

APPENDIX D

**STATISTICAL AND GEOCHEMICAL EVALUATION
OF SITE METALS DATA**

**STATISTICAL
(TIERS 1 AND 2)**

Statistical Comparison of Site and Background Data Range L – Lima Pond, Parcel 204(7) Fort McClellan, Alabama

1.0 Introduction

This report provides the Tier 1 and Tier 2 (Shaw E&I, 2003) site-to-background comparison results for Range L – Lima Pond, Parcel 204(7), at Fort McClellan in Calhoun County, Alabama. In the first step of the comparison, the maximum detected concentration (MDC) of each element is compared to two times the arithmetic mean of the background data (SAIC, 1998). Any metal that has an MDC greater than the background screening value is carried forward for Tier 2 evaluation, which includes the Slippage Test and the Wilcoxon Rank Sum Test (WRS). If either or both of these statistical tests cannot be done, the evaluation will include the Hot Measurement Test.

The methodology and results of the Tier 1 and Tier 2 comparisons are summarized in Tables 1 through 3, and described in more detail in the following sections. Site samples used in the site-to-background comparison include 7 groundwater samples, 6 sediment, and 6 surface water samples that were collected at the site.

Background distributions and screening values have been established for target analyte list metals in groundwater, sediment, and surface water for Fort McClellan (SAIC, 1998).

2.0 Comparison Methodology

This section describes the statistical techniques that were employed in the Range L, Parcel 204(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 several simultaneous tests is recommended for a valid and complete comparison of site

Table 1

Summary of Tier 1 and Tier 2 Site to Background Comparison for Groundwater
Range L, Parcel 204(7)
Fort McClellan, Calhoun County, Alabama

Metals	Frequency of Detection	Tier 1 Evaluation ^a	Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	6 / 7	Passed	NA	NA	NA	
Antimony	0 / 7	NA	NA	NA	NA	
Arsenic	0 / 7	NA	NA	NA	NA	
Barium	7 / 7	Passed	NA	NA	NA	
Beryllium	0 / 7	NA	NA	NA	NA	
Cadmium	0 / 7	NA	NA	NA	NA	
Calcium	7 / 7	Failed	Passed	Failed	NA	Yes
Chromium	1 / 7	Failed	NA ^d	NA ^e	Failed	Yes
Cobalt	1 / 7	Passed	NA	NA	NA	
Copper	1 / 7	Passed	NA	NA	NA	
Iron	6 / 7	Passed	NA	NA	NA	
Lead	0 / 7	NA	NA	NA	NA	
Magnesium	7 / 7	Passed	NA	NA	NA	
Manganese	2 / 7	Passed	NA	NA	NA	
Mercury	0 / 7	NA	NA	NA	NA	
Nickel	0 / 7	NA	NA	NA	NA	
Potassium	2 / 7	Failed	Passed	NA ^e	Failed	Yes
Selenium	1 / 7	Failed	NA ^d	NA ^e	Passed	
Silver	0 / 7	NA	NA	NA	NA	
Sodium	6 / 7	Passed	NA	NA	NA	
Thallium	0 / 7	NA	NA	NA	NA	
Vanadium	1 / 7	Passed	NA	NA	NA	
Zinc	0 / 7	NA	NA	NA	NA	

NA = not applicable; MDC = maximum detected concentration

a Tier 1 evaluation (site MDC compared to 2 x the background mean) per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or WRS test cannot be performed.

d Slippage test is not performed on data sets for which the maximum background value is a nondetect.

e WRS test is not performed on data sets containing 50% or more nondetects.

Table 2

Summary of Tier 1 and Tier 2 Site to Background Comparison for Sediment
Range L, Parcel 204(7)
Fort McClellan, Calhoun County, Alabama

Metals	Frequency of Detection	Tier 1 Evaluation ^a	Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	6 / 6	Failed	Failed	Failed	NA	Yes
Antimony	0 / 6	NA	NA	NA	NA	
Arsenic	6 / 6	Failed	Passed	Failed	NA	Yes
Barium	6 / 6	Failed	Passed	Failed	NA	Yes
Beryllium	5 / 6	Failed	Passed	Failed	NA	Yes
Cadmium	2 / 6	Failed	Passed	NA ^d	Failed	Yes
Calcium	6 / 6	Passed	NA	NA	NA	
Chromium	6 / 6	Failed	Passed	Failed	NA	Yes
Cobalt	6 / 6	Failed	Failed	Failed	NA	Yes
Copper	6 / 6	Failed	Passed	Failed	NA	Yes
Iron	6 / 6	Failed	Passed	Failed	NA	Yes
Lead	6 / 6	Failed	Passed	Failed	NA	Yes
Magnesium	6 / 6	Passed	NA	NA	NA	
Manganese	6 / 6	Failed	Failed	Failed	NA	Yes
Mercury	6 / 6	Passed	NA	NA	NA	
Nickel	6 / 6	Failed	Failed	Failed	NA	Yes
Potassium	6 / 6	Failed	Passed	Failed	NA	Yes
Selenium	0 / 6	NA	NA	NA	NA	
Silver	0 / 6	NA	NA	NA	NA	
Sodium	6 / 6	Passed	NA	NA	NA	
Thallium	4 / 6	Failed	Failed	Failed	NA	Yes
Vanadium	6 / 6	Failed	Passed	Failed	NA	Yes
Zinc	6 / 6	Failed	Failed	Failed	NA	Yes

NA = not applicable; MDC = maximum detected concentration

a Tier 1 evaluation (site MDC compared to 2 x the background mean) per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or WRS test cannot be performed.

d WRS test is not performed on data sets containing 50% or more nondetects.

Table 3

**Summary of Tier 1 and Tier 2 Site to Background Comparison for Surface Water
Range L, Parcel 204(7)
Fort McClellan, Calhoun County, Alabama**

Metals	Frequency of Detection	Tier 1 Evaluation ^a	Slippage Test ^b	Wilcoxon Rank Sum Test ^b	Hot Measurement Test ^{b,c}	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	6 / 6	Passed	NA	NA	NA	
Antimony	0 / 6	NA	NA	NA	NA	
Arsenic	5 / 6	Failed	Passed	NA ^e	Failed	Yes
Barium	6 / 6	Failed	Passed	Passed	NA	
Beryllium	0 / 6	NA	NA	NA	NA	
Cadmium	0 / 6	NA	NA	NA	NA	
Calcium	6 / 6	Passed	NA	NA	NA	
Chromium	0 / 6	NA	NA	NA	NA	
Cobalt	6 / 6	Failed	NA ^d	NA ^e	Failed	Yes
Copper	4 / 6	Passed	NA	NA	NA	
Iron	6 / 6	Passed	NA	NA	NA	
Lead	6 / 6	Passed	NA	NA	NA	
Magnesium	6 / 6	Passed	NA	NA	NA	
Manganese	6 / 6	Failed	Passed	Failed	NA	Yes
Mercury	0 / 6	NA	NA	NA	NA	
Nickel	6 / 6	Failed	Passed	NA ^e	Passed	
Potassium	0 / 6	NA	NA	NA	NA	
Selenium	0 / 6	NA	NA	NA	NA	
Silver	0 / 6	NA	NA	NA	NA	
Sodium	6 / 6	Passed	NA	NA	NA	
Thallium	0 / 6	NA	NA	NA	NA	
Vanadium	0 / 6	NA	NA	NA	NA	
Zinc	5 / 6	Failed	Passed	NA ^e	Failed	Yes

NA = not applicable; MDC = maximum detected concentration

a Tier 1 evaluation (site MDC compared to 2 x the background mean) per **Selecting Site-Related Chemicals for Human Health and Ecological Risk Assessments for FTMC, Revision 2**, Technical Memorandum, 24 June 2003 by Paul Goetchius.

b Part of Tier 2 evaluation per the above referenced memo.

c Performed only when the Slippage test and/or WRS test cannot be performed.

d Slippage test is not performed on data sets for which the maximum background value is a nondetect.

e WRS test is not performed on data sets containing 50% or more nondetects.

versus background distributions (U.S. Environmental Protection Agency [EPA], 1989, 1992, and 1994; U.S. Navy, 2002).

Analytes that fail the Tier 1 and Tier 2 comparisons are subject to a geochemical evaluation to determine if the elevated concentrations are due to natural processes or if they represent potential contamination.

2.1.1 Tier 1 - In this step of the background screening process, the maximum detected concentration (MDC) of the site data set is compared to the background screening value of two times the background mean (SAIC, 1998). Elements for which the site MDC does not exceed the background screening value are considered to be present at background concentrations, and are not considered site-related chemicals. Elements for which the site MDC exceeds the background screening value undergo further evaluation (Tier 2).

2.1.2 Tier 2 –

Slippage Test – The nonparametric Slippage test is designed to detect a difference between the upper tails of two distributions, and has been recommended for use in site-to-background comparisons to identify potential localized, or hot-spot, contamination (U.S. Navy, 2002). The test is performed by counting the number (K) of detected concentrations in the site data set that exceed the maximum background measurement, and then comparing this number to a critical value (K_c), which is a function of the number of background samples and the number of site samples. If $K > K_c$, then potential contamination is indicated and the analyte will be subjected to geochemical evaluation. If $K \leq K_c$, then localized contamination is not suspected.

Critical values tables for site and background data sets up to size $n = 50$ are provided in U.S. Navy (2002). Critical values for larger data sets are calculated using the test statistic provided in Rosenbaum (1954). In this report, the Slippage test is performed at the 95 percent confidence level. The test cannot be performed if the maximum background value is a nondetect, because the actual concentration in that sample is unknown.

Wilcoxon Rank Sum Test. The nonparametric WRS test is designed to detect a difference between the medians of two data sets, and has been recommended for use in site-to-background comparisons to identify slight but pervasive contamination (EPA, 2000; U.S. Navy, 2002). 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 mid-rank. 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 0.2, then there is a statistically significant difference between the medians at the 80 percent confidence level. A Type I error involves rejecting the null hypothesis when it is true. If the p-level is greater than 0.2, then there is no reasonable justification to reject the null hypothesis at the 80 percent confidence level. It can therefore be concluded that the medians of the two data sets are similar, and it can be assumed to be drawn from the same population.

If the p-level is less than 0.2, then the medians of the two distributions are significantly different at the 80 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 0.2, 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 comparison (EPA, 1989 and 1992). 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 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. Accordingly, the box plots are a necessary adjunct to the WRS test. 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.

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 (95th UTL) 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. To perform the test, each analyte's site MDC is compared to the background 95th UTL 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 threshold value, then hot-spot contamination is not indicated.

2.1.3 Geochemical Evaluation

If an analyte fails the statistical tests described above then a geochemical evaluation is performed to determine if the elevated concentrations are caused by natural processes. The methodology and results of the geochemical evaluation are provided separately.

3.0 Results of the Site-to-Background Comparisons

This section presents the results of the site-to-background comparisons for 23 TAL metals in the Range L, Parcel 204(7) groundwater, sediment, and surface water samples. Tables 1 through 3 summarize the Tier 1 and Tier 2 test results for each media as discussed in the following sections. Slippage test results and WRS test results are discussed in detail below. The corresponding box plots are also discussed below and are provided in Attachment 1.

3.1 Groundwater

This section presents the results of the site-to-background comparisons for 23 metals in unfiltered groundwater samples.

Ten metals (antimony, arsenic, beryllium, cadmium, lead, mercury, nickel, silver, thallium, and zinc) had no detected results in the site samples and are not considered any further. Nine metals had no detected concentrations, passing the Tier 1 evaluation. These metals (aluminum, barium, cobalt, copper, iron, magnesium, manganese, sodium, and vanadium) are considered to be within the range of background and will not be included in any further evaluation or discussion.

The remaining four metals are carried forward for Tier 2 evaluation. The results of these comparisons are discussed in detail below and summarized in Table 1. Box plots are provided in Attachment 1.

Calcium

Tier 1 Evaluation

One detected concentration in the site samples exceeds the background screening value of 56.49 mg/L.

Tier 2 Evaluation

Slippage Test

The critical value, K_c , for calcium is 2, and no site samples exceed the maximum background measurement ($K=0$). Because $K < K_c$, calcium passes the Slippage test.

WRS Test

The p-level of 0.052 indicates a weak agreement between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than the corresponding values in background (Figure 1-1). The site maximum is less than that of background.

Conclusion

Because calcium in groundwater failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Chromium

Tier 1 Evaluation

There is no background screening value for chromium. One site sample had a detected result.

Tier 2 Evaluation

Slippage Test

The maximum value for chromium is a nondetect, so the Slippage test was not performed.

WRS Test

The WRS test was not performed because the site and background data sets contain more than 50 percent nondetects.

Box Plot

The site minimum, interquartile range, and maximum exceed the corresponding background values (Figure 1-1). The shapes and locations of the background and site box plots are influenced by the high percentage of nondetects (100 percent and 86 percent, respectively), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC exceeds the background 95th percentile of 0.0168 mg/L.

Conclusion

Because chromium in groundwater failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Potassium

Tier 1 Evaluation

One detected result exceeds the background screening value of 7.195 mg/L.

Tier 2 Evaluation

Slippage Test

K_c for potassium is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, potassium passes the Slippage test.

WRS Test

The WRS test was not performed because the site data set has more than 50 percent nondetects.

Box Plot

The site minimum, 25th percentile, and median are higher compared to the corresponding background values (Figure 1-2). The site 75th percentile and maximum fall below the respective background values. The shape and location of the site box plot are influenced by the high percentage of nondetects (71 percent), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC of potassium exceeds the background 95th percentile of 16 mg/L.

Conclusion

Because potassium in groundwater failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Selenium

Tier 1 Evaluation

No background screening value is available for selenium. One site sample has a detected result.

Tier 2 Evaluation

Slippage Test

The Slippage test was not performed because the maximum value in the background samples is a nondetect.

WRS Test

The WRS test was not performed because the site and background data sets have more than 50 percent nondetects.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-2). The site maximum is much less than the background maximum value. The shapes and locations of the background and site box plots are influenced by the high percentage of nondetects (100 percent and 86 percent, respectively), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC is less than the background 95th percentile of 0.0971 mg/L.

Conclusion

Selenium is considered to be within the range of background, based on the Tier 2 evaluation.

3.4 Sediment

This section presents the results of the site-to-background comparisons for 23 TAL metals for Range L sediment samples. Three metals, antimony, selenium, and silver, had no detected concentrations in sediment. No further discussion of these elements is included.

Four metals, calcium, magnesium, mercury, and sodium, had no site samples exceeding their respective background screening value. Because they passed the Tier 1 evaluation these metals are considered to be within the range of background and are not included in further testing and discussions.

The remaining sixteen metals were carried forward for Tier 2 evaluation and are discussed in detail below. Box plots are provided in Attachment 1.

Table 2 summarizes the Tier 1 and Tier 2 results for sediment.

Aluminum

Tier 1 Evaluation

Six site samples exceed the background screening value of 8,593 mg/kg.

Tier 2 Evaluation

Slippage Test

The critical value, K_c , for aluminum is 2, and four site samples exceed the maximum background measurement. Because $K > K_c$, aluminum fails the Slippage test.

WRS Test

The WRS test p-level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

Box plots for the site and background data sets are provided in Figure 1-3. The site minimum, interquartile range, and maximum are higher than the corresponding background values.

Conclusion

Because aluminum in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Arsenic

Tier 1 Evaluation

Four site samples exceed the background screening value of 11.33 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for arsenic is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, arsenic passes the Slippage test.

WRS Test

The WRS test p-level of 0.00346 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-3). The site maximum is slightly lower than that of background.

Conclusion

Because arsenic in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Barium

Tier 1 Evaluation

Two site samples exceed the background screening value of 98.91 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for barium is 2, and one site sample exceeds the maximum background measurement. Because $K < K_c$, barium passes the Slippage test.

WRS Test

The p-level of 0.024 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-4).

Conclusion

Because barium in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Beryllium

Tier 1 Evaluation

Four site samples exceed the background screening value of 0.97 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for beryllium is 2, and 2 site samples exceed the maximum background measurement. Because $K \leq K_c$, beryllium passes the Slippage test.

WRS Test

The p-level of 0.00138 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, interquartile range, and the maximum are higher than the corresponding background values (Figure 1-4).

Conclusion

Because beryllium in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Cadmium

Tier 1 Evaluation

Two site samples exceed the background screening value of 0.43 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for cadmium is 2, and 2 site samples exceed the maximum background measurement. Because $K \leq K_c$, cadmium passes the Slippage test.

WRS Test

No WRS test was performed because the site data set contains more than 50 percent nondetects.

Box Plot

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-5). The shape and location of the site box plot are influenced by the high percentage of nondetects (67 percent) and the replacement values of one-half the reporting limit rather than detected concentrations.

Hot Measurement Test

The site MDC exceeds the background 95th percentile of 0.787 mg/kg.

Conclusion

Because cadmium in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Chromium

Tier 1 Evaluation

One site sample exceeds the background screening value of 31.15 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for chromium is 2. No site samples exceed the maximum background measurement. Because $K < K_c$, chromium passes the Slippage test.

WRS Test

The p-level of 0.025 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher with respect to the corresponding background values (Figure 1-5). The site maximum is less than that of background.

Conclusion

Because chromium in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Cobalt

Tier 1 Evaluation

Six site samples exceed the background screening value of 11.01 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for cobalt is 2, and 6 site samples exceed the maximum background measurement. Because $K > K_c$, cobalt fails the Slippage test.

WRS Test

The p -level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-6).

Conclusion

Because cobalt in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Copper

Tier 1 Evaluation

All 6 site samples exceed the background screening value of 17.12 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for copper is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, copper passes the Slippage test.

WRS Test

The p -level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher as compared to the corresponding background values (Figure 1-6). The site maximum is less than that of background.

Conclusion

Because copper in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Iron

Tier 1 Evaluation

Four of the site samples exceed the background screening value of 35,267 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for iron is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, iron passes the Slippage test.

WRS Test

The p-level of 0.0053 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-7). The site maximum is less than that of background.

Conclusion

Because iron in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Lead

Tier 1 Evaluation

Four site samples exceed the background screening value of 37.82 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for lead is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, lead passes the Slippage test.

WRS Test

The p-level of 0.0018 indicates a good agreement between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-7). The site maximum is less than that of background.

Conclusion

Because lead in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Manganese

Tier 1 Evaluation

Five site samples exceed the background screening value of 712.31 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for manganese is 2, and 3 site samples exceed the maximum background measurement. Because $K > K_c$, manganese fails the Slippage test.

WRS Test

The p -level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, interquartile range, and the maximum are higher than the respective background values (Figure 1-8).

Conclusion

Because manganese in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Nickel

Tier 1 Evaluation

All six of the site samples exceed the background screening value of 13.02 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for nickel is 2, and 6 site samples exceed the maximum background measurement. Because $K > K_c$, nickel fails the Slippage test.

WRS Test

The p -level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-8).

Conclusion

Because nickel in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Potassium

Tier 1 Evaluation

Five of the site samples exceed the background screening value of 1,013.48 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for potassium is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, potassium passes the Slippage test.

WRS Test

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

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-9). The site maximum is less than that of background.

Conclusion

Because potassium in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Thallium

Tier 1 Evaluation

Four of the site samples exceed the background screening value of 0.13 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for thallium is 2, and 4 site samples exceed the maximum background measurement. Because $K > K_c$, thallium fails the Slippage test.

WRS Test

The p-level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-9).

Conclusion

Because thallium in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Vanadium

Tier 1 Evaluation

Four site samples exceed the background screening value of 40.87 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for vanadium is 2, and one site sample exceeds the maximum background measurement. Because $K < K_c$, vanadium passes the Slippage test.

WRS Test

The p-level < 0.001 indicates a significant difference between the site and background distributions.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-10). The site maximum is just slightly elevated as compared to that of background.

Conclusion

Because vanadium in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Zinc

Tier 1 Evaluation

Six site samples exceed the background screening value of 52.74 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for zinc is 2, and 4 site samples exceed the maximum background measurement. Because $K > K_c$, zinc fails the Slippage test.

WRS Test

The p-level < 0.001 indicates strong agreement between the site and background distributions.

Box Plot

The site minimum, interquartile range, and maximum are higher than the respective background values (Figure 1-10).

Conclusion

Because zinc in sediment failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

3.5 Surface Water

This section presents the results of the site-to-background comparisons for the 23 metals tested in surface water samples at Range L, Parcel 204(7). Ten metals (antimony, beryllium, cadmium, chromium, mercury, potassium, selenium, silver, thallium, and vanadium) had no detected concentrations in the site samples and are not discussed any further.

Seven metals (aluminum, calcium, copper, iron, lead, magnesium, and sodium) had no detected concentrations exceeding their respective background screening values. These metals are considered to be within the range of background based on the Tier 1 evaluation, and will not be tested or discussed further.

The remaining six metals (arsenic, barium, cobalt, manganese, nickel, and zinc) were carried forward for Tier 2 evaluation. The results of these tests are discussed in detail below. Box plots are provided in Attachment 1.

Table 3 summarizes the Tier 1 and Tier 2 results for surface water.

Arsenic

Tier 1 Evaluation

Five site samples exceed the background screening value of 0.00217 mg/L.

Tier 2 Evaluation

Slippage Test

The critical value, K_c , for arsenic is 2. No site samples exceed the maximum background measurement ($K = 0$). Because $K < K_c$, arsenic passes the Slippage test.

WRS Test

The WRS test was not performed because the background data set has more than 50 percent nondetects.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-11). The shape and location of the background box plot are influenced by the high percentage of nondetects (86 percent) and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC for arsenic exceeds the background 95th percentile of 0.0034 mg/L.

Conclusion

Because arsenic in surface water failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Barium

Tier 1 Evaluation

One site sample exceeds the background screening value of 0.0754 mg/L.

Tier 2 Evaluation

Slippage Test

K_c for barium is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, barium passes the Slippage test.

WRS Test

The WRS test p-level of 0.83 indicates excellent agreement between the background and site distributions.

Box Plot

The site 25th percentile and maximum are lower compared to that of background (Figure 1-11). The site minimum, median, and 75th percentile are slightly higher than the corresponding background values.

Conclusion

Barium in surface water passes the Tier 2 evaluation and is considered to be within the range of background.

Cobalt

Tier 1 Evaluation

No background screening value is available for cobalt, and all six site samples have detected results.

Tier 2 Evaluation

Slippage Test

The maximum value for cobalt is a nondetect, so the Slippage test was not performed.

WRS Test

The WRS test was not performed because the background data set contains more than 50 percent nondetects.

Box Plot

The site minimum and interquartile range are higher than their respective background values (Figure 1-12). The shape and location of the background box plot are influenced by the high percentage of nondetects (100 percent), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC for cobalt exceeds the background 95th percentile of 0.025 mg/L.

Conclusion

Because cobalt in surface water failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Manganese

Tier 1 Evaluation

All six site samples exceed the background screening value of 0.565 mg/L.

Tier 2 Evaluation

Slippage Test

K_c for manganese is 2, and one site sample exceeds the maximum background measurement. Because $K < K_c$, manganese passes the Slippage test.

WRS Test

The WRS test p-level < 0.001 indicates a significant difference between the background and site distributions.

Box Plot

The site minimum and interquartile range are significantly higher than the corresponding background values (Figure 1-12). The site maximum is just slightly higher compared to the same background value.

Conclusion

Because manganese in surface water failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Nickel

Tier 1 Evaluation

All six site sample exceeds the background screening value of 0.0225 mg/L.

Tier 2 Evaluation

Slippage Test

K_c for nickel is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, nickel passes the Slippage test.

WRS Test

The WRS test was not performed because the background data set contains more than 50 percent nondetects.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-13). The site maximum is less than that of background. The shape and location of the background box plot are influenced by the high percentage of nondetects (95 percent), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC for nickel is less than the background 95th percentile of 0.04 mg/L.

Conclusion

Nickel passed the Tier 2 evaluation and is considered within the range of background.

Zinc

Tier 1 Evaluation

Four site samples exceed the background screening value of 0.04035 mg/L.

Tier 2 Evaluation

Slippage Test

K_c for zinc is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, zinc passes the Slippage test.

WRS Test

The WRS test was not performed because the background data set contains more than 50 percent nondetects.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-13). The site maximum is less than that of background. The shape and location of the background box plot are influenced by the high percentage of nondetects (91 percent), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test

The site MDC for zinc exceeds the background 95th percentile of 0.0456 mg/L.

Conclusion

Because zinc in surface water failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

4.0 Summary and Conclusions

The statistical methodology used to compare samples taken from Range L, Parcel 204(7), and background data sets for 23 elements in groundwater, sediment, and surface water include a comparison of the site MDC to the background screening value, Tier 1 evaluation. Analytes that failed this comparison were subjected to the Slippage test and WRS test. Box-and-whisker plots were prepared to visually compare the two data sets and properly interpret the WRS test results. For elements with data sets that did not allow for either the Slippage test or WRS test to be performed, the Hot Measurement test was used. Analytes that failed these statistical tests, Tier 2 evaluation, are carried forward for Tier 3 geochemical evaluation to determine if natural processes can explain the elevated concentrations.

Tables 1 through 3 summarize the statistical comparison test results and show the metals carried forward for geochemical evaluation.

