



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

Stacey Telesz on behalf of
Alan Seech, Ph.D.

SOIL & GROUNDWATER
REMEDICATION

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Presentation Outline



- Definition of *In Situ* Chemical Reduction (ISCR)
- DARAMEND® ISCR Reagents
- Three Case Studies with economics
- Sustainability
- Questions



What is *In Situ* Chemical Reduction (ISCR)?

- The term in-situ chemical reduction (ISCR) can be used to describe any reductive remediation technology based on transfer of electrons from reduced metals (ZVI, ferrous iron) or reduced minerals (magnetite, pyrite) to the contaminants, such as chlorinated VOCs.
- ISCR uses dechlorination pathways different from those active in biologically mediated reductive dechlorination.
- The major dechlorination pathway promoted by ISCR technology is β -elimination, which supports complete dechlorination of TCE and PCE with less accumulation of metabolites such as cis-DCE and VC than pure enzymatic systems.
- Permeable reactive barriers, known as PRBs, constructed using ZVI are probably the most well-known and broadly applied example of ISCR, with more than 200 constructed worldwide over the past 18 years.

DARAMEND® ISCR Reagents



- Patented combination of slow-release carbon and nutrients with micro-scale ZVI (20% to 50% w/w)
- Stimulates bacteria by providing carbon and nutrients
- Generate very strong reducing conditions that promote reductive dehalogenation reactions
- 2% to 5% by weight required to treat most soils to remedial goals
- Sustainable Solution
 - scrap metal
 - food production by-products



DARAMEND® ISCR Reagents



- Combined biological/chemical reduction technology
- Low cost treatment to remediate light to moderate contamination in situ in a large area as opposed to excavation/dig and haul.
- Standard land farming/agriculture equipment is needed for implementation.
- More than 2,000,000 tons of soil, sediment, and other wastes have been successfully treated to date.



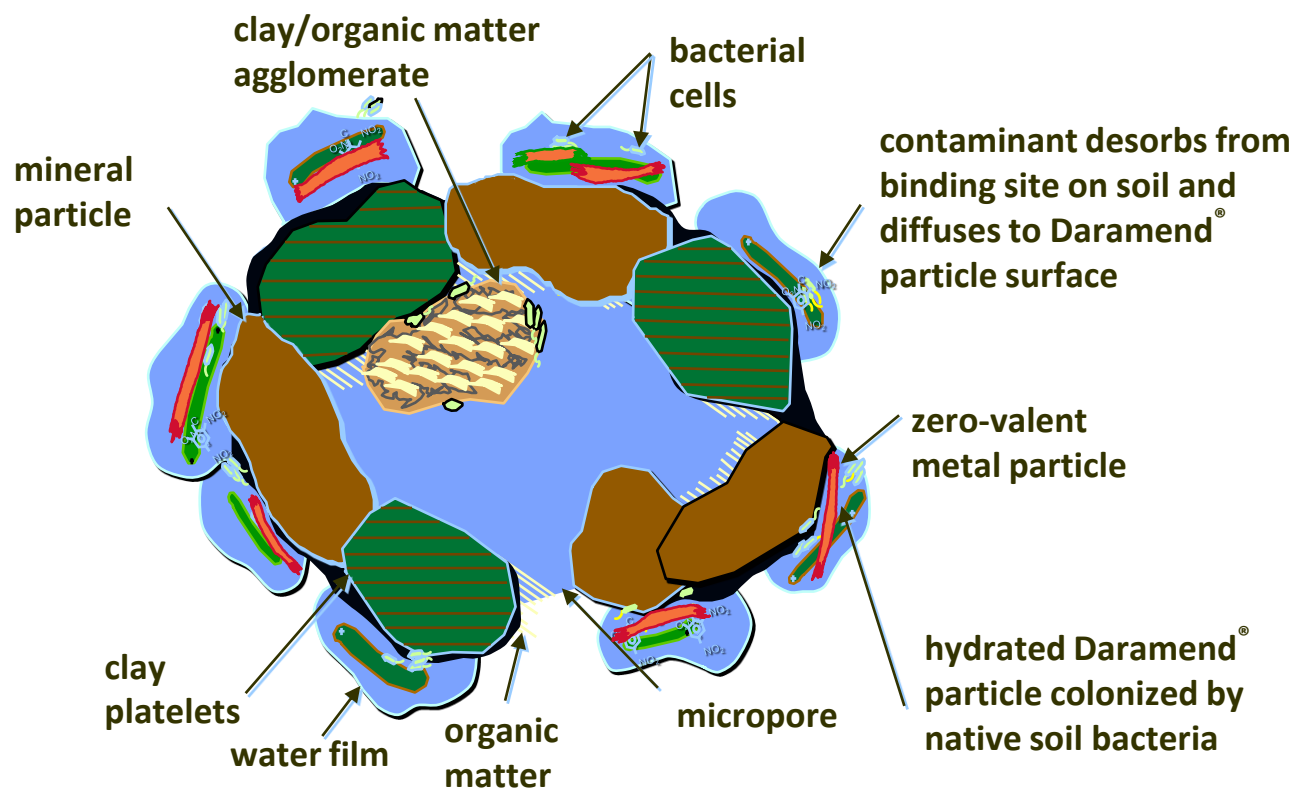
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DARAMEND® ISCR Reagents



