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Occurrence, Fate, and Remediation of the Emerging Contaminant 1,2,3-Trichloropropane

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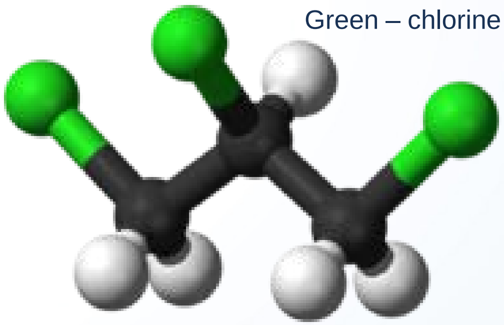
Why is 1,2,3-Trichloropropane an Emerging Concern for Groundwater?

- 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



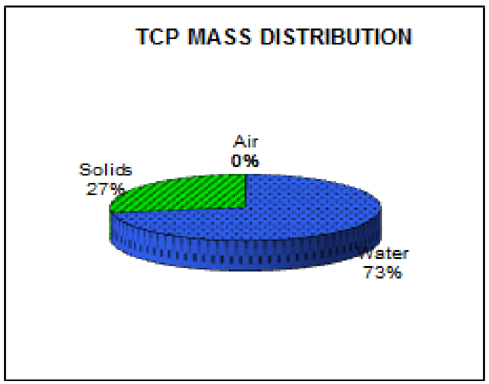
- Typically found at:
  - Ag-chem facilities, chemical manufacturing/storage facilities, military bases
  - Supply wells, particular those in agricultural areas (non-point sources)
- Classified as a likely or potential carcinogen to humans
  - EPA, US Health & Human Services, American Conference of Governmental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

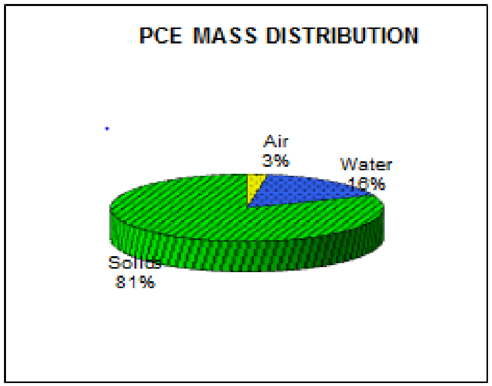
Why is 1,2,3-Trichloropropane an Emerging Concern for Groundwater?

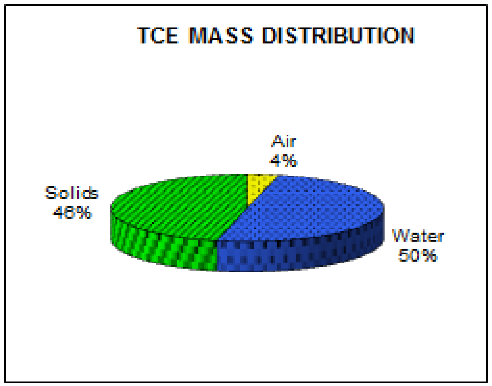
Low Vapor Pressure & Henry's Constant

Low Koc

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.

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Current Regulatory Climate

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. 2013):
	  • **0.003 µg/L** Cancer HRL
	  • **0.7 µg/L** Non-Cancer HRL

New Jersey	• **0.03 µg/L** Suggested MCL (est. 2009)
Other States?	• Coming Soon?

