Bioremediation of Soils Containing Organic Explosives Compounds Using ZVI/Organic Carbon Reagents

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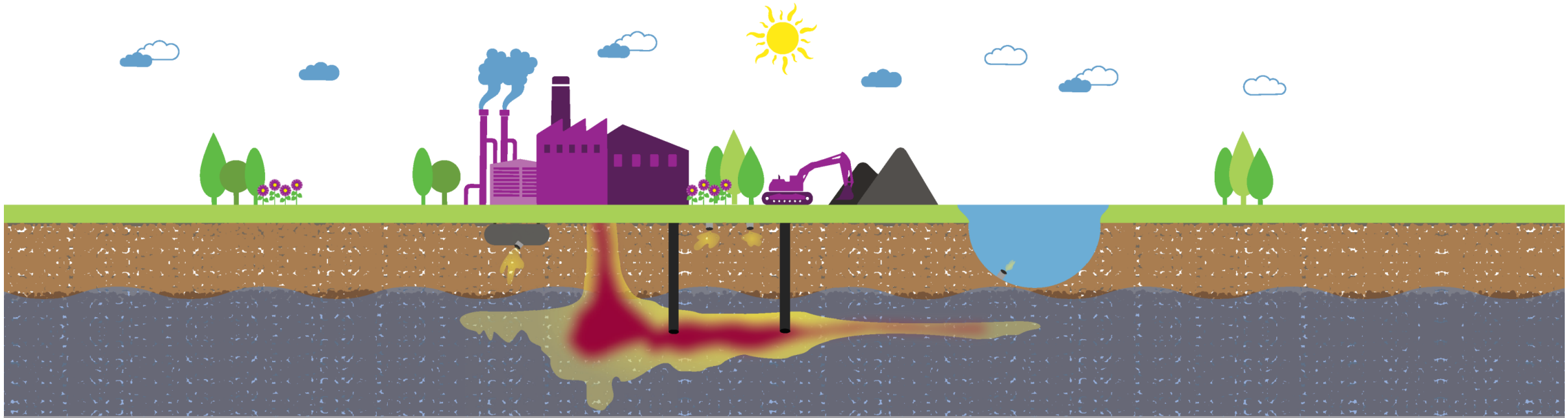
Presentation Outline

- Daramend® Overview
- Treatment Mechanisms
- Daramend ® Performance Data, Site Pilot, and Site Full-scale
- Questions and Answers

Evonik Soil & Groundwater Remediation
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

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

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

Metals Remediation
- MetaFix® Reagents

BioGeoChemical
- GeoForm® Reagents

NAPL Stabilization
- ISGS® Technology

Daramend® Family of Reagents

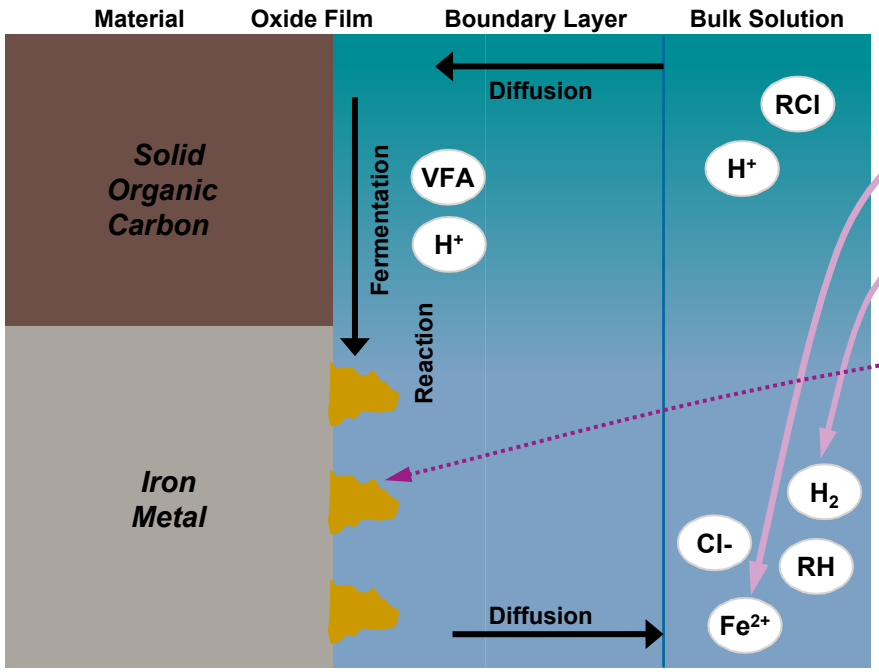
Attribute	Daramend®	Daramend® Metals	Daramend® Plus
High Surface Area Hydrophilic Plant Fiber	✓	✓	✓
Slow-release Organic Carbon & Nutrients (N, P, S)	✓	✓	✓
Microscale ZVI	✓	✓	✓
Soluble Sulfate Salts	-	✓	-
Activated Carbon	-	-	✓
Emulsifying Agent	✓	✓	✓
pH Balanced	✓	✓	✓
Applicability	Pesticides, cVOCs,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

