RECEIVED
FEB 28
CPD

Task IV.A
FY 89 CZ173

ADEM

TECHNICAL REPORT

COASTAL PROGRAM

SEDIMENT CHEMISTRY

BASELINE STUDY

QE571 .H35 1991

QE
571
.H35
1991

ALABAMA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
1751 CONG. W. L. DICKINSON DRIVE • MONTGOMERY, AL 36130

A SEDIMENT CHEMISTRY BASELINE STUDY OF COASTAL ALABAMA

By:

Gary L. Halcomb

Coastal Program
Alabama Department of Environmental Management
2204 Perimeter Rd.
Mobile, Alabama

November 1991

US Department of Commerce
NOAA Coastal Services Center Library
2234 South Hobson Avenue
Charleston, SC 29405-2413

DISCLAIMER

The mention of trade names or brand names in this document is for illustrative purposes only and does not constitute an endorsement by the Alabama Department of Environmental Management, the Alabama Department of Economic and Community Affairs or the National Oceanic and Atmospheric Administration.

TABLE OF CONTENTS

Acknowledgments II

List of Figures and Tables III

Executive Summary 1

Introduction 3

Materials and Methods 8

Results 12

Discussion 25

Conclusion 28

Bibliography 29

Appendix A: Normal scores vs metal values, all sample sites.

Appendix B: Metal vs Aluminum values, all sample sites.

Appendix C: Normal scores vs metal values, clean sites.

Appendix D: Metal vs Aluminum values, clean sites.

ACKNOWLEDGEMENTS

This report was funded in part by the Alabama Department of Economic and Community Affairs, Office of the Governor of the State of Alabama; and in part by a grant from the Office of Ocean and Coastal Resources Management, National Oceanic and Atmospheric Administration, United States Department of Commerce. The author wishes to express his kindest appreciation to Carolyn Merryman, David Wigger and Clinton Townsend of the ADEM Mobile Branch Laboratory for their diligence and many long hours spent processing and analyzing the samples. Thanks also to Mark Register, Nancy Van Antwerp, Michael Boyle, Al Hickey and Kelly Williams for their invaluable assistance collecting the samples. Regards also are extended to Dr. Steven Schropp, Dr. Herbert Windom and Dr. Wayne Isphording for their advice and technical assistance in preparing this paper.

LIST OF TABLES AND FIGURES

Table 1: Station locations, latitudes and longitudes 11

Table 2: Probability plot coefficients for normality of metals data 15

Table 3: Correlation coefficients for metals vs aluminum ... 16

Table 4: Results of regression analyses using aluminum as the independent variable and other metals as dependent variables 17

Table 5: Sediment metals data 18

Table 6: Probability plot coefficients for normality of metals data, "clean" sites data 22

Table 7: Correlation coefficients for metals vs aluminum, "clean" sites data 23

Table 8: Results of regression analyses using aluminum as the independent variable and other metals as dependent variables, "clean" sites data 24

Figure 1: Locations of sample stations 10

Figure 2: Test case, lead in sediment at Station DR-1 27

EXECUTIVE SUMMARY

This report details the application of the concept of utilizing aluminum as a "normalizing factor" for interpreting metals data in coastal sediments. Accurate interpretation of such information is often complicated by the various factors influencing metals concentration in sediments. These factors may be natural, like the geology of the drainage basin and sediment grain size to name a couple, or they may be anthropogenic such as wastewater discharges from industrial processes, development of offshore hydrocarbon resources and shipyard activity. Utilization of aluminum as a so-called "geochemical normalizer" allows for an accounting of the natural variability of metals in sediments and for the identification of sediments enriched with metals relative to expected natural concentrations.

The principle of utilizing aluminum as a "normalizing factor" is based on the constant relationships existing between metals and aluminum in the earth's crust and in natural sediments. This concept has been successfully employed by investigators in other states for developing a method for identifying anthropogenic enrichment of coastal sediments.

Samples of sediments from coastal Alabama were collected and analyzed for their metals content. Metal/aluminum regressions, correlations and prediction limits were calculated and graphical plots of these relationships were constructed. The results indicate statistically significant relationships between aluminum and eight other metals. Metals data from coastal sediments can now be plotted on

these diagrams of the relationships assessed to determine if the metals content of the sample is within natural ranges or represents an enriched area.

The efforts of this study accomplished several objectives, these being: 1) verifying the validity of applying the concept of aluminum as a "normalizing factor" for the sediments of coastal Alabama, 2) defining metal/aluminum relationships for "clean" sediments in coastal Alabama, 3) tentitive identification of areas of potentially enriched sediments, and 4) incorporation of a thorough and comprehensive Q&A program evaluating performance of the laboratory through use of reference standards and participation in an intercalibration exercise.

INTRODUCTION

The estuaries of coastal Alabama have become subjects of increasing concern relative to environmental stresses from developmental activities. These stresses may be in the form of industrial and municipal wastewater discharges, urban non-point sources, agricultural runoff, dredging and port and marina development. Of particular interest is the potential of these activities for enriching aquatic environments with heavy metals.

The sources of heavy metal enrichment are numerous and varied. These sources range in size from metal plating shops discharging small quantities on an intermittant basis to large facilities discharging millions of gallons daily of treated wastewater containing various heavy metals. Lead from the exhaust emissions of engines burning leaded gasoline also ends up in aquatic environments as a result of atmospheric deposition and direct input from boat motors. Additional sources common to coastal areas include the marine paints and surface coatings utilized in the shipbuilding industry. These preparations, designed for protection against corrosion and inhibition of the growth of fouling organisms, are based on heavy metal formulations toxic to many species of estuarine life. The uncontrolled release of these materials from the removal of old paint by sandblasting and the spray application of new coatings has, over the years, been a long standing source of metal enrichment to aquatic environments. A more recent and controversial source of potential enrichment of metals in the environment has been the development of offshore hydrocarbon reserves. The exploration and

production activities characterizing offshore development are accompanied by the use of clay-based drilling fluids and the generation of considerable quantities of geological formation cuttings from the well hole. The resultant waste drilling fluids and cuttings are rich in metals not common to estuarine sediments. The uncertain potentials for adverse impacts to aquatic ecosystems from these numerous sources have prompted federal and state regulatory agencies to examine more closely the effects of metal enrichment on sediment quality.

Consequently, needs have arisen for the investigation of the metal content of sediments throughout the Alabama coastal area. Specific needs from a regulatory perspective are:

1. Determination of "backround" levels of metals in sediments of the entire coastal area, or in other words the concentrations of metals atttributable to natural causes.
2. Development of a "standardized" method for sampling and analyzing sediments and interpreting the data for meaningful results.
3. Application of a "standardized" method along with a database of natural levels of metals in sediments in order to ascertain the degree of metal enrichment resulting from anthropogenic sources.
4. Identification of potential "hot spots" or areas of highly enriched sediments which may constitute a hazard to aquatic life and may require remediation.

Previous studies of sediment chemistry in coastal Alabama, Malatino

(1980) and Isphording (1985 and 1987), delt with Mobile Bay and Mississippi Sound but did not examine the smaller estuaries or tributary streams. Although these previous studies generated a useful database for future reference of metals in sediments the investigators did not delve into developing a standardized method for identifying polluted sediments.

Schropp and Windom (1988) and Windom et al (1989) examined metal concentrations in estuarine sediments from coastal Florida and Georgia and developed a method for identifying metal enrichment due to anthropogenic activities. This method is based on the naturally occurring relationships between aluminum and other metallic elements. These relationships allow for the identification of polluted sediments by using aluminum as a reference element. The basis for this method is that aluminum occurs naturally in all estuarine sediments and the concentrations of other metals tend to vary with the concentration of aluminum. These naturally occuring proportions of metals relative to aluminum have been reported by several investigators (Turekian and Wedepohl, 1961; Taylor, 1964; Duce et al, 1976) to be fairly constant. This allows for the use of aluminum as a reference element or "normalizing factor" for identifying sediments enriched by anthropogenic activities. This concept has been used to examine metal pollution in the Savannah River estuary (Goldberg, 1979) and lead pollution in the Mississippi River (Trefey et al, 1985).

Although the principle of using aluminum as a "geochemical normalizer" was successfully employed in the above mentioned studies

it cannot be assumed that this applies to coastal Alabama. The geology of the drainage basins of the study area is characterized by clays exceptionally rich in aluminum (Isphording, pers. comm.) which could skew the statistical distribution of aluminum data. A non-normal distribution of such data complicates interpretation of results making reliable determinations of contaminated areas a difficult task (Sokal and Rohlf, 1969; Schropp and Windom, 1988). Other metallic elements, barium for example, are also naturally abundant in the clays of the area (Isphording, pers. comm.), these too might compound the difficulty of identifying anthropogenically enriched sediments. An additional complicating factor for Mobile Bay is the history of releases of aluminum enriched clays and stormwater runoff from the tailings ponds of an aluminum extraction facility previously operated in Mobile by The Aluminum Company of America. Although this facility has not operated in nearly a decade, stormwater runoff and the loss of spent bauxite ore from breaches in the walls of the tailings ponds have contributed some enrichment, albeit of an unknown magnitude and significance, to the lower Mobile River and Mobile Bay.

This study applied the concept of utilizing aluminum as a normalizing factor to metal concentrations in sediments of coastal Alabama. The goal of this effort being a standardized method for sampling, analyzing and objectively interpreting metals data for sediments. In acheiving that goal a valuable database was compiled and preliminary identification of enriched areas was accomplished.

The results indicated that aluminum does account for most of the

variability of other metals except mercury. The scarcity of natural sources of mercury in the drainage basins of the study area would appear to account for this lack of covariance (Isphording, pers. comm.; Schropp, pers. comm.).

MATERIALS AND METHODS

Sediment samples (cores) were collected from 53 stations in coastal Alabama (Figure 1), the latitude and longitude coordinates of these stations are given in Table 1. The sites sampled encompassed a wide variety of sediment types ranging from aluminum and iron rich clays of the Mobile River Delta and upper Mobile Bay to the coarse grained silica rich sands of lower Perdido Bay. A K-B type core sampler (Wildlife Supply Co., cat. no. 2402-A12) equipped with a cellulose-acetate-butyrate liner tube was used for retrieval of sediment samples from sites where the water depth was greater than one meter; where the water depth was less than one meter samples were collected by utilizing the liner tubes as hand core samplers. The upper five centimeters of each core was placed in a clean glass jar and capped with a teflon lined lid. Samples were collected in triplicate, two samples for immediate processing and the third sample was "archived" in a freezer for future analyses in case of widely varying results between the first two.

Preparation of sediments for analyses began with oven drying samples at 60°C followed by weighing out a 0.25 gram portion of each. Each weighed portion was then placed in a 30 mL teflon cup to which was added nitric acid, hydrofluoric acid and perchloric acid. The teflon cups were then heated on a hotplate at ca. 120°C, each cup remaining on the hotplate until the sample had been totally digested, acid was added to each cup as needed until digestion was completed. Once the sample was digested, heating was continued until the sample volume was reduced to approximately 1 mL to which 2.5% nitric acid was added to bring the

sample volume up to 25 mL. Samples were then analyzed with a Perkin-Elmer 3030-B atomic absorption spectrophotometer (AA) using a flame furnace for Al, Fe and Zn and a graphite furnace for As, Ba, Cd, Cr, Cu and Pb. A Perkin-Elmer 460 AA equipped with cold vapor apparatus was used for analyses of samples for Hg.

The mean values of the analyses of replicate samples were utilized as data for statistical comparisons. Statistical procedures employed in this study are detailed in Sokal and Rohlf (1969) and Filliben (1975).

Quality of analytical technique was assured through particpation in the intercomparison exercise for sediment metal analyses (FDER, 1991). This exercise involved the digestion and analyses of standard reference sediments from the National Institute of Standards and Technology (NIST SRM 1646) and the National Research Council of Canada (NRC BCSS-1 and BEST-1). Coastal sediments of a variety of types were also incorporated in the intercomparison exercise. Analytical results obtained by the ADEM Mobile Branch Laboratory were compared to those of other labs participating in the exercise. These results indicate a high degree of reliability in the analytical data produced by the ADEM lab. In addition to participation in the intercalibration exercise, ADEM laboratory personnel routinely checked performance of their digestion technique and analytical instruments by testing samples of reference material during the course of this study.

FIGURE 1
Locations of Sample Stations

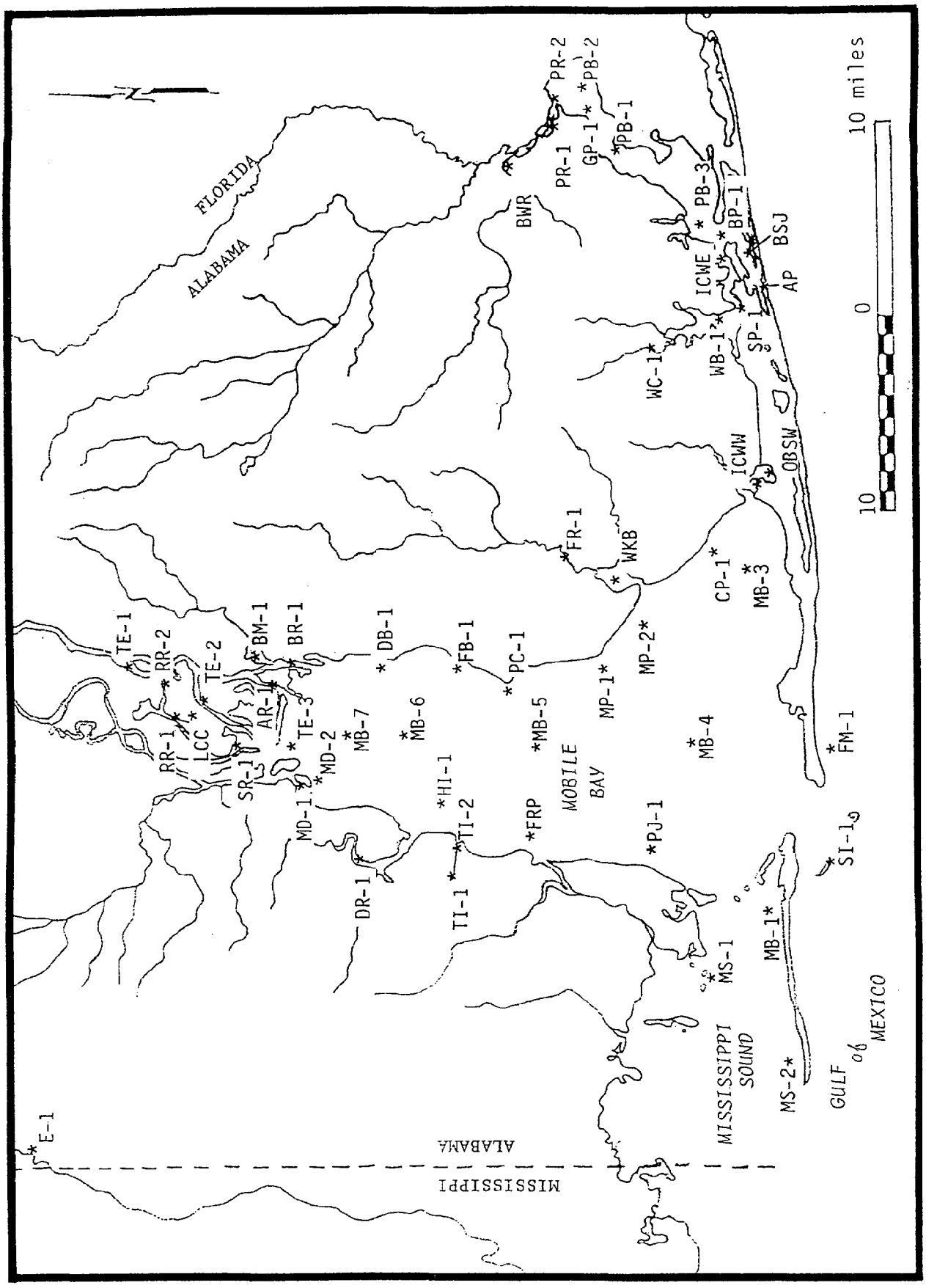


Table 1

STATION LOCATIONS
LATITUDE - LONGITUDE

STATION	NORTH LATITUDE	WEST LONGITUDE
MB-1	30°15.88′	88°10.45′
MB-3	30°18.26′	88°51.01′
MB-4	30°20.88′	87°59.53′
MB-5	30°26.52′	87°59.16′
MB-6	30°32.29′	87°59.04′
MB-7	30°36.80′	87°59.00′
SR-1	30°42.46′	88°42.46′
RR-1	30°45.79′	87°58.69′
RR-2	30°46.15′	87°56.82′
LCC-1	30°43.92′	87°58.78′
TR-1	30°46.98′	87°56.47′
TR-2	30°43.90′	87°58.28′
TR-3	30°40.49′	88°00.40′
MD-1	30°39.20′	88°02.75′
MD-2	30°38.52′	88°02.66′
DR-1	30°36.38′	88°06.55′
HI-1	30°31.40′	88°03.20′
PC-1	30°29.10′	87°56.19′
FB-1	30°31.62′	87°54.66′
DB-1	30°35.79′	87°55.63′
BR-1	30°40.50′	87°55.43′
BM-1	30°41.69′	87°55.34′
AR-1	30°41.09′	87°56.09′
MP-1	30°26.35′	87°56.65′
MP-2	30°23.59′	87°54.01
WKB-1	30°23.80′	87°49.72′
FR-1	30°23.72′	87°49.36′
CP-1	30°20.04′	87°48.97′
TI-1	30°31.74′	88°08.50′
TI-2	30°31.77′	88°07.14′
FRP-1	30°27.60′	88°04.12′
PJ-1	30°22.74′	88°06.04′
MS-1	30°17.10′	88°13.26′
MS-2	30°13.62′	88°18.37′
E-1	30°51.70′	88°24.92′
ICWW	30°16.54′	87°45.15′
OB-SW	30°15.75′	87°44.36′
BWR-1	30°29.00′	87°26.45′
PR-1	30°27.23′	87°25.03′
PR-2	30°26.83′	87°23.60′
GP-1	30°24.90′	87°24.03′
PB-1	30°24.45′	87°29.84′
PB-2	30°25.56′	87°22.58′
PB-3	30°19.84′	87°30.00′
SP-1	30°17.78′	87°34.65′
WC-1	30°20.72′	87°36.09′
ICWE	30°17.93′	87°32.46′
BP-1	30°18.32′	87°30.93′
BSJ-1	30°17.57′	87°31.43′
AP-1	30°16.45′	87°33.23′
SI-1	30°12.10′	88°05.10′
FM-1	30°13.20′	87°59.60′

RESULTS

Application of the concept of utilizing aluminum as a reference element in conjunction with parametric statistical analyses demands that the data for metals have constant variance and a normal distribution. The test for constant variance was performed by constructing plots of sample means versus sample standard deviations for each metal. Standard deviations were proportional to mean values for all metals. Mean values for metals were then converted to log-10 values and plotted against standard deviations. The proportionality between mean values and standard deviations was removed indicating the presence of constant variance in the data set.

Presence of normal distribution was determined by calculating normal scores for a sample size of N=53 and plotting them against the data for sediment metals concentration. The presence of a relatively linear plot indicating a normal distribution. This procedure was performed for both absolute concentrations and for log-10 transformed values. Some elements, aluminum, chromium and iron, appeared to fit a normal distribution using absolute concentrations whereas others, arsenic and cadmium, required a log-10 transformation to conform to a normal distribution. The remaining elements, barium, copper, lead, mercury and zinc, failed this graphical test for normal distributions regardless of using untransformed or transformed data. Graphical representation of these results are shown in Appendix A. Presence of normal distributions was tested in a more rigorous manner using the probability plot coefficient test (Filliben, 1975). Obtaining a significantly high correlation coefficient between normal scores and

metals data leads to the acceptance of the null hypothesis (Ho) of normality and the rejection of the alternative hypothesis (Ha) of non-normality, results of this test are shown in Table 2. Untransformed arsenic, barium, cadmium, copper, mercury, lead and zinc deviated from normality. Untransformed aluminum, chromium and iron values fit a normal distribution. Log-10 transformed arsenic, cadmium and zinc data produced normal distributions but transformed data for barium, copper and lead yielded coefficients just short of the critical value. Both untransformed and log-10 transformed data for mercury failed to conform to a normal distribution.

The untransformed values for aluminum were utilized as the independent variable for all comparisons in this study. Untransformed values for chromium and iron served as dependent variables for those elements; log-10 transformed data were utilized as the dependent variable sets for arsenic and cadmium. As mentioned above the data for barium, copper, lead and zinc did not exhibit a normal distribution; however, when samples that were suspected of being enriched were removed from the data set these elements also exhibited a normal distribution. Once again, mercury failed to conform to a normal distribution even as a "trimmed" set of data. A discussion of "trimming" the data set and analyses of data from "clean" sites follows later in this section.

Having examined the data for normality and constant variance the next step was to determine the strength of metal/aluminum relationships. Correlation coefficients were calculated for each metal and aluminum, these are listed in Table 3. Concentrations of all metals except

mercury were positively correlated with aluminum concentrations ($p<0.005$). Iron and chromium displayed the strongest relationships with aluminum; cadmium the weakest. Mercury showed a weak inverse correlation with aluminum and consequently was not referenced to aluminum values. Schropp and Windom (1988) found a similar inverse relationship between mercury and aluminum and also refrained from comparing mercury values to aluminum values.

The next step was to analyze the data for associations between the independent variable, aluminum, and dependent variables, other metals. Least squares regression analysis was used to evaluate the relationship between the metal concentrations and aluminum concentrations. Results of the regression analyses are presented in Table 4.

The results of the regression analyses were then utilized to calculate 95% prediction limits according to the procedure of Sokal and Rohlf (1969). Regression lines and prediction limits for each metal are plotted in Appendix B, superimposed on the metal vs aluminum graphs.

