National Defense Center for Energy and Environment

Development of Exposure Point Concentrations with Incremental Sampling Data – Comparing Means and Confidence Intervals of Discrete, Composite, and Incremental Sampling Environmental Study Data

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DoD Executive Agent

Office of the Assistant Secretary of the Army (Installations and Environment)

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Technology Transition – Supporting DoD Readiness, Sustainability, and the Warfighter

Report Documentation Page

Form Approved
OMB No. 0704-0188

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1. REPORT DATE **JUN 2010**	2. REPORT TYPE	3. DATES COVERED **00-00-2010 to 00-00-2010**
4. TITLE AND SUBTITLE **Development of Exposure Point Concentrations with Incremental Sampling Data - Comparing Means and Confidence Intervals of Discrete, Composite, and Incremental Sampling Environmental Study Data**		5a. CONTRACT NUMBER 5b. GRANT NUMBER 5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)		5d. PROJECT NUMBER 5e. TASK NUMBER 5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **National Defense Center for Energy and Environment (NDCEE),Concurrent Technologies Corporation,100 CTC Drive,Johnstown,PA,15904**		8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S) 11. SPONSOR/MONITOR'S REPORT NUMBER(S)
12. DISTRIBUTION/AVAILABILITY STATEMENT **Approved for public release; distribution unlimited**		
13. SUPPLEMENTARY NOTES **Presented at the NDIA Environment, Energy Security & Sustainability (E2S2) Symposium & Exhibition held 14-17 June 2010 in Denver, CO. U.S. Government or Federal Rights License**		
14. ABSTRACT		
15. SUBJECT TERMS		

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**72**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

Agenda

- Background
- Validation of Incremental Sampling Methods Compared to Traditional Sampling Approaches
  - Comparison of Means/Testing of the Null Hypothesis
    - ✓ 1-Way ANOVA & Validation w/Pairwise Comparison
- Determination of 95% Upper Confidence Intervals (UCI) & Scatterplot Comparison
- Conclusions & Recommendations
- Acknowledgements & Contact Information
- Bibliography & Backup Slides

Background (Cont'd.)

- The NDCEE demonstrated/validated *multi-increment*® sampling (MIS) in conjunction with U.S. EPA Method 8330B, as a tool for DoD site assessment.

- Comparison including the contrast of discrete, composite, and incremental sampling methods for shallow surface soils sampling.

- Findings included that MIS and 8330B is a more reproducible, cost efficient, and reliable means of soil sample analysis to improve the environmental quality and ultimately sustainability of DoD Ranges.

Background (Cont'd.)

Who cares?

- There are limitations to IS:
  - Is it *really* better? & How do I use it?
  - How do we apply IS data to site-specific criteria?
  - How do we apply IS to risk assessment?
  - How do we develop exposure point concentrations and how does it compare to traditional approaches (i.e., discrete & composite sampling)?

- This paper provides the comparison of means and develops 95% Upper Confidence Intervals (UCI) to further explore the benefits of IS approaches in application of exposure assessment in contrast to traditional approaches.

Background (Cont'd.)

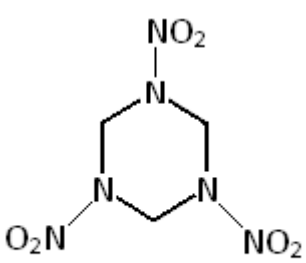
- Chemical energetic and propellant residues from detonation or manufacture of munitions and explosives of concern (MEC) at DoD sites may affect both the environment and human health.

- DoD sites potentially contaminated with munitions constituents:
  - Ammunition Plants
  - Training Ranges
  - Demolition Sites
  - Ammunition Test Sites
  - Storage Areas.

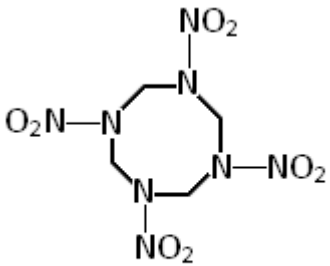
- Environmental safety must be maintained during:
  - Transition of land from government to public use
  - Site encroachment from residential housing, industrial growth, and expanding agricultural lands.

Background (Cont'd.)

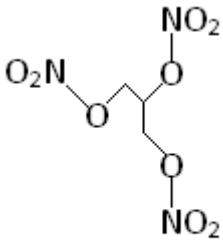
- Common Energetics and Propellants:
  - Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
  - Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
  - Nitroglycerin (NG)
  - 2,4-Dinitrotoluene (DNT)
  - Trinitrotoluene (TNT).



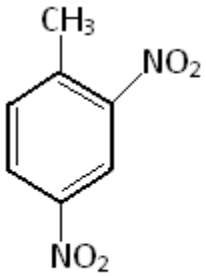
RDX



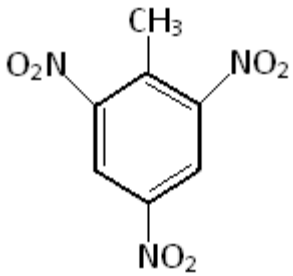
HMX



NG



DNT

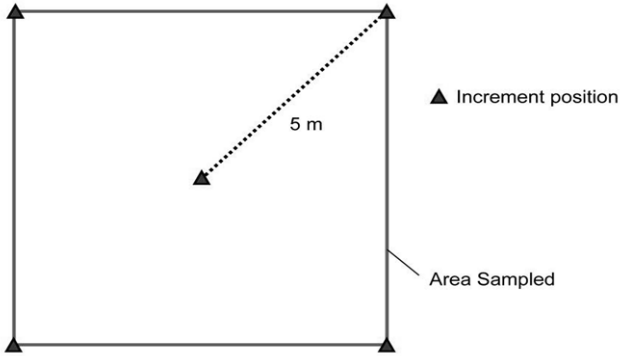


TNT

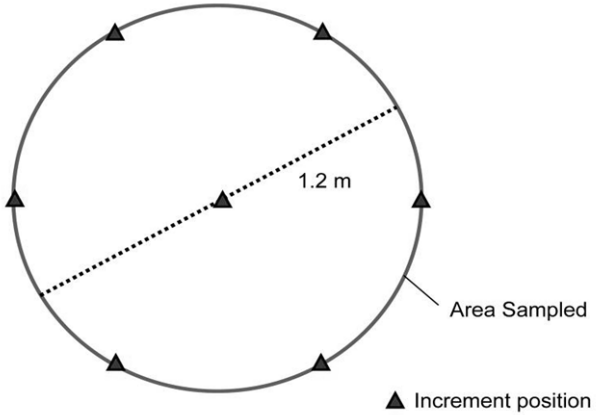
Traditional Sampling Methods

- Site divided into a set of decision (exposure) units.
- One or several discrete or small-scale composite soil samples collected to represent each decision unit.
- Analytical results assumed to be normally distributed (and representative).
- Mean (or 95% upper confidence limit) and estimates of uncertainty computed using normal statistics.

Box:



Wheel:



Multi-increment® Sampling (MIS)

- Developed by EnviroStat, Inc. and studied by the U.S. Army Corps of Engineers Cold Regions Research and Engineering Laboratory (U.S. ACE CRREL) for characterization of a wide variety of ranges in varying climatic and soil conditions.

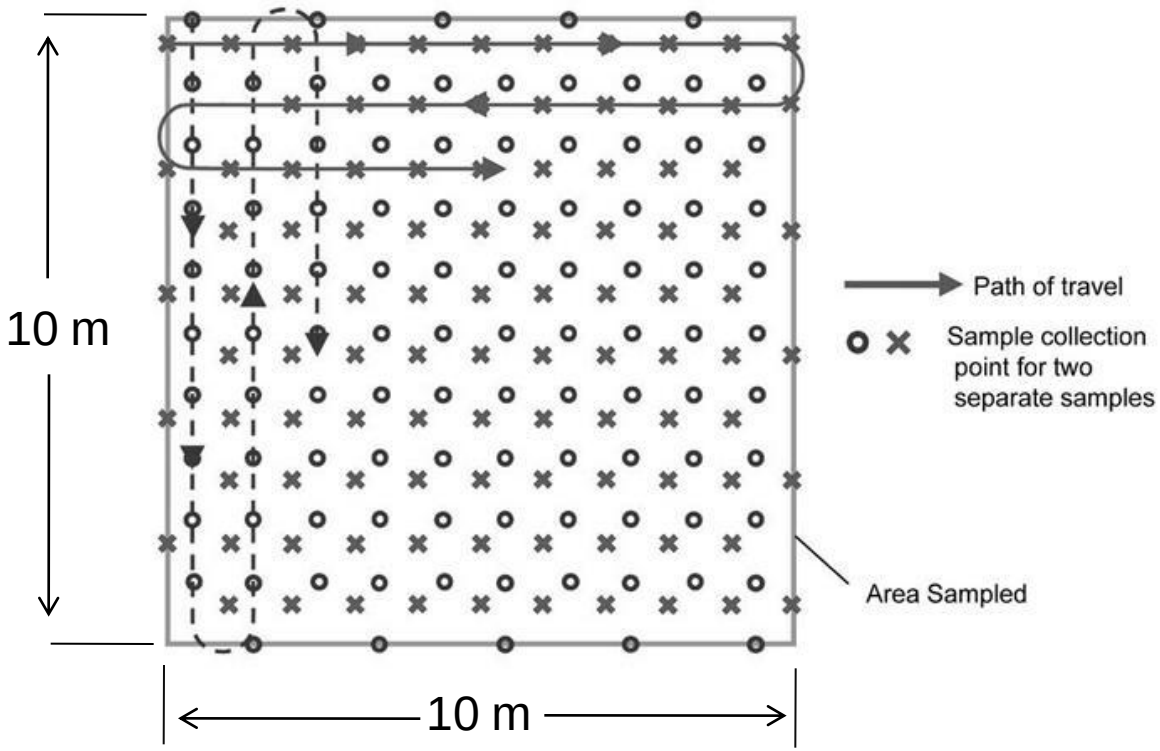
- Used to characterize the mean of the contaminant concentration in the decision unit (area of interest or exposure unit).

