Environmental Solutions

PeroxyChem

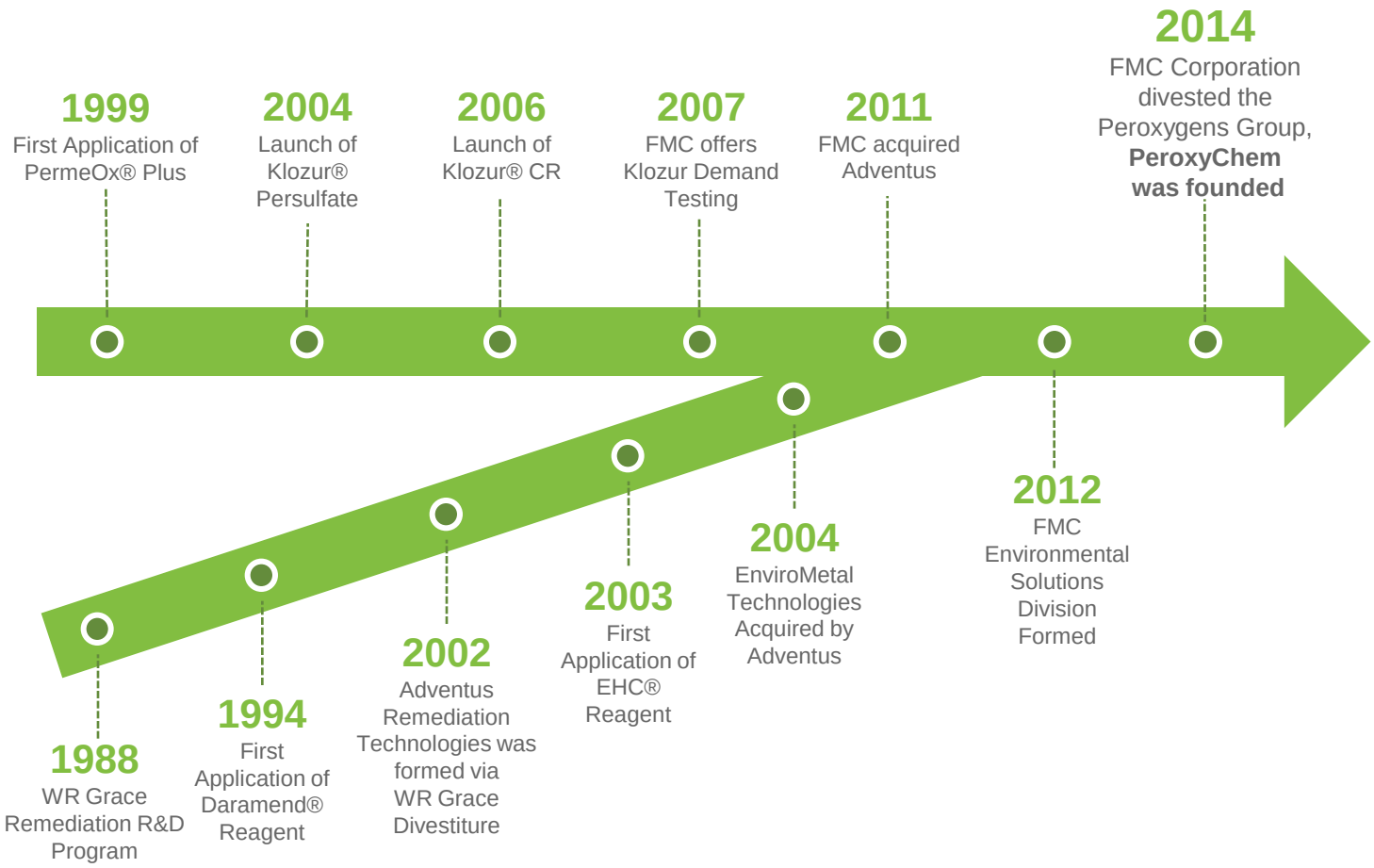
# DARAMEND® ISCR Reagent

*A Cost-effective Alternative to Excavation & Landfilling for the Remediation of Soils*

**Alan G. Seech, Ph.D.**
**PeroxyChem**

**3 December 2014**

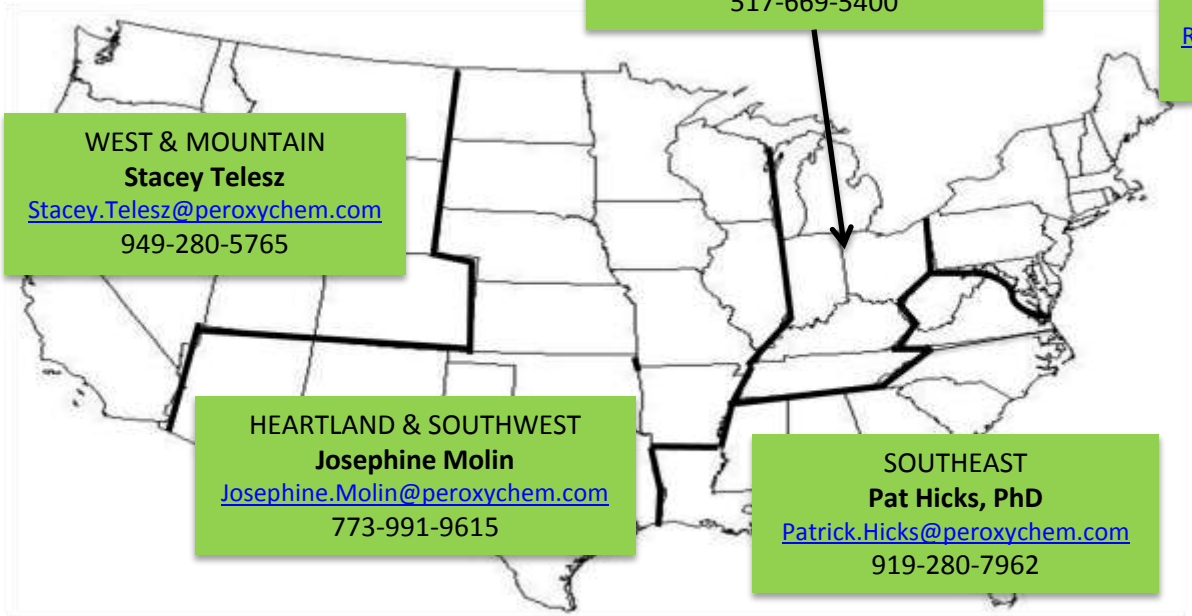
# New Name.
# Decades of Experience.



# Who We Are…


Expert Technical Team
Field-Proven, Diverse Technologies
Field Support
PeroxyChem
Environmental Solutions
R&D and Treatability Laboratories
Technical and Design Support
Mixing and Handling Equipment

# Environmental Solutions Team



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# Field-Proven Portfolio of Remediation Technologies Based on Sound Science

