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Virtual
remediationtechnologiessymposium2020
Together Apart

In Situ Chemical Reduction for Remediation of Soil Containing Chlorinated Pesticides, Herbicides

Presented by Jean Paré, P. Eng.

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Presentation Outline

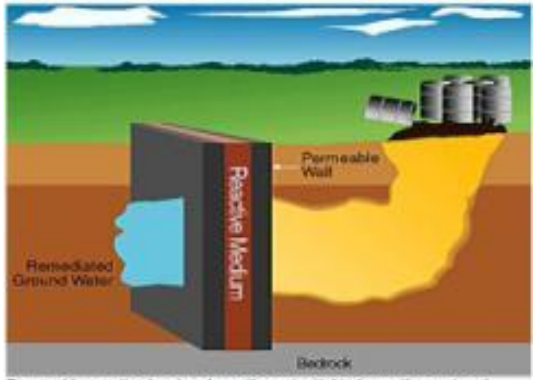
Virtual
remediationtechnologiessymposium2020
Together Apart

- ✓ About Chemco
- ✓ ISCR Chemistry and Biochemistry
- ✓ Daramend® Application Methodology
- ✓ Overview of Completed Projects
- ✓ Technology qualification & Design parameters
- ✓ Acknowledgement

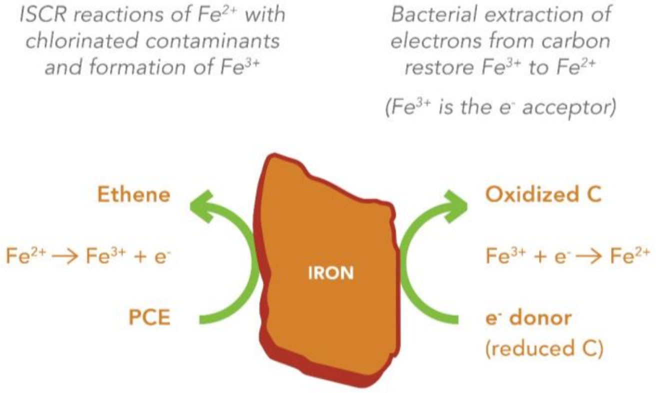
What is In Situ Chemical Reduction?

- ✓ 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



Permeable reactive barriers have the potential to lower the cost and increase the effectiveness of groundwater cleanup.



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
- ✓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

Pesticide Facts

Compound	Category	Solubility (mg/L)	K_{oc}	Soil Half-Life (low – high)	Observed DRE (%)
DDT	insecticide	0.03 – 0.09	151	2 – 15 years NPIC	60 – 99
DDD	DDT breakdown	0.09 – 0.10	150	70 – 294 days HEDR	
DDE	DDT breakdown	0.12 – 0.14	50	100 /16 days	
Dieldrin	insecticide	0.14	12	0.5 – 3.0 years HEDR	
Toxaphene	insecticide	3.0	295	0.2 – 11 years (ATSDR)	
Chlordane	insecticide			4 – 9.6 years NPIC	
Metolachlor	herbicide	493	190	15 – 70 days Extonet	
Lindane	insecticide, rodenticide	8.5	1,1	14 – 240 days HEDR	
2,4-D	herbicide	3,4	46	30 – 60 days (CDPR)	
PCP	biocide	1	30	178/23 days HEDR	
Bromacil	herbicide	815	69	275 days (USEPA)	
Tebuthiuron	herbicide	2500	80	12 -15 months (Cornell U)	

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

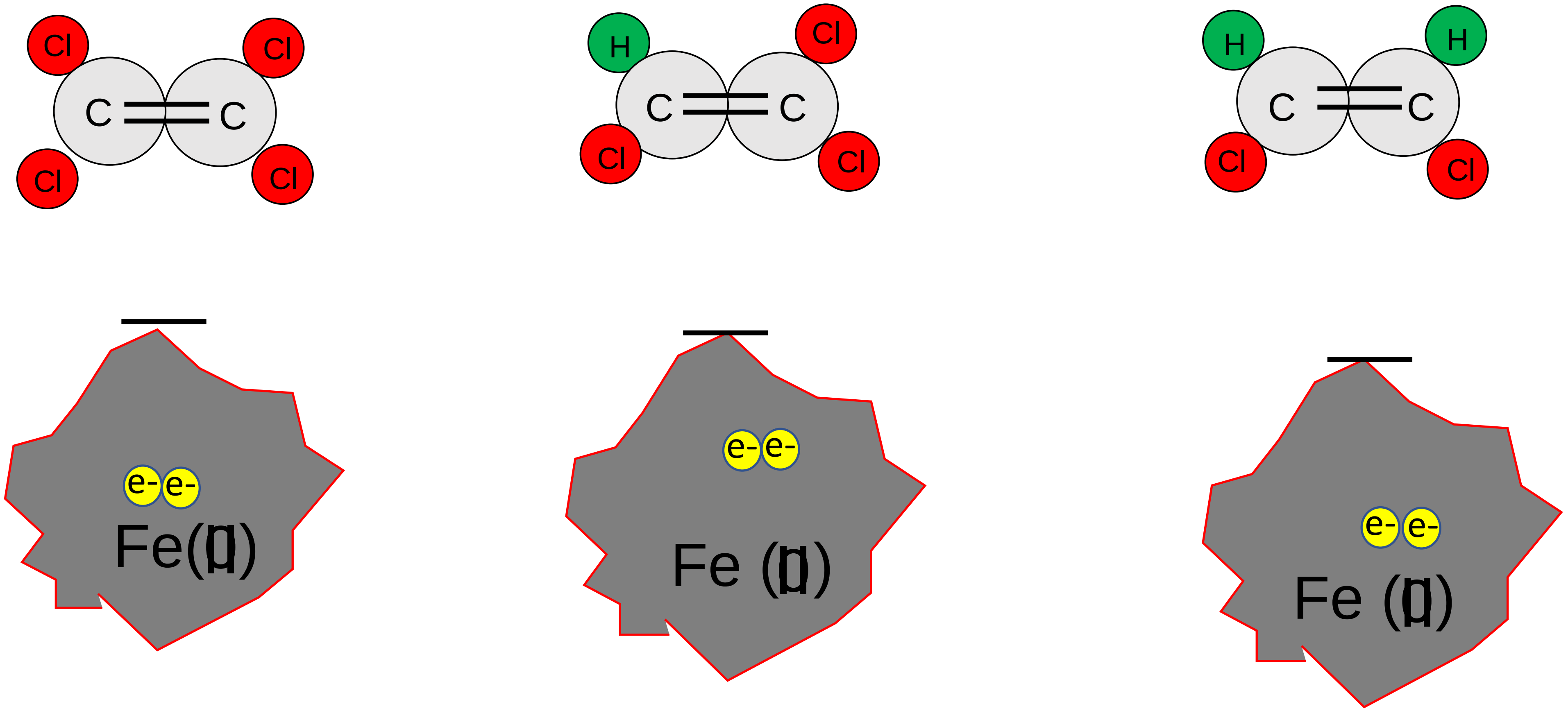
Direct Dechlorination Reactions with ZVI

