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Improving Mission Readiness Through Environmental Research

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Representative Sampling for Energetic Compounds at Military Training Ranges


Sampling near tank target YakimaTraining Center


Sampling near low-order 500 lb bomb, Camp Guernsey


Red crater at CFB Gagetown

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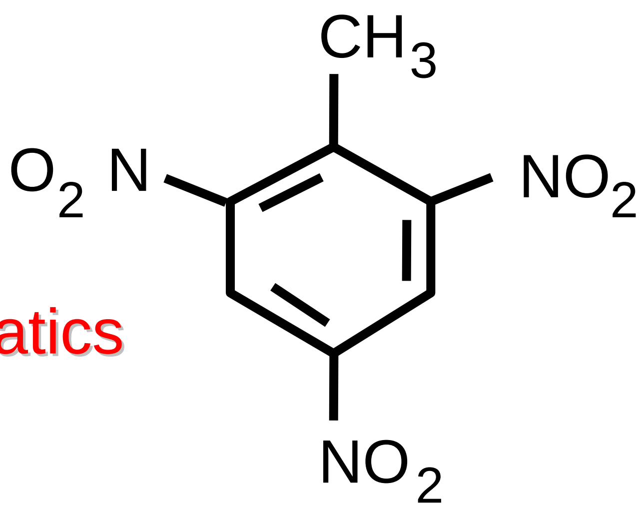
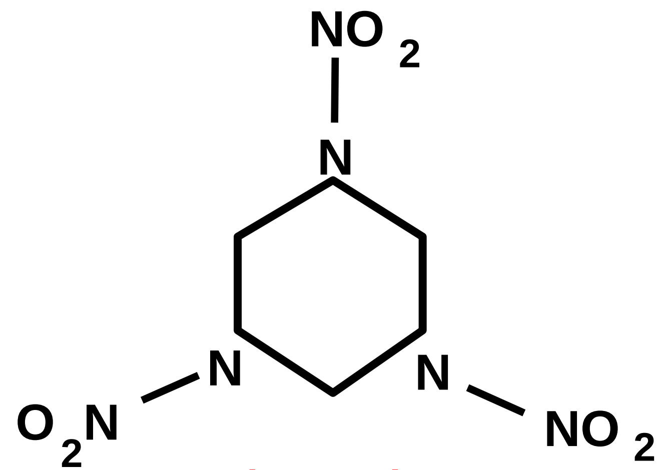
Major Classes of Energetic Chemicals Used by DoD

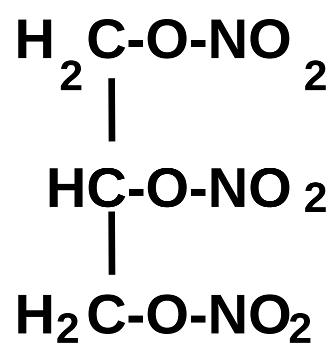
Nitroaromatics
(TNT)





Nitramines
(RDX)

Nitrate Esters
(NG)



Energetic Chemicals in Military Explosives

- Composition B (artillery/mortar)
  - 60% Military grade RDX (Contains about 10% HMX)
  - 39% Military grade TNT (Contains about 1% other TNT isomers and DNTs)
- Composition C4 (demolition explosive)
  - 91% Military Grade RDX
- Tritonal (Air Force Bombs)
  - Military grade TNT, aluminum
- Composition A4 (40-mm grenades)
  - Military grade RDX
- TNT (artillery)
  - Military grade TNT
- Composition H-6 (Air Force bombs)
  - Military grade RDX and TNT, aluminum
- Octol (Antitank rockets)
  - Military grade HMX and TNT

Energetic Chemicals in Military Gun Propellants

- Nitrocellulose (NC)

  Polymer used in all gun propellants
- Nitroglycerin (NG)

  Component of double and triple base propellants
- Nitroguanidine (NQ)

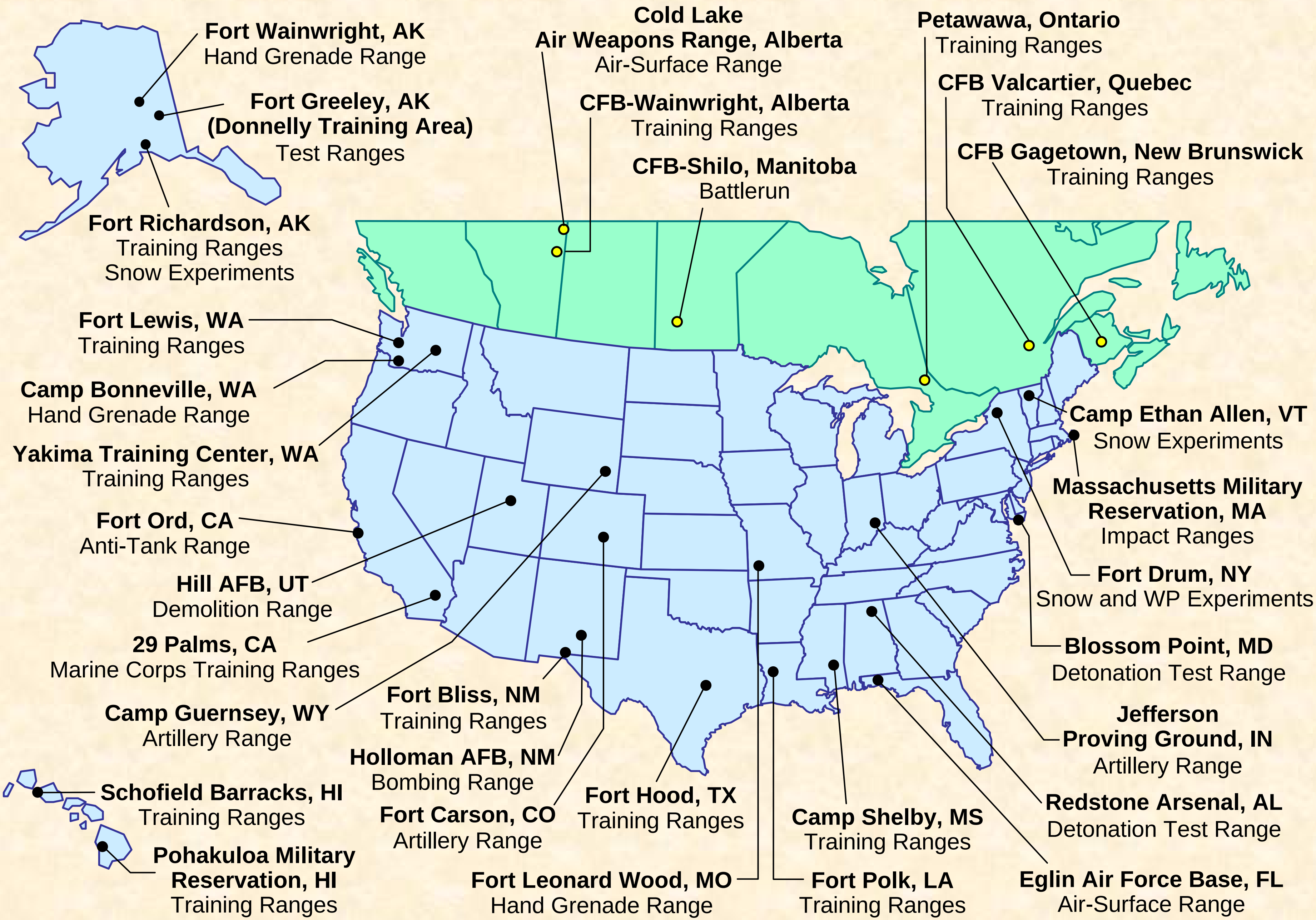
  Component of triple base propellants
- 2,4-Dinitrotoluene (2,4-DNT)

