Superoxide Catalysts for In-Situ Chemical Reduction

Second Southeastern In-Situ Soil and Groundwater Remediation Conference

Dan Bryant

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4+ Acre DNAPL Site

Carbon Tetrachloride + Chloroform DNAPL

Complex mix:

Reducible:
Carbon tetrachloride
Chloroform
Methylene chloride

Oxidizable:
Carbon disulfide
Chlorobenzene
Ethylbenzene
Methoxychlor
Anisole

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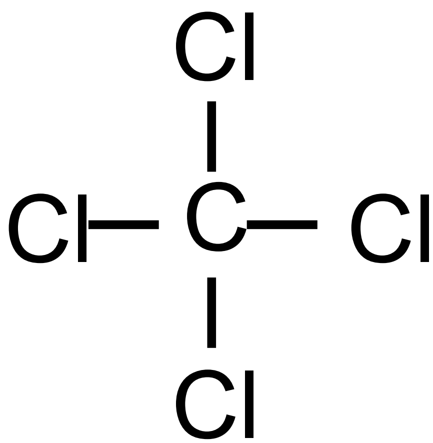
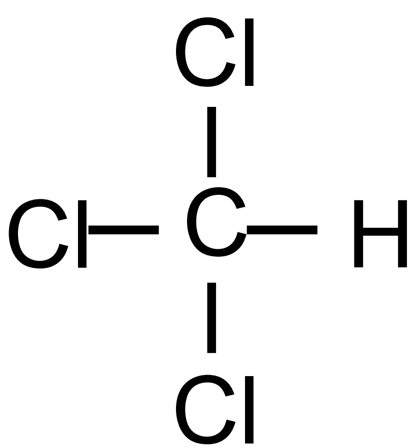
Chloromethanes cannot be oxidized



Carbon tetrachloride

No double carbon bonds



Chloroform

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Chemical *Reduction* during ISCO

Catalyzed peroxide reactions:

$H_2O_2 + Fe^{+2} \rightarrow OH\cdot + OH^- + Fe^{+3}$

$OH\cdot + Fe^{+2} \rightarrow OH^- + Fe^{+3}$

$Fe^{+3} + H_2O_2 \rightarrow H^+ + HO_2\cdot + Fe^{+2}$

$Fe^{+2} + HO_2\cdot \rightarrow Fe^{+3} + HO_2^-$

$Fe^{+3} + HO_2\cdot \rightarrow Fe^{+2} + O_2 + H^+$

$OH\cdot + H_2O_2 \rightarrow H_2O + \mathbf{O_2\cdot^-} + 2H^+$

$HO_2\cdot \rightarrow H^+ + \mathbf{O_2\cdot^-}$ ← **Superoxide (reductar**

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Manganese-Catalyzed Peroxide

Watts and coworkers:

Under acidic conditions:

$H_2O_2 + Mn^{+2} \rightarrow OH\cdot + OH^- + Mn^{+3}$

As pH approaches 6.8:

$Mn^{+2} + 2H_2O \rightarrow MnO_2(s) + 2e^- + 4H^+$

Hydroxyl radical production less efficient

At pH ≥6.8:

$Mn^{+4} + H_2O_2 \rightarrow Mn^{+3} + 2H^+ + O_2^{\bullet -}$

Only superoxide; no hydroxyl radicals

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Cannot distribute Mn^{+4}

- Inject $MnSO_4$ (precipitate Mn^{+4})
  - Very acidic
  - Require large pH shifts
- MnO_2 is solid
  - Fracture emplace?
  - Chelated Mn
  - Mn^{+2} valence state

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What about permanganate?

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2(s) + 4OH^-$$

$$Mn^{+7} \rightarrow Mn^{+4}$$

- Permanganate is already widely used in ISCO
- Permanganate solutions have a near-neutral pH
- Permanganate will oxidize certain COCs
- Preferential permanganate reduction in zones with highest concentration of organics
- MnO_2 catalyst is “fixed” as solid and not displaced by injection of additional liquids

Biggest Challenge: Stabilization

$$H_2O_2 + MnO_2 + 2H^+ \rightarrow Mn^{+2} + 2H_2O + O_2$$

$$Mn^{+2} + 2H_2O \rightarrow Mn(OH)_2 + 2H^+$$

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO_2 + 2H_2O$$

Net reaction: $2H_2O_2 \rightarrow 2H_2O + O_2$

Permanganate-MnO_2 amorphous, very fine

Extremely fast – H_2O_2 degraded in minutes

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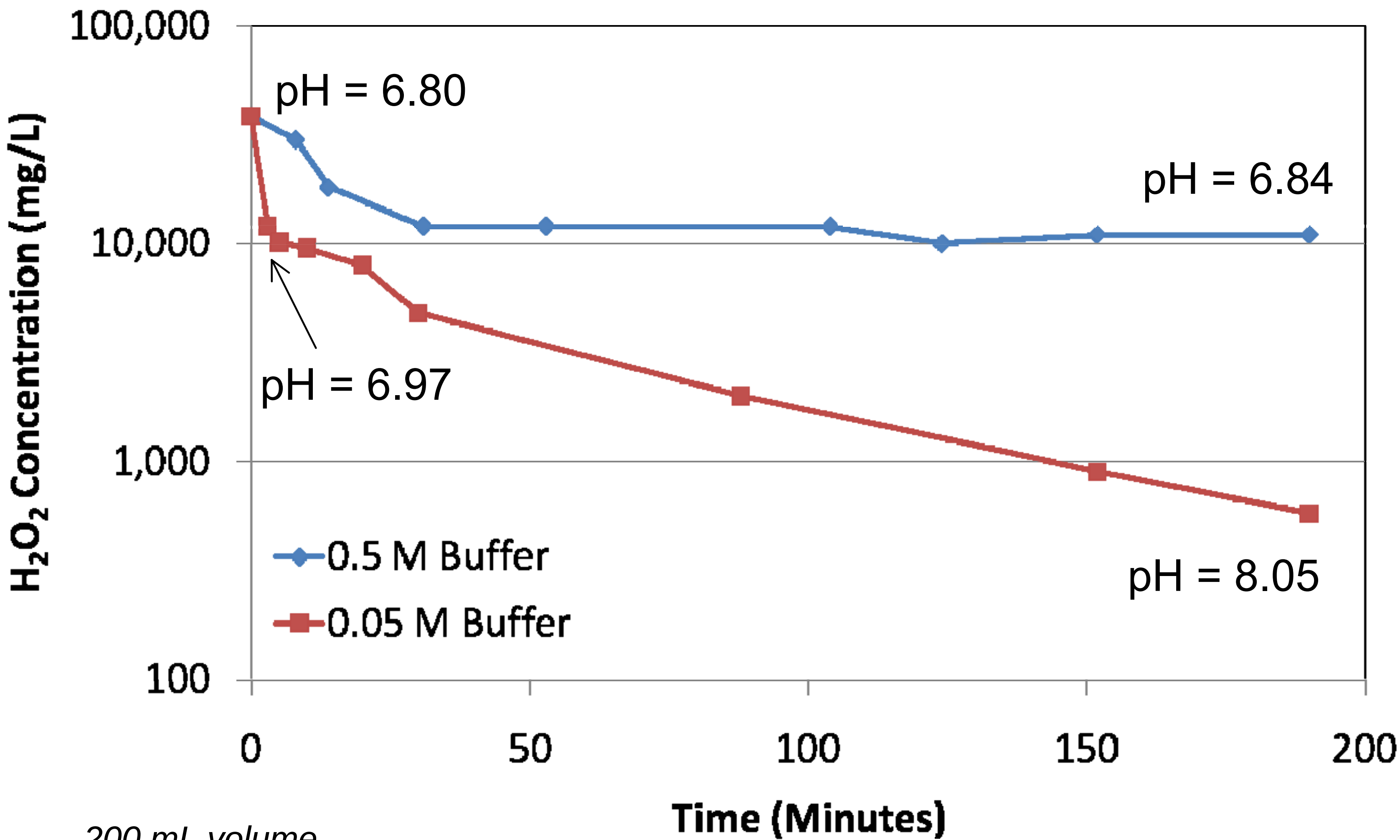
Phosphate Buffer



