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DREDGE DISPOSAL STUDY

SAN FRANCISCO BAY
AND ESTUARY

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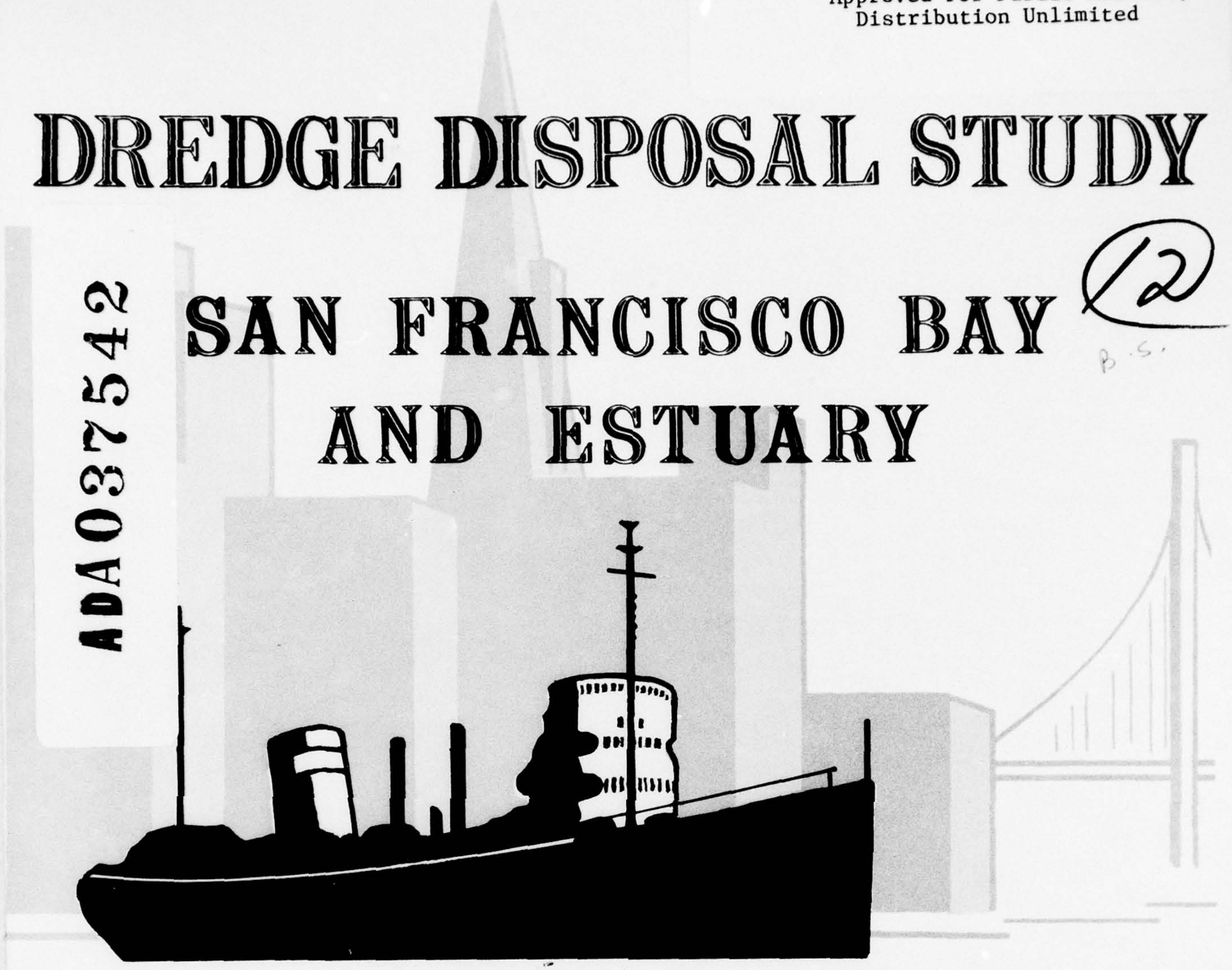

APPENDIX F

CRYSTALLINE MATRIX

JULY 1975

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DREDGE DISPOSAL STUDY SAN FRANCISCO BAY AND ESTUARY.

APPENDIX F.

CRYSTALLINE MATRIX STUDY,

11 JULY 1975

12 258p.

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U. S. Army Engineer District, San Francisco District
Corps of Engineers
100 McAllister Street
San Francisco, California 94102

FOREWORD

In April 1972, the San Francisco District of the United States Army Corps of Engineers initiated a three and one-half year $3.0 million study to quantify the impact of dredging and dredged material disposal operations on the San Francisco Bay and Estuarine environment. The study is generating factual data, based on field and laboratory studies needed for the Federal, State and local regulatory agencies to evaluate present dredging policies and alternative disposal methods.

The study is set up to isolate the questions regarding the environmental impact of dredging operations and to provide answers at the earliest date. The study is organized to investigate (a) the factors associated with dredging and the present system of aquatic disposal in the Bay, (b) the condition of the pollutants (biogeochemical), (c) alternative disposal methods, and (d) dredging technology. The study elements are intended first, to identify the problems associated with dredging and disposal operations and, second, to address the identified problems in terms of mitigation and/or enhancement. The division into separate but inter-related study elements provides a greater degree of expertise and flexibility in the Study.

This report presents the findings of Appendix F, Crystalline Matrix. The overall study will be the basis for preparation of a composite Environmental Impact Statement for Dredging Activities in San Francisco Bay System. A draft final report on the entire study is scheduled for completion in December 1975.

Main = 37727

The following is an index of appendices to be published in the Dredge Disposal Study:

	APPENDIX	REPORT	DATE PUBLISHED
		FINAL REPORT	
	A	Main Ship Channel (San Francisco Bar)	June 1974
	B	Pollutant Distribution	-
	C	Water Column (Water Column-Oxygen Sag)	-
	D	Biological Community	-
	E	Material Release	-
037 542	F	Crystalline Matrix	July 1975
	G	Physical Impact	-
543	H	Pollutant Uptake	-
	I	Pollutant Availability	-
	J	Land Disposal	October 1974
544	K	Marsh Development	-
	L	Ocean Disposal	-
	M	Dredging Technology	-

CONVERSION FACTORS

If conversion from the Metric to the British system is necessary, the following factors apply:

LENGTH

1 kilometer (km)=10^3 meters=0.621 statute miles=0.540 nautical miles
1 meter (m)=10^2 centimeters=39.4 inches=3.28 feet=1.09 yards=0.547 fathoms
1 centimeter (cm)=10 millimeters (mm)=0.394 inches=10^4 microns (μ)
1 micron (μ)=10^{-3} millimeters=0.000394 inches

AREA

1 square centimeter (cm^2)=0.155 square inches
1 square meter (m^2)=10.7 square feet
1 square kilometer (km^2)=0.386 square statute miles=0.292 square nautical miles

VOLUME

1 cubic kilometer (km^3)=10^9 cubic meters=10^{15} cubic centimeters=0.24 cubic statute miles
1 cubic meter (m^3) =10^6 cubic centimeters=10^3 liters=35.3 cubic feet=264 U.S. gallons=1.308 cubic yards
1 liter=10^3 cubic centimeters=1.06 quarts=0.264 U.S. gallons
1 cubic centimeter (cm^3)=0.061 cubic inches

MASS

1 metric ton=10^6 grams=2,205 pounds
1 kilogram (kg)=10^3 grams=2.205 pounds
1 gr (g)=0.035 ounce

SPEED

1 knot (nautical mile per hour)=1.15 statute miles per hour=0.51 meter per second
1 meter per second (m/sec)=2.24 statute miles per hour=1.94 knots
1 centimeter per second (cm/sec)=1.97 feet per second

TEMPERATURE

Conversion Formulas $^\circ C = \frac{^\circ F-32}{1.8}$ $^\circ F = 1.8(^\circ C) + 32$

PREFACE

As part of the San Francisco District's study of the environmental impact of dredging operations in San Francisco Bay and Estuary, an investigation was performed to ascertain the extent sediment-associated heavy metals and polychlorinated biphenyls (PCB's) may be made available to the biotic assemblage via release from the sediments as a consequence of dredging and disposal operations.

The intent of this program was not to develop a complete inventory of sediment quality throughout the authorized dredging areas in the Bay, but to cover a sufficiently broad range of sediment characteristics so as to obtain predictive tools that can be used for the range of sediments expected. Thus, sediments were characterized chemically from nine sites. Included were the following locations:

South Hampton Shoal Channel
Pinole Shoal Channel
Richmond Outer Harbor
Islais Creek Shoal
Oakland Outer Harbor (Seventh Street)
Oakland Outer Harbor (Turning Basin)
Oakland Inner Harbor
Redwood City Harbor
Mare Island Straits Channel

Laboratory characterizations of the sediments encompassed physical, chemical, and mineralogical parameters, including the content of heavy metals and PCB's. In addition to the above-mentioned characterizations, the relative distribution of the several metals between the various sediment phases and by inference, the metal chemical species were identified. This was achieved by use of sediment extractions under a variety of chemical conditions.

Finally, desorption experiments were conducted over the range of physical and chemical conditions expected to occur in dredging and disposal operations. These experiments were designed with the intent of obtaining correlations that would permit estimation of the biological and availability of contaminants for a range of sediments and a range of physical and chemical conditions when combined with other study elements.

Due to certain technical procedural uncertainties and the variety of options needed to be explored, the program was conducted in two phases. Phase I was exploratory in nature, selecting and firming up analytical and experimental procedures for subsequent application in Phase II.

To a large degree, the major uncertainty in the program was the probable concentration of the various heavy metals that would occur in solution in equilibrium with the sediment phase under the several possible chemical environments. Thus, the availability of heavy metals would control the choice of analytical methods that were necessary to accomplish the program. Further, the methods that were expected to be necessary were of the research type as opposed to routine analytical laboratory techniques. The range of cost per analysis could run from $15 for pulsed polarography to $500 per sample for neutron activation analysis. Thus, some flexibility had to be retained if meaningful results were to be obtained.

Completion of Phase I enabled the selection of proper analytical procedures and experimental methods to be applied in Phase II. In addition the scope of the investigation was limited such that the investigation could be more intensive with respect to the possible sorption and desorption of heavy metal. To that end the work being done with polychlorinated biphenyls and metals species characterization was negated and the number of sites or sediment types reduced to include material from Oakland Inner and Outer Harbors and Mare Island Strait only.

Laboratory characterizations of these sediments encompassed particle size (dispersed and nondispersed), pH, Eh, total sulfide content, organic carbon and organic nitrogen content, and heavy metal content including cadmium, copper, iron, lead, manganese, mercury and zinc. In addition, a series of extractions were performed in order to identify the relative distribution of the above heavy metals between various sediment phases and by inference the metal species involved. The Bay water samples from each location were collected and characterized as to heavy metal concentrations (cadmium, copper, iron, lead, manganese, mercury and zinc), organic carbon, organic nitrogen, free sulfide content, chloride content, Eh, and pH. The interstitial waters from the sediments were characterized as to their heavy metal concentrations, organic carbon, organic nitrogen, free sulfide content, Eh, and pH. The exchangeable extract solutions were characterized as to their heavy metal contents, free sulfides, and organic nitrogen.

Sorption-desorption batch experiments were conducted over the range of physical and chemical conditions expected to occur in dredging and disposal operations. Variables included salinity, Eh, contact time, sediment type, and sediment/solution ratio. Variables held constant at selected average values included temperature, pH, and trace metal content of the water. These experiments were designed to obtain correlations that permit estimation of the extent that cadmium, copper, lead, mercury and zinc become soluble when disturbed by dredging and disposal operations.

The results of this study will be integrated with the results obtained from the Water Column Study (Appendix C), Pollutant Uptake Study (Appendix H) and Pollutant Availability Study (Appendix I) to delineate the environmental consequences of displacing a contaminated sediment during a dredging and disposal operation and means of mitigating any adverse phenomena.

A Research Report

Characterization of San Francisco Bay Dredge Sediments — Crystalline Matrix Study

Contract Number DACWO7-73-C-0080

May 1975

To
U.S. Army Engineer District
San Francisco, California

Battelle
Pacific Northwest Laboratories

FINAL REPORT

CHARACTERIZATION OF SAN FRANCISCO BAY DREDGE SEDIMENTS - CRYSTALLINE MATRIX STUDY

By

R. J. Serne
B. W. Mercer

CONTRACT NUMBER DACW07-73-C-0080

MAY 1975

To

U. S. ARMY ENGINEER DISTRICT, SAN FRANCISCO
100 McAllister Street
San Francisco, California 94102

PACIFIC NORTHWEST LABORATORIES
a division of
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ABSTRACT

A study was undertaken to determine the quantity and nature of certain heavy metals (Cd, Cu, Hg, Pb, Zn) that may be released from selected San Francisco Bay sediments as a function of various physical and chemical parameters.

Ten sediment sampling stations in San Francisco Bay were selected to represent the range of sediment types and heavy metal concentrations which are involved in routine maintenance dredging and disposal. The sediment samples were characterized with respect to particle size, mineral content, total sulfide, organic carbon, cation-exchange-capacity, PCB and heavy metal contents.

For three regions a semi-selective chemical extraction procedure was utilized to determine the relative distribution of the heavy metals among the various geochemical phases. The greatest portions of heavy metals were found bound in clay or crystalline lattice-like and organic or sulfide-like sites.

A batch sorption-desorption experiment was performed to determine the fate of sediment bound heavy metals during simulated dredging activities. It was found that under oxygen rich conditions, statistically-significant larger concentrations of Cd, Cu, Pb, and Zn were found in the water column than were found under oxygen deficient conditions. Higher salinity waters also caused larger releases of cadmium and zinc than were found at low salinity. Length of agitation time in oxygen rich waters also affected the magnitude of release of copper, cadmium and zinc.

Mechanisms to explain the results are discussed as are relationships of the results to the environmental effects of dredging and disposal in San Francisco Bay. Elutriate trace metal concentration predictor equations and recommendations for future work are presented.

ACKNOWLEDGMENTS

The support of this project by the San Francisco District of the U. S. Army Corps of Engineers and the technical assistance and advice provided by T. H. Wakeman and J. F. Sustar of that office are gratefully acknowledged. The crew of the U.S.S. GRIZZLY and Corps divers Ron Ard, Doug Pirie, and Duncan Tharp who made the sample collection tasks a success are also gratefully acknowledged.

The authors wish to extend sincere appreciation to the following Battelle personnel whose contributions made this report possible: L. L. Ames, who conducted the X-ray diffraction studies; R. E. Wildung and T. R. Garland, who conducted the studies and wrote the sections on characterization of chemical species; J. A. Cooper and L. A. Rancitelli, who respectively provided the X-ray fluorescence and neutron activation analytical data; M. J. Mason, who performed the trace metal atomic absorption analyses; and R. G. Parkhurst, who performed the mercury analyses. The statistical testing and interpretations were performed with assistance from R. L. Buschbom, staff statistician. The contributions of J. A. Coates, R. G. Upchurch, J. L. Armantrout, and S. I. Thoreson, who performed many of the experiments; and Dee Parks, Nancy Painter, and Sheree Whitten, who prepared the manuscripts are also greatly appreciated. The administrative assistance of A. J. Shuckrow and W. H. Swift is also acknowledged.

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The many hours of excellent consultation provided by Dr. Ken Chen are sincerely appreciated.

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CHARACTERIZATION OF SAN FRANCISCO BAY DREDGE SEDIMENTS - CRYSTALLINE MATRIX STUDY - FINAL REPORT

INTRODUCTION

Dredging operations are required on a regular basis in the San Francisco Bay and Estuary to maintain deepwater shipping channels to various port facilities. The San Francisco District of the Corps of Engineers has responsibility for the major portion of the Bay dredging activities which involves the movement of an average of seven million cubic yards of dredged material annually.[1] Open water disposal of the dredged material within San Francisco Bay is currently restricted to five disposal sites.

Concern has arisen in recent years over the environmental impact of dredging activities in San Francisco Bay and other waterways of the country. In some instances, dredging and the disposal of dredged material are believed to have detrimental effects on the benthic and aquatic communities involved. Dredged material may contain relatively high concentrations of constituents such as finely divided sediments, degradable organics, and toxic materials including hydrogen sulfide, ammonia, heavy metals, polychlorinated biphenyls (PCB's), and pesticides. The removal and disposal of this dredged material may cause damage to the biological communities as a result of high turbidity levels, depression of dissolved oxygen, and the release of toxicants.

Although dredged material may contain high concentrations of objectionable material, it does not necessarily follow that the pollutants will cause damage to the biological community. In order to cause significant damage, the materials must be released or otherwise made available for reaction with constituents of the water (e.g., dissolved oxygen) or for absorption by various organisms. It is well known that not all of the pollutants in dredged material are available for release to water or for digestion by organisms. Many of the heavy metals, for example, are tightly held by sediments and are not released unless harsh chemical treatment is utilized.

Due to a paucity of basic information on pollutant availability from dredged material, regulatory agencies have taken a conservative approach on the disposal of this material. This approach has placed or threatened to place severe limitations on dredging activities in many areas including San Francisco Bay. In order to develop more accurate information concerning the effects of dredging activities in San Francisco Bay, the Corps of Engineers has undertaken a major study of the environmental impact of dredging in these waters.[2] Battelle-Northwest was contracted to perform the "Crystalline Matrix" portion of the overall study.

The principal objective of the Crystalline Matrix Study was to determine the extent to which sediment associated heavy metals may be released to the water column and made available to the estuarine ecosystem as a consequence of maintenance dredging and disposal operations in the San Francisco Bay. Conditions which may control the release of these pollutants include sediment characteristics (e.g., organic content, cation-exchange-capacity, and mineralogy), salinity, pH, Eh, temperature, and metal concentrations in both the water and sediments.

The Crystalline Matrix Study included the development of methods which can be used to help predict the impact of dredging and disposal on pollutant availability under conditions normally prevalent throughout San Francisco Bay. It was anticipated that these methods would rely on input data concerning sediment and water characteristics, and the results of sorption-desorption experiments aimed at determining the release or removal of pollutants under a range of conditions normally expected in the Bay. Hopefully, these methods will be useful in optimizing dredging and disposal practices so as to decrease the availability of pollutants to the ecosystem in this area.

The Crystalline Matrix Study was conducted in two phases. Phase 1 was exploratory in nature and was aimed largely at firming up analytical and experimental procedures for subsequent application in Phase 2. Major uncertainties existed as to the probable concentrations of various heavy metals that occur in the interstitial waters of the sediments and in the water to be contacted with the sediments. It is likely that very low concentrations of heavy metals will exist under certain conditions in the aqueous phase. Analytical methods for determining these very low metal concentrations are not necessarily routine procedures and may involve time consuming and costly techniques in some instances.

Phase 1, which was conducted over a five-month period, consisted of the following principal elements:

- Survey of the literature;
- Establishment of a sediment sampling method;
- Sample collection at ten locations;
- Evaluation of physical, chemical, and mineralogical characterization procedures;
- Investigation of sediment extraction and water analysis methods;
- Performance of scouting studies on sediment/water exchange; and
- Preliminary characterization of metal species in solution.

Phase 2, which was conducted over a seven month period, was a study to establish the sediment sorption-desorption characteristics of cadmium, copper, lead, mercury, and zinc in the range of physical and chemical conditions deemed significant in three specific dredging areas of San Francisco Bay.

The principal elements of Phase 2 consisted of the following tasks:

- Sampling the water and bottom sediments in three specified areas (Oakland Outer Harbor Turning Basin, Oakland Inner Harbor, and Mare Island Straits);

- Determination of the relative distribution of heavy metals throughout the various geochemical phases of the sediments by a semi-selective extraction procedure;
- Characterization of trace metal sorption-desorption phenomena as affected by salinity, Eh, contact time, sediment-solution ratio and sediment type; and
- Development of predictor relationships to be used in evaluating the extent that these trace metals become soluble when sediment is disturbed by dredging operations.

Studies on the effects of dredging on PCB mobilization and characterization of soluble trace metal speciation which were originally included in the Phase 1 scouting study were not included in the more comprehensive Phase 2 program.

LITERATURE SURVEY

A survey of the literature pertaining to the nature and concentration of heavy metals and PCB's in marine sediments and waters was undertaken to aid in establishing the mechanisms responsible for making these constitutents available to marine ecosystems. Pollutant availability to biological communities may occur as a result of direct ingestion of contaminated sediments by marine orgainsms or via the aqueous solution pathway (i.e., desorption from the sediments followed by sorption and/or ingestion by marine biota). A basic understanding of the chemistry of the sediment/water system is required as a basis for defining pollutant availability in future studies.

HEAVY METALS IN SEDIMENTS

Dissolved heavy metals in the open ocean waters and even in near shore waters close to man's activity occur at very low concentrations. Mechanisms which have been suggested as important forces which act to remove trace metals from the water column are precipitation of insoluble minerals and complexes, sorption onto suspended matter, bed sediment and small organisms, and incorporation into living tissue. Both inorganic (e.g., clays, hydrous oxides) and organic (e.g., plant detritus, animal tests) constituents of sediments are important sorbates.

Typical sediment concentrations of trace metals found in

TABLE I

TRACE METAL CONCENTRATIONS IN SEDIMENTS

Location	Sediment Type	Metal	Concent. (ppm)	Ref.
Indian Ocean	Deep-Sea	Cu	150-220	3
Delaware Bay	Near-Shore	Cu	60	4
		Pb	100	
		Hg	0.9	
		Cd	3.0	
Severn Estuary	Near-Shore	Cd	1.6-4.7	5
		Pb	150-200	
		Zn	420-590	
La Have River	River	Hg	.09-1.06	6
	Suspended Particles	Hg	3.59-34.4	
Lake Washington	Freshwater Surface	Pb	400	7
	30 cm and below	Pb	25	
Pacific	Pelagic Clays Avg.	Mn	4784	8
		Fe	50,669	
		Ni	211	
		Co	101	
		Cu	323	
		Pb	68	
		Cr	102	
Mobile Bay	Near-Shore	Pb	12-30	9
		Cu	10-104	
		Cd	.6-1.9	
Galveston Bay	Near-Shore Averages	Cu	19	10
		Pb	24	
		Hg	.1	
		Zn	51	
Corpus Christi	Bay	Zn	6-235	11
		Cd	.1-1.9	
	Industrial Harbor	Zn	235-11,000	
		Cd	2-130	
Firth of Clyde Scotland	Near-Shore Averages	As	8.0	12
		Cd	3.4	
		Cu	37	
		Fe	53,000	
		Mn	1,118	
		Ni	50	
		Pb	86	
		Zn	165	
Firth of Clyde	Sludge Dump Site Average	As	21	
		Cd	6.4	
		Cu	99	
		Fe	53,000	
		Mn	911	
		Ni	50	
		Pb	182	
		Zn	354	

TABLE I (CONT'D.)

Location	Sediment Type	Metal	Concent. (ppm)	Ref.
Rhode Island Sound	Range	Pb	8-56	13
		Hg	.2-.6	
		Zn	24-64	
San Diego Bay	Near Navy Waste Grounds	Pb	5-70	14
		Cr	25-225	
		Zn	25-240	
Baltimore Harbor	Unpolluted Average	Cd	1.3	15
		Cr	174	
		Cu	167	
		Pb	158	
		Mn	340	
		Hg	.7	
		Ni	40	
		Zn	440	
	Extremely Polluted Average	Cd	337	
		Cr	1993	
		Cu	966	
		Pb	1270	
		Mn	1012	
		Hg	6.3	
		Ni	33	
		Zn	3416	
Los Angeles Harbor	Silty Clay	As	27.9	16
		Cu	255.1	
		Cd	7.3	
		Cr	144.2	
		Fe	45,180	
		Mn	513	
		Ni	73.3	
		Pb	214.4	
		Zn	504.6	
		Hg	1.43	
	Sandy Silt	As	3.7	
		Cu	20.3	
		Cd	3.1	
		Cr	60.3	
		Fe	15,110	
		Mn	238	
		Ni	15.9	
		Pb	36.2	
		Zn	72.5	
		Hg	0.33	

marine and estuarine environments are shown in Table I on a dry weight basis.

The values presented in Table I have been selected to illustrate typical trace metal concentrations which are observed to vary over a wide range. Studies such as those of Crecelius and Piper,[5] Holmes, et al.[11] and Villa and Johnson[15] definitely showed increased concentrations of trace metals in regions of high industrialization. Much of the variability of trace metal concentrations probably reflects different geological source materials and types of sediments present. Averages for the Pacific Ocean pelagic clays[8] are often higher than near shore concentrations[9,10] in areas where man's activities might be expected to have increased the trace metal input.

Several studies of San Francisco Bay have generated data on the concentration of trace metals in sediments. The data presented in Table II indicate that the concentrations of trace metals in San Francisco Bay sediments are not exceptionally high compared to other developed ports such as Los Angeles and Baltimore Harbors. It appears that localized areas with high concentrations of trace metals[18,23] exist in San Francisco Bay and might be indicative of point source polluters. Data in Table II will be used to compare results of trace metal concentrations in sediments determined during this study.

TABLE II

TRACE METAL CONCENTRATIONS IN SAN FRANCISCO BAY SEDIMENTS (dry wt)

Location	Sediment Type	Metal	Concent. (ppm)	Ref.
Mare Island Straits	Surface Average	Ag	2.2	17
		As	12.5	
		Cd	2.2	
		Cu	87	
		Ni	90	
		Pb	57	
		Se	1.9	
		Zn	149	
		Hg	.47	
Islais Creek	Surface	Hg	6.9	18
Mare Island Strait	0-24 Inches	Cd	1.4-1.95	19
		Cu	29-33	
		Hg	.31	
		Pb	20-21	
		Zn	73-81	
Entire Bay	1-7 cm Average	Cd	1.22	20
	7-10 cm Average	Cd	0.93	
San Francisco Bar (Outside Golden Gate)	Surface Sand	Pb	4.8	21
		Hg	.08	
		Cd	2.08	
		Cu	1.7	
South Bay	Surface Average	Hg	.37	22
San Pablo Bay	Surface Average	Hg	.28	
Suisun Bay	Surface Average	Hg	.32	
Central Bay	Surface Average	Hg	.18	
San Francisco Bay	Surface Range	Pb	ND-10,000	23
	Surface Average	Pb	30	
	Surface Range	Cu	5-1500	
	Surface Average	Cu	30	

HEAVY METALS IN ESTUARINE WATERS

Data on the concentration of heavy metals in seawater is scarcer than sediment data because of the extremely low concentrations present. Sub parts per billion to several parts per billion seem to be typical values for marine waters. In order to measure these trace quantities in the presence of the comparatively large concentrations of chloride, sodium and other sea salts, highly sophisticated analytical techniques are required. Moreover, these techniques usually require complicated pretreatment steps which can be a significant source of contamination. Burrell[24] discussed the subject of analysis of trace metals in water in a recent book.

Selected values for the concentrations of heavy metals found in seawater, estuarine and interstitial waters are presented in Table III. These data represent the soluble concentrations of heavy metals. Solubility is usually operationally defined by filtration through a suitable pore size filter with 0.45μm being most commonly used.

The data presented in Table III show that interstitial waters[25,28] often are significantly enriched in soluble trace metals over open ocean waters. The data do not conclusively show that near-shore waters have significantly higher concentrations of trace metals than open ocean regions. The data of Holmes, et al.,[11] showed in this instance that highly polluted harbors can have very high trace metal concentrations in solution. No data for soluble trace metal concentrations in San Francisco Bay were found in the literature.

GEOCHEMICAL PARTITIONING OF THE TRACE METALS IN SEDIMENTS

Lee and Plumb[33] concluded after an extensive literature survey that the bulk chemical composition of sediments is not a useful index of potential environmental water quality problems

TABLE III

CONCENTRATIONS OF TRACE METALS IN MARINE WATERS

Location	Type	Metal	Concent. (ppb)	Ref.
Pacific Ocean	Interstitial	Cd	0.3-2.0	25
		Cu	0.9-16	
Open Oceans	Seawater	Cd	0.1	26
		Cu	3	
		Pb	0.03	
		Hg	0.2	
Atlantic	Coastal	Cd	0.15	27
		Cu	1.3	
		Pb	0.4	
Long Island Sound	Estuarine	Cd	0.23	
		Cu	2.5	
		Pb	0.4	
Loch Fyne Scotland	Interstitial	Cu	4-380	28
		Ni	8-66	
		Zn	14-480	
		Pb	5-74	
		Mn	200-1500	
		Fe	40-3860	
Pacific	Seawater Near-Shore	Cd	0.03-0.15	29
		Cu	1.0-1.7	
		Pb	0.4-1.0	
		Zn	4-12	
		Mn	0.4-0.7	
Pacific	Open Ocean	Cd	0.02	
		Cu	0.8	
		Pb	0.4	
		Zn	2.0	
		Mn	0.2	
Amchitka Alaska	Near-Shore	Pb	0.06-0.09	30
Bellingham Bay	Estuarine	Hg	0.03	
Atlantic	Estuarine	Cd	0.1	31
		Cu	1-4	
		Pb	.2-.9	
		Hg	0.2	
Pacific	Open Ocean	Zn	1.2-2.2	32
Los Angeles Harbor	Outside Breakwater	Ag	0.02	16
		Cu	0.10	
		Cd	0.15	
		Cr	0.74	
		Fe	5.5	
		Mn	0.8	
		Ni	0.04	
		Pb	0.05	
		Zn	0.2	
Corpus Christi Bay	Dissolved	Zn	4-6	11
		Cd	<2-3	
Corpus Christi Harbor	Dissolved	Zn	182-480	
		Cd	10-78	

because bulk analysis does not account for the varying impact of different chemical forms of an element. The weakness of total heavy metal analysis in sediments to predict damage to biological communities has led to attempts to differentiate geochemically various forms of the metals in the bulk sediment.

Basically the procedure is to attack sequentially the sediment with chemical reagents which selectively dissolve or release trace metals bound to different geological phases such as ion-exchange sites, carbonates, hydrous oxides, sulfides and organic detritus. Several extraction schemes have been proposed by Chester and Hughes,[34-36] Presley and Nissenbaum[37,38] and Engler, et al.[39]

In this study the procedure described by Engler, et al.,[39] was adopted and will be described in more detail in the Experimental Design section. This procedure was chosen over others because it attempts to maintain the sediments as close to the natural redox potential as possible during initial treatment steps.

The more mobile forms of trace metals in the bulk sediment would include metals in the interstitial water and on ion exchange sites. The least mobile forms of the metals would include metals bound in clay or silicate lattice sites. Of intermediate mobility would be trace metals bound to hydrous oxide surfaces, coprecipitated in carbonates or sulfides, and bound to organic matter. These phases are sensitive to oxidation-reduction and acid-base changes.

Studies reported by Gibbs[40] on two relatively unpolluted rivers (Amazon and Yukon) show that some heavy metals (Fe, Ni, Co, Cr, Cu and Mn) are largely distributed between precipitated metallic coatings on particulate matter and crystalline solids. Only a small fraction of these metals are held by ion exchange sites or by organic matter. Turekian and Scott[41] stated that ion exchange cannot be a major transport mode for trace elements. Their analyses showed no significant differences in the trace element contents of 20 to 2, 2 to 0.2, and less than 0.2 micron fractions of Brazos River sediments. This indicates that the fine fractions of this stream sediment do not contain a large amount of trace elements relative to the coarser fraction despite a generally higher cation-exchange-capacity of the finer material.

Chester and Hughes[34] investigated the distribution of nickel, iron, and manganese in North Pacific pelagic clay. The authors reported that the nickel was 56 percent bound in manganese nodules and 44 percent bound in clay lattices. There was no nickel bound to exchange sites. The total iron distribtuion was as follows: 1.5 percent bound in manganese nodules, 4 percent as marine formed iron oxides, and 95 percent detrital iron minerals. The distribution of manganese was 88 percent marine derived manganese nodules and 12 percent bound to clay lattices.

Chester and Hughes,[35] in a later article, reported studies on other trace metals including copper, lead, cobalt, nickel, chromium, and vanadium in the North Pacific pelagic clay. The total metals were chemically separated into three types: land derived (lithogeneous), nodular marine derived (hydrogeneous), and non-nodular marine derived. Table IV lists the results for the top 1-10 cm layer of sediment. The lithogenous contributions represent material which has been weathered from the continental area and in most cases represent atoms bound in the clay lattices. The hydrogeneous nodular fractions are bound to manganese-rich nodules. The non-nodular hydrogenous material represents metals bound in the hydrous iron-rich oxides. Adsorption to the exchange sites on the mineral surfaces can occur, but its importance in these samples appears negligible. Nearshore sediments may be affected by other processes such as sulfide precipitation and organic reactions, but as a first approximation the above results should be comparable to San Francisco Bay sediments.

Nissenbaum, et al.,[37] reported that the iron and heavy metal concentrations in the interstitial waters of sediment from a stagnant fjord exceeded the solubilities of their sulfides. Either a metastable phase, another metal complex, polysulfides, or some more complex mechanism must have been controlling the system.

Presley, et al.,[42] studied the trace metal distribution on the above sulfide-rich core. The only sources of sediment to the fjord are suspended sediment from low salinity water

TABLE IV

DISTRIBUTION OF TRACE ELEMENTS IN THE CHEMICALLY SEPARATED FRACTIONS[35]

	Total ppm	Lithogeneous (%)	Hydrogeneous Nodular (%)	Hydrogeneous Non-Nodular (%)
Cu	412	72	8	20
Pb	35	86	12	2
Ni	90	43	22	35
Cr	96	91	6	3
Co	92	32	65	3
V	141	78	8	14

and carbonaceous and siliceous organic matter from marine organisms. The organic carbon content of 2.5 to 4.5 percent is 2 to 3.5 times greater than that found in San Francisco Bay sediments. The carbonate content of 0.6 to 3.3 percent is also larger than that found in San Francisco Bay sediments during this study. The sediment was extracted with three different reagents. The first extraction (acetic acid in hydroxylamine hydrochloride) removes metals bound to carbonates, hydrous oxides, and some sulfides. The second extraction (30 percent hydrogen peroxide) removes metals bound to the sulfides and organic matter. The third extraction, residue dissolution, removes the lithogeneous mineral bound metals.

Table V lists the results of the Presley, et al.,[42] study for the upper 200 cm layer of sediment.

TABLE V

PERCENT OF TOTAL METAL IN EACH FRACTION[42]

	Extraction 1	Extraction 2	Extraction 3
Cu	4.8	52.4	42.8
Sr	29.0	0	71.0
Ni	10.9	9.8	79.3
Co	6.5	8.8	84.7
Zn	20.4	19.3	61.3

Other results indicated no correlation between the trace element content and the carbonate content. The trace metals that were chemically leachable were bound in amorphous oxides of iron and manganese, as sulfides and a minor contribution as exchangeable ions.

The high percentage of copper leached by the second fraction is probably an indication of the often proposed association of copper with organic matter.[42]

Nissenbaum[38] reported on the distribution of iron, manganese, strontium, copper, nickel, and zinc in a sediment core from the Sea of Okhotsk in the North Pacific off the coast of Siberia. His extraction procedure was similar to the one chosen for this study. The extractants used were (1) water, (2) hydrogen peroxide, (3) acetic acid, and (4) 6 N hydrochloric acid. The metals removed by these extractions are, respectively, (1) soluble ions; (2) organic and sulfide bound ions; (3) carbonate bound, exchangeable ions and some hydrous oxide bound ions; and (4) the remainder of hydrous oxide bound ions plus some metals in the clay lattice sites and silicate minerals.

Table VI lists the results as a percent of the total metal for the upper foot of sediment on trace metals of interest.

TABLE VI

PERCENT OF TOTAL METAL IN CHEMICAL EXTRACTIONS[12]

		Percent of Total Metal				
	Total ppm	H_2O	Peroxide	Acetic Acid	HCl	Residue
Cu	59	0	0	44.0	44.0	11.9
Ni	158	0.2	0	41.1	22.2	36.7
Zn	190	0.8	1.1	60.5	37.4	0

The percentage of organic carbon was 0.9 percent, which is slightly less than that in San Francisco Bay sediments. The particle size was coarser than that of typical San Francisco Bay sediment.

Hirst[3] studied the distribution of trace elements in the Gulf of Paria off the coast of Venezuela. Hirst showed that most of the Cr, V, Cu, Pb, and, to a lesser extent, Co and Ni, probably entered the basin of deposition structurally combined in the lattices of clay minerals weathered on land. The copper in the lattices tended to favor illite over montmorillonite. The small portion of nondetrital hydrogeneous copper (3-30 percent) found in the sediment could not be correlated to the organic content. The small portion of lead of nondetrital origin (1-10 percent) appeared tc be bound in the hydrous iron oxides.

The distribution of Hg, Pb, and Cu in surface sediments in San Francisco Bay Estuary have been reported by McCulloch, et al.,[22] and Peterson, et al.[23] These investigators found Hg, Pb, and Cu to be largely associated with the finer sediments in the Bay. Higher metal concentrations were found near the shoreline where the finer sediments migrate and where pollution sources may be located nearby. Automobile exhaust and sewage are considered to be major sources of pollutants in the Bay. Sediments high in sewage sludges in the New York Bight region[44] are reported to exhibit strong bonding characteristics for most metals. Even the strong action of boiling one molar hydrochloric acid was not capable of leaching metals such as Cu, Ni, Cr, Mn, Fe, and Zn from these sediments.

Mattraw,[45] in a study of an estuarine South Florida watershed, determined the percentage of the total metal content of sediments leachable with 1M ammonium acetate which is a standard procedure for determining ion exchangeable cations. The percentages of ion exchangeable metals to the total were Mn 2.7, Fe <0.02, Co 2.2, Cu 2.0, Zn 1.2, Cd 4.1, and Pb 3.0.

Walters and Wolery[46] extracted sediments from Lake Erie and determined the distribution of mercury in the extractants. They concluded that mercury was present in essentially three components: (1) high molecular weight organic acids (30-54 percent), (2) lower molecular weight organic acids believed to be held as insoluble complexes with iron under in situ conditions (5-20 percent), and (3) a sulfide and refractory organic component (24-62 percent). Interstitial water, sediment exchange sites and solid organic bases did not account for measurable amounts of mercury. Syers, et al.,[47] reported, however, that they found no consistent relationship between the concentration of Hg and other sediment components of potential interest (including organic matter) in a study of five freshwater lakes in Wisconsin.

It thus appears from the literature that the largest portions of trace metals, with the possible exception of mercury, in the bulk sediment are bound tightly in relatively inactive geochemical phases. Despite this fact, the minor proportions of metals bound to more mobile phases such as ion exchange sites if released may significantly increase the water concentrations of trace metals because of the very low natural water concentration.

SEDIMENT-WATER CHEMISTRY AND INTERACTION

The natural aqueous environment has been systematically modeled using the principle of chemical thermodynamic equilibrium. The basic concepts of this approach are nicely conveyed in the text by Stumm and Morgan.[48] The sediment, water and air are included in this approach. In the water phase, metal cations are free to interact with inorganic ligands such as chloride, carbonate and hydroxyl ions and organic ligands such as amino and humic acids. The complexes formed may or may not be soluble. The thermodynamic stability constants of these solubility and complex formation reactions can be used to estimate concentrations and speciation of trace metals in solution and to determine which solid phases should be present. The acidity and redox potential also affect speciation and have led to the pH-Eh diagram methods[48,49] of predicting stable mineral and soluble phases. Unfortunately, most of the predictions from these thermodynamic phenomenological models do not adequately describe the real system especially for trace metals. Two of the most serious drawbacks to the thermodynamic approach are the lack of adequate data and understanding of interactions at the solid-solution interface[50] such as ion exchange, adsorption and coprecipitation. These processes may be responsible for reducing the concentrations predicted by equilibrium solubility models. Several investigators[33,51] believe that sorption of trace metals by hydrous oxides of iron, aluminum and manganese may be the main control of the trace metals in natural environments especially freshwater regimes.

Soluble trace metals in marine waters very seldon exist as free cations. Burrell[24] believes that in seawater heavy metals exist predominatly as inorganic complexes. Zirino and Yamamoto[52] presented a model for speciation of copper, zinc, cadmium, and lead in seawater. The model which excludes polynuclear, organic and mixed ligand complexes predicts soluble copper to be presented in seawater (pH 8.1) as 90 percent $Cu(OH)_2°$ and 8 percent $CuCO_3°$; zinc as 17 percent Zn^{+2}, 62 percent $Zn(OH)_2°$, and 6.4 percent $ZnCl^+$ and 5.8 percent $ZnCO_3°$; cadmium as 51 percent $CdCl_2°$, 39 percent $CdCl^+$ and 6 percent $CdCl_3^-$; and lead as predominatly $PbCO_3°$ with some $PbCl^+$. All but the cadmium should exhibit dependence on pH. Anodic stripping of seawater at various pH values corroborated these predictions with lead, zinc, and copper scans changing but cadmium scans remaining stable.[52,53]

Gardiner[54] utilized a cadmium specific ion electrode and thermodynamic stability constants of inorganic ligands to calculate the complexing effects of natural humic materials and then predicted the speciation of cadmium in natural river, ground, and sewage effluent waters. In river waters 45-60 percent of the Cd was present as free Cd^{+2}, 10-24 percent as humic complexes, 5-21 percent as $CdCO_3°$ and less than 10 percent each $CdCl^+$, $CdOH^+$ and $CdSO_4$.

