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A GUIDE TO THE INTERPRETATION OF METAL CONCENTRATIONS IN ESTUARINE SEDIMENTS

Florida Department of Environmental Regulation
Coastal Zone Management Section

November 1987

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A GUIDE TO THE INTERPRETATION OF METAL CONCENTRATIONS IN ESTUARINE SEDIMENTS

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EXECUTIVE SUMMARY

This document describes an approach for interpreting metals concentrations in coastal sediments. Interpretation of environmental metals data is made difficult by the fact that absolute metals concentrations in coastal sediments are influenced by a variety of factors, including sediment mineralogy, grain size, organic content, and anthropogenic enrichment. The interpretive tool described herein provides a means of accounting for natural variability of metals and determining whether sediments are enriched with metals with respect to expected natural concentrations.

The interpretive tool is based on the relatively constant natural relationships that exist between metals and aluminum. "Clean" coastal sediments from throughout Florida were collected and their metals content determined. Metal/aluminum regressions and prediction limits were calculated and diagrams of metal/aluminum relationships constructed. Metals data from coastal sediments can be plotted on these diagrams to determine whether measured metal concentrations represent natural concentrations or metal enrichment.

There are several applications of this interpretive tool, including: 1) distinguishing natural versus enriched metals concentrations in coastal sediments, 2) comparing metals concentrations within an estuarine system, 3) comparing metals concentrations in different estuarine systems, 4) tracking the influence of pollution sources, 5) monitoring trends in metals concentrations over time, and 6) determining procedural or laboratory errors.

The guidance in this document is intended for use by regulatory agencies, consultants, and researchers. The geochemical and statistical bases for the interpretive tool, use of the tool, and its limitations are described. Diagrams suitable for reproduction and use as described herein are provided in the Appendix.

PREFACE

The work described in this document is part of broader efforts undertaken by the Florida Coastal Management Program to improve overall capabilities of the state for managing estuarine resources (the "Estuarine Initiative"). This part of the "Estuarine Initiative" suggests improvements in the way environmental data is used in regulatory and resource management decisions. Deficiencies in this area have played a major part in unnecessary regulatory delays, misperception of trends, and other problems in achieving balanced protection and use of coastal resources.

In this respect, the generation and interpretation of metals data have been of priority concern in identifying pollution problems. The purpose of this document is to describe a method for interpreting data on metals concentrations in estuarine sediments based on relationships that exist between metals in natural environments.

Information presented in this document represents refinements of previous work by the Florida Department of Environmental Regulation, Office of Coastal Management (FDER/OCM) and supersedes all previous FDER/OCM guidance concerning metal/aluminum relationships.

If you have any questions or comments about the use of the interpretive tool described in this document, please contact:

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MANAGEMENT ISSUES AND TECHNICAL BACKGROUND

Florida has an extensive coastline (approximately 11,000 miles) and an unusual diversity of estuarine types. Conditions in its many estuaries range from nearly pristine to localized severe degradation. Metals are of particular concern in terms of protecting and rehabilitating estuaries, not only because of their potential toxic effects, but also because high metals concentrations can be a signal for the presence of other types of pollution.

Estuarine management efforts generally suffer from several types of deficiencies in terms of understanding and dealing with metals pollution. Among these are the following:

1. Difficulty in comparing estuarine systems and establishing priorities for management actions.
2. Difficulty in distinguishing actual or potential problems from perceived problems.
3. Unnecessary delays in permitting, attributable to improper generation and interpretation of metals data.
4. Difficulty in establishing cost-effective means for assessing pollution trends and frameworks for understanding overall estuarine pollution.

The problem of understanding metals pollution has at least two major aspects. One aspect involves distinguishing those components attributable to natural causes from those attributable to man's activities. The second aspect involves determining whether metals in anthropogenically enriched sediments are potentially available for recycling to the water column or

through food chains in amounts likely to adversely affect water quality and living resources. Guidance in this document deals with the first aspect: the determination of natural versus unnatural concentrations of metals. In doing so, it sets the stage for addressing the second aspect: effects of enriched metal concentrations.

In order to address both of these aspects, it is necessary to have at least a general understanding of the geochemical processes that govern the behavior and fate of metals in estuaries and marine waters. Natural metal concentrations can vary widely among estuaries. In Florida, which has a wide range of estuarine types, this presents special difficulties for making statewide comparisons of estuarine systems and for making consistent, scientifically defensible regulatory decisions. The interpretive approach discussed in this document was developed to account for natural variability in metals concentrations and to help identify anthropogenic inputs.

The tool for interpreting metal concentrations in estuarine sediments is based on demonstrated, naturally occurring relationships between metals and aluminum. Specifically, natural metal/ aluminum relationships were used to develop guidelines for distinguishing natural sediments from contaminated sediments for a number of metals and metalloids commonly released to the environment due to anthropogenic activities. Aluminum was chosen as a reference element to normalize sediment metals concentrations for several reasons: it is the most abundant

naturally occurring metal; it is highly refractory; and its concentration is generally not influenced by anthropogenic sources.

To ensure that the information used to develop the interpretive tool was representative of the diverse Florida sediments, uncontaminated sediments from around the state were examined for their metal content and the natural variability of metal/aluminum relationships was statistically assessed.

This approach to the interpretation of metals data was initially described in two documents prepared by FDER/OCM: 1) "Geochemical and Statistical Approach for Assessing Metals Pollution in Estuarine Sediments" and 2) "Guide to the Interpretation of Reported Metal Concentrations in Estuarine Sediments". Information presented in this document represents further refinements of the approach, using an improved and expanded data base and a more rigorous statistical treatment of metal/aluminum relationships. This document supersedes all previous guidance by FDER/OCM concerning metal/aluminum relationships.

GEOCHEMICAL BASIS FOR AN INTERPRETIVE TOOL USING ALUMINUM AS A REFERENCE ELEMENT

Natural estuarine sediments are predominantly composed of river-transported debris resulting from continental weathering. A schematic representation of the weathering process is given in Figure 1. Acids formed in the atmosphere or from the breakdown of organic matter (e.g., carbonic, humic, fulvic acids) mix with water and form leaching solutions. These leaching solutions break down rocks and carry away the products in solution or as solid debris. The solid debris is composed chiefly of chemically resistant minerals, such as quartz and secondary clay minerals, which are the alteration products of other aluminosilicate minerals. The aluminosilicate clay minerals are represented by the general formula $M \cdot AlSiO4$, where M = naturally occurring metal that can substitute for aluminum in the aluminosilicate structure, Al = aluminum, Si = silicon, and O = oxygen. The metals are tightly bound within the aluminosilicate lattice.

The weathering solution also contains dissolved metals that have been leached from the parent rock. Because of their low solubilities, however, metals are present in the transporting solution (e.g., rivers) in very low amounts, on the order of nanomolar (10^{-9} liter^{-1}) concentrations. Thus, most of the metals transported by rivers are tightly bound in the aluminosilicate solid phases. As a consequence, during weathering, there is very little fractionation between the naturally occurring metals and aluminum.

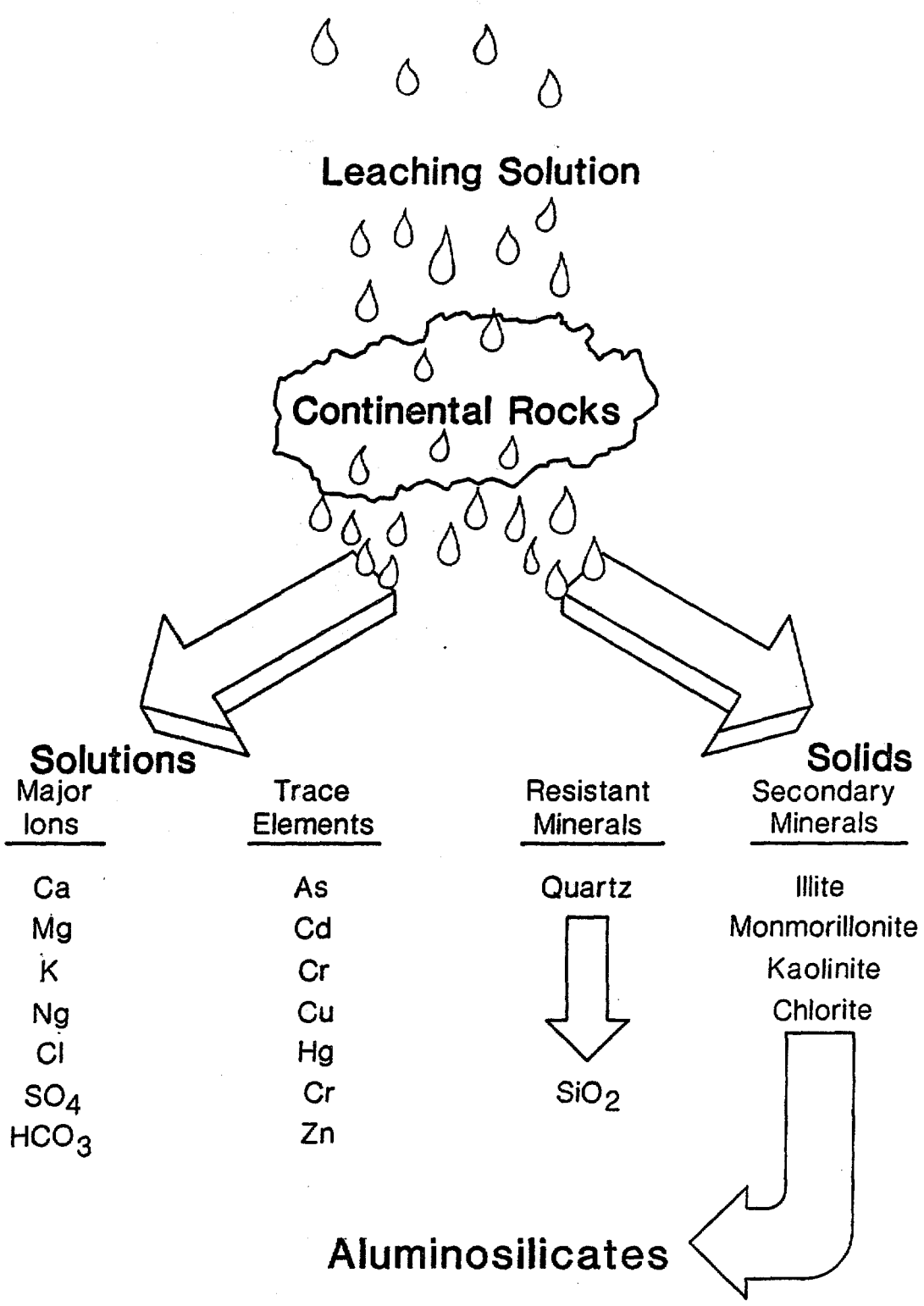

Figure 1. Schematic representation of the weathering process.

In general, when dissolved metals from natural or anthropogenic sources come in contact with saline water they quickly adsorb to particulate matter and are removed from the water column to bottom sediments. Thus, metals from both natural and anthropogenic sources are ultimately concentrated in estuarine sediments, not the water column.

Since much of the natural component of metals in estuarine sediments is chemically bound in the aluminosilicate structure, the metals are generally non-labile. The adsorbed anthropogenic or "pollutant" component is more loosely bound. Metals in the anthropogenic fraction, therefore, may be more available to estuarine biota and may be released to the water column in altered forms when sediments are disturbed (e.g., by dredging or storms).

Aluminum is the second most abundant metal in the earth's crust (silicon being the most abundant). Results from several studies have indicated that the relative proportions of metals and aluminum in crustal material are fairly constant (Martin and Whitfield, 1983; Taylor, 1964; Taylor and McLennan, 1981; Turekian and Wedepohl, 1961). This is not surprising given the lack of large-scale fractionation of metals and aluminum during weathering processes. The average metal concentration of various materials that make up the earth's crust are given in Table 1.

TABLE 1. Relative abundance of metals in crustal materials. Concentration in parts per million (Metal/aluminum ratio x 10-4).

	Average[1] Crust	Upper[2] Crust	Crustal[3] Rocks	Soils[3]	Deep-Sea[3] Sediments	Carbonate[4] Rocks
Aluminum	82,300	84,700	69,300	71,000	95,000	4,200
Arsenic	1.8 (.22)	-	7.9 (1.1)	6.0 (.85)	13.0 (1.4)	1.0 (2.4)
Cadmium	0.2 (.024)	-	0.2 (.029)	0.35 (.049)	0.23 (.024)	0.035 (.083)
Chromium	100 (12)	35 (4.1)	71 (10)	70 (9.8)	100 (11)	11 (26)
Copper	55 (6.7)	25 (3.0)	32 (4.6)	34 (4.8)	200 (21)	4 (9.5)
Iron	56,300 (6800)	35,000 (4100)	35,900 (5200)	40,000 (5600)	60,000 (6300)	3,800 (9000)
Lead	12.5 (1.5)	15 (1.8)	16 (2.3)	35 (4.9)	200 (21)	9 (21)
Manganese	950 (120)	600 (71)	720 (100)	1,000 (140)	6,000 (630)	1,100 (2600)
Mercury	0.08 (.0097)	-	-	-	-	0.04 (.095)
Nickel	75 (9.1)	20 (2.4)	49 (7.1)	50 (7.0)	200 (21)	20 (48)
Silver	0.07 (.0085)	-	0.07 (.010)	0.05 (.0070)	0.1 (.011)	0.1 (.24)
Zinc	70 (8.5)	52 (6.1)	127 (18)	90 (13)	120 (13)	20 (48)

[1]Taylor, 1964.
[2]Taylor and McLennan, 1981.
[3]Martin and Whitfield, 1983.
[4]Turekian and Wedepohl, 1961.

The relative constancy of composition of natural crustal material has been used as the basis of data interpretation by a number of geochemical investigators. Because of its high natural abundance and the relatively small inputs from anthropogenic sources, aluminum has been used to normalize metal data as an aid to 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. Goldberg et al. (1979) used metal/aluminum ratios to evaluate pollution

history recorded in sediments from the Savannah River estuary. Trefry et al. (1985) compared lead levels to those of aluminum in sediments of the Mississippi delta to assess the changes in relative amounts of lead pollution carried by the river over the past half century.

If a metal such as aluminum is to be useful to normalize metal concentrations for the purpose of distinguishing natural versus unnatural metal levels in sediments, it must explain most of the natural variance in the concentrations of the other metals. This assumption has been tested for natural sediments along the coast of Georgia (Figure 2, stations along transects HH - GA4). The results of the analysis of over three hundred sediment samples are presented in Figure 3. Metal concentrations are plotted against aluminum; regression lines and confidence limits are also plotted. These results indicate that for this geographic area aluminum does account for most of the variability of the other metals except cadmium. For cadmium, the low natural concentrations are such that analytical uncertainty introduces another source of variance.

The above shows that using aluminum to normalize natural metal concentrations is an approach that works, at least for a relatively localized area. But will this approach work for more diverse sediments such as those of coastal Florida?