β elimination (abiotic) pathway

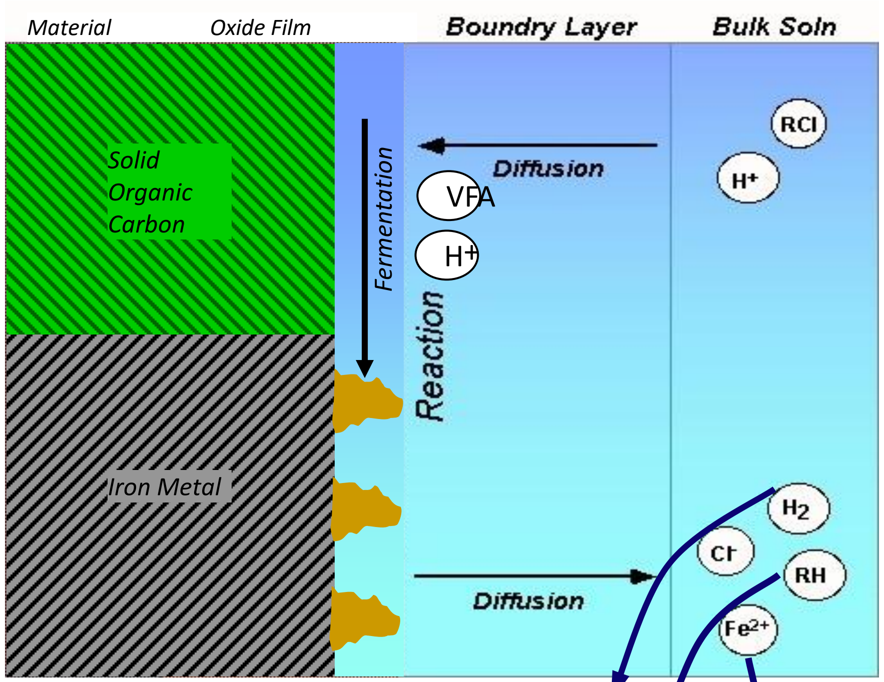
Tetrachloroethylene / Dichloroacetylene

Trichloroethylene / Chloroacetylene

Dichloroethylene / Acetylene



Carbon + ZVI Synergies Generate Multiple Dechlorination Mechanisms: ISCR



1. Direct Iron Effects:

Hydrocarbon generation:

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

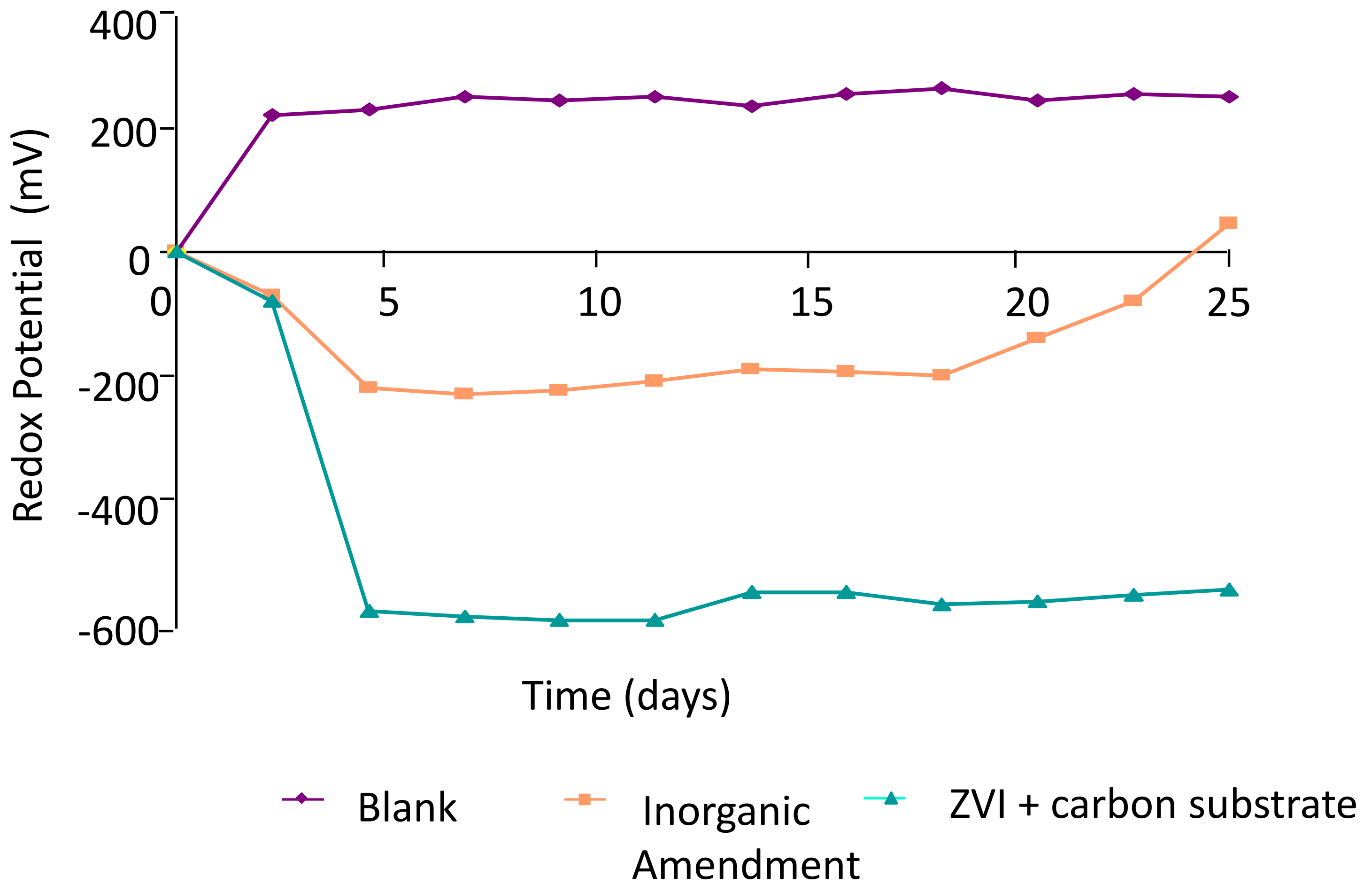
3. Biostimulation:

- 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



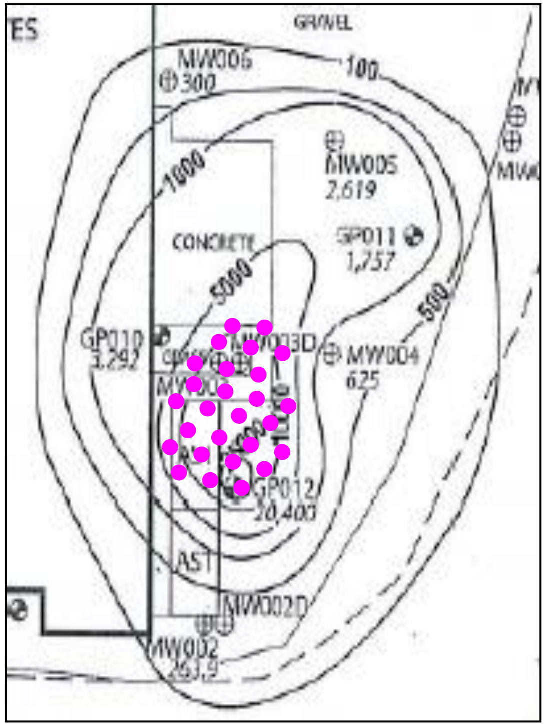
ZVI + Carbon substrate Synergy

ZVI (40%) + Solid Organic Carbon (50%) + Soluble Organic Carbon (10%) for in-situ integrated biological and chemical reduction (ISCR)

- ✓ Major, minor, and micro nutrients are provided
- ✓ Balances acidity (VFAs) and alkalinity (ZVI) to prevent acidification of groundwater
- ✓ ZVI (5 - 75 µm) protected from passivation by slow continuous release of VFAs as carbon ferments
- ✓ Very long life from 36 to 72 months
- ✓ Emplaced in slurry form via direct push injection, hydraulic/pneumatic fracturing, trenching or soil mixing
- ✓ Liquid injectable full soluble version available

