



# Calibration and Use of XRF for Hg Analysis of Bank Soils

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# Experimental Question

Can hand-held XRF analysis provide a low-cost real-time measure of Hg with sufficient accuracy and precision?

Why propose an alternative method?

- Sample Frequency
  - Nearly 5000 soil and sediment samples analyzed for Hg as a part of EcoStudy
  - Nearly 500 Hg soil samples already analyzed in 2015
- Cost
  - \$20/sample for Method 7471A
  - \$83/sample for Method 1631
  - Not including labor and shipping costs
- Time
  - Turnaround time on the order of weeks





# Experimental Design

- Method Comparison Study

## EPA Method 7471A

- 51 bank soil samples
- Lancaster Labs
- Routine QA

## Hand-held XRF

- 51 bank soil samples
- JMU ISAT Lab
- Calibration curve development; MDL determination; Triplicate analysis; precision and accuracy evaluation



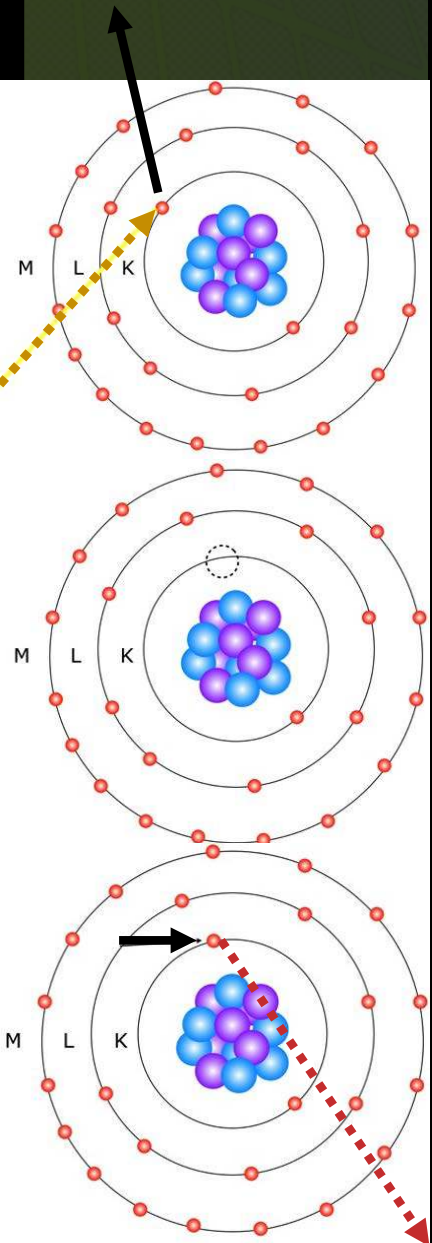
# Instrument Setup

| Parameter     | Value                                       |
|---------------|---------------------------------------------|
| Model         | Bruker Tracer III Handheld XRF Spectrometer |
| Voltage       | 0-40 kV                                     |
| Current       | 30 $\mu$ A                                  |
| Analysis Time | 60 s and 100 s                              |
| Filter        | Ti/Al/Cu                                    |

Instrument parameters  
were selected to  
optimize detection of  
Hg



# Instrument Principles

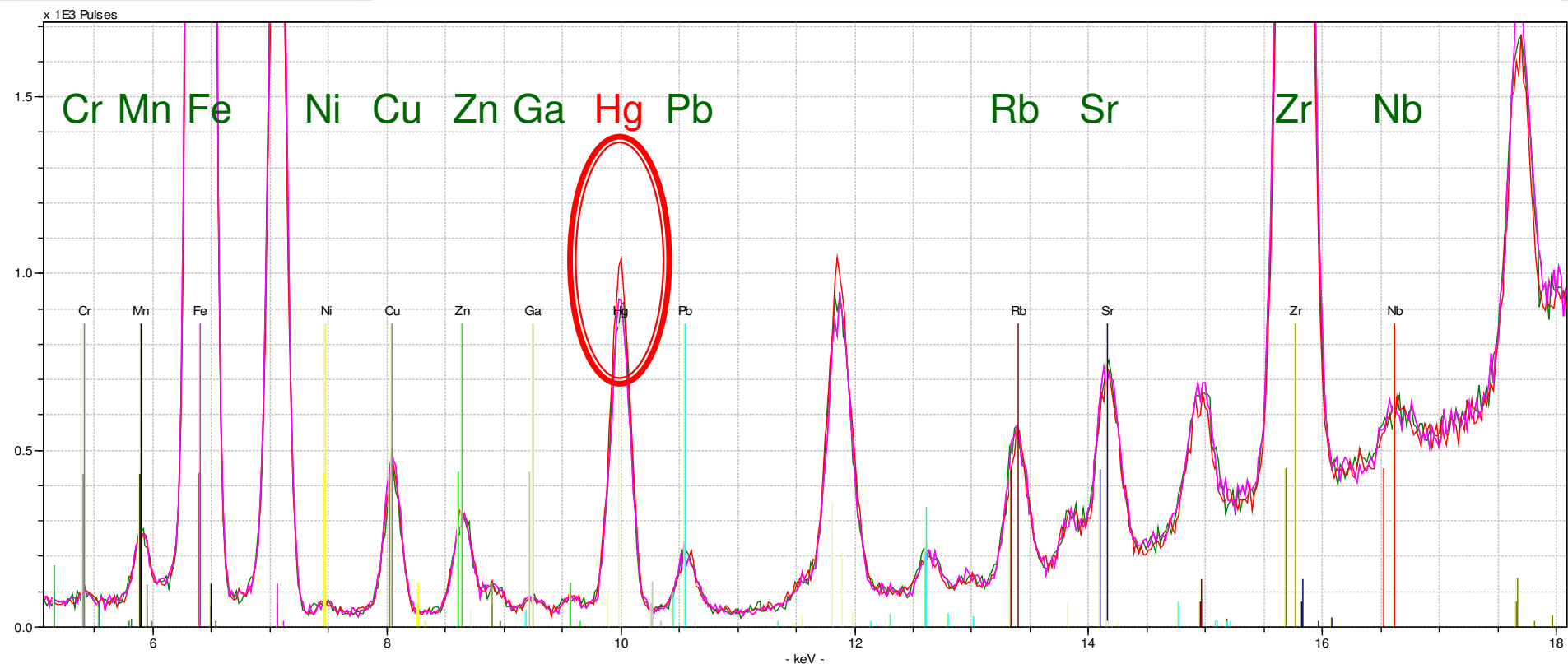


- Instrument produces x-rays that hit elements in the sample and expel inner shell electrons
- Outer shell electrons fill the void in the inner shell
- Drop in energy level releases a photon of energy in the x-ray spectrum
- Each element has a characteristic energy level of photons released