***In Situ* Chemical Oxidation**

1. Klozur® persulfate
2. Klozur® CR

***In Situ* Chemical Reduction**

3. EHC®
4. EHC® Liquid
5. Daramend®

***Aerobic Bioremediation***

6. Terramend®
7. PermeOx® Ultra

***Immobilization/Stabilization***

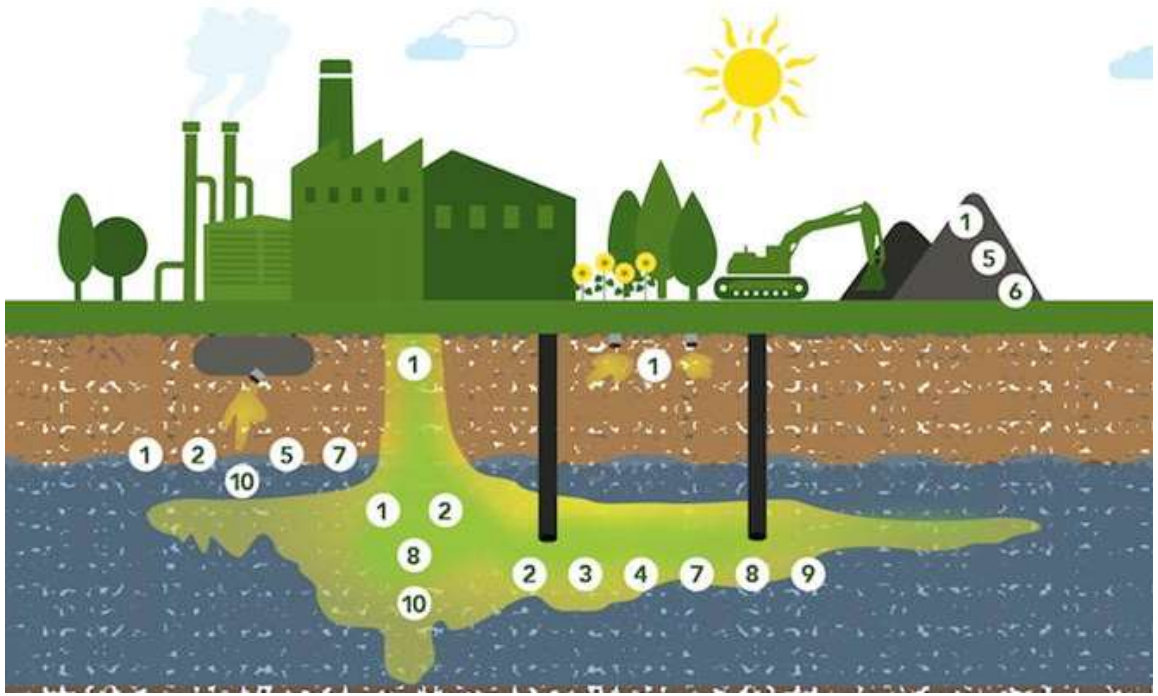
8. EHC® Metals and MetaFix™

***Enhanced Reductive Dechlorination***

9. ELS™

***NAPL Stabilization/Mass Flux Reduction***

10. ISGS™



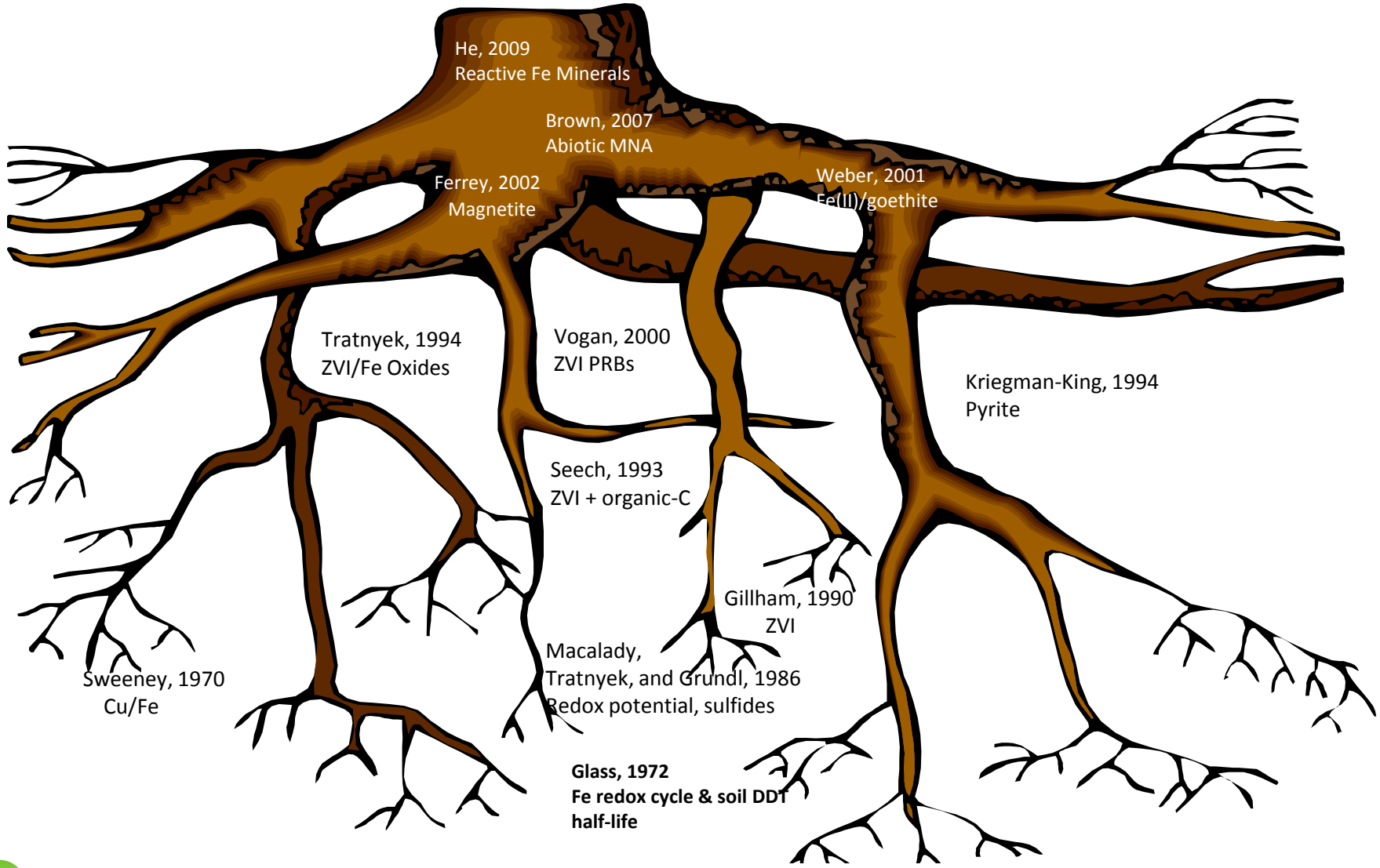
# Presentation Outline

- Definition of *In Situ* Chemical Reduction (ISCR)
- Key concepts important to the discussion
- Enhancement of iron reactivity by carbon fermentation: DARAMEND® ISCR Reagents
- Two example projects
- **Detailed case study (Todd Slater, Retia USA LLC)**
- Questions & Answers

# 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 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.
- Dechlorination pathways for pesticides are less well-understood; however, for some, such as DDT, we know the process all the way to ring cleavage and mineralization.
- Permeable reactive barriers, known as PRBs, constructed using ZVI are probably the most well-know and broadly applied example of ISCR, with more than 200 having been constructed worldwide over the past 18 years.

# The Roots of ISCR (after Brown, 2008)



# DARAMEND® ISCR Reagents

## *In Situ* Chemical Reduction

# 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 located in Lake Charles LA, Arlington OR, and Laraway IL
- More than 3,000,000 tons of soil, sediment, and other wastes have been successfully treated to date.

# DARAMEND® ISCR Reagents

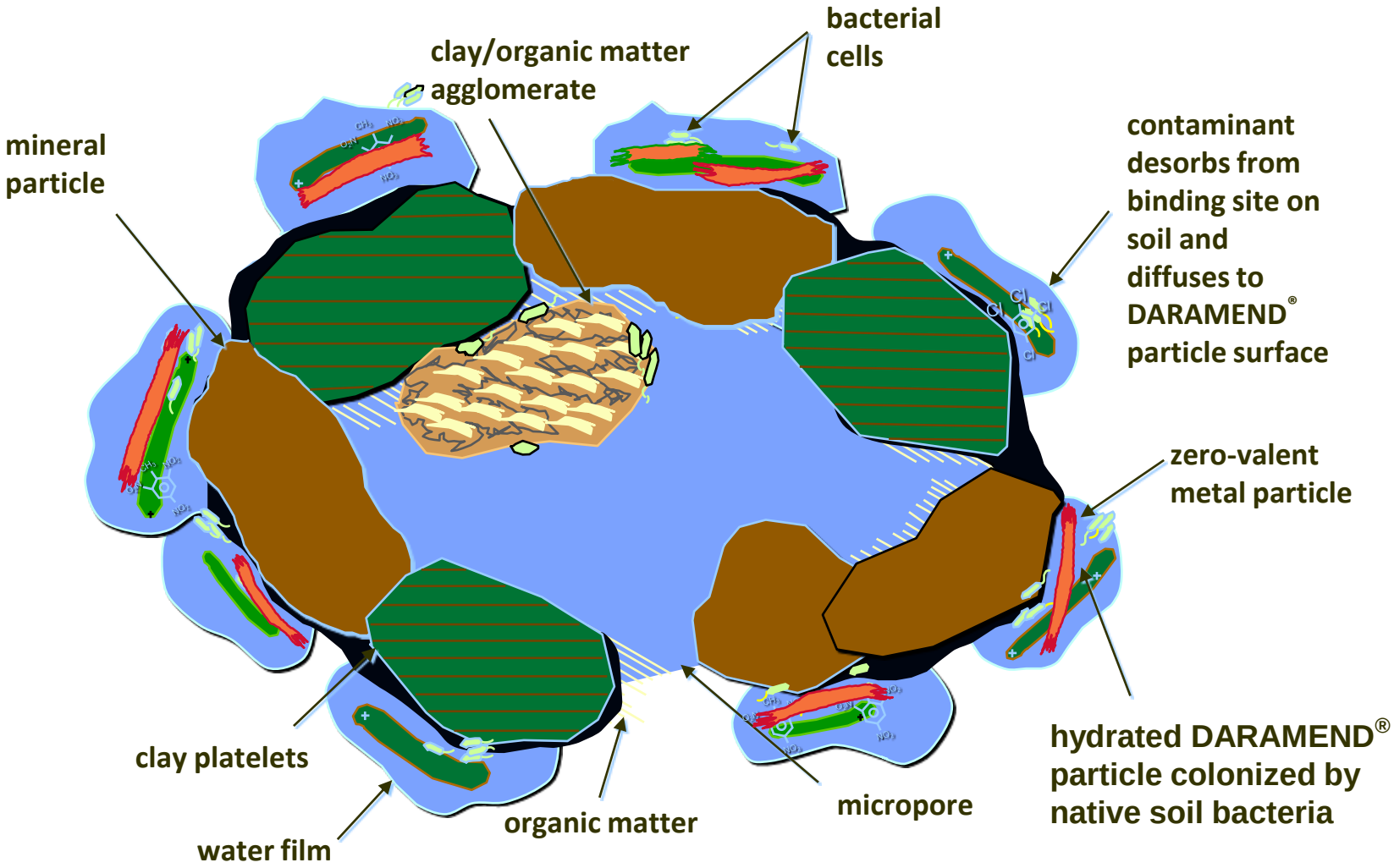
- A combined biological/chemical reduction technology
- Microbial (respiration) and chemical (ZVI corrosion) oxygen consumption combine to enable effective treatment of most halogenated and nitroaromatic organic compounds
- Applied in a cycled anaerobic/aerobic mode for chlorinated organics in soil, sediment, and other solid wastes (see next slide)
- Applied under anaerobic conditions for groundwater treatment (EHC® and EHC-M®)

# DARAMEND® ISCR Reagents

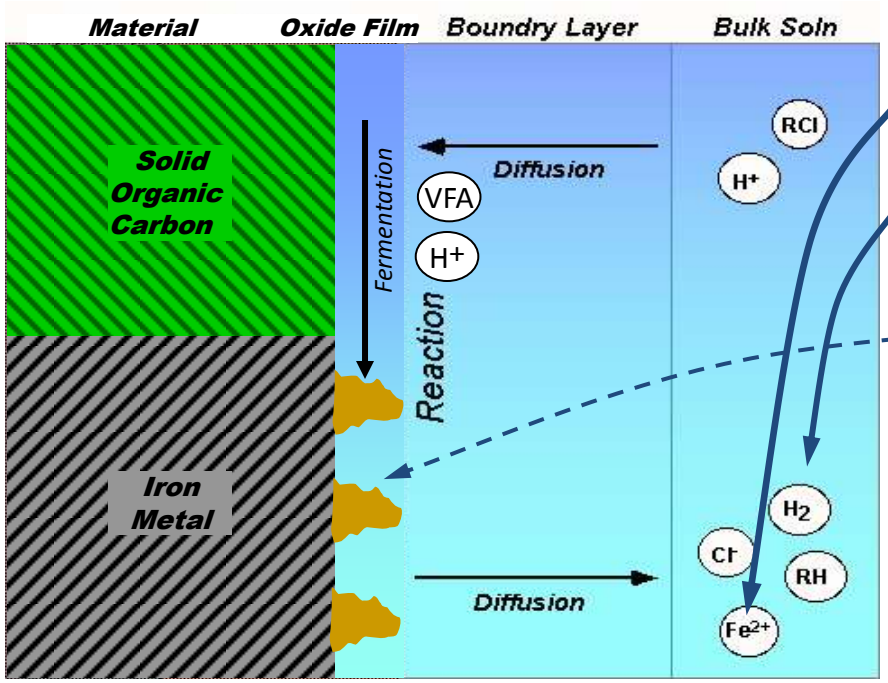
- Patented combination of slow-release carbon and nutrients with micro-scale ZVI (20% to 50% w/w)
- Stimulates indigenous bacteria by providing carbon and nutrients
- Generate very strong reducing conditions that promote reductive dehalogenation reactions
- 2% to 5% by weight required to treat most soils to remedial goals
- More than 3,000,000 tons of soil, sediment, and other wastes have been successfully treated to date.

