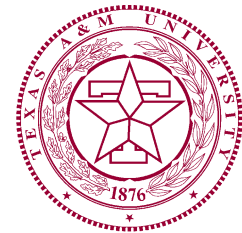# Reductive Dechlorination in Reactive CDFs

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Acknowledgements

◈ Texas Advanced Technology Program

◈ Mr. Sukil Son

Overview

◆ Reactive Containment/DSS

◆ Reductive Dechlorination

- Abiotic

- Biotic/abiotic

◆ Summary

Degradative Solidification/Stabilization

◈ Contain Metals and Organics
- Physical transport reduction
- Chemical immobilization

◈ Degrade Organics
- Oxidation
- Reductive dechlorination

Time for Degradation

◆ Transport

- Seepage (PCB half-times - 10^2-10^4 years)

  (WES, EEDP-02-19, 1996)

- Diffusion
- Volatilization

Leaching-Reaction Model

- First-order degradation
- Linear partitioning
- Fickian Diffusion
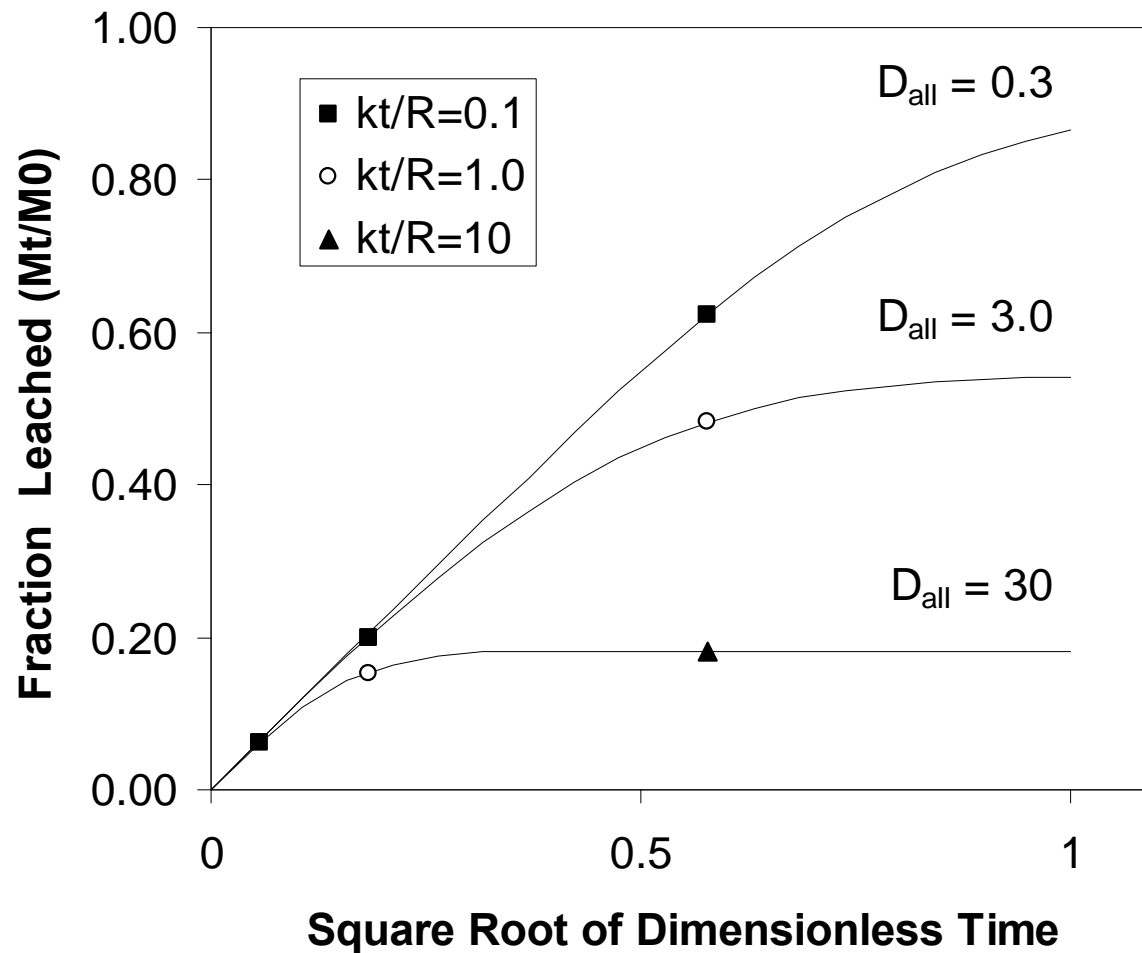
Leaching/Degradation

◆ First Damköhler ($D_{a,I}=kt/R$)
(for seepage, $D_{a,I}=k\theta/R = kL/Rv$)

◆ Second Damköhler ($D_{a,II}=kL^2/D_e$)

◆ Dimensionless time ($\bar{t}=D_e t/RL^2$)
  - $D_{a,I} = \bar{t} * D_{a,II}$

Leaching/Degradation

Leach Model Summary

- Ultimate Fraction leached
  - $=(D_{a,II})^{-0.5} = (D_e/kL^2)$, if $D_{a,II} > 1$
  - R has no effect
  - L is important

- If 90% ultimately degraded, $D_e = 5 \times 10^{-10}$ m^2/s, L=10 m
  - k = 0.016 yr^{-1} ($t_{1/2}$ = 44 yr = 16,000 days)
  - $k_{app} = k/R$

Required Half-lives

	Required Half-life (days)	
	90%	**99%**
Seepage (10^{-5}-10^{-7} cm/s)	80-8,000	8-800
Diffusion	16,000	160

