Fort Eustis MIS Study

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Purpose & Basic Characteristics

- Evaluate ability of MIS to provide representative mean concentrations of COCs
- Focus on specific facets of sample design, including
  - Grinding
  - Comparability between discrete samples & MIS
- Former skeet range (PAHs, Pb, As, Sb)
- Decision Unit (DU) design based on ecological habitats
- Here only present metals data

DU1 – 2.32 acre forested tidal wetland characterized by a predominately flat topography

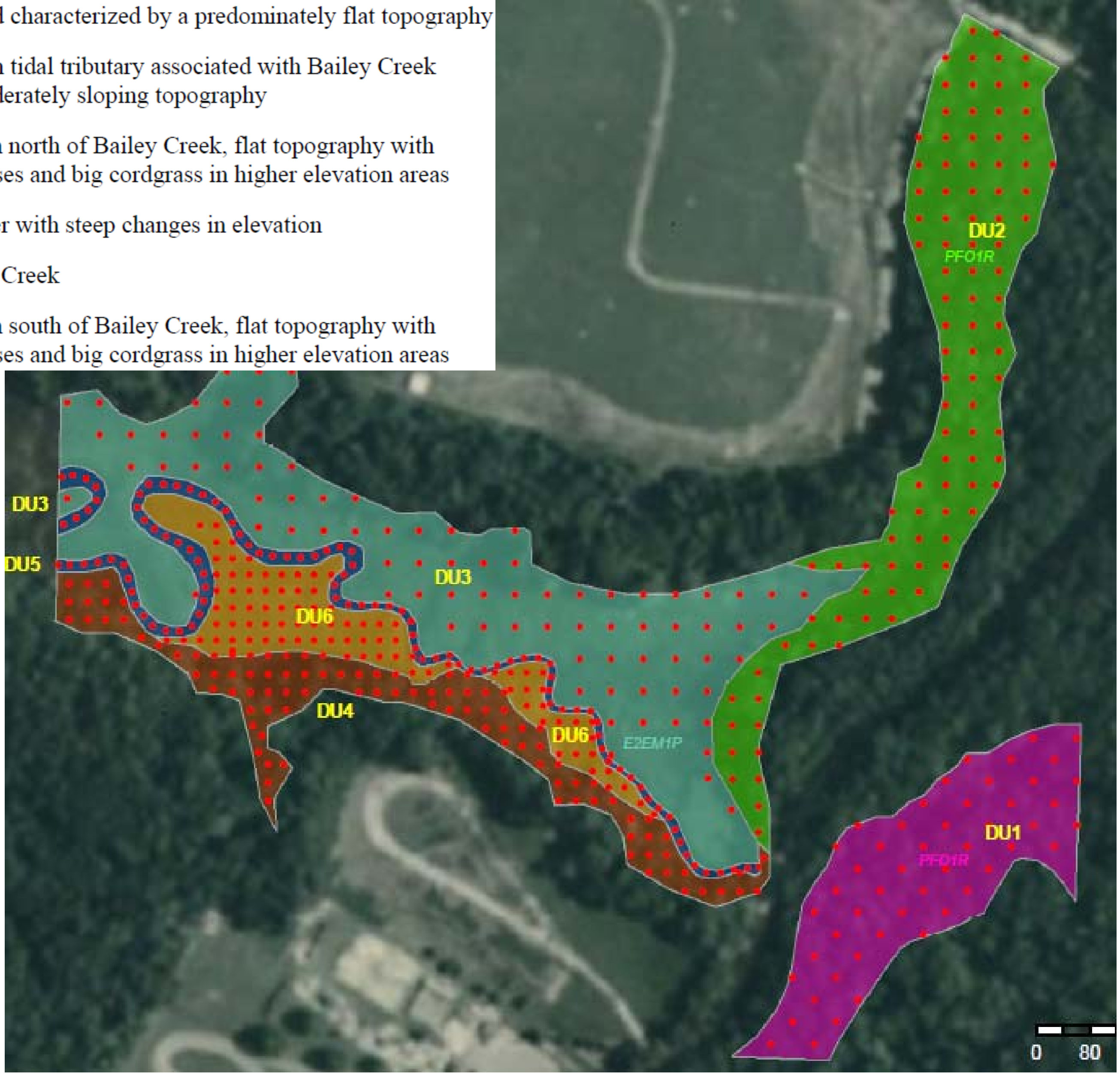
DU2 – 3.49 acre forested wetland with tidal tributary associated with Bailey Creek moving through, characterized by moderately sloping topography

DU3 – 5.203 acre brackish tidal marsh north of Bailey Creek, flat topography with saltmarsh cordgrass, saltmeadow grasses and big cordgrass in higher elevation areas

DU4 – 1.62 acre forested upland buffer with steep changes in elevation

DU5 – 0.88 acre stream bed of Bailey Creek

DU6 – 1.346 acre brackish tidal marsh south of Bailey Creek, flat topography with saltmarsh cordgrass, saltmeadow grasses and big cordgrass in higher elevation areas



Study Design

DU#	Field Replicate Sample (3)	Laboratory Pre-Grind Replicates (5) *	Laboratory Post-Grind Replicates (5)*	Laboratory Post-Grind Replicates (3)*	Discrete (49)
1	✓			✓	
2	✓	✓	✓		
3	✓			✓	
4	✓	✓	✓		✓
5	✓			✓	
6	✓	✓	✓		

* - Only 1 of the 3 field replicate samples from each DU was included in this portion of the evaluation. The other field replicates were simply sub-sampled once after sieving, drying and grinding.

Two Questions the Ft Eustis Data Can Address

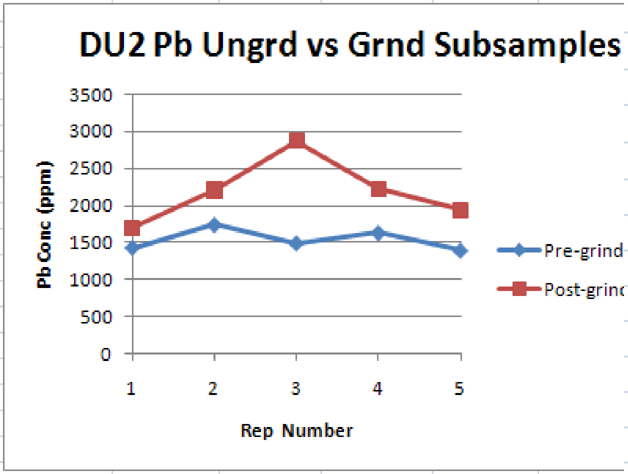
- Does grinding a sample increase the acid solubility of the matrix and release metals that would normally not be measured by ICP and that probably would not be bioavailable?
- Can incremental sampling produce data comparable to what would be obtained by a reasonably dense discrete sampling design?

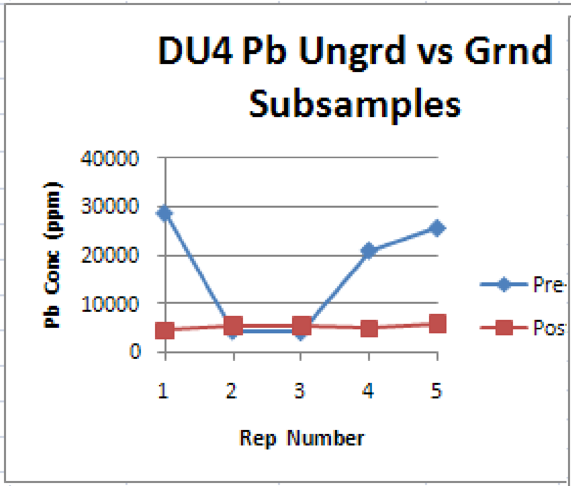
Does Grinding Increase Metal Solubilization During Digestion?