- In a lot of soils, hydrocarbons are absorbed, the soil becomes oily so bacteria does not like to grow on the particle.
- Daramend provides a non-toxic, hydrophilic, nutrient rich surface which bacteria can grow on and degrade the contaminants.



DARAMEND® ISCR Reagent Applications



Anaerobic/Aerobic - Applied in a cycled anaerobic/aerobic mode for chlorinated organics to polish out the dechlorination breakdown products.

- Chlorinated pesticides and herbicides
- Chlorinated methanes
- Chlorinated ethenes
- Chlorinated ethanes

Anaerobic

- Organic explosive compounds



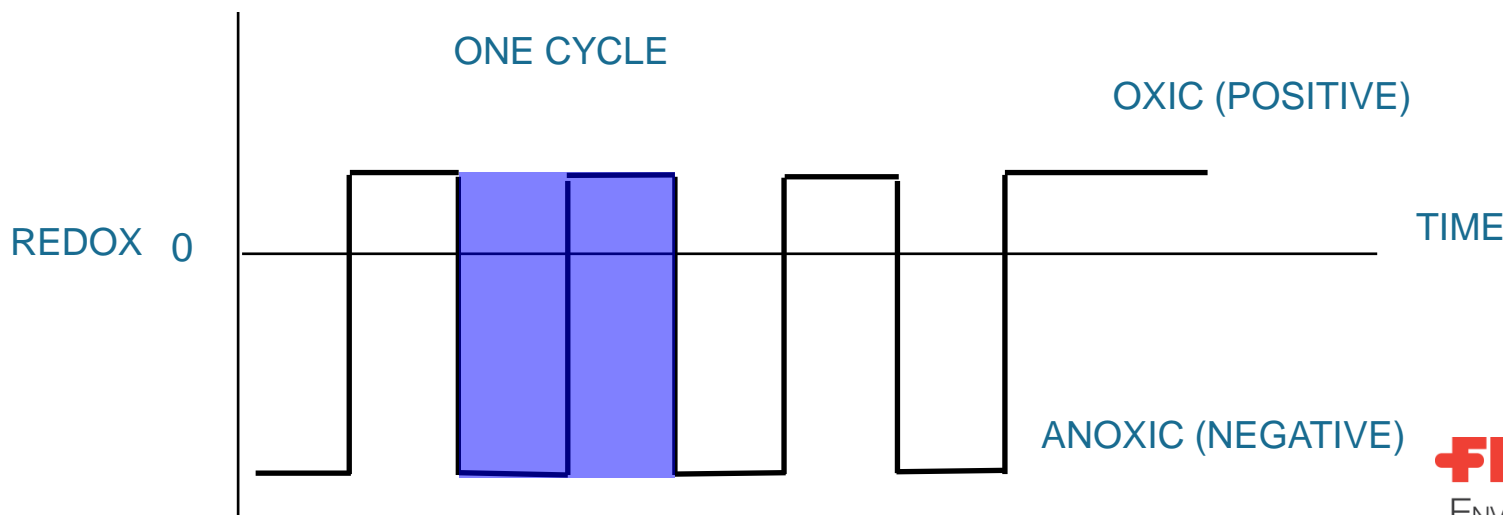
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Cycled Anaerobic/Aerobic DARAMEND®



