

Assessment of Trace Element Geochemistry of Hampton Roads Harbor and Lower Chesapeake Bay Area Sediments

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ABSTRACT / Acid extractable Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined in sediments from the Inner Virginia Shelf, and from shipping channels in the lower Chesapeake Bay and Hampton Roads, Virginia, harbor system. Data were evaluated by a variety of techniques. Levels of Cd, Cu, Pb, and Zn exceeded average crustal abundances for most of the study sites. Cumulative frequency curves suggested that

there were two major populations for all metals and perhaps a third and smaller one for Cd, Cr, and Mn. Plots of metal vs Fe indicated no anthropogenic inputs of metals for shelf and Chesapeake Bay channel sites, but suggested anthropogenic influences for all metals in several of the inshore sites. Enrichment factor calculations showed enrichment of Cd, Pb, and Zn with respect to average crustal abundances for all sites and of Cu for the industrial harbor system. A recommendation of this study for evaluation of environmental geochemical metals data is to utilize mean concentrations, cumulative frequency plots, and metal vs Fe and/or enrichment factor calculations when evaluating the pollution status of sediments.

Introduction

When assessing metal sediment concentrations for environmental studies, one major problem is the choice of methods of data analyses. One may attempt to evaluate the data on the basis of absolute metal concentrations, or choose between a variety of other methods, ranging from relatively simple ones like elemental ratios to more sophisticated, such as discriminant analysis.

Helz and others (1983) analyzed sediments from the Chesapeake Bay, Baltimore Harbor, and Elizabeth River for trace elements (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb). They calculated enrichment factors (EF) for the data using Al as the reference metal and average crustal shale values from Turekian and Wedepohl (1961) by the relations:

$$EF = \frac{(X/Al) \text{ sediment}}{(X/Al) \text{ Earth's crust}}$$

where X/Al is the ratio of the concentration of element X to Al. They found, in general, enrichment of Cd, Pb, and Zn in the bay and postulated that this resulted from: (1) atmospheric deposition, or (2) unrepresentative crustal abundance data—perhaps metal concentrations in Chesapeake Bay are anomalous compared to the average crustal abundances.

Using Fe-based enrichment factors, Helz and others (1983) compared their data to that from several other East Coast and Gulf Coast estuaries and found enrichment of Cd, Pb, and Zn in most cases. They

stated that Al concentrations in both the Hampton Roads and Baltimore Harbor sediments were high compared to the respective main Chesapeake Bay areas. In Hampton Roads, no consistent anthropogenic effect was found for Cr or V but Zn was highly enriched.

Goldberg and others (1978) collected and analyzed eight cores from the Chesapeake Bay (including one from the James River). They presented detailed metal concentrations for four of these cores and concluded, from the absolute concentrations, that surface metal contents were considerably enriched over those below 50 cm. This trend was not clearly evident in all cases.

Sommer and Pyzik (1974) used metal vs aluminum/metal ratios to evaluate metal-sediment associations of Chesapeake Bay sediments. They determined that Al was associated with clay minerals in bay sediments and used Al as an indicator of clay minerals. Linear relationships were found between Cu and Al/Cu, Pb and Al/Pb, Cr and Al/Cr, Mn and Al/Mn, but iron did not show a linear relationship. Sommer and Pyzik suggested that because of the linear relationships for Al and Cu, Pb, Cr and Mn, these elements were associated with the clay mineral portion of the sediment and that an alternate distribution mechanism (sulfides) was possible for Fe.

Johnson and Villa (1976) determined acid extractable metals in Elizabeth River sediments. They found that concentrations of all metals analyzed (Cd, Cu, Cr, Hg, Pb, Zn, Al, and Fe) were two to ten times greater than for sediments from the mid-Chesapeake Bay.

Distribution of metals generally reflected heavy industrial, commercial, and domestic inputs along the river. Their findings are reviewed in the discussion section.

Johnson and Villa (1976) discussed the work of Sommer and Pyzik (1974) and examined their data for metals in Elizabeth River sediments by the same metal vs Al/metal technique. No linear relationships with Al were found for Fe, Cr, Pb, or Cu. They concluded that either Al was not associated with clay minerals in the Elizabeth River as it was in the bay sediments, or non-linear relationships are indicative of anthropogenic sources rather than natural ones.

It seems highly unlikely that the association of Al with clay minerals (assuming these authors mean silicate clay minerals) would vary as postulated above, since Al is an inherent and abundant component of the clay mineral structure. Other forms of Al were undoubtedly present in sediments since the extraction techniques used by these workers would not significantly dissolve the silicate lattice. Whether or not these other forms of Al would be associated with silicate clay minerals may be questionable, but it is expected that these forms will be in the clay-sized fraction of sediments. Most of the Fe in sediments will be in the form of hydroxides or sulfides, depending on Eh, and in the clay-size fraction. The most relevant conclusion as to the association and distribution of Al and Fe, with respect to clay minerals, is that the forms of all three occur predominantly in the clay-sized sediment fraction. Many sediment forms of Al and Fe are relatively easily extracted; silicate clays are not.

Trefry and Presley (1976a and 1976b) used metal vs Fe graphs to characterize unpolluted sediments and to identify sediments thought to be polluted from anthropogenic sources. A population that occurred within the $\pm 95\%$ prediction interval about the best fit linear line was defined as natural, or unpolluted. Metal concentrations occurring outside of the 95% interval were postulated to indicate anthropogenic input. Rule (1982) discussed sediment metals in the lower Chesapeake Bay and Hampton Roads Harbor area as evaluated by the technique of Trefrey and Presley.

