Remediation of Soils Contaminated with Chlorinated Pesticides, Chlorinated Solvents, and Organic Explosive Compounds

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Our Presenter

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- M.Sc. (Soil Chemistry) and Ph.D. (Environmental Microbiology) at the University of Guelph in Canada
- Expertise in soil chemistry and reductive remediation techniques including pesticides, energetics, and metals
- 30 years of industry experience and product development, including Daramend®, Terramend®, EHC®, and MetaFix® technology portfolios
- Numerous patents, peer reviewed technical publications, and conference presentations
- Based in southern California

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Agenda

Treatment Methods

- ✓ Organic Carbon/ZVI Soil Amendments: Daramend®
- ✓ In-Situ or Ex-Situ Soil Mixing with Irrigation

Daramend® Family of Reagents

- ✓ Details on formulations
- ✓ Why these formulations?
- ✓ Overview of Daramend® treatment chemistry and biochemistry

Bench-scale Treatability Testing

- ✓ Benefits
- ✓ Representative Results

Project Snapshots

- ✓ Very Brief Case Studies

Questions & Answers

In Situ Treatment of Chlorinated Pesticides

Former Agricultural Site

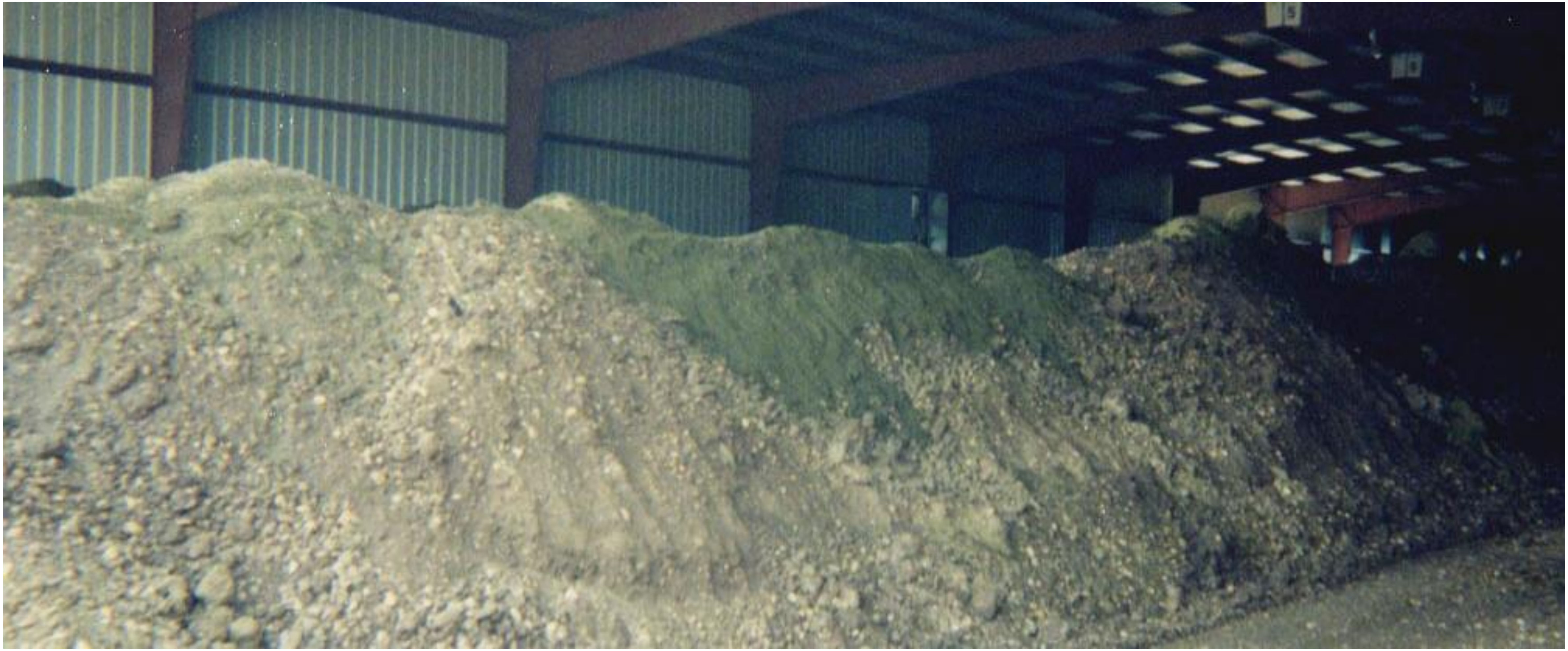
Ex Situ Treatment of PCE and TCE
Chemical Manufacturing Site

In-Situ Treatment of TNT in Wetland Sediment

US Navy Site, Virginia (0 – 2.5 m bgs)

Ex Situ Windrow Treatment of TNT and RDX

US Army Site



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Post-excavation Polishing of Residual cVOCs

Photos courtesy of Global Remediation Technologies, Inc. and Michigan Department of Environment Great Lakes and Energy

Daramend® Family of Reagents

Attribute	Daramend®	Daramend® Metals	Daramend® Plus
High Surface Area Hydrophilic Plant Fiber	✓	✓	✓
Slow-release Organic Carbon & Nutrients (N, P, S)	✓	✓	✓
Microscale ZVI	✓	✓	✓
Soluble Sulfate Salts	-	✓	-
Activated Carbon	-	-	✓
Emulsifying Agent	✓	✓	✓
pH Balanced	✓	✓	✓
Applicability	Pesticides, cVOCs, organic explosives	Pesticides, cVOCs, organic explosives, metals	Reductive Degradation & Physical Adsorption

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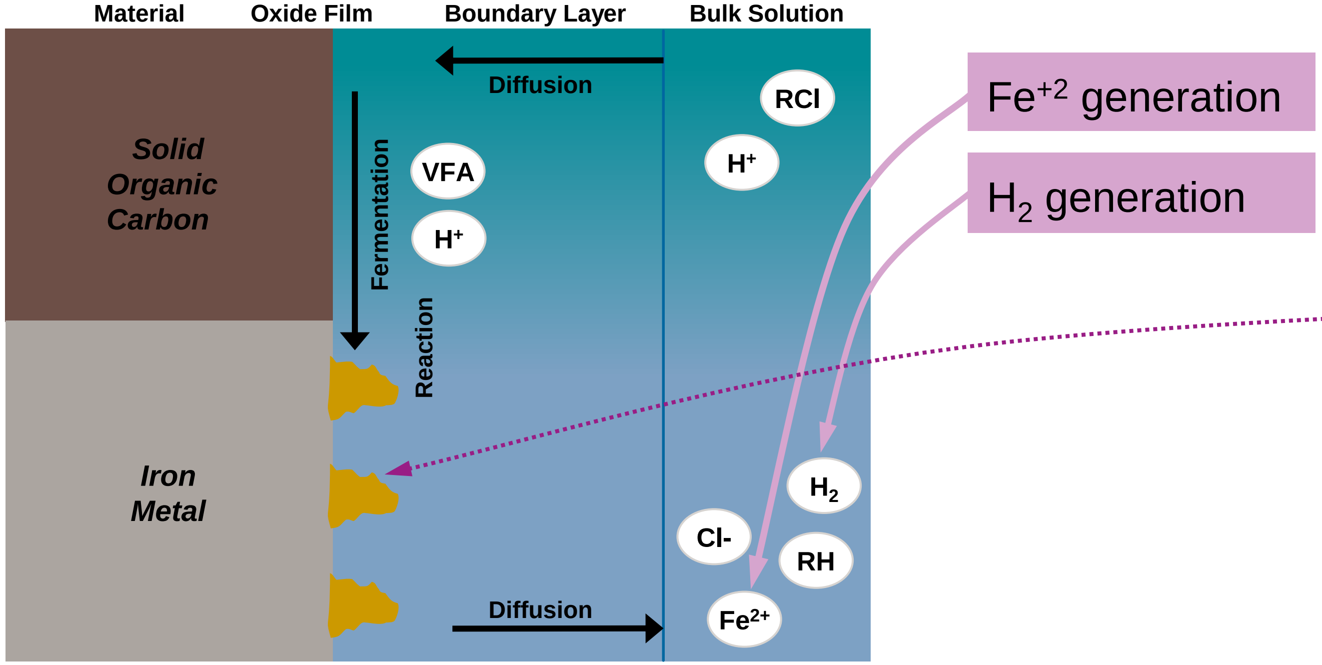
Benefits of Daramend® Formulations

Component	Benefits
High Surface Area Hydrophilic Plant Fiber	Increased soil water holding capacity & bioavailable water for increased microbial growth. Provides new, nontoxic surface area for microbial adhesion, overcomes acute soil toxicity. Continuous production of VFAs to increase ZVI reactivity and longevity.
Slow-release Organic Carbon & Nutrients (N, P, S)	Promotes synthesis of microbial enzymes active in degradation of aromatic compounds, avoids luxury consumption, promotes growth of both bacteria and fungi
Microscale ZVI	Strong reducing agent, high surface area, long-lasting source of ferrous iron. Source of alkalinity to balance acidity generated by fermentation of organic carbon.
Soluble Sulfate Salts	Provides sulfate for microbial sulfate reduction, enables generation of free sulfide needed for creation of biogenic iron sulfides. Promote stable precipitation of soluble heavy metals.
Activated Carbon	Strong adsorbent to reduce migration of soluble contaminants. Enable achievement of TCLP to enable less expensive off-site disposal for some applications.
Emulsifying Agent	Promote desorption of high MW and hydrophobic compounds (i.e., most OCPs) to increase contact with ZVI surfaces, ferrous iron in solution, and enzymatic degradation.