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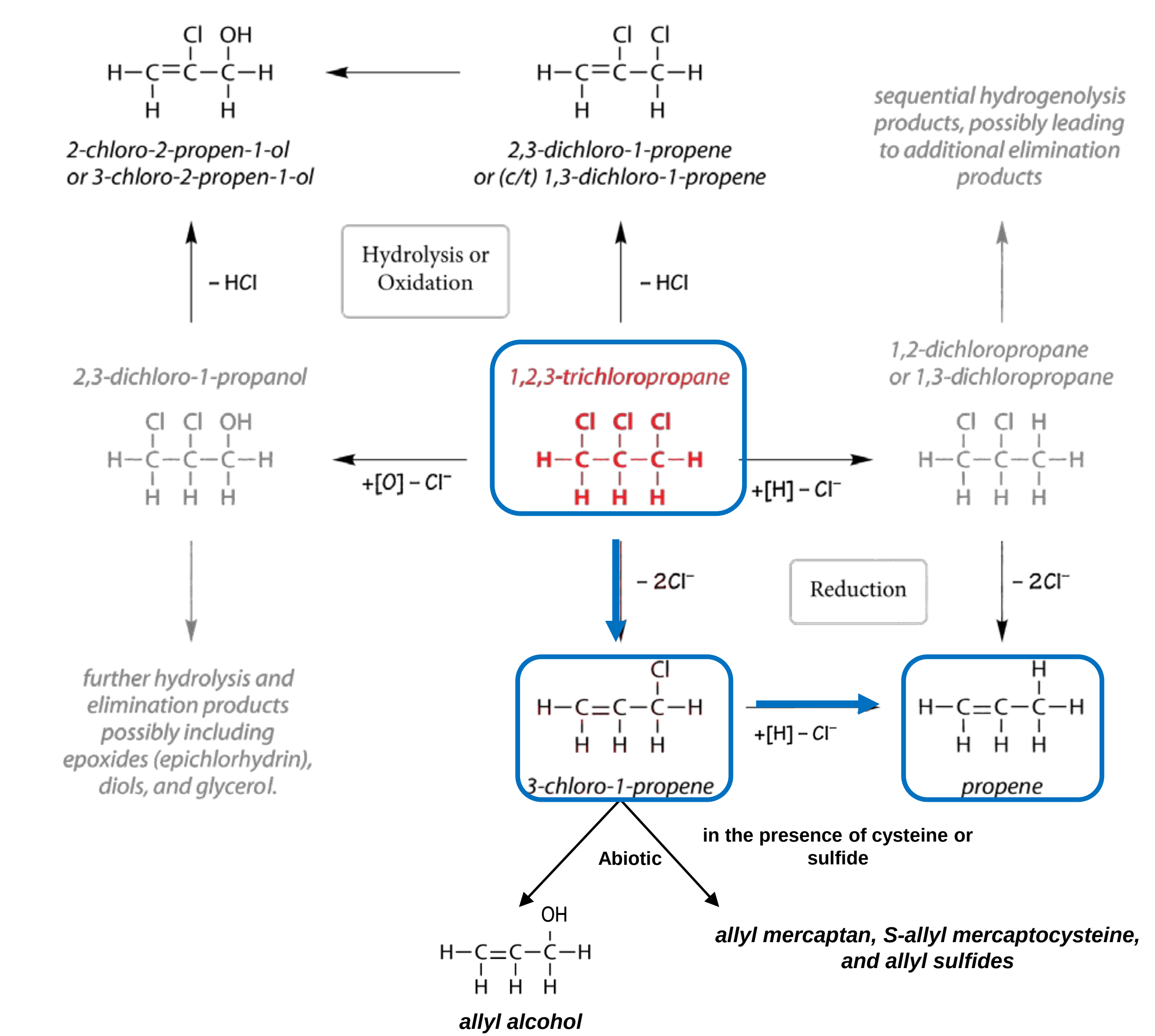
Groundwater Remediation

- 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 via Zero Valent Metals (ISCR)