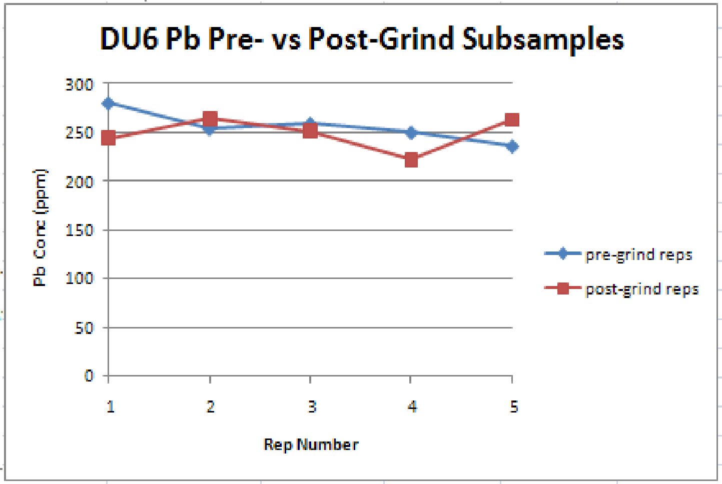
- Short answer: a qualified “No”, might depend on matrix
- Long answer: The evidence from 2 of the DUs is solidly against the conclusion that grinding elevates metal concentration results.
- Forested wetland DU (DU2) did show statistical elevation of Sb, As and Pb in ground vs unground samples.
  - Cannot be ruled out that something about the forested wetland matrix facilitates greater solubilization of Sb, As and Pb from ground samples.
  - But other metals in the DU’s data set did not show this pattern
  - There is another explanation for this observation

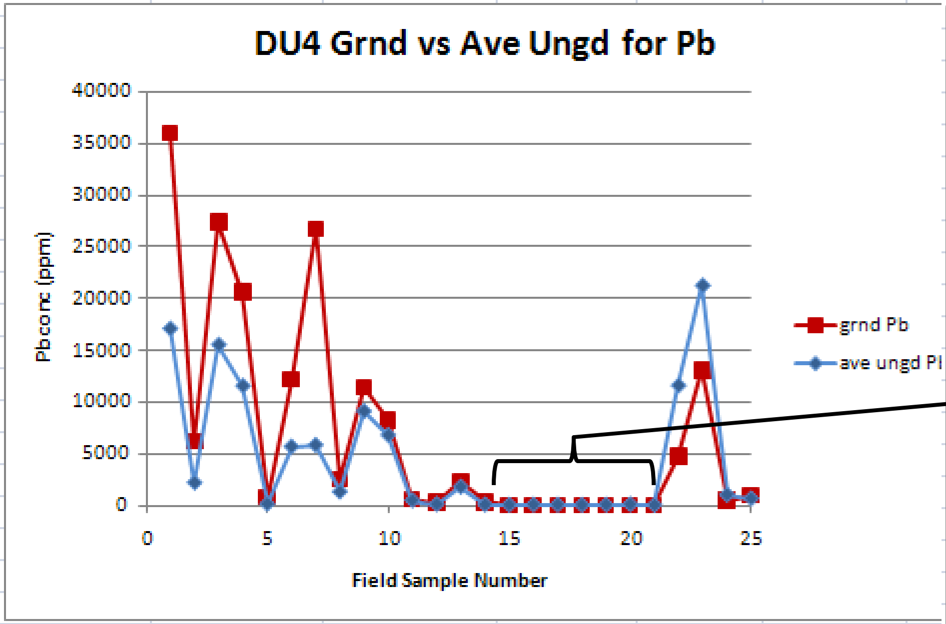
Ground vs. Unground for Pb (All DUs)

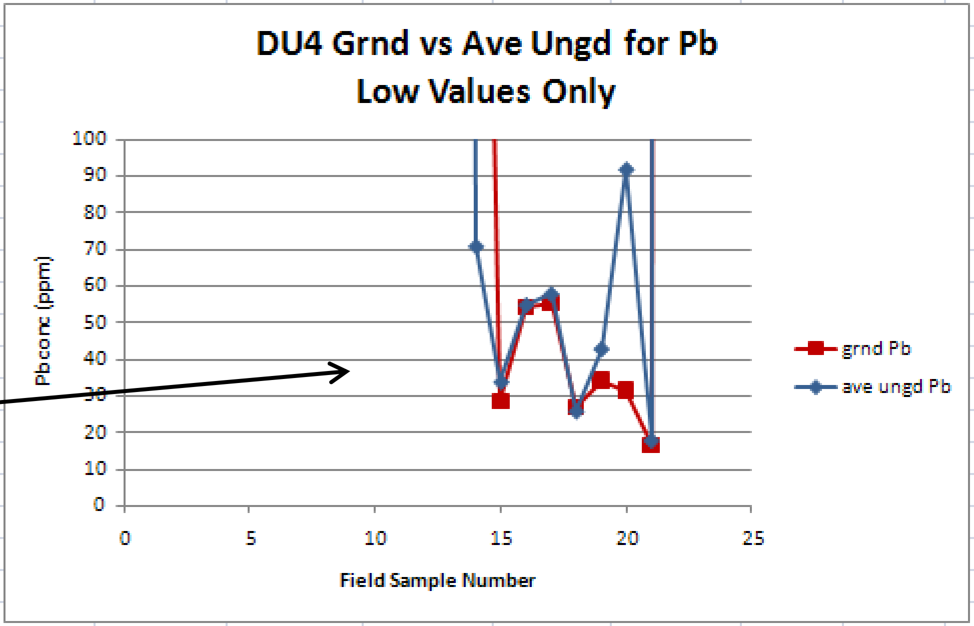
(Sb & As showed exact same pattern)











Why Do We Sometimes See Higher Metal Concentrations in Ground Samples?

- 1) Part of the explanation is simple chance. By chance, some ground sample results will be higher than unground sample results.
- This study looked at a large amount of data amenable to statistical analysis
  - Frequency of ground samples being higher is balanced by frequency of being lower or the same.

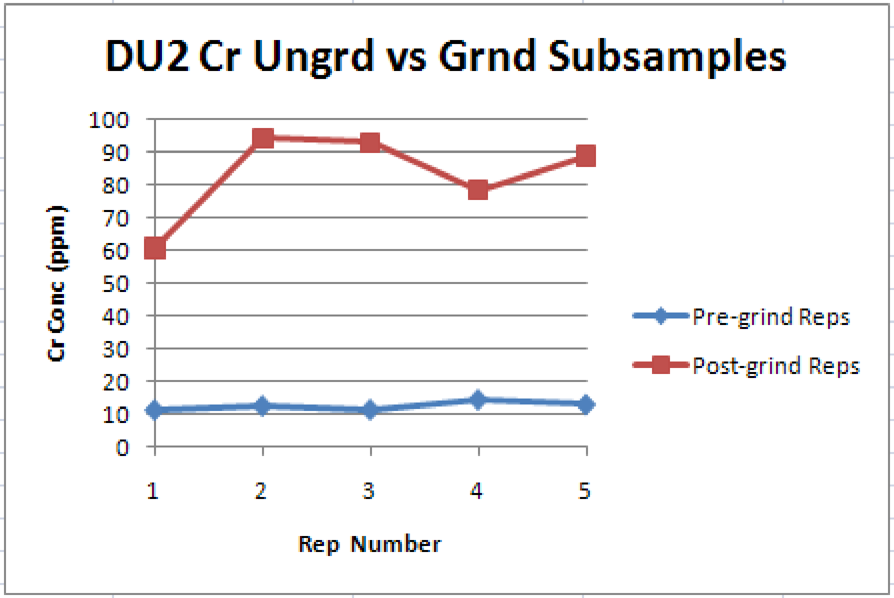
This study contained 4 experiments testing whether analyte concentrations increased after grinding. This table presents the results for Sb, As & Pb.