The analytical result of each metal was then plotted against its respective aluminum value. These are graphically represented in Appendix B. Superimposed on the graphs are the regression lines and 95% prediction bands for each metal/aluminum relationship. These results indicate a proportional relationship between the concentration of aluminum and the other metals except for mercury. Data for all metals is presented in tabular form in Table 5.

Table 2

Probability plot correlation coefficients
for normality of metals data.

Metal	Correlation Coefficient	
	Untransformed	LOG 10-Transformed
Aluminum	0.964 *	0.890 #
Arsenic	0.851 #	0.982 *
Barium	0.942 #	0.936 *
Cadmium	0.858 #	0.976 *
Chromium	0.974 *	0.913 #
Copper	0.912 #	0.949 #
Iron	0.966 *	0.882 #
Mercury	0.837 #	0.897 #
Lead	0.863 #	0.943 #
Zinc	0.788 #	0.962 *

* $p>0.005$ (Accept Ho; normal distribution)
# $p<0.005$ (Reject Ho; non-normal distribution)

Table 3

CORRELATION COEFFICIENTS FOR
METALS AND ALUMINUM

Metal	r
Arsenic	0.84*
Barium	0.68*
Cadmium	0.64*
Chromium	0.96*
Copper	0.83*
Iron	0.98*
Mercury	-0.13
Lead	0.84*
Zinc	0.86*

* $p < 0.005$

Table 4

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

Metal	a	b
Arsenic	0.14361943	0.00001621
Barium	23.9307788	0.00337917
Cadmium	-0.6197267	0.00000597
Chromium	6.34129908	0.00104977
Copper	0.47660139	0.00001151
Iron	544.383827	0.52196488
Mercury	-0.1700004	-0.0000008
Lead	0.46022156	0.00001311
Zinc	1.11002323	0.00001363

a = Y-intercept of regression line.
b = Slope of regression line.

Table 5

Sediment Metals Data

STATION	Aluminum	Arsenic	Barium	Cadmium	Chromium	Copper	Iron	Mercury	Lead	Zinc
MB-1	68,300	24.0	281.5	0.910	82.0	12.50	42,000	0.400	25.00	105.5
MB-3	96,900	82.5	251.5	0.560	90.0	25.20	53,400	0.520	22.95	139.0
MB-4	93,850	62.5	222.5	0.490	87.5	23.50	45,600	0.835	22.65	142.0
MB-5	98,600	70.5	209.0	0.590	91.0	21.25	50,100	0.610	22.75	173.5
MB-6	76,650	46.5	249.5	0.575	75.5	17.60	42,000	0.400	21.15	126.5
MB-7	64,950	34.5	250.0	0.575	68.0	15.05	33,050	0.400	17.95	105.5
RR-1	62,750	33.5	242.0	0.485	69.0	15.85	30,100	0.750	15.45	93.5
RR-2	75,000	46.0	313.5	0.550	77.5	20.30	35,950	0.450	18.15	94.0
SR-1	71,400	41.0	251.0	0.495	67.5	15.90	40,250	0.560	13.40	88.5
TR-1	65,450	40.5	366.5	0.540	68.0	19.70	32,150	0.400	17.90	141.5
TR-2	45,900	34.5	199.0	0.495	45.5	11.60	20,550	0.400	12.05	60.5
TR-3	34,650	21.0	118.0	0.515	48.5	8.50	19,300	0.400	8.00	68.5
LCC-1	78,650	19.0	346.0	0.790	112.5	21.50	40,950	0.400	16.00	180.0
AR-1	46,900	5.3	727.0	0.750	51.5	10.00	26,850	0.400	21.50	79.5
BM-1	46,250	12.0	27.0	0.510	40.0	11.50	24,200	0.400	19.50	94.0
BR-1	36,850	23.0	33.5	0.685	40.0	8.00	27,050	0.400	21.50	56.0
MD-1	88,400	106.0	263.5	1.150	107.5	27.50	46,450	0.400	34.00	202.0
MD-2	82,550	71.0	258.5	0.720	93.5	21.00	47,750	0.400	20.50	143.5
HI-1	67,000	5.5	217.5	0.615	80.0	30.50	34,150	0.400	15.50	94.0
DR-1	75,450	11.0	257.5	2.050	111.0	66.00	37,750	0.400	100.00	206.0
DB-1	53,400	23.5	30.0	0.580	55.0	12.00	30,800	0.400	18.50	84.0
FB-1	2,310	3.0	28.5	0.445	8.0	1.50	1,700	0.400	4.00	9.5
PC-1	5,220	3.0	17.5	0.385	17.0	1.75	3,185	0.400	5.00	10.0
ICW-W	5,555	2.0	4.0	0.505	12.0	1.50	4,800	0.400	3.00	8.0
OB-1	37,200	9.5	4.5	0.500	54.0	7.00	23,100	0.400	13.00	51.5
WB-S	74,350	14.0	15.5	0.810	89.5	11.00	30,250	0.400	27.00	82.5
ICW-E	11,105	6.5	22.0	0.295	3.6	3.85	948	0.400	2.50	18.5
PB-1	78,450	19.5	250.0	1.460	100.0	12.50	48,200	0.550	25.50	111.0
BP-1	3,300	2.0	9.0	0.245	2.9	0.90	219	0.400	1.50	11.0
AP-1	1,100	2.0	8.0	0.285	4.2	0.90	314	0.400	2.00	17.5
E-1	3,350	2.0	23.5	0.470	11.5	2.00	1,260	0.400	3.50	7.0
CP-1	9,800	1.6	84.0	0.300	19.0	3.95	8,190	0.950	6.65	21.0
FR-1	71,750	6.8	453.0	0.400	87.5	24.00	36,850	0.950	37.50	119.0
MP-1	86,700	8.0	464.5	0.400	100.0	25.00	44,900	0.900	29.00	136.0
MP-2	43,500	5.8	250.0	0.300	62.0	15.50	26,850	0.950	23.50	71.5
WKB-1	61,000	6.4	320.5	0.450	76.0	20.50	34,900	0.900	32.00	90.5
BWR-1	62,850	6.8	175.0	0.550	60.5	22.00	31,550	0.900	35.50	56.0
PR-1	58,050	4.8	193.0	2.250	62.0	18.50	26,600	0.950	33.50	77.0
TI-1	43,150	4.8	290.0	1.500	65.5	27.00	28,700	2.550	30.00	847.5
TI-2	66,050	4.9	400.0	0.400	88.5	19.00	33,400	1.250	26.00	92.0
FRP-1	73,500	7.1	389.5	0.450	104.0	24.00	42,850	1.350	29.50	175.0
PJ-1	8,700	1.4	63.0	0.250	16.0	2.80	5,845	1.250	5.50	16.0
MS-1	20,850	3.4	68.0	0.300	31.0	5.40	13,550	1.000	10.00	37.5
MS-2	1,021	0.9	4.7	0.300	7.0	1.10	917	1.000	2.00	7.0
BSJ-1	373	0.9	8.0	0.170	7.0	6.50	159	0.900	0.90	13.0
GP-1	29,100	2.0	163.5	0.240	38.5	15.00	15,900	0.900	14.70	52.5
PB-2	38,500	2.9	193.0	0.250	52.0	17.50	22,600	0.900	20.05	70.5
PB-3	1,365	0.9	7.5	0.090	8.0	7.00	659	0.900	3.20	31.5
PR-2	36,250	2.9	203.0	0.395	49.5	19.50	19,600	0.900	19.90	67.5
SP-1	1,855	0.9	8.5	0.215	10.5	8.00	925	0.900	1.50	14.5
WC-1	29,400	2.5	95.0	0.175	40.5	13.50	9,270	0.900	8.85	39.5
SI-1	857	0.9	12.5	0.090	1.9	3.80	774	0.900	0.65	3.2
FM-1	730	0.9	15.5	0.090	2.0	4.45	712	0.900	0.95	4.6

So far this exercise has demonstrated statistically significant relationships between aluminum and the metals arsenic, cadmium, chromium, iron and zinc. The metals barium, copper and lead did not fit a normal distribution but appeared to be somewhat skewed to the left indicating a data set enriched in these elements. Since the primary objective of selecting sample sites was the sampling of a broad spectrum of sediment types rather than selecting only those sites far removed from sources of potential contamination, there was the chance that some samples were enriched due to anthropogenic activity. The next part of the discussion deals with examination of a "clean" set of data.

As stated above, the intent of choosing the locations was directed more towards thouough coverage of the coastal area and a wide variety of sediment types rather than avoiding potentially contaminated areas. The observed lack of normality in the data for barium, copper and lead, combined with the potential for enrichment of the sediments of western Mobile Bay from urban non-point sources, the extensive industrial activity in the Mobile area and from the sources discussed in the introduction led to deleting from the data set those samples from the western half of Mobile Bay including the tributaries. Additional rationale for this action was provided by analyses of sample material from a ditch draining a bauxite tailings impoundment at the old ALCOA facility. This material was a fine grained "mud" typical of the contents of the impoundment. These results indicate that the material collected from the ditch was indeed enriched with aluminum far above that of any sample of natural sediment collected during this study. The nature and quantity of bauxite mud in the ditch together with the

direction of drainage (towards the Mobile River) appears to indicate that the tailings impoundments have been a likely source of metals enrichment to Mobile Bay.

Subsequent analyses were performed on this set of data, sample size N=38, referred to hereinafter as the "clean" data set.

Statistical analysis of the "clean" data set was handled the same as for the entire data set. Graphical plots of normal scores versus concentration values were constructed and the probability plot coefficient test was applied. The results of these proceedures indicate a normal distribution for the untransformed values of barium, chromium, copper, iron, lead and zinc, and for the log-10 transformed values of arsenic and cadmium. Graphical representation of these plots may be found in Appendix C and probability plot correlation coefficients in Table 6. The presence of homoscedasticity was tested by the same method as discussed earlier.

After determining that the "clean" set of data meets the requirements of parametric statistical analyses, the "clean" set was subjected to least squares regression analyses (Sokal and Rohlf, 1969). The results of which are presented in Table 7, correlation coefficients, and Table 8, regression equations. The correlation coefficients for the "clean" data set show a relationship between aluminum and metals approximately the same as those for the entire data set. Although "trimming" the data may not have strengthed the metal/aluminum relationships of the "clean" data set, it did result in normal

distributions for barium, copper and lead, indicating possible enrichment for these elements in sediments of western Mobile Bay.

The results of regression analyses were then utilized to calculate 95% prediction limits as with the entire data set. The graphical plots of metals vs aluminum complete with regression lines and 95% prediction limits for the clean data set are presented in Appendix D. As the reader will observe the width of the prediction limits vary among the different elements. This is a function of the correlation coefficents for the metal to aluminum relationships, as the magnitude of the correlation coefficents increase the width of the prediction limits decrease.

Table 6

Probability plot correlation coefficients
for normality of clean sites metals data.

Metal	Correlation Coefficient Untransformed	LOG 10-Transformed
Aluminum	0.955 *	0.919 #
Arsenic	0.868 #	0.978 *
Barium	0.963 *	0.903 #
Cadmium	0.837 #	0.978 *
Chromium	0.971 *	0.943 #
Copper	0.977 *	0.948 #
Iron	0.957 *	0.913 #
Mercury	0.861 #	0.853 #
Lead	0.968 *	0.949 #
Zinc	0.967 *	0.959 #

* $p > 0.01$ (Accept Ho; normal distribution)
# $p < 0.01$ (Reject Ho; non-normal distribution)

Table 7

CORRELATION COEFFICIENTS FOR
METALS AND ALUMINUM
"CLEAN SITES" DATA

Metal	r
Arsenic	0.81 *
Barium	0.69 *
Cadmium	0.66 *
Chromium	0.97 *
Copper	0.81 *
Iron	0.97 *
Mercury	-0.09
Lead	0.87 *
Zinc	0.93 *

* $p < 0.005$

Table 8

Results of regression analyses of data from "clean sites" using Aluminum as the independent variable and other metals as dependent variables.

Metal	a	b
Arsenic	0.172176	0.000015
Barium	4.259297	0.004070
Cadmium	-0.652876	0.000007
Chromium	4.335524	0.001102
Copper	0.449245	0.000012
Iron	395.383860	0.519763
Mercury	-0.194462	-0.000001
Lead	0.388669	0.000016
Zinc	1.049655	0.000015

a = Y-intercept of regression line.
b = Slope of regression line.

DISCUSSION

Application of the results of this study to monitoring efforts is fairly straightforward. The regression line and prediction limits of a specific metal to aluminum relationship from the "clean" set of data are reproduced on a graph either by hand or by means of computer graphics software. Then the value of a metal at a station is determined (utiliztion of mean values calculated from replicate or triplicate samples from each station is strongly recommended) and points representing the corresponding metal to aluminum values are plotted on the graph. If a point falls within the prediction limits then the metal is within the natural limits. If a point lies above the upper prediction limit then the sample is considered enriched in that specific metal. The greater the distance above the upper prediction limit, the greater the chance that the sample is from an enriched area and the greater the degree of enrichment of that sample.

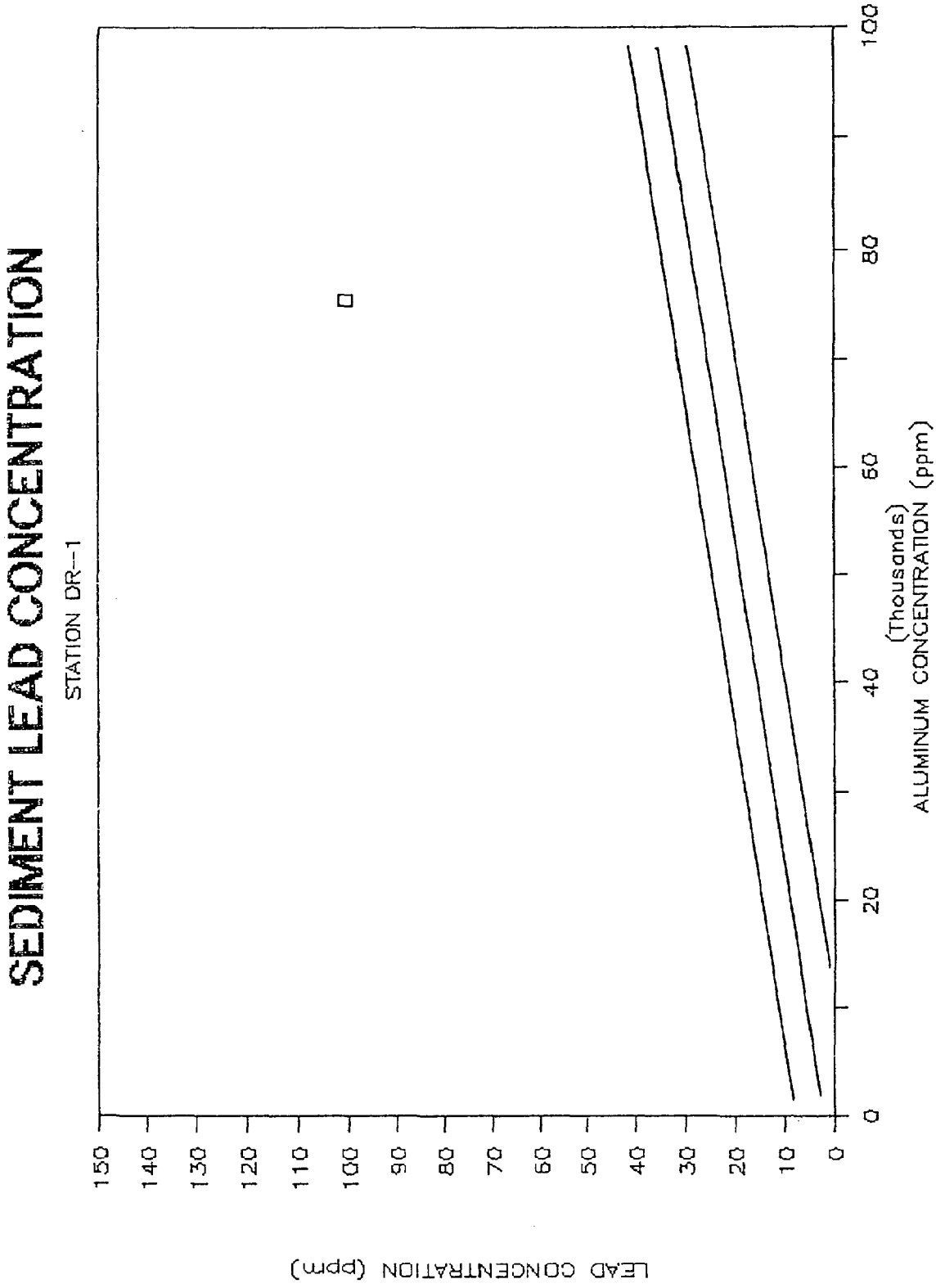
An example of this procedure is as follows. During our sampling we collected sediments from Dog River a tributary of Mobile Bay, this site is referenced to as station DR-1 in the data table and on the map. This stream as located in a extensively developed watershed and receives a considerable amount of stormwater runoff from paved roads, parking lots and other urban non-point sources. The site where sample DR-1 was collected is also a popular recreational area with a high density of boat traffic. Consequently this location has been subjected to years of exposure from emissions from boat motors and motor vehicles. Consultation of the data in Table 2 reveals this site to also be the one with the highest lead concentration of all sites sampled.

With this in mind site DR-1 was deleted from the clean data set and was chosen as a test case for evaluation of possible enrichment with lead. The value for lead at this location was then plotted on a graph of the lead/aluminum relationship. This example is illustrated in Figure 2 and shows the lead concentration to be well above the upper prediction limit. From this, it is reasonably certain to conclude that the sediments at this site are enriched with lead. This information along with knowledge of the geology and land use practices of the drainage basin would appear to indicate that exhaust emissions from internal combustion engines are the likely source of enrichment. Of course this preliminary assessment should be followed up with a more extensive survey of sediments in the river basin.

Although this method appears to be a useful tool for identifying areas of enriched sediments the author offers the following caveat so as to minimize the chance of misinterpretation of data. Points lying on or just above the upper prediction limit should be evaluated with caution. Such judgements are best made when assisted by analyses of samples from nearby stations and ancillary data such as proximity and nature of wastewater discharges and/or non-point sources. Also, the necesscity for utilizing the mean value of the analyses of duplicate or triplicate samples cannot be emphasied too strongly. Widely varying results for replicate samples from a station may be an indication of errors in the digestion and analytical procedures. Additionally, an effective laboratory Q&A program is invaluable for obtaining reliable results and if possible should incorporate certified reference sediments such as those available from the National Institute of Standards and Technology.

Figure 2

Sediment lead at Station DR-1



CONCLUSION

The results of this study appear to have established the existence of statistically significant relationships between aluminum and eight of the nine metals analyzed in "clean" sediments from Alabama estuaries. The relationships are defined by the regression lines for each metal vs aluminum, estimates of the ranges of values to be expected from samples of clean sediments in Alabama are given by the prediction limits. The regression lines and prediction limits of the "clean" data set can be used to identify unnatural concentrations of metals in sediments from Alabama estuaries.

This technique will be applied in the near future to a survey of shipyards in coastal Alabama. The objective of this study will be the evaluation of metals enrichment of sediments in and around shipbuilding facilities. These results are to be reported in a forthcoming document.

REFERENCES

Filliben, J.J. 1975. The probability plot correletion coefficient test for normality. Technometrics 17: 111-117.

Duce, R.A.; G.L. Hoffman; B.J. Ray; I.S. Fletcher; P.R. Walsh; E.J. Hoffman; J.M. Miller; J.L. Heffter; G.T. Wallace; J.L. Fasching and S.R. Pitrowicz. 1976. In: Marine Pollutant Transfer, Heath and Co., Lexington, MA. p 77.

Florida Department of Environmental Regulation, Coastal Zone Management Section. 1991. Results of intercalibration exercise for sediment metal analyses, draft report. FDER, Tallahassee, FL. 19 pp.

Goldberg, E.D., J.J. Griffin, V. Hodge, M. Kolde, and H. Windom. 1979. Pollution history of the Savannah River estuary. Environmental Science and Technology. 13: 588-594.

Isphording, W.C., and G.M. Lamb. 1985. Sedimentation, dispersal and partitioning of trace metals in coastal Mississippi-Alabama estuarine sediments. Mississippi-Alabama Sea Grant Consortium Project No. R/ER-4. 29 pp.

Isphording. W.C., and G.C. Flowers. 1987. Mobile Bay: The right estuary in the wrong place. In T.A. Lowery (ed.), Symposium on the natural resources of the Mobile Bay estuary. Alabama Sea Grant Extension Service. Sea Grant Publication No. 87-007

Malatino, A.M. 1980. Chemical quality of bottom sediment samples from Mobile Bay, Alabama. Geological Survey of Alabama. GSA Contract No. 80-3052. 23 pp.

Schropp, S.J. and H.L. Windom. 1988. A guide to the interpretation of metal concentrations in estuarine sediments. Florida Department of Environmental Regulation, Tallahassee, Florida. 44 pp w/ appendix.

Sokal, R.R. and F.J. Rohlf. 1969. Biometry: the principles and practice of ststistics in biological research. W.H. Freeman and Company, San Francisco. 776 pp.

Taylor, S.R. 1964. Abundance of chemical elements in the continental crust: a new table. Geochem. Cosmochem. Acta 28: 1273-1286.

Trefey, J.H.; S. Metz and R.P. Trocene. 1985. The decline in lead transport by the Mississippi River. Science 230: 439-441.

Turekian, K.K.; K.H. Wedepohl. 1961. Geol. Soc. Am. Bull. 72: 175-192.

Windom, H.L.; R.G. Smith and C. Rawlinson. 1989. Particulate trace metal composition and flux across the Southeastern U.S. Continental Shelf. Marine Chemistry, 27: 283-297.

Windom, H.L.; S.J. Schropp; F.D. Calder; J.D. Ryan; R.G. Smith; L.C. Burney; F.G. Lewis and C.H. Rawlinson. 1989. Natural trace metal concentrations in coastal marine sediments of the Southeastern United States. Environmental Science and Technology 23: 314-320.