Reductive Dechlorination

- R-Cl + 2 e$^-$ + H$^+$ = R-H + Cl$^-$
- Abiotic, Biotic, Abiotic/Biotic
- Various reductants
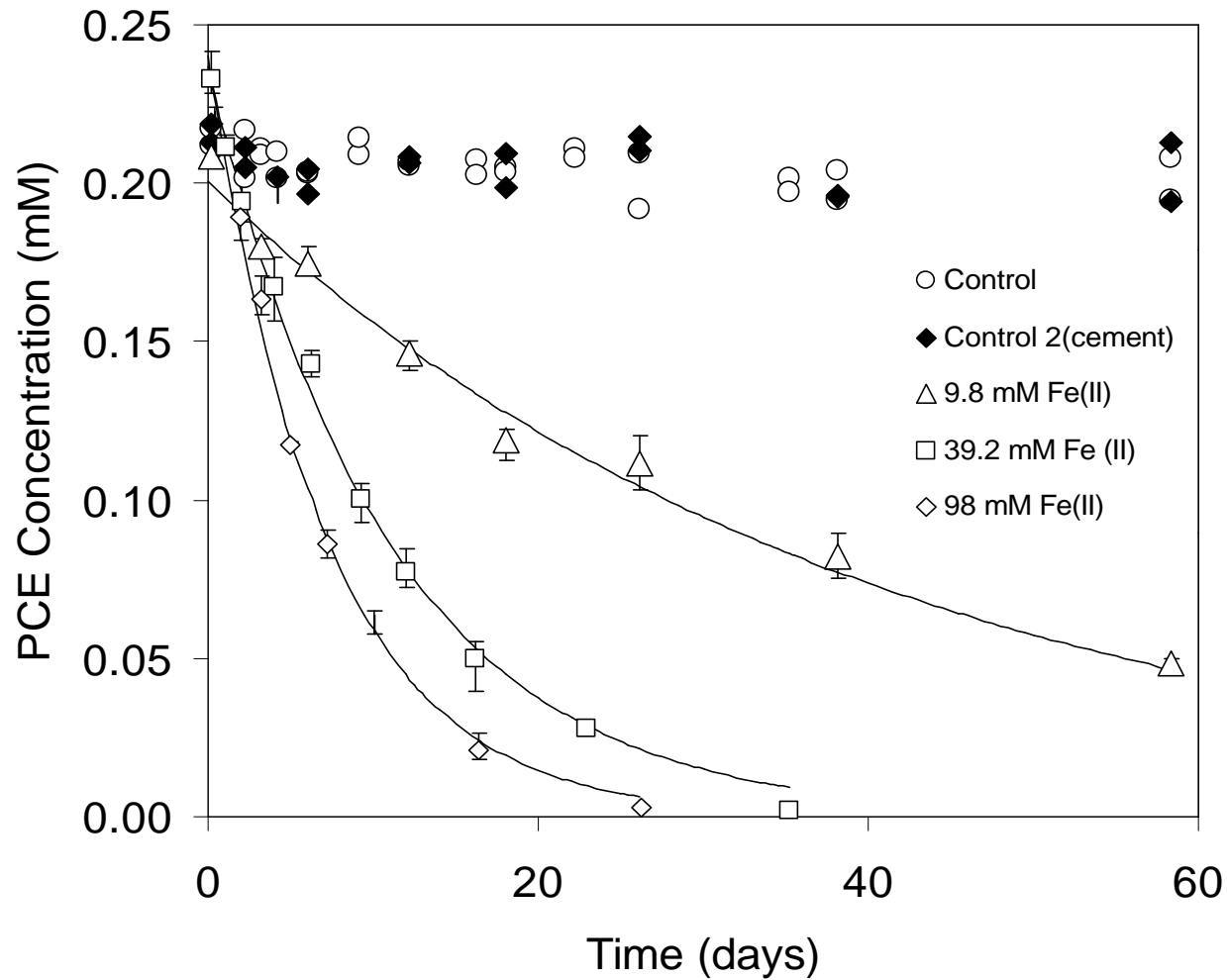
Potential reductants

- Zero-valent metals, bimetals (e.g. Fe, Fe/Pd)
- Fe(II) (solution, sorbed, solids)
- Sulfides, polysulfides
- Hydrogen
- Dithionite

