CHEMCO inc.
CANADIAN LEADER IN
ENVIRONMENTAL EXPERTISE
& SPECIALIZED PRODUCTS

EOS Remediation, LLC

Addressing High Concentration Solvent Sites with a Combined-Remedy: Emulsified Oil and ZVI

Presented by Jean Paré, P. Eng.
October 2021

remediation technologies symposium 2021

www.chemco-inc.com

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EOS Remediation, LLC

Presentation Outline

- ✓ About Chemco
- ✓ Introduction: Enhanced Reductive Dechlorination
- ✓ Properties of Emulsified Soybean Oil
- ✓ Design Parameters versus Site Conditions
- ✓ Case Study In-Situ Remediation Performance
- ✓ Acknowledgement

About us

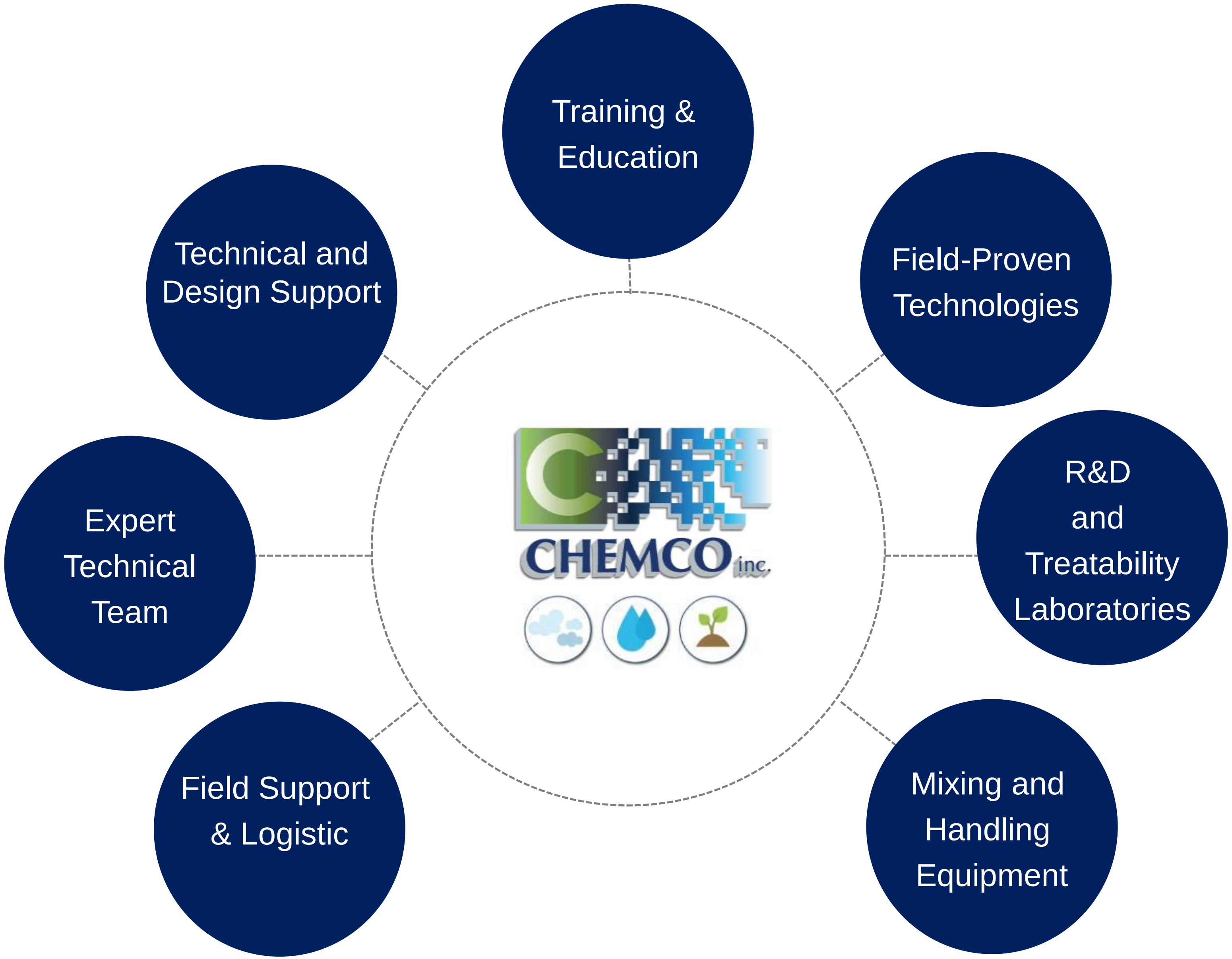
Canadian Company founded in 1988

- **Production and warehouses throughout Canada**
  - Quebec
  - Ontario
  - Alberta
  - British Columbia
- **Sectors of activity:**
  - Industrial and Municipal Potable & Waste Water
  - **Contaminated Soil and Groundwater**
  - Air, Odours and Atmospheric Emissions (Activated Carbon, filtering medias)
  - Process Water & Thermal Exchange Fluids (Glycols)
  - Drilling Fluids (Oil and Gas & Diamond exploration)
  - Aircraft De-icing Fluids

CANADIAN LEADER IN

ENVIRONMENTAL EXPERTISE
& SPECIALIZED PRODUCTS

- Chemical Oxidation
- Chemical Reduction
- Co solvent-Surfactant soil Washing
- Enhanced Bioremediation
- Permeable Reactive Barrier Amendments
- Metals Stabilization



Our product and services

Excellence & Science through proud Suppliers & Partners

ADVANCED OXIDATION TECHNOLOGY (AOT) *Since 2005*

PeroxyChem *Since 2005*

CARBONE CANADA INC *Since 2014*

BION BIOCONSERVACION *Since 2014*

CARUS® *Since 2014*

EthicalChem An Ethical Solutions, LLC Division *Since 2016*

EOS EOS Remediation, LLC *Since 2016*

ChemBio Formulation *Since 2017*

SiREM *Since 2017*

Höganäs *Since 2018*

Science-driven Environmental Remediation Products:
Development, Validation, Commercialization

- **Developer and Formulator of Remediation Technologies and Products**
  - **Emulsified vegetable oils for Chlorinated Compounds, Nitrates, Perchlorate, Hex Cr**
  - **Electron acceptors for BTEX, MTBE, GRO/DRO, TPH, Non-chlorinated compounds**
  - **Zero Valent Irons Abiotic Degradation and Sulfide Sequestration**
  - **pH Buffers for Aquifer Adjustment and Metals Immobilization**
  - **Research and Development in Emerging Contaminants**
- **In operation since 2002**
- **Headquartered in Research Triangle Park NC, USA**

EOS Remediation, LLC

CHEMCO inc.

The ONLY patented EVO technology in Canada (#2394068)

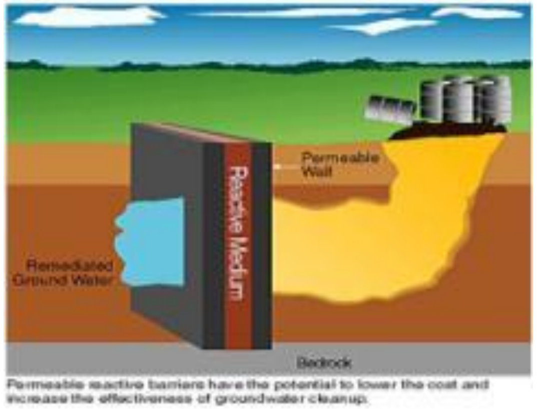
www.eosremediation.com

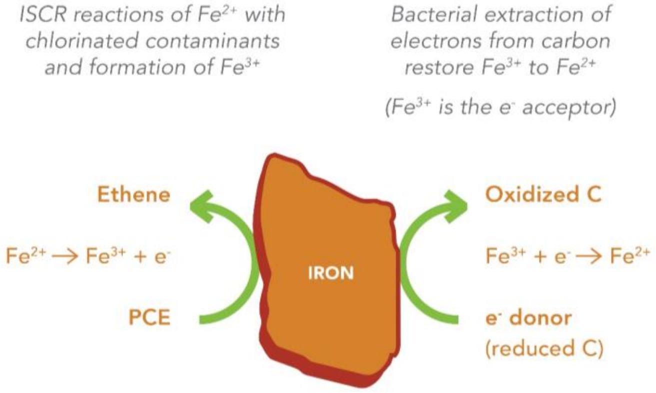
Woman-owned small business

What is In Situ Chemical Reduction?

- ✓ Introduction of a reducing material or generating reducing species to help degrade toxic organic compounds or immobilize metals in the desired area
- ✓ The most commonly used reductant is zero valent iron (ZVI)
- ✓ Possible introduction of organic substrates to produce enhanced conditions to conduct microbial reduction
- ✓ Degradation / Immobilization of contaminants by abiotic or biotic processes
- ✓ Transfer of electrons from reduced metals (ZVI, ferrous iron) or reduced minerals (magnetite, pyrite) to contaminants including chlorinated organics and heavy metals
- ✓ Permeable Reactive Barriers (PRB’s) constructed using ZVI = example of simple ISCR
- ✓ Combined ZVI/ fermentable carbon reagents are an example of advanced ISCR

Source: EPA





ISCR Terminology

- **Electron Donor**: reducing agents including elemental iron (ZVI), reactive minerals (iron sulfides)
- **Electron Donor**: fermentable organic carbon (many)
- **Electron Acceptor**: contaminants including pesticides (DDT, Dieldrin), herbicides (2,4-D), chlorinated solvents (PCE, TCE, CT), nitroaromatic explosive compounds (TNT, DNT), and heavy metals (arsenic, chromium)

Chemical Reduction Advantages

- ✓ Low Cost and Efficient. Sustainable Technology.
- ✓ Uses natural processes and groundwater flow.
- ✓ Easy to implement and using non dangerous material.
- ✓ Can be used by itself and with other treatment technology to remediate soils and groundwater.
- ✓ Simultaneous treatment of chlorinated organic compounds and heavy metals in the soil or water
- ✓ Usually NOT Applicable where contaminants are present at very high (i.e., % w/w) concentrations
- ✓ Combination of ZVI and a fermentable carbon (e.g. emulsified oils generally does not result in accumulation of toxic products of partial contaminant degradation (i.e., little or no VC from TCE)

Chemical Reduction
In Situ/Ex Situ – Application range

Chlorinated Compounds

- ✓ PCE, TCE, cDCE, 11DCE, VC
- ✓ 1122TeCA, 111TCA, 12DCA
- ✓ CT, CF, DCM, CM

Herbicides, Pesticides

- ✓ Toxaphène, Chlordane, Dieldrin, Pentachlorophenol

Energetics

- ✓ TNT, DNT, RDX, HMX, Perchlorate

Metals and metalloids

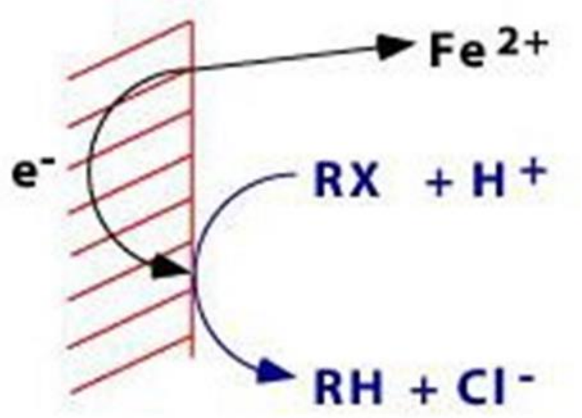
- ✓ As, Cr, Pb, Zn, Cd, Hg, Cu, Cr, Ni, Sb, Co

