Factors Affecting Enhanced In Situ Biological Reduction of 1,2,3-Trichloropropane in Groundwater: Case Studies from Central California

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Why is 1,2,3-Trichloropropane an Emerging Concern for Groundwater?

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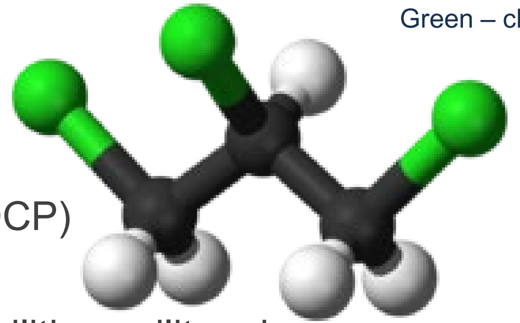
- Man-made compound
  - Formerly used as a chemical solvent and extraction agent
  - Chemical intermediate in the production of:
    - Other chemical intermediates
    - Agricultural fumigants
    - Specialty polymers and sealants
    - Commonly found with 1,2-dichloropropane (1,2-DCP)

Black – carbon
White – hydrogen
Green – chlorine



- Typically found at:
  - Ag-chem facilities, chemical manufacturing/storage facilities, military bases
  - Supply wells, particular those in agricultural areas (non-point sources)
- Classified as a likely or potential carcinogen to humans
  - EPA, US Health & Human Services, American Conference of Governmental Industrial Hygienists, NIOSH
  - Classified as a carcinogen by the State of California

Why is 1,2,3-Trichloropropane an Emerging Concern for Groundwater?

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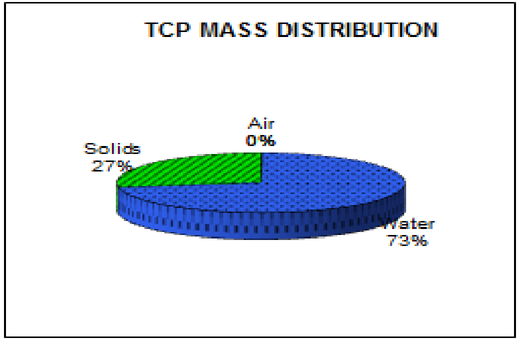
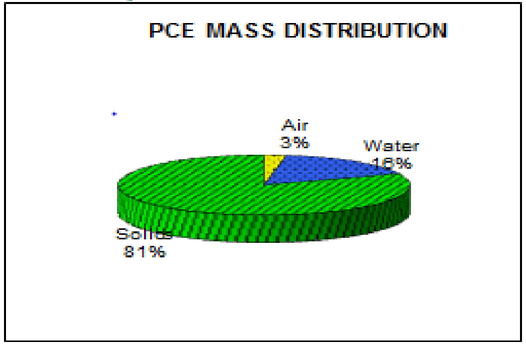
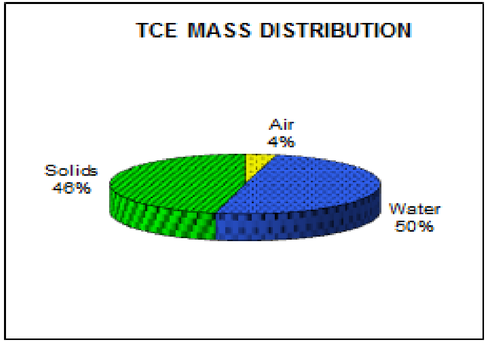
Low volatility and sorption

Property	1,2,3-TCP	1,1,1-TCA	TCE	1,2-DCA	Notes
Vapor Pressure	3.1	133.4	131.5	387	Torr (mm Hg) @ 25° C
Henry's Constant	2.3 – 3.4	167	93.7	11	x 10^{-4} atm m^3 $mole^{-1}$ @ 25° C
Solubility	1.75	1.3	1.1	8.61	g/L @ 20° C
K_{oc}	51	152	126		mL/g







- Little retardation – may form long, straight groundwater plumes
- Compared to chlorinated ethenes and chlorinated ethanes, TCP is less likely to sorb to solid material or partition into the vapor phase.

Current Regulatory Climate

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Federal	• USEPA tap water RSL is **0.00075 µg/L** • Listed on 2015 Draft Contaminant Candidate List 4 (CCL4)
California	• **0.0007 µg/L** Public Health Goal (est. 2009) • **0.005 µg/L** MCL (adopted 18 July 2017)
Hawaii	• State MCL of **0.6 µg/L** (est. 2011)
Minnesota	• Health Risk Limits (HRL) (est. 2011): • **0.003 µg/L** Cancer HRL
New Jersey	• **0.03 µg/L MCL** (est. 2018)
Other States?	• Coming Soon?