In Situ Intervention Strategies

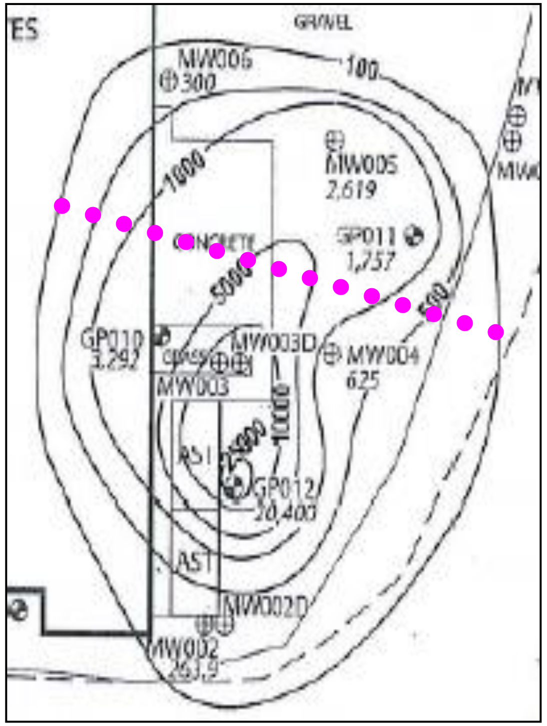
Source Area/ Hotspot Treatment



Dosing: 0.15 to 1% wt/wt

Spacing: 5 to 15 ft (DPT)

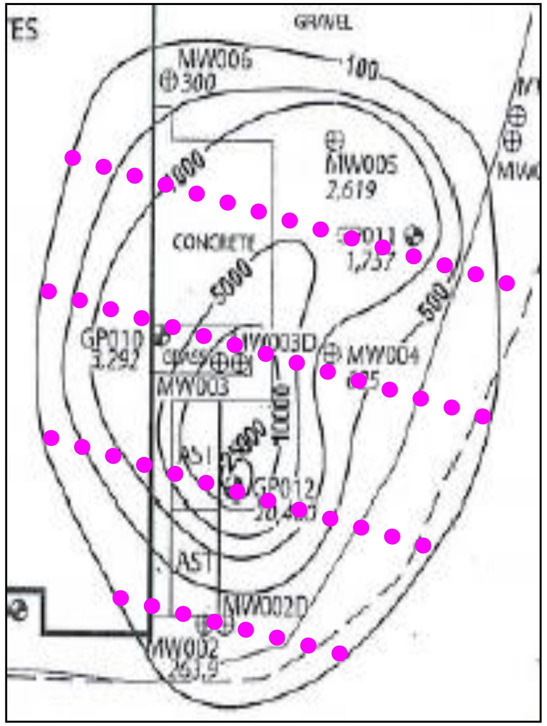
Injection PRB for Plume Control



Dosing: 0.4 to 1% wt/wt

Spacing: 5 to 10 ft (DPT)

