



2016 Study Update: Field and Lab Validation of XRF Method

Robert Brent

Hunter Wines, Joseph Luther



Review: 2016 Field Study Approach



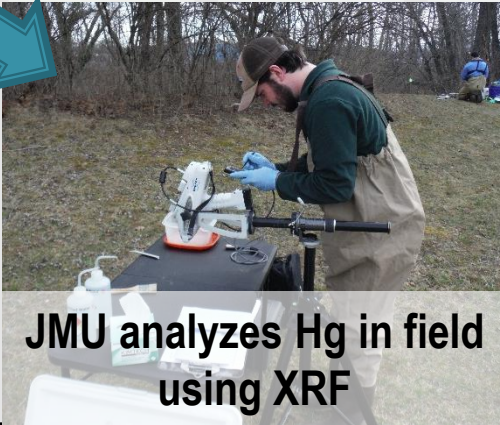
AECOM collected
cores or surficial soil



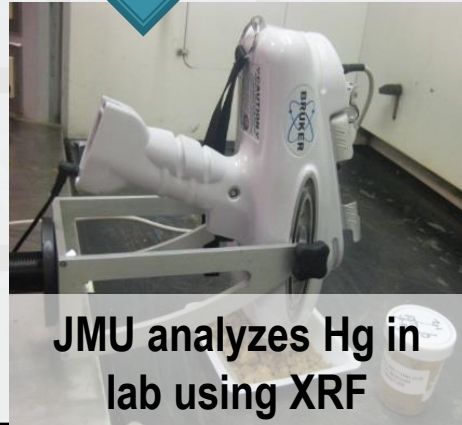
Samples shipped to Lancaster Labs
for Hg analysis using Method 7471A



AECOM homogenized
and characterized
composites



JMU analyzes Hg in field
using XRF



JMU analyzes Hg in
lab using XRF

2016 Field Study Details

- Dates: March 7-16, 2016
- Collected: 236 samples from 9 BMAs
- Hg Results:
 - 37% of samples were < MDL of 7.4 ppm
 - Hg levels ranged from < MDL – 1411 ppm
- QA Elements:

QA Sample	Frequency	Description
Blank	5% (5.5%)	Soil sample with ~1 ppm Hg
Hg Reference Material	5% (5.5%)	Soil sample with 245 ppm Hg
Sample Triplicates	15% (16%)	Analysis of 3 subsamples
Measurement Triplicates	5% (6.8%)	3 analyses of same subsample