- One 'cycle' consists of a reductive phase and an aerobic phase
- Reductive DARAMEND (fibrous organic carbon with ZVI) tilled into soil, water is added (80-90% soil water holding capacity) to initiate reductive phase.
- Very strong reducing conditions created with Eh readings commonly between -250 mV and -500 mV within 24 hours
- Static incubation for 5 to 8 days
- Soil tilled to initiate aerobic phase of 2 to 3 days duration
- Repeat if necessary



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DARAMEND® Fixed Site Treatment Facilities



- Waste Management is a licensee of the patented DARAMEND® ISCR technology and treats contaminated soils at permitted treatment facilities.
- Facilities are located in Lake Charles, LA, Calumet City, IL, and Laraway, IL
- Successful ISCR treatment of a range of soils, sediments, and other solid wastes since 2000.





Case Study 1 THAN Superfund Site Montgomery, Alabama

ISCR Treatment of Pesticides

THAN Superfund Site, Montgomery, AL



- T. H. Agriculture and Nutrition Superfund Site in Montgomery, Alabama
- Former agricultural chemical manufacturing facility
- Approximately 4,500 tons of soil contaminated with DDT, DDE, DDD, and Toxaphene
- On-site treatment in a 2 ft layer



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ISCR Treatment of Pesticides

THAN Superfund Site, Montgomery, AL



- Applied and incorporated 2% (w/w) DARAMEND amendments
- Irrigate amended soil to 90% of soil water holding capacity (approx. 30% moisture on a dry weight basis)
- Allow to stand undisturbed for about 7 days (variable dependent on weather)
- Aerate by tilling for 2 or 3 days
- Repeat as required



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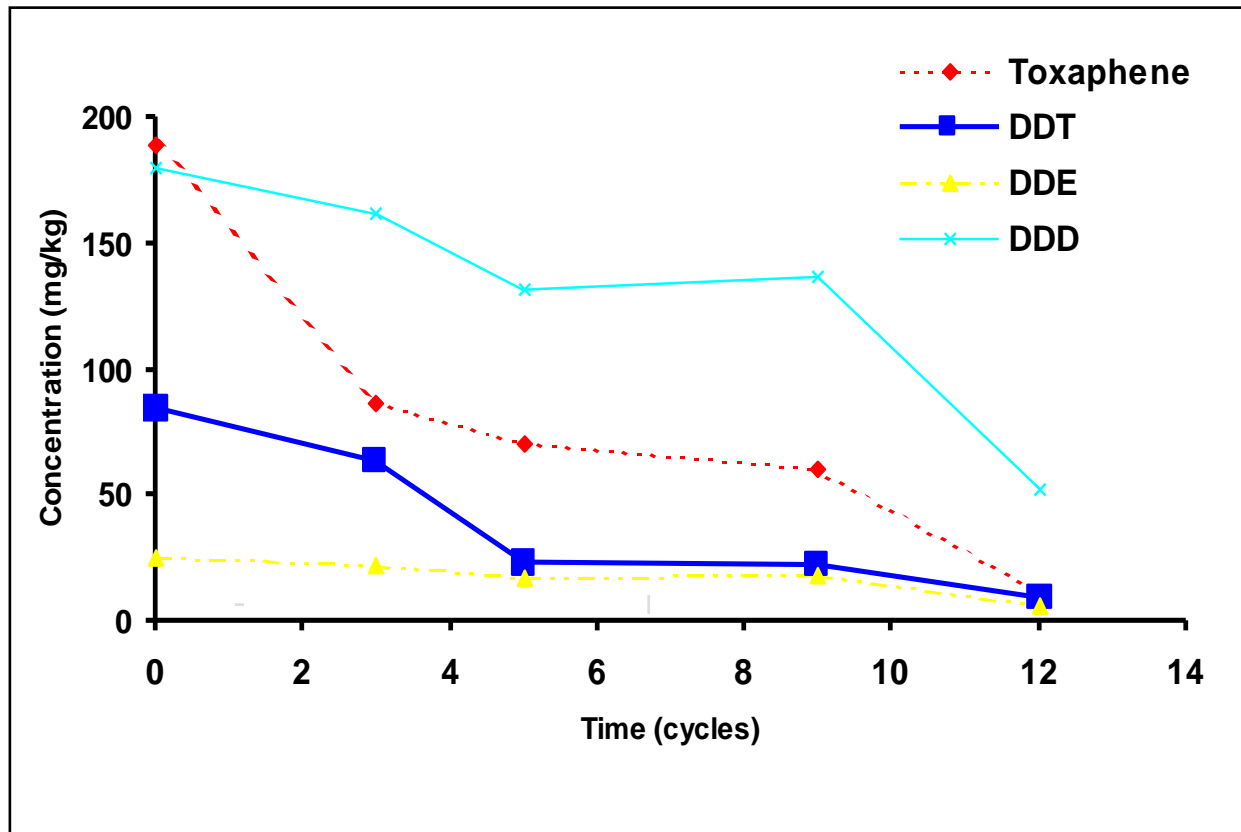
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ISCR Treatment of Pesticides

