Enhanced Aerobic Bioremediation of Soils Containing PAHs, PCP, Phthalates, and Petroleum Hydrocarbons

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Field-Proven Portfolio of Remediation Technologies

Chemical Oxidation
- Klozur® Persulfate Portfolio
  - Klozur® SP
  - Klozur® KP
  - Klozur® One
  - Klozur® CR
- Hydrogen Peroxide

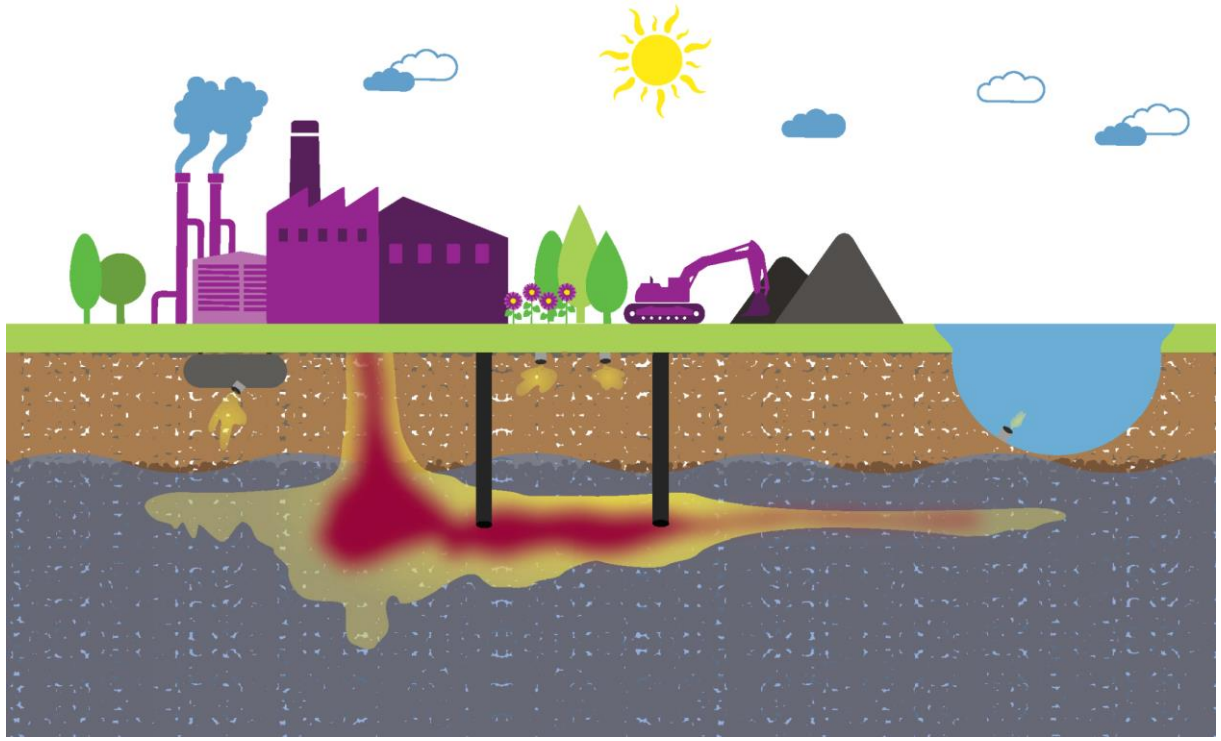
Aerobic Bioremediation
- Terramend® Reagent
- PermeOx® Ultra
- PermeOx® Ultra Granular

Metals Remediation
- MetaFix® Reagents

Chemical Reduction
- EHC® ISCR Portfolio
  - EHC® Reagent
  - EHC® Liquid
  - EHC® Plus
- Daramend® Reagent

Enhanced Reductive Dechlorination
- ELS® Microemulsion
- ELS® Liquid Concentrate
- ELS® Dry Concentrate

BioGeoChemical
- GeoForm® Reagents



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Our Presenter

Alan Seech, Ph.D.

Sr. Technology Applications Manager

Evonik Active Oxygens

Soil & Groundwater Remediation

Alan.Seech@evonik.com

- M.Sc. and Ph.D. degrees in Soil Chemistry and 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

1. Applicability
2. Terramend® Reagents
   - ✓Composition of Terramend® Carbon & Terramend® Inorganic reagents
   - ✓Compare and Contrast with traditional fertilizer-based approach
   - ✓Microbiology & Biochemistry during soil treatment
3. Bench-scale treatability approach and results
4. Project Snapshots (very brief case studies)
5. Questions & Answers

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Approaches to Aerobic Soil Bioremediation

- Traditional focus has been on supplying adequate inorganic nitrogen and phosphorus to support biodegradation of target hydrocarbons, adjusting soil water content, and soil mixing for aeration.
- Generally supplied in the form of commercial/agricultural fertilizer
- Target an “optimized” C:N:P ratio based on an estimate of bioavailable carbon including target compounds and native organic matter
- Commonly target C:N:P at 120:10:1 molar ratio
- This approach often fails because inorganic nutrients are used very quickly when bioavailable and are also lost through wasteful processes including luxury consumption, denitrification, and precipitation.
- This approach also fails to address the issue of low bioavailability of water in hydrophobic soils and the acute microbial toxicity created by some contaminants (e.g., PCP, Lindane)
- We use a different approach that is based on supplying nutrients, increasing bioavailable water, and overcoming acute microbial toxicity with our Terramend family of soil amendments.

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Terramend® Carbon, Terramend® Inorganic, and Daramend® Reagents

Attribute	Terramend® Carbon	Terramend® Inorganic	Daramend®	Daramend® Plus
High Surface Area Hydrophilic Plant Fiber	✓	✓	✓	✓
Slow-release Organic Carbon & Nutrients (N, P, S)	✓	✓	-	-
Rapid-release Organic Carbon & Nutrients (N, P, S)	-	-	✓	✓
Inorganic Nitrogen & Phosphorus	-	✓	-	-
Emulsifying Agent	✓	✓	✓	✓
pH Balanced	✓	✓	✓	✓
Microscale ZVI			✓	✓
Activated Carbon				✓

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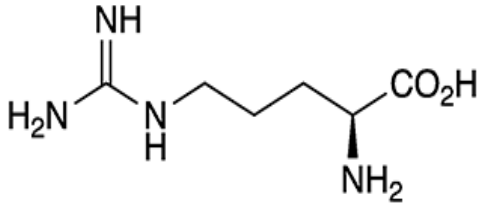
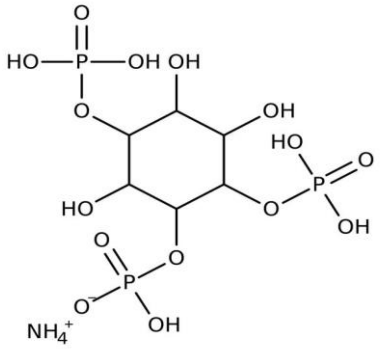
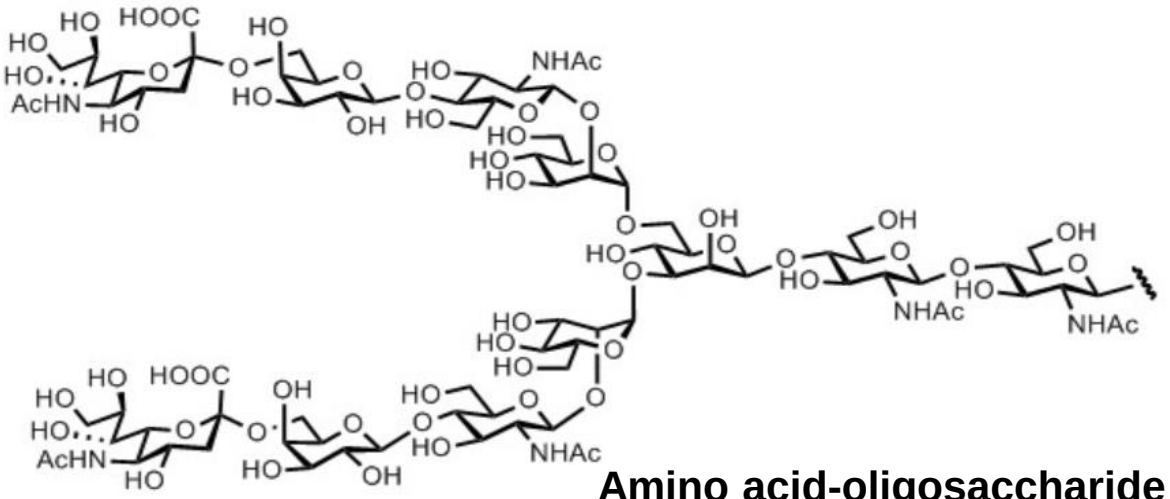
Rapid & Slow-release Organic Forms of Carbon, Nitrogen & Phosphorus in Terramend® Reagents



Arginine



Phytic acid



Amino acid-oligosaccharide

Carbon & Nutrients in Terramend® Reagents

- Between 4% and 10% in rapidly available forms including sugars, polysaccharides, and amino acids.
- More slowly-released forms including hemicellulose and amino acid-oligosaccharide structures
- Provides a range of rapidly and slowly released carbon and nutrients to support a variety of aerobic bioremediation applications
- Natural, sustainable, optimized food source for soil microorganisms

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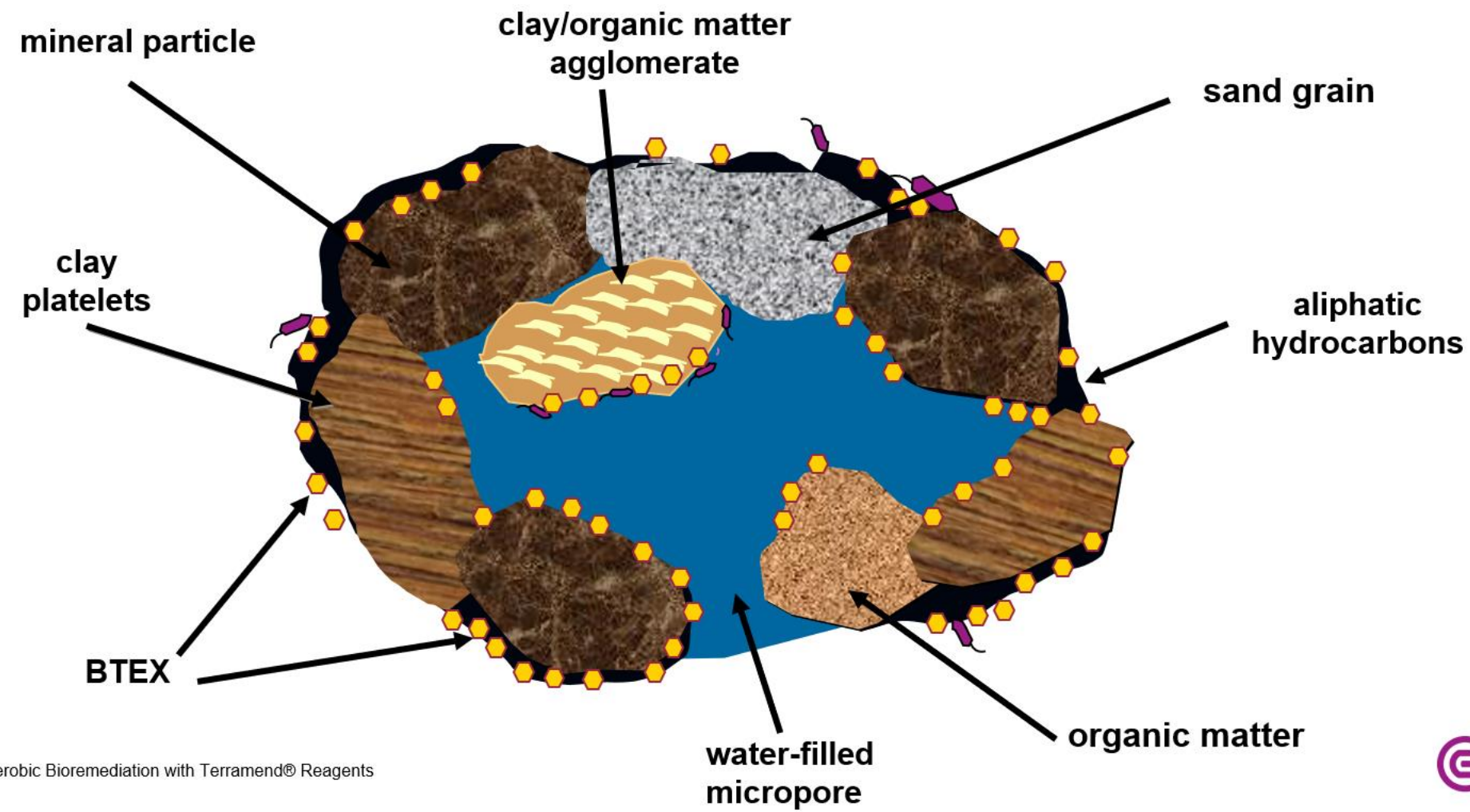
Terramend® Treatment Mechanism



