

ABSTRACT

The Distribution of Potentially Toxic Heavy Metals
in the Sediments of San Antonio Bay and
the Northwest Gulf of Mexico (May 1974)

John H. Trefry III, A.B., Syracuse University
Chairman of Advisory Committee: Dr. B.J. Presley

A total of 123 sediment samples from 48 locations in the northwest Gulf of Mexico, including San Antonio Bay and the Mississippi River Delta, were acid leached and analyzed for iron, manganese, lead, zinc, cadmium, copper, and nickel by atomic absorption spectrophotometry. HNO_3 and $\text{HNO}_3\text{-HCl}$ solutions leached 60-70% of the iron and 60 to more than 90% of the other metals from the sediments.

Heavy metal concentrations in the acid leachable fraction of the sediments were normalized against the acid leachable iron concentration by setting up a series of scatter plots. This provided a rapid method for indicating locations where heavy metal concentrations were above the expected natural sediment level.

The San Antonio Bay area sediments showed an overall low content of heavy metals. However, higher than natural levels were observed for cadmium, lead, and copper in the San Antonio-Guadalupe River System which feeds the bay. The northeastern extension of the bay, in the areas of the river mouths, also

showed slightly higher than expected levels of nickel, lead, and cadmium. The proposition that shell dredging operations in the bay remobilize significant quantities of toxic metals and make them available to the biota of the area does not appear to be true based on this study.

Most of the Mississippi Delta region showed higher metal concentrations in the surface sediments than in the subsurface sediments. Cadmium and lead were shown to be concentrated relative to iron over an extensive region at the mouth of the Mississippi River. Copper was anomalously high at two stations on the Mississippi River Delta. Cadmium appeared high at the entrance to Galveston Bay. No other significant heavy metal deviations were observed.

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I wish to thank Dr. B.J. Presley for serving as chairman of my committee, for providing financial assistance during the course of study, and for his continued interest and guidance in my work. Drs. D.R. Schink and R.B. Scott, who also served on my committee, offered valuable suggestions in reviewing my thesis and I wish to express my appreciation for their help.

I also wish to extend thanks to Mr. R.R. Sims, Mr. S. Feagley, Ms. S. Fay, Mr. R.F. Shokes, Mr. C.A. Page, and Dr. R.A. Feely who have all consistently helped in sampling, technical operations, and discussions. The drafting work of Dr. R. Fay and the typing of Ms. B. Scott have been greatly appreciated.

My wife Susan, who helped in sampling and typed the rough draft of this thesis, has been a constant source of support and encouragement and I offer her special thanks.

TO MY PARENTS

THE DISTRIBUTION OF POTENTIALLY TOXIC HEAVY METALS
IN THE SEDIMENTS OF SAN ANTONIO BAY AND
THE NORTHWEST GULF OF MEXICO

A Thesis

by

JOHN HAROLD TREFRY III

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INTRODUCTION

Heavy metal pollution - a statement of the problem

Increased accumulation of potentially toxic heavy metals in freshwater and coastal marine environments has attracted considerable attention in recent years. Irukayama (1966) showed a cause and effect relationship between methyl-mercury in shellfish and the occurrence of an unusual illness in the residents of the Minamata Bay area of Japan. Tatsumoto and Patterson (1963) have shown that introduction of industrial lead into the natural marine cycle is recent and that lead is presently being added to the ocean at a rate ten times greater than expected from natural weathering. Kobayashi (1970) correlated a high incidence of the bone disease "itai-itai" with contaminated rice paddies which had been irrigated with cadmium rich waters from Japan's Jintsu River Basin. The above considerations point to the twofold nature of the heavy metal problem which may be stated as follows:

- 1) Man is indiscriminately disposing of heavy metals in the seas, the inland waters, and the air.
- 2) Biological organisms, including man, have the ability to concentrate metals to such an extent that

consistent exposure to metal rich water or biota may cause the organisms to suffer physiological damage.

Input of heavy metals to our bays and oceans may come indirectly from contaminated rivers, streams, and runoff; or the input may come directly from discharges by vessels, aerial fallout, or the pumping of metal-rich wastes into estuaries or the sea from the shore. The incidence of contamination of rivers and streams by industrial wastes is world-wide. The Jintsu River in Japan has high concentrations of zinc, lead, and cadmium which are a result of wastewater discharges into the river from a mine (Kobayashi, 1970). The sediments in Sorfjord, Norway have unusually high levels of lead, cadmium, copper, and zinc which correlate positively with the locations of smelting plants (Skei et al., 1972). Locally, activity in the Houston Ship Channel has been shown to have resulted in high levels of mercury, lead, zinc, copper, cadmium, arsenic, and chromium (Hann and Slowey, 1972). In addition to these industrial and municipal sources of heavy metal contamination of inland waterways, land runoff from agricultural areas may carry metal bearing pesticides such as lead arsenate or copper sulfate. However, the degree to which this latter process contributes to the indirect addition of metals to our waters has not been clearly delineated.

Direct addition of the heavy metals chromium, copper,

lead, nickel, and zinc by solid waste dumping in New York Bight has resulted in a ten to one hundred times higher concentration of these metals in sediments near waste disposal sites than in uncontaminated sediments (Carmody et al., 1973). The deposition of copper sulfate on Dutch shores in March, 1965 increased the copper content of the coastal water from 3 to 500 $\mu\text{g/l}$ and resulted in a fish kill in excess of 100,000 individuals (Roskam, 1965). Johannesson (1955) and Guinn and Bellanca (1969) noted the presence of high levels of vanadium, nickel, manganese, and cobalt as nonvolatile metal porphyrins in crude oils. And, it is possible that tanker spills may introduce significant amounts of these metals to the oceans. Chow et al. (1973) have shown that the present flux of lead to the sediments of the Southern California basins is two to six times greater than natural rates. With the use of lead isotopic composition, they have shown that the lead excess is derived from combustion of lead gasoline additives which are transported aerially and deposited as atmospheric fallout.

As the above citations indicate, there are many examples of localized metal pollution due to the activities of man. The effects of this pollution have been most harmful in coastal areas and inland waters because these areas are closest to the sources of contamination, and because they are areas of most intense biological activity. Extension of near-shore metal

problems to global proportions is often dismissed because of the belief that the immense volume of the ocean will sufficiently dilute any contaminant. However, such consideration fails to account for damages which occur before the metals are dispersed or when they are concentrated by the marine biota (Riley and Chester, 1971).

The facet of the heavy metal pollution problem which is of most concern to mankind is the concentration of metals by organisms. Because of the ease of measuring the metal concentrations in some species, data supporting the observation of a higher level of heavy metals in the marine biosphere than the hydrosphere have been available for many years. Vinogradov (1953) has summarized most of the early investigations in his extensive monograph. Goldberg (1965) has collected more recent information on trace element concentrations in marine organisms.

To show the extent to which some organisms concentrate elements from seawater, an enrichment or concentration factor, which may be defined,

$$CF = \frac{\mu\text{g element/g organism, wet weight}}{\mu\text{g element/g seawater}}$$

is used by many investigators (Goldberg, 1965). Table I, taken from Brooks and Rumsby (1965), gives an indication of the magnitude of concentration factors in marine molluscs. Other investigators have shown similar values for concentration factors in marine algae (Stevenson et al., 1964), zooplankton (Martin, 1970),

TABLE I

Concentration factors for heavy metals in marine molluscs

Element	Concentration Factors		
	Scallop	Oyster	Mussel
Cd	2,260,000	318,000	100,000
Cu	3,000	13,700	3,000
Fe	291,500	68,200	196,000
Mn	55,500	4,000	13,500
Ni	12,000	4,000	14,000
Pb	5,300	3,300	4,000
Zn	28,000	110,300	9,100

From Brooks and Rumsby (1965, p. 523).

Note: Concentration factors in this table are based on the dry weight of these organisms. To approximate concentration factors in terms of wet weight, the above factors should be divided by 10 (Martin, 1970).

and echinoderms and coelenterates (Riley and Segar, 1970).

Another example of trace element enrichment by organisms is given by Kobayashi (1970) who found concentrations of lead and cadmium in tissues of humans who had eaten contaminated rice to be 10 to 100 times the concentrations in the rice.

Brooks and Rumsby (1965, p. 521) have summarized the following suggested mechanisms for trace element concentration:

- 1) Particulate ingestion of suspended material from seawater (Armstrong and Atkins, 1950).
- 2) Ingestion of elements via their preconcentration in food material (Bowen and Sutton, 1951).
- 3) Complexing of metals by coordinate linkages with appropriate organic molecules (Schubert, 1954); the incorporation of metal ions into physiologically important systems (Williams, 1953; Lehninger, 1950); and uptake by exchange, for example, onto mucous sheets of the oyster (Korringa, 1952).

Although the suggested pathways of element concentration are most reasonable, the role they play in a given individual or in a given geographic location is not fully understood. It does seem, however, that element concentration is very much a function of the individual, its habitat, and its feeding mechanisms.

While the observation of element concentration by organisms cannot be disputed, the magnitude of this enrichment as expressed

in listings such as Table I seems overwhelming. However, the marine molluscs listed in Table I are benthonic and thus live in close association with the sediments. This is reinforced by Brooks and Rumsby's statement that "...it was difficult to remove sedimentary material from the gills." Thus, in this case, it may be more reasonable to calculate concentration factors which are based on the enrichment of metals in the organism versus sedimentary concentrations rather than sea water concentrations. Such a compilation appears in Table II. It is interesting to note that these molluscs show a higher level of cadmium, lead, and zinc than sediments.

TABLE II

Concentration factors for heavy metals in marine molluscs based on sediment concentrations

Element	Concentration factors		
	Scallop	Oyster	Mussel
Cd	>12.45	> 1.75	> 0.5
Cu	0.088	0.402	0.088
Fe	0.040	0.009	0.027
Mn	0.160	0.015	0.039
Ni	0.027	0.009	0.032
Pb	> 3.2	> 2.0	> 2.4
Zn	> 2.83	> 11.03	> 0.91

Data from Brooks and Rumsby (1965).

Note: In this table

$$CF = \frac{\text{ug element/g organism, dry weight}}{\text{ug element/g sediment, dry weight}}$$

The above line of reasoning can be projected to the calculation of enrichment factors in pelagic species. These concentration factors could be based on metal concentrations in suspended material or some combination of water and particulates. Such considerations are, however, beyond the scope of this study. The important point is that continued misuse and disposal of metals will lead to a higher level of these potentially toxic contaminants in our waters and in organisms. Such a result could have only a harmful effect on mankind. It is thus important to monitor and regulate metal inputs, to determine toxicity levels of metals, and to discover the pathways of metal transportation in the environment.

Purpose of the study

The overall purpose of this study is to determine whether man is significantly contributing to the accumulation of heavy metals in the environments of San Antonio Bay, the Mississippi River Delta, and the coastal and deeper waters of the northwest Gulf of Mexico. The study uses the metal concentrations in the sediments to make the evaluation. The sediments are useful indicators of man-introduced metals because the vertical distribution of metals in the sediments allows one to examine the record of past elemental inputs and because the horizontal distribution of metals in the sediments enables one to locate

point sources of metal inputs.

The commonly accepted procedure for environmental measurement of heavy metals in the sediments involves an acid leach (EPA, 1969). One purpose of this study is to examine both the usefulness and thoroughness of the sediment acid leaching process. Such consideration will include a comparison of different acid leaches with total metal content.

To properly evaluate the significance of sediment metal concentrations, there are a number of factors which have usually been taken into consideration. These factors include the enrichment of metal concentrations by the presence of clay and organic carbon and the dilution of metal concentrations by the occurrence of quartz and carbonate (Potter et al., 1963; Moore, 1963; Piper, 1971). In addition to the above factors, it is also important to know both the natural and artificial sources of metal input for the particular area of study. The measurement and utilization of such parameters is an important part of this inquiry and one which has sometimes been neglected in environmental studies.

Since this investigation encompasses river, bay, deltaic, coastal, and deeper water sediments, a study of the relative metal concentrations of these areas is pertinent. The recent accumulation of knowledge on deep-sea sediments has sparked interest in examining the differences between near-shore and deep-sea sediments and in hypothesizing mechanisms for transport

of metals from the continents to the oceans (Goldberg and Arrhenius, 1958; Turekian and Imbrie, 1966; Turekian, 1968). A goal of this study is to point out the differences observed among the varied environments and how these observations relate to described mechanisms for the transport of metals to the deep sea.