Estuarine and coastal sediments of Florida contain natural metal-bearing phases. In south Florida, however, many sediments are carbonate-rich. Inspection of Table 1, indicates that

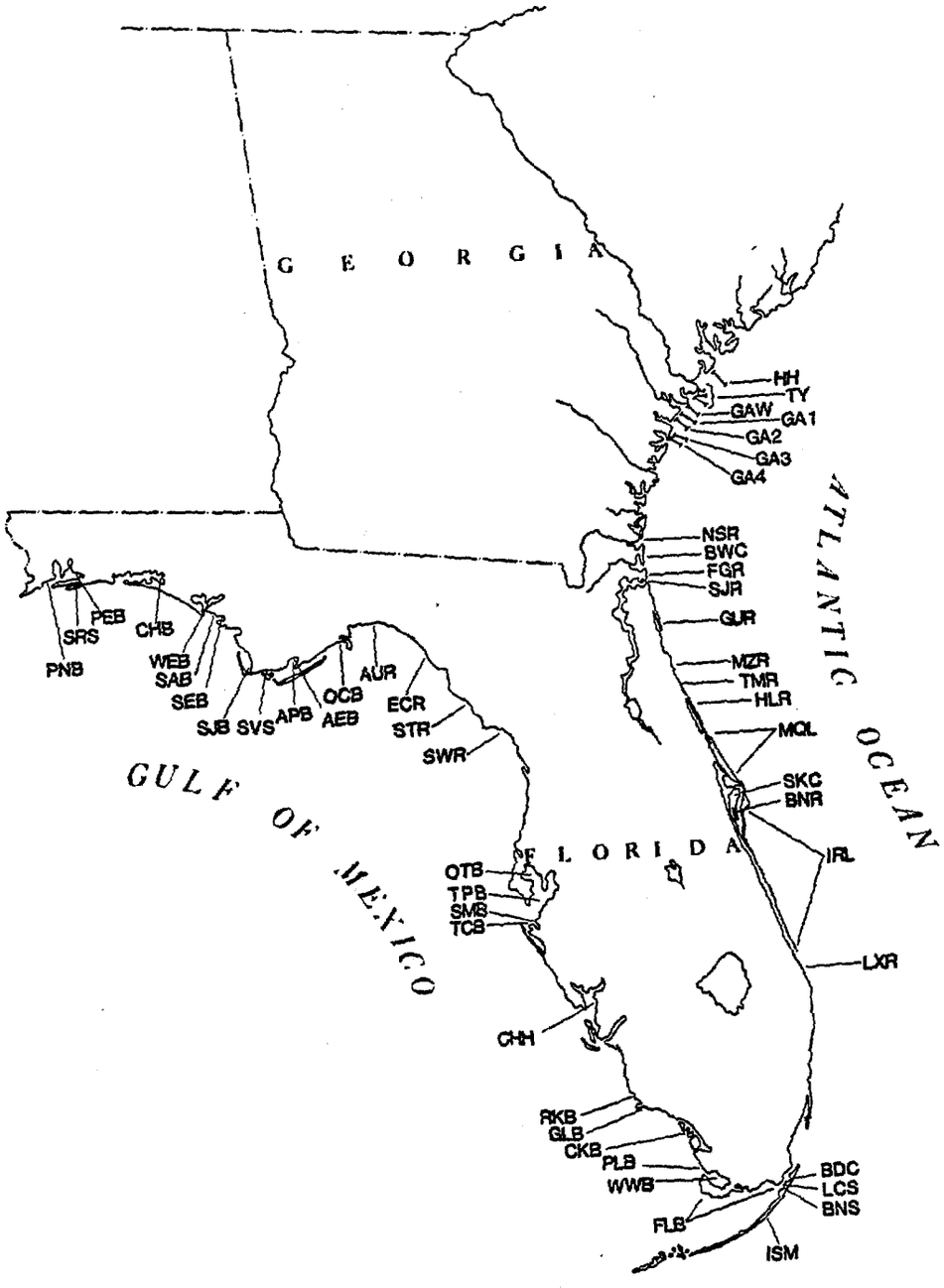

Figure 2. Locations of "clean" natural sediment sample collection sites.

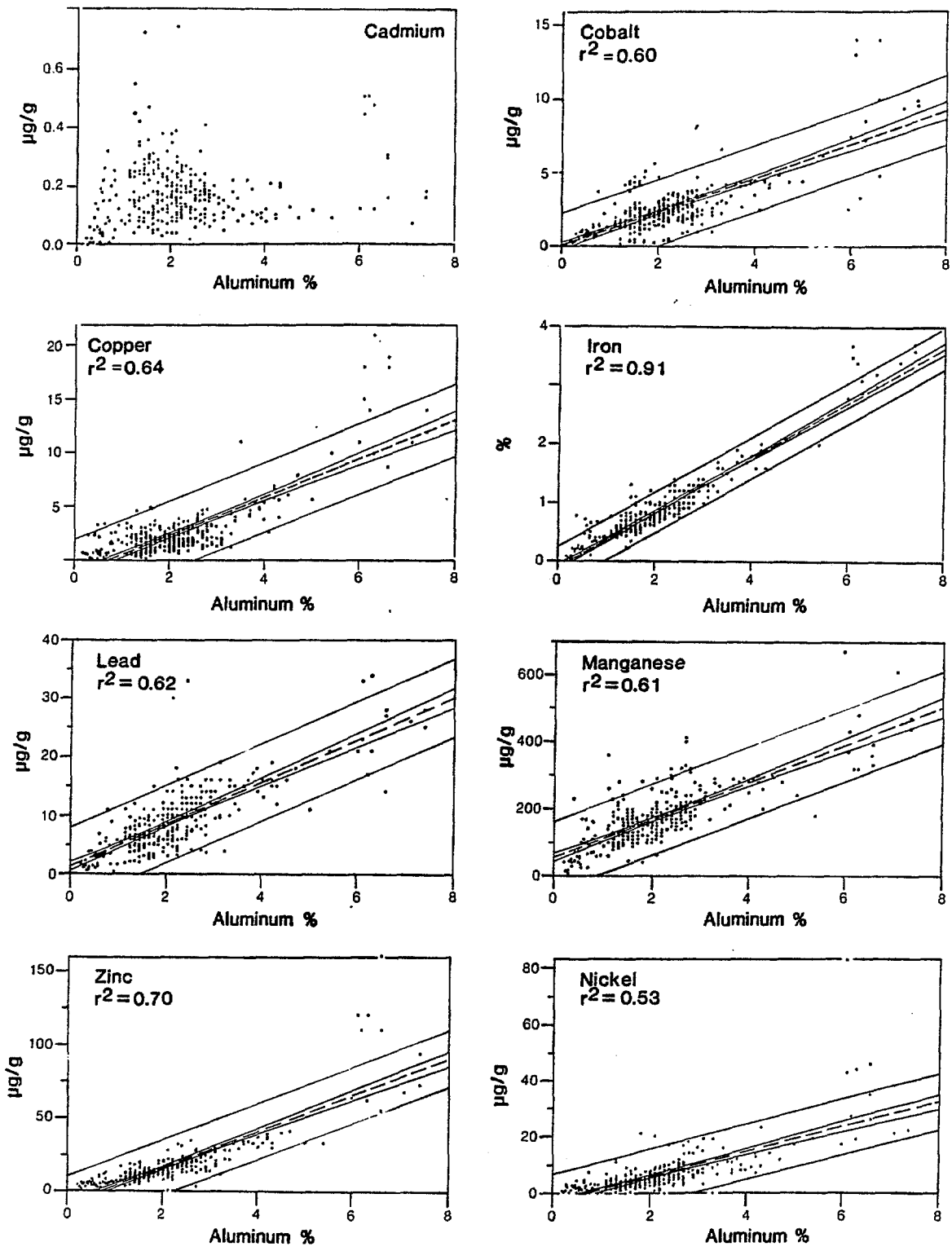

Figure 3. Metal aluminum relationships in sediments off the Georgia coast. Dashed line represents the linear regression line. Solid lines crossing the regression line represent the range in slope at the 95% confidence level. Outer solid lines define the 95% confidence band.

carbonate sediments have larger metal/aluminum ratios than other crustal rocks. Table 1 also suggests, however, that carbonates contain relatively smaller concentrations of most metals as compared to typical crustal material. It follows, therefore, that in a sediment containing a mix of aluminosilicates and carbonates, aluminosilicate minerals would still be the most important metal-bearing phase and that aluminum could still be used to normalize metal concentrations. Thus, aluminum concentrations should also be appropriate for normalizing metal levels in most estuarine and coastal sediments of Florida.

To test whether aluminum can be used to normalize metal concentrations in Florida coastal sediments, sediment samples from 103 stations in uncontaminated estuarine/coastal areas were collected and analyzed for aluminum and a number of environmentally and geochemically important metals. The areas involved encompassed a variety of sediment types ranging from terrigenous, aluminosilicate-rich sediments in northern Florida to biogenic, carbonate-rich sediments in southern Florida (Figure 2). These "clean" sites were selected subjectively, based upon their remoteness from known or suspected anthropogenic metal sources.

At each station, to ensure retrieval of undisturbed sediment samples, divers collected sediments in cellulose-acetate-butyrate cores. Sediment for metals analyses was taken from the upper five centimeters of each core. Duplicate samples were taken at each station and analyzed for nine metals (aluminum, arsenic, cadmium, chromium, copper, mercury, nickel, lead, zinc) according

to procedures specified by the United States Environmental Protection Agency (USEPA, 1982), with modifications to enhance accuracy and precision of data from saline environments (FDER/OCM, 1984).

The results of the metals analyses are plotted against aluminum in Figure 4. Superimposed on the graphs are the 95% confidence bands from the Georgia data. These results indicate that aluminosilicate minerals have a major influence on metal concentrations in natural sediments of Florida. It thus appears that sediment metal/aluminum relationships do indeed provide a basis for interpreting metals data from Florida coastal sediments.

DEVELOPMENT OF AN INTERPRETIVE TOOL USING METAL/ALUMINUM RELATIONSHIPS

This section outlines the statistical procedures used to develop a tool for assessing metals enrichment in Florida estuarine sediments, using the data from "clean" estuarine sediments and employing aluminum as a reference element. Two computer programs were used for statistical calculations: MINITAB (Ryan et al., 1982) and SYSTAT (Wilkinson, 1986).

Parametric statistical analyses require that the data under scrutiny have constant variance and be normally distributed. To examine the assumption of constant variance (homoscedasticity), plots of means versus standard deviations were generated for each

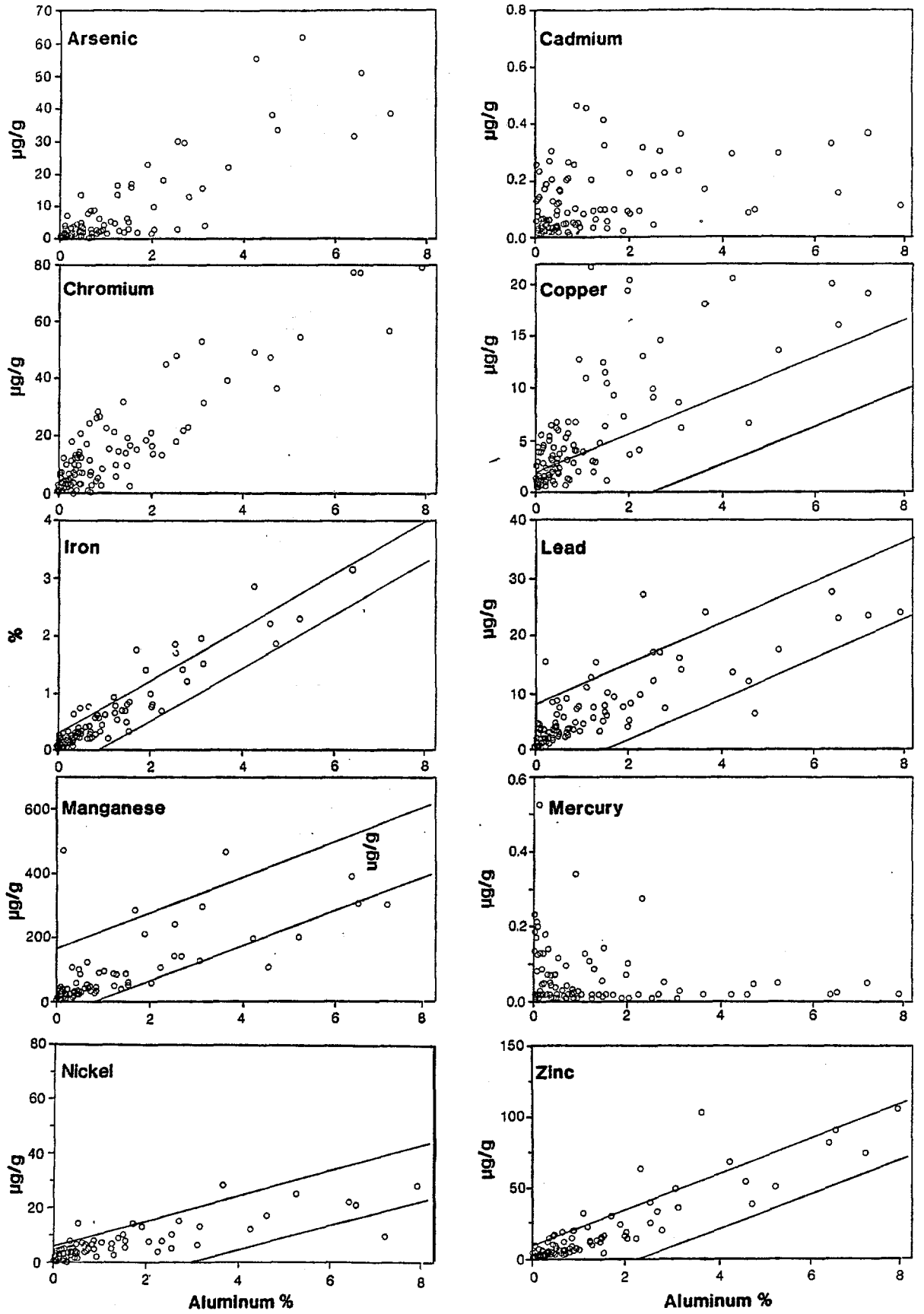

Figure 4. Metal/aluminum relationships in "clean" sediments from Florida estuaries.

metal. Standard deviations were proportional to mean values for all nine metals. After a $\log_{10}$ transformation, the proportionality between standard deviations and mean values was removed, indicating that the assumption of homoscedasticity was satisfied. Examples of these plots before and after transformation, using the data for chromium, are shown in Figure 5.

To examine the assumption of normality, normal score plots were created by calculating normal scores and plotting them against original data. Normal-score plots for untransformed and $\log_{10}$-transformed chromium are shown in Figure 6. The curvature in the plot for absolute chromium concentrations (Figure 6a) indicates that the data are not normally distributed, whereas the relatively linear plot for $\log_{10}$-transformed chromium (Figure 6b) indicates a normal distribution (Wilkinson, 1986). With the exception of nickel, $\log_{10}$ transformation of the remaining metals also appeared to produce normal distributions. The normal distributions of transformed data were confirmed using the probability plot correlation coefficient test (Filliben, 1975). With this test, the null hypothesis (H_O) of normality is examined relative to the alternative hypothesis (H_A) of non-normality. A significantly high correlation coefficient between normal scores and original data results in a failure to reject H_O (i.e., the data are normally distributed). Results of the test are shown in Table 2. Untransformed aluminum, arsenic, cadmium, chromium, copper, mercury, lead, and zinc deviated from normality, whereas

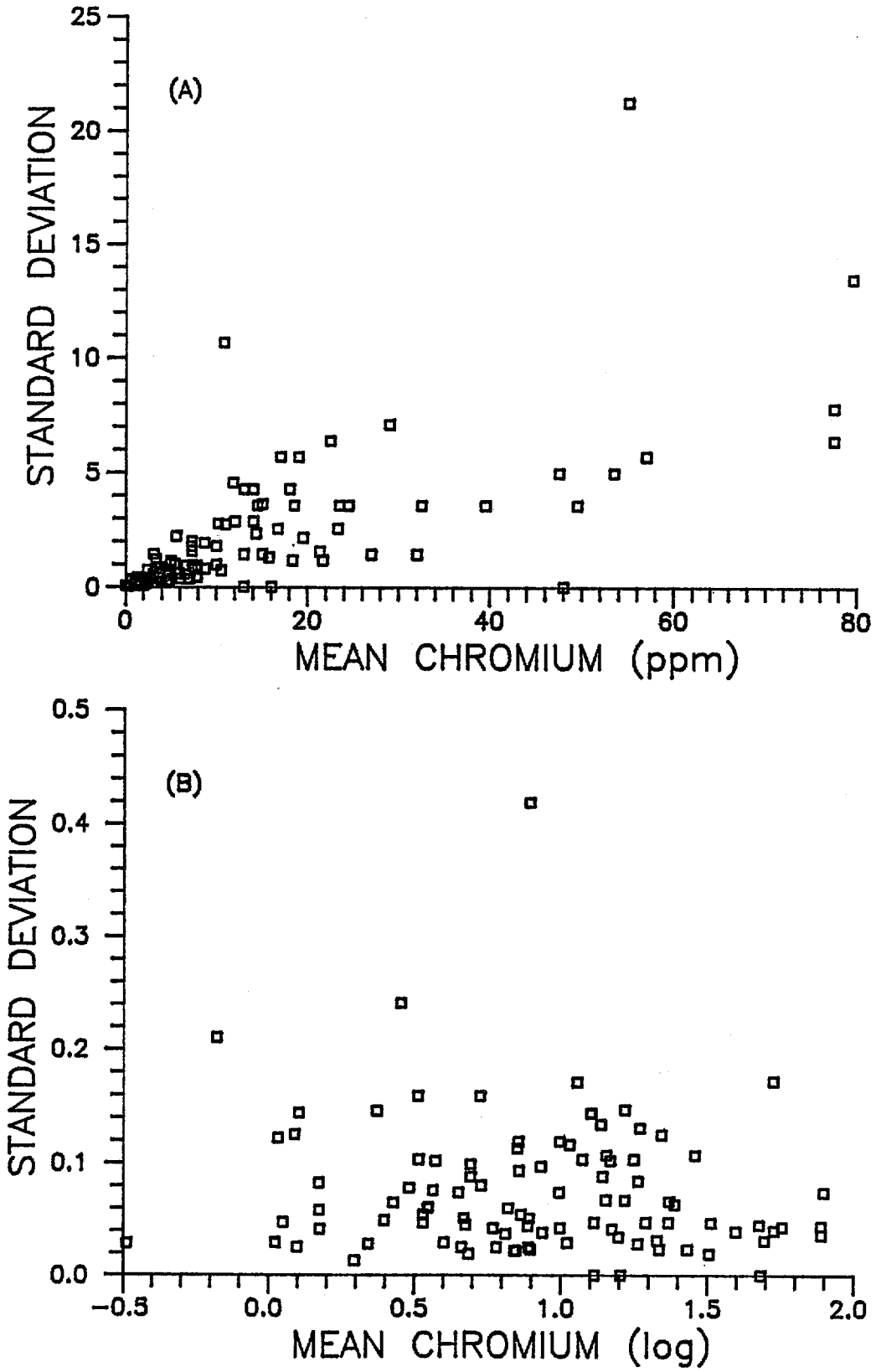

Figure 5. Mean value vs. standard deviation for chromium: A) untransformed data, B) log-transformed data.