# DARAMEND® ISCR Technology

## *How it works*



# Carbon Fermentation + ZVI Corrosion:
## Multiple Dechlorination Mechanisms




Fe+2 generation

$H_2$ generation

**ZVI Reactions:**

$Fe^0 \rightarrow Fe^{2+} + 2e^-$

$2H_2O \rightarrow 2H^+ + 2OH^-$

$2H^+ + 2e^- \rightarrow H_{2(g)}$

$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-$

**Production of organic acids (VFAs):**

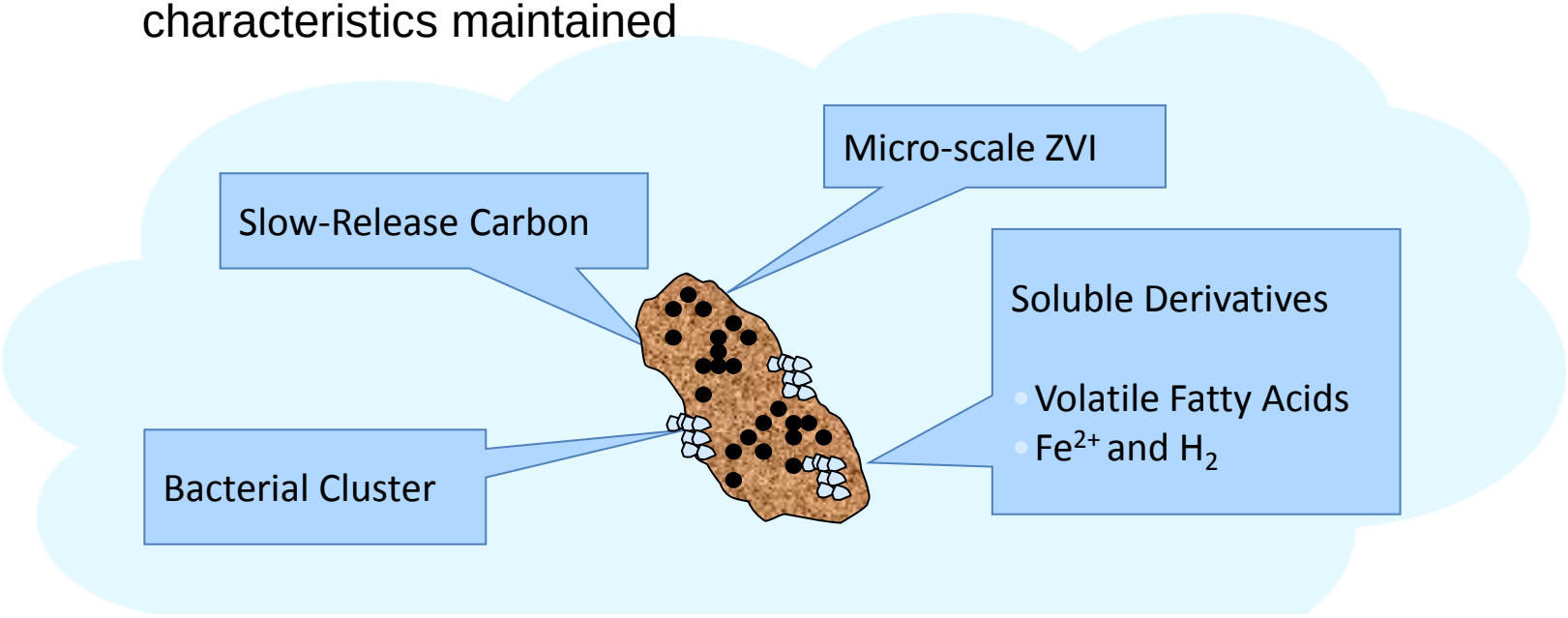
- Serves as electron donor for microbial reduction of CVOCs and other oxidized species such as $O_2$, $NO_3$, $SO_4$
- The release of acids keeps the pH down and thereby serve to reduce precipitate formation on ZVI surfaces to increase reactivity
- Increase rate of iron corrosion/$H_2$ generation

**Favorable thermodynamic conditions for dechlorination:**

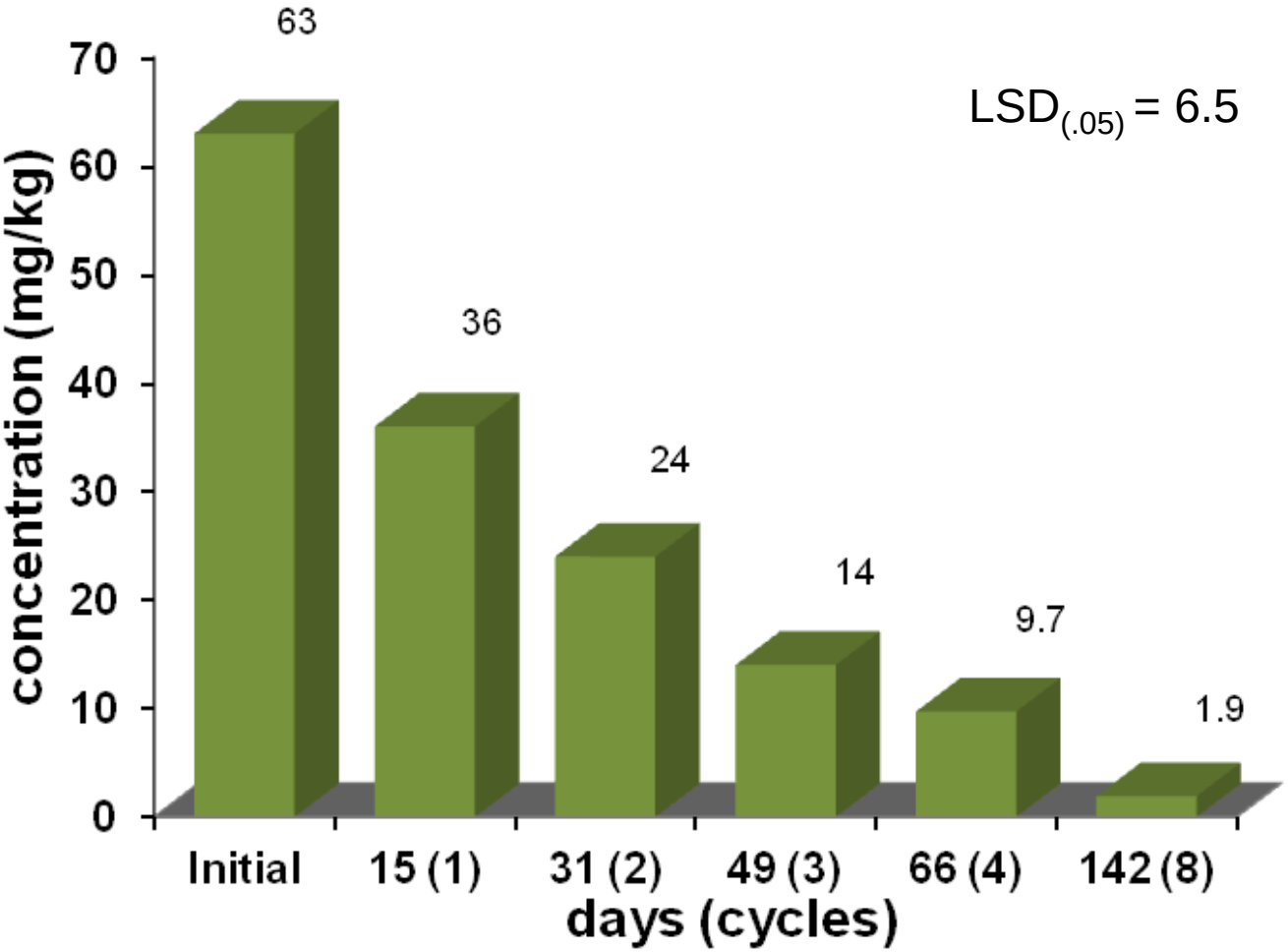
- Combined oxygen consumption from carbon fermentation and iron oxidation → Strongly reduced environment (-250 to -500 mV)
- High electron/$H^+$ pressure

# Attributes of DARAMEND® ISCR

1. Oxidized ZVI (alkaline) and fermenting carbon (acidic) are balanced producing circumneutral pHs in contrast to either alone.
2. Organic acids reduce or eliminate iron passivation – increasing the efficiency of ZVI by minimizing coating.
3. Synergistic thermodynamic effects from Fe + C
4. Low dosage = No bulking + In Situ practical + Geotechnical characteristics maintained



