that the concentration of organic nutrients in ground water was too low to support life.”
- “Ground water was considered pure and wholesome because it was protected by the soil mantle.”
- PCB and chlorinated aliphatics (TCE) were not biodegradable.
- Benzene and toluene were not considered biodegradable in the absence of oxygen.

25 years ago

1982:

Suflita et al. ***Dehalogenation: a novel pathway for the anaerobic biodegradation of haloaromatic compounds***. Science 218:1115-1117

1984:

Reinhard, et al. ***Occurrence and distribution of organic chemicals in two landfill leachate plumes***. EST 18:953-961.

20 years ago

1985:

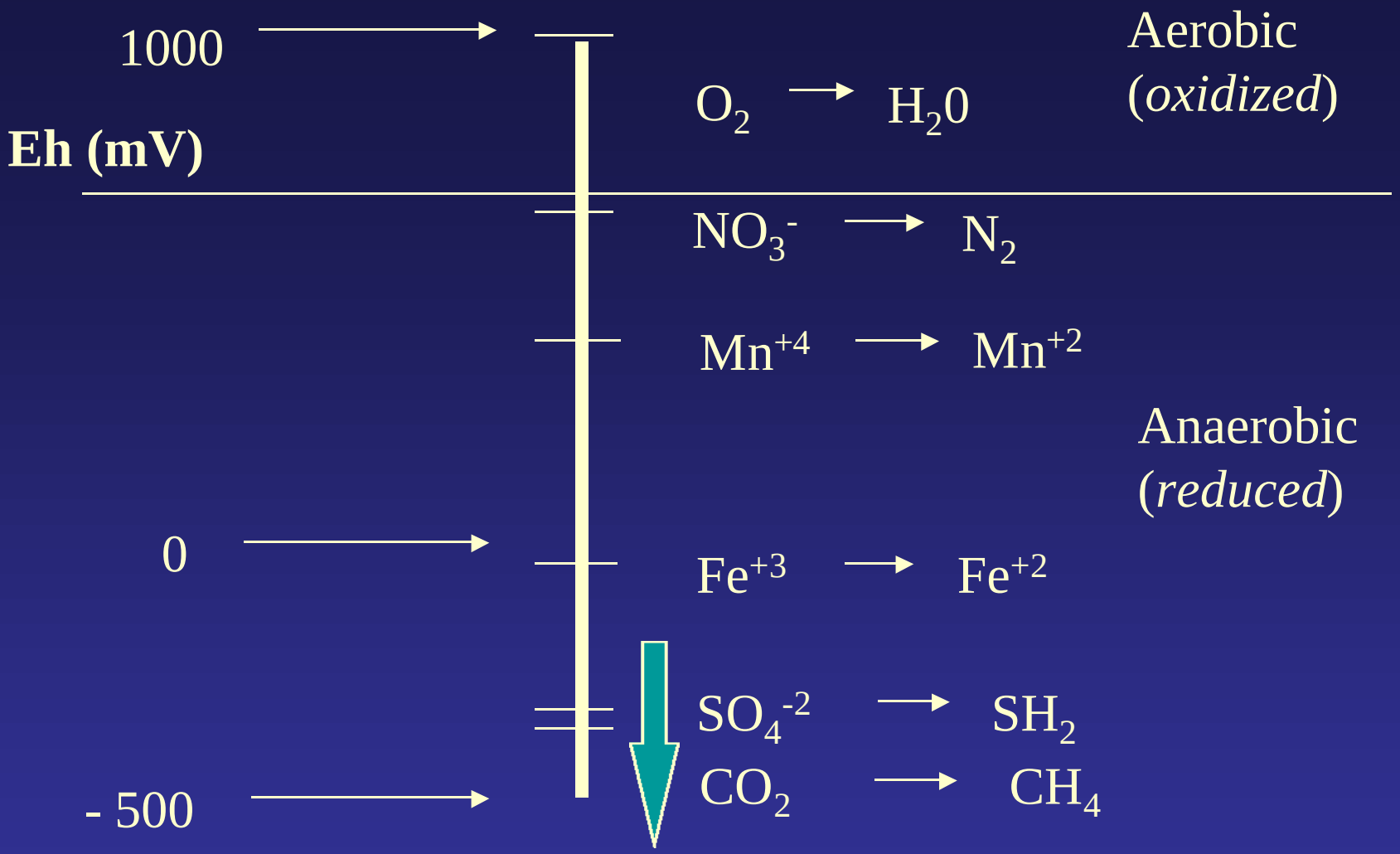
Kleopfer, R. et al. ***Anaerobic degradation of trichloroethylene in soil.*** EST 19:277-280.

