Sampling Error, the Major Contributor to Total Characterization Error for Energetic Compounds in Soil

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Soil Sampling and Subsampling Problems for Ranges

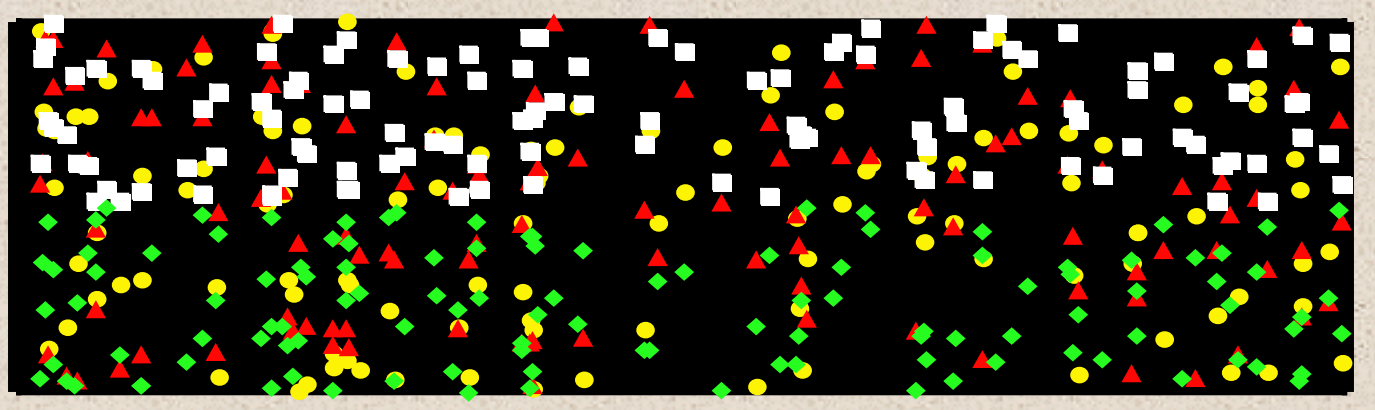
- **Collection of soil samples** in areas of extreme spatial heterogeneity
- **Laboratory subsampling** to preserve representativeness

Sampling Objectives

- What is the mean concentration?
- Are there “hot spots”?
- Has the mean concentration decreased?
- Was remediation successful?

Heterogeneity

- **Constitution** - complexity of the sample matrix (clay, silt, sand, organic matter, metallic debris, water, HE particles, propellant fibers)
- **Distributional** - segregation or non-random distribution of components of the sample



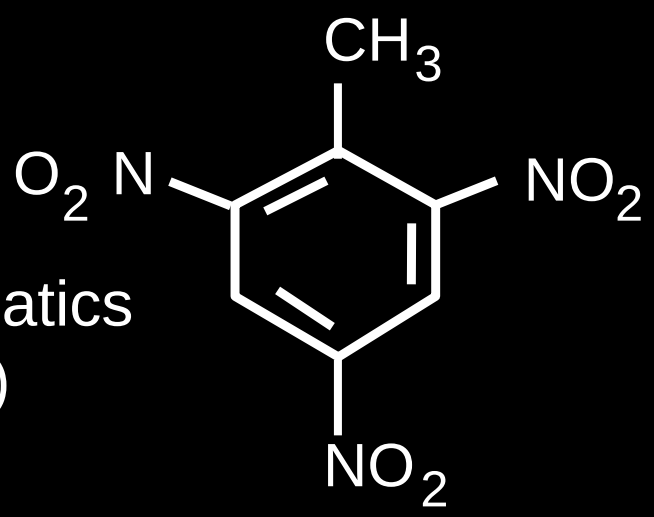
From *Pierre Gy's Sampling Theory and Sampling Practice*

Sampling Errors

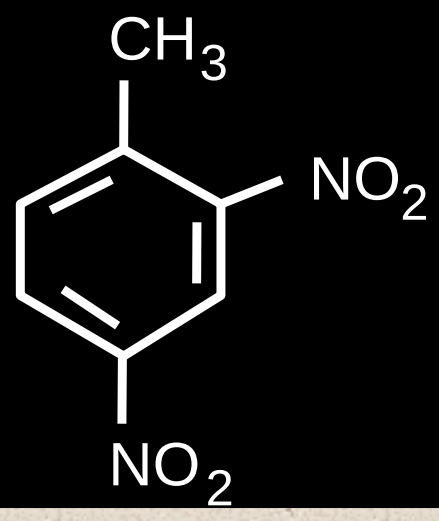
- **Fundamental** - Due to *composition* heterogeneity. Reduced by adequate sample size (all the different particles in proper proportions)
- **Grouping and Segregation** - Due to *distributional* heterogeneity. Reduced by multi-increment sampling and sampling through the heterogeneity.

Classes of Compounds

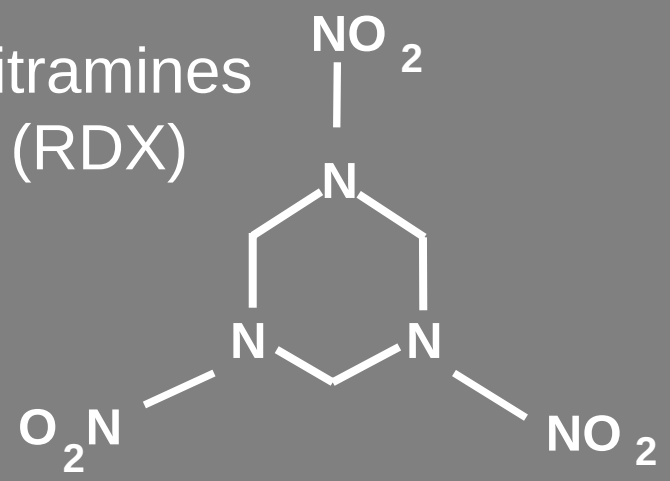
Nitroaromatics
(TNT)



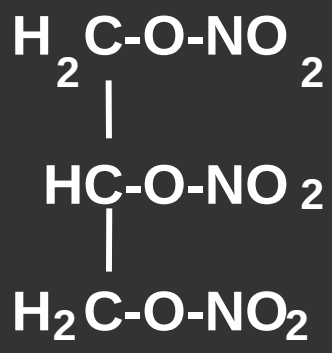
(2,4-DNT)



Nitramines
(RDX)