Under aerobic conditions you can target

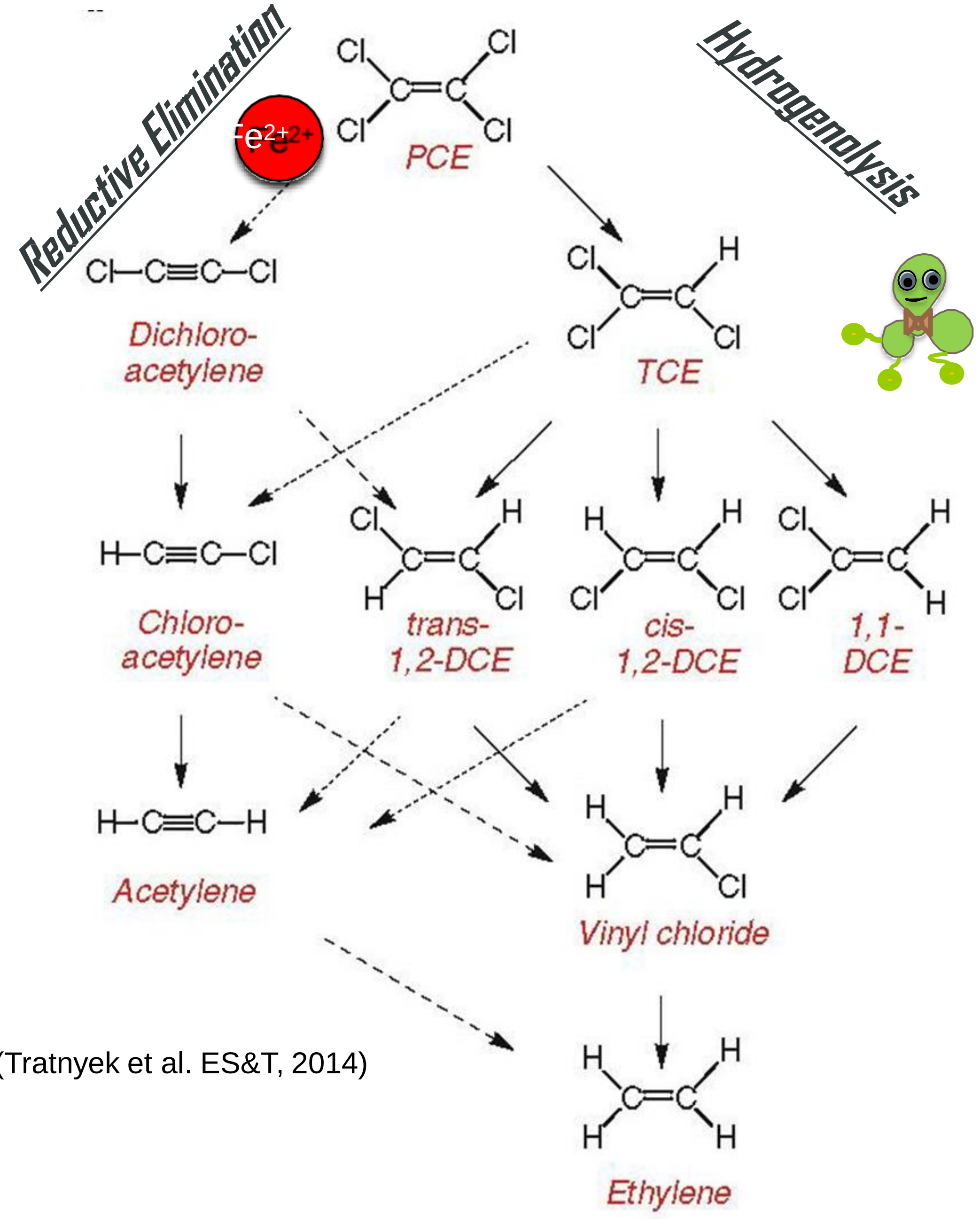
HAP, phthalates, perchlorate, petroleum hydrocarbon

- In Red: need to have an organic substrate and/or a ZVI/carbon combination

Abiotic Dechlorination



- CVOC (RX) must 'sorb' to metal surface
- RX loses Cl and gains H
- Requires direct contact between CVOC and iron particle

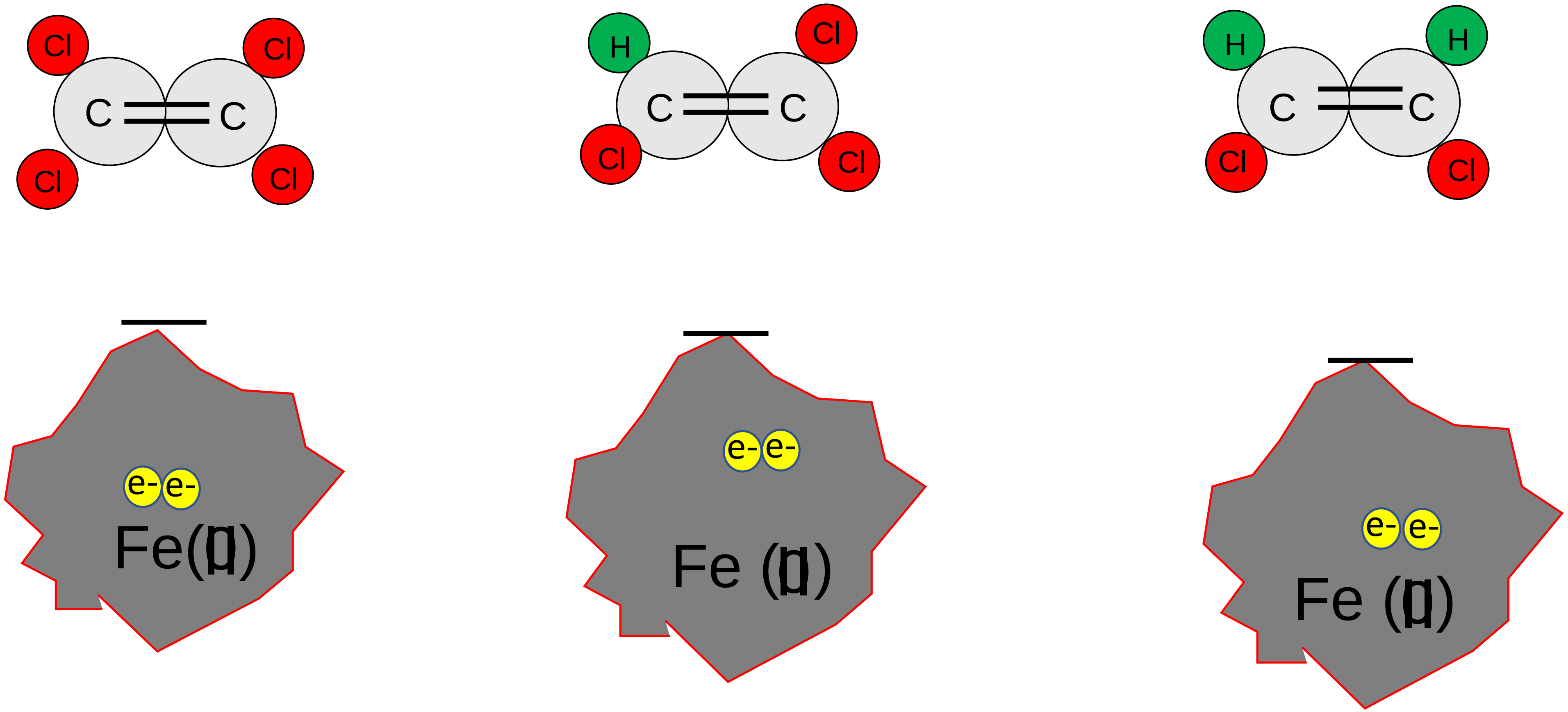


(Tratnyek et al. ES&T, 2014)

Direct Dechlorination Reactions with ZVI

β elimination (abiotic) pathway

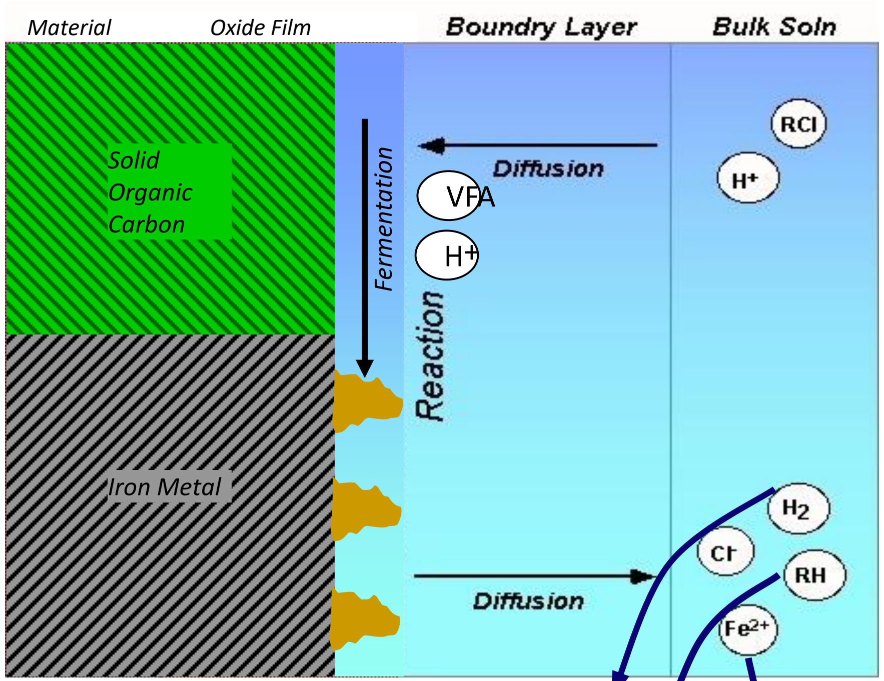
Tetrachloroethylene / Dichloroacetylene | Trichloroethylene / Chloroacetylene | Dichloroethene / Acetylene



Chemical Reduction-Mechanism

Mechanism	Material	Description
Direct Chemical Reduction	ZVI or Carbon Substrates	• Redox reaction at iron surface where solvent gains electrons and iron donates electrons • Abiotic reaction *via* beta-elimination
Indirect Chemical Reduction	ZVI or Carbon Substrates	• Surface dechlorination by magnetite and green rust precipitates from iron corrosion
Stimulated Biological Reduction	Carbon Substrates	• Anaerobic reductive dechlorination involving fastidious microorganisms • Strongly influenced by nutritional status and pH of aqueous phase
Enhanced Thermodynamic Decomposition	Carbon Substrates	• Energetics of dechlorination are more favorable under lower redox conditions generated by combination of ZVI and organic carbon

Carbon + ZVI Synergies Generate Multiple Dechlorination Mechanisms: ISCR



1. Direct Iron Effects:

Hydrocarbon generation:

