Results of X-Ray Fluorescence Screening Phase 1 Remedial Investigation – October 2007 Klau and Buena Vista Mines Superfund Site San Luis Obispo County, California

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INTRODUCTION

In order to provide efficient and comprehensive site coverage for nature and extent determination of metals contamination at the Klau Buena Vista Mine Super fund site, a field portable X-ray fluorescence (XRF) spectrometer was used to measure heavy metal concentrations over a systematic sampling grid. One hundred and fifty-three soil samples were split and analyzed for metals by XRF and by an off-site laboratory, the EPA Region 9 laboratory in Richmond, California. The off-site laboratory used inductively coupled plasma –atomic absorption spectrometer (ICP-AES) and cold vapor atomic absorption spectrometry (CVAAS) techniques for metals and mercury, respectively. The field portable XRF was a Niton Model XLt with a miniaturized X-Ray tube excitation source. This memorandum presents a brief description of XRF measurement techniques, the field procedures, and a comparison of the XRF and fixed laboratory results.

METHOD

XRF spectrometry is a non-destructive technique for determination of heavy metal concentrations. When a sample is irradiated with X-rays, inner shell electrons absorb the incident radiation and are promoted to higher energy levels, leaving lower energy vacancies. These vacancies are filled with electrons from outer electron shells. When these outer shell electrons cascade into the inner shell vacancies they emit characteristic energies. These characteristic energies produce the fluorescence spectrum which is proportional to the amount of analyte in the sample.

XRF is limited to measurement of analytes on the surfaces of materials. The accuracy and precision of XRF measurements may be affected by:

- Physical matrix effects such as particle size, uniformity, homogeneity, and surface condition;
- Moisture content greater than 10 percent resulting in attenuation of X-ray transmission
- Chemical or spectral interference from other analytes resulting in absorption or enhancement of X-ray signal;

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Because all of the XRF measurements were made in-situ, the largest source of error is expected to be the non-homogeneous sample surface. Because the soils at Klau and Buena Vista Mine were generally in the 80 to 90 percent solids range, moisture is not considered a significant source of error. There was no evidence of chemical or spectral interferences, although these interferences cannot be ruled out as a minor source of error for the Klau and Buena Vista Mine data.

Procedure

The in-situ measurements were conducted as follows:

The in-situ measurements were conducted as follows:

1. Large or non-representative debris was removed from the selected location.
2. The location chosen for analysis was smoothed and flattened in an area approximately 4" by 4", using a disposable spoon.
3. The location was smoothed and firmly tamped to provide as flat and smooth an area as possible.
4. The nose of the XRF, which was covered by x-ray film, was positioned against the X-ray film, the shutter released and the sample data collected for approximately 30 seconds.
5. Three areas within each 4" by 4" location were randomly analyzed.

Samples for the offsite laboratory were collected from the area prepared for *in situ* analysis by using the disposable scoop. The soil samples were placed into a resealable plastic bag.

Calibration

The XRF is supplied with an internal calibration which is updated each time the instrument is powered on. Niton uses the Compton normalization method to automatically correct for sample specific matrix effects. The XRF is calibrated internally at the factory on NIST standard reference soil samples. This internal calibration is used for subsequent field work, without need for adjustment of recalibration at other sites. The manufacturer provides a NIST reference material that is used to verify the internal calibration.

EVALUATION OF XRF RESULTS.

The following presents a comparison and assessment of the correlation between the laboratory and XRF results.

Field Quality Control Results

A National Institutes of Standards and Technology (NIST) Standard Reference Material (SRM) was analyzed daily as a calibration check standard (NIST SRM 2710). Figure 1 presents the percent recoveries obtained by analysis date. The minimum and maximum recoveries are presented in the table below for the five analytes that were present in the SRM at certified concentrations above the XRF RL.

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TABLE 1
Daily XRF Calibration Check Standard: NIST SRM 2710
Klau and Buena Vista Mine Phase I Investigation

Analyte	Lead	Arsenic	Mercury	Zinc	Copper
Concentration of SRM 2710 (mg/Kg)	5532	626	32.6	6952	2950
Minimum Percent Recovery	95.10	88.88	73.07	94.89	94.80
Maximum Percent recovery	100.79	127.69	142.36	102.38	104.42
Average Percent Recovery	97.89	106.63	99.94	98.96	99.31

The largest range of recoveries was observed for mercury although the averages for all analytes are well within the advisory 75 percent -125 percent recovery criteria presented in Standard Operating Procedure (SOP 11) (CH2M HILL, 2007). Based on the results for the calibration check, the XRF was capable of obtaining acceptable metals data for the elements of interest.