Chester and Voutsinou (1981) used diluted HCl to extract sediment metals and assessed the sediment's pollution status by examining absolute trace metal concentrations. They suggest that spatial contour maps of surface metal concentrations are a simple and effective manner to present results. Although proposing the use of this simple method, they point out that great care is necessary in choosing baseline metal levels.

Absolute amounts of trace elements are, to some degree, simply a function of sediment particle size.

Therefore, assessing a group of data based on variable sediment particle size must be done with caution. Even when the grain size is nearly homogeneous within a data set, the choice of baseline data must be made with care.

Sinex and Helz (1981) noted that certain unfractionated samples from the Chesapeake Bay contained higher trace element concentration than corresponding $<63 \mu\text{m}$ fractions. They postulated that the coarser-grained fraction contained fecal pellets, heavy minerals, aggregates of fine-grained materials, or sand grains with unusually thick coatings.

Shrader and others (1977) studied the distribution of several metals in different size fractions of stream sediments. They found that the concentration of some metals, notably Mn, was greater in the sand and clay fractions than in the silt fractions, with the highest concentrations often in the sand fractions. This phenomenon is most probably attributable to Mn oxide coatings on the sand grains.

If a data assessment technique can be utilized which inherently incorporates the influence (effect) of grain size on the trace metal content, then there would be no need to group the data by particle size, and a larger set of data can be compared.

Cumulative frequency graphs of metal concentrations have long been used (Siegel 1974) to determine the number of populations present in a group of samples. When a cumulative frequency curve for a given metal (metal concentrations vs number of occurrences for each concentration) is constructed on a semi-logarithmic scale, a single population is defined as a group of points which form a straight line. Multiple populations within a single (given) data set will give two or more straight-line segments on the graph.

Generally, the sediment fraction that contains the greatest concentrations of trace metal is, of course, the finer size. A very desirable method of assessing the trace metal status of sediments would be to analyze the $<63 \mu\text{m}$ material. In this manner, the variable effect of grain size will be eliminated. Most environmental studies utilize an unfractionated or $<2 \text{ mm}$ portion of sediments for the various determinations. Analyses of the $<63 \mu\text{m}$ fraction, while desirable, would entail additional time and labor often beyond that available for the research. The most useful technique should allow use of chemical data from unfractionated samples, be applicable to a wide range of sediment types, and minimize the difficulty in selection of baseline or reference concentrations. This article evaluates some of the available techniques utilizing sediment metal data from the lower Chesapeake Bay, Inner Virginia Shelf, and Hampton Roads Harbor system. A suggested scheme

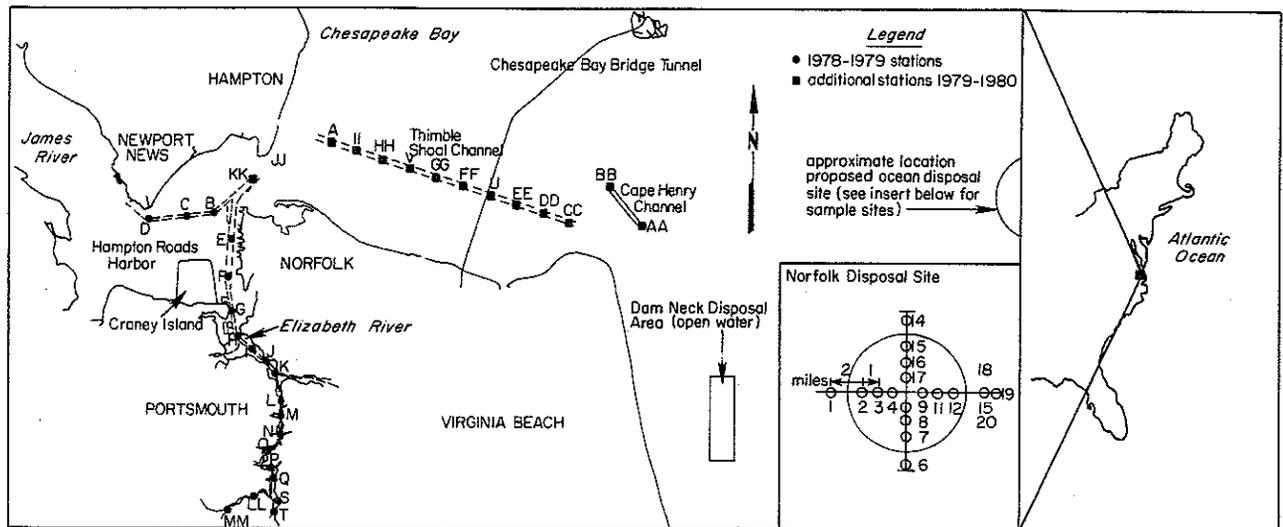


Figure 1. Study area.

for the data analyses of trace metals in sediments is presented in the summary.

Materials and Methods

The port of Hampton Roads, Virginia, is located within a major metropolitan area encompassed by Norfolk, Virginia Beach, Chesapeake, Portsmouth, Newport News, and Hampton (Fig. 1). Waters of this harbor are along one of the most industrialized coastal areas in the eastern part of the United States. The largest naval port in the world is located here. Navigation channels of this port system are maintained by the U.S. Army Corps of Engineers (COE). The COE dredges an annual average of 4.1 million m^3 of sediment from the port system channels. Approximately 60% of this material is classified as mud, clay, and silt and is taken primarily from the Hampton Roads/Elizabeth River portion. These are the most active industrial areas in the port system. The balance of the dredged materials consists of sand, gravel, and shell which comes from the Chesapeake Bay channels (Pequegnat and others 1978).