# Post Processing

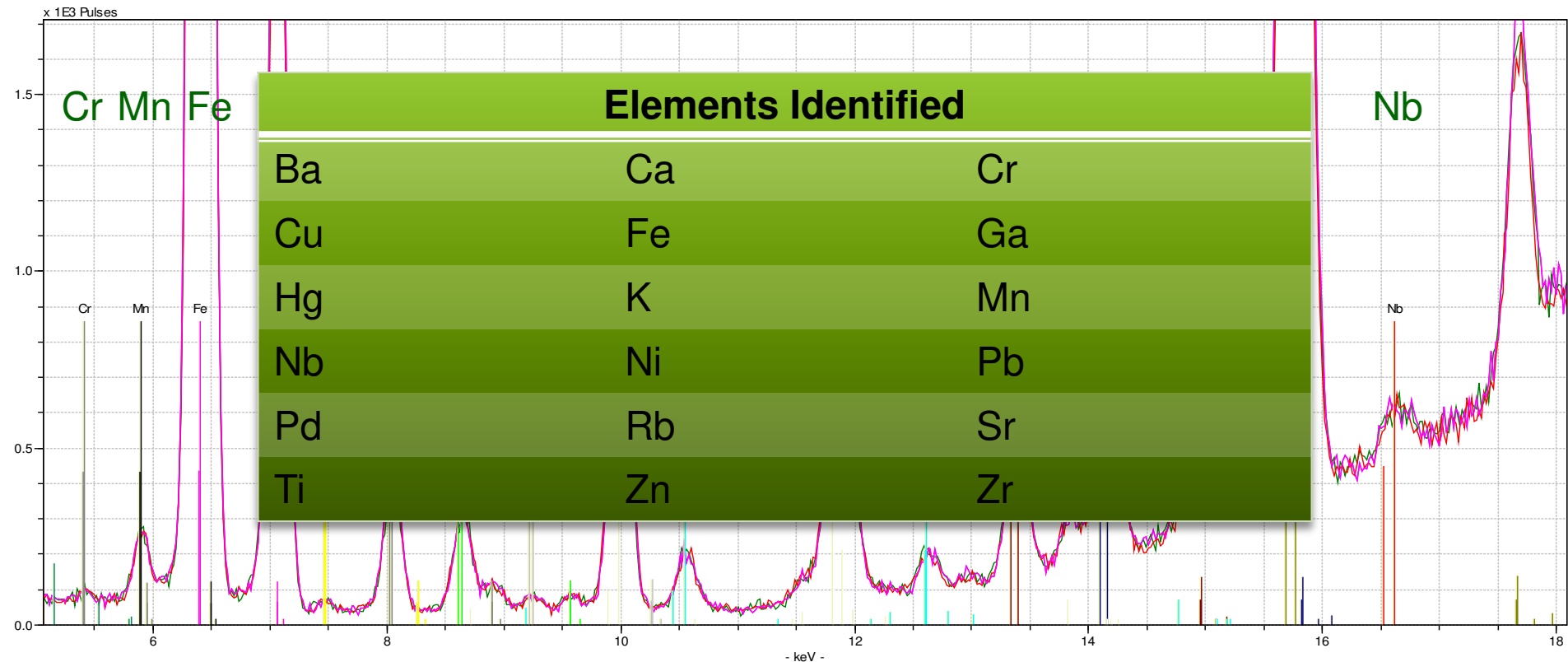
- Artax software used to analyze spectra
  - Bayesian deconvolution method modeled peaks and quantified electron counts for each element



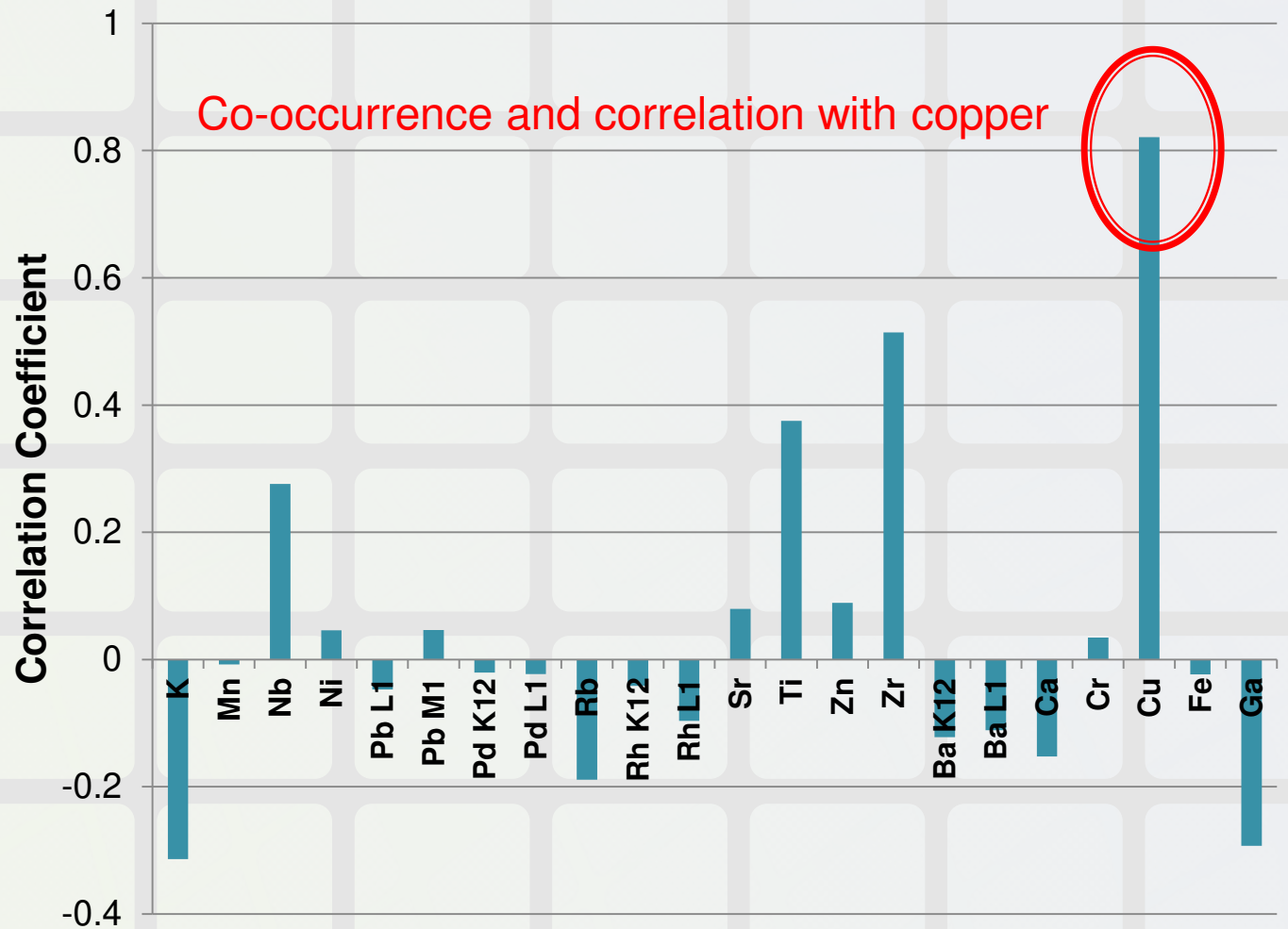


# Post Processing

- Artax software used to analyze spectra
  - Bayesian deconvolution method modeled peaks and quantified electron counts for each element