- Alternative surface soil sampling techniques often exhibit high standard deviation and skewed or non-reproducible results that do not provide solid evidence for decision making.

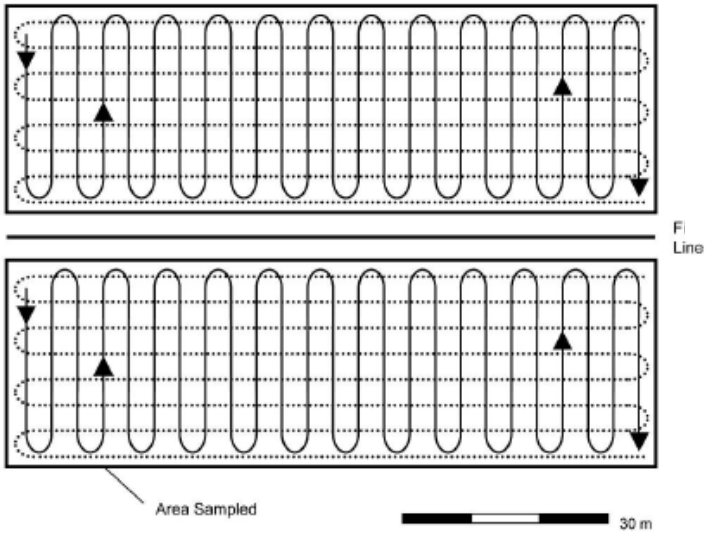
- MIS was developed to reduce representative issues noted with:
  - Discrete sampling
  - Composite sampling with limited increments.

MIS (Cont'd.)

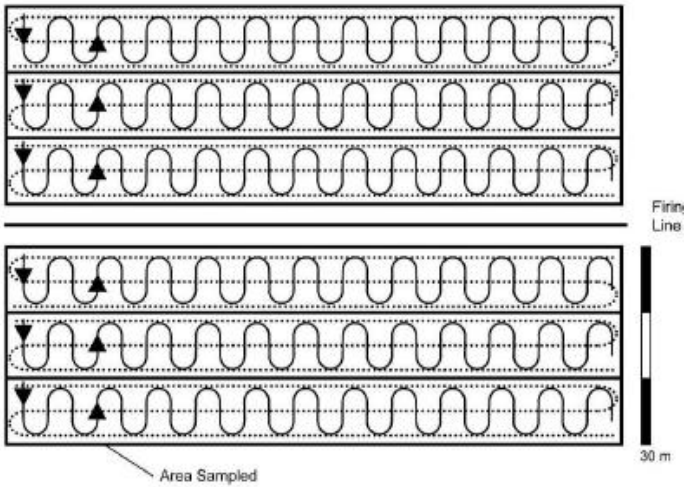
- Considers all increments of a chosen area, or decision unit, as a whole.



MIS (Cont'd.)Alternative Decision Units



a. Pattern to collect one multi-increment sample in a single 30-m wide decision unit.



b. Pattern to collect multi-increment samples in three 10-m-wide decision units.

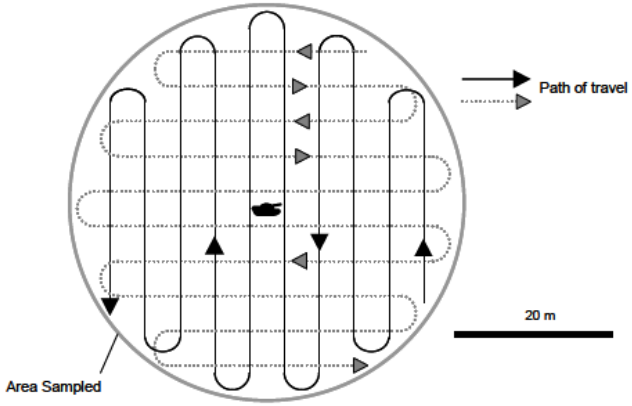


Figure 6. Systematic-random multi-increment sampling design surrounding a tank target at the impact area of an anti-tank range.

MIS (Cont'd.)

- A decision unit is chosen to represent a specific exposure unit or area of interest; can be various shapes/sizes depending upon contamination source. Typically 100 m^2 minimum.
- Depths studied for range characterization are shallow – typically 0 to 2.5 cm depth interval sampled. Depth may exceed 2.5 cm.
- Typically, 30-100 increments are recommended per decision unit; number, depth, size of increments vary with decision unit size.
- Ultimately, around 1kg of soil will be sampled (per decision unit) and sent to the laboratory.

Tools needed for MIS (Jenkins, 2009)

U.S. EPA Method 8330B

- Involves air drying, sieving, and pulverizing the entire sample.
- Unique to Method 8330B is the whole sample processing and incremental subsampling of the pulverized sample.
- Approximately 30 increments will be collected to create the subsample for extraction.
- "Smaller particle size and a larger portion analyzed yields better precision." (Bruce and Penfold, 2009).

MIS Benefits

- MIS promises the following benefits:
  - Results more precise and accurate.
    - Mean concentration closer to the perceived actual mean.
    - Smaller standard deviation among replicates.
    - A high degree of sampling reproducibility.
  - Cost effective.
    - Reduced human and analytical error due to reduced number of samples.
    - Reduced time performing field work (cost reduction).
    - Reduced analytical cost because fewer samples are needed to achieve reliable results.

MIS Benefits

- MIS meets the three fundamental principles of soil sampling
  - Accurate representation of the mean constituent concentrations in the decision unit.
  - High level of confidence for decision making.
  - Cost reduction for similarly accurate results compared to other methods.

Decision Unit Layout (NDCEE, 2009)

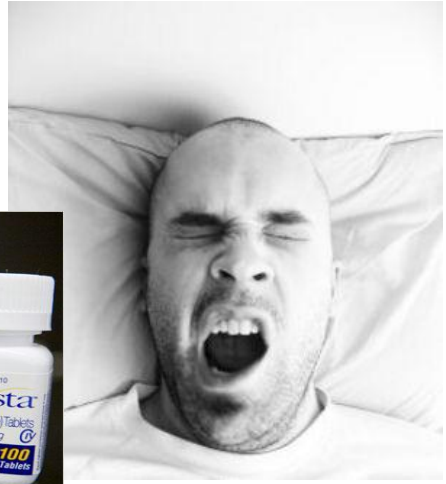
Collecting Increments (NDCEE, 2009)

NDCEE Project Data Evaluation Approach

- Sampling demonstrations at two diverse ranges - a live-fire bombing range with arid, sandy soils and a shoulder-fired grenade range with humid sandy loam soils
- Comparison of discrete, box, and wheel sampling methods to MIS
- Comparison of EPA Method 8330A (utilizing scoop off the top sampling) and EPA Method 8330B (whole sample processing)
- Preliminary assessment of two different EPA Method 8330B grinding methods (roller ball mill and ring and puck mill)
- Comparison of laboratory subsampling methods to bulk sample analysis
- Analysis of variance of field and laboratory sample replicates
- Cost Benefit Analysis.

Data Comparison Evaluation Approach

- Formation and Testing of the Null Hypothesis
- Statistical Comparison of Estimated Means
- 1-Way ANOVA & Validation w/Pairwise Comparison
- Determination of 95% Upper Confidence Intervals (UCI) & Scatterplot Comparison



Data Comparison

The primary question:

- Did the sampling and analysis approach influence the characterization and reporting of the mean concentration of contaminants (i.e., TNT)?
  - ✓ All samples are from within the same decision unit.
  - ✓ Not all observations in the same group will have exactly the same values.
  - ✓ However, in partitioning the variation in detections of TNT – we should only see within group variation and **NOT** variation among the groups.

Data Comparison

Sampling/Analysis Method	Concentrations of TNT mg/kg (0-2.5cm) Holloman AFB, New Mexico						
1 Discrete Samples	1900	230	210	11	37	200	**Basis for selection**: Highest Analytical Detection
2 Box Composite	1100	1800	1500	160	6400	3700	**Basis for selection**: Highest Analytical Detection
3 Wheel Composite	0.6	0.37	0.47	21000	42	90	**Basis for selection**: Highest Analytical Detection
4 IS R. Ball Mill – UV	1700	1700	1600	1300	2000	3300	**Basis for selection**: Highest Analytical Detection
5 IS R. Ball Mill – MS/MS	1600	1300	1400	1100	1500	2900	**Basis for selection**: Highest Analytical Detection
6 IS Ring/Puck – UV	1500	1400	1700	2100	1000	1700	**Basis for selection**: Highest Analytical Detection
7 IS Ring/Puck – MS/MS	1600	1400	1800	2300	1100	1500	**Basis for selection**: Highest Analytical Detection

NOTES:
All detected concentrations are presented. Data set includes replicates. Excluded are bulk values and/or means calculated using replicates.
All samples analyzed by Test America Laboratories, Inc., Denver, Colorado Laboratory.
All samples are dry weight corrected. Bulk dry weight corrections based on average % moisture of three laboratory replicates.