2. Indirect Iron Effects: Dissolved iron precipitates to reactive minerals

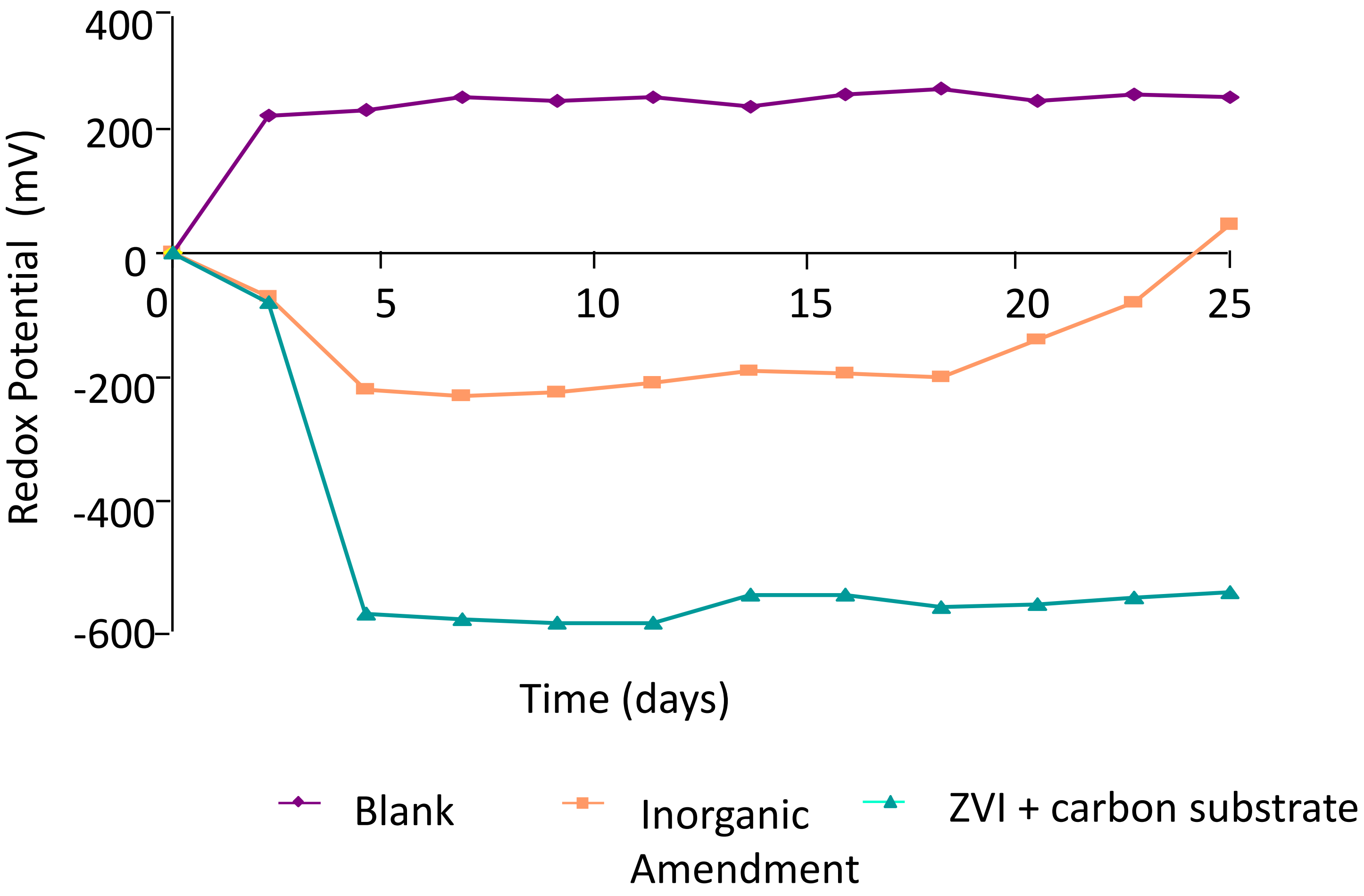
3. Biostimulation:

- Serve as electron donor and nutrient source for microbial activity
- VFAs reduce precipitate formation on ZVI surfaces to increase reactivity
- Facilitate consumption of competing electron acceptors such as O_2, NO_3, SO_4
- Increase rate of iron corrosion/H_2 generation

4. Enhanced Thermodynamics:

- Very low redox reached by addition of fermentable carbon and ZVI (-500 mV)
- Two processes simultaneously reduce Eh
- Enhances kinetics of dechlorination reactions via higher electron/H^+ pressure

Redox Potential evolution during a reductive phase treatment period



Enhanced Reductive Dechlorination

- There are more microbes in a teaspoon of healthy soil than there are
- humans on earth!
- As of 2018 there are an estimated 1 billion species of bacteria
- One group; dehalo-respiring Bacteria
  - Capable of breaking down PCE & TCE *(chlorinated solvents)*
  - Specific organism able to completely detoxify: *Dehalococcoides* (DHC)

…**BUT,** DEHALO COCCOIDES NEEDs HYDROGEN to grow

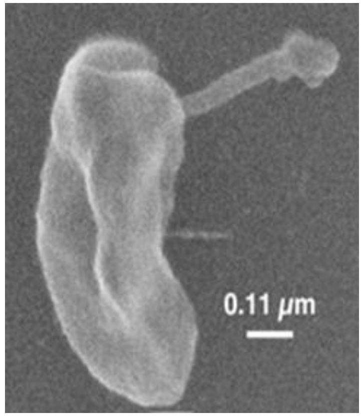
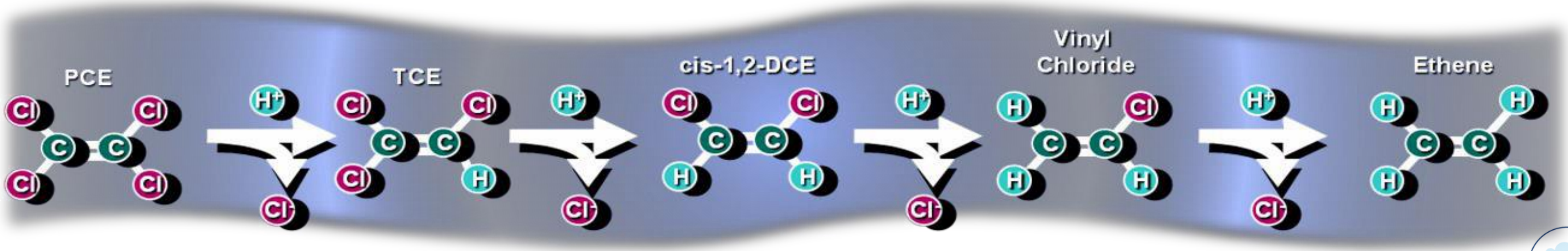


Image by the late Dr. Robert P. Apiarian and Jeanette Taylor, at the Integrated Microscopy & Micro analytical Facility (IM&MF), Department of Chemistry, Emory University, Atlanta, GA

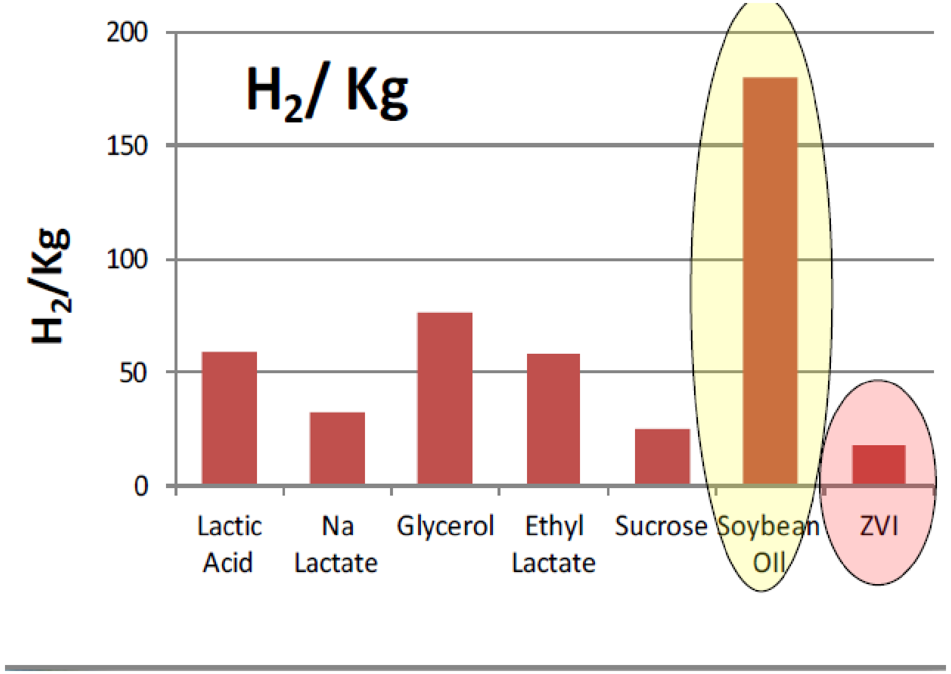


Biological breakdown of PCE to Ethene (reductive dichlorination)

Substrate selection: Hydrogen Factor + complexity = persistency

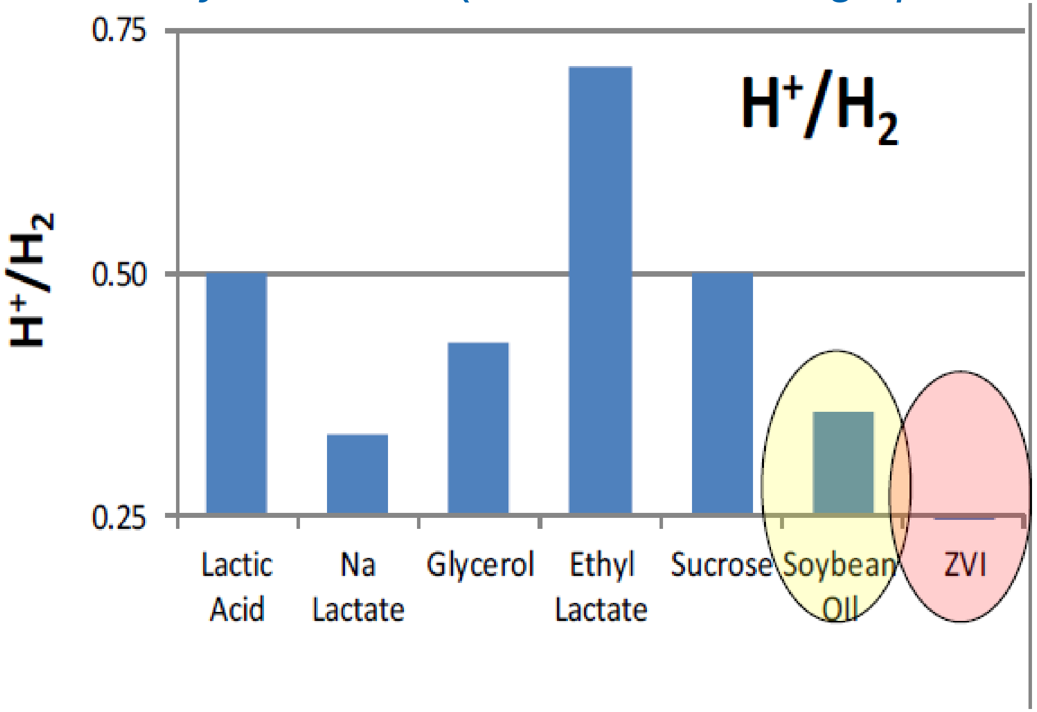
Substrate	Formula	MW	H_2O	H_2 per mole	H^+ per mole	H^+/H_2	H_2 / Kg
Lactic Acid	$C_3H_6O_3$	90	12%	6	3	0.50	59
Na Lactate	$C_3H_6O_3$	112	40%	6	3	0.33	32
Glycerol	$C_3H_8O_3$	92	0	7	3	0.43	76
Ethyl Lactate	$C_5H_{10}O_3$	118	2%	7	5	0.71	58
Sucrose (molasses)	$C_{12}H_{22}O_{11}$	342	65%	24	12	0.50	25
Soybean Oil	$C_{56}H_{100}O_6$	873	0	157	56	0.36	180
Lecithin	$C_{42}H_{82}NO_8P$	758	100%	122	39	0.321	124
ZVI	Fe^0	56	0	1	Consumes acidity		18

Bioremediation & pH



1. ***Soybean oil produces lots of hydrogen and moderate acidity***
2. ***ZVI produces a small amount of hydrogen but consumes acidity***

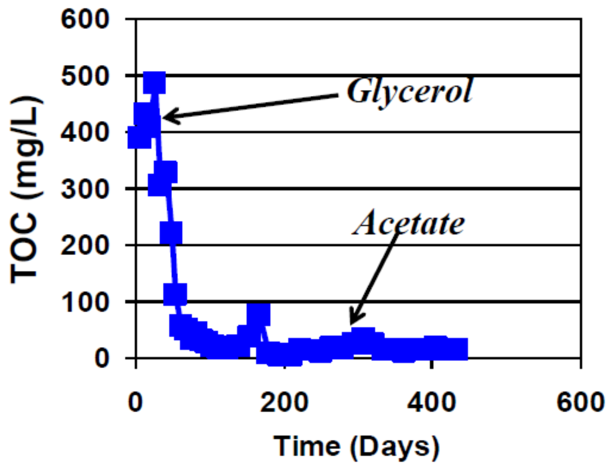
Acidity Produced (can & does change pH of the aquifer)