The effect of oyster shell dredging on central Texas bays has been a much debated subject. One proposed adverse effect of dredging concerns the heavy metals. It is possible that remobilization of metals in the sediments during the dredging process may increase the metal concentration of both the water and the finer grained, slower settling particles which form a new surface sediment layer in the dredge spoil. Such enrichment would have a potentially harmful effect on the biota of the area as the metals would be physically more available. This paper examines suspended matter and surface sediments from inside and outside dredge areas for the purpose of judging the effect of the dredging on the remobilization and surface accumulation of metals.

Survey of pertinent literature

The bays and coast of the northwest Gulf of Mexico, including the Mississippi River Delta, have been the subject of numerous papers; however, many of the publications have been concerned

with the geology and biology of the area. San Antonio Bay and the northern coast of the Gulf of Mexico were part of an intensive study under A.P.I. Project 51. As part of this project, Shepard and Moore (1955, 1960) reported on sedimentary structures, sediment particle sizes, total carbon and carbonate values for the sediments, and on sediment deposition rates for the Central Texas bays and coast. Also included in Project 51, Grim and Johns (1954) and Johns and Grim (1958) determined clay mineralogies and made total silicate analyses for a great number of sediment cores from San Antonio Bay, the Mississippi Delta, and the northern Gulf of Mexico. Hall (1973) has re-evaluated sediment texture, sedimentary structures, and mineralogy as part of his study of San Antonio Bay. A number of similar supportive geological studies for the northwest Gulf of Mexico are also available. These include the following: mineralogies and sedimentation rates for the Mississippi River Delta (Griffin, 1962); Mississippi River Delta mineralogies (McAllister, 1964); particle size and mineralogy data for the northern coast of the Gulf of Mexico (Scafe and Kunze, 1971); and particle size and mineralogical information for the Mississippi Delta (Tieh et al., 1973).

The two most extensive studies of metal distributions in the sediments of the northwest Gulf of Mexico are those of Tieh and Pyle (1972) and Holmes (1974). Included in the Tieh and Pyle (1972) study were iron, manganese, nickel, and zinc analyses

and a conclusion that, excluding manganese and zinc, there is little difference in the trace element content of near-shore and abyssal plain sediments. Holmes (1974) surveyed 1,304 surface sediment samples from the northern Gulf of Mexico shelf for 23 metals including iron, manganese, lead, copper, and nickel. The Holmes (1974) study showed high metal concentrations at Galveston Bay and the Mississippi Delta.

In addition to these major studies, Davis (1968) determined manganese, nickel, copper, zinc, and lead in the northwest Gulf of Mexico and Galveston Bay; Custodi (1971) measured mercury concentrations throughout the Gulf of Mexico; and Tieh et al. (1973) included manganese, iron, and nickel in their study of the inner continental shelf off the Louisiana coast. Hann and Slowey (1972), in an environmentally oriented study, analyzed the sediments of Galveston Bay and the Houston Ship Channel for ten potentially toxic metals. A heavy metal study of San Antonio Bay sediments does not appear in the literature.

A number of studies, not specifically concerned with the Gulf of Mexico, have increased our knowledge of methods for determining sources of metals, the pathways of metal transport, and factors controlling the concentration of metals in sediments (Goldberg and Arrhenius, 1958; Hirst, 1962; Moore, 1963; Piper, 1971; Shimp et al., 1971; and Frye and Shimp, 1973). These investigations have been a valuable source for ideas used in this study.

METHODS OF INQUIRY

Sampling

The sediment samples for this study were collected on four separate field investigations. Samples from San Antonio Bay, Texas were gathered on June 8 and 9, 1972 and January 27, 1973 from the 46 foot long shrimp boat Sandy. Six sampling stations off the central Texas coast were made during cruise 73-A-9 of Texas A&M University's R/V Alaminos (June 11-15, 1973). Sediments from the region of the Mississippi River Delta were taken in the period July 16-27, 1973 on cruise 73-L-2 of the University of Texas' R/V Longhorn. Sampling sites were located by visual piloting in San Antonio Bay and by LORAN positions aboard the Alaminos and the Longhorn.

In each case, the sediment samples were obtained with a two meter long, five centimeter diameter, gravity coring device equipped with a plastic liner. Upon retrieval of the core, the sediment was extruded on to a half-round PVC tray. Several sections were separated for metal determination, placed in plastic containers, and kept refrigerated until time of analysis. Special care was taken throughout the sampling operations to avoid heavy metal contamination which may occur if the sample is brought in contact with a metal surface. Initial sample preparation involved drying a 50-100 gram aliquot of wet sediment at

105°C and then reducing it to a fine powder with a porcelain lined Spex mixer-mill.

Acid leaching

For acid leaching of the sediments, a modification of the procedure of the Environmental Protection Agency (EPA, 1969) was used. Approximately two gram portions of dry, finely powdered sediment were weighed out and placed in tared 200 milliliter tall form Pyrex breakers. The samples were then heated for 8 hours at 450°C in a muffle furnace in order to ash the organic matter present. Our observations that there is no loss of the pertinent metals on heating to 450°C confirms those of Gorsuch (1970).

For the San Antonio Bay samples, the next step was to add 10 milliliters of concentrated, redistilled nitric acid to the ashed sediment and heat it on a hot plate to near dryness. The other samples were treated similarly except that the leaching solution consisted of 10 milliliters of the concentrated HNO_3 plus 5 milliliters of reagent grade 6 N HCl. Use of the latter leaching solution was found to increase the percentage of metal leached for all metals studied. The evolution of the leaching solution and comparative results of leaching experiments will be discussed in a later section.

The treated sample was then washed into a funnel and

filtered through Whatman #40 paper into a 25 milliliter stoppered graduated cylinder. Washing with 1 N HNO_3 was continued until the filtrate had a volume of 25 milliliters. The graduated cylinder was then shaken and the solution emptied into a 13 dram polystyrene snap-cap vial.

Lead, nickel, and copper, in all samples, and cadmium in the San Antonio Bay samples, were determined on the leached solution by direct aspiration into a Jarrell-Ash model 810 atomic absorption spectrophotometer. Iron, manganese, and zinc were determined after appropriate dilution by the same technique. The analytical wavelengths used for measurement and their respective sensitivities are listed in Table III. Standards were prepared in 1 N HNO_3 from Hartman-Leddon standard reference solutions.

Because the effects of the leaching solution vary with the nature of the sample, the preparation of standards with consistent matrices is very difficult. However, background absorbance due to the presence of large amounts of sodium, calcium and other elements in the acid leach make some correction imperative. One method of remedying the problem is to dilute the solution so that the effect of the background is negligible. This could be done for iron, manganese, and zinc in most of the samples. But, for the sediments analyzed in this study, low levels of lead, nickel, copper, and cadmium prohibited the diluting-out of their

TABLE III

Wavelengths, sensitivities, and precision for atomic absorption spectrophotometry

Element	Analytical Wavelength (nm)	Sensitivity (µg/mL/1% A)	Precision ¹ (%)	Flame Type ²	Non-absorbing Wavelength (nm)
Fe	248.3	0.07	<1	A/A	251.1
Mn	279.5	0.04	1-2	A/A	257.6
Pb	283.3	0.12	2	H/A	282.0
Zn	213.9	0.01	1	A/A	220.2
Cd	228.8	0.02	5	A/A	220.8
Cu	324.7	0.05	2	A/A	296.1
Ni	232.0	0.07	2	A/A	231.6

¹Precision was determined by averaging the % average deviation from the mean for replicate analyses of a number of samples.

²A/A = Acetylene/Air; H/A = Hydrogen/Air.

background matrices. Thus, to compensate for the problem, a non-absorbing wavelength near the analytical line of interest was used.

A non-absorbing wavelength for an element is one for which no absorbance is measured for relatively concentrated simple standards containing the element. However, when a sample with a substantial level of dissolved solids (eg. >1%) is aspirated, absorbance due to elements other than the element of interest is recorded by the non-absorbing wavelength. The analytical line for the element of interest records the absorbance due to the element plus the background matrix. Thus, by subtracting the absorbance measured by the non-absorbing wavelength from the absorbance of the analytical wavelength, one measures the true absorbance due to the element of interest. The non-absorbing wavelengths used in this study are listed in Table III.

The inability to make standards with proper background matrices may introduce one other problem. A background matrix may also have the effect of enhancing or, more often, depressing the absorbance signal. To properly correct for such a situation, it would be necessary to carry out a method of additions analysis while using the non-absorbing wavelength for background correction. A series of studies were carried out to determine the importance of this effect. In the cases of interest, namely lead, nickel, copper, and cadmium, the results, although not

extensive, showed a less than 5% depression of the absorbance signal due to the matrix effect.

In the analysis for cadmium, it was found that the absorbance due to the background matrix was often 50 to 80% of the total absorbance. To avoid this unsatisfactory condition, the cadmium content of a number of samples was determined with a Perkin-Elmer 303 atomic absorption spectrophotometer equipped with an HGA-2000 graphite atomizer. With this instrument, sensitivities 1000 times greater than those with the Jarrell-Ash spectrophotometer were obtainable. This permitted 500-1000 fold dilutions of the samples, thereby eliminating matrix problems.

Total dissolutions

To examine the thoroughness of the leaching process, total dissolution of 10 samples was carried out using HF-HNO₃ (Jeffery, 1970). Approximately 1 gram samples were dry-ashed at 450°C in a muffle furnace and then transferred to teflon beakers. A mixture of 10 ml of HF (48%) and 5 ml of 16 N HNO₃ was added to each sample and heated to dryness. The process was repeated twice, then the residue was dissolved in 5 ml of hot 2 N HCl. A reagent blank was also processed along with the samples.

The samples were filtered and diluted to 25 ml with 1 N HCl as described in the section on acid leaching. Analysis of lead, nickel and copper was made by direct aspiration into the

spectrophotometer and iron, manganese, and zinc were treated similarly after proper dilution. Background absorbance was monitored by using a non-absorbing wavelength as previously noted. The blank contained a small amount of zinc and apparently significant amounts of cadmium. For this reason, a measure of the thoroughness of acid leaching for cadmium does not appear in this study.

Calcium carbonate and organic carbon analysis

Calcium carbonate data from the San Antonio Bay area were available from Shepard and Moore (1955) and Ahr (1973). To supplement this data and to make analyses of the Mississippi River Delta and other coastal sediments, carbonate was determined by a manometric method (Presley, in preparation). The method is a modification of that described by Williams (1948) and involves the acidification of 1 gram of sediment (0-0.4g CaCO_3) with H_3PO_4 and the subsequent measurement of evolved CO_2 with a simple pressure gauge.

Organic carbon values from San Antonio Bay were available from Ahr (1973) and several independent measurements were made during this study using a Leco induction furnace. In this procedure, sediment samples (3-5g) were acidified in tared beakers to remove carbonate and then dried and reweighed to check weight change. From the carbonate free sediment, 0.25

gram samples were taken, mixed with copper oxide, tin, and iron accelerators and placed in the induction furnace apparatus. Carbon dioxide from the combustion of organic carbon was passed into a vacuum system, dried and purified, and measured manometrically.

Evaluating observed metal distributions

The main objective of this study is to make some conclusion about the observed metal distributions and how they do or do not show the influence of man. Where pollution is severe, the metal concentrations will be unmistakably high. However, where the metal concentrations in a given area show less than order of magnitude changes, it becomes more important to consider some of the factors which influence the normal distribution of metals in the sediments. It is only in this way that abnormalities can be elucidated.

The most common method for studying metal distributions has involved comparing metal concentrations with calcium carbonate, organic carbon, and percent clay. Depending on the area of study, one or more of these factors has been shown to have a significant effect on the metal distributions observed. For example, a large difference in metal concentrations may merely be a result of a dilution by a high carbonate concentration in one sample and not in another.

As a result of this investigation, it appears that the concentration of iron in the acid leachable fraction of the sediments shows a strong correlation with the trace metal content of a given sample. This may well be due to the ability of iron oxides and/or hydroxides to accumulate trace elements. Furthermore, the comparison of iron with trace metals seems to point out samples which have anomalous metal concentrations much the same way the other, more traditional factors have. This iron/trace-element relationship and its usefulness will be demonstrated more thoroughly in the results and discussion which follow.

RESULTS AND DISCUSSION

Sediment leaching

The use of a variety of leaching techniques to study the distribution of elements between different phases present in the sediments has received widespread attention (Hirst and Nichols, 1958; Mehra and Jackson, 1960; Chester and Hughes, 1967; Presley et al., 1972; Gibbs, 1973). For environmental studies of sediment metal concentrations, a strong acid leach has traditionally been used. The Environmental Protection Agency recommended a concentrated nitric acid leach in its 1969 Chemistry Laboratory Manual-Bottom Sediments. The philosophy behind such a rigorous treatment is that no greater concentration of metals than those removed by the leach are available to organisms.