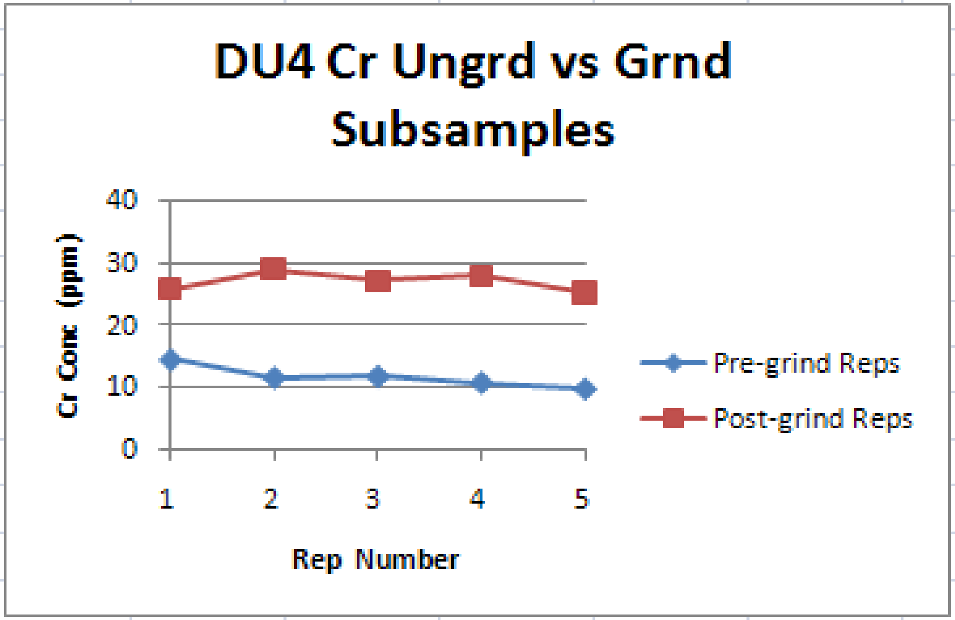
# of experiments finding the ground conc to be statistically:	Higher	The Same	Lower
Sb	3		1
As	2	1	1
Pb	2	2	

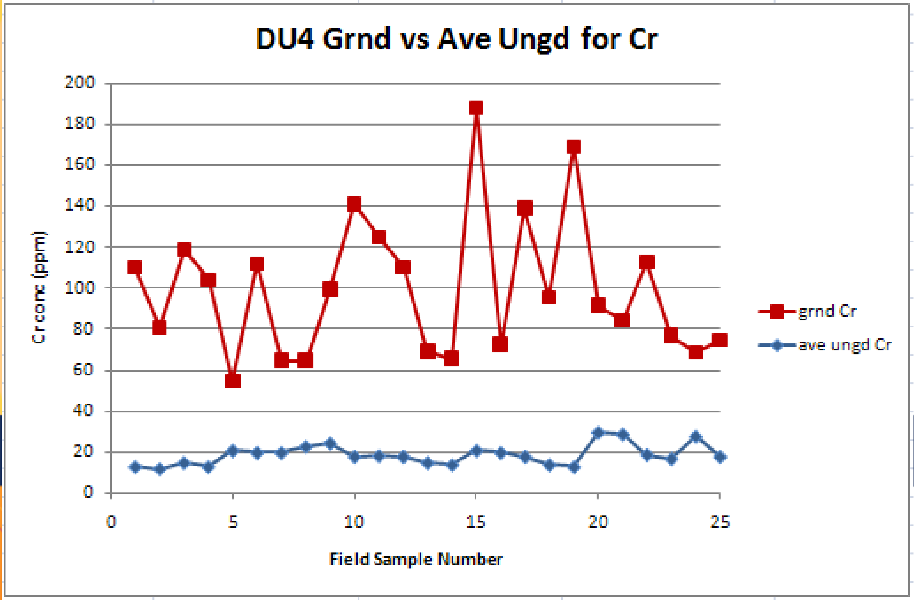
“Bleed” from Grinder Can Add Certain Metals

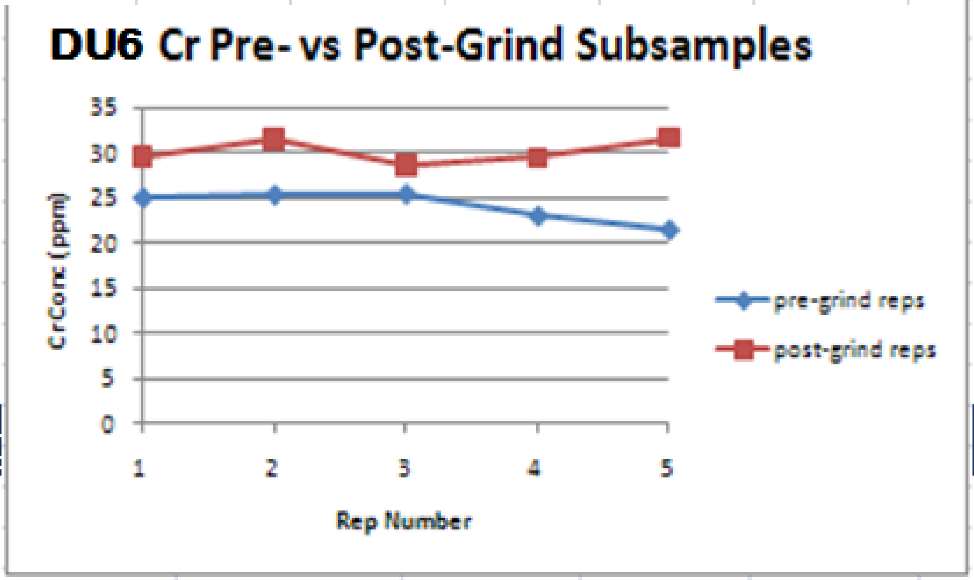
- This seems to be the case for Cr in this study.
- Cr was the only element with ground concentrations consistently higher than the corresponding unground samples’ concentrations.
- A stainless steel grinder was used.

