Application of FPXRF Technology and Field Expedient Sample Preparation Techniques

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Overview

Field-portable X-ray Fluorescence (FPXRF)

- Site screening procedure using a small, light weight, hand-held portable instrument.
- Measure inorganic elements when used with the proper radioisotope/X-ray source and the appropriate standards.
- Addresses the need for a *rapid* turnaround (~2 min./sample), *low-cost* method for the in situ analysis of inorganic contaminants.
- Traditional laboratory methods = days to weeks per sample to complete; significantly higher cost.
- Capable of the simultaneous analysis of up to 25 elements.
- Some FPXRF instruments have multiple radioisotope sources allowing the researcher to expand the list of analytes and to select the source which will provide the best quantitation of the element(s) of concern.

RCRA Analytes by FPXRF

- Antimony (Sb)
- Arsenic (As)
- Barium (Ba)
- Cadmium (Cd)
- Chromium (Cr)
- Cobalt (Co)
- Copper (Cu)
- Lead (Pb)
- Mercury (Hg)
- Nickel (Ni)
- Selenium (Se)
- Silver (Ag)
- Thallium (Tl)
- Tin (Sn)
- Vanadium (V)
- Zinc (Zn)

Non-RCRA Analytes by FPXRF

- Aluminum (Al)
- Calcium (Ca)
- Iron (Fe)
- Magnesium (Mg)
- Manganese (Mn)
- Molybdenum (Mo)
- Phosphorus (P)
- Potassium (K)
- Rubidium (Rb)
- Silicon (Si)
- Strontium (Sr)
- Thorium (Th)
- Titanium (Ti)
- Zirconium (Zr)

“Light" elements (Z<16/12) cannot be detected

- Lithium (Li), Beryllium (Be), Sodium (Na)

