

**Development of an Interpretive Tool for Assessment of Metal
Enrichment in Florida Freshwater Sediment**

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DEVELOPMENT OF AN INTERPRETIVE TOOL FOR ASSESSMENT OF METAL
ENRICHMENT IN FLORIDA FRESHWATER SEDIMENT

Prepared for

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EXECUTIVE SUMMARY

Metals are a ubiquitous natural component of the sediments that lie beneath Florida's lakes, rivers, and streams. Natural metal concentrations in these sediments vary by orders of magnitude depending on the sediments' mineralogy, grain size and organic content. In addition to the naturally occurring metals, sediments may also contain metal contaminants from human activities. Unfortunately, the variability of the natural sediment metal concentrations sometimes makes it difficult to determine whether a measured metal concentration represents a natural or metal-enriched condition.

This document describes the development of an interpretive tool to determine whether metals in Florida freshwater sediments exceed expected natural concentrations. The interpretive tool provides users a simple way to account for the natural variability of metals in some of Florida's freshwater systems and to determine whether sediment is metal enriched.

The tool is based on the relatively constant relationships that exist between metals and two reference elements — aluminum and iron — in natural sediments. “Clean” lake, stream, and spring sediments samples from north and central Florida provided the natural reference concentrations to describe metal/aluminum and metal/iron linear regressions and prediction limits. Metals data from freshwater sediment samples can be compared to the prediction limits to determine whether the metal concentrations exceed expected natural ranges. The Microsoft Excel™ spreadsheet that accompanies this document allows the users to easily plot metals data from freshwater sediments for comparison to the prediction limits.

Applications of this interpretive tool include 1) distinguishing natural versus enriched metals concentrations in freshwater sediments, 2) comparing metals concentrations between and within freshwater systems, 3) tracking the influence of pollution sources, 4) monitoring trends in metals concentrations over time, and 5) screening for procedural or laboratory errors.

The audience for this document includes regulatory agencies, consultants, and researchers. The document addresses the regulatory and managerial reasoning behind the development of sediment quality criteria, the geochemical and statistical bases for this interpretive tool, and limitations of the tool. Appendices A and B provide metal/aluminum and metal/iron diagrams suitable for reproduction and use and a brief explanation of the Excel spreadsheet user interface.

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Note:

The Florida Department of Environmental Protection has reviewed this report and approved it for publication. Such approval does not signify that the methods and guidance necessarily represent the policies of the Florida Department of Environmental Protection, nor does mention of any trade name or commercial product constitute endorsement or recommendation for its use.

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1.0 INTRODUCTION

The sediments that lie beneath Florida's lakes, rivers, and streams are comprised of loose particles of sand, clay, silt, and other substances that have settled to the bottom of these water bodies from natural and anthropogenic processes. Metals are ubiquitous natural components of these sediments. Metal concentrations in uncontaminated sediments vary by orders of magnitude depending on the sediments' mineralogy, grain size, organic content, and post-depositional physicochemical processes (diagenesis). In addition to the naturally occurring metals, sediments may also contain contaminant metals from human activities. Unfortunately, the variability of the natural sediment metal concentrations sometimes makes it difficult to determine whether a measured metal concentration represents a natural or metal-enriched condition.

Metal concentrations in bottom sediments, at the sediment water interface or even in the suspended sediments themselves, can exceed the metal concentration in the overlying water body by several orders of magnitude (Lee and Jones-Lee, 1993; Horowitz, 1991). In the past, however, water quality studies focused mostly on the detection of contaminants in the water column and ignored the fact that sediments may act as large sinks or reservoirs of contamination (USEPA, 2000; Horowitz, 1991; Loring 1991). Many past studies also failed to recognize that remobilization of metals from contaminated sediment can cause water quality problems (USEPA, 1999).

Several mechanisms contribute to metal remobilization from contaminated sediment. First, sediment and associated contaminants may be resuspended by dredging, agitation from boat propellers, storms, floods, runoff, and activities of bottom dwelling creatures (Lee and Jones-Lee, 1993; Horowitz, 1991). Second, changes in physicochemical conditions, such as pH or dissolved oxygen, can dissolve sediment-bound trace metals and make them available to enter the food chain (Horowitz, 1991). Finally, some inorganic or inert constituents can degrade or react with other constituents to create more soluble forms with higher toxicity (e.g., mercury to methyl-mercury) (Horowitz, 1991).

Contaminated sediments may affect an ecosystem at several levels, usually beginning with small creatures that inhabit the bottom (benthic environment). The small benthos may ingest and retain contaminants. When larger animals feed on these contaminated organisms, they take the contaminants into their bodies. The uptake of contaminants along the food chain is known as bioaccumulation. As this process continues up the food chain, an increase in contaminant

concentration may occur as larger animals consume greater numbers of smaller animals. This process is known as biomagnification.

These processes demonstrate that sediment contamination can significantly affect fish and shellfish, waterfowl, freshwater and marine mammals, and humans (USEPA, 1999). Given their potential toxic effects, potential threats to public health, and potential as indicators of other types of pollution, high metal concentrations are of particular concern in habitat protection and rehabilitation. Unfortunately, due to the variable concentration of naturally occurring sediment metals, identification of sediment metal contamination can be difficult.

This document describes development of an interpretive tool for screening Florida freshwater sediment metal data to determine whether metal concentrations are within natural ranges. Using data from relatively simple laboratory analyses of bulk sediment samples, the interpretive tool provides a mechanism for screening sediments to determine whether measured metal concentrations represent a natural or metal-enriched condition. This document discusses the rationale for this tool, describes procedures used to develop the tool, and provides graphs and a Microsoft Excel spreadsheet for use in application of the tool.

2.0 SEDIMENT QUALITY ASSESSEMENT: A BRIEF OVERVIEW

In the late 1970s, the Federal Water Quality Administration (FWQA) developed the Jensen Criteria, a rigorous and costly set of standards related to the disposal of contaminated sediments (Lee and Jones-Lee, 1993). In the 1980s, the United States Army Corps of Engineers (USACE) conducted a series of studies to address the issue of contamination in dredged material. In 1991, the USACE and United States Environmental Protection Agency (USEPA) published the *Green Book* (USEPA and USACE, 1991) that addressed a four-step methodology — the Tiered Testing Approach — designed to evaluate the contaminant status and toxicity of dredged material proposed for ocean disposal. The *Green Book* preceded a series of more recent studies that led to the implementation of several federal programs and regulations that address contamination in aquatic sediments.

Under the Water Resources Development Act of 1992 (WRDA), the USEPA began the comprehensive National Sediment Quality Survey (NSQS). In 1997, USEPA, in its “Incidence and Severity of Sediment Contamination in Surface Waters of the United States” (USEPA, 1997) reported to Congress that contaminated sediments existed in “all regions and in every state,” in all types of water bodies. The report also identified “areas of concern” along the Atlantic and Pacific coasts, in the Gulf of Mexico, the Great Lakes, and along inland waterways. Following the release of this report, the USEPA announced, in 1998, its Contaminated Sediment Management Strategy (USEPA, 1998). The Strategy included a policy framework describing specific actions to reduce the ecological and human health risks posed by contaminated sediment and provided the bases for the implementation of a comprehensive research program to develop Sediment Quality Criteria (SQC). The same year, the USACE and USEPA published *The Inland Testing Manual*, which extended the application of the Green Book methodology to all open water disposals of dredged material (USEPA and USACE, 1998) and addressed compliance with the water quality guidelines of Section 401(b)(1) of the Clean water Act. In 2000, the USEPA published a set of criteria and methodologies to test and interpret bioaccumulation from sediments of several metals and organic contaminants (USEPA, 2000).

The works and studies cited above focused on the biological effects of contaminants and on the use of biological indicators as a mean to evaluate the potential risks to public health or aquatic ecosystems. They did not provide simple guidelines to interpret sediment metal concentrations. The evaluation of sediment quality from the methods described in those studies is fairly complicated

and costly. Frequently, regulatory agencies require a simple method to determine whether sediments contain metals above natural background (baseline) levels.

Recognizing the need for a simple method to screen estuarine sediment data for evidence of metal contamination, the Florida Department of Environment Protection (FDEP) in 1988 prepared an interpretative tool for sediment metals in Florida estuaries. The interpretative tool is based on the relatively constant relationships that exist between metals and aluminum in natural sediments. By normalizing metal concentrations to aluminum, the tool allows a simple determination of whether estuarine sediment metals are within or outside of the expected natural ranges. Very simple to apply, the tool relies on metal concentration data from total digestion ($\text{HF} + \text{HNO}_2 + \text{HClO}_4$) of bulk sediment samples. Others have developed similar tools based on uncontaminated reference sediments or on historical data from sediment cores from specific sites or regions.

In a subsequent effort, the FDEP developed a set of metals interpretative guidelines based on a comprehensive review of biological responses to coastal sediment contamination (MacDonald, 1994). This tool also uses metal concentration data from strong acid digestion of bulk sediment samples. Since both the FDEP tools rely on absolute metal concentrations, they provide a simple method to screen estuarine sediment quality data to determine whether the measured metal concentrations represent metal enrichment or potential harm to estuarine ecosystems. Such tools and guidelines constitute cost-effective means to help establish priorities for water and sediment quality regulatory or management actions.

The freshwater metals interpretative tool described in this document follows the same reference element normalization approach as FDEP's estuarine metals interpretation tool (Schropp and Windom, 1988).

3.0 GEOCHEMICAL BASIS FOR THE NORMALIZATION OF SEDIMENT METAL CONCENTRATIONS

3.1 Sources of Metals in Sediments

The weathering of rocks and soils is one of the major sediment sources in nature. Physical processes slowly break rocks into smaller particles. Acids formed in the atmosphere or during the breakdown of organic matter (e.g., carbonic acids) form leaching solutions which break down rocks and carry away the products in solution or as solid chemically resistant mineral debris. Because of their low solubility, metals occur in the transporting solution (e.g., rivers) in very low concentrations. Most naturally occurring metals that rivers transport are tightly bound in the solid mineral debris.

Weathering is not the only source of trace metals in sediments. Organic material also carries trace metals (e.g., Hg and Cd). Naturally and anthropogenically derived non-detrital metals can also become associated with fine-grained inorganic and organic material during transportation and deposition and add to the total metal concentration in sediments (Loring, 1991).

Natural sediment metal concentrations tend to vary spatially by several orders of magnitude depending on the grain size, mineral source, and chemical composition of the sediments and water body (Cooke and Drury, 1998; Loring, 1991; Shiff and Weisberg, 1999; Schropp and Windom, 1988; Weisberg, et al., 2000). Most anthropogenic metallic contaminants are supplied in solution or in association with fine-grained suspended solid and colloidal inorganic and organic particles. These particles are usually deposited in areas of low hydrodynamic energy along streams or are transported all the way to lakes, estuaries, or the ocean during times of increased river flow (Loring, 1991; Simpson et al., 2000).

In spite of input and transport dissimilarities, both natural and anthropogenic metals tend to accumulate together in sediments. As a result, separating and quantifying natural and anthropogenic metal contents becomes difficult.

To compensate for the natural variability of trace metals in sediments and to detect and quantify anthropogenic metal contributions, metal concentrations may be normalized to a common parameter (Cooke and Drury, 1998; Loring, 1991; Shiff and Weisberg, 1999; Schropp and Windom, 1988; Weisberg, et al., 2000). One example of a normalization technique is to compare

metal concentrations to a reference element. The reference element (e.g., aluminum or iron) must originate from non-anthropogenic sources in order to establish a reference baseline for natural concentrations and metal to reference element ratios. In streams, metal to reference element ratio comparisons between upstream and downstream samples determine whether metals in samples downstream of a contaminant source exceed expected natural levels (Cooke and Drury, 1998). Introduced in Chapter 2, FDEP's estuarine sediment interpretative tool — relying on aluminum as its reference element — employs the metal to reference element normalization technique with a statewide database of “clean” reference estuarine sediments.

3.2 Sediment Mineralogy

Tables 3.1 and 3.2 show the average metal concentrations of various materials that make up the earth's crust and their ratios to aluminum and iron. After silicon, aluminum and iron are the most abundant metals in the earth's crust. Studies have indicated that the relative proportions of metals to aluminum and iron in crustal material are fairly constant (Taylor, 1964; Turekian and Wedepohl, 1961). Aluminum, a major component of clay minerals, is usually associated with fine-grained aluminosilicate minerals. Iron in most sediment exists in a ferrous form as a structural component of the aluminosilicates (Cooke and Drury, 1998; Lee and Lee-Jones, 1993; Trefrey et al. 1992). Iron can also occur in sediment as a separate sulfide phase (Trefrey et al. 1992) or as iron oxide “coating” of metals (Lee and Lee-Jones, 1993; Trefrey et al., 1992).

The relative constancy of composition of natural crustal materials formed the basis for a variety of studies of metal data interpretation. For example, Duce et al. (1976) compared metal/aluminum ratios in atmospheric dust samples to that of average crustal material to estimate the relative atmospheric enrichment of metals due to anthropogenic sources. Studies to identify or assess the extent of contamination in freshwater and coastal sediments using a reference element normalization approach have employed various reference elements including:

- aluminum (Cooke and Drury, 1998; Daskalakis and O'Connor, 1995; Goldberg et al., 1979; Loring, 1987, 1988, 1990, 1991; Rediske et al., 1999; Schropp and Windom, 1988; Schropp et al., 1990; Simpson et al., 2000; Trefry and Presley, 1976; Trefry et al., 1985; Tuchman et al., 1998; Weisberg et al., 1999; Windom et al., 1989)
- iron (Cooke and Drury, 1998; Daskalakis and O'Connor 1995; Loring 1987, 1988, 1990, 1991; Rediske et al. 1999; Shiff & Weisberg 1999; Simpson et al. 2000; Trefry et al. 1992)

Table 3.1 Relative Abundance of Metals in Crustal Materials (concentration in mg/kg)

	Crust ^(a)	Upper Crust ^(b)	Crustal Rocks ^(c)	Soils ^(c)	Deep-Sea Sediments ^(c)	Carbonate Rocks ^(d)
Aluminum	82,300	84,700	69,300	71,000	95,000	4,200
Arsenic	1.8	-	7.9	6	13	1
Barium	425	-	-	-	-	10
Cadmium	0.2	-	0.2	0.35	0.23	0.035
Chromium	100	35	71	70	100	11
Copper	55	25	32	34	200	4
Iron	56,300	35,000	35,900	40,000	60,000	3,800
Lead	12.5	15	16	35	200	9
Lithium	20	-	-	-	-	5
Mercury	0.08	-	-	-	-	0.04
Nickel	75	20	49	50	200	20
Silver	0.07	-	0.07	0.05	0.1	0.1
Titanium	0.57	-	-	-	-	400
Vanadium	135	-	-	-	-	20
Zinc	70	52	127	90	120	20

(a) Taylor, 1964.

(b) Taylor and McLennan, 1981.

(c) Martin and Whitfield, 1983.

(d) Turekian and Wedepohl, 1961.

Table 3.2 Metal/Aluminum and Metal/Iron Ratios in Crustal Materials ($\times 10^{-4}$)

	Crust		Upper Crust		Crustal Rocks		Soils		Deep-Sea Sediments		Carbonate Rocks	
	Aluminum	Iron	Aluminum	Iron	Aluminum	Iron	Aluminum	Iron	Aluminum	Iron	Aluminum	Iron
Aluminum	-	14618	-	24200	-	19304	-	17750	-	15833	-	11053
Arsenic	0.22	0.32	-	-	1.1	2.2	0.85	1.5	1.4	2.17	2.4	2.6
Barium	51.6	75.5	-	-	-	-	-	-	-	-	23.8	26.3
Cadmium	0.024	0.036	-	-	0.029	0.056	0.049	0.088	0.024	0.038	0.083	0.092
Chromium	12	17.8	4.1	10.0	10	19.8	9.8	17.5	11	16.7	26	28.9
Copper	6.7	9.8	3	7.1	4.6	8.9	4.8	8.5	21	33.3	9.5	10.5
Iron	6841	-	4100	-	5200	-	5600	-	6300	-	9000	-
Lead	1.5	2.2	1.8	4.3	2.3	4.5	4.9	8.8	21	33.3	21	23.7
Lithium	2.4	3.6	-	-	-	-	-	-	-	-	11.9	13.1
Mercury	0.0097	0.014	-	-	-	-	-	-	-	-	0.095	0.105
Nickel	9.1	13.3	2.4	5.7	7.1	13.6	7	12.5	21	33.3	48	52.6
Silver	0.0085	0.012	-	-	0.01	0.019	0.007	0.013	0.011	0.017	0.24	0.26
Titanium	0.07	0.10	-	-	-	-	-	-	-	-	952	1053
Vanadium	16.4	24	-	-	-	-	-	-	-	-	47.6	52.6
Zinc	8.5	12.4	6.1	14.9	18	35.4	13	22.5	13	20	48	52.6

- lithium (Loring, 1990; Loring,1991)
- manganese (Simpson et al., 2000) and
- total organic carbon (Daskalakis and O'Connor 1995, Trefrey et al. 1992, USEPA and USACE, 1991,1998).

3.3 Normalization of Trace Metal Data to Reference Elements

In order to use reference elements to normalize metal data and to detect unnatural metal concentrations in sediments, one must make two assumptions. First, anthropogenic sources or environmental influences such as diagenic processes cannot influence the reference element concentrations (Loring, 1991; Shiff & Weisberg, 1999; Schropp and Windom, 1988). Second, the naturally occurring concentrations of the metal of interest must covary proportionally to the reference element. That is, as the concentration of the normalizing element varies (e.g., with changing mineralogy or particle size), the concentration of the metals will change proportionally.

4.0 STATISTICAL BASIS FOR METAL TO REFERENCE ELEMENT NORMALIZATION

According to several studies (Loring, 1987; Loring, 1988; Loring, 1991; Schiff & Weisberg, 1999; Schropp and Windom, 1988; Trefry et al. 1992; Weisberg et al. 2000), several criteria must be met to evaluate sediment metals by reference element normalization. Criteria include availability of a reference data set from uncontaminated sediment samples with substantial grain size variation, normally distributed sample data, a strong significant linear relationship (at least at the 95% confidence level) between the metal and the normalizer, and a measurement of the laboratory error. With these criteria met, one can apply simple statistical procedures to evaluate sediment metals. The remainder of this chapter discusses the statistical approach followed to develop the freshwater sediment metals assessment tool. Chapter 5 describes the reference data set obtained for this work.

4.1 Data Normality Assessment

The normality of the metal data can be assessed visually by plotting normal scores against the original data or statistically by performing a normality test. The Shapiro-Wilks' W normality test used in this work assumes that if the W statistic is significant, the null hypothesis (H_0) — “the sample is normally distributed” — should be rejected (StatSoft, Inc., 1999). The p-level in this test is used to measure the statistical significance of the W statistic. The p-level represents the probability of error in accepting that the observed values are normally distributed. In other words, it assumes that if the p-value of the W-statistic is less than 0.01 (99% confidence level), there is only a 1% chance of erroneously rejecting H_0 (i.e. classifying a normal distribution as non-normal). Data transformation (e.g. \log_{10} transformation) may be required to obtain a normally distributed data set.

With normality established, application of least squares regression analysis assesses the linear relationships between metals and potential normalizers. This work applies the methodology described in Sokal & Rohlf (1995) to establish and measure the strength of the linear regressions for each metal/normalizer pair. The strength of a linear regression is measured by its correlation coefficient (r). The significance of r is measured based on a statistical table that lists the critical values for correlation coefficients (Rohlf and Sokal, 1995). Stronger relationships correspond to higher correlation coefficients

Regression relationships can be strongly influenced by the presence of outlying data. Hawkins (1980) defined an outlier as “an observation that deviates so much from other

observations as to arouse suspicions that it was generated by a different mechanism.” Outliers in a reference sediment metals data set may arise from different sources including laboratory error, sampling a site with an unknown contaminant source, or other factors.

4.2 Outliers Identification

For this tool, identification and selective removal of data outliers follows a methodology adapted from Shiff and Weisberg (1999) and Weisberg et al. (2000). This methodology requires normal distribution of the regression residuals. The regression residuals are the differences between the estimated points on the regression line and the observed data. Application of this methodology involves testing the residuals for normality using the Shapiro-Wilks' W test and then, if necessary, removing an outlier (i.e. the data point with the largest residual), recalculating the regression line, and testing the new regression residuals for normality. The process continues until the residuals meet the normality criterion. Figure 4.1 illustrates a potential outlier on the zinc/aluminum regression plot.

4.3 Regression Analysis and Prediction Limits

With all the statistical criteria met, reference data sets representative of natural metal concentrations are ready for further analysis. The linear regression describes the relationship between the metal and the normalizer.

Upper and lower 95% prediction limits, calculated following the methodologies described in Sokal & Rohlf (1995) and Rohlf and Sokal (1995), “predict the outcome of future samples from the same population” (Sokal and Rohlf, 1995). For this application the prediction limits describe the expected standard error of any new uncontaminated sediment sample collected in similar Florida freshwaters systems. In other words, the prediction limits establish the expected range of variation of the natural metal concentrations.