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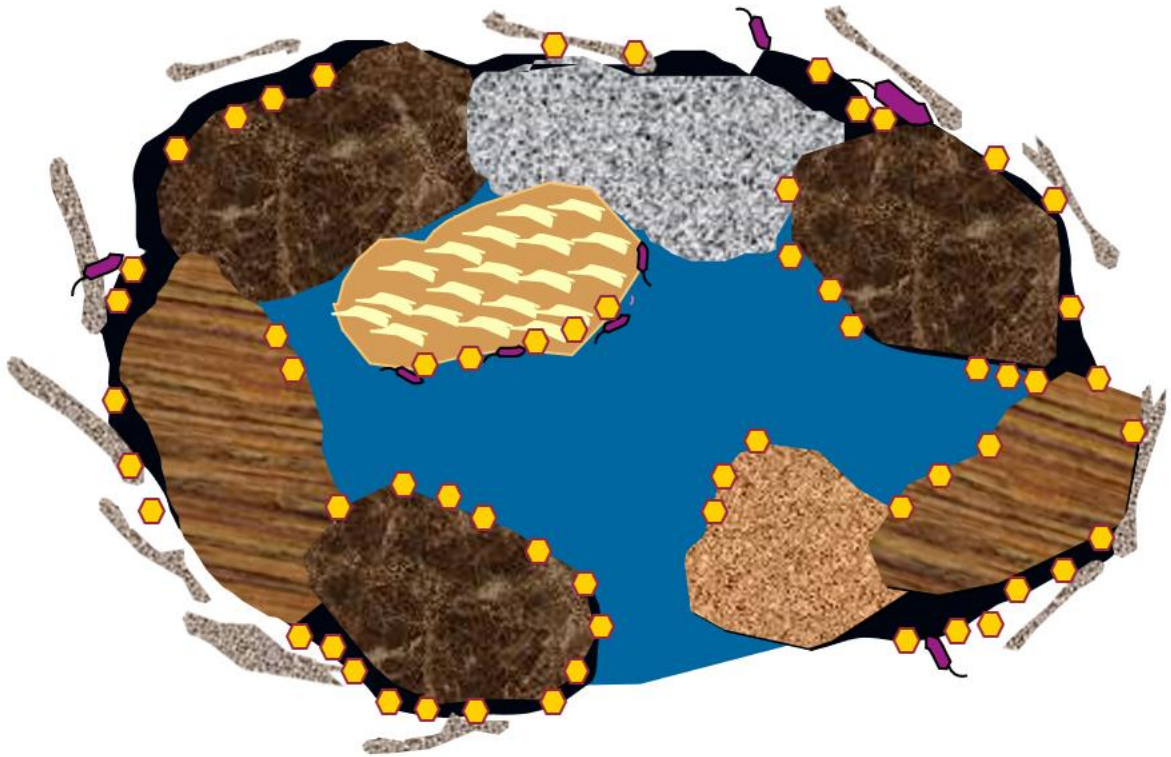
Terramend® Treatment Mechanism

Terramend® Added



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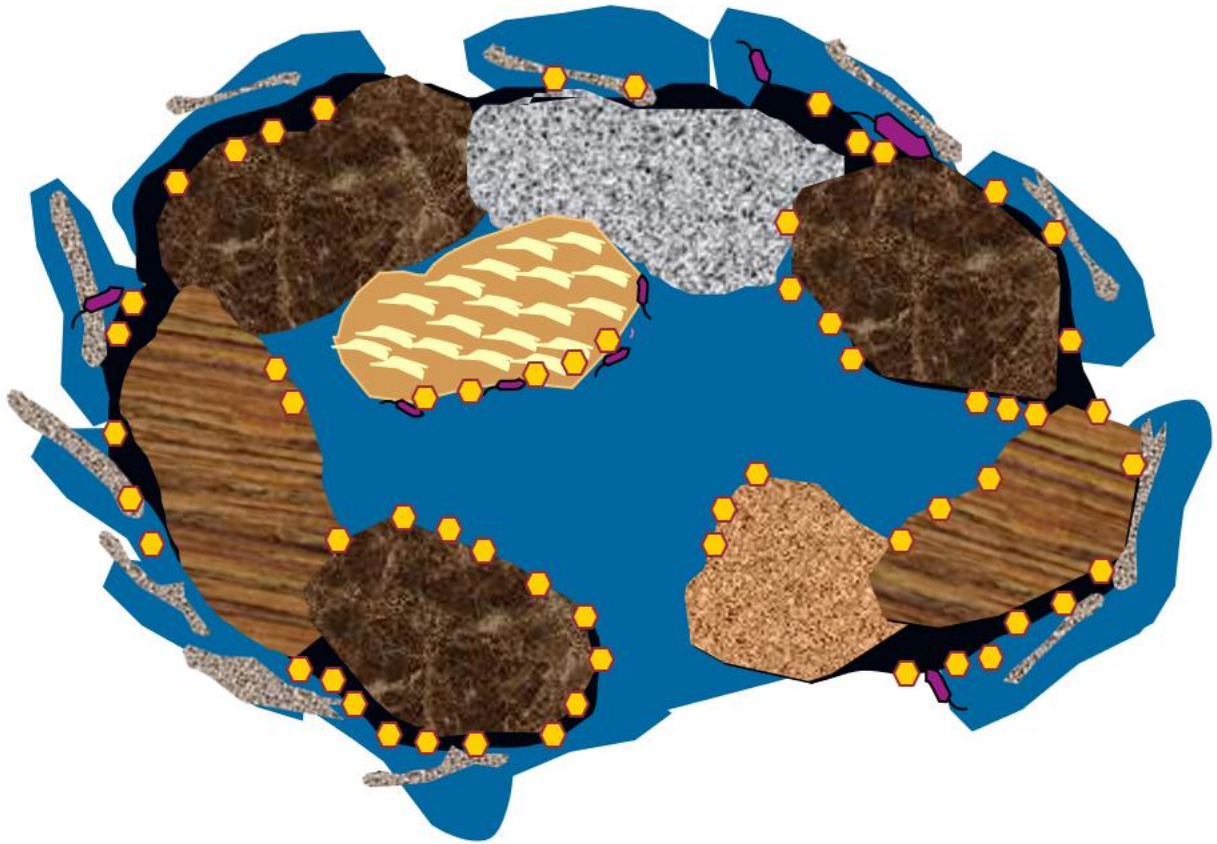
Terramend® Treatment Mechanism

Terramend® Hydrated



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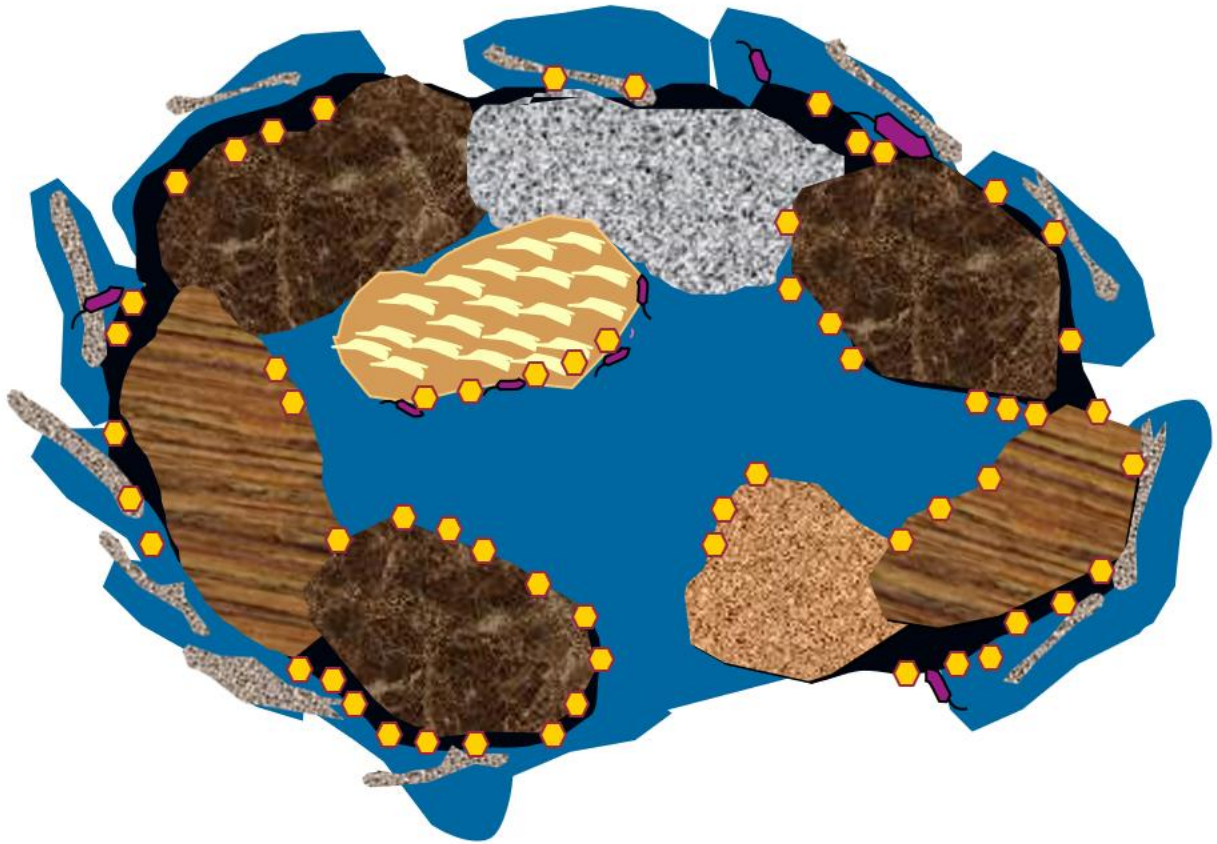
Terramend® Treatment Mechanism