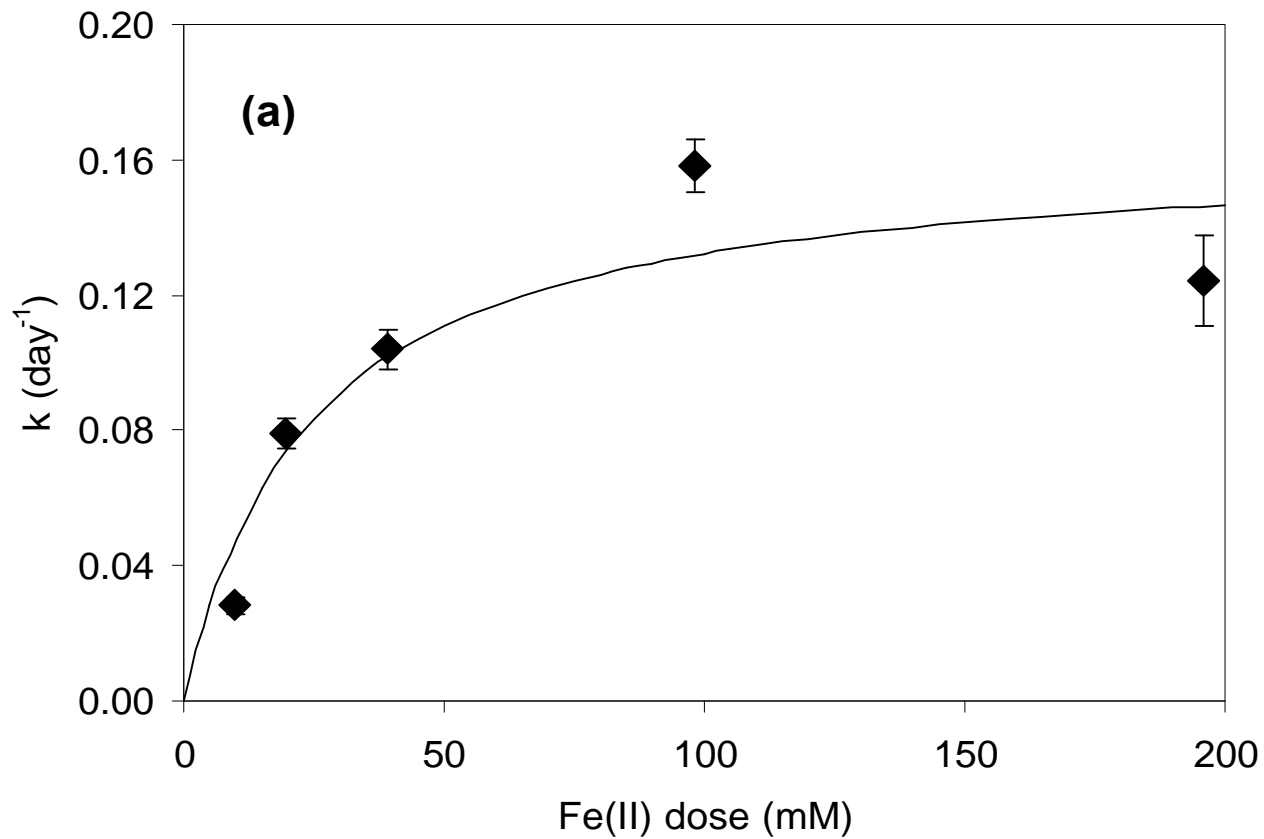# Carrier/bulk reductant

- Vitamin B_{12}/Ti(III), dithiothreitol
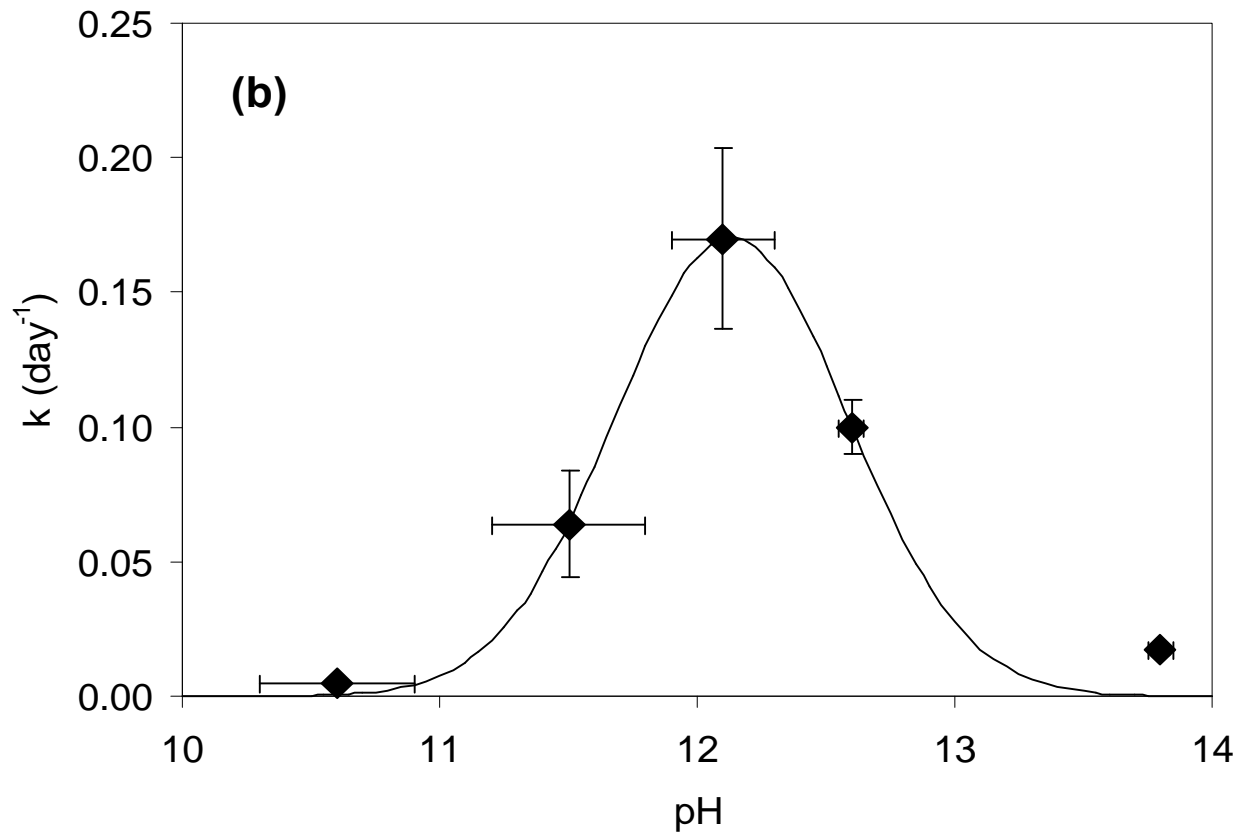- Other biochemicals/organics ?