THAN Superfund Site, Montgomery, AL



- Performance Data showing the break down of DDT
- 12 Cycles were completed (around 10 days each) – 120 days total
- You can save money but it will take some time.



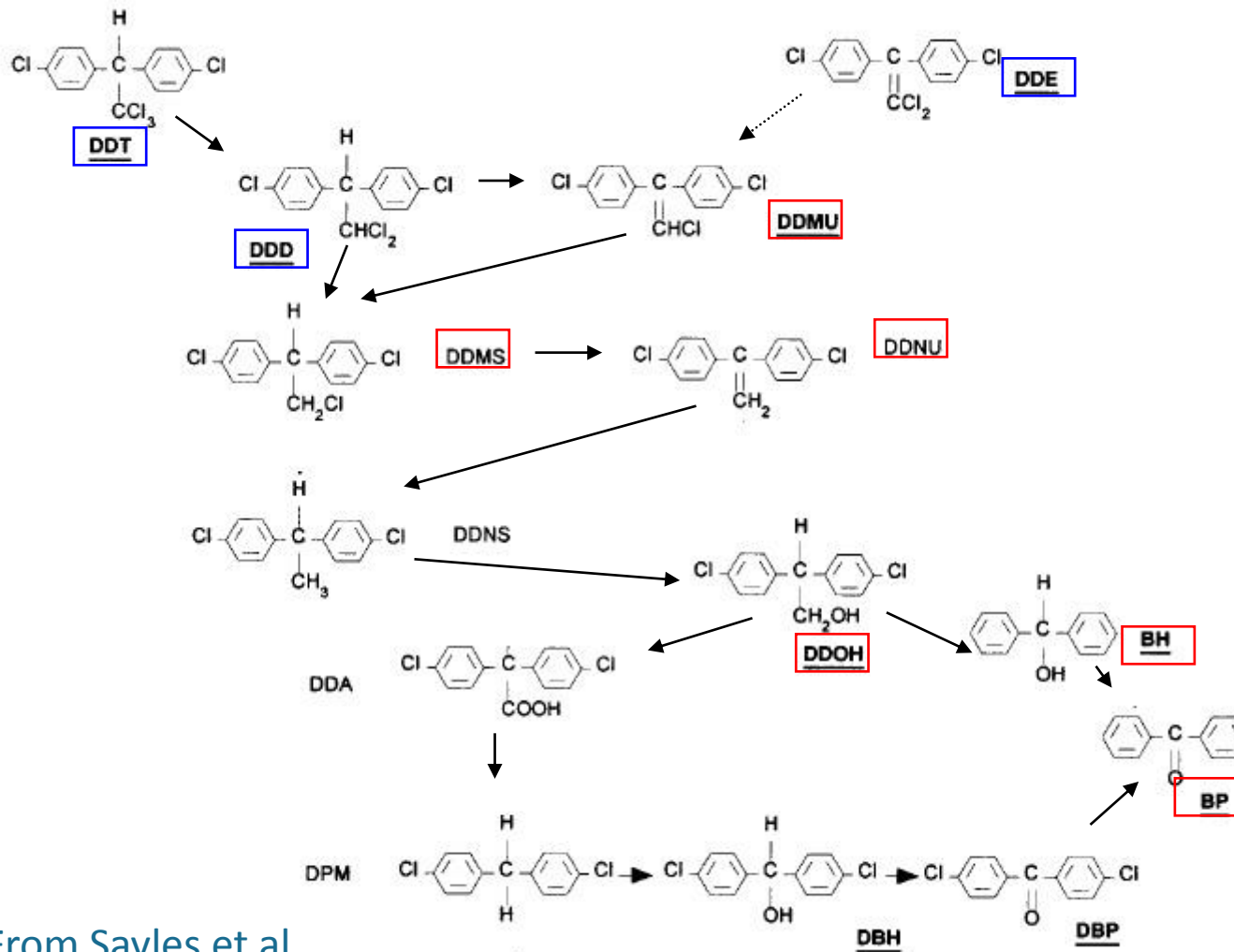
Economics



- Costs are variable and dependent on:
 - Excavation requirements
 - Initial contaminant concentrations
 - Remediation Goals
 - Number of cycles needed
- Treatment Costs ranged from \$30/ton to \$63/ton
 - Average treatment cost was \$55/ton

What was the fate of the DDT?

Dechlorination (anaerobic)



From Sayles et al.
(1997)

What was the fate of the DDT?

Ring opening/Mineralization?



- Radioisotope (^{14}C -DDT) Fate Studies:
 - Confirmed Daramend process broke DDT down to carbon dioxide
 - Slow but significant production of ^{14}C - CO_2
 - Recovery of added ^{14}C in DDT as carbon dioxide was about 7% in 150 days
 - After 150 days the rate of ^{14}C - CO_2 release had decreased to about 1% per month
- Stable isotope (^{13}C -DDT) Fate Studies:
 - Indicated dichlorobenzophenone (DBP) was the major breakdown product, which is in agreement with the published literature on how DDT breaks down.
 - It was further broke down to carbon dioxide.



Case Study 2 Former Agricultural Site Toronto, Ontario

ISCR Treatment of Pesticides

Former Agriculture Site, Toronto, ONT



- 33 acre site, former apple orchards and strawberry farms converted into residential homes.
- 50 years of farming resulted in elevated DDT, DDE, Dieldrin
- Looked at potential dig & haul but with the location of the site and location of the landfill it would have required 1500 truckloads of contaminated soil to be hauled through residential neighborhoods.
- When looking for an alternative to dig & haul they found Daramend.
- Lab studies confirmed their remedial goals could be achieved and had positive results.