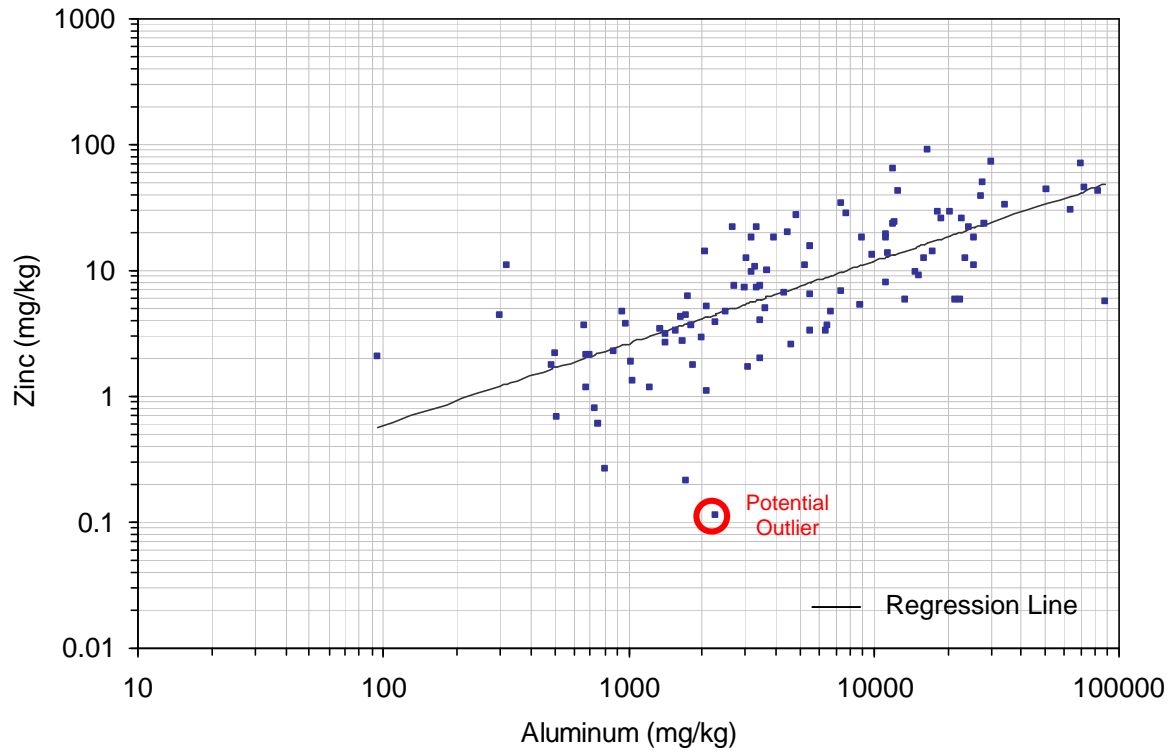


Figure 4.1 Regression Plot of a Zinc/Aluminum Relationship Showing a Potential Outlier

5.0 SITE SELECTION, SAMPLE COLLECTION AND ANALYSIS

5.1 Site Selection

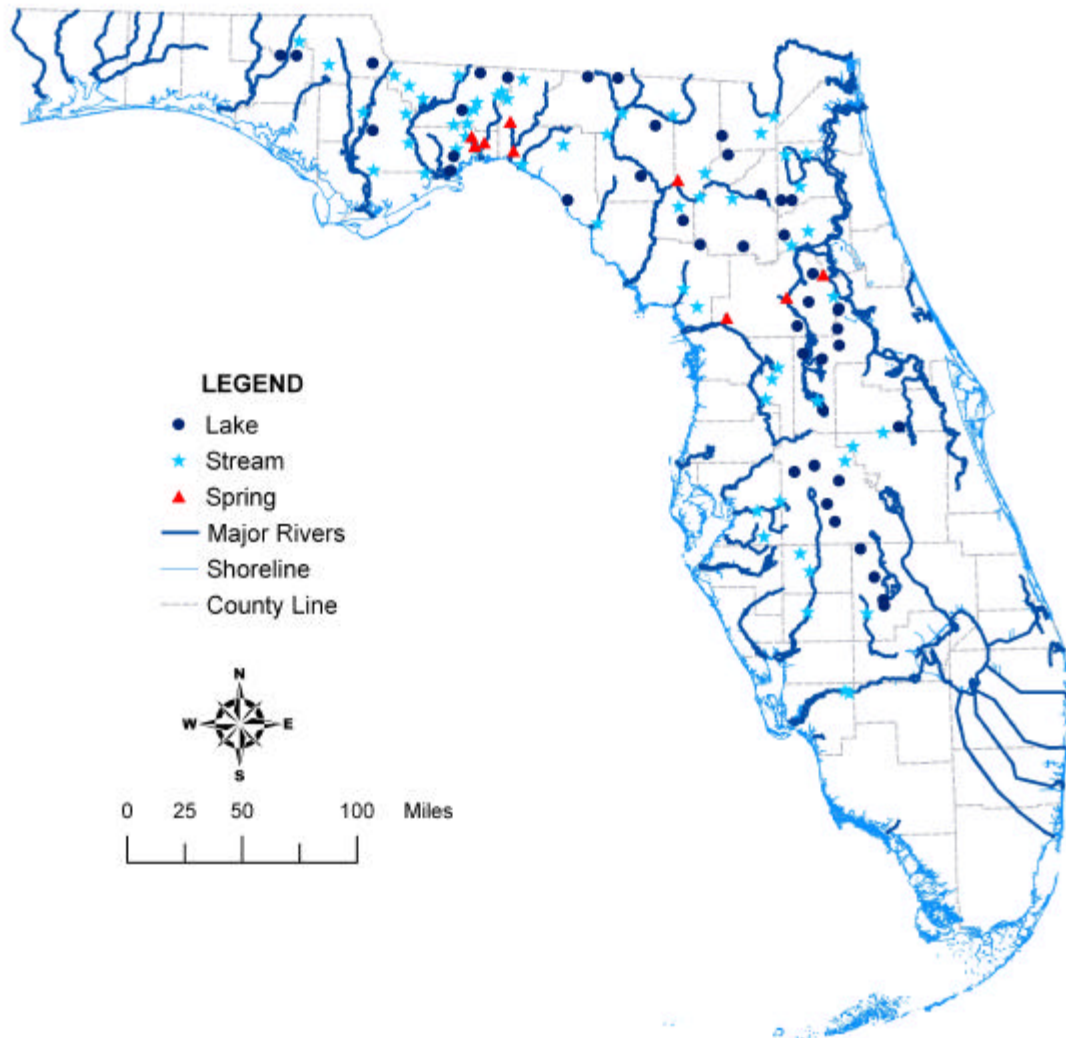
Florida has an extensive network of freshwater systems. Conditions in many of these systems range from nearly pristine to localized, severe degradation. The first step taken to develop this interpretative tool consisted of finding remote, “clean” sampling sites representative of the different freshwater systems (springs, streams, and lakes) in Florida and analyzing sediments from these sites for their metal concentrations. For the purposes of this work, “clean” sites refer to locations where the influences of known or suspected anthropogenic metal sources within the watershed appear minimal or nonexistent. Where possible, stations were co-located with FDEP Biocriteria reference sites, which have been tested and established as a statewide reference for healthy biological communities.

The Florida Department of Environmental Protection (FDEP) collected 121 sediment samples between August and November of 1997 from 111 stations in lakes, streams, and springs in Florida (Figure 5.1). Duplicate samples from the same sampling station were collected at 10 of the 111 locations. Duplicate values were averaged and used as a single sample. Some reported metal concentrations fell below the analytical method detection limits. These values were kept in the data set when the laboratory had a high level of confidence that the values were accurate. When this was not the case, the values were removed from the data set.

5.2 Sample Collection and Chemical Analysis

FDEP staff, using a polycarbonate piston corer (Fisher *et. al.* 1992), collected one sediment core at each site. The core was extruded and transferred into pre-cleaned containers, preserved on ice at 4°C and shipped to Skidaway Institute of Oceanography for analysis. Field collection, field decontamination, and handling of samples followed Standard Operating Procedures (SOP) included within Quality Assurance plan number 970114.

Location of each station was recorded using a Trimble Pro XL differentially corrected Global Positioning System (DGPS). DGPS data collection followed FDEP Division of Water Facilities (now Water Resource Management) GPS standard protocols, ensuring 5 meter accuracy (FDEP 1998).



GIS data source: Florida Department of Environmental Protection



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 Jacksonville, FL 32256

Figure 5.1 Sediment Sample Locations

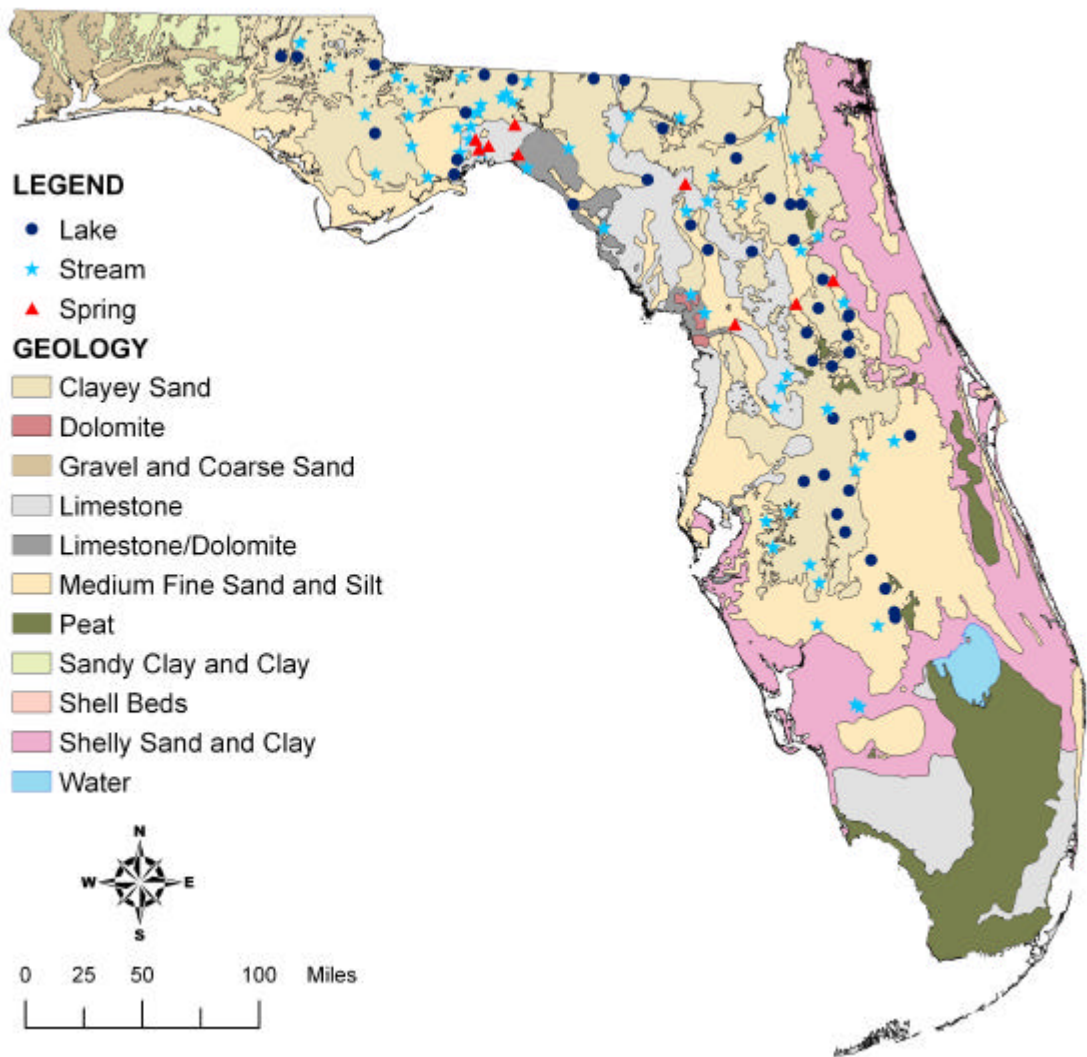
Skidaway Institute of Oceanography analyzed the samples. Total digestion of the sediment for trace metals analyses used nitric, perchloric, and hydrofluoric acids. Following digestion, the samples were analyzed for aluminum, arsenic, barium, cadmium, chromium, copper, iron, lead, lithium, manganese, nickel, silver, titanium, vanadium, and zinc by inductively coupled plasma-mass spectrometry (ICP-MS). Mercury was quantified by ICP-MS (isotope dilution) methods (Smith, 1993). Total organic carbon and total organic nitrogen were analyzed using a Perkin Elmer Model 240C elemental analyzer. FDEP Central Laboratory in Tallahassee determined the sediment grain size with standard sieve analysis.

Laboratory quality assurance/quality control procedures included instrument calibration, replication of some analyses, percent recoveries of spiked blanks, and analyses of standard reference materials.

5.3 Sample Characteristics

The sediment samples represent sites with different hydrological and geological characteristics within central and northwest Florida. Of the 111 sampling stations, 43 were in lakes, 59 in streams (creeks and rivers), and 9 in springs or spring runs. Figure 5.2 shows sampling locations in relation to Florida's geology. As shown, most of the samples represent areas dominated by aluminosilicate sediments, carbonates or a mix of both, with grain sizes ranging from fine sand and silt to coarser shelly sand and clays.

Table 5.1 describes the ranges of metal concentration and total organic carbon content in the sediment samples. The ranges of metal concentrations illustrate the difficulty in interpretation of sediment metals data.



GIS data source: Florida Department of Environmental Protection



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Figure 5.2 Sediment Sample Location Relative to Florida Geology

Table 5.1 Data Set Characteristics

	Concentrations (mg/kg)				
	Number of Samples	Minimum	Average	Maximum	Standard Deviation
Aluminum	111	94.87	10,793.	87,611.	16,901.
Arsenic	111	0.005	1.57	25.18	2.96
Barium	111	2.30	53.17	419.82	72.95
Cadmium	83	0.005	0.43	11.60	1.36
Chromium	110	0.16	23.25	570.78	58.63
Copper	111	0.04	4.69	38.05	6.39
Iron	111	29.11	3,953.	48,388.	6,263.
Lead	111	0.30	6.33	42.53	7.78
Lithium	111	0.78	5.07	36.08	5.49
Mercury	95	0.001	0.04	0.36	0.06
Nickel	111	0.13	5.62	66.95	8.89
Silver	110	0.003	0.08	0.50	0.10
Titanium	110	30.21	1,072.91	5,930.80	1,156.50
Vanadium	111	0.18	19.17	209.79	34.31
Zinc	105	0.11	14.19	91.23	16.93
Total Organic Carbon (%)	101	0.003	6.83	52.39	1.14

6.0 DEVELOPMENT OF AN INTERPRETIVE TOOL

As discussed in Chapter 3, several normalizers may lend themselves to sediment metals data evaluation. This study examined the strength of the relationship between metals and six potential normalizers — aluminum, iron, titanium, lithium, vanadium, and total organic carbon.

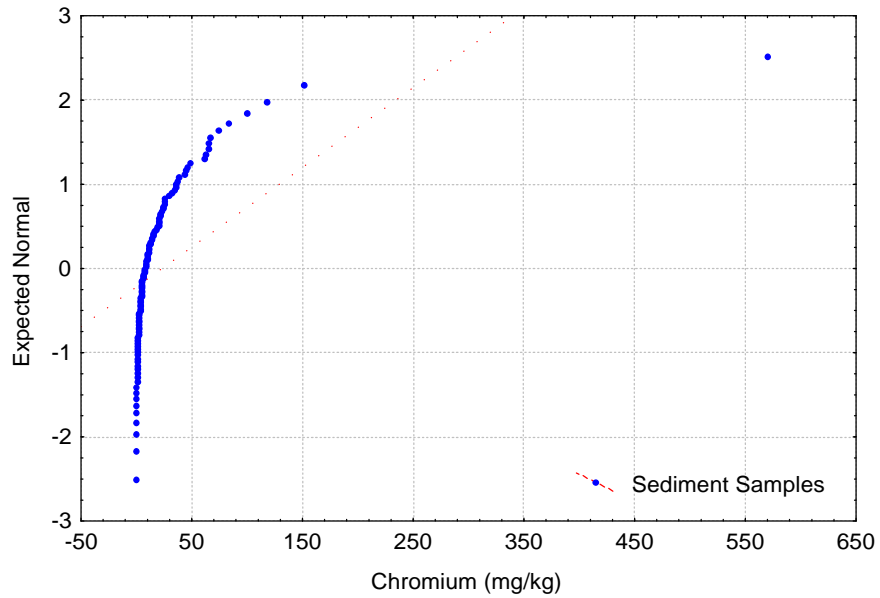
6.1 Normality Assessment of Sediment Metal Data

The normal score plots and the Shapiro-Wilks' W normality test for each metal and potential normalizer were calculated using the STATISTICA™ software package (StatSoft, Inc, 1999). Both the results of the Shapiro-Wilks' W normality test and the normal score plots for each metal show that the raw data were not normally distributed. With the exception of lithium, the application of a \log_{10} transformation to the data brought the data distribution to normality (Table 6.1). Figure 6.1 shows an example of normal score plots for the non-normal raw chromium data and for the normal \log_{10} transformed chromium data. The remaining analyses were performed on the \log_{10} -transformed data.

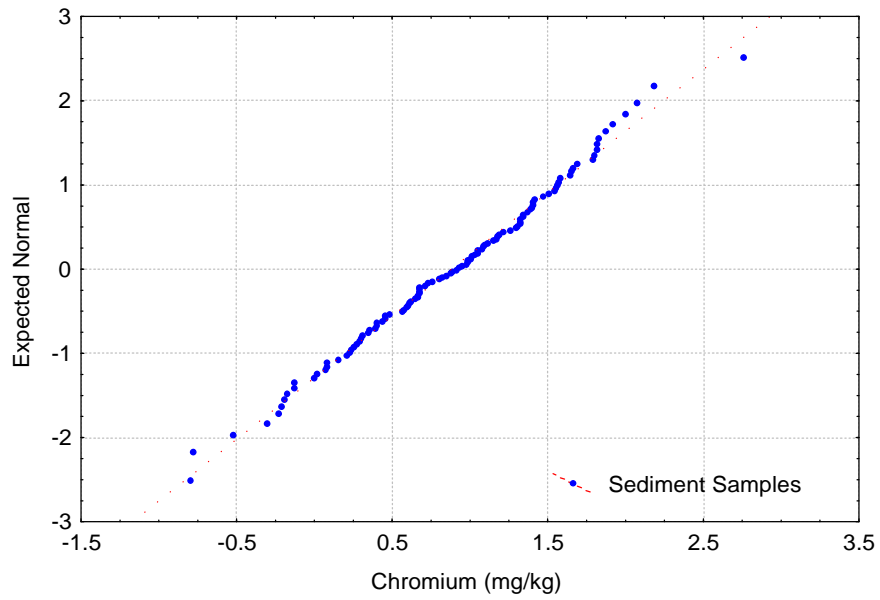
Table 6.1 Results of the Shapiro-Wilks' W Normality Test for Metals and Potential Normalizers — Raw Data

	Number of Samples	Raw Data W-Value	P-Value	Normal ^(a) Distribution	Log ₁₀ -Transformed W-Value	P-Value	Normal ^(a) Distribution
Aluminum	111	0.620	0.000	No	0.988	0.422	Yes
Arsenic	111	0.462	0.000	No	0.979	0.080	Yes
Barium	111	0.677	0.000	No	0.978	0.059	Yes
Cadmium	83	0.287	0.000	No	0.977	0.138	Yes
Chromium	110	0.333	0.000	No	0.994	0.909	Yes
Copper	111	0.581	0.000	No	0.992	0.761	Yes
Iron	111	0.599	0.000	No	0.983	0.181	Yes
Lead	111	0.711	0.000	No	0.989	0.470	Yes
Lithium	111	0.572	0.000	No	0.925	0.000	No
Mercury	95	0.535	0.000	No	0.969	0.022	Yes
Nickel	111	0.683	0.000	No	0.981	0.126	Yes
Silver	110	0.704	0.000	No	0.986	0.305	Yes
Titanium	110	0.783	0.000	No	0.980	0.089	Yes
Total Organic Carbon	101	0.636	0.000	No	0.971	0.026	Yes
Vanadium	111	0.535	0.000	No	0.993	0.814	Yes
Zinc	105	0.669	0.000	No	0.979	0.088	Yes

^(a) 99% significance level (p-value < 0.01)



Raw Data (non-normal distribution)



Log₁₀-transformed Data (normal distribution)