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ATTACHMENT 1

Figure 1-1

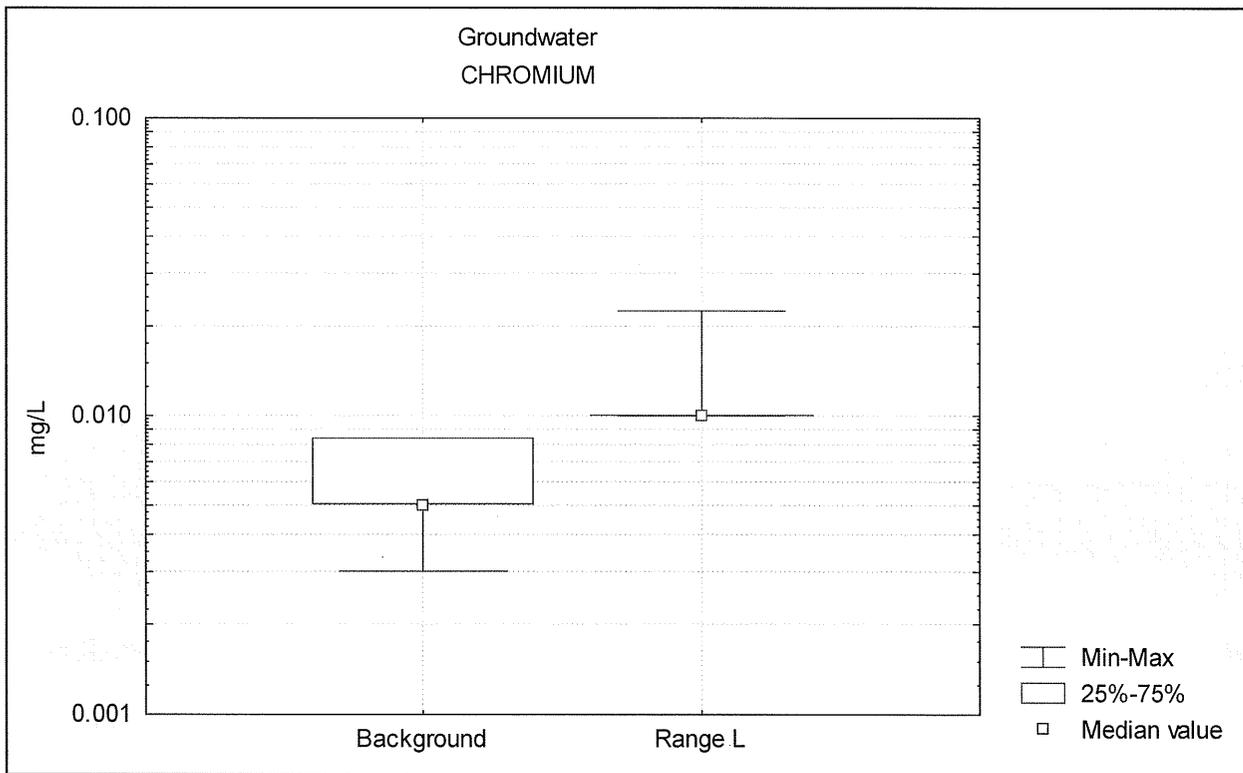
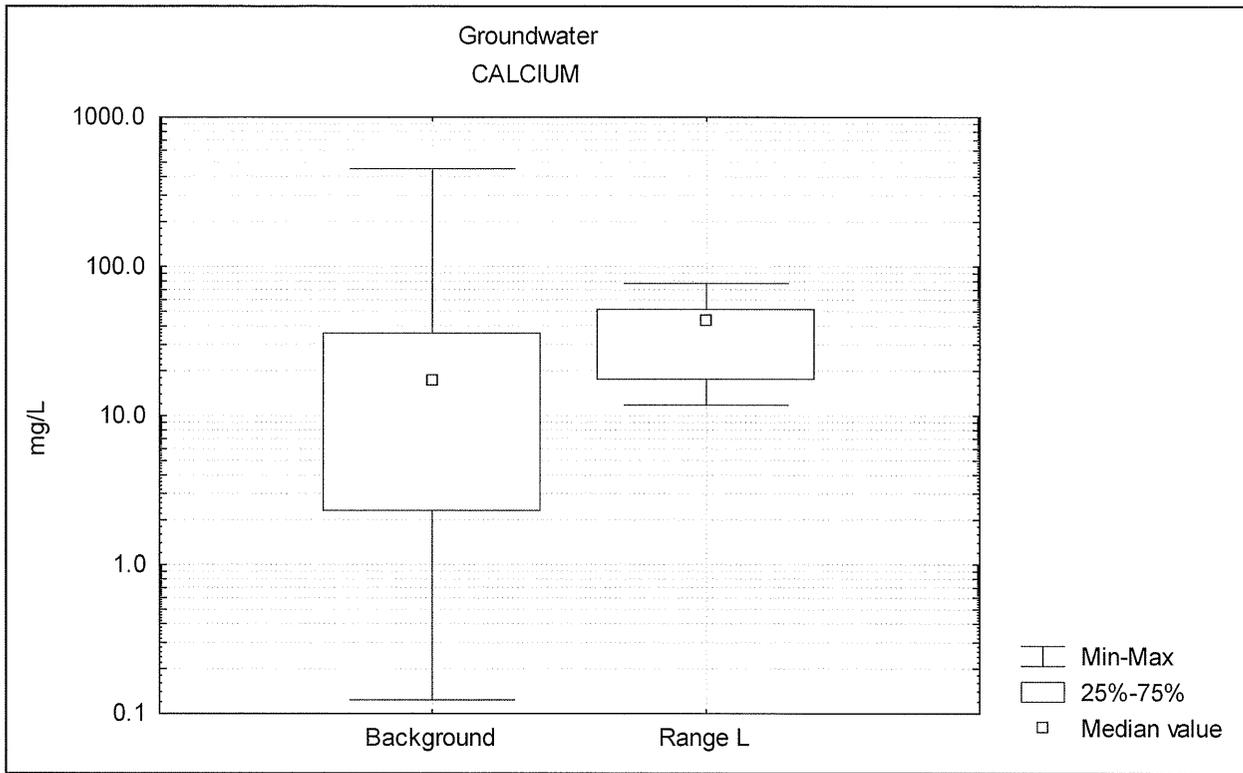


Figure 1-2

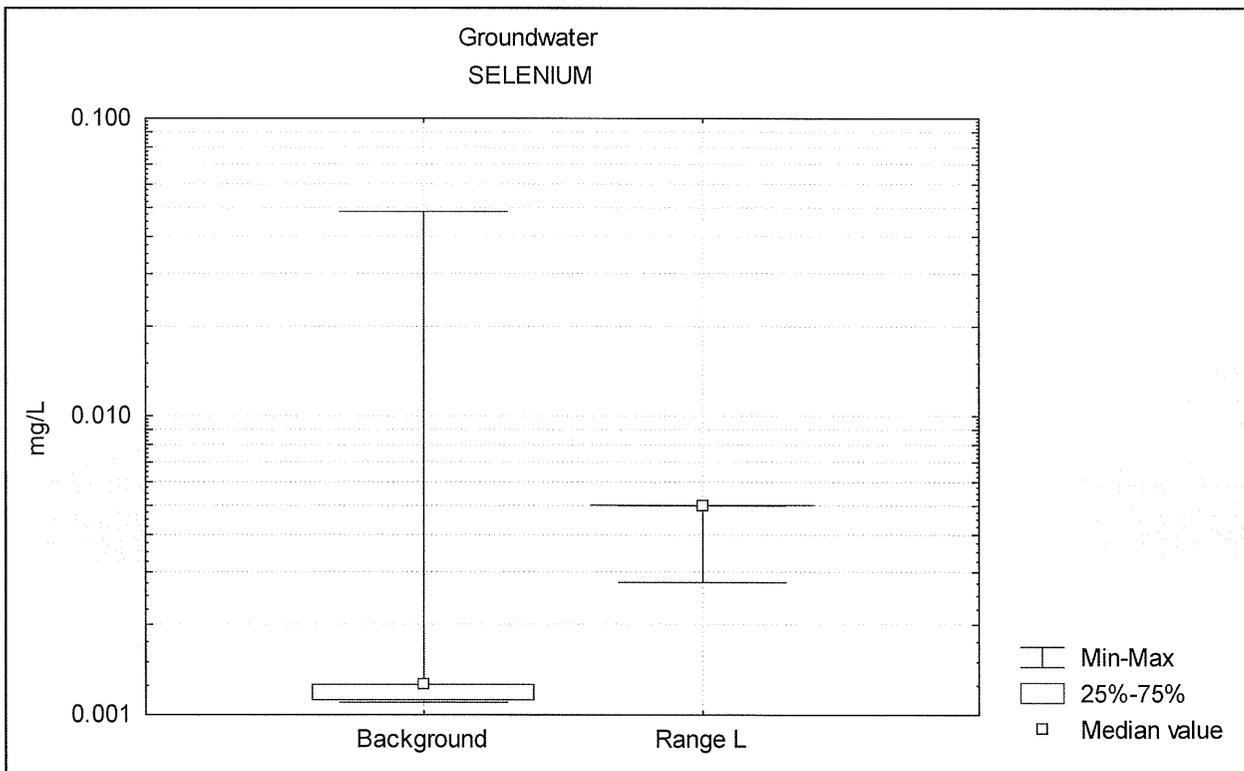
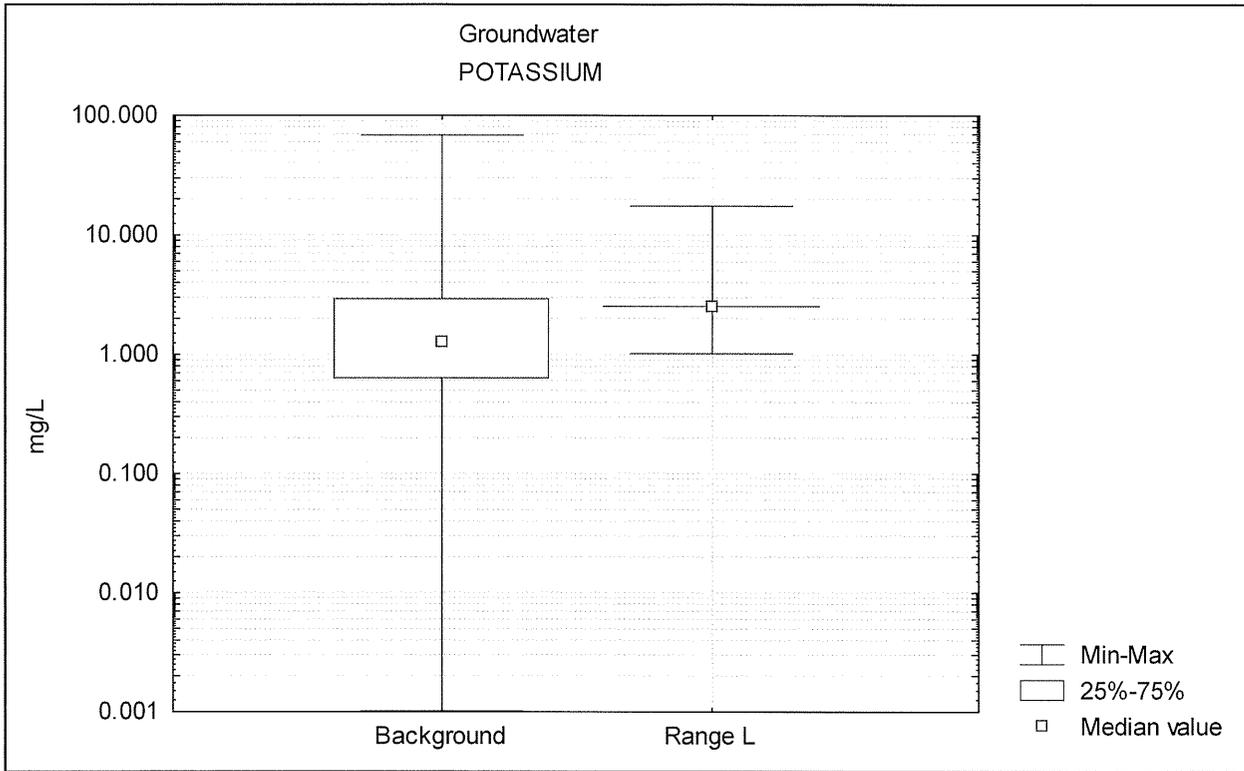


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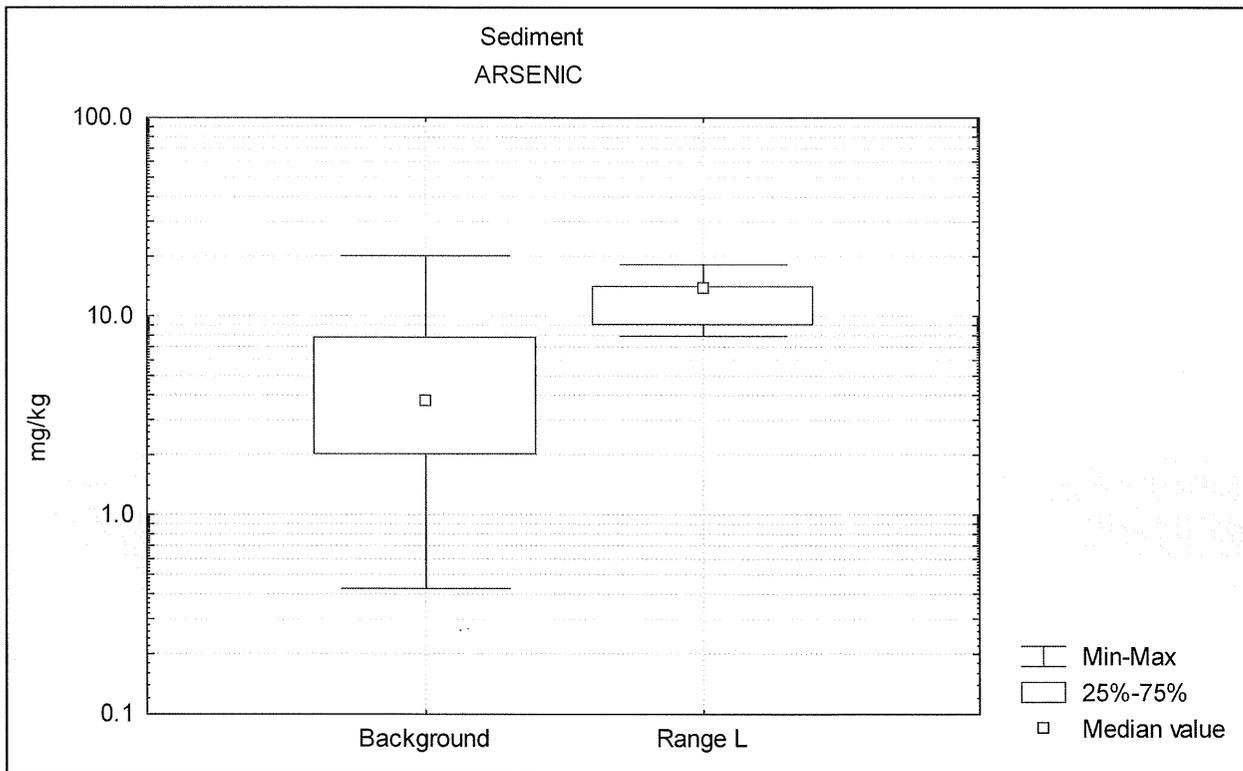
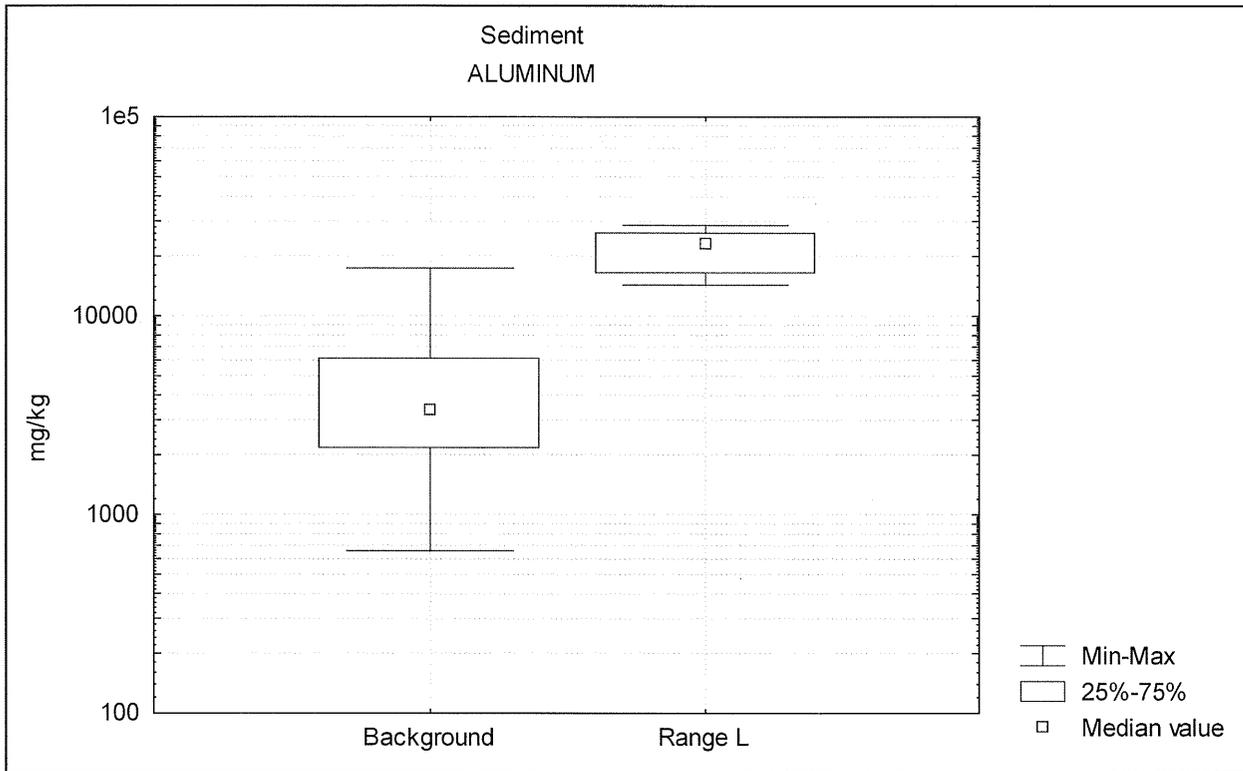


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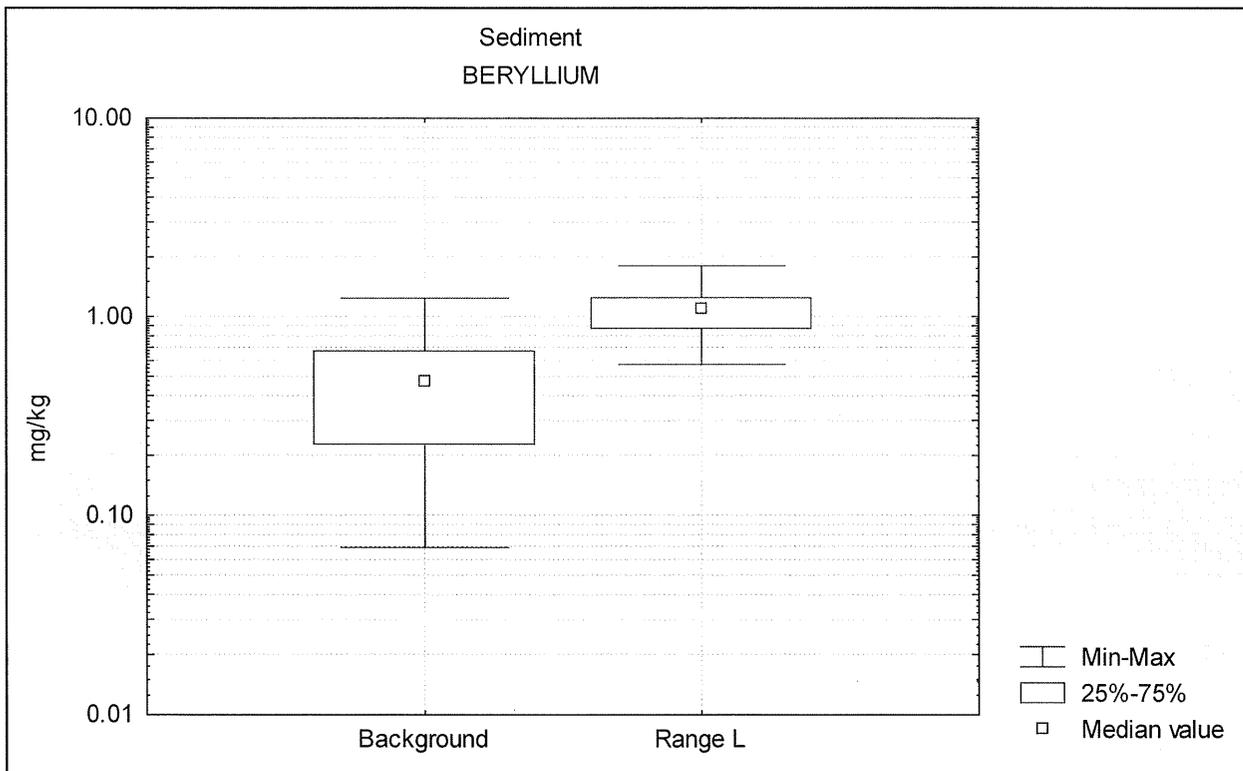
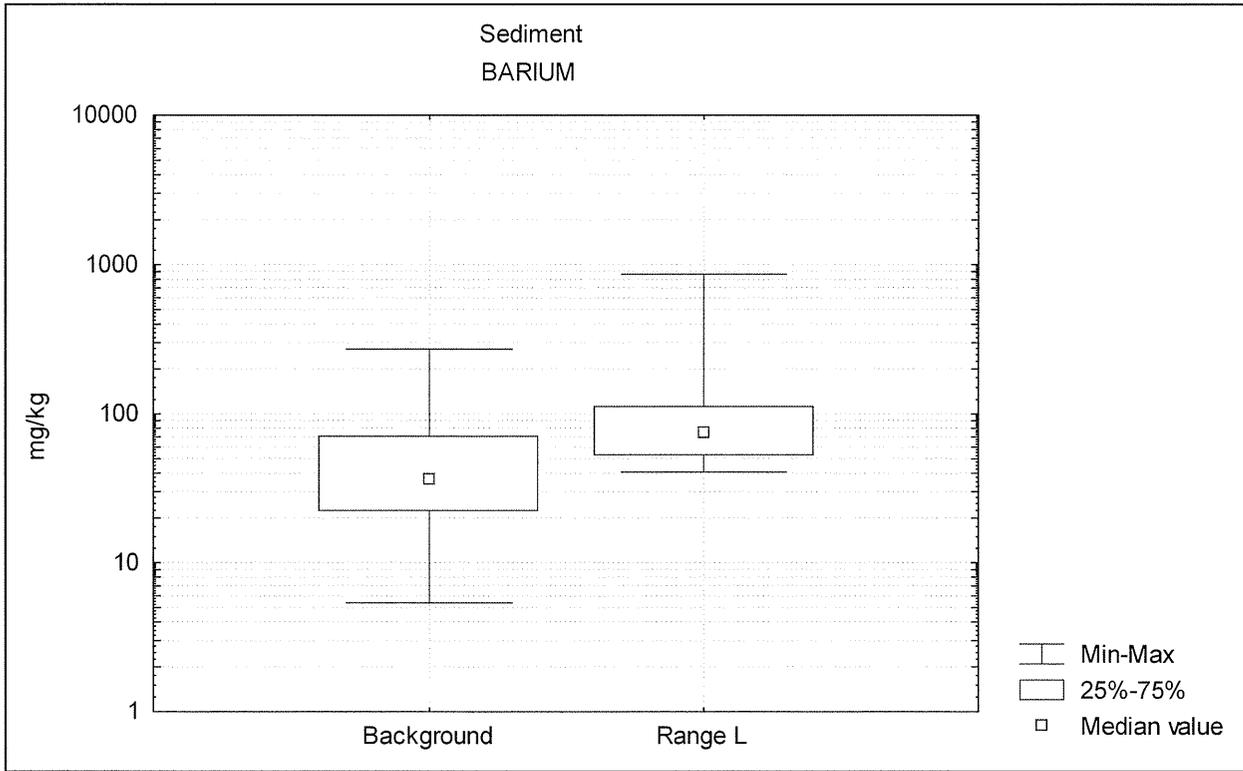


