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Full-Scale Alkaline Hydrolysis of Organic Explosives in Soil

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Presentation Overview

- Explosives at defence sites in North America
- Conventional remediation approaches
- Innovative options
- Successful case histories
- Further applications

Distribution of Explosives Contamination at Defense Facilities

- Organic explosives and their residues prevalent at:
  - army ammunition sites
  - ordnance sites
  - range sites
  - other federal manufacturing and storage facilities
- Predominant organic explosives are
  - trinitrotoluene (TNT)
  - dinitrotoluenes (DNTs), and
  - royal demolition explosive (RDX)

Conventional Remedies for Organic Explosives

- Biological Treatment: Feasible but can be slow and cumbersome
- Chemical Oxidation:
  - Employs application of strong oxidants such as hydrogen peroxide, sodium permanganate, or sodium persulfate,
  - Largely unproven, and
  - Could require repeated applications making the process prohibitively expensive
- Stabilization:
  - Difficult for organic explosives
  - Disposal issues
- Existing limitations call for an innovative approach

Case Study – Site Description

- Volunteer Army Ammunitions Plant
- Government-Owned/Contractor-Operated facility
- Primarily used for the production and storage of TNT
- Built 1941 to 1943 in support of World War II effort, then Korean and Vietnam conflicts; production ceased in 1977
- In addition to extensive nitroaromatics contamination, metals contamination also present resulting from acid production in support of TNT manufacturing.

Innovative Treatment of Explosives

- CMS recommended excavation, stabilization, and offsite disposal for explosives
- Remedial goals required innovation
  - effective treatment of large quantity of soil
  - cost and schedule constraints
- Implemented in-house laboratory bench-scale tests to evaluate chemical treatment using:
  - chemical oxidants (traditional)
  - alkaline hydrolytic and catalytic agents

Alkaline Hydrolysis Process

- Destroys contaminants via nucleophilic substitution
  - Strong nucleophile (hydroxide ion) attacks electrophile
  - Displacement of a leaving (functional) group
- Ring instability and cleavage
- End products such as formate and nitrite/nitrate