  Energetic plasticizer in some single base propellants

Physical and Chemical Properties of Energetic Chemicals

- Most are solids at environmental temperatures
- Sources often particulate and deposited at soil surface
- Low aqueous solubilities
- Surface contamination of "chunks" can persist for long periods
  (50-100 years) - particularly in arid areas
- RDX does not degrade rapidly under aerobic conditions
- Once dissolved, RDX can migrate rapidly through vadose zone to ground water for sites with shallow groundwater, permeable soils, and moderate rainfall
- TNT readily biotransforms and migration much slower than RDX
- Compounds are relatively non-volatile (10^{-4} to 10^{-14} torr) - samples can be homogenized (or composited) without losses
- Thermally labile - some can decompose upon heating

Field Experiments



Research on Deposition of Energetic Residues

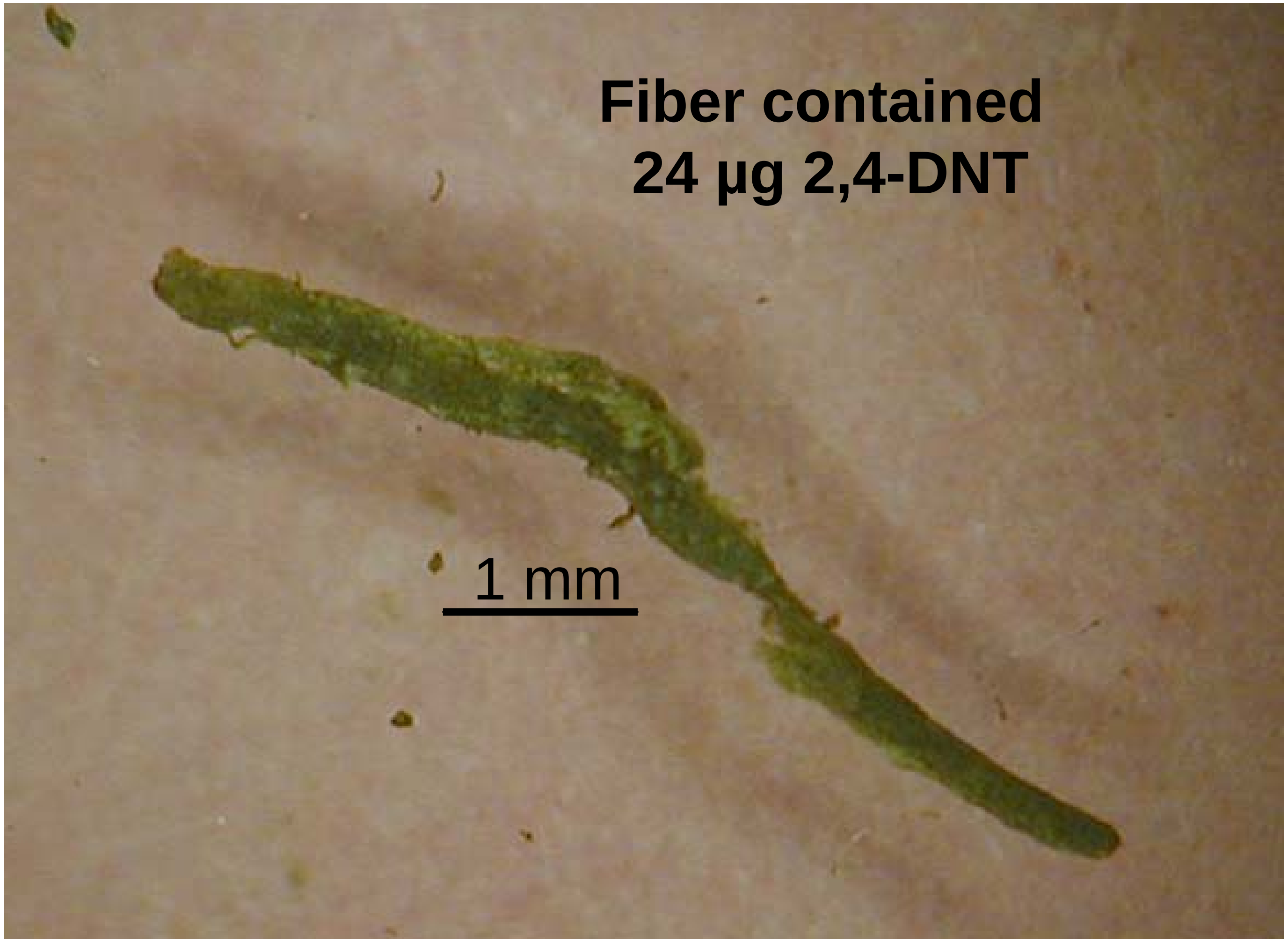
- Firing points

  Residues deposited as fibers and particles of burnt and unburnt propellant

- Impact areas

  Residues deposited as small particles of explosive from low-order (partial) detonations