Increase in Cr with Grinding





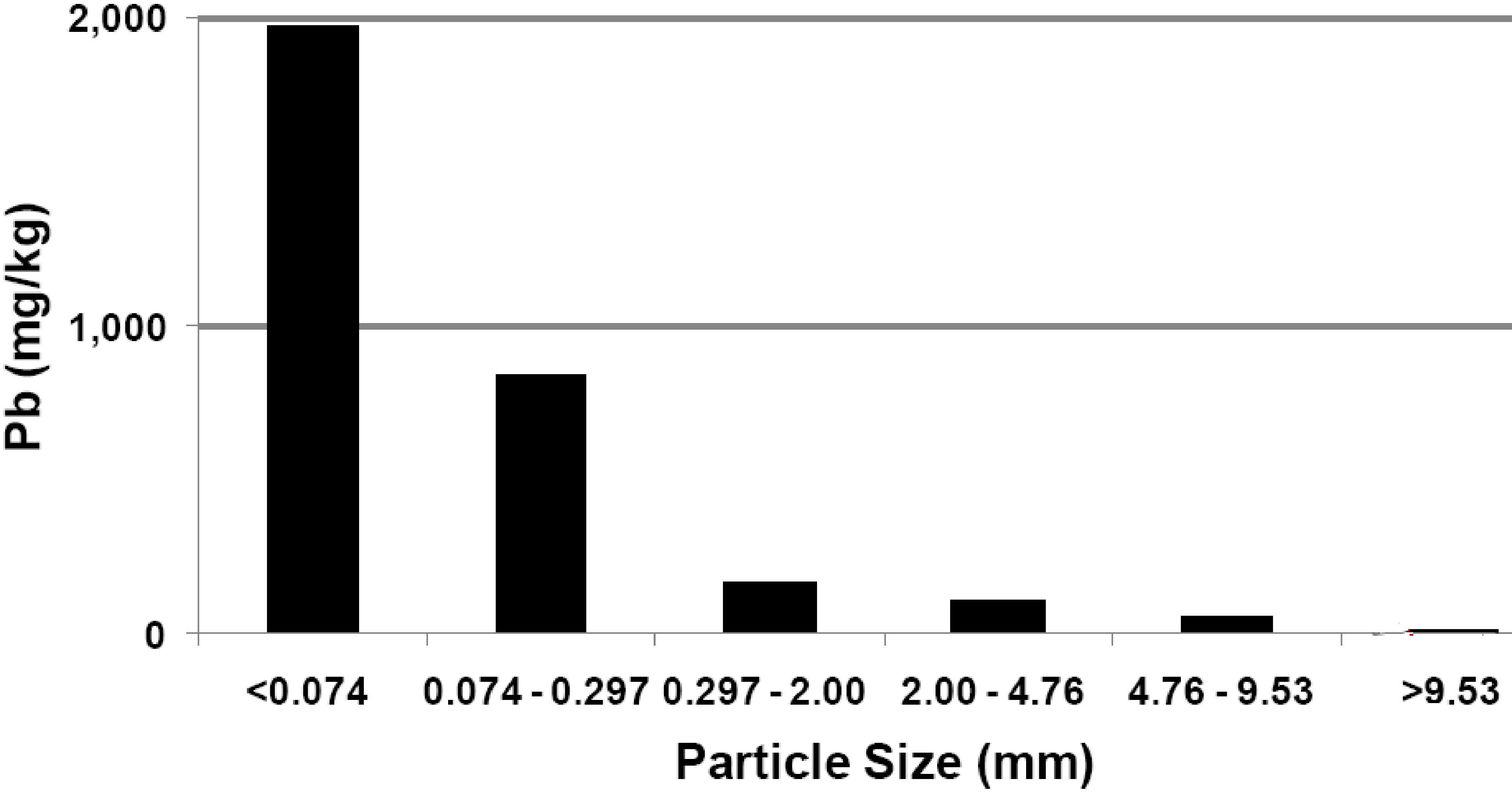




Particle Effects Can Make It Appear that Ground Conc's Are Higher than Unground

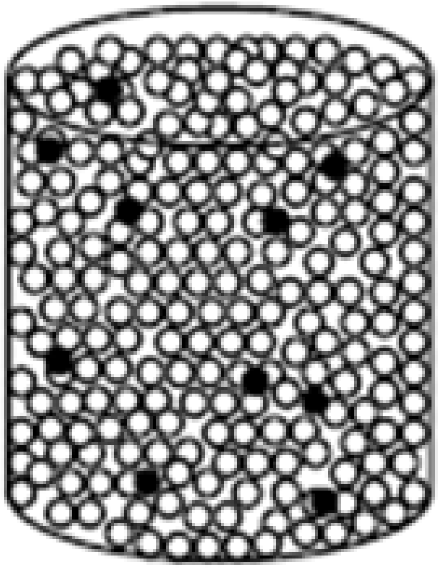
- Given the particulate nature of soil, this is to be expected
- It is well-known that contaminants concentrate in the very small particle size fractions
- For Pb shot, this happens in several ways
  - Corrosion via OC, DO and Eh (Cao et al, 2003)
  - Dust from firing and abrasion by travel through soil (Hardison et al, 2004)

Particle Size Analysis of Pb from Another Firing Range



What Are “Particle Effects”?

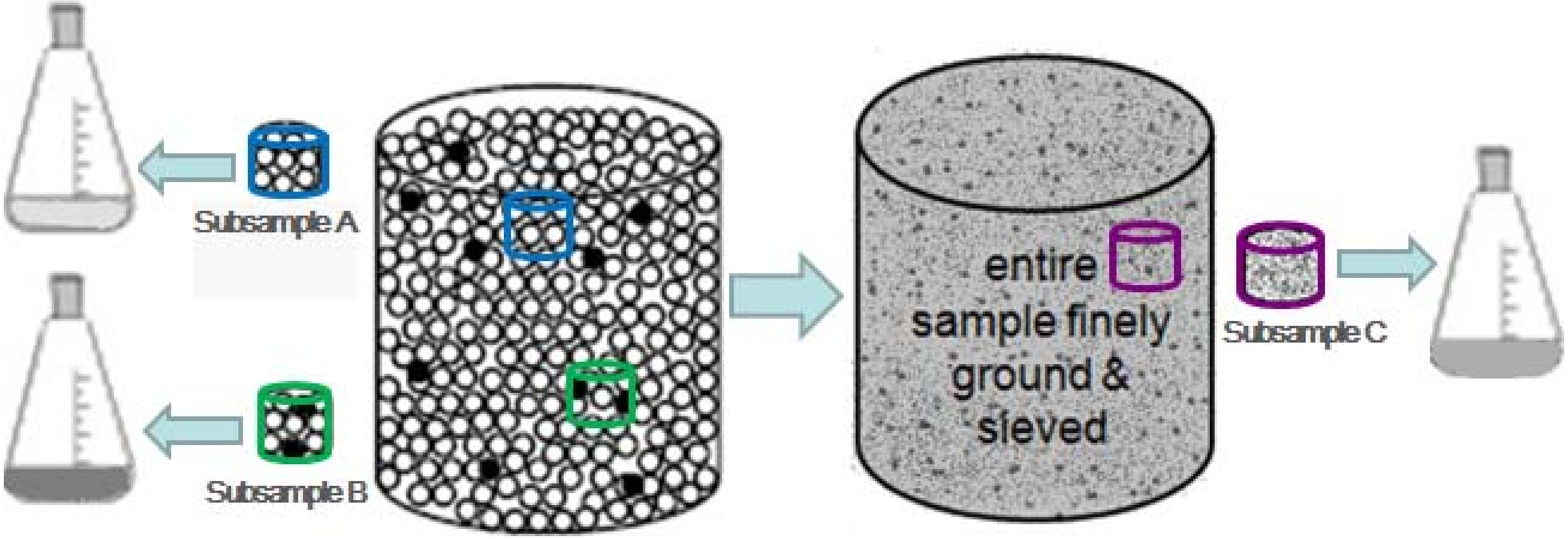
- = a soil particle heavily laden with contaminant
- ○ = a soil particle carrying less contaminant