Groundwater Remediation

- Groundwater ex situ treatment feasible but potentially costly
  - GAC effective, but long residence time required
  - Advanced oxidation processes may also be effective
- In situ remediation is most effective but not widely tested
  - Potentially costly for dilute plumes
  - Includes:
    - Biological Reduction (ISBR)
    - Chemical Oxidation (ISCO)
    - Chemical Reduction: Zero Valent Metals (ISCR)

In Situ Biological Reduction (ISBR)- Timeline

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- **Since 2000** — Biostimulation at numerous sites; mixed results and unknown/unclear degradation mechanism and pathway
- **~2010** – Dihaloelimination of chlorinated propanes by *Dehalogenimonas* recognized (Bowman et al, 2012)
- **2014** – Commercially-available testing of *Dehalogenimonas* (Dhg) (SiREM's Gene-Trac® Dhg) and discovery of Dhg in SiREM's KB-1® Plus bioaugmentation culture
- **~2015** – Laboratory scale testing to understand and develop TCP degradation using Dhg
- **2016** – First-to-field bioaugmentation pilot scale study
- **2018** – Full-scale field implementation of bioaugmentation

1,2,3-TCP Degradation Pathway

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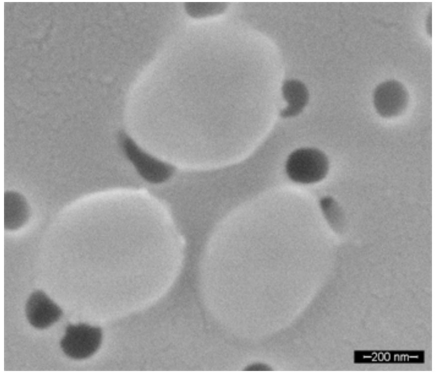
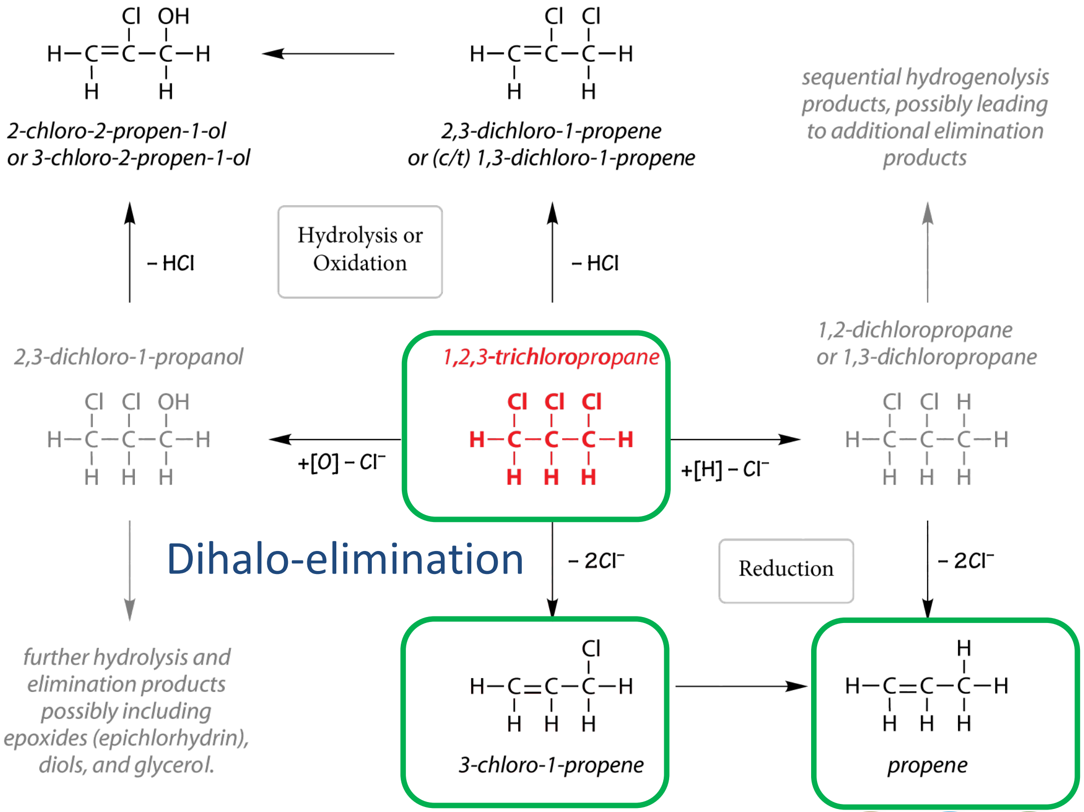
Strains of *Dehalogenimonas spp*[1]

