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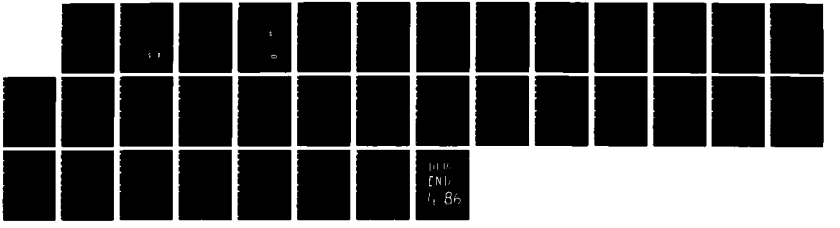

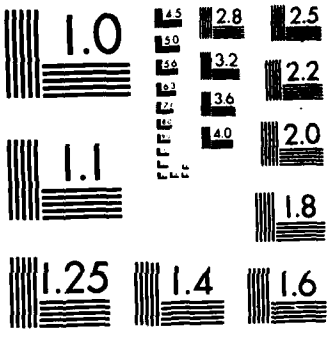

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CHEMICAL EXTRACTIONS OF HEAVY METALS IN SEDIMENTS AND METAL UPTAKE BY PALAEMONETES PUGIO AND MERCENARIA MERCENARIA

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US Army Corps
Of Engineers
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Report B- 21

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ABSTRACT

Sediments from four sites in the Hampton Roads Harbor and Elizabeth River system were subjected to solid phase bioassays using Palaemonetes pugio and Mercenaria mercenaria. A reference sediment from an offshore potential disposal site was included. Metal levels in both organisms after exposure to the sediments varied little between sites. There was essentially no difference in metal uptake between organisms exposed to the test sediments and to the reference sediment. Based on these results, all of the test sites would be acceptable for ocean disposal with respect to the metals tested. Metals concentrations in Palaemonetes were generally greater than in Merceneria. The amounts of metals extracted from the sediments were in the order of Conc HNO_3 + H_2O_2 > 1 N HNO_3 > DTPA. Differences in metal levels in the Conc HNO_3 + H_2O_2 and DTPA extracts from different sediments were generally significant and were related to sediment type and sampling location. Since there was no significant difference in the concentrations in tissue for either organism, there was no correlation of metal uptake with sediment extraction method. Out of four sites and seven metals studied with two test organisms, only four instances of bioaccumulation occurred. Using data from sediment extractable metals and metal/Fe ratios, Palaemonetes were enriched with respect to the sediment in Cr, Cu, Ni, Pb, and Zn; Mercenaria were enriched in Pb and Zn.

INTRODUCTION

Because of the increasing amounts of toxic metals from anthropogenic sources in the sedimentary environment, various means for determining their effects on marine organisms have been devised. Reaction to the uptake of metals ranges from the obvious toxic responses to those of chronic and sub-chronic effects. Chronic levels of metals in organisms and any chronic response are often difficult to detect or assess. These levels are of importance since prolonged chronic levels or synergims of various metals and/or other toxicants can cause undue stress on the organisms. The most direct way to assess the degree of biological uptake of toxic metals from sediments is to collect and analyze the sediments and organisms dwelling therein. The problems to this general approach are many. The collection of sufficient biomass, or of desired species is often difficult. The task is frequently impossible if the sediment in question contains high levels of toxicants, low dissolved oxygen, nutrients, or other factors which result in a few to no organisms being present.

Because of these and other difficulties, laboratory bioassay techniques have been developed. The need to standardize procedures, test organisms, and other factors led to the development of the "Implementation Manual" by the Environmental Protection Agency (EPA) and U.S. Army Corps of Engineers (COE) (1978). Although there are several advantages to laboratory bioassays, there are also some drawbacks, primary of which is the time and cost for these tests. The Ocean Dumping criteria require that for evaluation of sediment toxicity a three-phase (liquid, suspended-solid, and solid) bioassay be used for each sample. If proper replication of sediment samples and

multiple test organisms are used, the task of testing a large number of sediments becomes enormous and costly. Raymond W. Alden, III (personal communication) adopted the suspended solid phase bioassay for use as a screening test for large numbers of sediment samples. This method was found to work very well as a screening technique; however, the development of a relatively rapid, simple, and inexpensive method for initial screening of sediments for toxic metals availability would be very useful. The possibility that this might be accomplished using a chemical extractant of the sediment is very inviting. Although it is realized that a single extractant would not be expected to work for all metals or organisms, even a series of extractants may be an advantageous alternative to the bioassay method.

Chemical extractants have been successfully used for both major and trace metals in soils for many years (Mortvedt et al., 1982). Some researchers and reviewers (Pequegnat et al., 1978) argue that, at present, research indicates that no simple extractant can be developed to predict biological availability of sediment trace metals. While this is probably true, a less than simple chemical extractant scheme may be possible to attain and prove less costly and time consuming than bioassays techniques, especially for screening purposes.