1986:

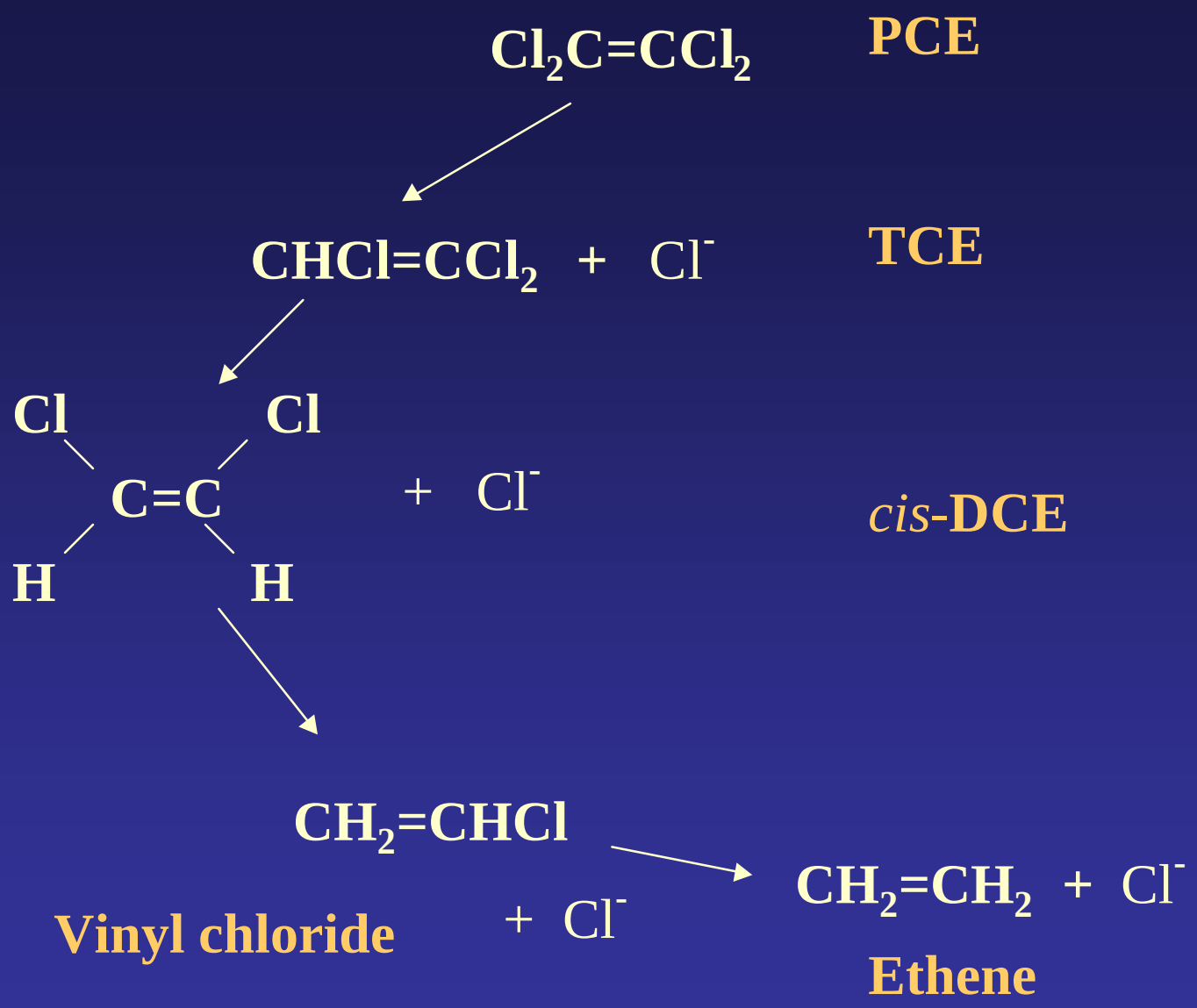
Wilson, B. et al. ***Biotransformation of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: a microcosm study.*** EST 20:997-1002.

1987:

Brown, J. et al. **Polychlorinated biphenyl dechlorination in aquatic sediments**. Science 236:709-712.



1994 (from Bouwer)


$Cl_2C=CCl_2$
PCE
$CHCl=CCl_2$ + Cl^-
TCE
Cl
Cl
C=C
H
H
+ Cl^-
cis-DCE
$CH_2=CHCl$
Vinyl chloride
+ Cl^-
$CH_2=CH_2$ + Cl^-
Ethene

10 years ago

1995:

Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater. Air Force Center for Environmental Excellence

