

## LEACHING AND BIOASSAY STUDIES ON THE SIGNIFICANCE OF HEAVY METALS IN DREDGED SEDIMENTS

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### ABSTRACT

The presence of heavy metals in dredged sediments has prompted the development of dredged material disposal criteria. The criteria are designed to try to minimize the adverse environmental impact of chemical contaminants in dredged sediments on water quality at the dredging and dredged material disposal site. Dredged material disposal criteria are often based on the bulk chemical content of the sediments. Bulk chemical criteria are not technically valid, since the amounts of heavy metals available in sediments are not related to the total content of the metals in the sediments.

Studies have been initiated to examine the release of heavy metals from dredged sediments from various locations in the U.S. These studies have shown that for sediments tested thus far, the only heavy metal that is released in potentially significant amounts to possibly be adverse to water quality at a dredged-material, disposal-site water column is manganese. All other heavy metals tested were either sorbed, not released, or released in sufficiently small quantities to not significantly change the concentrations of heavy metals at an open water dredged material disposal site. Bioassays of the elutriates of dredged sediments were conducted to examine the toxicity of released metals and other contaminants to aquatic organisms. The toxicity of the sediment elutriates was insufficient to be adverse to aquatic organisms at a typical open water disposal site water column.

### RÉSUMÉ

La présence de métaux lourds dans les sédiments dragués a contribué à l'élaboration de critères relatifs à l'élimination des matériaux dragués. Les critères ont été conçus pour tenter de minimiser les effets nuisibles des substances chimiques contaminantes dans les sédiments dragués sur la qualité de l'eau dans les zones de dragage et d'élimination des sédiments dragués. Les critères relatifs à l'élimination des matériaux dragués sont souvent basés sur la teneur brute en produits chimiques des sédiments. Ces critères ne sont pas valables du point de vue technique, car la quantité de métaux lourds disponible dans les sédiments n'est pas liée à la teneur totale en métaux des sédiments.

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On a entrepris des études pour examiner la libération de métaux lourds par les sédiments dragués à divers endroits aux Etats-Unis. Ces études ont montré que dans le cas des sédiments analysés jusqu'à présent, le manganèse est le seul métal lourd qui est libéré en quantités suffisamment importantes pour contaminer l'eau dans la colonne d'eau au lieu d'élimination des matériaux dragués. Tous les autres métaux lourds analysés étaient soit adsorbés, soit retenus, soit libérés en quantités insuffisantes pour changer de façon significative les concentrations de métaux lourds dans une zone découverte d'élimination des sédiments dragués constituée d'un plan d'eau. Des épreuves biologiques ont été effectuées sur les produits de lavage des sédiments dragués pour examiner la toxicité des métaux libérés et d'autres substances contaminantes pour les organismes aquatiques. La toxicité des produits de lavage des sédiments était insuffisante pour nuire aux organismes aquatiques dans une colonne d'eau découverte typique d'une zone d'élimination constituée d'un plan d'eau.

## INTRODUCTION

Sediments dredged from waterways near urban and industrial centers often have elevated concentrations of heavy metals. This situation has prompted the U.S. EPA and its predecessor organization to adopt dredged material disposal criteria which are based on the bulk chemical characteristics of the sediments. These criteria emphasize that if the concentrations of heavy metals in the sediments exceed an arbitrarily established number, the sediments are classified as polluted and special provisions must be made for their disposal.

Over 400 million cubic yards of sediments are dredged in the U.S. each year at a cost of approximately \$200 million (Lee 1975). In some parts of the U.S., use of alternate methods to dispose of dredged material considered polluted has caused a significant increase in the cost of maintenance of waterways. In some areas, dredging has been halted completely because no suitable site for disposal of the "polluted" sediments could be found.

Examination of the aqueous environmental chemistry of heavy metals associated with natural water sediments would cause one to question the validity of using bulk chemical criteria to judge the effects of dredged material disposal on water quality. It is well known that one way to detoxify solutions of excessive concentrations of heavy metals is to add suspended material which will sorb the heavy metals and greatly reduce their availability to aquatic organisms. Lee and Plumb (1974) have presented an extensive discussion of the factors influencing the release of heavy metals and other contaminants from dredged sediments, with particular reference to the lack of technical validity to bulk sediment dredged material disposal criteria.

In 1973, the U.S. EPA and the U.S. Corps of Engineers developed a leaching procedure designed to ascertain the amounts of chemical contaminants

that might be released to the water column during disposal of hydraulically dredged sediments. This procedure, (U.S. EPA 1973a,b; Keeley and Engler 1974) termed the Elutriate Test, originally involved vigorously mixing one part by volume of proposed dredged sediment with four parts of disposal site water. The mixture was settled for one hour, followed by centrifugation and filtration. The chemical characteristics of the filtrate were then compared to the disposal site water characteristics. In the original version of the Elutriate Test, if the concentrations of contaminants in the elutriate exceeded 1.5 times the ambient concentrations at the disposal site water column, the sediment was termed "polluted." Recently this procedure was modified (U.S. EPA 1975) to include substitution of dredging site water for the disposal site water and exclude the arbitrary 1.5 factor. Instead, comparison of the test results to the comparable disposal site water column characteristics was instituted on a case-by-base basis. Such factors as the rate and amount of mixing at the disposal site, the ambient concentrations of contaminants in this region and the amount of release of contaminants from the dredged sediments are considered.

During the past several years a study has been conducted on the factors influencing the results of the Elutriate Test. Sediments from a wide variety of locations in the U.S. were subjected to this test, or modifications thereof, in order to determine the amounts of heavy metals and other contaminants released. Further, the elutriates for many of these sediments have been used in bioassay tests in order to ascertain acute lethal toxicity. This paper summarizes the results of these studies on the release of heavy metals from waterway sediments and the toxicity of their elutriates to selected aquatic organisms.

## CHARACTERISTICS OF THE ELUTRIATE TEST

The Elutriate Test is designed to simulate the conditions which will prevail upon disposal of hydraulically dredged material in open waters. These conditions represent the optimum opportunity for the release of heavy metals from dredged sediments because the sediments are slurried in an approximate one-to-four volume ratio with dredging site water and then either dumped from a hopper dredge or discharged from a pipeline dredge to the receiving water. Other types of dredging such as mechanical dredging, which involves the use of clamshell or drag lines and the loading of barges, result in a much denser dredged sediment mixture. When dumped, this usually descends to the bottom in a more or less cohesive mass. Little of the sediment interacts with the water column.

Lee *et al.* (1975b) discussed the factors influencing the results of the Elutriate Test based on studies conducted on sediments from a wide variety of U.S. waterways. These studies included sediments from Mobile, Alabama; Ashtabula, (Lake Erie) Ohio; San Francisco, California; Los Angeles, California and Bridgeport, Connecticut. Sediments were also collected from the Trinity River and Houston Ship Channel and Galveston, Texas City, Corpus Christi, Port Aransas and Port Lavaca in Texas. The factors that may influence the Elutriate Test that have been investigated include sediment-water ratio, shaking time, agitation method, sample size, settling time, sample storage time, salinity, water type, and oxygen status. This paper will present a summary of heavy metal results from these tests and bioassays of the elutriates. The complete data from these studies are available in Lee *et al.* (1975a,b).

Experimental techniques are presented in Lee *et al.* (1975b). In general, these have involved selecting sediments from a U.S. waterway with a sediment grab or corer, and transferring these under ice *via* air freight to the University of Texas at Dallas. Sediments and water are stored at 4°C for a minimum amount of time before conducting the Elutriate Tests and bioassays. The analytical procedure for the heavy metals utilized the APDC-MIBK extraction procedure (APHA *et al* 1971; U.S. EPA 1974) followed by atomic absorption flame techniques.

The bioassays were conducted with *Palaemonetes pugio* (grass shrimp) obtained from the Gulf Specimen Company, Panacea, Florida. The elutriates were decanted after having settled for one hour and the organisms were placed in these elutriates and observed for periods up to four days. The number of dead grass shrimp was determined at approximately 12 hour intervals. All bioassays were static.