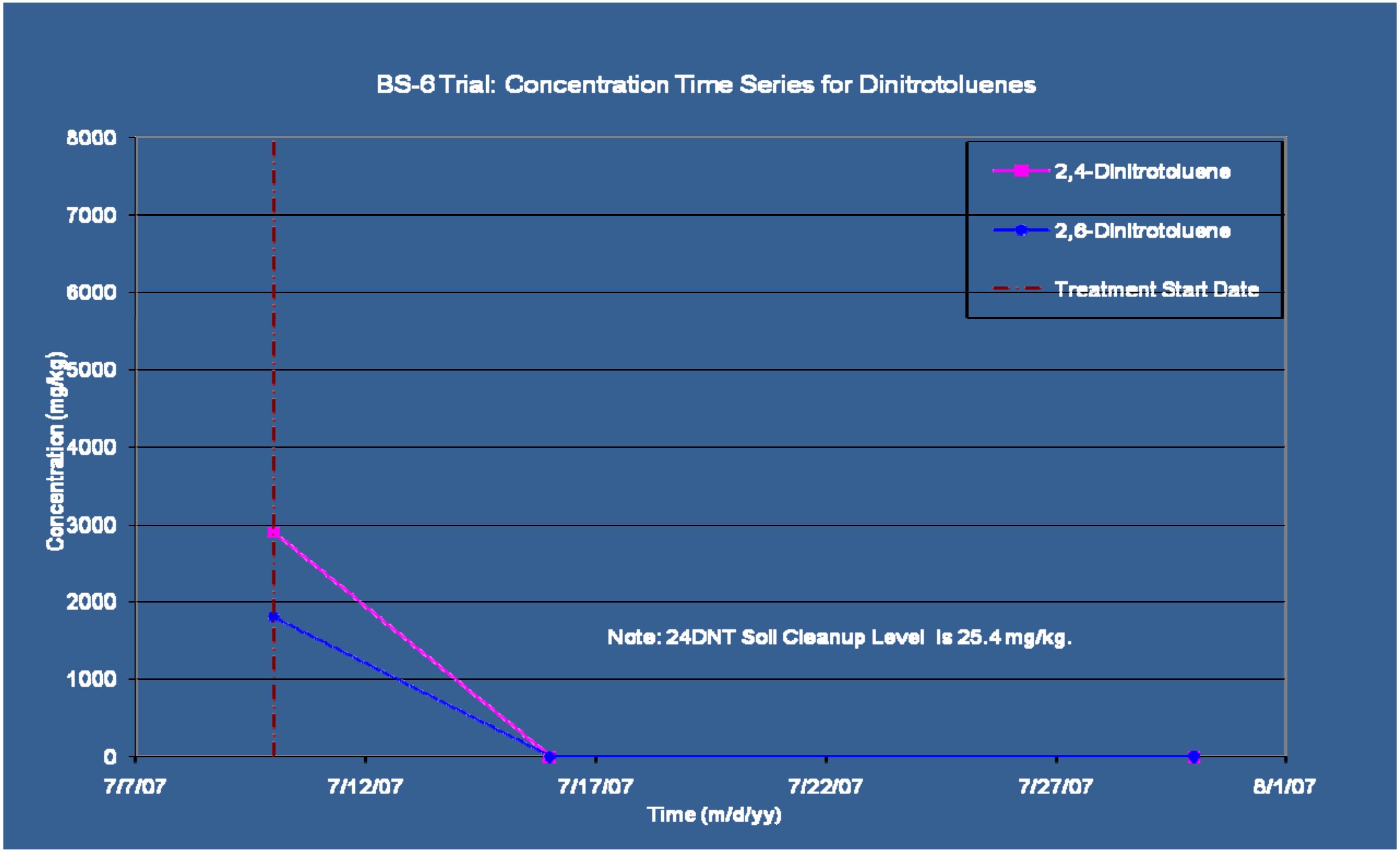
Bench-Scale Set-up

- Soil pan studies
- Varying quantities of selected chemical amendments
- Water added to achieve saturation
- Mixing
- Effectiveness sampling included:
  - pH (SW9040) and moisture content
  - Nitrates and nitrites (E300)
  - Explosives (SW8330B)