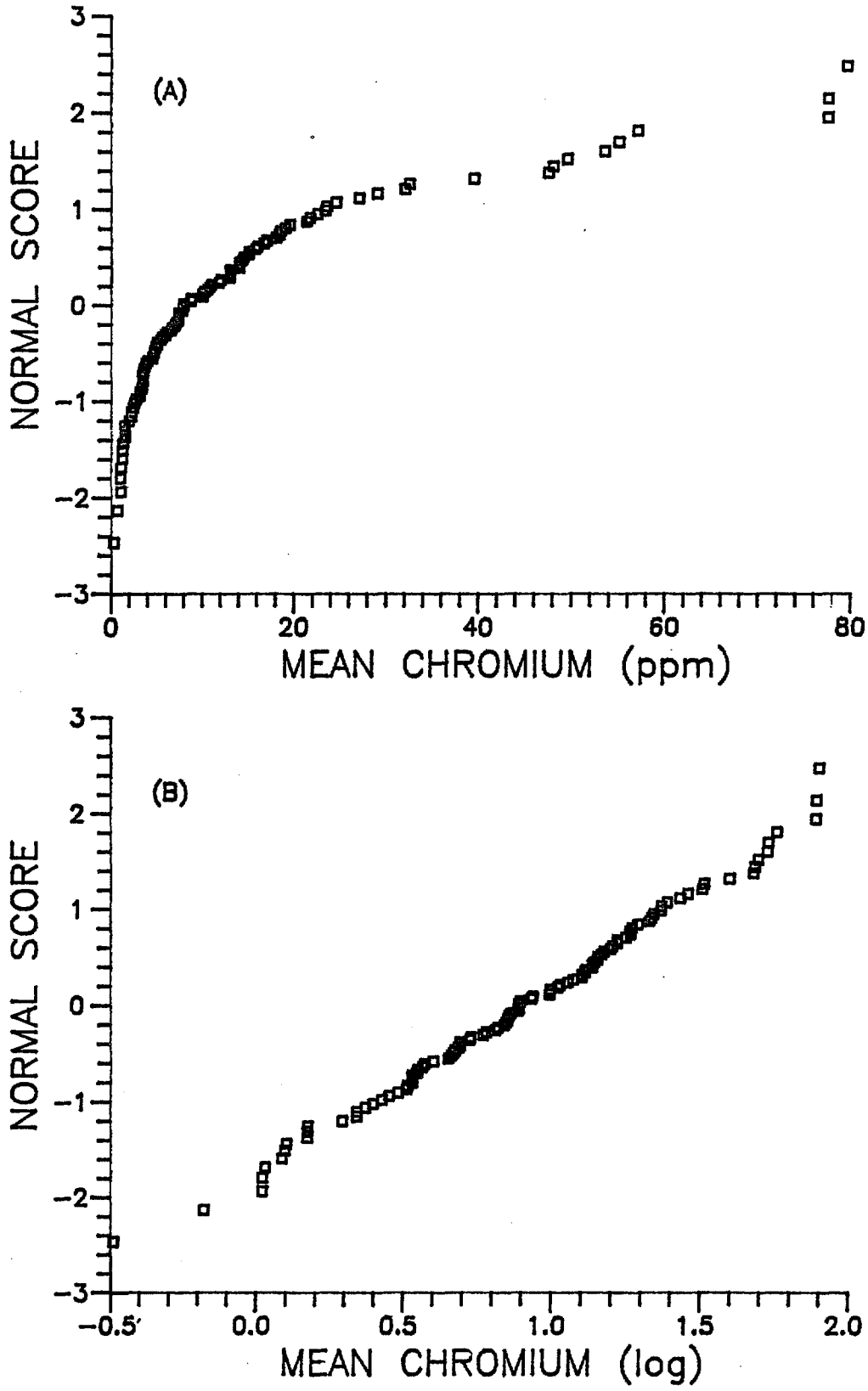

Figure 6. Normal score vs. chromium value:
A) untransformed data, B) log–transformed data.

TABLE 2. Results of probability plot correlation coefficient tests for normality of metals data.

		Correlation Coefficient	
Metal	N	Untransformed	Log_{10}-transformed
Aluminum	103	0.817[c]	0.991[a]
Arsenic	98	0.752[c]	0.988[a]
Cadmium	103	0.920[c]	0.990[a]
Chromium	102	0.847[c]	0.996[a]
Copper	101	0.870[c]	0.992[a]
Mercury	92	0.898[c]	0.981[b]
Nickel	78	0.880[c]	0.986[a,d]
Lead	103	0.885[c]	0.991[a]
Zinc	103	0.778[c]	0.984[b]

[a] $p > 0.05$ (Accept H_o; normal distribution)
[b] $0.05 > p > 0.01$ (Accept H_o; normal distribution)
[c] $p < 0.01$ (Reject H_o; non-normal distribution)
[d] N = 75, Three points (Ni < 0.2 ppm) were removed from data set.

the log_{10}-transformed metals did fit a normal distribution. Log_{10}-transformed nickel data were not normally distributed, being skewed toward low nickel concentrations. The three lowest nickel values (Ni < 0.2 ppm) were removed from the data set, normal scores recalculated, and the remaining nickel data did conform to a normal distribution. For all nine metals, the remainder of the work was performed on log_{10}-transformed data. Metal/aluminum relationships for arsenic, cadmium, chromium copper, mercury, nickel, lead, and zinc are shown in Figure 7. Concentrations of seven metals, arsenic, cadmium, chromium,

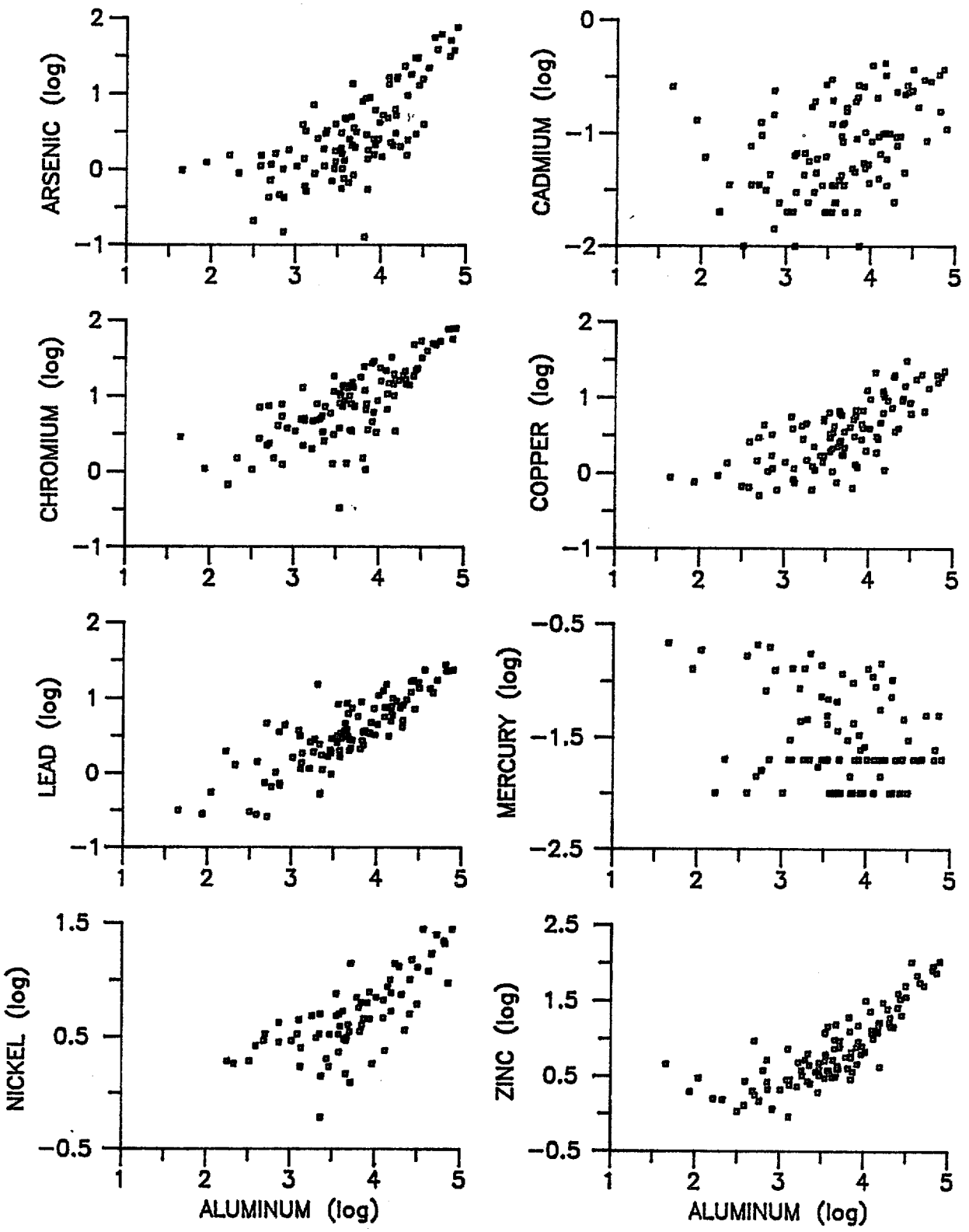

Figure 7. Metal/aluminum relationships for log-transformed metals in clean Florida estuarine sediments.

copper, nickel, lead, and zinc, were positively correlated with aluminum ($p < 0.005$). The strength of the relationships varied among metals as indicated by the magnitude of the correlation coefficient, with cadmium having the weakest relationship (Table 3). Mercury exhibited a weak inverse relationship with aluminum and therefore was excluded from further analysis. The problem of dealing with mercury is discussed in a later section.

TABLE 3. Correlation coefficients for metals and aluminum.

Metal	r	N
Arsenic	0.71[a]	98
Cadmium	0.39[a]	103
Chromium	0.74[a]	102
Copper	0.73[a]	101
Mercury	-0.29[a]	92
Nickel	0.78[a]	75
Lead	0.84[a]	103
Zinc	0.82[a]	103

[a]$p < .005$

Since the selection of stations with "clean" sediment was subjective, it is possible that any given sample was somewhat enriched with one or a combination of metals. In order to minimize the possibility that metal-enriched samples were included in the final data set, metal/aluminum ratios were calculated for arsenic, cadmium, chromium, copper, nickel, lead, and zinc and the probability plot correlation coefficient test

was used to determine whether the ratios were normally distributed. If the correlation coefficient test indicated deviations from normality, data points with the largest metal/aluminum ratio were removed (assuming that high ratios were possibly indicative of anthropogenic enrichment) and the process repeated until the metal/aluminum ratios fit a normal distribution. Results are shown in Table 4. Data points for three metals (cadmium, zinc, lead) were deleted from the data set using this procedure.

TABLE 4. Results of probability plot correlation coefficient tests for normality of metal/aluminum ratios.

	"Clean" data		"Trimmed-clean" data	
Ratio	N	r	N	r
Arsenic/aluminum	98	0.988[a]	98	0.988[a]
Cadmium/aluminum	103	0.969[c]	102	0.983[b]
Chromium/aluminum	102	0.988[a]	102	0.988[a]
Copper/aluminum	101	0.988[a]	101	0.988[a]
Nickel/aluminum	75	0.911[c]	72	0.987[a]
Lead/aluminum	103	0.955[c]	93	0.993[a]
Zinc/aluminum	103	0.934[c]	99	0.985[b]

[a] $p > 0.05$ (Accept H_0; normal distribution).
[b] $0.05 > p > 0.01$ (Accept H_0; normal distribution).
[c] $p < 0.01$ (Reject H_0; normal distribution).

Nickel again presented a different case, with the distribution of nickel/aluminum ratios being skewed toward low ratios. After removal of three points with the lowest

nickel/aluminum ratios, the remaining nickel/aluminum ratios fit a normal distribution. The metals data set resulting from the deletion of points was called the "trimmed clean" data set and was used for subsequent analyses.

Having ascertained that the data does meet the assumptions of normality and homoscedasticity, and having examined metal/aluminum ratios for outlying data points, the data were then analyzed using parametric statistical procedures. Least squares regression analysis, using aluminum as the independent variable and other metals as dependent variables, was used to fit regression lines to the metals of the "trimmed clean" data set (Sokal and Rohlf, 1969). Results of the regressions are presented in Table 5. Correlation coefficients for three of the "trimmed" metals (cadmium, lead, zinc) were greater than those for the original data, indicating the relationship between these metals and aluminum in the "trimmed clean" data set was strengthened by removing the suspect points. Y-intercepts of the regression lines are less than zero because the data were $\log_{10}$-transformed.

Using the regression results, 95% prediction limits were calculated according to Sokal and Rohlf (1969). Regression lines and prediction limits for each metal are plotted in Figures 8-14, superimposed over data points from the "trimmed clean" data set. The relative width of the prediction limits vary among the different metals, depending on the magnitude of the correlation between the metal and aluminum. Metals with the largest correlation coefficients (i.e., lead & zinc) have the narrowest prediction limits.