Pre-Mobilization Sampling and Analysis

During pre-mobilization site reconnaissance, the XRF was used in-situ to select locations containing a range of mercury concentrations. Samples from these locations were collected, homogenized, and split for analysis by both the XRF and the EPA Region 9 laboratory. The purpose of the collection and analysis of these split samples was to provide site matrix samples of known concentration to be used as stability check samples for the XRF in the field.

The selected samples were analyzed for mercury, cadmium, chromium, cobalt, and zinc in triplicate by both XRF and the Region 9 laboratory using inductively coupled plasma spectroscopy (ICP) and cold vapor atomic absorption spectroscopy (CVAA). The samples were analyzed by the XRF in the ex-situ mode using both the analysis cup provided with the instrument and using a zip-lock bag. The use of the zip-lock bag is a closer approximation to the variability encountered when performing direct, in-situ soil measurements while the cup presents a denser, more uniform surface to the incident X-rays. The Table 2 summarizes the comparison for mercury, the primary chemical of concern at the site.

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TABLE 2
Comparison of Mercury Results in Pre-Mobilization Samples Analyzed by Field XRF and ICP/CVAA
Klau and Buena Vista Mine Phase I Investigation

Standard	Average Lab (mg/kg)	Average XRF (Analyzed in Cup) (mg/kg)	RPD	Average XRF (Analyzed in Bag) (mg/kg)	RPD
M06WRT	9533	3723	88	2550	116
N20RF	4433	1811	84	782	140
O23BVR	3867	698	139	913	124
L07WKP	743	65	168	44	178
R13CTA	1267	128	163	87	174

Based on the relative percent difference between the samples, the comparison between the XRF results and the Region 9 laboratory results is poor.

Figure 2 presents a correlation plot of these results. A perfect correlation would be represented by a correlation coefficient (r) of unity and a slope of one as indicated by the 45 degree line (providing the scale of the x and y axis are identical). The correlation coefficient for the comparison of the XRF and laboratory results is 0.98, indicating that the results are well correlated, but the slope is 0.43, less than one, indicating a significant high bias in the laboratory results compared to the XRF results. The source of this bias is unknown.

The XRF results obtained for the five pre-mobilization samples analyzed during the main field sampling activities were stable and repeatable. However, while the precision of the XRF analysis of the pre-mobilization samples during the main field sampling and analysis activities is good, the correlation with the laboratory results remained poor. The source of the disparity between the XRF and laboratory results is unknown.

Comparison of In-Situ XRF and Off-site Laboratory Project Sample Results
A similar analysis of field XRF and laboratory results for the principle analytes of concern, arsenic, chromium, nickel, and mercury obtained during the Phase 1 field event, was performed. Table 3 presents a summary of the maximum and minimum RPDs, correlation coefficients, slope of the linear regression line, and the average and standard deviation for the RPD. All split sample results from the background, judgmental, and systematic locations were used for this preliminary comparison.

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TABLE 3
Correlation Statistics
Klau and Buena Vista Mine Phase I Investigation

Analyte	Maximum RPD	Minimum RPD	Average RPD	RPD Standard Deviation	Correlation Coefficient (r)	Slope	Bias (XRF with respect to ICP)
Arsenic	175	5	68	39	0.68	1.1	Negligible
Chromium[1]	192	2	114	49	0.82	7.4	High
Mercury	198	0.55	49	40	0.61	1.9	High
Mercury (<200 mg/kg)	198	0.55	49	40	0.40	0.81	Low
Nickel	179	0.24	30	37	0.89	1.2	Negligible

1 Chromium results obtained by XRF are not considered reliable as the calibration standard is at a concentration well below the XRF RL.

Plots illustrating the correlation between the XRF measurements and the off-site laboratory results are presented in Figures 3 thru 7 for the above listed analytes. The laboratory results were corrected for percent solids so that the results are compared on a wet weight basis. In some cases, certain data were excluded as described below:

- Figure 3, Arsenic Correlation Plot:

The surface and subsurface samples from the Klau and Buena Vista Mine waste rock pile and the western retort were eliminated due to the large difference between the field XRF and laboratory results. The differences are considered the result of non-representative sampling of the non homogeneous matrix.

