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Engineer Research and Development Center

Proposed Changes for USEPA Method 3050B, Metals Digestion, Incorporating Incremental Sampling Methodology

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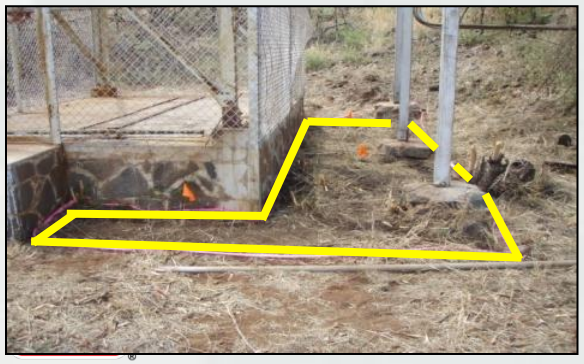
Surface Soil Sampling Issues

- Non-representative results using conventional grab surface soil sampling at military sites with metallic residues
- Inability to replicate results (duplicates) with grab sampling
- Poor precision of grab sample results yields large uncertainties when estimating the mean and calculating 95% upper confidence limits (UCLs)
- High grab sample result uncertainties problematic when reported concentration is near a regulatory action level
- Increasing State regulatory insistence to apply Incremental Sampling Methodology (ISM) for all soil sampling

Decision Units (DUs)

The volume of soil where samples are to be collected and decisions made based on the resulting data.