The variety of chemical extractants is nearly endless. Those that are most likely to be initially tested are the ones already successfully used for trace metals in soils. Most of the marine sediment extracting (or leaching) techniques have been concerned with determining the partitioning in various chemical phases with no direct interest to the bioavailability

(Hirst and Nicholls, 1958; Chester and Hughes, 1967; Presley et al., 1972; Gibbs, 1973). Diks and Allen (1983) studied the uptake of Cu in suspensions from four river sediments by tubificid worms. They extracted the Cu from five different fractions of the sediment and attempted to relate its uptake by the worms to the concentrations of these five phases. They found a high correlation between uptake of Cu and its amount present in the manganese oxide/easily reducible phase. Other researchers have studied dredged material but were still primarily concerned with metal partitioning (Brannon et al., 1976; Chen et al., 1976).

This method of assessing potential bioavailability is receiving increased interest and attention. Depending on the chemical nature of the sediment, the determination of metals in these different chemical fractions may have merit. A major problem in comparing metals extracted in these various phases to their biological uptake is that the entire fraction of each is dissolved. Biologically available metals may occur primarily in one of these phases or may be the most loosely-bound portion in several phases. A method is needed that will extract those metals easily available to biological organisms regardless of the phase in which they exist. This paper presents the results from the testing of three extraction methods.

The types of chemical extractants may conveniently be divided into three groups: (1) acids, (2) chelates; and (3) salts. The standard sediment extractant utilized in the author's laboratory is hot, concentrated HNO_3-plus-30% H_2O_2. While being far from a bulk metal extractant, this is, of course, a rather severe treatment. This mixture is expected to remove metals associated with hydrous oxides, carbonates, and organic matter and

to strongly leach the remaining constituents. Metals thus extracted should be well above the maximum concentrations ever expected to affect any organisms or be released by any chemical changes to which the sediments may be subjected. Because of the reasons given, plus the fact that a large data base has already been established using this extractant on lower Chesapeake Bay area sediments, it was included in the bioavailability study.

Weak acid (0.01 - 1.0 N) extractants are commonly used by many soil test laboratories for estimating trace metal availabilities. The acidic nature of soils and plant root exudates make such extractants very appropriate. For marine organisms and sediments, these solutions may seemingly be less applicable. Acid extractants may, however, simulate conditions encountered in the gut of many organisms that ingest sediments. Gates and Travis (1969) found that pH 4 was the lowest known for benthic invertebrate guts. Only small amounts of metal would be released at this pH. Vertebrate digestive tracts are commonly at pH values of 3 or less. In all cases, of course, there are mechanisms of uptake and organisms and soil/sediment interactions that are not yet thoroughly documented.

Malo (1977) used 0.3 N HCl to extract aquatic sediments but was primarily interested in the metals associated with the "acid extractable oxides."

Pequegnat and Presley (1978) used 1 N HNO_3 to extract marine sediments as an estimate of bioavailability. They stated that the 1 N concentration was practical where large amounts of $CaCO_3$ are present. Because of their work and the fact that a stronger concentration of HNO_3 was used in the first procedure, the 1 N concentration was chosen as the second of the test extractants in the current study.

Extractants containing chelates have been most recently introduced in the field of soil testing (Lopez and Graham, 1971; Lindsay and Norvell, 1969a, b; Rule and Graham, 1976). Chelates are of interest as extractants because of their natural presence in organisms and their particular affinity for trace elements. Two of the most widely used chelates as soil extractants are ethylenediaminetetra acetic acid (EDTA) and diethylenetriamine pentaacetic acid (DTPA). The latter chelate was chosen as an extractant in the present study.

Salt solutions (0.10 to 1.0 N) have long been used as metal extractants in soils. They are most commonly used for major metals. Since marine systems already are at such salt concentrations, these solutions are not expected to be effective as a primary extractant for trace metals in marine/estuarine sediments.

The present report utilizes data obtained when sediments from dredging sites in the Hampton Roads Harbor and Elizabeth River, Virginia, were tested for toxicity by a solid phase bioassay method utilizing the grass shrimp Palaemonetes pugio and clam Mercenaria mercenaria.

MATERIALS AND METHODS

The Port of Hampton Roads, Virginia, is located within the major metropolitan area encompassed by Norfolk, Virginia Beach, Chesapeake, Portsmouth, Newport News, and Hampton (Figure 1). The waters of this harbor are along one of the most industrialized coastal areas in the eastern part of the United States.

Sediments for the bioassays were collected from four dredging sites in the Hampton Roads Harbor and Elizabeth River (Figure 1). Site D was located at the western end of the Newport News Channel in Hampton Roads Harbor, near major shipyard facilities and ship anchorages. Site E was adjacent to the large naval base in the Harbor. Site H was near the confluence of the Western Branch and main stem of the Elizabeth River. This area is downstream of the most heavily industrialized portion of the river. Site P was located in a lightly industrialized area near the upper reach of the Southern Branch of the Elizabeth River. A brief sediment description is presented in Table 1. Ten grabs were taken at each site using a $0.76m^3$ clamshell grab and material from each was composited to obtain test sediment for each size. Bioassays were started the day following sediment collection. The ten-day solid phase bioassays utilized methods as described by the EPA and COE (1978). The grass shrimp Palaemonetes pugio and the clam Mercenaria mercenaria were used as test organism in these bioassays. The organisms were collected in non-industrial areas and acclimated to the conditions of $20^{\circ}C$ temperature and 30 ppt. salinity before the beginning of the bioassay. Organisms were then acclimated in 30 L aquaria to reference sediment taken from a potential offshore disposal site located in nearshore shelf waters of the Atlantic

Ocean, approximately 20 km off the mouth of the Chesapeake Bay. The organisms were then exposed to sediments from the four test sites with one additional group exposed to only the reference sediment as a control. All rediment sites (including reference) were replicated six times. Further details concerning the study area, sediments, and bioassay methods may be obtained from Alden and Young (1982). At the end of the 10-day bioassay, samples of the sediments and both types of organisms were taken from each of the tanks for metals analyses. Sediment samples were dried at $<40^{\circ}C$, crushed to pass a 2mm stainless steel sieve, and stored until extracted. Both organisms were purged for 24 hours in 30 ppt. salinity water. Palaemonetes were rinsed uickly with deionized water and dried at $60^{\circ}C$. Mercenaria were washed with deionized water, shucked and the tissue and fluids dried at $60^{\circ}C$. Tissue samples were analyzed within two weeks of collection.

