Generating Quality Metals Data at Sites using Field-Portable XRF

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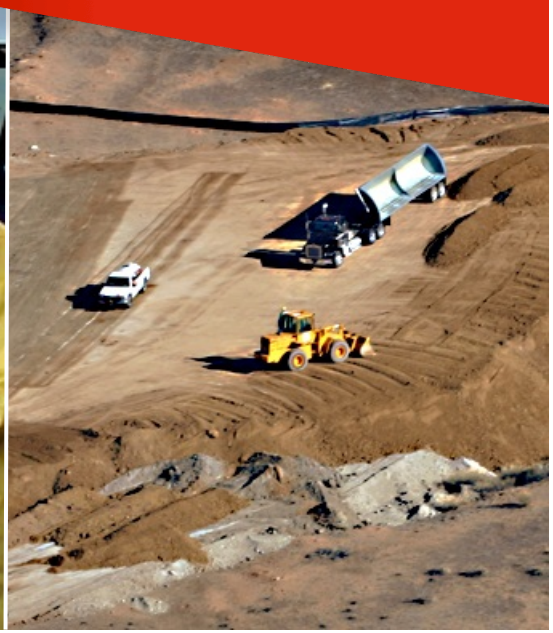

What is Quality Data?

- Quality data is of known and documented quality appropriate for its intended use.
- Quality data can thus include both screening and definitive data, depending on the end use of the data.
- Field-portable XRF can generate both screening and definitive data, depending on the instrumentation used; and the sample collection, preparation and analytical procedures employed.

How Do We Document the Quality of the Data?

- **Accuracy**: The degree of agreement of a measurement to an accepted reference or true value.
  - ✓ *Accuracy is demonstrated by use of NIST-traceable calibration checks and splits with off-site laboratories, where appropriate*

- **Precision**: The measure of variability between individual sample measurements under prescribed conditions.
  - ✓ *Precision is demonstrated by measuring a minimum of 3 replicate samples, with a goal of %RSDs of less than 20%*
  - ✓ *This is the same criteria used in EPA Methods 6010 and 6020*

How Do We Document the Quality of the Data?

- **Representativeness**: The degree to which data accurately and precisely express a characteristic of a population, parameter variations at a sampling point, or an environmental condition.
  - ✓ *The robust sample preparation steps and "flipping" the sample between replicates ensures the method provides data that is representative.*
  - ✓ *Formalized preparation and analytical requirements in written SOPs also ensures representative data.*

Generating Quality Metals Data using XRF

Key Elements of Methodology?

- Based on EPA Method 6200
- Comprehensive SOPs covering both sample preparation and analysis
- Key elements of the methodology include:
  - ✓ *Preparation of the samples*
  - ✓ *Use of multiple NIST-traceable standards*
  - ✓ *Replicate analyses of all samples*
  - ✓ *Monitoring of %RSD of key elements*

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Standard Operating Procedure

Field Analytical Methods: Olympus Innov-X X-50 and X-5000 Portable X-Ray Fluorescence (XRF) Analyzers for Metals in Soil

PR-TC-02.05.02.05 v1.3

Date: 18 Dec 2012

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Standard Operating Procedure

Field Analytical Methods: Innov-X Alpha 4400 Portable X-Ray Fluorescence Analyzer (XRF) for Metals in Soil

PR-TC-02.05.02.01 v1.2

Reviewed by: Dennis Rich Date: 30 September 2009

Reviewed by: Kristen Carylon, Senior Chemist Date: 30 September 2009

Approved by: Jeffrey Hess, Director Technical Services Date: 30 September 2009

Review / Revision History:

Version	Changes	Affects Section/Pages	Review / Revision Date	Approval*
1.0	Initial release	–	30 Sep 2009	–
1.1	Updated NIST soil standards and values	App. B / pgs. 19–30	02 Jan 2014	J Hess
1.2	Updated organization name. No other changes needed.	All	6 Aug 2014	

* Approval required for reviews and minor changes only. Substantive revisions to the technical requirements contained in the SOP require review and approval by the signatures to the SOP.