Daramend® Treatment Mechanisms

Carbon Fermentation + ZVI Corrosion: Synergy Promotes Multiple Dechlorination Mechanisms



ZVI Reactions:

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

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

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

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

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

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

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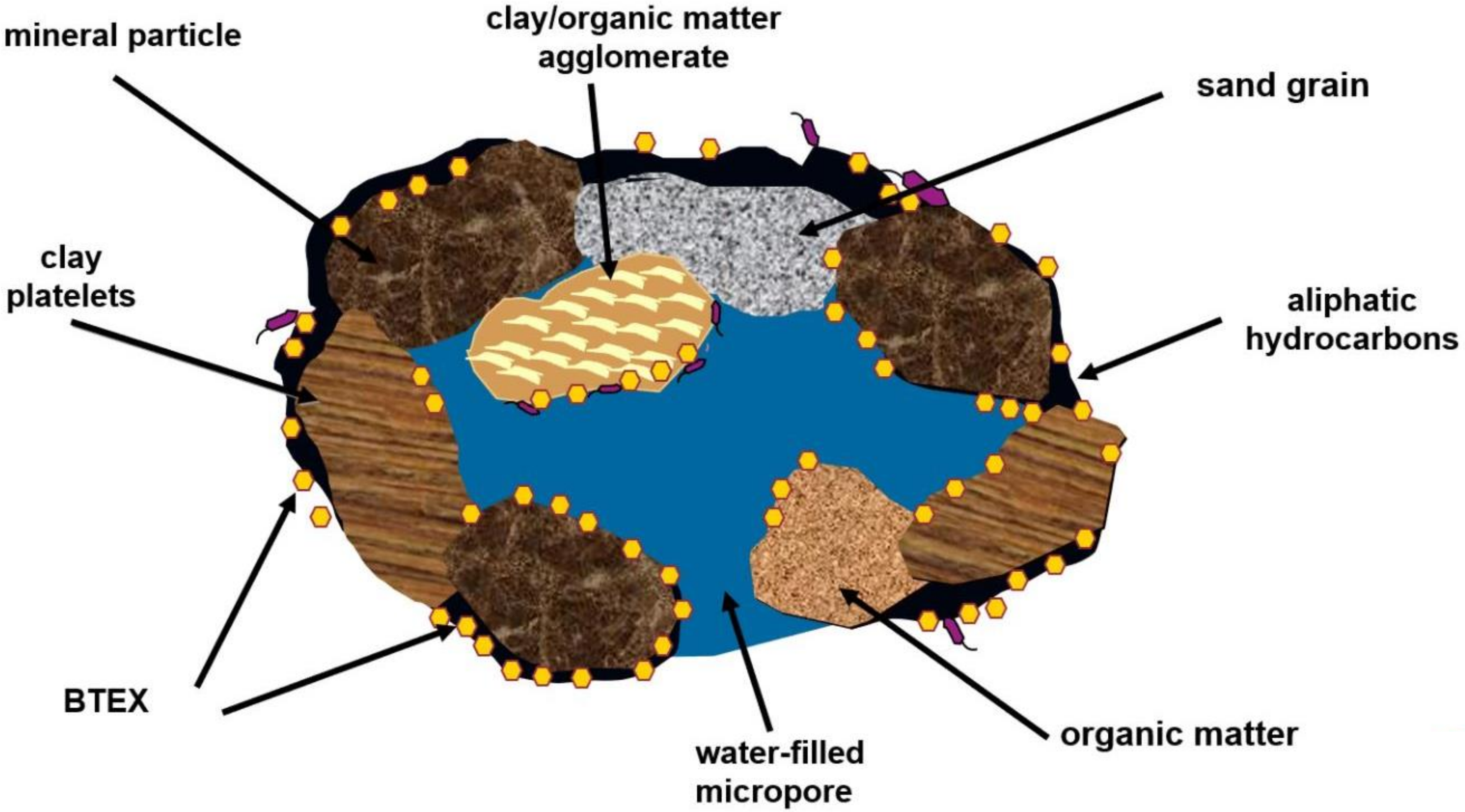
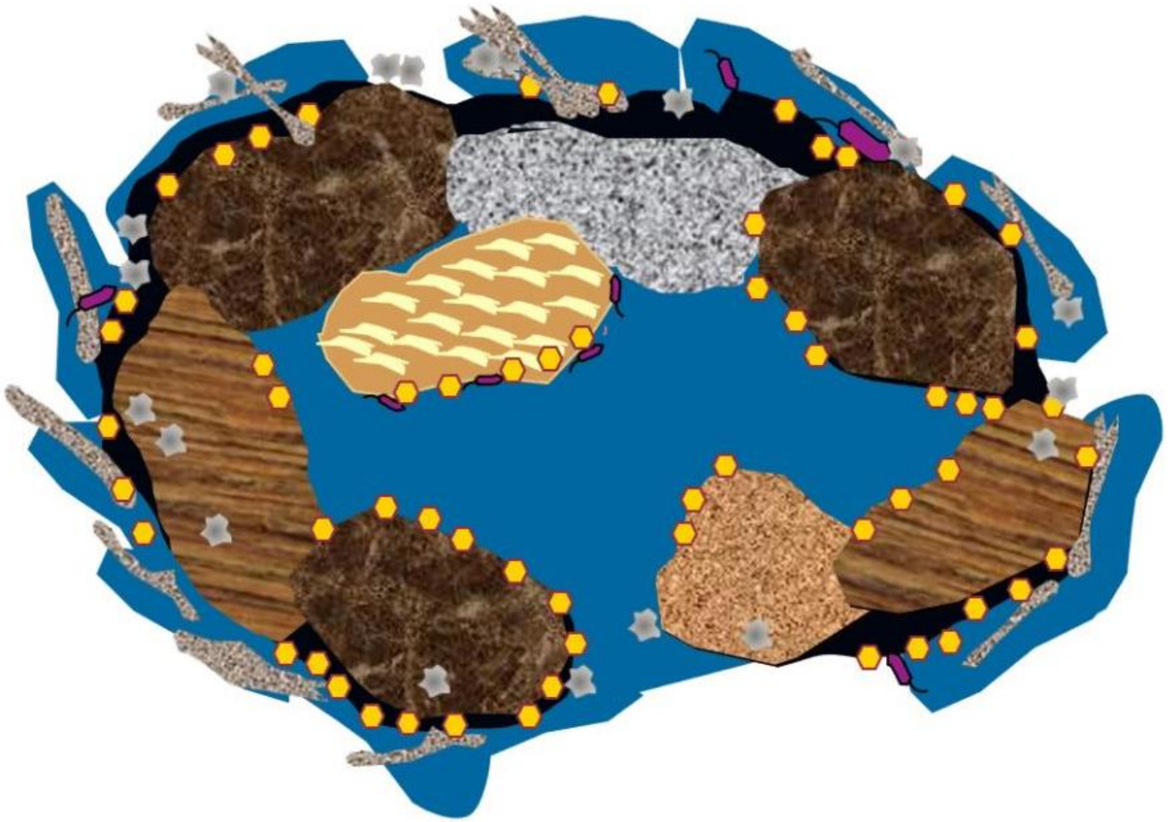
Daramend® Treatment Mechanism



