Environmental Solutions

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Effective Biotreatment of Soils Containing TNT, DNT, ANT, RDX, HMX, and Tetryl with Daramend® Reagent

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PeroxyChem is a company of Evonik Industries AG

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Presentation Outline

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- PeroxyChem Overview
- Daramend® and other PeroxyChem ISCR Reagents (composition, applicability)
- Basics of ISCR Chemistry and Biochemistry
- Reductive Degradation of Organic Explosive Compounds in Soil
- Daramend ® Performance Data: Bench-scale, Pilot-scale, Full-scale
- Soil Treatment Case Study
- Questions and Answers

Field-Proven Portfolio of Remediation Technologies Based on Sound Science

Chemical Oxidation

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

Chemical Reduction

- EHC ISCR Portfolio
  - EHC® Reagent
  - EHC® Liquid
  - EHC® Plus
- Daramend® Reagent
- Zero Valent Iron

Aerobic Bioremediation

- Terramend® Reagent
- PermeOx® Ultra
- PermeOx® Ultra Granular

Enhanced Reductive Dechlorination

- ELS® Microemulsion
- ELS® Liquid Concentrate
- ELS® Dry Concentrate

Metals Remediation

- MetaFix® Reagents

BioGeoChemical

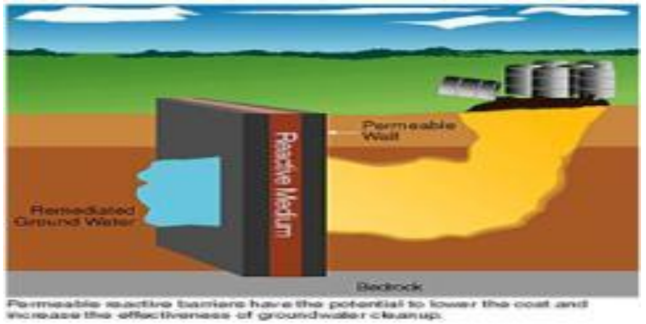
- GeoForm™ Reagents

PeroxyChem ISCR Reagents

Attribute	Daramend® Reagent	EHC® Reagent	EHC® Metals	EHC® Plus	GeoForm™ ER	GeoForm™ Soluble	MetaFix® Reagents
ORP	strongly reduced	strongly reduced	strongly reduced	strongly reduced	strongly reduced	reduced	reduced
Slow-release Carbon	✓	✓	✓	✓	✓	✓	-
Soluble Carbon	-	-	-	-	✓	✓	-
Nutrients	✓	✓	✓	✓	✓	✓	-
pH Buffer	-	-	-	-	✓	✓	✓
ZVI	✓	✓	✓	✓	✓	-	-
Ferrous Iron	-	-	-	-	✓	✓	-
Sulfate	-	-	✓	-	✓	✓	-
Iron Oxides	-	-	-	-	-	-	✓
Iron Sulfide	-	-	-	-	-	-	✓
Activated Carbon	-	-	-	✓	-	-	✓
Applicability	Pesticides, chlorinated solvents, organic explosives in soil and sediment	Pesticides, chlorinated solvents, organic explosives in groundwater	As for EHC and most heavy metals	As for EHC and provides adsorption mechanism	As for EHC Metals and formation of reactive minerals	Fully soluble "ISCR Light"	Metals

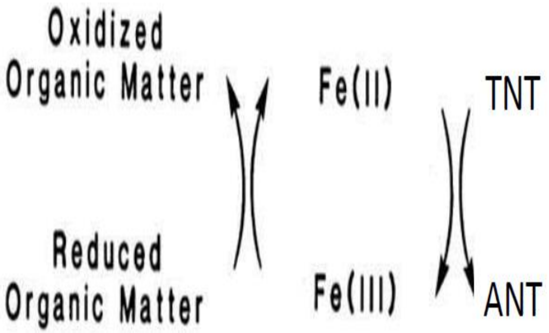
What is *In Situ* Chemical Reduction?

- Transfer of electrons from reduced metals (ZVI, ferrous iron) or reduced minerals (magnetite, pyrite, ferruginous clay) to contaminants including chlorinated organics, nitroaromatics, and certain heavy metals.
- Microbial processes play an important role in creation of chemistry suitable for ISCR by removing dissolved oxygen & nitrate, converting sulfate to sulfide, and reducing Fe^{+3} to Fe^{+2}.
- Limiting parameters in soil or groundwater may include supply of metabolizable carbon, availability of and form of iron, and the availability of sulfate.
- Reactive minerals can be formed *in situ* when chemistry and biochemistry are favorable, and the required reactants are available.
- We know that the thermodynamics of dehalogenation and reduction of nitro groups become more favorable as Eh becomes more negative.



ZVI Reactions:

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$
$$2H_2O \rightarrow 2H^+ + 2OH^-$$
$$2H^+ + 2e^- \rightarrow H_{2\,(g)}$$
$$R\text{-}Cl + H^+ + 2e^- \rightarrow R\text{-}H + Cl^-$$



Why *In Situ* Chemical Reduction?

- Robust technology proven successful at hundreds of sites worldwide
- Multiple treatment mechanisms including direct chemical reduction, biostimulation, enhanced thermodynamic conditions
- Degradation pathways have been confirmed for most target compounds
- Destroys target compounds and therefore eliminates long term liability
- Eliminates O&M costs and can enable site closure
- Broadly applicable: most chlorinated organics, most nitro-substituted organic explosive compounds
- Often removes heavy metals simultaneous with destruction of organic target compounds

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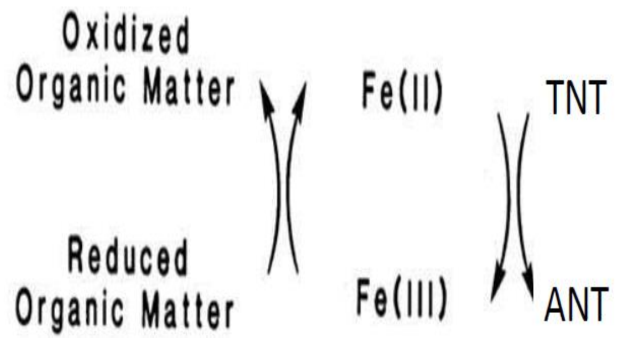
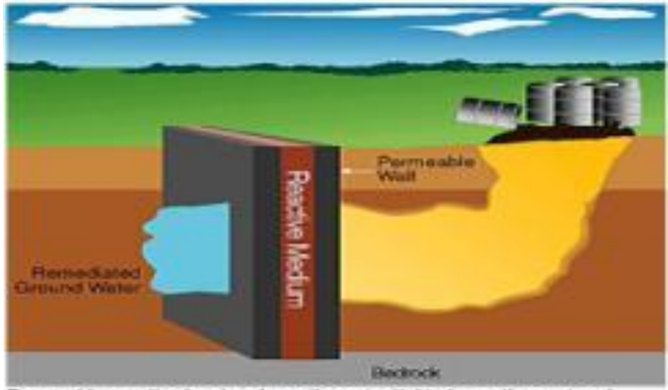
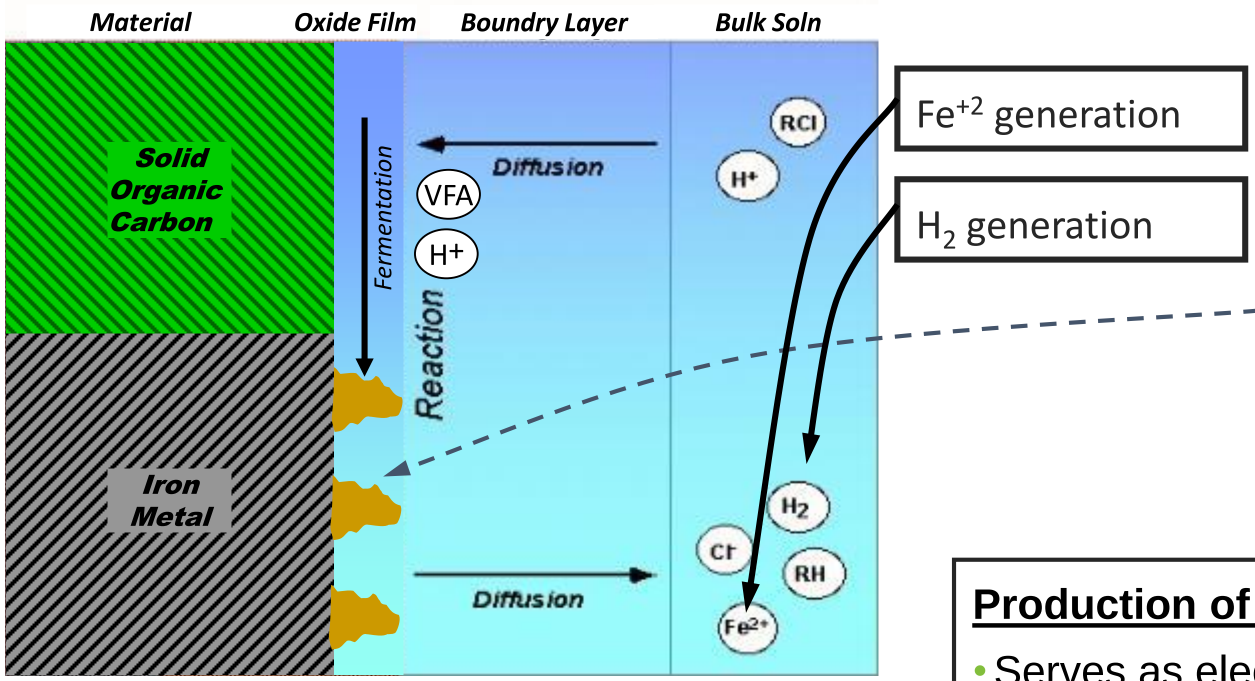




Permeable reactive barriers have the potential to lower the cost and increase the effectiveness of groundwater cleanup.