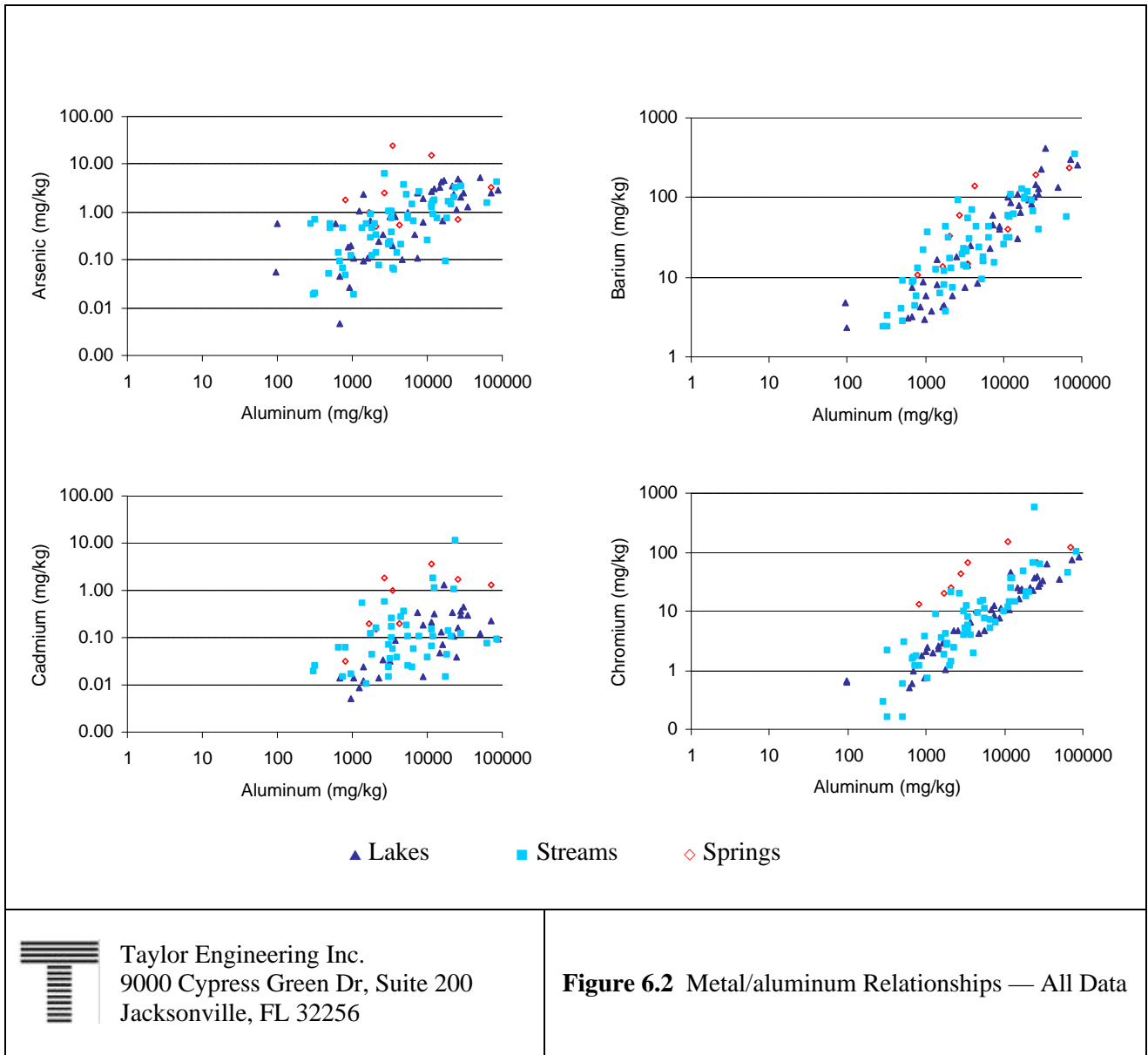


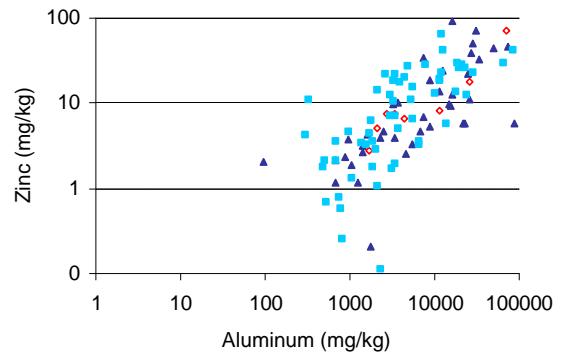
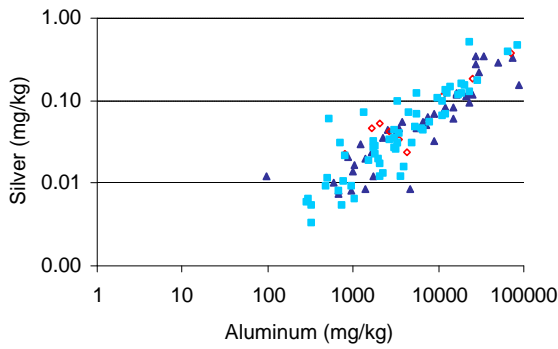
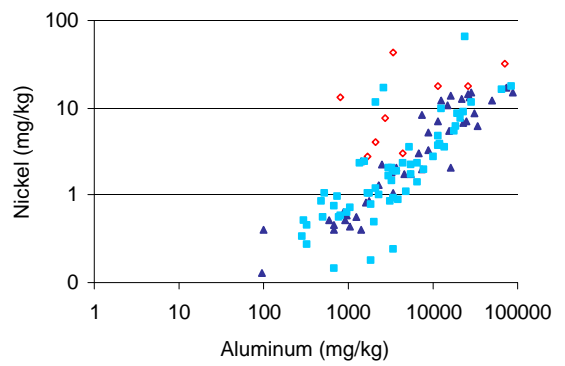
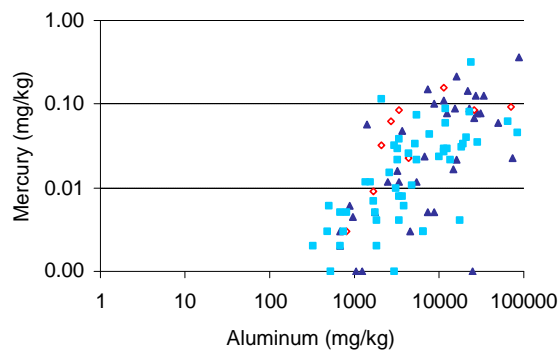
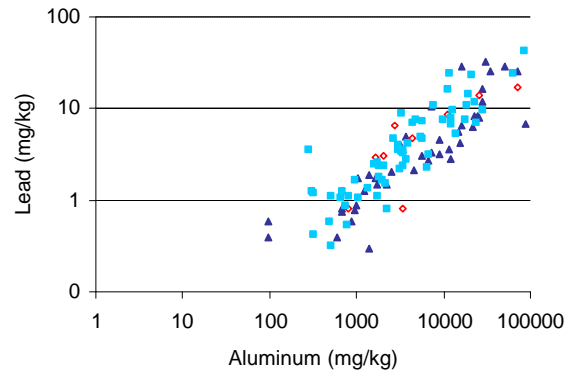
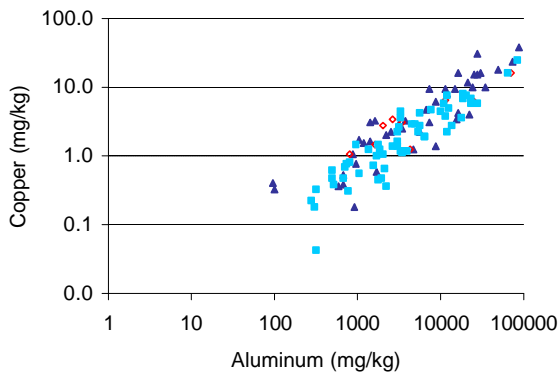
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Figure 6.1 Normal Probability Plots

6.2 Assessment of the Relationship Between Metals and Normalizers

All metals exhibited a positive relationship with all potential normalizers — aluminum, lithium, iron, titanium, total organic carbon and vanadium. Simply stated, as the concentration of the normalizer increased, the concentration of the metal also increased. Figure 6.2 provides an example of this trend using aluminum as the normalizer.





▲ Lakes ■ Streams ◇ Springs



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Figure 6.2 (Continued) Metal/aluminum Relationships — All Data

Figure 6.2 suggests that in some cases separating the data by type of freshwater system greatly improves the strength of the relationships between the metals and aluminum. As examples, the chromium, copper, and lead plots indicate that in these lake sediment metals are more strongly correlated to aluminum than metals in stream and spring sediments; chromium data from spring sediments have a second linear pattern. With additional data, separate metal/normalizer relationships might be apparent for each type of freshwater system. However due to the limited number of lake, spring and stream samples, all data were kept together and used as a single data set for this work.

6.3 Assessment of the Strength of Metals and Potential Normalizers Relationships

Table 6.2 lists the correlation coefficients for each pair of metal and potential normalizer calculated for all \log_{10} -transformed data.

Table 6.2 Correlation Coefficients from the Linear Regression Between Metals Data, and Six Potential Normalizers

Metals	Sample Size	Correlation coefficients for each potential normalizer					
		Aluminum	Iron	Vanadium	Total Organic Carbon	Titanium	Lithium
Arsenic	111	0.622	0.718	0.713	0.625	0.318	0.485
Barium	111	0.874	0.746	0.816	0.455	0.601	0.636
Cadmium	83	0.468	0.578	0.681	0.523	0.202	0.413
Chromium	110	0.850	0.871	0.949	0.578	0.586	0.632
Copper	111	0.895	0.844	0.871	0.651	0.710	0.620
Lead	111	0.868	0.783	0.807	0.457	0.694	0.628
Mercury	95	0.666	0.723	0.698	0.739	0.404	0.469
Nickel	111	0.807	0.806	0.861	0.621	0.470	0.676
Silver	110	0.889	0.753	0.863	0.546	0.774	0.719
Zinc	105	0.705	0.728	0.712	0.453	0.524	0.492

All correlation coefficients in Table 6.2 are significant at the 99% significance level (Rohlf & Sokal, 1995). However, the correlation coefficients for aluminum, iron, and vanadium are greater than those for titanium, lithium, and total organic carbon. Based on these results, aluminum, iron and vanadium appear good candidates for reference elements. Among the three, aluminum has the highest correlations with barium, copper, lead and silver; iron has the highest (best overall) correlations with arsenic and zinc; and vanadium has the highest correlations with cadmium, chromium and nickel.

Despite vanadium's favorable potential as a reference element, most studies have employed either aluminum or iron as reference elements. Aluminum and iron are the second and third most abundant element in the earth's crust. In comparison with iron and aluminum, vanadium's concentration in the earth's crust and in carbonate rocks (Taylor, 1964; Turekian and Wadepohl, 1961) is several orders of magnitude lower. The total concentrations of aluminum and iron are therefore less likely to be affected by human activities. Also, aluminum and iron are more commonly measured in sediment samples. These characteristics support the elimination of vanadium as a reference element.

6.4 Outlier Removal

For those metal and reference element pairs with non-normal residuals, the methodology described in Chapter 4 was applied to remove outliers. Tables 6.3 and 6.4 show correlation coefficients for the metal/aluminum and metal/iron linear regressions. The same tables also show the results of the Shapiro-Wilks' *W* normality test applied to the regression residuals.

With aluminum as the reference element, chromium, nickel, and zinc regression residuals did not meet the normality criterion. Removal of one outlier from the original zinc data set, six from the nickel data set, and seven from the chromium data set brought the regression residuals into normality. The outliers included — seven data points streams, and six from springs. With iron as the reference element, six metal data sets did not meet the normality criterion. Removal of one outlier from the lead, mercury, silver, and zinc data sets and two outliers from the chromium and nickel data sets brought the regression residuals into normality. The outliers included — two data points from lakes, four from streams, and two from springs. Throughout the remainder of this report, the term “trimmed data set” refers to the data set with outliers removed. The remaining evaluations were performed on the trimmed data set.

Tables 6.5 and 6.6 show the correlation coefficients for the trimmed data set as well as the results from the regression residuals normality test. Typically, the outliers were either the highest or the lowest metal concentrations in the data set. As expected, correlation coefficients for the targeted data sets improved greatly with removal of the outliers.

Table 6.3 Metal/Aluminum Regression Correlation Coefficients and Regression Residuals Normality Test Results

Metal	Sample Size	Correlation Coefficient	W-Value Raw Data	P-Value	Normal ^(a) Distribution
Arsenic	111	0.622	0.993	0.869	Yes
Barium	111	0.874	0.983	0.185	Yes
Cadmium	83	0.468	0.964	0.020	Yes
Chromium	110	0.850	0.923	0.000	No
Copper	111	0.895	0.981	0.126	Yes
Lead	111	0.868	0.987	0.362	Yes
Mercury	95	0.666	0.978	0.118	Yes
Nickel	111	0.807	0.900	0.000	No
Silver	110	0.889	0.972	0.019	Yes
Zinc	105	0.705	0.956	0.002	No

^(a) 99% significance level (p-value < 0.01)

Table 6.4 Metal/Iron Regression Correlation Coefficients and Regression Residuals Normality Test results

Metal	Sample Size	Correlation Coefficient	W-Value Raw Data	P-Value	Normal ^(a) Distribution
Arsenic	111	0.718	0.981	0.122	Yes
Barium	111	0.746	0.991	0.652	Yes
Cadmium	83	0.578	0.982	0.276	Yes
Chromium	110	0.871	0.944	0.000	No
Copper	111	0.844	0.969	0.011	Yes
Lead	111	0.783	0.965	0.005	No
Mercury	95	0.723	0.950	0.001	No
Nickel	111	0.806	0.939	0.000	No
Silver	110	0.753	0.962	0.003	No
Zinc	105	0.728	0.944	0.000	No

^(a) 99% significance level (p-value < 0.01)

Table 6.5 Metal/aluminum Regression Correlation Coefficients and Residuals Normality Test Results — Trimmed Data

Metal	Sample Size	Correlation Coefficient	W-Value Final Data	P-Value	Normal ^(a) Distribution
Mercury	95	0.666	0.978	0.118	Yes
Nickel	105	0.894	0.976	0.058	Yes
Copper	111	0.895	0.981	0.126	Yes
Zinc	104	0.727	0.982	0.177	Yes
Arsenic	111	0.622	0.993	0.869	Yes
Lead	111	0.868	0.987	0.362	Yes
Silver	110	0.889	0.972	0.019	Yes
Cadmium	83	0.468	0.964	0.020	Yes
Chromium	103	0.895	0.970	0.018	Yes
Barium	111	0.874	0.983	0.185	Yes

^(a) 99% significance level (p-value < 0.01)

Table 6.6 Metal/iron Regression Correlation Coefficients and Residuals Normality Test Results — Trimmed Data

Metal	Sample Size	Correlation Coefficient	W-Value Final Data	P-Value	Normal ^(a) Distribution
Mercury	94	0.768	0.975	0.069	Yes
Nickel	109	0.844	0.982	0.145	Yes
Copper	111	0.844	0.969	0.011	Yes
Zinc	104	0.748	0.971	0.023	Yes
Arsenic	111	0.718	0.981	0.122	Yes
Lead	110	0.810	0.988	0.432	Yes
Silver	109	0.782	0.974	0.036	Yes
Cadmium	83	0.579	0.981	0.276	Yes
Chromium	108	0.898	0.977	0.054	Yes
Barium	111	0.746	0.991	0.652	Yes

^(a) 99% significance level (p-value < 0.01)

Tables 6.5 and 6.6 show that the correlation coefficients for barium, copper, lead, nickel, and silver in the trimmed data set are higher with aluminum as the reference element; in contrast, the correlation coefficients for arsenic, cadmium, chromium, mercury, and zinc are higher with iron as the reference element. Cadmium has the weakest relationship with either normalizer as demonstrated by its correlation coefficients below 0.60.

6.5 Regression Analysis and Predictions Limits

Figures 6.3 and 6.4 present the metals data regression lines and 95% prediction limits for metal/aluminum and metal/iron relationships. The range of the prediction limits varies depending on the metal concentrations and strength of the regressions. Higher correlation coefficients result in narrower prediction limits (e.g. copper or nickel). As mentioned in Chapter 4, the prediction limits provide a valid statistical estimate of the range of metal concentrations one can expect from uncontaminated sediments in Florida freshwater sediments.

The trimmed data sets final regression lines and respective 95% prediction limits provide an interpretative tool to screen for metals enrichment. When sediment metals concentrations from freshwater samples fall within the range of the upper and lower prediction limits, those metals can be considered within expected natural ranges. Metal concentrations that exceed the upper prediction limits may represent a metal enriched condition.