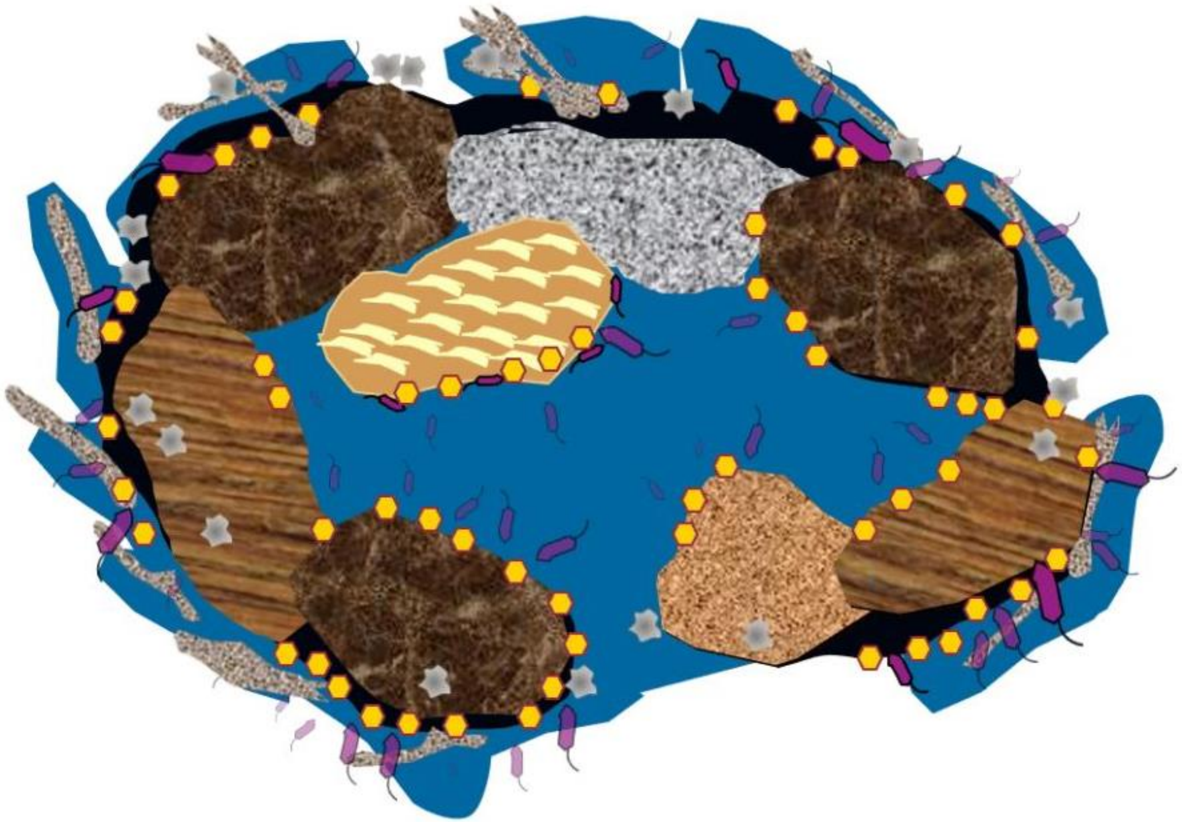
Daramend® Treatment Mechanism

Daramend® Hydrated



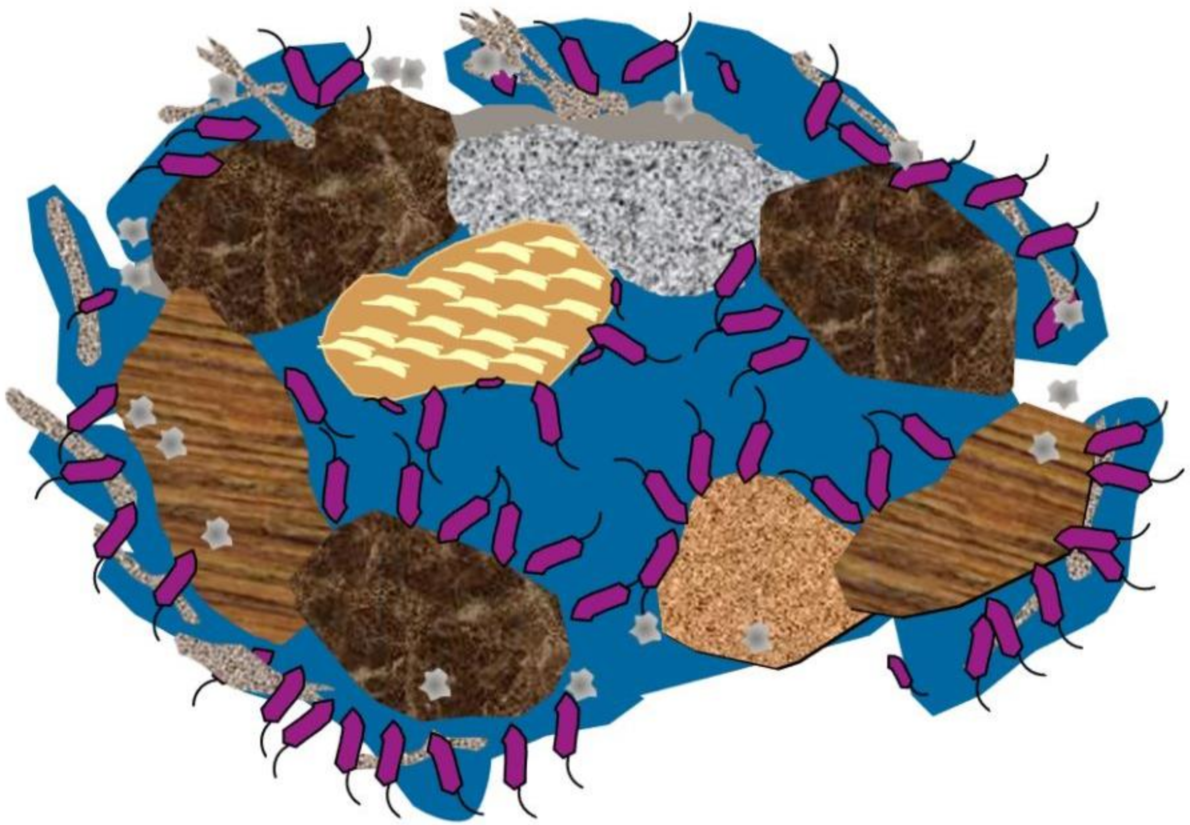
Daramend® Treatment Mechanism

Bacteria Grow



Daramend® Treatment Mechanism

Contaminants Destroyed



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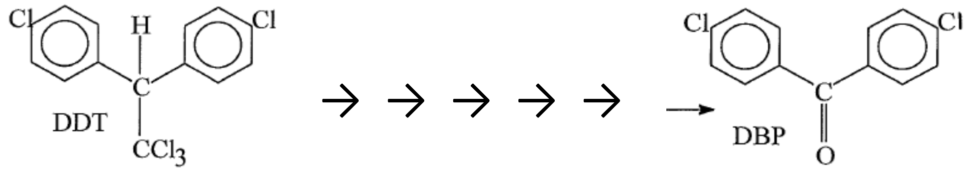
The fate of the DDT in Soil during Daramend® Treatment

Ring Cleavage and Slow Mineralization to CO_2

1. **Radioisotope (^{14}C-DDT) Fate Studies:**
   - Main fates were adsorption to soil solids and conversion to carbon dioxide (i.e., no measurable volatilization)
   - 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

2. **Stable isotope (^{13}C-DDT) Fate Study:** indicated p,p'-Dichlorobenzophenone was the major breakdown product:



3. **Other Chlorinated Pesticides:** it is reasonable to assume similar reductive dehalogenation pathways for other chlorinated pesticides with eventual mineralization to CO_2

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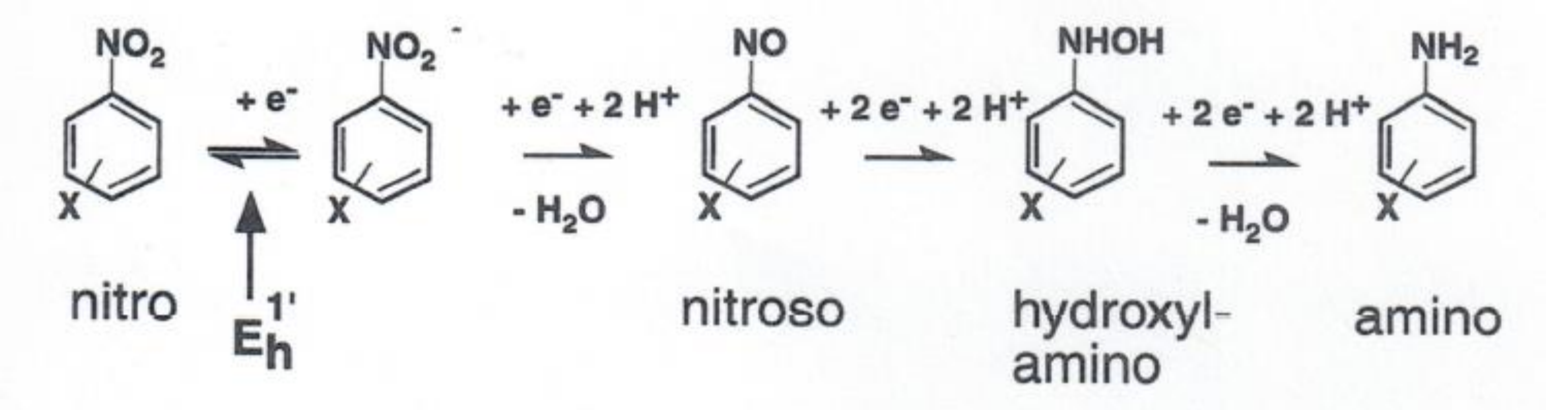
Reductive Degradation of Nitroaromatics



Haderlein, S., Hofstetter, T., and Schwartzenbach, R. In: Biodegradation of Nitroaromatic Compounds and Explosives. 2000. Eds.: Spain, J., Hughes, J, and Knackmuss, H.-J.

1. Sequential reductive degradation of nitro groups through intermediate compounds to fully reduced amino end product (reference).
2. Requires 6 e^- for complete reduction of each $^{-}NO_2$ group and 18 e^- for each TNT molecule
3. Suggests that effective treatment of OE with achievement of low residual concentrations is best achieved with a long-lasting source of reducing equivalents (e.g., long-lasting organic carbon + ZVI)