- Figures 5 and 6, Mercury Correlation Plots:

Two correlation plots were prepared for the mercury results based on concentration ranges. Figure 3 presents all of the mercury data excluding the results from several judgmental locations with concentrations above 500 mg/kg. This was done to improve this initial graphical presentation. The actual agreement between these high concentration results is similar to that obtained using the whole data set and there was little change in the correlation coefficient or slope by limiting the concentration range. In a similar manner, the plot of the results below 200 mg/kg (Figure 6) has essentially the same statistics as Figure 5.

All data for chromium and nickel were used for preparation of Figures 4 and 7, respectively.

CONCLUSION

The linear regress ion analysis was evaluated based on the guidance in EPA Method 6200, *Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment* (EPA, 2007) which recommends a correlation coefficient of 0.7 or greater between results from XRF and off-site laboratory analysis. When this criterion is met, the

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XRF results may be considered suitable for use as screening level data. For the analyses performed at this site, the mercury correlation coefficients for the two concentration ranges plotted are slightly below this value. However, the average RPD is not excessive for non-homogenous soils analyzed by two different methodologies compared to an acceptance criteria for sample replicates of 35 percent (EPA, 2002). Because of the inherent increased variation expected from in-situ measurements, the XRF and laboratory results are considered sufficiently correlated to meet the project objectives despite correlation coefficients slightly below the recommended acceptance criterion. Chromium is a notable exception as the value in the NIST High standard is well below the XRF RL so the XRF results for chromium are not considered reliable.

As indicated in the previous sections of this memorandum, the daily XRF calibration verification was acceptable, indicating that the XRF was performing correctly. While the correlation between the XRF and off-site laboratory results from the main field sampling and analysis activities are considered adequate to meet the project goals, the comparison of the pre-mobilization results from the XRF and offsite laboratory results is not considered adequate. There are two possible explanations for the disparity between the pre-mobilization results:

- The concentration of the XRF calibration standard used to establish the factory set internal calibration is 32.6 mg/kg, well below the concentrations of the pre-mobilization split samples reported by the offsite laboratory.
- The pre-mobilization split samples were not prepared by drying and sieving to a uniform particle size as recommended by EPA Method 6200 which would improve the correlation between the two sets of results.

The NIST SRM used for XRF calibration verification is the highest concentration certified reference material available. The majority of the concentrations measured by XRF in the Klau and Buena Vista Mine soils were higher than this value. For these reason, the majority of the XRF results were based on extrapolation, assuming calibration linearity over all concentrations, rather than interpolation which is the more accurate procedure. It is likely that the XRF is not perfectly linear over concentrations ranges of several orders of magnitude and that changes in the slope of the calibration curve over the range of concentrations measured is responsible for the poor comparability observed in the pre-mobilization sample results. Overall, the comparability for the samples analyzed during the main field activities is better compared to the pre-mobilization sample results, due in part, to the number of sample results within at least one order of magnitude from the concentration of the calibration standard.

The manufacturer, Niton, has been contacted and is evaluating several samples using alternative calibration modes to assist in finding an explanation for the differences between the XRF and off-site laboratory pre-mobilization sample results.

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United States Environmental Protection Agency. 2004b. *Contract Laboratory Program National Functional Guidelines for Inorganic Data Review*, OSWER 9240.1-35, EPA 540-R-01-008. July.

