APPENDIX H

STATISTICAL AND GEOCHEMICAL EVALUATIONS OF SITE METALS DATA

STATISTICAL
(TIERS I AND II)

Statistical Comparison of Site and Background Data
Training Area T-31, Parcels 184(7) and 185(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 Training Area T-31, Parcels 184(7) and 185(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 test 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 5, and described in more detail in the following sections. Site samples used in the site-to-background comparison include 11 surface soil samples (0 to 1 foot below ground surface [bgs]), 8 subsurface soil samples (2 to 8 feet bgs), 7 groundwater samples, 1 sediment sample, and 1 surface water sample that were collected at the site.

Background distributions and screening values have been established for target analyte list metals in surface soil, subsurface soil, 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 Training Area T-31 site-to-background comparison.

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,

Table 1

Summary of Tier 1 and Tier 2 Site to Background Comparison for Surface Soil
Training Area T-31, Parcels 184(7) and 185(7)
Fort McClellan, Calhoun County, Alabama

Metals	Frequency of Detection	Tier 1 Evaluation[a]	Tier 2 Evaluation: Slippage Test[b]	Tier 2 Evaluation: Wilcoxon Rank Sum Test[b]	Tier 2 Evaluation: Hot Measurement Test[b,c]	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	11 / 11	Failed	Passed	Failed	NA	Yes
Antimony	1 / 11	Failed	NA[d]	NA[e]	Passed	
Arsenic	11 / 11	Passed	NA	NA	NA	
Barium	11 / 11	Failed	Passed	Failed	NA	Yes
Beryllium	5 / 11	Failed	Passed	NA[e]	Passed	
Cadmium	0 / 11	NA	NA	NA	NA	
Calcium	10 / 11	Passed	NA	NA	NA	
Chromium	11 / 11	Passed	NA	NA	NA	
Cobalt	11 / 11	Passed	NA	NA	NA	
Copper	9 / 11	Failed	Passed	Passed	NA	
Iron	11 / 11	Passed	NA	NA	NA	
Lead	11 / 11	Failed	Passed	Passed	NA	
Magnesium	11 / 11	Failed	Passed	Failed	NA	Yes
Manganese	11 / 11	Passed	NA	NA	NA	
Mercury	4 / 11	Failed	Passed	NA[e]	Failed	Yes
Nickel	11 / 11	Passed	NA	NA	NA	
Potassium	5 / 11	Failed	Passed	NA[e]	Passed	
Selenium	2 / 11	Failed	Passed	NA[e]	Failed	Yes
Silver	1 / 11	Failed	Passed	NA[e]	Failed	Yes
Sodium	3 / 11	Passed	NA	NA	NA	
Thallium	0 / 11	NA	NA	NA	NA	
Vanadium	11 / 11	Passed	NA	NA	NA	
Zinc	10 / 11	Failed	Passed	Passed	NA	

NA = not applicable

a Tier 1 evaluation 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 Wilcoxon Rank Sum (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 Subsurface Soil
Training Area T-31, Parcels 184(7) and 185(7)
Fort McClellan, Calhoun County, Alabama

Metals	Frequency of Detection	Tier 1 Evaluation[a]	Tier 2 Evaluation: Slippage Test[b]	Tier 2 Evaluation: Wilcoxon Rank Sum Test[b]	Tier 2 Evaluation: Hot Measurement Test[b,c]	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	8 / 8	Failed	Passed	Failed	NA	Yes
Antimony	1 / 8	Failed	NA[d]	NA[e]	Passed	
Arsenic	8 / 8	Passed	NA	NA	NA	
Barium	8 / 8	Passed	NA	NA	NA	
Beryllium	3 / 8	Passed	NA	NA	NA	
Cadmium	0 / 8	NA	NA	NA	NA	
Calcium	5 / 8	Passed	NA	NA	NA	
Chromium	8 / 8	Passed	NA	NA	NA	
Cobalt	8 / 8	Passed	NA	NA	NA	
Copper	8 / 8	Passed	NA	NA	NA	
Iron	8 / 8	Passed	NA	NA	NA	
Lead	8 / 8	Passed	NA	NA	NA	
Magnesium	8 / 8	Failed	Passed	Failed	NA	Yes
Manganese	8 / 8	Passed	NA	NA	NA	
Mercury	1 / 8	Passed	NA	NA	NA	
Nickel	8 / 8	Passed	NA	NA	NA	
Potassium	5 / 8	Failed	Passed	Failed	NA	Yes
Selenium	0 / 8	NA	NA	NA	NA	
Silver	0 / 8	NA	NA	NA	NA	
Sodium	2 / 8	Passed	NA	NA	NA	
Thallium	0 / 8	NA	NA	NA	NA	
Vanadium	8 / 8	Passed	NA	NA	NA	
Zinc	8 / 8	Passed	NA	NA	NA	

NA = not applicable

a Tier 1 evaluation 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 Wilcoxon Rank Sum (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 3

Summary of Tier 1 and Tier 2 Site to Background Comparison for Groundwater
Training Area T-31, Parcels 184(7) and 185(7)
Fort McClellan, Calhoun County, Alabama

Metals	Frequency of Detection	Tier 1 Evaluation[a]	Tier 2 Evaluation: Slippage Test[b]	Tier 2 Evaluation: Wilcoxon Rank Sum Test[b]	Tier 2 Evaluation: Hot Measurement Test[b,c]	Carried Forward for Tier 3 Geochemical Evaluation
Aluminum	3 / 7	Failed	Passed	Passed	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	Passed	NA	NA	NA	
Chromium	0 / 7	NA	NA	NA	NA	
Cobalt	1 / 7	Passed	NA	NA	NA	
Copper	0 / 7	NA	NA	NA	NA	
Iron	5 / 7	Passed	NA	NA	NA	
Lead	1 / 7	Passed	NA	NA	NA	
Magnesium	7 / 7	Passed	NA	NA	NA	
Manganese	7 / 7	Failed	Passed	Failed	NA	Yes
Mercury	0 / 7	NA	NA	NA	NA	
Nickel	0 / 7	NA	NA	NA	NA	
Potassium	5 / 7	Passed	NA	NA	NA	
Selenium	0 / 7	NA	NA	NA	NA	
Silver	0 / 7	NA	NA	NA	NA	
Sodium	5 / 7	Failed	Passed	Passed	NA	
Thallium	0 / 7	NA	NA	NA	NA	
Vanadium	0 / 7	NA	NA	NA	NA	
Zinc	0 / 7	NA	NA	NA	NA	

NA = not applicable

a Tier 1 evaluation 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 Wilcoxon Rank Sum (WRS) test cannot be performed.

Table 4

Summary of Tier 1 and Tier 2 Site to Background Comparison for Sediment
Training Area T-31, Parcels 184(7) and 185(7)
Fort McClellan, Calhoun County, Alabama

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

NA = not applicable

a Tier 1 evaluation 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 Wilcoxon Rank Sum (WRS) test cannot be performed.

Table 5

Summary of Tier 1 and Tier 2 Site to Background Comparison for Surface Water
Training Area T-31, Parcels 184(7) and 185(7)
Fort McClellan, Calhoun County, Alabama

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

NA = not applicable

a Tier 1 evaluation 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 of less than 5 samples.

the use of several simultaneous tests is recommended for a valid and complete comparison of site 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 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 either of 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 in Appendix H.

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 Training Area T-31 surface soil, subsurface soil, groundwater, sediment, and surface water samples. Tables 1 through 5 summarize the Tier 1 and Tier 2 test results for each media as discussed in the following sections. Statistical test results are discussed in detail below. Box plots are also discussed below and are provided in Attachment 1.

3.1 Surface Soil

Twenty-three TAL metals were evaluated in the Training Area T-31 surface soil. Two metals (cadmium and thallium) had no detected concentrations in surface soil. No further discussion of these metals is included.

Nine metals (arsenic, calcium, chromium, cobalt, iron, manganese, nickel, sodium, and vanadium) had no detected concentrations above their respective background screening values, passing the Tier 1 evaluation. These metals are considered within the range of background and will not be tested or discussed any further.

The remaining 12 metals underwent Tier 2 evaluation. The statistical test results and box plots are discussed in detail below:

Table 1 summarizes the Tier 1 and Tier 2 test results for surface soil.

Aluminum

Tier 1 Evaluation

One site sample exceeds the background screening value of 16,306 milligrams per kilogram (mg/kg).

Tier 2 Evaluation

Slippage Test

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

WRS Test
The WRS test p-level of 0.02 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 1-1. The site minimum and interquartile range are higher than the corresponding background values. The site maximum is less than that of background.

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

Antimony

Tier 1 Evaluation
One site sample exceeds the background screening value of 1.99 milligrams per kilogram (mg/kg).

Tier 2 Evaluation
Slippage Test
The maximum value for antimony is a nondetect, so the Slippage test was not performed.

WRS Test
The WRS test was not 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 1-1). The shape and location of the site 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 of antimony is less than the background 95th percentile of 7.14 mg/kg.

Conclusion
Antimony in surface soil passed the Tier 2 evaluation and is considered to be within the range of background.

Barium

Tier 1 Evaluation
One site sample exceeds the background screening value of 123.94 mg/kg.

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 0.128 indicates a weak agreement between the site and background distributions.

Box Plot
The site minimum and interquartile range are higher than the corresponding background values (Figure 1-2). The site maximum is less than that of background.

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

Beryllium
Tier 1 Evaluation
One site sample exceeds the background screening value of 0.8 mg/kg.

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

WRS Test
The WRS test was not 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 1-2). The shape and location of the site box plot are influenced by the percentage of nondetects (55 percent), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test
The site MDC for beryllium is less than the background 95th UTL of 1.189 mg/kg.

Conclusion
Because beryllium in surface soil passed the Tier 2 evaluation, it is considered to be within the range of background.

Copper

Tier 1 Evaluation

Three site samples exceed the background screening value of 12.71 mg/kg.

Tier 2 Evaluation

Slippage Test

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

WRS Test

The WRS test p-level of 0.725 indicates a strong agreement between the site and background distributions.

Box Plot

The site 25th percentile and median are lower than the corresponding background values (Figure 1-3). The site minimum, 75th percentile, and maximum are higher than the corresponding background values.

Conclusion

Copper in surface soil is considered to be within the range of background.

Lead

Tier 1 Evaluation

Three site samples exceed the background screening value of 40.05 mg/kg.

Tier 2 Evaluation

Slippage Test

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

WRS Test

The WRS test p-level of 0.61 indicates a strong agreement between the site and background distributions.

Box Plot

The site 25th percentile and median are lower than the corresponding background values (Figure 1-3). The site minimum, 75th percentile, and maximum are higher than the corresponding background values.

Conclusion

Lead in surface soil is considered to be within the range of background.

Magnesium

Tier 1 Evaluation

Two site samples exceed the background screening value of 1,033 mg/kg.

Tier 2 Evaluation
Slippage Test
K_c for magnesium is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, magnesium 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 1-4). The site maximum is lower compared to that of background.

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

Mercury

Tier 1 Evaluation
One site sample exceeds the background screening value of 0.08 mg/kg.

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

WRS Test
No WRS test was performed because the site and background data sets contain more than 50 percent nondetects.

Box Plot
The site minimum, interquartile range, and maximum are higher than the corresponding background values (Figure 1-4). The shape and location of the background and site box plots are influenced by the high percentage of nondetects (66 percent and 64 percent, respectively), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test
The site MDC of mercury is greater than the background 95th percentile of 0.125 mg/kg.

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

Potassium

Tier 1 Evaluation
Two site samples exceed the background screening value of 799.76 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 WRS test was not performed because the site data set contains more than 50 percent nondetects.

Box Plot

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

Conclusion

Potassium in surface soil is considered to be within the range of background.

Selenium

Tier 1 Evaluation

Two site samples exceed the background screening value of 0.48 mg/kg.

Tier 2 Evaluation

Slippage Test

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

WRS Test

No WRS test was performed because the site and background data sets contain more than 50 percent nondetects.

Box Plot

The site minimum and interquartile range are higher than the corresponding background values (Figure 1-5), and the site maximum is less than that of background. The shape and location of the background and site box plots are influenced by the high percentage of nondetects (99 percent and 82 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 0.563 mg/kg.

Conclusion

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

Silver

Tier 1 Evaluation

One site sample exceeds the background screening value of 0.36 mg/kg.

Tier 2 Evaluation

Slippage Test

K_c for silver is 2, and one site sample exceeds the maximum background measurement. Because $K < K_c$, silver 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 1-6). The shape and location of the site 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 of silver exceeds the background 95th percentile of 0.774 mg/kg.