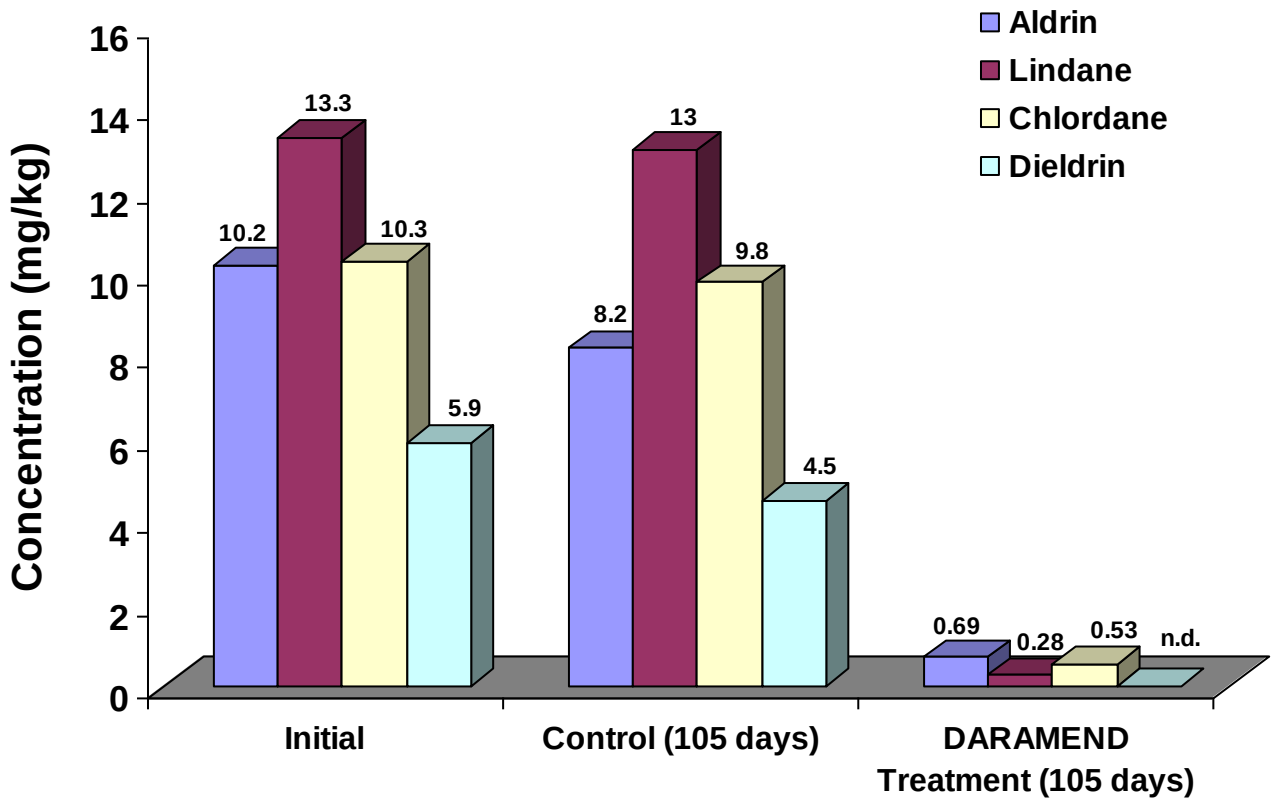
# Influence of DARAMEND® treatment on Toxaphene concentration in Southeastern U.S. soil




$LSD_{(.05)} = 6.5$

Data points represent mean of four replicates

# Influence of DARAMEND® treatment on Aldrin, Lindane, Chlordane, and Dieldrin concentrations in soil



# DARAMEND® ISCR Reagent Applications

Cycled Anoxic/Aerobic

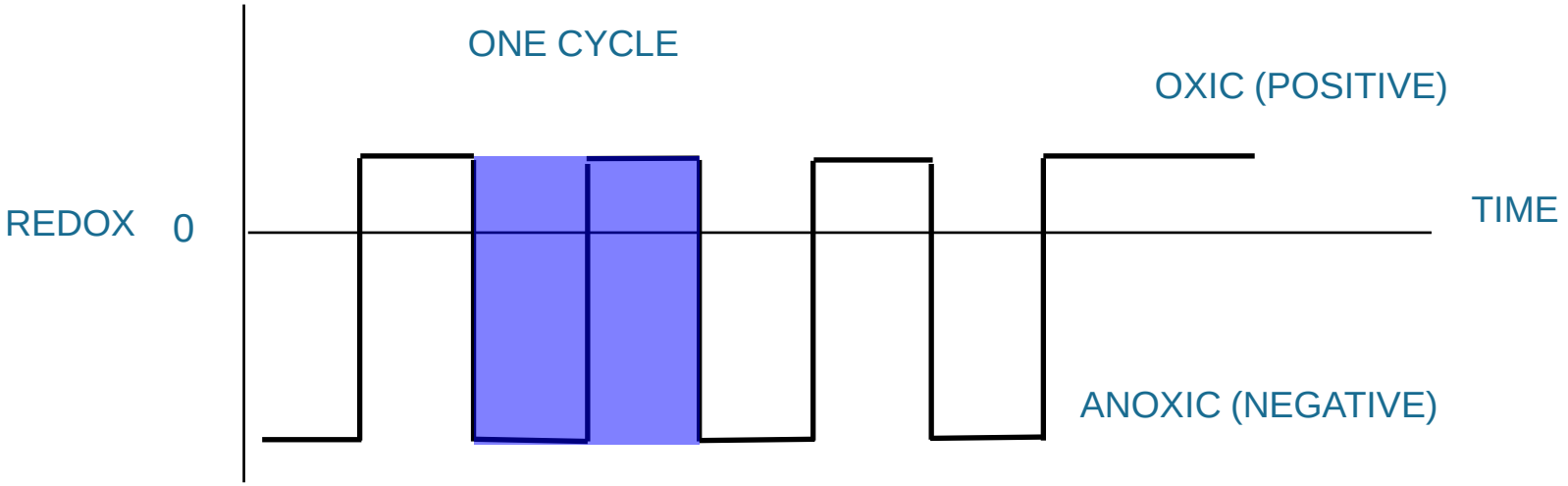
- Chlorinated pesticides and herbicides
- Chlorinated methanes
- Chlorinated ethenes
- Chlorinated ethanes

Anaerobic

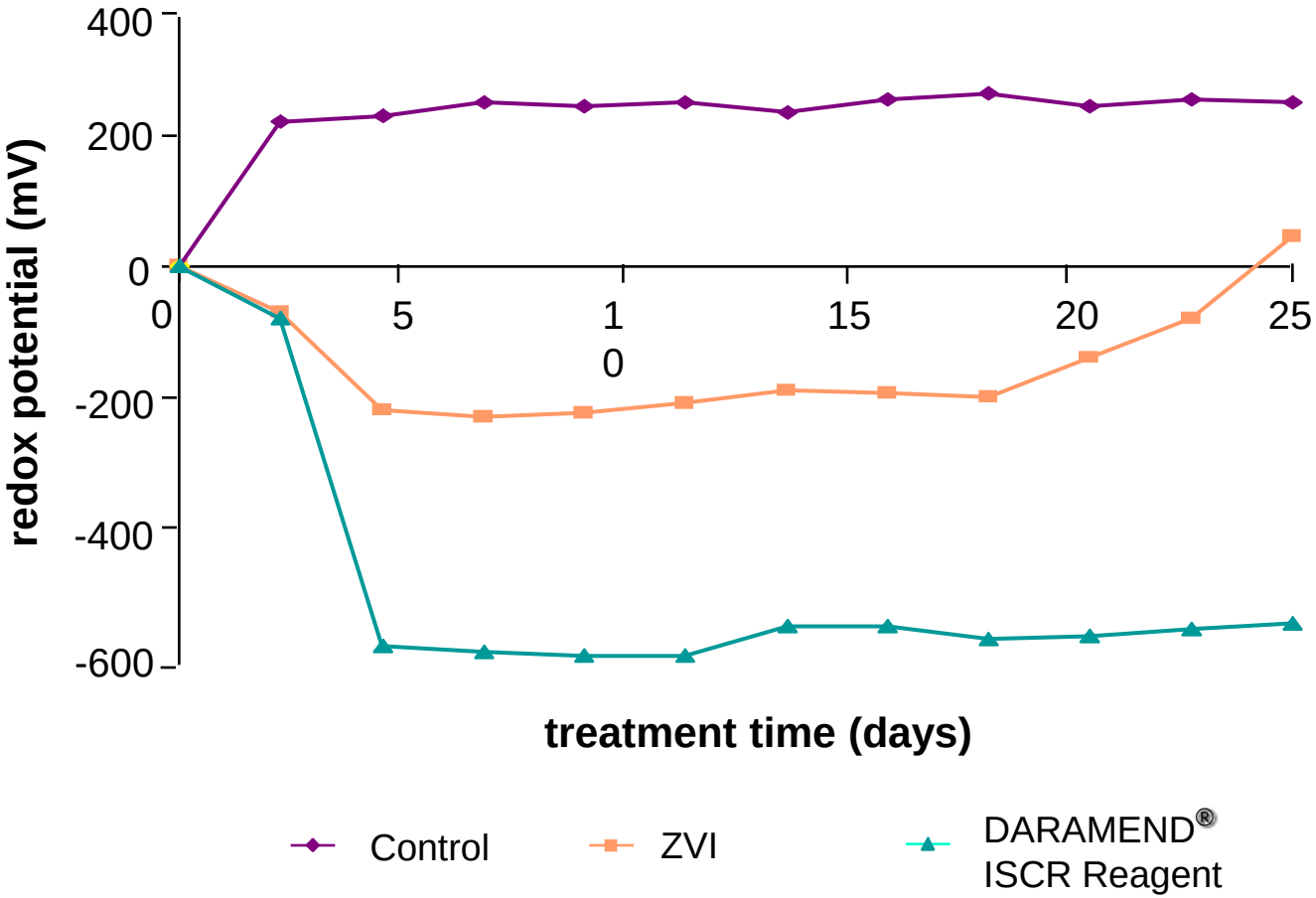
- Organic explosive compounds

# Cycled Anaerobic/Aerobic DARAMEND®

- One ‘cycle’ consists of a reductive phase and an aerobic phase
- Reductive DARAMEND (food grade insoluble + soluble 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