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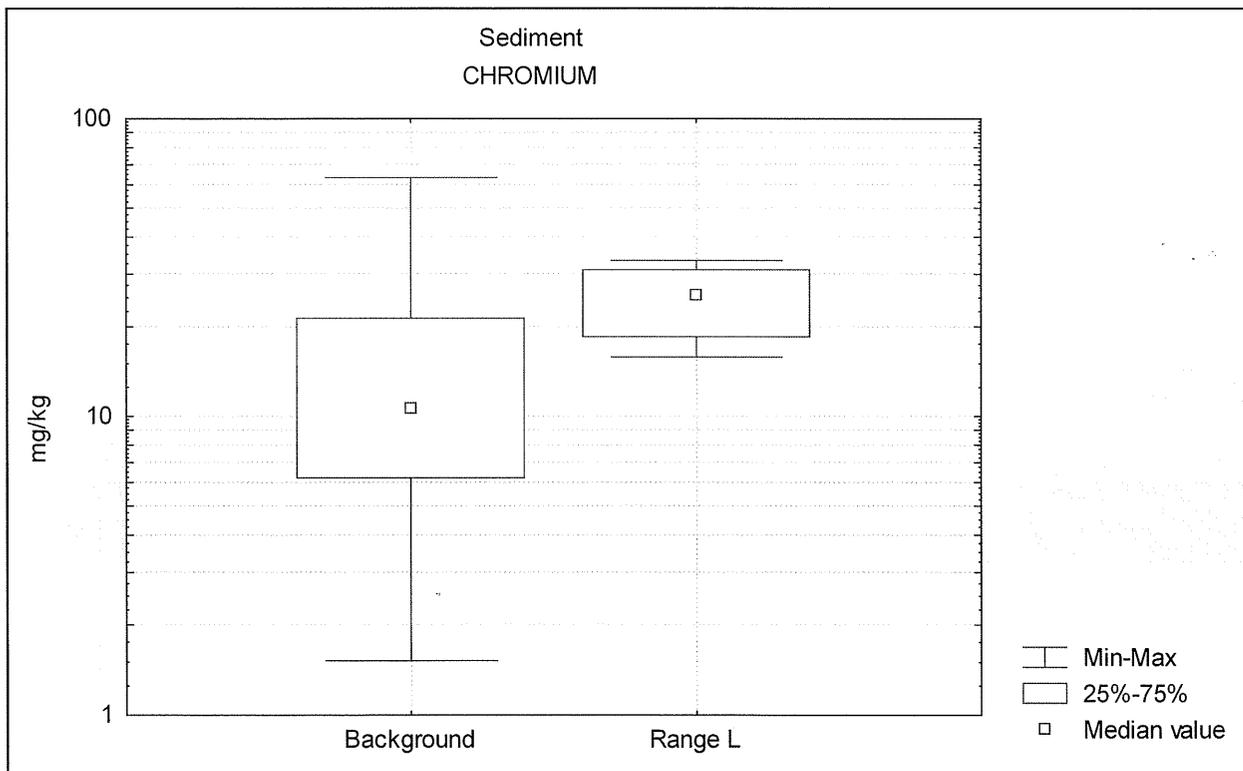
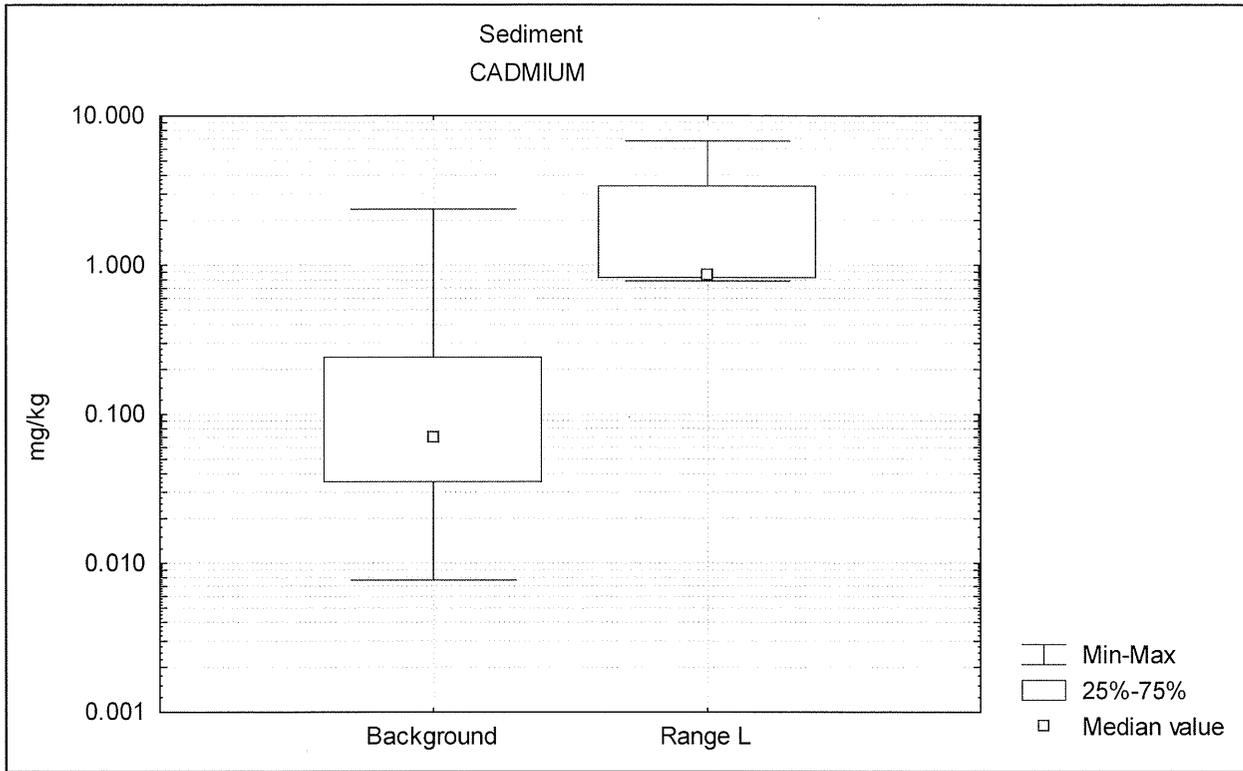


Figure 1-6

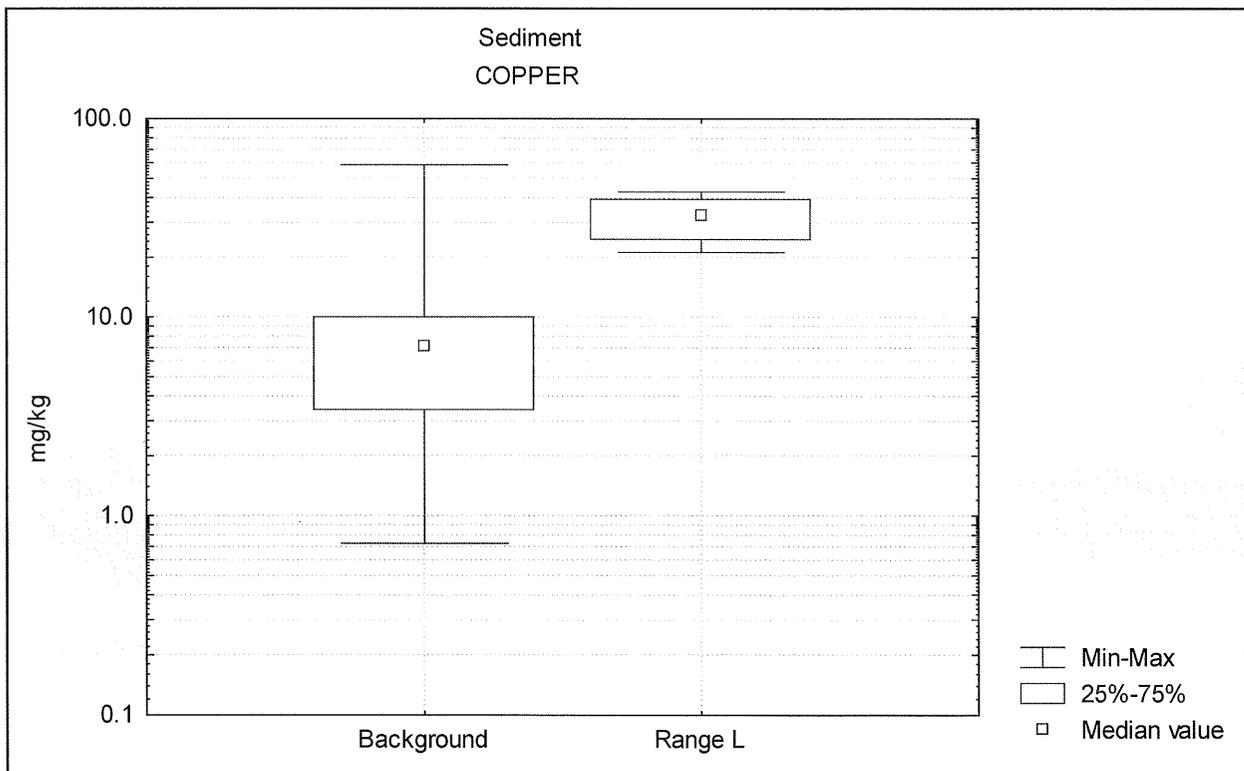
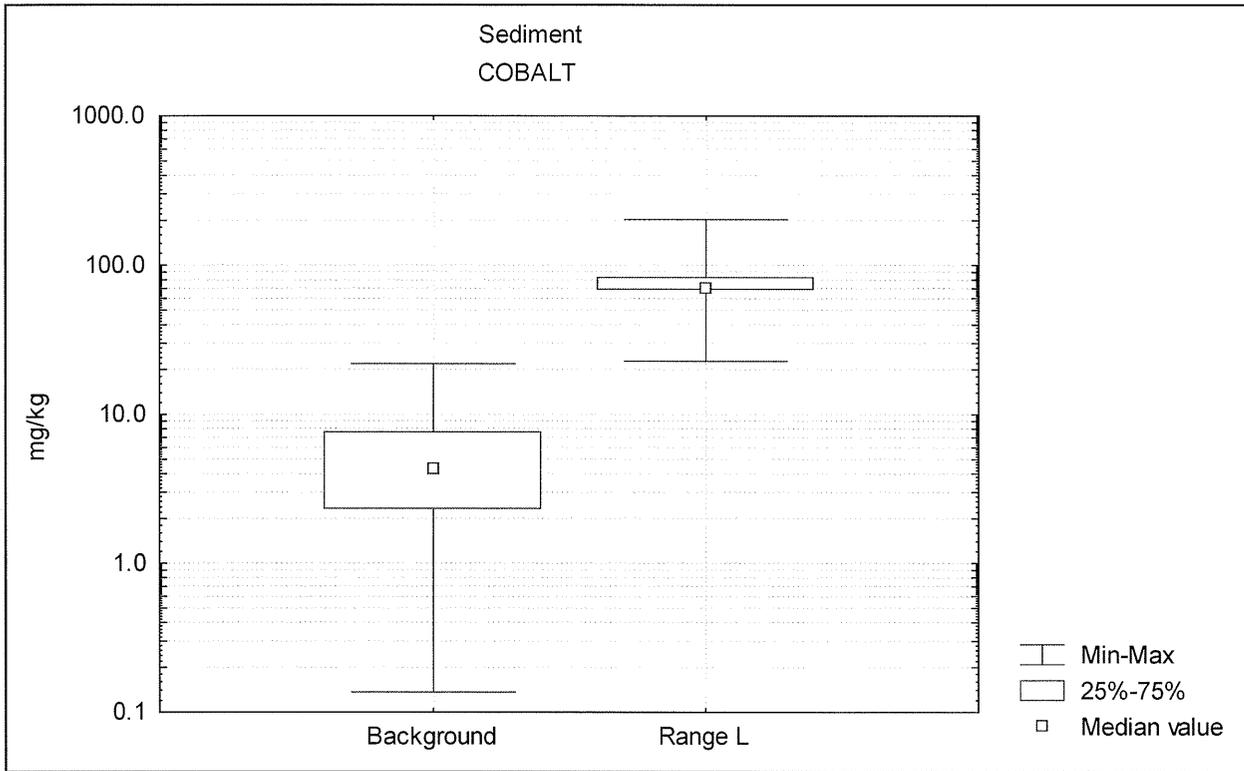


Figure 1-7

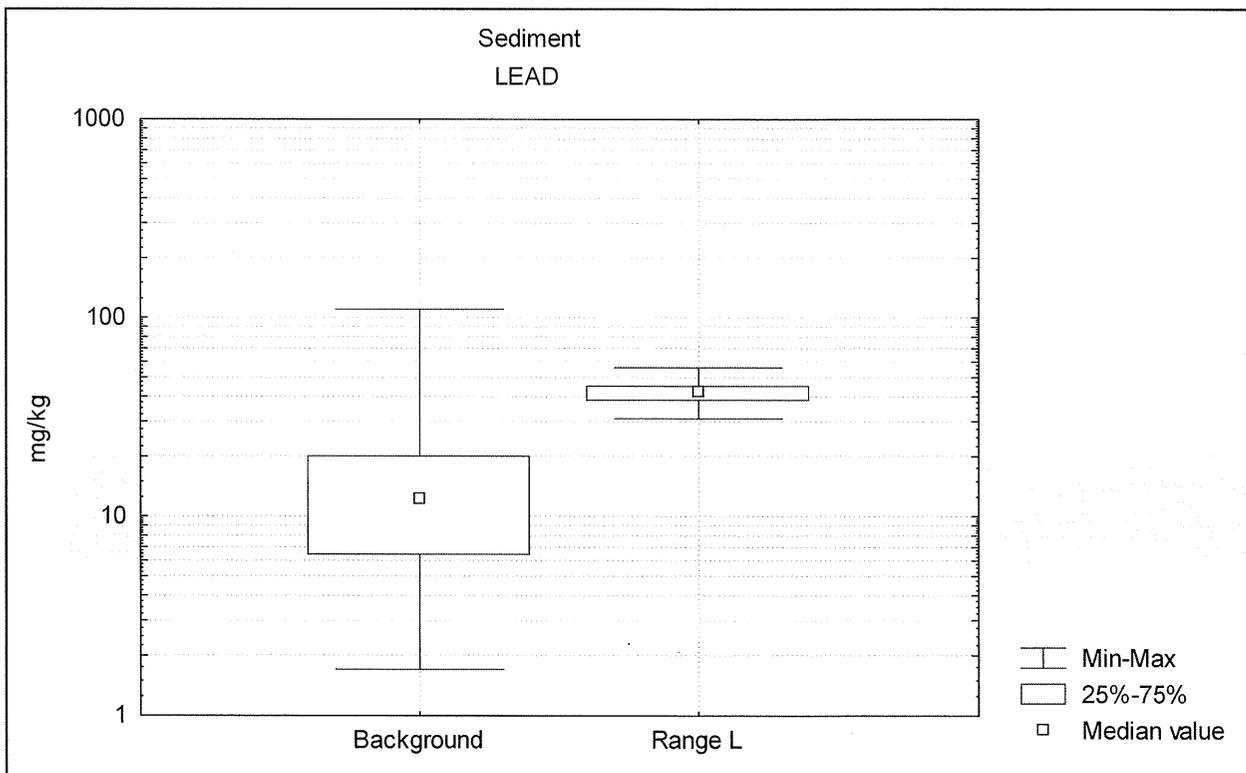
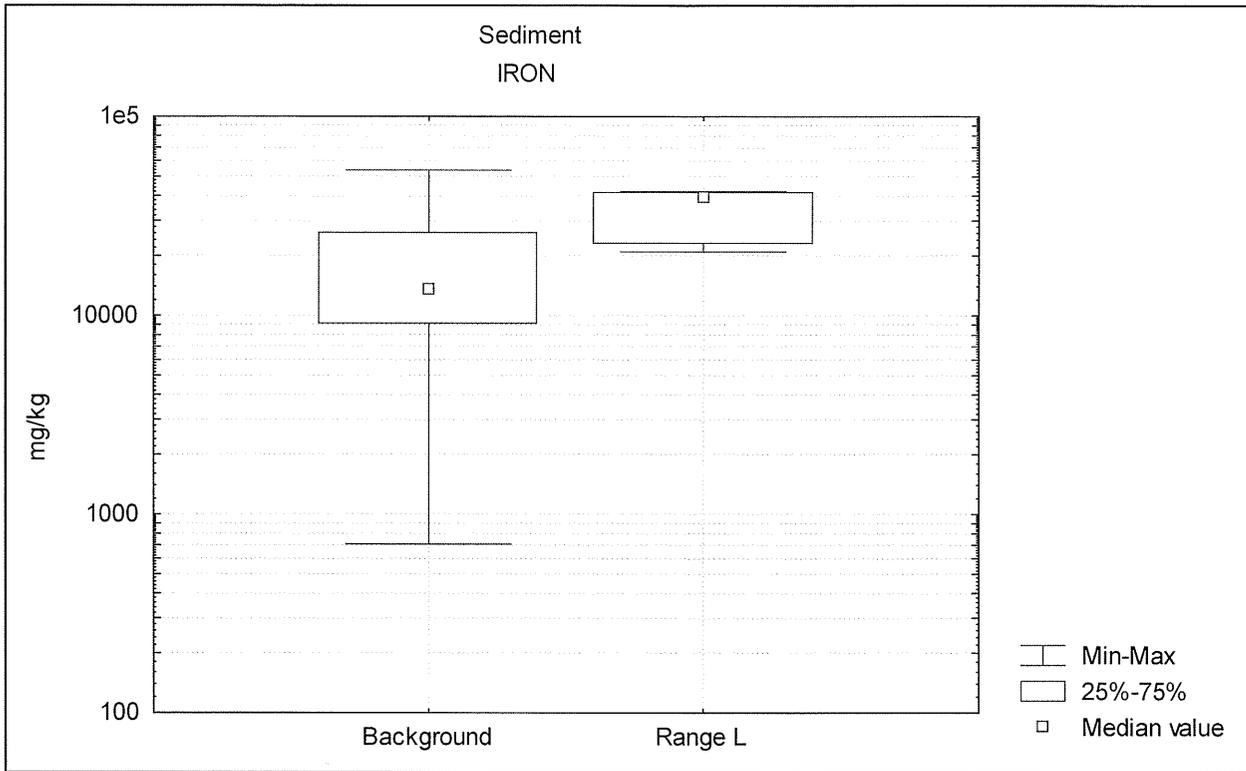


Figure 1-8

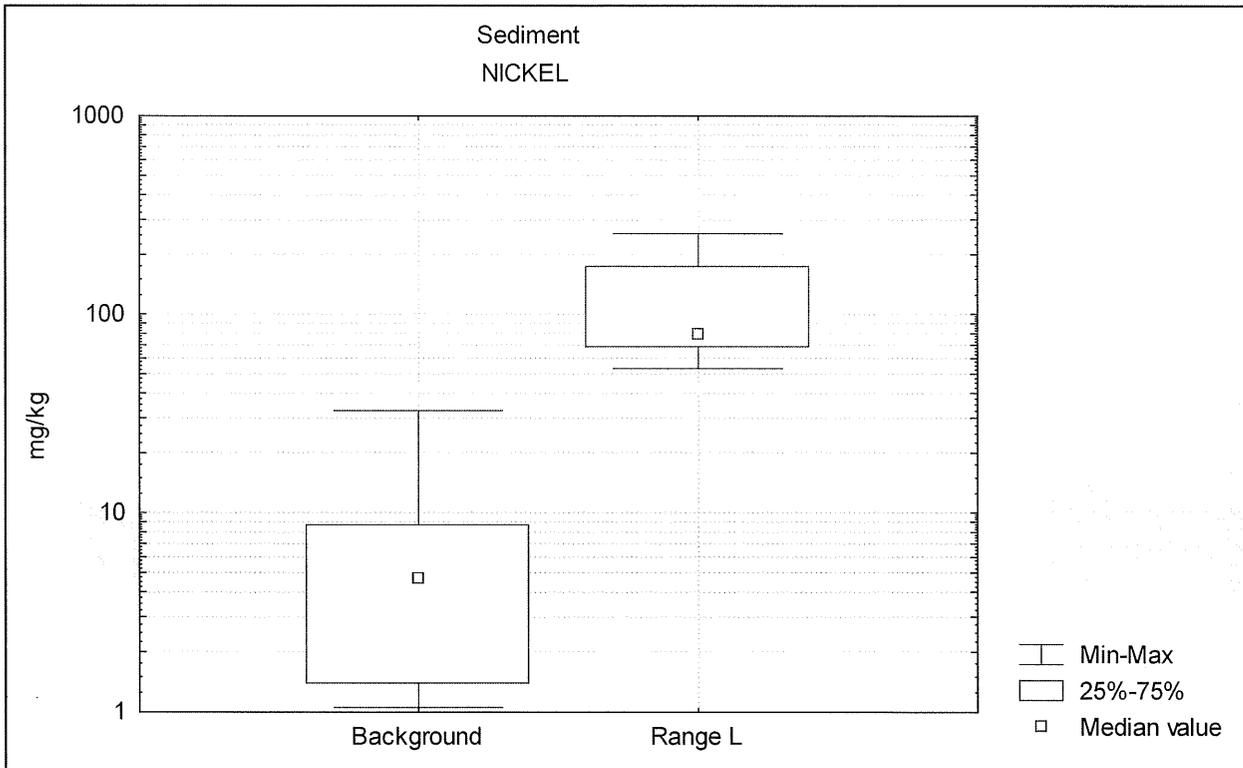
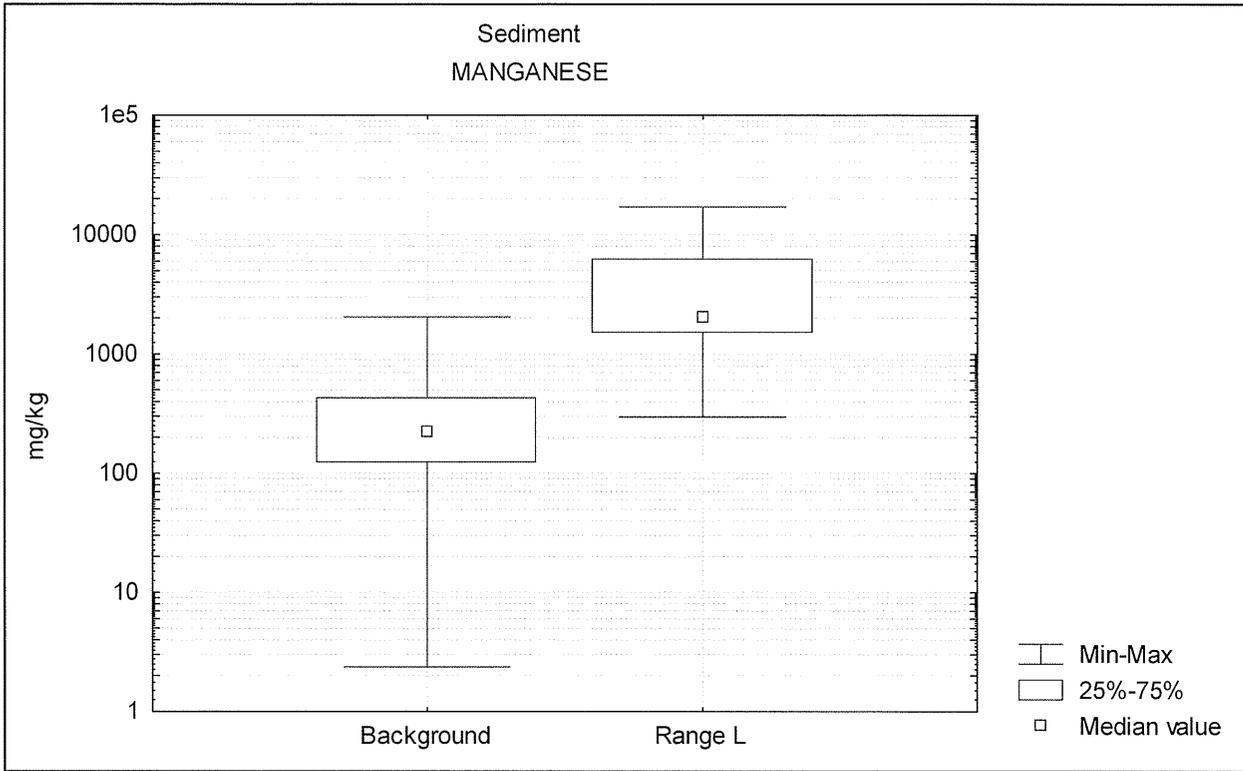