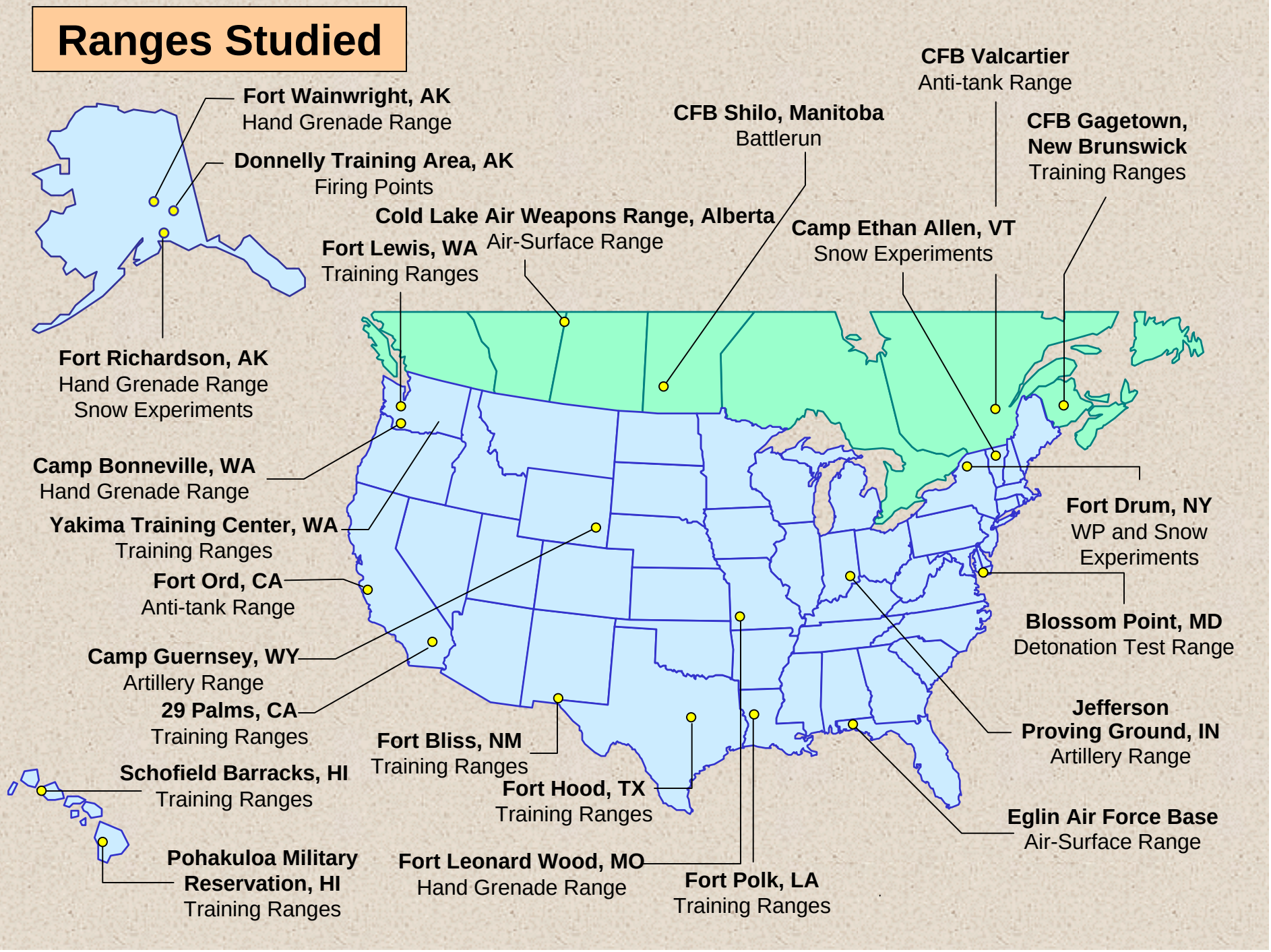
Nitrate Esters
(NG)



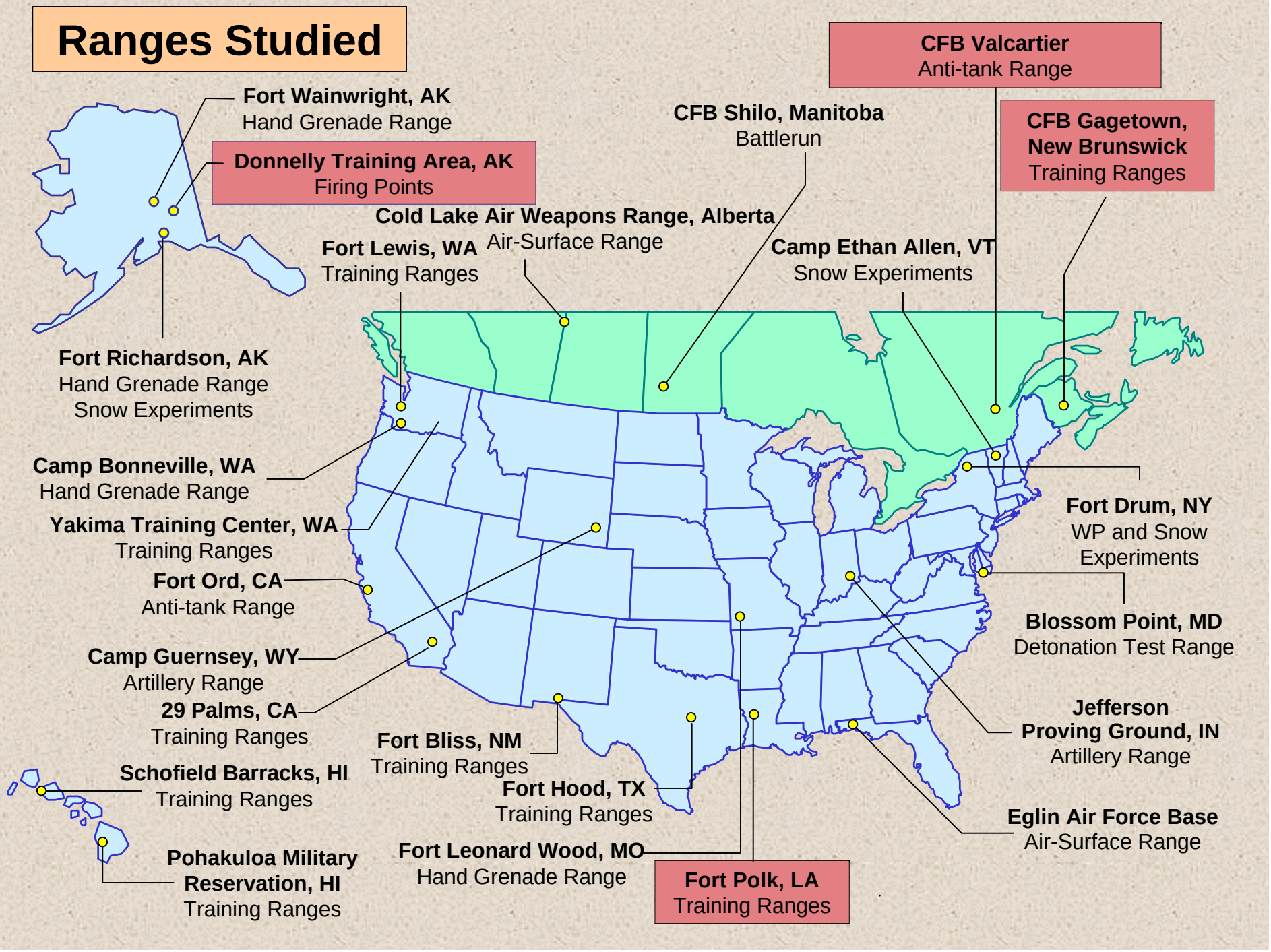
Physical and Chemical Properties of Explosive Chemicals