Benefits of Daramend® Formulations

Component	Benefits
High Surface Area Hydrophilic Plant Fiber	Increases soil WHC & bioavailable H_2O. Provides surface area for microbes, overcoming acute toxicity. Produces VFAs to increase ZVI reactivity and longevity.
Slow-release Organic Carbon & Nutrients (N, P, S)	Promotes enzymatic synthesis, avoids luxury consumption, promotes bacteria & fungi.
Microscale ZVI	Strong reducing agent, source of ferrous iron. Provides alkalinity to balance carbon source fermentation.
Soluble Sulfate Salts	Provides sulfate for reductive sulfide generation => biogenic iron sulfides. Precipitates soluble heavy metals.
Activated Carbon	Strong adsorbent of soluble contaminants. Enable reductions to TCLP for disposal
Emulsifying Agent	Promotes desorption of high MW and hydrophobic compounds (i.e., OCPs) to enhance degradation rates.

Daramend® Treatment Mechanisms

Carbon Fermentation + ZVI Corrosion: Synergy Promotes Multiple Dechlorination Mechanisms



Fe^{+2} generation

H_2 generation

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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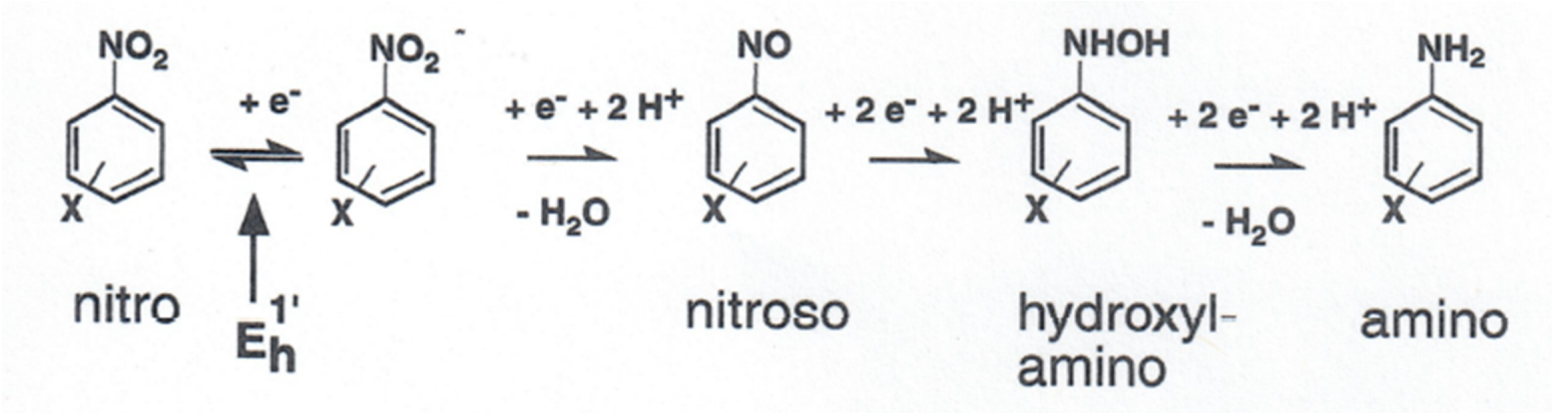
General Daramend Process Overview

1. Apply Daramend
2. Mixing/Tilling
3. Watering
4. Reaction processing & monitoring
5. More recalcitrant compounds (OCPs) require process cycling
6. Typical application rates of 2-5 wt% overall, cycled rates vary

