1.0 XRF Analyses Performance Evaluation

1.1 Scope and Application

Due to the time and monetary costs associated with conventional analytical methods for measuring the concentrations of inorganic elements in environmental media, field-portable measurement technologies have been increasingly proposed as alternative approaches. These approaches often provide rapid and cost-effective results for site characterization and assessment. Field-portable X-Ray Fluorescence (XRF) analysis is one such technology that allows quick measurement of soil concentrations of inorganic elements.

Previous demonstration of method applicability (DMA) studies have evaluated the performance of XRF technologies to measure the concentrations of inorganic elements in a range of soil and sediment types (EPA 1998a, 1998b, 2006). These studies have concluded that the incorporation of XRF technologies in environmental sampling strategies can offer significant savings in time and costs compared to conventional fixed laboratory analyses. The purpose of this section is to evaluate the performance of the Innov-X XRF analyzer for the field screening and qualification of total uranium and molybdenum concentrations in soil samples at the Former Harshaw Chemical Site (hereafter, the site). The primary objectives of this report are to (1) quantify XRF accuracy and precision in measuring total uranium and molybdenum concentrations through XRF Quality Control (QC) analyses, (2) summarize the detection limits and analytical errors associated with the XRF analyses for total uranium and molybdenum, and (3) compare XRF analyses of total uranium concentrations to conventional fixed laboratory methods. Collectively, these objectives will be used to determine the applicability of XRF technology in determining the soil concentrations of total uranium and molybdenum at the site. The section concludes with recommendations about how best to deploy XRF technologies at the site in the future.

1.2 The INNOV-X System

Weighing approximately 3.3 lbs, the Innov-X XRF analyzer (hereafter, XRF) is a handheld field-portable device for measuring inorganic element concentrations in environmental media. The XRF generates x-rays from an internal x-ray tube that provides excitation energy to cause elements to emit characteristic x-rays (fluorescence). XRF spectroscopy analyzes the characteristic wavelengths of the fluorescent x-rays by counting the number of x-rays at a given wavelength, converting the counts to electronic pulses, and assigning the pulses to a unique element according to wavelength.

The XRF deployed at the site can be used to measure prepared soil samples in cups, soils samples in plastic bags through the bag walls, and in situ soil surfaces. The system was calibrated to report 25 elements. Molybdenum and uranium were of particular interest.

XRF measurement time can affect XRF performance as measured by detection limits and measurement uncertainty. In general, longer measurement times will result in lower detection limits and more accurate and precise measurements. However, there are other factors that may also affect XRF data quality. They include:

1) Variability in sample moisture content,
2) Spectral interferences between two or more elements,
3) Matrix effects (matrix type, heterogeneity), and
4) General levels of other inorganic elements.

1.3 Sample Collection, Preparation, and Analysis

The samples analyzed by XRF and referenced in this section included reference standard samples of known total uranium and molybdenum concentrations and soil core samples collected at the site. A Geoprobe was used to collect all site-specific soil core samples. All XRF analyses were conducted *ex situ*, following the sample preparation methods described in the *SOP for XRF Analysis of Soils* (SAIC 2006b), hereafter *XRF SOP*.

Soils were air dried prior to sample preparation and XRF analysis. A portable soil moisture gauge was used to confirm that soil moisture was $\leq$ 20% by weight prior to analysis. Soil sample aggregates were crushed prior to XRF soil sample analysis. As described in the *XRF SOP*, the majority of XRF soil sample analyses were performed on dried, crushed, bagged soil samples, with a minimum of four 30-second XRF measurements per bag, two measurements per side. The XRF unit was set to report the average concentrations observed for the four measurements. The purpose of four readings was to control for contaminant heterogeneity within bagged samples.

In the case of soil cores, 6-inch depth intervals were homogenized and treated as individual samples for XRF purposes.

The target XRF elements for this project were molybdenum and uranium. Uranium isotopes are the primary radionuclides of concern at the site. As discussed elsewhere in the RIR, uranium at the site is expected to be composed of uranium isotopes that are either at naturally occurring ratios, or slightly depleted from a U-235 perspective. Consequently one would expect very strong correlations between U-238 activity concentrations (as measured by gamma or alpha spectroscopy) and total uranium content in soil samples.

2.0 Performance Evaluation Approach and Results

This section presents the approach for evaluating the performance of the XRF and observed results.

2.1 XRF Quality Control (QC) Analyses

XRF QC measurements were recorded in order to monitor the calibration and performance of the instrument. These procedures involved XRF measurements of commercial reference standard samples and measurements of site-specific soil samples. XRF QC measurements were obtained according to Section 7.0 of the *XRF SOP*. The objectives of the QC analyses were divided into three broad categories:

1) Standard calibration checks (instrument accuracy)
2) XRF repeatability and intrinsic variability (instrument precision)
3) Sample homogeneity (sample preparation and sub-sampling)

2.1.1 Standard Calibration Checks

This section evaluates the XRF measurements of calibration standards according to Section 7.3 of the *XRF SOP*. Calibration/operational reference standards were obtained from the R.T. Corporation in Laramie, WY, for the following elements and concentrations:

- Natural uranium – 50 ppm
- Molybdenum – 50 ppm
- Natural uranium/molybdenum (combined) – 100 ppm each
- Natural uranium – 150 ppm
- Molybdenum – 150 ppm

These standards were composed of fine-grained clay loam. In addition, one archived sample (HSSB1184) with known uranium concentrations (U238 – 34.1 pCi/g [102.3 ppm]) was available as a calibration check. Three additional calibration standards used previously at the Rattlesnake Creek (RSC) FUSRAP site were provided by USACE. These standards were also manufactured by the R.T. Corporation and were composed of sand and silt matrices and consisted of the following:

- Natural uranium – 100 ppm (RSC Sand)
- Natural uranium – 200 ppm (RSC Sand)
- Natural uranium – 100 ppm (RSC Silt)

Prior to the commencement of field sampling activities, a number of XRF calibration checks were performed using these reference standards. These calibration checks were performed on 29 November 2006, and were referred to as pre-field work calibration checks. It was determined that the RSC silt matrix calibration standard was most representative of the soil nature at the site; as such, the XRF was internally calibrated for the RSC silt standard. Additional calibration checks were performed during the course of field sampling, from 4 December – 21 December 2006. These calibration checks were performed at the beginning, middle, and end of each work day and were referred to as on-going calibration checks. Table 1 lists the total number of pre-field work calibration samples analyzed with the XRF for total uranium and molybdenum. Table 2 lists the total number of on-going calibration checks performed with the XRF for total uranium and molybdenum.

Table 1. Pre-field work XRF analyses of QC standards for total uranium and molybdenum.

Reference Standard	Media	N[1]
50 ppm U	Clay	10
100 ppm U	Sand	10
100 ppm U	Clay	10
150 ppm U	Clay	11
200 ppm U	Sand	10
200 ppm U	Silt	10
HSSB1184 (U)	Site-Specific	21
50 ppm Mo	Clay	10
100 ppm Mo	Clay	10
150 ppm Mo	Clay	11

[1] N – Total number of XRF analyses attempted for each standard.

Table 2. On-going XRF analyses of QC standards for total uranium and molybdenum.

Reference Standard	Media	N[1]
50 ppm U	Clay	48
100 ppm U	Sand	3
100 ppm U	Clay	4
150 ppm U	Clay	58
200 ppm U	Sand	4
200 ppm U	Silt	10
50 ppm Mo	Clay	28
100 ppm Mo	Clay	4
150 ppm Mo	Clay	32

[1] N – Total number of XRF analyses attempted for each standard.

2.1.1.1 *XRF Accuracy* – To evaluate the accuracy of the XRF, pre-field work calibration measurements (Table 1) were compared to the standard concentrations from which the XRF measurements were obtained. The reference standard concentrations were considered to be the benchmarks in this comparison. Although there may be some uncertainty surrounding the reference standard concentration, this uncertainty is assumed to be minimal. XRF accuracy was evaluated via a number of methods. Percent difference between the XRF and the reference standard was calculated for each of the QC measurements. This was calculated as the absolute percent difference between XRF and standard total uranium concentrations, such that:

Equation 1

Percent Difference = [*ABS* (XRF – Reference Standard) / Reference Standard] x 100

Where

Percent Difference	= The absolute percent change in XRF result from the standard.
ABS	= The absolute value
XRF	= The reported XRF concentration for total uranium
Reference Standard	= The reference standard concentration for total uranium

As discussed in the EPA Method 6200 for XRF analysis of environmental media, XRF accuracy is acceptable if it is within 20% of the reference value.

XRF accuracy was also evaluated by calculating the 95% confidence interval[1] for the mean XRF measurement and comparing the standard concentration to the confidence interval. Accuracy was determined based upon whether the confidence interval contained the standard concentration. The average measurement error reported by the XRF for replicate standard measurements was also compared to the observed standard deviation of concentrations in the resulting data set.

Attempts to improve instrument calibration for the fine-grained and coarse-grained calibration standards indicated the instrument could not be calibrated to provide comparable accuracy across the entire range of grain sizes represented by the standards. As a result, the final instrument calibration settings were based on the relatively coarse-grained RSC silt calibration standard because it was considered more representative of site-specific soil samples to be analyzed during field activities.

Prior to the commencement of field sampling, a total of 127 measurements of the QC standards were collected with the XRF for total uranium and 64 were analyzed for the presence of molybdenum (Tables 1 & 3). Table 3 summarizes the XRF analyses of the QC standards at the various standard concentrations and media types. With the exception of the site-specific sample (HSSB1184), measurement acquisition times for these samples were 120 seconds; the acquisition time for HSSB1184 was 30 seconds.

Initial calibration tests for these standards indicated XRF instrument accuracy varied by standard concentration and was influenced by matrix type. The XRF appeared to be most accurate for the reference standard to which it was calibrated (RSC silt [200 ppm U]), as evident by the low mean percent difference, similarity between the average reported error and the standard deviation, and the measure of the 95% confidence interval (Table 3). The 95% confidence interval of the mean XRF result contained the standard concentration only for the reference standard to which the XRF was calibrated. For all other reference standards, the standard concentration was outside of the calculated 95% confidence interval. This may be due to the narrow 95% confidence intervals (Table 3), which indicates the presence of matrix effects. The variation in response caused by the matrix may be due to differences in attenuation of both the incident X-rays into the sample and the emitted X-rays from metals in the sample in conjunction with the way metals are distributed within matrices of the different types.

[1] Technique used depended upon the distribution of the data. Calculated using Pro UCL software.

The XRF largely underestimated total uranium concentrations in the fine-grained clay reference standards as the 95% confidence interval was below the standard concentration (Table 3). The XRF appeared to overestimate total uranium concentrations in the site-specific reference standard as the 95% confidence interval exceeded the standard concentration (102.3 ppm). Overall, XRF measurements for molybdenum showed greater accuracy than those for total uranium. XRF measurements of the 3 molybdenum reference standards resulted in highest accuracy at the greatest concentration (150 ppm Mo), moderate accuracy at the lowest concentration (50 ppm Mo), and the lowest accuracy at the intermediate concentration (100 ppm Mo) (Table 3).