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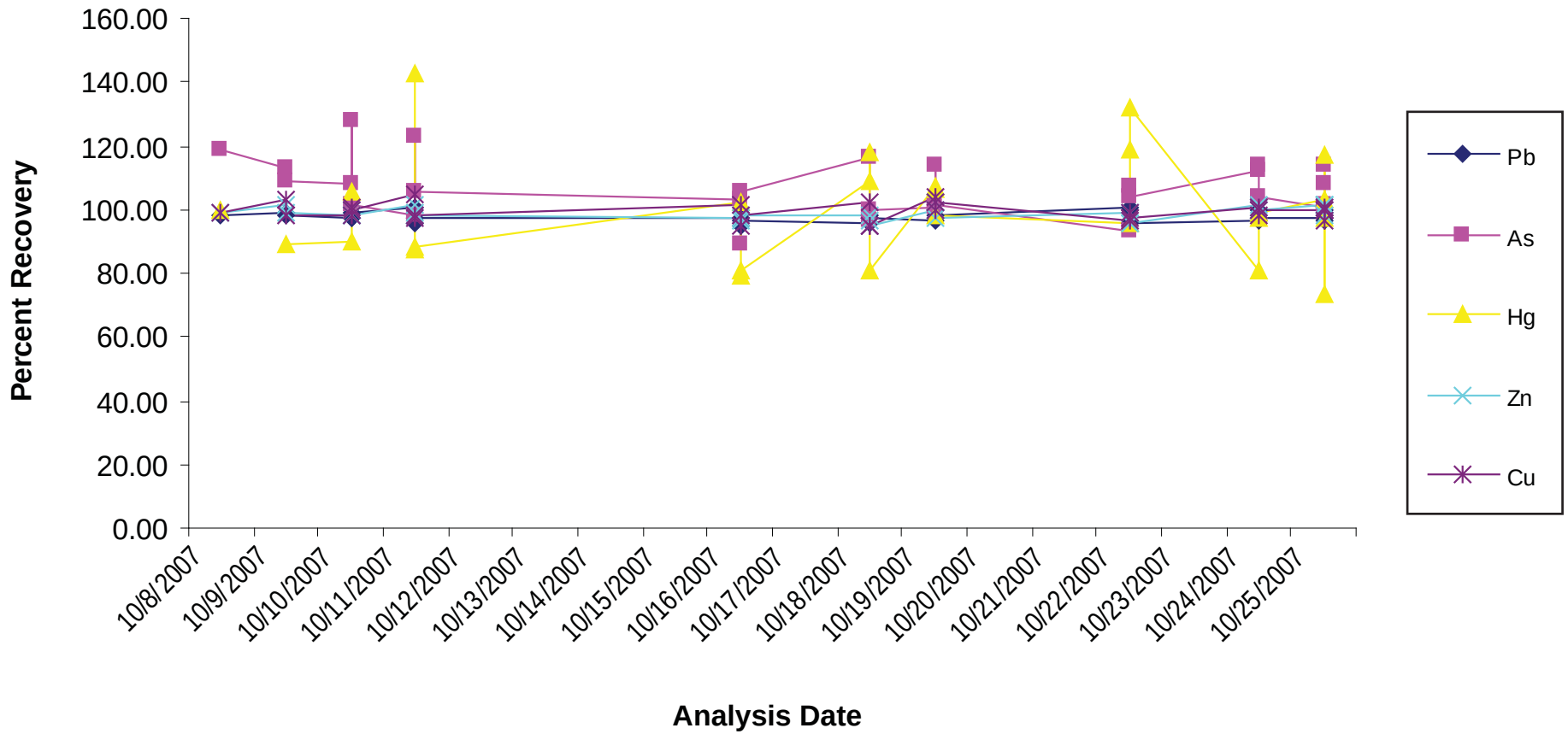

FIGURE 1
DAILY XRF CALIBRATION CHECK STANDARD: NIST SRM 2710
PHASE 1 KLAU BUENA VISTA MINE INVESTIGATION
SAN LUIS OBISPO COUNTY, CALIFORNIA

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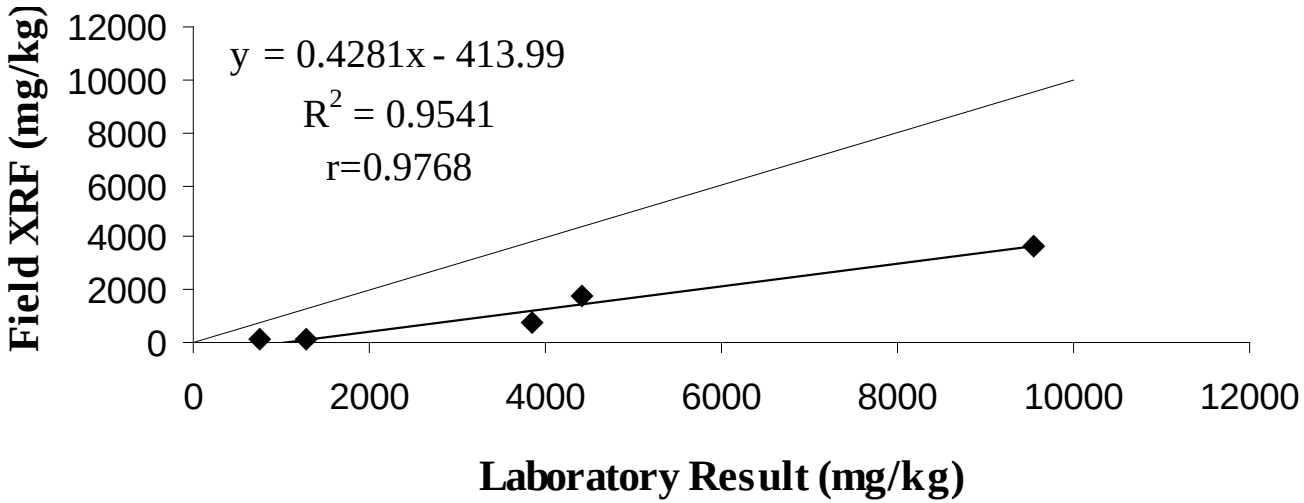