Organisms (usually five per sample) were dissolved using 22.4 M redistilled HNO_3 + 30% H_2O_2. Sediment samples were extracted by each of the following methods: (1) Hot, concentrated (15.4 M) redistilled HNO_3 + 30% H_2O_2 for six hours, filtered through pre-rinsed Whatman No. 42 filter paper; (2) 1 N HNO_3 (after neutralization of carbonates), shaken for two hours, centrifuged, if necessary filtered; and (3) 0.005 M DTPA in 0.10 M NaOAc, shaken for four hours, centrifuged, filtered if necessary. Metals analyses for Cr, Cu, Fe, Mn, Pb, Ni, and Zn were performed by atomic absorption spectrophotometry (AAS) using a Perkin-Elmer 603. Standards were prepared in the appropriate matrix for the various extracts. Quality control materials used were SRM No. 1654 (River Sediment) and SRM No. 1566 (Oyster tissue) from the National Bureau of Standards.

Linear regression analyses were performed with the metal concentrations of either Palaemonetes or Mercenaria as the dependent variable and sediment concentrations from the three extractions as the independent variables. Regression analyses were also done in the same manner using metal concentrations normalized to the iron concentration (metal/Fe). One-way ANOVA/ Duncan's Range analyses were conducted on the data set to test replicate homogeneity and to compare site means from the sediment extractions and for the tissue concentrations using both the metal concentration and the iron-normalized coefficients. All statistical packages were from the SPSS manual (Nie, 1975).

RESULTS AND DISCUSSION

ANOVA/Duncan's Range Test showed that the replicate values for all data sets (sediment extractions and tissue concentrations) constituted statistically similar subsets at the 95% confidence level. Variances for all data sets were shown to be homogeneous by Bartlet's test.

Organism Uptake-Bioaccumulation

There were 56 instances of possible uptake, but significant uptake occurred in only 3 cases. The only statistically significant difference between sites in uptake of metals by Palaemonetes was for Cu (Table 2). (Note the two significantly different groups, a and b, for Site P and the Reference Site.) Organisms from Site P sediments contained higher levels than those from the Reference Site and this is the only instance of bioaccumulation by Palaemonetes. In many cases, metal concentrations for the shrimp from the test sediments were less than those from the Reference sediment.

There were significant differences in metal uptake between sites by Mercenaria in only two cases (Table 2). Clams from Site D had statistically greater Fe concentrations than from all other sites, including the Reference sediment. Concentrations for Pb were significantly less from Site E than from Reference Site organisms; Pb concentrations from all other sites were the same as for the Reference Site. Mercenaria concentrations of Zn were greater from Site P exposure than from other sediments; tissue levels of Zn from all other sediments were statistically the same. There were only

two instances of bioaccumulation (one each for Fe and Zn) by Mercenaria. Although the means for several tissue metal concentrations for many sites were less from the test sites than for the Reference Site, they were not statistically different due to the high variability of the data.

Two of the three instances of bioaccumulation were for metals from Site P sediments. Chemically extractable sediment metals were significantly less for Site P than for any of the other test sites; extractable metals from Site P were very similar to those from the Reference Site. Even so, the biological availability of Cu and Zn appears to be greatest at Site P.

The similarity of metals concentrations of organisms exposed to the reference and test sediments suggests either similar bioavailabilities for all sediments and/or mechanisms of organism regulation of metals content. These observations were also made by Cross et al. (1970) when studying Mn, Fe, and Zn uptake by polychaetous worms.

Tissue concentrations from organisms exposed to the Reference sediment appear to be rather high for several of the metals. Unfortunately, data for background levels in the animals for this bioassay were not available. In a previous bioassay, Palaemonetes were sampled after laboratory acclimation (background) as well as after exposure to the Reference sediments. Reference sediments for both bioassays were taken from the same offshore area. Tissue concentrations for several metals after exposure to the Reference sediment were similar for both data sets. There was an increase in tissue concentrations of some metals (Cr, Mn, Ni, Pb) after exposure to the Reference sediment (Table 3). This may indicate greater amounts of biologically available metals in the Reference sediments than for those at the collection site or may reflect depuration by the organisms during the

acclimation period. Sediment metal concentrations from the Reference Site were low (discussed below) and sediment metals from the collection site were not determined.

Based on the results of this bioassay, all of the sites tested should be acceptable for ocean disposal with respect to metals. There was bioaccumulation in only one instance for Palaemonetes and two instances for Mercenaria.