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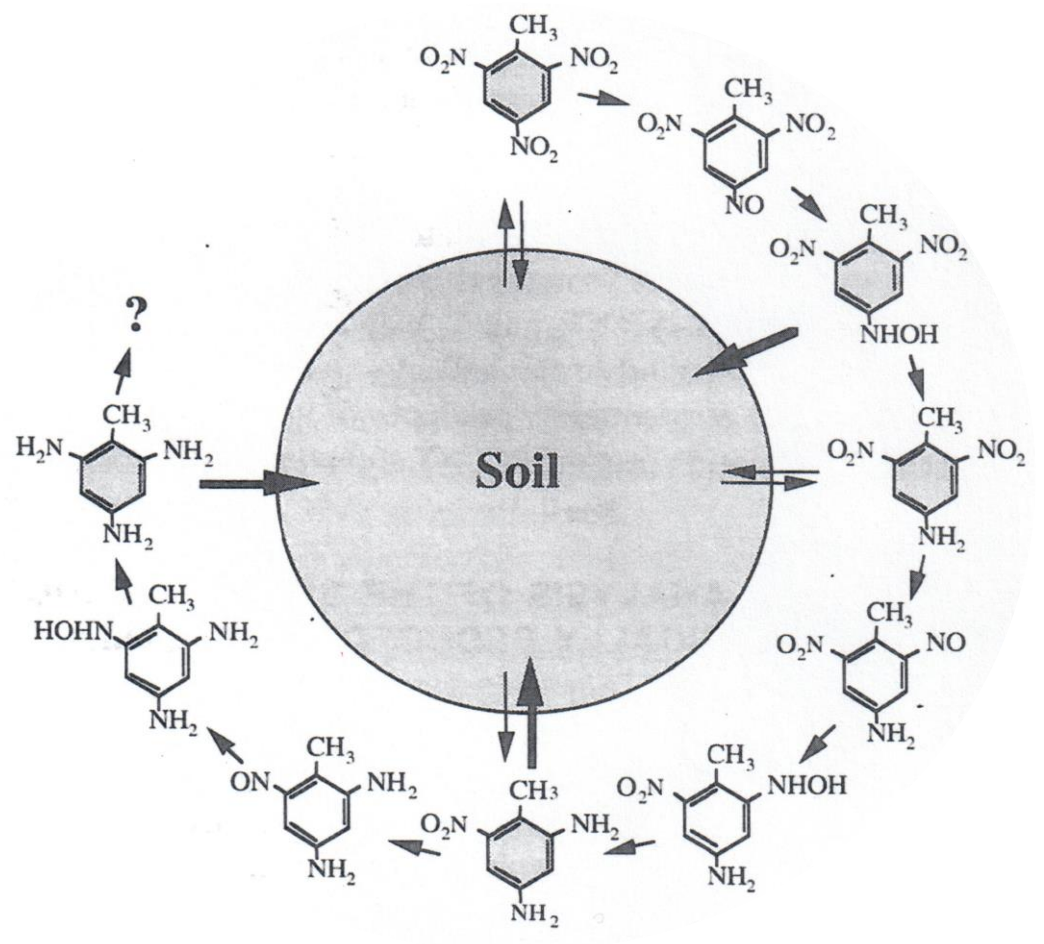
Fate of Nitroaromatics During Reductive Treatment



Fate of Organic Explosives in Soil

1. NO_2 groups are less strongly adsorbed
2. NH_2 groups are highly reactive and strongly adsorbed
3. Some reversibility so long as at least one NO_2 group is present
4. Structure with three NH_2 groups (TAT) is highly reactive and will polymerize or be adsorbed irreversibly
5. Highlights the importance of preventing accumulation of partial reduction products such as mono and diamino nitrotoluenes
6. Adsorption is so strong that adsorbed TAT is not released even by alkaline or acid hydrolysis
7. Supported by soil toxicology studies

Lenke, H., Achtnich, C., and Knackmuss, H.-J. In: Biodegradation of Nitroaromatic Compounds and Explosives. 2000. *Eds*.: Spain, J., Hughes, J, and Knackmuss, H.-J.

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Bench-scale Treatability Testing

Objectives:

- ✓ confirm adequate reduction in COI concentrations
- ✓ estimate required reagent dosage, acceptable treatment time

Methodology:

- ✓ representative soil sample in glass microcosms
- ✓ evaluate dose response
- ✓ approved extraction and analysis methods

Representative Results:

- ✓ major pesticides and organic explosives
- ✓ Lindane, Chlordane, Dieldrin, Toxaphene, TNT

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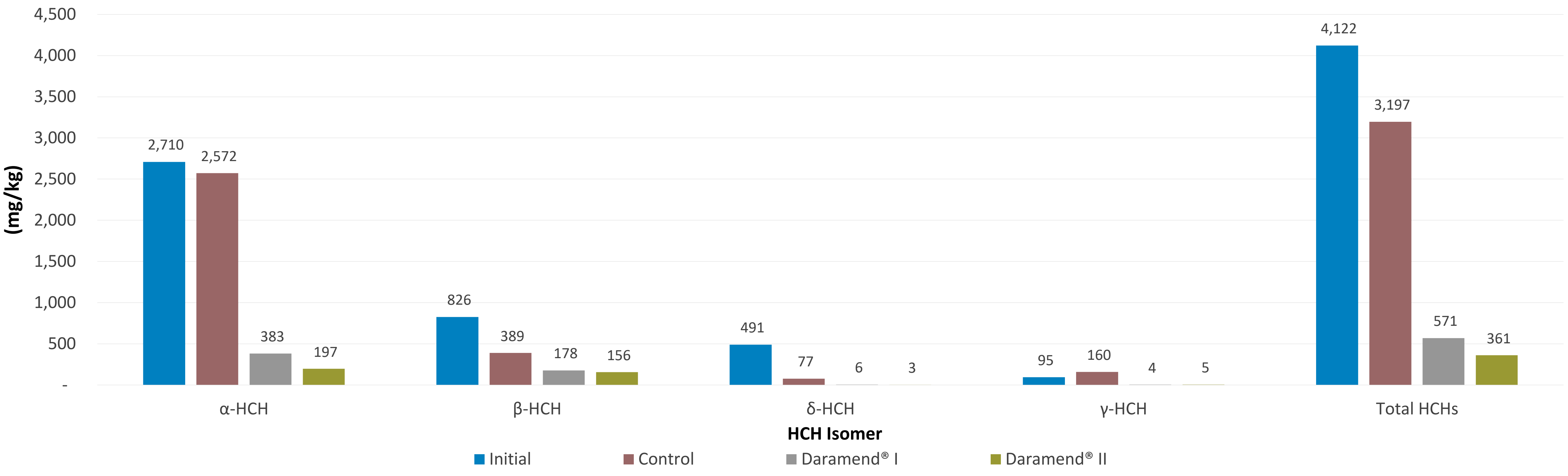
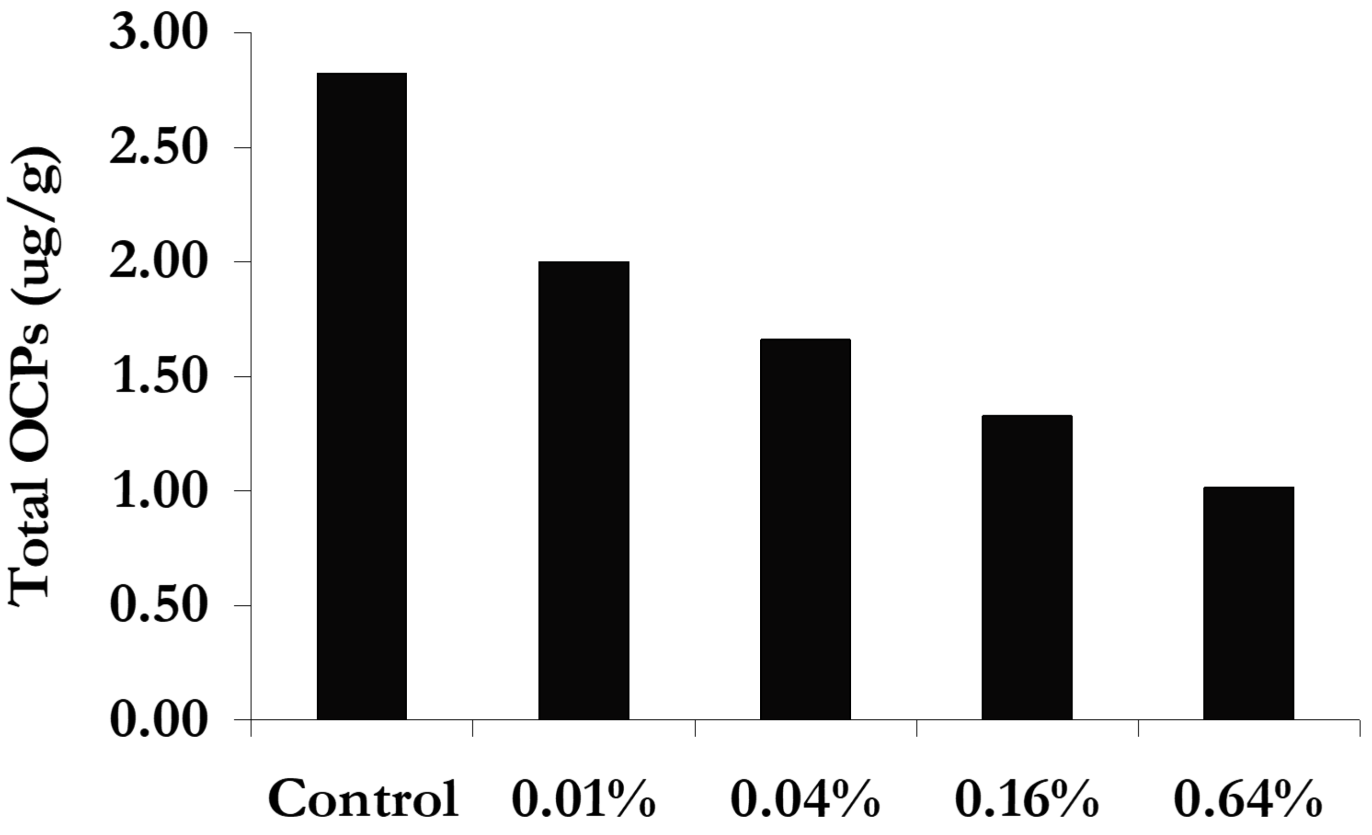
Daramend® Bench Scale Results:
Influence of Daramend® treatment on HCH isomer concentrations in soil



- ✓ Daramend formulations differed in grade of ZVI
- ✓ Nearly complete removal of δ-HCH and γ-HCH isomers
- ✓ Daramend II achieved better destruction of α-HCH
- ✓ α-HCH and β-HCH isomers have higher acute toxicity
- ✓ γ-HCH was the driver (Lindane)
- ✓ Field application used the more effective formulation

Daramend® Bench Scale Results:
Influence of Daramend dosage on pesticide removal (Florida soil)