Propellant Fiber Deposited from 105-mm Howitzer



Residues from 105-mm Propellant at Firing Points

Residues are deposited as burned and unburned fibers of nitrocellulose
(6% of unburned fiber weight is 2,4-DNT)

- Average measured fiber length: – 3 mm
- Average mass of 2,4-DNT: – 12 μg / fiber
- If soil concentration is 1 mg/kg, then you have only about 80 fibers / kilogram of soil

Composition B particles from low-order 81-mm mortar

Residues of Composition B Deposited at Impact Areas

- Particles (chunks) of Composition B deposited range in size from micrometer to centimeter
- Soil sized particles are defined as < 2 mm
- One 1-mm spherical particle of Composition B:
  - weighs about 0.9 mg
  - contains ~ 0.50 mg of RDX
    0.35 mg of TNT
    0.05 mg of HMX
- If the soil concentration is 1 mg/kg of RDX, a kilogram sample contains only 2 of these 1-mm particles

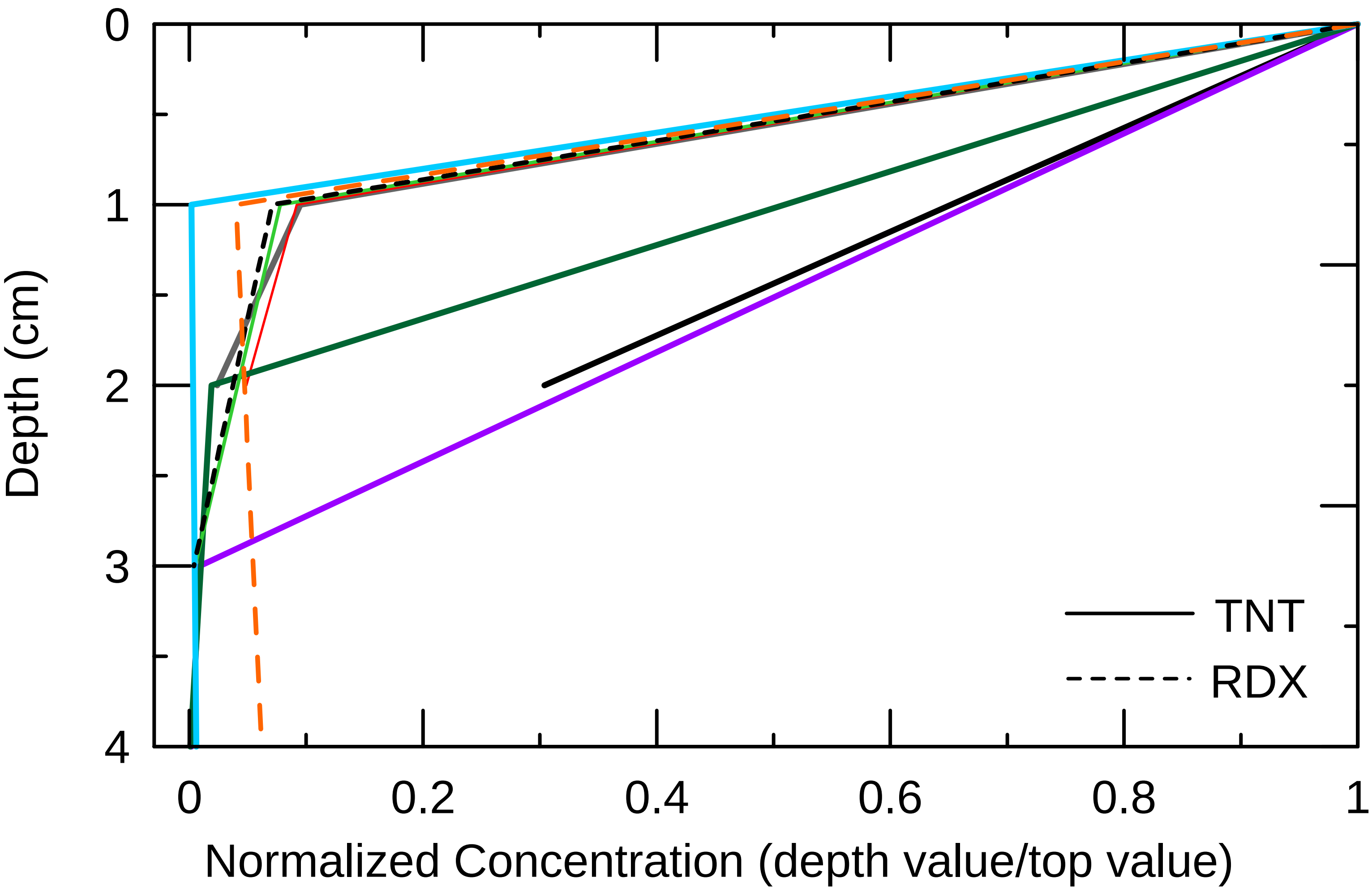
What is the Multi-increment Sampling Approach?