The formation of soluble inorganic ligands can increase the concentration of certain trace metals and retard metal sorption into the sediment. Krenkel, et al.,[55] report the adsorption of inorganic mercury by sediment components is reduced by increased chloride concentrations. The magnitude of this loss depends on the composition of the sediment and the type of scavengers contained therein. Exceptions to this observation were found for sediments containing organic amines or mercaptans. Feick, et al.,[56] also found that the addition of NaCl or $CaCl_2$ to fresh water can cause significant release of Hg from the sediments contained therein. Their data also show increased Hg sorption with increased organic matter content of freshwater sediments. In contrast to these studies, Bothner and Carpenter[57] report that both inorganic and methyl mercury are fairly rapidly taken up by the natural assemblage of Columbia River particulates. Desorption experiments indicate that at least half of each of these forms are readily desorbed by filtered river water but subsequent leaches with seawater removed little additional Hg.

The importance of organic complexes in the soluble speciation of trace metals is still controversial. Stumm and Bilinski[58] caution that a sufficient concentration of ligands must be available to form complexes of a particular metal. Concentrations of dissolved organic matter in natural waters typically range from 0.2 to 2 mg of organic carbon per liter which corresponds to about $10^{-7.5}$ to $10^{-5.5}$ moles per liter of ligands. Because there is a large number of organic species present, many potential chelate-formers must typically be present at concentrations of 10^{-6} M or less. The functional groups usually encountered in dissolved organic substances, such as $-COOH$, $-NH_2$, $-OH$, $-SH$, show little specificity toward individual metal ions. Therefore, the coordination tendency of most ligands will be satisfied with Ca^{+2} and Mg^{+2}, which are present at concentrations at least a thousandfold greater than those of the trace metals or chelate-forming substances. Contrary anodic stripping evidence was presented by Matson,[59] Fitzgerald[60] and Dehlinger, et al.[27] Matson[59] found a significant portion of the copper and lead and smaller portions of cadmium and zinc to be bound to what appeared to be soluble organic material. Fitzgerald[60] presented stability constant arguments and experimental data which refute Stumm and and Bilinski[58]. Fitzgerald found 63 percent of seawater copper off Woods Hole, Massachusetts, to be organically bound and 70 percent of the soluble copper concentration in the Sargasso Sea to be organically bound.

Barcia, et al.,[61] studied the mobilization of trace metals in water by TPP (tripolyphosphate, the convential detergent builder) and NTA and EDTA (two potential replacements for TPP). The results showed that the chelating agents applied in concentrations of 0.2-5 ppm sometimes increased the concentration of iron, manganese, lead, and zinc in water above contaminated sediment. EDTA increased all four metal concentrations whereas TPP and NTA caused increases in only iron concentration probably because these organics were quickly degraded. In flowing systems there was very little evidence that the chelating agents influenced the release of heavy metals from the sediment into the water.

Soluble organic complexes do not necessarily retard the sorption of the trace metals as evidenced by organic complex-sediment adsorption. Siegel[67] found that zinc complexes with glycine, an amino acid, were strongly bound to cation exchangers, particularly clay. The binding of the monovalent zinc glycinate was almost as strong as that of the divalent zinc ion which illustrates the marked effect of the organic component on the binding of the complex. Monovalent ions are normally not bound as strongly as multivalent ions to ion exchangers. Soluble organic complexes may play a significant role in sediment-water equilibrium under certain conditions.

When solutions of trace metals come in contact with solid phases, the concentration of the metal usually decreases. This association with the solid phase has been attributed to a number of processes such as ion exchange, adsorption and coprecipitation. Cranston and Buckley[6] found that soluble Hg released via industrial effluents to the LaHave River and estuary appeared to be quite rapidly adsorbed by suspended particulate matter and bottom sediments. Suspended particulates had concentrations of 3.59 to 34.4 ppm mercury. They also found that the smaller size particles sorbed more mercury which supports the hypothesis that adsorption is related to the specific surface area. Bothner and Carpenter,[57] after spiking Columbia River water with inorganic and methyl mercury radioisotopes found that between 50-75 percent of both species became associated with suspended particulates. Desorption experiments led them to conclude that a fraction of the bound mercury was "non specifically" bound and thus was easily released but at least half of the mercury was tightly held in "specific" sites.

Gardiner[63] studied the adsorption of cadmium in natural fresh waters onto sediments, clay, silica and humic material. In most cases adsorption occurred very rapidly with equilibrium being reached in two minutes. Gardiner found that as the cadmium concentration was increased, the more active sediment sites were saturated first and less active sediment sites with corresponding lower sorption specificity were then employed. This is similar to Bothner and Carpenter's[57] "non specific" and "specific" sites. Gardiner concluded that adsorption of cadmium on mud controls the concentration of cadmium in fresh water and that humic material appears to be the major component of sediment responsible for the adsorption.

Ion exchange type mechanisms are implicated by several researchers as being important in determining the sorption-desorption of trace metals. Kharker, et al.,[64] observed that trace elements adsorbed from freshwater solutions by particulate matter are always released to a greater or lesser extent on contact with seawater. Displacement of the sorbed ions by magnesium and sodium ions in seawater was presumed to be the desorption mechanism. Studies reported by Johnson, et al.,[65] show that particle bound Cr and Sc would not be displaced but that much of the Mn would be released to seawater. Zinc was intermediate in its affinity for sediments. These authors indicate that "specific adsorption" is largely responsible for bonding of the zinc to the particulate matter. Sodium and magnesium ions are, therefore, less effective than transition metal ions (e.g., Cu^{+2} and Co^{+2}) for desorption of the zinc.

Mattraw[45] found decreases in the concentrations of manganese, iron and zinc bound to exchangeable sites on suspended sediments brought down a river into Chokoloskee Bay in Florida. A plot of the percentage exchange bound metals versus the salinity of the water showed that the cation competition of the saline water explained the maganese decrease. Similar decreases in exchange bound metals were present for iron and zinc but the decreases were not statistically significant. Copper, cadmium and lead showed no decrease from exchangeable sites upon contact with saline water.

Robertson, et al.,[66] have described the transport of the radionuclides of manganese, cesium, europium, cobalt, zinc, scandium and iron from the effluents of the Hanford reactors to the Columbia River and subsequently the Pacific Ocean. The ions rapidly become associated with suspended particulates and bottom sediments. Leaching of radionuclides from the sediments by river water to form soluble species is apparently small. During spring runoff large amounts of fine sediment are resuspended and often transported out into the Pacific Ocean. A seawater leach of some river sediment revealed that 40 percent of the manganese, 10 percent of the cesium, 5 percent of the europium, 3 percent of the cobalt, and about 1 percent or less each of the zinc, scandium and iron was rapidly released. It thus appears that simple ion-exchange phenomena do not adequately explain the adsorption-desorption events observed so that other mechanisms should be considered.

As stated earlier, several researchers believe the hydrous oxides of manganese, iron and aluminum are major scavengers of trace metals. Anderson, et al.,[67] performed laboratory sorption experiments on silver by poorly crystallized manganese oxides. All manganese oxides studied sorbed significant quantities of silver and the sorption capacity increased both with increasing pH and with decreasing solution ionic strength. Silver sorption maxima were not directly related to surface area but appeared to vary with the amount of occluded sodium and potassium present in the manganese oxide. The important processes involved in the uptake of silver by the poorly crystallized manganese oxides were considered to be surface exchange for manganese, potassium, and sodium as well as exchange for structural manganese, potassium, and sodium.

Bondietti, et al.,[68] performed sorption experiments for Cd on aluminum and iron oxides and several clay minerals from simulated river waters. Distribution coefficients, Kd, (the ratio of cadmium adsorbed per unit weight of adsorbate to the equilibrium solution concentration) showed the iron oxide to sorb approximately twice as much cadmium as the aluminum oxide and more than four times as much cadmium as illite, weathered shale, muscovite and biotite.

In a freshwater stream carrying trace amounts of radioactive wastes from Oak Ridge, Jenne and Wahlberg[69] found that ^{60}Co was sorbed by the natural manganous and ferric oxides.

Loganathan and Burau[70] studied the sorption of cobalt, zinc, calcium, and sodium by hydrous manganese oxide at pH 4. During the sorption of Co and Zn, Mn was released to the solution suggesting some structural exchange. Calcium and sodium appeared to exchange only with surface bound hydrogen sites. Zinc exchanged with both surface hydrogen sites and structural Mn^{+2}. Cobalt, in addition to these two sites, also interchanged with structural Mn^{+3}.

Lockwood and Chen[71] found dramatically increased sorption of mercury by hydrous manganese oxides from both fresh and saline waters at the pH at which $Hg(OH)_2^{\circ}$ was calculated to be the predominant species. Addition of chloride ion caused desorption of mercury and a shift of mercury sorption to higher pH where $Hg(OH)_2^{\circ}$ again would predominate. Thus, it appears that Hg^{+2} and mercury chloride complexes either do not sorb or are weakly adsorbed to hydrous oxide surfaces. Similar mercury sorption results are reported in the review of Leckie and James[50] and the work of Parks.[72] Leckie postulates that similar hydrolyzed species, $M(OH)^{m-x}$, for other trace metals are the forms which associate with hydrous oxides.

One effect of organics, the formation of soluble complexes with trace metals, has been discussed. Particulate organic materials present in sediments can act as strong scavengers.

Organic materials such as humic and fulvic acids and detergents containing the functional groups hydroxyl, carboxyl, sulfhydryl and amino acids show significant sorption capacities. In seawater the presence of divalent cations can cause the precipitation of metal fulvates and humates with possible co-precipitation of trace elements.[73] Feick, et al.[56,74] found highly organic sediments to bind more mercury from freshwaters than low organic sediments in batch sorption tests. Mercury partitioning between sediments and water was 10^4 times greater for highly organic than for sandy sediments. The association of mercury with organic material in the sediment also was shown by Walters and Wolery.[46]

Windom[75] has suggested that the decrease in soluble iron, manganese and copper in river waters upon entering the Atlantic Ocean may be caused by preferential flocculation of organic complexes.

Bioconcentration of trace metals by plant and animal tissue and the subsequent settling of detritus and biological skeletons may also be important, especially for the short term deposition of trace elements.

The effects of organic material in sediments is hard to separate from oxidation-reduction phenomena. Sediments with organic carbon contents as low as one percent on a dry weight basis often contain large quantities of reduced material, especially sulfides.[76] The organic content acts as a food source for bacteria which deplete the oxygen supply while decomposing the organics. Sulfates are then utilized as oxygen sources with the resultant formation of sulfide. The solubility of trace metals in the presence of sulfides is extremely low. Thus, the reductive precipitation of trace metals especially co-precipitation with iron sulfides may be very important. Moyer and Budinger[20] found high concentrations of cadmium in sediments in San Francisco Bay which showed the characteristic black coloration of reduced sediments due to iron sulfide presence. Feick, et al.,[74] found that oxidation of freshwater sediments by allowing them to dry decreased their ability to sorb mercury in subsequent laboratory testing.

The oxidation-reduction environment of the sediment and water system definitely will influence the mobilization of trace metals. Two opposing views have been expressed. One thought is that trace metals will be more soluble under reduced conditions because of efficient scavenging of metals by hydrous oxide formation under oxidized conditions. The opposite view is that the extremely low solubility of trace metals in the presence of sulfides which occur under reducing conditions would make trace metals more soluble under oxidizing conditions. Evidence supporting the first view is found in the following literature which concludes trace metals may be more soluble in reduced environments. Brooks, et al.,[25] found iron and nickel to be enriched in interstitial waters taken from reduced sediments in comparison to oxidized interstitial waters at the sediment surface. Windom[77] explained an observed initial decrease of iron, copper, and zinc at a dredge discharge pipe and subsequent increase back to the initial metal concentrations to be caused by rapid oxidation followed by reduction. The initial oxidation of iron caused scavenging of other trace metals by the flocculating hydrous oxides. The subsequent increase in trace metal concentration in the water occured when fresh oxide precipitates were reduced again in the bottom sediments.

Evidence indicating that trace metals are more mobile under oxidizing conditions is presented below. Lopez-Diaz[78] performed batch type leach tests on freshwater sediments under oxidized and anoxic conditions. At concentrations of three to four grams of sediment per liter of solution, it was observed that under oxidized conditions the release rate of copper was almost twice that of tests performed under anoxic conditions (1.5μg Cu/l/day vs 0.8μg Cu/l/day). Less copper was released in distilled water than in natural lake waters which suggests that a soluble complex may have been formed in the natural water with a resultant increase in soluble copper. Holmes, et al.,[11] found effluent enriched Corpus Christi harbor water, which was oxgenated, to be much enriched in zinc and cadmium as compared to bottom waters which were anoxic. In summer, as the harbor stagnated, Cd and Zn were found to precipitate in anoxic sulfide bearing waters. During winter, waters with more oxygen content were found to desorb sulfide bound metals.

Lu and Chen [79] reported on laboratory experiments very similar to those carried out in this study. Sediment samples from Los Angeles Harbor were contacted with seawater in a ratio of about 4 liters wet sediment to 16-20 liters of seawater. The oxygen contents in some trials were kept at near saturation, other experiments were kept at low oxygen contents (0-1 ppm) and still other containers were maintained at a total sulfide concentration of 20-30 ppm simulating very reduced conditions. Metal concentrations in the water column were monitored and compared with the concentrations in the original seawater. The trace metals Cd, Cu, Ni, Pb, Zn, Fe, and Mn were found to be released under oxidizing conditions. Ag, Cr, and Hg did not show significant increases under oxidizing conditions. Under reducing conditions large amounts of iron and manganese were released into the water column. In general, the concentrations in the water column under the slightly oxidizing conditions were intermediate with significant release of iron and manganese and small releases of copper, nickel, lead, and zinc. The authors concluded that the transport phenomena were controlled by the chemical environment of the water. The release under oxidizing conditions was the result of soluble complex formation most likely carbonate, chloride, and organic. Under reducing conditions iron and manganese were released as the result of dissolution of previously insoluble hydrous oxides. Trace metals were inhibited from mobilizing by the formation of extremely insoluble sulfides.

The desorption of trace metals associated with sludge and sewage effluents upon mixing and dilution under aerobic conditions into seawater was shown by Rohatgi and Chen.[80] In most cases Cd, Cu, Ni, Pb, and Zn were found to be released to a greater extent than Cr, Fe, and Mn. The percentage release of trace metals from suspended particulates in a primary-secondary sewage effluent upon aerobic mixture and 5X dilution in seawater were Cd 93-95, Cu 67-69, Ni 57-63, Pb 53-58, and Zn 38-44. In general, the release was observed to occur in two stages: a rapid initial release, followed by a slower, long term release. The authors attributed these releases to the oxidation of organic particulates containing the metals, the oxidation of metal sulfides, surface desorption of the metals upon dilution and soluble complex formation both inorganic and organic.

Hendricks and Young[81] showed that a release of trace metals from sewage associated particulates actually occurred at a Southern California outfall.

Sediment-water chemical interactions are a complex subject. It appears that no one process such as complexation, acidity, redox reaction, adsorption, ion exchange or precipitation contols the mobilization or sequestration of trace metals in a natural system. In most instances multiple processes are probably acting in concert to control the concentration and behavior of trace metals in aquatic systems. The observed net result will probably be similar to the process which predominates for each case.

POLYCHLORINATED BIPHENYLS IN MARINE ENVIRONMENTS

An interdepartmental task force from five departments of the Executive Branch of the U.S. Government reported in 1972 that there were few data on the removal, disappearance, and sequestration of PCB's in soils and bottom sediments of rivers, lakes, estuaries, or the ocean.[82] The task force reported 3.1 to 5.8 ppb PCB in sewage sludge from San Francisco treatment facilities. Typical seawater values were reported as a few parts per trillion. Sediments generally contain a few parts per billion to hundreds of parts per million off industrial outfalls. The task force reported one desorption study conducted by D. R. Nimmo. A sandy silt containing 61 ppm PCB's was shaken with initially clean seawater. The final PCB concentration in solution was 3.5 ppb. A silt sediment containing 30 ppm PCB's supported a seawater solution concentration of 0.5 ppb.

Goldberg[83] reports that very few data are available on the concentrations of PCB's in seawater. Goldberg quotes personal communication with Olney (University of Rhode Island) that PCB's in northeastern U.S. coastal waters range from 0.05 to 4.15 ppb. Values in the North Atlantic open ocean waters ranged from 0.01 to 0.20 ppb.

Harvey, Steinhauer and Teal[84] reported a North Atlantic surface water average of 0.035 ppb and a 200 m depth average of 0.010 ppb. The PCB concentration decreased with depth. Atmospheric transport was hypothesized as the cause of PCB concentrations in the open ocean. No relationship between PCB concentration and proximity to land was observed. Goldberg quotes Barrett (National Marine Fisheries Service, La Jolla, California) that the near shore Pacific Ocean waters contain an average of 0.001 ppb PCB's. The larger differences between the Pacific and Atlantic Ocean values coupled with the small number of determinations shows the need for additional work.

Chen and Wang[16] determined the bulk sediment concentration of three forms of PCB's in Los Angeles Harbor. PCB 1254 concentrations ranged from 70.4 to 366 ppb, PCB 1260 concentrations ranged from 7 to 34 ppb and PCB 1242 ranged from 96 ppb to 304 ppb.

STUDIES ON THE ENVIRONMENTAL EFFECTS OF DREDGING

Sediments in many coastal estuaries and harbors are highly enriched in nutrients and possible harmful substances such as heavy metals, petrochemicals and chlorinated hydrocarbons. Many of these areas require frequent dredging to permit navigation and there is great environmental concern over the potential degradation that dredging may cause.

Two isolated instances of potential damage to the environment were found in the literature. Servizi, et al.,[85] found that dredging of Bellingham Bay sediments may cause a substantial oxygen depletion and release of hydrogen sulfide. The dredged material was heavily influenced by pulp waste from nearby paper mills and was, therefore, atypical. Hydrogen sulfide concentrations reached 4 ppm in a water column during the simulated dredging. Undoubtedly dilution would occur in the real environment, but concentrations as low as 0.3 ppm H_2S were found to be toxic to salmon and trout.

Kneip, et al.,[86] studied the effects of dredging sediments near the discharge from a nickel-cadmium battery plant adjacent to the Hudson River. During dredging, the dissolved cadmium concentration reached a maximum of 50μg/l which was 10 to 50 times higher than concentrations before dredging for any tidal state. The authors concluded that the distribution patterns of both dissolved and insoluble cadmium in the water column were increased by dredging but that the long term after effects of dredging needed to be further defined. This case is also a typical in that sediment concentrations of cadmium near the plant discharge range from 3000 to 50,000 ppm which is extraordinarily high compared to other "polluted" bays (See Table I).

Most environmental studies of the effects of dredging reported in the literature conclude that damage to water quality and biological life is minimal or often apparently nonexistent. The Navy Oceanographic Office[87] conducted a multiphase monitoring program in a disposal site off the mouth of the St. Johns River, Florida. Over an eighty day period, 571,000 cubic yards of material were removed by a hopper dredge. The spoil, if evenly distributed over the spoil site, would have covered the bottom with 5 inches of material. No conclusive drop in oxygen saturation could be detected after dredging. Heavy metal analyses were also performed on the water at the disposal site. Immediately following dredge spoiling, the mean lead content dropped slightly, but was not statistically significant.

No significant difference in cadmium concentration was observed, but a small decrease with depth after the disposal was observed. Zinc and copper concentrations both dropped slightly after the dredge spoils disposal but most of the change was due to a decrease in river runoff influence. The sediments in the disposal area showed that much of the finer material present after spoiling was removed by currents or covered over by advection of coarser grained material. Based on biological monitoring carried out seven months following the cessation of dumping operations, there appeared to be no appreciable permanent impairment in the condition of the benthic community.

Slotta, et al.,[88] reported on the effects of hopper dredging and in-channel spoiling in Coos Bay, Oregon. The particle size distribution for the spoil site showed a six fold increase in median grain size caused by a loss of fines. The dredge site and spoils site tended to return to the original conditions by natural and man made causes. The volatile solids of the dredged material changed from 10 percent before dredging to 8 percent after spoiling, thus supporting the hypothesis that organics were being dispersed during suspension. The authors found no measurable free sulfides at any sites either before or after dredging. Total sulfides in the sediments were 0-600 ppm. It was hypothesized that as long as sufficient available iron (II) is present in the sediment-water interface, essentially all of the hydrogen sulfides produced will be rapidly transformed to insoluble iron sulfides. Heavy metals were not studied during this work. The authors concluded that one can anticipate that dredging, unless extensive, will not produce significant changes in benthic systems which routinely experience physical disruption by natural seasonal high runoffs, tidal cycles, or man's activities. Within physically unstable benthic systems dramatic short term environmental impacts due to dredging should not be anticipated; however, chronic conditions resulting from activities made possible by dredging may be of greater importance. The general approach of measuring background conditions and then comparing them to conditions during and immediately after dredging operations becomes less applicable when chronic conditions tend to dominate acute impacts. In summary, with the exception of two low dissolved oxygen readings a few minutes after spoiling, the only water parameter change on dredging in Coos Bay was an increase in turbidity.

Westley, et al.,[89] reported on the environmental effects of maintenance dredging in southern Puget Sound. Evaluation of the data for Olympia Harbor revealed that neither the clamshell nor the pipeline method of removing bottom material from the harbor had any measurable effect on water quality. However, the disposal of the dredged material did affect the water quality parameters, suspended solids and turbidity. Barge dumping caused very localized and short term increases in ammonia, BOD, and organic phosphate. Bioassay studies showed no unusual toxicity related to the pipeline dredging to salmon, oyster, clam larvae or phytoplankton. In the case of pipeline spoiling, no major changes occurred in the benthic community at the disposal sites while in the barge disposal sites, a decrease in abundance and diversity of macroscopic benthic organisms did occur. However, complete eradication did not occur even in the areas of heaviest dumping. A single site site which revisited showed evidence of restoration in progress. Four months after active spoiling, native geoducks were found over the entire spoil site including areas covered by three feet of spoils.

Saila, et al.,[13] reported on the impact of dredge spoil disposal in Rhode Island. They found that a few benthic species were able to reach the surface after burials of over 20 centimeters. Mortality of marine animals, including fish and lobster was doubtful because of their ability to withstand high concentrations of suspended solids. Lack of oxygen in spoil sediments may have restricted the colonization of infauna but the overlying water probably never became anoxic. Spoils one to three years old yielded large numbers of species indicating the spoils lacked gross toxic or repellent properties.

May[90,91] has studied several dredging operations in Alabama. General conclusions of his first study are briefly stated below. Hydraulic channel, shell dredging and open water spoil disposal have had little significant immediate effect on water quality in Alabama estuaries. Almost all (96 percent) of the sediment discharged by dredges settled very rapidly and was transported by gravity along the bottom as a cohesive flocculated density layer and potentially harmful components (such as heavy metals) of the mud were not dissolved into the water. There was a limited, temporary reduction in benthic organisms in areas influenced by dredging. Hydraulic dredging in Bon Secour Bay, Alabama, when compared to weather, was an insignificant contributor to the overall sediment movement in the bay. In salt water, even with salinities below 1 ppt, fine sediments flocculated rapidly and settled. Barged spoils settled so rapidly that the area of low oxygen was confined to areas of extremely high suspended solids concentrations in the mud flow.

In the second study[91] May found that dredging a polluted harbor using confined spoil disposal did not degrade water quality. Quality of the water returned to the waterway was better than that in the stream before or during dredging due to an increase in dissolved oxygen and removal of solids and hydrogen sulfide. There was no significant increase in trace metals in the return waters from the confined dikes. The spoils were near paper mill effluent outfalls and contained pulp fibers with 15-41 percent volatile solids and a high chemical oxygen demand. Hydrogen sulfide was often detectable and fish kills occurred frequently. Before and during dredging, bottom waters in the area had zero dissolved oxygen content. Surface water oxygen contents ranged from 0 to 2.6 ppm while the spoil area overflow dissolved oxygen varied form 4.2 to 5.2 ppm. Trace metals present in the dredged sediment; Pb up to 180 ppm, Zn up to 1900 ppm, Cd up to 6 ppm, Cu up to 293 ppm, and Hg up to 2 ppm on a dry weight basis; did not dissolve since levels in the return water were not significantly different from levels in the stream. Values reported for the concentrations of trace metals in the stream were Pb 20 to 200 ppb, Zn 20-40 ppb, Cd <10-20 ppb, Cu 10-50 ppb, and Hg <1-1.6 ppb which are high compared to many recent published values such as presented in Table III.

Windom and Stickney[92,77] reported on both diked and undiked disposal operations. Twenty-four water quality studies were performed before, during, and after dredging. In general, only suspended solids increased in the water column. A possible release of mercury was observed in one instance but not repeated at other areas. In fact, a decrease in copper, lead and zinc was found in water taken from the discharge pipe and weir outlet during and right after dredging. Scavenging by ferric hydroxides was the suspected mechanism.

Windom[31] summarized much of his work on the environmental effects of dredging and stated that the only place where water quality problems are likely to occur during pipeline dredging is at the point of discharge from the spoil area. He also observed at a pipeline dredge site in Brunswick Harbor with diked disposal that the slurry taken from the pipeline initially showed lower soluble heavy metals than predredging conditions. However, after storage in large polypropylene containers, the soluble metals iron, copper, and lead increased to levels above predredging values after 15 days. Interestingly, free copper, Cu^{++}, as measured by anodic stripping showed no change during or after dredging. Windom suggested that this is the result of the scavenging of copper complexes by iron hydroxide flocs in preference to coprecipitation of free copper. Control of metal concentrations by iron precipitation was described in Windom's earlier works.[77,92] That explanation, however, suggested that oxidation and precipitation of the reduced iron released from the sediment during dredging resulted in the coprecipitation of trace metals. Subsequent accumulation and reduction of the sediment and iron precipitates was thought to bring about the release of the metals. Windom now feels this hard to explain when one considers the insolubility of the sulfide compounds of the metals. Windom's new explanation of the observed metal changes appears to be that iron hydroxide flocs preferentially scavenge organic complexes. Upon reduction, these stable organic complexes are allowed to diffuse back into the water column. The free cation species of the metals apparently are not influenced to any significant degree as judged by the anodic stripping results. Zinc and mercury reacted differently by decreasing in concentration with time of storage and may reflect uptake by the microphytes.

STUDIES ON THE EFFECTS OF DREDGING IN SAN FRANCISCO BAY

Boyd, et al.,[93] estimated the annual maintenance dredging operations in the San Francisco Bay area to be 7.1 million cubic yards of which 97 percent was removed by hopper dredges. Ninetynine percent of the spoil was disposed by open water release. The open water disposal may be viewed as an extension of natural sediment resuspension except that open water disposal often results in the resuspension of large volumes of sediments over a relatively short period of time into a relatively small area. The grain size classification of the San Francisco Bay spoil was estimated by Boyd, et al.,[93] to be 68 percent silt and clay, 15 percent mixed silt and sand, and 17 percent sand and gravel.

Field and laboratory studies[94] were carried out by the Fish and Wildlife Service on hopper disposal operations in certain reaches of San Francisco and San Pablo Bays. Measurable effects of spoil disposal were not apparent in deep channel areas. In other areas, it was concluded that the dredging and disposal operations significantly reduced the number and species composition of benthic organisms and demersal fish. Although some of the species were reestablished in a few months, during the study period the species diversity index did not return to the level measured prior to the dredging.

The Corps of Engineers, San Francisco District, studied[21] the effects of dredging the San Francisco Bar directly outside the Golden Gate in the Pacific Ocean and subsequent disposal south of the site. The dredged material was found to meet EPA criteria (see reference 93, page 32) with the exception of the zinc level in two samples. The water quality data were insufficient to form a basis for overall analysis of the dredging impact but generally the data did not show significant increases. The bottom life appeared to be burrowing types apparently capable of sustaining themselves under sediment accumulation at the disposal site. The study concluded that due to the nature of the indigenous species, natural turbid waters and only minor deposition in the spoils area, no harmful smothering effects occurred.

Brown and Caldwell[95] studied the dissolved oxygen conditions of the water surrounding a disposal site near Mare Island Straits. The dredged material contained 8.5 percent volatile solids, had a 4.5 percent chemical oxygen demand and contained 14-290 ppm total sulfides on a dry weight basis. The hopper barge had a capacity of 3000 cubic yards which were released over a time interval of approximately two minutes and a distance interval of about 200 yards. The material tended to drop rapidly to the bottom with little mixing with the receiving waters. Six successive releases were monitored and the results showed only very transient oxygen depressions which subsided within one to eight minutes after release.

Recently, investigators at the Lawrence Berkeley Labs[17] studied the concentration of lead in the water and heavy metal concentrations of benthic organisms before, during, and after dredging operations in Mare Island Strait. Their preliminary conclusions are that there is no indication that dredging is a significant factor in the dynamics of trace metals in Mare Island Strait as compared with other phenomena.

In summary, studies to date on the acute or short term environmental impact of dredging and disposal in general have been shown to increase temporarily turbidity, to decrease temporarily dissolved oxygen and possibly to smother certain benthic organisms. Open water disposal, which is extensively utilized in San Francisco Bay, showed few effects on turbulent high energy regimes.

EXPERIMENTAL METHODS

SAMPLING OF WATER AND SEDIMENTS

Phase 1 and Phase 2 sampling occurred August 14-17, 1973 and June 17-19, 1974 respectively. The first sampling included the ten locations shown in Figure 1. Sites were chosen by Corps of Engineer personnel to represent typical types of sediment in dredging zones with emphasis on ability to relocate the sampling station. During the second sampling trip only stations 2,3,8, and a new water sampling location inland of Golden Gate (near Alcatraz Island) were visited.

Water samples were collected in 1 gallon and 13 gallon polyethylene containers. Containers were rinsed once with dilute acid (5 percent HNO_3) and several times with distilled water. Before use in the field, the containers were rinsed with surface water from the location sampled. The method of collection for surface waters was to have SCUBA divers swim away from the ship with a closed bottle, open the cap and allow the containers to fill. The thirteen gallon containers were brought on deck with the aid of a winch. Mid-depth and bottom waters were obtained by SCUBA divers carrying empty containers to the respective depth and opening the caps.

Three types of core sampling tubes were fabricated for use in collecting the sediment samples. The first sampler consisted of a 10 cm ID polyvinyl chloride (PVC) pipe, the second consisted of a 5 cm ID plexiglas tube and the third

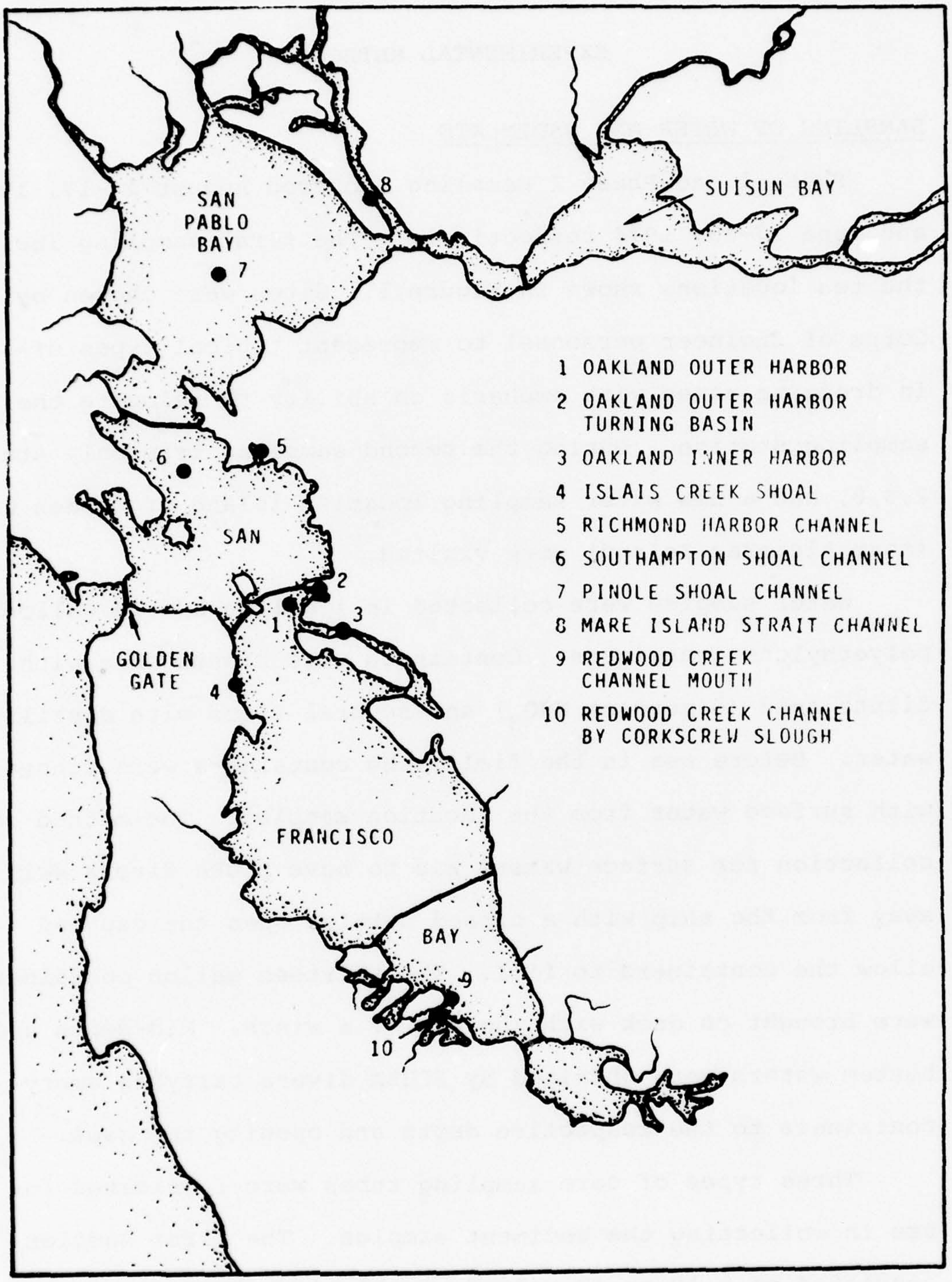

FIGURE 1. LOCATION OF SAMPLING STATIONS

consisted of 12 cm ID aluminum pipe. All types of tubes were 51 cm long and were fitted with caps having a 1.6 cm hole in the top center of the cap. The volumetric capacity of the PVC, plexiglas, and aluminum tubes was 4000, 1000, and 6000 cc, respectively. The PVC pipe was used to prevent possible metal contamination of the sediment samples while the aluminum pipe was used to prevent possible sorption of polychlorinated biphenyl (PCB) compounds by the sample tube. The plexiglas cores were used to collect sediments to measure Eh, pH, total sulfides and to allow visual inspection of cored material before total disruption of the vertical layering. Divers collected the sediment samples by pushing the sampling tubes into the sediment in a vertical direction in most instances. The hole in the cap of the sampling tube allowed the water above the sediment surface in the tube to escape. When the top of the tube was nearly flush with the surface of the sediment, a rubber stopper was inserted in the hole of the cap to prevent loss of the sample as the tube was withdrawn from the sediment. Another cap was placed over the open end of the tube as it was withdrawn from the sediment.

Large bulk samples of sediment to be used in sorption-desorption experiments were collected during the second sampling period at the same times as core samples. Containers utilized by SCUBA divers were polyethylene lined five gallon paint cans. The cans were filled on the bottom by pushing them into the soft sediment at about a forty-five degree angle until full. Lids were placed on the cans before return to the surface to inhibit sediment from washing out of the containers. On board the ship any void space at the top of the cans was filled with seawater to exclude air and the lids with rubber O-rings were secured with flanges to make an air tight seal.

The sediment collected in PVC, plexiglas, five gallon cans and water samples were packed in ice on board ship and during transit and placed in cold storage at 4°C before being utilized. The samples collected in aluminum tubes were frozen with dry ice on the boat, shipped and stored in a frozen condition. A description of the exact sample locations and field observations are presented in Table VII.

BULK SEDIMENT CHARACTERISTICS

Eh and pH

The plexiglas cores were taken into a portable inert atmosphere after the ship returned to the dock. Visual inspections, Eh and pH were measured under a nitrogen atmosphere within three hours of the sampling. pH, Eh and reference electrodes were placed directly into the sediment and measurements made after 15-30 minutes.

Particle Size Distribution

Sediment particle size was determined by both dispersed and non-dispersed methods utilizing the hydrometer approach.[96,97] For the dispersed analysis, sediment was contacted with a ten

TABLE VII

SEDIMENT DESCRIPTION

PHASE 1 - AUGUST 14-17, 1973

LOCATION	MOORING	SEDIMENT DESCRIPTION	SAMPLES TAKEN ALUMINUM	SAMPLES TAKEN PVC	REMARKS
Oakland Outer Harbor (Seventh Street)	Buoy "3" Fl 4 sec 8	Top few inches mud, hard underlayer	#1 Vertical #2 Horizontal	#1 Vertical #2 Horizontal	#2 Samples contained more water than #1 samples
Oakland Outer Harbor Turning Basin	Northern dock by U. S. Army cranes, across from first crane	Black mud for more than 2 ft depth	#1 Vertical #2 Vertical	#1 Vertical #2 Vertical	High solids content
Oakland Inner Harbor	Southern dock at Alameda Army supply dock	Black soft mud for more than 2 ft depth	#1 Vertical #2 Vertical	#1 Vertical #2 Vertical #3 Vertical #4 Vertical	#2 Samples taken 100 ft further east from #1 sample location; much debris on bottom
Islais Creek Shoal	Docked on south side about one-third of the way in	Black soft mud for more than 2 ft depth	#1 Vertical #2 Vertical	#1 Vertical #2 Vertical	No debris evident
Richmond Harbor Channel	Docked on east side at Terminal # 3	Black soft mud for more than 2 ft depth	#1 Vertical #2 Vertical	#1 Vertical #2 Vertical	Debris evident; sediments smelled oily; #2 taken 100 ft north
Southampton Shoal Channel	Tied off Buoy "ISS" on S.E. corner of channel	Brownish sand	#1 Vertical #2 Vertical	#1 Horizontal #2 Vertical #3 Vertical #4 Lost	#1 Aluminum only half full; #4 PVC lost when boat moved, pulling diver away from sampling tube
Pinole Shoal Channel	Tied off northern black can, Buoy # 5	Top 5.5 inches--brownish sand/mud; 4 inches--black mud to bottom--gray mud	#1 Vertical #2 Vertical	#1 Vertical #2 Vertical	Looked for sand with grab samples but could not find
Mare Island Strait Channel	Moored off west cable crossing	Black mud	#1 Vertical #2 Vertical	#1 Vertical #2 Vertical	Strong current; brown colored water; water at other locations colored green
Redwood Creek Channel at the mouth	Moored off Buoy "5", 130 ft S.W. into channel	Black mud	#1 Vertical #2 Vertical #3 Vertical	#1 Vertical	Samples contain much water; #1 PVC--most lost in transit
Redwood Creek Channel by Corkscrew Slough	Moored off buoy marked "15" on Chart 5531	Black mud	#1 Vertical	#1 Vertical #2 Vertical #3 Vertical	Samples contain much water; lost end cap on #3 PVC

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TABLE VII (Cont'd.)

SEDIMENT DESCRIPTION

PHASE 2 - JUNE 17-19, 1974

LOCATION	MOORING	SEDIMENT DESCRIPTION	SAMPLES TAKEN	REMARKS
Oakland Outer Harbor Turning Basin	Northern dock by U. S. Army cranes	Black mud Very soft	2 - PVC cores 1 - Plexiglas 4 - 5 gal. cans	Collection went smoothly; weather was slight drizzle
Oakland Inner Harbor	Southern dock at Alameda Army supply dock	Black soft mud	2 - PVC Cores 1 - Plexiglas 4 - 5 gal. cans	Area had just recently been dredged
Mare Island Strait Channel	Moored off W. cable crossing	Brown mud	2 - PVC Cores 1 - Plexiglas 4 - 5 gal. cans	Water very turbid; Strong current on divers

percent calgon (sodium hexameta-phosphate) solution for 18 hours, and distilled water was used for the supporting liquid in the actual measurement. For the non-dispersed analysis, sediment was contacted with synthetic seawater at the same salinity as determined to be present at the mid-depth of the water column above the sediment. The same seawater was used as the supporting liquid during the hydrometer measurements. Hydrometer readings were corrected for the density differences in the supporting liquid.

Mineral Content of the Sediment

After pretreatment[98] to remove carbonates, organics and iron oxides, mineral contents were determined by X-ray diffraction on sediments collected in Phase 1.

The effects of ethylene glycol on the interlayer distances were also determined.

Cation-Exchange-Capacity

The cation-exchange-capacity was measured by the method described by Routson, Wildung, and Serne[99] on sediments collected during Phase 1. The procedure consisted of placing 0.5 g of sediment in a fritted glass tube, removing the carbonates with a 1 N strontium solution at pH 5, saturating the exchange sites with a 1 N strontium solution at pH 7, and equilibrating the sediment with a 0.05 N strontium-^{85}Sr traced solution at pH 7. Entrained solution is washed from the sediment and the sorbed ^{85}Sr activity in the sediment is measured.