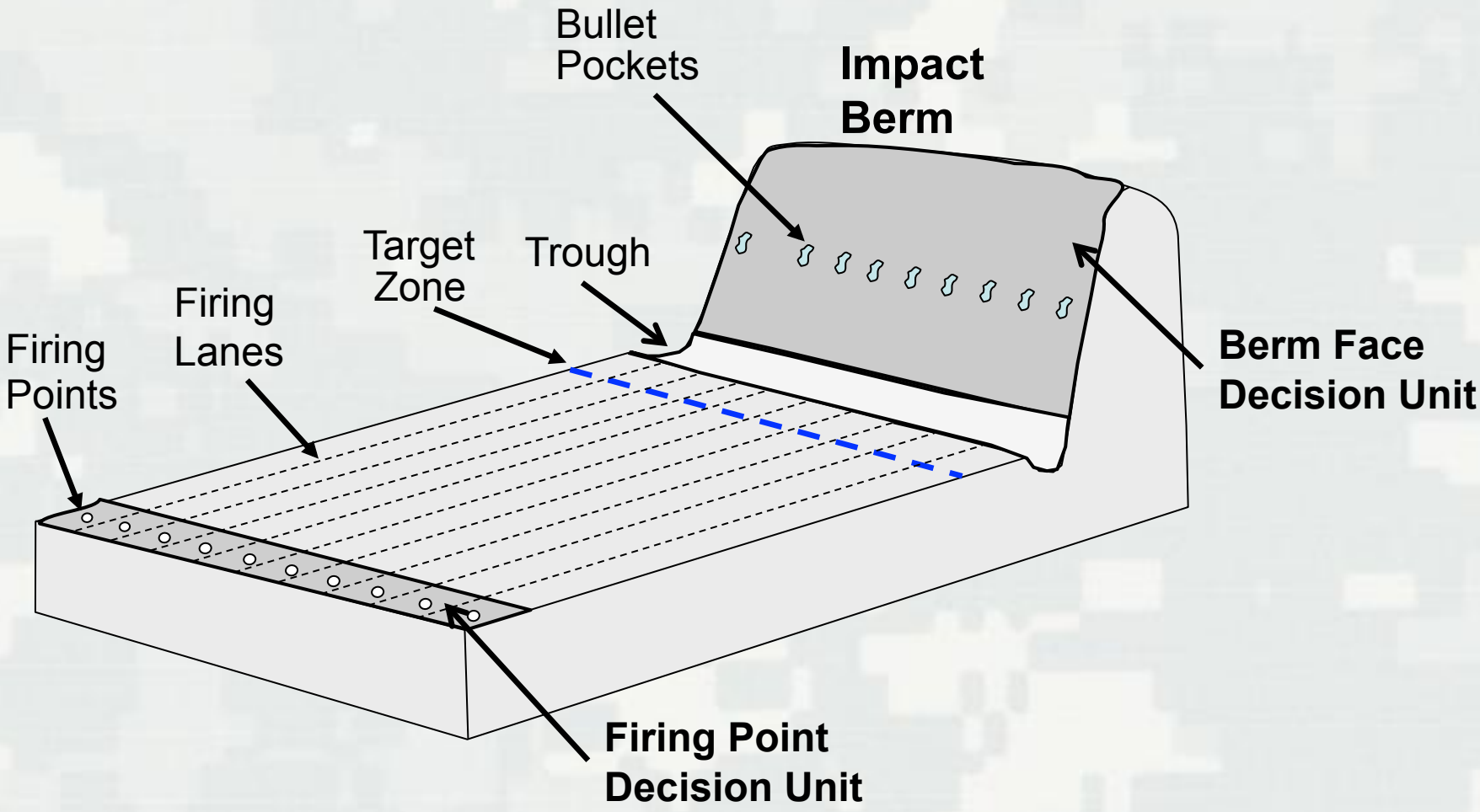
Source Areas



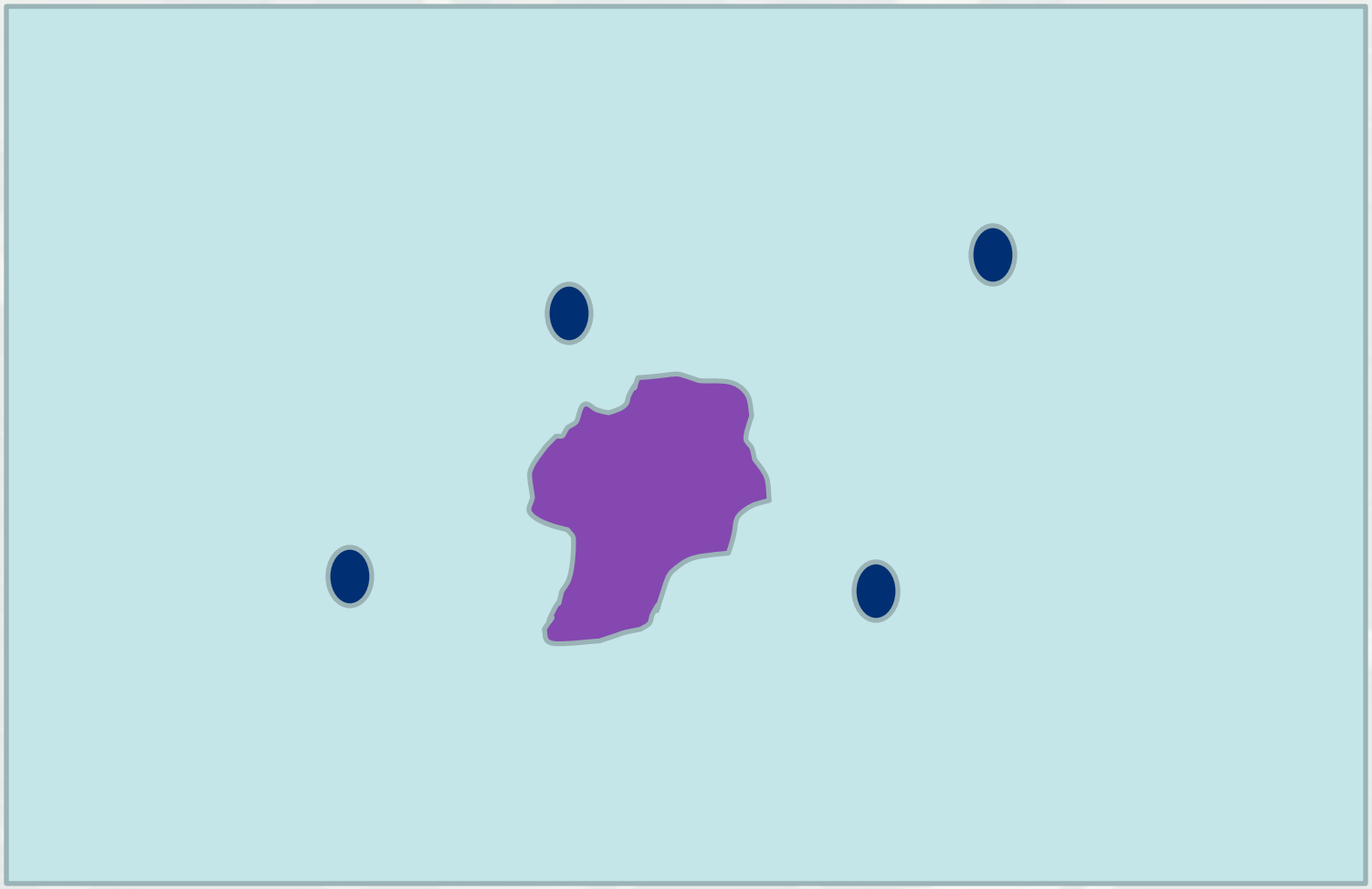
Exposure Areas

Size, shape, and type of DU are an outcome of systematic planning and depend on site specific data quality objectives.