# Redox Potential in Soil during Reductive Phase



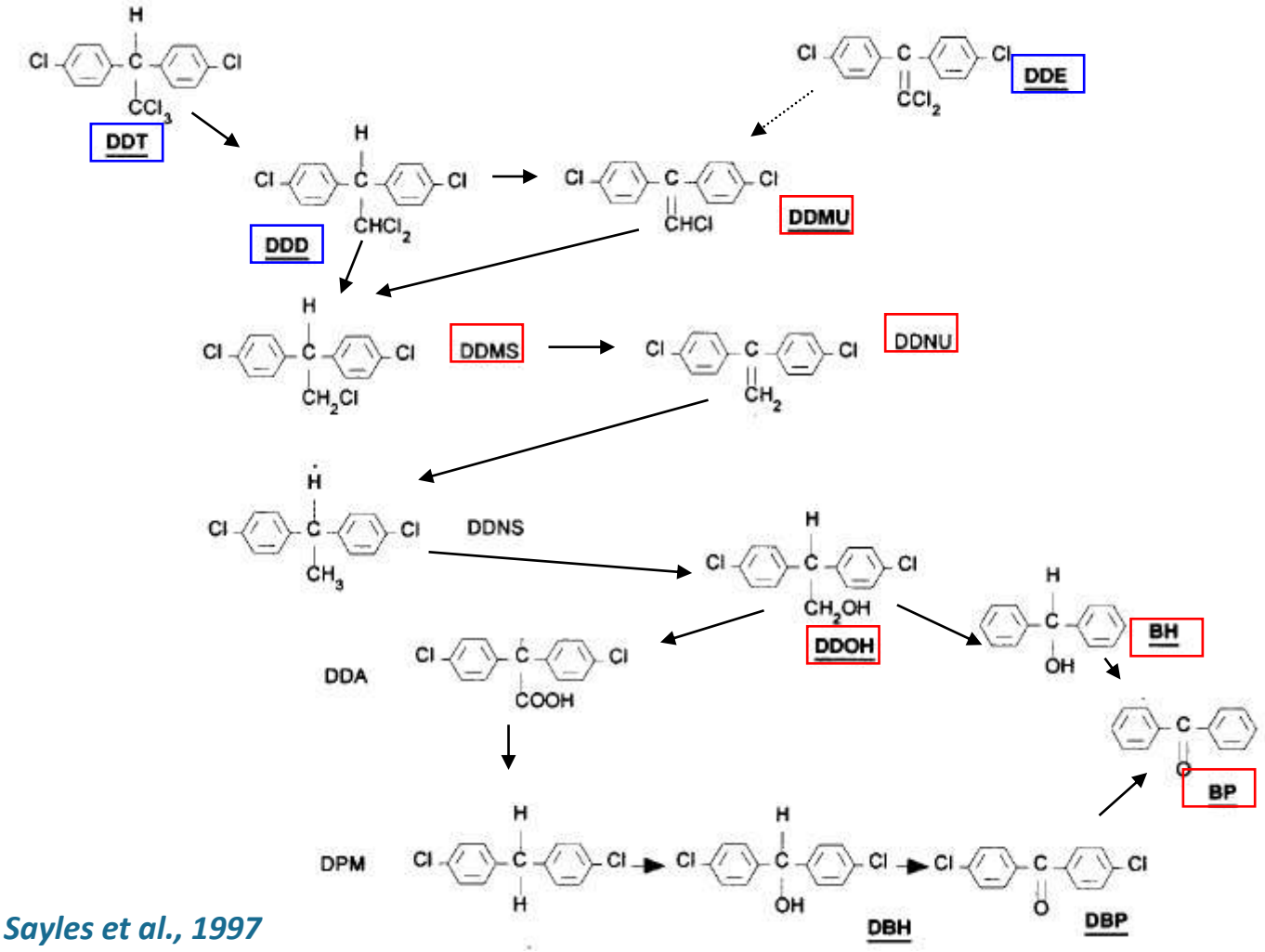

***Note: soil pH does not change***

# Demonstrated efficacy on OCPs and cVOCs

| | |
|---|---|
| DDT, DDD, DDE | √ |
| Toxaphene | √ |
| Chlordane | √ |
| Dieldrin, Endrin | √ |
| Lindane & other HCHs | √ |
| 2,4-D, 2,4,5-T | √ |
| Atrazine | √ |
| Chlorobenzenes | √ |
| Chloroethenes, Chloroethanes | √ |
| Chloromethanes | √ |

# What is the fate of the DDT?

## Reductive Dechlorination)




*From Sayles et al., 1997*

# What was the fate of the DDT?

## Ring cleavage and slow mineralization

- **Radioisotope ($^{14}$C-DDT) Fate Studies:**
  - Main fate was conversion to carbon dioxide
  - Slow but significant production of $^{14}C\text{-}CO_2$
  - Recovery of added $^{14}$C in DDT as carbon dioxide was about 7% in 150 days
  - After 150 days the rate of $^{14}C\text{-}CO_2$ release had decreased to about 1% per month
- **Stable isotope ($^{13}$C-DDT) Fate Studies indicated dichlorobenzophenone was the major breakdown product**

# What does it cost?

- Variable and dependent on:
  - Excavation requirements
  - Initial COI identity and concentration
  - Remedial goals
- DARAMEND® cost is generally from $15/ton to $75/ton of treated soil.
- Labor, equipment, and analytical will be additional costs.
- Economies of scale

# DARAMEND® Case Studies

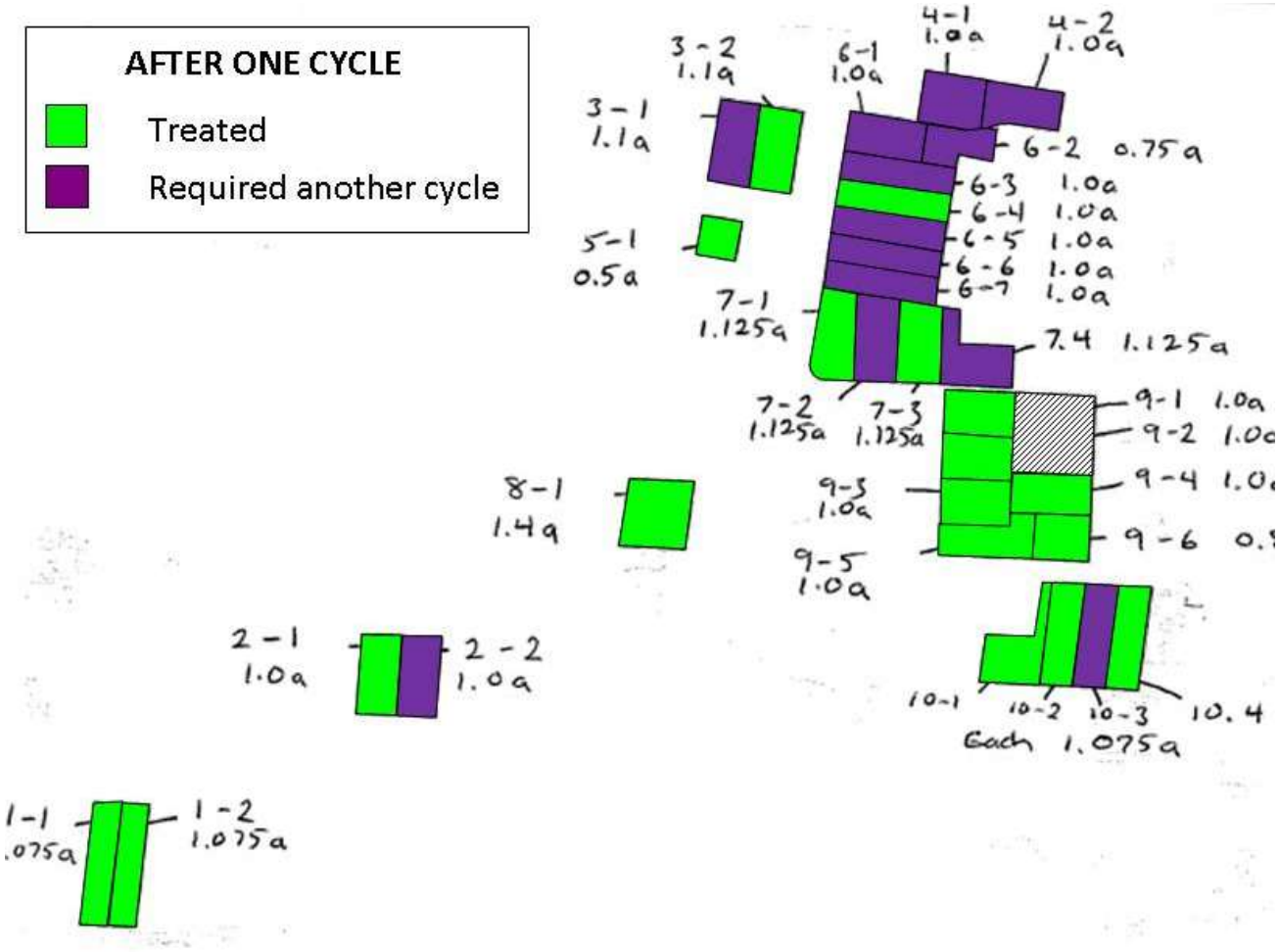
## Project Example #1
## Former Agricultural Site near Toronto