- Pooling of several individual increments from within the decision unit
- Typically used to obtain a more reliable estimate of the mean concentration
- Reduces analytical costs compared with multiple discrete samples
- Normalizes data

Sampling Depth

- At firing points, residues are associated with NC polymeric propellants and remain at the surface
- At impact areas, residues are particulates from low-order detonations and ruptured rounds and the bulk also remains at the surface
- For most ranges, we recommend a sampling depth of 2.5 to 5 cm
- Including deeper soil just dilutes the concentrations

Normalized Depth Concentration Profiles for Soils at Various Ranges



Tools for Multi-Increment Sampling

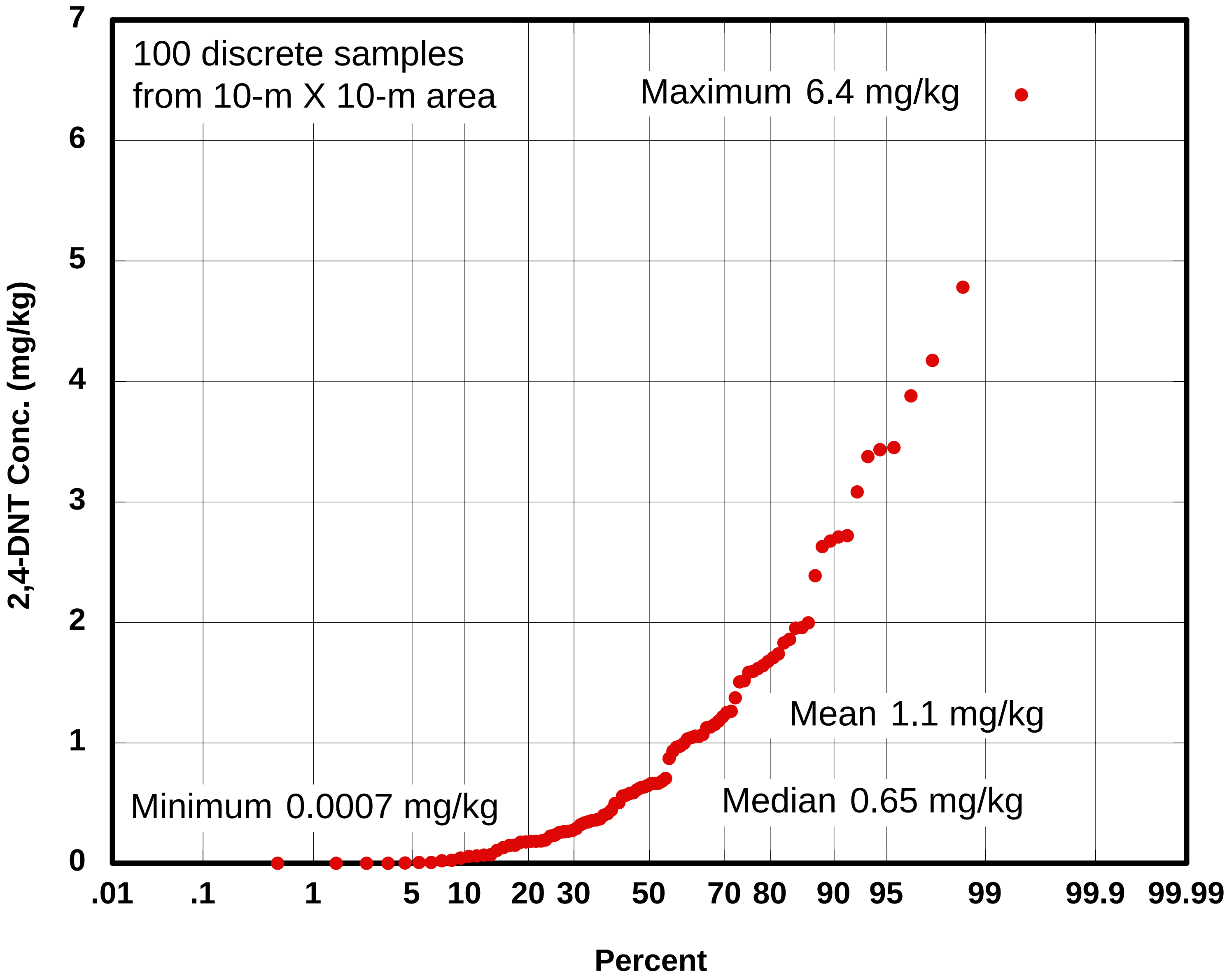
Sampling Experiment for 105-mm Howitzer Firing Point, Donnelly Training Area, AK

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?

Comparison: Discrete samples collected in 1-m x 1-m cells within a 10-m X 10-m grid. 30-increment samples collected randomly throughout entire 10-m X 10-m grid.