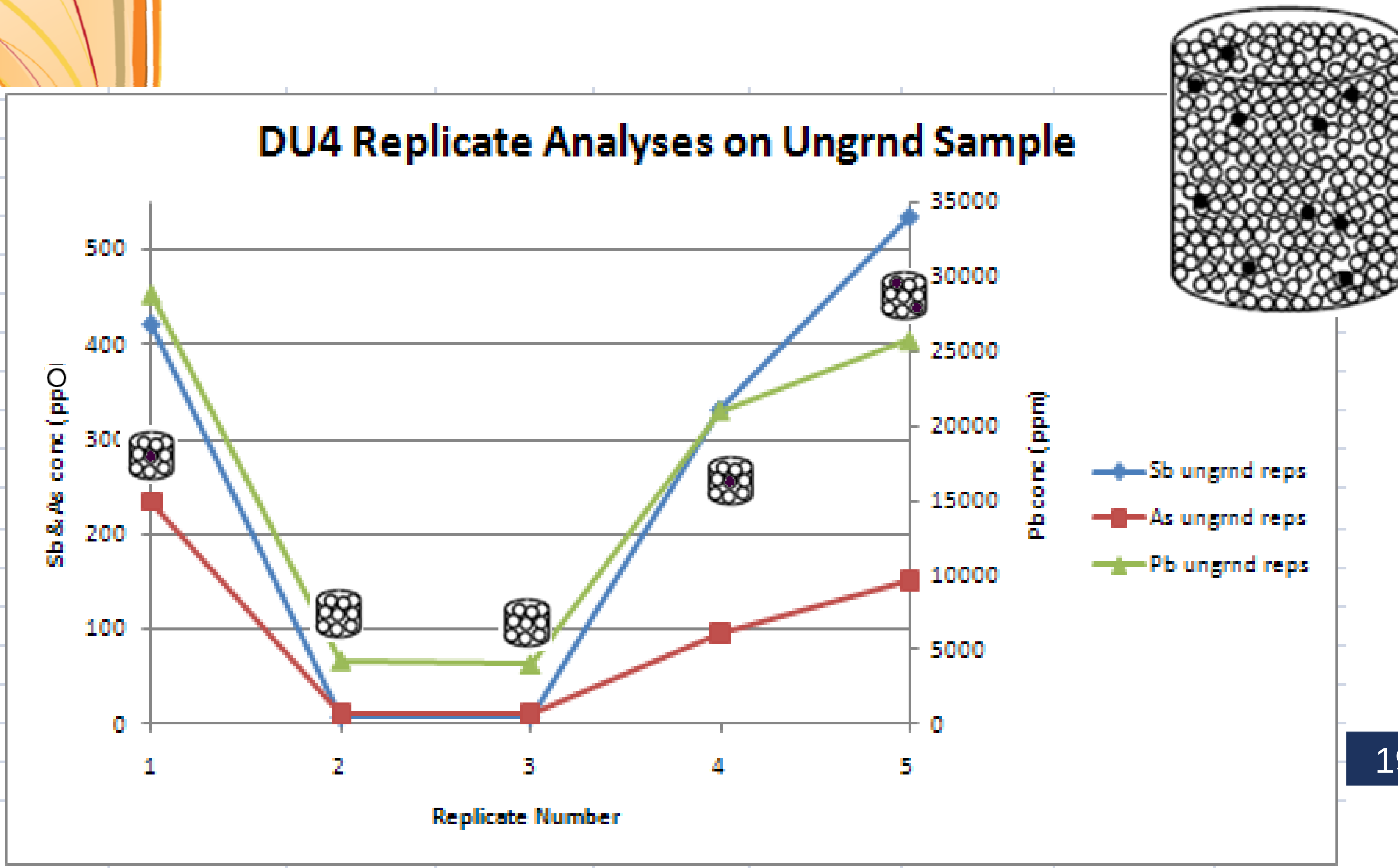
Cartoon of field sample from an impacted area

Subsampling a Particulate Material

Small subsamples & large particles => data variability
Reduction of particle size required for more representative sampling
Can reduce, but not entirely eliminate particle effects!
Grinding creates a physical average for sample

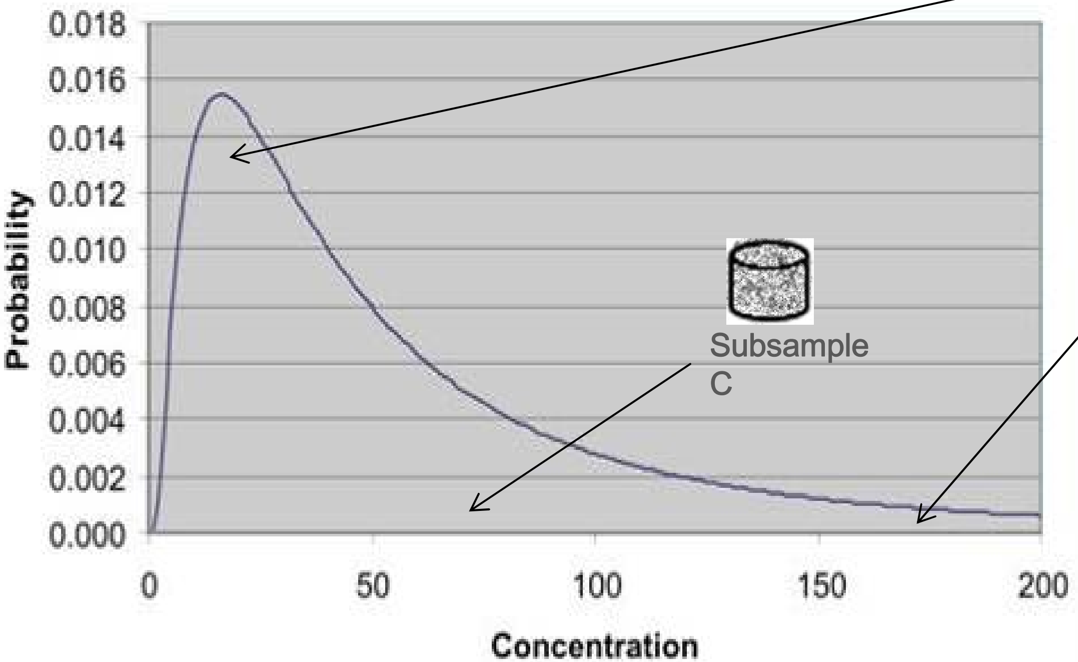


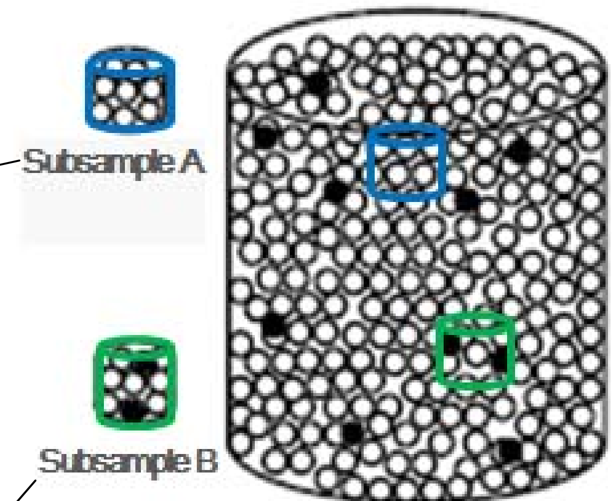
Unground Samples and Data Variability



Fluctuations in Sb, As & Pb Conc

- For a mild to moderately contaminated soil, more likely to get Subsample A rather than B.
- Produces lognormal data populations.