The chemical characteristics of the bioassay solutions were determined. One of the principal differences between the bioassay elutriates and the heavy metal elutriates was that standard ASTM sea water was used for the bioassay elutriates. This solution had a salinity of approximately 30‰ (ASTM 1966). Additional details on the bioassay procedure can be found in Lee *et al.* (1975b).

## SUMMARY OF PREVIOUSLY REPORTED ELUTRIATE TEST RESULTS FOR HEAVY METALS

Some of the results of these studies were previously presented in a paper by Lee *et al.* (1975a) and in reports by Lee *et al.* (1975b, 1976). A summary of these previously reported results concerning the release of heavy metals from waterway sediments is presented below.



Elutriate Tests were performed on Trinity River sediments obtained a few miles below the location where the City of Dallas discharges wastewater to the river. These tests showed that the only heavy metals released in moderate amounts were manganese and iron; there was no release of lead, copper, cadmium and zinc. Considerable problems were encountered in obtaining reproducible results with the Standard Elutriate Test on the Trinity River sediments.

A series of tests were made on Mobile Bay, Alabama, sediments which investigated the effect of varying the shaking period from 15 minutes to 30, 60, and 90 minutes. These results showed manganese release, with no release of zinc, cadmium, lead and copper. No significant differences were noted between the 30 and 90 minute shaking periods. The 15 minute shaking period results were often different, which indicated that at least 30 minutes of agitation was necessary to adequately promote the release of heavy metals.

The Mobile Bay sediments were also tested with respect to methods of agitation, and it was found that the method of agitation did not play an important role in the release of heavy metals in the Elutriate Test. These tests indicated a significant release of manganese, with zinc and copper removal and no change in cadmium and lead content. Iron was released in the sediments which had been mechanically stirred, but not in those which had been shaken on a wrist action shaker.

It was decided that the problem of obtaining reproducible results was related to the amounts of oxygen entering the flask during the agitation period. The degree of oxygenation of the sediments controlled the redox conditions within the test and, most importantly, the form of iron. Iron in the iron hydroxide form is known to be an excellent scavenger of heavy metals. However, reduced forms, such as ferrous iron, have little or no scavenging ability. In order to obtain a more well-defined, reproducible oxidation-reduction condition, air or nitrogen gas was vigorously bubbled through the Elutriate Test solution for the 30 minute agitation period. To obtain oxic conditions, compressed air was used. Oxygen-free nitrogen was used to achieve anoxic conditions.

A series of tests utilizing air and nitrogen gas for mixing were conducted on the Houston Ship Channel Turning Basin sediments. These sediments, which were heavily contaminated with heavy metals, released only manganese in significant amounts. Significant removal of zinc from the solutions occurred. Copper, cadmium, and iron concentrations did not change in the test employing compressed air agitation. Replicate Elutriate Tests showed excellent agreement and supported the use of dissolved gas agitation versus mechanical agitation or stirring as a means of producing the mixing condition prescribed in the Elutriate Test.

Houston Ship Channel sediment tests conducted with oxygen-free nitrogen showed greater release of manganese than occurred under oxic conditions. Also, large amounts of iron, lead, copper and, to a lesser extent, cadmium were released. It is apparent from these results that iron hydroxide formed during an oxic, 30 minute agitation period is an effective scavenger for many of the heavy metals released during the Elutriate Test.

A series of Elutriate Tests was conducted with Ashtabula Harbor (Lake Erie) sediments and Lake Erie water. Particular attention was given to the liquid-solid ratio and the length of the settling period. In these tests there were no differences in the test water for zinc, copper, cadmium and lead in either a 5 percent or 20 percent sediment of the total elutriate volume for a one or 24 hour settling period. Manganese, and to a lesser extent, iron, were released from these sediments with the amount of release dependent on the amount of sediment present in the test. No difference in manganese release was noted between the one and 24 hour settling periods. However, in the 10 percent sediment of the total elutriate volume test, amounts of iron were larger for the one hour than for the 24 hour settling period. The reverse trend was noted for the 20 percent sediment elutriate volume tests. A bioassay test was conducted with *Daphnia magna* with 5, 10 and 20 percent sediment of the total elutriate volume. The results of this test (Lee *et al.* 1975b) showed no *Daphnia* deaths during the 96 hour test period. Both the 5 and 10 percent tests showed reproduction of *D. magna*.

The manganese content of the bioassay test solution ranged from 2700  $\mu\text{g/l}$  for the 5 percent sediment to over 9000  $\mu\text{g/l}$  for the 20 percent sediment. All the other heavy metals were approximately 10  $\mu\text{g/l}$  or less in these test conditions. The ammonia nitrogen content ranged from 1 mg/l to more than 5 mg/l.

In the series of tests conducted on the Corpus Christi sediments, primary emphasis was given to the effect of the type of water on the leaching of heavy metals. The results of these tests showed the release of manganese and the removal of zinc in the more saline Corpus Christi Bay waters (specific conductance more than 37,000  $\mu\text{mhos/cm}$ ) while the manganese appeared to be removed and the zinc unchanged in deionized waters. There was no effective release of copper, cadmium, lead or iron in either test water.

A bioassay test using *P. pugio* and Corpus Christi Site 3 sediments showed no deaths of *P. pugio* in 24 hours for 5, 10 or 20 percent sediment of the total elutriate volume tests. One *P. pugio* died in the 5, 10 and 20 percent sediment tests after 48 hours, and two *P. pugio* died in the 5 and 10 percent sediment after 72 hours. No additional deaths occurred in the 96 hour period. These results indicate that Corpus Christi Site 3 sediment elutriates are moderately toxic to *P. pugio*.

In summary, it has been found that manganese is the only heavy metal consistently released in all of the oxic Elutriate Tests. The amount of manganese released was somewhat, although not directly, proportional to the amount of sediments present. In general, zinc was removed from the test water by the sediments. No relationship was found between the heavy metal content of individual metals and their amounts released in the Elutriate Test.

## RELEASE OF HEAVY METALS FROM U.S. WATERWAY SEDIMENTS

The results of studies that have been completed on the release of heavy metals and the corresponding bioassay tests for selected sediments throughout the U.S. are now presented.

### Bridgeport, Connecticut Sediments

Sediments collected at Bridgeport, Connecticut were tested with water collected off Eaton's Neck, New York (Long Island Sound) in a series of Elutriate Tests of variable sediment composition and settling time. During the course of the tests, an increase in pH and decrease in dissolved oxygen concentration were apparent, as the sediment exerted a strong oxygen demand.

Leaching results for heavy metals appear in Table 1. These data illustrate that results were statistically identical for replicate samples allowed to settle

TABLE 1

Combined effects of various percentage sediments and settling times: Elutriate Test results; Bridgeport sediments ( $\mu\text{g/l}$ ).

Sample	Manganese		Zinc		Copper		Cadmium		Lead		Iron	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Eaton's Neck Test	60	—	10.5	—	6.4	—	2.3	—	4.5	—	32	—
Water												
5% ( 1 hr)	82	4	6.8	0	4.2	3.2	1.8	0	3.8	0.4	32	5
5% (24 hr)	78	4	11.5	4.9	5.9	0.6	2.4	0.1	3.8	0.4	45	8
10% ( 1 hr)	92	25	7.5	2.9	5.5	1.1	2.0	0.2	3.0	0	26	4
10% (24 hr)	90	0	5.8	1.1	4.9	0.4	2.0	0.4	4.8	0.4	16	1
20% ( 1 hr)	100	14	3.5	0	2.8	0.1	2.0	0.1	4.5	0	38	8
20% (24 hr)	120	7	5.0	2.1	9.0	5.4	2.1	0.1	4.8	0.4	33	4

Mean ( $\bar{X}$ ) and standard deviation (S) computed from 2 replicate analyses.