COASTAL PROGRAM

SEDIMENT CHEMISTRY

BASELINE STUDY

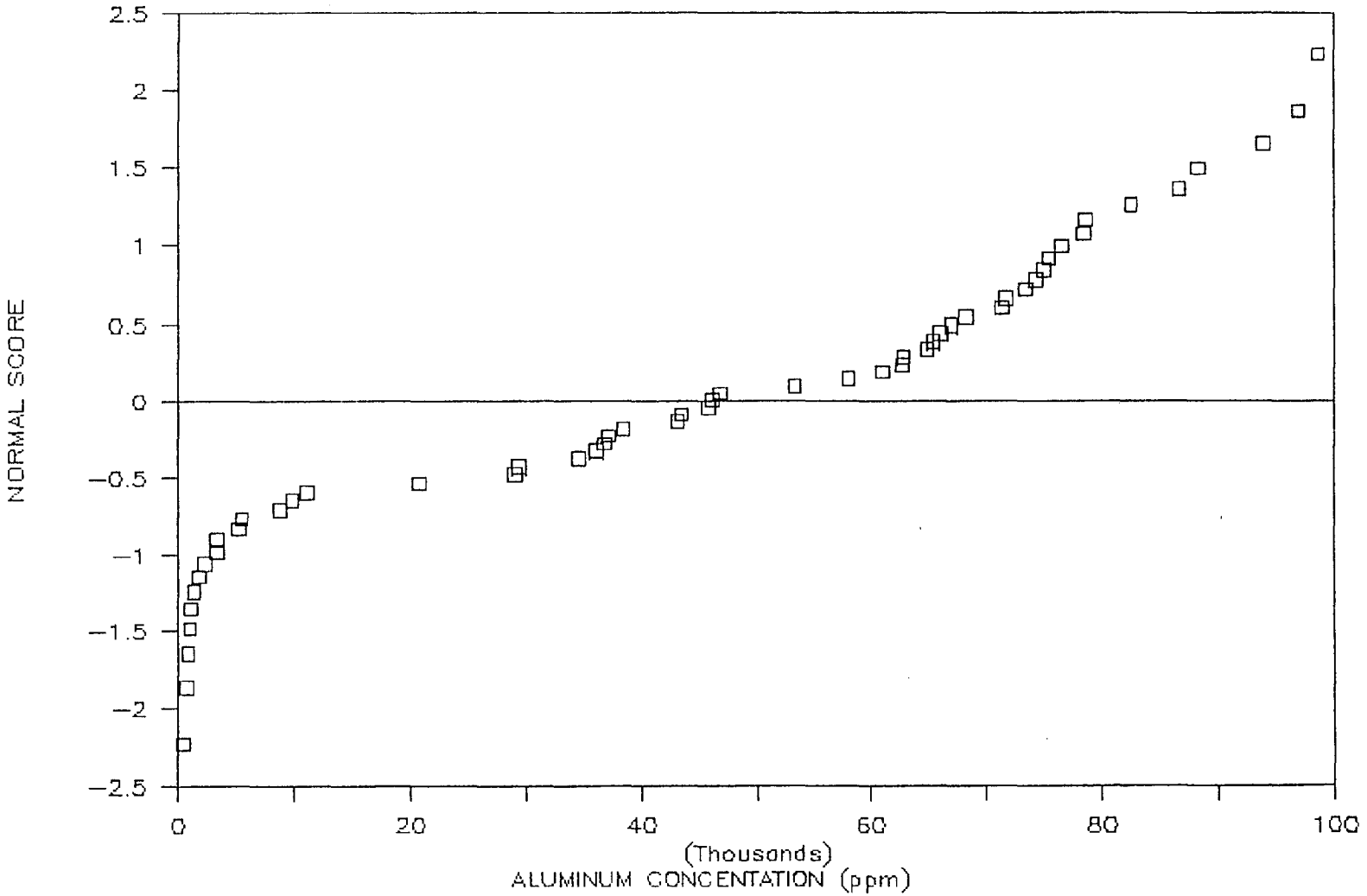
APPENDIX A

NORMAL SCORES

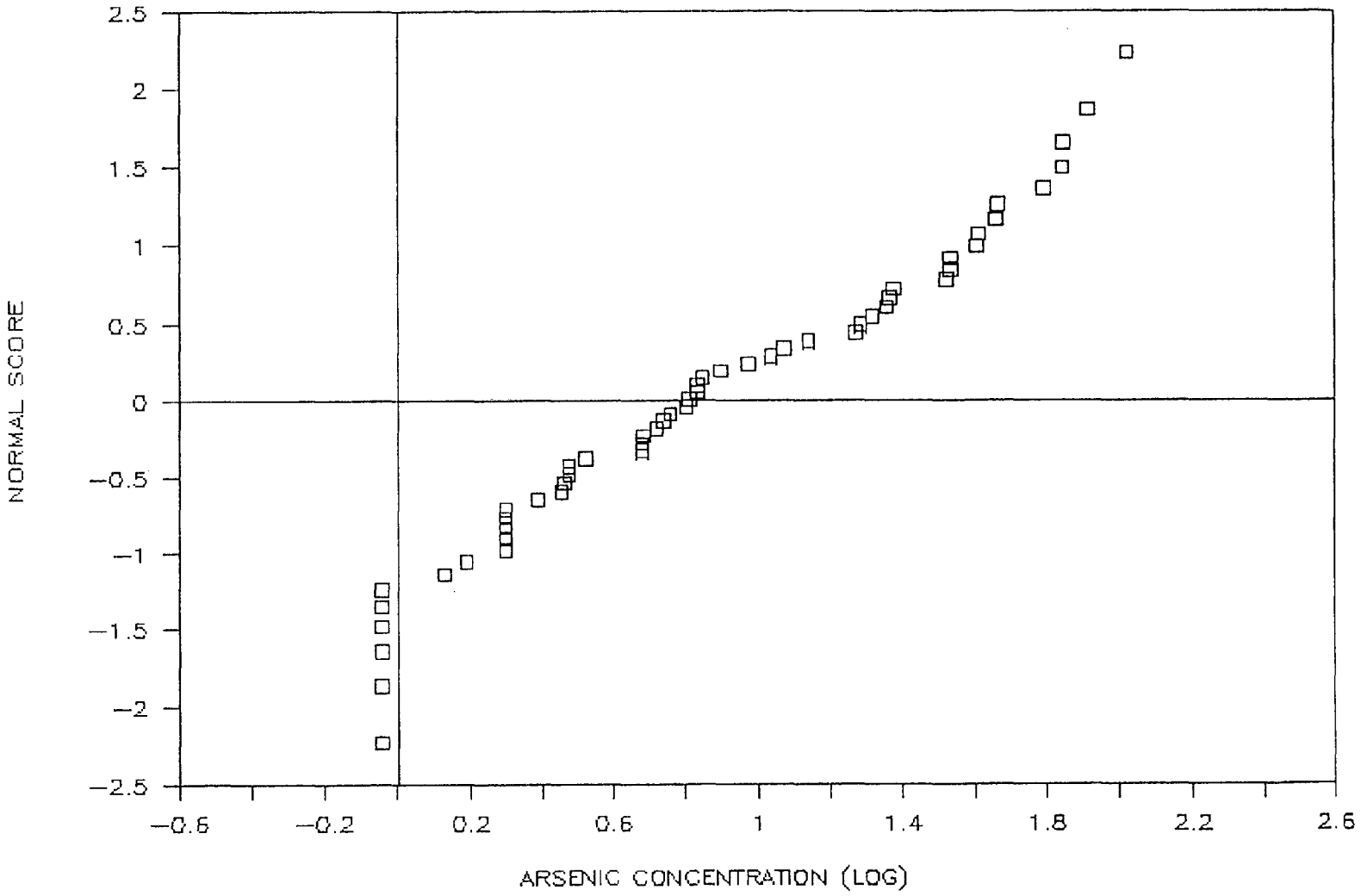
VS

METAL VALUES

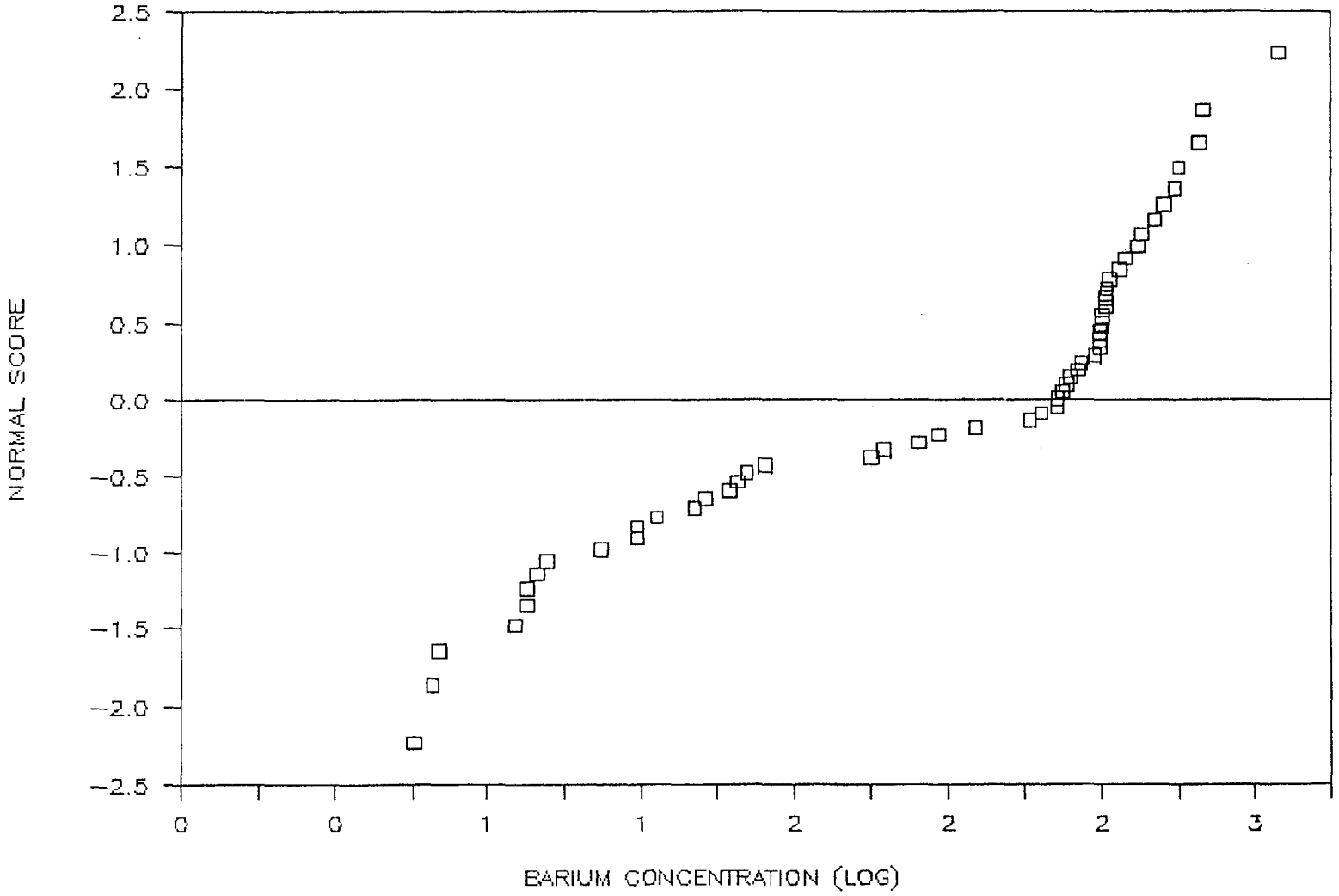
NORMAL SCORE VS ALUMINUM VALUE



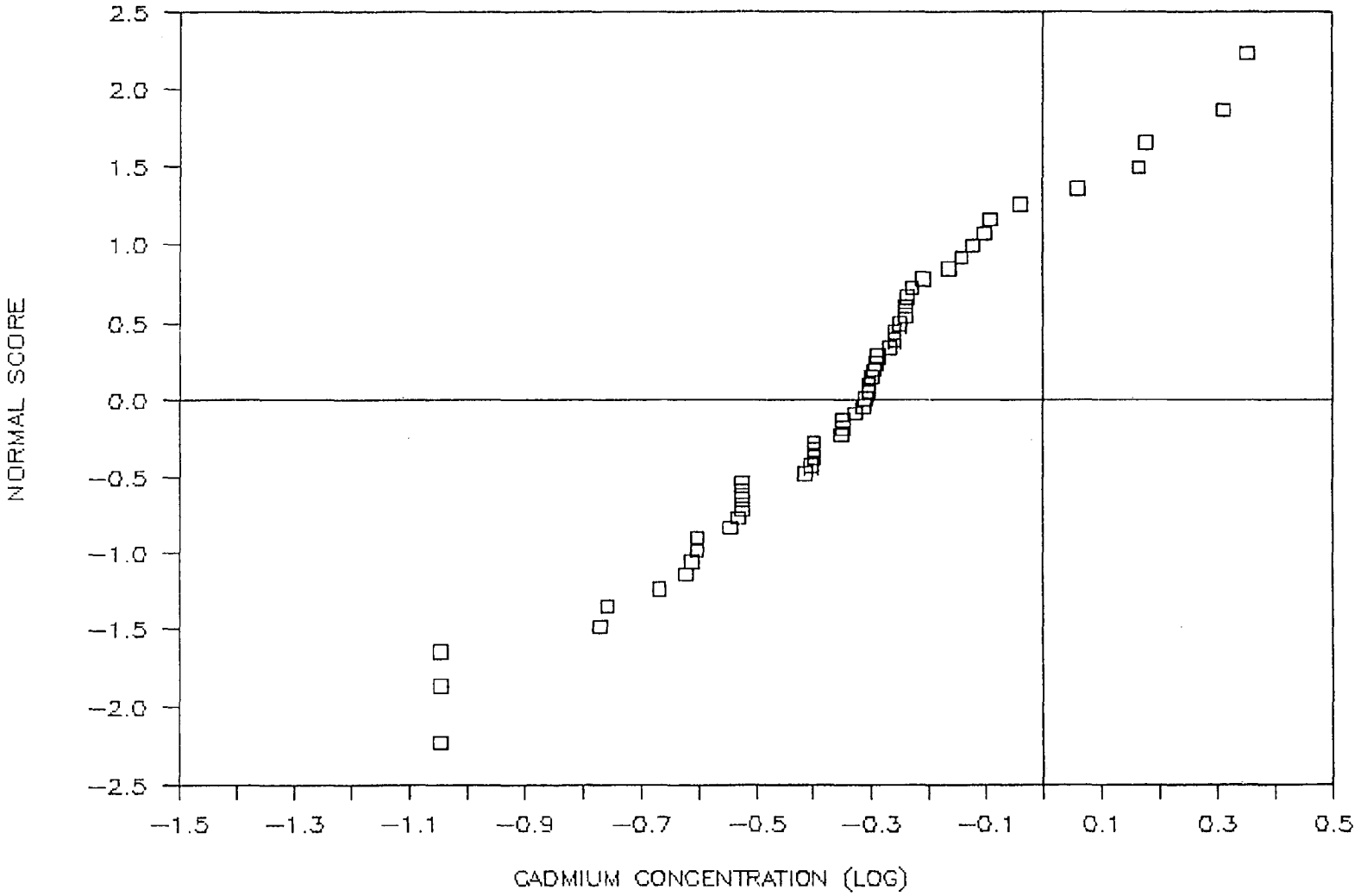
NORMAL SCORE VS ARSENIC VALUE



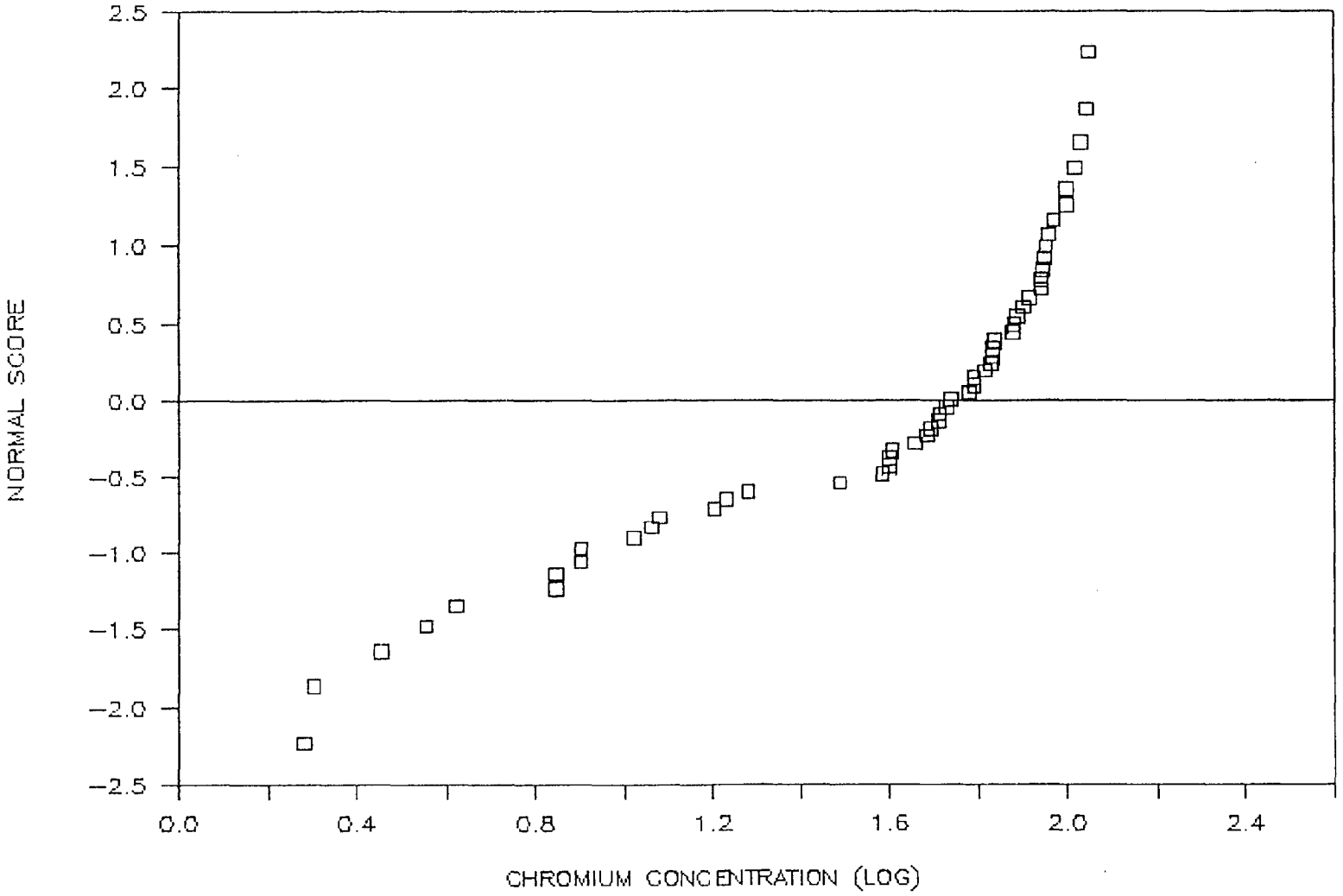
NORMAL SCORE vs BARIUM VALUE



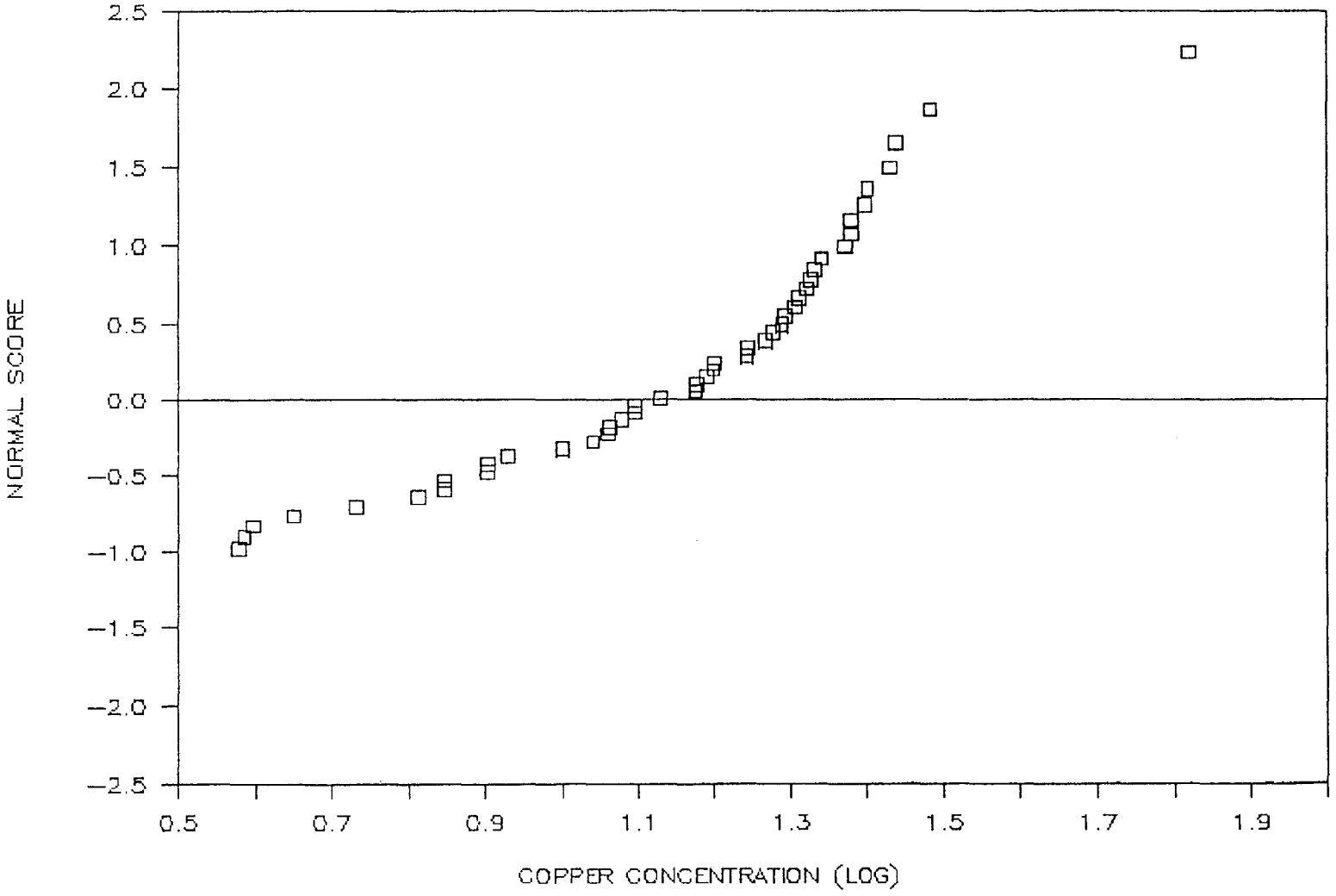
NORMAL SCORE vs CADMIUM VALUE



