Enhanced Bioremediation of Soil Contaminated with Pentachlorophenol

Alan G. Seech, Ph.D.
Senior Manager of Technology Applications
Soil & Groundwater Remediation
Evonik Corporation

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Agenda

- 1. Pentachlorophenol
- 2. Perspective on Aerobic Bioremediation of Soil
- 3. Terramend® Reagents
 - ✓ Composition of Terramend® Carbon & Terramend® Inorganic reagents
 - √ Microbiology & Biochemistry during soil treatment
- 4. Bench-scale treatability approach and results
- 5. Project Snapshots (two short case studies)
- 6. Questions & Answers



Physical, Chemical, & Toxicological Properties of Pentachlorophenol

Parameter	PCP	Notes
CAS No.	87-86-5	-
Chemical Formula	C ₆ HCl ₅ O	-
Molecular Weight (g/mol)	266.3	-
Vapor Pressure (mm Hg, 25°C)	0.0001	Naphthalene = 0.087 TCE = 69
Water Solubility (mg/L at 20°C)	20	Naphthalene = 32 TCE = 1,280
pK _a (25°C)	4.7	n/a
Octanol/Water K _p (25°C)	3.25	Naphthalene = 3.29 TCE = 2.61
LD ₅₀ (rat, mg/Kg)	27	Naphthalene = 490 TCE = 7,208
LC ₅₀ (trout, µg/L)	44	Naphthalene = 110 TCE = 2,000







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.
- Nutrients are 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 sometimes 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, PAHs, high MW TPH).
- We use a different approach that is based on supplying organic nutrients, increasing bioavailable water, and overcoming acute microbial toxicity with our Terramend® family of organic soil amendments.



Terramend® Carbon, Terramend® Inorganic Reagents

Attribute	Terramend [®] Carbon	Terramend® Inorganic
High Surface Area Hydrophilic Plant Fiber	✓	✓
Slow-release Organic Carbon	✓	✓
Slow-release Organic Nitrogen and Phosphorus	✓	✓
Inorganic Nitrogen & Phosphorus	-	✓
Emulsifying Agent	✓	✓
pH Buffer	\checkmark	-



Influence of Terramend® Dosage on Soil Water Holding Capacity and pH

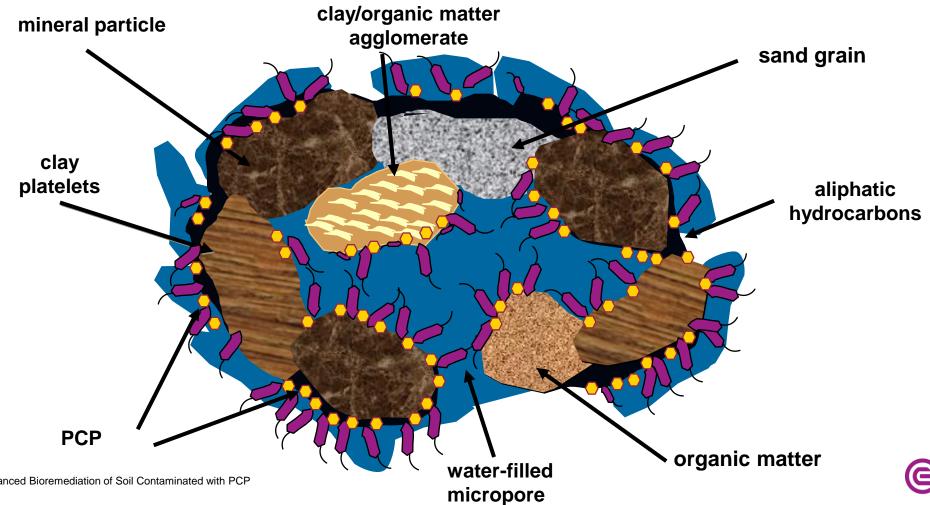
Sandy loam soil (Industrial Wood Preserving Site)