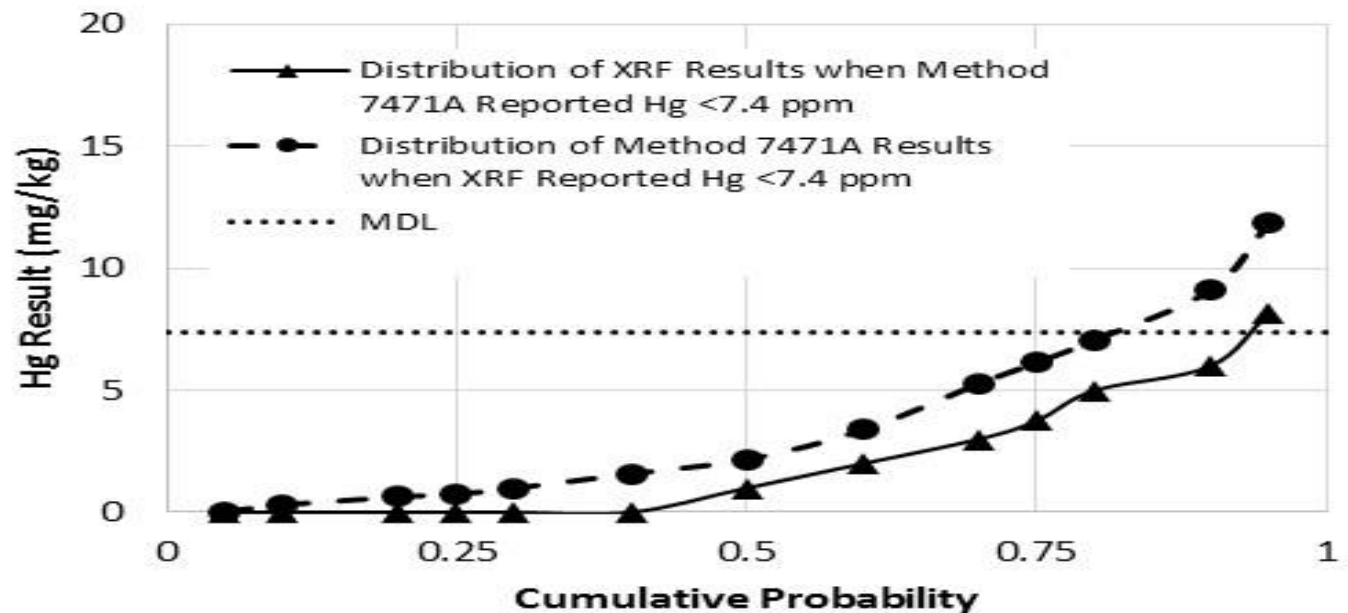
2016 Lab Details

- Dates: May 9-26, 2016
- Reanalyzed: 244 samples collected in March and previously analyzed by Lancaster Labs
 - Including 13 field duplicates
 - No samples >1000 ppm

QA Sample	Frequency	Description
Blank	15%	Soil sample with ~1 ppm Hg
Hg Reference Material	15%	Soil sample with 245 ppm Hg
Sample Triplicates	100%	Analysis of 3 subsamples
Measurement Triplicates	100%	3 analyses of same subsample
Matrix Spike Samples	10 spikes	North River soil spiked with 1-1000 ppm Hg

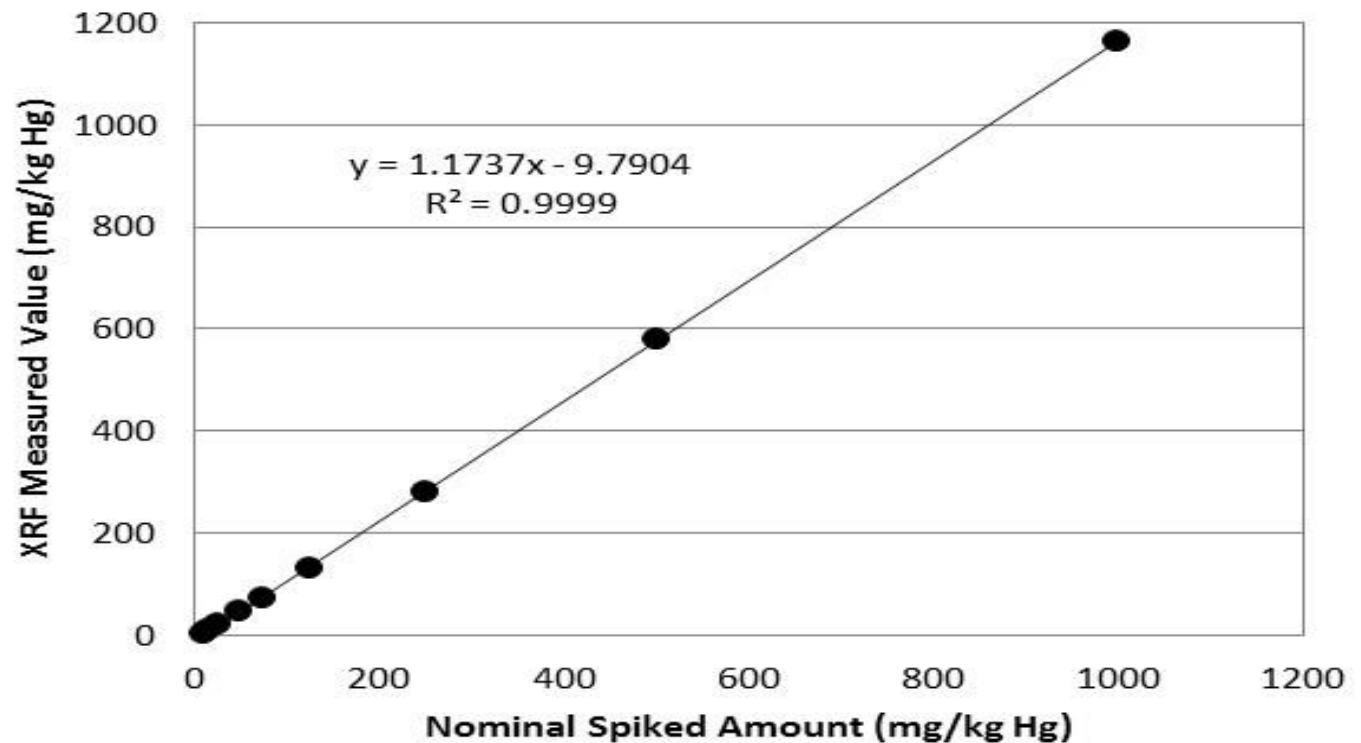
Results: Accuracy of Detection

- Blank QA samples
 - Of 71 blanks analyzed, 100% were measured as <7.4 ppm
- Field samples
 - Of 90 field samples measured as <7.4 ppm by Method 7471A, 93% agreed with XRF results