Carbon Fermentation & ZVI Corrosion: Synergy That Promotes Multiple Reduction Mechanisms



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

Favorable thermodynamic conditions for reduction and 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 reduces precipitate formation on ZVI surfaces (increases and extends reactivity)
- Increase rate of iron corrosion/H_2 generation

Influence of Eh on Dechlorination of CCl_4

Olivas, Y., Dolfing, J., and Smith, G.B., 2002

Thermodynamics: Stronger Reducing Conditions Result in More Dechlorination

 Environ. Toxicol. Chem. 21, 2002 495

Table 3. Redox potential and degradation rates[a]

Ti (III) citrate[c]	*Eh* (mV) at pH 7[d]	CCl_4 rates in nmol/h/mg ± SD[b]			$CHCl_3$ rates in nmol/h/mg ± SD[b]		
		Live[e]	HR[f]	Abiotic[g]	Live	HR	Abiotic
0.0	+534	0	0	0	0	0	0
0.6	−104	0.01 ± 0.006	0.002 ± 0.002	0	0.03 ± 0.01	0.02 ± 0.02	0.02 ± 0.004
2.5	−223	0.09 ± 0.05	0.07 ± 0.05	0.002 ± 0.002	0.051 ± 0.01	0.06 ± 0.01	0.03 ± 0.005
10.0	−280	0.14 ± 0.04	0.28 ± 0.08	0.10 ± 0.02	0.04 ± 0.002	0.08 ± 0.01	0.05 ± 0.01
15.0	−348	0.31 ± 0.02	0.55 ± 0.11	0.14 ± 0.05	0.04 ± 0.02	0.09 ± 0.02	0.06 ± 0.01

[a] Rates were drawn from linear portions of the degradation curves.
[b] Standard deviation.
[c] Titanium citrate concentration in millimols.
[d] Redox potential in millivolts based on the standard hydrogen electrode.
[e] Live sludge.
[f] Heat-resistant, autoclaved sludge.
[g] No sludge inoculum.

1. Strong positive relationship between lower Eh and more rapid dechlorination (↑30x for CCl_4)
2. Also improved removal of chloroform, but to a lesser degree.
3. Observed in both biotic and abiotic systems.

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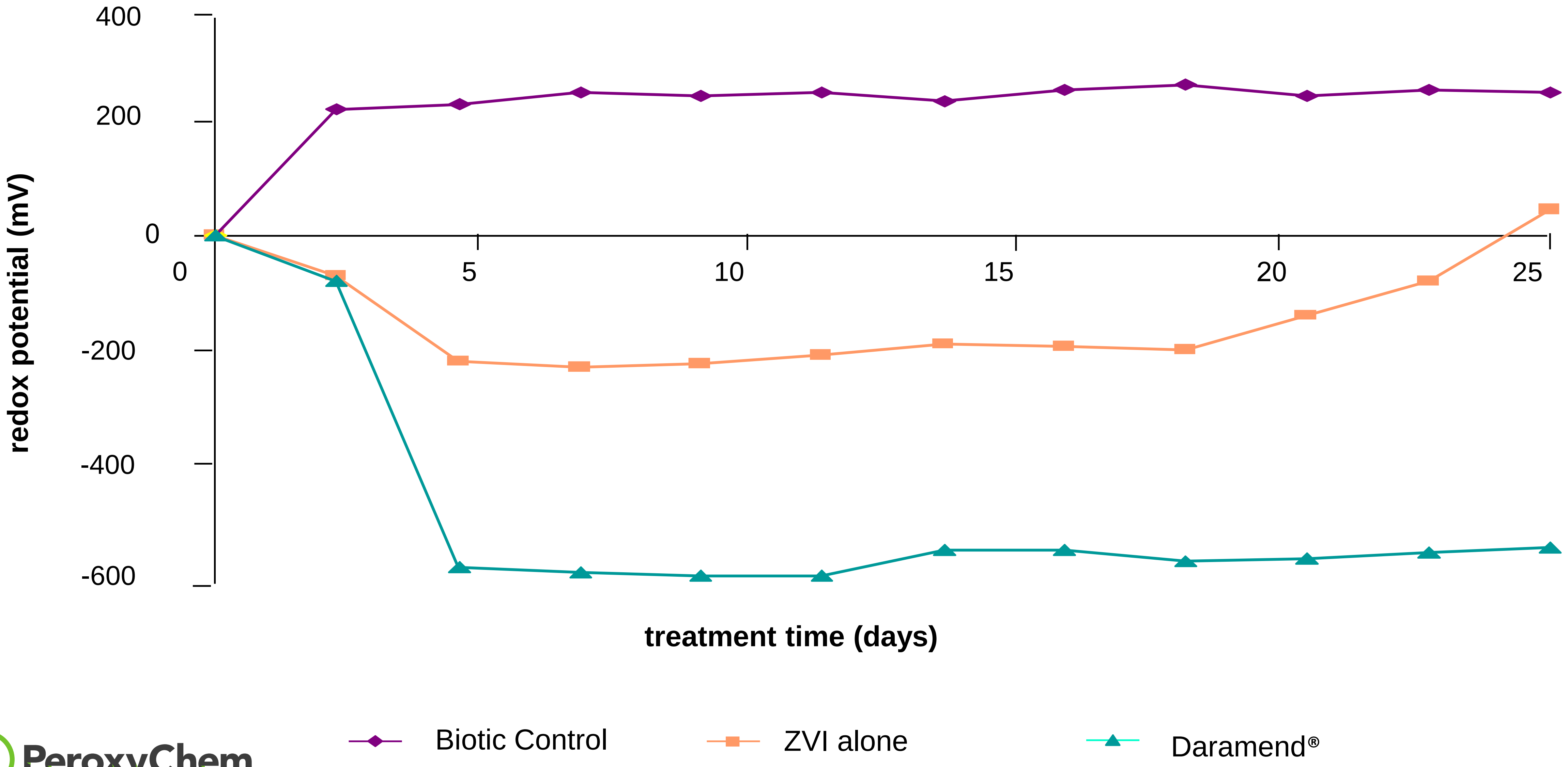
Daramend® Reagent Controls Redox Potential in Saturated Soil



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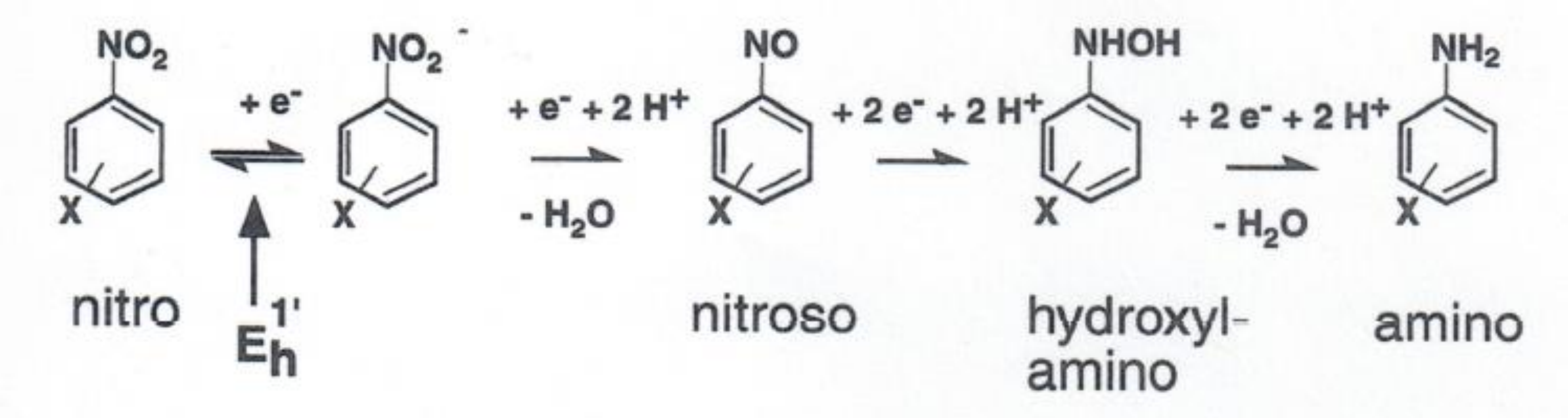
Daramend® for Organic Explosive Compounds in Soil

- Promotes both chemical and biological reduction of target compounds (TNT, DNTs, ANTs, RDX, HMX, Tetryl, nitrocellulose, nitroglycerin, nitrobenzene)
- Daramend® reagents are composed of micro-scale zero valent iron + solid organic carbon, and food grade binding agent
- Organic component designed to provide a long-lasting, hydrophilic, source of carbon and nutrients while preventing strong adsorption of target compounds – which slows degradation (contrast with mulch, EVO, compost mix, or ZVI alone
- Microscale ZVI (Fe^0) promotes chemical dehalogenation while labile organic carbon + nutrients push microbial growth and removal of oxygen/nitrate/sulfate
- Together these processes drive soil to a strongly negative Eh
- Strongly negative, long-lasting reducing conditions prevent accumulation of partial breakdown products
- Typical dosages are between 2.0% and 5.0% w/w of soil

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.

