APPENDIX K

STATISTICAL AND GEOCHEMICAL EVALUATION OF METALS DATA

SOILS

Comparison of Site and Background Soil Data for the Small Weapons Repair Shop, Parcel 66(7), at Fort McClellan, Calhoun County, Alabama

Summary

An integrated statistical and geochemical evaluation of 23 elements in soil was performed for the Small Weapons Repair Shop, Parcel 66(7), at Fort McClellan. Concentrations of arsenic, chromium, iron, lead, manganese, mercury, sodium, thallium, and vanadium were demonstrated to be within range of background. Elevated concentrations of aluminum, barium, beryllium, calcium, cobalt, copper, magnesium, nickel, potassium, selenium, and zinc were shown to be naturally occurring. The available data do not indicate inorganics contamination in the Parcel 66(7) soil samples.

1.0 Introduction

This report provides the methodology and results of the comparisons of concentrations of inorganic constituents in soil samples from background areas versus samples from the Small Weapons Repair Shop, Parcel 66(7), at Fort McClellan in Calhoun County, Alabama. Site samples used in the site-to-background comparison include the three surface soil samples (0 to 1 foot below ground surface [bgs]) and three subsurface soil samples (varying depths from 3 to 7 feet bgs) that were collected during the 1999 site investigation.

Background distributions and screening values have been established for target analyte list metals in surface soil (0 to 1 foot bgs), subsurface soil (1 to 10 feet bgs), and combined (surface and subsurface) soil for Fort McClellan (IT Corporation, 2002). Because there are no significant differences between the background distributions of inorganic constituents in surface and subsurface soil, the combined (surface and subsurface) soil data set is considered the primary reference for background. Greater confidence can be placed in the combined background summary statistics because they are based on a larger data set (122 samples, for most analytes) than the individual surface and subsurface soil intervals (67 and 55 samples each, for most analytes). Accordingly, the background screening values used in the following site-to-background comparisons are based on the combined soil data set.

2.0 Comparison Methodology

This section describes the statistical and geochemical evaluation techniques that were employed in the Parcel 66(7) site-to-background comparisons.

2.1 Statistical Procedures

Contamination can be caused by a variety of processes that yield different spatial distributions of elevated contaminant concentrations. Slight but pervasive contamination can occur from non-point-source releases, and can result in slight increases in contaminant concentrations in a large percentage of samples. Localized, or "hot-spot," contamination can result in elevated concentrations in a small percentage of the total number of site samples. No single two-sample statistical comparison test is sensitive to both of these modes of contamination. For this reason, the use of multiple simultaneous tests is recommended for comparison of site and background distributions (U.S. Environmental Protection Agency [EPA], 1989, 1992, and 1994; U.S. Navy, 1998 and 1999).

The Wilcoxon rank sum (WRS) test is sensitive to slight but pervasive contamination, but is not sensitive to localized or more extreme hot-spot situations. The background threshold comparison, or "hot-measurement test," is effective in identifying localized contamination, but is not sensitive to slight but pervasive contamination. The WRS test and hot measurement test are thus complementary. In addition to these tests, box-and-whisker plots are useful for visually comparing the site and background distributions and for properly interpreting the results of the WRS test.

Hot Measurement Test. The hot measurement test consists of comparing each site measurement with a concentration value that is representative of the upper limit of the background distribution (EPA, 1994). Ideally, a site sample with a concentration above the background screening value would have a low probability of being a member of the background distribution, and may be an indicator of contamination. It is important to select such a background screening value carefully so that the probability of falsely identifying site samples as contaminated or uncontaminated is minimized.

The 95th upper tolerance limit (UTL_{95}) is recommended as a screening value for normally or lognormally distributed analytes and the 95th percentile is recommended as a screening value for nonparametrically distributed analytes (EPA, 1989, 1992, and 1994). Site samples with concentrations above these values are not necessarily contaminated, but should be considered suspect.

The UTL_{95} or 95^{th} percentile of the background distributions for 23 elements in Fort McClellan soil are provided in Table 1. To perform the test, each analyte's site maximum detected concentration (MDC) is compared to the background UTL_{95} or 95^{th} percentile, in accordance with the type of background distribution. If the site MDC exceeds the background screening value, then that analyte will undergo a geochemical evaluation. If the MDC does not exceed the background threshold value, then hot-spot contamination is not indicated.

Wilcoxon Rank Sum Test. The WRS test has been recommended for use in site-to-background comparisons (U.S. Navy, 1998 and 1999; EPA, 2000). In this report, the WRS test is performed when the site and background data sets each contain less than 50 percent nondetects (i.e., measurements reported as not detected below the laboratory reporting limit). The WRS test will not be performed on data sets containing 50 percent or more nondetects. The medians of such data sets are unknown, and hence the test results would lack sufficient power to yield reliable results.

The WRS test compares two data sets of size n and m ($n > m$), and tests the null hypothesis that the samples were drawn from populations with distributions having the same medians. To perform the test, the two sets of observations are pooled and arranged in order from smallest to largest. Each observation is assigned a rank; that is, the smallest is ranked 1, the next largest is ranked 2, and so on up to the largest observation, which is ranked ($n + m$). If ties occur between or within samples, each one is assigned the midrank. Next, the sum of the ranks of smaller data set m is calculated. Then the test statistic Z is determined,

$$Z = \frac{W - m(m+n+1)/2}{\sqrt{mn(m+n+1)/12}}$$

Where:

W = Sum of the ranks of the smaller data set
m = Number of data points in smaller group
n = Number of data points in larger group.

This test statistic Z is used to find the two-sided significance. For instance, if the test statistic yields a probability of a Type I error (p-level) less than 0.05, then there is a statistically significant difference between the medians at the 95 percent confidence level. A Type I error involves rejecting the null hypothesis when it is true. If the p-level is greater than 0.05, then there is no reasonable justification to reject the null hypothesis at the 95 percent confidence level. It can therefore be concluded that the medians of the two data sets are similar, and can be assumed to be drawn from the same population.

If the p-level is less than 0.05, then the medians of the two distributions are significantly different at the 95 percent confidence level. This can occur if the site data are shifted higher or lower than the background data. If the site data are shifted higher relative to background, then contamination may be indicated, and the analyte in question will be carried on for geochemical evaluation; however, if the site data are shifted lower relative to background, then contamination is not indicated. If the p-level is greater than 0.05, then pervasive site contamination is not suspected.

Box Plots. A quick, robust graphical method recommended by the EPA to visualize and compare two or more groups of data is the box plot (EPA, 1989 and 1992). An example box plot is provided in Figure 1. These plots provide a summary view of the entire data set, including the overall location and degree of symmetry. The box encloses the central 50 percent of the data points so that the top of the box represents the 75^{th} percentile and the bottom of the box represents the 25^{th} percentile. The small box within the larger box represents the median of the data set. The upper whisker extends to the maximum point and the lower whisker extends to the minimum point. Nondetect results are set equal to one-half of the reporting limit for plotting purposes.

For each analyte, box plots of site and background data are placed side by side to visually compare the distributions and qualitatively determine whether the data sets are similar or distinct. As described previously, the WRS test may indicate that the medians of the site and background data sets are significantly different. Examination of the box plots will confirm whether that difference is caused by site data that are shifted higher or lower relative to background.

2.2 Geochemical Evaluation

If an analyte fails either of the statistical tests described in Section 2.1, then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The importance of geochemical evaluations in distinguishing between site and background data sets has been recognized in the industry (EPA, 1995; U.S. Navy, 1998 and 1999; Barclift, *et al.*, 2000). When properly evaluated, geochemistry can provide mechanistic explanations for apparently high, yet naturally occurring, constituents. Anomalous samples that may represent contamination can also be readily distinguished from uncontaminated samples.

The geochemical evaluation is based on the natural associations of trace elements with specific minerals in the soil matrix. For instance, arsenic, vanadium, nickel, and selenium are usually associated with iron oxide minerals. If a soil sample has a high percentage of iron oxide minerals, then it is expected to have proportionally higher concentrations of associated trace elements.

As an example, the absolute concentrations of arsenic and iron can vary by several orders of magnitude at a site, but the arsenic/iron ratios in each sample are usually quite constant at a given site as long as no contamination is present (Daskalakis and O'Connor, 1995). If a sample has some naturally occurring arsenic plus additional arsenic from an herbicide or some other source, then it will have an anomalously high ratio relative to the other uncontaminated samples. These ratios thus serve as a powerful technique for identifying contaminated samples.

The evaluation includes the generation of plots in which arsenic concentrations in a set of samples are plotted on the y-axis, and the corresponding iron concentrations are plotted on the x-axis. The slope of a best-fit line through the samples is equal to the average arsenic-to-iron background ratio. If the samples with the highest arsenic concentrations plot on the same linear trend as the other samples, then it is most probable that the elevated concentrations are natural, and are caused by proportionally higher iron oxide content in those samples. If the site samples with elevated arsenic concentrations plot above the trend displayed by the uncontaminated samples, then there is evidence that those samples have an excess contribution of arsenic, and contamination may be indicated.

Each trace element is associated with one or more minerals in the soil matrix. Arsenic, vanadium, and selenium form anionic species in solution and are associated with iron oxides, which maintain a positive surface charge. Divalent metals such as barium, cadmium, lead, and zinc tend to form cationic species in solution and are attracted to clay mineral surfaces, which maintain a negative surface charge. These trace elements would be evaluated against aluminum, which is a major component of clay minerals. Manganese oxide minerals also have an affinity to adsorb cations such as barium and cobalt; these trace elements would be evaluated against manganese.

3.0 Results of the Site-to-Background Comparisons

Aluminum

Hot Measurement Test: None of the site samples exceeds the background screening value of 17,981 milligrams per kilogram (mg/kg).

WRS Test: The p-level of 0.006 indicates poor agreement between the site and background distributions.

Box Plot: A box plot comparing the data sets is shown in Figure 2. The minimum, 25th percentile, median, and 75th percentile of the site data are higher than the respective background values. The site maximum is below the background maximum.

Geochemical Evaluation: Aluminum is the second most abundant of the 23 elements analyzed in the site soil samples, with a mean concentration of 11,807 mg/kg (approximately 1.2 weight percent). Aluminum is a primary component of common soil-forming minerals such as clays, feldspars, and micas. The Parcel 66(7) soil boring logs note that clay is the predominant soil type in several of the sampled intervals. If a soil sample is enriched in clays or other aluminum-bearing minerals, then that sample is expected to contain high concentrations of aluminum and associated trace elements. The site samples with high aluminum concentrations contain high concentrations of trace elements such as barium, beryllium, and zinc. For example, plots of beryllium versus aluminum and zinc versus aluminum reveal a linear trend (see the Barium, Beryllium, and Zinc evaluations, below). The site samples with high barium, beryllium, and zinc concentrations also contain high aluminum concentrations, and lie on the trend formed by the background samples. These observations support the contention of a natural origin for aluminum, barium, beryllium, and zinc in the site samples.

Conclusion: Aluminum detected in the site samples is naturally occurring.

Antimony

Hot Measurement Test: One hundred percent of the site samples are nondetect for antimony. Site reporting limits range from 6.6 to 8 mg/kg, so it is not possible to determine if all of the site antimony concentrations are below the background screening value of 7.14 mg/kg.

WRS Test: The WRS test was not performed because the site data set contains 100 percent nondetects.

Box Plot: The site data set is characterized by 100 percent nondetects, so the site box plot reflects the replacement values of one-half the reporting limit (Figure 3). The site plot is elevated with respect to background because the site samples have significantly higher reporting limits (one to two orders of magnitude higher, in many cases).

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Arsenic

Hot Measurement Test: None of the site samples have arsenic concentrations that exceed the background screening value of 32.42 mg/kg.

WRS Test: The p-level of 0.807 indicates excellent agreement between the site and background distributions.

Box Plot: The minimum, 25th percentile, and median of the site data are higher than their respective background values (Figure 4). The site 75th percentile and maximum are below the corresponding background values.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Arsenic in the site samples is most likely naturally occurring.

Barium

Hot Measurement Test: None of the site samples exceeds the background screening value of 242 mg/kg.

WRS Test: The p-level of 0.009 indicates poor agreement between the site and background distributions.

Box Plot: The minimum, 25th percentile, median, and 75th percentile of the site data are higher than the corresponding background values (Figure 5). The site maximum is below the background maximum.

Geochemical Evaluation: As discussed in Section 2.2, clay minerals, which contain aluminum, have an affinity to adsorb divalent cations such as barium. A plot of barium versus aluminum reveals a generally linear trend with a positive slope (Figure 6). Samples with high barium concentrations also contain high aluminum, and the site samples lie on the trend formed by the background samples. This indicates that barium is associated with clay minerals at a relatively constant ratio. Barium detected in the site samples is natural.

Conclusion: The elevated barium concentrations are observed in samples with high aluminum content. Barium in the site samples is naturally occurring.

Beryllium

Hot Measurement Test: Two samples exceed the background screening value of 1.502 mg/kg.

WRS Test: The p-level of 0.0006 indicates a significant difference between the site and background distributions.

Box Plot: The minimum, 25th percentile, median, and 75th percentile of the site data are higher than the respective background values (Figure 7). The site and background maxima are similar.

Geochemical Evaluation: A plot of beryllium versus aluminum reveals a weak linear trend (Figure 8). The site samples with high beryllium concentrations have high aluminum, and all of the site samples lie on the trend defined by the background samples.

Conclusion: The elevated beryllium concentrations are observed in samples with high aluminum content. Beryllium in the site samples is naturally occurring.

Cadmium

Hot Measurement Test: One hundred percent of the site samples are nondetect for cadmium. The site reporting limits range from 0.55 to 0.67 mg/kg, so cadmium concentrations in the site samples are below the background screening value of 1.2 mg/kg.

WRS Test: No WRS test was performed because the site data set contains 100 percent nondetects.

Box Plot: The location and shape of the site box plot reflects the high percentage of nondetects (100 percent), the narrow range of reporting limits (0.55 to 0.67 mg/kg), and the higher reporting limits relative to the background data (Figure 9).

Geochemical Evaluation: Lower reporting limits for the site data would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data.

Calcium

Hot Measurement Test: One sample exceeds the background screening value of 5,490 mg/kg.

WRS Test: The p-level of 0.001 indicates poor agreement between the site and background distributions.

Box Plot: The site minimum, 25th percentile, median, 75th percentile, and maximum are all higher than their respective background values (Figure 10).

Geochemical Evaluation: Calcium occurs in common soil minerals such as carbonates, clays, and feldspars. Calcium and magnesium have similar chemical properties, and magnesium often substitutes for calcium in minerals. Figure 11 contains a plot of magnesium versus calcium. The site samples with high calcium concentrations also contain high magnesium, and lie on the trend established by the background samples. This indicates that the calcium is most likely natural.

Conclusion: Calcium concentrations detected in the site samples are naturally occurring.

Chromium

Hot Measurement Test: None of the site samples exceeds the background screening value of 56.3 mg/kg.

WRS Test: The p-level of 0.813 indicates excellent agreement between the site and background distributions.

Box Plot: The minimum, 25th percentile, and median of the site data set are elevated with respect to background (Figure 12). The 75th percentile and maximum of the site data set are below their respective background values.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Chromium in the site samples is most likely naturally occurring.

Cobalt

Hot Measurement Test: One sample exceeds the background screening value of 36.3 mg/kg.

WRS Test: The p-level of 0.045 indicates weak agreement between the site and background distributions.

Box Plot: The minimum, 25th percentile, median, and 75th percentile of the site data set are higher than the respective background values (Figure 13). The site maximum is below the background maximum.

Geochemical Evaluation: A plot of cobalt versus manganese reveals a strong linear trend, and the samples with high cobalt concentrations also have high manganese (Figure 14). The site samples lie on the trend established by the background samples. These observations suggest that cobalt in the site samples is associated with manganese oxides.

Conclusion: The elevated cobalt concentrations are observed in samples with elevated manganese content. Cobalt in the site samples is naturally occurring.

Copper

Hot Measurement Test: Three samples exceed the background screening value of 25.9 mg/kg.

WRS Test: The p-level of 0.001 indicates a significant difference between the site and background distributions.

Box Plot: The site minimum, 25th percentile, median, and 75th percentile are higher than their respective background values (Figure 15). The site maximum is below the background maximum.

Geochemical Evaluation: A plot of copper versus iron exhibits a linear trend (Figure 16). The site samples with the highest copper concentrations also contain the highest iron concentrations, and lie on the trend defined by the other samples. These concentrations are most likely natural.

Conclusion: The elevated copper concentrations are observed in samples with high iron content. Copper in the site samples is naturally occurring.

Iron

Hot Measurement Test: None of the site samples exceeds the background screening value of 56,312 mg/kg.

WRS Test: The p-level of 0.173 indicates acceptable agreement between the site and background distributions.

Box Plot: The site minimum, 25th percentile, median, and 75th percentile are higher than the corresponding background values (Figure 17). The site maximum is below the background maximum.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background. It is worth noting that iron is the most abundant element of the 23 elements analyzed in the site soil samples, with a mean concentration of 25,195 mg/kg (2.5 weight percent). It is commonly present in soil in the form of iron oxide minerals, which have an affinity to adsorb trace elements such as arsenic, nickel, selenium, and vanadium. If a soil sample contains a high proportion of iron oxides, then it is expected to contain high concentrations of iron and associated trace elements. As discussed in the Copper and Nickel evaluations, plots of copper versus iron and nickel versus iron reveal linear trends. The site samples with high iron concentrations contain high concentrations of these trace elements, and lie on the trends formed by the background samples. These observations support the contention of a natural origin for iron, copper, and nickel in the site samples.

Conclusion: Iron concentrations in the site samples are naturally occurring.

Lead

Hot Measurement Test: None of the site samples exceeds the background screening value of 60.5 mg/kg.

WRS Test: The p-level of 0.447 indicates strong agreement between the site and background distributions.

Box Plot: The minimum and 25th percentile of the site data are elevated with respect to background (Figure 18). The medians of the two data sets are similar, the 75th percentiles are similar, and the site maximum is below the background maximum.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Lead in the site samples is most likely naturally occurring.

Magnesium

Hot Measurement Test: Four samples exceed the background screening value of 5,545 mg/kg.

WRS Test: The p-level of <0.0001 indicates a significant difference between the site and background distributions.

Box Plot: The site minimum, 25th percentile, median, and 75th percentile are higher than the corresponding background values (Figure 19). The site maximum is below the background maximum.

Geochemical Evaluation: Magnesium is probably present in site soil in the form of mica, clay, and carbonate minerals. As discussed in the Calcium evaluation, calcium and magnesium have similar chemical properties, and magnesium often substitutes for calcium in minerals. A plot of magnesium versus calcium shows a linear trend (Figure 11); the site samples with high magnesium concentrations generally contain high calcium, and lie on the trend established by the background samples. This indicates that the magnesium is most likely natural.

Conclusion: Magnesium in the site samples is naturally occurring.

Manganese

Hot Measurement Test: None of the site samples exceeds the background screening value of 4,120 mg/kg.

WRS Test: The p-level of 0.644 indicates strong agreement between the site and background distributions.

Box Plot: The minimum and 25th percentile of the site data are higher than the corresponding background values (Figure 20). The medians of the two data sets are similar, and the site 75th percentile and maximum are lower than the respective background values.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Manganese in the site samples is most likely naturally occurring.

Mercury

Hot Measurement Test: None of the site samples exceeds the background screening value of 0.094 mg/kg.

WRS Test: No WRS test was performed because the background data set contains 59.8 percent nondetects.

Box Plot: The site minimum and median are higher than their respective background values (Figure 21). The 25th percentiles are similar, and the site 75th percentile and maximum are lower than the corresponding background values.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Mercury in the site samples is most likely naturally occurring.

Nickel

Hot Measurement Test: Four samples exceed the background screening value of 16.9 mg/kg.

WRS Test: The p-level of 0.003 indicates poor agreement between the site and background distributions.

Box Plot: The minimum, 25th percentile, median, 75th percentile, and maximum of the site data are elevated with respect to background (Figure 22).

Geochemical Evaluation: A plot of nickel versus iron reveals a weak linear trend (Figure 23). The site samples with high nickel generally contain high iron, and plot on the trend formed by the background samples. The nickel concentrations are most likely natural.

Conclusion: The elevated nickel concentrations are observed in samples with elevated iron content. Nickel in the site samples is most likely naturally occurring.

Potassium

Hot Measurement Test: None of the site samples exceeds the background screening value of 831 mg/kg.

WRS Test: The p-level of 0.001 indicates a significant difference between the site and background distributions.

Box Plot: The minimum, 25th percentile, median, and 75th percentile of the site data set are higher than the corresponding background values (Figure 24). The site maximum is below the background maximum.

Geochemical Evaluation: Potassium is present in minerals that also contain aluminum, such as feldspars, micas, and clays. Figure 25 reveals a linear relationship between potassium and aluminum, and samples with high potassium concentrations also contain high aluminum. The site samples plot on the trend formed by the background samples. Elevated potassium in the site samples is most likely natural.

Conclusion: Potassium in the site samples is naturally occurring.

Selenium

Hot Measurement Test: All five detected concentrations exceed the background screening value of 0.571 mg/kg. The single nondetect sample has a reporting limit of 0.55 mg/kg, which is below the background screening value.

WRS Test: No WRS test was performed because the background data set contains 98.4 percent nondetects.

Box Plot: The site minimum, 25th percentile, median, 75th percentile, and maximum are all higher than the respective background values (Figure 26). The background data set is characterized by a high percentage of nondetects (98.4 percent), so the background box plot reflects the replacement values of one-half the reporting limit.

Geochemical Evaluation: As discussed in Section 2.2, selenium is typically associated with iron oxide minerals in soil. A plot of selenium versus iron reveals a linear trend (Figure 27). The site samples with the highest selenium concentrations also have the highest iron concentrations, indicating that the selenium in the site samples is probably associated with iron oxides.

Conclusion: The elevated selenium concentrations are observed in samples with elevated iron concentrations. Selenium detected in the site samples is most likely naturally occurring.

Silver

Hot Measurement Test: One-hundred percent of the site samples are nondetect for silver. The site reporting limits range from 1.1 mg/kg to 1.3 mg/kg, so it cannot be determined if silver concentrations in the site samples exceed the background screening value of 0.803 mg/kg.

WRS Test: The WRS test was not performed because the site data set contains 100 percent nondetects.

Box Plot: The site data set is characterized by a high percentage of nondetects (100 percent), so the shape and location of the box plot are defined by the replacement values of one-half the reporting limit (Figure 28). The site box plot is higher than the background box plot because the site samples have significantly higher reporting limits.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Sodium

Hot Measurement Test: None of the site samples exceeds the background screening value of 560 mg/kg.

WRS Test: The p-level of 0.0002 indicates a significant difference between the site and background distributions. The reason for this difference is that the site data are lower than the background data.

Box Plot: The 25^{th} percentile, median, 75^{th} percentile, and maximum of the site data are below the respective background values (Figure 29). The site minimum is above the background minimum.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Sodium in the site samples is most likely naturally occurring.

Thallium

Hot Measurement Test: Neither of the two detected concentrations exceeds the background screening value of 6.62 mg/kg. Site reporting limits range from 1.1 to 1.3 mg/kg, so thallium concentrations in the nondetect samples are below the background screening value.

WRS Test: No WRS test was performed because the site data set contains 67 percent nondetects.

Box Plot: The site data set contains 67 percent nondetects, so the shape and location of the site box plot are largely determined by the narrow range of reporting limits (1.1 to 1.3 mg/kg) (Figure 30). The site plot is higher than the background plot because the site detected concentrations and reporting limits are significantly higher than the background detected concentrations.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: The detected thallium concentrations are most likely naturally occurring. However, lower reporting limits would be required to adequately compare the site and background data sets.

Vanadium

Hot Measurement Test: None of the site samples exceeds the background screening value of 90.5 mg/kg.

WRS Test: The p-level of 0.364 indicates good agreement between the site and background distributions.

Box Plot: The minimum and 25th percentile of the site data set are higher than the respective background values (Figure 31). The site median, 75th percentile, and maximum are lower with respect to background.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Vanadium in the site samples is most likely naturally occurring.

Zinc

Hot Measurement Test: Three samples exceed the background screening value of 71.3 mg/kg.

WRS Test: A WRS test p-level of 0.002 indicates poor agreement between the site and background distributions.

Box Plot: The site minimum, 25th percentile, median, and 75th percentile are elevated with respect to background (Figure 32). The site maximum is below the background maximum.

Geochemical Evaluation: A plot of zinc versus aluminum reveals a linear trend (Figure 33). The site samples with high zinc concentrations also contain high aluminum, and lie on the trend defined by the background samples. This indicates that zinc is associated with clay minerals at a relatively constant ratio, and is natural.

Conclusion: The elevated zinc concentrations are observed in samples with elevated aluminum concentrations. Zinc detected in the site samples is naturally occurring.