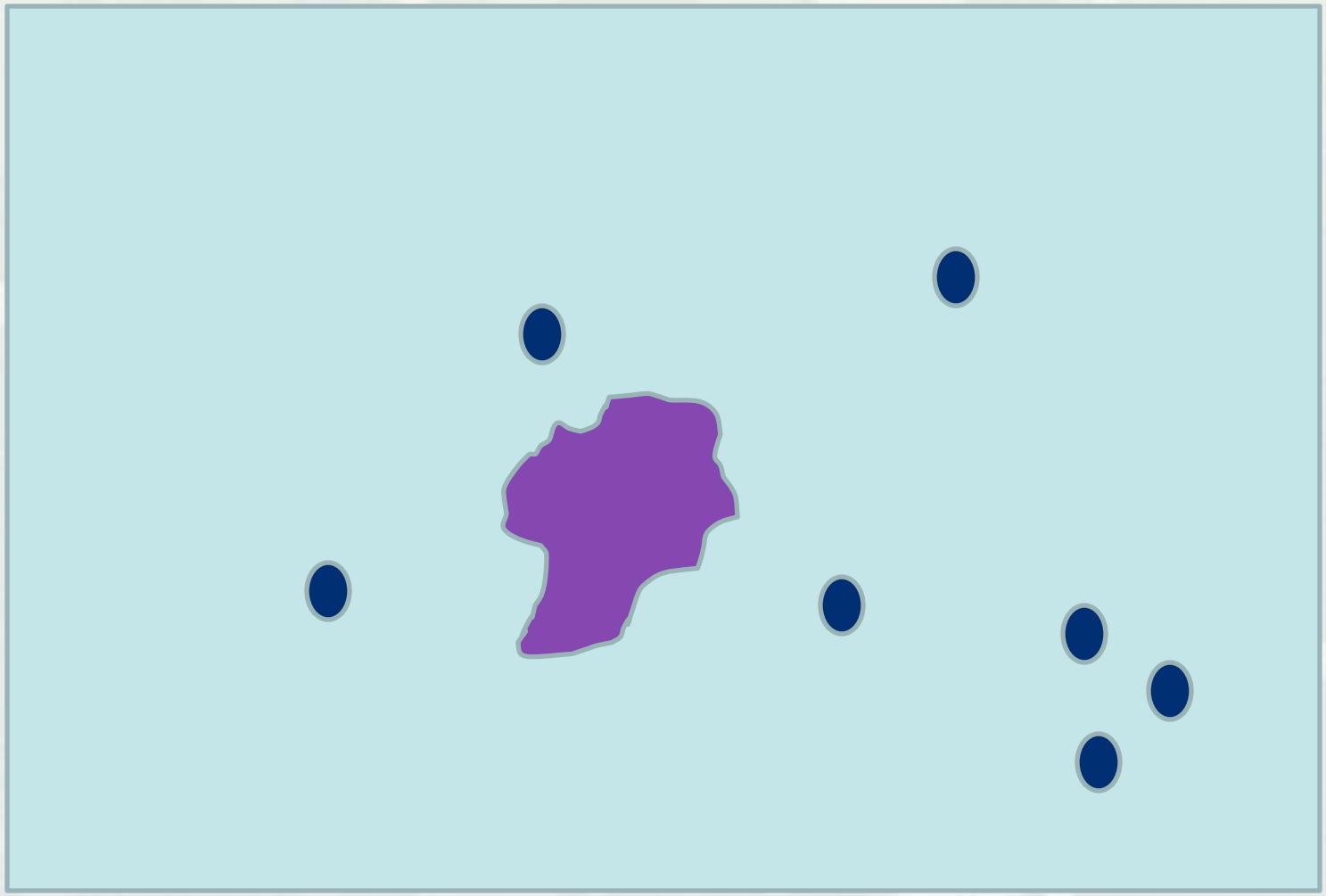
Typical Small Arms Range



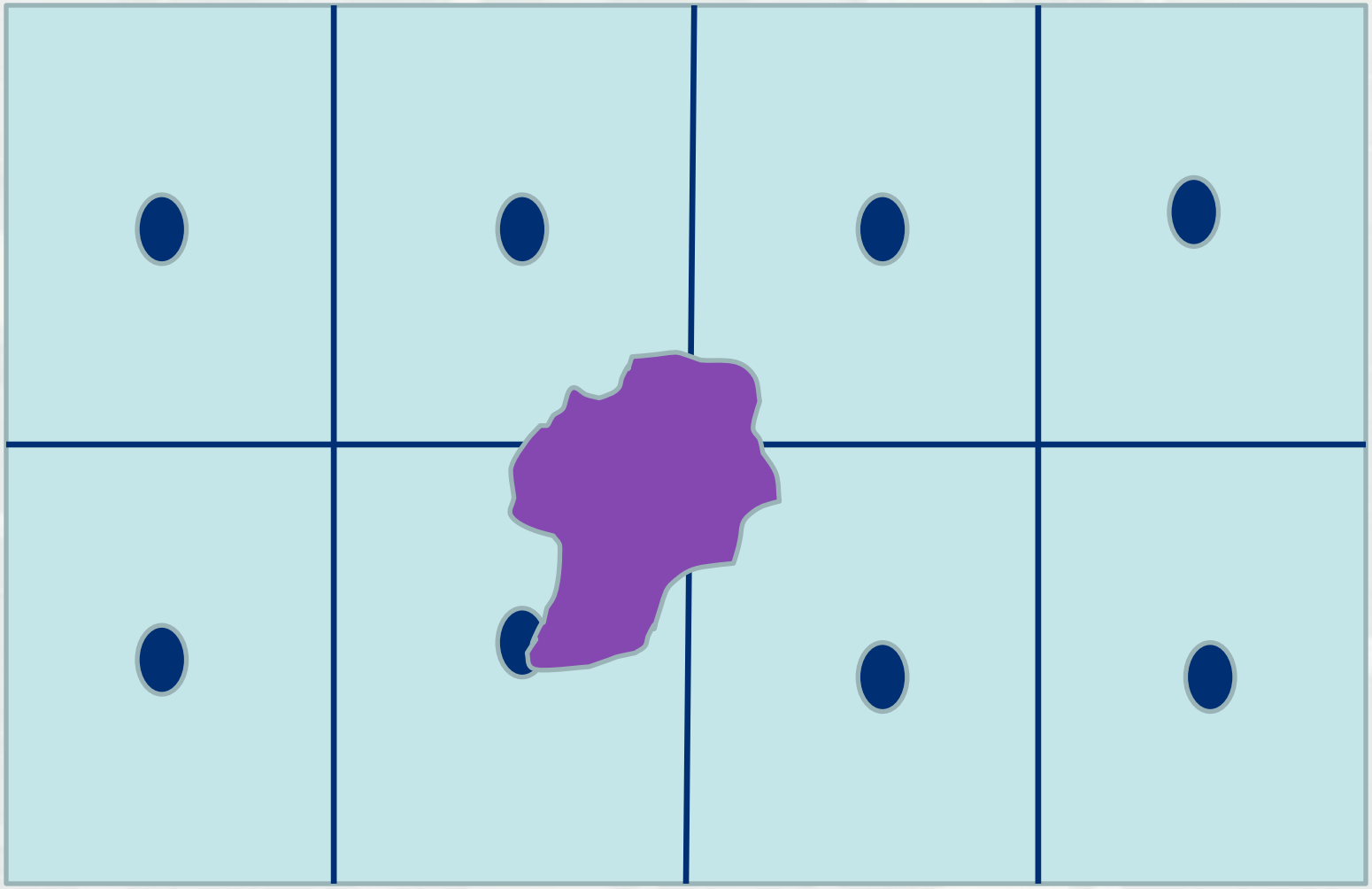
Conventional Random Sampling



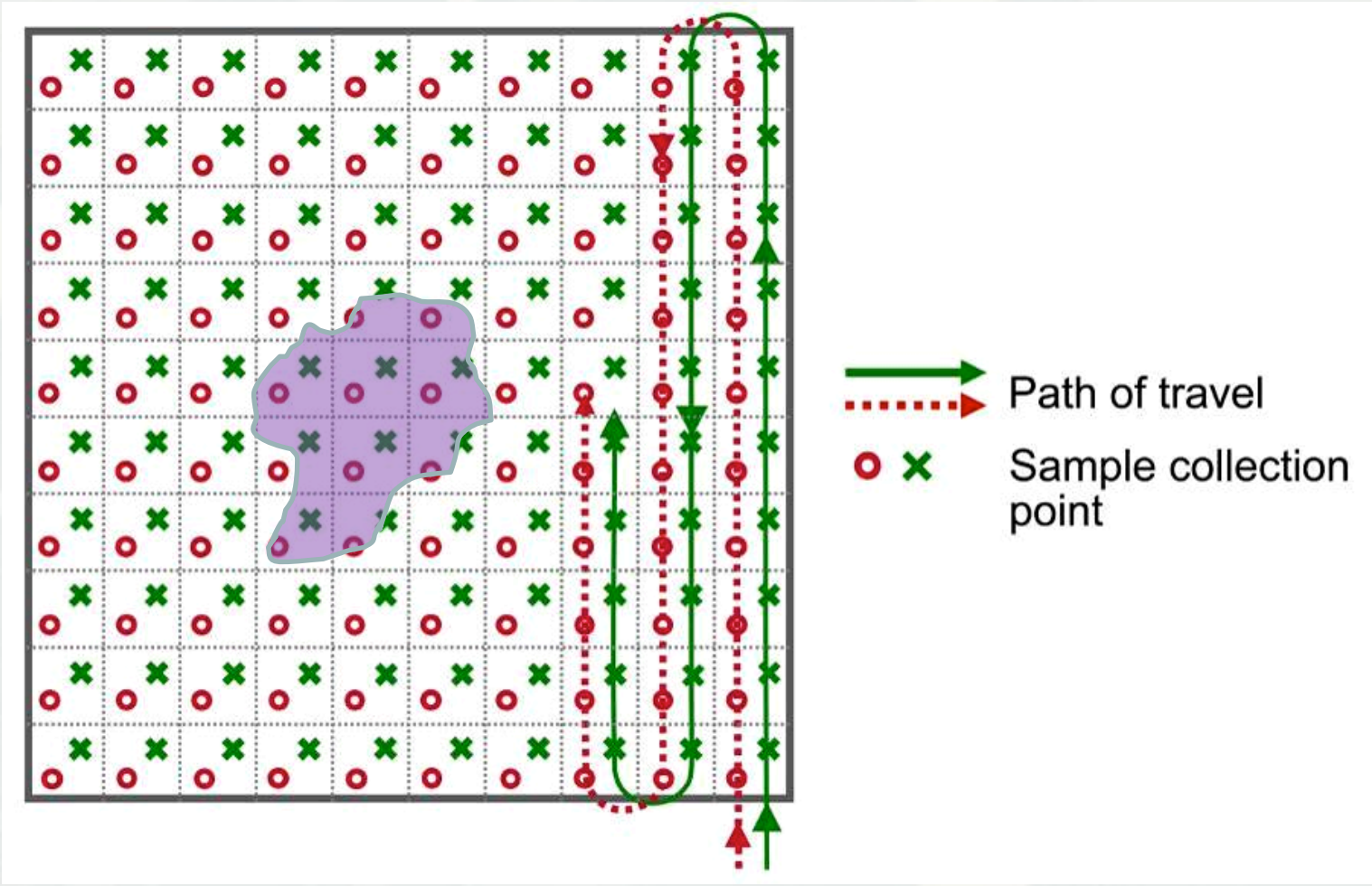
Conventional Biased Sampling



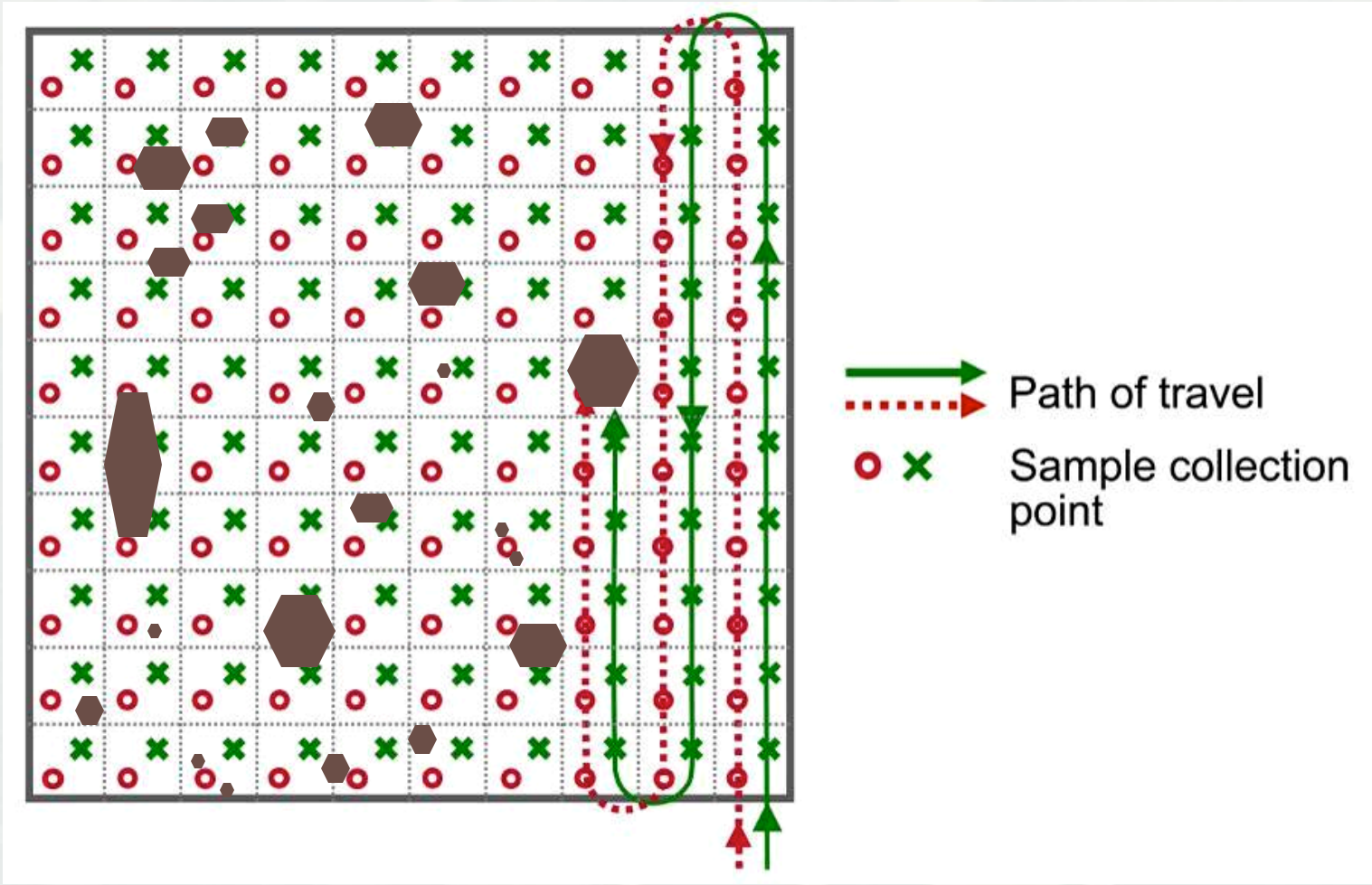
Conventional Grid-Centered Sampling



Incremental Sampling Methodology (ISM)