The cation-exchange-capacity can be calculated from the specific activity of the ^{85}Sr in the equilibrating solution and the activity in the sediment. In order to percolate the solution through the fine Bay sediment samples in fritted tubes within a reasonable length of time, the samples were mixed with 1.5 g of clean beach sand. The beach sand had a very low exchange capacity of 0.038 meq/100 g and did not significantly influence the results. The 1.5 g of added beach sand increased the ^{85}Sr activity by only one percent and was therefore neglected.

Sediment Total Sulfide Content

Total acid soluble sulfides in the sediment samples were determined on the iced samples (PVC) and several of the frozen cores (AL) by the iodometric titration procedure.[100] The samples from PVC cores obtained during Phase 2 were manipulated in an inert atmosphere and all analyses performed within fourteen days of sampling. The PVC cores had remained sealed and stored at 4°C until analyses were performed.

Organic Carbon Content of the Sediment

Total organic carbon was determined on freeze dried sediment by direct combustion[101] after treatment with HCl to remove carbonates. Analyses were performed by Schwarzkopf Microanalytical Laboratory.[102]

Carbonate Content

The carbonate content of the sediment was determined by the calcimeter[103] method in which the evolved carbon dioxide was volumetrically captured as the sediment was acidified by addition of HCl. Dried sediment samples were acidified in a slurry in silver nitrate solution. The silver nitrate solution sequestered the evolved H_2S from the sediment but did not affect CO_2 evolution from sediments or sodium carbonate standards.

Carbonate was also estimated by difference from samples which were directly combusted with and without HCl treatment.

Total Kjeldahl Nitrogen, Ammonia and Organic Nitrogen Contents

During Phase 2, wet sediments from the PVC cores were analyzed for total Kjeldahl nitrogen and ammonia by standard methods[100] with the evolved ammonia determined colorimetrically with Nessler's reagent. Organic nitrogen was calculated by difference.

Heavy Metal Concentrations in the Sediment

Wet sediments from the cores were centrifuged to remove as much water as possible. Portions of the centrifuged sediment were freeze dried while other portions were oven dried at 100°C for fourty-eight hours. All samples were then ground and mixed in a porcelain mortar. A few samples were washed with distilled water before freeze drying to compare with unwashed results. In Phase 1 three analytical techniques were used to measure trace metals in the sediment: X-ray fluorescence, instrumental neutron activation, and total digestion with subsequent analysis by atomic absorption. In Phase 2 only atomic absorption techniques were used.

Energy dispersive X-ray fluorescence was performed on pellets formed from oven dried and ground sediments. Elemental calibration was performed utilizing NBS geological materials.

Instrumental neutron activation was performed on both freeze dried and oven dried and ground sediments placed in special polyethylene vials. The vials were irradiated with thermal neutrons and subsequent activation products counted without chemical separations on Ge-Li gamma detectors. Again calibration was performed with use of NBS geological materials.

The total digestion procedure utilized in this study is that of Smith and Windom[104] with minor modifications. One half to one gram of dry sediment was placed in a Teflon beaker and digested for two hours with 15 ml of HF and 10 ml of HNO_3. After two hours, 2 ml of $HClO_4$ were added and the beaker heated until perchloric acid fumes subsided. The sample was heated to dryness and redissolved in 6M ultrapure nitric acid. Final volumes of ten milliliters were carefully measured and samples were stored in pre-cleaned polyethylene vials until atomic absorption analyses were performed. Reagent blanks were acquired with the identical procedure without the sediments.

Trace metal concentrations were determined by the methods of known additions[105] utilizing standard flame and graphite furnace atomic absorption with deuterium background correction (Perkin Elmer 503 AA and HGA 2000 Furnace).

Total Mercury Concentration of the Sediments

The determination of total mercury was accomplished by both neutron activation on freeze dried samples and by flameless atomic absorption.[75,106] In the latter case, wet sediment was digested in nitric acid, permanganate, and persulfate on a water bath at 60°C overnight. The resultant solution was then treated with hydroxylamine hydrochloride to reduce excess oxidizing reagents. Stannous chloride was added to reduce the mercury to its elemental form. The mercury was next purged with nitrogen gas which carried the volatile mercury through a silver foil trap. Mercury was captured as an amalgam on the foil while organic and moisture vapors were vented. The silver foil was then rapidly heated and mercury driven through a quartz absorption cell. The mercury absorption peak was measured with a strip chart recorder receiving the spectrophometer signal. Standard mercury solutions were used to calibrate the instrumentation.

PCB's and Chlorinated Insecticides

Sediment samples from the aluminum coring tubes used in Phase 1 were analyzed for PCB's, DDT, DDE, and DDD by the Wisconsin Alumnae Research Foundation[107] utilizing gas chromatographic techniques.[108] Aurochlor 1254 was the PCB form used to calibrate the instrumentation.

WATER ANALYSES

Salinity

During Phase 1 decanted solutions from the centrifuged sediment samples were analyzed for salinity using a conductivity meter. Salinities were determined from the conductivity data by plotting a curve of dilutions of standard seawater versus conductivity. During Phase 2, surface, mid-depth and extracted interstitial waters were analyzed for chloride contents by coulometric silver titration. Salinity was then calculated from chlorinity values utilizing Knudsen's equation,[109] $S\ ^\circ/_{\circ\circ} = 1.805\ Cl\ ^\circ/_{\circ\circ} + .03$.

Eh and pH

Oxidation-reduction potential (Eh) and pH were measured with platinum and glass electrodes respectively versus the calomel reference electrode.

Total Free Sulfide Content of the Waters

A specific ion electrode determination of sulfide contents was unsuccessful below concentrations of 0.1 ppm; therefore the methylene blue photometric procedure[100] described in Standard Methods was adopted. Seawater samples spiked with sodium sulfide were used to prepare a standard curve.

Total Soluble Organic Carbon Content of the Waters

Soluble organic carbon contents of water samples were determined using a Beckman 914 carbon analyzer.

Total Kjeldahl and Ammonia Nitrogen

The Kjeldahl nitrogen and ammonia nitrogen contents of water samples were determined as described in Standard Methods[100] within two weeks. Water samples were preserved by the addition of 1.5g/ℓ sulfuric acid.

Trace Metal Concentration of the Waters

The mercury concentrations of the water samples were obtained by the flameless atomic absorption method described for the sediments with the exception that the oxidative digestion step was shortened from overnight to four hours. The mercury samples obtained during Phase 2 were not filtered but were preserved with ultrapure nitric acid to pH 1-1.5 and 10 ml/liter of 6% potassium permanganate solution. The reported mercury values thus included any mercury released by the suspended solids upon acidification.

Other trace metals (Cd, Cu, Fe, Pb, and Zn) were measured on Phase 2 samples that had been filtered through 0.45µ millipore filters and acidified to pH 1-1.5 with ultrapure nitric acid (ALFA Chemical Company). Heavy metals were determined by flame and flameless graphite furnace atomic absorption after chelation with 1% APDC (ammonium pyrolidine dithiocarbamate), extraction into MIBK (methyl isobutyl ketone) and back extraction into 6N ultrapure nitric acid. The method is derived from the works of Brooks, et al.,[110] and Segar and Gonzalez.[111] Four hundred milliliters of filtered water was pH adjusted to 4-5 with sodium hydroxide or ultrapure nitric acid in a polyethylene separatory funnel, after which four ml of 1% APDC prepared daily as described by Smith and Windom[104] were added. The funnel was briefly shaken, 20 ml of redistilled MIBK added, and the funnel shaken for 30 minutes on a laboratory shaker. The mixture was then allowed to separate for 15 minutes. The water phase was transfered and saved. Ten ml of 6N ultrapure acid were then added to the MIBK phase in the separatory funnel and shaken for 20 minutes. The phases were allowed to separate for 15 minutes and the acid phase was removed and stored at 4°C in the dark until atomic absorption measurements were performed. The resultant acid-extracted MIBK phase was discarded. The saved water phase was re-extracted with another dose of APDC and MIBK and then respiked with known concentrations of heavy metals and used as standards. The respiked water standards were treated exactly like water samples throughout the chelation, extraction, and acid back extraction. The back extraction into nitric acid was used because the MIBK phase chelated metals were found to be unstable with time. The back-extracted acid samples remained stable for at least several days. All original sample filtering, extraction and storage procedures were carried out in non-glass containers which had been scrupulously cleaned by soaking for two days in dilute nitric acid and thoroughly rinsed with ultrapure water as suggested by Chen.[79,112]

SEMI-SELECTIVE SEDIMENT EXTRACTION PROCEDURE

During Phase 1 a sediment extraction procedure similar to Nissenbaum's work was utilized. For Phase 2, however, a procedure developed by Engler[39] and co-workers at the Corps of Engineers Waterways Experiment Station was used because it is more applicable to anaerobic sediments.

Wet sediment samples were manipulated during the early extractions under an inert atmospher to minimize contact with air. Inexpensive disposable glove bags from I^{2}R, Cheltenham, Pennsylvania were used to act as inert chambers. High grade nitrogen or argon from standard cylinders was constantly bled through the bags to inhibit oxidation. Oxygen concentrations in the bags were monitored with an O_2 membrane probe to ensure the absence of leaks and sufficient inert gas flow.

The extractants, approximate ratios of sediment to reagents utilized, and the geochemical phases which are expected to be dissolved in each step are presented in Table VIII. For specific details the Engler, et al.,[39] reference should be consulted.

The metals cadmium, copper, and lead were determined on the interstitial waters and chemical extracts by known addition techniques on a Perkin Elmer 503 atomic absorption spectrophotometer in the graphite furnace mode with deuterium background correction.

The metals manganese, iron, and zinc were determined on the interstitial waters and chemical extracts by known addition techniques on a Perkin Elmer 503 atomic absorption spectrophotometer in the flame mode. Background correction was utilized on zinc but was not necessary for the other metals.

Mercury was determined after wet oxidation in the interstitial waters and chemical extracts by cold vapor atomic absorption techniques previously described. After it was determined that none of the reagents caused matrix effects, the mercury concentrations were calculated from standard curves in spiked distilled water.

Reagent blanks were determined for metals and appropriate corrections made before the metal concentrations in each extract were calculated.

TABLE VIII

SEMI-SELECTIVE EXTRACTION PROCEDURE

	Extractant	Atmosphere	Dry Soil (g)/Reagent (ml)	Geochemical Phase
1.	Centrifuge or Filter Press	Inert	100-300g	Interstitial water
2.	1-1.5 M Ammonium Acetate pH7	Inert	20-30g/100 mls	Exchangeable Phase
3.	0.1 M Hydroxylamine Hydrochloride pH 2 HNO_3	Up to Addition of Reagents Inert	3-5g/130 mls	Manganous Oxides, Some Amorphous Iron Oxides, Carbonates
4.	Hydrogen Peroxide Leach 1 M Ammonium Acetate pH 2	Air	3-5g/30 mls H_2O_2 100 mls NH_4OAC	Organics, Sulfides
5.	Sodium Citrate And Sodium Dithionite	Air	3-5g/2g Dithionite 20g Citrate 120 ml H_2O	Iron Oxides
6.	Nitric, Hydrofluoric Perchloric Acids*	Air	0.5g/10 mls NHO_3 10 mls HF 2 mls $HClO_4$	Residual Alumino Silicates Clay Minerals and Total Metals

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*NOTE: Residual samples for mercury determinations were not totally digested. Mercury residuals were determined by cold vapor A.A. as discussed in the determination of total Hg in sediments section.

RADIOISOTOPE CHECK OF APDC-MIBK-HNO_3 WATER EXTRACTION PROCEDURE

Radioactive tracers, ^{65}Zn, ^{109}Cd, ^{54}Mn, and ^{59}Fe, were added separately to water at two salinities (29‰ and 1.5‰). The ^{54}Mn, ^{109}Cd and ^{65}Zn were carrier free with approximate specific activities of 100 μC/μg. Approximately 10 μC of each isotope were spiked into respective 500 ml water samples. The samples were shaken overnight to allow short term equilibration of the radiotracers. The spiked water samples were extracted at pH 4-5 with APDC-MIBK. Extraction time was 30 minutes followed by a 15 minute phase separation. Samples from both the remining aqueous phase and MIBK phase were counted to determine the distribution of radioactivity. The MIBK phase was then back-extracted with 6N nitric acid for 20 minutes. The acid phase and organic phase were then separated and counted for radioactivity.

FACTORIAL DESIGN SORPTION-DESORPTION BATCH EXPERIMENTS

Under nitrogen atmosphere, wet sediment was quantitatively added by volume to one liter polypropylene centrifuge bottles at the approximate solids-to-solution ratio desired. Sediment volumes were 15 ml, 75 ml, and 300 ml. The bottles were then filled with 600 ml of seawater at the appropriate salinity (1°/oo, 15°/oo, 29°/oo) again under nitrogen. The 29°/oo seawater was from Alcatraz Island, the 15°/oo was a combination of waters from Mare Island and Oakland Inner Harbor, and the 1°/oo was a dilution of the 15°/oo water with distilled-deionized water. To develop two different oxidation reduction potentials, half the samples were sparged with argon for 10 minutes to maintain reduced conditions and half the samples were sparged with air or oxygen for 10-30 minutes to develop the oxidized condition. Sealed bottles were then agitated at 10°C in a dark environmental chamber for one of the desired time periods (1, 24, or 144 hours). At the appropriate time, the container was removed from the shaker and small samples removed for slurry pH, Eh, and dissolved oxygen content measurements. The reduced samples were obtained under a nitrogen atmosphere. The sealed bottles were then centrifuged for 30 minutes. The centrate solutions were vacuum filtered through 0.45μ filters in all plastic filtering apparatus. The reduced condition samples were filtered under a nitrogen atmosphere and oxidized samples were filtered in air. After filtering, portions of the water samples were extracted at pH 4-5 with APDC-MIBK, then back-extracted with 6N ultrapure nitric acid. The resultant heavy metal concentrations were then measured by flame (Zn, Fe) and graphite furnace (Cu, Pb, Cd) atomic absorption. A separate portion of the filtered elutriate was utilized to measure the mercury content directly by cold vapor atomic absorption. Samples of the original $1^{\circ}/_{\circ\circ}$, $15^{\circ}/_{\circ\circ}$, and $29^{\circ}/_{\circ\circ}$ waters were extracted after filtration and compared with the subsequent elutriates to determine whether significant sorption or desorption was occurring. Absolute ppb metal concentrations for the water and elutriate samples were determined by constructing standard curves from addition of known amounts of trace metals into "clean" (twice extracted) seawaters samples at the appropriate salinities and performing identical APDC-MIBK, HNO_3 extractions on the spiked samples.

CHARACTERIZATION OF METAL SPECIES IN SOLUTION

Sediments

Sediments from three locations in San Francisco Bay (Southampton Shoal Channel, Oakland Inner Harbor Channel, and Redwood Creek Channel by Corkscrew Slough, see Figure 1) were chosen for initial studies on the basis of the previously determined range in metal concentrations. Duplicate sediment cores were taken from each site. One set was frozen and another set was stored at 4°C. Investigations reported herein were conducted with cores stored at 4°C.

Separation of Sediment Interstitial Waters

Individual sediment cores were thoroughly mixed and subsampled (approximately 500 g) in triplicate during mixing. The sediment and interstitial water were separated by gravity filtration (∿24 hrs) through a Whatman #1 filter paper as described by Hajek and Wildung.[101] The contents of total sediment solids were determined by further subsampling (approximately 10 g) and drying (60°C) for 24 hours.

Analyses of Sediment Interstitial Waters

The sediment interstitial waters were analyzed for mercury, copper, zinc, pH, and total salt content. Mercury was determined in solution by reduction to the elemental state with stannous chloride, aspiration of the metal vapor through a quartz cell, and quantification using flameless atomic absorption spectroscopy. Copper and zinc were determined directly in solution using flame atomic absorption techniques and comparison to appropriate standard curves prepared in an aqueous solution of sodium chloride (10,000 ppm). The interstitial water pH was measured using a combination electrode. No sodium corrections were made. Total salt content was measured by evaporation of an aliquot (approximately 20 ml) of the interstitial water to dryness and drying the residue (60°C) for 24 hours.

Analyses of Sediments

The sediment was analyzed for mercury, copper, zinc, carbon, hydrogen, nitrogen, and ash content. The metals were determined using the techniques described for interstitial waters after solubilization of the metals in the sediment. Mercury was solubilized by digestion with aqua regia, whereas copper and zinc were solubilized by digestion with concentrated nitric acid. Carbon, hydrogen, nitrogen, and ash contents were determined by microcombustion techniques.[101]

Molecular Weight Fractionation

Interstitial waters and sediment extracts utilizing boiling water and ammonium acetate as solvents (as previously described) were employed in all investigations to further characterize the metal in sediment aqueous phases. The reasons for selection of these solutions are discussed later.

The aqueous extractions were concentrated and fractionated according to molecular weight using Amicon Diaflo® ultrafiltration membranes in a cell (60 ml volume) equipped with a stirrer over the membrane and maintained at 4°C in an ice bath. The two membranes used were UM05 and UM10 (>500 molecular weight and >10,000 molecular weight, respectively). The extracts were filtered under pressure (55 psi, He) and the concentrate (approximately 15 percent of the original volume) analyzed for the appropriate metal. Filtrate from the higher molecular weight fraction was employed for subsequent fractionations at lower molecular weights.

Characterization of Molecular Weight Fractions

Molecular weight fractions were further characterized using Sephadex separation in conjunction with measurements of differential refractive index and metal concentration in the separated fractions. In addition, thin-layer chromatography and thin-layer electrophoresis were employed to further characterize separate fractions containing sufficient quantities of the metals.

Sephadex Separations

An aliquot (1 ml) of the >10,000 molecular weight fraction isolated as described above was lyophilized (freeze-dried) and resuspended in distilled water (100 microliters). This entire volume was applied to a column (1.5 x 30 cm) containing Sephadex G-100 (Fine) gel which has an exclusion limit of molecular weight >100,000. The materials were eluted (10 ml/hr) with distilled water. Eluant was collected in volumes appropriate to isolation of distinctly different fractions from the column as indicated by measurements of differential refractive index (relative to distilled water alone). A similar procedure was followed for the 500 to 10,000 and the <500 molecular weight fractions, except the gel used was Sephadex G-25 (Fine) which has an exclusion limit of molecular weight >5,000. After collection of the appropriate fractions, the copper content of each fraction was measured by atomic absorption techniques employing the graphite furnace and known addition.

Thin-Layer Electrophoresis

An aliquot (5μl) of the fraction containing the highest copper concentration in the effluent from the G-100 gel column was spotted in the center of conventional precoated thin-layer chromatographic plate (0.25 mm layer of MN-300 cellulose). After drying, the plate was sprayed with a pH 6.6 buffer containing glacial acetic acid, pyridine, and water (7:200:4000), placed on the cooling block of a Desaga/Brinkman electrophorator and voltage adjusted to 400 mv. The current at this voltage was 5 mA. On completion of electrophoresis (20 min), the plate was removed from the migration chamber and dried. After drying, spots were visualized using two techniques. A bromcresol green stain (detects organic acids and their salts) was applied to one plate and another plate, prepared in a similar manner, was stained with 2', 7' dichlorofluorescein (detects lipids and esters of fatty acids) and visualized under ultraviolet light.

Although additional separation on the thin layer plates is normally obtained by chromatographic separation in a second dimension with an ascending solvent, this was not undertaken because the fraction used was of a molecular weight >10,000 and separation by thin-layer chromatographic methods was expected to be minimal.

RESULTS AND DISCUSSION

The results of the Crystalline Matrix study together with a discussion of the findings are presented in this section of the report. Emphasis in the discussion has been placed on the environmental significance of the findings to the dredging situation in San Francisco Bay. The order of discussion follows the sequence used in the experimental design section with bulk sediment and water results first, followed by the results of the semi-selective extraction, radioisotope work, factorial design sorption-desorption experiment and solution chemical speciation work.

BULK SEDIMENT PARAMETER RESULTS

Eh and pH

The Eh and pH of sediments collected during Phase 2 were measured under an inert atmosphere shortly after the sampling ship returned to the dock. Results presented below show that in general the sediments appear to be in a reduced state in which manganese and possibly iron would be present in their reduced (divalent) state. The studies of Patrick[113—115] and coworkers have shown that at pH values between 7 and 8 in waterlogged soils the more mobile Mn^{+2} becomes predominant at +100 to -100 mv and S^{-2} begins to form in the region of -150 mv. Disturbance of these reduced sediments by actions such as dredging would allow some oxidation to take place in the water column. The effects of this change in Eh were studied in the sorption-desorption experiment and will be discussed later.

Results of the sediment Eh and pH determinations from Phase II sampling are listed below. It is possible that the 15-30 minutes allowed for electrode equilibration was not sufficient. Therefore the Eh values may under estimate the magnitude of the reduced state in the sediment.

Location	Sediment Color	Depth From Surface (cm)	Mean pH	Eh (mv)
Mare Island	Brown	0-30	7.20 ± .05	+138 ± 30
Mare Island	Brown	30-60	7.05 ± .05	+ 22 ± 30
Turning Basin	Brown	0-20	6.62 ± .05	- 73 ± 30
Turning Basin	Brown/ Black	20-40	6.60 ± .05	- 75 ± 30
Turning Basin	Black	40-60	6.77 ± .05	- 79 ± 30
Oakland Inner	Black	0-20	7.38 ± .05	- 37 ± 30
Oakland Inner	Black	20-40	7.40 ± .05	-43.5 ± 30
Oakland Inner	Black	40-60	7.35 ± .05	- 18 ± 30

PARTICLE SIZE DISTRIBUTION

The particle size distributions of the Bay sediments were determined to aid in characterization of the sediments, to aid the estimation of physical dispersion, and to gain insight into the importance of clay chemistry. Results for dispersed samples during Phase 1 and 2 are presented in Table IX. The three locations which were sampled ten months apart may provide some insight into temporal changes. The slight increase in sand content and decrease in clay content evidenced by the Phase 2 samples may reflect the fact that spring rains and runoff had just ended. The high rains and runoff may have the effect of

TABLE IX

PARTICLE SIZE DISTRIBUTION

Sample	Type*	Study Phase**	Particle Size***
Oakland Outer Harbor (Seventh Street)	PVC 1 V	1	50-22-28
	PVC 2 H	1	31-30-39
	AL 1 V	1	59-17-24
Oakland Outer Harbor Turning Basin	PVC 1 V	1	2-28-70
	PVC 2 V	1	6-25-69
	AL 1 V	1	3-28-69
	PVC V	2	11-38-51
Oakland Inner Harbor	PVC 1 V	1	16-26-58
	PVC 2 V	1	31-21-48
	PVC V	2	22-33-45
Islais Creek Shoal	PVC 1 V	1	6-34-60
	PVC 2 V	1	7-33-60
	AL 1 V	1	
Richmond Harbor Channel	PVC 1 V	1	6-32-62
	PVC 2 V	1	9-33-58
Southampton Shoal Channel	PVC 1 H	1	91-5-4
	PVC 2 V	1	91-3-7
Pinole Shoal Channel	PVC 1 V	1	12-38-49
	PVC 2 V	1	9-33-58
Mare Island Strait Channel	PVC 1 V	1	6-43-51
	PVC 2 V	1	8-38-53
	AL 1 V	1	8-41-51
	PVC V	2	12-46-42
Redwood Creek Channel at the mouth	PVC 1 V	1	8-35-57
	AL 3 V	1	5-37-58
	AL 1 V	1	6-35-59
Redwood Creek by Corkscrew Slough	PVC 1 V	1	12-31-56

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* Samples taken in PVC or aluminum (AL) pipe in a vertical (V) or horizontal (H) position. (V) cores 0-60 cm thoroughly mixed.

** Phase 1, August 1973; Phase 2, June 1974.

***Values represent average percent sand, percent silt, and percent clay, rounded to the nearest percent respectively (Sand >50μ, silt 50μ-2μ, and clay <2μ) seasonally scouring some of the fines. The Oakland Inner Harbor and Mare Island differences may also reflect the fact that dredging had occurred between samplings.

The effects on particle size distribution of freezing the samples during storage were investigated during Phase 1 and the effects of dispersing the sediments before analyses were determined in Phase 2. The results shown in Table X. Freezing does not appear to alter the particle size distribution unless freezing breaks down clay particles into even smaller clay particles which cannot be detected from these data. Differences in the Oakland Outer Harbor data probably reflect sampling heterogeneity. During sample collection at this location, the divers encountered difficulty in obtaining vertical cores. The coring device would penetrate only a few inches of sediment; at which point the coring devices were tipped and horizontal cores were taken. It appeared to the divers that a surface sand layer was underlaid by a compacted clay.

The use of dispersing agents dramatically affects the particle size distribution. Without dispersion the aggregate sediment flocculates and shows very little mass acting as <2μ clay material. The tendency to form aggregates should diminish the creation of large turbidity plumes during dredging and disposal. Similar flocculation and rapid settling during disposal operations were reported by Brown and Caldwell[95] and May.[90] The data also show an apparent change in particle size distribution with depth in Oakland Inner Harbor and Oakland Outer Harbor Turning Basin.

TABLE X

EFFECTS OF FREEZING AND DISPERSING AGENT ON PARTICLE SIZE

Location		% Sand	% Silt	% Clay
Redwood Creek Channel at Mouth	(Frozen) AL 1	6.1	35.2	58.7
	(Iced) PVC 1	7.7	35.4	56.8
Mare Island Straits	(Frozen) AL 1	8.0	40.5	51.5
	(Iced) PVC 1	6.3	43.1	50.6
Oakland Outer Harbor Turning Basin	(Frozen) AL 1	2.8	28.2	69.0
	(Iced) PVC 1	2.1	27.7	70.2
Oakland Outer Harbor	(Frozen) AL 1	59.2	17.1	23.7
	(Iced) PVC 1	49.5	22.5	28.0
Mare Island Straits	Dispersed 0-60 cm	12.2	45.8	42.0
	Non-Dispersed 0-60 cm	12.7	87.3	0.0
Oakland Outer Harbor Turning Basin	Dispersed 0-30 cm	5.6	38.6	55.8
	Non-Dispersed 0-30 cm	17.4	82.6	0.0
	Dispersed 30-60 cm	16.0	37.9	46.1
	Non-Dispersed 30-60 cm	24.4	75.6	0.0
Oakland Inner Harbor	Dispersed 0-30 cm	15.4	36.4	48.2
	Non-Dispersed 0-30 cm	19.8	75.1	5.1
	Dispersed 30-60 cm	27.5	30.1	42.4
	Non-Dispersed 30-60 cm	31.2	67.5	1.3

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The bottom of the cores had more sand and less clay content than the surface 30 centimeters. Without additional data it is difficult to determine the cause of the particle size distribution changes. The data may show a variation of transport energy over a period of years or if the data reflect seasonal variations the sedimentation rate must be very high.

With the exception of the Southampton Shoal location, all areas may be classified as clays and silty clays. In most cases, the material appears to be in a reduced, possibly anaerobic, state, rich in total sulfides and could create substantial immediate oxygen demand and turbidity problems. Observations of disposal operations by Brown and Caldwell[95] appear to show that these effects are not large enough to evoke concern. Observations during the dredging itself are lacking.

MINERAL CONTENT OF SEDIMENTS

The centrifuge method[98] was used to separate particle sizes for X-ray diffraction analysis. The X-ray diffraction data used to determine the mineral content of the sediments are presented in Table XI.

X-ray diffraction studies of the sediments included determination of the effects of ethylene glycol on the interlayer distances. Layers of water are usually present between the lattice sheets of the clay minerals. Treating the sample with ethylene glycol replaces the water and causes shifts in the X-ray diffraction peaks. Ethylene glycol saturated clays generally have a distinct interlayer distance which aids in the mineral

TABLE XI

MINERALS VERSUS PARTICLE SIZE

74μ to 20μ	quartz, feldspar, mica, chlorite
20μ to 5μ	quartz, feldspar, hydrous mica, chlorite
5μ to 2μ	minor quartz, feldspar, hydrous mica, chlorite, some montmorillonite
2μ to 0.2μ	hydrous mica, chlorite, montmorillonite
<0.2μ	montmorillonite

identification. A collapse or expansion of interlayer distance upon treatment with ethylene glycol is indicative of minerals with high ion exchange capacity. X-ray diffraction data obtained following treatment of the sediment samples with ethylene glycol indicate that only the montmorillonite interlayers changed. Therefore, of the clay minerals identified, the montmorillonite will be the greatest contributor of ion exchange capacity to the bulk sediment.

The detection limit for X-ray diffraction is between 5 and 10 percent mineral content. Since it is very difficult to quantify the results from the X-ray diffraction plots, only a qualitative determination of the montmorillonite content of the Bay sediments was made. The percentage of the total sample weight in each of the size fractions X-rayed and the qualitative determinations of montmorillonite are given in Table XII. Summation of the weights

TABLE XII

PARTICLE SIZE DISTRIBUTION OF SEDIMENT-CLAY FRACTION AND QUALITATIVE RESULTS FOR MONTMORILLONITE CLAY

	Percent of Total for Each Size Fraction					% Total Sample With Montmorillonite Detected	
Sample Location	<.2μ	.2--2μ	2-5μ	5--20μ	20-75μ		CEC*
Oakland Outer Harbor	8.5M**	14.4M	6.3	9.3	17.3	23.9	15.9
Oakland Outer Harbor Turning Basin	24.7M	28.1M	16.3M	21.4	9.4	69.1	35.2
Oakland Inner Harbor	16.4M	26.2	14.6	17.5	13.2	16.4	26.2
Islais Creek Shoal Channel	22.1M	25.1	14.2	19.4	19.2	22.1	33.1
Richmond Harbor Channel	23.3M	22.9M	13.9M	22.5	16.3	60.1	32.2
Southampton Shoal Channel	0.8M	1.2	1.6	2.0	2.4	0.8	10.3
Pinole Shoal Channel	12.2M	20.8M	13.4	24.5	21.0	33.0	31.1
Mare Island Straits Channel	18.1M	21.2M	13.1M	22.1M	22.5	75.5	28.1
Redwood Creek Channel at Mouth	14.0M	27.8M	12.8	19.7	24.8	41.8	30.3
Redwood Creek Channel at Corkscrew Slough	13.3M	25.7M	13.5	21.0	17.5	39.0	33.4

*CEC = Cation Exchange Capacity

**M denotes montmorillonite detected

of the separate fractions in which montmorillonite was detected and comparison of this weight with the bulk cation-exchange-capacity will allow a qualitative correlation. The correlation must be qualitative because the percentage of montmorillonite in each size fraction is not known. A sample with slightly greater than 10 percent montmorillonite content is weighted the same as a sample with much higher montmorillonite content. The correlation between cation-exchange-capacity and weight percentage of sample with montmorillonite present appears weak compared to the correlations with particle size and organic content.

CATION-EXCHANGE-CAPACITY

Table XIII presents the cation-exchange-capacity results in units of millequivalents/100 grams. The data do not show any conclusive difference between frozen and iced cores. However, Oakland Outer Harbor data show substantial scatter. The diving records indicate that the first cores were taken vertically and the second cores were taken horizontally at the Oakland Outer Harbor location which is believed to account for the variability of the data. The high value for the Pinole Shoal Channel frozen core could also have been caused by sampling variability. The diving records for Pinole Shoal show that the cores had distinct layering in color and particle size appearance.

Pearson, et al.,[116] report cation-exchange-capacities of 2.3 to 66.1 meq/100 g with a median value of 19.6. The sediments in this study show a much smaller range and a median value of

TABLE XIII

CATION-EXCHANGE CAPACITY DATA

Sample Location	Sample Type	No. of Determi- nations	Sample Average (meq/100g)	Location Average (meq/100g)
	Clean Beach Sand	7	0.088	
Oakland Outer Harbor	AL 1	2	11.8	
	PVC 1	2	15.2	15.9
	PVC 2	2	20.7	
Oakland Outer Harbor Turning Basin	AL 1	2	37.5	
	PVC 1	2	36.0	35.2
	PVC 2	3	33.2	
Oakland Inner Harbor	AL 1	3	24.7	
	PVC 1	2	28.6	26.2
	PVC 2	2	26.0	
Islais Creek Shoal	AL 1	4	33.4	
	PVC 1	2	33.4	33.1
	PVC 2	2	32.0	
Richmond Harbor Channel	AL 1	3	33.7	
	PVC 1	2	32.0	30.6
	PVC 2	2	26.1	
Southampton Shoal Channel	AL 2	1	11.9	
	PVC 1	2	9.5	10.6
	PVC 2	2	10.4	
Pinole Shoal Channel	AL 1	3	34.1	
	PVC 1	2	28.4	31.1
	PVC 2	2	29.3	
Mare Island Shoal Channel	AL 1	2	29.5	
	PVC 1	3	26.2	28.1
	PVC 2	2	29.6	
Redwood Creek Channel at Mouth	AL 1	2	31.0	
	PVC 1	3	29.3	30.3
	PVC 2	2	31.2	
Redwood Creek Channel at Corkscrew Slough	PVC 1	2	33.4	33.4

29.5 meq/100 g. The cation-exchange-capacity data correlate well with the particle size data, i.e., the lower capacities are found with the low clay content sediments. Pearson, et al.,[116] also found that the cation-exchange-capacity was very closely related to the particle size distribution. The low exchange values were found in high sand content sediments.

Cation-exchange-capacity also correlates with the organic content. Sediments with high organic carbon content also tend to have high exchange capacities.

As noted in the literature review section of this report, clay minerals with high cation-exchange-capacities are capable of sorbing metals. Whether the exchangeable ions will be mobilized during dredging and disposal needs to be investigated but the preponderence of clay material with the above cation-exchange-capacities certainly makes the exchange process of potential importance in San Francisco Bay.

TOTAL SULFIDE CONTENT OF SEDIMENT

Total acid soluble sulfides in the sediment samples were determined on the iced samples (PVC) and several of the frozen cores (AL) during Phase 1. Sulfide in the three locations revisited in Phase 2 were also measured with the top (0-30 cm) and bottom (30-60 cm) of the cores differentiated. The results presented in Table XIV show variability of about ±20 percent with larger variations in several samples. The accuracy of the sulfide data on the frozen cores is not expected to be as good as that of the iced cores because the sampling technique of

TABLE XIV

ACID SOLUBLE SULFIDE CONTENT OF SEDIMENT
PHASE 1

Sample	Type*	Total Sulfide (ppm)**
Oakland Outer Harbor (Seventh Street)	PVC 1 V	223
	PVC 2 H	490
	AL 1 V	60
Oakland Outer Harbor Turning Basin	PVC 1 V	1040
	PVC 2 V	825
	AL 1 V	1230
Oakland Inner Harbor	PVC 1 V	1120
	PVC 2 V	1480
	AL 1 V	1430
Islais Creek Shoal	PVC 1 V	1920
	PVC 2 V	1900
	AL 1 V	1910
Richmond Harbor Channel	PVC 1 V	2000
	PVC 2 V	1250
	AL 2 V	1380
Southampton Shoal Channel	PVC 1 H	4
	PVC 2 V	5
	AL 2 V	393***
Pinole Shoal Channel	PVC 1 V	213
	PVC 2 V	266
	AL 1 V	260
Mare Island Strait Channel	PVC 1 V	185
	PVC 2 V	1000
	AL 1 V	365***
Redwood Creek Channel at the mouth	PVC 1 V	1020
	AL 3 V	1150
	AL 1 V	952
Redwood Creek by Corkscrew Slough	PVC 1 V	570
	AL 1 V	1210***

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*Samples taken in PVC or aluminum (AL) pipe in a vertical (V) or horizontal (H) position

**Dry weight basis

***Dewatered frozen core samples stored in contact with air for a period of 3.5 weeks. Results may be low by a factor of 2.

TABLE XIV (Cont'd.)

ACID SOLUBLE SULFIDE CONTENT OF SEDIMENT
PHASE 2

Sample	Depth (cm)	Total Sulfide (ppm dry wt.)	Mean Percent Solids
Oakland Outer Harbor Turning Basin	0-30	290 ± 14[†]	30.2 ± .1
	30-60	1850 ± 160	42.9 ± .2
Oakland Inner Harbor	0-30	1840 ± 380	39.0 ± .3
	30-60	2760 ± 120	43.3 ± .8
Mare Island Strait Channel	0-30	7 ± 5	34.8 ± .5
	30-60	45 ± 20	34.6 ± .1

[†] ± one standard deviation

removing portions of the frozen core from several locations and mixing is not as representative of the total core as in the case of a sample from a total well-mixed iced core.

The areas of higher sand content have the lowest sediment sulfide contents (Southampton Shoal, Pinole Shoal and Oakland Outer Harbor) possibly showing that the regions are areas of high energy with adequate ventilation with oxygen rich waters. Also these areas contain low organic carbon contents which act as the energy source for the bacteria to convert the sulfates to sulfides.

The Phase 2 data show significant differences in sulfide contents of the surface sediments and deeper sediments. In all three cases the surface layer contains less sulfides possibly caused by oxygen diffusion into the surface from the water column. No detailed studies were performed on thin sections to ascertain whether a thin oxygenated layer was present at the surface. The Oakland Outer Harbor Turning Basin samples from Phases 1 and 2 compare after averaging the sulfide content for the entire core. The sulfide content of the Oakland Inner Harbor appears to be higher during Phase 2. Since this area had recently been dredged, the samples may represent deep sediments from previous years. Phase 2 Mare Island sediment was a rich brown color and was described by Wakeman[117] as being atypical. The sulfide content of this sediment was very low and may represent freshly deposited material from the spring river runoff.

The high sulfide contents are in the range of values reported by Chen and co-workers[16,79] for sediments in Los Angeles Harbor. These data represent further evidence that the fine silt and clay which constitute the bulk of material dredged in San Francisco Bay are in the reduced state. Dredging and disposal may cause oxidation and because sulfides of the trace metals are extremely insoluble, the oxidation may cause some metal mobilization. This phenomenon is discussed in more detail in the portion of the report dealing with the sorption-desorption experiments.

TOTAL ORGANIC CARBON AND CARBONATE CONTENT

The total organic carbon, ash, and carbonate contents are reported in Table XV. The organic carbon contents of the silt and clay sediments generally are in the range 1.3-1.6 percent. Sand sediments have lower organic carbon contents, 0.1-1.0 percent.

Pearson, et al.,[116] report a median value of 1.1 percent organic carbon in San Francisco Bay. The data in Table XV indicate a median value for organic carbon of 1.4 percent.

In general, the organic matter content of the San Francisco Bay sediments is average for nearshore sediments. As reported by several investigators,[116,118] the organic matter content is inversely related to the sand content. Sandy sediments tend to be poor in organic matter because they accumulate in agitated, well-ventilated waters where the light organic matter is either washed away or swiftly oxidized by virtue of an adequate oxygen supply.

TABLE XV

ORGANIC CARBON AND CARBONATE DATA

Phase 1	Sample Type*	Organic Carbon%	Ash	Carbonate Content% by Difference	Carbonate Content by Calcimeter%
Oakland	PVC 1	1.10	83.7	0	0.25
Outer	PVC 1	0.63	92.8	0.15	
Harbor	PVC 2	1.06	88.18	3.35	
Oakland Outer	AL 1	1.72	86.7	0.55	0.39
Harbor Turning	PVC 1	1.63	95.9	1.90	
Basin	PVC 2	1.58	82.6	0.45	
Oakland	AL 1	1.16	92.0	0	0.63
Inner	PVC 1	1.49	83.4	0.25	
Harbor	PVC 2	0.97	96.7	0.45	
Islais	AL 1	-	-	-	0.42
Creek	PVC 1	1.76	82.7	0.65	
Shoal	PVC 2	1.79	85.3	0.35	
Richmond	AL 2	1.40	86.9	0.65	0.85
Harbor	PVC 1	1.56	88.8	0.30	
Channel	PVC 2	1.48	84.8	1.10	
Southampton	AL 1	-	-	-	0.09
Shoal	PVC 1	0.05	87.6	0.25	
Channel	PVC 2	0.14	95.9	0.00	
Pinole	AL 1	-	-	-	1.31
Shoal	PVC 1	1.17	85.7	0.25	
Channel	PVC 2	1.08	79.6	0.40	
Mare Island	AL 1	1.56	88.3	1.55	0.42
Channel	PVC 1	1.34	86.4	0.65	
at Mouth	PVC 2	1.33	76.6	0.15	
Redwood Creek					
Channel by	PVC 1	1.33	82.2	5.55	3.30
Corkscrew					
Slough					
Phase 2					
Oakland Outer	0-30	1.28±.04	87.7	-	0.43
Harbor Turning	30-60	1.64±.01	85.6	-	0.29
Basin					
Oakland Inner	0-30	1.62±.05	87.2	-	0.38
Harbor	30-60	1.55±.03	87.8	-	0.42
Mare Island	0-30	1.56±.01	87.7	-	0.59
Straits	30-60	1.49±.08	87.2	-	0.15
Channel					

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*Samples taken in PVC or aluminum (AL) pipe in a vertical (V) or horizontal (H) position. (0-30) surface sample and (30-60) deeper samples were taken during Phase 2.

