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TECHNICAL REPORT

A SURVEY OF THE WATER QUALITY AND SEDIMENT CHEMISTRY OF SELECTED SITES IN MOBILE DELTA SYSTEM

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ALABAMA DEPARTMENT OF ENVIRONMENTAL MANAGEMENT
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A Survey of the Water Quality
and Sediment Chemistry
of Selected Sites in the
Mobile Delta System

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TABLE OF CONTENTS

LIST OF TABLES AND FIGURES

EXECUTIVE SUMMARY

Water and sediment samples were collected from seven sites in the Mobile River Delta. These samples were analyzed for base/neutral extractables, organochlorine pesticides, organophosphorous pesticides and phenoxy acid herbicides. Sediment samples were also analyzed for a suite of eleven metals.

Results of this study indicate the presence of sediments enriched with chromium, copper, lead, mercury and zinc. Also, sediments collected near a petroleum storage terminal were contaminated with polycyclic aromatic hydrocarbons. Other sediments from sites relatively undeveloped and rural were found to contain phthalates. Some possibilities as to the potential sources of contamination are discussed. None of the sediments samples contained detectable concentrations of pesticides or herbicides

Analyses of water samples failed to detect any of the organic compounds in the four groups for which scans were performed on a GC-MS.

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INTRODUCTION

The estuaries of coastal Alabama, like those of most coastal states, have been the focus of numerous investigations into the effects of anthropogenically induced environmental stress. Environmentally stressful activities include but are not limited to industrial and municipal wastewater discharges, stormwater runoff from industrial facilities, urban non-point sources, and drainage from agricultural fields.

To date, water quality and sediment chemistry surveys have primarily concentrated on the effects of point source discharges. Most hydrological and sedimentological studies investigating the effects of development in coastal Alabama have been directed towards ascertaining the impacts of a particular effluent on its receiving water and documenting the improvements (hopefully) of the water and sediment due either to better treatment of wastewaters or elimination of discharges. However, there still exists a need for investigating some of the impacts of non-point sources (urban, industrial and agricultural) on aquatic environments. Of particular interest is the potential of these activities for enriching aquatic environments with heavy metals and toxic organic compounds.

The sources of such contamination are numerous and varied. The metallic element lead being a good example. Lead from the exhaust emissions of engines burning leaded gasoline ends up in aquatic environments as a result of atmospheric deposition. Other significant sources of lead are urban stormwater runoff from paved streets and parking lots and direct input from boat motors (Isphording and Flowers, 1987; Schropp and Windom, 1988; Baudo et al, 1990). Organics such as polycyclic aromatic hydrocarbons enter aquatic environments from spills at loading docks and leaks from storage facilities (Marion et al, 1987). Pesticides and fertilizer from residential lawns and agricultural fields are present in surface runoff to streams (NOAA, 1989).

The uncertainty of the extent and magnitude of adverse impacts to aquatic ecosystems from these numerous sources has prompted federal and state regulatory agencies to examine more closely the effects of non-point sources on water and sediment quality. Of additional relevance to coastal Alabama is the conclusion of some investigators that the sediment characteristics of Mobile Bay (high content of smectite clay and organic carbon) predisposes the Bay to accumulate and retain heavy metals and organics in concentrations potentially harmful to aquatic life (Isphording and Flowers, 1987).

Consequently, needs have arisen for the investigation of the non-point source contamination of water and sediments throughout the Alabama coastal area. Specific needs from the Department's perspective are:

1. Ascertain the impacts to estuaries from spills and leaks from petroleum storage facilities along lower Mobile River
2. Determine if industrial stormwater discharges have significantly altered water and sediment chemistry in the lower Mobile River
3. Examine the tributaries of Mobile Bay for signs of heavy

metal and organic contamination resulting from urban and agricultural runoff.

4. Identification of potential "hot spots" or areas of highly enriched sediments which may constitute a hazard to aquatic life and possibly require remediation or special management during dredging.

Studies previously conducted by the Department, of water quality in coastal Alabama primarily have been routine trend monitoring or short-term intensive sampling of the effects of a specific discharge on a receiving water. Past surveys of sediment chemistry were directed towards establishing baseline conditions and correlations between aluminum and other metals (Halcomb, 1991), and the impacts on estuarine systems from shipyard activities (Halcomb, 1992). The results of the shipyard survey, which also included water column sampling, were instrumental in identifying impacts to water quality and sediment chemistry from various non-point sources related to shipbuilding.

The discovery of sediments enriched with heavy metals and petroleum hydrocarbons in and around shipyards prompted the Department to further investigate the water and sediment quality of the Mobile Delta and its tributaries. This time, for possible impacts from the petroleum storage terminals and other industrial facilities along the lower Mobile River. Also to be examined in ths report are some of the impacts accompanying other anthropogenic activities.

MATERIALS AND METHODS

Water and sediment samples were collected from 7 stations in the Lower Mobile Delta (Figure 1 and Table 1). A K-B type core sampler (Wildlife Supply Co., catalog number 2402-A12) equipped with a cellulose-acetate-butyrate liner tube was utilized for retrieval of sediment samples. The upper five centimeters of each core was placed in a clean glass jar and capped with a teflon lined lid. Five replicate samples were collected at each station, two samples for metal analyses, two for organic scans and the fifth sample was "archived" in a freezer for future analyses in case of widely varying results between the first two. Water samples were obtained by means of a 6.2 liter Kemmerer bottle (Wildlife Supply Co., cat. no. 1560-C25) and were stored in 3.8 liter brown glass jugs with teflon lined caps. All water samples were taken at a depth of one meter and only a single sample was collected at each station. Samples were stored on ice following collection and throughout transport to the laboratory.

The stations MR-1 and MR-2, in the Mobile River, were selected for for evaluating potential impacts from the numerous petroleum storage facilities along the west bank of the river. Although some of these facilities have operated under NPDES regulations for a number of years, stormwater drainage and dock areas have been subject to little, if any, control. Station TM-1, at the mouth of Threemile Creek, was chosen for evaluating potential impacts from petroleum storage terminals and the effects from urban non-point sources. Station CC-1, at the confluence of the Mobile River with Chickasaw Creek, was located for examining the possibility of contamination from the industrial facilities along

Chickasaw Creek and urban runoff in the North Mobile area. The station in Bay Minette Creek, BMC-1, was sited for the examination of an area receiving drainage from agricultural operations and residential developments. The remaining two stations, MR-3 in the Mobile River and TR-1 in the Tensaw River, were chosen as "reference stations" well upstream of the other stations sampled in this study and removed from the drainage from urban Mobile.

All samples were collected within 30 meters of the streambank and in depositional zones in relatively shallow water, less than 3 meters total station depth.

Preparation of sediments for metals 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, Cd, Cr, Cu, Mn, Pb and Sn. A Leeman Labs Model PS-200 automated mercury analyzer was utilized for analyses of samples for Hg.

Sediments were prepared for organic analyses according to EPA

Method 3550 (sonication extraction procedure) and EPA Method 3640 (gel permeation clean-up procedure) for base/neutral compounds, organochlorine pesticides and organophosphorous pesticides. EPA Method 8150 was employed for the extraction and clean-up of phenoxy herbicides.