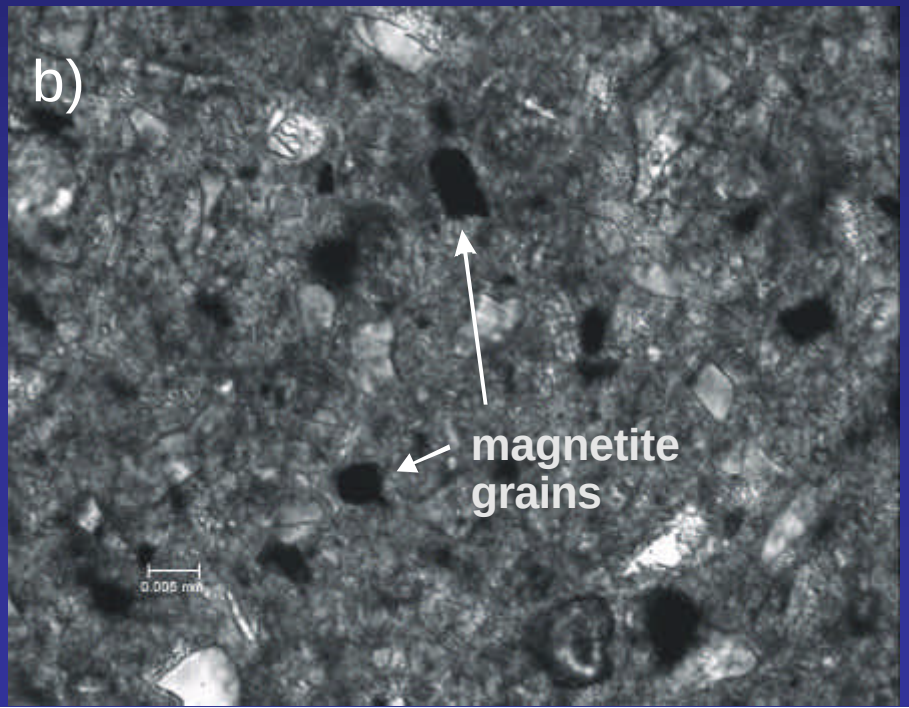
1998:

Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. U.S. EPA

2002:

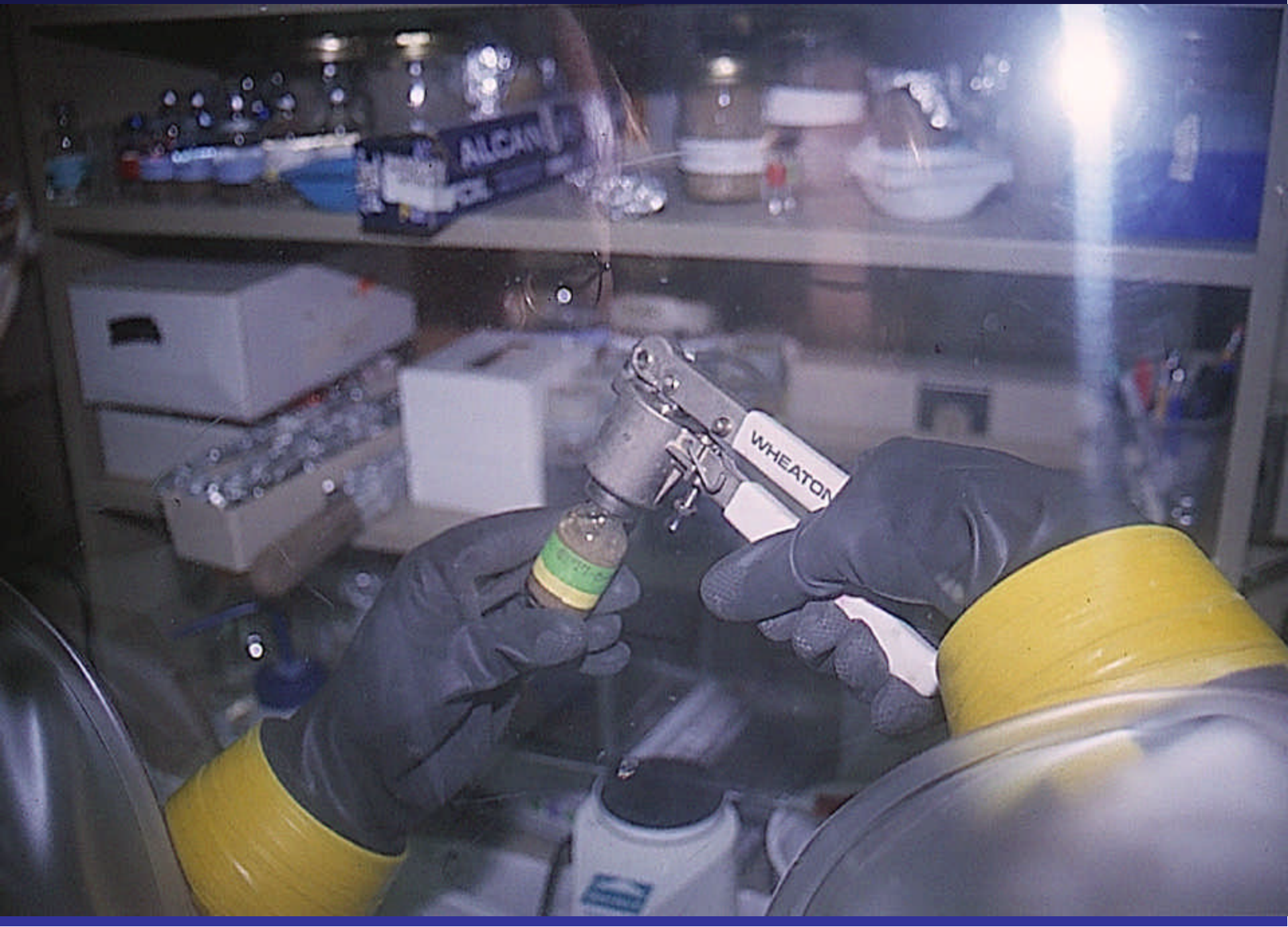
Lee, W., and B. Batchelor. Abiotic reductive dechlorination of chlorinated ethylenes by iron-bearing soil minerals. 1. Pyrite and magnetite. EST **36:**5147-5154.

