Incremental Sampling Methodology (ISM) for Metals: Number of Increments and Milling Necessity

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Soil Sampling Issues

- Unrepresentative results using conventional grab soil sampling at military ranges with energetic & metallic residues
- Poor precision for grabs (e.g., for duplicates)
- Large uncertainty at concentrations near decision limits
- Increasing State regulatory insistence for Incremental Sampling Methodology (ISM) for soils

- USEPA SW-846 work group to update Method 3050B to Method 3050C with ISM. By late 2015?
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

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Metallic Residues

9-mm Pistol
5.56-mm Rifle
7.62-mm MG
.50-caliber MG
Incremental Sampling Methodology (ISM)

Project Planning
- Conceptual Site Model Development
- Data Quality Objectives
  - Decision Unit Identification
  - Sample Depth Determination
  - Number of Increments per Decision Unit/Sample
  - Number of Replicates Per Decision Unit

Field Implementation
- Sample Tool Selection
- Decision Unit Field Delineation
  - Field Splitting
  - Collection of Soil Sample
  - Air Drying
  - Sieving
  - >2-mm Size Fraction
- Milling < 2-mm Size Fraction
  - Splitting
  - Subsampling
  - Digestion
  - Analysis

Sample Preparation

Analysis

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Decision Units (DUs)

**Volume** of soil to be sampled for which a decision needs to be made using the sample results.

- **Source Areas**: Size, shape, and type of DU determined during systematic planning and depend on Data Quality Objectives (DQOs).
- **Exposure Areas**: Size, shape, and type of DU determined during systematic planning and depend on Data Quality Objectives (DQOs).
Incremental Sampling

Path of travel

Sample collection increment
Can ISM samples be split in the field to reduce the mass that needs to be shipped to and processed in the laboratory?
Field Cone-and-Quartered Splits

Boxplot of Sb (mg/kg)

Boxplot of Cu (mg/kg)

Boxplot of Pb (mg/kg)

Boxplot of Zn (mg/kg)
Background Metals

Boxplot of Ba (mg/kg)

Boxplot of Co (mg/kg)

Boxplot of Ni (mg/kg)

Boxplot of V (mg/kg)
Number of Increments
### Number of Increments vs. Relative Standard Deviation

<table>
<thead>
<tr>
<th>ISM</th>
<th>Percent Relative Standard Deviation (RSD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>20</td>
<td>27</td>
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<tr>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>100</td>
<td>3</td>
</tr>
<tr>
<td>200</td>
<td>6</td>
</tr>
</tbody>
</table>

$m = \text{number of increments per MI sample}$
Lead Concentration vs. Number of Increments of ISM Field Replicates

Weighted Mean = 2589 mg/kg for n=100
Number of Increments ($m$) for Small Arms Metals (Sb, Pb, Cu, & Zn)
Bootstrap Simulation: Number of Increments per ISM Sample

Mean of 48 grab samples = 432 mg/kg

300 bootstrap replicates for each value of m
Distributions of Simulated Bootstrap Lead Means

Distribution of means becomes Gaussian & variability decreases as \( m \) increases, consistent with central limit theorem (CTL)

Mean of Pb from \( m \) Increments (mg/kg)

Number of Bootstrap Means

m = 5  m = 7  m = 10  m = 15  m = 20  m = 25  m = 30  m = 35
Bootstrap Standard Error of Mean Simulation

**Equation:**

\[ y \approx 2000 \times^{-1} \]

\[ r^2 \approx 0.99 \]
To mill or not mill: Whether ‘tis nobler in the mind to not mill and suffer the slings and arrows of outrageous fortune or to mill to obtain reproducible results...
## Milled and Unmilled Comparison

<table>
<thead>
<tr>
<th>Subsample Replicates</th>
<th>Metals Conc. (mg/kg)</th>
<th>Metals Conc. (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu</td>
<td>Pb</td>
</tr>
<tr>
<td>1</td>
<td>2,600</td>
<td>360</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
<td>330</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>920</td>
</tr>
<tr>
<td>4</td>
<td>110</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>130</td>
<td>280</td>
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<tr>
<td>6</td>
<td>140</td>
<td>2,800</td>
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<tr>
<td>7</td>
<td>860</td>
<td>1,600</td>
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<td>1,500</td>
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<tr>
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<td>1,900</td>
<td>380</td>
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<tr>
<td>12</td>
<td>120</td>
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<tr>
<td>13</td>
<td>130</td>
<td>290</td>
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<tr>
<td>14</td>
<td>120</td>
<td>300</td>
</tr>
<tr>
<td>15</td>
<td>110</td>
<td>820</td>
</tr>
</tbody>
</table>