1,2,3-TCP Degradation Pathway



Note: Degradation products transient in water and rarely observed

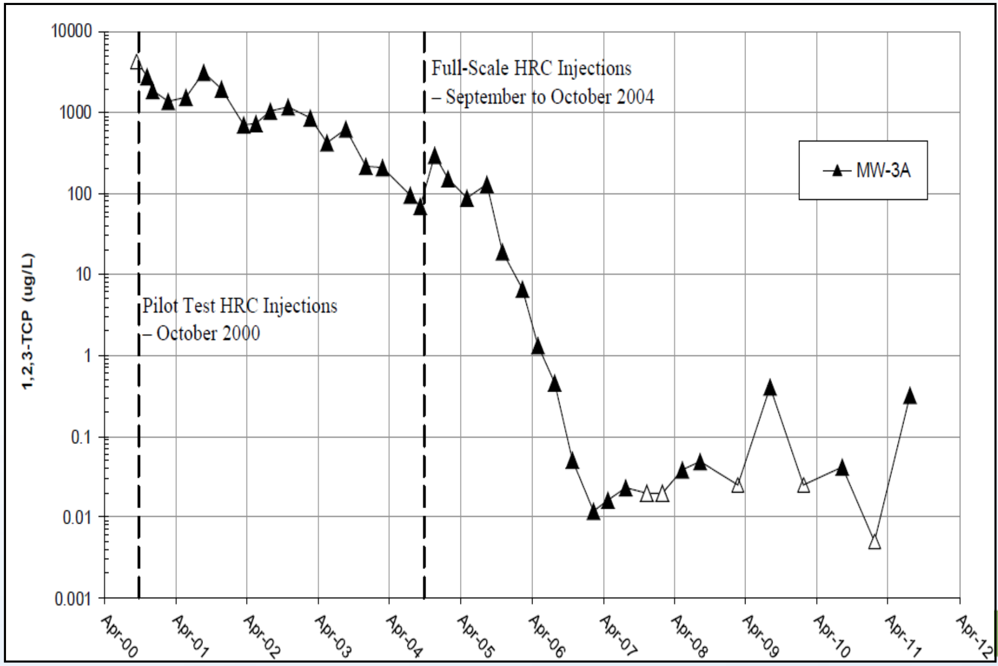
Primary pathway observed for ISBR and ISCR

In Situ Biological Reduction (ISBR)

- **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

ISBR - Case Study # 1

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



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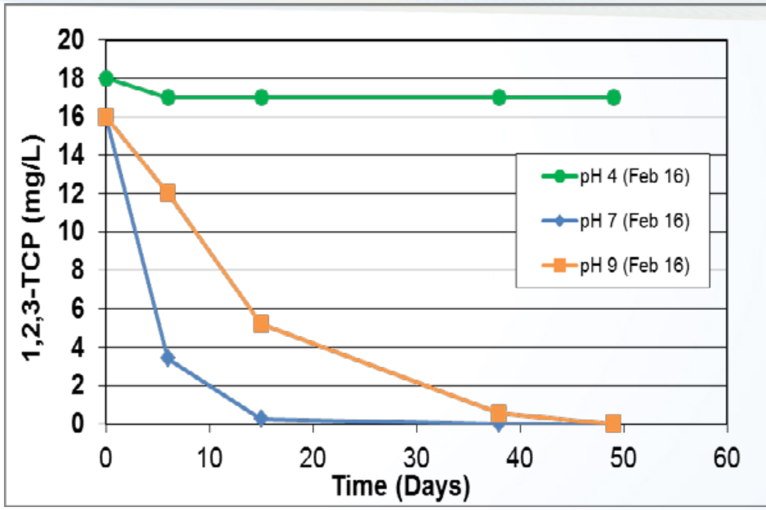
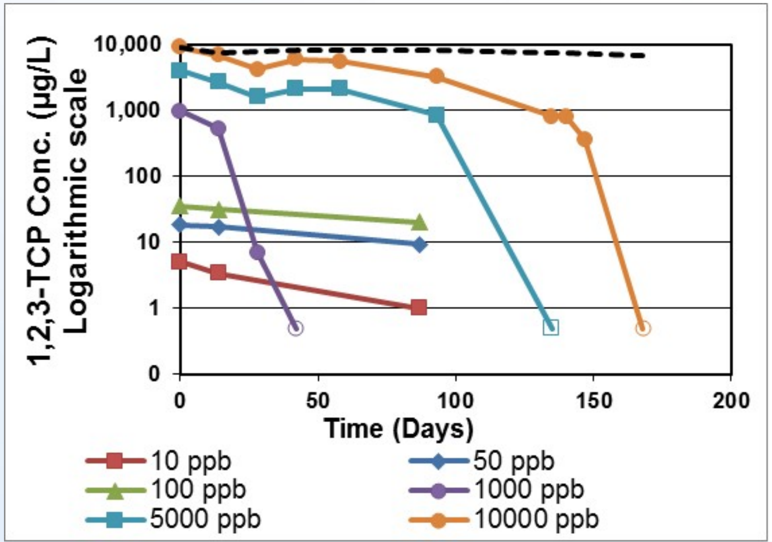
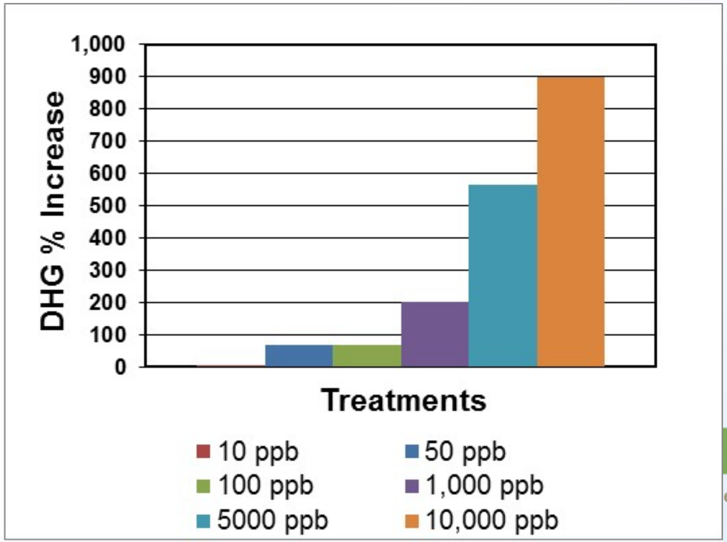
- **2014-Present** – Geosyntec/SiREM R&D to understand and develop ISBR for TCP remediation
  - Degradation pathway
  - KB-1®Plus inoculum size, culture acclimation, degradation rates
  - Evaluated practical concentration & pH ranges for effective ISBR
  - Mechanisms for degradation via biostimulation alone
- **2016-Present** – First field demonstration for bioaugmentation