- Sequential reductive degradation of nitro groups with through intermediate compounds to fully reduced amino end product (reference).
- Requires 6 e^- for complete reduction of one $-NO_2$ group and 18 e^- for TNT
- Suggests that effective treatment of OE with achievement of low residual concentrations is best achieved with a long-lasting source of reducing equivalents

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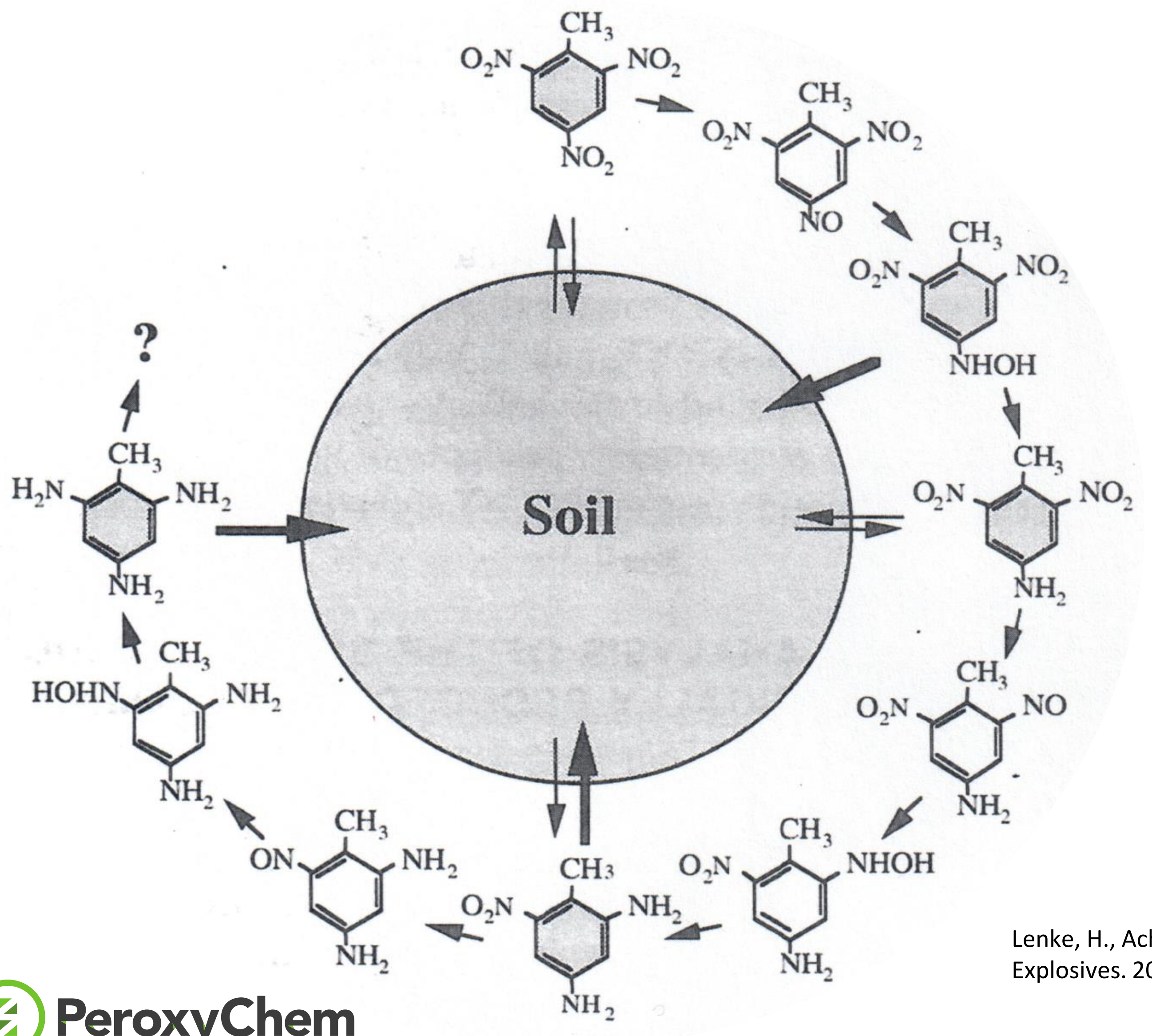
Fate of Nitroaromatics During Reductive Treatment



Adsorption of Reductive Degradation Products

- NO_2 groups are less strongly adsorbed
- NH_2 groups are highly reactive and strongly adsorbed
- Some reversibility as long as at least on NO_2 group is present
- Structure with three NH_2 groups (TAT) will be adsorbed irreversibly
- Highlights the importance of preventing accumulation of partial reduction products such as mono and diamino nitrotoluenes
- Adsorption is so strong that adsorbed TAT is not released even by alkaline or acid hydrolysis
- 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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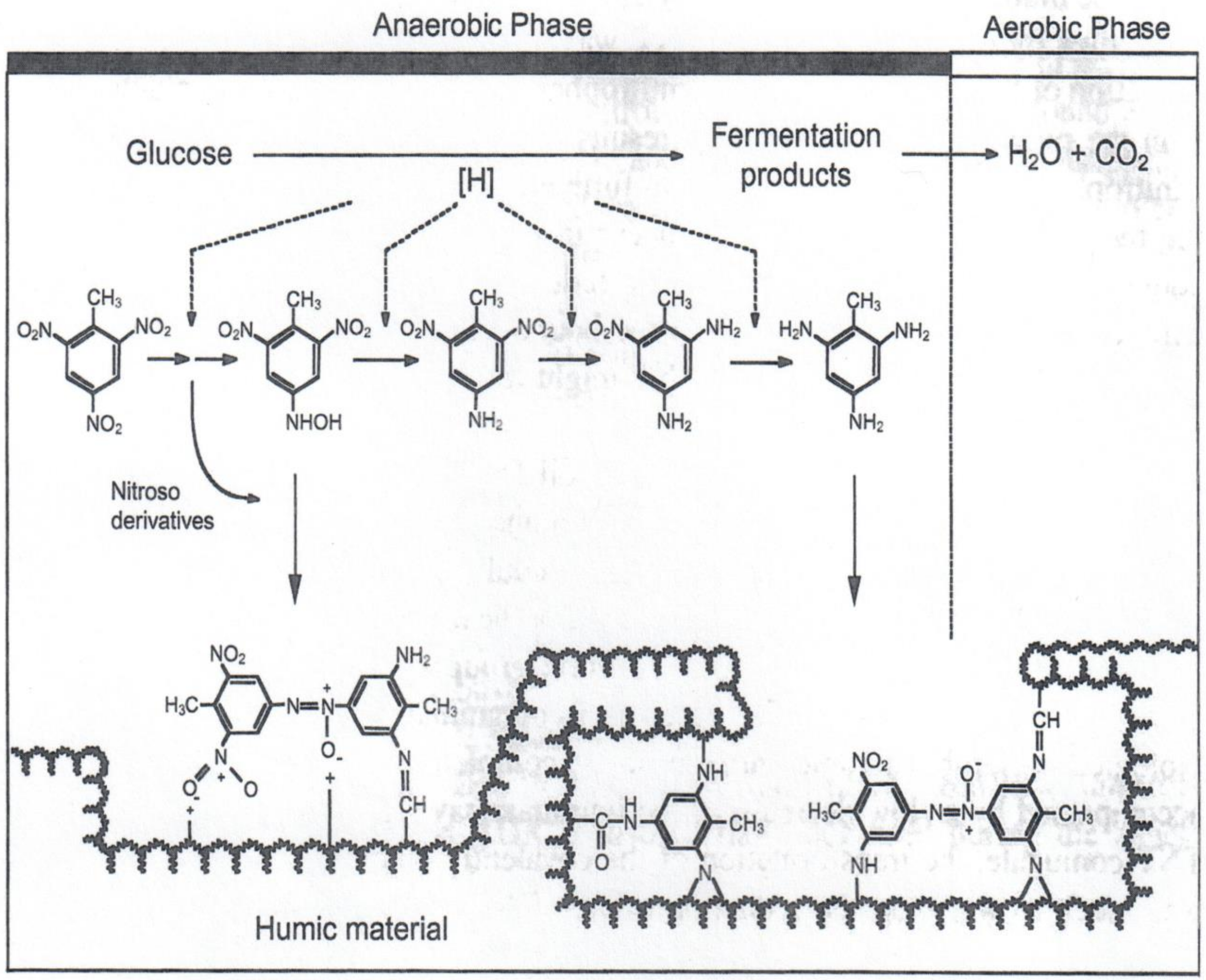
Fate of TNT During Reductive Soil Treatment