As previously mentioned, the cation-exchange capacity of the sediments increases as the organic content increases. Therefore, the organic content may be an important sink for heavy metals and thus its contribution to metal transport should be considered for the fine grained sediments in San Francisco Bay.

Agreement between the carbonate data determined by the difference between total carbon and organic carbon with the carbonate data determined by calcimeter (CO_2 evolution and volume measurement) is generally good considering the low carbonate content and the nature of the analytical methods employed. Pearson, et al.,[116] reported by difference a median carbonate content of 0.85 percent. Carbonate values for Oakland Outer Harbor (PVC 2) and Redwood Creek by Corkscrew Slough (PVC 1) are much larger than those for the other samples analyzed. A total sample weight of only 0.10 to 0.15 g was used in the total carbon analysis, whereas the total sample weight for the calcimeter procedure was 6.0 to 10.0 grams. The small sample size utilized for the total carbon analysis, coupled with the possibility of carbonate rich particles such as shell fragments being present, could lead to greater variability in the carbonate results in the "by difference" method.

There do not appear to be any significant differences in the organic carbon or carbonate data in the Phase 1 and 2 samples taken ten months apart.

The ash content should represent all the nonvolatile geological matter present. As expected, the sediment consists mainly of this nonvolatile geological material.

TOTAL NITROGEN AND AMMONIA NITROGEN CONTENT

During Phase 2 total nitrogen and ammonia nitrogen contents of the sediments were determined for both the top and bottom of the cores with results as presented in Table XVI. Organic nitrogen is calculated by difference from total Kjeldahl and ammonia nitrogen determinations.

There appears to be a loss of organic nitrogen in the sediments with depth which would reflect the process by which bacteria decompose organic nitrogen to ammonia under reducing conditions.[119] The Mare Island 0-30 centimeter sample shows a higher ammonia nitrogen content than does a composite of the 0-60 cm core, possibly signifying different sediment types. The increase in ammonia content with depth in the Turning Basin and Oakland Inner cores accounts for only about 50 percent of the decrease in organic nitrogen measured. Ammonia possibly diffuses out of the pore water or is converted to nitrate in the surface oxidized layer and escapes into the water column.

Pearson, et al.,[116] reported total nitrogen contents of fine grain (<30% sand) sediments in San Francisco Bay to range between 820-3180 ppm N with a median value of 1380. The low sand content sediments had the highest nitrogen contents. All the samples exceeded the criterion set up by FWQA for open water disposal which was set at 1000 ppm TKN.[93]

TABLE XVI

SEDIMENT NITROGEN DATA

Location	Depth (cm)	Number of Determinations	TON* (ppm N)	NH_3-N* (ppm N)
Mare Island	0-30	3	330 ± 340	222 ± 91
Mare Island	0-60	3	1580 ± 110	11 ± 19
Turning Basin	0-30	3	4410 ± 1710	230 ± 30
Turning Basin	30-60	3	3380 ± 750	460 ± 60
Oakland Inner	0-30	3	3110 ± 590	265 ± 25
Oakland Inner	30-60	3	2470 ± 450	570 ± 105

*Dry weight basis

HEAVY METAL CONTENT OF SEDIMENT

Analytical results obtained by X-ray fluorescence, neutron activation and atomic absorption for the heavy metals Cd, Cu, Fe, Hg, Mn, Pb, and Zn in the sediment samples are presented in Tables XVII and XVIII. Atomic absorption was the only technique utilized during Phase 2.

Results for copper by X-ray fluorescence are much higher than those reported by others as shown in Table II. Atomic absorption values agree with LBL's recent work.[17] Cadmium, mercury and zinc values are in the same range as shown in Table II.

A comparison of heavy metal concentrations from Phase 2 with data from Phase 1 shows that the X-ray fluorescence copper data are too high and the lead data from Phase 1 may be

TABLE XVII

SEDIMENT TOTAL HEAVY METAL CONTENT
DRY WEIGHT BASIS
PHASE 1

Sample	Type	Cd (ppm)	Cu (ppm)		Fe (ppt)		Hg (ppm)	Mn (ppm)		Pb (ppm)		Zn (ppm)
		AA	XRF	AA	XRF	NAA	AA	XRF	NAA	XRF	AA	XRF
Oakland Outer Harbor	PVC 1 V	0.66	106	-	34.0	33.2	0.26	376	-	30	27	105
	PVC 2 H	--	111	-	42.4	40.1	0.47	460	485	38	-	150
Turning Basin	PVC 2 V	--	170	-	61.9	55.7	0.48	463	390	89	-	212
	PVC 2 V	--	145	-	55.3	--	0.67	350	-	68	-	189
Oakland Inner Harbor	PVC 1 V	1.25	170	121	51.5	49.6	1.02	493	430	102	130	214
	PVC 2 V	--	207	-	49.6	--	1.13	449	-	118	-	230
Islais Creek Shoal	PVC 1 V	1.60	165	77	56.0	51.3	0.62	540	395	85	70	218
	PVC 2 V	--	164	-	59.7	--	0.64	534	-	95	-	247
Richmond Harbor	PVC 1 V	1.31	143	76	51.4	50.8	0.56	488	430	63	91	196
	PVC 2 V	--	157	-	59.0	--	0.60	460	-	71	-	234
Southampton Shoal	PVC 1 H	--	56	-	41.1	51.3	0.05	609	-	13	-	91
	PVC 2 V	--	78	-	45.6	48.0	0.03	820	520	6	-	90
Pinole Shoal	PVC 1 V	--	126	-	58.2	55.2	0.32	851	710	12	-	140
	PVC 2 V	--	136	-	56.9	--	--	624	-	38	-	161
Mare Island Strait	PVC 1 V	0.61	142	71	59.6	52.4	0.64	814	-	50	63	181
	PVC 2 V	--	138	-	57.8	53.4	0.47	837	620	40	-	160
Redwood Creek Mouth	PVC 1 V	0.89	121	60	54.7	48.1	0.56	902	610	51	-	174
	AL 3 V	--	104	-	55.1	--	0.32	750	-	56	-	177
Redwood Creek Corkscrew Slough	PVC 1 V	--	172	-	51.3	45.9	0.41	790	590	85	-	266

XRF = X-ray fluorescence; AA = Atomic absorption; and NAA = Neutron activation
-- = No determination made

TABLE XVIII

SEDIMENT TOTAL HEAVY METAL CONTENT
DRY WEIGHT BASIS
PHASE 2

Location	Depth (cm)	# Determinations	Cd (ppm)	Cu (ppm)	Fe (ppt)	Hg (ppm)	Mn (ppm)	Pb (ppm)	Zn (ppm)
Mare Island	0-30	3	0.81 ± .35*	93 ± 3	76.3 ± 3.9	0.362 ± .06	1124 ± 23	35 ± 1	204 ± 13
Mare Island	0-60	3	0.48 ± .12	89 ± 1	87.4 ± 6.1	0.603 ± .01	1036 ± 15	32 ± 2	162 ± 10
Turning Basin	0-30	3	0.91 ± .28	73 ± 1	45.6 ± .6	0.635 ± .16	512 ± 11	51 ± 3	177 ± 7
Turning Basin	30-60	3	0.70 ± .58	86 ± 3	52.3 ± 4.5	0.610 ± .08	552 ± 39	55 ± 30	187 ± 11
Oakland Inner	0-30	3	1.56 ± .48	118 ± 7	56.8 ± 1.7	1.01 ± .17	531 ± 35	81 ± 3	222 ± 3
Oakland Inner	30-60	3	1.06 ± .02	114 ± 2	65.5 ± 9.2	1.27 ± .34	535 ± 27	78 ± 20	247 ± 33

*one standard deviation

too high. The metals cadmium, manganese, iron, mercury and zinc agree. There is a significant increase in manganese and iron and a possible decrease in lead concentrations found in the Mare Island Phase 2 samples in comparison with Phase 1 values. This is further supporting evidence that the Phase 2 sediments at this location are atypical.

The coarse grained sediments from Southampton Shoal, Pinole Shoal and Oakland Outer Harbor show the lowest concentrations of copper, mercury, lead and zinc which suggests that higher concentrations of trace metals are associated with fine sediments. The location of Southampton Shoal and Pinole Shoal in the middle of San Francisco's bays may have some bearing on the lower trace metal concentrations since the bulk of "pollutional" input from man's activities would be expected to occur in nearshore locations. The highest sulfide and organic contents were also found in the nearshore sediments with highest trace metal contents. In comparison to some grossly contaminated areas and heavily industrialized harbors referenced in Table I, the trace metal contents of San Francisco Bay sediments are not excessive. The significance of these concentrations to the environmental impact of dredging is difficult to assess and it must be stressed that bulk metal analysis of sediments is <u>not</u> a useful index of potential environmental water quality problems because the many chemical forms of metals present in the sediment do not have equal impact.

Linear regression analyses of total heavy metals contents versus total iron, aluminum and sulfur are presented in Appendix A. Results show moderately significant positive correlation for copper and zinc with the sediment total iron content and for copper with the sediment total aluminum content. The total heavy metals (Pb, Cu, Zn, and Hg) correlate highly with the sediment total sulfur content. The strong correlation with total sulfur may indicate that the heavy metals are associated with a sulfur phase such as insoluble sulfides. In addition, total metal analyses performed by neutron activation and X-ray fluorescence are presented in Appendix A.

PCB AND SELECTED PESTICIDES IN SEDIMENT

Results of determinations of PCB, DDT, DDE, DDD and Dieldrin contents of the sediment are presented in Table XIX. The values given for DDD and DDT represent a maximum estimate of the amount of these compounds present. Four of the samples were hydrolyzed to eliminate possible interference from DDD and DDT to the PCB determinations. This treatment did not significantly alter the initial PCB values which indicates relatively low concentrations of DDD and DDT. The PCB results for Oakland Outer Harbor, Islais Creek Shoal, and Richmond Harbor Channel are higher than results[120] reported previously for these areas. However, the previous results indicate considerable sample variability. PCB values are in the same ranges as values from Los Angeles Harbor, while DDD and DDE values are considerably lower.[16]

TABLE XIX

CONCENTRATION OF PCB'S AND PESTICIDES IN SEDIMENT SAMPLES

Sample Location	Dry Weight Basis (ppm)				
	DDE	DDD	DDT	PCB	Dieldrin
Southampton Shoal Channel*	0.002	0.007	0.006	0.030	<0.001
Oakland Inner Harbor	0.041	0.091	0.118	0.833	0.001
Oakland Outer Harbor Turning Basin	0.011	0.029	0.037	0.239	0.002
Redwood Creek Channel at Mouth	0.007	0.014	0.021	0.137	0.006
Redwood Creek Channel at Corkscrew Slough	0.002	0.006	0.004	0.052	0.001
Oakland Outer Harbor	0.009	0.016	0.012	0.099	0.002
Mare Island Straits Channel	0.010	0.017	0.007	0.084	0.001
Richmond Harbor Channel*	0.024	0.083	0.065	0.189	0.005
Islais Creek Shoal	0.010	0.026	0.032	0.280	0.002
Pinole Shoal Channel	0.001	0.002	0.002	0.026	<0.001

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*Samples taken from AL 2 cores. All other samples were taken from AL 1 cores.

WATER PARAMETER RESULTS

Salinity, pH, Eh and Hydrogen Sulfide Data

The salinity of the interstitial waters taken from Phase 1 cores is shown in Table XX. Phase 2 water salinities, pH, Eh and hydrogen sulfide data are presented in Table XXI. Salinity values for the Mare Island Straits area show the effect of dilution by freshwater from the Napa river. Anderlini, et al.,[17] found values as low as 1-3‰ throughout the water column during a winter rain storm. The seasonal variation in salinity at other stations is much less (0.5 to 4.0‰).[116]

Free hydrogen sulfide values in interstitial water and mid-depth water are shown in Table XXI. Sulfides determinations were performed in a time span of 2 to 8 hours after sample collection. In all cases the concentrations of H_2S were below detection limits. During Phase 1 similar values (<0.05 ppm) were found on cores which had been stored about 30 days before being opened. It appears that if hydrogen sulfide is formed in the interstitial waters it is quickly transformed to insoluble complexes such as FeS as Slotta, et al.,[88] suggest or dissipates before building up to measurable levels.

Total Nitrogen and Soluble Organic Carbon Content

The total Kjeldahl nitrogen and soluble organic carbon contents were measured on both mid-depth waters and interstitial waters centrifuged out of the sediment. Results are presented in Table XXII.

TABLE XX

SALINITY OF INTERSTITIAL WATER
PHASE 1

Sample	Type*	S°/₀₀
Oakland Outer Harbor (Seventh Street)	PVC 1 V PVC 2 H	26.92 26.96
Oakland Outer Harbor Turning Basin	PVC 1 V PVC 2 V	26.96 26.29
Oakland Inner Harbor	PVC 1 V PVC 2 V	25.96 25.96
Islais Creek Shoal	PVC 1 V PVC 2 V	26.29 26.62
Richmond Harbor Channel	PVC 1 V PVC 2 V	27.71 27.29
Southampton Shoal Channel	PVC 1 H PVC 2 V	- -
Pinole Shoal Channel	PVC 1 V PVC 2 V	22.63 21.80
Mare Island Strait Channel	PVC 1 V PVC 2 V	16.77 15.39
Redwood Creek Channel at the Mouth	PVC 1 V AL 3 V	- 27.29
Redwood Creek by Corkscrew Slough	PVC 1 V	25.63

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*Samples taken in PVC or aluminum (AL) pipe in a vertical (V) or horizontal (H) position.

TABLE XXI

WATER PARAMETERS
PHASE 2

Location	Type	pH	Eh (mv)	H_2S (ppm)	S ($^{\circ}/_{oo}$)
Mare Island	S				10.4 ± .4
Mare Island	M	7.72 ± .05	+317 ± 30	<.05	15.0 ± .1
Mare Island	IW	7.39 ± .05	+296 ± 30	<.1	
Turning Basin	M	7.55 ± .05	+258 ± 30	<.05	26.3 ± .3
Turning Basin	IW	6.75 ± .05	Missing	<.1	
Oakland Inner	S				26.0 ± .3
Oakland Inner	M	7.60 ± .05	+280 ± 30	<.05	26.5 ± .2
Oakland Inner	IW	7.58 ± .05	+ 45 ± 30	<.1	
Alcatraz	S				29.4 ± .5

S = Surface waters
M = Mid-depth waters
IW = Interstitial waters

Pearson, et al.,[116] reported ammonia values for the entire San Francisco Bay north of Dunbarton Bridge (which is located south of Redwood City) to be between 0.1 and 0.2 ppm. No values of TKN were taken in the Bay during this study in any regions which were sampled during their study.

TABLE XXII

NITROGEN AND CARBON CONTENTS OF WATERS

Location	Type	No. of Samples	TKN (ppm N)	NH_3 (ppm N)	TOC (ppm C)
Turning Basin	M	3	0.48 ± .12	<0.3	8.1 ± 0.6
	IW	1 for N 3 for C	6	-	211.0 ± 15.0
Oakland Inner Harbor	M	3	0.36 ± .27	<0.3	7.6 ± 1.2
	IW	1 for N 3 for C	<1	-	11.0 ± 3.0
Mare Island Straits	M	3	<0.3	<0.3	12.4 ± 1.9
	IW	1 for N	<1	-	12.0 ± 1.0

M = Mid-depth water
IW = Interstitial water
\- = Not measured

The organic carbon content and TKN of the interstitial waters from the Oakland Outer Harbor Turning Basin appear to be significantly increased over values in the overlying water. The other areas show no large solubilization of organic carbon or nitrogen in the interstitial waters.

Trace Metal Concentrations in Water

The trace metal contents of the mid-depth waters from Mare Island, Oakland Inner Harbor and Oakland Outer Harbor Turining Basin and the surface waters near Alcatraz Island are shown in Table XXIII. The Alcatraz sample was not filtered and acidified as were the other samples prior to storage. Analyses were performed after sixty days of storage in an unlighted cold room at 4°C. The effects of storage for this length of time are not known but serious errors might have occurred. The Alcatraz sample was taken from a large 13 gallon container just prior to analysis. The sample was not acidified nor had the water been filtered before storage. The high cadmium and copper values for this sample may reflect contamination from the carboy which was not as meticuously cleaned before usage as containers for the other samples. The low iron value compared to the other samples may reflect iron precipitation from the unacidified water during storage.

RESULTS OF THE SEMI-SELECTIVE EXTRACTION PROCEDURE

Determinations of the relative distribution of heavy metals in the various geochemical phases of the sediment were made for both the top and bottom of cores taken at Oakland Outer Harbor

TABLE XXIII

HEAVY METAL CONTENTS OF WATER SAMPLES*

	Cd (ppb)	Cu (ppb)	Pb (ppb)	Zn (ppb)	Fe (ppb)	Hg (ppb)**
Mare Island	0.14±.01	2.62±.04	0.14±.01	4.6±1.2	2.8±1.1	0.11±.01
Oakland Inner Harbor	0.30±.04	2.32±.10	0.89±.02	10.3±1.8	8.0±1.4	0.67±.04
Oakland Outer Harbor Turning Basin	0.24±.02	2.08±.04	0.58±.02	16.2±6.3	5.5±0.7	0.19±.04
Alcatraz***	1.74±.33	10.50±.80	0.24±.20	9.0 1.8	<2	<0.08

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* Alcatraz sample surface water, all others mid-depth.
** Hg samples were not filtered.
***Alcatraz samples were not filtered and acidified before storage.

Turning Basin, Oakland Inner Harbor and Mare Island Strait Channel. Results of these analyses are presented in Tables XXIV, XXV, and XXVI. The top sediment refers to the 0-30 centimeter depth and the bottom refers to the 30-60 centimeter depth. The numbers reported are the average of three samples except for a few cases where one sample gave a very different value than the others and was excluded. Separate sediment samples were totally digested and total heavy metal contents determined to allow comparison with the sum extracted by the various chemicals. In all but four cases, the sum of extractable metals agrees within ±30 percent with the heavy metal content found by total digestion of a separate sample. In twenty-seven cases, the agreement is within ±10 percent. Tables XXVII through XXXIII present the percentages of total metals extracted by each treatment. The cadmium data in Table XXVII shows no differences between the top and bottom parts of the cores. The hydrogen peroxide phase released 82 to 97 percent of the cadmium. The remainder of the

TABLE XXIV

TURNING BASIN CHEMICAL EXTRACTION RESULTS

EXTRACTANT		Cd ppm	Cu ppm	Hg ppm	Pb ppm	Zn ppm	Mn ppm	Fe ppt
Interstitial Water	Top	<.01	0.1	.00	.0	0.1	5	0.0
	Bottom	<.01	0.1	.00	.0	0.1	5	0.0
Ammonium Acetate	Top	.00	2.3	.00	.4	2.8	42	0.7
	Bottom	.00	0.0	.00	.1	0.6	9	0.3
Hydroxylamine Hydrochloride	Top	.00	0.6	.00	1.0	2.7	75	2.7
	Bottom	.00	0.5	.00	.0	0.4	43	2.2
Hydrogen Peroxide	Top	.56	22.5	.39	21.5	55.3	118	3.6
	Bottom	1.24	33.2	.04	24.6	82.3	105	5.4
Sodium Dithionite Citrate	Top	.00	0.0	-	0.1	25.2	31	22.6
	Bottom	<.01	0.0	-	0.0	2.3	21	13.7
Residual	Top	.05	46.5	.20	22.7	118.3	381	42.6
	Bottom	.04	49.9	.66	30.3	105.7	345	38.3
Sum	Top	.62	72.0	.59	44.8	204.3	648	72.3
	Bottom	1.28	83.7	.71	55.0	191.3	523	54.9
Total Digestion	Top	.91	72.8	.63	50.7	177.0	512	45.6
	Bottom	.71	86.4	.61	54.9	186.8	552	52.3

TABLE XXV

OAKLAND INNER HARBOR CHEMICAL EXTRACTION RESULTS

EXTRACTANT		Cd ppm	Cu ppm	Hg ppm	Pb ppm	Zn ppm	Mn ppm	Fe ppt
Interstitial Water	Top	0.00	0.3	0.00	0.0	0.1	1	0.0
	Bottom	0.00	0.3	0.00	0.0	0.1	1	0.0
Ammonium Acetate	Top	0.00	0.0	0.00	0.2	0.1	24	0.1
	Bottom	0.00	0.3	0.00	0.1	0.4	19	0.0
Hydroxylamine Hydrochloride	Top	0.00	0.1	0.00	0.1	4.7	67	1.9
	Bottom	0.00	0.4	0.00	0.0	0.3	57	1.6
Hydrogen Peroxide	Top	1.31	69.6	0.06	46.2	141.4	86	4.5
	Bottom	1.06	75.2	0.04	27.4	154.5	90	3.9
Sodium Dithionite-Citrate	Top	0.01	4.9	-	0.0	0.0	27	16.0
	Bottom	0.01	0.0	-	0.0	0.0	24	19.0
Residual	Top	0.08	58.8	1.05	44.9	133.8	378	34.0
	Bottom	0.04	51.2	1.20	45.2	94.4	335	42.0
Sum	Top	1.40	133.8	1.11	91.4	280.0	581	56.6
	Bottom	1.11	127.1	1.24	72.7	249.8	525	66.5
Total Digestion	Top	1.56	118.3	1.01	80.7	222.0	531	56.8
	Bottom	1.06	113.6	1.27	78.2	247.1	525	65.5

TABLE XXVI

MARE ISLAND CHEMICAL EXTRACTION RESULTS

EXTRACTANT		Cd ppm	Cu ppm	Hg ppm	Pb ppm	Zn ppm	Mn ppm	Fe ppt
Interstitial Water	Top	.00	.2	.00	.0	.0	2	0.0
	Bottom	.00	.0	.00	.0	.0	2	0.0
Ammonium Acetate	Top	.01	.1	.00	.1	1.2	208	0.0
	Bottom	.00	.0	.00	.1	0.5	220	0.3
Hydroxylamine Hydrochloride	Top	.02	.5	.00	.0	10.5	262	1.1
	Bottom	.06	.0	.00	.0	7.0	215	2.7
Hydrogen Peroxide	Top	.51	37.1	.09	21.8	53.2	244	4.3
	Bottom	.32	28.0	.12	15.8	40.1	252	3.5
Sodium Dithionite Citrate	Top	.00	10.3	-	6.8	13.9	40	29.
	Bottom	.00	3.8	-	4.6	2.3	61	33.3
Residual	Top	.01	42.6	.30	15.6	122.0	422	41.8
	Bottom	.01	49.6	.23	17.6	103.1	393	48.6
Sum	Top	.55	90.8	.39	44.2	200.8	1176	76.8
	Bottom	.39	81.4	.34	38.0	153.0	1141	91.4
Total Digestion	Top	.62	92.6	.36	35.1	204.3	1124	76.3
	Bottom	.42	89.2	.60	31.7	161.6	1036	87.4

TABLE XXVII

PERCENTAGE OF CADMIUM EXTRACTED BY EACH CHEMICAL TREATMENT

EXTRACTANT	Mare Island Top	Mare Island Bottom	Turning Basin Top	Turning Basin Bottom	Inner Harbor Top	Inner Harbor Bottom
Interstitial Water	0.0	0.0	<1.6	<0.8	0.0	0.0
Ammonium Acetate	1.8	0.0	0.0	0.0	0.0	0.0
Hydroxylamine Hydrochloride	3.6	15.4	0.0	0.0	0.0	0.0
Hydrogen Peroxide	92.7	82.1	90.3	96.9	93.6	95.5
Sodium Citrate Dithionite	0.0	0.0	0.0	<0.8	0.7	0.9
Residual	1.8	2.6	8.1	3.1	5.7	3.6

TABLE XXVIII

PERCENTAGE OF COPPER EXTRACTED BY EACH CHEMICAL TREATMENT

EXTRACTANT	Mare Island Top	Mare Island Bottom	Turning Basin Top	Turning Basin Bottom	Inner Harbor Top	Inner Harbor Bottom
Interstitial Water	0.2	0.0	0.1	0.1	0.2	0.2
Ammonium Acetate	0.1	0.0	3.2	0.0	0.0	0.2
Hydroxylamine Hydrochloride	0.6	0.0	0.8	0.6	0.1	0.3
Hydrogen Peroxide	40.9	34.4	31.2	39.7	52.0	59.2
Sodium Citrate Dithionite	11.3	4.7	0.0	0.0	3.7	0.0
Residual	46.9	60.9	64.6	59.6	43.9	40.3

TABLE XXIX

PERCENTAGE OF MERCURY EXTRACTED BY EACH CHEMICAL TREATMENT

EXTRACTANT	Mare Island Top	 Bottom	Turning Basin Top	 Bottom	Inner Harbor Top	 Bottom
Interstitial Water	0.0	0.0	0.0	0.0	0.0	0.0
Ammonium Acetate	0.0	0.0	0.0	0.0	0.0	0.0
Hydroxylamine Hydrochloride	0.0	0.0	0.0	0.0	0.0	0.0
Hydrogen Peroxide	23.1	35.3	66.1	5.6	5.4	3.2
Sodium Citrate-Dithionite	-	-	-	-	-	-
Residual	76.9	67.6	33.9	93.0	94.6	96.8

TABLE XXX

PERCENTAGE OF LEAD EXTRACTED BY EACH CHEMICAL TREATMENT

EXTRACTANT	Mare Island Top	Mare Island Bottom	Turning Basin Top	Turning Basin Bottom	Inner Harbor Top	Inner Harbor Bottom
Interstitial Water	0.0	0.0	0.0	0.0	0.0	0.0
Ammonium Acetate	0.2	0.3	0.9	0.2	0.2	0.1
Hydroxylamine Hydrochloride	0.0	0.0	2.2	0.0	0.1	0.0
Hydrogen Peroxide	49.3	41.6	48.0	44.7	50.5	37.7
Sodium Citrate-Dithionite	15.4	12.1	0.2	0.0	0.0	0.0
Residual	35.3	46.3	50.7	55.1	49.1	62.2

TABLE XXXI

PERCENTAGE OF ZINC EXTRACTED BY EACH CHEMICAL TREATMENT

EXTRACTANT	Mare Island Top	Mare Island Bottom	Turning Basin Top	Turning Basin Bottom	Inner Harbor Top	Inner Harbor Bottom
Interstitial Water	0.0	0.0	0.0	0.1	0.0	0.0
Ammonium Acetate	0.6	0.3	1.4	0.3	0.0	0.2
Hydroxylamine Hydrochloride	5.2	4.6	1.3	0.2	1.7	0.1
Hydrogen Peroxide	26.5	26.2	27.1	43.0	50.5	61.8
Sodium Citrate-Dithionite	6.9	1.5	12.3	1.2	0.0	0.0
Residual	60.8	67.4	57.9	55.3	47.8	37.8

TABLE XXXII

PERCENTAGE OF MANGANESE EXTRACTED BY EACH CHEMICAL TREATMENT

	Mare Island		Turning Basin		Inner Harbor	
EXTRACTANT	Top	Bottom	Top	Bottom	Top	Bottom
Interstitial Water	0.2	0.2	0.8	1.0	0.2	0.2
Ammonium Acetate	17.7	19.3	6.5	1.7	4.1	3.6
Hydroxylamine Hydroxhloride	22.3	18.8	11.6	8.2	11.5	10.9
Hydrogen Peroxide	20.7	22.1	18.2	20.1	14.8	17.1
Sodium Dithionite-Citrate	3.4	5.3	4.8	4.0	4.6	5.1
Residual	35.9	34.4	58.8	66.0	65.1	63.8

TABLE XXXIII

PERCENTAGE OF IRON EXTRACTED BY EACH CHEMICAL TREATMENT

EXTRACTANT	Mare Island Top	Mare Island Bottom	Turning Basin Top	Turning Basin Bottom	Inner Harbor Top	Inner Harbor Bottom
Interstitial Water	0.0	0.0	0.0	0.0	0.0	0.0
Ammonium Acetate	0.0	0.3	1.0	0.5	0.2	0.0
Hydroxylamine Hydrochloride	1.4	3.0	3.7	4.0	3.4	2.4
Hydrogen Peroxide	5.6	3.8	5.0	9.8	8.0	5.9
Sodium Citrate-Dithionate	38.5	36.4	31.3	25.0	28.3	28.6
Residual	54.4	53.2	58.9	69.8	60.1	63.2

cadmium from the Turning Basin and Oakland Inner Harbor samples was found in the residual phase. Some of the Mare Island cadmium appeared to be released in the hydroxylamine hydrochloride phase.

The copper data in Table XXVIII also show no significant differences between the tops and bottoms of the cores. Between 31 and 59 percent with an average of 43 percent of the copper was released in the hydrogen peroxide extract. Between 40 and 65 percent of the copper with an average of 53 percent was extracted from the residual phase. Five to 10 percent of the copper in the Mare Island sediment appeared to be released in the sodium dithionite-citrate reduction step.

The mercury data presented in Table XXIX show mercury extractable in only two phases. Three to 66 percent of the mercury was released in the hydrogen peroxide treatment. Thirty-four to 97 percent of the mercury was found in the residual phase. The highly reducing sodium dithionite-citrate phase interfered with the method chosen to determine mercury. Over 100 ml of potassium permanganate solution had to be added to oxidize the sample and added a blank contamination larger than the resultant signal. Direct analysis of the sodium dithionite solution without oxidation gave no mercury signals. From the sum of mercury found in all other extracts and comparison with the total mercury in the sediment it appears that any contribution by the sodium dithionite-citrate phase would be small. The top and bottom sediments from the Turning Basin core appear to show differences in the geochemical makeup of the mercury.

Table XXX shows the lead results. Again there appears to be no significant differences in lead extractability between the tops and bottoms of the cores. Thirty-eight to 50 percent of the lead present in the sediments was extracted by the hydrogen peroxide treatment. The average for the three cores was 45 percent extractable by the hydrogen peroxide. Thirty-five to 62 percent of the lead with an average of 50 percent was found in the residual sediment. About 14 percent of the Mare Island lead was extracted in the sodium dithionite reduction treatment.

Table XXXI represents the zinc data. There does not appear to be any difference between the top and bottom of the cores with respect to zinc release. An average of 54 percent of the zinc was found in the residual phase. An average of 39 percent of the zinc was extracted by the hydrogen peroxide treatment. Both the Mare Island and Turning Basin sediments showed some zinc extracted during the reducing treatments of hydroxylamine hydrochloride and sodium dithionite, but the Oakland Inner Harbor sediment showed negligible release under these treatments.

Table XXXII shows the manganese results. No significant differences in the release of manganese between the top and bottom is evident. An average of 54 percent of the manganese was found in the residual sediment, 19 percent was released by treatment with hydrogen peroxide, and 14 percent was extracted by the hydroxylamine hydrochloride. Mare Island sediment had a significantly higher total manganese content and showed about twice the percentage release during the hydroxylamine hydrochloride reduction step.

Table XXXIII contains the iron data. No large differences between the tops and bottoms nor the three geographical locations are evident. An average of 60 percent of the iron is extractable in the residual phase. Thirty-one percent of the iron was released in the sodium dithionite-citrate reduction treatment and six percent was released by treatment with hydrogen peroxide.

Thus far, in the present discussion, no detailed discussion of these results in terms of geochemical phases has been attempted. Recently some criticism of the semi-selective extraction procedure has surfaced. The criticism revolves around the fact that as a chemical treatment dissolves a phase releasing trace metals, some other component in the sediment may rapidly sorb the metal before the solution is separated from the sediment. Bearing this in mind and assuming the above phenomenon is minimal, it appears that the hydrogen peroxide treatment is significant. This extractant oxidizes many of the organics and sulfide forms in the sediment. The organic, sulfide like phases contained 92 percent of the cadmium, 45 percent of the lead, 43 percent of the copper, 39 percent of the zinc, 23 percent of the mercury, 19 percent of the manganese, and 6 percent of the iron.

A significant amount of most of the metals was found in the residual phase which represents metals bound in mineral lattice sites which are essentially inert to moderate chemical attack. Seventy-seven percent of the mercury, 60 percent of the iron, 54 percent of the manganese and zinc, 53 percent of the copper, 50 percent of the lead, and 4 percent of the cadmium were found in the residual state.

Thirty-one percent of the iron was extracted by the sodium dithionite-citrate treatment which dissolves hydrous iron oxides and coprecipitated metals, but only 0.4 percent of the cadmium, 3 percent of the copper, 5 percent of the lead, and 4 percent of the zinc was found in this extract. From these results, it appears that the hydrous oxide coprecipitation and surface exchange of other trace metals is not a significant sink for trace metals in San Francisco Bay sediments. Fourteen percent of the manganese was extracted by the hydroxylamine hydrochloride treatment which reduces and dissolves manganous hydrous oxides. From the data present, manganous oxides also do not appear to be a significant sink for the heavy metals in San Francisco Bay sediments.

The interstitial water heavy metal contents were determined directly by atomic absorption using known addition techniques. Despite the use of a deuterium background corrector, the non-specific absorption present in the high salt solutions probably causes these results to be high. Not enough sample could be squeezed from the sediment to obtain the necessary volume to run the APDC-MIBK extraction which would be the preferred method of analysis.

These results, when compared to the data presented in the literature survey,[35,38,42,43] in general agree that at least 50 to 75 percent of the copper, lead and zinc are found in unreactive mineral sites. Because the extraction schemes differ and most of the published data are on sediments with oxidized surface layers extending down to about two feet, comparison of the significance of hydrous oxide and organic-sulfide phases is difficult. The data of Presley, et al.,[42] for anoxic sediments in a marine fjord may closest resemble the Bay sediments. Comparison for the distribution of copper and zinc is shown in Table XXXIV.

TABLE XXXIV

DISTRIBUTION OF COPPER AND ZINC IN PERCENT

Phase	Cu		Zn	
	Fjord	SF	Fjord	SF
Carbonates, Fe-Mn Oxides, some sulfides	20	5	5	3
Sulfides, organics	19	39	53	43
Residual minerals	61	54	43	53

Recent work on Mobile Bay and Los Angeles Harbor sediments utilizing the Engler, et al.,[39] procedure also indicates that the hydrogen peroxide and residual extracts contain the largest portions of trace metals.[121,122] Interstitial waters and exchangeable contributions are negligible while hydrous oxide phases appear to account for only 5-10 percent of the trace metal distribution.

The hydrogen peroxide oxidation step releases significant amounts of the bound trace metals in San Francisco Bay sediments. Because most of the Bay sediments are in a reduced state, the dredging disturbance which may increase the oxidation of the disturbed sediments has the potential to increase mobilization. Simulated disturbance, as carried out in the laboratory sorption-desorption experiments, is discussed later in this report.

It is interesting to note that linear regression results show that the total heavy metal contents of the San Francisco Bay sediments correlate with the total sulfur contents, as discussed in Appendix A. These results also suggest that sulfides play an important role in the movement of trace metals within San Francisco Bay. As stated earlier, there was a very large increase in the dissolved organic content of the Turning Basin interstitial water compared to the overlying water and interstitial waters from the other locations. However, there was no significant increases in soluble heavy metal content in the Turning Basin interstitial water and thus no effect on metal mobilization can be substantiated.

RADIOTRACER STUDY AND VERIFICATION OF TRACE METAL EXTRACTION PROCEDURE

Before the large factorial design experiment to determine whether agitated dredge spoils would release heavy metals to the water column was initiated, a detailed study was made of the APDC-MIBK extraction and HNO_3 back extraction. Concern developed after reviewing the literature and not finding adequate data on the efficiency of the APDC-MIBK extraction and no data on nitric acid back extraction efficiency. One article[123] showed that for liquid coexisting with sewage sludges, the procedure extracted only 10-30 percent of the zinc, copper and cadmium as compared to aliquots of the solution which were acid digested, taken to dryness and then rediluted before APDC-MIBK extraction. On the other hand, Peterson[124] reported no loss of lead extractability for either the addition of 7 ppm of natural soluble organic material or the addition of EDTA to a normality of 5×10^{-5} to lake waters in which the APDC-MIBK extraction procedure was being used to determine lead contents.

Radiotracers added to seawater of 29‰ and 1.5‰ were shaken overnight to allow equilibration with natural soluble species. All of the isotopes but ^{59}Fe appeared to remain in solution. Some of the iron apparently precipitated or sorbed onto the container walls. The low salinity case showed a loss of six percent of the initial ^{59}Fe activity. The high salinity case showed a loss of 20 percent of the initial ^{59}Fe activity.

The results of the extraction by APDC of trace metals from the water into the MIBK phase are shown in Table XXXV.

TABLE XXXV

PERCENT RADIOISOTOPE EXTRACTED FROM WATER BY APDC-MIBK

	Fe	Cd	Zn	Mn
High Salinity	76±11	97±1	99±1	16±1
Low Salinity	81±5	97±1	99±1	17±1

It was found the manganese would not extract into the MIBK under these conditions. The pH of the seawater was dropped to 3 and subsequently 2 but manganese still would not extract. A second APDC-MIBK extraction of the iron samples increased the percentage of activity removed from the water to 92%±4% for the high salinity case and 93%±3% for the low salinity case.

During the experiment it was also discovered that if the seawater pH was dropped to 2.9 cadmium would not quantitatively extract into the APDC-MIBK phase. Moyer and Budinger[20] confirm that high acid solutions inhibit the chelation and removal of cadmium into the MIBK phase. They found that pH values below 2.5 inhibit the cadmium extraction.

Back extraction into the nitric acid followed and results are presented in Table XXXVI.

TABLE XXXVI

PERCENT RADIOISOTOPE EXTRACTED FROM MIBK BY 6N HNO_3

	Fe	Cd	Zn	Mn
High Salinity	100±1	100±1	100±1	Not Run
Low Salinity	100±1	100±1	100±1	

From this experiment it was determined that the described procedure of APDC-MIBK extraction and 6N HNO_3 back extraction was satisfactory for iron, cadmium and zinc at both low and high salinities. The above results can only be applied to the radioactive portions of the trace metals present in the seawaters. There is still the question brought up by several investigators as to whether APDC-MIBK will extract trace metals tightly bound to soluble organics in the water. It is not possible to state conclusively that all the trace metals of interest were removed from the seawater but the radioisotopes were allowed to equilibrate sixteen hours before extraction so that the dissolved organics did have a chance to sequester the radiotracers also. From the results only iron showed an extraction percentage significantly below 100 percent.

From specific activity values (μc/μg) reported in the Methods section it was determined that the concentration of radioisotopes added to the seawater were in the range of concentrations normally found. Added concentrations are presented in Table XXXVII.

TABLE XXXVII

CONCENTRATION OF RADIOACTIVE
ELEMENTS ADDED TO SEAWATER

	Added ppb	Original ppb
Mn	0.2	--
Fe	1-5	2
Cd	0.4	0.15
Zn	0.2	6.6

No gamma ray emitting isotopes of lead or copper were available to investigate the efficiency of the extraction and back extraction procedures for these elements.

In a separate experiment a seawater sample taken near Alcatraz Island with a salinity of 29 ppt was subdivided into numerous aliquots each of which was analyzed for trace metals. The samples were extracted with APDC-MIBK and back extracted with 6N HNO_3 acid. Precision of analysis for each metal is presented in Table XXXVIII.

TABLE XXXVIII

TRACE METAL ANALYSIS PRECISION BY APDC-MIBK-HNO_3 EXTRACTIONS

	Number of Determinations	Standard Deviation %
Cd	11	14
Cu	12	5
Pb	10	17
Zn	7	11
Fe	8	32
Mn	would not extract	

Four Alcatraz seawater samples were subjected to three successive extractions with APDC-MIBK and the resultant MIBK phases were back extracted with 6N HNO_3. The average values of the percent of the total extracted metal obtained in each successive extract are presented in Table XXXIX.

TABLE XXXIX

AVERAGE PERCENT OF METAL EXTRACTED IN EACH SUCCESSIVE EXTRACT

	Extracts			
Metal	1	2	3	Σ
Cu	90	9	1	100
Zn	93	7	0	100
Fe	95	5	0	100
Cd	90	8	2	100
Pb	100	-	-	100

The lead determinations were difficult because the values always hovered around the detection limit controlled by the instrument and extracted ultrapure water blanks. In all four cases of the first lead extraction, a signal greater than an extracted ultrapure water signal was obtained. For the second and third extracts of the seawater samples, the lead values were the same or less than the extracted ultrapure water blank.

From the described experiments it was decided that one extraction of a seawater sample at salinities between 1.5 and 29‰ would be adequate to remove 90 percent or more of the metal for copper, cadmium and zinc, and 80-90 percent of the iron. Lead appears to be low in the samples and hindered by a persistent blank signal. Back extraction with 6N ultrapure nitric acid appears satisfactory and allows sample storage for at least several days. The competition of soluble organics to the metal extractability is probably minimal because the San Francisco Bay waters and elutriates from the sorption-desorption experiment had soluble organic contents of only 10-20 ppm.