Overall, a moderate level of accuracy was observed for XRF measurements of all reference standards. For most pre-field QC standard analyses, mean percent difference was approximately 20% or less and the average reported XRF error was similar to the reported standard deviation for the mean XRF result (Table 3). Noticeable differences between mean reported XRF error and the reported standard deviation for total uranium occurred at low standard concentrations (i.e., 50 ppm) and among clay or site-specific matrix types (Table 3). Measurements of the 50 ppm U clay matrix reference standard resulted in the lowest accuracy assessment. The mean percent error for this reference standard was the greatest among all reference standards evaluated (35.05%) and the average reported XRF error was nearly two times greater than the reported standard deviation (Table 3). For the most part, XRF measurements of the RSC reference standards (coarse-grained silt/sand material) were more accurate as compared to the XRF measurements of fine-grained clay and site-specific reference standards.

The differences observed between the clay and sand matrix types for the 100 ppm U reference standards (Table 3) may also be attributed to spectral interference of the XRF analysis by molybdenum. Molybdenum was present in equal concentration to total uranium in the clay reference standard; this element was absent from the sand matrix reference standard. Molybdenum is a natural element occurring at elevated concentrations in the soils at the site and may interfere with the XRF analysis of total uranium isotopes. However, these elements exhibit contrasting spectral energy levels from their K- and L- shell electrons, respectively ($K\alpha_1$, Mo: 17.5, U: 98.4; $L\alpha_1$, Mo: 2.3, U: 13.6), and there is no published documentation describing spectral interferences between uranium and molybdenum. It is more likely that the difference in XRF measurements of total uranium in the 100 ppm Mo/U clay and 100 ppm U sand reference standards is due to matrix effects rather than spectral interference.

XRF measurements of on-going calibration standards (Section 2.1.3) appeared to exhibit greater accuracy than the pre-field work calibration standards. There were more numerous XRF measurements of the on-going QC standards than there were for the pre-field work standards. Because XRF accuracy was higher for the more numerous on-going calibration dataset, XRF accuracy was likely stronger than that indicated by the pre-field work data.

Table 3. Summary of pre-field work XRF analyses of QC standards by media nature used to calibrate the instrument. Analyses of the 100 ppm U clay matrix and 100 ppm Mo clay matrix standards (highlighted) were obtained from the same standard in which both elements were combined in equal concentration.

			XRF Result (ppm)							
Standard Concentration (ppm)	Media Type	N[1]	Mean (ppm)	Average Reported XRF Error (ppm)[2]	Standard Deviation of the XRF Result (ppm)[3]	Minimum XRF Result (ppm)	Maximum XRF Result (ppm)	Lower 95% Confidence Limit of the Mean (ppm)[4]	Upper 95% Confidence Limit of the Mean (ppm)[4]	Mean Absolute Percent Difference (%)
50 U	Clay	8/10 (80%)	32.48	10.97	5.87	24.22	39.41	28.55	36.41	35.05
100 U	Clay	10/10 (100%)	79.58	8.31	8.36	63.82	87.11	74.37	84.43	20.42
100 U	Sand	10/10 (100%)	88.92	3.05	2.99	84.20	94.21	87.19	90.65	11.08
150 U	Clay	11/11 (100%)	119.90	8.58	6.80	104.00	128.10	116.10	123.70	20.04
200 U	Sand	10/10 (100%)	175.00	4.02	4.18	168.2	183.4	172.60	177.4	12.52
200 U	Silt	10/10 (100%)	199.3	5.61	5.83	193	209.3	195.90	202.7	2.40
102.3 U (HSSB1184)	Site-Specific	21/21 (100%)	123.10	9.37	7.94	104.10	132.86	120.10	126.10	20.36
50 Mo	Clay	10/10 (100%)	54.67	3.67	4.67	48.47	62.52	51.97	57.37	9.94
100 Mo	Clay	10/10 (100%)	120.60	4.12	4.48	114.40	128.70	118.00	123.20	20.58
150 Mo	Clay	11/11 (100%)	153.80	4.28	3.26	148.90	158.30	152.10	155.50	2.76

[1] N – Number of XRF analyses in which the analyte was detected to the total number of XRF analyses. Percent of analyses detected is in parentheses.
[2] The average of the reported instrument uncertainty (ppm) of XRF analyses in which total uranium or molybdenum was detected.
[3] The standard deviation calculated from the mean result (ppm) of XRF analyses in which total uranium or molybdenum was detected.
[4] Lower and upper 95%confidence limits of the mean XRF result (ppm) were calculated based upon the data distribution using Pro UCL software.

2.1.1.2 *XRF Measurement Error as a Function of Standard Concentration* — Statistical analyses were conducted to determine the relationship between systematic instrument calibration error and element concentration and to determine if matrix effects influenced the reported XRF measurements. The XRF performance measure investigated in these analyses was percent difference (Equation 1).

To examine matrix effects on XRF analyses, statistical analyses were performed to compare XRF percent difference and reported uncertainty among matrix types. Due to the nature of sampling, it was difficult to discern matrix effects from spectral interferences in the same analysis. For this evaluation, therefore, only similar standard concentrations analyzed in multiple media types were used. The standard concentrations analyzed in different media types (Table 1) include total uranium 100 ppm (clay & sand) and total uranium 200 ppm (sand and silt). Based upon the type of statistical distribution of the calculated percent difference for these reference standards, these data were compared between matrix types using parametric or nonparametric statistics as appropriate.

Statistical analyses indicated an overall negative relationship between mean percent difference and standard concentration[1] , which supports the observations in Section 2.1.1.1 that describe improved XRF accuracy at greater standard concentrations. When analyzed separately, the relationship between mean percent difference and standard concentration is similar between element parameters. For both uranium and molybdenum, mean percent difference decreases along an increasing standard concentration gradient, indicating that XRF systematic bias decreases at higher element concentrations (Figure 1). This effect was observed only within the concentration range represented by the reference standards; inferences on the mean percent difference for concentrations outside of this range are speculative. Because only three reference standards were analyzed for molybdenum (Table 1; Figure 1), the trend for this element should be interpreted with caution.

[1] The data were analyzed using a Spearman Rank Correlation (α=0.05); SAS 9.1.

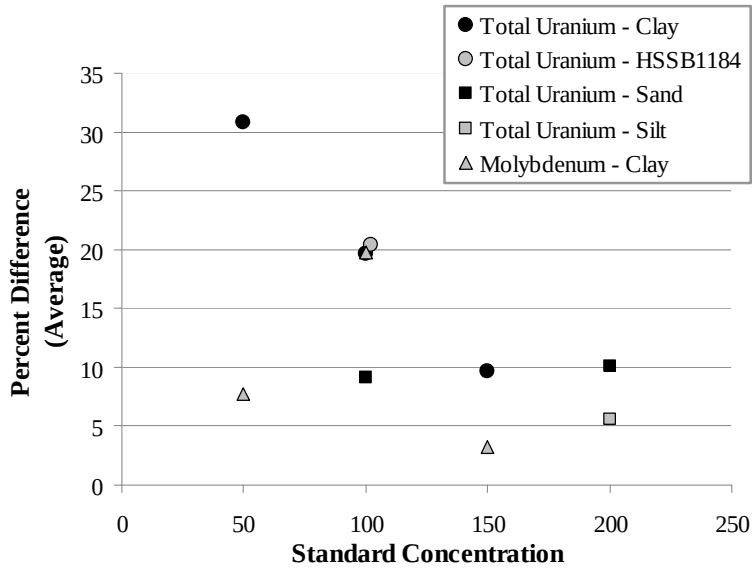

Figure 1. Average percent difference between the reported XRF measurement and the standard concentration along standard concentrations.

2.1.2 XRF Precision and Sample Heterogeneity

Evaluations of XRF precision and intrinsic variability were conducted according to Sections 7.4 through 7.6 of the *XRF SOP*; only XRF measurements for total uranium concentrations were included in evaluations of instrument precision and intrinsic variability. Subsets of pre-field work (Section 2.1.1.1) and on-going QC standards (Section 2.1.1.3) were used to evaluate XRF precision and quantify intrinsic variability associated with sample preparation and analysis. The number and types of samples included in these evaluations are listed in Table 4. In total, the XRF measurements were used to make three evaluations: 1) instrument precision, 2) small-scale sample variability within sample cups, and 3) bagged sample intrinsic variability. Precision (described in Section 2.1.2.1) refers to the ability of the XRF to determine the same result for repeated measurements of the same sample. Small-scale variability and bagged sample intrinsic variability are indicative of heterogeneity in total uranium concentrations within the sample. Small-scale variability within sample cups refers to the amount of variability introduced at a fine scale by moving the sample cup in between repeated XRF measurements of the same sample. Bagged sample intrinsic variability ("sample intrinsic variability") refers to the amount of variability present within an entire bagged sample among XRF measurements of different locations on the bag.

Table 4. XRF analyses of QC standards and site-specific samples used to evaluate XRF repeatability and quantify intrinsic variability within the sample.

Sample Source	Group	Objective	Acquisition Time (sec)[1]	N[2]
Standard	150 ppm - move[3]	Small-Scale Variability	30	10
Standard	150 ppm – no move[4]	Precision	30	10
Site	HSSB1184 - move	Small-Scale Variability	30	10
Site	HSSB1184 – no move	Precision	30	10
Site	SB0155-A1	Intrinsic Variability	120	5
Site	SB0155-B1	Intrinsic Variability	120	5
Site	SB0155-A2	Intrinsic Variability	120	5
Site	SB0155-B2	Intrinsic Variability	120	5
Site	SB0155-A3	Intrinsic Variability	120	5
Site	SB0155-B3	Intrinsic Variability	120	5
Site	SB0155-A4	Intrinsic Variability	120	5
Site	SB0155-B4	Intrinsic Variability	120	5
Site	SB0155 - Detect	Screening Reproducibility	30	5
Site	SB0040 - Non-Detect	Screening Reproducibility	30	5

[1] Acquisition Time – Amount of time (sec) between instrument counts.
[2] N – Number of XRF analyses recorded for each sample. Recorded as the aggregate of analyses within each acquisition time.
[3] Samples analyzed to investigate small scale variability involved moving the sample cup in between measurements.
[4] Samples analyzed to investigate precision involved XRF measurements without the movement of the sample cup in between measurements.

2.1.2.1 *XRF Precision* —This evaluation determined the precision of the XRF for total uranium measurements. Two approaches were used to evaluate XRF precision: a comparison of the average reported errors and standard deviations for pre-field work calibration standards (Section 2.1.1.1) and an evaluation of two other QC samples selected to determine XRF precision (*XRF SOP*, Section 7.4; Table 4). In the latter approach, one reference standard (150 ppm) and one site-specific sample (HSSB1184) were repeatedly analyzed 10 times at the same location *without* moving the sample cup in between measurements. The purpose of cup placement was to control for within-cup heterogeneity contributing to observed variability in replicate XRF measurements.

XRF measurements of the precision samples in Table 4 (150 ppm U Standard, HSSB1184) were evaluated by calculating XRF relative standard deviation, such that:

Equation 2

$$RSD = (SD / \text{Mean Concentration}) \times 100$$

Where
RSD = Relative Standard Deviation
SD = Standard Deviation

For these analyses, the precision of the XRF for total uranium concentrations was categorized, based on the calculated RSD for each sample source (*from* EPA 2006 and EPA Method 6200): very low variability (RSD less than 5%), low variability (5% < RSD < 10%), somewhat variable (10% < RSD < 20%), or high variability (RSD above 20%). Only two

samples were analyzed with the XRF for this evaluation, thus, the RSD for each sample was directly categorized. A separate evaluation was performed by comparing the average reported XRF error for the replicate measurements of each sample to the observed replicate measurement standard deviation. The purpose of this comparison was to evaluate the instrument's ability to estimate analytical error for individual measurements.