Incremental Sampling Methodology (ISM)



Conventional Sampling Versus ISM

Activity	Grab	ISM
Deterministic Sampling	√	
Decision Unit Layout		√
Field Splitting	√	
Air Drying		√
Sieving		√
Milling/Grinding		√
Subsampling		√
Larger Aliquot		√

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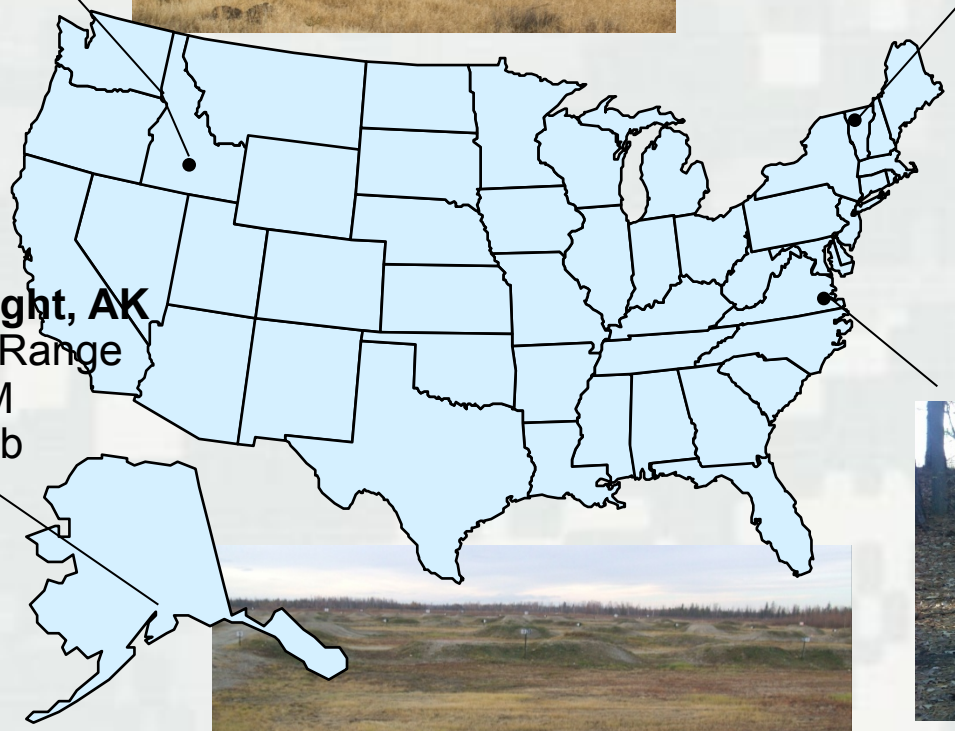
Performance Assessment

- **ISM versus Grab samples**
- **Number of increments/decision unit**
- Field splitting appropriateness
- **Milling necessity**
- **Milling equipment comparisons**
- Milling sample cross-contamination
- **Puck Mill and Roller Mill optimum milling interval**
- Digestion mass evaluation
- Digestion time
- Digestion reagent mixture
- Digestion subsampling preparation
- Blank material selection

Demonstration Sites

Kimama, ID
Small Arms Range
21 ISM
30 Grab

Camp Ethan Allen, VT
Small Arms Range
43 ISM
36 Grab

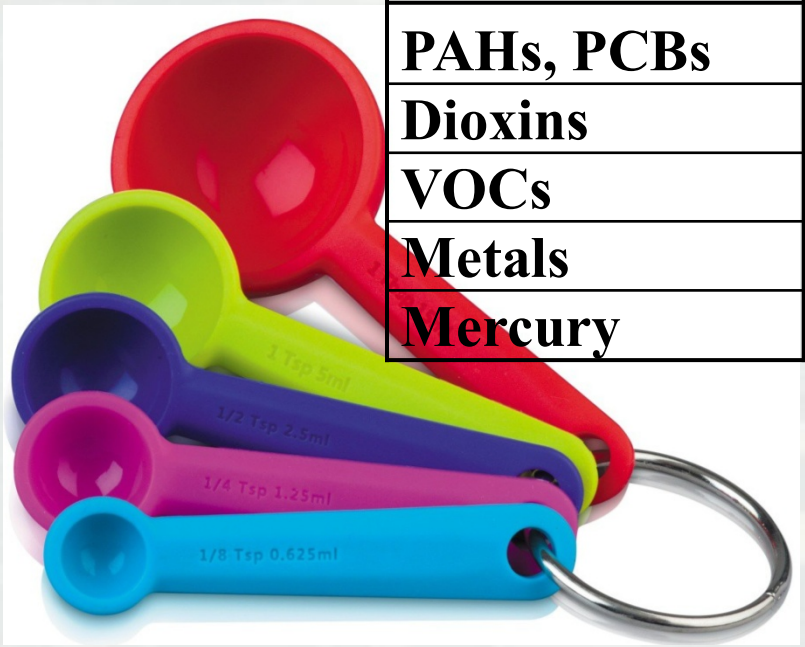


Fort Wainwright, AK
Small Arms Range
63 ISM
52 Grab

Fort Eustis, VA
Small Arms Range
27 ISM
33 Grab

How Representative is Your Grab Sample?

Contaminant Category	Mass Analyzed by Lab	Approximate Kitchen Equivalent
PAHs, PCBs	30g	1 1/2 tbl
Dioxins	10g	1/2 tbl
VOCs	5g	~ 1 tsp
Metals	1g	~ 1/8 tsp
Mercury	0.5g	~ 1/16 tsp



Discrete sampling field tools (approximately to scale)

Assuming Soil Density = 1.3

1 tablespoon (15ml) = 20g

1 teaspoon (5ml) = 6.5g

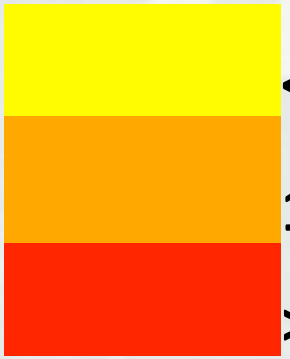
1/2 tsp (2.5ml) = 3g

1/8 tsp (0.6ml) = 0.8g

Small Arms Range Grab Sample Results
Lead (mg/kg)

951	868	1061	2868	217	2623	1767	1213	692	44
938	2307	319	19,038	1060	1952	3537	9235	5328	79,020
127	352	1204	1977	809	986	2840	4858	2349	1848