The extraction of manganese should be performed at a pH near neutrality[24] and great speed must be utilized because of severe instability of manganese in MIBK.[125]

RESULTS OF THE FACTORIAL DESIGN BATCH SORPTION-DESORPTION EXPERIMENT

The purpose of the large factorial design batch sorption-desorption experiment was to determine the effects of the variables sediment type, solids-to-solution ratio, contact time, salinity of the water and oxidation-reduction potential on the release or uptake of heavy metals associated with the sediment. The independent variables and the values chosen are presented in Table XL.

TABLE XL

FACTORIAL DESIGN INDEPENDENT VARIABLES

	High	Medium	Low
Salinity	29‰	15‰	1‰
Agitation	144 hrs	24 hrs	1 hr
Sediment	Inner Harbor	Turning Basin	Mare Island
Solids-To-Solution Ratio	190 g/l dry wt.	60 g/l dry wt.	9 g/l dry wt.
Oxidation Reduction Potential	Oxidizing	---	Reducing

Raw data including the agitation times, solids-to-solution ratio, slurry pH, Eh, dissolved oxygen content, initial salinity of the water and final elutriate concentrations of selected metals are presented in Tables XLI-XLIII.

In the case of oxidizing conditions, it was initially desired to stabilize the dissolved oxygen of the system at a value near natural saturation, 8-9 ppm. Sparging the system with air proved satisfactory to achieve this goal for low solids content samples. However, for all samples above, the 9 g/l solids content, it was necessary to sparge the system with pure oxygen. This latter technique resulted in final dissolved oxygen concentrations which were highly variable, often times

TABLE XLI

MARE ISLAND SORPTION-DESORPTION DATA

	Time (hrs)	Solids g/l	pH	DO ppm	Eh* mv	S‰ ‰	Cd ppb	Cu ppb	Fe ppb	Pb ppb	Zn ppb	Hg ppb
1	139.5	184.0	7.3	0.2	-180	1	0.120	10.0	25	0.13	4.9	<0.08
2	139.5	56.0	7.2	0.2	-140	1	0.006	4.6	13	0.30	2.0	<0.08
3	140.5	9.7	7.7	0.2	+ 20	1	0.275	2.4	2	--	1.9	<0.04
4	21.8	163.0	7.6	0.04	-190	1	0.200	3.0	10	0.06	4.1	<0.08
5	21.8	62.0	7.8	0.04	-190	1	0.008	1.5	53	<0.05	4.0	<0.08
6	22.5	9.0	7.9	0.6	+ 30	1	0.015	1.6	4	--	2.9	<0.04
7	1.5	178.0	7.5	0.2	-190	1	0.073	7.4	345	0.16	11.0	<0.08
8	1.5	54.0	7.8	0.2	-180	1	0.028	7.7	152	0.21	10.7	<0.08
9	1.5	13.0	8.1	0.1	-200	1	0.038	2.6	240	--	8.5	<0.04
10	139.5	185.0	7.3	0.2	-180	15	0.037	5.0	2412	0.08	3.5	<0.08
11	140.5	59.0	7.4	0.04	-120	15	0.187	4.6	1060	<0.05	7.2	<0.08
12	140.5	9.2	8.2	0.2	+ 40	15	0.102	1.4	2	--	3.3	<0.04
13	21.8	183.0	7.3	0.05	-180	15	0.126	2.2	1938	<0.05	5.2	<0.08
14	22.2	57.0	6.6	0.04	-160	15	0.037	1.3	1168	<0.05	9.6	<0.08
15	22.5	10.0	8.0	0.2	+ 30	15	0.094	1.9	55	--	4.5	<0.04
16	1.5	185.0	7.2	0.2	-190	15	0.084	6.8	2295	0.16	12.5	<0.08
17	1.5	56.0	7.5	0.04	-160	15	0.028	1.5	738	0.10	7.2	<0.08
18	1.5	12.4	7.9	0.1	-200	15	0.023	1.9	539	--	6.0	<0.04
19	140.5	187.0	7.4	0.04	-180	29	0.660	12.0	4747	0.55	<.2	<0.08
20	140.5	56.0	7.6	0.2	-130	29	0.202	7.2	505	0.15	11.9	<0.08
21	140.5	10.8	8.2	0.2	+ 50	29	0.077	2.4	154	--	3.9	<0.04
22	22.2	187.0	6.5	0.1	-180	29	0.044	5.2	4756	0.05	0.9	<0.08
23	22.2	57.0	6.6	0.1	-170	29	0.116	1.5	808	0.13	8.2	<0.08
24	22.5	10.0	7.9	0.15	+ 40	29	0.200	2.2	20	--	2.9	<0.04
25	1.5	185.0	7.2	0.04	-170	29	0.660	2.8	4221	0.09	<.2	<0.08
26	1.5	57.0	7.3	0.04	-170	29	0.152	2.2	1414	<0.05	8.3	<0.08
27	1.5	11.3	7.9	0.1	-220	29	0.060	2.2	1334	--	4.5	<0.04

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*vs Calomel reference electrode

TABLE XLI (CONT'D.)

	Time (hrs)	Solids g/1	pH	DO ppm	Eh* mv	S‰ ‰	Cd ppb	Cu ppb	Fe ppb	Pb ppb	Zn ppb	Hg ppb
28	142.0	178.0	7.2	9.2	+150	1	0.146	11.4	2	0.34	6.2	<0.08
29	139.5	54.0	7.3	>15.0	+140	1	0.025	7.2	6	0.82	7.3	<0.08
30	142.0	11.4	7.2	9.1	+190	1	0.036	2.9	2	--	5.8	<0.04
31	21.8	188.0	7.2	>15.0	+140	1	0.033	6.5	9	0.12	5.0	<0.08
32	21.8	63.0	7.6	8.4	+120	1	0.021	6.4	5	0.59	6.8	<0.08
33	23.0	10.2	7.5	8.7	+140	1	0.064	5.0	3	--	7.2	<0.04
34	1.5	180.0	7.7	>15.0	+ 90	1	0.145	11.3	32	0.21	4.3	<0.08
35	1.5	62.0	7.8	8.7	+ 80	1	0.116	6.6	12	0.56	7.6	0.09
36	1.5	10.9	8.0	8.8	+130	1	0.021	2.5	2	--	1.0	0.04
37	139.5	167.0	6.9	12.4	+120	15	1.140	8.6	10	0.10	13.8	0.08
38	140.5	59.0	7.1	11.4	+140	15	0.369	6.1	4	<0.05	10.2	<0.08
39	142.0	9.9	8.0	9.2	+210	15	0.333	4.5	2	--	36.3	<0.04
40	21.8	177.0	7.2	>15.0	+140	15	0.651	6.3	6	0.76	22.4	<0.08
41	22.2	56.0	7.4	11.0	+120	15	0.264	6.2	5	0.06	8.8	<0.08
42	23.0	13.6	7.6	8.6	+140	15	0.219	3.8	2	--	6.2	<0.04
43	1.5	179.0	7.4	>15.0	+110	15	0.451	9.2	6	0.26	11.8	<0.08
44	1.5	56.0	7.8	>15.0	+180	15	0.192	3.8	2	0.15	7.9	<0.08
45	1.5	10.0	7.9	8.9	+150	15	0.280	2.6	2	--	4.5	<0.04
46	142.0	185.0	6.9	13.6	+170	29	2.860	11.9	6	0.83	22.4	<0.08
47	140.5	58.0	7.0	13.0	+140	29	1.565	7.8	2	0.78	14.0	<0.08
48	142.0	10.9	8.1	8.8	+220	29	0.575	5.2	2	--	10.3	<0.04
49	22.2	185.0	7.2	>15.0	+120	29	1.640	5.5	5	0.09	10.8	<0.08
50	22.2	59.0	7.4	>15.0	+120	29	1.053	6.0	7	0.18	10.1	<0.08
51	23.0	12.0	7.5	8.6	+150	29	0.450	4.2	2	--	9.8	<0.04
52	1.5	185.0	7.4	>15.0	+140	29	1.130	7.7	12	0.18	15.1	<0.08
53	1.5	60.0	7.7	14.0	+130	29	0.687	3.9	6	0.09	16.1	<0.08
54	1.5	12.1	8.0	8.8	+150	29	0.310	3.2	2	--	10.3	<0.04

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*vs Calomel reference electrode

TABLE XLII

TURNING BASIN SORPTION-DESORPTION DATA

	Time (hrs)	Solids g/l	pH	DO ppm	Eh* mv	S‰ ‰	Cd ppb	Cu ppb	Fe ppb	Pb ppb	Zn ppb	Hg ppb
1	141.5	147.0	7.5	0.05	-220	1	<0.005	3.1	2778	0.25	5.9	<0.08
2	143.5	45.0	7.9	0.2	-210	1	<0.005	5.3	69	0.34	3.9	<0.08
3	141.5	8.2	7.8	0.2	- 20	1	0.017	1.6	2	--	7.5	<0.04
4	22.5	149.0	7.0	0.05	-240	1	0.005	2.8	735	<0.05	4.2	<0.08
5	25.2	46.0	7.3	0.1	-250	1	<0.005	4.2	175	<0.05	19.5	<0.08
6	22.0	7.0	8.0	0.2	-190	1	<0.005	1.4	208	--	7.6	<0.04
7	1.5	149.0	7.6	0.3	-250	1	0.068	2.8	2260	0.10	33.2	<0.08
8	1.5	47.0	7.9	0.4	-240	1	0.090	1.0	155	0.25	8.4	<0.08
9	1.5	8.0	7.9	0.2	-240	1	0.043	1.7	412	--	6.7	<0.04
10	141.5	147.0	7.4	0.05	-220	15	0.025	3.4	4420	0.25	0.6	<0.08
11	139.2	46.0	7.6	0.05	-190	15	0.012	2.0	2120	<0.05	11.5	<0.08
12	141.5	8.6	8.1	0.2	- 70	15	0.022	0.5	164	--	1.9	<0.04
13	22.5	146.0	7.0	0.05	-230	15	<0.005	4.4	4270	<0.05	<0.5	<0.08
14	19.0	44.0	7.3	0.1	-240	15	<0.005	0.8	5528	0.25	0.5	<0.08
15	22.0	8.9	8.0	0.1	-230	15	0.049	0.7	1428	--	11.0	<0.04
16	1.5	148.0	7.5	0.3	-230	15	0.045	1.4	5528	<0.05	0.5	<0.08
17	1.5	46.0	7.6	0.3	-210	15	<0.005	1.2	631	<0.05	<0.5	<0.08
18	1.5	8.4	8.0	0.1	-220	15	0.045	1.8	2142	--	6.6	<0.04
19	140.8	150.0	7.3	0.05	-210	29	<0.005	3.4	3912	0.36	<0.5	<0.08
20	141.8	48.0	7.5	0.05	-220	29	<0.005	1.6	3282	0.25	<0.5	<0.08
21	141.5	7.9	8.1	0.2	- 10	29	0.029	0.7	39	--	4.3	<0.04
22	21.8	146.0	7.1	0.1	-230	29	0.062	1.4	13568	0.33	3.2	<0.08
23	22.8	44.0	7.4	0.1	-240	29	0.005	0.7	6282	0.05	1.2	<0.08
24	22.0	7.3	7.9	0.1	-230	29	0.041	0.9	1029	--	9.8	<0.04
25	1.5	146.0	7.3	0.3	-220	29	0.005	1.3	13635	0.26	<0.5	<0.08
26	1.5	53.0	7.4	0.4	-210	29	<0.005	1.2	9595	0.26	<0.5	<0.08
27	1.5	8.0	8.1	0.1	-230	29	0.071	2.6	2625	--	9.4	<0.04

*vs Calomel reference electrode

TABLE XLII (CONT'D.)

	Time (hrs)	Solids g/l	pH	DO ppm	Eh* mv	S‰ ‰	Cd ppb	Cu ppb	Fe ppb	Pb ppb	Zn ppb	Hg ppb
28	143.5	145.0	7.2	5.7	+ 90	1	0.264	12.7	2	0.48	5.7	<0.08
29	143.5	46.0	7.6	9.2	+110	1	0.050	7.9	7	0.48	5.2	<0.08
30	141.5	9.2	7.4	12.6	+260	1	0.027	2.9	2	--	4.5	<0.04
31	27.2	149.0	7.8	8.2	+110	1	<0.005	3.1	25	0.14	3.0	<0.08
32	25.2	45.0	8.0	8.8	+110	1	0.017	4.0	8	0.27	3.6	<0.08
33	22.0	6.6	7.6	8.4	+100	1	<0.005	1.6	2	--	5.4	<0.04
34	1.5	153.0	7.5	3.2	- 40	1	0.020	4.5	9	0.22	4.1	<0.08
35	1.5	46.0	7.9	8.2	+ 60	1	0.010	3.2	7	0.10	2.1	<0.08
36	1.5	8.0	8.3	8.0	+ 80	1	0.012	1.6	4	--	4.0	<0.04
37	139.3	146.0	7.2	>15.0	+ 90	15	0.730	8.4	3	0.31	21.9	<0.08
38	139.3	46.0	7.4	8.6	+130	15	0.400	4.9	2	0.60	10.8	<0.08
39	141.5	8.3	7.6	8.4	+280	15	0.148	4.2	2	--	6.4	<0.04
40	27.2	146.0	7.7	6.3	+110	15	0.058	2.4	39	0.28	23.8	<0.08
41	21.0	46.0	7.4	7.0	+ 90	15	0.225	1.6	100	0.91	2.2	<0.08
42	22.0	8.3	7.5	8.4	+125	15	0.258	1.2	2	--	6.0	<0.04
43	1.5	150.0	7.5	8.8	- 20	15	0.032	3.2	4	0.31	3.0	<0.08
44	1.5	48.0	7.6	7.2	+ 60	15	0.013	1.5	8	0.36	2.6	<0.08
45	1.5	8.0	8.1	8.2	+110	15	0.013	1.4	3	--	6.6	<0.04
46	139.2	146.0	7.1	13.5	+130	29	1.990	8.5	2	0.46	19.5	<0.08
47	143.5	46.0	7.3	8.4	+110	29	0.548	6.0	4	0.36	15.6	<0.08
48	141.5	9.5	7.5	13.0	+260	29	0.500	4.0	2	--	8.2	<0.04
49	21.8	148.0	7.6	8.0	+ 30	29	0.022	2.4	12	0.47	14.9	<0.08
50	22.8	47.0	7.3	7.4	+100	29	0.060	2.0	2	0.34	6.6	<0.08
51	22.0	7.8	7.7	8.6	+130	29	0.114	1.4	2	--	3.9	<0.04
52	1.5	152.0	7.4	7.6	- 20	29	0.049	1.8	2	0.45	1.9	<0.08
53	1.5	46.0	7.7	7.5	+ 40	29	0.016	1.4	4	0.36	2.4	<0.08
54	1.5	8.6	8.1	8.1	+120	29	0.050	1.6	3	--	9.8	<0.04

*vs Calomel reference electrode

TABLE XLIII

OAKLAND INNER HARBOR SORPTION-DESORPTION DATA

	Time (hrs)	Solids g/l	pH	DO ppm	Eh* mv	S‰ ‰	Cd ppb	Cu ppb	Fe ppb	Pb ppb	Zn ppb	Hg ppb
1	143.5	191.0	7.2	0.05	-230	1	0.041	4.0	190	0.25	4.3	<0.08
2	143.5	60.0	7.2	0.05	-210	1	0.026	1.4	156	0.25	3.8	<0.08
3	141.5	9.2	8.4	0.10	-100	1	0.071	1.4	2	--	6.6	<0.04
4	27.2	193.0	7.2	0.05	-240	1	0.056	5.3	352	0.60	26.4	<0.08
5	25.2	56.0	7.3	0.05	-230	1	0.058	4.0	82	0.22	2.4	<0.08
6	22.0	8.4	8.4	0.3	+100	1	0.065	4.5	4	--	6.7	<0.04
7	1.5	190.0	8.1	0.1	-230	1	0.043	3.2	451	0.24	5.2	<0.08
8	1.5	56.0	8.2	0.1	-230	1	0.058	3.5	116	0.14	7.3	<0.08
9	1.5	8.8	8.5	0.2	- 60	1	0.008	3.7	94	--	0.4	<0.04
10	139.3	190.0	7.2	0.05	-230	15	0.032	1.5	3686	<0.02	<0.2	<0.08
11	139.3	63.0	7.5	0.05	-200	15	0.009	2.7	588	<0.02	3.1	<0.08
12	141.5	10.6	8.2	0.10	- 80	15	0.054	<0.5	498	--	7.9	<0.04
13	27.2	196.0	7.2	0.05	-240	15	0.028	1.2	2640	0.14	<0.2	<0.08
14	21.0	64.0	7.2	0.05	-230	15	0.038	2.0	820	0.38	6.2	<0.08
15	22.0	9.8	8.1	0.20	+180	15	0.046	1.4	64	--	13.3	<0.04
16	1.5	190.0	8.0	0.10	-230	15	0.020	4.0	2603	0.28	2.9	<0.08
17	1.5	60.0	7.9	0.05	-240	15	0.035	2.2	446	<0.02	3.8	<0.08
18	1.5	10.5	8.1	0.10	- 40	15	0.028	1.6	12	--	20.1	<0.04
19	139.2	193.0	7.3	0.05	-230	29	0.011	1.4	2676	<0.02	<0.2	<0.08
20	143.5	62.0	7.5	0.05	-230	29	0.008	1.6	1565	<0.02	<0.2	<0.08
21	141.5	9.3	8.2	0.20	- 40	29	0.065	<0.5	309	--	6.1	<0.04
22	21.8	190.0	7.2	0.05	-240	29	0.042	1.6	3854	<0.02	0.6	<0.08
23	22.8	60.0	7.2	0.05	-250	29	0.041	1.7	1906	0.13	6.8	<0.08
24	22.0	7.2	8.1	0.20	+128	29	0.033	1.2	39	--	6.9	<0.04
25	1.5	194.0	7.6	0.05	-220	29	0.032	2.1	1616	<0.02	2.0	<0.08
26	1.5	63.0	7.9	0.05	-240	29	0.035	2.8	2444	<0.02	1.0	<0.08
27	1.5	9.4	8.1	0.20	- 40	29	0.038	1.5	14	--	1.4	<0.04

*vs Calomel reference electrode

TABLE XLIII (CONT'D.)

Cont'd.

	Time (hrs)	Solids g/l	pH	DO ppm	Eh* mv	S%• %•	Cd ppb	Cu ppb	Fe ppb	Pb ppb	Zn ppb	Hg ppb
28	138.5	194.0	7.8	6.3	+120	1	0.118	24.4	13	0.05	18.2	<0.08
29	138.5	60.0	7.6	>15.0	+140	1	0.143	16.6	4	0.14	9.3	<0.08
30	140.0	7.7	7.2	8.9	+190	1	0.070	2.9	12	--	11.3	<0.04
31	20.8	190.0	8.1	>15.0	+ 60	1	0.064	14.7	16	0.73	10.0	<0.08
32	20.8	58.0	8.3	>15.0	+ 40	1	0.048	8.6	10	0.11	5.5	<0.08
33	21.0	9.8	8.5	8.3	+130	1	0.036	3.7	3	--	23.8	<0.04
34	1.5	189.0	8.3	8.0	+100	1	0.060	6.0	11	0.26	4.1	<0.08
35	1.5	50.0	8.5	13.0	+ 70	1	0.026	4.6	5	0.19	5.2	<0.08
36	1.5	9.0	8.2	8.8	+110	1	0.022	2.3	2	--	11.9	<0.04
37	138.5	186.0	7.2	2.8	+100	15	0.737	7.3	6	0.32	28.6	<0.08
38	141.0	64.0	7.2	14.0	+150	15	1.624	16.4	4	0.18	34.8	<0.08
39	140.0	7.5	7.8	8.9	+200	15	0.473	3.9	2	--	31.0	<0.04
40	20.8	190.0	7.9	>15.0	+ 70	15	0.092	7.2	12	0.44	11.0	<0.08
41	22.5	62.0	8.1	12.6	+100	15	0.064	5.6	5	0.38	3.4	<0.08
42	21.0	10.5	7.9	8.2	+160	15	0.059	1.8	2	--	6.4	<0.04
43	1.5	183.0	8.1	13.6	+ 10	15	0.055	5.4	12	0.48	3.8	<0.08
44	1.5	62.0	8.2	13.0	+ 30	15	0.046	2.6	4	0.62	3.4	<0.08
45	1.5	9.0	8.0	8.8	+130	15	[illegible]	0.9	11	--	1.9	<0.04
46	141.0	192.0	7.0	7.9	+150	29	4.620	20.0	4	0.48	73.2	<0.08
47	141.0	63.0	7.2	13.5	+130	29	5.590	17.8	4	0.25	50.4	<0.08
48	140.0	8.0	7.9	9.1	+220	29	1.470	3.2	2	--	81.0	<0.04
49	22.5	193.0	8.0	14.5	+120	29	0.048	6.0	20	0.32	4.5	<0.08
50	22.5	65.0	8.1	13.0	+130	29	0.351	6.0	12	0.35	4.7	<0.08
51	21.0	10.5	8.0	8.2	+170	29	0.046	1.4	2	--	7.5	<0.04
52	1.5	193.0	8.2	5.6	+ 20	29	0.160	4.4	46	0.50	25.0	<0.08
53	1.5	61.0	8.1	13.5	+ 60	29	0.029	2.7	5	0.50	13.2	<0.08
54	1.5	9.0	8.0	8.6	+130	29	0.066	1.8	2	--	7.2	<0.04

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*vs Calomel reference electrode

abnormally high (>15 ppm) and sometimes quite low (1-4 ppm).

The Eh values for the reducing conditions are consistent and compare favorably with low dissolved oxygen content samples. The dissolved oxygen (DO), redox potential (Eh) and pH were taken on the slurry at the end of the shaking period. The Eh values are raw data vs the calomel reference electrode. To convert to values vs the hydrogen electrode, +240 mv should be added to each. The trace metal contents shown are the elutriate waters after contact with the sediment. Unfortunately, all the low solids extractions were completed before analyses showed a lead contamination problem in the MIBK, therefore, results are not shown. The change in the mercury concentrations from <0.08 ppb to <0.04 ppb for the low solids content is not significant. It reflects an improvement in the detection limit for measuring mercury between the times that the higher solids experiments and the low solids experiments were performed.

The original concentrations of trace metals in the three salinity waters before contact with the sediment are reported in Table XLIV. Both filtered (0.45μ) and unfiltered values are shown in Table XLIV. It appears that for the 15‰ and 1‰ waters the lead concentrations in the unfiltered samples are significantly higher than after filtration. The 15‰ water sample had a high suspended solids content because the water from Mare Island Straits was very turbid. The 1‰ water was a dilution of the 15‰ water. The 29‰ water was from off Alcatraz Island and contained very little suspended solids.

TABLE XLIV

TRACE METAL CONCENTRATIONS IN ORIGINAL WATER, (ppb)

	Cd	Cu	Fe	Pb	Zn	Hg
Filtered 1‰	0.03±0.01	1.1±.2	<2.	<0.05	1.9±0.5	<0.08
Unfiltered 1‰	0.03±0.01	0.8±.3	<2.	0.23±0.11	1.3±0.2	<0.08
Filtered 15‰	0.18±0.07	3.6±.2	<2.	0.32±0.2	9.6±0.9	<0.08
Unfiltered 15‰	0.23±0.06	3.6±.2	3.±.5	2.31±1.2	9.9±1.3	<0.08
Filtered 29‰	2.21±0.70	10.7±.6	<2.	0.28±0.1	8.8±0.8	<0.08
Unfiltered 29‰	1.74±0.33	10.5±.8	<2.	0.24±0.2	9.0±1.8	<0.08

The raw data presented in Table XLI, XLII, and XLIII show pronounced differences in trace metal concentrations in the elutriate waters at the two oxidation-reduction potentials. In the cases of copper, cadmium, lead, and zinc higher concentrations were found in solution under oxidizing conditions than under reducing conditions. Iron acts in the opposite sense with a higher concentration found in the elutriate under reducing conditions. The statistical t-test was run on the difference between the concentrations of trace metals at the two redox potentials and results are shown in Table XLV.

The mercury data are all below the detection limit and thus show that very little mercury was soluble under either redox condition. The sediment apparently sorbs mercury effectively under either redox condition.

Figures 2-6 show the average elutriate concentrations of the iron, cadmium, copper, lead and zinc respectively for each sediment and each salinity under both low and high oxgen conditions. The average elutriate concentrations represent the

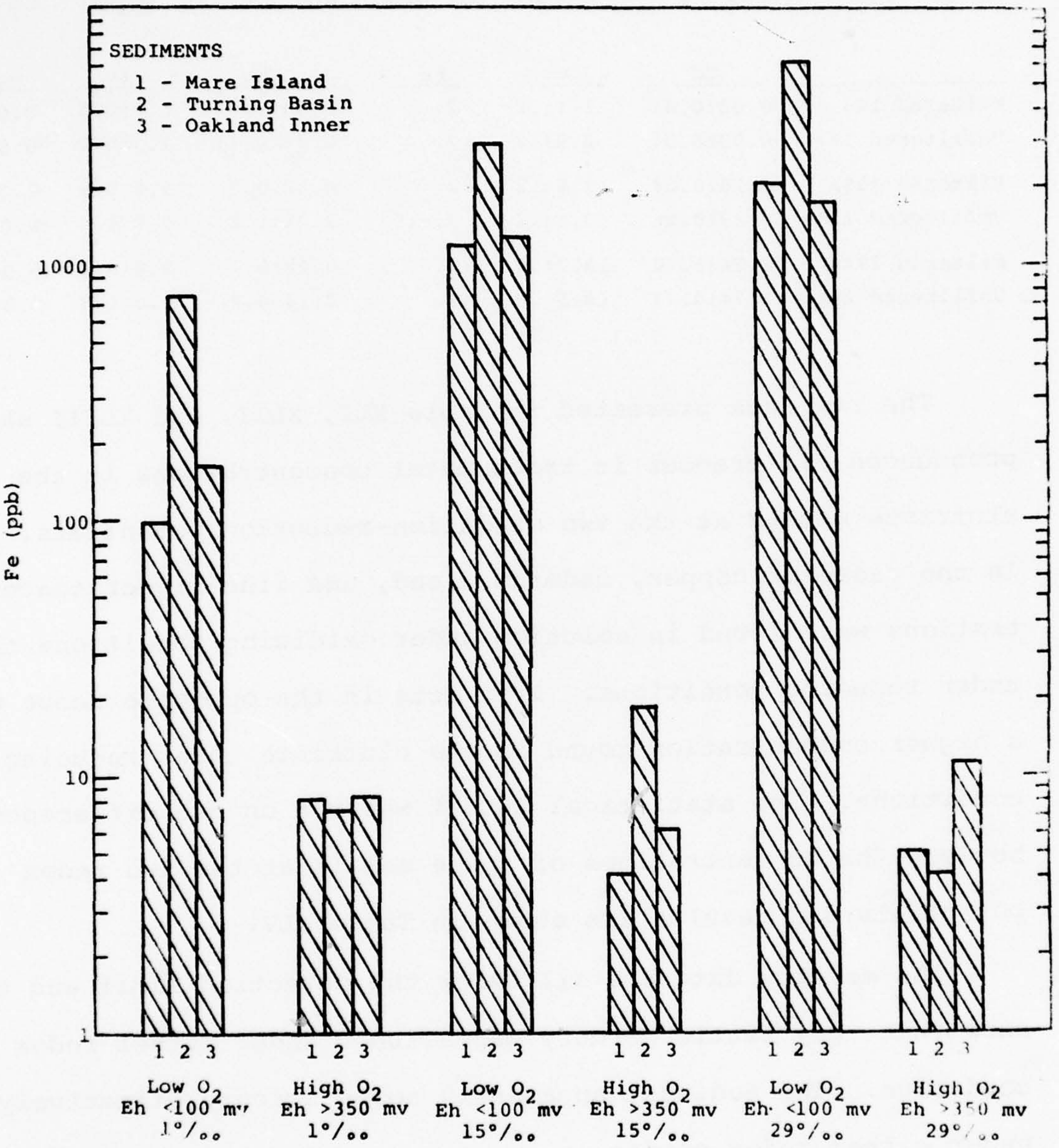


FIGURE 2. ELUTRIATE IRON CONCENTRATIONS

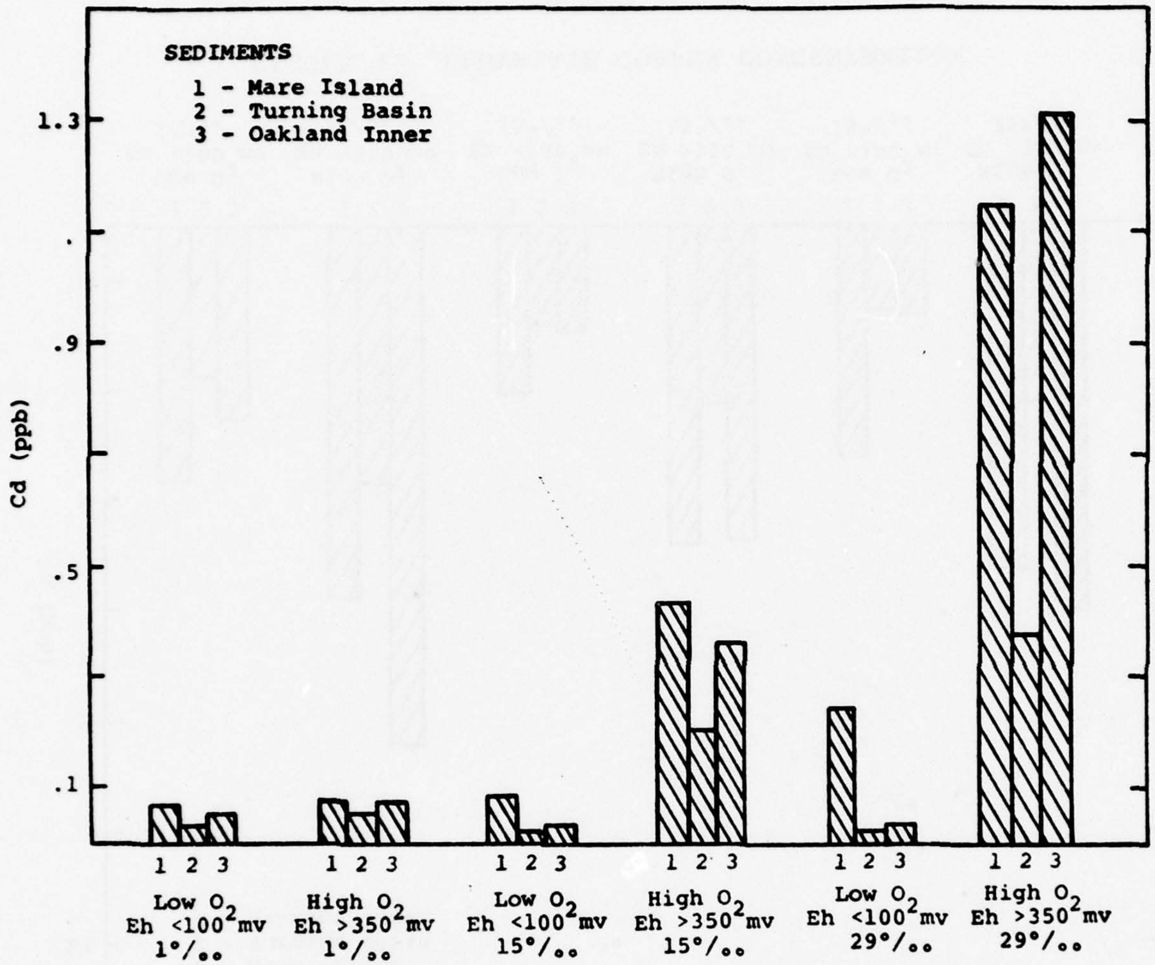


FIGURE 3. ELUTRIATE CADMIUM CONCENTRATIONS

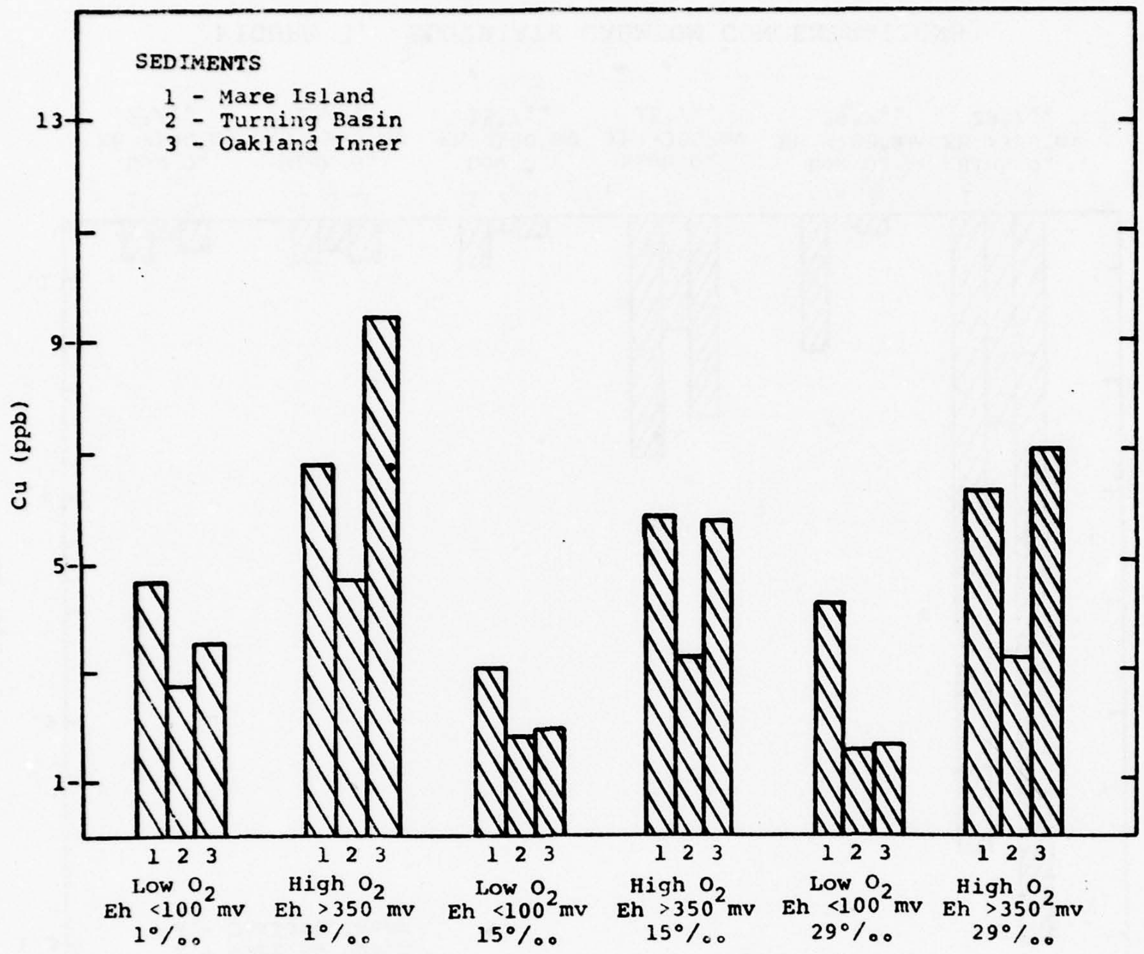


FIGURE 4. ELUTRIATE COPPER CONCENTRATION

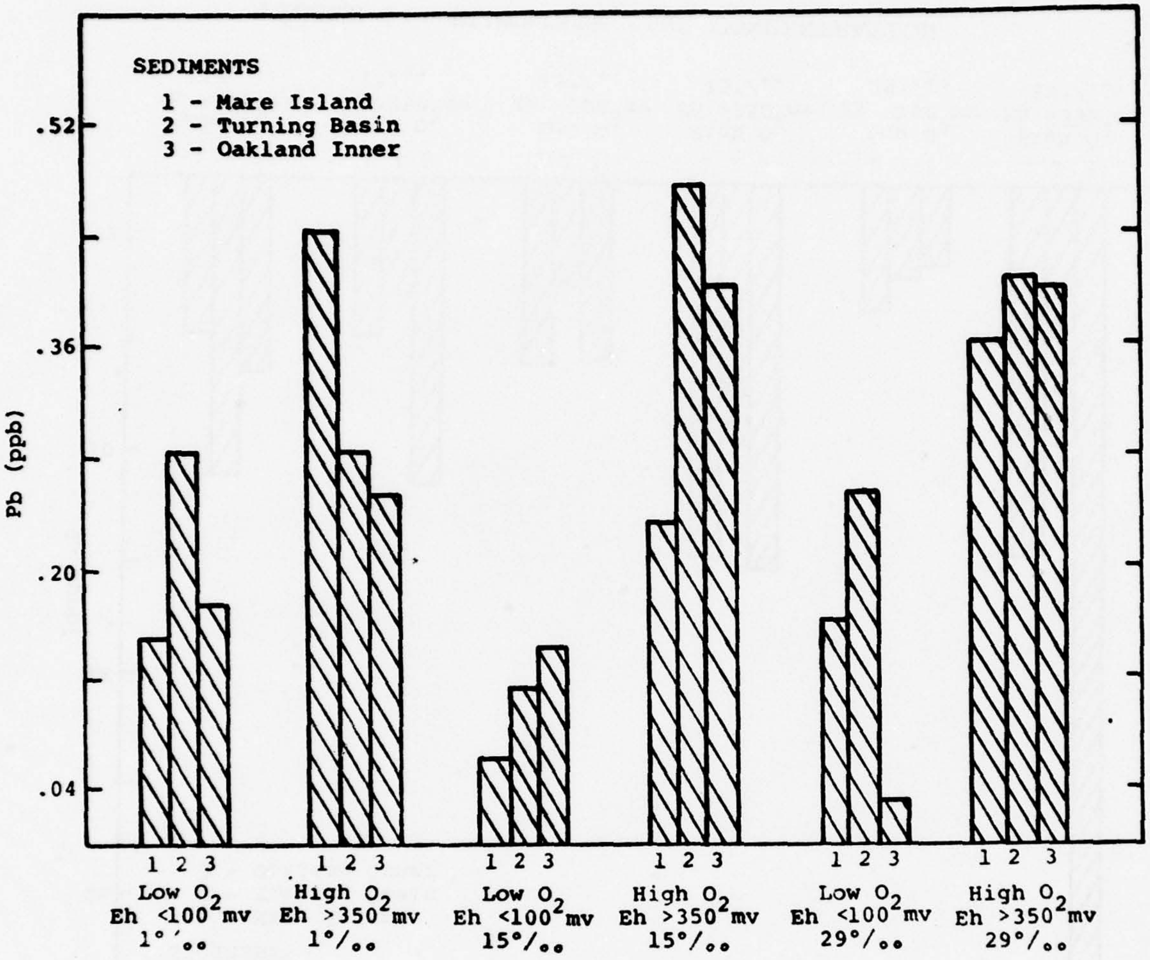


FIGURE 5. ELUTRIATE LEAD CONCENTRATION

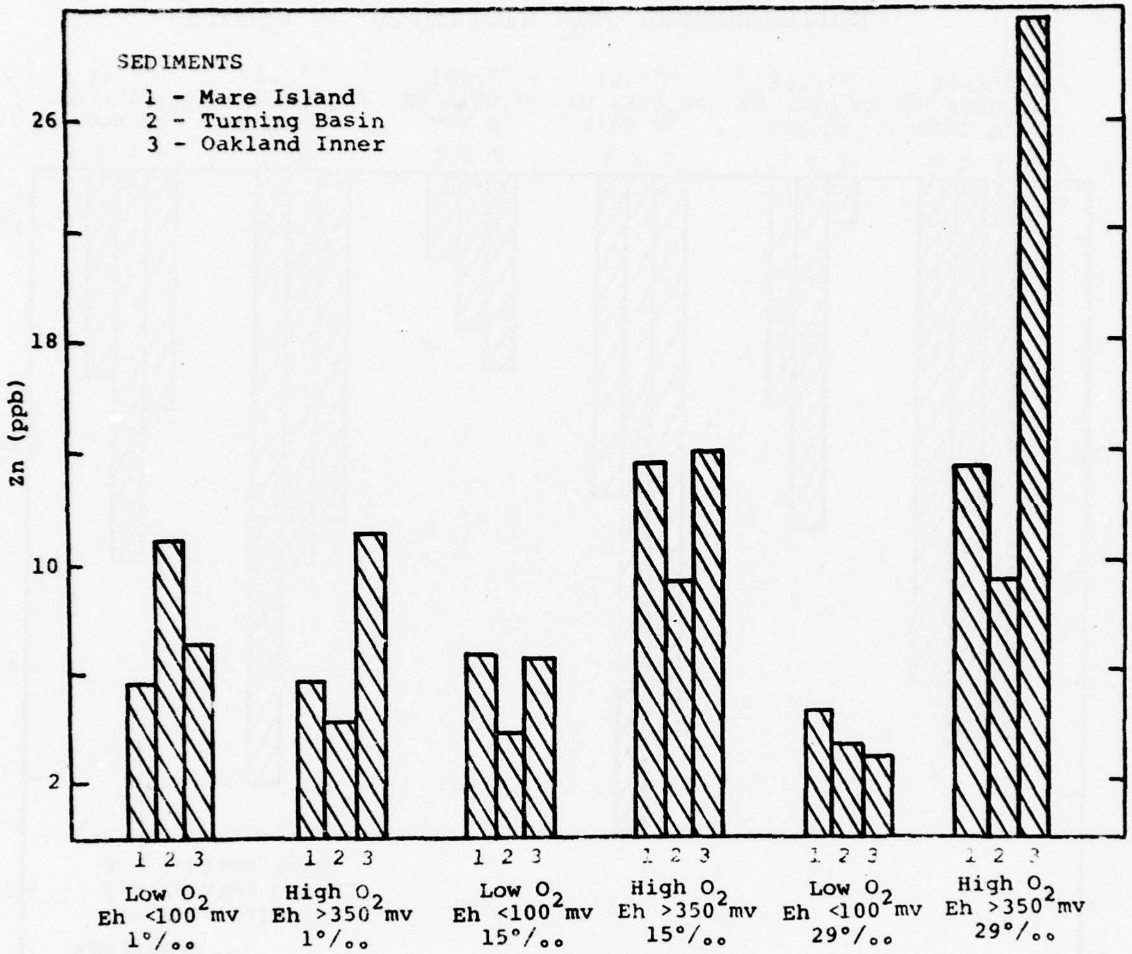


FIGURE 6. ELUTRIATE ZINC CONCENTRATION

TABLE XLV

T-TEST RESULTS FOR DIFFERENCES IN METAL CONTENT DUE TO REDOX POTENTIAL DIFFERENCES

	Mare Island	Turning Basin	Oakland Inner Harbor
Cd	t = 3.86	t = 2.37	t = 2.14
Significance	99.9%	97%	95%
Cu	t = 6.90	t = 3.69	t = 4.22
Significance	99.9%	99.5%	99.9%
Fe	t = 3.82	t = 4.37	t = 4.23
Significance	99.9%	99.9%	99.9%
Pb	t = 3.65	t = 4.62	t = 3.72
Significance	99.5%	99.9%	99.5%
Zn	t = 3.17	t = 0.69	t = 2.94
Significance	99.5%	50%	99.0%

average of nine data points (3 agitation times x3 solids/solution ratios) for iron cadmium, copper and zinc and six data points (3 agitation times x2 solids/solution ratios) for lead.