As described earlier, the leaching solution used for the San Antonio Bay sediments was concentrated nitric acid. Prior to acidification, the samples had been pre-treated by heating to 450°C in a muffle furnace. This procedure is not included in the EPA method which uses H₂O₂ to oxidize organic matter. The EPA procedure also involves the adding and heating of HNO₃ to dryness twice. cursory studies showed the two leaches to be similar and thus use of the EPA procedure was rejected because it involved considerably more handling, chemicals, time, and led to foaming and mechanical loss of sample.

Later, during the course of this study, it became apparent that an HNO_3 -HCl solution increased the leached concentrations of iron and the other metals considerably. This more effective solution was thus adopted for further analyses. No direct comparison of the HNO_3 -HCl leaching method of this study with the EPA method is presently available. However, a comparison study with J.F. Slowey showed that the EPA and HNO_3 -HCl leaches consistently remove metals to within a 10% variation.

For the purposes of this investigation, the HNO_3 and HNO_3 -HCl leaching solutions have been compared for their thoroughness in removing metals. The total metal content of a number of sediments was determined by complete dissolution of the sediments in HF- HNO_3 to measure the degree of leaching accomplished by these two procedures. The results of this brief study, which appear in Table IV, show clearly that the HNO_3 -HCl solution is more effective in removing metals than the HNO_3 alone.

The amount of material leached by any given solution is, of course, a function of the type of sample used. One can see from the standard deviations given in Table IV that there is considerable variation in the removal of some of the trace metals from the leaching study. And, the average percent leached is very much biased by the choice of sample. For example, San Antonio Bay samples tended to have a lesser percent of the total metal content leached than open Gulf of

TABLE IV

Comparison of average percent metal leached from a variety of samples by two different acid treatments

Leaching Solutions	Fe leached		Mn leached		Pb leached		Zn leached		Cu leached		Ni leached	
	Ave. %	% of total	Ave. ppm	% of total	Ave. ppm	% of total	Ave. ppm	% of total	Ave. ppm	% of total	Ave. ppm	% of total
16N HNO ₃	1.82	59±6	721	81±6	16.6	79±9	68.1	61±11	12.2	61±16	23.4	79±14
16N HNO ₃ - 6 N HCl	2.20	71±3	771	87±5	18.0	86±10	76.2	69±20	14.8	76±14	26.4	89±8

Total dissolution	Ave. Fe(%)	Ave. Mn(ppm)	Ave. Pb(ppm)	Ave. Zn(ppm)	Ave. Cu(ppm)	Ave. Ni(ppm)
Hf-HNO ₃	3.10	886	20.9	110.4	19.5	29.7

Mexico sediments. The results are too limited to make any detailed comment on this observation. It seems logical that the acid leach removes most of the iron and manganese oxides and hydroxides with their associated trace-metals. Yet, the degree to which the clay mineral structure is disrupted has not been thoroughly investigated. The sample differences observed are, then, most likely a result of differences in the mineralogy of metal bearing phases.

A study of the amounts of iron, manganese, and chromium leached in a variety of HCl solutions for Bay of Roquebrune sediments yielded 61% Fe, 89% Mn, and 65% Cr with 12 N HCl (Fukai, 1965). Jones (1973) found that approximately 75% of the zinc, 60% of the cadmium, and most all the lead and copper were removed by a rigorous nitric acid and subsequent HNO_3 -HCl treatment. These results compare favorably with those found in this study.

Whether acid leaching of sediments is a viable method for environmental work is an important and unanswered question. The relative simplicity, reproducibility, and high metal yields are factors which favor its use. One must, however, be aware that the nature of the sediment sample and the leaching solution will effect the total percent of metal removed.

Heavy metal distribution - San Antonio Bay Area

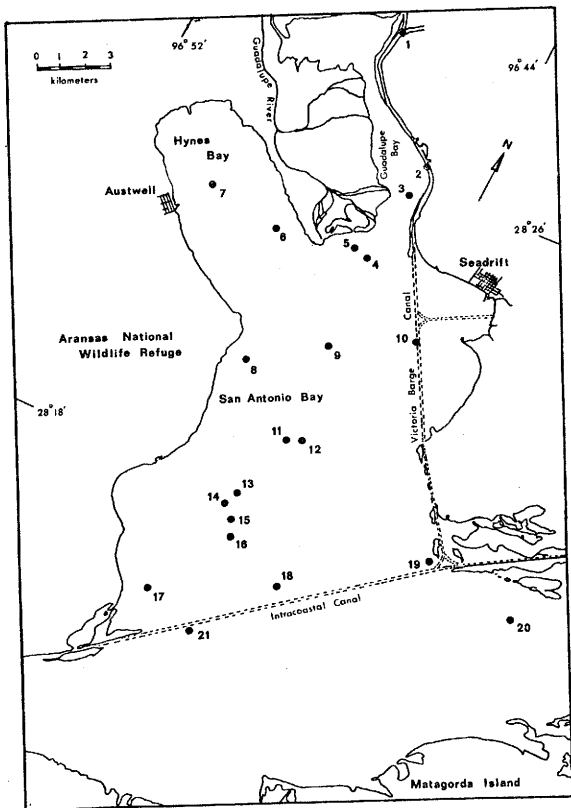
This study of heavy metal distribution in San Antonio Bay

and the surrounding area was part of an Environmental Impact Assessment on the effects of shell dredging. The study area is located on the central Texas coast as shown in the outlined area of Figure 9 (p. 57). A more detailed map of the bay (Fig. 1) shows that the San Antonio-Guadalupe River system, which enters the bay from the north, has built its delta southward into San Antonio Bay to form Hynes and Guadalupe Bays. San Antonio Bay proper, which has an average depth of less than two meters, is cut by the Intracoastal and Victoria Barge Canals.

The shallow bay water is well mixed and carries an average of 100 ppm total suspended matter (this study). There is a strong and seasonably variable north to south salinity gradient which is about $0-10^{\circ}/\text{oo}$ in winter and $0-25^{\circ}/\text{oo}$ in summer (Hall, 1973). Fresh water circulates southward along the west coast of the bay from the Guadalupe River and more saline water moves northwestward along the east coast of the bay from neighboring Matagorda Bay (Hall, 1973). The normal diurnal tidal fluctuation is 7.6 centimeters; however, hurricanes and high river runoff on occasion have increased normal water levels by up to 3.4 meters (Hall, 1973). Such drastic changes can obviously result in considerable mixing in the sediment column.

A total of 24 sediment cores were taken in the San Antonio Bay area. The locations of 21 of the sampling sites are shown on Figure 1. The remaining three cores were taken with a one

Fig. 1. Sampling sites in the San Antonio Bay area.



meter hand coring device several miles upstream in the rivers which feed into San Antonio Bay. Their locations, in order of decreasing distance from the bay, are as follows: river sample #1 is from the Guadalupe River at Rte. 236 near Guero, Texas; river sample #2 is from the San Antonio River at Rte. 239, Charco, Texas; and river sample #3 is from the Guadalupe River (after it joins with the San Antonio River) at Rte. 35.

The acid leachable heavy metal content was determined for 51 San Antonio Bay sediment samples after treatment with the HNO_3 leaching solution. Iron, manganese, lead, zinc, cadmium, copper, and nickel concentrations for these samples are listed in Appendix A. Precision was established by making replicate analyses on ten of the samples. A summary of the San Antonio Bay area data appears below in Table V.

TABLE V

Summary of leachable heavy metal concentrations for San Antonio Bay sediments

	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
Range	1.65 to 0.19	423 to 60	14.4 to 3.3	51.7 to 5.6	0.5 to 0.02	8.3 to 1.6	20.3 to 2.6
Mean	1.04	210	9.5	32.7	0.2	4.0	9.9
Stand. Dev. (of the mean)	0.36	79	2.7	10.3	0.09	1.5	3.6
Precision	± 0.04	± 6	± 0.7	± 0.9	± 0.02	± 0.5	± 1.0

Calculated average total heavy metal values for the San Antonio Bay area sediments are compared in Table VI with the total distributions found in Buzzards Bay, Massachusetts (Moore, 1963) and the deeper sediments of Lake Michigan (Frye and Shimp, 1973). Sediments of the upper 15 centimeters of Lake Michigan show considerable contamination and therefore were not used for comparative purposes. Because it is difficult to compare leachable metal concentrations from different studies, the total concentrations of the San Antonio sediments were used in Table VI. These were determined by calculating the metal concentrations on a carbonate-free basis and applying the average percent-leached-factor to convert to totals. With this adjustment, the iron, manganese, and zinc values of San Antonio Bay appear similar to those of Lake Michigan, yet higher than those of Buzzards Bay. The low copper, lead, and nickel values in San Antonio Bay may be indicative of lower natural levels in the bay area or man-influenced increases in the other areas. All three studies show overall lower metal concentrations than average shale or deep-sea clay.

The horizontal distribution of each of the seven heavy metals in the bay is quite similar. Figure 2 shows the lead concentrations in the surface sediments to be lower along the shoreline with higher values in the central part of the bay, south of the Guadalupe River Delta. Each of the other elements

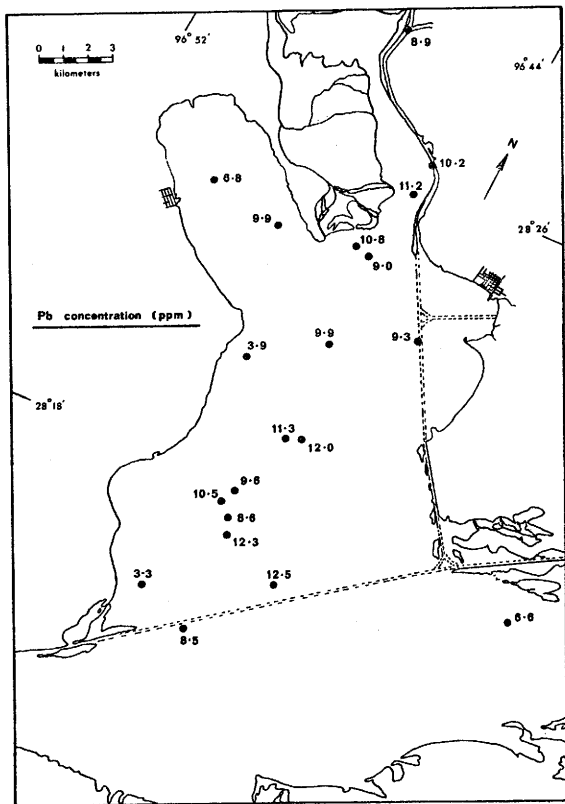
TABLE VI

Calculated average total heavy metal concentrations of San Antonio Bay sediments and comparisons with other studies

	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
San Antonio Bay area (this study)	2.19	322	14.9	66.6	0.2 ¹	8.2	15.6
Buzzards Bay, Massachusetts (Moore, 1963)	1.47	180	27	51	-	18	11
Lake Michigan (from depths >15 cm) (Frye and Shimp, 1973)	2.49	387	20	66	-	20	35
Average shale (Krauskopf, 1967)	4.7	850	20	80	0.3	57	95
Deep-sea clay (Turekian and Wedepohl, 1961)	6.5	6700	80	165	0.42	250	225

¹Acid leachable concentration.

Fig. 2. Lead concentration (ppm) in San Antonio Bay area surface sediments.



shows a similar pattern.

According to previous discussion, carbonate and organic carbon concentrations, as well as sediment particle sizes, may influence heavy metal distribution. Calcium carbonate data, available from Shepard and Moore (1955), Ahr (1973), and this study, is tabulated in Appendix B. The means and standard deviations of each investigator's data are as follows: Shepard and Moore (1955), $21.4 \pm 4.5\%$ CaCO_3 ; Ahr (1973), $21.3 \pm 5.3\%$ CaCO_3 ; this study, $19.4 \pm 5.1\%$ CaCO_3 . It is evident that the calcium carbonate content is reasonably high, yet rather uniform. The high levels of carbonate may contribute to the low metal levels in the bay because CaCO_3 is usually low in heavy metals (Graf, 1962). However, a series of scatter plots showed a low correlation between metal concentrations and carbonate content. This is most likely a result of the narrow range of carbonate values.