- 1,2,3-TCP, 1,2-DCP, 1,1,2,2-TeCA, 1,1,2-TCA, 1,2-DCA degrading
- Strictly anaerobic
- Hydrogen (electron donor)





[1] Moe et al, 2009.
SEM image by W.G. Henk and J. Yan, Louisiana State University, Baton Rouge, LA

Case Study #1

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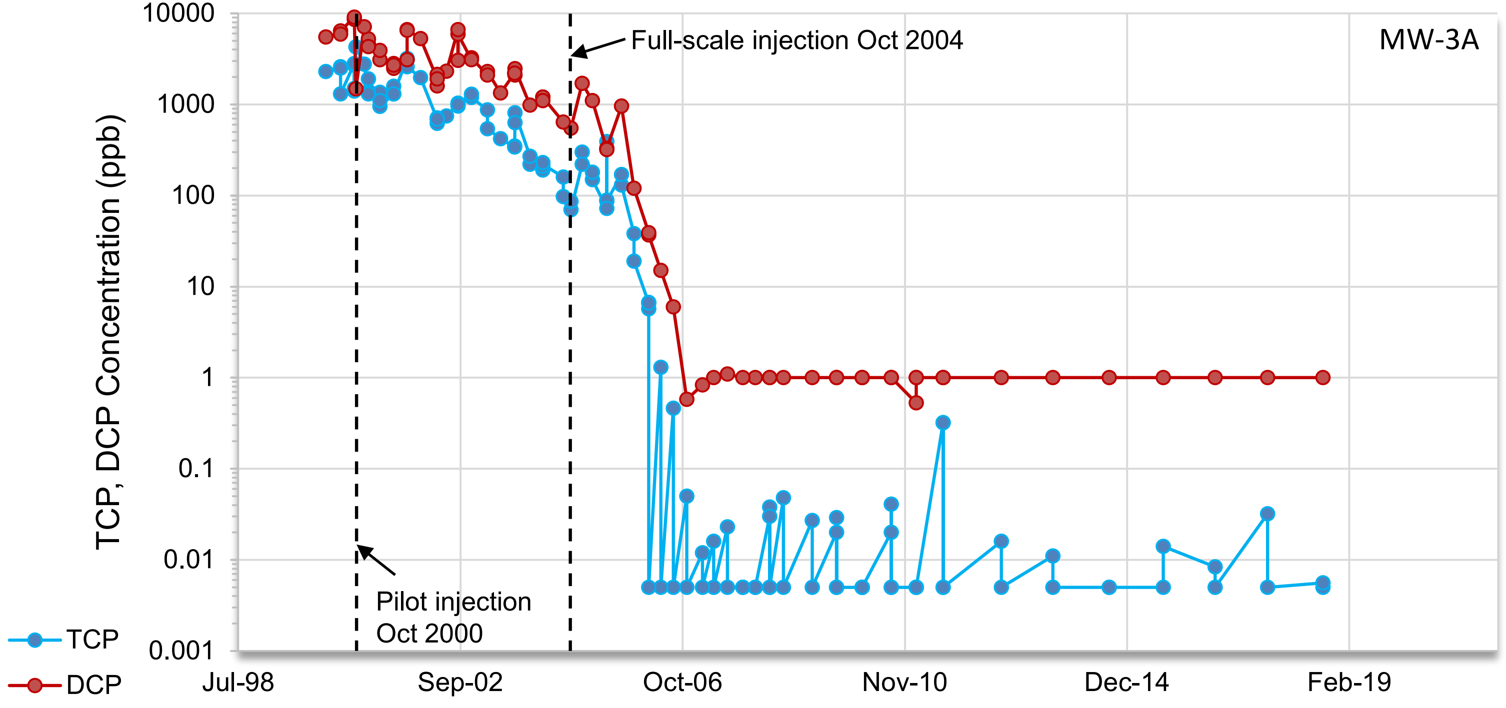
- Direct push injections of a slow-release electron donor
- Successful long-term reduction of TCP (and 1,2-DCP)
- Pilot led to full-scale implementation
- Understanding of remedial mechanisms remained unclear
- Recent Dhg testing inconclusive
  - ~9 years after full-scale injections