Data Comparison

The most important activity:

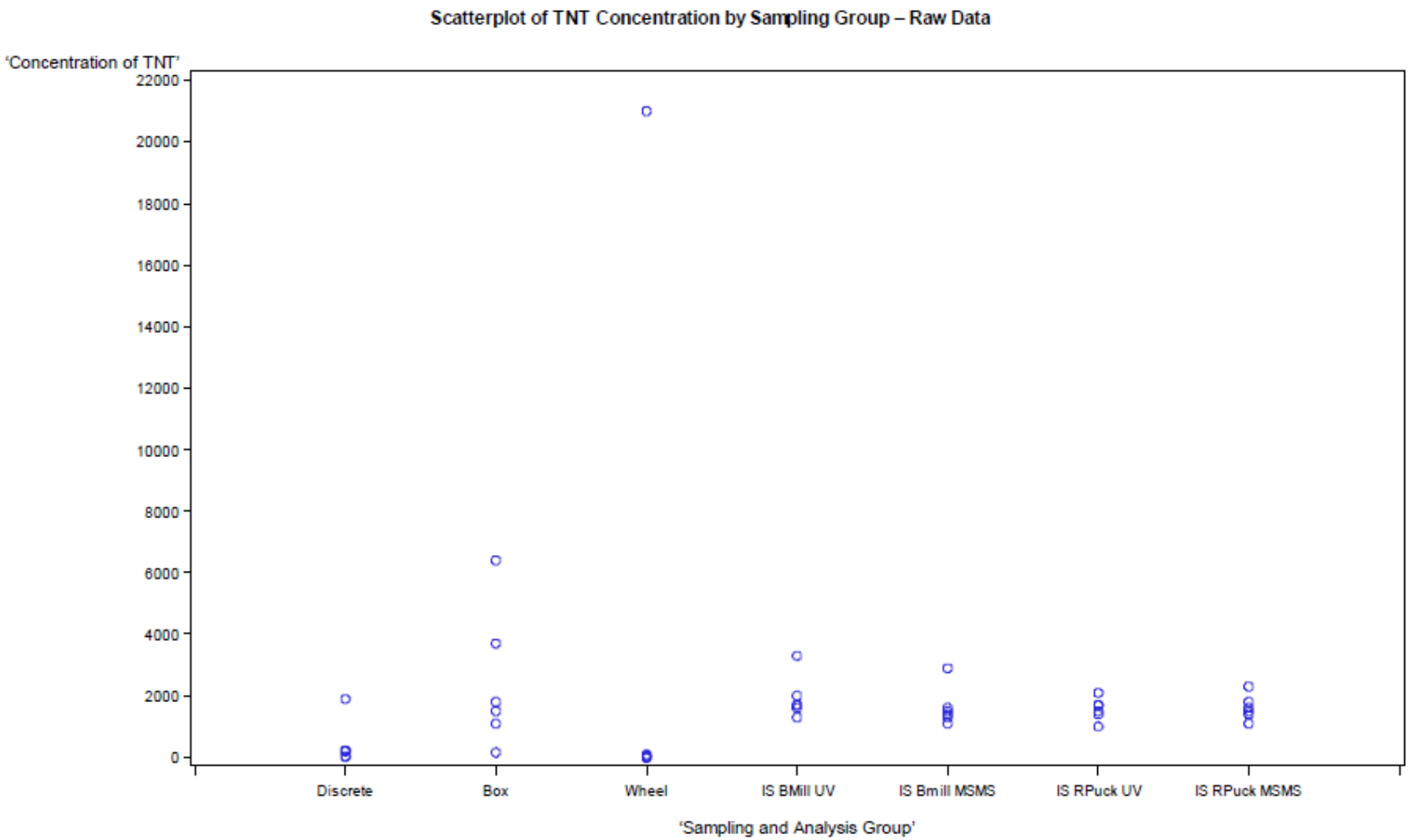
Plot your data.

Data Comparison

The second most important activity:

Plot your data.

Data Comparison



Data Comparison

- Based on your visual examination of the plot, do you believe the collection and analysis method influences the reported mean concentration of TNT?

Data Comparison

- Based on your visual examination of the plot, do you believe the collection and analysis method influences the reported mean concentration of TNT?
  - It appears that the collection method **does not** influence the characterization of the mean concentration of the data.
  - However, It appears that within group variance may be an issue across data collection methods.

Data Comparison - Null Hypothesis

- The ANOVA (Analysis of Variance) (developed by Sir Robert Fisher) is a procedure for testing the equality of two or more means.

- The *F* statistic (named in honor of Sir Robert Fisher) (a mean square ratio) is used to test the null hypothesis that group means are equal against the alternative hypothesis that there is inequality.
  - ✓ If the *F* statistic is unity (one) the null is true.
  - ✓ If the *F* statistic is a large one, the null hypothesis is false.

- For additional information on the application of ANOVA, see Forthofer, Lee, and Hernandez (2007). *Biostatistics: A Guide to Design, Analysis, and Discovery.* Academic Press, Burlington, MA.

Data Comparison - Null Hypothesis

- The following summarizes carrying out a 1-way ANOVA in testing the null hypothesis that the means are identical:

Null Hypothesis

H_0: Reported mean concentration of TNT is the same in all groups (i.e., $\mu_1 = \mu_2 = \mu_3 = \mu_4 = \mu_5 = \mu_6 = \mu_7$).

Alternative Hypothesis

H_a: Mean concentration is <u>not</u> the same in all 7 groups (inequality among means).

ANOVA *F* test

- Using an α=0.05, combined with the visual inspection of the plot provided above, the <u>null is accepted</u> on the *F test*.

- It can be concluded that sampling approach <u>does not affect</u> the reported mean concentration at this site. <u>I.e., the mean concentration does not differ by sampling and analysis type</u>.

```
Analysis of Variance on Differences by Sampling Type
00:22 Wednesday, March 31, 2010

                    The GLM Procedure
              Class Level Information
Class          Levels    Values
group               7    1 2 3 4 5 6 7
Number of Observations Read          42
Number of Observations Used          42
```

```
Analysis of Variance on Differences by Sampling Type
00:22 Wednesday, March 31, 2010

                    The GLM Procedure

Dependent Variable: tntconc   'Concentration of TNT'
                                          Sum of
Source                  DF        Squares     Mean Square    F Value    Pr > F
Model                    6     32064710.4       5344118.4       0.47    0.8282
Error                   35    400829683.0      11452276.7
Corrected Total         41    432894393.4

R-Square     Coeff Var      Root MSE    tntconc Mean
0.074071      180.1857      3384.121        1878.130

Source                  DF      Type I SS     Mean Square    F Value    Pr > F
group                    6    32064710.36      5344118.39       0.47    0.8282
Source                  DF    Type III SS     Mean Square    F Value    Pr > F
group                    6    32064710.36      5344118.39       0.47    0.8282
```

Pairwise Comparison Verification

- Although the null hypothesis of equal means in was not rejected, an exploratory series of pairwise t tests was conducted using SAS to validate that means do not differ from the others.
  - ✓ NOTE: The use of multiple comparison procedures is not recommended when the null is not rejected. However, exceptions may occur when comparisons were planned as a part of the investigation.
  - ✓ Fisher's Least Significant Difference (LSD) method was applied using SAS.

Pairwise Comparison Verification

All Pairwise Comparisons on Differences by Sampling Approach
00:22 Wednesday, March 31, 2010

The GLM Procedure
Least Squares Means

group	tntconc LSMEAN	LSMEAN Number
1	431.33333	1
2	2443.33333	2
3	3522.24000	3
4	1933.33333	4
5	1633.33333	5
6	1566.66667	6
7	1616.66667	7

Least Squares Means for effect group
Pr > |t| for H0: LSMean(i)=LSMean(j)

Dependent Variable: tntconc

i/j	1	2	3	4	5	6	7
1		0.3102	0.1227	0.4472	0.5424	0.5649	0.5480
2	0.3102		0.5843	0.7956	0.6810	0.6564	0.6748
3	0.1227	0.5843		0.4216	0.3403	0.3237	0.3361
4	0.4472	0.7956	0.4216		0.8789	0.8522	0.8722
5	0.5424	0.6810	0.3403	0.8789		0.9730	0.9932
6	0.5649	0.6564	0.3237	0.8522	0.9730		0.9797
7	0.5480	0.6748	0.3361	0.8722	0.9932	0.9797	

NOTE: To ensure overall protection level, only probabilities associated with pre-planned comparisons should be used.

Pairwise Comparison Verification

- Table 1 below summarizes that all comparisons were determined to be not significant (using an α=0.05).

Table 1. Summary of Pairwise t-Test Comparison Validation (Determined to be Not Significant) Within the Sampling Groups When Comparing Means.

i/j	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Comments
Group 1		NS	NS	NS	NS	NS	NS	None are Different
Group 2	NS		NS	NS	NS	NS	NS	None are Different
Group 3	NS	NS		NS	NS	NS	NS	None are Different
Group 4	NS	NS	NS		NS	NS	NS	None are Different
Group 5	NS	NS	NS	NS		NS	NS	None are Different
Group 6	NS	NS	NS	NS	NS		NS	None are Different
Group 7	NS	NS	NS	NS	NS	NS		None are Different

Assumptions

Limitations & Concerns:

- Before trusting the results of this ANOVA, it is important to remember that this analysis is based on a number of assumptions:
  - Independent observations;
  - Random samples from respective populations;
  - Populations have common variances; and,
  - Residuals are normally distributed.

Assumptions

Limitations & Concerns:

- The independent and random sampling assumption is verified:
  - ✓ Sampling and analysis plan & personal communication with the sampling specialists.
  - ✓ These elements are not easily tested with formal procedures.