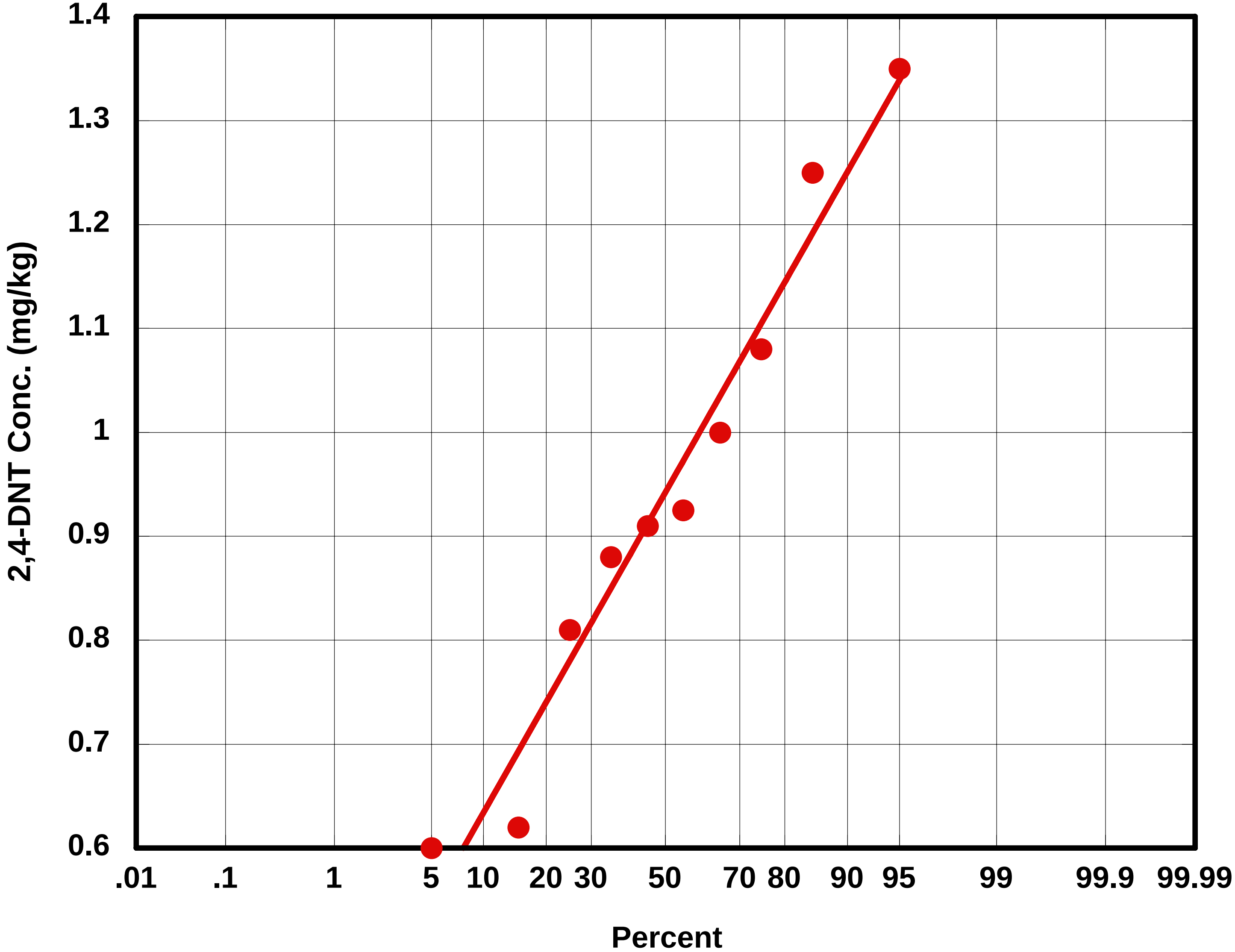
Results:	Discrete	Multi-increment
Number of Samples:	100	10
Minimum:	0.0007 mg/kg	0.60 mg/kg
Maximum	6.4 mg/kg	1.35 mg/kg
Mean:	1.1 mg/kg	0.94 mg/kg
Standard Deviation:	1.2 mg/kg	0.24 mg/kg
Median:	0.65 mg/kg	0.92 mg/kg
Distribution:	Skewed	Gaussian

Normal Probability Plot: 100 Discrete Samples



Normal Probability Plot:

Ten 30-Increment Composite Samples



Central Limit Theorem Applied to Multi-increment (MI) Sampling

- As the number of individual increments in each sample gets “large enough,” the distribution of replicate samples can be approximated by a normal distribution, regardless of the shape of the distribution of individual increments.
- “Large enough” - For most populations, the number of increments must be at least 30.

Firing Point - 2,4-DNT mg/kg within 10 x 10-m area at 105-mm howitzer training range

100 discretes (1 x 1-m sub grids)

– Mean	1.1
– Median	0.65
– Min	0.0007
– Max	6.4
– Pro UCL	1.3

Multi-increment Samples

– 10, 30-increment (random)
  - Pro UCL 1.1

– 4, 30-increment (random)
  - Pro UCL

1.3, 1.1, 1.1, 1.4, 1.1

Pro UCL - Discrete samples

N = 7*

1.6, 3.6, 5.4, 0.72**, 1.1

N = 15*

2.6, 2.8, 2.5, 2.4, 2.4

N = 30*

1.6, 1.4, 1.1, 1.5, 1.5

* Set of random discrete sample values

** false negative

Firing Point - NG mg/kg within 10 x 10-m area at Law Rocket training range

100 discretes (1 x 1-m sub grids)

- Mean 0.645
- Median 0.403
- Min 0.023
- Max 3.37
- Pro UCL 0.562

Multi-increment Samples

- 1, 30-increment (random)
  - 0.80

Pro UCL - Discrete samples

N = 7*

0.82, 0.57, 0.32, 1.2, 0.74

N = 15*

0.74, 0.76, 0.69, 0.86, 0.68

N = 30*

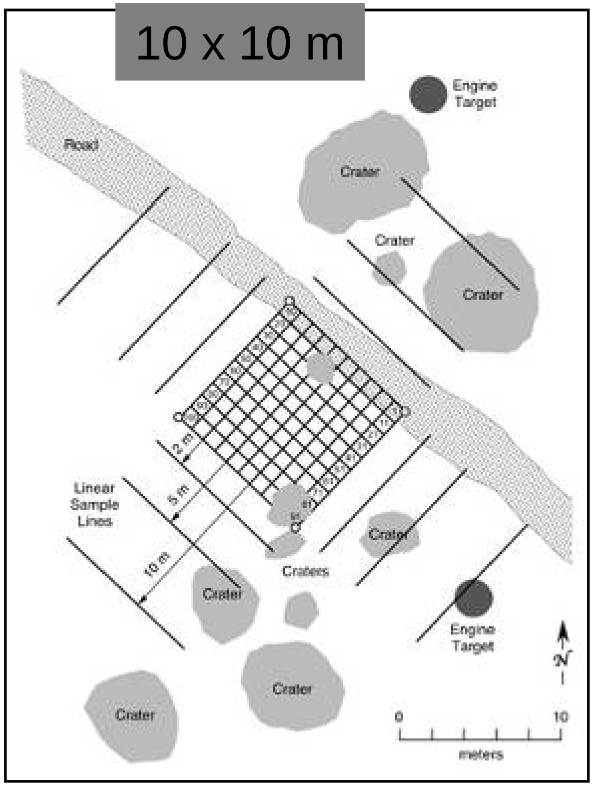
0.74, 0.65, 0.56, 0.54, 0.93

* Set of random discrete sample values

** false negative

Sampling Experiment at an Artillery/Mortar Range Impact Area

10-m x 10-m chunk residue "Hot Spot"