Figure 1-9

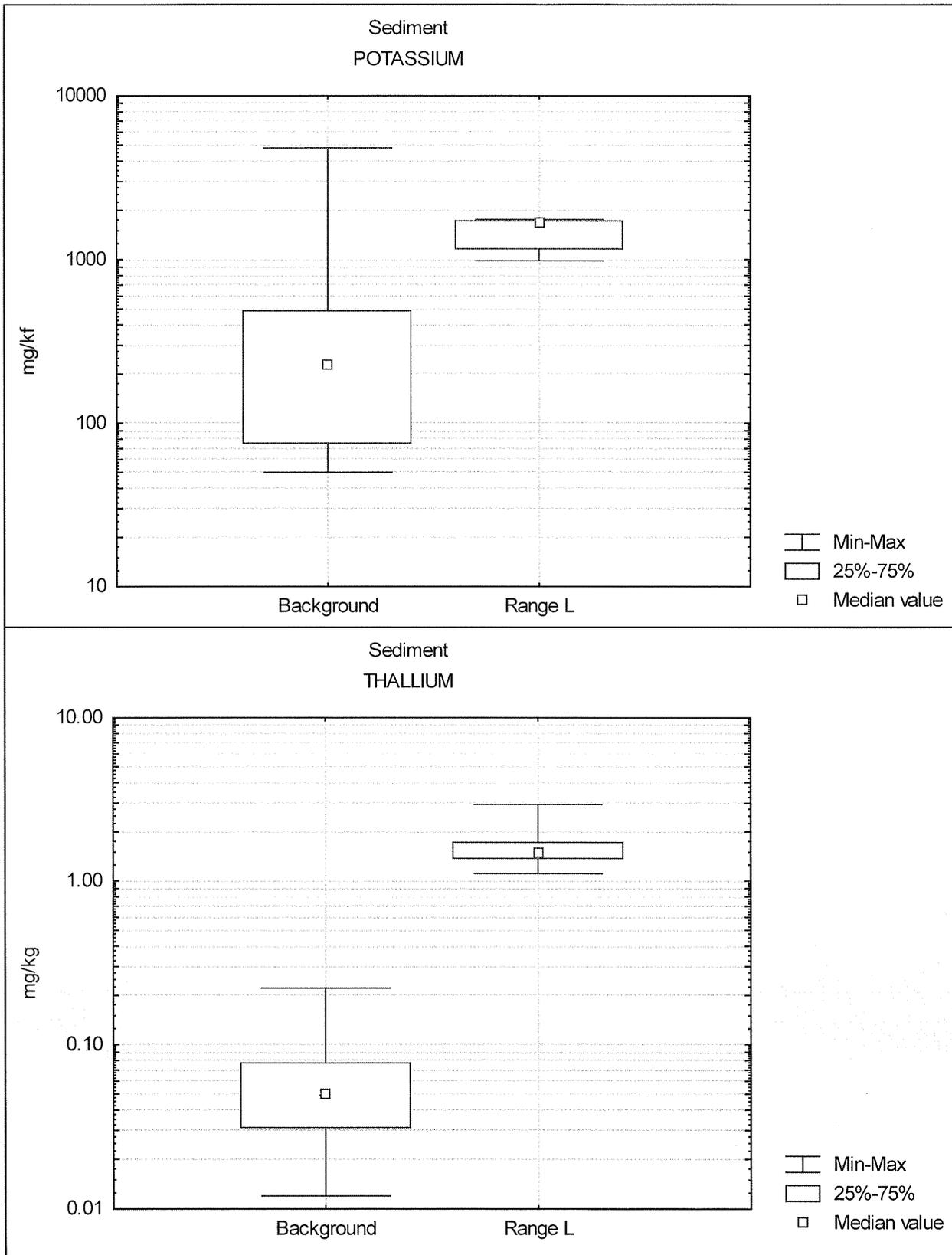


Figure 1-10

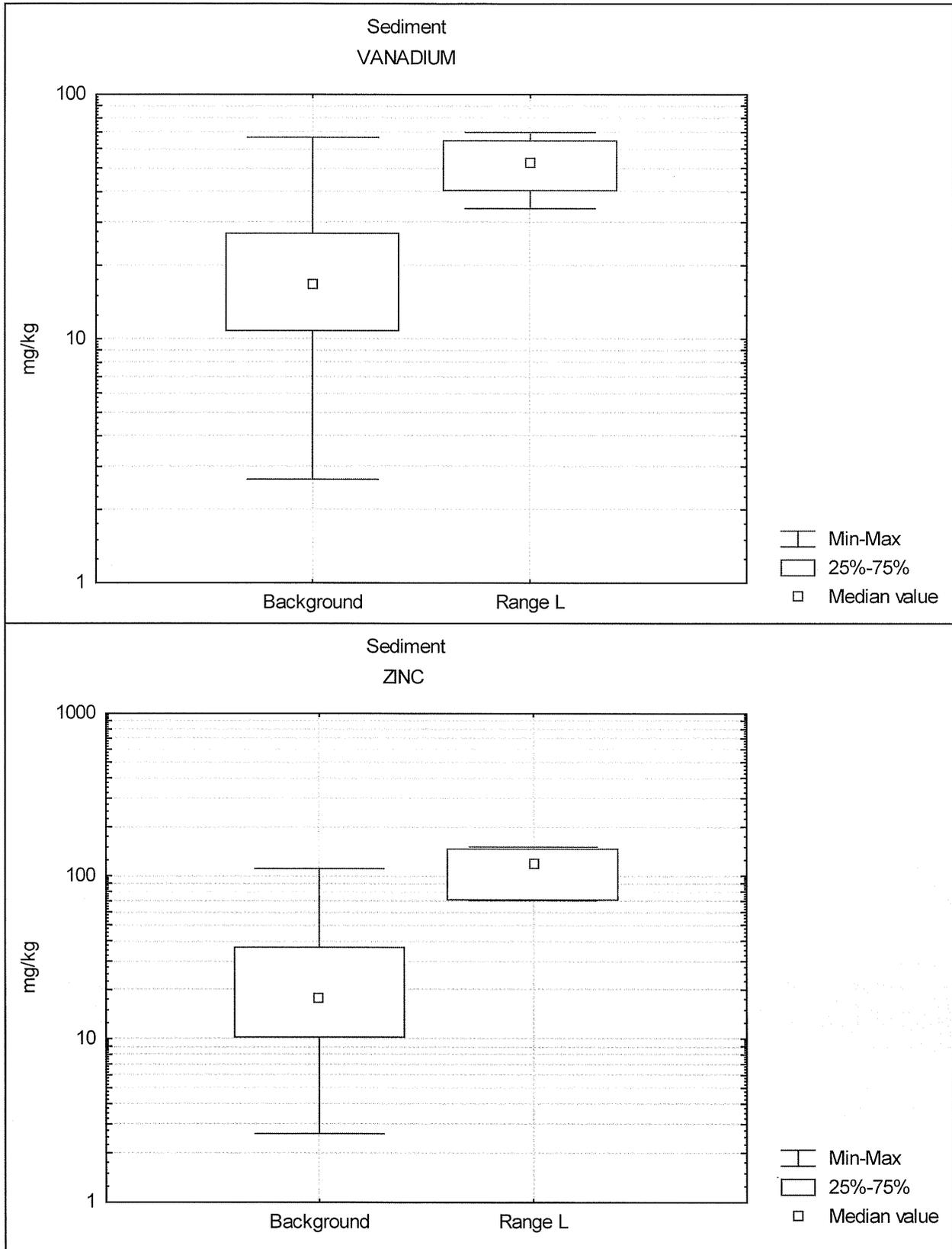


Figure 1-11

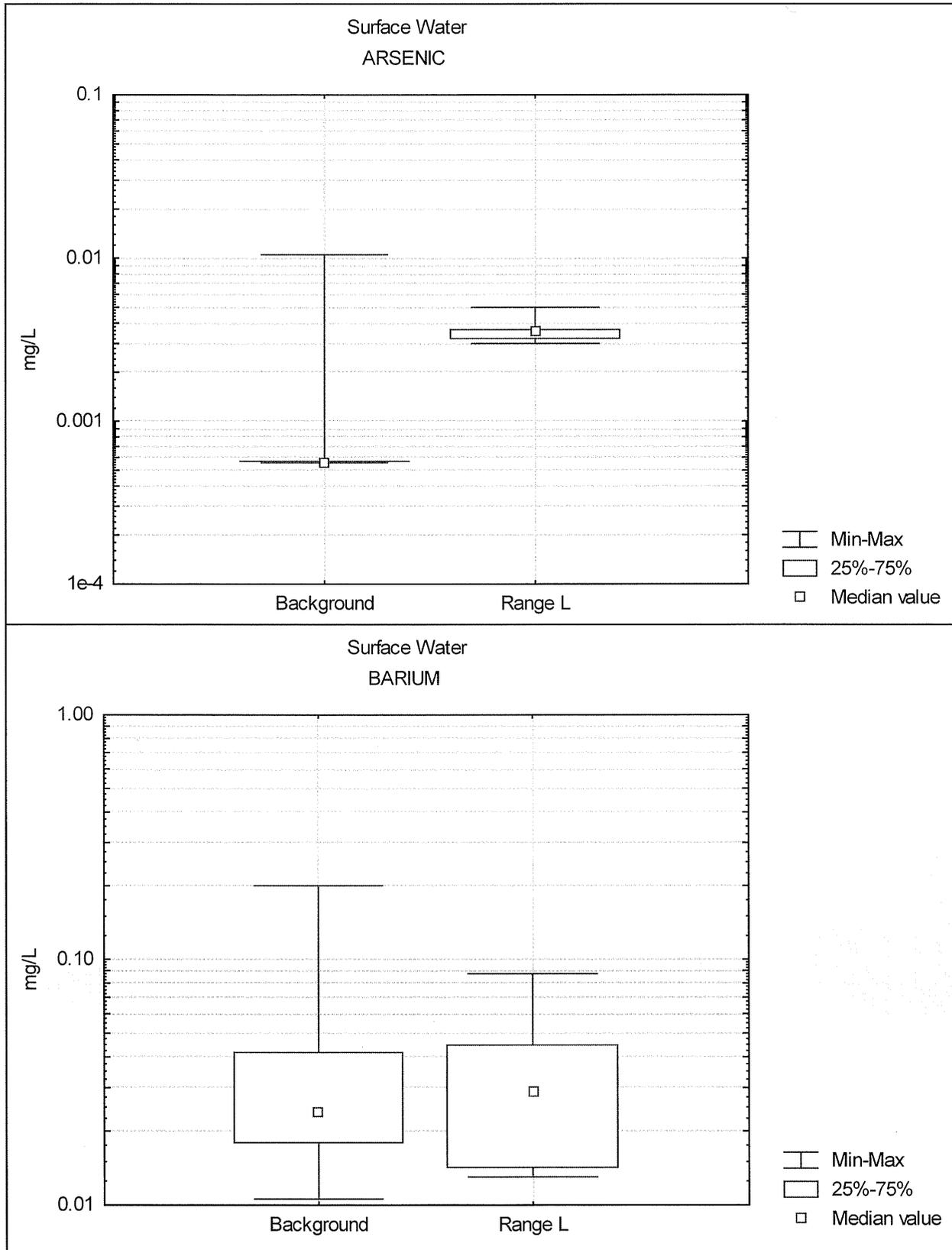


Figure 1-12

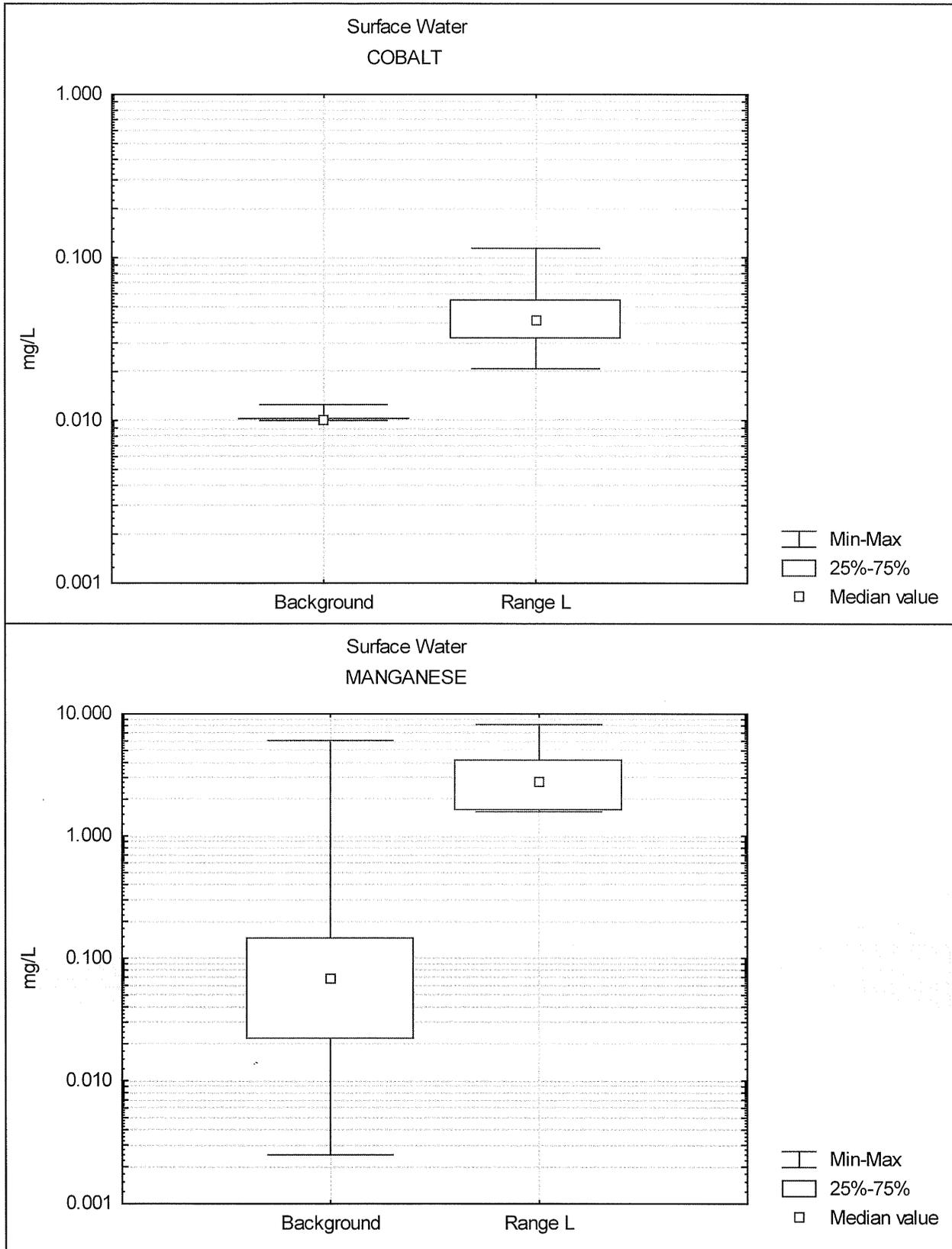
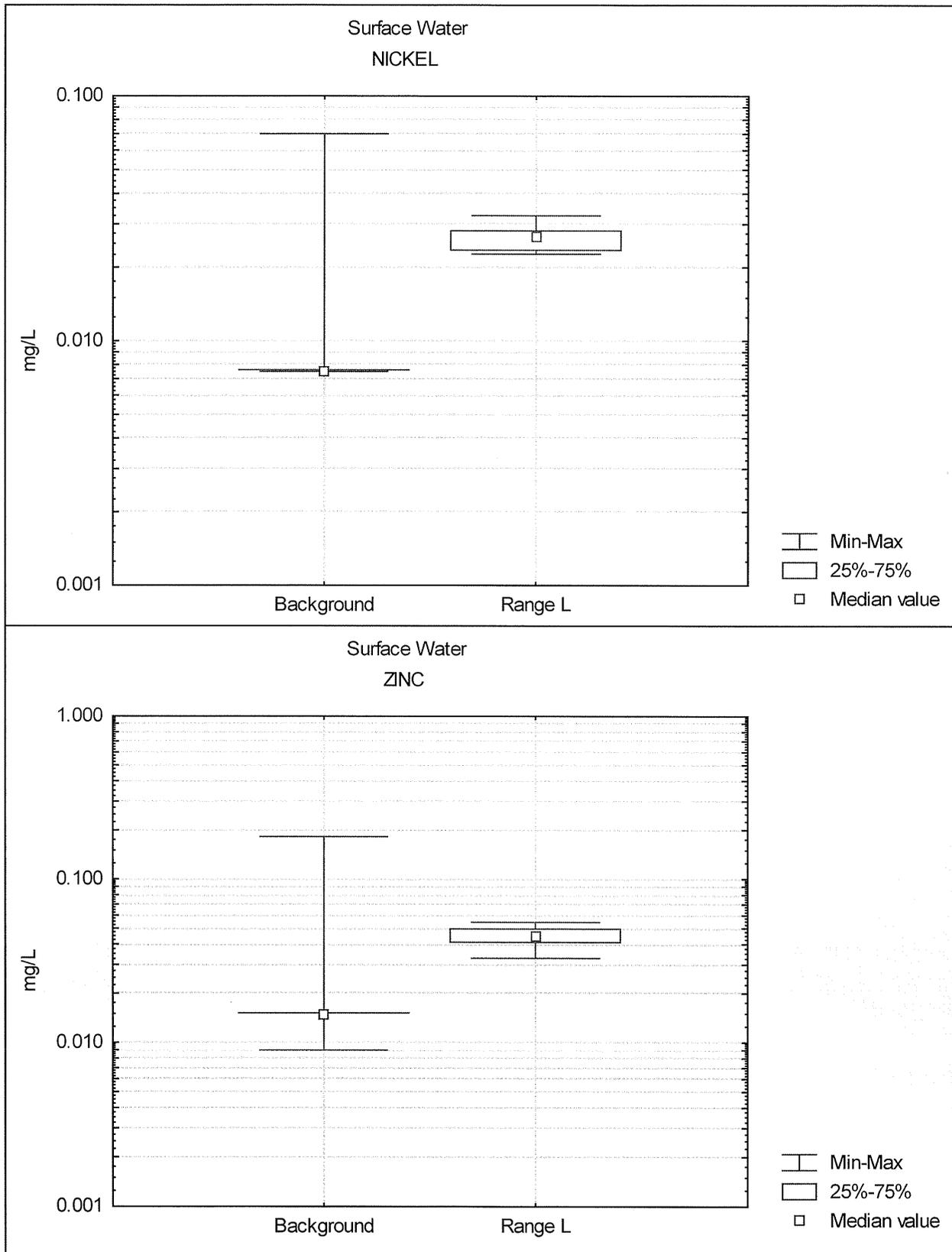


Figure 1-13



**GEOCHEMICAL
(TIER 3)**

Geochemical Evaluation of Metals in Site Media Range L – Lima Pond, Parcel 204(7) Fort McClellan, Alabama

1.0 Introduction

This report provides the results of a geochemical evaluation of inorganic constituents in sediment, groundwater, and surface water samples from Range L, Parcel 204(7), at Fort McClellan in Calhoun County, Alabama. Sixteen elements in sediment, three elements in groundwater, and four elements in surface water failed statistical comparison to background. A geochemical evaluation was performed to determine if the elevated concentrations are naturally occurring or if they contain a component of contamination.

Site samples included in the evaluation consist of six sediment samples collected in April 2002; seven unfiltered groundwater samples collected in January 2003; and six unfiltered surface water samples collected in April 2002. All of the site samples were analyzed for the full suite of 23 target analyte list (TAL) metals. Installation-wide background data for TAL metals in sediment, groundwater, and surface water are provided in the background study report (Science Applications International Corporation, 1998) and are used in the following evaluation.

2.0 Geochemical Evaluation Methodology

Naturally occurring trace element concentrations in environmental media commonly exceed regulatory screening criteria or fail statistical comparison to background data sets. Trace element distributions in uncontaminated soil and sediment tend to have very large ranges (two to three orders of magnitude are not uncommon), and are highly right-skewed, resembling lognormal distributions. These trace elements are naturally associated with specific minerals, and the preferential enrichment of a sample with these minerals will result in elevated trace element concentrations. It is thus important to be able to identify these naturally high concentrations and distinguish them from potential contamination.

If an analyte fails statistical comparison to background as described in the “Statistical Comparison of Site and Background Data, Range L – Lima Pond, Parcel 204(7),” 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 (U.S. Environmental Protection Agency, 1995; Barclift, *et al.*, 2000; U.S. Navy, 2002; Myers and Thorbjornsen, 2004). 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. This section describes the geochemical evaluation techniques that were employed in the site-to-background comparisons for Range L. Additional supporting information on these techniques is provided in the installation-wide work plan (IT Corporation, 2002) and Shaw Environmental's technical memorandum dated June 24, 2003.

It should be noted that the geochemical evaluations rely in part on professional judgment and qualitative assessment is a necessary part of the process. Samples that plot off the linear trend on a correlation plot are certainly suspect, but because all uncertainty cannot be eliminated from the evaluation, such plots cannot be construed as definitive proof of contamination. However, anomalous samples should be flagged as suspect and their results used as a basis for further investigation, risk assessment, or remediation, as appropriate. The combination of statistical evaluations (Tiers 1 and 2) and geochemical evaluation (Tier 3) as presented in this appendix is effective in reducing the occurrences of decision errors relative to consideration of statistics or geochemistry alone.

2.1 Soil and Sediment

The geochemical evaluation is based on the natural associations of trace elements with specific minerals in the soil or sediment matrix. As an example, arsenic in most uncontaminated oxic soils is almost exclusively associated with iron oxide minerals (Bowell, 1994; Schiff and Weisberg, 1997). (The term "iron oxide" is used here to include oxides, hydroxides, oxyhydroxides, and hydrous oxides of iron.) This association of arsenic with iron oxides is a result of the adsorptive behavior of this particular trace metal in an oxic soil environment. Arsenic is present in oxic soil pore fluid as negatively charged oxyanions (HAsO_4^{-2} , H_2AsO_4^-) (Brookins, 1988). These anions have strong affinities to adsorb on the surfaces of iron oxides, which maintain a strong positive surface charge (Electric Power Research Institute, 1986). If a soil sample has a high percentage of iron oxides, then it is expected to have a proportionally higher concentration of arsenic.

The absolute concentrations of arsenic and iron can vary by several orders of magnitude at a site, but the arsenic/iron ratios in the samples are usually quite constant 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 detected arsenic concentrations in a set of samples are plotted on the y-axis, and the corresponding detected iron concentrations are plotted on the x-axis. The slope of a best-fit line through the samples is equal to the average As/Fe 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 the preferential enrichment of iron oxides 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.

These trends may be linear or may have some curvature to them. The adsorption of a trace element on a mineral surface can usually be described by a linear isotherm over a limited range of concentrations, but a two-parameter curved fit (such as a Freundlich or Langmuir isotherm) can be more appropriate for some trace elements over a broader range of concentrations. The trace-versus-major element correlations are referred to as “linear trends” for convenience in this report, even though there may be some degree of curvature to the natural relationship.

Each trace element is associated with one or more minerals in the soil matrix. Vanadium and selenium, along with arsenic, 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 oxides also have an affinity to adsorb divalent cations such as barium, cobalt, and lead (Kabata-Pendias, 2001). These trace elements would be evaluated against manganese.

2.2 Groundwater and Surface Water

Elevated concentrations of inorganic constituents in groundwater and surface water samples may be due to naturally high dissolved concentrations, the presence of suspended particulates in the samples, reductive dissolution, or contamination resulting from site activities. This section discusses the major geochemical processes considered during the evaluation of groundwater and surface water analytical data.

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. The same concepts involved in the evaluation of soil and sediment data also apply to groundwater and surface water data: 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 ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) and hydroxides [$\text{Al}(\text{OH})_3$]; and iron oxide (Fe_2O_3), iron hydroxide [$\text{Fe}(\text{OH})_3$], and iron oxyhydroxide ($\text{FeO} \cdot \text{OH}$) 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 (Hem, 1985; Stumm and Morgan, 1996), with higher aluminum concentrations being a qualitative indicator of the mass of suspended clay minerals. 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 (Hem, 1985).

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; they maintain 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 and thus tend to concentrate on clay surfaces (Electric Power Research Institute, 1984; Brookins, 1988). Arsenic, selenium, and vanadium are usually present under oxidizing conditions as oxyanions, 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 $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0$, and $\text{Cr}(\text{OH})_4^-$, depending on pH (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) would be plotted against aluminum (x-axis). If all of the samples display a common linear trend, then it is most likely that the 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 Zn/Al ratio. If some samples plot above the linear trend established by the other samples, then those samples have an anomalously high Zn/Al ratio, and most likely contain excess zinc that cannot be explained by these natural processes.

These trends may be linear or may have some curvature to them. The adsorption of a trace element on a mineral surface can usually be described by a linear isotherm over a limited range of concentrations, but a two-parameter curved fit (such as a Freundlich or Langmuir isotherm) can be more appropriate for some trace elements over a broader range of concentrations. The trace-versus-major element correlations are referred to as “linear trends” for convenience in this report, even though there may be some degree of curvature to the natural relationship.

Alternative techniques for assessing the effects of suspended particulates on trace element concentrations are the evaluation of correlations of trace element concentrations versus turbidity, evaluation of correlations of trace element concentrations versus total suspended solids (TSS), and comparison of analyses of filtered versus unfiltered splits of samples. 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. Filtered splits were not obtained for the Range L groundwater and surface water samples, so comparisons of filtered versus unfiltered element concentrations cannot be performed.

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.

Effects of Reductive Dissolution. Iron and manganese oxides concentrate several trace elements such as arsenic, selenium, and vanadium on mineral surfaces, as discussed above. In

soils and sedimentary aquifers, these elements are almost exclusively associated with iron and manganese oxide minerals and grain coatings, as long as the redox conditions are moderate to oxidizing.

The release of organic contaminants such as fuels or chlorinated solvents can establish local reducing environments caused by anaerobic microbial degradation of the organic compounds. The establishment of local reducing conditions can drive the dissolution of iron and manganese oxides, which become soluble as the redox potential drops below a threshold value. Dissolution of these oxide minerals can mobilize the trace elements that were adsorbed on the oxide surfaces, which is a process termed “reductive dissolution.” Several investigations have documented the mobilization of arsenic, selenium, and other trace elements under locally reducing redox conditions (Sullivan and Aller, 1996; Nickson, *et al.*, 2000; Belzile, *et al.*, 2000).

Evidence for reductive dissolution would be a correlation between elevated trace elements (arsenic, selenium, and vanadium in particular) versus lower redox conditions. Low redox conditions can be identified by local depressions in oxidation-reduction potential (ORP) or dissolved oxygen (DO) measurements, or the presence of reducing gases such as hydrogen, methane, ethane, or ethene. Anaerobic microbes can also reduce sulfate to sulfide and nitrate to ammonia, resulting in local depressions in sulfate and nitrate concentrations, and local detections of sulfide and ammonia. In areas impacted by chlorinated solvents, additional evidence for the establishment of anaerobic reducing conditions is the presence of *cis*-1,2-dichloroethene and/or vinyl chloride, which are reductive dechlorination products resulting from the microbial degradation of trichloroethene or tetrachloroethene under anaerobic conditions.