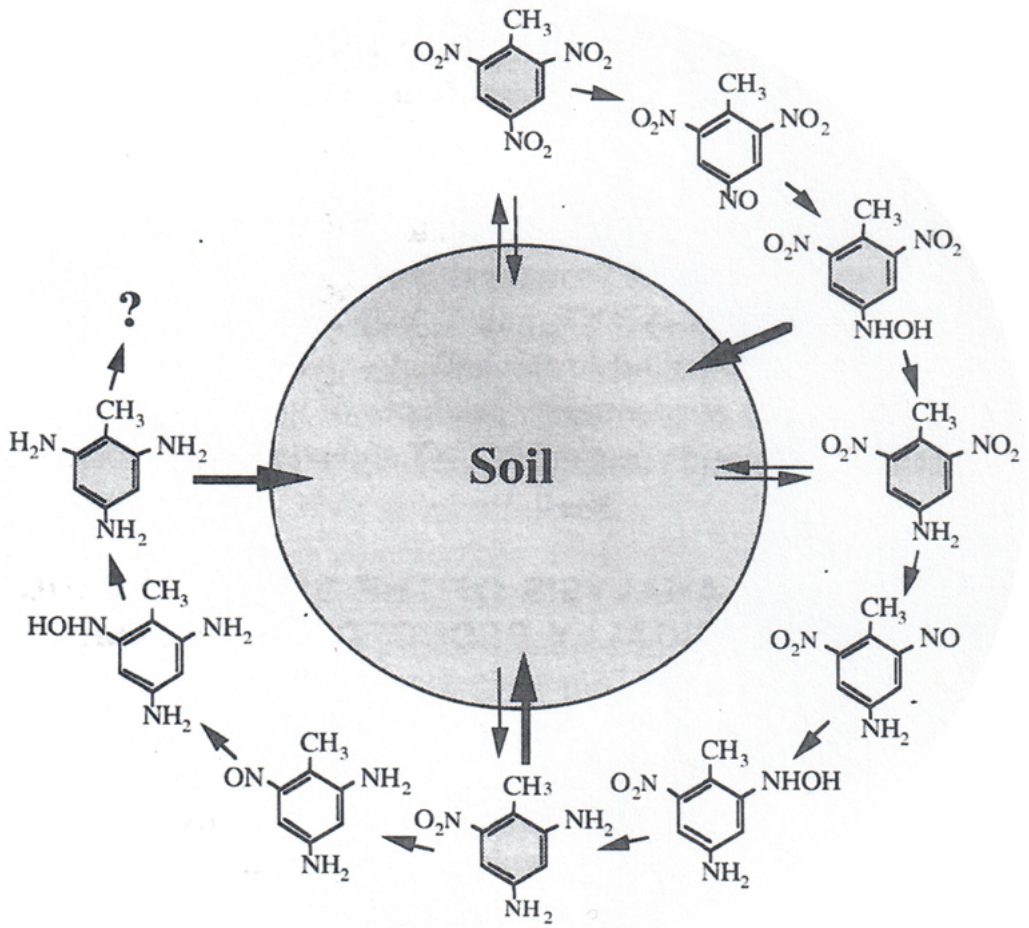
Reductive Degradation of Nitroaromatics



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 to fully reduced amino groups.
2. Requires 6 e^- for each NO_2 group and 18 e^- for each TNT molecule
3. Strongly electronegative, long-lasting reducing conditions prevent accumulation of partial breakdown products (i.e., long-lasting organic carbon + ZVI)

Fate of Nitroaromatics During Reductive Treatment



Fate of Organic Explosives in Soil

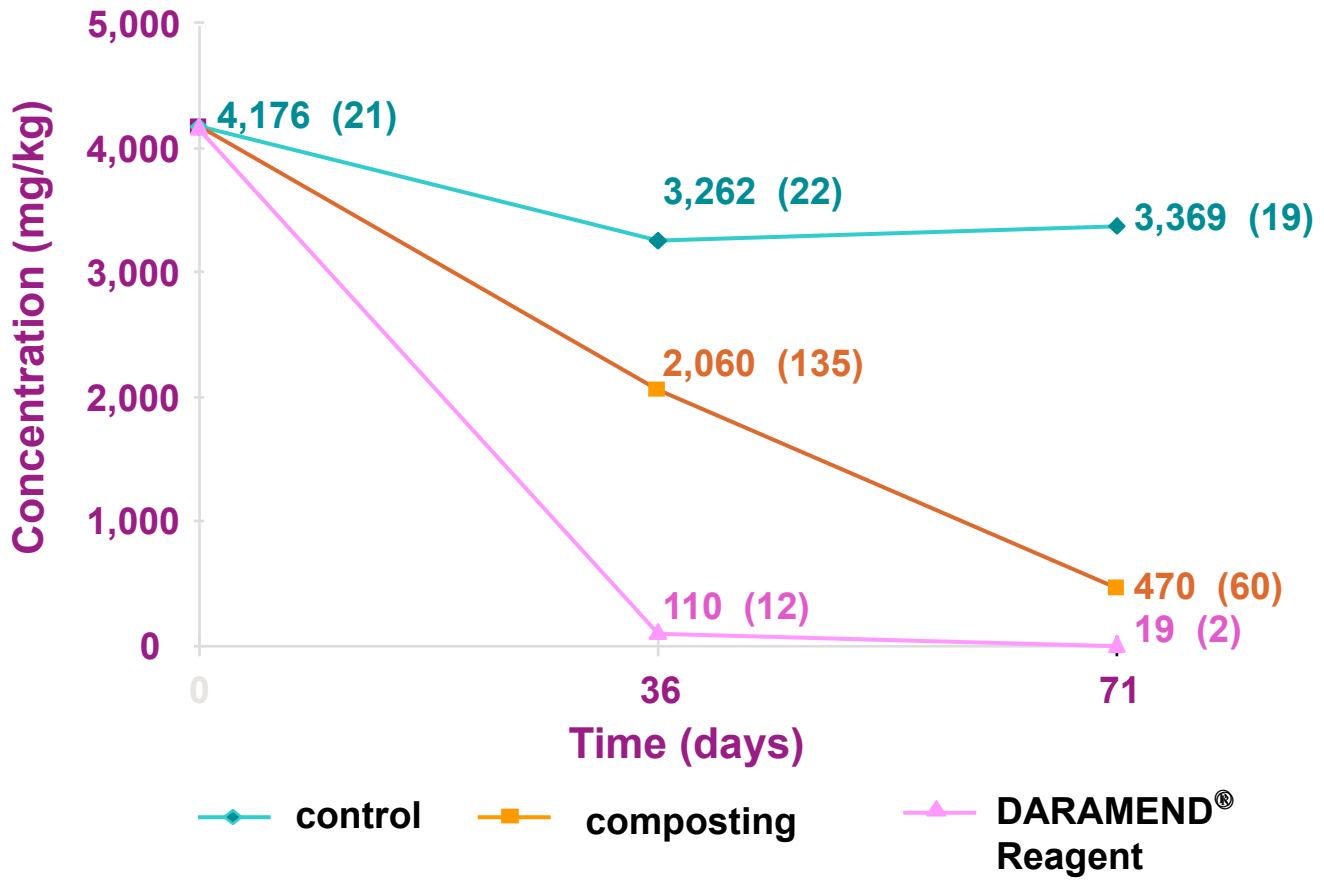
1. NO_2 groups less strongly adsorbed
2. NH_2 groups strongly adsorbed
3. Some reversibility when NO_2 group is present
4. Three NH_2 groups (TAT) is adsorbed irreversibly
5. Highlights the importance of preventing accumulation of partial reduction products such as mono and diamino nitrotoluenes
6. TAT is not desorbed hydrolysis or silylation
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.