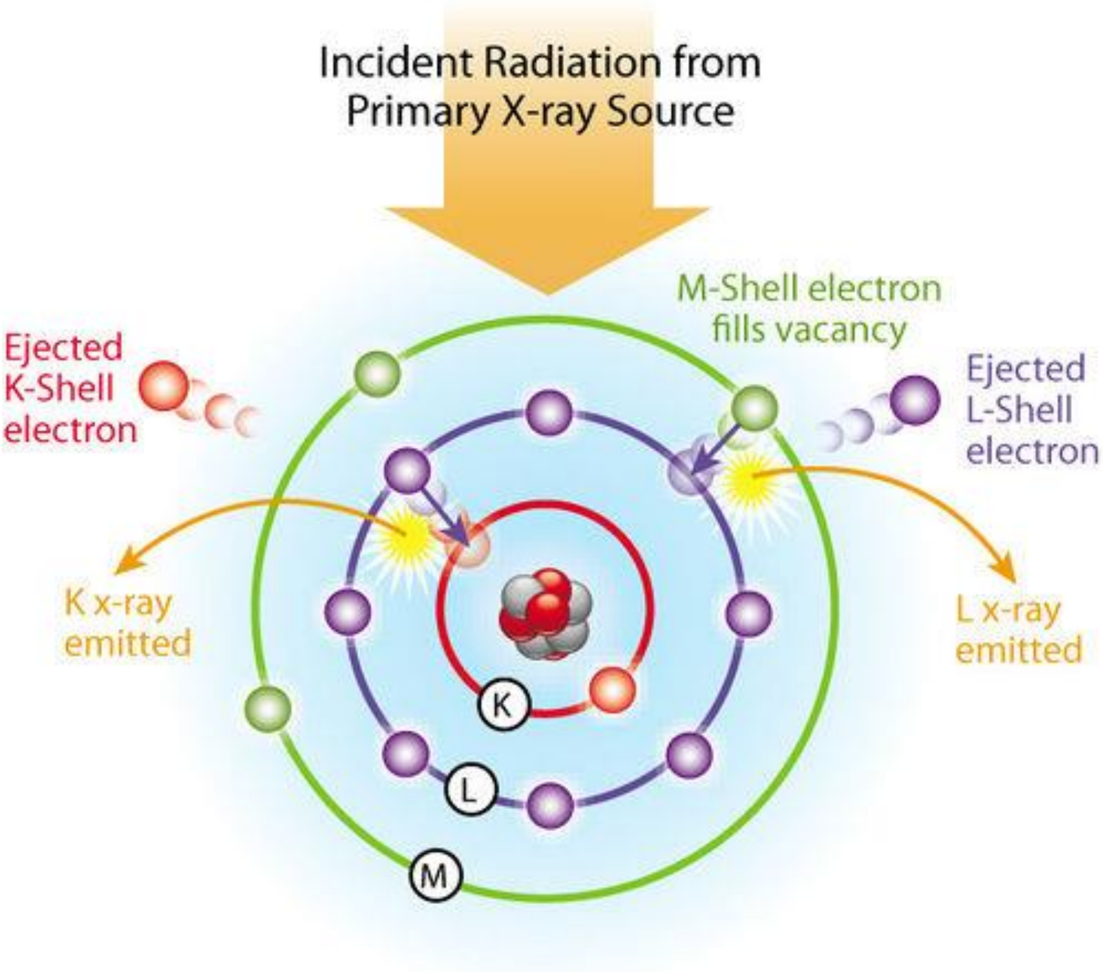
FPXRF Screening Method

- Rapid “field” screening procedure.
- Requires confirmatory lab analysis (e.g., AA, ICP-AES, ICP-MS).
- Lower detection limits are typically above the toxicity characteristic regulatory level for most RCRA analytes.
- Often can be used to meet project-specific data quality objectives (DQOs).
- Fast, powerful, cost effective technology for site characterization.

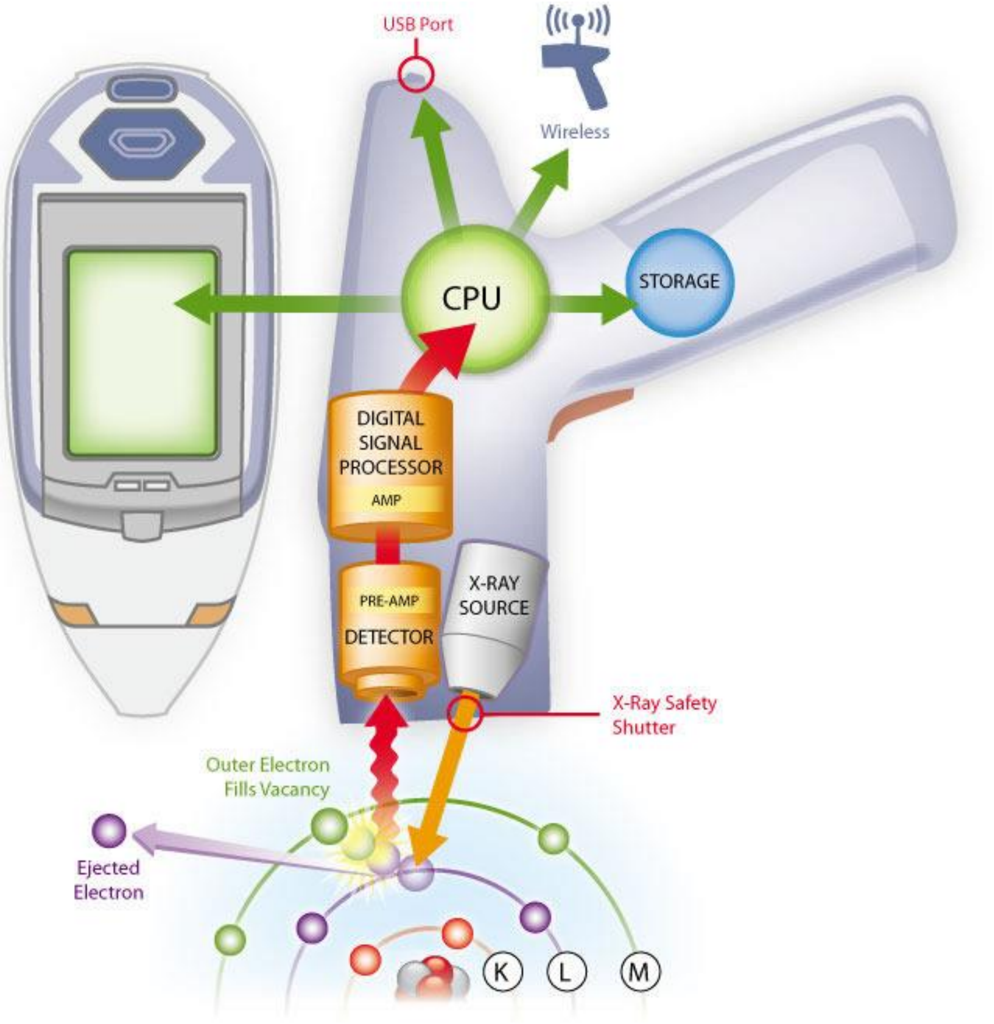
Principle of X-ray Fluorescence

The principle of X-ray fluorescence is based on the fact that each element will fluoresce in a unique and characteristic way when “excited.”

