EPA 8330B: Issues and Status

Environmental Monitoring and Data Quality Workshop

April 2014

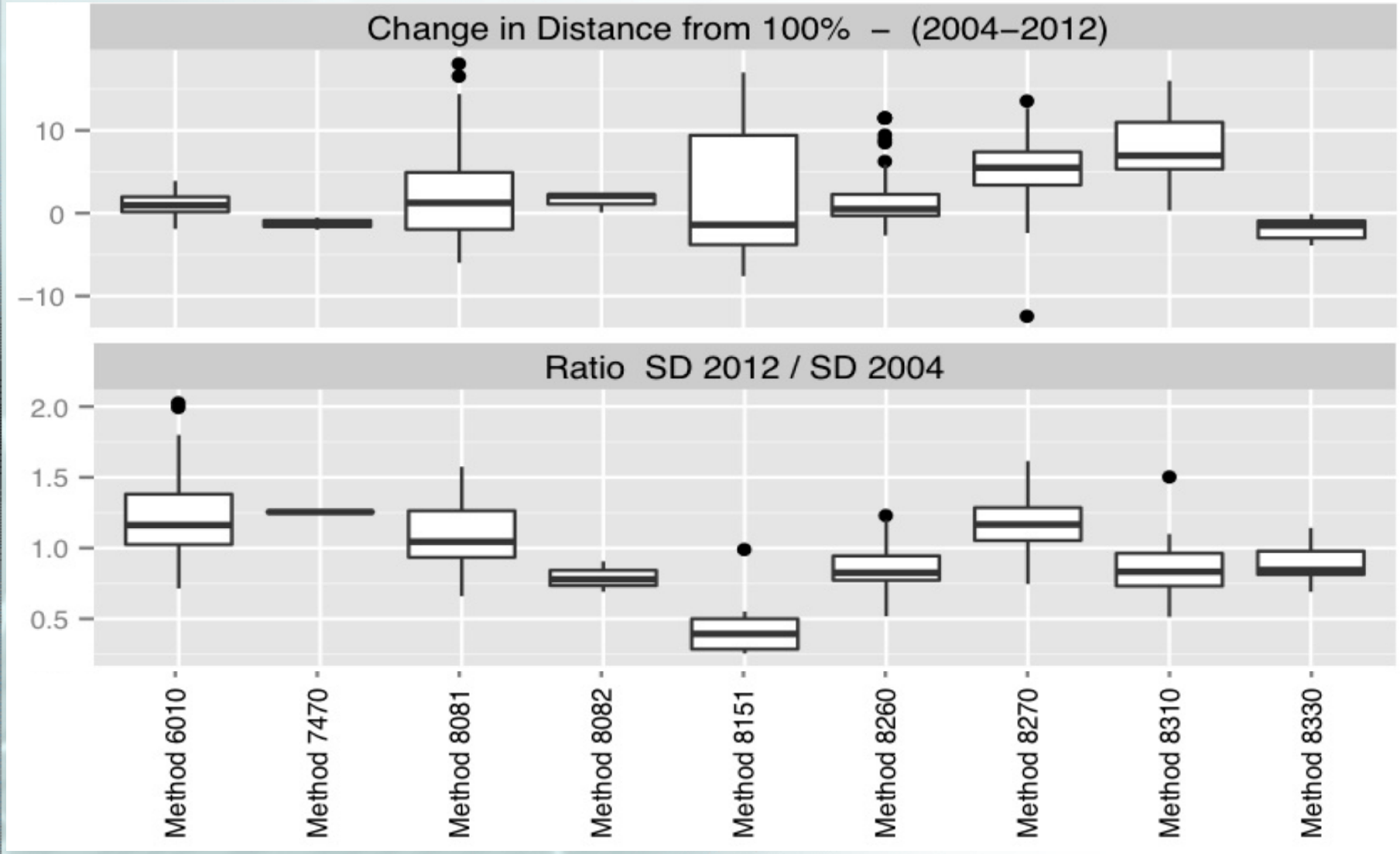
Ed Corl
NAVSEA LQAO

8330B Session Overview

- **Ed Corl (NAVSEA LQAO)- Current status, overview of QSM Version 5 LCS limits, FAQ's, path forward.**
- **Dr. Tom Georgian (USACE)- Problems associated with drying.**
- **Dr. Chung-Rei Mao (USACE)- Problem associated with alkaline hydrolysis of explosive constituents.**
- **Janice Willey (NAVSEA LQAO)- 8330B QSM Version 5 specifics.**
- **Panel discussion Q&A.**

- EPA 8330- 1994
- DoD LCS Control Limits May 2004
- 8330B- Revision2- October 2006
- 8330A- Revision1 February 2007
- EDQW Guide for Implementing 8330B July 2008
- DoD LCS Control Limits- July 2013

LCS Comparison



8330 LCS Comparison

	2004 mean	LCL	UCL	2013 mean	LCL	UCL
1,3,5-Trinitrobenzene	99	73	125	101.9	80.8	123
1,3-Dinitrobenzene	102.3	79	126	104.2	84.1	124.4
2,4-Dinitrotoluene	101.9	80	124	102.3	81.7	123
2,6-Dinitrotoluene	100.2	78	122	102.4	86.1	118.8
(TNT)	98.5	57	140	100.2	75.1	125.2
2-Amino-4,6-dinitrotoluene	102	80	124	103.8	86.5	121
2-Nitrotoluene	101.2	80	123	102	83.9	120.1
3-Nitrotoluene	99.9	77	122	103.3	79.1	127.4
4-Amino-2,6-dinitrotoluene	101	79	124	104.2	84	124.3
4-Nitrotoluene	100.6	76	125	102.2	82.6	121.8
(RDX)	103	72	134	103.1	82.4	123.8
Nitrobenzene	100.4	77	124	103.9	80.1	127.7
(HMX)	100	74	126	99.1	76.6	121.7
Nitroglycerin				97.2	72.6	121.8
PETN				100.9	78.4	123.4
Tetryl				101.8	66	137

- Analytical Differences- 8330B added:
- Nitroglycerin
- PETN
- 3,5-Dinitroaniline
- Dual UV 254/210 nm or diode array, HPLC, GC-ECD, or other techniques
- Appendix A- MIS
- Sampling, drying, sieving, grinding

EPA Method 8330B released in 2006 calls for drying and sieving (10 mesh or 2 mm) entire sample →

Should drying and sieving be performed In the laboratory? What about the LCS?

← Entire portion <2 mm subjected to grinding, then subsampling is conducted using a MIS technique in the laboratory

Contamination from carry-over?

From: Chuck Tomljanovic, NDCEE/CTC, E2S2, June 2010.

2008 EDQW Implementation guide

- A laboratory control sample (LCS) consisting of a solid reference material containing all reported analytes, must go through the grinding process and be analyzed with each batch.

DoD Environmental Data Quality Workgroup

Guide for Implementing EPA SW-846 Method 8330B

Introduction:

In November of 2006 the Environmental Protection Agency (EPA) published method 8330B.[1] The method provides instruction for the trace analysis of explosives and propellant residues by high performance liquid chromatography (HPLC). The method includes an appendix (A), which describes sampling methodologies for collecting and processing representative samples for analysis.

Issue:

Method 8330B introduces several concepts that are new or are a change from 8330 and 8330A. The sampling and analytical modifications in 8330B are collectively intended to decrease the effects of sampling and subsampling error caused by the compositional and distributional heterogeneity typically encountered in solid environmental media at military training ranges. Various studies have shown that concentrations of energetic residues at military training ranges that were measured using the procedures in 8330B were statistically more representative relative to traditional sampling and analytical protocols[2,3,4]. However, it is uncertain as to whether some of the new concepts utilized in 8330B represent viable sampling and analytical procedures that can be adopted within other SW-846 methodologies or if all of these concepts have practical application to environmental investigations other than military training ranges. Therefore, the application of these sampling and sample preparation techniques to constituents other than those listed in 8330B should be applied with great caution. Like most SW-846 methods, 8330B is a guidance method that provides for flexibility in the choice of apparatus, materials, reagents, and supplies. The objectives of this paper are to highlight those steps that represent a change from historical sampling and analytical methodologies, to provide recommendations as to the appropriate use of the concepts presented in Method 8330B, and to provide recommended minimum method QC requirements for laboratories performing Method 8330B.

Scope:

This paper addresses all aspects of Method 8330B. For simplicity, Method 8330B has been separated into three phases: sampling, preparation/extraction, and analysis. The methodologies that represent changes in each phase, and key issues associated with those

1

http://www.denix.osd.mil/edqw/Index.cfm

2008 EDQW Implementation guide cont.-

- Grinding equipment must be thoroughly cleaned between the processing of separate samples and grinding blanks must be processed and analyzed to ensure cross-contamination is not occurring.

- Although Method 8330B is scoped to include soils and sediments, there is evidence that drying samples with high moisture content (e.g., sediment) can significantly affect recoveries.

http://www.denix.osd.mil/edqw/Index.cfm

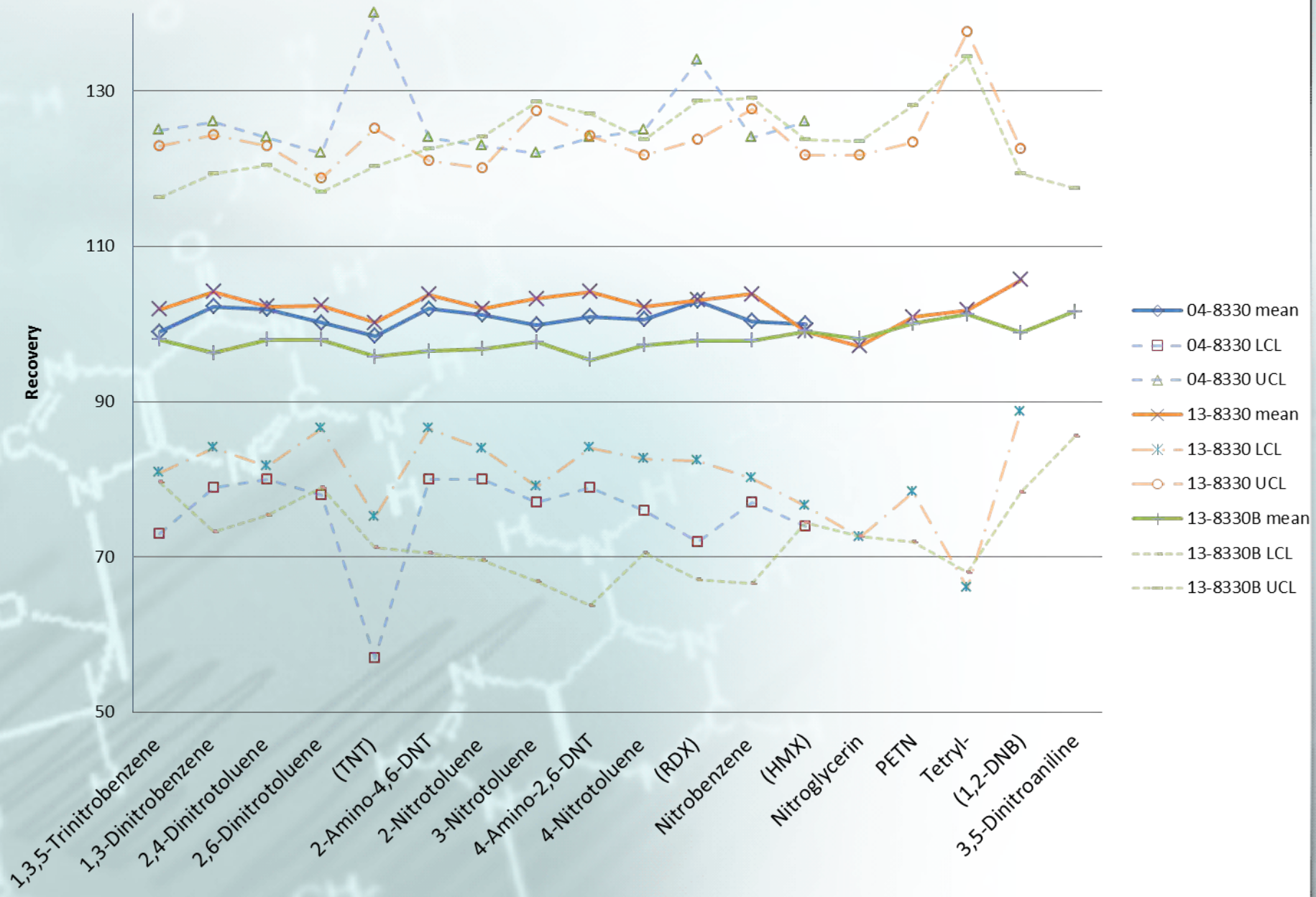
2004 LCS Evaluation

- 8 data sources
- 160-212 records
- Allowed variation in procedures
- Limits established using a 2-phase statistical approach
- Remove outliers (Youden/Grub)
- (ANOVA) between different method-specific parameters
- Pool data as appropriate
- Set control limits (*CL* = mean ± 3*SD)*
- Poor performer (LCL<10% identified)-Tetryl 10-150% CL's
- Allowable sporadic failures approach (>5% total analytes)

2013 LCS Evaluation

- 9 data sources
- 326-618 records
- Allowed variation in procedures
- Remove outliers (Tukey)
- (ANOVA) between different method-specific parameters
- Pool data as appropriate
- Set control limits (*CL* = mean ± 3*SD)*
- More records used
- Separated 8330 and 8330B

8330 LCS comparison



- Grinding- Method 8330B suggests grinding of samples to a particle size of <75 µm. This is a change from the previous Method 8330 which directs particle size reduction to 30 mesh (595 µm).
- Sieving- Not required in previous 8330 method
- Drying- procedures for drying to constant weight
- Laboratory Subsampling Procedures- not provided in previous version
- Extraction of additional sample mass (10g)
- Holding Times?
- Grinding Blanks- not required previously

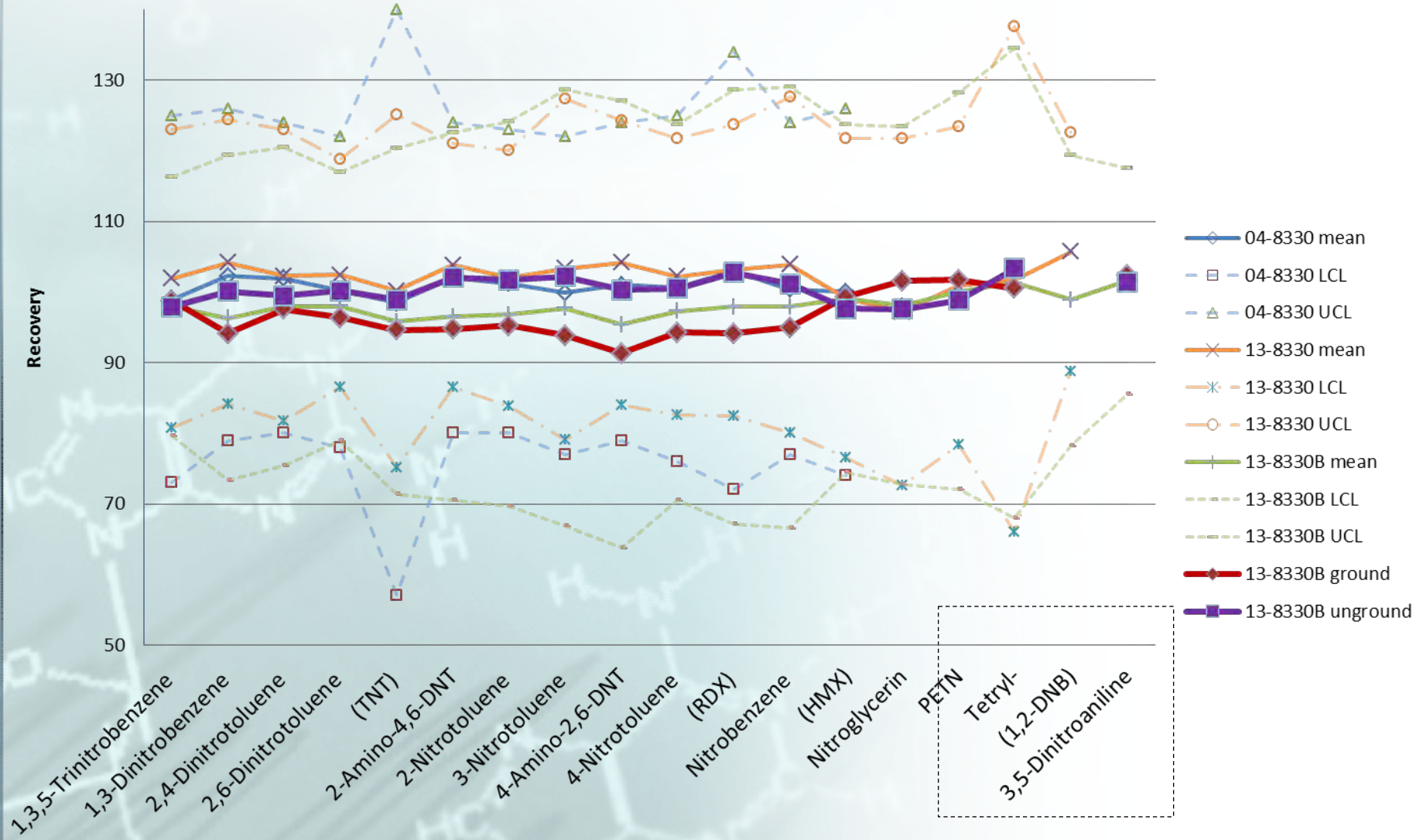
9 labs submitted data in 2013 data call for 8330B:

Prep methods identified:

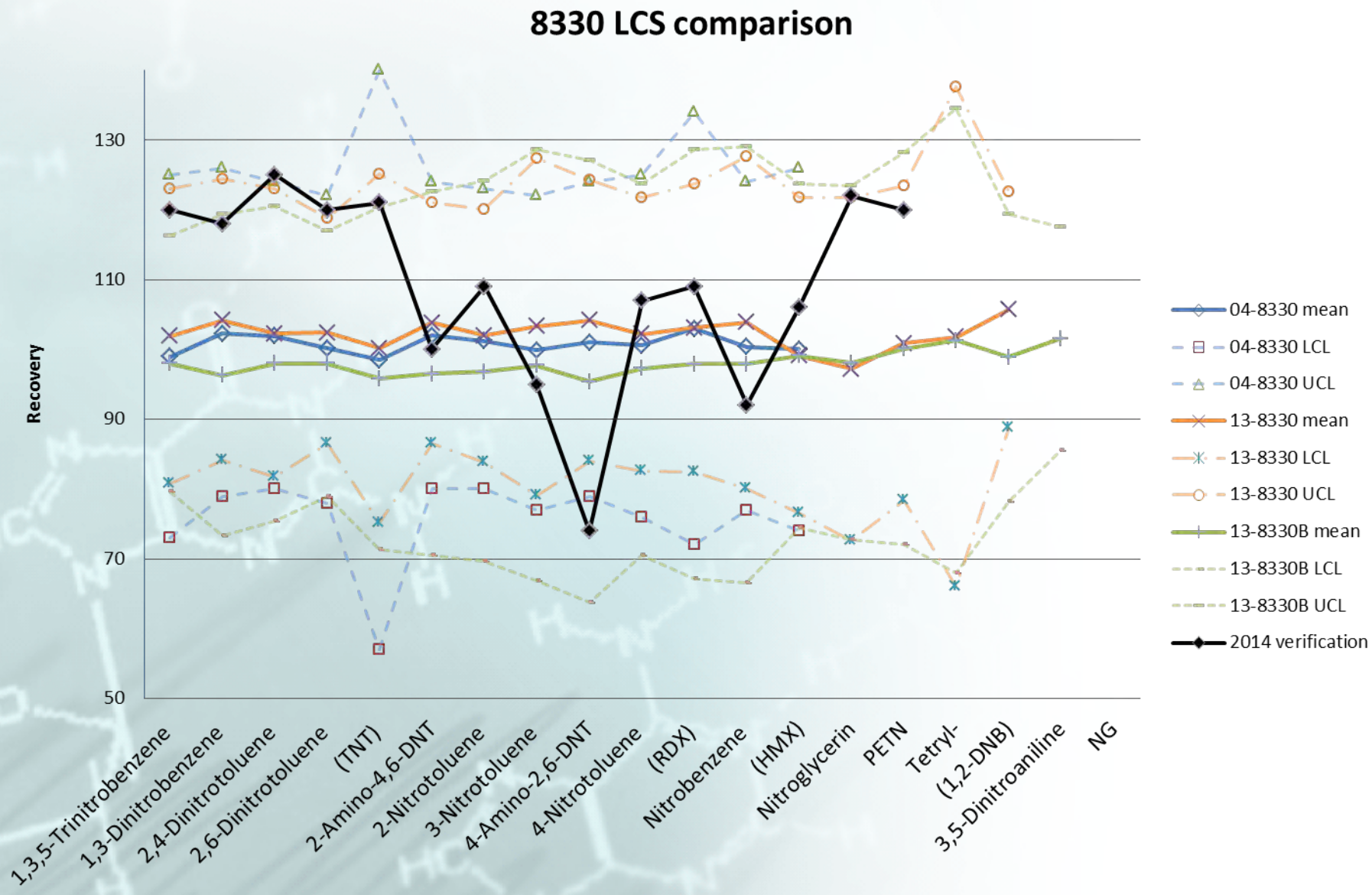
3550 grind
SW846 3535A
SW846 8330B
grinding in prep
SW8330
GRIND_SHAKE
SHAKER
Grinding/SW3535
8330_sonication

Some labs identified no-grinding in the cleanup method field
Concentration range 0.1 – 8 ppm for most compounds
Concentration range 0.8 – 40 ppm for nitroglycerin and PETN

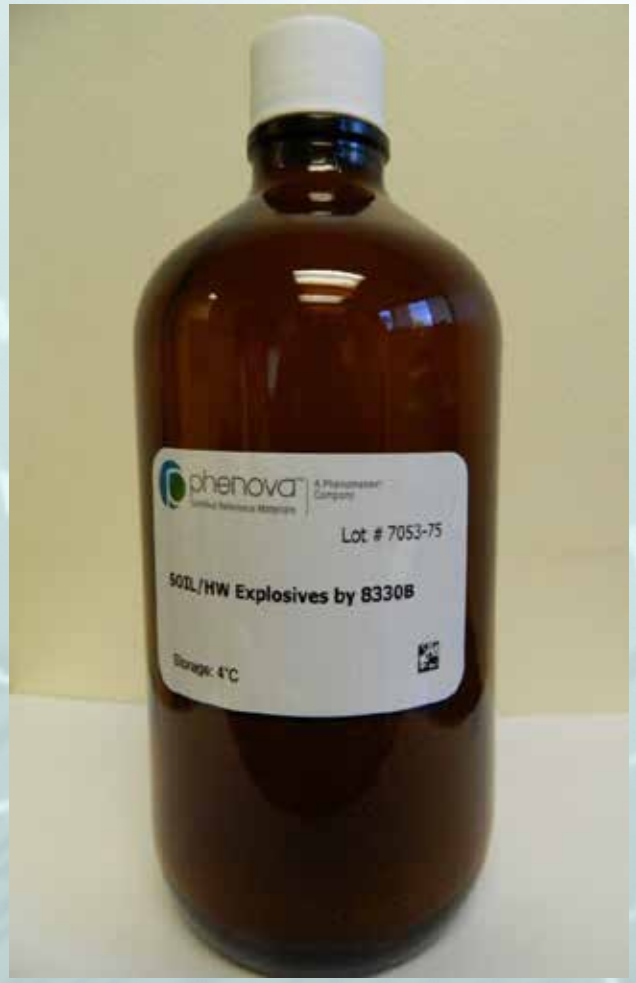
8330 LCS comparison



- Appreciable difference between ground/unground 2013 LCS data
- Not a robust data set for some compounds
- Control limits calculated for pooled data still met



Single lab witness/verification of ERA reference standard suggests QSM Version 5 limits are achievable



There are standard reference materials available.

The material MUST be ground prior to extraction and analysis.

Lab may not dilute material.

May not contain all analytes (tetryl) which will have to be spiked.

Frequently Asked Questions:

Q Is sieving necessary and can it be performed in the field?

A A 2mm nominal sieving is required and should be performed in the laboratory.

Q The QSM requires that the reference material go through the same processing steps as typical samples. So, am I required to sieve and dry the reference standard in order to utilize it as my LCS?

A No, the objective of the LCS is to measure lab performance in a similar but ideal matrix (best case scenario). However, the reference material must go through typical grinding procedures.

Q Wouldn't it make sense for the EDQW to perform an additional data call and correct the LCS limits for the affects of drying?

A No. The affects of drying are dependent upon the type of soil, porosity, moisture content, and analyte of concern.

Frequently Asked Questions Continued:

Q Can a laboratory simply spike a clean sand matrix with a liquid spike to create the LCS?

A The LCS should be a reference material. However, any analytes that are not contained in the reference material may be spiked prior to grinding. There is evidence of low recoveries from spiked sand.

Q Do I have to grind 1Kg of reference material with each batch?

A No, as this is cost prohibitive. Smaller aliquots can be ground and then subsamples extracted with each batch. The reference material should not be diluted.

Q Are grinding blanks required?

A Yes. Grinding blanks are required to evaluate the potential affects of carry-over contamination and shall be performed prior to grinding field samples, after every 10 samples, and at the end of the batch. These grinding blanks may be composited for analysis, however, at least one grinding blank per batch must be analyzed.

Frequently Asked Questions Continued:

Q Are spikes added before or after grinding?

A Both matrix spikes and surrogates are added to the matrix after grinding but prior to extraction.

Q QSM Version 5, Appendix B, Table 3 describes a soil sampling triplicate. Is this the same as the field sample triplicate or sample duplicate?

A No, the soil sampling triplicate described in the QSM, is designed to evaluate potential laboratory bias during the sub-sampling due to heterogeneity of the sample post grinding. Field sample triplicates (or field replicates) collected during incremental sampling events and sample duplicates collected during discrete sampling events, are samples that are co-located in the field that are used to determine the heterogeneity of the site and representativeness of the samples, or the field error.

Q Could you provide some clarification on the hold time for 8330B?

A Soil samples should be treated just like the analysis of base neutral acids (semi-volatiles) in soil samples, which require that hold time start after samples are collected in the field and end with solvent addition.

- If the proper material is used and protocols are followed laboratories should have no problem meeting the QSM LCS limits.

- Project-specific performance criteria (QAPP) always take precedent over QSM or method.

- In-house laboratory control limits for the LCS must demonstrate the laboratory's ability to meet the project's MQOs.

- The EDQW is considering a 8330B web training session.

Laboratory Control Sample (LCS) Dying Studies for Method 8330B

Dr. Thomas Georgian

Chemist

Omaha, NE

April 2014

US Army Corps of Engineers

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To answer an elusive seemingly insoluble conundrum – “a riddle, wrapped in a mystery, inside an enigma” – that has plagued both scientists and philosophers for some time to the very brink of despair.

When testing for explosives by Method 8330B, why aren’t the laboratory control samples (LCSs) dried with the environmental soil samples?

LCS Drying Study

- Unpublished research conducted in June 2008 by the USACE Cold Regions Research and Engineering Laboratory (Alan Hewitt).
- Study was done using 500-g soil standards from Environmental Resources Associate (ERA) that are commonly used as LCSs for Method 8330B. Standard contains 15 of 17 explosives in 8330B:
  - 4-Am-2,6-DNT, 2-Am-4,6-DNT, 1,3-DNB, 2,4-DNT, 2,6-DNT, HMX, NB, 2-NT, 3-NT, 4-NT, RDX, 1,3,5-TNB, 2,4,6-TNT, NG, & PETN
  - Standard lacks Tetryl & 3,5-DNA

ERA Solid Standard for Method 8330B

- ERA provides certified values ("as determined by volumetric and gravimetric measurements") for the solid standard.
- As smaller quantities of the same material are used for PT samples for Method 8330A, ERA also provides recovery ranges for Method 8330A.
- Note: ERA does not provide PT acceptance ranges for Method 8330B.

Experimental Design

- ERA standard (previously refrigerated for > 6 months) was not ground but air dried at room temperature (20 – 22°C) for up to 5 days (120 hours).
- Five replicate sub-samples were analyzed for explosives by Method 8330B at time *t* = 0, 1, 2, 3, 4, and 5 days.
- Mean concentrations and recoveries were plotted against time.

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Compound	Mean %R $t = 0$ *	ERA WLs**	%RSD
4-Am-2,6-DNT	89	46 – 98	3.2
2-Am-4,6-DNT	108	56 – 108	3.5
DNB	100	69 – 116	0.6
2,4-DNT	98	64 – 120	0.3
2,6-DNT	102	60 – 122	0.7
HMX	105	54 – 115	3.6
NB	79	58 – 119	3.3
2-NT	93	67 – 117	2.1
3-NT	92	69 – 124	3.6
4-NT	97	62 – 123	0.7
RDX	95	60 – 116	2.3
TNB	106	58 – 116	2.7
TNT	100	61 – 104	0.7
NG	103		1.2
PETN	107		5.1

* Recoveries calculated from ERA certified values.