Nutrients Released



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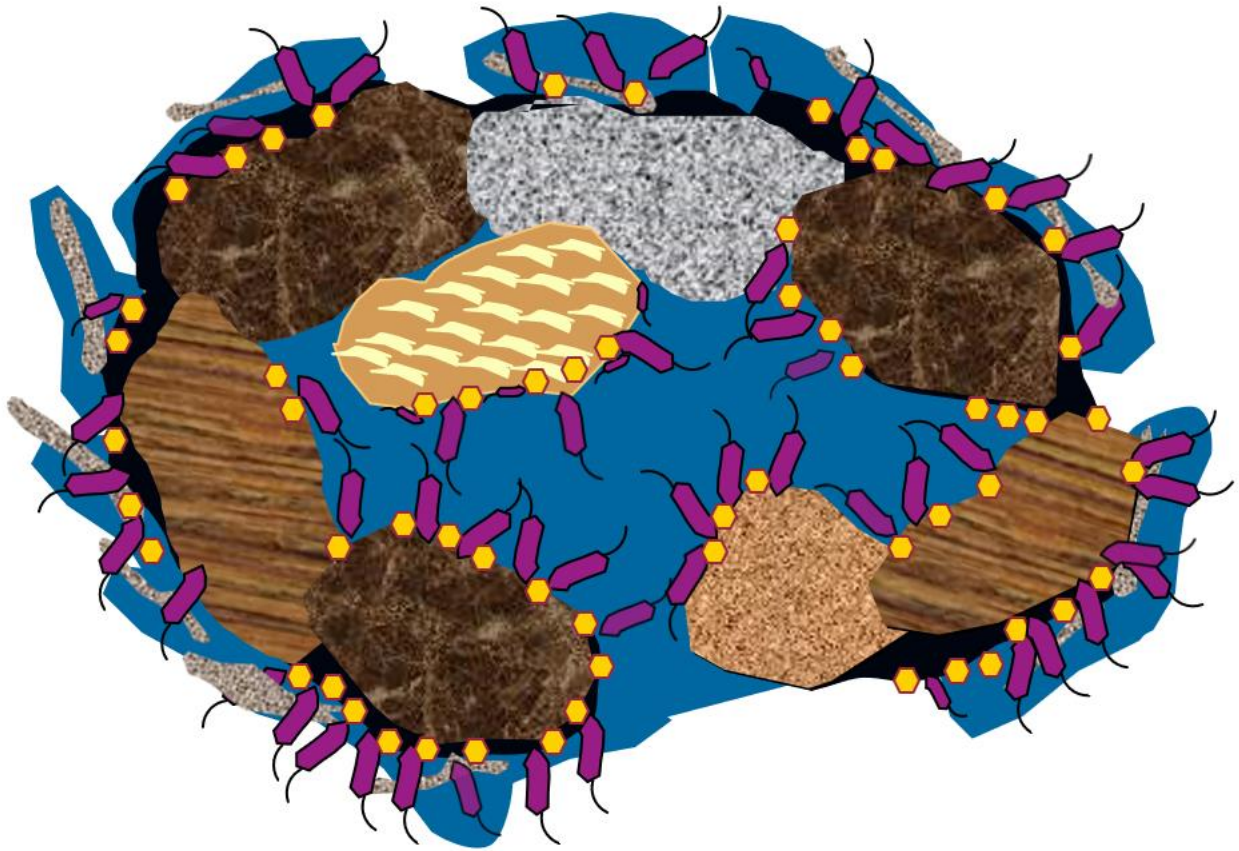
Terramend® Treatment Mechanism

Bacteria Grow



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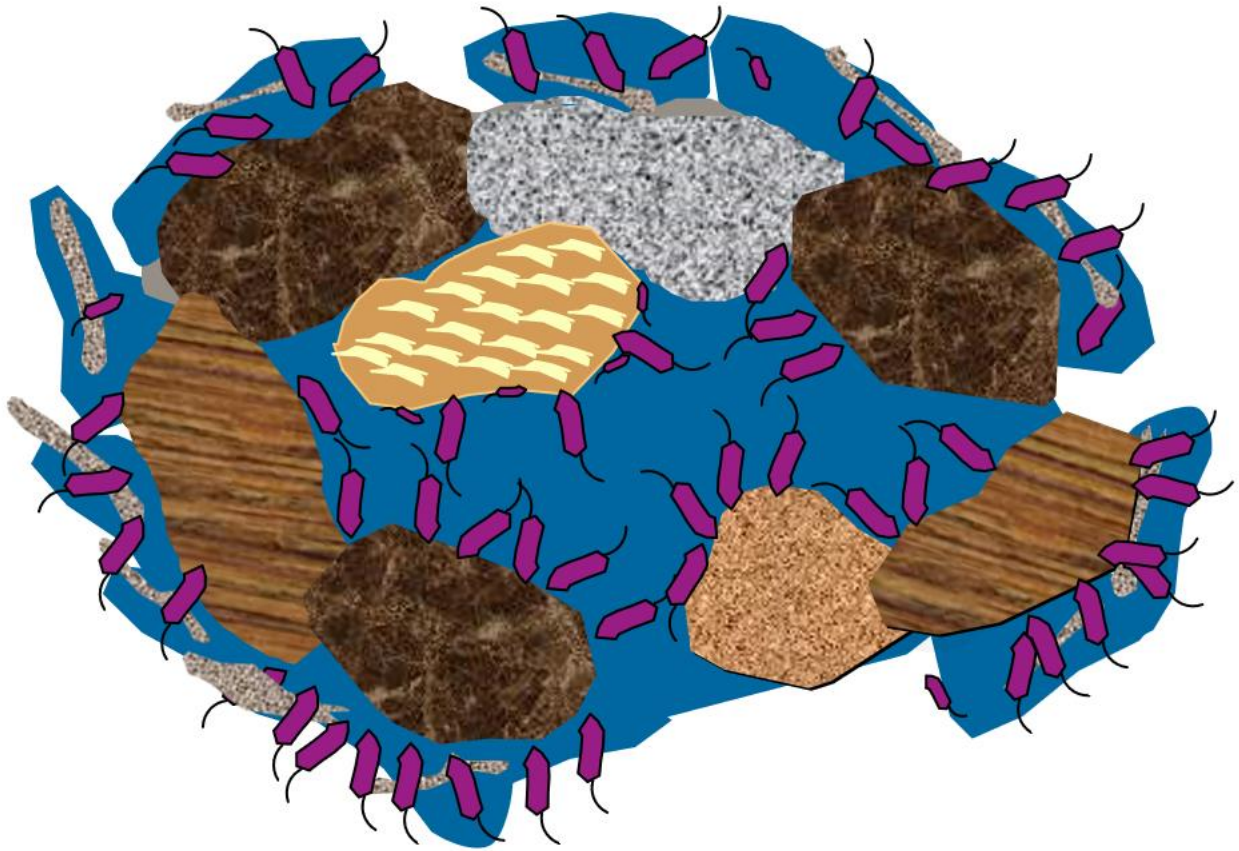
Terramend® Treatment Mechanism

Contaminants Destroyed



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In Situ Terramend Treatment of PAHs, PCP, and Mineral Oil Industrial Wood Preserving Site

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Ex Situ Treatment of Chlorinated Phenols
Chemical Manufacturing Site

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In Situ Treatment of Herbicides and Chlorinated Pesticides
Former Agricultural Site

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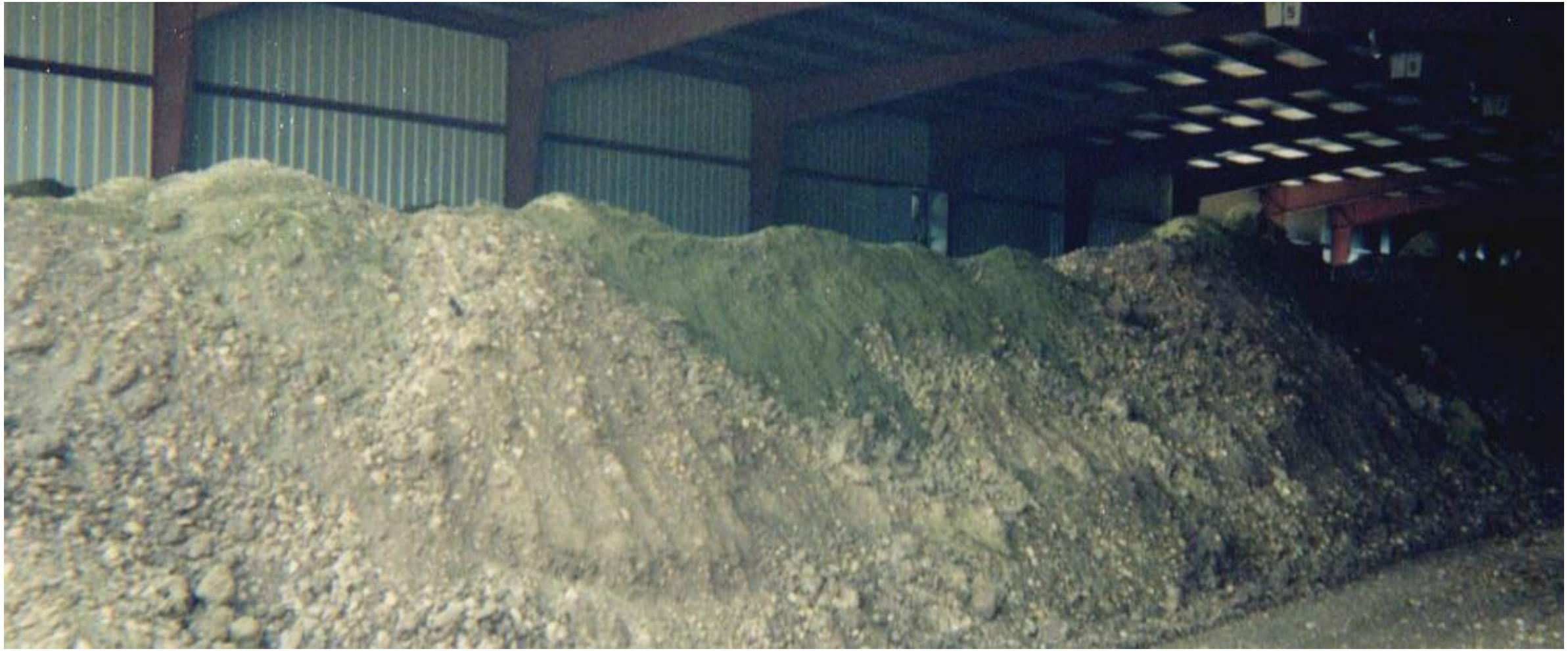
Windrow Treatment of Petroleum Hydrocarbons and PAHs



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Bench-scale Treatability Testing

- ✓ Objectives
- ✓ Methodology
- ✓ Results for PCP, Lindane, and Petroleum Hydrocarbons