200 mL volume
500 mg MnO_2
Peroxide = 1.9%

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Bench Test Set-Up

- Batch reactor / soil slurry tests
- 500 g composited soil
- 1,500 mL homogenized groundwater
- 20 g MnO_2 (precipitated from TCE/$KMnO_4$)
- 200 mL 1.0 *M* phosphate buffer pH = 6.8
- Soil, groundwater, volatilization
  – VOST tube (Tenax/Anasorb)

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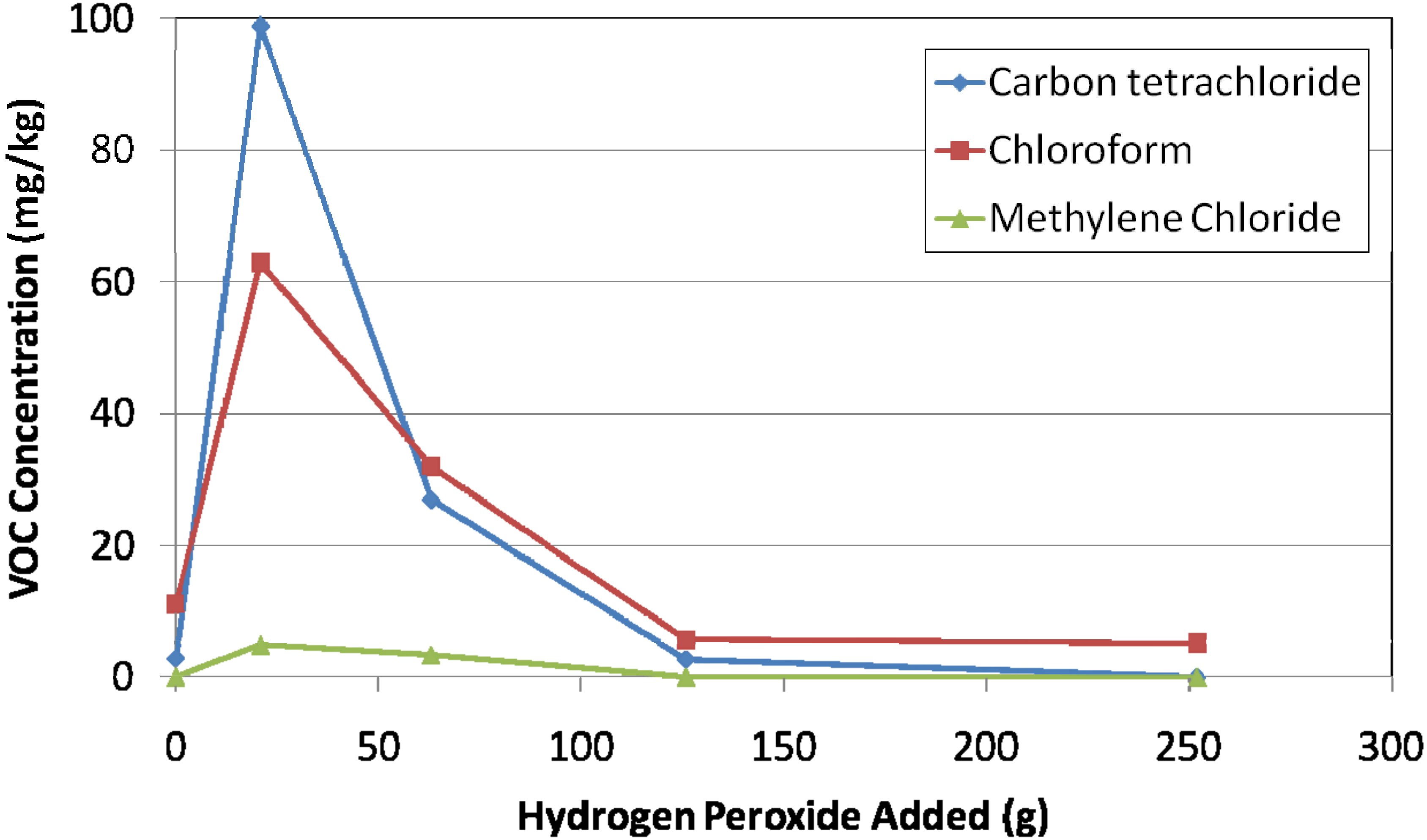
Bench Test Soil Data - Chloromethanes



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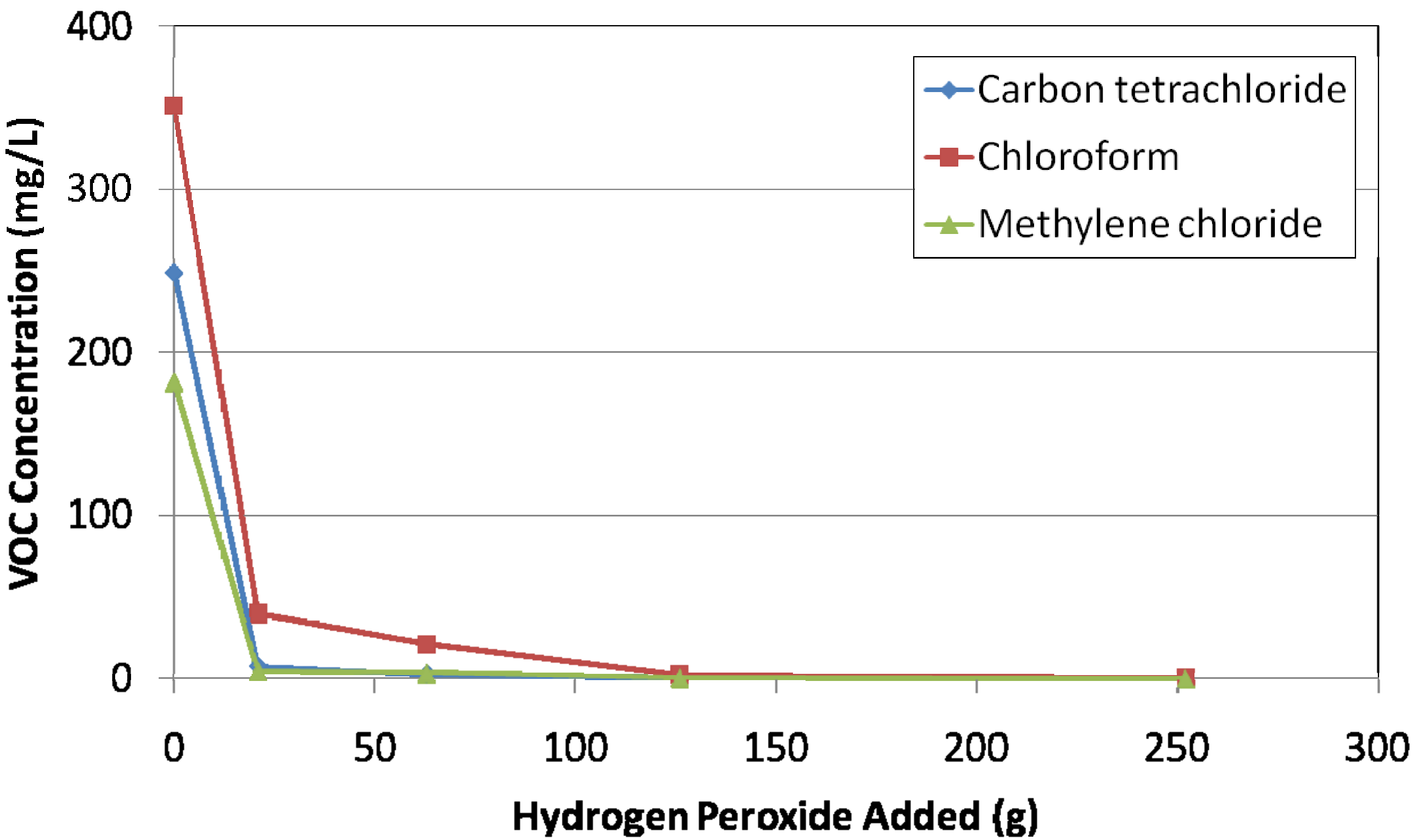
Bench Test Water Data – Chloromethanes