** Warning limits = mean ± 2 std dev.

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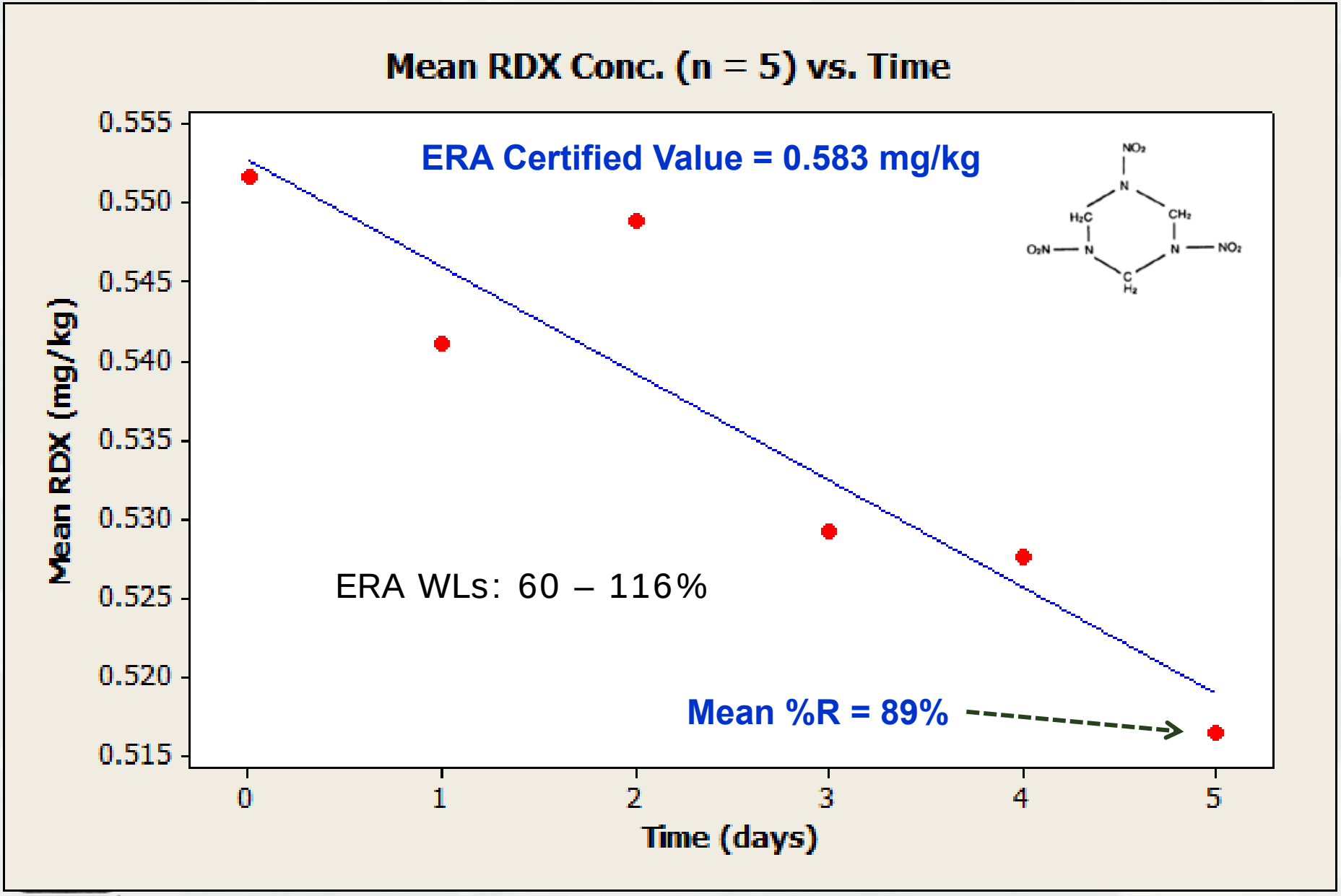
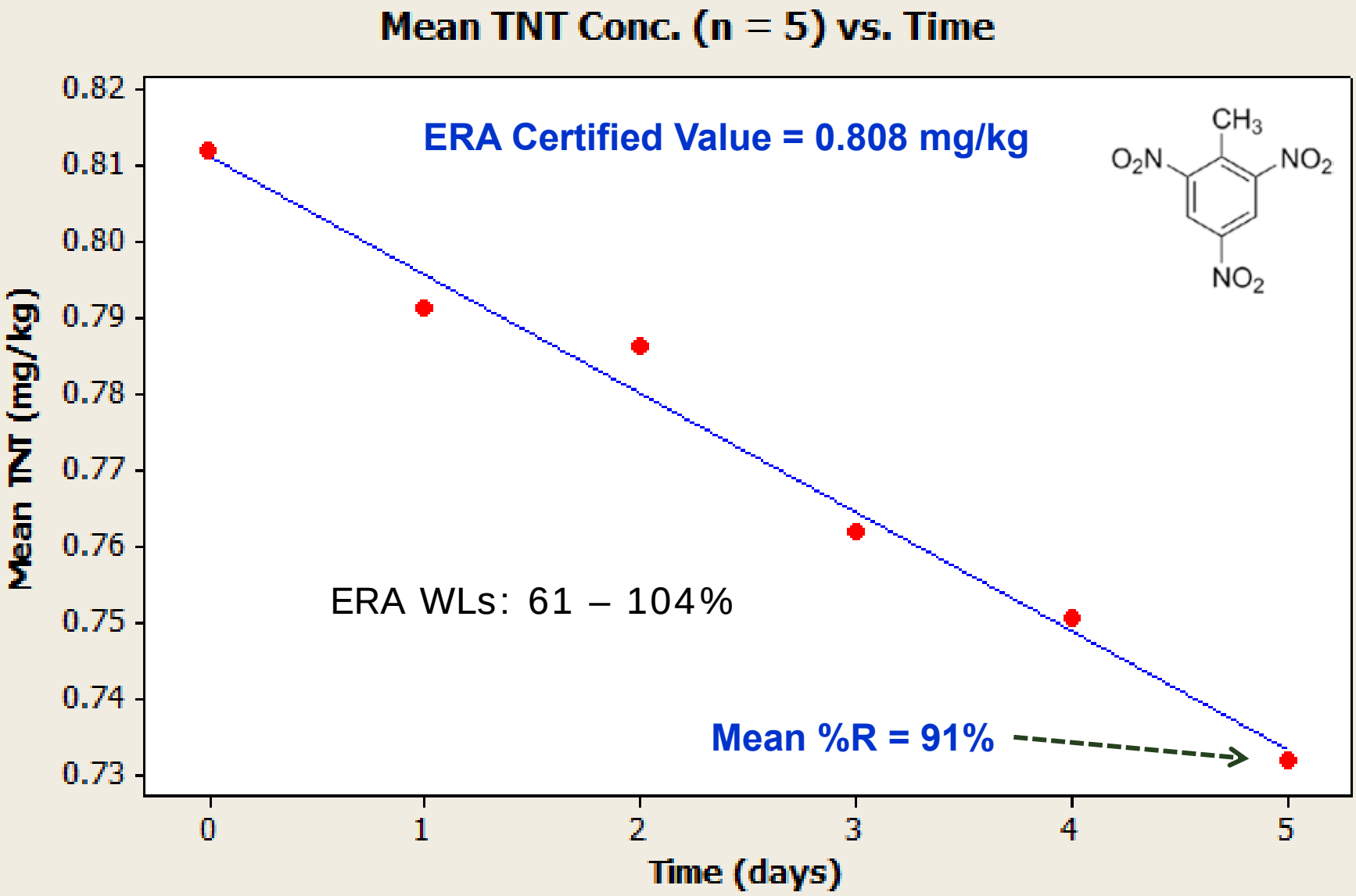
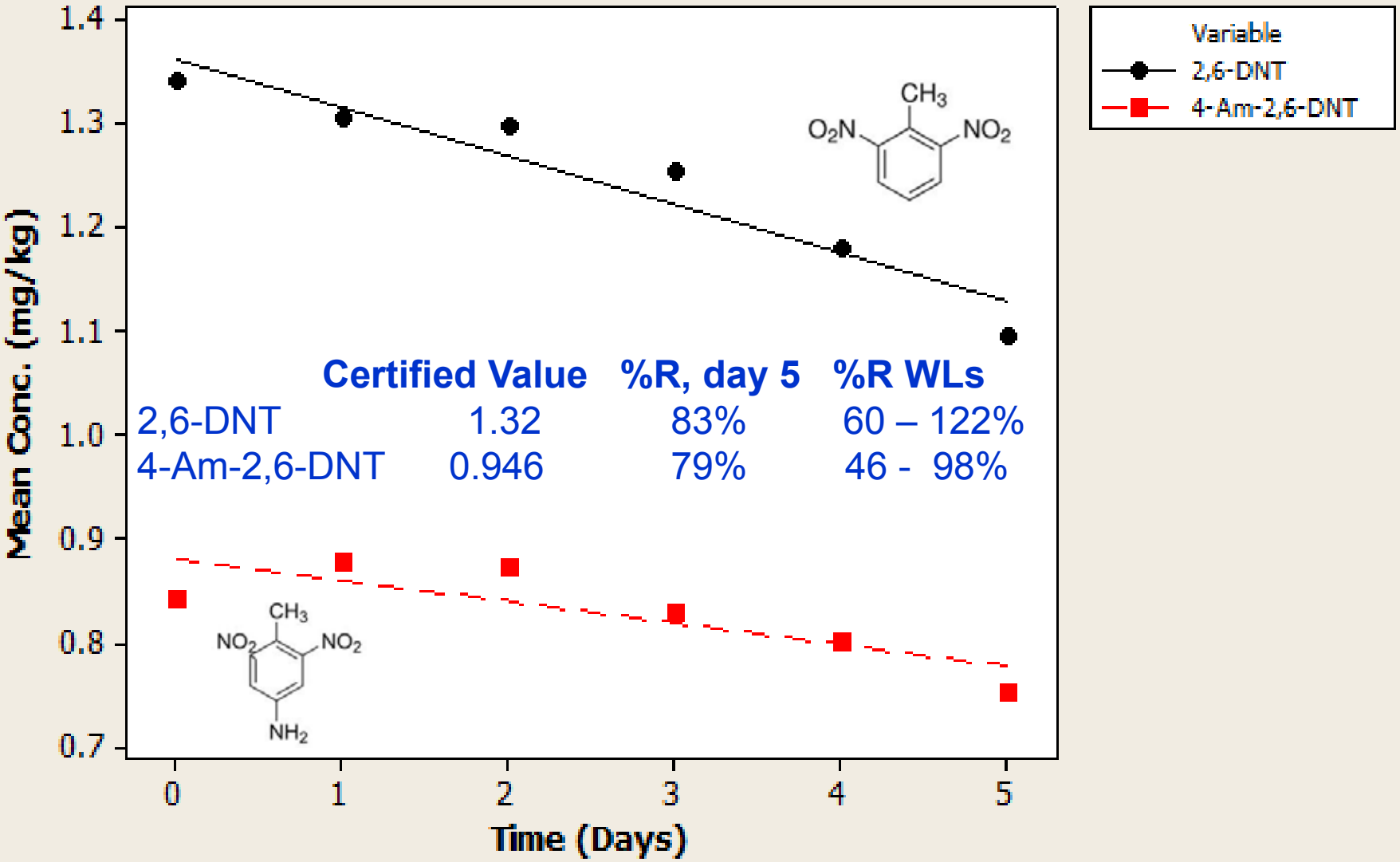
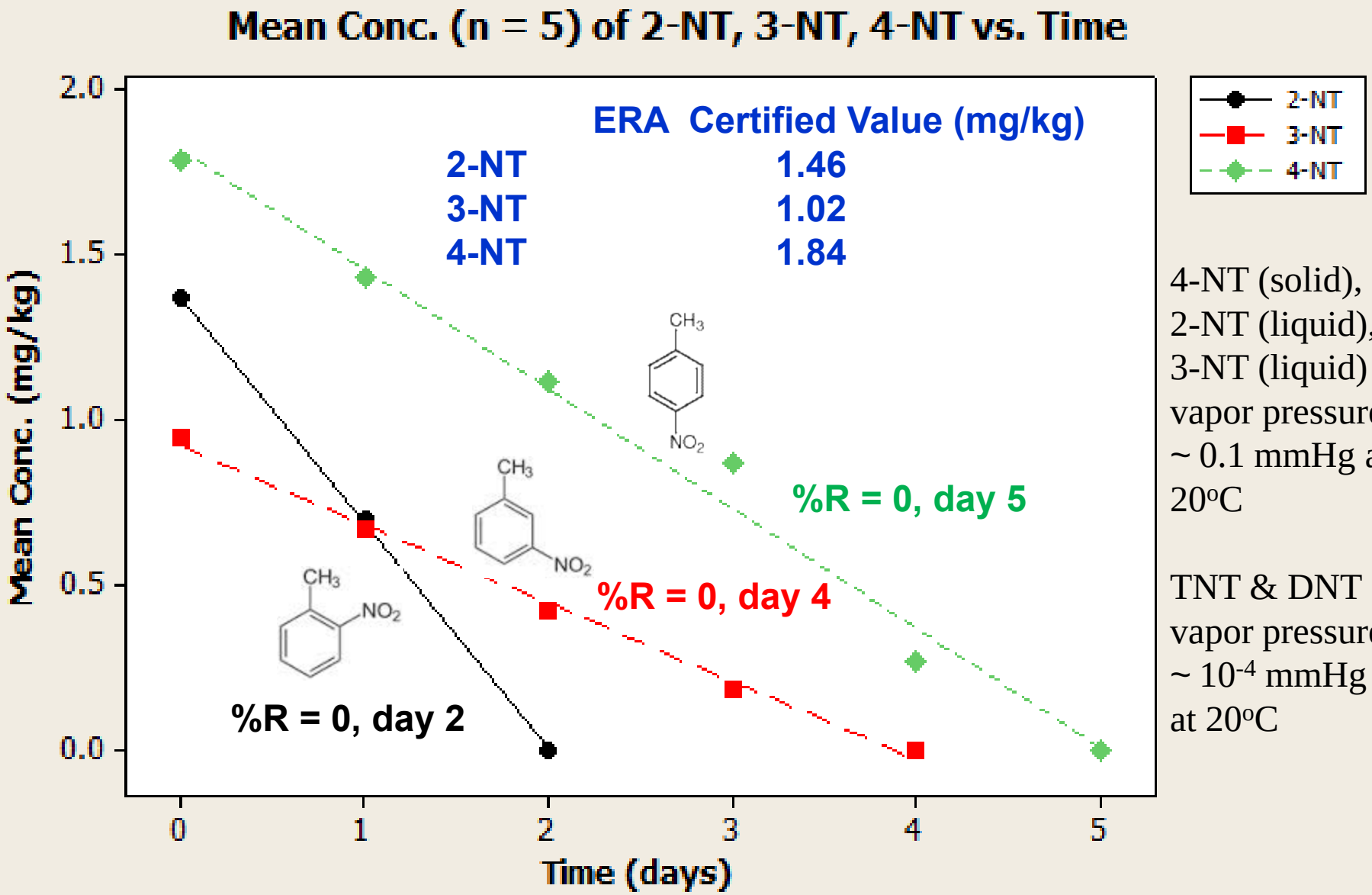

Mean RDX Conc. (n = 5) vs. Time
ERA Certified Value = 0.583 mg/kg
ERA WLs: 60 – 116%
Mean %R = 89%
Mean RDX (mg/kg)
0.555
0.550
0.545
0.540
0.535
0.530
0.525
0.520
0.515
0
1
2
3
4
5
Time (days)


Mean TNT Conc. (n = 5) vs. Time
ERA Certified Value = 0.808 mg/kg
CH3
O2N
NO2
NO2
ERA WLs: 61 – 104%
Mean %R = 91%
Mean TNT (mg/kg)
0.82
0.81
0.80
0.79
0.78
0.77
0.76
0.75
0.74
0.73
0
1
2
3
4
5
Time (days)

Mean Conc. (n = 5) of 2,6-DNT and 4-Am-2,6-DNT vs. Time

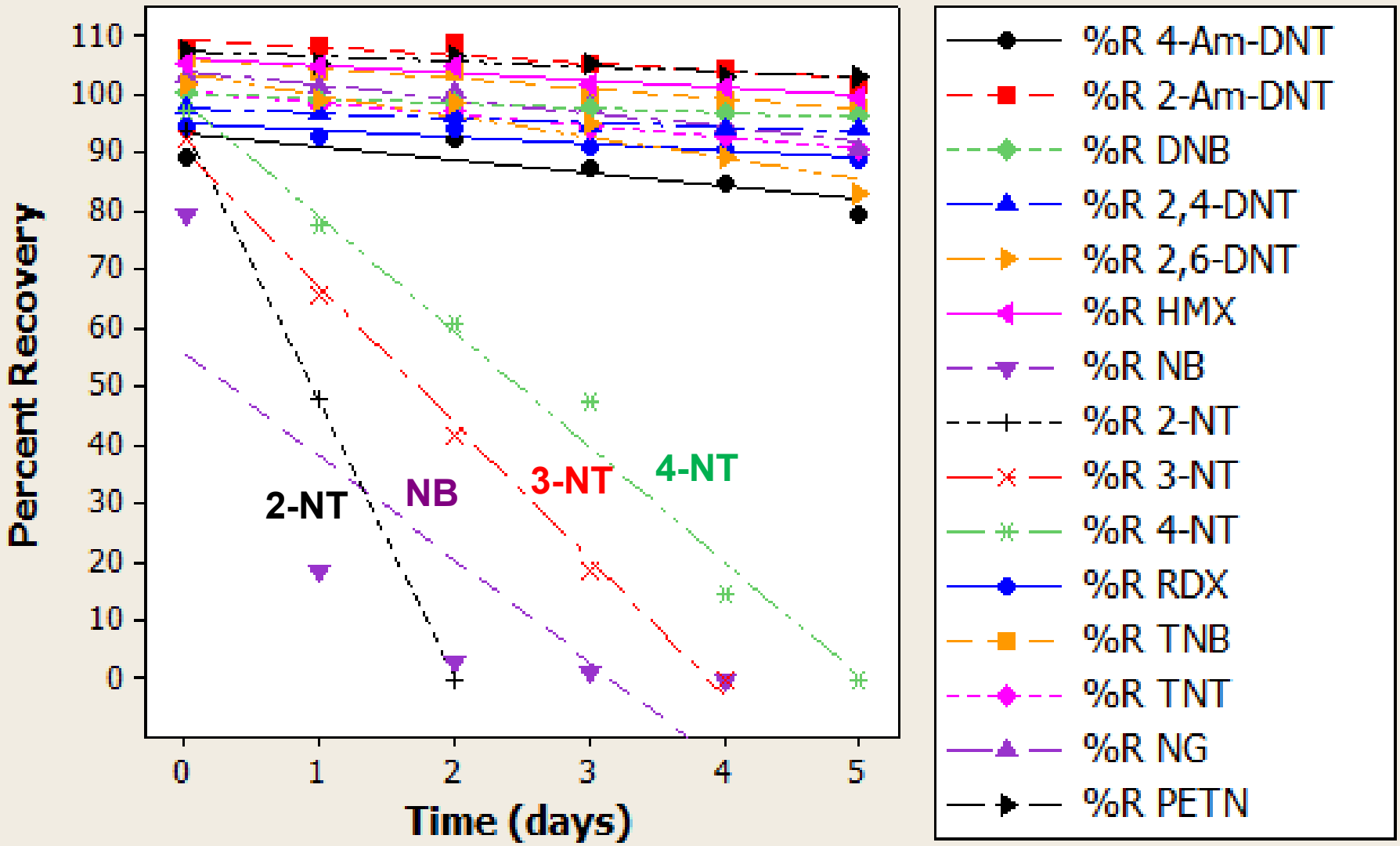


	Certified Value	%R, day 5	%R WLs
2,6-DNT	1.32	83%	60 – 122%
4-Am-2,6-DNT	0.946	79%	46 - 98%