XRF Theory


Incident Radiation from
Primary X-ray Source
M-Shell electron
fills vacancy
Ejected
K-Shell
electron
Ejected
L-Shell
electron
K x-ray
emitted
L x-ray
emitted
K
L
M

Applied XRF Theory



Method Sensitivity
(Lower Detection Limit)

- Analyte of interest
- Type of detector used (GOLDD™ technology)
- Type of excitation source (X-ray source)
- Strength of the excitation source
- Count times used to irradiate the sample (60s)
- Physical matrix effects (moisture)
- Chemical matrix effects
- Interelement spectral interferences

GOLDD™ technology

- **Thermo Scientific Niton FXL, Niton XL3t, and the Niton XL2 FPXRFs**
- **Geometrically Optimized**
  - Geometry of detector optimized to be as close to sample as possible
  - Increased voltage from 40 kV to 50 kV
- **Large Drift Detector**
  - Large surface area detector
  - Process over 180,000 detector events/sec
- **X-ray tube source instead of radioactive source (Niton XL3t, Innov-X FP-XRF)**

Interferences

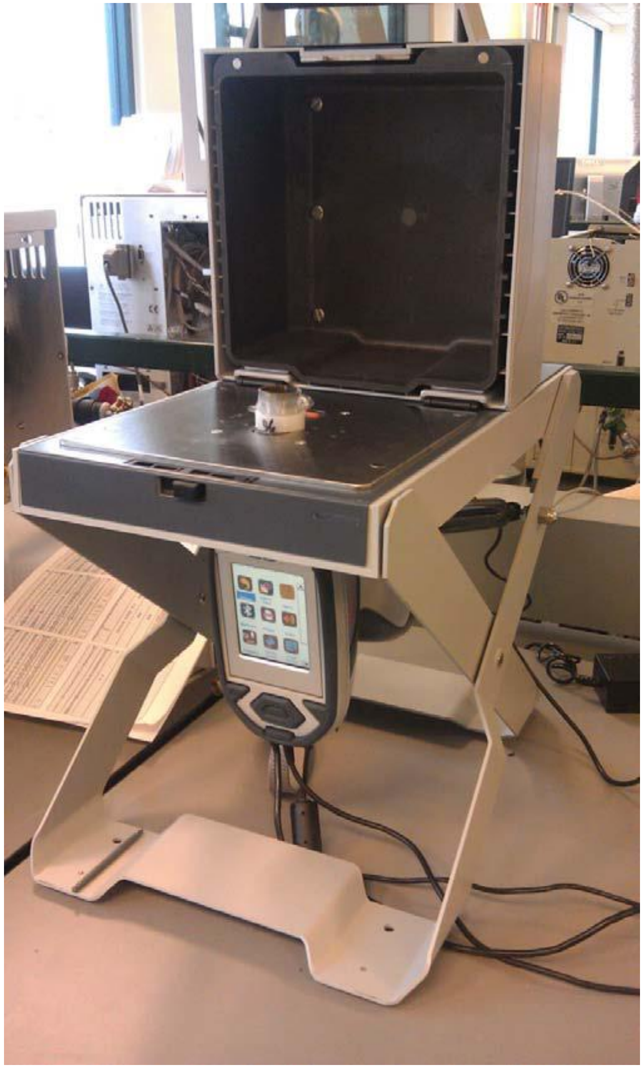
- Instrument precision is the least significant source of error
- User- or application-related error is generally more significant and varies with each site and method used.
- Some sources can be minimized or controlled by the instrument operator, but others cannot.