A final assessment of XRF precision involved the analysis of pre-field work calibration standards (Section 2.1.1.1) by comparing the mean relative instrument error to the standard concentration. A statistical evaluation[1] was performed to associate relative instrument error with standard concentration to determine if instrument precision was influenced by media concentration. This analysis evaluated the systematic bias of the XRF instrument for measurements of pre-field work calibration standards. For all XRF measurements, it was expected for absolute XRF errors to increase with increasing sample concentration. Relative instrument errors, however, were expected to decrease along increasing sample concentrations.

A summary of the repeated XRF measurements of the standard and site-specific sample for total uranium concentration is shown in Table 5. The calculated RSD (Equation 2) indicated a high level of precision for the XRF for both samples (low variability; RSD between 5% and 10%). The calculated RSD for repeated measurements of both sources were similar. The RSD for the repeated measurements of the standard is 8.02 %, whereas the RSD for the repeated measurements of the site-specific sample is 5.59 % (Table 5). Comparisons of the average reported error to the standard deviation for these samples revealed that the average reported error was similar to the standard deviation for both samples (Table 5). This observation indicates that, for the replicate measurements of these samples, the XRF exhibited an acceptable level of precision in determining total uranium concentrations.

Table 5. Evaluation of XRF precision for the presence of total uranium in two samples.

Source	N	Mean (ppm)	Median (ppm)	Min (ppm)	Max (ppm)	Standard Deviation (ppm)	Average Reported Error (ppm)	Relative Standard Deviation of the XRF Result (% RSD)
Standard (150 ppm)	10	162.11	163.24	143.76	180.08	13.00	17.62	8.02 %
HSSB1184 (site-specific)	10	124.43	125.60	112.58	132.56	6.95	9.65	5.59 %

For all pre-field work calibration samples analyzed, the average relative instrument errors were less than 20% (Figure 2). Statistical analyses indicated that, overall, relative systematic XRF calibration error decreased with increasing standard concentration (Figure 2). As expected for all XRF measurements of the site soil samples, the absolute reported XRF errors increased with increasing sample concentration, and the relative instrument errors decreased (square-root function) with increasing sample concentrations (Figure 3). These observations confirm that relative XRF precision improved at greater total uranium concentrations. Further investigation of the complete XRF dataset for total uranium concentrations in site soils revealed that an

[1] The data were analyzed using Spearmen Rank Correlations by standard concentration (α=0.05); SAS 9.1.

acceptable level of precision based upon EPA Method 6200 (≤ 20% RSD) was attained for soil samples with reported total uranium concentrations greater than 35 ppm (Figure 3B).

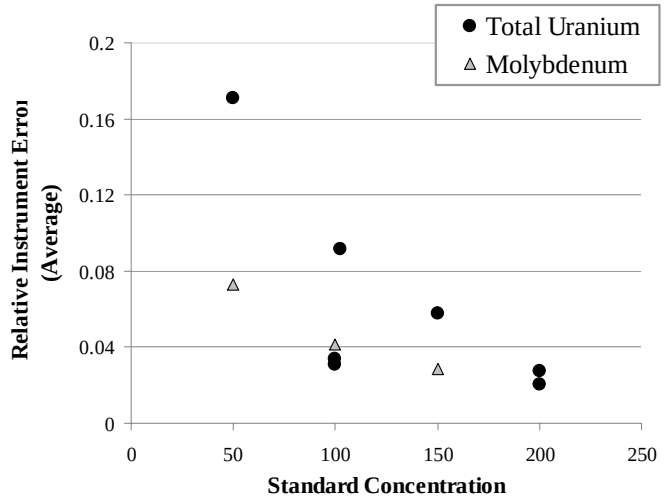

Figure 2. Average relative instrument error along standard concentrations. Relative instrument error is equal to the ratio of the average reported XRF error to the standard concentration.

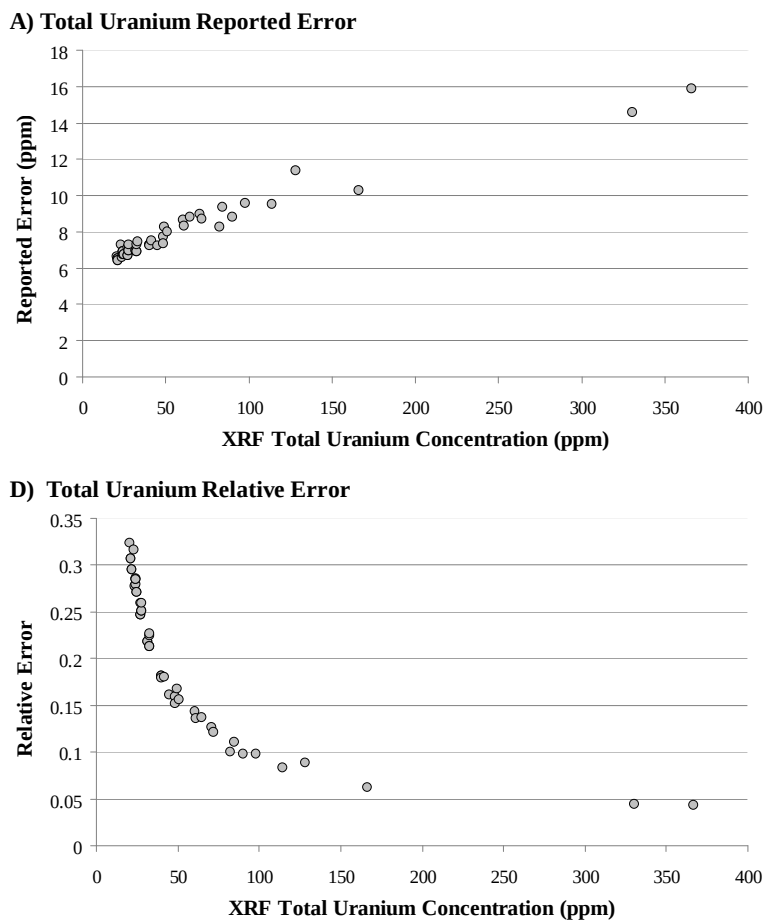

Figure 3. Relationship between XRF total uranium concentrations and A) absolute XRF errors and B) relative XRF errors for all XRF measurements of site soil samples.

2.1.2.2 *Sample Small-Scale and Intrinsic Variability*. - This demonstration evaluated the small-scale and intrinsic variability in XRF measurements associated with sample preparation and analysis (*XRF SOP*, Section 7.5). This analysis evaluated samples undergoing two different analysis methods: 1) Samples in cups which were repeatedly analyzed but *with* replacement of the sample cup in between measurements, and 2) Bagged samples in which different locations across the bag were analyzed.

Two prepared samples in cups (one standard, one site-specific) were analyzed 10 times with replacement of the sample cup in between measurements (Table 4). The movement of the sample cup between measurements may introduce fine-scale variability in the XRF measurements due to fine-scale heterogeneity in total uranium, other elements, or the physical matrix composition in the sample. A different site-specific soil core sample (SB0155) divided into 4 bags representing 4 soil depth intervals was analyzed with the XRF by collecting 5 measurements on each side of the sample bag – one measurement in each corner and one measurement in the center. The purpose of this approach was to determine the level of uranium concentration heterogeneity within bagged samples, and to determine if 4 measurements per bag (the protocol for site data collection) were sufficient to provide an acceptable estimate of uranium concentration per bag. Bagged samples were not homogenized beyond crushing aggregates. Sample intrinsic variability in total uranium concentrations may be evident by analyzing the variability in concentrations from repeated measurements located in different areas of a bagged sample. Finally, two bagged samples were each analyzed 5 times using site protocols (i.e., 4 measurements per bag) to further evaluate the sufficiency of 4 measurements per bag as an estimator of bag uranium concentrations. Small-scale variability and bagged sample intrinsic heterogeneity in total uranium concentrations were quantified by calculating the relative standard deviation (RSD; Equation 2). Variability was categorized based on the calculated RSD: very low (RSD < 10%), low (10% < RSD < 20%), moderate (20% < RSD < 30%), high (30% < RSD < 50%) or very high (RSD above 50%). The RSD was also compared to XRF reported error.

A final assessment involved a comparison of the average reported error for the replicate measurements of each sample bag to the reported standard deviation for the XRF measurements. The purpose of this evaluation was to determine the amount of variability attributable to sample heterogeneity versus XRF precision. This information can be used to develop future sampling protocols accounting for small- and large-scale sample heterogeneity. Multiple measurements of bagged samples serve as a potentially cost-effective alternative to preparing and homogenizing samples prior to cup measurements by XRF.

A summary of the repeated XRF measurements for small-scale and intrinsic variability is shown in Table 6. The results indicate that small-scale variability is very low, as the RSD for standard and site-specific samples are below 10% (Table 6A). Furthermore, there does not appear to be much effect of sample cup replacement in between measurements on the XRF analysis as the variability (RSD) in XRF measurements without cup replacement (Table 5) is similar to the variability in XRF measurements with cup replacement (Table 6A).

Table 6. Evaluation of XRF performance to quantify sample heterogeneity in total uranium concentrations. A) Summary of XRF analyses for total uranium used to quantify small-scale sample variability at one location on the sample bag. B) Summary of XRF analyses for total uranium used to quantify intrinsic sample variability at different locations of the sample bag.

A) Small-Scale Sample Heterogeneity

Source	N	Mean (ppm)	Median (ppm)	Min (ppm)	Max (ppm)	Standard Deviation (ppm)	Average Reported Uncertainty (ppm)	Relative Standard Deviation (% RSD)
Standard (150 ppm)	10	160.49	155.16	139.36	182.63	14.47	17.74	9.01 %
HSSB1184 (site-specific)	10	122.04	124.25	104.10	132.86	9.38	9.56	7.69 %

B) Sample Bag Intrinsic Heterogeneity

Depth Interval (ft)	Side	N	Mean (ppm)	Median (ppm)	Min (ppm)	Max (ppm)	Standard Deviation (ppm)	Average Reported Uncertainty (ppm)	Relative Standard Deviation (% RSD)
0.5 - 1.0	A	5	320.66	333.35	272.33	370.87	44.78	7.03	13.96
	B	5	389.66	393.69	375.67	402.02	11.31	7.98	2.90
	Total	10	355.16	373.27	272.33	402.02	47.65	7.50	13.42
1.0 - 1.5	A	5	35.98	32.53	30.68	47.45	7.02	3.68	19.50
	B	5	29.88	25.21	21.12	47.31	10.34	3.53	34.62
	Total	10	32.93	31.09	21.12	47.45	8.93	3.60	27.13
3.5 - 4.0	A	5	18.13	14.97	11.86	33.56	9.02	3.34	49.73
	B	5	21.42	20.70	16.43	26.96	4.21	3.36	19.64
	Total	10	19.78	18.56	11.86	33.56	6.86	3.35	34.67
5.0 - 5.5	A	5	25.75	26.59	18.05	30.52	4.66	3.54	18.10
	B	5	18.34	19.24	15.67	20.01	1.82	3.34	9.93
	Total	10	22.05	19.77	15.67	30.52	5.13	3.44	23.28

However, sample intrinsic variability was much greater when different locations on the sample bag were measured with the XRF. This was observed among the 5 repeated measurements on each side of the sample bag and among all 10 repeated measurements on both sides of the sample bag. The RSD for any one group of analyses ranged from 2.90% to 49.73% (Table 6B). Overall, there was slightly less intrinsic variability for repeated measures of one side of the sample bag (A or B) than for repeated measures on both sides of the sample bag (Total). This observation indicates that XRF measurements on both sides of the sample bag were necessary to fully quantify the amount of bagged sample intrinsic variability. For all 4 depth intervals, the average RSD for the 10 repeated measurements on both sides of the sample bag was 24.63%, whereas the average RSD for the 5 repeated measurements on each side of the sample bag was 21.05%. There were subtle differences between average reported error and standard deviation for the samples analyzed for small-scale variability (Table 6A). However, the disparity between average reported error and standard deviation were substantially greater among the samples analyzed for intrinsic variability. For the most part, the standard deviations of the XRF results for these samples were more than twice the average reported uncertainties

(Table 6B). This observation further indicates that greater variability in total uranium concentrations (as reported by the XRF) exists within the bagged sample than what can be attributable to instrument error (precision).