The large naval base (Fig. 1) is located adjacent to sites E and F; sites G-I are on the main stem of the Elizabeth River, where there is moderate industrial activity (fuel facilities and chemical companies). The highly industrialized area, with private and naval shipyards, oil storage and creosoting facilities, and fertilizer companies occur along sites K, L, and M. A less densely developed area in the upper reaches of the Elizabeth River is represented by sites P, Q, S, T.

Sediments from the highly industrialized segments are presently disposed at Craney Island, a diked dis-

posal area (Fig. 1). With normal maintenance, dredging, and disposal operations, the Craney Island site will be available for several years but has a finite lifetime. Plans are also being made to deepen the port of Hampton Roads from the present 13.8 m depth to 17 m to accommodate deeper draft vessels. Should the deepening occur, the filling of Craney Island would be greatly accelerated. A multidisciplinary study was designed to investigate if open ocean disposal of sediments from various areas within the port system would be ecologically acceptable.

Sediment samples were collected to use in various types of bioassays, for particle size analyses, and for metals analysis. Sediment samples collected for all these various purposes were analyzed for trace metals.

One hundred and seventy-nine sediment samples were collected over a three-year period from 46 stations in the navigation channels in the lower Chesapeake Bay (Thimble Shoal and Cape Henry channels), Hampton Roads Harbor, and the Elizabeth River (main stem and southern branch). Samples from a proposed offshore disposal site on the Inner Virginian Shelf about 27 km from the bay mouth were also included.

The sampling pattern for the offshore area is shown in Figure 1. All other samples, in the navigation channels, were taken at one-mile intervals using navigation buoys as site markers. At each site, four samples were taken across the channel, between the buoys.

Sediment samples were collected using a Shipek grab or a 0.76 m^3 clamshell grab. Care was taken to avoid contamination from the samplers, and the samples were placed in plastic bags for transport to the laboratory. Sediments were dried at $<40^\circ C$, crushed

Table 1. Mean concentrations for sediment metals (mg/kg except Fe, which is %).

	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Norfolk Disposal Site	.07 ± 0.05 ^a	3.4 ± 1.9	6.7 ± 3.6	1.1 ± .8	.559 ± .288	83 ± 41	4.1 ± 2.1	2.7 ± 1.7	15 ± 7
Thimble Channel—Outer	.14 ± .08	3.12 ± 2.7	4.3 ± 4.8	1.5 ± 1.0	.606 ± .295	65 ± 50	5.2 ± 3.0	6.6 ± 1.5	14 ± 7
Thimble Channel—Inner	.27 ± .12	4.86 ± 3.7	5.3 ± 6.6	4.3 ± 3.6	1.05 ± .563	101 ± 75	9.5 ± 5.2	11 ± 5.6	33 ± 22
Newport News Channel	.44 ± .23	7.8 ± 2.7	12.9 ± 11.6	6.2 ± 4.0	1.39 ± .710	123 ± 84	8.1 ± 9.0	15 ± 7	44 ± 24
Inner Hampton Roads	.91 ± .30	16.6 ± 3.7	50.1 ± 7.3	35.6 ± 8.7	3.47 ± .371	623 ± 180	58 ± 15	53 ± 11	207 ± 54
Lower Elizabeth River (main)	2.00 ± 1.11	15.5 ± 5.2	52.6 ± 6.6	75.4 ± 36.5	3.62 ± .551	398 ± 87	43 ± 15	93 ± 39	495 ± 197
Mid-Elizabeth River	2.75 ± .86	11.6 ± 4.7	56.4 ± 22.7	142.1 ± 80.0	3.16 ± 1.25	251 ± 111	29 ± 11	157 ± 79	413 ± 242
Upper Elizabeth River	1.18 ± .51	9.7 ± 4.0	43.9 ± 16.5	70.8 ± 55.0	2.39 ± .982	157 ± 82	38 ± 22	89 ± 53	196 ± 103

^a Ranges are ± 1 Standard Deviation.

Table 2. Site and legend and description of sediment type.

Area	Sites included	# of samples	Sediment type
Norfolk Disposal Site	Numbered sites	49	fine sands
Thimble Channel—outer	AA thru EE,U	35	coarse sands
Thimble Channel—inner	FF thru II,V,A	26	coarse/fine sands; silts
Newport News Channel	B,C,D	13	silts/clays; sands; shell
Inner Hampton Roads	E,F	9	silts/clays
Lower Elizabeth River (main)	G,H,I	12	clays/silts
Mid-Elizabeth River	K,L,M	12	clays/silts
Upper Elizabeth River	P,Q,S,T	16	clays/silts

Table 3. Average crustal abundance data from Taylor (1964).