Physical Matrix Effects

- Particle size
  - very large particles may skew results
- Uniformity
  - Distribution of very fine grain material in coarser matrix
- Homogeneity
  - Largest impact on comparability with confirmatory lab samples
- Surface condition
- Moisture
  - 5 – 20% minimal impact, saturated samples moisture can be major source of error. Oven dry, do not microwave

Sample Position

- X-ray signal decreases as the distance from the source increases.
- Inconsistent positioning of samples in front of the probe window is a potential source of error
- Minimized by maintaining the same distance between the window and each sample.



Sample Position

Chemical Matrix Effects

- Due to differences in the concentrations of interfering elements.
  - Spectral interferences (peak overlaps)
  - X-ray absorption and enhancement phenomena.
- Both effects are common in soils contaminated with heavy metals.

  e.g., Fe tends to absorb copper Cu x-rays, reducing the intensity of the Cu measured by the detector, while chromium Cr will be enhanced at the expense of Fe because the absorption edge of Cr is slightly lower in energy than the fluorescent peak of iron.

Case Study 1 - Wisconsin

- Arsenic Sediment Removal Project
- Develop a rapid assessment tool to directly measure total As content of the wet dredge material (DM) without the drying typically required by USEPA Method 6200.
- FPXRF prone to signal interference when analyzing high moisture content samples
- Comparison was made between the accuracy of the XRF versus ICP-OES.