FIGURE 2
CORRELATION BETWEEN AVERAGE ICP AND FIELD XRF MERCURY RESULTS PRE-MOBILIZATION SAMPLES
PHASE 1 KLAU BUENA VISTA MINE INVESTIGATION
SAN LUIS OBISPO COUNTY, CALIFORNIA

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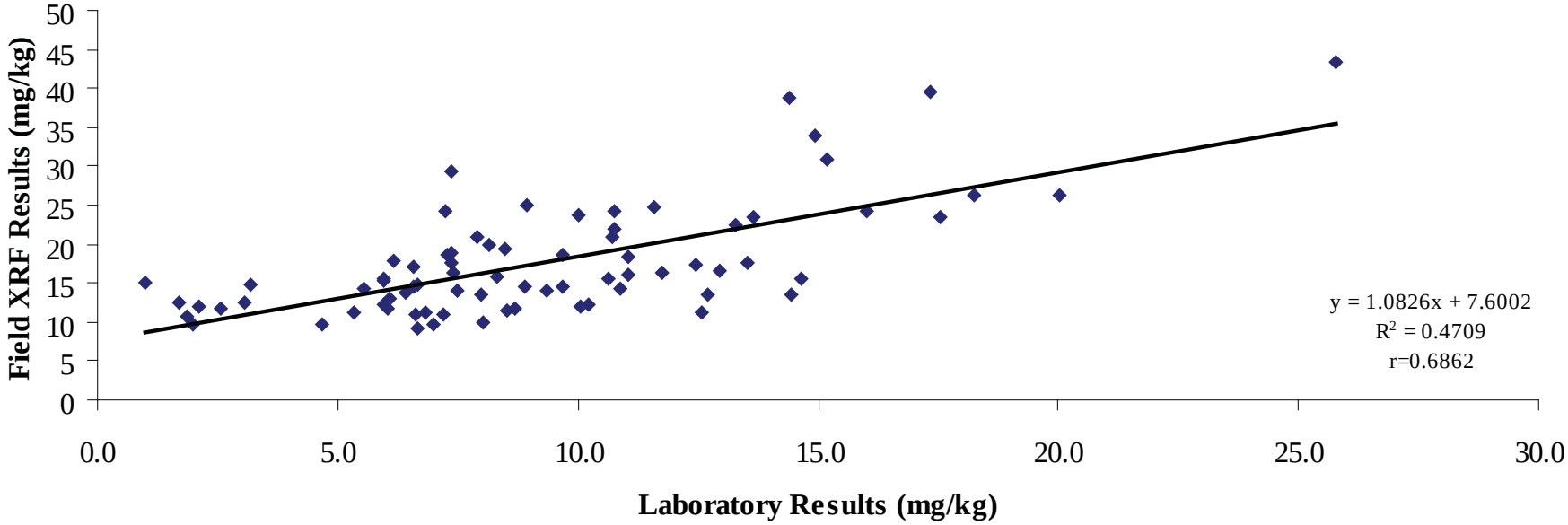

FIGURE 3
ARESENIC CORRELATION PLOT
FIELD XRF VERSUS LABORATORY RESULTS
PHASE 1 KLAU BUENA VISTA MINE INVESTIGATION
SAN LUIS OBISPO COUNTY, CALIFORNIA