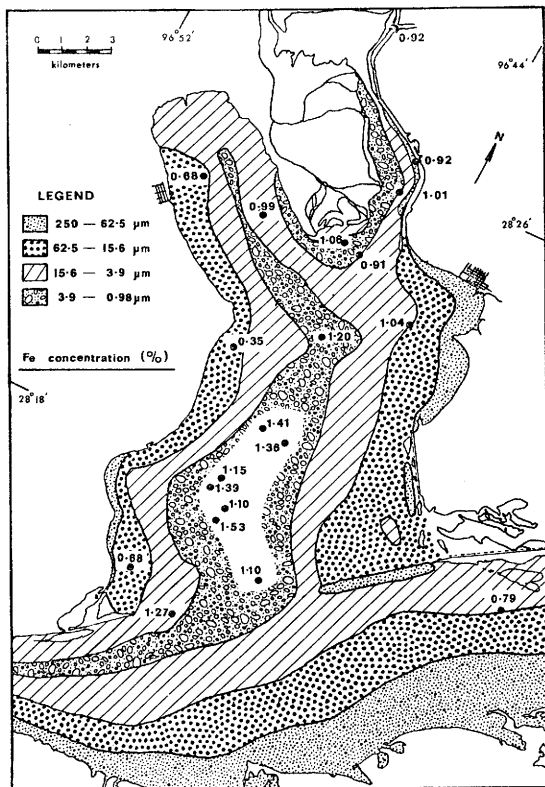
The organic carbon content of the San Antonio Bay sediments was determined for a limited number of samples by Ahr (1973) and in this study (see Appendix B). The means and standard deviations are $0.65 \pm 0.15\%$ organic carbon (Ahr, 1973) and $0.68 \pm 0.30\%$ organic carbon (this study). As in the carbonate study, the values are rather uniform and there is a very low correlation between sediment metal concentrations and organic carbon content.

Mean particle size data for the bay sediments, presented in Figure 3, are from Hall (1973). Superimposed on the grain size map are the iron values determined by this study. The pattern of lower metal values near shorelines and higher metal values in the central part of the bay is again observed. However, it is now evident that sand size particles ($>62.5\mu\text{m}$) predominate near the coastline and clay size particles ($<3.9\mu\text{m}$) are found in the central bay, south of the Guadalupe River Delta. A linear regression analysis of the iron and % clay content yields a correlation coefficient of 0.82. The correlation increases to 0.87 when the iron is calculated on a carbonate-free basis.

It appears that particle size is a major distribution-controlling factor for iron concentration in San Antonio Bay sediments. By plotting the other surface sediment metal concentrations on the mean grain size map, one continues to observe higher metal content where there is more fine grained material. The only discrepancies of note are nickel values at stations 1, 2, and 3, and the cadmium value at station 3. The river samples, which are not shown on the grain size map, are higher than the average bay sediments in lead, cadmium and copper. These few anomalies will be considered momentarily.

Changes in metal concentration with depth in the sediment column were not consistent. In some cores, concentrations decreased with depth while in others the concentrations increased.

Fig. 3. Mean grain size map of San Antonio Bay area surface sediments with surface sediment iron concentrations (%) superimposed (Grain size data from Hall, 1973).



It was observed that in most cases these vertical variations were similar for all elements. To evaluate the vertical dimension more fully, eleven cores for which the sediment mean grain size was less than $15.6 \mu\text{m}$ were considered. Surface sediment concentrations for these eleven cores were averaged and compared with the average deeper sediment values of the same eleven cores (Table VII). The mean depth of the non-surface samples was greater than 100cm. The top sections showed slightly higher values for iron, lead, zinc, copper, and nickel. However, considering the stipulated error limits (Table V), the top and bottom concentrations are all very nearly equivalent.

The next logical step in this study of vertical distributions is to arrive at a time over which the metal concentrations may have remained the same. Shepard and Moore (1955) calculated a sedimentation rate of 23 centimeters per 100 years for San Antonio Bay from carbon-14 dating. Moore (1955) used forams to arrive at a San Antonio Bay sedimentation rate of 21 centimeters per 100 years. Although the sedimentation rate is not uniform throughout the bay, these data represent a reasonable approximation. The crudest of calculations would thus yield a maximum age of 400-500 years for the deeper sediments analyzed in this study. This calculated age is based on an ideal sediment column in which sediments are gradually buried

TABLE VII

Concentrations of heavy metals in surface sediments vs. subsurface sediments
in San Antonio Bay

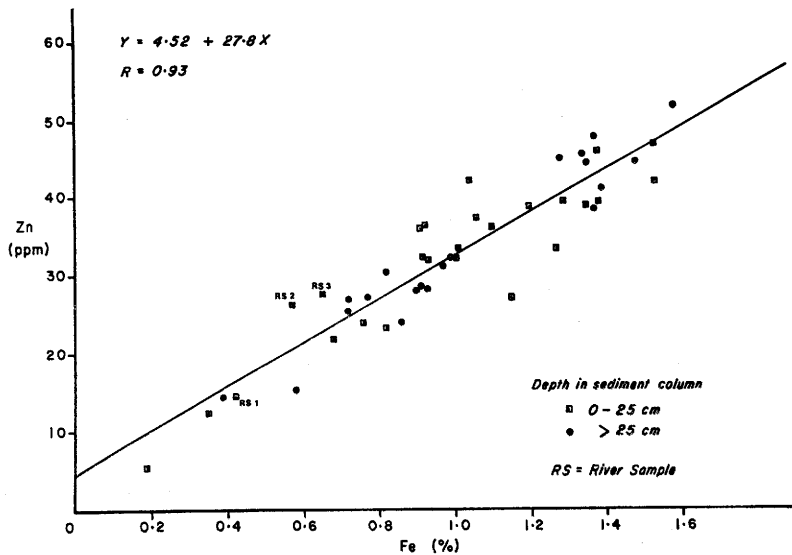
Depth in Sediment Column		Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
Surface sediments (0-15cm)	Mean	1.15	226	10.0	37.1	0.2	4.2	12.1
	Range	1.53-0.91	280-194	12.3-8.5	46.8-31.9	0.2-0.1	5.8-2.5	20.3-7.9
Subsurface sediments (ave. depth) 100cm	Mean	1.16	246	9.8	37.2	0.2	4.2	10.9
	Range	1.58-0.72	314-107	15.9-5.4	51.7-26.8	0.3-0.1	8.1-2.1	15.1-5.4

and remain undisturbed. However, the simple observation of a small boat stirring up the sediments of the less than two meter deep bay water destroys any thoughts of ideal behavior. Bio-turbation, tides, storm surges, and dredging certainly make significant contributions to the mixing of the sediments. Thus, while the 24 meter deep sediments dated by Moore may be 9500 years old, it is difficult to extrapolate an age to sediments only one meter deep.

An interesting insight into the heavy metal distributions of the San Antonio Bay area is derived from examining scatter plots of element ratios. Figure 4 shows zinc concentrations plotted as a function of the iron values. The close correlation of zinc with iron in the acid leached portion of the sediments supports the assumption that trace elements, such as zinc, are associated with mixtures of oxides and/or hydroxides of iron. Furthermore, the significant correlation of leachable iron with percent clay discussed earlier is indicative of increased adsorption of these iron oxides and hydroxides on fine clay surfaces.

It may be assumed that the strong linear relationship of zinc and iron is a function of the natural zinc to iron ratio resulting from rock weathering in the San Antonio-Guadalupe River basin. It follows, then, that the introduction of zinc into the bay area from non-natural sources would result in data

Fig. 4. Scatter plot of zinc vs. iron concentrations for San Antonio Bay area sediments.



points which deviate from linearity on the zinc to iron scatter plot. This, of course, assumes that artificial sources of iron would not be high enough to influence the greater than 1% iron naturally present. Such normalizing of trace element values to iron may well serve as a useful indicator of man-introduced heavy metals.

Figures 5 and 6 show nickel versus iron and lead versus iron scatter plots for the San Antonio Bay sediments. Both plots show an overall linear relationship. Points which deviated from the general linear trends by several times the error limits of the analysis were statistically rejected in the regression analysis leading to the equation for the line, but are shown on the diagrams.

Nickel concentrations (Fig. 5) deviate considerably from the expected values at sampling sites 1, 2, and 3 and to a lesser extent at sites 4 and 5. Lead (Fig. 6) shows anomalous values in the three river samples, in the surface sediment at site 18, and in one deeper sediment sample from stations 5 and 11. Although not schematically presented in this study, manganese showed no anomalous values; copper was deviant in the three river samples, in surface sediments at sites 3 and 10, and in one deeper sediment sample at stations 1 and 21; and cadmium appeared high in the three river samples, in the surface sediments at station 3, and in a deeper sediment sample of site 6.

Fig. 5. Scatter plot of nickel vs. iron concentrations
for San Antonio Bay area sediments.

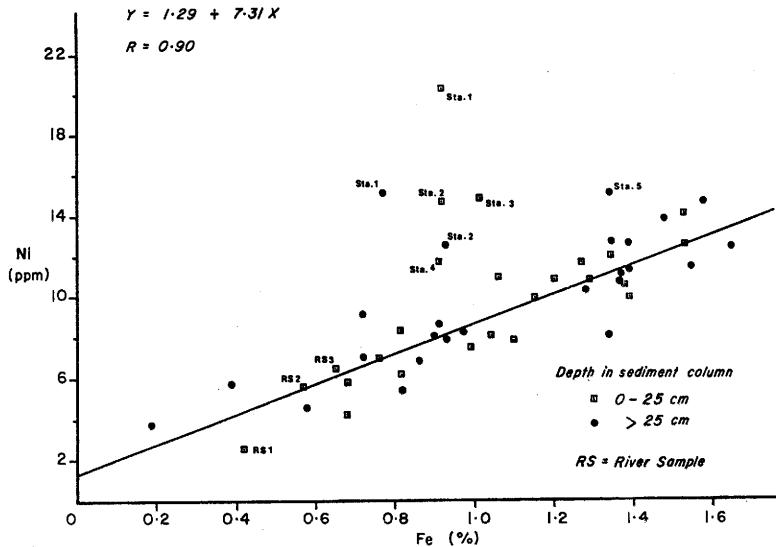
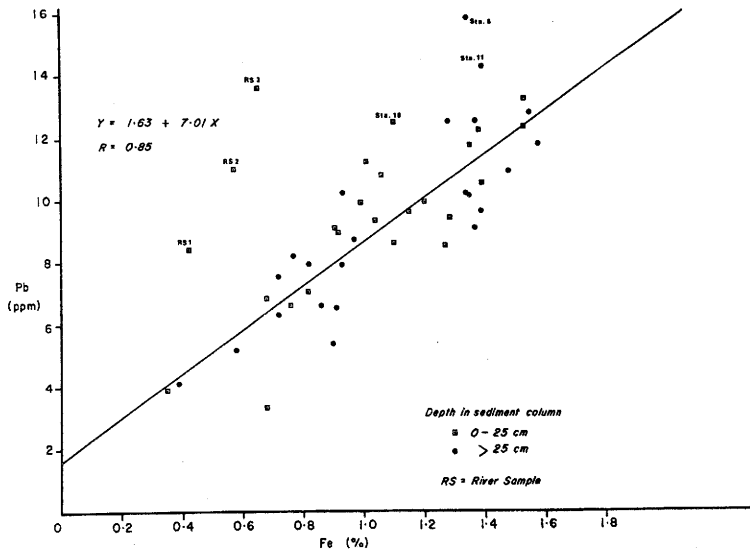


Fig. 6. Scatter plot of lead vs. iron concentrations
for San Antonio Bay area sediments.



In order to make a more conclusive study of the normalizing to iron process, heavy metal analyses of sediments from Galveston Bay, Texas (Hann and Slowey, 1972), an area known to show contamination, were plotted versus iron. A sample plot of zinc to iron is shown in Figure 7. Stations 1, 10, and 11 appear anomalously high. The same three stations showed deviations from linearity for lead, arsenic, chromium, cadmium, mercury, and copper. These high areas are near the Houston Ship Channel and the industrial area of Texas City, respectively. Furthermore, the Houston Ship Channel showed no significant metal to iron correlation (see Fig. 8). And, when the least-squares line from Galveston Bay was superimposed on the channel data, the anomalies were most dramatic.

At the low metal levels of near-shore sediments, it appears that normalization of these trace constituents to iron is useful in isolating anomalous values. This process is especially helpful where the deviations are more subtle than those of the Houston Ship Channel. However, the task of relating the anomalies to a particular artificial source is more difficult.

Shell dredging - San Antonio Bay

Oyster shell dredging in San Antonio Bay annually produces over 5 million cubic meters of shell material (Bouma, 1973). This represents about 66% of the total shell production in all

Fig. 7. Scatter plot of zinc vs. iron concentrations for Galveston Bay sediments (Data from Hann and Slowey, 1972).