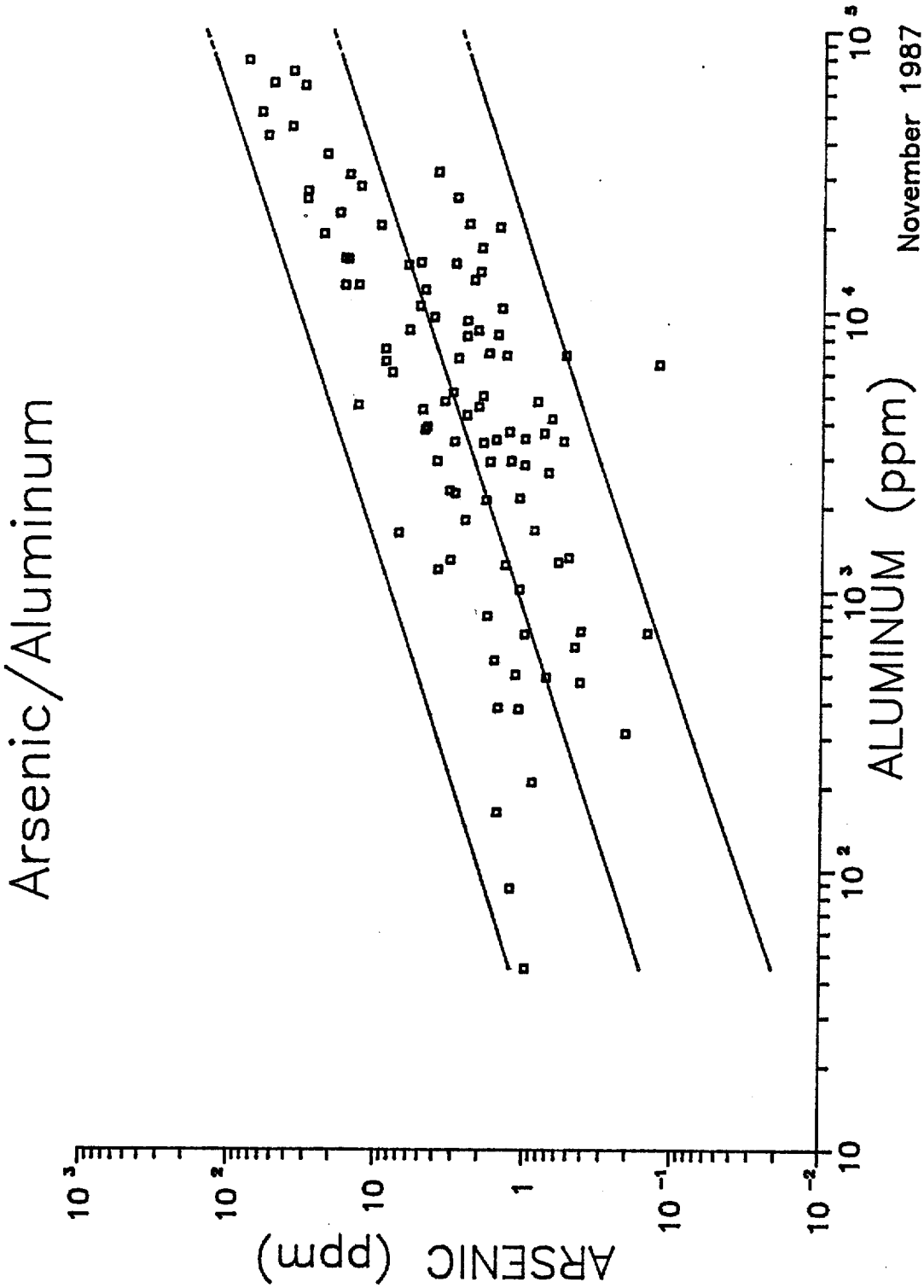

Figure 8. Arsenic/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

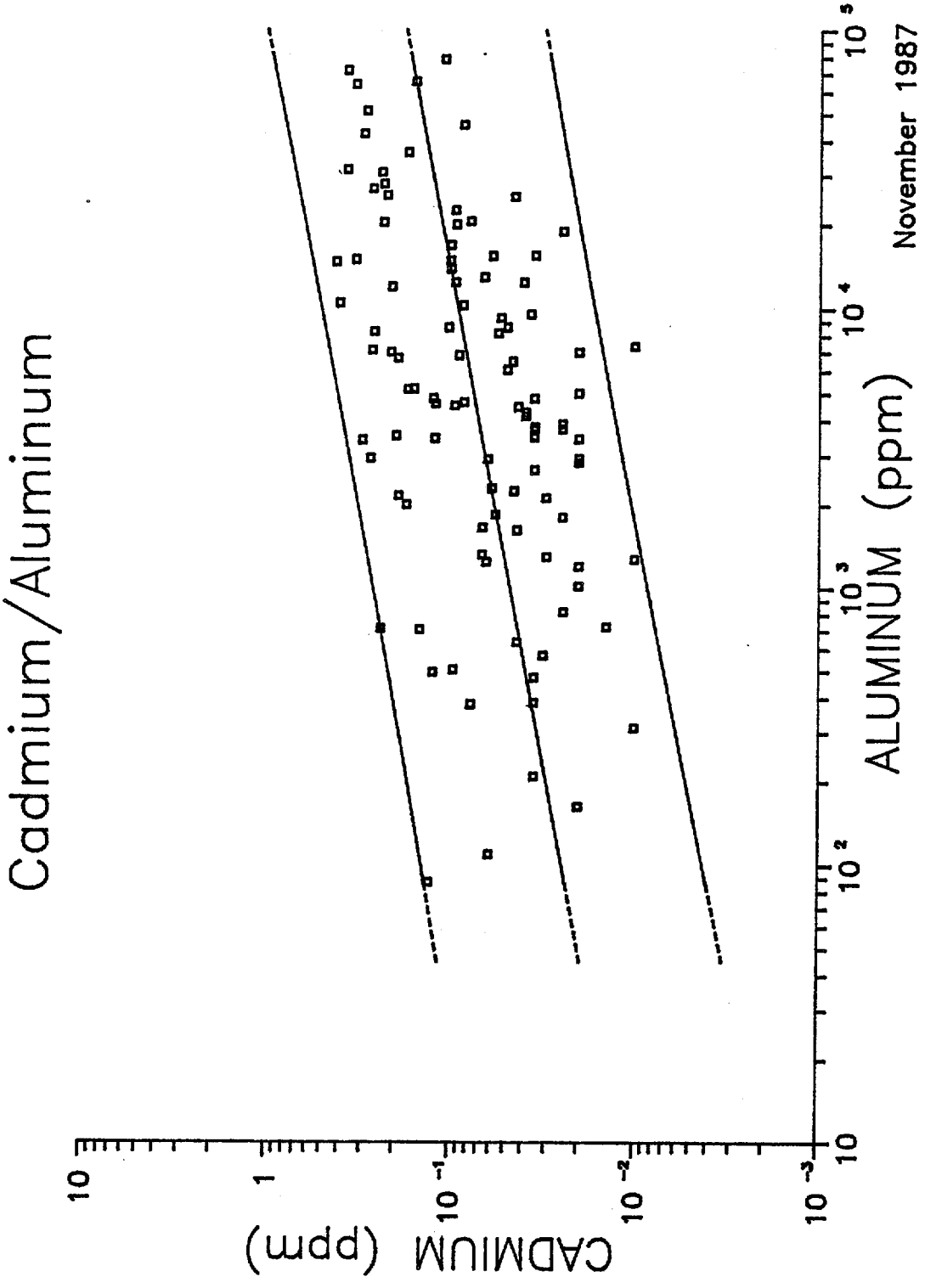

Figure 9. Cadmium/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

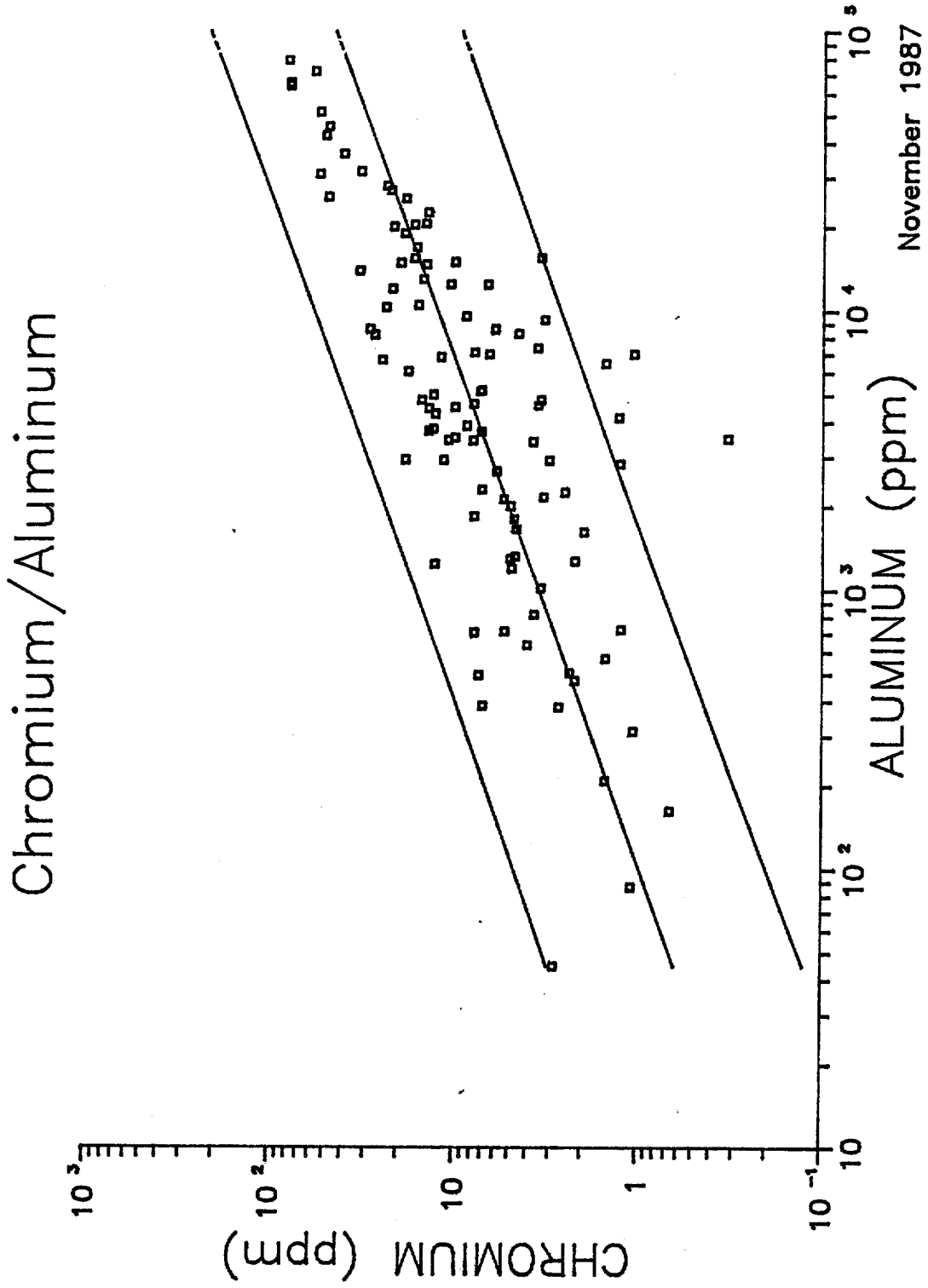

Figure 10. Chromium/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

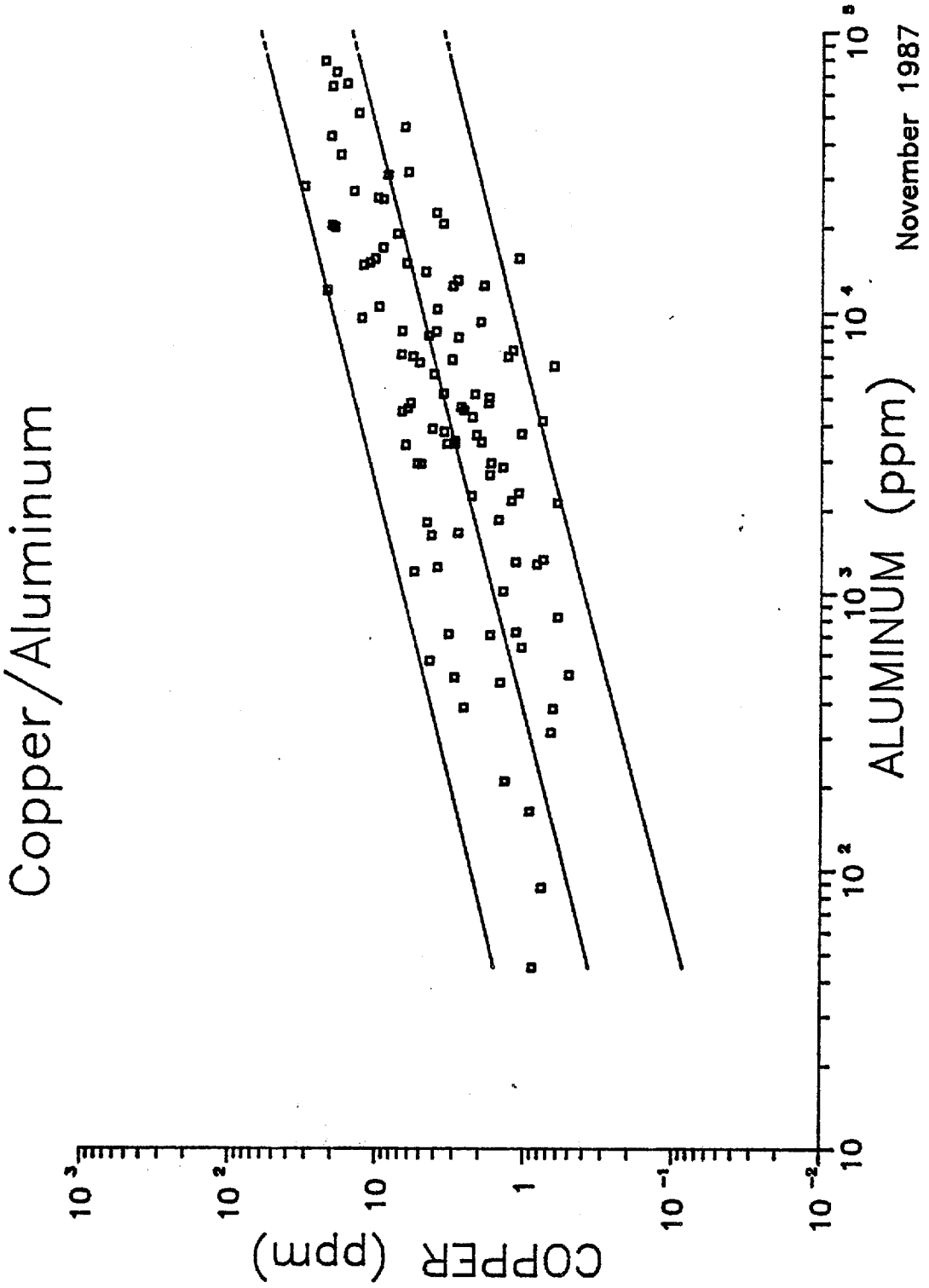

Figure 11. Copper/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

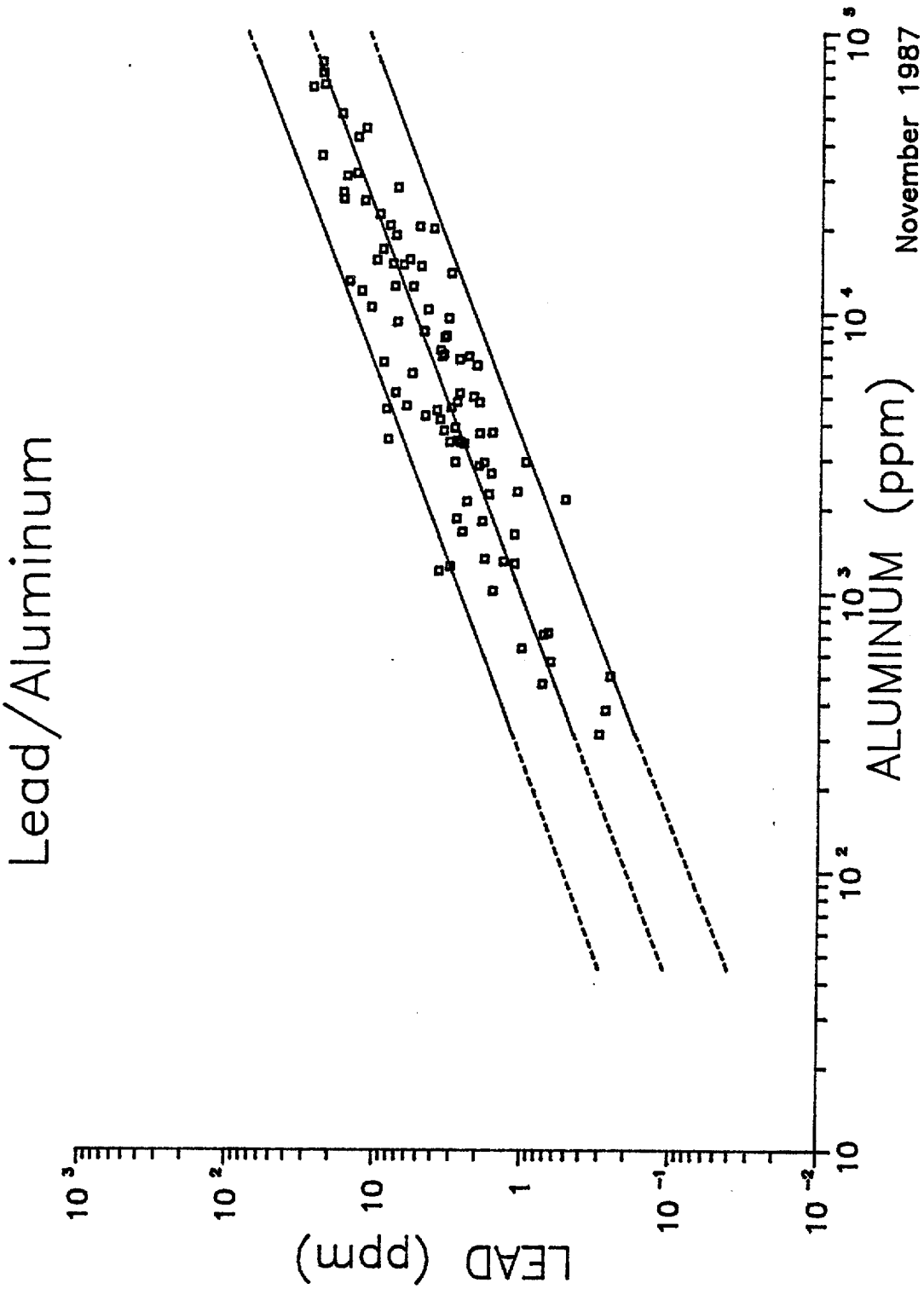

Figure 12. Lead/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

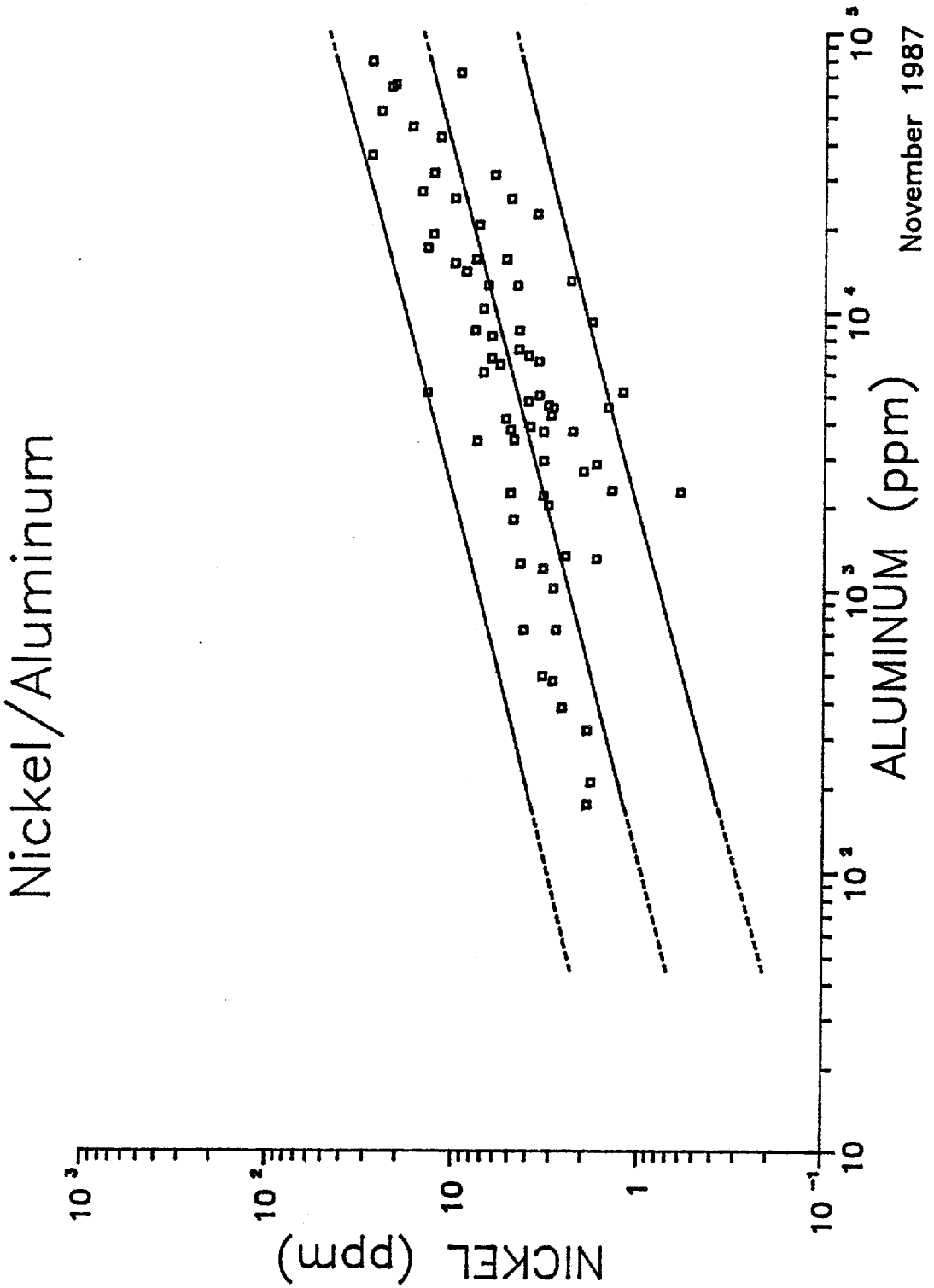

Figure 13. Nickel/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

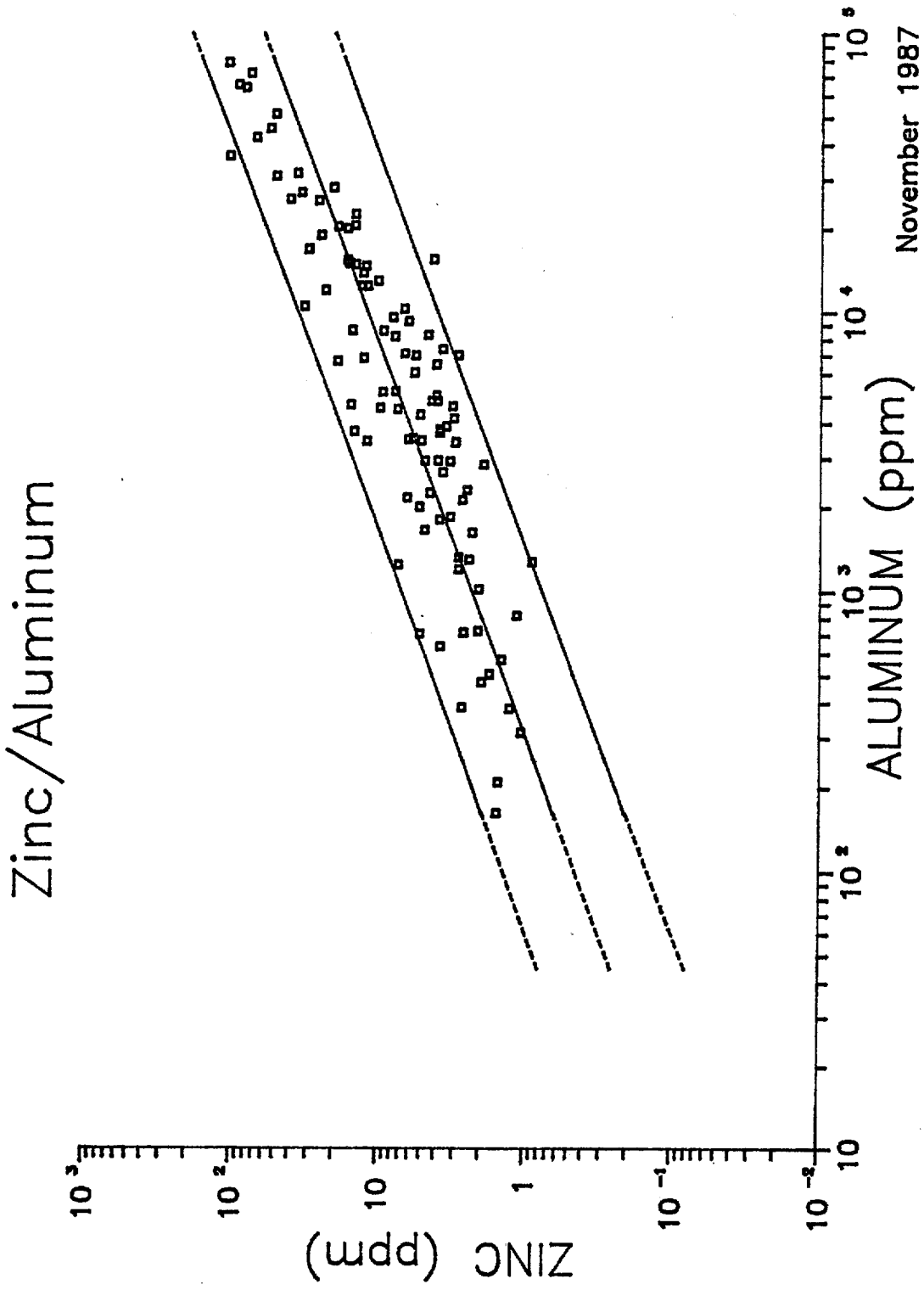

Figure 14. Zinc/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

TABLE 5. Results of regression analyses using aluminum as the independent variable and other metals as dependent variables.

Metal	n	r[a]	a[b]	b[c]
Arsenic	98	0.71	-1.8	0.63
Cadmium	102	0.45	-2.2	0.29
Chromium	102	0.74	-1.1	0.55
Copper	101	0.73	-1.2	0.48
Nickel	72	0.72	-0.81	0.40
Lead	93	0.90	-2.1	0.73
Zinc	99	0.88	-1.8	0.71

[a]Correlation coefficient.
[b]Y-intercept of regression line.
[c]Slope of regression line.

Thus far, it has been demonstrated that statistically significant relationships exist between aluminum and six of the metals examined in "clean" sediments. The calculated regression lines define metal/aluminum relationships and the prediction limits provide a valid statistical estimate of the range of values to be expected from samples taken from clean sediments in Florida. The regression lines and prediction limits presented here can be used to identify unnatural concentrations of metals in Florida estuarine sediments. A similar approach, using iron as the reference element, was taken by Trefry and Presley (1976) to evaluate metals concentrations in northwestern Gulf of Mexico sediments.

USING THE INTERPRETIVE TOOL

Model figures with regression lines and prediction limits are presented in the Appendix. The figures are constructed on a log-log scale to facilitate plotting; absolute metal concentrations can be plotted on the figures without the necessity of $\log_{10}$-transformation. These figures can be reproduced and routinely used to determine whether samples from Florida estuarine sediments are enriched with metals. To do this, a mean value of each metal (derived from replicate or triplicate values) at a station is calculated and points representing corresponding metal and aluminum values are plotted on the appropriate figures. The sediment is judged to be natural or "metal-enriched" depending on where the points lie relative to the regression lines and prediction limits. If a point falls within the prediction limits, then the sediment metal concentration is within the expected natural range. If a point falls above the upper prediction limit, then the sediment is considered to be metal- enriched. Prior to making a determination of "enrichment", however, the accuracy of the analytical results should be confirmed, since an unusual point can also be indicative of procedural errors. Furthermore, since the results are being evaluated with respect to a 95% prediction limit, some points from "clean" stations will lie outside the prediction limit. The farther from the prediction limit, the greater the likelihood that the sample does indeed come from a metal-enriched sediment. Also, greater distance above the prediction limit indicates a greater degree of enrichment.

Points that lie closely above the upper prediction limit must be interpreted in light of available ancillary information about possible sources of metal contamination and information from other nearby stations. Likewise, some points from "clean" sediments will fall below the lower prediction limit. Points that are far below the lower prediction limit should be considered suspect and examined for analytical errors.

APPLICATIONS OF THE INTERPRETIVE TOOL

The interpretive tool using metal and aluminum relationships allows results of sediment chemical analyses to be used for a variety of environmental information needs, including:

1. Distinguishing natural versus enriched metals concentrations in coastal sediments. The degree of enrichment can also be estimated based on the deviation from the expected natural range.
