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CANADIAN LEADER IN ENVIRONMENTAL SOLUTIONS

Optimizing Bioremediation of Recalcitrant Soil Contaminants in Canada's Cold Climate

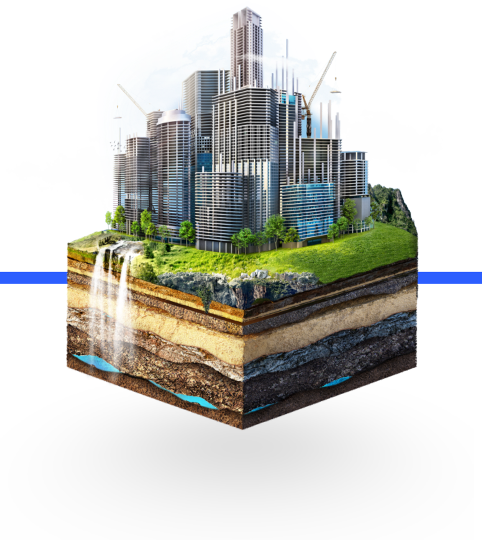
Bioremediation Symposium

Austin, Texas, May 2023

Presented by

Jean Paré, P. Eng., Chemco

BATTELLE



Presentation Agenda

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

Acknowledgements

Victor Bachmann, BSc., AiT.

Dr. Alan G. Seech

Bruce Tunnicliffe, M.A.Sc., P.Eng.

First - Establishing the fact about Canada cold climate

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A bit of History - Reductive Dehalogenation of Pesticides

ABIOTIC REDUCTION OF NITRO AROMATIC PESTICIDES

IN ANAEROBIC LABORATORY SYSTEMS

DESIGNED TO MODEL DISSOLVED ORGANIC MATTER

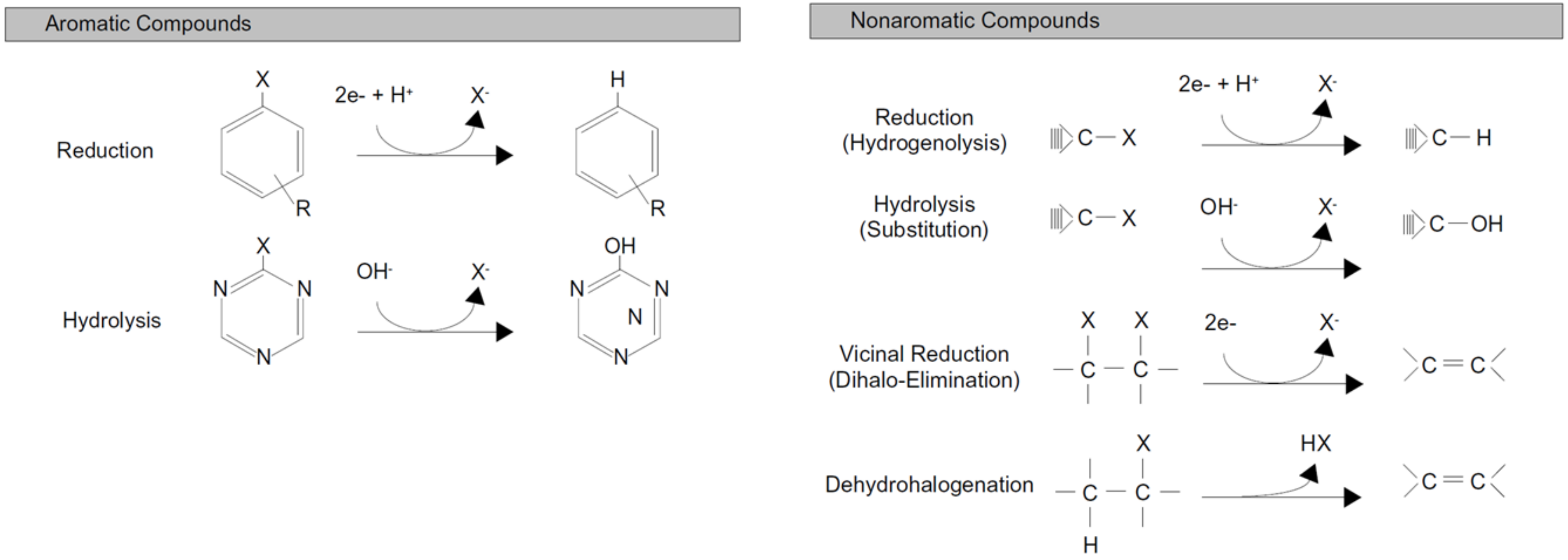
by

Paul G. Tratnyek

August 1987

- Doctoral research focused on reductive degradation of nitroaromatic pesticides
- Focused on electron transfer from redox acitve natural organic compounds to nitro groups on the pesticides

A bit of History – Anaerobic Reductive Dehalogenation of Pesticides



Source - Kuhn and Suflita, 1989a

A bit of History – Anaerobic Reductive Dehalogenation of Pesticides

US005411664A

United States Patent [19]
Seech et al.

[11] **Patent Number: 5,411,664**
[45] **Date of Patent: May 2, 1995**

[54] **METHOD FOR DEHALOGENATION AND DEGRADATION OF HALOGENATED ORGANIC CONTAMINANTS**

[75] Inventors: **Alan G. Seech**, Mississauga; **James E. Cairns**, Toronto; **Igor J. Marvan**, Mississauga, all of Canada

[73] Assignee: **W. R. Grace & Co.-Conn.**, New York, N.Y.

[21] Appl. No.: **126,343**

[22] Filed: **Sep. 24, 1993**

[30] **Foreign Application Priority Data**

Sep. 28, 1992 [CA] Canada 2079282

[51] **Int. Cl.**[6] **C02F 1/58**
[52] **U.S. Cl.** **210/602**; 210/610; 210/615; 210/631; 210/757; 210/908; 210/909; 134/42
[58] **Field of Search** 210/601, 602, 610, 611, 210/615–617, 631, 679, 747, 754, 757, 908, 909; 134/39, 40, 42

[56] **References Cited**

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Primary Examiner—Thomas Wyse
Attorney, Agent, or Firm—Howard J. Troffkin

