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

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Chemco Inc.

SMART Remediation
Edmonton, AB | March 11, 2020
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CANADIAN LEADER IN ENVIRONMENTAL EXPERTISE & SPECIALIZED PRODUCTS

PeroxyChem

Chemical reduction for the treatment of soil & groundwater contaminated with chlorinated pesticides, herbicides & metals

Presented by Jean Paré, P. Eng.
March 2020

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Presentation Agenda

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

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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

www.chemco-inc.com

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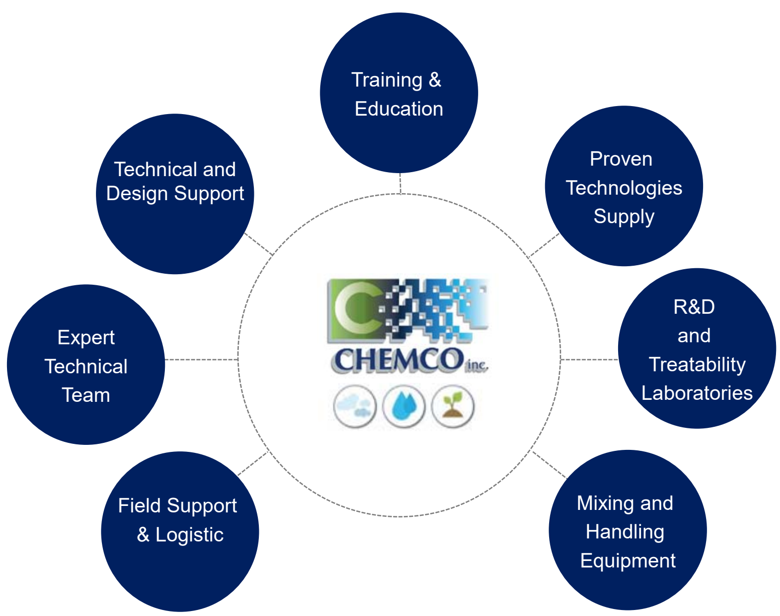
CANADIAN LEADER IN
ENVIRONMENTAL EXPERTISE
& SPECIALIZED PRODUCTS

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



Our product and services

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CHEMCO inc.

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 Remediation, LLC *Since 2016*

ChemBio Formulation *Since 2017*

IVEY-SOL® Surfactant Technology www.iveyinternational.com *Since 2017*

SiREM *Since 2017*

Höganäs *Since 2018*

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Typical site remediation technique

- ✓Dig and Haul
- ✓Pump and Treat
- ✓Soil Vapour Extraction under vacuum with or without air/steam injection
- ✓Chemical Oxidation In Situ//Ex Situ
- ✓Chemical Reduction In Situ//Ex Situ
- ✓Monitored Natural Attenuation
- ✓Enhanced Bioremediation
- ✓Risk Analysis
- ✓Soil Washing
- ✓Phytoremediation
- ✓Reactive Barriers
- ✓Thermal degradation/desorption

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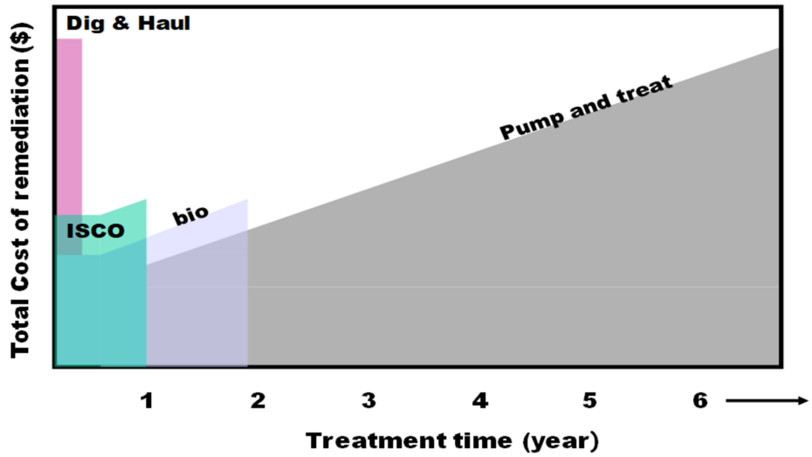
Treatment Evaluation

Remediation time and cost



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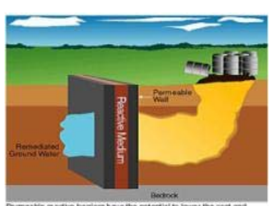
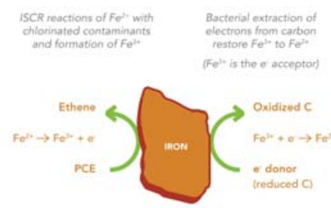
What is In Situ Chemical Reduction?