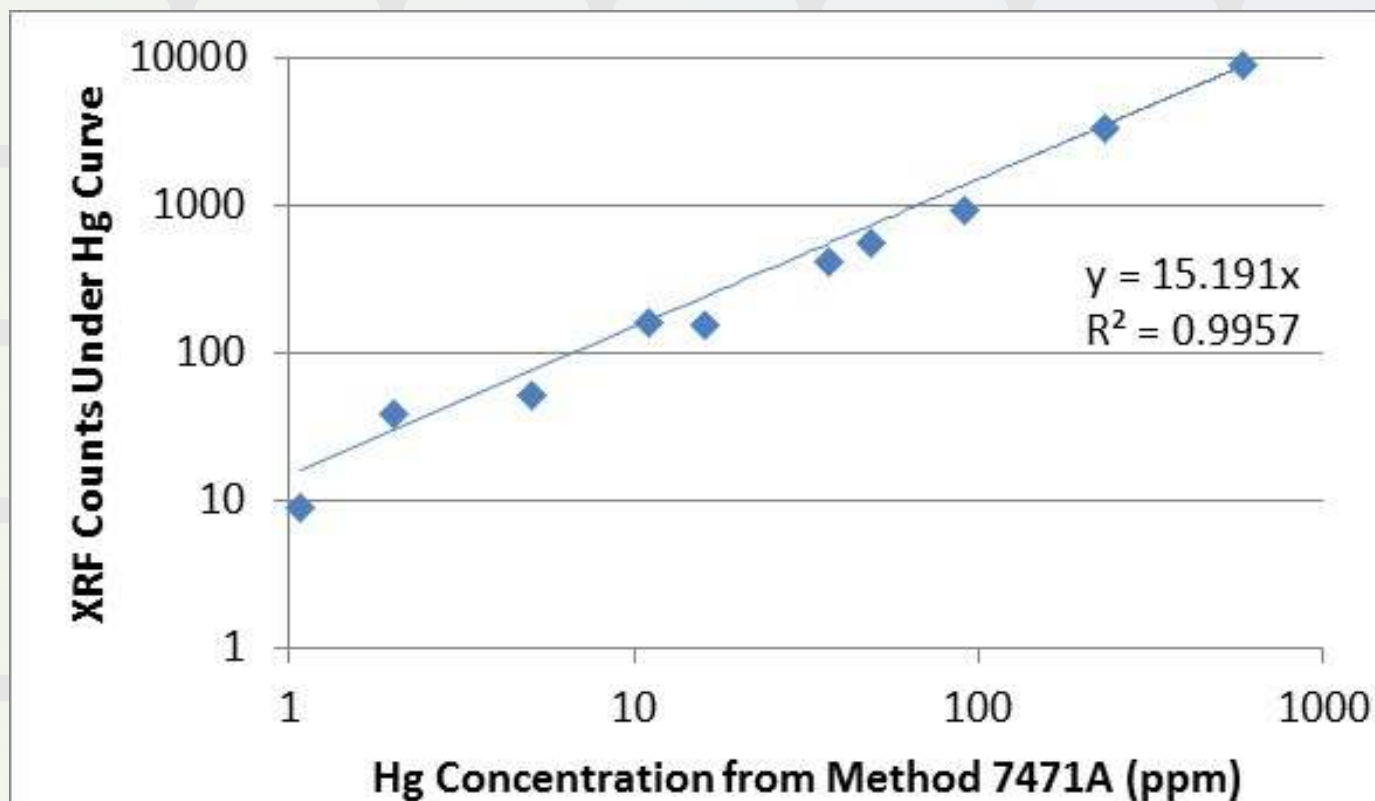
# Element Comparisons





# Calibration

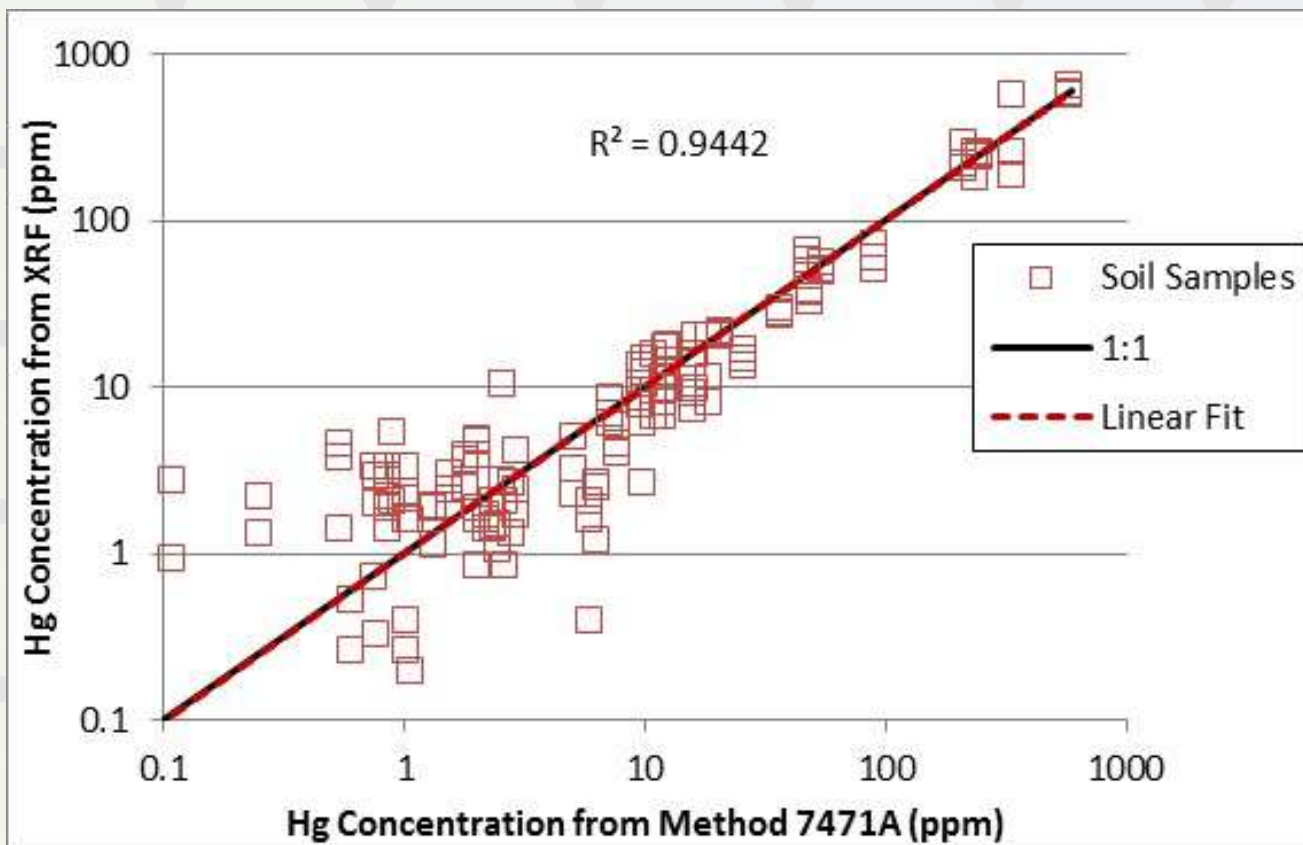
- 10 samples of known Hg conc. ranging from 1.07 to 587 ppm