Sediment Extractions

With only the exception of Mn at Site P and the Reference Site, metal concentrations extracted by Conc HNO_3 + H_2O_2 were significantly different between the various sites for all metals (Table 2). The amounts extracted were related to both the location and characteristics of the sediments. The (offshore) Reference sediment was a medium to coarse-grained sand with minor amounts of shell debris. Site P is upriver from the major industrial activity and this is reflected in the low amounts of extracted metals. Material from Site P was approximately 50% shell debris with the balance being fine sand (Table 1). Sites D, E, and H were fine-grained (silty clays) sediments in the highly industrialized areas of Hampton Roads Harbor and Elizabeth River (Figure 1) and had correspondingly greater levels of extractable metals. Ranking of the sites in order of increasing amounts of Conc HNO_3 + H_2O_2 extractable metals gives Ref Site < Site P < Site E < Site D < Site H. The only exception to this ranking is that the greatest level of extracted Mn was found at Site D.

Metal concentrations extracted by 1 N HNO_3 showed patterns similar to those from Conc HNO_3. For most sites, the amounts extracted by the 1 N HNO_3 were significantly lower than those for Conc HNO_3 for corresponding sediments. The exceptions to this occurred with Mn, Ni, and Pb levels in Site P samples. Only the Pb value appears to be greater for the 1 N than for the Conc HNO_3 and this difference appears to be related to the volume of acid used in the Conc HNO_3 extractant and the sediment carbonate content. Extracted metal levels in the two HNO_3 methods are most similar for the Reference Site and Site P sediments. This similarity is probably due to the high amount of shell and sand material in these samples and the low metal input from anthropogenic sources. The shell material will be, of course, easily dissolved by either of these acid concentrations.

Using the DTPA extraction, much lower concentrations of metals were obtained than in either of the two HNO_3 methods. One anomalous exception was for Ni extracted from the reference sediment where the DTPA extracted amount was greater than for 1 N HNO_3 and equal to the Conc HNO_3 extracted concentration. For most metals, the DTPA extracted concentrations were significantly different for the various sites. As with the HNO_3 methods, DTPA extracted levels were most similar between Site P and the Reference Site. The DTPA results show that there are different amounts of easily removable (extractable) metals in the sediments; these do not correlate with the 1 N HNO_3 extraction method (Table 4). Generally there was not a good correlation between metals extracted by any of the three methods (Table 4). The consistently good correlation for extracted Mn and Zn for all methods suggests that the chemical forms of these two differ from the other metals and are similarly affected by the three extractions.

Animal-Sediment Interactions

Since there was essentially no difference in metal uptake from the various sediments, regression analysis of tissue concentrations of both Palaemonetes and Mercenaria against concentrations extracted from sediments showed no significant correlations. The three extractants discussed herein cannot be used to predict uptake of metals by Palaemonetes pugio or Mercenaria mercenaria from the sediments in this bioassay. Sediment extractions showed that the levels of extractable metals in these sediments varied greatly. DTPA values indicated that there were significantly different amounts of easily extractable metals, yet organism uptake was not a function of these concentrations. Two of the three isolated cases of bioaccumulation occurred on the sediment with the least amount of extractable metals. As indicated in an earlier section, the mechanisms of organism-sediment interaction are not yet well understood.

Organism Enrichment

When studying organisms collected from various environments, organism enrichment of metals relative to sediment metals is sometimes determined. Organism enrichment of metals is measured by comparing tissue concentrations with sediment extracted concentrations (Cross et al., 1970). Certainly the choice of sediment extractant may determine if enrichment occurs, yet this is a convenient method of comparing metal concentrations of organisms exposed to different sediments.

Based on ANOVA/Duncan's Range Test for metal/Fe ratios, Palaemonetes were enriched with respect to the sediment in Cr, Cu, Ni, Pb, and Zn using

data from either of the three extractants, and enriched in Mn with respect to Conc HNO_3 and 1 N HNO_3 extracted levels. Mercenaria were enriched in Pb and Zn with respect to all three extractants and in Mn when using the Conc HNO_3 extract data (Tables 5 and 6).

Metal/Fe ratios are often used to eliminate the effect of ingested (or other) sediment when determining enrichment or bioaccumulation. A potential problem with this method, of course, is that Fe may also be enriched or bioaccumulated. The normally high amounts of sediment Fe in relation to other metals usually prevents this type of problem from occurring. In other words, the amount of Fe uptaken by organisms in relation to its sediment concentration is much greater than for any other metal (Table 2). Unpublished research by this author suggests that the use of metal/Al data might be more informative, but much more research is needed.

SUMMARY

Uptake of metals by Palaemonetes pugio and Mercenaria mercenaria varied little as a function of the concentration in sediment to which they were exposed including the reference sediment. Only three instances of bioaccumulation were noted and based on these results, the test site sediments should be acceptable for ocean disposal. Since metal uptake did not vary as a function of sediment concentration, regression analyses of tissue concentrations against sediment extracted levels showed no correlations. It is postulated that either the bioavailabilities of metals are similar for all sediments or the organisms are able to regulate tissue concentrations from these test sediments.

All extractants removed variable amounts of metals from the sediments with the extracted concentrations in the order of Conc HNO_3 + H_2O_2 > 1 N HNO_3 > DTPA. The Conc HNO_3 and DTPA were better discriminators between sediments than was 1 N HNO_3. The order of extracted metal concentrations was generally Ref Site < Site P < Site E < Site D < Site H.