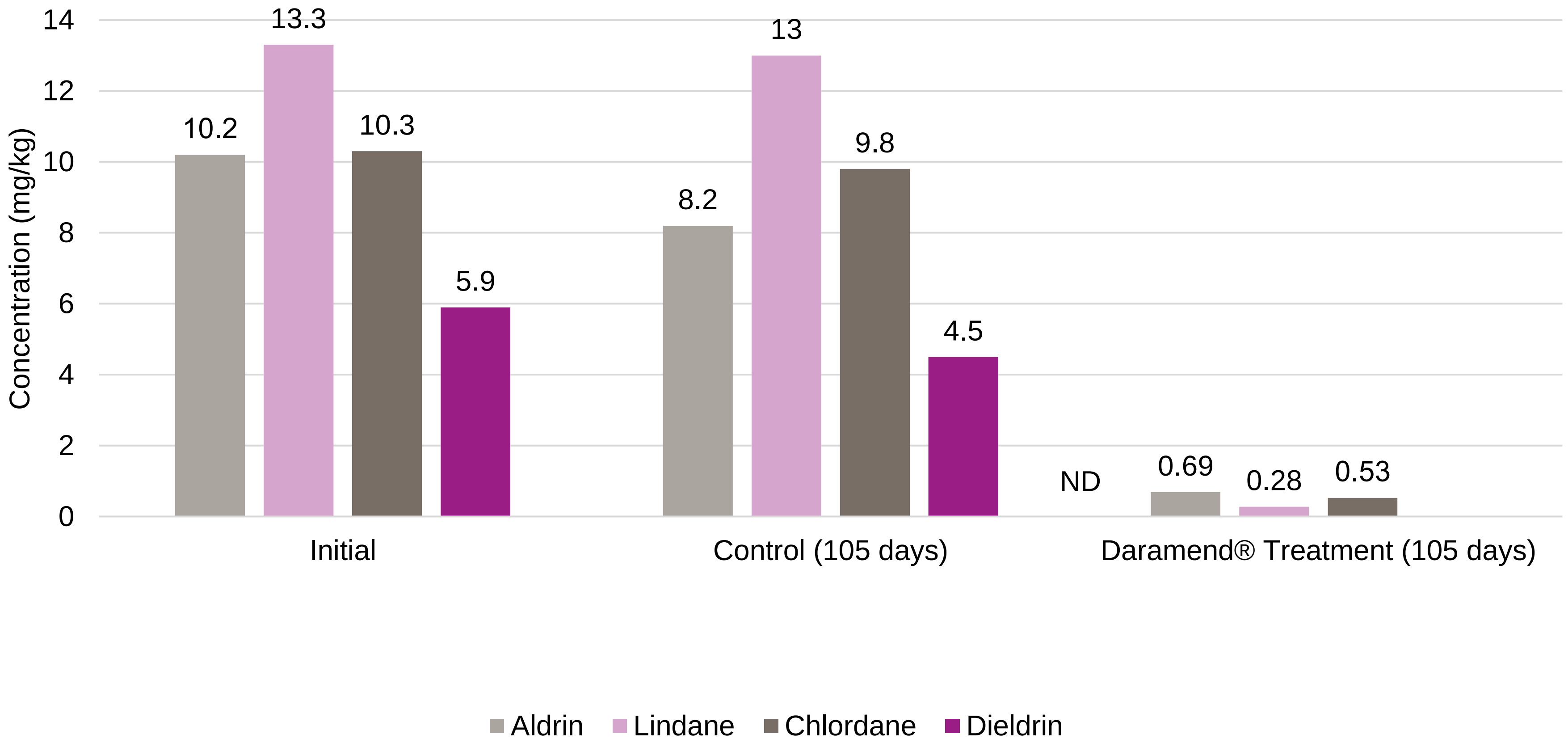
Data points represent mean of three replicates

Daramend® Dosage Response

- Example of relationship between Daramend® dosage and Chlordane + Dieldrin degradation
- Four treatment cycles completed over a period of 36 days
- Based on this result and evaluation of reagent cost and available time soil treatment was conducted at 0.5% w/w

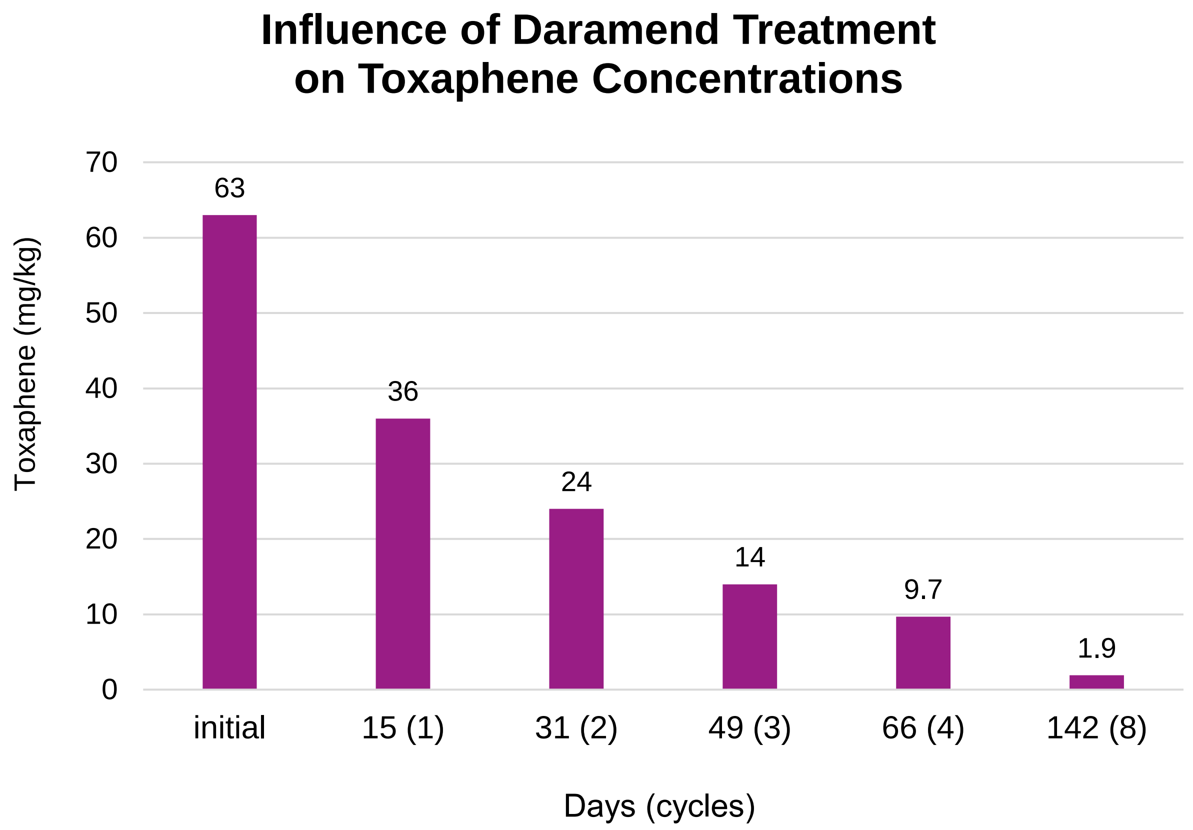
Daramend® Bench Scale Results:
Treatment of Aldrin, Lindane, Chlordane, and Dieldrin in Louisiana soil

Chlorinated Pesticide Concentrations after Daramend® Treatment



Aldrin, Lindane, Chlordane, and Dieldrin are some of the most recalcitrant chlorinated pesticides

Daramend® Bench Scale Results:
Influence on Toxaphene concentration in Soil from Alabama Site