Treatment	Dosage (% w/w)	WHC (% w/w)	pH (14 days)
Control		16.6	6.6
Terramend® Carbon	0.5	18.4	6.8
Terramend® Carbon	1.0	20.7	6.9
Terramend® Carbon	2.0	24.1	7.0
Terramend® Carbon	4.0	27.3	7.2
Terramend® Carbon	6.0	30.5	7.2

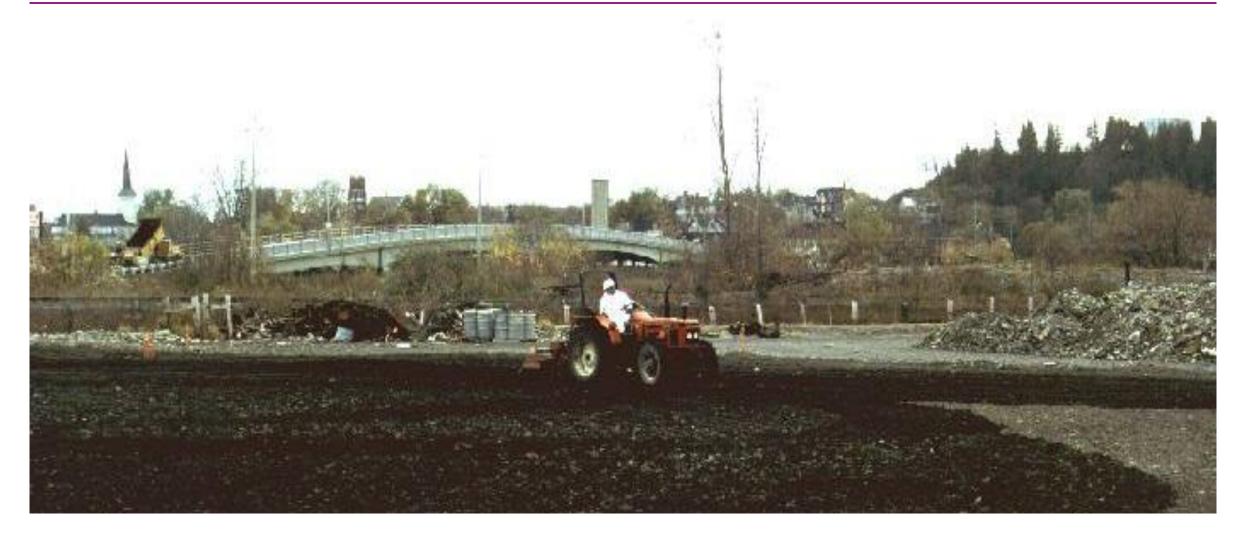


Terramend® Treatment Mechanism

Contention Desirable ed



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





Ex Situ Treatment of Chlorinated Phenols

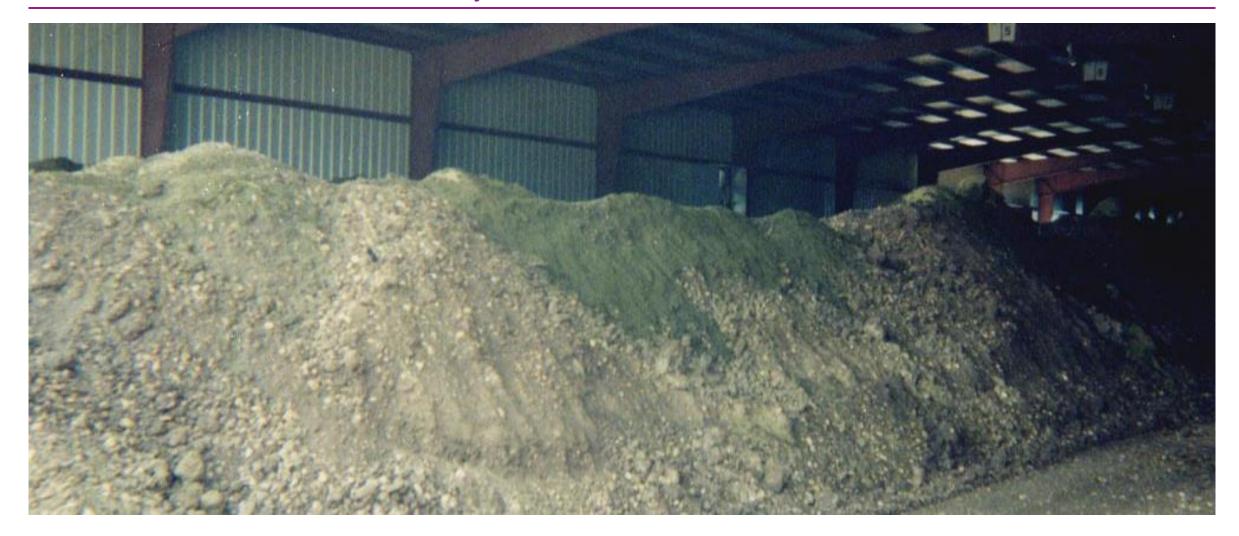
Chemical Manufacturing Site





Windrow Treatment of PAHs and TPH

Permitted Soil Treatment Facility





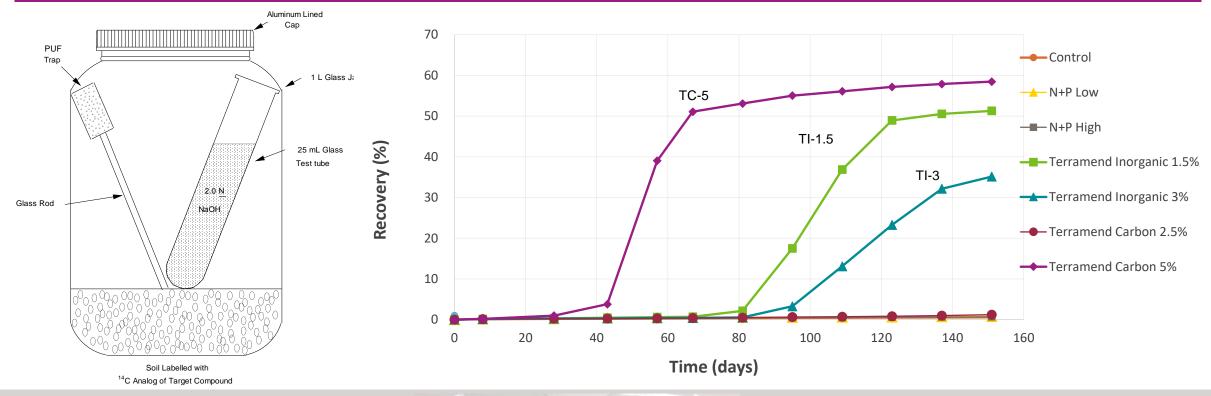
Bench-scale Treatability Testing

- ✓ Objectives