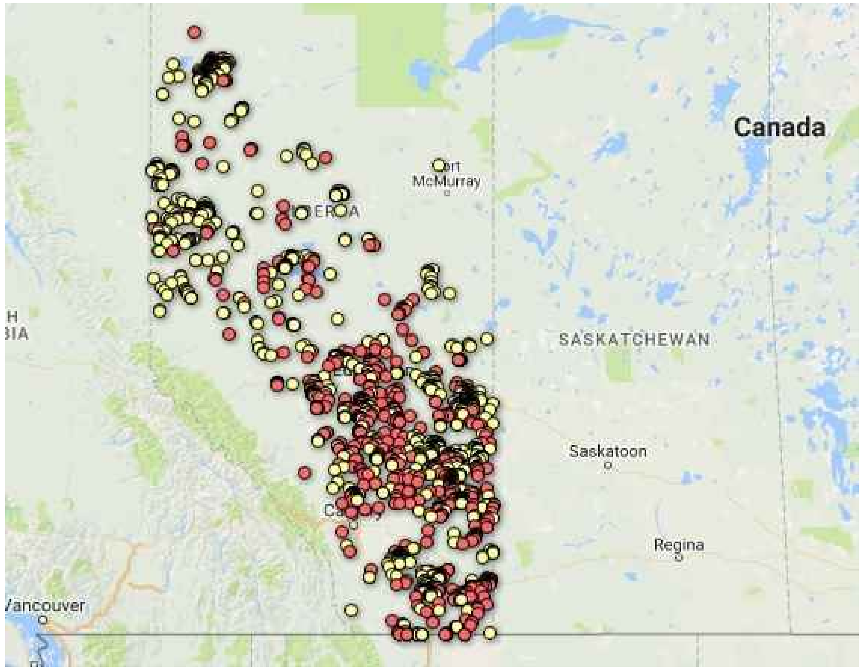
[57] **ABSTRACT**

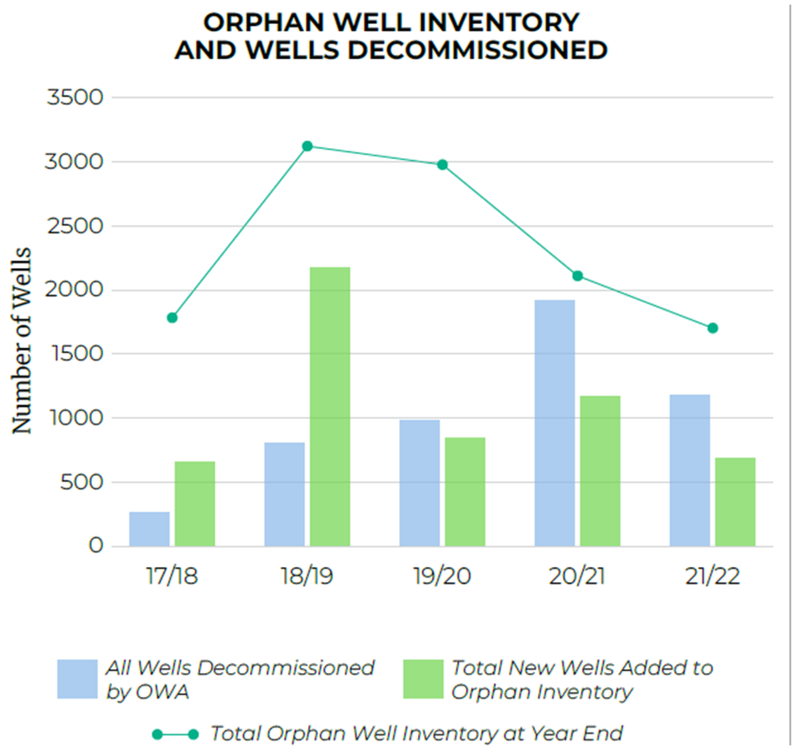
A method of creating an environment which promotes dehalogenation and/or degradation of halogenated organic chemical contaminants in water, sediment, or soil by adding a combination of fibrous organic matter and certain multi-valent metal particles to the water, sediment or soil.

20 Claims, No Drawings

- Discovered that a blend of ZVI and nutrient rich organic carbon supported better destruction of chlorinated pesticides than either ZVI alone or organic carbon alone

Orphan Well issue in Alberta





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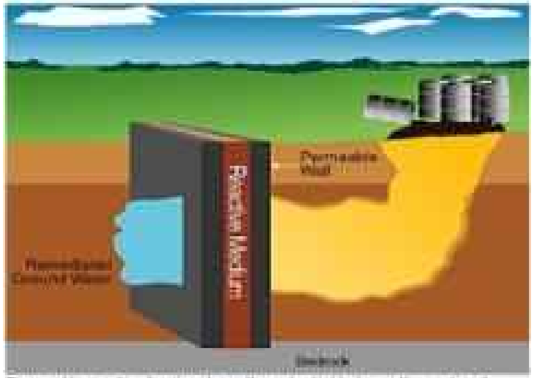
What is In Situ Chemical Reduction?

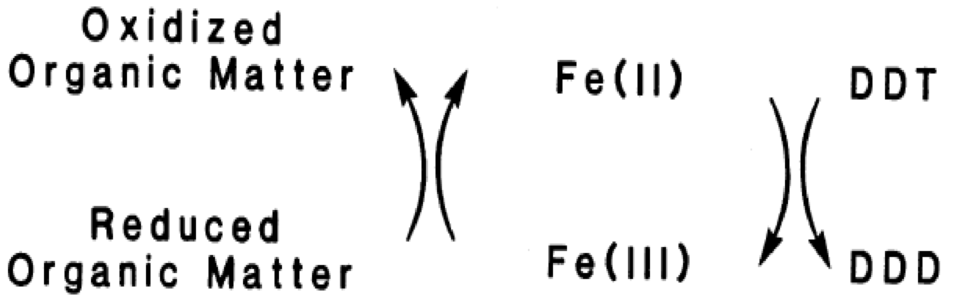
- Introduction of a reducing material or generating reducing species to help degrade toxic organic compounds or immobilize metals in the desired area
- Degradation / Immobilization of contaminants by abiotic or biotic processes
- Transfer of electrons from reduced metals (ZVI, ferrous iron) or reduced 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 enhanced ISCR using microbial reduction



Source: EPA

Chemical Reduction on recalcitrant pesticides

- Many pesticides are too large, insoluble, resistant to movement across microbial membranes to by biodegraded by bacteria
- For these compounds dehalogenation and degradation are mediated in the soil's aqueous phase but outside the microbial cell
- Microbial processes play an important role in the creation of solution chemistry suitable for enhanced reductive dehalogenation (i.e., thermodynamics)
- Elemental iron powder (ZVI) promotes chemical dehalogenation while high quality organic carbon + nutrients pushes microbial growth and oxygen/nitrate/sulfate consumption
- Together these processes drive the soil under treatment to a highly reduced state (i.e. strongly negative Eh)
- Applied in a cycled anaerobic/aerobic mode for chlorinated organics in soil



Source: Tratnyek, 1987 (after Glass, 1972)

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Chemical Reduction Advantages

- **Low Cost and Efficient**. Sustainable Technology. Typical dosages are between 0.1% w/w and 0.5% w/w per treatment cycle
- Uses natural processes and/or groundwater flow when used in situ.
- Easy to implement and using **non dangerous material.**
- Can be used by itself and with other treatment technology to **remediate both soils and groundwater.**
- **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**