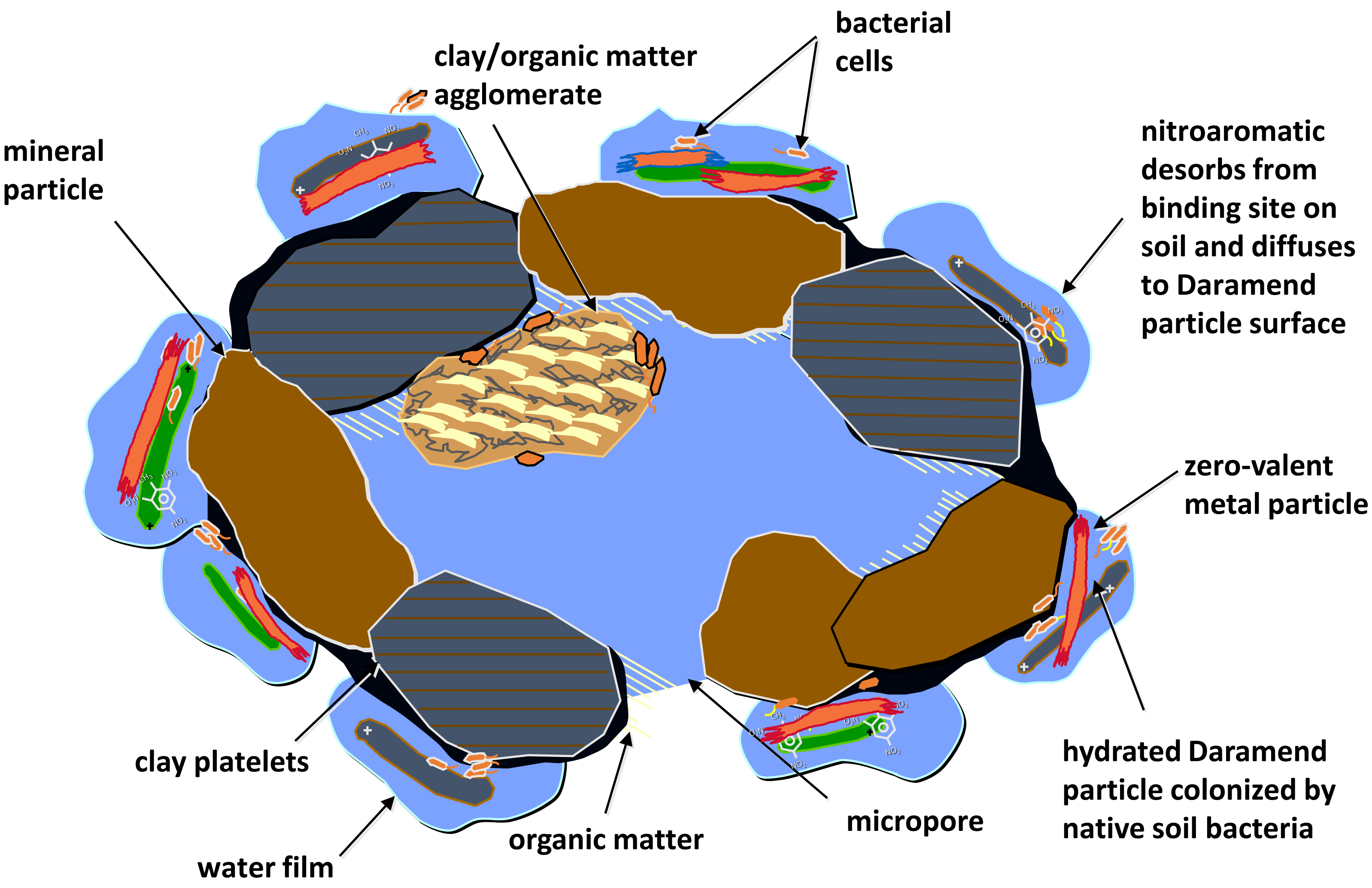


TNT Reduction Products are Incorporated into Soil Organic Matter

- Amino groups ($^{-}NH_2$) are highly reactive
- Subject to covalent incorporation into soil organic matter
- ^{14}C and ^{15}N NMR studies indicate that the fate of TNT during reductive treatment is covalent binding of the reduction products into soil humic and fulvic material
- An adequate supply of Fe^{+2} is critical to full removal and detoxification of TNT and its breakdown products

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.

Daramend® Treatment of Nitroaromatics and Organic Explosive Compounds



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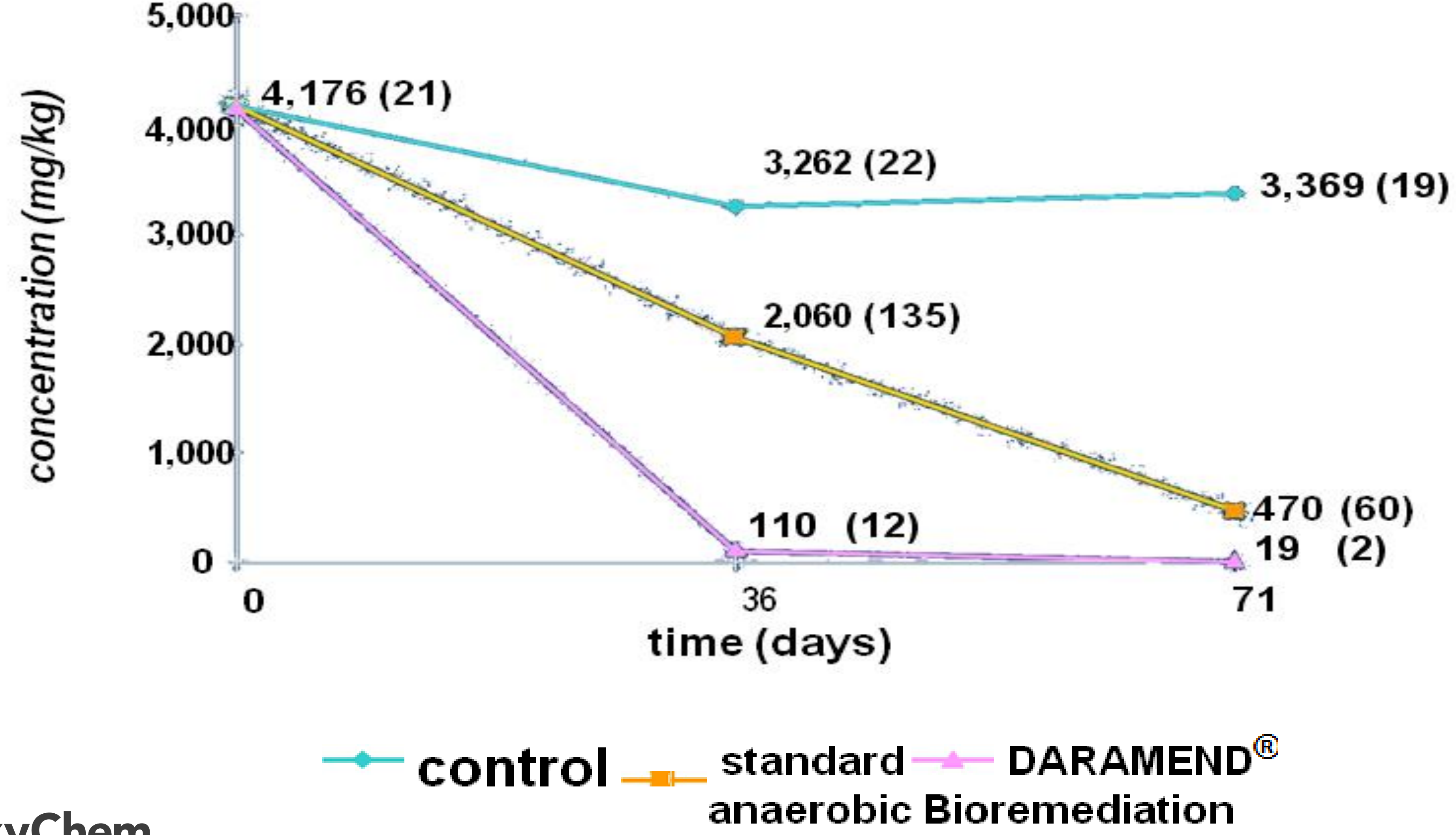
Bench-scale Performance Daramend® Reagent for Organic Explosive Compounds