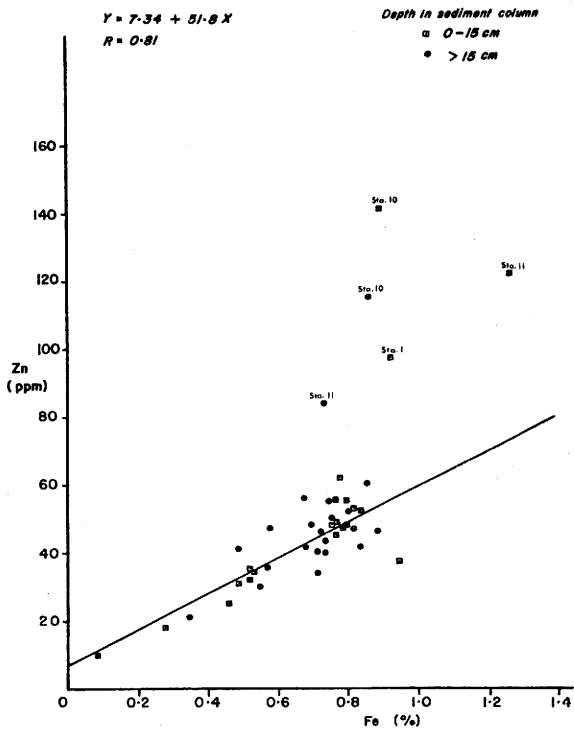
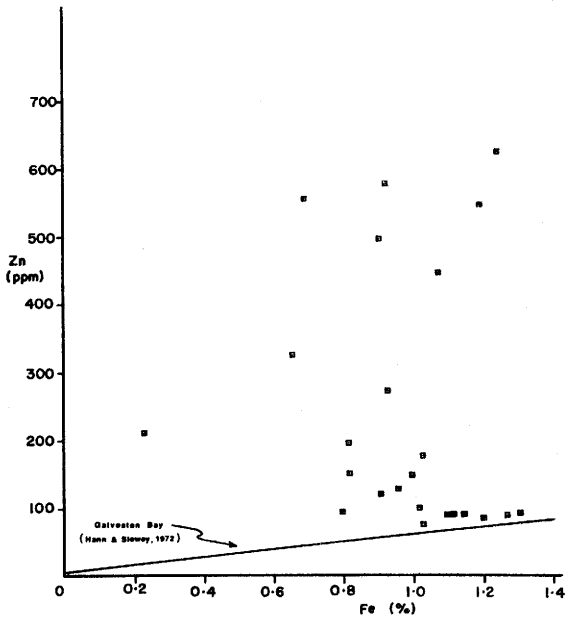


Fig. 8. Scatter plot of zinc vs. iron concentrations for Houston Ship Channel surface sediments (Data from Hann and Slowey, 1972).



Texas bays. San Antonio Bay is also a rich nursing ground for shrimp. The purpose of the Environmental Impact Assessment was to determine what effect the dredging operations had on the biota of the bay and the adjacent bird sanctuary in the Aransas National Wildlife Refuge.

The most common concerns of dredging and spoil disposal operations in estuarine waters are the adverse effects of increased turbidity and reduced dissolved oxygen content of the waters due to dredging (Bella and McCauley, 1972). However, secondary considerations focus on the potential of adding toxic metals, pesticides, or H_2S to the water column as a result of disturbing the large reservoir which the sediments may represent. With reference to metals, analyses of San Antonio Bay water samples for cadmium, lead, manganese, copper, arsenic, and mercury yielded very low concentrations which would be more typical of clear sea water far from shore than estuarine water (Presley, 1973). A possible explanation given for the observed low values was adsorption of the metals onto the surfaces of the abundant suspended matter.

If the dredging process resulted in the remobilization of sediment metals, then one would expect this increase to be observed in the water, which it was not, or in the suspended matter, or the very fine particles which have slowly settled and formed a new sediment surface. One suspended matter sample

from a dredged area and one from a non-dredged area of the bay were subjected to a nitric-hydrochloric acid leach. The trace element concentrations for both samples plotted within normal ranges on the metal to iron scatter plots for the San Antonio Bay area.

Finally, five pairs of sampling stations had been taken such that one of each pair was obtained from within a dredge cut and the other sample was taken at a considerable distance from the corresponding dredged area. Surface sediment concentrations for the five dredged areas have been averaged and compared with those for the five undredged areas (Table VIII).

TABLE VIII

Surface sediment metal concentrations in dredged vs. non-dredged areas of San Antonio Bay

	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
Dredged areas	1.24	262	10.1	38.4	0.2	4.5	10.6
Non-dredged areas	1.29	251	11.3	39.1	0.2	4.4	11.5

Surface sediments in the dredged and undredged areas are, within error limits, equivalent.

From the preceding data, it appears that there has not been any significant remobilization of heavy metals due to dredging in San Antonio Bay. These results substantiate those of Ahr (1973) who found that dredging did not increase

the number of favorable sites for pesticide adsorption and did not create a hazard by resuspending large amounts of chlorinated hydrocarbons.

Heavy metal distribution - Northwest Gulf of Mexico

Scruton (1956) determined that 70-75% of the annual sediment load of the Mississippi River initially moves westward into the area of the northwest Gulf of Mexico. The sediment load of the Mississippi River comes from the drainage of about one-half the total land area of the United States and represents two-thirds of the United States' river-borne suspended material (Curtis et al., 1973). Several major cities dispose of municipal and industrial wastes in the Mississippi River and vast farm areas are also drained by the river. For these reasons, study of the discharge area of the Mississippi River, namely the delta region and the northwest Gulf of Mexico, is a useful way of assessing the extent to which heavy metal disposal from the activities of man is impinging on the marine environment.

Twenty-four sediment cores from the northwest Gulf of Mexico, including the Mississippi River Delta, were chosen for this study. The locations of nine of the sampling sites are shown on Figure 9. The positions of the remaining 15 sites are plotted on the expanded scale map of the Mississippi River Delta region (Fig. 10). Sediments from this area were taken

Fig. 9. Locations of San Antonio Bay area, Mississippi River Delta region, and other sampling sites on the northwest coast of the Gulf of Mexico.

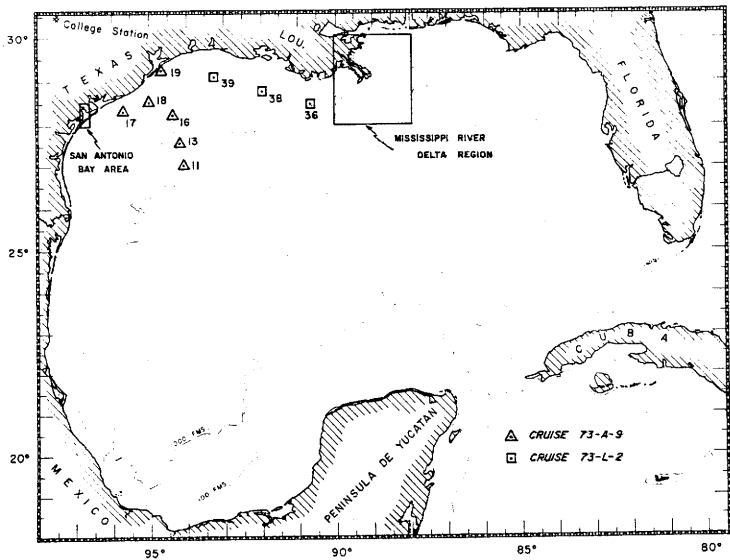
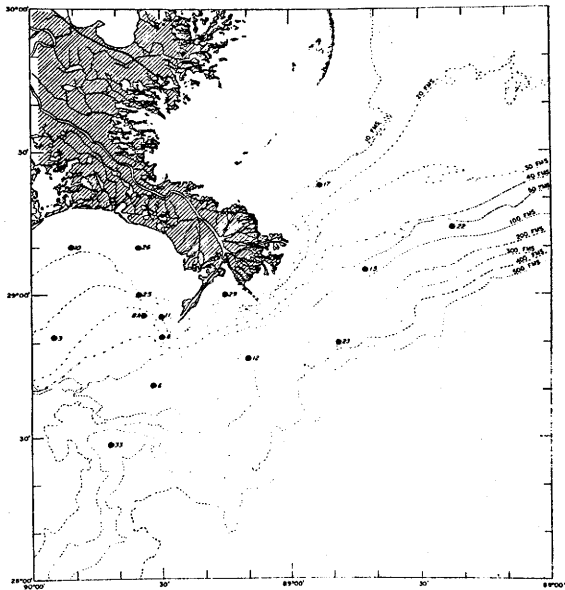


Fig. 10. Sampling sites in the Mississippi River Delta region.



from waters which ranged in depth from 7.6 to 1210 meters and had surface water salinities of 13 to 35⁰/oo. Sediment pore waters all had salinities between 33 and 36⁰/oo. Positions, water depth, and salinity data for the 24 stations are tabulated in Appendix C.

A total of 72 sediment samples from the 24 northwest Gulf of Mexico sites were acid leached with the HNO₃-HCl leaching solution. The iron, manganese, lead, zinc, cadmium, copper, and nickel concentrations determined for these samples are listed in Appendix D. A summary of the data appears below in Table IX.

TABLE IX

Summary of leachable heavy metal concentrations of northwest Gulf of Mexico sediments

	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
Range	3.34 to 0.53	2067 to 61	34.4 to 4.9	132.3 to 17.6	0.8 to 0.02	24.8 to 2.0	38.8 to 5.1
Mean	2.18	462	16.5	73.8	0.3	11.4	22.6
Stand. Dev. (of the mean)	0.72	340	7.1	26.5	0.2	5.2	8.2
Precision	±0.05	±9	±0.9	±2.1	±0.03	±0.8	±1.6

By calculating the leachable metal concentrations of this study on a carbonate-free basis and applying the average percent-leached-factor, a total sediment value was obtained for the northwest Gulf of Mexico sediments. These revised data are

compared with the studies of other investigators in Table X. The northwest Gulf of Mexico sediments have consistently higher metal concentrations than those of San Antonio Bay. The manganese, zinc, and copper values of Davis (1968) are about the same as the northwest Gulf of Mexico concentrations of this study. Lower values obtained by the Holmes (1974) study are a result of a greater number of shallow water sampling sites and the reporting of the data as a geometric mean. The shelf sediments of this study and the comparative studies have lead, zinc, and cadmium values equivalent with average shale, yet lower than deep-sea clay.

Calcium carbonate concentrations for the northwest Gulf of Mexico samples studied, excluding 73-A-9 stations 11 and 13, averaged only 3.3% and showed little variation (see Appendix D). There is, also, no consistent trend in carbonate content versus metal concentrations for these samples. Organic carbon was determined for only a few samples but showed higher values at the mouth of the Mississippi River ($0.90 \pm 0.18\%$ organic carbon) than in the remaining areas of the northwest Gulf of Mexico ($0.46 \pm 0.15\%$ organic carbon).

Particle size data from Tieh et al. (1973) show clay percentages of from 21 to 52% in the area of Southwest Pass and from 0 to 15% in the area of stations 36, 38, and 39 off the coast of Louisiana. The Tieh et al. (1973) study also shows a high correlation of iron concentration with the percent

TABLE X

Calculated average total heavy metal concentrations of northwest Gulf of Mexico sediments and comparisons with other studies

	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
Northwest Gulf of Mexico (this study)	3.17	549	19.9	110.6	0.3 ¹	15.5	26.3
San Antonio Bay area (this study)	2.19	322	14.9	66.6	0.2 ¹	8.2	15.6
Shelf of No. Gulf of Mexico (Davis, 1968)	-	498	<50	86	-	20	63
Northwest shelf and slope, Gulf of Mexico, (Holmes, 1974) ²	1.51	401	24	-	-	10	19
Gulf of Mexico (<15% CaCO ₃) (Tieh and Pyle, 1972)	3.45	1284	-	67	-	-	93
Average shale (Krauskopf, 1967)	4.7	850	20	80	0.3	57	95
Deep-sea clay (Turekian and Wedepohl, 1961)	6.5	6700	80	165	0.42	250	225

¹ Acid leachable concentration.

² Metal values expressed as the geometric mean.

clay in the northwest Gulf of Mexico.

An analysis of the heavy metal distribution in the surface sediments of the Mississippi River Delta region shows higher values in the immediate area of Southwest Pass. A decreasing horizontal gradient of metal concentrations extends in a southwestward direction from the pass. The path of the gradient approximates that of surface currents and sediment flow (Scruton, 1956). Lead and cadmium show this pattern quite well (Figs. 11 and 12). In the other areas of the delta and along the coast of western Louisiana and eastern Texas the sediment metal concentrations are lower than at Southwest Pass. One obvious exception to this pattern is the high cadmium value at 73-A-9 station 19 which is located just outside Galveston Bay.