Reductive Technology Contaminant Applicability

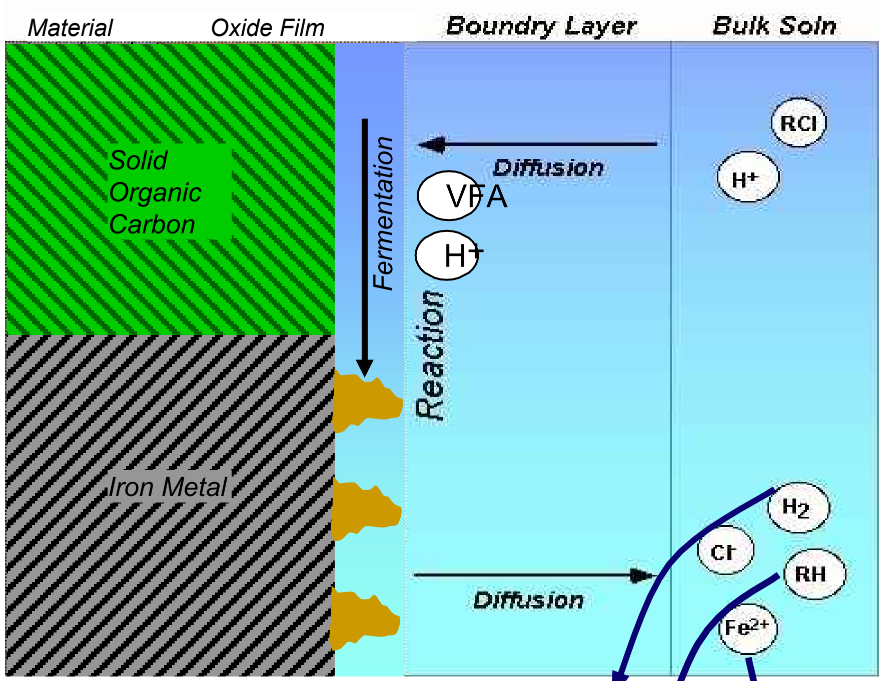
Cycled Anoxic/Aerobic or Anaerobic DegradationPathways

- 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

Carbon + ZVI Synergies Generate Multiple Dechlorination Mechanisms: ISCR



1. Direct Iron Effects:

Hydrocarbon generation:

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

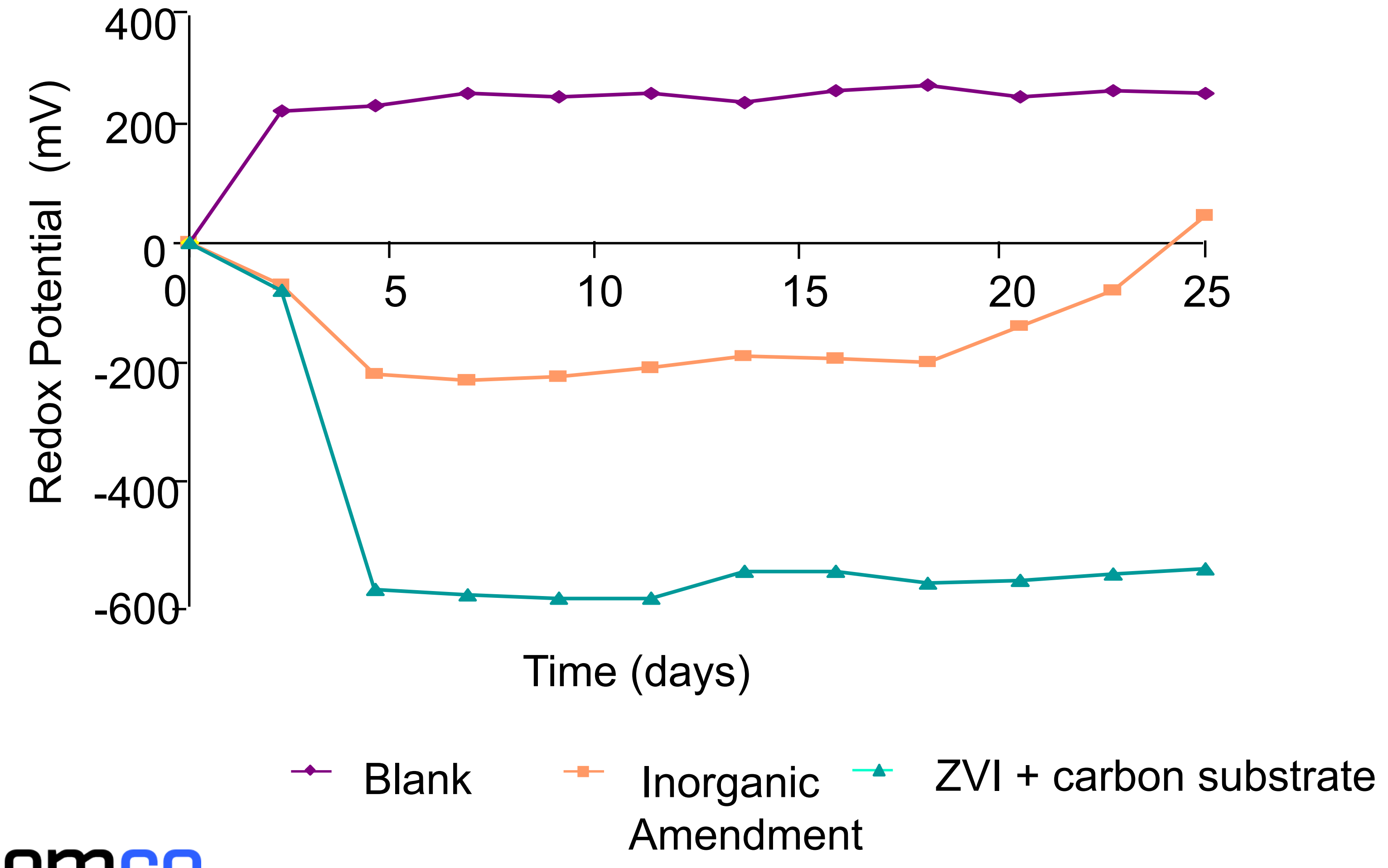
3. Biostimulation:

- 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



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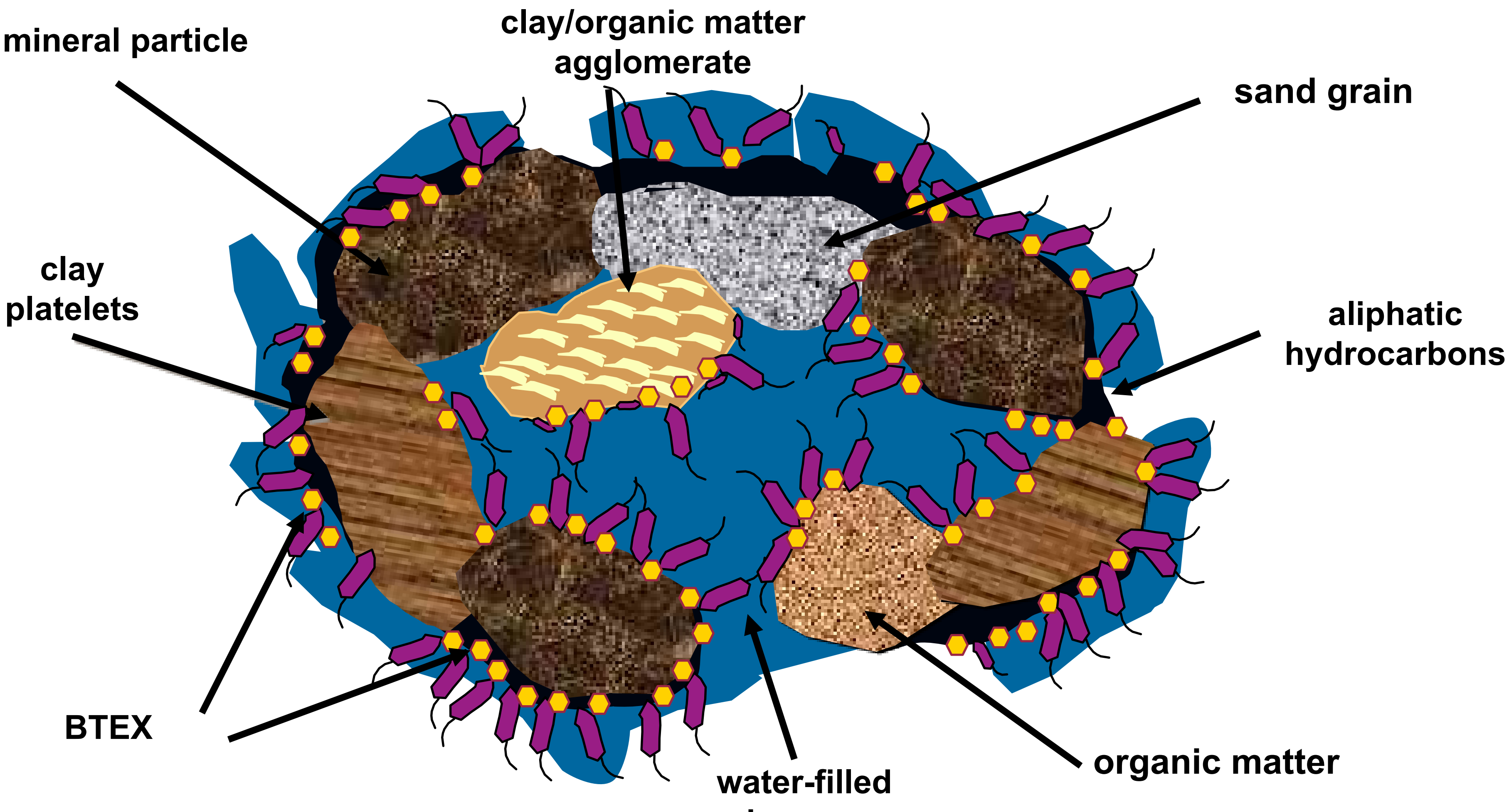
Daramend® Treatment Mechanism



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 and reduced leachability

Daramend® *vs* Anaerobic Composting

Parameter	Composting	Daramend®
Redox Strength	Moderate, subject to nature of available compost substrates	Very strong, results form combined biological and chemical reduction chemistry
Treatment Mechanisms	Enzymatic biological as facilitated by growth of bacteria and fungi	Enzymatic biological as facilitated by bacteria and fungi + Chemical reduction by reactive ZVI and Fe2+ + Enhanced Thermodynamics (strong negative Eh)
Soil Physical Properties	Large volume increase, may have poor geotechnical properties	No change in volume or geotechnical properties
Tolerance of High Acute Toxicity	Soil is diluted by compost volume, acute toxicity of blend is reduced	Chemical degradation insensitive to acute toxicity and reduces toxicity sufficiently to allow microbial growth.
Sustainability	May be positive or negative subject to local availability of substrates	Most sustainable, produces from natural byproducts, recycled iron, small carbon footprint

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

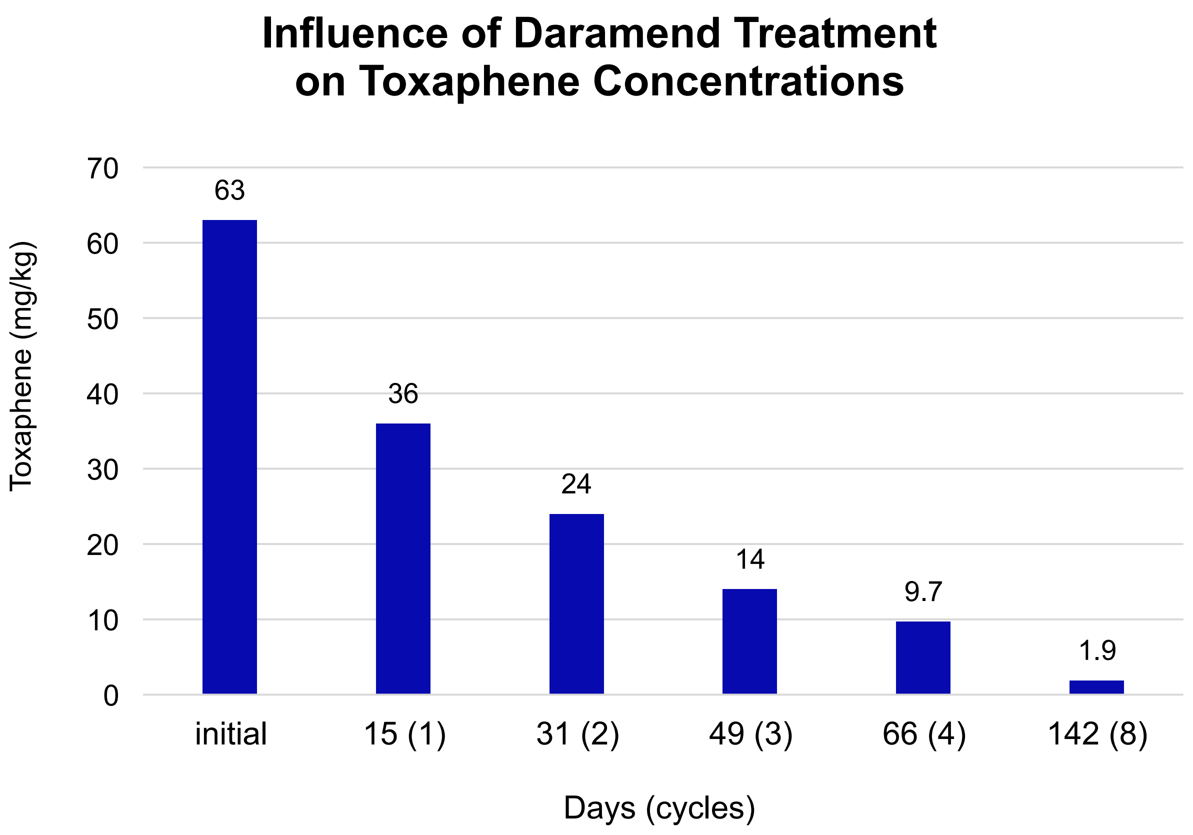
Design and Field Measurements Requirement