4-NT (solid), 2-NT (liquid), 3-NT (liquid) vapor pressure ~ 0.1 mmHg at 20°C

TNT & DNT vapor pressure ~ 10^{-4} mmHg at 20°C


Percent Recoveries of 15 Explosives vs. Time
Percent Recovery
110
100
90
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
Time (days)
2-NT
NB
3-NT
4-NT
%R 4-Am-DNT
%R 2-Am-DNT
%R DNB
%R 2,4-DNT
%R 2,6-DNT
%R HMX
%R NB
%R 2-NT
%R 3-NT
%R 4-NT
%R RDX
%R TNB
%R TNT
%R NG
%R PETN

Second LCS Study

- Five replicates of the ERA LCS were processed under four different experimental conditions:
  - UG Unground analyzed immediately
  - OUG Opened unground LCS analyzed at 30 min.
  - 90G Ground for 90 sec in puck mill
  - 4-60G Ground for 4 60-sec cycles in puck mill

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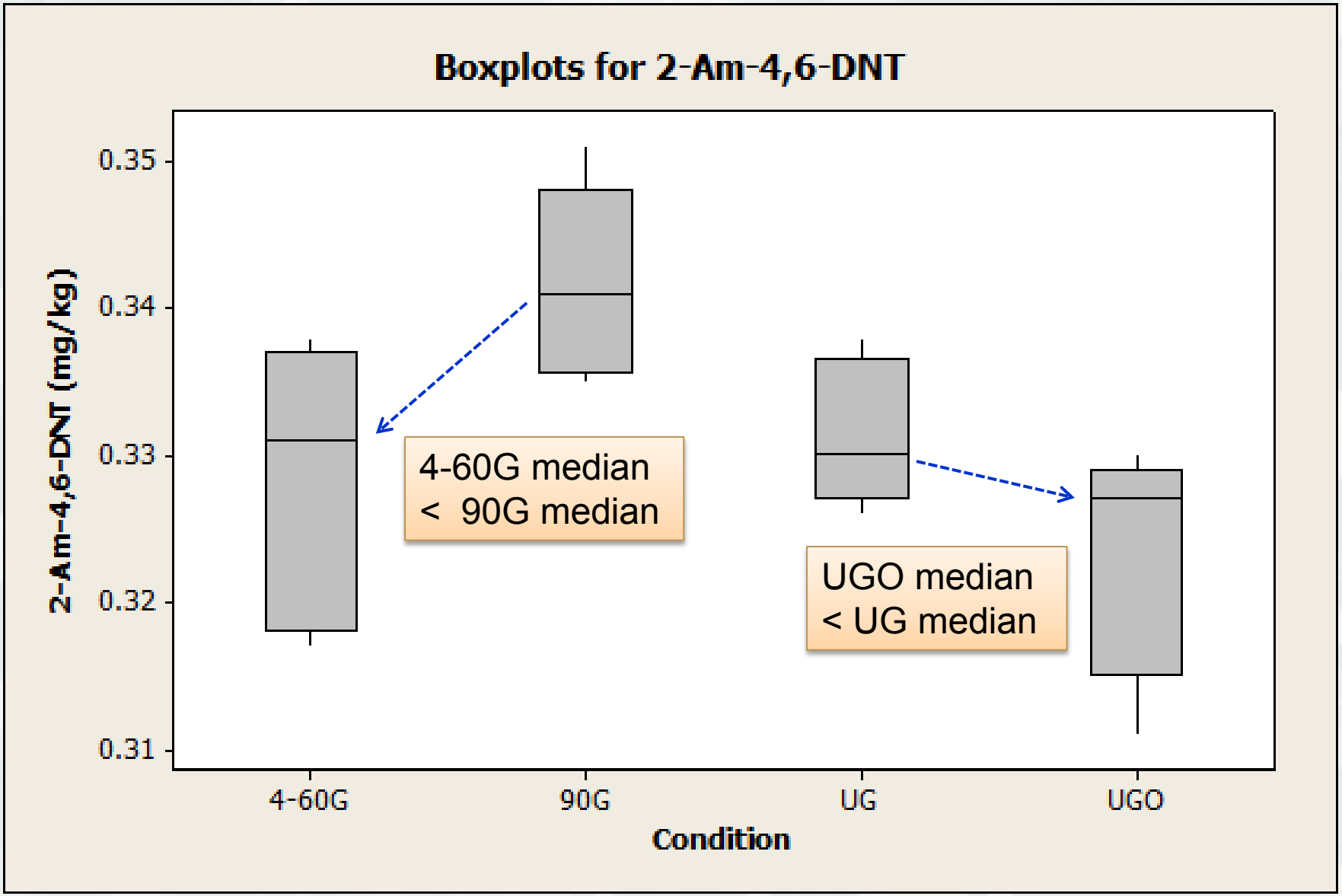
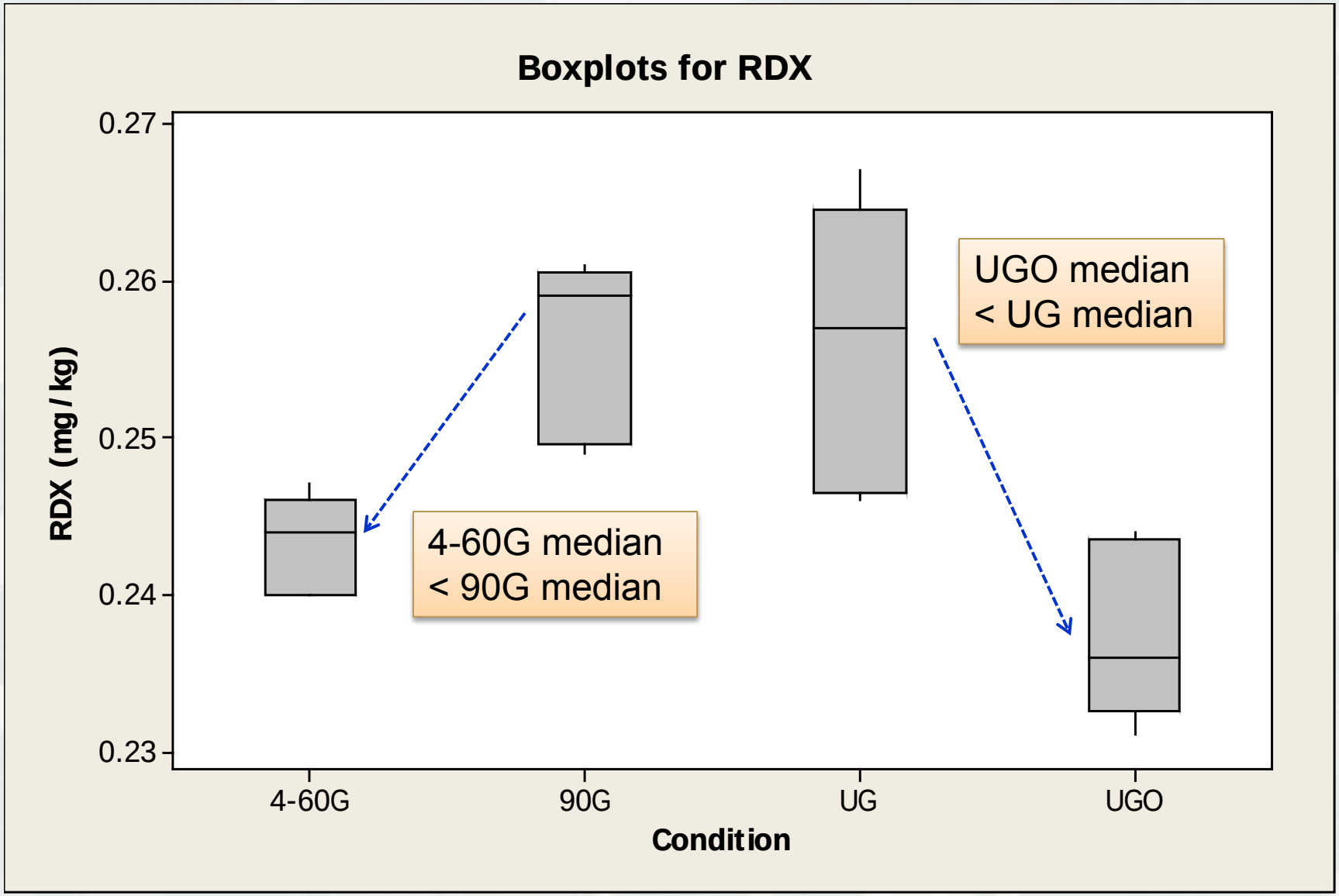

Boxplots for 2-Am-4,6-DNT
2-Am-4,6-DNT (mg/kg)
0.35
0.34
0.33
0.32
0.31
4-60G
90G
UG
UGO
Condition
4-60G median
< 90G median
UGO median
< UG median



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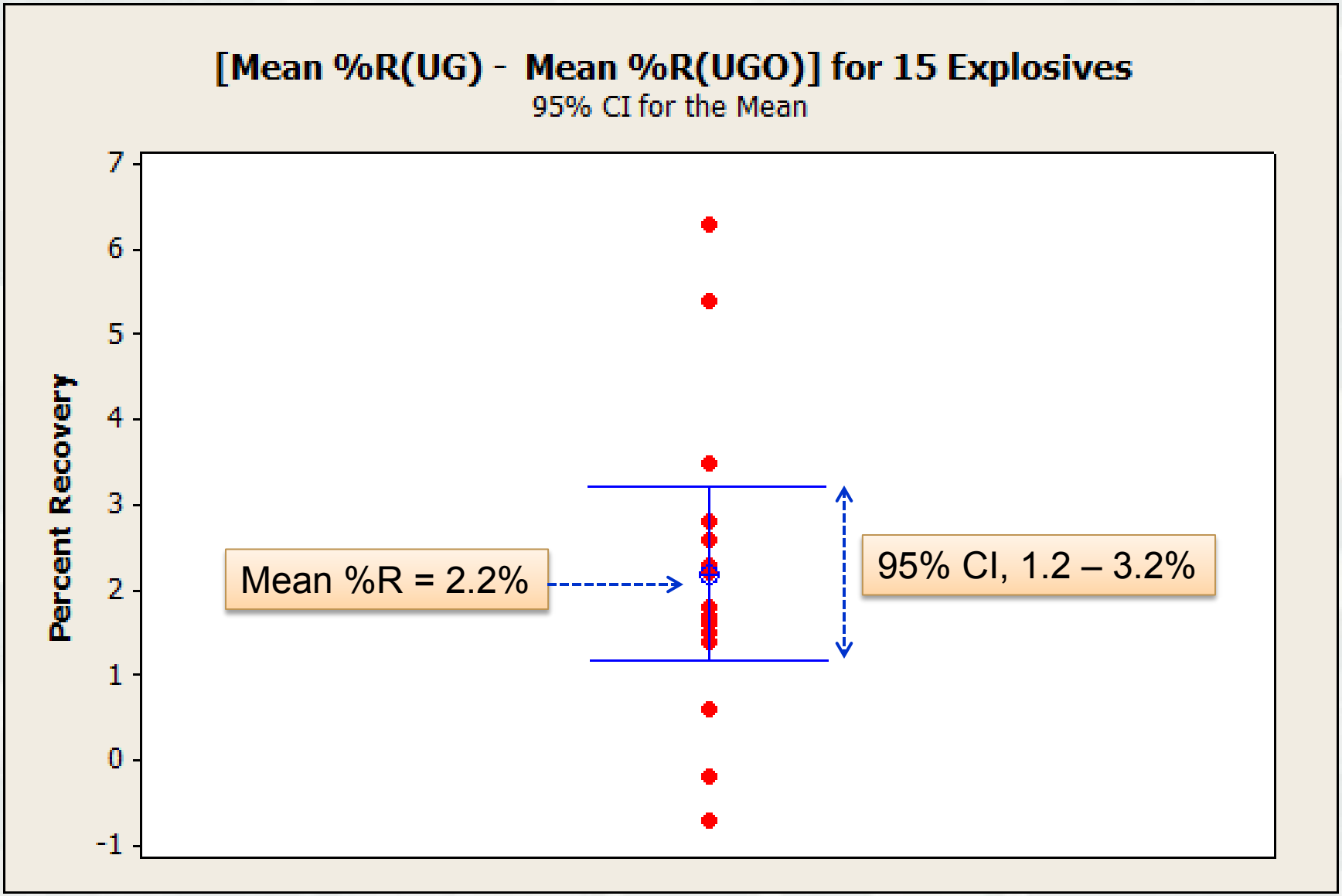

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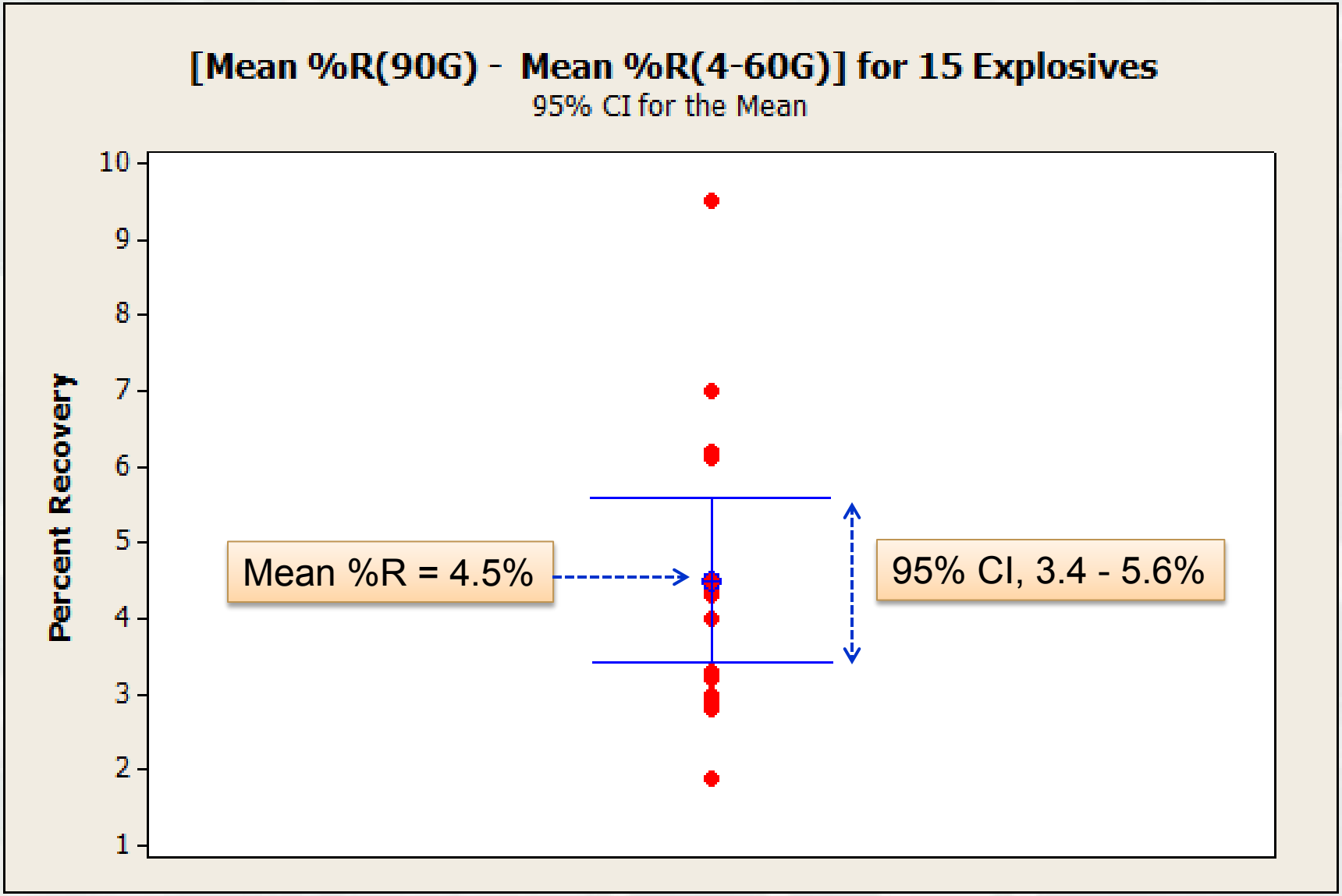