Performance Data Daramend® Reagent for Organic Explosive Compounds

Degradation and Toxicity

TNT and Total Amino Compounds



Numbers in parentheses indicate total amino compounds by EPA 8330 Method.

Weldon Springs, MO Site

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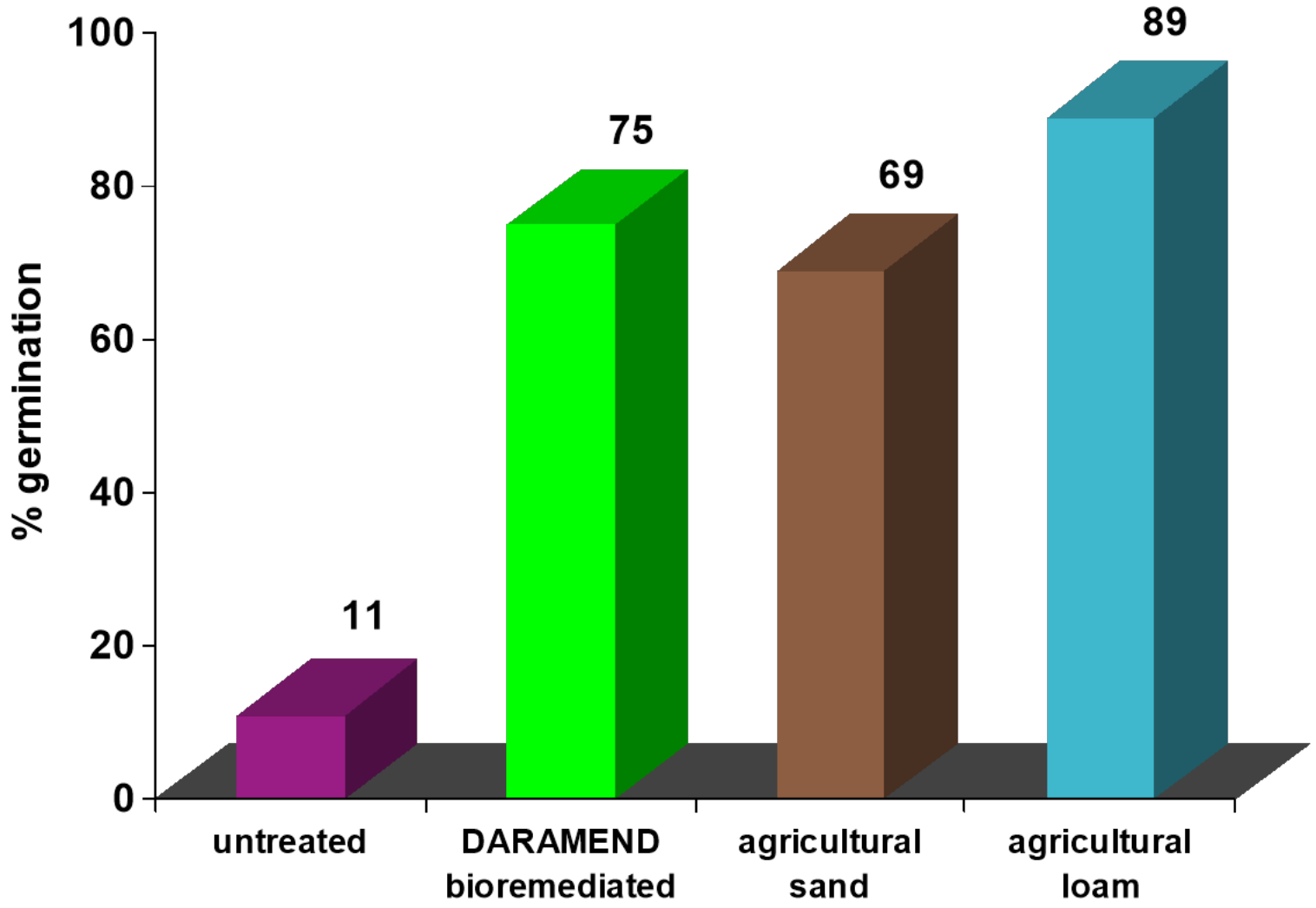
Degradation and Toxicity

