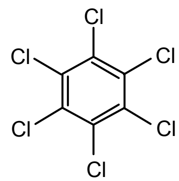
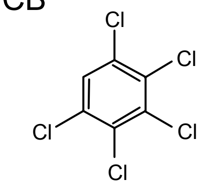
Zero-valent iron's effectiveness at dehalogenating chlorobenzenes and its feasibility as a reactive cap

Shawn Moderow and Danny Reible
University of Texas at Austin
Department of Civil, Architectural and Environmental Engineering

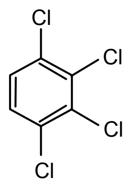
Chlorobenzenes, CBs



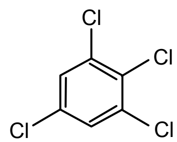
Hexachlorobenzene, HCB



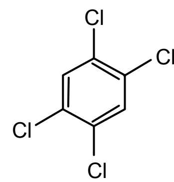
Pentachlorobenzene, PeCB



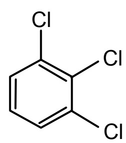
1,2,3,4-Tetrachlorobenzene



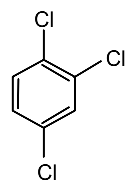
1,2,3,5-Tetrachlorobenzene



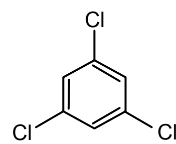
1,2,4,5-Tetrachlorobenzene



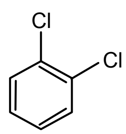
1,2,3-Trichlorobenzene



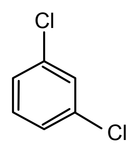
1,2,4-Trichlorobenzene



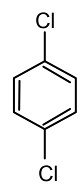
1,3,5-Trichlorobenzene



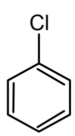
1,2-Dichlorobenzene



1,3-Dichlorobenzene

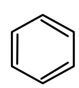


1,4-Dichlorobenzene



Monochlorobenzene

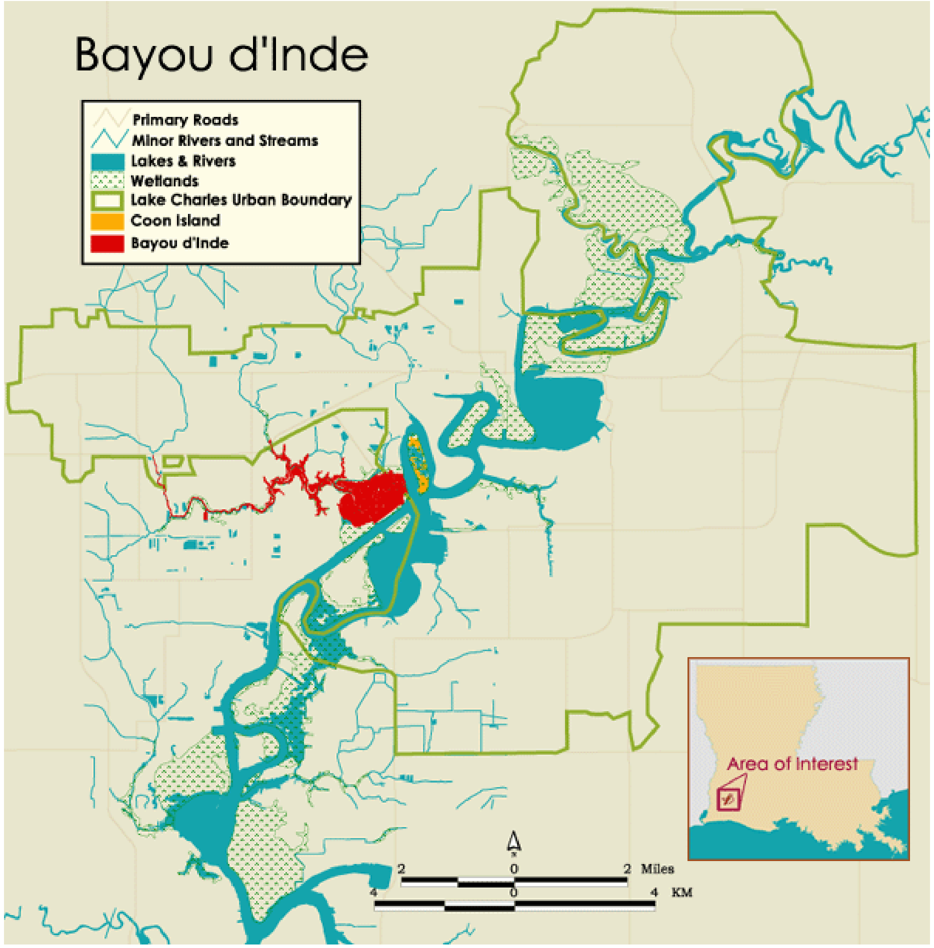
Benzene



- Used in the manufacturing of pesticides, herbicides, dyestuff and rubbers
- Range of chemical and physical properties.
- High MW CBs strongly sorbing.
- Low MW CBs are very volatile.