Dilution-corrected



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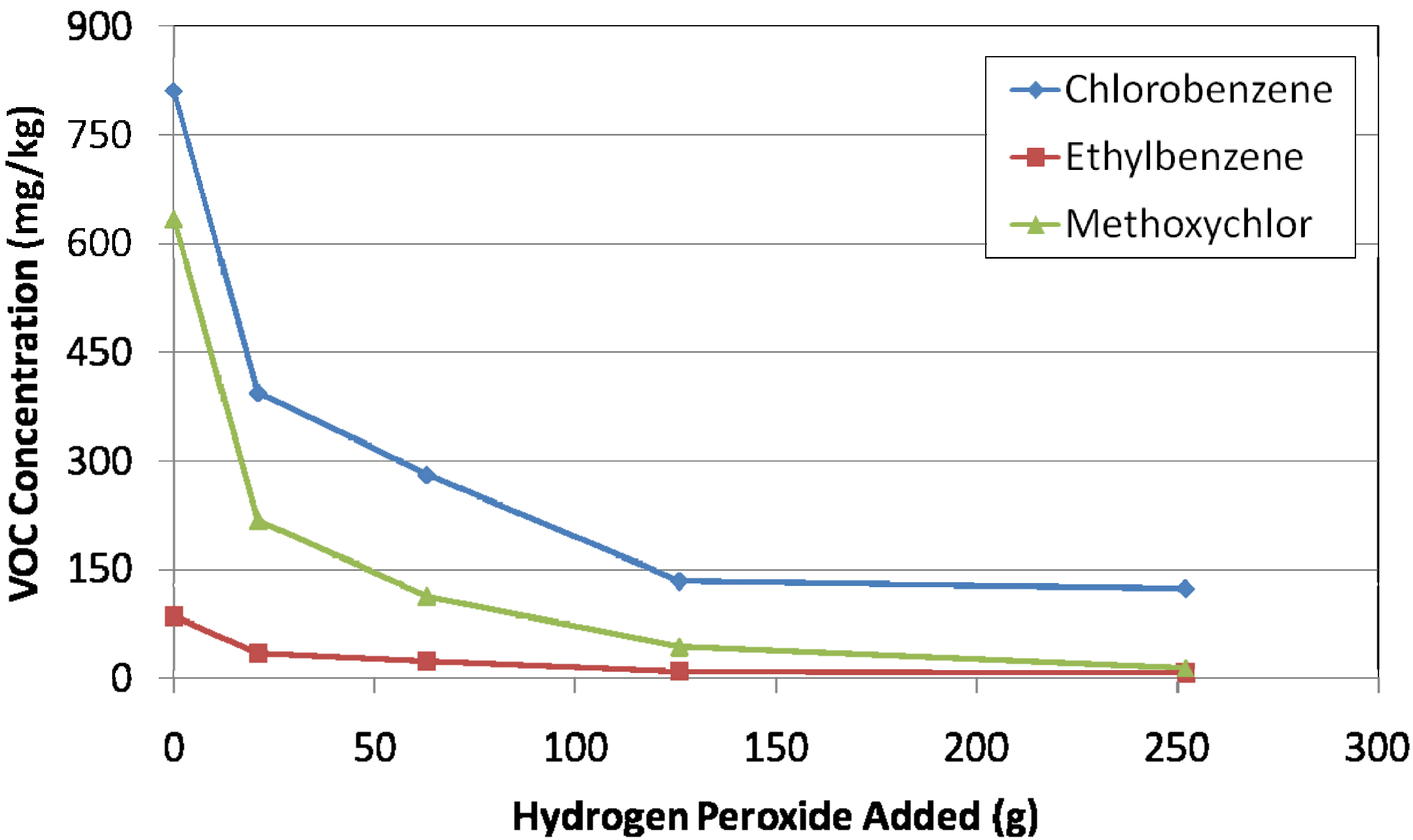
Bench Test Soil Data - Aromatics



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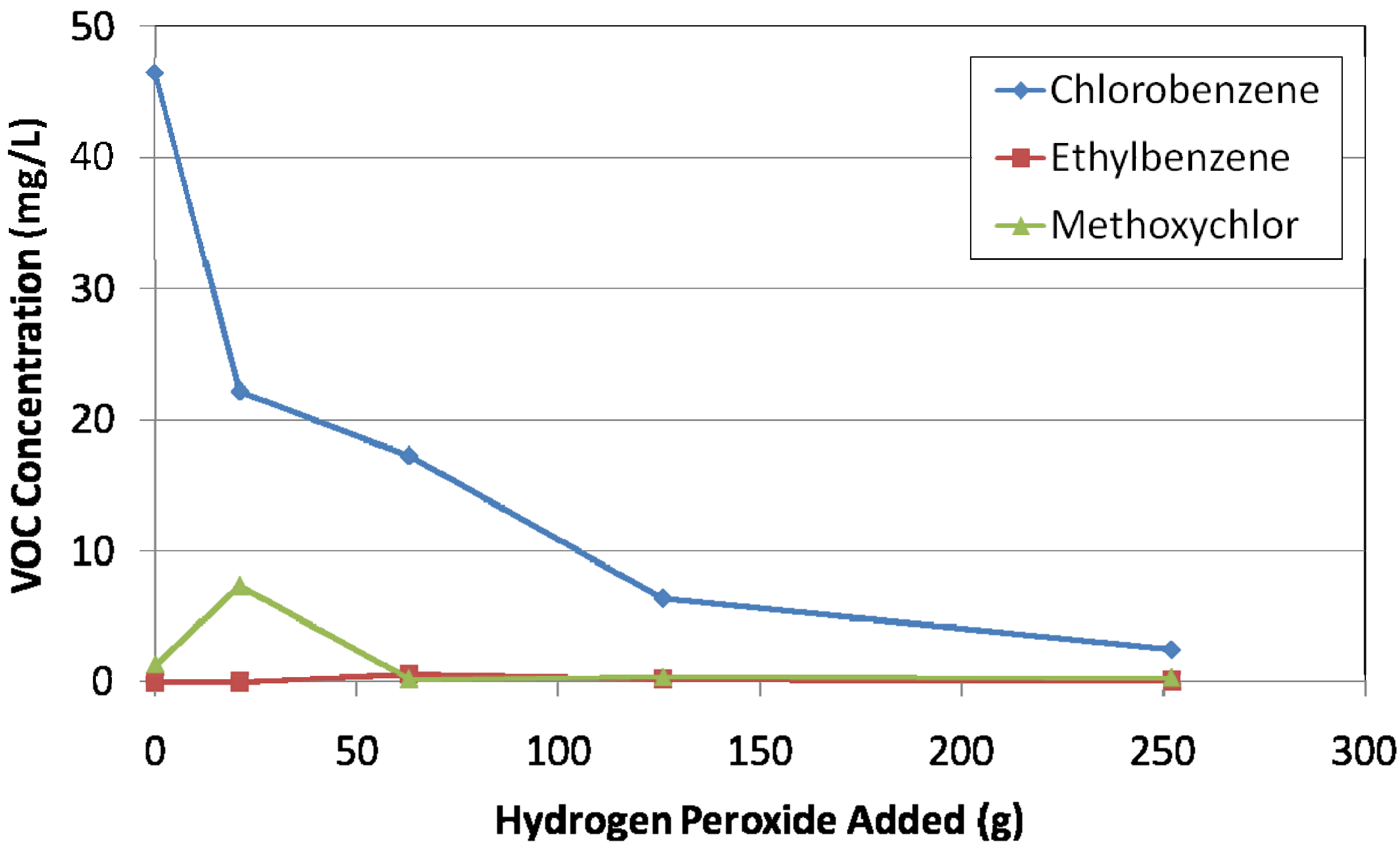
Bench Test Water Data – Aromatics