Using metal/Fe ratios, Palaemonetes were enriched with respect to the sediment in Cr, Cu, Ni, Pb, and Zn using data from either of the three extractants and Mercenaria were enriched in Pb and Zn utilizing levels from any of the three extractants.

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TABLE 1. Sediment Descriptions.

REFERENCE SITE	Medium to coarse sand; none collected >2mm, numerous small shell fragments, no visible O.M.
SITE P	Approximately 17% of sampled material was >2mm and was all shell hash - this was not chemically analyzed.
	<2mm: about 50% shell debris, the rest is fine sand with very minor amounts of mud - no visible O.M.
SITE D	Fine gray mud, no sand, minor trace of shell debris, some O.M.
SITE E	Fine gray mud with some very fine sand, minor trace of shell debris, some O.M.
SITE H	Fine gray mud, no sand, minor trace of shell fragments, some O.M.

TABLE 2. Mean and standard deviation (mg/kg, dry wt.) for sediment extractions and tissue concentrations. Each mean is an average of six replications.

SITE	SEDIMENT EXTRACTION			TISSUE CONCENTRATION	
	DTPA	1 N HNO_3	HNO_3-H_2O_2	SHRIMP	CLAM
			CR		
REF	0.4 ± 0.3^{a}	0.8 ± 0.0^{a}	3.0 ± 0.6^{a}	48.5 ± 43.1^{a}	4.6 ± 3.0^{a}
d	0.6 ± 0.3^{a}	6.1 ± 0.3^{d}	43.4 ± 3.1^{d}	41.5 ± 45.9^{a}	2.6 ± 3.0^{a}
e	0.4 ± 0.0^{a}	3.5 ± 0.5^{b}	29.6 ± 0.9^{c}	27.8 ± 32.4^{a}	1.6 ± 2.4^{a}
h	0.8 ± 0.2^{b}	5.7 ± 0.5^{d}	49.4 ± 4.4^{e}	5.6 ± 9.3^{a}	1.2 ± 1.9^{a}
p	0.9 ± 0.0^{b}	4.3 ± 0.5^{c}	9.6 ± 0.9^{b}	17.1 ± 21.7^{a}	6.8 ± 11.6^{a}
			CU		
REF	0.2 ± 0.3^{a}	0.5 ± 0.1^{a}	1.1 ± 0.6^{a}	241.4 ± 26.0^{a}	16.8 ± 2.3^{bc}
d	0.7 ± 0.1^{b}	6.8 ± 0.1^{d}	13.6 ± 0.8^{d}	257.0 ± 33.7^{ab}	15.0 ± 2.9^{ab}
e	1.9 ± 0.1^{c}	5.4 ± 0.3^{c}	10.2 ± 0.3^{c}	330.0 ± 83.9^{ab}	13.9 ± 2.7^{a}
h	5.3 ± 0.0^{d}	12.0 ± 0.5^{e}	23.2 ± 1.9^{e}	273.1 ± 40.6^{ab}	13.4 ± 1.5^{a}
p	0.4 ± 0.3^{a}	4.7 ± 0.1^{b}	5.3 ± 0.2^{b}	352.0 ± 143.1^{b}	19.5 ± 2.2^{c}
			FE		
REF	28.4 ± 3.8^{a}	760.0 ± 129.0^{a}	2763.0 ± 278.0^{a}	78.5 ± 21.0^{a}	156.1 ± 10.4^{a}
d	119.1 ± 4.9^{c}	10307.0 ± 1277.0^{d}	31704.0 ± 1891.0^{d}	108.9 ± 41.6^{a}	183.4 ± 25.1^{b}
e	251.4 ± 4.4^{d}	5927.0 ± 2216.0^{c}	23142.0 ± 857.0^{c}	136.0 ± 49.2^{a}	154.3 ± 28.5^{a}
h	341.5 ± 11.3^{e}	6667.0 ± 635.0^{c}	38246.0 ± 2063.0^{e}	124.6 ± 69.0^{a}	139.1 ± 14.3^{a}
p	63.9 ± 4.6^{b}	2969.0 ± 834.0^{b}	7070.0 ± 239.0^{b}	141.1 ± 84.0^{a}	141.9 ± 17.9^{a}
			MN		
REF	9.8 ± 1.6b	26.2 ± 5.8^{a}	42.2 ± 5.7^{a}	16.9 ± 10.9^{a}	18.0 ± 7.9^{a}
d	111.7 ± 3.8^{e}	324.8 ± 9.8^{e}	481.2 ± 36.5^{d}	12.0 ± 6.3^{a}	15.1 ± 9.6^{a}
e	62.0 ± 2.1^{c}	136.0 ± 10.1^{c}	257.0 ± 4.9^{b}	20.6 ± 10.6^{a}	15.4 ± 4.2^{a}
h	70.1 ± 1.2^{d}	186.0 ± 23.2^{d}	390.9 ± 11.1^{c}	15.5 ± 10.5^{a}	13.5 ± 3.7^{a}
p	3.4 ± 0.2^{a}	59.3 ± 2.1^{b}	54.9 ± 1.1^{a}	14.5 ± 6.0^{a}	10.0 ± 3.6^{a}

CONTINUED

TABLE 2. Concluded.