- **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

Bench-scale Treatability Testing

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



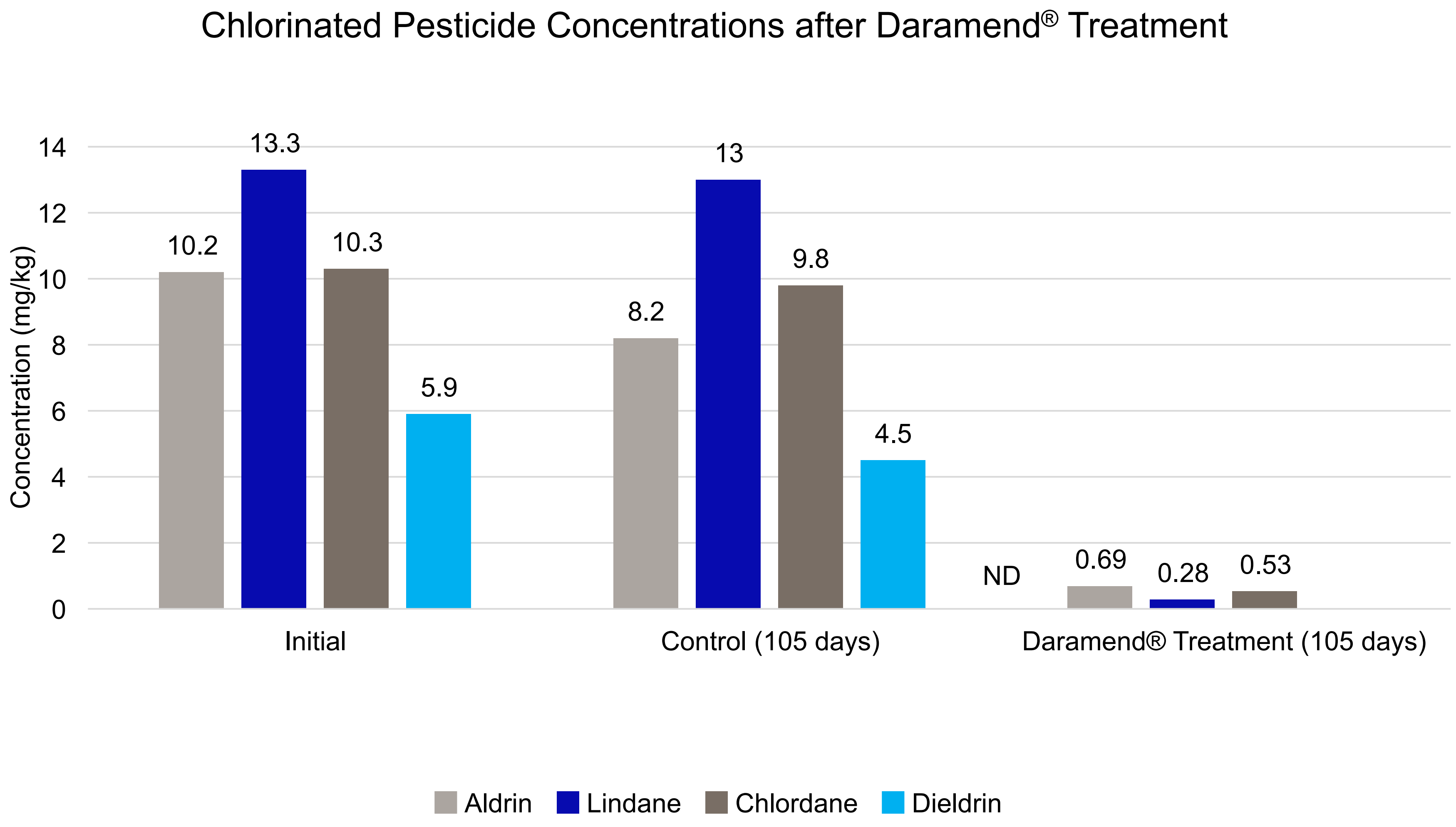
Data points represent mean of four replicates; $LSD_{(0.05)}$ = 6.5

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.
- Dependent on-site conditions, COCs, and concentrations, 2-3 cycles may be required in order to establish reductive conditions.
- Once reductive conditions are established contaminant removal response increases significantly
- Mixing is optional for treatment of OE

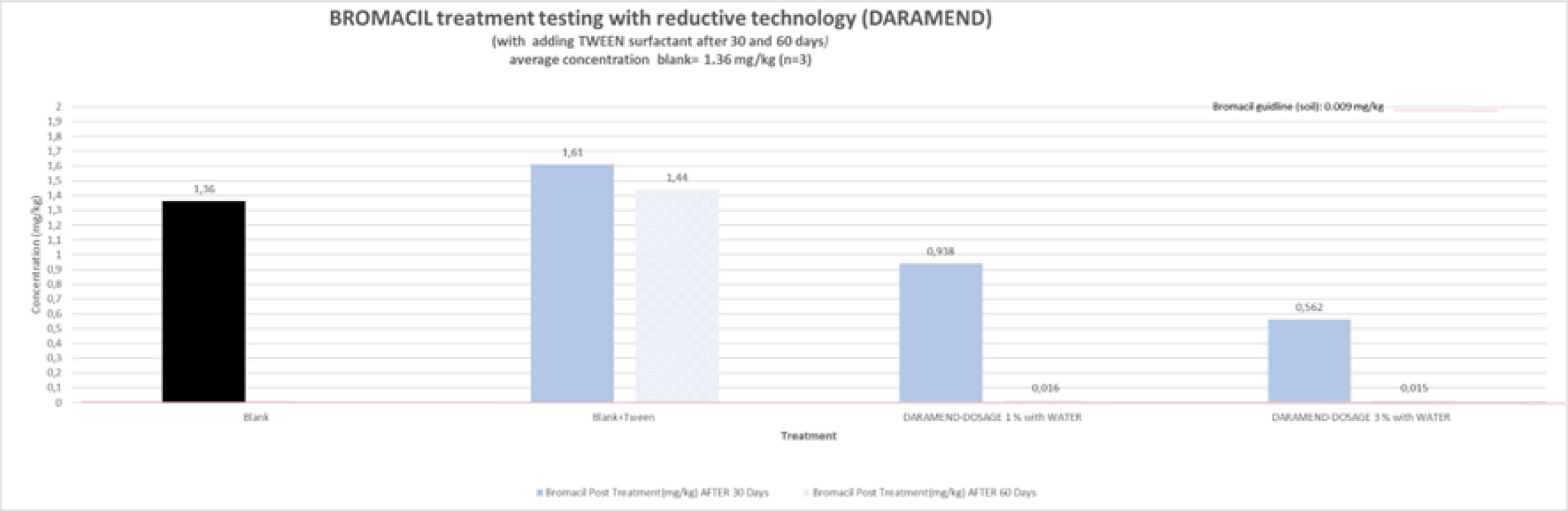
Daramend® Bench Scale Results:

Treatment of Aldrin, Lindane, Chlordane, and Dieldrin in Louisiana soil



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

Daramend® Bench Scale Results:
Treatment of Bromacil in Alberta soil



Removal of 98.8 % after 60 days (1 % w/w dosage rate)

Removal of 98.9 % after 60 days (3 % w/w dosage rate)

Case studies

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

Surface soil to a depth of 24” (60 cm)