Properties of Emulsified Soybean Oil

- **Soybean oil hydrolysis**
  - 1 glycerol ($C_3H_8O_3$)
  - 3 long chain fatty acids ($C_{18}H_{32}O_2$)
  - Fermentation releases both H_2 and fatty acids
- **PCE & TCE → DCE**
  - Use BOTH H_2 and acetate (short-chain fatty acid)
- **DCE & VC → Ethene**
  - Use ONLY H_2
  - H_2 turns over very rapidly (Fe(III), SO_4, CH_4)
  - H_2 only occurs near fermentable carbon
- **Sources of Hydrogen**
  - Vegetable oil
  - Proprionate, butyrate, valerate, , ,
  - NOT acetate

TOC in Emulsion Treated Columns

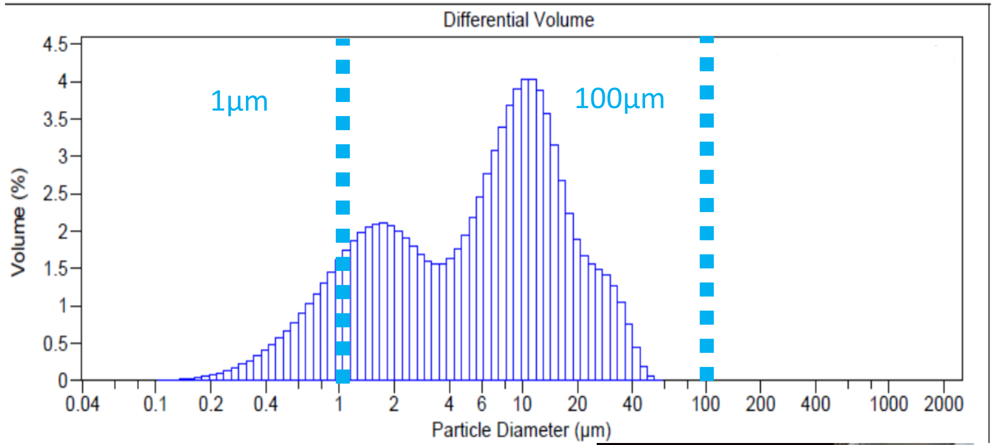


EOS Substrate Properties

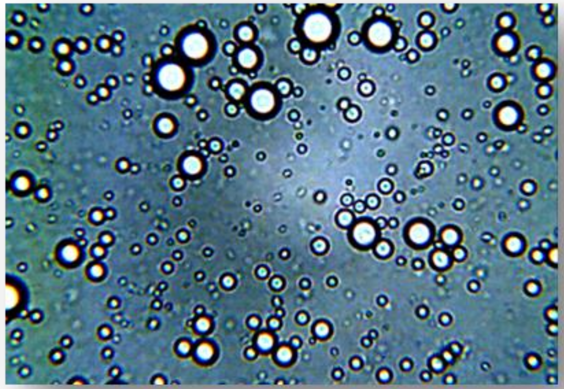
Properties of “water-less” oil products

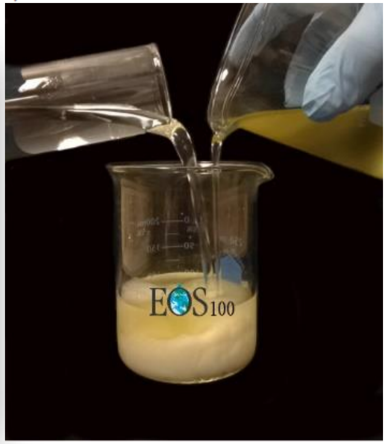
EOS 100

Oil droplet diameter (PSD Analysis)



at 1000x

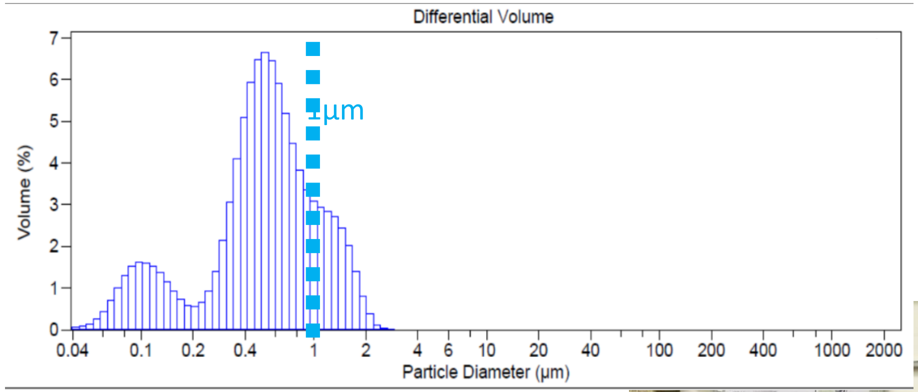




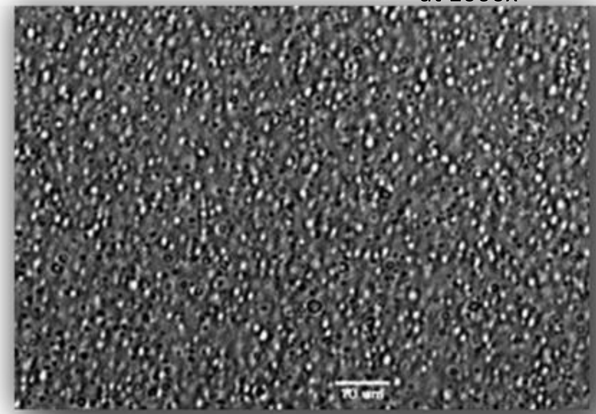
Mean Droplet ~ 10 microns

Properties of traditional EVO products

EOS Pro



at 1000x

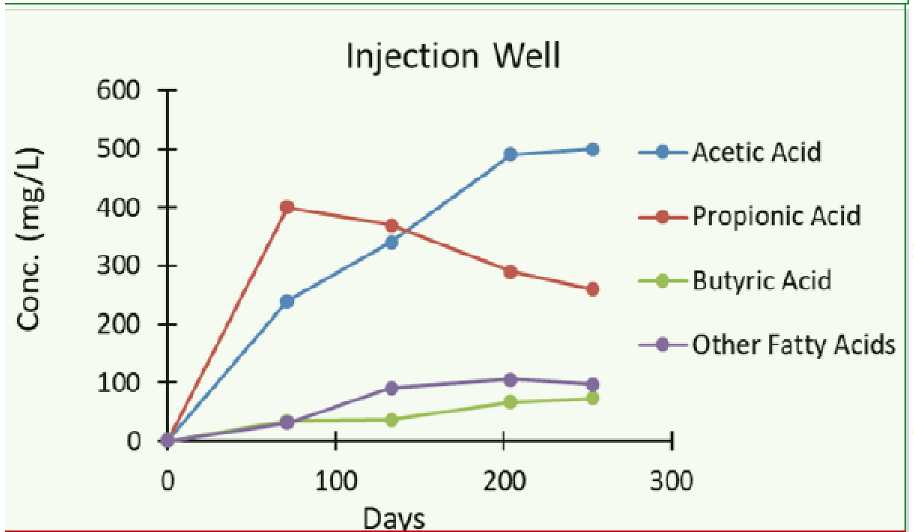


IBC Tot

Mean Droplet ~ 1 micron

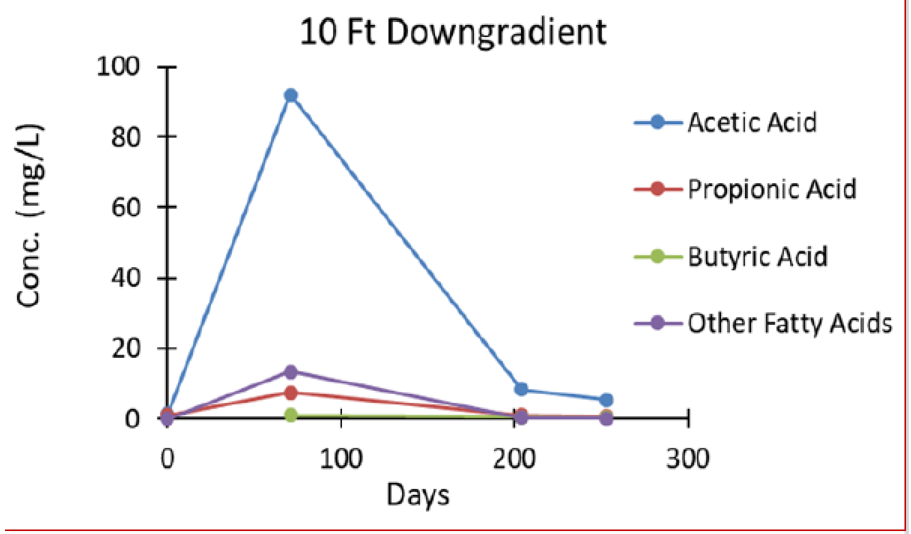
Distribution of Amendment is key

***Complete** dechlorination of TCE → Ethene (non-toxic)*

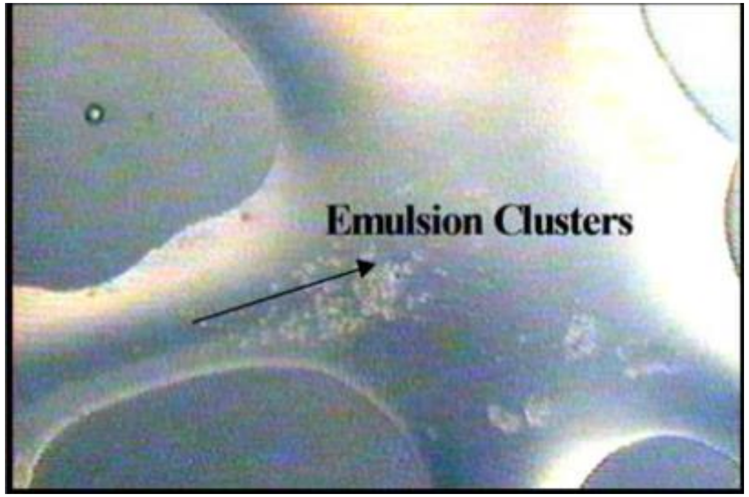


Technology is working

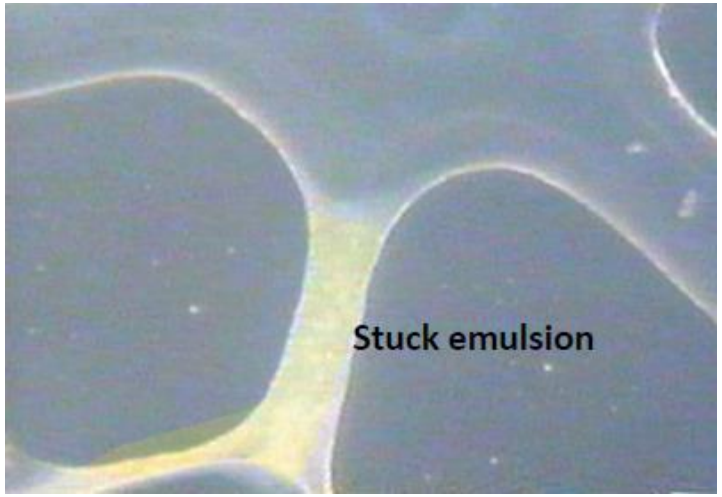
***Good** TCE → DCE but **Poor** DCE → Ethene*