Large differences between elutriate concentrations under low oxygen conditions and under high oxygen conditions are apparent for all metals. Several of the metals, iron, cadmium and zinc show increasing elutriate concentrations with increasing salinity. Elutriate concentrations of each metal often differ greatly from one sediment to another. The differences in elutriate concentrations versus sediment will be discussed later. Differences in elutriate concentrations versus the other independent variables were statistically analyzed by analysis of variance techniques.

The sediments were analyzed separately as were the two redox conditions for each sediment. Thus six sets of data were analyzed:

1. Mare Island - oxidized
2. Mare Island - reduced
3. Turning Basin - oxidized
4. Turning Basin - reduced
5. Oakland Inner - oxidized
6. Oakland Inner - reduced

Each set consisted of the dependent variables (trace metal concentrations) and three independent variables at three levels: S‰, agitation time, and solids content. In the case of lead, values were available for only two levels of solids content. F test statistics were performed to determine which independent variables and first order interactions show significantly different trace metal concentrations at the different levels. Results are presented in Tables XLVI and XLVII for the reduced and oxidized redox potentials respectively. Under reducing conditions there was no significant difference in the cadmium or lead concentrations at the levels of independent variables studied. The zinc data show two sporadic significant variables for the Mare Island sediment.

It appears that varying the solids content has an effect on the concentration of copper found in solution under low oxygen conditions. For all three sediments more copper was found in solution at the highest solids content and the least copper in solution was present at the lowest solids content.

TABLE XLVI

SIGNIFICANT VARIABLES UNDER REDUCING CONDITIONS (Eh <100 mv)

	S‰	Time	Solids	Interactions S‰ x Time	S‰ x Solids	Time x Solids
Mare Island Cd						
Turning Basin Cd						
Inner Harbor Cd						
Mare Island Cu		X	X			
Turning Basin Cu			X			
Inner Harbor Cu	X					
Mare Island Fe	X		X		X	
Turning Basin Fe	X		X			
Inner Harbor Fe	X		X			
Mare Island Pb						
Turning Basin Pb						
Inner Harbor Pb						
Mare Island Zn		X	X			
Turning Basin Zn						
Inner Harbor Zn						

TABLE XLVII

SIGNIFICANT VARIABLES UNDER OXIDIZING CONDITIONS (Eh >350 mv)

				Interactions		
	S‰	Time	Solids	S‰ x Time	S‰ x Solids	Time x Solids
Mare Island Cd	X	X	X	X	X	
Turning Basin Cd	X	X			X	
Inner Harbor Cd	X	X			X	
Mare Island Cu		X	X			X
Turning Basin Cu	X	X	X			
Inner Harbor Cu		X	X			
Mare Island Fe			X			
Turning Basin Fe						
Inner Harbor Fe			X			
Mare Island Pb						
Turning Basin Pb						
Inner Harbor Pb						
Mare Island Zn	X					
Turning Basin Zn	X	X	X			
Inner Harbor Zn	X	X		X		

For the iron in solution under reducing conditions, both salinity and the solids content significantly affected the concentration found in the elutriate. For all three sediments the higher the salinity the higher the concentration of iron found in the elutriate. The solids content data show the same increasing trend in iron concentration in the elutriate with increasing solids content. Figures 7 and 8 show the mean iron concentrations in the elutriate at the different levels of salinity and solids content.

Elutriates that are oxidized show significantly different cadmium concentrations at the three levels of salinity and three agitation times. The salinity effect on the cadmium concentration under oxidizing conditions shows high elutriate cadmium values at higher salinities. At longer agitation times more cadmium is found in solution than at short agitation times. Figures 9 and 10 show average cadmium concentrations at the different salinity and agitation times.

The copper elutriate data show that under oxidizing conditions time and solids content significantly affect the final copper concentration for all three sediments. Salinity shows significant effects only for the Turning Basin sediment with average concentrations of 4.6 ppb, 3.2 ppb and 3.2 ppb at 1‰, 15‰, and 29‰ respectively.

For all three sediments more copper was found in the elutriate at the longest agitation time than at the shorter times for the high oxygen conditions. Also as the solids content of the

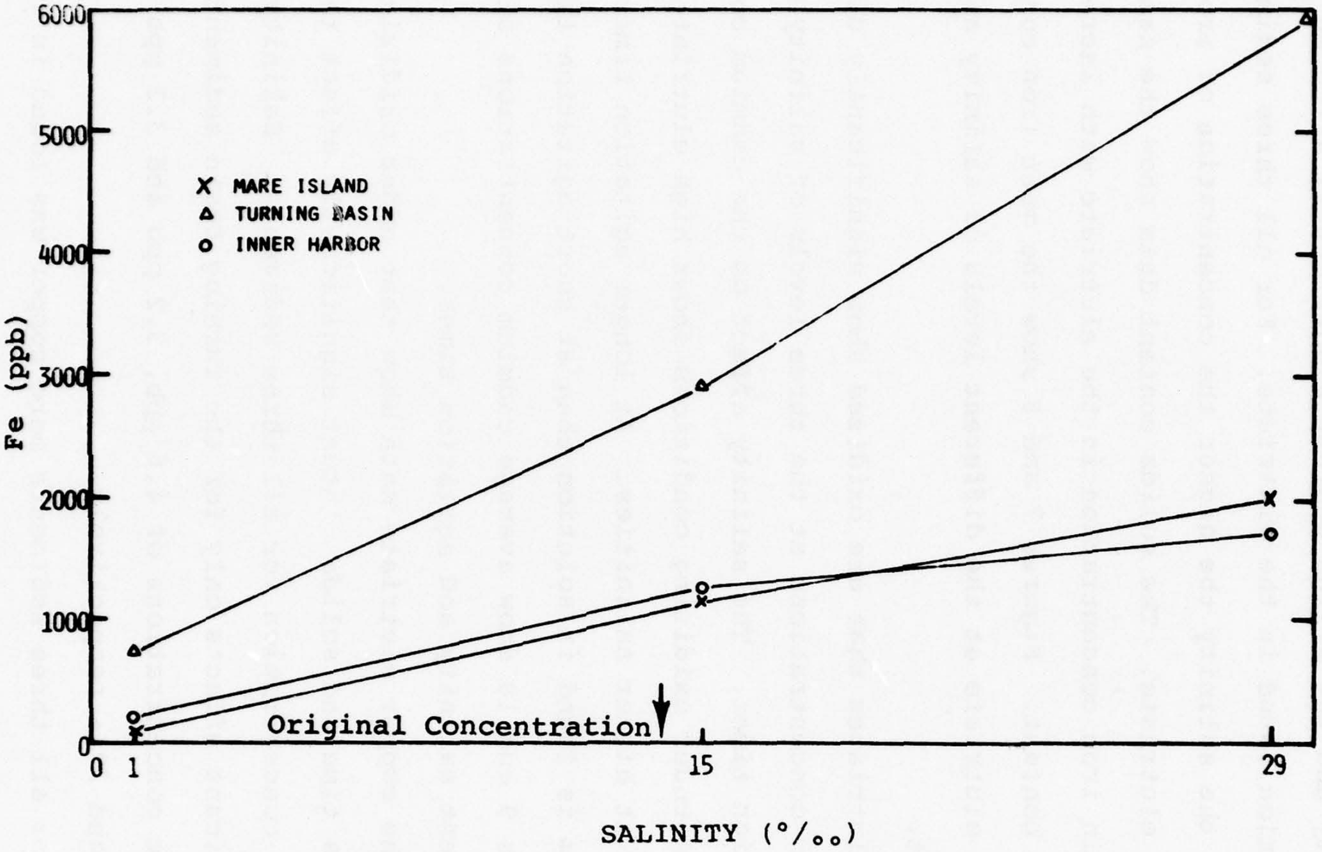


FIGURE 7. AVERAGE IRON CONCENTRATION VS SALINITY FOR REDUCING CONDITIONS (LOW OXYGEN CASES)

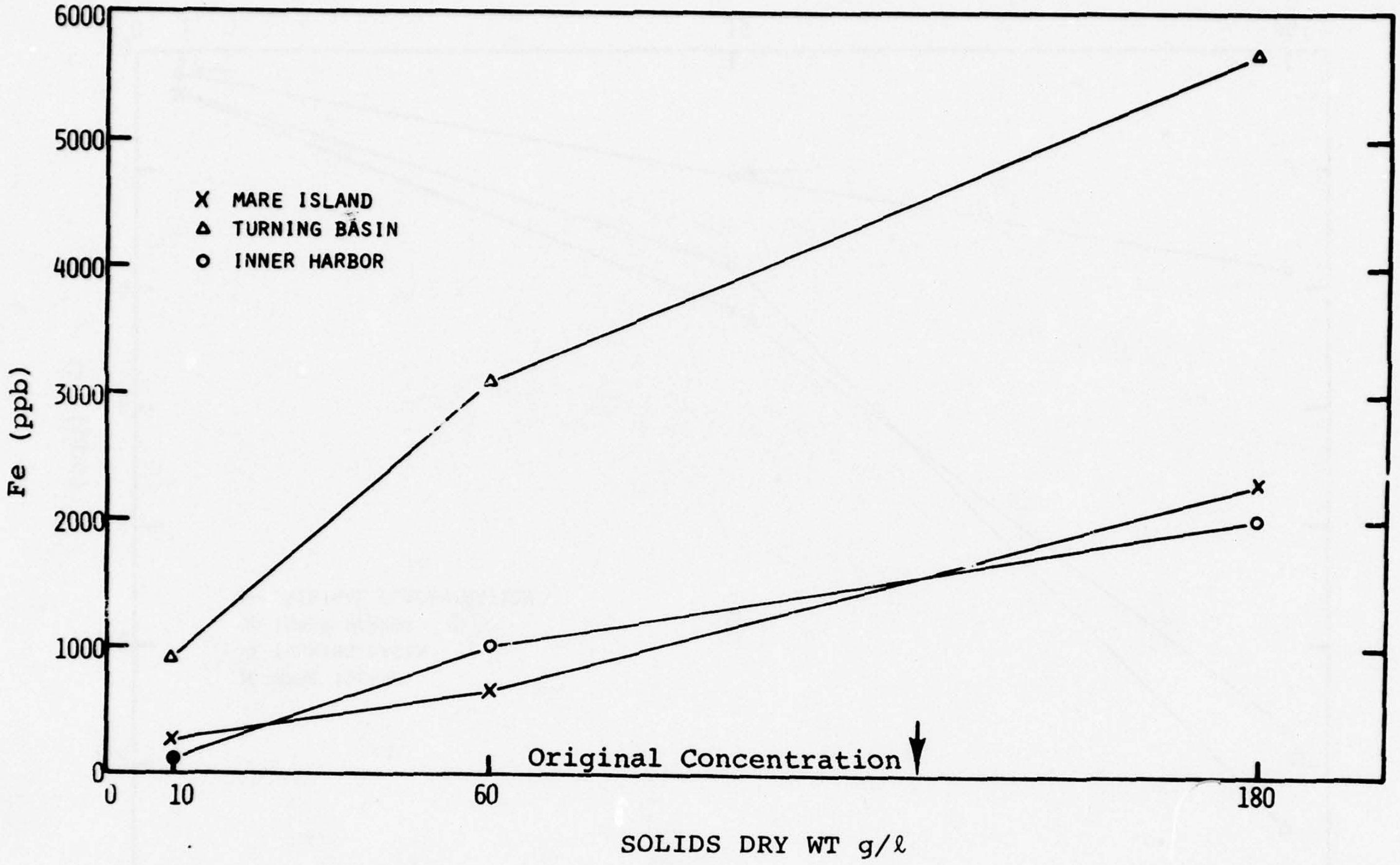


FIGURE 8. AVERAGE IRON CONCENTRATION VS SOLIDS CONTENT FOR REDUCING CONDITIONS (LOW OXYGEN CASES)

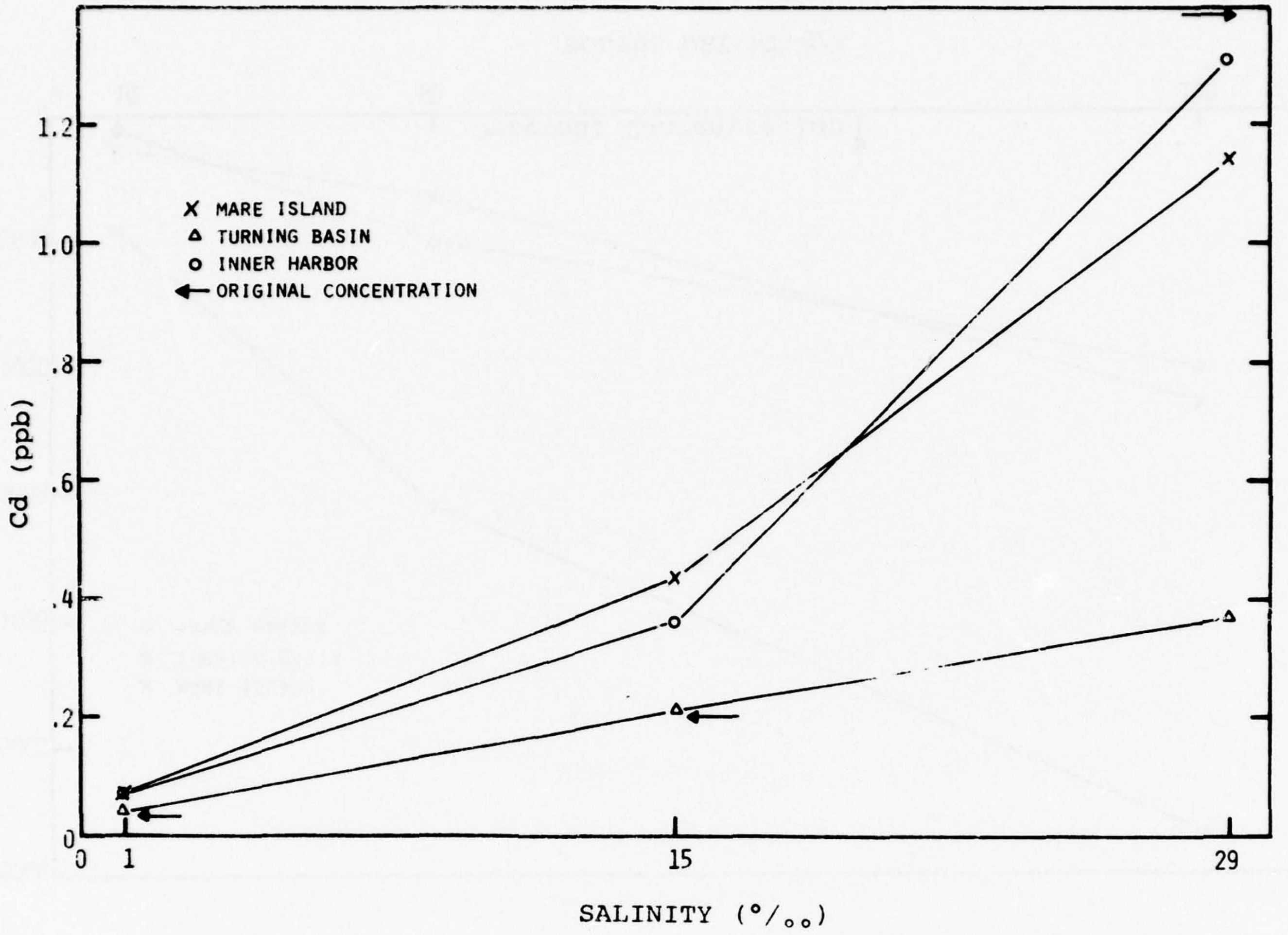


FIGURE 9. AVERAGE CADMIUM CONCENTRATION VS SALINITY FOR OXIDIZING CONDITIONS (HIGH OXYGEN CASES)

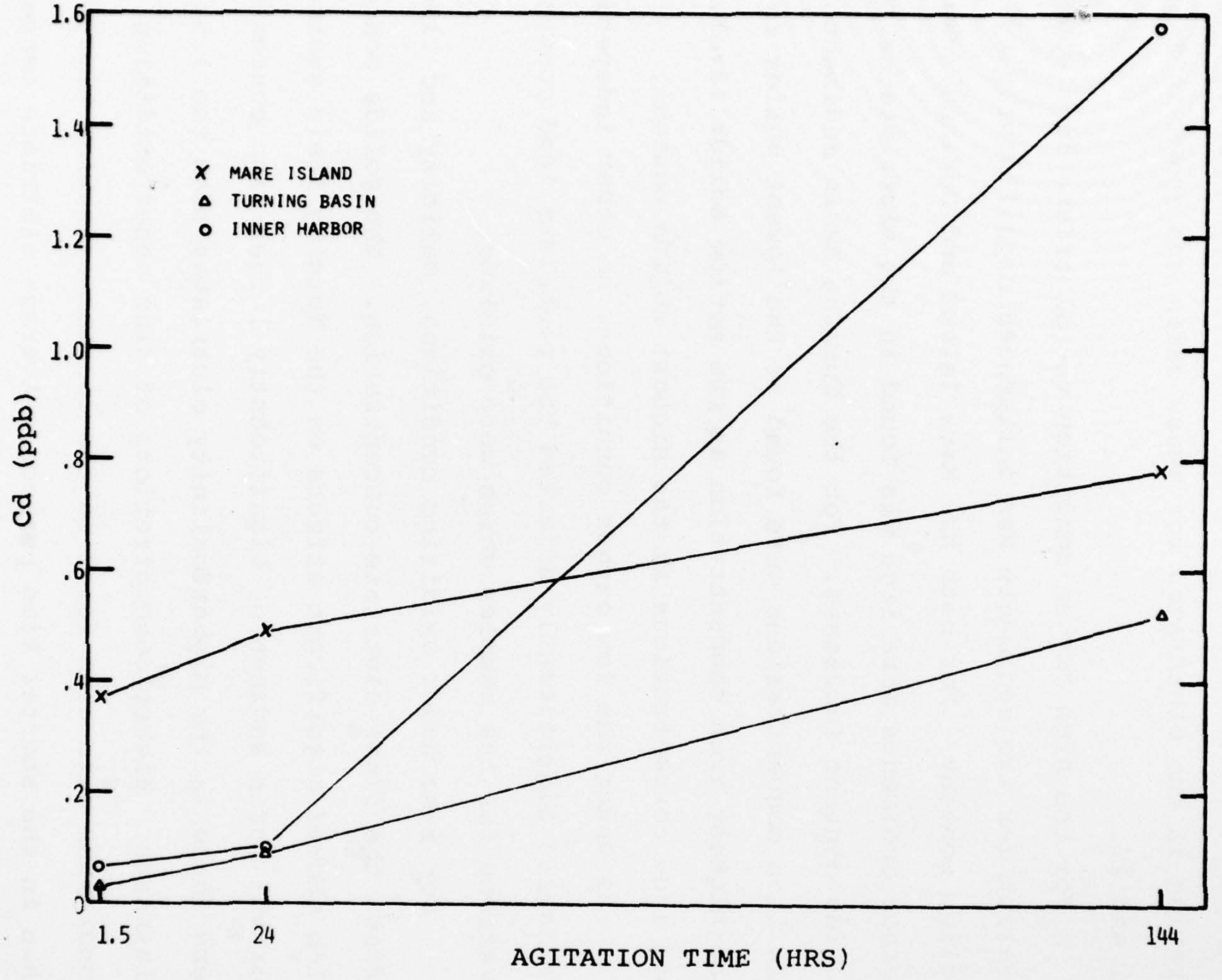


FIGURE 10. AVERAGE CADMIUM CONCENTRATION VS TIME FOR OXIDIZING CONDITIONS (HIGH OXYGEN CASES)

sediment increased so did the copper concentration in the elutriate for the oxidized condition. Average copper concentration in the elutriates for these cases are shown in Figures 11 and 12.

For the high oxygen condition the elutriate iron concentration for two sediments was influenced significantly by the solids content. For both the Mare Island and Oakland Inner Harbor sediments more iron was found in the elutriate as the solids content increased. For the Turning Basin sediment, low iron concentrations were found at the lowest solids ratio, the highest iron concentration at the medium solids level, and mid iron concentrations at the highest solids content.

As under the low oxygen conditions, no other independent variables significantly affected the elutriate lead concentrations for the samples which were oxidized.

For zinc under oxidizing conditions, salinity and time affect the final elutriate concentration. The solids content also showed significant effects on the Turning Basin sediment. For all three sediments, significantly larger zinc concentrations were found in the higher salinity elutriates than the 1.5‰ elutriate. Higher concentrations of zinc under oxidizing conditions were also found in the longest agitation time samples than in the shorter time periods. Average elutriate concentrations versus salinity and time are plotted in Figures 13 and 14. Significantly higher zinc was found in samples with the highest solids content for the Turning Basin sample.

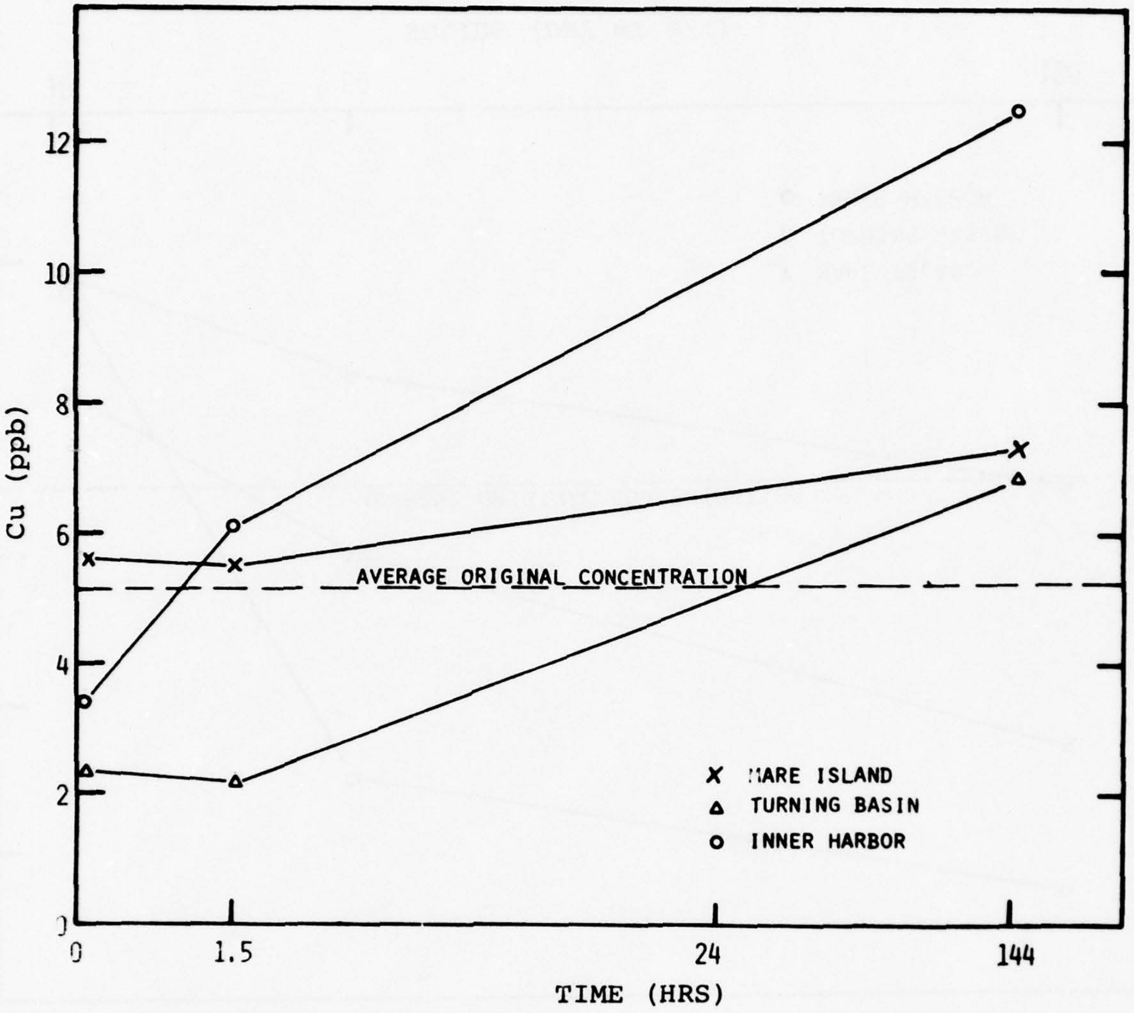


FIGURE 11. AVERAGE COPPER CONCENTRATION VS TIME FOR OXIDIZING CONDITIONS (HIGH OXYGEN CASES)

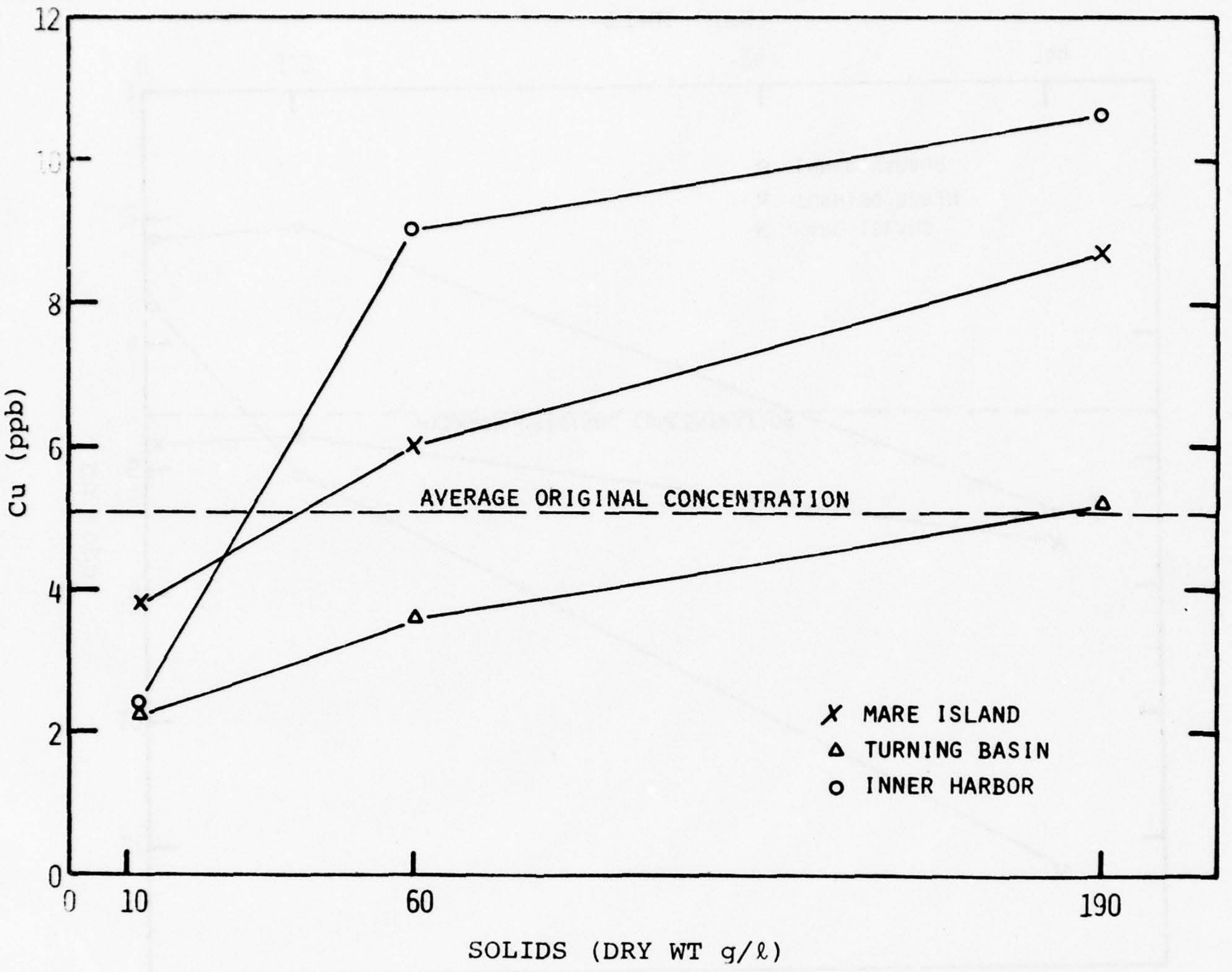


FIGURE 12. AVERAGE COPPER CONCENTRATION VS SOLIDS FOR OXIDIZING CONDITIONS (HIGH OXYGEN CASES)

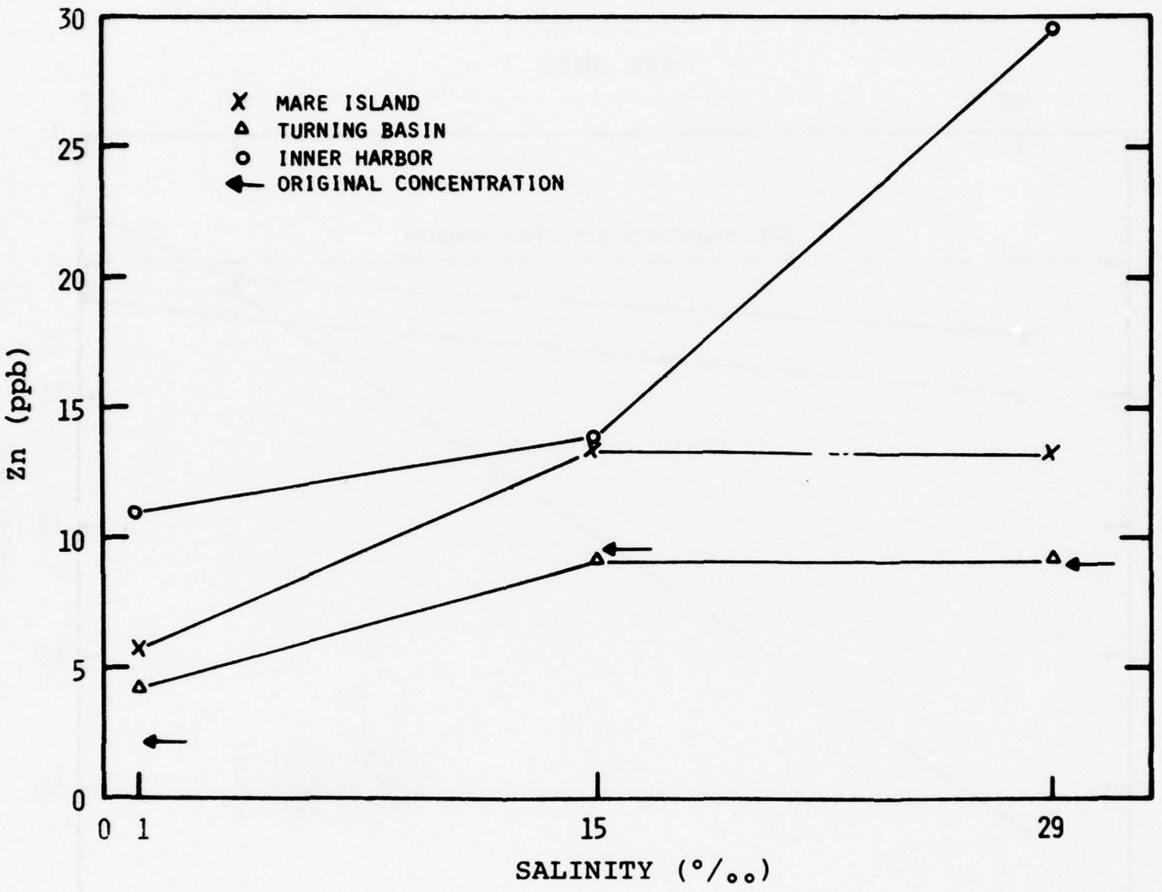


FIGURE 13. AVERAGE ZINC CONCENTRATION VS SALINITY FOR OXIDIZING CONDITIONS (HIGH OXYGEN CASES)

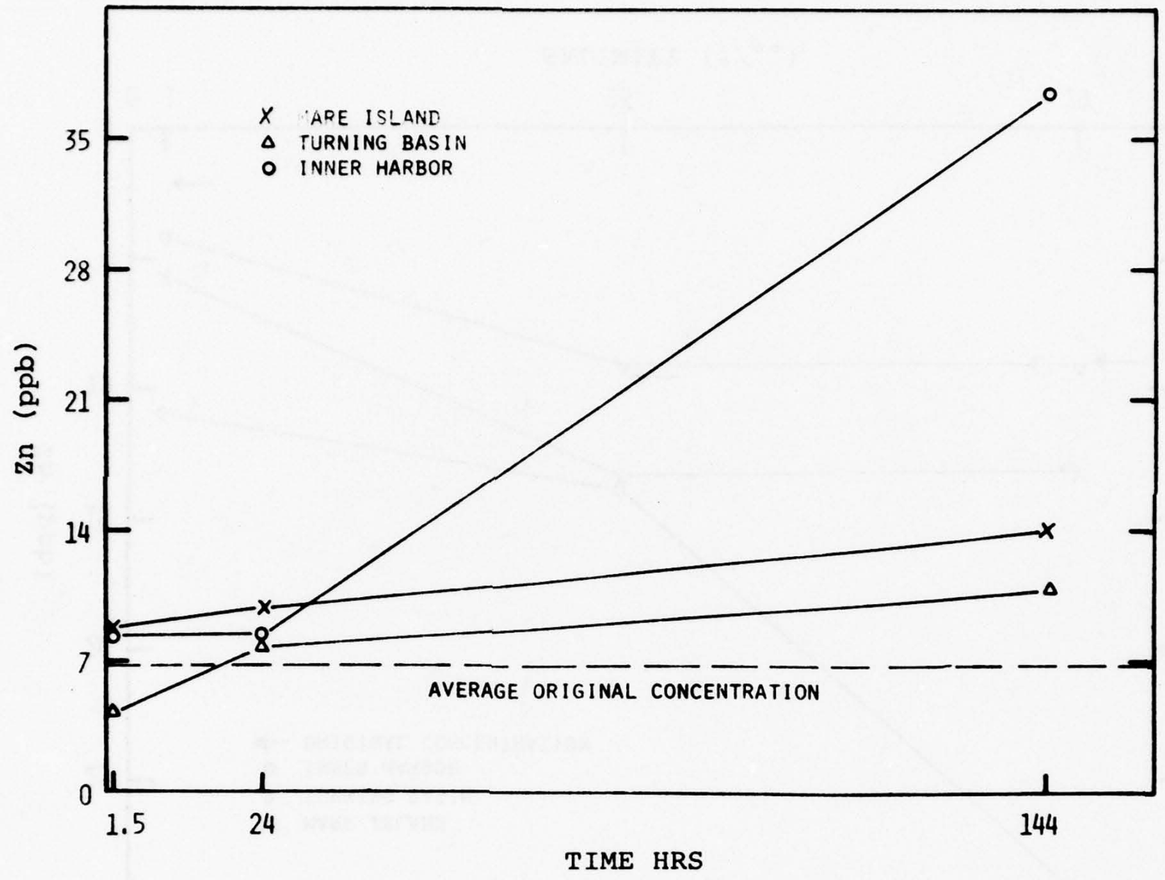


FIGURE 14. AVERAGE ZINC CONCENTRATION VS TIME FOR OXIDIZING CONDITIONS (HIGH OXYGEN CASES)

The above statistical testing of the elutriate concentrations of each sediment separately leads to the following conclusions. For the variables tested the oxidation-reduction potential and dissolved oxygen content appear to be the most significant environparameters which control the final elutriate concentration of the metals studied. The trace metals cadmium, copper, lead, and zinc all showed significantly higher concentrations in elutriates that were oxidized. Under reducing conditions and in the presence of sulfides these metals would be very susceptible to sediment incorporation as insoluble sulfides. Perhaps this is the controlling mechanism which caused very low soluble concentrations of these trace metals in elutriates in contact with reduced San Francisco Bay sediments. Under oxidized conditions inorganic soluble complexes with Cl^-, HCO_3^-, and SO_4^- and organic soluble complexes with fulvic and humic acids may allow the higher concentrations found in the elutriates. Hydrous iron, aluminum and manganese oxides and silicate clays would compete with the soluble complexes to keep the elutriate concentrations low.

Iron, and by inference manganese, act in an opposite manner with higher concentrations found in the reduced elutriates than were found in the oxidized elutriates. This may be explained by the increased solubility of the lower valence species (Fe^{+2} and Mn^{+2}) over the chemical species found under oxidizing conditions. At the observed 7 to 8 pH, iron and manganese under oxidizing conditions readily precipitate as amorphous hydrous oxides.

No differences were detectable in the solubility of mercury in the elutriates. In all cases the elutriate concentration of mercury was below the detection limit of the analytical procedure utilized. Similar results on the effect of redox potential on elutriate concentrations of trace metals were found by Lu and Chen[79] while studying Los Angeles Harbor sediments.

The effects of salinity, when significant, showed higher elutriate concentrations at higher salinities. This phenomenon could be explained by the increase in inorganic ligand-metal soluble complexes which could form at the elevated ligand concentrations present in higher salinity waters.

A second explanation for the increase in elutriate trace metals with increasing salinity is that the greater cation concentrations of Ca^{++}, Mg^{++} and Na^{+} would compete for the finite ion exchange sites on the sediments. Although the semi selective extraction results appear to show the relative distribution of trace metals sorbed on exchangeable sites is insignificant, the extremely small releases (parts per billion) of cadmium, copper, lead and zinc could be explained by release from exchangeable sites. On the other hand if exchangeable trace metal release was the source of the increase in elutriate concentrations, any trace metal capable of ion-exchange would have been expected to increase with salinity and not just selected metals as observed.

A third explanation which is inherent in the sorption-desorption experiment is the fact that the independent variable redox condition or dissolved oxygen content, which was very importai was not precisely controlled in the experiment.

The dissolved oxygen contents of the elutriates were compared to determine whether the salinity effects found might actually have been caused by slightly varying redox potentials for the various salinities. T-test results showed no significant differences in the dissolved oxygen contents at the various salinities. Thus the salinity effects are probably real. Salinity significantly influenced the cadmium and zinc elutriate concentrations under oxidizing conditions and significantly affected the iron concentrations under reducing conditions. The lack of effects on the lead and minor effects on copper may signfy that soluble inorganic complexes of these two metals are not important. Zirino and Yamimoto[52] presented a speciation model for trace metals in seawater which showed that at the mean pH value of these batch experiments (7.6±0.4), copper would be 75 percent $Cu(OH)_2°$ and thus not dependent on salinity. At higher pH values or lower salt contents the $Cu(OH)_2°$ form becomes even more dominate. At pH 7.6, the soluble zinc distributes between $ZnCl^+$ (20%), Zn^{++} (45%), $Zn\ (OH)_2°$ (20%) and $Zn\ (SO_4)°$ (10%) and thus an increase in salinity which would increase Cl^- and SO_4^{-2} might result in the formation of more soluble zinc complexes. The cadmium speciation is rather insensitive to pH and at values near 7.6 show a distribution of 50 percent $CdCl_2°$ and 40 percent $CdCl^+$. Thus total soluble cadmium complexes would be sensitive to salinity as was found. At pH 7.6 lead would be 60 percent $PbCO_3°$, 25 percent $PbCl^+$ and 10 percent $PbCl_2°$ and thus sensitive to salinity which is contrary to the results of this experiment. It must be kept in mind that this theoretical model excludes organics and other inorganic mixed ligand complexes which may be of importance in seawater.