Dilution-Corrected



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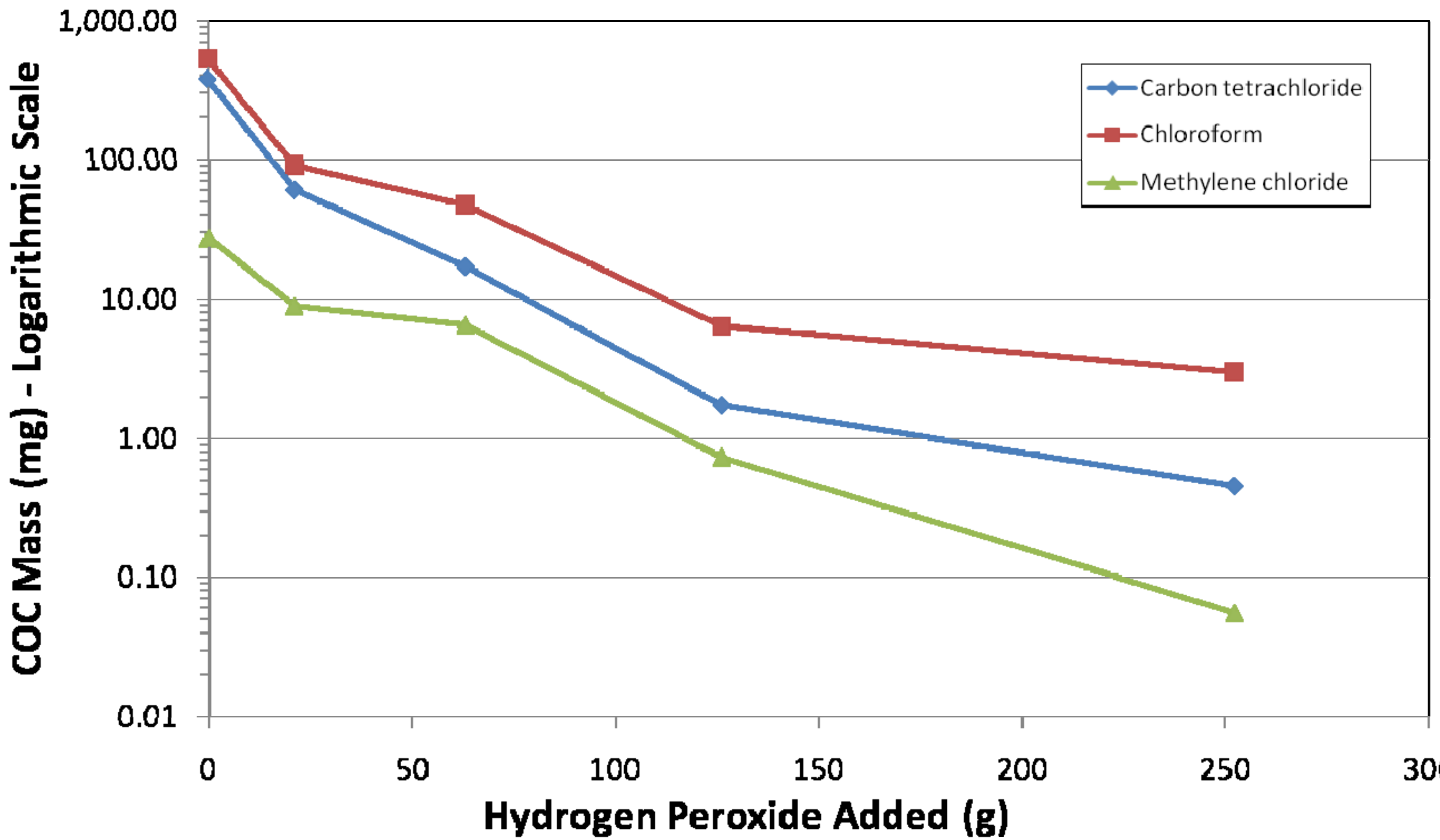
Contaminant Mass – Chloromethanes

Includes volatilized mass



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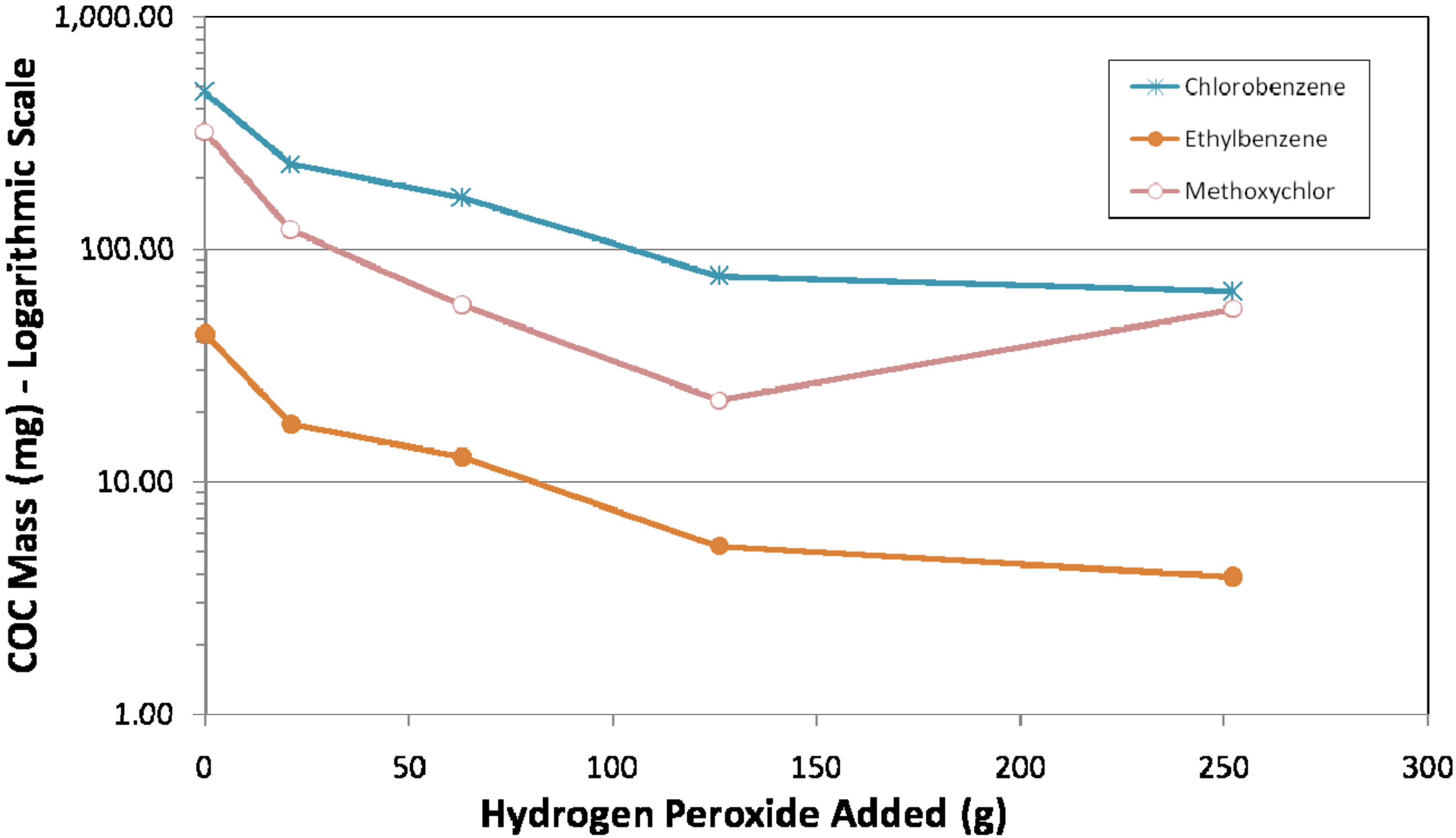
Contaminant Mass – Aromatics