4.0 Summary and Conclusions

The methodology used to compare the site and background data sets for 23 elements in soil consists of a combination of a hot measurement test, the nonparametric two-sample

Wilcoxon rank sum test, and box-and-whisker plots. Analytes that failed either of the statistical tests were subjected to a geochemical evaluation to determine if the elevated concentrations could be explained by natural processes. Concentrations of arsenic, chromium, iron, lead, manganese, mercury, sodium, thallium, and vanadium were demonstrated to be within range of background.

Aluminum, barium, beryllium, calcium, cobalt, copper, magnesium, nickel, potassium, selenium, and zinc failed at least one statistical test and were subjected to geochemical evaluation. For these elements, the elevated concentrations could be explained as most likely resulting from the preferential enrichment of samples with minerals such as clays, iron oxides, or manganese oxides, which naturally concentrate specific trace elements. The available data do not indicate inorganics contamination in the six Parcel 66(7) soil samples.

5.0 References

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ATTACHMENT 1

TABLES

Table 1

Background Screening Values (H_m) for Combined (Surface and Subsurface) Soils
Fort McClellan
Calhoun County, Alabama

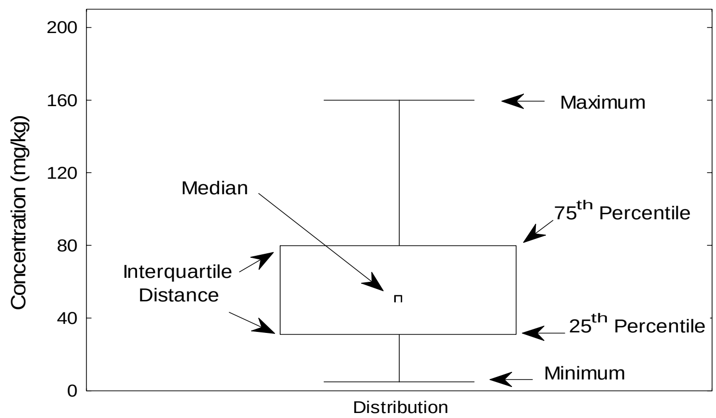
Analyte	H_m (mg/kg)
Aluminum	17,981
Antimony	<7.14
Arsenic	32.42
Barium	242.0
Beryllium	1.502
Cadmium	<1.2
Calcium	5,490
Chromium	56.3
Cobalt	36.3
Copper	25.9
Iron	56,312
Lead	60.5
Magnesium	5,545
Manganese	4,120
Mercury	0.094
Nickel	16.9
Potassium	831
Selenium	<0.571
Silver	<0.803
Sodium	560.0
Thallium	<6.62
Vanadium	90.5
Zinc	71.3

mg/kg - Milligram(s) per kilogram.

ATTACHMENT 2

FIGURES

Figure 1
Example Box Plot



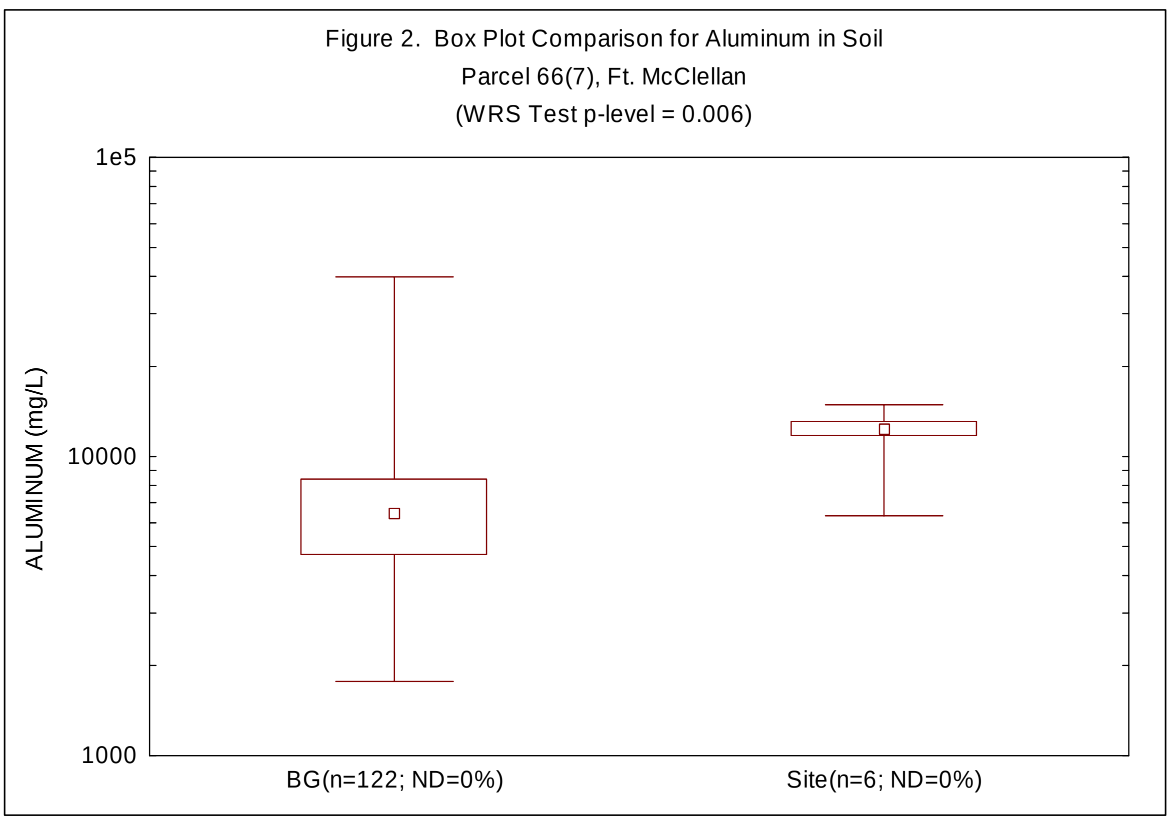


Figure 3. Box Plot Comparison for Antimony in Soil
Parcel 66(7), Ft. McClellan

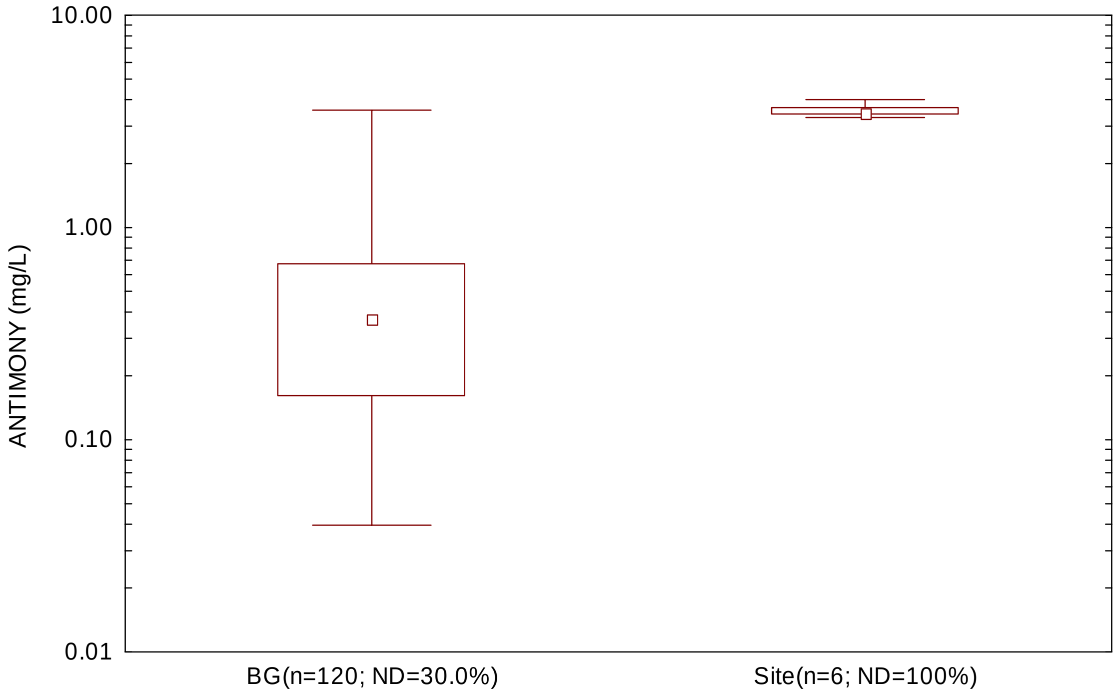


Figure 4. Box Plot Comparison for Arsenic in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.807)

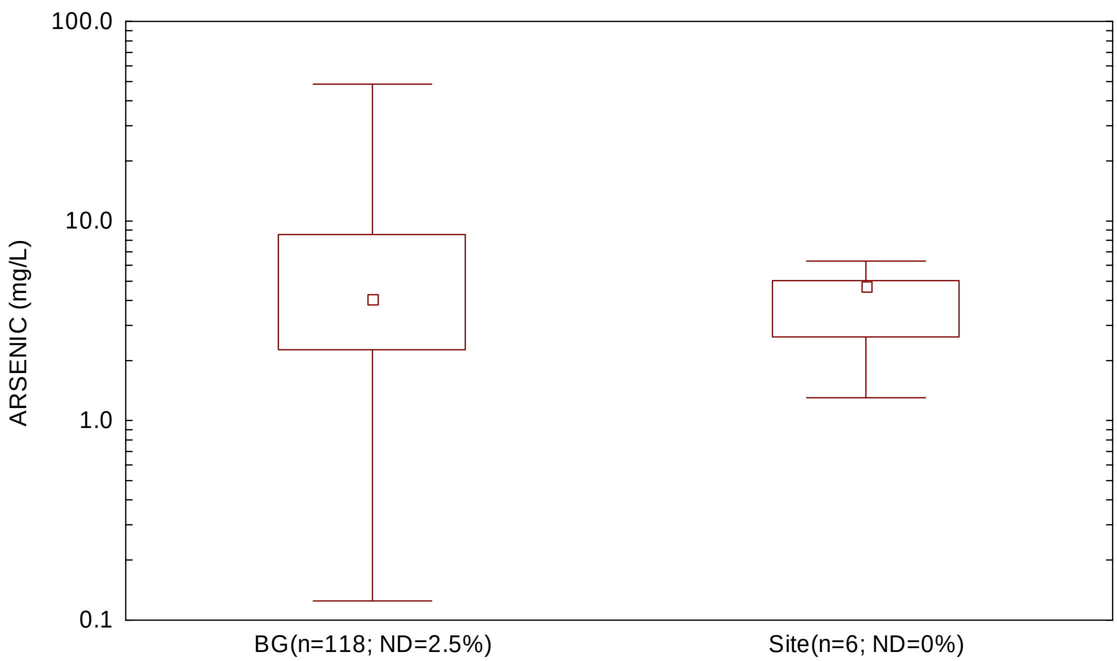


Figure 5. Box Plot Comparison for Barium in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.009)

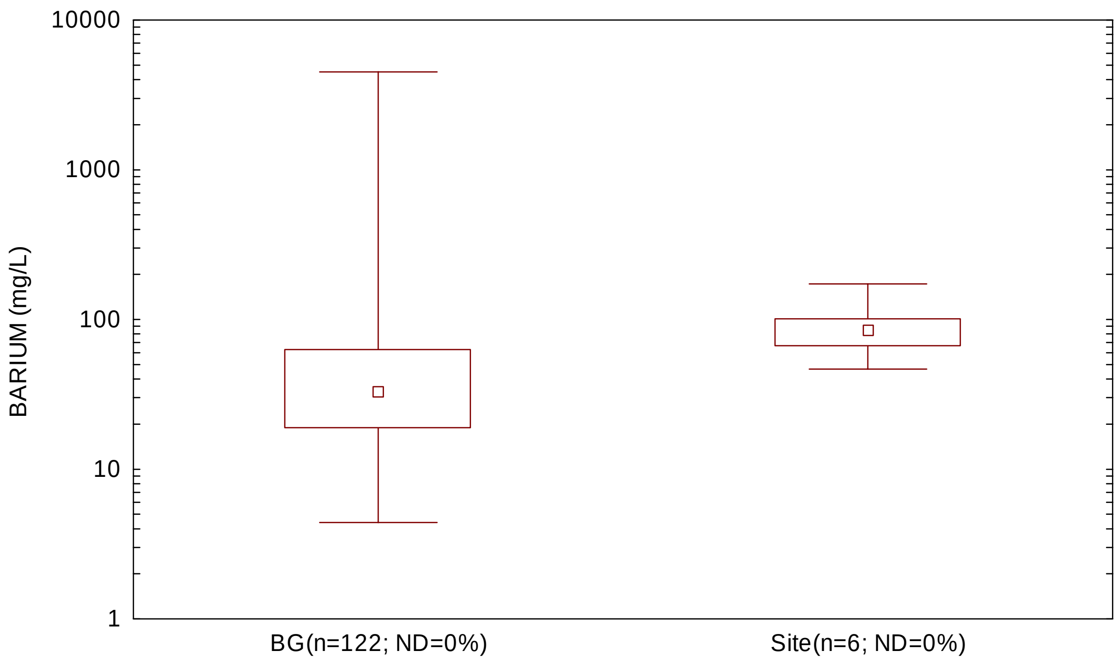
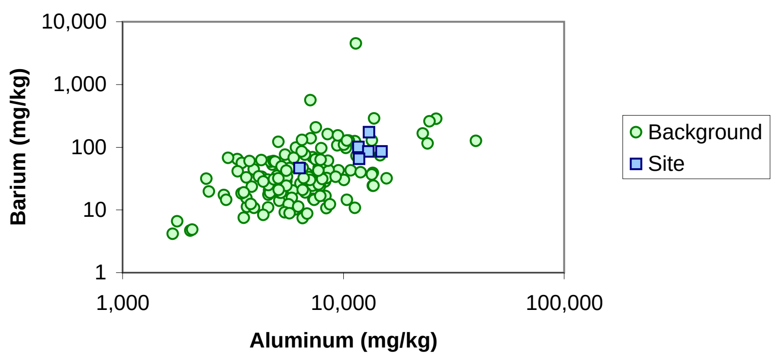


Figure 6. Barium vs. Aluminum in Soil



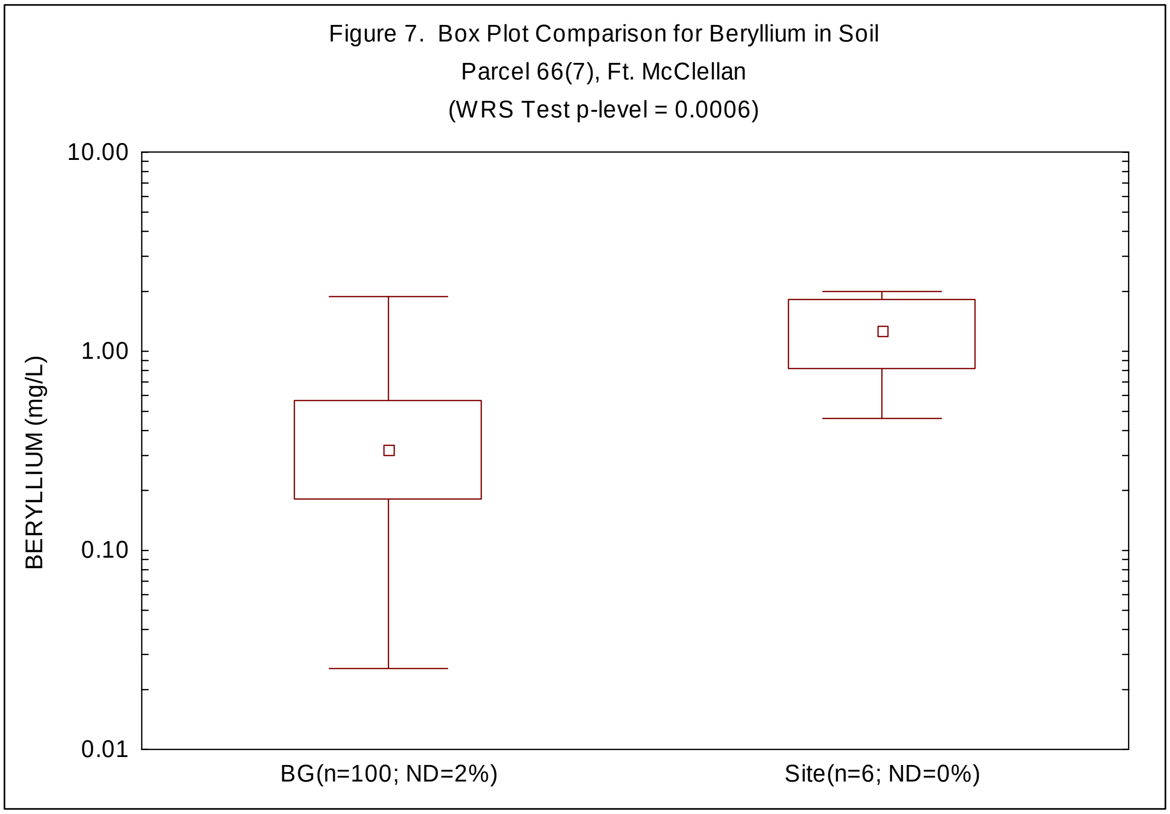


Figure 7. Box Plot Comparison for Beryllium in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.0006)
10.00
1.00
0.10
0.01
BERYLLIUM (mg/L)
BG(n=100; ND=2%)
Site(n=6; ND=0%)

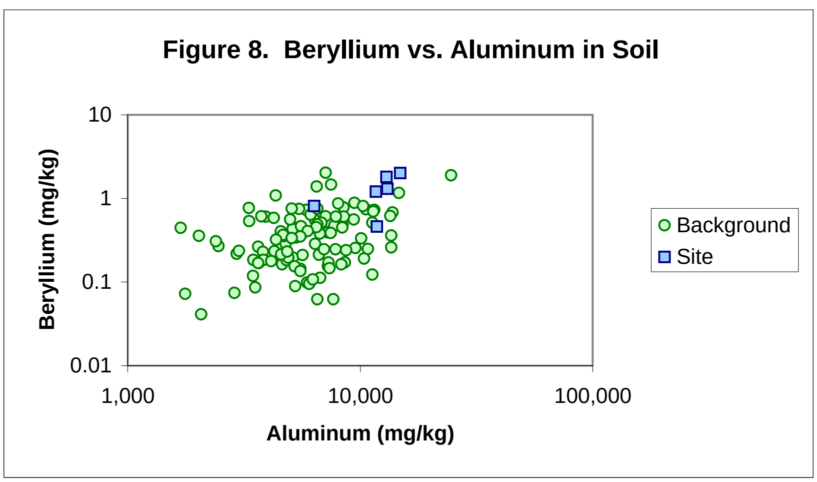


Figure 8. Beryllium vs. Aluminum in Soil
10
1
0.1
0.01
Beryllium (mg/kg)
1,000
10,000
100,000
Aluminum (mg/kg)
Background
Site

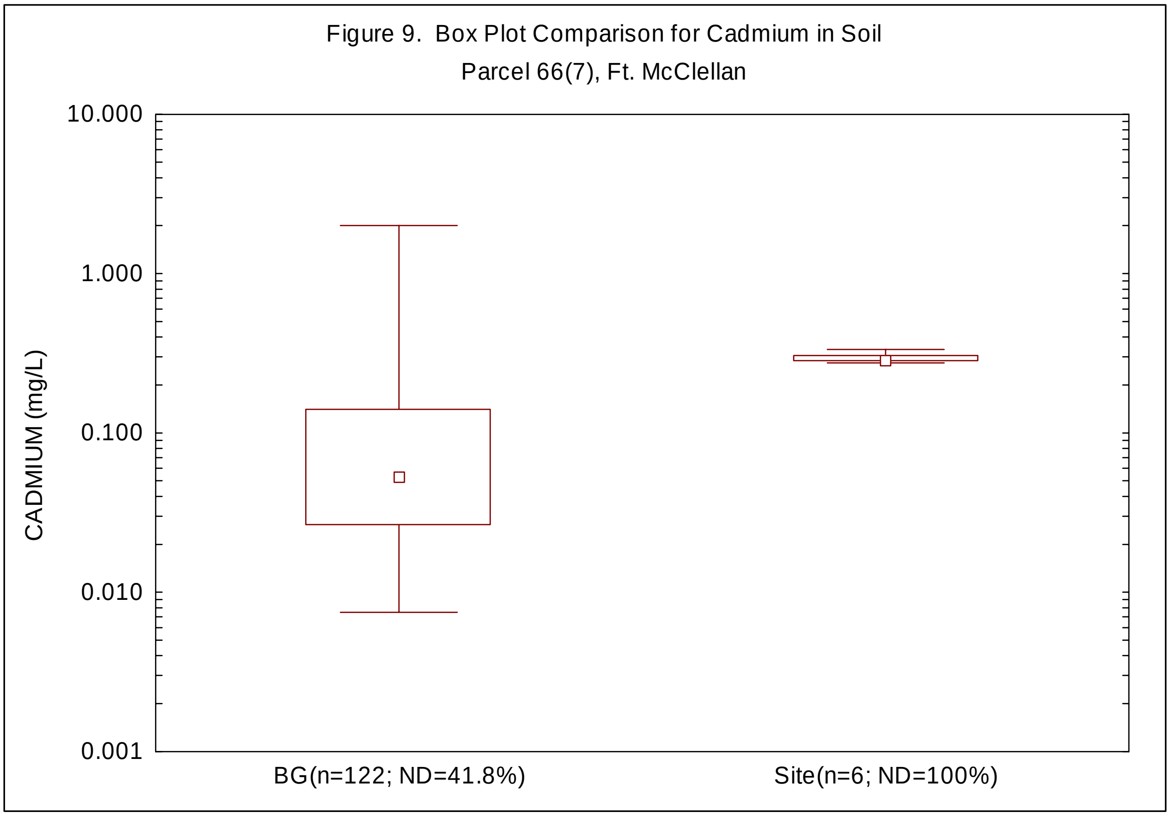


Figure 9. Box Plot Comparison for Cadmium in Soil
Parcel 66(7), Ft. McClellan
10.000
1.000
0.100
0.010
0.001
CADMIUM (mg/L)
BG(n=122; ND=41.8%)
Site(n=6; ND=100%)

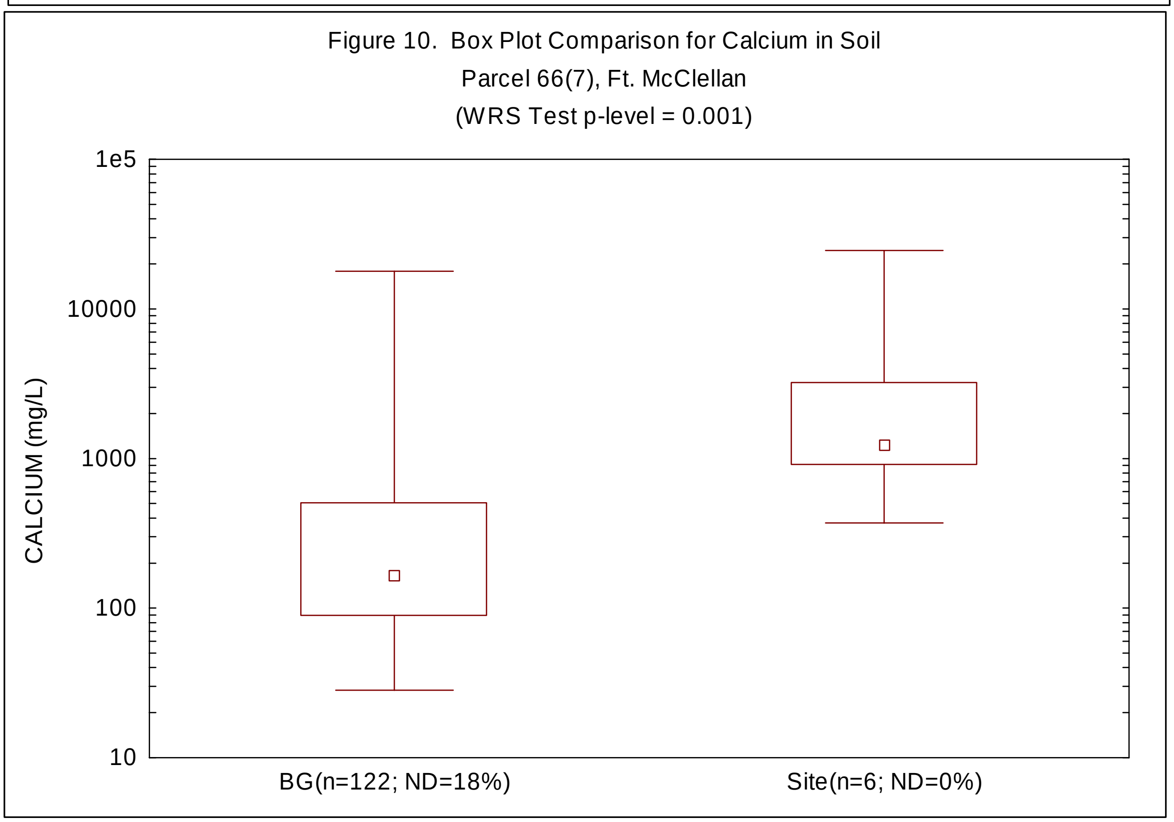


Figure 10. Box Plot Comparison for Calcium in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.001)
1e5
10000
1000
100
10
CALCIUM (mg/L)
BG(n=122; ND=18%)
Site(n=6; ND=0%)