Dash (—) indicates no standard deviation computed; value obtained by standard addition method.

one or 24 hours. At all percentage sediment contents tested, Cu, Cd, and Pb concentrations remained unchanged. No iron release could be documented. An apparent trend for removal of zinc is evident as zinc concentrations were lower in the elutriates than in the corresponding test water.

Relatively small manganese releases were observed in these leaching tests. The amount of Mn release increased as a function of total mass of sediment in the system.

Table 2 presents the results of the bioassays using *P. pugio* as the test organism. Examination of this table shows that some toxicity to *P. pugio* for the Bridgeport, Connecticut, sediments was found after about 48 hours, with the greatest toxicity found for the 10 percent sediment content test. The

TABLE 2

Response of *P. pugio* to varying sediment percent of total Elutriate volume as a function of time for Bridgeport sediments.

Time (hr)	Number of <i>P. pugio</i> living at varying sediment percentages							
	0%		1%		5%		10%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
24	10	10	10	10	10	10	9	10
48	9	10	8	8	9	8	6	7
72	9	10	8	7	8	7	5	5
96	8	10	8	7	8	7	5	4

A and B are replicates.

Chemical characteristics of the Elutriate Test bioassay for Bridgeport sediments.

Parameter	Control	Percent sediment of total Elutriate volume		
		1%	5%	10%
D.O. (mg/l)	5.7	4.8	4.6	4.6
pH	7.3	7.3	7.5	7.5
Temp. ( $\pm 0.1^\circ\text{C}$ )	21.0	21.0	21.0	21.0
Ammonia (mg-N/l)	0.65	2.2	5.7	8.8
Zn ( $\mu\text{g/l}$ )	12.6	22.9	9.3	9.4
Cd ( $\mu\text{g/l}$ )	5.2	5.3	5.2	5.0
Cu ( $\mu\text{g/l}$ )	6.8	9.8	8.5	9.0
Fe ( $\mu\text{g/l}$ )	22.0	136.2	123.2	154.8
Mn ( $\mu\text{g/l}$ )	75.0	70.0	80.0	115.5
Pb ( $\mu\text{g/l}$ )	9.5	8.8	9.0	8.8

chemical characteristics of the Elutriate Test solution used for the bioassays are also presented in Table 2. These results show that most heavy metal concentrations were under  $20\text{ }\mu\text{g/l}$ , with iron and manganese approximately equal (about  $100\text{ }\mu\text{g/l}$ ). The ammonia content of these solutions ranged from 2 to almost  $9\text{ mg/l}$  ammonia nitrogen. It is possible that the acute toxicity is related to the ammonia content, since such concentrations of heavy metals probably would not cause acute toxicity.

### **Texas City and Houston Ship Channel, Morgan's Point, Texas Sediments**

A series of sediment and water samples for metals leaching studies in the Elutriate Test were collected at Houston Ship Channel, Morgan's Point (HSC-MP) and Texas City (TCC) navigation channels. These areas are frequently dredged. In the region where the samples were collected, the Texas City Channel is heavily industrialized and receives industrial wastes from several petrochemical plants and one refinery. Samples were collected with grab samplers at TCC 1 (mid-channel in the Turning Basin), TCC 2 (a half-mile below the Turning Basin) and TCC 3 (at mile 3 of the ship channel).

Additional samples were collected off Morgan's Point in the Houston Ship Channel.

**Texas City Channel Site 1 Sediments.** Several Elutriate Tests were performed using Texas City Channel Site 1 (TCC 1) sediments in order to examine the effects of the length of settling period and amount of sediment in the test mixture on the likelihood of metals release.

The tests used 5 and 20 percent sediment by volume. Duplicates of each were allowed to settle for one hour or 24 hours. Dissolved oxygen was at near saturation values immediately after air stirring but decreased during settling, reaching the lowest value ( $4.2\text{ mg/l}$ ) after 24 hours.

Results of the tests for metals are listed in Table 3. Relatively large quantities of manganese were released in these Elutriate Tests. Samples settled for 24 hours showed increases of 10 and 20 times the test water concentration in tests containing 5 and 20 percent sediments, respectively. The resulting elutriate manganese concentrations were  $0.6$  and  $1.1\text{ mg/l}$ . Smaller amounts of manganese were released in samples settled for one hour. The 20 percent sediment content test showed twice the Mn release observed in the 5 percent sediment content test.

Zinc removal from the test water was evident. The amount removed was unrelated to percentage sediments of the total volume or length of settling

TABLE 3

Elutriate Tests results: Texas City Channel Site 1 ( $\mu\text{g/l}$ ).

Sample	Mn		Zn		Fe		Cu		Ni		Cr		Pb		Cd		Hg	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
TCC 1 Test Water	52	8	13.3	0.6	4.6	2.6	5.4	0	4.1	1.5	11.1	2.5	3.6	1.2	1.8	0.1	0.27	0.01
5% (1 hr)	262	52	4.8	3.9	17.8	1.1	4.6	4.0	11.4	3.1	108.4	8.1	3.9	2.4	5.5	1.9	0.08	0.01
5% (24 hr)	551	13	5.1	0.9	14.8	8.2	4.2	1.6	9.5	1.9	41.4	5.6	4.1	0.7	3.8	0.6	0.01	0.01
20% (1 hr)	626	48	4.7	2.6	19.9	5.1	2.2	0.2	14.7	0.6	159	10	4.5	1.9	5.9	1.1	0.22	0.01
20% (24 hr)	1063	35	3.2	1.0	27.1	4.5	1.8	0.4	9.5	1.9	134.9	14	5.2	2.9	3.9	1.2	0.10	0.01

Note: Elutriate samples are labeled according to percent sediment content of the total elutriate mixture and length of settling period.

 $\bar{X}$  denotes mean; S denotes standard deviation.

TABLE 4

Results of Elutriate Test: Texas City Channel Site 1 sediment (Samples stored for 81 days after collection)\* ( $\mu\text{g/l}$ ).

Sample	Mn		Zn		Cu		Cd		Cr		Ni		Pb		Fe		Hg	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
TCC 1 Test Water	<2	~0	8.2	4.7	3.0	0.1	0.9	0.0	2.9	0.3	5.3	0.2	<1.0	~0	8.5	2.3	0.009	0.004
TCC 1 20%	539	26	10.9	0.4	3.5	0.4	1.0	0.0	3.7	0.1	9.5	2.5	<1.0	~0	20.2	0.7	0.035	0.008
TCC 1 5%	269	26	9.5	5.0	3.3	0.2	1.1	0.1	2.6	0.2	6.3	1.1	<1.0	~0	34.6	1.1	0.026	0.004

Mean ( $\bar{X}$ ) and Standard Deviation (S) computed from two replicate determinations.

\*Compare to Elutriate Test results of Table 3.

period. Zinc concentration declined from  $13.3 \mu\text{g/l}$  in the test water to about  $5 \mu\text{g/l}$  in the elutriate, a greater than 50 percent decrease.

Some iron release was observed in all samples. The amount of release showed no statistically significant difference between one or 24 hour settling times. Iron concentrations in the elutriates were as high as  $27 \mu\text{g/l}$ ; the test water concentration was  $4.6 \mu\text{g/l}$ .

There was apparent removal of copper. The amount of copper removed increased with increases in the percentage sediment content of the Elutriate Test mixture. Results were not statistically different for 1 and 24 hour settling periods.

Nickel was released in small quantities. The amount of release was greater in the samples settled for the shorter time period. Greater Ni release was observed with the larger percentage sediment content test. Releases of twice or three times the test water concentration were observed.

Significant amounts of chromium release were found. Chromium concentrations increased from  $11 \mu\text{g/l}$  in the test water to  $159 \mu\text{g/l}$  in a 20 percent sediment content test. The amount of chromium released was a function of increasing sediment content in the test. In addition, larger releases were observed in the samples settled for one hour.