Effect on Tomato Seed Germination in Organic Explosive Contaminated Soil



Raritan Arsenal

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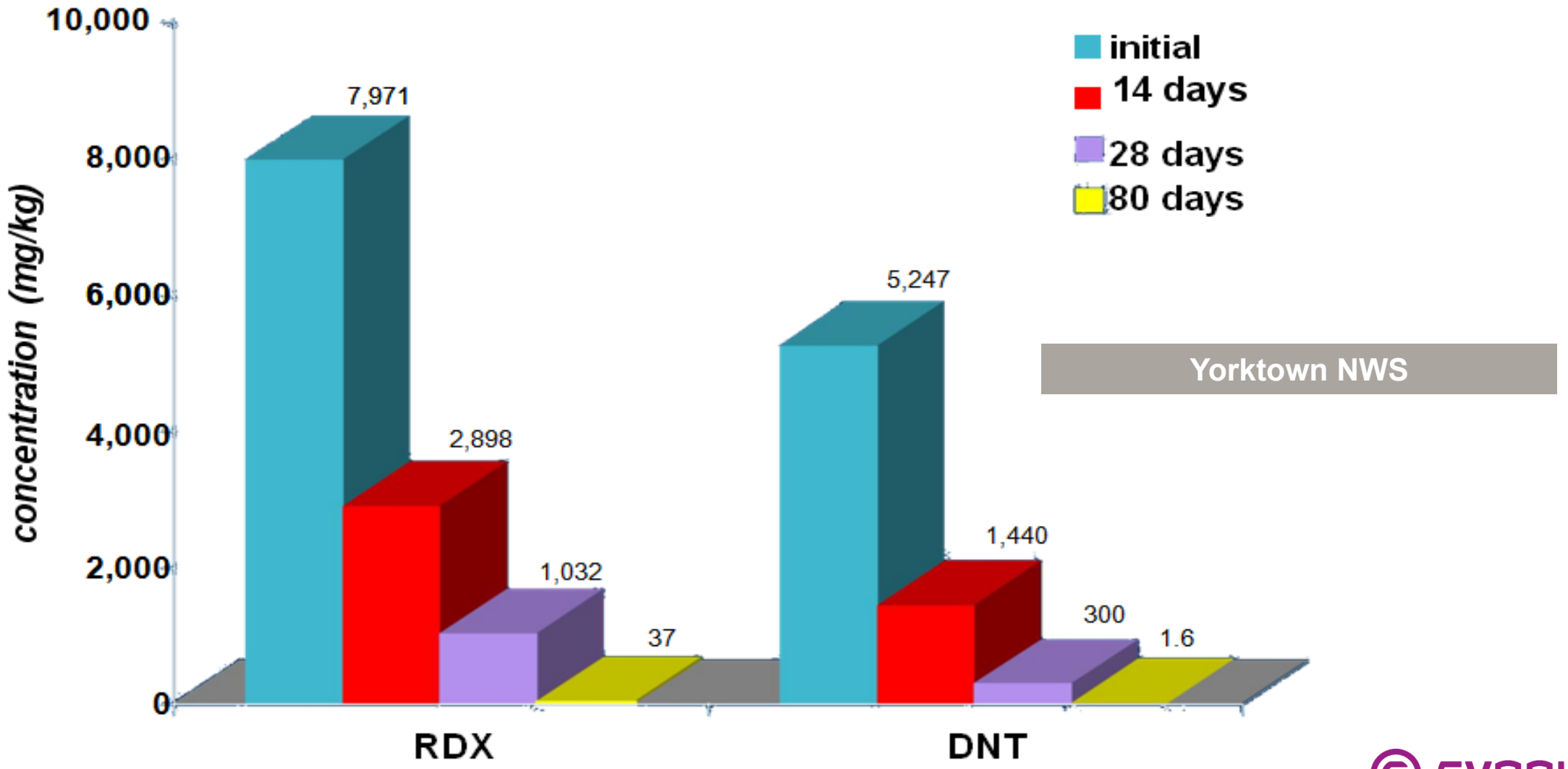
Influence of Daramend® Treatment on RDX and DNT in Soil