# DARAMEND® ISCR Reagent

## 33 acre Agricultural Site: near Toronto (DDT, DDE, Dieldrin)

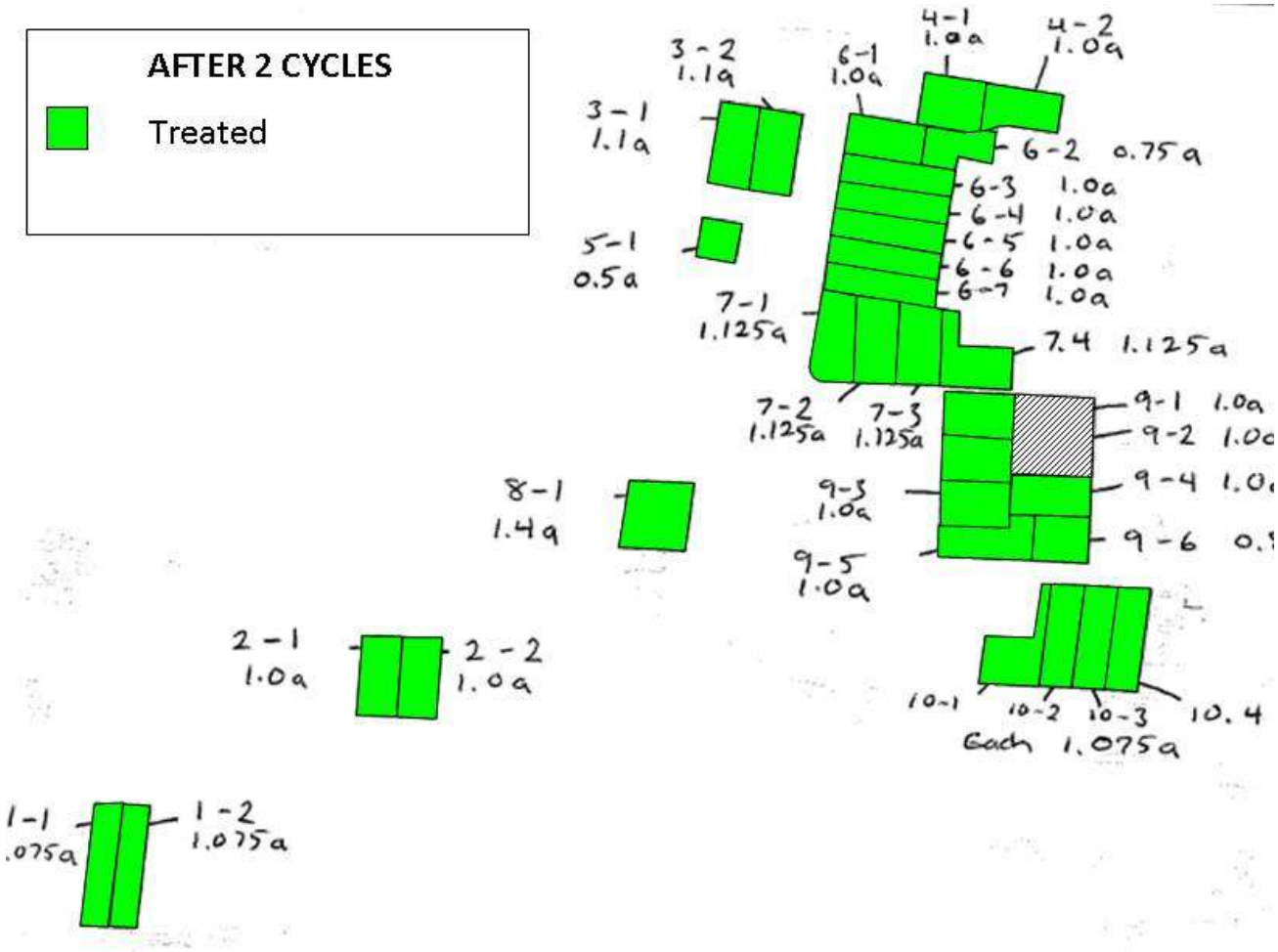
# Treatment Results After One Cycle

## 33 acre Agricultural Site: Toronto Canada



# Treatment Results After Two Cycles

## 33 acre Agricultural Site: Toronto Canada



# Treatment Results After One and Two Cycles

## 33 acre Agricultural Site: Toronto Canada

Data for plots treated after one cycle

| Constituent | 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 plots that received a second cycles

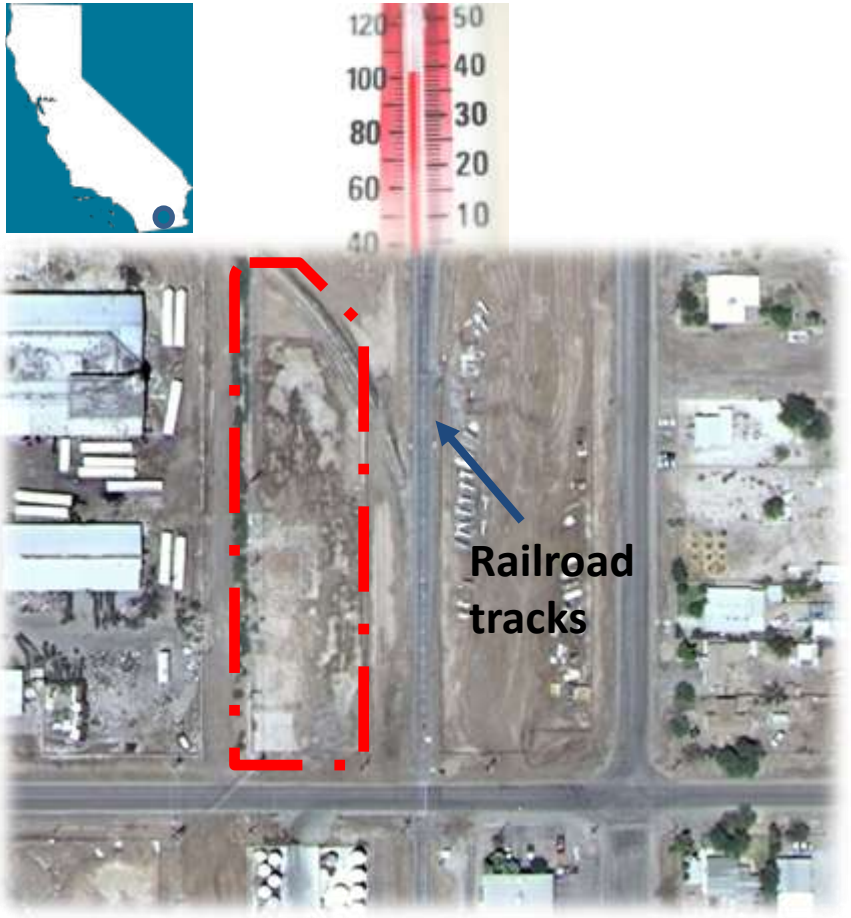
| Constituent | Initial Concentration (mg/kg) | Concentration After 1st Cycle (mg/kg) | Concentration After 2nd Cycle (mg/kg) | Final % Removal |
|---|---|---|---|---|
| DDT | 2.05 | 2.00 | 0.66 | 68% |
| DDE | 2.37 | 1.98 | 0.80 | 66% |
| Dieldrin | 0.110 | 0.080 | 0.028 | 65% |

# DARAMEND® ISCR Treatment

## Project Example #2
## Industrial Site in Southern California

# Industrial Site, Southern California

- ~1 acre property in Southern CA
- Desert climate
- Fenced and vacant, previous strong odor
- Property is leased by client from Union Pacific Railroad (UPRR)
- Organochlorine pesticides, including Toxaphene, DDT, DDE, Chlordane
- Majority of COCs confined to top 2-3 ft of soil
- Zoning is rail-industrial
  - <50 feet from railroad tracks
  - 0.25 mile to nearest resident



# Industrial Site, Southern California

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

# Results
## Industrial Site, Southern California

- Reduction in grid samples achieved cleanup goals
  - *All but 2 locations reduced pesticide concentrations to less than residential CHHSLs*
  - *These two attained industrial CHHSLs*
  - *Toxaphene in particular 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

# Economics

| DARAMEND® 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 = about 4,400 tons