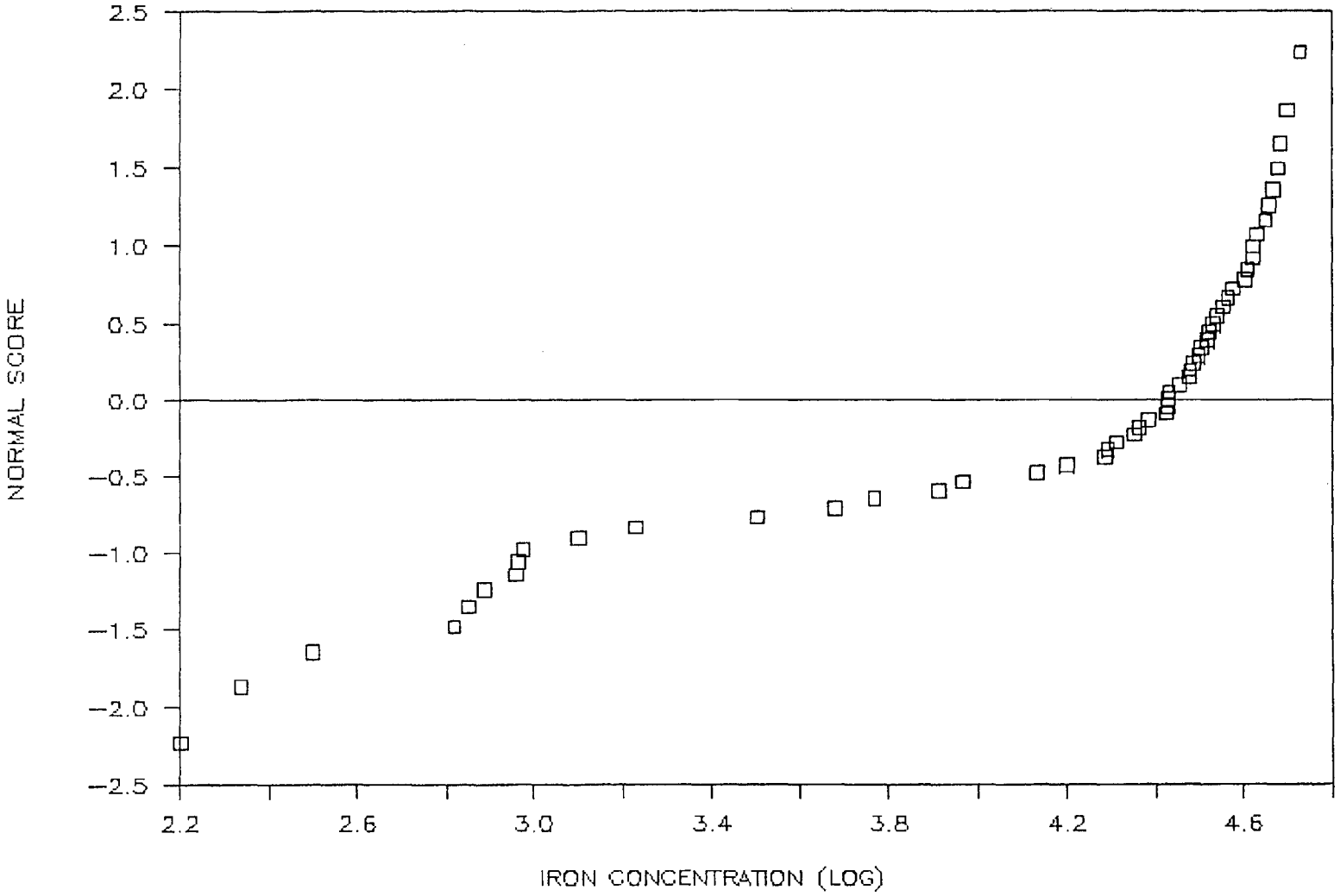
NORMAL SCORE vs CHROMIUM VALUE



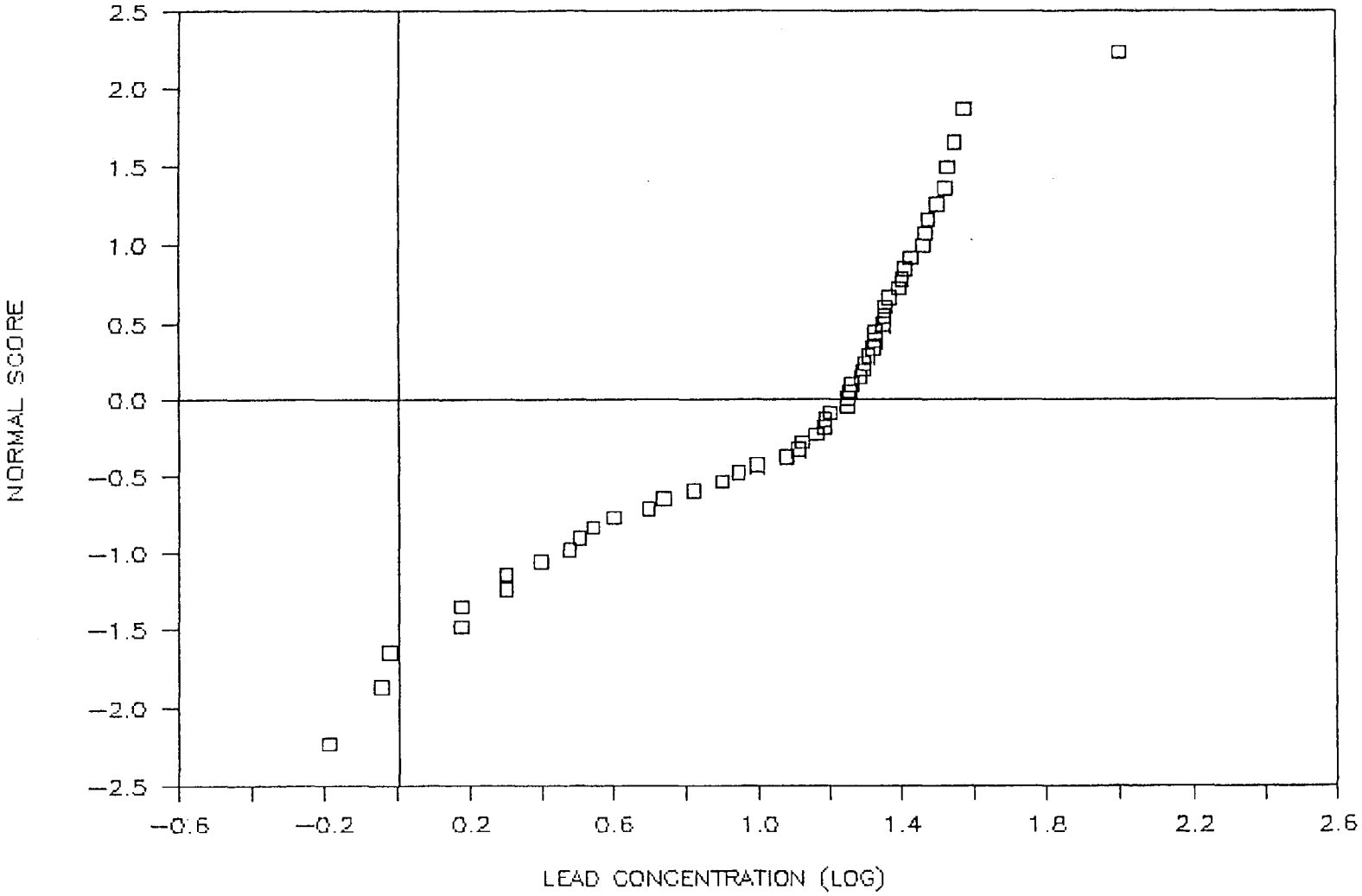
NORMAL SCORE vs COPPER VALUE



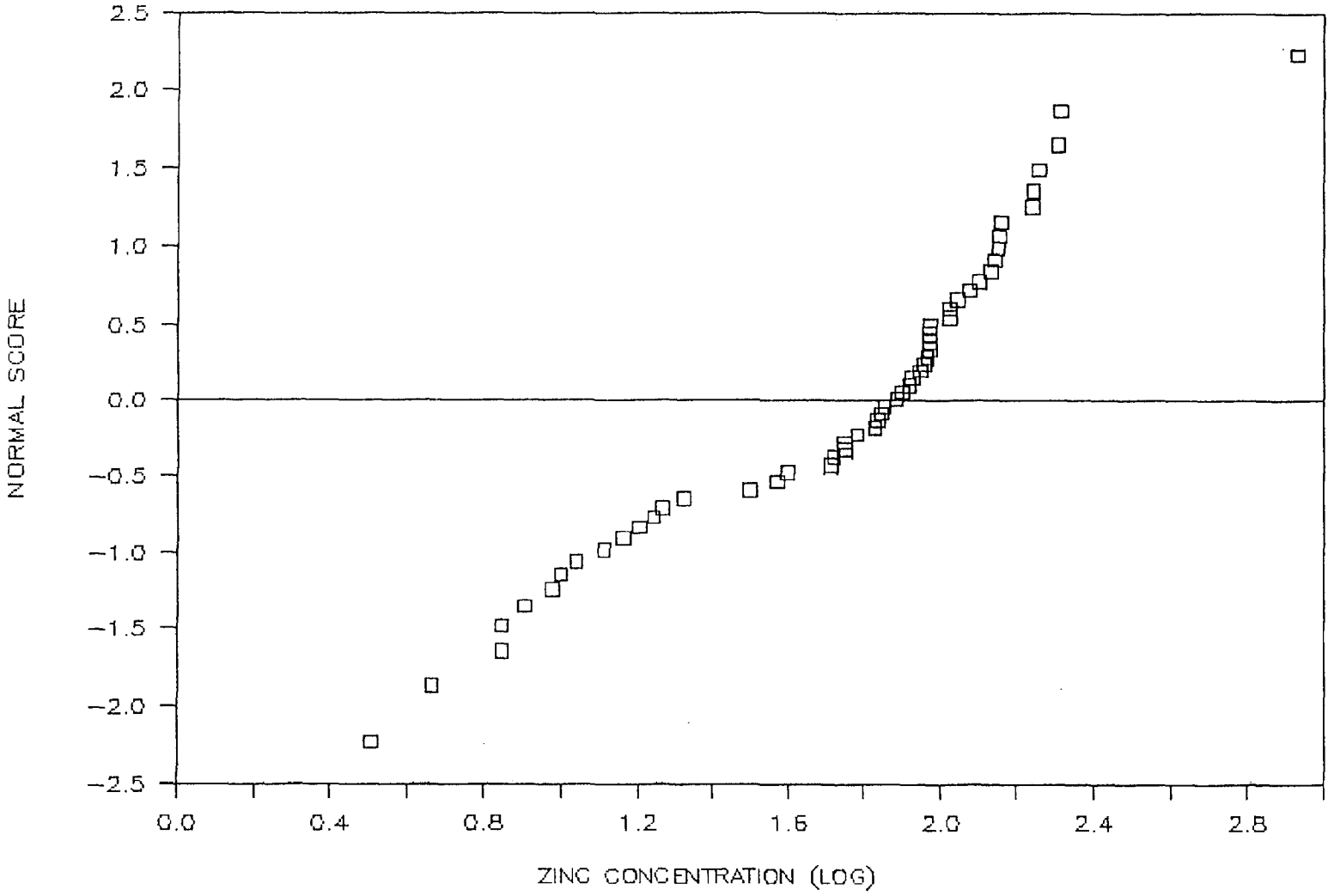
NORMAL SCORE vs IRON VALUE



NORMAL SCORE vs LEAD VALUE



NORMAL SCORE vs ZINC VALUE



COASTAL PROGRAM

SEDIMENT CHEMISTRY

BASELINE STUDY

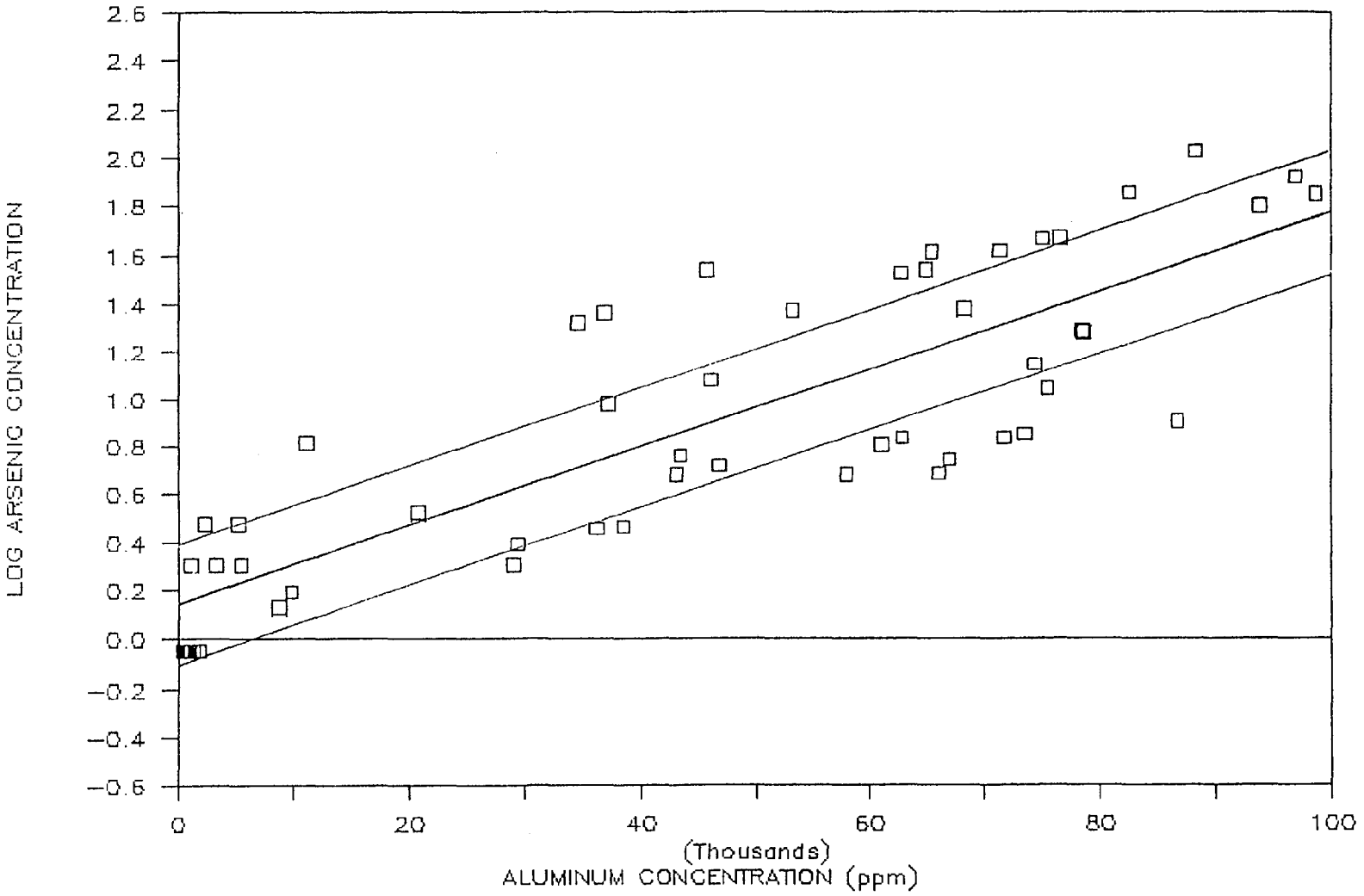
APPENDIX B

METAL VALUES

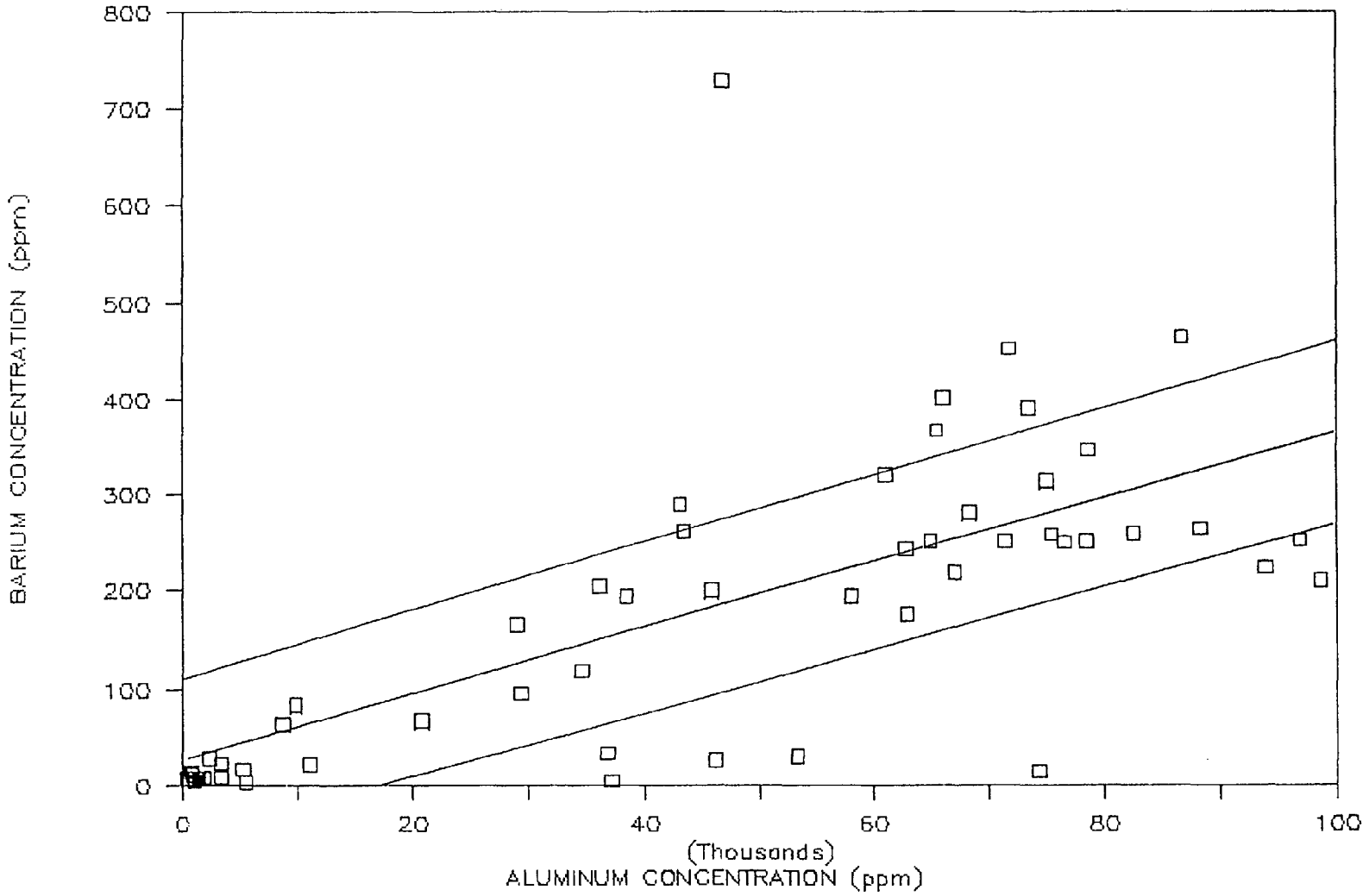
VS

ALUMINUM VALUES