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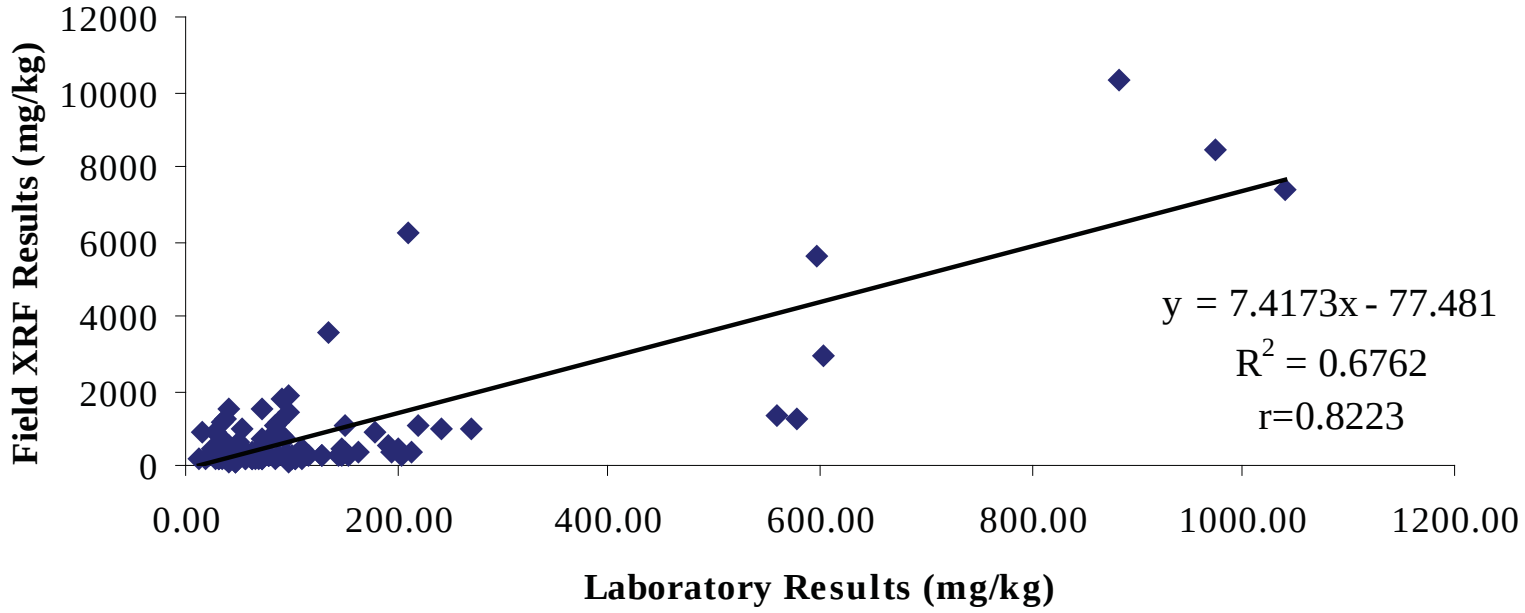

FIGURE 4
CHROMIUM CORRELATION PLOT
FIELD XRF VERSUS LABORATORY RESULTS
PHASE 1 KLAU BUENA VISTA MINE INVESTIGATION
SAN LUIS OBISPO COUNTY, CALIFORNIA