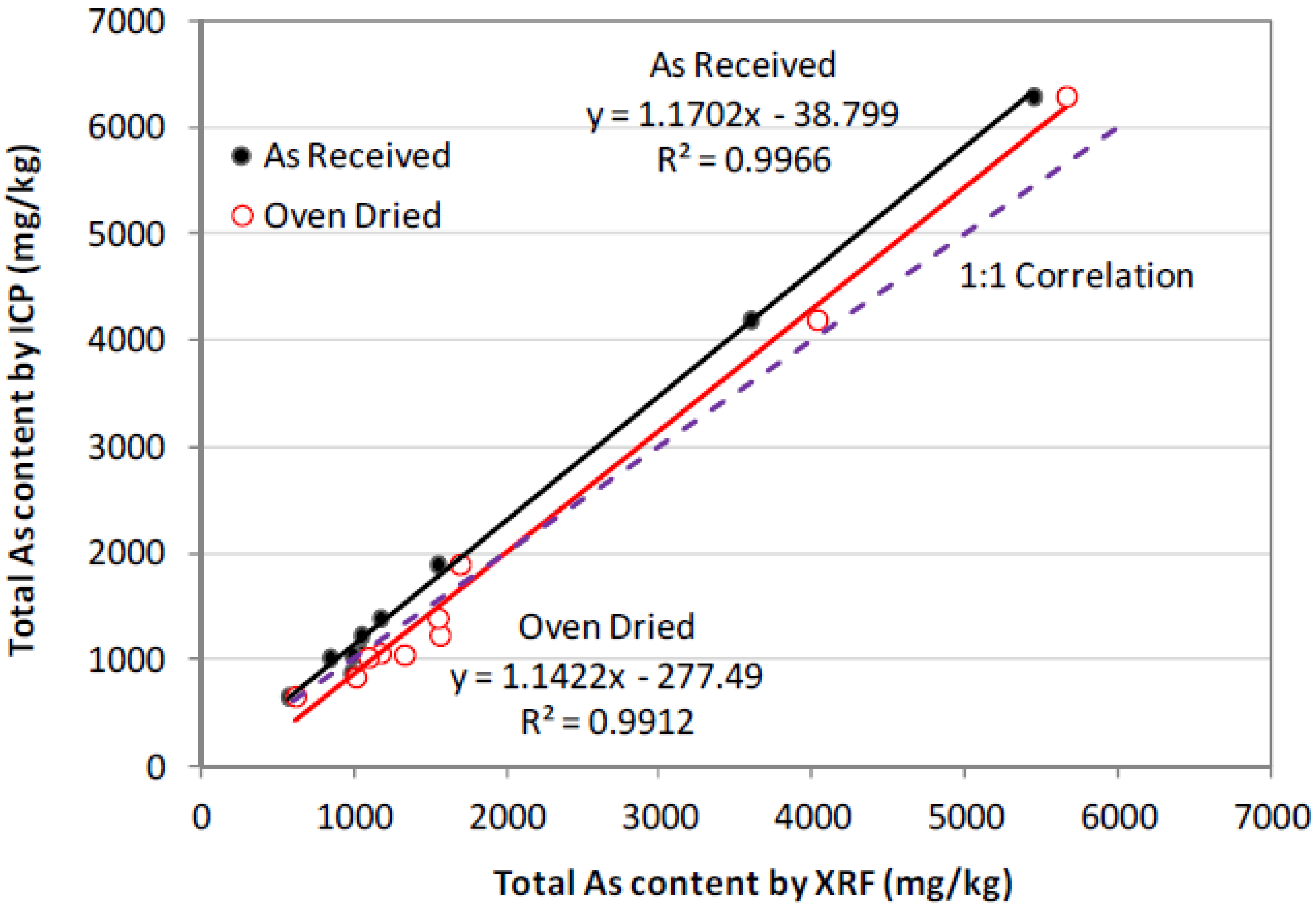
DM Source Materials

- Two main types of DM at the project site
  - Soft, fresh DM primarily comprised of fine-grained material and organic matter typically has the highest total (7,000 mg/kg) and TCLP As (40 mg/L).
  - Semi-consolidated material (SCM) of silty-sandy with moderate total As contents (2,000 mg/kg), but elevated leaching (TCLP-As 30 mg/L).
- Materials selected to evaluate high variability in terms of soil type and total As of the DM characteristic of the project site.

Testing Method

- Thermo Fisher Niton FPXRF model XL3t 600
- Manufacture test stand.
- Each DM sample was analyzed for total As at field moisture and oven-dried.
- DM samples homogenized with a wood spatula, then placed in a sample cup with a Mylar film cover.
- Sample time was integrated over 30 seconds.
- Same DM samples were dried at 105°C for 2.5 hours, then ground.
- Dried sample was analyzed in the same manner as the as-received material.

Results


7000
6000
5000
4000
3000
2000
1000
0
Total As content by ICP (mg/kg)
● As Received
○ Oven Dried
As Received
y = 1.1702x - 38.799
R² = 0.9966
1:1 Correlation
Oven Dried
y = 1.1422x - 277.49
R² = 0.9912
0
1000
2000
3000
4000
5000
6000
7000
Total As content by XRF (mg/kg)

Conclusions

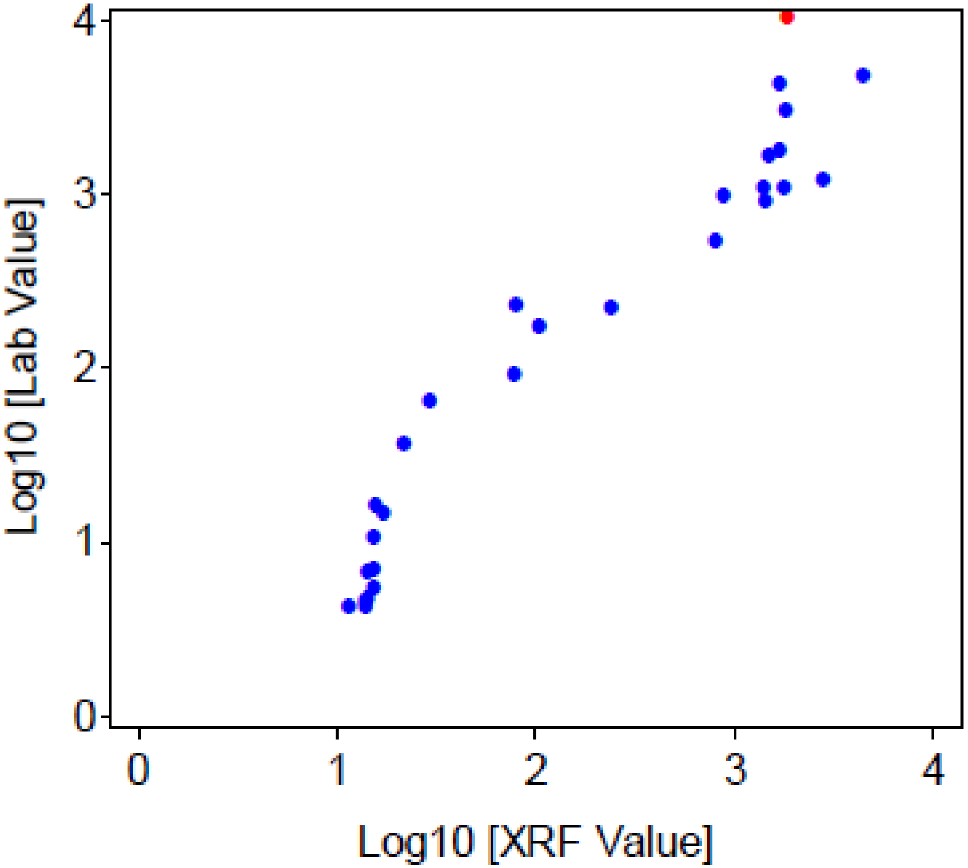
- Very high correlation between wet and/or dry XRF measurements and those analyzed by USEPA Method 6010.
- Since the bias is consistent, there is no significant value in drying materials or additional sample preparation before XRF analysis.
- Wet XRF samples must be well homogenized and free of large debris such as rocks or twigs
- Split samples should be analyzed by USEPA Method 6010 (or the equivalent) at prescribed intervals during field operations