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Generating Quality Metals Data using XRF

Innov-X Alpha 4000 Handheld XRF

Convenient handheld detector with limits of detection (LOD) well below EPA Method 6200 guidelines

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10-40kV, 10-50 µA X-ray tube

Silicon PIN diode detector (<230 eV resolution)

Olympus X-5000 Benchtop XRF

Lower LOD and shorter analysis times than typical handheld detector, due to a more powerful x-ray tube and more sensitive detector

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50kV, 200 µA x-ray tube

Large-area silicon drift detector (<165 eV resolution)

Sample Collection and Processing

- Collect representative samples of the geologic materials
- Describe the samples on the sample collection logs
- For granular samples:
  - ✓ Remove visible debris and note description of debris on the sample collection logs
  - ✓ If the samples are wet (> 20% moisture), then dry in an onsite oven
  - ✓ Sieve the samples using a #10 mesh (2 mm) sieve to remove organic materials and smaller debris
  - ✓ Optionally, further homogenize the samples by crushing and passing through a #100 sieve (same as rock samples on next page)

Sample Collection and Processing

- For solid samples, crush the samples using a Plattner Mortar
- Sieve to pass a #100 mesh sieve to homogenize the samples
- Place the samples in small plastic bags for analysis

Instrument Startup and Calibration

- Power on the unit and allow it to warm up
- Standardize the unit using a "coin" of known metallic content
- Perform an initial calibration verification (ICV), consisting of replicate analyses of:
  - ✓ *A blank sample (synthetic quartz)*
  - ✓ *A minimum of 2 NIST traceable standards of different target analyte concentrations*

Continuing and Ending Calibration

- Continuing calibration verifications (CCVs) are performed during the day (typically at 4-hour intervals)
- A closing CCV is performed at the end of each day
- If a CCV fails, samples analyzed after the last successful CCV and prior to the unsuccessful CCV are reanalyzed

Sample Analysis

- Place the sample on the XRF analyzer and initiate analysis
- 3 consecutive measurements are performed for each sample, flipping or rotating the sample bag between each measurement
- The %RSD for the 3 replicate measurements is calculated for each target analyte
- If the %RSD is > 20%, an additional 3 replicate measurements are performed

Sample Analysis

- The readings for the 3 measurements is averaged, and the averaged result is used as the reported concentration for the sample.

- For samples with 2 sets of 3 measurements, the average of the set of 3 measurements with the lowest %RSD for the target analytes is selected

Example Daily Analytical Logbook

Log of Analysis – X-5000 X-Ray Fluorescence Instrument

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Project Name: _____ Project Number/Task Code: _____

Sample ID	Date	Time	Analyst	Instrument Serial No.	Mode	Scan Length[1] (seconds)	No. of Scans[2]
Sample Description/Comments:							

Sample ID	Date	Time	Analyst	Instrument Serial No.	Mode	Scan Length[1] (seconds)	No. of Scans[2]
Sample Description/Comments:							

(1) Default length of scans is 120 seconds per beam.
(2) A minimum of three (3) scans are required for definitive analysis, or until the relative standard deviation of the scans is less than 20% for those target elements with values greater than 2x of their approximate instrument reporting limit.