Conclusion

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

Zinc

Tier 1 Evaluation

Two site samples exceed the background screening value of 40.64 mg/kg.

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 p-level of 0.385 indicates a good agreement between the site and background distributions.

Box Plot

The site minimum and maximum are lower than the corresponding background values (Figure 1-6). The site and background medians appear to be the same. The site 25th and 75th percentiles are higher than those of background.

Conclusion

Zinc in surface soil is considered to be within the range of background.

3.2 Subsurface Soil

Twenty-three TAL metals were evaluated in Training Area T-31 subsurface soil. Four metals (cadmium, selenium, silver, and thallium) had no detected concentrations in the subsurface soil samples. No further discussion of this metal is included.

Fifteen metals (arsenic, barium, beryllium, calcium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, sodium, vanadium, and zinc) had no detected concentrations above the background screening values, passing the Tier 1 evaluation. These metals are considered within the range of background and no further testing or discussion of these elements is included.

The remaining four metals underwent Tier 2 evaluation. The statistical tests and box plots are discussed in detail below.

Table 2 summarizes the Tier 1 and Tier 2 test results for subsurface soil.

Aluminum

Tier 1 Evaluation

Five site samples exceed the background screening value of 13,591 mg/kg.

Tier 2 Evaluation

Slippage Test

The critical value, K_c, for aluminum is 2. No site samples exceed the maximum background measurement. Because $K < K_c$, aluminum 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 1-7). The site and background maximums appear to be the same.

Conclusion

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

Antimony

Tier 1 Evaluation

One site sample exceeds the background screening value of 1.31 mg/kg.

Tier 2 Evaluation
Slippage Test
The maximum value for antimony is a nondetect, so the Slippage test was not performed.

WRS Test
The WRS test was not 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 1-7). The shape and location of the site box plot are influenced by the high percentage of nondetects (87 percent), and the replacement values of one-half the reporting limit, rather than detected concentrations.

Hot Measurement Test
The site MDC of antimony is less than the background 95th percentile of 7.14 mg/kg.

Conclusion
Antimony in subsurface soil passed the Tier 2 evaluation and is considered to be within the range of background.

Magnesium
Tier 1 Evaluation
Two site samples exceed the background screening value of 766.24 mg/kg.

Tier 2 Evaluation
Slippage Test
K_c for magnesium is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, magnesium 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 1-8). The site maximum is less than that of background.

Conclusion
Because magnesium in subsurface soil failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Potassium
Tier 1 Evaluation
Four site samples exceed the background screening value of 710.74 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 0.003 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 1-8). The site maximum is less than that of background.

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

3.3 Groundwater

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

Thirteen metals (antimony, arsenic, beryllium, cadmium, chromium, copper, mercury, nickel, selenium, silver, thallium, vanadium, and zinc) had no detected results in the site samples and are not discussed any further.

Seven metals had no detected concentrations that exceeded their respective background screening values, passing the Tier 1 evaluation. These metals (barium, calcium, cobalt, iron, lead, magnesium, and potassium) are considered to be within the range of background, and will not be included in any further evaluation or discussion.

The remaining three metals (aluminum, manganese, and sodium) underwent Tier 2 evaluation. The results of the statistical tests are discussed in detail below and summarized in Table 3. Box plots are provided in Attachment 1.

Aluminum

Tier 1 Evaluation
One site sample exceeds the background screening value of 2.335 mg/L.

Tier 2 Evaluation
Slippage Test
The K_c for aluminum is 2, and no site samples exceed the maximum background measurement. Because $K < K_c$, aluminum passes the Slippage test.

WRS Test
The p-level of 0.98 indicates excellent agreement between the site and background distributions.

Box Plot
The site median, 75th percentile, and maximum are lower than the corresponding background values (Figure 1-9). The site minimum and 25th percentile are higher than the corresponding background values.

Conclusion
Aluminum in groundwater is considered to be within the range of background.

Manganese

Tier 1 Evaluation
Three site samples exceed the background screening value of 0.5805 mg/L.

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

WRS Test
The p-level of 0.089 indicates weak agreement 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 manganese in groundwater failed statistical comparison to background, it will be carried forward for Tier 3 geochemical evaluation.

Sodium

Tier 1 Evaluation
One site sample exceeds the background screening value of 14.846 mg/L.

Tier 2 Evaluation
Slippage Test
The K_c for sodium is 2, and no site samples exceed the maximum background measurement for sodium. Because $K < K_c$, sodium passes the Slippage test.

WRS Test
The p-level of 0.0897 indicates weak agreement between the site and background distributions. The box plot description describes the site data as lower than that of background.

Box Plot
The site interquartile range and maximum are lower than the corresponding background values (Figure 1-10). The site minimum is slightly higher than that of background.

Conclusion
Sodium in groundwater is considered to be within the range of background.

3.4 Sediment

This section presents the results of the site-to-background comparisons for 23 TAL metals for the Training Area T-31 sediment sample. Nine metals (antimony, beryllium, cadmium, cobalt, mercury, selenium, silver, sodium, and thallium) had no detected concentrations in sediment. No further discussion of these elements is included.

The remaining 14 metals (aluminum, arsenic, barium, calcium, chromium, copper, iron, lead, magnesium, manganese, nickel, potassium, vanadium, and zinc) had no detectable concentrations exceeding their respective background screening values. Because these metals passed the Tier 1 evaluation, they are considered to be within the range of background and will not be tested or discussed any further.

Table 4 summarizes the results for sediment.

3.5 Surface Water

This section presents the results of the site-to-background comparisons for the 23 metals tested in the surface water sample from Training Area T-31. Fourteen metals (aluminum, antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, mercury, nickel, silver, vanadium, and zinc) had no detected concentrations in the site sample and are not discussed any further.

Six metals (barium, calcium, iron, manganese, potassium, and sodium) had no detected concentrations exceeding their respective background screening values. These metals are considered within the range of background based on the Tier 1 evaluation, and will not be tested or discussed further.

The remaining three metals (magnesium, selenium, and thallium) underwent Tier 2 evaluation. The results of these tests are discussed in detail below. Box plots are provided in Attachment 1.

Magnesium

Tier 1 Evaluation

One site sample exceeds the background screening value of 10.972 mg/L.

Tier 2 Evaluation

Slippage Test

The critical value, K_c, for magnesium is 1. No site samples exceed the maximum background measurement. Because $K < K_c$, magnesium passes the Slippage test.

WRS Test

The site data set consists of one sample, and the WRS test is not performed on data sets less than 5.

Box Plot

The box plot is not created because the site data set has just one sample.

Hot Measurement Test

The site MDC for magnesium is less than the background 95th UTL of 50.536 mg/L.

Conclusion

Magnesium in surface water passed the Tier 2 Evaluation and is considered to be within the range of background.

Selenium

Tier 1 Evaluation

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

Tier 2 Evaluation

Slippage Test

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

WRS Test

The site data set consists of one sample, and the WRS test is not performed on data sets less than 5.

Box Plot

The box plot is not created because the site data set has just one sample.

Hot Measurement Test

The site MDC for selenium is less than the background 95th percentile of 0.005 mg/L.

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

Thallium

Tier 1 Evaluation
One site sample exceeds the background screening value of 0.00249 mg/L.

Tier 2 Evaluation
Slippage Test
K_c for thallium is 1, and 1 site sample exceeds the maximum background measurement. Because $K \leq K_c$, thallium passes the Slippage test.

WRS Test
The site data set consists of one sample, and the WRS test is not performed on data sets less than 5.

Box Plot
The box plot is not created because the site data set has just one sample.

Hot Measurement Test
The site MDC for thallium exceeds than the background 95th percentile of 0.002 mg/L.

Conclusion
Because thallium 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 site data from Training Area T-31, Parcels 184(7) and 185(7) and the background data for 23 TAL elements in surface soil, subsurface soil, groundwater, sediment, and surface water includes 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 Wilcoxon rank sum test. Box-and-whisker plots were prepared to visually compare the two data sets and properly interpret the WRS test results. If the Slippage test and/or the WRS test could not be performed, the Hot Measurement test was included as part of the Tier 2 statistical evaluation. Analytes that underwent Tier 2 evaluation and failed any component of the statistical site-to-background comparison are carried forward for Tier 3 geochemical evaluation to determine if natural processes can explain the elevated concentrations.

Tables 1 through 5 summarize the comparison test results and the metals carried forward for geochemical evaluation.

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ATTACHMENT 1

Figure 1-1

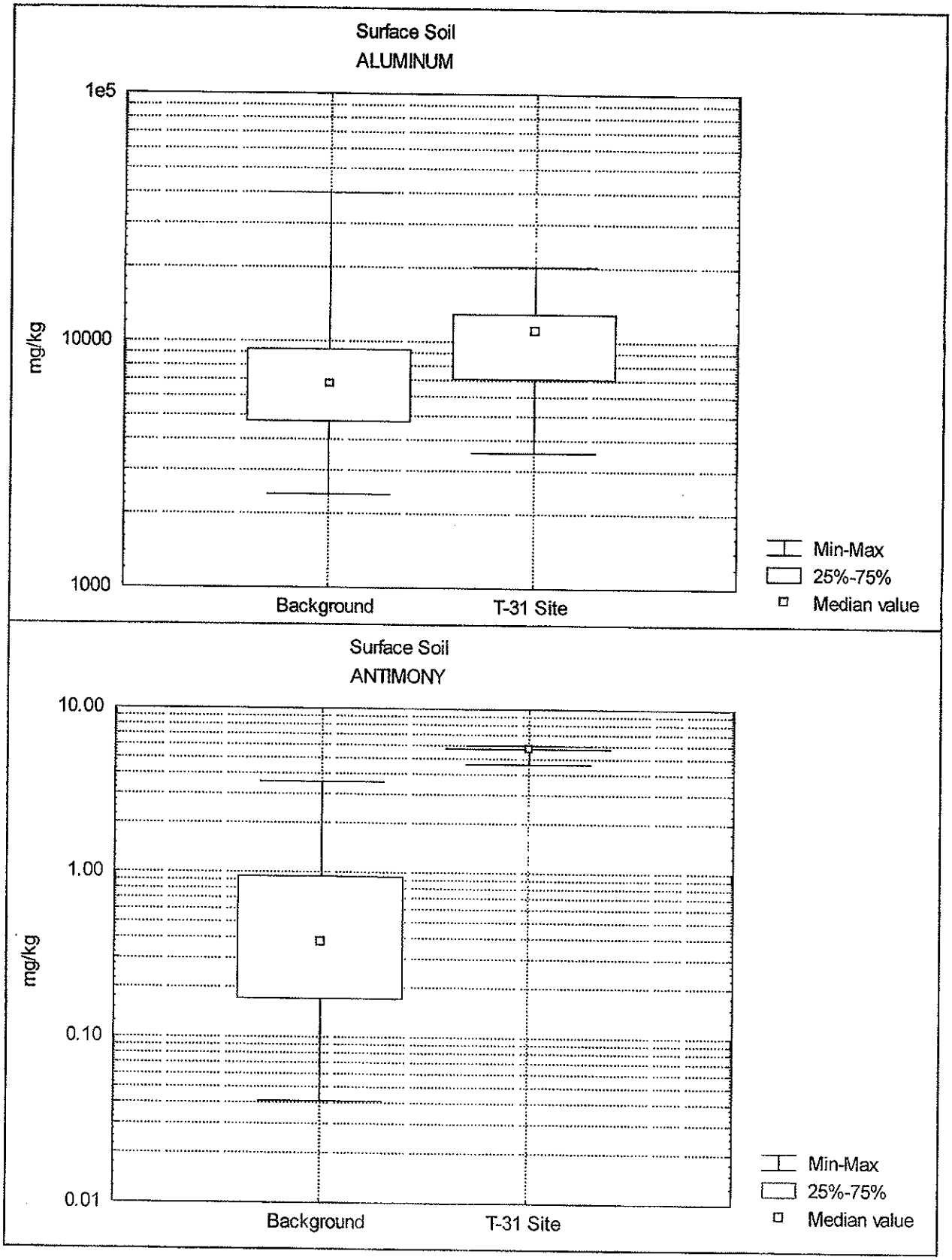
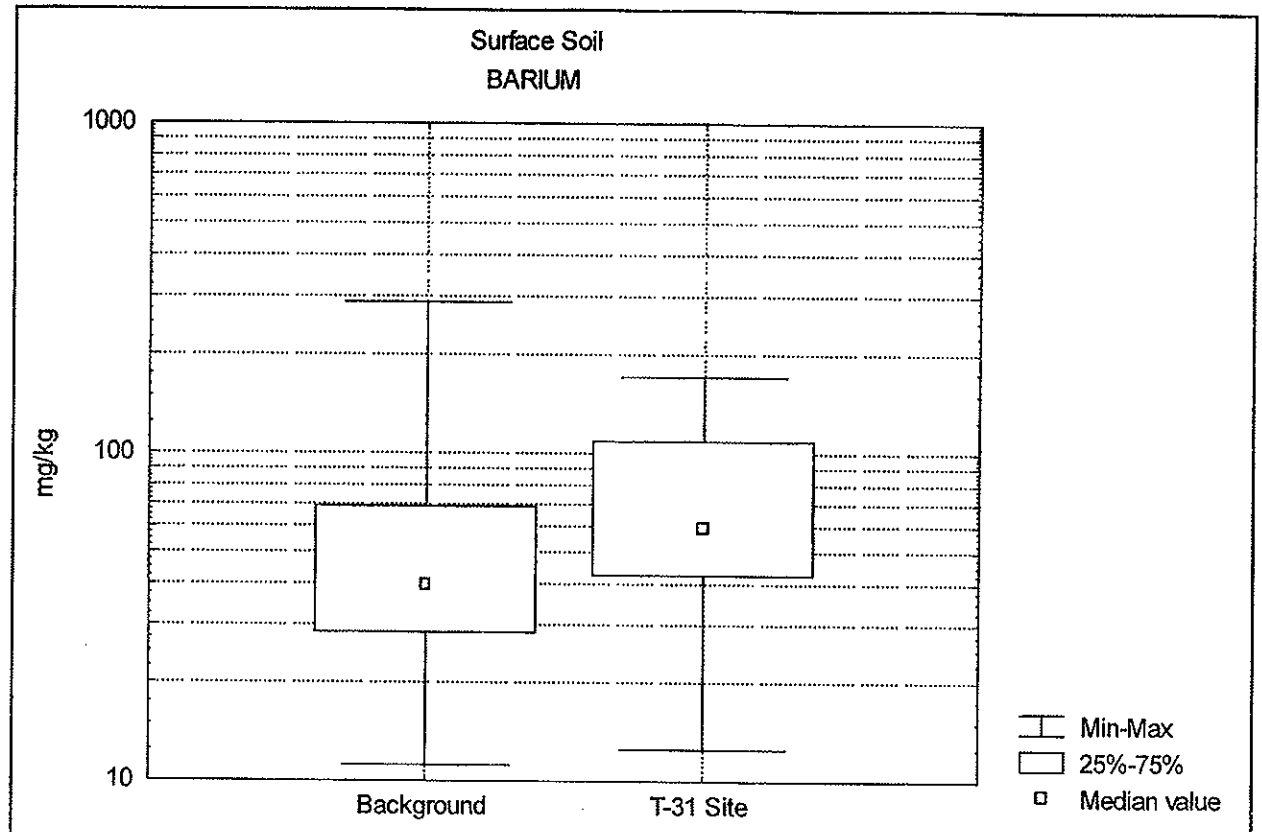