Figure 11. Magnesium vs. Calcium in Soil

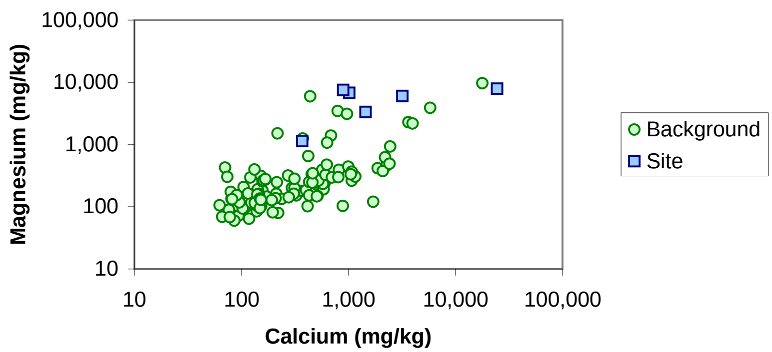
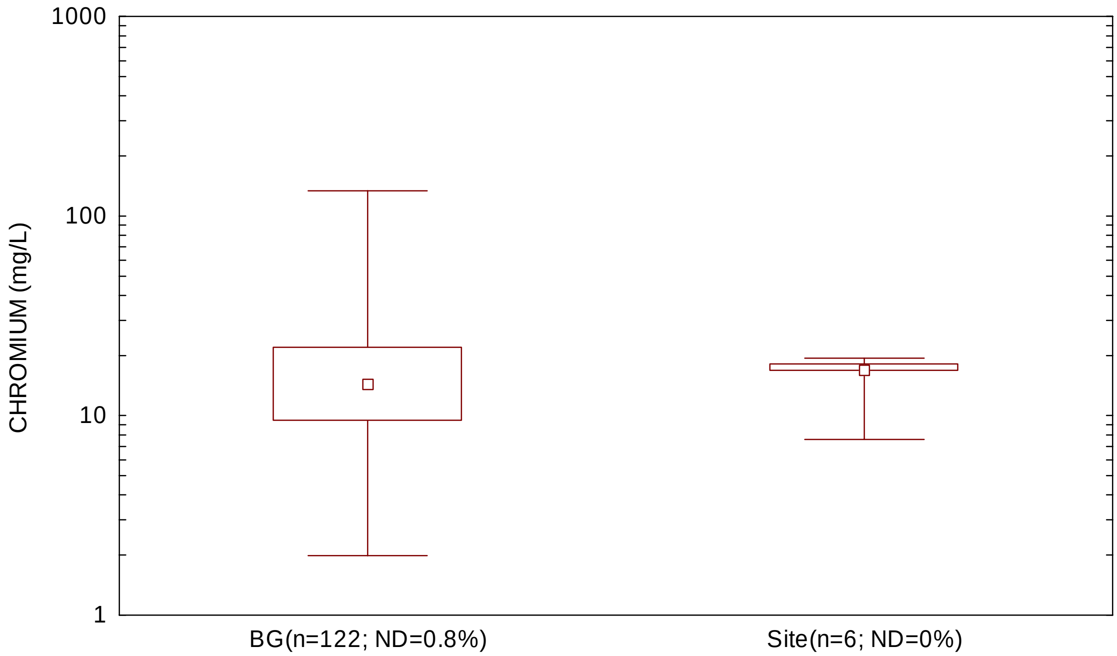


Figure 12. Box Plot Comparison for Chromium in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.813)



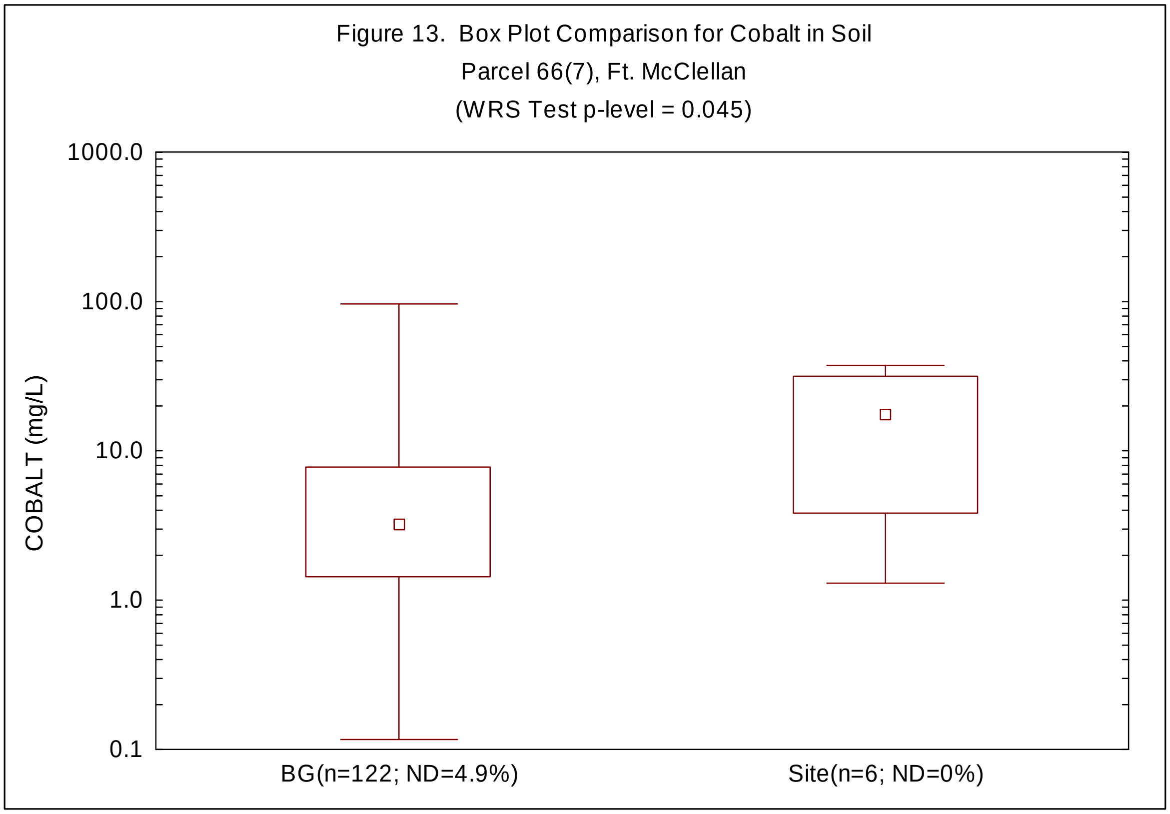


Figure 13. Box Plot Comparison for Cobalt in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.045)
COBALT (mg/L)
1000.0
100.0
10.0
1.0
0.1
BG(n=122; ND=4.9%)
Site(n=6; ND=0%)

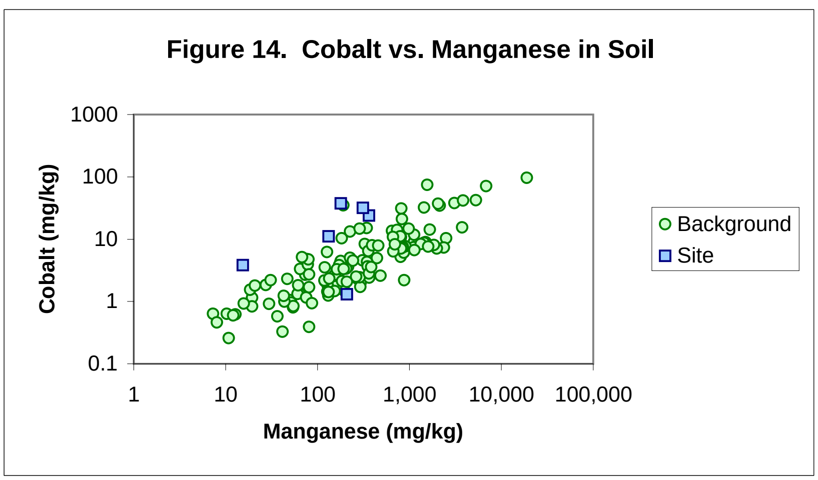


Figure 14. Cobalt vs. Manganese in Soil
Cobalt (mg/kg)
1000
100
10
1
0.1
1
10
100
1,000
10,000
100,000
Manganese (mg/kg)
Background
Site

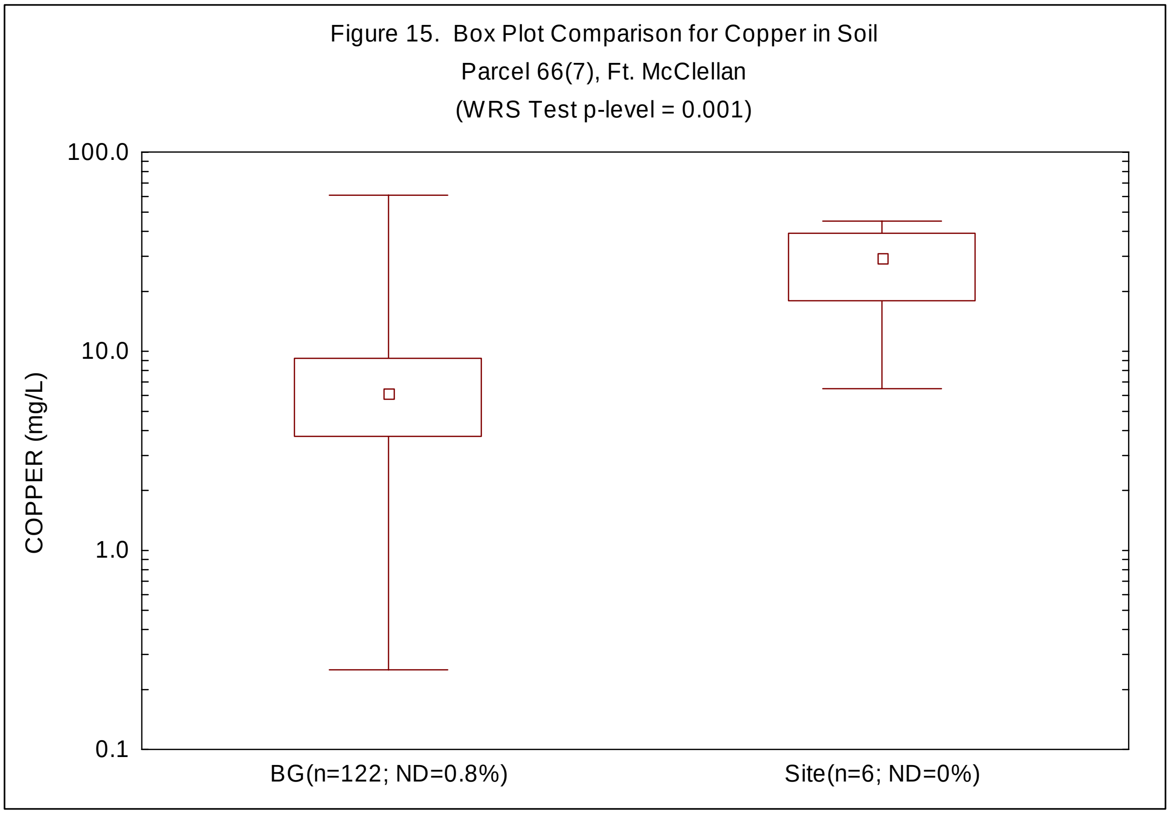


Figure 15. Box Plot Comparison for Copper in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.001)
100.0
10.0
1.0
0.1
COPPER (mg/L)
BG(n=122; ND=0.8%)
Site(n=6; ND=0%)

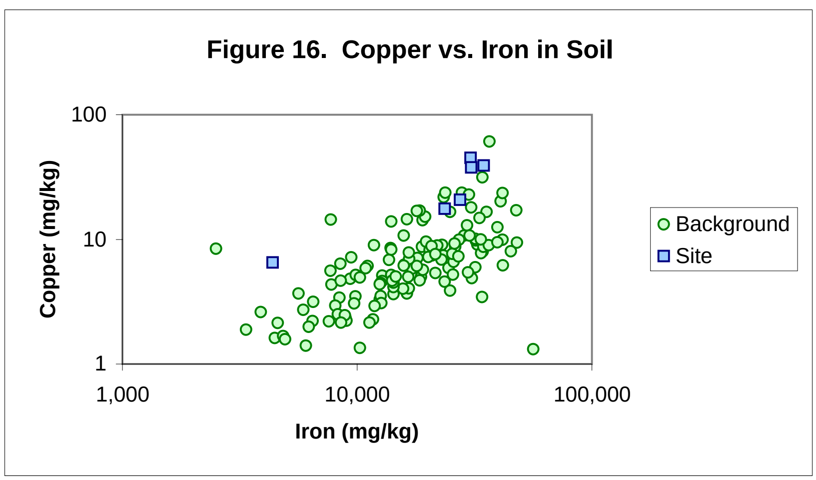


Figure 16. Copper vs. Iron in Soil
100
10
1
Copper (mg/kg)
1,000
10,000
100,000
Iron (mg/kg)
Background
Site

Figure 17. Box Plot Comparison for Iron in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.173)

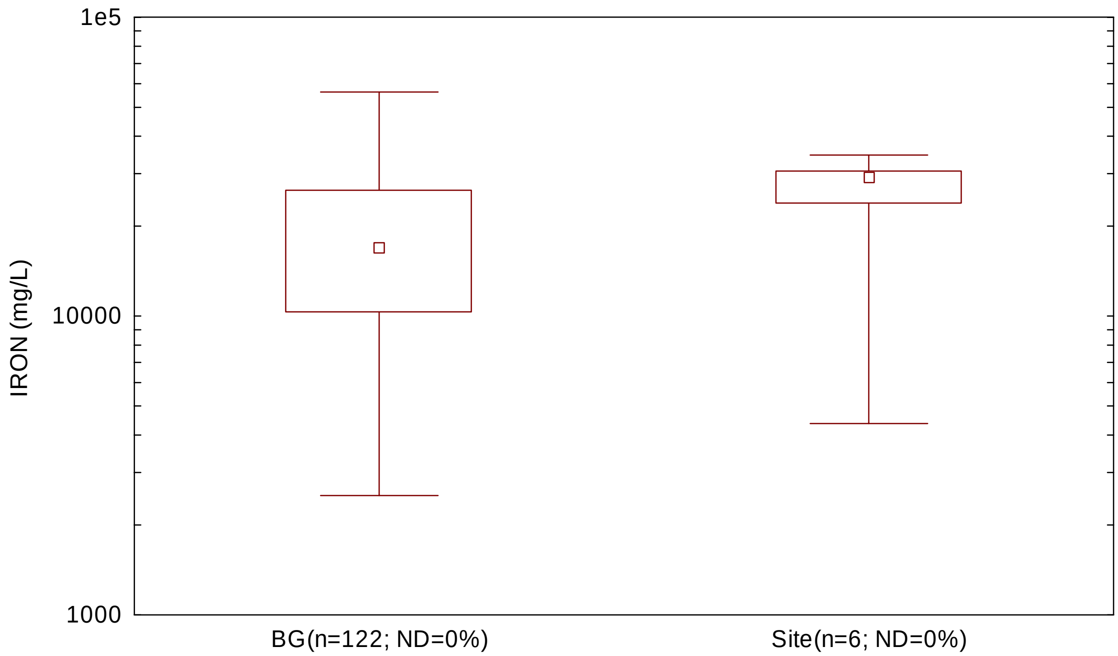


Figure 18. Box Plot Comparison for Lead in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.447)

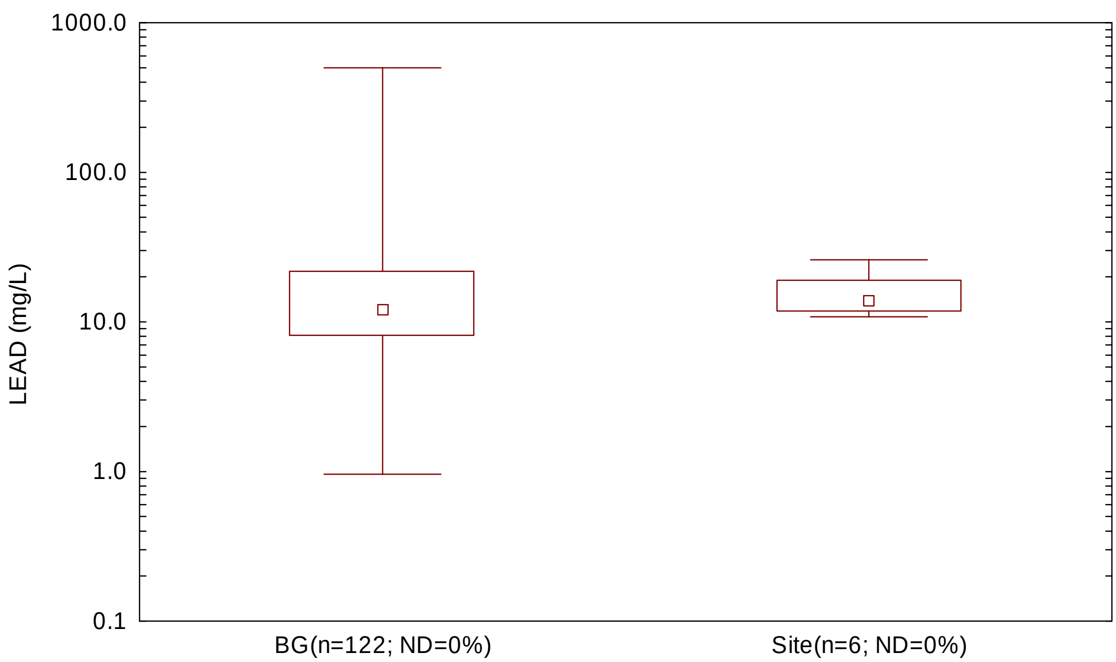


Figure 19. Box Plot Comparison for Magnesium in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = <0.0001)

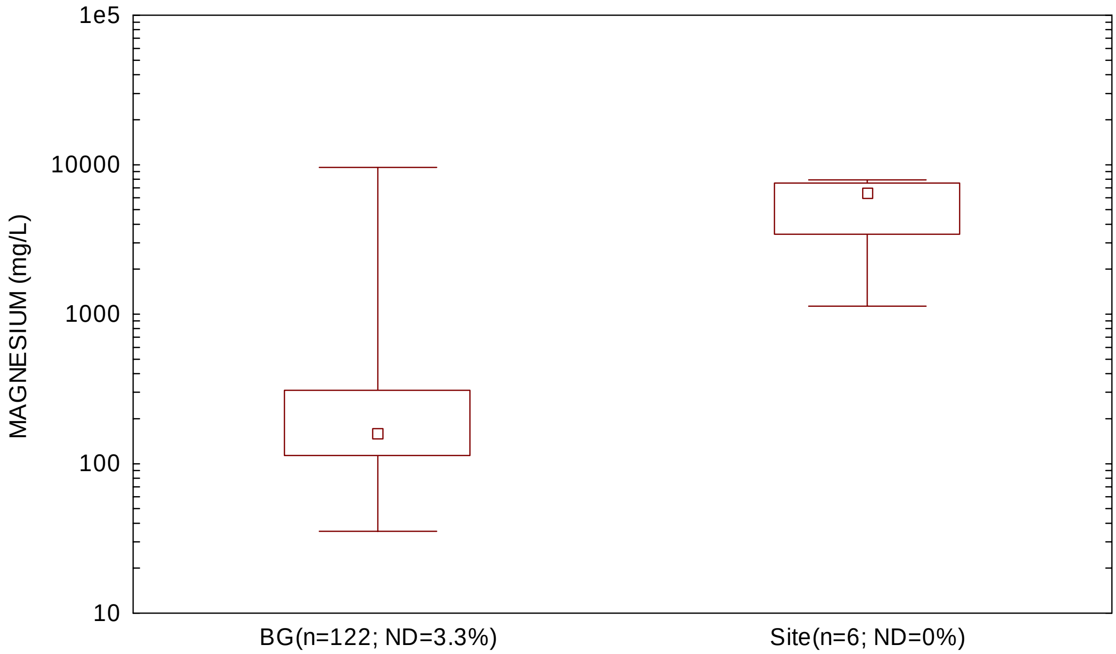


Figure 20. Box Plot Comparison for Manganese in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.644)

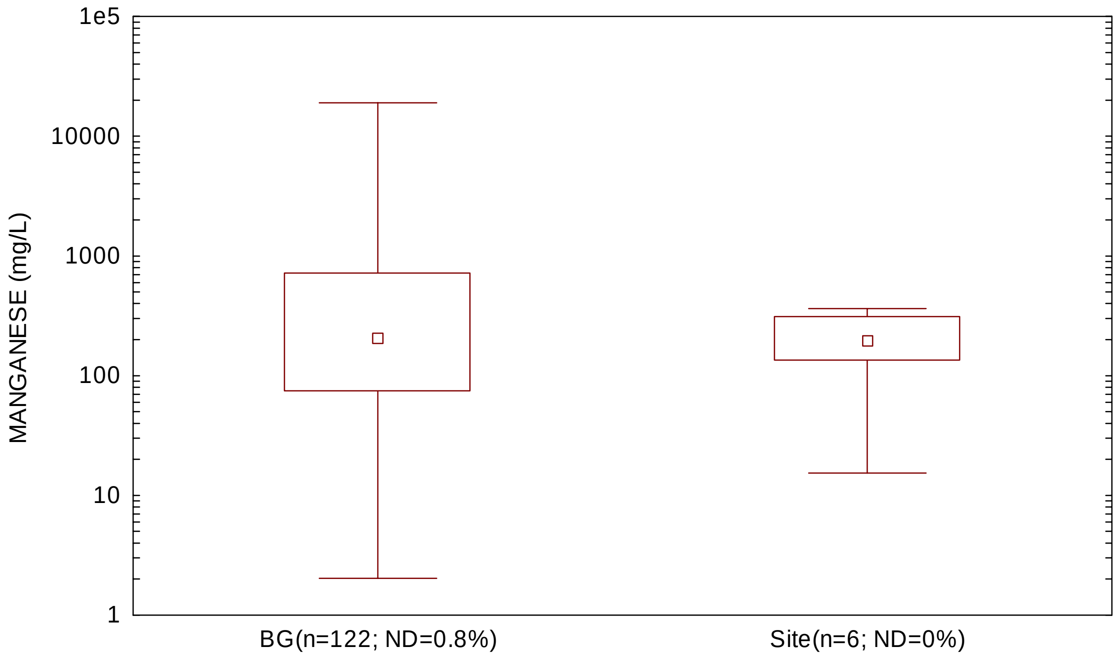


Figure 21. Box Plot Comparison for Mercury in Soil
Parcel 66(7), Ft. McClellan

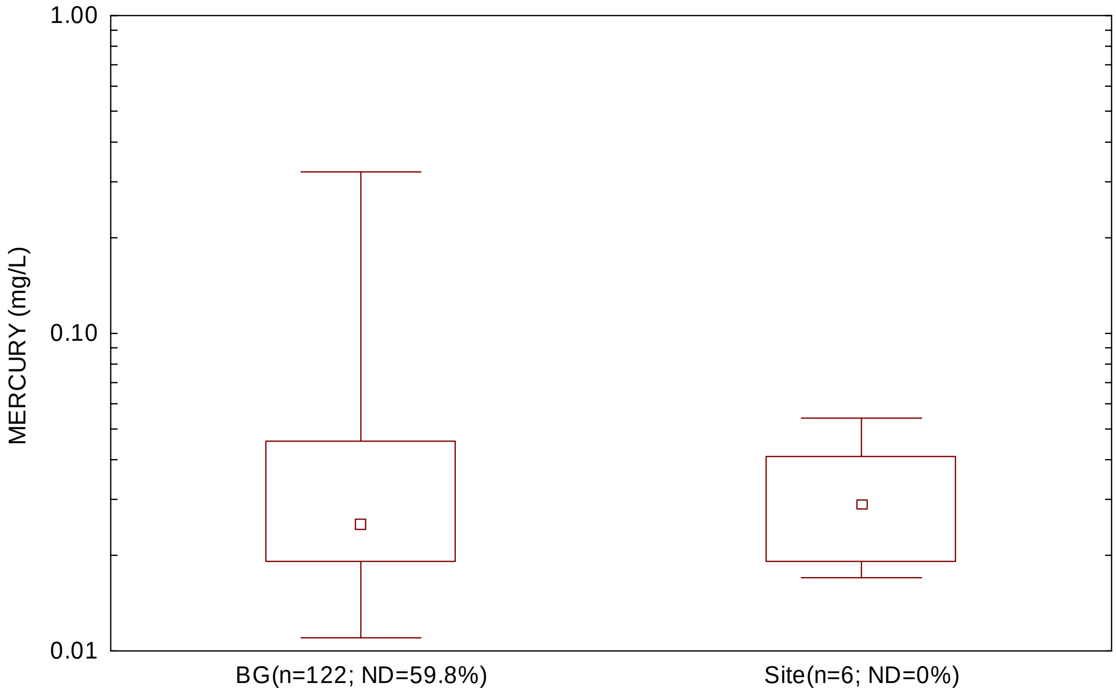
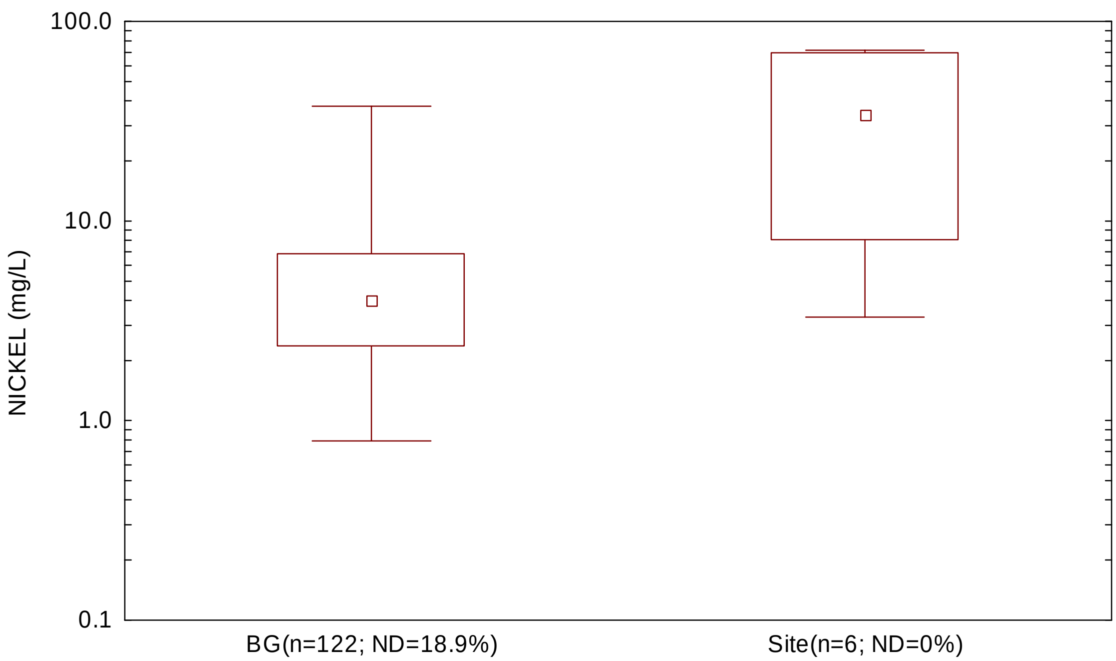