- Most are **solids** at environmental temperatures
- Sources often **particulate** at soil surface
- Low aqueous solubilities, slow rates of dissolution
- Surface contamination with “chunks” can persist for long periods (50-100 years) - particularly in arid areas
- Once dissolved, RDX can migrate rapidly through vadose zone to ground water
- TNT readily biotransforms
- Relatively **non-volatile**
- Thermally labile - can decompose upon heating

Ranges Studied



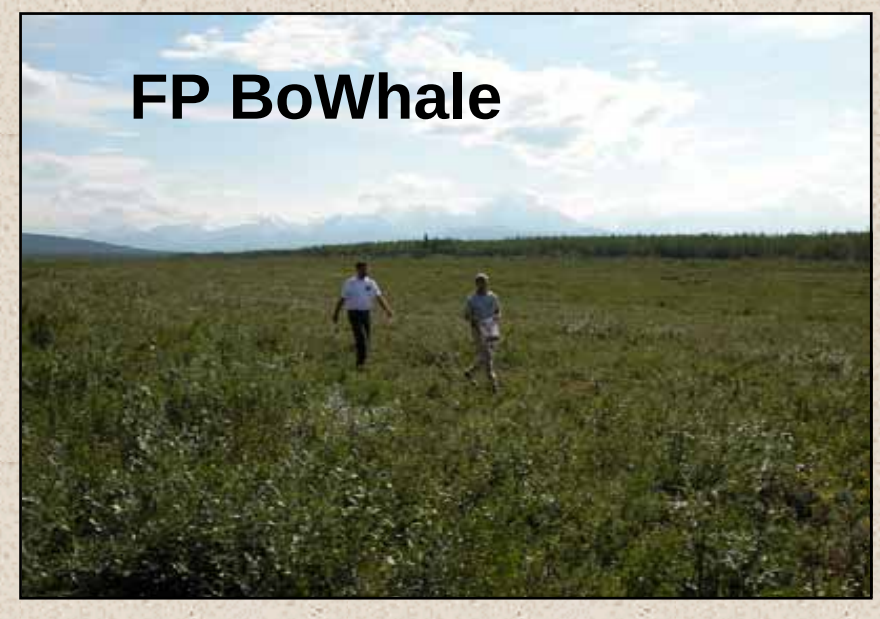
Ranges Studied



Sources of Propellant-Residues at Firing Points

Burning of Excess Propellant

Donnelly Training Area (AK) Firing Points



Some Propellant Compositions

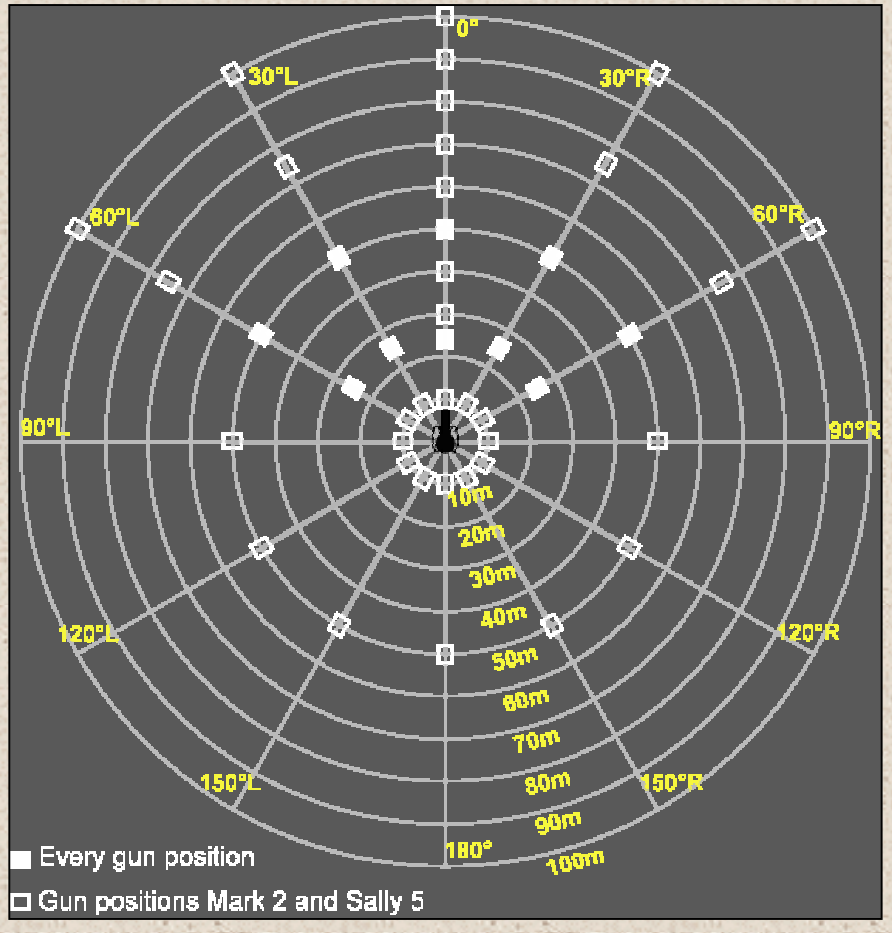
M1: 85% Nitrocellulose, 9% DNT, 5% Dibutylphthalate, 1% Diphenylamine (105-mm howitzers)

M10: 84.2% Nitrocellulose, 9.9% DNT, 4.9% Dibutylphthalate, 1% Diphenylamine (60-mm mortars)

M9: 57.75% Nitrocellulose, 40% Nitroglycerin, 1.5% Potassium Nitrate, 0.75% Ethyl Centralite (81-mm mortars)

M7: 54.6% Nitrocellulose, 35.5% Nitroglycerin, 7.8% Potassium Perchlorate (LAW Rocket)