Case Study#1



MW-3A
Full-scale injection Oct 2004
Pilot injection
Oct 2000
TCP, DCP Concentration (ppb)
10000
1000
100
10
1
0.1
0.01
0.001
Jul-98
Sep-02
Oct-06
Nov-10
Dec-14
Feb-19
TCP
DCP

ISBR Development

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- Evaluate sensitivity to site specific parameters
  - pH
  - Concentration range
  - Presence of co-contaminants
  - In-situ conditions
- Biostimulation
  - Amendment type
- Bioaugmentation
  - Culture growth conditions
  - Dhg population

Lessons from ISBR Development

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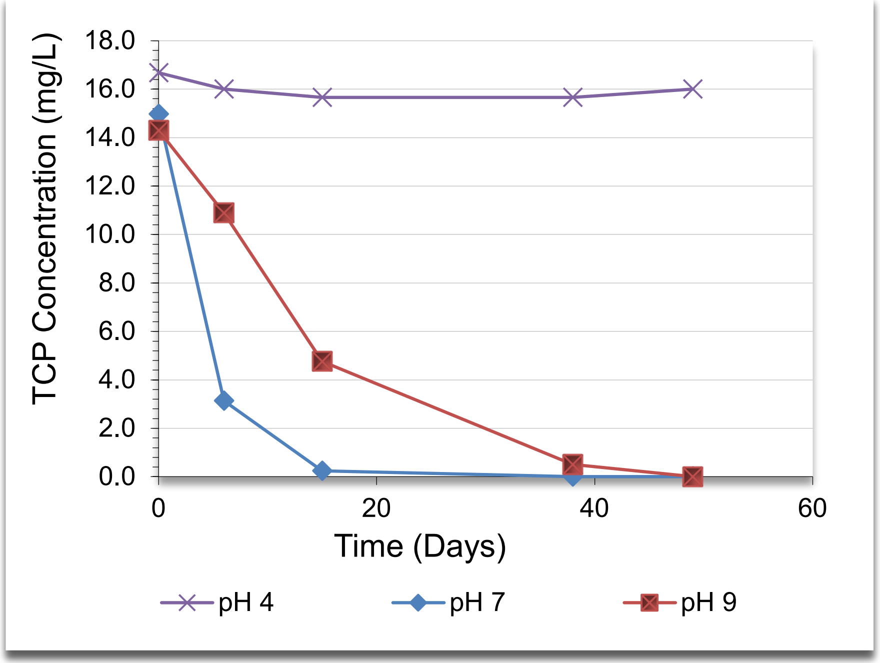
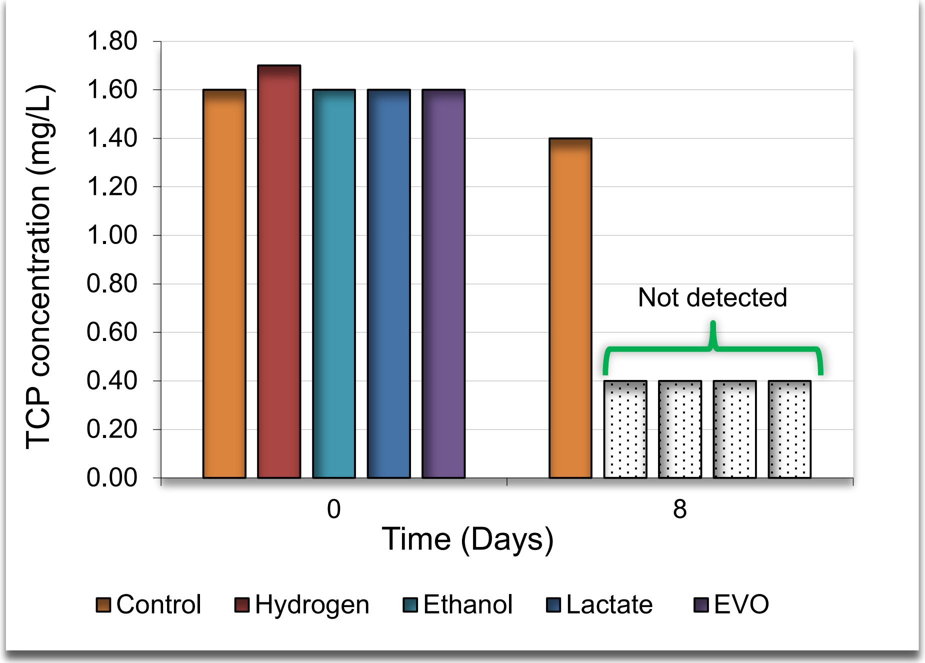
Effect of pH



