Missouri Department of Natural Resources

# Combining XRF Field Measurement with Incremental Sampling


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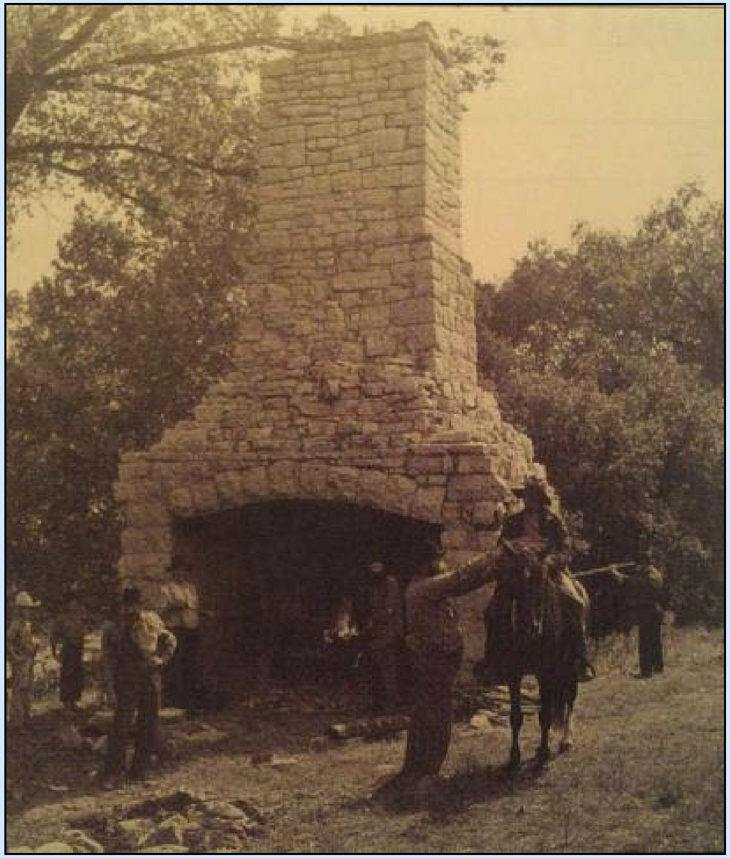
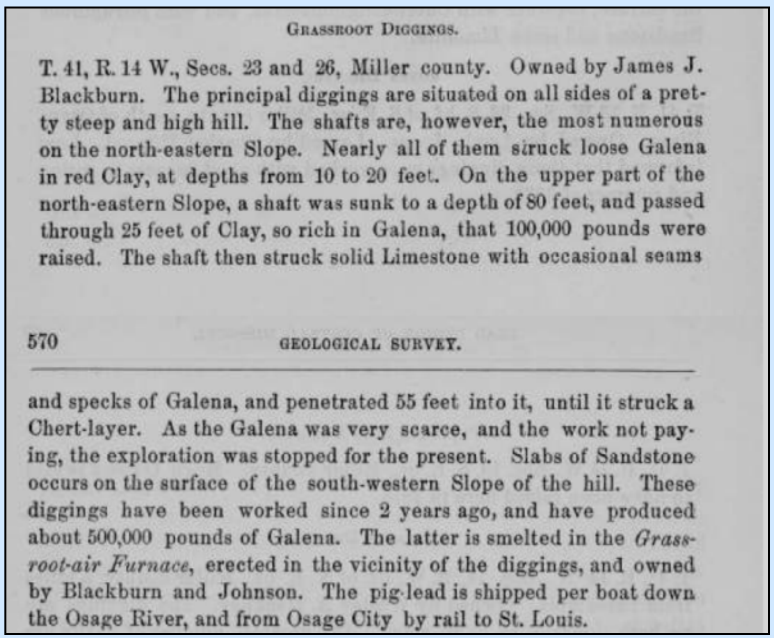


# X-Ray Fluorescence (XRF)

- "Point & shoot" metals analysis
- Measure by
  - Gun window directly on ground (drawback is high sampling error)
  - Prepared soil in special cup (typically soil is ground)
  - Prepared soil in plastic bag: average multiple shots per bag (reduces sampling error without grinding; check for bias from the plastic)

# Former Sites of Galena Mine and Lead Smelter

## Records on mining & production



GRASSROOT DIGGINGS.