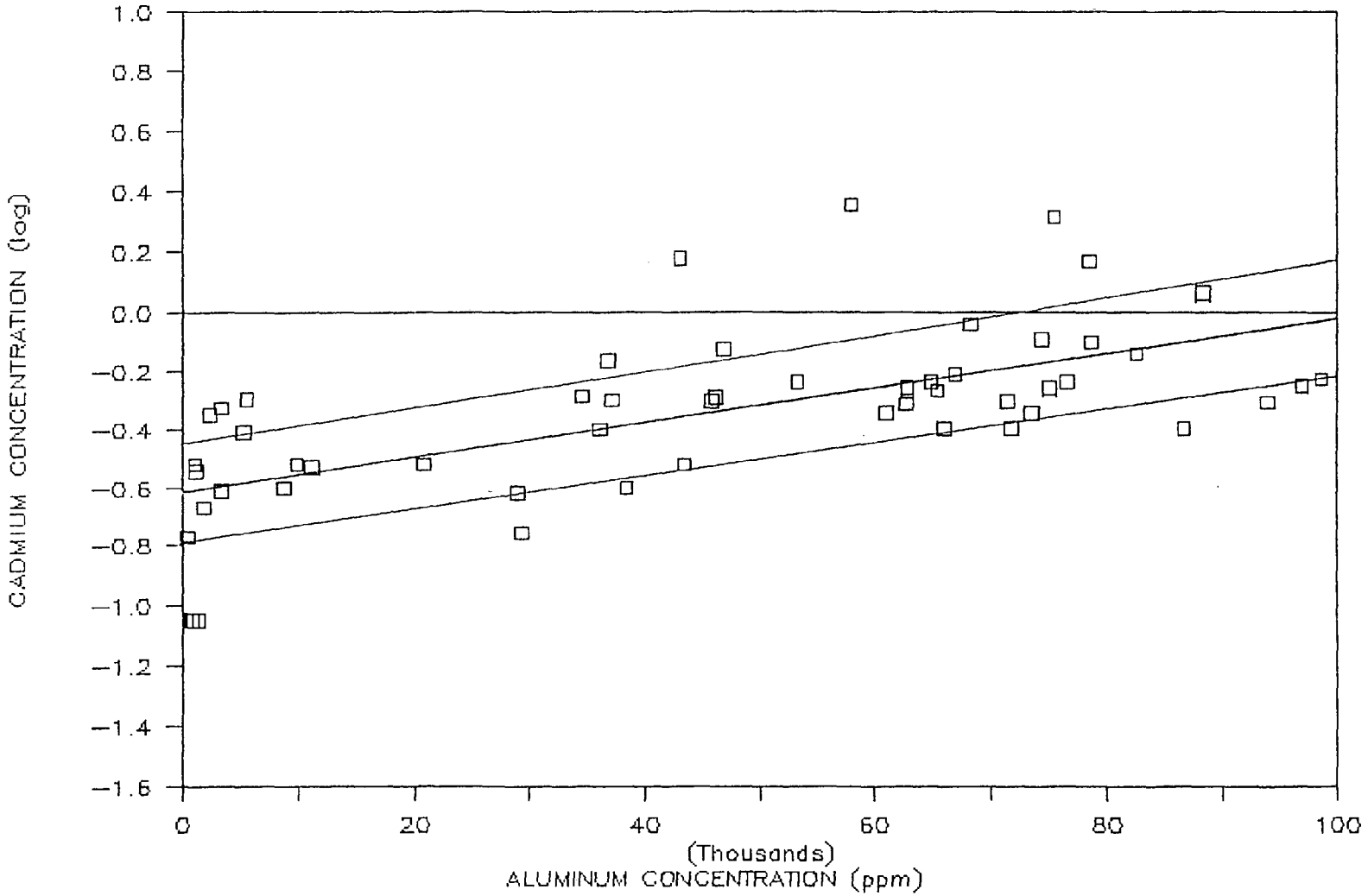
LOG ARSENIC / ALUMINUM



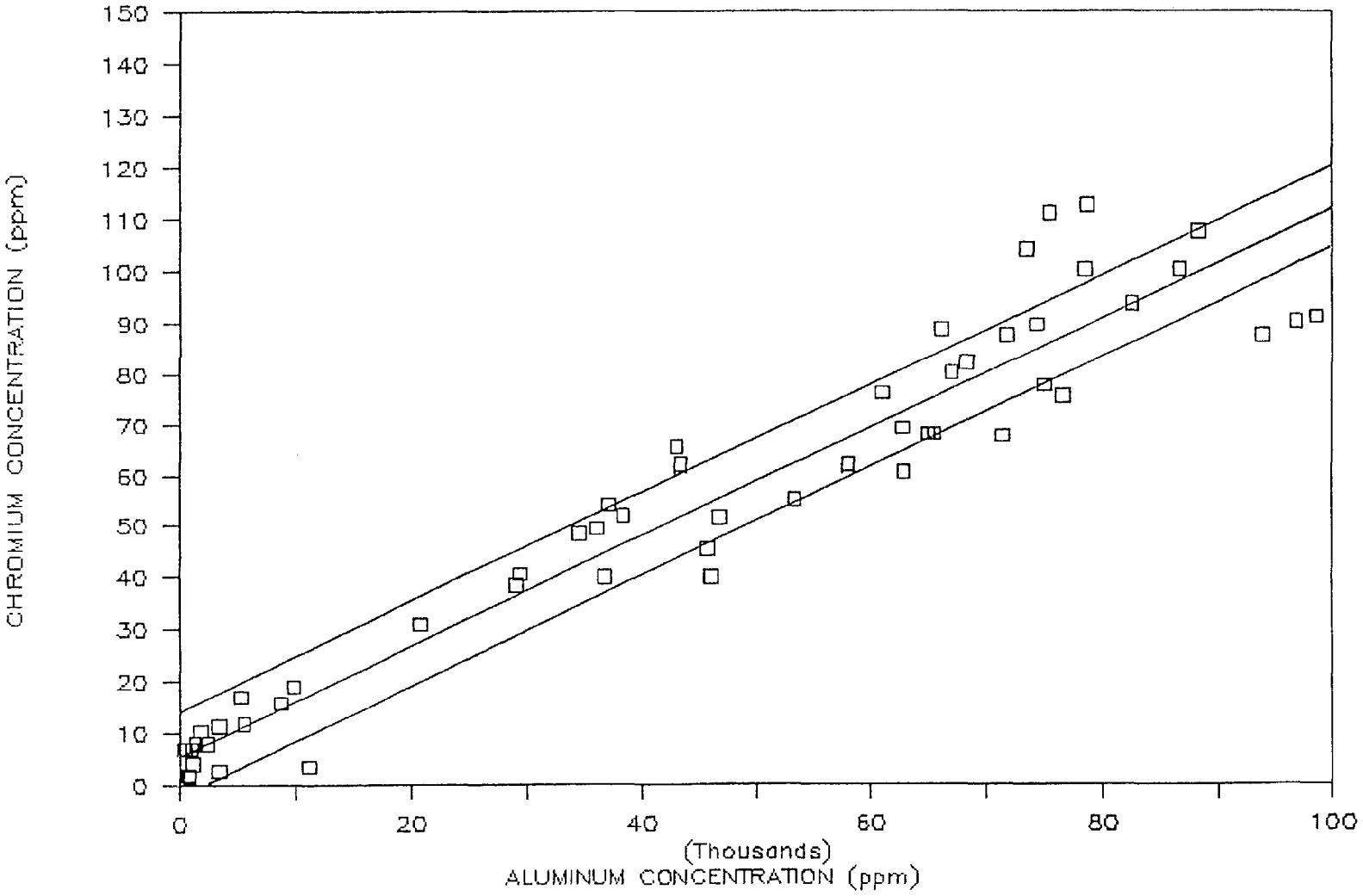
BARIUM / ALUMINUM



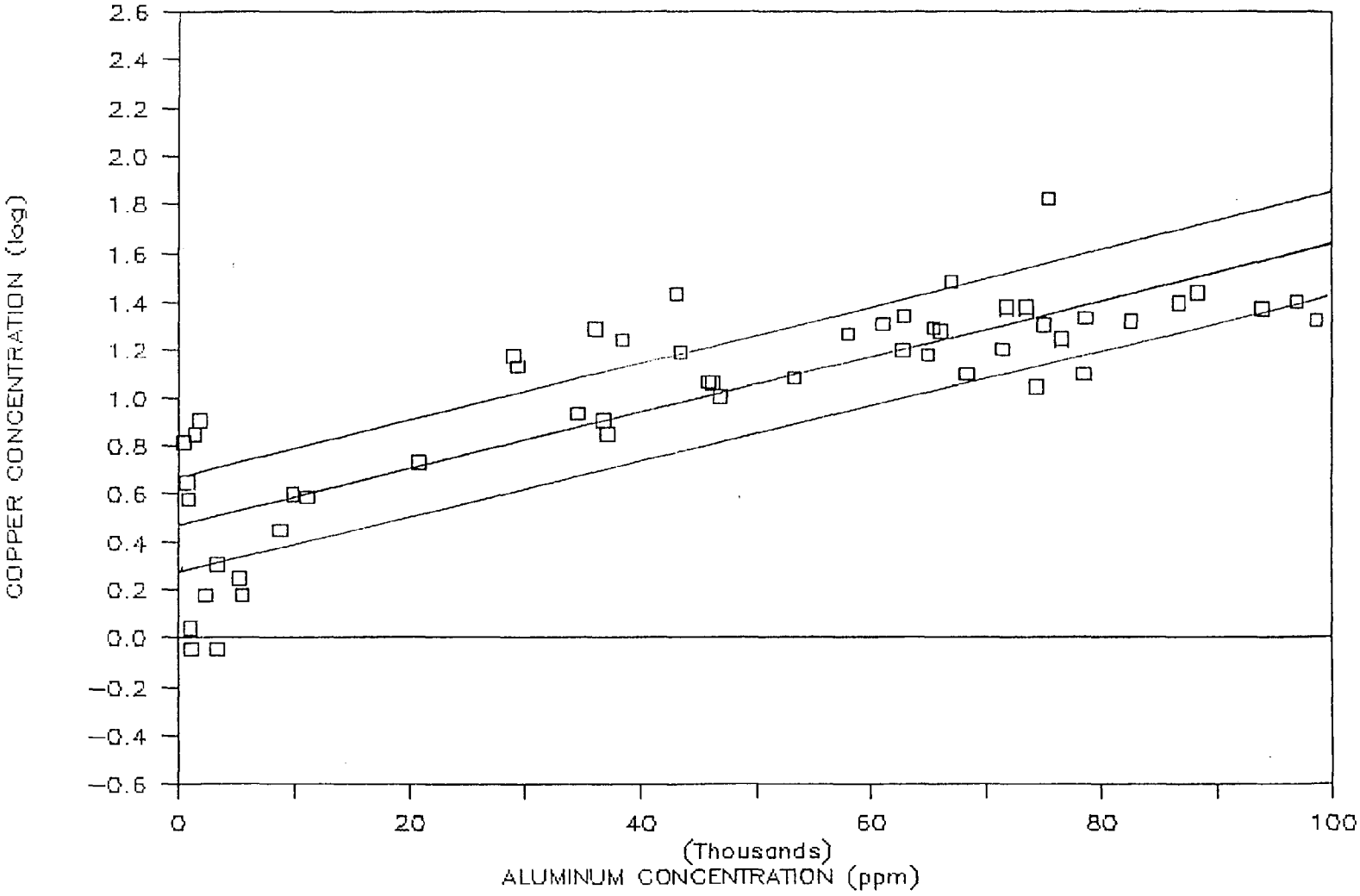
LOG CADMIUM / ALUMINUM



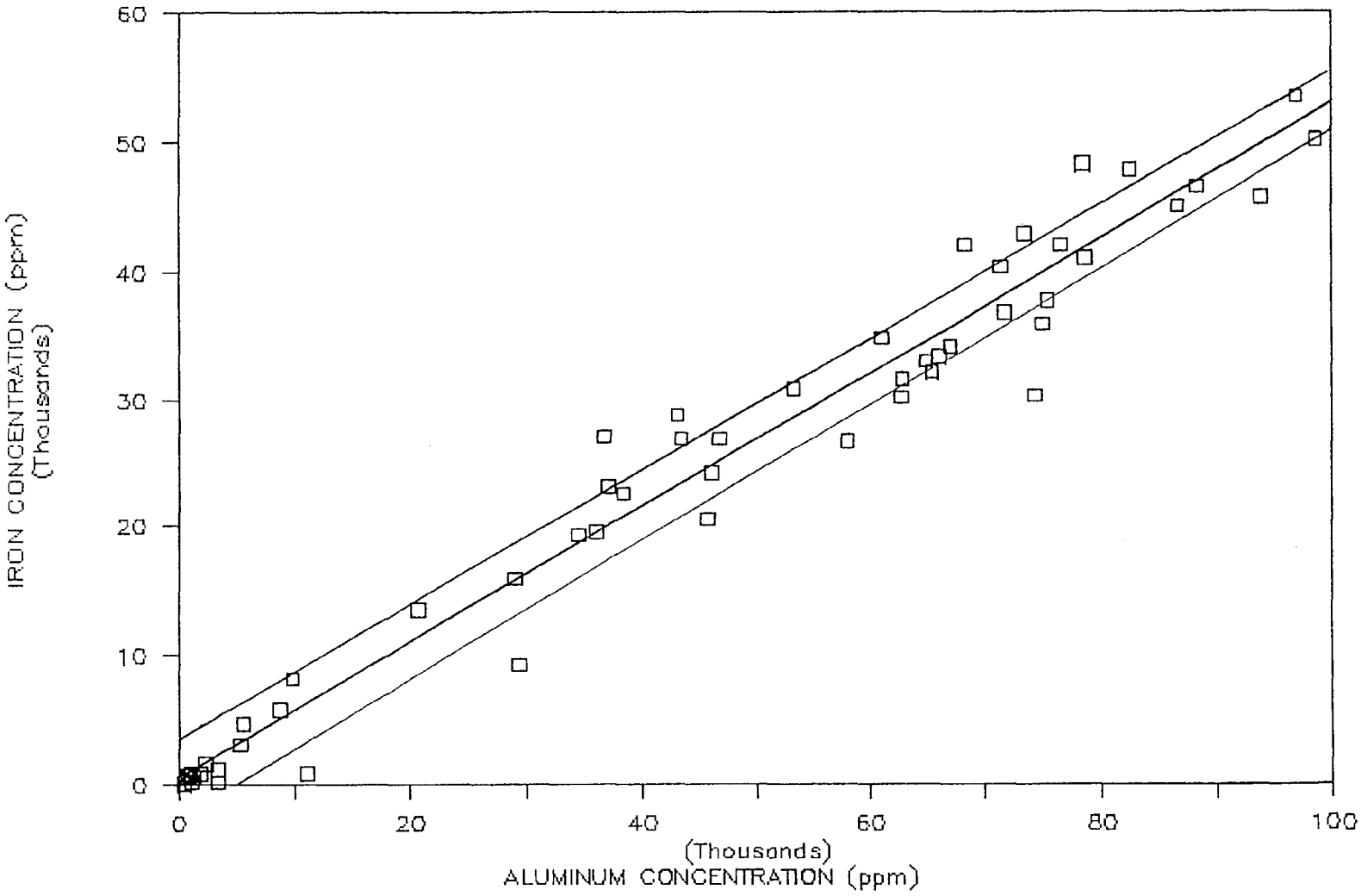
CHROMIUM / ALUMINUM



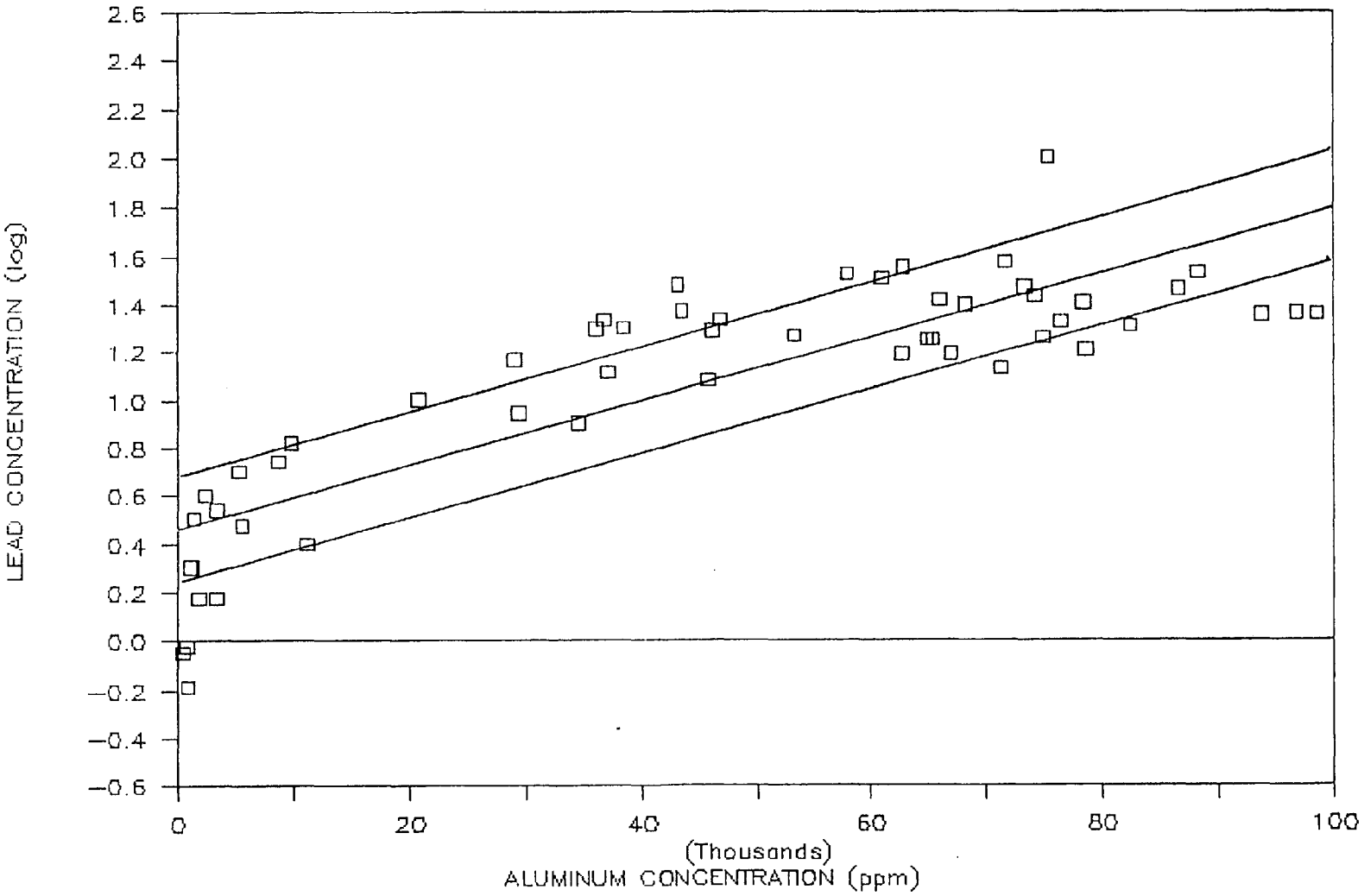
LOG COPPER / ALUMINUM



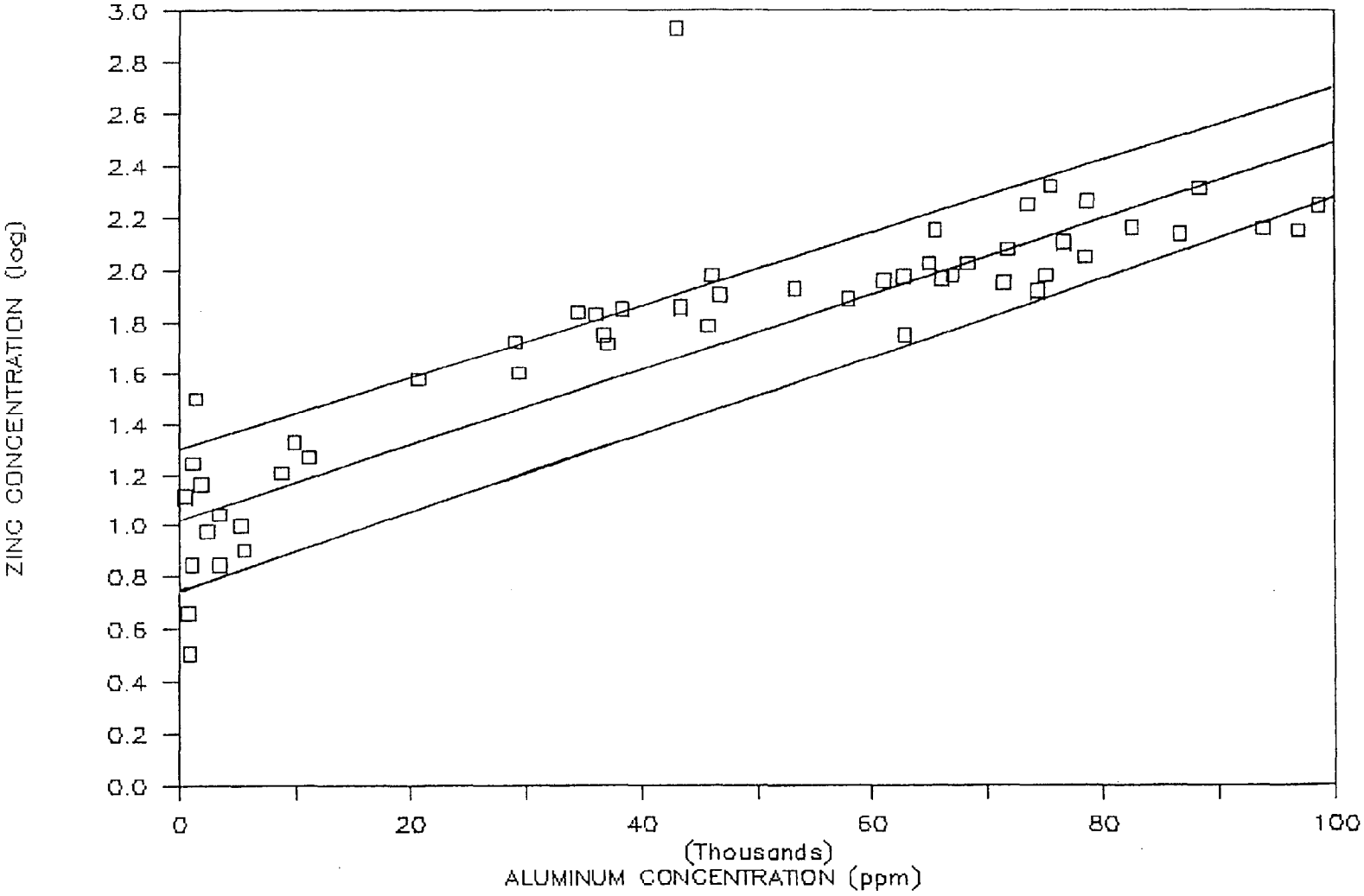
IRON / ALUMINUM



LOG LEAD / ALUMINUM



LOG ZINC / ALUMINUM



COASTAL PROGRAM

SEDIMENT CHEMISTRY

BASELINE STUDY