Includes volatilized mass



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Bench Test Conclusions

- Phosphate buffer controls pH and stabilizes reaction
- All of the COCs are readily destroyed:
  - Chloromethanes by superoxide reduction.
  - Aromatics by hydroxyl radical oxidation.
- DNAPL was destroyed.
- Superoxide degradation pathway not fully resolved.
  - Phosgene not detected.

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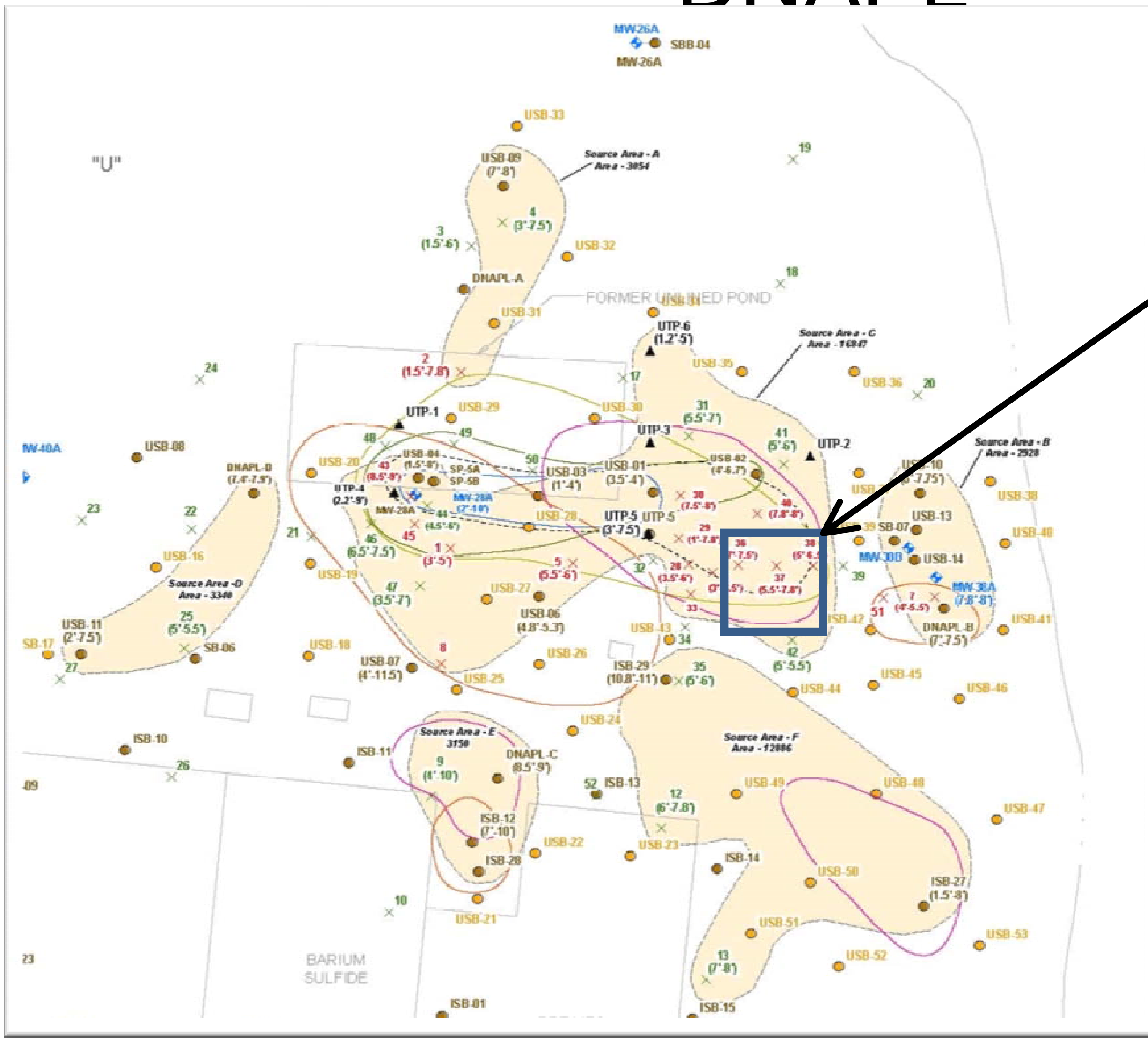
4+ Acre DNAPL Site

Carbon Tetrachloride + Chloroform DNAPL



Field Pilot Test
50 ft x 50 ft area
4,800 gal $NaMnO_4$ 4%
2,800 gal 1*M* buffer
26,000 gal 11% H_2O_2