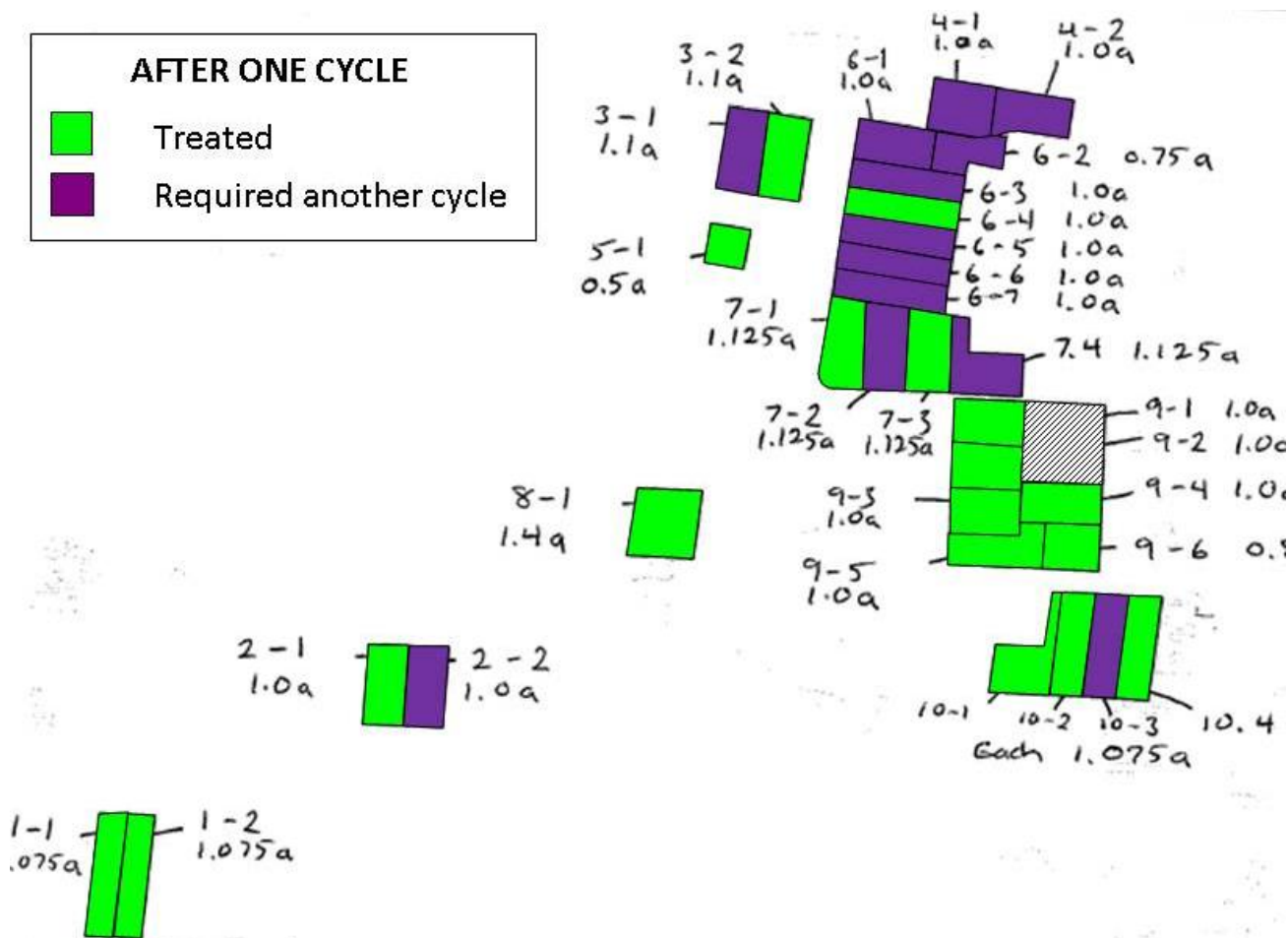


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