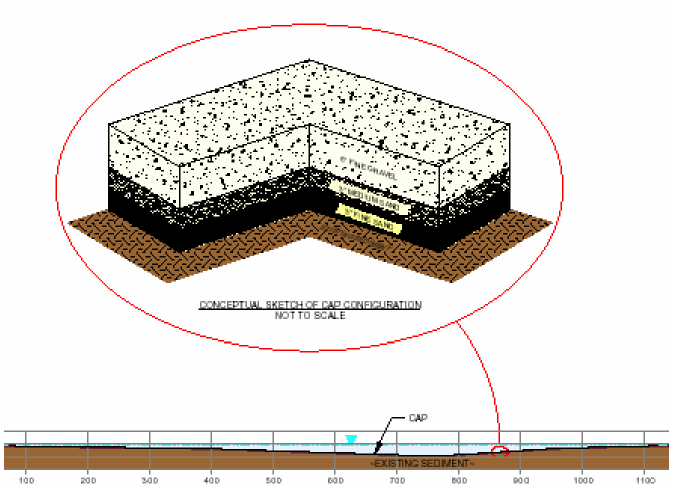
Bayou d'Inde (Bayou Den)

- Tributary of the Calcasieu River (Calc-a-shoe) outside Lake Charles, Louisiana that has received discharge of metals, PAH, PCBs, CBs, and other chlorinated organics.
- Primarily contaminated with HCB.
- Natural attenuation has been ineffective at reducing HCB contamination (Yeh and Pavlostathis, 2004).



Sediment Capping

- Improve quality of aquatic habitat
  - Stabilize sediments
  - Physically isolate sediment contaminants from benthic organisms
  - Reduce contaminant flux to benthos and water column
  - Improve surficial substrate



Sand caps

- Majority of existing caps
- Effective for contaminants strongly sorbed to solid phase of underlying sediment
- Easy to place with minimal intermixing
- Generally erosion resistant compared to existing bottom but, if necessary, can be supplemented with armoring layer
- Often provides much-needed diversity to bottom substrate
- Drives sediment layer anaerobic

Active Capping

Provides an opportunity for treatment in addition to passive containment

- Sorption and sequestration
- Chemical and biological treatment

From a variety of materials, Zero-Valent Iron (ZVI) was chosen for investigation as an active capping material for the use in the Bayou d'Inde. Why?

- ZVI has been shown to be effective at reducing chlorinated aliphatics and PCBs
  - Can HCB be reduced to less chlorinated benzenes?
  - Results of literature review inconclusive
- Iron is an relatively inexpensive and nontoxic material.

Goals

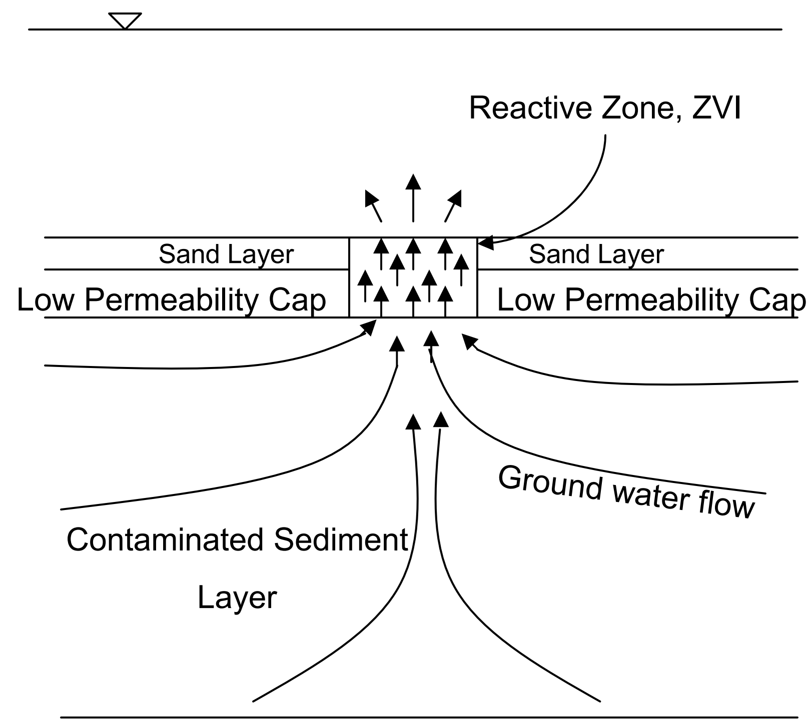
- Assess ZVI potential for reducing chlorobenzenes.

  - Published reports have shown mixed results on the reactivity of ZVI and CBs.