- ✓ Methodology
- ✓ Results for PCP

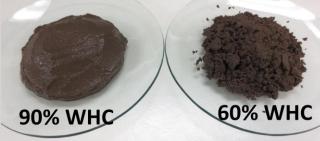


Bench-scale Treatability Testing for Soil Contaminated with PCP

Mineralization of ¹⁴C-PCP to ¹⁴C-CO₂



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

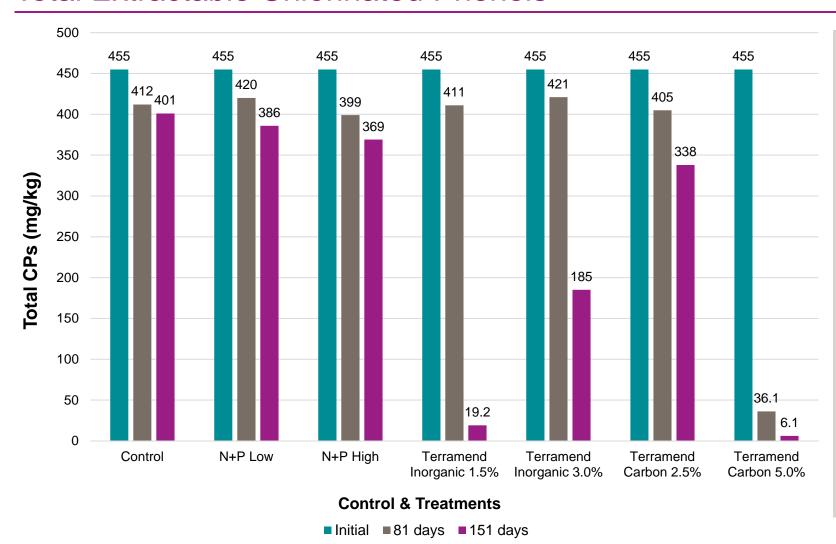


- Terramend® Carbon at 5% w/w performed best
- Best performance: high WHC + fully aerobic
- Hydrophobic soil with acutely toxic COI
- Poor response to both N+P nutrient treatments



Bench-scale Treatability Testing for PCP in Soil

Total Extractable Chlorinated Phenols



- ✓ Very good agreement between mineralization of ¹⁴C-PCP and reduction in total extractable CP