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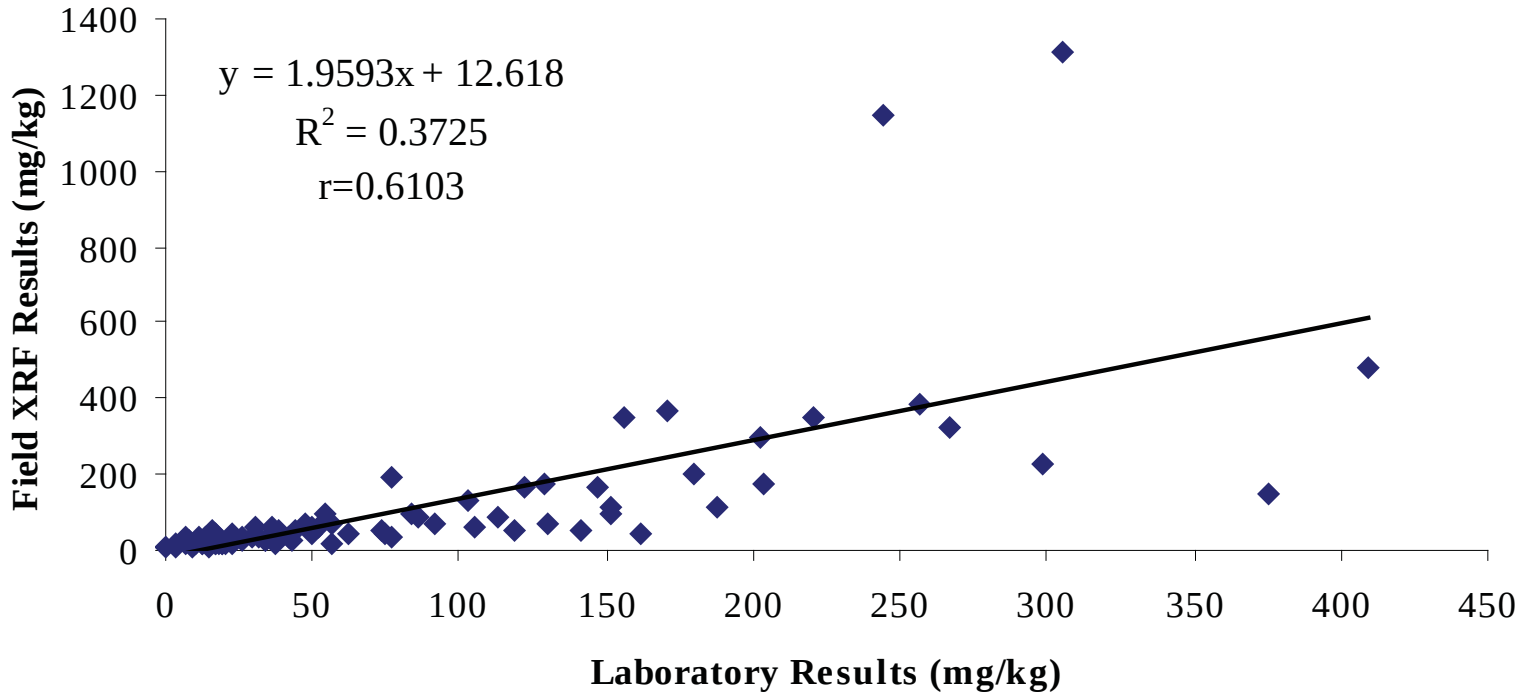

FIGURE 5
MERCURY CORRELATION PLOT
FIELD XRF VERSUS LABORATORY RESULTS
PHASE 1 KLAU BUENA VISTA MINE INVESTIGATION
SAN LUIS OBISPO COUNTY, CALIFORNIA

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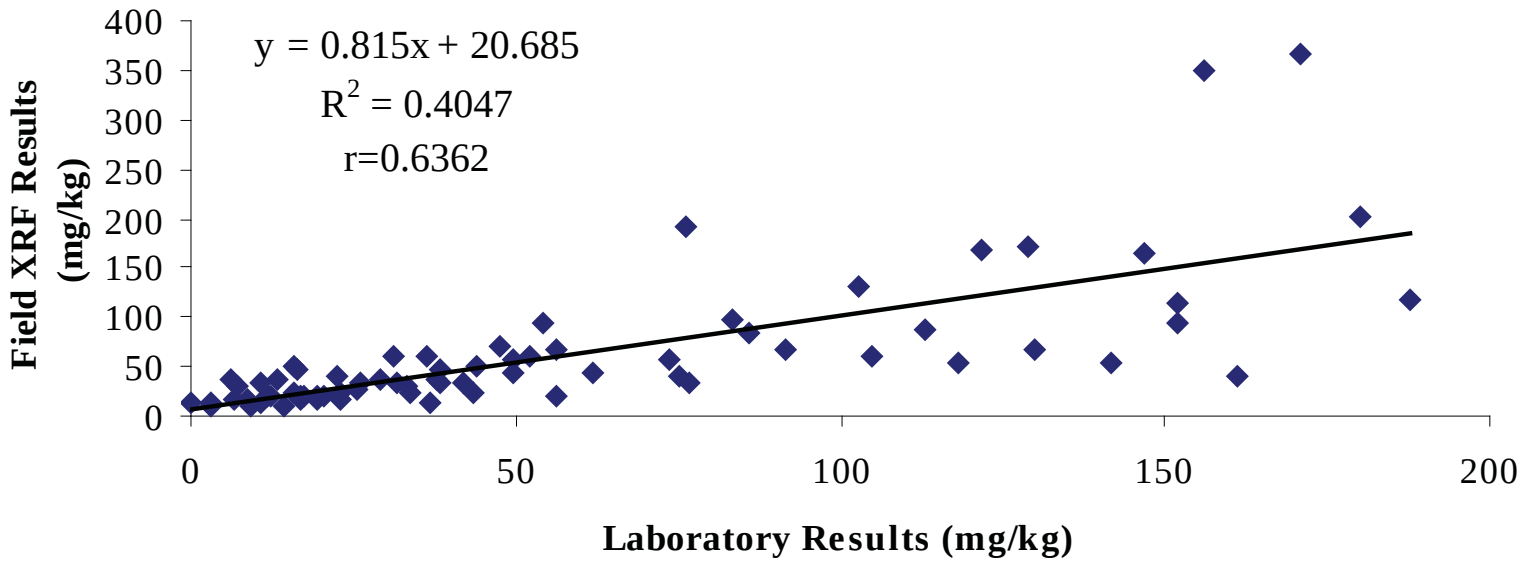