Assumptions

Limitations & Concerns:

- The equal variance assumption was examined informally with the aforementioned scatterplot.
  - ✓ It is reasonable that the two extreme values from the composite sampling and analysis approach raise a cause for potential concern (i.e., composite sampling had variances that potentially differ from the discrete and incremental sampling and analysis approaches).

- Additional research and analysis is needed to assess the normality of the residuals in the context of ANOVA for this data set and others.
  - ✓ Equal variance assumption can be tested formally with Bartlett's test or Levene's test. Levene's test is presented below.

Levene's Test for Equal Variances

Levene's Test for equal variances among TNT data sets.

- As with other tests, a <u>small</u> p-value indicates the null hypothesis of equal variances should be rejected.
- The Levene test of equal variances for the data set <u>does NOT</u> reject the null.

Analysis of Variance for TNT Concentrations
00:22 Wednesday, March 31, 2010

The GLM Procedure
Levene's Test for Homogeneity of tntconc Variance

ANOVA of Squared Deviations from Group Means

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
group	6	1.868E16	3.114E15	1.52	0.2014
Error	35	7.184E16	2.053E15		

Analysis of Variance for TNT Concentrations
00:22 Wednesday, March 31, 2010

The GLM Procedure

Level of group	N	tntconc Mean	tntconc Std Dev
1	6	431.33333	725.56176
2	6	2443.33333	2260.81106
3	6	3522.24000	8562.39239
4	6	1933.33333	706.16334
5	6	1633.33333	643.94617
6	6	1566.66667	366.96957
7	6	1616.66667	407.02170

Normality Tests – Shapiro-Wilk/KS

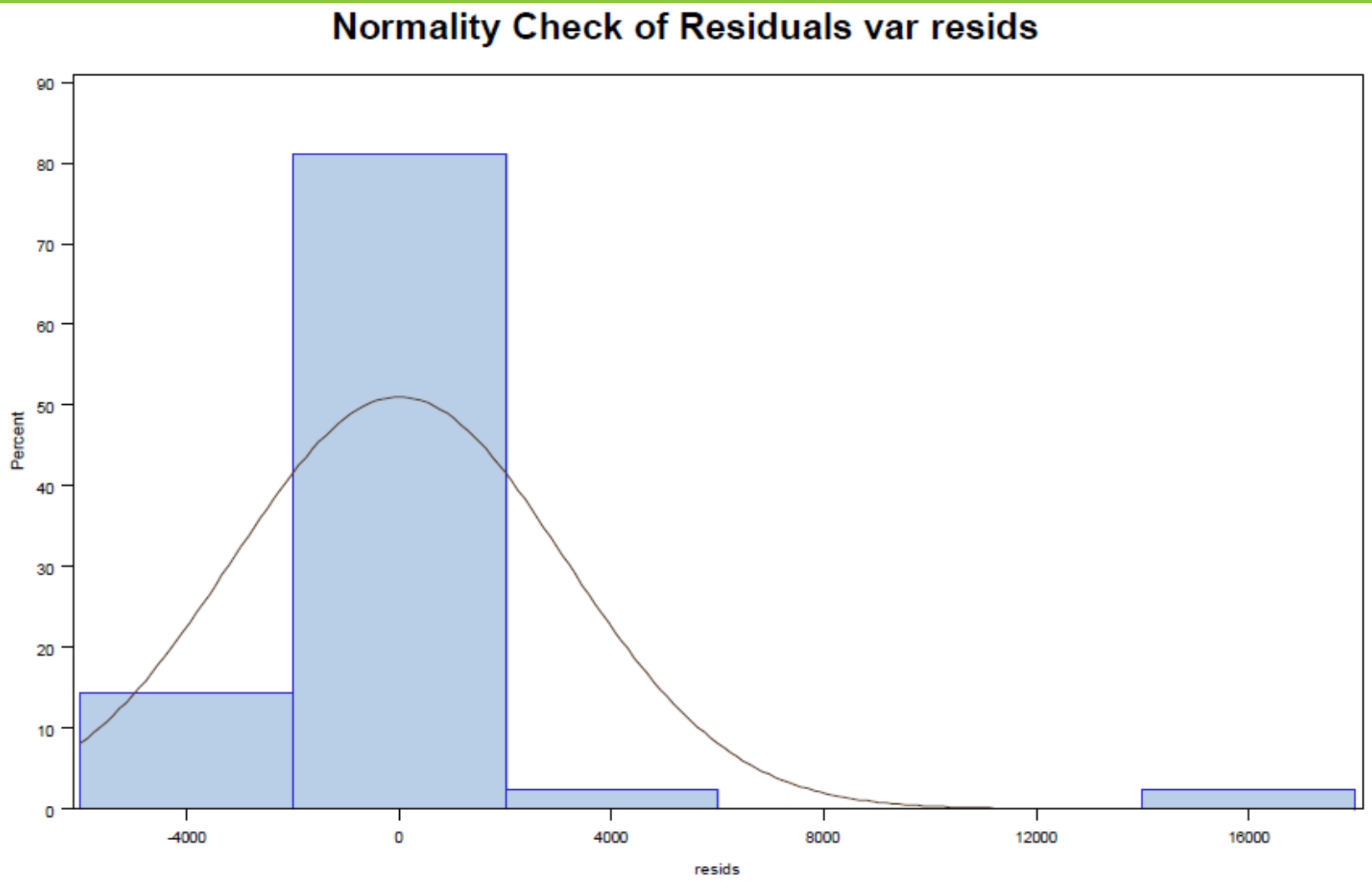
- The Normality assumption for residuals may be examined informally using histograms, q-q plots, and/or formal tests such as Shapiro-Wilk or Kolmogorov-Smirnov tests.
- Those tests were conducted for this data set and are presented below.

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.531026	Pr < W	<0.0001
Kolmogorov-Smirnov	D	0.286145	Pr > D	<0.0100
Cramer-von Mises	W-Sq	1.089852	Pr > W-Sq	<0.0050
Anderson-Darling	A-Sq	5.667553	Pr > A-Sq	<0.0050

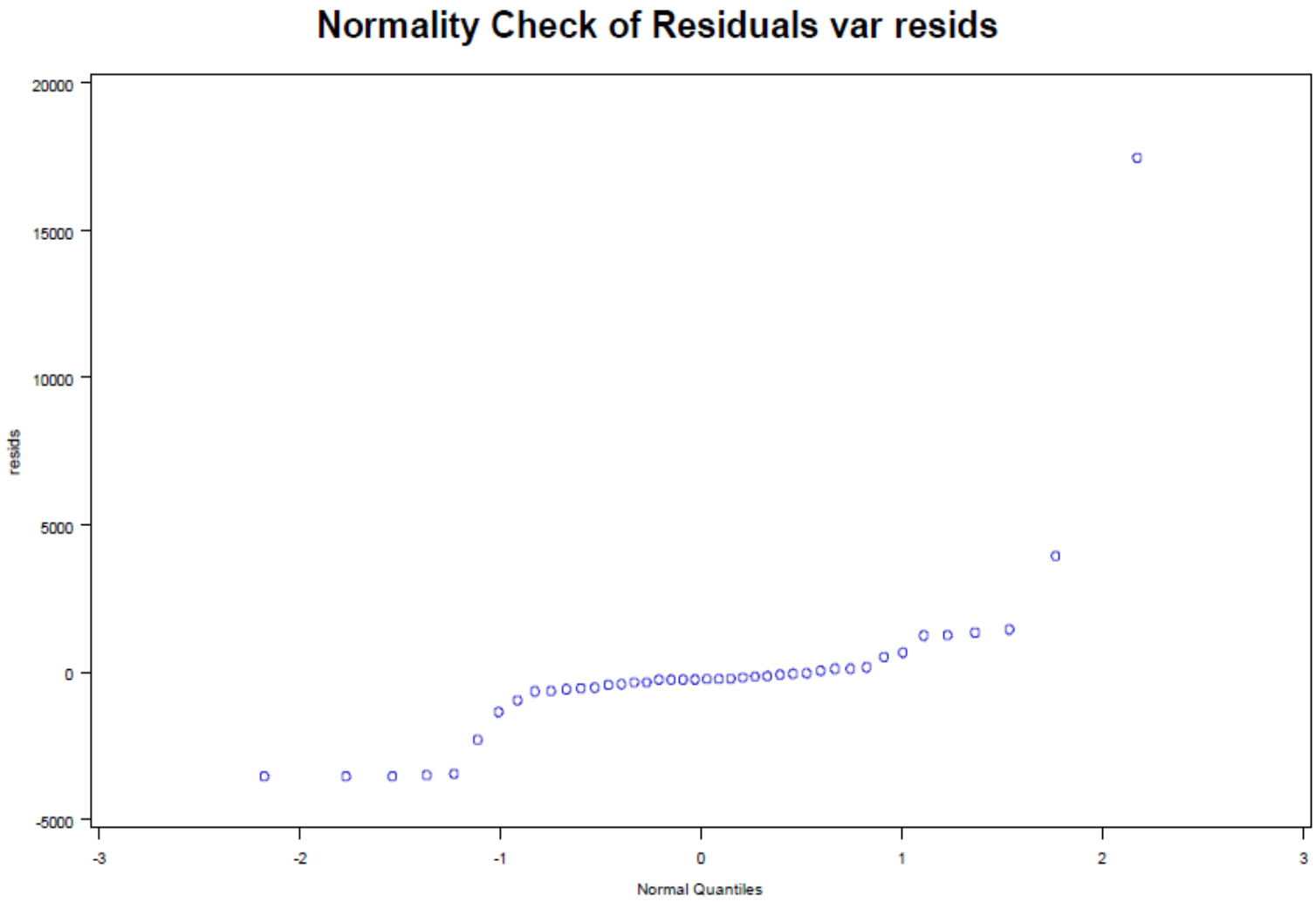
Quantiles (Definition 5)

Quantile	Estimate
100% Max	17477.760
99%	17477.760
95%	1468.667
90%	1266.667
75% Q3	133.333
50% Median	-226.333

Normality Tests – Residuals Histogram



Normality Tests – Q/Q Plot



Assumption Issues

- We can conclude that we would reject the null assumption of normality based on the informal and formal tests. It appears that normality assumption may be unreasonable for this set of residuals using this data set.
  - **NOTE:** However**,** ANOVA procedures work reasonably well with small departures from the normality assumption. More weight may be placed on the interpretation of the variances evaluation (Forthofer, Lee, and Hernandez, 2007).
- We can conclude that there is some difference among groups in the degree of variation; However, this difference does not appear to be very great.
- As an option, we can continue the analysis looking at SAS evaluation without the outliers, which would most likely show conformity to all assumptions. We can suggest the TNT in the composite sampling approach may be associated with tritinol based on personal communications with the field specialists.