Surface Soil
ALUMINUM
1e5
10000
1000
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value
Surface Soil
ANTIMONY
10.00
1.00
0.10
0.01
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-2


Surface Soil
BARIUM
1000
100
10
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

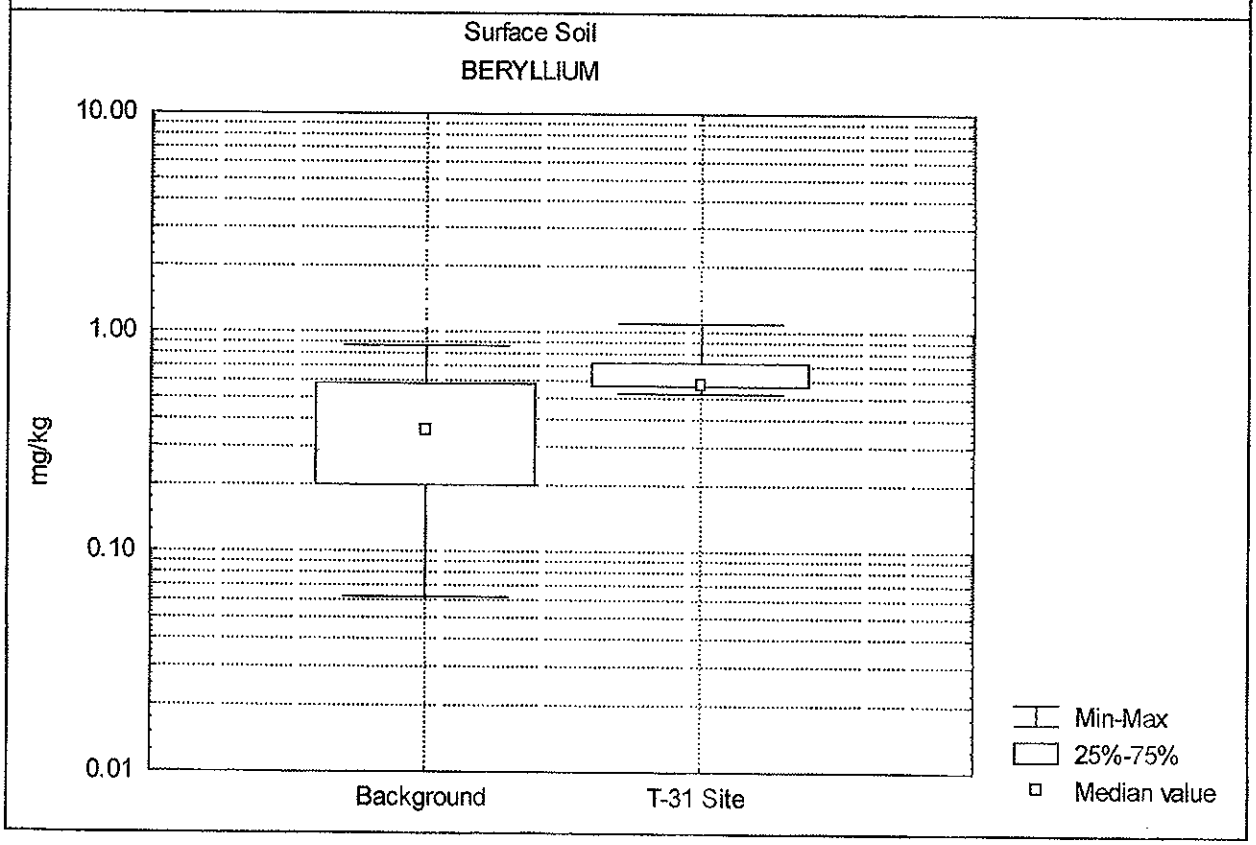

Surface Soil
BERYLLIUM
10.00
1.00
0.10
0.01
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-3

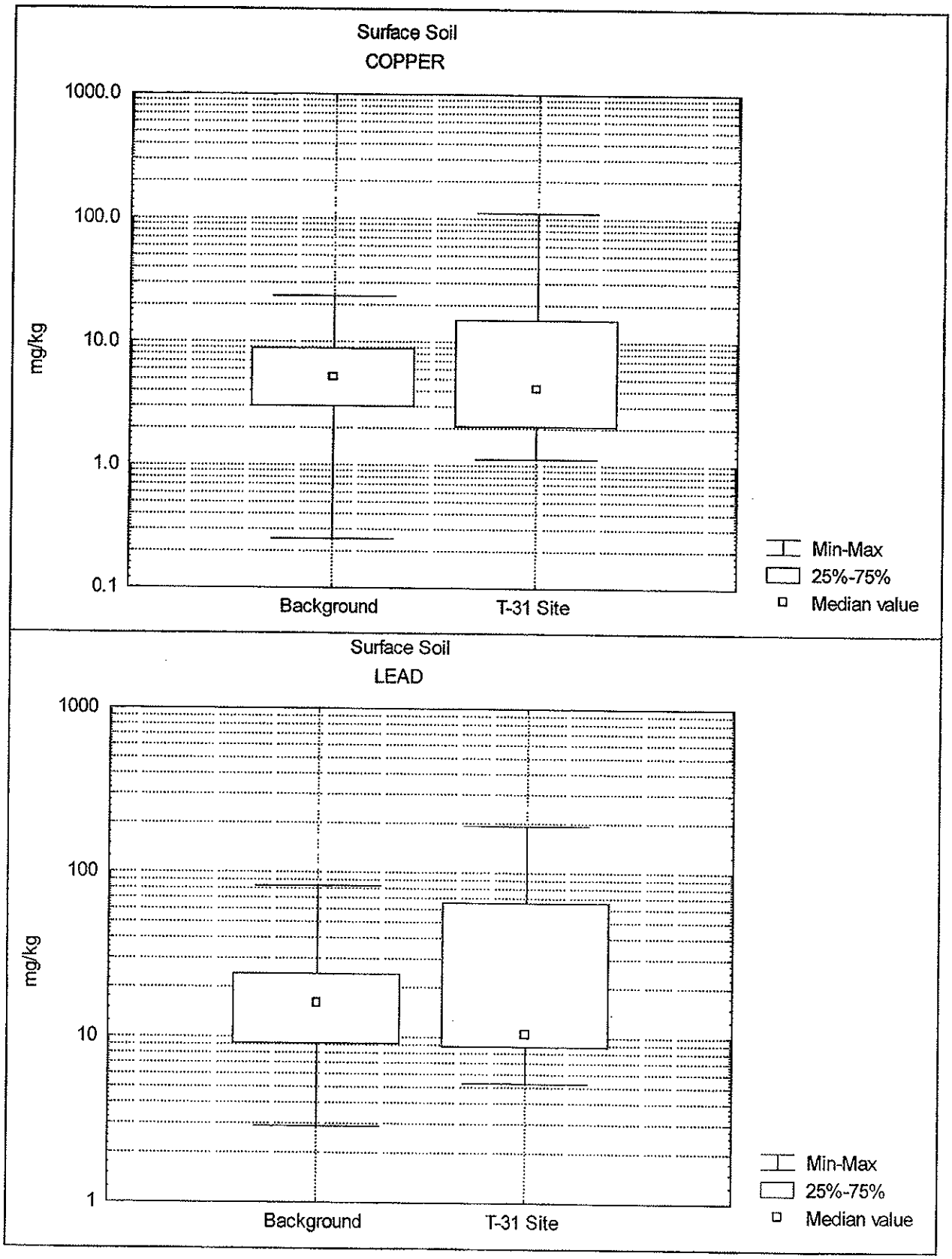

Surface Soil
COPPER
1000.0
100.0
10.0
1.0
0.1
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value
Surface Soil
LEAD
1000
100
10
1
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-4

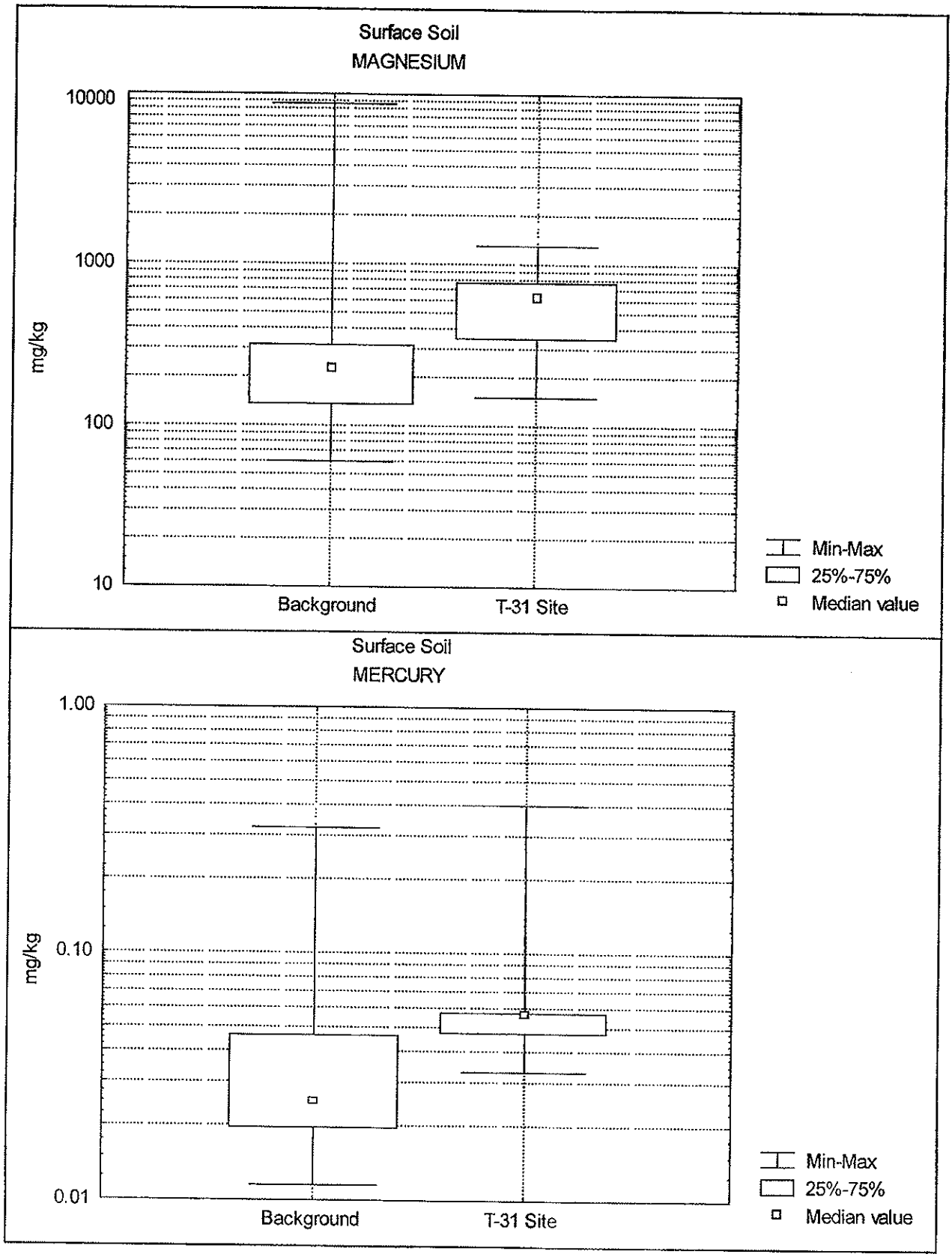

Surface Soil
MAGNESIUM
10000
1000
100
10
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value
Surface Soil
MERCURY
1.00
0.10
0.01
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-5