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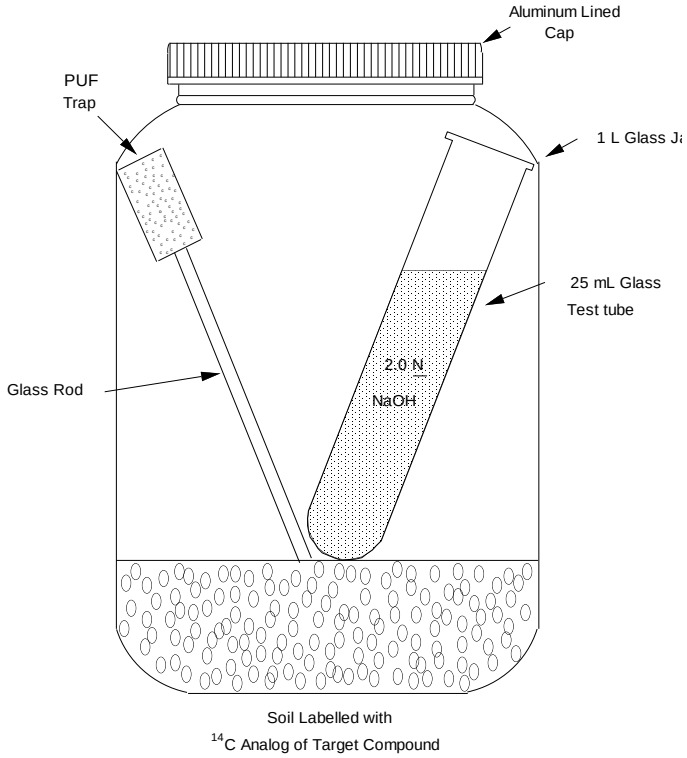
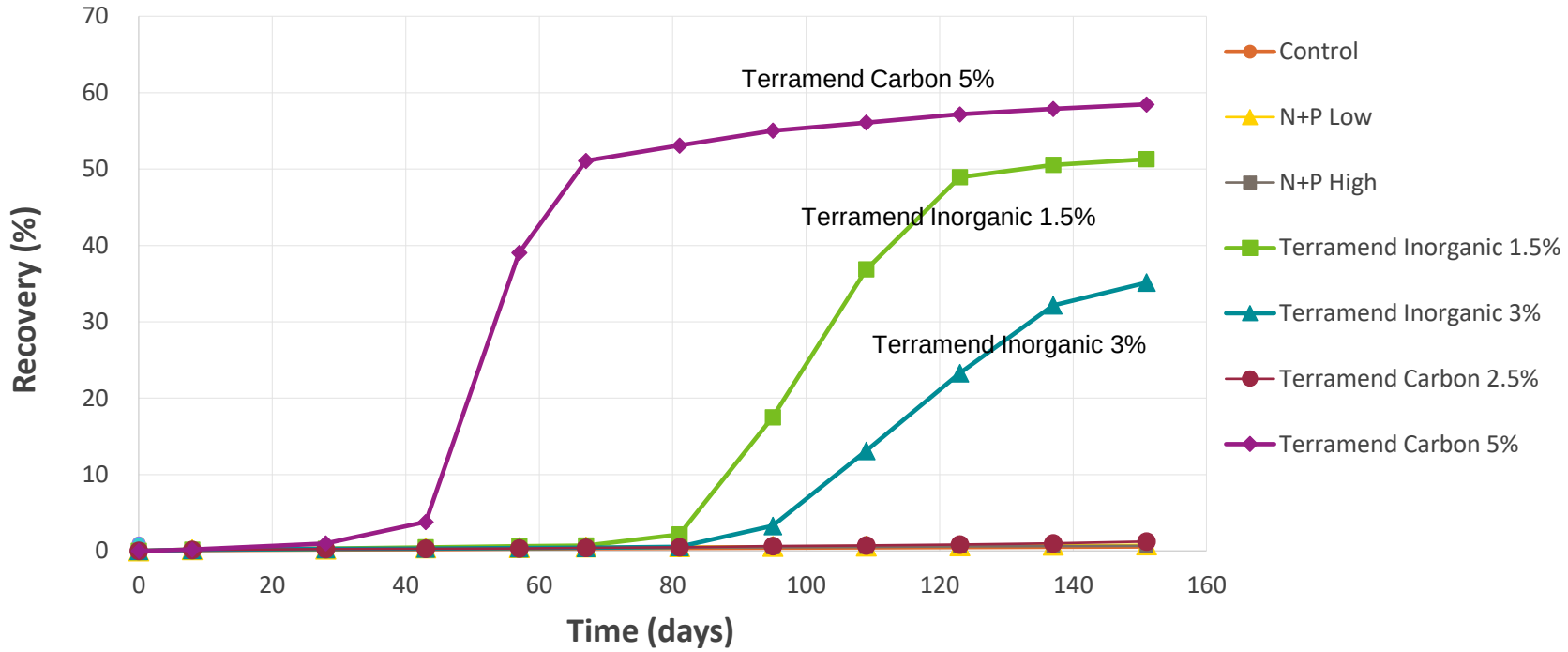
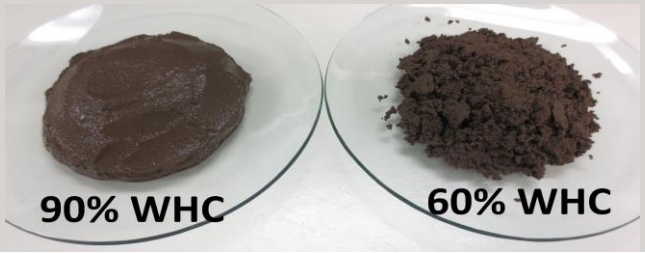
Bench-scale Treatability Testing for PCP in Soil

Mineralization of ^{14}C-PCP to ^{14}C-CO_2





- Documents complete biodegradation of PCP
- Compares performance of reagents & dosages
- Supported by traditional extraction & GC analysis



- Terramend® Carbon at 5% w/w performed best
- Order of performance same as increase in soil WHC
- Hydrophobic soil with acutely toxic COI
- Poor response to both N+P nutrient treatments

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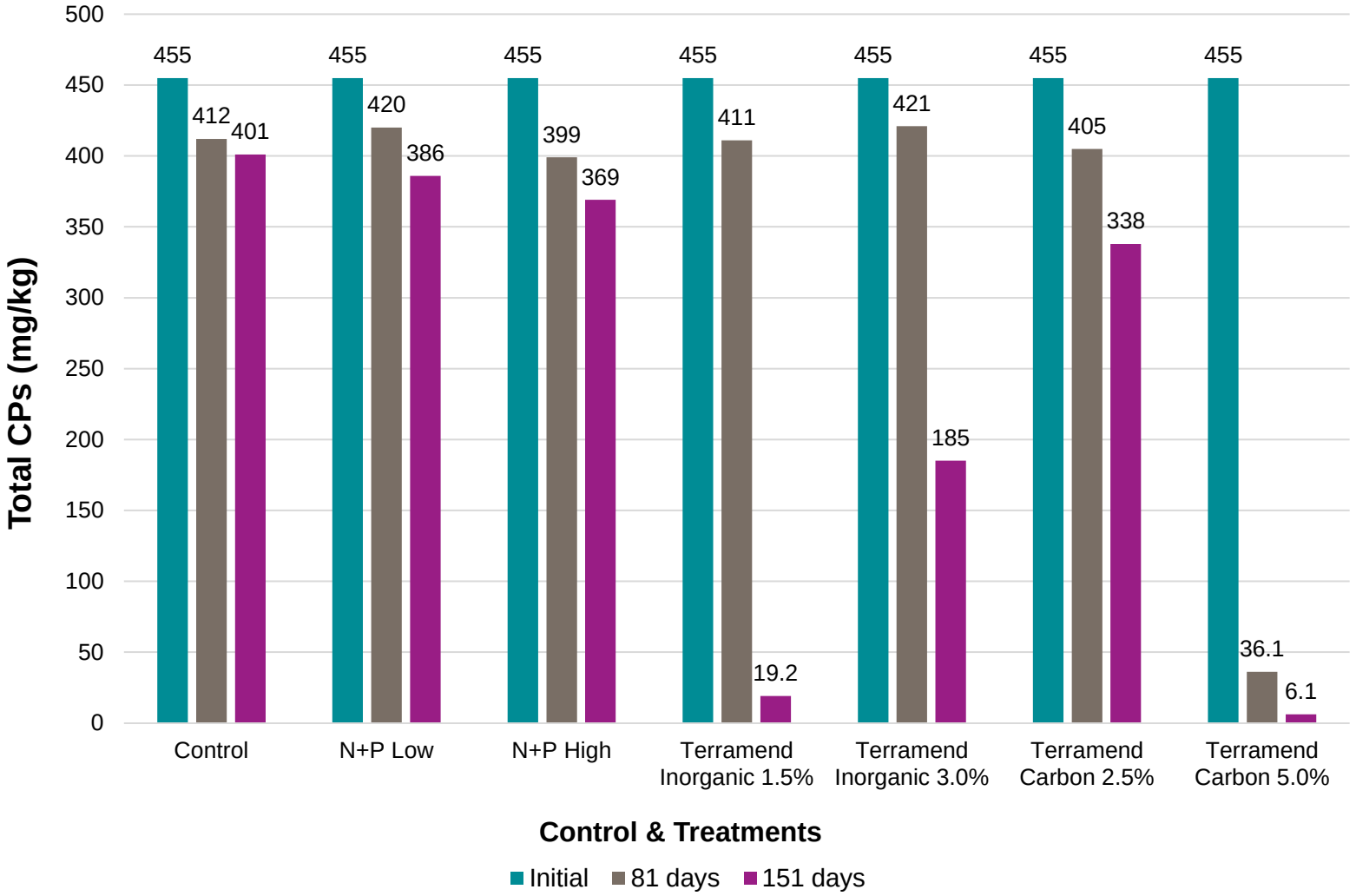
Bench-scale Treatability Testing for PCP in Soil
Total Extractable Chlorinated Phenols



- ✓ Very good agreement between mineralization of ^{14}C-PCP and reduction in total extractable CPs
- ✓ Treatments that supported greatest conversion of radiolabeled PCP to CO_2 also achieved lowest residual CP concentrations
- ✓ Higher dose of slowly-released Terramend Carbon provided large increase in soil WHC without turning soil anaerobic
- ✓ More rapidly-released Terramend Inorganic at the higher dose may have resulted in less oxic conditions in this soil
- ✓ Inorganic N+P was ineffective regardless of dosage

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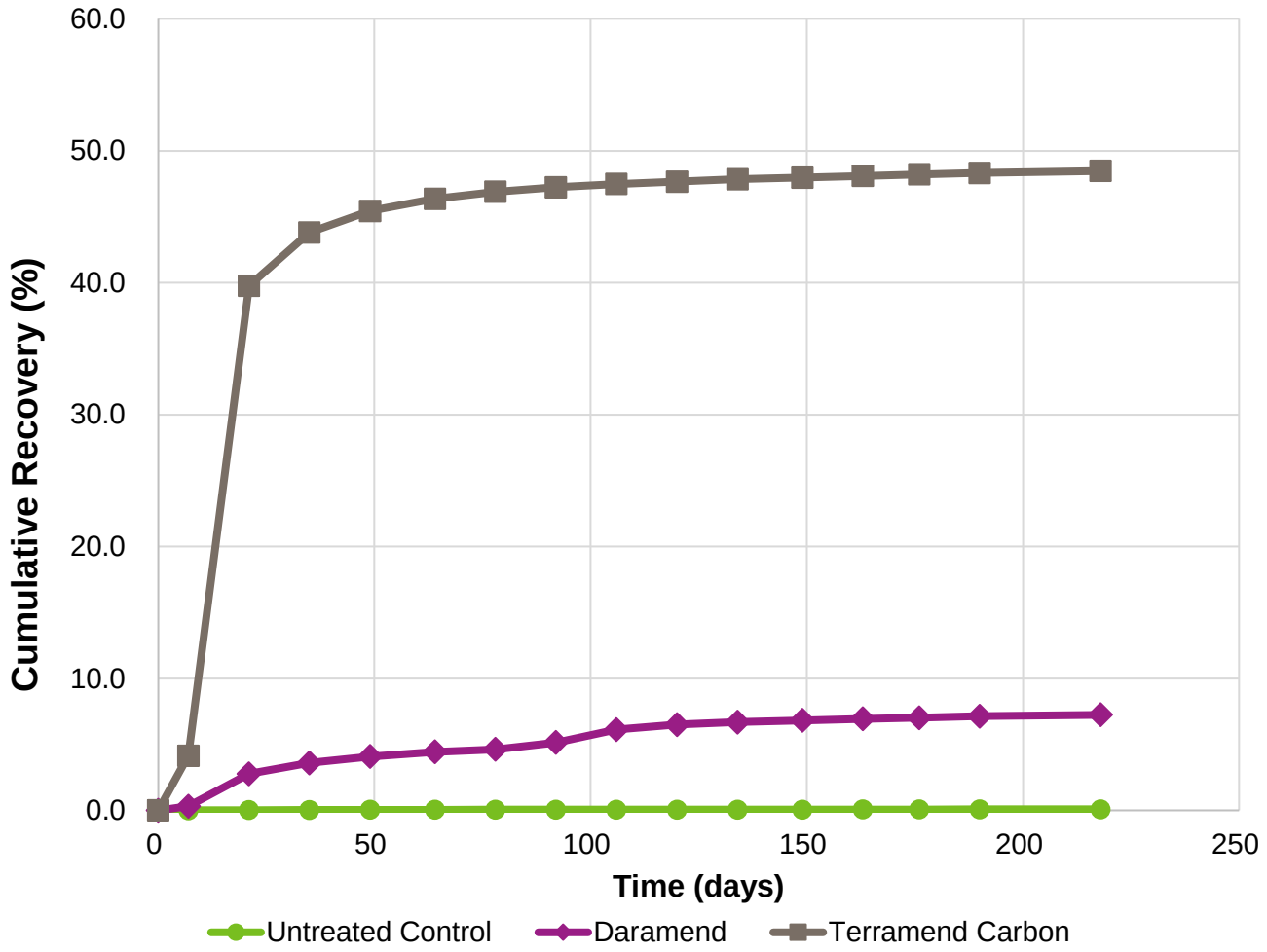
Bench-scale Treatability Testing for Lindane in Soil