3.0 Results of the Geochemical Evaluation of Multiple Elements in Sediment

This section presents the results of the geochemical evaluation of aluminum, arsenic, barium, beryllium, cadmium, cobalt, copper, iron, lead, manganese, nickel, potassium, thallium, vanadium, and zinc in sediment samples from Range L. Correlation plots are provided in Attachment 1.

Aluminum

Aluminum is the second most abundant of the 23 elements analyzed in the site sediment samples, with a mean concentration of 21,900 mg/kg (2.2 weight percent). Aluminum is a primary component of common minerals such as clays, feldspars, and micas. Iron oxides are also common minerals in soil and sediment, and occur as discrete mineral grains or as coatings on silicate minerals (Cornell and Schwertmann, 2003). Clays and iron oxides tend to exist as very

fine particles, so both aluminum and iron are enriched in samples with finer grain sizes. A plot of aluminum versus iron concentrations provides a qualitative indicator of the relative abundance of these minerals in site sediment (Figure 1). The background samples form a generally linear trend with a positive slope, and all of the site samples lie on this trend. The site samples have higher aluminum concentrations than most of the background samples, but they also have proportionally higher iron. This indicates a natural source for the aluminum detected in the site samples. The location of the site samples near the top of the background trend (i.e., slightly higher Al/Fe ratios relative to those of some of the background samples) suggests that the site samples are preferentially enriched in clays relative to background. It is important to note that clays and iron oxides adsorb specific trace elements (as discussed in Section 2.1), so the samples that plot in the upper right portion of the trend in Figure 1 – including all of the site samples – are expected to contain naturally higher concentrations of trace elements relative to most of the background samples.

Conclusion

Aluminum detected in the site sediment samples is naturally occurring.

Arsenic

As explained in Section 2.1, arsenic is present in oxic pore fluid as oxyanions and has a strong affinity to adsorb on iron oxides, which maintain a positive surface charge. A positive correlation between arsenic and iron concentrations is thus expected for uncontaminated sediment samples under oxic conditions. The background samples form a generally linear trend with a positive slope in a plot of arsenic versus iron (Figure 2). The site samples contain higher arsenic concentrations than many of the background samples, but they also contain proportionally higher iron and lie on the linear trend. These observations indicate that arsenic in the site samples is associated with iron oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Arsenic detected in the site sediment samples is naturally occurring.

Barium

Manganese oxides have a strong affinity to adsorb divalent cations (such as Ba^{2+} , Co^{2+} , and Pb^{2+}), due to the large surface area and high negative surface charges of these minerals. If a sediment sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements such as barium. A plot of barium versus manganese reveals a common linear trend with a positive slope for the site and background samples (Figure 3). Site sample MJ1006 contains the highest barium concentration of the site and background data sets (863 J mg/kg), but it also contains the highest manganese concentration (17,100 mg/kg) and lies on the linear trend. This indicates that barium in the site samples is associated with manganese oxides at ratios consistent with those of the background samples, and is natural.

This conclusion is supported by the comparison of site and background Ba/Mn ratios. Figure 4 displays the barium concentrations of the site and background sediment samples (y-axis) versus their corresponding Ba/Mn ratios (x-axis). If a site sample contained excess barium from a

contaminant source, then it would exhibit an anomalously high Ba/Mn ratio relative to background and would plot to the right of the background samples in Figure 4. No such samples are observed in the plot. All of the site samples, including sample MJ1006, exhibit Ba/Mn ratios that are within the background range.

Conclusion

Barium detected in the site sediment samples is naturally occurring.

Beryllium

Beryllium is commonly present in soil and sediment as the divalent cation (Be^{2+}), under natural conditions. Manganese oxides have a strong affinity to adsorb divalent cations, due to the large surface area and high negative surface charges of these minerals. If a sediment sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements such as beryllium. The site and background samples form a generally linear trend with a positive slope in a plot of beryllium versus manganese (Figure 5). The site samples with high beryllium concentrations also have proportionally higher manganese content and lie on the trend established by the background samples. These observations indicate that beryllium detected in the site samples is associated with manganese oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Beryllium detected in the site sediment samples is naturally occurring.

Cadmium

Cadmium is commonly present in soil and sediment as the divalent cation (Cd^{2+}), under natural conditions. Manganese oxides have a strong affinity to adsorb divalent cations, due to the large surface area and high negative surface charges of these minerals. If a sediment sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements such as cadmium. Most of the background samples form a generally linear trend with a positive slope in a plot of cadmium versus manganese (Figure 6). Samples MJ1004 and MJ1005 contain the only detectable cadmium in the site data set (3.37 mg/kg and 6.67 mg/kg). They have higher cadmium concentrations than the background samples, but they also have proportionally higher manganese content (as well as high aluminum) and lie on the trend established by the background samples. The elevated cadmium in these two samples is due to the preferential enrichment of minerals such as manganese oxides, and is natural.

Conclusion

Cadmium detected in the site sediment samples is naturally occurring.

Chromium

As discussed in Section 2.1, chromium can be present in sediment as various species with different charges, and thus it can adsorb on several different types of minerals including iron oxides and clays. A plot of chromium versus iron reveals a collinear trend for the site and background samples (Figure 7). The site samples with the highest chromium concentrations also contain the highest iron concentrations, and lie on the trend established by the other samples.

These observations indicate that chromium in the site samples is associated with iron oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Chromium detected in the site sediment samples is naturally occurring.

Cobalt

Manganese oxides have a strong affinity to adsorb divalent cations (such as Ba^{2+} , Co^{2+} , and Pb^{2+}), due to the large surface area and high negative surface charges of these minerals. If a sediment sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements such as cobalt. A plot of cobalt versus manganese reveals a common linear trend with a positive slope for the site and background samples ($R^2 = 0.89$ and 0.64 , respectively) (Figure 8). The site samples have higher cobalt concentrations than the background samples, but they also contain proportionally higher manganese and lie on the linear trend. These observations indicate that cobalt in the site samples is associated with manganese oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Cobalt detected in the site sediment samples is naturally occurring.

Copper

Copper has an affinity to adsorb on the surfaces of minerals such as clays and iron oxides (Kabata-Pendias, 2001). Positive correlations for copper versus aluminum or copper versus iron are commonly observed for uncontaminated sediment samples. A plot of copper versus aluminum is provided in Figure 9. Most of the background samples form a linear trend with a positive slope, and all of the site samples lie on this trend. The site samples have higher copper concentrations than most of the background samples, but they also have proportionally higher aluminum content. These observations indicate that copper in the site samples is associated with clays at ratios consistent with those of the background samples, and is natural.

Conclusion

Copper detected in the site sediment samples is naturally occurring.

Iron

Iron is the most abundant of the 23 elements analyzed in the site soil samples, with a mean concentration of 34,400 mg/kg (3.4 weight percent). The iron in the samples is dominantly present as iron oxides, which are common minerals in soil and sediment and which occur as discrete mineral grains or as coatings on silicate minerals (Cornell and Schwertmann, 2003). As explained in the Aluminum evaluation, a plot of aluminum versus iron can be used to qualitatively assess the relative abundance of clays and iron oxides in site sediment (Figure 1). The background samples form a generally linear trend with a positive slope, and all of the site samples lie on this trend. The site samples have higher iron concentrations than many of the background samples, but they also have proportionally higher aluminum. This indicates that the site samples are preferentially enriched in clays and iron oxides relative to the background samples, and that the iron has a natural source. The positive correlations observed for arsenic

versus iron and vanadium versus iron – and the absence of outliers in the correlation plots – provides additional evidence for a natural source for iron in the site samples (see the Arsenic evaluation, above, and the Vanadium evaluation, below).

Conclusion

Iron detected in the site sediment samples is naturally occurring.

Lead

Manganese oxides have a strong affinity to adsorb divalent cations (such as Ba^{2+} , Co^{2+} , and Pb^{2+}), due to the large surface area and high negative surface charges of these minerals. If a sediment sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements such as lead. A plot of lead concentrations versus manganese concentrations is provided in Figure 10. The site and background samples form a common linear trend with a positive slope. The site samples with high lead concentrations also exhibit Pb/Mn ratios that are similar to those of the background samples, and lie on the linear trend. These observations indicate that lead in the site samples is associated with manganese oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Lead detected in the site sediment samples is naturally occurring.

Manganese

Manganese is the third most abundant of the 23 elements analyzed in the site data set, with a mean concentration of 4,871 mg/kg (0.5 weight percent). The manganese is dominantly present as manganese oxides, which are common minerals in soil and sediment. Manganese oxides, along with clays and iron oxides, tend to exist as very fine particles, so manganese is enriched along with aluminum and iron in samples with finer grain sizes. The site samples have higher manganese concentrations relative to background most likely because they have a higher proportion of finer grain sizes (note that the elevated aluminum concentrations suggest that the site samples are enriched in clays; see the Aluminum evaluation, above). Manganese oxides have a strong affinity to adsorb specific trace elements such as barium, nickel, and cobalt. The positive linear correlations observed for barium versus manganese, beryllium versus manganese, cobalt versus manganese, and nickel versus manganese indicate a natural source for these elements in the site samples (Figures 3, 5, 8, and 11).

Conclusion

Manganese detected in the site sediment samples is naturally occurring.

Nickel

Nickel is commonly present in soil and sediment as the divalent cation (Ni^{2+}), under natural conditions. Manganese oxides have a strong affinity to adsorb divalent cations, due to the large surface area and high negative surface charges of these minerals. If a sediment sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements such as nickel. A plot of nickel versus manganese reveals a strong linear trend with a positive slope for the site samples ($R^2 = 0.93$) (Figure 11),

which reflects the affinity for nickel adsorption on manganese oxides. The site samples with the highest nickel concentrations also have proportionally higher manganese and lie on the linear trend. This indicates that the elevated nickel in the site samples is due to the preferential enrichment of manganese oxides relative to the background samples, and that the nickel is naturally occurring.

Evaluation of the site and background Ni/Mn ratios indicates that the nickel in the site samples is associated with manganese oxides at ratios consistent with those of the background samples. Figure 12 displays the nickel concentrations of the site and background sediment samples (y-axis) versus their corresponding Ni/Mn ratios (x-axis). If a site sample contained excess nickel from a contaminant source, then it would exhibit an anomalously high Ni/Mn ratio relative to background and would plot to the right of the background samples in Figure 12. No such samples are observed in the plot. All of the site samples exhibit Ni/Mn ratios that are within the background range.

Conclusion

Nickel detected in the site sediment samples is naturally occurring.

Potassium

Potassium is a common constituent of minerals such as clays, which also contain aluminum as a primary component. Positive correlations between potassium and aluminum concentrations are thus commonly observed for uncontaminated samples. A plot of potassium concentrations versus aluminum concentrations is provided in Figure 13. The site and background samples form a common, generally linear trend with a positive slope ($R^2 = 0.87$). The site samples exhibit K/Al ratios that are similar to those of the background samples, indicating a natural source for the potassium in the site samples.

Conclusion

Potassium detected in the site sediment samples is naturally occurring.

Thallium

Thallium concentrations in sediment are often controlled through adsorption on iron oxides and manganese oxides. Positive correlations for thallium versus iron or thallium versus manganese are commonly observed for uncontaminated samples. A plot of detected thallium concentrations versus manganese concentrations is provided in Figure 14. The site samples form a linear trend with a positive slope, and the sample with the highest thallium concentration also has the highest manganese concentration. This indicates that the elevated thallium in the site samples is due to the preferential enrichment of manganese oxides relative to the background samples, and that the thallium is naturally occurring.

Figure 15 provides another perspective of the data, and displays the thallium concentrations of the site and background sediment samples (y-axis) versus their corresponding Tl/Mn ratios (x-axis). If a site sample contained excess thallium from a contaminant source, then it would exhibit an anomalously high Tl/Mn ratio relative to background and would plot to the right of the background samples in Figure 15. No such samples are observed in the plot. All of the site samples exhibit Tl/Mn ratios that are within the background range.

It is important to note that all four thallium detections in the site data set are estimated (“J”-qualified) concentrations below the reporting limit, and that such values are highly uncertain. In comparison, the background data set is characterized by unestimated detected concentrations and lower reporting limits. The site reporting limits range from 3.14 to 3.79 mg/kg, with a mean of 3.44 mg/kg. Reporting limit data are not available for the background detections, but their unestimated concentrations of 0.012 to 0.221 mg/kg suggest that the background reporting limits are one to two orders of magnitude lower than the site reporting limits. These background concentrations are reported to lower concentrations than the site samples and have uncertainty due to their proximity to the reporting limit. This uncertainty causes the scatter observed at lower concentrations in the correlation plot (Figure 14).

Conclusion

Thallium detected in the site sediment samples is naturally occurring.

Vanadium

As discussed in Section 2.1, vanadium is present in oxic pore fluid as oxyanions and has a strong affinity to adsorb on iron oxides, which maintain a positive surface charge. A positive correlation between vanadium and iron concentrations is thus expected for uncontaminated sediment samples under oxic conditions. The background samples form a linear trend with a positive slope in a plot of vanadium versus iron (Figure 16). The site samples have higher vanadium concentrations than many of the background samples, but they also have proportionally higher iron and lie on the background trend. This indicates that vanadium in the site samples is associated with iron oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Vanadium detected in the site sediment samples is naturally occurring.

Zinc

Zinc in soil and sediment is commonly associated with clay minerals and hydrous iron and aluminum oxides (Kabata-Pendias, 2001), so positive correlations for zinc versus aluminum and zinc versus iron are expected for uncontaminated samples. The site samples and most of the background samples form a common, generally linear trend with a positive slope in a plot of zinc versus iron (Figure 17). The site samples contain higher zinc concentrations than most of the background samples, but they also contain proportionally higher iron. This indicates that zinc in the site samples is associated with iron oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Zinc detected in the site sediment samples is naturally occurring.

4.0 Results of the Geochemical Evaluation of Multiple Elements in Groundwater

This section presents the results of the geochemical evaluation of calcium, chromium, and potassium in the seven unfiltered groundwater samples from Range L. Correlation plots are provided in Attachment 1.

Field-measured pH readings for the groundwater samples range from 5.28 to 8.17 standard units, with a median of 6.73 and mean of 6.43. These values indicate near-neutral to neutral pH conditions at the sample locations. Field-measured DO readings range from 2.24 to 8.25 mg/L, with a median of 5.21 mg/L and mean of 5.60 mg/L, and ORP readings range from +205 to +482 millivolts (mV), with a median of +325 mV and mean of +321 mV. These values suggest oxidizing redox conditions at all of the sample locations. Turbidity measurements range from 1 to 6.6 nephelometric turbidity units (NTU), with a median of 3.4 NTU and mean of 3.7 NTU. These readings indicate that the site samples did not contain a significant mass of suspended particulates. It should be noted that field readings are not available for the background groundwater samples.

Calcium

Calcium was detected in all seven site groundwater samples. Calcium and sodium are both major dissolved constituents in groundwater, and their concentrations often covary in uncontaminated samples. The background samples form a generally linear trend with a positive slope in a plot of calcium versus sodium (Figure 18). The site samples have higher calcium concentrations than some of the background samples, but they have Ca/Na ratios that are consistent with those of the background samples and they all lie on the background trend. These observations indicate a natural source for the calcium in the site samples.

Conclusion

Calcium detected in the site groundwater samples is naturally occurring.

Chromium

Chromium was detected in only one of the seven unfiltered groundwater samples (sample MJ3006, collected from well RL-G05 on 01/06/03), at a concentration of 0.0225 mg/L. The remaining site samples are nondetect for chromium, at a reporting limit of 0.02 mg/L. As noted in Section 2.2, chromium can be present in groundwater as a mixture of aqueous species with different charges, and thus it can adsorb on different surfaces, including clay and iron oxide minerals. Positive correlations for chromium versus aluminum concentrations and chromium versus iron concentrations are commonly observed for uncontaminated samples, under natural conditions.

Aluminum was detected in six of the seven unfiltered groundwater samples, and iron was detected in all seven samples (one of the iron concentrations has a “B” validation qualifier, but is

treated as a detected concentration for the purposes of this evaluation). As discussed previously, aluminum concentrations in excess of approximately 1 mg/L in neutral pH groundwater indicate the presence of suspended clays. Aluminum will be present in solution at a pH below about 4.0, but the Range L groundwater pH readings are higher than this and are generally neutral (see the discussion of field readings, above), so the aluminum in the site samples is expected to be present in particulate form. Iron concentrations in excess of approximately 1 mg/L in neutral-pH, moderate to oxidizing groundwater conditions indicate the presence of suspended iron oxides. The Range L field readings indicate oxidizing redox conditions at the sample locations, so the iron in the site samples is expected to be present primarily as suspended iron oxides.

A plot of aluminum versus iron can be used as a qualitative indicator of the amount of suspended particulates in the groundwater samples (Figure 19). The site samples and the majority of background samples form a linear trend with a positive slope, indicating that both elements are present in particulate form in these samples. The site samples contain lower aluminum concentrations than many of the background samples, indicating that they contain a lower mass of suspended clay minerals.

A plot of chromium versus aluminum is provided in Figure 20. Comparison to background is precluded by the lack of detectable chromium in the background samples. However, groundwater samples with detectable chromium that were collected at other Fort McClellan sites are included in the following evaluation for comparative purposes. These sites include Range J (Parcel 202[7]), the Former Tank Ranges (Parcels 92Q, 93Q, 107Q, 133Q, and 134Q), and monitoring wells located in the vicinity of Parcel 233(7). All of these non-Range L samples are referred to below as the “reference” samples.

In Figure 20 it can be seen that the reference samples with high chromium concentrations also contain high aluminum. This suggests that the elevated chromium in these samples is associated with suspended clays, and is natural. Range L sample MJ3006, however, has the highest chromium of all the samples depicted on the plot, but contains only moderate aluminum (as well as low iron) and lies above the general trend formed by the reference samples. There may be a component of contamination in this sample.

Figure 21 provides another perspective of these data sets, and displays the chromium concentrations of the site and reference samples (y-axis) versus their corresponding Cr/Al ratios (x-axis). Sample MJ3006 exhibits the highest Cr/Al ratio and lies to the right of the reference samples. This anomalously high Cr/Al suggests that the sample may contain excess chromium from a contaminant source.

Conclusion

The chromium concentration in groundwater sample MJ3006 is anomalously high and may contain a component of contamination. The remaining site samples are nondetect for chromium.

Potassium

Potassium was detected in two of the seven site groundwater samples. Potassium and sodium are both major dissolved constituents in groundwater, and their concentrations often covary in uncontaminated samples. The site and background samples form a common, generally linear

trend with a positive slope in a plot of potassium versus sodium (Figure 22). The site sample with the highest potassium concentration also has proportionally higher sodium, and lies on the background trend. These observations indicate a natural source for the potassium detected in the site samples.

Conclusion

Potassium detected in the site groundwater samples is naturally occurring.

5.0 Results of the Geochemical Evaluation of Multiple Elements in Surface Water

This section presents the results of the geochemical evaluation of arsenic, cobalt, manganese, and zinc in the six unfiltered surface water samples from Range L. Correlation plots are provided in Attachment 1.

Field-measured pH readings for the surface water samples range from 5.15 to 7.67 standard units, with a median of 5.73 and mean of 6.03. These values indicate near-neutral to neutral pH conditions at most of the sample locations, with slightly acidic conditions at sample location RLR-204-SW/SD06 (sample number MJ2007; pH of 5.15). Field-measured DO readings range from 9.07 to 15.7 mg/L, with a median of 9.19 mg/L and mean of 10.6 mg/L, and ORP readings range from +190 to +285 mV, with a median of +205 mV and mean of +223 mV. These values indicate oxidizing redox conditions at all of the sample locations. Turbidity measurements range from 1 to 50 NTU, with a median of 10 NTU and mean of 15 NTU. Although most of the site samples did not contain a significant mass of suspended particulates (10 NTU or lower for five of the six samples), sample MJ2001 contained a relatively high mass of suspended particulates (50 NTU; sample location RLR-204-SW/SD01). It should be noted that field readings are not available for the background surface water samples.

Arsenic

Arsenic was detected in five of the six unfiltered surface water samples. As discussed in Section 2.2, arsenic is usually present in neutral pH, oxidizing waters as an oxyanion and tends to concentrate on iron oxide surfaces, which maintain a positive surface charge. A positive correlation between arsenic and iron concentrations is expected for uncontaminated samples under those conditions. Field readings indicate oxidizing redox conditions at all of the sample locations and neutral-range pH conditions at most locations, so arsenic concentrations in the site samples are expected to be controlled primarily by adsorption on iron oxides.

Aluminum and iron were detected in all six samples. As discussed previously, aluminum concentrations in excess of approximately 1 mg/L in neutral pH groundwater indicate the presence of suspended clays. Aluminum will be present in solution at a pH below about 4.0, but the Range L surface water pH readings are higher than this and are generally neutral, so the

aluminum in the site samples is expected to be present in particulate form. Iron concentrations in excess of approximately 1 mg/L in neutral-pH, moderate to oxidizing groundwater conditions indicate the presence of suspended iron oxides. The field readings indicate oxidizing redox conditions at the sample locations, so the iron in the site samples is expected to be present primarily as suspended iron oxides.

A plot of aluminum versus iron can be used as a qualitative indicator of the amount of suspended particulates in the surface water samples (Figure 23). The site and background samples form a collinear trend with a positive slope, indicating that both elements are present in particulate form in the samples. The site samples contain lower iron concentrations than many of the background samples, indicating that they contain a lower mass of suspended iron oxides. The positive correlation between iron and TSS concentrations ($R^2 = 0.60$) provides additional evidence that the iron is present dominantly in particulate form.

A plot of arsenic versus iron is provided in Figure 24. The site samples and most of the background samples form a common linear trend with a positive slope. The site samples contain only moderate amounts of arsenic relative to the background samples – the site concentrations range from 0.003 J mg/L to 0.00366 J mg/L, similar to the mean background concentration of 0.0038 mg/L. They contain proportional amounts of iron, and lie near the center of the linear background trend. This indicates that the arsenic in the site samples is associated with suspended iron oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Arsenic detected in the site surface water samples is naturally occurring.

Cobalt

Cobalt was detected in all six unfiltered surface water samples. Under oxidizing groundwater conditions, cobalt concentrations are commonly controlled by adsorption on iron oxides and manganese oxides (Hem, 1985). Field readings for the site samples indicate oxidizing redox conditions; the site Al/Fe ratios suggest the presence of suspended clays and iron oxides, and the Manganese evaluation (below) indicates that the manganese detected in the site samples is associated to some degree with suspended particulates. Given these observations, cobalt concentrations in site groundwater are expected to be at least partly controlled by adsorption on suspended particulates such as iron oxides and manganese oxides.

A plot of cobalt versus manganese is provided in Figure 25. Comparison to background is precluded by the lack of detectable cobalt in the background samples. However, the site samples exhibit a strong positive correlation ($R^2 = 0.98$); sample MJ2006 contains the highest cobalt concentration of the site data set (0.114 mg/L), but it also contains the highest manganese concentration (8.18 mg/L) and lies on the linear trend established by the other samples. This suggests that the elevated cobalt is due to the presence of suspended manganese oxides, and that the cobalt is natural.

Conclusion

Cobalt detected in the site surface water samples is naturally occurring.

Manganese

Manganese was detected in all six unfiltered surface water samples. Manganese usually displays complex behavior in natural systems because of three possible valence states (+2, +3, and +4), which each have different solubilities and sorptive properties (Hem, 1985). Manganese is similar to iron in that it is soluble under reducing conditions but has very low solubilities under oxidizing conditions. Field readings for the site samples indicate oxidizing redox conditions at all of the sample locations. It is thus expected that manganese in the site samples may be primarily associated with suspended particulates.

A plot of manganese versus iron is provided in Figure 26. The background samples form a generally linear trend with a positive slope and the site samples lie on or, particularly in the case of sample MJ2006, slightly above the background trend. Sample MJ2006 contains the highest manganese concentration of the site data set (8.18 mg/L) but it also contains the highest TSS concentration (93 mg/L) (Figure 27). The positive correlation between manganese and TSS concentrations in the site data set ($R^2 = 0.87$) suggests that the manganese is due to the presence of suspended particulates, and that it is natural.

Conclusion

Manganese detected in the site surface water samples is naturally occurring.

Zinc

Zinc was detected in five of the six unfiltered surface water samples. Zinc concentrations in neutral-pH waters are commonly controlled through adsorption on suspended iron oxides (Drever, 1997), so a positive correlation for zinc versus iron is expected for uncontaminated samples under those conditions. A plot of zinc versus iron is provided in Figure 28. The background samples with detectable zinc form a linear trend with a positive slope. The site samples contain relatively low amounts of zinc relative to the background samples – the site concentrations range from 0.0329 J mg/L to 0.0545 J mg/L, below the mean background concentration of 0.087 mg/L. They contain proportional amounts of iron, and lie on the lower portion of the linear background trend. These observations indicate that zinc in the site samples is associated with suspended iron oxides at ratios consistent with those of the background samples, and is natural.

Conclusion

Zinc detected in the site surface water samples is naturally occurring.

6.0 Summary

This section summarizes the results of the geochemical evaluations of selected elements in sediment, groundwater, and surface water samples from Range L.

Sediment. Geochemical evaluation indicates that all detected concentrations of aluminum, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, potassium, thallium, vanadium, and zinc in the site sediment samples are naturally occurring.