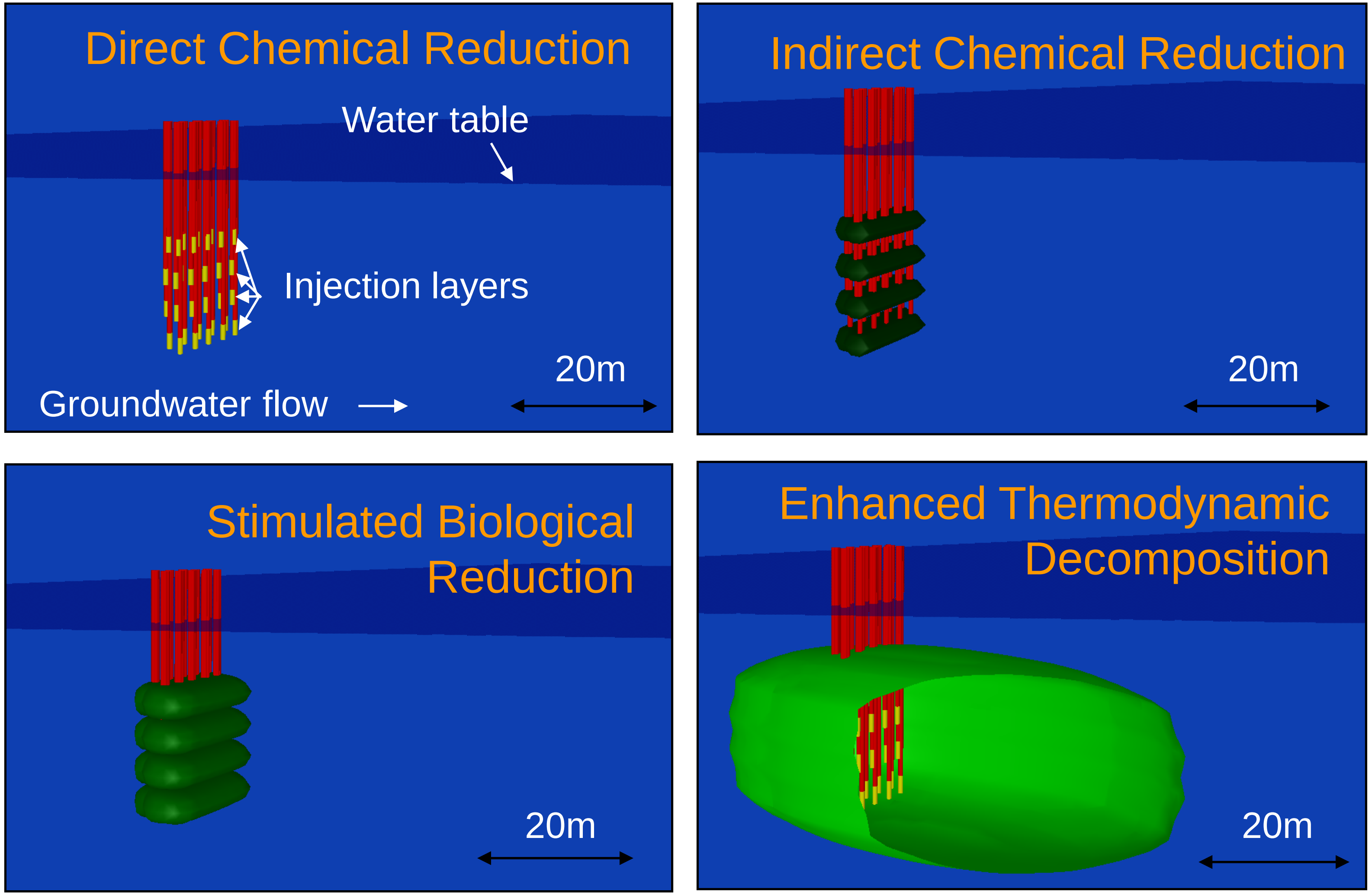
Poor oil distribution



- Emulsion transport is very similar to colloid transport (e.g. bacteria)
  - Small oil droplets (~ 1 µm) easily pass through most pores (30 - 100 µm)

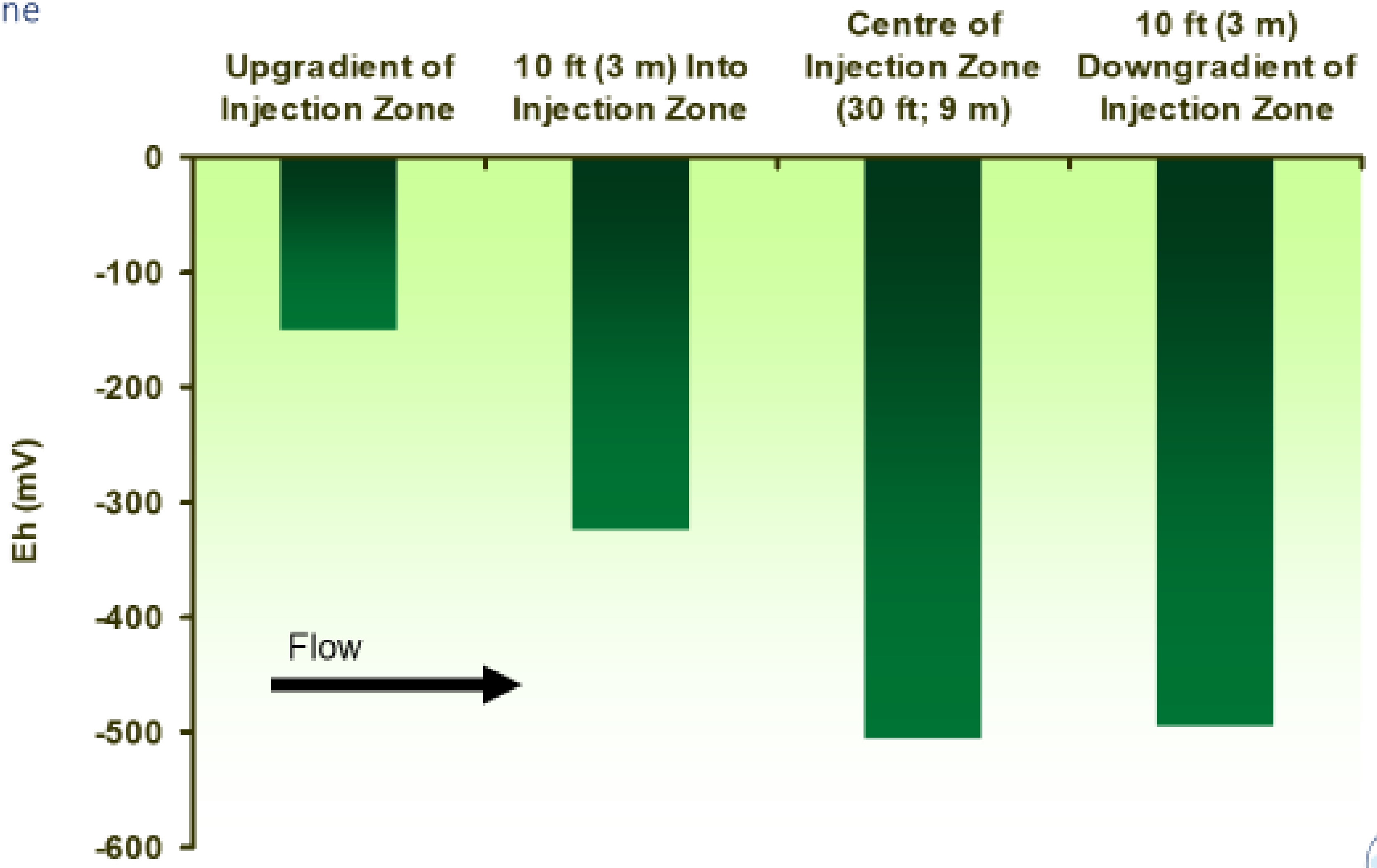


ZVI + Carbone Synergies brings multiples dechloration mechanism



ZVI + FOC blend influence on Redox potential in the subsurface aquifer

60 ft (18 m) injection zone

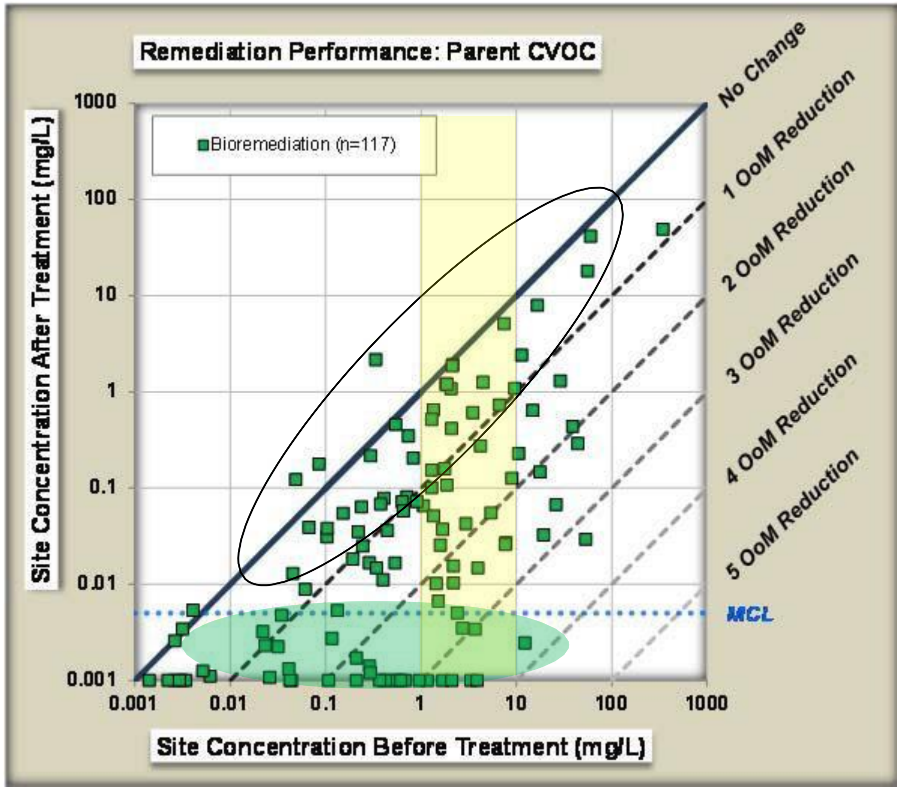


Source: URS

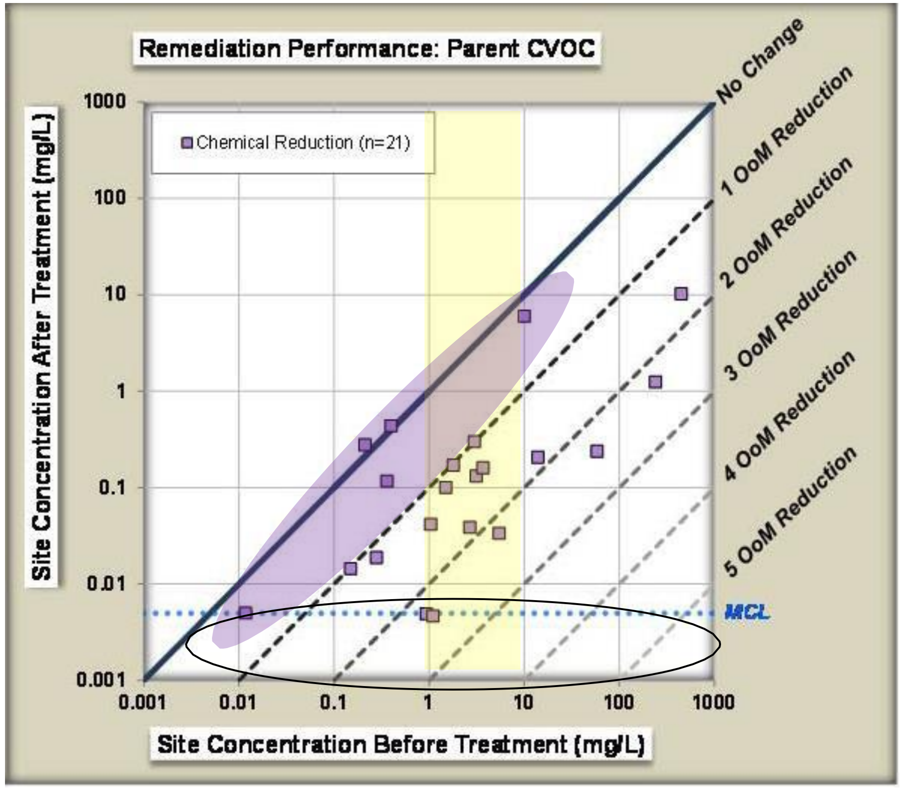
In-Situ Remediation Performance Database

- *Bio vs ZVI*
  - *Bio more common at lower concentration sites*
  - *ZVI more common at high concentration sites*

(McGuire et al., ESTCP 2016)



Dependency on site conditions
High chance of reaching MCL
Cost ~$35 to $228 per m³



Better overall reductions
Low chance of reaching MCL
Cost ~$82 to $334 per m³

Technology Sweet Spot

ERD with EOS (EVO) ONLY

- ***Low to Moderate (10 mg/L) CVOC concentrations***
- ***Single contaminant group***
  - ***PCE, TCE, cDCE, VC***
  - ***TCA, DCA, CA***
  - ***CT, CF, DCM***
  - ***TNT, RDX, HMX, ClO4***
  - ***Metals and rads***
- ***Neutral pH***
- ***Can manage low pH with buffer (CoBupH)***

ERD with ZVI

DNAPLs (CVOCs >25 mg/L)

- ***Contaminant mixtures***
  - ***TCA and TCE***
- ***No pH limitation***
- ***Contact is key***
- ***Smaller source areas “hot spots”***
- ***Jump start bioremediation***

<u>There is an option to use both</u>

- Utilize same redox conditions
- Both produce hydrogen
- No cross-interaction

EOS ZVI

Combination of micro-scale zero valent iron and EOS 100.