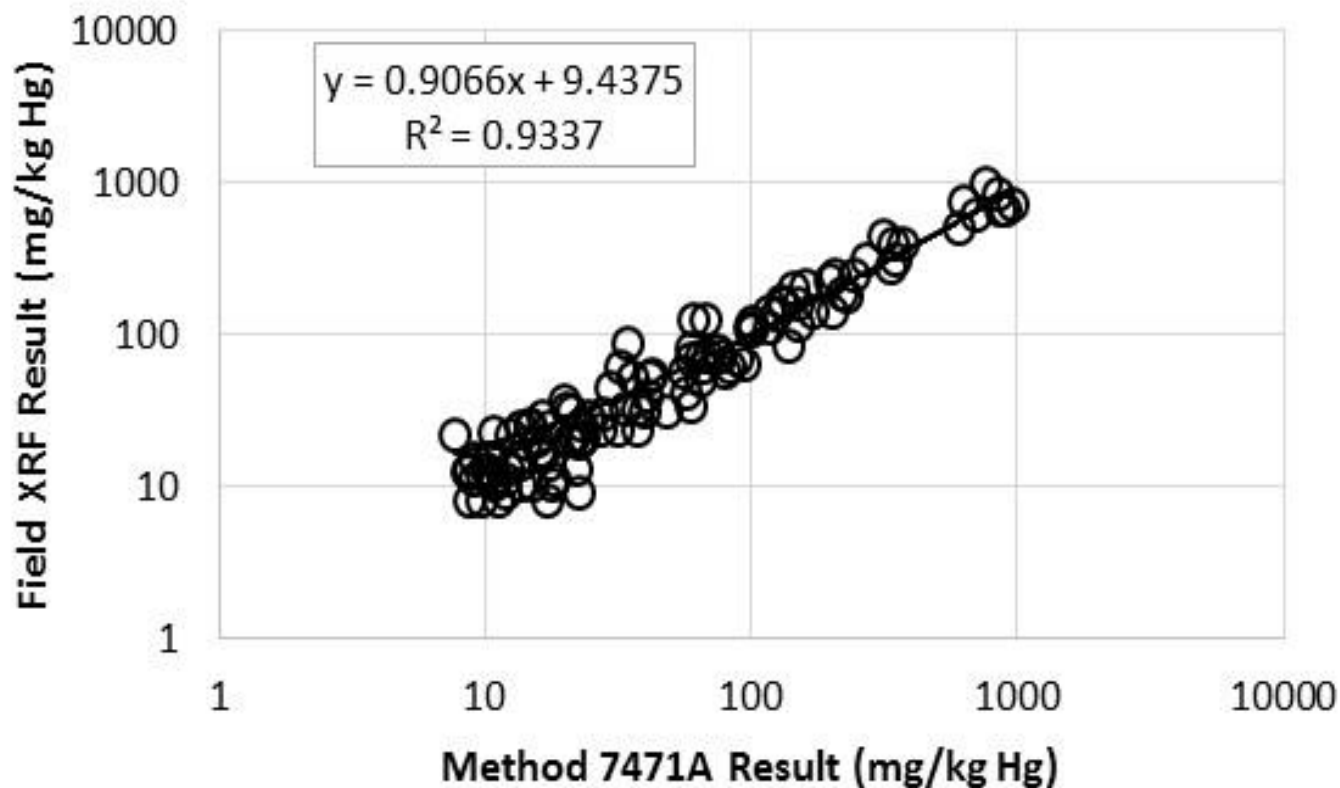
Results: Accuracy of Spiked Samples

- Matrix Spike Samples
 - Very good recovery: Average = 102%
 - Excellent fit: $R^2 = 0.9999$