Analyses for base/neutral compounds in sediments were performed according to EPA Method 8270. Pesticide analyses were conducted by the procedures of EPA Method 8080; herbicides in sediments were determined by EPA Method 8150.

Water samples were extracted and analyzed according to EPA Method 625 for base/neutral compounds, EPA Method 608 for chlorinated pesticides and EPA Method 615 for phenoxy herbicides.

A Finnigan Incos 50 gas chromatograph/mass spectrometer was utilized for analyses of water and sediments for base/neutrals. A Perkin Elmer gas chromatograph equipped with an electron capture detector was employed for determination of pesticides and herbicides in water and sediments

A complete list of organic compounds analyzed and the lower detection limits (dry weight basis for sediments) utilized for this study may be found in Table 2.

Quality of laboratory analyses 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 also were 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. Additionally, both the the ADEM Mobile Branch Laboratory and the Central Laboratory participate in laboratory quality assurance programs conducted annually by the U.S.EPA and NOAA. An in house Q/A program conducted by the Department provides further assurance of quality. Laboratory personnel monitor their techniques and the performance of analytical instruments by routinely testing samples of certified reference material during the course of this and other studies.

This survey applied the method developed by Schropp and Windom (1988) 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; Halcomb, 1991) to be fairly constant, allowing 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), lead pollution in the Mississippi River (Trefey et al, 1985) and heavy metal contamination in and around shipyards in coastal Alabama (Halcomb, 1992).

The analytical result of each metal (average of the station duplicates) was then plotted against its respective aluminum value. These are graphically represented in the Appendix. Superimposed on the graphs are the regression lines and 95% prediction limits for each metal/aluminum relationship as would be expected to occur in uncontaminated sediments. Methods for calculating regression lines, prediction limits and other statistical procedures utilized in this report are detailed in Sokal and Rohlf (1969). The bases for determining the metal/aluminum relationships are described by Schropp and Windom (1987) and Halcomb (1991).

Additionally, the results of sediment metal analyses were compared to a database of metal concentrations of clean sediments. This database was generated through a previous study conducted by ADEM of metal concentrations in sediments of coastal Alabama. The details of this study and the database are described by Halcomb (1991).

At the time of this report the Department does not have a similar method for normalizing the concentration of organic compounds against either aluminum or any other reliable reference factor. Therefore, the data for organic compounds were examined from a perspective of presence or absence of organics and referencing concentrations to data from other studies of organic compounds in estuarine sediments.

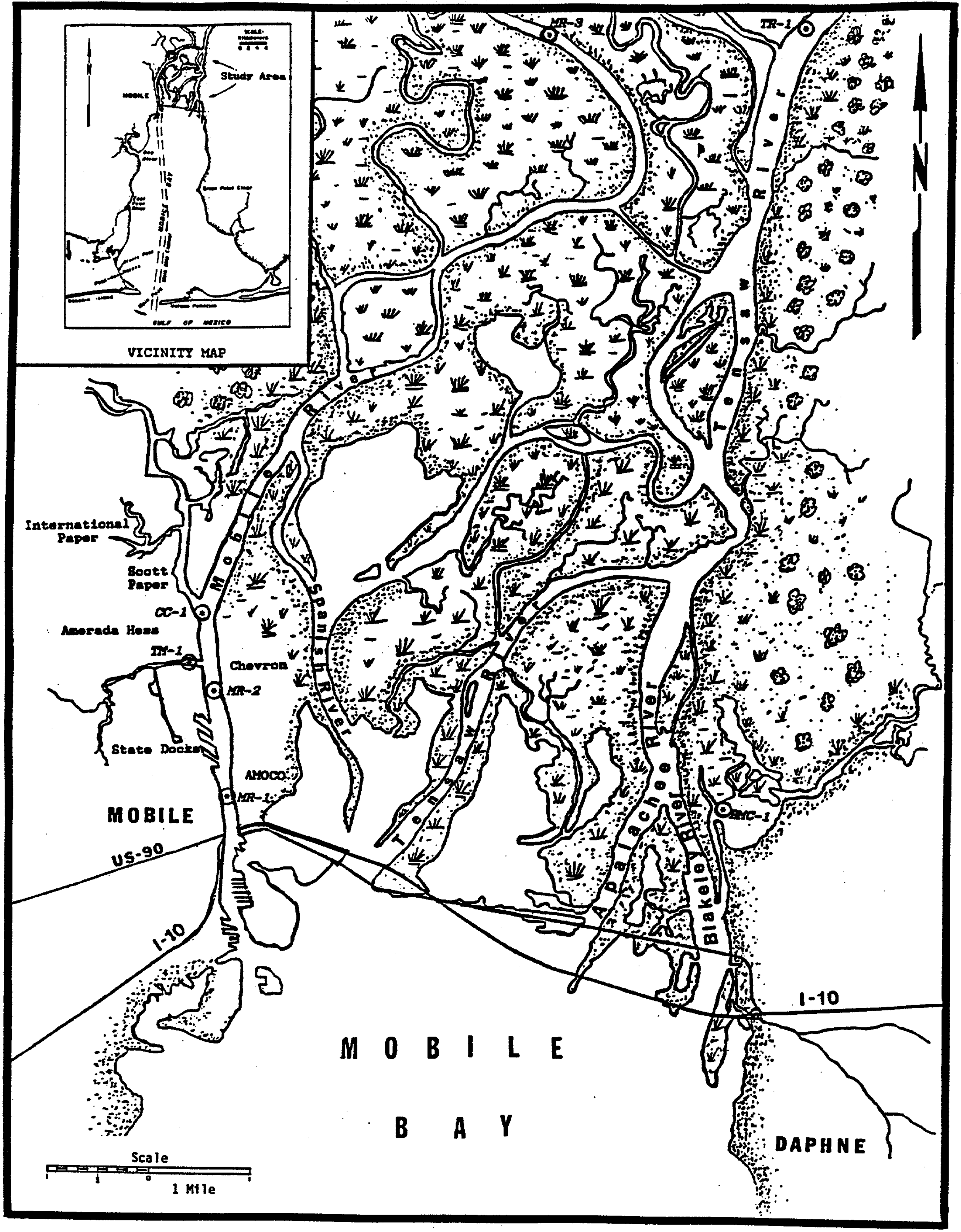


FIGURE 1

Locations of Sample Stations

TABLE 1

Locations of sites sampled for this study

Station designation	Description of location
MR-1	Lower Mobile River at the loading dock of the AMOCO Oil Co. terminal.
MR-2	Lower Mobile River near the Chevron Oil Co refinery on Blakeley Island.
MR-3	Mobile River approximately two miles upstream of the CSX rail bridge.
TM-1	Threemile Creek at the creek mouth near the loading dock of the Amerada Hess terminal.
CC-1	Chickasaw Creek at its confluence with the Mobile River.
TR-1	Tensaw River approximately two miles upstream of the CSX rail bridge.
BMC-1	Bay Minette Creek.