- ✓ 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.



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ISCR in the Remediation Market

- ✓ **Best suited to treatment of large volumes of lightly to moderately impacted materials. Generally not applicable in situations where contaminants are present at very high (i.e., %w/w) concentrations**
- ✓ **Has the unique advantage of being able to simultaneously treat chlorinated organic compounds and heavy metals in the soil or water**

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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 both soils and groundwater.**

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Reductive Technology Contaminant Applicability

Cycled Anoxic/Aerobic or Anaerobic Degradation Pathways

- ✓ Chlorinated pesticides and herbicides
- ✓ (DDD, DDT, DDE, Toxaphene, Lindane, Chlodane, Dieldrin, Aldrin)
- ✓ Organic explosives (RDX, TNT)
- ✓ Chlorinated solvents (xCE, VC)
- ✓ Metals Precipitation in GW (

Aerobic Degradation Pathways

- ✓ Wood treatment chemicals (PAHs & PCP)
- ✓ Manufactured gas plant PAHs
- ✓ Phthalates
- ✓ Perchlorate
- ✓ Petroleum hydrocarbon

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Typical ISCR Reagents

- ✓Promote combined chemical/biological reduction of contaminants
- ✓Micro-scale or macro-scale zero valent iron + solid/liquid organic carbon and food grade binding agent
- ✓Metals control can come with the same formulation but supplemented with a source of sulfide depending on the contaminant (i.e. sulfate salts)
- ✓Applied in a cycled anaerobic/aerobic mode for chlorinated organics in soil
- ✓Applied in a fully anaerobic mode for organic explosive compounds in soil
- ✓Applied under anaerobic conditions for groundwater treatment

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Amendments Containing ZVI

- EHC®, EHC Plus®
- Daramend®
- Trap & Treat® BOS 100®
- EZVI (Emulsified ZVI)
- FerroBlack®
- AquaZVI™ and MicroZVI™
- Sulfidated ZVI
- Cleanit® Media (Sponge ZVI)
- Many others…

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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

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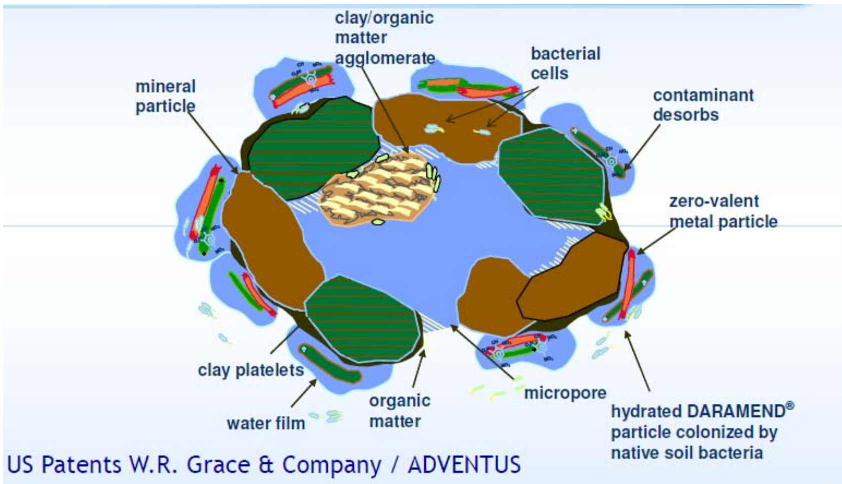
ZVI + Carbon substrate Synergy



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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