Collectively, these observations illustrate the effect of sample heterogeneity on small-scale and intrinsic variability in site-specific soil samples. The effect of sample heterogeneity on small-scale variability in these samples was minimal as the calculated RSD was less than 10% and the average reported error was similar to the observed replicate standard deviation (Table 6A). The effect of sample heterogeneity on intrinsic variability across the entire bagged sample, however, was more substantial as evident by the greater RSD calculations over all the bagged samples and the greater disparities between the average reported uncertainties and standard deviations (Table 6B). These observations confirm that sample heterogeneity contributes to much greater variability in XRF measurements at larger scales (within bagged samples) than at finer scales. As a result, these observations suggest that the collection of 4 XRF measurements on both sides of the sample bag was sufficient to quantify the average concentration and the bagged sample heterogeneity.

2.1.2.3 *XRF Bagged Sample Screening Reproducibility*. - This demonstration evaluated the reproducibility of XRF measurements for screening purposes (*XRF SOP*, Section 7.6). Two site-specific bagged soil samples were analyzed with XRF for this evaluation (Table 4). One sample was known to contain detectable concentrations of total uranium (Detect sample), whereas the other sample was known to contain non-detectable concentrations of total uranium (Non-Detect sample). Each bagged sample was analyzed with the XRF in 5 replicates to determine the reproducibility of the screening level measurement. Each replicate consisted of four measurements per bag, two on each side of the bag.

To evaluate the reproducibility of the XRF screening results, the XRF-reported concentration and error for total uranium were investigated. In particular, data completeness was assessed to determine whether each of the 5 replicate XRF measurements provided correct results for both the Detect sample and for the Non-Detect sample. The relative standard deviation (RSD; Equation 2) based on the reported XRF concentration was calculated for the Detect sample to determine the amount of relative variability in reported total uranium concentrations.

A summary of the evaluation for XRF screening reproducibility is shown in Table 7. The data were 100% complete for the XRF measurements of the Detect sample and no detectable results were observed for the Non-Detect sample (Table 7). The mean reported error for the Detect samples was 15.6 ppm total U. These observations confirm the reliability of the XRF to reproduce appropriate screening-level results based on measurements of site-specific soil samples. The narrow range of reported total uranium concentrations for the Detect sample and low RSD (Table 7) indicates that variability in XRF results were minimal. These observations suggest that the collection of 4 XRF measurements per aggregate sample (as defined in the *XRF SOP*) is sufficient to provide reliable screening-level results. Furthermore, the performance of the XRF when analyzing the Non-Detect sample indicates that XRF reported error can be used to estimate the XRF limit of detection (LOD) for soil samples in which total uranium was not detected. A further discussion of the LOD for XRF measurements of the site soil samples is provided in Section 2.2.

Table 7. Reproducibility of XRF screening results. XRF reported concentration (total uranium, ppm) among replicate analyses of two sample types.

Sample ID	Detect[1]	Mean (ppm)	Standard Deviation (ppm)	Relative Standard Deviation (% RSD)	Median (ppm)	Min (ppm)	Max (ppm)
Detect	5/5	366.5	10.1	2.7	369.0	350.5	377.2
Non-Detect	0/5	-	-	-	-	-	-

[1] Detect – Number of XRF analyses in which the analyte (total U) was detected to the total number of XRF analyses.

2.1.3 *Analyses of On-Going QC XRF Measurements* – Standard calibration checks were also conducted by the operator at the start and end of each workday using at least two standard samples for total uranium. Measurement acquisition time for these samples was 120 seconds. In total, 191 on-going QC measurements were recorded from reference standards at various standard concentrations and media types (Table 2). A subset of these on-going QC measurements was also used to evaluate instrument precision and intrinsic variability (Section 2.1.2). Summary statistics for the reported XRF measurements of the on-going calibration checks are shown in Table 7. For all calibration standards, XRF detection was 100%. The purpose of the on-going XRF QC calibration measurements was to evaluate the instrument's accuracy during the field sampling period and determine whether instrument accuracy degradation occurred. This was accomplished by relating XRF readings to instrument sequential reading numbers and comparing the on-going XRF results to the pre-field work XRF results.

To investigate for internal instrument degradation in XRF measurements, reported XRF results for molybdenum and total uranium were associated with the reported reading number, which is the daily sequential analysis number that is tracked in-between electronic data downloads from the XRF unit. If instrument performance degradation, or drift, occurred in the XRF then an association would exist between the reading number and the reported XRF total uranium concentration. Performance degradation could result in negative or positive instrument bias. A statistical analysis[1] was conducted to determine the association of reported XRF concentrations with the sequential reading number by standard concentration. Only those reference standards in which $N \geq 20$ were included in this statistical analysis (Tables 2 & 8). A separate evaluation was performed on the entire dataset in which the mean reported XRF error was directly compared to the standard deviation of the dataset. The purpose of this direct comparison was to determine how much variability in the on-going QC measurements was explained by measurement error as reported by the XRF and how much was attributable to systematic bias.

[1] The data were analyzed with separate Spearman Rank Correlations by standard concentration (α=0.05); SAS 9.1.

The relationships between XRF results for molybdenum and uranium and reading number for those reference standards with a sufficient number of measurements are shown in Figure 4. A negative relationship between XRF result and the daily sequential reading number was statistically determined for only total uranium; no statistical relationship existed for molybdenum (Figure 4). It is possible that this effect is due to differences in spectral energy levels for molybdenum and total uranium (see Section 2.1.1.1 for a discussion of spectral energy levels). For XRF measurements of total uranium, these results indicate that system degradation did occur as the reported XRF value decreased over time. The slopes of the regression equations of the best-fit trend line for these reference standards were -0.10 and -0.21 (Figure 4B & 4D). Based upon these results, total reduction in XRF response over the course of an entire day was between 10 and 21%.

For on-going XRF calibration tests of standards where $N \geq 20$, the average reported XRF error is substantially less than the reported standard deviation for total uranium (Table 8). For analyses of molybdenum, the average reported XRF error and the standard deviation are more similar. Compared to the pre-field work calibration tests (Section 2.1.1), the disparity between the average reported XRF error and reported standard deviation is greater for the on-going calibration results, indicating the presence of measurement variability that was larger than could be explained by measurement error alone. This was consistent with the trends observed in Figures 4B and 4D.

Statistical analyses[1] were performed to determine if differences existed between the pooled pre-field work and on-going XRF measured concentrations for total uranium and molybdenum, paired by standard concentration. Based upon these analyses, there were no distinguishable differences between pre-field work XRF results for molybdenum and on-going XRF results for molybdenum (Figure 5A). However, there were differences in reported XRF total uranium concentration between QC sample types (Figure 5B). For the most part, reported XRF concentrations for total uranium differed more at lower standard concentrations (i.e., 50 ppm U) than at higher standard concentrations. XRF reported total uranium concentrations differed between pre-field and on-going QC sample types at every standard concentration, except 200 ppm U. Despite the degradation in reported XRF total uranium concentrations occurring within on-going XRF calibration measurements, the on-going XRF results exhibited improved accuracy compared to the pre-field work XRF calibration measurements (Figure 5B). With the exception of the 200 ppm U reference standard, the on-going XRF calibration measurements for total uranium were closer to the target standard concentration than were the pre-field work calibration standards. As discussed in Section 2.1.1.1, because XRF accuracy was higher for the more numerous on-going calibration dataset, XRF accuracy was likely stronger than that indicated by the pre-field work data.

Collectively, these results indicate that system degradation had occurred over sequential XRF measurements collected during the course of a day. Degradation was observed in the decreasing trend in XRF results for total uranium (Figure 4) and the greater disparity between average reported XRF error and standard deviation (Table 8). Discharge of the XRF battery is the most plausible explanation for the observations of daily degradation of the XRF measurements. The ability of the XRF to analyze the concentrations of elements is a function of

[1] The data were analyzed with separate T-Tests by standard concentration (α=0.05); SAS 9.1.

the amount of energy supplied to the x-ray tube to excite and quantify element electrons. As the power supply is depleted in the XRF in-between charges, the weakened power supply may affect the XRF result. Measures to minimize this effect include charging the XRF battery at regular times of the day (i.e., over lunch-time) or keeping fully-charged spare batteries in possession to be exchanged on a frequent basis throughout the day as needed. As discussed in EPA Method 6200, X-ray tubes have no intrinsic lifetime limit and produce a constant output over their lifetime; thus, degradation in XRF measurements over time is unlikely to be due to degradation within the x-ray tube.

Table 8. Summary of on-going XRF analyses of QC standards by media nature used to calibrate the instrument. Analyses of the 100 ppm U clay matrix and 100 ppm Mo clay matrix standards (highlighted) were obtained from the same standard in which both elements were combined in equal concentration.

			XRF Result (ppm)				
Standard Concentration (ppm)	Media Type	N[1]	Mean (ppm)	Average Reported XRF Error (ppm)[2]	Standard Deviation of the XRF Result (ppm)[3]	Minimum XRF Result (ppm)	Maximum XRF Result (ppm)
50 U	Clay	48/48 (100%)	62.44	8.02	12.62	36.54	88.62
100 U	Clay	4/4 (100%)	110.68	8.54	16.78	87.70	125.71
100 U	Sand	3/3 (100%)	101.66	3.18	3.42	98.41	105.25
150 U	Clay	58/58 (100%)	150.78	11.80	18.51	102.95	191.60
200 U	Sand	4/4 (100%)	191.67	4.16	1.45	190.08	193.01
200 U	Silt	10/10 (100%)	182.34	5.43	4.99	175.06	189.45
50 Mo	Clay	28/28 (100%)	48.42	3.63	3.98	40.30	57.43
100 Mo	Clay	4/4 (100%)	117.82	4.11	5.81	109.36	122.43
150 Mo	Clay	32/32 (100%)	151.96	4.48	6.49	136.35	171.05

[1] N – Number of XRF analyses in which the analyte was detected to the total number of XRF analyses. Percent of analyses detected is in parentheses.
[2] The average of the reported instrument uncertainty (ppm) of XRF analyses in which total uranium or molybdenum was detected.
[3] The standard deviation calculated from the mean result (ppm) of XRF analyses in which total uranium or molybdenum was detected.