DTA Firing Points: 105-mm Howitzers

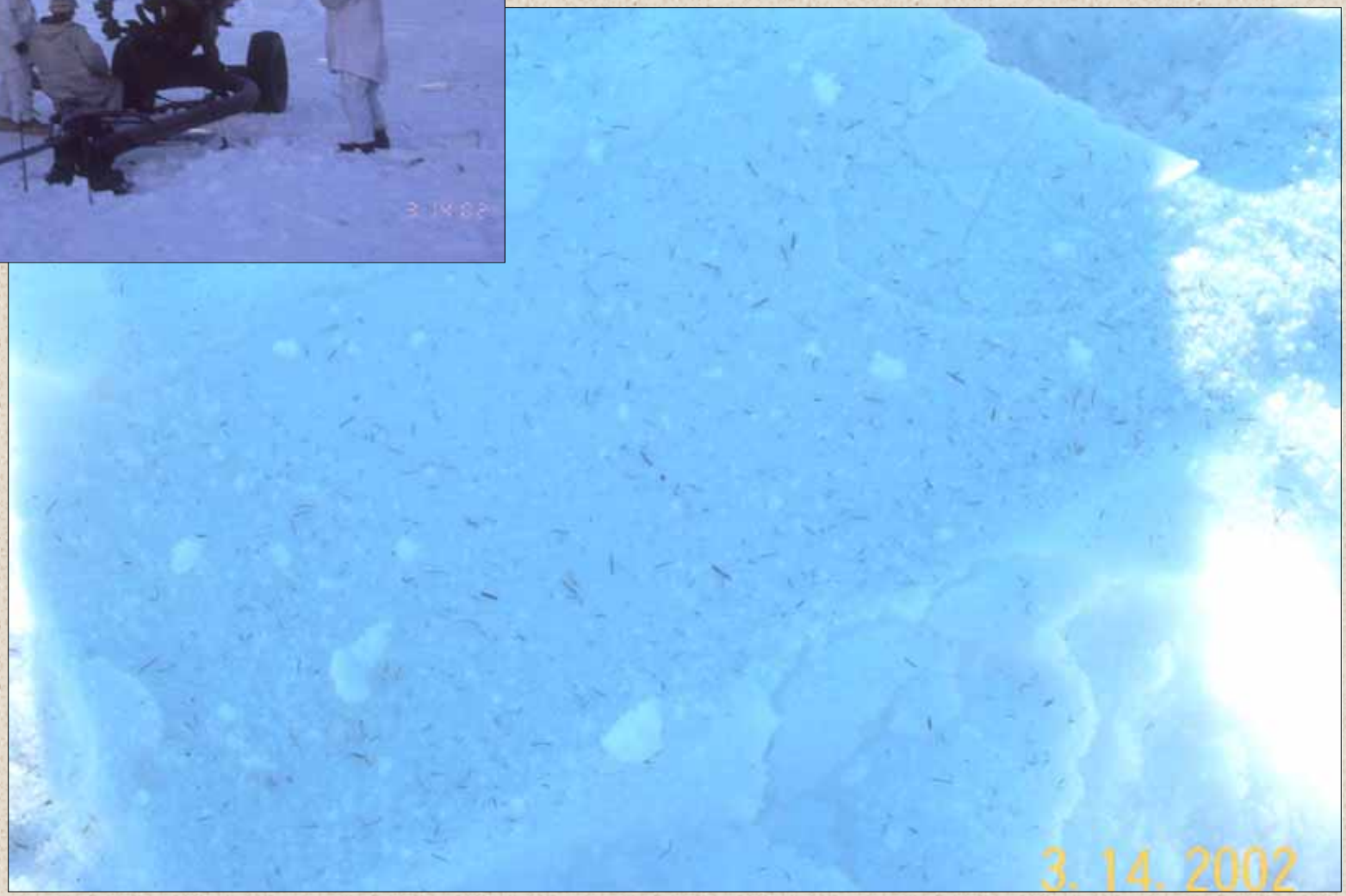


2,4-DNT Concentration (µg/g)	Vegetated	Unvegetated
June 2002 (within one week of firing)		
mean	0.66	1.1
median	0.19	0.12
max	5.8	19
July 2002 (five weeks after firing)		
mean	0.99	1.4
median	0.27	0.17
max	7.4	32

Propellant Residues at Donnelly Training Area 105-mm Firing Points

- 2,4-DNT easily detectable in surface samples
- Large error associated with laboratory subsampling and field duplicates