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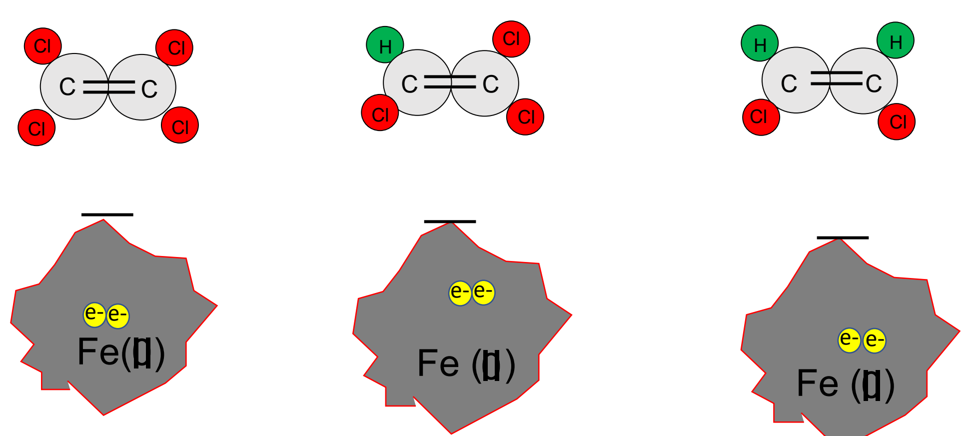
β elimination (abiotic) pathway



3/18/2020

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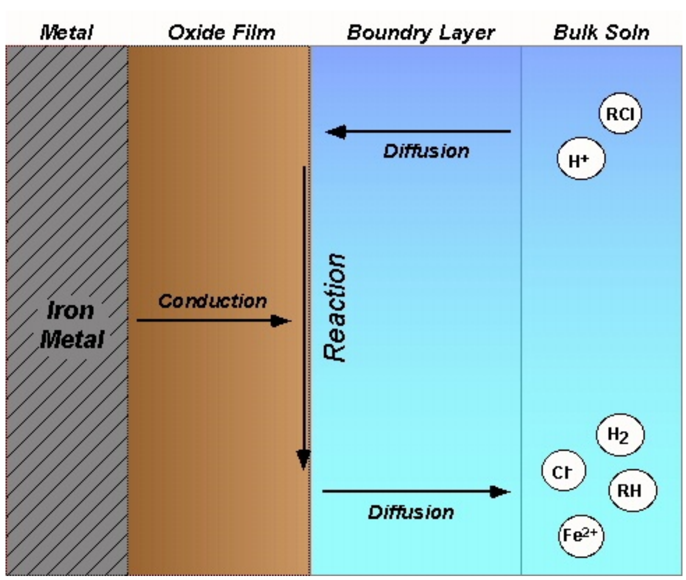
Direct Dechlorination Reactions with ZVI



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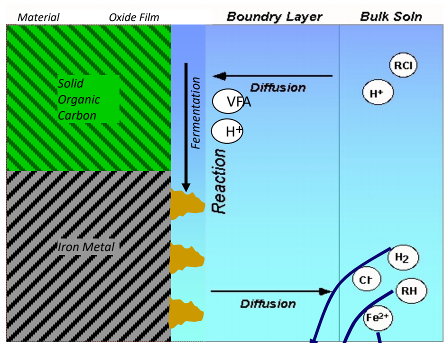
Carbon + ZVI Synergies Generate Multiple Dechlorination Mechanisms: ISCR



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

1. Direct Iron Effects:

Hydrocarbon generation:

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

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

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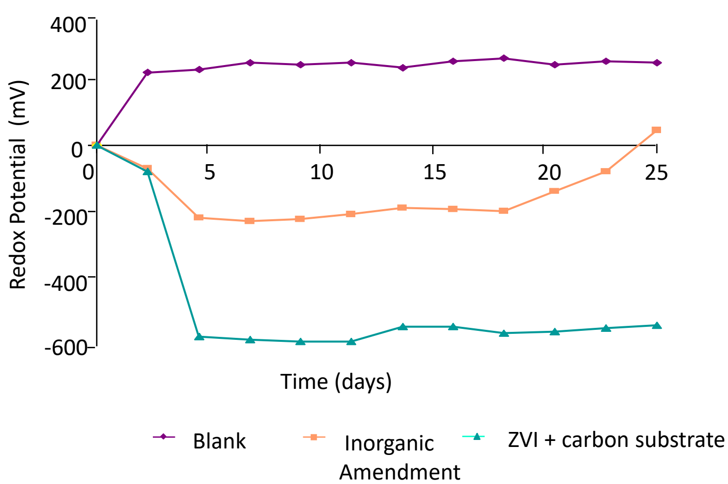
Redox Potential evolution during a reductive phase treatment period