Other heavy metals showed varying results. Elutriate Pb concentrations did not change significantly from the test water concentrations. Cadmium concentration of the elutriates appeared slightly higher than those in the test water, indicating limited release of cadmium. Results were not statistically different for the different sediment percentage elutriates or the different settling times. The mercury determinations, however, showed apparent removal of mercury. The amount of mercury removed was larger with the small sediment content sample and longer settling period.

In summary, in this set of tests, only manganese and chromium were released in readily measurable amounts. Iron, nickel, lead, and cadmium showed small releases. Zinc, mercury, and possibly copper were removed.

**Effect of Sediment Storage.** Oxidizing Elutriate Tests, performed 81 days after samples were collected and stored at  $4^{\circ}\text{C}$ , showed different metals leaching behavior in TCC 1 sediments (Table 4). The amount and trend of Mn release were similar to those of early tests on the same samples, with increasing release observed as a function of increasing suspended mass of sediments. In similar leaching tests performed shortly after sample collection, release of Cd, Ni, and Cr and removal of Zn had been statistically significant. After prolonged storage of these materials at  $4^{\circ}\text{C}$ , leaching showed neither release nor removal of Cu, Cd, Cr, Pb, Ni, and Zn. Small amounts of Fe were released both times. Both tests agreed only in results for Mn, Fe, and Pb.

**Effect of Anoxic/Oxic Conditions.** In order to simulate possible environmental conditions of dredging and dredged material transport and disposal, the sediment and water mixture was leached anoxically (sparging  $N_2$  gas) for 20 minutes and then aerated for 10 minutes.

Sample metal analysis data presented in Table 5 indicate statistically significant release of manganese in both elutriates. Greater release was observed in the 20 percent sediment content test (up to 1.5 mg/l) than the 25 percent sediment content test (0.5 mg/l Mn). For zinc, chromium, cadmium, and lead, concentrations were not statistically different between the elutriates and test water.

### **Leaching Studies of Morgan's Point and Texas City Channel Sites 2 and 3 Sediments**

Water and sediments from Morgan's Point and from the Texas City Channel Sites 2 and 3 were subjected to oxidizing Elutriate Tests. These were combined to obtain 5 and 20 percent sediment by volume mixtures. Leaching data for metals are presented in Table 6 for Morgan's Point and Table 7 for TCC 2 and 3.

No statistically significant change in Zn concentration was observed between elutriates of Morgan's Point and Morgan's Point test water. The TCC 2 samples showed what appeared to be slight release. The amount of release was greater for the lower percentage sediments (5 percent). Elutriates of TCC's showed little deviation from the test water Zn concentration. Only the 5 percent sediment test produced a small statistically significant decrease in Zn. These results are rather unusual since experience with other sediments indicates a general tendency for Zn removal.

Copper concentrations in test waters for the three sites (MP, TCC 2 and TCC 3) were very low, generally less than  $2 \mu\text{g/l}$ . The Cu concentrations of the elutriate obtained from the three different sediments and these waters were also at this low level, which approaches the detection limits of the analytical method. Neither release, nor removal of Cu, was observed for any of these materials at either sediment content used.

A small difference exists between the elutriates' nickel concentrations and those of the corresponding test waters. These differences may not be of significance but do suggest a potential trend for release of nickel in all but three systems in question.

Large releases of Mn occurred in all Elutriate Tests of these sediments. The Morgan's Point sediment showed release of 0.5 to 2 mg/l Mn. The original test water concentration was 0.004 mg/l. The amount released in the 5 percent sediment content sample appeared to have been higher than that



TABLE 5  
Elutriate Tests results: Texas City Channel Site 1 under anoxic-aerated conditions\* ( $\mu\text{g/l}$ ).

Sample	Mn		Zn		Cu		Cd		Cr		Ni		Pb		Fe	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	0	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
TCC 1 Test Water	209	22	13.5	1.0	2.5	0.2	1.8	0.1	1	0	4.3	0.0	8.3	1.2	6.1	0.0
TCC 20%	1551	42	9.1	-	2.6	0.8	2.3	0.2	1	0	18.6	3.4	11.2	2.1	14.7	3.1
TCC 1 25%	475	-	14.0	2.8	1.7	-	2.1	-	1	0	18.5	-	9.8	-	19.2	-

$\bar{X}$  denotes mean; S denotes standard deviation computed from duplicates.

Dash (-) indicates no standard deviation can be computed; single determination.

\*Samples were stirred with nitrogen gas 20 minutes, then with air 10 minutes.

TABLE 6  
Elutriate Test results on Morgan's Point sediments (HSC) ( $\mu\text{g/l}$ ).

Sample	Zn		Cu		Ni		Mn		Fe		Pb		Cr		Hg		Cd	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Morgan's Point Test Water	14.9	-	1.3	-	2.6	-	4.1	-	11.6	-	<1.0	-	<2.0	-	0.041	-	<0.3	-
Morgan's Point 5%	15.6	2.4	<1.0	~0	4.0	0.8	1920	103	3.4	2.1	<1.0	~0	5.0	4.2	0.028	-	<0.3	~0
Morgan's Point 20%	14.8	1.3	<1.0	~0	1.6	-	507	7	1.5	0.6	1.3	0.3	6.0	2.8	0.086	-	<0.3	~0

Dash (-) denotes standard deviation cannot be computed.

$\bar{X}$  denotes mean; S denotes standard deviation.

TABLE 7  
Elutriate Test results on Texas City Channel Sites 2 and 3 sediments ( $\mu\text{g/l}$ ).

Sample	Zn		Cu		Ni		Mn		Fe		Pb		Cr		Hg		Cd	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
TCC 2 Test																		
Water	8.7	-	<1.0	-	7.8	-	4.9	-	<1.0	-	1.0	-	<2.0	-	0.028	-	<0.3	-
TCC 2-5%	14.3	0.6	<1.0	~0	12.9	0.3	296	11	1.7	1.2	2.0	0	10.3	7.0	0.048	-	<0.3	~0
TCC 2-20%	10.7	0.8	<1.0	~0	9.8	0	472	53	1.6	0	2.0	0	3.7	2.3	0.014	-	<0.3	~0
TCC 3 Test																		
Water	19.3	-	1.7	-	4.6	-	11.8	-	<1.0	-	<1.0	-	<2.0	-	0.099	-	<0.3	-
TCC 3-5%	15.7	0.4	<1.0	~0	6.9	1.1	3970	17	<1.0	~0	3.2	2.3	<2.0	~0	0.034	-	<0.3	~0
TCC 3-20%	17.0	2.7	1.2	0.8	8.1	0	5760	170	<1.0	~0	1.6	0	4.0	0	0.034	-	<0.3	~0

Dash (-) denotes standard deviation cannot be computed.

$\bar{X}$  denotes mean; S denotes standard deviation.

released from the 20 percent sediment content test. Texas City Channel Site 2 sediment Elutriate Tests resulted in moderate Mn release (approaching 0.5 mg/l Mn in solution). The Mn content of the test water was 0.005 mg/l and reached 0.296 mg/l and 0.472 mg/l for 5 and 20 percent sediment content, respectively. The largest Mn releases, 4 to 6 mg/l, were observed in the TCC 3 sediment Elutriate Tests. Mn concentrations in these ranged from 0.012 mg/l in the test water to 3.97 mg/l in the 5 percent sediment content test and 5.76 mg/l in the 20 percent sediment content test. These high levels are potentially toxic to some organisms.

Iron concentrations in the three test waters in question were very low. For Morgan's Point, the test water concentration was 11.6  $\mu\text{g/l}$  and the resulting elutriates showed iron contents under 5  $\mu\text{g/l}$ . TCC 2 and TCC 3 elutriates evidenced no change from the test water Fe concentration ( $< 1 \mu\text{g/l}$ ), regardless of the amounts of sediment in the test mixture.

Lead concentrations in all samples were near 1  $\mu\text{g/l}$ . No statistically significant changes could be observed in any of the elutriates.

Apparent release of Cr occurred in the various Elutriate Tests; however, this was not statistically significant because of the relatively large standard deviations. Thus, no changes in the Cr concentration of the parent waters can be supported from these data. Chromium levels remained at near the detection limit of 2  $\mu\text{g/l}$ .