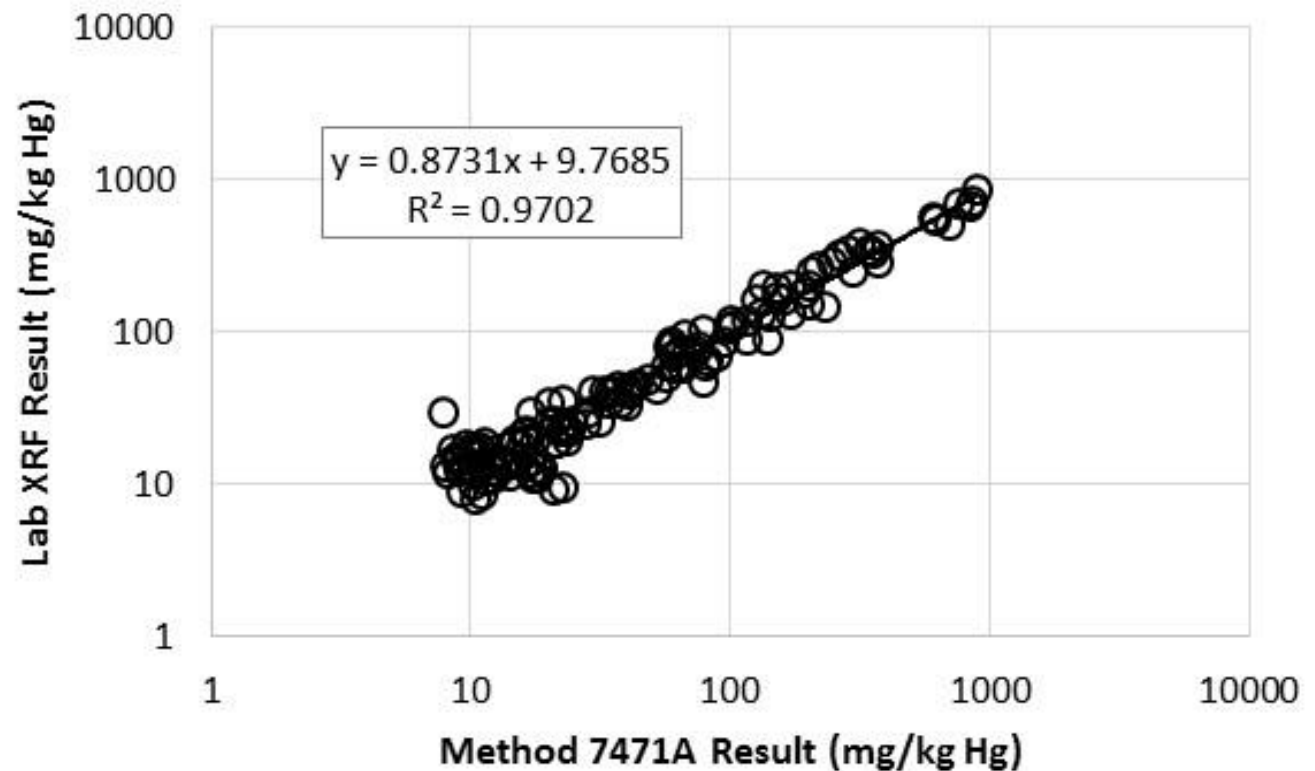
Results: Accuracy of Field XRF Measurements

- Field XRF Measurements
 - Very good agreement with Method 7471A: $R^2 = 0.9337$



Results: Accuracy of Lab XRF Measurements

- Lab XRF Measurements
 - Agreement increases slightly in lab: $R^2 = 0.9702$



Results: Precision of Field XRF Measurements

- Field XRF Measurements
 - Precision is comparable to (and slightly more precise than) Method 7471A

Statistic	XRF Field Precision		Method 7471A Precision
	Measurement Triplicates	Sample Triplicates	Field Duplicates
N	16	33	39
Mean CV	3.0%	19%	25%
25%tile CV	1.2%	9.6%	4.4%
Median CV	1.9%	18%	19%
75%tile CV	4.7%	29%	26%
95%tile CV	8.5%	43%	95%