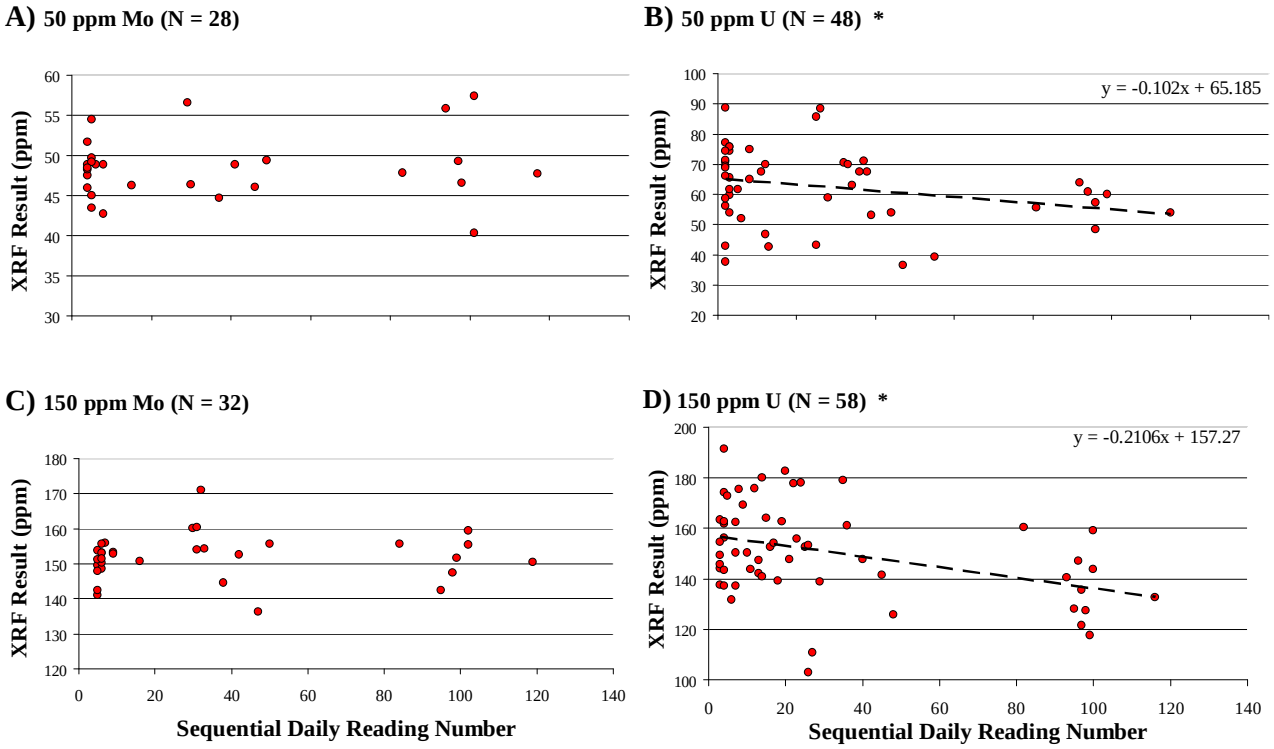

Figure 4. Association between XRF result (ppm) and sequential daily reading number for on-going calibration tests of reference standards during field sampling activities. The sequential reading number refers to the ordinal daily XRF measurement. Statistical significance (α=0.05) is denoted by *, which includes the best-fit trend line and regression equation.

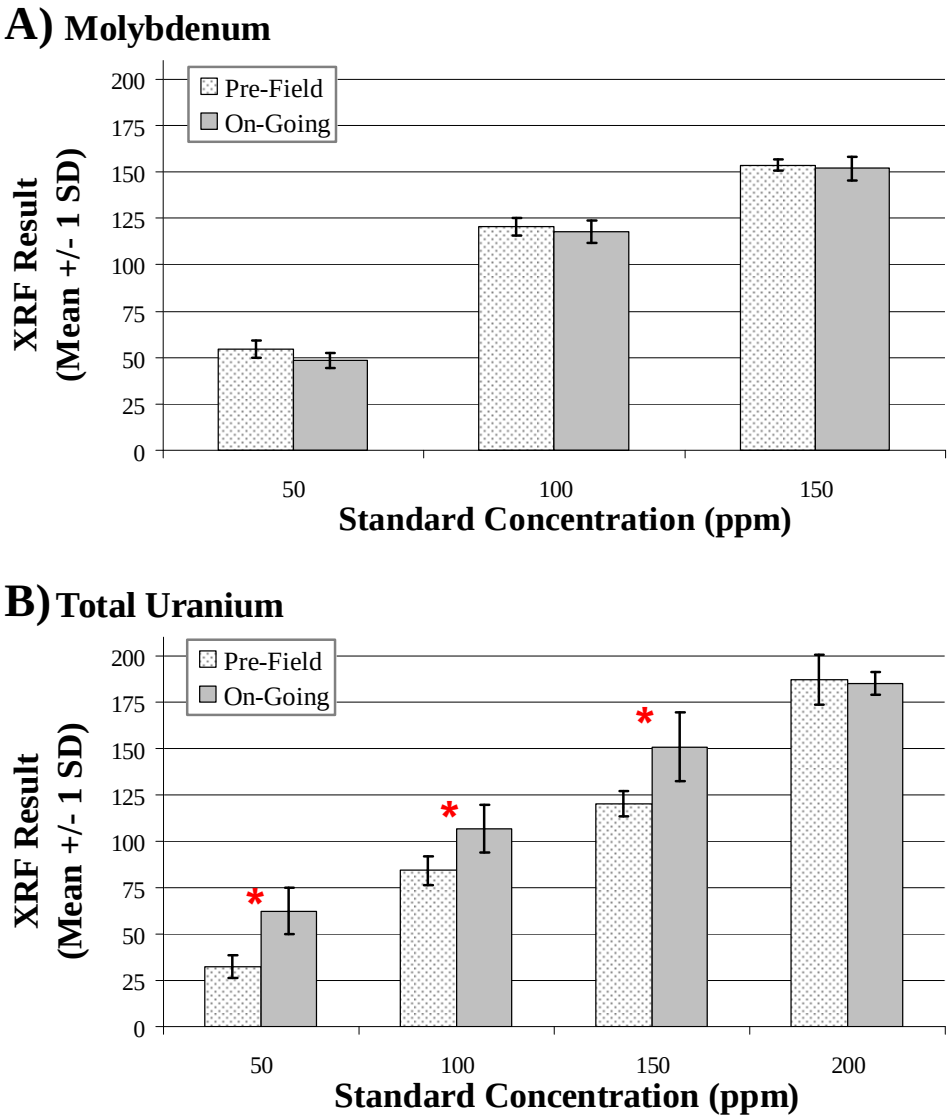

Figure 5. Comparison of reported XRF concentrations for A) molybdenum and B) total uranium between the pre-field work and on-going QC calibration standards. A statistical difference in mean reported concentrations (α=0.05) is denoted by *.

2.2 XRF Limits of Detection (LOD)

XRF reported LOD is influenced by a variety of factors including the presence of other elements, matrix nature and composition, XRF settings (i.e., aggregate mode), and the relationship between reported concentration and reported error. XRF reported LOD is also a function of measurement time – the reported LOD decreases as measurement time increases up to a threshold point in time at which the LOD becomes static. Quantification of the XRF limit of detection (LOD) in conjunction with information gathered concerning XRF accuracy, precision,

and laboratory-referenced comparability can improve the quantitative applicability of the XRF for site characterization purposes.

To best quantify XRF LOD for a particular element, it is recommended in EPA Method 6200 that XRF LOD performance be compared to certified laboratory-referenced analyses of the same sample to identify the lowest certified concentration that can be measured with the XRF. Statistical evaluations using only the XRF reported LOD may support this determination.

At the site, the XRF was used to screen for total uranium concentrations from soil core samples collected at 59 station locations. In total, 791 distinct XRF measurements were recorded to detect the concentration of molybdenum and total uranium from 6-inch depth intervals. Soil core samples analyzed at multiple depth intervals produced multiple discrete XRF analyses. For some locations, these discrete XRF measurements were pooled and the composite XRF result for the soil core station location was compared against laboratory analyses of a composite sample formed from the soil core. In total, there were 95 composite soil samples that corresponded to 675 depth intervals with discrete XRF observations. Laboratory analyses were performed to detect only total uranium and uranium isotopes for a subset of the discrete and composite soil samples; thus, the XRF lower limit of detection was not certified for molybdenum. Laboratory analysis of the site soil samples included alpha spectroscopy for U-238 and gamma spectroscopy for U-238. The following explores the range of total uranium concentrations for those samples in which uranium was detected by the XRF and the LOD for those samples in which uranium was not detected. The XRF LOD for non-detect samples was then compared to paired laboratory-referenced results to determine the lower limit of detection. Laboratory-determined U-238 activity concentrations were multiplied by a factor of 3 to provide an estimated total uranium mass-based concentration. Additional statistical evaluations were performed on the LODs for non-detect samples. The following analysis is divided into two main categories:

1) Detection Limits All XRF Measurements (N = 791)
2) XRF Detection Limits as Determined by Split Laboratory Analyses (N = 159)

2.2.1 Detection Limits and Analytical Errors of All XRF Measurements

Discrete XRF analyses were conducted at 6-inch depth intervals from the 59 station locations at the Former Harshaw Chemical Site. These analyses were performed in XRF aggregate mode to measure total uranium, with 4 thirty-second acquisitions contributing to a single measurement from a bagged soil sample. As such, the reported total uranium XRF concentration and error represents the average across all 4 aggregated analyses.

Only the XRF reported LOD (for non-detect samples) is evaluated in this section. The XRF method LOD for total uranium was statistically determined for non-detect site soil samples by evaluating the central measures (mean, median) and range of reported individual XRF LOD values. The instrument-reported LOD values, in turn, are a function of measurement uncertainty, which is a function of counting statistics. A summary of the reported XRF LOD for those site soil samples in which the elements were not detected is provided in Table 9.

Table 9. Summary of discrete XRF soil samples collected at the site in which the elements were not detected (assumed to be the reported LOD).

Element	N[1]	XRF Variable	Mean (ppm)	Median (ppm)	Minimum (ppm)	Maximum (ppm)
Molybdenum	765	Reported LOD	18.0	18.0	14.7	26.0
Total Uranium	743	Reported LOD	17.1	16.2	12.3	205.4

[1]N - The number of observations for all discrete XRF measurements in which the element was not detected (Total N = 791).

Molybdenum and total uranium were not detected in 765 and 743, respectively, of 791 discrete XRF measurements (Table 9). For non-detected molybdenum samples, the mean reported uncertainty was 18.0 ppm (range: 14.7 – 26.0 ppm). For non-detected total uranium samples, the mean uncertainty (assumed to be the instrument-reported LOD) was 17.1 ppm (range: 12.3 – 205.4 ppm). The elevated maximum reported uncertainty (205.4 ppm) for a non-detect total uranium sample warranted special consideration. Further investigation of the reported uncertainties revealed that this maximum value was an anomaly, apparently due to the elevated concentrations of collocated arsenic (As; 29,167 ppm) and lead (Pb; 446,773 ppm). Extreme values have a greater effect on the reported mean and range; however, the median is generally unaffected by extreme values. As such, the median total uranium value was used to statistically determine the XRF LOD. The median value represents the middle of the dataset, where 50% of the values are above the median and 50% of the values are below the median. Based upon the median value, the statistical XRF LOD was determined to be 16.2 ppm for uranium.

These results indicate that the statistically determined XRF LOD for molybdenum and total uranium was 18.0 ppm and 16.2 ppm, respectively. Only the statistical XRF LOD could be determined for molybdenum. Laboratory-confirmation of the XRF LOD for total uranium is discussed in Section 2.2.2

2.2.2 Laboratory-Confirmed XRF Detection Limits

As mentioned in Section 2.2, a subset of the total XRF analyses of the site soils was split for confirmatory laboratory analysis. These procedures were consistent with those provided in Section 7.7 of the *XRF SOP*. Laboratory analyses were performed to detect only uranium isotopes; thus, confirmation of the XRF LOD for molybdenum could not be performed. Instead, the comparability between the statistical XRF LOD (Section 2.2.1) and the split laboratory analyses for total uranium was used to determine whether there was good agreement between the statistical XRF LOD and the laboratory-confirmed LOD for total uranium. The result of this comparison for uranium might reasonably be extended to other metals, including molybdenum. For the purposes of this evaluation, all reported laboratory concentrations were used regardless of whether the reported concentration was qualified (estimated) or not.