Mineralization of ^{14}C-Lindane to ^{14}C-CO_2



Radioisotope Fate Study

- Industrial soil from Lindane manufacturing site
- Tracked conversion of ^{14}C-γ-hexachlorocyclohexane (Lindane) to ^{14}C-CO_2 in glass microcosms
- Compared untreated control to soil amended with Terramend® Carbon (3.0%) or Daramend® (4.0%)
- Literature says half life of Lindane should be shorter under anaerobic conditions
- Our results differed as we found more rapid and more substantial biodegradation of Lindane under optimized aerobic conditions than under highly reduced anaerobic conditions (ORP = -450 mV)

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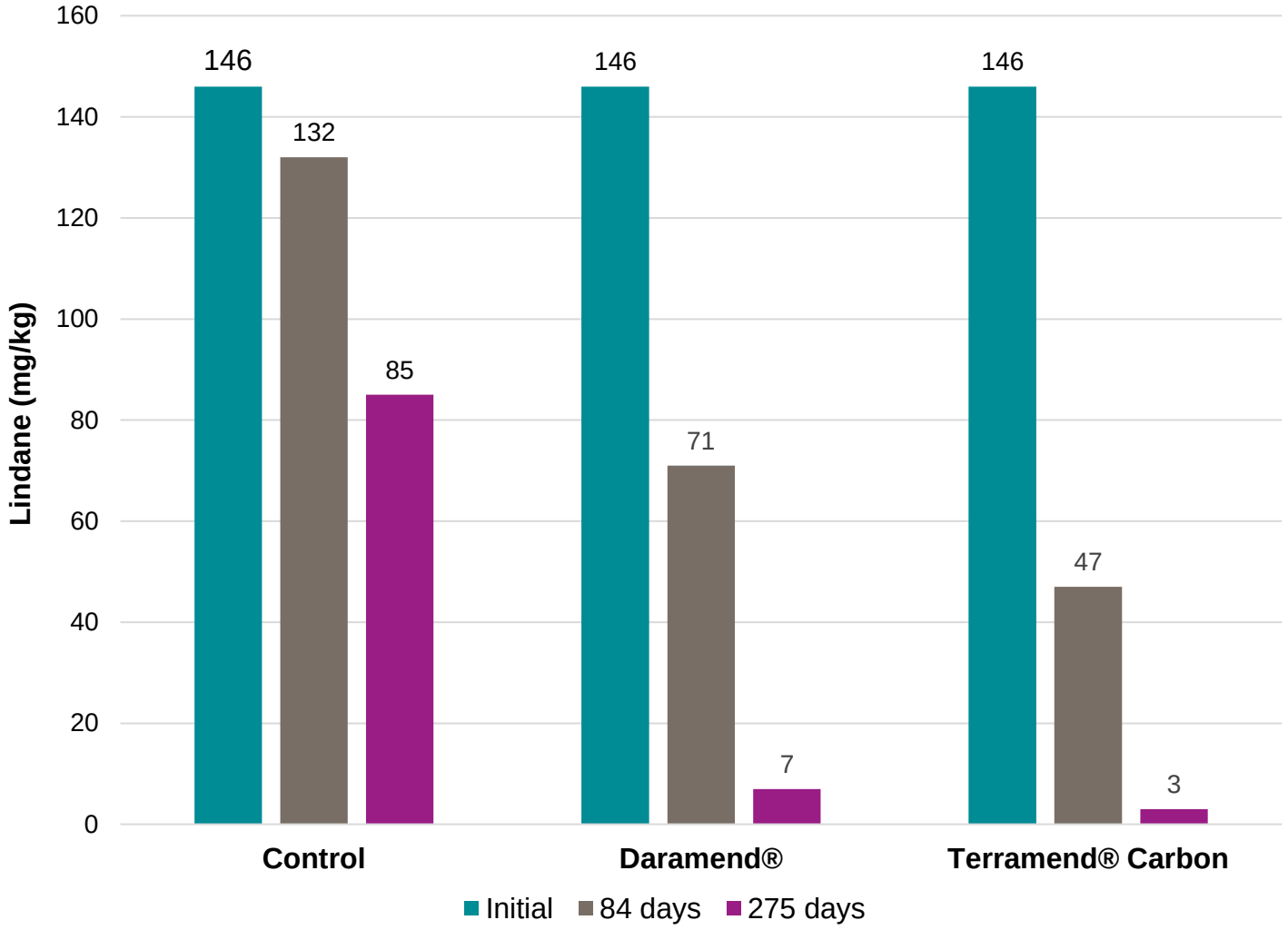
Bench-scale Treatability Testing for Lindane in Soil
Total Extractable Lindane



- Total extractable Lindane by EPA 3540 and 8081B
- Total extractable Lindane was in good agreement with results from mineralization of added ^{14}C-Lindane to CO_2
- Both reductive dechlorination (Daramend®) and aerobic bioremediation (Terramend® Carbon) were effective in degradation of Lindane in this soil
- Isolates of *Sphingomonas japonicum* and several other bacteria have been shown to use Lindane as sole source of carbon and energy through aerobic dechlorination and hydroxylation and ring cleavage
- Extracellular enzymes produced by soil fungi have also been shown to degrade Lindane

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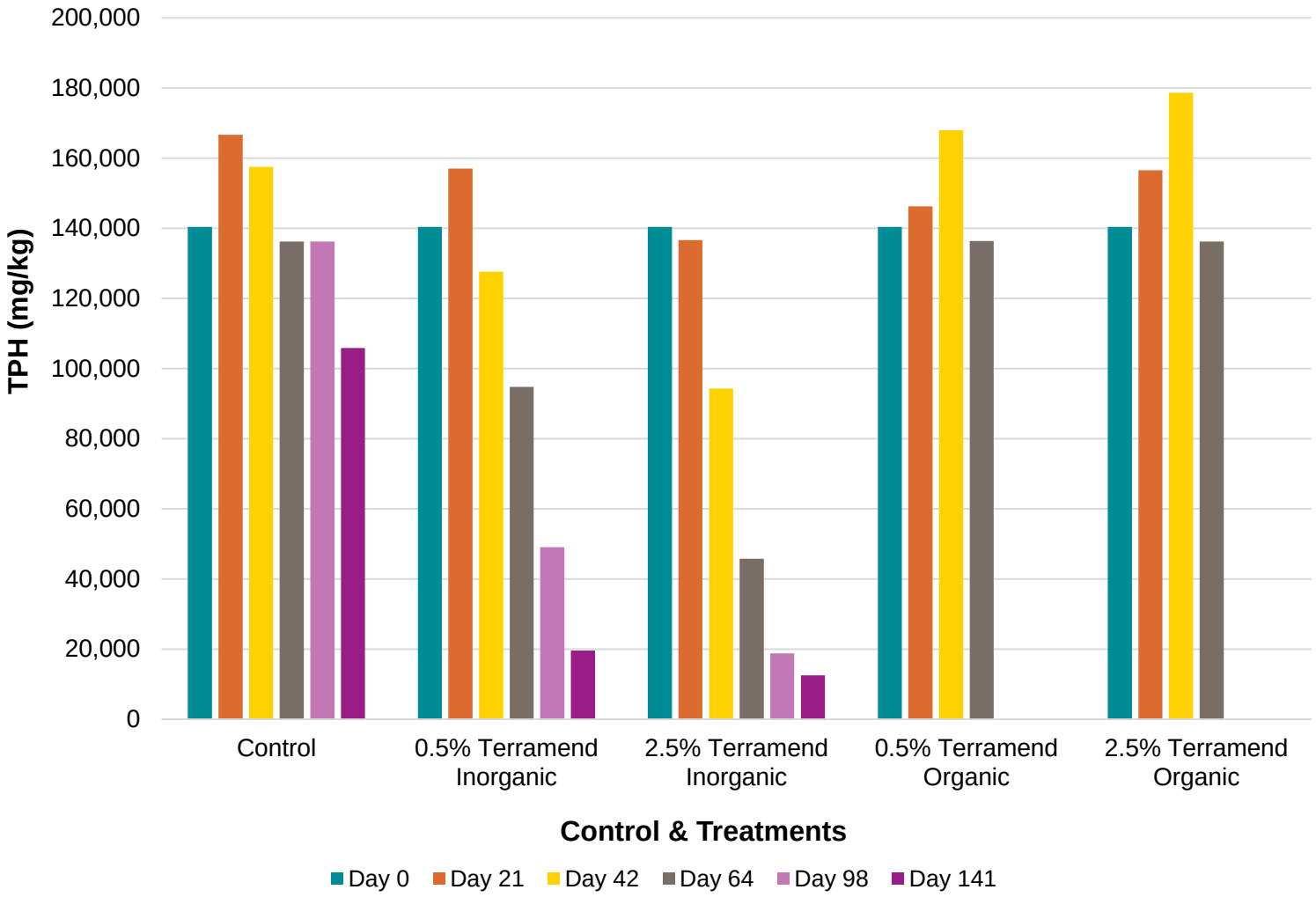
Bench-scale Treatability Testing

Terramend® Treatment of Stabilized Drill Cuttings



- Very high TPH drill cuttings from oil extraction
- Initial treatment was stabilization with wood much followed by aerobic tillage; however, this approach did not achieve the desired degree of TPH reduction
- The as-received drill cuttings (already treated with wood mulch at 10% w/w) were subjected to 141 days of Terramend treatment at RT with weekly aeration by mixing
- Sharp difference in response to Terramend Inorganic vs Terramend Carbon.
- Most effective treatment was the higher dosage of Terramend Inorganic
- TPH was reduced by 91% in response to this treatment

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Project Snapshots

1. Terramend® Inorganic Treatment of Aged Hydraulic Oil and Diesel Fuel
2. Terramend® Carbon Treatment of Bis(2-ethylhexyl) Phthalate
3. Terramend® Carbon Treatment of PAHs, PCP, and Mineral Oil TPH
4. Terramend® Carbon Treatment of MGP PAHs
5. In Situ Daramend® Treatment of Chlorinated Pesticides

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Project Snapshot 1

Terramend® Inorganic

Ex Situ Treatment of Hydraulic Oil & Diesel Fuel

- Midwest Industrial site
- Former agricultural equipment repair facility
- Approximately 4,400 tons of soil treated on-site

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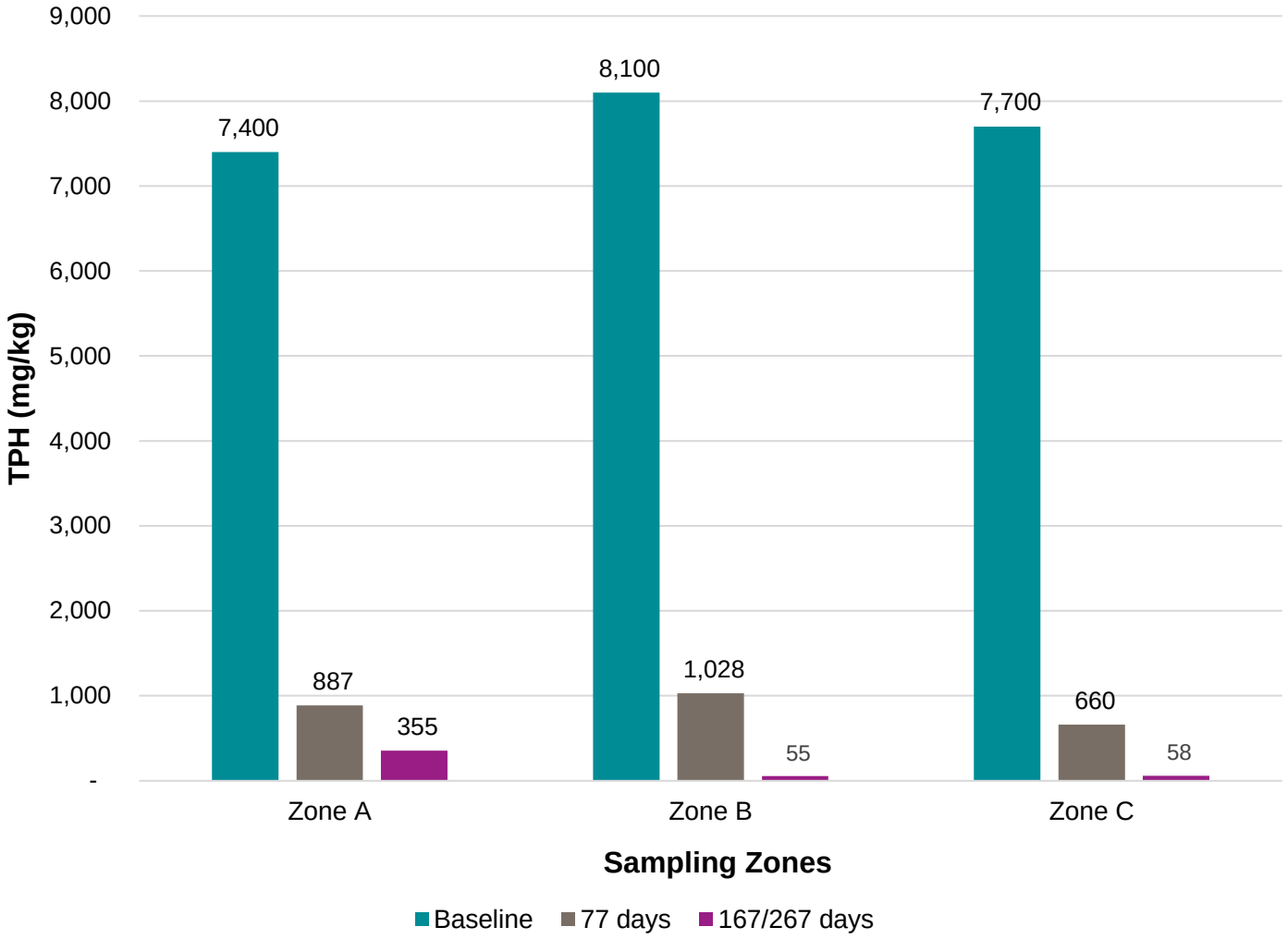
Bioremediation of Hydraulic Oil + Diesel Fuel Contaminated Soil with Terramend® Inorganic Reagent