The Hg data seemingly show removal in the Morgan's Point 5 percent sediment elutriate and release in the 20 percent sediment content test. For the TCC 2 samples, this trend was reversed; there was apparent release in the 5 percent elutriate and removal in the 20 percent elutriate sediment content. The TCC 3 Elutriate Tests results clearly suggested Hg removal from the test water as there was a threefold reduction in concentration. The Hg levels in all samples, however, remained at less than 0.1  $\mu\text{g/l}$ . Previous Elutriate Tests on other sediments had also shown a tendency for Hg removal.

Cadmium in all samples remained below detection level, less than 0.3  $\mu\text{g/l}$ . No change was observed in any of the elutriates.

### Bioassay Tests on Texas City and Morgan's Point Sediment Samples

Table 8 presents the results of a 96 hour bioassay using *P. pugio* on Texas City Channel Site 1 sediments. Examination of the table shows that no toxicity to *P. pugio* was found in 96 hours for the 5 and 10 percent sediments, with a slight toxicity noted after 24 hours for the 20 percent sediment of the total elutriate volume. Table 9, which presents the characteristics of the bioassay test water for this test, shows that the total ammonia

TABLE 8

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Texas City Channel Site 1.

Time (hr)	Control*		Percent sediment of total Elutriate volume*					
			5%		10%		20%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
12	10	10	10	10	10	10	10	10
24	10	10	10	10	10	10	9	9
36	10	10	10	10	10	10	8	8
48	10	10	10	10	10	10	8	8
60	10	10	10	10	10	10	8	8
72	10	10	10	10	10	10	8	8
84	10	10	10	10	10	10	8	8
96	10	10	10	10	10	10	8	8

A and B are replicate bioassays.

\*Figures represent number of organisms alive during 96 hr bioassay.

TABLE 9

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Texas City Channel Site 1.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	23.5	8.1	7.1	46,100	0.03	<0.01	2.0
Control B	23.5	8.1	7.0	46,000	0.05	<0.01	2.0
5% A	22.0	8.1	3.9	30,800	4.03	0.16	33.0
5% B	22.0	8.1	3.9	30,700	4.00	0.16	33.0
10% A	22.0	8.2	2.6	24,800	5.46	0.27	30.0
10% B	22.0	8.2	2.6	24,900	5.60	0.28	29.0
20% A	21.0	8.2	2.2	24,200	7.31	0.34	26.0
20% B	21.0	8.2	2.2	24,200	7.71	0.36	27.0

A and B are replicate bioassay tests.

nitrogen content for the 20 percent sediment contained approximately 7 mg/l as nitrogen, with approximately 0.35 mg/l present as unionized ammonia.

Tables 10, 11, 12 and 13 present the results for the bioassays using *P. pugio* for Texas City Channel Site 2 and Site 3 sediments, with the

TABLE 10

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Texas City Channel Site 2.

Time (hr)	Control*		Percent sediment of total Elutriate volume*					
			5%		10%		20%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
12	10	10	10	10	10	10	10	10
24	10	10	10	10	9	10	10	9
36	10	10	10	10	9	10	9	9
48	10	10	9	10	9	9	9	8
60	10	10	9	10	9	9	8	8
72	10	10	9	9	9	9	8	8
84	10	10	9	9	9	9	8	8
96	10	10	9	9	9	9	8	8

A and B are replicate bioassays.

\*Figures represent number of organisms alive during 96 hr bioassay.

TABLE 11

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Texas City Channel Site 2.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	23.5	8.1	7.0	46,100	0.03	<0.01	2.0
Control B	23.5	8.1	7.0	46,000	0.05	<0.01	2.0
5% A	22.0	8.2	3.7	24,200	2.25	0.11	48.0
5% B	22.0	8.2	3.6	24,200	2.25	0.11	48.0
10% A	22.0	8.3	2.0	24,000	3.12	0.20	26.0
10% B	22.0	8.3	2.0	24,000	3.20	0.20	26.0
20% A	21.8	8.3	1.8	29,000	3.74	0.23	23.0
20% B	21.6	8.3	1.7	29,000	3.65	0.23	22.0

A and B are replicate bioassay tests.

corresponding characteristics of the test solutions. Site 3 sediments were similar to Texas City Site 1 sediments in that approximately 6 mg/l of ammonia nitrogen were present. Both Site 2 and Site 3 sediments show essentially no toxicity to *P. pugio* with at most only one or two organisms

TABLE 12

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Texas City Channel Site 3.

Time (hr)	Control*		Percent sediment of total Elutriate volume*					
			5%		10%		20%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
12	10	10	10	10	9	9	9	8
24	10	10	9	10	9	9	8	8
36	10	10	9	10	9	9	8	8
48	10	10	9	9	9	9	8	8
60	10	10	9	9	9	9	8	8
72	10	10	9	9	9	9	8	8
84	10	10	9	9	9	9	8	8
96	10	10	9	9	9	9	8	8

A and B are replicate bioassays.

\*Figures represent number of organisms alive during 96 hr bioassay.

TABLE 13

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Texas City Channel Site 3.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	23.0	8.1	6.5	39,000	0.04	<0.01	<0.1
Control B	23.0	8.1	6.5	39,000	0.04	<0.01	<0.1
5% A	23.0	8.0	4.2	31,800	2.64	0.09	53.0
5% B	23.0	8.0	4.2	36,500	2.64	0.09	53.0
10% A	23.0	7.8	1.6	37,800	4.12	0.09	58.0
10% B	23.0	7.8	1.5	33,000	4.10	0.09	58.0
20% A	23.0	7.8	1.3	30,800	6.06	0.13	52.0
20% B	23.0	7.8	1.3	38,500	6.10	0.13	52.0

A and B are replicate bioassay tests.

dying after a period of several days in the 5 to 20 percent sediment elutriates. Elutriate Test heavy metals results from the Texas City sediments show that none of heavy metals should be present in sufficient concentrations in these sediments to cause acute toxicity.

The results for the Morgan's Point sediments (Tables 14 and 15) show a slightly higher toxicity to *P. pugio* than the Texas City sediments. Morgan's Point is at the mouth of the Houston Ship Channel and receives all of the persistent toxicants that are dumped into the channel in the form of municipal and industrial wastes. It is interesting to note that even with such a

TABLE 14

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Morgan's Point, Texas.

Time (hr)	Control*		Percent sediment of total Elutriate volume*					
			5%		10%		20%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
12	10	10	10	10	9	9	8	8
24	10	10	9	9	8	9	8	8
36	10	10	9	9	8	8	7	8
48	10	10	9	9	8	8	7	8
60	10	10	9	9	8	8	7	8
72	10	10	9	9	8	8	7	8
84	10	10	9	9	8	8	7	7
96	10	10	9	9	8	8	7	6

A and B are replicate bioassays.

\*Figures represent number of organisms alive during 96 hr bioassay.

TABLE 15

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Morgan's Point, Texas.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	20.8	8.1	7.2	35,000	0.04	<0.01	2.0
Control B	20.8	8.1	7.2	35,000	0.04	<0.01	2.0
5% A	20.5	7.9	5.5	38,200	1.33	0.03	60.9
5% B	20.5	7.9	5.5	38,300	1.33	0.03	70.0
10% A	20.5	7.7	2.3	38,000	2.97	0.04	42.0
10% B	20.5	7.7	2.4	37,900	2.97	0.04	42.0
20% A	20.5	7.7	1.9	37,000	3.64	0.05	21.0
20% B	20.5	7.7	2.0	36,900	3.64	0.05	20.0

A and B are replicate bioassay tests.

tremendous toxic waste load into the channel, the toxicity of the sediments to *P. pugio* was relatively slight over the four day test period.