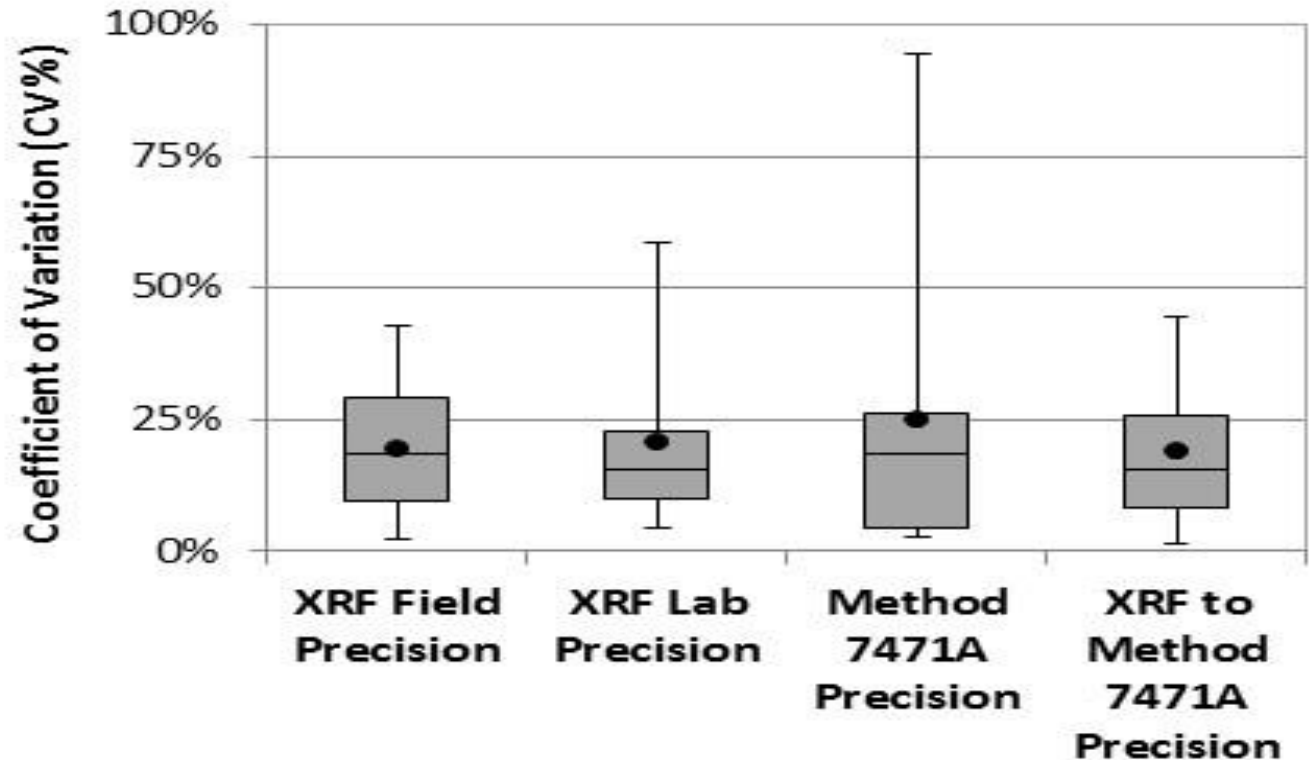
Results: Precision of Lab XRF Measurements

- Lab XRF Measurements
 - Precision is comparable to (and slightly more precise than) Method 7471A

Statistic	XRF Laboratory Precision		Method 7471A Precision
	Measurement Triplicates	Sample Triplicates	Field Duplicates
N	135	135	39
Mean CV	9.9%	21%	25%
25%tile CV	2.6%	10%	4.4%
Median CV	6.0%	15%	19%
75%tile CV	15%	23%	26%
95%tile CV	30%	59%	95%