TABLE 2

Organic compounds analyzed and lower detection limits utilized

Base/Neutral Compounds

Parameter	Detection Limits Water(ug/L)	Sediments(ug/g)
Bis (2-chloroethyl) ether	5.00	0.33
1,3-Dichlorobenzene	"	"
1,4-Dichlorobenzene	"	"
1,2-Dichlorobenzene	"	"
Bis (2-chloroisopropyl) ether		
Hexachloroethane	Note: These detection limits apply to all base/neutral compounds	
N-nitroso-di-n-propylamine		
Nitrobenzene		
Isophorone		
Bis (2-chloroethoxy) methane		
1,2,4-Trichlorobenzene		
Naphthalene		
Hexichlorobutadiene		
Hexachlorocyclopentadiene		
2-Chloronapthalene		
Acenapthylene		
Dimethylphthalate		
2,6-Dinitrotoluene		
Acenaphthene		
2,4-Dinitrotoluene		
Fluorene		
4-Chlorophenyl phenyl ether		
Diethyl phthalate		
N-nitrosodiphenylamine		
1,2-Diphenylhydrazine		
4-Bromophenyl phenyl ether		
Hexachlorobenzene		
Phenanthrene		
Anthracene		
Dibutyl phthalate		
Fluoranthene		
Pyrene		
Benzidene		
Butyl benzyl phthalate		
2,3,7,8-Tetrachlorodibenzo-p-dioxin		
Benzo (a) anthracene		
Chrysene		
3,3'-Dichlorobenzidene		
Bis (2-ethylhexyl) phthalate		
Di-n-octyl phthalate		
Benzo (b) fluoranthene		
Benzo (k) fluoranthene		
Benzo (a) pyrene		
Indeno (1,2,3-cd) pyrene		
Dibenzo (a,h) anthracene		
Benzo (g,h,i) perylene		
N-nitrosodimethyl amine		

TABLE 2 cont.

Organochlorine Pesticides

Parameter	Detection Limits Water(ug/L)	Sediments(ug/g)
Aldrin	0.030	0.004
a-BHC	0.030	0.004
b-BHC	0.040	0.050
d-BHC	0.030	0.004
g-BHC	0.020	0.003
Chlordane	0.040	0.005
4-4'-DDD	0.100	0.010
4-4'-DDE	0.080	0.010
4-4'-DDT	0.100	0.010
Dieldrin	0.040	0.005
Endosulfan I	0.080	0.010
Endosulfan II	0.090	0.010
Endosulfan sulfate	0.080	0.010
Endrin	0.060	0.010
Endrin Aldehyde	0.100	0.010
Heptachlor	0.040	0.005
Heptachlor Epoxide	0.020	0.003
Methoxychlor	0.200	0.030
Mirex	0.200	0.030
Toxaphene	0.400	0.050

Organophosphorous Pesticides

Parameter	Detection Limits Water(ug/L)	Sediments(ug/g)
Diazinon	0.010	0.002
Parathion	0.015	0.002
Methyl Parathion	0.012	0.002
Ethion	0.010	0.001
Phosdrin	0.050	0.007
Malathion	0.030	0.004

Phenoxy Acid Herbicides

Parameter	Detection Limits Water(ug/L)	Sediments(ug/g)
2,4 D	0.05	0.001
2,4,5 T	0.04	0.001
Silvex	0.04	0.001

Note: All concentrations for sediments are expressed on a dry wt. basis.

RESULTS

WATER ORGANICS

The analytical results of water samples indicate no detectable quantities of any of the organic compounds for which these samples were analyzed. Any organics that might have been present in the water at the time of sampling were in such dilute concentrations as to be below the lower detection limits of the analytical procedures utilized for this study.

SEDIMENT ORGANICS

Of the seven sites investigated, only MR-1, TR-1 and BMC-1 were found to have sediments containing detectable concentrations of any of the organic compounds analyzed by the GC-MS scans. The specific organics found and their concentrations are listed in Table 3.

The presence of the PAH contamination at MR-1 should not be totally unexpected due to the station's proximity to the petroleum storage facilities along the west bank. These compounds also were discovered in sediments and shellfish from Mobile Bay by other investigators (Marion et al., 1987 and NOAA, 1988). The presence of bis(2-ethylhexyl) phthalate in the sediments of the study area is not surprising either. Phthalates have been found in bivalves from Mobile Bay and the Mobile Delta during previous research conducted by Marion et al. (1987). These materials are widely utilized in paints, varnishes and plastics (EPA, 1980).

TABLE 3

Organic compounds detected in sediments

Station	Parameter	Concentration
MR-1	Benzo(k)fluoranthene	1.96 ug/g
	Fluoranthene	2.60 ug/g
	Pyrene	2.35 ug/g
	Pheneanthrene	2.21 ug/g
TR-1	Bis(2-ethylhexyl)phthalate	0.60 ug/g
BMC-1	Bis(2-ethylhexyl)phthalate	1.50 ug/g

Note: All concentrations are expressed on a dry wt. basis.

SEDIMENT METALS

The results of sediment metal analyses are listed in Table 4. These values are the averages of the duplicate samples collected at a station. Graphical depictions of these results are shown in the Appendix. The graphs of metals verus aluminum shown in the Appendix are the analytical values of the samples collected during this study plotted against regression lines and 95% prediction limits of metals versus aluminum relationships as observed for clean sediments during the baseline study of 1990 (Halcomb, 1991). The regression equation for each relationship is given in the upper left corner of the graphs.

The reader will observe there are no plots for the elements manganese, mercury and tin. For mercury this is due to the poor correlation between mercury and aluminum thereby making such a plot of little or no use, Schropp and Windom (1988) and Halcomb (1991). For manganese and tin such plots have been omitted because of the lack of a sufficently large enough database for coastal Alabama sediments in order to establish reliable regression lines and 95% prediction belts between these elements and aluminum. Expansion of the "clean" sediment database through additional sampling will be necessary before this method may be applied to evaluations of manganese or tin enrichment in sediments.

Sediment data for both the arsenic vs. alumuinum and cadmium vs. aluminum relationships reveal no discernable enrichment of sediments with these elements in the areas sampled. The chromium vs aluminum plot indicates the presence of a slight degree of enrichment in Bay Minette Creek (BMC-1), Chickasaw Creek (CC-1) and Tensaw River (TR-1). More pronounced enrichment of sediments with chromium was detected in the Mobile River at MR-1 and MR-3 and in Threemile Creek (TM-1).

The plot of the copper vs. aluminum relationship shows two of the Mobile River stations (MR-2 & MR-3) as very slightly enriched, data points just above the upper confidence limit. Two other stations, MR-1 and TM-1, exhibit a somewhat noticeable enrichment with copper at concentrations approximately twice that of the expected upper limit.

The data for lead analyses reveal the presence of significant enrichment at two sites. The sediments from the mouth of Threemile Creek (TM-1) and the Mobile River (MR-1) contained lead at concentrations two times and five times greater, respectively, than the amount predicted by the upper limit of the "clean sediment" relationship.

The plot of the zinc data indicates the five stations along the Mobile River (MR-1, MR-2, MR-3, CC-1 and TM-1) possess concentrations of this metal greater than that to be expected given the same aluminum concentration. Although stations MR-2 and CC-1 are only slightly over the upper prediction limit, the sediments from stations MR-1, MR-3 and TM-1 contained zinc in amounts approximately fifty percent greater than the concentrations predicted by the "clean sediment" relationship.