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Compound	Mean %R* 90G	Mean %R* 4-60G	ERA WLs**
4-Am-2,6-DNT	95	89	46 – 98
2-Am-4,6-DNT	105	101	56 – 108
DNB	98	95	69 – 116
2,4-DNT	95	93	64 – 120
2,6-DNT	98	95	60 – 122
HMX	97	91	54 – 115
NB	84	80	58 – 119
2-NT	98	93	67 – 117
3-NT	92	90	69 – 124
4-NT	94	91	62 – 123
RDX	88	83	60 – 116
TNB	100	95	58 – 116
TNT	96	93	61 – 104
NG	96	87	
PETN	102	95	

* $n = 5$

** Warning limits = mean ± 2 std dev.

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Summary of Results

- After 5 days of drying at room temperature, NB and the NT isomers volatilized producing 0% recoveries; the 11 remaining explosives were negatively biased by an average of » 10%
- Concentrations of the unground LCS decreased about 2% on the average after only 30 min of drying.
- Increasing the grinding time from 90 sec to 240 sec. (4 60-sec cycles) decreased the recoveries of the 15 compounds by an average of 4% - 5%.

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Conclusions

- The ERA solid standard (LCS) should **not** be air dried but processed (e.g., ground) **immediately** with the environmental samples.
- Excessive grinding of the LCS should be avoided as this will negatively bias the results.
- The recoveries of the ground LCS for Method 8330B will likely fall well within the ERA acceptance ranges for the unground Method 8330A PT samples.

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Neutralization of Alkaline Hydrolysis Treated Soils for SW-8330B Analysis

Presenters

Chuck Coyle, P.E. and Chung-Rei Mao, Ph.D.

Environmental and Munitions Center of Expertise

US Army Engineering and Support Center, Huntsville, AL

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US Army Corps of Engineers
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Overview

- Alkaline hydrolysis treatment of explosives contaminated soils.
- Issues with SW-8330B analysis of alkaline hydrolysis treated soils.
- Acid neutralization of alkaline hydrolysis treated soils for SW-8330B analysis.
- Summary and recommendations.

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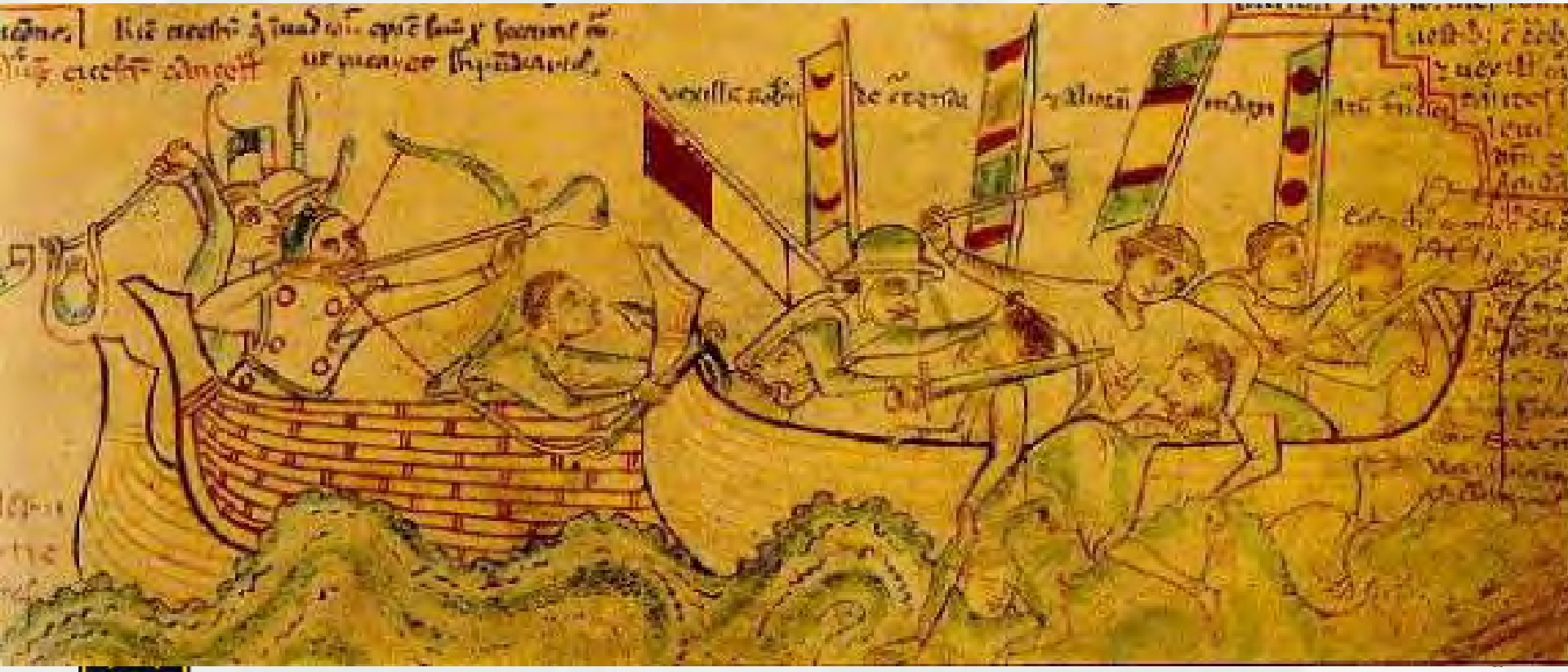
Caustic History

- *1217, Henry III, Battle of Sandwich*



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Caustic History

§ Transformation of TNT in basic solutions

- Janowsky, J. V. (1891). “Ueber eine reaction der dinitrokörper,” *Berichte* 24, 971

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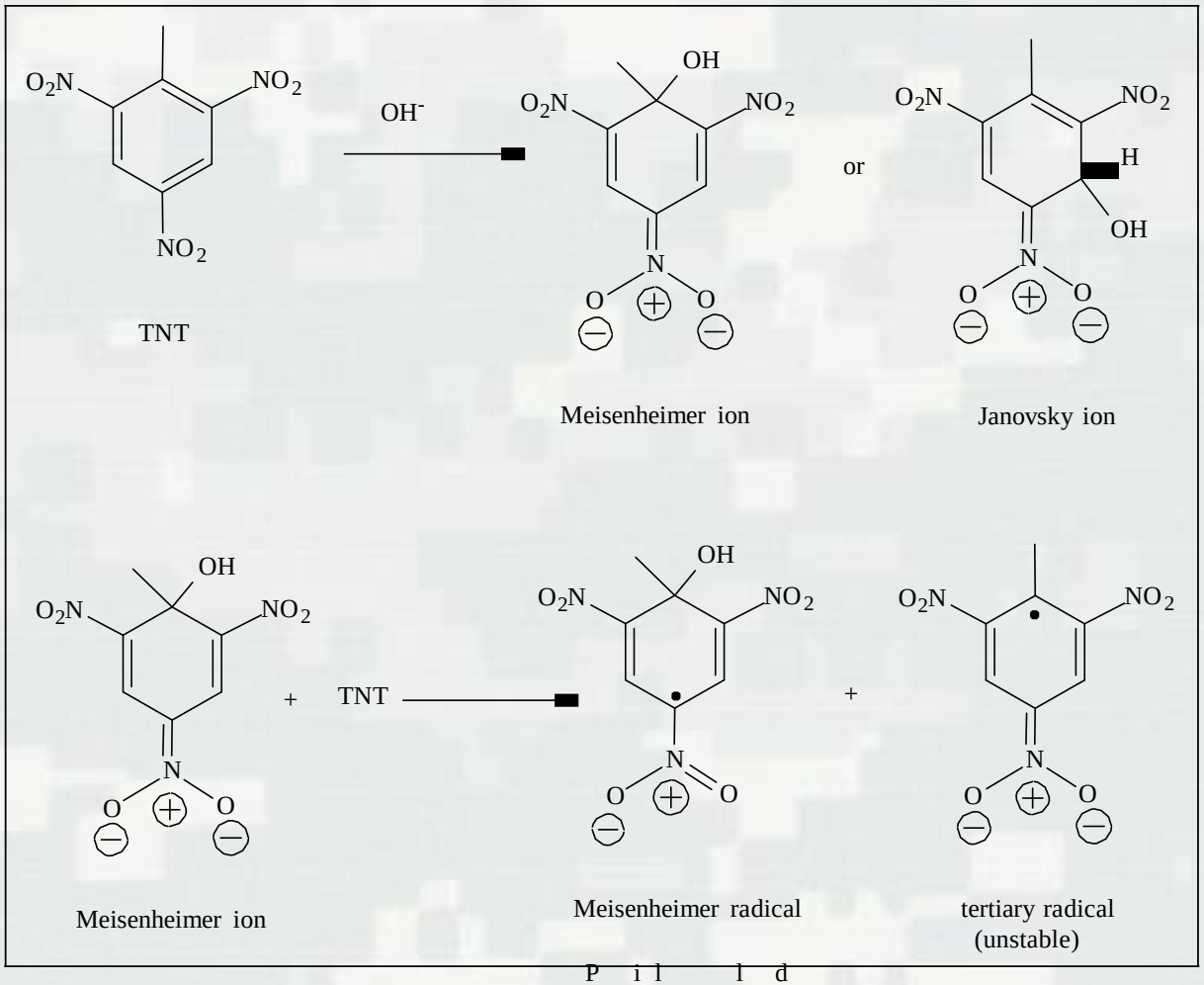

Figure 2-4. Proposed TNT reaction mechanism illustrating formation of a Meisenheimer or Janowski complex and radicals. Possible structure of long-lived (tertiary) radical is illustrated in the bottom right corner.

Alkaline Hydrolysis

- **Uses:**
  - Ø to prevent migration of contaminants from active training ranges.
  - Ø for bulk soil treatment.
- **Contaminants: TNT & RDX.**
- **Pug mill is used to mix hydrated lime (HL) $Ca(OH)_2$ or NaOH into soil with target pH of ~11 – 12.**
- **Rapid destruction of TNT & RDX.**
- **pH of AH treated soil usually reverts back toward neutral with time.**

Explosives-Contaminated Soil Treatment Timeline

- *Incineration*
  - 1987 Cornhusker
  - 1994 Savannah ADA
  - 1997 Mead NOP
- *Composting*
  - *1995 Umatilla, full-scale*
- *Alkaline Hydrolysis*
  - *2005-2007 Ft Jackson HGR*
  - *2007 Volunteer AAP*

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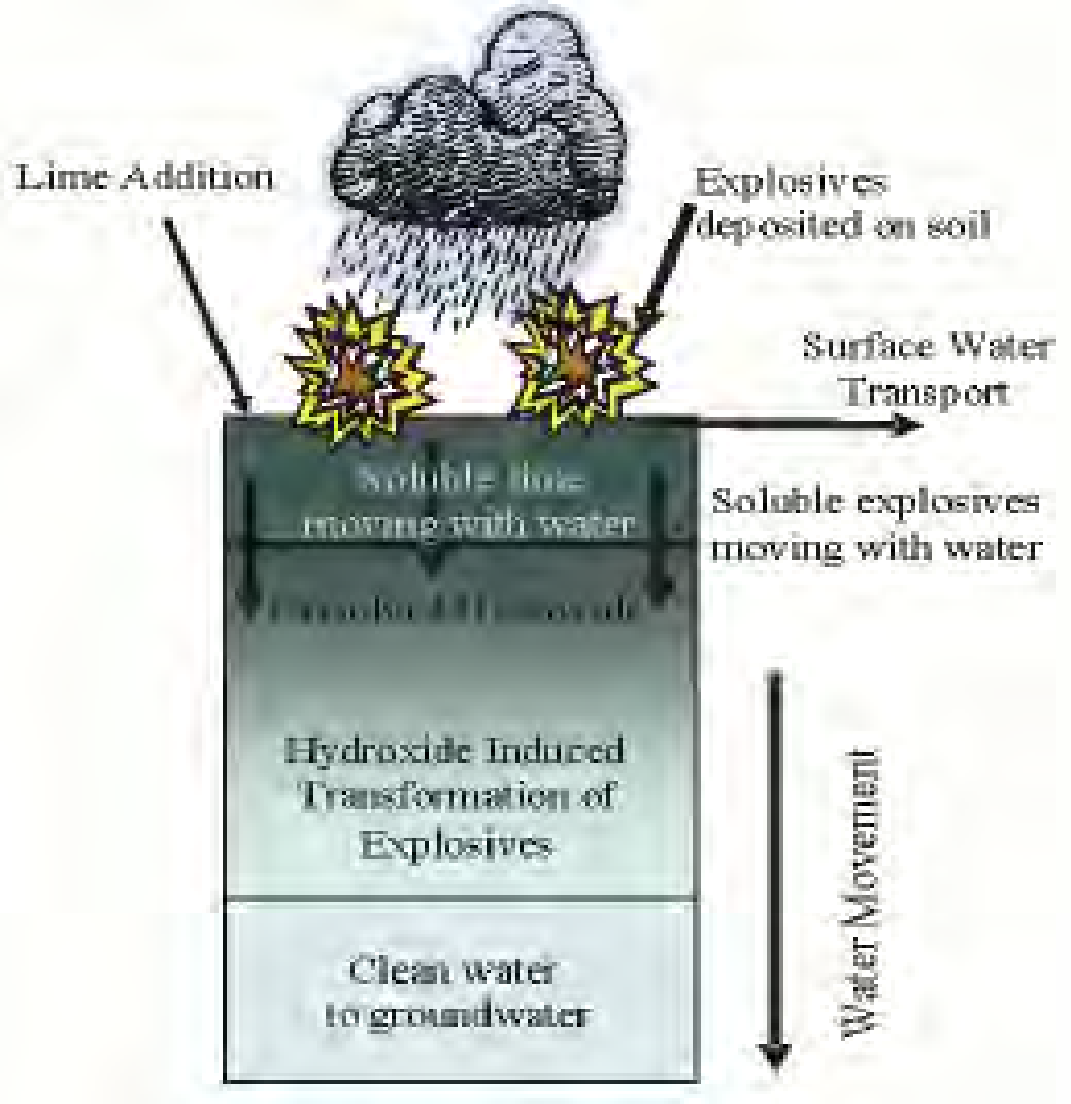
Schematic of Alkaline Hydrolysis