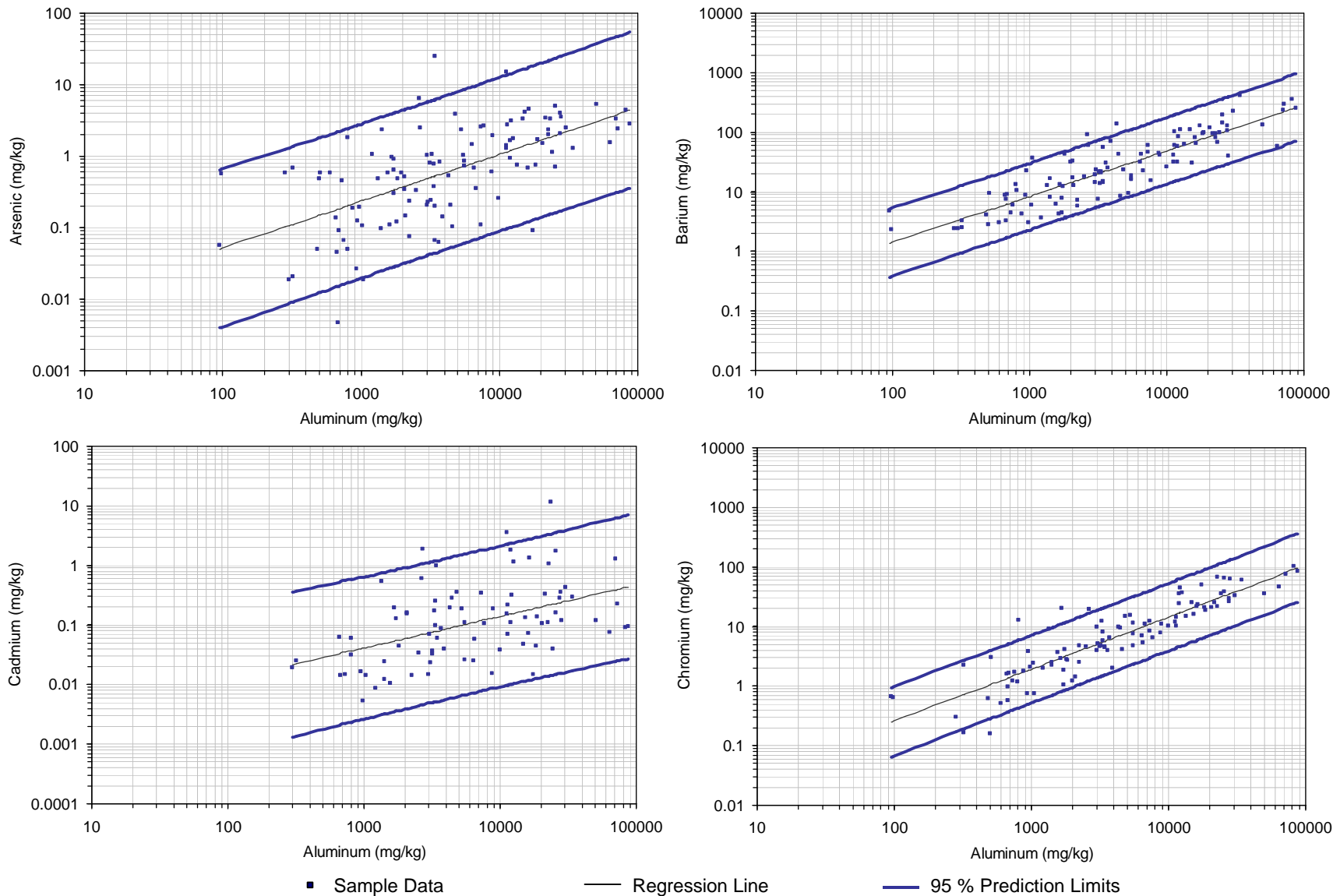
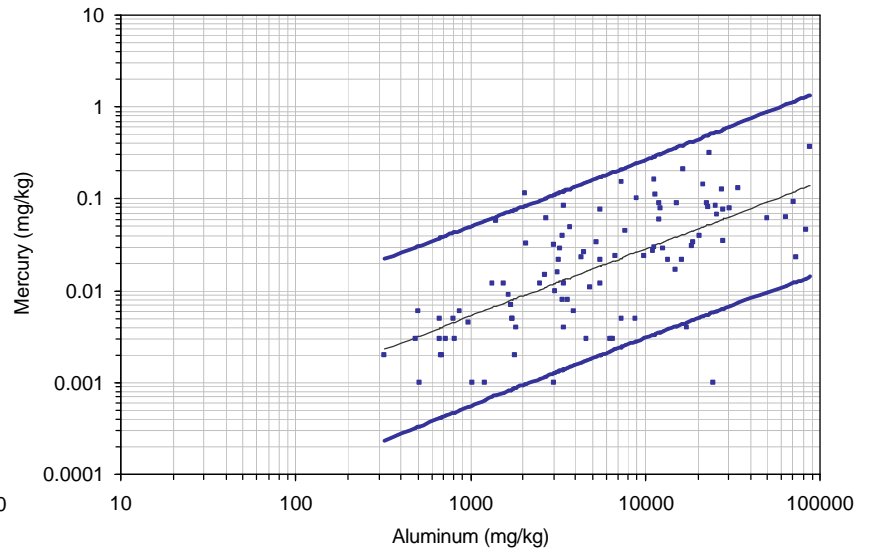
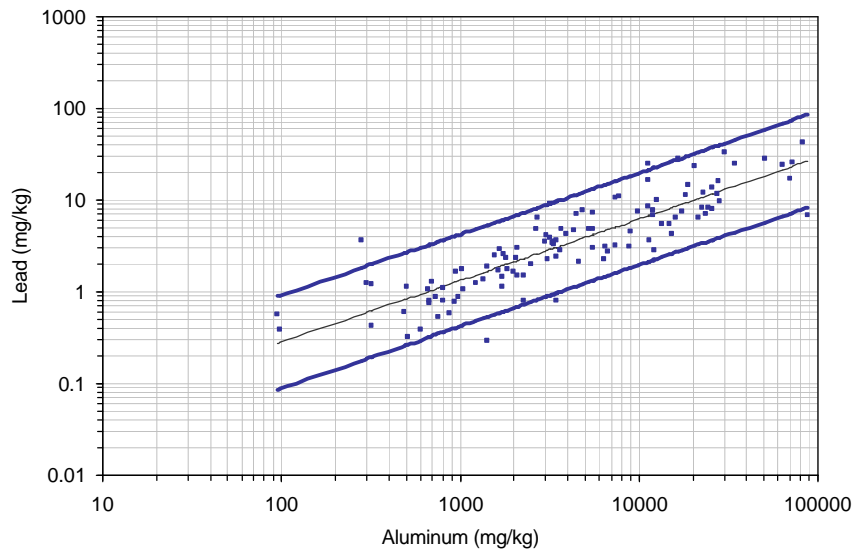
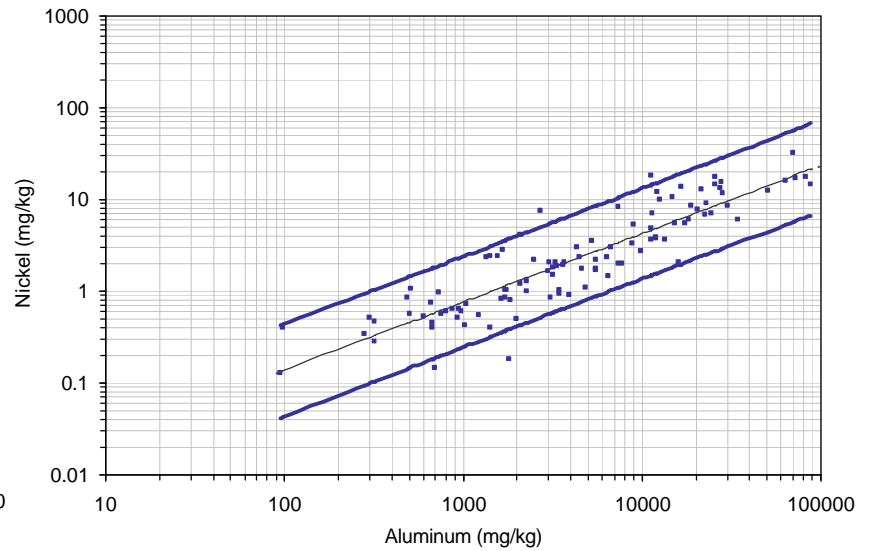
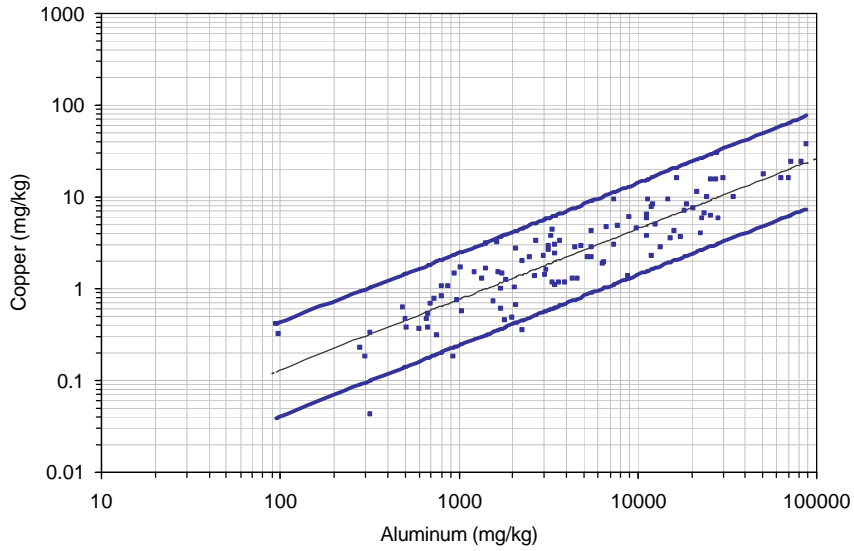


Figure 6.3 Metal/Aluminum Regression Lines with the 95 % Prediction Limits



Sample Data
 Regression Line
 95 % Prediction Limits

Figure 6.3 (Continued) Metal/Aluminum Regression Lines with the 95 % Prediction Limits

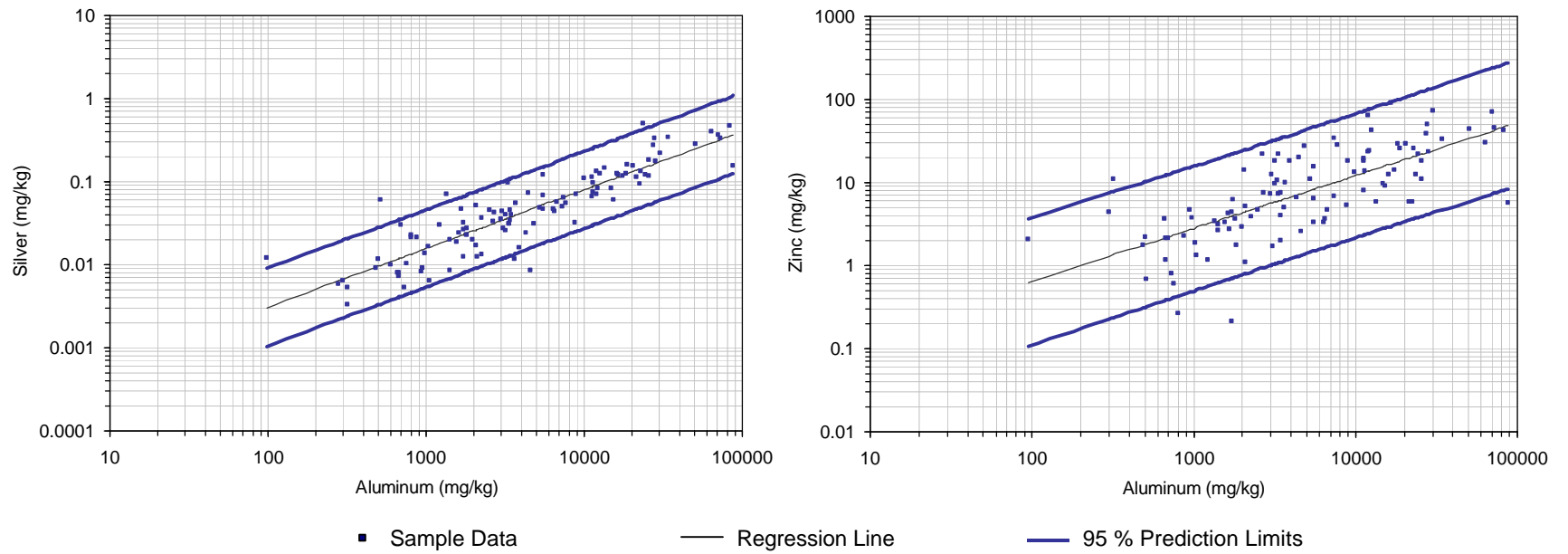


Figure 6.3 (Continued) Metal/Aluminum Regression Lines with the 95 % Prediction Limits

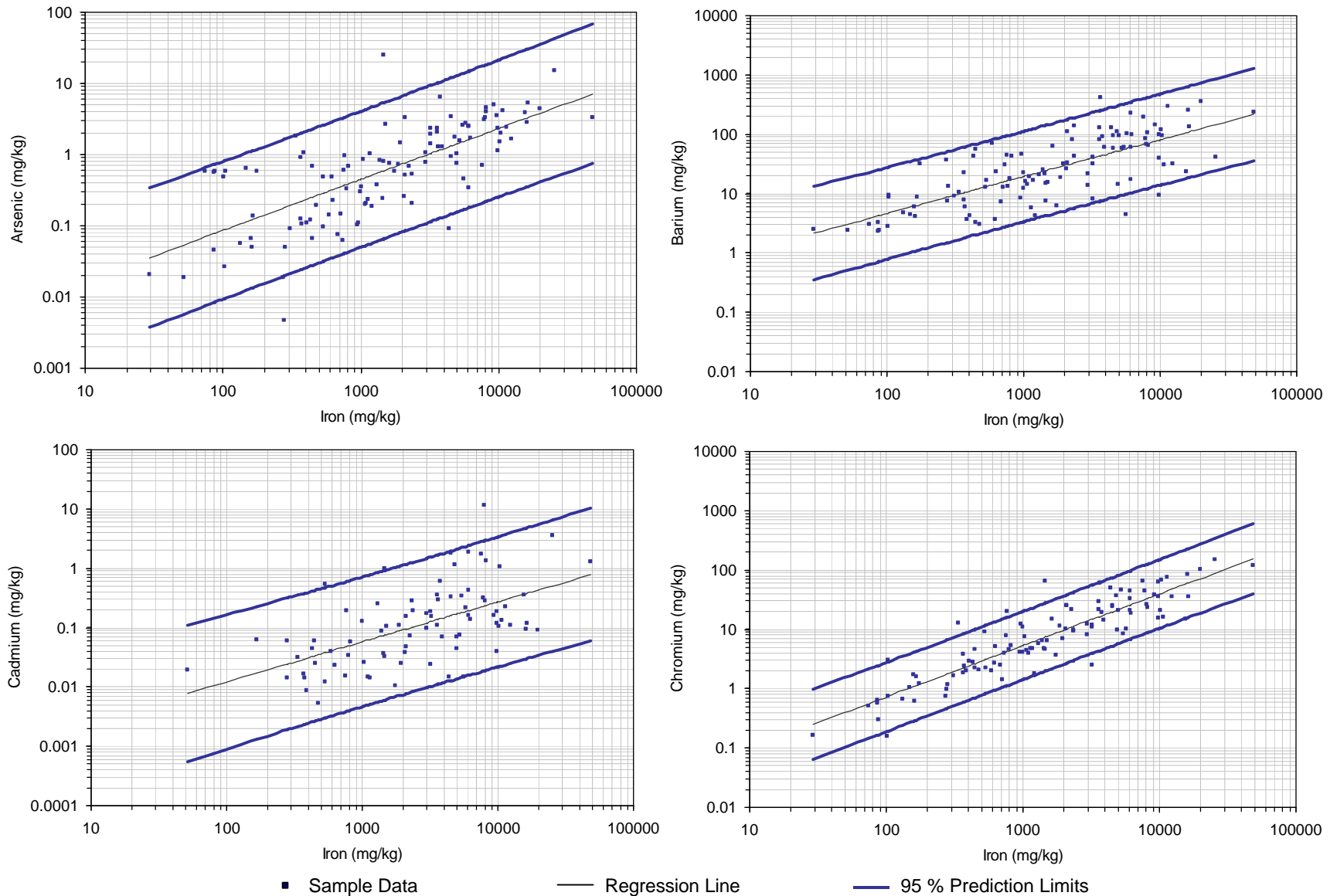


Figure 6.4 Metal/Iron Regression Lines with the 95 % Prediction Limits

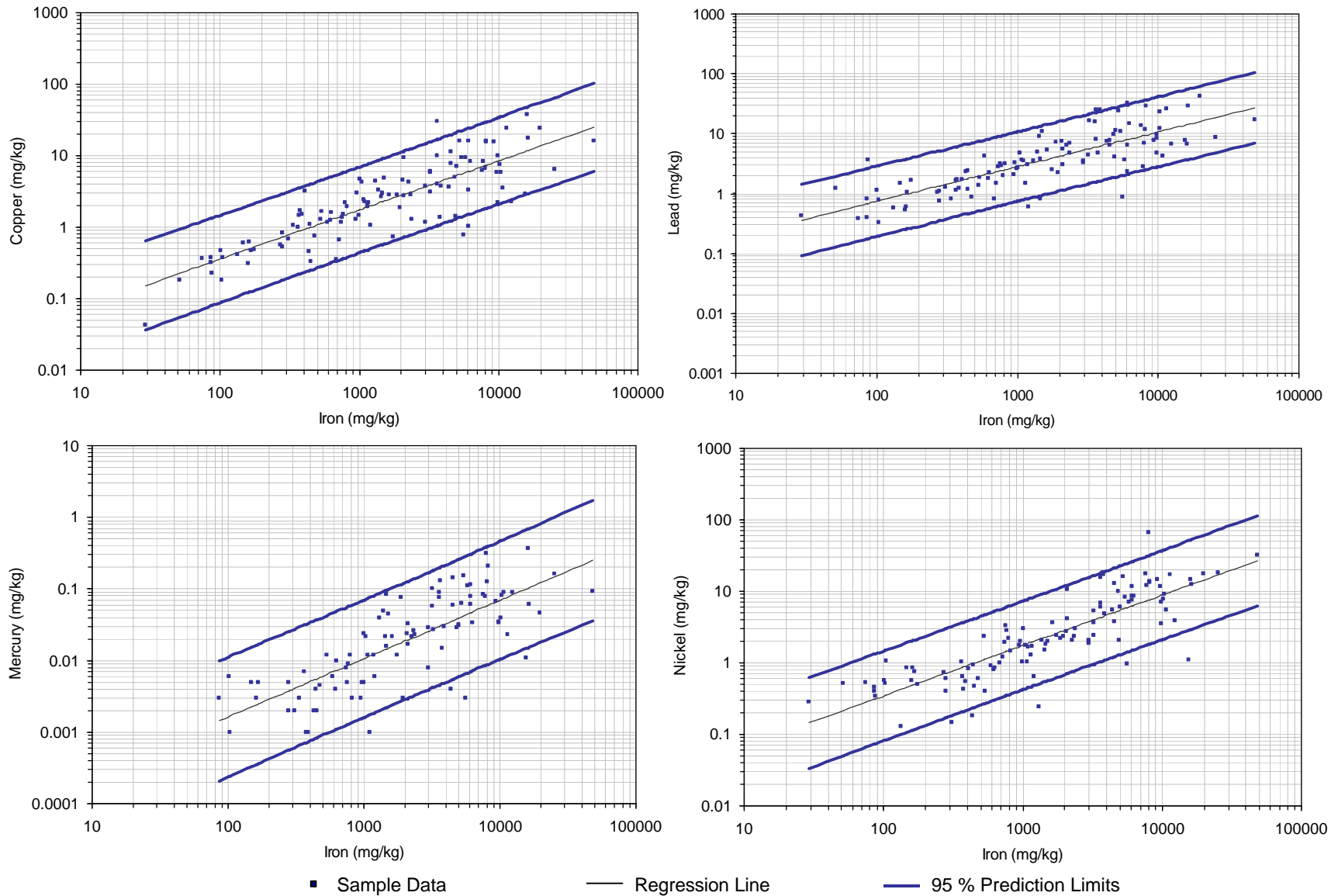


Figure 6.4 (Continued) Metal/Iron Regression Lines with the 95 % Prediction Limits

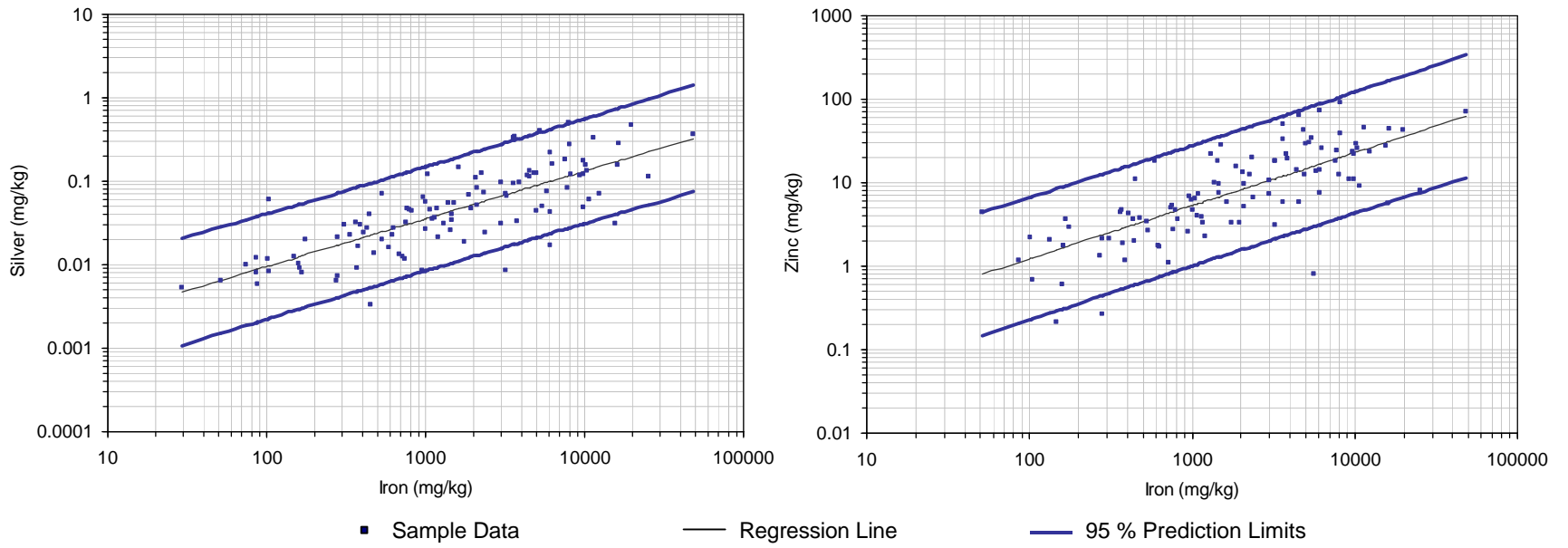


Figure 6.4 (Continued) Metal/Iron Regression Lines with the 95 % Prediction Limits

6.6 Application of the Interpretative Tool

The freshwater sediment metals interpretative tool comprises a set of graphs (Appendices A and B) and an interactive Microsoft Excel™ spreadsheet that accompanies this report. The user can plot absolute metal concentrations on copies of the graphs included in Appendices A and B. Alternatively, the interactive tool guides the user through data entry, plotting, and printing. Figure 6.5 shows a sample application of the tool to hypothetical copper/aluminum concentrations for three different samples.

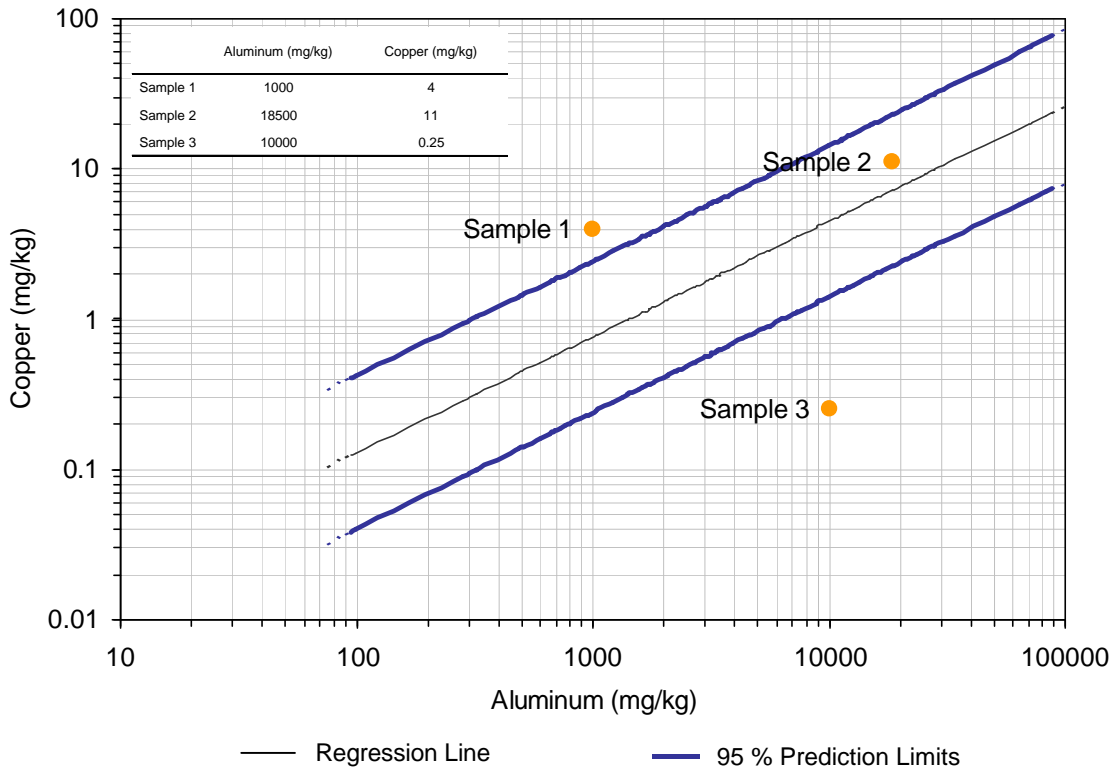


Figure 6.5 Interpretative Tool Example

A sediment falls into either natural or “metal-enriched” classification depending on where the points lie relative to the prediction limits. If a data point falls within the prediction limits (Sample 2), then the sediment metal concentration is within the expected natural range for freshwater systems in Florida. If a data point plots above the upper prediction limit (Sample 1), the sediment may be metal enriched. These data illustrate the point that one should not assume, for a given data set, that samples with highest metal concentrations are most likely contaminated.