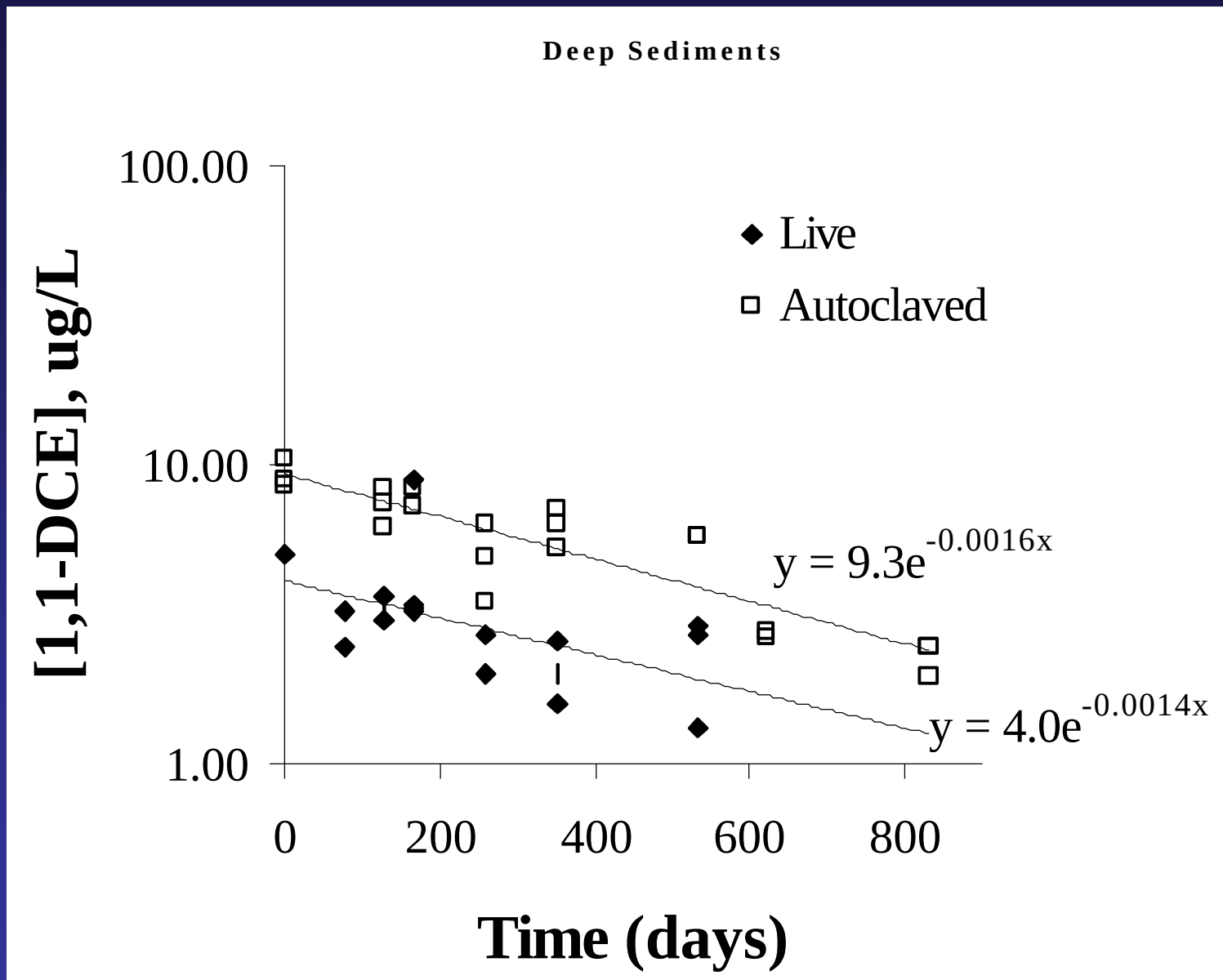

a)
0.05 mm

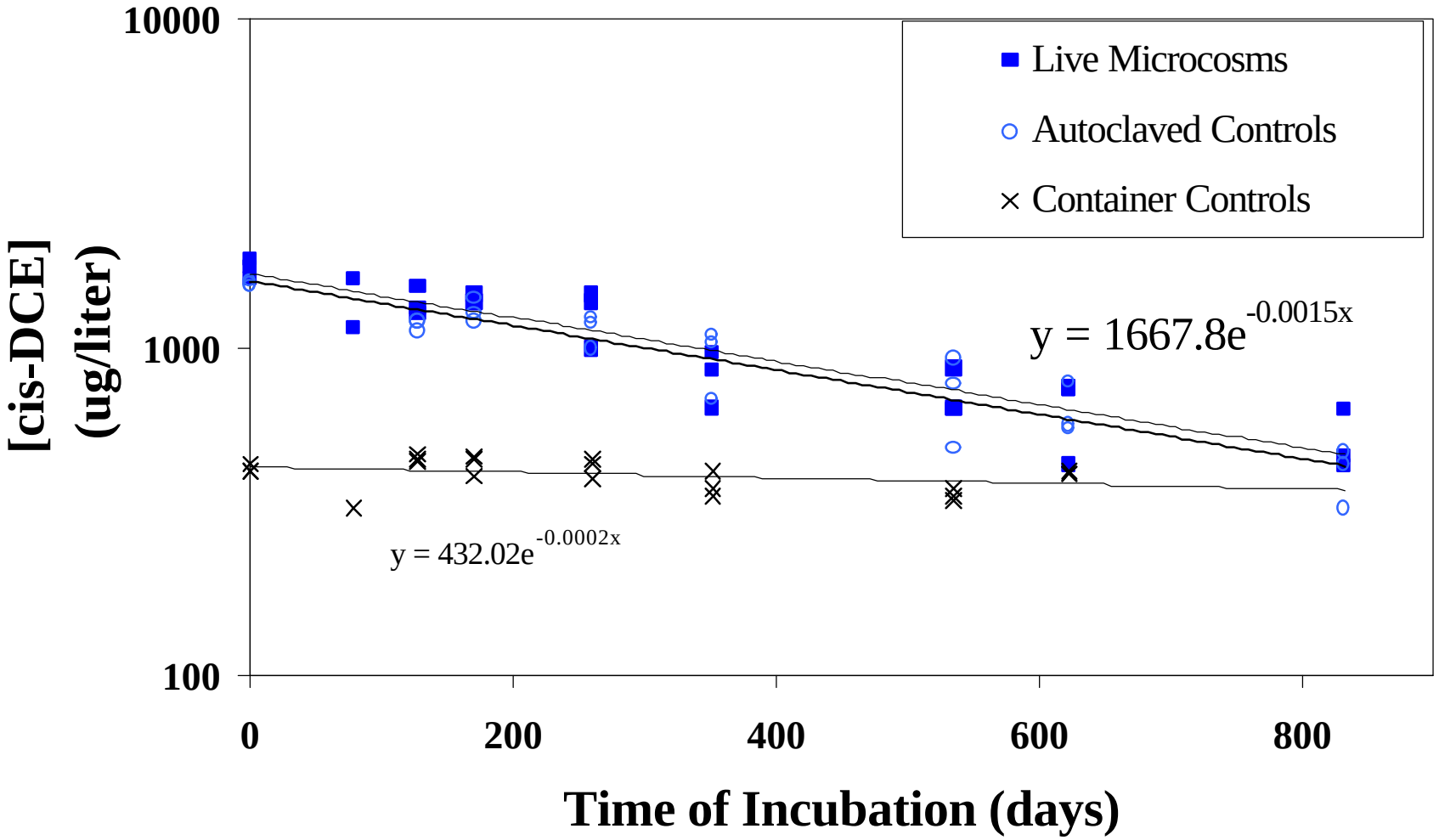

b)
magnetite
grains
0.005 mm

Iron content in TCAAP sediments

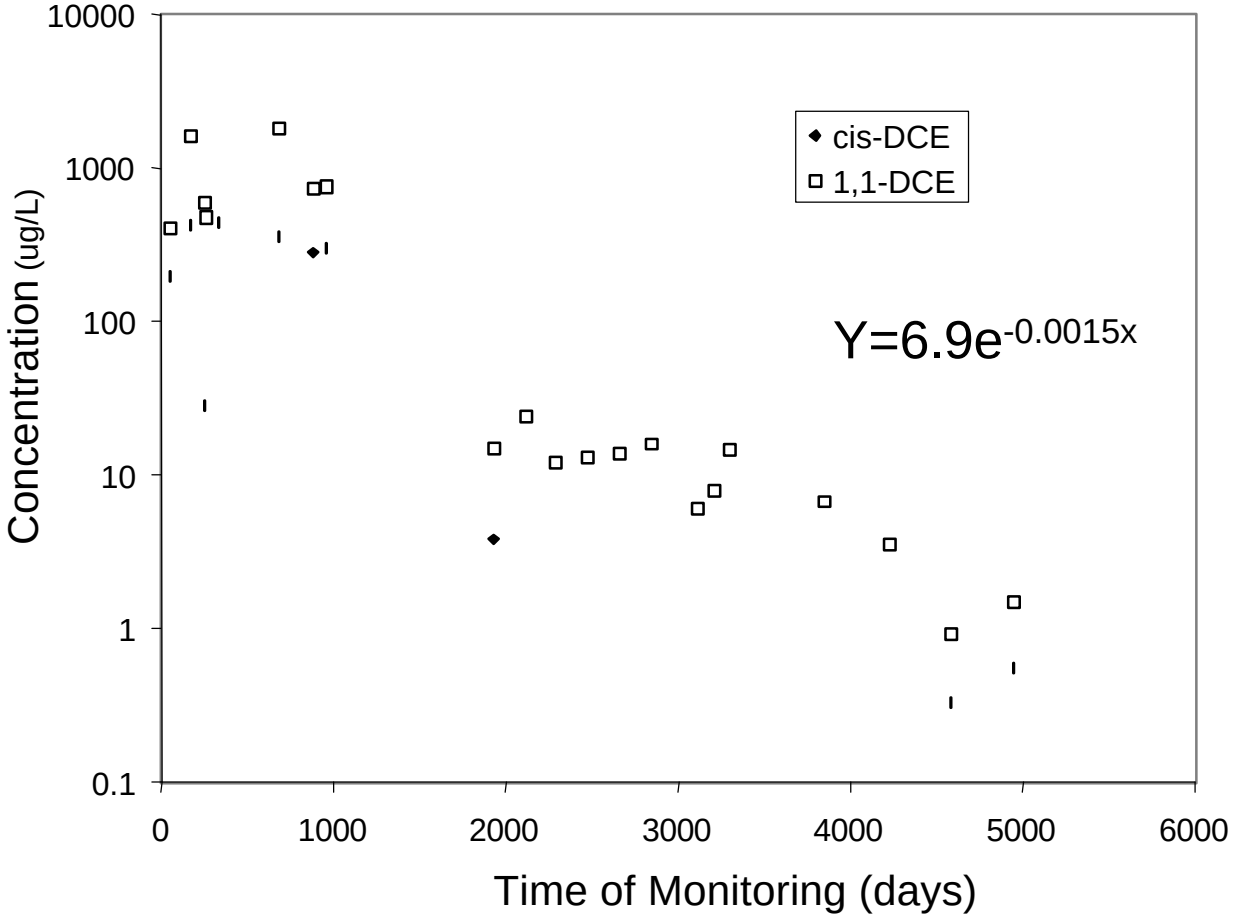
Depth Below Water Table (Approx ft)	Total (XRF)	Total (Nitric Acid)	Bioavailable
0-5	7,820 ± 110	6,515	556 ± 15
10	12,450 ± 1820	10, 251	649 ± 109
15-20	11,190 ± 1250	9,164	567 ± 112


WHEATON


Deep Sediments
100.00
10.00
1.00
[1,1-DCE], ug/L
Live
Autoclaved
y = 9.3e-0.0016x
y = 4.0e-0.0014x
0
200
400
600
800
Time (days)


10000
1000
100
[cis-DCE] (ug/liter)
0
200
400
600
800
Time of Incubation (days)
Live Microcosms
Autoclaved Controls
Container Controls
y = 1667.8e-0.0015x
y = 432.02e-0.0002x

Monitoring well near contaminant source at TCAAP



Cis-DCE rates of removal (per year)

Location	Living	Autoclaved Control
Shallow, reduced	0.55	0.57
Intermediate, Reduced	2.30	2.28
Deep, Oxidized	0.43	0.31

- TCAAP sediments are 0.3 wt% magnetite.
- Magnetite accounts for 25% of total iron in the sediments.
- There is ample magnetite in the sediments to reduce all of the DCE added to the microcosms.