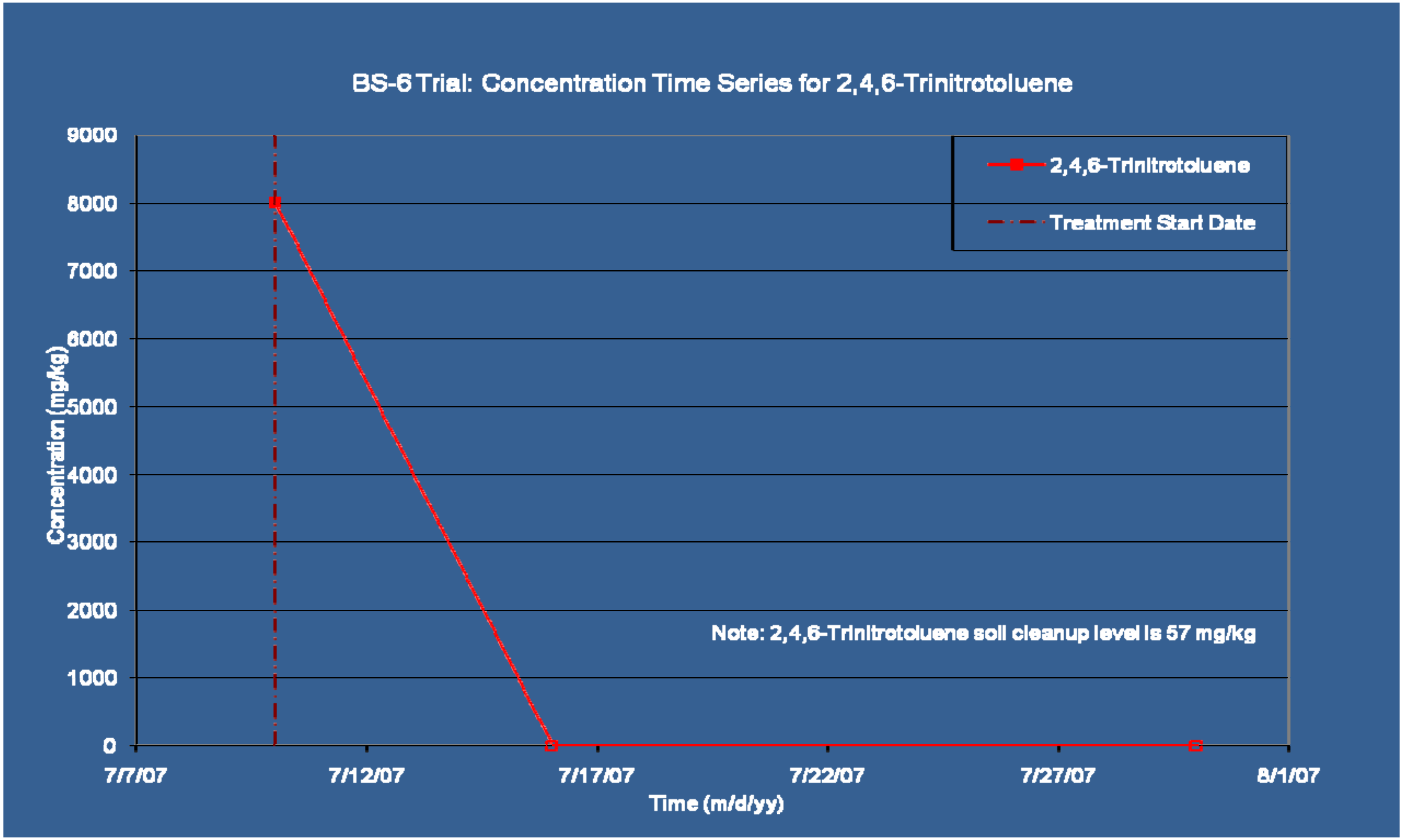
Results Of Bench-scale Studies

- Bench-scale results indicated:
  - High levels of explosives could be treated rapidly (within a week) using an alkaline hydrolytic agent
  - “Material Balance” indicated complete treatment with no accumulation of organic daughter products
  - Nitrites are the largest identifiable end product (denitrification could be required)
  - Treatment in the field would be feasible and economical

Results Of Bench-scale Studies



Results Of Bench-scale Studies



Denitrification Bench-Scale Study

- Evaluate citric acid as an organic substrate to determine its potential to treat elevated nitrate and nitrite concentrations in soil resulting from chemical destruction of TNT and DNT
  - Citric acid was chosen as the organic substrate because it:
    - serves as a carbon source for denitrification bacteria
    - lowers the pH to neutral conditions
- Estimate the time required for treatment and the kinetics of chemical degradation