Effect of amendment type



Lessons from ISBR Development

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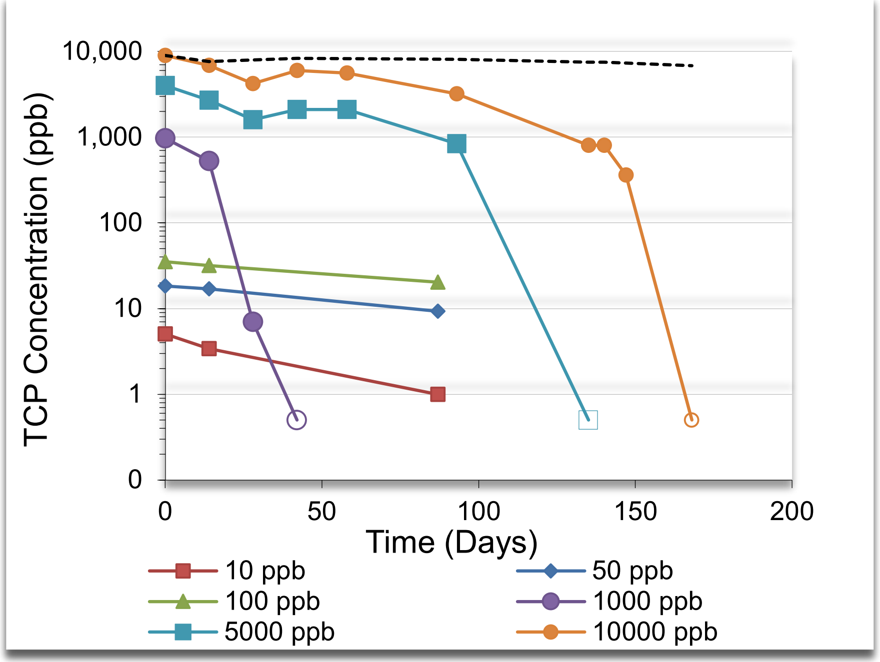
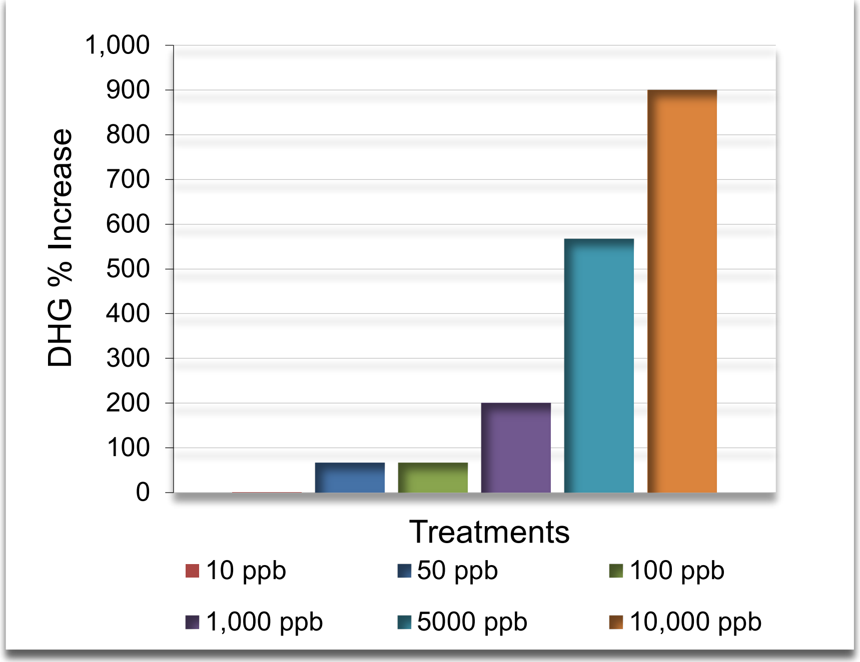
Effect of concentration