Practical Ranges for Successful ISBR

- pH Ranges
  - Successful degradation at pH 5-9
  - Unsuccessful at pH 4
  - Optimal pH appears to be around 7-8
- Concentration Ranges
  - Degradation observed in laboratory from <10 to 10,000 ppb TCP
  - Optimal range observed 1,000 – 10,000 ppb







ISBR - Case Study # 2

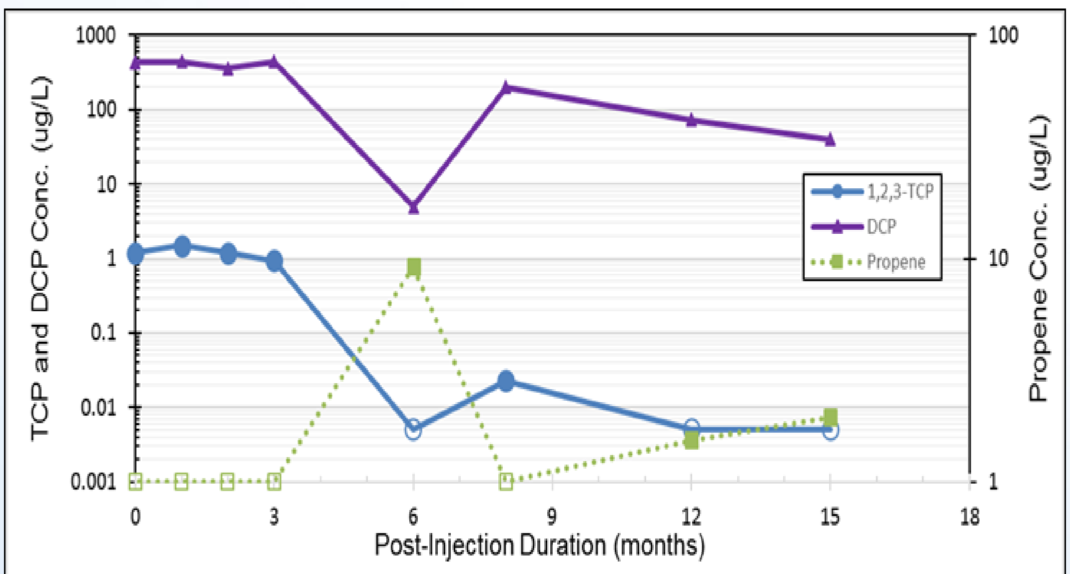
- Former agricultural chemical facility

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	10 mg/L (MCL)
Sulfate	415 mg/L	250 mg/L (Secondary MCL)

