Update on ESTCP Project ER-0918: Field Sampling and Sample Processing for Metals on DoD Ranges

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**Update on ESTCP Project ER-0918: Field Sampling and Sample Processing for Metals on DoD Ranges**

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Presented at the 2011 DoD Environmental Monitoring & Data Quality Workshop (EMDQ 2011), 28 Mar - 1 Apr, Arlington, VA.
Project Team

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- Anthony Bednar: ERDC-EL
- Thomas Georgian: HNC@EMCX
- Larry Penfold: Test America
- Diane Anderson: APPL Laboratories
Technical Objectives

- Demonstrate improved data quality for metal constituents in surface soils on military training ranges by coupling multi-increment sampling with modifications to sample preparation and analysis methods such as:
  - Sample processing involving grinding
  - Sub-sampling to build the digestate aliquot
  - Digestion Issues (mass, acid ratio, time)
  - Laboratory processing protocol applicable to both metals and energetics
Experimental Design – Task 1

- Multi-increment versus grab samples
- Number of increments per decision unit
- Grinding necessity
- Digestion mass evaluation
- Digestion time
- Blank material identification and assessment
- Puck Mill metal carry over assessment (cross contamination)
- Grinder comparisons
- Puck Mill and Roller Mill optimum grinding interval
- Appropriateness of field splitting
- Subsampling for digestate preparation
Experimental Design – Task 1

Task 1 Activities

Task 4 Activities

Note: Each level consists of 15 replicates
Soil Test Material

- Site: Camp Ethan Allen, VT
- Range Type: Small Arms (Pistol, Rifle)
- Decision Unit: Berm Face – 3 by 30 m
- Soil Type: Silty sand, low CEC, low OM, pH~ 5
- Metal Content: 100’s to low 1,000’s ppm
- Samples Collected
  - Grab/discrete using grid-node approach – 30
  - Multi-increment using systematic random, 7 replicates of 5, 10, 20, 30, 50, 100 increments
  - One 200 increment sample ~ 25 kg
Soil Test Material
## Multi-Increment vs Grab Samples

<table>
<thead>
<tr>
<th></th>
<th>Sb mg/kg</th>
<th>Cu mg/kg</th>
<th>Pb mg/kg</th>
<th>Zn mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Grab</strong>&lt;br&gt;(n=30)</td>
<td>Mean 88</td>
<td>300</td>
<td>5060</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>Std. Dev. 375</td>
<td>132</td>
<td>14,437</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>RSD (%) 426</td>
<td>44</td>
<td>285</td>
<td>27</td>
</tr>
<tr>
<td><strong>MI-30</strong>&lt;br&gt;(n=7)</td>
<td>Mean 23</td>
<td>573</td>
<td>2664</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Std. Dev. 3.3</td>
<td>85</td>
<td>367</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>RSD (%) 14</td>
<td>15</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td><strong>MI-50</strong>&lt;br&gt;(n=7)</td>
<td>Mean 17.6</td>
<td>457</td>
<td>2156</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>Std. Dev. 1.8</td>
<td>96</td>
<td>243</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>RSD (%) 10</td>
<td>21</td>
<td>11</td>
<td>10</td>
</tr>
</tbody>
</table>
Number of Increments per Decision Unit

Scatterplot of StDev vs Increments

mg/kg

Increments

StDev

0 500 1000 1500 2000 2500 3000 3500

0 20 40 60 80 100

Variable

Al, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Al, Sb, Sr, V, W, Zn
Number of Increments per Decision Unit

**Boxplot of Pb (mg/kg) by Number of Field Increments**

- **Medians**
- **95th Percentile Range**
- **IQR**

**Number of Field Increments**

5, 10, 20, 30, 50, 100

**Pb (mg/kg)**

1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500

*Note: The diagram illustrates the distribution of Pb levels across different numbers of field increments, showing medians, 95th percentiles, and interquartile ranges.*
<table>
<thead>
<tr>
<th></th>
<th>Sb mg/kg</th>
<th>Cu mg/kg</th>
<th>Pb mg/kg</th>
<th>Zn mg/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-Ground</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>14</td>
<td>360</td>
<td>1600</td>
<td>66</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>10</td>
<td>90</td>
<td>630</td>
<td>11.3</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>71</td>
<td>25</td>
<td>39</td>
<td>17</td>
</tr>
<tr>
<td>Ground</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>23</td>
<td>550</td>
<td>2720</td>
<td>77</td>
</tr>
<tr>
<td>Std. Dev.</td>
<td>1.6</td>
<td>100</td>
<td>120</td>
<td>8.7</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>7.0</td>
<td>18</td>
<td>4.4</td>
<td>11</td>
</tr>
</tbody>
</table>