Confidence Intervals Development

- Confidence Intervals (95% UCI) on the mean are used to estimate exposure point concentrations (EPC) in risk assessment.

- There are a number of ways to estimate the UCI depending on the distribution of the dataset (none is ideal in all):
  - Classical Student's *t* statistic (normal distribution or assumed normal);
  - Land H-statistic (log-normal distribution);
  - Chebyshev (non-parametric/non-distribution).

- The appropriate procedure should be reviewed with your risk assessor, regulator, or statistician, etc. for determining the appropriateness of selected calculation (U.S. EPA, 2002).

Confidence Intervals Development

- 95% Confidence Intervals (95% UCI) were estimated using SAS for each dataset to represent typical exposure point concentrations that could be use in risk assessment.

- <u>Limitations:</u>
  - ✓ SAS w/Student's t.
  - ✓ Limited data set (n=6).
  - ✓ Cannot confidently determine distribution.
  - ✓ Statistical power is low.
  - ✓ Chebyshev's procedure may be more appropriate.

1: DISCRETE

Basic Confidence Limits Assuming Normality

Parameter	Estimate	95% Confidence Limits	
Mean	431.33333	-330.09704	1193
Std Deviation	725.56176	452.90146	1780
Variance	526440	205120	3166702

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	1.456177	Pr > |t|	0.2051
Sign	M	3	Pr >= |M|	0.0313
Signed Rank	S	10.5	Pr >= |S|	0.0313

Quantiles (Definition 5)

Quantile	Estimate
100% Max	1900
99%	1900
95%	1900
90%	1900
75% Q3	230
50% Median	205

Confidence Intervals Development

2: BOX COMPOSITE

Basic Confidence Limits Assuming Normality

Parameter	Estimate	95% Confidence Limits	
Mean	2443	70.75763	4816
Std Deviation	2261	1411	5545
Variance	5111267	1991532	30745881

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	2.647245	Pr > |t|	0.0456
Sign	M	3	Pr >= |M|	0.0313
Signed Rank	S	10.5	Pr >= |S|	0.0313

Quantiles (Definition 5)

Quantile	Estimate
100% Max	6400
99%	6400
95%	6400
90%	6400
75% Q3	3700
50% Median	1650

3: WHEEL COMPOSITE

Basic Confidence Limits Assuming Normality

Parameter	Estimate	95% Confidence Limits	
Mean	3522	-5463	12508
Std Deviation	8562	5345	21000
Variance	73314563	28565966	441010221

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	1.007626	Pr > |t|	0.3599
Sign	M	3	Pr >= |M|	0.0313
Signed Rank	S	10.5	Pr >= |S|	0.0313

Quantiles (Definition 5)

Quantile	Estimate
100% Max	21000.00
99%	21000.00
95%	21000.00
90%	21000.00
75% Q3	90.00
50% Median	21.30

Confidence Intervals Development

4: IS Ball Mill UV

Basic Confidence Limits Assuming Normality

Parameter	Estimate	95% Confidence Limits	
Mean	1933	1192	2674
Std Deviation	706.16334	440.79281	1732
Variance	498667	194298	2999637

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	6.706211	Pr > |t|	0.0011
Sign	M	3	Pr >= |M|	0.0313
Signed Rank	S	10.5	Pr >= |S|	0.0313

Quantiles (Definition 5)

Quantile	Estimate
100% Max	3300
99%	3300
95%	3300
90%	3300
75% Q3	2000
50% Median	1700

5: IS Ball Mill MS MS

Basic Confidence Limits Assuming Normality

Parameter	Estimate	95% Confidence Limits	
Mean	1633	957.55327	2309
Std Deviation	643.94617	401.95635	1579
Variance	414667	161569	2494351

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	6.212993	Pr > |t|	0.0016
Sign	M	3	Pr >= |M|	0.0313
Signed Rank	S	10.5	Pr >= |S|	0.0313

Quantiles (Definition 5)

Quantile	Estimate
100% Max	2900
99%	2900
95%	2900
90%	2900
75% Q3	1600
50% Median	1450

Confidence Intervals Development

6: IS Ring Puck UV

Basic Confidence Limits Assuming Normality

Parameter	Estimate	95% Confidence Limits	
Mean	1567	1182	1952
Std Deviation	366.96957	229.06534	900.03471
Variance	134667	52471	810062

Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	10.45736	Pr > |t|	0.0001
Sign	M	3	Pr >= |M|	0.0313
Signed Rank	S	10.5	Pr >= |S|	0.0313

Quantiles (Definition 5)

Quantile	Estimate
100% Max	2100
99%	2100
95%	2100
90%	2100
75% Q3	1700
50% Median	1600

7: IS Ring Puck MS MS

Basic Confidence Limits Assuming Normality

Parameter	Estimate	95% Confidence Limits	
Mean	1617	1190	2044
Std Deviation	407.02170	254.06620	998.26712
Variance	165667	64550	996537

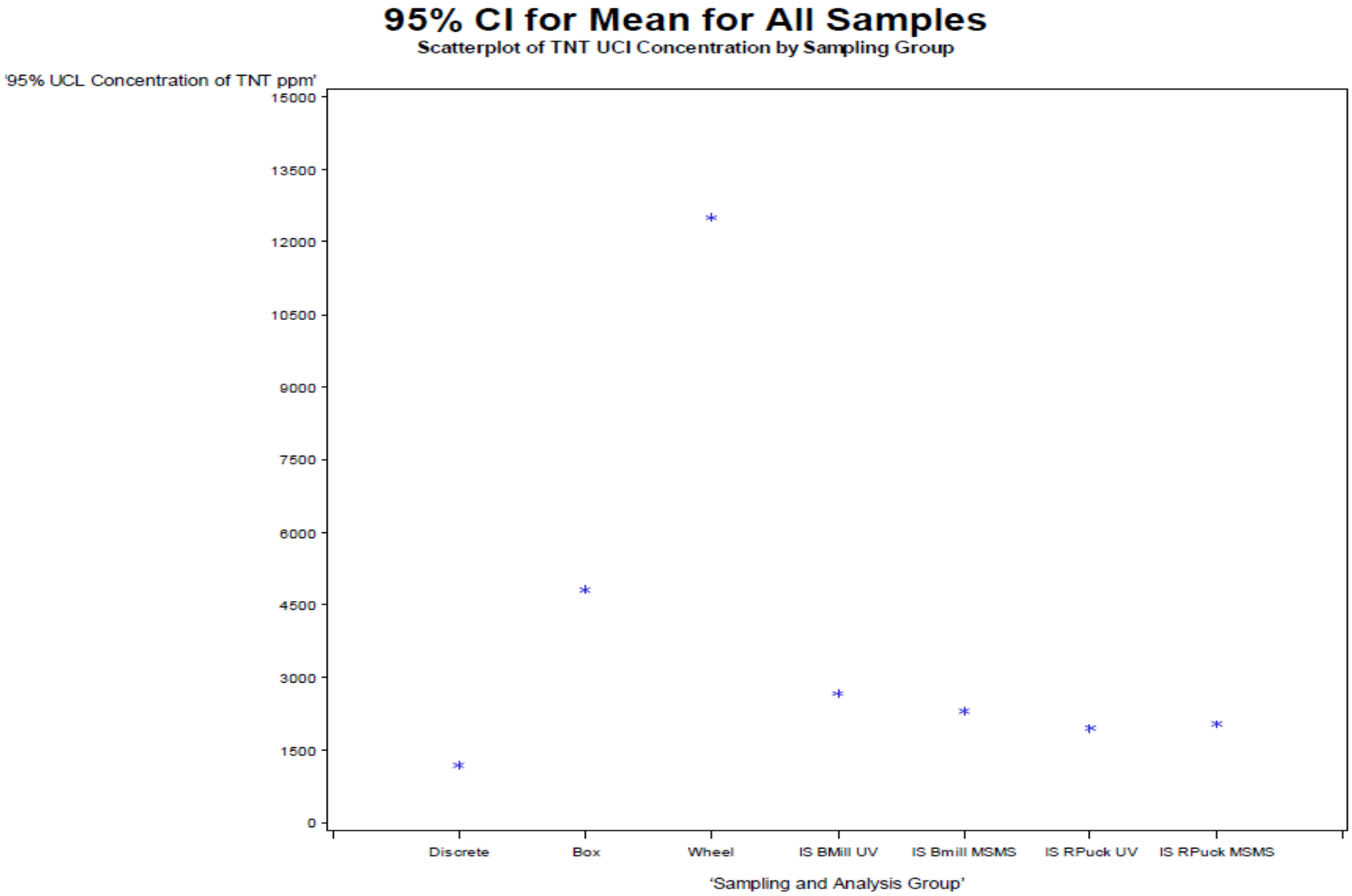
Tests for Location: Mu0=0

Test	-Statistic-		-----p Value------	
Student's t	t	9.729232	Pr > |t|	0.0002
Sign	M	3	Pr >= |M|	0.0313
Signed Rank	S	10.5	Pr >= |S|	0.0313