# Analysis Results

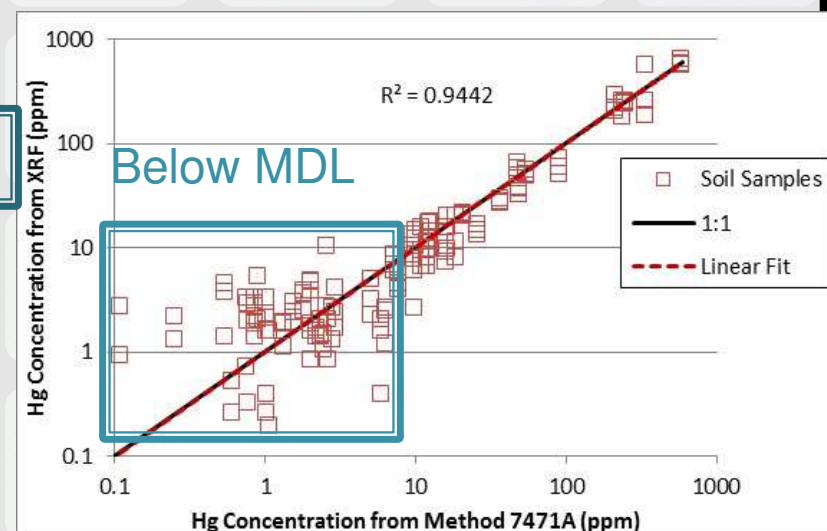
- All samples, all replicates analyzed according to calibration.



# Method Detection Limit

- Sample containing 10 ppm Hg
- 10 duplicate analyses conducted
- Calculated MDL as concentration that can be distinguished from zero with 95% confidence
- At 60 sec
  - MDL = 7.4 ppm
- At 100 sec
  - MDL = 3.4 ppm

Method 7471A  
MDL ~ 0.11

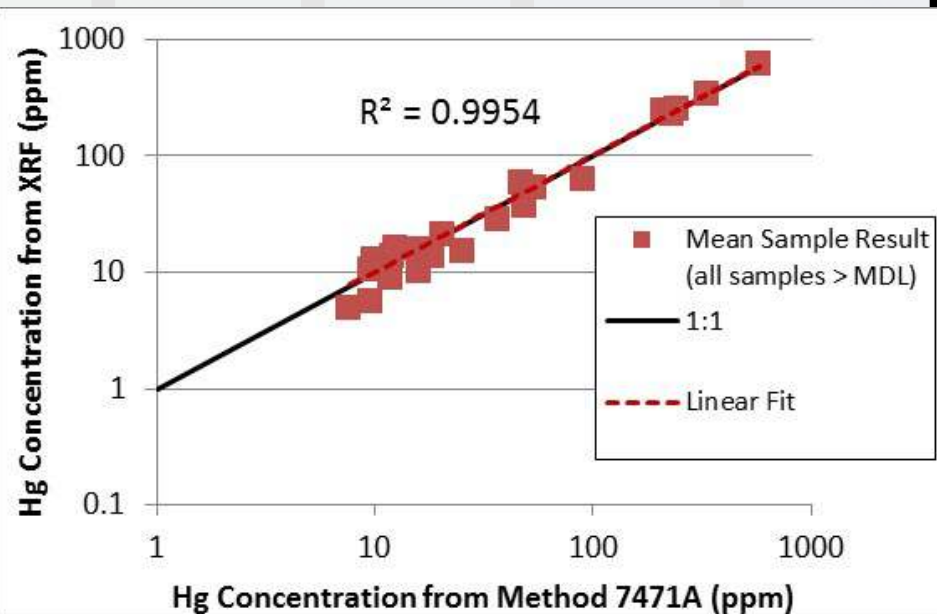
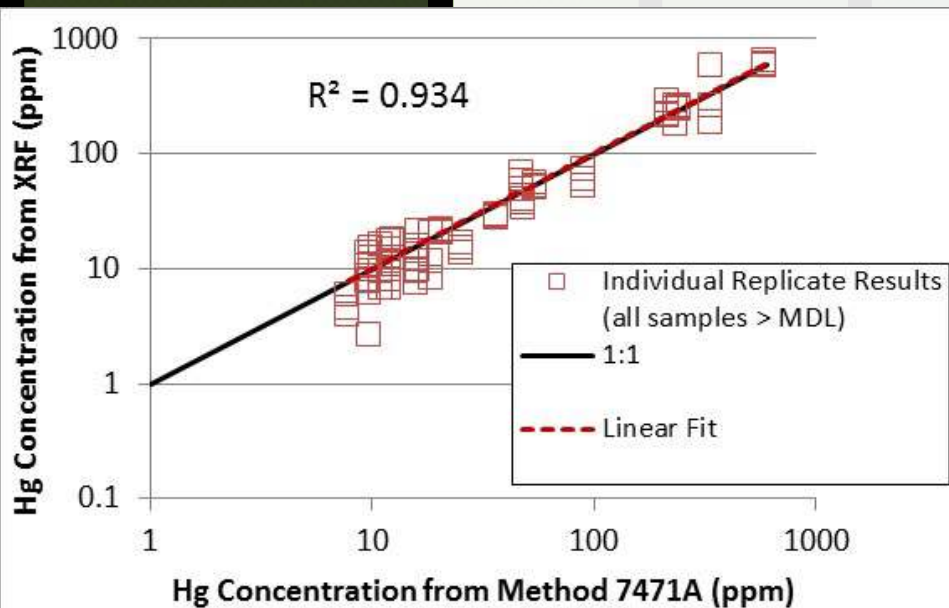