Before making a determination of “enrichment,” one must confirm the accuracy of the analytical results. A point above the prediction limits can also indicate procedural errors or natural variation. Similarly, metal concentrations below the lower prediction limit (Sample 3), may be due to procedural error, natural variability, or, perhaps, reference element contamination. Since the interpretative tool is based on 95% prediction limits a few metal concentrations from uncontaminated sediments will be outside of these limits.

If procedural errors can be ruled out, the greater the distance above the upper prediction limit, the greater the likelihood that the sample comes from a metal-enriched sediment. Points that plot closely above or below the upper prediction limit must be interpreted in light of available additional information about possible sources of metal contamination (e.g., sewage or wastewater outfalls) and information from other nearby stations.

7.0 LIMITATIONS OF THE INTERPRETIVE TOOL

The approach presented in this document provides an interpretive tool for evaluating metals concentrations in freshwater sediments in Florida. The use of this tool requires knowledge of local conditions and the application of professional judgment and common sense. The user should keep the following points in mind when applying this interpretive tool.

1) The interpretive tool is meaningless without reliable data. Thus collection of sediment samples should follow FDEP approved methodologies for the collection of uncontaminated samples.

2) Metals analyses must follow techniques appropriate for freshwater sediments. Because naturally occurring aluminum, iron and other metals are tightly bound within the crystalline structure of the sediment minerals, the methods for metals analyses should include complete sediment digestion. If aluminum or iron are not completely released by a strong acid digestion, metal to aluminum or metal to iron ratios may appear unusually high.

3) Aluminum concentrations in the reference data set ranged from 94 to 87,700 (mg/kg), while iron concentrations ranged from 29 to 48,400 mg/kg. The reference data set, to the extent possible in this project, represents various types of natural “clean” sediments found in Florida's freshwater systems. The majority of samples recovered from Florida freshwater sediments will likely have aluminum and iron concentrations within the above range. To extend the applicability of the interpretive tool to sediments containing aluminum and iron concentrations beyond these ranges, the prediction limits have been extrapolated upward to concentrations of 100,000 mg/kg aluminum and 50,000 mg/kg iron and downward to 90 mg/kg aluminum and 25 mg/kg iron. The dashed lines in the figures indicate extrapolations. Although a reasonable approach, any interpretations based on the extrapolated lines should include a qualifying statement acknowledging that the data in question exceed the range of the “clean” data set. Any samples containing greater than 100,000 mg/kg aluminum or 50,000 mg/kg iron concentrations should receive special scrutiny to detect evidence of contamination or analytical error.

4) At stations where a metal concentration exceeds the upper 95% prediction limit, the sediment may be considered metal enriched. One must not immediately assume, however, that a finding of “enrichment” is indicative of a problem. Some samples from natural “clean” sediments

will contain metals whose concentrations exceed the 95% prediction limit. Interpretation of metal concentrations with these metal/aluminum and metal/iron relationships must also take into consideration sediment grain size, mineralogy, hydrology, proximity to sources of metals and, if possible, method detection limits and laboratory errors.

5) The majority of the freshwater sediment samples used to build the sediment metals database from which this tool was developed came from central peninsular and north Florida. Therefore, this tool should be used to evaluate sediments from the same region.

8.0 RECOMMENDATIONS

The freshwater sediment metals interpretive tool described herein was developed from a data set comprised of lake, stream, and spring samples from central peninsular and north Florida. Although similar metal to reference element relationships could exist in sediments from other parts of Florida, the interpretive tool should be used with a cautionary note outside of central peninsular and north Florida. Additional data are needed to expand the geographic range of the freshwater metals interpretive tool. Specifically, sediment samples from south Florida and far northwest Florida freshwater systems should be obtained and incorporated into the “clean” sediment database. The data should then be reanalyzed to determine whether a single freshwater interpretive tool could be further developed for statewide use.

As noted in Section 6.2, separation of the metals data into separate data sets for lakes, streams, and springs might result in stronger correlations between metals and reference elements. However, segregation of the present metals data set by water body type results in too few data for reliable analysis of each type. Therefore, the freshwater metals interpretive tool was developed with the combined data from all water body types. The advantage of this approach is that the tool is simple to use. For example, a user is not required to determine when a “spring” run has become a “stream” or a slow moving “stream” has become a “lake”. Nonetheless, if additional metals data are collected as recommended above, those data should be evaluated to determine whether separate interpretive tools should be developed for each water body type.

The reader of this document is cautioned not to interpret finding of any exceedence to represent an estimate of bioavailable metals. This tool does not address the complex nature of contaminant bioavailability or toxicity; other methods are available to test site-specific contaminant bioavailability or toxicity. Additionally, the reader is directed to use other tools to further interpret the meaning of metals exceedences, such as the Consensus-Based Sediment Quality Guidelines (MacDonald et. al, 2000), the companion evaluation of the predictive ability of these Guidelines for Florida (MacDonald, 2001; MacDonald and Ingersoll, 2002).

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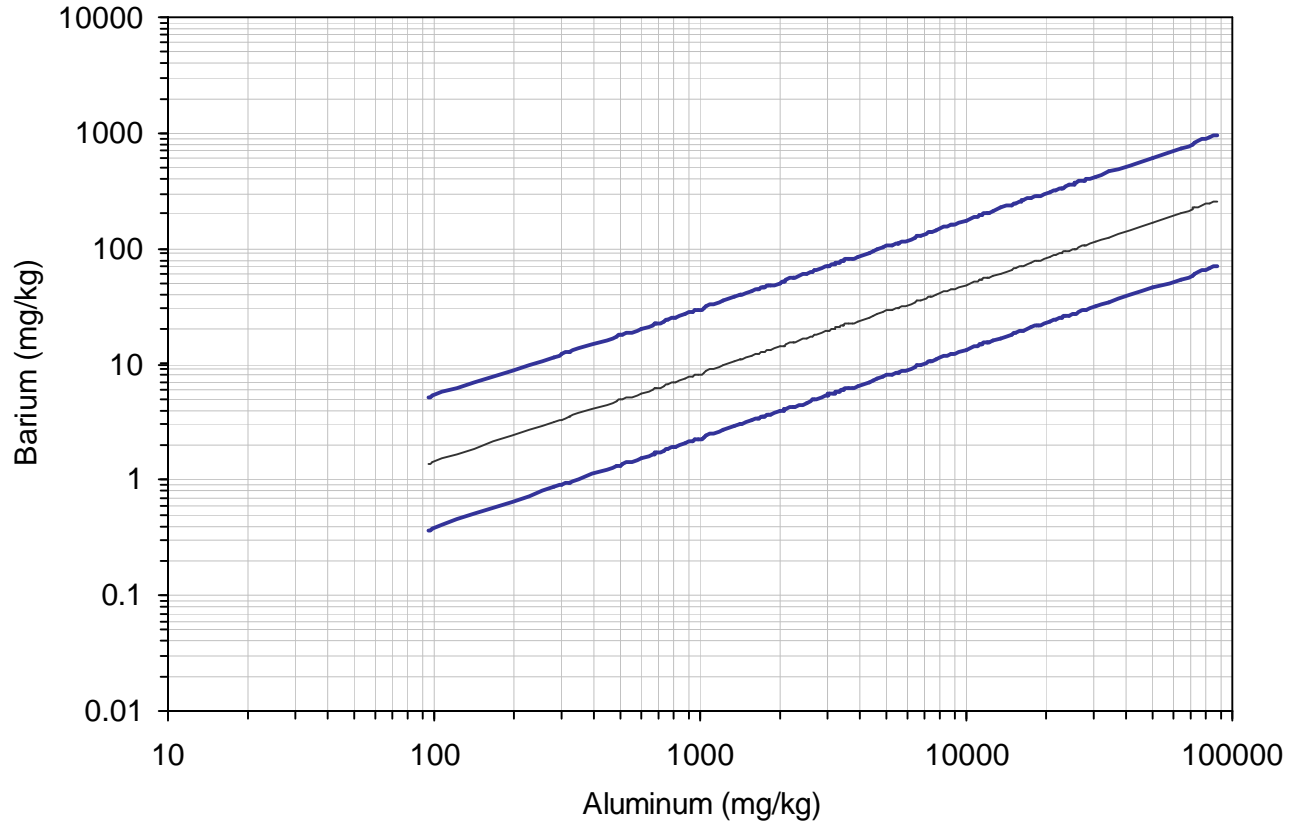
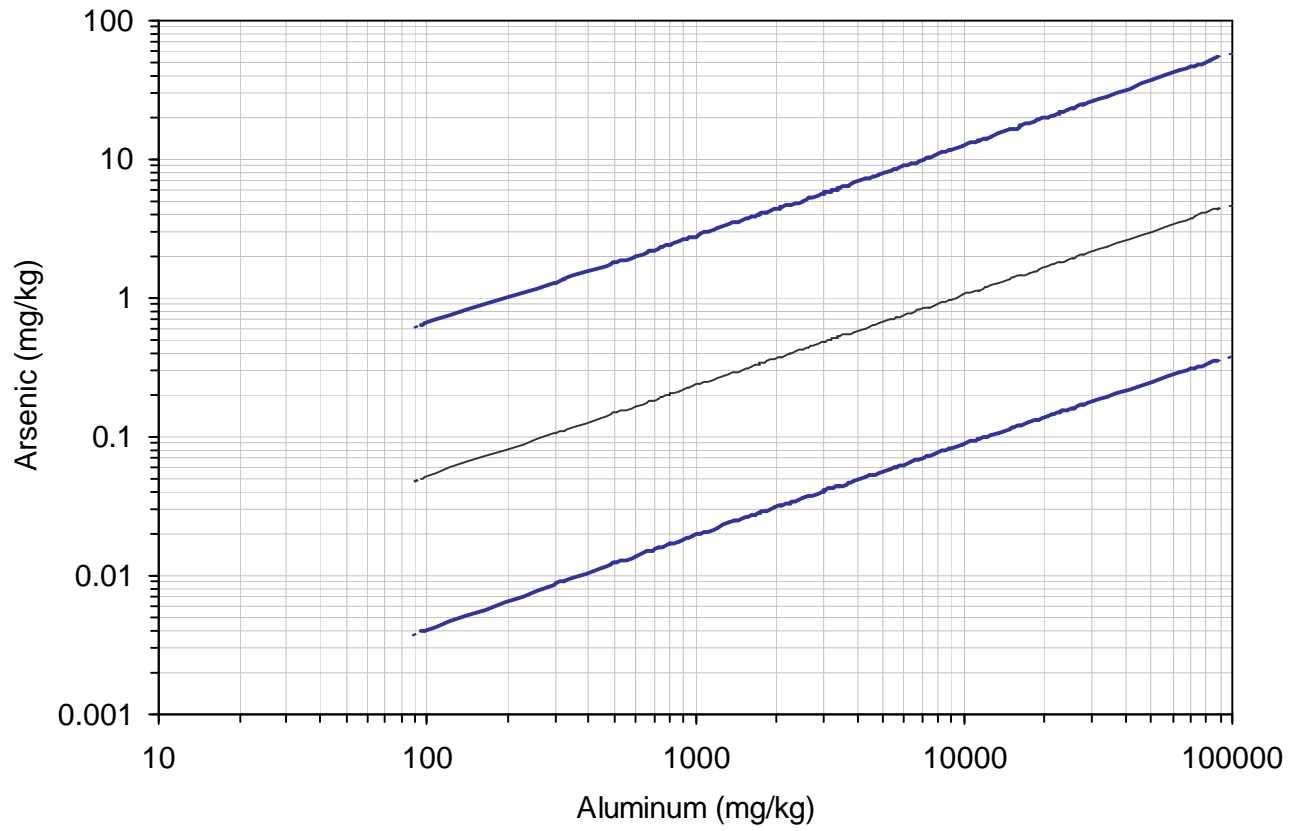
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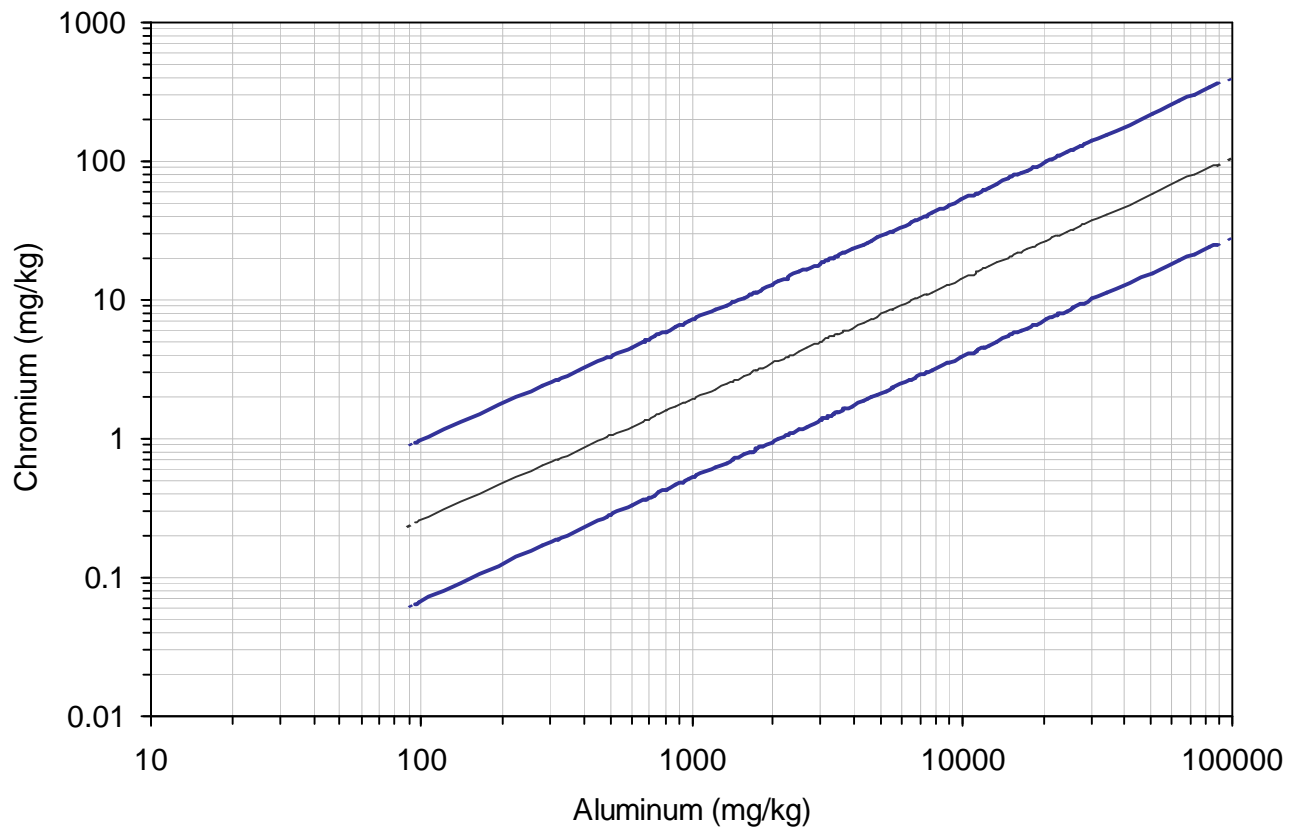
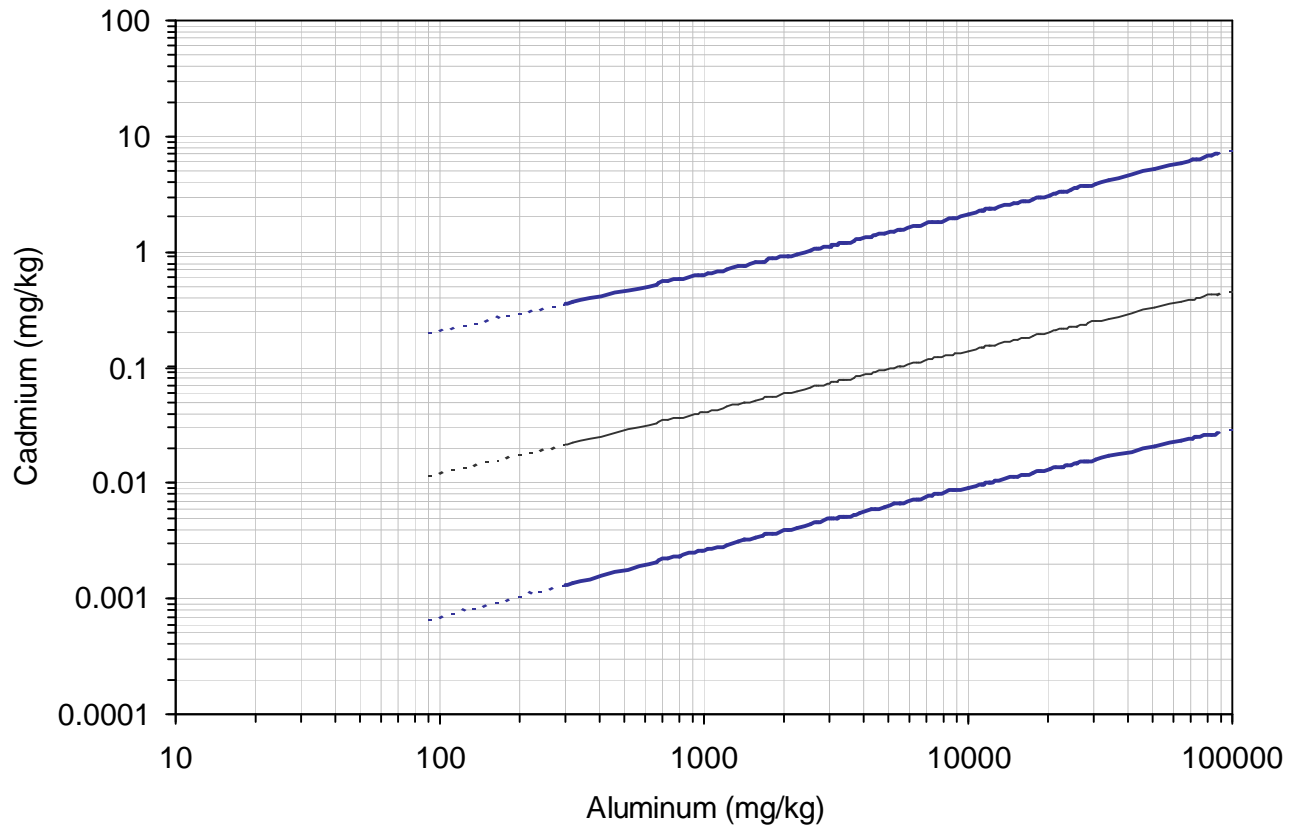
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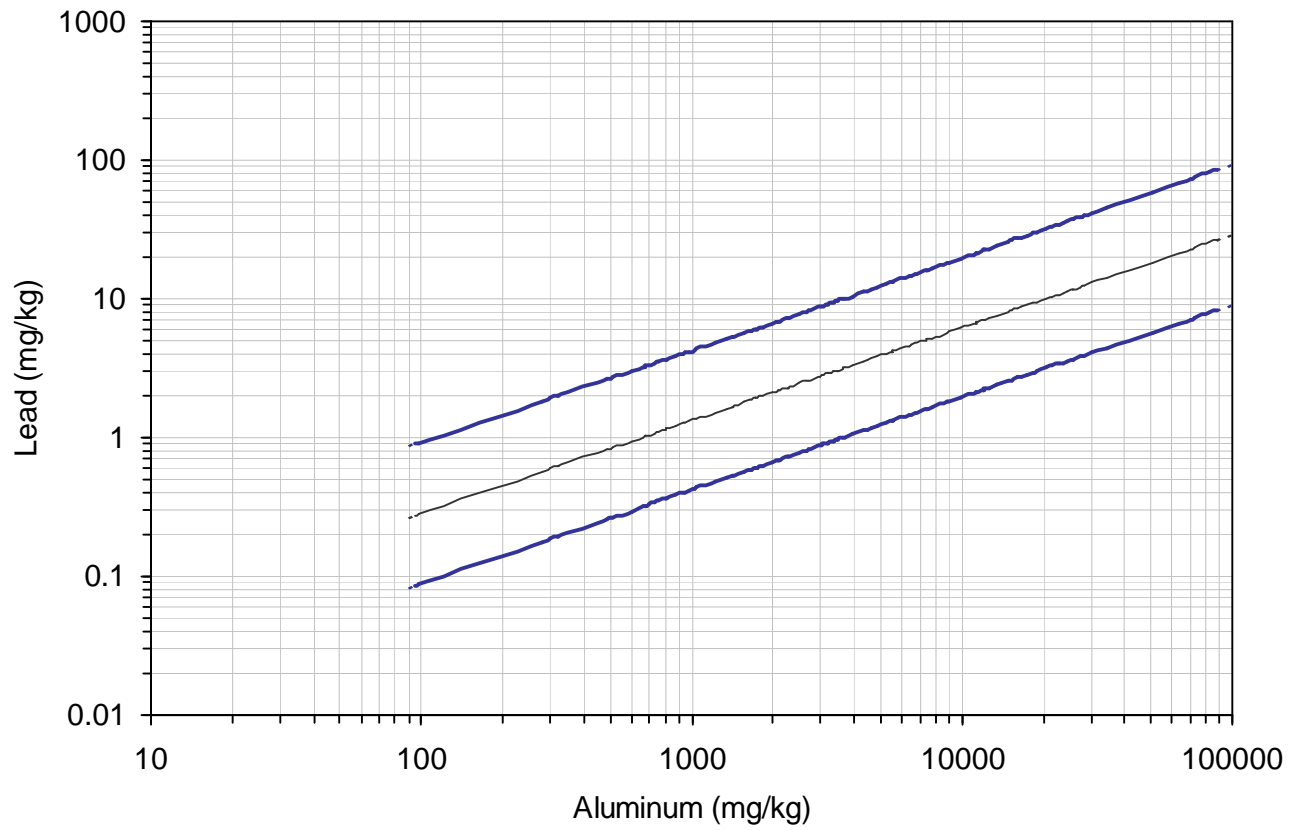
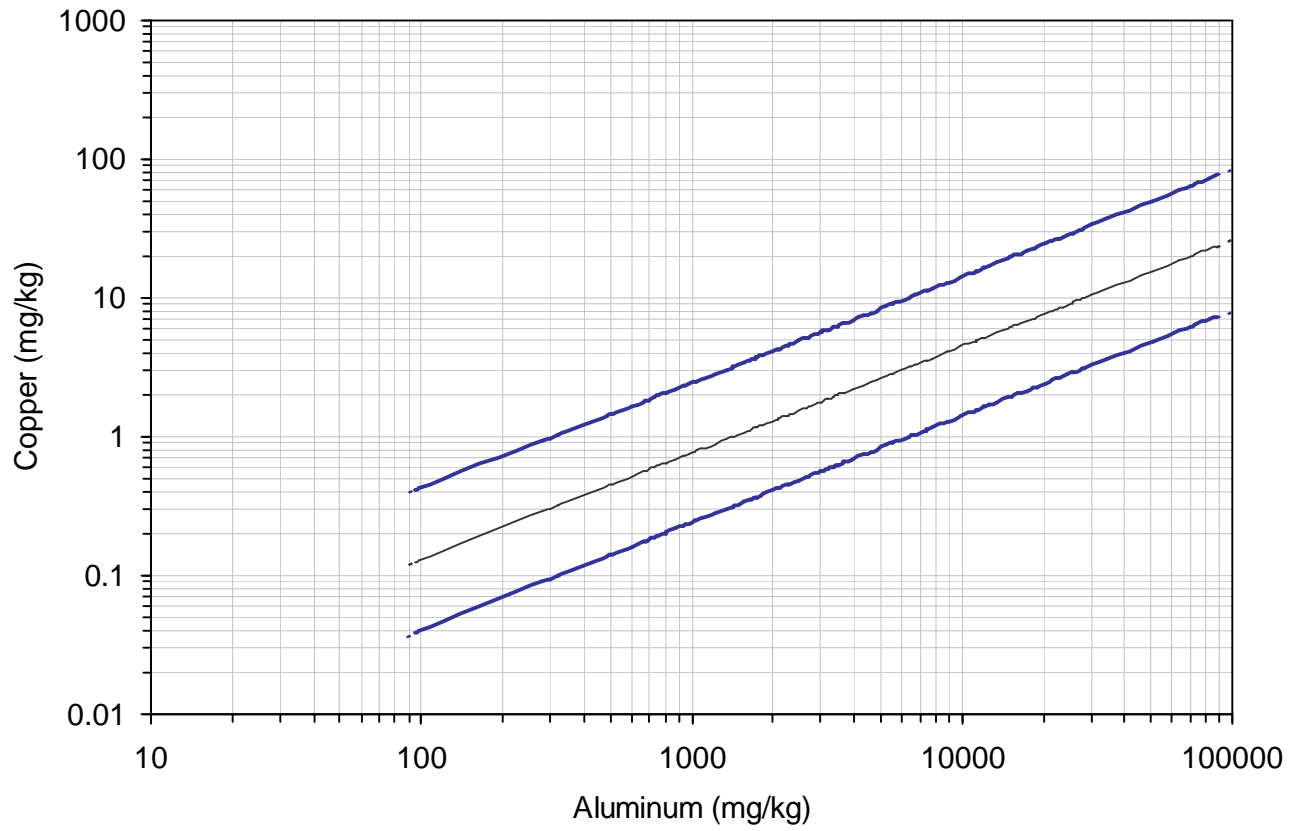
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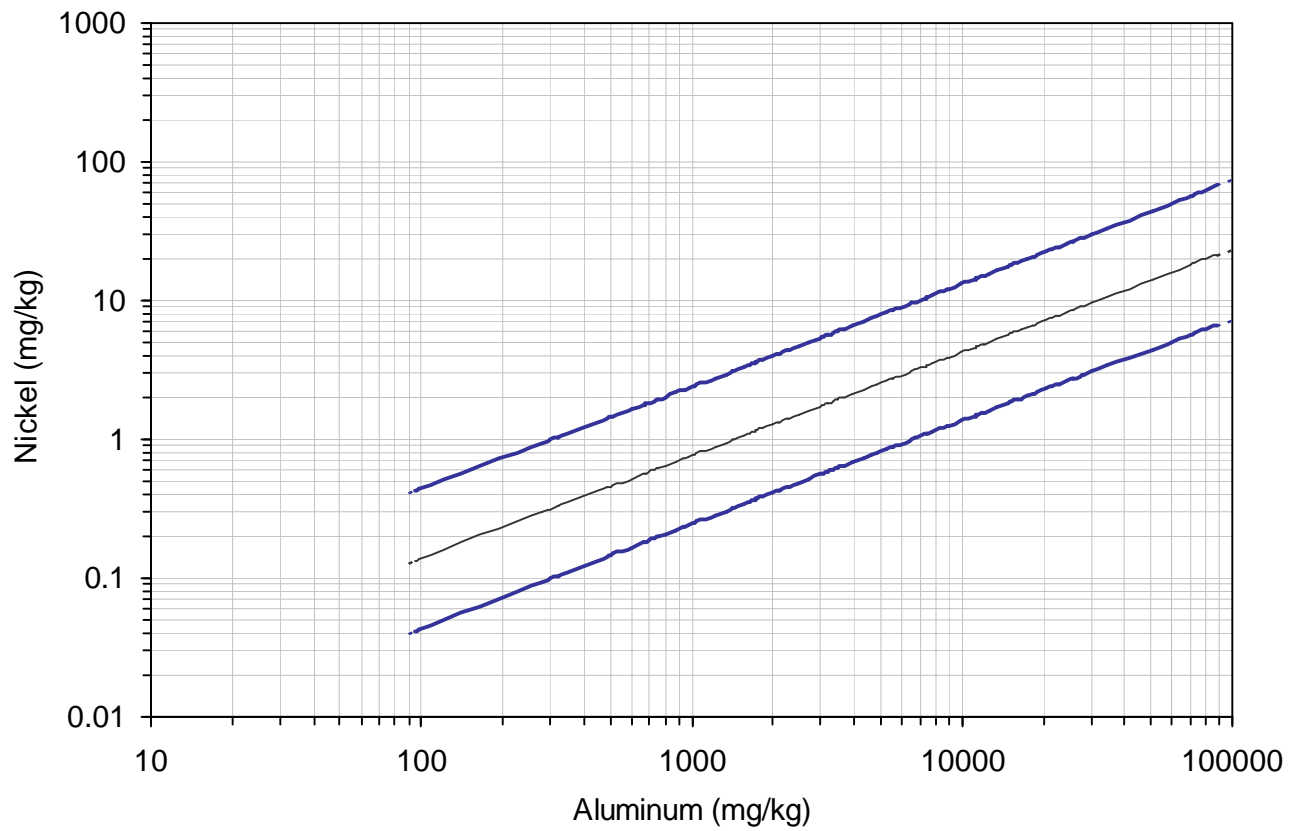
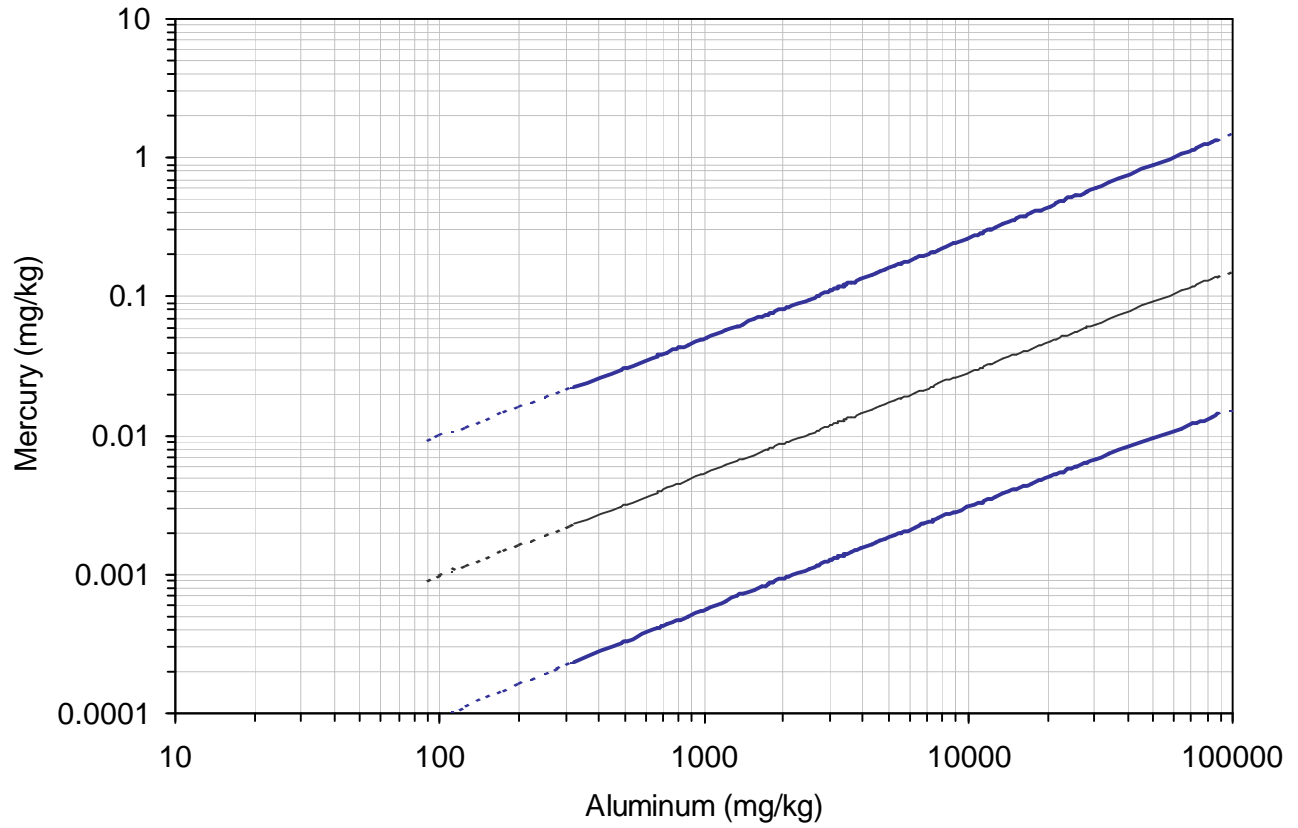
APPENDIX A