TCAAP Site 102

Site 102 ground water chemistry

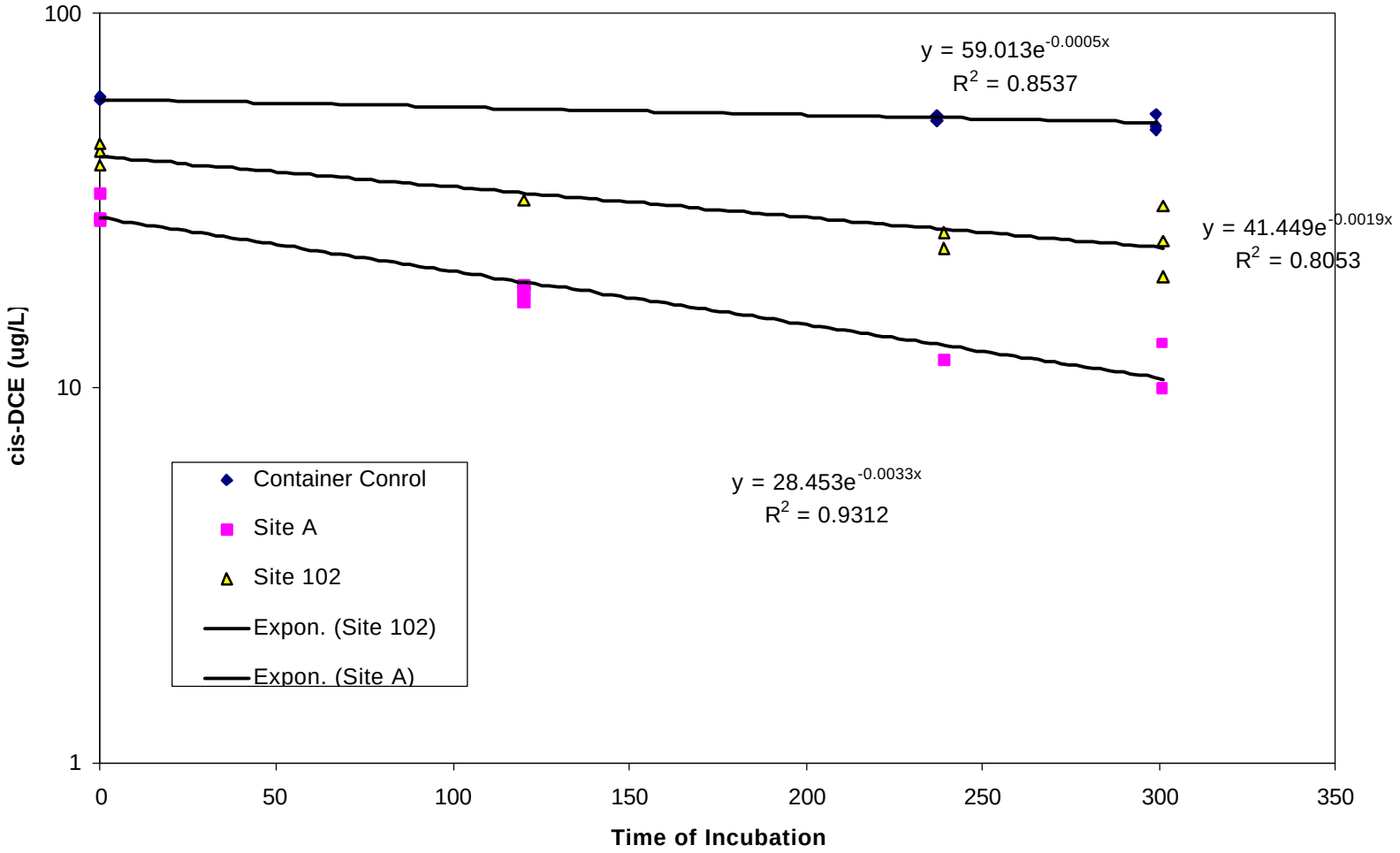
	DO	NO_3^-	Mn^{+2}	Fe^{+2}	SH_2	CH_4	Ethene
01U579	1.6	4.	0.7	ND	ND	0.01	ND
01U580	2.6	4.	.02	ND	ND	ND	ND
01U581	0.7	ND	> 0.7	ND	ND	0.06	ND
01U582	4.6	ND	ND	ND	ND	ND	ND

(Concentrations in ppm)

Site A and Site 102 Microcosms

- Ground water sediment was air dried.
- Microcosms were prepared under aerobic conditions.
- Microcosms were heat-killed.
- The microcosms were sealed and incubated for 300 days on the lab bench and sampled quarterly.

cis-DCE


100
10
1
cis-DCE (ug/L)
0
50
100
150
200
250
300
350
Time of Incubation
y = 59.013e-0.0005x
R2 = 0.8537
y = 41.449e-0.0019x
R2 = 0.8053
y = 28.453e-0.0033x
R2 = 0.9312
Container Conrol
Site A
Site 102
Expon. (Site 102)
Expon. (Site A)

Site 102
Lab and Field Attenuation rates

- TCE
  - Microcosms: 1.1 yr^{-1}
  - Field data: 8.7 yr^{-1}
- DCE
  - Microcosms: 0.7 yr^{-1}
  - Field data: 9.8 yr^{-1}