Zero valent iron and self emulsifying oil provide a combined abiotic and biotic degradation. No water-formula means no loss of reducing power unti ready for injection. A variety of ZVIs sizes and types can be used in EOS ZVI t meet the site and budget needs.

We can source iron powders too if no oil is requested.

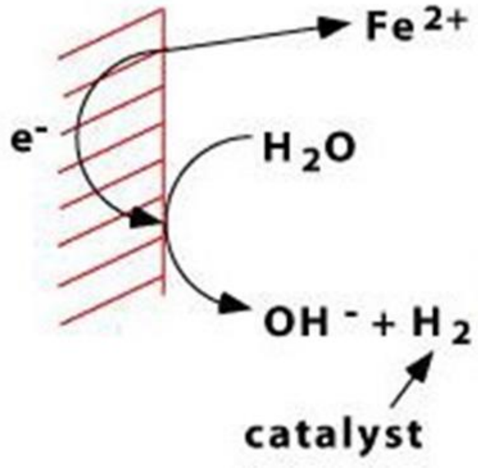
- 50% Zero Valent Iron
- 41% Soybean Oil
- ~7% Food-grade Surfactant
- ~1.67g/cc

Compare to eZVI (NASA) 10-17% by weight ZVI

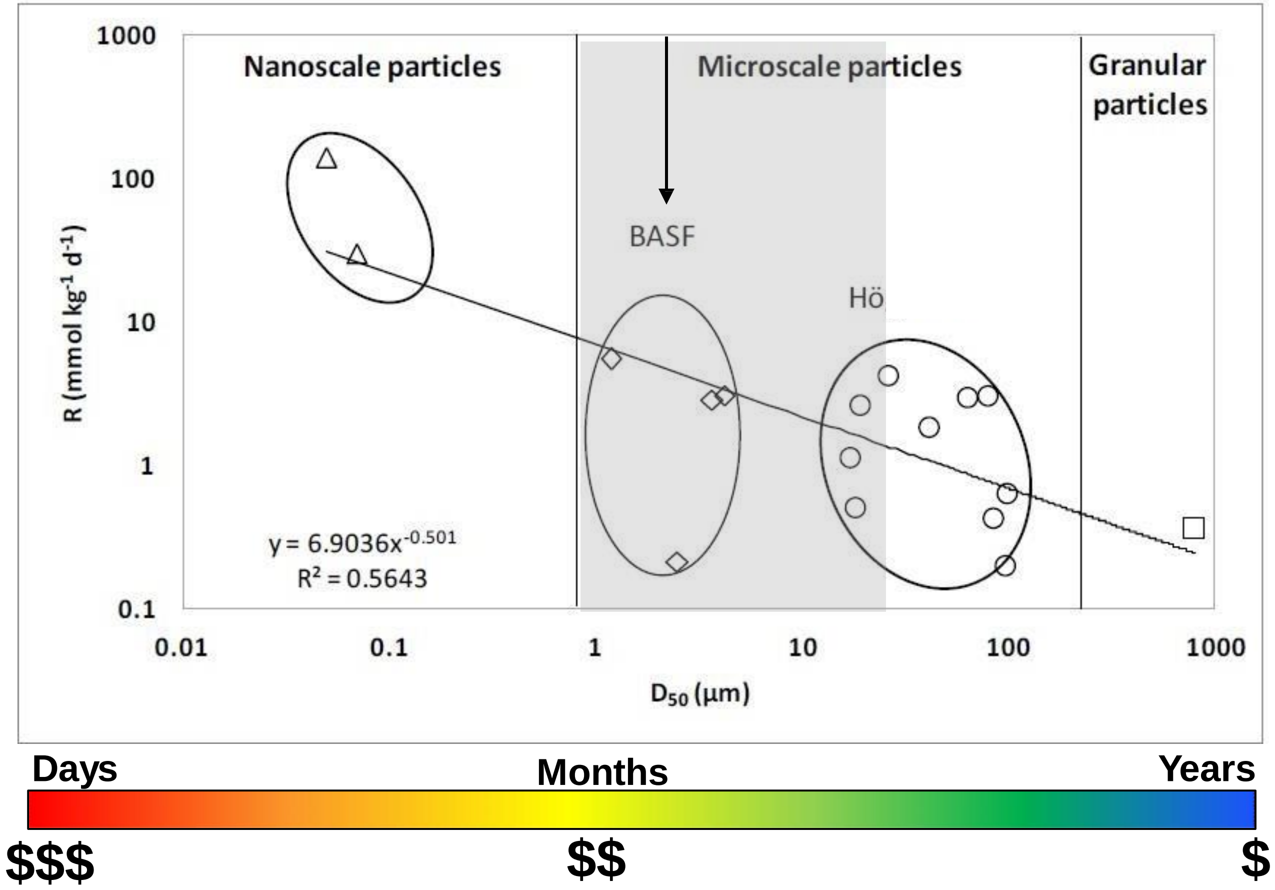
Oil-water emulsion: short shelf life 60% higher cost on lbs. of iron basis

ZVI Reactivity & Surface Area

- Trade-off between: Reactivity, injectability, cost
- H_2O ❼ $OH^- + H_2$ at metal surface
- H_2 use for biological ERD



Best diameter for injection



(Velimirovic et al. 2014; Tratnyek and Johnson, 2006)

Bench Scale Laboratory testing

- ✓ Site groundwater and aquifer material needs to be used.
- ✓ Proper sampling and sample handling is essential to avoid sample alteration (aeration) that may result in testing artifacts.
- ✓ Flow through column tests are preferable to batch test.
- ✓ Field pilot-scale test are strongly recommended as a feasibility step, either following the lab evaluation or stand alone, for As treatment especially.

Design and Field Measurements Requirement

- ✓ Total concentration in soil and groundwater of targeted metals
- ✓ Dissolved (field filtered) metals concentrations
- ✓ pH, Redox Potential (Eh), Dissolved Oxygen
- ✓ Cation scan (calcium, sodium, magnesium, silicon)
- ✓ Anion Scan (chloride, sulfate, nitrate)
- ✓ Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC)
- ✓ Alkalinity

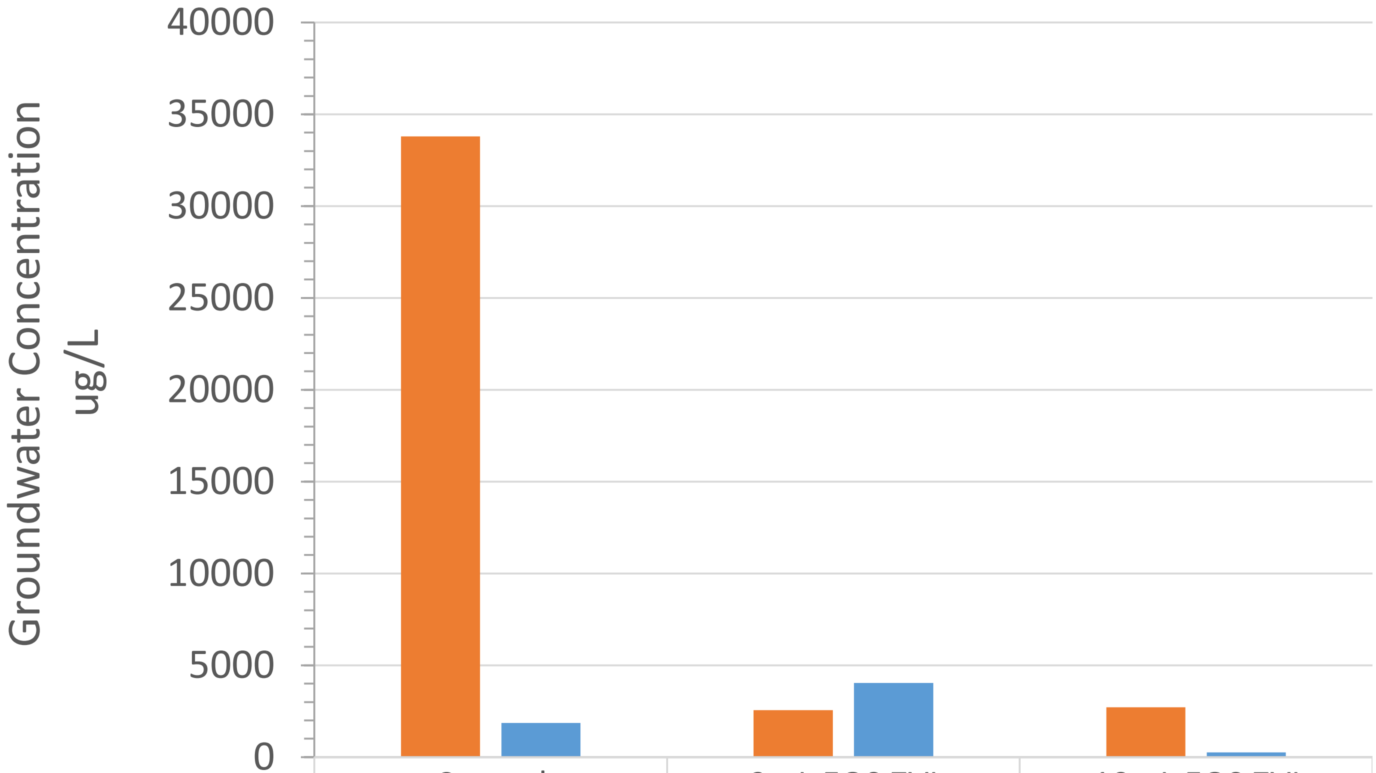
These parameters are used to assess the applicability of an ISCR approach and for optimizing the application rate. The same parameters are also recommended monitoring parameters