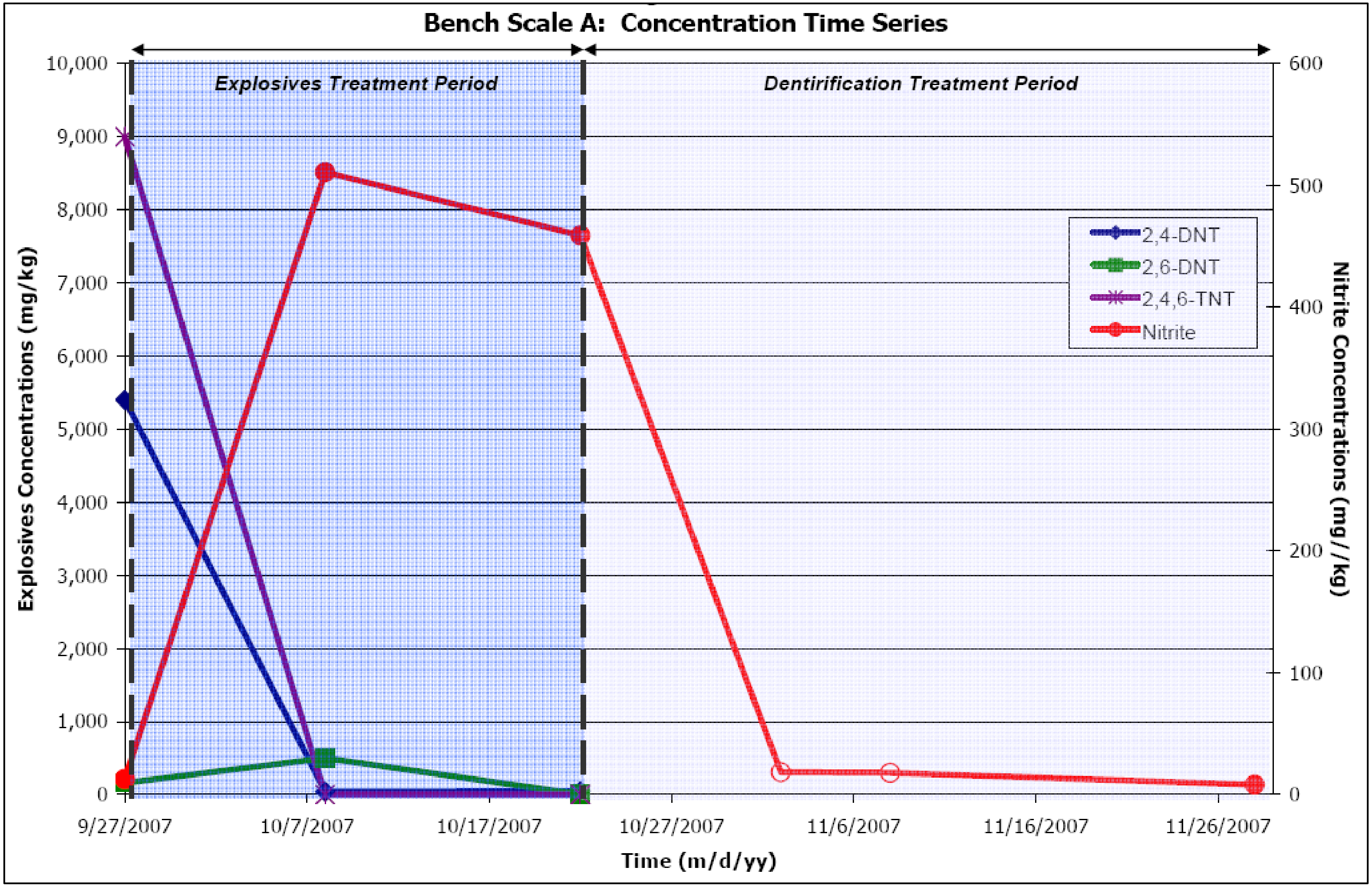
Bench-Scale Study – Set-Up

- Two soil pan tests containing approximately 4 kg each of soil from contaminated area
- Phase I – soil pan tests underwent alkaline hydrolysis to remediate the nitroaromatic compounds in soil
- Once treatment was complete (approximately 2 weeks), the denitrification bench-scale began (Phase II)
- Citric acid waste was added to one of the soil pan tests, denoted as BS-A; no citric acid was added to BS-B (control)
- Citric acid was added and mixed using mixing spoons