Propellant Fibers

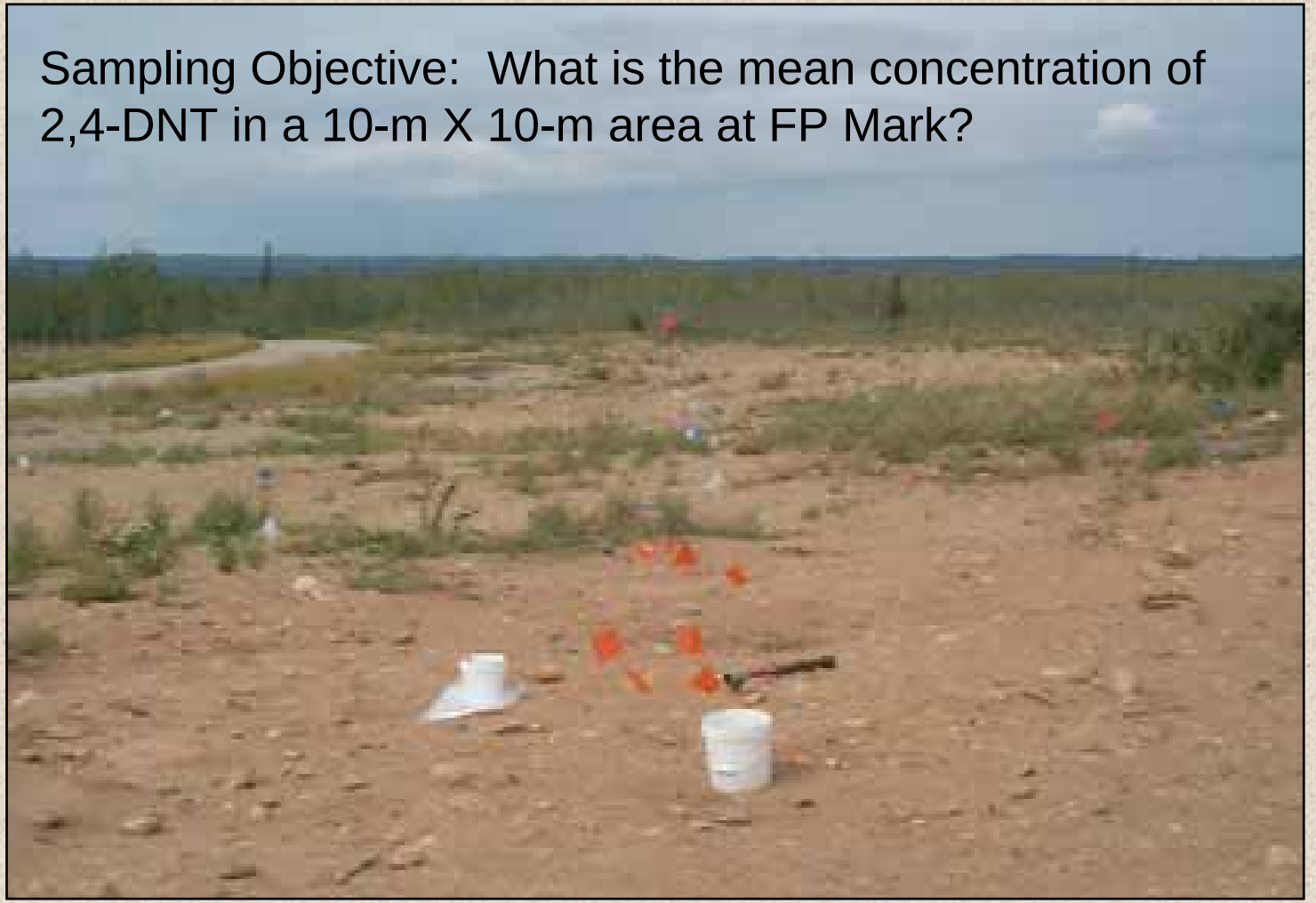


2,4-DNT
Soil Cleanup Levels

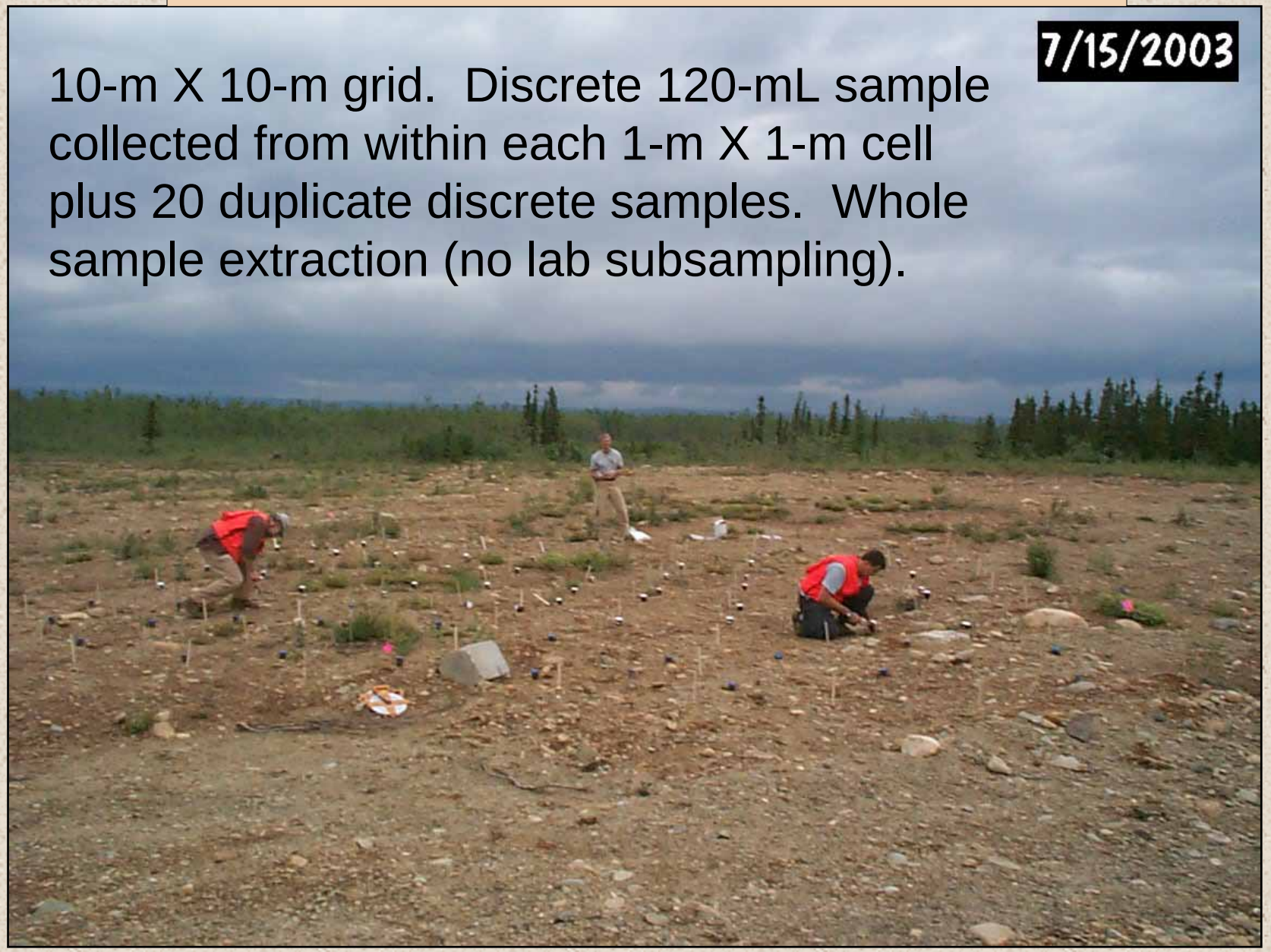
AK Department of Environmental Conservation

Migration to Groundwater	0.005 µg/g
Ingestion	**12 µg/g**

105-mm Howitzer Firing Point



105-mm Howitzer Firing Point



10-m X 10-m grid. Discrete 120-mL sample collected from within each 1-m X 1-m cell plus 20 duplicate discrete samples. Whole sample extraction (no lab subsampling).

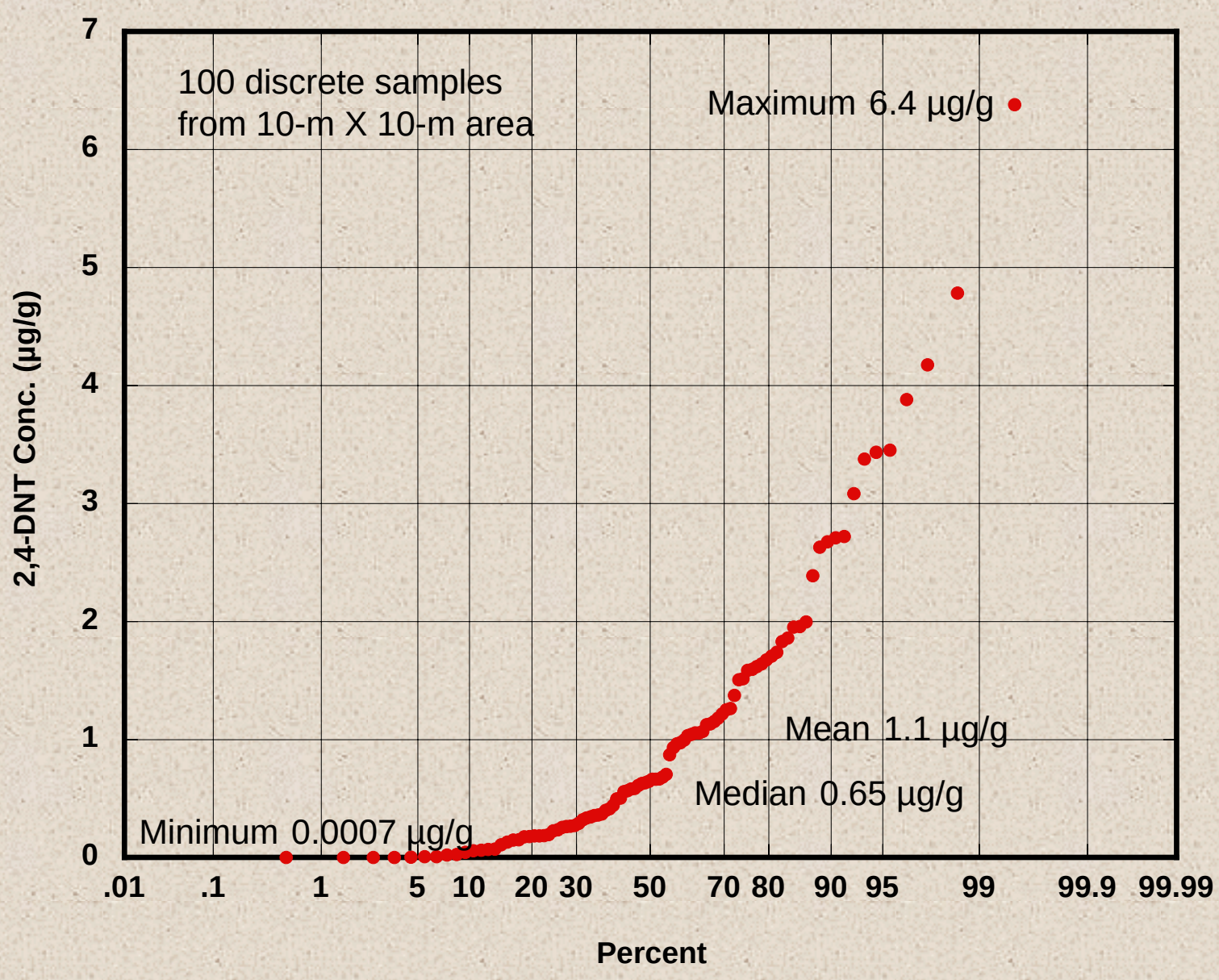
Sampling Objective: What is the mean concentration of 2,4-DNT in a 10-m X 10-m area at a 105-mm Howitzer Firing Point (FP Mark)?