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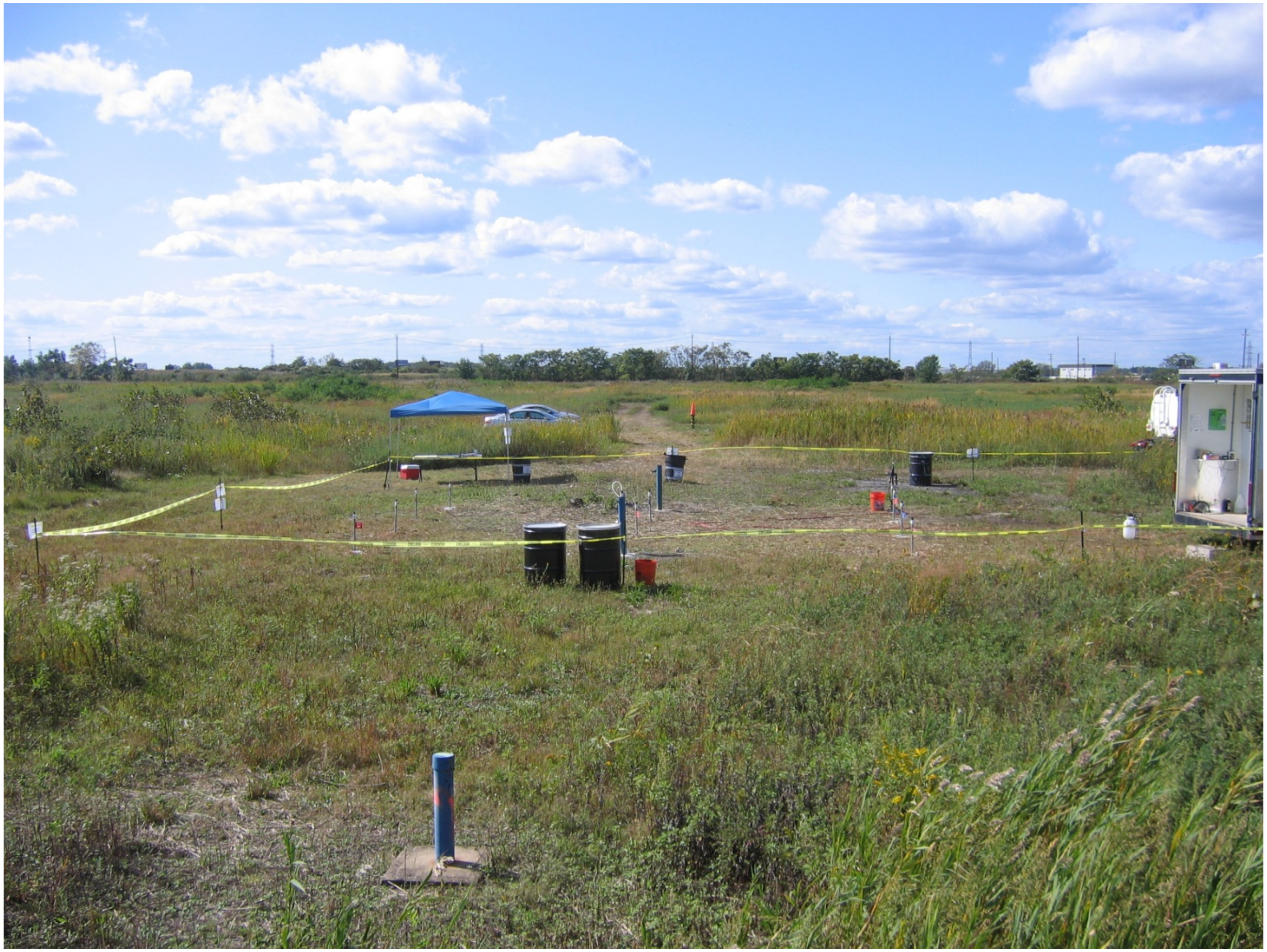
Field Pilot Test



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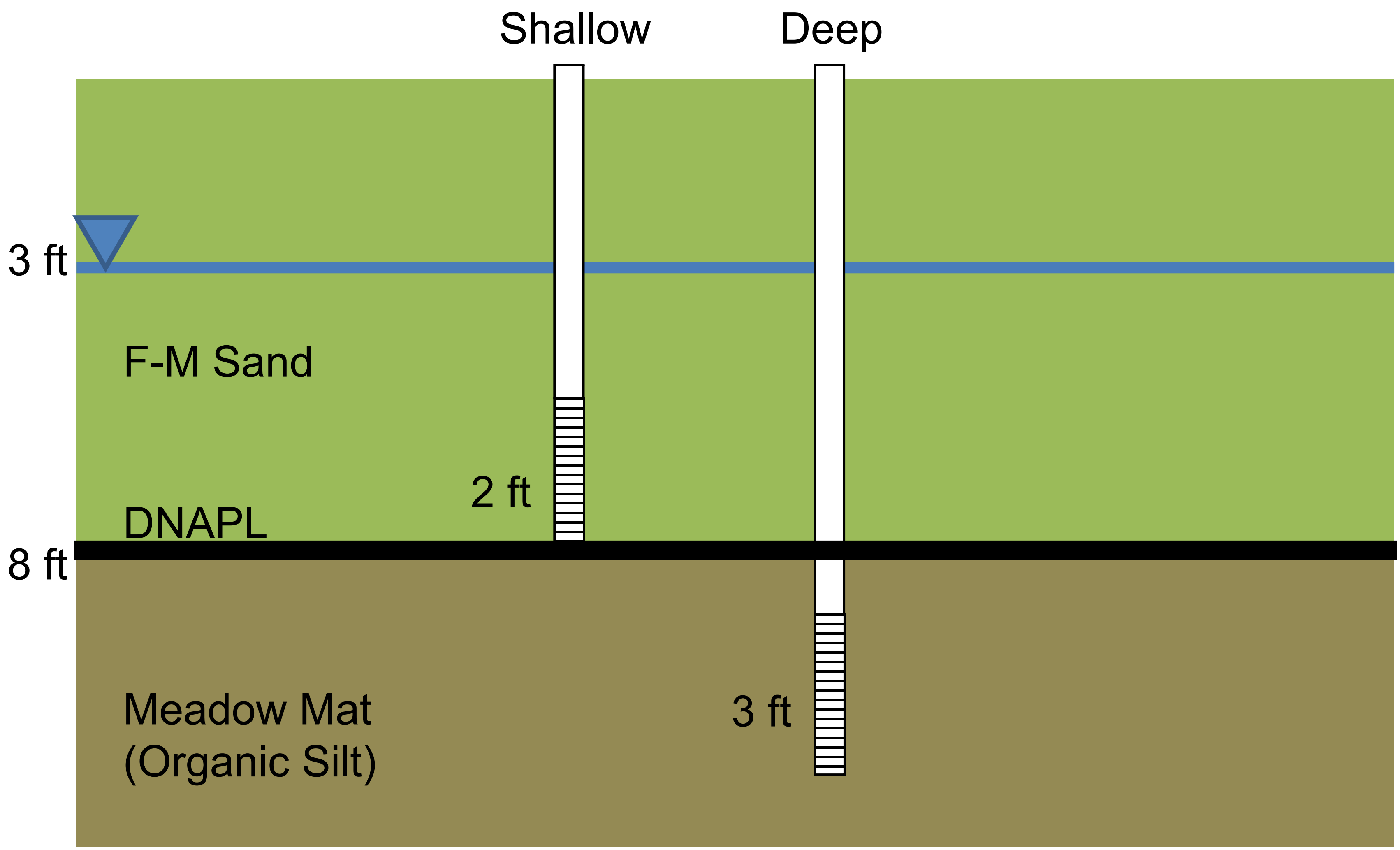
Conceptual Cross Section



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Sequence of Events

- Baseline sampling
  - Challenge #1: Groundwater pH 3-4
- Permanganate injection phase
- Sampling to confirm permanganate degradation
  - Groundwater pH remains 3-4
- Sodium hydroxide injection
  - Inject at pH 8.5-9, establish stable pH 6.5-8
- Phosphate buffer injection
- Peroxide injection