Residual metabolites from use of DDT as an insecticide

Major target compound was DDE

Case Study 1

34 acre Agricultural Site – DDT, DDE, Dieldrin

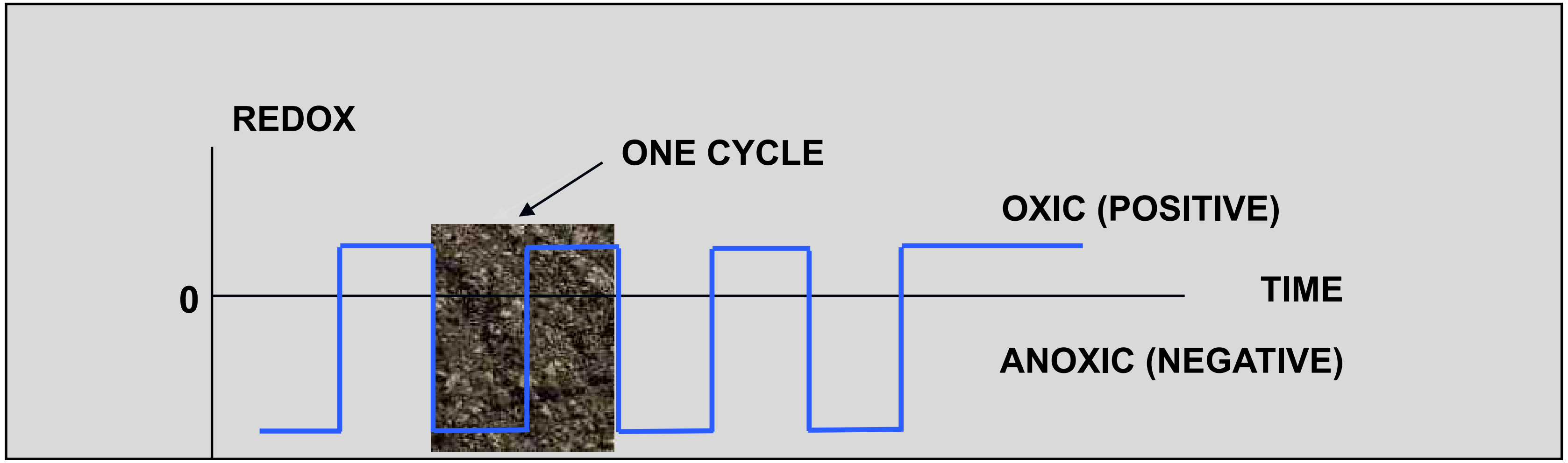



In Situ Daramend Treatment

Chlorinated Pesticides and Herbicides in Soil

In Situ Daramend Redox Cycling

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



Results After One & Two Cycles

Data for area treated after one cycle

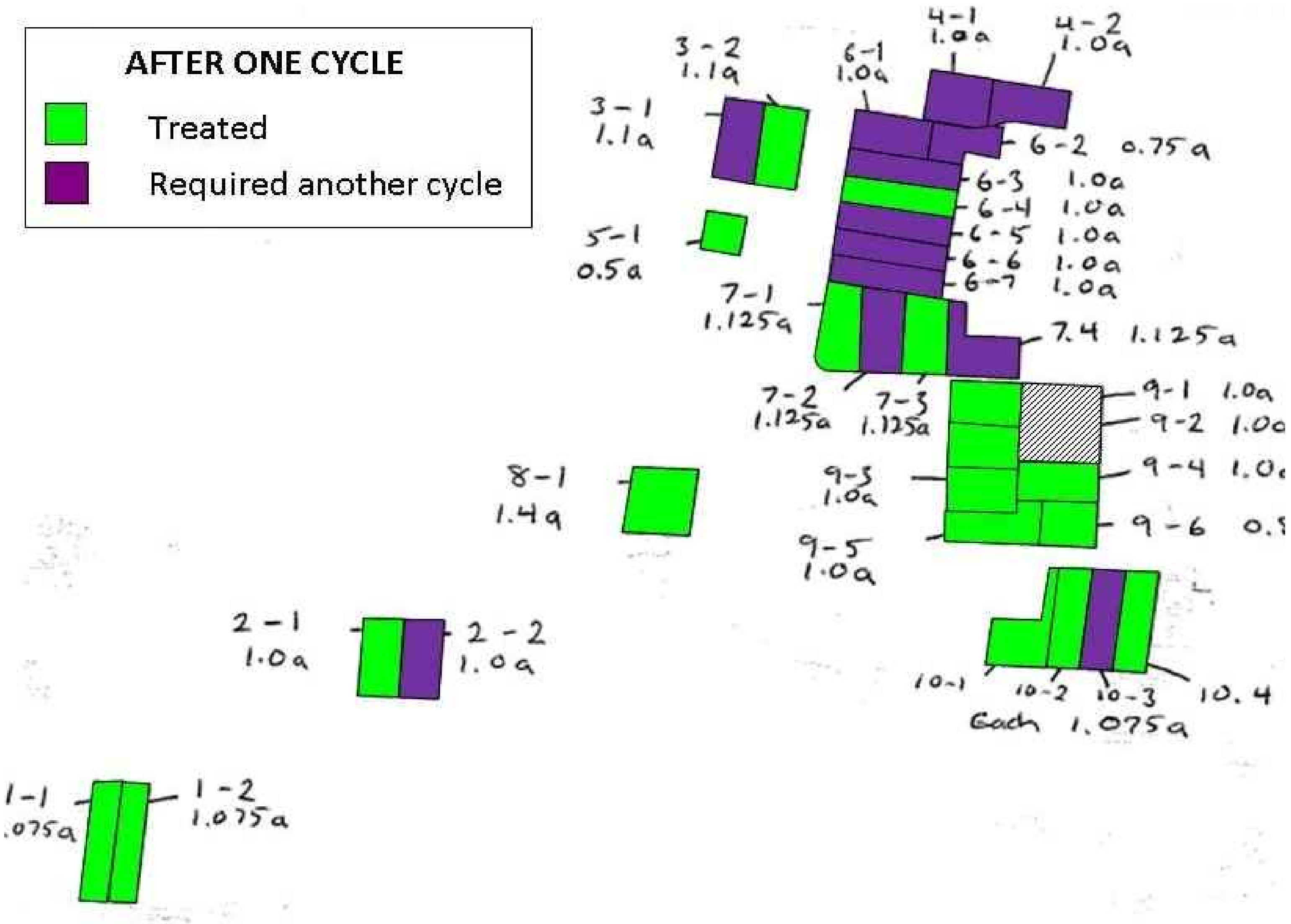
Compound	Initial Concentration (mg/kg)	Concentration After 1st Cycle (mg/kg)	Final % Removal
DDT	1.90	0.98	49%
DDE	2.38	1.11	53%
Dieldrin	0.064	0.040	38%