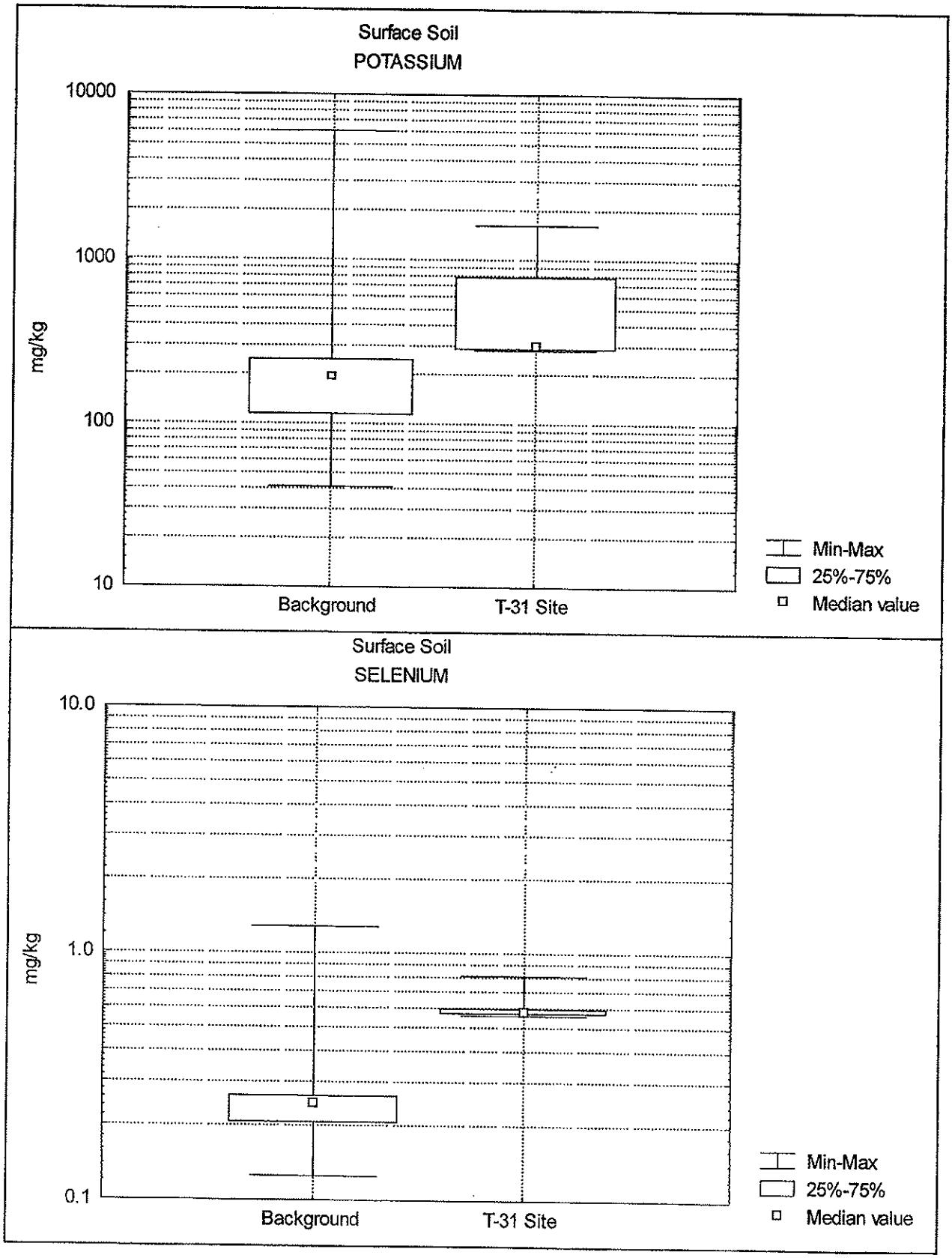

Surface Soil
POTASSIUM
10000
1000
100
10
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value
Surface Soil
SELENIUM
10.0
1.0
0.1
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-7

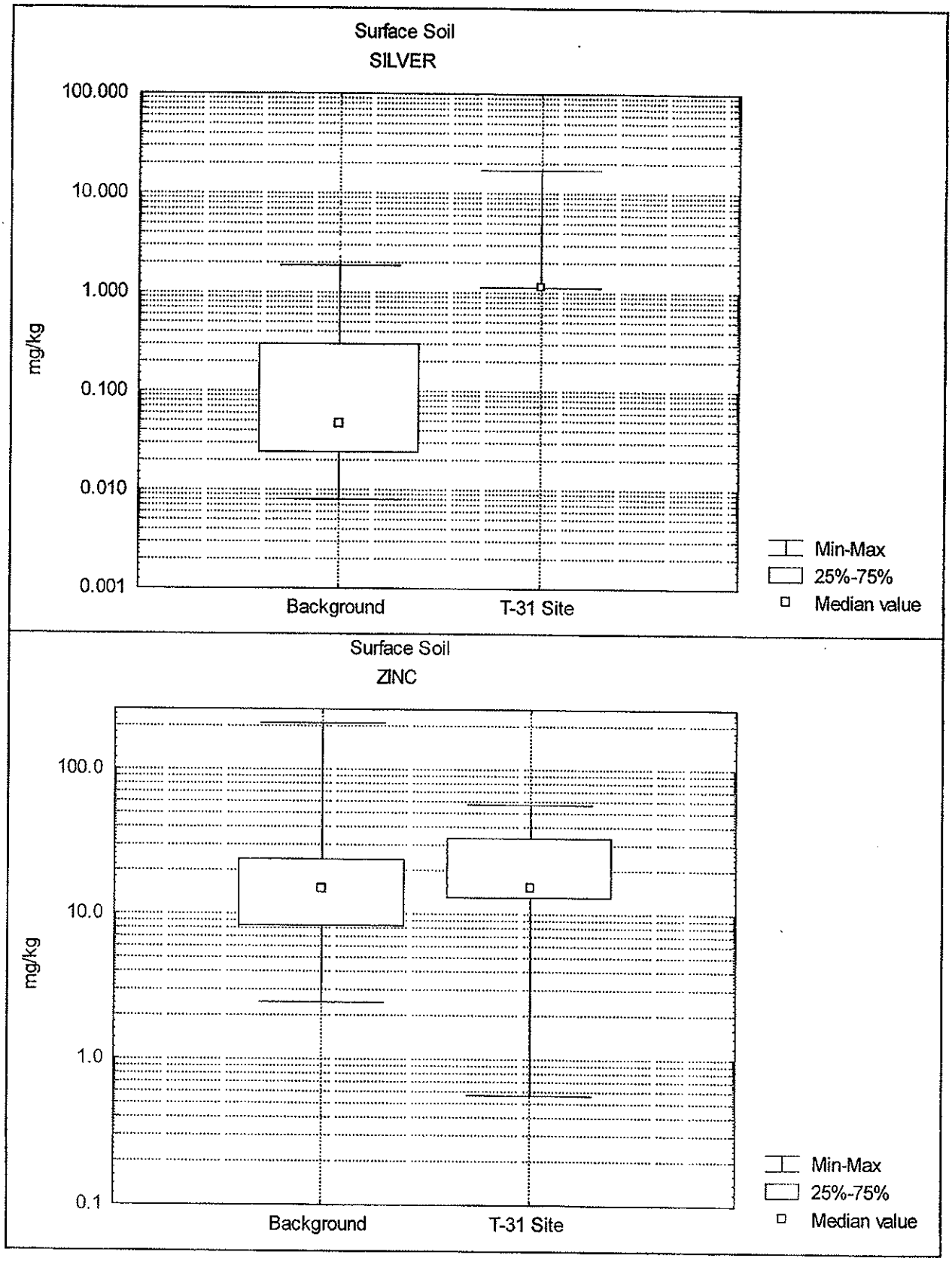

Surface Soil
SILVER
100.000
10.000
1.000
0.100
0.010
0.001
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value
Surface Soil
ZINC
100.0
10.0
1.0
0.1
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-7

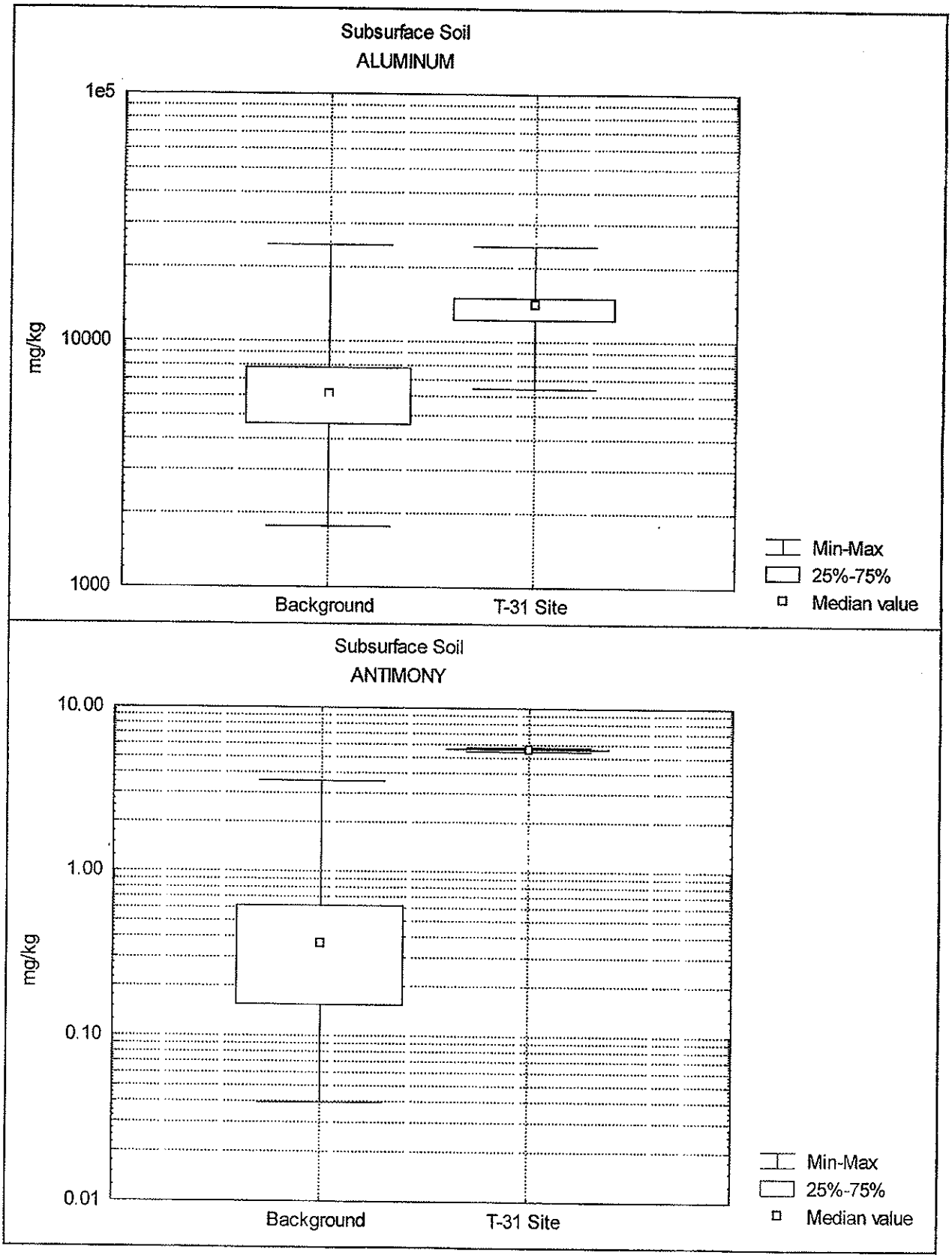

Subsurface Soil
ALUMINUM
1e5
10000
1000
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value
Subsurface Soil
ANTIMONY
10.00
1.00
0.10
0.01
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-8