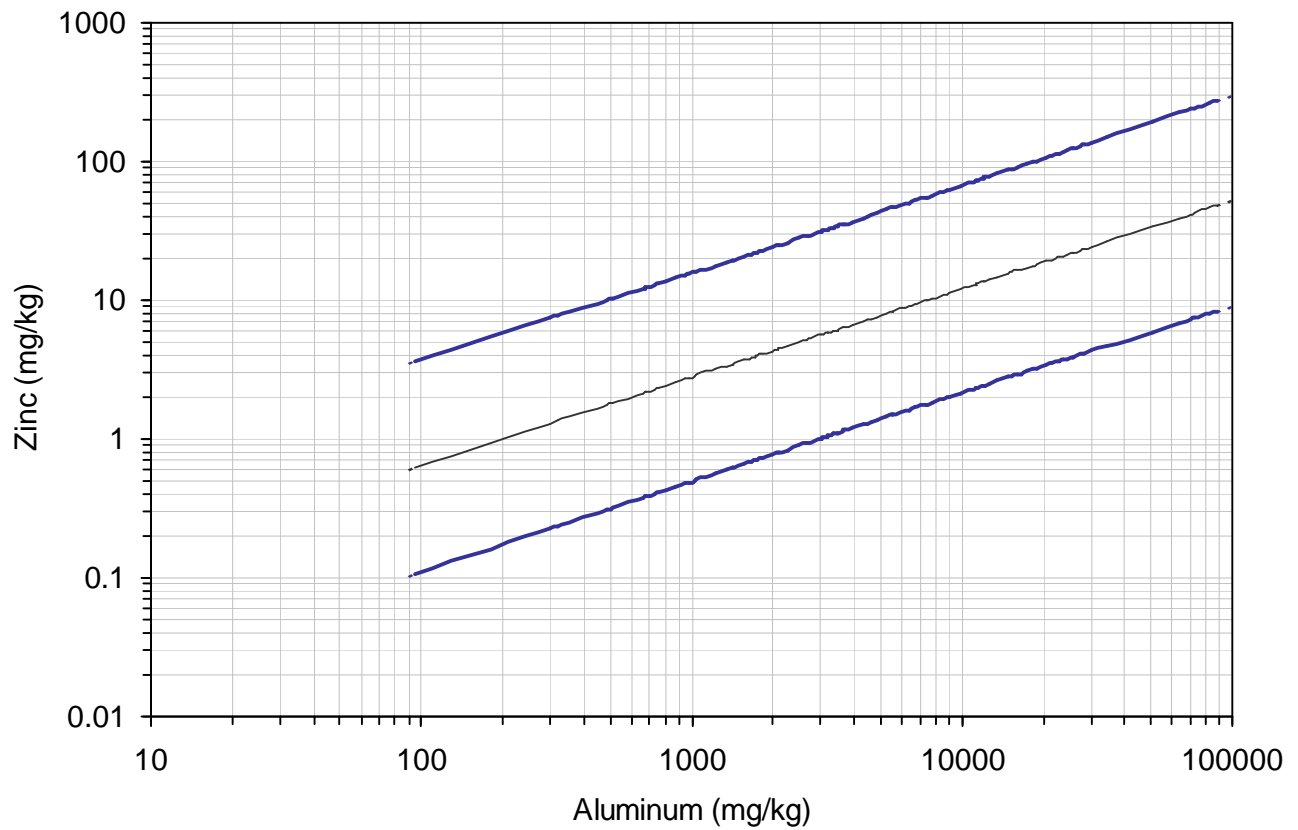
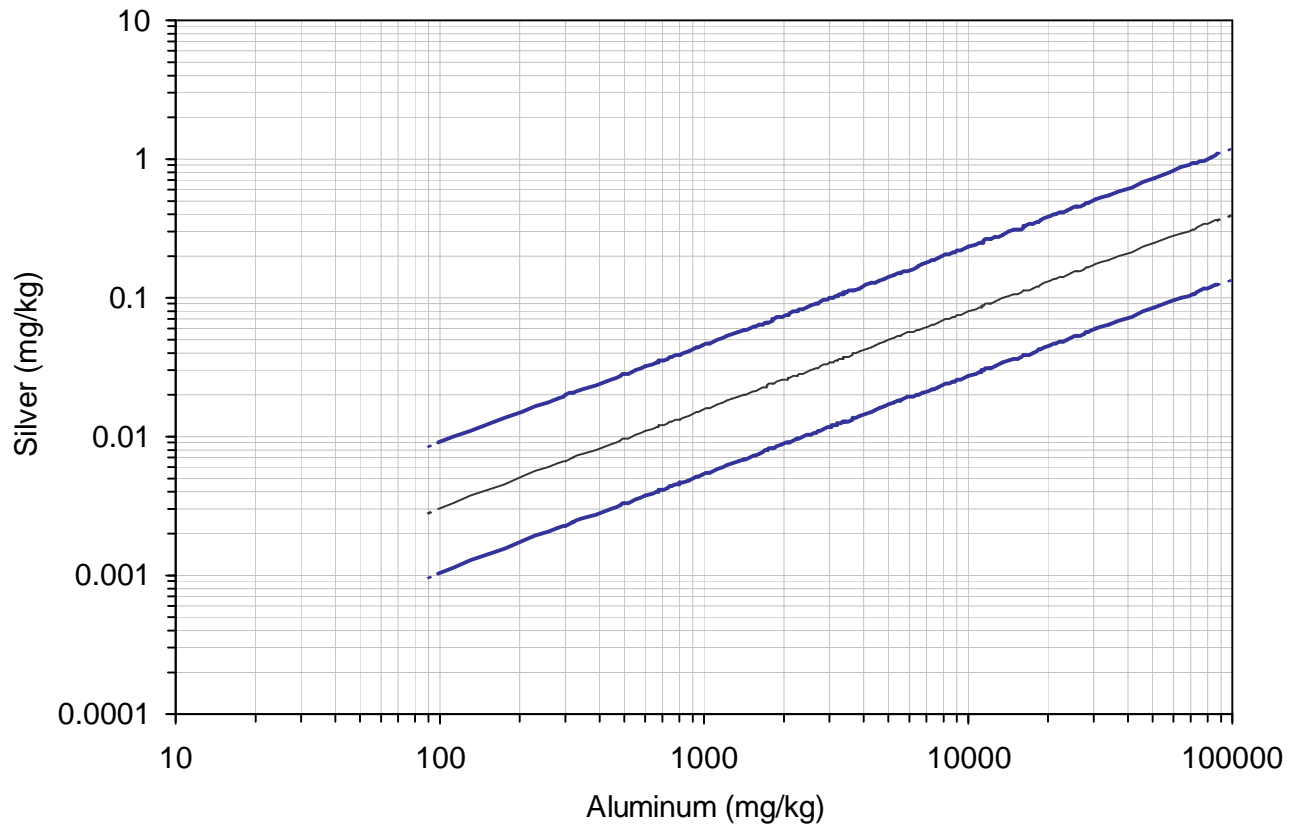
METAL/ALUMINUM DIAGRAMS