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

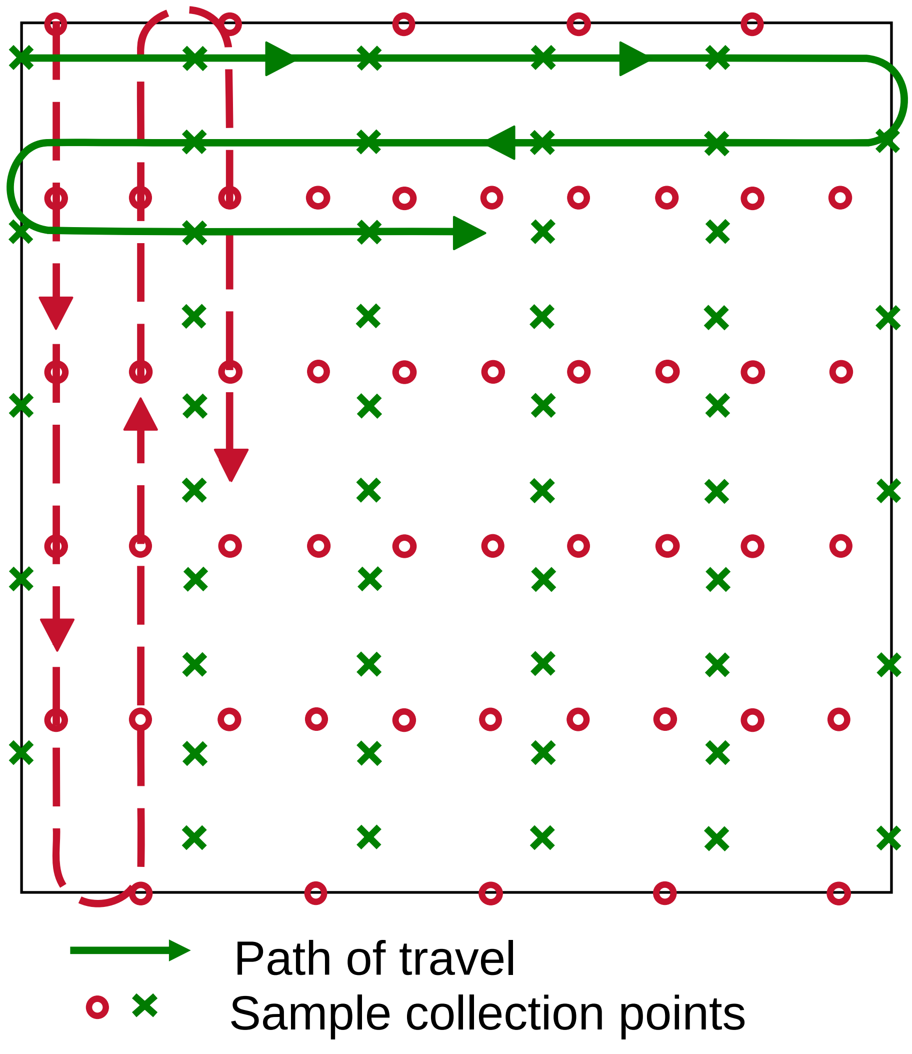
RDX Concentrations (mg/kg) in a 10- x 10-m chunk residue "Hot spot" area on artillery/mortar impact range

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
- Mean 71 mg/kg
- Loading: 300 g RDX
  100 g chunks
  200 g top 2.5 cm soil

Pattern of multi-increment sample collection using systematic-random sampling design



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

Comparison: Discrete samples collected in 1-m x 1-m cells within a 10-m X 10-m grid, 25-increment samples collected randomly within entire 10-m X 10-m grid.

Results:	Discrete	Random-MI	Sys.-Random-MI Simulated
Number:	100	10	4
Minimum:	0.037mg/kg	4.6 mg/kg	33 mg/kg
Maximum:	2390 mg/kg	290 mg/kg	100 mg/kg
Mean:	71 mg/kg	54 mg/kg	71 mg/kg
Std. Dev.	315 mg/kg	86 mg/kg	43 mg/kg
Median:	1.8 mg/kg	25 mg/kg	75 mg/kg
Distribution:	Skewed	Skewed	??

Multi-Increment Sampling Experiment at an Artillery/Mortar/Bombing Impact Range

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

Comparison: Three totally random 25-increment samples versus three 25-increment samples collected using a systematic-random design from within 10-m X 10-m area.

Results:

	Totally Random-MI	Systematic-Random-MI
Number:	3	3
Minimum:	0.24 mg/kg	0.31 mg/kg
Max:	0.78 mg/kg	0.37 mg/kg
Mean:	0.49 mg/kg	0.34 mg/kg
Std. Dev.:	0.27 mg/kg	0.033 mg/kg
Median:	0.45 mg/kg	0.34 mg/kg

Impact Range - RDX mg/kg within 10 x 10-m area around low-ordered 81 mm mortar

100 discretes (1 x 1-m sub grids)

- Mean 70.9
- Median 1.79
- Min 0.0007
- Max 2390
- Pro UCL 96.4

Multi-increment Samples

- 10, 25-increment (random)
  - Pro UCL 120
- 4, 25-increment (systematic-random)
  - Pro UCL 110

Pro UCL

N = 7*

4.6**, 2.7, 9.0, 1300, 12

N = 15*

320, 240, 1300, 4.0, 1300

N = 30*

1100, 49, 310, 120, 410

N = 50*

550, 240, 90, 130, 170

* Set of random discrete values

** False negative

RDX Concentrations (mg/kg)