The length of agitation time appears to significantly effect the elutriate concentrations of cadmium, copper and zinc under oxidizing conditions. At the longest agitation time, the elutriate concentrations were found to be largest for the above metals. This possibly signifies a kinetic effect. The formation of soluble complexes should occur rapidly and therefore, the kinetic effect must be caused by other phenomena. One explanation of the time effect could be that the oxidation of the reduced sediment takes several days to complete. A t-test check of the observed dissolved oxygen contents versus agitation times showed no significant differences,but a similar test of the observed Eh values versus agitation times showed significant differences for all three sediments. The Eh's measured for the one hour agitation times were significantly different (more positive) than Eh values after 24 or 144 hours. Therefore, a redox dependent mechanism cannot be ruled out as being the cause of the time differences in elutriate concentrations.

The solids content of the slurry significantly affected the elutriate concentrations of iron and copper under both redox conditions. The higher the solids content of the sample the larger the elutriate concentration of these metals. One explanation for the iron could be that at the higher solids content more suspended particles less than 0.45μ were probably present in the elutriate. Since small particulates of high iron content are found in seawater the higher iron contents found may reflect the greater particulates in the filtered elutriate. The results may also just reflect the larger source of trace metals in the sediment which could release more metals if adsorption mechanisms are somewhat less powerful than desorption or dissolution mechanisms. Also the dissolved oxygen contents of the various solids contents varied significantly in one third of the possible combinations. The dissolved oxygen differences could cause an over-estimation of the significance of the solids effects.

The effects of different types of sediment are difficult to assess from the data obtained during this experiment. The three sediments utilized show very little variation (<20%) in clay content, cation-exchange-capacity, total organic content, total zinc, and total copper content and only moderate (>30%) variation in total cadmium, lead and iron contents. The only bulk parameter which showed significant differences was the sediment total sulfide content.

An analysis of variance test on all the data lumped together shows that the sediment type was of less significance than other variables. Table XLVIII lists the order of significance in explaining the variation of elutriate concentrations of each of the independent variables in the factorial batch tests. The data show that the sediment type does not significantly aid in the understanding of the elutriate concentrations in this

TABLE XLVIII

ORDER OF SIGNIFICANCE OF INDEPENDENT VARIABLES

Order	Cd	Cu	Fe	Zn	Pb
1	DO	DO	DO	DO	DO
2	S‰	Solids	Solids	Time	Solids
3	Time	Time	S‰	Sediment	Sediment
4	Sediment	Sediment	Sediment	S‰	Time
5	Solids	S‰	Time	Solids	S‰

DO = Dissolved oxygen content of elutriate
S‰ = Initial salinity
Time = Agitation time
Solids = Solids to solution ratio
Sediment = Type of sediment

experiment. Whether in general the bulk parameters of the sediment can be used to significantly aid in the understanding of trace metal concentrations in elutriates needs further investigation. This investigation utilized only three sediment types and unfortunately, few of the bulk parameters of the chosen sediments varied substantially. The resluts are further confounded by the fact that the final elutriate dissolved oxygen contents of the Turning Basin samples were significantly lower than the Oakland Inner Harbor and Mare Island samples. Because the dissolved oxygen content appears to be the most significant parameter studied, the lack of adequate control of the oxygen contents may over-emphasize the difference in elutriate trace metals observed between sediments.

Lu and Chen's[79] results on two types of sediments showed much larger differences in bulk parameters such as clay contents, total organic carbon, total sulfide contents and total heavy metals contents. The amount of trace metals transported across an equal sediment-water interface under oxidizing conditions was found to be larger for a silty sand than for a silty clay despite the fact that the sand had significantly lower total concentrations of trace metals.

The sorption-desorption data were also compared to see whether the elutriate water concentrations increased over the original values. This type of comparison is important when trying to interpret the change in water quality of a given water by disturbances such as dredging and has been suggested as a legal criterion for determining whether a disturbance is detrimental to the environment.[126] Analysis of the raw data for each individual case to see whether the elutriate water concentrations increased over the original values shows much scatter. In order to present a clearer picture, the ratio of the average elutriate concentration at each salinity, redox condition and sediment to the respective initial water concentrations are shown in Figures 15-19. The elutriate concentration represents the averaging of nine data points for the iron, cadmium, copper and zinc (3 agitation times x3 solids/solution ratio) and six data points for lead (3 agitation times x2 solids/solution). Initial water concentrations for each salinity are from Table XLIV.

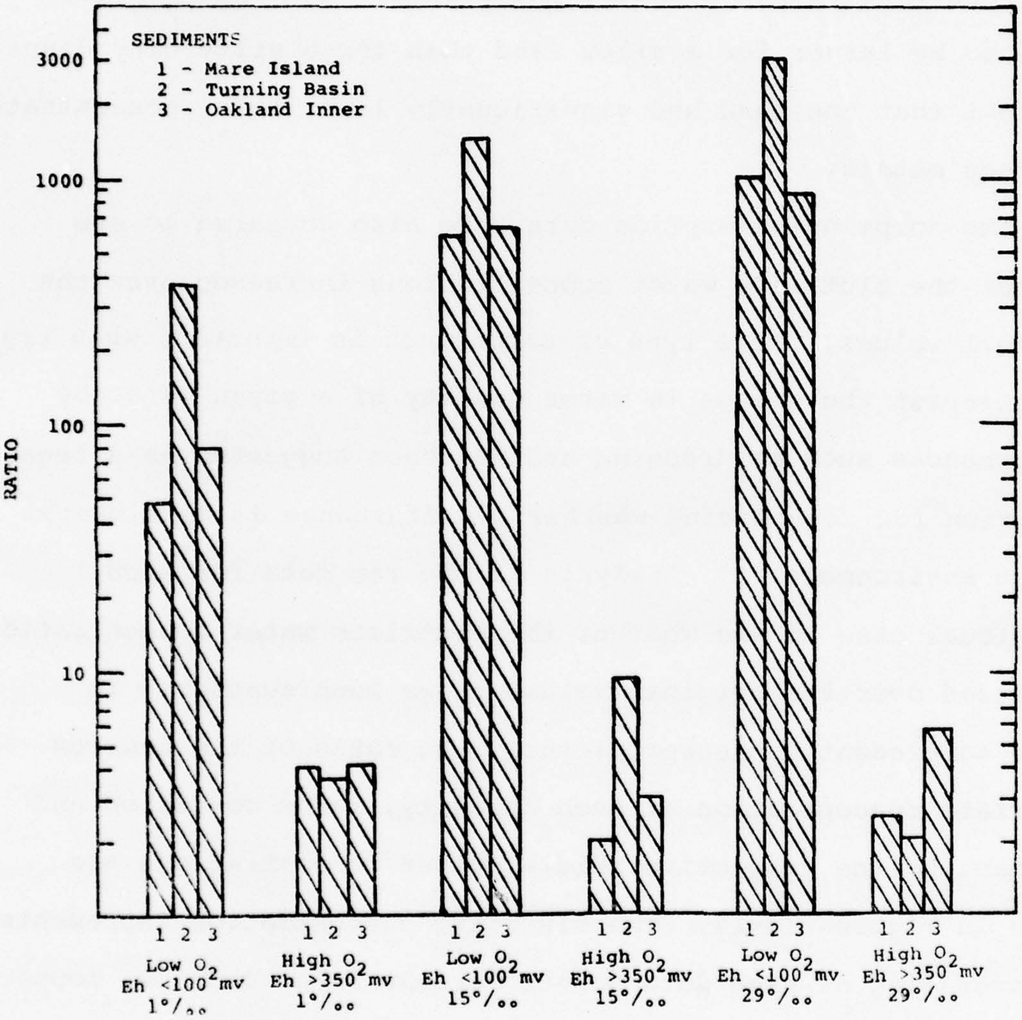


FIGURE 15. IRON RATIO OF ELUTRIATE TO ORIGINAL WATER

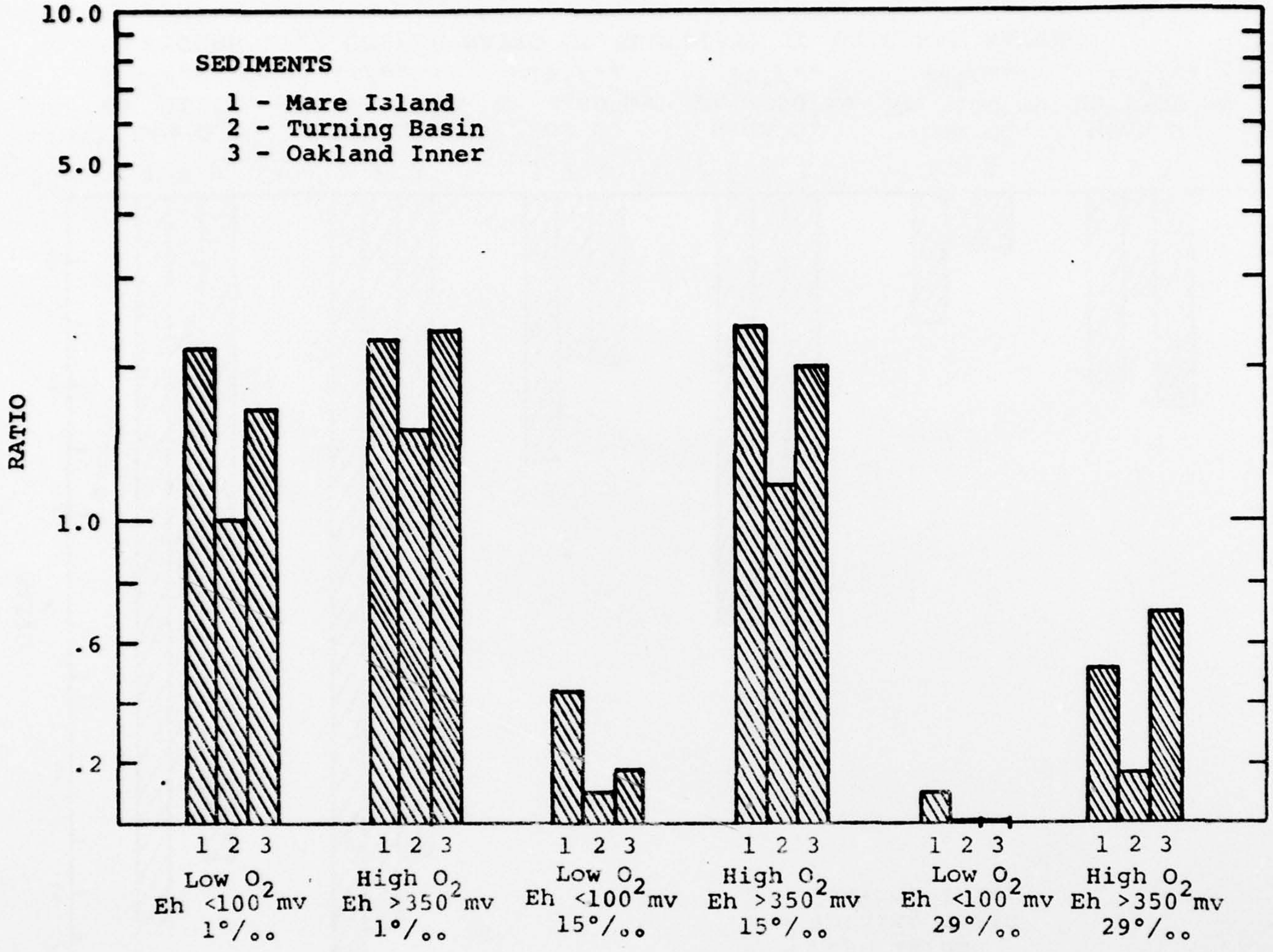


FIGURE 16. CADMIUM RATIO OF ELUTRIATE TO ORIGINAL WATER

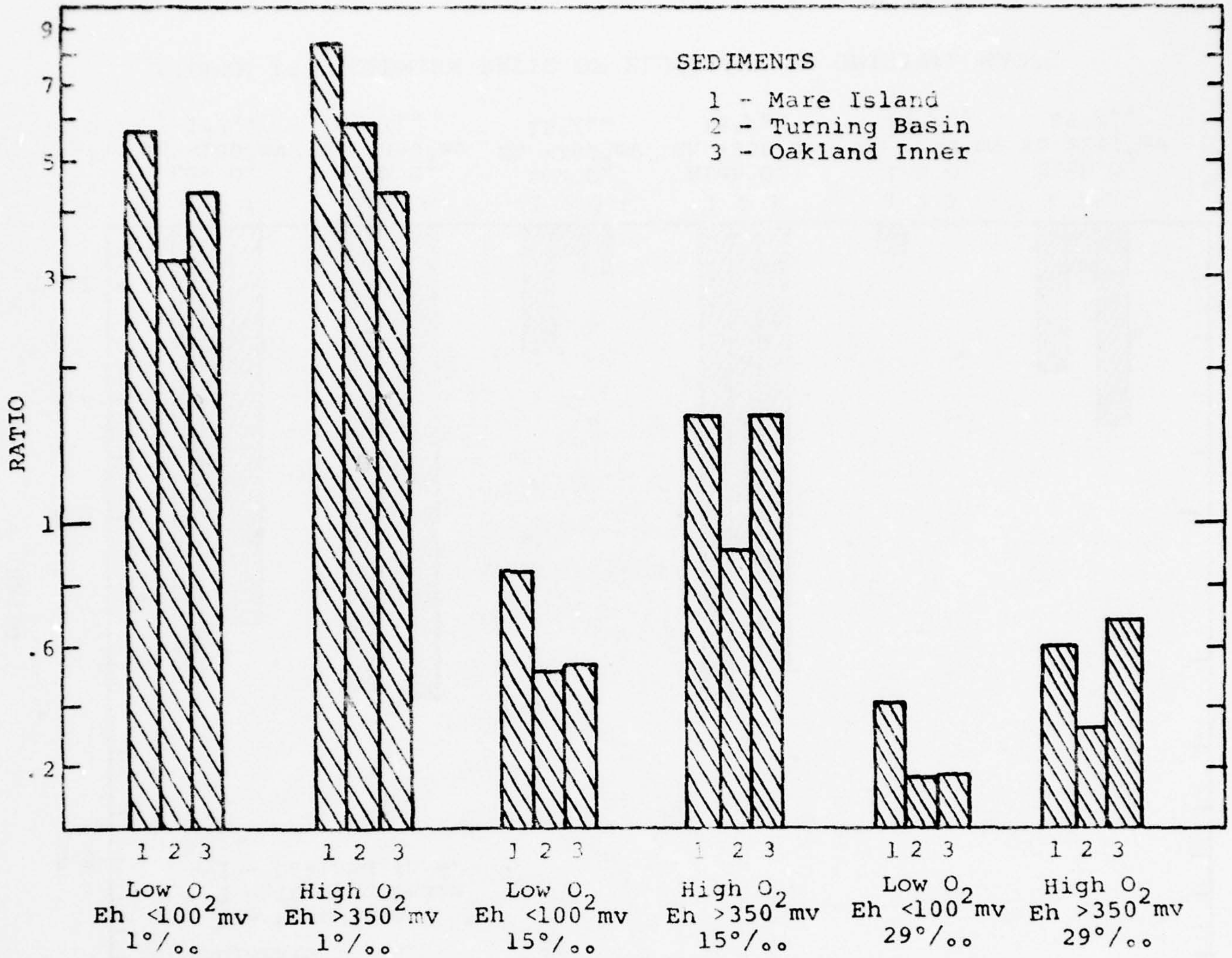
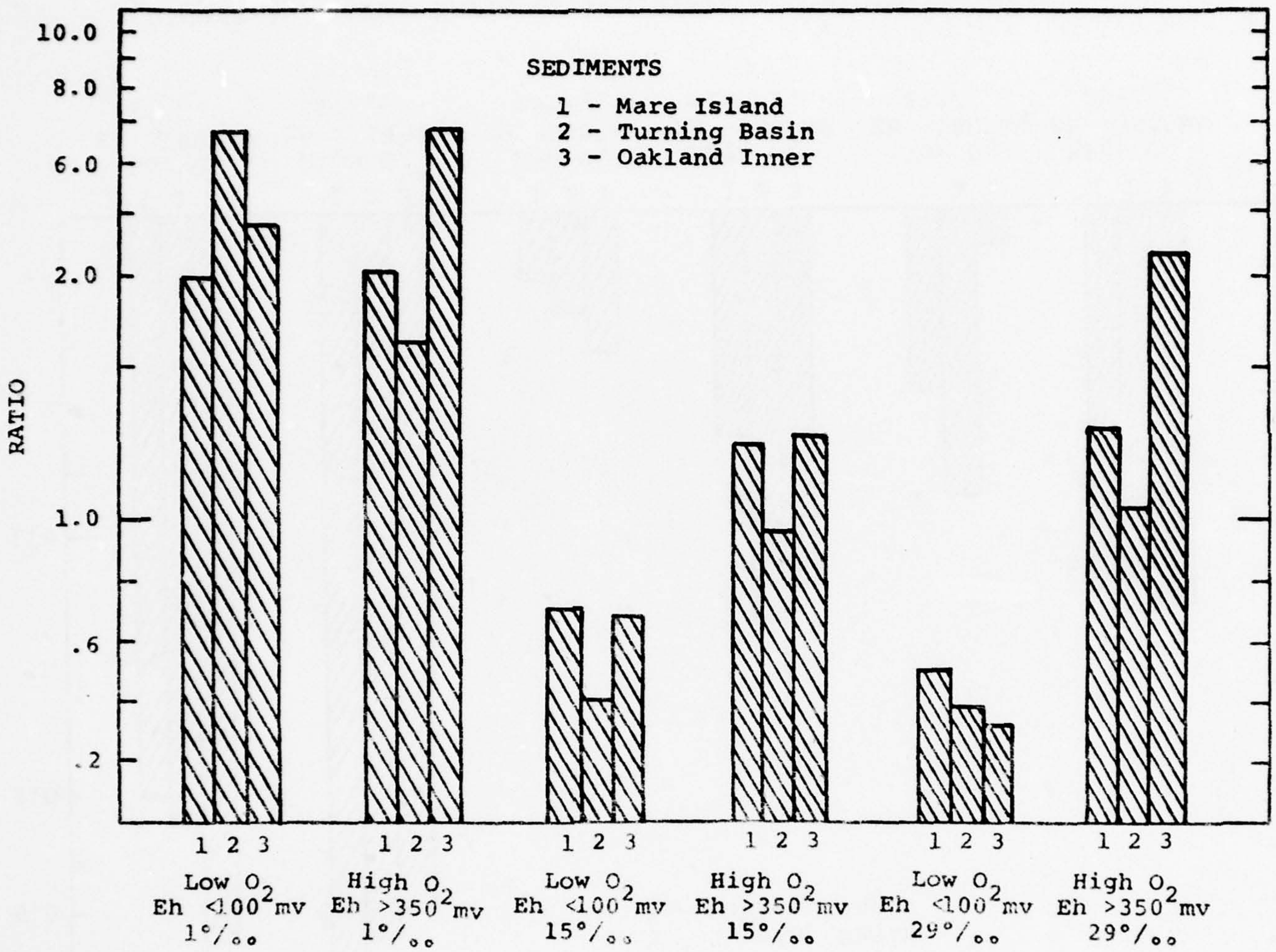


FIGURE 17. COPPER RATIO OF ELUTRIATE TO ORIGINAL WATER



GURE 18. ZINC RATIO OF ELUTRIATE TO ORIGINAL WATER

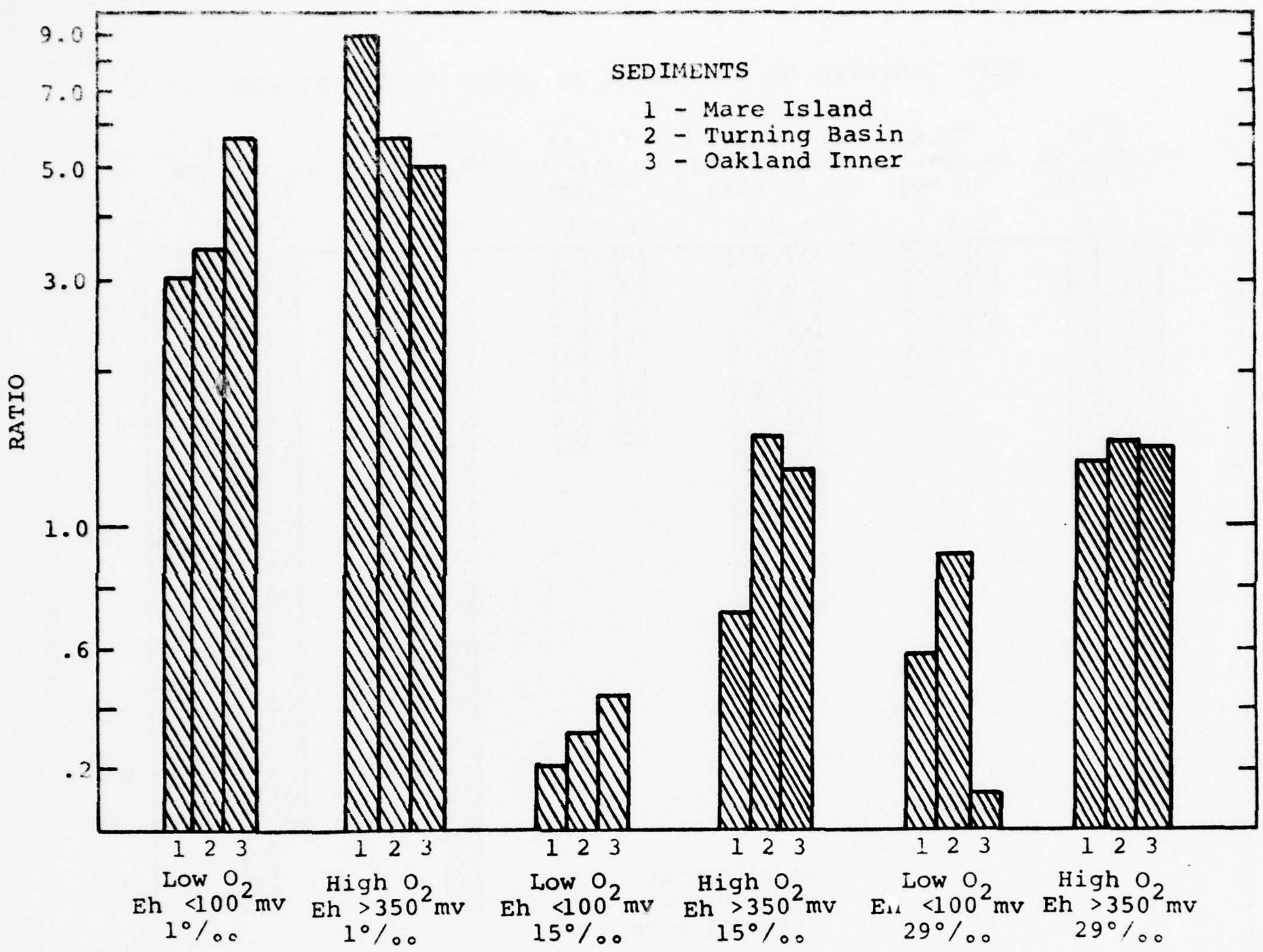


FIGURE 19. LEAD RATIO OF ELUTRIATE TO ORIGINAL WATER

An elutriate/original water ratio greater than one represents net release from the sediments while a ratio less than one represents net sorption by the sediments.

Figure 15 shows that under both redox conditions at all three salinities for all three sediments iron is released to the water. The magnitude of the release is much higher under reducing conditions than oxidizing conditions and increases with increasing salinity under the reducing conditions.

Figure 16 shows that at the low salinity and at both redox conditions for all three sediments cadmium is released. At the $15^{\circ}/_{\circ\circ}$ salinity the reduced condition exhibits net sorption of cadmium while the oxidized condition exhibits net release. At the high salinity all six cases show net sorption. The release at the low salinity may reflect the fact that the original water was not a natural sample but was an arbitrary mixture of estuarine water with distilled water. The mixture may thus be trace metal deficient in comparison to a natural $1^{\circ}/_{\circ\circ}$ water. The $29^{\circ}/_{\circ\circ}$ original water sample appeared to be contaminated because of an anomously high cadmium concentration. It thus appears that the net sorption (at high salinity) in the sorption-desorption experiment may reflect the unnaturally high original concentration possibly caused by an inadequately cleaned container.

The copper data presented in Figure 17 exhibit the same trends as the cadmium. Again the low salinity cases show net desorption while the high salinity cases show net adsorption. The use of the distilled water and suspected contaminated high salinity water appear to be biasing the resluts. The 15°/oo cases show net release under oxidizing conditions and net sorption under reducing conditions. The original 15‰ copper concentration agrees more closely with values found in the Bay and reported in Table XXIII.

The zinc data shown in Figure 18 again show net desorption in all cases at the low salinity, again possibly caused by the unnatural dilution with distilled water. The original 15‰ and 29‰ waters agree with values found naturally in San Francisco Bay presented in Table XXIII. At these higher salinities the data again show net release under oxidizing conditions and net sorption under reduced conditions.

Figure 19 shows that lead trends are very similar to the just mentioned zinc results. The 1‰ cases show large net desorption while the other two salinities with original concentrations closer to values reported in the Bay show a net sorption of lead under reducing conditions and a net release in five out of six oxidizing cases.

In the cases where the original water concentrations of the trace metals cadmium, copper, lead and zinc agree with values reported for San Francisco Bay waters it appears that a net release occurs under oxidizing conditions. The ratio of the elutriate to original water trace metal concentrations for these cases generally range from 1 to 1.6. In only one case, the zinc concentrations for the Oakland Inner Harbor at 29°/oo, does the ratio exceed 2. Only in the case of iron are the ratios and thus release of a great magnitude.

Predictor Relationships

The results of the factorial design sorption-desorption experiment were used to develop multiple regression predictor equations for the final elutriate concentrations of the metals cadmium, copper, iron, lead and zinc. Mercury predictor equations were not developed because all the experimental results were below the detection limit of the analytical method employed.

The analysis of variance results reported in this section show that interaction terms between the main variables (salinity, dissolved oxygen content, agitation time, and solids content) seldom significantly affect the final elutriate metal concentrations. Therefore, to develop predictor equations for each sediment type, the four main variables listed above were utilized. The squared term of each main variable was also added to the initial models but did not significantly improve the predictability of the elutriate metal concentrations. Logarithmic transformations of the sorption-desorption elutriate data were also investigated and in two cases improved the regression equation. The simplest predictor equations for the metal concentrations which include all the significant variables are presented in Table XLIX. The multiple correlation coefficients (r) which estimate the "goodness of fit" of the predicted metal concentrations to the observed concentrations are also given. An r value of ±1 signifies perfect fit while the r^2 value represents the fraction of variance in the metal concentrations that the model explains.

TABLE XLIX

PREDICTOR EQUATIONS FOR EACH SEDIMENT

Mare Island Sediment

$\text{Cd} = -.320+.040(\text{DO})+.021(\text{S‰})+.002(\text{time}) \qquad r = .72$

$\text{Cu} = 1.21+.178(\text{DO})+.016(\text{time})+22.941(\text{solids}) \qquad r = .78$

$\text{Fe} = -43.246-100.426(\text{DO})+35.870(\text{S‰})+7688.246(\text{solids}) \qquad r = .75$

$\text{Zn} = 3.313+.450(\text{DO})+.106(\text{S‰})+.011(\text{time}) \qquad r = .51$

$\text{Pb} = .134+.015(\text{DO}) \qquad r = .40$

Turning Basin Sediment

$\text{Cd} = -.166+.029(\text{DO})+.005(\text{S‰})+.001(\text{time}) \qquad r = .60$

$\text{Cu} = .071+.183(\text{DO})+.017(\text{time})+14.808(\text{solids}) \qquad r = .72$

$\text{Fe} = 545.294-.033(\text{DO})+99.589(\text{S‰})+15389.160(\text{solids}) \qquad r = .67$

$\ln\text{Zn} = 1.218+.094(\text{DO})-.022(\text{S‰})+.001(\text{time}) \qquad r = .42$

$\text{Pb} = .190+.021(\text{DO}) \qquad r = .52$

Inner Harbor Sediment

$\text{Cd} = .611+.048(\text{DO})+.022(\text{S‰})+.006(\text{time}) \qquad r - .55$

$\ln\text{Cu} = .178+.090(\text{DO})+.002(\text{time})+4.498(\text{solids}) \qquad r = .70$

$\text{Fe} = 133.223-80.478(\text{DO})+26.639(\text{S‰})+4935.165(\text{solids}) \qquad r = .67$

$\text{Zn} = 2.320+.812(\text{DO})+.261(\text{S‰})+.107(\text{time}) \qquad r = .51$

$\text{Pb} = .165+.015(\text{DO}) \qquad r = .48$

where

Cd, Cu, Fe, Zn, Pb = the metal concentrations (ppb),
DO = dissolved oxygen content of slurry (ppm),
S‰ = salinity of original water (ppt),
time = agitation time (hrs), and
solids = solid content (g/ml).

Tables L, LI AND LII list the observed and regression equation predicted values for the cadmium, copper, iron and zinc elutriate concentrations for each sediment.

The predictor equations in general explain 20 to 60 percent of the variability in the elutriate data. The lack of better predictive capabilities emphasizes the fact that the final elutriate concentration is the net result of several competing processes. The data show much scatter which is partially a reflection of the difficulty of analyzing trace metals in the sub and low parts per billion range. Besides the analytical precision problems, other variables not monitored may be important parameters controlling the fate of the trace metals.

As stated previously, the bulk sediment parameters do not appear to be good indices of the resultant water quality of natural waters. The samples utilized in this experiment compound the problems associated with attempts to correlate sediment parameters with the resultant elutriate trace metal concentrations for three reasons. First only three different sediments were tested. To study the ability of sediment characteristics to predict resultant concentrations of trace metal concentrations in solution many different sediments should be studied. Second the three sediments chosen were very similar in particle size, organic content, cation-exchange-capacity and total trace metal content. Only the total sulfide contents varied significantly. To aid in determining the effects of bulk sediment characteristics on the elutriate trace metal concentrations, sediments with wide

TABLE L

MARE ISLAND METAL CONCENTRATIONS (ppb) IN ELUTRIATES

Sample No.	Cd		Cu		Fe		Zn	
	OBS	PRE	OBS	PRE	OBS	PRE	OBS	PRE
1	0.120	-0.039	10.0	7.6	25	1387	4.9	5.1
2	0.006	-0.039	4.6	4.7	13	403	2.0	5.1
3	0.275	-0.037	2.4	3.6	2	47	1.9	5.1
4	0.020	-0.258	3.0	5.3	10	1242	4.1	3.7
5	0.008	-0.258	1.5	2.9	53	465	4.0	3.7
6	0.015	-0.234	1.6	1.9	4	2	2.9	3.9
7	0.073	-0.288	7.4	5.4	345	1341	11.0	3.5
8	0.028	-0.288	7.7	2.5	152	388	10.7	3.5
9	0.038	-0.292	2.6	1.5	240	83	8.5	3.5
10	0.370	0.259	5.0	7.7	2412	1897	3.5	6.6
11	0.187	0.254	4.6	4.8	1060	944	7.2	6.5
12	0.102	0.260	1.4	3.6	2	55	3.3	6.6
13	0.126	0.040	2.2	5.8	1938	1897	5.2	5.2
14	0.037	0.041	1.3	2.9	1168	929	9.6	5.2
15	0.094	0.048	1.9	1.8	55	552	4.5	5.3
16	0.084	0.010	6.8	5.5	2295	1897	12.5	5.0
17	0.028	0.003	1.5	2.5	738	921	7.2	4.9
18	0.023	0.006	1.9	1.5	539	580	6.0	5.0
19	0.660	0.551	12.0	7.7	4747	2431	<0.2	8.0
20	0.202	0.558	7.2	4.7	505	1407	11.9	8.1
21	0.077	0.558	2.4	3.7	154	1060	3.9	8.1
22	0.044	0.341	5.2	5.9	4756	2425	0.9	6.6
23	0.116	0.341	1.5	2.9	808	1425	8.2	6.7
24	0.200	0.343	2.2	1.8	20	1059	2.9	6.7
25	0.660	0.301	2.8	5.5	4221	2415	<0.2	6.4
26	0.152	0.301	2.2	2.5	1414	1431	8.3	6.4
27	0.060	0.303	2.2	1.5	1334	1074	4.5	6.5
28	0.146	0.330	11.4	9.1	2	437	6.2	9.2
29	0.025	0.561	7.2	7.3	6	-1099	7.3	11.8
30	0.036	0.326	2.9	5.3	2	-834	5.8	9.1
31	0.033	0.349	6.5	8.5	9	-68	5.0	10.4
32	0.021	0.081	6.4	4.5	5	-367	6.8	7.5
33	0.064	0.095	5.0	3.4	3	-803	7.2	7.6
34	0.145	0.312	11 3	8.0	32	-130	4.3	10.2
35	0.116	0.057	6.6	4.2	12	-404	7.6	7.4
36	0.021	0.061	2.5	3.1	2	-807	1.0	7.4
37	1.140	0.753	8.6	9.4	10	53	13.8	12.1
38	0.369	0.714	6.1	6.8	4	-196	10.2	11.6
39	0.333	0.628	4.5	5.3	2	-353	36.3	10.7
40	0.651	0.646	6.3	8.3	6	349	22.4	11.9
41	0.264	0.485	6.2	4.8	5	-179	8.8	10.1
42	0.219	0.389	3.8	3.4	2	-264	6.2	9.0
43	0.451	0.609	9.2	8.0	6	365	11.8	11.7
44	0.192	0.609	3.8	5.2	2	-581	7.9	11.7
45	0.280	0.362	2.6	3.1	2	-322	4.5	8.9
46	2.860	1.104	11.9	10.0	6	1054	22.4	14.1
47	1.565	1.076	7.8	7.0	2	137	14.0	13.8
48	0.575	0.909	5.2	5.2	2	197	10.3	12.0
49	1.640	0.944	5.5	8.5	5	913	10.8	13.4
50	1.053	0.944	6.0	5.6	7	-55	10.1	13.9
51	0.450	0.687	4.2	3.4	2	226	9.8	10.5
52	1.130	0.907	7.7	8.2	12	913	15.1	13.2
53	0.687	0.867	3.9	5.1	6	52	16.9	12.7
54	0.310	0.656	3.2	3.1	2	206	10.3	10.4

NOTE: OBS = observed and PRE = predicted.

TABLE LI

OAKLAND OUTER HARBOR TURNING BASIN METAL CONCENTRATIONS (ppb) IN ELUTRIATES

Sample No.	Cd		Cu		Fe		Zn	
	OBS	PRE	OBS	PRE	OBS	PRE	OBS	PRE
1	<0.005	0.036	3.1	4.7	2778	2890	5.9	4.0
2	<0.005	0.043	5.3	3.3	69	1271	3.9	4.0
3	0.017	0.041	1.6	2.7	2	704	7.5	4.0
4	0.005	-0.128	2.8	2.7	735	2931	4.2	3.4
5	<0.005	-0.122	4.2	1.2	175	1319	19.5	3.4
6	<0.005	-0.124	1.4	0.6	208	686	7.6	3.5
7	0.068	-0.149	2.8	2.4	2260	2838	33.2	3.4
8	0.090	-0.147	1.0	0.9	155	1235	8.4	3.4
9	0.043	-0.152	1.7	0.3	412	701	6.7	3.4
10	0.025	0.111	3.4	4.7	4420	4285	0.6	2.9
11	0.012	0.108	2.0	3.2	2120	2730	11.5	2.9
12	0.022	0.115	0.4	2.7	164	2105	1.9	2.9
13	<0.005	-0.054	4.4	2.6	4270	4279	<0.5	2.5
14	<0.005	-0.057	0.8	1.1	5528	2683	0.5	2.5
15	0.049	-0.053	0.7	0.6	1428	2143	11.0	2.5
16	0.045	-0.075	1.4	2.3	5528	4217	0.5	2.5
17	<0.005	-0.075	1.2	0.8	631	2647	<0.5	2.5
18	0.045	-0.081	1.8	0.2	2142	2135	6.6	2.4
19	<0.005	0.183	3.4	4.7	3912	5735	<0.5	2.1
20	<0.005	0.185	1.6	3.2	3282	4165	<0.5	2.1
21	0.029	0.189	0.6	2.7	39	3488	4.3	2.2
22	0.062	0.021	1.4	2.6	13568	5646	3.2	1.8
23	<0.005	0.023	0.7	1.1	6282	4077	1.2	1.8
24	0.041	0.022	0.8	0.6	1029	3512	9.8	1.8
25	0.005	-0.001	1.3	2.3	13635	5580	<0.5	1.8
26	<0.005	0.002	1.2	1.0	9595	4116	<0.5	1.8
27	0.071	-0.006	2.6	0.2	2625	3523	9.4	1.8
28	0.264	0.202	12.7	5.8	<3	974	5.8	6.7
29	0.050	0.303	7.9	4.9	7	-1718	5.2	9.4
30	0.027	0.399	2.9	5.0	<3	-3419	4.5	12.8
31	<0.005	0.114	3.1	4.3	<25	201	3.0	7.4
32	0.017	0.129	4.0	2.8	8	-1599	3.6	7.8
33	<0.005	0.113	1.6	2.1	<2	-2057	5.4	7.5
34	0.020	-0.066	4.5	2.9	9	1931	4.1	4.5
35	0.010	0.079	3.2	2.3	7	-1384	2.1	7.2
36	0.012	0.073	1.6	1.7	4	-1902	4.0	7.0
37	0.730	0.539	8.4	7.4	3	- 720	21.9	11.7
38	0.400	0.354	4.9	4.7	<3	- 123	10.8	6.4
39	0.148	0.352	4.2	4.2	<3	- 637	6.4	6.3
40	0.058	0.134	2.4	3.9	39	2183	23.8	4.5
41	0.225	0.145	1.6	2.4	100	411	2.2	4.8
42	0.258	0.187	1.2	2.1	<3	- 637	6.0	5.5
43	0.032	0.170	3.2	3.9	4	1410	3.0	5.5
44	0.013	0.124	1.5	2.1	8	375	2.6	4.8
45	0.013	0.153	1.4	1.7	<3	- 575	6.6	5.2
46	1.990	0.571	8.5	7.1	<3	1174	19.5	7.5
47	0.548	0.429	6.0	4.8	4	1337	15.6	4.6
48	0.500	0.559	4.0	5.0	<3	- 761	8.2	7.1
49	0.022	0.249	2.4	4.1	12	3041	14.9	3.9
50	0.060	0.234	2.0	2.5	<3	1687	6.6	3.6
51	0.114	0.267	1.4	2.1	<3	683	3.9	4.1
52	0.049	0.210	1.8	3.7	<3	3236	1.9	3.6
53	0.016	0.207	1.4	2.2	4	1638	2.4	3.6
54	0.050	0.224	1.6	1.7	3	862	9.8	3.8

NOTE: OBS = observed and PRE = predicted.