	Element								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
μg/g ^a	0.2	25	100	55	5.63%	950	75	12.5	70

^a Except Fe, which is %.

and passed through a 2-mm stainless steel sieve, and stored in plastic bags. Sediment grain-size analysis was performed on the samples collected from the Chesapeake Bay channels and the offshore site as a part of the contracted study. Analyses of grain size of the Hampton Roads and Elizabeth River samples were conducted where time permitted. Portions (2–6) g of the <2-mm samples were extracted as follows. Fifteen ml of redistilled, concentrated (15.4 M) HNO₃ were added to the samples, which were allowed to sit overnight at room temperature and were then heated at 100°C for 4 h. Five ml of 30% H₂O₂ were added and the mixtures heated for an additional 2 h. The extract was filtered through acid-washed Whatman no. 2 filter paper and diluted with ultrapure deionized water to a final acid concentration of 10%. The metals Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined by flame Atomic Absorption Spectrophotometry using a Perkin-Elmer 603 instrument. All data were calculated on a dry weight basis. Statistical calculations were conducted using the Statistical Packages for Social Sciences (SPSS) by Nie and others (1975).

Results and Discussions

Average sediment metal concentrations for different areas are shown in Table 1. The areas are defined by site groups in Table 2. Except for Pb, concentrations of metals are similar for the Norfolk Disposal Site (NDS) area and Outer Thimble Channel. The Inner Thimble Channel sediments, closer to inshore activities, have a slight but consistent increase in all metals concentrations. The NDS sediments, generally lowest in metal concentration, are fine sands, while the Thimble Channel sediments range from coarse sands to fine material which is responsible for some of the concentration increase.

Starting in the Inner Thimble Shoal Channel, the general pattern shows an increase in metal concentrations toward the industrialized portions of the Elizabeth River. Levels of Cd, Cu, Pb, and Zn exceeded average crustal abundances (Taylor 1964, Table 3) in several sites close to industrial activities. Concentrations of Cd and Pb showed the greatest elevation above crustal abundances (>10X), and this increase occurred for a greater number of sites than for other metals.

Maximum concentrations of Cd, Cr, Cu, and Pb occurred in sediments from the most highly industrialized area in the mid-Elizabeth River, while maximum values for Fe and Zn were found in the lower Elizabeth River. The highest values for both Mn and Ni occurred in the inner Hampton Roads sediments. The concentration pattern (Table 1) of Mn and Ni, and to

Table 4. Means and standard deviations of trace metals in Elizabeth River sediments from the current study and from Johnson and Villa (1976).^a

Metal (mg/kg)	Main stem		Southern branch	
	1974, EPA ^b	1979, Rule ^b	1974, EPA ^b	1979, Rule ^b
Cd	5.3 ± 5.5	2.0 ± 1.1	2.3 ± 1.6	2.3 ± 1.6
Cr	47 ± 26	52 ± 6.6	40 ± 30	57 ± 17
Cu	38 ± 43	75 ± 36	82 ± 91	130 ± 69
Fe	28834 ± 8043	36208 ± 5512	25092 ± 8145	31815 ± 9736
Pb	70 ± 68	93 ± 39	106 ± 101	149 ± 62
Zn	386 ± 404	459 ± 197	287 ± 263	363 ± 197

^a Sites were chosen from the current study to correspond with the areas sampled by Johnson and Villa (1976).

^b Sampling for the Johnson and Villa study was conducted in 1974, and in the Elizabeth River for the current study in 1979.

a lesser extent of Mn and Co, suggests a geochemical association between these elements in the sediments. Geochemical association of Mn with Ni and Co has frequently been reported (Siegel 1974, Levinson 1980).

Concentrations of all metals decreased in the uppermost Elizabeth River, reflecting the lower level of industrialization, but values in these sediments were still greater than those in the Thimble Shoal Channel and NDS area, and exceeded the average crustal abundance for Cd, Cu, Pb, and Zn.

Although there were no statistically significant differences in average concentrations of trace elements extracted from Elizabeth River sediments during the present study (sampled in 1979) and the levels measured by Johnson and Villa (1976) (sampled in 1974, Table 4), the ranges for most metals for this study were much narrower than for the study of Johnson and Villa. A more severe extraction procedure was used in the current study, and the higher mean values may have resulted from the removal of a greater amount of metals from the sediments. Although the average Johnson and Villa's values were somewhat lower, there were several instances where maximum found values exceeded those for the present study. This may have resulted from slightly different sampling patterns or it may indicate a change in the distribution pattern of the metals.

There is, of course, a variation in grain size (Table 2) over the study area, which causes some of the differences in trace metal levels; however, variations in metal concentrations also exist in similar grain-sized samples (such as in the Elizabeth River). Such observations are common in geochemical studies. Analyzing the <63 μm fraction of sediments may help to resolve this problem. Since it was not possible in the current study to analyze the <63 μm fraction, the approach was to utilize a method of data analysis which might account for grain-size effect.

For each metal analyzed, cumulative frequency graphs were constructed utilizing the entire data set. All curves had two distinct straight-line portions indicating two major populations present. Diagrams for Cd, Cu, Cr and Mn (Figs. 2 and 3) show the variety of curves obtained. The population defined by the near-vertical segment (low metal concentrations) includes the Norfolk Disposal Site and Thimble Shoal Channel sediments. The nearly horizontal segment (higher range of concentrations) includes the Hampton Roads Harbor and Elizabeth River sediments. The portion of the curves for Cd, Cr, and Mn between the larger near-vertical and near-horizontal segments may indicate that a third population is present.

The data were then divided into three groups based on geographic areas, sedimentological and geochemical characteristics, and cumulative frequency curves. The three groups were Norfolk Disposal Site (OFFSHORE); Thimble Shoal Channel (CHANNEL); and sites from the Hampton Roads Harbor and Elizabeth River (INSHORE).