Plume Treatment



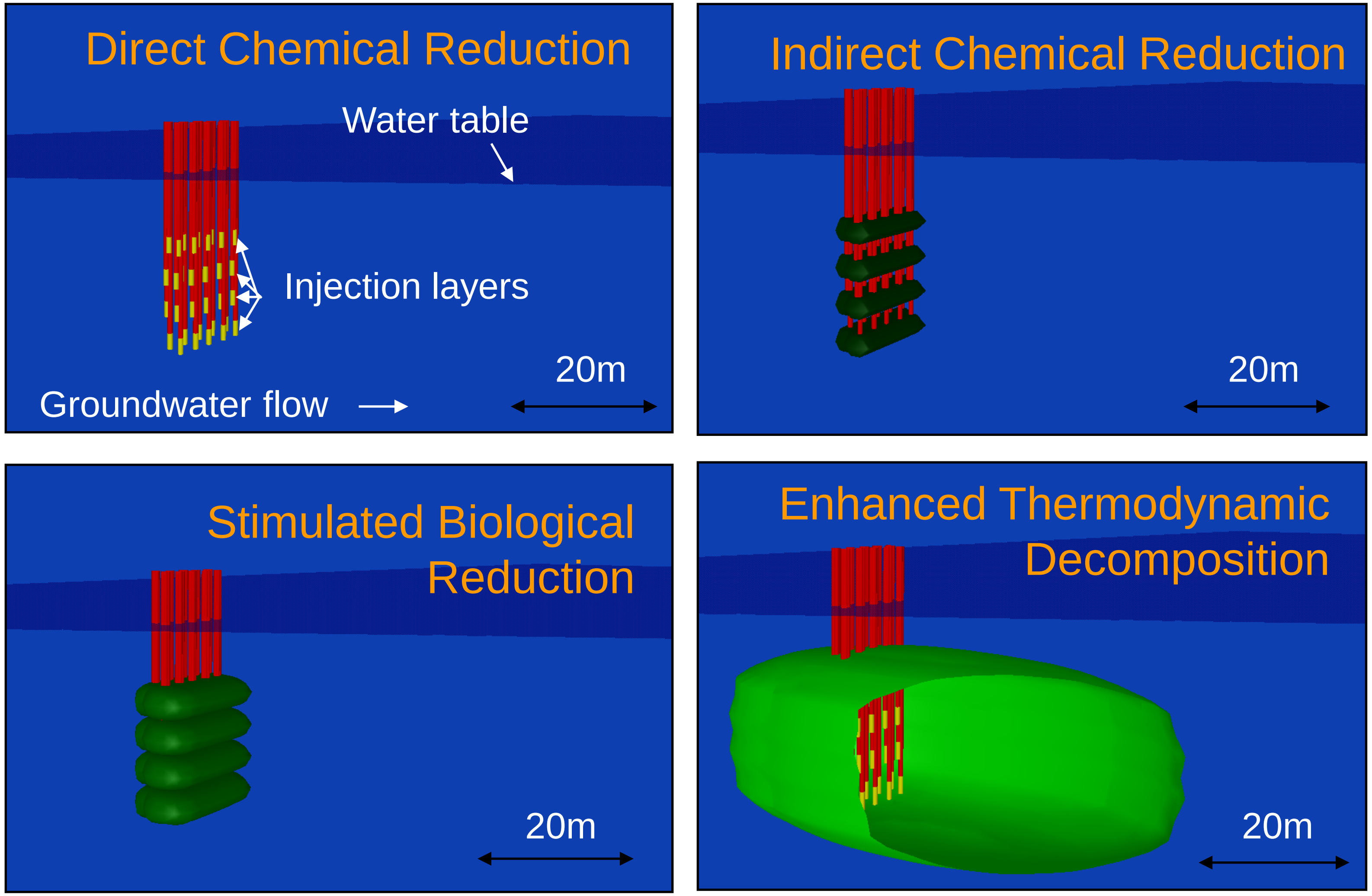
Dosing: 0.05 to 0.2% wt/wt

Line Spacing: based on 1 year g.w. travel distance

In Situ Application Methods for Soil and Groundwater Treatment

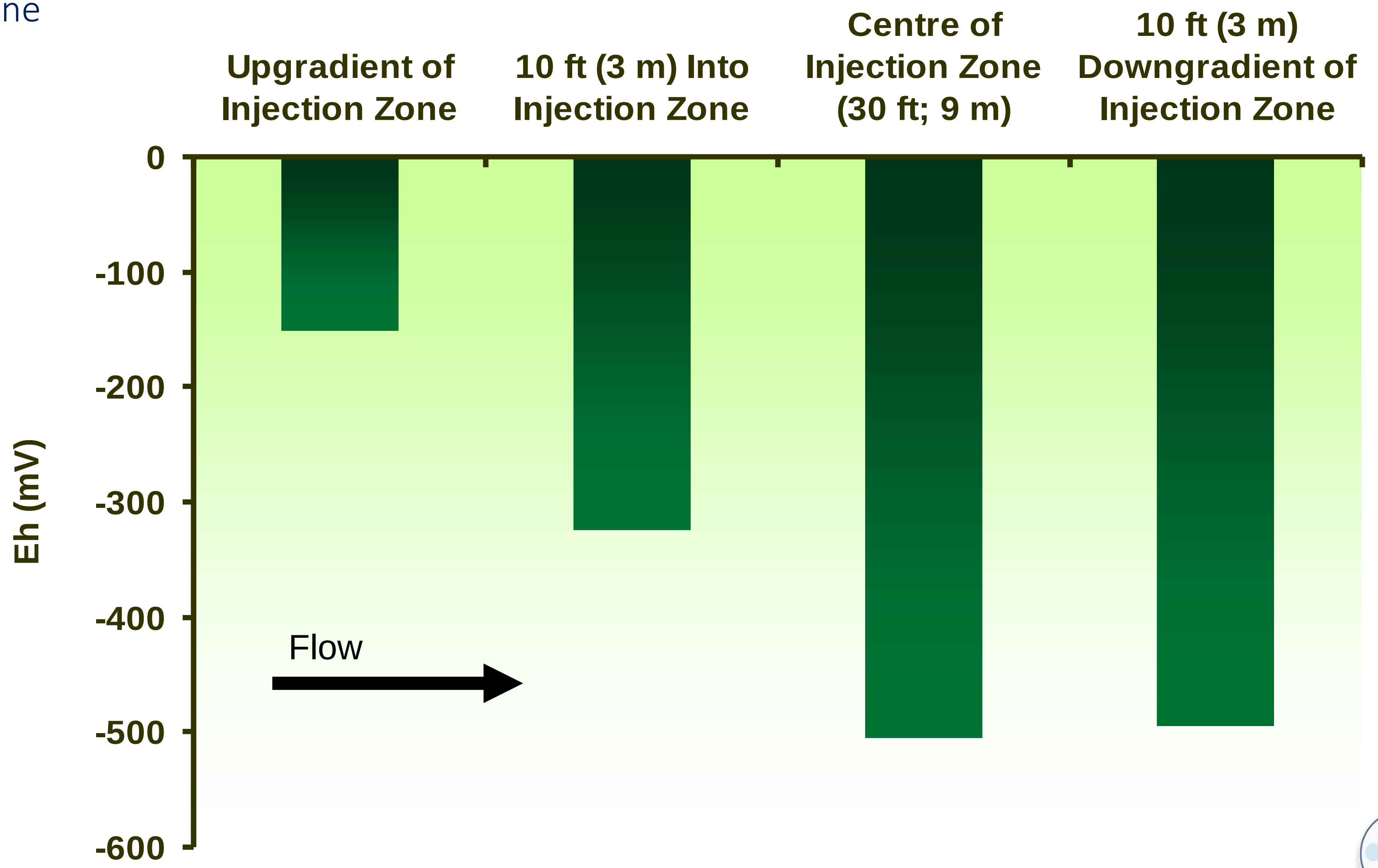
- ✓ **Direct Placement:**
  - ✓ Trenching
  - ✓ Excavations
  - ✓ Deep soil mixing
- ✓ **Injection Methods:**
  - ✓ Direct injection
  - ✓ Well injections (EHC-A)
  - ✓ Hydraulic fracturing
  - ✓ Pneumatic fracturing
  - ✓ Jetting

ZVI + Carbone Synergies brings multiples dechloration mechanism



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

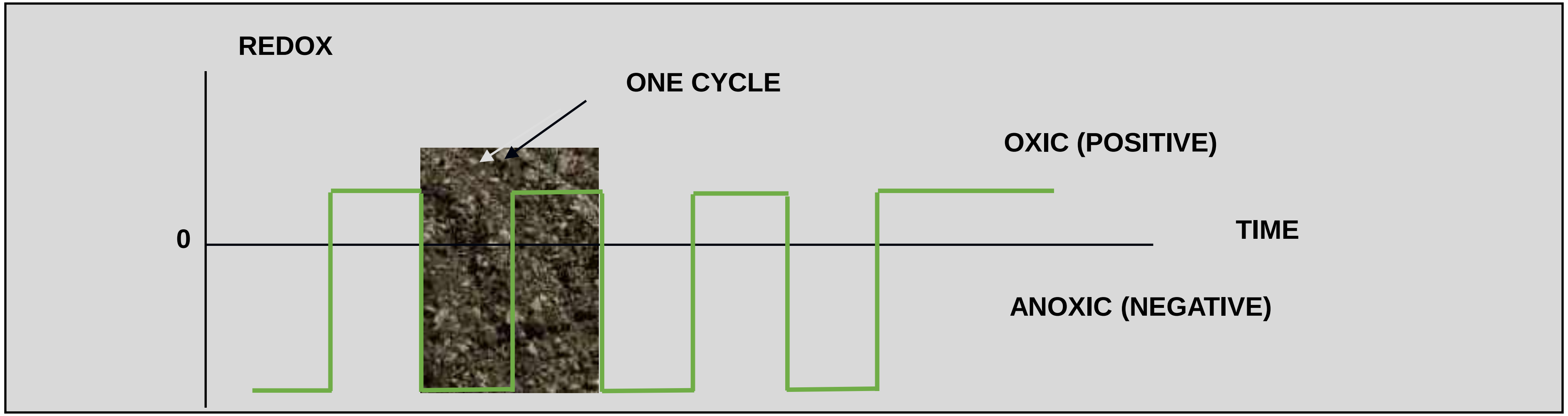
60 ft (18 m) injection zone



Source: URS

Cycled Anoxic/Aerobic ZVI+Carbon

- ✓ One 'cycle' consists of a reductive phase and an aerobic phase
- ✓ Reductive amendment (fibrous organic carbon with ZVI) tilled into soil and water added to initiate reductive phase
- ✓ Soil tilled to initiate aerobic phase
- ✓ Amendment composition and dosage soil specific



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

In Situ Treatment of Pesticides in Soil to Achieve Residential Remediation Standards

Case Study 1

Target Compounds: DDT, DDE, and Dieldrin

Confidential Home Builder Site
34 acres formerly in apple orchard and strawberry fields
Soil impacts to 60 cm bgs
Remedial Goals were 1.4 mg/kg for DDT and 1.1 mg/kg for DDE