Method: Discrete samples collected in 1-m x 1-m cells within a 10-m X 10-m grided area.

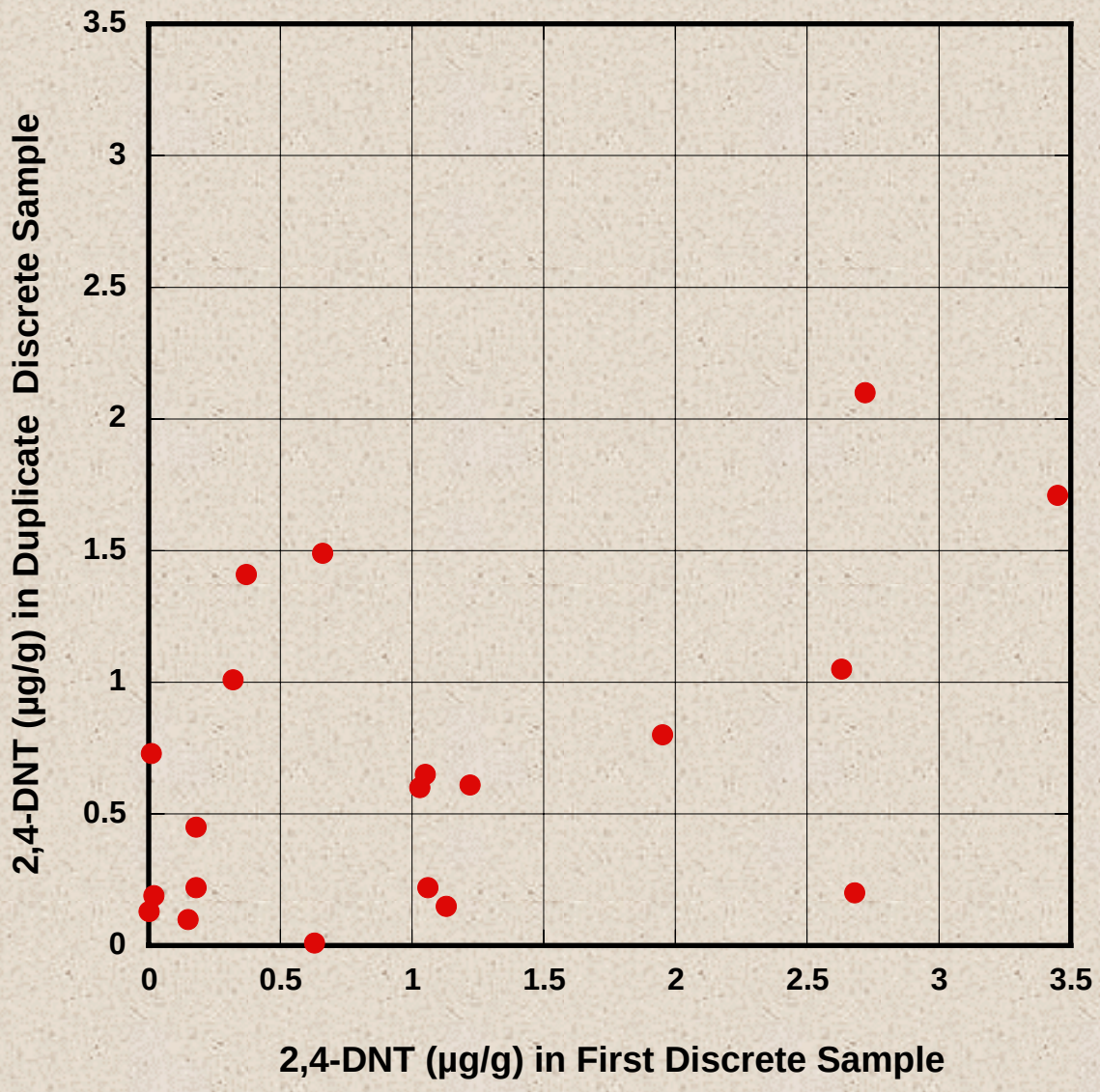
Results:

Number of Samples:	100
Minimum:	0.0007 µg/g
Maximum	6.4 µg/g
Mean:	1.1 µg/g
Standard Deviation:	1.2 µg/g
Median:	0.65 µg/g

Normal Probability Plot: 100 Discrete Samples



Sampling Objective: What is the short range (within 1-m^2) spatial variability of 2,4-DNT (µg/g) at FP Mark?



Individual discrete samples are useless for representing 2,4-DNT concentrations in a 1-m^2 area.

Composite Sampling

- Pooling of several individual samples (multi-increment sampling)
- Typically used to obtain an estimate of the mean concentration
- Reduces analytical costs
- Normalizes data