On-Site Treatment of Industrial Soil

- 4,400 tons treated in HDPE lined biocell with soil in a layer of 24” (60 cm) thickness
- Hydraulic oil and diesel fuel (C_{16} – C_{35})
- Calcareous sandy loam, neutral pH, low organic matter
- Terramend® Inorganic dosage of 3.0% w/w in split application (2.0% at start and 1.0% on day 90)
- Soil water content maintained near 60% WHC
- Aeration by tillage twice weekly for the first month, with tillage reduced to weekly thereafter
- Each data point represents the mean of 5 composite samples with each composite created by blending 10 grab samples from full depth of treatment

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Project Snapshot 2

Terramend® Carbon
On-Site Treatment of Phthalates
in Excavated Soil

- Industrial site in eastern New Jersey
- Former chemical industry facility
- Approximately 600 tons of soil treated on-site
- Two 300-ton batches in biocell

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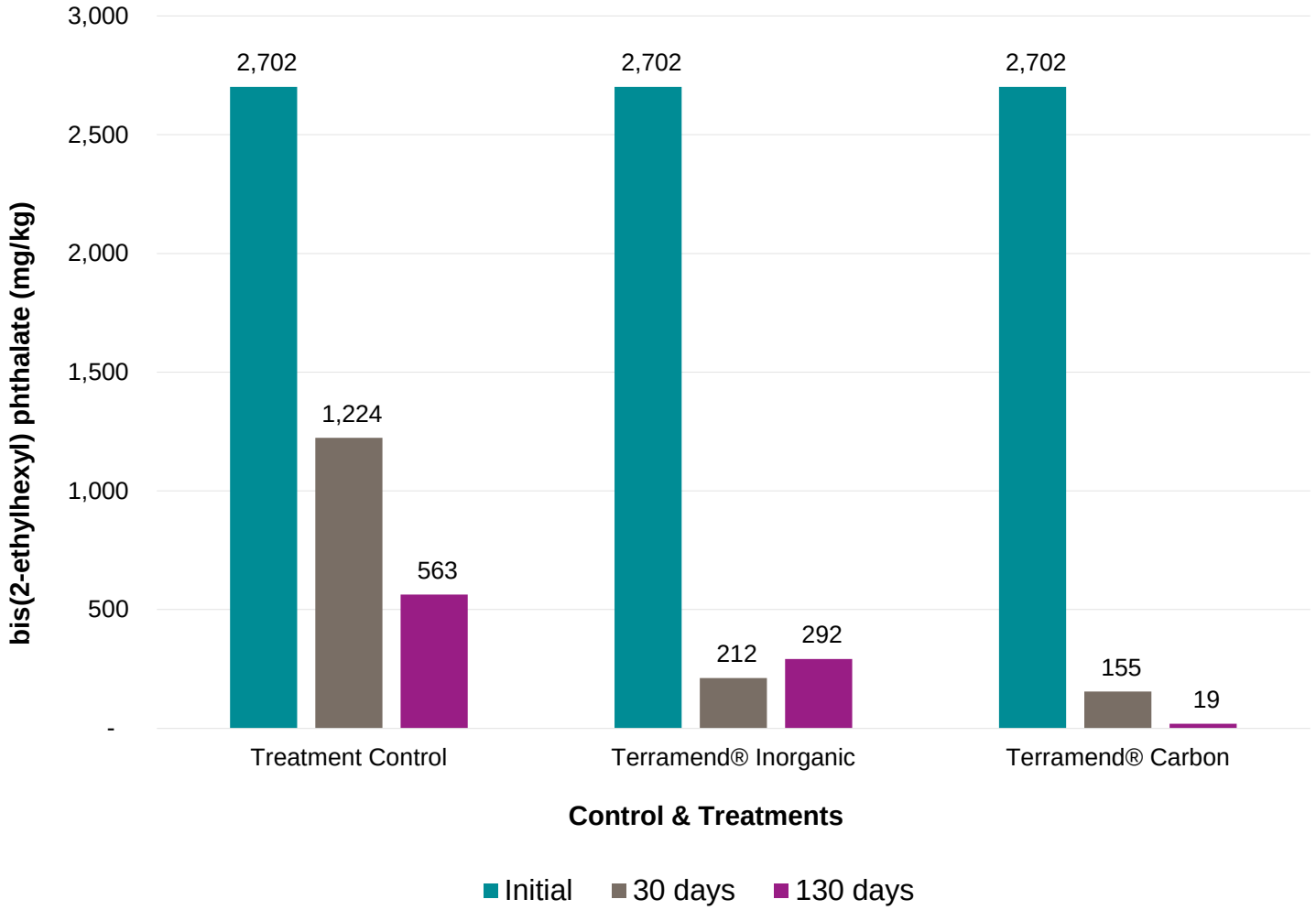
Bench-scale Treatability Testing Results

Bis(2-ethylhexyl) phthalate in New Jersey Chemical Industry Soil



Interpretation of Results

- Low solubility of phthalate makes it relatively slow to degrade
- Terramend® Inorganic at 2.0% w/w and Terramend® Carbon at 3.0% w/w.
- Longer lasting reagent (Terramend® Carbon) was better suited
- High native organic matter and fine-grained texture made it more difficult to maintain aerobic conditions in soil treated with Terramend® Inorganic
- Possible that native bacteria produced more biosurfactant under lower nutrient status in soil with Terramend® Carbon
- Visible fungal growth on soil with Terramend® Carbon

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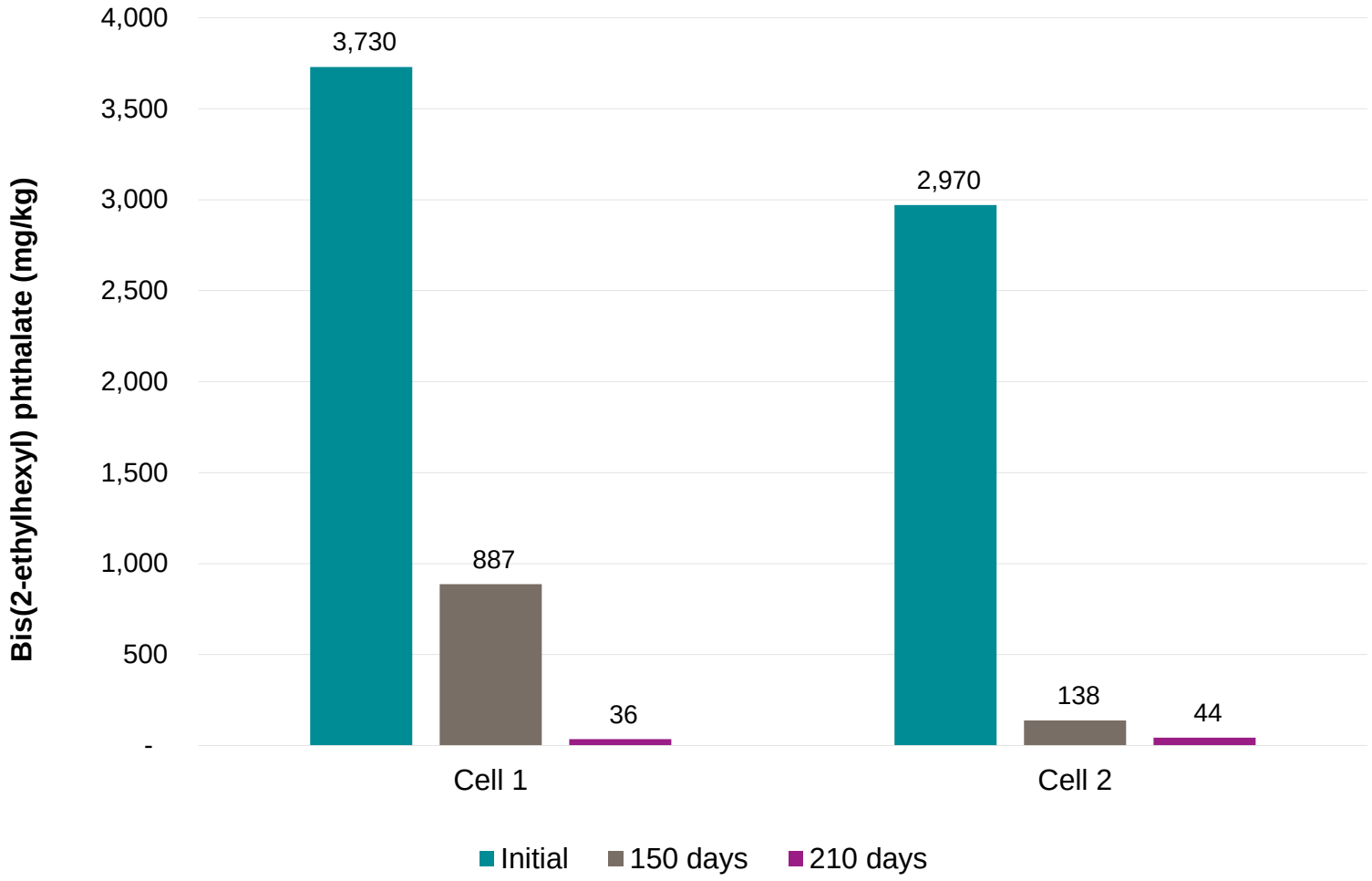
Terramend® Inorganic Treatment of Bis(2-ethylhexyl) Phthalate

Ex situ On-Site Treatment in New Jersey



- Ex situ soil treatment on-site in New Jersey
- Terramend formulation and dosage established during bench-scale treatability testing
- Soil moisture set to 60% WHC by spray irrigation system
- Reagent dosage of 3.0% w/w for both
- Slowly released carbon and nutrients was proven more effective
- Visible fungal growth on soil treated with Terramend® Carbon

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Project Snapshot 3

Terramend® Carbon

Ex Situ Treatment of PAHs, PCP, and Petroleum Hydrocarbons

- Industrial Wood Preserving Site
- On-site treatment of excavated soil in HDPE-lined cell
- 1,200 tons/year in batch system