Performance criteria RSD < 15% for lab replicates (for concentrations > 100)
Soil Post Grinding
Grinding Necessity

Boxplot of Pb by Method

- Medians
- IQR
- 95th Percentile
- Range
- Outlier
- G
- UG

Pb (mg/kg)

mg/kg

3500
3000
2500
2000
1500
1000

Method
Performance Assessment – Sample Processing (Grinding) of Soil

- **Puck Mill**
  - Fe, Mn, Cr, V

- **Roller Mill**
  - Alumina cans polyethylene
  - Liner, ceramic balls

- **Pulvisette**
  - Mortar and Pestle
  - Ceramic
  - Agate balls
Grinder Comparisons

RSD (%)
Grinder Comparisons

Boxplot of Pb (mg/kg) by Grinder Type

Grinder Type

- Ball Mill-16
- Ball Mill-20
- Puck
- Puck Ring
- Pulvisette
- UG-EL
- UG-TA

Pb (mg/kg)
Roller Mill Optimum Grinding Interval
Roller Mill Optimum Grinding Interval

mg/kg

8 hrs
12 hrs
16 hrs
20 hrs

Al  Ba  Cd  Co  Cr  Cu  Fe  Mg  Mn  Ni  Pb  Sb  V  Zn
Roller Mill Optimum Grinding Interval

Boxplot of Pb (mg/kg) by Grinder Type

Increasing Grinding time (hrs)
 Scatterplot of StDev vs Mass

Panel variable: Variable
## Digestion Time

<table>
<thead>
<tr>
<th>Metal</th>
<th>$M_{24}$ (mg/kg)</th>
<th>$M_{48}$ (mg/kg)</th>
<th>Metal</th>
<th>$M_{24}$ (mg/kg)</th>
<th>$M_{48}$ (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>5678</td>
<td>6075</td>
<td>Mn</td>
<td>223.9</td>
<td>242.8</td>
</tr>
<tr>
<td>Ba</td>
<td>30.29</td>
<td>32.09</td>
<td>Ni</td>
<td>12.24</td>
<td>11.67</td>
</tr>
<tr>
<td>Cd</td>
<td><strong>1.825</strong></td>
<td>1.050</td>
<td>P</td>
<td>612.3</td>
<td><strong>630.0</strong></td>
</tr>
<tr>
<td>Co</td>
<td>8.60</td>
<td><strong>8.935</strong></td>
<td>Pb</td>
<td>2718</td>
<td>2893</td>
</tr>
<tr>
<td>Cr</td>
<td>221.2</td>
<td><strong>242.1</strong></td>
<td>Sb</td>
<td><strong>22.61</strong></td>
<td>20.59</td>
</tr>
<tr>
<td>Cu</td>
<td>542.5</td>
<td>498.2</td>
<td>Sr</td>
<td>21.51</td>
<td><strong>23.80</strong></td>
</tr>
<tr>
<td>Fe</td>
<td>16920</td>
<td><strong>17293</strong></td>
<td>V</td>
<td>15.14</td>
<td><strong>16.32</strong></td>
</tr>
<tr>
<td>Mg</td>
<td>2121</td>
<td><strong>2259</strong></td>
<td>Zn</td>
<td>75.80</td>
<td>79.88</td>
</tr>
</tbody>
</table>

$M_{24}$, $M_{48}$ = Median 24- and 48-hr digestions, respectively
Issues

- Analysis error is still greater than expected between laboratories, believed associated with volume of acid used during digestion
- Considerable mass of metal remains in over size fraction (typically discarded)
- Ongoing question of impact of sample preparation method changes to risk determination
- Poor recovery of antimony is evident with conventional analysis; new digestion process needed