Figure 22. Box Plot Comparison for Nickel in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.003)



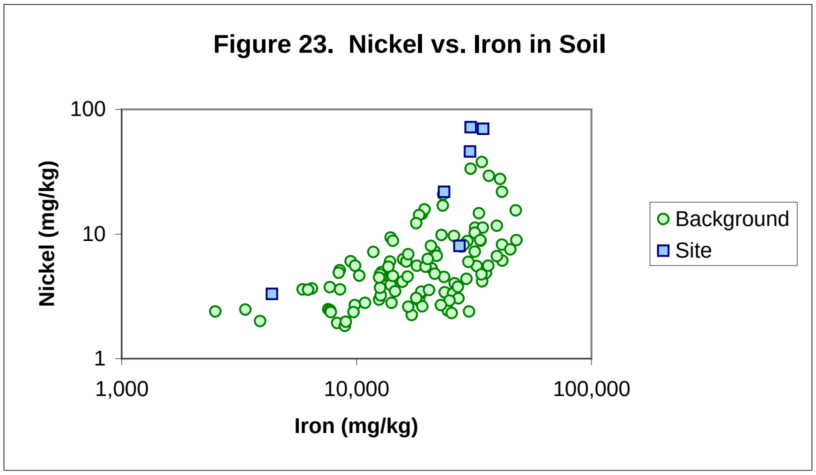


Figure 23. Nickel vs. Iron in Soil
Nickel (mg/kg)
100
10
1
1,000
10,000
100,000
Iron (mg/kg)
Background
Site

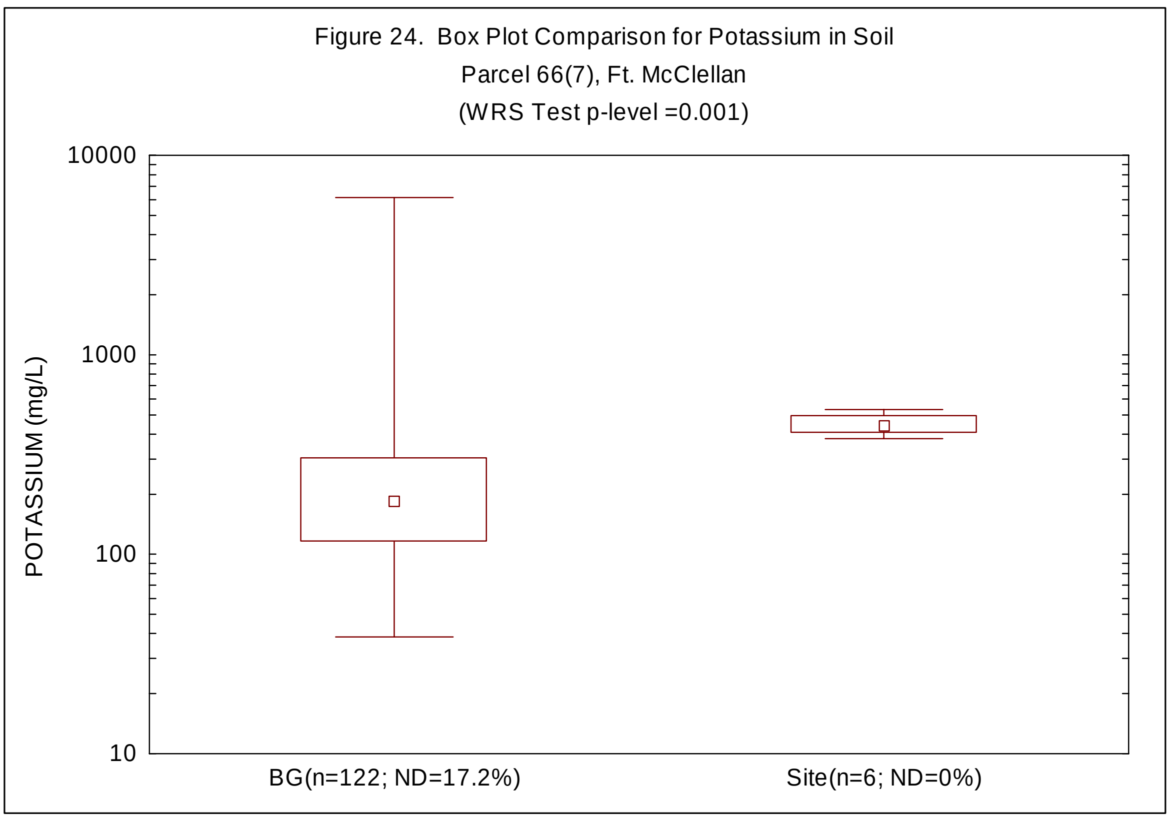


Figure 24. Box Plot Comparison for Potassium in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level =0.001)
POTASSIUM (mg/L)
10000
1000
100
10
BG(n=122; ND=17.2%)
Site(n=6; ND=0%)

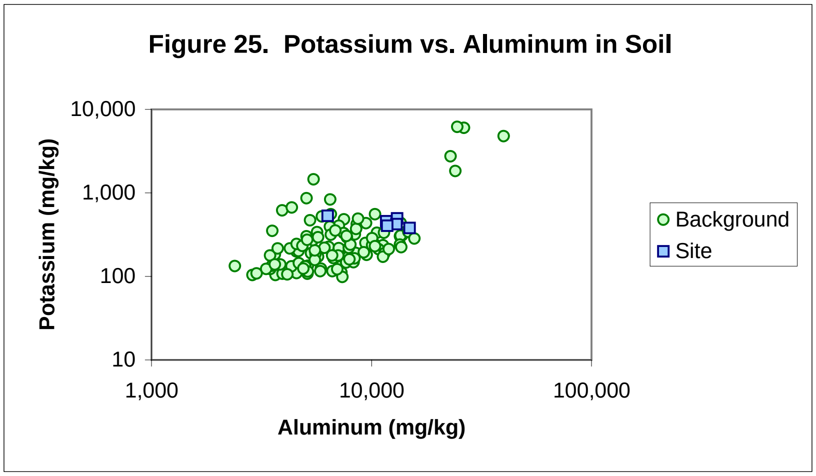


Figure 25. Potassium vs. Aluminum in Soil
10,000
1,000
100
10
Potassium (mg/kg)
1,000
10,000
100,000
Aluminum (mg/kg)
Background
Site

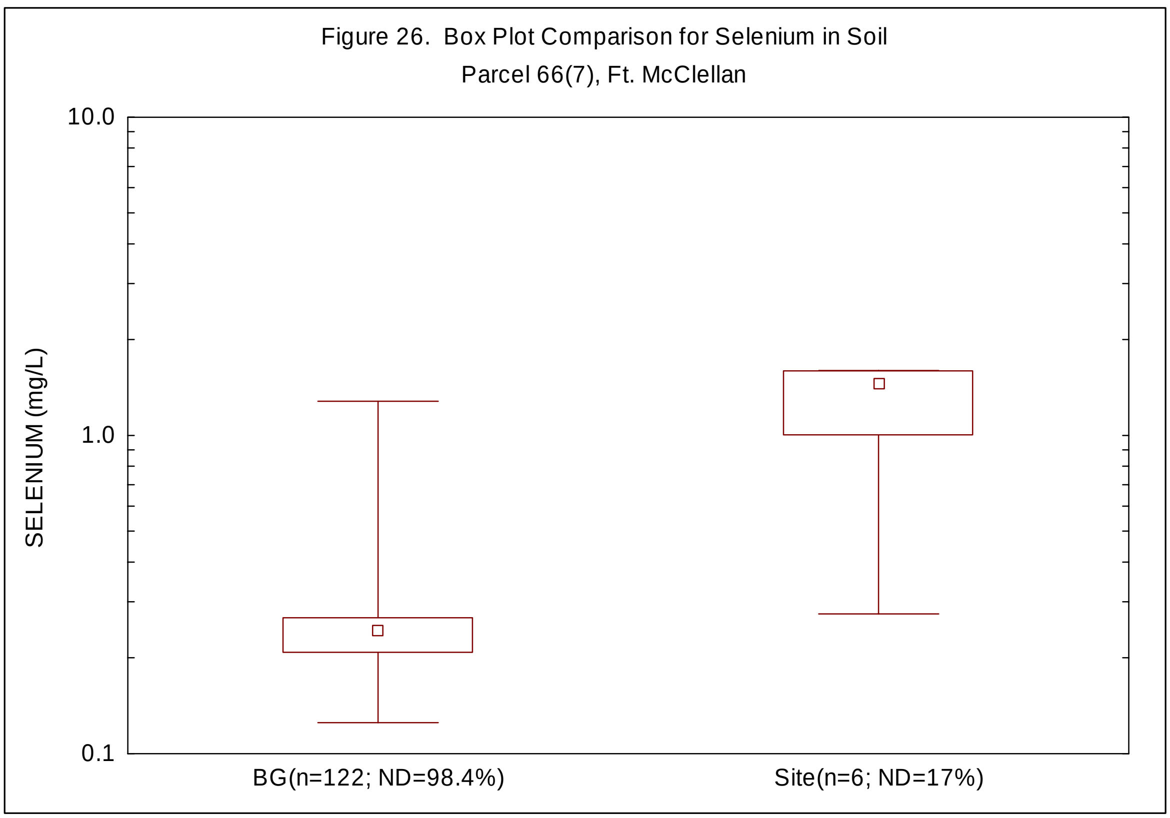


Figure 26. Box Plot Comparison for Selenium in Soil
Parcel 66(7), Ft. McClellan
10.0
1.0
0.1
SELENIUM (mg/L)
BG(n=122; ND=98.4%)
Site(n=6; ND=17%)

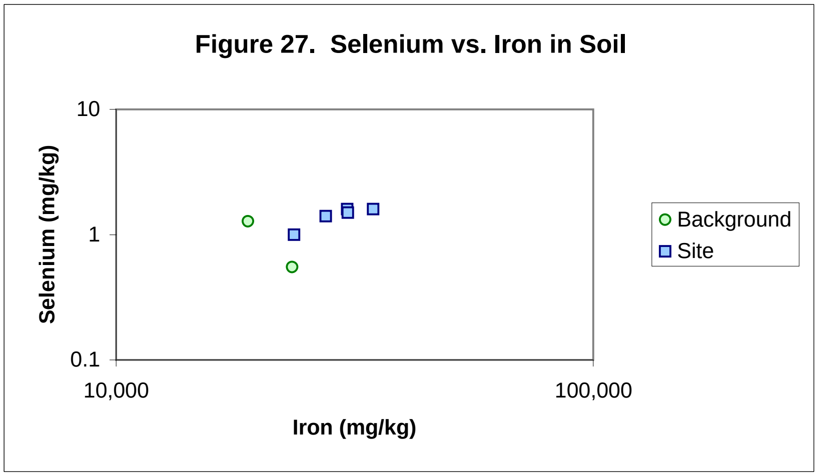


Figure 27. Selenium vs. Iron in Soil
10
1
0.1
Selenium (mg/kg)
10,000
100,000
Iron (mg/kg)
Background
Site

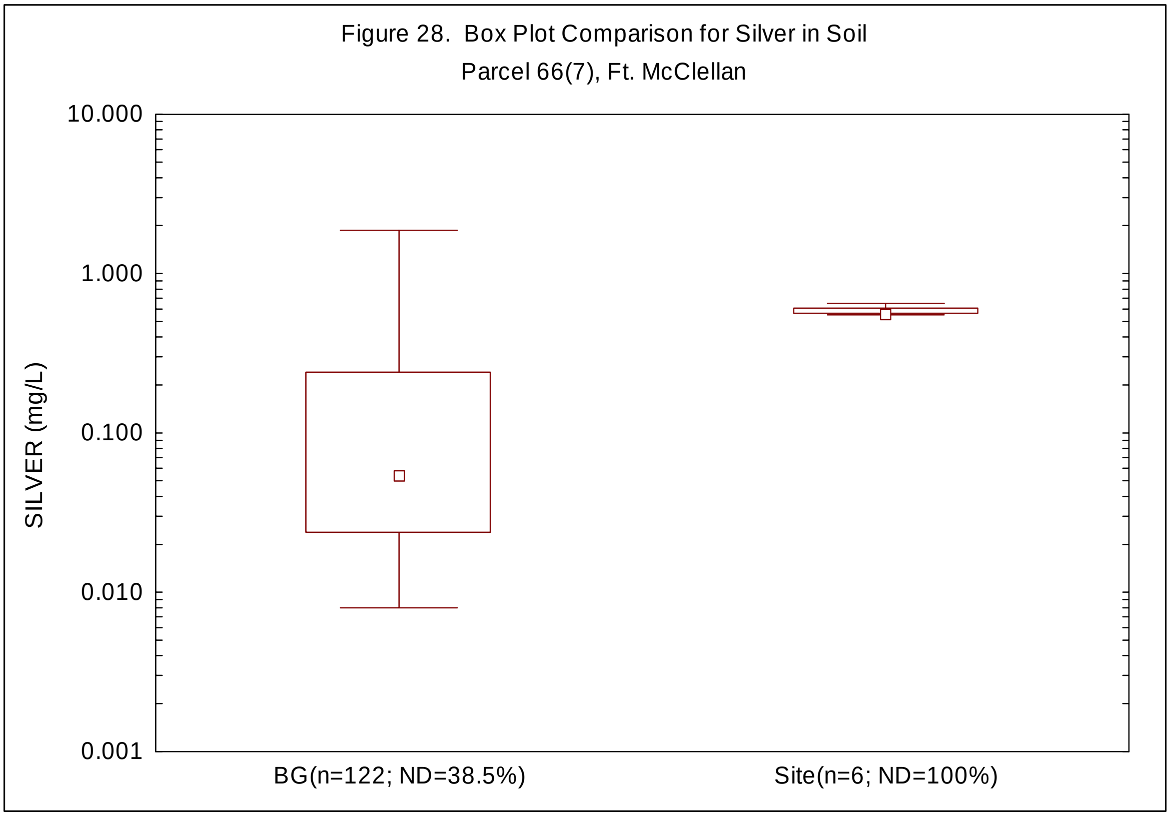


Figure 28. Box Plot Comparison for Silver in Soil
Parcel 66(7), Ft. McClellan
10.000
1.000
0.100
0.010
0.001
SILVER (mg/L)
BG(n=122; ND=38.5%)
Site(n=6; ND=100%)

Figure 29. Box Plot Comparison for Sodium in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.0002)

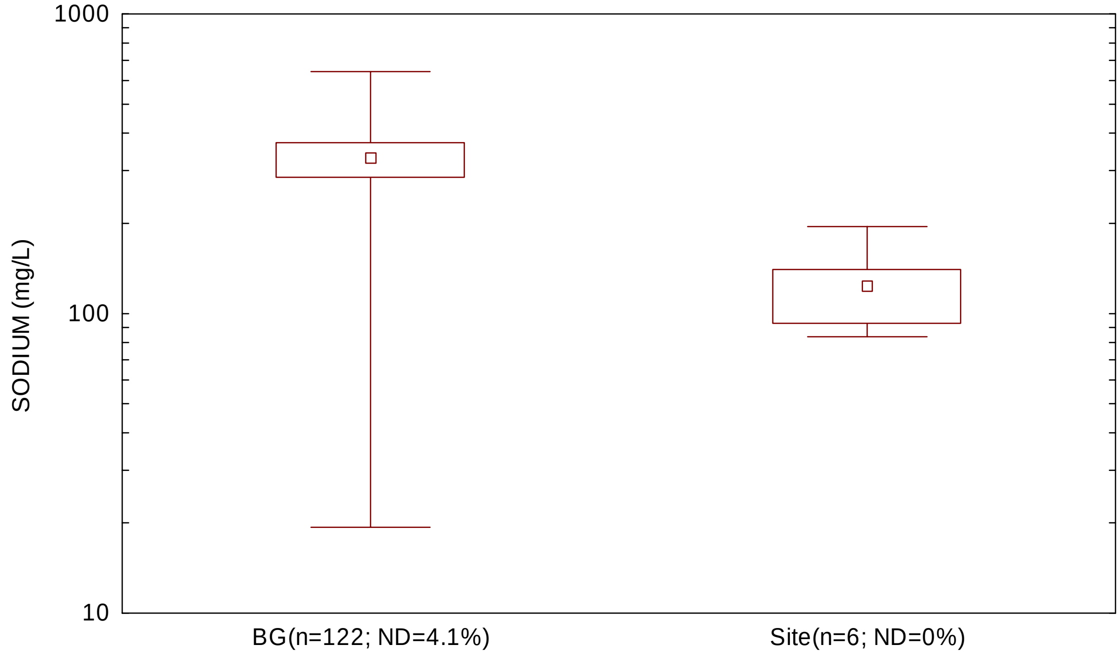


Figure 30. Box Plot Comparison for Thallium in Soil
Parcel 66(7), Ft. McClellan

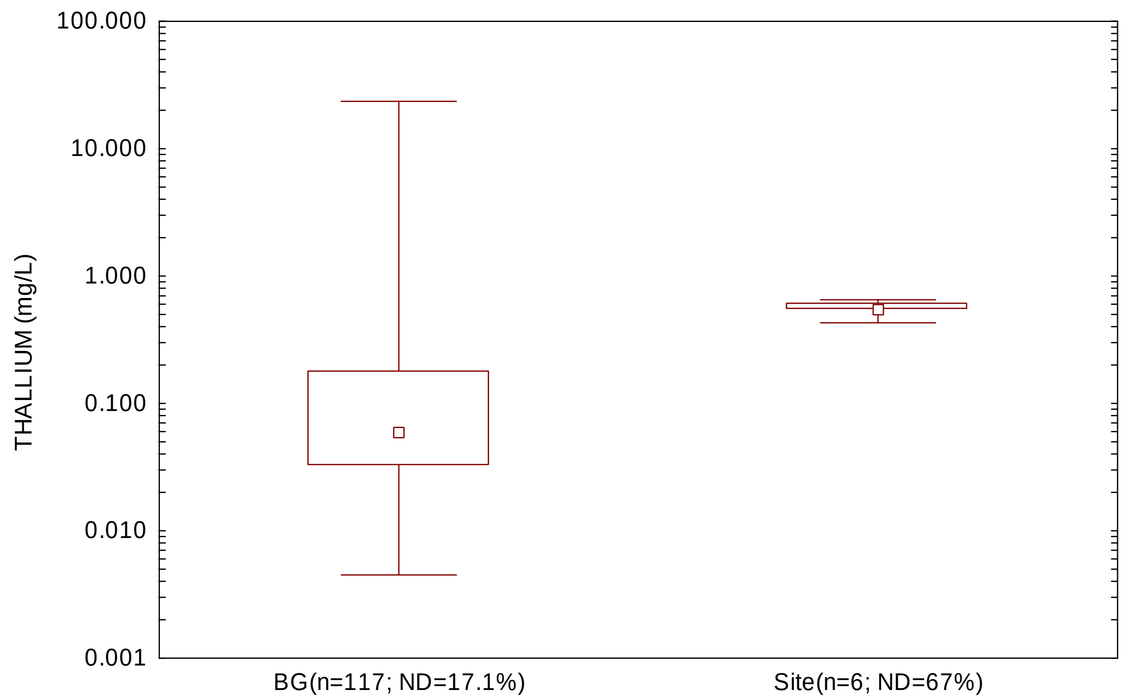


Figure 31. Box Plot Comparison for Vanadium in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.364)

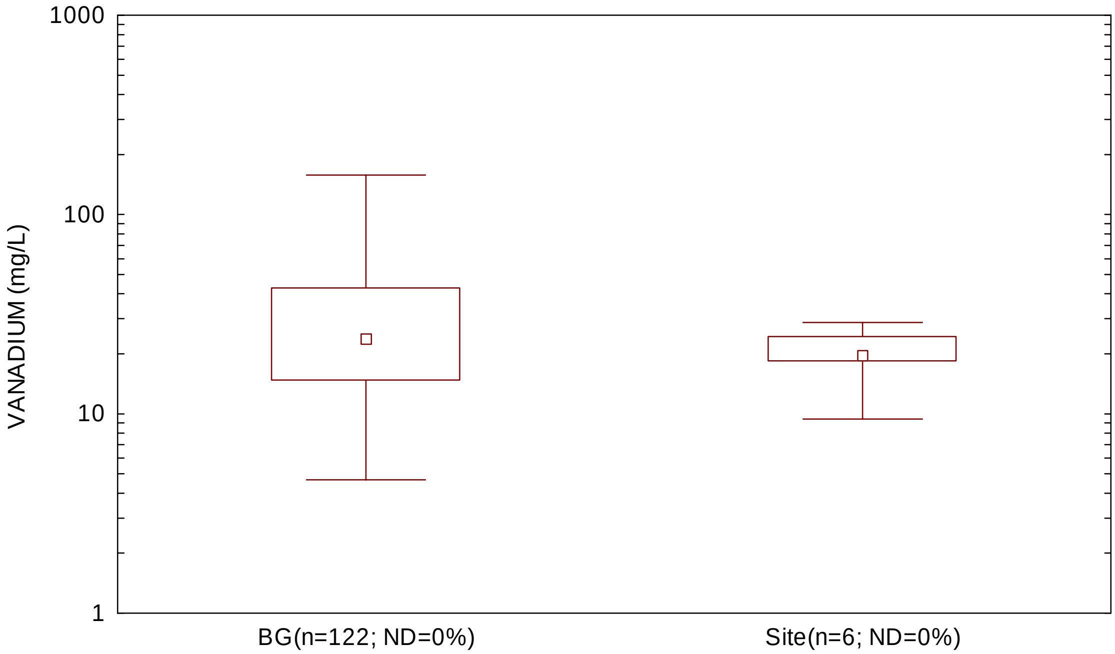


Figure 32. Box Plot Comparison for Zinc in Soil
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.002)

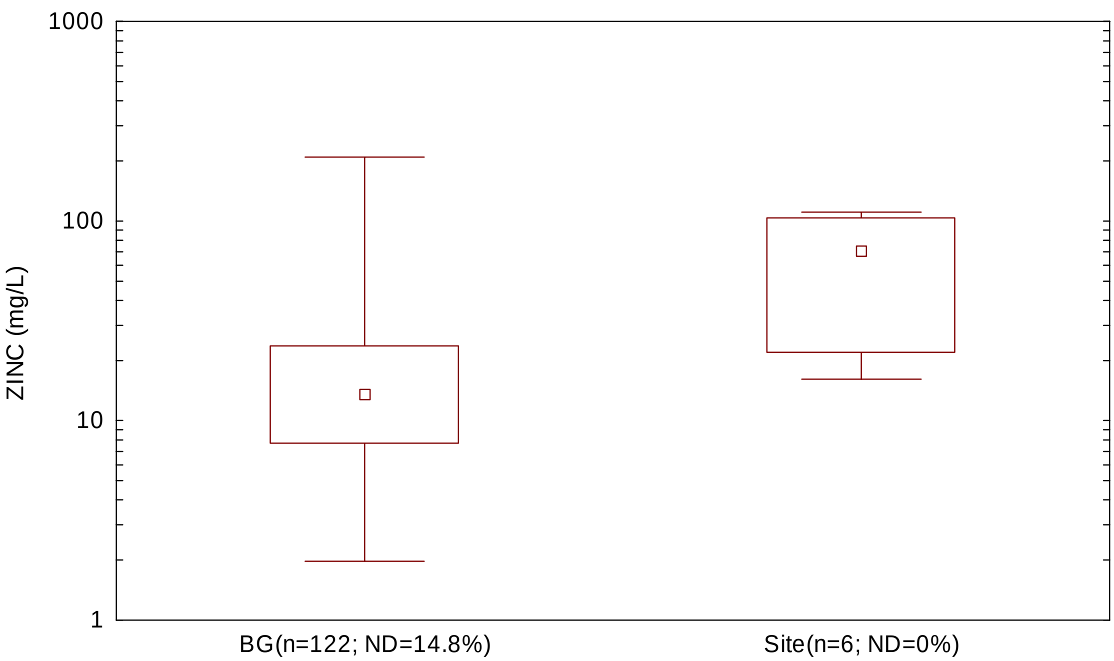
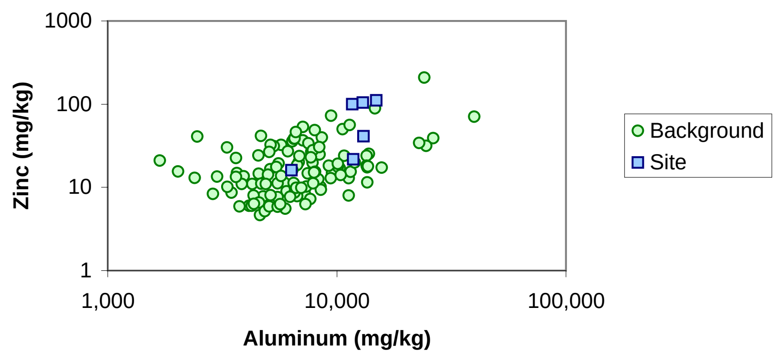


Figure 33. Zinc vs. Aluminum in Soil



GROUNDWATER

Comparison of Site and Background Groundwater Data for the Small Weapons Repair Shop, Parcel 66(7), at Fort McClellan, Calhoun County, Alabama

Summary

An integrated statistical and geochemical evaluation of 23 elements in groundwater was performed for the Small Weapons Repair Shop, Parcel 66(7), at Fort McClellan. Concentrations of aluminum, barium, nickel, and potassium were determined to be within range of background. Elevated concentrations of calcium, magnesium, and sodium were determined to be naturally occurring. The manganese concentration in sample KJ3001 (from monitoring well PPMP-75-GP01) may be elevated due to reductive dissolution, which is a secondary effect of the VOC contamination in groundwater at that location.