In a 30- x 30-m area at an artillery/mortar impact range Fort Richardson, AK

0.0	0.05	0.02	0.0	0.0	0.0	0.16	0.44	0.86	6.89
0.0	0.0	0.02	0.05	0.03	0.0	0.0	119	172	1.51
0.0	0.0	0.0	0.0	0.0	0.03	0.04	40.2	4.47	0.55
0.0	0.0	0.0	0.0	0.04	0.15	0.03	0.7	0.37	0.21
0.0	0.07	0.0	0.0	0.0	0.0	0.0	62.5	0.05	0.02
0.0	0.03	0.0	0.0	0.0	0.0	0.0	0.25	0.03	0.04
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.17	0.0	0.13
0.0	0.0	0.0	0.11	0.0	0.06	0.0	4.34	121	2.90
0.0	0.0	0.0	0.03	0.0	0.0	0.0	0.21	0.07	0.46
0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.07	0.14	6.10

← 30-m →

100 Discrete samples

- Mean = 5.5
- Median = <d
- Max = 172

100-increment samples (n=4)

2.9, 5.6, 11.8, 8.5

Concentration (mg/kg)

- < d
- 0.01 – 1.0
- 1 – 10
- >10

Impact Range - RDX mg/kg within 30 x 30-m area around low-ordered 120 mm mortar

100 discretes (3 x 3-m sub grids)

– Mean	5.46
– Median	0.0
– Min	0.0
– Max	172
– Pro UCL	16.3

Multi-increment Samples

– 4, 100-increment (systematic-random)
  - Pro UCL 11.9

Pro UCL

N = 7*
0.33**, 0.11, 0.31, 0.64, 55

N = 15*
61, 43, 2.2, 58, 2.8

N = 30*
41, 22, 1.5, 28, 13

N = 50*
16, 27, 32, 1.2, 14

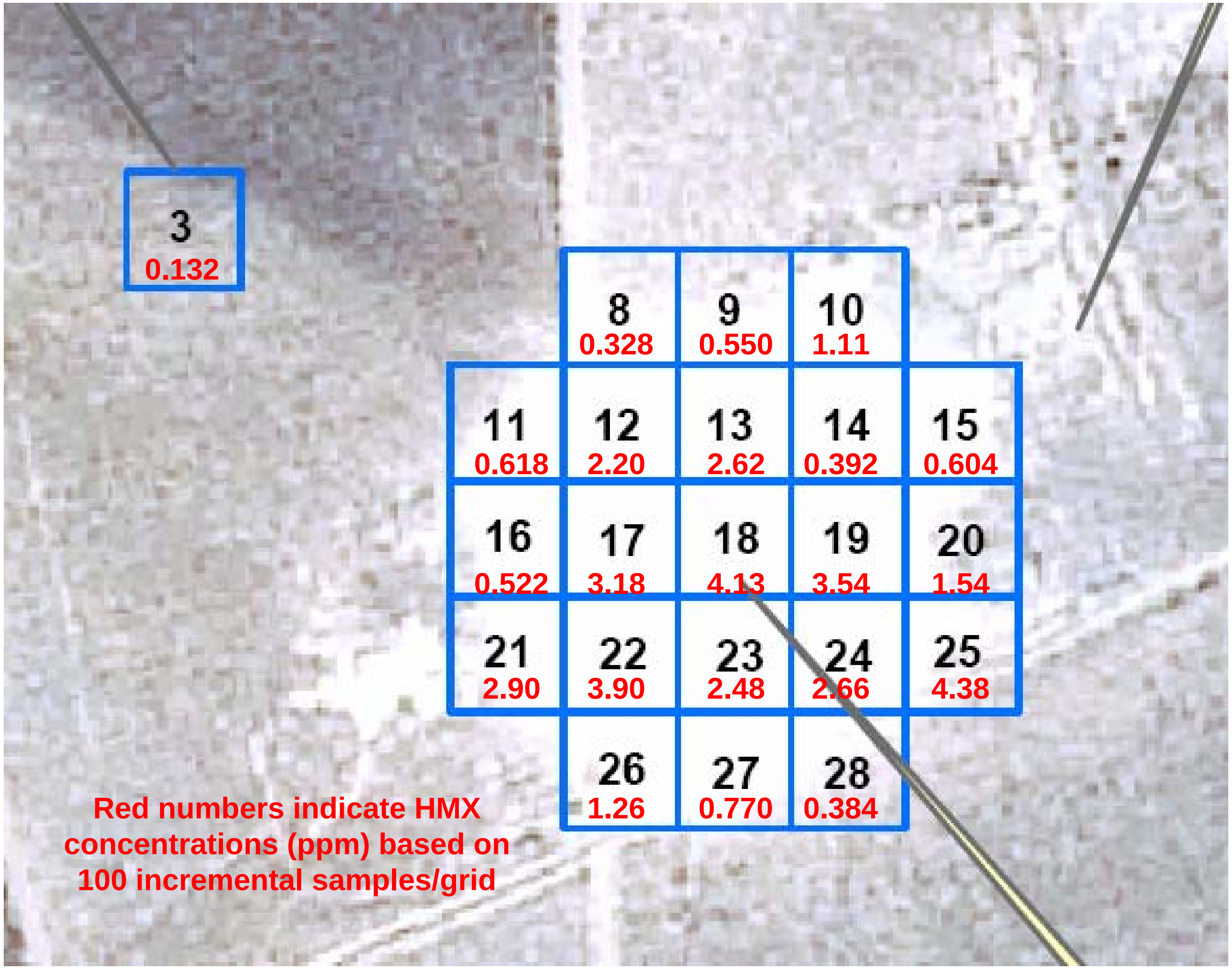
* Set of random discrete values
** False negative

Demolition of Missile Motors

Detonation (one minute later)