Case Study – 2

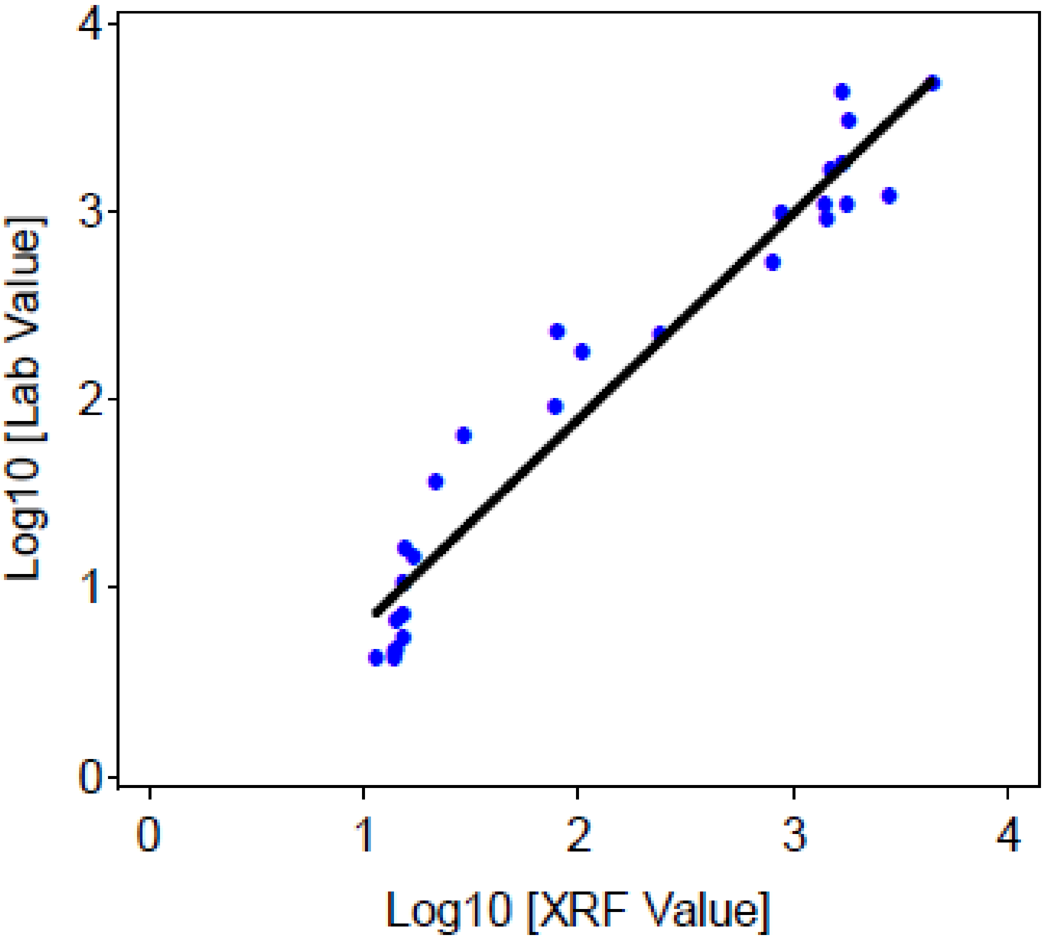
- Oven-dried surface and subsurface soil samples analyzed for Pb using FPXRF
- Splits were submitted for ICP-MS confirmatory analysis
- Correlation and regression analyses were used to compare XRF and laboratory ICP data for Pb using soil XRF-Lab pairs (n = 28)
- One pair of data was found to be an “influential pair” due to large disparity between the XRF and Lab reported values.
- The influential pair was removed from the regression analysis