### **Leaching Studies with Galveston Entrance Channel Buoy 1 Sediments**

Results of Elutriate Tests under oxidizing leaching conditions for sediments collected at Buoy 1 of the Galveston Entrance Channel appear in Table 16. This buoy is located approximately five miles seaward at the entrance to the Galveston Entrance Channel in the Gulf of Mexico. In general, considering the proximity to sources of industrial and domestic pollution, sediments from Buoy 1 were the least contaminated of all the sediments that were examined.

Increasing amounts of Mn release were observed as the amount of sediment in suspension was increased. Manganese concentrations in excess of 1 mg/l resulted. Under oxidizing conditions, the differences between the test water and elutriate concentrations of Zn, Cu, Cd, Ni, Pb, Fe, and Hg were not statistically different.

Tables 17 and 18 present the results of the Elutriate Test using *P. pugio* for the Galveston Entrance Channel sediment from Buoy 1 and the chemical characteristics of the bioassay test solution. Examination of Table 18 shows a slight toxicity to *P. pugio* in the 20 percent sediment elutriate after 36 hours, with no additional toxicity beyond that period.

### **Leaching Studies with Galveston Inner Bar Channel, Buoys 9 and 11 Sediments**

The metals leaching potential of the Buoys 9 and 11 sediments and the effect of different leaching water on the results of the Elutriate Test were studied. These sediments were combined with corresponding water from their disposal site off Galveston in the Gulf of Mexico. The tests utilized 5 and 20 percent sediment by volume elutriate mixtures and were conducted under oxidizing conditions. Results are summarized in Table 19. These buoys are located in the Gulf of Mexico in the Galveston Entrance Channel just seaward of a line between Galveston Island and Bolivar Peninsula. In general, sediments in this area would be classified as uncontaminated, or slightly contaminated, based on proximity to major pollution sources.

A small amount of Zn was apparently removed in Elutriate Tests of Buoy 9 and Buoy 11 sediments and corresponding waters. The Zn concentration was approximately 50 percent of the test water concentration. In tests using disposal site water, these same sediments showed essentially no effect on



TABLE 16  
Elutriate Tests results: Galveston Entrance Channel Buoy 1 sediment ( $\mu\text{g/l}$ ).

Sample	Mn		Zn		Fe		Cu		Ni		Cr		Pb		Cd		Hg	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Buoy 1 Test Water	2.6	0.0	3.5	1.1	5.2	0.6	1.9	0.1	2.9	0.4	1.6	0.0	<1.0	~0	1.2	0.1	0.006	~0
Buoy 1 20%	1165	11	9.2	4.4	7.0	0.3	2.5	0.6	4.6	1.1	2.3	0.3	<1.0	~0	1.2	0.2	0.018	0.00
Buoy 1 5%	370	8	7.3	2.9	10.3	4.6	2.9	0.4	5.8	1.8	2.6	0.3	<1.0	~0	1.2	0.6	0.026	0.02

$\bar{X}$  denoted mean; S denotes standard deviation.

TABLE 17

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Galveston Entrance Channel-Buoy 1.

Time (hr)	Control*		Percent sediment of total Elutriate volume*					
			5%		10%		20%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
12	10	10	10	10	10	10	10	10
24	10	10	10	10	10	10	10	10
36	10	10	10	10	10	10	9	8
48	10	10	10	10	10	10	9	8
60	10	10	10	10	10	10	9	8
72	10	10	9	10	10	10	9	8
84	10	10	9	9	10	10	9	8
96	10	10	9	9	10	10	9	8

A and B are replicate bioassays.

\*Figures represent number of organisms alive during 96 hr bioassay.

TABLE 18

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Galveston Entrance Channel-Buoy 1.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	24.0	8.2	6.8	50,000	0.57	0.03	0.4
Control B	24.0	8.2	6.8	50,000	0.57	0.03	0.4
5% A	23.8	8.2	5.7	60,000	1.35	0.07	59.0
5% B	23.6	8.2	5.7	60,000	1.37	0.07	59.0
10% A	23.6	8.2	5.4	58,000	1.62	0.09	54.0
10% B	23.5	8.2	5.4	58,000	1.62	0.09	54.0
20% A	23.5	8.1	2.5	58,000	2.14	0.09	29.0
20% B	23.5	8.1	2.4	58,000	2.20	0.09	28.0

A and B are replicate bioassay tests.

the Zn concentration of the test water, in that the elutriates showed the same Zn concentration as the test water regardless of the sediment and percentage sediment content.

In these Elutriate Tests, there was a general trend toward removal of Cu from solution. Although Cu levels were quite low in all site test waters (less

TABLE 19  
Elutriate Test results for Galveston Entrance Channel (Buoys 9 and 11) sediments ( $\mu\text{g/l}$ ).

Sample	Mn		Zn		Cu		Cr		Pb		Cd		Fe		Hg*	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Offshore Disposal Site																
Water	40.3	-	12.4	-	3.7	-	8.0	-	4.0	-	<0.3	-	<1.0	-	0.041	-
Buoy 9:																
Site Water	17.2	-	12.4	-	2.5	-	<2.0	-	2.1	-	<0.3	-	<1.0	-	0.069	-
5%-Site	1010	8	5.0	5.0	<1.0	-	10.0	-	2.0	0	<0.3	-	<1.0	-	0.034	-
5%-Offshore	467	39	13.7	0.2	<1.0	-	5.1	0	3.1	1.4	<0.3	-	<1.0	-	1.034	-
20%-Offshore	1780	101	15.4	1.1	<1.0	-	5.9	1.1	1.1	1.3	<0.3	-	<1.0	-	0.028	-
Buoy 11:																
Site Water	48	-	16.0	-	1.4	-	<2.0	-	4.0	-	<0.3	-	<1.0	-	0.021	-
5%-Site	1780	3	8.3	1.0	<1.0	-	6.0	3.0	5.0	1.4	<0.3	-	<1.0	-	0.020	-
5%-Offshore	1840	40	12.8	1.4	1.0	0.3	4.0	0	4.0	0	<0.3	-	<1.0	-	0.021	-
20%-Offshore	5050	58	13.7	1.2	<1.0	-	4.5	0.7	5.0	1.4	<0.3	-	<1.0	-	0.014	-

Notes: Buoys 9 and 11 sediments were combined with water from the sediment sampling sites and from the offshore disposal site (off-shore) in the percentages given.

Mean ( $\bar{X}$ ) and standard deviation (S) computed from duplicate determinations.

Dash (-) indicates S cannot be computed.

\*Based on single determination.

than  $4\text{ }\mu\text{g/l}$ ) the elutriates obtained from Buoys 9 and 11 sediments showed removal of Cu (less than  $1.0\text{ }\mu\text{g/l}$  in all cases). Results were similar for both sediments, each of the individual test waters used and at both sediment contents. Data for chromium suggest that a small release of this metal may have occurred, but this cannot be firmly established from the available data.

Large releases of Mn were apparent in Elutriate Tests of these sediments. Water from the Buoy 9 site showed  $17.2\text{ }\mu\text{g/l}$  Mn, and the corresponding 5 percent elutriate resulted in  $1,010\text{ }\mu\text{g/l}$  Mn, a more than fiftyfold increase. Buoy 11 sediment (5 percent sediment content elutriate) with water from this same site showed a Mn concentration of  $1780\text{ }\mu\text{g/l}$  (compared to  $40.3\text{ }\mu\text{g/l}$  in the test water), a greater than fortyfold increase. Release of Mn also occurred when disposal site water was used as test water for these sediments. Using Buoy 9 sediment, the resultant 5 percent elutriate Mn concentration was  $467\text{ }\mu\text{g/l}$ , or about half the release obtained with Buoy 9 water. Using disposal site water, the sediment content test exhibited Mn levels of  $1780\text{ }\mu\text{g/l}$ .

Buoy 11 sediments produced higher Mn releases when tested in disposal site water rather than Buoy 11 water. Manganese concentrations reached  $1840\text{ }\mu\text{g/l}$  and  $5050\text{ }\mu\text{g/l}$  in the 5 and 10 percent elutriates, respectively. These Mn releases are comparable to those observed for Morgan's Point and Texas City Channel sediments in oxidizing Elutriate Tests.