Groundwater. Geochemical evaluation indicates that the detected concentrations of calcium and potassium in the site groundwater samples are naturally occurring. The chromium concentration in sample MJ3006 (collected from well RL-G05 on 01/06/03) is anomalously high relative to the reference element concentrations, and may contain a component of contamination. The other site samples are nondetect for chromium.

Surface Water. Geochemical evaluation indicates that the detected concentrations of arsenic, cobalt, manganese, and zinc in the site surface water samples are naturally occurring.

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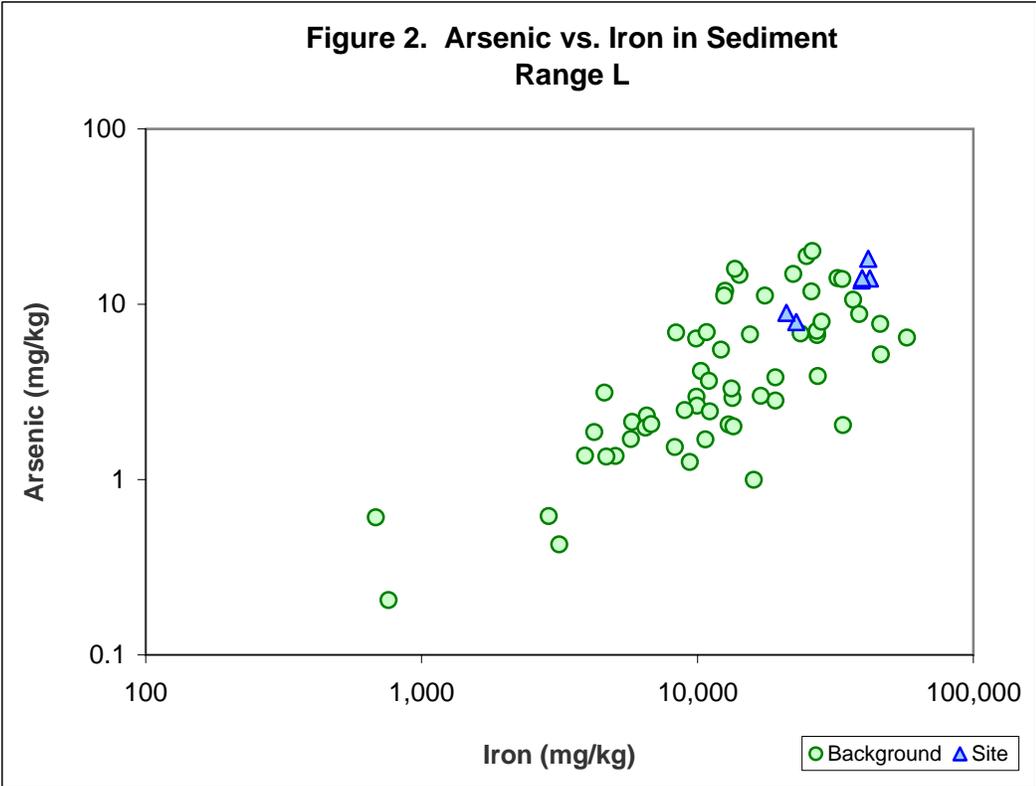
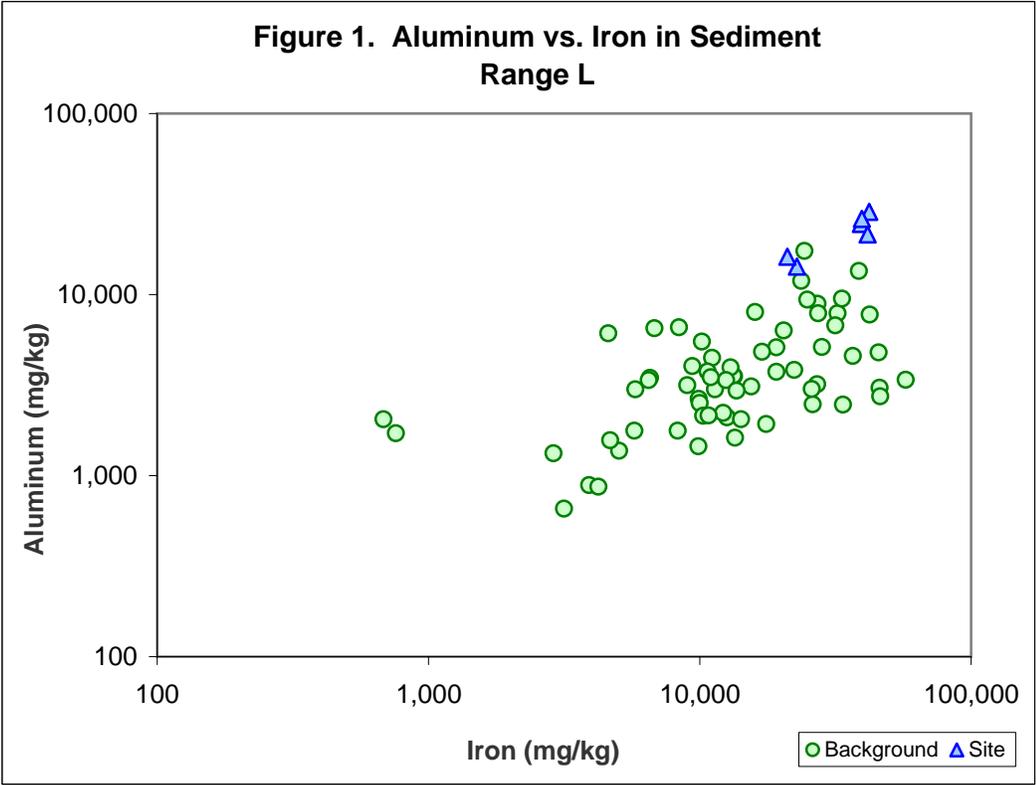
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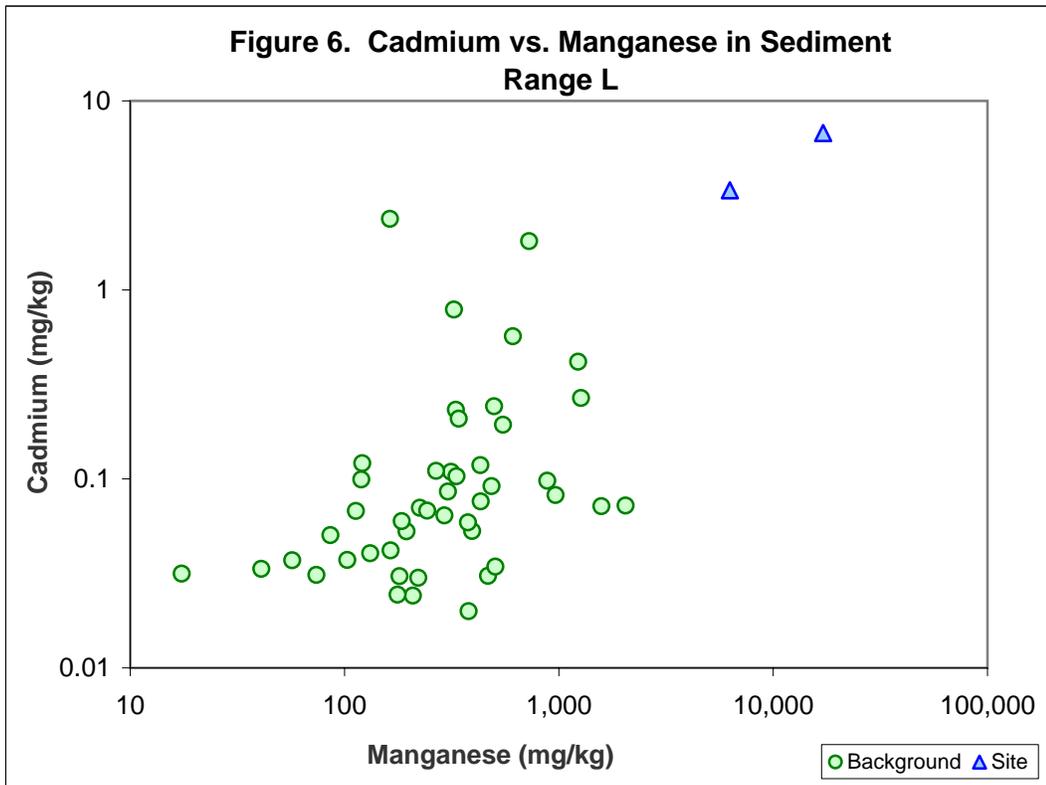
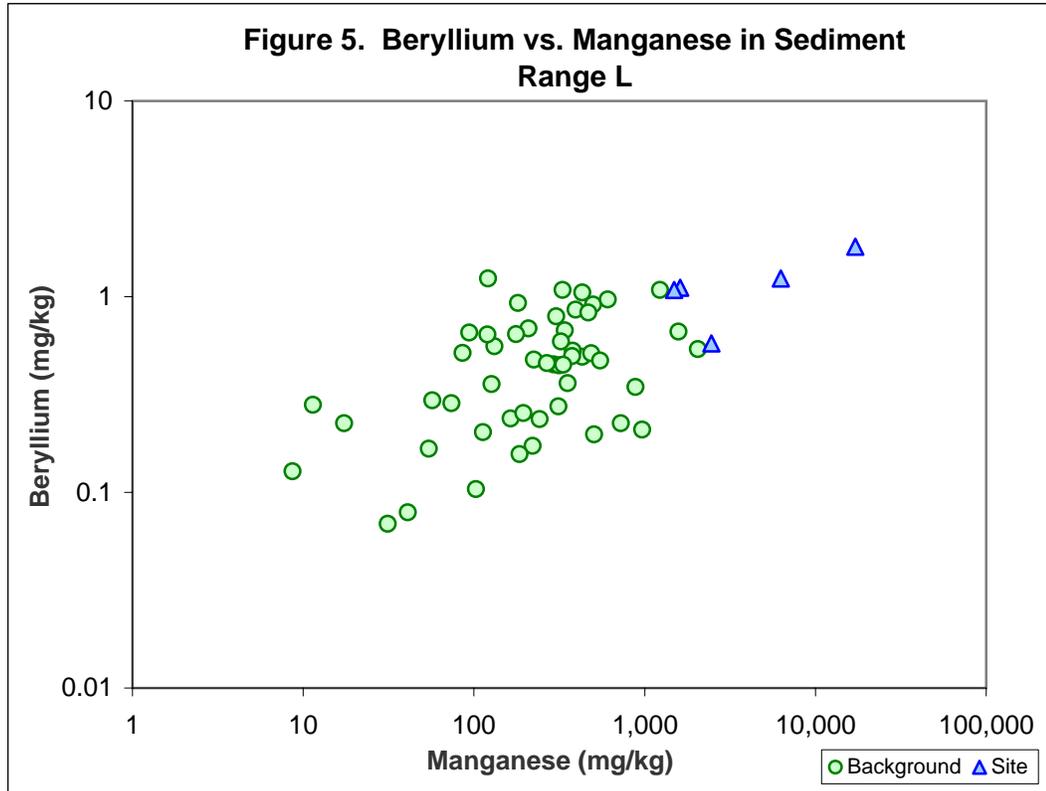
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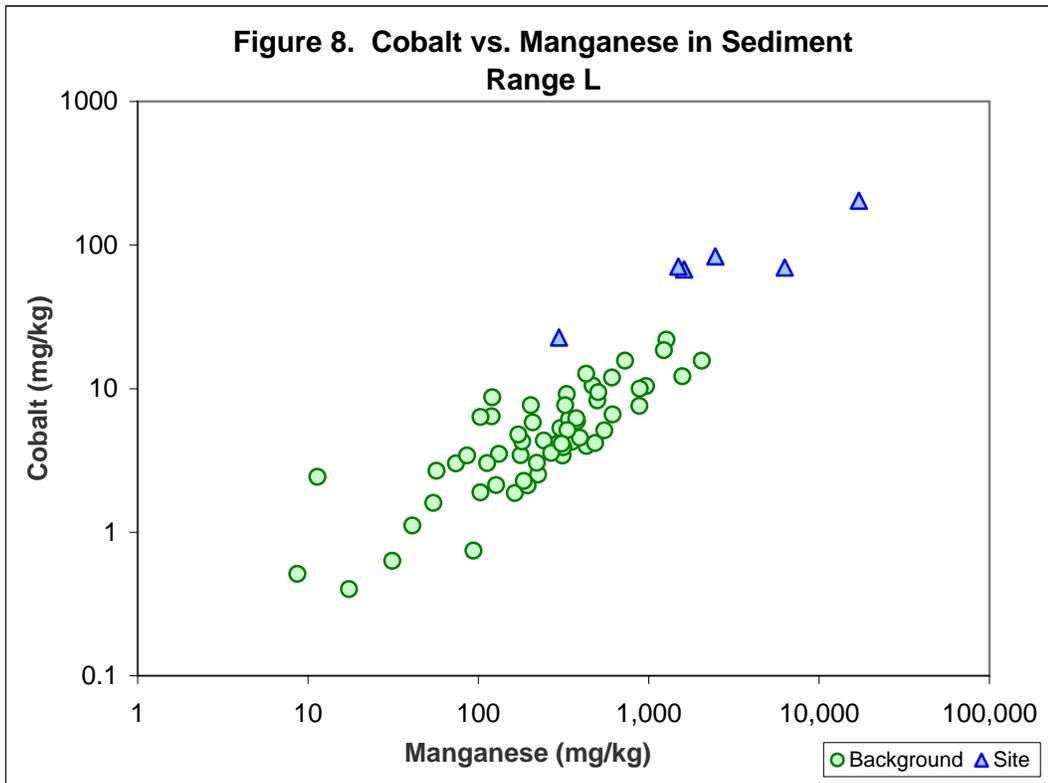
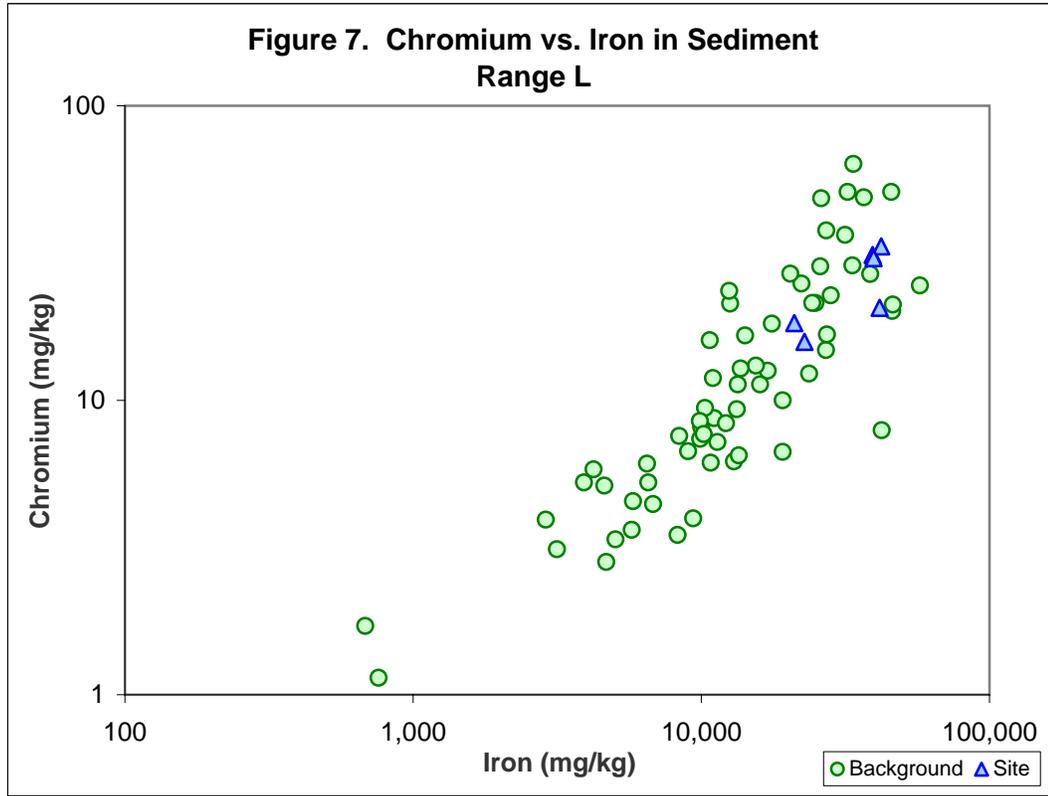
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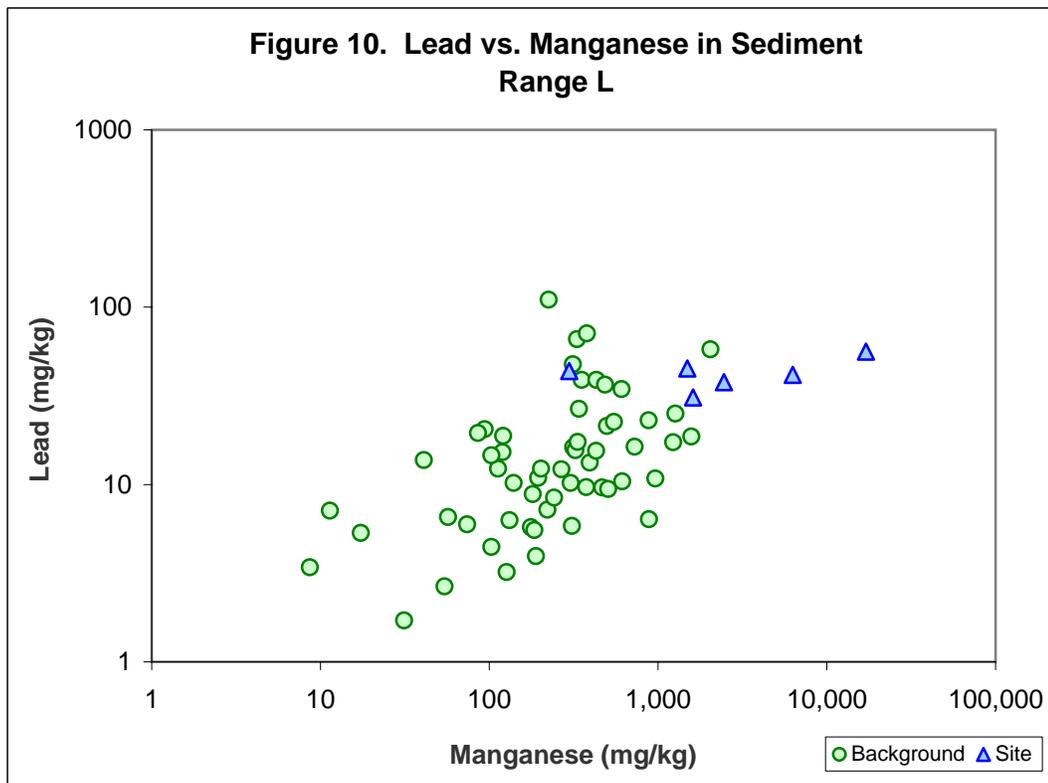
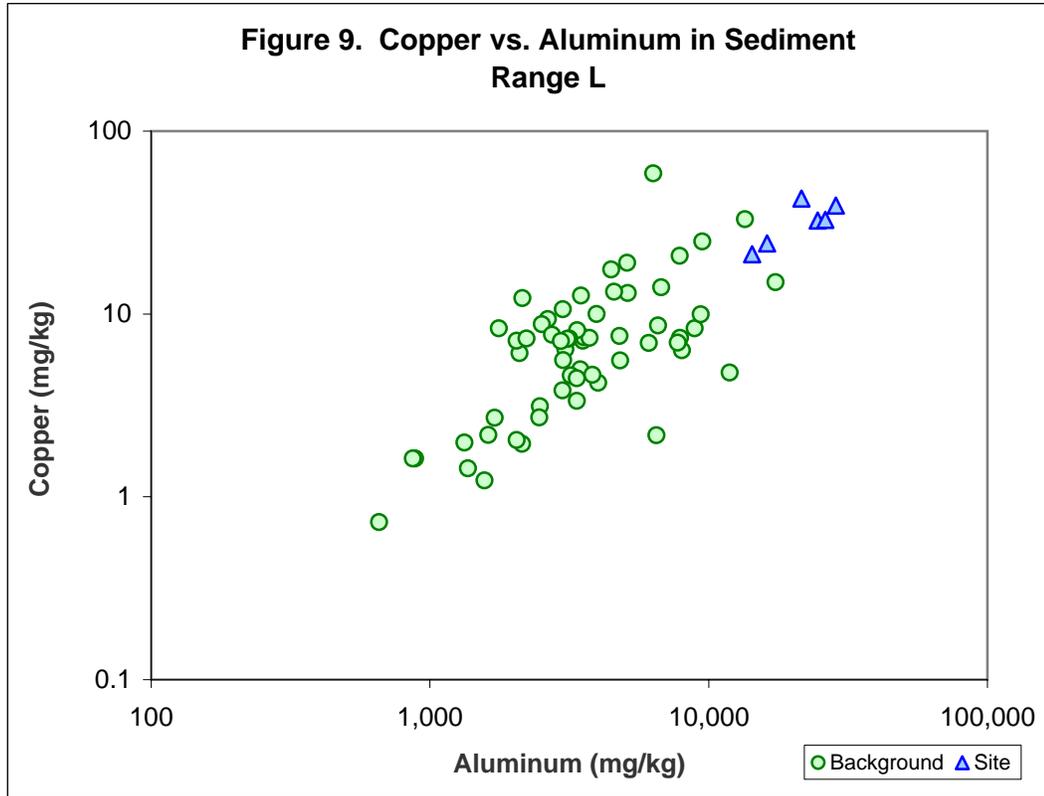
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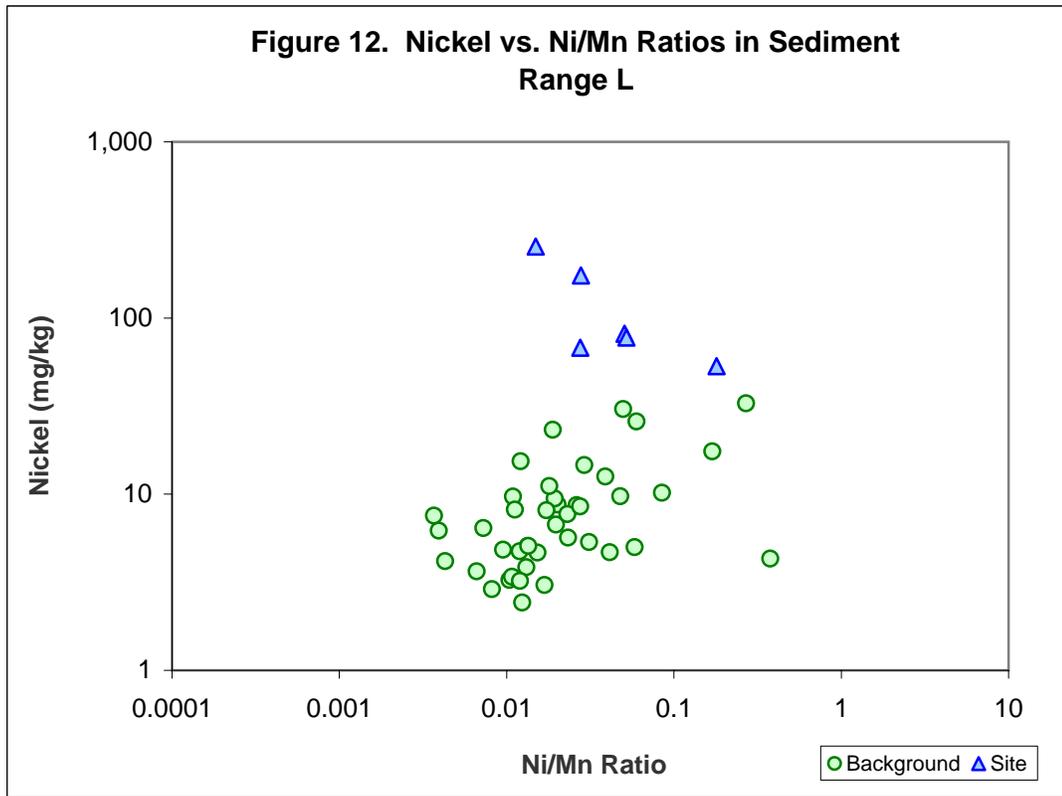
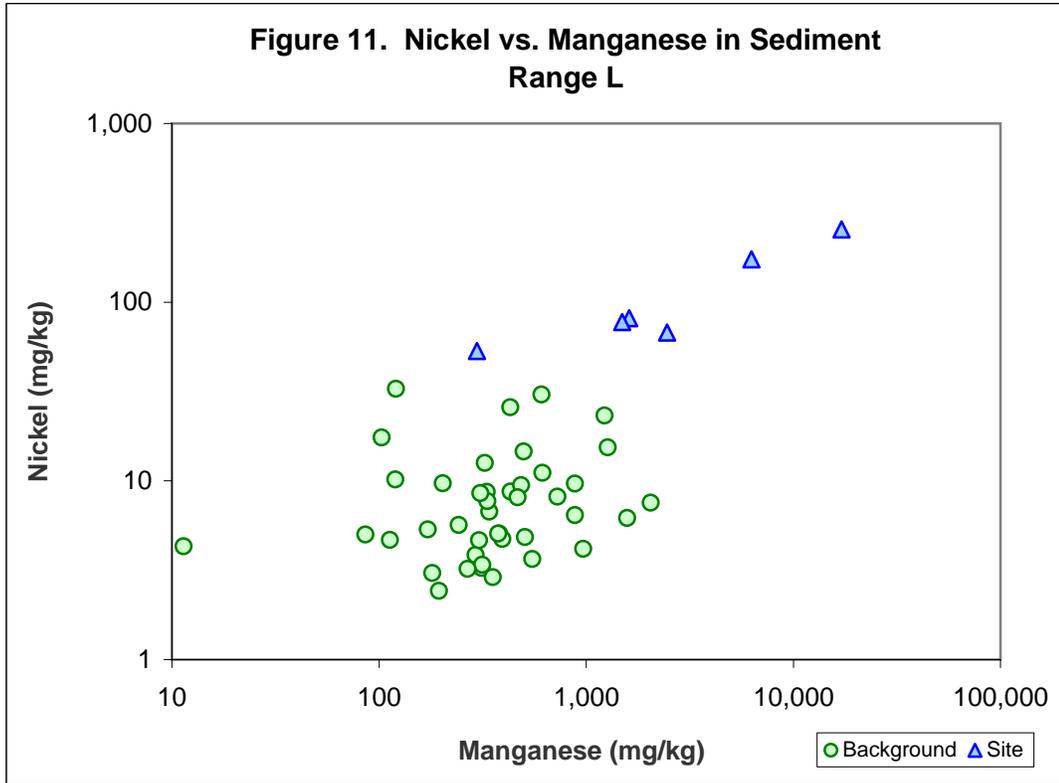
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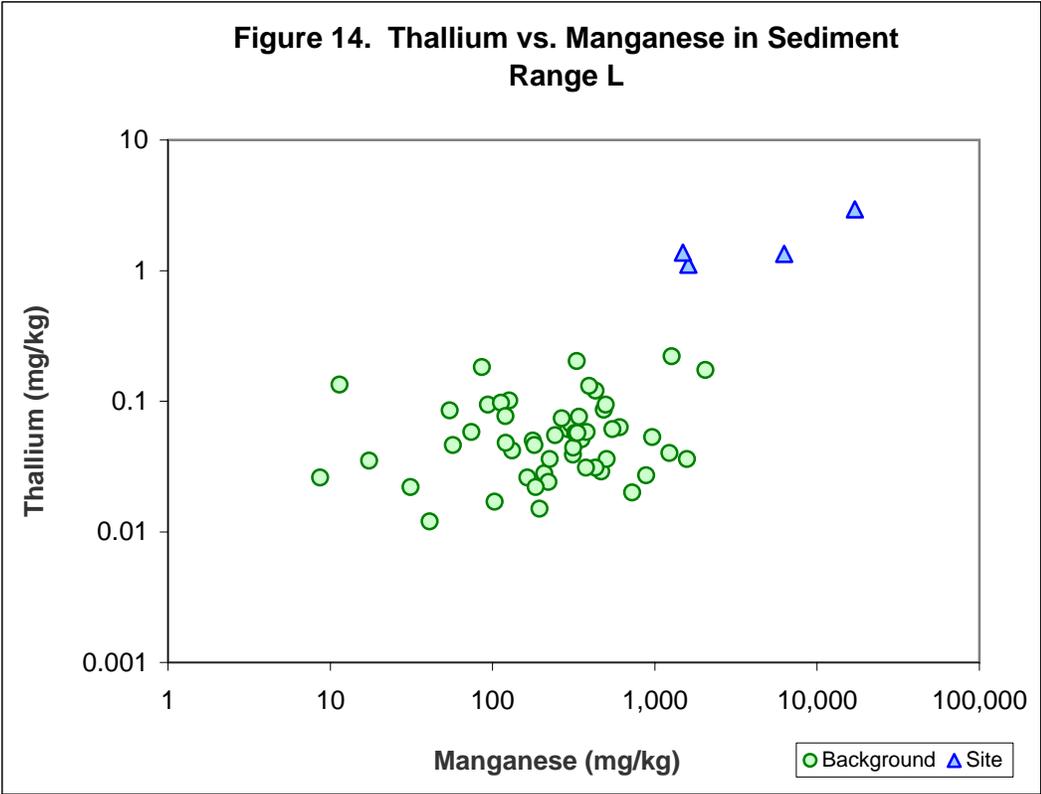
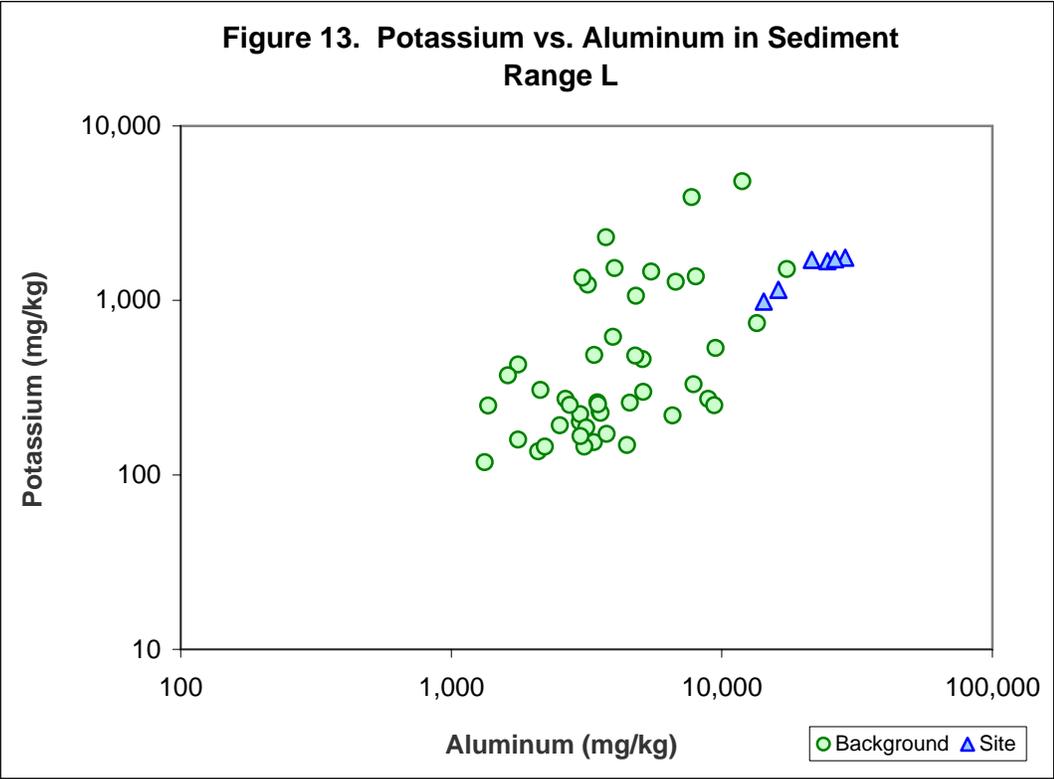