T. 41, R. 14 W., Secs. 23 and 26, Miller county. Owned by James J. Blackburn. The principal diggings are situated on all sides of a pretty steep and high hill. The shafts are, however, the most numerous on the north-eastern Slope. Nearly all of them struck loose Galena in red Clay, at depths from 10 to 20 feet. On the upper part of the north-eastern Slope, a shaft was sunk to a depth of 80 feet, and passed through 25 feet of Clay, so rich in Galena, that 100,000 pounds were raised. The shaft then struck solid Limestone with occasional seams

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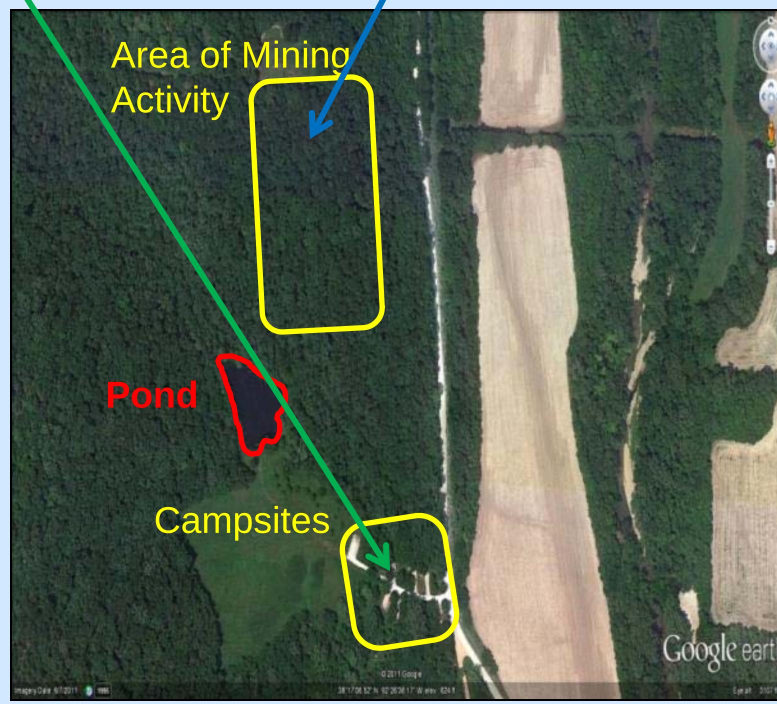
and specks of Galena, and penetrated 55 feet into it, until it struck a Chert-layer. As the Galena was very scarce, and the work not paying, the exploration was stopped for the present. Slabs of Sandstone occurs on the surface of the south-western Slope of the hill. These diggings have been worked since 2 years ago, and have produced about 500,000 pounds of Galena. The latter is smelted in the *Grass-root-air Furnace*, erected in the vicinity of the diggings, and owned by Blackburn and Johnson. The pig-lead is shipped per boat down the Osage River, and from Osage City by rail to St. Louis.



# Site Photos

Mine Shaft

Campground

Campsite size =
1500 sq ft each

# Study Questions

- Does the mean Pb concentration in the fine particulate fraction (<250 µm = 60 mesh) of surface soil (0-2 inches) in any campsite exceed the risk-based screening level?
- Does the mean Pb concentration in the subsurface (2-4 inches, fine fraction) in the 2 campsites where the smelter was located (#1 and #2) exceed the risk-based screening level?