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

# FULL-SCALE BIOREMEDIATION OF PESTICIDE-IMPACTED SOIL
# THAN SUPERFUND SITE, MONTGOMERY, ALABAMA

Todd Slater, Retia USA LLC

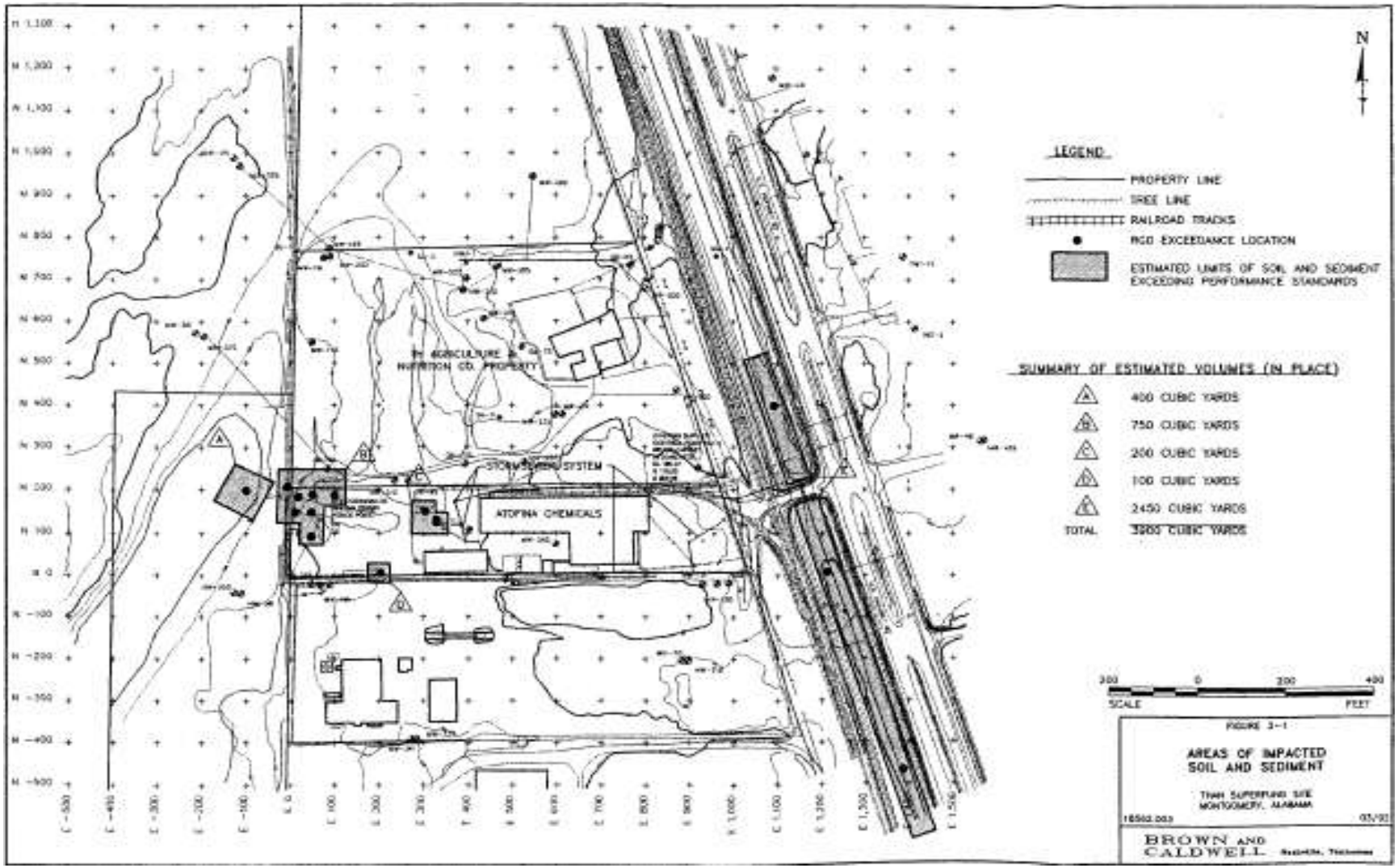
# Presentation Outline

- Site Information
- Application Methods
- Results
- Conclusion

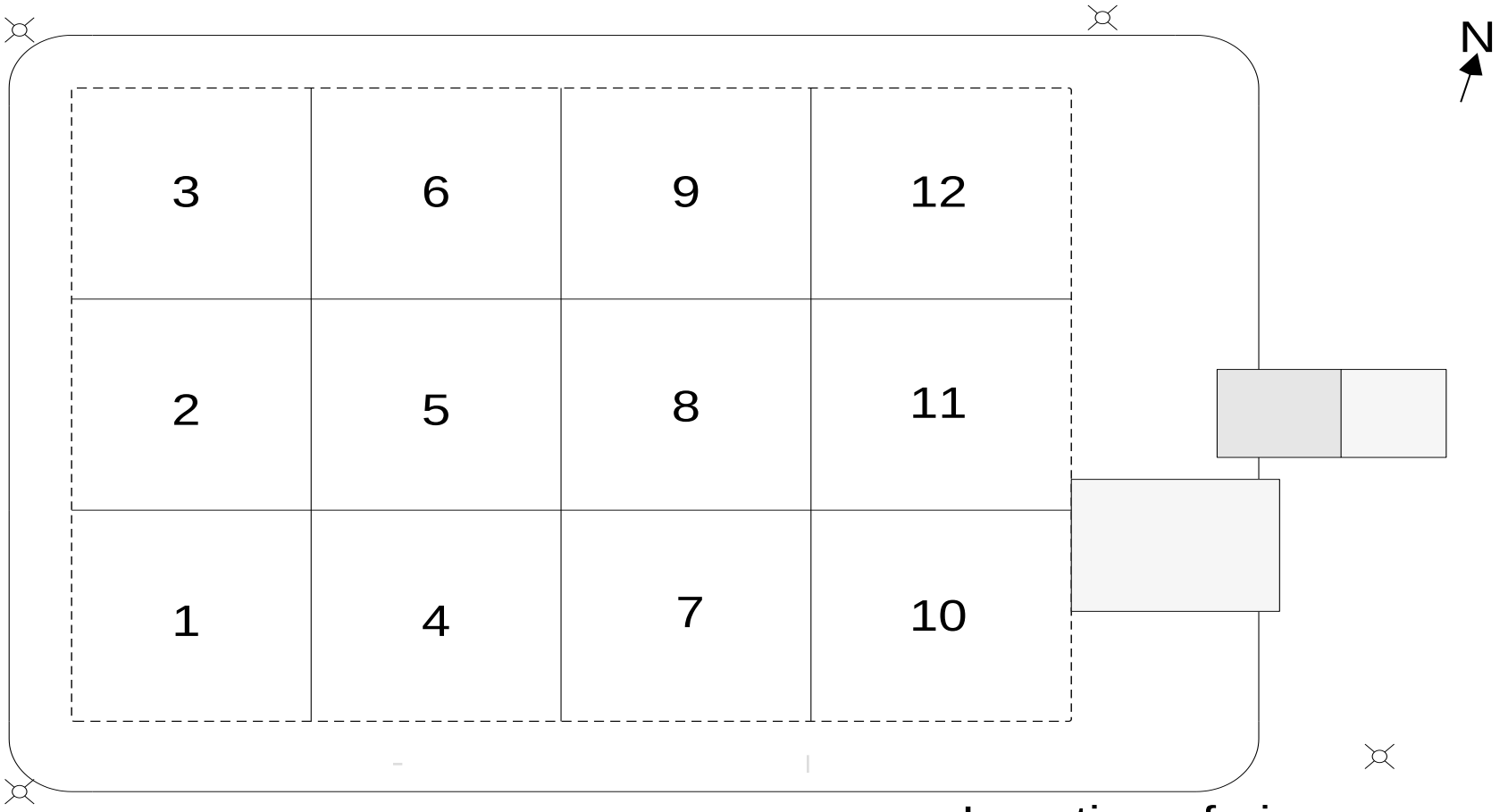
# Site Background

- T. H. Agriculture & Nutrition Superfund Site in Montgomery, Alabama
- Former agricultural chemical blending and formulating facilities
- Approximately 4,800 tons of soil and sediment from drainage ditch contaminated with DDT, DDE, DDD, and Toxaphene
- Placed in on site treatment bed at a depth of approximately 2 feet

# Site Background



# Treatment Bed Schematic



# DARAMEND® Soil Remediation at THAN Site

# DARAMEND® Soil Remediation at THAN Site

# Treatment Protocol

- 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

# DARAMEND® Soil Remediation at THAN Site

# DARAMEND® Soil Remediation at THAN Site

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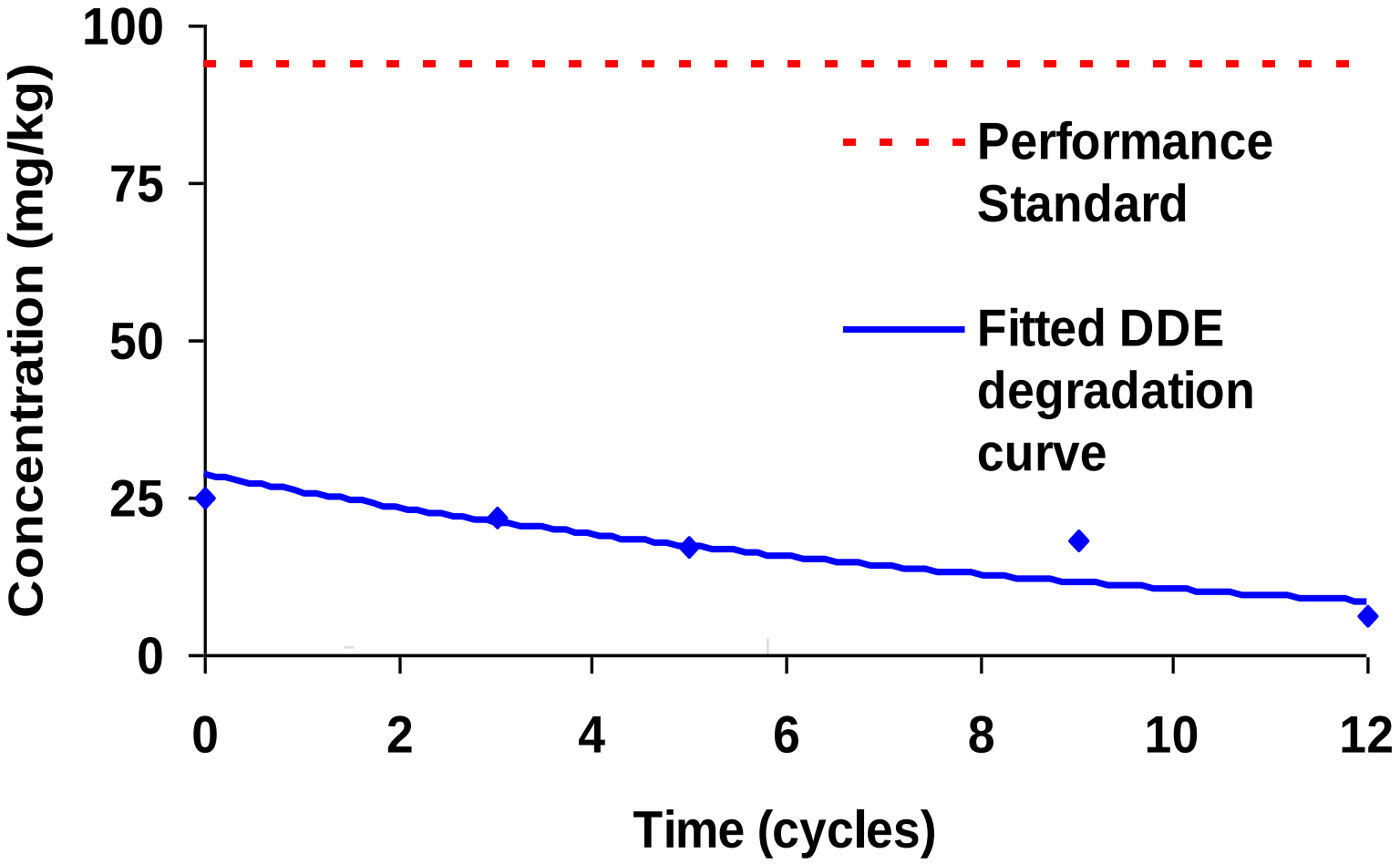
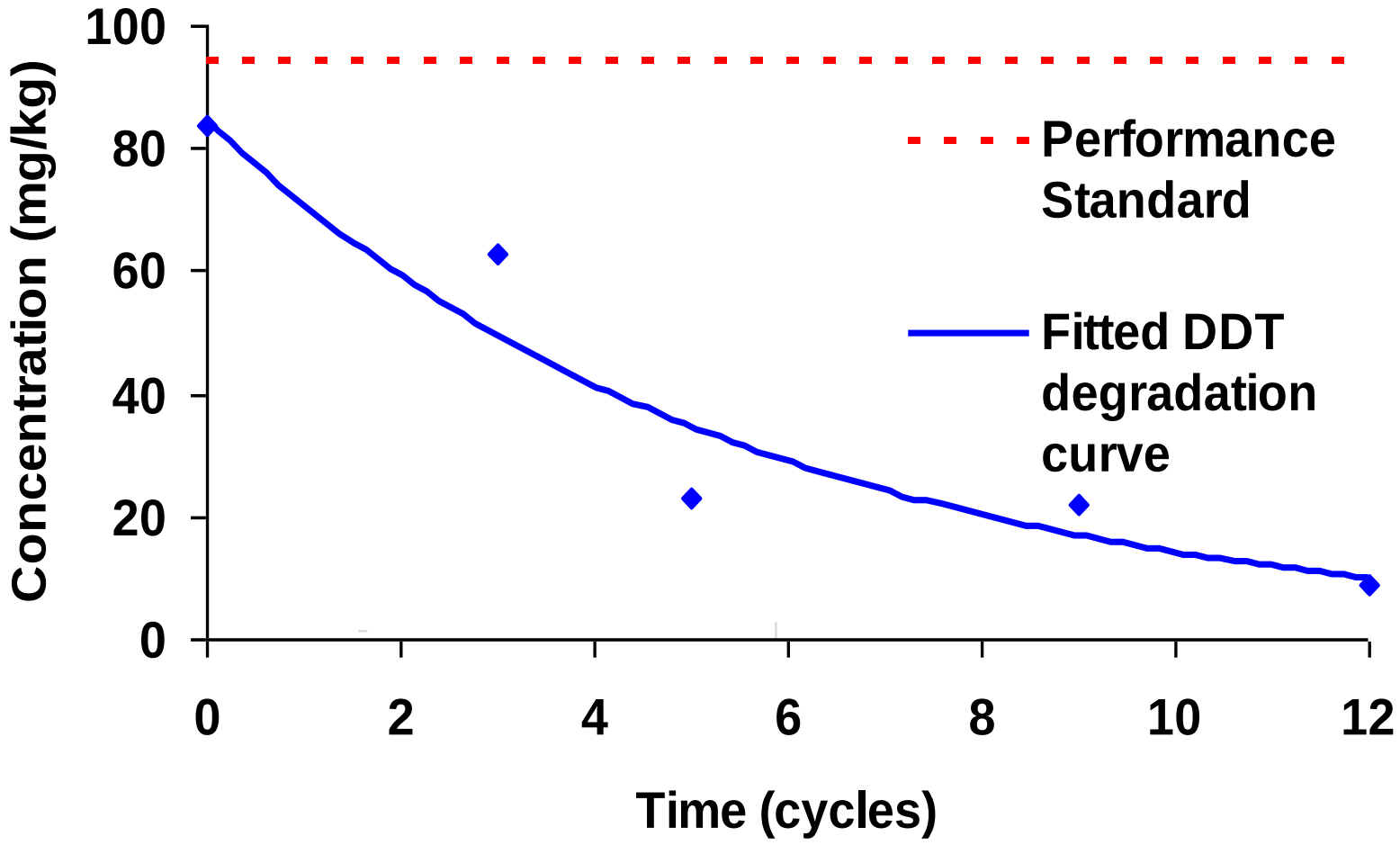
# DARAMEND® Soil Remediation at THAN Site