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Pilot Study

Tooele Army Depot
Tooele, UT

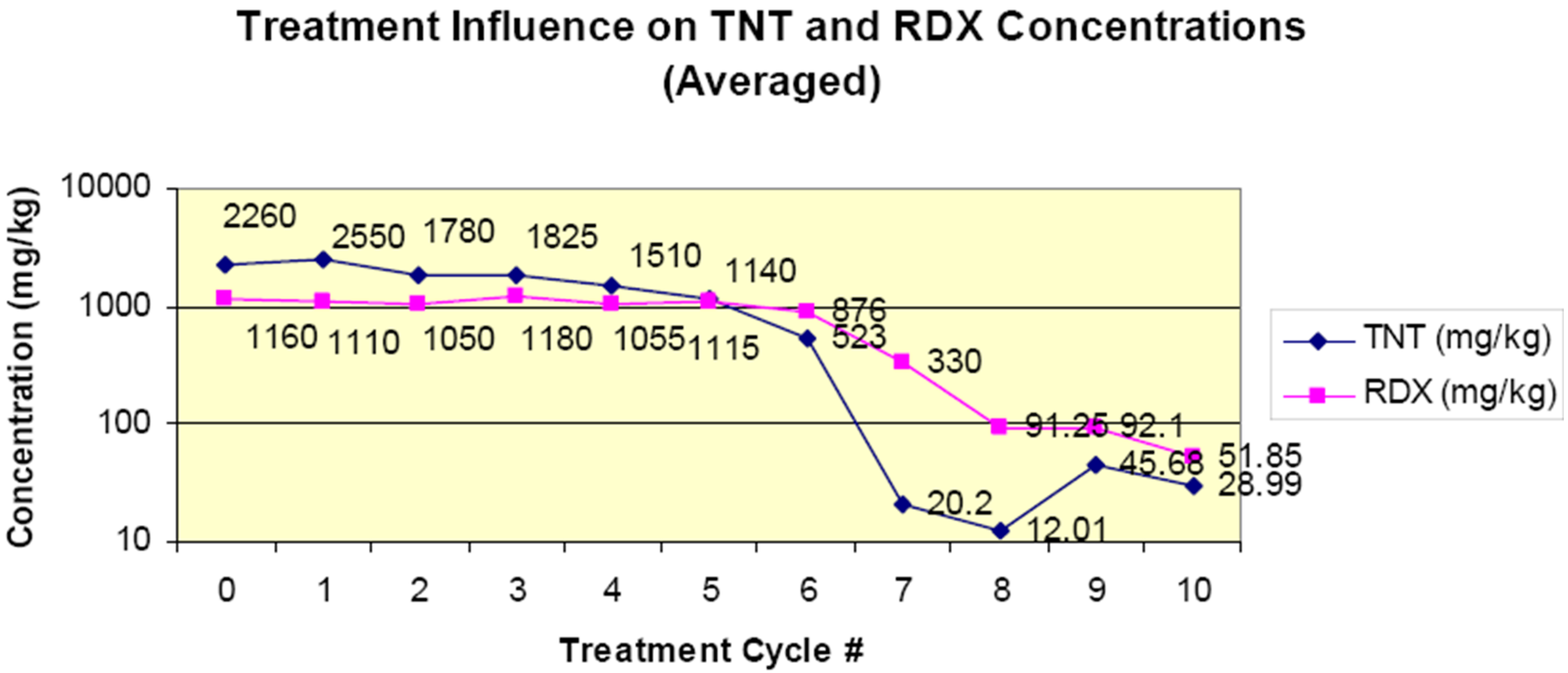
Project Background

1. Tooele Army Depot (TEAD, Near Salt Lake City)
2. TNT Washout Facility (SWMU-10)
3. ~10,000 CY Soil
4. TNT and RDX (up to 2500 and 1000 mg/kg)
5. Exposure Pathway
6. Treatment Goals (TNT – 86 mg/kg; RDX – 31 mg/kg)
7. Selected Remedy

Implementation - Pilot Study

- 7 CY Soil treated in Greenhouse
- Soils initially cool and soil relatively dry
- Increased moisture (62% -92%) and temps (13-40 C) in later cycles
- ORP from +75 at start to -550 mV at end
- Cycles typically 0.5 to 1 wt% DARAMEND®

Pilot Results



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Pilot Lessons Learned

Primary

Process Controls

- Maintain soil temp at 25 C or higher
- Target 90% soil WHC

Secondary

Process Observations

- ORP
- Odor
- Soil Consistency
- Fungus

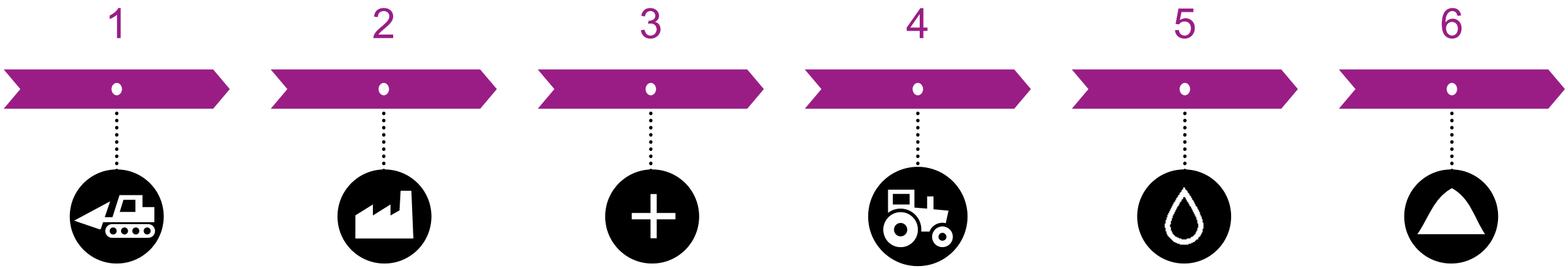
Full Scale Case Study

Tooele Army Depot
Tooele, UT

Implementation - Full Scale

- Conducted inside building (2008)
- ~3000 CY/batch
- 3.5 wt% DARAMEND/batch
- 8900 CY treated