Analysts Signature: _____ Date: _____

Example Daily Analytical Spreadsheet

Sample ID	Processed Date	Run Time	Reading	As	As +/-	Cr	Cr +/-	Pb	Pb +/-	As Average	%RSD (As)	Cr Average	%RSD (Cr)	Pb Average	%RSD (Pb)
Cal Check			1												
SiO2-062714-r1	27-Jun-14	180	2	<2.0		<1.7		<2.5							
SiO2-062714-r2	27-Jun-14	180	3	<2.0		<1.7		<2.5		0.0	NA	0	NA	0	NA
SiO2-062714-r3	27-Jun-14	180	4	<2.0		<1.6		<2.6							
2710a-062714-r1	27-Jun-14	180	5	1561	12	35	4	5560	25						
2710a-062714-r2	27-Jun-14	180	6	1582	12	35	4	5559	25	1566.3	0.9%	34	6.9%	5557	0.1%
2710a-062714-r3	27-Jun-14	180	7	1556	12	31	4	5552	25						
2711a-062714-r1	27-Jun-14	180	8	108	4	54	3	1427	8						
2711a-062714-r2	27-Jun-14	180	9	107	4	58	3	1414	8	106.0	2.5%	55	5.6%	1422	0.5%
2711a-062714-r3	27-Jun-14	180	10	103	4	52	3	1424	8						
MRSED-01-0.5-r1	27-Jun-14	180	11	46	2	92	4	245	3						
MRSED-01-0.5-r2	27-Jun-14	180	12	51	2	88	4	293	3	49.0	5.4%	88	4.5%	291	15.5%
MRSED-01-0.5-r3	27-Jun-14	180	13	50	2	84	4	335	3						
SiO2-062714-r4	27-Jun-14	180	14	<2.0		<1.6		<2.6							
SiO2-062714-r5	27-Jun-14	180	15	<2.0		<1.5		<2.5		0.0	NA	0	NA	0	NA
SiO2-062714-r6	27-Jun-14	180	16	<2.0		<1.6		<2.5							
2710a-062714-r4	27-Jun-14	180	17	1577	12	37	4	5547	25						
2710a-062714-r5	27-Jun-14	180	18	1591	12	39	4	5565	25	1577.7	0.8%	36	10.0%	5550	0.3%
2710a-062714-r6	27-Jun-14	180	19	1565	12	32	4	5537	24						
2711a-062714-r4	27-Jun-14	180	20	109	4	52	3	1431	8						
2711a-062714-r5	27-Jun-14	180	21	101	4	51	3	1436	8	107.3	5.3%	51	2.0%	1435	0.3%
2711a-062714-r6	27-Jun-14	180	22	112	5	50	3	1438	8						

Representative Precision and Accuracy Study

- Multiple (9 or more) readings of NIST standard 2710a were taken using 3 different XRF instruments:
  - ✓ 2 Innov-X Alpha handheld units (SN #6009 and 9767)
  - ✓ 1 Olympus X-5000 benchtop unit

Instrument	Alpha-6009	Alpha-9767	X-5000	Alpha-6009	Alpha-9767	X-5000
Element	Arsenic			Lead		
NIST 2710A	Published Value: 1,540 ± 10 ppm			Published Value: 5,520 ± 30 ppm		
Average	1,800 ppm	1,570 ppm	1,590 ppm	5,460 ppm	4,930 ppm	5,570 ppm
RSD	1.40%	1.20%	1.70%	0.74%	0.79%	0.68%
% Recovery	117%	102%	104%	98.8%	89.2%	101%

Where Has XRF Been Used?