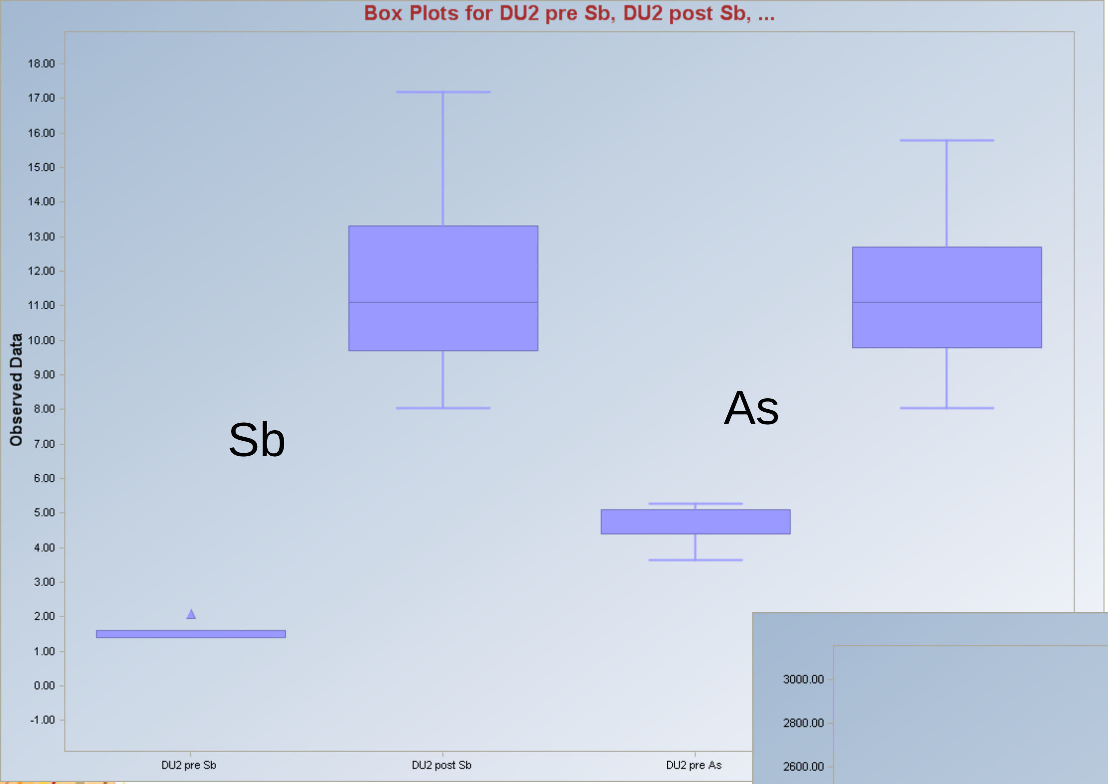


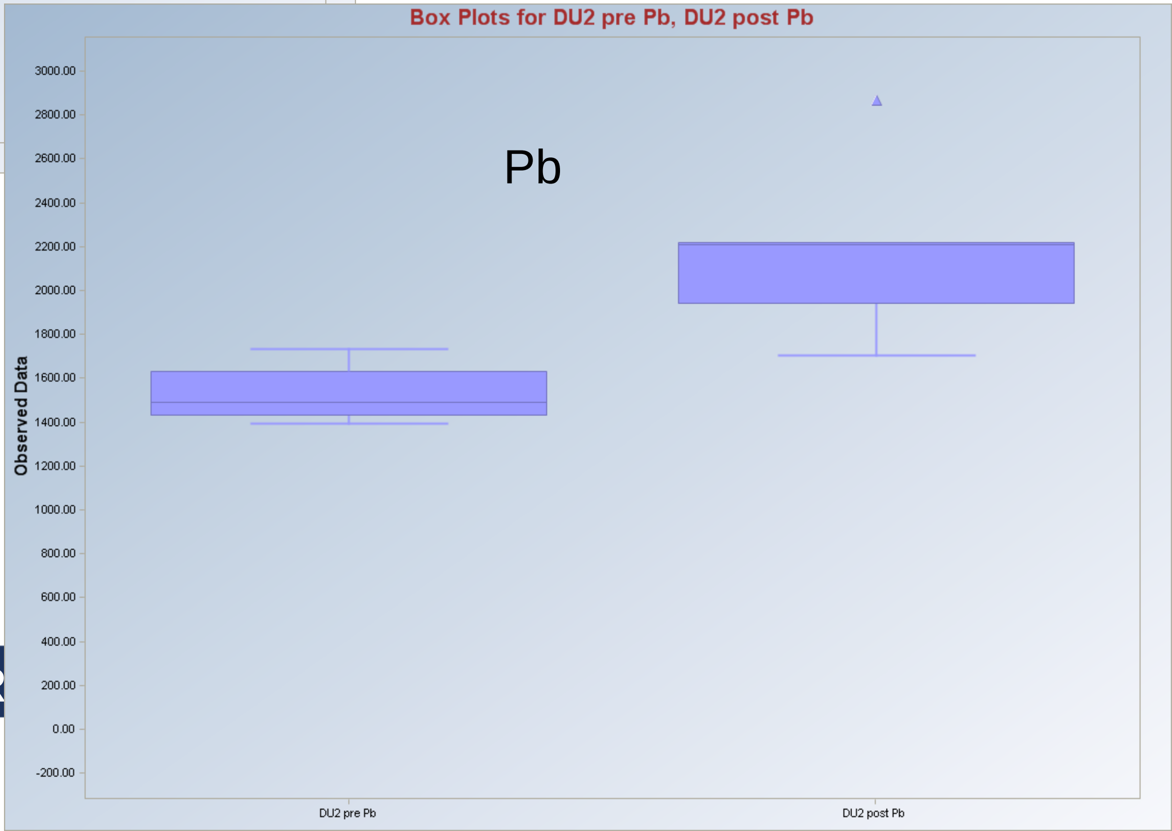
Average conc for ground samples higher than the unground results, which are very common

Did Grinding Markedly Reduce Variability?

- Sometimes
  - Hg consistently saw decreased variability across all DUs
  - Other metals and DUs were variable
- All samples had been sieved
  - Possibly the sieving was as effective as grinding in this case