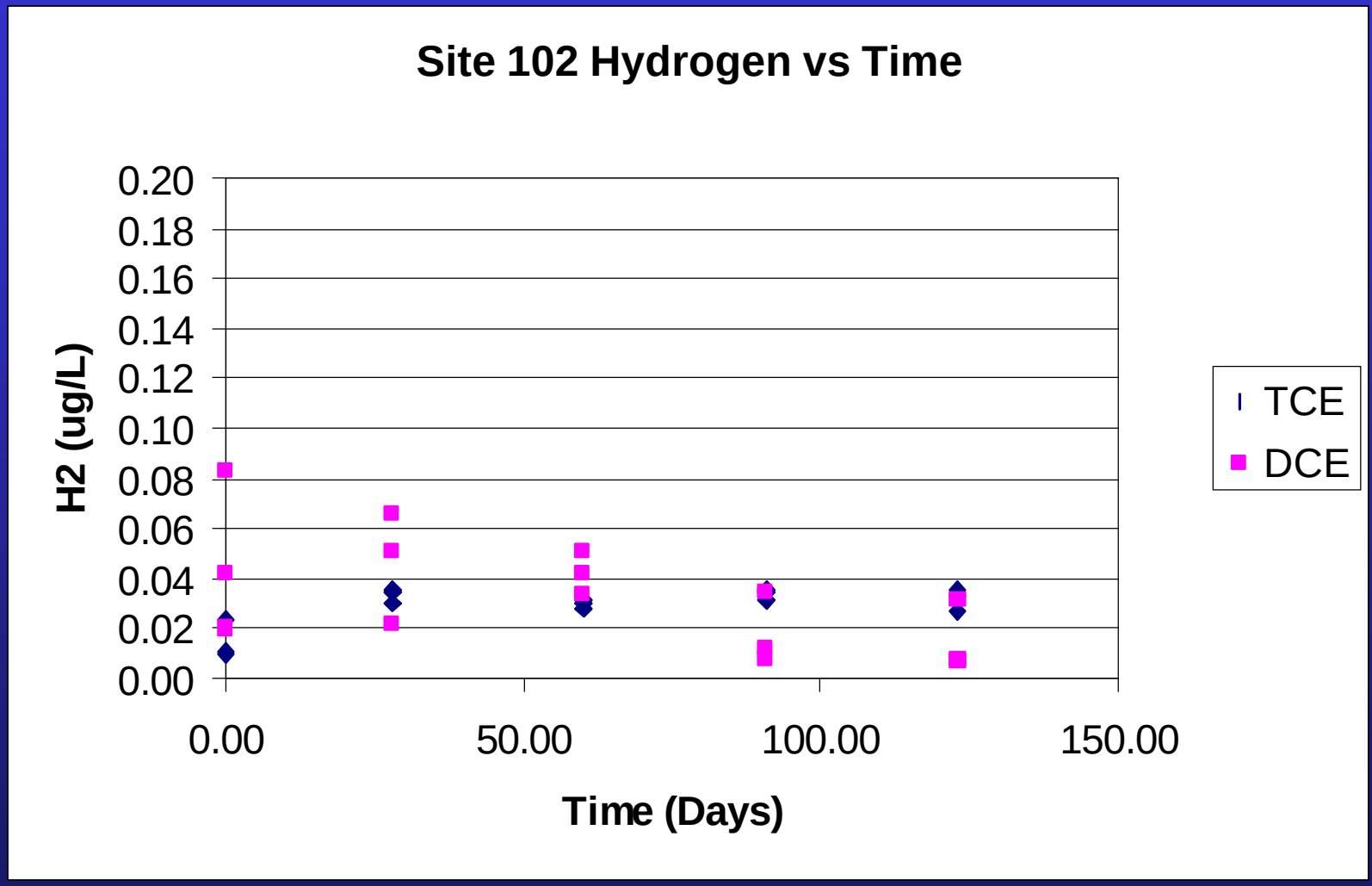
- Non-biological mechanisms may be more important than biological reductive dehalogenation for chlorinated solvents.

- Natural attenuation studies should consider the possibility of abiotic degradation processes for chlorinated solvents.

- Abiotic degradation products of chlorinated ethenes are not present.
- Screening for abiotic degradation of chlorinated ethenes is not yet possible.
- Demonstrating abiotic degradation in ground water:
  - Contaminant fate and transport modeling
  - Microcosms

Future work

- What is the mechanism of non-biological degradation of chlorinated aliphatic compounds (*What is happening*)?
- Are there inexpensive field indicators of abiotic degradation processes in ground water (*Is it happening*)?
- How prevalent is abiotic degradation of chlorinated aliphatic compounds in ground water (*How much is it happening*)?
- Other chlorinated contaminants?


Site 102 Hydrogen vs Time
H2 (ug/L)
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.00
50.00
100.00
150.00
Time (Days)
TCE
DCE