Zero-valent Iron

- MicroScale ZVI - 0.14 m^2/g, 70% < 44 µm diameter.
- Reactive Nanoscale Iron Particles (RNIP) – 33.1 m^2/g, ~ 70 nm

Funnel and Gate design for ZVI active capping

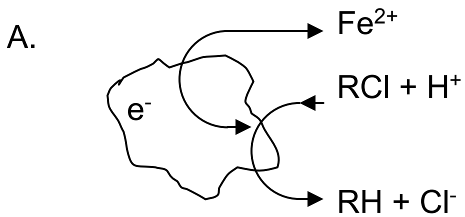


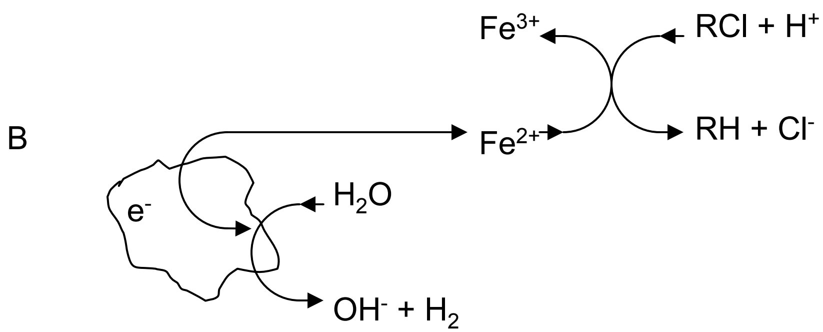
Zero-Valent Iron Chemistry

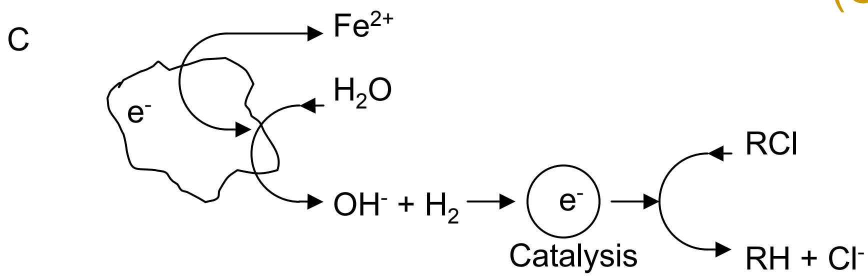
$$Fe^0 = Fe^{2+} + 2e^-$$

$$\underline{RCl + 2e^- + H^+ = RH + Cl^-}$$

$$Fe^0 + RCl + H^+ = RH + Cl^- + Fe^{2+}$$







(A) Reduction by zero-valent iron.

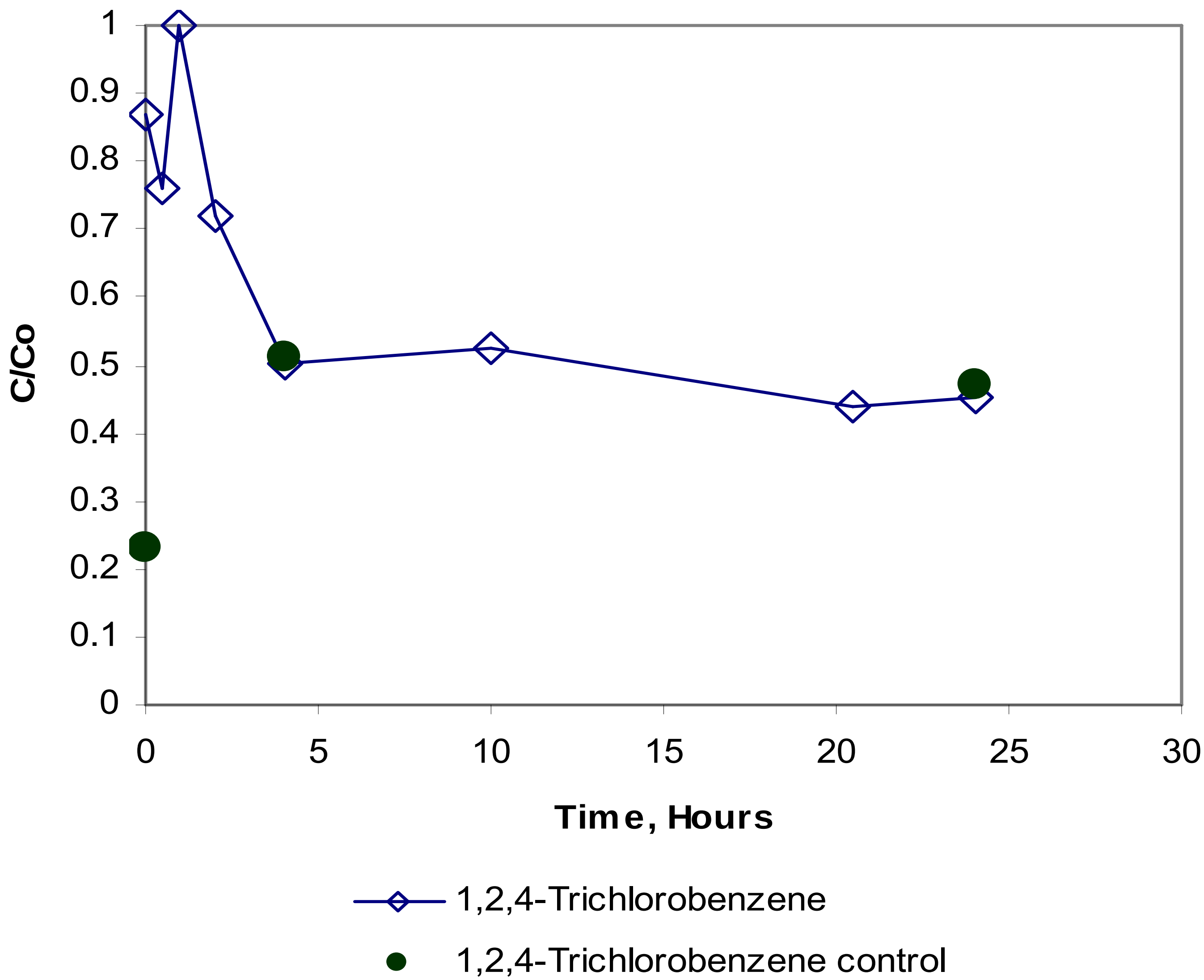
(B) Reduction by Fe^{2+}.