It is assumed that for natural sediment conditions (no anomalous metal concentrations), the relationship between Fe and another metal will form a linear trend (Trefrey and Presley 1976a and 1976b). Should the concentration of Fe change because of changing mineralogy, sediment particle size (which usually changes mineralogy), or other naturally occurring phenomena, the concentration of the other metal will change with a constant relation to Fe. If a scatterplot of metal vs Fe is constructed and a regression line with 95% prediction band is graphed, then the natural geochemical population of a given data set is defined. That means there is a 95% probability that the points that fall within the prediction interval belong to the normal population and those that are outside of this band are from a different (or anomalous) population.

Metal vs Fe concentrations were plotted for the OFFSHORE, CHANNEL, and INSHORE data groups and

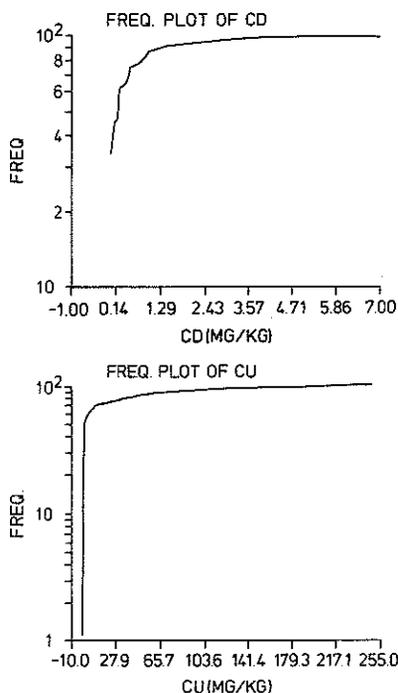


Figure 2. Cumulative frequency curves for Cd and Cu.

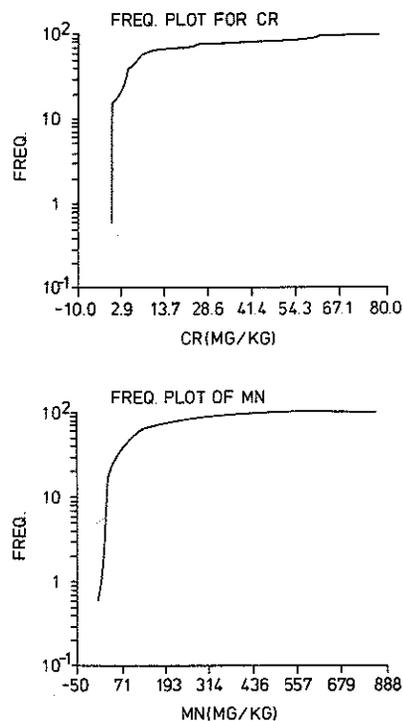


Figure 3. Cumulative frequency curves for Cr and Mn.

also for all data for each metal. Representative plots are shown in Figure 4.

Even though the metal concentrations vary greatly between the data sets in Figure 4, the same scale was used for comparative purposes. Correct scaling of OFFSHORE Cu for evaluation as a single data set is shown in Figure 5a. The slope and nature of the curves for the OFFSHORE and CHANNEL samples (Fig. 4a, 4b) are very similar, and no doubt the samples are from an unpolluted environment. Metal concentrations are low and all points fall within the 95% prediction interval.

When all sites of two data sets belong to the same population, they fall along the same line of the metal/Fe curves. Those samples having coarser sediments with low metal concentrations lie on the lower portion near the ordinant; those samples having finer sediments with resulting higher metal concentrations lie further to the right but along the same line. The data in Table 1 show that the Thimble Channel sediments vary in metal content. The outer channel sites are generally more similar to the OFFSHORE than those in the inner channel. However, the OFFSHORE and CHANNEL samples form one population for Cu and when placed together fall along the same line. When samples are from different geochemical populations, having different metal/Fe ratios, they tend to form lines of different slopes on the same graph. The Cr/Fe diagram

in Figure 5b is a very good example of what appears to be two populations in one data set. The upper group of samples to the left fits closely with the points for a similar OFFSHORE graph (Fig. 5c), while the other points lie along a distinctly different curve. The OFFSHORE and CHANNEL data for Cr/Fe horizontal row of points are from relatively coarse, clean sands in the Thimble Shoal Channel; they have very low and similar Cr concentrations.

The distribution for the INSHORE sediment data (Fig. 4c) is totally different from the other two groups. The points are widely scattered and the 95% prediction interval is relatively wide. Even so, several points are above this band, indicating anomalously high values. Although there is some particle-size variation in the INSHORE group, sediments are predominantly silt-sized or less. The anomalously high values are from sites along the highly industrialized portion of the Elizabeth River.

Each of the metal/Fe (Cu/Fe) diagrams in Figure 4a, 4b, 4c have included similar grain-sized material. The coarser, low metal content OFFSHORE and CHANNEL sediments gave similar curves with few anomalous points. The INSHORE data, with mostly silt and clay-sized materials, gave a scatterplot with widely spread points, a wide prediction interval, and several anomalous points.