Effect of Daramend® Reagent on TNT and Total Amino Concentrations at USACE Weldon Spring MO Site



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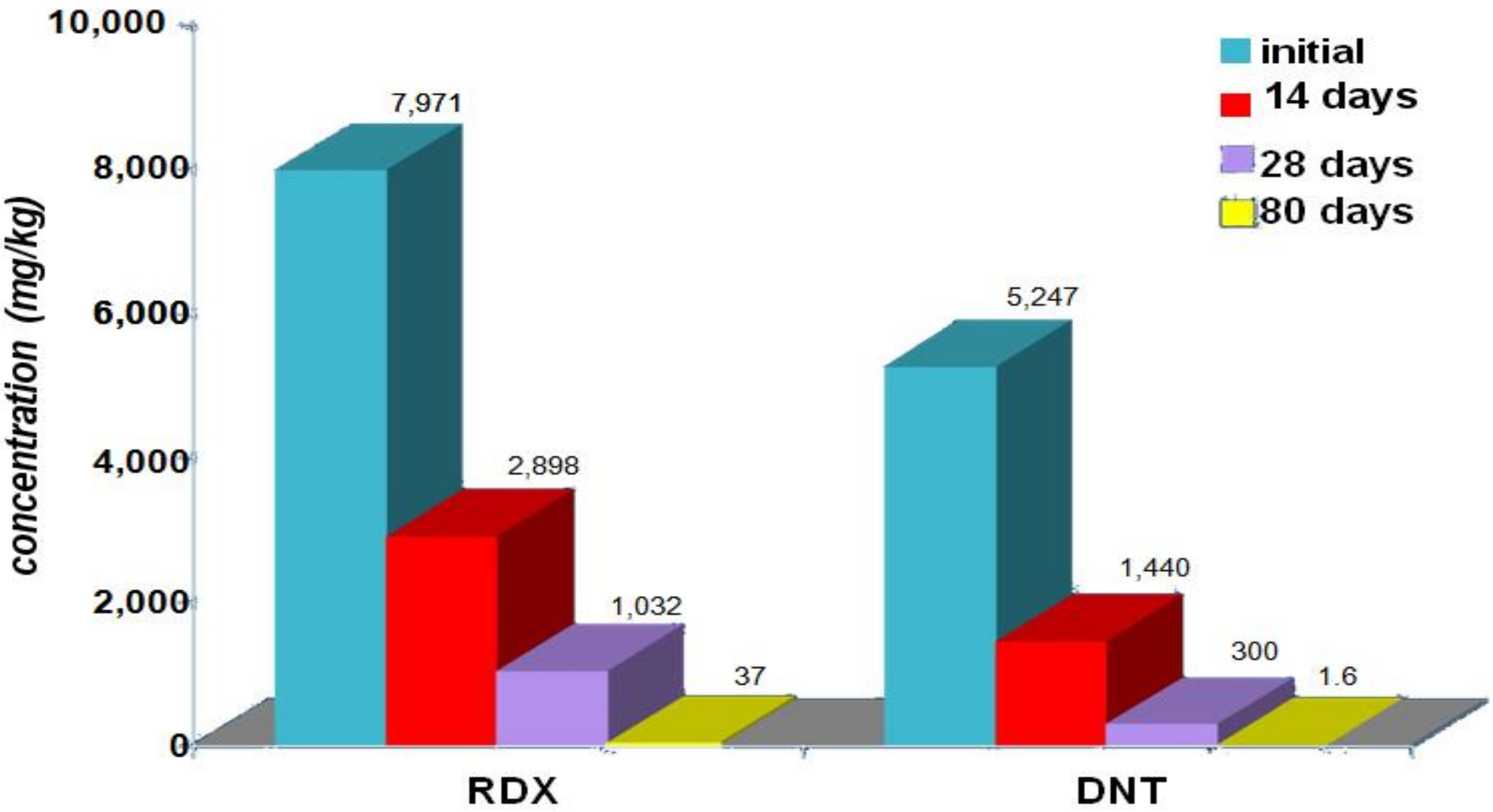
Influence of Daramend® Treatment on RDX and DNT in Soil



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Pilot-scale Technology Demonstration

Extended Monitoring

Confidential Industrial Site

NE USA

Kennedy Jenks Consultants

Pilot-scale Treatment of TNT in Soil

Experimental Design

- Soil was loaded into purpose-made 10 y^3 open-top steel boxes.
- The experimental design included:
  - Static control (no mixing, no water)
  - Watered control mixed only once
  - Watered control mixed every 14 days
- The treatments included:
  - Organic amendment (wood mulch, 10% w/w) with water but mixed only once,
  - Organic amendment (wood mulch, 10% w/w) with water, mixed every 14 days,
  - Six Daramend® treatments (2%, 3%, 4% w/w, either single application with single mixing or sequential dosing with repeated mixing).

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Pilot-scale Treatment for TNT in Soil

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Experimental Design (cont.)

- Daramend® reagent is a blend of micro-scale ZVI and processed plant fiber.
- Daramend dosages were 2%, 3%, and 4% (w/w soil).
- Three treatments received the entire mass of Daramend at the start of treatment and were mixed only once.
- The other three Daramend treatments received the reagent in five smaller doses, each separated by 14 days and accompanied by mixing.
- Water content in all but the static control was maintained near the soil's water holding capacity throughout the project

Monitoring of Indicator Parameters

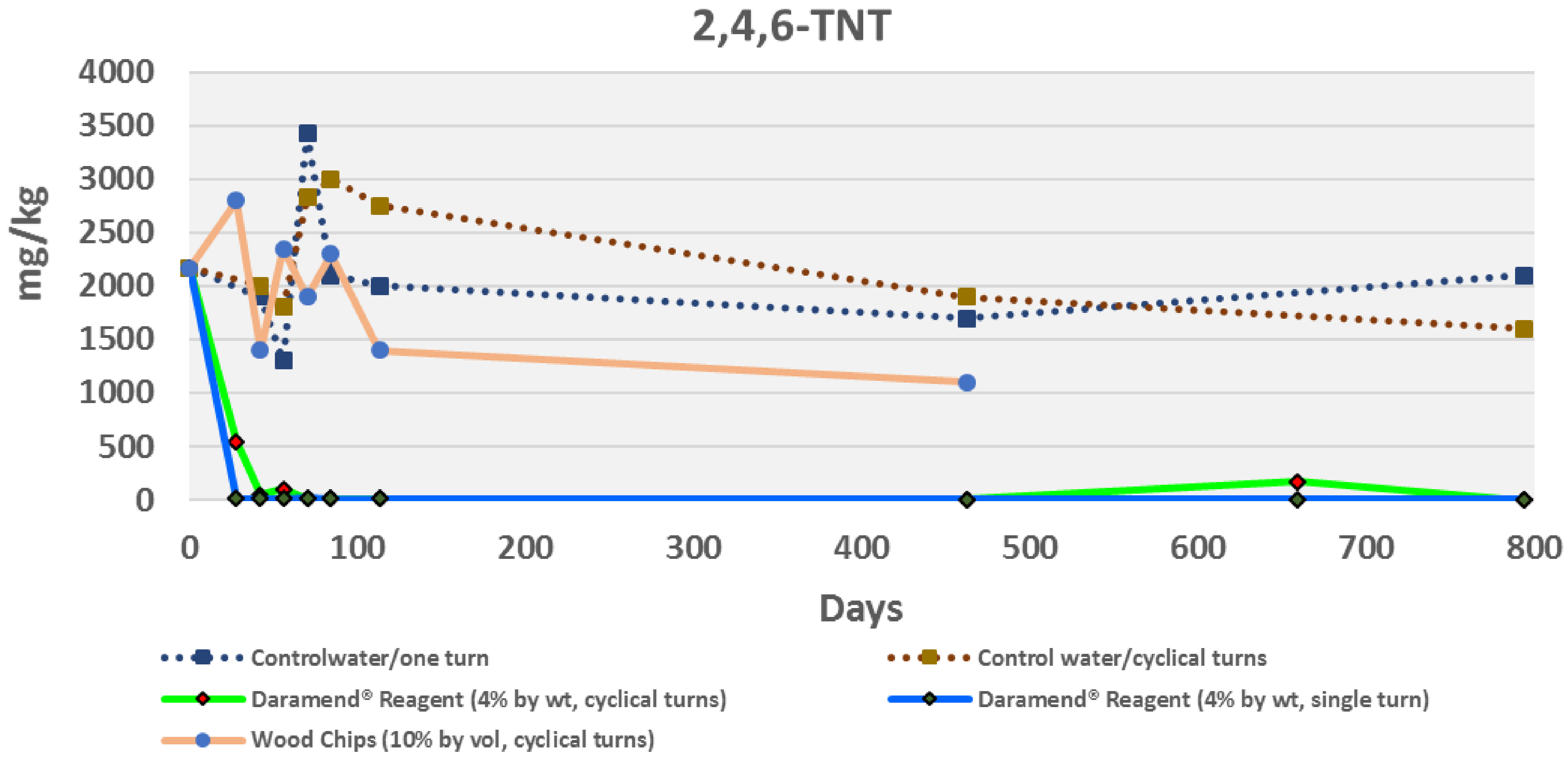
TNT and Breakdown Products

Extended Post Treatment Monitoring

Preliminary Indications: Soil pH and Eh

- Soil pH ranged from 5.0 to 7.0 and there was no apparent relationship between soil amendment type or dosage and changes in soil pH over time.
- Redox potential in the control soil and remained positive throughout the 204-day monitoring period.
- Redox potentials in the soil treated with wood mulch were initially between +170 mV and +223 mV and dropped somewhat to between +70 mV and +80 mV by the end of the monitoring period.
- Redox potentials in the soil treated with Daramend were initially between +137 mV and +253 mV, became strongly negative by day 3 of the monitoring period, and ultimately fell to as low as -390 mV.