When the same sediments were leached in disposal site water, there was apparent removal of chromium. Concentrations decreased from  $8\text{ }\mu\text{g/l}$  in the site water to  $6\text{ }\mu\text{g/l}$  or less in the elutriates. Results for 5 and 20 percent sediment content tests were similar. More Cr was apparently removed with Buoy 11 sediment than with Buoy 9 sediment.

Low concentrations (less than  $4\text{ }\mu\text{g/l}$ ) of Pb occurred in the test waters and elutriates. There was no statistically significant change in the Pb concentration of the test waters for any of the conditions tested. Lead was neither released to, nor removed from, Buoy 9 and Buoy 11 sediments.

Cadmium levels remained at less than the detection limit ( $< 0.3\text{ }\mu\text{g/l}$ ) in all cases, indicating no release or removal of Cd.

Iron was barely detectable and remained at less than  $1\text{ }\mu\text{g/l}$  regardless of treatment water or sediment amount. Mercury was removed from solution as a function of increasing sediment percentage in the system.

Table 20 presents the results of the bioassays using *P. pugio* for the Galveston Entrance Channel Buoy 9 sediments. Only the 10 percent sediment of the total elutriate volume was used in the bioassay. No toxicity to *P. pugio* was found. Physical and chemical characteristics of the bioassay test water are presented in Table 21. The results show very small amounts of ammonia release; all other conditions are typical of those found for waters in this region. Table 22 presents the results of the bioassay tests for *P. pugio* from

TABLE 20

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Galveston Entrance Channel-Buoy 9.

Time (hr)	Control*		Percent sediment of total Elutriate volume*	
			10%	
	A	B	A	B
0	10	10	10	10
12	10	10	10	10
24	10	10	10	10
36	10	10	10	10
48	10	10	10	10
60	10	10	10	10
72	10	10	10	10
84	10	10	10	10
96	10	10	10	10

A and B are replicate bioassays.

\*Figure represents number of organisms alive during 96 hr bioassay.

TABLE 21

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Galveston Entrance Channel-Buoy 9.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	24.0	8.2	6.8	50,000	0.57	0.03	0.4
Control B	24.0	8.2	6.8	50,000	0.57	0.03	0.4
10% A	24.0	8.1	6.7	58,000	0.81	0.03	98.0
10% B	24.0	8.1	6.7	58,000	0.80	0.03	98.0

A and B are replicate bioassay tests.

Buoy 11, in the Entrance Channel just north of Galveston Island. These tests show no toxicity to *P. pugio* in the 5 and 10 percent sediment of elutriates, with one grass shrimp dying after 24 hours in one replicate of the 20 percent elutriate, and after 48 hours in the other replicate.

Table 23 presents the physical and chemical characteristics of the test water. It shows that a maximum ammonia concentration of approximately 2 mg/l as N was present in the 20 percent sediment elutriate.

TABLE 22

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Galveston Entrance Channel-Buoy 11.

Time (hr)	Percent sediment of total Elutriate volume*							
	Control*		5%		10%		20%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
12	10	10	10	10	10	10	10	10
24	10	10	10	10	10	10	9	10
36	10	10	10	10	10	10	9	10
48	10	10	10	10	10	10	9	9
60	10	10	10	10	10	10	9	9
72	10	10	10	10	10	10	9	9
84	10	10	10	10	10	10	9	9
96	10	10	10	10	10	10	9	9

A and B are replicate bioassays.

\*Figures represent number of organisms alive during the 96 hr bioassay.

TABLE 23

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Galveston Entrance Channel-Buoy 11.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	23.0	8.1	6.5	39,000	0.04	<0.01	<0.1
Control B	23.0	8.1	6.5	39,000	0.04	<0.01	<0.1
5% A	22.5	7.9	4.8	36,500	0.80	0.02	93.0
5% B	22.5	7.9	4.8	36,500	0.80	0.02	93.0
10% A	22.5	7.8	4.8	37,000	0.97	0.02	>100.0
10% B	22.5	7.8	4.8	37,000	0.99	0.02	>100.0
20% A	22.0	7.8	2.2	35,000	1.99	0.04	>100.0
20% B	22.0	7.8	2.2	35,000	2.0	0.04	>100.0

A and B are replicate bioassay tests.

## Leaching of San Francisco Bay Area Sediments

Samples of sediment and water from the San Francisco Bay area were obtained at dredging locations in Mare Island and near Rodeo Flats. Chemical characteristics of the elutriates from these sediments are found in Table 24.

TABLE 24  
Results of reducing conditions Elutriate Tests: Mare Island sediments ( $\mu\text{g/l}$ ).

Sample	Mn		Fe		Zn		Ni		Cd		Cu		Pb	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Mare Island Test Water	13.7	4.0	74.5	8.7	117.8	0.0	117.2	2.4	1.2	2.4	43.9	1.5	5.6	1.0
Elutriate A	6.9	0.0	500.0	29	18.7	0.7	117.2	0.0	0.6	0.0	25.7	1.0	8.0	0.9
Elutriate B	9.1	0.6	463.0	36	17.4	0.3	117.9	6.8	1.4	0.3	19.5	0.1	7.3	0.0
Elutriate C	5.2	2.5	393.0	9	17.2	0.3	20.0	1.0	0.6	0.0	21.5	1.0	9.5	0.7

Mean ( $\bar{X}$ ) and standard deviation (S) computed from duplicate analyses.

Elutriate samples were treated as follows:

- A—Sample prepared, agitated, settled and centrifuged under nitrogen gas atmosphere, then filtered with compressed air.
- B—Sample prepared in air, then agitated, settled, centrifuged and filtered under  $\text{N}_2$ .
- C—Sample completely processed under nitrogen gas atmospheres.

Under oxidizing Elutriate Test conditions, the Rodeo Flats material produced a small to moderate Mn release and effective (97 percent) removal of Zn from solution (Table 24). No significant changes from the test water concentration were observed in the Cu, Cd, Pb, and Fe elutriate concentrations. Leaching of Mare Island sediment did not show any change in Mn concentration under oxidizing conditions (Table 25). The absence of Mn release in these samples is in marked contrast with findings for sediments from various locations across the U.S. under similar conditions. Also, small amounts of Cu and Fe appeared to be released. No change was observed for Cd or Pb.

Leaching of Mare Island under reducing conditions (anoxic tests) did not result in manganese release as previously reported for oxidizing conditions (Table 14). Under reducing conditions, large amounts of Fe were released. Slight releases of Pb occurred while Cu appeared to be slightly removed. Cadmium concentrations did not change. Removal of Zn and Ni from solution proceeded readily under reducing conditions.

Apparent release of nickel occurred, the amount of release being the same in both tests. Similar small apparent releases of iron were also observed in the two elutriates.

In comparison to the Elutriate Test data in Table 25 (performed under oxidizing conditions), the results of these anoxic-aerated tests agree for the

TABLE 25

Elutriate Tests results: San Francisco Bay Area sediments ( $\mu\text{g/l}$ ).

Sample	Mn		Fe		Zn		Cu		Cd		Pb	
	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S	$\bar{X}$	S
Rodeo Flats Test Water	30	—	3.0	—	32	—	2.2	—	0.3	—	2.3	—
Rodeo Flats 5%	138	13	4.3	1	1.5	0.9	1.8	0.7	0.4	0.1	1.7	0.9
Rodeo Flats 20%	160	42	13.5	1	1.1	0.4	1.6	0.6	0.5	0.1	<1.0	—
Mare Island Test Water	<30	—	8.5	—	20	—	2.6	—	0.3	—	<1.0	—
Mare Island 5%	32	4	81	13	0.9	0.1	4.4	0.1	0.1	0.1	<1.0	—
Mare Island 20%	<30	—	62	4	1.4	0.7	3.6	0.4	0.3	0.1	<1.0	—

Dash (—) denotes standard deviation cannot be computed.