Although a predictable relationship for mercury vs. aluminum has not been developed for Alabama sediments, several of the sites sampled showed an indication of mercury enrichment. This decision was based on a recommended guideline of 0.21 mg/kg of mercury in sediments as an upper limit concentration for "clean" or unenriched sites (Schropp, personal communication). According to Schropp, this value is utilized by a number of researchers in the southeast and gulf coastal area as a "cut-off point" for judging sediments as contaminated by anthropogenic sources of mercury. Employing this guideline indicates that sediments collected from stations MR-2, MR-3, CC-1 and BMC-1 contain enriched concentrations of mercury. Such enrichment was slighly evident at MR-3 and BMC-1 but was more pronounced at CC-1 and MR-2.

TABLE 4

Sediment Metals Data
Mobile Delta Survey 1992

STATION	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Sn	Zn
MR-1	24,840	3.4	0.14	52	19.0	21,700	0.168	133	75.5	3.4	84
MR-2	28,275	3.2	0.24	35	14.0	17,825	1.474	141	14.5	2.3	68
MR-3	12,200	4.0	0.26	56	10.8	18,800	0.374	258	13.4	1.0	70
CC-1	18,800	1.4	0.13	39	10.5	16,200	0.498	106	12.8	2.4	56
TM-1	9,825	1.4	0.14	53	17.0	20,900	0.178	114	23.0	4.4	65
BMC-1	12,750	4.8	0.20	36	8.2	13,150	0.345	166	10.3	1.0	36
TR-1	13,158	2.5	0.12	29	5.5	12,805	0.091	298	8.6	1.0	24
AVERAGE	17,121	3.0	0.17	43	12.1	17,340	0.447	174	22.6	2.2	58
MAXIMUM	28,275	4.8	0.26	56	19.0	21,700	1.474	298	75.5	4.4	84
MINIMUM	9,825	1.4	0.12	29	5.5	12,805	0.091	106	8.6	1.0	24
STD DEV	6,536	1.2	0.05	10	4.5	3,240	0.439	69	22.0	1.2	19

NOTE: All concentrations are the averages of duplicate samples and are expressed as mg/kg on a dry weight basis.

DISCUSSION

The results of this study identified the presence of anthropogenic enrichment of some form or another in the sediments of all sites sampled. Specifically, elevated concentrations of chromium, copper, lead, mercury, zinc, PAHs and phthalates were discovered. Metallic enrichment is especially evident in the Mobile River and Threemile Creek.

The sources of the chromium enrichment would appear to be numerous and varied considering the widespread occurance at stations BMC-1, MR-1, MR-3, CC-1, and TM-1 . Chromium is utilized in a variety of applications including corrosion resistant surface coatings, wood preservatives and corrosion inhibitors for recirculating cooling systems. The latter application involving poisonous chromate preparations (Nordell, 1951; Betz Laboratories, 1976; Baudo, 1990). Potential sources of corrosion inhibiting chromate compounds might be the industrial facilities employing recirculating water cooling systems and maintenance operations at the shipyards for steam powerplants. Some contribution to chromium enrichment might also have been made by historical wastewater discharges and spills at a wood products treatment plant (no longer in operation) in the Threemile Creek Basin.

The elevated concentrations of copper observed at MR-1 and TM-1 might be attributed to biocidal treatments utilized in industrial cooling waters, antifoulant surface coatings and wood preservatives. The specific activities presenting potential historical and ongoing sources of copper enrichment to the study area are, sandblasting/painting activities at local shipyards, cooling system and boiler blowdown and wood preserving operations.

Excessive concentrations of lead were also discovered at MR-1 and TM-1. Station MR-1 was sited next to a loading dock at a bulk petroleum storage terminal along the western bank of the Mobile River. A possible cause of the high lead levels at this site might the spills and leaks of leaded gasoline likely to have occured at such a facility over the years. This station also was the site of polycyclic aromatic hydrocarbon contamination as discussed in the review of organic data. The lead comtamination at TM-1 might be due in part to similar spills and runoff from the petroleum storage terminals at Magazine Point; however, the absence of detectable hydrocarbons at TM-1 may indicate the lead enrichment to be more a result of lead from exhaust emissions.

The elevated levels of zinc detected in sediments of Mobile River and Threemile Creek reflect enrichment from several potential sources. Zinc is also a component of the chromate preparations utilized in cooling waters (Nordell, 1951; Betz Laboratories, 1976). Discharge of such untreated waters has the potential for significantly increasing zinc concentrations in receiving waters and sediments. Zinc was also present in abnormally high concentrations at station MR-3, well upstream of the petroleum storage terminals and industrial operations in the Blakeley Island/Threemile Creek portion of the lower Mobile River. This would appear to indicate contributions to zinc enrichment from upstream sources, possibly along the upper Mobile and lower Tombigbee Rivers.

Although no relationship for either manganese or tin versus aluminum has been developed for clean sediments in coastal Alabama, the concentrations observed in this study appear to be, for the most part, within the ranges of relatively natural concentrations reported by other investigators (Isphording and Lamb, 1985; Isphording and Flowers, 1987; Malatino, 1980 and NOAA, 1988). Exceptions to this being the slightly enriched tin concentrations at MR-1, MR-2, CC-1 and TM-1. The shipyards proximate to these stations are likely sources of this condition.

Previous studies of sediment chemistry by ADEM (Halcomb, 1991) and others (Schropp and Windom, 1988 and Isphording, pers. comm.) have concluded that no reliable relationship exists between mercury and aluminum or any normalizing element. Therefore, evaluation of sediment data for mercury contamination usually relies on comparing concentrations from "suspect" sites with concentratons from "clean" reference sites. As mentioned in the previous section this study employed the guideline concentration of 0.21 mg/kg mercury as an upper limit for "clean" sediments. The levels of mercury detected at four of the seven sites sampled in this study exceeded this limit. The most likely sources of mercury enrichment would appear to be wastewater discharges from the chlorine production facilities in the Mobile area.

The relatively volatile and mobile nature of mercury in aquatic environments is demonstrated by the presence of mercury enrichment in sediments of Bay Minette Creek (BMC-1). Bay Minette Creek is well removed from industrial and municipal discharges and the mercury responsible for contaminating this site is likely to have travelled from the western side of the Mobile Delta, possibly from as far as the Tombigbee River.

The PAHs detected at station MR-1 are indicators of spills of gasoline, diesel fuel and other petroleum products from the offloading of barges and other operations at the bulk storage terminals along the west bank of the lower Mobile River. As discussed above this station was also a site of lead enrichment; the most pronounced of all locations sampled during this study.

In a study of organics in the tissue of bivalve mollusks Marion et. al. (1987) detected PAH compounds, as well as other compounds, in oysters and clams from Mobile Bay. The concentrations observed in the shellfish study were highest for samples collected in the northwestern portion of the bay and in the areas of high density boat traffic, especially the tributaries to the western side of Mobile Bay.

Phthalates, such as those found in the sediments from BMC-1 and TR-1, are ubiquitous in estuarine sediments of developed areas (Marion et al., 1987 and EPA, 1980). This class of compounds is contained in a multitude of plastic products, solvents and varnishes. One avenue of entry for these compounds into aquatic systems is from the innumerable plastic containers discarded on a daily basis. The phthalates contained in plastic trash slowly leach out and, as in the case of plastic litter in and along the water, end up in sediments and shellfish.