Case Study 1

34 acre Agricultural Site – DDT, DDE, Dieldrin

Results After One & Two Cycles

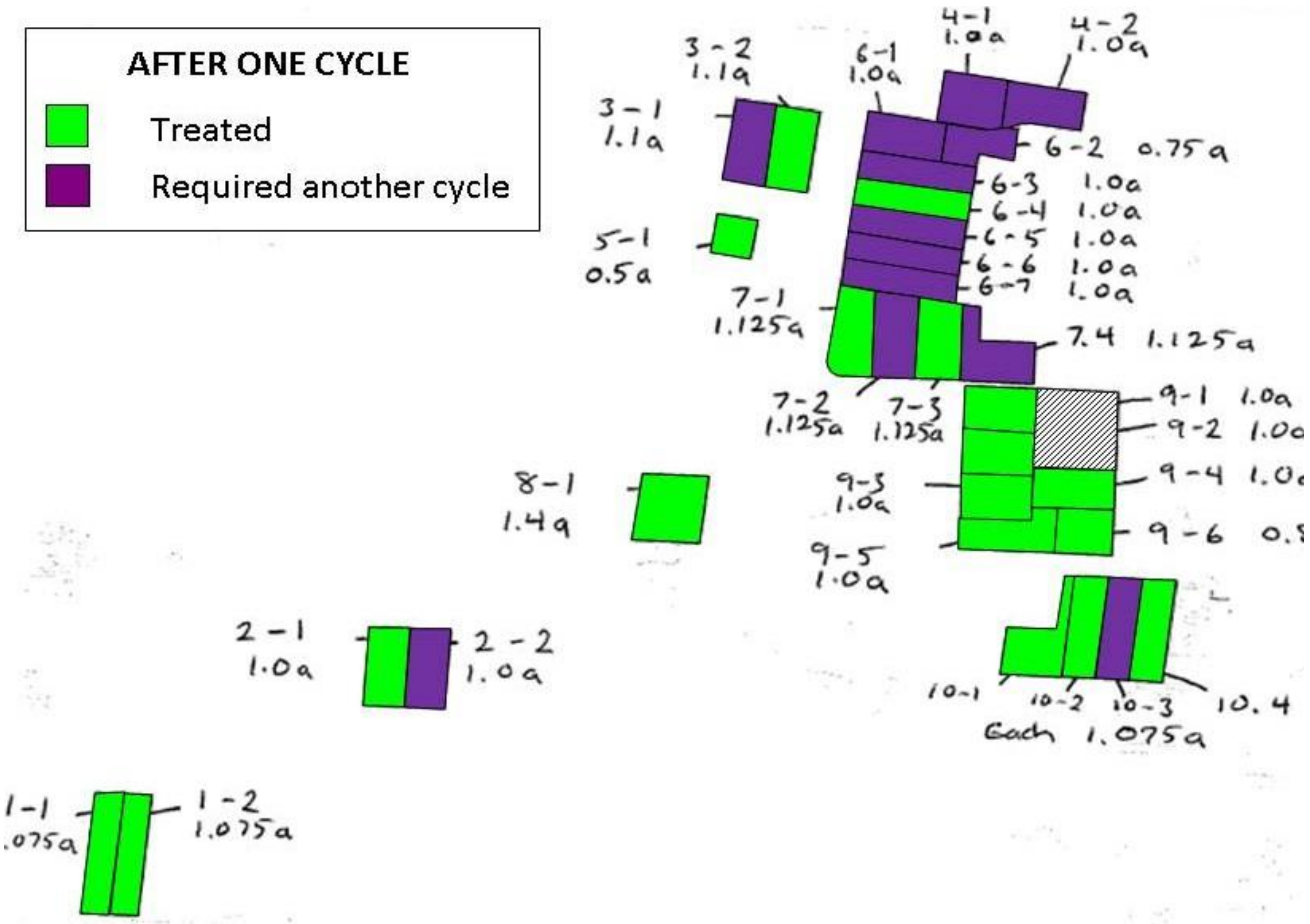
Data for area treated after one cycle

Compound	Initial Concentration (mg/kg)	Concentration After 1st Cycle (mg/kg)	Final % Removal
DDT	1.90	0.98	49%
DDE	2.38	1.11	53%
Dieldrin	0.064	0.040	38%

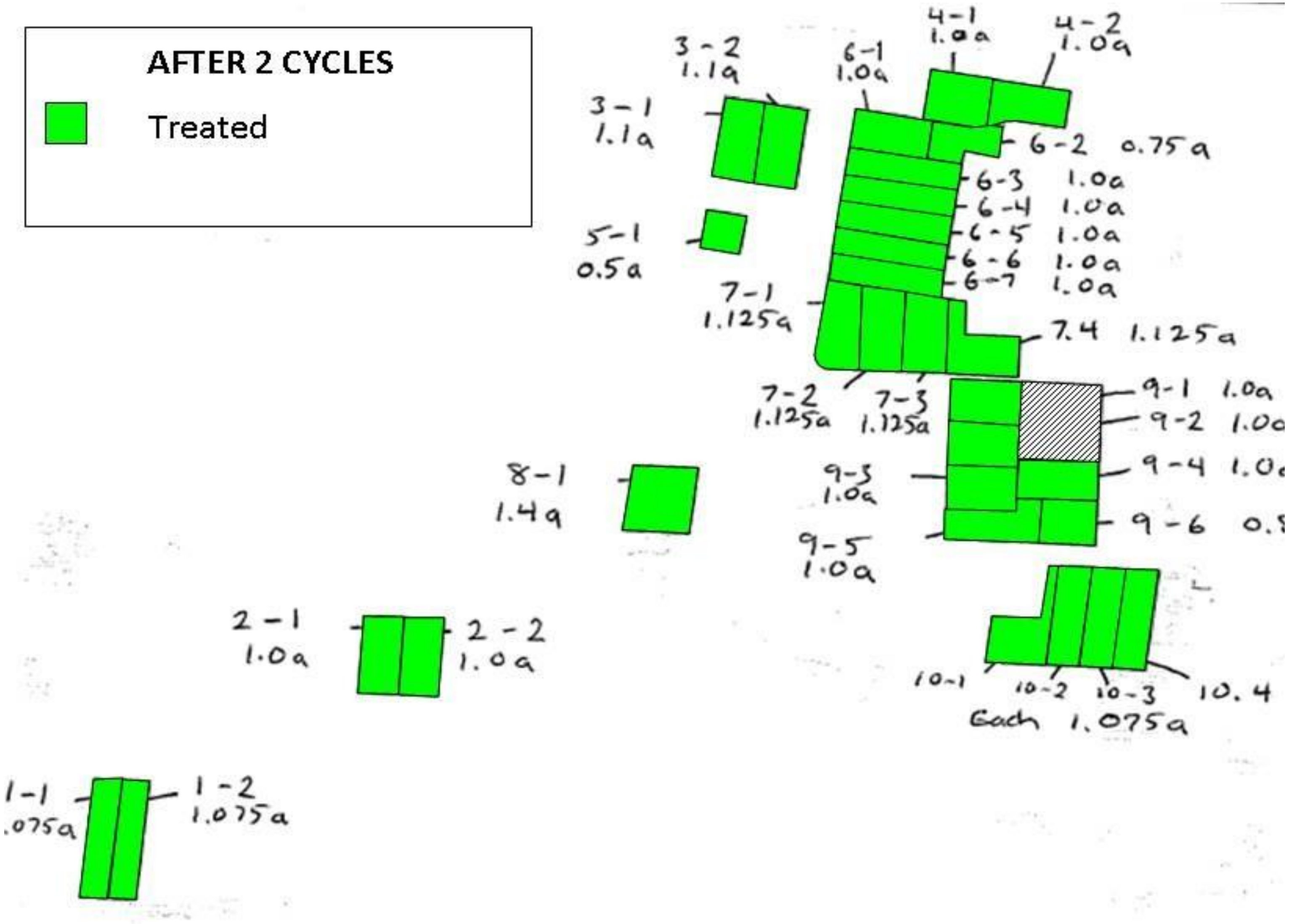
Data for area that required a second cycle

Compound	Initial Concentration (mg/kg)	Concentration After 1st Cycle (mg/kg)	Concentration After 2nd Cycle (mg/kg)	Final % Removal
DDT	2.05	2.00	0.66	68%
DDE	2.37	1.98	0.80	66%
Dieldrin	0.110	0.080	0.028	65%