APPENDIX C

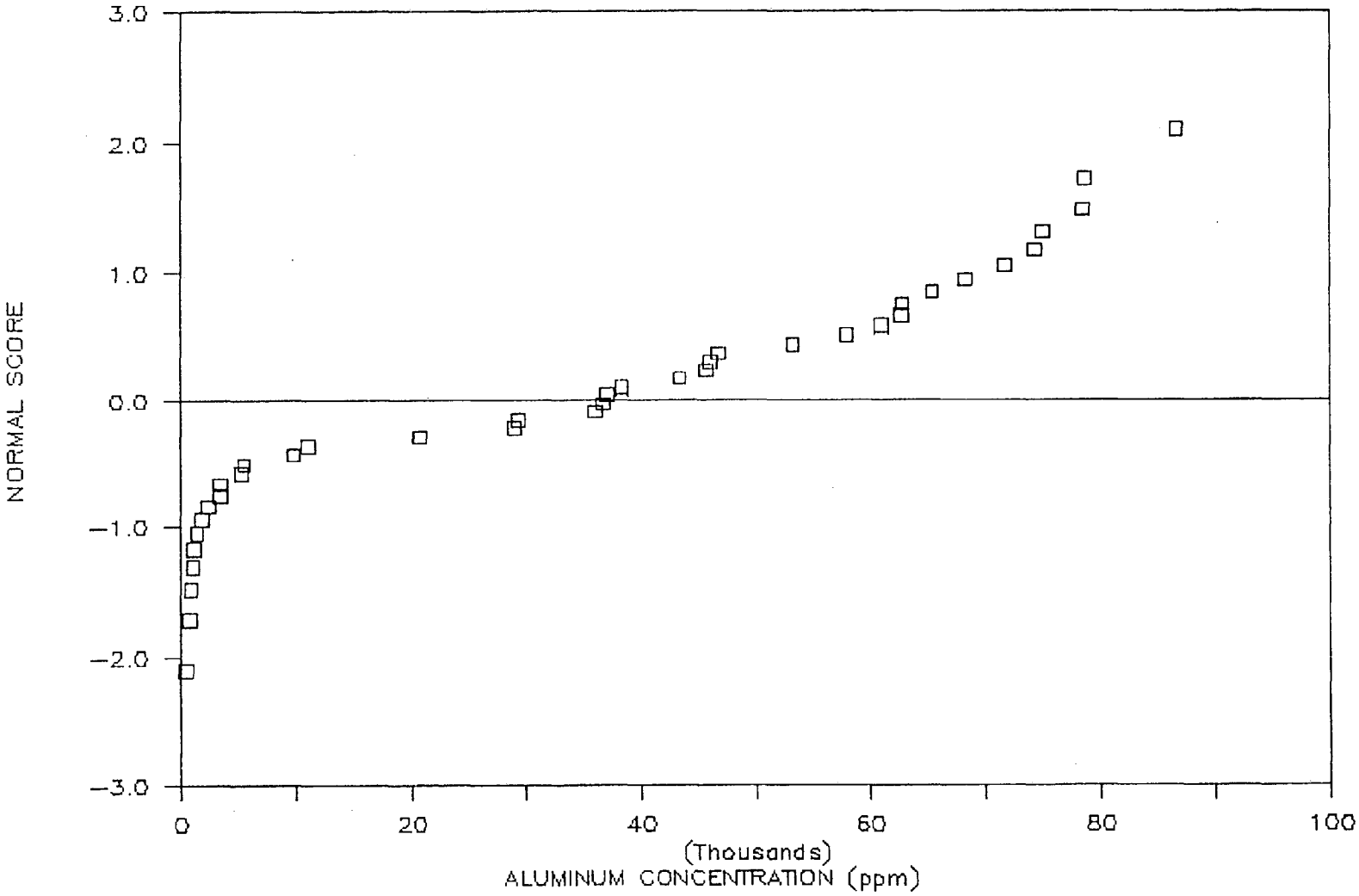
NORMAL SCORES

VS

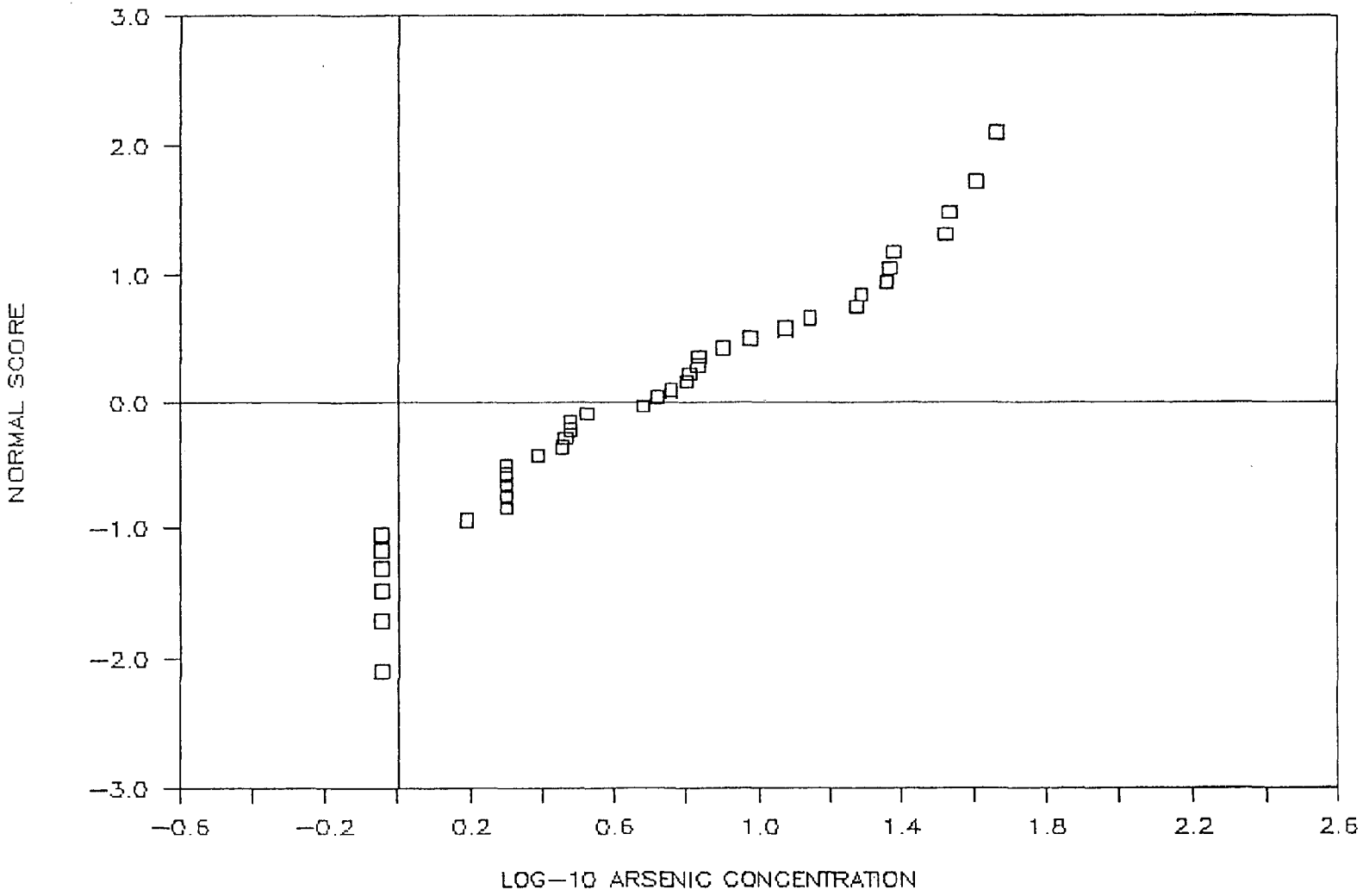
METAL VALUES

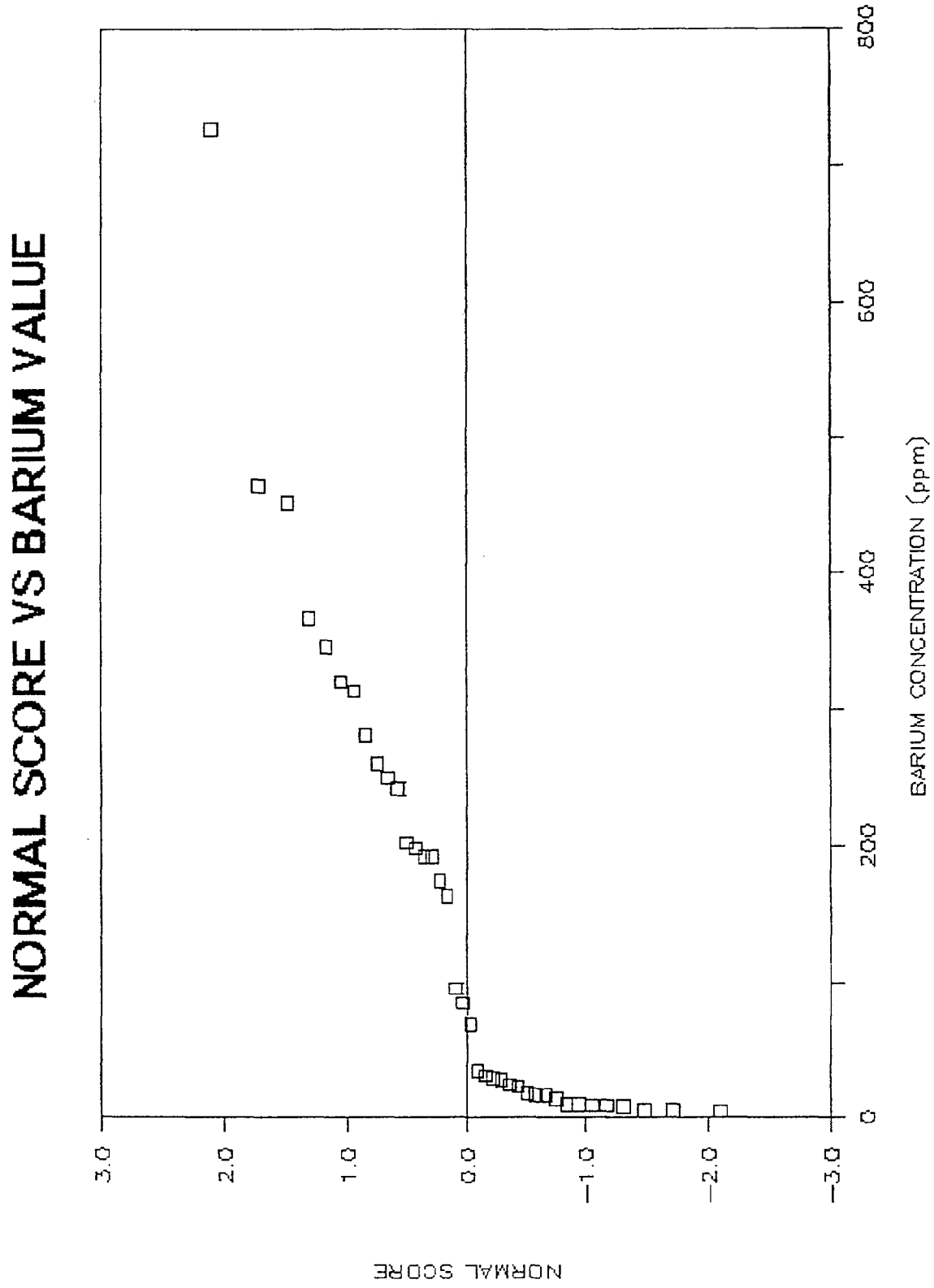
"CLEAN" DATA

NORMAL SCORE VS ALUMINUM VALUE

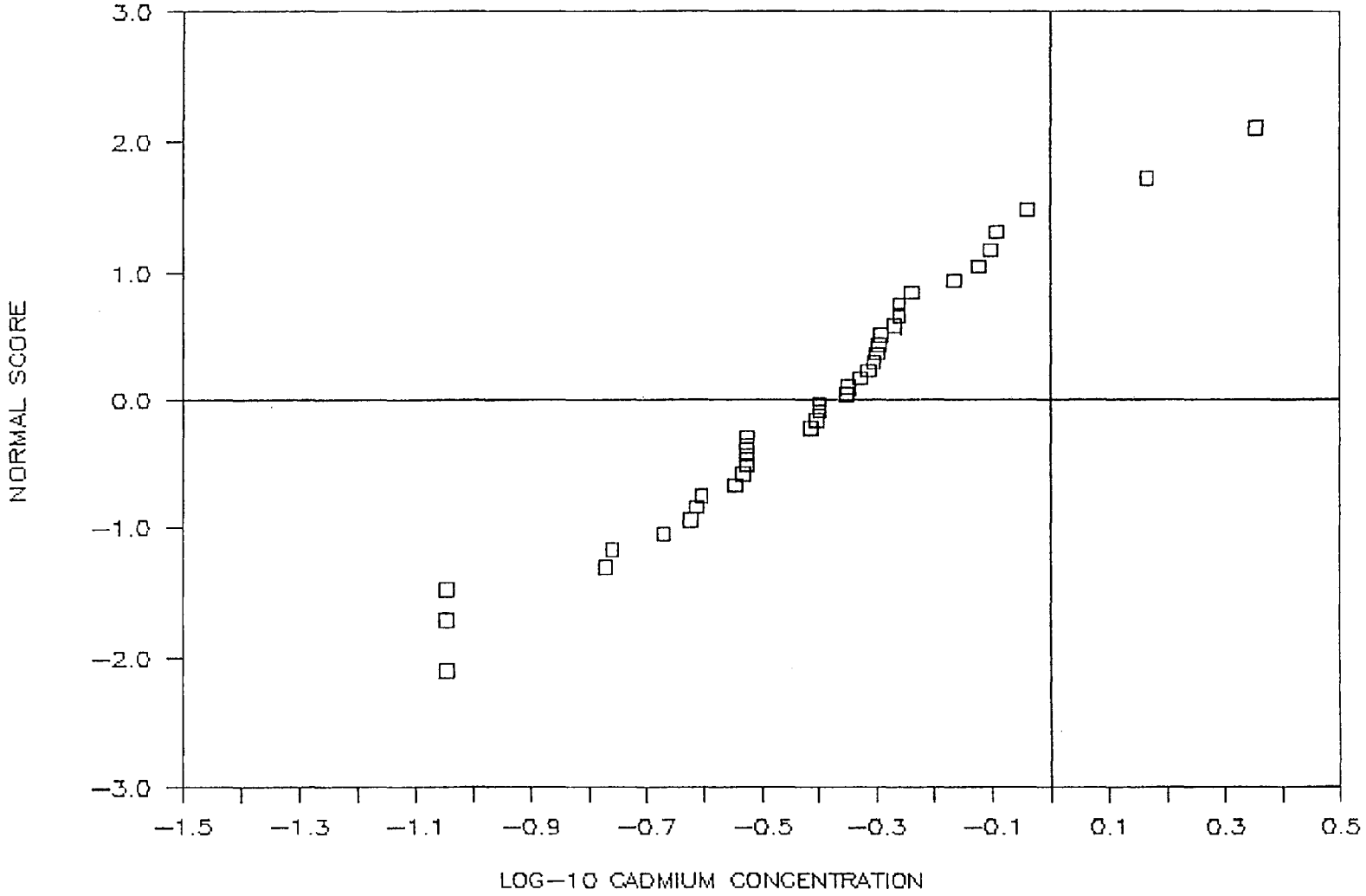


NORMAL SCORE VS ARSENIC VALUE

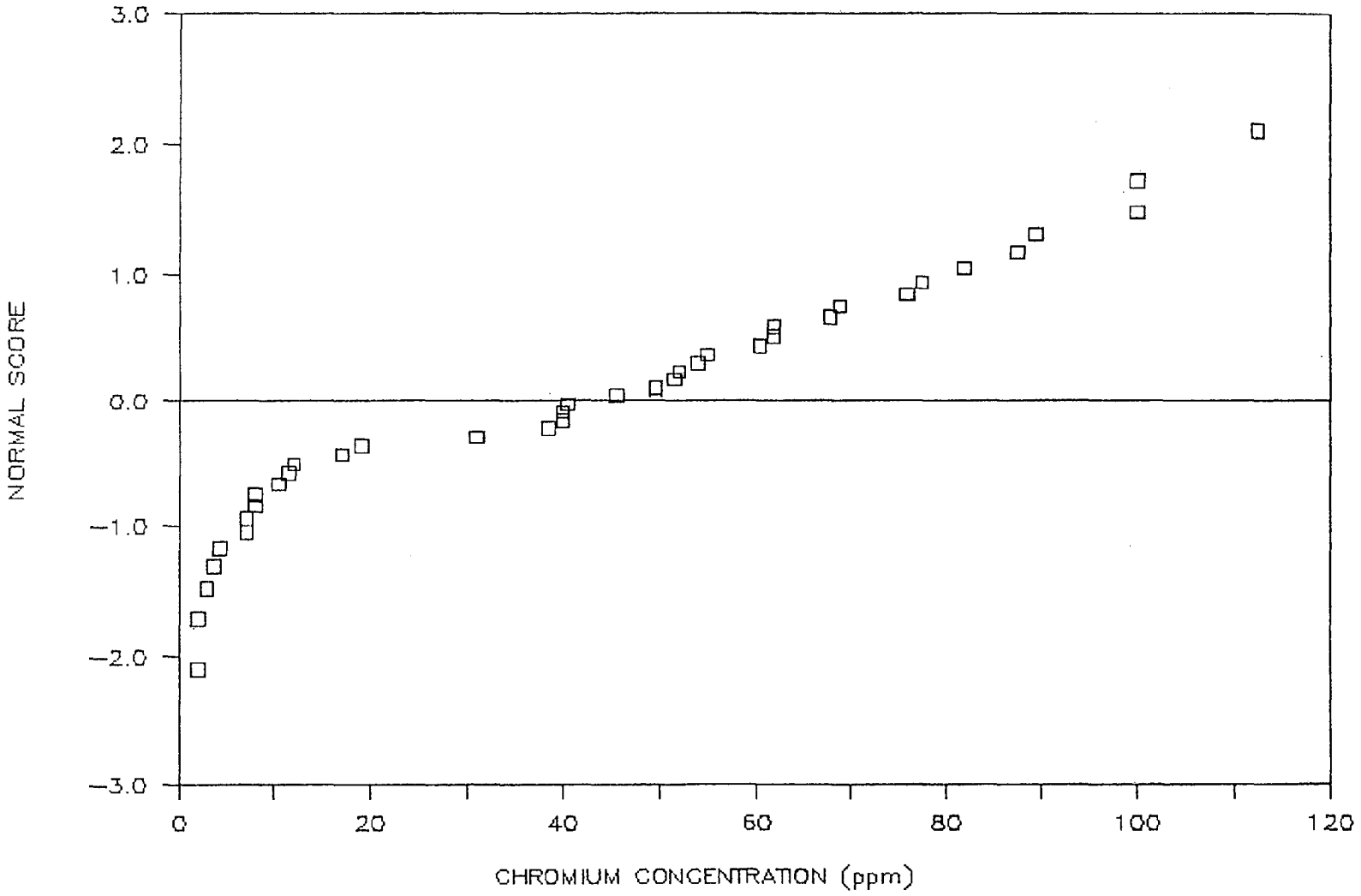



NORMAL SCORE VS BARIUM VALUE
NORMAL SCORE
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
0
200
400
600
800
BARIUM CONCENTRATION (ppm)