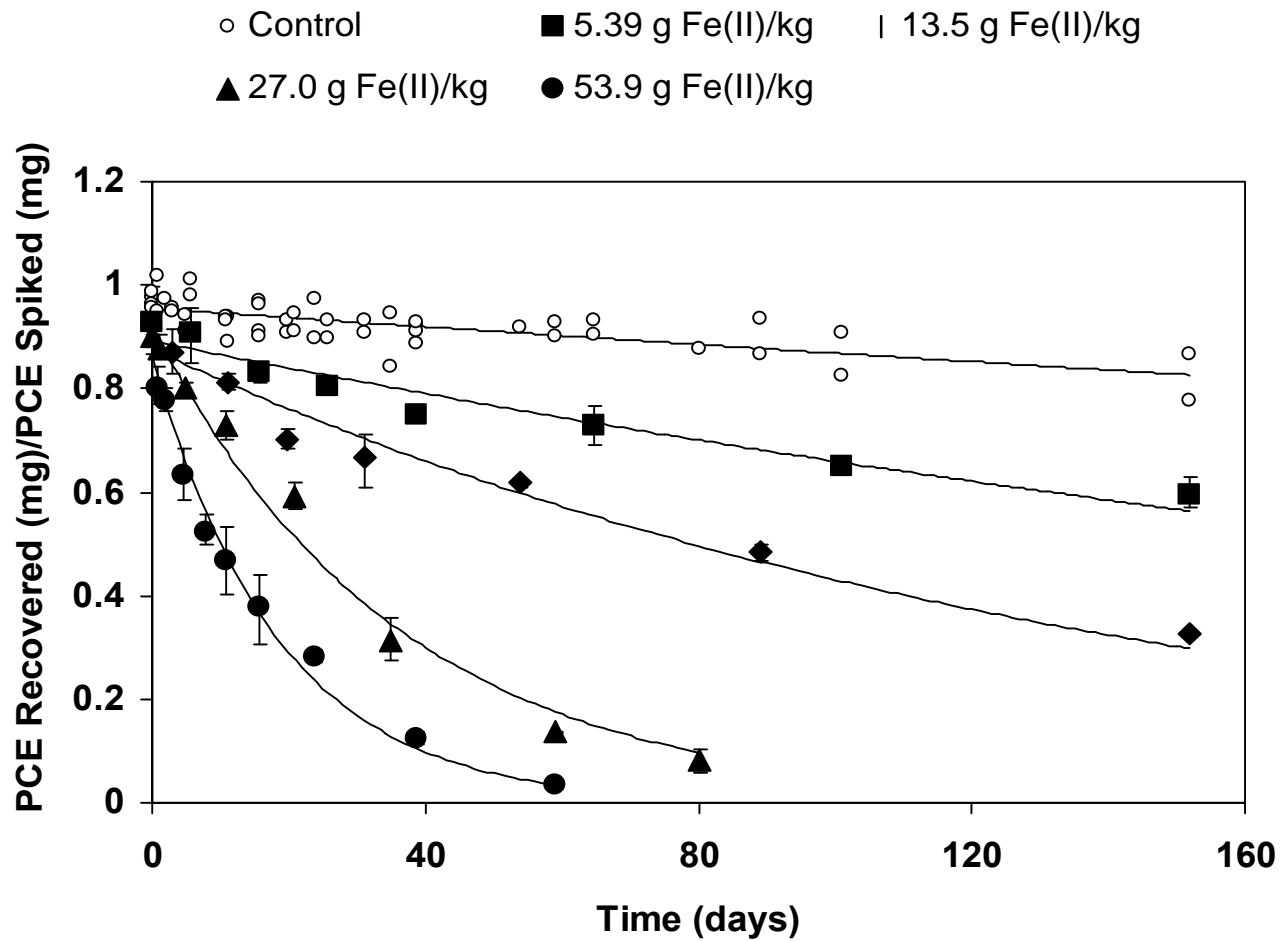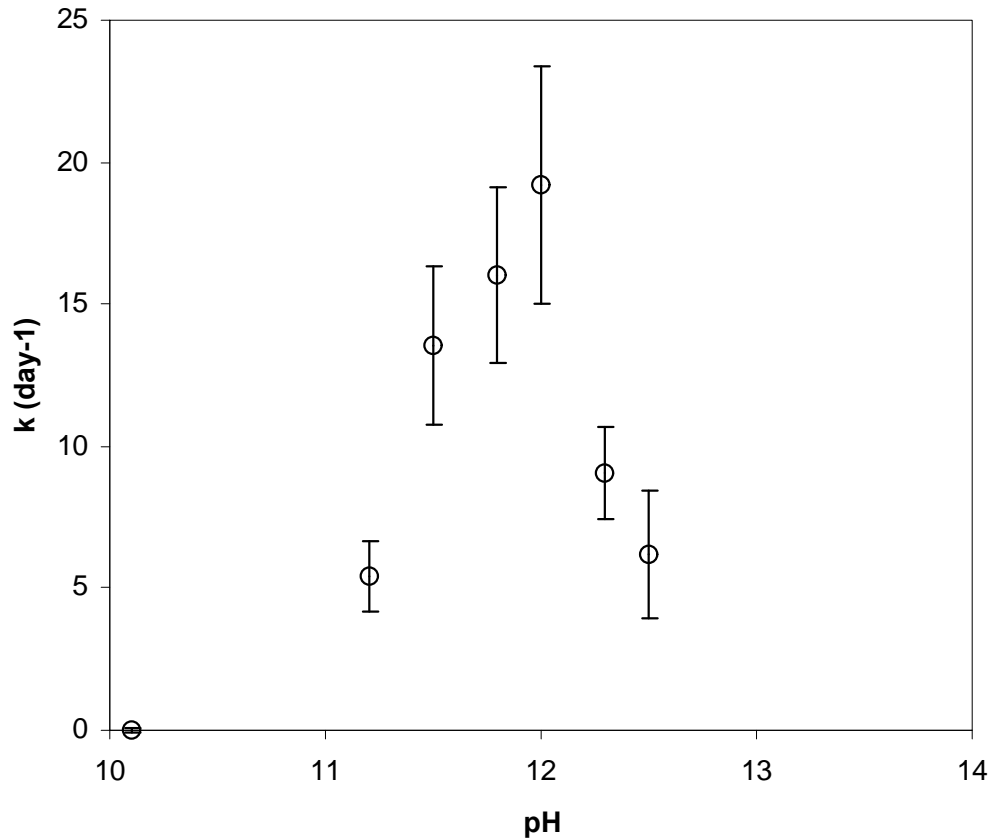# PC-based DSS for PCE