FIGURE 6
MERCURY CORRELATION PLOT
FIELD XRF VERSUS LABORATORY RESULTS
LESS THAN 200mg/kg
PHASE 1 KLAU BUENA VISTA MINE INVESTIGATION
SAN LUIS OBISPO COUNTY, CALIFORNIA

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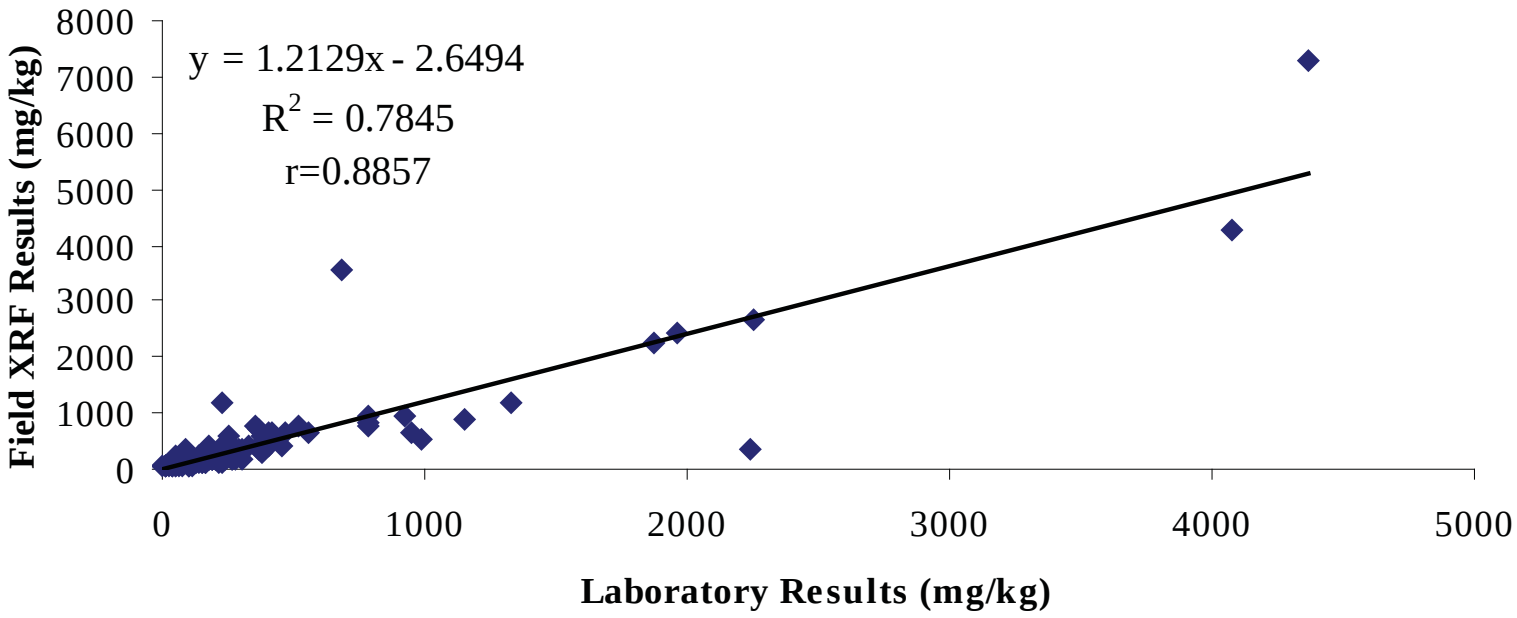

FIGURE 7
NICKEL CORRELATION PLOT
FIELD XRF VERSUS LABORATORY RESULTS
PHASE 1 KLAU BUENA VISTA MINE INVESTIGATION
SAN LUIS OBISPO COUNTY, CALIFORNIA

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