(C) Catalyzed hydrogenolysis.

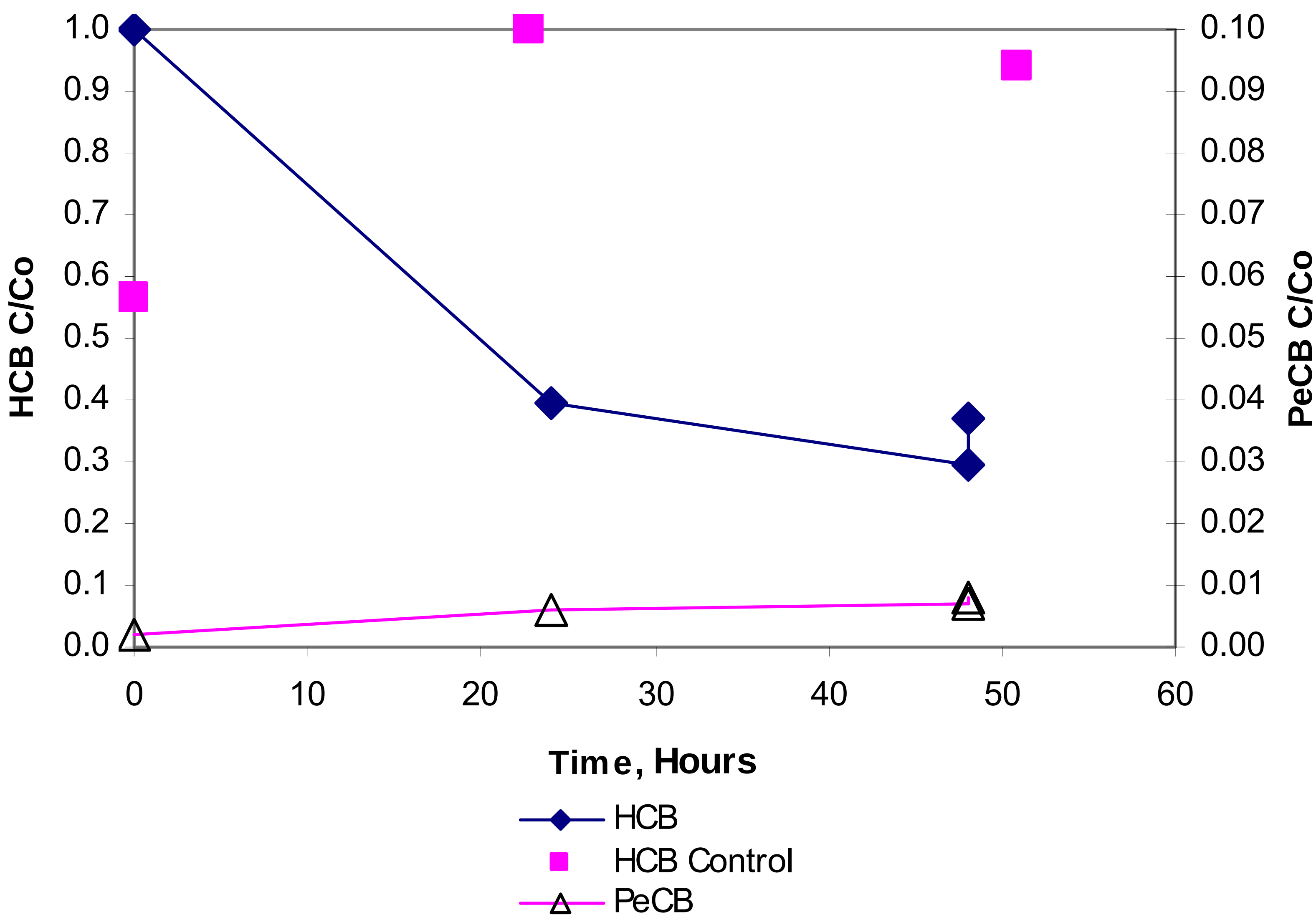
Preliminary Experiments

- Batch tests
  - 20 ml aqueous solution in 40 ml vials
  - pH ~7
  - ~8 grams of acid pretreated MicroScale Fe^0
  - Anaerobic Environment
  - ~3.2 μM Chlorobenzene isomer