SITE	SEDIMENT EXTRACTION: DTPA	SEDIMENT EXTRACTION: 1 N HNO_3	SEDIMENT EXTRACTION: HNO_3 - H_2O_2	TISSUE CONCENTRATION: SHRIMP	TISSUE CONCENTRATION: CLAM
SITE			**NI**		
REF	1.0 ± 0.3[a]	0.1 ± 0.2[a]	1.0 ± 0.5[a]	35.0 ± 15.7[a]	8.2 ± 6.3[a]
d	2.5 ± 0.4[c]	6.5 ± 0.4[c]	28.0 ± 1.8[d]	30.3 ± 13.9[a]	11.5 ± 4.8[a]
e	2.9 ± 0.3[d]	3.9 ± 0.5[b]	16.3 ± 1.4[c]	59.5 ± 46.0[a]	9.2 ± 4.3[a]
h	4.4 ± 0.3[e]	7.1 ± 0.3[d]	31.2 ± 1.9[e]	23.5 ± 20.4[a]	6.5 ± 2.7[a]
p	1.9 ± 0.4[b]	10.0 ± 0.3[e]	9.1 ± 1.5[b]	31.2 ± 38.6[a]	10.2 ± 4.7[a]
			PB		
REF	0.8 ± 0.0[a]	3.5 ± 1.4[a]	3.8 ± 1.7[a]	8.0 ± 4.5[a]	24.7 ± 11.0[b]
d	0.8 ± 0.0[a]	11.3 ± 0.0[c]	17.2 ± 0.8[c]	10.8 ± 12.8[a]	14.6 ± 8.3[ab]
e	4.0 ± 0.0[b]	8.9 ± 0.9[b]	13.6 ± 0.4[b]	12.0 ± 7.8[a]	12.0 ± 4.4[a]
h	9.5 ± 0.9[c]	18.0 ± 0.8[d]	27.3 ± 2.2[e]	13.5 ± 11.9[a]	10.1 ± 10.2[ab]
p	0.8 ± 0.0[a]	30.0 ± 1.0[e]	22.0 ± 1.2[d]	19.2 ± 8.1[a]	23.1 ± 15.1[ab]
			ZN		
REF	0.6 ± 0.3[a]	4.1 ± 0.8[a]	6.2 ± 0.6[a]	131.7 ± 15.0[a]	99.9 ± 9.3[a]
d	5.5 ± 0.3[c]	24.3 ± 0.3[c]	78.1 ± 5.7[d]	130.5 ± 23.5[a]	93.9 ± 9.6[a]
e	10.1 ± 0.4[d]	24.9 ± 1.1[c]	59.1 ± 1.9[c]	161.6 ± 68.7[a]	94.8 ± 9.1[a]
h	33.0 ± 0.4[e]	62.6 ± 2.2[d]	128.9 ± 4.1[e]	114.4 ± 17.4[a]	92.4 ± 10.2[a]
p	4.5 ± 0.2[b]	12.5 ± 0.5[b]	14.1 ± 0.7[b]	169.9 ± 62.5[a]	116.0 ± 9.0[b]

Within a column, for each metal, means with the same letters are not significantly different at the 95% confidence level using the Duncan's Range Test.

TABLE 3. Metal concentrations (mg/kg, dry wt.) of *Palaemonetes* from acclimation tank (Background) and after exposure to Reference sediment.

	CR	CU	FE	MN	NI	PB	ZN
BACKGROUND	1.5 ± 1.2	163 ± 10.7	40.4 ± 6.6	9.7 ± 3.7	<2.5	<2.5	92.5 ± 3.4
REFERENCE SEDIMENT	12.1 ± 14.2	140 ± 7.8	47.7 ± 21.4	15.5 ± 9.0	19.3 ± 21.0	25.1 ± 3.0	95.1 ± 8.2

TABLE 4. Correlation and R^2 values between extraction methods.

R VALUES

	Cr	Cu	Fe	Mn	Ni	Pb	Zn
CONC HNO_3 vs DTPA	.1061	.8727	.8142	.9733	.8147	.5906	.8769
CONC HNO_3 vs 1 N HNO_3	.2586	.7593	.6725	.8862	.0171	.5285	.8767
1 N HNO_3 vs DTPA	.6214	.6504	.3252	.8881	.0242	-.1644	.9584

R^2 VALUES

	Cr	Cu	Fe	Mn	Ni	Pb	Zn
CONC HNO_3 vs DTPA	.0113	.7642	.6629	.9473	.6637	.3488	.7690
CONC HNO_3 vs 1 N HNO_3	.0669	.5765	.4523	.7854	.0003	.2793	.7686
1 N HNO_3 vs DTPA	.3861	.4230	.1085	.7887	.0004	.0270	.9185

TABLE 5. Mean and standard deviation of metal/Fe ratios for sediment extractions and tissue concentrations. Each mean is an average of six replications.