For some XRF-laboratory splits, the discrete XRF measurements were pooled and the average XRF measurement for soil core intervals contributing to the composite sample was compared against laboratory analyses of the composite sample. In total, 159 XRF samples were

split for confirmatory laboratory analysis, of which 95 were XRF composite samples and 64 were XRF discrete samples. Two different laboratory methods were employed to determine total uranium concentrations: alpha spectroscopy for U-238 and gamma spectroscopy for U-238. The purpose of this evaluation was to determine the laboratory-confirmed XRF LOD for total uranium and compare the laboratory methods for analyzing total uranium in the site soils.

A summary of the XRF-laboratory split analyses for total uranium in site soils is shown in Table 10. Composite and discrete split samples were investigated separately to determine the effects of sample aggregation on XRF and laboratory results. Of the 159 split samples, 131 contained non-detectable XRF concentrations of total uranium; 28 contained detectable concentrations of total uranium. To confirm the XRF LOD with the laboratory procedures, the range of XRF LODs for non-detect split samples were compared to the range of reported laboratory results (Table 10A). For composite non-detect split samples, mean XRF LOD was 17.4 ppm (range: 13.8 – 26.2 ppm). For discrete non-detect split samples, mean XRF LOD was 16.8 ppm (range: 12.2 – 205.4 ppm). This dataset included the same anomalous observation described in Section 2.2.1 (XRF LOD: 205.4 ppm). Overall, the range of alpha spectrometry results for total uranium was not as comparable to the XRF LOD as was the range of gamma spectrometry results (Table 10A). In total, the mean XRF reported LOD was 18.7 ppm total uranium (range: 12.2 – 205.4 ppm). The range of alpha spectrometry was 0.2 to 255.0 ppm total uranium, whereas the range of gamma spectrometry results was 0.0 to 24.5 ppm total uranium. There was an additional anomalous observation in reported alpha spectrometry total uranium results. For one observation (sample no. HSSB1516), the XRF did not report detectable levels of total uranium yet the alpha spectroscopy method resulted in total uranium concentrations of approximately 255.0 ppm. The gamma spectroscopy estimated total uranium concentration for this sample was a qualified result at 3.15 ppm, which is a much more likely representation of the true total uranium concentration for a sample in which total uranium was not detected with the XRF. It is possible that laboratory error may have occurred in the alpha spectroscopy analyses of this sample. Because of the anomalous value in alpha spectroscopy total uranium results, only gamma spectroscopy results were evaluated further and compared with the statistical XRF LOD. A comparison of the alpha and gamma spectroscopy results with XRF results is provided in Section 2.3.

Table 10. Summary of XRF and Split Laboratory Analyses for Total Uranium.

A) Alpha and Gamma Spectroscopy Results for Split Non-Detect XRF Samples

Sample Type	N[1]	Variable (ppm)	Mean	Median	Min	Max	Standard Deviation
Composite	82	XRF Reported LOD	17.4	17.6	13.8	26.2	2.2
		Total U (Alpha Spectroscopy)[2]	7.8	3.9	0.2	255.0	27.9
		Total U (Gamma Spectroscopy)[3]	4.6	3.2	0.0	24.5	4.6
Discrete	49	XRF Reported LOD	20.9	16.8	12.2	205.4	27.1
		Total U (Alpha Spectroscopy)[2]	5.7	3.5	0.8	63.4	9.4
		Total U (Gamma Spectroscopy)[3]	4.2	2.6	0.0	23.6	5.0
Total	131	XRF Reported LOD	18.7	17.2	12.2	205.4	16.6
		Total U (Alpha Spectroscopy)[2]	7.0	3.7	0.2	255.0	22.8
		Total U (Gamma Spectroscopy)[3]	4.4	3.0	0.0	24.5	4.8

B) Alpha and Gamma Spectroscopy Results for Split Detected XRF Samples

Sample Type	N[1]	Variable (ppm)	Mean	Median	Min	Max	Standard Deviation
Composite	13	XRF Result	24.5	18.5	12.0	64.8	17.7
		XRF Reported Uncertainty	13.8	13.9	8.3	16.4	2.1
		Total U (Alpha Spectroscopy)[2]	23.8	20.0	11.1	60.4	13.9
		Total U (Gamma Spectroscopy)[3]	22.6	16.1	8.4	59.7	15.8
Discrete	15	XRF Result	102.8	70.7	20.6	366.4	104.8
		XRF Reported Uncertainty	9.3	8.6	6.6	15.9	2.7
		Total U (Alpha Spectroscopy)[2]	100.2	75.0	3.2	538.0	127.3
		Total U (Gamma Spectroscopy)[3]	119.9	77.1	22.2	450.0	133.8
Total	28	XRF Result	66.5	34.9	12.0	366.4	86.1
		XRF Reported Uncertainty	11.4	11.9	6.6	16.4	3.3
		Total U (Alpha Spectroscopy)[2]	64.7	33.9	3.2	538.0	99.9
		Total U (Gamma Spectroscopy)[3]	74.7	30.4	8.4	450.0	108.8

[1] The number of valid observations for all split laboratory measurements (N = 159).

[2] Alpha spectroscopy for total uranium, as estimated by U-238.

[3] Gamma spectroscopy for total uranium, as estimated by U-238.

The laboratory LOD_{50} value was calculated to confirm the XRF total uranium LOD with laboratory results. The LOD_{50} value represents the laboratory concentration at which 50% of the XRF measurements detect the element of interest; the other 50% of the XRF measurements report a non-detect value for the element of interest. To calculate the LOD_{50} value for total uranium, all split soil samples (N = 159; Table 10) were binned by gamma spectroscopy result. A total of 6 bins were created, each of which contained at least 9 observations. The midpoint of one bin contained the statistical XRF LOD for total uranium calculated in Section 2.2.1 (16.2 ppm). A graph was created to illustrate the proportion of observations within each bin that

detected total uranium concentrations. The midpoint of the bin that is closest to 50% detection represents the LOD_{50} value.

The proportion of XRF measurements that detected total uranium in each bin are shown in Figure 6. The LOD_{50} at which nearly 50% of the XRF observations were detected was 10.3 ppm total uranium. At the midpoint gamma spectroscopy concentration, nearly 45% of the XRF results detected total uranium (Figure 6). The results of this evaluation indicate that the true LOD for total uranium, as determined by the LOD_{50} for gamma spectroscopy results, was 10.3 ppm. This confirms the expectation presented in Section 2.2.1 that the XRF slightly overestimates the LOD for non-detect results.

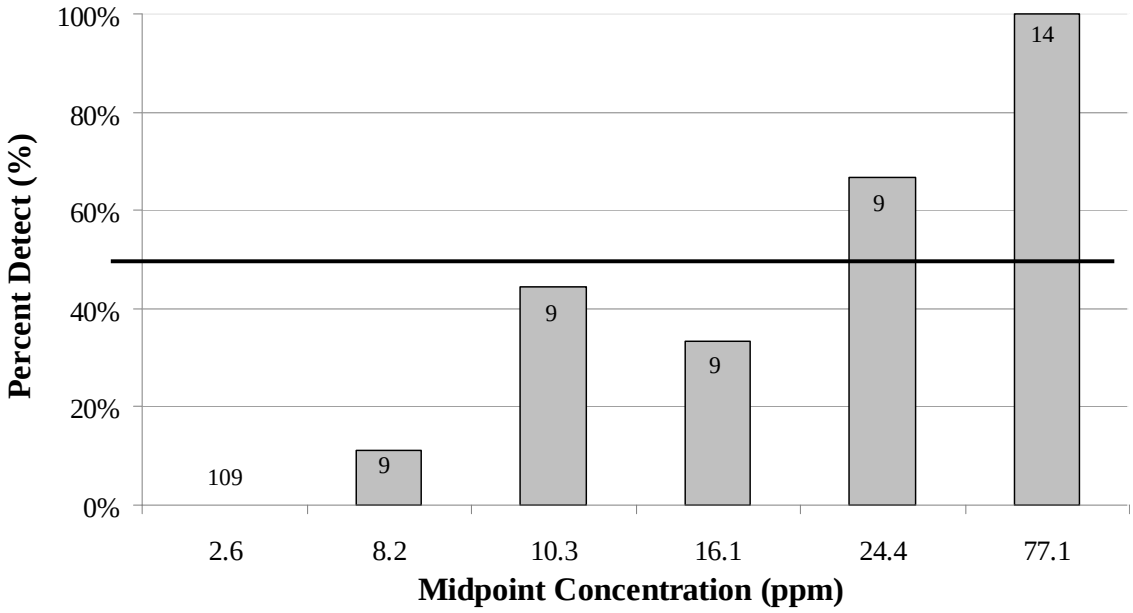

Figure 6. Percent of XRF measurements that detected total uranium concentrations along midpoints of binned gamma spectroscopy results. The proportion of XRF observations was used to determine the LOD_{50} value. The horizontal reference line refers to 50% detection. Numbers within or above each bar represent the total number of observations included in the bin.

2.3 Comparability Assessment

This section evaluates the comparability of the XRF and laboratory analytical datasets according to Section 7.7 of the *XRF SOP* and Section 13.7 of EPA Method 6200. Comparability between XRF datasets and fixed laboratory results may be used as empirical means to calibrate the instrument or check an instrument calibration, or to evaluate the appropriateness of different laboratory methods. For the purposes of this XRF evaluation, two comparability evaluations were performed: 1) association between XRF reported molybdenum and total uranium concentrations, and 2) associations between XRF reported total uranium concentrations and the fixed laboratory analytical results for total uranium. Meeting the objectives of these evaluations involved determining if a relationship existed between the two target analytes in the XRF dataset; determining the relationship between XRF reported total uranium concentrations and the fixed laboratory analytical results to confirm XRF accuracy; and to evaluate the comparability of XRF results with each of the two laboratory methods to determine the laboratory analytical method that best explains the XRF data.

2.3.1 Relationship Between XRF Molybdenum and XRF Total Uranium

A statistical evaluation was performed to determine the relationship between XRF reported molybdenum and total uranium concentrations. This analysis was performed for the entire XRF dataset using discrete XRF measurements of the site soil core samples. See Table 9A in Section 2.2.1 for a summary of XRF measurements in which molybdenum or total uranium was detected. A total of 26 and 48 discrete XRF analyses of site soils reported detectable concentrations of molybdenum and total uranium, respectively (Table 9A). XRF detectable concentrations of both molybdenum and total uranium were collocated in 9 discrete soil samples. Table 11 summarizes the XRF results for molybdenum and total uranium in those site soil samples in which both elements were detected.

Table 11. Summary of XRF results for site soil samples in which molybdenum and total uranium were detected (N = 9).