Influence of Daramend® Reagent and Soil Mixing on TNT Concentration in Soil



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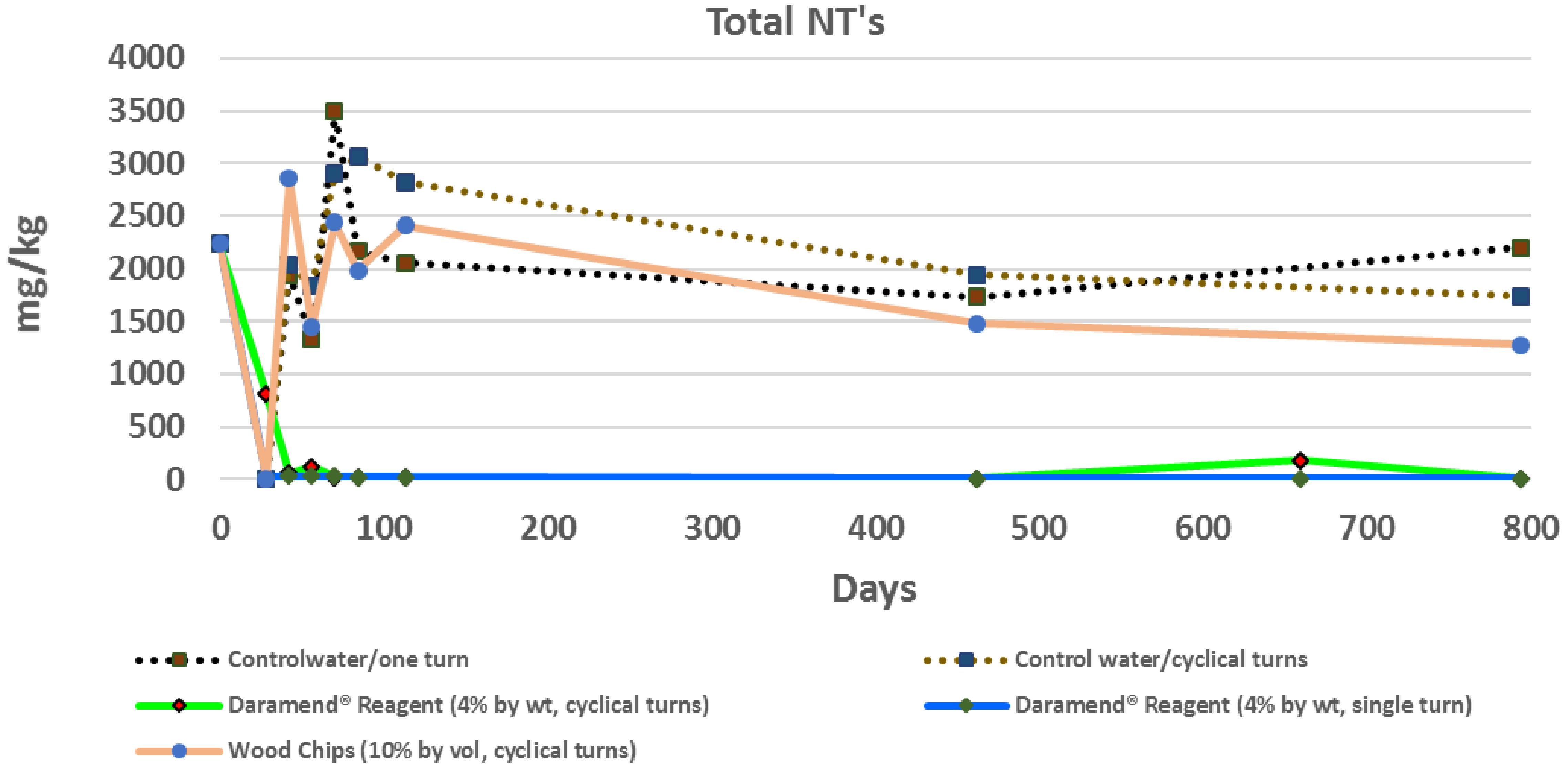
Influence of Daramend® Reagent and Soil Mixing on Total Nitrotoluene Concentration in Soil



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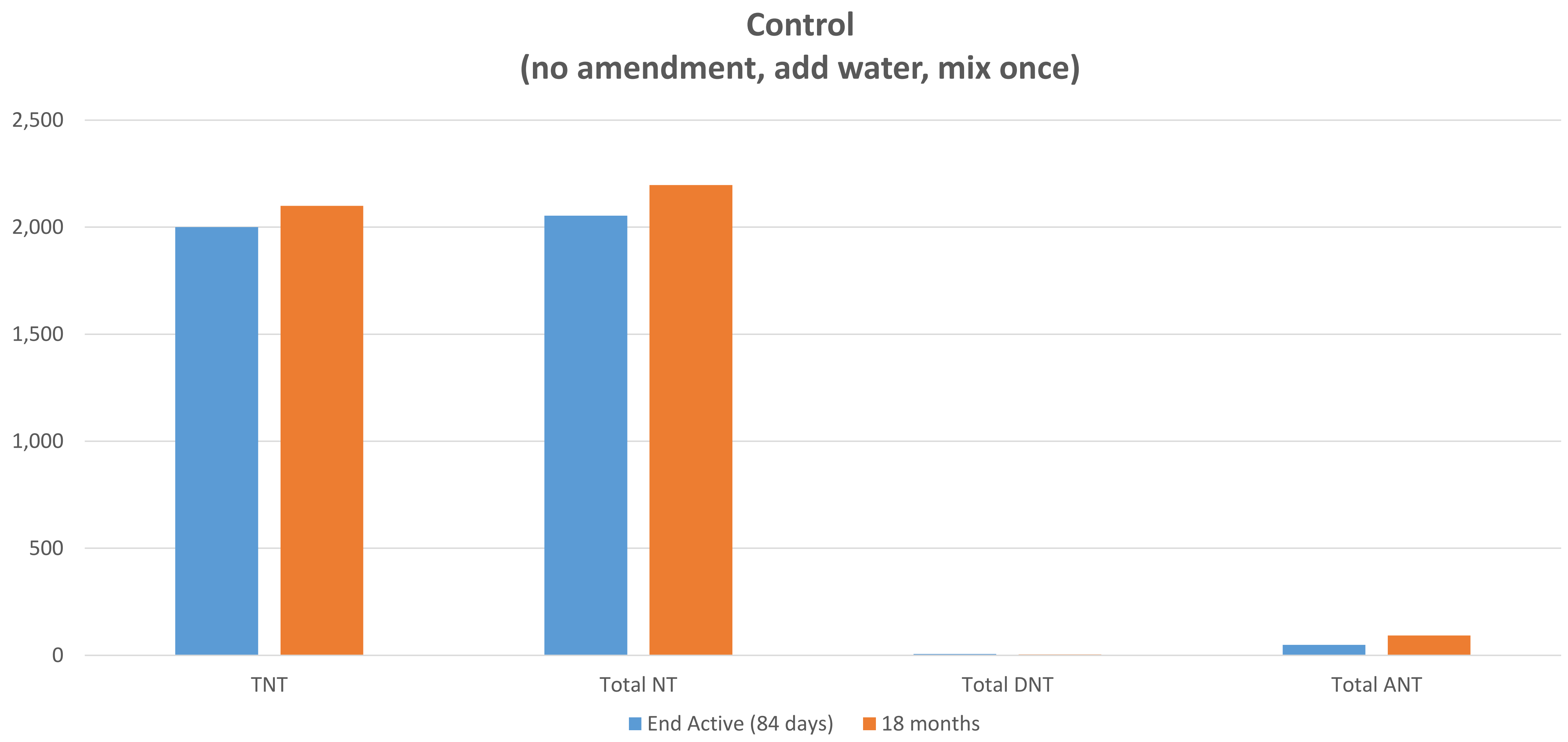
Extended Post Treatment Monitoring