Legend



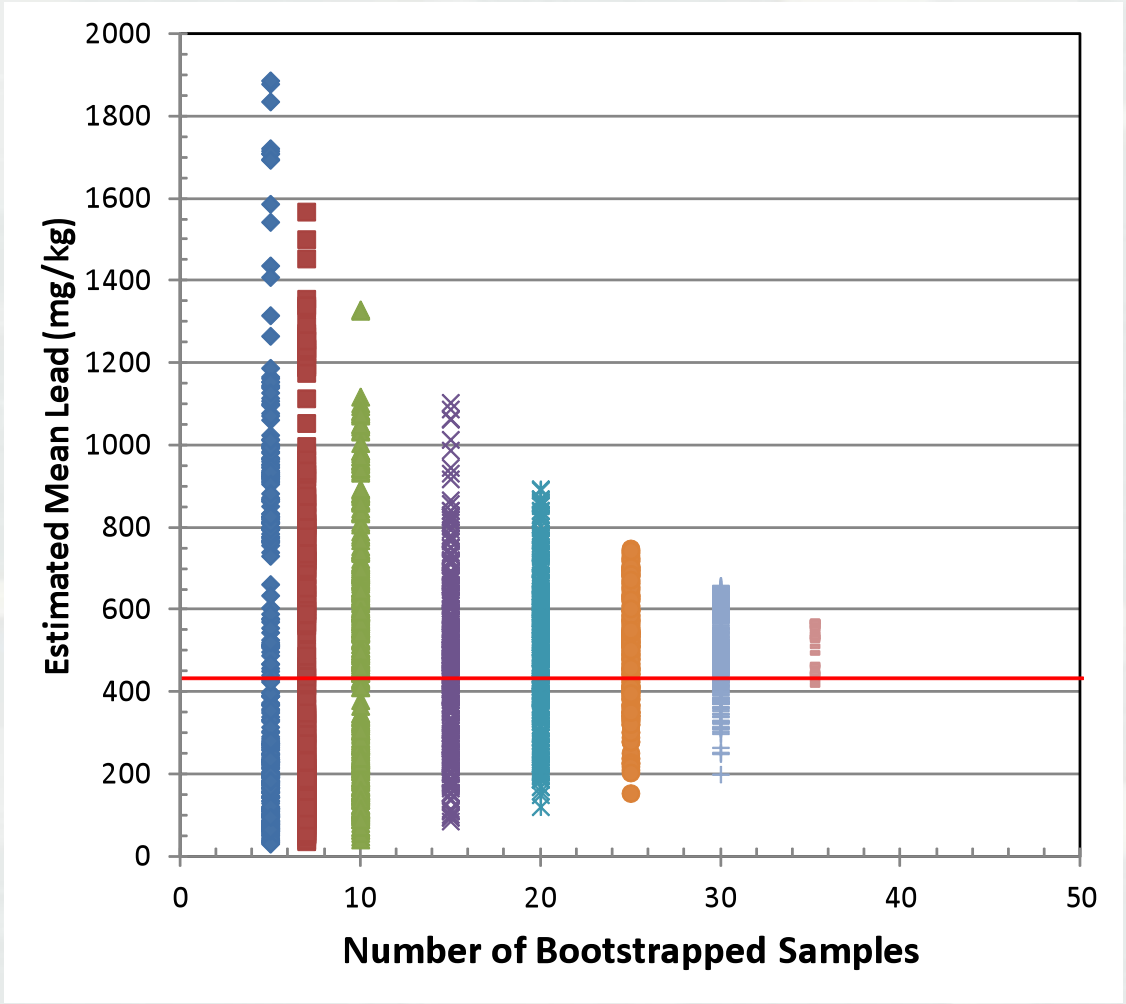
<1,000

1000-10,000

>10,000

n	30
Mean	5060
Median	1238
Min	43.9
Max	79020
STD	14438
RSD (%)	285

Number of Grab Samples versus Estimate of Mean



Small Arms Range Results for Seven Grab Samples, Lead (mg/kg)

951		1061	2868		2623				
			19,038		1952		9235		

Mean 10075
Median 951
RSD (%) 42

951							1213		44
							9235		
127					986			2349	

Mean 2129
Median 986
RSD (%) 151

938				1060				5328	79,020
127						2840	4858		

Mean 13453
Median 2840
RSD (%) 215

ISM versus Grab Samples

Gridded Grab

951	868	1061	2868	217	2623	1767	1213	692	44
938	2307	319	19,038	1060	1952	3537	9235	5328	79,020
127	352	1204	1977	809	986	2840	4858	2349	1848

Lead (mg/kg)

	<1,000
	1000-10,000
	>10,000

Biased Random Grab

555					1930			1851	
		479							
		501					1650		

	ISM (100-inc)	Grab	Grab
	Systematic Random	Grid	Biased Random
n	7	30	6
Mean	2,717	5,060	1,161
Median	2,718	1,238	1,103
Min	2,440	44	479
Max	2,936	79,020	1,930
RSD	4	285	62

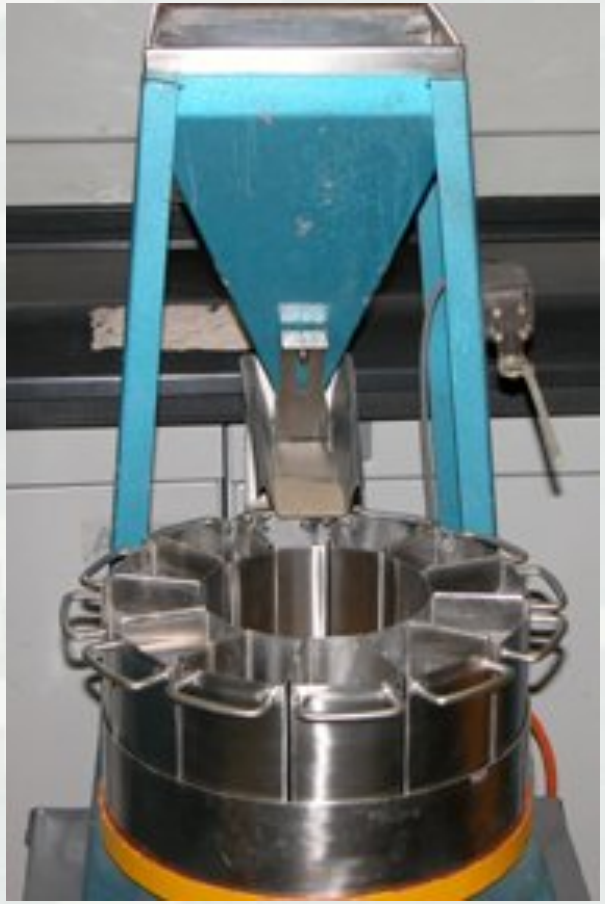
Probability of finding 1 hotspot with six grab samples is 44%. Finding both is 8%

Number of ISM Increments Needed

ISM	Percent Relative Standard Deviation (RSD)									
n	Al	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
5	3	10	22	4	4	3	25	25	6	9
10	8	6	162	4	4	4	32	63	5	154
20	27	121	26	22	18	26	30	50	32	15
30	3	7	15	10	4	3	14	15	6	6
50	3	15	21	10	2	4	11	11	6	10
100	3	7	26	4	2	2	17	17	3	15
200	6	3	18	4	5	2	4	7	1	11
n = number of increments per MI sample										

Replicate Comparison for Small Arms Range Berm Soil

Subsample Replicates	Metals Conc. (mg/kg) Cu	Pb	Metals Conc. (mg/kg) Sb	Cu
1	**2,600**	360	5.5	99
2	110	330	5.0	90
3	300	920	7.6	87
4	**110**	300	4.3	99
5	130	280	4.3	**130**
6	140	**2,800**	**16**	90
7	860	1,600	12	88
8	540	330	4.6	99
9	1,200	850	4.2	83
10	130	1,500	4.5	98
11	1,900	380	4.9	99
12	120	330	4.3	110
13	130	**290**	**3.7**	**80**
14	120	300	4.1	87
15	110	820	8.2	84