# Reality Check

The Incremental Sampling IDEAL:

30 increments per incremental sample (IS)

3 replicate ISs per DU

Total of 10 DUs (6 surface DUs + 2 bkgd DUs + 2 subsurface DUs)

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= 900 increments of surface soil + 180 hand-dug pits

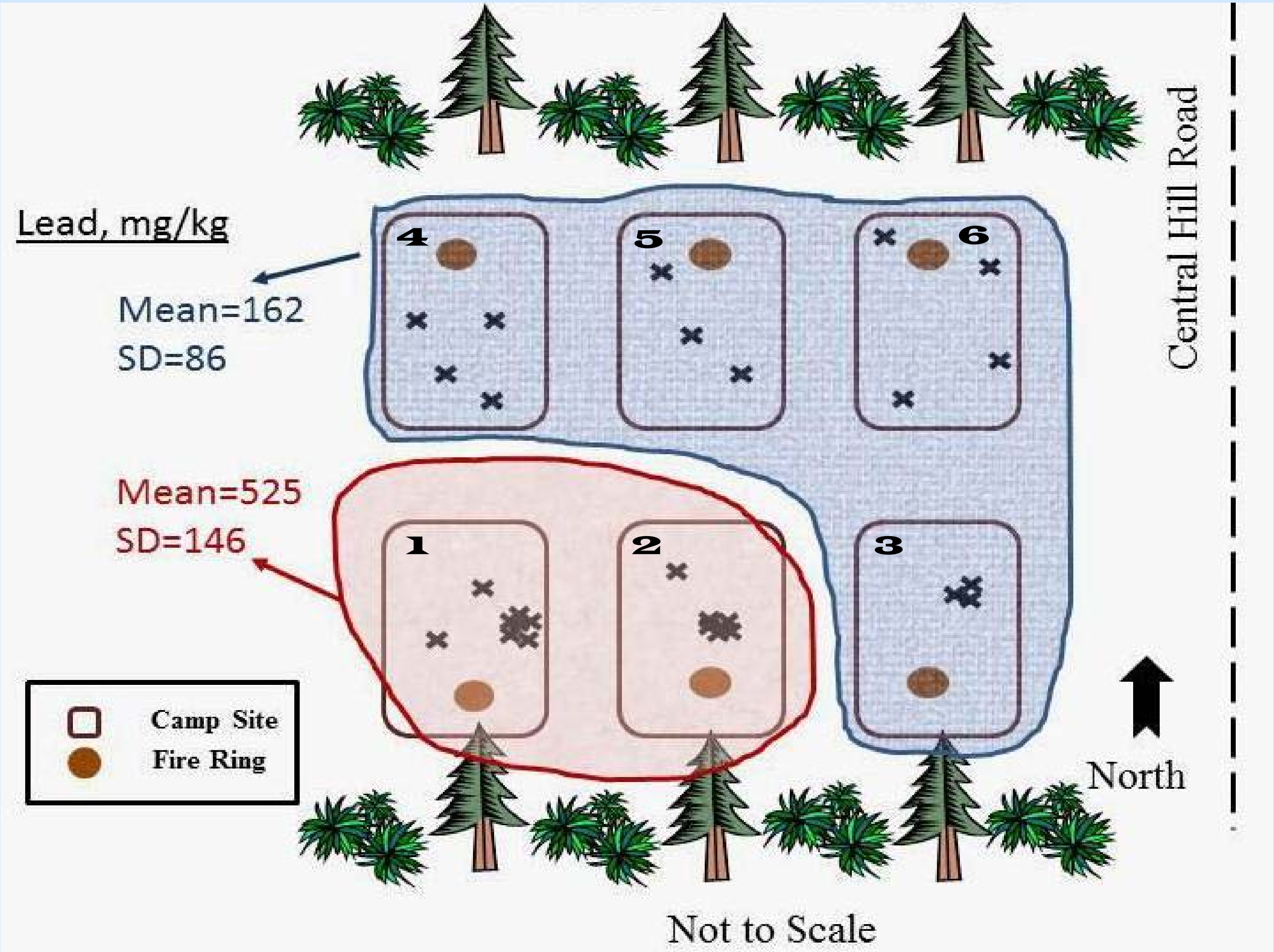
Would bust grant budget; really needed given that the campsites are only 1500 sq ft each?