As in the San Antonio Bay area study, use of the iron to trace metal ratio is a rapid and seemingly reliable method for elucidating anomalous heavy metal concentrations. The zinc versus iron scatter plot for the northwest Gulf of Mexico (Fig. 13) shows only one or two possible deviations from the strong positive linear relationship. However, the lead versus iron scatter plot (Fig. 14) reveals a far greater number of anomalies. It is most interesting to note that the sampling sites which are high in lead relative to iron (stations 6, 8, 8A, 11, 25, and 29) are those which are in the main sediment

Fig. 11. Distribution of lead in the surface sediments
of the northwest Gulf of Mexico.

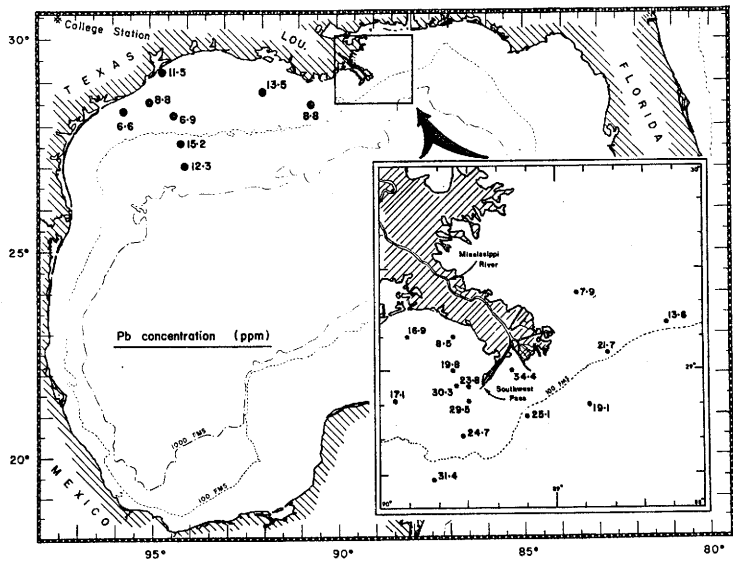


Fig. 12. Distribution of cadmium in the surface sediments
of the northwest Gulf of Mexico.

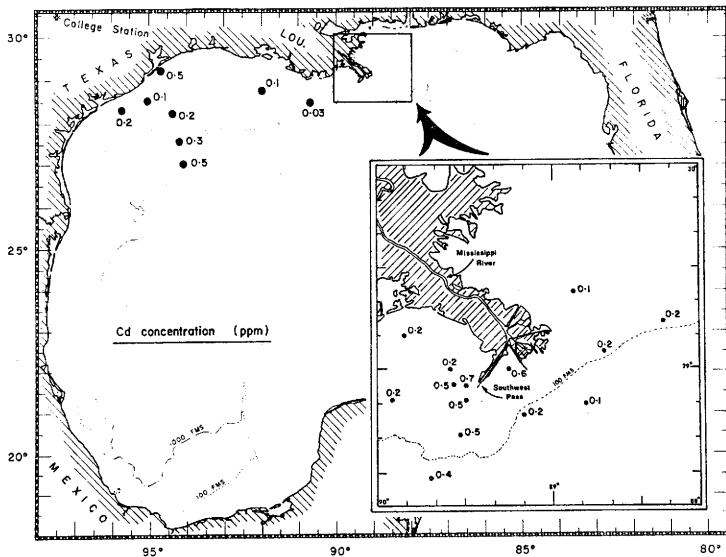


Fig. 13. Scatter plot of zinc vs. iron concentrations for northwest Gulf of Mexico sediments.

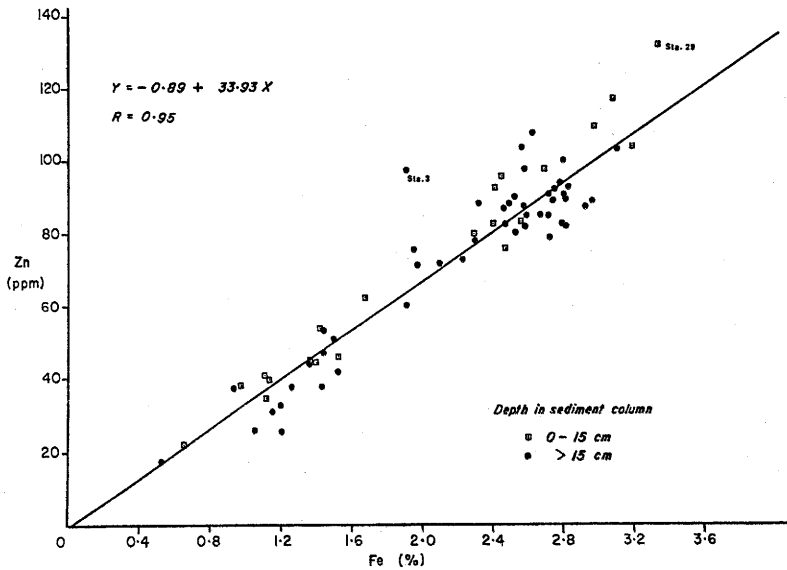
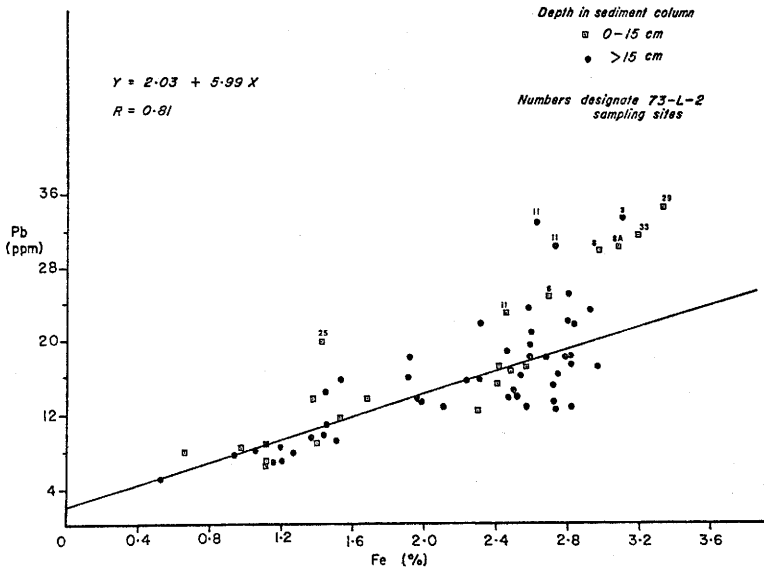


Fig. 14. Scatter plot of lead vs. iron concentrations for northwest Gulf of Mexico sediments.



transport path from the Southwest Pass area.

The heavy metal to iron scatter plots are not all presented in this paper. The observed relationships are summarized as follows: manganese shows exceptionally large deviations from the standard line in surface sediments at deep-water stations 33(73-L-2) and 11(73-A-9) as well as smaller deviations in the subsurface sediments at sampling site 11(73-A-9); nickel behavior is similar to that of manganese in deep-water stations 11 and 33; copper concentrations are high relative to iron in the surface sediments of 73-L-2 stations 8 and 29 and throughout the entire 125 centimeters of sediment at 73-A-9 site 11; cadmium is high in surface sediments at 73-L-2 sites 6, 8, 8A, 11, and 29, in the surface sediments of 73-A-9 stations 11 and 19, and in the subsurface sediments of stations 11(73-L-2) and 19 (73-A-9).

In summary, the acid leachable concentrations of lead and cadmium, and to a lesser extent copper, were higher relative to iron in the sediments of the Southwest Pass area of the Mississippi River. Cadmium was also high just outside Galveston Bay. Manganese and nickel, and in one core, copper, showed enrichment in the sediments of the deep water stations off the Mississippi Delta and the central Texas coast. While the Mississippi River mouth anomalies seem indicative of man-introduced metals, the more isolated deep-water deviations may

be due to an enrichment process which has been observed in deep-sea sediments. The latter point will be considered momentarily.

The scatter plot for lead vs. iron (Fig. 14) showed that anomalous lead values were not entirely restricted to the surface sediments. Sampling sites 8 and 11 on the Mississippi Delta gave high lead values in the subsurface sediments as well. To investigate the vertical dimension more fully, surface and subsurface sediment metal concentrations from the Southwest Pass area have been compared with the remaining area of the Mississippi Delta and with the western section of the northwest Gulf of Mexico (Table XI).

An increased level of iron and most of the other heavy metals in the surface versus subsurface sediments is observed for the Mississippi Delta region. A slightly lower relative metal level is observed in the deeper sediments of the western part of the study area.

With the exception of lead and cadmium in the surface sediments of the Southwest Pass area, the heavy metal values for the northwest Gulf of Mexico are quite normal in their ratio to iron (i.e. they plot on the linear portion of the metal vs. iron scatter plots). Lead and cadmium, then, seem to show an enrichment in the more recent sediments at the mouth of the Mississippi River.

TABLE XI

Surface vs. subsurface sediment metal concentrations for selected areas of the northwest Gulf of Mexico

Area	Depth in sediment core (cm)	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
Southwest Pass (Sta. 6,8,8A, 11,33)	0-20	2.89	632 ¹	27.9	104.8	0.5	15.3	31.5
	>20 (ave=90)	2.71	543	21.2	90.2	0.4	14.1	27.8
Mississippi River Delta area (Sta. 3,10,12, 23,38)	0-20	2.53	468	18.3	87.5	0.2	12.6	24.7
	>20 (ave=100)	2.29	472	16.4	81.5	0.2	12.1	24.7
Western N.W. Gulf of Mexico (Sta. 13,16,17, 18,19)	0-15	1.52	270	9.8	49.7	0.2	6.4	15.5
	>15 (ave=60)	1.71	179	11.4	52.0	0.2	7.2	15.9

¹Mn concentration from Sta. 33 (1982ppm) not included.

The overall increase in metal concentrations in surface versus subsurface sediments is a rather interesting observation. A number of cores (stations 3, 6, 8, 8A, 12, 15, 23) show marked and consistent decreases in acid leachable metal content with depth. This leads to speculation on possible increased input of iron and associated heavy metals over time. Dean et al. (1972) have listed the seven heavy metals of this study, including iron, in their list of the ten heavy metals of most immediate environmental concern. Perhaps all seven metals are showing an increased flux into the marine environment as a result of man's activities, with lead and cadmium increasing at a faster rate than the others.

As in the San Antonio Bay study, any attempt to determine a meaningful difference in age between sediments in the 0-20 centimeter interval and deeper sediments is complicated by a number of factors. Ludwig (1971) has calculated a sedimentation rate of 2.5 centimeters per 100 years for the Mississippi fan sediments deeper than the 100 fathom isobath. Sedimentation rates as high as 1 centimeter per year have been calculated in the mainstream of the Mississippi River. Station 33 (at > 100 fathoms) shows markedly higher metal concentrations in the top 5 centimeters (see Appendix D). It is not, however, until greater than 30 centimeters that any leveling off of metal values appears to occur. At station 8A the higher metal levels are observed in the 0-10 centimeter interval. Although values

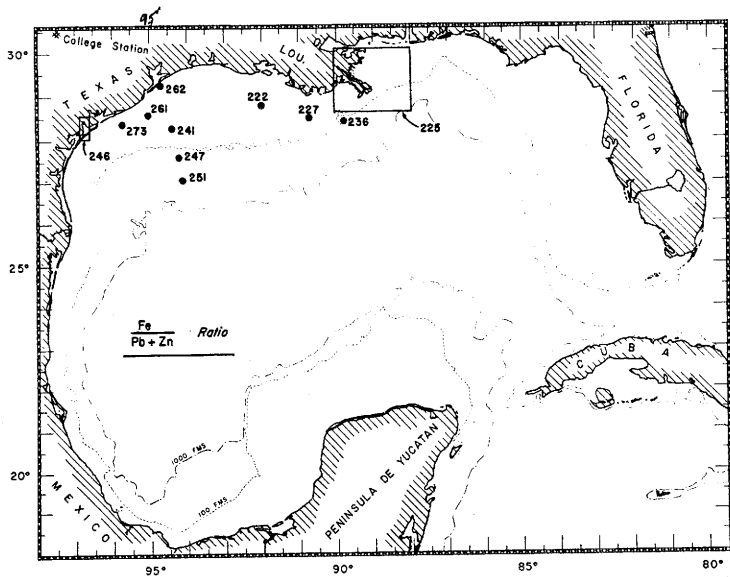
within the 10-30 centimeter region were not determined, the concentrations are quite consistent in sediments deeper than 30 centimeters. Based on a sedimentation rate of 50 centimeters per 100 years, the crudest of estimates would reveal that the increased metal levels of station 8A and the immediate South-west Pass area have occurred over the past 50-100 years.