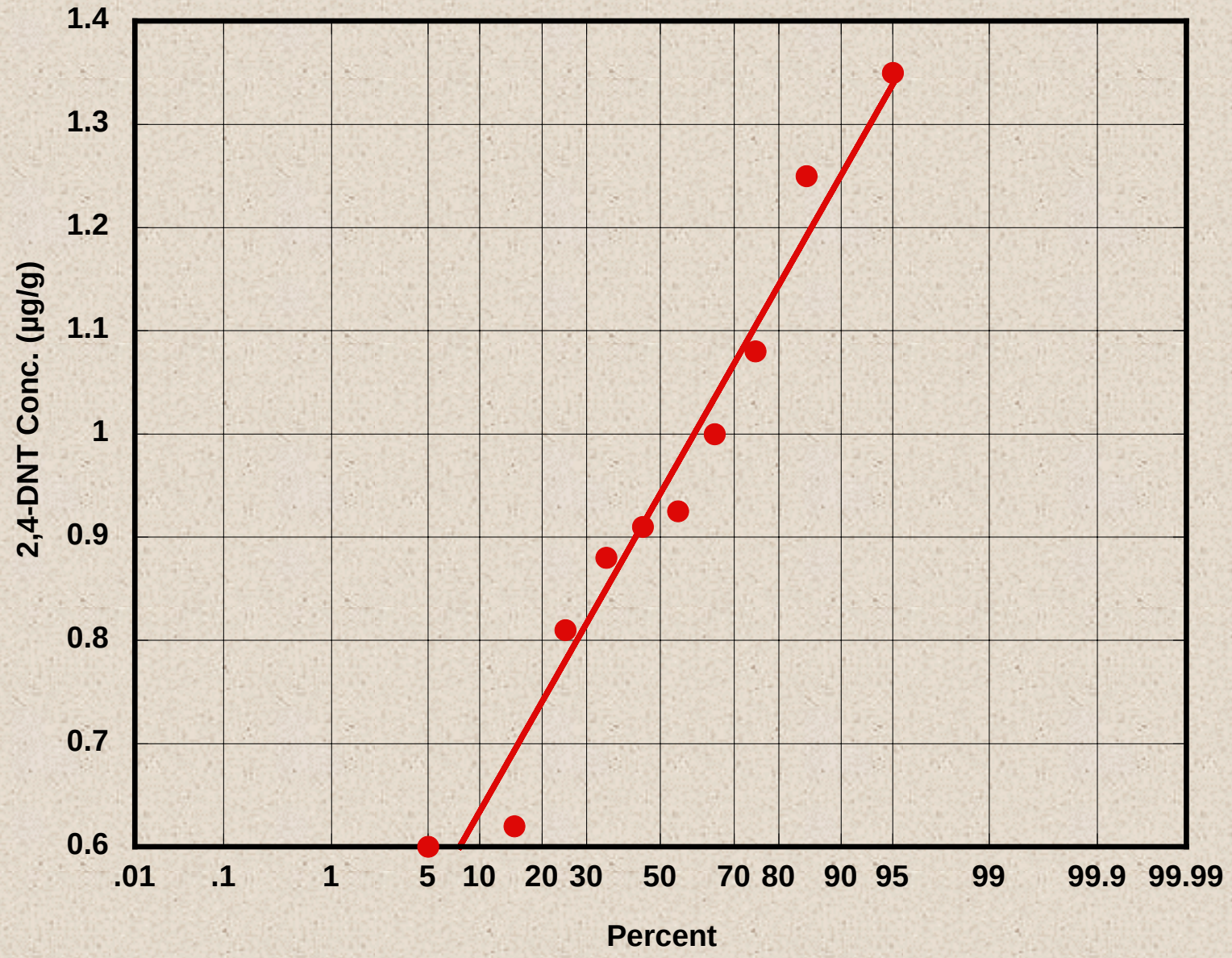
Sampling Objective: What is the mean concentration of 2,4-DNT in a 10-m X 10-m area at FP Mark?

Method: Ten 30-increment samples from random locations within 10-m X 10-m area.

Results:

Number of Samples:	10
Minimum:	0.60 µg/g
Max:	1.35 µg/g
Mean:	0.94 µg/g
Standard Deviation:	0.24 µg/g
Median:	0.92 µg/g

Normal Probability Plot: Ten 30-Increment Composite Samples



Discrete Samples vs Multi-Increment Composite Samples

- Can a single discrete sample represent a 10-m X 10-m area at a 105-mm howitzer firing point? **NO**
- Can a single discrete sample represent a 1-m X 1-m area at a 105-mm howitzer firing point? **NO**
- Are the data from 100 discrete samples normally distributed? **NO**

Recommendations:

To determine mean concentration: collect replicate **multi-increment (composite) samples**.

To determine spatial heterogeneity: collect replicate **discrete samples**.

Sampling Objective: Determine mean concentration of 2,4-DNT at a 105-mm howitzer firing point (FP Mark: 90-m X 120-m area).

Method 1: Single sampler collects ~50 increment composite samples. Seven replicates.

Method 2: Five samplers each collect a ~50 increment composite sample.

Method 3: Five samplers each collect a ~200 increment composite sample.

Sampling Objective: Determine mean concentration of 2,4-DNT at a 105-mm howitzer firing point (FP Mark: 90-m X 120-m area).

Method 1: Single sampler collects ~50 increment composite samples. Seven replicates.

Range 0.32 to 0.56 µg/g. Mean 0.47 µg/g. Median 0.50 µg/g.

Method 2: Five samplers each collect a ~50 increment composite sample.

Range 0.43 to 0.73 µg/g. Mean 0.59 µg/g. Median 0.62 µg/g.

Method 3: Five samplers each collect a ~200 increment composite sample.

Range 0.40 to 0.76 µg/g. Mean 0.56 µg/g. Median 0.58 µg/g.

CFB-Valcartier Anti-tank Range

Major Munition Fired
66-mm M72 LAW Rocket

Propellant

- Double-based – nitrocellulose, nitroglycerin

Explosive used in warhead

- Main charge – octol (70%HMX, 30% TNT)
- Booster – RDX

Sampling 10-m X 10-m Grid at Anti-Tank Firing Point

Sampling Objective: What is the mean concentration of NG in a 10-m X 10-m area at an anti-tank firing point?

Method: Discrete samples collected in 1-m x 1-m cells within a 10-m X 10-m grided area.

Results:

Number of Samples:	100
Minimum:	0.023 µg/g
Max:	3.3 µg/g
Mean:	0.64 µg/g
Standard Deviation:	0.67 µg/g
Median:	0.40 µg/g

Sampling Objective: What is the mean concentration of NG in a 10-m X 10-m area at an anti-tank firing point?

Method: Ten 30-increment samples from random locations within 10-m X 10-m area (mathematical simulation using discrete concentration estimates).

Results:

Number of Samples:	10
Minimum:	0.34 µg/g
Max:	0.93 µg/g
Mean:	0.65 µg/g
Standard Deviation:	0.17 µg/g
Median:	0.69 µg/g

Sampling Objective: What is the mean concentration of HMX in a 10-m X 10-m area at an anti-tank range?

Method: Discrete samples collected in 1-m x 1-m cells within a 10-m X 10-m grided area.

Results:

Number of Samples:	100
Minimum:	8.3 µg/g
Max:	1920 µg/g
Mean:	454 µg/g
Standard Deviation:	463 µg/g
Median:	290 µg/g

Sampling Objective: What is the mean concentration of HMX in a 10-m X 10-m area at an anti-tank range?

Method: Ten 30-increment samples from random locations within 10-m X 10-m area (mathematical simulation using discrete concentration estimates).

Results:

Number of Samples:	10
Minimum:	322 µg/g
Max:	532 µg/g
Mean:	394 µg/g
Standard Deviation:	63 µg/g
Median:	381 µg/g

CFB-Gagetown Anti-tank Range

CFB-Gagetown Anti-tank Range

Sampling Strata Based on Target Locations, Ordnance Debris, Water-cover, and Vegetation

CFB-Gagetown Anti-tank Range
Sampling Stratum: Elevated Berm Around and Between Targets

- Four samplers collecting two samples each
- Eight composite samples composed of >44 increments each
- Increments collected at approximately 5-m intervals over an area 110-m long and 20 to 40 m wide.