2. Comparing metal concentrations within an estuary. Absolute metal concentrations in coastal sediments will vary depending on many factors, including sediment grain size, mineralogy, and anthropogenic metal sources. Normalizing metals to the reference element, aluminum, allows comparisons of metal concentrations among sites within an estuary.
3. Comparing investigative results from different estuaries. By normalizing metal concentrations to aluminum, an assessment of relative metal enrichment levels can be made, allowing estuaries to be ranked according to specific metal enrichment problems.

4. Tracking the influence of a pollution source. As illustrated in the next section, it is possible to determine the extent of metal-enriched sediments. Delineation of the extent of metal-enrichment can help focus attention on real, rather than perceived, problems.
5. Monitoring trends in metal concentrations over time. By periodically examining sediments at permanent sampling stations or along known pollution gradients, the technique may provide a much-needed device for cost-effective monitoring of the overall "pollution climate" of estuaries.
6. Determining procedural or laboratory errors. The location of points on the metal/aluminum figures can signal possible errors, which could include sample contamination in the field or laboratory, as well as analytical or reporting errors.

LIMITATIONS OF THE INTERPRETIVE TOOL

The approach presented in this document provides an interpretive tool for evaluating metals concentrations in estuarine sediments. Use of the tool requires knowledge of local conditions and the application of professional judgement and common sense. The following points should be kept in mind when using this interpretive tool.

1) The interpretive tool is useless without reliable data. Results from single, non-replicated samples should never be used. Ideally, sediment samples should be collected in triplicate. If budget constraints dictate analysis of only

duplicate samples, the third sample should be archived. In the event of a disparity in the results of replicate analyses, the archived sample should be retrieved and analyzed to resolve the problem.

2) Sediment metals must be carefully analyzed using techniques appropriate for saline conditions and capable of providing adequate detection limits. Because naturally-occurring aluminum and other metals are tightly bound within the crystalline structure of the sediment minerals, the methods for metals analyses must include complete sediment digestion. If aluminum is not completely released by a thorough digestion, metal to aluminum ratios may appear to be unusually high.

3) Mercury presents special problems, both in the laboratory and in the interpretation of results. Since mercury is more volatile than the other metals, a different digestion procedure, employing a lower temperature than for the other metals, must be used. Also, natural mercury concentrations are very near routine analytical detection limits, where precision and accuracy are reduced. Furthermore, mercury's apparent weak inverse relationship with aluminum precludes the use of aluminum as a reference element.

To deal with mercury, assume that the maximum mercury value in the "clean" sediment data set (0.21 ppm mercury) represents the maximum mercury concentration to be found in natural sediments of Florida. For the purpose of evaluating sediment samples, those containing less than 0.21 ppm mercury can be considered as typical of clean sediments. Samples with greater

than 0.21 ppm mercury should be suspected as being enriched and should be interpreted similarly to those other metals that fall outside of the 95% prediction limits.

4) Similar to mercury, natural concentrations of cadmium are also low and are near normal analytical detection limits. Because of this, analytical precision and accuracy are reduced and special care must be taken to obtain accurate laboratory results.

5) Aluminum concentrations in the data set from which these guidelines were prepared ranged from 47 to 79,000 ppm. The data set is, to the extent possible in this project, representative of various types of natural "clean" sediments found in Florida estuaries. The majority of samples recovered from Florida estuarine sediments will have aluminum concentrations within this range.