Quantiles (Definition 5)

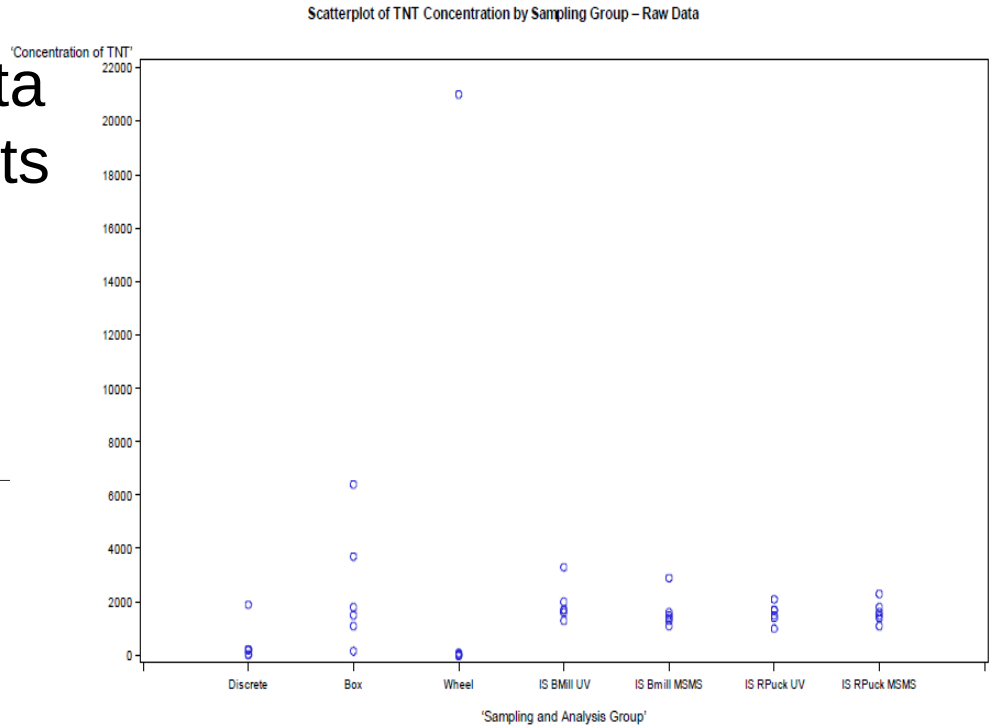
Quantile	Estimate
100% Max	2300
99%	2300
95%	2300
90%	2300
75% Q3	1800
50% Median	1550

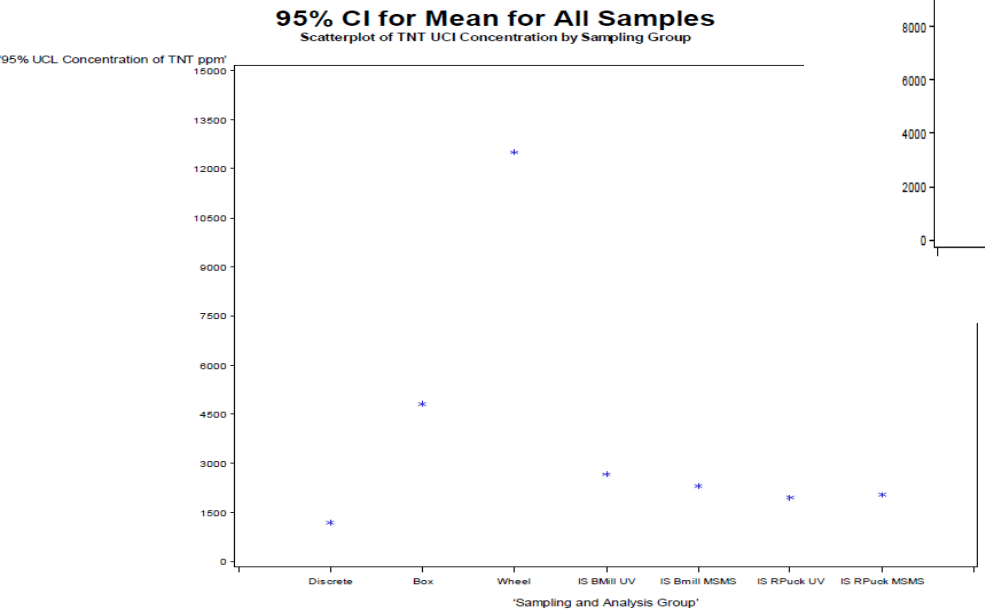
Confidence Intervals Development



Confidence Intervals Development

- Comparison of Raw Data and 95%UCI Scatterplots





Conclusions

- Did the sampling and analysis approach influence the characterization and reporting of the mean concentration of contaminants (i.e., TNT)?

  – **No.**

  (But this is <u>great</u> news…)

(…An option for a consistent, faster, and less expensive defensive sampling method for vast tracts of land is always welcome…right?)

Conclusions

- Incremental sampling did, shows these benefits:
  - Results more precise and accurate with mean concentration closer to the perceived actual mean.
  - Smaller standard deviation among replicates and a higher degree of sampling reproducibility.
  - Cost effective for expansive tracks of land.
  - Reduced human and analytical error due to reduced number of samples.
  - Reduced time performing field work (cost reduction).
  - Reduced analytical cost because fewer samples were needed to achieve reliable results.

Conclusions (Cont'd.)

- Most importantly, MIS meets the three fundamental principles of soil sampling:
  - Accurate representation of the mean constituent concentrations in the decision unit.
  - High level of confidence for decision making.
  - Cost reduction for similarly accurate results compared to other methods.

MIS Limitations

- DoD research focused primarily on application for shallow surface soil sampling at ranges.
  - Application for contaminants other than energetics residues limited to date; metal co-contaminants can not yet be evaluated alongside – potential grinding impacts.
  - Some depth profiling completed (apparent cost savings likely decrease with depth unless drilling).
- Goal must be to determine mean concentration of contaminant in area of interest.
  - MIS has better chance of including hotspots in an MI sample than typically discrete sampling, however the mean concentration overall will be what is determined.
- MIS in field must go hand in hand with whole sample analysis in laboratory (Laboratory protocols must be examined to ensure compatibility with MI sampling).

Future of MIS

- Continued studies of MIS in the sustainability of DoD and other sites.
- Expanding use of MIS to include metals and other contaminants. Among parameters to be considered include:
  - Impact of grinding;
  - Whole sample processing; and,
  - Sampling depth.
- Expanding list of regulatory authorities approving or requiring MIS for range characterization.

National Defense Center for Energy and Environment

Points of Contact

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This work was funded through the Office of the Assistant Secretary of the Army (Installations and Environment) and conducted under contract W74V8H-04-D-0005 Task 0527 A3. The views, opinions, and/or findings contained in this paper are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision unless so designated by other official documentation.

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Backup Slides

Development of Exposure Point Concentrations with Incremental Sampling Data – Comparing Means and Confidence Intervals of Discrete, Composite, and Incremental Sampling Environmental Study Data

E2S2 Denver, CO
June 14th, 2010

Mr. Chuck Tomljanovic, CHMM, MSEM
CTC/NDCEE

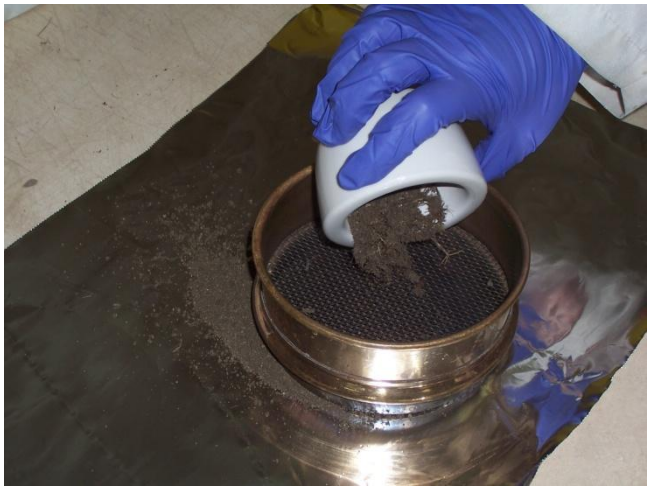
Co-authors: Dr, C. Dan Volz, Ms. Diane Roote, and Ms. Alyssa Gormish

Laboratory Analyses of Energetics by EPA Method 8330A

- Traditional analytical method for surface soil samples resulting from discrete, box, and wheel methods
- Per typical lab protocol, subsampling under 8330A consists of taking a “scoop off the top” of the soil (in-transit settling of sample can lead to unrepresentative lab subsample even from field composite)
- Per 8330A, this subsample is ground with mortar and pestle, screened w/ 30 mesh sieve, then subjected to HPLC/UV extraction and analysis
- Modifications to 8330A for this project
  - 10 Mesh (2 mm) sieve size
  - Include nitrogylcerin as a target analyte