1.0 Introduction

This report provides the methodology and results of the comparisons of the concentrations of inorganic constituents in unfiltered groundwater samples from background areas versus samples from the Small Weapons Repair Shop, Parcel 66(7) at Fort McClellan in Calhoun County, Alabama. Site samples used in the site-to-background comparison include the three unfiltered groundwater samples that were collected during the 1999 site investigation. Background distributions and screening values have been established for target analyte list (TAL) metals in unfiltered groundwater at Fort McClellan (IT Corporation, 2002), and are used in the following comparisons.

2.0 Comparison Methodology

This section describes the statistical and geochemical evaluation techniques that were employed in the Parcel 66(7) site-to-background comparisons.

2.1 Statistical Procedures

Contamination can be caused by a variety of processes that yield different spatial distributions of elevated contaminant concentrations. Slight but pervasive contamination can occur from non-point-source releases, and can result in slight increases in contaminant concentrations in a large percentage of samples. Localized, or "hot-spot," contamination can result in elevated concentrations in a small percentage of the total number of site samples. No single two-sample statistical comparison test is sensitive to both of these modes of contamination. For this reason, the use of multiple simultaneous tests is recommended for comparison of site and background distributions (U.S. Environmental Protection Agency [EPA], 1989, 1992, and 1994; U.S. Navy, 1998 and 1999).

The Wilcoxon rank sum (WRS) test is sensitive to slight but pervasive contamination, but is not sensitive to localized or more extreme hot-spot situations. The background threshold comparison, or "hot measurement test," is effective in identifying localized contamination, but is not sensitive to slight but pervasive contamination. The WRS test and hot measurement test are thus complementary. In addition to these tests, box-and-whisker plots are useful for visually comparing the site and background distributions and for properly interpreting the results of the WRS test.

Hot Measurement Test. The hot measurement test consists of comparing each site measurement with a concentration value that is representative of the upper limit of the background distribution (EPA, 1994). Ideally, a site sample with a concentration above the background screening value would have a low probability of being a member of the background distribution, and may be an indicator of contamination. It is important to select such a background screening value carefully so that the probability of falsely identifying site samples as contaminated or uncontaminated is minimized.

The 95th upper tolerance limit (UTL_{95}) is recommended as a screening value for normally or lognormally distributed analytes and the 95th percentile is recommended as a screening value for nonparametrically distributed analytes (EPA, 1989, 1992, and 1994). Site samples with concentrations above these values are not necessarily contaminated, but should be considered suspect.

The UTL_{95} or 95th percentile of the background distributions for 23 elements in unfiltered groundwater are provided in Table 1. To perform the test, each analyte's site maximum detected concentration (MDC) is compared to the background UTL_{95} or 95th percentile, in accordance with the type of background distribution. If the site MDC exceeds the background screening value, then that analyte will undergo a geochemical evaluation. If the MDC does not exceed the background screening value, then hot-spot contamination is not indicated.

Wilcoxon Rank Sum Test. The WRS test has been recommended for use in site-to-background comparisons (U.S. Navy, 1998 and 1999; EPA, 2000). In this report, the WRS test is performed when the site and background data sets each contain less than 50 percent nondetects (i.e., measurements reported as not detected below the laboratory reporting limit). The WRS test will not be performed on data sets containing 50 percent or more nondetects. The medians of such data sets are unknown, and hence the test results would lack sufficient power to yield reliable results.

The WRS test compares two data sets of size n and m ($n > m$), and tests the null hypothesis that the samples were drawn from populations with distributions having the same medians. To perform the test, the two sets of observations are pooled and arranged in order from smallest to largest. Each observation is assigned a rank; that is, the smallest is ranked 1, the next largest is ranked 2, and so on up to the largest observation, which is ranked ($n + m$). If ties occur between or within samples, each one is assigned the midrank. Next, the sum of the ranks of smaller data set m is calculated. Then the test statistic Z is determined,

$$Z = \frac{W - m(m+n+1)/2}{\sqrt{mn(m+n+1)/12}}$$

Where:

W = Sum of the ranks of the smaller data set
m = Number of data points in the smaller group
n = Number of data points in the larger group.

This test statistic Z is used to find the two-sided significance. For instance, if the test statistic yields a probability of a Type I error (p-level) less than 0.05, then there is a statistically significant difference between the medians at the 95 percent confidence level. A Type I error involves rejecting the null hypothesis when it is true. If the p-level is greater than 0.05, then there is no reasonable justification to reject the null hypothesis at the 95 percent confidence level. It can therefore be concluded that the medians of the two data sets are similar, and can be assumed to be drawn from the same population.

If the p-level is less than 0.05, then the medians of the two distributions are significantly different at the 95 percent confidence level. This can occur if the site data are shifted higher or lower than the background data. If the site data are shifted higher relative to background, then contamination may be indicated, and the analyte in question will be carried on for geochemical evaluation; however, if the site data are shifted lower relative to background, then contamination is not indicated. If the p-level is greater than 0.05, then pervasive site contamination is not suspected.

Box Plots. A quick, robust graphical method recommended by the EPA to visualize and compare two or more groups of data is the box plot (EPA, 1989 and 1992). An example box plot is provided in Figure 1. These plots provide a summary view of the entire data set, including the overall location and degree of symmetry. The box encloses the central 50 percent of the data points so that the top of the box represents the 75th percentile and the bottom of the box represents the 25th percentile. The small box within the larger box represents the median of the data set. The upper whisker extends outward from the box to either 1.5 times the interquartile distance (i.e., range between 25th and 75th percentiles) or to the maximum point, whichever is larger. The lower whisker extends either 1.5 times the interquartile distance or to the minimum point, whichever is smaller. Values outside the whiskers are shown as circles representing distinct points. Nondetect results are set equal to one-half of the reporting limit for plotting purposes.

For each analyte, box plots of site and background data are placed side by side to visually compare the distributions and qualitatively determine whether the data sets are similar or distinct. As described previously, the WRS test may indicate that the medians of the site and background data sets are significantly different. Examination of the box plots will confirm whether that difference is caused by site data that are shifted higher or lower relative to background.

2.2 Geochemical Evaluation

If an analyte fails either of the statistical tests described in Section 2.1, then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The importance of geochemical evaluations in distinguishing between site and background data sets has been recognized in the industry (EPA, 1995; U.S. Navy, 1998 and 1999; Barclift, *et al.*, 2000). When properly evaluated, geochemistry can provide mechanistic explanations for apparently high, yet naturally occurring, constituents. Anomalous samples that may represent contamination can also be readily distinguished from uncontaminated samples.

Groundwater samples often contain elevated concentrations of inorganic constituents. Common reasons for these elevated concentrations include naturally high dissolved concentrations, the presence of suspended particulates in the samples, or contamination resulting from site activities. One primary mechanism that is examined in this Parcel 66(7) groundwater site-to-background comparison is the presence of suspended particulates, as discussed in the following section.

Effects of Suspended Particulates. The presence of trace elements adsorbed on suspended particulates can greatly increase trace element concentrations as reported by an analytical laboratory. These adsorbed trace elements are not in true solution, and can be removed by settling or filtration. Samples containing trace elements adsorbed on suspended clay particulates should show a positive correlation with aluminum concentrations, and samples containing trace elements adsorbed on suspended iron oxides should show a positive correlation with iron concentrations. These correlations are evaluated by generating x-y plots of the concentrations of an elevated trace metal versus aluminum or iron (depending on the trace element).

The most common suspended particulates in groundwater samples are clay minerals, hydrous aluminum oxides ($Al_2O_3 \cdot nH_2O$), and hydroxides [$Al(OH)_3$]; and iron oxide (Fe_2O_3), iron hydroxide [$Fe(OH)_3$], and iron oxyhydroxide ($FeO \cdot OH$) minerals, collectively referred to as "iron oxides." All clay minerals contain aluminum and have low solubilities over a neutral pH range of 6 to 8. Measured concentrations of aluminum in excess of ~1 milligram per liter (mg/L) indicate the presence of suspended clay minerals, with higher aluminum concentrations being a qualitative indicator of the mass of suspended clay minerals (Stumm and Morgan, 1970; Hem, 1985). Iron also has a very low solubility under neutral pH and moderate to oxidizing redox conditions, so that measured iron concentrations in excess of ~1 mg/L under these conditions indicate the presence of suspended iron oxides.

The presence of suspended clay or iron oxides in groundwater samples has particular importance in the interpretation of trace element concentrations. Most clay particles maintain a negative surface charge under neutral pH conditions, and have a strong tendency to adsorb positively charged (cationic) aqueous species. Iron oxides display the opposite behavior, maintaining a positive surface charge under neutral pH conditions, and have a strong tendency to adsorb negatively charged (anionic) aqueous species.

Barium, lead, and zinc are usually present in groundwater as divalent cations (Ba^{+2}, Pb^{+2}, Zn^{+2}) and thus tend to concentrate on clay surfaces (Electric Power Research Institute [EPRI], 1984; Brookins, 1988). Arsenic, selenium, and vanadium are usually present under oxidizing conditions as oxyanions ($HAsO_4^{-2}$, $HSeO_3^-$, $H_2VO_4^-$), and thus tend to concentrate on iron oxide surfaces (Bowell, 1994; Hem, 1985; Pourbaix, 1974; Brookins, 1988).

Chromium can be present in groundwater as a mixture of aqueous species with different charges such as $Cr(OH)_2^+$, $Cr(OH)_3^0$, and $Cr(OH)_4^-$ (EPRI, 1984). The positive, neutral, and negative charges on these species result in the distribution of chromium on several different types of sorptive surfaces, including clay and iron oxide minerals.

As an example, the concentrations of zinc (y-axis) can be plotted against aluminum (x-axis) for site and background samples. If the site and background samples display a common linear trend, then it is most likely that the elevated zinc concentrations are due to the presence of suspended clay minerals in the samples. The slope of a best-fit line through the points is equal to the average zinc/aluminum ratio. If some site samples plot above the trend established by the background samples, then those site samples have an anomalously high zinc/aluminum ratio, and most likely contain excess zinc that cannot be explained by these natural processes.

An alternative technique for assessing the effects of suspended particulates on trace element concentrations is the evaluation of correlations of trace element concentrations versus turbidity. Turbidity measurements are qualitative, and do not distinguish between suspended clay minerals, iron oxides, and natural organic material, so this approach lacks the resolution provided by trace element versus aluminum or trace element versus iron correlations. Despite these limitations, correlations of trace elements versus turbidity are still useful for providing independent confirmation of the conclusions reached by evaluation of the aluminum and iron ratios.

If the concentrations of trace elements in unfiltered samples are correlated with aluminum or iron, then they are most likely adsorbed to the surfaces of suspended particulates. If these correlations are linear, then the elevated concentrations are most likely natural.

3.0 Results of the Site-to-Background Comparisons

Aluminum

Hot Measurement Test: None of the site samples exceeds the background screening value of 5.95 milligrams per liter (mg/L).

WRS Test: A p-level of 0.915 indicates excellent agreement between the site and background distributions.

Box Plot: A box plot comparing the data sets is shown in Figure 2. The site box plot lacks whiskers because of the small sample size (three). The site median is below the background median.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background. It should be noted that aluminum has very low solubilities, on the order of a few tens of micrograms per liter, under neutral pH conditions (Hem, 1985). Detectable concentrations of aluminum in neutral pH groundwater indicate the presence of suspended particulates, such as clay minerals, hydrous aluminum oxides, and aluminum hydroxides.

Conclusion: Aluminum concentrations detected in groundwater are within range of background, and are most likely naturally occurring.

Antimony

Hot Measurement Test: All three of the site samples are nondetect for antimony. The site reporting limit is 0.06 mg/L, so it cannot be determined if the site antimony concentrations are above the background screening value of 0.01 mg/L.

WRS Test: The WRS test was not performed because the site and background data sets contain 100 and 96.2 percent nondetects, respectively.

Box Plot: The site and background data sets are characterized by high percentages of nondetects (greater than 96 percent), so the box plots are defined by the replacement values of one-half the reporting limit (Figure 3). The site data are higher than background because the site data set has a higher reporting limit (0.06 mg/L) than most of the background samples.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Arsenic

Hot Measurement Test: All three of the site samples are nondetect for arsenic. The site reporting limit of 0.01 mg/L is below the background screening value of 0.117 mg/L.

WRS Test: The WRS test was not performed because the site and background data sets contain 100 and 83.9 percent nondetects, respectively.

Box Plot: The shape and location of the site box plots reflect the high percentage of nondetects (100 percent), the replacement value of one-half the reporting limit, and the high reporting limit relative to background (Figure 4).

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Barium

Hot Measurement Test: None of the site samples exceeds the background screening value of 0.472 mg/L.

WRS Test: The p-level of 0.830 indicates excellent agreement between the site and background distributions.

Box Plot: The site median is slightly below the background median (Figure 5). The site minimum is similar to the background 25th percentile and the site maximum is similar to the background 75th percentile.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Barium in the site samples is most likely naturally occurring.

Beryllium

Hot Measurement Test: All three of the site samples are nondetect for beryllium. The site reporting limit is 0.005 mg/L, so none of the site concentrations exceed the background screening value of 0.005 mg/L.

WRS Test: The WRS test was not performed because the site and background data sets contain 100 and 72.2 percent nondetects, respectively.

Box Plot: The shape and location of the site box plot reflect the high percentage of nondetects (100 percent) and the replacement value of one-half the reporting limit (Figure 6). The site plot is higher than the background plot because the site data set has higher reporting limits.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Cadmium

Hot Measurement Test: All three of the site samples are nondetect for cadmium. The reporting limit of 0.005 mg/L is below the background screening value of 0.00678 mg/L.

WRS Test: No WRS test was performed because the site and background data sets contain 100 and 64.3 percent nondetects, respectively.

Box Plot: The location and shape of the site box plot reflect the high percentage of nondetects (100 percent) and replacement values of one-half the reporting limit (Figure 7). The site plot is elevated with respect to background because the site data set is characterized by a higher reporting limit.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Calcium

Hot Measurement Test: Two of the site samples exceed the background screening value of 71.4 mg/L.

WRS Test: The WRS test p-level of 0.024 indicates weak agreement between the site and background distributions.

Box Plot: The site median is higher than the background median (Figure 8). The site maximum is below the background maximum.

Geochemical Evaluation: Magnesium and calcium are major cations in groundwater, and they are also two of the dominant ions in groundwater associated with shale (Brownlow, 1996). The soil boring logs for monitoring wells PPMP-75-GP01, -02, and -03 indicate that shale is the predominant lithology at the depths where the water table was encountered. A plot of magnesium versus calcium reveals a linear trend, and the samples with high calcium also contain high magnesium (Figure 9). The site samples lie on the trend formed by the background samples. This indicates that calcium in the site samples is natural.

Conclusion: Calcium concentrations detected in the site samples are naturally occurring.

Chromium

Hot Measurement Test: All three of the site samples are nondetect for chromium. The site reporting limit of 0.01 mg/L is below the background screening value of 0.0168 mg/L.

WRS Test: No WRS test was performed because the site and background data sets both contain 100 percent nondetects.

Box Plot: The site and background data sets are both characterized by 100 percent nondetects, so the box plots reflect the replacement values of one-half the reporting limit (Figure 10). The site reporting limit is similar to the median background reporting limit.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Cobalt

Hot Measurement Test: All three of the site samples are nondetect for cobalt. The site reporting limit is 0.05 mg/L, so it is not possible to determine if cobalt concentrations in the site samples exceed the background screening value of 0.0202 mg/L.

WRS Test: The WRS test was not performed because the site and background data sets contain 100 and 94.4 percent nondetects, respectively.

Box Plot: The site and background box plots reflect the high percentages of nondetects (greater than 94 percent) and the replacement values of one-half the reporting limit (Figure 11). The site plot is elevated with respect to the background plot because the site data set has a higher reporting limit.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Copper

Hot Measurement Test: All three of the site samples are nondetect for copper. The site reporting limit is 0.025 mg/L, so none of the site concentrations exceed the background screening value of 0.207 mg/L.

WRS Test: The WRS test was not performed because the site and background data sets contain 100 and 81.5 percent nondetects, respectively.

Box Plot: The site and background box plots reflect the high percentages of nondetects (greater than 81 percent) and replacement values of one-half the reporting limit (Figure 12). The site plot is elevated with respect to the background plot because the site reporting limit is higher than most of the background reporting limits.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Iron

Hot Measurement Test: None of the site samples exceeds the background screening value of 22 mg/L.

WRS Test: A p-level of 0.642 indicates strong agreement between the site and background distributions.

Box Plot: The medians of the two data sets are similar (Figure 13). The site maximum is below the background maximum.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background. It is worth noting that iron has a very low solubility under neutral pH and moderate to oxidizing redox conditions, so that measured iron concentrations in excess of ~1 mg/L under these conditions indicate the presence of suspended iron oxides.

Conclusion: Iron concentrations in the site samples are most likely naturally occurring.

Lead

Hot Measurement Test: All three of the site samples are nondetect for lead. The reporting limit of 0.003 mg/L is below the background screening value of 0.0434 mg/L.

WRS Test: The WRS test was not performed because the site and background data sets contain 100 and 60 percent nondetects, respectively.

Box Plot: The site box plot is defined by the high percentage of nondetects (100 percent) and the replacement value of one-half the reporting limit (Figure 14).

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: The observed concentrations of lead are most likely naturally occurring.

Magnesium

Hot Measurement Test: Two of the site samples exceed the background screening value of 22 mg/L.

WRS Test: A p-level of 0.006 indicates poor agreement between the site and background distributions.

Box Plot: The site median is higher than the background median (Figure 15). The site and background maxima are similar.

Geochemical Evaluation: As discussed in the Calcium evaluation, magnesium and calcium are major cations in groundwater and are two of the dominant ions in groundwater associated with shale (Brownlow, 1996). A plot of magnesium versus calcium reveals a linear trend, and the samples with high magnesium concentrations also have high calcium concentrations (Figure 9). The site samples lie on the trend formed by the other samples, suggesting that magnesium in the site samples is natural.

Conclusion: Magnesium concentrations detected in the site samples are naturally occurring.

Manganese

Hot Measurement Test: None of the manganese concentrations in the site samples exceed the background screening value of 4.134 mg/L.

WRS Test: The p-level of 0.186 indicates acceptable agreement between the site and background distributions.

Box Plot: The site median is higher than the background median, and the site maximum is lower than the background maximum (Figure 16).

Geochemical Evaluation: The results of the statistical comparisons indicate that the site data are within range of background and that a geochemical evaluation is not required. It should be noted, however, that sample KJ3001 (from monitoring well PPMP-75-GP01) contains the highest site manganese concentration; the lowest Eh and dissolved oxygen field readings; and detectable concentrations of several VOCs, including trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC). DCE and VC are reductive dechlorination products that result from the microbial degradation of TCE under anaerobic conditions. These data suggest that degradation of VOCs may be causing a locally reducing environment in the vicinity of well PPMP-75-GP01. Such an environment can drive the dissolution of iron oxides and manganese oxides, which become soluble as the redox potential drops below a threshold value. If this is the case, the elevated manganese concentration in sample KJ3001 may be a secondary effect of the VOC contamination, and represents mobilization of naturally occurring manganese.

Conclusion: Manganese concentrations observed in the three site samples are statistically within range of background. However, the manganese concentration observed in sample KJ3001 (from monitoring well PPMP-75-GP01) may be elevated due to the reductive dissolution caused by VOC contamination in groundwater at that location, and reflects the mobilization of naturally occurring manganese.

Mercury

Hot Measurement Test: All three of the site samples are nondetect for mercury. The site reporting limit of 0.0002 mg/L is below the background screening value of 0.000243 mg/L.

WRS Test: No WRS test was performed because the site and background data sets both contain 100 percent nondetects.

Box Plot: The site and background box plots reflect the high percentages of nondetects (100 percent) and similarity in reporting limits between the two data sets (Figure 17).

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Nickel

Hot Measurement Test: The single detected concentration is an estimated quantitation that is below the background screening value of 0.0343 mg/L. The site reporting limit is 0.04 mg/L, so it is not possible to determine if nickel concentrations in the two nondetect samples are below the background screening value.

WRS Test: The WRS test was not performed because the site and background data sets contain 67 and 100 percent nondetects, respectively.

Box Plot: The locations and shapes of the box plots reflect the high percentages of nondetects (67 percent or greater) and difference in reporting limits between the two data sets (Figure 18).

Geochemical Evaluation: A geochemical evaluation is not required because the single detected concentration is within range of background. However, lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: The observed concentration of nickel is most likely naturally occurring.

Potassium

Hot Measurement Test: None of the site samples exceeds the background screening value of 16 mg/L.

WRS Test: The p-level of 0.068 indicates acceptable agreement between the site and background distributions.

Box Plot: The site median is higher than the background median (Figure 19). The site maximum is lower than the background maximum.

Geochemical Evaluation: A geochemical evaluation is not required because the site data are within range of background.

Conclusion: Potassium in the site samples is most likely naturally occurring.

Selenium

Hot Measurement Test: All three site samples are nondetect for selenium. The site reporting limit of 0.005 mg/L is below the background screening value of 0.0971 mg/L.

WRS Test: No WRS test was performed because the site and background data sets both contain 100 percent nondetects.