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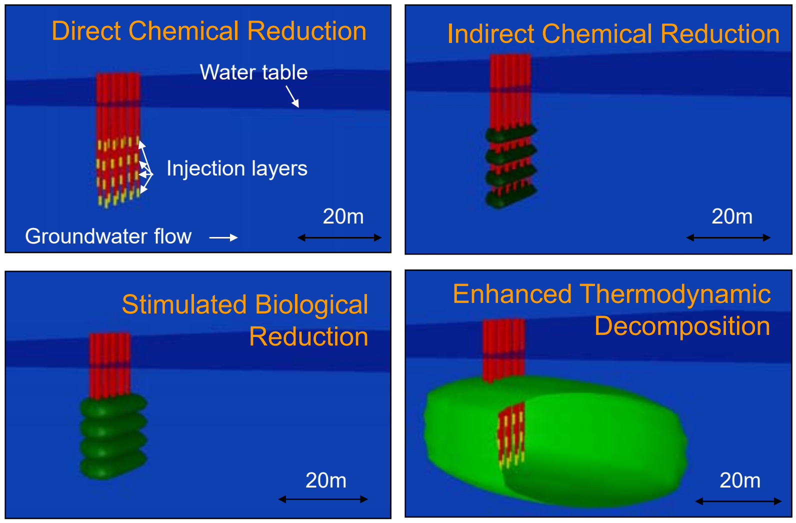
ZVI + Carbone Synergies brings multiples dechloration mechanism



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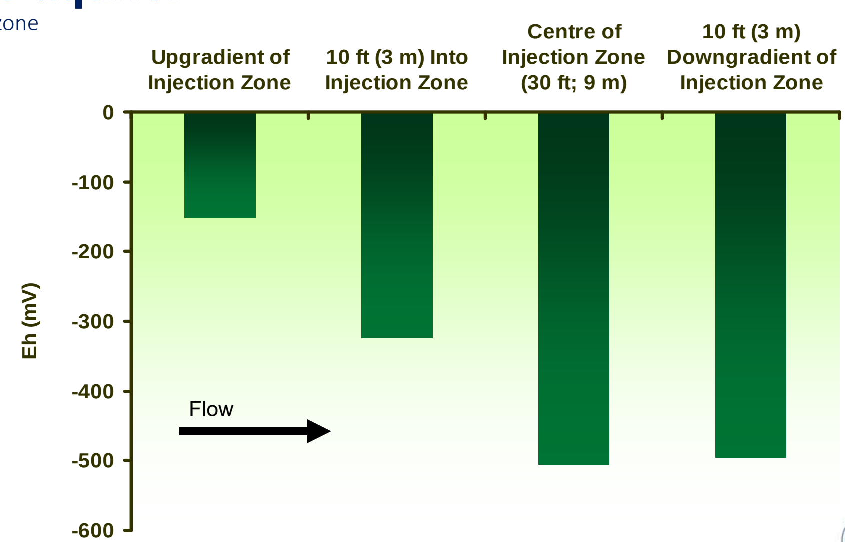
ZVI + FOC blend influence on Redox potential in the subsurface aquifer

60 ft (18 m) injection zone



Source: URS

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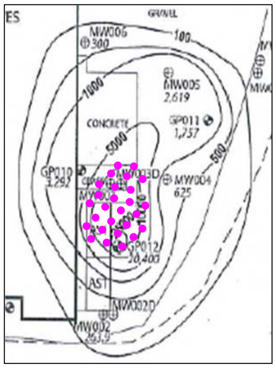
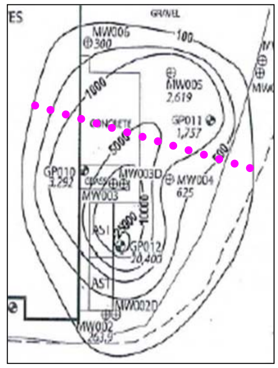
In Situ Intervention Strategies