Results After One Cycle

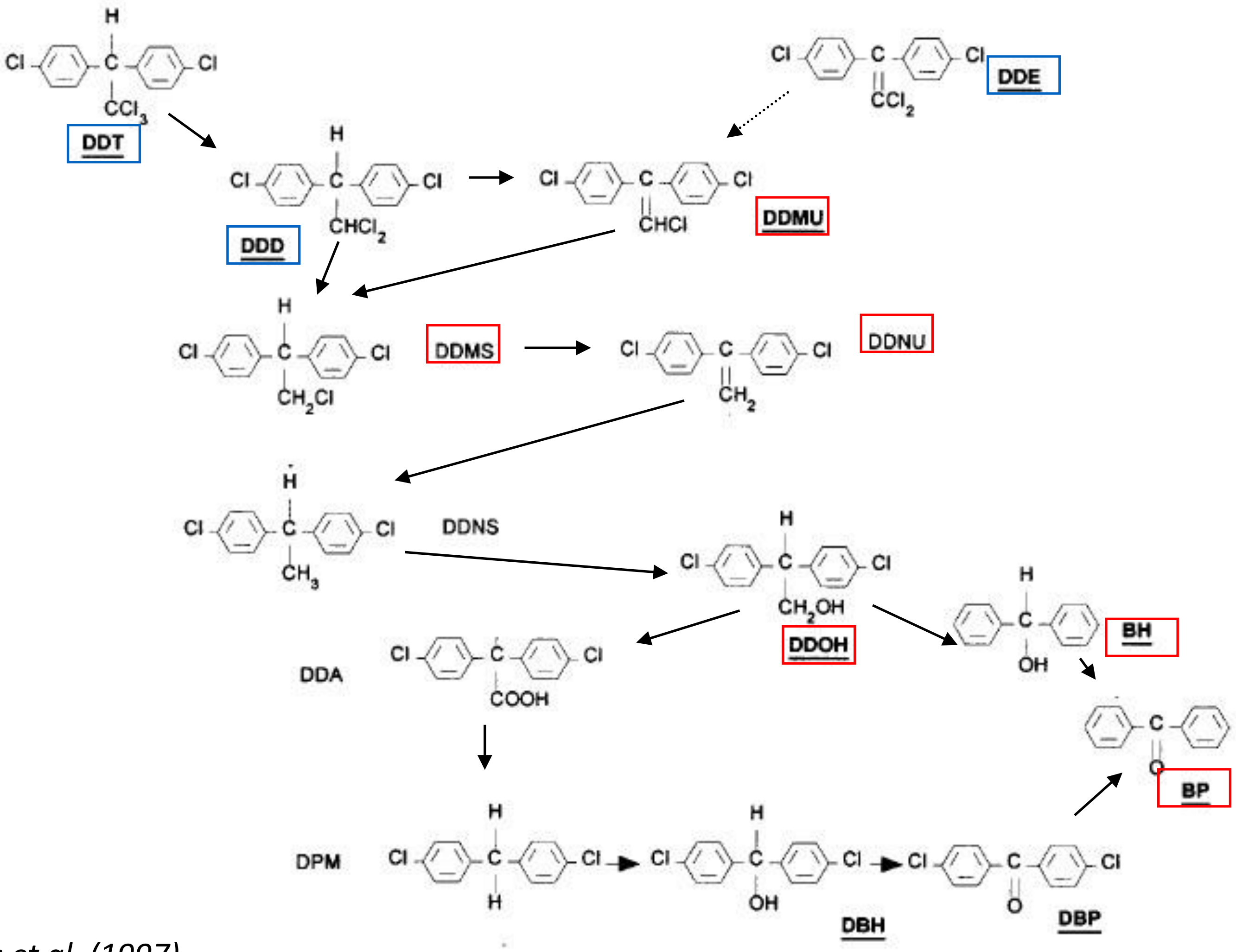


Results After Second Cycle



What was the Fate of DDT?

Dechlorination (anaerobic)



From Sayles et al. (1997)

What was the Fate of DDT?

Ring Opening and Mineralization?

- Radioisotope (14C-DDT) Fate Studies:
  - ✓ Main fate was conversion to carbon dioxide
  - ✓ Slow but significant production of 14C-CO2
  - ✓ Recovery of added 14C in DDT as carbon dioxide was about 7% in 150 days
  - ✓ After 150 days the rate of 14C-CO2 release had decreased to about 1% per month

- Stable isotope (13C-DDT) Fate Studies indicated dichlorobenzophenone was the major breakdown product

Case Study 2

Target Compounds: Dieldrin and Chlordane

Agricultural Site in Florida
Land was used to produce sweet corn, peppers, and tomatoes for over 30 years
Dieldrin was the driver with a RG of 15 µg/kg
Must achieve residential soil remediation standards

Case Study 2

Pesticide-impacted Site, Palm Beach County FL

Treatment Protocol

- ✓Applied and incorporated 0.5% (w/w) Daramend Reagent using standard 4-wheel drive agricultural tractor and specialized deep penetration (24”) rotary tiller
- ✓Irrigate amended soil to 90% of soil water holding capacity (approx. 30% moisture on a dry weight basis) to create the anaerobic phase of each cycle
- ✓Allow to stand undisturbed for 6 days (variable dependent on weather)
- ✓Aerate by tilling on day 7 to create the aerobic phase of each cycle
- ✓Re-apply Daramend on day 8 and repeat the anaerobic/aerobic cycling process as required to attain required pesticide removal

Daramend Bulk Bags

Tillage Equipment

Observations

- ✓Redox potential was measured 24 h after incorporation of Daramend Reagent at 13 points in each of the two treatment plots
- ✓The mean redox potentials measured in the North and South plots were -126 mV and - 458 mV, respectively
- ✓Soil pH levels in the North and South plots were 6.7 – 7.0 and 6.7 – 7.1, respectively

Pesticide Removal Results

Compound	Concentration (µg/kg)		RDE (%)[1]
	Initial	Final	
Dieldrin	48.4	11.6	**76**
α-Chlordane	8.5	4.1	**51**
γ-Chlordane	13.9	4.1	**71**
Total COC[2]	**70.8**	**19.8**	**72**

1. Removal and Destruction Efficiency
2. Contaminants of Concern

Case Study 2 Conclusions

- ✓Daramend successfully reduced the concentrations of all target compounds to less than the performance standards
- ✓Treatment was completed within a reasonable timeframe and on budget
- ✓Very cost effective method for treating soil containing low levels of organochlorine pesticides

Daramend for Residential: Summary

- ✓ treatment is a proven, low cost approach to treatment of surface soils containing chlorinated pesticides
- ✓ The Daramend reagent has evolved and improved over the past 20 years to the point where residential treatment standards can often be reached.
- ✓ Cost is always less than most alternatives, commonly as little as 25% to 40% of the cost of excavation/transportation/landfill/backfill
- ✓ Treatment time is generally between 3 and 6 months, subject to site conditions and weather
- ✓ A very cost effective method for treating soil containing low levels of organochlorine pesticides

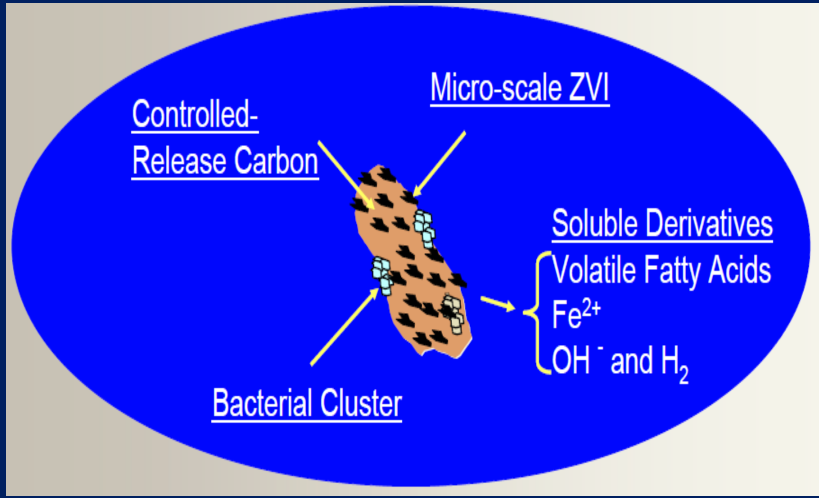
Case Study Conclusions

✓Daramend successfully reduced the concentrations of all target compounds to less than the performance standards

✓Treatment was completed within a reasonable timeframe and on budget

✓Very cost effective method for treating soil containing low levels of organochlorine pesticides

Case Study 3 - Project
2,4-D, 2,4,5T, and DDT
Uniroyal, Elmira ON, Canada
1997



Project One Summary & Lessons Learned

Figure 1. Influence of DARAMEND treatment on 2,4-D concentration.

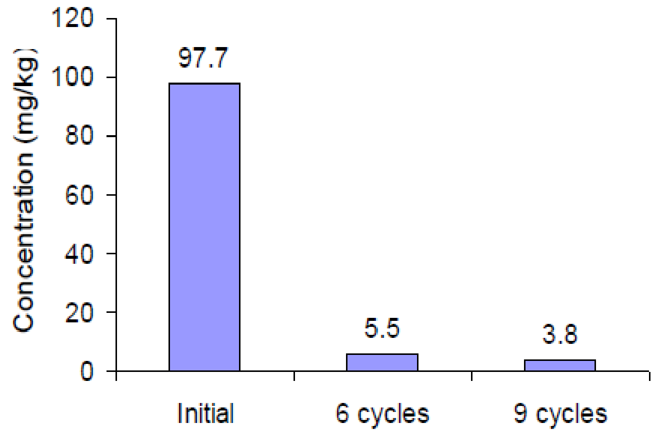


Figure 2. Influence of DARAMEND treatment on 2,4,5-T concentration.