Variable	Mean (ppm)	Median (ppm)	Minimum (ppm)	Maximum (ppm)	Standard Deviation (ppm)
Mo Reported Concentration	30.6	26.3	21.8	47.4	10.2
Total U Reported Concentration	144.8	97.9	23.8	366.4	122.3
Mo Reported Uncertainty	7.0	6.9	6.5	7.7	0.4
Total U Reported Uncertainty	10.3	9.5	6.6	15.9	3.0

The purpose of this evaluation was to determine whether detectable concentrations of molybdenum and total uranium (as reported by XRF) were associated throughout the site. The association in reported XRF concentrations would indicate the reported concentration of one element that can be explained by the reported concentration for the other element. A linear regression analysis was performed to determine the linear relationship between the two variables, using XRF total uranium concentrations as the explanatory (predictor) variable and XRF molybdenum concentrations as the response variable. Regression analysis is advantageous in establishing linear relationships between variables through the calculation of three factors: the y-intercept of the linear relationship, the slope of the linear relationship, and the coefficient of

determination (R^2). The R^2 value is indicative of the proportion of the response variable explained by the predictor variable; it is often used to determine the strength of the association (Sokal and Rohlf 1995). These factors were used to determine the linear relationship between the two variables based upon the following equation:

Equation 3

$$Y = b*X + a$$

Where

Y	= The response variable.
b	= The slope of the linear relationship.
X	= The explanatory variable.
a	= The y-intercept of the linear relationship.

For the 9 discrete site soil samples in which detectable concentrations of molybdenum and total uranium were collocated, the regression analysis indicated that a linear relationship between total uranium and molybdenum concentrations did not exist ($R^2 = 0.24$). Further investigation revealed that the linear relationship was obscured by a single influential observation (sample no. HSSB1580) where the reported total uranium concentration was 23.8 ppm and the reported molybdenum concentration was 47.4 ppm. Compared to the other samples included in this evaluation the total uranium reported concentration for this influential observation approached the XRF LOD for site soils (see Section 2.2.2). The XRF total uranium concentrations for the other samples included in this evaluation were above 50 ppm. Omitting the influential observation from the analysis resulted in a strong positive linear relationship between the element concentrations for the remaining samples (Figure 7). The R^2 value for this relationship was 0.977, indicating that approximately 98% of the variability in reported XRF molybdenum concentrations was explained by the variability in total uranium XRF concentrations.

This evaluation indicates that, for those samples in which molybdenum and total uranium were detected with XRF, concentrations of the two elements were correlated. As XRF total uranium concentrations approach the XRF LOD, however, the relationship between total uranium and molybdenum becomes obscured and molybdenum concentrations may be greater than total uranium concentrations (Figure 7). Another caveat surrounding this conclusion is that there were a number of samples in which only one element (but not the other) was detected. Of the XRF observations in which either molybdenum or total uranium were detected, there were 17 observations in which only molybdenum was detected; there were 39 observations in which only total uranium was detected. Because there was a greater number of XRF observations in which only one element was detected (N = 56) than those in which both elements were detected (N = 9), it is not possible to conclude that an association in exists for these two elements over all XRF observations. This conclusion is thus restricted to those XRF observations in which both elements were detected.

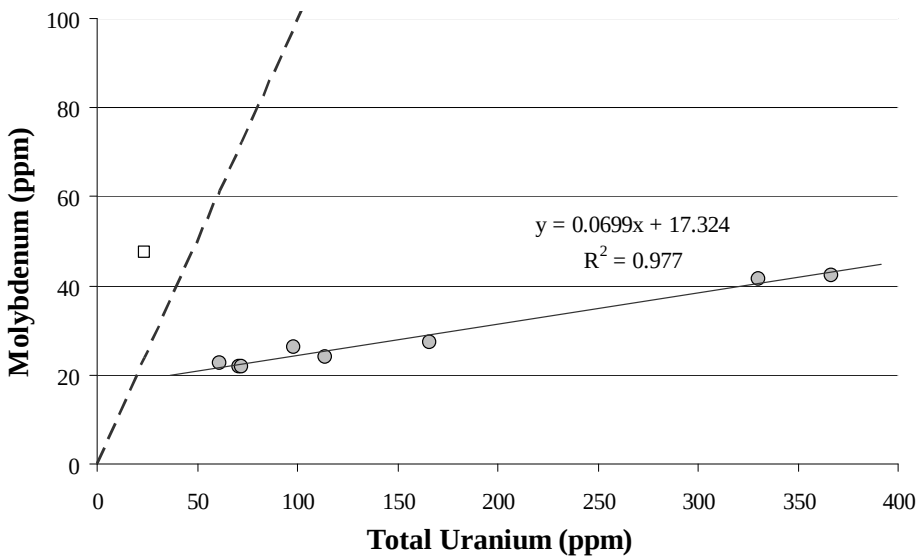

Figure 7. Relationship between XRF molybdenum and total uranium concentrations. The 45-degree line (dashed) denotes a 1:1 relationship. One anomalous observation (open square) was excluded from analysis. Analysis: linear regression; $\alpha = 0.05$; SAS 9.1.

2.3.2 Relationship Between XRF and Alpha Spectroscopy Methods

A statistical evaluation was performed to determine the comparability between XRF and alpha spectroscopy methods for determining total uranium concentrations in the site soils. This analysis was performed for the entire XRF split sample dataset using composite and discrete site soil core samples. Only composite samples in which at least one discrete measurement reported detectable XRF total uranium concentrations were included in this analysis. For these composite samples, all non-detect discrete observations were replaced with ½ the LOD as reported by the XRF and the mean of all discrete results so determined was substituted as the XRF concentration to be compared to the laboratory results. See Table 10B in Section 2.2.2 for a summary of the XRF and alpha spectroscopy analyses for total uranium concentrations for all split samples. For this comparability evaluation, however, only XRF concentrations greater than two-times the laboratory-confirmed LOD (10.3 ppm) were included (N = 20). To relate alpha spectroscopy total uranium results to XRF results, a linear regression analysis was used following Equation 3 and the procedures outlined in Section 2.3.1. The response variable for this analysis was the alpha spectroscopy total uranium concentration; the explanatory variable was the XRF total uranium concentration.

For the 28 split soil samples in which total uranium was detected, the regression analysis indicated that a linear relationship existed between XRF total uranium concentration and alpha spectroscopy total uranium concentration (Figure 8). The R^2 value for this relationship was approximately 0.45, indicating that nearly 45% of the variation in alpha spectroscopy total uranium concentrations was explained by variation in XRF total uranium concentrations. The slope of the linear relationship was 0.80 and the y-intercept was 15.24. Two observations appeared to significantly deviate from the regression trend for this analysis. Both of these anomalous observations occurred at elevated XRF total uranium concentrations (Figure 8). This

has resulted in a wider 95% confidence interval for the mean alpha spectrometry results. A comparison of this relationship to the relationship between XRF and gamma spectrometry is provided in Section 2.3.4.

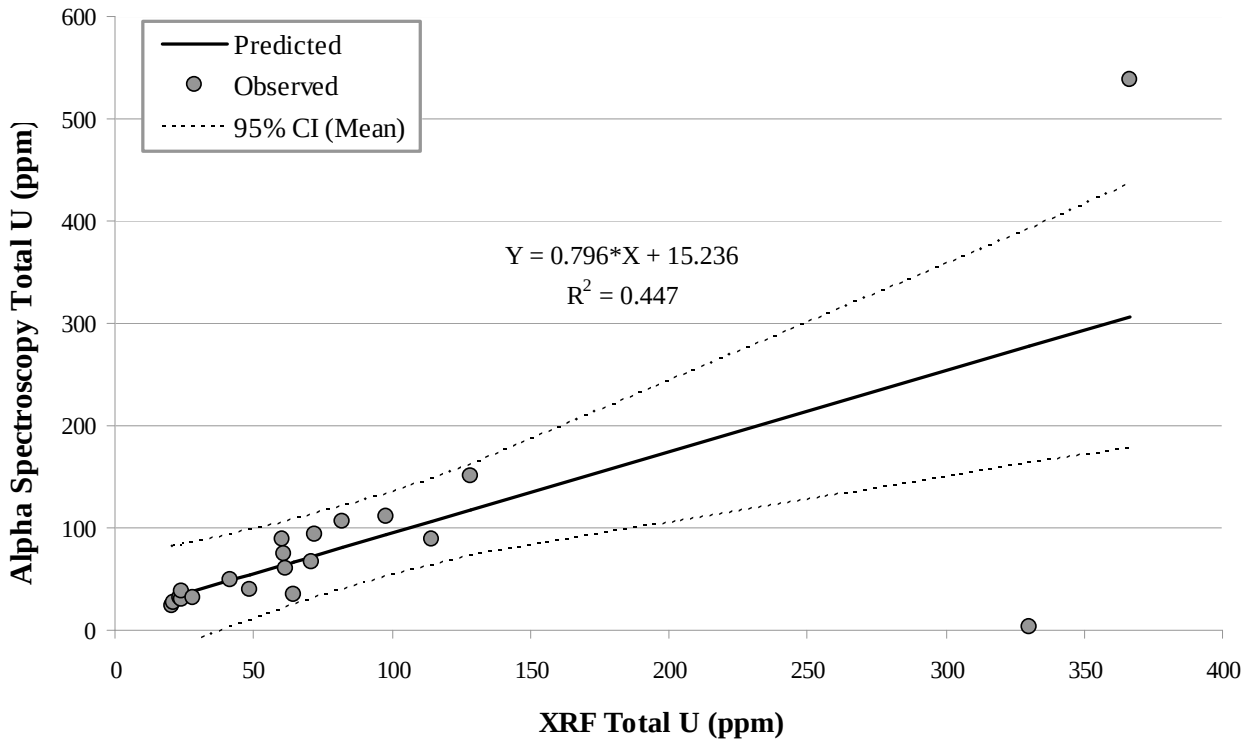

Figure 8. Relationship between XRF total uranium and alpha spectroscopy total uranium concentrations. The best-fit trend line (solid line) is shown for all observations in which XRF total uranium was detected for the split samples. Also shown is the 45-degree line (dashed) denoting a 1:1 relationship between reported concentrations and the 95% confidence interval (dotted line) for the mean alpha spectroscopy total uranium concentration.

2.3.3 Relationship between XRF and Gamma Spectroscopy Methods

A statistical evaluation was performed to determine the relationship between XRF and gamma spectroscopy methods for determining total uranium concentrations in the site soils. The same approach as described in Section 2.3.2 was used to determine the relationship between XRF total uranium and gamma spectroscopy total uranium concentrations. See Table 10B for a summary of the XRF and gamma spectroscopy analyses for total uranium concentrations.

For the 20 split soil samples in which XRF total uranium was greater than two-times the laboratory-confirmed LOD, the regression analysis indicated that a linear relationship existed between the XRF and gamma spectroscopy results (Figure 9). The R^2 value for this relationship was approximately 0.98, indicating that over 95% of the variation in gamma spectroscopy total uranium concentrations was explained by variation in XRF total uranium concentrations. The slope of the linear relationship was 1.26 and the y-intercept was -10.54 (Figure 9). There were no apparent outliers in the gamma spectroscopy dataset and comparability between XRF and

gamma spectroscopy was less variable then alpha spectroscopy, as evident by the narrow 95% confidence interval around the predicted gamma spectroscopy results (Figure 9).