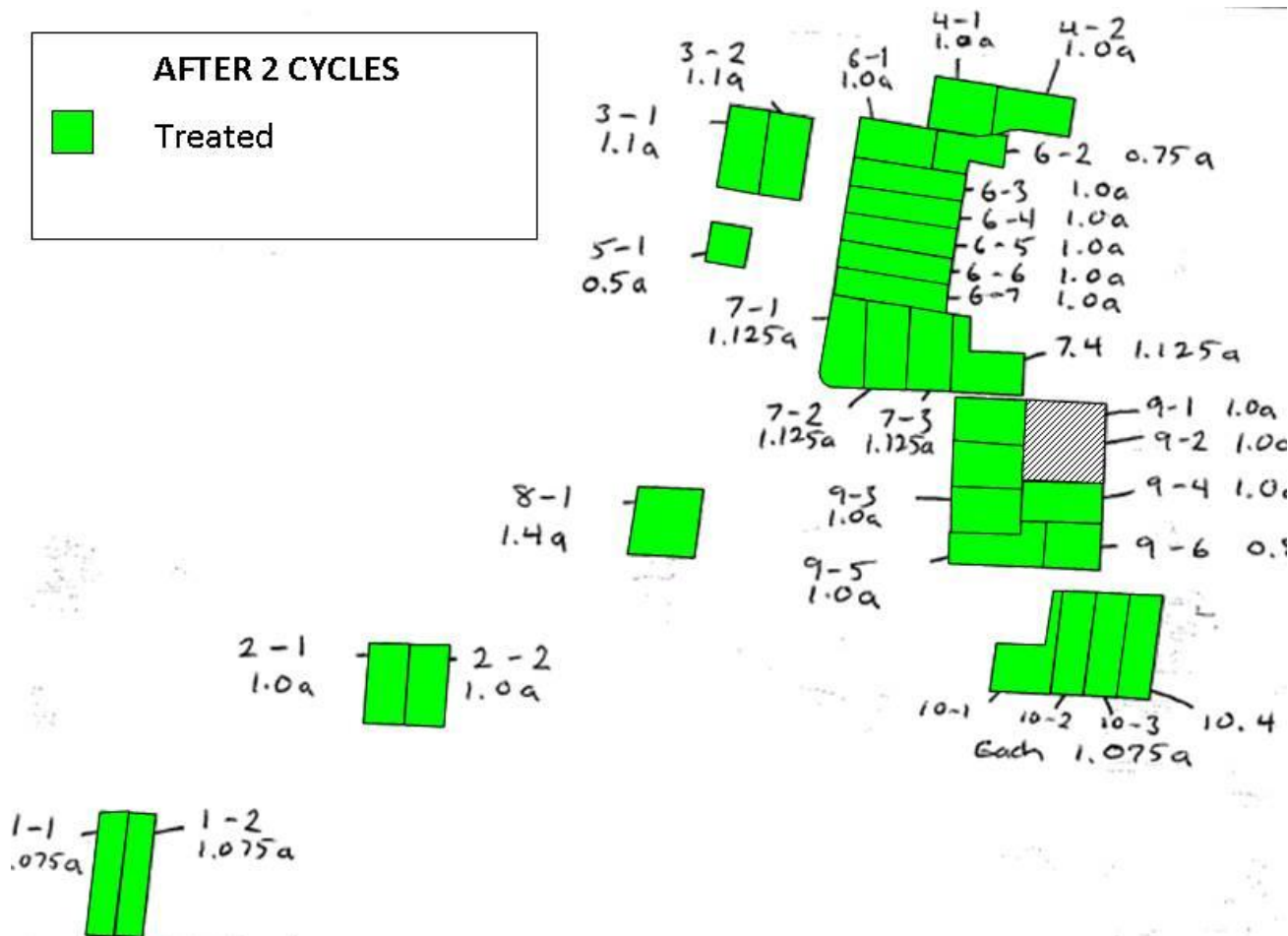
Treatment Results After One Cycle