As is evidenced by the results of this study the "reference stations", as were termed MR-3, TR-1 and BMC-1, showed signs of anthropogenic enrichment. Such an outcome does not invalidate the usefulness of the "reference stations" as points of reference. Although these stations apparently are not of unblemished pristine quality they do indicate the cause of lead enrichment in sediments to be more from urban non-point sources and the bulk petroleum terminals than from industrial sources upstream of Mobile. These stations also help illustrate the apparent fact that the sediments in the lower Mobile River and Threemile Creek have been enriched with copper and tin by sources somewhat proximate to Threemile Creek and the harbor area. The "omnipresent nature" of chromium and phthalate enrichment in sediments of developed areas also is born out by the data from stations TR-1 and BMC-1. Finally, the presence of zinc enrichment in the sediments from the Mobile River side of the delta (including MR-3) and the accompanying lack of such enrichment on the Tensaw River side (TR-1 and BMC-1) is evidence of a source of this metal located downstream of the divergence of the Mobile and Tensaw Rivers.

CONCLUSION

The concept of metal versus aluminum relationships following the method of Schropp and Windom (1988) and developed for Alabama sediments during previous surveys (Halcomb, 1991 and 1992) was sucessfully employed for evaluating sediment enrichment. These relationships revealed the presence of metal enrichment in some sediments of the study area. Specific metals were, in several cases, attributed to certain anthropogenic activities. Motor vehicle and boat traffic, biocidal formulations and industrial uses of metallic compounds are potential sources of metal enrichment to sediments of the study area. Spills and other releases of leaded gasoline from storage terminals and associated loading operations also appear to be significant contributors to elevated metal concentrations in sediments. Enrichment of sediments with chromium also was observed at sites well removed from urban and industrial development (BMC-1 and TR-1) and is evidence of the far reaching effects of these activities.

Other forms of sediment contamination observed during this investigation were PAH compounds at a petroleum products loading dock and phthalates at a couple of locations. Such findings compliment previous research into organic contamination revealing, as previously known, organics are/have been input to aquatic environments through various pathways and to many places. The discovery of phthalates in sediments from "reference sites" in rural areas is truly indicative of the widespread environmental impacts of human society.

This study failed to detect any traces of pesticides or herbicides in either the water or sediment of the sites sampled. These substances will be part of the focus in future efforts investigating the impact of residential and agricultural development in local watersheds. Also not found in the course of this survey were signs of arsenic enrichment. Excessive concentrations of this metal have been reported in sediments of Mobile Bay through previous research conducted by Isphording and Flowers (1987), Halcomb (1991) and U.S.EPA (personal communication with Dr. Kevin Summers, EPA Gulf Breeze Lab). This survey did not include samples from the same sites as the those studies and failure to detect the above mentioned contaminants is more likely an indication of the "patchy" distribution of some of these materials rather than procedural error on our part. Also, the failure to detect pesticides and herbicides might be a hopeful indication that contamination by these compounds is subsiding in some locations

Obviously, additional investigations into the nature of non-point source impacts and the extent and magnitude of sediment enrichment are needed before full and effective management of Alabama coastal resources are realized.

REFERENCES

Betz Laboratories Inc. 1976. Handbook of industrial water conditioning. Betz Laboratories, Trevose, PA. 344pp.

Baudo, R; J.P. Giesy and H. Muntau. 1990. Sediments:chemistry and toxicity of in-place pollutants. Lewis Publishers, Chelsea, MI. 405pp.

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.

Halcomb, G.L. 1992. A survey of the water quality and sediment chemistry of shipyards in coastal Alabama. Alabama Department of Environmental Management, Mobile, Alabama. 23pp w/ appendices.

Halcomb, G.L. 1991. A sediment chemistry baseline study of coastal Alabama. Alabama Department of Environmental Management, Mobile, Alabama. 30pp w/ appendicies.

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

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.

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.

Marion, K.R., S.A. Barker and R.L. Settine. 1987. Organic pollutant levels in bivalves of Mobile Bay. 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

National Oceanic and Atmospheric Administration (NOAA). 1989. Agricultural pesticide use in estuarine drainage areas:a preliminary summary for selected pesticides. The National Coastal Pollutant Discharge Inventory. 32pp w/ appendices.

National Oceanic and Atmospheric Administration (NOAA). 1988. A summary of selected data on chemical contaminants in sediments collected during 1984, 1985, 1986 and 1987. National Status and Trends Program for Marine Environmental Quality, progress report. NOAA Technical Memorandum NOS OMA 44. 15pp w/appendices.

Nordell, E. 1951. Water treatment for industrial and other uses. Reinhold Publishing Corp., New York, New York. 526pp.

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 statistics 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.

U.S. Environmental Protection Agency. 1980. Ambient Water Quality for for Phthalate Esters. Pub. No. 440/5-80-067.

U.S. Environmental Protection Agency. 1983. Methods for Chemical Analyses of Water and Wastes. EPA 600/4-79-020. Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency.

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.