Effect on Dhg population



Case Study #2

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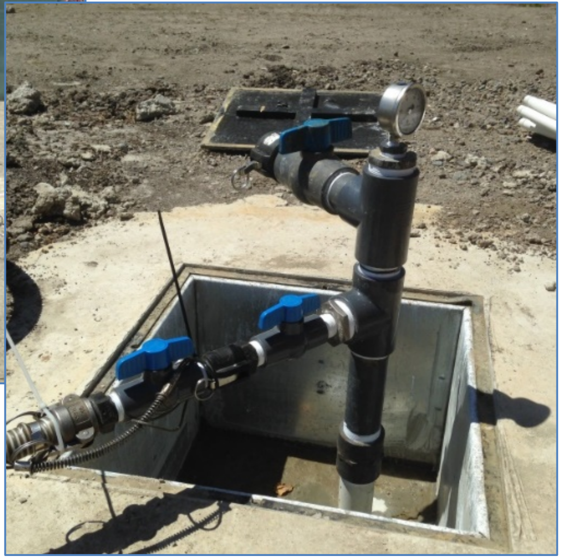
- Former agricultural chemical facility

Constituent	Max Site Conc.	State Goal
1,2,3-TCP	72 µg/L	0.005 µg/L (MCL)
1,2-DCP	680 µg/L	5 µg/L (MCL)
Nitrate (as N)	1,800 mg/L	--
Sulfate	415 mg/L	--

- Treatability study elements
  - Biostimulation with lactate and emulsified vegetable oil (EVO)
  - Bioaugmentation with KB-1®Plus
- Promising results with KB-1®Plus bioaugmentation

Case Study#2

- First-to-field bioaugmentation
- Injections - mid-May 2016
  - EVO/lactate electron donor
  - Bioaugmentation with KB-1®Plus (Dhg enriched)
  - Dhg not enriched on TCP