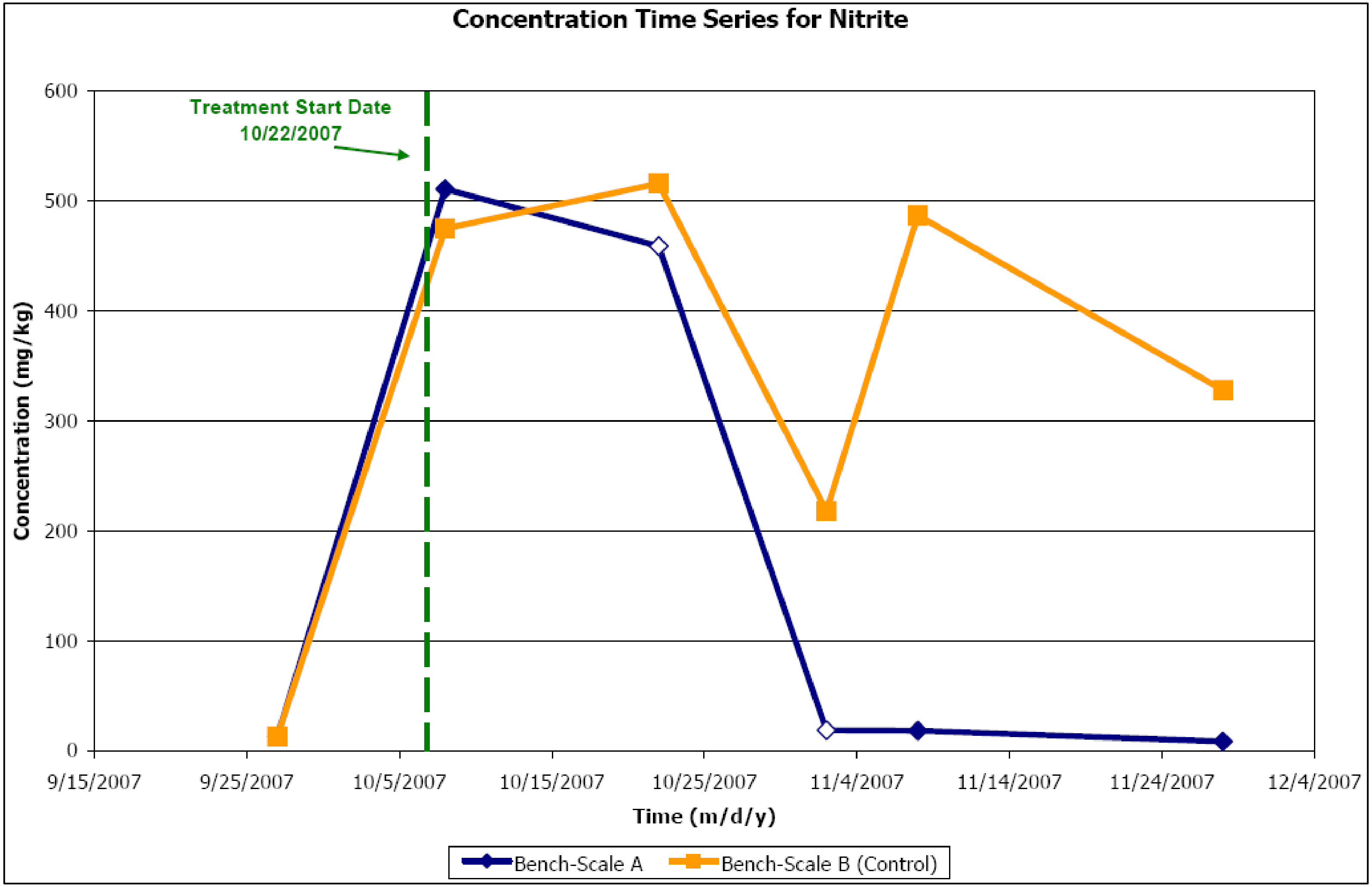
Bench-Scale Study – Results

- Both test trials showed a substantial decrease in nitroaromatic compounds
  - Total DNT and 2,4,6-TNT exhibited greater than a 99% percent decrease in concentrations over the course of the two-week treatment
- Nitrate was not formed in significant concentrations compared to baseline results indicating very little oxidation from nitrite to nitrate
- Nitrite concentrations decreased from 511 mg/kg to non-detect levels during the first twelve days
- The degradation rate for nitrite was calculated to be 0.292 day^{-1}

Denitrification Study: Results



Denitrification Study: Results



Field Pilot Study Results

- 230 m^3 excavated soil in bermed area (~ 30 m by 15 m)
- Designed amounts of alkaline agent and catalyst
- Implemented mixing, moisture, monitoring, and evaluation

COC	Baseline (July 31, 2007)	August 6, 2007 (mg/kg)
1,3,5-TNB	5	0.066
2,4-DNT	800	1.6
2,6-DNT	12	1.5
2,4,6-TNT	230	0.64
Amino-DNTs	ND	0.82
Nitrotoluenes	ND	0.48

Field Pilot Study

Full-Scale Treatment

- Full Scale Ex Situ Treatment
  - Soils excavated and treated within asphalt-lined pond
  - 230 m^3 increments
  - Alkaline and catalytic reagents evenly spread
  - Conventional construction equipment
  - In-house moisture and mixing design
  - pH – primary indicator for uniform physical and chemical mixing of chemicals

Full-Scale Treatment

Full-Scale Treatment

- Full Scale Ex Situ Treatment Results
  - 86,000 m^3 (ex situ) completed treatment (100%)
  - 70 tonnes total nitroaromatic mass removed (>94%)
  - Treated soils below cleanup targets for DNT (25.4 mg/kg)
    - 42% < 2.54 mg/kg for 2,4-DNT (20x rule)
    - Average 2,4-DNT in remaining piles 6.9 mg/kg
- Technology has been examined for groundwater