Variations in metal concentrations between near-shore and deep-water sediments

The varied nature of the samples analyzed in this study and the characteristics of the leaching process used lend themselves to a consideration of the observed differences and similarities between the metal concentrations of near-shore and deep-water sediments. Such consideration is important in any attempt to follow the flux of metals from the continents to the deep sea.

An increase in the acid leachable metal content of the sediments from the inland rivers to San Antonio Bay and on to the near-shore and deeper waters of the Gulf of Mexico is clearly observable. Lead and zinc concentrations increase in a rather constant ratio to iron from near-shore to deep-water sediments (Fig. 15). The relative constancy of the ratio is indicative of the association of lead and zinc with the iron phase of the sediments. However, a greater than 10% variance in the $\frac{\text{Fe}}{\text{Pb}+\text{Zn}}$ ratio is observed between the Mississippi Delta sediments and

Fig. 15. Iron to lead plus zinc ratios for the northwest Gulf of Mexico (with average values for the San Antonio Bay and Mississippi Delta areas).

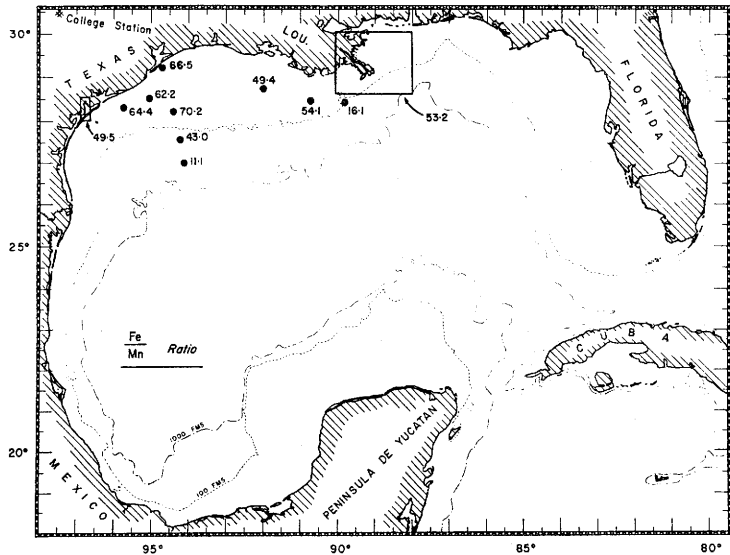


the western northwest Gulf of Mexico sediments. This deviation appears to point out the greater than natural levels of lead which are emanating from the Mississippi River.

A significant increase in the manganese concentration of the acid leached fraction of the sediments from near-shore to deep water has been previously pointed out. Figure 16 re-emphasizes this increase by showing a sharp change in the iron to manganese (Fe/Mn) ratio from shallow to deep water. Copper and nickel show this same trend, but to a lesser extent. It seems possible that the large increase in the manganese oxide and/or hydroxide phase may have resulted in an associated increase of copper and nickel.

Turekian (1967) points out that in deeper waters the sediments are composed of a greater number of finer particles. These particles, which have a higher surface area, may adsorb higher levels of iron and manganese oxides and hydroxides. Trace elements are scavenged by and become associated with these oxides and hydroxides. Because finer grained material stays in suspension longer, it is this material, with its higher levels of certain adsorbed metals, which is transported to the deep sea. The question of interest concerns the point at which the majority of the metals become associated with the iron and manganese phases. Wedepohl (1960) proposes that the metals are gradually adsorbed from deep-sea water on the high surface area particles. Turekian (1967) hypothesizes that the metals are

Fig. 16. Iron to manganese ratios for surface sediments of the northwest Gulf of Mexico (with average values for the San Antonio Bay and Mississippi Delta areas).



adsorbed by the finer grained material in the rivers and that the metals are retained by these fine grained particles which are then transported to the deep sea.

This study has not been directed at answering this complex geochemical question. Most likely, both theories contribute to the observed deep-sea sediment enrichment of metals. Nevertheless, the more important consideration for this investigation is the ultimate fate of the metals and their availability to organisms.

While sediment metal concentrations are markedly higher in the deep sea, Goldschmidt (1937) and Goldberg and Arrhenius (1958) have shown that potentially toxic metals are relatively quickly removed to the sediments and that the bulk of sediments are deposited in the near-shore environment. The present study showed that greater than natural levels of lead and cadmium are in the sediments at the mouth of the Mississippi River. The concentrations appear to be greater in samples taken nearest the river mouth. This observed deposition of excesses fits the Goldschmidt and Goldberg and Arrhenius models.

If the bulk of the potentially toxic metals are being deposited in near-shore waters, it is important to know how available these metals are to organisms. The large amount of coarse sediment material and detritus being deposited at high rates in near-shore areas lowers metal concentrations considerably. This, in turn, reduces the absolute levels of metals

available to the important food source that coastal organisms represent. However, the degree to which organisms may accumulate metals and the levels of metal toxicity are still basically unanswered questions.

CONCLUSIONS

Studies of acid leaching of sediments have shown that there is considerable variability in the concentrations of heavy metals removed. This is a function of both the leaching solution and the nature of the sample. The value of the leach is that heavy metals are removed in a rather consistent ratio to iron in near-shore sediments. This study shows that scatter plots of the acid leachable heavy metal concentration versus the acid leachable iron concentration are useful indicators of man-introduced contamination.

The San Antonio Bay area sediments have a very low natural heavy metal concentration. However, a few locations in the area have sediment metal contents which exceed expected natural levels.

The San Antonio-Guadalupe River system, which feeds into San Antonio Bay, has higher than natural levels of lead, cadmium, and copper. The rivers drain the relatively large and industrial cities of San Antonio and Victoria, Texas. From the normalizing to iron scatter plots of this study, it appears that metal discharge into the river system has accounted for an approximate 50% increase in the expected natural surface river sediment content of lead, cadmium, and copper.

Nickel concentrations in the sediments of the Guadalupe Bay section of the San Antonio Bay area are anomalously high.

The rivers which feed into the bay do not show this trend. However, the presence of a large chemical company (plastics) upstream along the Victoria Barge Canal is a possible prospect for raising the natural nickel level of the area.

San Antonio Bay proper appears to have remained relatively free from metal contamination during its recent history. However, there are slight increases being observed at the mouth of the Guadalupe River. This is a subtle, yet positive indication of increased growth and industrialization in this central Texas area. Should the rivers continue to support a high "man-introduced" load of potentially toxic heavy metals, the bay may, in time, show the effects more seriously.

It seems clear that dredging operations in San Antonio Bay do not in any way redistribute heavy metals so as to make them more available to the biota of the area. This is most likely a function of the low natural levels of heavy metals in the bay. An important contributing factor is that dredging was not found to provide abundant surfaces for pesticide or metal adsorption (Ahr, 1973).

The open northwest Gulf of Mexico does not presently show an alarmingly high level of heavy metals in the sediments. However, surface sediments in the region of the Mississippi River Delta are 7-10% higher in iron and from 10-30% higher in other heavy metals than subsurface sediments. Cadmium and lead show 10-50% deviations from their expected ratios to iron

in the area of Southwest Pass. This anomaly extends over a rather wide range of area and gives a positive indication that large excesses of lead and cadmium are being transported to the Mississippi Delta.

The sediments of the western sector of the northwest Gulf of Mexico do not show widespread heavy metal contamination. Although Galveston Bay is known to be partially polluted with heavy metals (Hann and Slowey, 1972), any extension of this trend into the open Gulf of Mexico is limited.

Increased levels of manganese, nickel, and copper in deep-water sediments do not appear to be a function of man-introduced contamination. These metal "excesses" are due to a partially explained phenomenon whereby finer grained material adsorbs greater amounts of iron and manganese oxides and hydroxides. These oxides and hydroxides, in turn, selectively scavenge metals. In order to expand the iron normalization process to the deep sea, the use of an iron plus manganese base for comparison may be necessary.

While the heavy metal contamination of rivers, bays, and inland waterways is well documented, this study shows that the extension of this problem to open coastal waters of the Gulf of Mexico is very restricted. However, the increased level of heavy metals observed at the Mississippi River Delta represents both an important record of recent input and an ominous forecast for the future.

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A P P E N D I C E S

APPENDIX A

Heavy metal composition of San Antonio Bay sediments

Station	Depth of Core Section (cm)	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
RS 1 ***	0-6	0.42	74	8.4#	14.4	0.33#	4.3#	2.6
RS 2 ***	0-8	0.57	165	11.0#	26.2	0.43#	8.3#	5.6
RS 3 ***	0-15	0.65	198	13.6#	27.5	0.44#	6.3#	6.5
	0-15	0.92	195	8.9	36.3	0.18	3.9	20.3#
1 **	75-90	0.82	164	7.9	30.4	-	5.0#	5.4
	130-145	0.77	107	8.2	27.3	0.12	3.5	15.1#
	20-35	0.92	217	10.2	32.2	0.18	3.8	14.7#
2 **	55-70	0.93	188	10.2	31.9	0.11	3.3	12.6#
	93-108	1.65	204	9.7	35.0	-	6.9	12.5
	0-15	1.01	202	11.2	33.2	0.27#	5.8#	14.8#
3 **	70-85	1.55	423	12.8	-	-	5.4	11.5
	130-145	0.39	76	4.1	14.5	0.10	2.1	5.8
	0-15	0.91	197	9.0	36.0	0.20	2.9	11.8#
4 **	70-85	0.93	264	7.9	28.2	0.24	3.2	7.9
	143-158	0.91	185	6.5	28.5	0.23	2.1	8.6
5 **	0-15	1.06	280	10.8	37.2	0.18	2.5	11.0
	119-134	1.34	-	15.9#	45.5	0.24	4.1	15.1#
6 **	0-15	0.99	194	9.9	31.9	0.16	3.4	7.5
	55-70	0.72	178	6.3	26.8	0.29#	2.8	9.2

APPENDIX A (continued)

Station	Depth of Core Section (cm)	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
7 **	0-25	0.68	174	6.8	21.9	0.18	2.2	5.8
8 **	0-15	0.35	60	3.9	12.5	0.03	1.8	-
9 **	0-15	1.20	198	9.9	38.7	0.18	4.1	10.9
	158-173	0.90	164	5.4	28.1	0.20	2.9	8.1
10 *	0-25	1.04	176	9.3	42.0	0.11	5.5#	8.1
	75-100	0.97	175	8.7	31.0	0.11	2.9	8.2
11 *	0-25	1.53	342	13.2	42.0	-	5.8	12.6
	75-100	1.39	340	14.4#	41.0	0.17	4.8	12.6
11 **	0-15	1.29	264	9.4	39.4	0.21	4.8	10.8
	75-90	1.35	290	10.1	44.4	0.15	3.3	12.7
	145-160	1.58	281	11.8	51.7	0.22	5.1	14.7
12 *	0-25	1.38	268	12.2	45.8	0.20	4.6	10.6
	75-100	1.48	336	10.9	44.5	0.17	4.1	13.9
12 **	0-15	1.35	249	11.7	38.9	0.17	5.2	12.0
	140-155	1.39	280	9.6	41.4	0.17	3.9	11.4
13 *	0-25	1.15	195	9.6	27.0	0.20	4.4	10.0
	75-100	1.34	258	10.2	-	-	3.4	8.0
14 *	0-25	1.39	287	10.5	38.3	0.20	4.9	10.0
	75-100	0.19	128	10.9	5.6	0.20	1.6	3.8
15 **	0-15	1.10	220	8.6	36.2	0.23	4.1	7.9
	160-175	1.28	268	12.5	45.0	0.24	4.5	10.4

APPENDIX A (continued)

Station	Depth of Core Section (cm)	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)
16 **	0-15	1.53	264	12.3	46.8	0.18	5.4	14.1
	110-125	1.37	282	12.5	47.8	0.21	4.5	10.7
17 *	0-25	0.68	62	3.3	-	-	1.8	4.3
18 *	0-25	1.10	253	12.5‡	-	-	3.6	8.3
19 *	75-100	0.58	101	5.1	15.2	0.02	2.6	4.6
20 *	0-25	0.76	139	6.6	24.0	0.04	2.8	7.0
	75-100	0.72	137	7.5	25.4	0.04	2.4	7.0
20 **	0-15	0.82	118	7.0	23.3	-	3.0	6.2
	35-50	0.86	150	6.6	23.9	0.05	3.0	6.8
21 **	0-15	1.27	221	8.5	33.3	0.08	4.0	11.7
	160-175	1.37	314	9.1	38.4	0.11	8.1‡	11.1
Average %								
Relative Precision		3.7	3.0	7.8	2.8	9.0	12.5	10.4

* Samples of June 8 and 9, 1972.