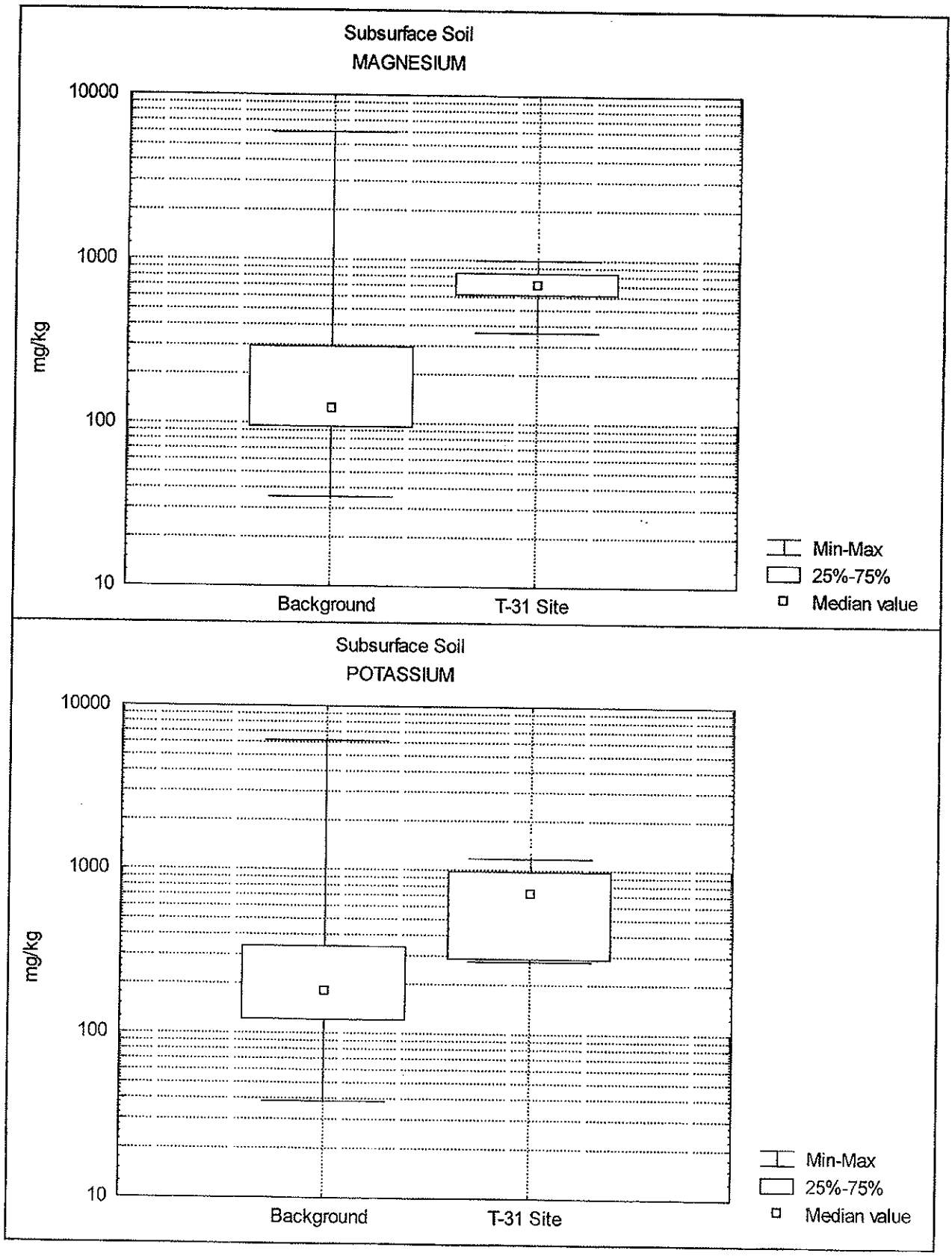

Subsurface Soil
MAGNESIUM
10000
1000
100
10
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value
Subsurface Soil
POTASSIUM
10000
1000
100
10
mg/kg
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-9

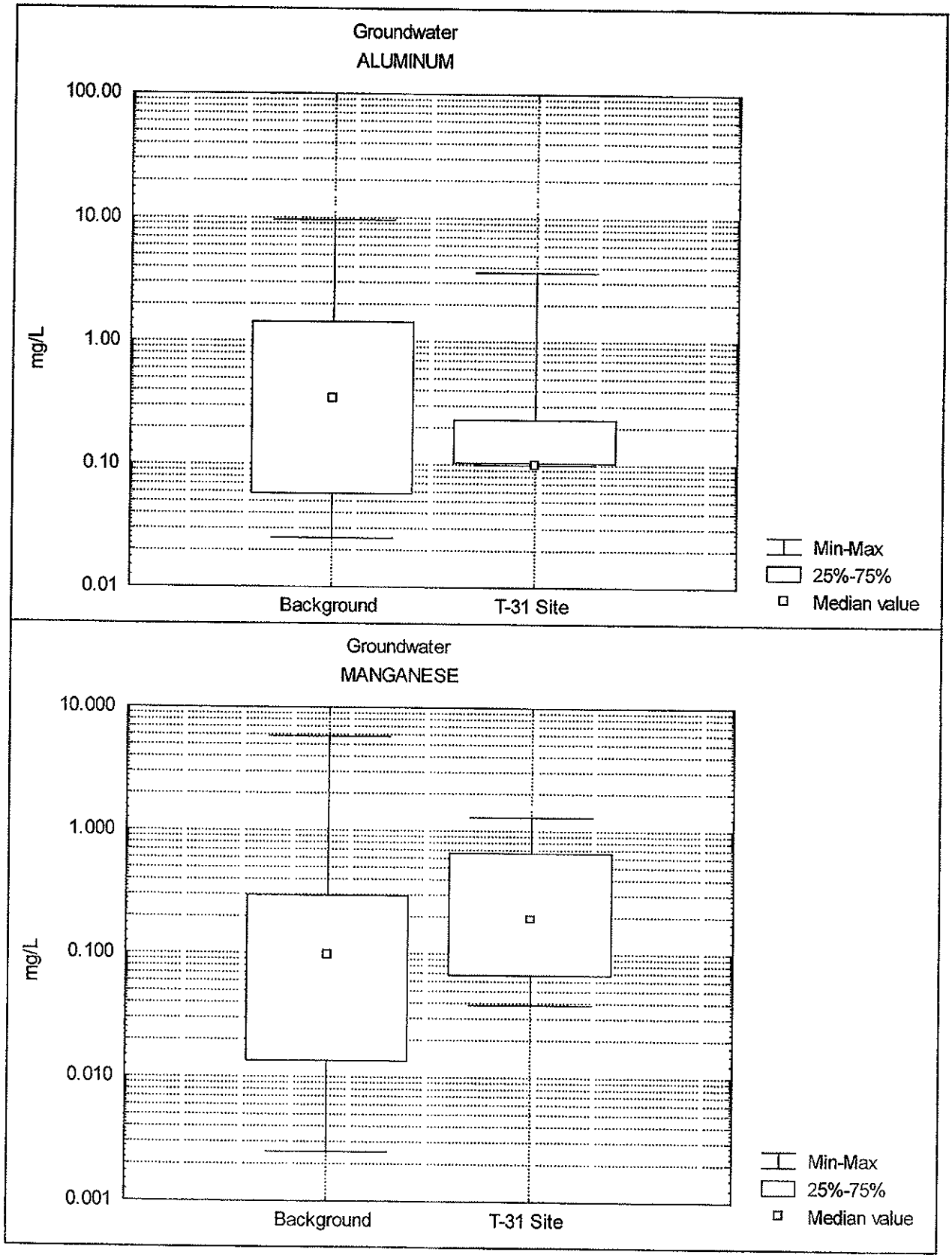
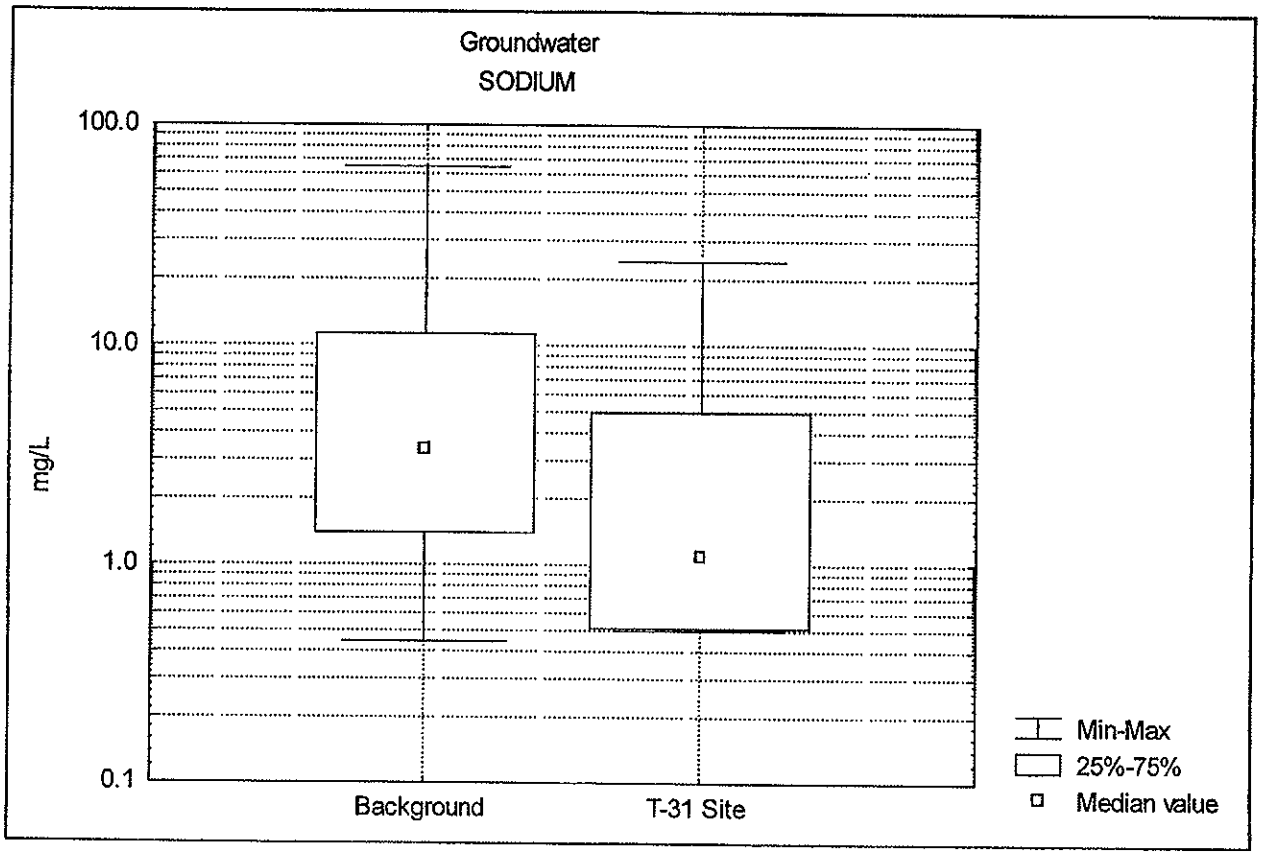

Groundwater
ALUMINUM
100.00
10.00
1.00
0.10
0.01
mg/L
Background
T-31 Site
Min-Max
25%-75%
Median value
Groundwater
MANGANESE
10.000
1.000
0.100
0.010
0.001
mg/L
Background
T-31 Site
Min-Max
25%-75%
Median value

Figure 1-10


Groundwater
SODIUM
100.0
10.0
1.0
0.1
mg/L
Background
T-31 Site
Min-Max
25%-75%
Median value

GEOCHEMICAL
(TIER III)

Geochemical Evaluation of Metals in Soil, Groundwater, and Surface Water
Training Area T-31, Parcels 184(7) and 185(7)
Fort McClellan, Alabama

1.0 Introduction

This report provides the results of a geochemical evaluation of inorganic constituents in soil, groundwater, and surface water samples from Training Area T-31, Parcels 184(7) and 185(7), at Fort McClellan in Calhoun County, Alabama. Seven elements in soil, one element in groundwater, and one element 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 eleven surface soil samples (obtained from a depth of 0 to 0.5 foot below ground surface [bgs] and 0 to 1 foot bgs) collected in October and November 2001; eight subsurface soil samples (various depths ranging from 2 to 8 feet bgs) collected in October 2001; seven unfiltered groundwater samples collected in December 2001; and one unfiltered surface water sample collected in November 2001. Installation-wide background data for TAL metals in soil, 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. Trace element distributions in uncontaminated soil 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 soil-forming 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 for Training Area T-31," 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 Training Area T-31.