- Treatability study elements
  - Biostimulation with lactate and emulsified vegetable oil (EVO)
  - Bioaugmentation with KB-1®Plus
- Promising results with KB-1®Plus bioaugmentation
- Initiated pilot test in May 2016

ISBR - Case Study # 2

- First-to-field bioaugmentation
- Injections - mid-May 2016
  - EVO/lactate electron donor
  - Bioaugmentation with KB-1®Plus
- Results
  - Slow growth of Dhg population
  - Degradation lag period ~ 6 months



In Situ Chemical Reduction via Zero Valent Metals

- **Since Mid-2000s** - Use of zero valent metals has been evaluated and applied at TCP sites (bench- and pilot-scale)
  - Zero valent metal formulations assessed for TCP remediation include Zero Valent Iron (ZVI), Zero Valent Zinc (ZVZ), proprietary mixtures of ZVI and other compounds (e.g., EHC®)
- **2014** - Geosyntec completed first field demonstration using ZVZ in conjunction with Navy and OHSU. Additional R&D pending under ESTCP grant.

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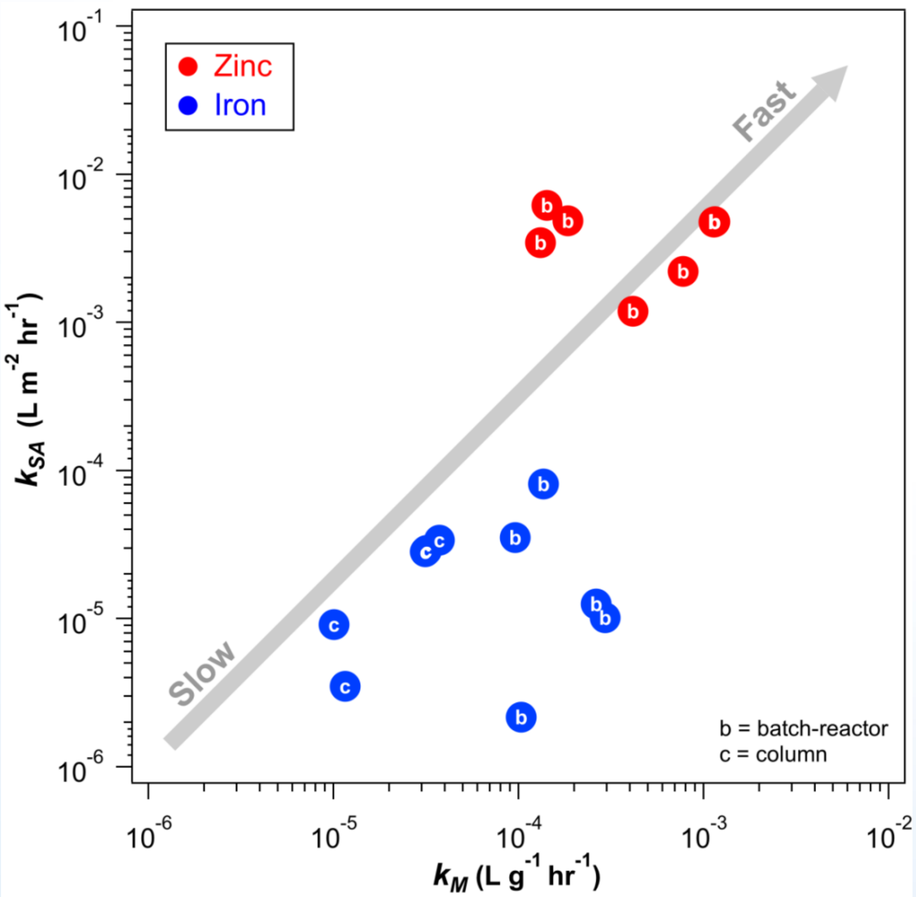
Comparison of TCP Degradation by ZVI and ZVZ