CFB-Gagetown Anti-tank Range

Sampling Stratum: Elevated Berm Around and Between Targets

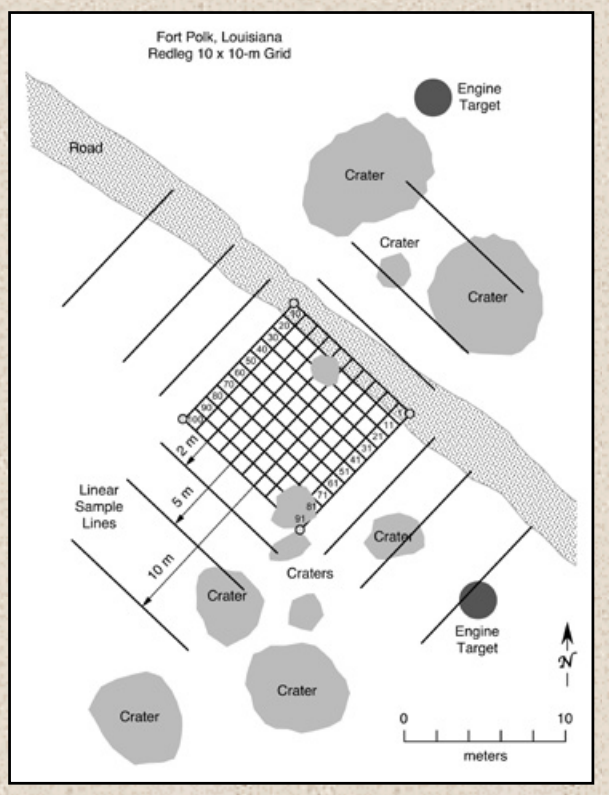
	Concentration (µg/g)			
	HMX		NG	
Sampler A:	1040	430	71	27
Sampler B:	424	414	22	26
Sampler C:	444	536	24	65
Sampler D:	270	354	16	20
Mean	490		34	
Std. Dev.	235		21	
Median	430		25	

CFB-Gagetown Anti-tank Range
Sampling Strata: Road and Vegetated Areas

	Concentration (µg/g)					
	HMX			NG		
Road		320	386		17	6.7
Vegetated Area 1		52	61		2.7	6.7
Vegetated Area 2	240	550	320	35	56	35

Artillery/Mortar Range - Ft. Polk, LA

Ft. Polk 10-m x 10-m Grid



Cobble-size pieces of Composition B (60/40 RDX/TNT)

Sampling Objective: What is the mean concentration of RDX in a 10-m X 10-m area at an artillery/mortar impact area?

Method: Discrete samples collected in 1-m x 1-m cells within a 10-m X 10-m grided area.

Results:

Number of Samples:	100
Minimum:	0.037 µg/g
Maximum	2390 µg/g
Mean:	71 µg/g
Standard Deviation:	315 µg/g
Median:	1.8 µg/g

Sampling Objective: What is the mean concentration of RDX in a 10-m X 10-m area at an artillery/mortar impact area?

Method: Ten 25-increment samples from random locations within 10-m X 10-m area.

Results:

Number of Samples:	10
Minimum:	4.6 µg/g
Max:	290 µg/g
Mean:	54 µg/g
Standard Deviation:	86 µg/g
Median:	25 µg/g

Ft. Polk 10-m x 10-m Grid: Concentration (µg/g) in 25-Increment Composite Samples

Field Sample #	HMX	RDX	TNT	4-Am-DNT	2-Am-DNT
1	4.5	51	22	0.48	0.61
2	0.59	4.6	0.75	0.5	0.62
3	1.0	8.1	1.1	0.48	0.44
4	32	290	110	1.9	1.4
5	2.1	19	5	0.42	0.43
6	8.3	78	21	0.77	0.79
7	3.2	26	9.7	0.56	0.56
8	3.3	25	5.4	0.66	0.78
9	2.7	24	4.6	0.45	0.52
10	2.3	17	2.8	0.44	0.53
Min	0.59	4.6	0.75	0.42	0.43
Maximim	32	290	110	1.9	1.4
Mean	6.0	54	18	0.67	0.67
Std. Dev.	9.4	86	33	0.45	0.28
Median	3.0	25	5.2	0.49	0.59

RDX Concentrations (µg/g) in a 10-m X 10-m Area at an Artillery/Mortar Impact Area

17.1	1.27	0.829	0.908	10.9	4.44	0.437	0.354	1.52	0.067
0.805	24.1	7.73	0.539	0.260	0.233	0.366	1.93	0.731	0.138
30.8	1.40	12.5	0.342	0.074	1.11	0.18	0.076	7.11	0.187
12.7	138	53.7	3.85	4.94	1.22	4.63	0.470	2.41	1.06
331	9.70	3.96	1.44	3.67	0.243	3.21	0.254	1.03	0.073
7.52	5.65	1.97	0.571	4.84	19.9	0.825	0.122	1.46	0.070
1.65	1.56	8.51	10.6	2.24	25.2	7.15	0.248	0.175	0.037
48.3	13.3	3.36	6.93	889	21.8	3.75	0.618	0.193	0.081
1.18	1.03	64.3	557	1790	2390	11.3	1.65	0.335	0.263
8.86	3.50	5.02	42.7	385	24.9	3.64	0.96	0.526	0.161

10-m

- Hotspots two to three meters in size
- Increments for composite samples should spaced to include hotspots (systematic random)

Conclusions

- **For 100 discrete samples from each of the 10-m X 10-m areas sampled:**

  The median was always less than the mean.

  Individual discrete samples underestimated the mean most of the time.

  Standard deviations were equal or greater than the mean.

  Statistical analyses based on normal distributions would be invalid.

Conclusions

- **For 10 multi-increment composite samples from the 10-m X 10-m areas at firing points and anti-tank ranges:**

  The medians were similar to the means.

  Standard deviations were less than the means.

  Estimates of the means were normally distributed.

Conclusions

Nature of deposition affects the ability to collect repeatable samples.

Artillery/mortar impact areas have hotspots with chunks of High Explosive.

Adequate (repeatable) sampling methods are being developed and tested.

Sampling needs to be stratified (based on targets, ordnance debris, and substrate).

Acknowledgments

- US Army Alaska - Douglas Johnson
- ERDC - John Cullinane
- US Army Corps of Engineers - June Mirecki
- SERDP - Bradley Smith, Dr. Jeff Marqusee and Robert Holst
- AEC - John Buck and Martin Stutz
- CHPPM - Barrett Borrey, Ken Mioduski, and Mike Brown
- EOD support teams
- Range control and base environmental personnel
- Sampling teams from ERDC, DRDC (Canada), USACHPPM, and Sacramento District Corps of Engineers
- Kevin Bjella, Nancy Perron, Dennis Lambert, Jane Mason, CRREL