Source Area/
Hotspot Treatment



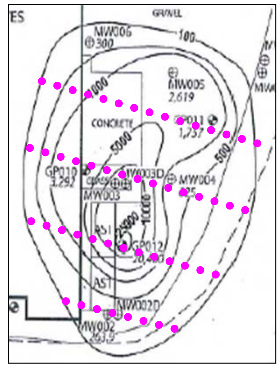
Dosing: 0.15 to 1% wt/wt
Spacing: 5 to 15 ft (DPT)

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

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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

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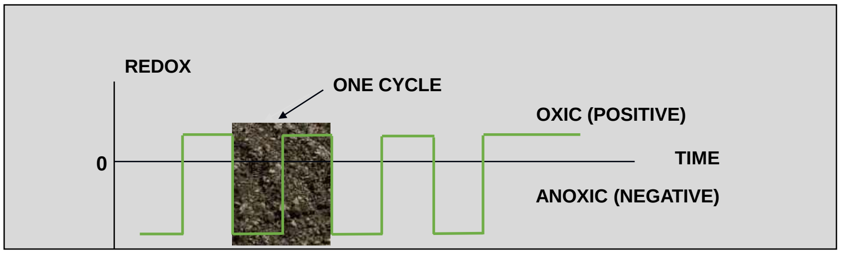
Ex Situ Daramend Redox Cycling

- Cycling between reductive and oxidative phases
- Reagent composition and dosage are site specific



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Ex Situ Daramend Treatment

Source: Vertex Environmental

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Ex Situ Daramend Treatment

Chlorinated Pesticides and Herbicides in Soil

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Ex Situ Daramend Treatment

Sediment Treatment above Clay Confining Layer

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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.

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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

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

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Pesticide Facts

Compound	Category	Solubility (mg/L)	K_{oc}	Soil Half-Life (low – high)	Observed DRE (%)
DDT	insecticide	0.03 – 0.09	151,000	2 – 15 years NPIC	60 – 99
DDD	DDT breakdown	0.09 – 0.10	150,000	70 – 294 days HEDR	
DDE	DDT breakdown	0.12 – 0.14	50,000	100 /16 days	
Dieldrin	insecticide	0.14	12,000	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	1,100	14 – 240 days HEDR	
2,4-D	herbicide	3,400	46	30 – 60 days (CDPR)	
PCP	biocide	1,000	30	178/23 days HEDR	

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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

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Case Study 1

34 acre Agricultural Site – DDT, DDE, Dieldrin

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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%

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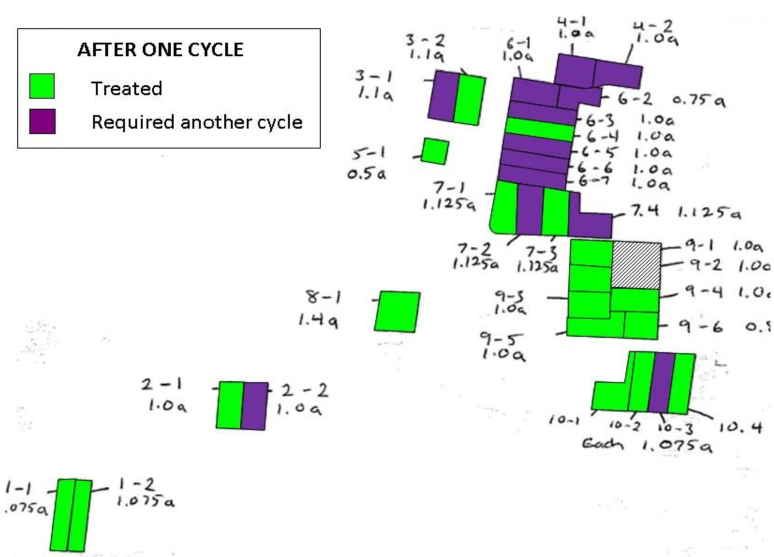
Results After One Cycle