Data for area that required a second cycle

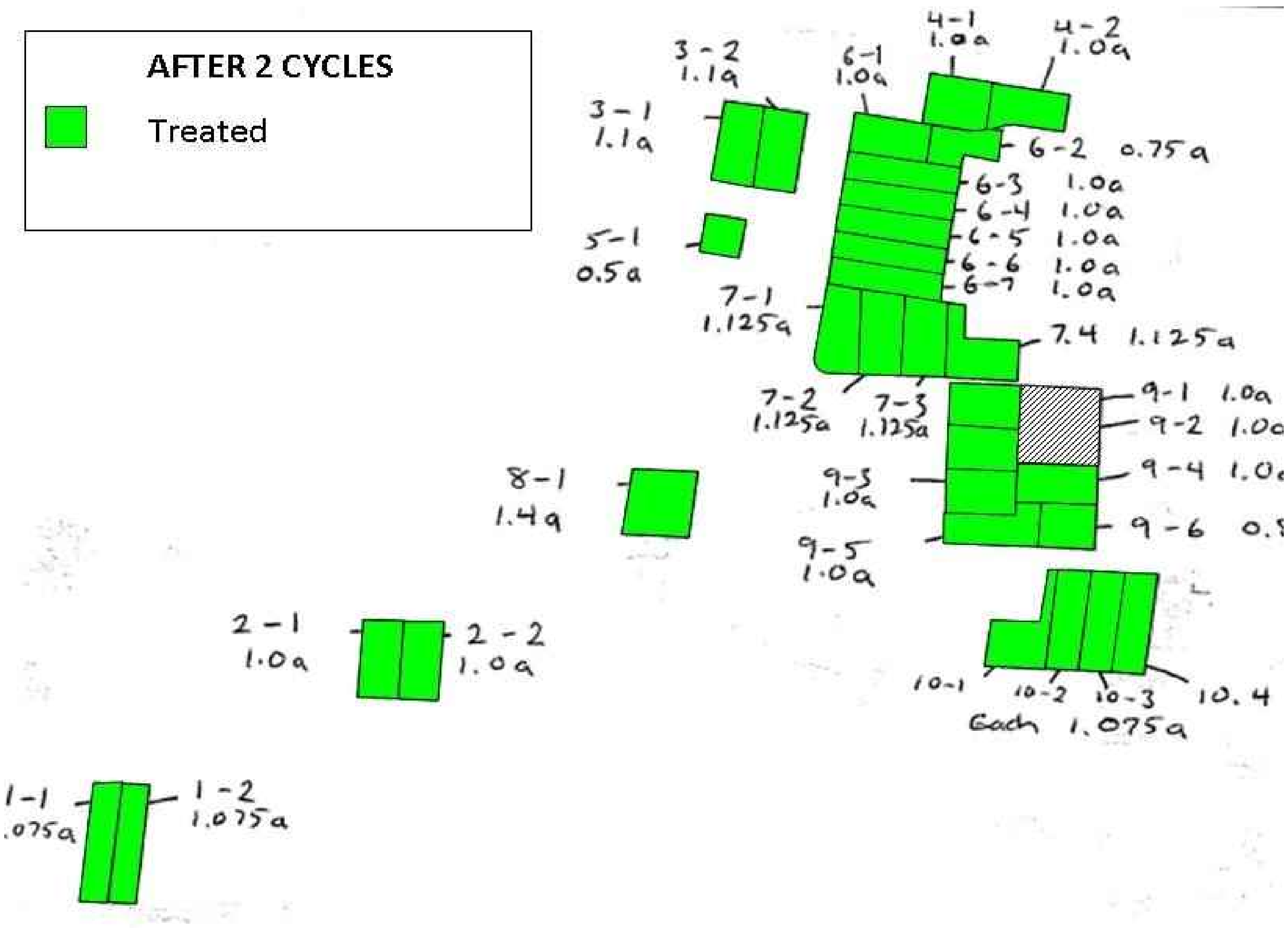
Compound	Initial Concentration (mg/kg)	Concentration After 1st Cycle (mg/kg)	Concentration After 2nd Cycle (mg/kg)	Final % Removal
DDT	2.05	2.00	0.66	68%
DDE	2.37	1.98	0.80	66%
Dieldrin	0.110	0.080	0.028	65%

- Initial pesticide concentrations were lower than had been treated before
- No apparent relation between initial concentration and response to treatment
- Residential treatment standards were achieved quite easily with low dosage of Daramend
- When concentrations are low (<5 mg/kg) spatial variability in pesticide concentrations makes analytical challenging
- In this soil, removal efficiency for DDT, DDE, and Dieldrin were roughly equivalent, which is quite surprising
- Long term use of “Bordeaux Mix” (copper sulfate) for mildew control: sulfate → sulfide → native reactive iron sulfides?

Results After One Cycle

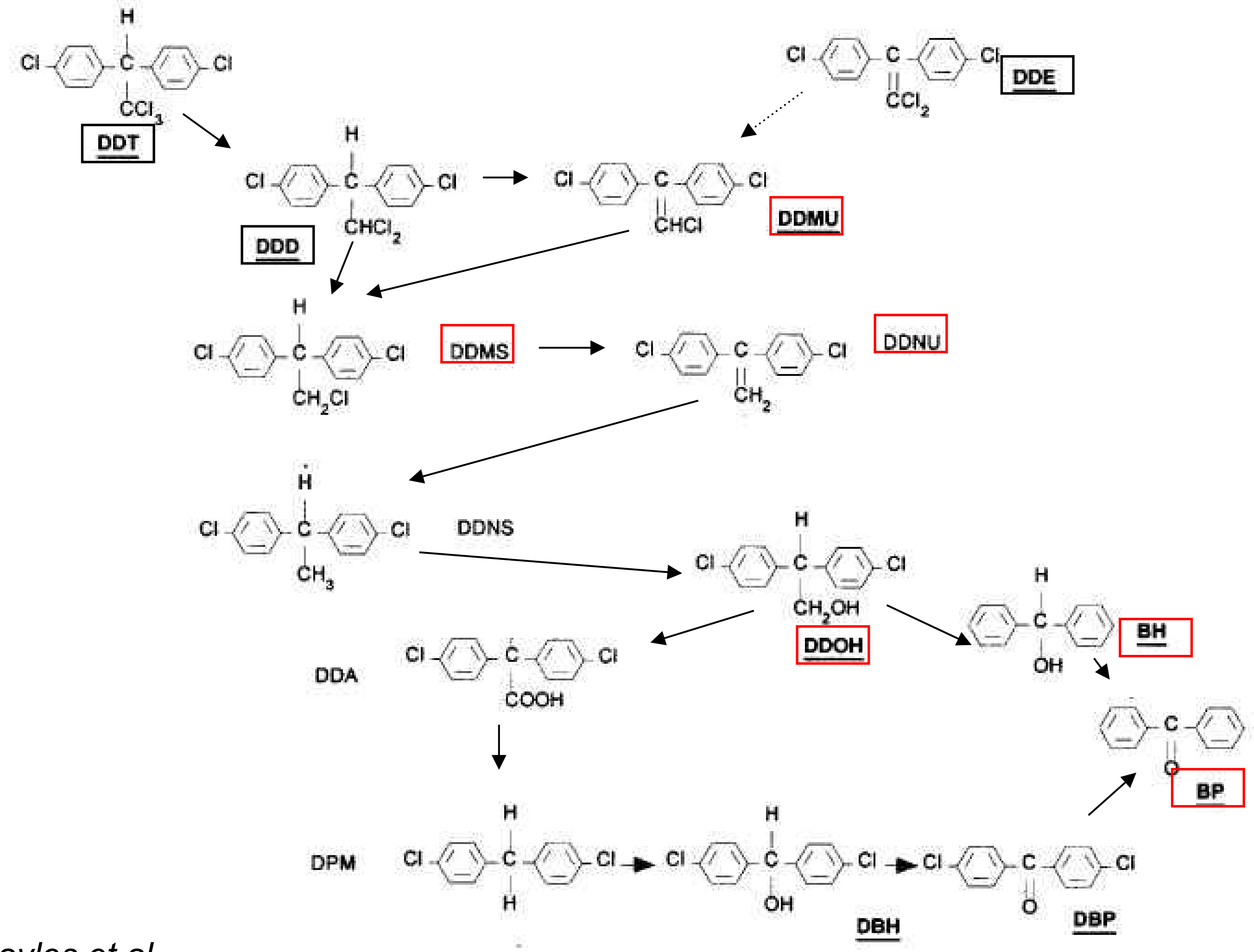


Results After Second Cycle



What was the Fate of DDT?