Case Study #2

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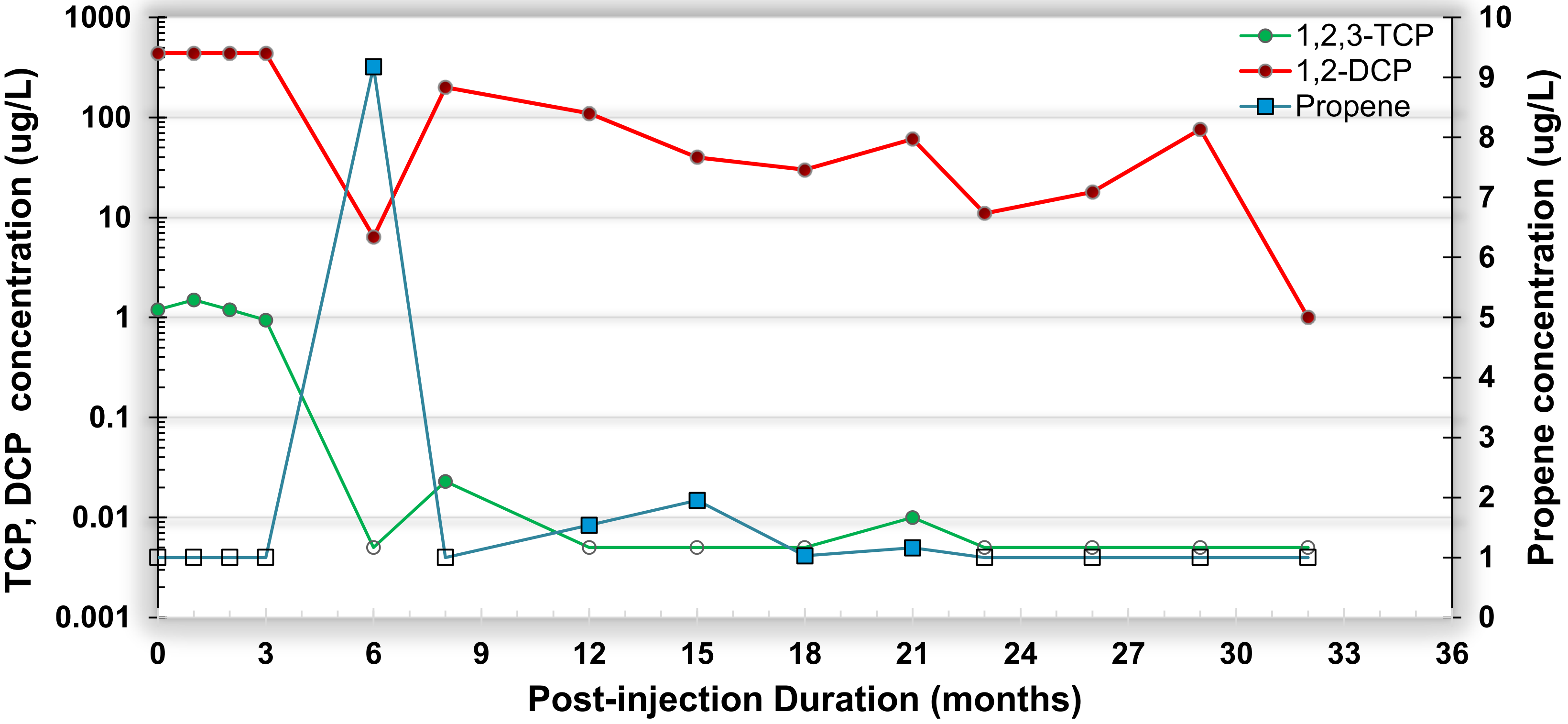
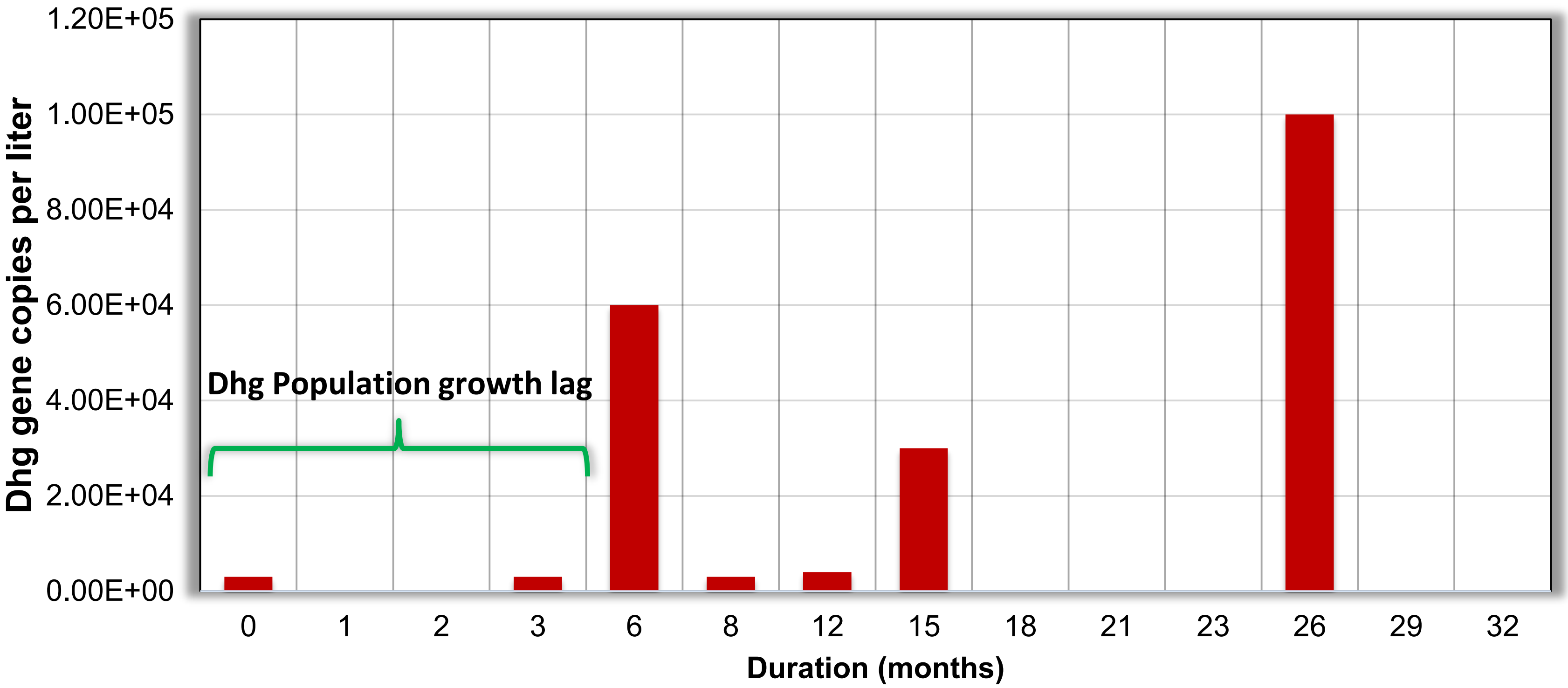