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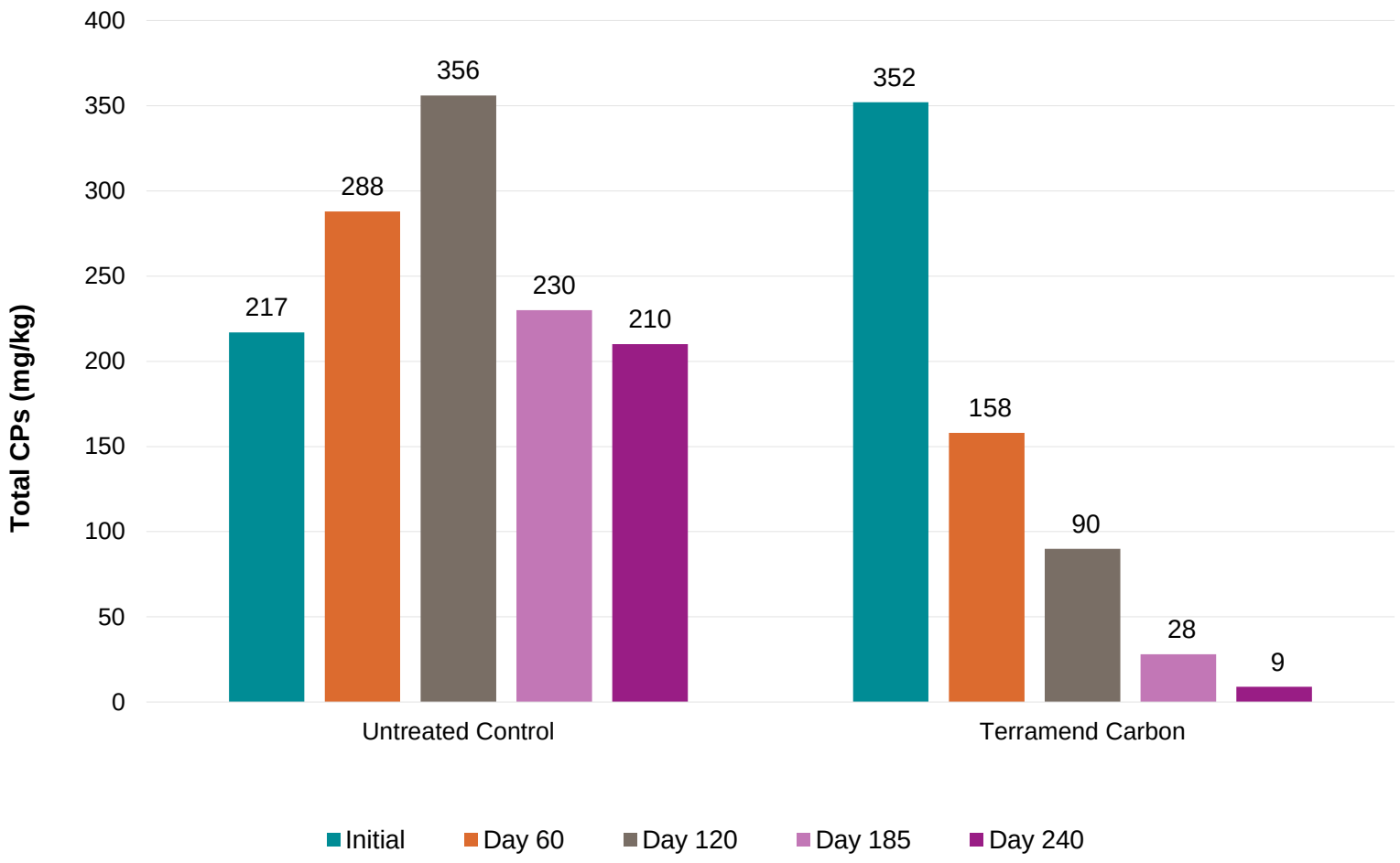
Ex Situ Bioremediation of Wood Treatment Soil with Terramend® Carbon



- Industrial wood preserving site in operation since 1950
- Pressure treatment using creosote and PCP in mineral oil
- Batch treatment of 1,200 tons/year over three years
- Excavated soil in HDPE-linde bioremediation cell
- Covered to extend treatment season in cool climate area
- First batch included monitoring of untreated control soil simultaneous with Terramend Carbon treated soil
- Also treated 4,800 tons of lightly impacted soil in situ (0 – 24” bgs)

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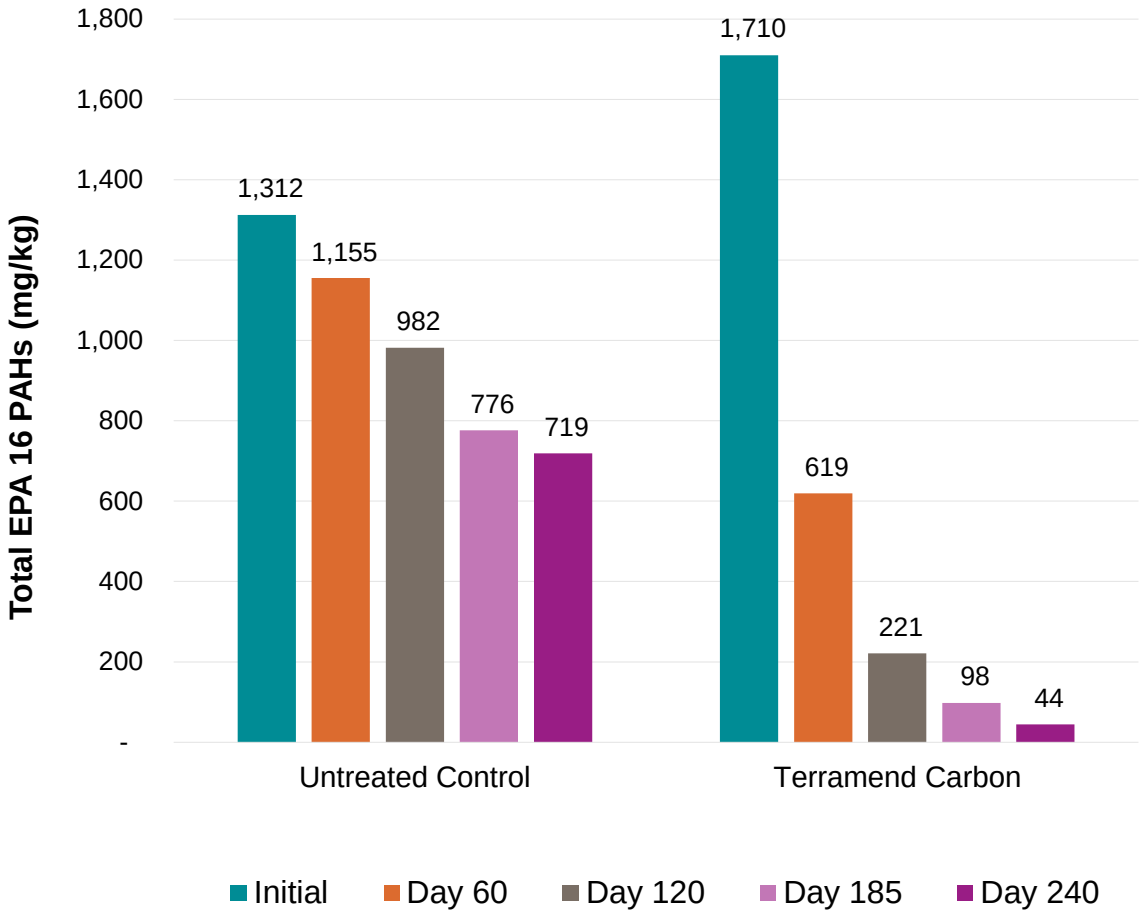
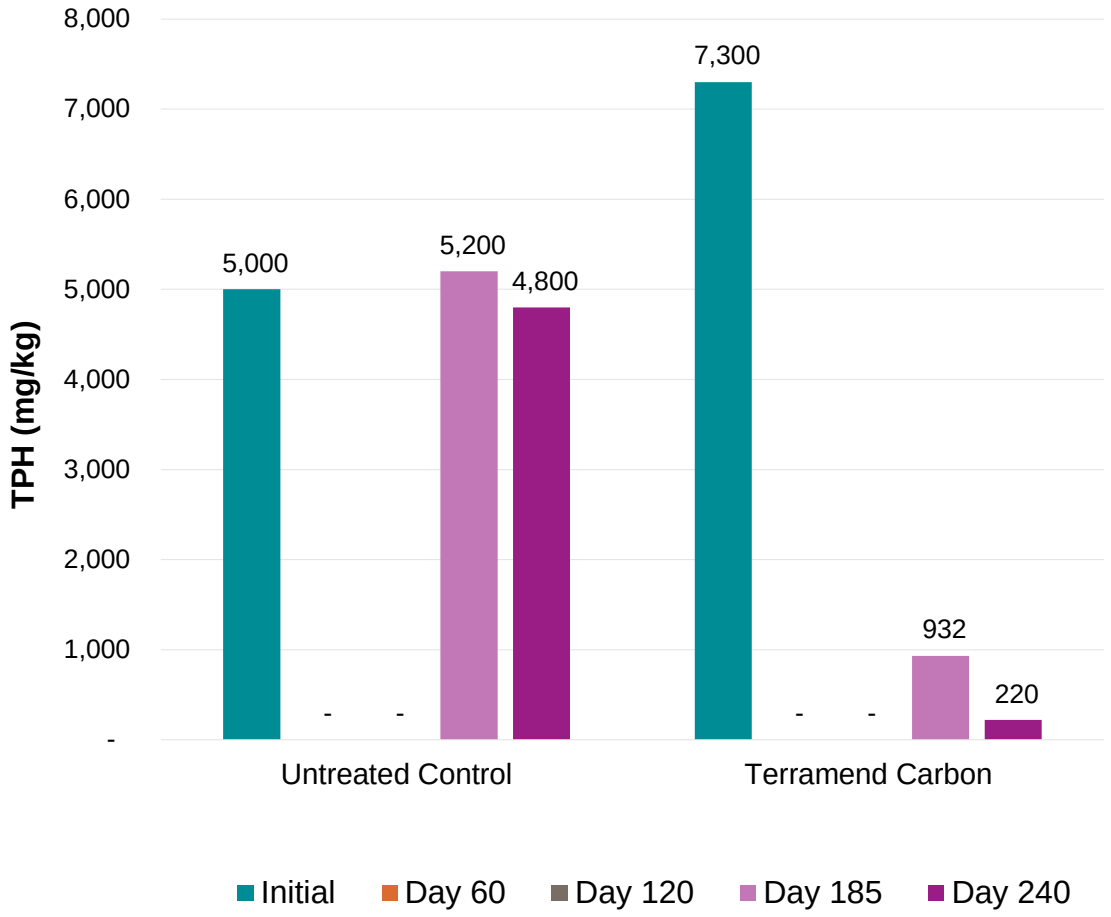
Treatment of PAHs and Petroleum Hydrocarbons





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Project Snapshot 4

Terramend® Carbon

Ex Situ Treatment of PAHs at MGP Site

- Pacific Northwest Manufactured Gas Plant Site
- On-site treatment of excavated soil in biocell