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 arsenic/iron background ratio. If the samples with the highest arsenic concentrations plot on the same linear trend as the other samples, then it is most probable that the elevated concentrations are natural, and are caused by 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.

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 ($Al_2O_3 \cdot nH_2O$) and hydroxides [$Al(OH)_3$]; and iron oxide (Fe_2O_3), iron hydroxide [$Fe(OH)_3$], and iron oxyhydroxide ($FeO \cdot OH$) minerals, collectively referred to as "iron oxides." All clay minerals contain aluminum and have low solubilities over a neutral pH range of 6 to 8. Measured concentrations of aluminum in excess of ~1 milligram per liter (mg/L) indicate the presence of suspended clay minerals (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, maintaining a positive surface charge under neutral pH conditions, and have a strong tendency to adsorb negatively charged (anionic) aqueous species.

Barium, lead, and zinc are usually present in groundwater as divalent cations 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, depending on pH (Electric Power Research Institute, 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 zinc/aluminum ratio. If some samples plot above the linear trend established by the other samples, then those samples have an anomalously high zinc/aluminum ratio, and most likely contain excess zinc that cannot be explained by these natural processes.

Alternative techniques for assessing the effects of suspended particulates on trace element concentrations are the evaluation of correlations of trace element concentrations versus turbidity, 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.

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 (TCE) or tetrachloroethene under anaerobic conditions.

3.0 Results of the Geochemical Evaluation of Multiple Elements in Soil

This section presents the results of the geochemical evaluation of aluminum, barium, magnesium, mercury, potassium, selenium, and silver in soil samples from Training Area T-31. Correlation plots are provided in Attachment 1.

Aluminum

Aluminum is the most abundant element analyzed in the site soil samples, with a mean concentration of 12,320 mg/kg (1.2 weight percent). Aluminum is a primary component of common soil-forming minerals such as clays, feldspars, and micas. Aluminum also substitutes for ferric iron in iron oxide minerals, and can adsorb on iron oxide surfaces (Cornell and Schwertmann, 2003). Iron is the second most abundant element analyzed in the site soil samples (mean concentration of 11, 291 mg/kg; 1.1 weight percent), and is mostly present as iron oxides, which are common soil-forming minerals. Clays and iron oxides tend to exist as very fine particles, so both aluminum and iron are enriched in samples with finer grain sizes. The site soil boring logs note that clay or clay with some sand are the predominant soil types in many of the sampled intervals, which indicates that the site samples contain a high percentage of fine-grained material.

A plot of aluminum versus iron concentrations provides a qualitative indicator of the relative abundance of clay and iron oxide minerals in site soil (Figure 1). Site surface soil samples are represented by open triangles, site subsurface soil samples by filled triangles, and background soil samples by filled circles. For both soil intervals, the site samples exhibit slightly higher aluminum concentrations than most of the background samples and lie on or slightly above the general background trend (Figure 1). However, the site samples are linear ($R^2 = 0.73$ and 0.77 for the surface and subsurface intervals, respectively), indicating that Al/Fe ratios in the site samples are relatively constant. These observations suggest that the site samples are enriched in clays and other aluminum-bearing minerals relative to the background samples, and that the aluminum has a natural source. It is important to note that clays and iron oxides adsorb specific trace elements (as discussed in Section 2.1), so samples that plot on the upper end of the trend in Figure 1 are expected to contain proportionally higher concentrations of trace elements.

<u>Conclusion</u>

Aluminum detected in the site soil samples is naturally occurring.

Barium

Manganese oxides have an affinity to adsorb divalent cations such as barium and cobalt (Kabata-Pendias, 2001). If a soil sample contains a high proportion of manganese oxides, then it is expected to contain high concentrations of manganese and associated trace elements. The site and background samples form a collinear trend in a plot of barium versus manganese (Figure 2). The site samples with the highest barium concentrations also contain the highest manganese concentrations, and lie on the trend established by the other samples. These observations indicate that barium in the site samples is associated with manganese oxides at a relatively constant ratio, and is natural.

Conclusion

Barium detected in the site soil samples is naturally occurring.

Magnesium

Magnesium is a common component of minerals such as clays and micas, which contain aluminum as a primary constituent, so positive correlations between magnesium and aluminum concentrations in soil are often observed. A plot of magnesium versus aluminum reveals a generally linear trend for most of the background samples, and the site samples lie on this trend ($R^2 = 0.83$ and 0.76 for the site surface and subsurface intervals) (Figure 3). The site samples with high magnesium concentrations also exhibit proportionally higher aluminum content. These observations indicate a natural source for the elevated magnesium in the site samples.

Conclusion

Magnesium detected in the site soil samples is naturally occurring.

Mercury

Mercury concentrations in soil are commonly controlled through organic complex formation (Kabata-Pendias, 2001), so weak correlations between mercury and iron or mercury and aluminum are often observed, even in uncontaminated soil samples. The background samples form a weak linear trend with a positive slope in a plot of mercury versus iron (Figure 4). Most of the site samples lie on this trend. Mercury in these site samples is associated with clays at ratios consistent with those of the background samples, and is natural. Site surface soil sample TL0011, however, contains the highest mercury concentration of the site and background data sets (0.4 mg/kg) but only moderate iron (as well as only moderate aluminum and manganese), and lies above the background trend. There may be a component of contamination in this sample, which was collected from location CWM-184-DEP01.

Conclusion

The mercury concentration in surface soil sample TL0011 is anomalously high relative to the major elements, and may contain a component of contamination. Mercury detected in the other site soil samples is naturally occurring.

Potassium

Potassium and magnesium are common constituents of soil-forming minerals such as clays. Most of the background samples form a generally linear trend in a plot of potassium versus magnesium (Figure 5). The site samples are highly linear ($R^2 = 0.89$ and 0.95 for the surface and

subsurface intervals, respectively), and they all lie on the background trend. The site samples with the highest potassium also have proportionally higher magnesium, and lie on the trend established by the other samples. These observations indicate a natural source for potassium in the site samples.

Conclusion
Potassium detected in the site soil samples is naturally occurring.

Selenium

As explained in Section 2.1, selenium has a strong affinity to adsorb on iron oxides in oxic soils, so a positive correlation between selenium and iron is expected for uncontaminated soil samples. Comparison to background is hindered because of the high percentage of nondetects in the background data set. A plot of selenium versus iron is provided in Figure 6. The two site samples with detectable selenium and one of the background samples form a linear trend with a positive slope. Selenium in these samples is associated with iron oxides at a relatively constant ratio, and is natural.

Conclusion
Selenium detected in the site soil samples is naturally occurring.

Silver

A plot of silver versus iron is provided in Figure 7. Site surface soil sample TL0011 contains the highest silver concentration of the site and background data sets (17.1 mg/kg), but only moderate iron (as well as only moderate aluminum and manganese), and lies well above the trend formed by the background samples. This indicates that there may be a component of contamination in this sample, which was collected from location CWM-184-DEP01.

Conclusion
The silver concentration in surface soil sample TL0011 is anomalously high relative to the reference elements, and may contain a component of contamination.

4.0 Results of the Geochemical Evaluation of Manganese in Groundwater

This section presents the results of the geochemical evaluation of manganese in the seven unfiltered groundwater samples from Training Area T-31. Correlation plots are provided in Attachment 1.

Field-measured pH readings for the site groundwater samples range from 5.27 to 8.23 standard units, with a mean of 7.05. These values indicate neutral conditions at most of the groundwater sample locations. Field-measured DO readings range from 7.02 to 11.49 mg/L, with a mean of 9.98 mg/L, and ORP readings range from +44 to +425 millivolts (mV), with a mean of +271 mV. These values suggest oxidizing conditions at the sample locations. Turbidity

measurements range from 1.9 to 96 nephelometric turbidity units (NTU), with a mean of 18.5 NTU and median of 6.1 NTU, indicating that most of the samples did not contain a significant mass of suspended particulates. It should be noted that field readings are not available for the background samples.

Manganese

Manganese was detected in all seven site groundwater samples, with concentrations ranging from 0.0386 J to 1.29 mg/L. Manganese behaves similarly to iron in that it is redox-sensitive and soluble only under reducing conditions. Reducing conditions can be natural, or can be caused by the anaerobic degradation of chlorinated solvents or fuels. However, field readings for the site samples indicate oxidizing conditions at all of the sample locations, and the few VOCs (acetone, bromomethane, chloroform, and TCE) detected in the site samples are present at estimated concentrations below the reporting limit. Furthermore, no correlation is observed between manganese and TCE, which was detected in only three of the site samples. Under these conditions, both manganese and iron are expected to be present primarily as suspended particulates.

A plot of manganese versus iron is provided in Figure 8. Four of the site samples lie on the general background trend. The three site samples with the highest manganese concentrations (0.617, 0.662, and 1.29 mg/L) lie slightly above the trend formed by the majority of background samples. However, these concentrations are well below the background maximum of 5.82 mg/L, so any contamination, if present, would not be significant. None of the site samples exhibits excess manganese relative to background, suggesting a natural source for the manganese in the site samples.

Conclusion

Manganese detected in the site groundwater samples is naturally occurring.

5.0 Results of the Geochemical Evaluation of Thallium in Surface Water

This section presents the results of the geochemical evaluation of thallium in the single unfiltered surface water sample from Training Area T-31. Correlation plots are provided in Attachment 1.

The field-measured pH reading for the site surface water sample is 7.36 standard units, the DO reading is 6.69 mg/L, and the ORP reading is +141 mV. These values indicate neutral-pH, oxidizing conditions at the sample location. The turbidity measurement of 2.3 NTU indicates that the sample did not contain a significant mass of suspended particulates. It should be noted that field readings are not available for the background samples.

Thallium

Thallium was detected in the site surface water sample at a concentration of 0.0435 mg/L. Thallium concentrations are often controlled in surface water by adsorption on suspended iron oxides, and can be mobilized under reducing conditions if the oxides become soluble. Reducing conditions can be natural, or can be caused by the anaerobic degradation of chlorinated solvents or fuels. However, the field readings suggest oxidizing conditions at the sample location (see description above) and no VOCs were detected in the sample. Under these conditions, thallium is expected to be sorbed on suspended particulates such as iron oxides.

A plot of thallium versus iron is provided in Figure 9. Comparison to background is hindered because only one background sample contains detectable thallium. The site sample has higher thallium than the background sample, but it also has higher iron. These observations suggest that thallium in the site sample is primarily associated with suspended iron oxides, and that it is natural.

Conclusion

Thallium detected in the site surface water sample is naturally occurring.

6.0 Summary

This section summarizes the results of the geochemical evaluations of selected elements in soil, groundwater, and surface water samples from Training Area T-31.

Soil. Geochemical evaluation indicates that all of the aluminum, barium, magnesium, potassium, and selenium concentrations detected in the site surface and subsurface soil samples are naturally occurring. The mercury and silver concentrations in surface soil sample TL0011 (collected from location CWM-184-DEP01) are anomalously high relative to the reference element concentrations, and may contain a component of contamination. Mercury and silver concentrations detected in the other soil samples are naturally occurring.

Groundwater. Geochemical evaluation indicates that manganese concentrations detected in the site groundwater samples are naturally occurring.

Surface Water. Geochemical evaluation indicates that thallium detected in the site surface water sample is naturally occurring.