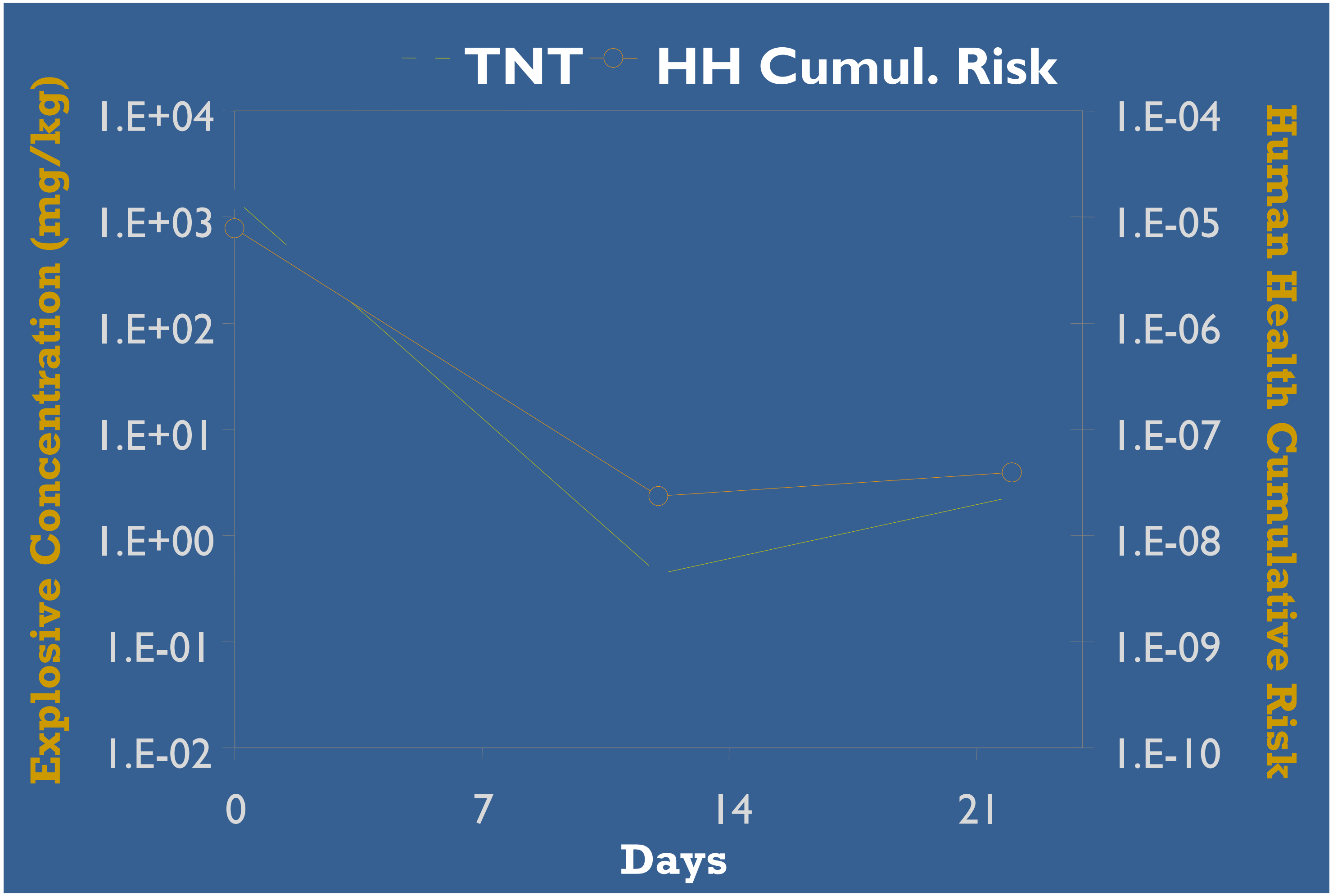
Full-Scale Treatment

- Remaining contaminated soils were treated in situ
- Results indicate in situ treatment is effective and comparable to ex situ treatment
- To date, 11,500 m^3 of contaminated soil has been successfully treated in situ – site has been closed