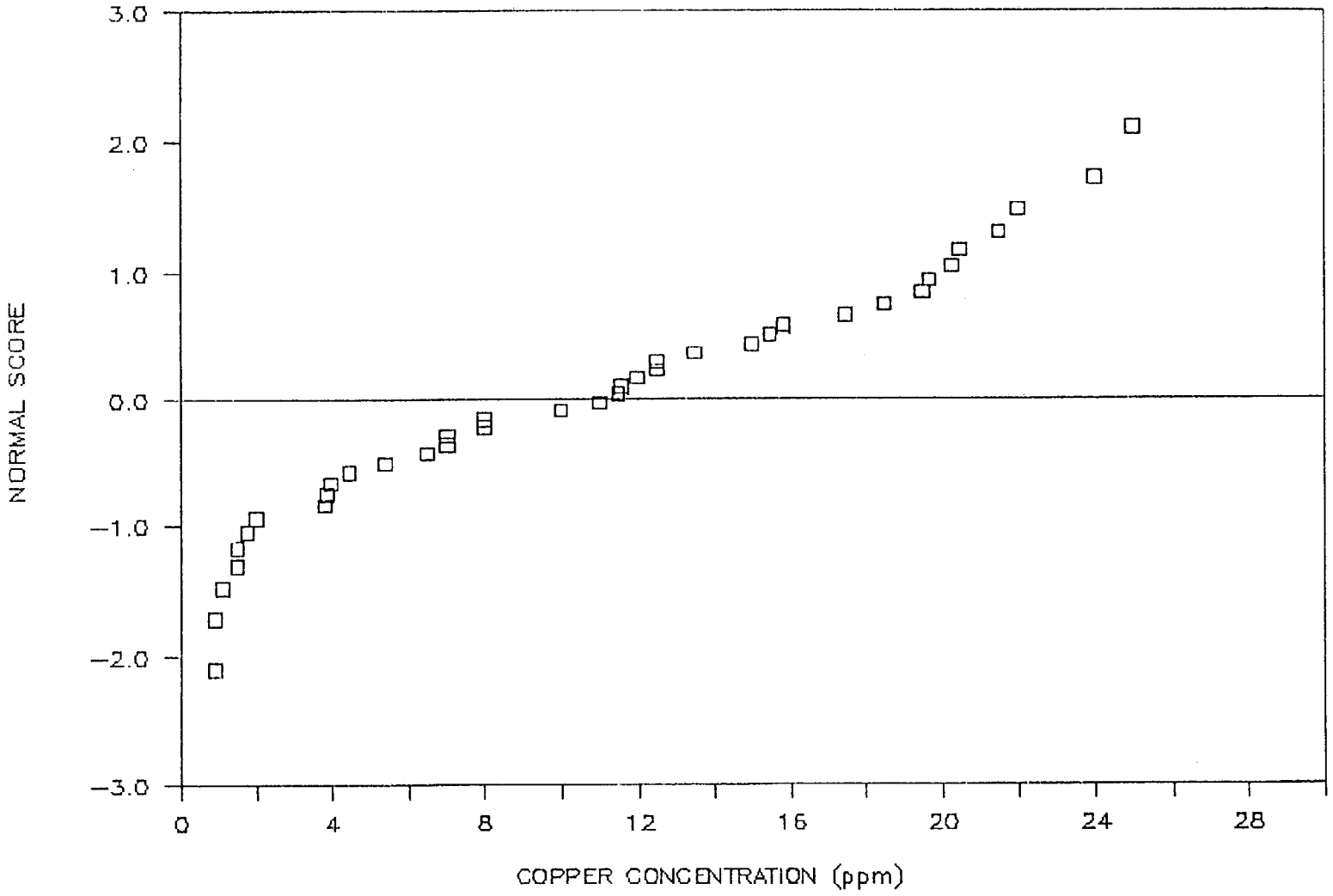
NORMAL SCORE VS CADMIUM VALUE



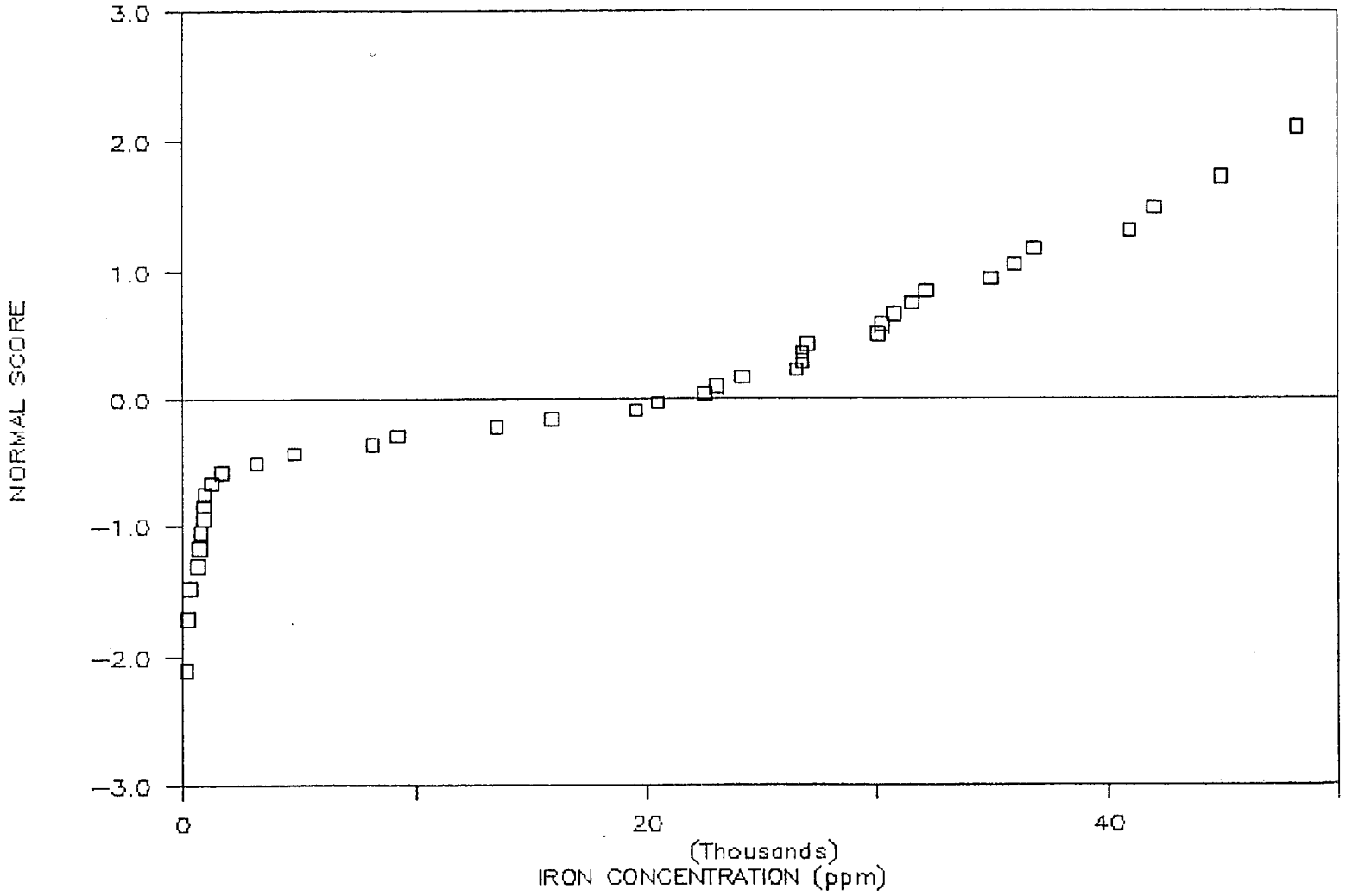
NORMAL SCORE VS CHROMIUM VALUE



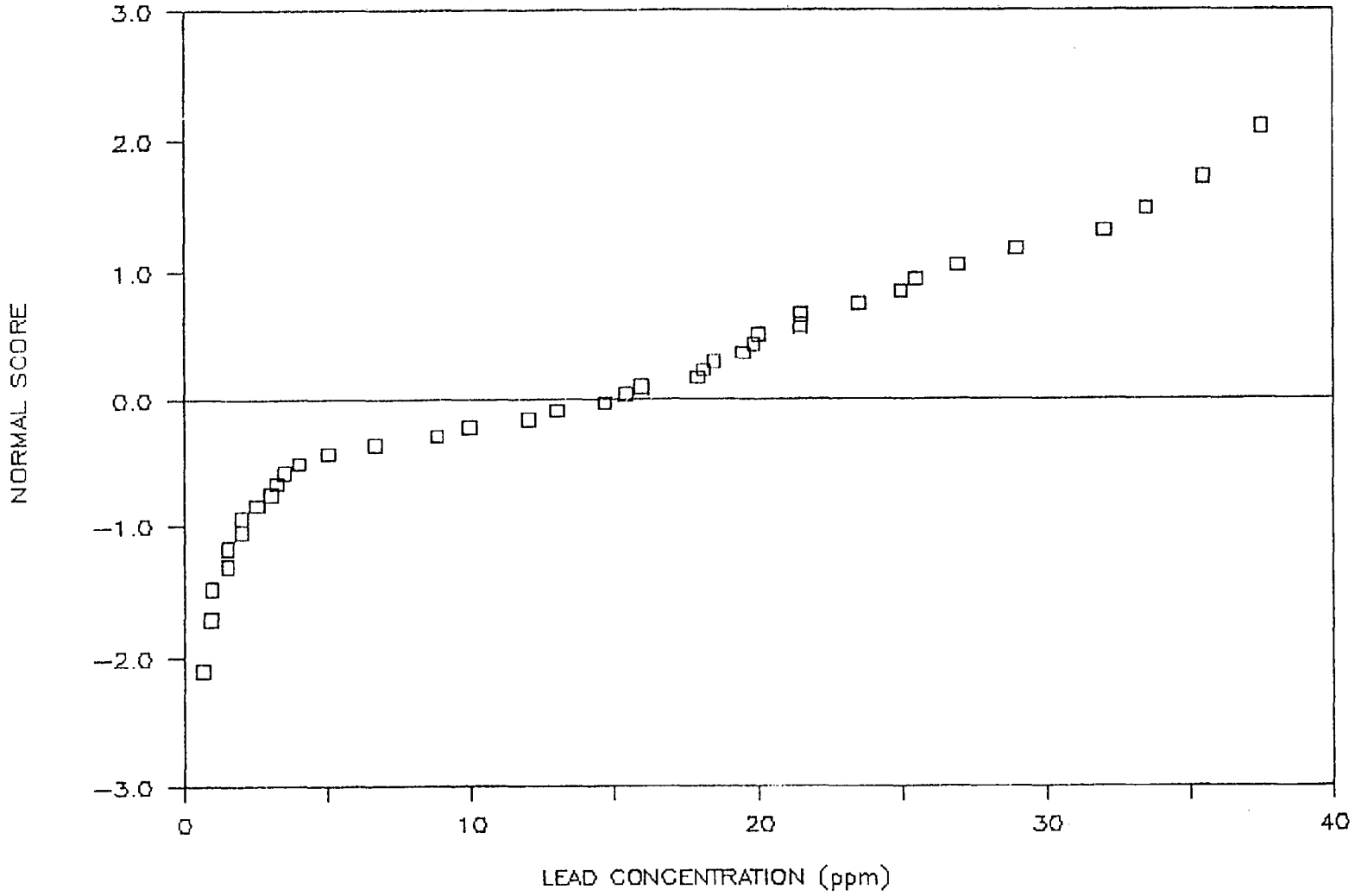
NORMAL SCORE VS COPPER VALUE

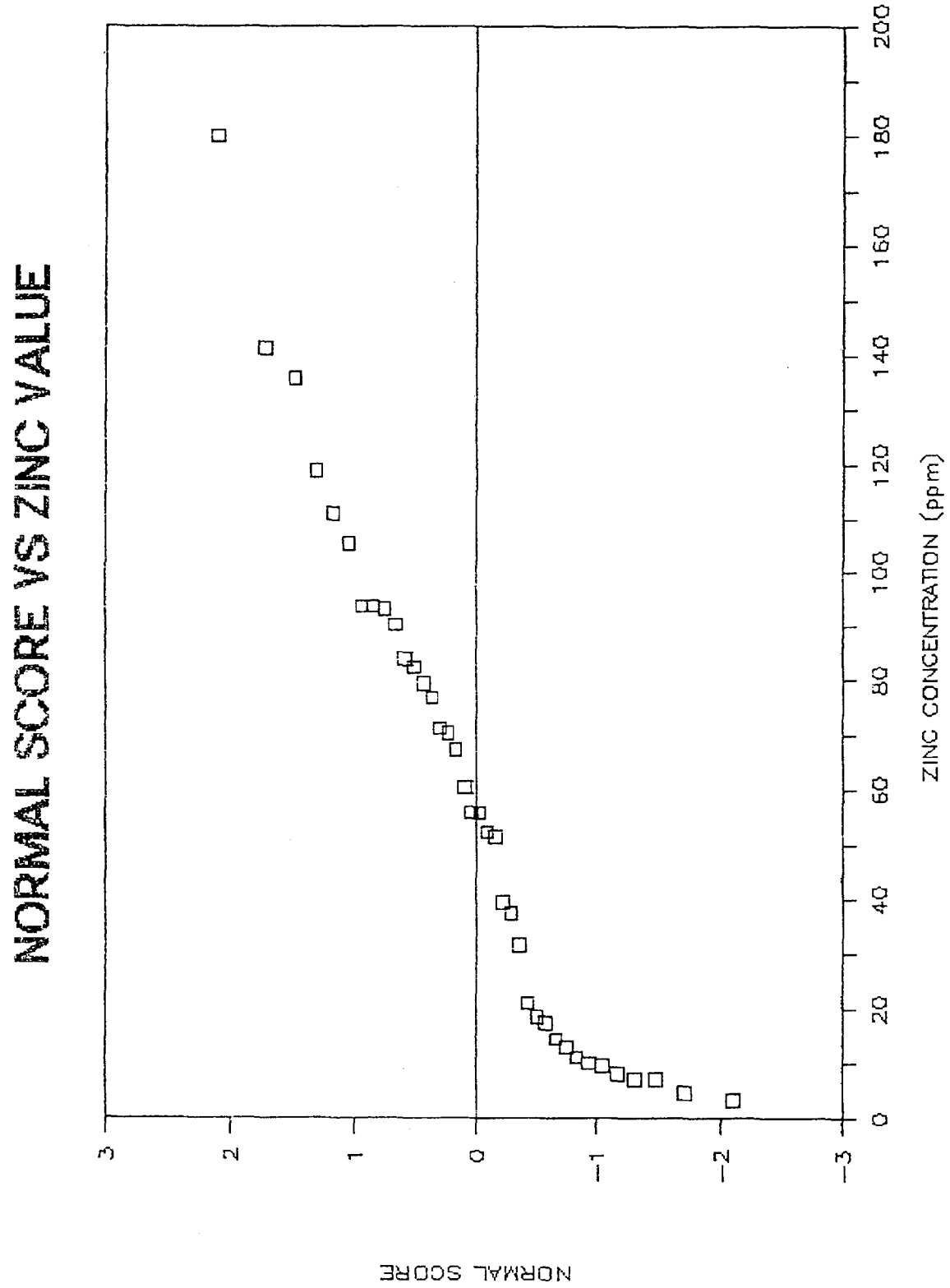


NORMAL SCORE VS IRON VALUE



NORMAL SCORE VS LEAD VALUE




NORMAL SCORE VS ZINC VALUE
NORMAL SCORE
3
2
1
0
-1
-2
-3
0
20
40
60
80
100
120
140
160
180
200
ZINC CONCENTRATION (ppm)