Some clay-rich sediments, however, especially in northwest Florida, may contain aluminum concentrations exceeding 79,000 ppm. Kaolinite, illite (muscovite), montmorillonite, and chlorite, four commonly occurring marine clays, contain aluminum concentrations of approximately 21%, 20%, 15%, and 10%, respectively (calculated based on chemical formulas for the clay minerals given in Riley and Chester, 1971). Theoretically, therefore, the maximum aluminum concentration in a natural marine sediment is about 210,000 ppm (21%), if the sediment is composed of pure kaolinite. Since sediments are not pure clay, the aluminum concentration in estuarine sediment samples should be considerably less than this theoretical maximum and only in a few

instances should aluminum concentrations exceed 100,000 ppm (10% aluminum). Any samples containing greater than 100,000 ppm aluminum should be examined carefully for evidence of contamination or analytical error.

In order to extend the applicability of the interpretive tool to sediments containing aluminum in excess of 79,000 ppm, the regression lines and prediction limits have been extrapolated out to an aluminum concentration of 100,000 ppm.[1] The extrapolations are indicated on the figures by dashed lines. This is considered to be a reasonable approach. However, any interpretations based on the extrapolated lines should be qualified with a statement acknowledging that the data in question exceeds the range of the "clean" data set from which these guidelines were prepared.

6) During the construction of the "trimmed clean" data set, some points containing low aluminum values were removed from the cadmium, lead, nickel, and zinc data. Since, however, the lowest overall aluminum value was 47 ppm, the regression lines and prediction limits for these four metals have been extrapolated down to an aluminum value of 47 ppm. These extrapolations are also indicated by dashed lines.

7) At stations where a metal's concentration exceeds the 95% prediction limit, the metal must be considered "enriched". One must not immediately assume, however, that a finding of "enrichment" is indicative of a problem. There is a probability that some samples from natural "clean" sediments will contain metals whose concentrations exceed the 95% prediction limit.

[1]Since the calculations were done on $\log_{10}$-transformed data, the extrapolation was from 4.9 to 5.0 log units. Aluminum values in the data set ranged from 1.7 to 4.9 log units.

Interpretation of metal concentrations using these metal to aluminum relationships must also take into consideration sediment grain size, mineralogy, coastal hydrography, and proximity to sources of metals. In the following section are two examples of the use of this metals interpretive tool.

EXAMPLES

The following two examples show how the interpretive tool is used in combination with ancillary information to evaluate metals data from an estuarine system. For the first example, consider the hypothetical situation shown in Figure 15. The estuary has a single major freshwater source, a river entering at its northern end. Hydrographic studies have shown that water circulation in the estuary is to the west-southwest from the mouth of the river and then seaward along the western shore. The estuarine sediment is mostly mud with a strip of fine sand along the shoreline. The estuary is still in a "pristine" state with no known anthropogenic sources of metal along its shores or in the river. Sediments from Stations 1 - 9 were collected and analyzed for chromium.

Results of the chromium analyses are shown in Figure 16. Several points are illustrated by these results. Chromium concentrations vary with sediment grain size, being greatest at the stations with finest sediment. However, despite the differences in absolute chromium concentrations, Stations 1, 3, 4, 5, 6 and 8 all have metal values falling within the natural range. Station 2, although statistically enriched with chromium, does not in practice appear indicative of any problem since, it is

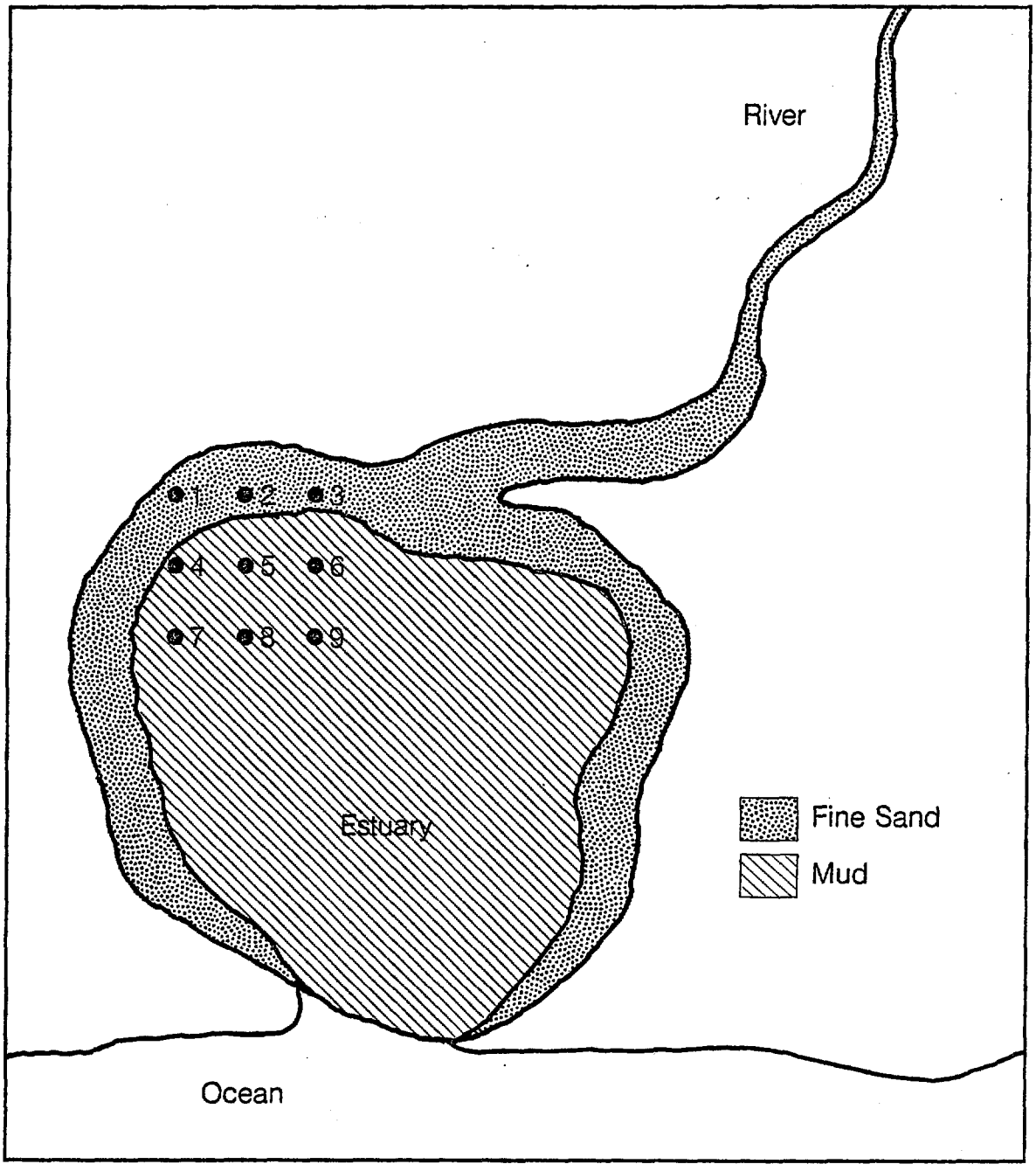

Figure 15. Hypothetical estuary showing sampling stations and sediment grain size.

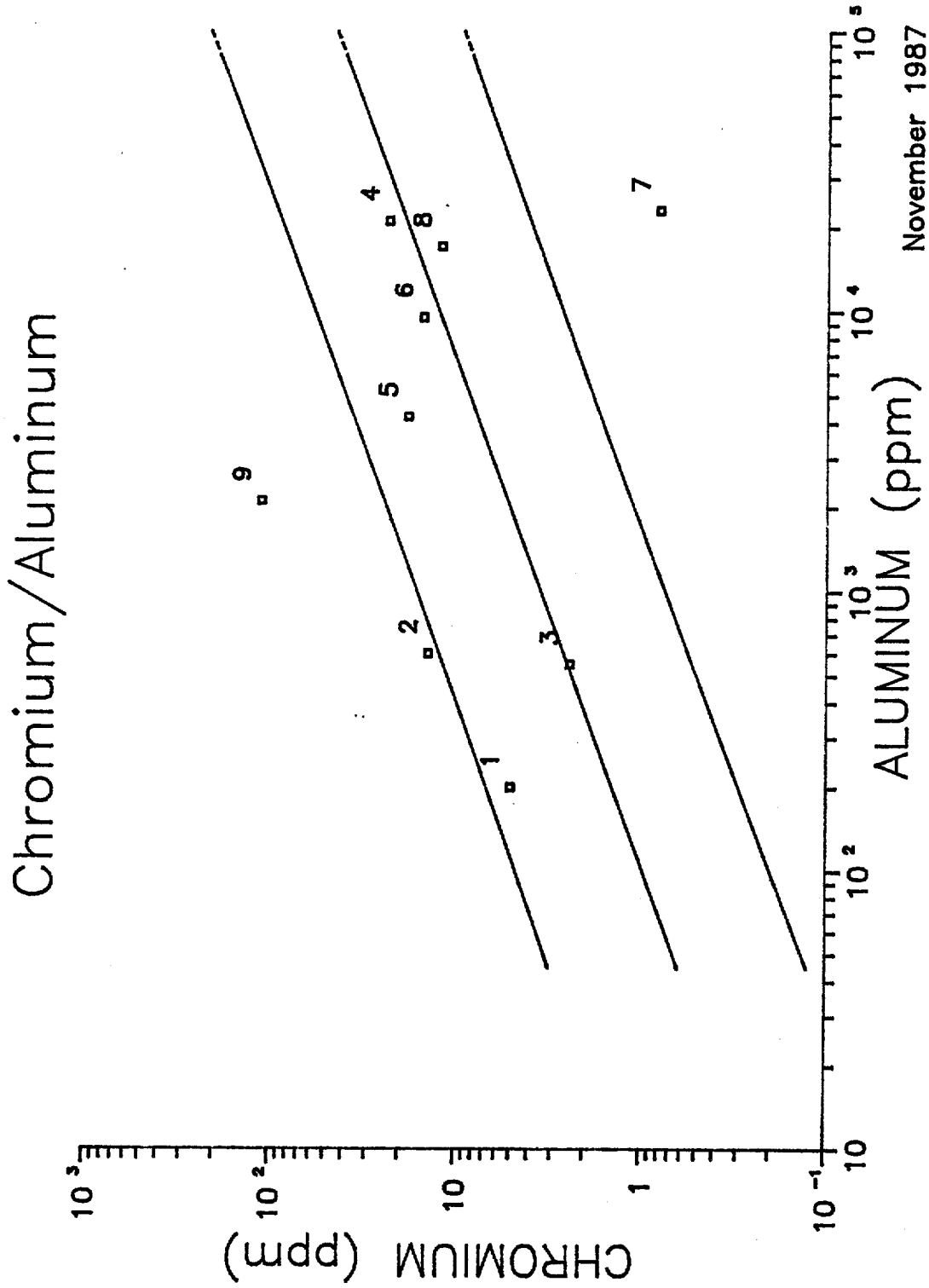

Figure 16. Chromium results from hypothetical estuarine sampling stations shown in Figure 15.

only slightly above the prediction limit and since the surrounding stations (Sta. 1, 3, 4, 5, 6) all have chromium concentrations within the natural range. Stations 7 and 9 each have chromium values that lie far outside the 95% prediction limit. The chromium value from Station 7 is unusually low which, since the aluminum value is reasonable given the aluminum concentrations of the other similar stations, indicates a possible laboratory error. There are at least three possible explanations for the anomalously high chromium value at Station 9: 1) the sample was contaminated, 2) there was a laboratory error, or 3) there is an unusual and unknown source of chromium in this area. Given the conditions described for this example, the first two possibilities are most likely. To examine these, one needs to review the field data sheets (to identify any field sampling problems), laboratory logbooks, and the original raw data. Occasionally, spurious data from a single replicate can greatly alter mean concentrations at a site, so the data should be examined for outliers. If the latter two possibilities can be ruled out, then further investigations to determine the source of the chromium are in order.

For the second example, consider the situation shown in Figure 17. Conditions are the same in this hypothetical estuary as they were for the previous example, except for the presence of an urbanized area in the northwest portion of the system. Drainage from the urban area enters the estuary and is a potential source of metal contamination. Sediment samples are taken at the locations indicated and analyzed for chromium; results of the analyses are plotted in Figure 18.

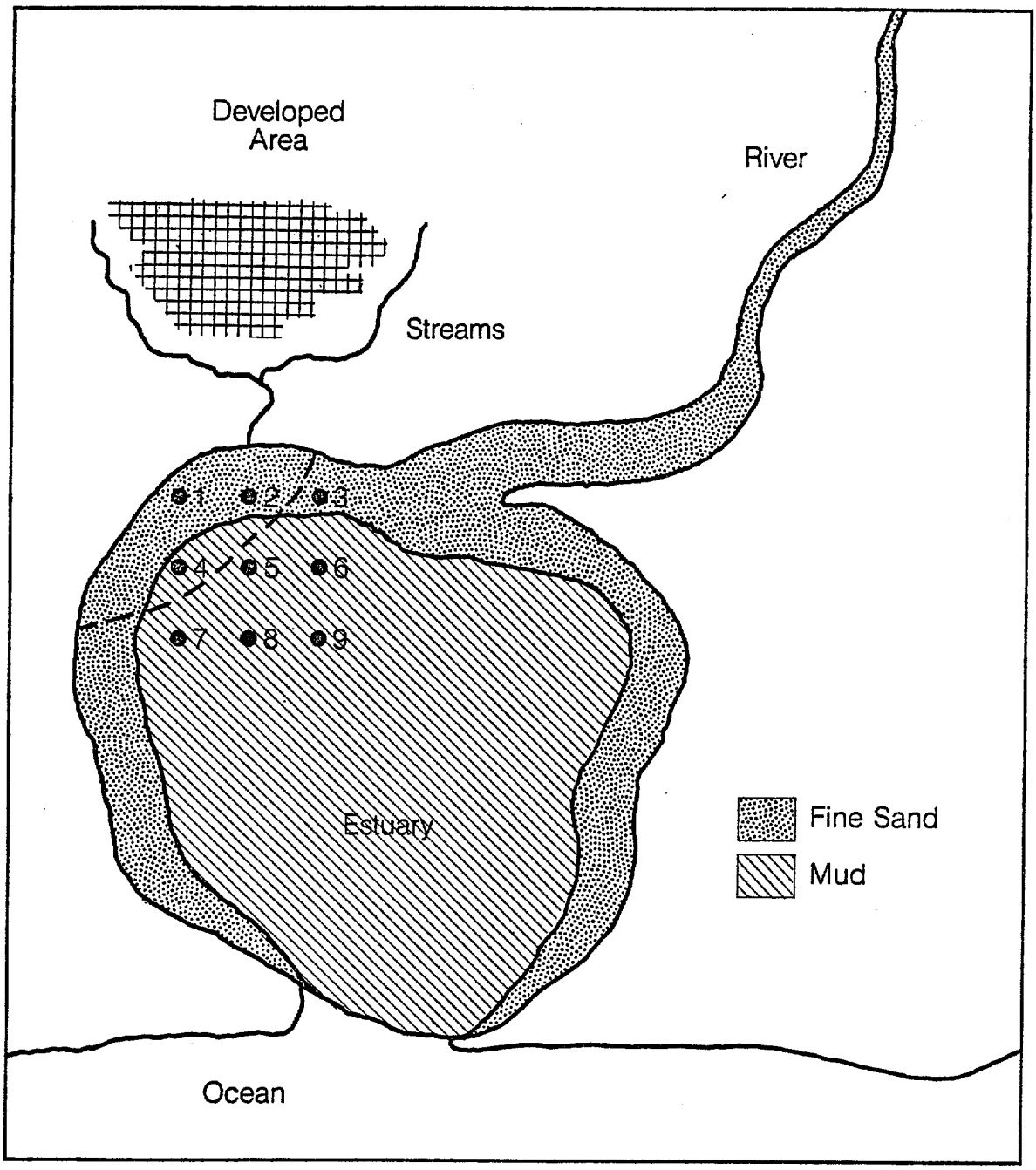

Figure 17. Hypothetical estuary showing metal source, sampling stations, and sediment grain size. Dashed line indicates extent of elevated chromium concentrations.