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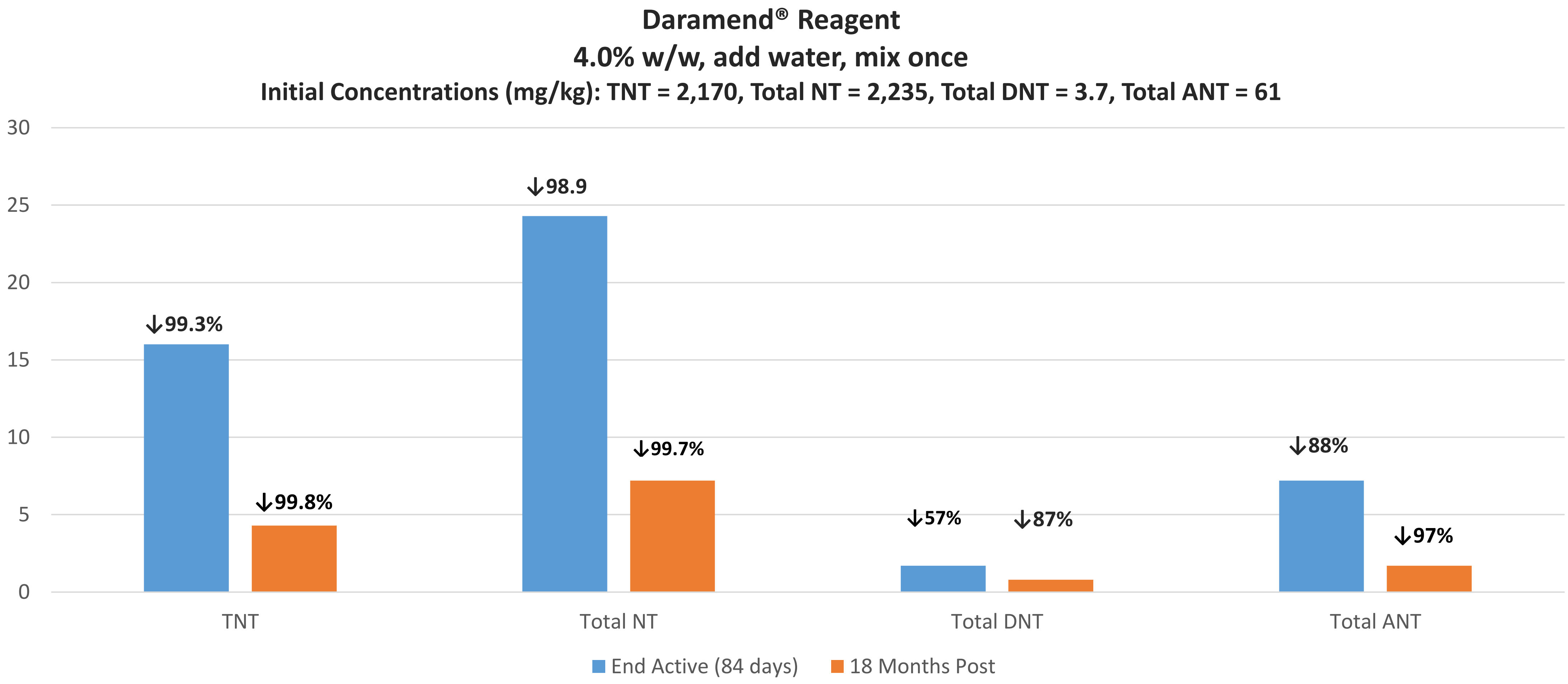

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Pilot-scale Demonstration Summary

- Reducing conditions were not established in the untreated control and soil treated with wood mulch whether mixed or static.
- TNT was not extensively degraded in the control or wood mulch treatments. Amino compound concentrations increased by as much as 3x in the wood much treatments.
- Strong reducing conditions were established by each of the Daramend® treatments and the highest Daramend® dosage produced strongest reducing conditions
- The concentrations of TNT and its breakdown products remained quite stable in the controls and the wood mulch treatments, whether the soil was mixed or left to static.
- The NJDEP residential soil remediation standards for TNT, 2,6-DNT, 2,4-DNT, 2-A-4,6-DNT, and 4-A-2,6-DNT were all achieved in response to Daramend® treatment.
- No advantage gained from repeated small Daramend® applications with additional mixing versus single application with single mixing
- TNT and amino compound concentrations continued to decrease in Daramend® treated soil during extended monitoring over 18 months.

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Case Study

Naval Weapons Station Yorktown

Yorktown VA

Daramend® at Naval Weapons Station Yorktown

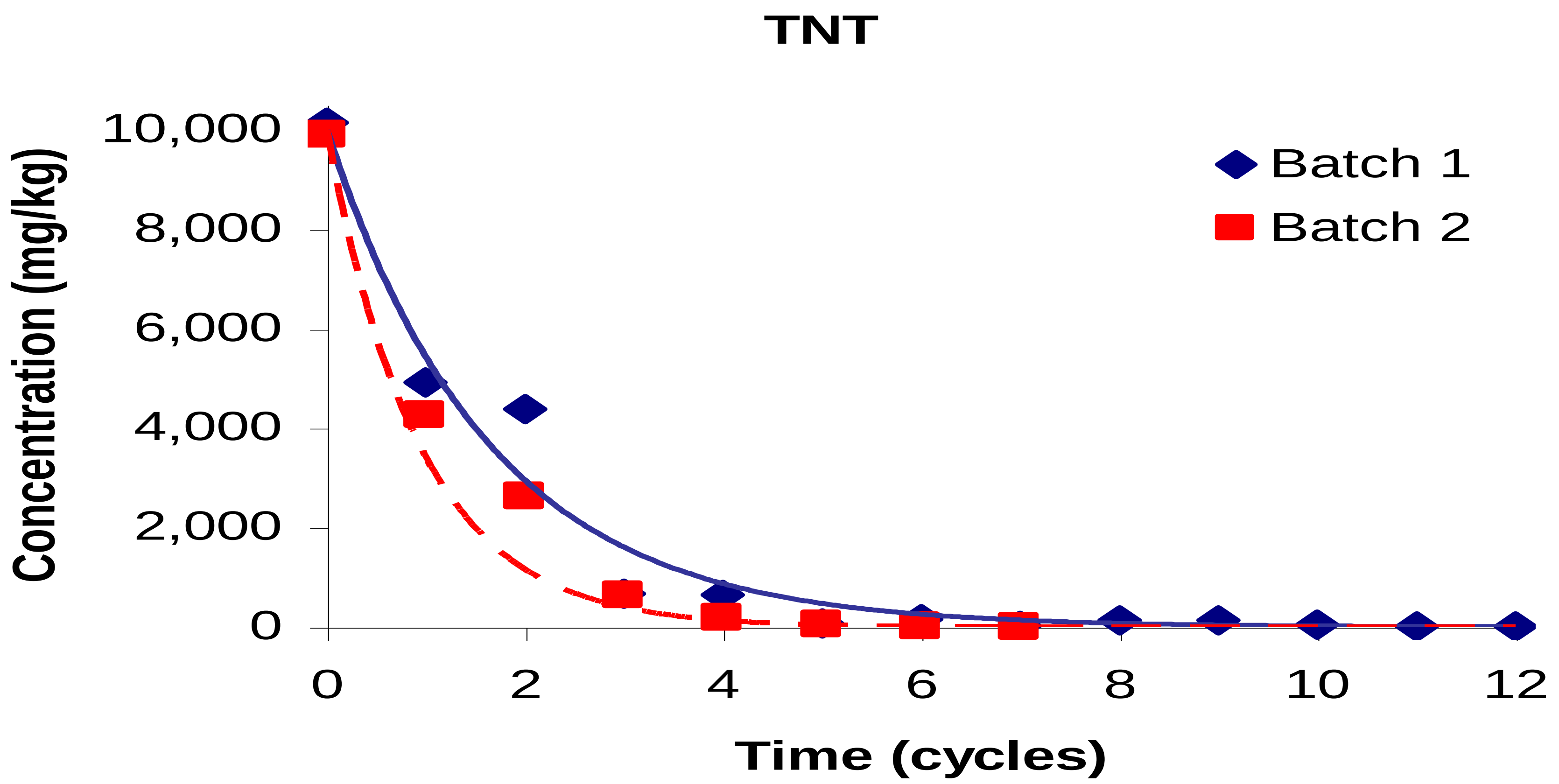
- 8,400 y^3 soil (*ca*. 12,000 tons)
- Soil TNT concentrations as high as 43,000 mg/kg (average about 10,000 mg/kg)
- Treatment goals were 14 mg/kg for TNT and 5 mg/kg for RDX
- Daramend® was selected through the FS Process
- Ex-situ treatment of soil and sediment (impacted by effluent from washout of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