Daramend® Implementation Steps – Tooele Site



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Soil Excavation

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Soil Placement

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DARAMEND® Addition

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Soil Tilling

Water Addition

Create Piles

Fungus

Full Scale Results

- Single DARAMEND® Addition
- Additional declines over time
- Little Process Data Collected
- Slow Water Additions (1 week)
- Product Cost $62/CY
- 8900 CY treated
- $4.75 million under budget
- Dosage ~5% of Conventional Composting
  - 3.5 wt % DARAMEND
  - 70 wt % Organic Matter for Compost

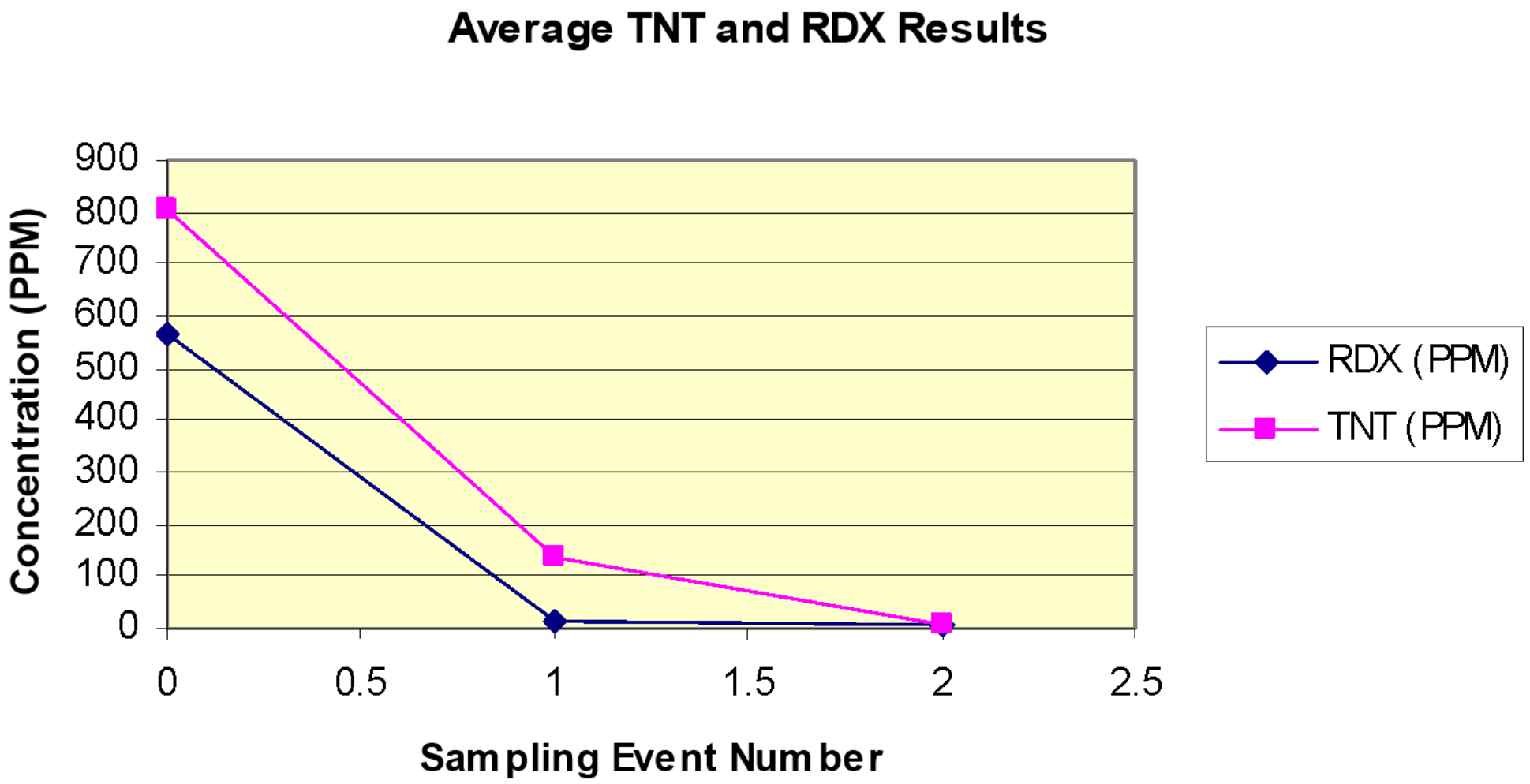
Batch 1 Data

	Treatment Goal	Initial*	Post Treatment*	One Week Post-Treatment**
RDX (PPM)	**31**	563	13	6
TNT (PPM)	**86**	802	138	7