Sb, As, Pb in **DU2**: variability & conc rose for ground samples





Box plots of 5 replicates each

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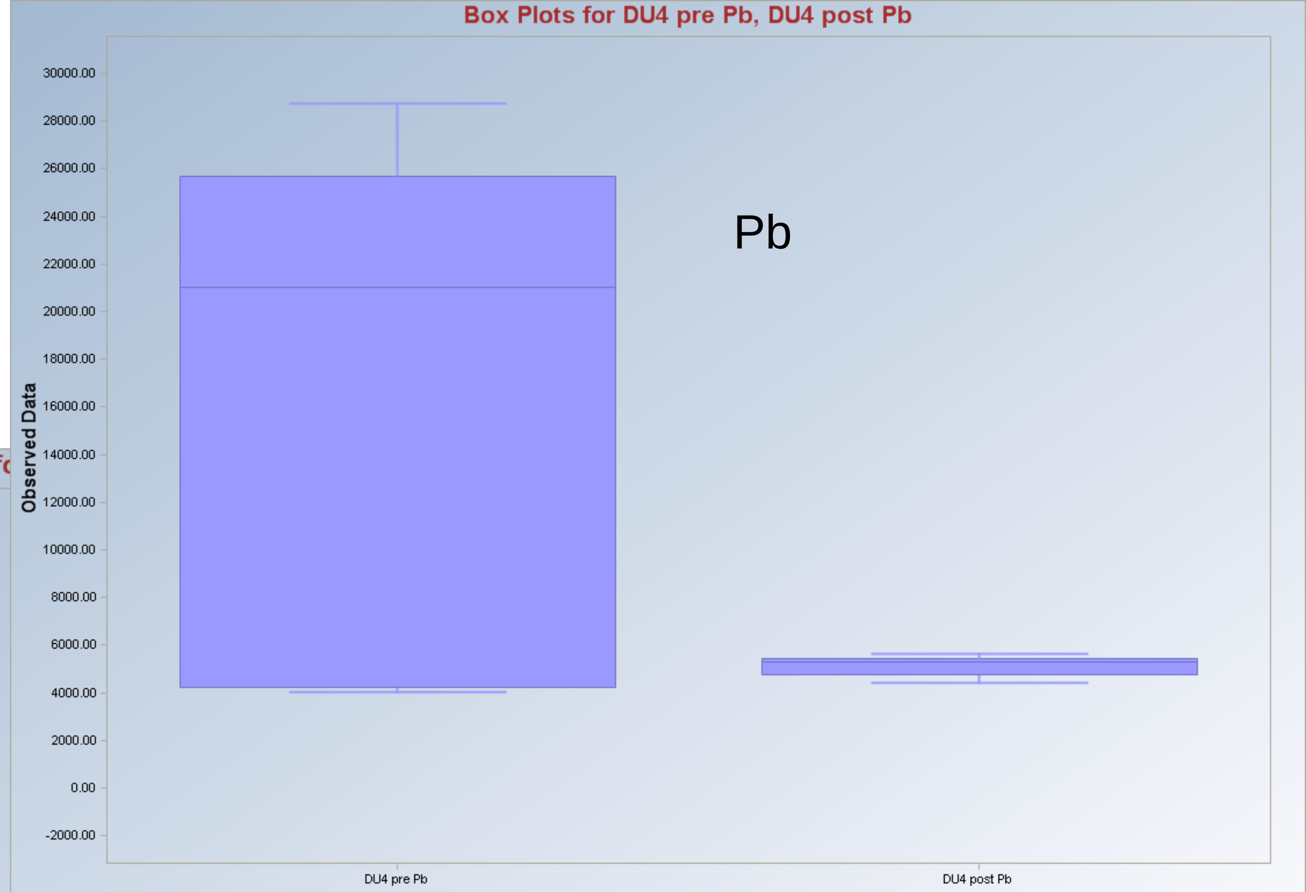
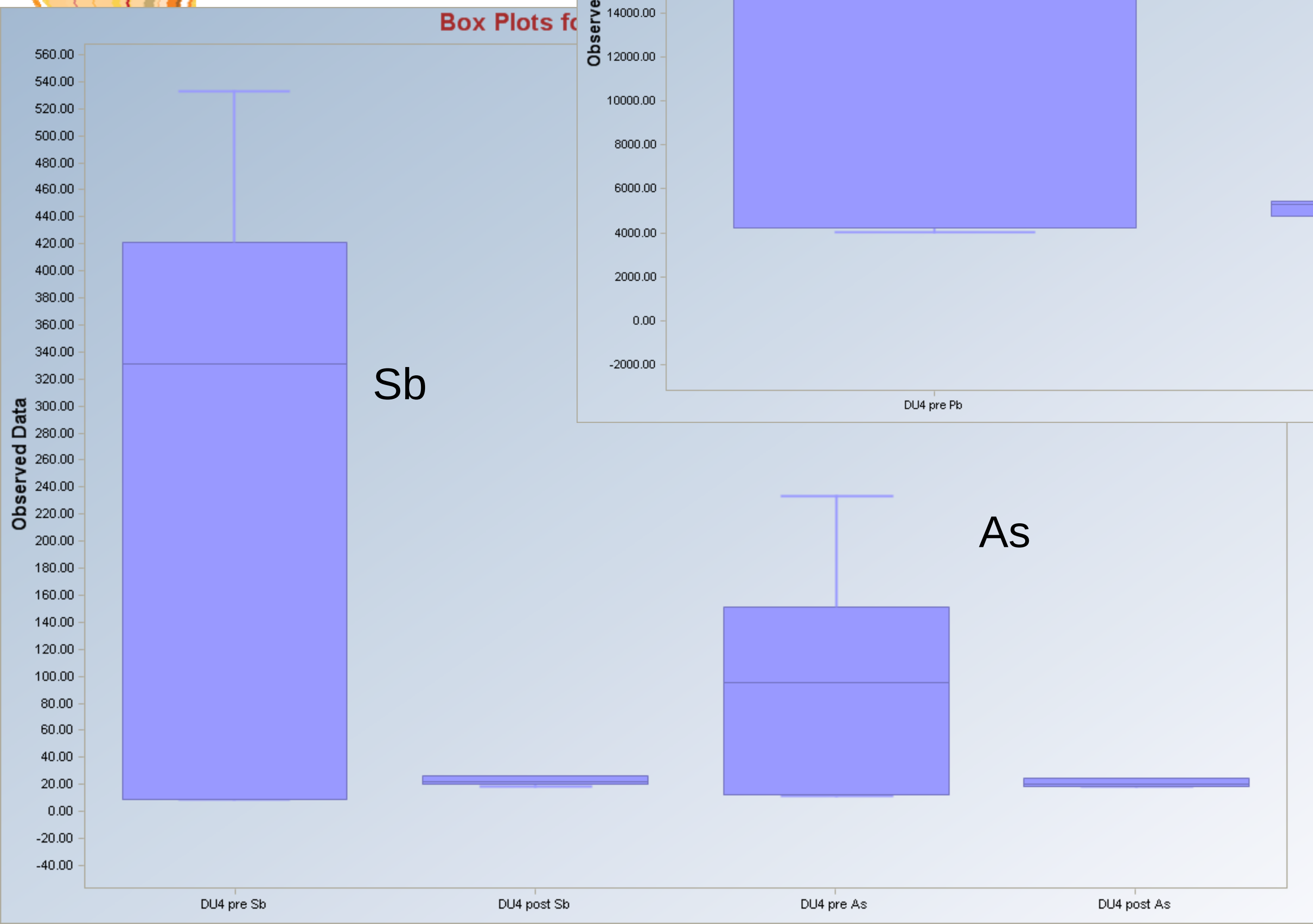
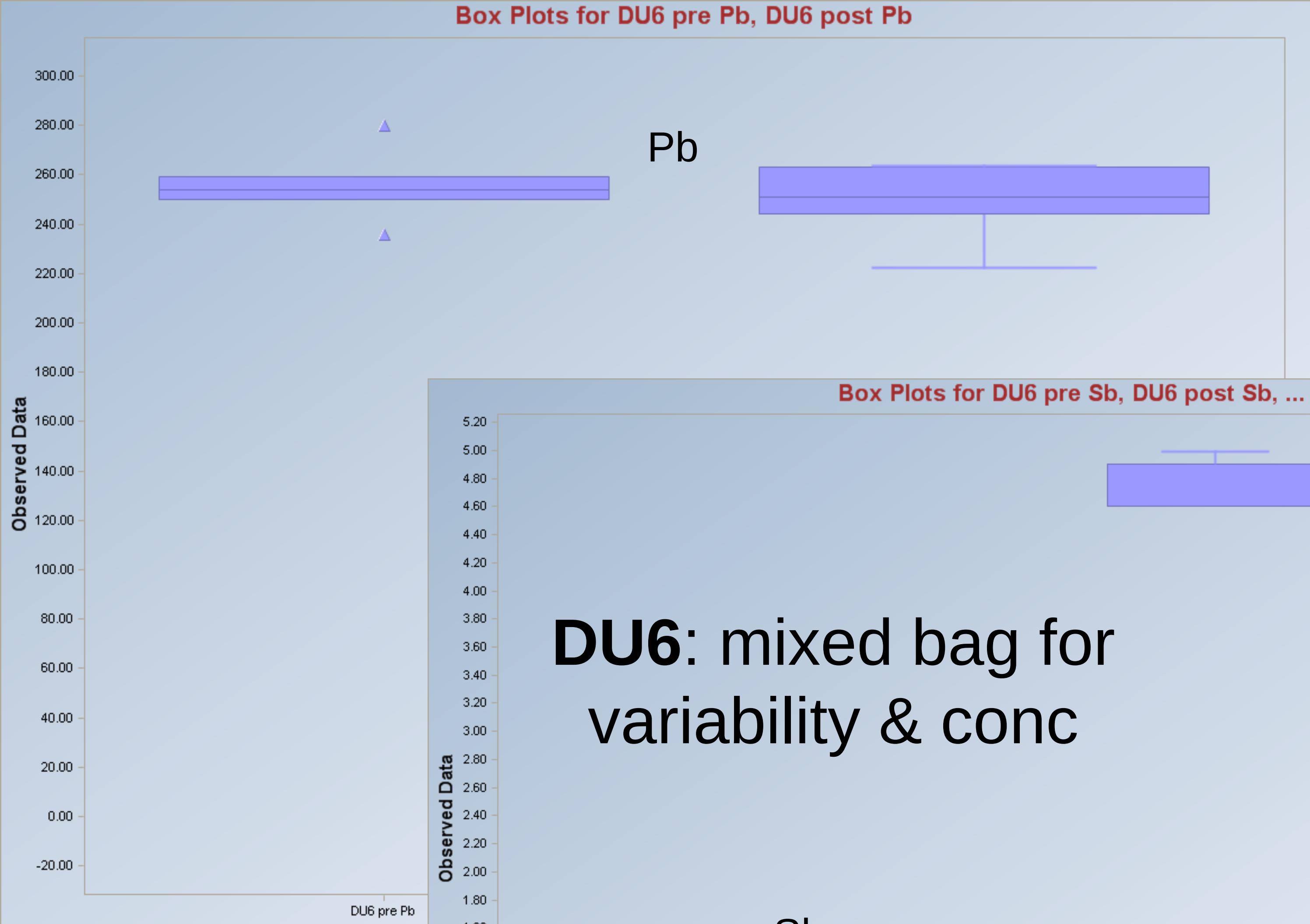
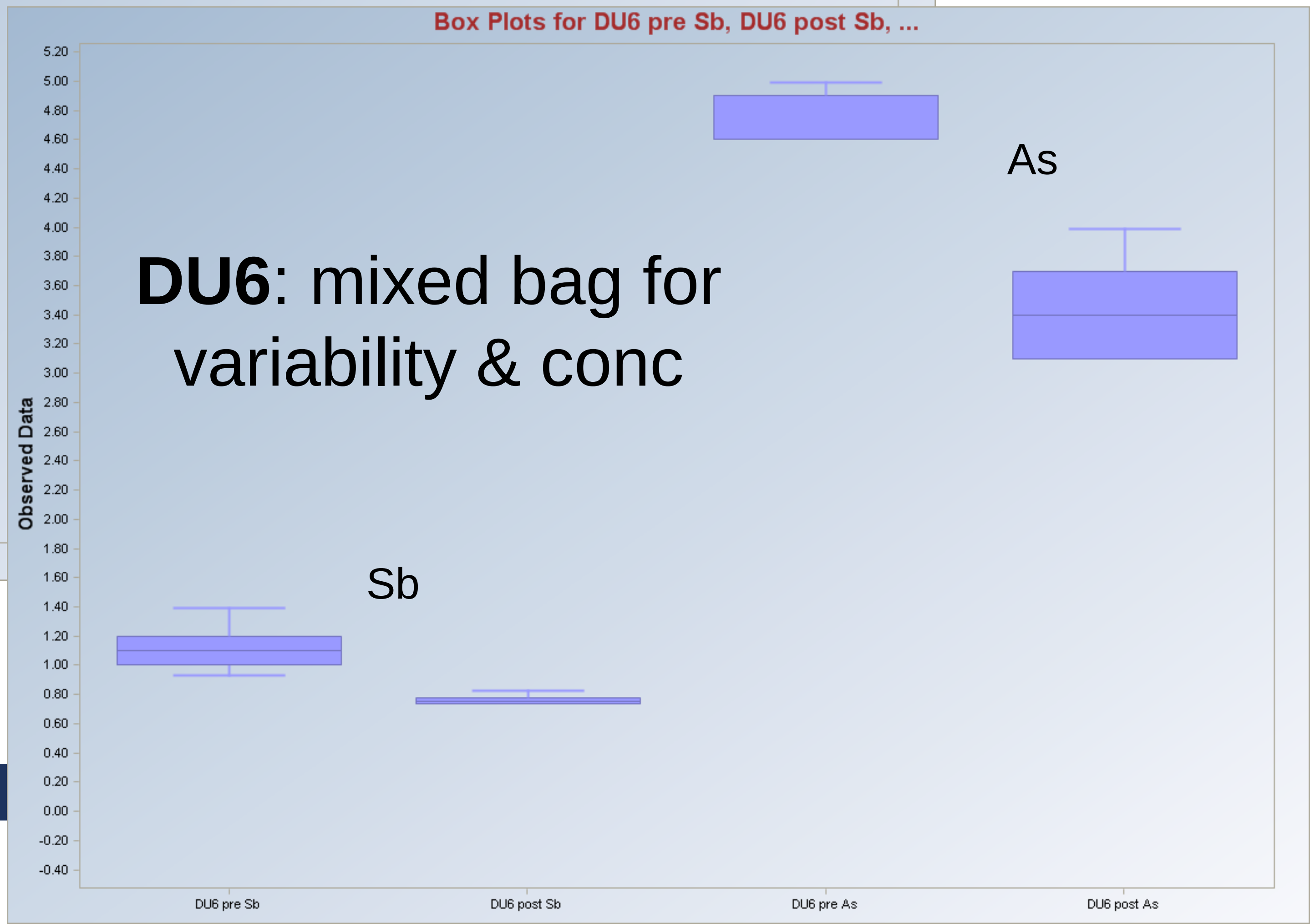
DU4: variability dropped; conc dropped