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ATTACHMENT 1

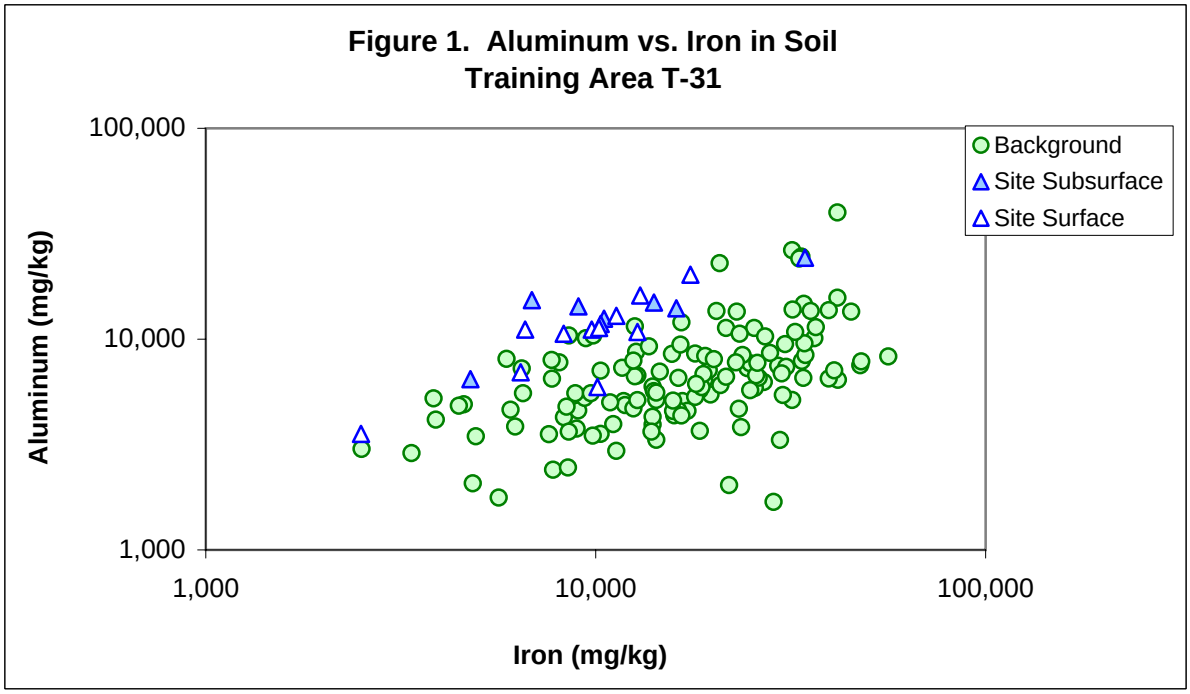
Figure 1. Aluminum vs. Iron in Soil
Training Area T-31
100,000
10,000
1,000
Aluminum (mg/kg)
1,000
10,000
100,000
Iron (mg/kg)
Background
Site Subsurface
Site Surface

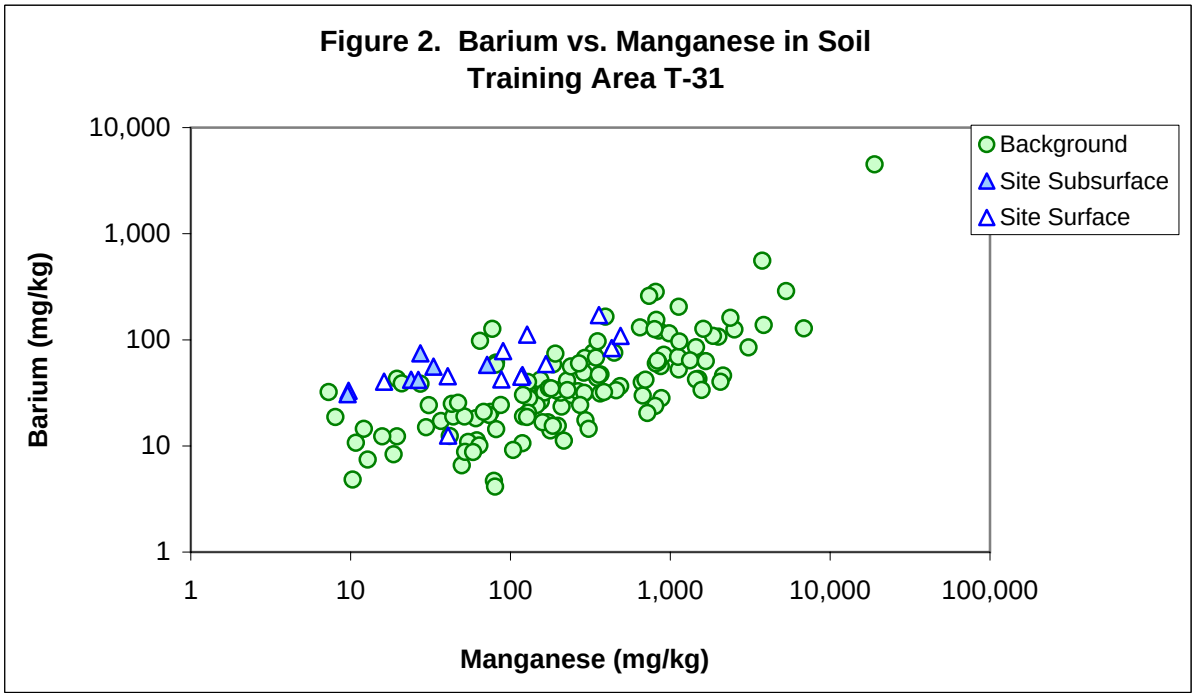
Figure 2. Barium vs. Manganese in Soil
Training Area T-31
10,000
1,000
100
10
1
Barium (mg/kg)
1
10
100
1,000
10,000
100,000
Manganese (mg/kg)
Background
Site Subsurface
Site Surface

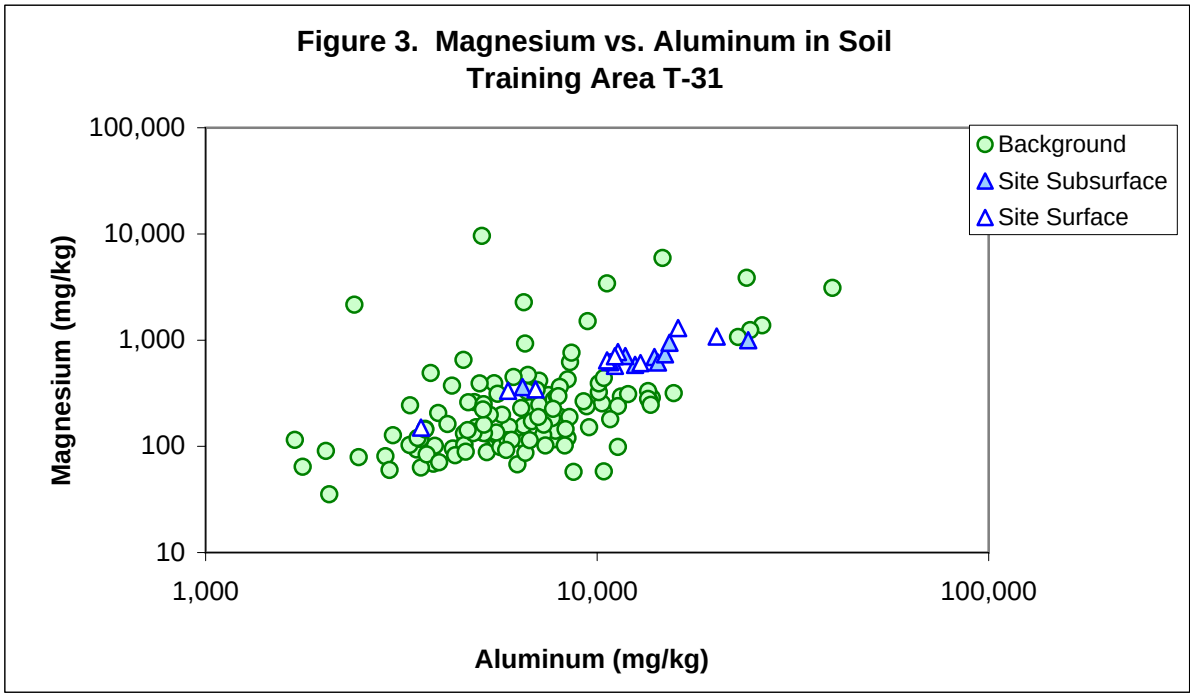
Figure 3. Magnesium vs. Aluminum in Soil
Training Area T-31
100,000
10,000
1,000
100
10
Magnesium (mg/kg)
1,000
10,000
100,000
Aluminum (mg/kg)
Background
Site Subsurface
Site Surface

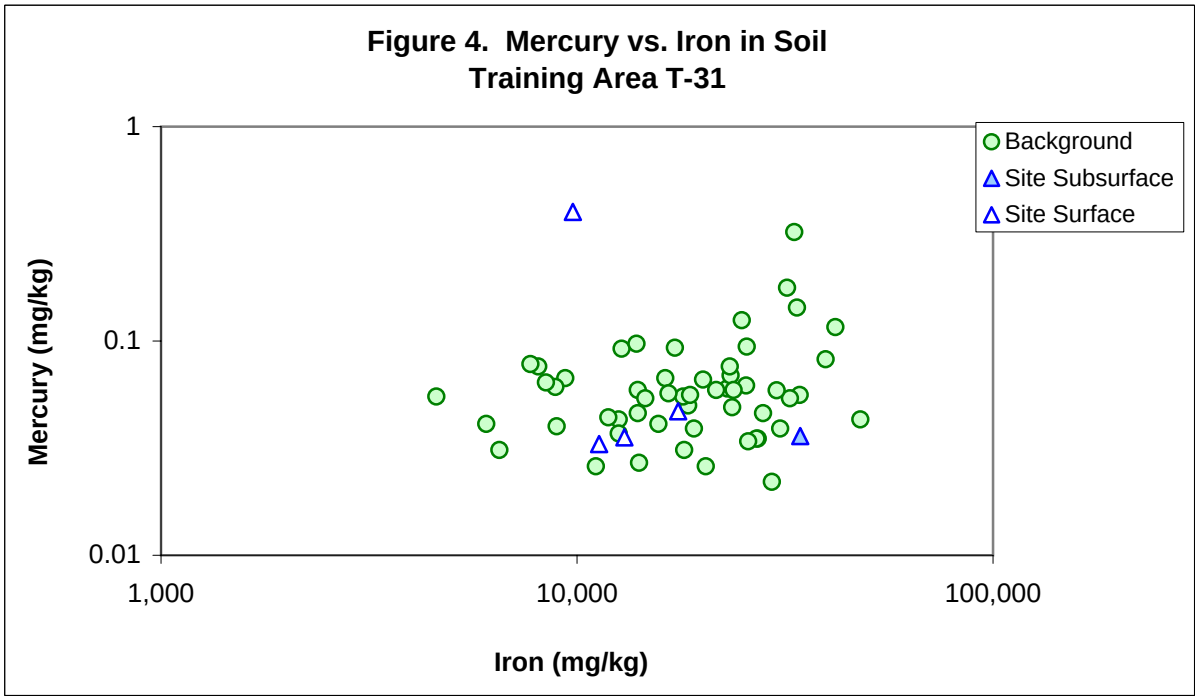
Figure 4. Mercury vs. Iron in Soil
Training Area T-31
1
0.1
0.01
Mercury (mg/kg)
1,000
10,000
100,000
Iron (mg/kg)
Background
Site Subsurface
Site Surface