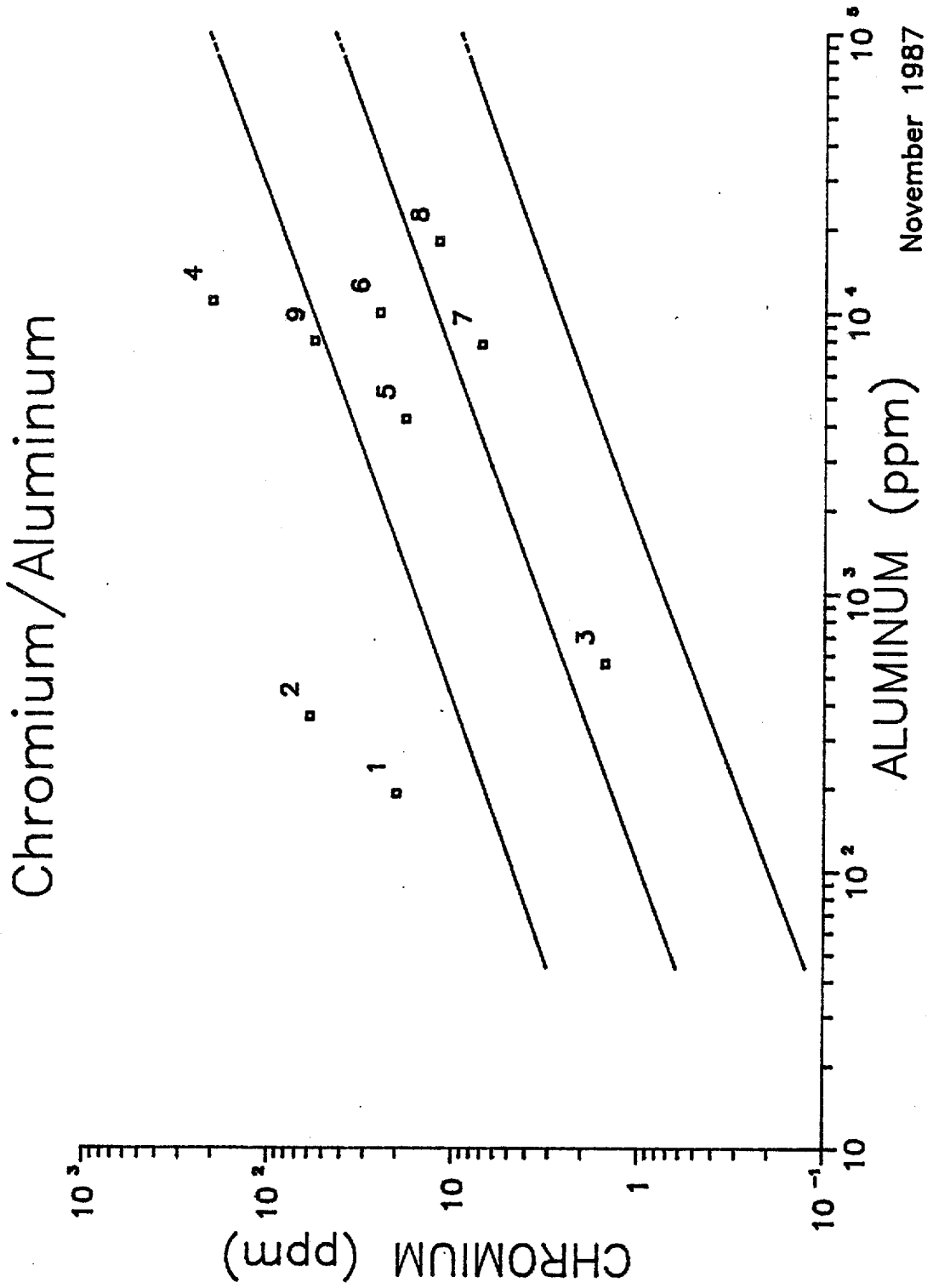

Figure 18. Chromium results from hypothetical estuarine sampling stations shown in Figure 17.

Based on the information described above, the extent of elevated chromium concentrations is indicated by the dashed line in Figure 17. Chromium from the pollution source appears to be accumulating in the sediments at stations 1, 2, and 4. Chromium concentrations at these stations lie outside the 95% confidence interval and, assuming they have been checked for errors, can be considered indicative of chromium-enriched sediment. Stations 3, 5, 6, 7, 8 do not have elevated chromium levels and thus appear to be outside the range of influence of the chromium source. Note that the absolute concentration of chromium at Station 1 is less than that at Stations 5 and 6 but Station 1 is considered to be enriched with chromium. Station 9 has a chromium value just outside the 95% prediction limit but given its location and the metal concentrations at the surrounding stations, the station is judged to be unpolluted.

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APPENDIX

This appendix contains blank metal/aluminum figures with regression lines and 95% prediction limits. Extrapolated portions of the lines are represented by dashed lines (see explanation in text). Metals data can be plotted on these figures as described in the text for assessment of metal enrichment in estuarine sediments.