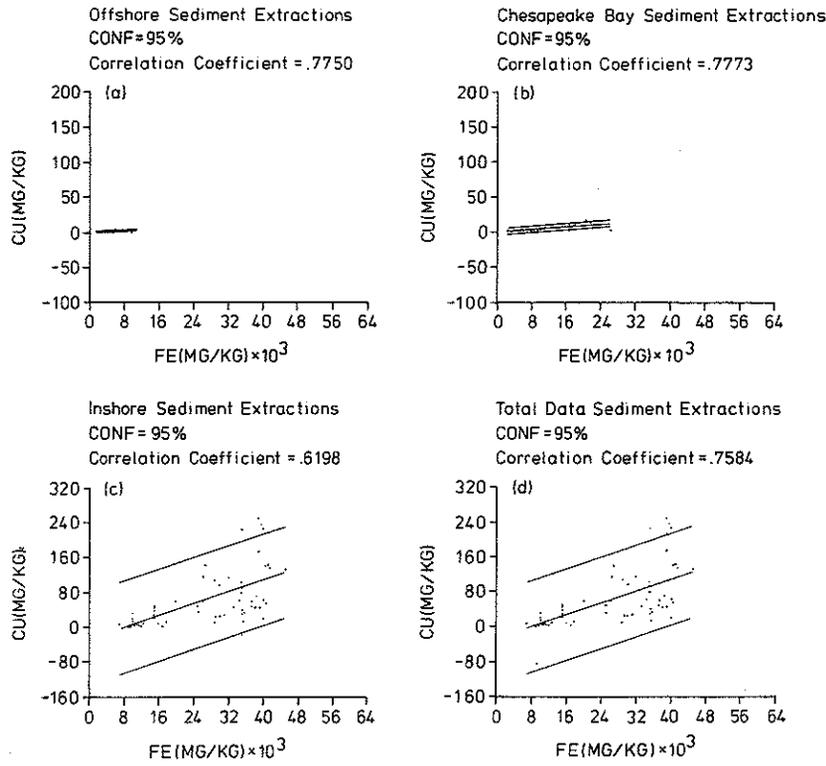


Figure 4. Scatterplots for Cu vs Fe with the 95% prediction interval.

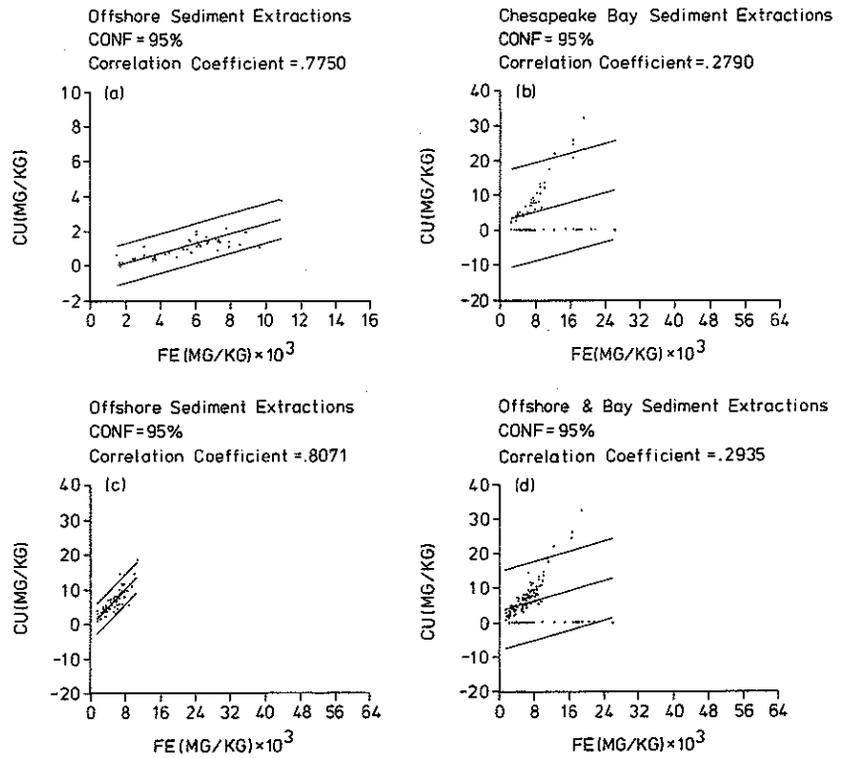


Figure 5. Scatterplots for Cu vs Fe and Cr vs Fe with the 95% prediction interval.

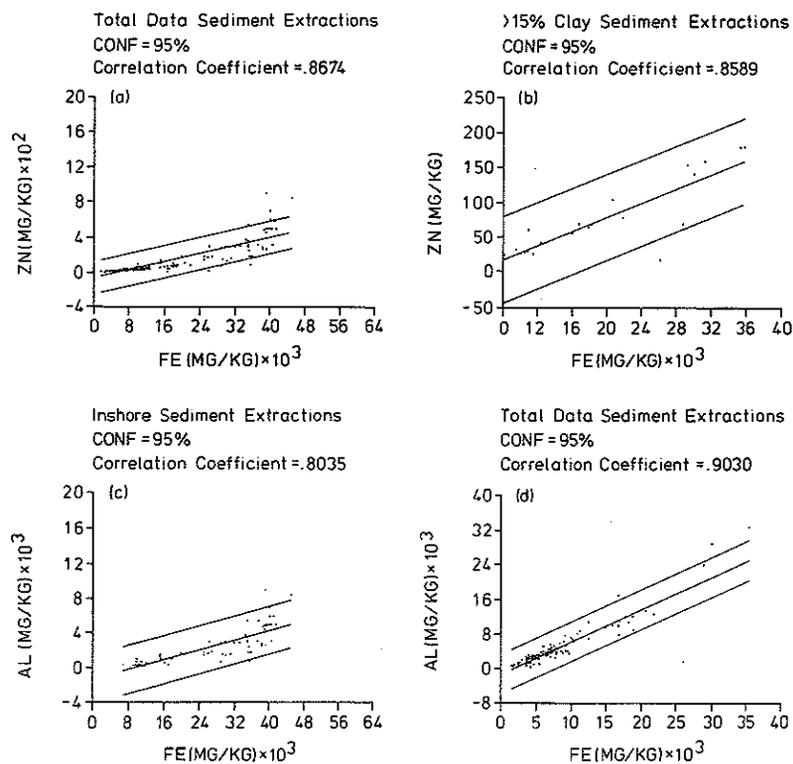


Figure 6. Scatterplots for Zn vs Fe and Al vs Fe with the 95% prediction interval.