Kinetics of TCP degradation by ZVZ and ZVI



Sarathy, Tratnyek, et al., 2010

Figure format

- Surface area normalized rate constant (k_{SA}) vs. mass normalized rate constant (k_M)
- Good for complex comparisons of kinetics
- Reactivity increases up and to the right

Observations

- Both ZVZ and ZVI produce relevant degradation rates, but ZVZ rates significantly faster than ZVI

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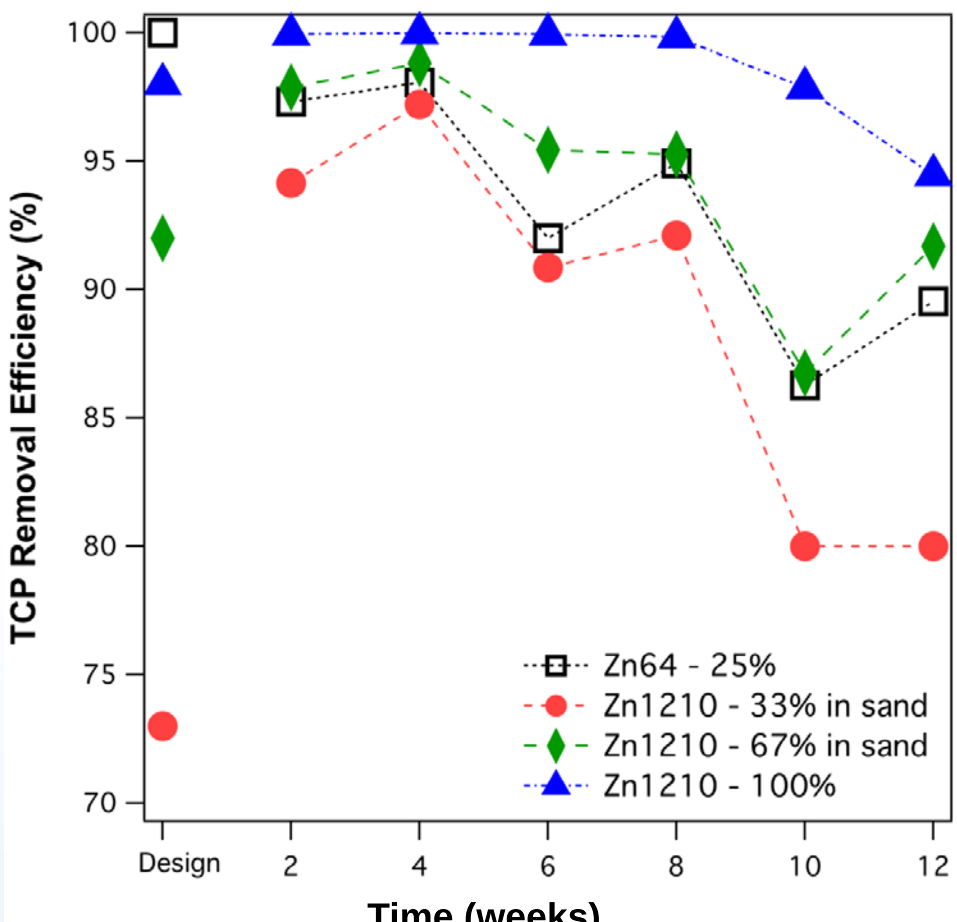
ZVZ Field-Scale Column Results

- Field-scale column testing conducted
  - 25% Zn64 Dust/75% Sand
  - 33% Zn1210 Powder/67% Sand
  - 67% Zn1210 Powder/33% Sand
  - 100% Zn1210 Powder
- All Zn1210 columns met 1,2,3-TCP treatment goal
  - Treatment efficiency declined over 12 weeks of operation
- Hydrogen gas produced
- Effluent dissolved zinc (0.04 to 0.20 mg/L) was below secondary MCL (5 mg/L)



Salter-Blanc, Suchomel, et al., 2012

ZVZ Pilot Study

- Military facility located in Southern California
  - 1,2,3-TCP present in source well at concentrations up to 10 µg/L, eventual remedial objective for 1,2,3-TCP expected to be 0.5 µg/L
- Pneumatic fracturing injections completed in July 2014 –injected ~14,000 pounds of Zn1210
  - Main issues – surfacing, process challenges (pump plugging, etc.)