Sample #1 **Sample #2**

Performance Assessment – Sample Processing (Milling) of Soil

Puck Mill

Fe, Mn, Cr, V

Roller Mill

Alumina cans polyethylene Liner, ceramic chips

Pulvisette

Agate balls

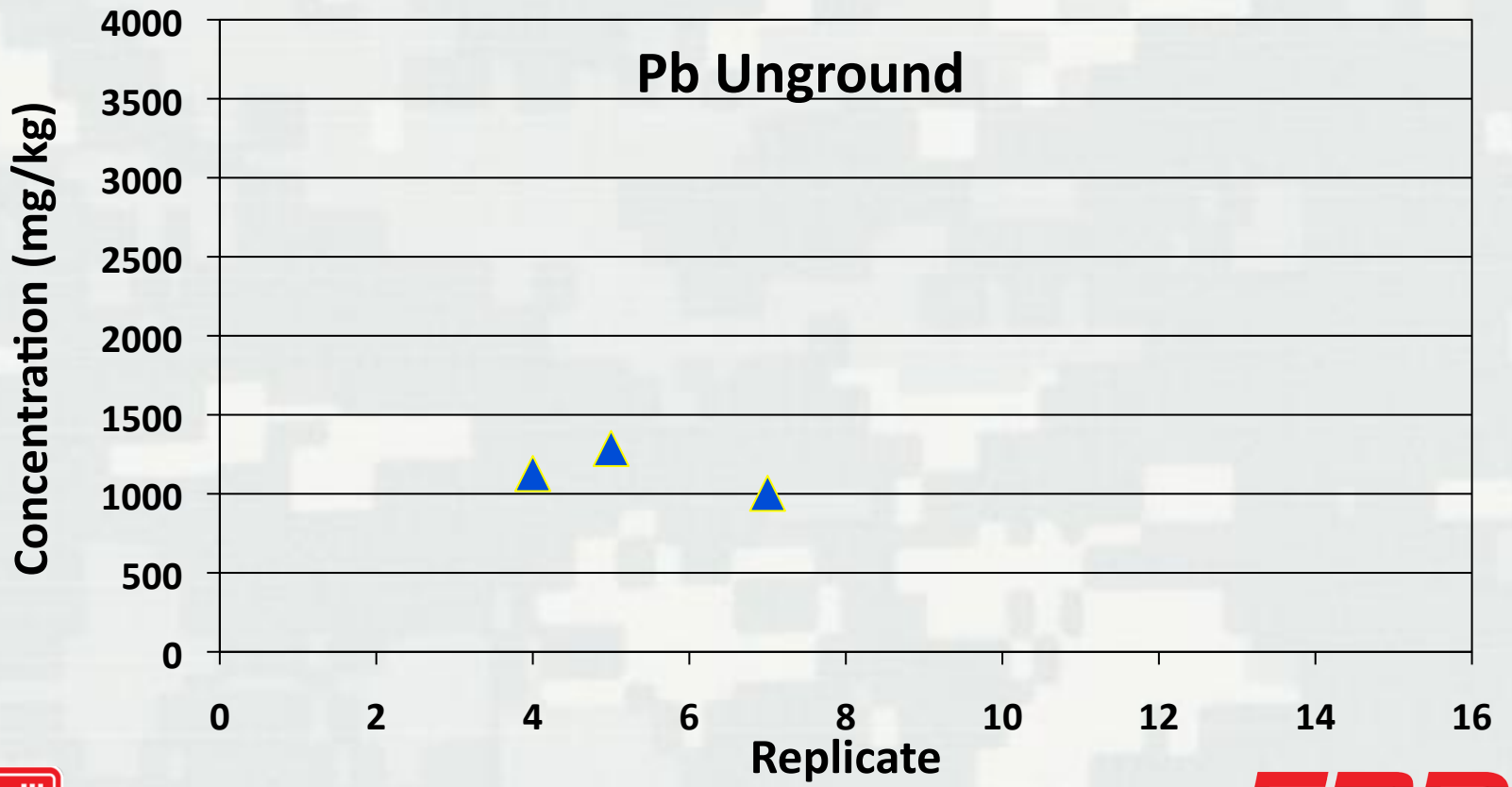
Mortar and Pestle

Ceramic

Milling Equipment Comparisons

	Percent Relative Standard Deviation (RSD)									
Machine Type	Al	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
Unground #1	4	5	**257**	4	4	7	**61**	**116**	4	**162**
Unground #2	2	5	**25**	1	1	2	**39**	**69**	NA	**17**
Mortar & Pestle	5	4	**39**	4	3	3	**32**	**55**	4	**28**
Puck Mill #1	5	4	10	4	4	4	15	**21**	5	5
Puck Mill #2	1	2	15	4	2	1	4	7	2	10
Puck Mill #3	5	1	**16**	3	2	2	4	5	2	11
Puck & Ring Mill	6	5	5	4	5	5	5	8	5	6
Ball Mill	1	1	3	1	1	1	1	8	1	2
NA-not analyzed, Bolded values > 15%										

To Mill or Not To Mill



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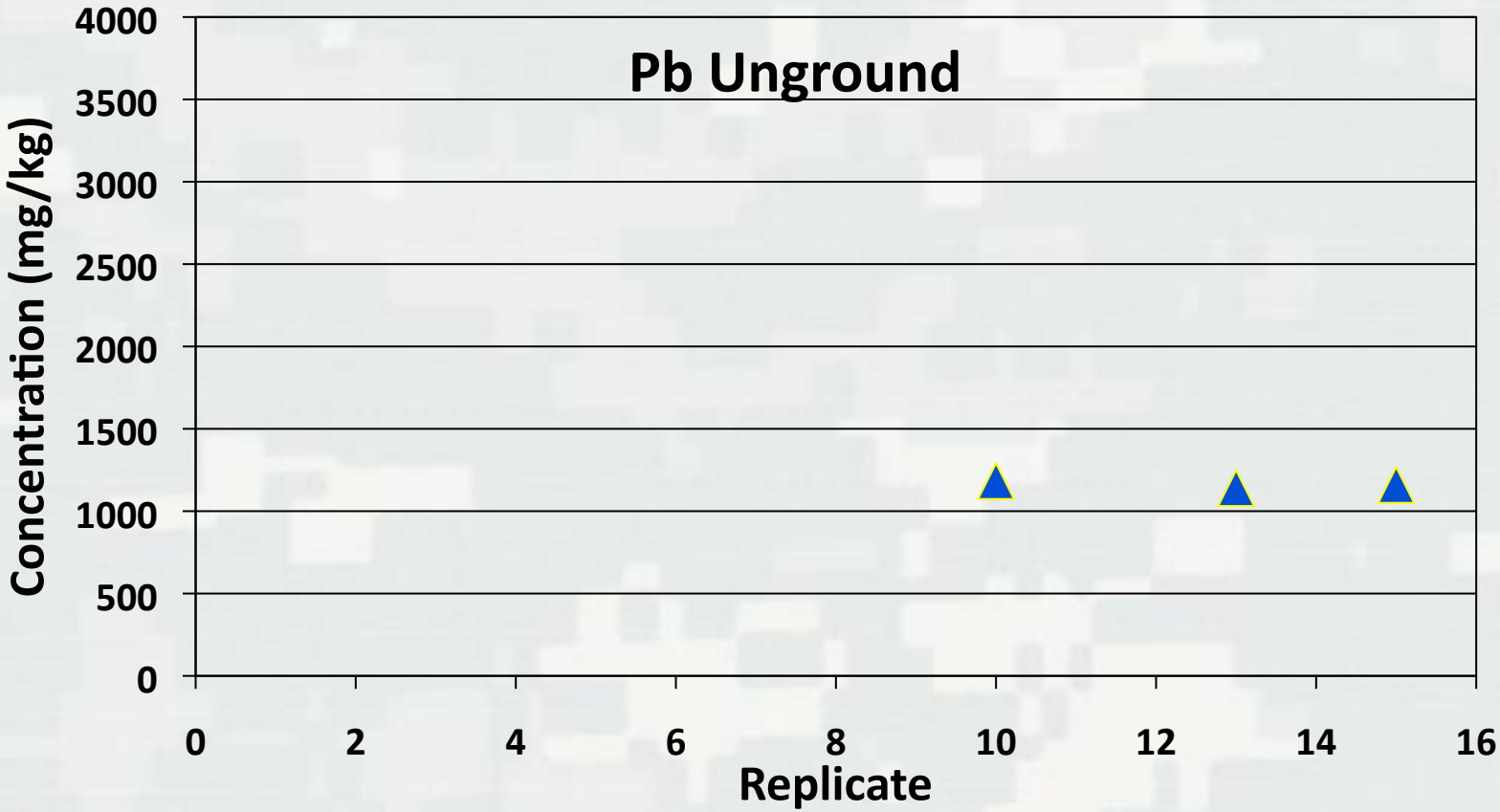