- ✓ Treatments that supported greatest conversion of radiolabeled PCP to CO₂ 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 resulted in some oxygen stress.
- Inorganic N+P was less effective regardless of dosage



Project Snapshots

- 1. Terramend® Carbon Treatment of PCP, PAHs, and TPH (mineral oil)
- 2. Terramend[®] Carbon Treatment of PCP



Project Snapshot 1

Terramend® Carbon

Ex Situ Treatment of PAHs, PCP, and TPH (mineral oil)

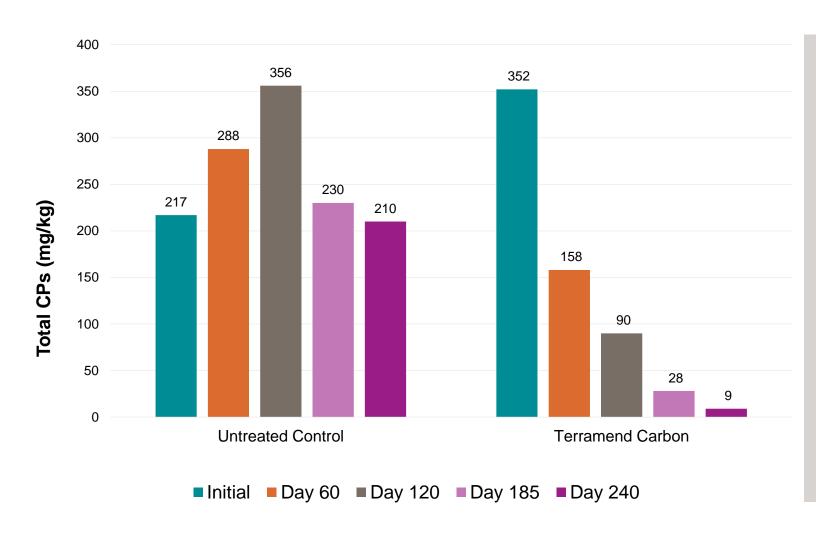


- Industrial Wood Preserving Site
- On-site treatment of excavated soil in HDPE-lined cell
- 1,200 tons/year in batch system
- Pressure treatment with PCP in mineral or as well as creosote