Results

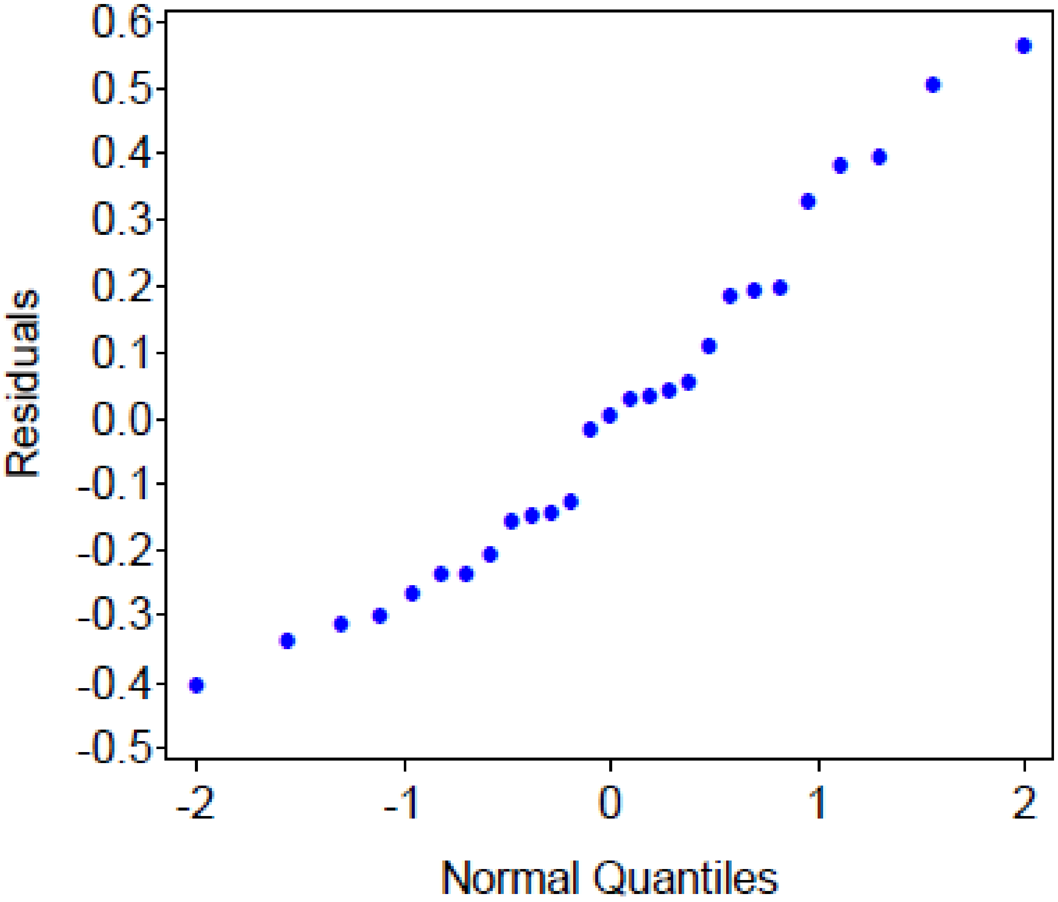
- **XRF-Lab pairs with influential pair shown in red**



Regression



Probability Plot of Regression Residuals



- reasonable adherence of the residuals (difference between measured and modeled values) to a normal distribution

Conclusions

Advantages

- Low cost analyses
- Ease of operation
- Portable, moves to any site
- Rapid results (real time)
- Surface sampling

Limitations

- Complex data interpretation (for geostatistical investigations)
- Matrix variability
- Type of soil influences results
- Interelement interferences
- Less sensitive than a complete CLP analysis

Questions?

Case Study – 3

- FPXRF used in mobile “lab” to analyze soil samples in an ex-situ manner from various grid locations from the OU-4 project in Region 6 of the Tar Creek Superfund Site
- Developed dedicated sample analysis