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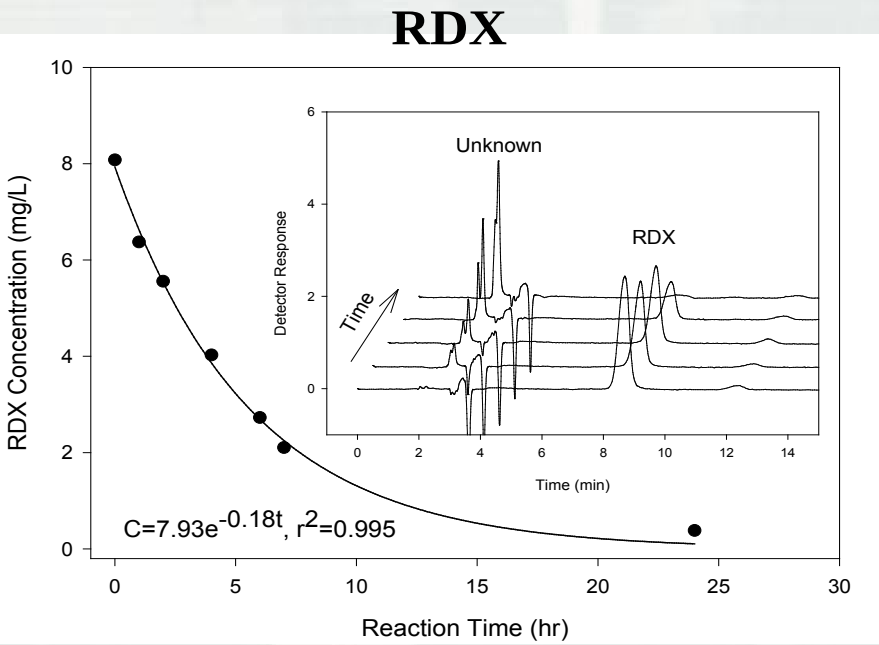
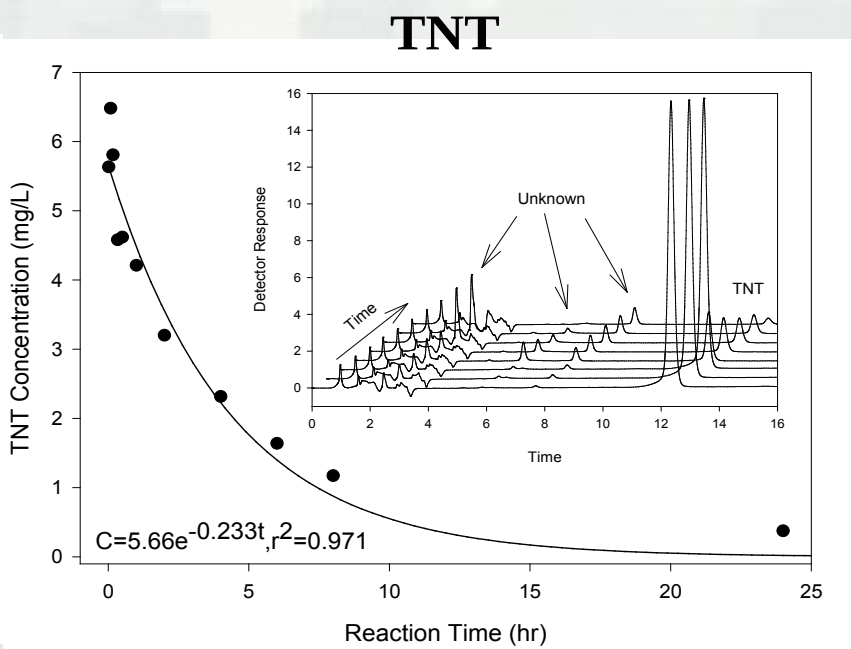
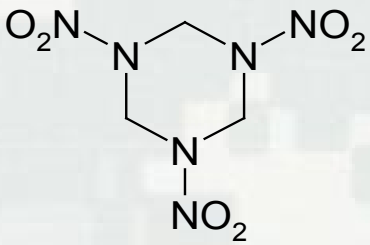
Alkaline Hydrolysis





- **RDX**
- **Aqueous**
- **pH=12**
- **Half Life ≈ 5 hrs**



- **TNT**
- **Aqueous**
- **pH=11.5**
- **Half Life < 2 hrs**

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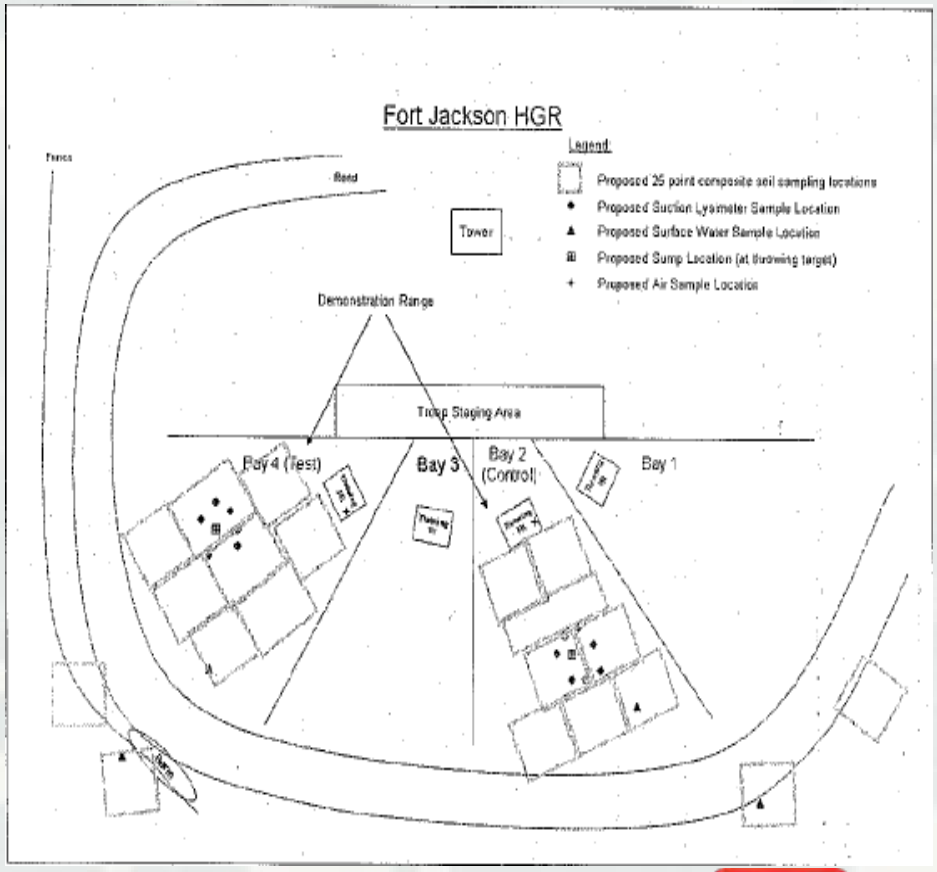
Alkaline Hydrolysis

Initial Pilot Study at Fort Jackson HGR (ER-0216)

- **Objectives:**
  - Ø **Reduce RDX and TNT by 90% in pore water and surface water.**
  - Ø **Reduce metals (Zn, Cr, Cu, and Pb) by 90% in pore water and surface water.**
- **1% HL added to elevate soil pH to 11 (1 ton of lime added to a depth of 6”) using hydroseeder and mixed with rotor-tiller.**



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Alkaline Hydrolysis

Initial Pilot Study at Fort Jackson HGR (ER-0216)

Sampling Date	Bay 4 (Limed) Avg RDX Conc. (ppm)			Rain Between Sample Events (inches)	Post Lime % Soil Moisture
	Pre Lime	Post Lime	% Change		
Apr 06	4.21	<1.75[1]	>58%	0.12	2.21
Oct 06[2]	0.42	<0.08	>59%	3.2	6.36
Jan 07	<0.09	<0.10	No Change	0	6.83

1 Report limit (0.02 ppm) used in calculations where '<' present.
2 Pre-lime samples taken in Jul; approximately 30 days between liming and post liming samples.

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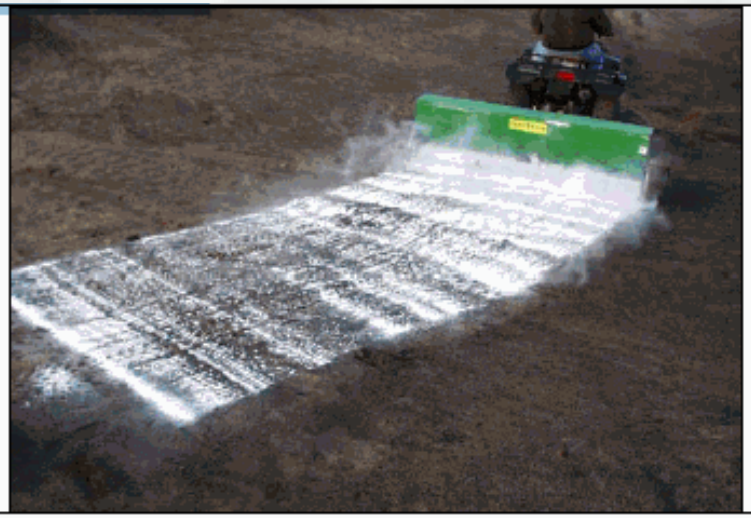
Alkaline Hydrolysis

Fort Jackson Remagen HGR

- 1 ton of lime to elevate pH ≥ 11.5
- 1% lime per 6 inch depth for Bay 4

Mixing lime into range at Fort Jackson



Lime application at Fort Jackson

Application

- Cost ~ $400.00 / ton
- This range is limed quarterly
- Spread bags by hand or with drop spreader
- Disc into soil
- Required less than 2 hours labor

Alkaline Hydrolysis

- **Topical Application Approach**
  - **HL rate at 0.5% of dry soil weight to raise shallow soil pH to 11.**
  - **Initially HL is topically applied using a drop spreader and then mixed in the top 6" of soil in the test area using a disc.**

Example Topical Liming

Area	4.5 acres = 196,000 sq. ft.
Depth	0.5 ft.
Soil Volume	98,000 cubic ft.
Soil Density (estimated)	1.6 g/cm^3 = 100 lb/ft^3
Quantity of Lime	Soil Volume * Soil Density * Lime rate (0.5%)
Total Quantity of Lime	49,000 lb. = 24.5 tons
Lime Density	2.24 g/cm^3 = 140 lb/ft^3
Lime volume required	13 cubic yards

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2013-0805 remed pad decon of windrow turner before maintenance

AH Application in Daily Life

How to Fix A Clogged Drain?

Option (1) Toilet Plunger

Option (2) AH with Drano

Winner: (2) AH of esters/amides by hydroxide ion attack of carbonyl carbon

AH Transformation

- **AH destroys explosives via nucleophilic substitution.**
  - Strong nucleophile (OH^-) attacks electrophile.
  - Displacement of a leaving (functional) group.
  - Ring cleavage.
- **Transformation occurs rapidly in soil pore water.**
  - Explosives residues degrade rapidly in soils with high pH and moisture content.
  - End products are small molecules (e.g., NO_2^-, N_2O_2, N_2, NH_3, HCHO, HCOOH, and CO_2), which are easy for biodegradation.

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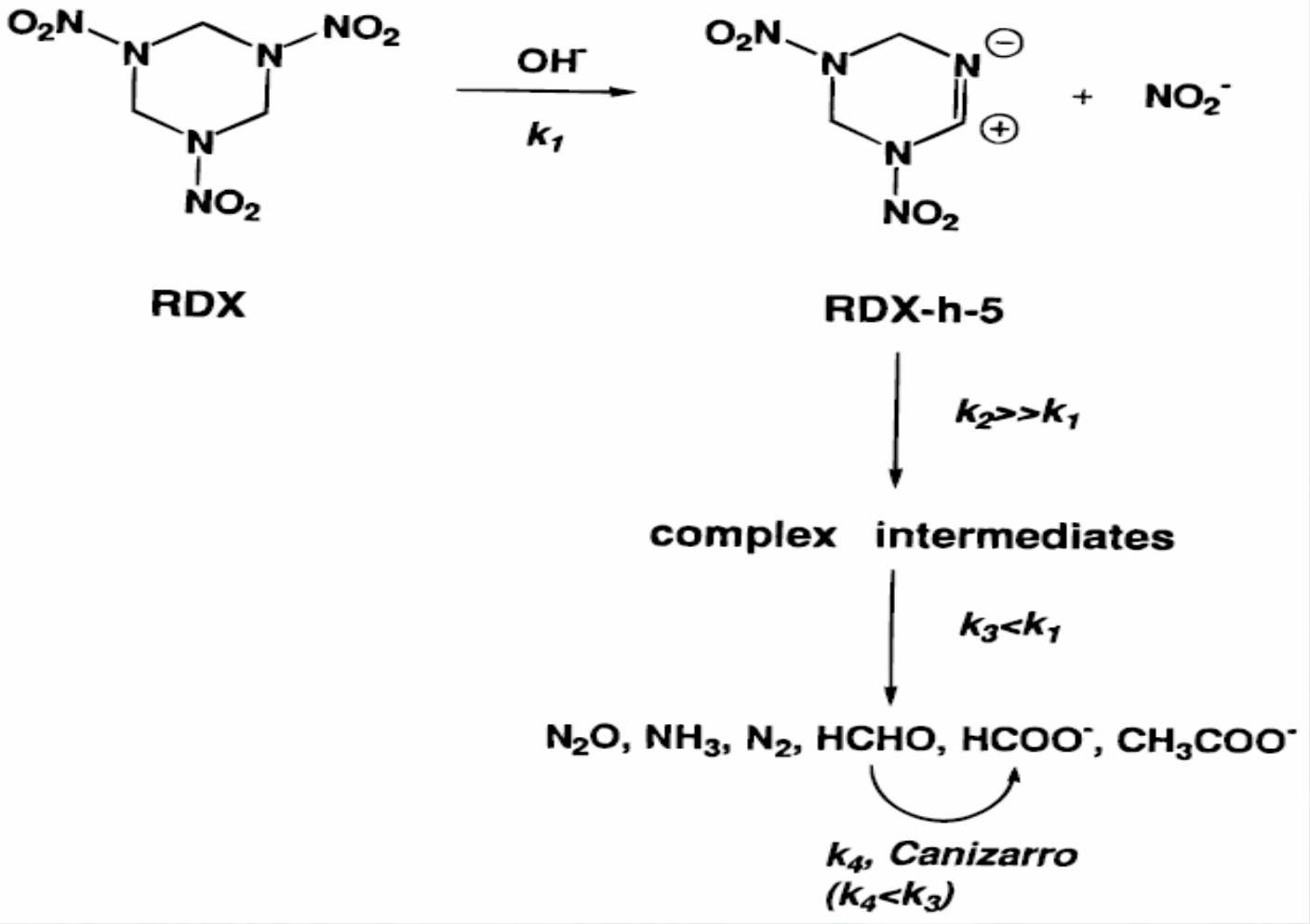
Mechanism of AH Transformation



Source: Heilmann et al., Environ, Sci. Technol., 30, 1996

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Kinetics of AH Transformation

- Nucleophilic transformation – pseudo 1st order with pH >10.
- AH rates are affected by soil pH, moisture content, temperature, compounds, time, etc.
  - NaOH: higher pH >12 for faster AH rate.
  - HL: high pH last longer for AH.
- AH rates for soil treatment:
  - TNT > RDX > HMX.
  - Half-lives are about 0.15 days for TNT and 0.28 days for RDX in soil at pH >10.
  - AH rates increase with increasing pH.

Conceptual Model for AH

- Caustic materials dissolve into and raise pH of soil pore water.
- Explosives desorb/dissolve into soil pore water.
  - Ø Sorption « soil particle size, organic carbon content, temperature, cation, etc.
  - Ø Dissolution « time, temperature, pH, explosives type, explosives particle size, etc.
- Explosives destruction via AH occurs in soil pore water with high pH >10.

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Analytical Issues with AH Treated Soil

- SW-8330B data of AH treated soils at times showed poor precision.
- Matrix spike/matrix spike duplicate (MS/MSD) showed false degradation in field samples.
- False degradation occurred if residual caustic materials and moisture present in the samples.
- HL has lower water solubility than NaOH and is more prone to false degradation than NaOH.