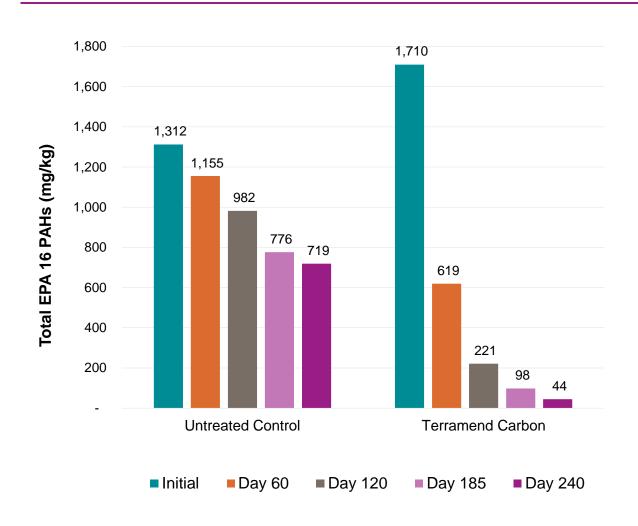
Ex Situ Bioremediation of Wood Treatment Soil with Terramend® Carbon

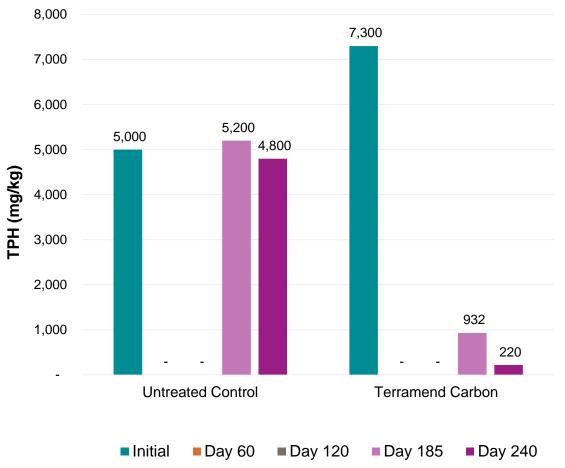


- Industrial wood preserving site
- Pressure treatment using creosote and PCP in mineral oil since 1950
- Batch treatment of 1,200 tons/year over three years
- Excavated soil in HDPE-lined bioremediation cell
- Covered to extend treatment season in cool climate area
- First batch included monitoring of untreated control soil simultaneous with Terramend Carbon treated soil
- Reagent cost between \$25 and \$55/ton of treated soil



Treatment of PAHs and Petroleum Hydrocarbons







Influence of Terramend® Treatment on Soil Toxicity

As Indicated by Earthworm Mortality

Soil Condition	Mean Mortality at 28 Days ¹ (<u>Eisinia fetida</u>)		
	Control (excavated soil)	Terramend [®] Treated	
As Received	100%	100%	
Post Treatment	100%	0%	

Notes:

1. Mean of three replicate microcosms with 12 earthworms per microcosm.



Project Snapshot 2

Terramend® Carbon Ex Situ Treatment of PCP at Chemical Industry Site



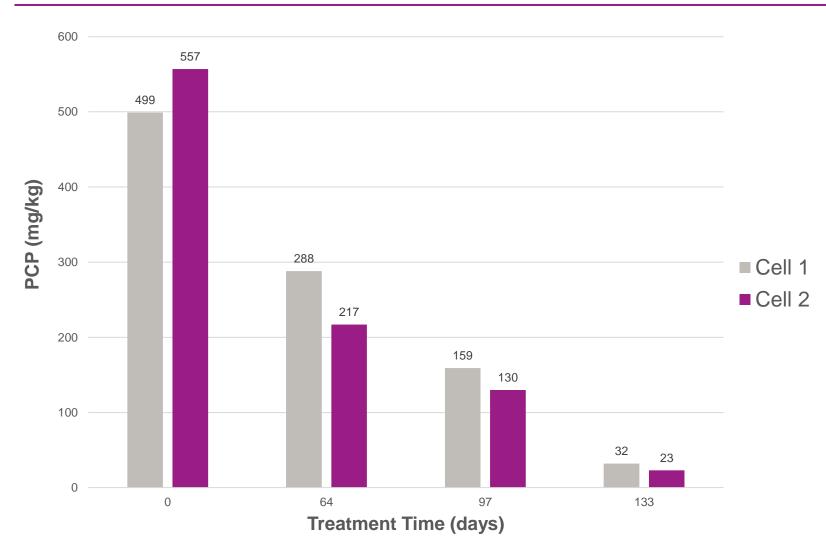




- On-site treatment of excavated soil in biocell
- Initial PCP concentrations up to 2,800 mg/kg
- Chlorinated phenols alone (i.e., without PAHs or TPH)