Box Plot: The locations and shapes of the site and background box plots reflect the high percentages of nondetects (100 percent) and replacement values of one-half the reporting limit (Figure 20). The site plot is higher than the background plot because the site data set has higher reporting limits than most of the background samples.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Silver

Hot Measurement Test: All three site samples are nondetect for silver, with a reporting limit of 0.01 mg/L. None of the samples exceeds the background screening value of 0.01 mg/L.

WRS Test: No WRS test was performed because the site and background data sets contain 100 and 98.2 percent nondetects, respectively.

Box Plot: The locations and shapes of the site and background box plots reflect the high percentages of nondetects (greater than 98 percent) and replacement values of one-half the reporting limit (Figure 21). The site plot is higher than the background plot because the site data set has higher reporting limits.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Sodium

Hot Measurement Test: Two of the site samples exceed the background screening value of 49.028 mg/L.

WRS Test: The p-level of 0.006 indicates poor agreement between the site and background distributions.

Box Plot: The site median is higher than the background median (Figure 22). The site maximum is below the background maximum.

Geochemical Evaluation: Sodium is a major dissolved constituent in groundwater, and along with calcium and magnesium it is a dominant cation in groundwater associated with shale (see the Calcium evaluation, above). A plot of sodium versus calcium reveals a generally linear trend (Figure 23). The site samples with the highest sodium concentrations also contain the highest calcium concentrations, and lie on the trend formed by the background samples. This indicates that sodium in these samples is probably natural.

Conclusion: Sodium concentrations in the site samples are naturally occurring.

Thallium

Hot Measurement Test: All three site samples are nondetect for thallium. The site reporting limit is 0.01 mg/L, so none of the nondetect samples contain thallium concentrations above the background screening value of 0.01 mg/L.

WRS Test: No WRS test was performed because the site and background data sets contain 100 and 88 percent nondetects, respectively.

Box Plot: Both data sets are characterized by a high percentage of nondetects (88 percent or greater), so the locations and shapes of the box plots reflect the replacement value of one-half the reporting limit (Figure 24). The site plot is higher than the background plot because the site data set is characterized by a higher reporting limit.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Vanadium

Hot Measurement Test: All three site samples are nondetect for vanadium. The site reporting limit is 0.05 mg/L, so it is not possible to determine if any of the site samples contain vanadium at concentrations above the background screening value of 0.0276 mg/L.

WRS Test: No WRS test was performed because the site and background data sets contain 100 and 96.3 percent nondetects, respectively.

Box Plot: Both data sets are characterized by a high percentage of nondetects (greater than 96 percent), so the locations and shapes of the box plots reflect the replacement value of one-half the reporting limit (Figure 25). The site plot is higher than the background plot because the site data set is characterized by a higher reporting limit.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

Zinc

Hot Measurement Test: All three site samples are nondetect for zinc. The site reporting limit of 0.02 mg/L is below the background screening value of 1.155 mg/L.

WRS Test: No WRS test was performed because the site and background data sets contain 100 and 55.6 percent nondetects, respectively.

Box Plot: The site plot reflects the high percentage of nondetects (100 percent) and the replacement value of one-half the reporting limit (Figure 26). The site plot is lower than the background plot because the site samples have a lower reporting limit than many of the background samples.

Geochemical Evaluation: Lower reporting limits would be required to perform a geochemical evaluation.

Conclusion: Lower reporting limits are required to adequately compare the site and background data sets.

4.0 Summary and Conclusions

The methodology used to compare the Parcel 66(7) and background data sets for 23 elements in unfiltered groundwater consists of a combination of a hot measurement test, the nonparametric two-sample Wilcoxon rank sum test, and box-and-whisker plots. Analytes that failed either of the statistical tests were subjected to a geochemical evaluation to determine if the elevated concentrations could be explained by natural processes. Concentrations of aluminum, barium, nickel, and potassium were determined to be within range of background.

Calcium, magnesium, and sodium failed at least one statistical test and were subjected to geochemical evaluation. These elevated concentrations are due to the presence of major cations that naturally occur in groundwater. Manganese concentrations detected in the three site samples are statistically within range of background. However, the manganese concentration in sample KJ3001 (from monitoring well PPMP-75-GP01) may be elevated due to reductive dissolution caused by VOC contamination in groundwater at that location. The manganese concentration observed in this sample may represent the mobilization of naturally occurring manganese.

5.0 References

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ATTACHMENT 1

TABLES

Table 1

Background Screening Values (H_m) for Groundwater
Fort McClellan
Calhoun County, Alabama

Analyte	H_m (mg/L)
Aluminum	5.95
Antimony	<0.01
Arsenic	<0.117
Barium	0.472
Beryllium	<0.005
Cadmium	<0.00678
Calcium	71.4
Chromium	<0.0168
Cobalt	0.0202
Copper	0.207
Iron	22
Lead	<0.0434
Magnesium	22
Manganese	4.134
Mercury	<0.000243
Nickel	<0.0343
Potassium	16
Selenium	<0.0971
Silver	<0.01
Sodium	49.028
Thallium	<0.01
Vanadium	<0.0276
Zinc	1.155

mg/l - Milligram(s) per liter.

ATTACHMENT 2

FIGURES

Figure 1
Example Box Plot

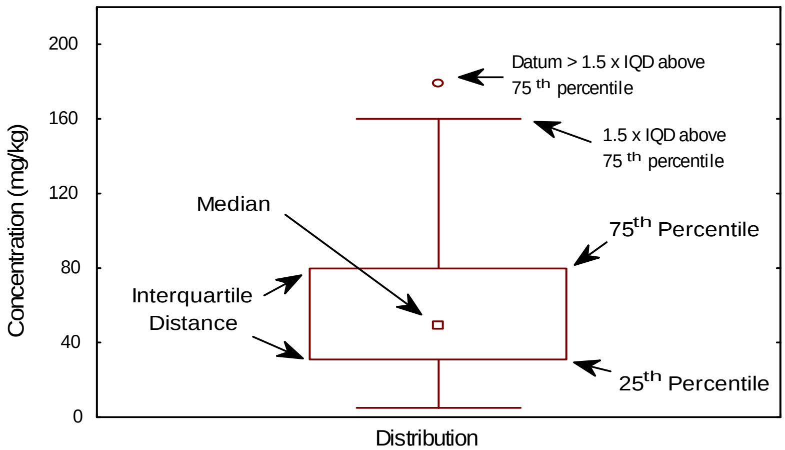


Figure 2. Box Plot Comparison for Alumium in Groundwater
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.915)

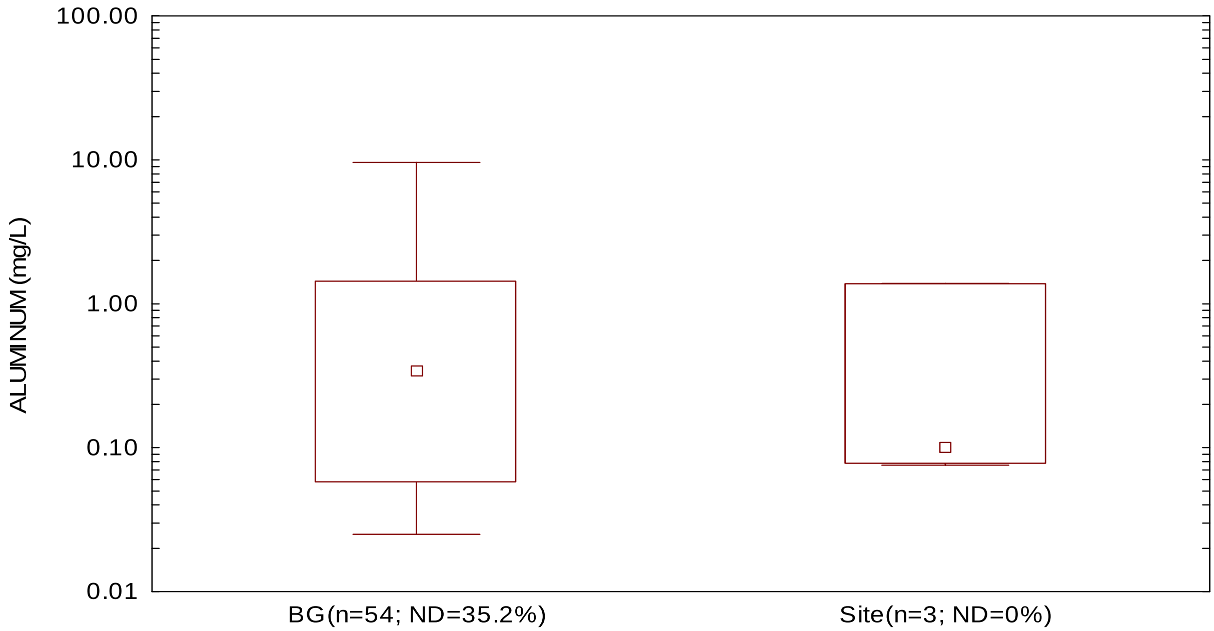


Figure 3. Box Plot Comparison for Antimony in Groundwater
Parcel 66(7), Ft. McClellan

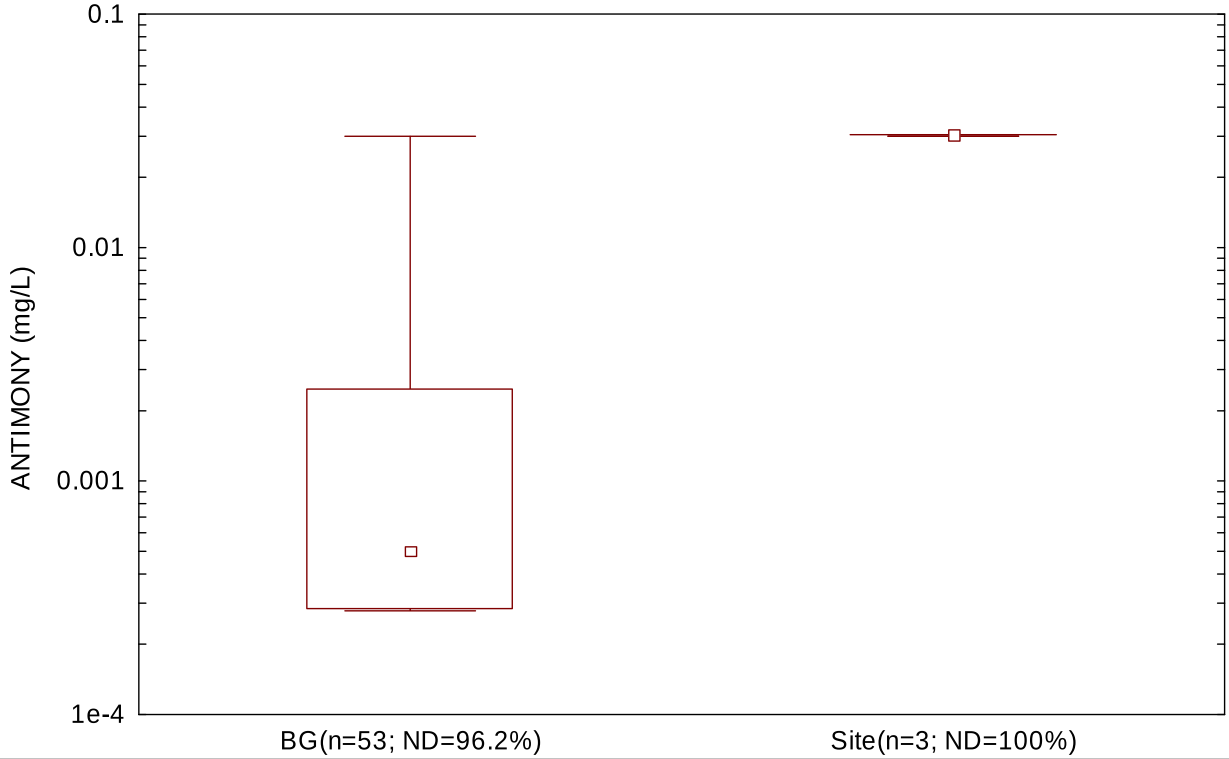


Figure 4. Box Plot Comparison for Arsenic in Groundwater
Parcel 66(7), Ft. McClellan

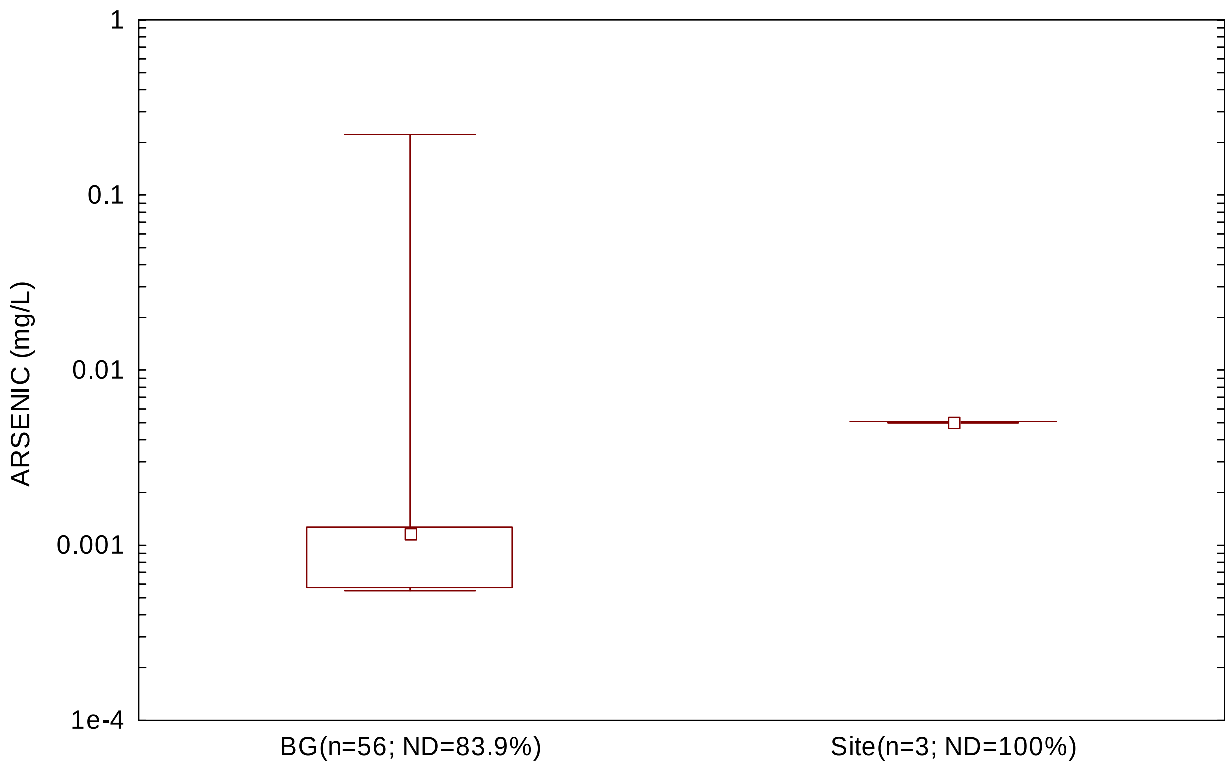


Figure 5. Box Plot Comparison for Barium in Groundwater
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.830)

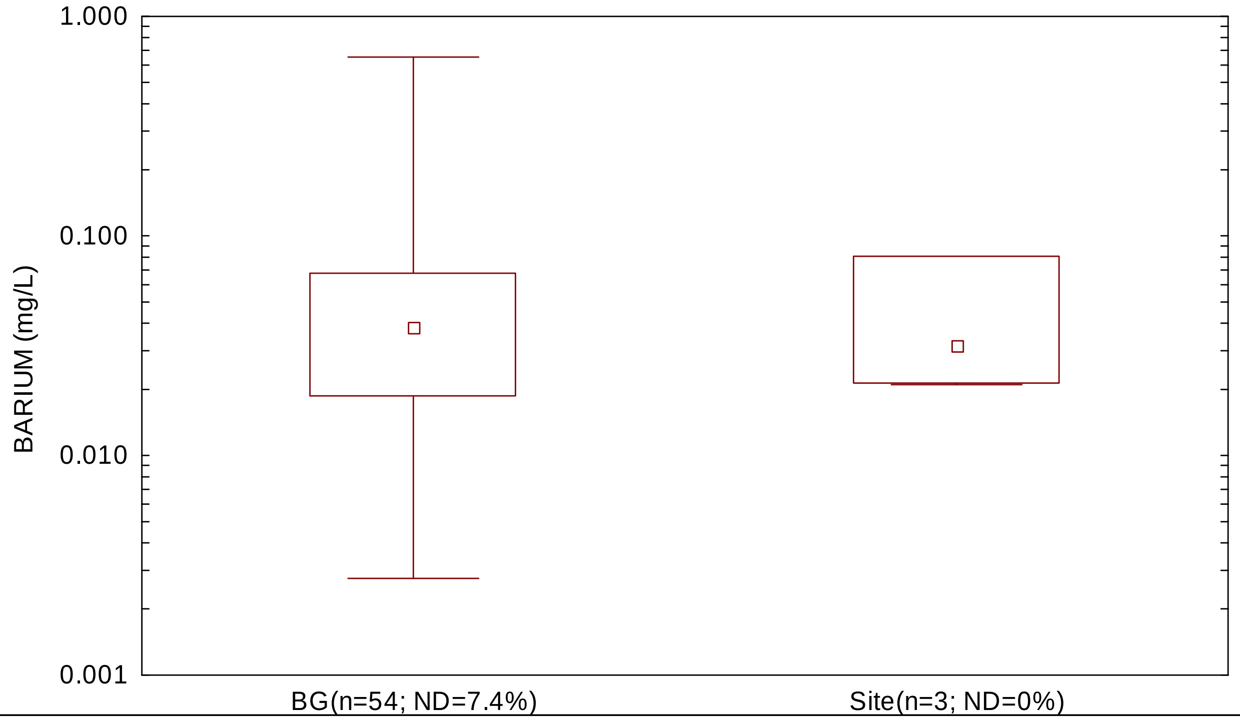


Figure 6. Box Plot Comparison for Beryllium in Groundwater
Parcel 66(7), Ft. McClellan

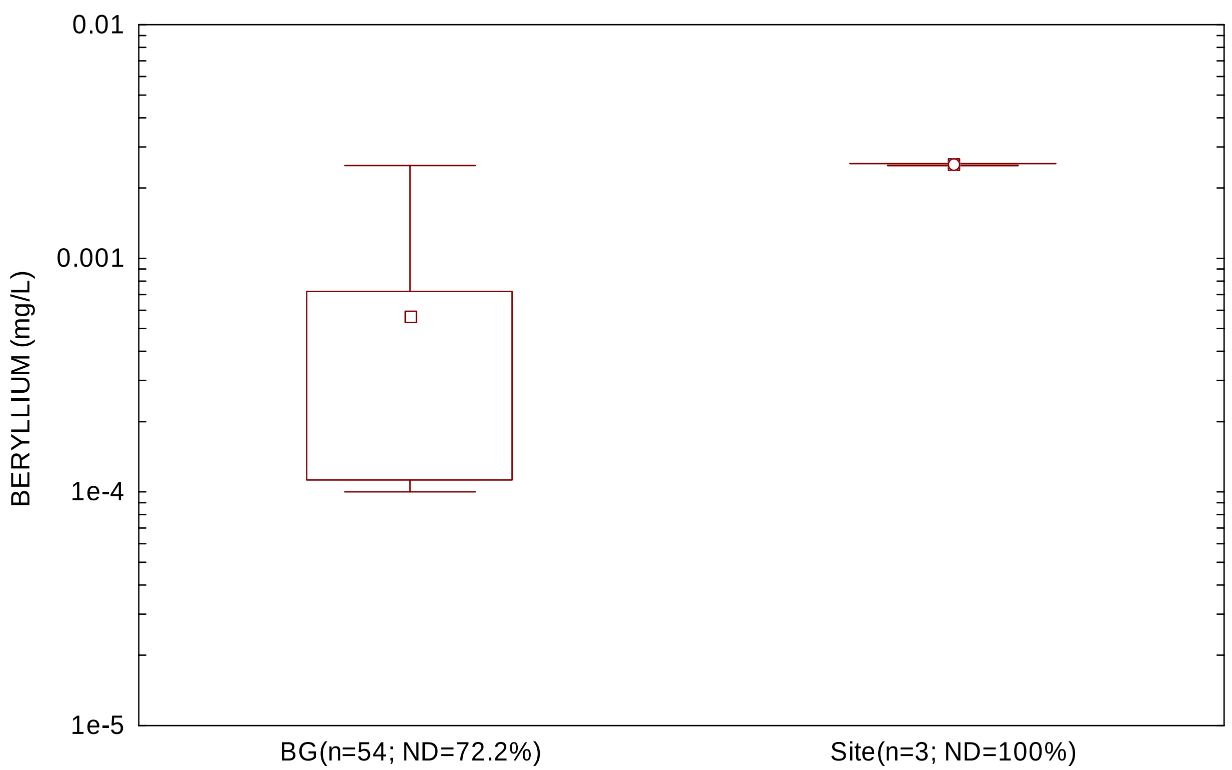


Figure 7. Box Plot Comparison for Cadmium in Groundwater
Parcel 66(7), Ft. McClellan

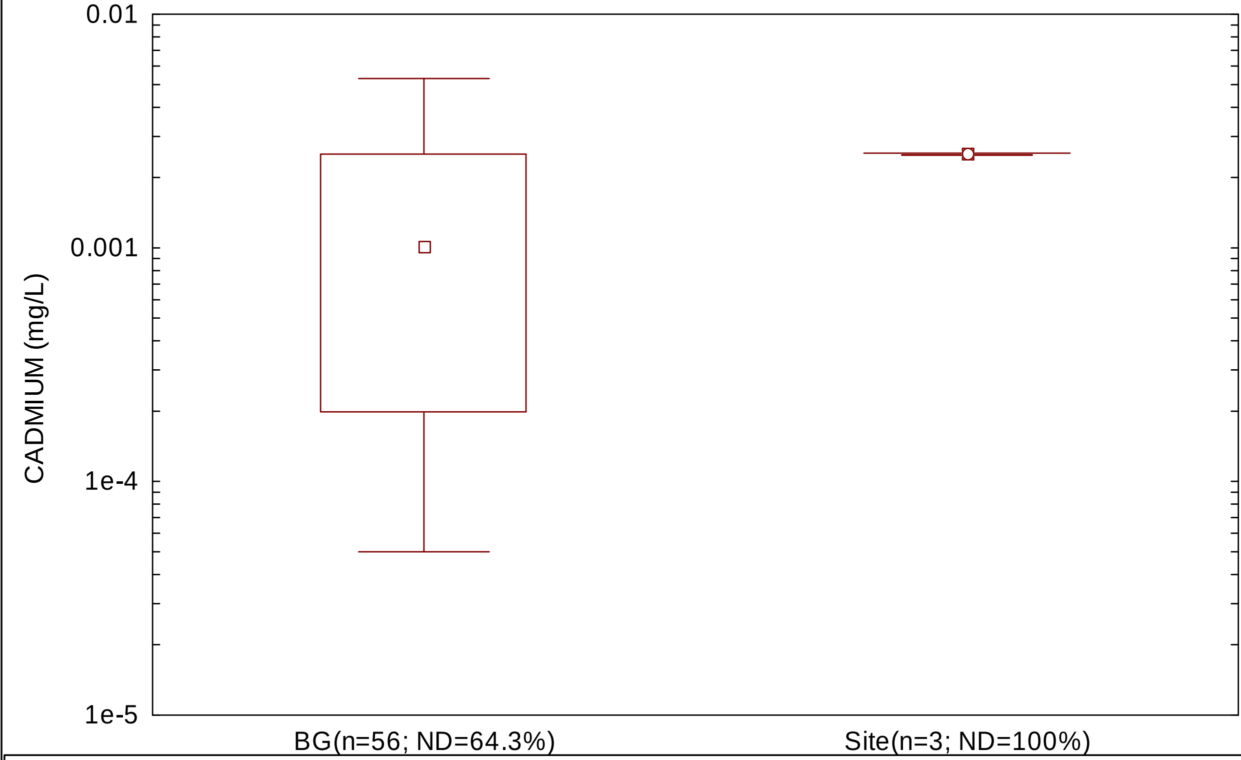
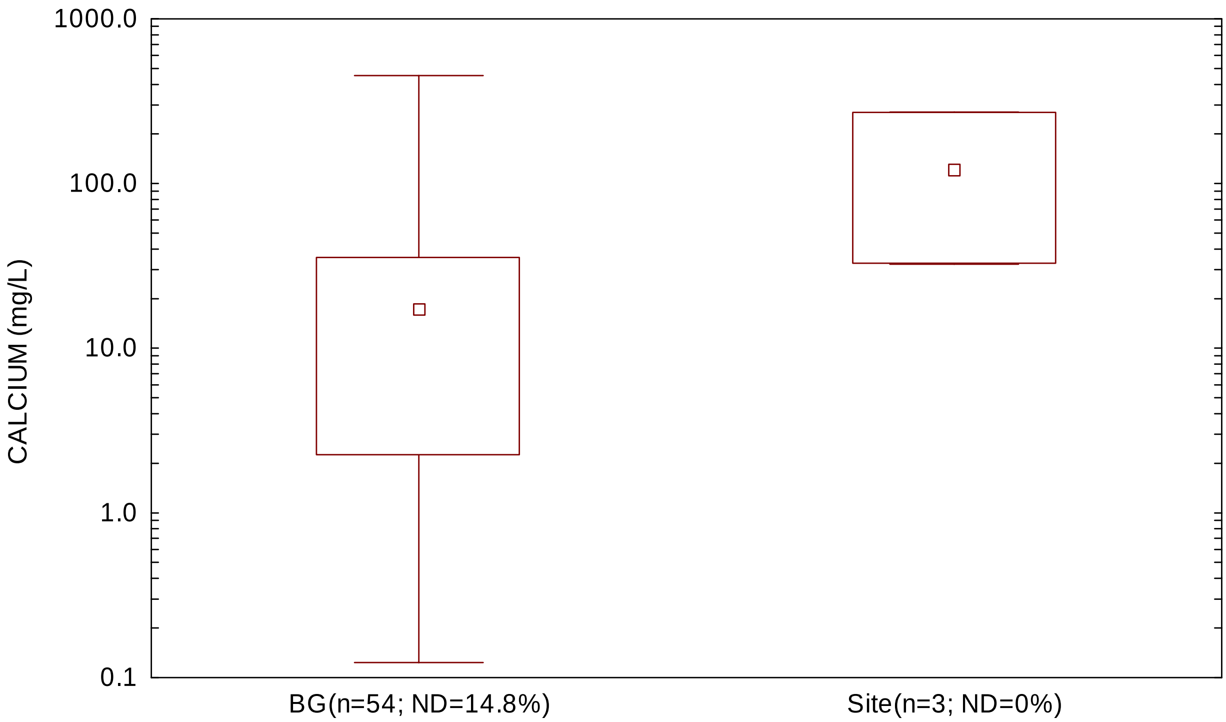