	SEDIMENT EXTRACTION			TISSUE CONCENTRATION	
SITE	DTPA	1 N HNO_3	CONC HNO_3	SHRIMP	CLAM
			CR		
REF	.0153 ± .0119^{b}	.0011 ± .0002^{b}	.0011 ± .0002^{a}	.6472 ± .6070^{b}	.0299 ± .0206^{a}
d	.0048 ± .0022^{a}	.0006 ± .0001$_{a}$	.0014 ± .0001^{b}	.3376 ± .2399^{ab}	.0154 ± .0173^{a}
e	.0016 ± .0000^{a}	.0006 ± .0001$_{a}$	.0013 ± .0001^{b}	.2061 ± .1673^{a}	.0096 ± .0150^{a}
h	.0024 ± .0006^{a}	.0009 ± .0001$_{ab}$	.0013 ± .0001^{b}	.0887 ± .1426^{a}	.0084 ± .0131^{a}
p	.0141 ± .0010^{b}	.0016 ± .0006$_{c}$	.0014 ± .0001^{b}	.0962 ± .0819^{a}	.0493 ± .0867^{a}
			CU		
REF	.0078 ± .0086^{a}	.0006 ± .0002^{a}	.0004 ± .0002^{a}	3.2727 ± .9287^{a}	.1084 ± .0190^{a}
d	.0056 ± .0009^{a}	.0007 ± .0001^{ab}	.0004 ± .0000^{a}	2.6562 ± 1.0495^{a}	.0821 ± .0138^{a}
e	.0077 ± .0005^{a}	.0010 ± .0003^{b}	.0004 ± .0000^{a}	2.6832 ± 1.1215^{a}	.0936 ± .0312^{a}
h	.0155 ± .0005^{a}	.0018 ± .0002^{c}	.0006 ± .0000^{b}	2.6977 ± 1.1444^{a}	.0966 ± .0093^{a}
p	.0055 ± .0051^{b}	.0017 ± .0005^{c}	.0008 ± .0000^{c}	2.9719 ± 1.3895^{a}	.1404 ± .0294^{b}
			MN		
REF	.3521 ± .0889^{c}	.0344 ± .0043^{c}	.0153 ± .0016^{c}	.2221 ± .1256^{b}	.1161 ± .0525^{b}
d	.9382 ± .0415^{d}	.0320 ± .0047^{bc}	.0152 ± .0012^{c}	.1265 ± .0686^{ab}	.0788 ± .0375^{ab}
e	.2468 ± .0052^{b}	.0259 ± .0096^{ab}	.0111 ± .0004^{b}	.1712 ± .1000^{ab}	.0990 ± .0124^{ab}
h	.2054 ± .0063^{b}	.0279 ± .0014^{abc}	.0102 ± .0003^{b}	.1227 ± .0271^{ab}	.0960 ± .0174^{ab}
p	.0533 ± .0024^{a}	.0216 ± .0065^{a}	.0078 ± .0002^{a}	.1123 ± .0362^{a}	.0712 ± .0265^{a}

CONTINUED

TABLE 5. Concluded.

SITE	SEDIMENT EXTRACTION: DTPA	SEDIMENT EXTRACTION: 1 N HNO_3	SEDIMENT EXTRACTION: CONC HNO_3	TISSUE CONCENTRATION: SHRIMP	TISSUE CONCENTRATION: CLAM
			NI		
REF	.0373 ± .0153[b]	.0002 ± .0004[a]	.0004 ± .0002[a]	.4389 ± .1659[a]	.0527 ± .0402[a]
d	.0207 ± .0031[a]	.0006 ± .0001[ab]	.0009 ± .0001[c]	.3520 ± .3186[a]	.0621 ± .0253[a]
e	.0115 ± .0011[a]	.0007 ± .0002[ab]	.0007 ± .0001[b]	.4393 ± .2449[a]	.0596 ± .0273[a]
h	.0128 ± .0014[a]	.0011 ± .0001[b]	.0008 ± .0000[bc]	.2595 ± .2625[a]	.0473 ± .0213[a]
p	.0299 ± .0058[b]	.0036 ± .0010[c]	.0013 ± .0002[d]	.2078 ± .2359[a]	.0743 ± .0410[a]
			PB		
REF	.0282 ± .0036[d]	.0046 ± .0019[b]	.0014 ± .0005[b]	.1053 ± .0528[a]	.1578 ± .0695[ab]
d	.0066 ± .0003[a]	.0011 ± .0002[a]	.0005 ± .0000[a]	.0895 ± .0677[a]	.0830 ± .0527[ab]
e	.0159 ± .0003[c]	.0016 ± .0005[a]	.0006 ± .0000[a]	.1110 ± .1148[a]	.0825 ± .0425[ab]
h	.0279 ± .0032[d]	.0027 ± .0003[ab]	.0007 ± .0000[a]	.0952 ± .0341[a]	.0689 ± .0621[a]
p	.0124 ± .0009[b]	.0109 ± .0032[c]	.0031 ± .0003[c]	.1651 ± .0804[a]	.1704 ± .1185[b]
			ZN		
REF	.0201 ± .0087[a]	.0054 ± .0010[b]	.0022 ± .0002[b]	1.8076 ± .6184[a]	.6401 ± .0466[b]
d	.0460 ± .0022[c]	.0024 ± .0003[a]	.0025 ± .0002[c]	1.3426 ± .5504[a]	.5170 ± .0646[a]
e	.0401 ± .0012[b]	.0047 ± .0016[b]	.0026 ± .0001[c]	1.2380 ± .3655[a]	.6268 ± .0897[ab]
h	.0966 ± .0032[e]	.0095 ± .0011[c]	.0034 ± .0001[d]	1.1540 ± .5482[a]	.6689 ± .0965[b]
p	.0703 ± .0038[d]	.0045 ± .0012[b]	.0020 ± .0000[a]	1.4507 ± .6708[a]	.8311 ± .1502[c]

Within a column, for each metal, means with the same letters are not significantly different at the 95% confidence level using the Duncan's Range Test.