Laboratory Analysis of Energetics by EPA 8330B

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



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

Laboratory Analysis of Energetics by EPA 8330B

- 8330B allows either HPLC/UV or HPLC/MS
- Additional evaluations per 8330B for this project
  - Two different grinding techniques will be used for MI samples (roller ball mill and ring and puck mill)
  - Both UV and MS will be used as detectors for a subset of extracts and results compared

Laboratory Analysis of Energetics by EPA 8330B

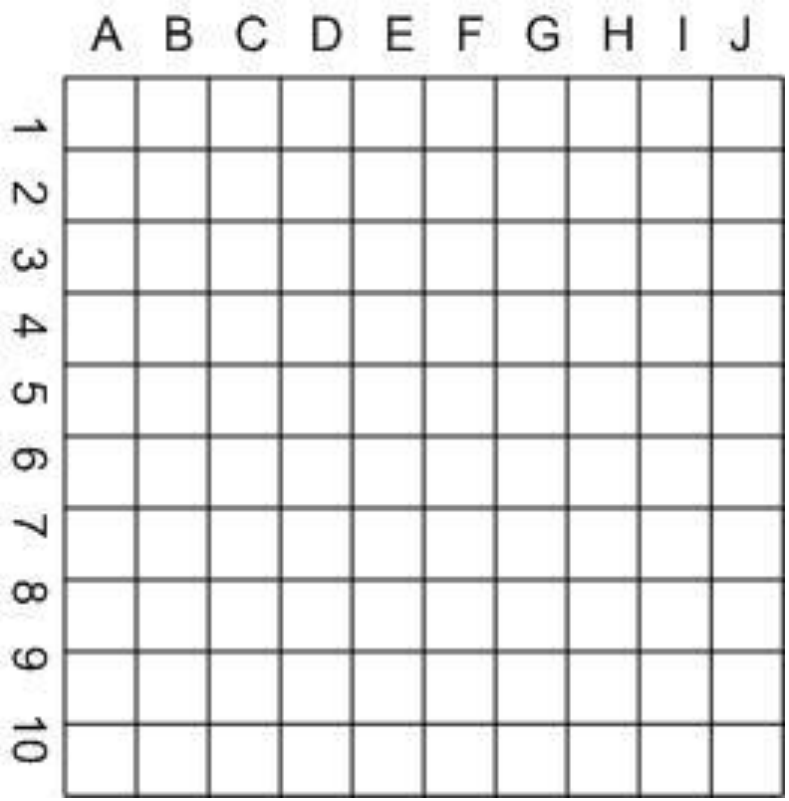
- Not all laboratories have an acceptable 8330B/IS sub-sampling Standard Operating Procedure (SOP) or certification to perform
  - Must have enough space to allow samples to air dry
  - Must have a grinding tool with dust control to prevent cross-contamination
  - Must have an SOP for MIS sub-sampling

NDCEE Demonstration/Validation

- Field sampling at Red Rio Bombing Range, Live Drop Impact Area, Holloman AFB completed March 24, 2009.
- Field sampling at shoulder-fired grenade launcher range, DoD site in the humid northwest region completed May 7, 2009 and July 28, 2009.
- Sample analysis being completed at TestAmerica Laboratories, Inc., Denver, CO.
- Full results are available for Holloman AFB and preliminary results are available for Fort Lewis.

Collecting Increments (NDCEE, 2009)

Holloman AFB Decision Unit



- 10 m x 10 m decision unit adjacent to crater of low order detonation of 500 pound bomb.
- Tritonal (2,4,6-Trinitrotoluene (TNT) with aluminum) prime contaminant of potential concern.
- Collected four field replicates each of discrete, box, wheel, MIS ball mill, and MIS puck mill samples.
- All samples 0 – 2.5 cm depth, dry, loose fine to coarse sand with very little vegetation.
- 100 increments collected for multi increment (MI) samples.

Holloman Discrete/Composite Results (mg/kg)

	4-A-DNT		2-A-DNT		2,4-DNT		TNB		TNT	
H-Discrete1-I4	2.10	J	2.90	J	<2.60		6.60		1900	
H-Discrete1-I4-R1	2.10		2.40	J	0.47		6.00		230	
H-Discrete1-I4-R2	2.30		2.30	J	0.42		6.30		210	
H-Discrete1-I4-Bulk	2.30	J	3.00	J	<2.70		5.30		2000	
H-Discrete2-B2	2.10		2.70		<0.25		0.61		11	J
H-Discrete3-B8	4.70		4.90		0.10	JJ	0.82		37	
H-Discrete4-A9	3.60		4.70		0.18	JJ	0.19	J	200	
H-Box1-G3	4.00		4.80	J	0.82	JJ	13.0		1100	
H-Box1-G3-R1	4.70		5.50	J	1.20	JJ	13.0		1800	
H-Box1-G3-R2	3.90		4.90	J	2.00	JJ	13.0		1500	
H-Box1-G3-Bulk	4.90		5.50	J	1.20	JJ	14.0		3300	
H-Box2-H8	1.50	J	2.40	JJ	0.38		4.3	J	160	
H-Box3-H4	2.40	J	4.00	J	6.40	JJ	30.0		6400	
H-Box4-H8	1.90	J	2.30	J	1.40	JJ	7.3		3700	
H-Wheel1-I8	0.087	J	0.15	J	<0.28		<0.28		0.60	
H-Wheel1-I8-R1	0.087	J	0.15	J	<0.30		<0.30		0.37	
H-Wheel1-I8-R2	0.130	J	0.20	J	<0.27		<0.27		0.47	
H-Wheel1-I8-Bulk	0.11	J	0.20	J	<0.30		<0.30		0.81	
H-Wheel2-F4	3.00		<2.80		5.60	JJ	64.0		21000	
H-Wheel3-B5	3.60		4.20		0.15	JJ	0.61		42	
H-Wheel4-H7	1.90		2.30		0.30		1.60		90	

Holloman IS Results (mg/kg)

	HPLC/UV					HPLC/MS/MS				
	4-A-DNT	2-A-DNT	2,4-DNT	TNB	TNT	4-A-DNT	2-A-DNT	2,4-DNT	TNB	TNT
H-IS-Ball1	4.40	4.90 J	1.50	8.60	1700	4.60 J	3.90 J	1.20 J	6.20 J	1600
H-IS-Ball1-R1	4.30	4.70 J	1.40	8.60	1700	5.40 J	4.30 J	1.50 J	6.80 J	1300
H-IS-Ball1-R2	4.50	5.00 J	1.40	8.60	1600	3.50 J	4.00 J	1.30 J	7.50 J	1400
H-IS-Ball1-Bulk	5.40	7.10 J	0.930 JJ	8.60	1600	4.30 J	6.10 J	1.30 J	7.20 J	1600
H-IS-Ball2	3.80	4.90 J	0.870 JJ	9.60	1300	5.70 J	5.60 J	1.30 J	11.00	1100
H-IS-Ball3	5.40	5.50 J	1.000 JJ	12.0	2000	4.20 J	4.60 J	1.30 J	9.90 J	1500
H-IS-Ball4	8.10	6.30 J	0.780 JJ	8.30	3300	7.00 J	5.40 J	1.30 J	8.10 J	2900
H-IS-Puck1	2.50	3.40 J	1.000 JJ	7.60	1500	3.50 J	2.30 J	1.40 J	5.50 J	1600
H-IS-Puck1-R1	2.40	3.20 J	1.000 JJ	7.00	1400	3.10 J	1.90 J	1.50 J	5.50 J	1400
H-IS-Puck1-R2	2.60	3.60 J	1.100	7.90	1700	3.10 J	3.30 J	1.50 J	6.70 J	1800
H-IS-Puck1-Bulk	2.50	4.30 J	1.40	9.70	1900	2.60 J	2.80 J	1.70 J	6.30 J	1500
H-IS-Puck2	2.70	3.80 J	1.10 JJ	11.0	2100	5.60 J	3.10 J	1.40 J	8.80 J	2300
H-IS-Puck3	2.50	3.70 J	0.64 JJ	7.90	1000	2.50 J	3.00 J	1.00 J	6.30 J	1100
H-IS-Puck4	2.60	3.70 J	0.79 JJ	8.30	1700	4.10 J	1.10 J	3.00 J	7.20 J	1500

NDCEE Dem/Val Holloman AFB Results

Holloman Data TNT (mg/kg), Laboratory Replicates Comparison

Sample Type	Replicates			Bulk	Mean	Range	Std Dev	% RSD	Rel % Diff	Range % diff		RSD Rank	RPD Rank
	1	2	3							High	Low		
Discrete	1900	230	210	2000	780	210-1900	970	124	-87.8	-5.1	-162	7	7
Box	1100	1800	1500	3300	1467	1100-1800	351	23.9	-76.9	-58.8	-100	5	6
Wheel	0.6	0.37	0.47	0.8	0.48	0.37-0.6	0.12	24.0	-50.0	-28.6	-73.5	6	5
MIS-Ball-HPLC	1700	1700	1600	1600	1667	1600-1700	57.7	**3.46**	**4.1**	6.1	0.0	1	1
MIS-Ball-MS/MS	1600	1300	1400	1600	1433	1300-1600	153	**10.7**	**-11.0**	0.0	-20.7	3	3
MIS-Puck-HPLC	1500	1400	1700	1900	1533	1400-1700	153	**9.96**	**-21.4**	-11.1	-30.3	2	4
MIS-Puck-MS/MS	1600	1400	1800	1500	1600	1400-1800	200	**12.5**	**6.5**	18.2	-6.9	4	2

Rule of Thumb: RSD for laboratory replicates should be <20% for MIS (Rieck, 2008)

NDCEE Dem/Val Holloman AFB Results (Cont'd.)