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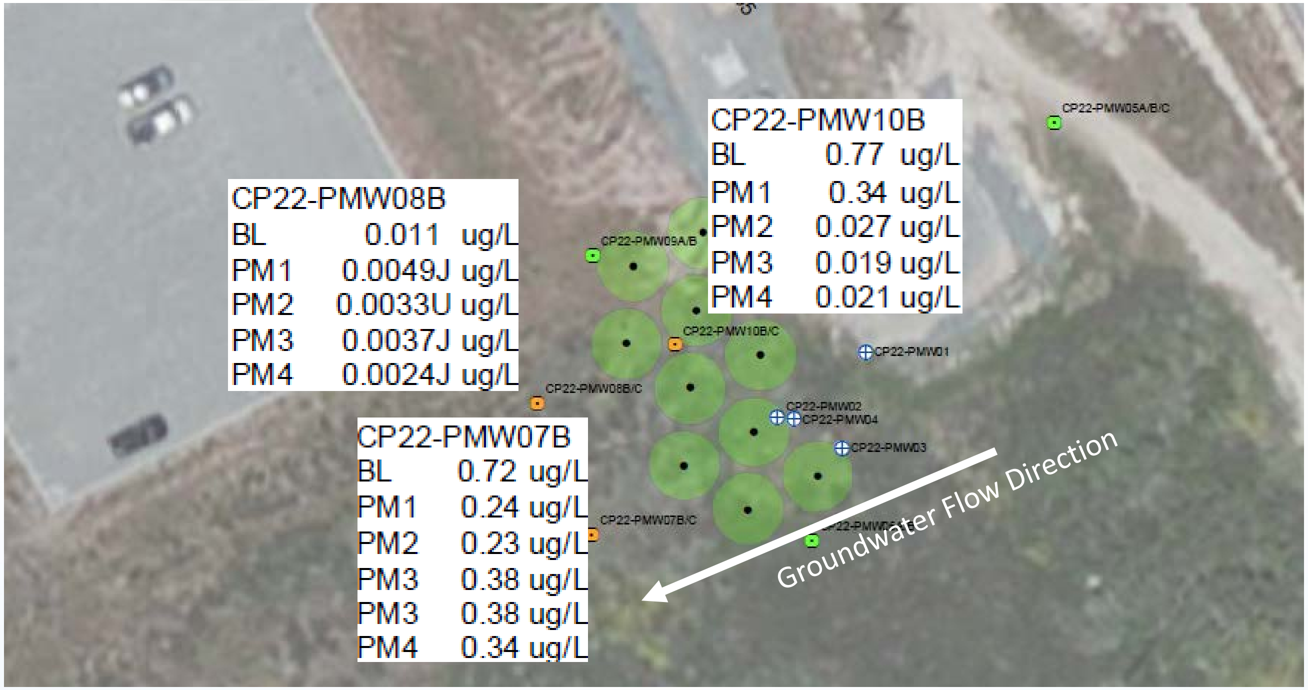
ZVZ Pilot Study Initial Results



- TCP degradation by ZVZ ongoing over year of post-injection monitoring
- No observed impacts to groundwater flow or secondary water quality impacts

Conclusions/Summary

- 1,2,3-TCP is an emerging challenge
  - Relatively high toxicity -> Low regulatory levels
  - Degradation pathway not well understood until now
- On-going advances in situ remediation provides more robust remedial technology alternatives for consideration
  - ISBR parameters appear to be similar to chlorinated ethenes/ethanes
    - Potentially similar costs for implementation, with initial concentration considerations
  - ISCR with ZVZ appears to be effective at low initial concentrations
    - Long-term validation of technology is ongoing

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