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Analytical Issues with AH Treated Soil

- Air-dried soils may contain high moisture and pH.
- Acetonitrile (ACN) extraction in an ultrasonic bath for 18 hours helps explosives dissolution into soil pore water.
- AH may occur rapidly during ACN extraction.
- Need to check and adjust soil pH between 5 – 8 or to the background soil pH prior to sample drying, extraction, and analysis.

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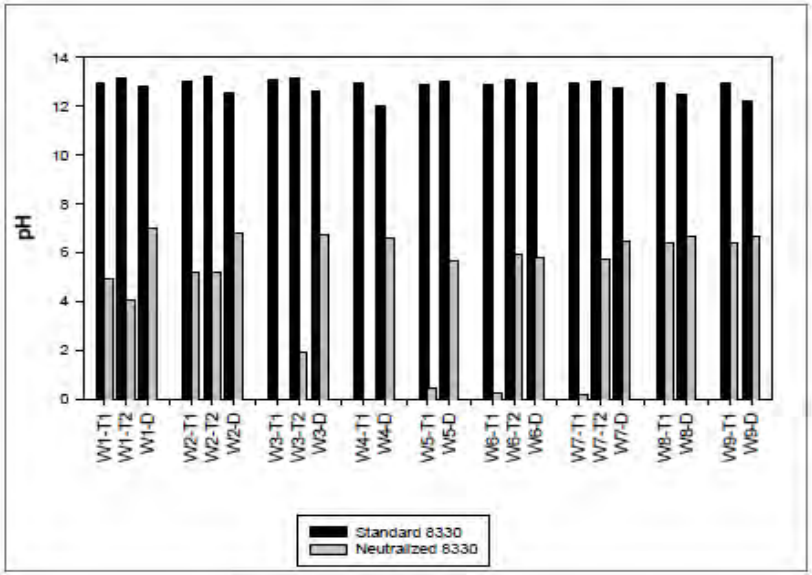
Lab Study of Neutralization

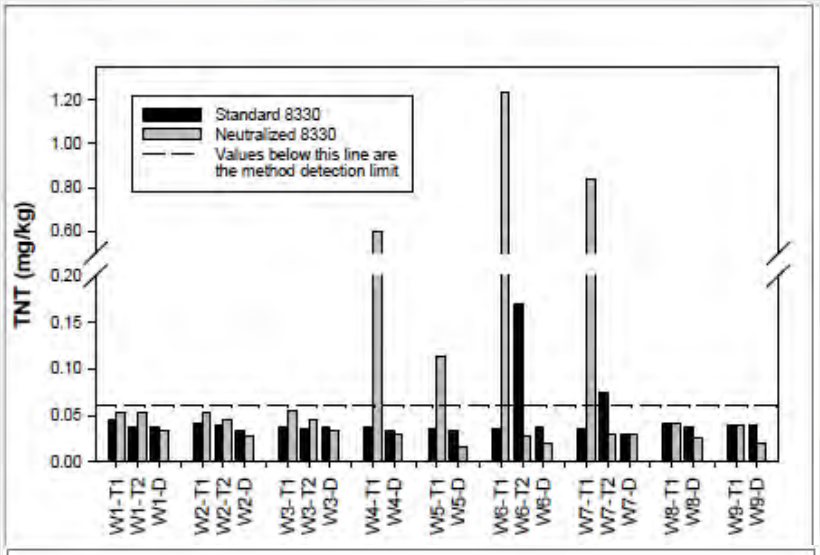
- Collected soils containing TNT/DNT and undergoing AH treatment from PBOW.
- Analyzed "non-neutralized" and "neutralized", AH treated soil samples in triplicates using SW-8330B.
- SW-8330B analysis:
  - HPLC with C-18 & CN columns and UV detector.
  - Mobile – 50:50 MeOH:H_2O at 1.0 mL/min.
  - 25 µL injection volume.
  - MDL = 20 µg/L.

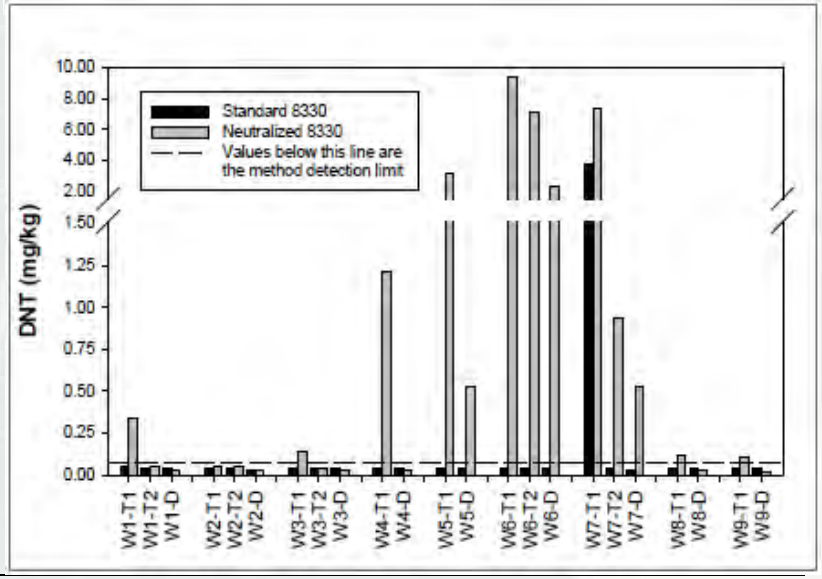
Source: Larson et al., ERDC/EL TR-12-14 (2012)

Lab Study of Neutralization

Effects of neutralization on pH, [TNT], and [DNT] of soils collected from PBOW remediation site.







Source: Larson et al., ERDC/EL TR-12-14 (2012)

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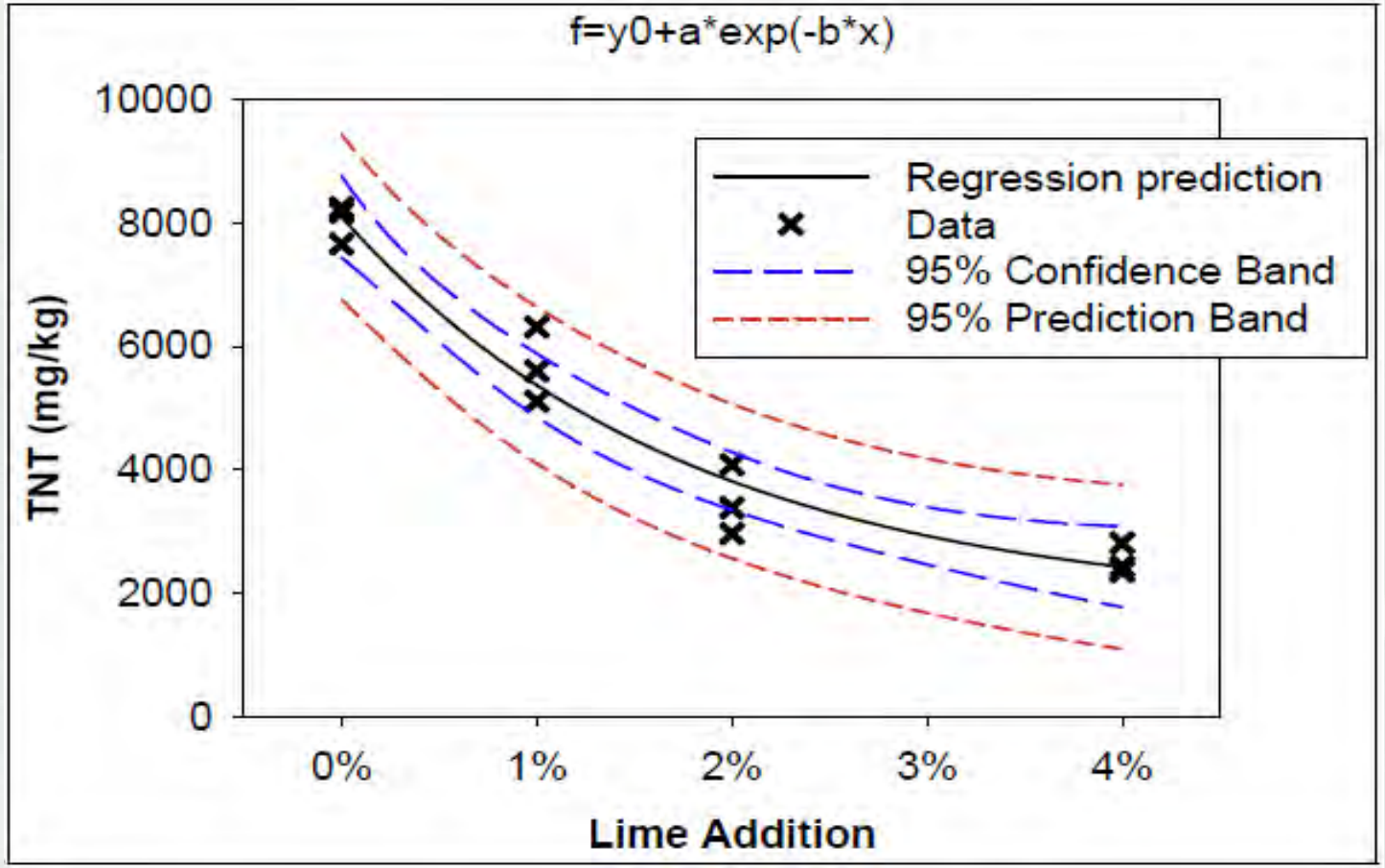
Lab Study Variables

Condition	Moisture	DI	Lime	Lime	Acidified
A	21.5%	3.00 mL	0%	0.00 g	
B	21.5%	3.00 mL	2%	0.30 g	
C	21.5%	3.00 mL	2%	0.30 g	X
D	11.5%	1.50 mL	2%	0.30 g	
E	6.5%	0.75 mL	2%	0.30 g	
F	1.5%	0.00 mL	2%	0.30 g	
G	21.5%	3.00 mL	4%	0.60 g	
H	21.5%	3.00 mL	1%	0.15 g	
I	21.5%	3.00 mL	0%	0.00 g	X

Source: Larson et al., ERDC/EL TR-12-14 (2012)

AH of TNT vs. Lime

Non-Linear Regression of Lime as a Variable with 20% Soil Moisture



Source: Larson et al., ERDC/EL TR-12-14 (2012)

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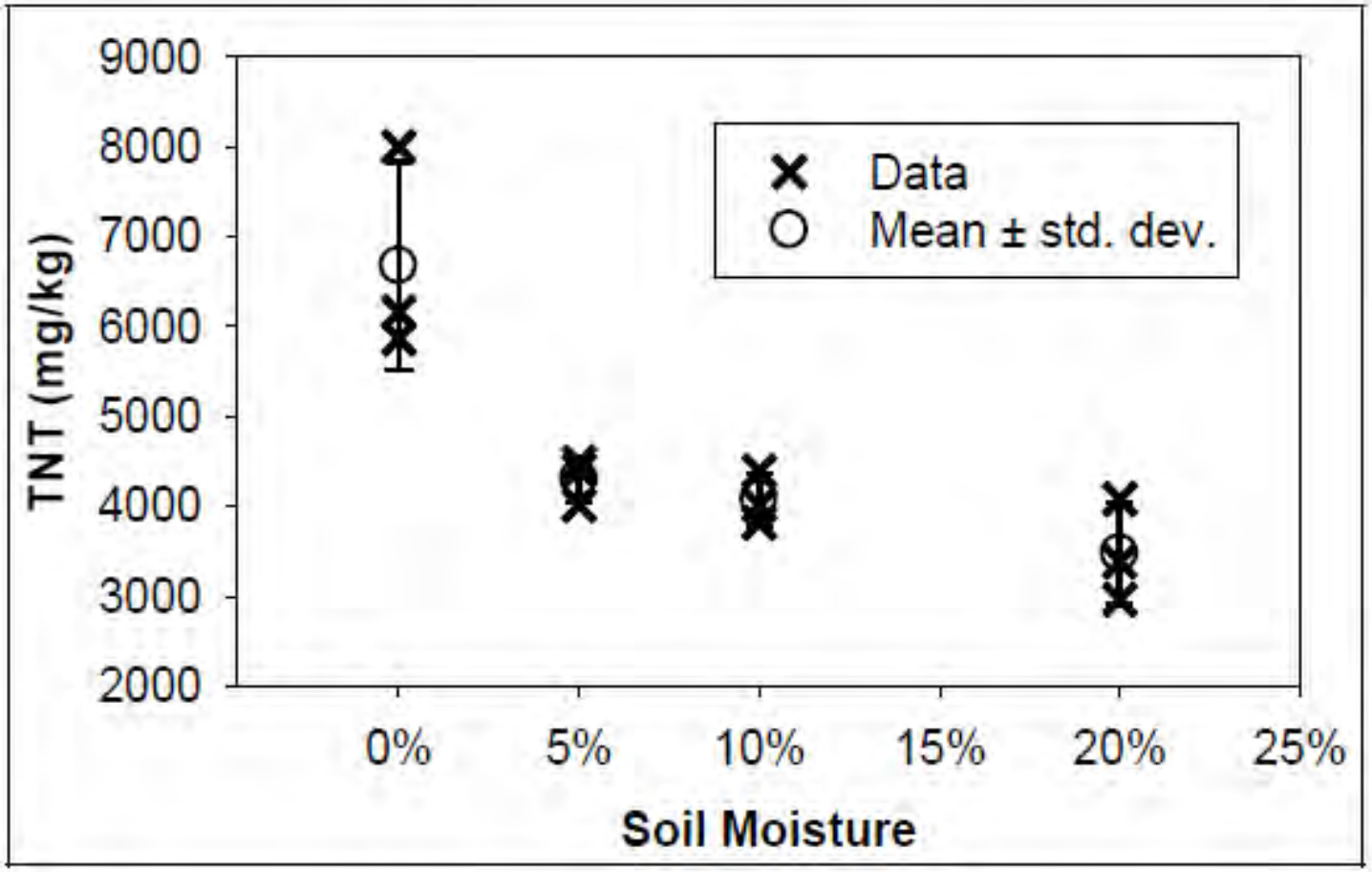
AH of TNT vs. Soil Moisture

Variable Moisture with 2% Lime Addition



Source: Larson et al., ERDC/EL TR-12-14 (2012)

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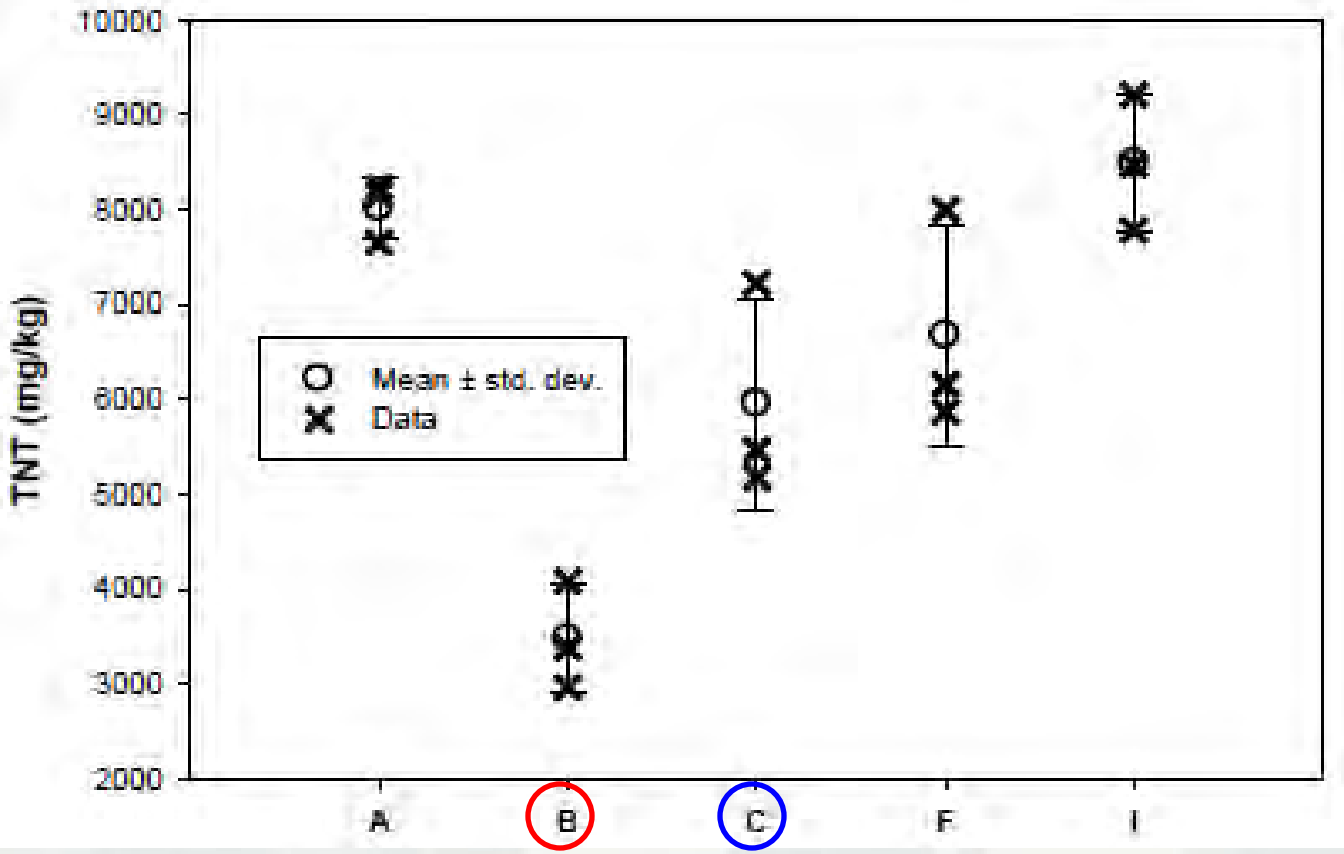
Effect of Neutralization

Effect of Pre-Extraction Acidification of Soil



A: 20% moisture/0% lime; B: 20% moisture/2% lime; C: 20% moisture/2% lime/acidified; F: 1.5% moisture/2% lime; I: 20% moisture/0% lime/acidified.