# Pilot Study Approach

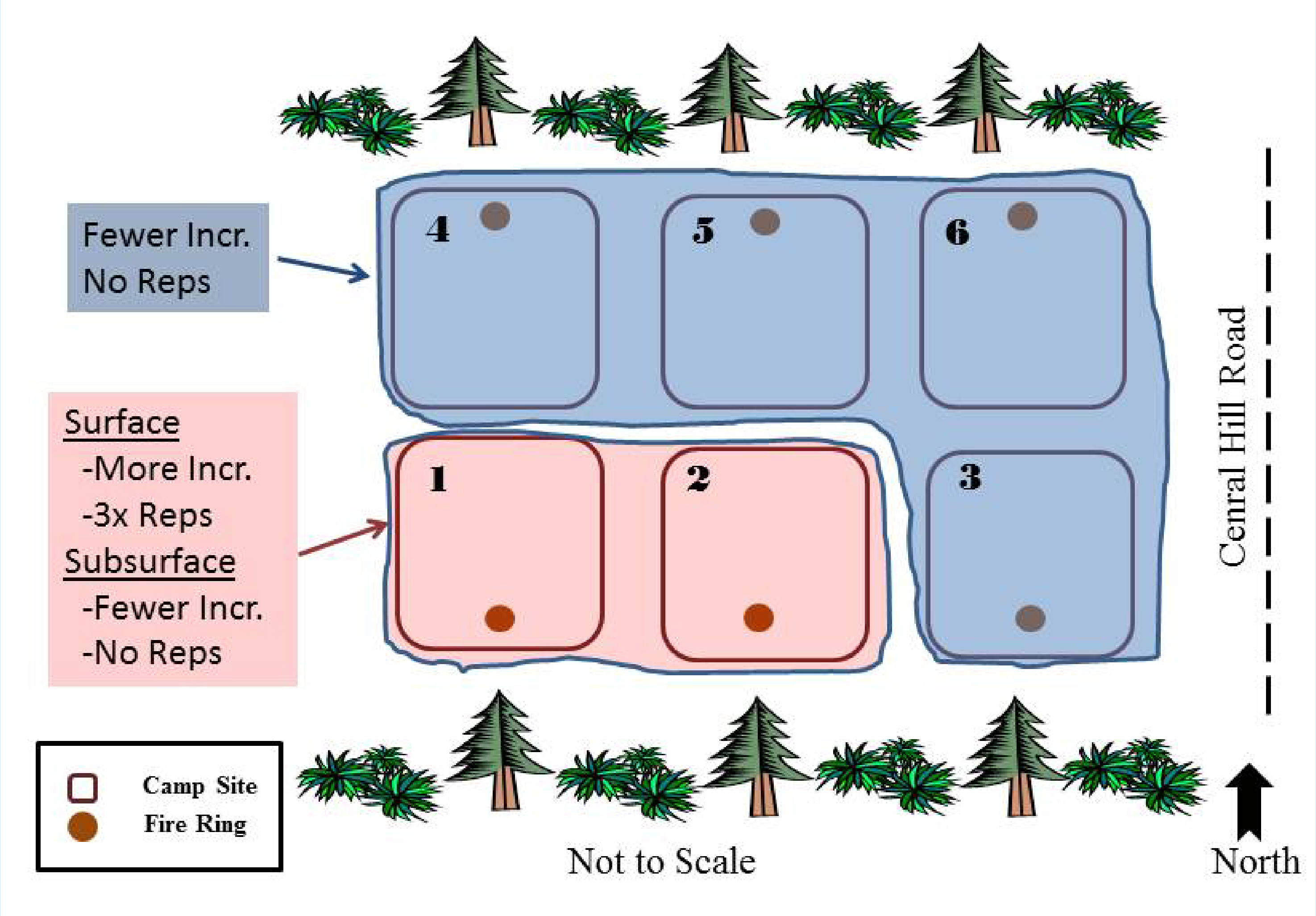
Use in-situ XRF to

- Estimate mean & variability across campsites
- Identify high conc areas
- Design a site-specific IS approach