Case study 1

Dry Cleaner Site, CAlifornia

Tight Clay Site

Treatability Study using EOS ZVI



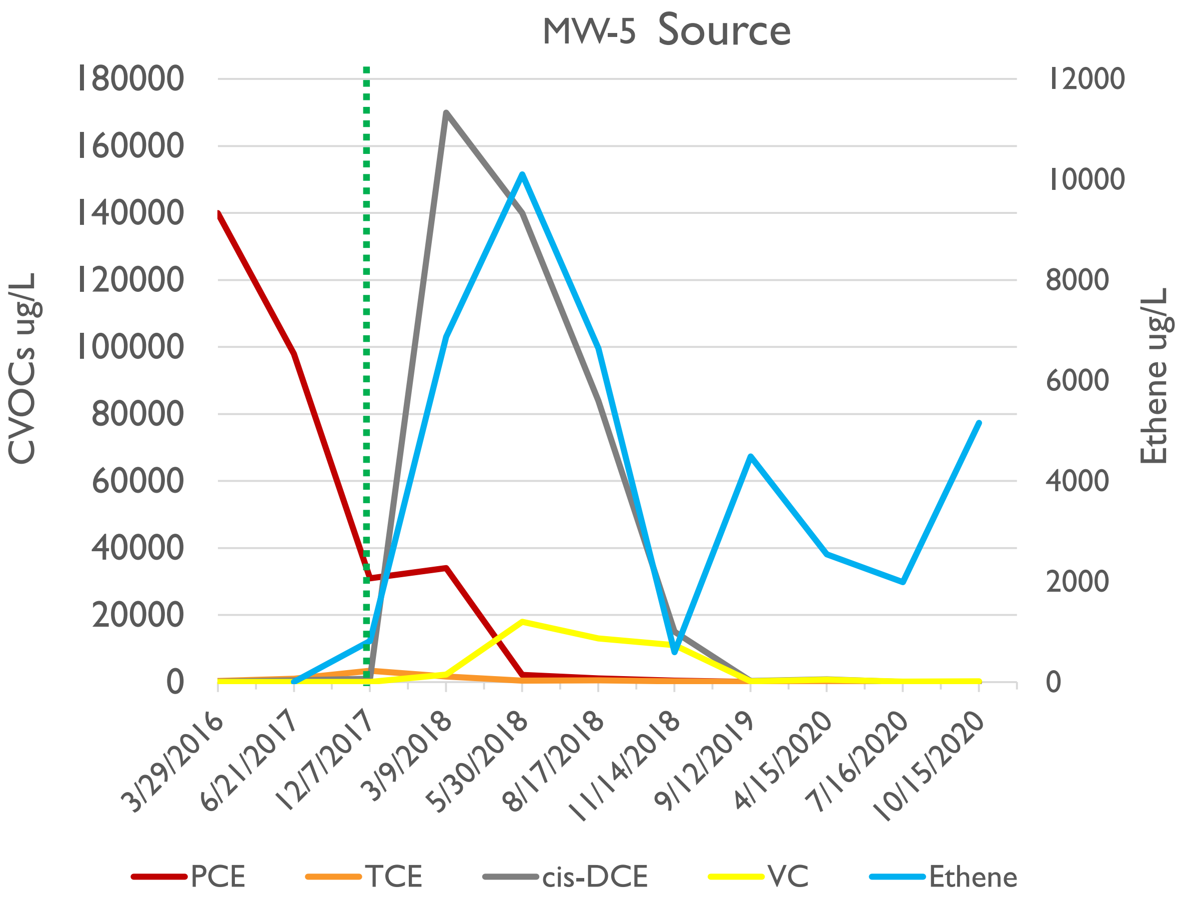
	Control	2mL EOS ZVI	10mL EOS ZVI
Trichloroethene	33800	2560	2710
Cis-1,2-Dichloroethene	1860	4030	263

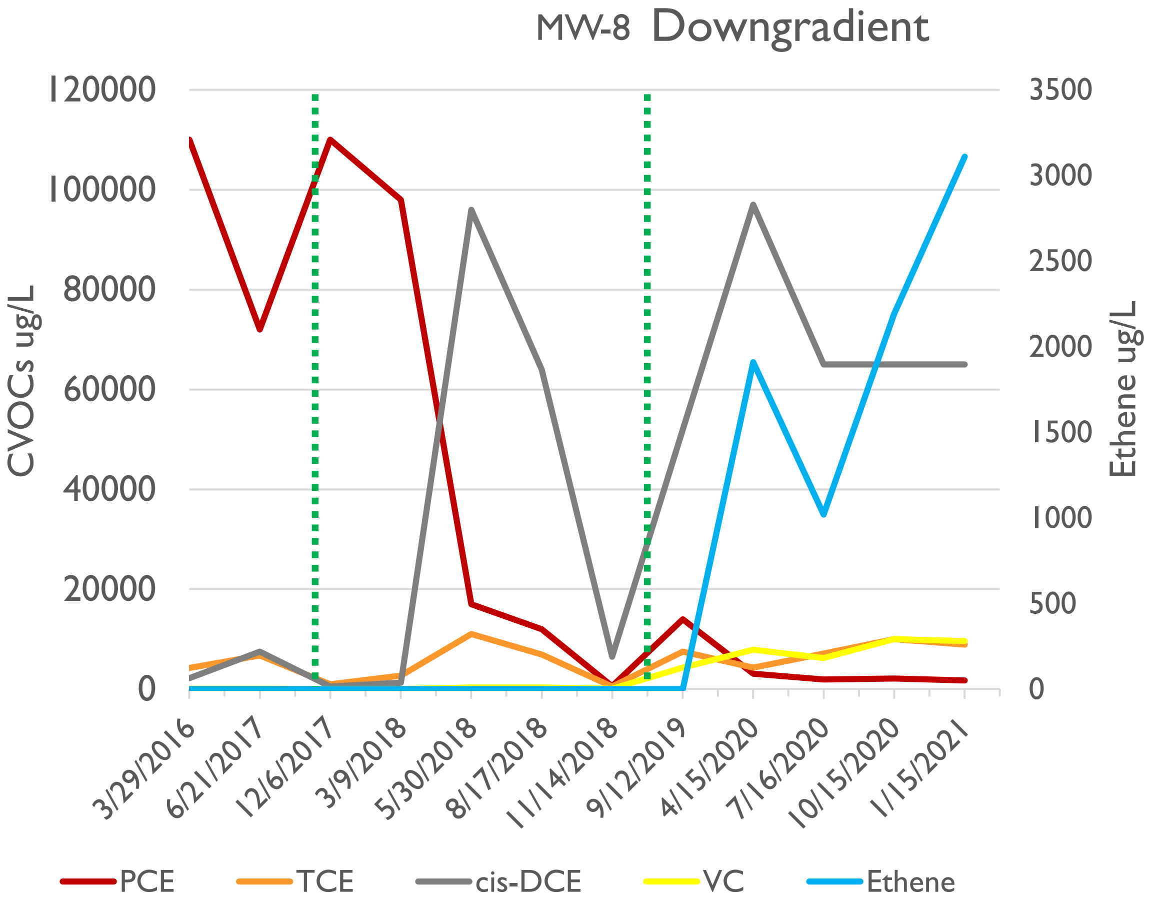
Third party consultant performed a 1 week treatability study:

- Each microcosm contained 115 mL of groundwater and 30 g of soil
- Performed two doses; 2mL and 10mL of the EOSZVI
- Samples were collected and measured in duplicate

Case Study 1 with EOS Pro and ZVI

DPT injection of EOS Pro, BAC-9 and ZVI at a dry-cleaning site; subsurface was Silt with some Sand





Injection event

Case study 2

Operating Industrial Site, Brampton, ON

Tight Clay Site

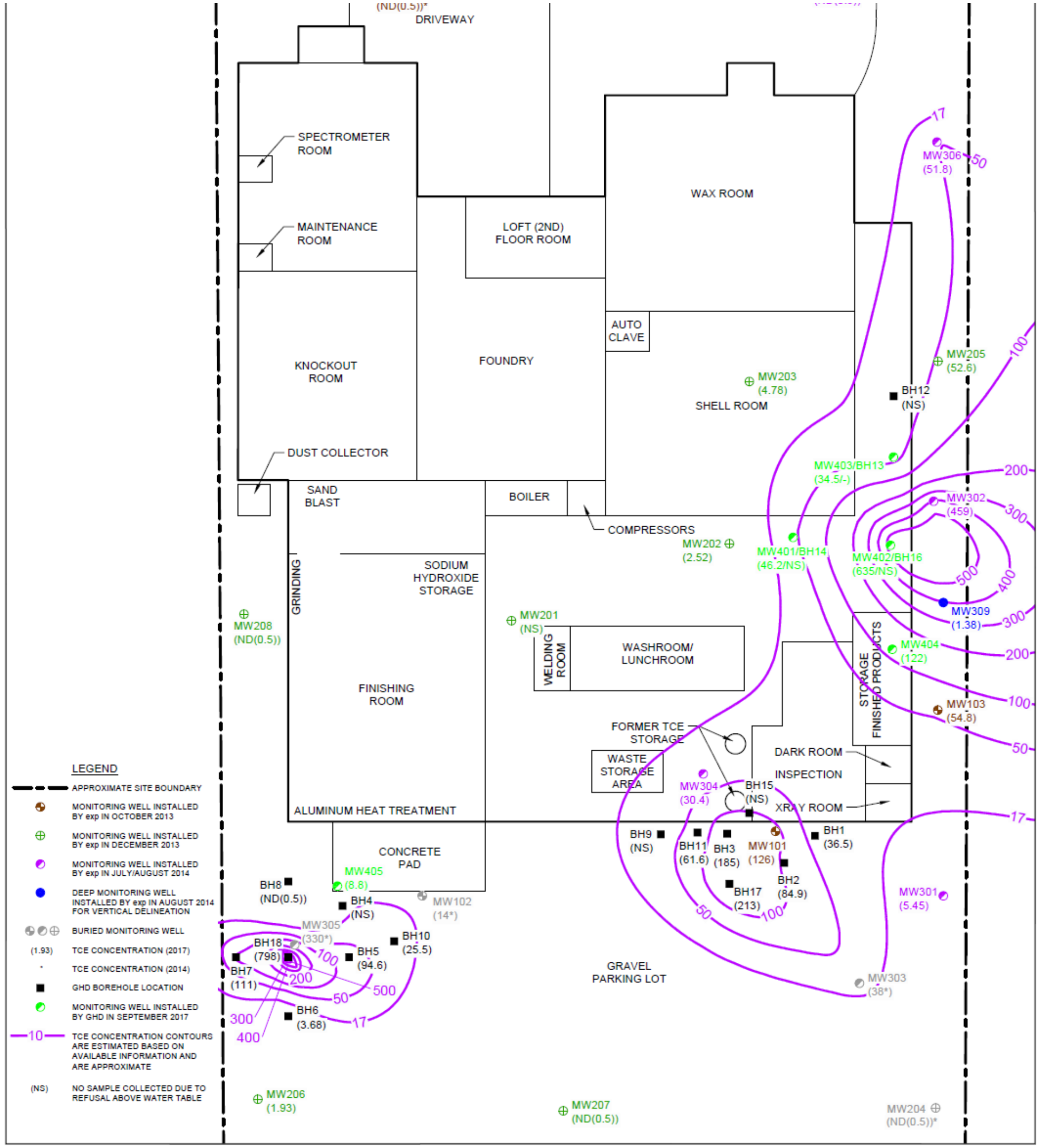


Figure 1 – TCE Plume Contour – October 2017

Case Study 2 - Operating Industrial Site, Brampton, ON

- ❑ 30 years old cVOC impact in the Saturated Zone
- ❑ Contamination located around 3.0 to 5.0 mbgs
- ❑ Tight Clay Aquifer
- ❑ Very low level remediation criteria for cVOC
- ❑ Mix of reducing fermentable carbon & soluble iron as the selected amendment (EHC-L®)
- ❑ Injectant Concentration optimize to represent about 10 % of the effective pore volume
- ❑ Slow injection process in clay over 8 weeks using direct push