TABLE 6. Mean and standard deviation of metal/Fe ratios for the averages of all replications by extraction method or tissue concentration. Each mean is an average of 30 replications.

	CR	CU	MN	NI	PB	ZN
DTPA	.0076 ± .0078[a]	.0084 ± .0056[a]	.3591 ± .3129[d]	.0224 ± .0123[a]	.0182 ± .0089[a]	.0546 ± .0272[a]
1 N HNO_3	.0010 ± .0005[a]	.0012 ± .0006[a]	.0284 ± .0072[ab]	.0012 ± .0013[a]	.0042 ± .0039[a]	.0053 ± .0026[a]
CONC HNO_3	.0013 ± .0002[a]	.0005 ± .0002[a]	.0019 ± .0031[a]	.0008 ± .0003[a]	.0013 ± .0010[a]	.0025 ± .0005[a]
SHRIMP	.2752 ± .3566[b]	2.8563 ± 1.0828[b]	.1509 ± .0857[c]	.3385 ± .2512[b]	.1132 ± .0749[b]	1.3986 ± .5693[b]
CLAMS	.0225 ± .0417[a]	.1042 ± .0289 [a]	.0922 ± .0343[bc]	.0592 ± .0312[a]	.1125 ± .0812[b]	.6568 ± .1363[c]

Within a column, for each metal, means with the same letters are not significantly different at the 95% confidence level using the Duncan's Range Test.

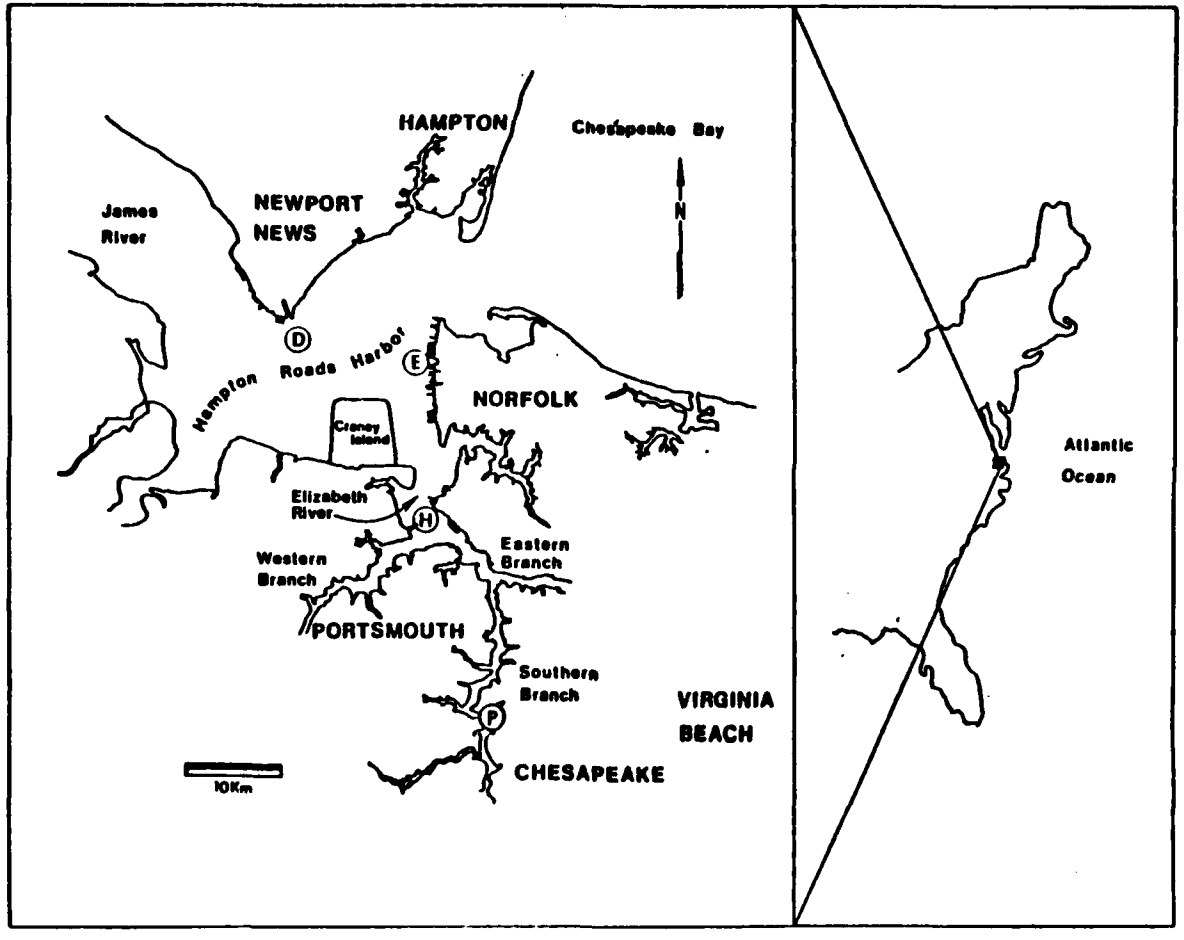

FIGURE 1. Study area: sediment collection sites in the Port of Hampton Roads, Virginia.

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