Fort Eustis MIS Study

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FRTR Meeting, May 5, 2011
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
<table>
<thead>
<tr>
<th>DU#</th>
<th>Field Replicate Sample (3)</th>
<th>Laboratory Pre-Grind Replicates (5)*</th>
<th>Laboratory Post-Grind Replicates (5)**</th>
<th>Laboratory Post-Grind Replicates (3)*</th>
<th>Discrete (49)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>5</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>6</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

* - 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 subsampled 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.

<table>
<thead>
<tr>
<th># of experiments finding the ground conc to be statistically:</th>
<th>Higher</th>
<th>The Same</th>
<th>Lower</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>3</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>As</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pb</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>
“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

**DU2 Cr Ungrd vs Grnd Subsamples**

- Cr Conc (ppm)
  - Rep Number

**DU4 Cr Ungrd vs Grnd Subsamples**

- Cr Conc (ppm)
  - Rep Number

**DU4 Grnd vs Ave Ungd for Cr**

- Cr Conc (ppm)
  - Field Sample Number

**DU6 Cr Pre- vs Post-Grind Subsamples**

- Cr Conc (ppm)
  - Rep Number
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

DU4 Replicate Analyses on Ungrnd Sample

- Sb & As conc. (ppm)
- Pb conc. (ppm)

Replicate Number

- Sb ungrnd reps
- As ungrnd reps
- Pb ungrnd reps
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.

![Graph showing probability distribution for Subsample A and Subsample B.]

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
DU4: variability dropped; conc dropped

Box plots of 5 replicates each
Box plots of 5 replicates

**DU6:** mixed bag for variability & conc

Box Plots for DU6 pre Pb, DU6 post Pb

Box Plots for DU6 pre Sb, DU6 post Sb, ...
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

<table>
<thead>
<tr>
<th>Parameter (DU4)</th>
<th>Sb</th>
<th>As</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean for 49 discrete samples</td>
<td>38</td>
<td>28</td>
<td>6817</td>
</tr>
<tr>
<td>Mean for triplicate ISs</td>
<td>38</td>
<td>28</td>
<td>6680</td>
</tr>
<tr>
<td>RPD between means</td>
<td>1%</td>
<td>1%</td>
<td>2%</td>
</tr>
<tr>
<td>Std Dev for 49 discrete samples</td>
<td>51</td>
<td>32</td>
<td>8740</td>
</tr>
<tr>
<td>Std Dev for triplicates ISs</td>
<td>33</td>
<td>16</td>
<td>3745</td>
</tr>
<tr>
<td>Data distribution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gamma</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-parametric</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gamma</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ProUCL recommended 95% UCL</td>
<td>53</td>
<td>47</td>
<td>10185</td>
</tr>
<tr>
<td>95% t-UCL for triplicate ISs</td>
<td>94</td>
<td>54</td>
<td>12994</td>
</tr>
<tr>
<td>Are the 2 results statistically equivalent?</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
</tbody>
</table>
## Comparability Summary for All Elements

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