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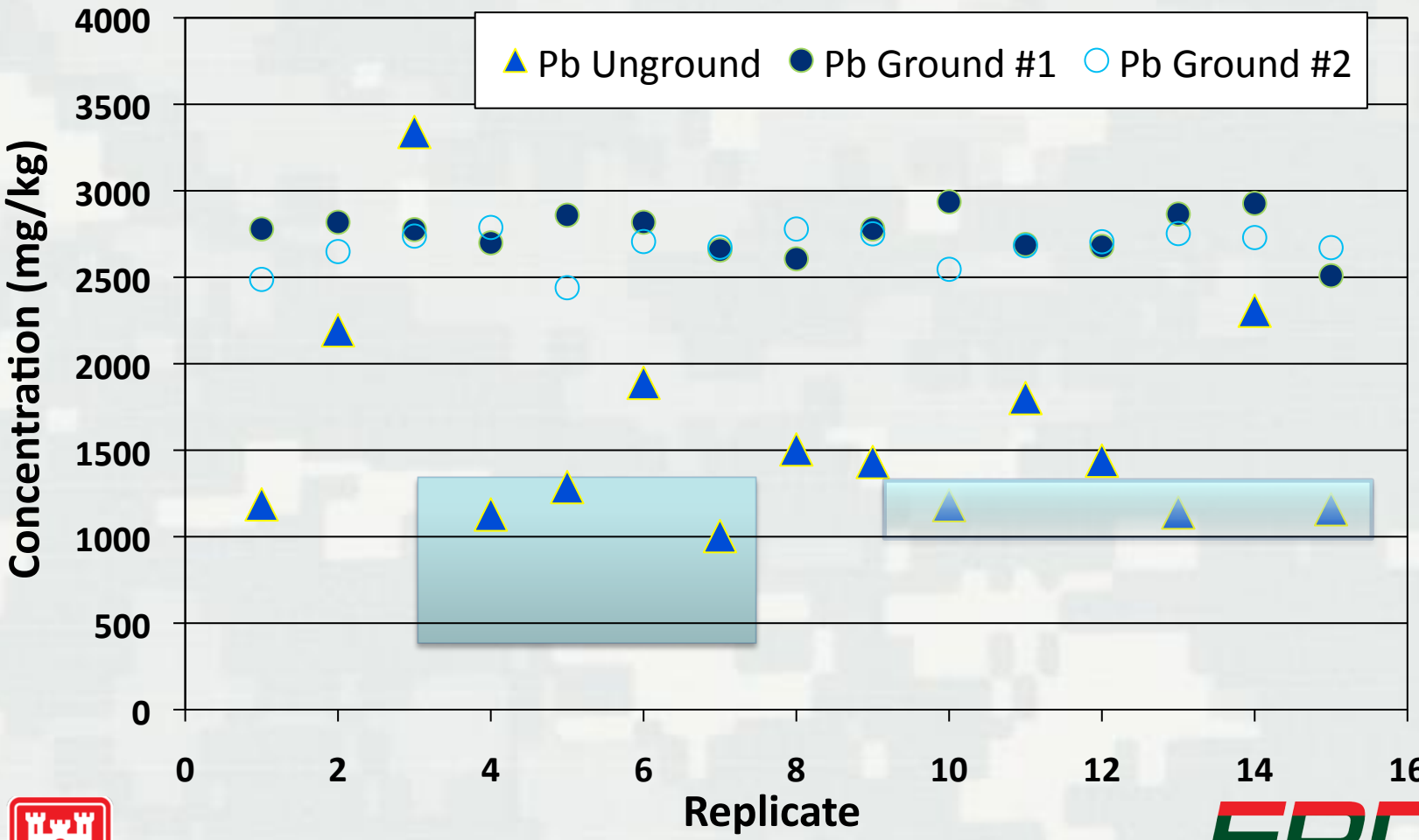
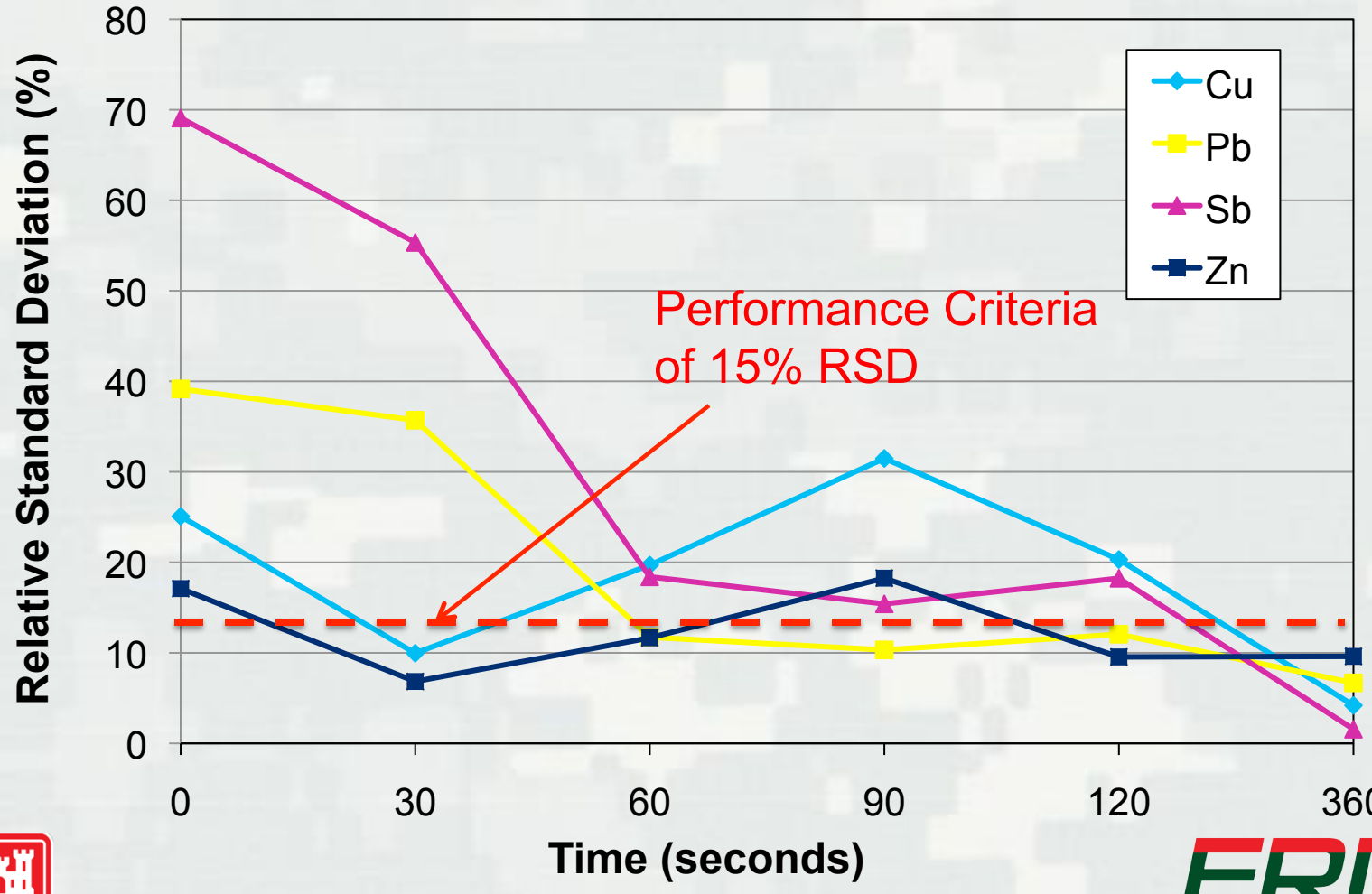
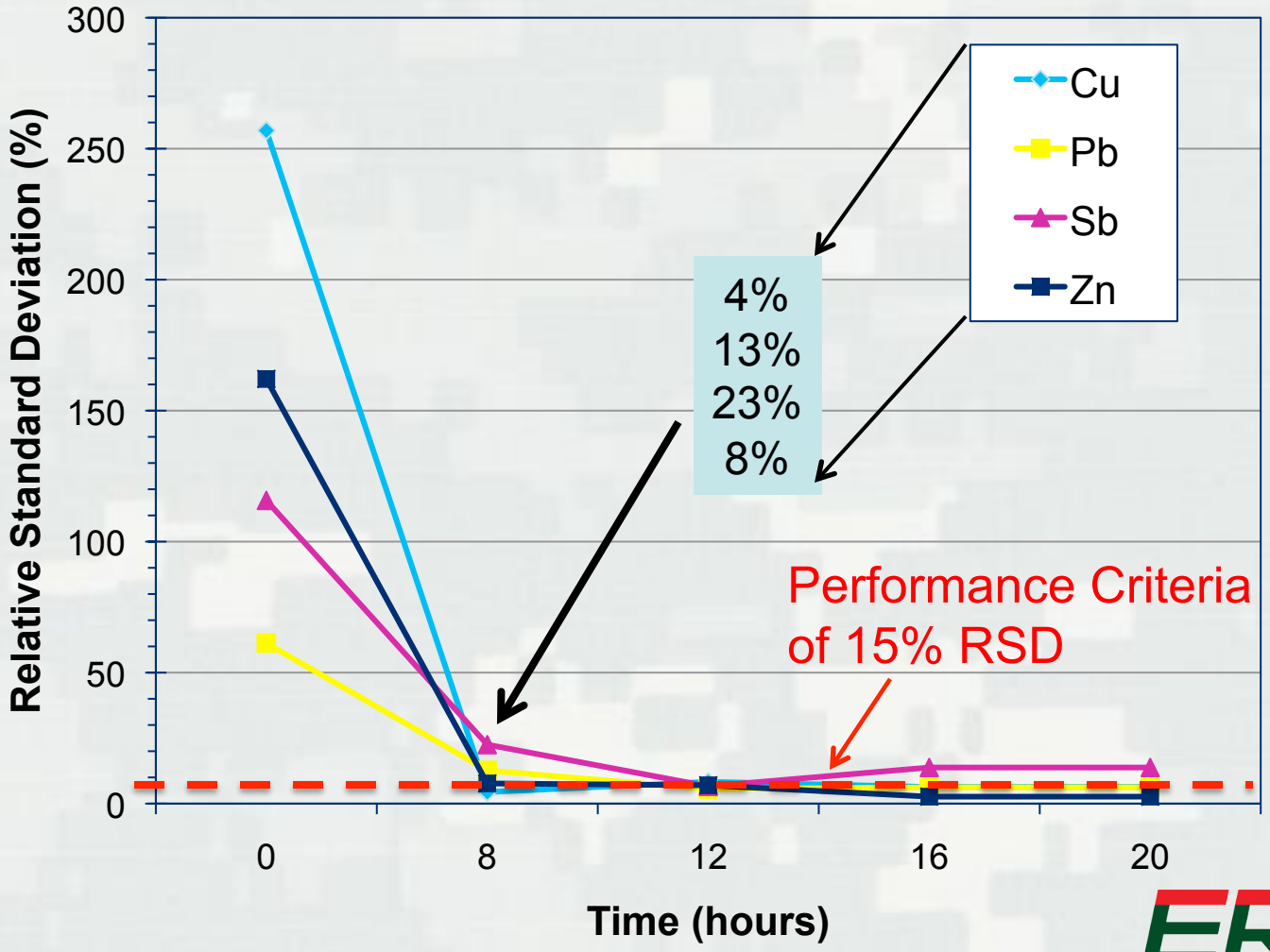