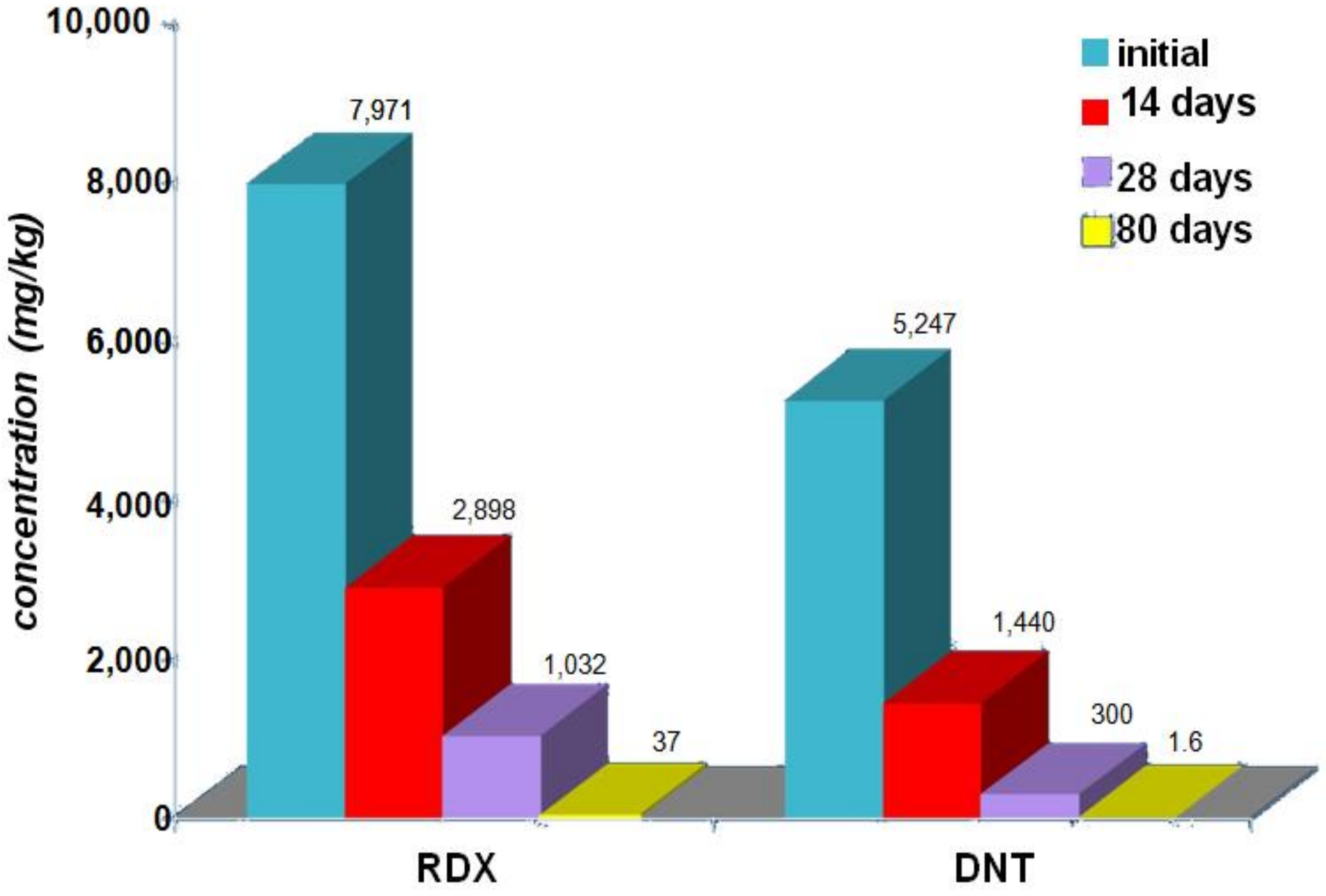


Data points represent mean of four replicates; $LSD_{(0.05)}$ = 6.5

Daramend® Treatment O&M

- Example of a linear relationship between number of cycles and treatment efficacy
- A treatment cycle involves addition of Daramend®, soil mixing, and irrigation.
- This bench test allowed us to document that the RG for Toxaphene (17 mg/kg) could be achieved in this soil
- Once reductive conditions are established contaminant removal response increases significantly

Influence of Daramend® Treatment on RDX and DNT in Soil



- ✓ Soil from chemical industry site in Wisconsin
- ✓ DNT is more toxic and resistant to degradation than TNT
- ✓ Excellent removal of both compounds
- ✓ Total Daramend® dosage was 3.0% w/w

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Project Snapshots

1. In Situ Daramend® Treatment of Chlorinated Pesticides (Toronto, ON)
2. In Situ Daramend® Treatment of Chlorinated Pesticides (El Centro, CA)
3. Ex Situ Daramend® Treatment of PCE and TCE (Seattle, WA)
4. In Situ Daramend® Treatment of cVOCs (Oxnard, CA)
5. Ex Situ Daramend® Treatment of TNT and RDX (Yorktown NWS)

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Project Snapshot 1

Daramend® Reagent

In Situ Treatment of Chlorinated Pesticides

Residential Treatment Standards

- Former agricultural site for residential development
- In situ treatment of 34 acres (14 hectares)
- About 110,000 tons of soil in total
- Surface soil to a depth of 24” (60 cm)
- Residual metabolites from use of DDT as an insecticide
- Major target compound was DDE

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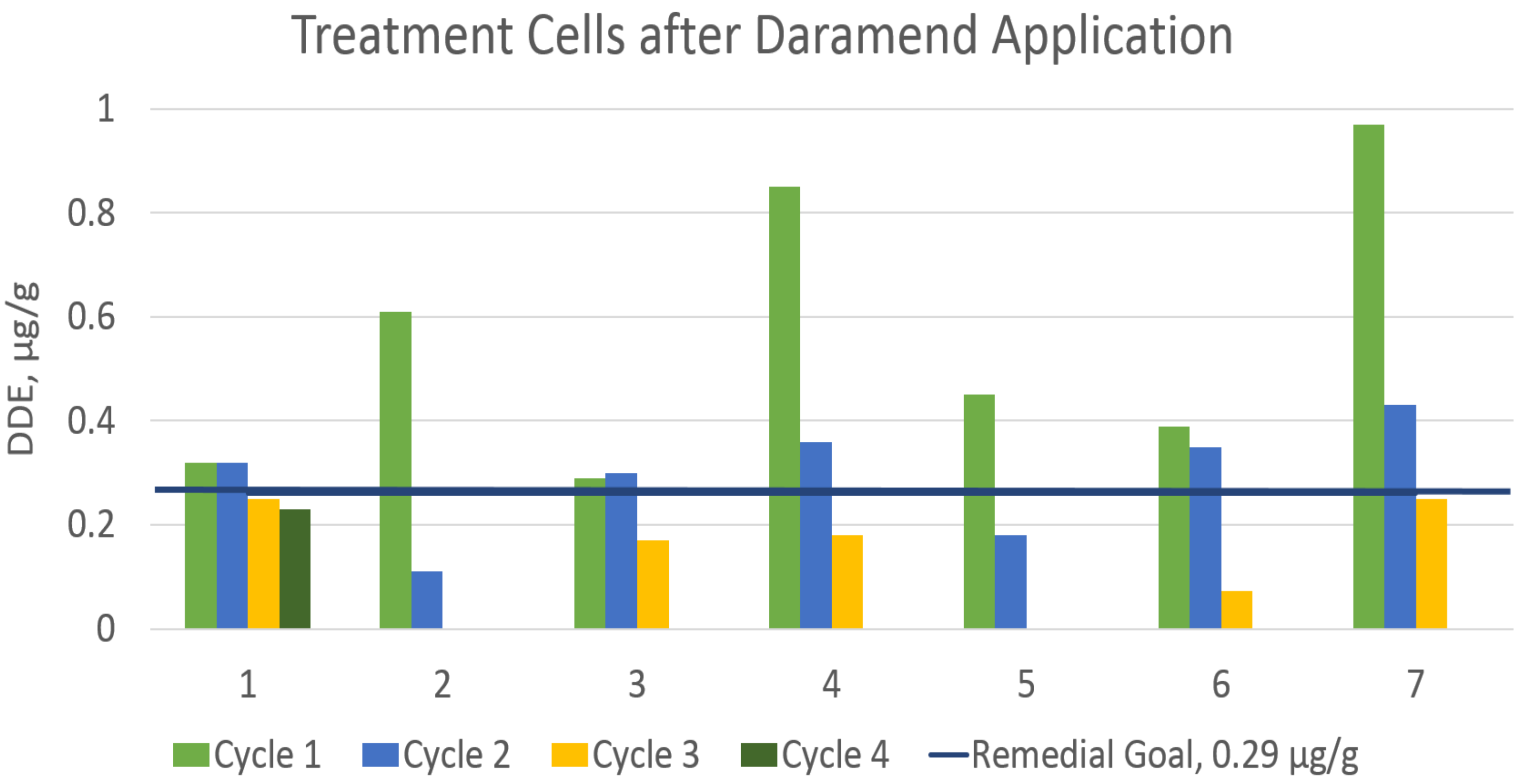
In Situ Treatment of DDE at Former Agricultural Site

Remediation for Residential Development



Achievement of Residential Land Use Criteria

- Treatment of large areas in situ sharply reduces total cost as compared to excavation and off-site disposal
- Total cost including Daramend® reagent, equipment, and labor was less than US$50,000/acre
- Equivalent to about $14/ton of treated soil

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Project Snapshot 2:

Daramend® Treatment of Toxaphene and DDT

Industrial site in Imperial Valley, CA

Industrial Treatment Standards

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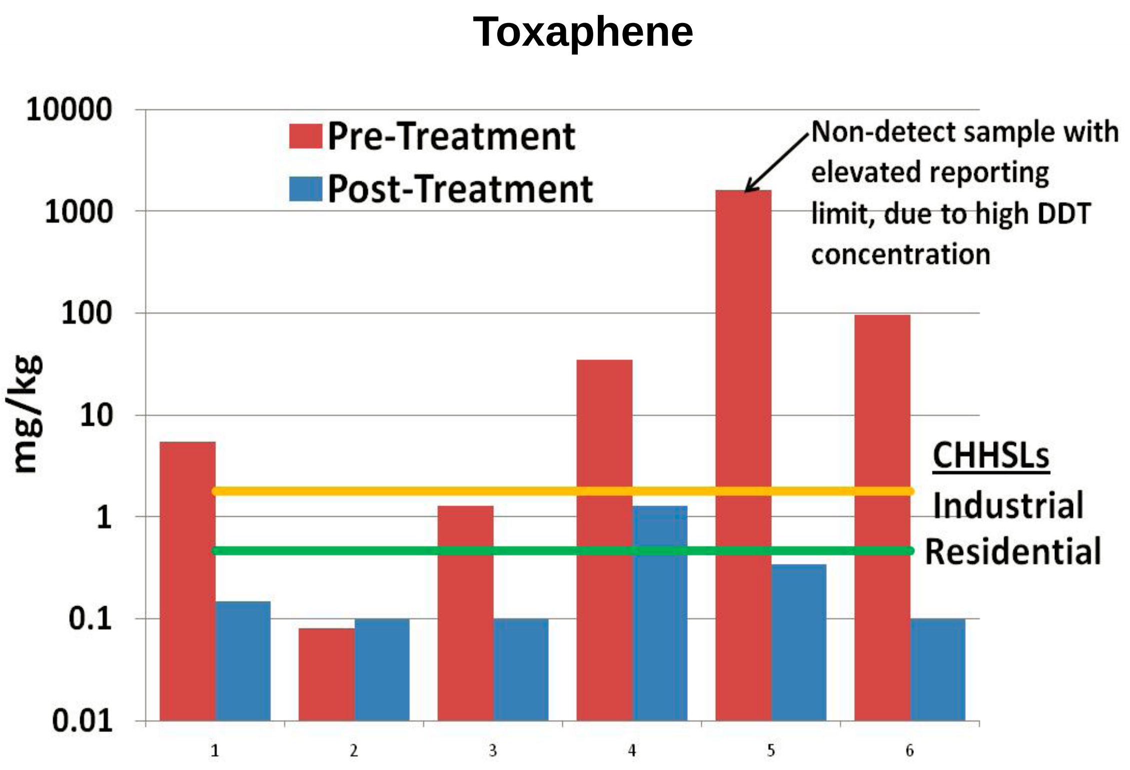
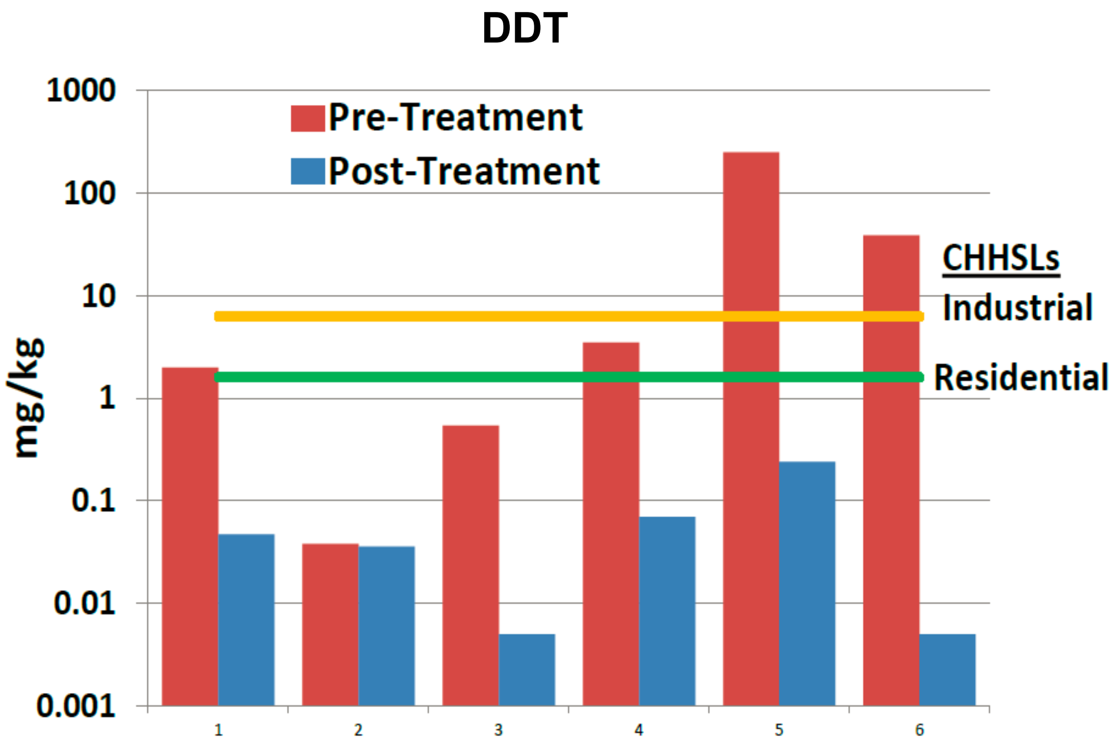
Industrial site in Imperial Valley, CA
Daramend® Treatment of Toxaphene and DDT





- Industrial treatment standards achieved with only one treatment cycle for all the sampling zones (note log scale)
- Residential treatment standards achieved with only one treatment cycle for all but one sampling zone
- Very high removal efficiencies and low residuals achieved for both DDT and Toxaphene
- Presence of elemental sulfur may have enhanced removal; similar observation at other pesticide sites

Project Snapshot 3:

Daramend® Treatment of TCE and PCE In Excavated Soil

Industrial Site, Seattle WA

- Industrial site near Seattle
- Former chemical manufacturing facility
- Soil with PCE as high as 3,800 mg/kg and TCE as high as 220 mg/kg
- Remedial goals were 19 mg/kg for PCE and 1.2 mg/kg for TCE
- Excavated soil was placed in on site treatment cell at a depth of 24”
- Dosage of 1% w/w per cycle and both remedial goals achieved after three treatment cycles

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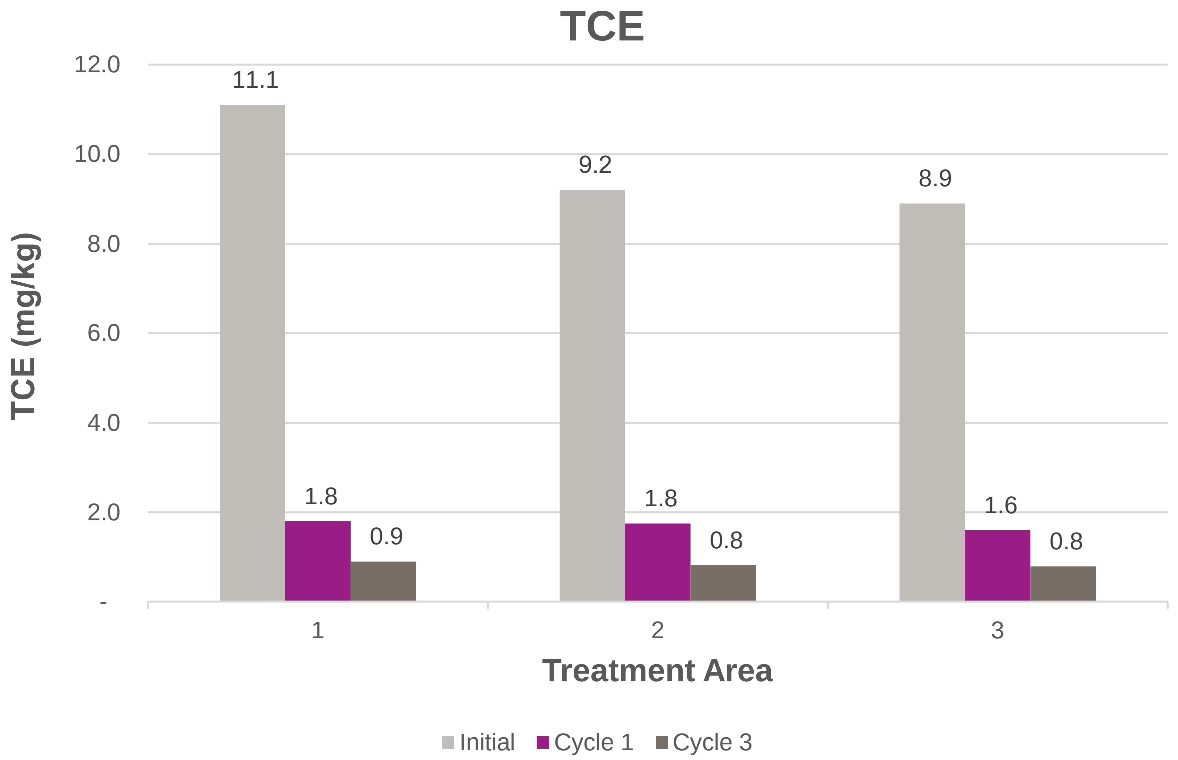
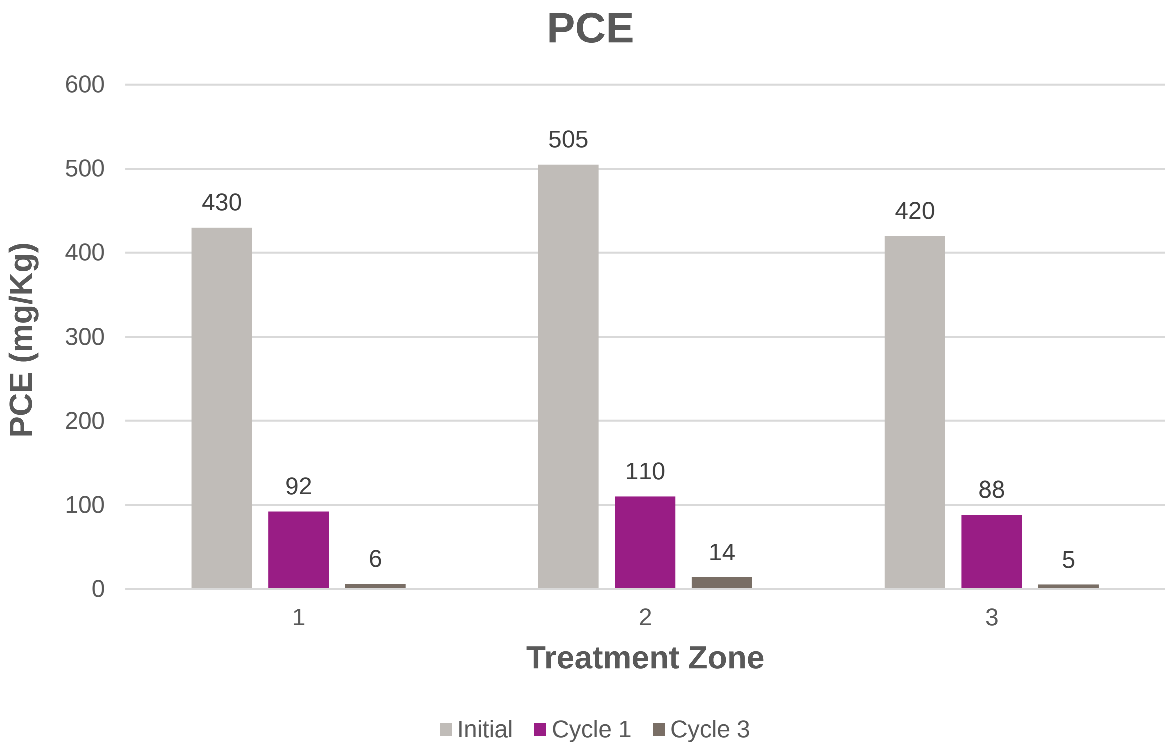
Industrial Site near Seattle WA