# Results of In-Situ XRF



# Incremental Sampling Design



# Collecting IS Samples

# IS Sample Processing

# Real-time Data Processing

| | | | |
|---|---|---|---|
| | **Campsite 1** | | 30-incr |
| | **Replicate 1** | | |
| | **0-2"** | | |
| Bagged Replicate Readings | | Instrmnt Result (ppm Pb) | Instrmnt Error (as SD) |
| Bag reading 1 | | 1251 | 18 |
| 2 | | 1308 | 18 |
| 3 | | 1303 | 19 |
| 4 | | 1434 | 19 |
| | **Mean** | 1324.0 | |
| | **SD** | 77.7 | |
| | **%RSD** | 5.9 | |
| **2-sided CLs** | n = | 4 | |
| | Bag 95%LCL = | 1200 | |
| | Bag 95%UCL = | 1448 | |

## A QC Check for XRF

| **XRF Instrument Precision Check** | | | | Reading | Inst Error |
|---|---|---|---|---|---|
| Bag reading 1 | | | | 455 | 10 |
| 2 | Campsite 4 Bag | | | 477 | 11 |
| 3 | | | | 450 | 10 |
| 4 | | | | 459 | 10 |
| 5 | | | | 450 | 10 |
| 6 | | | | 455 | 10 |
| 7 | | | | 459 | 10 |
| | | | **Mean** | 460.3 | |
| | | | **SD** | 11.8 | |

Note: Instrument is not moved between these replicate shots

# Summary of Data

| Campsite # | DU depth | # incr | # IS repls | Result/mean | SD of repls |
|---|---|---|---|---|---|
| 1 | 0-2 in | 30 | 3 | 1316 | 75 |
| 1 | 2-4 in | 15 | 1 | 1724 | N/A |
| 2 | 0-2 in | 30 | 3 | 2331 | 284 |
| 2 | 2-4 in | 15 | 1 | 3571 | N/A |
| 3 | 0-2 in | 15 | 1 | 106 | N/A |
| 4 | 0-2 in | 15 | 1 | 444 | N/A |
| 5 | 0-2 in | 15 | 1 | 310 | N/A |
| 6 | 0-2 in | 15 | 1 | 190 | N/A |
| Future C-site | 0-2 in | 15 | 1 | 134 | N/A |
| Bkgd #1 | 0-2 in | 30 | 1 | 42 | N/A |
| Bkgd #2 | 0-2 in | 30 | 1 | 32 | N/A |

# Partitioning Sources of Error

from 3 IS Repls → Total measurement error (SD)

from 4 readings on the bag → Analytical + sample processing error (SD)

by subtraction → Field-scale (between-IS) error (SD)

| (0-2 in) | Total measurement error (SD) | Analytical + sample proces-sing error (SD) | Field-scale (between-IS) error (SD) | Mean | UCL |
|---|---|---|---|---|---|
| Campsite 1: | 75 | 50 | 56 | 1316 | 1442 |
| Campsite 2: | 284 | 35 | 282 | 2331 | 2809 |

Reducing uncertainty requires more increments per incremental sample

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# 95% UCLs for Campsites 1 & 2 Surface DUs

- Calculated from results of 3 (30-incr each) replicate ISs
- Each replicate result represents a physical mean
- Example for DU1:

| DU 1 Repl. | Pb, mg/kg |
|---|---|
| 1 | 1,324 |
| 2 | 1,386 |
| 3 | 1,237 |
| Grand Mean | 1,316 |
| SD ($SE_{mean}$) | 75 |
| %RSD | 6 |

$$tUCL_{1-\alpha} = \overline{X} + t_{1-\alpha,n-1}\left(\frac{s}{\sqrt{n}}\right)$$

$$tUCL_{95} = 1{,}316 + 2.92\left(\frac{75}{\sqrt{3}}\right) = 1{,}442\ ppm$$

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# 95% UCLs for Campsites 1 & 2 Subsurface DUs