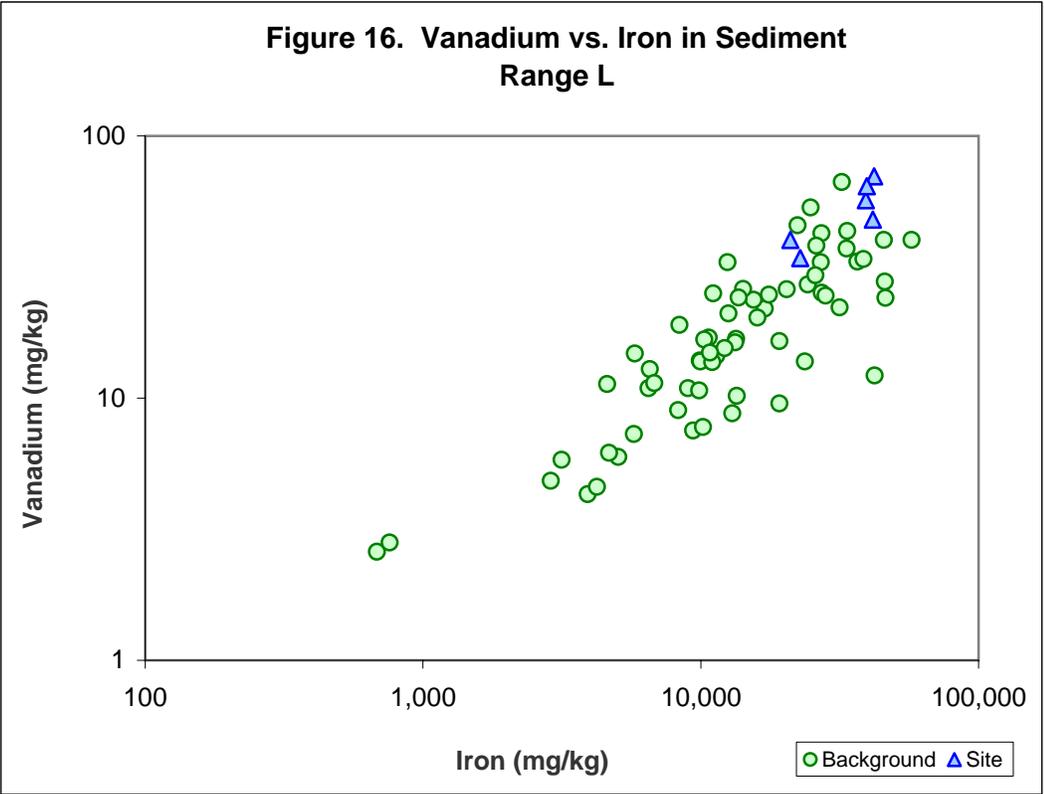
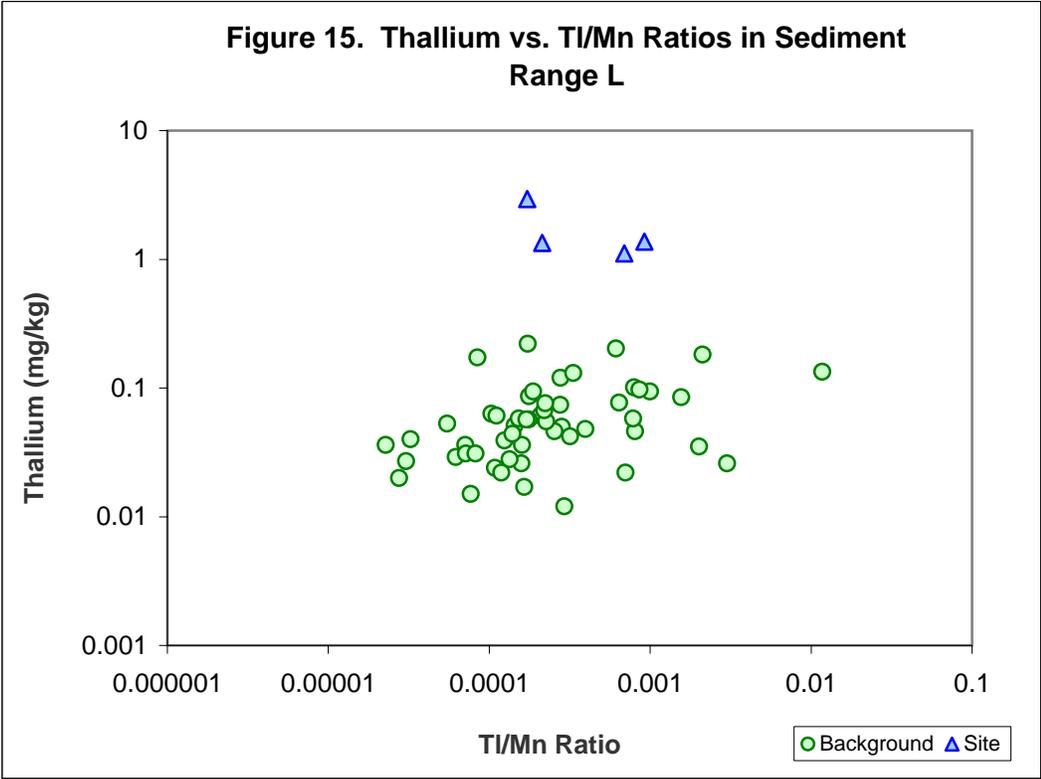


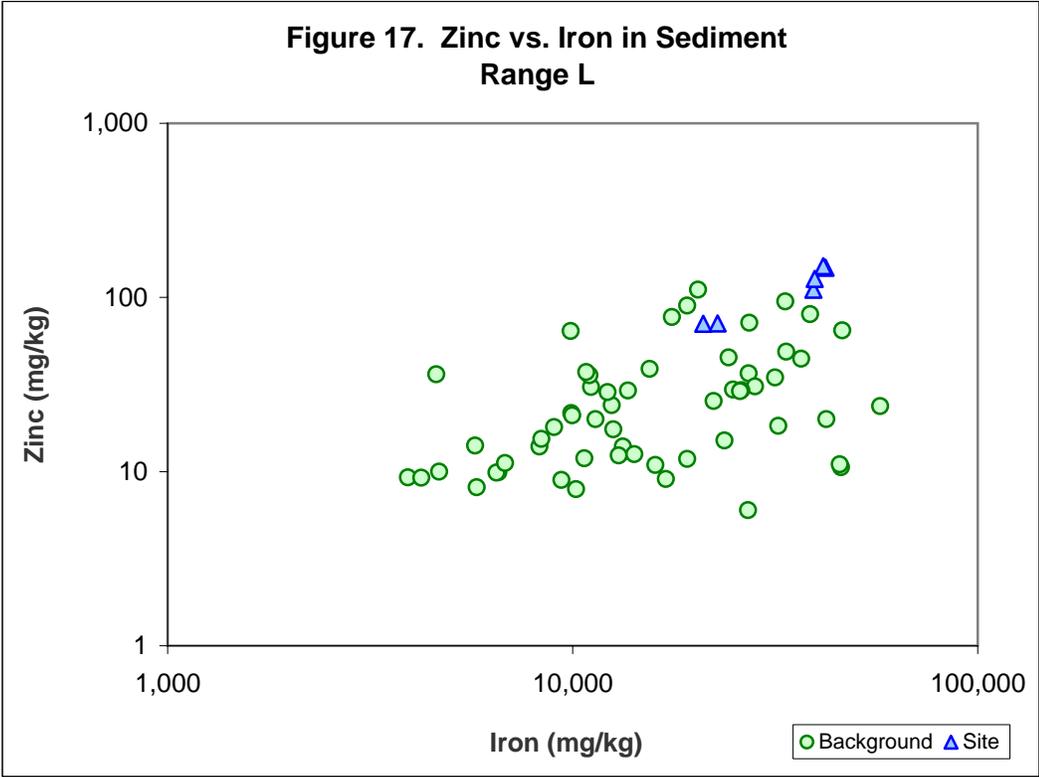


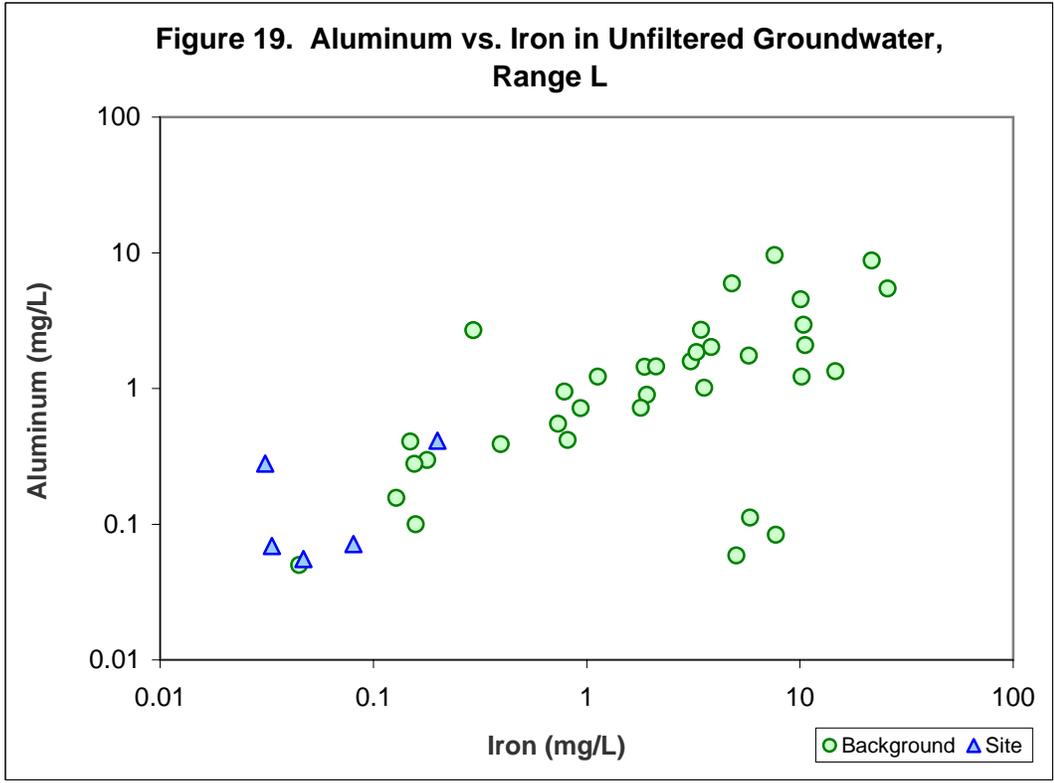
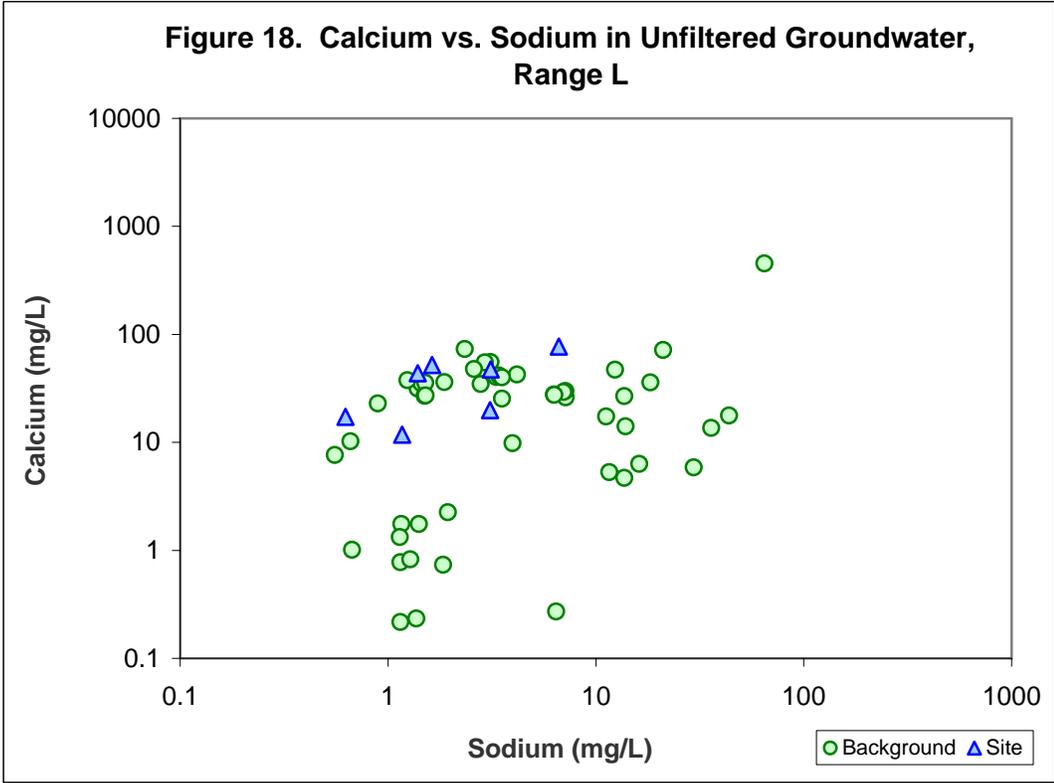












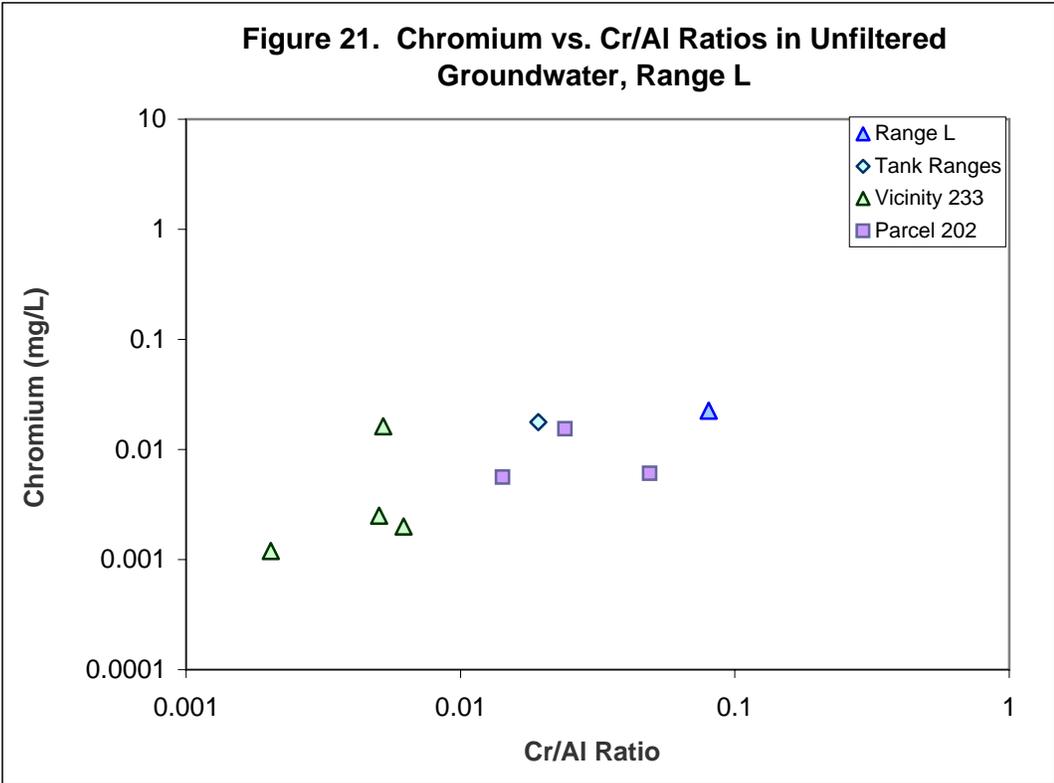
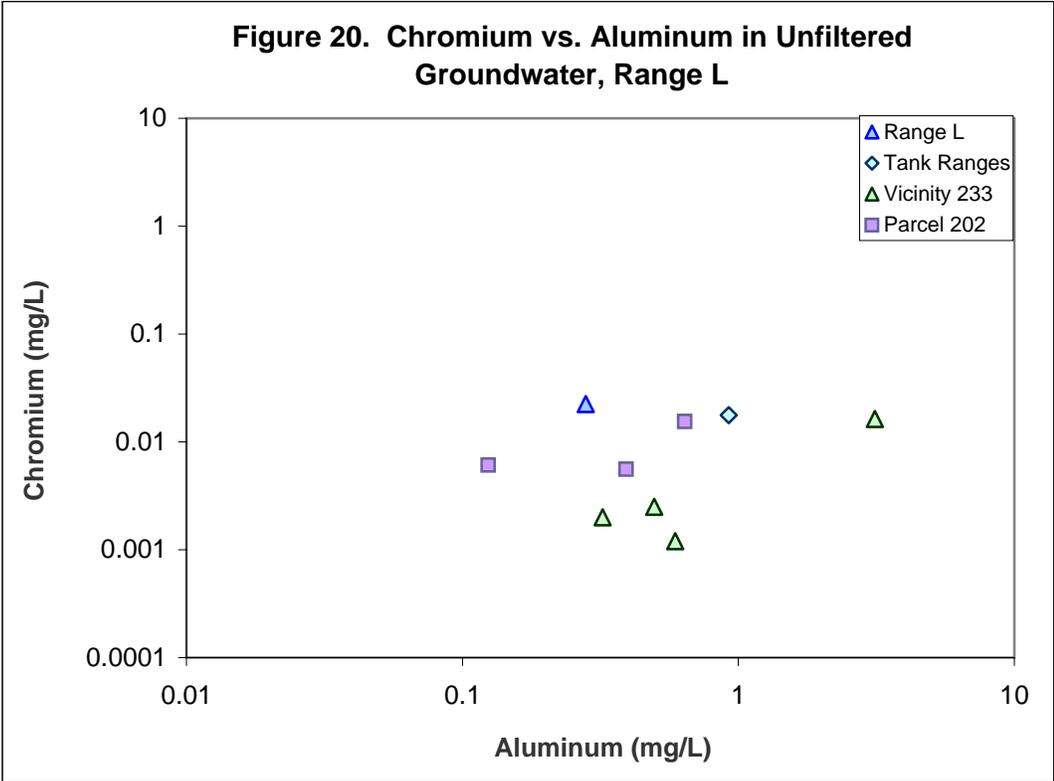
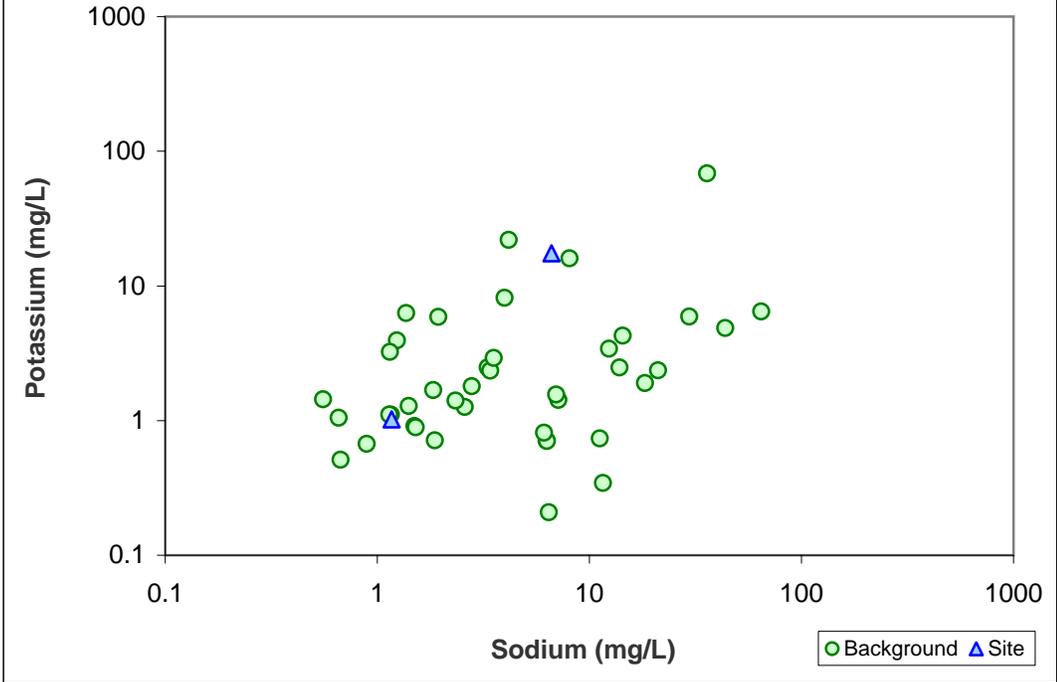