Figure 8. Box Plot Comparison for Calcium in Groundwater
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.024)



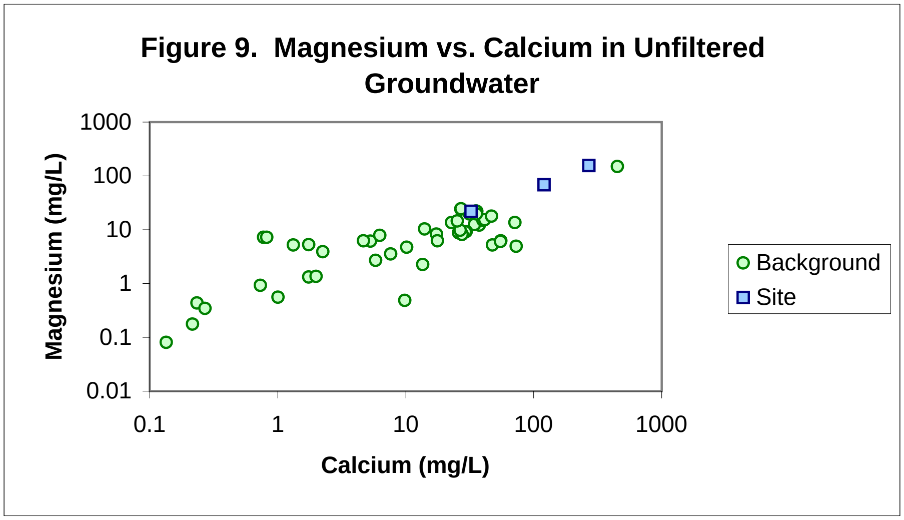


Figure 9. Magnesium vs. Calcium in Unfiltered Groundwater
Magnesium (mg/L)
1000
100
10
1
0.1
0.01
0.1
1
10
100
1000
Calcium (mg/L)
Background
Site

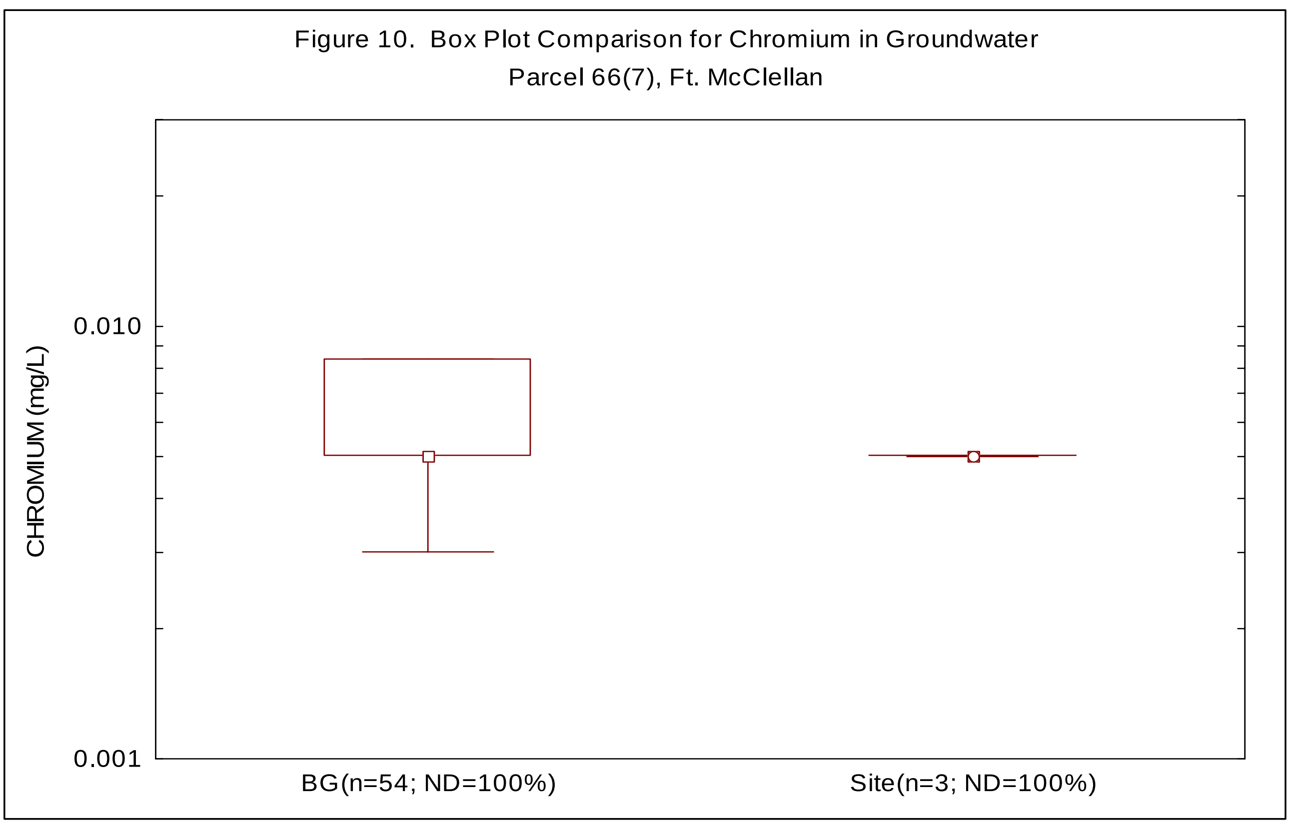


Figure 10. Box Plot Comparison for Chromium in Groundwater
Parcel 66(7), Ft. McClellan
CHROMIUM (mg/L)
0.010
0.001
BG(n=54; ND=100%)
Site(n=3; ND=100%)

Figure 11. Box Plot Comparison for Cobalt in Groundwater
Parcel 66(7), Ft. McClellan

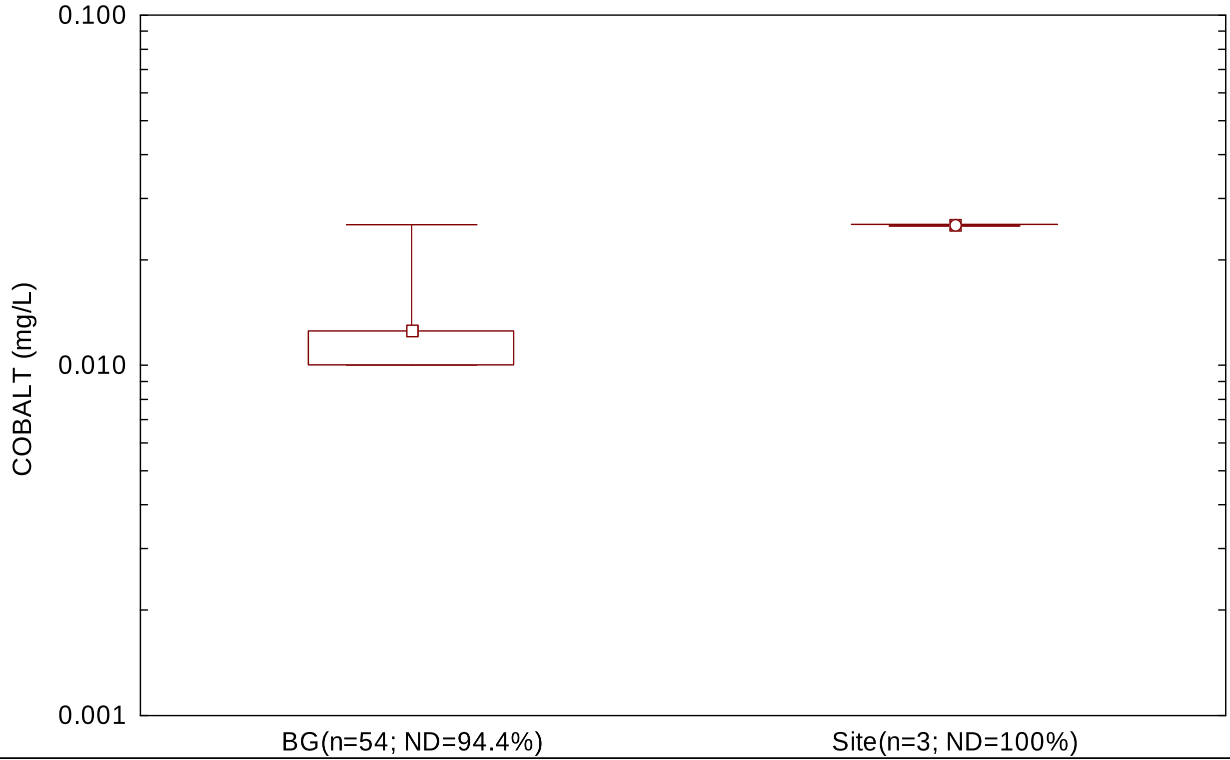


Figure 12. Box Plot Comparison for Copper in Groundwater
Parcel 66(7), Ft. McClellan

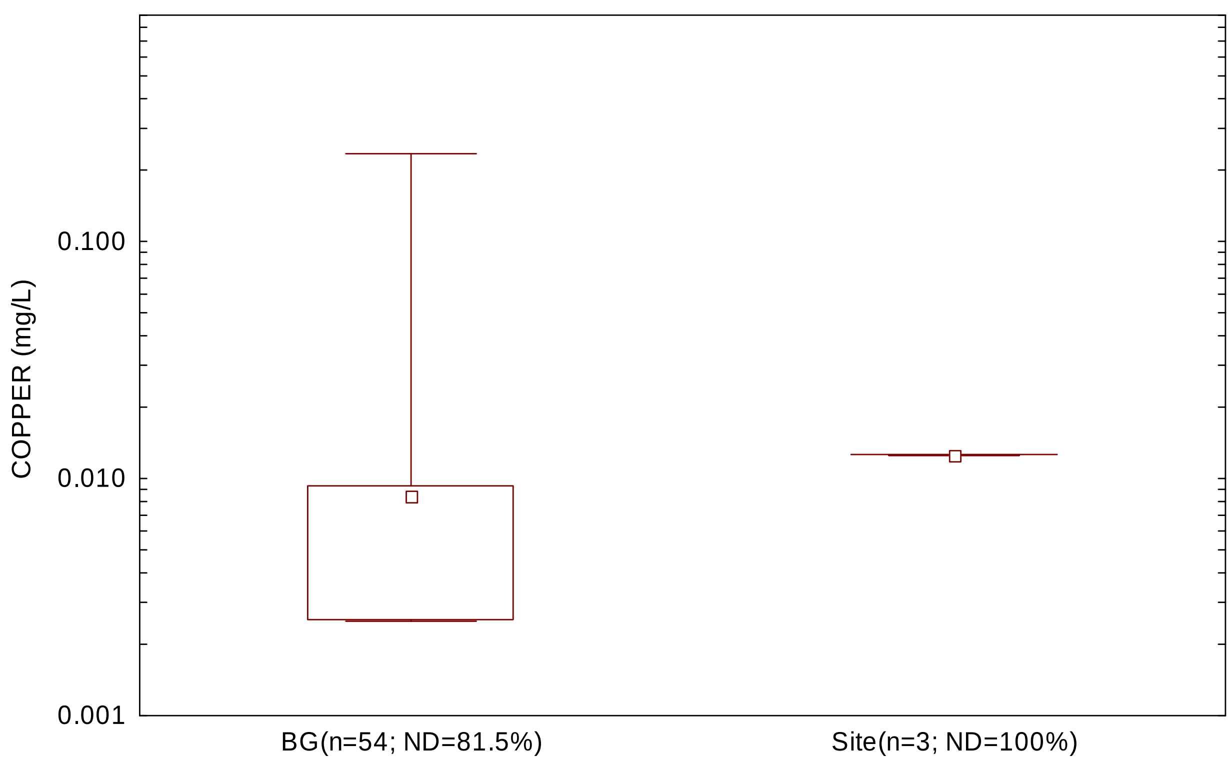


Figure 13. Box Plot Comparison for Iron in Groundwater
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.642)

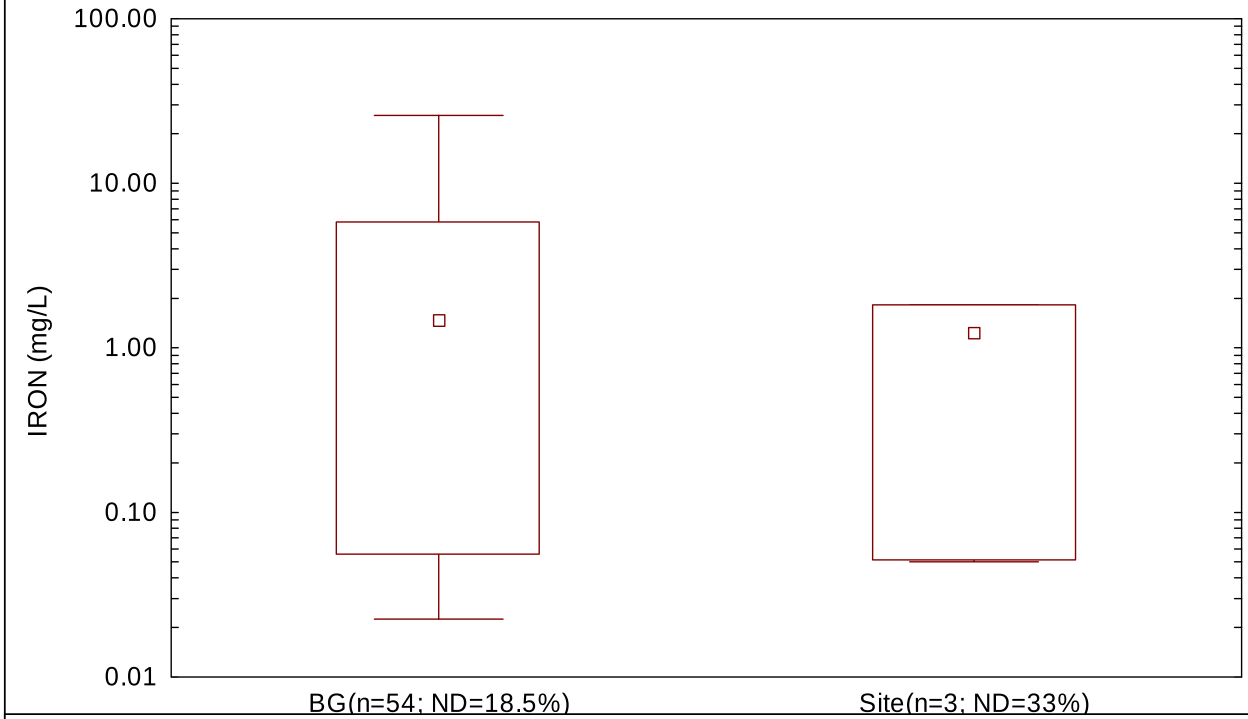


Figure 14. Box Plot Comparison for Lead in Groundwater
Parcel 66(7), Ft. McClellan

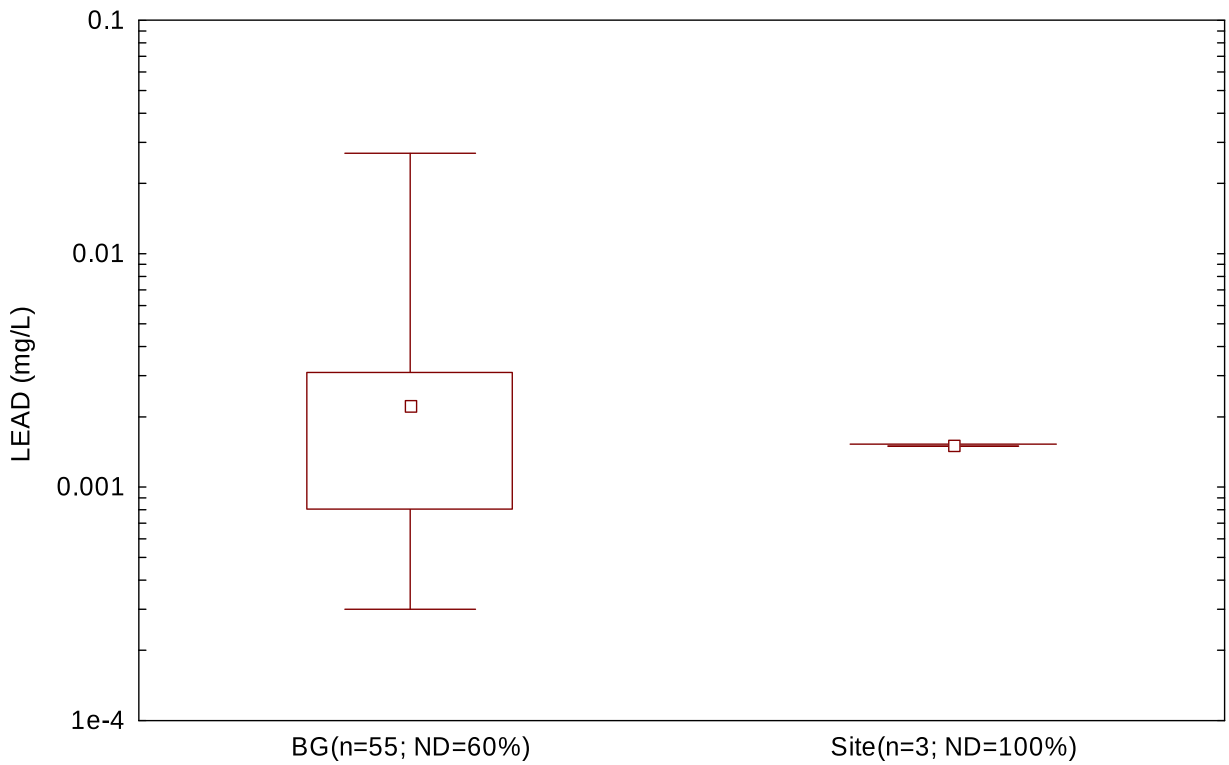


Figure 15. Box Plot Comparison for Magnesium in Groundwater
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.006)

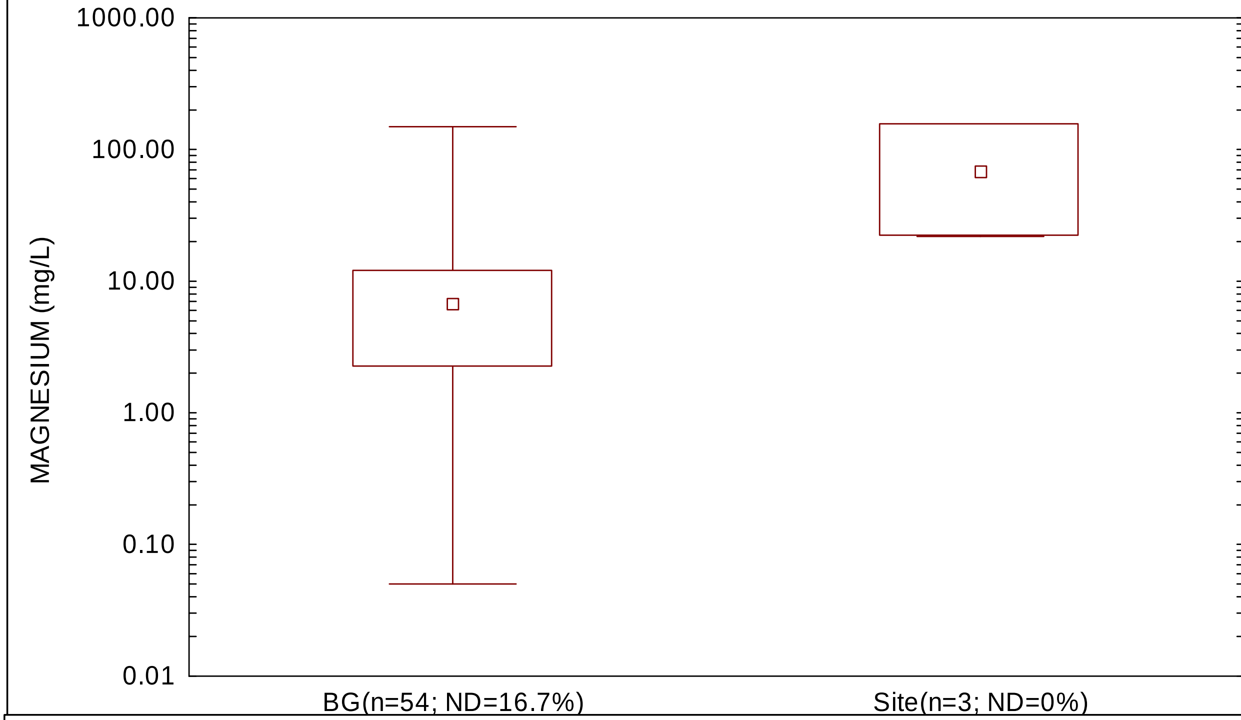


Figure 16. Box Plot Comparison for Manganese in Groundwater
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.186)

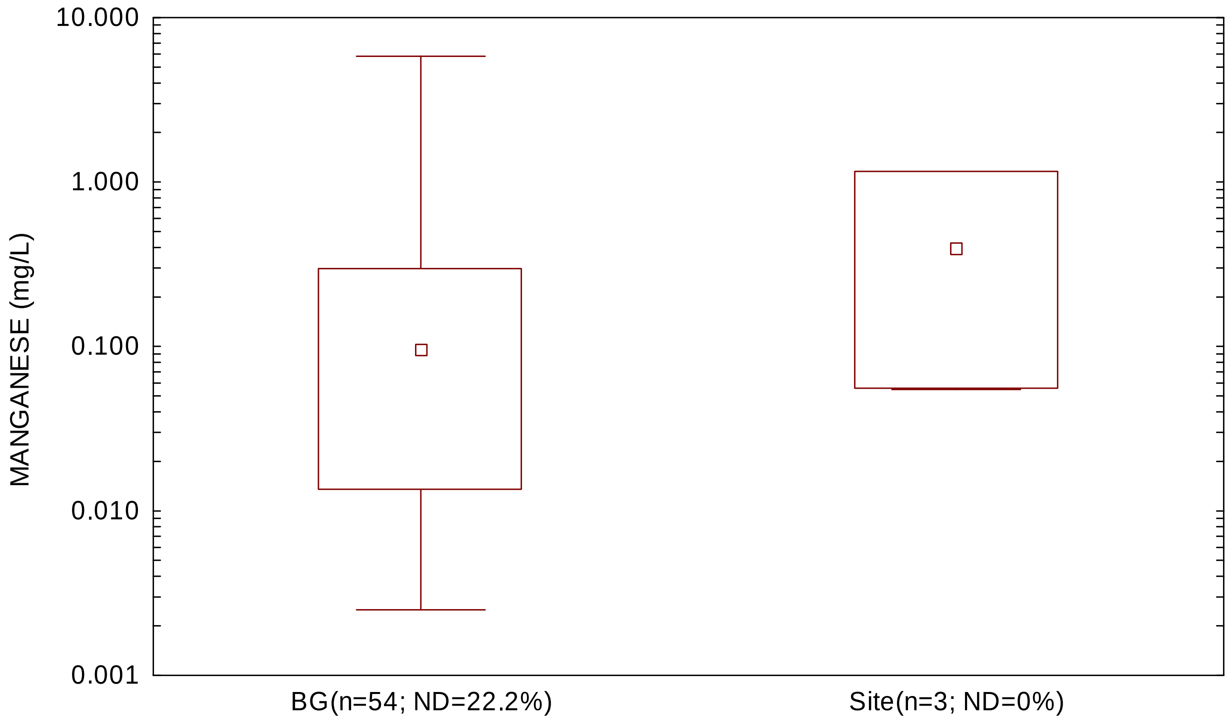


Figure 17. Box Plot Comparison for Mercury in Groundwater
Parcel 66(7), Ft. McClellan