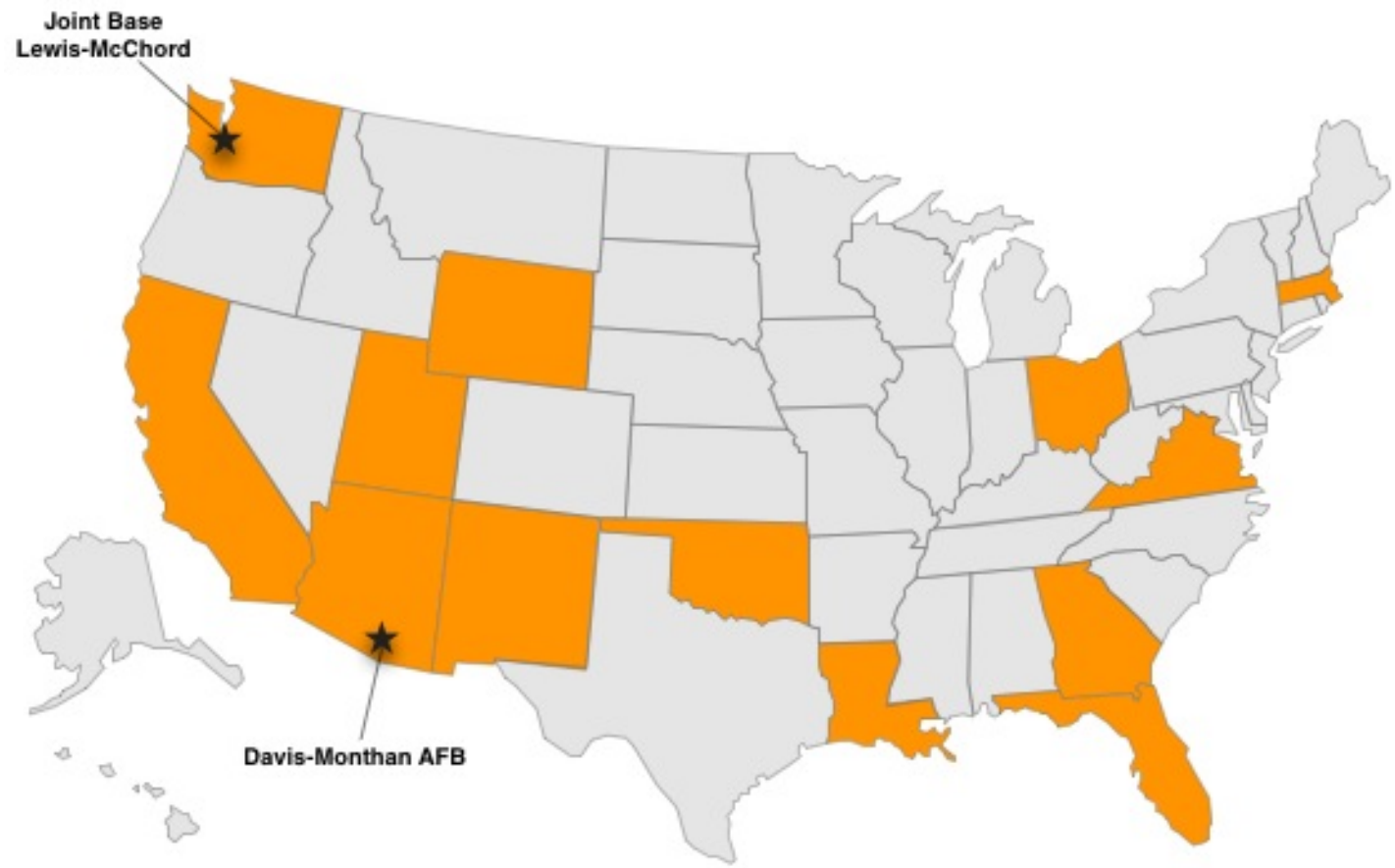
- Gilbane has employed field-portable XRF to characterize metals and metalloids in geologic materials at many sites throughout the U.S., including:

  1) *lead in soils and sediment at munitions response areas (MRAs)*

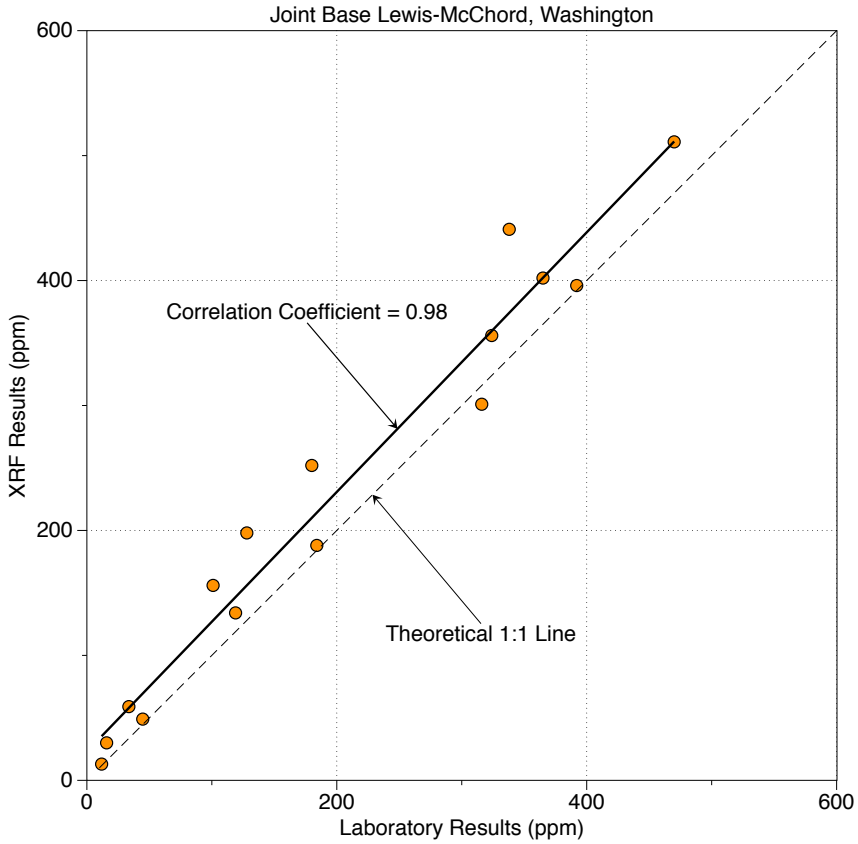
  2) *arsenic and heavy metals in rock, soil and sediment at a former naval facility in mountains of Southern California*

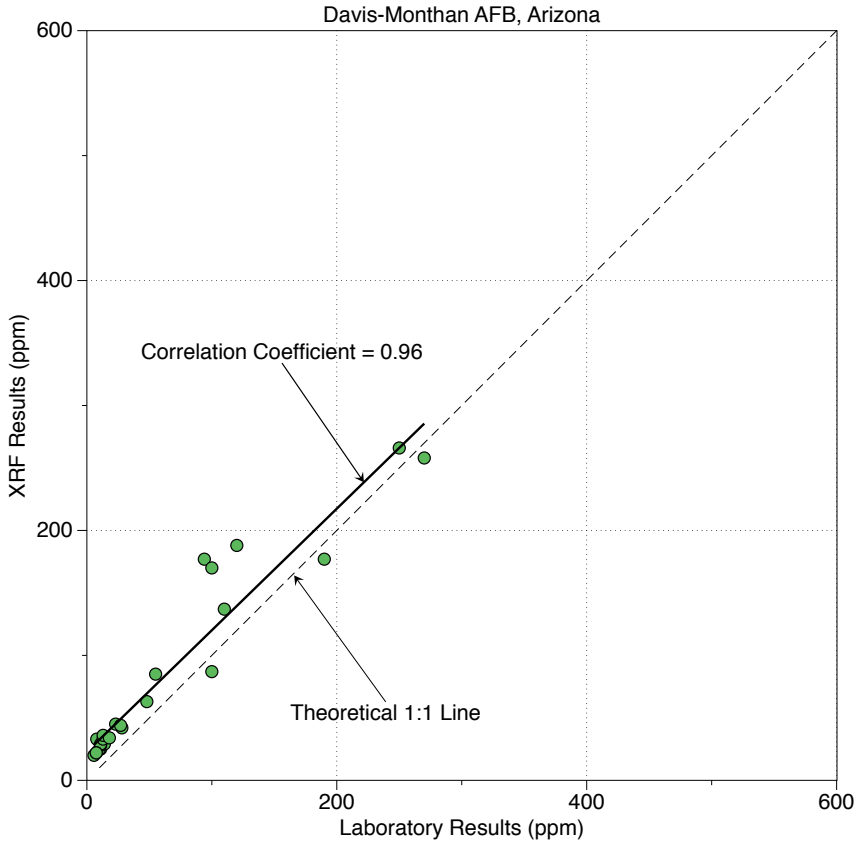
- For the Southern California site, field-portable XRF was subjected to 3rd party validation and yielded definitive data accepted by state regulators to support site closure.