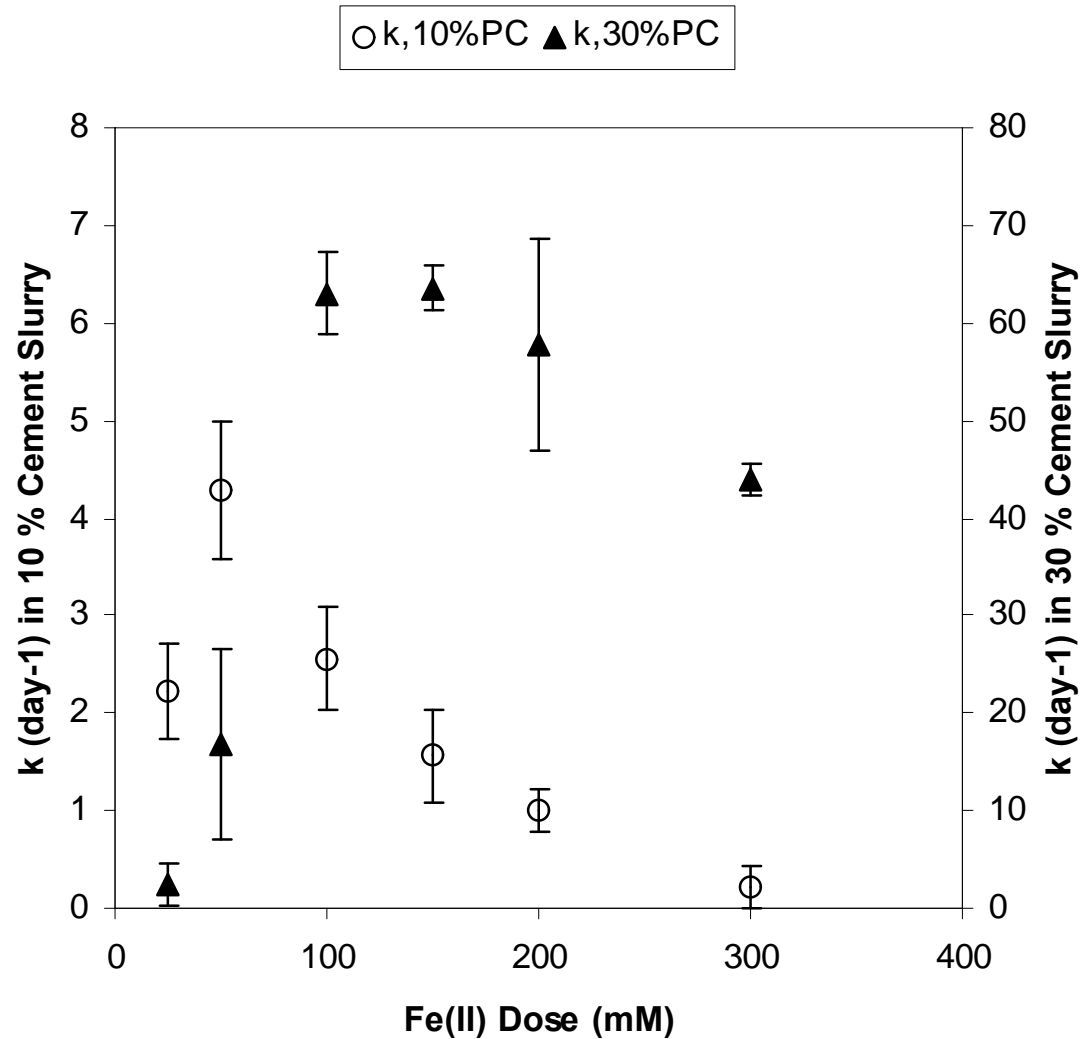# Effect of Fe(II) Dose

Effect of pH

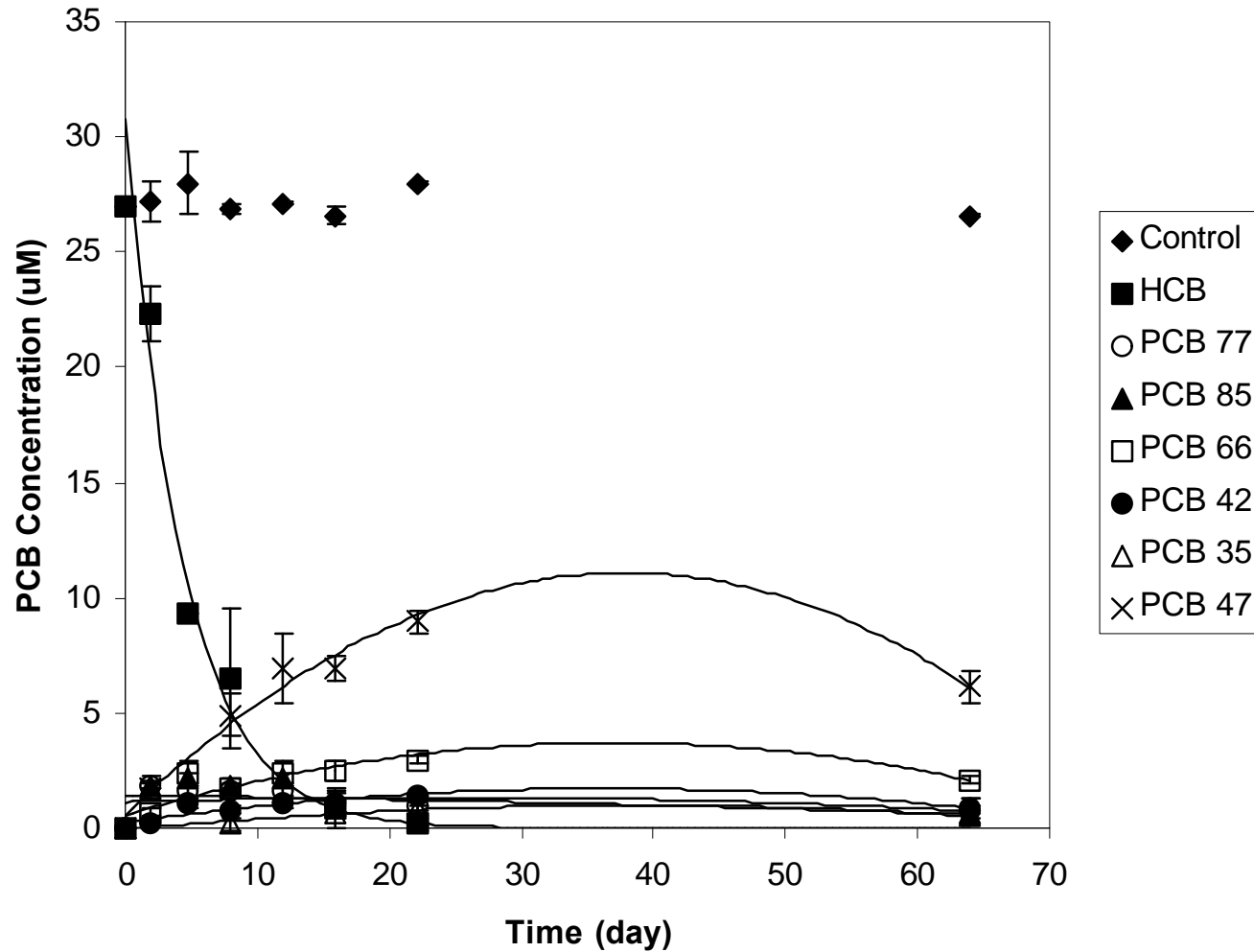# Solid Phase Reaction
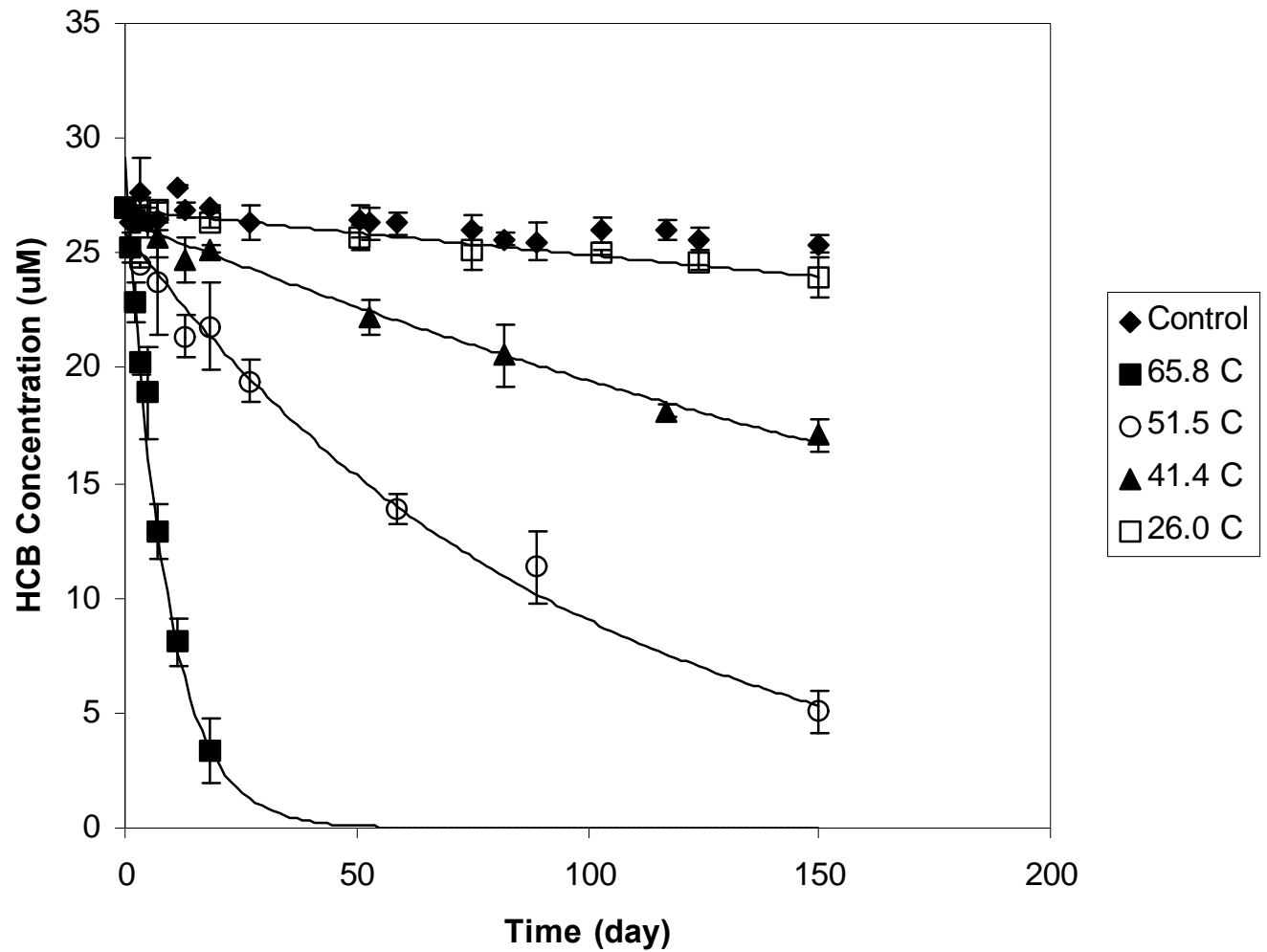
PC-based DSS for HCB (IUPAC No. 128)

◆ Effect of pH

Effect of Fe(II), PC Doses

Products

Effect of Temperature

Apparent Half-lives

◆ Optimum pH, Fe(II), PC
- 1.1 day at 66° C
- 150 day at 26 ° C (calculated)

◆ Affected by R
- 100 in experiments
- 64,000 to 81,000 in sediments
  (WES, EEDP-02-19, 1996)

PC-based DSS - Active Reductant

◆ Fe(II) in solution

◆ Fe(II) sorbed on surfaces

◆ Fe(II) in new compound
  - Green rust (LDH)
  - Substituted calcium chloraluminate (LDH)