  - Run over 24- 48 hrs
  - CB recovery with injection of Hexane, 10 - 20 min
  - Continuously shaken using Shaker table

Preliminary Results (Trichlorobenzene)



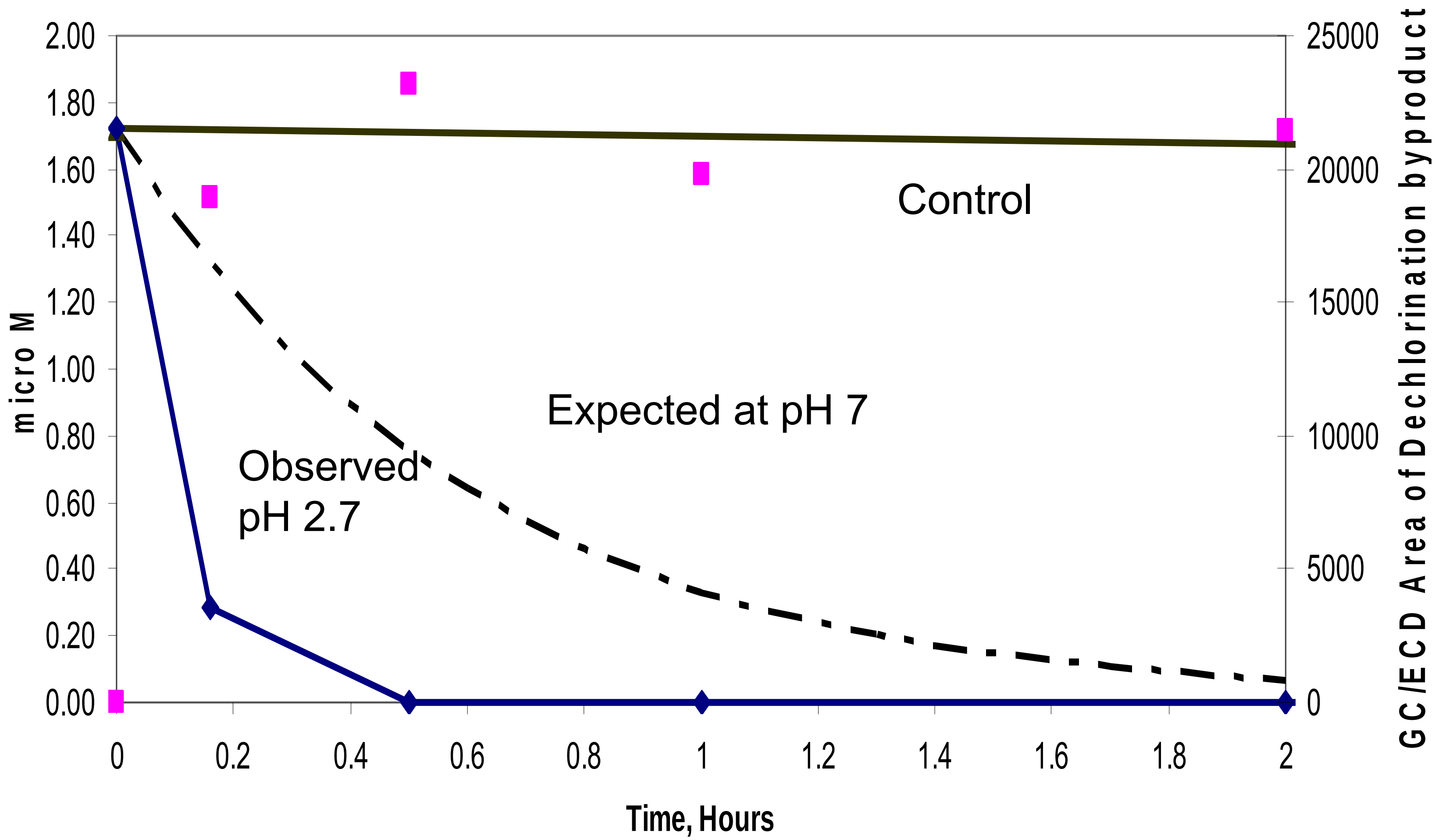
Preliminary Results (Hexchlorobenzene)