Holloman Data TNT (mg/kg), Field Sampling Comparison

Sample Type	Replicates				Mean	Range	Std Dev	% RSD	RSD Rank
	1	2	3	4					
Discrete	1900	11	37	200	537	11-1900	913	170	6
Box	1100	160	6400	3700	2840	160-6400	2810	98.9	5
Wheel	0.6	21000	42	90	5280	0.60-21000	10500	199	7
MIS-Ball-HPLC	1700	1300	2000	3300	2080	1300-3300	866	**41.6**	3
MIS-Ball-MS/MS	1600	1100	1500	2900	1780	1100-2900	780	**43.8**	4
MIS-Puck-HPLC	1500	2100	1000	1700	1580	1000-2100	457	**28.9**	1
MIS-Puck-MS/MS	1600	2300	1100	1500	1630	1100-2300	499	**30.6**	2
Rule of Thumb: RSD for Field Replicates should be <30% for MIS (Rieck, 2008)									

NDCEE Dem/Val Results

- In the field:
  - MIS procedures resulted in much better reproducibility for field replicates than discrete, box, or wheel methods, close to 30% RSD goal except at extremely heterogeneous site.
  - MIS provided superior samples:
    - At Holloman AFB bombing range, with scattered titronal (TNT with aluminum) chunks on the surface of non-vegetated arid sandy soils.
    - At Fort Lewis firing points, with microscopic NG embedded in nitrocellulose fibers in grassy, humid sandy loam soils.
  - MIS procedures provide data more representative of the true mean of the contaminant concentration within the decision unit, based on the smaller variance between the field replicates (total sampling error).

NDCEE Dem/Val Results (Cont'd.)

- In the laboratory:
  - MIS subsampling procedure (Method 8330B) led to superior reproducibility for lab replicates compared to scoop off the top and mortar and pestle grinding (Method 8330A).
  - MIS subsamples provided a more representative subsample in comparison to the bulk sample analysis over the scoop off the top method at Holloman AFB and Fort Lewis.
  - For crystalline energetics such as TNT, roller ball mill and ring and puck mill grinding methods may be roughly equivalent in effectiveness. The puck mill may be more effective for contaminants found in nitrocellulose fibers such as NG, though dem/val final results are still out.

NDCEE Dem/Val Results (Cont'd.)

- <u>In the laboratory (cont'd.):</u>
  - UV detection appeared to provide slightly better reproducibility than MS/MS. MS/MS may be favored in some cases regardless, including when lower detection limits are needed, and for complex sample matrices (Penfold, 2008).

NDCEE Dem/Val CBA Results

- Cost comparisons based on three replicate MIS samples compared to 30 discrete samples assumed to provide equivalent data, based on previous research.
- Labor cost:
  - Lower for MIS compared to discrete sampling method that could yield equivalent quality data. With a coring tool, 100 MIS increments plus replicates take about the same time as a few discrete samples. For one 100 m^2 decision unit, a two-person team may take twice as much time to collect 30 discrete samples as to collect three replicate 100-increment MI samples.
- Analytical cost savings:
  - With MIS, fewer analyses required to yield equivalent data
  - For single 100 m^2 decision unit, analytical cost > 3x higher for 30 discrete samples than for three MI sample replicates, including appropriate laboratory quality control samples.
  - Offsets higher shipping costs for larger samples and use of 8330B instead of 8330A.
- Overall cost 189% higher for 30 discrete samples compared to three MI sample replicates for single decision unit.
- Indirect cost benefits may result from higher confidence in reproducible results:
  - Reduced demand for confirmation sampling
  - More straight-forward decision process.

SAS Code (SAS, 2010)

```
**** isdataTNT_HAFB.sas
**** Carry out 1-way Analysis of Variance (ANOVA) on Mean
**** Concentrations of TNT Within Seven Sampling and Analysis groups.
options ls=75 ps=55;

data TNTdata;
input tntconc group @@;
label
tntconc = 'Concentration of TNT'
group = 'Sampling and Analysis Group';
cards;
1900  1 230 1 210 1 11  1 37  1 200 1 1100      2 1800      2 1500
      2 160       2 6400      2 3700      2 .6  3 .37 3 .47 3 21000
      3 42        3 90        3 1700      4 1700      4 1600      4
1300  4 2000      4 3300      4 1600      5 1300      5 1400      5
1100  5 1500      5 2900      5 1500      6 1400      6 1700      6
2100  6 1000      6 1700      6 1600      7 1400      7 1800      7
2300  7 1100      7 1500      7;
run;
```

SAS Code

```
**** Format the Scatterplot for Readability.;
proc format;
value grouptype
0=' '
1='Discrete'
2='Box'
3='Wheel'
4='IS BMill UV'
5='IS Bmill MSMS'
6='IS RPuck UV'
7='IS RPuck MSMS'
8='  '
;
run;

symbol v=circle;
proc gplot data=TNTdata;
title2 'Scatterplot of TNT Concentration by Sampling Group - Raw Data';
format group grouptype.;
plot tntconc * group /haxis=(0 to 8 by 1) hminor=0
vaxis=(0 to 22000 by 2000)vminor=0;
run;

proc print data= TNTdata;
title1      'Data in TNTdata Data Set';
var tntconc group;
run;
```

SAS Code

```
proc univariate data=TNTdata plot normal;
var tntconc group;
title2 'Univariate Descriptive Statistics';
run;

**** Carry out 1-Way ANOVA on the TNT Data;
proc glm data=TNTdata;
title1 'Analysis of Variance on Differences by Sampling Type';
class group;
model tntconc=group;
run;

**** Complete Pairwise Comparisons of Diet Data;
proc glm data=TNTdata;
title1 'All Pairwise Comparisons on Differences by Sampling Approach';
class group;
model tntconc=group;
lsmeans group/pdiff=all adj=t;
run;

**** Complete Levene's Test for Equal Variances.;
proc glm data=TNTdata;
title1 'Analysis of Variance for TNT Concentrations';
class group;
model tntconc=group;
means group/hovtest=levene;
run;
```

SAS Code

```
**** Obtain residuals and carry out normality check.;
proc glm data=TNTdata;
title1 'Obtain residuals for normality nheck.';
class group;
model tntconc=group;
output
out=resids
residuals=resids;
run;

proc univariate data=resids normal;
title1 'Normality Check of Residuals'
var resids;
qqplot resids/normal;
histogram resids/normal;
run;
```

SAS Code

```
****CONFIDENCE INTERVALS AS PART OF THE PROC UNIVARIATE OUTPUT
(VARIANCE UNKONWN)
data group1;
input discrete @@;
cards;
1900  230  210 11  37 200;
run;
proc univariate data=group1
cibasic alpha=0.05;
title1 "95% CI for Mean for Discrete Samples";
var discrete;
run;

data group2;
input box @@;
cards;
1100 1800 1500 160 6400 3700;
run;
proc univariate data= group2
cibasic alpha=0.05;
title1 "95% CI for Mean for Box Composite Samples";
var box;
run;

data group3;
input Wheel @@;
cards;
.6 .37 .47 21000 42 90 ;
run;
proc univariate data= group3
cibasic alpha=0.05;
title1 "95% CI for Mean for Wheel Samples";
var Wheel;
run;
```

```
data group4;
input isballuv @@;
cards;
1700 1700 1600 1300 2000 3300;
run;
proc univariate data=group4
cibasic alpha=0.05;
title1 "95% CI for Mean for IS Ball Mill UV Samples";
var isballuv;
run;

data group5;
input isballmsms @@;
cards;
1600 1300 1400 1100 1500 2900;
run;
proc univariate data=group5
cibasic alpha=0.05;
title1 "95% CI for Mean for IS Ball Mill MS MS Samples";
var isballmsms;
run;

data group6;
input ispuckuv @@;
cards;
1500 1400 1700 2100 1000 1700;
run;
proc univariate data=group6
cibasic alpha=0.05;
title1 "95% CI for Mean for IS Ring Puck UV Samples";
var ispuckuv;
run;

data group7;
input ispuckmsms @@;
cards;
1600 1400 1800 2300 1100 1500;
run;
proc univariate data=group7
cibasic alpha=0.05;
title1 "95% CI for Mean for IS Ring Puck MS MS Samples";
var ispuckmsms;
run;
```

SAS Code

```
**** exposuredataTNT_HAFB.sas
**** Scatterplot of 95% UCI for Sampling Data
**** TNT Within Seven Sampling and Analysis groups.
options ls=75 ps=55;

data ucldata;
input tntucl fgroup @@;
label
tntucl = '95% UCL Concentration of TNT ppm'
fgroup = 'Sampling and Analysis Group';
cards;
1193 1 4816 2 12508 3 2674 4 2309 5 1952 6 2044 7;
run;


**** Format the Scatterplot for Readability.;
proc format;
value ucltype
0=' '
1='Discrete'
2='Box'
3='Wheel'
4='IS BMill UV'
5='IS Bmill MSMS'
6='IS RPuck UV'
7='IS RPuck MSMS'
8='  '
;
run;

options ls=75 ps=55;
symbol v=star;
proc gplot data= ucldata;
title1 "95% CI for Mean for All Samples";
title2 'Scatterplot of TNT UCI Concentration by Sampling Group';
format fgroup ucltype.;
plot tntucl * fgroup /haxis=(0 to 8 by 1) hminor=0
vaxis=(0 to 15000 by 1500)vminor=0;
run;

proc print data= ucldata;
title1      'Data in TNT UCI data Data Set';
var tntucl fgroup;
run;
```