# Results >MDL

All Replicates

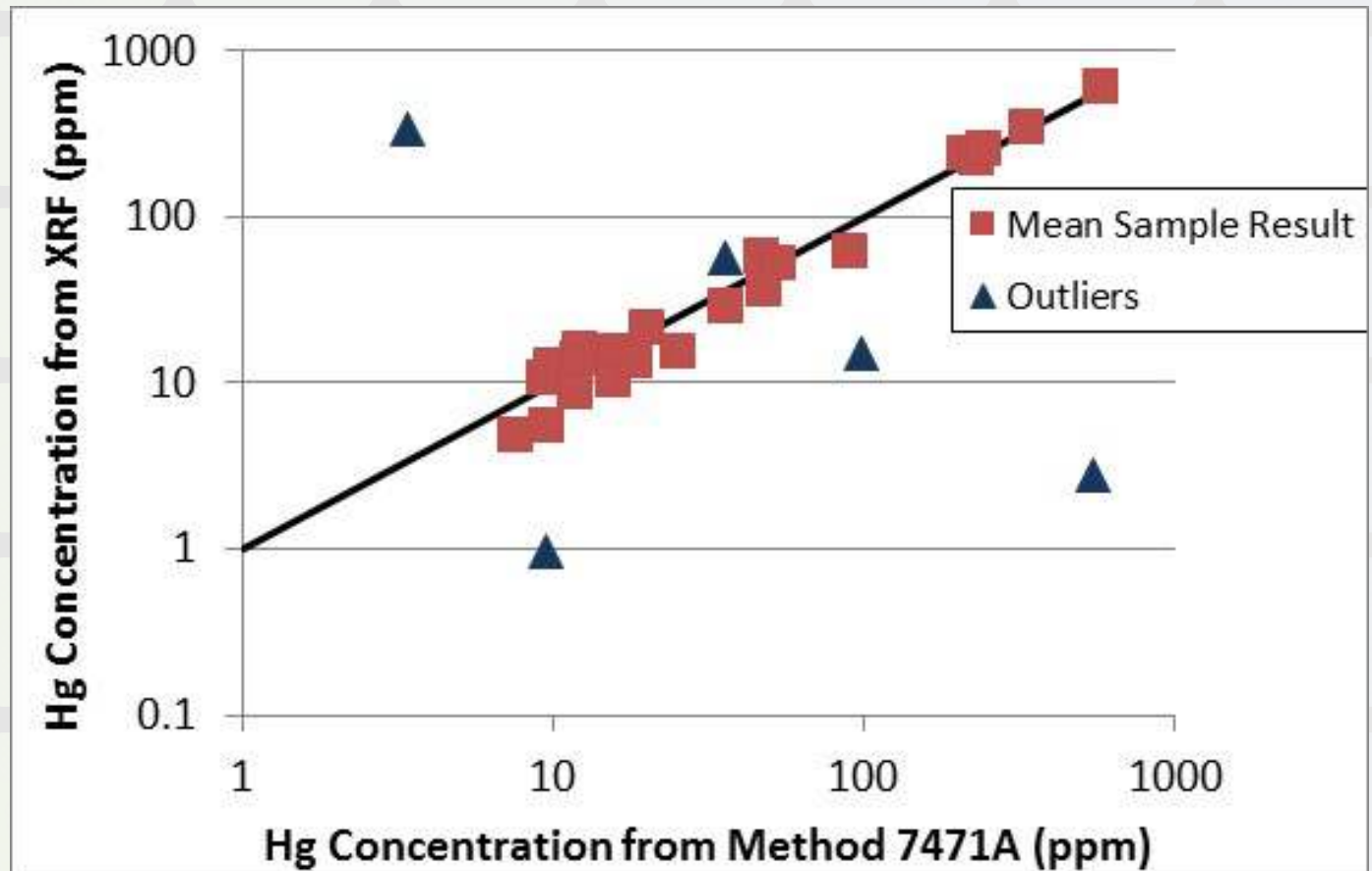
Mean Results





# Outliers

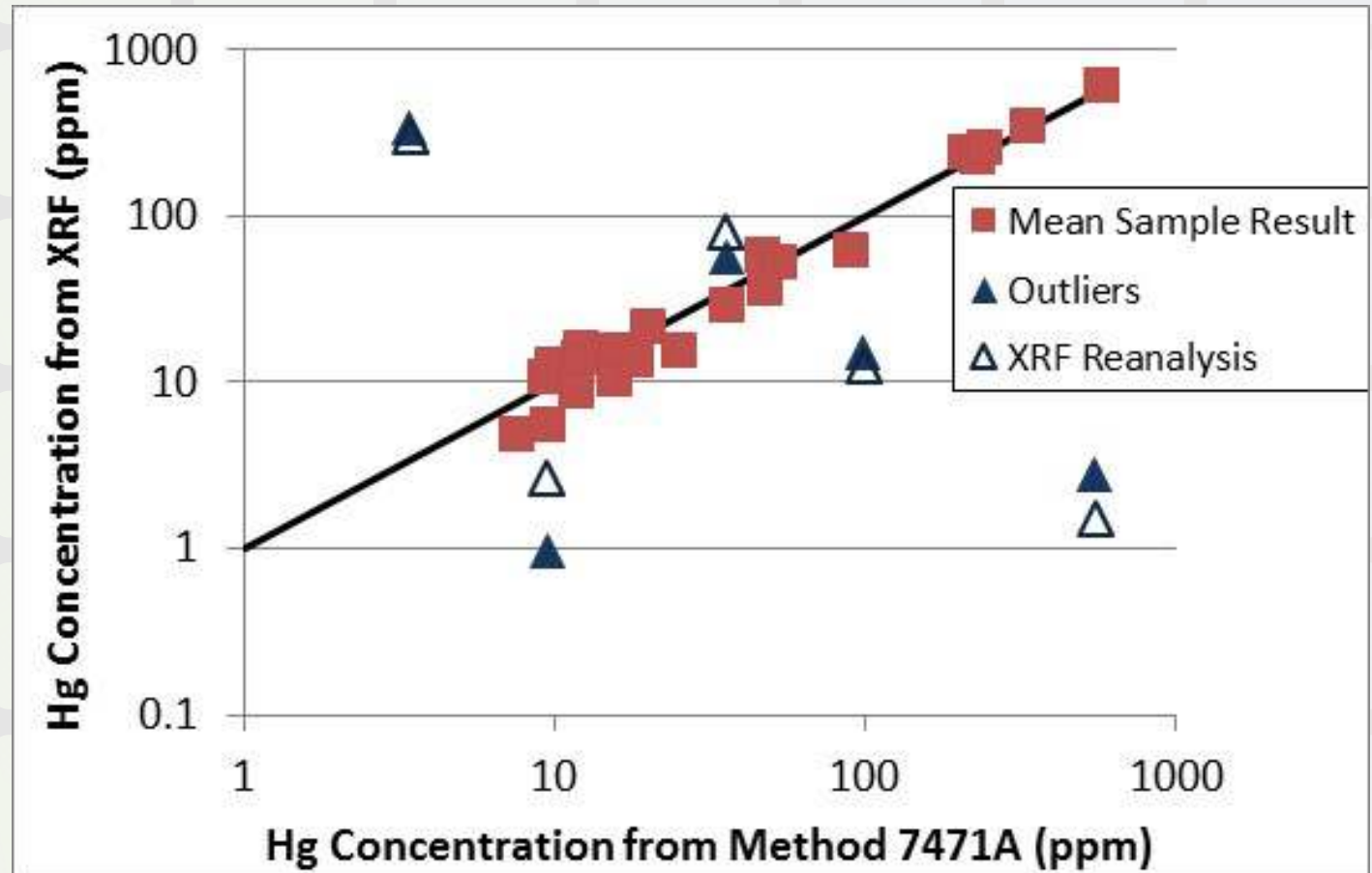
- Outliers identified?