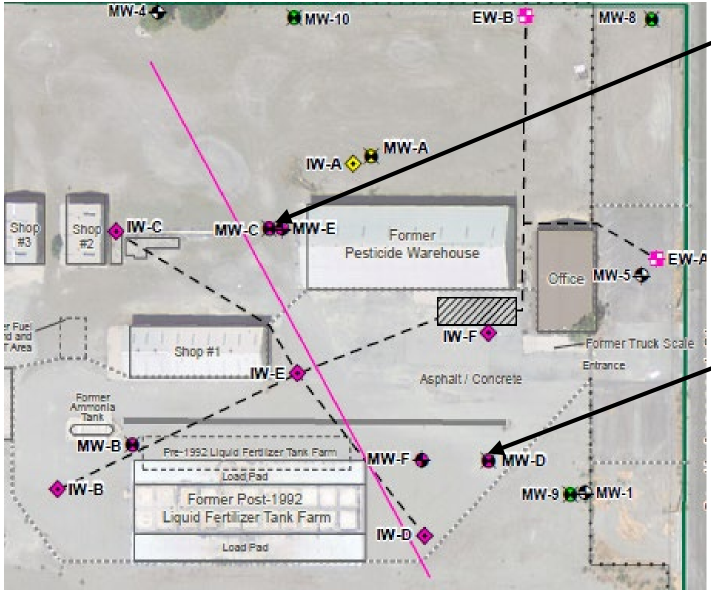
Case Study#2

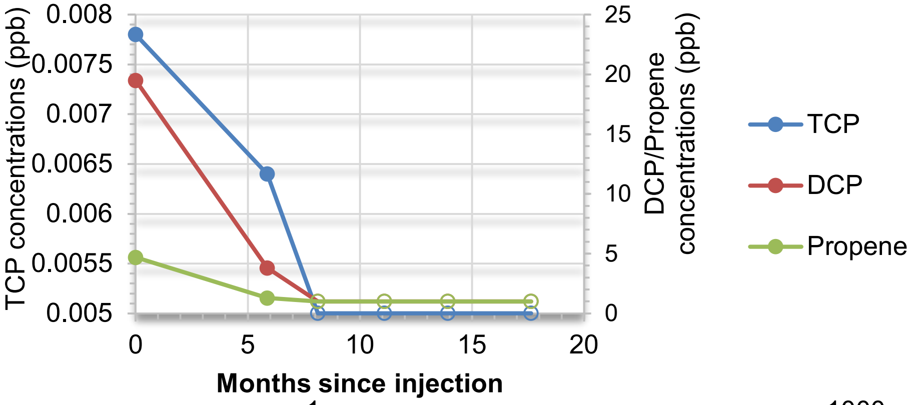


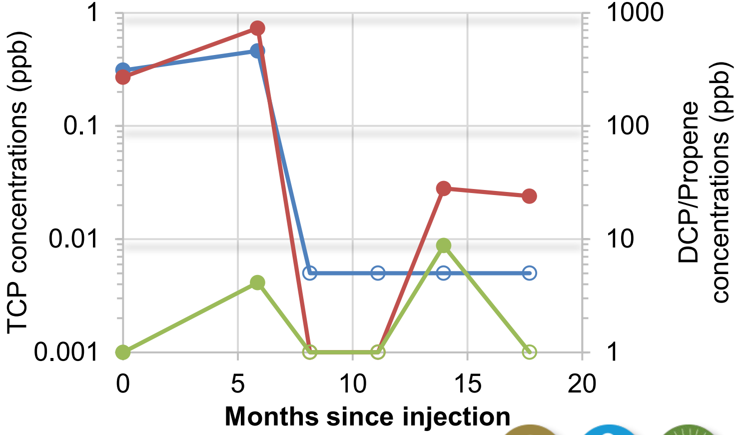
1.20E+05
1.00E+05
8.00E+04
6.00E+04
4.00E+04
2.00E+04
0.00E+00
Dhg gene copies per liter
Dhg Population growth lag
0
1
2
3
6
8
12
15
18
21
23
26
29
32
Duration (months)

Case Study#2

- **Full-scale Implementation**
  - ISB Recirculation System
  - Dhg enriched on low TCP concentrations







Conclusions/Summary

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- 1,2,3-TCP is an emerging challenge
  - Relatively high toxicity -> Low regulatory levels
  - Limited effective remedial applications
  - Biodegradation pathway not well understood until now

- ISBR parameters appear to be similar to chlorinated ethenes/ethanes
  - Potentially similar costs for implementation, with initial concentration considerations
  - Site specific conditions must be considered for effective implementation

Team & Acknowledgements

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