Dechlorination (anaerobic)



From Sayles et al. (1997)

What was the Fate of DDT?

Ring Opening and Mineralization?

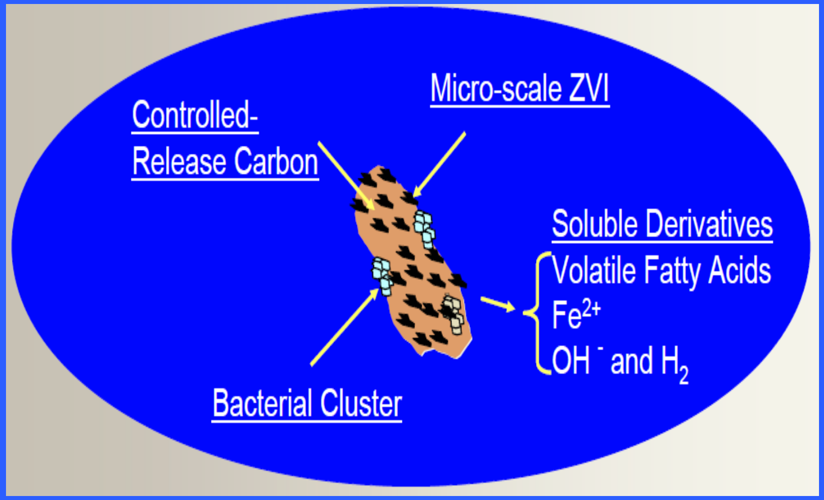
- Radioisotope (14C-DDT) Fate Studies:
  - ✓ Main fate was conversion to **carbon dioxide**
  - ✓ Slow but significant production of 14C-CO2
  - ✓ Recovery of added 14C in DDT as carbon dioxide was about 7% in 150 days
  - ✓ After 150 days the rate of 14C-CO2 release had decreased to about 1% per month
- Stable isotope (13C-DDT) Fate Studies indicated dichlorobenzophenone was the major breakdown product

Case Study 1 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 2

2,4-D, 2,4,5T, and DDT
Uniroyal, Elmira ON, Canada



Project 2: Summary & Lessons Learned

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

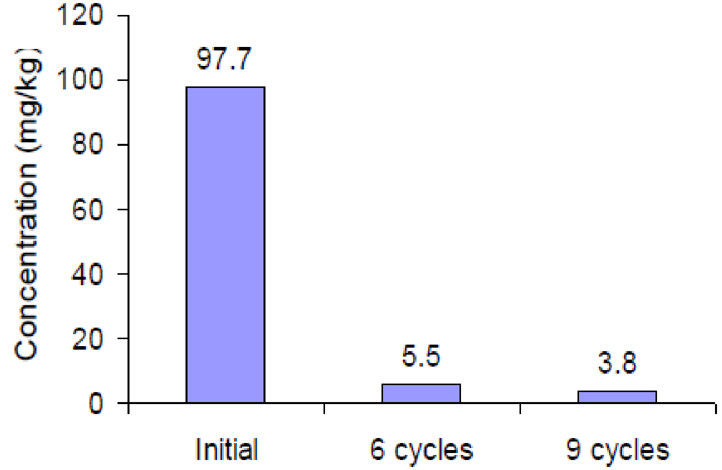


Figure 2. Influence of DARAMEND treatment on 2,4,5-T concentration.

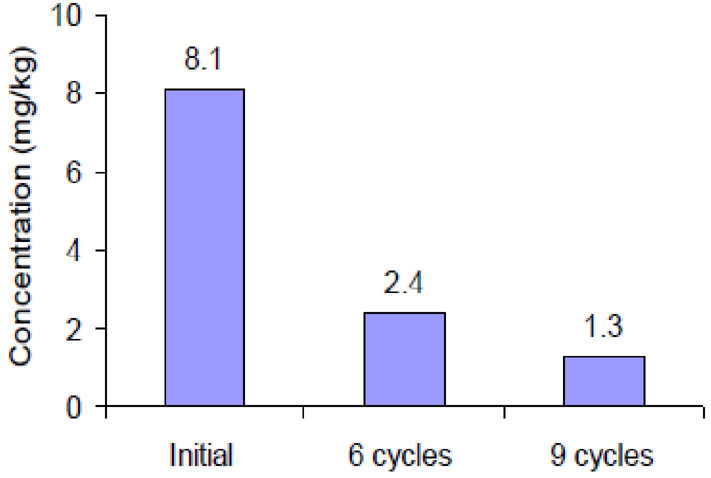
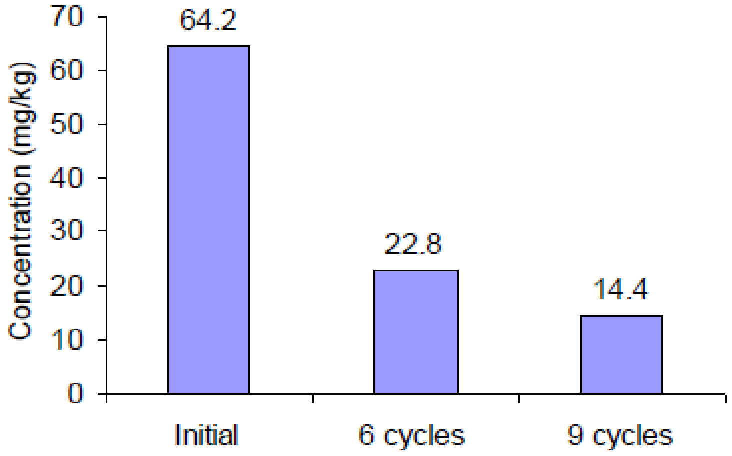


Figure 3. Influence of DARAMEND treatment on DDX concentration.



- ✓ **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: much higher labour requirement**
- ✓ **Raioisotope studies indicated that 2,4-D were rapidly converted to ^{14}C-CO_2 but 2,4,5-T and DDT were much slower**
- ✓ **Bench-scale studies on a range of soil samples indicated that total 2,4-D + 2,4,5-T concentrations above 400**

Daramend for Residential: Summary

- treatment is a **proven, low cost destructive approach** to treatment of surface soils containing chlorinated and other halogenated 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

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Thank you for your attention !!
Questions ?!?

May 2023

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