# Outliers

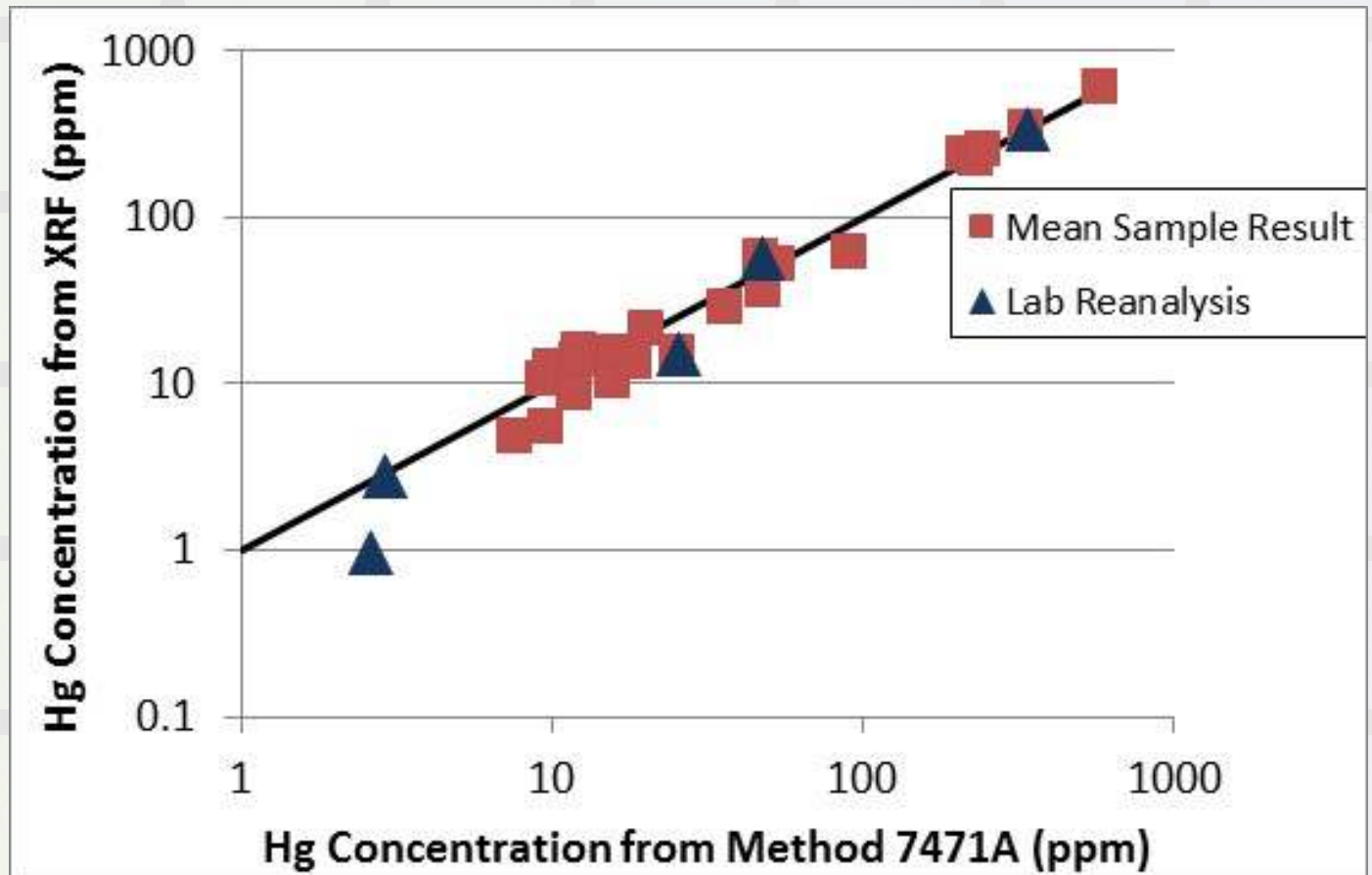
- XRF Reanalysis





# Outliers

- Lab Reanalysis

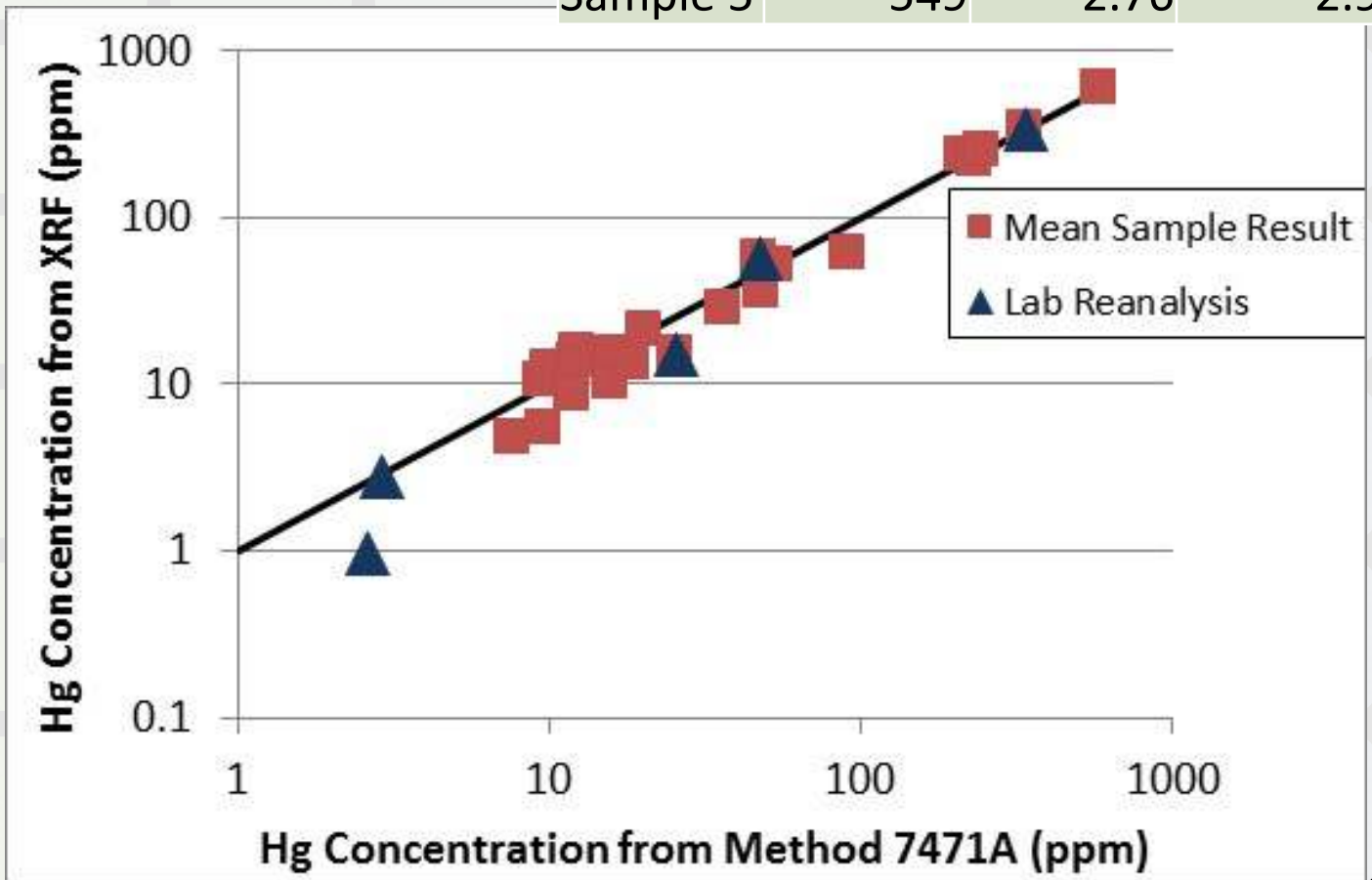




# Outliers

- Lab Reanalysis

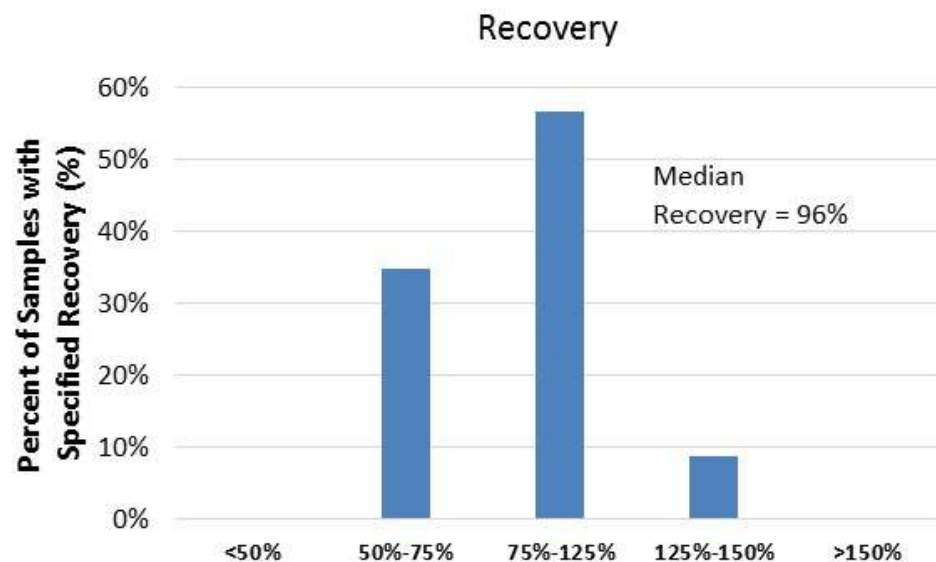
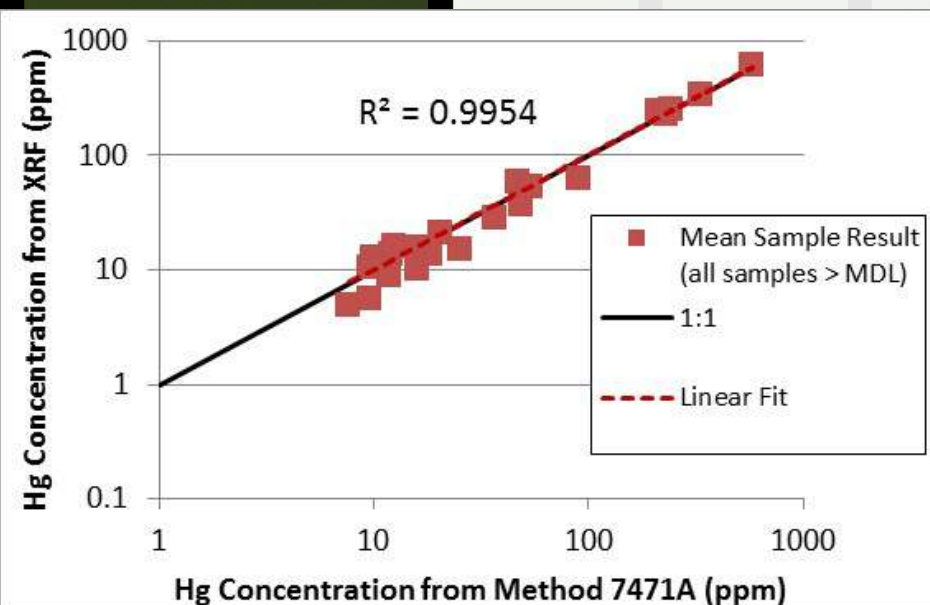
|          | Lab Result | XRF Result | Lab Re-analysis |
|----------|------------|------------|-----------------|
| Sample 1 | 3.42       | 338        | 336             |
| Sample 2 | 9.48       | 0.965      | 2.62            |
| Sample 3 | 35.8       | 57.4       | 47.5            |
| Sample 4 | 98.2       | 14.9       | 25.5            |
| Sample 5 | 549        | 2.76       | 2.9             |