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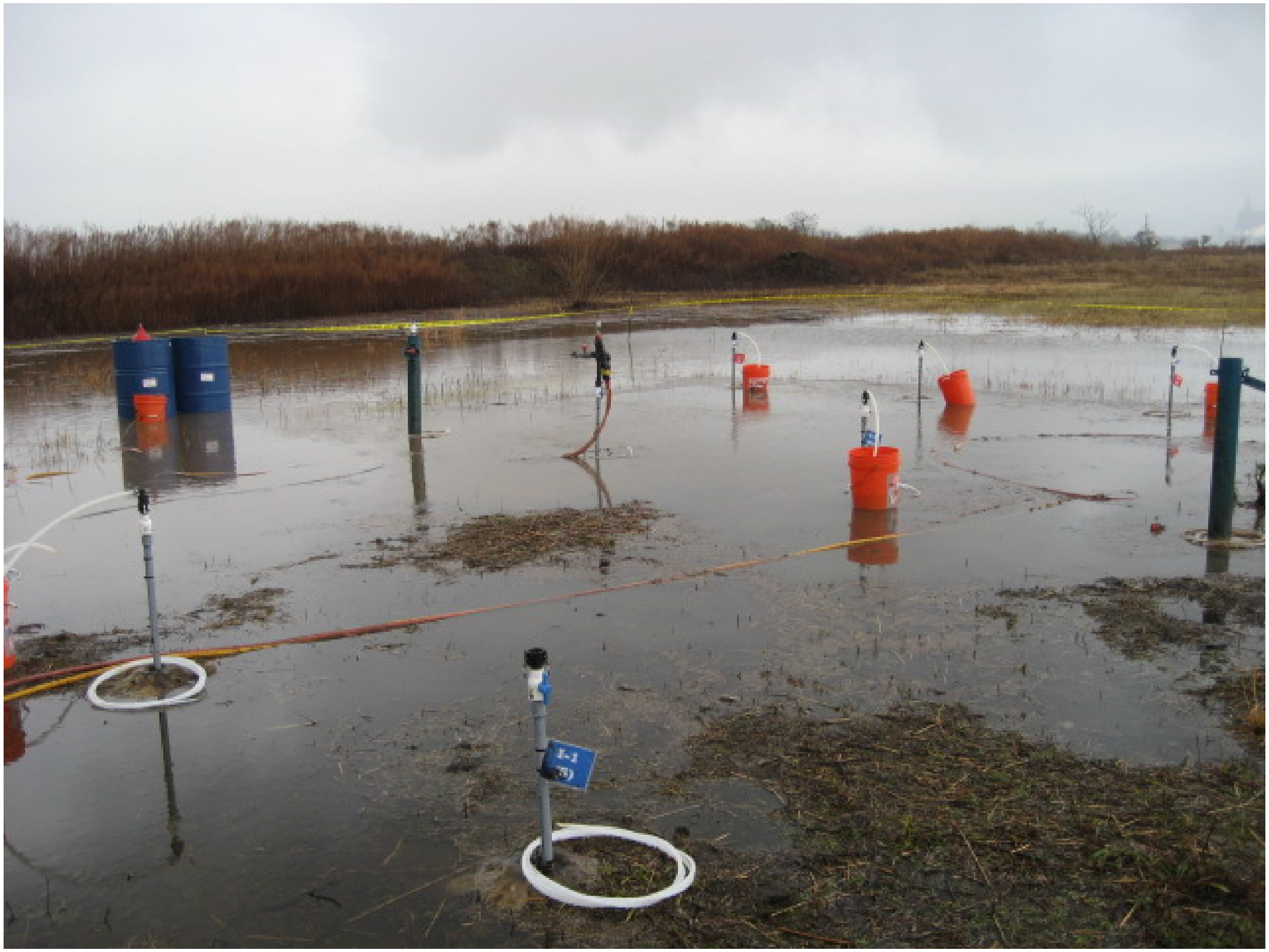
Challenge #2

November Nor'easter



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Standing Water Provided ROI

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Intermediate Products

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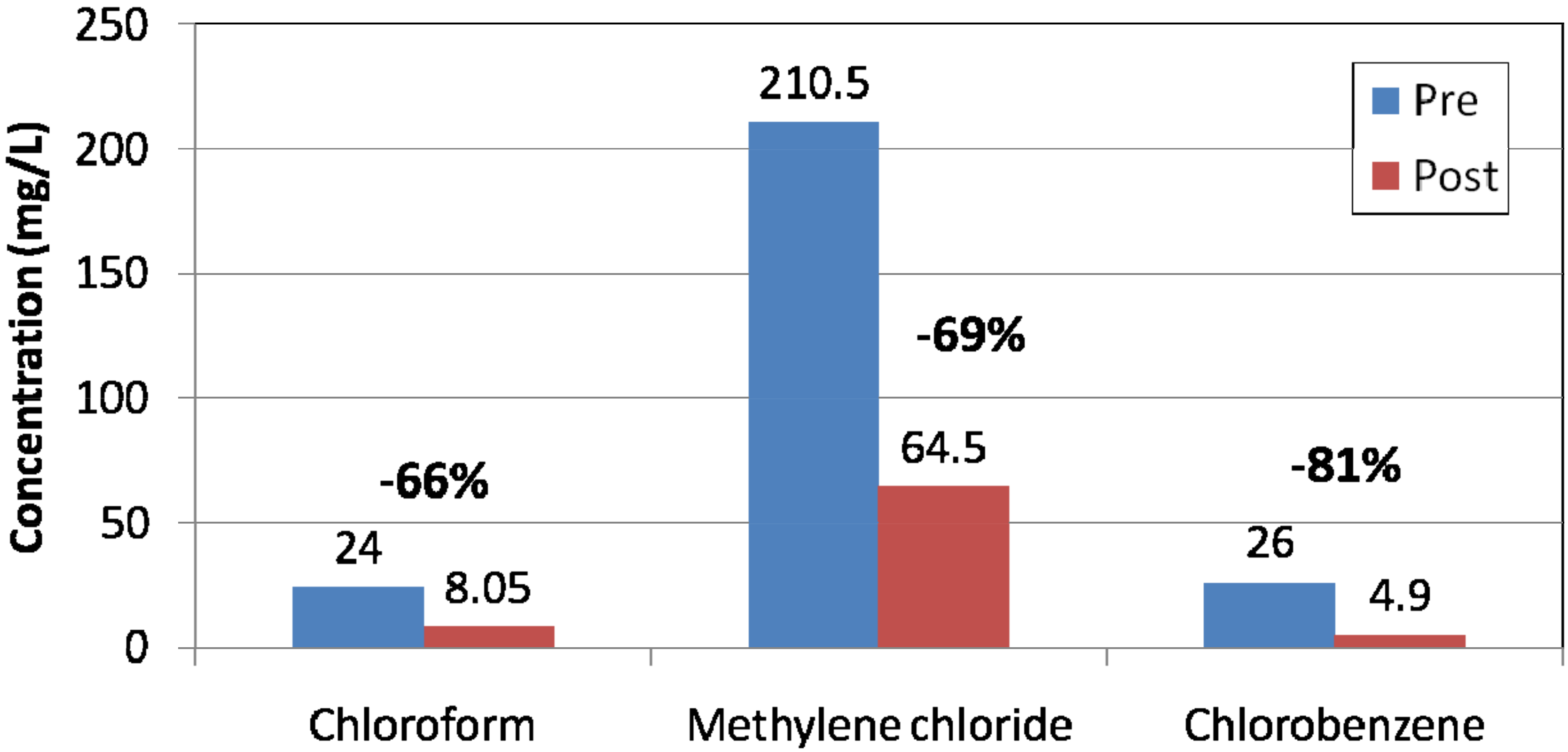
Pilot Test Results - Groundwater