Example 1 – Lead in Soil at MRAs



Representative Results for Lead in Soil

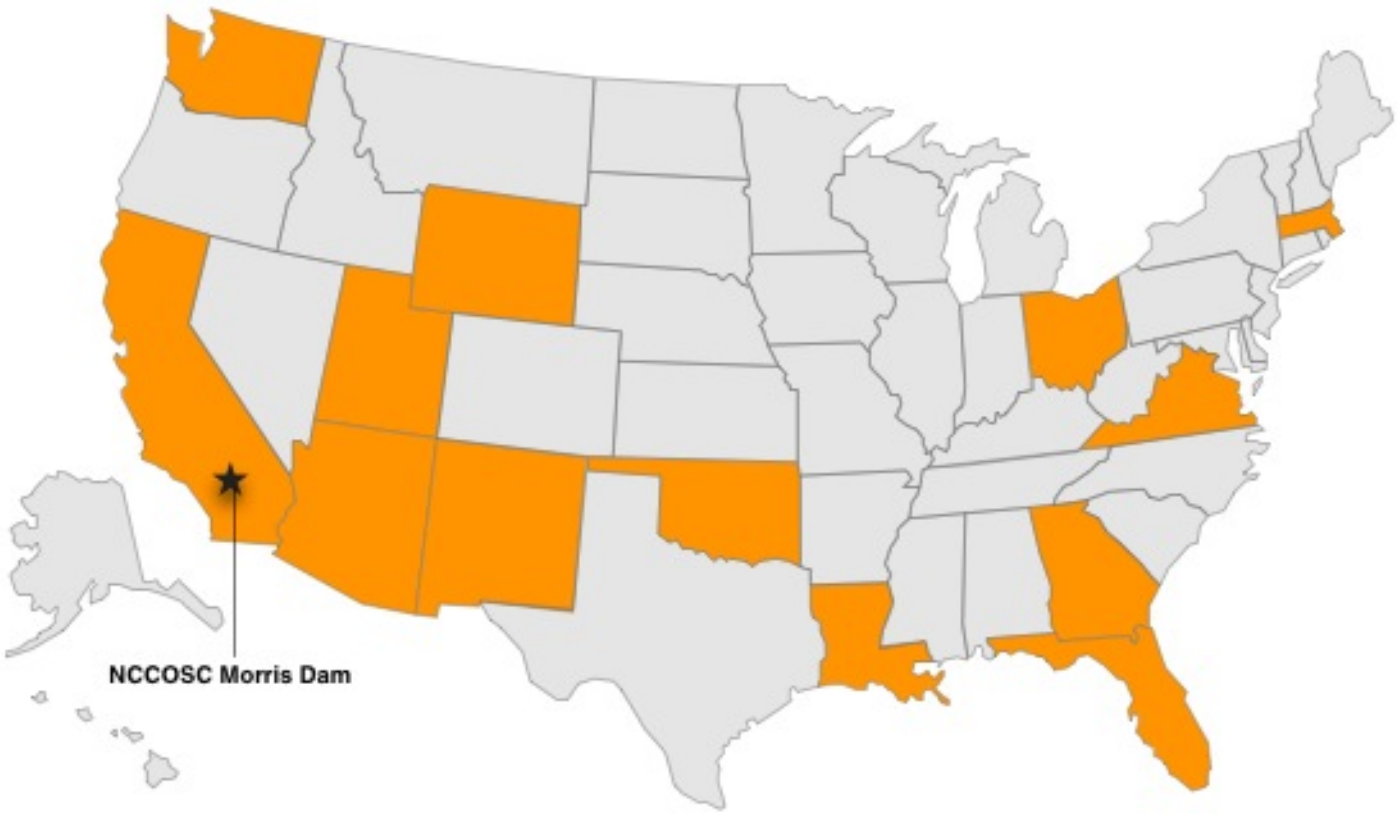




Representative Results for Lead in Soil

- Over 2,780 samples analyzed at more than a dozen active military facilities throughout the U.S., with an average correlation coefficient of 0.945
- Sites with samples containing lead up to 600 ppm (1.5x the RSL) exhibited very high correlation (0.9-1.0), and low %RSD (<10%)
- Sites with samples containing lead above 600 ppm still exhibited high correlation (0.7-0.9), but with moderate to high %RSD (often >20%)

Example 2 – Arsenic in Geologic Materials in California

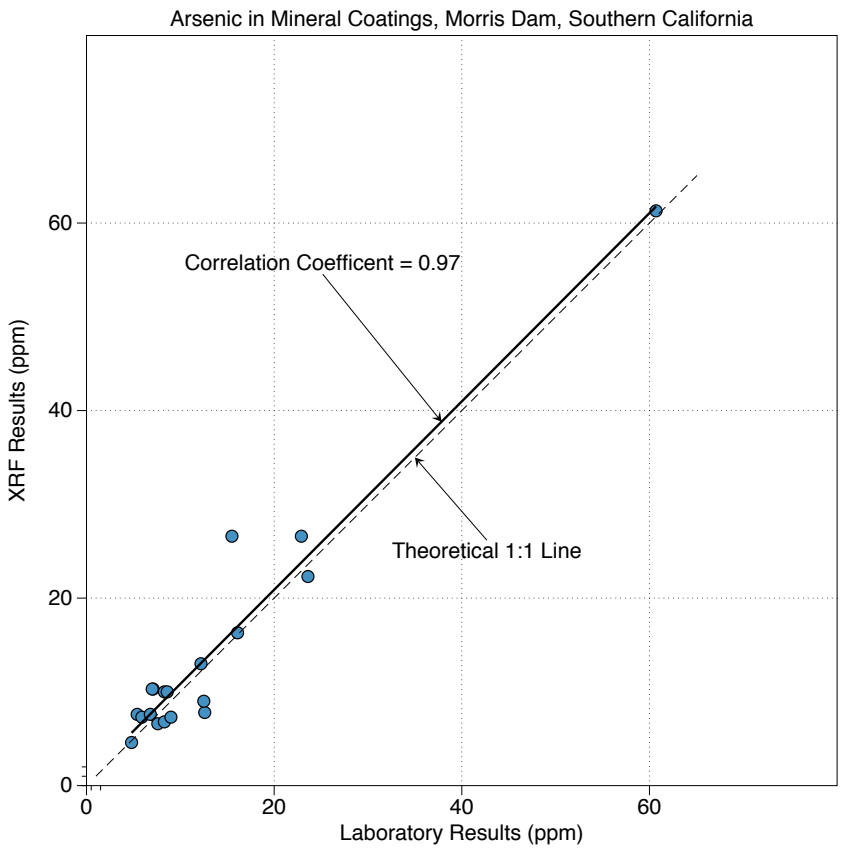


Representative Results for Arsenic in Soil and Sediment

- Three rounds of onsite XRF analyses:
  - ✓ *'Screening' analysis during removal of 10,000 CY of crushed rock backfill impacted with organic and inorganic contaminants*
  - ✓ *'Definitive' analysis during geochemical study of bedrock following completion of NTCRA*
  - ✓ *'Definitive' analysis during geochemical study of sediments in adjacent reservoir*
- Limited 'confirmation' analyses performed during geochemical studies, due to As being present in resistant mineral phases from regional hydrothermal mineralization
- EPA digestion methods only yield 'environmentally available' metals and metalloids