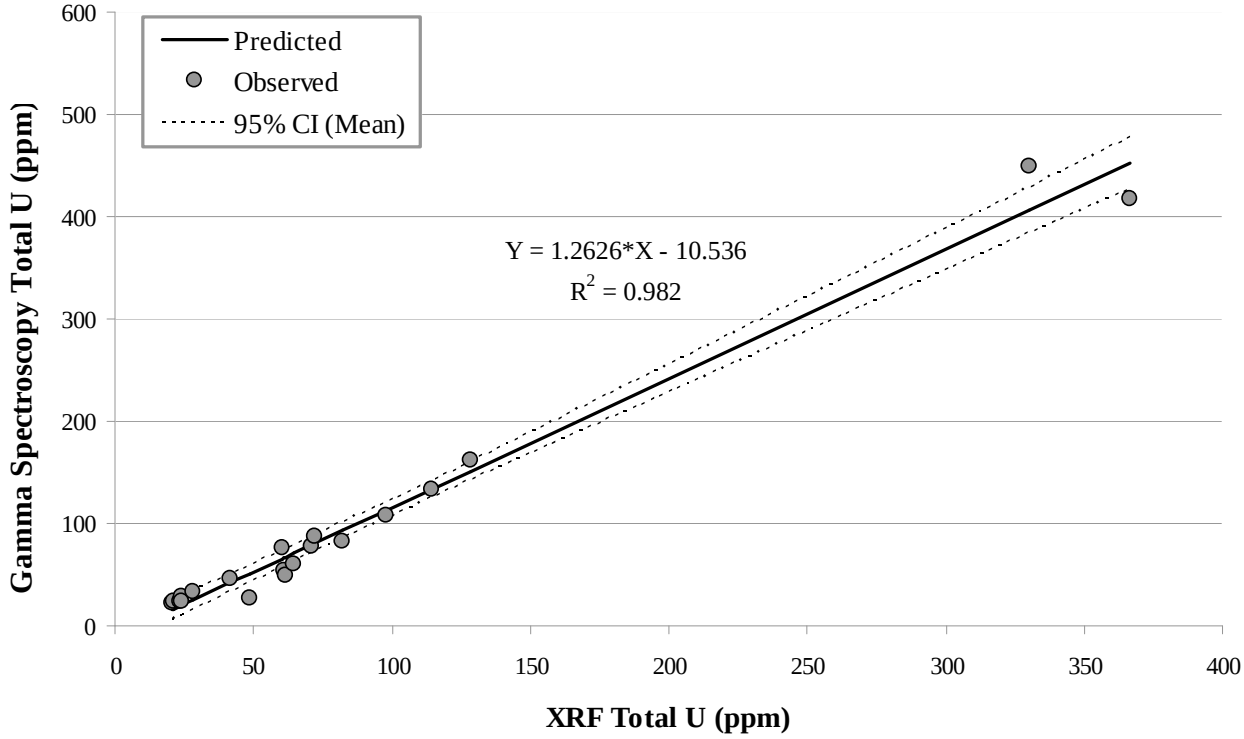

Figure 9. Relationship between XRF total uranium and gamma spectroscopy total uranium concentrations. The best-fit trend line (solid line) is shown for all observations in which XRF total uranium was detected for the split samples. Also shown is the 45-degree line (dashed) (denoting a 1:1 relationship) and the 95% confidence interval (dotted line) for the mean gamma spectroscopy total uranium concentration.

2.3.4 Comparing the XRF-Laboratory Relationship between Analytical Methods

This section compares the relationships between the XRF and the two laboratory analytical methods to detect total uranium concentrations. The purpose of this evaluation was to determine whether alpha or gamma spectroscopy was the more appropriate analytical method to compare with XRF measurements of site soils. This evaluation was based upon the regression analyses conducted in Sections 2.3.2 and 2.3.3.

A number of similarities and differences were apparent when the relationships were examined. In analyses of both analytical methods, a statistical relationship between the XRF and the analytical result was observed. Furthermore, the XRF result was approximately within 20% - 26% of the reported laboratory result (based upon slope). Due to the presence of influential observations in the dataset, the analysis for alpha spectroscopy total uranium indicated a weaker and more uncertain relationship with XRF total uranium concentrations. The R^2 value for the alpha spectroscopy analysis was 0.45 with a much wider 95% confidence interval for the mean alpha spectroscopy result (Figure 8). On the other hand, the analysis for gamma spectroscopy

indicated a stronger and less uncertain relationship with XRF total uranium concentrations. For this analysis, the R^2 value was 0.95 with a much narrower 95% confidence interval (Figure 9).

Based upon these observations, gamma spectroscopy appeared to be the more appropriate laboratory method for confirming XRF total uranium concentration in site soils. The main factor influencing the relationship for both analyses was the presence/absence of influential observations. There were two influential observations recorded under the alpha spectroscopy analysis; influential observations were absent from the gamma spectroscopy analysis. These influential observations may have been introduced into the alpha spectroscopy results through sample preparation. Alpha spectroscopy employs a more intensive laboratory method than either gamma spectroscopy or XRF, involving different sample sizes and sub-sampling steps. As such, differences owing to sample heterogeneity between alpha spectroscopy and either gamma spectroscopy or XRF, which involve more similar procedures, might accrue.

As discussed in Section 2.1.1.2, the XRF was internally calibrated to coarse-grained silt matrix reference standards prior to its use at the site. The strong positive relationship between the XRF total uranium results and the gamma spectroscopy results indicates that the calibration was appropriate for the site soils.

3.0 Conclusions

This section summarizes the performance of the XRF to detect molybdenum and total uranium concentrations in site soils. Recommendations for future field sampling plans are also discussed.

3.1 XRF Performance

A variety of methods were used to evaluate the performance of the XRF to determine molybdenum and total uranium concentrations. These include accuracy assessments (Sections 2.1.1.1, 2.1.1.2, and 2.3.4), an assessment of XRF precision (Section 2.1.2.1), XRF screening-level reproducibility (Section 2.1.2.3), and XRF system degradation (Section 2.1.3). The samples in these evaluations were prepared and analyzed according to the *XRF SOP*.

3.1.1 XRF Accuracy

XRF accuracy was greatest for standards containing silt matrix, intermediate for sand matrix standards, and lowest for fine-grained clay matrix standards. Despite the apparent matrix effects observed, XRF accuracy was adequate for all matrix types as the calculated mean percent difference for all standards was approximately equal to or less than 20%. These results indicate that the differences in XRF accuracy across matrix types are due to the internal calibration of the device to the silt matrix standard. A trend was also observed indicating that XRF accuracy improves at increasing concentrations of the target element.

Comparability assessments of the XRF results for the site soil samples and the gamma spectroscopy results for total uranium confirm that the internal calibration of the XRF against the coarse-grained silt matrix standard was appropriate to provide accurate and reliable results for

total uranium at the site. The XRF results exhibited a close relationship with the gamma spectroscopy results (Figure 9), as the predicted gamma spectroscopy results for total uranium was within 20% of the XRF results. These observations confirm that the accuracy of the XRF is sufficient to provide comparable results against laboratory gamma spectroscopy results.

3.1.2 XRF Precision

The XRF exhibited excellent precision, as measured by the low variability between repeated measurements of the same location within a sample (RSD < 10%). Furthermore, the average reported error (instrument error) was low (< 20%) and was similar to the standard deviation for the repeated measurements. These observations confirm that the precision of the XRF is sufficient to provide consistent results for total uranium at the site.

3.1.3 XRF Screening-Level Reproducibility

For this evaluation, the XRF results were 100% accurate with respect to correct outcomes for determination of detection or non-detection. Furthermore, there was low variability in the reported XRF concentration for the sample in which total uranium was detected; there was also low variability in the reported LOD for the sample in which total uranium was not detected. These observations confirm that reported XRF measurements are sufficient for quantitative screening-level purposes. The low variability in these reported measurements also support the observations of XRF precision.

3.1.4 XRF Performance over a Work Day

This evaluation indicated that XRF response over the course of a work day was reduced by 10% to 21% for measurements of total uranium. However, no similar XRF response reduction occurred for molybdenum calibration measurements. The reduced uranium response result may be due to battery discharge over the course of the day, as the X-ray tube excitation energy output is dependent upon the power supply. Methods to minimize instrument degradation include charging the battery at regular intervals throughout the day or exchanging with a fully charged battery.

3.1.5 XRF LOD for Total Uranium

For all XRF analyses of site soils, the median reported XRF LOD for samples in which total uranium was not detected was 16.2 ppm. Laboratory-determined XRF LOD was evaluated for the split soil samples that were analyzed with both XRF and laboratory methods. The laboratory-confirmed XRF LOD was approximately 10.3 ppm. These observations confirm the expectation that the reported XRF LOD is slightly greater than the true LOD. With respect to the field investigation level for the site (44 ppm [30 pCi/g] total uranium), both of these LOD values are low enough to provide appropriate screening-level results for total uranium.

3.2 Sample Heterogeneity

The effects of sample heterogeneity on reported total uranium concentrations were assessed by examining small-scale and bagged sample variability (Section 2.1.2.2). These analyses were conducted to determine the amount of variability introduced by the sample preparation and analysis procedures described in the *XRF SOP*.

3.2.1 Small-Scale Sample Variability

Small-scale sample variability, defined as the localized variability in a soil sample as determined by removing and replacing the sample cup, was very low (RSD < 10%), indicating that small-scale variability was minimized following the sample preparation and analysis protocols described in the *XRF SOP*.

These results indicate that the current XRF protocol is sufficient to manage small-scale variability in total uranium concentrations.

3.2.2 Bagged Sample Intrinsic Variability

Bagged sample intrinsic variability, defined as the broader-scale variability throughout an entire bagged sample, ranged from 2.90% to 49.73% RSD. There was greater variability observed along both sides of the sample bag than within one side of the sample bag. These observations indicate that greater variability in total uranium concentrations (as reported by the XRF) exists within the bagged sample than what can be attributed to instrument error (precision).

Due to greater heterogeneity along both sides of the sample bag, XRF protocols should also include an approach to quantify sample bag intrinsic variability using measurements collected from both sides of the bagged sample.

3.3 Relationship Between XRF Reported Molybdenum and Total Uranium

XRF reported total uranium and molybdenum concentrations were evaluated to determine whether elevated total uranium and molybdenum concentrations were collocated (Section 2.3.1). With the exception of one sample in which total uranium was detected at a low concentration, there was a positive relationship between XRF reported molybdenum and total uranium concentrations. For XRF observations in which both elements were detected, elevated molybdenum and total uranium concentrations were strongly positively associated, indicating that some soil locations may have been contaminated with a residue containing both elements in a relatively constant ratio.

Due to the limited number of XRF observations in which both elements were detected (N = 9), it is not possible to conclude that an association exists for these two elements over all XRF observations. This conclusion is thus restricted to those XRF observations in which both elements were detected.

3.4 Comparability Between XRF and Laboratory Spectroscopy Methods

Comparisons of the XRF results to laboratory results using spectroscopy methods were used to evaluate overall comparability of XRF to laboratory methods and to determine which laboratory method produced results most comparable to XRF results for soils.

For XRF comparisons with alpha spectroscopy results, the relationship was relatively weak ($R^2 = 0.45$) and yielded much more variable estimates of the true total uranium concentrations as determined by the 95% confidence interval. The XRF comparisons with gamma spectroscopy results, on the other hand, resulted in a much stronger relationship ($R^2 = 0.98$) and yielded less variable estimates of the true total uranium concentrations. There were two anomalous observations in the alpha spectroscopy dataset; there were no apparent anomalous values in the gamma spectroscopy dataset.

According to EPA Method 6200, XRF data can be considered definitive if the correlation coefficient (r) is greater than or equal to 0.90. In this evaluation, the regression coefficient to compare XRF and gamma spectroscopy total uranium concentrations ($R^2 = 0.98$) corresponds to a correlation r-value of 0.99. Thus, XRF and gamma spectroscopy methods are highly comparable with respect to analysis of total uranium in site soils. Thus, it is concluded that XRF measurements of site soils provide reliable and accurate quantitative results for molybdenum and total uranium, which would be suitable for meeting a number of potential future site remediation needs.

4.0 References

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