Nanoscale Fe, Fe/Pd
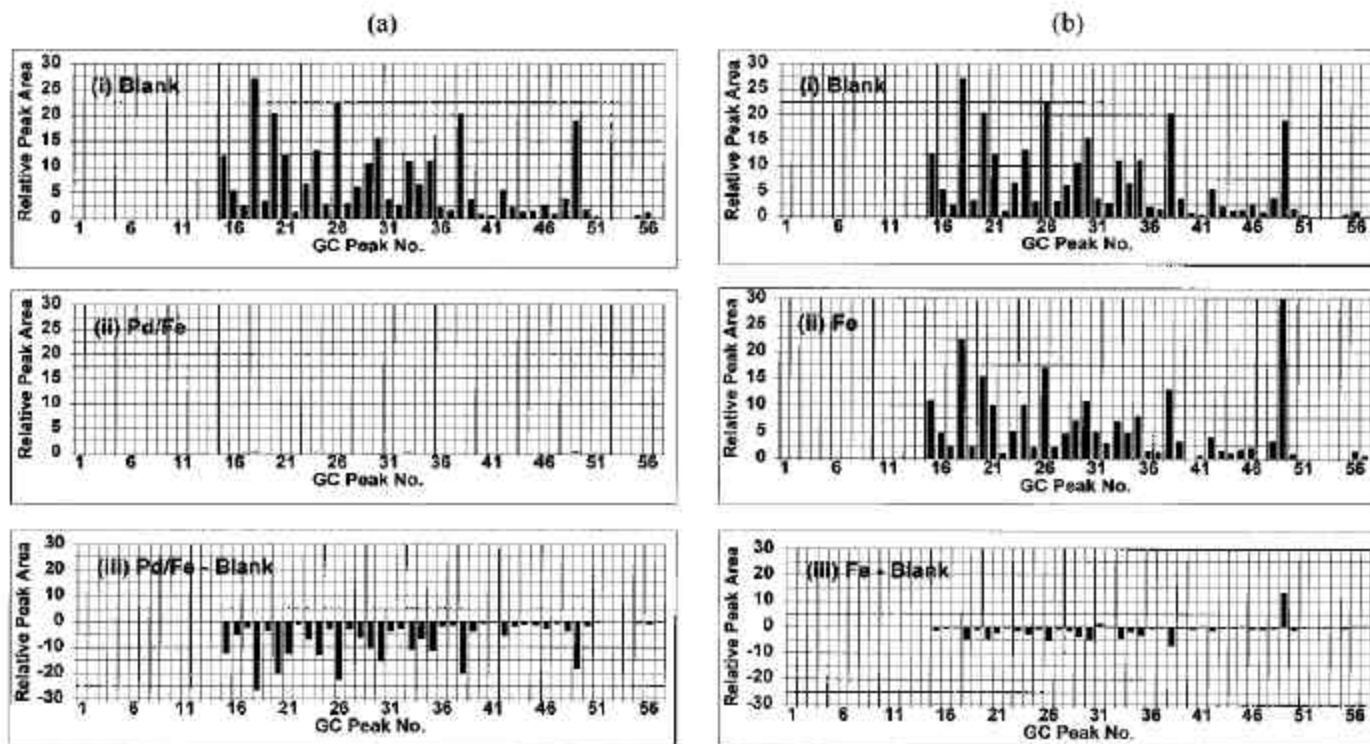
Wang and Zhang, ES&T, 31:2154-2156, 1997.

FIGURE 3. Changes in GC relative peak areas of an Aroclor 1254 solution in 17 h with (a) nanoscale Pd/Fe particles and (b) nanoscale Fe particles. GC peaks in (i) were from blank samples. Peaks in (ii) were from samples containing the nanoscale Fe or Pd/Fe particles. Peaks in (iii) were the difference between (ii) and (i) and represented the net degradation. Initial PCB concentration was 5 mg/L. Metal to solution ratio was 5 g/100 mL.

Vitamin B$_{12}$

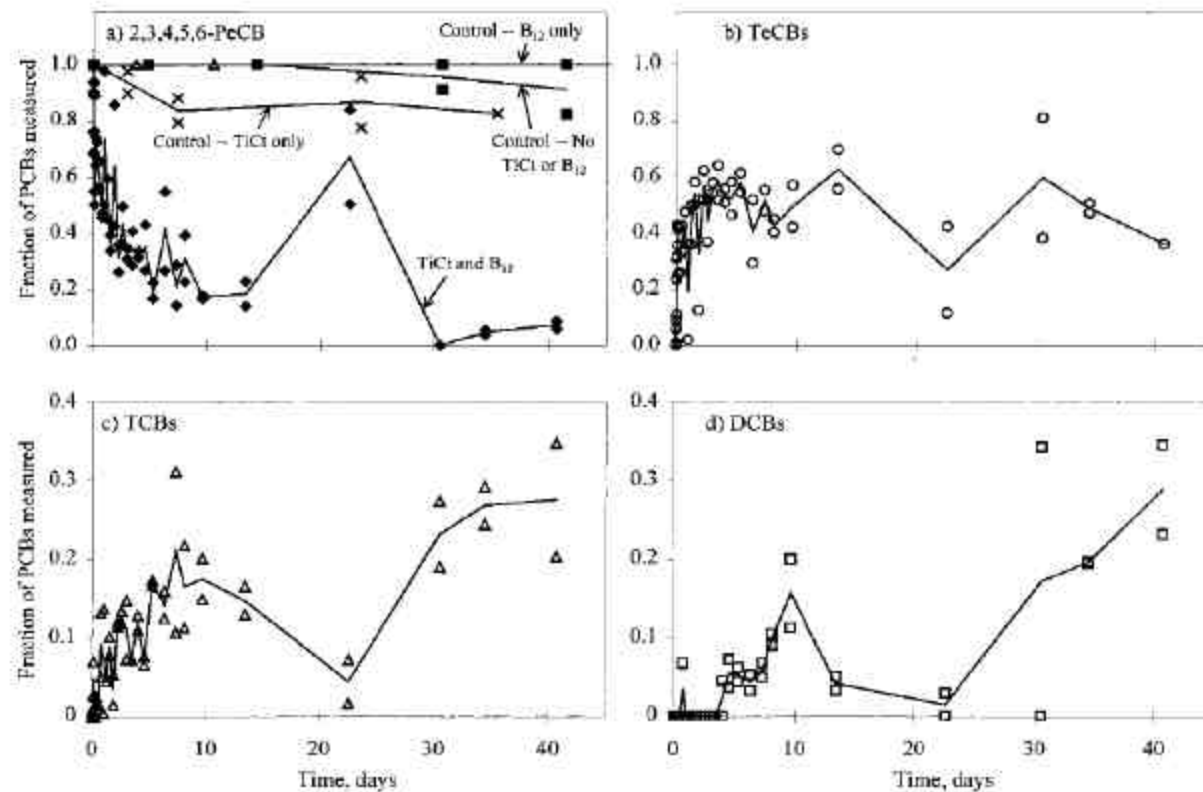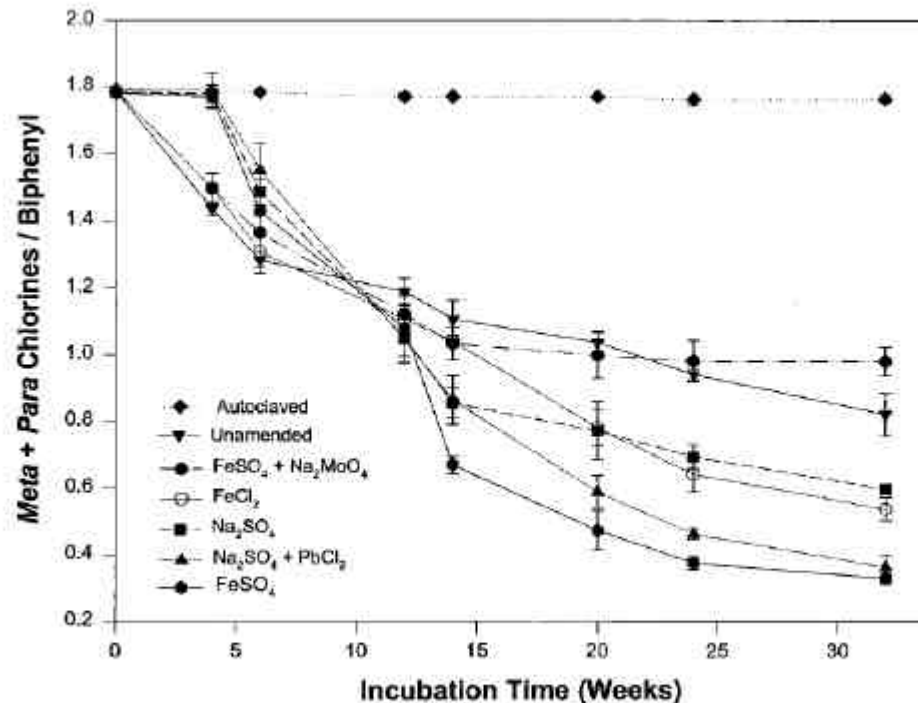Wood, Trobaugh, and Carter, ES&T, 33: 857-863, 1999.