** Samples of January 27, 1973.

*** Samples of May 20, 1973 (RS = River samples).

‡ Values which deviate from a linear relationship when plotted vs. iron.

APPENDIX B

Calcium carbonate and organic carbon concentrations of surface sediments from the San Antonio Bay area

Station	% CaCO ₃			% Organic carbon	
	Moore and Shepard (1955) ¹	Ahr (1973) ²	This Study	Ahr (1973) ²	This Study
RS 1	-	-	16.5	-	0.62
RS 2	-	-	15.2	-	-
RS 3	-	-	21.8	-	-
1	21.9	-	17.4	-	1.04
2	28.7	23.4	-	-	-
3	22.2	24.9	24.5	0.64	-
5	27.1	22.6	22.6	0.79	-
6	23.5	27.4	-	0.77	-
8	7.5	19.9	9.0	0.35	0.18
9	19.4	-	23.5	0.58	-
11	22.2	22.2	28.7	0.87	0.82
15	20.3	-	23.7	-	-
17	23.3	20.3	-	0.58	-
21	22.6	-	20.4	0.64	-

¹Samples are from same approximate area as those of this study.

²Samples are near-bottom suspended material at same locations as those of this study.

Note: A number of carbonate and organic carbon values were determined for deeper sediments. The carbonate values were, in most cases, very similar and the organic carbon values were somewhat lower at depth.

APPENDIX C

Sampling sites in the northwest Gulf of Mexico - Cruise 73-L-2

Station Number	Latitude Longitude	Water Depth (m)	Surface Water Salinity (‰)
3	28°51'00"N 89°54'30"W	50.3	16.3
6	28°40'45"N 89°31'30"W	108.2	16.6
8	28°51'00"N 89°29'30"W	59.7	20.5
8A	28°55'30"N 89°34'00"W	53.3	15.7
10	29°10'00"N 89°50'30"W	15.8	24.0
11	28°55'15"N 89°29'30"W	36.6	14.6
12	28°46'30"N 89°10'00"W	224.9	15.9
15	29°05'00"N 88°42'30"W	101.8	13.5
17	29°23'00"N 88°53'00"W	20.1	27.5
22	29°14'30"N 88°22'30"W	117.3	16.7
23	28°50'00"N 88°48'30"W	649.2	17.4
25	29°00'00"N 89°35'00"W	22.8	18.5
26	29°10'00"N 89°35'00"W	9.6	13.0

APPENDIX C (continued)

Station Number	Latitude Longitude	Water Depth (m)	Surface Water Salinity ($^{\circ}/\text{oo}$)
29	29 $^{\circ}$ 00'00"N 89 $^{\circ}$ 15'30"W	7.6	16.0
33	28 $^{\circ}$ 28'30"N 89 $^{\circ}$ 41'30"W	643.7	20.2
36	28 $^{\circ}$ 32'30"N 90 $^{\circ}$ 43'15"W	22.9	24.4
38	28 $^{\circ}$ 40'30"N 92 $^{\circ}$ 03'15"W	28.0	25.8
39	29 $^{\circ}$ 04'30"N 93 $^{\circ}$ 19'30"W	21.9	30.3

Sampling sites in the northwest Gulf of Mexico - Cruise 73-A-9

Station Number	Latitude Longitude	Water Depth (m)	Surface Water Salinity ($^{\circ}/\text{oo}$)
11	27 $^{\circ}$ 00.8'N 94 $^{\circ}$ 06.1'W	1210	34.4
13	27 $^{\circ}$ 33.2'N 94 $^{\circ}$ 15.0'W	672	35.0
16	28 $^{\circ}$ 18.7'N 94 $^{\circ}$ 17.3'W	55	29.9
17	28 $^{\circ}$ 17.7'N 95 $^{\circ}$ 45.6'W	27	30.7
18	28 $^{\circ}$ 35.8'N 95 $^{\circ}$ 02.5'W	27	30.7
19	29 $^{\circ}$ 13.7'N 94 $^{\circ}$ 38.6'W	16	29.5

APPENDIX D

Heavy metal, carbonate, and organic carbon data for the northwest Gulf of Mexico -
Cruise 73-L-2

Station	Depth of Core Section (cm)	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)	CaCO ₃ (%)	Organic Carbon (%)
3	10-20	2.42	460	17.1	92.4	0.21	9.5	24.3	2.5	0.68
	60-70	2.47	498	13.6	82.8	0.24	10.8	25.0	2.7	-
	90-100	2.24	478	15.5	72.7	-	10.4	21.6	5.1	0.57
	160-170	1.91	539	15.8	*97.5	0.24	12.6	23.6	3.4	0.69
6	0-10	2.70	433	24.7	97.5	*0.50	12.2	28.4	6.5	-
	70-80	2.31	406	15.6	78.0	0.31	8.4	23.5	4.9	-
	130-140	2.47	460	18.7	86.8	0.39	8.5	26.2	4.9	-
8	10-20	2.98	721	*29.5	109.8	*0.47	*21.7	30.6	1.8	1.07
	30-40	3.11	584	*33.3	103.1	-	11.4	33.0	1.3	-
	60-70	2.59	624	19.5	87.1	*0.45	11.2	26.3	2.3	0.94
	90-100	2.60	645	20.8	85.3	0.36	14.6	26.8	2.5	-
8A	0-10	3.09	771	*30.3	117.5	*0.49	12.8	30.8	3.3	-
	30-40	2.80	529	22.1	99.6	-	13.4	27.1	2.2	-
	70-80	2.93	586	23.2	87.3	-	15.4	-	1.4	-
	90-100	2.84	460	21.8	92.6	0.26	15.0	29.0	1.7	-
	120-130	2.82	453	17.2	89.3	0.22	13.5	27.4	1.3	-
10	0-10	2.57	571	16.9	83.4	0.25	15.5	26.7	-	-
	60-70	2.75	548	16.2	92.7	0.14	15.4	25.3	-	-
	100-110	2.59	695	18.0	82.1	0.25	16.6	26.5	-	-
	140-150	2.50	606	14.4	88.1	0.29	16.1	30.2	-	-

APPENDIX D (continued)

Station	Depth of Core Section (cm)	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)	CaCO ₃ (%) ³	Organic Carbon (%)
11	10-20	2.46	603	*23.8	95.4	*0.67	13.9	29.0	1.4	0.97
	30-40	2.74	543	*30.2	89.2	*0.78	16.4	-	1.5	-
	50-60	2.63	591	*32.8	*107.8	*0.62	12.8	30.2	-	-
	80-90	1.45	364	14.2	53.2	0.36	8.4	17.7	-	-
	150-160	2.32	458	21.7	88.6	*0.59	15.1	26.9	2.0	0.60
	190-200	2.59	493	23.4	97.2	-	15.3	26.8	2.0	-
12	10-20	3.12	406	25.1	105.8	0.19	15.7	27.8	2.7	-
	60-70	2.81	288	25.0	90.1	0.17	11.4	26.8	2.0	-
	110-120	2.68	338	18.0	85.0	0.23	9.7	26.2	4.8	-
15	0-2	2.83	383	21.7	104.0	0.25	12.8	28.6	-	-
	12-22	2.48	233	16.6	75.9	0.17	13.2	23.7	7.5	-
	52-62	0.94	128	7.6	37.3	0.20	6.2	11.6	7.7	0.28
	72-82	0.53	61	4.9	17.6	-	5.3	5.1	9.5	-
17	Grab	0.66	136	7.9	22.1	0.10	2.0	9.7	-	-
22	0-10	1.38	226	13.6	45.0	0.22	7.0	13.6	-	-
	50-60	2.11	290	12.7	71.7	0.17	9.5	20.8	-	-
	80-90	1.16	148	6.8	30.8	0.24	5.7	7.2	-	-
	110-120	1.20	114	8.4	25.7	0.27	5.2	9.1	-	-
23	7-17	2.84	565	19.1	93.7	0.10	15.5	28.2	-	-
	37-47	2.54	362	16.1	80.3	0.20	13.0	25.0	-	-
	77-87	1.92	303	17.9	60.1	-	9.5	24.0	-	-
25	0-10	1.43	289	*19.8	53.7	0.22	5.1	16.9	-	-

APPENDIX D (continued)

Station	Depth of Core Section (cm)	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Cd (ppm)	Cu (ppm)	Ni (ppm)	CaCO ₃ (%)	Organic Carbon (%)
26	0-5	0.98	138	8.5	37.8	-	5.0	11.9	1.8	-
	10-20	1.06	171	8.0	26.0	-	6.2	13.1	2.0	-
29	0-5	3.34	715	*34.4	*132.3	*0.60	*21.3	33.3	-	-
	0-5	3.20	*1982	*31.4	104.0	0.37	16.1	*38.8	3.1	-
33	25-35	2.97	531	17.0	88.8	0.41	-	27.9	2.5	-
	45-55	2.79	508	18.0	93.5	0.20	15.5	25.0	-	-
	55-65	2.72	656	15.0	84.9	-	12.1	28.8	4.0	0.79
	115-125	2.81	555	18.1	82.6	-	14.6	27.9	4.8	-
	145-155	2.82	688	12.6	82.3	0.32	12.8	31.3	5.7	1.06
36	10-20	1.12	207	8.8	40.6	0.03	5.0	13.8	-	-
38	0-5	1.68	340	13.5	62.3	0.09	6.9	16.4	-	-
	75-85	1.96	435	13.5	75.3	0.14	10.0	21.9	-	-
	145-155	1.98	571	13.3	71.4	0.09	9.6	20.0	-	-
39	48-58	1.20	235	7.0	32.6	0.17	6.6	10.2	-	-

APPENDIX D (continued)

Heavy metal, carbonate, and organic carbon data for the northwest Gulf of Mexico -
Cruise 73-A-9

Station	Depth of Core Section (cm)	Fe (%)	Mn (ppm)	Pb (ppm)	Zn (ppm)	Gd (ppm)	Cu (ppm)	Ni (ppm)	CaCO ₃ (%)	Organic Carbon (%)
11	0-15	2.30	*2067	12.3	79.4	*0.50	*18.6	30.4	27.5	0.30
	60-75	2.57	*952	12.5	103.3	0.42	*24.8	*44.2	20.7	-
	110-125	2.52	*990	13.7	90.0	0.38	*22.6	31.6	16.3	0.52
13	0-15	2.41	560	15.2	82.2	0.34	12.9	27.3	13.5	-
	60-75	2.73	342	12.3	78.7	0.28	17.8	26.1	8.0	-
	95-110	2.72	255	13.1	85.9	-	18.1	26.9	15.9	-
16	0-15	1.13	161	6.9	40.0	0.20	4.2	10.2	8.3	-
	45-60	1.45	164	10.7	47.1	0.08	5.1	15.1	2.5	-
	90-105	1.44	137	9.7	37.6	0.12	4.5	13.3	2.5	-
17	0-15	1.12	174	6.6	34.4	0.15	3.6	11.2	2.7	0.36
	30-45	1.27	184	7.8	37.7	0.12	3.7	11.0	2.2	-
	55-70	1.37	211	9.5	44.0	0.14	5.0	12.5	2.6	0.41
18	0-15	1.40	225	8.8	44.8	0.08	4.7	14.0	2.6	-
	55-70	1.51	236	9.2	50.8	0.02	4.6	13.7	2.8	-
19	0-15	1.53	230	11.5	46.9	*0.54	7.0	14.9	1.5	0.45
	15-30	1.53	56	15.5	41.8	*0.52	-	13.3	1.0	0.37
Average %										
Relative Precision		2.3	2.0	5.3	2.8	10.4	6.8	7.4	<2	-

*Values which deviate from a linear relationship when plotted vs. iron.

VITA

Mr. John Harold Trefry, III was born to Mr. and Mrs. John Harold Trefry, Jr. on September 2, 1947, in Boston, Massachusetts.

He lived in Quincy, Massachusetts, and attended public schools until his graduation from North Quincy High School in June, 1965. He then enrolled at Syracuse University in September, 1965 and graduated with an A.B. degree in Zoology in June, 1969.

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