## Steps 1 & 2

- No replicates collected (no DU-specific SD); 15 incr per IS
- Derive subsurface SD using relationship between Std Error of the mean (= the SD of the IS replicates) & SD of the increments

Step 1

$$SE_{mean(90incr)} = SD_{repls} = SD_{90incr} \div \sqrt{n}$$

$$SD_{90incr} = SD_{repls}\sqrt{n}$$

$$SD_{90incr} = 75\sqrt{90} = 710$$

↑

SD of the 3 IS replicates (of 30 incr each) for DU 1 (surface soil)

Step 2

Now calculate SE when have 15 incr.

$$SE_{mean(15incr)} = \frac{SD_{90incr}}{\sqrt{n}}$$

$$SE_{mean(15incr)} = \frac{710}{\sqrt{15}} = 183$$

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# 95% UCLs for Campsites 1 & 2 Subsurface DUs
## Step 3

- We now have an estimate for the SD between 3 simulated replicates of 5 increments each
- Using equation for t-UCL as before:

$$tUCL_{1-\alpha} = \overline{X} + t_{1-\alpha,n-1}\left(\frac{s}{\sqrt{n}}\right)$$

For DU 1 subsurface:

$$tUCL_{95} = 1{,}720 + 2.92\left(\frac{183}{\sqrt{3}}\right) = 2{,}033\,ppm$$

↑

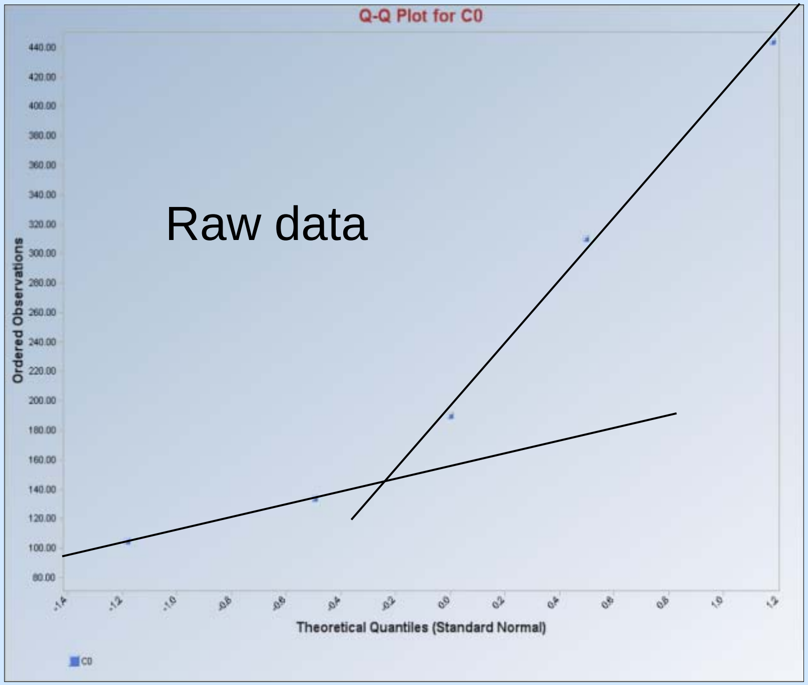
Pb conc from the single 15-incr. subsurface IS;
treated as a simulated average of 3 replicate 5-incr ISs