$\bar{X}$  denotes mean; S denotes standard deviation.



behavior of Zn, Cu, Cd, Cr, Pb, and Fe. Substantially greater amounts of manganese were released in the partially anoxic system of the later tests than in the oxidizing tests. In addition, nickel release was observed in the nitrogen-treated system, while no significant change was observed in the aerated system.

The bioassays of the Mare Island and Rodeo Flats sediments are presented in Tables 26 and 27, with the corresponding physical and chemical data for these tests in Tables 28 and 29. Examination of Tables 26 and 27 shows a slight toxicity of Mare Island sediment to *P. pugio* after 24 hours, with 2 grass shrimp dying in the 20 percent sediment elutriate in the 4-day period. For the Rodeo Flats sediments, a somewhat higher toxicity was noted, with 4 of the grass shrimp dying in the 20 percent sediment elutriate after 36 hours. A comparison of the physical and chemical characteristics of these test systems shows approximately the same ammonia and dissolved oxygen concentrations. The difference in the toxicity of these two sediments from the same general region is not apparent from either the heavy metal or general data available at this time.

TABLE 26

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Mare Island, California.

Time (hr)	Percent sediment of total Elutriate volume*							
	Control*		5%		10%		20%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
12	10	10	10	10	10	10	10	10
24	10	10	10	10	10	10	10	10
36	10	10	10	9	10	9	9	9
48	10	10	10	9	10	9	9	9
60	10	10	10	9	9	9	9	9
72	10	10	10	9	9	9	9	9
84	10	10	10	9	8	9	8	8
96	10	10	10	9	8	9	8	8

A and B are replicate bioassays.

\*Figures represent number of organisms alive during 96 hour bioassay.

TABLE 27

Mortality of *P. pugio* during 96 hour acute bioassay as a function of percent sediment of total Elutriate volume: Rodeo Flats, California.

Time (hr)	Percent sediment of total Elutriate volume*							
	Control*		5%		10%		20%	
	A	B	A	B	A	B	A	B
0	10	10	10	10	10	10	10	10
12	10	10	9	10	9	9	8	9
24	10	10	9	10	9	9	7	8
36	10	10	9	10	8	7	6	9
48	10	10	9	10	8	7	6	8
60	10	10	9	10	8	7	6	8
72	10	10	9	10	7	7	6	8
84	10	10	9	10	7	7	6	8
96	10	10	9	10	7	7	6	8

A and B are replicate bioassays.

\*Figures represent number of organisms alive during 96 hr bioassay.

TABLE 28

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Mare Island, California.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	21.0	7.9	7.3	37,000	0.04	<0.01	1.0
Control B	21.0	7.9	7.3	37,000	0.04	<0.01	1.0
5% A	20.2	7.7	4.9	34,000	0.19	<0.01	73.0
5% B	20.3	7.7	5.3	34,000	0.20	<0.01	70.0
10% A	20.2	7.4	4.9	34,000	0.49	<0.01	58.0
10% B	20.2	7.4	4.9	34,000	0.50	<0.01	62.0
20% A	20.0	7.4	4.4	34,000	1.44	0.01	33.5
20% B	20.0	7.4	4.5	34,000	1.55	0.01	40.0

A and B are replicate bioassay tests.

## DISCUSSION

Previously reported results as well as those reported in this paper show more or less consistently that manganese is the only heavy metal released at

TABLE 29

Chemical and physical parameters of bioassay Elutriate water after the one hour settling period: Rodeo Flats, California.

Sample	Temp. (°C)	pH	D.O. (mg/l)	Spec. cond. (μmhos/cm)	Ammonia (total mg/l as N)	NH <sub>3</sub> (mg/l)	Turbidity (NTU)
Control A	23.0	8.0	7.1	38,000	0.08	<0.01	1.0
Control B	23.0	8.0	7.1	38,000	0.07	<0.01	1.0
5% A	22.0	7.8	5.1	39,000	0.76	0.01	62.0
5% B	22.0	7.8	5.4	39,000	1.05	0.02	70.0
10% A	22.5	7.7	4.6	40,000	1.85	0.03	60.0
10% B	22.5	7.7	4.9	37,000	1.85	0.03	58.0
20% A	22.0	7.7	4.7	40,000	1.86	0.03	45.0
20% B	22.0	7.7	4.6	40,000	1.85	0.03	50.0

A and B are replicate bioassay tests.

potentially significant levels during the Elutriate Test. A more or less consistent pattern of zinc removal from the test water has also been observed. Copper, nickel, lead, cadmium, chromium and mercury generally show little or no change in the oxic Elutriate Test. Some of these metals, as well as iron, show large release under anoxic test conditions. For manganese, the only metal consistently released, the amount of release was dependent to some extent on the amount of sediment present. However, no relationship has been found between the amount of manganese, or for that matter any other heavy metal present in the sediments and the amount of release that occurs in oxic Elutriate Tests.

Bioassay tests using either *Daphnia magna* or *P. pugio* (Lee *et al.* 1975b) have detected limited toxicity of the elutriates to these two organisms during a 24 to 48 hour period. For some sediments, a definite though not pronounced toxicity was found for the 20 percent sediment elutriate after 3-4 days of exposure. These results are particularly significant in that they indicate that in a typical dredged material disposal dump or pipeline discharge outside of the mixing zone immediately adjacent to the discharge, the likelihood of any toxicity to aquatic organisms in the water column is quite small. Further, the results of chemical leaching tests (Elutriate Tests) and bioassays of the elutriates have shown that there is essentially no likelihood of toxicity to water column organisms from the typical barge or hopper dredge dump (Lee *et al.* 1975a). Moreover, the likelihood of chronic toxicity to aquatic organisms in the water column from dredged material dumping in open waters is also quite remote because of the usual intermittent nature of

such operations and the rapid dilution that occurs at most open water sites. A series of bioassay tests of the elutriates from many of the sediments that have been tested thus far show that little or no acute toxicity exists for *P. pugio* (grass shrimp) for marine or estuarine sediments and *Daphnia* for freshwater sediments. The results of the bioassay tests are presented in a paper by Lee *et al.* 1975a. There is, however, some concern over acute and chronic toxicity to water column organisms from pipeline dredge discharges. Depending upon the mixing characteristics of the receiving waters, there is a region near the pipeline discharge area where the concentrations of contaminants can exceed the acute lethal and even chronic toxicity levels (if the organisms stay in the area throughout their lifetime which is a remote possibility) for all water column organisms.

## CONCLUSIONS

Based on studies on the leaching of heavy metals from waterways throughout the U.S. and bioassay tests on the leachates, it is concluded that although the heavy metals present in some U.S. waterway sediments would cause them to be classified as grossly contaminated based on bulk chemical criteria, they constitute little or no hazard to aquatic life in the disposal site water column. A possible exception to this generalization would be highly contaminated dredged sediments disposed of in areas of restricted circulation and mixing, especially in association with pipeline dredging operations.

It is recommended that the Elutriate Test be utilized on a routine basis to check for possible exceptional situations, in which a contaminant in the sediments could be released in sufficient concentrations to be adverse to aquatic life at the disposal site water column. The Elutriate Test should be conducted with a well-defined oxygen status using the compressed air agitation in order to simulate conditions at the disposal site.

Research is needed on the development of a benthic organism bioassay test which could determine the potential significance of chemical contaminants associated with dredged sediments once they are re-deposited on the bottom at the disposal site. Primary emphasis in this test should be toward determining acute and chronic toxicity to benthic and epibenthic organisms of potential ecological or commercial significance. In addition, consideration should be given to the possibility of food web accumulation of heavy metals and other contaminants from dredged material disposal in open waters.

In association with these studies, studies are also needed on the environmental impact of confined and unconfined dredged sediment disposal in water and on land as discussed by Lee (1975). It is possible that due to

overflow of the supernatant and fine material to nearby watercourses, the present methods of on-land disposal of what are classified as polluted sediments may be more ecologically harmful than the formerly used, less expensive methods of open water disposal.

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