Disclaimer

- The views expressed in this presentation are those of the author and do not necessarily reflect the views or policies of the U.S. Environmental Protection Agency.
Proposal

- Use the TNI / NELAC Fields of Proficiency Testing (FoPT) regression equations to establish laboratory control sample (LCS) control limits
EPA Region 8

- 6 states
- 27 Tribal Nations
- 15 National Parks
Region 8 Laboratory

- Full service laboratory
- NELAP accredited
  - Drinking water
  - Non-potable water
- Field sampling support
- Certifying Officers for drinking water
- PSL for Wyoming
Analytical Areas

- **Metals**
  - ICP-OES
  - ICP-MS
- **Wet chemistry**
  - Anions
  - Alkalinity
- **GC**
  - GRO / BTEX
  - DRO
  - EDB / DBCP
- **GC/MS**
  - VOCs
  - SVOCs
- **HPLC**
  - Pesticides
  - PPCPs
- **Microbiology**
LCS Control Limits - Sources

- DoD LCS Study
- Method requirements
- TNI / NELAC FoPT regression equations?
DoD LCS Study

- Published 2004
- Focused on nine SW 846 methods
- Based on empirical data
  - Performed in cooperation with ACIL
  - Over 20 participating laboratories
    - Doing work for DoD
    - Considered to be “good performing”

- Used to establish benchmarks for DoD
  - PT regression equations considered a “benchmark”
    - PT limits generally less stringent than LCS Study limits
PT Regression Equations

- Three matrices
  - Drinking water
  - Non-potable water
  - Solid and chemical materials
- Based on empirical data
- Acceptance criteria
  - Mean recovery: $a \cdot \text{conc} + b$
  - Standard deviation: $c \cdot \text{conc} + d$
- Reviewed and updated periodically
  - TNI SOP 4-101
**Comparison to LCS Study as Benchmark**

<table>
<thead>
<tr>
<th>LCS Study</th>
<th>PT Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nine methods</strong></td>
<td><strong>Twelve+ methods</strong></td>
</tr>
<tr>
<td>- Water</td>
<td>- Water</td>
</tr>
<tr>
<td>- Solids</td>
<td>- Solids - limited</td>
</tr>
<tr>
<td><strong>Unique analyses</strong></td>
<td>- Drinking water - limited</td>
</tr>
<tr>
<td>- Explosives</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- GRO</td>
</tr>
<tr>
<td></td>
<td>- DRO</td>
</tr>
<tr>
<td></td>
<td>- Anions</td>
</tr>
<tr>
<td></td>
<td>- 2 Aroclors</td>
</tr>
<tr>
<td></td>
<td>- 7 Aroclors, including PCBs in oil</td>
</tr>
<tr>
<td></td>
<td>- Miscellaneous analytes</td>
</tr>
<tr>
<td><strong>No concentration dependence</strong></td>
<td><strong>Concentration dependent</strong></td>
</tr>
</tbody>
</table>
Ground Rules for Comparing acceptance criteria with LCS Study

- Use non-potable water equations
- Use a mid-range concentration
- Focus on overall properties of analytical groups
Comparison to LCS Study as Benchmark - Metals in Water

<table>
<thead>
<tr>
<th>LCS Study</th>
<th>PT Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean recovery</strong></td>
<td><strong>Mean recovery</strong></td>
</tr>
<tr>
<td>- 24 analytes (including Hg)</td>
<td>- 28 analytes (including Hg)</td>
</tr>
<tr>
<td>- 98.7%</td>
<td>- 99.7%</td>
</tr>
<tr>
<td><strong>Standard deviation</strong></td>
<td><strong>Standard deviation</strong></td>
</tr>
<tr>
<td>- 4.2%</td>
<td>- 5.1%</td>
</tr>
</tbody>
</table>

Method 200.7: ± 15%
Method 200.8: ± 15%
Comparison to LCS Study as Benchmark - Volatiles in Water

**LCS Study**
- Mean recovery
  - 69 analytes (including surr)
  - 98.5%
- Standard deviation
  - 10.9%

**PT Equations**
- Mean recovery
  - 33 analytes
  - 98.4%
    - a(ave): 0.982
- Standard deviation
  - 12.0%
    - c(ave): 0.113
## Comparison to LCS Study as Benchmark - Semivolatiles in Water

<table>
<thead>
<tr>
<th>LCS Study</th>
<th>PT Equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean recovery</td>
<td>Mean recovery</td>
</tr>
<tr>
<td>- 69 analytes (including surr)</td>
<td>- 62 analytes</td>
</tr>
<tr>
<td>- 77.7%</td>
<td>- 77.3%</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>- 12.1%</td>
<td>- 17.9%</td>
</tr>
<tr>
<td></td>
<td>a(ave): 0.759</td>
</tr>
<tr>
<td></td>
<td>c(ave): 0.168</td>
</tr>
</tbody>
</table>
Extension to Other Analyses

Anions

- 7 analytes
- Mean recovery: 99.8%
  - a(ave): 0.998
- Standard deviation: 5.9%
  - c(ave): 0.048
- Method 300.0: ± 10%
- R8L:
  - Mean recovery: 97.6%
  - Standard deviation: 4.6%
Extension to Other Analyses
Gas Range Organics

- Analyte: GRO
- Mean recovery: 106.1%
  - a: 1.068
- Standard deviation: 25.1%
  - c: 0.216
- R8L (MS detection):
  - Mean recovery: 95.5%
  - Standard deviation: 7.0%
  - Use ± 30% for BTEX compounds
Extension to Other Analyses

Diesel Range Organics

- Analyte: DRO
- Mean recovery: 73.1%
  - a: 0.779
- Standard deviation: 19.3%
  - c: 0.136
- R8L LCS:
  - Mean recovery: 86.6%
  - Standard deviation: 12.3%
Extension to Other Analyses
PCBs in Water

- 7 Aroclors
- Mean recovery: 88.6%
  - $a(\text{ave})$: 0.878
- Standard deviation: 18.0%
  - $c(\text{ave})$: 0.192
Conclusions

- LCS Study and PT regression equations lead to similar results
  - Especially true for mean recoveries
  - Use ± 2 SD for in-house limits?
- When the analytical process includes extraction, the mean recoveries will be less than 100%
- The a term is most important in determining the %R
- Both the c and d terms are important in determining the standard deviation
  - Increasingly true as concentration decreases
Advantages of Using PT Regression Equations

- Provide a benchmark for analyses not in the LCS Study
  - Examples: DRO analysis, PCBs in oil
  - Use in absence of in-house statistical limits

- Control limits are concentration dependant
  - Slight

- Have regular review with periodic updates
  - Get DoD out of the business of maintaining
Questions?