Source: Larson et al., ERDC/EL TR-12-14 (2012)

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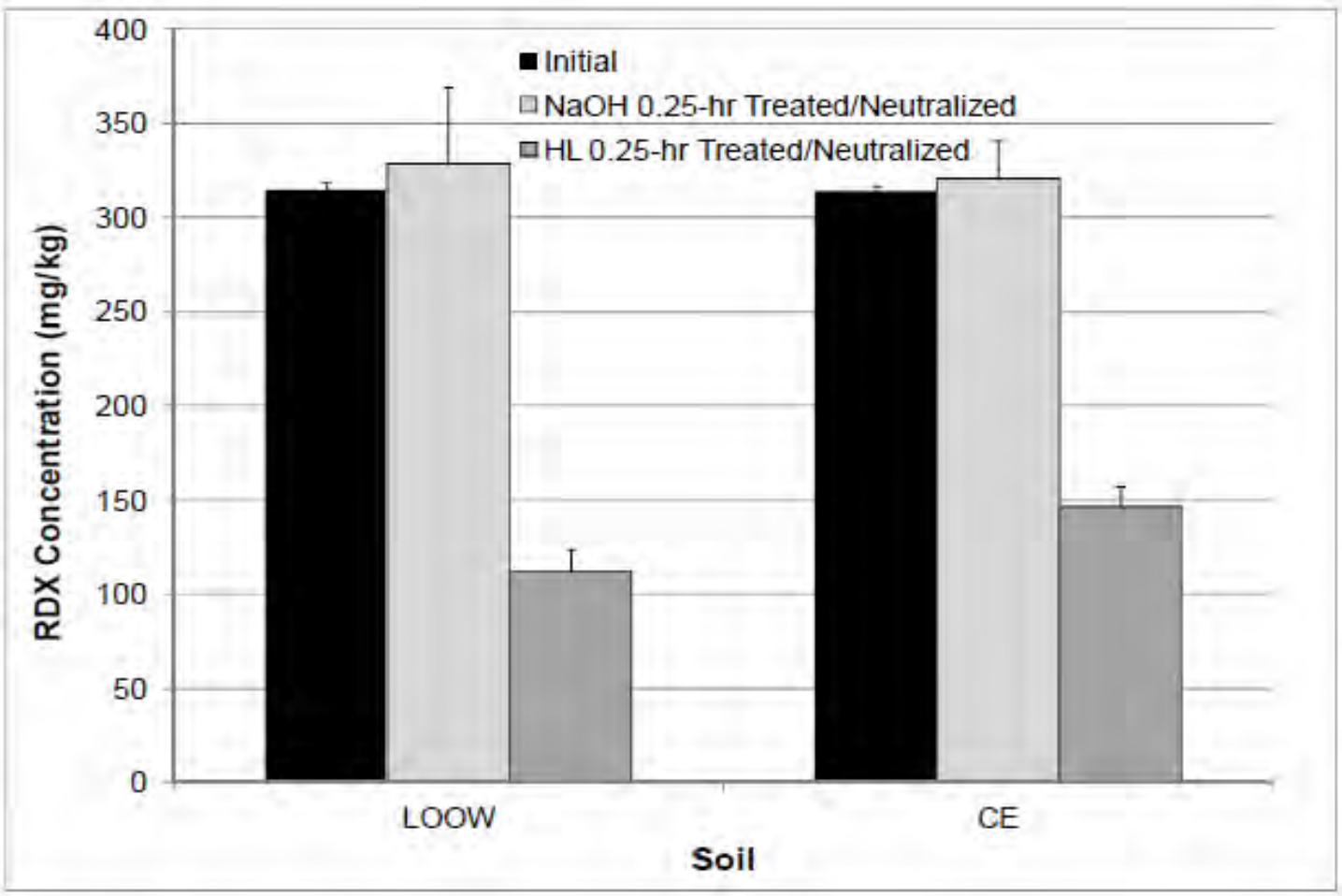
Lab Study of Neutralization

AH with NaOH or HL; Neutralized with Buffer (NaH_2PO_4)



Source: Larson et al., ERDC/EL TR-12-14 (2012)

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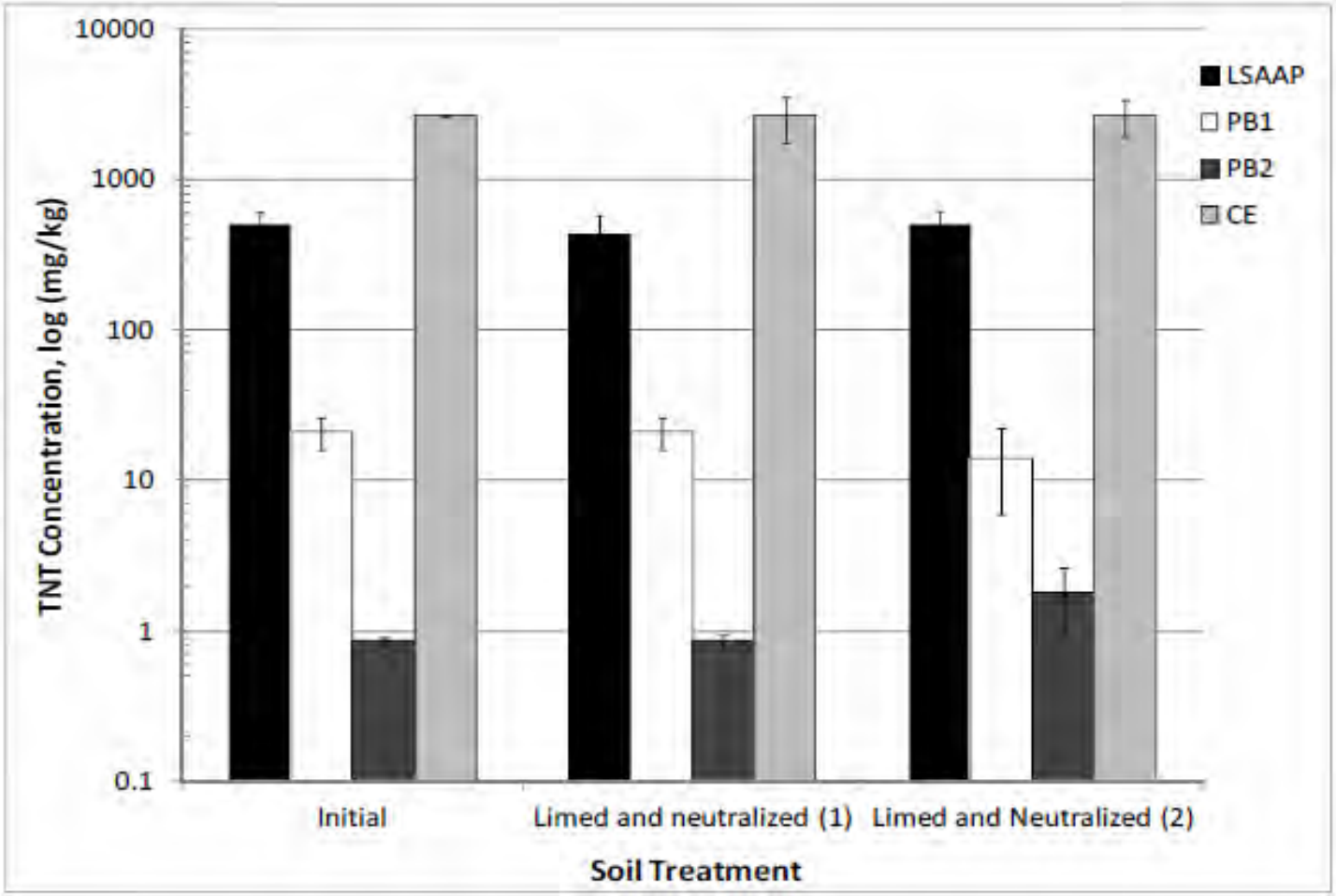
Lab Study of Neutralization

AH with HL; Neutralized with (1) Buffer or (2) Acid + Buffer



Source: Larson et al., ERDC/EL TR-12-14 (2012)

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Neutralization Procedures

- **EDRC-EL developed procedures:**
  1) Check pH of treated soil – prepare a 1:10 soil:water slurry, mix well, allow sit for 1 hr, and check overlying solution pH with a pH meter.
  2) If soil pH ≤9, neutralization is not required and follow SW-8330B.
  3) If pH >9, neutralization with a combination of a strong acid (3N HCl) and buffer solution (5M NaH_2PO_4) is required.
  4) The HCl concentration and volume added per gram of soil must be optimized for specific soil type, caustic type, caustic added, and time elapsed since alkalization. A starting point could be 1 g soil:1 ml 3N HCl.
  5) Add 3N HCl solution to the soil and mix. When gas evolution diminishes and is not re-activated upon mixing, add the 5M NaH_2PO_4 buffer solution at 1 g soil:1mL 5M NaH_2PO_4.
  6) Allow sample to equilibrate at room temperature for 10 minutes with occasional stirring to ensure full wetting of the soil.
  7) Check the solution pH using a pH test strip to ensure pH is in 5 – 8 range.

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Neutralization Procedures

- **EDRC-EL developed procedures (continued):**
  8) **If the mixture pH is <5, add additional 5M NaH_2PO_4 buffer solution. If the pH cannot be elevated >5 with <3 mL of 5M NaH_2PO_4 per gram of soil, repeat the process with a lower concentration and/or volume of strong acid.**
  9) **After the pH is sufficiently reduced with the strong acid addition to eliminate residual caustic and then elevated with the buffer solution, the soil mixture is transferred to a low temperature drying system for water evaporation.**
  10) **When samples are dried to a constant weight, samples are homogenized, subsampled, extracted, and analyzed as described in SW-8330B.**
  11) **Care should be taken to avoid reducing the soil and or soil/slurry pH <4 for prolonged periods as DNTs are susceptible to acid hydrolysis. If this occurs, reduce the acid concentration in order to facilitate raising the pH to the 5 – 8 range upon buffer addition.**

Source: Felt et al., ERDC/EL Draft Letter Report Sioux Army Depot (2012)

Summary/Recommendations

- AH is a safe, effective, and cost-efficient method for treating explosives contaminated soils with successful field applications since 2007.
- Combination of residual caustic materials and moisture in AH treated soils can lead to false degradation. AH with HL with lower solubility are more prone to false degradation than NaOH.
- AH treated soil samples may be neutralized on-site or immediately upon received at the lab prior to air dry, extraction, and analysis.
- ERDC-EL developed detailed acid neutralization procedures using HCl and NaH_2PO_4.

Summary/Recommendations

- The amount of neutralization materials depends on the amount and type of caustic materials added, the analyte of concern, and the amount of caustic materials remain.
- Care must be taken to ensure that acid neutralization does not result in acid reactions that degrade RDX and DNTs.
- For AH treated soils, the SOW should include acid neutralization of all post-treatment samples to ensure pH = 5 – 8 or the background soil pH.
- Recoveries of MS/MSD guard against low biased or false negative SW-8330B results.
- Proposed to USEPA for SW-8330B update.

Questions/Comments?

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DoD QSM Version 5.0 SW-846 EPA Method 8330B Specific Requirements

Janice Willey
NAVSEA LQAO
April 9, 2014
EMDQ Workshop

- *DoD Quality Systems Manual Version 5.0* (July 2013)

  http://www.denix.osd.mil/edqw/

- SW-846 EPA Method 8330B *"Nitroaromatics, Nitramines and Nitrate Esters by High Performance Liquid Chromatography (HPLC)"*

  http://www.epa.gov/osw/hazard/testmethods/sw846/new_meth.htm

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SW-846 EPA METHOD 8330B

- *Sample Preparation*
  - Ø Drying
  - Ø Sieving
  - Ø Grinding
  - Ø Subsampling
  - Ø Extraction
- *Sample Analysis*
  - Ø Calibration and Calibration Verification
  - Ø Batch QC Criteria
  - Ø Confirmation

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SAMPLE PREPARATION

- *Soil Drying*
  - ü Ambient temperature
  - ü Constant mass

- *Soil Sieving*
  - ü *Weigh entire sample*
  - ü *Sieve with 10 mesh sieve*
  - ü *Weigh portion that does not pass thru sieve*

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SAMPLE PREPARATION

- *Soil Grinding*
  - ü Reduce particle size to < 75 µm demonstrated by passing through a 200 mesh sieve
  - ü Grinding Blanks

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SAMPLE PREPARATION

- *Soil Subsampling*
  - ü 30 or more randomly located increments
  - ü Total mass approximately 10 grams
  - ü Triplicate subsample

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SAMPLE PREPARATION

- *Soil Sample Extraction*
  - ü 10 gram Subsample
  - ü Add surrogates and matrix spikes prior to addition of 20 mL of ACN
  - ü 18 hours on platform shaker or in cooled ultrasonic bath
  - ü Filter with 0.45 µm PTFE filter

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SAMPLE PREPARATION

- *Water Sample Extraction*

ü SPE, resin-based phase (EPA SW-846 Method 3535)

ü QC required is Method Blank, LCS, MS, and MSD

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SAMPLE ANALYSIS

- *Calibration*
  - ü Minimum of 5 calibration points
  - ü Lowest calibration level at or below LOQ
  - ü Three options on criteria
  - ü Must be met for all target analytes and surrogates

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SAMPLE ANALYSIS

- *Calibration Verifications*
  - ü Initial Verification (second source) and Continuing Verification
    - Must meet ±20% criteria for all target analytes and surrogates
    - Corrective Actions

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SAMPLE ANALYSIS

- *Batch QC*
  - ü Method Blank: no analytes detected >½ LOQ
  - ü LCS, MS, MSD, Surrogates: limits depend on technology used (LCS/MS/MS, LC/MS, or HPLC)
  - ü Triplicates: RSD <20%

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SAMPLE ANALYSIS

- *Confirmation*
  - ü Not required if LC/MS or LC/MS/MS is primary analysis
  - ü All detections above the DL
  - ü RPD ≤40%

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