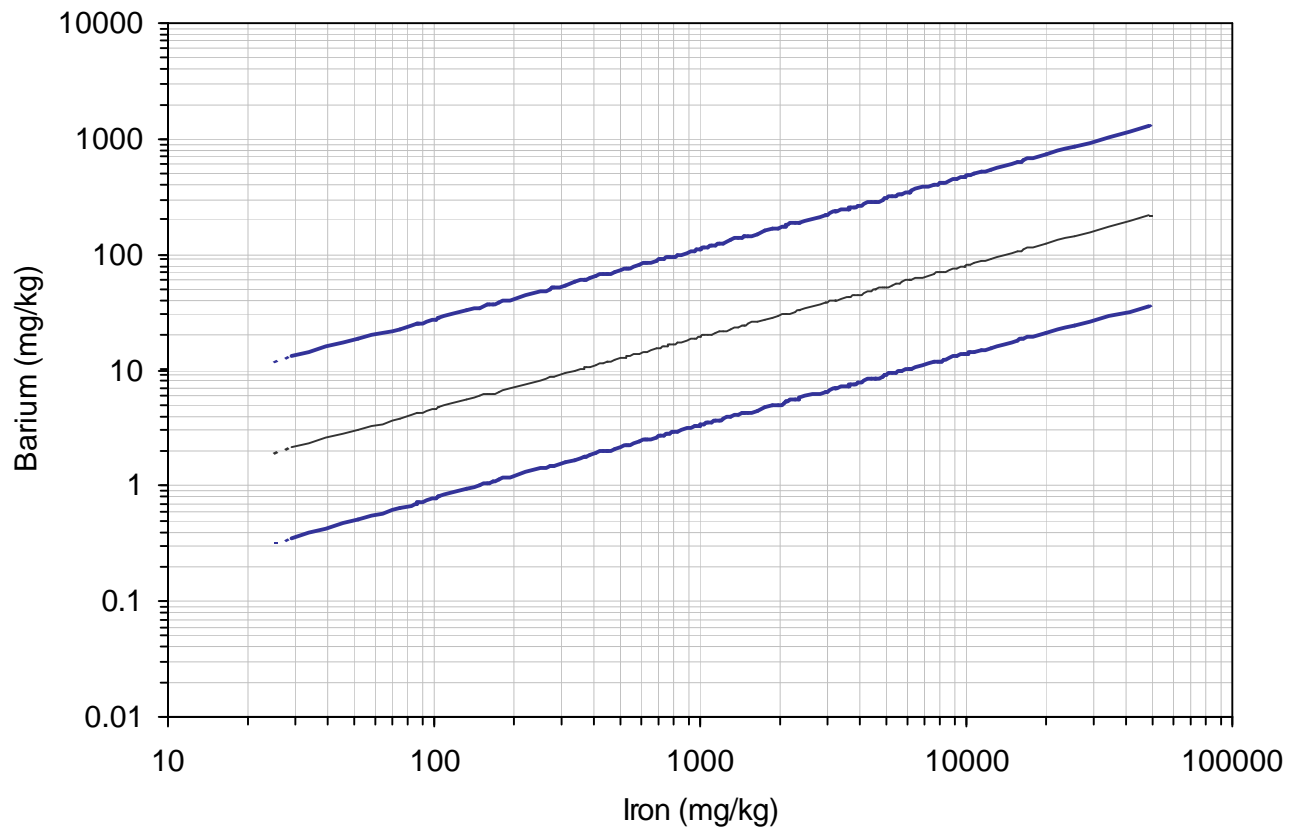
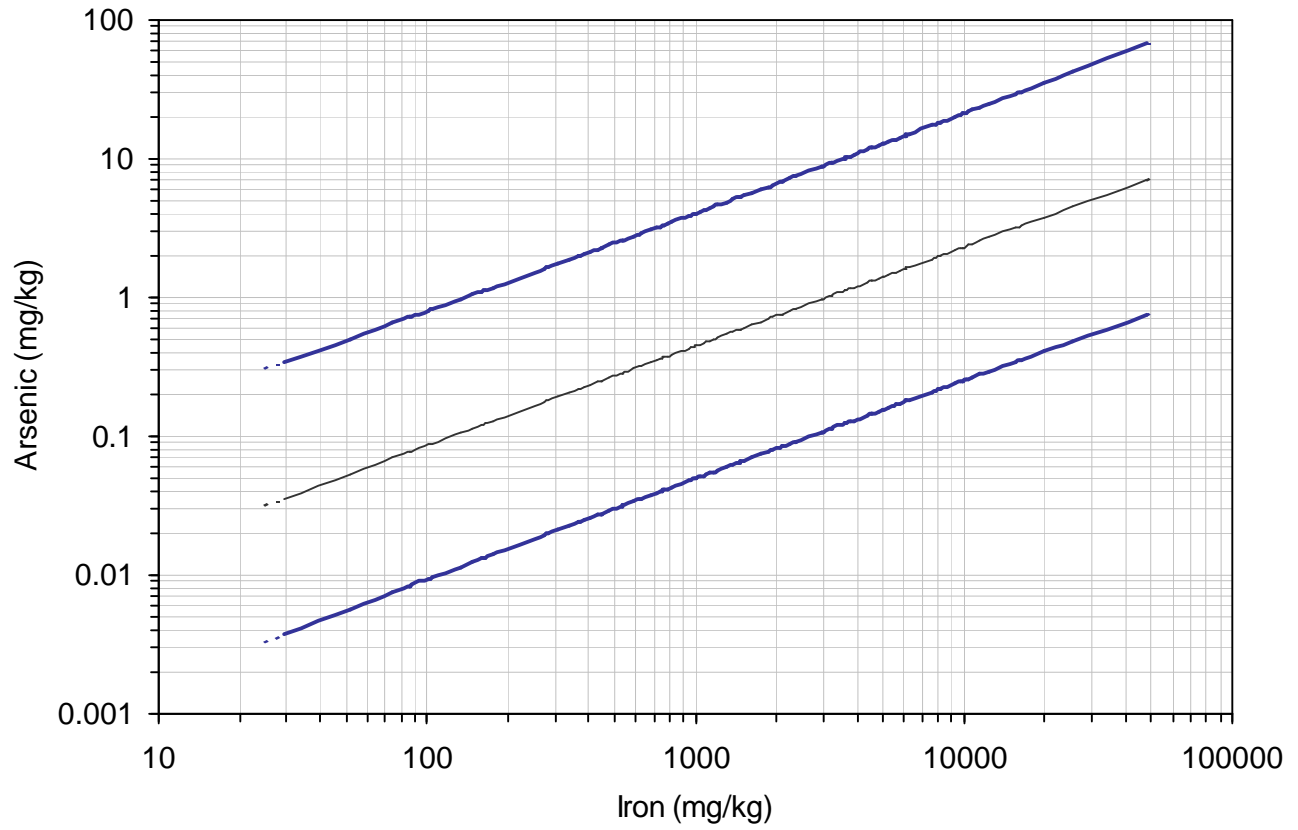


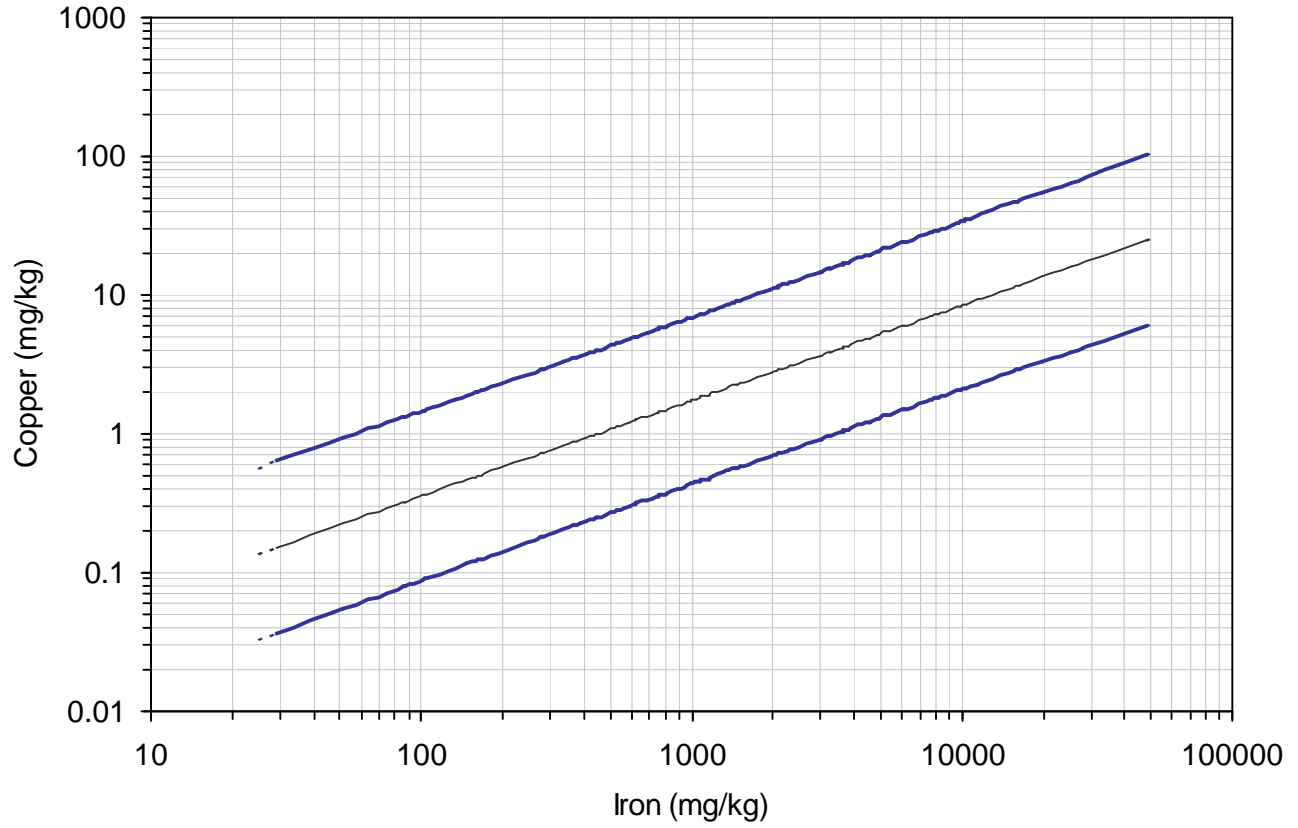
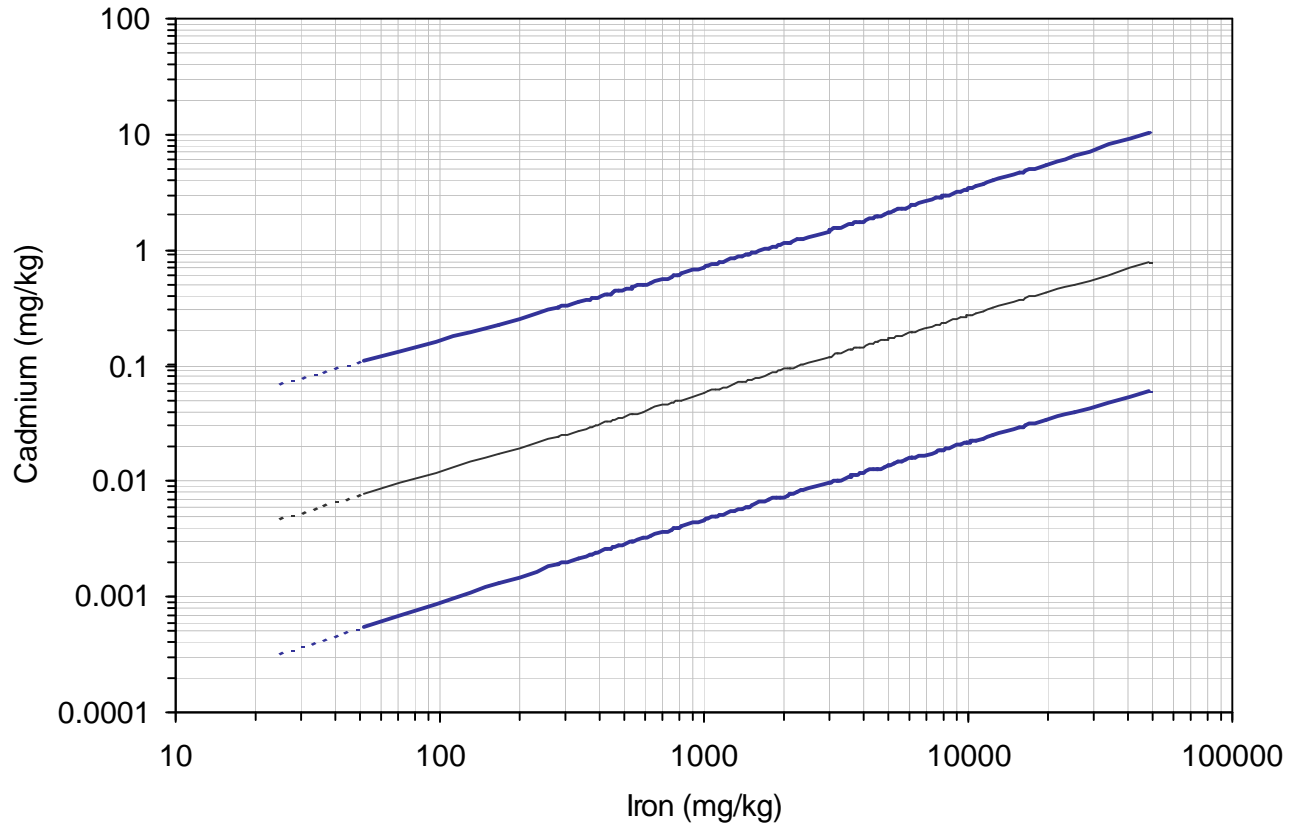


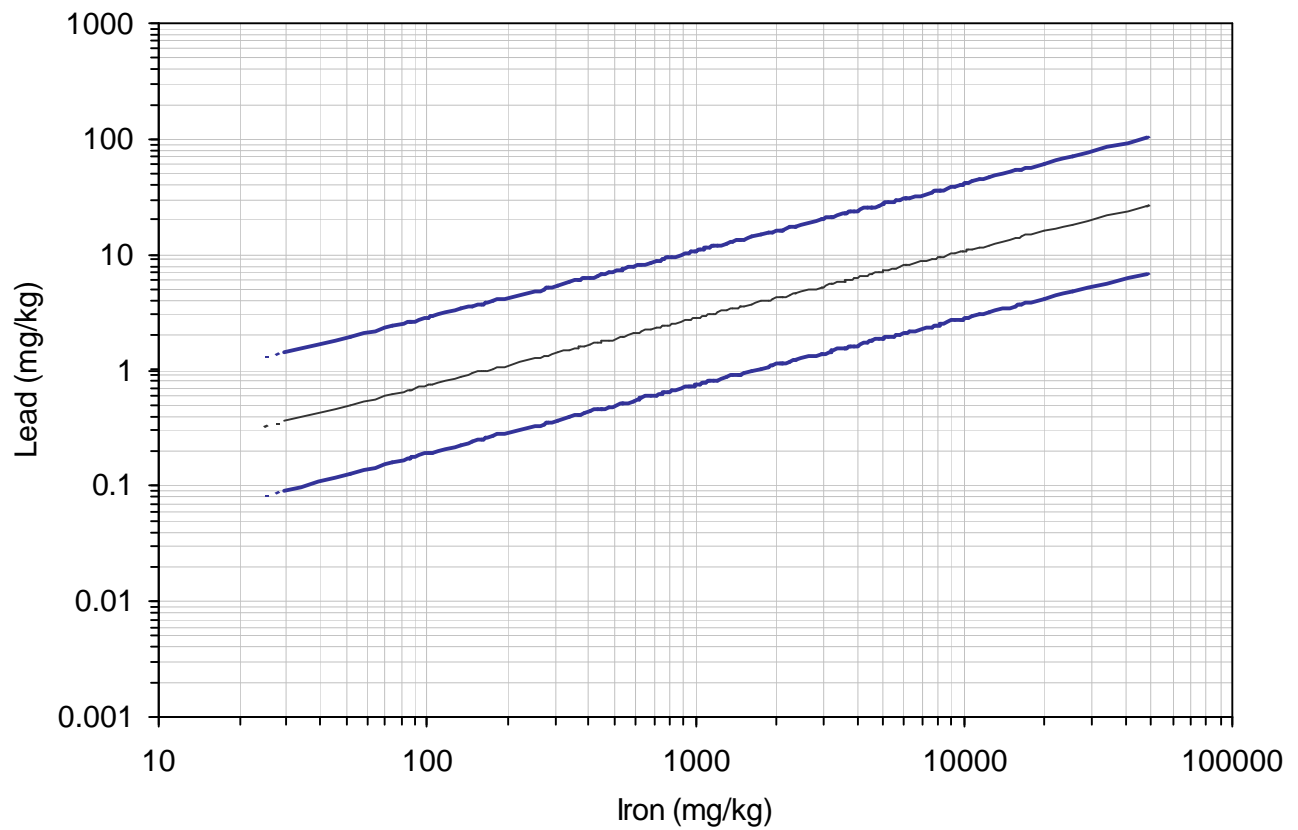
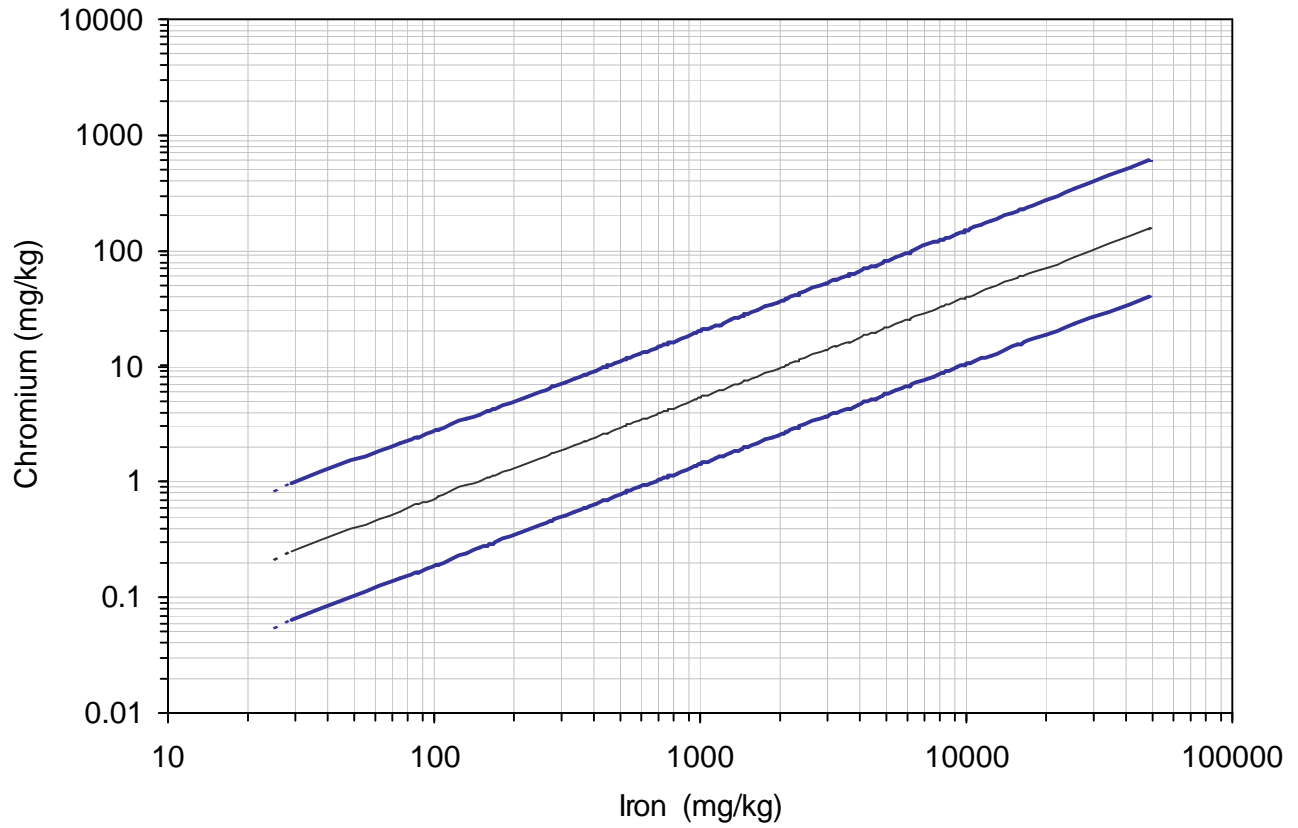