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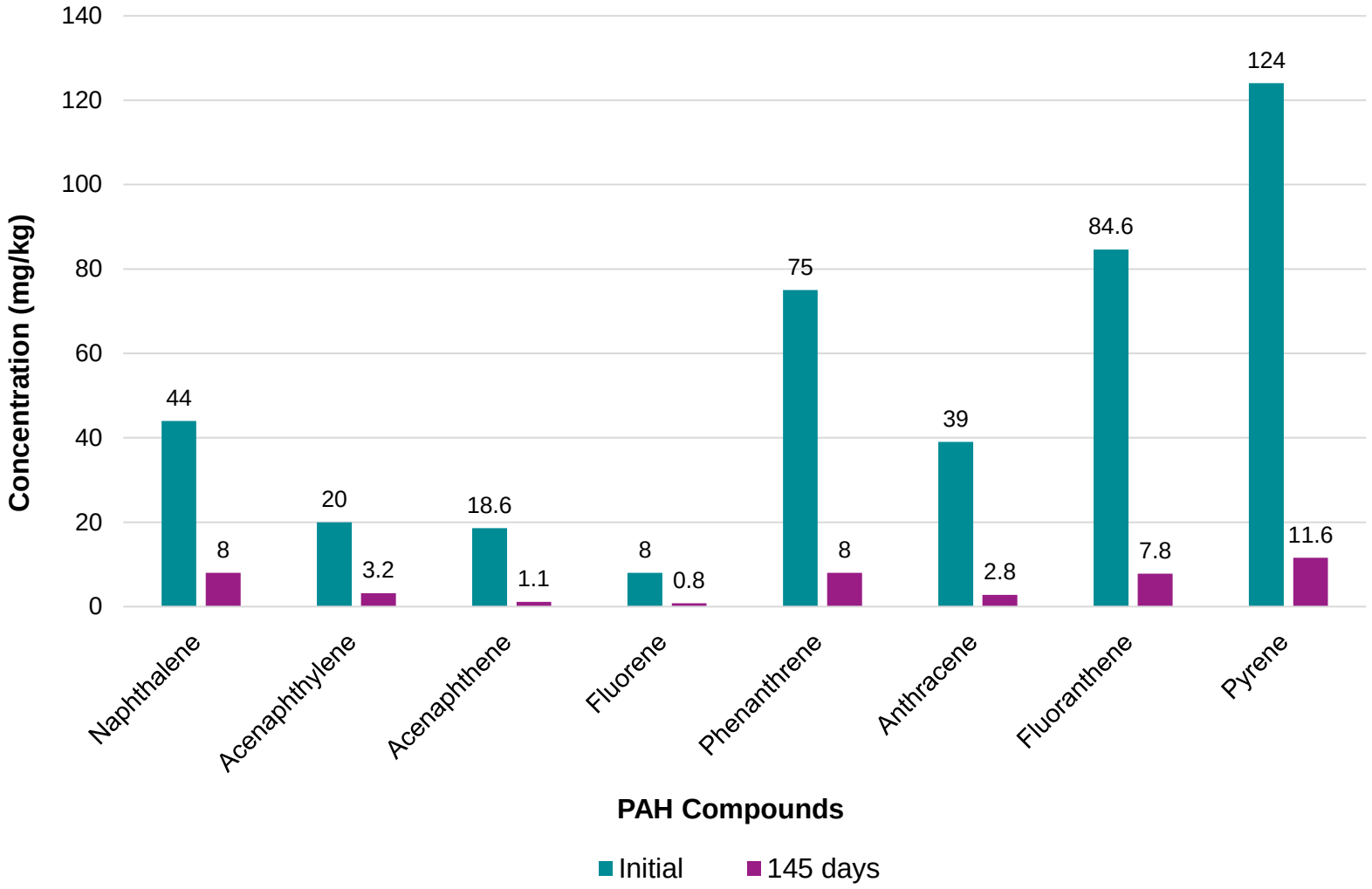
Ex situ Terramend® Treatment of PAHs
Pacific Northwest MGP Site



Lower MW PAH Compounds

- Pacific Northwest MGP Site
- Excavated soil in HDPE-lined Biocell
- Terramend Carbon application at 4.0% w/w
- Weekly tillage for aeration
- Removal efficiencies of 90% or more for most of the lower molecular weight PAHs

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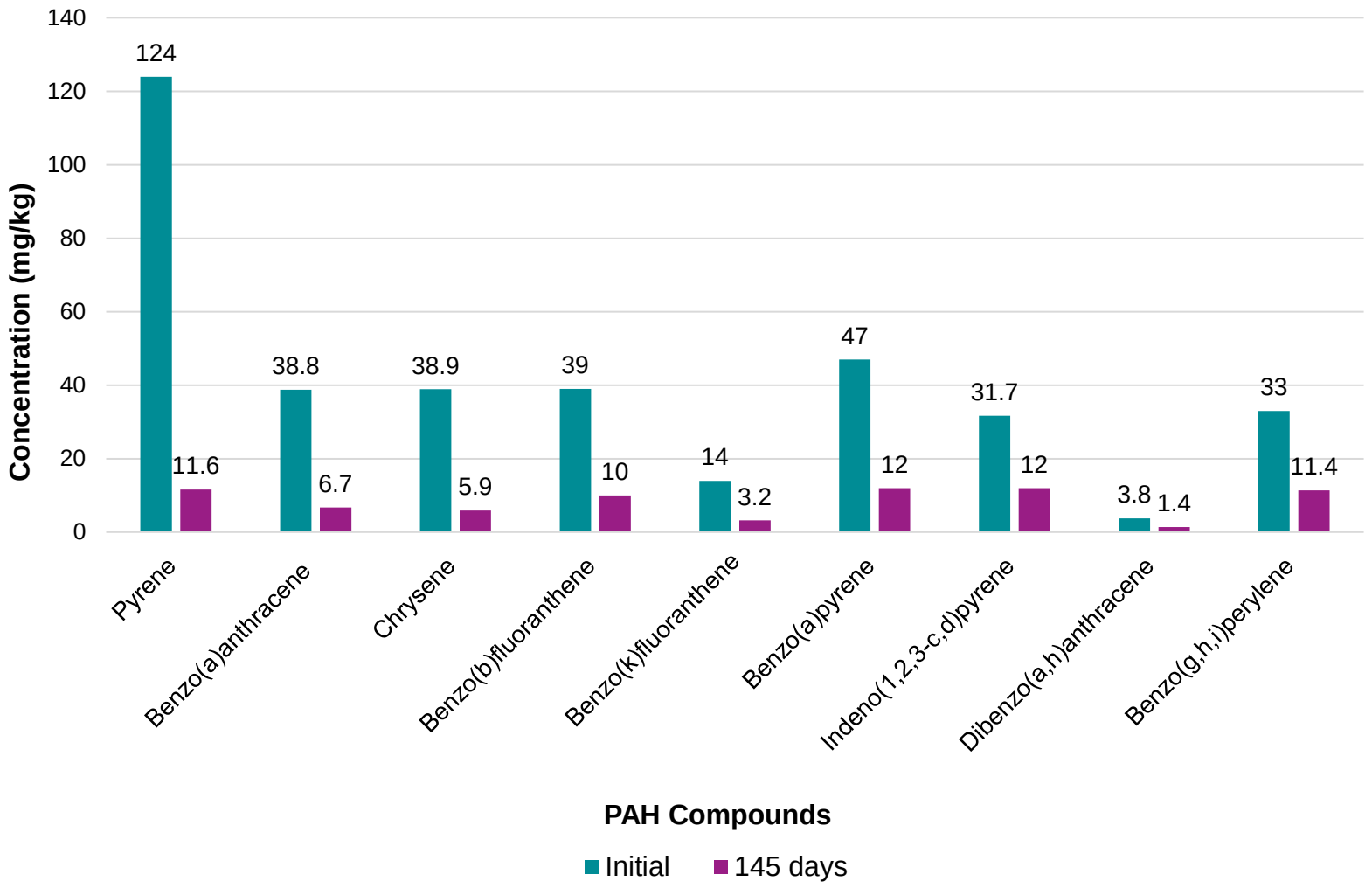
Ex situ Terramend® Treatment of PAHs

Pacific Northwest MGP Site



Higher MW PAH Compounds

- Good treatment efficiency on even high molecular weight PAHs
- Lower removal efficiencies than for the lower MW (more soluble) PAHs
- Removal efficiencies between 60% and 85% for most of the higher MW PAHs
- Somewhat lower removal efficiency than for creosote soils
- Possibly related to acute soil toxicity?

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Project Snapshot 5

Daramend®

In Situ Treatment of Chlorinated Pesticides

- 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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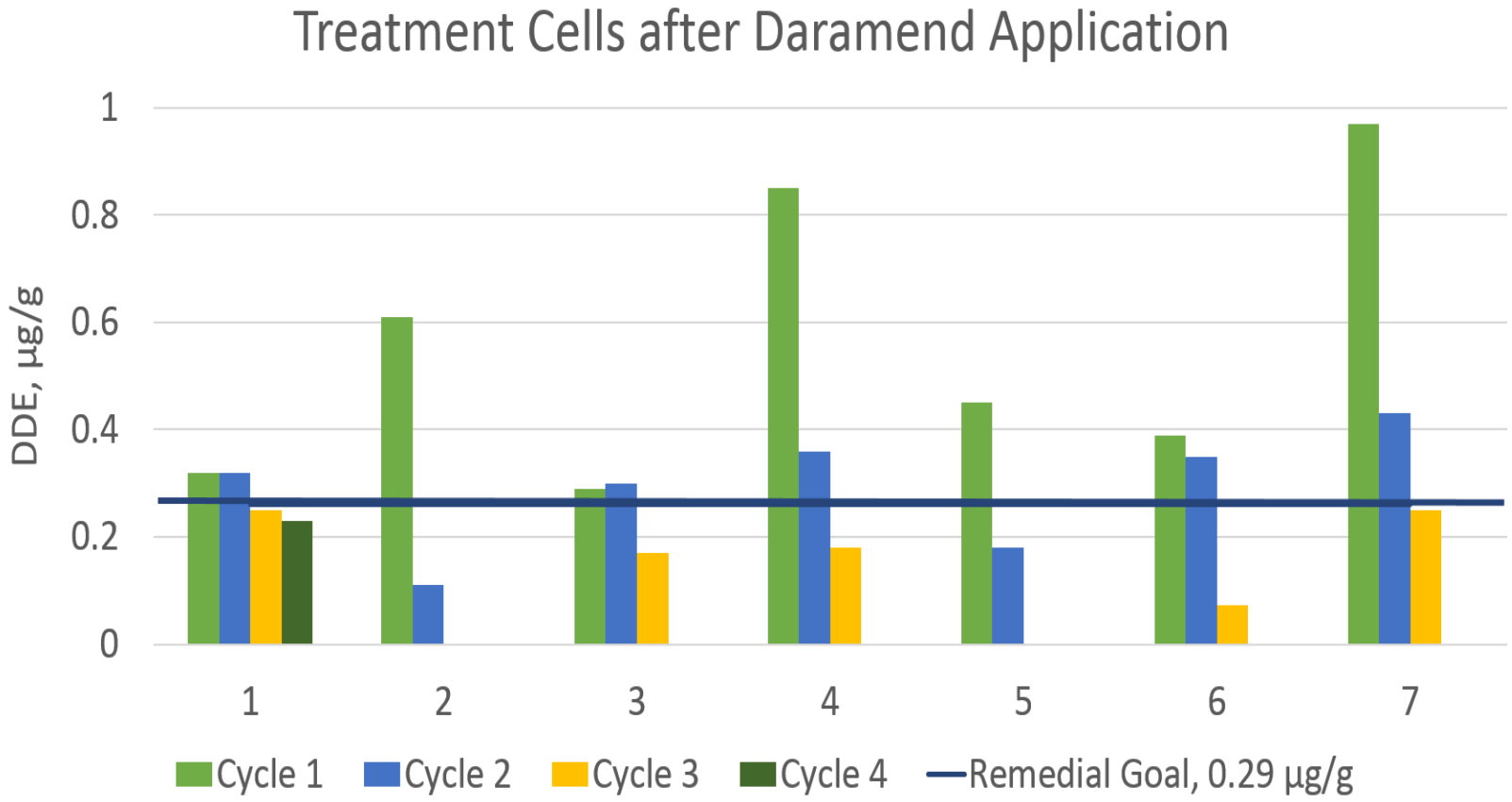
In Situ Treatment of DDE at Former Agricultural Site

Remediation for Residential Development



Achievement of Residential Land Use Criteria

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

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Terramend® Reagents Summary

- ✓ Proven performance on PAHs, chlorinated phenols, phthalates, bunker oil, diesel fuel, and Lindane
- ✓ Excellent performance in simultaneous removal of PCP + PAHs + Petroleum Hydrocarbons for wood treatment sites
- ✓ Supported by experienced staff including bench-scale treatability and optimization capability
- ✓ Sustainable and economical alternative to off site disposal for many soils, sediments, and even many industrial process wastes
- ✓ Excellent 25-year worldwide track record in many field-scale applications

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Available Terramend® Case Studies

- ✓ PAHs
- ✓ PCP
- ✓ Bunker Oil
- ✓ Diesel Fuel
- ✓ Phthalates
- ✓ Lindane
- ✓ Wood Preserving Sites
- ✓ MGP sites
- ✓ Lindane

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Questions are Welcome!

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