When data from all sites are shown on the same graph (Fig. 4d), less satisfactory results are obtained. One obvious difference is that the 95% prediction band has been compressed. The large number of OFFSHORE and CHANNEL samples that occur near the ordinant along the x-axis had the effect of compressing the confidence band. Even so, only three additional samples fall above the line as being described as having anomalously high Cu values.

As a more direct test of the influence of particle size on the metal/Fe graphs, samples for which particle size analysis had been conducted were selected. Figure 6a shows Zn vs Fe for all data available and for only those samples having >15% clay (Fig. 6b). Because of the nature of the study area sediments, most of these data are from the INSHORE sites. All INSHORE data are shown in Figure 6c. The graph of Zn vs Fe for >15% clay samples gives a regression line and 95% prediction interval which fit the data much better than in the case of all data. When other metals were grouped according to clay or silt and clay content, graphs were similar to that in Figure 6b. The more narrow confidence band is again evident for all data (Fig. 6a vs Figure 6c). It appears that the major difficulty with the all-data diagrams is with the great number of data points (from OFFSHORE and CHANNEL) lying together near the ordinant, and not with the particle-size dif-

ference. Improved evaluation of the lower concentration sample (OFFSHORE and CHANNEL sands) can be accomplished by graphing them separately or as one group (Fig. 5c). Evaluation of INSHORE data set was affected only slightly by the all-data plot.

Another method for assessing geochemical data is the enrichment factor, EF (Zollar and others 1974, Sinex and Helz 1981). The EF is defined for this data analysis as:

$$EF = \frac{(X/Fe) \text{ sediment}}{(X/Fe) \text{ Earth's crust}}$$

where X/Fe is the ratio of the concentration of element X to Fe. Anthropogenic inputs of Fe are relatively small compared to natural sources (Helz 1976), so Fe was chosen as the element for normalization. Aluminum is also used as the element for normalization (Zollar and others 1974, Helz and others 1983) and thought by these workers to perhaps be more desirable than Fe. Since Al data were not available for all sediments in the current study, Fe and Al could not be compared, nor could Al be used. For the samples where both Fe and Al analysis were available, plots of Fe vs Al gave a correlation of 0.90 (Fig. 6d).

The major assumption, or perhaps limitation, of this method is the use of average crustal abundance data. A study area may be either enriched or depleted

Table 5. Mean enrichment factors for sediments of the study areas^a

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
Norfolk Disposal Site	5.9 ± 6.6 ^b	1.4 ± 1.0	0.7 ± 0.2	0.2 ± 0.1	0.8 ± 0.2	0.6 ± 0.2	2.5 ± 2.3	2.0 ± 0.6
Thimble Channel—outer	6.1 ± 4.0	1.8 ± 0.9	0.4 ± 0.2	0.3 ± 0.1	0.7 ± 0.7	0.6 ± 0.2	5.1 ± 1.8	1.9 ± 0.5
Thimble Channel—inner	7.3 ± 2.4	1.2 ± 0.3	0.4 ± 0.3	0.4 ± 0.2	0.5 ± 0.2	0.7 ± 0.2	4.9 ± 1.8	2.4 ± 0.5
Newport News Channel	10.0 ± 6.0	1.3 ± 0.3	0.5 ± 0.3	0.5 ± 0.2	0.5 ± 0.2	0.4 ± 0.3	5.2 ± 2.4	2.6 ± 0.9
Inner Hampton Roads	7.3 ± 1.9	1.1 ± 0.2	0.8 ± 0.1	1.0 ± 0.2	1.0 ± 0.2	1.2 ± 0.2	6.8 ± 0.8	4.7 ± 0.8
Lower Elizabeth River (main)	15.0 ± 7.9	1.0 ± 0.3	0.8 ± 0.1	2.3 ± 1.4	0.7 ± 0.1	0.9 ± 0.4	11.6 ± 4.2	9.9 ± 3.2
Mid-Elizabeth River	22.9 ± 10.4	0.8 ± 0.2	1.0 ± 0.1	4.3 ± 1.3	0.5 ± 0.0	0.7 ± 0.0	21.1 ± 4.6	9.7 ± 3.3
Upper Elizabeth River	14.5 ± 3.6	0.9 ± 0.2	1.1 ± 0.4	2.7 ± 1.3	0.4 ± 0.1	1.2 ± 0.4	15.8 ± 1.7	6.4 ± 1.2

^a Enrichment factors (EF) were calculated for individual samples in each location area and an average EF for the area then calculated.

^b Ranges are ± 1 Standard Deviation.

in relation to the average crustal abundance and still be free of anthropogenic inputs. This method does, however, give a common reference point for comparison. A value of 1 would mean neither enrichment nor depletion in relation to the Earth's crust. The crustal abundance data of Taylor (1964) were used to compute the EF for all data in this article. Sinex and Helz (1981) state that the EF is not very sensitive to the choice of reference material, and if average shale data were used instead of average crustal abundance, the enrichment factors would change by less than 10% except for Cd, Pb, and Zn, which would decrease approximately 40%–50%.