Detonation Crater

HMX Concentrations (mg/kg) for 100-m x 100-m grids



Field Replicates for Missile Demolition Range (100-m x 100-m grids)

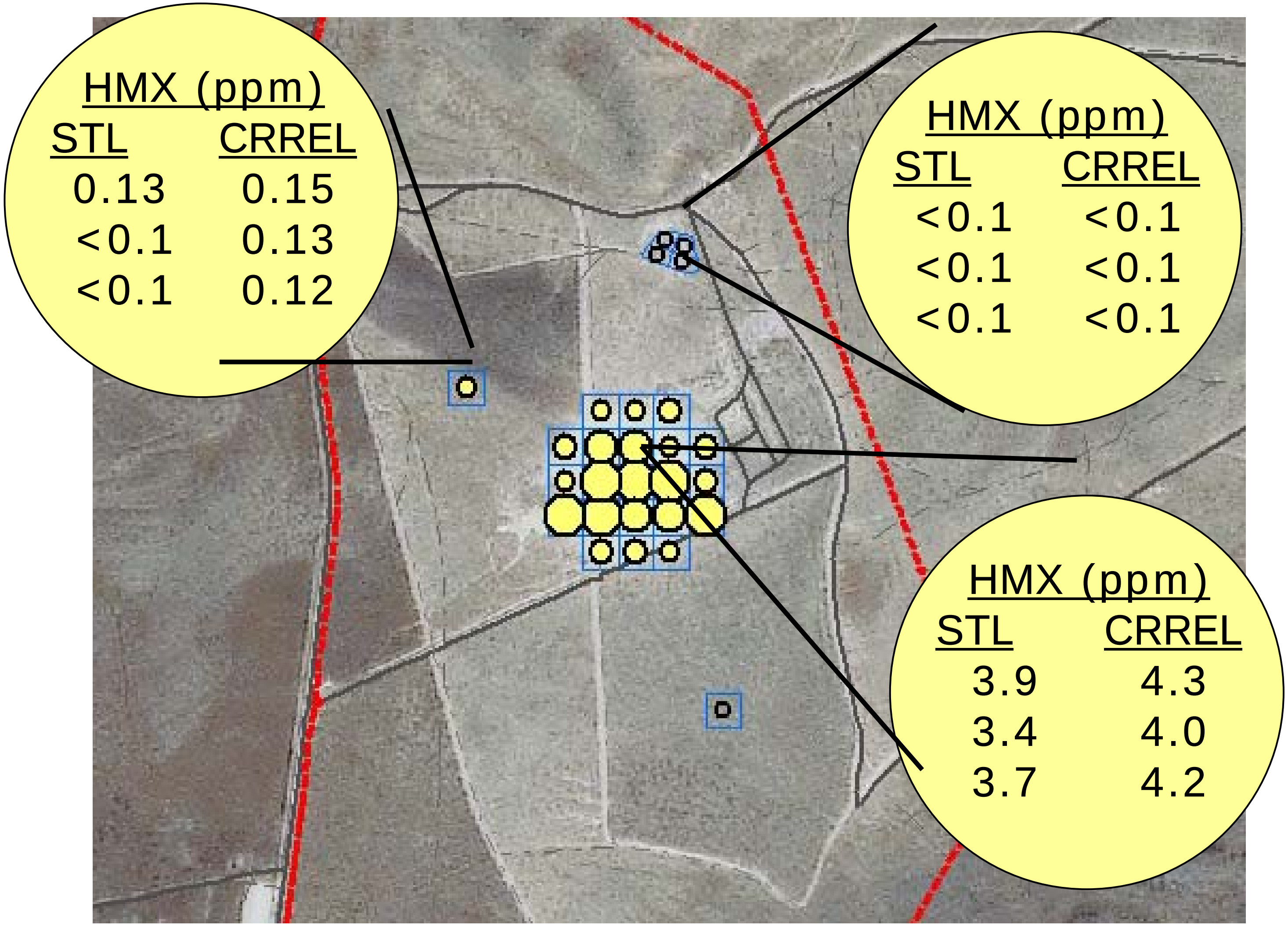
Triplicate 100-increment samples using a systematic-random design for four **100-m X 100-m** grids

HMX Concentration (mg/kg)

Grid 3	Grid 6	Grid 18	Grid 31
0.146	<0.04	4.26	<0.04
0.126	<0.04	3.96	<0.04
0.124	<0.04	4.16	<0.04
Mean=0.132		Mean=4.13	
RSD = 9.2%		RSD = 3.7%	

For this example, the MI sampling was done by a contractor.

Replicate Multi-increment Results



Discrete Samples vs Multi-Increment Samples

- Large range in data for discrete samples – much smaller range in multi-increment samples
- Distribution of discrete data always non normal – distribution of data from multi-increment samples often normal
- Median from discrete sample almost always less than mean – thus most discrete samples underestimate mean
- Median and mean concentrations generally similar for multi-increment samples
- Use of multi-increment samples often eliminates problem of dealing with "less than" data
- Recommendation – collect replicate systematic multi-increment samples to represent decision unit

Major Sampling Issues

- How many increments are necessary to overcome spatial heterogeneity within the decision unit?
  - Recommend 30 to 100
- How should increments be collected (totally random or with some systematic component)?
  - Recommend systematic-random sampling design
- What should the sample mass be to overcome compositional heterogeneity?
  - Recommend a minimum of 1 kg
- How large of an area can be adequately characterized with a multi-increment sample?
  - Experiments have been successful for areas as large as 100 m X 100 m (1 hectare)
- What should the sampling depth be?
  - Experiments indicate most residues are present in top 5 cm

Overall Recommendations for Sampling of Ranges

- Stratify ranges into functional areas
- Divide functional areas into decision units of a hectare or less
- Collect multi-increment samples from within each decision unit using a systematic-random pattern (*n* from 30 to 100)
- Collect field replicate samples to provide estimate of total uncertainty
- Do the job once and do it right!