**Sample #1**

**Sample #2**

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To Mill or Not To Mill (1)

Lead - Unmilled

Replicate

Concentration (mg/kg)

0 5 10 15

20
To Mill or Not To Mill (2)

![Graph showing concentration of lead unmilled](image)
To Mill or Not To Mill (3)

Graph showing the concentration levels of Pb in samples with and without grinding. The graph plots concentration (mg/kg) against replicate number, with different symbols representing Pb Unground, Pb Ground #1, and Pb Ground #2.
Digestion Mass for Milled & Unmilled Samples

Boxplot of Pb (mg/ kg)

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Probability of One Lead Particle by Aliquot Mass for Unmilled Soil

- **Probability**
  - Y-axis: 0 to 1

- **Aliquot Mass (g)**
  - X-axis: 0.5 to 100

- **Lead Concentration (mg/kg)**
  - 400
Probability of One Lead Particle by Aliquot Mass for Unmilled Soil
SAR Metal Concentration by Puck Mill Milling Time

Boxplot of Pb (mg/kg)

Boxplot of Cu (mg/kg)

Boxplot of Sb (mg/kg)

Boxplot of Zn (mg/kg)
SAR Metal Concentration by Ball Mill Milling Time

Boxplot of Pb (mg/kg)

Boxplot of Sb (mg/kg)

Boxplot of Cu (mg/kg)

Boxplot of Zn (mg/kg)
Milling by Device Type

Boxplot of Pb (mg/ kg)

Grinder Type

Ball Mill  MP  Puck #1  Puck #2  Puck & Ring  Unmilled #1  Unmilled #2

Pb (mg/ kg)

5000
4000
3000
2000
1000

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### Performance Assessment

<table>
<thead>
<tr>
<th>Activity</th>
<th>Yes</th>
<th>No</th>
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<tbody>
<tr>
<td><strong>ISM, 30+ increments</strong></td>
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<tr>
<td>Grab Sampling</td>
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<td>√</td>
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<tr>
<td>Field Splitting</td>
<td></td>
<td>√</td>
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<tr>
<td>Sieving</td>
<td>√</td>
<td></td>
</tr>
<tr>
<td><strong>Milling necessity</strong></td>
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<td></td>
</tr>
<tr>
<td>Increased digestion mass</td>
<td>√</td>
<td>√</td>
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<tr>
<td>Increased digestion time</td>
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<td>√</td>
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<tr>
<td>Subsampling</td>
<td>√</td>
<td></td>
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</table>
No ISM-Lite
# Cost Comparison

<table>
<thead>
<tr>
<th></th>
<th>Grab</th>
<th>ISM</th>
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<tbody>
<tr>
<td>Systematic Project Planning</td>
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<td>$</td>
</tr>
<tr>
<td>Site Preparation</td>
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<td>Field Sampling</td>
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<td>Laboratory Sample Processing</td>
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<td>Analysis</td>
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<td>Data Validation</td>
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<tr>
<td><strong>Per Sample Cost</strong></td>
<td>$$-$$</td>
<td>$$-$$$</td>
</tr>
<tr>
<td><strong>Number of Samples</strong></td>
<td>###</td>
<td>#</td>
</tr>
<tr>
<td><strong>Total Project Cost</strong></td>
<td>$$-$$$</td>
<td>$$-$$</td>
</tr>
</tbody>
</table>
Conclusions

- Field splitting not recommended when metal particles expected
- Minimum of 30-increments per ISM sample
- Number of increments is a function of expected degree of heterogeneity
- Larger digestion aliquot in lieu of milling does not work
- Milling is necessary when metal particles are present
- Marginal improvements in data quality with larger digestion aliquots for milled samples
- Recommend 5 minutes milling with Puck and 8 hours with Roller Mills
References

References (Continued)