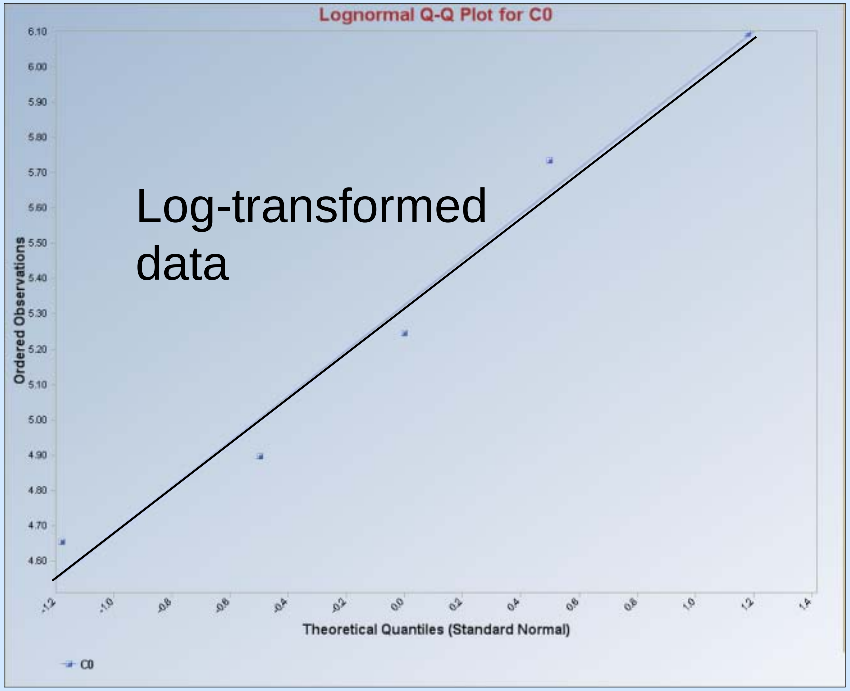
# Deriving UCLs For Campsites 3-6 & F

- By *in-situ* XRF: low concentrations & low variability
- Surface (0-2 inches) only
- 15 increments per IS; 1 IS per DU so no within-DU SD
- Group Campsites 3-6 & F together
- Use ProUCL to plot the low conc group’s data (n = 5); calculate group’s SD & UCL

# Statistical Distribution for Low-conc DUs

## ProUCL Q-Q Plots



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# Low-conc DU Group UCL Calculation

ProUCL output

| General Statistics | | | |
|---|---|---|---|
| Number of Valid Observations | 5 | Number of Distinct Observations | 5 |
| **Raw Statistics** | | **Log-transformed Statistics** | |
| Minimum | 105 | Minimum of Log Data | 4.654 |
| Maximum | 444 | Maximum of Log Data | 6.096 |
| Mean | 236.6 | Mean of log Data | 5.326 |
| Median | 190 | SD of log Data | 0.592 |
| SD | 140 | | |
| Std. Error of Mean | 62.62 | | |
| Coefficient of Variation | 0.592 | | |
| Skewness | 0.889 | | |

ics

| Lognormal Distribution Test | |
|---|---|
| Shapiro Wilk Test Statistic | 0.961 |
| Shapiro Wilk Critical Value | 0.762 |
| Data appear Lognormal at 5% Significance Level | |
| **Assuming Lognormal Distribution** | |
| 95% H-UCL | 643.1 |
| 95% Chebyshev (MVUE) UCL | 504.6 |
| 97.5% Chebyshev (MVUE) UCL | 620.9 |
| 99% Chebyshev (MVUE) UCL | 849.3 |

UCL for the low conc group (DUs 3-6 & F) = 505 mg/kg

# Putting An Upper Bound on Uncertainty For the Means of Individual DUs

- Mean of ISs from DUs 3-6, F = 237mg/kg
- Mean-to-UCL width for *between*-DU variability 505-237 = 268

Use as a conservative estimate of *within*-DU uncertainty

| DU | Pb IS Result, ppm | Measure of Uncertainty | Pb Mean + Uncertainty, ppm |
|---|---|---|---|
| 3 | 105 | 268 | 373 |
| 4 | 444 | 268 | 712 |
| 5 | 310 | 268 | 578 |
| 6 | 190 | 268 | 458 |
| F | 134 | 268 | 402 |

These will be compared to the screening level

# Summary

- Field analytical method (XRF) used to firm CSM & guide IS design
- <30 increments reasonable since DU areas are very small
- Estimates of variability extrapolated across DUs that belong to the same concentration population
- Penalty paid in higher UCLs, but acceptable given distance from SL