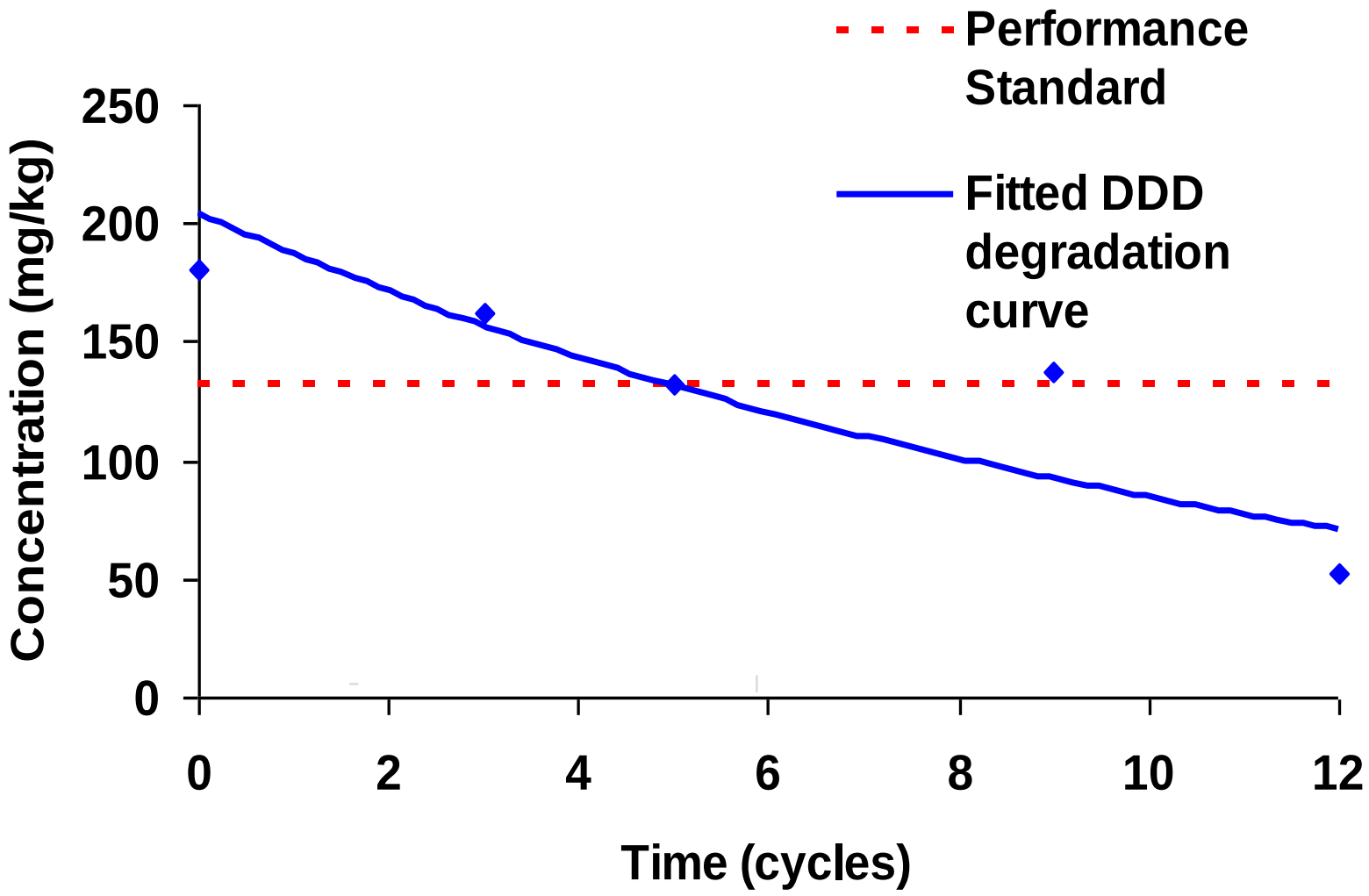
# THAN Results (DDE)



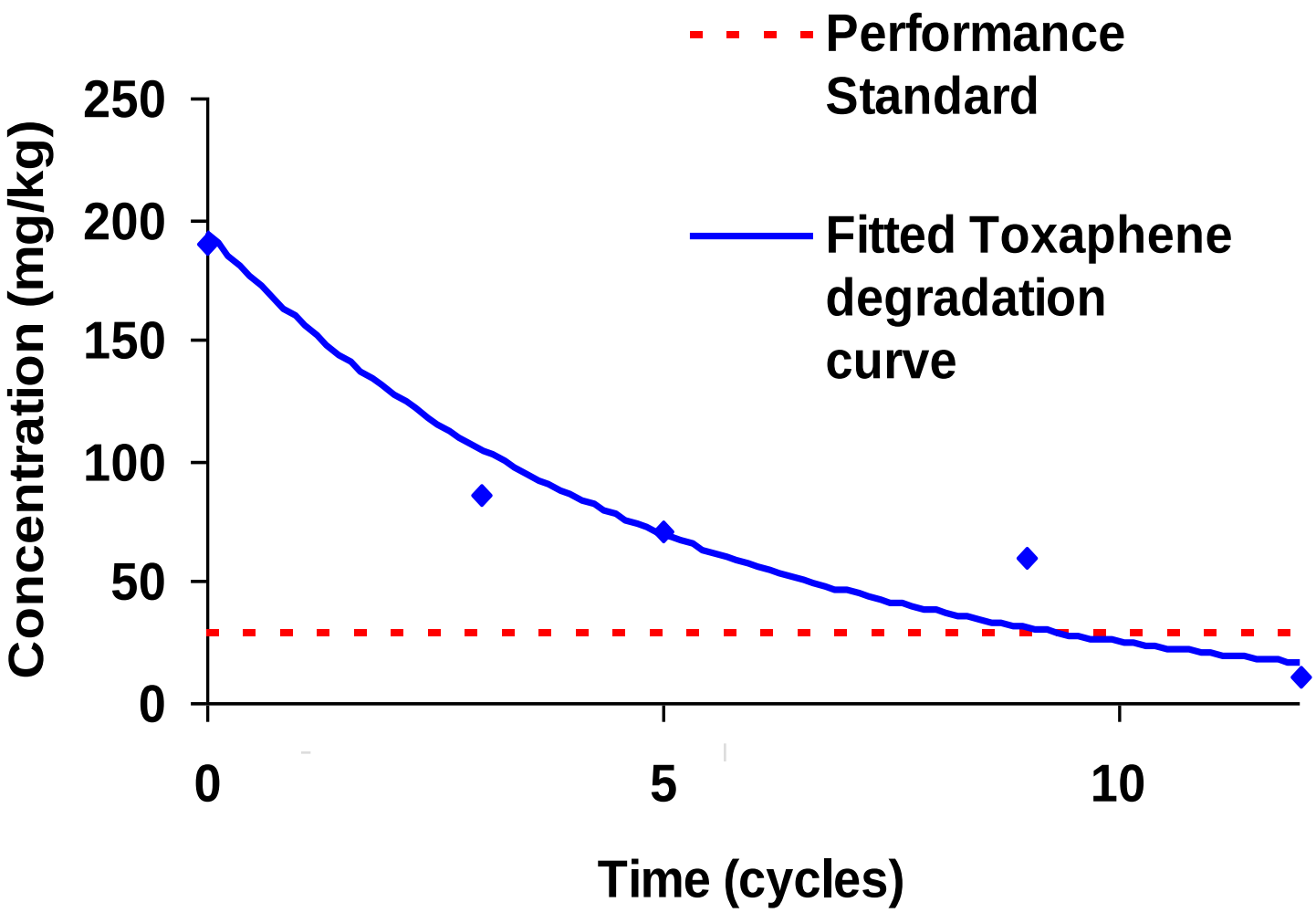
# THAN Results (DDT)



# THAN Results (DDD)



# THAN Results (Toxaphene)



# Results

## (Mean of all Zones)

| Compound | Concentration (mg/kg) | | RDE (%) |
|---|---|---|---|
| | Initial | Final | |
| Toxaphene | 189 | 11 | 95 |
| DDT | 84 | 9 | 89 |
| DDD | 180 | 52 | 71 |
| DDE | 25 | 6 | 76 |
| **Total COC** | **478** | **78** | **84** |

# Results

## (Heavily Contaminated Zones)

| Compound | Concentration (mg/kg) | | RDE (%) |
|---|---|---|---|
| | Initial | Final | |
| Toxaphene | 720 | 10.5 | 99 |
| DDT | 227 | 15 | 93 |
| DDD | 590 | 87 | 85 |
| DDE | 65 | 8.6 | 87 |
| **Total COC** | **1,602** | **121.1** | **92** |

# Post Treatment

# What did it cost?

- Mean treatment cost was $55 per ton
- The range was from $29/ton to $63/ton
- Subject to number of treatment cycles needed to reach performance standards
- Initial target compound concentrations were the main driver

# Conclusions

- **DARAMEND® treatment successfully reduced the concentrations of all target compounds to below the performance standards**
- **Treatment was completed within a reasonable timeframe and on budget**
- **Sampling zones with concentrations originally considered outside the scope of the performance warranty were nevertheless treated successfully**
- **EPA and ADEM approved of RA completion**

# Questions are Welcome!

For more information please contact:

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**www.peroxychem.com/remediation**

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