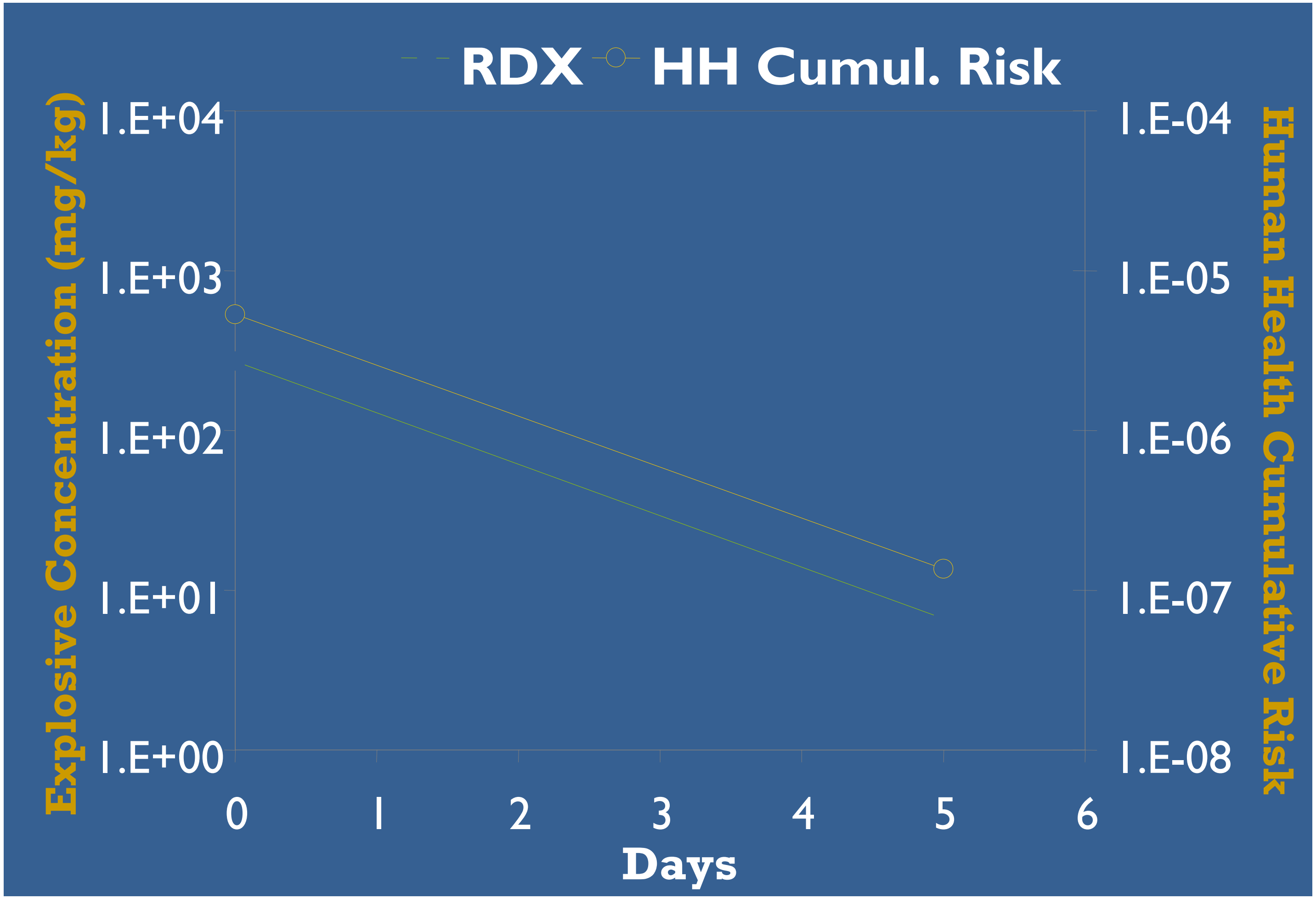
Second Case Study

- Over 13,000 m^3 of soil treated
- Summer 2008 – successful demonstration of bench-scale, pilot-scale, and currently full-scale using out technology experience at VOAAP
- July – October 2009 – completed and confirmed the treatment of soil in one season

High TNT Concentration
604 KG of TNT destroyed in 21 days



High RDX Concentration
113 KG of RDX destroyed in 5 days



Applications

- Can be applied to other sites
- In-situ vadose zone and saturated zone applications
- Variety of alkaline hydrolytic agents
- Range of application/mixing regimes
- Application in colder environments
- Application to other contaminants
- Presence of co-contaminants

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Questions