COASTAL PROGRAM

SEDIMENT CHEMISTRY

BASELINE STUDY

APPENDIX D

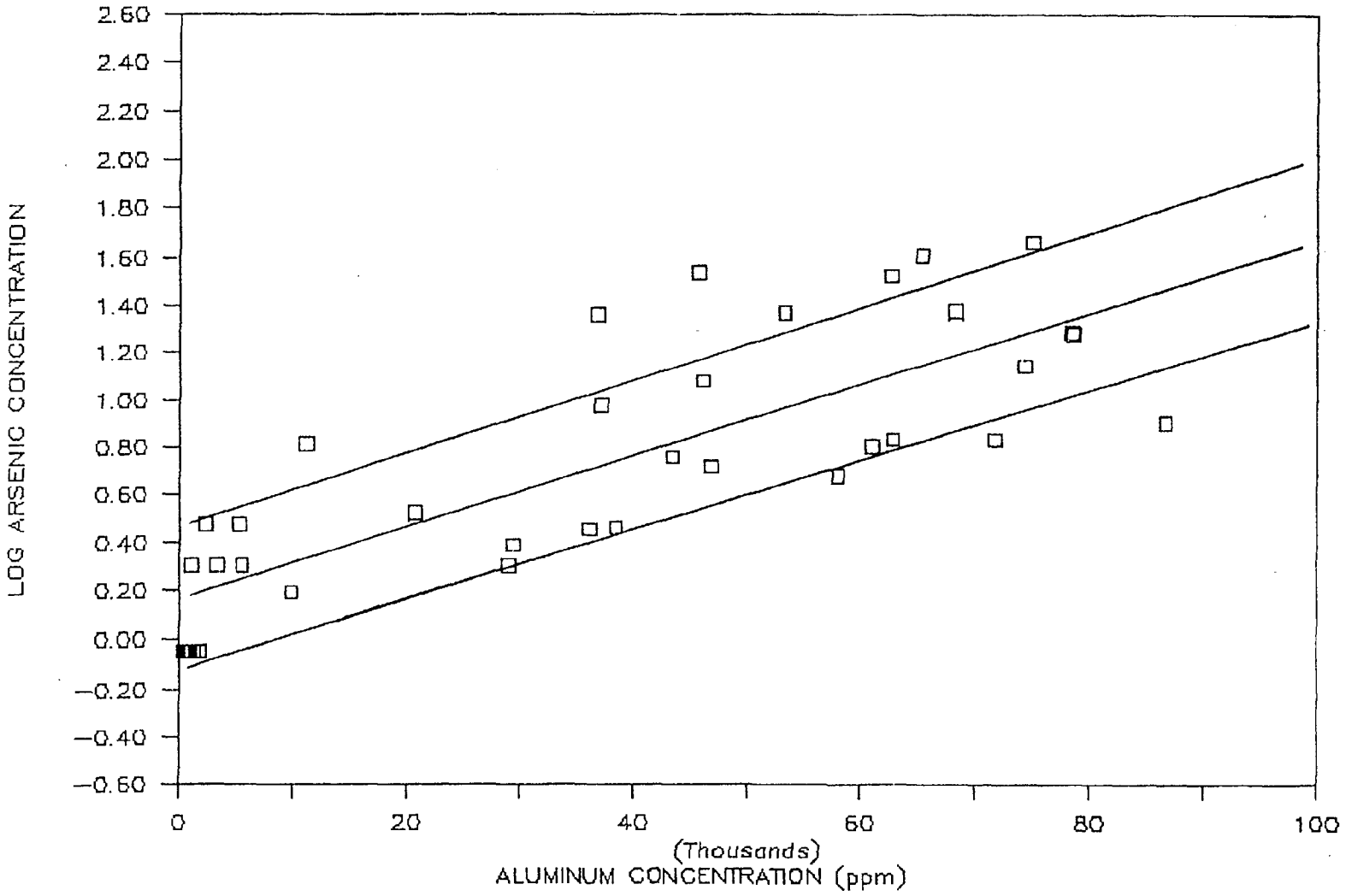
METAL VALUES

VS

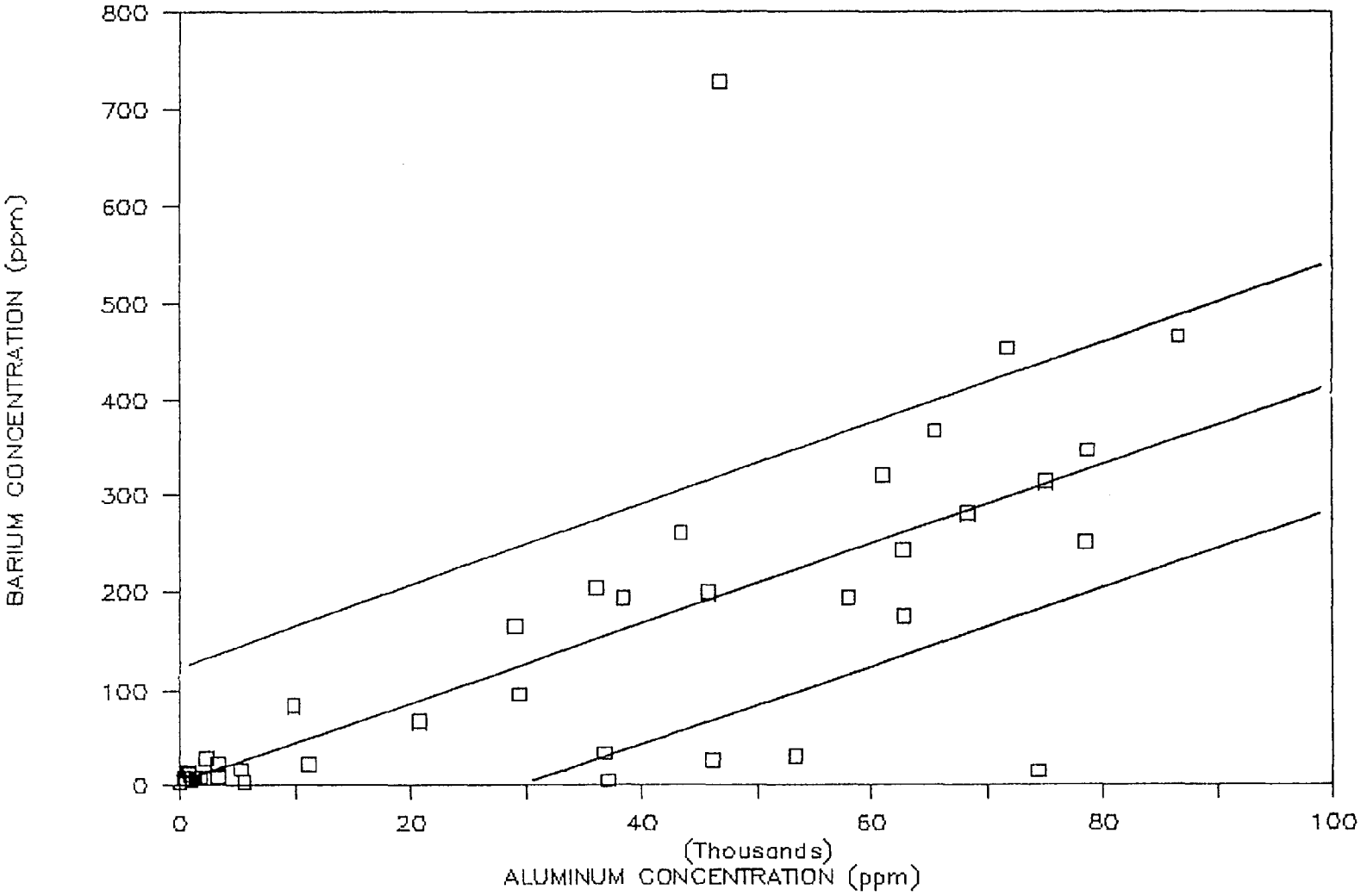
ALUMINUM VALUES

"CLEAN" DATA

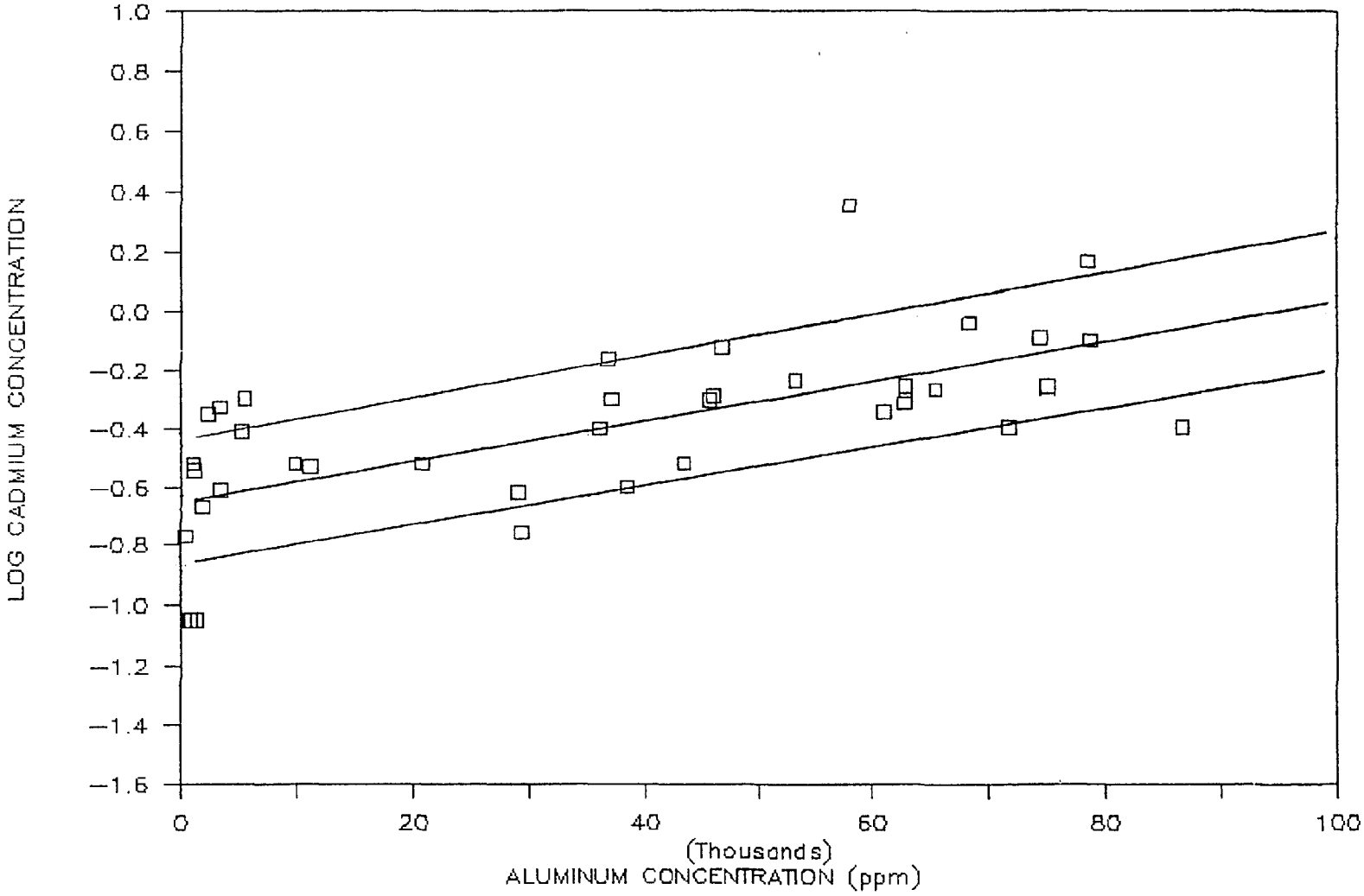
LOG ARSENIC / ALUMINUM



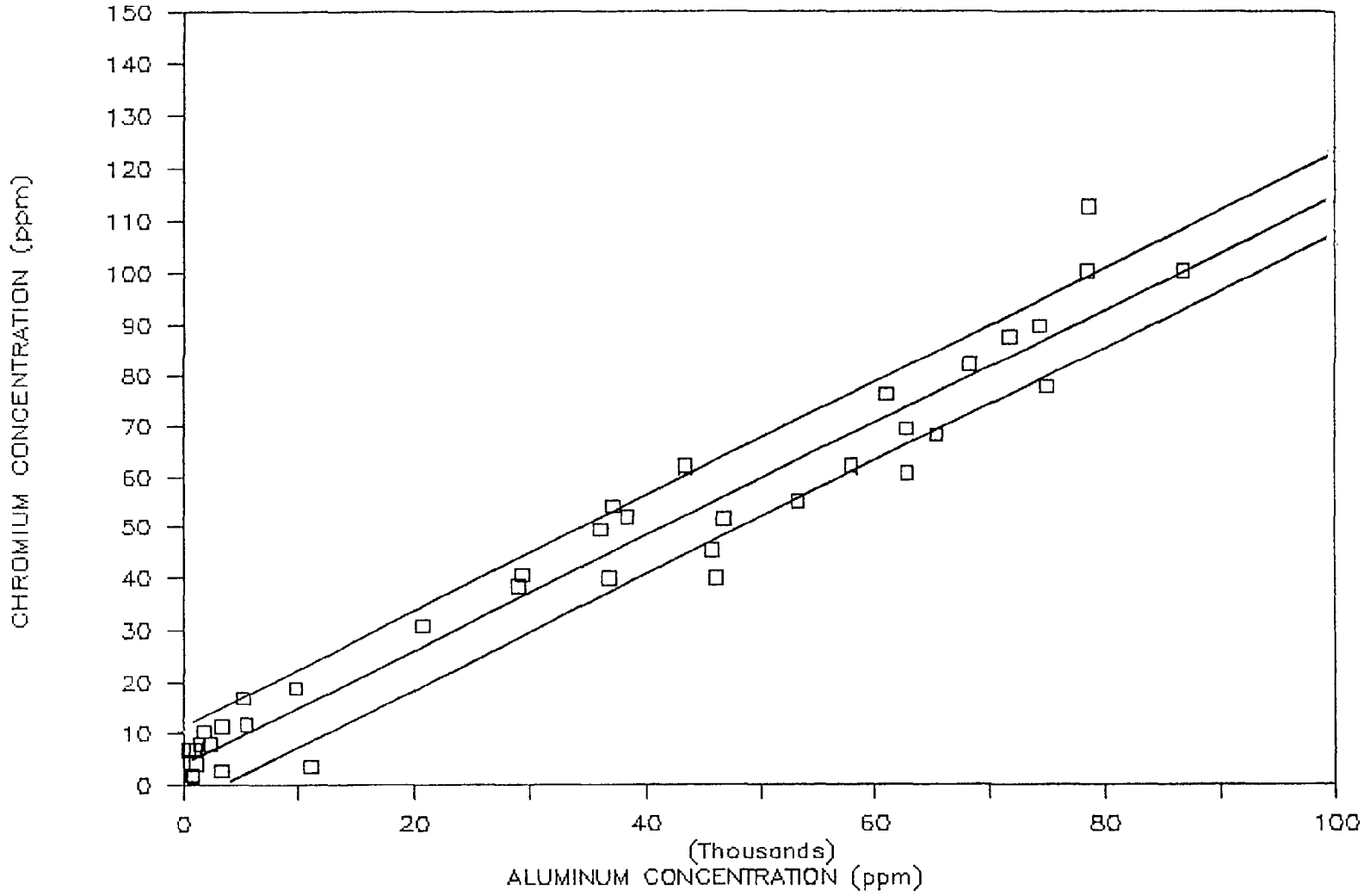
BARIUM / ALUMINUM



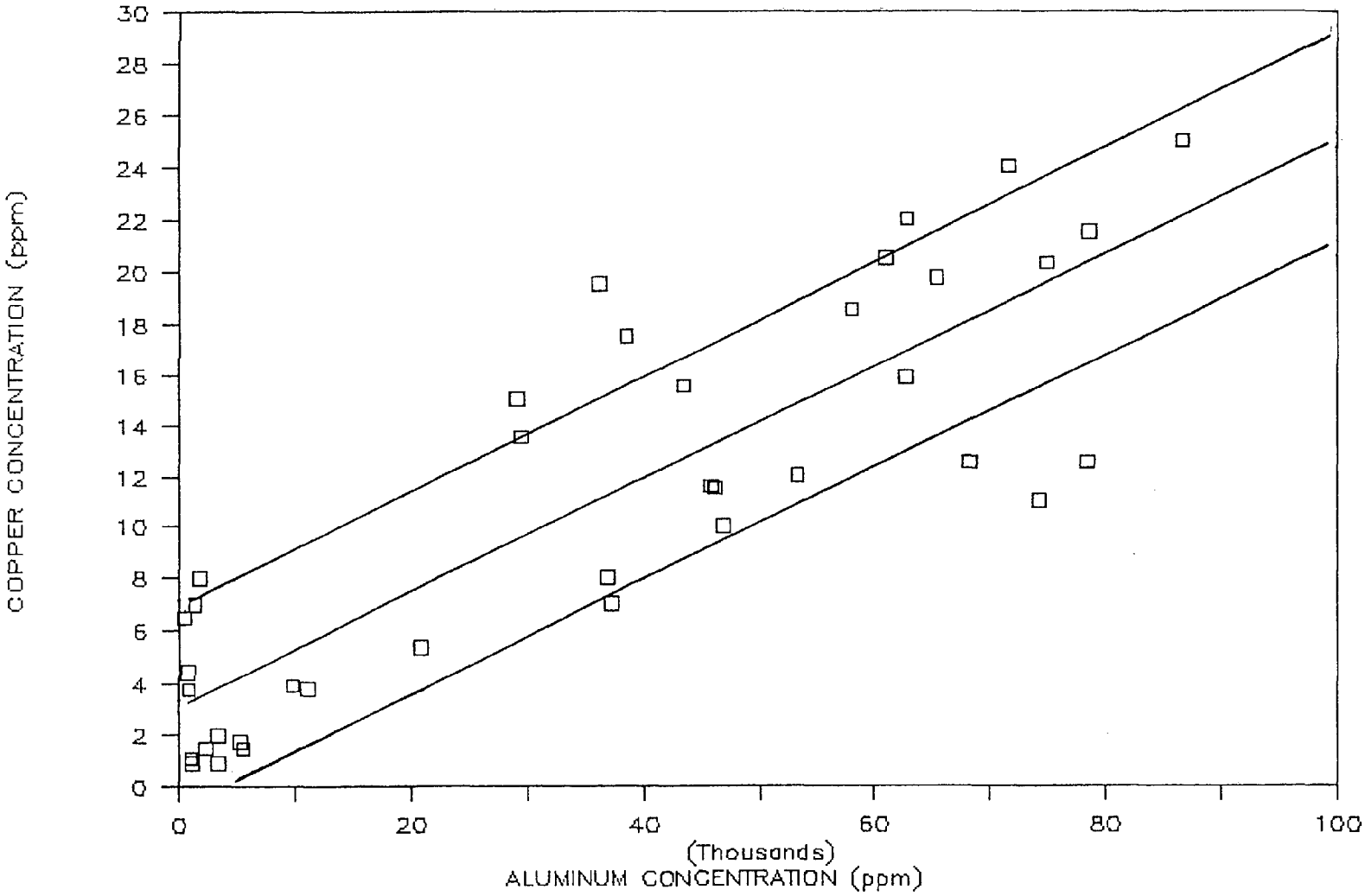
LOG CADMIUM / ALUMINUM



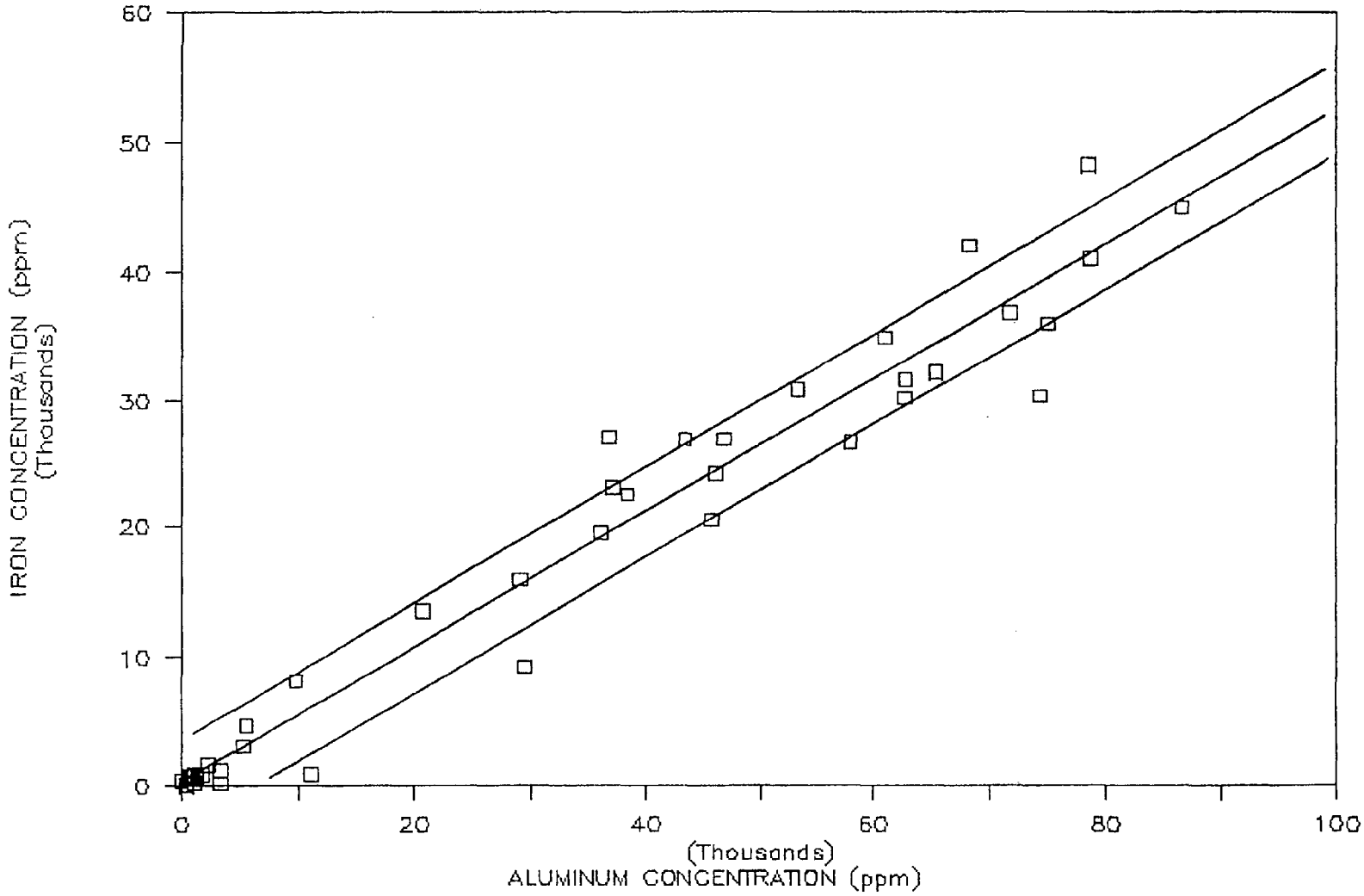
CHROMIUM / ALUMINUM



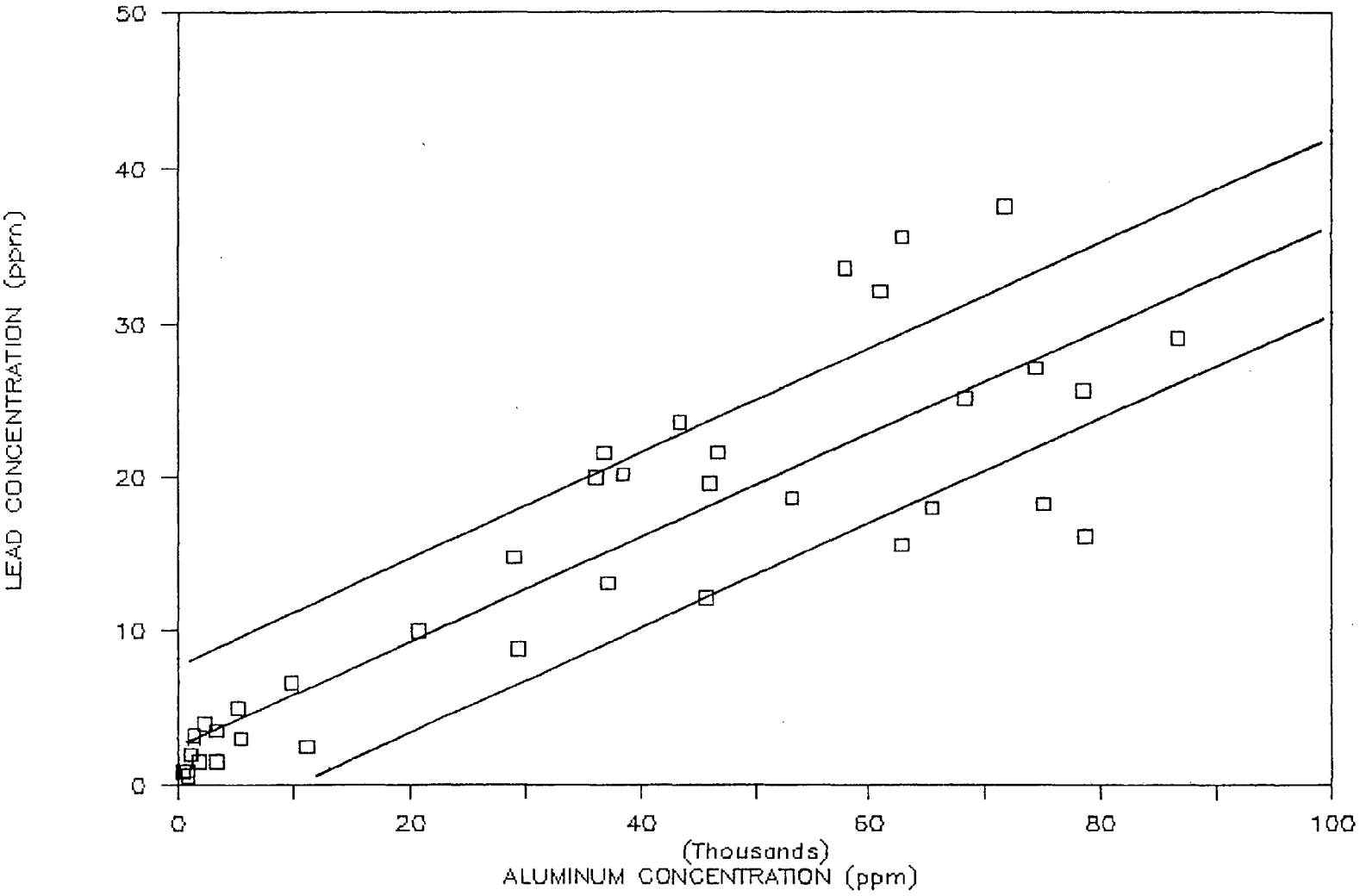
COPPER / ALUMINUM



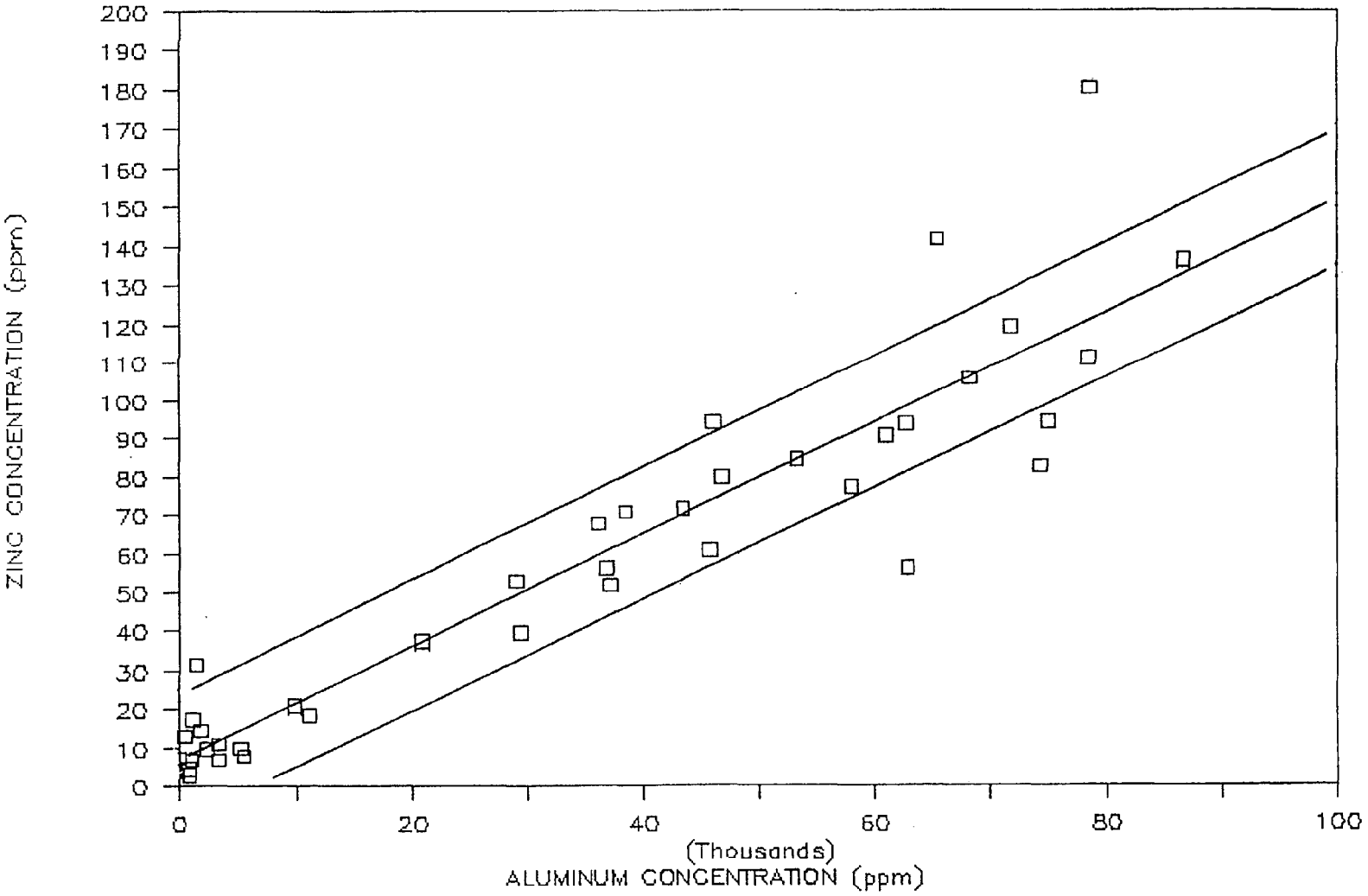
IRON / ALUMINUM



LEAD / ALUMINUM



ZINC / ALUMINUM



NOAA COASTAL SERVICES CENTER LIBRARY
3 6668 14104 8100