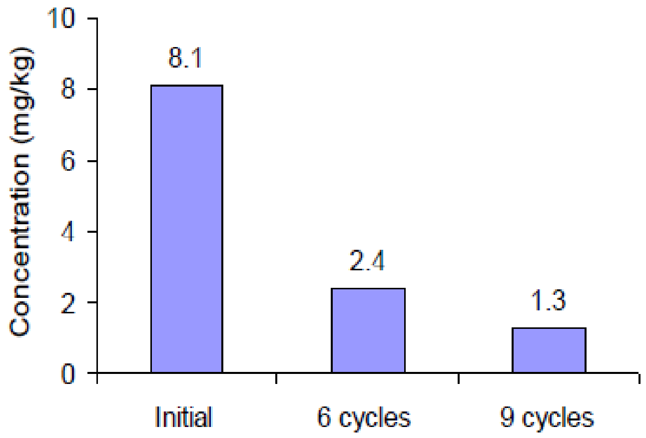
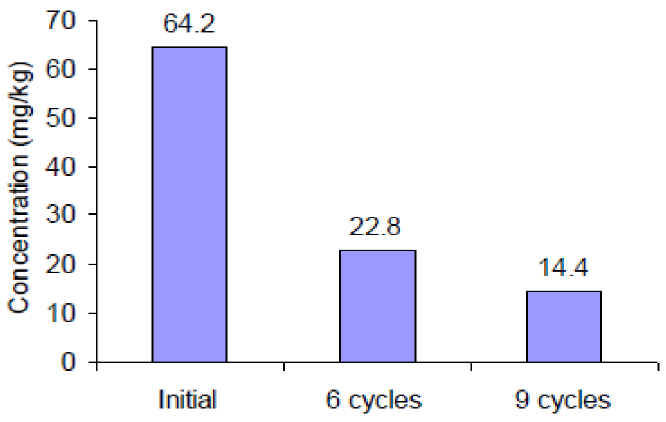


Figure 3. Influence of DARAMEND treatment on DDX concentration.



- ✓ 2,4-D was reduced by 96% from 97.7 mg/kg to 3.8 mg/kg while 2,4,5-T was reduced by 84% from 8.1 mg/kg to 1.3 mg/kg
- ✓ DDT was reduced by 91% from 53.5 mg/kg to 4.7 mg/kg
- ✓ DDX (i.e., sum of DDT, DDD, & DDE) was reduced by 78% from 64.2 mg/kg to 14.4 mg/kg (Removal DDT >> DDE > DDD)
- ✓ Monitoring of atmosphere inside treatment cell indicated supplied air was essential: resulted in much higher labor requirement
- ✓ Radioisotope studies indicated that both 2,4-D was substantially converted to 14-C-CO2 but 2,4,5-T was not
- ✓ Bench-scale studies on a range of soil samples indicated that total 2,4-D + 2,4,5-T concentrations above 400 mg/kg were inhibitory

Case Study Project 4
Metolachlor® and DDT
CIBA Geigy, Cambridge ON, Canada
1996



Project Two Summary & Lessons Learned

Table 1 - Initial and Final Concentrations of Target Compounds [3]

Plot		Initial Concentration (mg/kg)				Final Concentration (mg/kg)			
	Sample	2,4-D	Dinoseb	Atrizine	Metolachlor	2,4-D	Dinoseb	Atrizine	Metolachlor
A	Zone 1	(0.4)[1]	(0.4)	1.5	68	(1.0)	(1.0)	(1.5)	(1.0)
	Zone 2	(0.4)	(0.4)	4.7	84	(1.0)	(1.0)	(1.5)	(1.0)
	Zone 3	3.7	(0.4)	13.0	48	(1.0)	(1.0)	(1.5)	(1.0)
	Zone 4	2.8	(0.4)	17.0	54	(1.0)	(1.0)	(1.5)	(1.0)
	Zone 5	1.2	(0.4)	15.0	82	(1.0)	(1.0)	(1.5)	(1.0)
B	HM[2]	(0.4)	(0.4)	4.5	170	(1.0)	(1.0)	(1.5)	38
	HM[3]	-	-	-	-	(4.0)	(4.0)	(6.0)	11.8
C	Static control	(0.4)	(0.4)	1.0	37	2.3	(1.0)	3.9	56
	Untreated Material[4]	-	-	-	-	(1.0)	(1.0)	4.9	2.0

1 - Values in parenthesis represent MDL for compounds reported as non detectable
2 - Sample collected from entire 60 cm depth
3 - Sample collected from top 30 cm only
4 - Near berm around treatment area (uncontaminated soil)

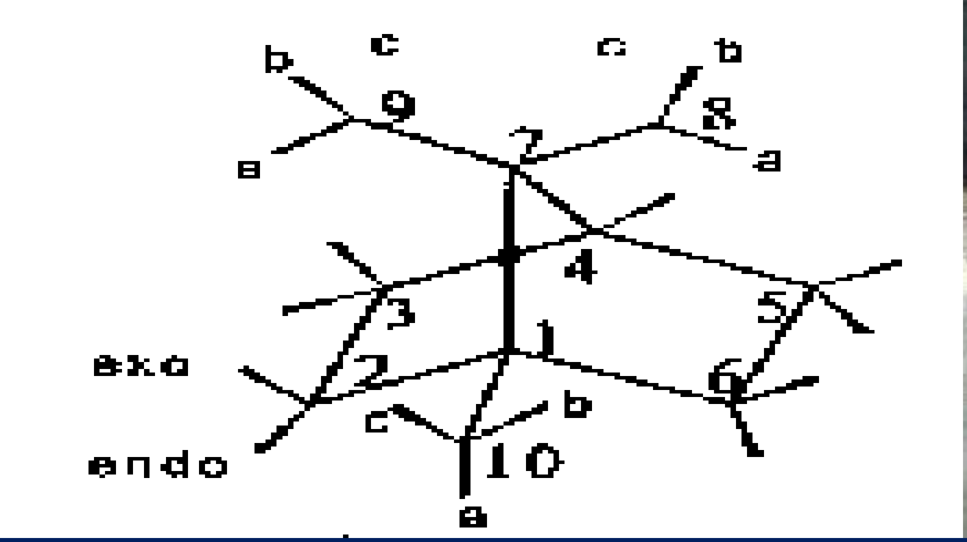
Table 2 - Metolachlor Concentrations (mg/kg) [3]

Area	Initial	Day 2	Day 7	Day 28	Day 208	Day 306	Day 454	Day 565
Main Treatment cell[1]	67	72	65	53	27	14	3.1	ND
HM cell[2]	170	140	140	110	78	57	42	38
Static Control cell	37	NS	49	87	63	57	66	56

1- Average of 5 zones
2- Sample collected from entire 60 cm depth
NS- Not sampled
ND- Not detected (below 1.0 mg/kg)