FIGURE 2. Results of sediment ampule experiment: (a) 2,3,4,5,6-PeCB fraction with time in active and control samples; (b–d) TeCB, TCB, and DCB sums with time in active samples. TiCt represents the reductant, titanium(III) citrate.

Biotic/Abiotic (PCB)

Zwiernik, Quensen, and Boyd, ES&T, 32: 3360-3365, 1998.

FIGURE 1. Effects of FeSO₄ amendments on anaerobic microbial dechlorination of Aroclor 1242. Rates and extents of dechlorination were determined by comparing changes in the average number of meta + para chlorines per biphenyl (no ortho dechlorination was observed). Error bars indicate standard error of triplicate samples. Unamended samples served as positive controls to establish indigenous dechlorination activity; autoclaved samples served as negative biological controls.

Biotic/Abiotic (CF)

Weathers, Parkin and Alvarez, ES&T, 31: 880-893, 1997
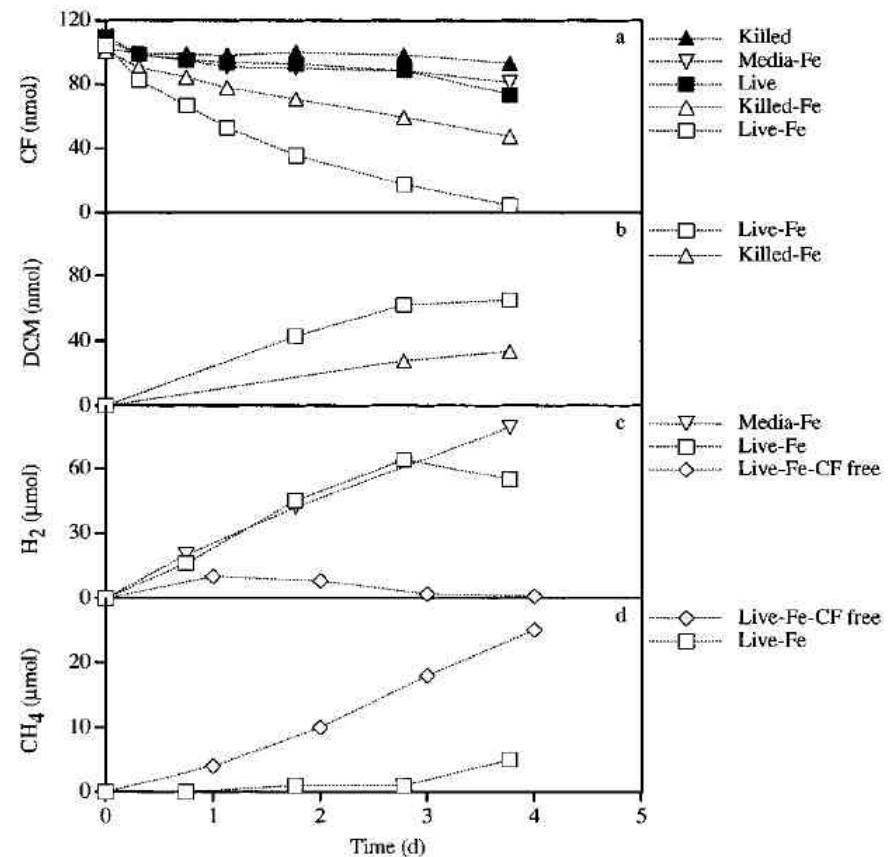
FIGURE 1. CF degradation (a), DCM formation (b), hydrogen evolution and utilization (c), and methane production (d) in batch reactors containing 2 g of iron filings and killed or live cells, or mineral medium. Filled symbols indicate treatments that were not amended with iron. All incubations received CF except those designated CF free.

Summary - Abiotic

◆ **PC-based DSS**
- Probably too slow in sediments
- Produce active agent

◆ **Fe, Fe/Pd**
- Extend to aqueous
- Extend to macro-scale

◆ **Fe(II) minerals**
- green rust, magnetite
- FeS, FeS_2,

Summary – Abiotic/Biotic

- FeSO$_4$
- Fe
- Electron carriers (Vit B$_{12}$?)
- Others?

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