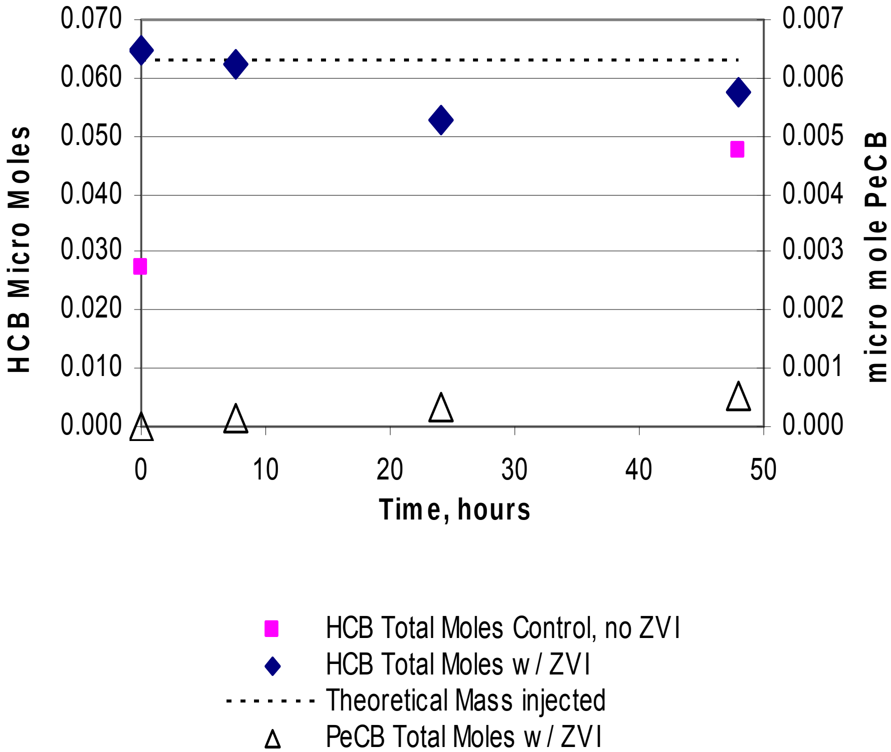
Experimental Adjustments

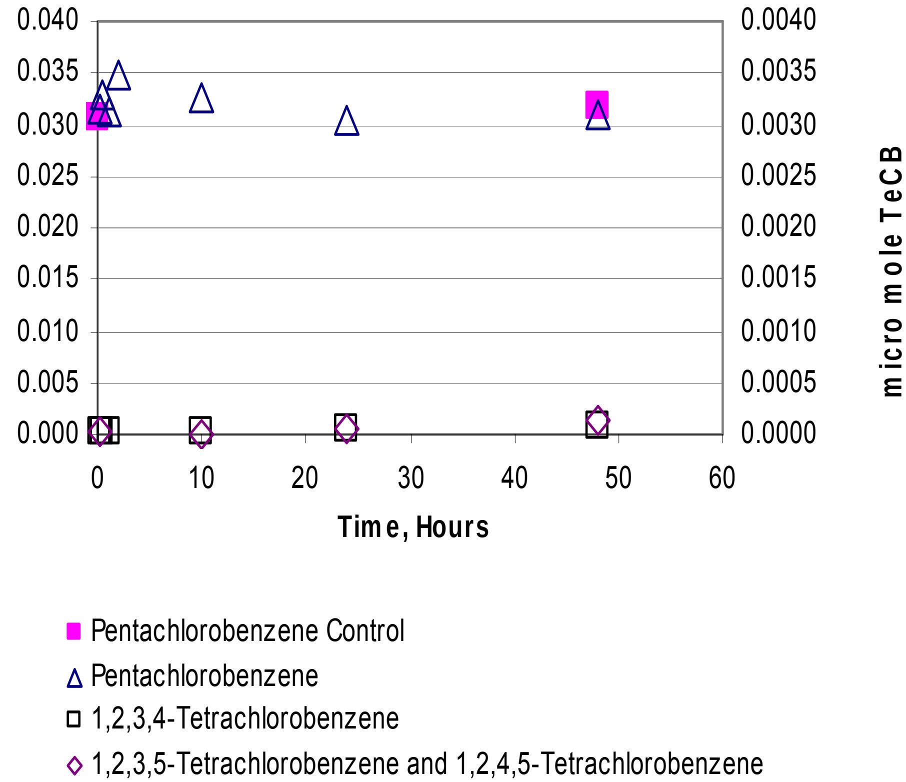
- Ensure iron activity
- Longer extraction times to recover reactant sorbed to iron
- Enhance mixing throughout with tumbler (relative to shaker table)
- Lower pH (2.7) to maximize potential for reductive dechlorination