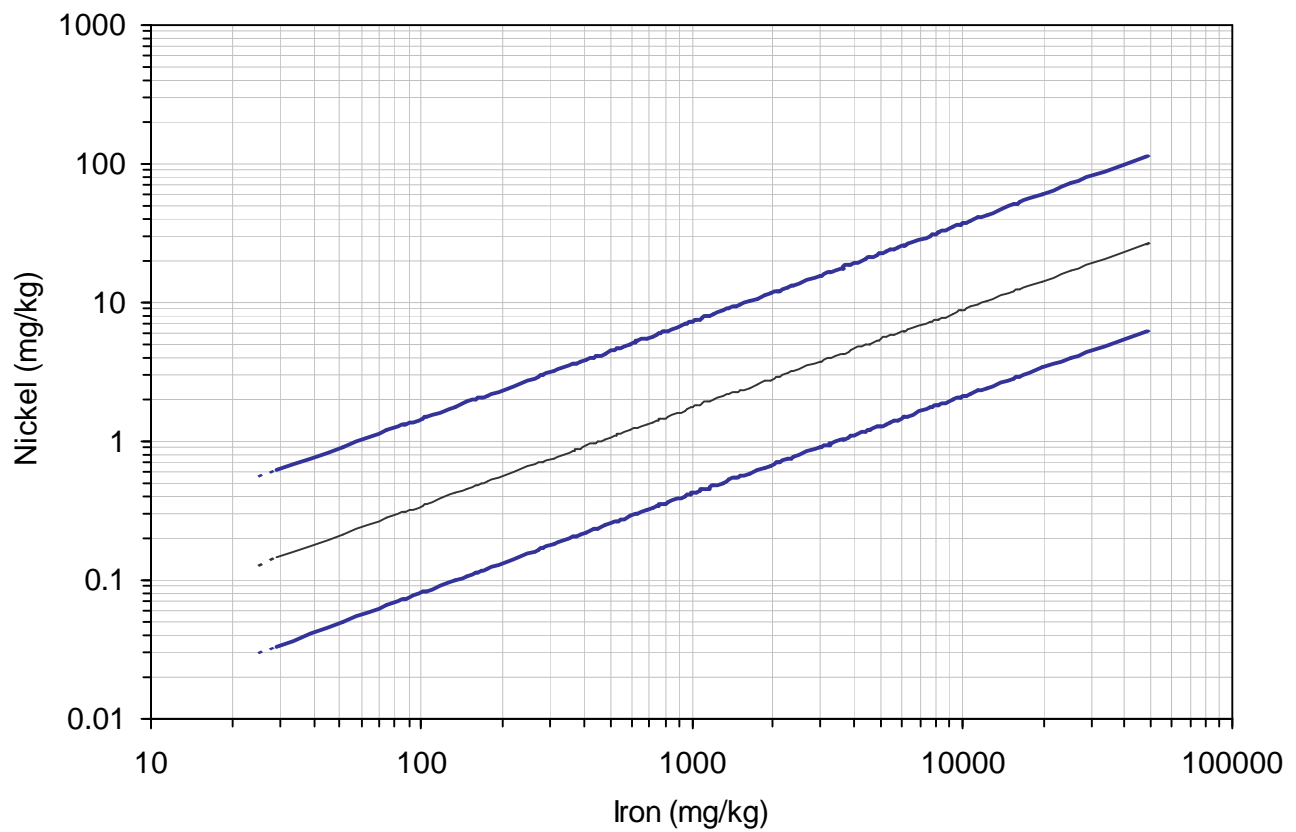
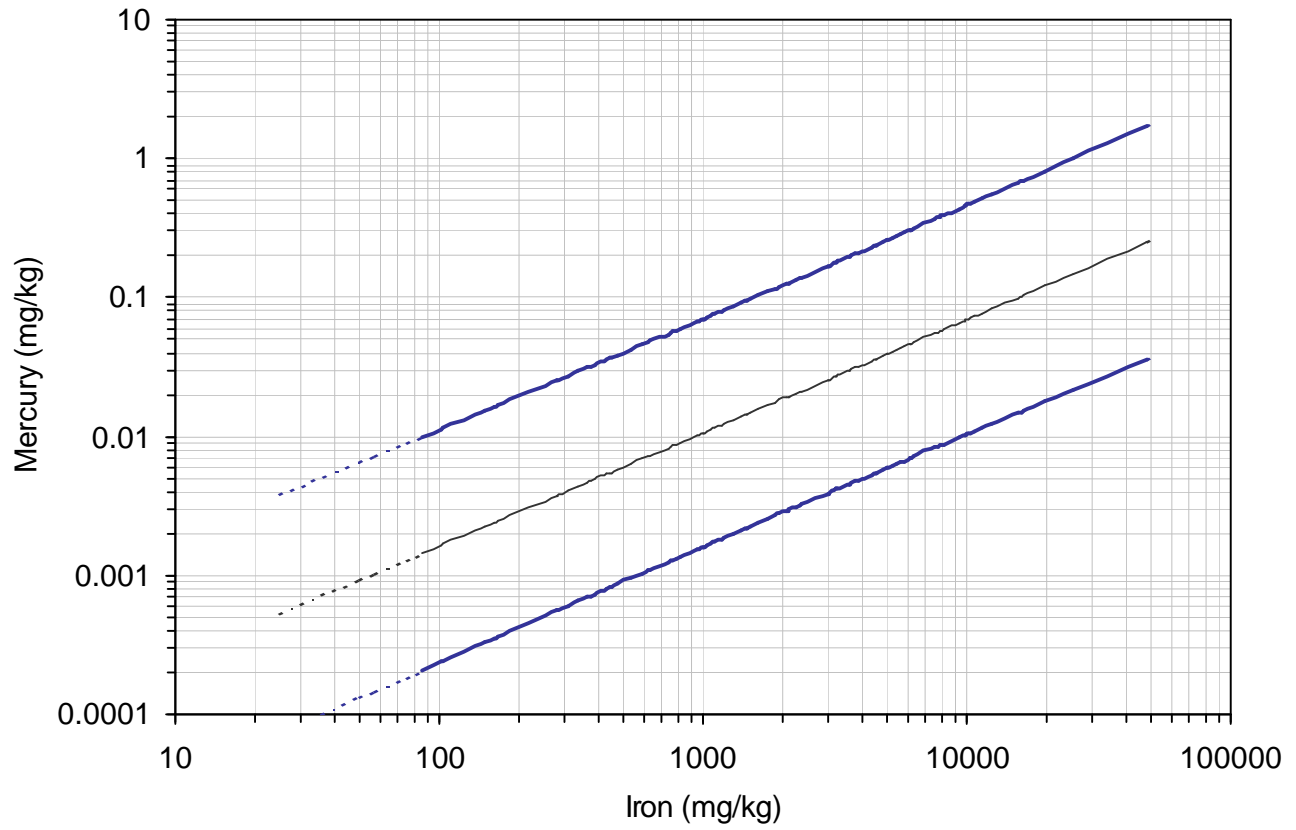
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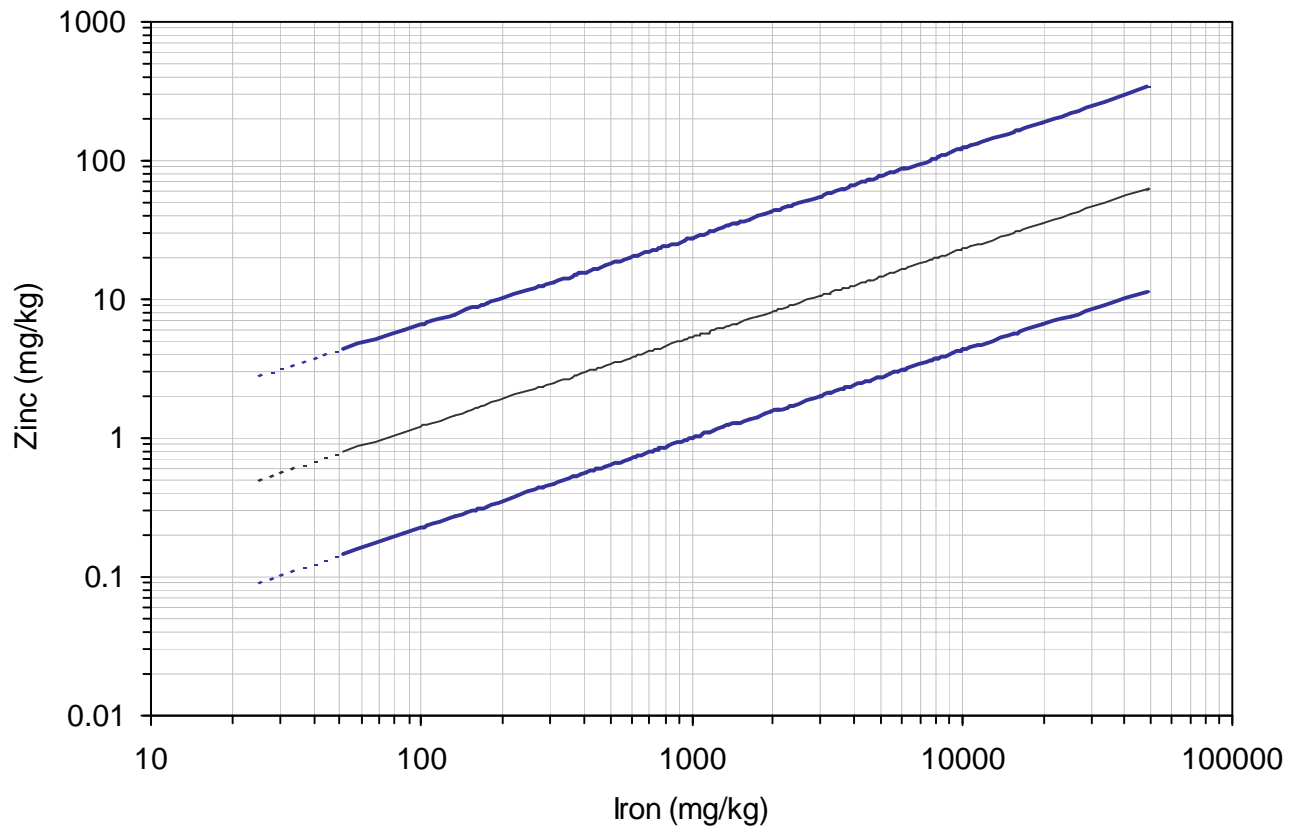
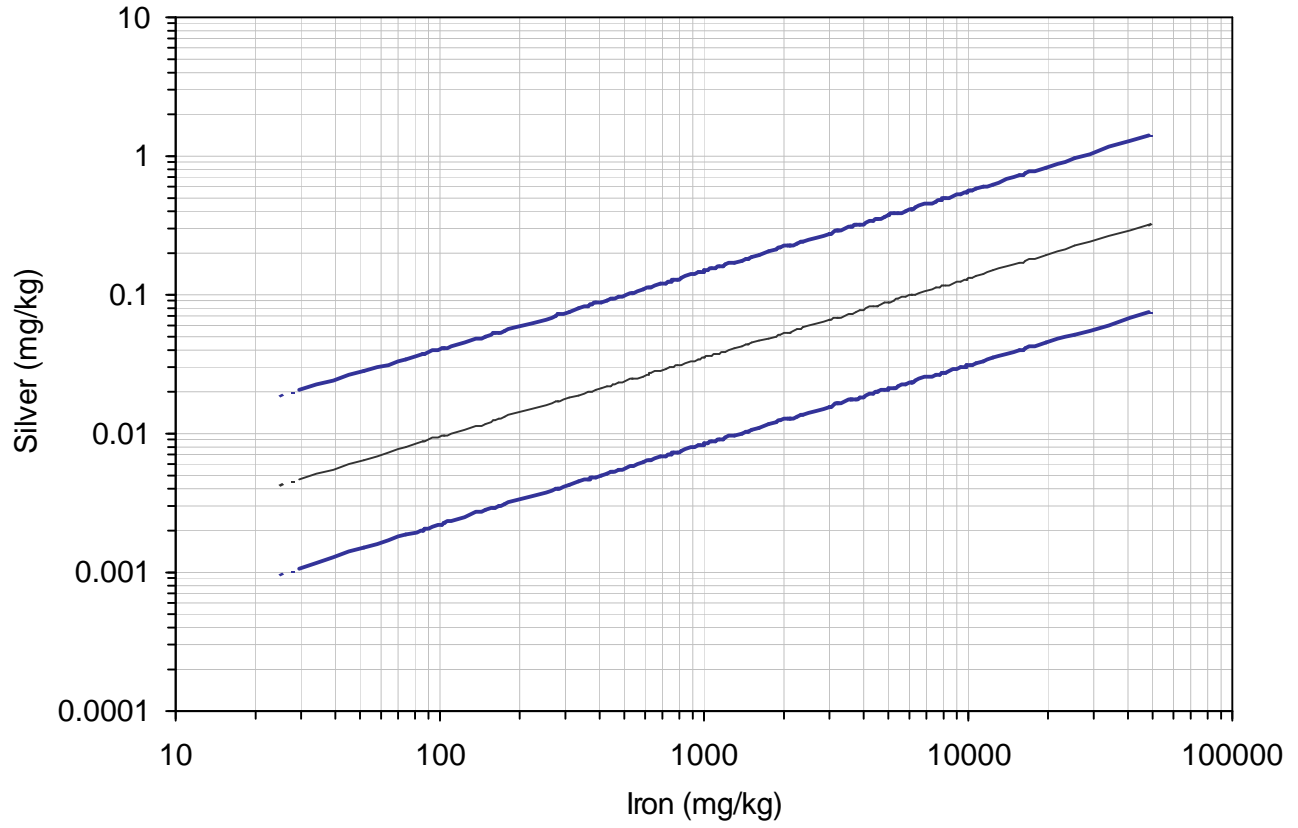
METAL/IRON DIAGRAMS











APPENDIX C

EXCEL[™] INTERPRETATIVE TOOL

Interpretative Tool for Assessment of Metal Enrichment in Florida Freshwater Sediments

Developed by Alexandra Carvalho, Ph.D. & Steven Schropp, Ph.D.



Taylor Engineering Inc
9000 Cypress Green Dr. Suite 200
Jacksonville, Florida 32256

For



Florida Department of Environmental Protection
Tallahassee, Florida

Start

May 2002

This workbook is a companion tool to the "Development of An Interpretive Tool for Assessment of Metal Enrichment in Florida Freshwater Sediment" report. The user should consult this report for guidance on data quality and interpretation of results before using the workbook.

Interpretative Tool
Contact Information

Click the "Start"
button to load the
Interpretative tool.

Click the "OK"
button to fill in the
origin and
characteristics of the
metal data set, the
laboratory contact
and user
information.

Metals Data Set Description

Name: _____
Sample Location: _____
Sampling Date: _____ through _____ Number of Samples: _____
Collected by: _____
Address: _____ Phone: _____
City: _____ State: _____ Zip: _____

Laboratory Contact

Laboratory: _____
Address: _____ Phone: _____
City: _____ State: _____ Zip: _____

Interpretative Tool User Information

Prepared by: _____ Date: _____
Address: _____ Phone: _____
City: _____ State: _____ Zip: _____

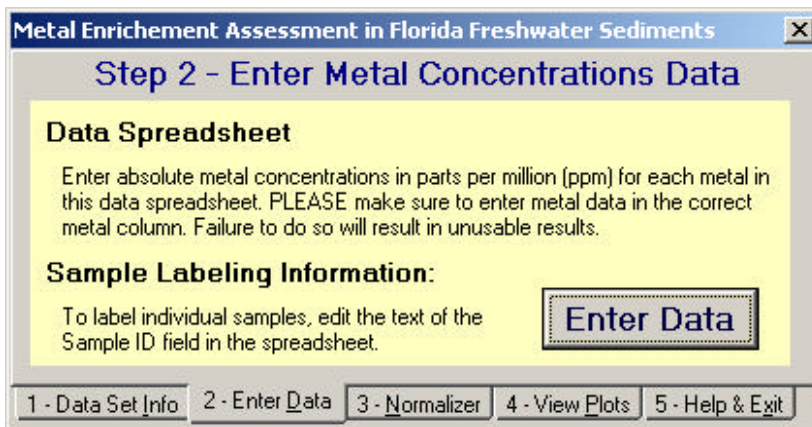
Continue

After filling in the
current screen click
the "Continue"
button". It will take
you to the metal
data spreadsheet.

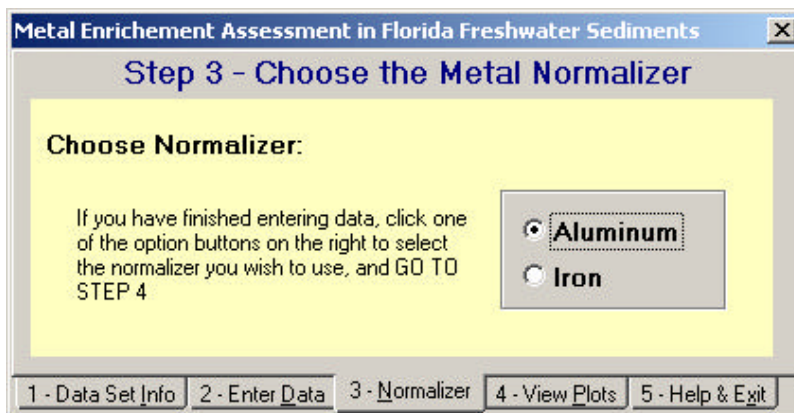
	Click Here When Finished Entering Data											
Sample ID	Aluminum (Al)	Iron (Fe)	Arsenic (As)	Barium (Ba)	Cadmium (Cd)	Chromium (Cr)	Copper (Cu)	Lead (Pb)	Mercury (Hg)	Nickel (Ni)	Silver (Ag)	Zinc (Zn)
Sample 1												
Sample 2												
Sample 3												
Sample 4												
Sample 5												
Sample 6												
Sample 7												
Sample 8												
Sample 9												
Sample 10												
Sample 11												
Sample 12												
Sample 13												
Sample 14												
Sample 15												
Sample 16												
Sample 17												
Sample 18												
Sample 19												
Sample 20												
Sample 21												
Sample 22												
Sample 23												
Sample 24												

Enter or Paste the metal data and sample ID in the proper columns.

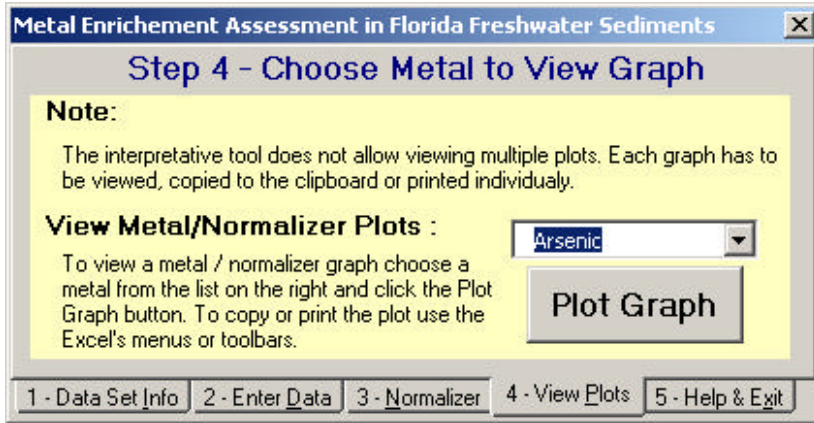
Once finished click the "Click Here When Finished Entering the Data" button to continue. to Step 3



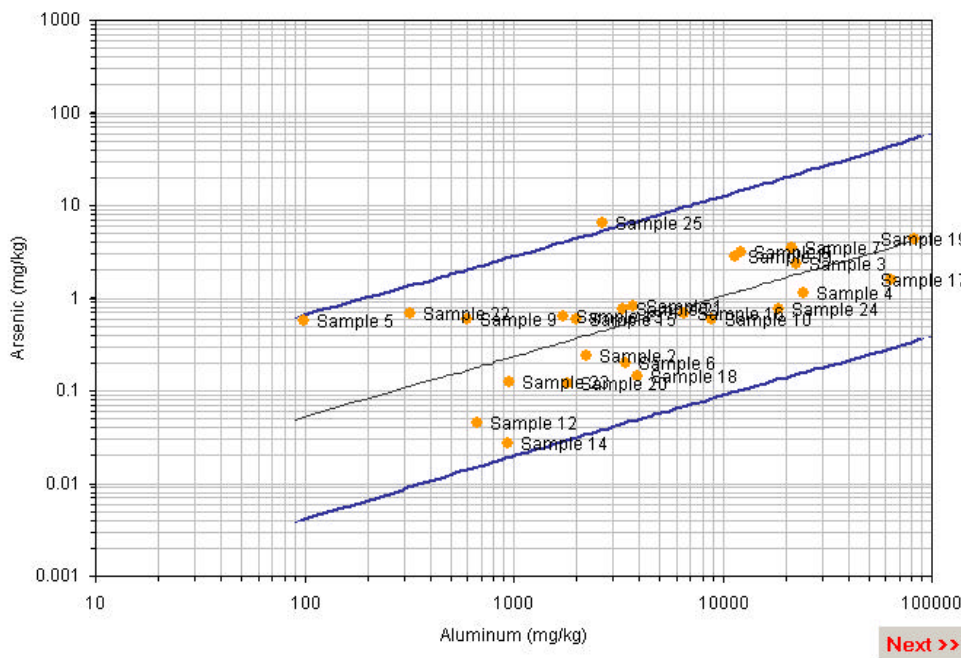
NOTE: To revise the metal data choose Step 2 in the tool tab and then click the "Enter Data" button.



Only one normalizer can be chosen each time. Choose the metal normalizer and then click Step 4 in the tool tab to continue.

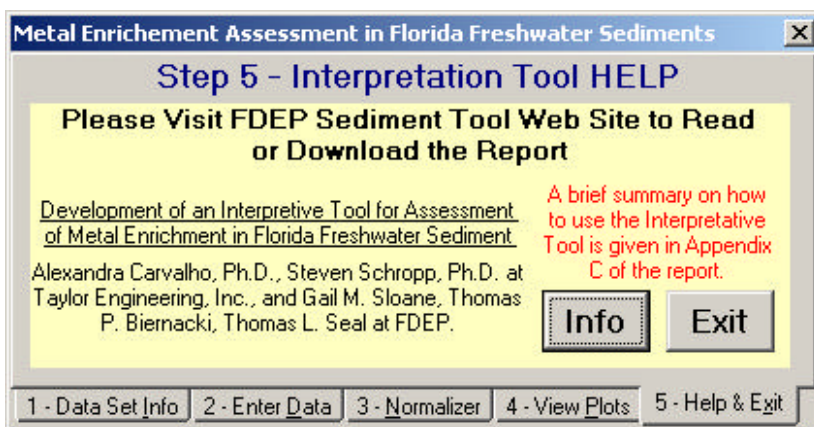


Choose a metal to plot against the previously chosen normalizer. Your data will be displayed in a graph window.



Data will be displayed in a similar Graph Window. The thick lines represent the upper and lower 95% prediction limits. The thin line represents the regression equation.

To print the graph use Excel's menus and toolbars. To plot more graphs click the "Next" button.



Step 5 in the Tool tab references the report that accompanies this Tool.

To finish using the Interpretive Tool, click the "Exit" button or use the Excel "Exit" buttons or the "File" menu.

Note: The Sediment Tool Web Site is Currently Under Construction. Please check the FDEP main website for an update.