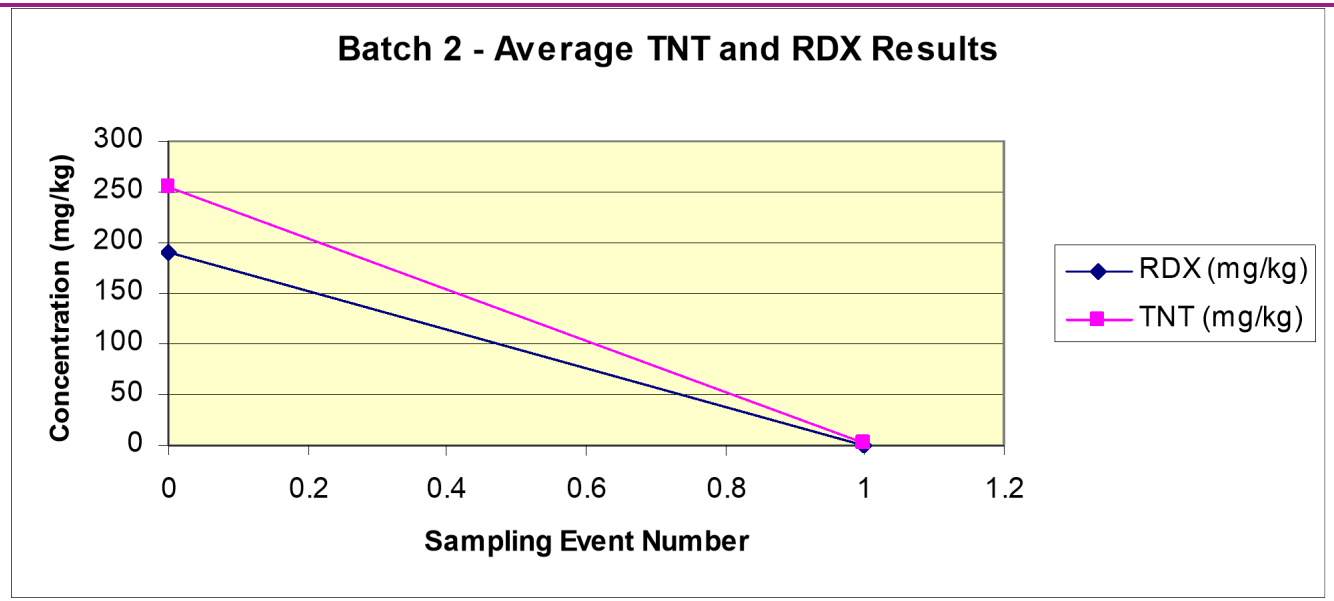
* Average of six samples

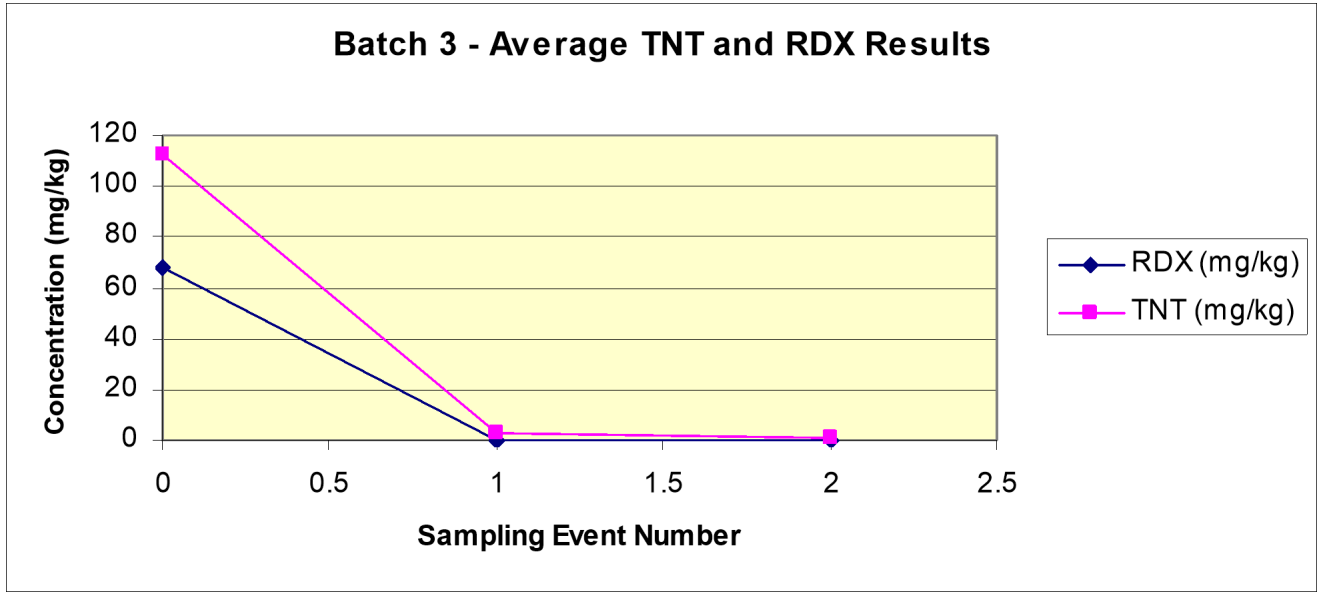
** Average of three samples (re-sample of highest areas)

Batch 1 Data, cont.



Batch 2 and Batch 3 Results





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Daramend® Technology Summary

- ✓ 25-year track record with a wide range of soil conditions
- ✓ Proven effective for treatment of organic explosive compounds, as well as most chlorinated pesticides, herbicides, cVOCs
- ✓ Economical alternative to off site disposal.
- ✓ Promotes contaminant destruction over sequestration or relocation.
- ✓ Sustainable low carbon footprint approach that enables soil recycling/reuse.

Questions?

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