APPENDIX

GRAPHICAL PLOTS

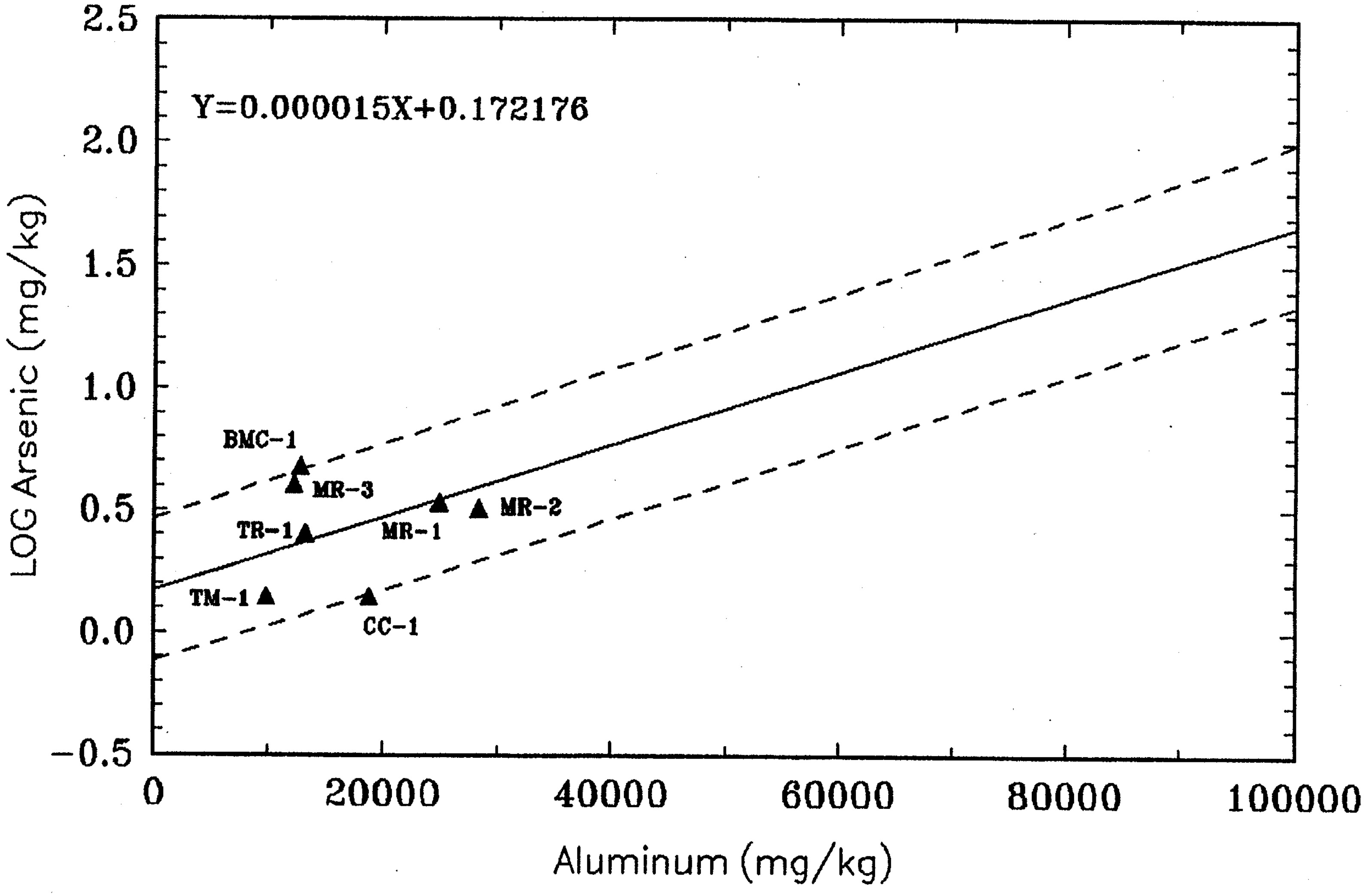
OF METALS

VERSUS ALUMINUM

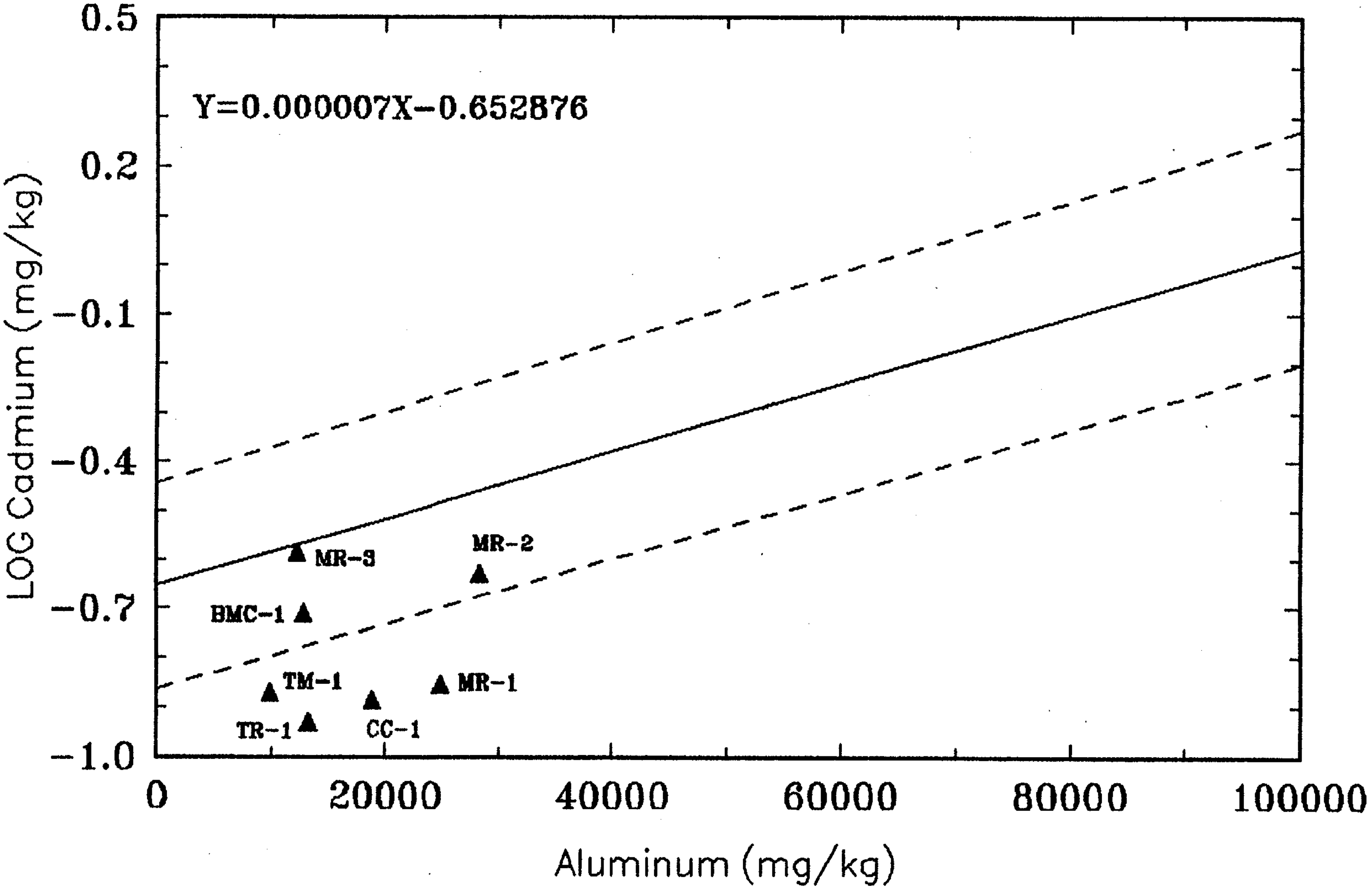
IN SEDIMENTS

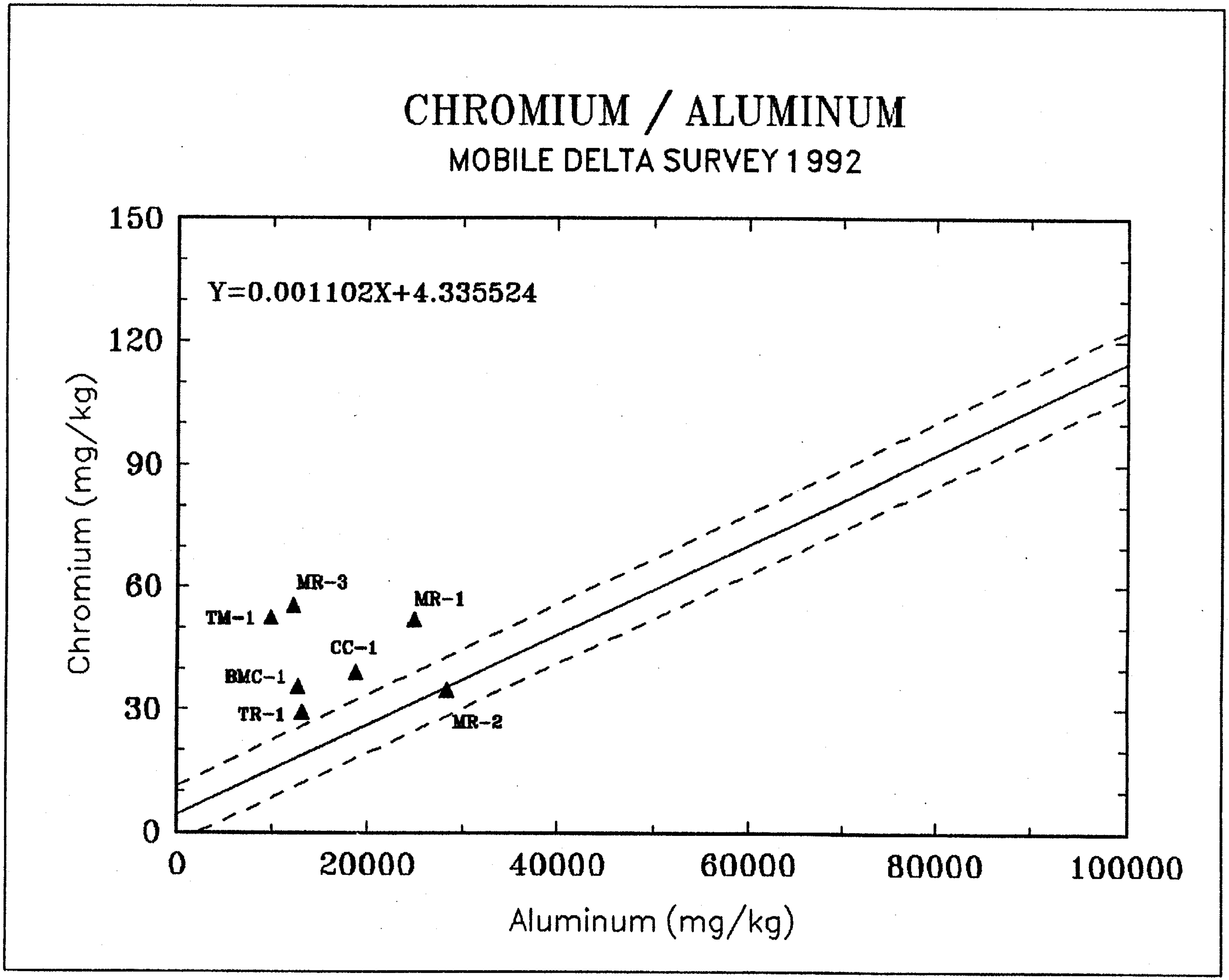
ARSENIC / ALUMINUM

MOBILE DELTA SURVEY 1992



CADMIUM / ALUMINUM