Influence of Daramend® on TCE and PCE Concentrations





- ✓ **Soil mixing with irrigation**
- ✓ **Total Daramend® dosage was 2.0% w/w (1.0% + 0.5% +0.5%)**
- ✓ **Treatment cycle duration of 7 to 10 days**
- ✓ **Reagent cost was $27/ton of treated soil**

- ✓ **Treatment standards achieved after completion of three cycles (TCE = 1.2 mg/kg; PCE = 19 mg/kg**
- ✓ **Soil Eh dropped from +120 mV to -450 mV at 48 hours after application of Daramend + water**

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Project Snapshot 4

Daramend® Treatment of TNT in Soil

Naval Weapons Station Yorktown, Yorktown VA

- 8,400 y^3 soil (ca. 12,000 tons)
- Soil TNT concentrations as high as 43,000 mg/kg (average about 10,000 mg/kg)
- Treatment goals were 14 mg/kg for TNT and 5 mg/kg for RDX
- Daramend® was selected through the FS Process
- Ex Situ Treatment of soil and sediment (impacted by effluent from washout of TNT manufacturing plant)
- Engineered HDPE biocell, covered to prevent flooding and allow extended treatment season
- Completed seven batches (1,200 y^3/batch)

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Project Snapshot 4
Naval Weapons Station Yorktown VA

Naval Weapons Station Yorktown

TNT Concentrations before and after Daramend® Treatment

Sampling Zone	Batch #1		Batch #2		Batch #3		Batch #4	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
	TNT (mg/kg)							
1	14,000	4.1	240	4.0	1,520	0.6	12,400	2.0
2	7,900	6.5	3,500	5.6	2,400	10.4	5,700	12.0
3	12,000	3.1	1,600	7.1	1,560	0.5	43,400	2.4
4	17,000	7.0	38,650	3.6	8,000	1.0	351	1.3
5	19.0	2.6	7,000	0.3	2,210	2.7	929	1.3
6	5,100	5.7	5,900	3.3	15,500	11.5	192	1.0
7	33,000	8.8	9,300	1.8	30,200	5.7	19.5	1.2
8	1,300	2.9	31,873	1.2	10,900	2.0	5,870	1.1
9	8,400	14.0	1,000	14.0	40,400	9.5	333	0.8
10	2,800	6.8	1.7	4.0	40,900	8.8	12,000	12.6
Mean	**10,151**	**6.2**	**9,906**	**4.5**	**15,359**	**5.3**	**8,119**	**3.6**

Treatment Protocol

- ✓ Daramend dosage of 1.0% w/w for first cycle and 0.5% w/w for subsequent cycles
- ✓ Each treatment cycle includes addition of Daramend, tillage, irrigation, and a post irrigation reaction period of 7 – 10 days
- ✓ Soil moisture content set to 70% to 80% of WHC
- ✓ Lower soil moisture content for treatment of organic explosive compounds than for chlorinated pesticides

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Naval Weapons Station Yorktown

RDX Concentrations before and after Daramend® Treatment

Sampling Zone	Batch #1		Batch #2		Batch #3		Batch #4	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
	RDX (mg/kg)							
1	140	2.8	10	0.6	185	0.2	154	0.2
2	260	1.8	92	1.0	230	0.4	123	3.9
3	260	5.0	40	0.5	120	0.3	44.6	0.1
4	210	4.3	930	0.7	500	0.3	6.7	0.2
5	0.5	2.5	150	0.5	250	12.0	9.0	0.2
6	510	1.6	160	0.3	185	0.5	3.9	0.3
7	560	2.5	290	0.5	2,500	0.4	0.3	0.2
8	12	2.5	850	0.7	1,000	0.1	6.5	1.4
9	74	2.5	24	0.7	2,500	2.9	1.8	0.3
10	70	2.0	0.8	0.5	3,430	2.4	92.9	0.3
Mean	**209**	**3.0**	**255**	**0.6**	**1,090**	**2.0**	**44.0**	**0.7**

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Project Snapshot 5

Oceanfront Residential Development
Daramend® Treatment of cVOCs
Southern California

- 52,000 tons of sandy soil amended with Daramend® and used for backfill
- Daramend® dosage was 0.8% w/w
- Thorough mixing to achieve good distribution
- Annual downgradient groundwater monitoring conducted for 8 years
- Excellent treatment of all cVOCs

Backfill with Sand/Daramend® Mixture

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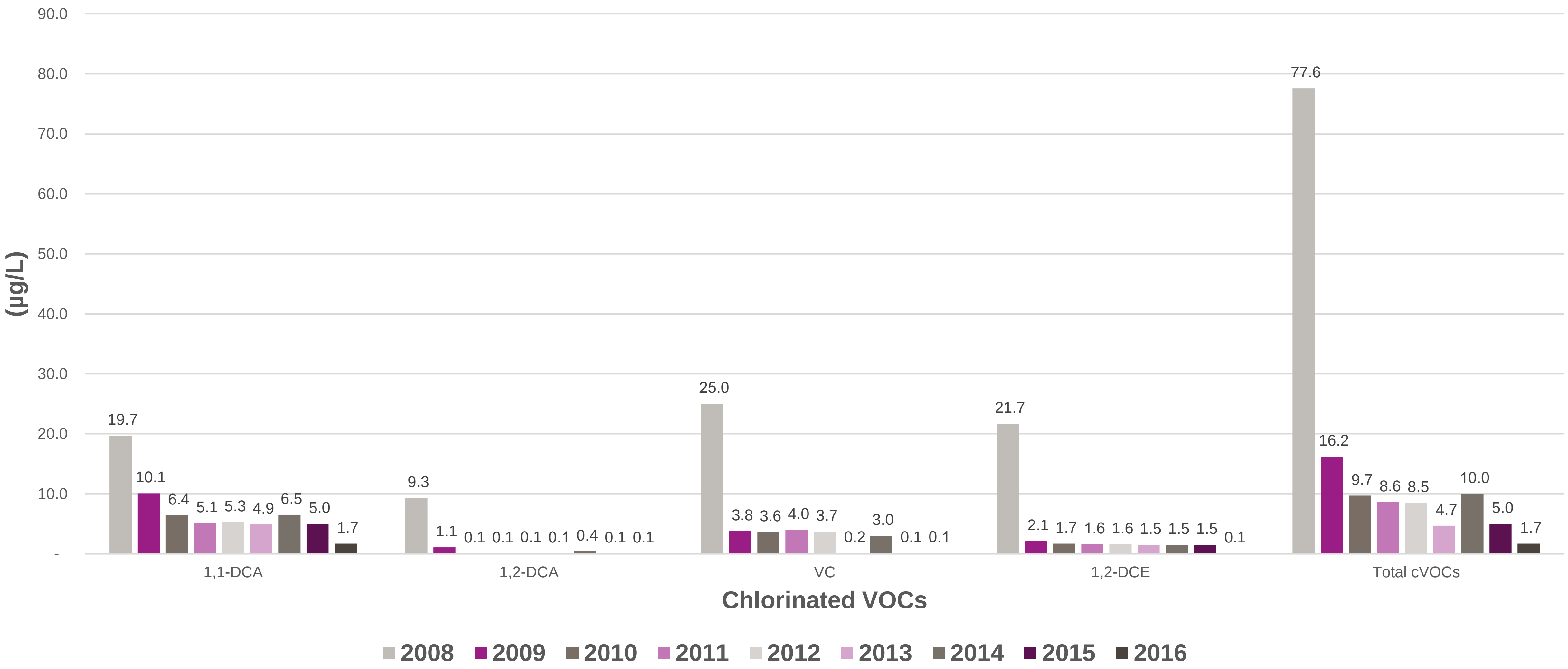
Oceanfront Site, Southern California cVOCs

Concentrations before and after Daramend® Treatment



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Daramend® Reagents Summary

- ✓ Excellent 25-year track record in treatment at hundreds of sites with a wide range of soil conditions
- ✓ Proven effective for treatment of most chlorinated pesticides, herbicides, cVOCs, and organic explosive compounds
- ✓ Economical alternative to off site disposal for many soils, sediments, and industrial wastes based on contaminant destruction as opposed to sequestration of relocation
- ✓ Sustainable low carbon footprint approach to soil remediation that allows reuse of soil for agriculture or construction

Daramend® Case Studies

- ✓ DDT, DDD, DDE
- ✓ Toxaphene
- ✓ Lindane & other BHCs
- ✓ Dieldrin
- ✓ Chlordane
- ✓ 2,4-D & 2,4,5-T
- ✓ Metolachlor

- ✓ TNT & DNT
- ✓ RDX
- ✓ HMX
- ✓ Tetryl
- ✓ TCE & PCE
- ✓ 1,2-DCA
- ✓ CT & CF

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Questions are Welcome!

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