Overall Average: -74%

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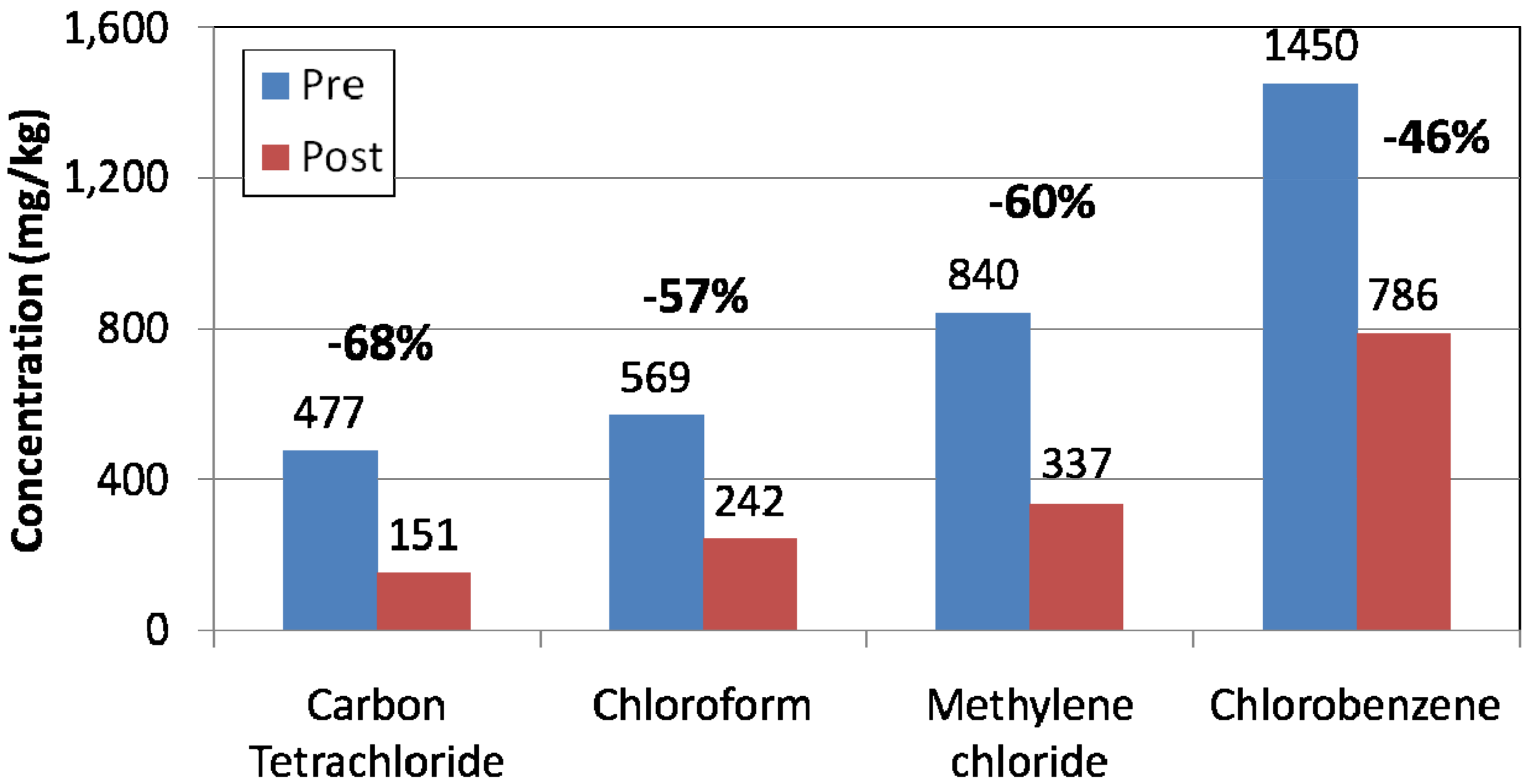
Pilot Test Results – Soil

VOCs decrease in 9 out of 12 locations



Overall Average: -65%

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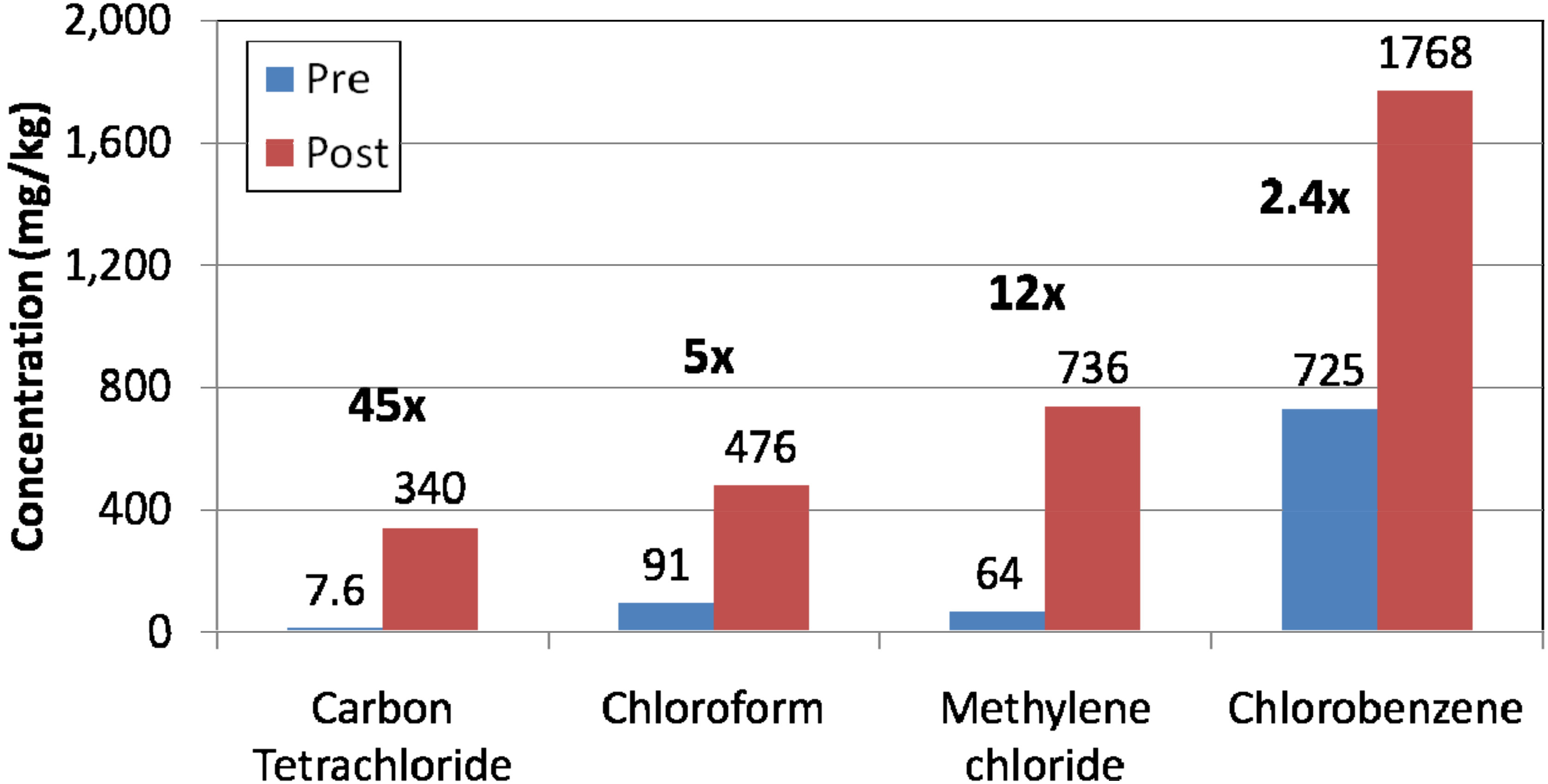
Pilot Test Results – Soil

VOCs increase in 3 out of 12 locations



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Conclusions

- Mn^{+4} catalyzes superoxide (reductant)
- Use permanganate to distribute Mn
  - Organic matter reduces $Mn^{+7} \rightarrow Mn^{+4}$ (MnO_2)
- Phosphate buffer – stabilizer, pH control
- Peroxide – reductant and oxidant
- Natural soils: Fe to catalyze OH•
- Field pilot: Positive but need to optimize

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