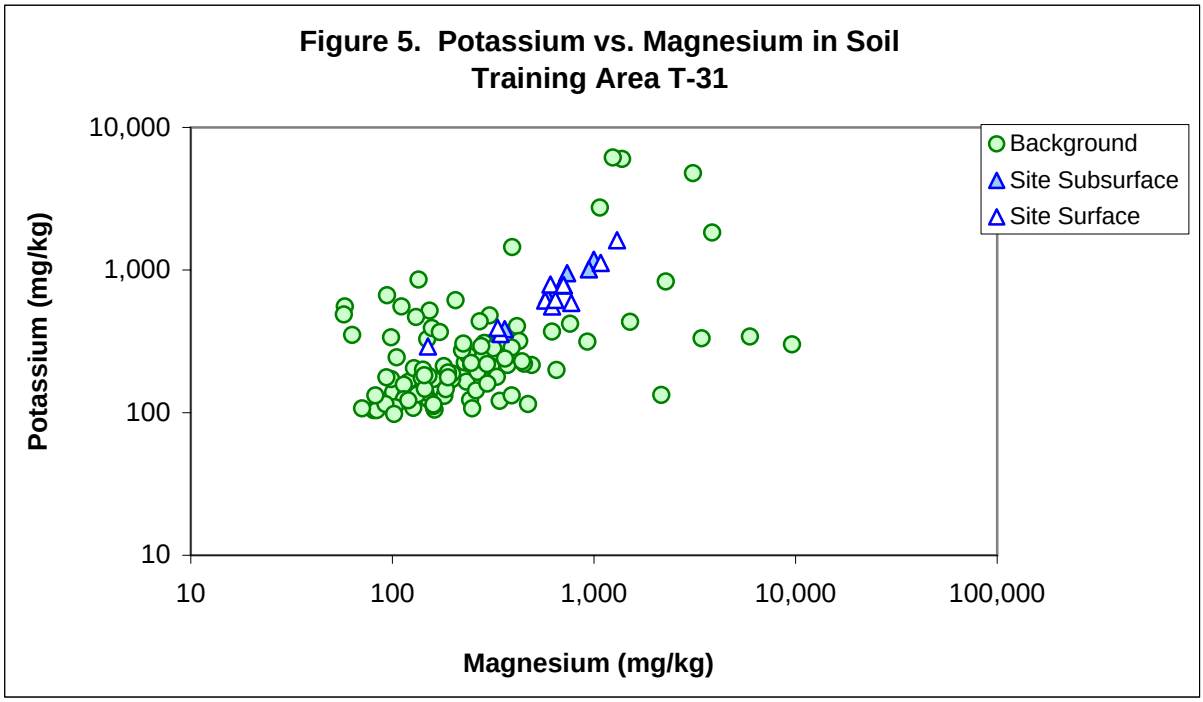
Figure 5. Potassium vs. Magnesium in Soil
Training Area T-31
Potassium (mg/kg)
10,000
1,000
100
10
10
100
1,000
10,000
100,000
Magnesium (mg/kg)
Background
Site Subsurface
Site Surface

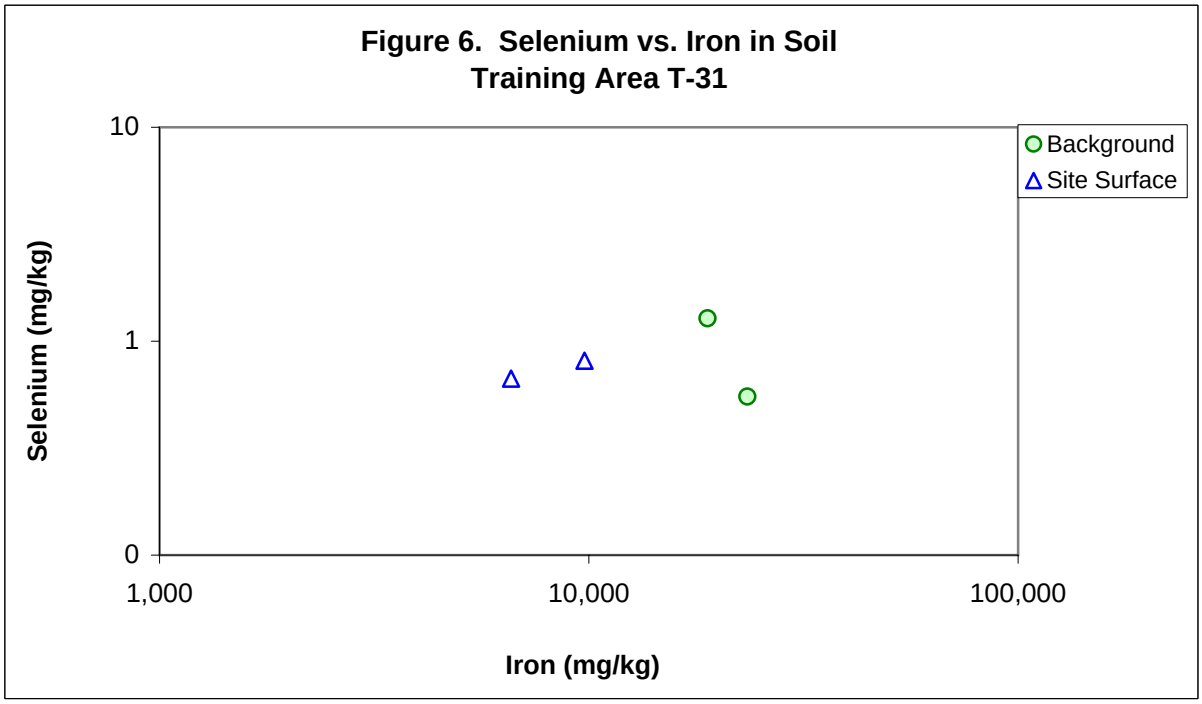
Figure 6. Selenium vs. Iron in Soil
Training Area T-31
Selenium (mg/kg)
10
1
0
1,000
10,000
100,000
Iron (mg/kg)
Background
Site Surface

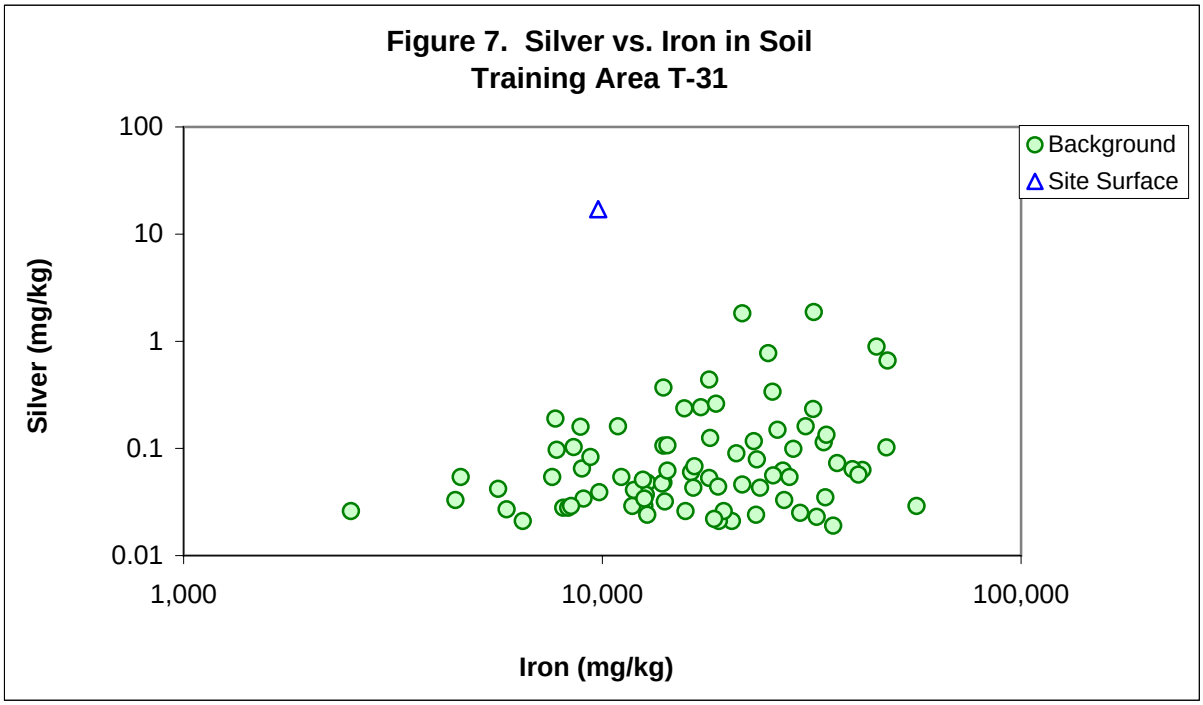
Figure 7. Silver vs. Iron in Soil
Training Area T-31
Silver (mg/kg)
100
10
1
0.1
0.01
1,000
10,000
100,000
Iron (mg/kg)
Background
Site Surface

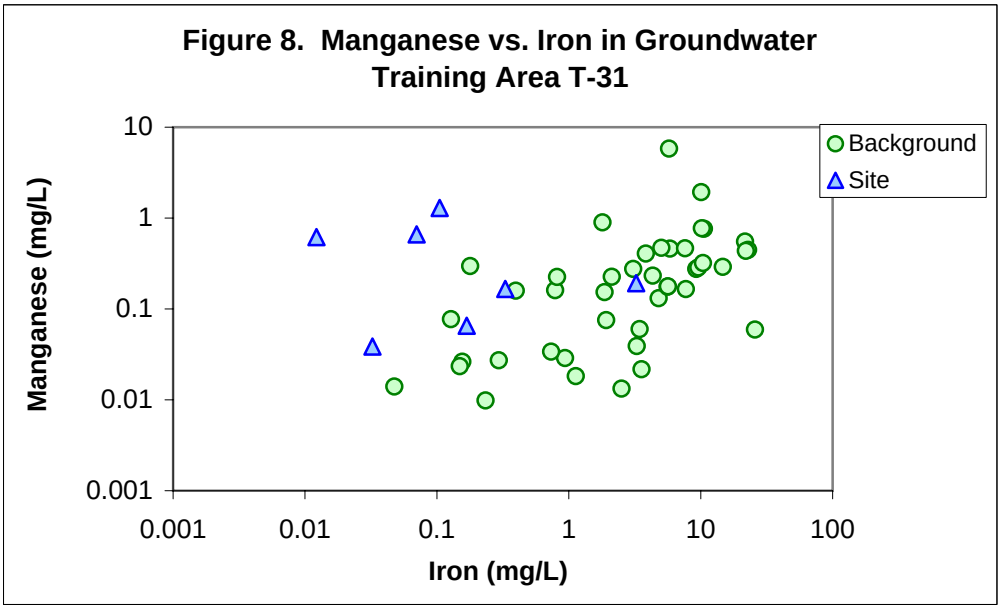
Figure 8. Manganese vs. Iron in Groundwater
Training Area T-31
Manganese (mg/L)
10
1
0.1
0.01
0.001
0.001
0.01
0.1
1
10
100
Iron (mg/L)
Background
Site

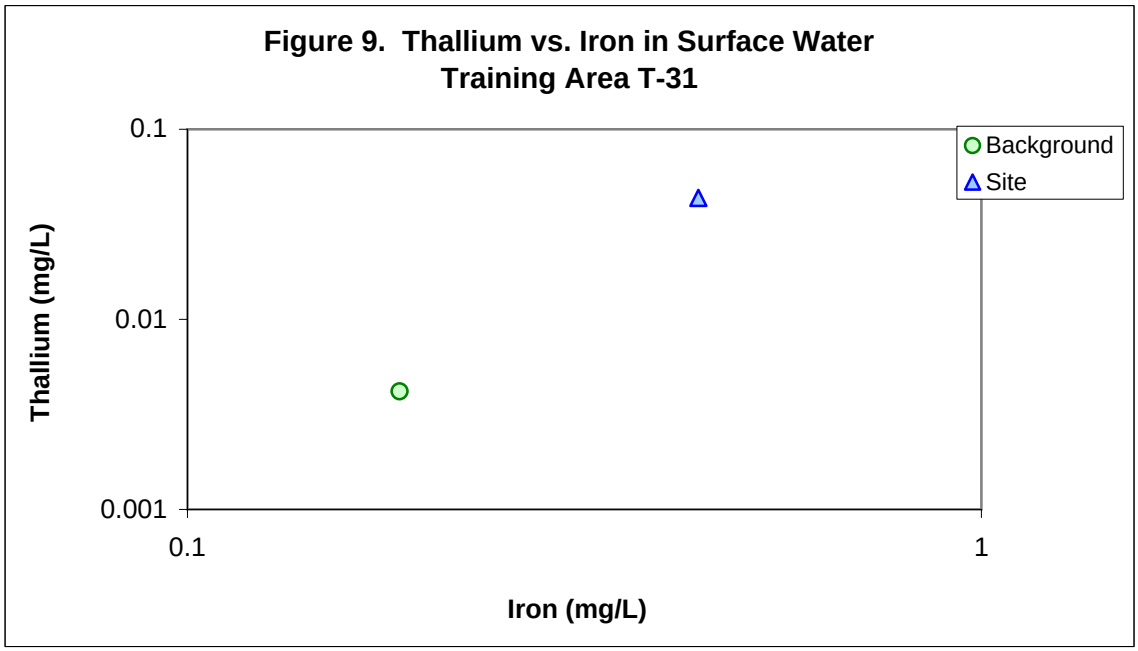
Figure 9. Thallium vs. Iron in Surface Water
Training Area T-31
0.1
0.01
0.001
Thallium (mg/L)
0.1
1
Iron (mg/L)
Background
Site