Case Study 2 - Operating Industrial Site, Brampton, ON

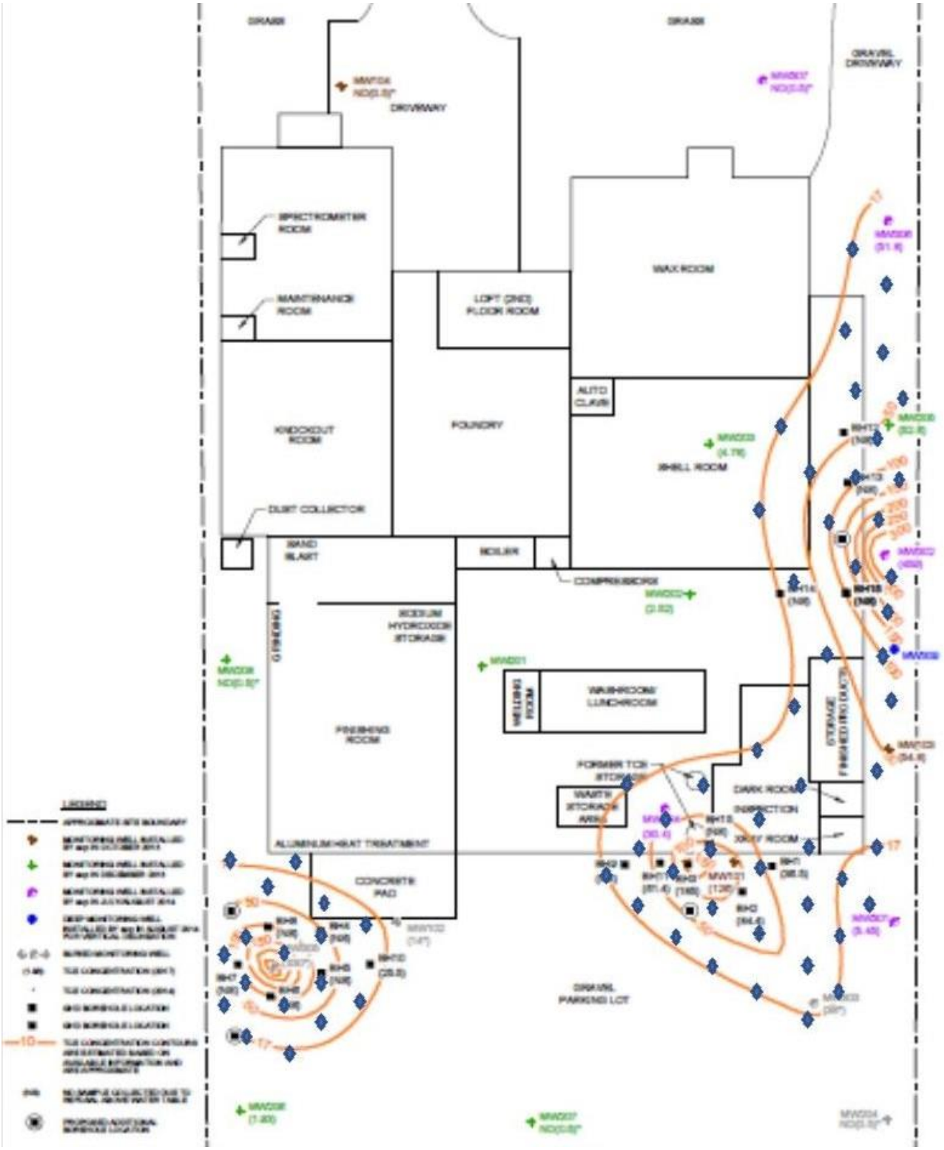


Figure 2 – Injection Grid – May 2018

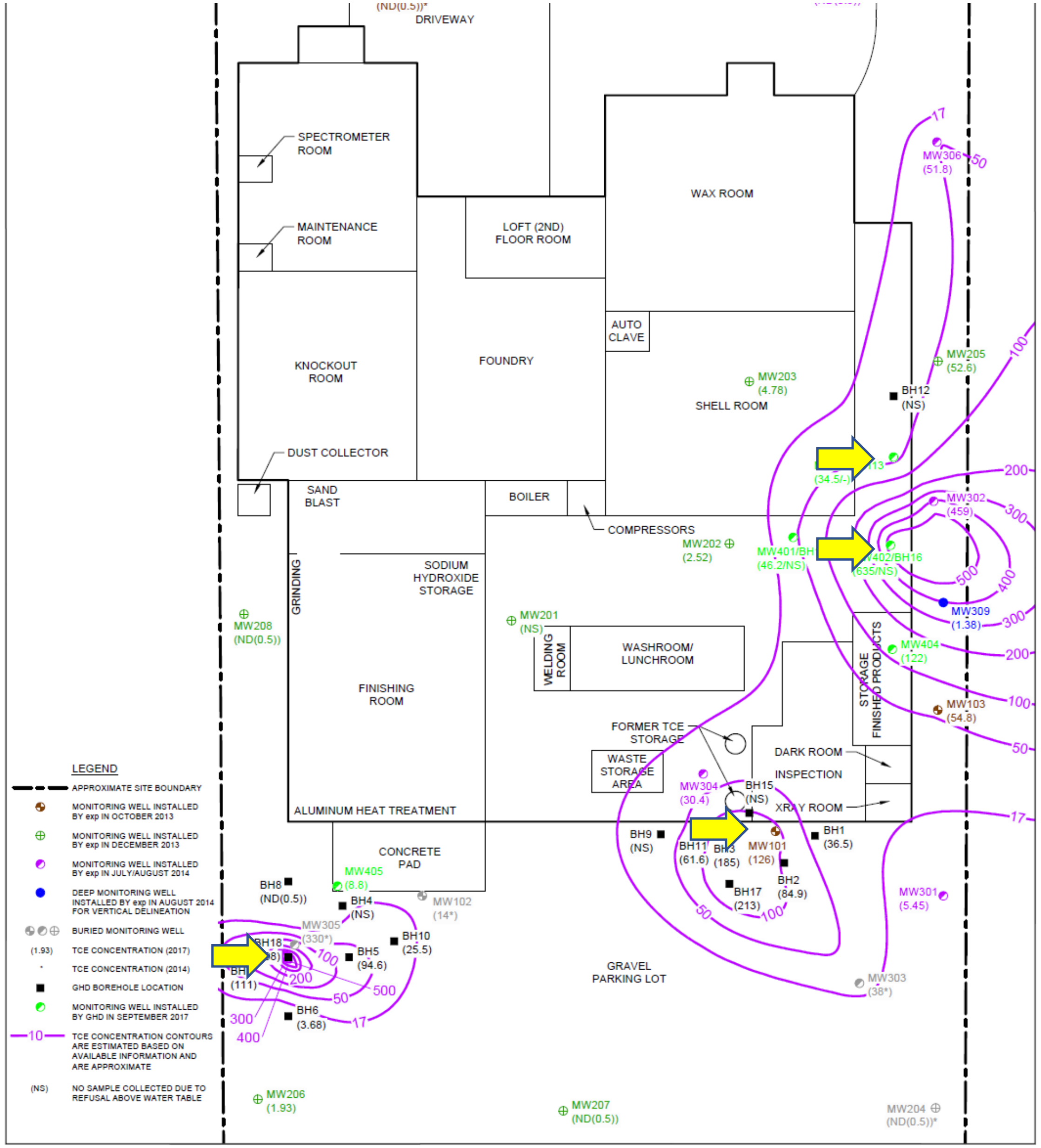


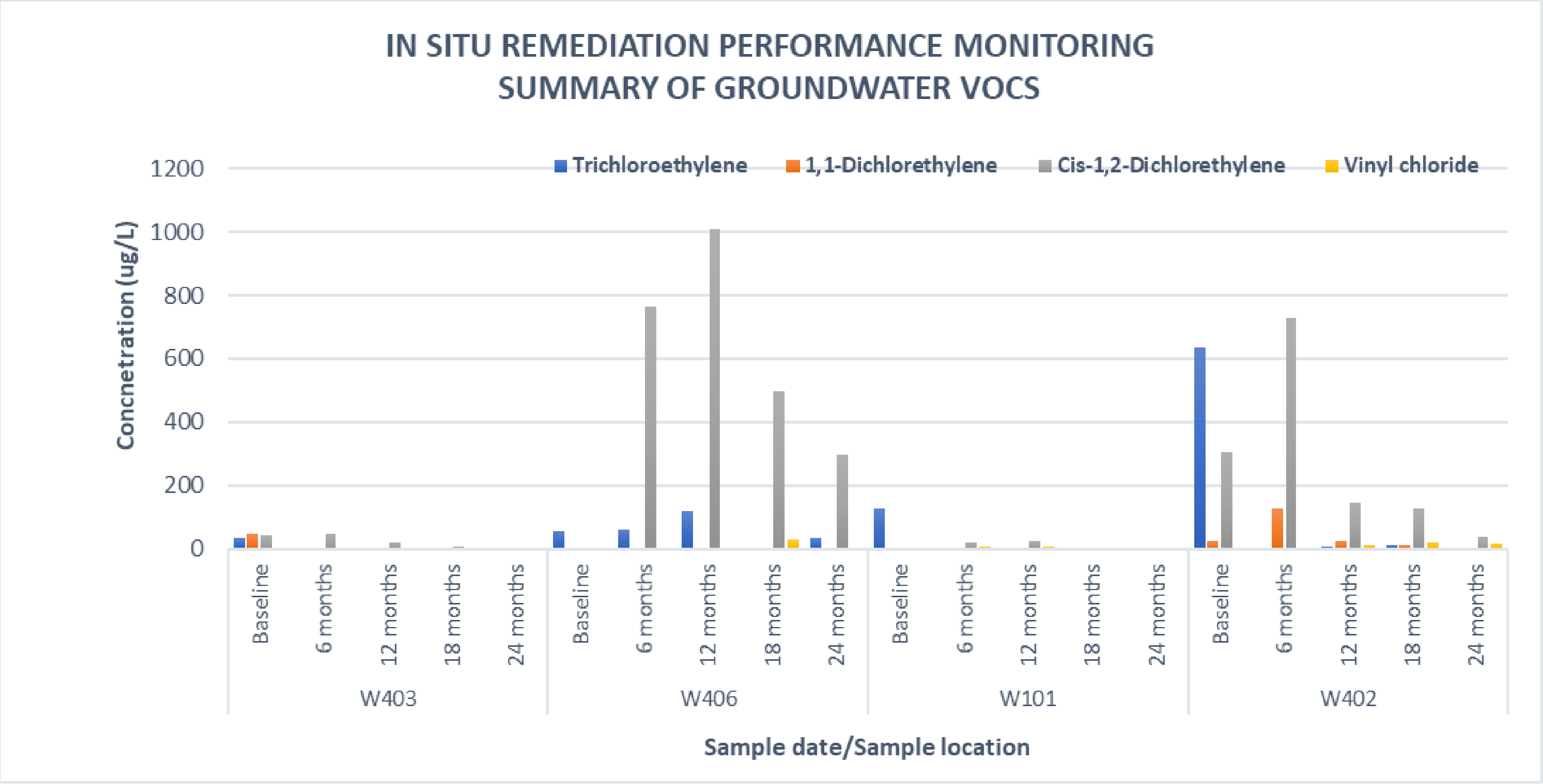
Figure 1 – TCE Plume Contour – October 2017

Case Study 2 – Post injection monitoring Results

	MECP Table 3 - GW standards	W403					W406					W101					W402				
		Baseline	6 months	12 months	18 months	24 months	Baseline	6 months	12 months	18 months	24 months	Baseline	6 months	12 months	18 months	24 months	Baseline	6 months	12 months	18 months	24 months
Trichloroethylene	17	34,5	<0,50	<0,50	<0,50	<0,50	56,6	63	118	4,98	32,6	126	3,22	1,45	<0,50	4,85	635	1,27	9,92	11,2	1,22
1,1-Dichlorethylene	17	48,6	<0,50	<0,50	<0,50	<0,50	<0,50	2,38	2,96	1,35	0,59	2,21	<0,50	<0,50	<0,50	<0,50	26,8	130	23,6	14,5	3,15
Cis-1,2-Dichlorethylene	17	43,4	49,8	21,7	7,57	2,31	2,25	765	1010	497	295	2,25	22,4	25,2	<0,50	3	304	727	148	127	37,8
Vinyl chloride	1,7	1,32	1,39	3,68	3,55	1,54	<0,50	0,8	<5,0	31,5	2,65	<0,50	6,31	9,53	<0,50	1,38	2,6	5,12	13,5	19,7	17,4

Performance Monitoring Results :

In-Situ Remediation Program Brampton, Ontario



Case Study 2 - Summary & Conclusions

- Highly anaerobic and reducing for over 24 months

- Plume pulled back from the property line and off-site migration of TCE was prevented

- Post injection changes in geochemical parameters indicate that chemical and microbiological treatment of TCE and daughter products has occurred in wells MW-101 and MW-402, MW-403 & MW-406 which were under the influence of EHC-L

- EHC-L combined remedy met the site-specific remedial objectives while limiting the vinyl concentration build-up

Reagent Mixing Station

Acknowledgements

- ✓EOS Remediation
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- ✓Hoganas
- ✓Peroxychem *becoming* Evonik

Thank you for your attention !

Have a good day !

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