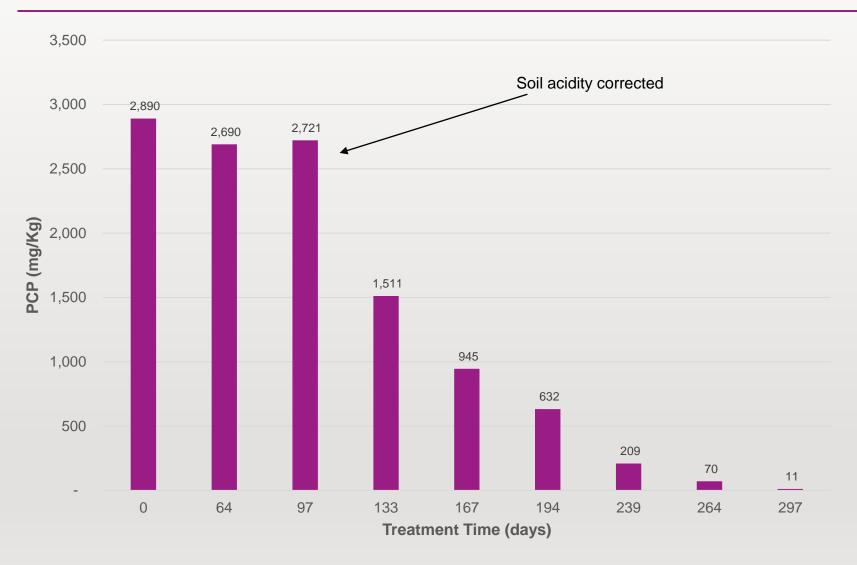
Ex Situ Bioremediation of Wood Treatment Soil with Terramend® Carbon



- Ex-situ treatment of 5,500 tons soil in double HDPE-lined biocell
- PCP Remedial Goal: 50 mg/kg
- Reagent dosage between 2.0% and 4.0% w/w
- Weekly tillage to maintain aerobic conditions
- Soil water content monitored and adjusted by spray irrigation
- pH monitored and adjusted if required using dolomite
- Lower CPs also removed
- Average reagent cost was \$39/ton of treated soil



Ex Situ Bioremediation of Wood Treatment Soil with Terramend® Carbon



- Hottest zone in this batch (200 tons)
- Soil pH dropped from 6.6 to 3.9
- pH adjusted with Ca(OH)₂ on day 108
- Treatment times presented exclude 150 days when soil temperature was below 10°C.
- Terramend® and Ca(OH)₂ cost for this zone was \$84/ton of treated soil
- Lesson Learned: don't trust that pH will be stable from batch to batch or zone to zone.



Summary and Lessons Learned

- ✓ PCP concentrations as high as 2,800 mg/kg can be treated without dilution of soil when soil is amended with Terramend® Carbon reagent.
- ✓ PCP + PAHs + Petroleum Hydrocarbons can be removed at the same time in soil at industrial wood treatment sites
- ✓ Soils with very high PCP concentration may be subject to acidification during aerobic bioremediation, possibly due to release of Cl and formation of HCl
- ✓ Properly managed aerobic bioremediation can provide a sustainable, economical alternative to off site disposal for soil contaminated with PCP, PAHs, and petroleum hydrocarbons.



Questions are Welcome!



Alan Seech, Ph.D.

Technology Applications Manager Evonik Active Oxygens

E. Alan.Seech@evonik.com T. +1 949-514-1068 3334 East Coast Highway, #114 Corona Del Mar, California 92625

Evonik Soil & Groundwater Remediation remediation@evonik.com www.evonik.com/remediation