Results: Precision Comparison With Method 7471A

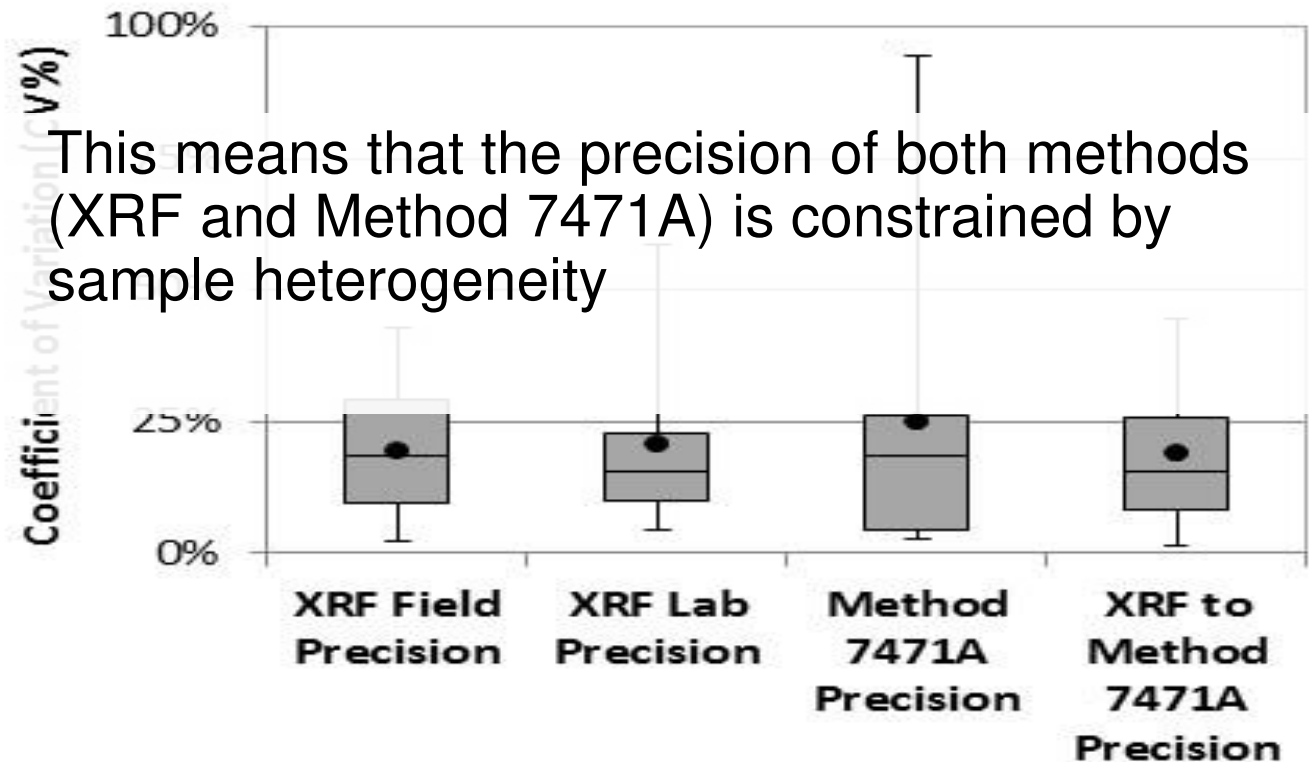
- No difference between precision of XRF and Method 7471A measured on field duplicates or between XRF and 7471A results on same sample



Results: Precision Comparison With Method 7471A

- No difference between precision of XRF and Method 7471A measured on field duplicates or between XRF and 7471A results on same sample

- This means that the precision of both methods (XRF and Method 7471A) is constrained by sample heterogeneity



Summarized Findings

- Accuracy of detection at the 7.4 ppm level is very good – general agreement at the detection level between methods
- Accuracy throughout the range of 7.4 to 1000 ppm is very good – based on comparison with Method 7471A and comparison to known spiked amounts
- Precision is comparable to Method 7471A and constrained by sample heterogeneity
- In summary, XRF method produces quick, real-time Hg results with equivalent accuracy and precision to the traditional analytical methods



Demonstrated and Potential Uses

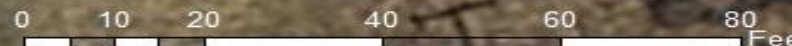
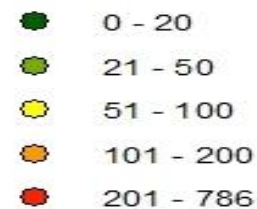
1. More efficient bank characterization
 - Ability to increase density of transects in response to Hg levels
 - Provides quicker results and avoids field re-deployments





Surficial Soil Composites

Hg (ppm)



Protocol

- Bracket each surficial soil transect that has more than two intervals >20 ppm Hg with additional transects as close as 25 ft.