Puck Mill Optimum Grinding Interval



Roller Mill Optimum Grinding Interval



Comparison Method 3050B to 3050C

Activity	Method 3050B/ Conventional Sampling	Method 3050C/ Incremental Sampling Method
Field sampling	Not explicitly addressed. Typically, grab samples are collected from biased locations	Addressed in Appendix using ISM
Sample mass	200 g	1-2 kg
Sample drying	Optional, not typical	Yes
Sieving	If appropriate use a #10 sieve, samples are typically not sieved	Yes, using a #10 (2-mm) sieve
Milling	Milling is typically not done.	Yes, using appropriate mechanical grinders such as puck or roller mills
Laboratory sub-sampling	No	Yes, using 20-30 increments
Sub-sample mass.	0.5 - 2 g wet weight or 1 g dry weight	2 - 10 g dry weight

Environmental Status

- ITRC issued ISM guidance, Feb 2012. http://www.itrcweb.org/ISM-1/
- AK, HI issued regulatory requirements for ISM, 2010-12
- Other States in progress of developing guidance
- USEPA issued Federal Facilities Forum Issue Paper: *Site Characterization for Munitions Constituents*.
- EPA-505-S-11-01.

  http://www.epa.gov/fedfac/pdf/site_characterization_for_munitions_constituents.pdf
- ERDC-CRREL issued ESTCP reports on recommendations, demonstration, and cost & performance
- ERDC-CRREL working with USEPA to modify Method 3050B, new guidance, Method 3050C, 2015?

ERDC ISM Documentation

- Clausen et al. 2013. *Cost and Performance of Incremental Sampling Methodology (ISM) for Metallic Residues, ESTCP Project ER200918.* ERDC/CRREL TR-13-10. http://acwc.sdp.sirsi.net/client/search/asset/1030100
- Clausen et al. 2013. *Demonstration of Incremental Sampling Methodology for Soil Containing Metallic Residues.* ERDC/CRREL TR-13-9. http://acwc.sdp.sirsi.net/client/search/asset/1030080
- Clausen et al. 2013. *Incremental Sampling Methodology (ISM) for Metallic Residues.* ERDC/CRREL TR-13-5. http://acwc.sdp.sirsi.net/client/search/asset/1029240

ERDC ISM Documentation (Cont.)

- Clausen *et al.* 2012. *Evaluation of Sampling and Sample Preparation Modifications for Soil Containing Metal Residues.* ERDC TR-12-01. http://acwc.sdp.sirsi.net/client/search/asset/1006020
- Clausen *et al.* 2012. *Metal Residue Deposition from Military Pyrotechnic Devices and Field Sampling Guidance.* ADA562327. http://handle.dtic.mil/100.2/ADA562327
- Clausen *et al.* 2010. Sample preparation and digestion considerations for determining metal deposition at small arms ranges. *Int. J. Env. Anal. Chem.* **90**(12):903-921. http://www.tandfonline.com/doi/abs/10.1080/03067310903353495

DOD/USACE ISM Documentation

- DoD. 2014 (In Review). OACSIM Guidance on Implementation of Incremental Sampling (IS) of Soil for the Military Munitions Response Program.
- USACE. 2014 (In Press). Technical Guidance for Military Munitions Response Actions. IGD 14-01. Dec 2013. (to be published as EM 200-1-15)
- DoD. 2013. Environmental Field Sampling Handbook. April 2013. http://denix.osd.mil/edqw/upload/DoD-Environmental-Field-Sampling-Handbook.pdf
- USACE. 2009. - Implementation of Incremental Sampling of Soil for Military Munitions Response Program. IGD 09-02. July 2009. http://www.itrcweb.org/ism-1/references/IGD_9-02v2.pdf

Conclusions

- Conventional grab soil samples do not yield a representative result of the area of interest (DU) when metallic residues are present
- Small grab sample populations have high error for situations with heterogeneously distributed contaminants
- Grab sample error can be reduced by increasing population size, however question of affordability
- Incremental Sampling Methodology (ISM) yields results representative of the area of interest
- ISM yields lower total error, which is quantifiable
- ISM requires far fewer samples than conventional grab samples and results in lower total project cost

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