Hexachloroethane



Results - pH 2.7





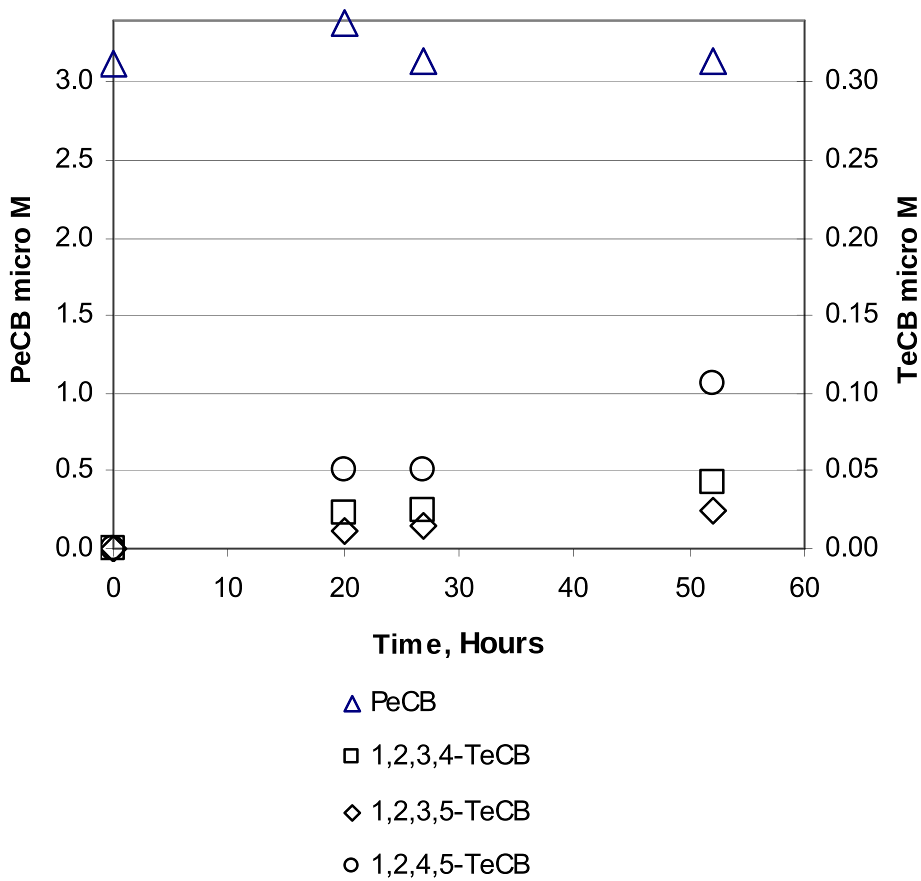
- Observed reductions in HCB and PeCB were 0.8% and 0.7 %.
- Observed reductions in 1,2,3,4-TeCB, 1,2,3,5-TeCB and 1,2,4,5-TeCB were negligible (0.04, 0.05 and 0 %, respectively)

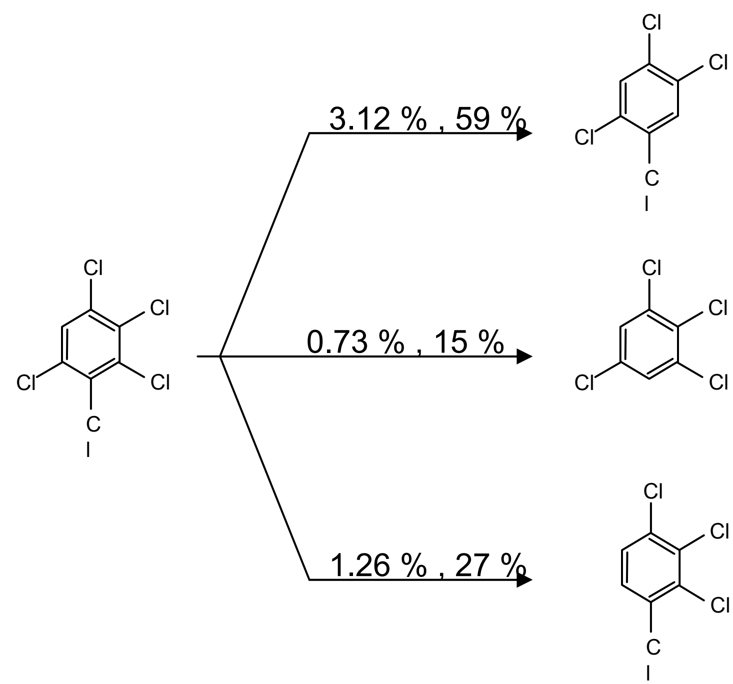
Micro vs Nano Iron

- Nanoscale iron requires much lower iron loading rate compared with microscale to achieve equivalent surface areas per gram.