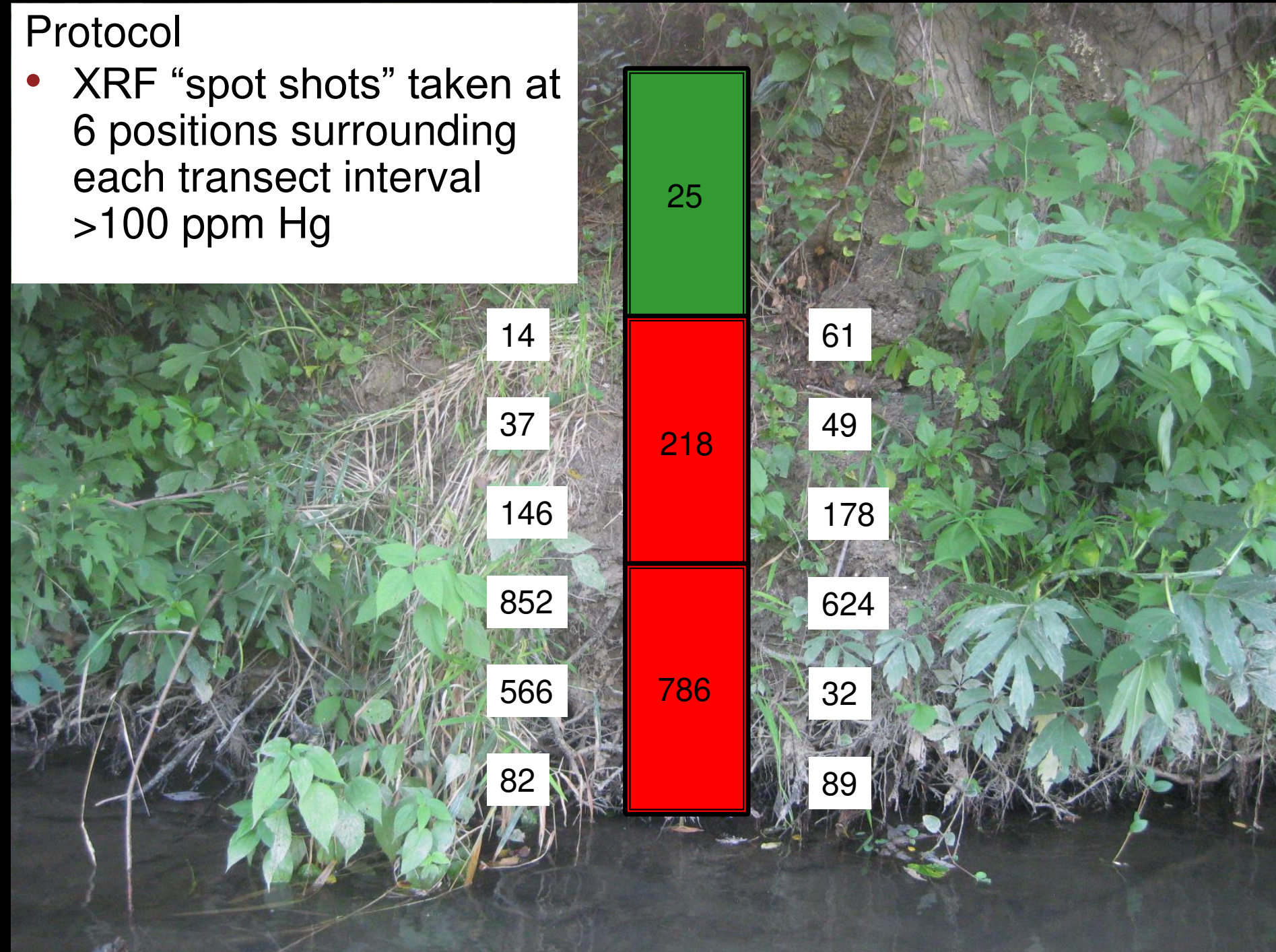
Demonstrated and Potential Uses

1. More efficient bank characterization
 - Ability to increase density of transects in response to Hg levels
 - Provides quicker bank characterization results and avoids field re-deployments
2. Confirmation and delineation of high Hg bank soils



Protocol

- XRF “spot shots” taken at 6 positions surrounding each transect interval
>100 ppm Hg



Demonstrated and Potential Uses

1. More efficient bank characterization
 - Ability to increase density of transects in response to Hg levels
 - Provides quicker bank characterization results and avoids field re-deployments
2. Confirmation and delineation of high Hg bank soils
3. Quick investigation of interesting features (highly eroding banks, tree falls, etc.)





26

19

38

<7.4

<7.4

Demonstrated and Potential Uses

1. More efficient bank characterization
 - Ability to increase density of transects in response to Hg levels
 - Provides quicker bank characterization results and avoids field re-deployments
2. Confirmation and delineation of high Hg bank soils
3. Quick investigation of interesting features (highly eroding banks, tree falls, etc.)
4. Confirmation of removal extents during construction