The enrichment factors, computed for individual samples within each location group and averaged to obtain the group value are shown in Table 5. Elements that show definite enrichment are Cd, Cu, Pb, and Zn. The greatest enrichment occurs, as expected, in the heavily industrialized Elizabeth River. Cadmium and Pb show the greatest enrichment, with Zn next and the least for Cu. The enrichment patterns are almost identical for Cu, Pb, and Zn, and slightly different for Cd. The seemingly high enrichment factors for Cd and Pb for the OFFSHORE and Thimble Channel sediments are probably due to the relatively low concentrations for Fe. Cadmium and Pb concentrations in these sediments were very low; several will have to be reanalyzed with larger aliquots to give values above detection limits. Given the nature of the sediments (sands) and the very low Fe values, these enrichment factors should be cautiously interpreted. Even though the OFFSHORE samples are defined as being enriched, the absolute concentrations of Cd and Pb obviously indicate no need for environmental concern. The enrichment factors for Cd, Cu, Pb, and Zn are within the range of values computed by Sinex and Helz (1981) for various East Coast and Gulf Coast estuaries. Enrichment factors for Co, Cr, Mn, and Ni were at, or below one.

The data comparison with Johnson and Villa (1976) are presented in Table 6. Strong enrichment of Cd,

Table 6. Comparison of enrichment factors from the current data with those from Johnson and Villa (1976) for the Elizabeth River.

Metal	Main stem		Southern branch	
	1974, EPA	1979, Rule	1974, EPA	1979, Rule
Cd	59 ± 74 ^a	15 ± 7.9	23 ± 12	19 ± 9.4
Cr	1.0 ± 0.9	0.8 ± 0.1	0.8 ± 0.4	1.0 ± 0.1
Cu	1.4 ± 1.5	2.3 ± 1.4	3.1 ± 2.7	4.0 ± 1.3
Pb	12 ± 12	12 ± 4.2	18 ± 14	21 ± 4.0
Zn	11 ± 11	10 ± 3.2	9 ± 6	8 ± 2.9

^a Ranges are ± 1 Standard Deviation.

Pb, and Zn is evident in both sets of data. However, there was an apparent decrease in the enrichment factor for Cd from 1974 to 1979 in the lower portion of the Elizabeth River (main stem). This decrease most likely resulted from reduced input of wastes and wastewater from a chemical plant along the river. Factors for Cr are unity (or near) in all cases, and there has been no change for Cu, Pb, or Zn since 1974.

Summary and Conclusions

The mean concentrations for extractable sediment metals were evaluated with respect to average crustal abundances. Levels of Cd, Cu, Pb, and Zn exceeded average crustal abundances for most of the study sites. Mean values for Cd, Cr, Cu, Fe, Pb, and Zn were not statistically different from samples measured in 1974 in the Elizabeth River. The range of values for the current study was much more narrow than in 1974.

Cumulative frequency curves suggested that there were two major geochemical populations for all metals and perhaps a third and smaller one for Cd, Cr, and Mn.

Graphs of metal vs Fe indicated that sediments from the Norfolk Disposal Site and the Thimble Shoal Channel were not anthropogenically affected and, for most metals, were slightly different in their geochemical nature. Diagrams for INSHORE data were

very different and indicated that several sites were enriched well above natural levels. Grouping of sediments as a function of particle size gave less scatter of the points and identified anomalously high samples. On the basis of present results, it is recommended that segregation of samples based on general particle size (sand or silt and clay) be done before plotting metal vs Fe.

When the data were evaluated using the enrichment factor (EF), Cd, Cu, Pb, and Zn showed enrichment with respect to crustal abundances. In general, metal concentrations in the NDS sediments were low; unusually low Fe values resulted in high EFs for Pb and Zn but especially for Cd. Although these sediments may be enriched in Cd, the concentration is low and would not be of environmental concern. When this type of data is presented, both sample concentrations and EF data should be included to allow for clear interpretation of the significance of the data.

Both the metal vs Fe graphs and the EF identified anomalous metal concentrations. The metal vs Fe diagrams identified anomalous concentrations for a greater number of elements than did the EF. An advantage of plotting the metal vs Fe is that there is no dependence on average abundance data which may not be appropriate for the study area sediment.

Metal concentrations, metal vs Fe graphs, and enrichment factors all identified the same sections of the study area as most affected by anthropogenic sources. Each of these means of data evaluation contributes unique and useful information and all should be included in data evaluation.

A suggested approach to geochemical data analysis is to: (1) evaluate metal concentrations using appropriate crustal abundances, (2) construct cumulative frequency graphs, (3) construct metal vs Fe diagrams utilizing particle size grouping, and/or (4) calculate enrichment factors choosing appropriate reference data. In all instances, the metal concentrations as well as plots or enrichment factors should be presented.

Metal concentration values from this and other studies (such as Sinex and Helz 1981) are obtained from partial sediment extractions, while the crustal abundances reflect total values for a given material. The EFs so calculated are conservative estimates and may actually be greater than the calculated values. Interpretation of the EFs must therefore be made with the method of extraction in mind and may vary from study to study. Interpretation of the results based on the extraction method can lead to estimation of the potential environmental impact based on enrichment of a given metal, that is, high enrichment factors ob-

tained using weak chemical extraction could be of greater environmental concern than the similar factors from strong extractants.

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