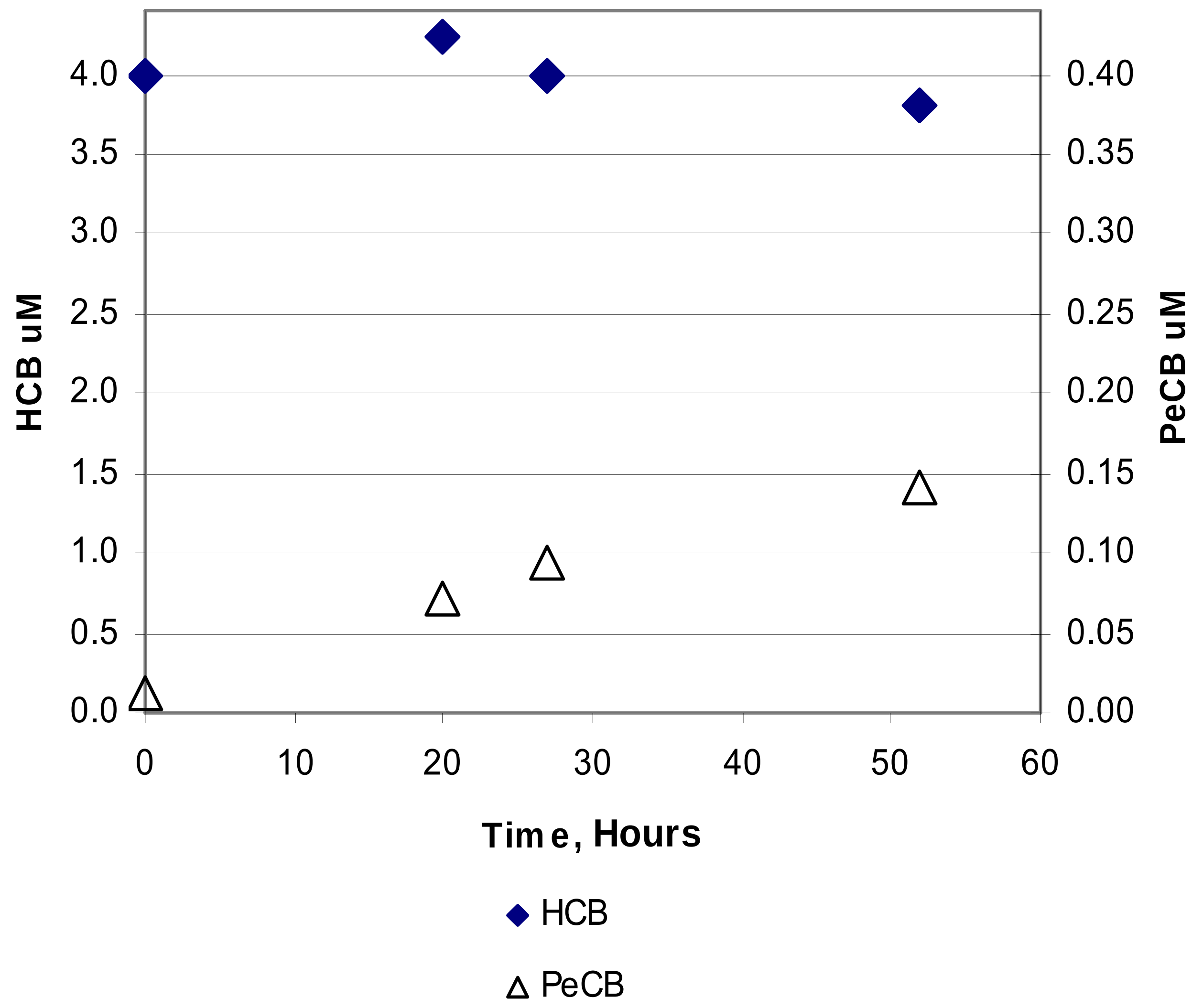
	Microscale	Nanoscale
Iron loading g/L	400	6.3
Surface Area m2/g	0.14	33.1
SA conc m2/L	56	209

Nanoscale Iron Reduction of PCB





Nanoscale Iron Reduction of HCB



Summary

	Percent Reduction			
	Microscale Fe		NanoScale Fe	
	pH 7	pH 2.7	pH 7	pH 2.7
	24 / 48 hrs	24 / 48 hrs	24 / 48 hrs	24 / 48 hrs
HCB	0.61 / 0.78	0.50 / 0.80	0.30 / 0.36	2.22 / 3.33
PeCB	--	0.34 / 0.69	--	2.70 / 5.11
1,2,3,5-TeCB	--	0.05	--	--
1,2,4,5-TeCB	--	0	--	--
1,2,3,4-TeCB	--	0.04	--	--
1,2,4-TCB	0	--	--	--

Conclusions

- ZVI has shown limited reactivity with CBs
- ZVI cannot be recommended as a reactive capping material for the purpose of reducing CBs.
- Larger MW CBs have greater reactivity with ZVI (HCB>PeCB>TeCBs, although all show small reactivity).