Box plots of 5 replicates each





DU6: mixed bag for variability & conc

Box plots of 5 replicates

Next Question: Are Incremental Sampling Data Comparable to Discrete Data Sets with a High Number of Samples?

Only 1 DU (DU4) Addressed this Question

- Are MI results within the confidence interval of the dense discrete data set?
  - DU4: had 49 discrete samples
  - ProUCL used to determine statistical distribution of each metal analyte and its 95% UCL
- MI results were triplicates: calculated a DU average and a 95% UCL(t) for each analyte

Discrete to MIS Comparability for Sb, As and Pb

Parameter (DU4)	Sb	As	Pb
Mean for 49 discrete samples	**38**	**28**	**6817**
Mean for triplicate ISs	**38**	**28**	**6680**
RPD between means	1%	1%	2%
Std Dev for 49 discrete samples	**51**	**32**	**8740**
Std Dev for triplicates ISs	**33**	**16**	**3745**
Data distribution	**Gamma**	**Non-parametric**	**Gamma**
ProUCL recommended 95% UCL	**53**	**47**	**10185**
95% t-UCL for triplicate ISs	**94**	**54**	**12994**
Are the 2 results statistically equivalent?	yes	yes	yes

Comparability Summary for All Elements

Parameter	Elements
RPD between DS & IS means <5%	Al, Sb, As, Be, Pb, Hg, Ni
RPD between DS & IS means >5 & <10%	Co, Fe, V, Zn
RPD between DS & IS means >10 & <25%	Ba, Cu
RPD between DS & IS means >25 & <50%	Mn
RPD between DS & IS means >50 & <100%	Cd, Ca, Cr
RPD between DS & IS means >100%	None
DS & IS data sets that are statistically equivalent	Al, Sb, As, Ba, Be, Ca, Co, Cu, Fe, Pb, Mn, Hg, Ni, V, Zn
DS & IS data sets that are statistically different	Cd (DS mean = 0.27; IS mean = 0.13), Cr (transfer from grinder)

Summary

- The concern that grinding samples would produce non-representative high metals results is partially laid to rest by the project
  - Until more experience accumulated, should probably check any unusual matrices
- Incremental sampling does produce data comparable to a discrete sampling design when there is a high density of discrete samples.