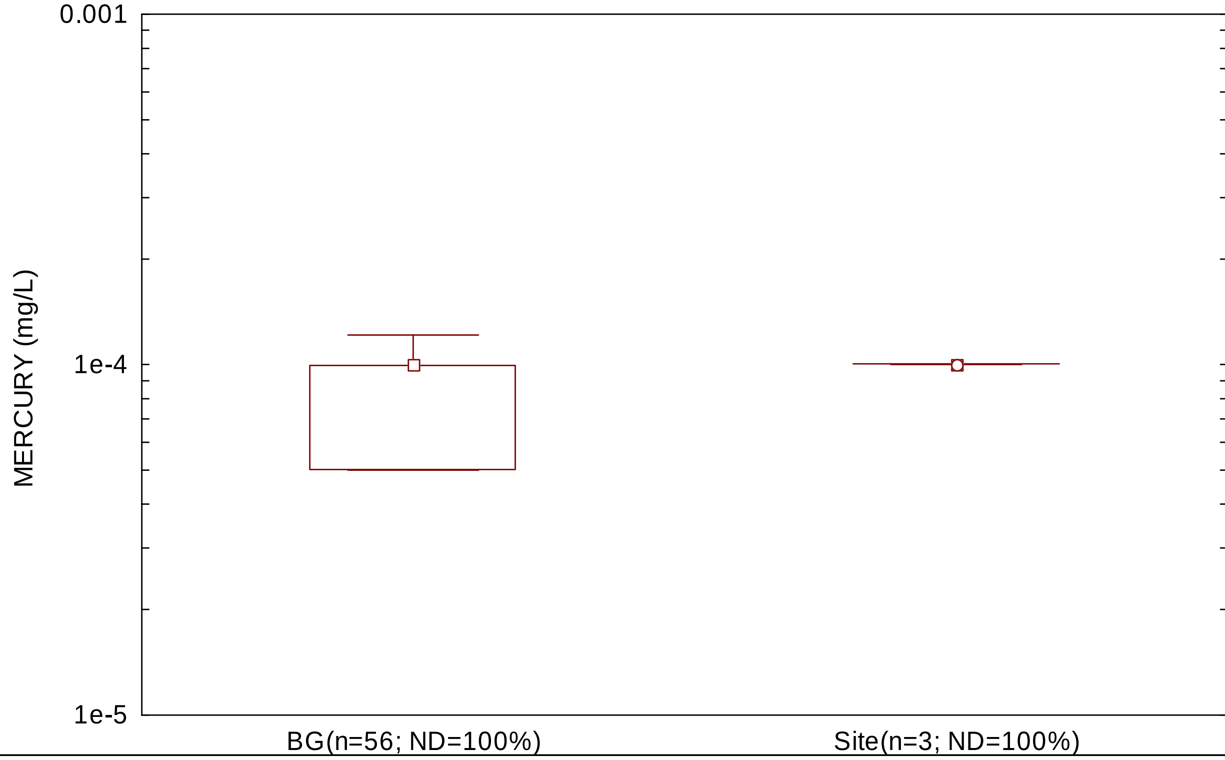


Figure 18. Box Plot Comparison for Nickel in Groundwater
Parcel 66(7), Ft. McClellan

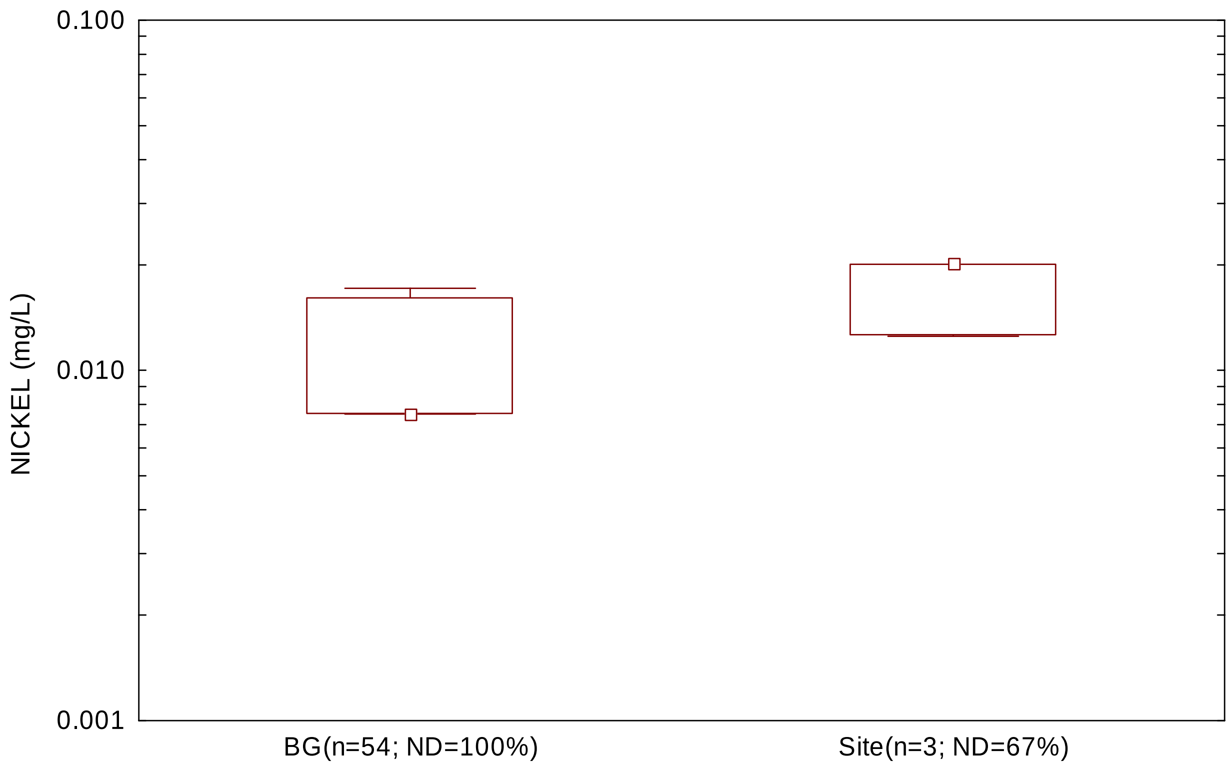


Figure 19. Box Plot Comparison for Potassium in Groundwater
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.068)

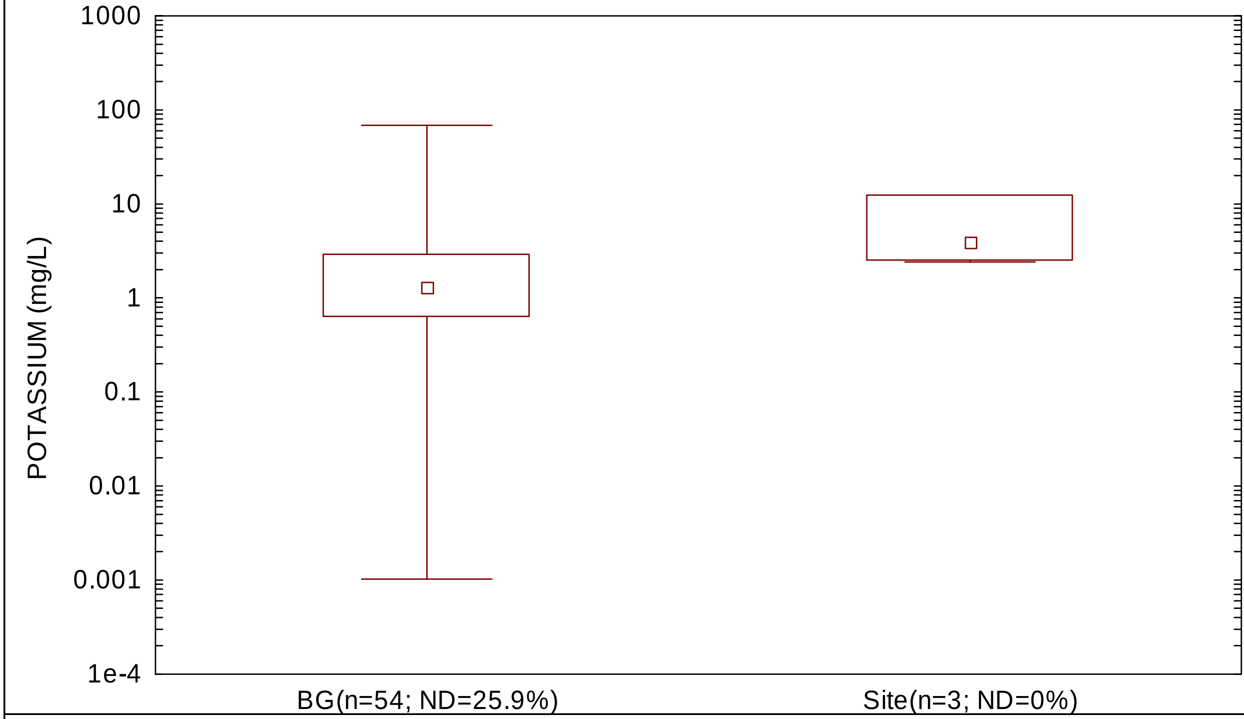


Figure 20. Box Plot Comparison for Selenium in Groundwater
Parcel 66(7), Ft. McClellan

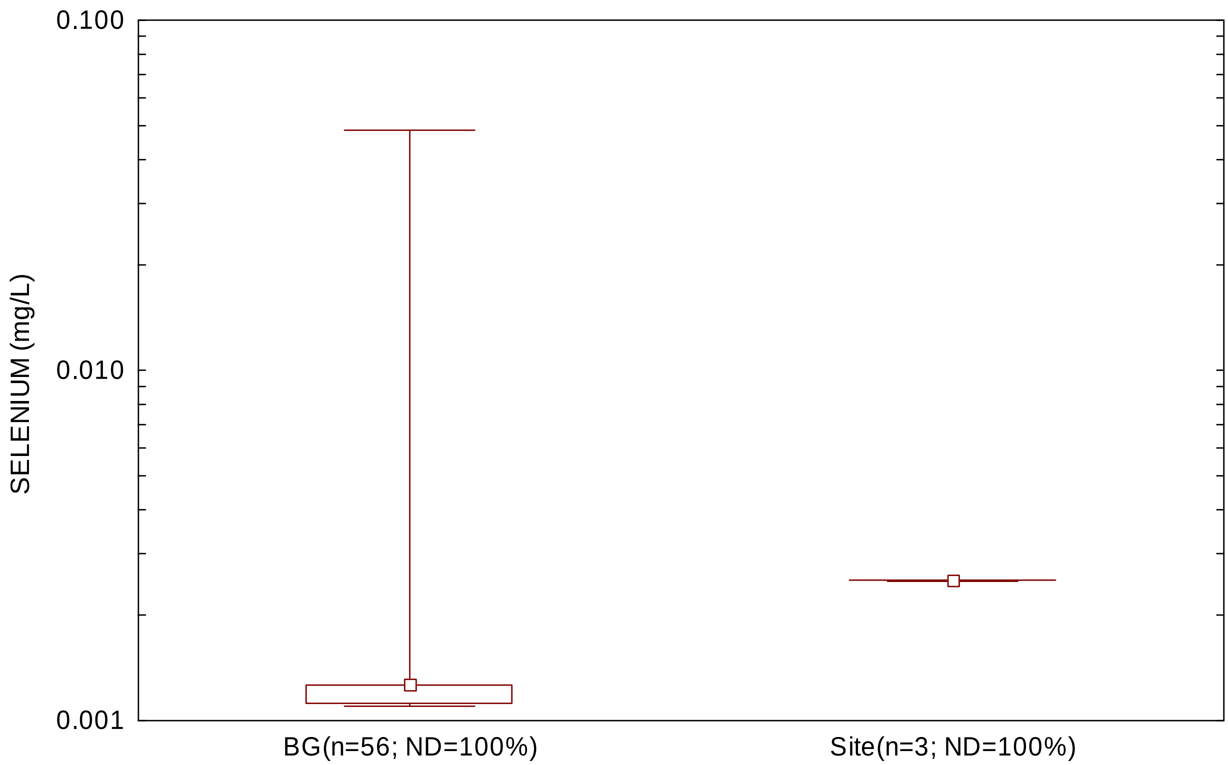
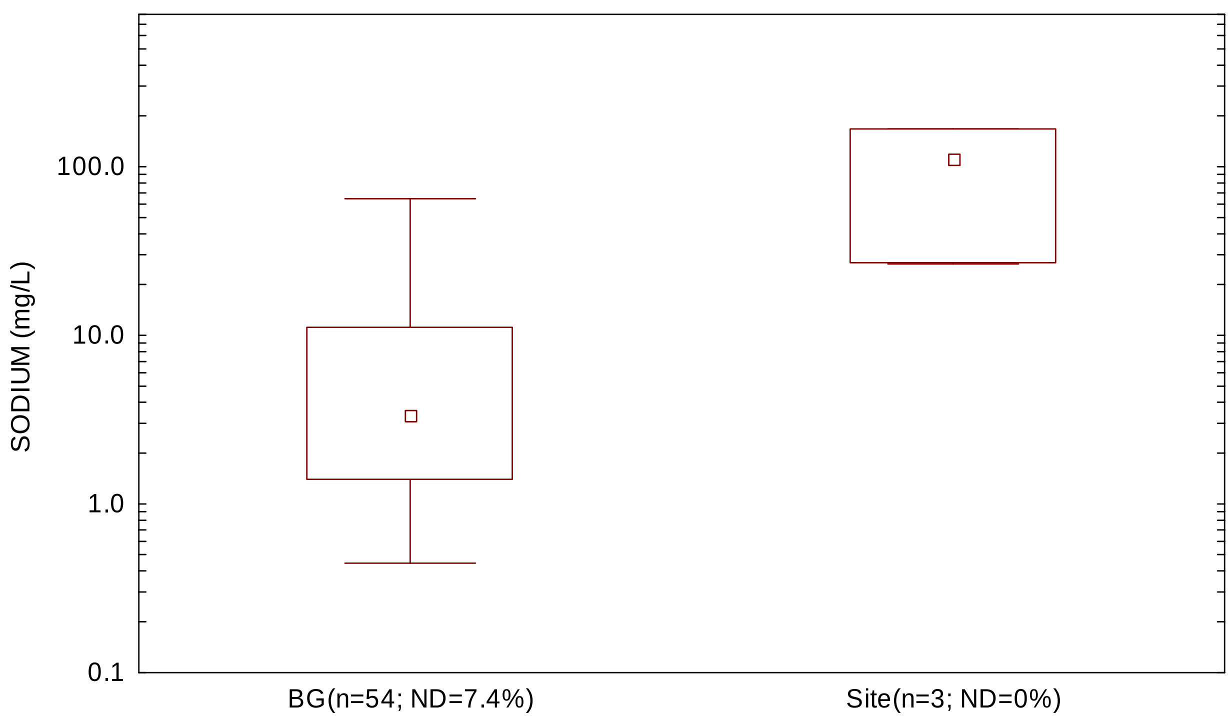


Figure 21. Box Plot Comparison for Silver in Groundwater
Parcel 66(7), Ft. McClellan

Figure 22. Box Plot Comparison for Sodium in Groundwater
Parcel 66(7), Ft. McClellan
(WRS Test p-level = 0.006)



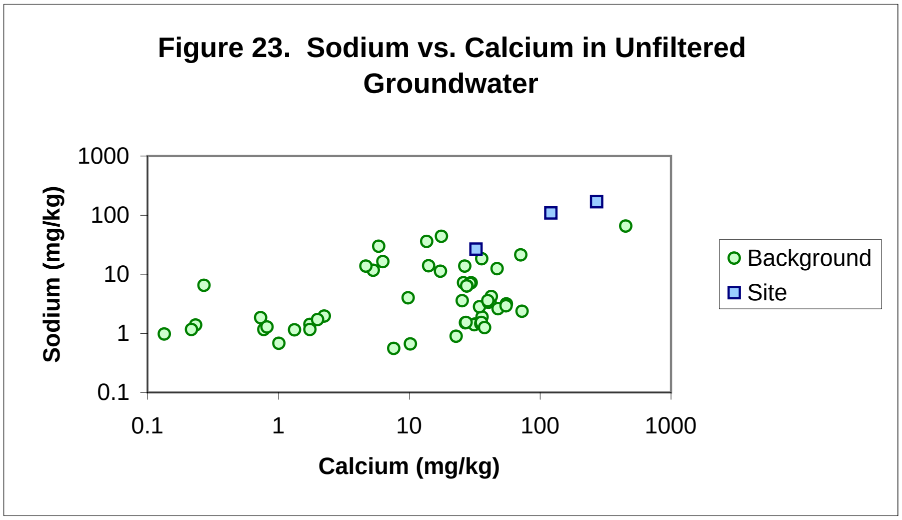


Figure 23. Sodium vs. Calcium in Unfiltered Groundwater
1000
100
10
1
0.1
Sodium (mg/kg)
0.1
1
10
100
1000
Calcium (mg/kg)
Background
Site

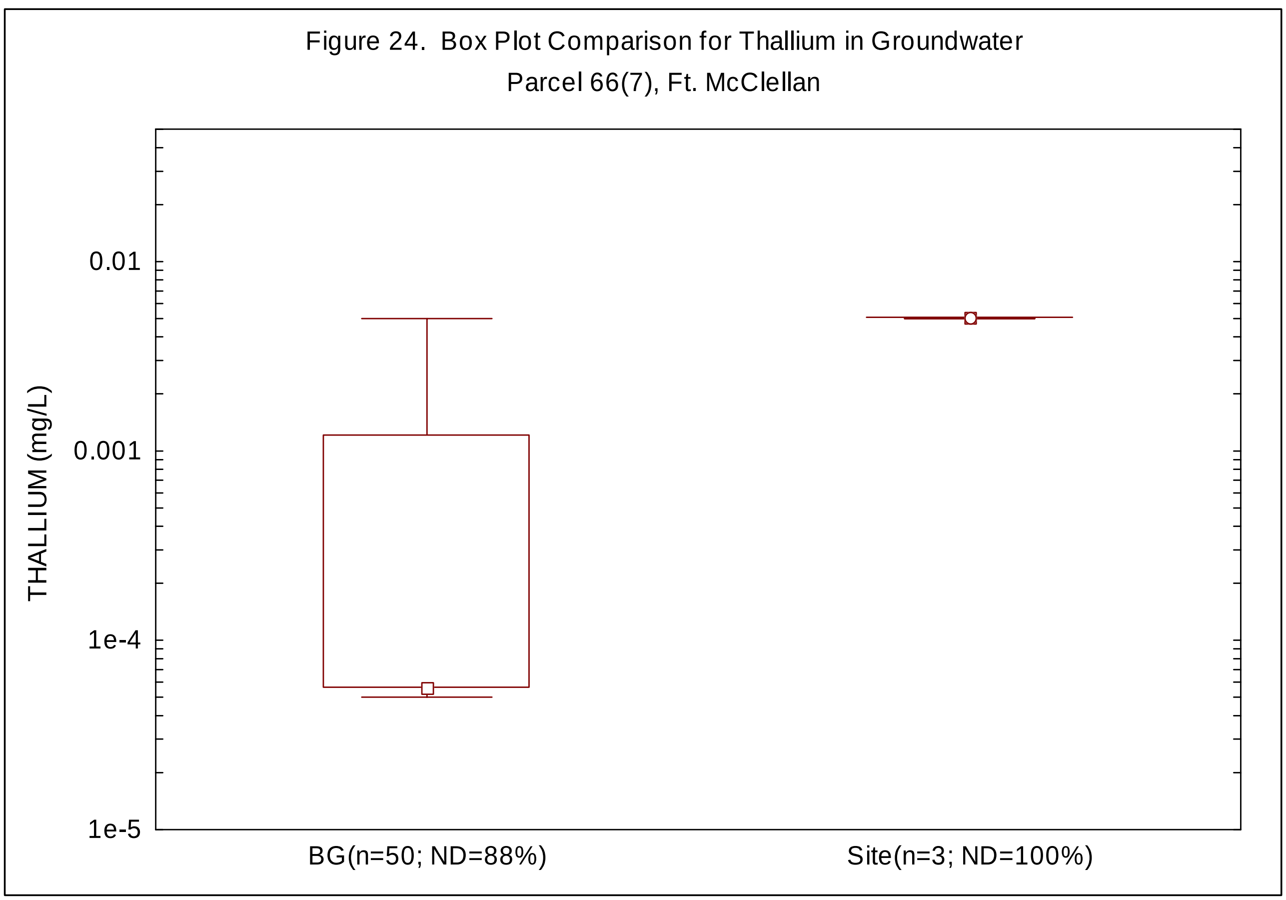


Figure 24. Box Plot Comparison for Thallium in Groundwater
Parcel 66(7), Ft. McClellan
THALLIUM (mg/L)
0.01
0.001
1e-4
1e-5
BG(n=50; ND=88%)
Site(n=3; ND=100%)

Figure 25. Box Plot Comparison for Vanadium in Groundwater
Parcel 66(7), Ft. McClellan

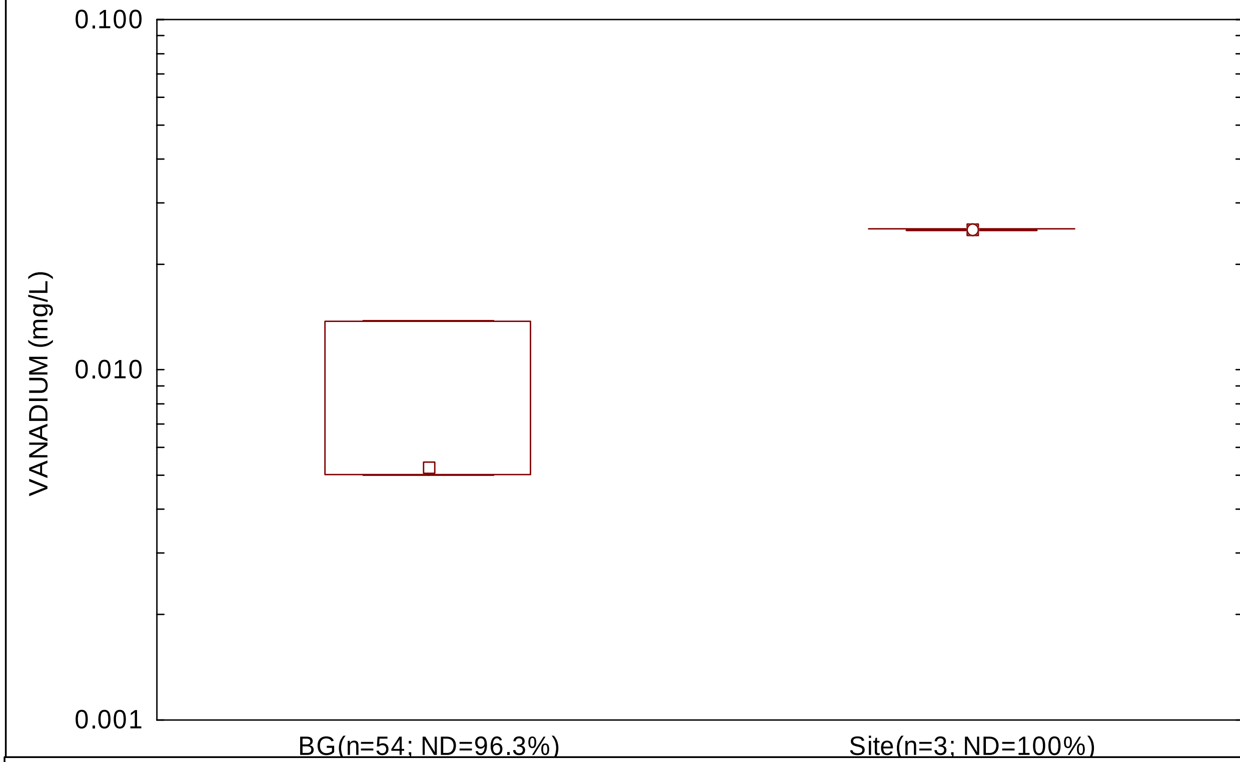


Figure 26. Box Plot Comparison for Zinc in Groundwater
Parcel 66(7), Ft. McClellan