Figures

FIGURE A1. Arsenic/aluminum regression line with 95% prediction limits A-3

FIGURE A2. Cadmium/aluminum regression line with 95% prediction limits A-4

FIGURE A3. Chromium/aluminum regression line with 95% prediction limits A-5

FIGURE A4. Copper/aluminum regression line with 95% prediction limits A-6

FIGURE A5. Nickel/aluminum regression line with 95% prediction limits A-7

FIGURE A6. Lead/aluminum regression line with 95% prediction limits A-8

FIGURE A7. Zinc/aluminum regression line with 95% prediction limits A-9

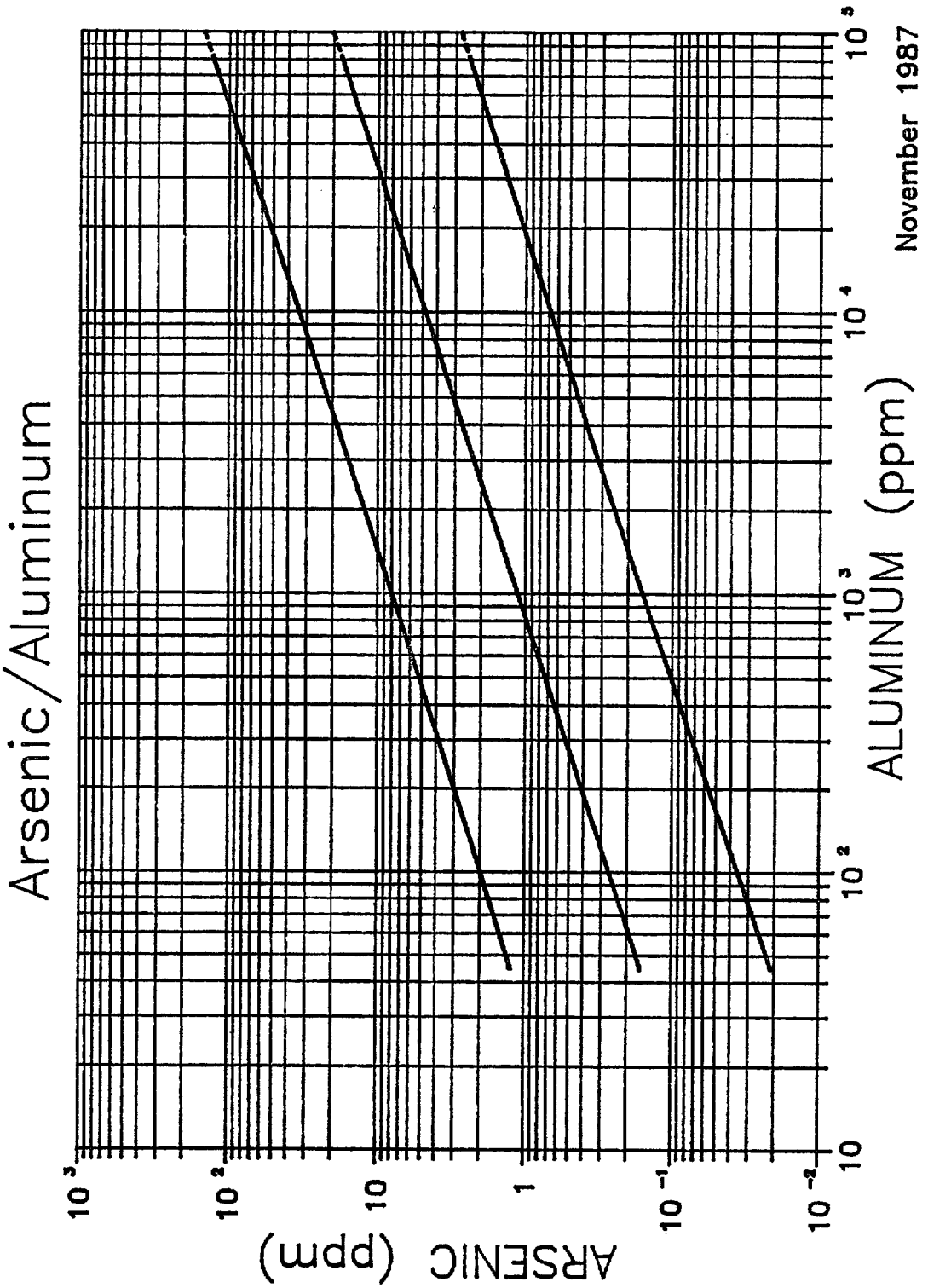

Figure A1. Arsenic/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

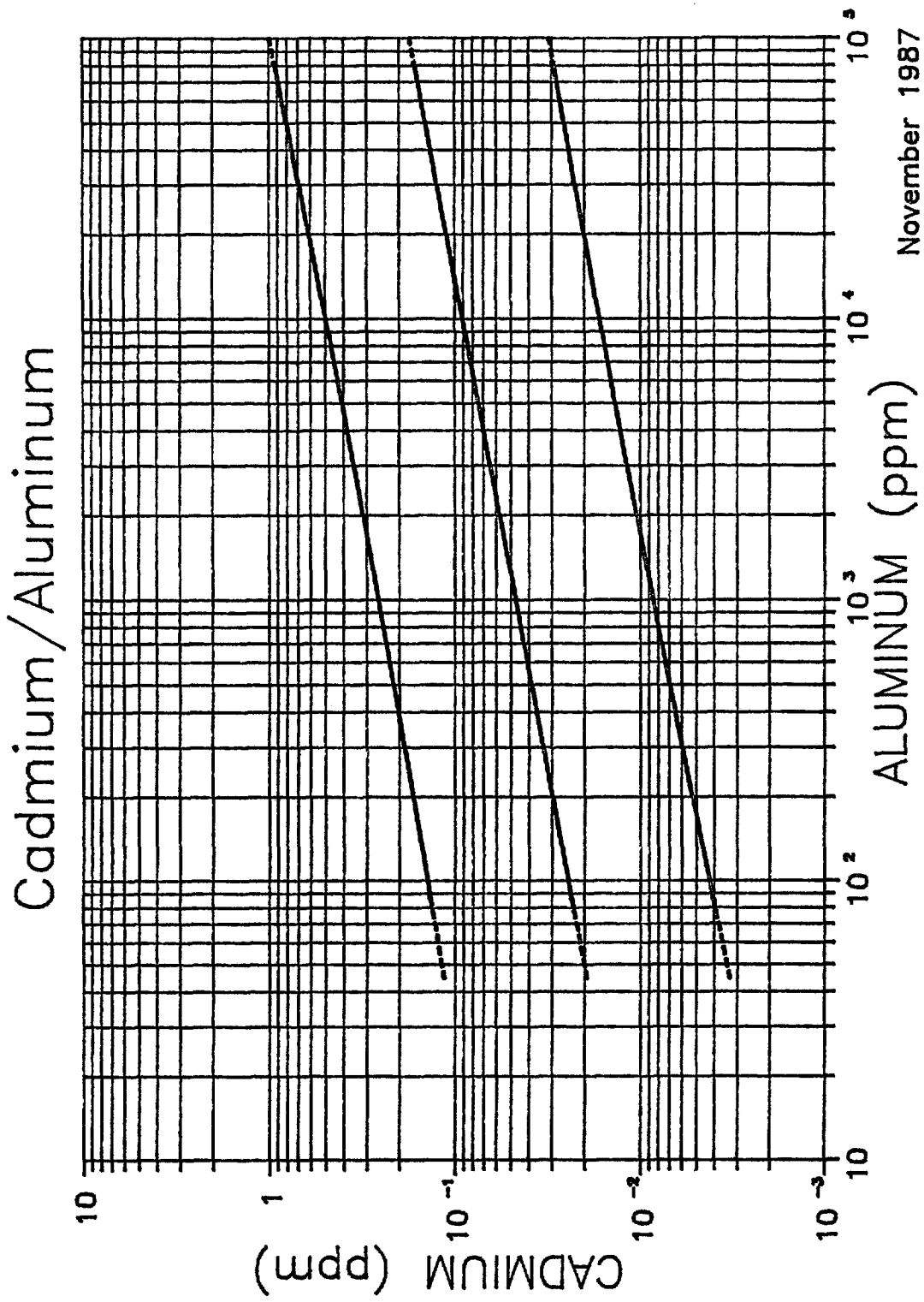

Figure A2. Cadmium/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

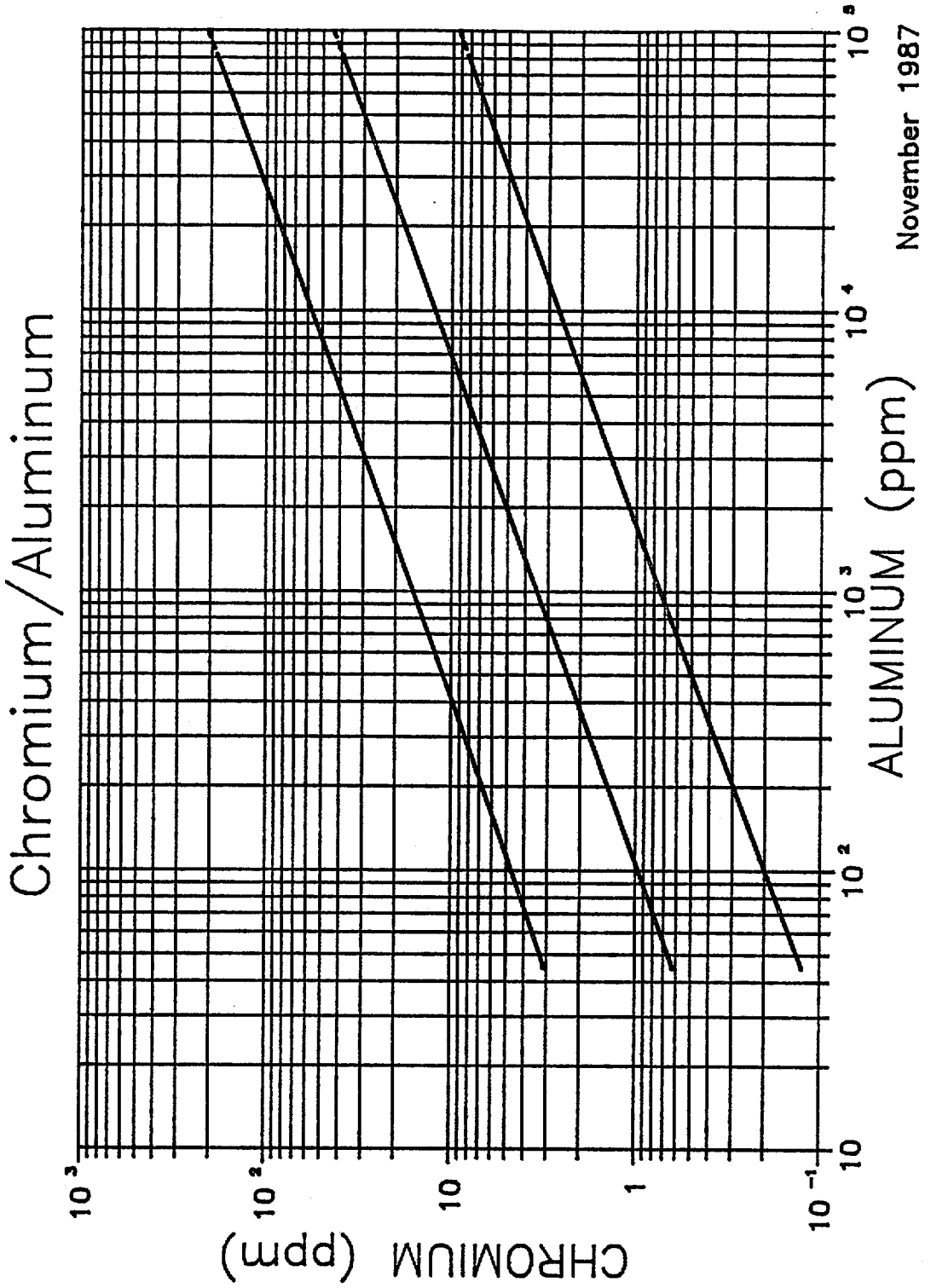

Figure A3. Chromium/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

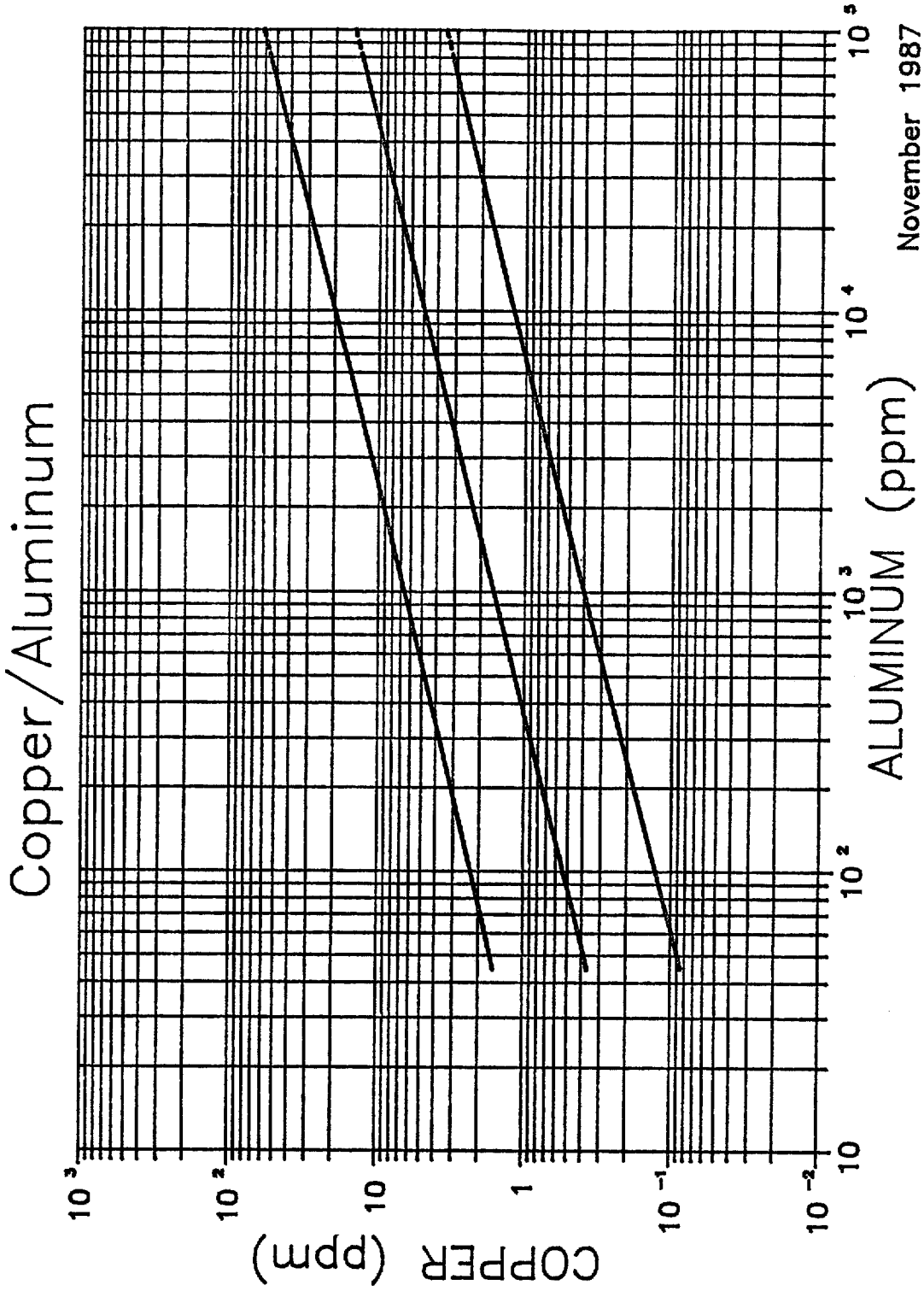

Figure A4. Copper/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

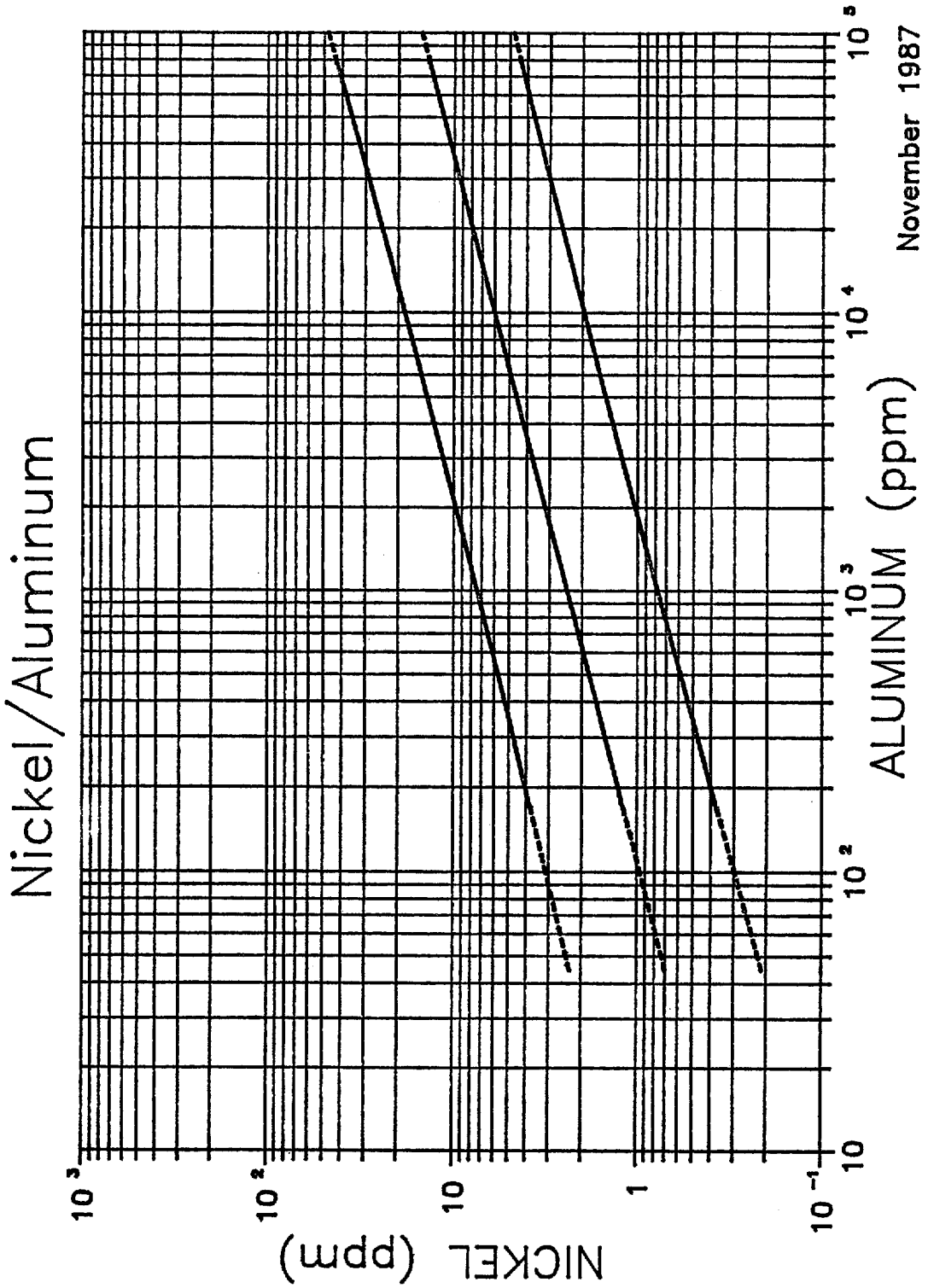

Figure A6. Nickel/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

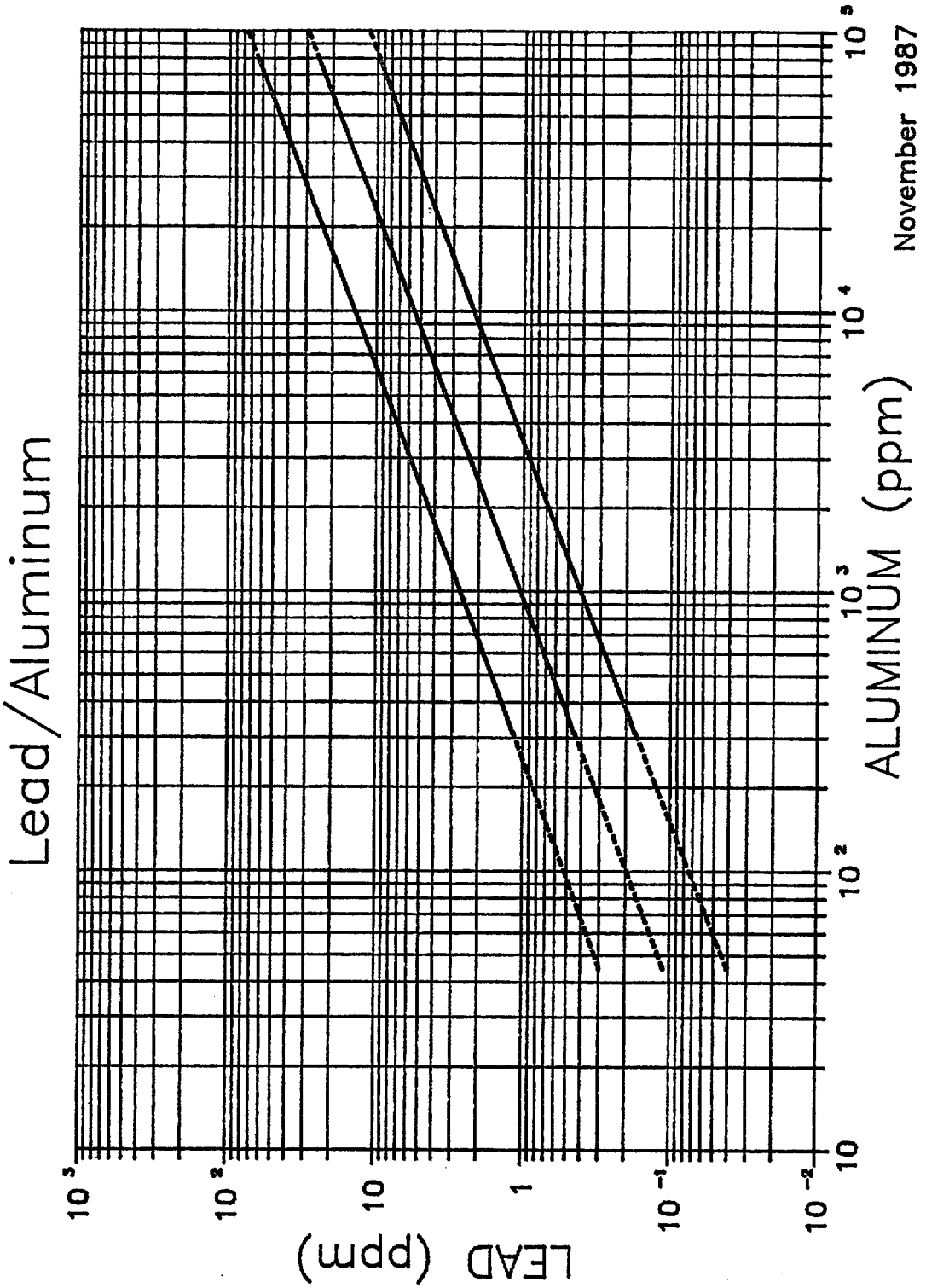

Figure A5. Lead/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).

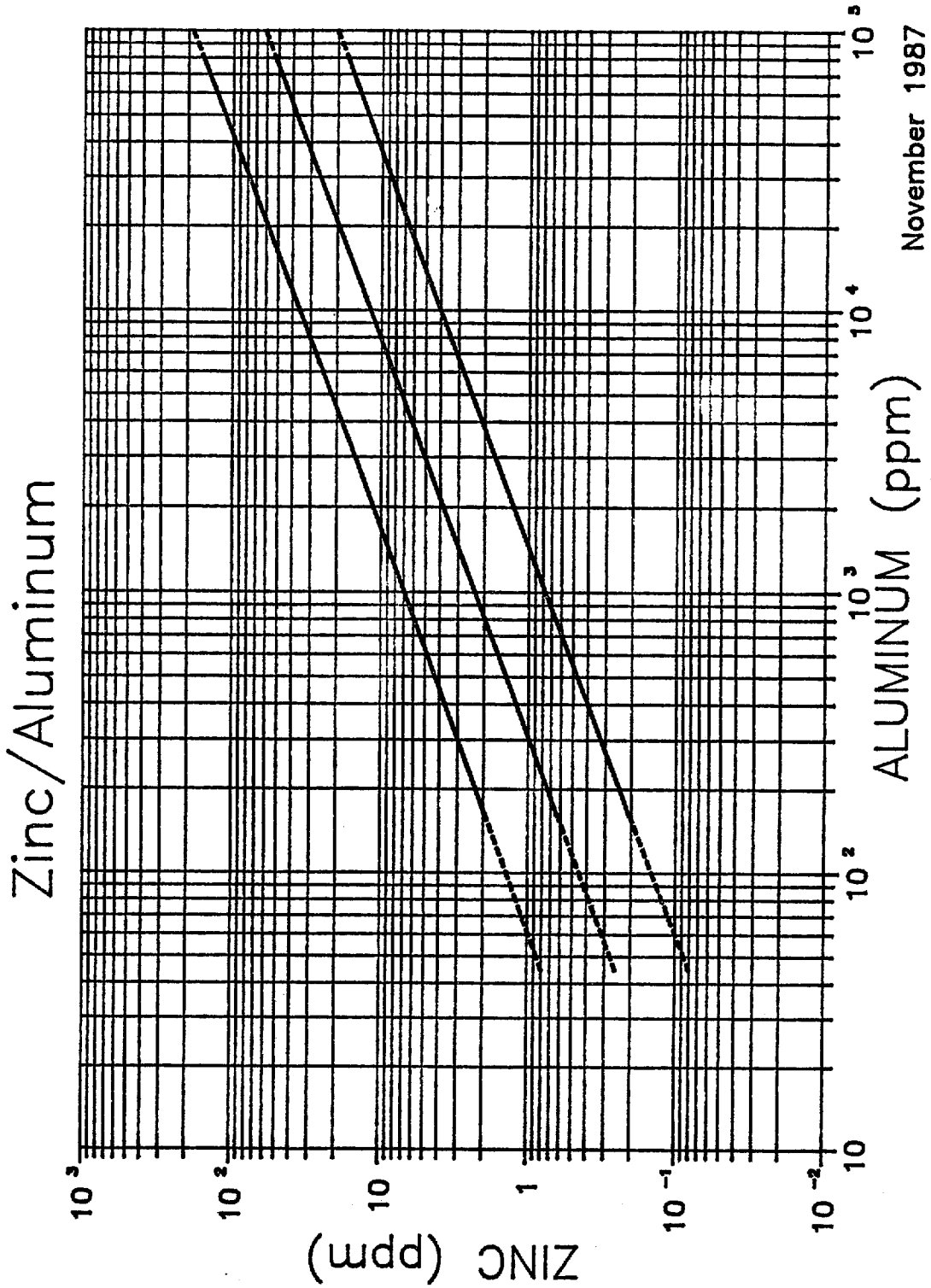

Figure A7. Zinc/aluminum regression line with 95% prediction limits. Dashed line indicates extrapolation (see text for explanation).