# Accuracy – Comparison with Known

- $R^2$  of known vs measured regression
- Recovery = measured/known \* 100
  - Includes both XRF measurement variability and Method 7471A measurement variability

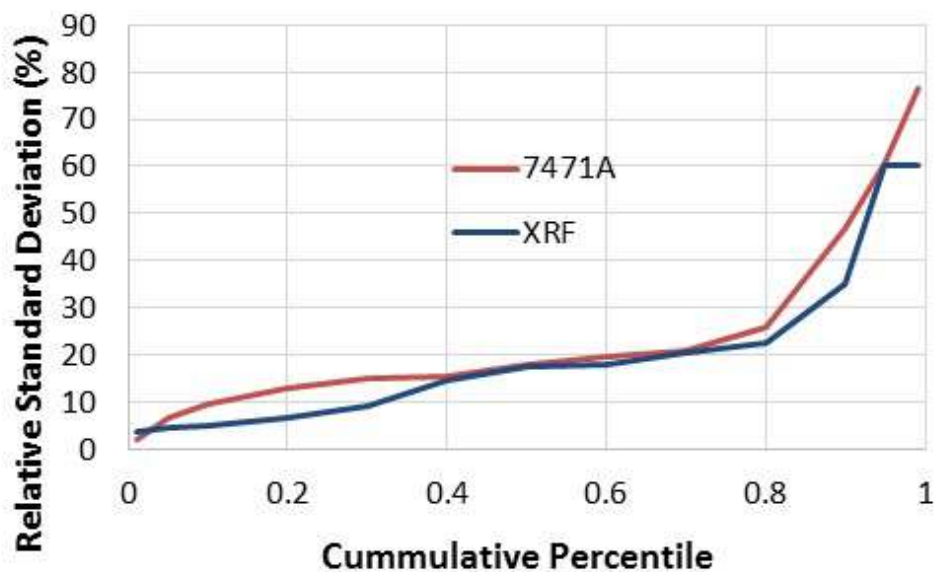




# Precision – Duplicate Analysis

- Relative Standard Deviation (RSD or CV)
  - Duplicate standard deviation / duplicate mean \* 100
- Relative Percent Difference (RPD)
  - Duplicate range / duplicate mean \* 100

Precision Estimate

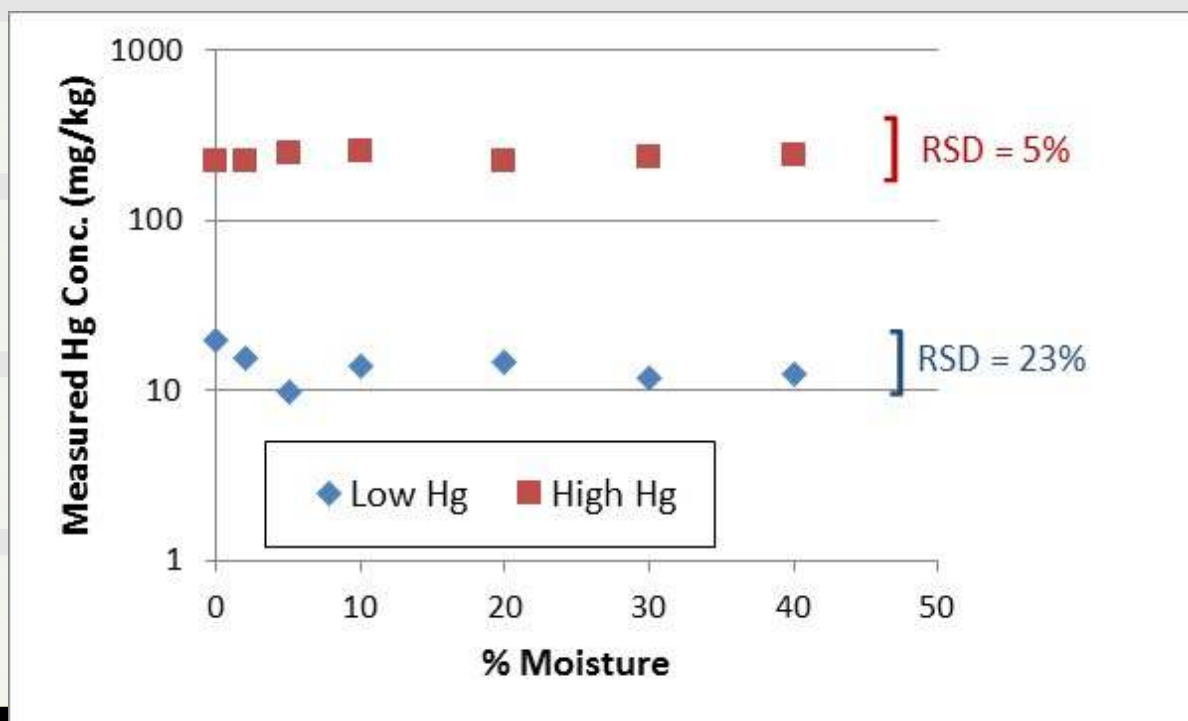


|     |        | Method<br>7471A | XRF<br>Method |
|-----|--------|-----------------|---------------|
| RSD | N      | 28              | 23            |
|     | Mean   | 23              | 23            |
|     | Median | 18              | 18            |
|     | Range  | 1-81            | 3-60          |
| RPD | N      | 28              | 23            |
|     | Mean   | 33              | 44            |
|     | Median | 25              | 35            |
|     | Range  | 1-115           | 6-113         |



# Moisture Investigation

- XRF measurements tested on samples adjusted to varying moisture levels
  - Low Hg = 18.6 mg/kg; High Hg = 214 mg/kg
  - Moisture Levels = 0, 2, 5, 10, 20, 30, 40%





# Conclusions



|   | Criteria        | Description                                                                                 |
|---|-----------------|---------------------------------------------------------------------------------------------|
| ✓ | Cost            | Only labor cost; no lab or shipping costs                                                   |
| ✓ | Turnaround Time | 60 sec (or 100 sec)                                                                         |
| ✓ | Detection Limit | 7.4 ppm (@ 60 sec); 3.4 (@ 100 sec); below thresholds for determining bank management areas |
| ✓ | Accuracy        | Acceptable accuracy; Median recovery = 96%; avoids errors from sample handling              |
| ✓ | Precision       | Acceptable precision; Mean RSD = 23%; precision identical to Method 7471A                   |
| ✓ | Interference    | Moisture not a significant interference                                                     |



# Future Work

- Additional Lab Validation
  - Spiked samples
- Field Validation
  - Comparison of:
    - In situ XRF field measurement before sampling
    - XRF field measurement on collected sample
    - XRF lab measurement on collected sample
    - Method 7471A lab measurement on collected sample
- Analysis of banks in next 2 miles of river (2-4 miles)
  - Hg measurement and mapping using XRF and GPS