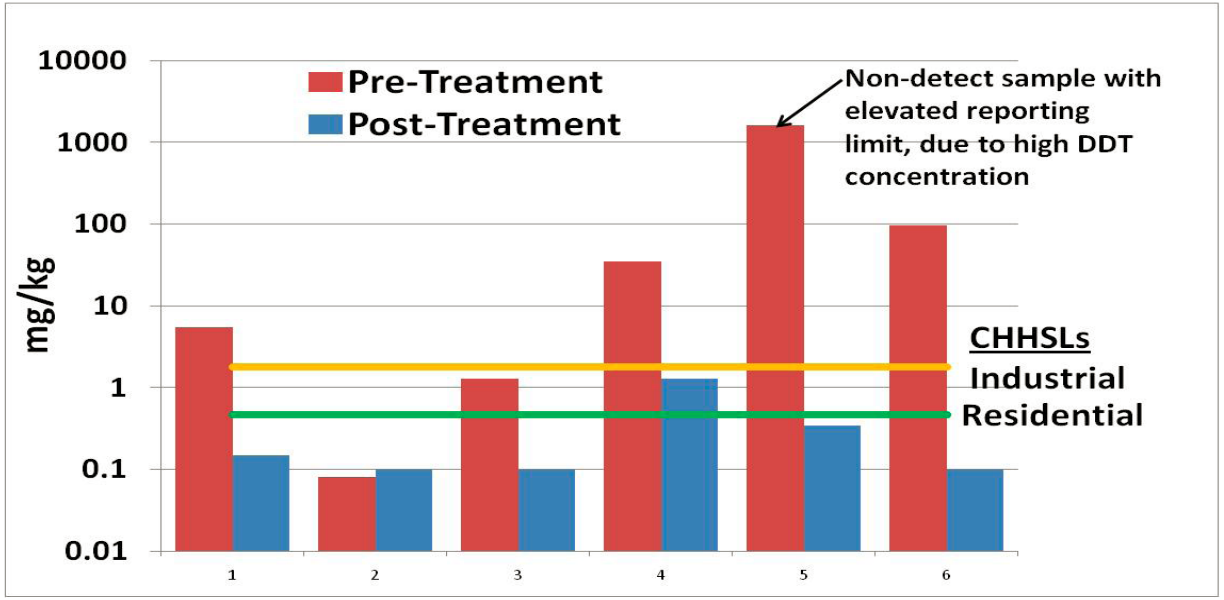
- ✓ Metolachlor® was reduced by >99% in the main treatment area from 67 mg/kg to <0.5 mg/kg
- ✓ Removal efficiency was lower in the high Metolachlor ® treatment area (only 78% from 170 mg/kg to 38 mg/kg
- ✓ Metolachlor ® removal rate was relatively slow, as compared to other pesticides at between 10% and 15% per treatment cycle

Case Study Project 5
Confidential Industrial Site, Imperial Valley CA
Toxaphene, DDT
2009

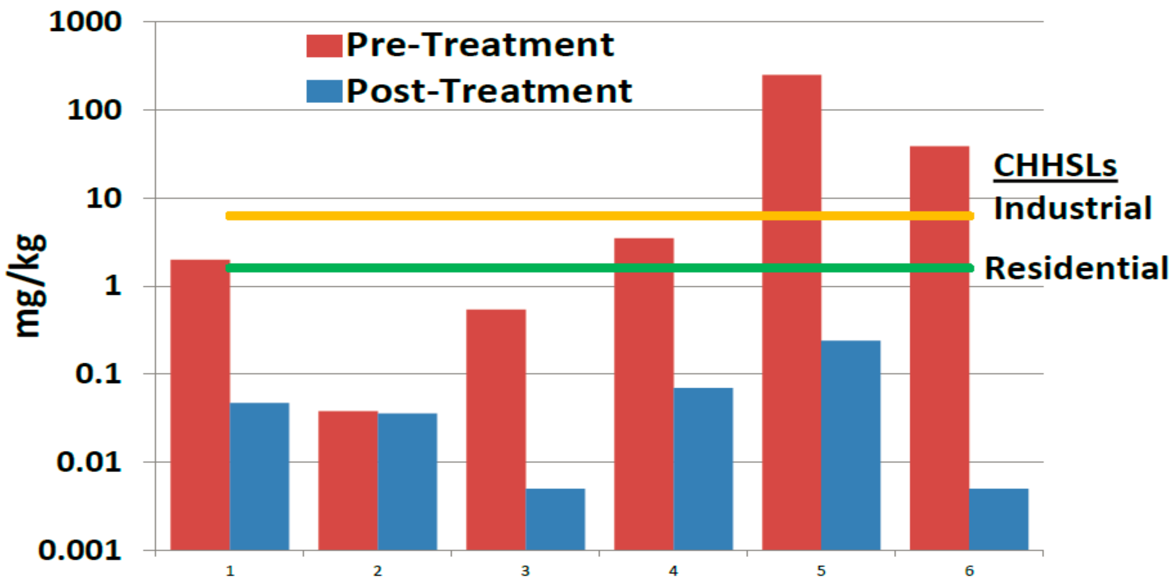


Project Summary & Lessons Learned

Toxaphene Concentrations



DDT Concentrations



- ✓ Residential treatment standards achieved with only one treatment cycle
- ✓ Very high removal efficiencies and low residuals achieved for both DDT and Toxaphene
- ✓ Presence of elemental sulfur?

About us

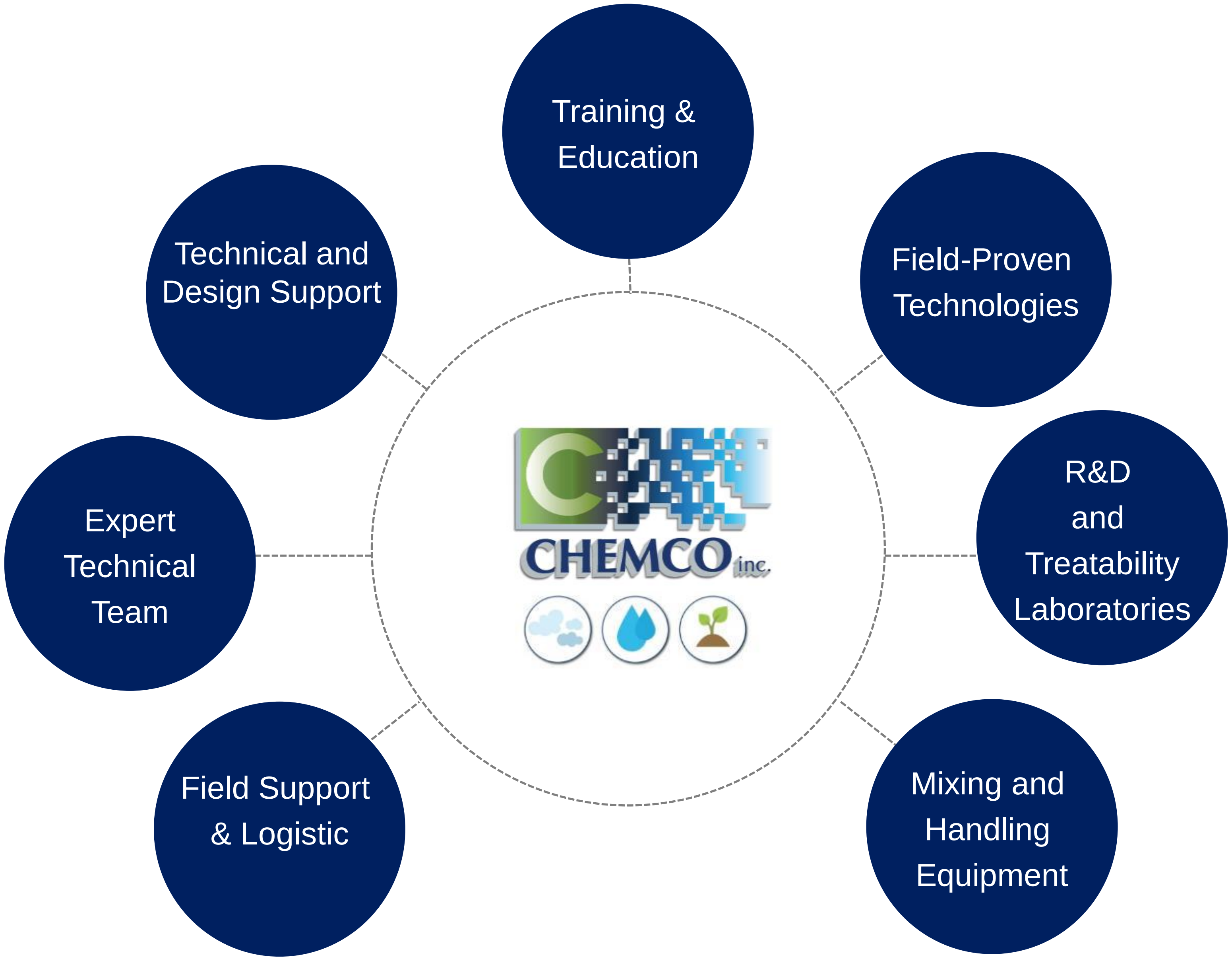
Canadian Company founded in 1988

- **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



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Höganäs *Since 2018*

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Thank you for your attention !
Have a good day !!!

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