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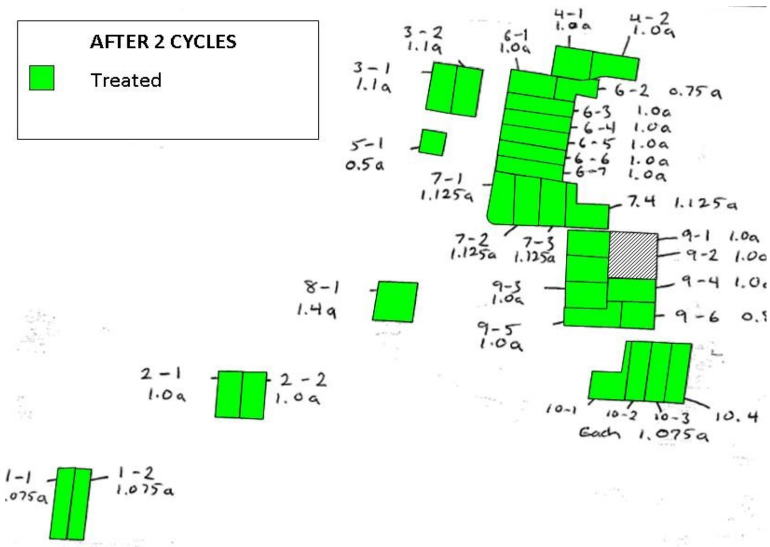
Results After Second Cycle



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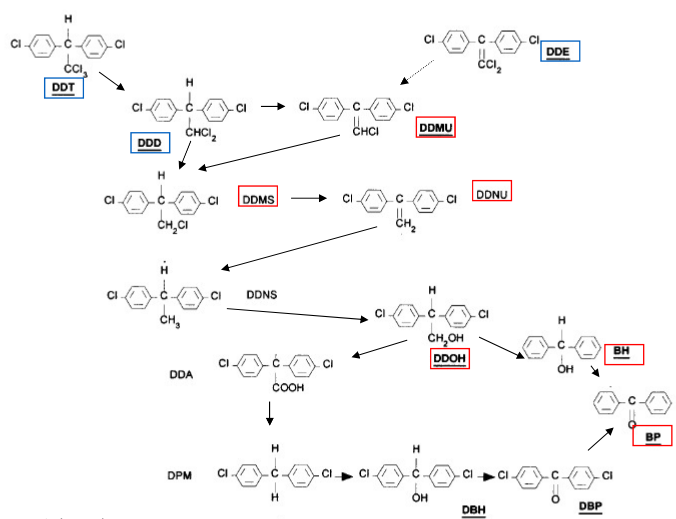
What was the Fate of DDT?

Dechlorination (anaerobic)



From Sayles et al. (1997)

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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

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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

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Case Study 2

Pesticide-impacted Site, Palm Beach County FL

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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

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Daramend Bulk Bags

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Tillage Equipment

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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

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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

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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

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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

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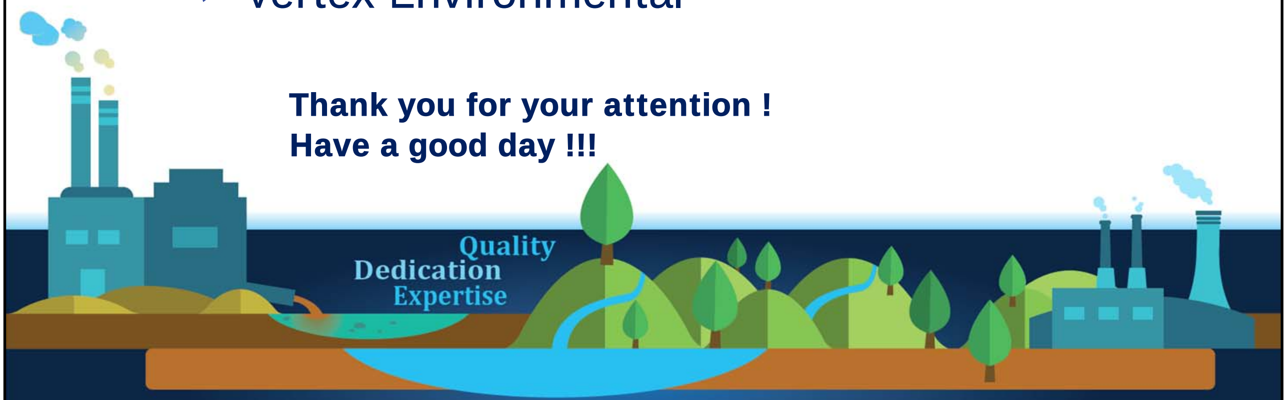
Acknowledgements

- ✓ Peroxychem
- ✓ Vertex Environmental

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



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