NWS Yorktown: Biocell Construction

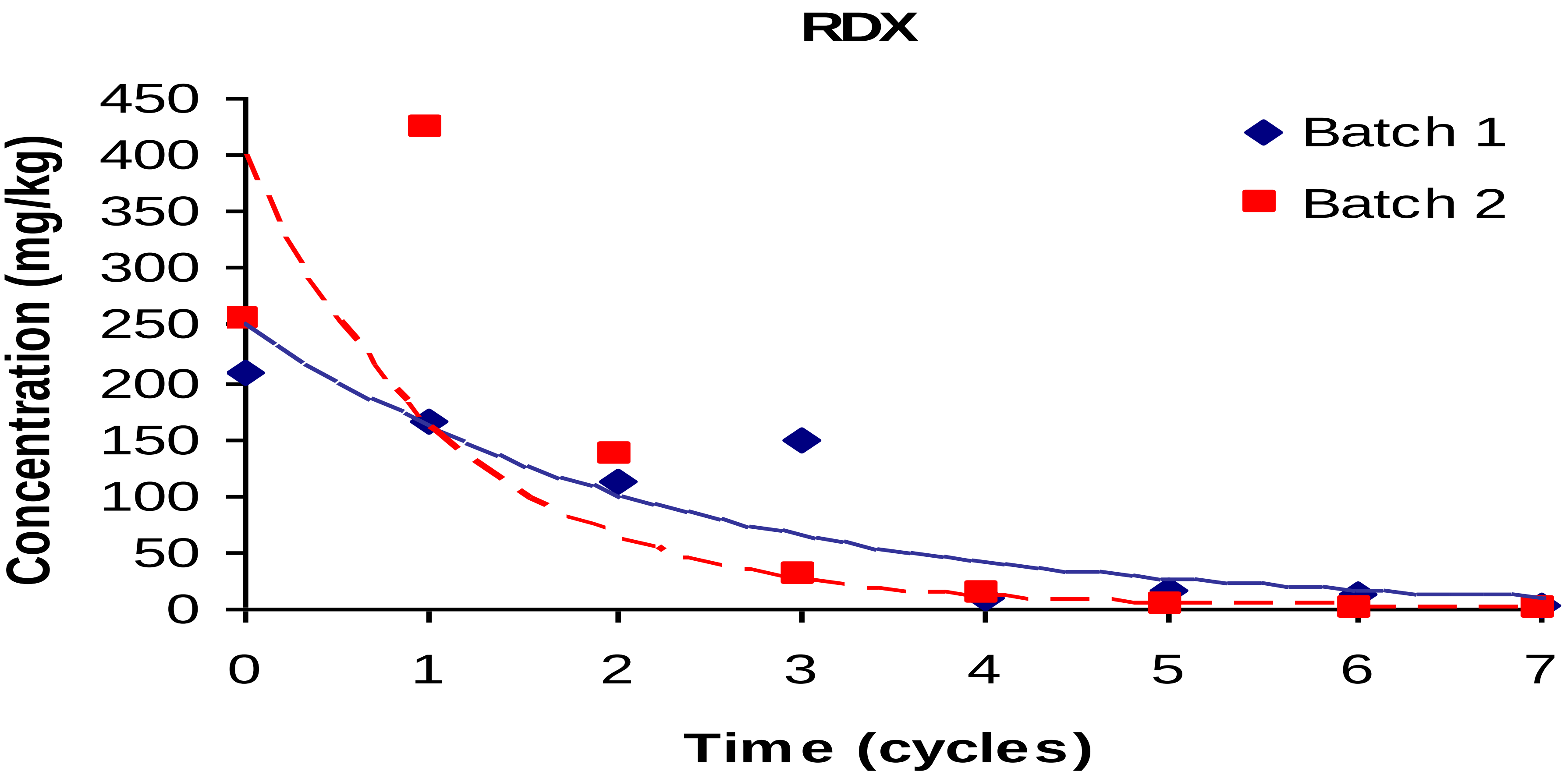
NWS Yorktown: Biocell Loading

NWS Yorktown: Biocell Cover Construction

NWS Yorktown: TNT Treatment Results



NWS Yorktown: RDX Treatment Results

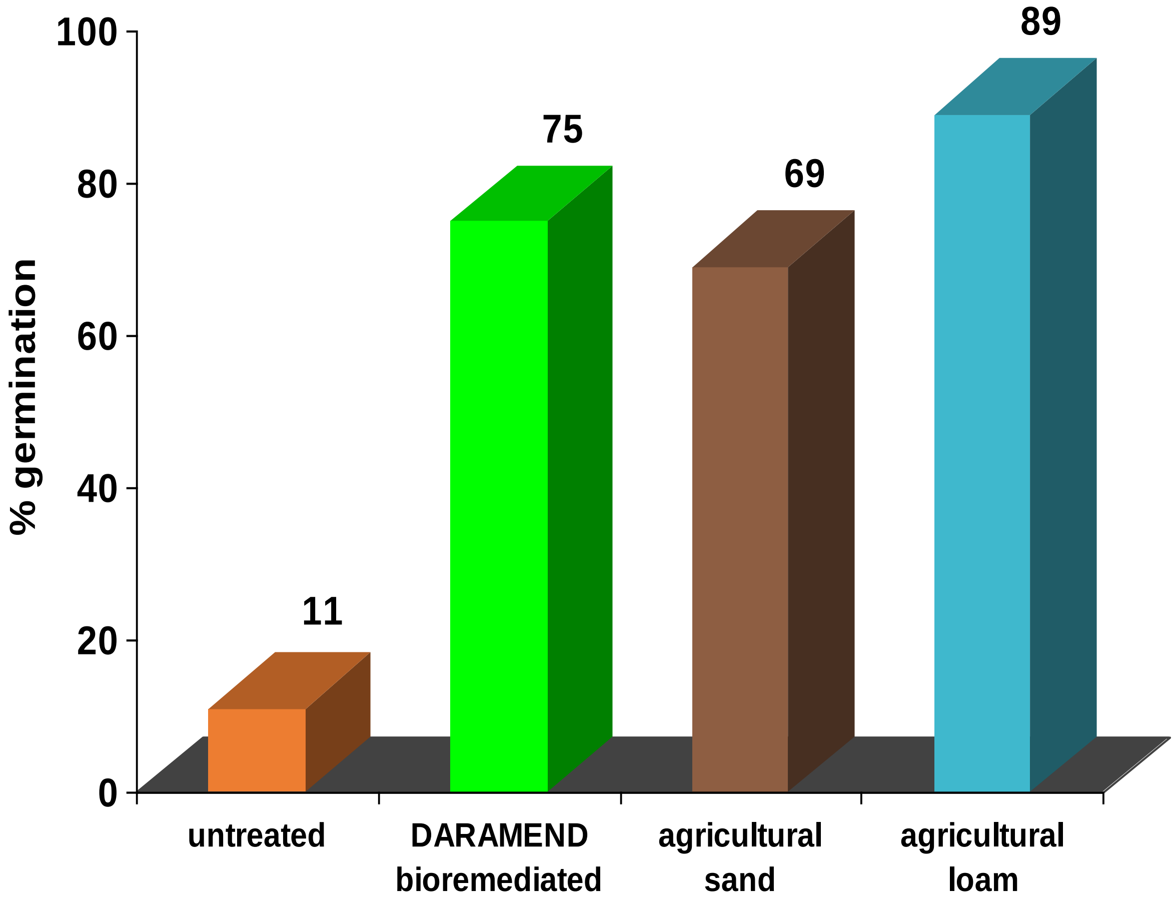


Influence of Daramend® Treatment on TNT Concentrations in NWS Yorktown Soil

TNT Concentration (mg/kg)

Sampling Zone	Batch One		Batch Two		Batch Three		Batch Four	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
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	2.6	7,000	0.25	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	1.2.0	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**

Influence of Daramend® Treatment on Tomato Seed Germination
NWS Yorktown Soil



- Soil collected from zones 1, 2, and 3 of batch 4 (before and after treatment)
- Pretreatment TNT about 20,000 mg/kg and post treatment about 5 mg/kg
- Tomato (*Solanus lycopersicum*) seed germination comparison
- Soil moisture adjusted to 60% WHC
- No addition of nutrients
- Incubation at room temperature (20±2°C)

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Completed Daramend® Projects

- ✓ **Iowa Army Ammunition Plant, Middletown IA** (RDX, HMX, TNT)
- ✓ **Yorktown Naval Weapons Station, Yorktown VA** (TNT, RDX)
- ✓ **Joliet Army Ammunition Plant, Joliet IL** (RDX, DNT)
- ✓ **Raritan Arsenal, Edison NJ** (TNT)
- ✓ **Tooele Army Ammunition Depot, Tooele UT** (RDX, TNT)
- ✓ **Hawthorne Army Depot, Hawthorne NV** (RDX, TNT, HMX, TNB)

Comparative Soil Treatment Costs

Technology	Mobilization/Demobilization	Treatment	Total
	Unit Cost ($/ton treated soil)		
Daramend®	75	90	165[1]
Windrow Composting	75	150	225[1]
Bioslurry	105	204	309[1]
Alkaline Hydrolysis	105	130	235[2]

1. Estimates based on treatment of 25,000 tons of RCRA hazardous soil (Jerger, D. and Woodhull, P. *In*: Biodegradation of Nitroaromatic Compounds and Explosives. 2000. *Eds*.: Spain, J., Hughes, J, and Knackmuss, H.-J.
2. Estimate based on available literature data.

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Questions & Answers

Discussion