Agricultural Site: Toronto Canada



Treatment Results After Two Cycles

Agricultural Site: Toronto Canada



Treatment Results After One and Two Cycles

Agricultural Site: Toronto Canada



Data for plots treated after one cycle

Constituent	Initial Concentration (mg/kg)	Concentration After 1 st 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 plots that received a second cycles

Constituent	Initial Concentration (mg/kg)	Concentration After 1 st Cycle (mg/kg)	Concentration After 2 nd 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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Case Study 3 Industrial Site Southern California

Daramend® Case Study

Industrial Site, Southern CA



Site Background

- ~1 acre property in Southern CA
- Fenced and vacant, previous strong odor
- Property is leased by client from Union Pacific Railroad (UPRR)
- Zoning is rail-industrial

Chemicals of Concern

- Organochlorine pesticides
 - Primarily Toxaphene
 - Lesser extent: DDT, DDE, chlordane
- Majority of COCs confined to top 2-3 ft of soil
- Source areas excavated



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Daramend® Case Study

Full-Scale Application



- Application rate determination:
 - 0.7% w/w
- Tillage and cycle application
 - Tillage work required dust control
 - Tractor-tiller used to spread and incorporate DARAMEND® reagent





Daramend® Case Study Summary

- After one cycle, reduction in grid samples achieved site remediation cleanup goals of industrial CHHSLs.
 - All but 2 locations reduced pesticide concentrations to less than residential CHHSLs
 - Toxaphene had high degradation rates
- Regulatory agency familiar with technology
- No negative comments from public
- Applicable to agricultural fields with shallow contamination
- Costs significantly lower than excavation and landfill



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Economics



DARAMEND ISCR Treatment Cost = \$16/ton (1 application)

On-site Tech Support	\$19,600
Equipment Rental	\$11,500
DARAMEND ISCR Reagent	\$27,700
Delivery of product and equipment	\$11,500
TOTAL:	\$70,300

Excavation Unit Cost = \$103/ton

Excavation	\$83,000
Soil Import, Backfill, & Compaction	\$54,000
Waste Disposal (\$72/ton as non-RCRA)	\$314,000
TOTAL:	\$451,000

*0.8 acres @ 2.5 ft bgs z 4,400 tons

**US costs typically range ~\$29 - \$63/ton



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Treated Pesticides and Herbicides



DDT, DDD, DDE	✓
Toxaphene	✓
Chlordane	✓
Dieldrin	✓
Lindane & other HCHs	✓
2,4-D	✓
2,4,5-T	✓
Endrin	✓
Alachlor, Metolachlor	✓
Atrazine	✓

Any Questions?



Dr. Alan Seech

Director - Soil & Groundwater Remediation

FMC Environmental Solutions

Phone: 949-514-1068

Alan.Seech@fmc.com

www.environmental.fmc.com

Stacey Telesz

Technical Sales Manager

FMC Environmental Solutions

Phone: 949-280-5765

Stacey.Telesz@fmc.com

www.environmental.fmc.com



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