MOBILE DELTA SURVEY 1992



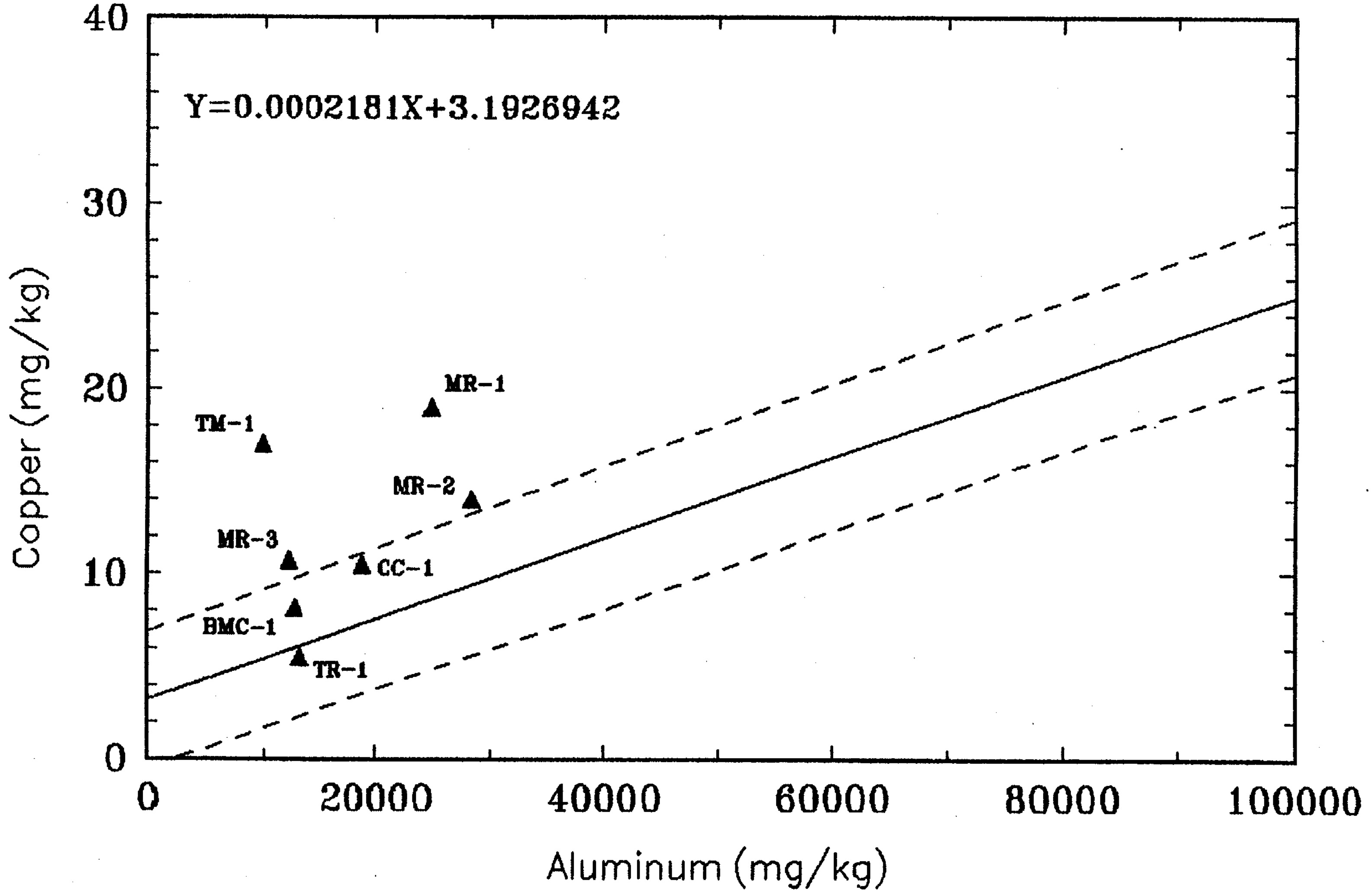


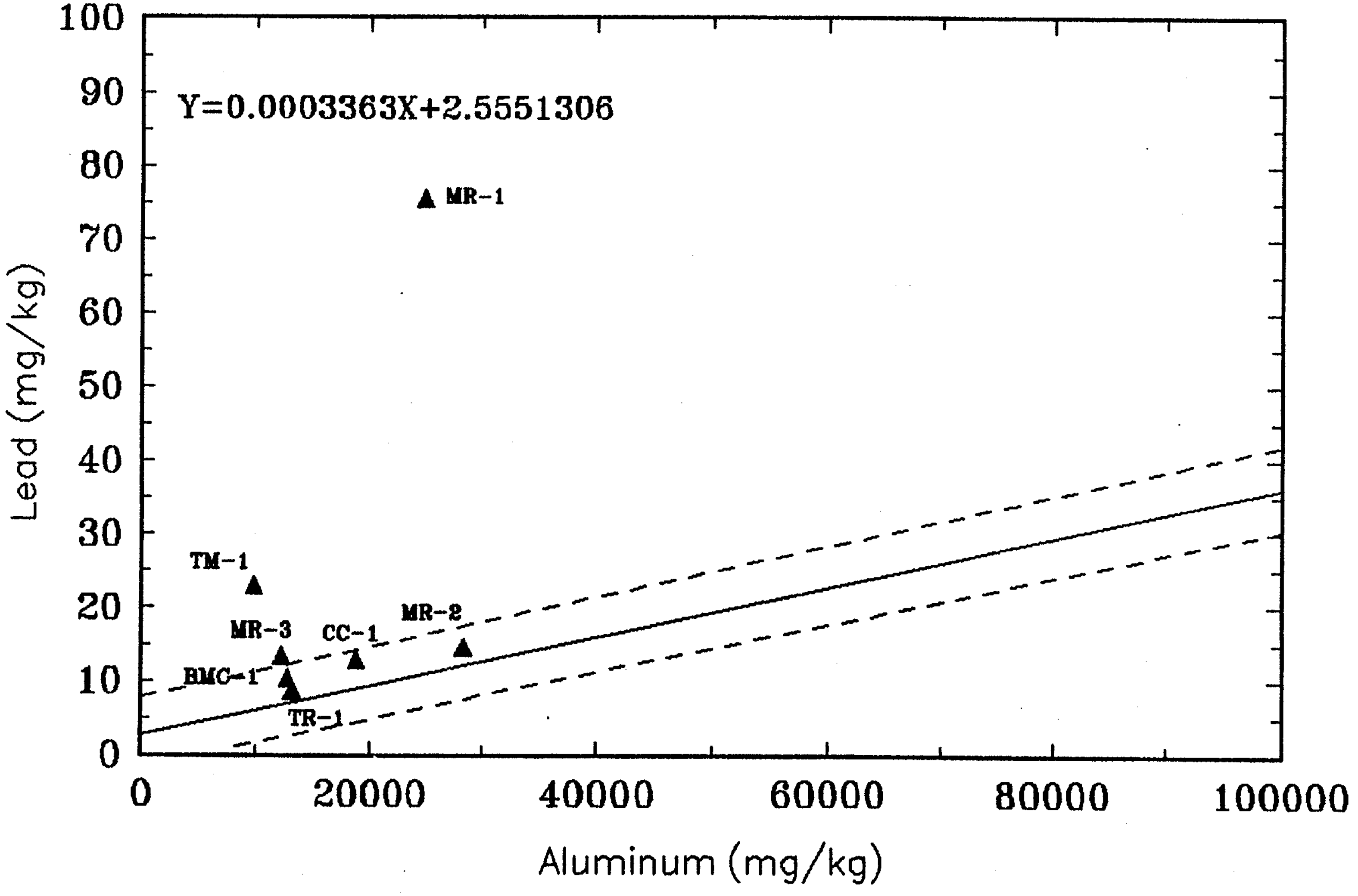
CHROMIUM / ALUMINUM

MOBILE DELTA SURVEY 1992

COPPER / ALUMINUM

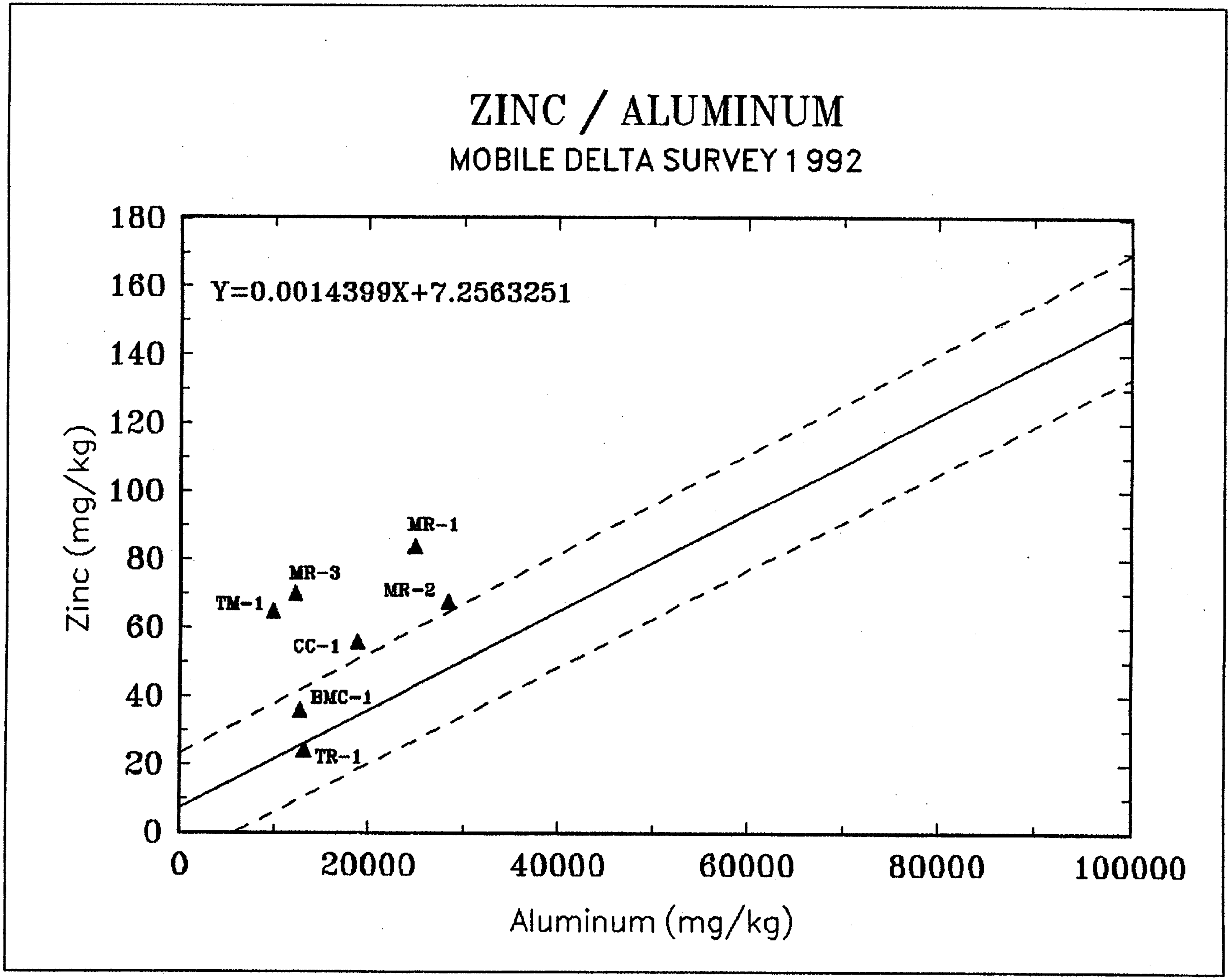
MOBILE DELTA SURVEY 1992





LEAD / ALUMINUM

MOBILE DELTA SURVEY 1992


ZINC / ALUMINUM
MOBILE DELTA SURVEY 1992
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Zinc (mg/kg)
180
160
140
120
100
80
60
40
20
0
Aluminum (mg/kg)
0
20000
40000
60000
80000
100000
MR-1
MR-3
TM-1
MR-2
CC-1
BMC-1
TR-1