Figure 22. Potassium vs. Sodium in Unfiltered Groundwater, Range L



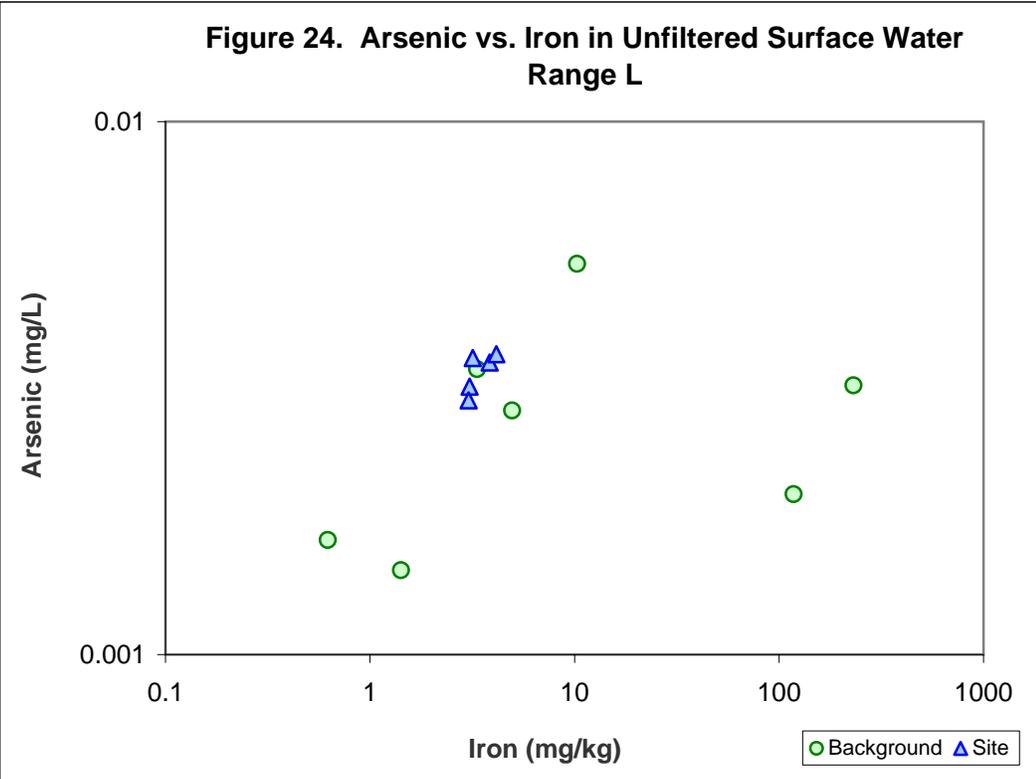
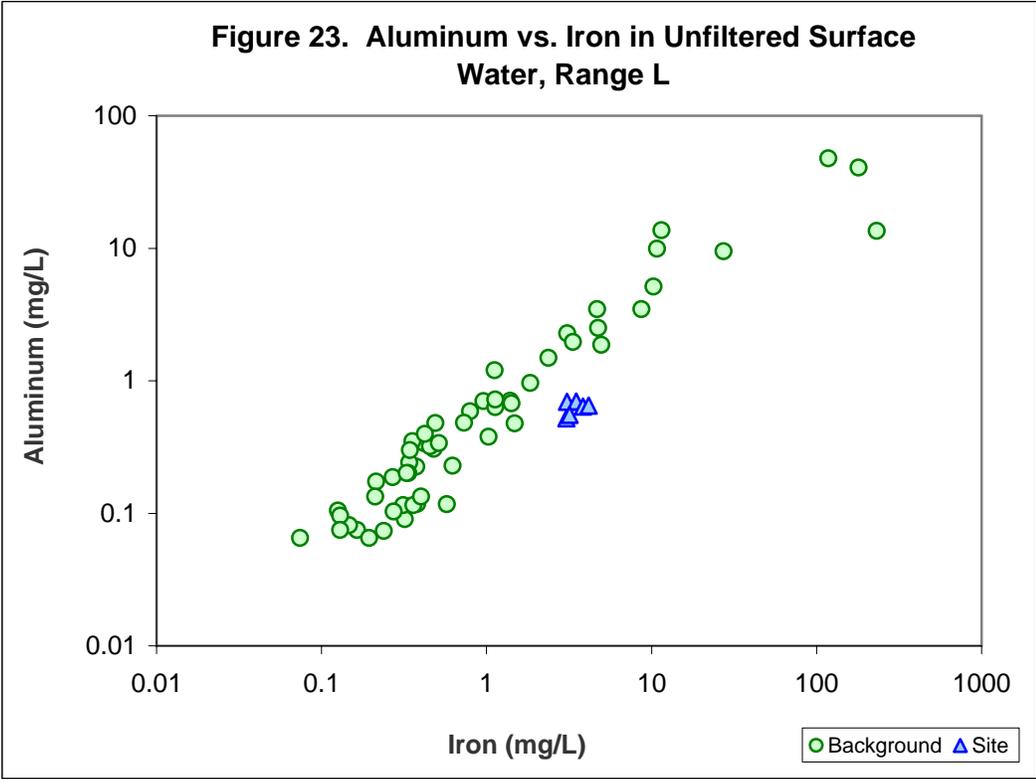


Figure 25. Cobalt vs. Manganese in Unfiltered Surface Water, Range L

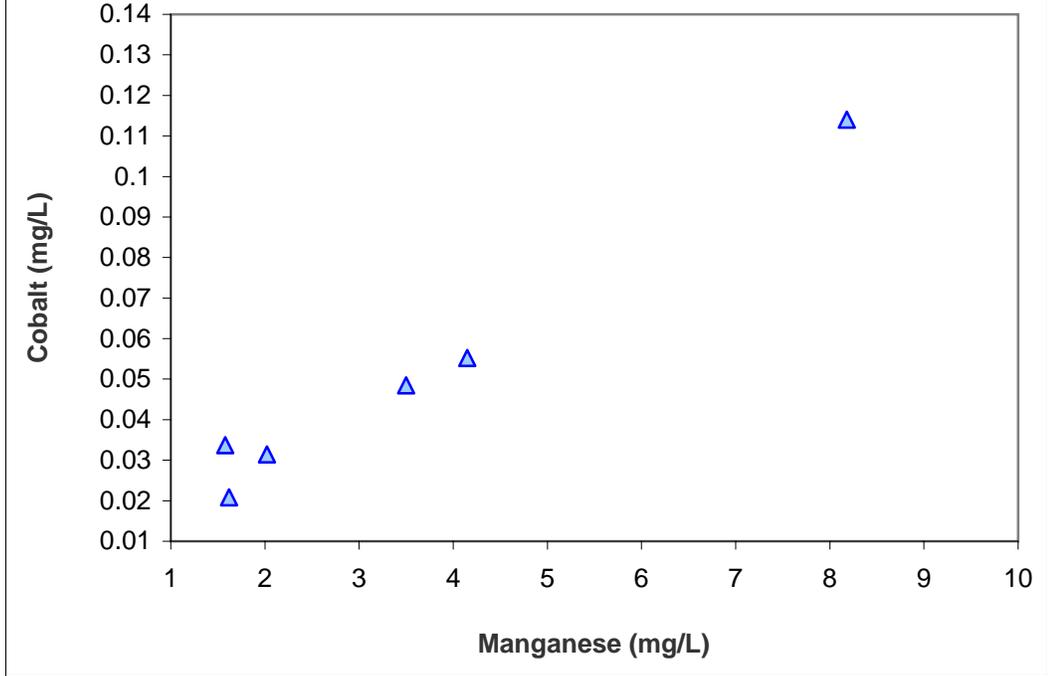
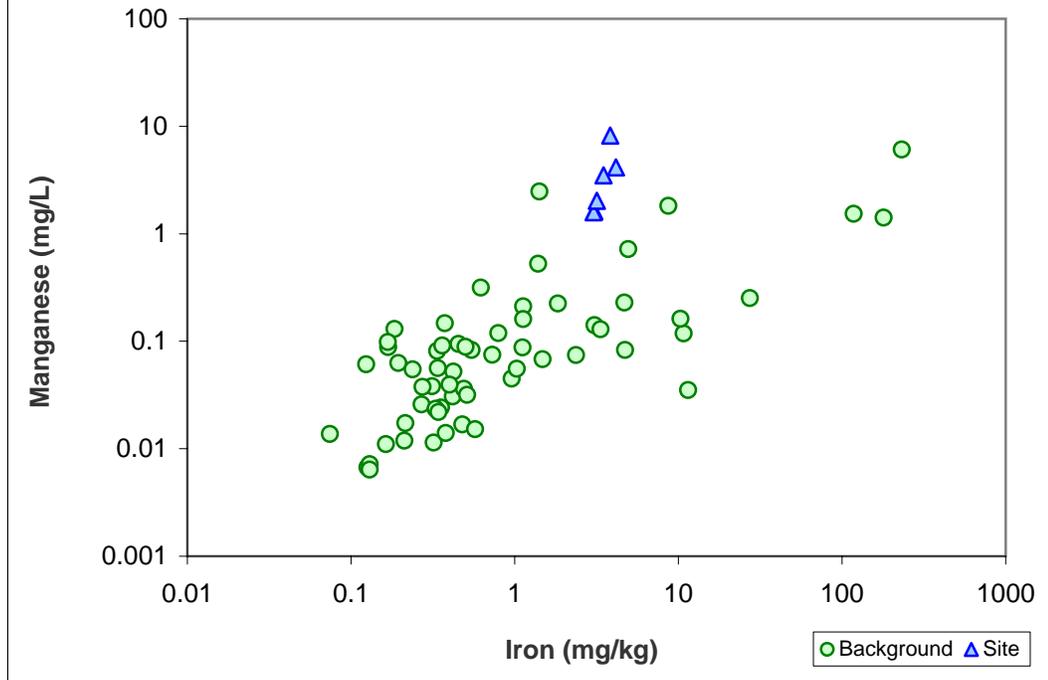
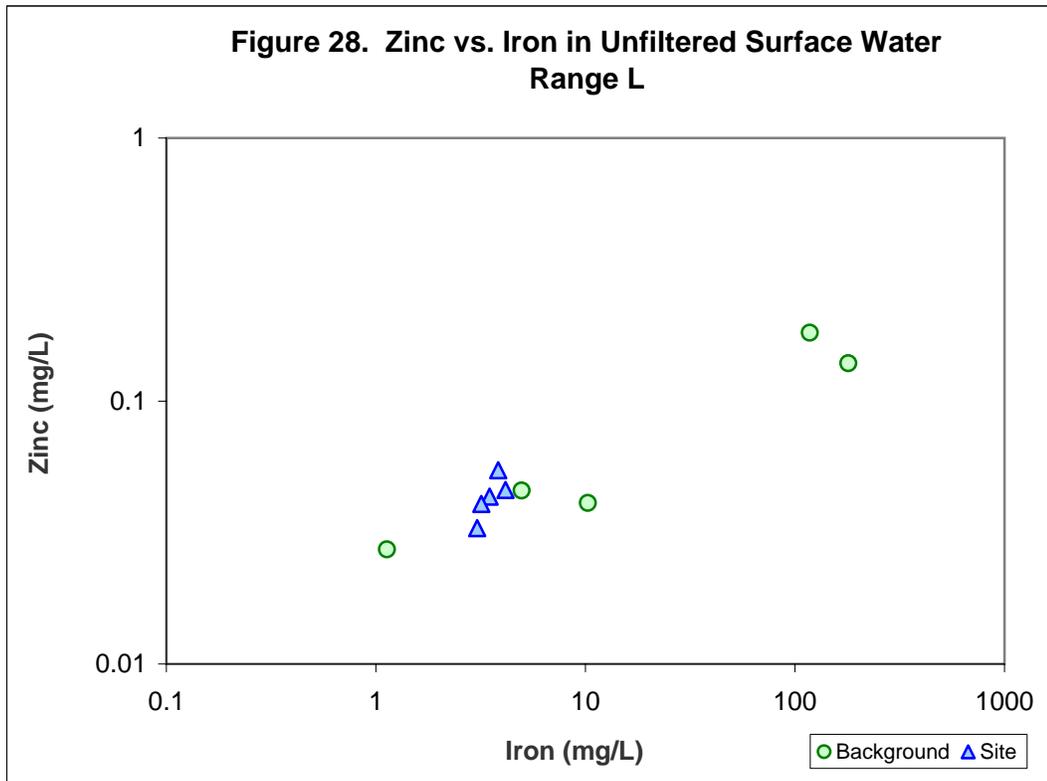
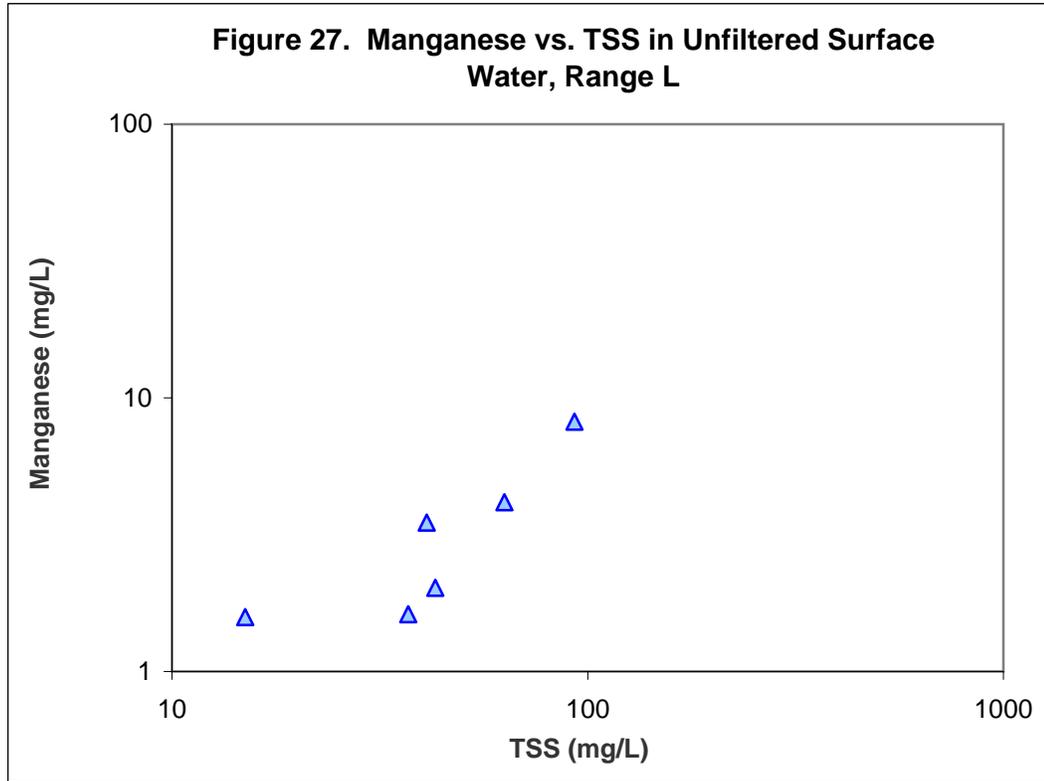


Figure 26. Manganese vs. Iron in Unfiltered Surface Water, Range L





RESPONSE TO COMMENTS

**Response to Alabama Department of Environmental Management Comments
Supplemental RI Results, Range L – Lima Pond, Parcel 204(7)
Fort McClellan, Calhoun County, Alabama
May 2003**

Comments from Stephen A. Cobb, Chief, Governmental Hazardous Waste Branch, Land Division, dated January 21, 2004.

Comment 1: The disposition of the other areas of parcel 204(7) (i.e., outside the boundary of the pond) is unclear to the Department. ADEM understands that the Army's initial RI effort identified contamination in the soil located outside the boundary of the pond. Specifically, the Army found that the soil contains human health Chemicals of Concern (metals) and COPECs (metals and benzyl alcohol) (page 2, paragraph 4). The Army's Supplemental RI data and remedy only address the pond area itself.

The July 2000 Remedial Investigation/Baseline Risk Assessment report containing RI data for Range L-Lima Pond states that the EPA risk level for all noncancer hazard indexes (HIs) and cancer risks are $HI < 1$ and cancer risk $< 1 \times 10^{-6}$ (Final RI/BRA Report, p. 8-5). No recommendation or conclusion is drawn regarding the soil contamination either in the RI/BRA report or the Supplemental RI Results report.

A "No further action" (NFA) designation for the soil and subsurface soil does not appear warranted until these issues are further explained and resolved. The Army should provide the status and recommendation for the parcel in its entirety.

Response 1: Comments noted. The parcel boundary is limited to the pond itself. Areas outside of Lima Pond will be addressed in the remedial investigation of the Former Toxic Gas Area, Parcel 211(7).

Comment 2: The Site Specific Work Plan for this investigation states that semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs) were present in the surface water of the pond and the nearby intermittent stream. However, the nearby stream apparently has not been re-sampled for verification, and the Army has presented no conclusions regarding the prior contaminants identified in the stream. The level of contamination present in the stream should be addressed, as well any related recommendations for remediation.

Response 2: See previous response.

Comment 3: Figure 2 shows a topographic map of the area; however, except for one contour (575 ft MSL), topographic contours are not provided on the map.

Thus, ADEM cannot decipher the upgradient or downgradient direction of the stream relative to the pond. As a result, ADEM cannot determine if runoff from the land around Lima pond area may potentially impact the stream.

Response 3: See response to Comment No. 1.

Comment 4: **The Army should provide a more detailed description of the proposed remedy, and present how the remedy will eliminate or appropriately reduce long term ecological risk. The Army states that it will collect confirmatory soil samples after the work is completed to verify that the area is clean. However, the scope of the proposed confirmatory sampling is not defined. When developing the proposed remedy, the Army should support its assertions with analytical data and define any anticipated land use controls that may be warranted to address future land use(s).**

Response 4: Comment noted. This type of information is typically provided in a closure plan or remedial action plan.

**Response to U.S. Environmental Protection Agency Comments
Draft Supplemental RI Results, Range L, Lima Pond, Parcel 204(7)
Fort McClellan, Calhoun County, Alabama
February 2004**

Comments from Doyle T. Brittain, U.S. Environmental Protection Agency, Senior Remedial Project Manager, dated June 12, 2003.

Specific Comments

Comment 1: **Page 2. The section on Supplemental Field Activities should contain a brief discussion of the rationale behind the selection of the surface water and sediment sampling locations.**

Response 1: Agree. Text was added explaining the rationale for selecting the surface water and sediment sampling locations.

Comment 2: **Appendix B. The reason for using chain of custody forms is to allow the reconstruction of the custody of the samples from time of collection until time of receipt by the analytical laboratory. This is accomplished by signatures at the appropriate locations on the appropriate forms. The sampling records in this appendix will not allow for the reconstruction of the COC for the following reasons.**

- **On all but six of the sample collection logs (SCLs), the sampling team blocks contained initials, not signatures as required by the guidance. Anyone can print someone else's name.**
- **On five of the SCLs, the sampling team block contained printed names, not signatures.**
- **On the remaining SCL, the sampling team members were not identified.**
- **The name of the person who signed the relinquished block on all of the chain of custody (COC) forms does not appear on the sample collection logs.**
- **On five of the COC forms, the received by block contains a printed name, not a signature.**

Response 2: Disagree. The main thrust of the reviewer's comment regards chain of custody yet the first three bullets above address irregularities with the sample collection logs (SCL). Chain of custody is documented on the COC form as noted by the reviewer in the comment. While Shaw agrees that the SCLs should have been

thoroughly completed as a matter of course, the irregularities therein do not invalidate the chain of custody because that is not their purpose.

With regard to the fourth bullet, Shaw followed the procedures outlined in Section 6.1.7.1 *Field Custody Procedures* presented in the *Draft Installation-Wide Sampling and Analysis Plan*, Revision 3, February 2002 (SAP). This sections states, "The sampling team, sample coordinator, and site manager will maintain overall responsibility for the care and custody of the samples until they are transferred or properly dispatched to the on-site screening facility and/or fixed-based laboratory." In addition, SAP Section 6.1.7.2 *Transfer of Custody and Shipment* states, "General custody of the sample will be maintained by the sample collection team members from the time of collection in the field through preparation and shipment to the laboratory. The main custody transfer will occur when the sample shipment is received into the laboratory from the field and is documented." Similar language is also provided in the QAP.

Using these two sections as guidance, all Shaw field personnel who are responsible for the collection of field samples (which includes the sample coordinator and the site manager) were considered part of the "sample team." No custody transfer record was considered necessary among members of the *same* sample collection team. If another contractor, a subcontractor to Shaw, the Army, or other personnel had collected samples and transferred them to Shaw for processing or analysis, then the transfer of custody of those samples would have been formally recorded using a COC form.

Multiple sample technicians were responsible for collecting samples and completing the sample collection logs. The samples and logs were funneled to the Shaw sample coordinator, who then reviewed the documentation, inventoried all of the samples collected, and compiled a single COC record to list all the samples collected (daily) for transfer to the receiving analytical laboratories. Therefore, the sample coordinator's signature on the form represents the transfer of custody from the Shaw sample team in the field to the analytical laboratory personnel (per Section 6.1.7.2 of the SAP). Shaw believes that this is satisfactory custody transfer documentation and, therefore, does not agree this indicates that sample custody was not maintained as stated in the comment. Shaw personnel followed the same chain-of-custody procedures that have been in effect since the beginning of the FTMC project in 1998. It is perplexing that until now these issues have never been called into question.

However, in light of recent comments received by EPA, Shaw has changed its COC procedures to include a separate COC for each sample collection team. Each sample collection team will submit samples, COCs, and SCLs to the sample coordinator. The SCLs and COCs will be reviewed by the sample coordinator prior to taking possession of the samples and signing the COC. This process will be repeated for each sample collection team in the field. The

COCs will then be copied for the field records and maintained onsite. The original forms will be transmitted to the office for filing in the project central files. In future reports, this appendix will include all "supplementary" sample team COCs to document intra-team custody transfers and all SCLs.

Regarding the last bullet: Is EPA implying that someone's "signature" can only be made through cursive writing? If an individual willingly marks a document and affirms that the mark is indeed his own, then the manner in which that mark is made and the form that mark takes are irrelevant.

Response to National Guard Bureau Comments
Draft Supplemental RI Results for Range L – Lima Pond, Parcel 204(7)
Fort McClellan, Calhoun County, Alabama (dated May 2003)

Comments from Gerald I. Walter, Chief, Environmental Programs Division, dated February 12, 2004.

Comment 1: The current investigation suggests that the contamination in all media has been substantially abated from previous levels. Please indicate this trend in the Conclusions and Recommendations Section.

Response 1: Agree. The “Conclusions and Recommendations” section was revised to indicate the decreasing trend in contamination levels at the site.

Comment 2: We anticipate that the Lima Pond area would not be used for any purpose other than a military training range. The NGB concurs with the recommendation that the fence be removed and this area re-graded to eliminate the training safety hazard. We also agree that a confirmatory sample should be taken to ensure no residual contamination is present and the results documented. Indicate the future land use for the acreage will be military training in the Conclusions and Recommendations Section. A copy of this letter will be forwarded to DA, US Army Garrison, ATTN: Environmental Restoration Manager (Ms. Karen Pinson), 291 Jimmy Parks Blvd, Fort McClellan, AL 36205-9000, and LTC Barrontine and Mr. Case, ALARNG.

Response 2: Comments noted. The “Conclusions and Recommendations” section was revised to indicate that the future land use will be military training.