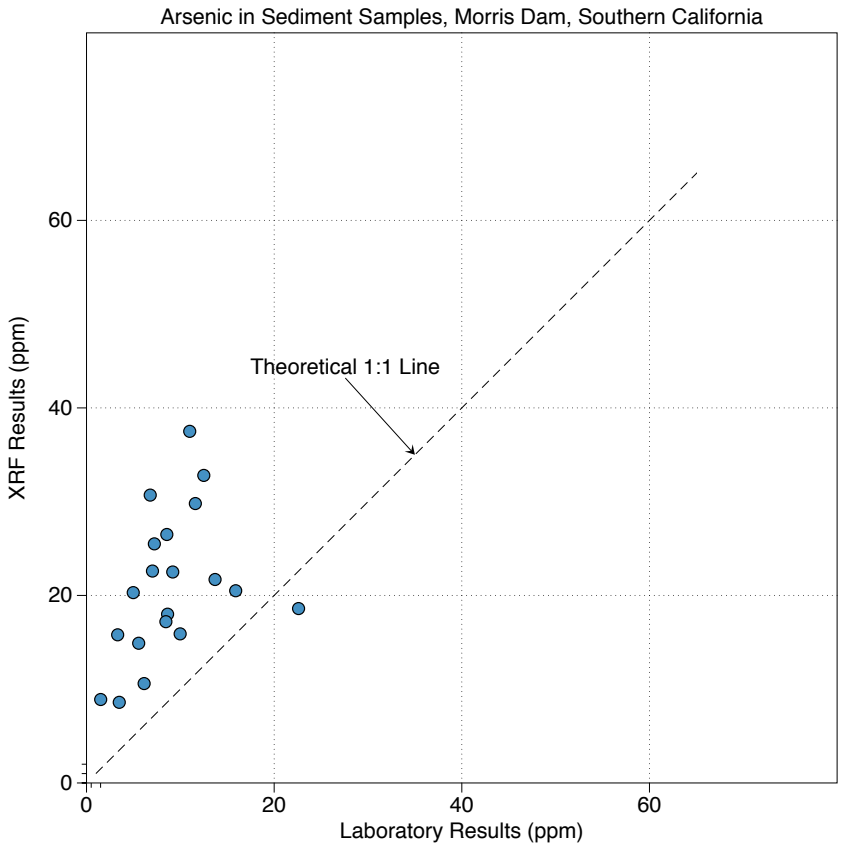
Representative Results for Arsenic in Mineral Coatings

- 'Screening' performed using handheld XRF (Alpha)
- Analyses performed on coatings present on rocks in fractured bedrock
- 19 samples analyzed for As by XRF and EPA 6010, with a correlation coefficient of 0.97, with
- Good match with 1:1 line



Representative Results for Arsenic in Sediment

- 'Definitive' analysis performed using benchtop XRF (X-5000)
- Analyses performed on coarse-grained sediments
- 20 samples analyzed for As by XRF and EPA 6020, with
  - ✓ *poor correlation*
  - ✓ *Poor match with 1:1 line*
- However, poor correlation was expected based on other geochemical analyses



Representative Results for Arsenic in Soil and Sediment

- XRF analysis of mineral coatings showed very high correlation with EPA methods
  - ✓ *Due in large part to the weathered state of the mineral coatings (hydrothermal minerals are no longer the dominant As-bearing phase)*
- XRF analyses performed on sediments showed poor correlation
  - ✓ *Due to the presence of hydrothermal minerals as the dominant As-bearing phase*
- Presence of As in hydrothermal mineralization was confirmed by optical petrography, x-ray diffraction, and electron microprobe

Conclusions

- Field portable XRF is a valuable tool for characterizing metals in a variety of geological materials
- Systematic testing methodology can produce data of known and documented quality appropriate for a variety of uses, including evaluation of human and ecological risk

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