TABLE LII

OAKLAND INNER HARBOR METAL CONCENTRATIONS (ppb) IN ELUTRIATES

Sample	Cd		Cu		Fe		Zn	
No.	OBS	PRE	OBS	PRE	OBS	PRE	OBS	PRE
1	0.041	0.252	4.0	3.6	190	1102	4.3	12.7
2	0.026	0.252	1.4	2.0	156	454	3.8	12.7
3	0.071	0.265	1.4	1.6	2	197	6.6	12.9
4	0.056	-0.462	5.3	3.0	352	1110	26.4	0.2
5	0.058	-0.461	4.0	1.6	82	432	2.4	0.2
6	0.065	-0.447	3.2	1.3	4	177	6.7	0.4
7	0.043	-0.575	3.2	2.8	451	1089	5.2	-1.8
8	0.058	-0.575	3.5	1.6	116	428	7.3	-1.8
9	0.008	-0.571	3.7	1.3	95	187	0.4	-1.7
10	0.032	0.563	1.5	3.6	3686	1469	<0.2	16.2
11	0.009	0.578	2.7	2.1	588	842	3.1	16.7
12	0.054	0.576	0.4	1.6	498	577	7.9	16.7
13	0.028	-0.150	1.2	3.0	2640	1496	<0.2	3.8
14	0.038	-0.139	2.0	1.7	820	845	6.2	4.0
15	0.046	-0.141	1.4	1.3	64	565	13.3	4.0
16	0.020	-0.264	4.0	2.8	2603	1462	2.9	1.8
17	0.035	-0.267	2.2	1.6	446	825	3.8	1.8
18	0.028	-0.264	1.6	1.3	12	576	20.1	1.8
19	0.011	0.889	1.4	3.7	2676	1857	<0.2	20.3
20	0.008	0.889	1.6	2.0	1565	1211	<0.2	20.3
21	0.065	0.891	0.4	1.6	309	936	6.1	20.3
22	0.042	0.172	1.6	2.9	3854	1839	0.6	7.7
23	0.041	0.172	1.7	1.6	1906	1198	6.8	7.7
24	0.033	0.170	1.2	1.3	39	925	6.9	7.6
25	0.032	0.044	2.1	2.9	1616	1859	2.0	5.4
26	0.035	0.044	2.8	1.6	3444	1213	1.0	5.4
27	0.038	0.051	1.5	1.3	14	936	1.4	5.6
28	0.118	0.551	24.4	6.5	13	610	18.2	17.8
29	0.143	0.964	16.6	7.8	4	- 751	9.3	24.9
30	0.070	0.683	2.9	3.6	12	- 518	11.3	20.1
31	0.064	0.262	14.7	11.3	16	- 109	10.0	12.6
32	0.048	0.250	8.6	6.2	10	- 760	5.5	12.3
33	0.036	-0.067	3.7	2.7	3	- 460	23.8	6.9
34	0.060	-0.200	6.0	5.8	11	449	4.1	4.6
35	0.026	0.038	4.6	4.8	5	- 639	5.2	8.7
36	0.022	-0.162	2.3	2.8	<3	- 504	11.9	5.3
37	0.737	0.695	7.3	4.6	6	1225	28.6	18.6
38	1.624	1.240	16.4	7.3	4	- 278	34.8	28.0
39	0.473	0.994	3.9	3.6	<3	- 146	31.0	23.8
40	0.092	0.573	7.2	11.3	12	263	11.0	16.2
41	0.064	0.457	5.6	5.1	5	- 175	3.4	14.2
42	0.059	0.239	1.8	2.7	<3	- 75	6.4	10.5
43	0.055	0.377	5.4	9.3	12	341	3.8	12.8
44	0.046	0.348	2 6	5.1	4	- 207	3.4	12.3
45	0.092	0.149	0.9	2.8	11	- 131	1.9	8.9
46	4.020	1.264	20.0	7.5	4	1218	73.2	26.7
47	5.590	1.530	17.8	6.9	4	130	50.4	31.3
48	1.470	1.315	3.2	3.6	<3	213	81.0	27.6
49	0.048	0.858	6.0	10.9	20	691	4.5	19.4
50	0.351	0.787	6.0	5.4	12	180	4.7	18.2
51	0.046	0.550	1.4	2.7	<3	298	7.5	14.1
52	0.160	0.308	4.4	4.7	46	1408	25.0	9.9
53	0.029	0.683	2.7	5.3	5	120	13.2	16.4
54	0.066	0.450	1.8	2.7	<3	258	7.2	12.4

NOTE: OBS = observed and PRE = predicted.

ranges in bulk parameters should be used. Finally, the trace metal contents of natural sediments may not be evenly distributed among the sediment volume regardless of how well the samples are mixed. This natural heterogeneity may well be the cause of much of the scatter and would be a serious weakness in many study approaches.

Despite the above limitations, statistical analysis of the sorption-desorption data was performed on each metal. Independent variables included the slurry dissolved oxygen content, original salinity, agitation time, solids to solution ratio as before, plus the sediment clay content, sediment cation-exchange capacity, organic carbon content, total sulfide content and total concentration of each heavy metal. The values for cation-exchange-capacity were determined during Phase 1 and not on the actual material utilized in the batch sorption-desorption experiment.

The statistical method utilized was step-wise regression which builds multiple regression equations one variable at a time starting with the most significant variable and ending when the multiple correlation coefficient is no longer improved.

The best predictor equation for each metal is presented in Table LIII. The order in which the independent variables occur corresponds to the importance of that parameter in explaining the variability of the elutriate trace metal concentration.

The improvement in the multiple regression equations upon addition of bulk sediment parameters is small. Combining all three sediments and utilizing only the variables used in the

TABLE LIII

METAL PREDICTOR EQUATIONS

$$\text{Cd} = .197+.039(\text{DO})+.016(\text{S‰})+.003(\text{time})-.019(\text{CEC}) \qquad r = .55$$

$$\begin{aligned}\text{Cu} = {} & 12.438+.282(\text{DO})+19.583(\text{solids})+.020(\text{time})-.072(\text{CEC}) \\ & -.095(\text{clay})+9.831(\text{carbon}) \qquad r = .69\end{aligned}$$

$$\begin{aligned}\text{Fe} = {} & 15139.51-145.126(\text{DO})+8667.708(\text{solids})+53.183(\text{S‰}) \\ & +207.249(\text{CEC})+5979.340(\text{carbon}) \qquad r = .61\end{aligned}$$

$$\text{Zn} = -13.569-.502(\text{DO})+.041(\text{time})+.080(\text{HM})+.108(\text{S‰}) \qquad r = .40$$

$$\text{Pb} = .142+.016(\text{DO})+.006(\text{clay}) \qquad r = .48$$

where

Cd, Cu, Fe, Zn, Pb are ppb

DO = slurry dissolved oxygen content (ppm)

S‰ = original water salinity (ppt)

Solids = solids to solution ratio (dry g/ml)

Time = agitation time (hrs)

CEC = cation-exchange capacity (meq/100g)

Clay = clay content (%)

Carbon = organic carbon content (%)

HM = heavy metal content of sediment (ppm) factorial design experiment yielded regression equations almost as large. Without bulk sediment parameters added to the model, the correlation coefficients were; Cd 0.54, Cu 0.67, Fe 0.56, Zn 0.34 and Pb 0.44.

The predictor equations presented in Tables XLIX and LIII may be correctly used to predict metal concentrations in elutriates only over the range of variables presented in Table LIV.

TABLE LIV

RANGE OF VALUES FOR THE INDEPENDENT VARIABLES

Variable	Range
Salinity	1 to 29 ppt
Dissolved Oxygen	.05 to 15 ppm
Agitation Time	1 to 144 hrs
Solids-to-Solution Ratio	.009 to .190 g/ml
Clay	40 to 60 %
Cation-Exchange-Capacity	26 to 35 meq/100g
Organic Carbon	1 to 1.7 %

When conditions vary significantly from these ranges, the equations should not be used without explicit reservations. To estimate water concentrations of trace metals under natural conditions of suspended solids concentrations in San Francisco Bay, further work is necessary. The results to date more satisfactorily simulate the physical turbulence present during the dredging procedure than events which occur naturally or after spoils disposal.

The step-wise regression analyses also showed that the total heavy metal content correlates with total sulfide content but

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since only three types of sediment were studied the resultant correlations need more verification. The correlation "r" values for the heavy metals-sulfide relationship were 0.999, 0.971, 0.881 and 0.711 for lead, cadmium, zinc and copper respectively.

In summary it appears that the best predictor equations are derived from treating the data from each sediment separately. The dissolved oxygen content of the slurry in every case is the most important independent variable. Salinity, agitation time and solids content also appear to be better predictors than bulk sediment parameters. More work with larger ranges of sediment types would be advisable to substantiate this conclusion.

Preliminary Characterization of Metal Species in Solution

Metals in the interstitial waters are considered to be in a dynamic equilibrium with the sediment solid phase. Interstitial waters were selected for initial testing because it is likely that these waters represent the most available source of metals to the biota, and it was expected that this fraction would serve as a control to evaluate the effect of subsequent chemical extractions of the sediments on metal species in solution. The concentrations of metals and their distribution in sediments and interstitial waters are given in Tables LV and LVI. The pH and salt contents of interstitial waters are given in Table LVII. In all cases, the concentration of metal in the interstitial waters did not exceed 5 percent of the total metal in the sediment. Sediments from Redwood Creek exhibited the largest quantities

TABLE LV

CONCENTRATION OF MERCURY, ZINC, AND COPPER IN SAN FRANCISCO BAY SEDIMENTS AND INTERSTITIAL WATERS

	Metal Concentrations (µg/g)*					
	Mercury		Zinc		Copper	
Location	Sediment	Interstitial Waters	Sediment	Interstitial Waters	Sediment	Interstitial Waters
Southampton Shoal	0.20	.000012	86	.060	29	0.90
Oakland Inner Harbor	0.86	.000067	220	.010	76	0.80
Redwood Creek	0.49	.000098	180	.010	110	0.80

---

*Sediment values on a dry weight (60°C, 24 hrs.) basis

TABLE LVI

DISTRIBUTION OF MERCURY, ZINC, AND COPPER IN INTERSTITIAL WATERS

Location	Total Solids (%)	Metal in Interstitial Waters (%)* Mercury	Zinc	Copper
Southampton Shoal	70	0.0023	0.025	1.14
Oakland Inner Harbor	44	0.0058	0.0043	0.63
Redwood Creek	41	0.100	0.027	4.64

---

*% metal in interstitial water = $\frac{\mu g/g \text{ in water} \times \text{wt. water}}{\mu g/g \text{ in sediment} \times \text{wt. sediment}} \times 100$

TABLE LVII

pH AND TOTAL SALT CONTENT OF INTERSTITIAL WATERS

Location	pH	Total Salt Content (%)*
Southampton Shoal	7.3	5.1 ± 0.3
Oakland Inner Harbor	7.6	3.8 ± 0.1
Redwood Creek	7.2	4.6 ± 0.9

---

*Total salt ± S.E. (n=3) was determined by evaporating 20 ml aliquots of the interstitial water to dryness followed by drying of the resulting salt residue (24 hrs., 60°C).

of metals in the interstitial waters relative to total metal content. Mercury was present at the highest levels in the interstitial waters (Table LV) of sediments containing the largest quantities of organic carbon (Table LVIII). The reverse was true in the case of zinc. In contrast, the copper content of the interstitial waters remained relatively constant, regardless of organic carbon content.

In addition to the interstitial waters, the boiling water and ammonium acetate extractions were selected for further characterization because these solvents tend to extract low-molecular weight organic materials most likely to be released from sediments and enter the aquatic food web and because more drastic extractions utilized in other phases of this study may be expected to modify the chemical form of the low-molecular weight organic materials.

Copper was selected for further study because of the concern regarding its presence in San Francisco Bay sediments and because it was present in sufficient quantities in the appropriate extracts for detailed chemical characterization. The sediment from Oakland Inner Harbor was selected for extraction as it contained the highest concentration of copper.

A major portion of the copper in the extracts was associated with materials of <10,000 molecular weight (Table LIX). Only the boiling water extracts contained significant material of molecular weight greater than 10,000. Of the materials less than molecular weight 10,000, the copper in the interstitial

TABLE LVIII

CARBON, HYDROGEN, NITROGEN, AND ASH CONTENT OF SAN FRANCISCO BAY SEDIMENTS (%)*

Location	Carbon	Hydrogen	Nitrogen	Ash
Southampton Shoal	0.75	0.53	0.08	93.8
Oakland Inner Harbor	1.84	0.93	0.17	87.7
Redwood Creek	1.96	1.01	0.18	85.4

*Based on dry weight (60°C, 24 hrs.)

TABLE LIX

DISTRIBUTION OF COPPER IN MOLECULAR WEIGHT FRACTIONS OF OAKLAND INNER HARBOR SEDIMENT EXTRACTS

	Molecular Weight Fractions of		
Extract	< 500	500-10,000	> 10,000
		%	
Interstitial Water	47	53	0
Boiling Water	58	16	26
Ammonium Acetate	92	8	0

---

*Molecular weight equivalent to globular organic polymer water was evenly distributed in the <500 molecular weight and 500-10,000 molecular weight fractions but was primarily present in the <500 molecular weight fraction of the boiling water and ammonium acetate extracts.

Sephadex gel fractionation is a relatively convenient way to separate compounds on the basis of molecular size. Sephadex consists of grains of cross-linked dextrans and the degree of cross-linkage determines the porosity of the gel. Separation of molecules of different size is based on the degree of diffusion into the grains in the column of a given porosity. If it is assumed that the material to be separated does not react with the column, molecules which exceed the exclusion limit are eluted first and molecules which are sufficiently small to enter the grain are eluted last. Separation of molecules partially excluded occurs between these limits. This latter phenomenon may occur when the solute reacts with the column or is of a size which does not completely penetrate the inner portion of the grain.

The differential refractive index, i.e., the change in refractive index of the eluant from the column compared to that of the eluting solution alone, was chosen as indicative of the total solute concentration in the column effluent. This information served as a basis for selection of the appropriate fraction volumes which were subsequently analyzed for copper.

The results of Sephadex separation of the >10,000 molecular weight fraction are illustrated in Figure 20. The volume

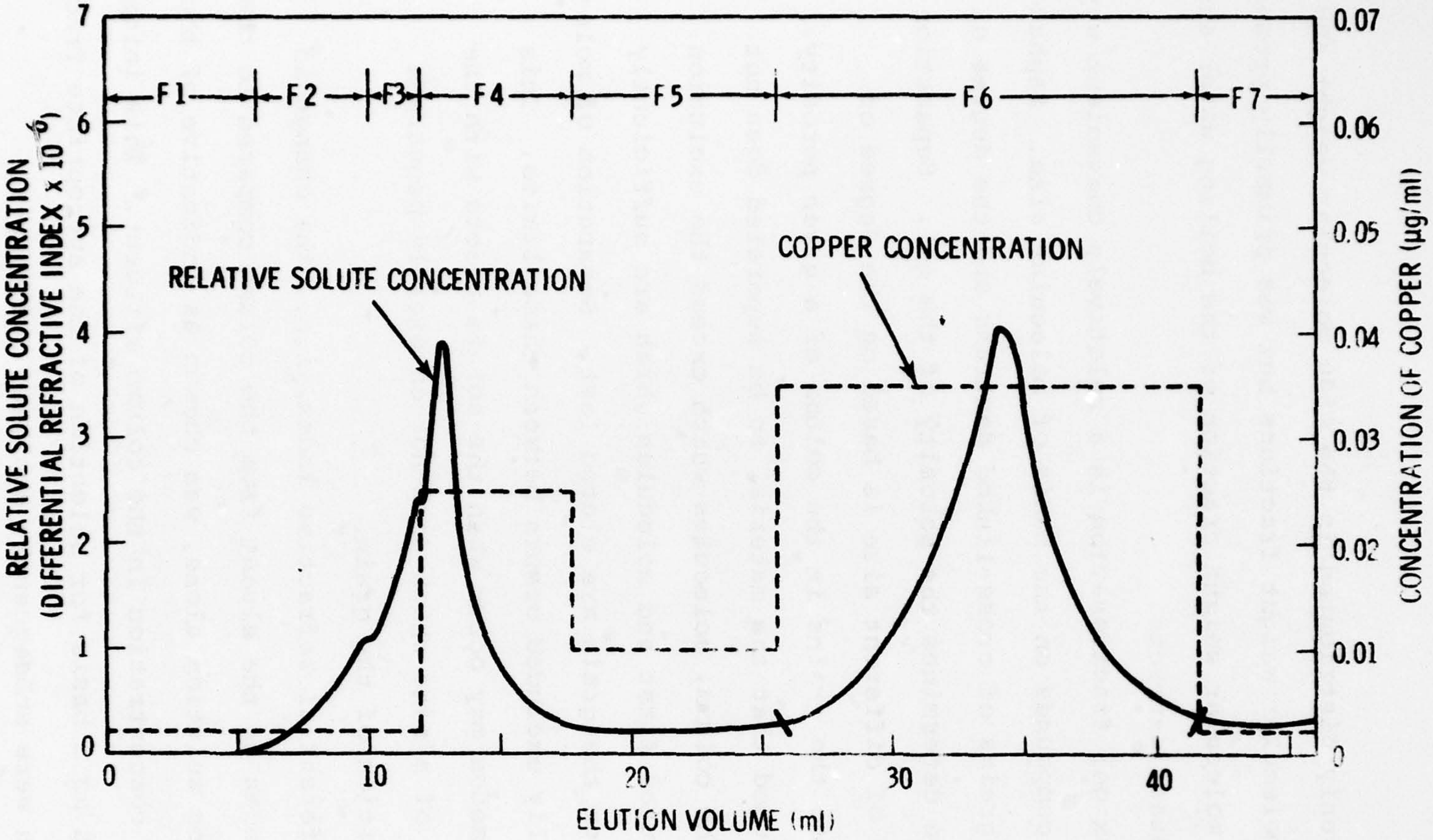

FIGURE 20. SEPARATION BY SEPHADEX GEL (G-100) CHROMATOGRAPHY OF COPPER-CONTAINING LIGANDS IN THE GREATER THAN 10,000 MOLECULAR WEIGHT FRACTION (BOILING WATER EXTRACT) OF SEDIMENT FROM INNER HARBOR, SAN FRANCISCO BAY. RELATIVE SOLUTE CONCENTRATION OF ELUTION FRACTION NUMBER 6 (F6) IS SHOWN ON A SCALE OF 10^{-4}.

equivalent to the exclusion limit for this column was 13 ml. Compounds excluded from the gel and thus equivalent to an organic, globular polymer of molecular weight >100,000 were eluted from the column after elution of approximately 13 ml. Molecules which corresponded to an equivalent molecular weight of <10,000 would have been eluted from the column with a 21 ml volume. A major portion of the solute was eluted in a subsequent extract (F6), likely as a result of reaction with the gel which reduced migrational velocity. This fraction, which exhibited a yellow color, also contained the highest concentration of copper. However, copper was also associated with molecules of equivalent molecular weight >100,000 (F4).

The Sephadex gel employed in separation of the 500-10,000 and <500 molecular weight fractions had an exclusion volume of 16 ml. The major fraction of total solute and of the copper in the 500-10,000 molecular weight fraction was associated with compounds less than the upper exclusion limit (F5 and F6, Figure 21). The highest concentration of copper was associated with unresolved materials in F5.

There were four major classes of materials resolved in the <500 molecular weight fraction (Figure 22). As in the case of the 500-10,000 molecular weight fraction, the major portion of the total solute and of the copper (F3-F6) was in materials of sizes less than the upper exclusion limit. Of particular importance is the fact that the majority of the copper was present

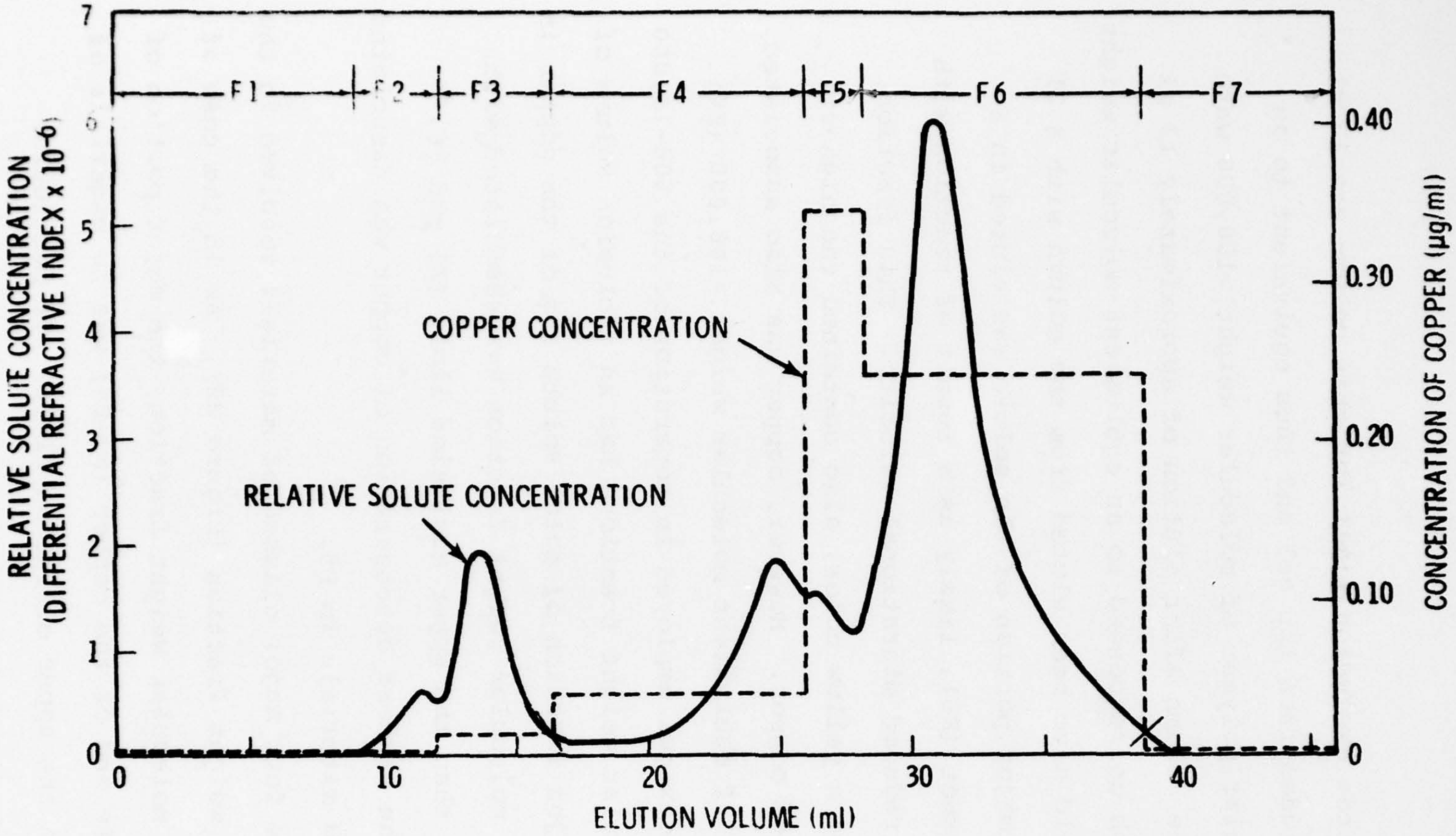

FIGURE 21. SEPARATION BY SEPHADEX GEL (G-25) CHROMATOGRAPHY OF COPPER-CONTAINING LIGANDS IN THE 500 TO 10,000 MOLECULAR WEIGHT FRACTION (BOILING WATER EXTRACT) OF SEDIMENT FROM INNER HARBOR, SAN FRANCISCO BAY. RELATIVE SOLUTE CONCENTRATION OF ELUTION FRACTION NUMBER 4-6 (F4-F6) IS SHOWN ON A SCALE OF 10^{-4}.

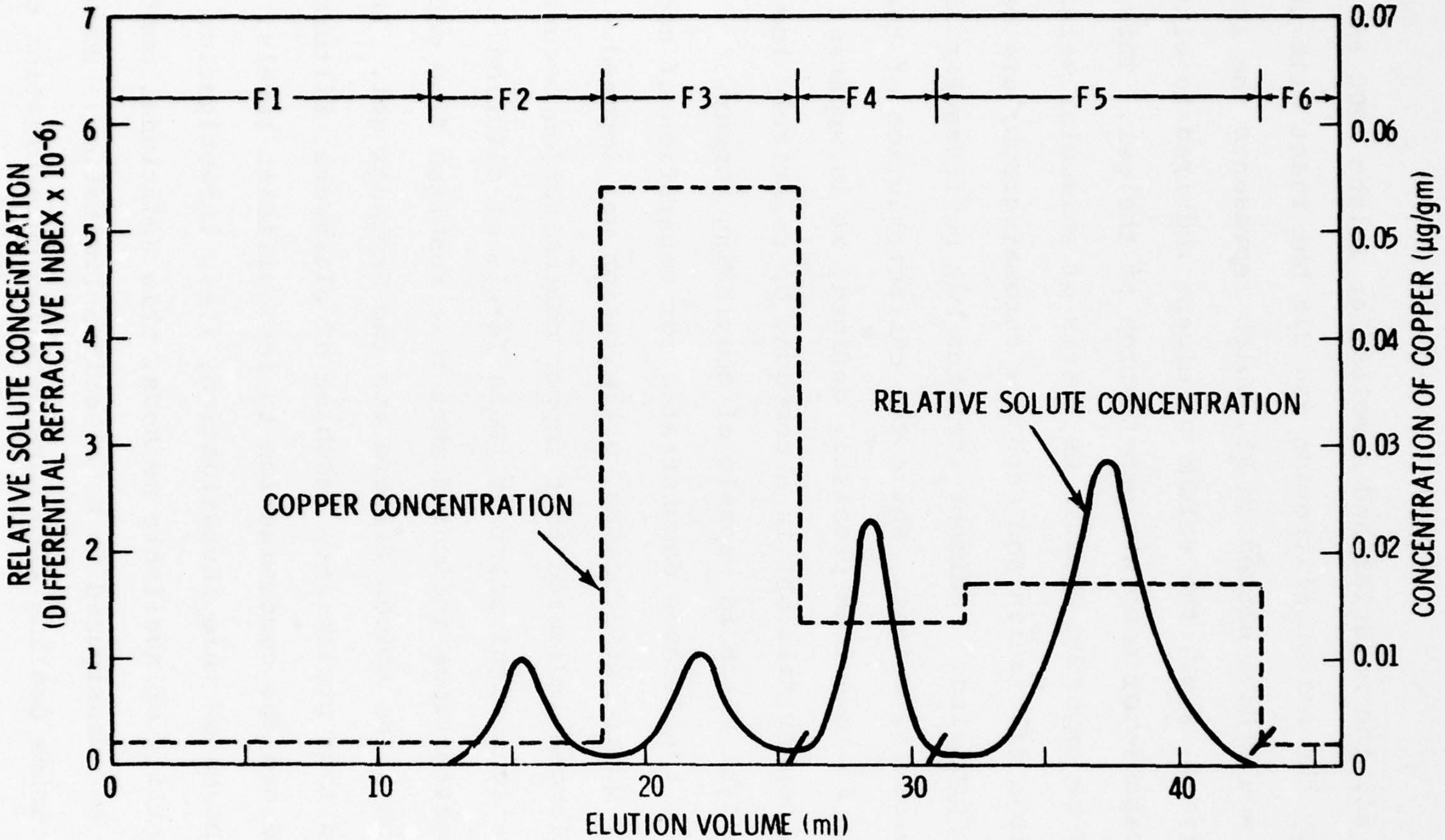

FIGURE 22. SEPARATION BY SEPHADEX GEL (G-25) CHROMATOGRAPHY OF COPPER-CONTAINING LIGANDS IN THE LESS THAN 500 MOLECULAR WEIGHT FRACTION (BOILING WATER EXTRACT) OF SEDIMENT FROM INNER HARBOR, SAN FRANCISCO BAY. RELATIVE SOLUTE CONCENTRATION OF FRACTION NUMBER 4 (F4) AND FRACTION NUMBER 5 (F5) ARE SHOWN ON A SCALE OF 10^{-5} AND 10^{-4} RESPECTIVELY.

in F3. If all the material had a molecular weight <500 as suggested by the Amicon filtration and did not react with the column, it would have eluted in F5, which represents the lower exclusion limit, i.e., the volume of eluant required to elute molecules capable of complete penetration of the gel. This anomaly may be expected because estimates of molecular weight in both Amicon filtration and Sephadex chromatography are based on globular proteins. Sediment isolates may be irregular in size and molecular weight. While the characteristics of the component in F3 cannot be precisely defined, it is apparent that it is not a copper salt but is a compound of relatively low molecular weight which is capable of complexing copper.

Although the methods demonstrated for separation of copper ligands were quite satisfactory, a limitation was imposed. Material balances indicated that copper contamination occurred in concentrations significant at these levels of dilution. Further investigations indicated that this resulted from copper present in both the Amicon filters and the Sephadex gel. It was demonstrated that preliminary leaching of glassware, filters, and gels reduced the contamination to insignificant levels. For the purposes of this investigation, i.e., investigation of the applicability of available methods, this additional contamination was not considered to be a serious limitation. However, in future studies dealing with more detailed determination of the chemical form of copper and other metals, preliminary purification procedures must be employed.

Identification of the chemical form of metal ligands requires isolation of the compounds in relatively pure form from the sediment complex. In the studies discussed above, initial purification was demonstrated for at least 5 compound classes containing copper. These materials varied in apparent molecular weight from ionic species to >100,000. It is likely that these compound classes contained several different compounds of approximately the same molecular size and of unknown individual affinity for copper. Several options are now available to separate and fully characterize these materials. Considerable improvement in resolution of individual compounds can be obtained with Sephadex by re-eluting separated fractions through the same column or by alteration of column size, gel porosity, and eluant composition. The fractions containing highest concentrations of copper may also be subjected to additional chemical and physical separations. In the present studies, thin-layer electrophoresis and thin-layer chromatography were employed in a preliminary manner for this purpose. The results are described below.

The solubility in water, color, chromatographic characteristics, and affinity for copper suggested that F6 in the >10,000 molecular weight fraction contained aromatic and acidic components. This information allowed development of thin-layer electrophoretic procedures tailored for these materials. The results of the application of thin-layer electrophoretic techniques to materials in F6 are illustrated in Figure 23. This fraction contained at

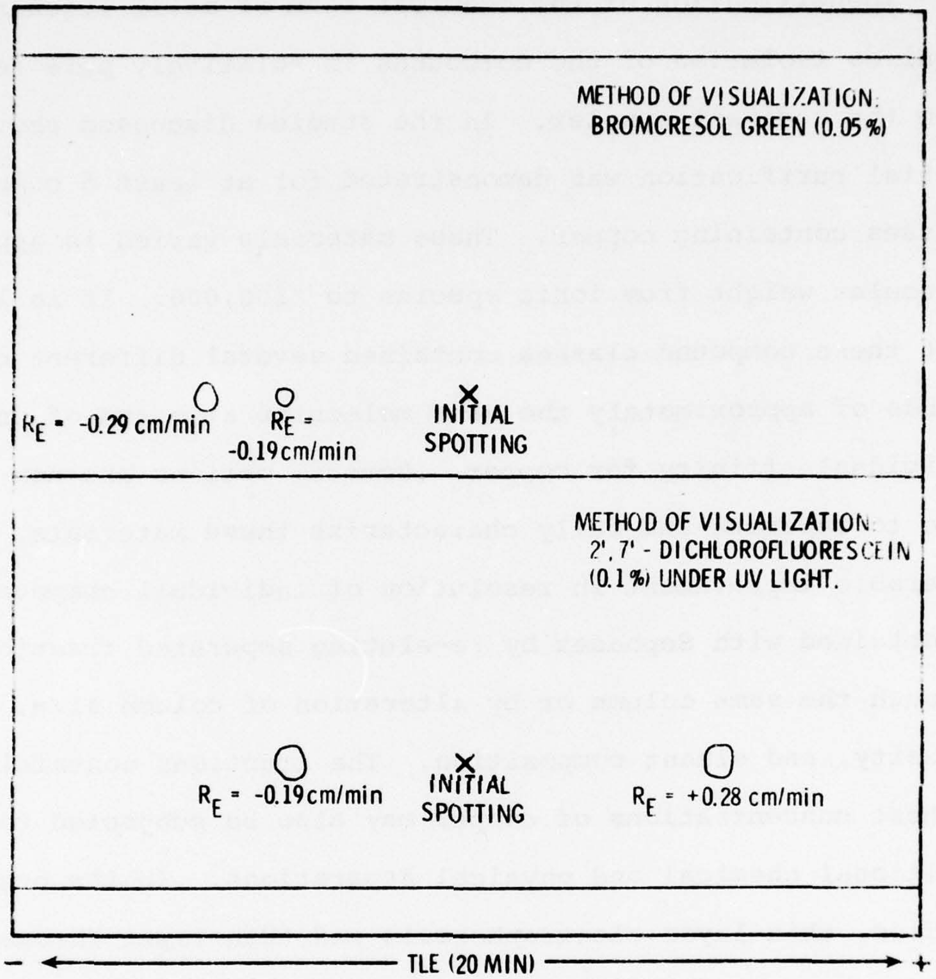

FIGURE 23. THIN LAYER ELECTROPHORETIC SEPARATIONS OF CONSTITUENTS IN SEPHADEX GEL (G-100) FRACTION 6 OF THE GREATER THAN 10,000 MOLECULAR WEIGHT FRACTION (BOILING WATER EXTRACT) OF SEDIMENT FROM INNER HARBOR, SAN FRANCISCO BAY

least three highly mobile compounds. Two of these compounds were positively charged, whereas one was negatively charged. This information may now be employed in kinetic studies to determine the potential for release of metal complexes from sediments and in biological studies to estimate accumulative and toxicological effects of metal entrance into the overlying water. Furthermore, the isolated materials may be extracted from the thin layer plate and subjected to further chemical characterization using infrared and ultraviolet spectroscopy, gas chromatography, and mass spectroscopy. Final identification of the compounds would provide a basis for detailed assessment of hazards with a degree of sophistication previously unavailable in environmental studies of this nature.

SUMMARY AND CONCLUSIONS

A survey of the literature pertaining to the nature and concentration of heavy metals and PCB's in estuarine sediments and waters along with possible mechanisms of transport was conducted. Literature relating to the effects of dredging with emphasis on the fate of heavy metals was also reviewed.

Samples of sediments and waters from various locations in San Francisco Bay were collected. Physical, chemical and mineralogical characterizations of the sediment and chemical characterization of the estuarine waters were carried out. A semi-selective extraction procedure was used to determine the relative distribution of trace metals among the various geochemical phases. A large sorption-desorption batch experiment was performed to determine the effects of oxidation-reduction potential, salinity, agitation time, solids-to-solution ratio and sediment type on the release of trace metals into the water column. Multiple regression equations to predict the elutriate concentrations were developed from the sorption-desorption data. The major findings of the Crystalline Matrix Study are summarized below.

LITERATURE SURVEY

- The concentrations of the heavy metals Pb, Cu, and Zn in sediments from industrialized bays typically range between 50-200 ppm. The concentrations of Cd and Hg from these bays range between 0.1-5 ppm. The available literature reported values for San Francisco Bay fall within these ranges. Instances of extreme values up to thousands of parts per million can be found in highly industrialized harbors such as Baltimore.

- The concentrations of trace metals in nearshore bay waters typically range from subparts per billion to tens of parts per billion.
- In general, knowledge of mechanisms for sorption and release of heavy metals in estuarine sediments includes several mechanisms none of which has been shown to predominate.
- Binding mechanisms for heavy metals include 1) lattice sites in mineral phases; 2) sorption by iron, manganese, and aluminum hydrous oxides; 3) precipitation as insoluble mineral phases such as sulfides, carbonates, oxides and hydroxides; 4) sequestration by organic matter especially humic acids; and 5) ion exchange.
- Release of heavy metals from the sediment may occur as a result of 1) cation competetion for ion exchange sites; 2) oxidation of anaerobic sediments including sulfide phases and organic debris; 3) reduction of hydrous ferric oxides; 4) formation of soluble inorganic and organic complexes; and 5) biological interactions.
- Information concerning sorption or release of PCB's in estuarine environments is very scarce but it appears from one study that sediments can be a sink for PCB's.

- In the majority of the literature reviewed, dredging activities which have been studied did not cause substantial releases of heavy metals to the water column. The most common effects of dredging were increased turbidity and transitory decreases in water oxygen content. In certain instances disposal operations briefly increased turbidity and caused smothering of benthic communities.

Bulk Sediment Parameters

- The pH and Eh of sediments from three locations in the Bay ranged from 6.6 to 7.4 and +140 to -80 mv, respectively.
- Most of the sediments sampled were clay and silty clay sediments with 40-70 percent of the sediment consisting of <2μm particulates. Two areas, Southhampton Shoal Channel and Oakland Outer Harbor, were predominatly sand. The clay particles in the Bay were agglomerated and had falling velocities like silt particles if dispersing agents were not used.
- The main clay mineral found in the Bay sediments was montmorillionite which contributes a substantial cation-exchange-capacity.
- The cation-exchange-capacity (CEC) ranged from 10.6 to 35.2 meq/100g. The CEC was largest in sediments with high clay contents and high organic contents.
- The clay sediments in general contained 1000-3000 ppm total sulfide and thus represent a reduced environment. It appears that the upper 30 centimeters of sediment contain

substantially less total sulfide than the sediments found at the 30-60 centimeter depth.

- The organic carbon content for the clay sediments varied only slightly with a range from 1.2 to 1.7 percent. Southampton Shoal Channel, a sand, contained only 0.1 percent organic carbon. In general the carbonate content of the Bay sediments was lower than 0.5 percent. One sediment, Redwood Creek Channel by Corkscrew Slough, had a carbonate content of 3-5 percent.
- Total organic nitrogen values ranged from 0.2 to 0.4 percent N at the three samples analyzed. Ammonia concentrations ranged between 200-500 ppm N in these samples. All the samples exceeded the FWQA criterion of 0.1 percent TKN for open water disposal.
- The total heavy metal contents of the sediment in general followed the pattern of higher concentrations in the clay sediments and lower concentrations in sand sediments. Highest cadmium concentrations were found at Oakland Inner Harbor and Islais Creek (1.6 ppm). Other regions contained 0.4-1.3 ppm Cd. Highest copper concentration was found at Oakland Inner Harbor (120 ppm) with other regions ranging from 60-90 ppm. Highest mercury concentration was found at Oakland Inner Harbor (1.2 ppm) with other regions ranging from 0.03 to 0.67 ppm. The highest lead concentration again appeared to occur at Oakland Inner Harbor. High zinc concentrations (230-250 ppm) were found at Oakland Inner Harbor, Islais Creek Shoal and Richmond Harbor.

- The PCB content of the sediment was low in the open Bay sands (30 ppb) and higher in the nearshore clays (130-830 ppb). Selected pesticides appeared low in the Bay sediments ranging from 1-100 ppb.
- Linear regression correlations of the total trace metal contents with the total iron, aluminum and sulfur contents showed very significant correlations of Pb, Cu, Zn, Hg with total sulfur content in the sediment. Only Cu and Zn showed moderate correlation with total iron and Cu showed a moderate correlation with total aluminum in the sediment.
- When the sediment was high in one metal it invariably was high in the other metals with·Zn-Cu-Pb correlating very strongly. This suggests a common source for the trace metals or common sorption-desorption mechanisms controlling the metals.

<u>Water Parameters</u>

- The salinities of the water samples ranged from a surface low of 10°/oo and an interstitial water low of 15°/oo at Mare Island to a high salinity of 29°/oo near Alcatraz Island. Most channel and interstitial waters contained 26-27°/oo salinity.
- Free hydrogen sulfide concentrations in the waters (both surface and interstitial) were undetectable (<0.1 ppm) with measurements taken three hours after collection of water and sediments.

- The total Kjeldahl nitrogen content of waters including interstitial waters was low. Excepting the interstitial water from the Oakland Outer Harbor Turning Basin, soluble organic carbon contents ranged from 8-12 ppm. The Turning Basin intersititial water orgainc content was 200 ppm.
- Trace metal contents of filtered mid-depth waters from three locations had 0.1-0.3 ppb Cd, 2.1-2.8 ppb Cu, 0.1-0.9 ppb Pb and 5-16 ppb Zn. Unfiltered mercury concentrations ranged from 0.1-0.7 ppb.

Semi-Selective Extraction Results

- A significant amount of most of the metals was found in the residual phase which represents metals bound in mineral lattice sites that are essentially inert to moderate chemical attack. Seventy-seven percent of the mercury, 60 percent of the iron, 54 percent of the manganese and zinc, 53 percent of the copper, 50 percent of the lead and 4 percent of the cadmium were found in the residual phase.
- The hydrogen peroxide chemical treatment released significant amounts of the metals; 92 percent of the cadmium, 45 percent of the lead, 43 percent of the copper, 39 percent of the zinc, 23 percent of the mercury, 19 percent of the manganese, and 6 percent of the iron. This treatment should release organic and sulfide like phases which may be quite sensitive to oxidation during dredging.

- The chemical extractants which should release metals sorbed by hydrous oxides did not appear to contain significant amounts of trace metals.

Sorption-Desorption Results

- Of the independent parameters studied; oxidation-reduction potential, salinity, agitation time, solids-to-solution ratio and sediment type, the oxidation-reduction potential had the greatest effect on the fate of trace metals. Under oxygen rich conditions significantly more copper, cadmium, lead and zinc were found in the elutriate solution than in elutriates under reduced conditions. Iron acted in an opposite manner with more iron found in solution under the reduced environment. One mechanism which may be the cause of these results is the release of trace metals bound to sulfide phases upon oxidation. The iron released under oxidized conditions probably precipitates as hydrous oxides which dissolve and form the more soluble Fe^{+2} species under reducing conditions.
- Salinity significantly influenced cadmium and zinc concentrations in oxygen rich samples and iron in oxygen deficient conditions. In each case more metals were found in higher salinity elutriates than in the 1‰ water. Two possible mechanisms which may explain this observation are the formation of soluble inorganic complexes with the increased chlorides, carbonates and sulfates or the release of trace

metals bound to ion exchangeable sites with the greater cation competition of more saline waters.

- The length of agitation time significantly affected the release of cadmium, copper and zinc under oxidizing conditions. More metals were released at the longer shaking periods, suggesting that a kinetic mechanism may be playing a role in the fate of the trace metals. Possibly the oxidation of sulfide or organically bound trace metals occur over a time interval of the order of several days to weeks to attain a steady state equilibrium.
- The solids-to-solution ratio significantly affected the release of copper and iron in both oxidation-reduction states. More of these metals were found in the elutriates separated from the high solids content samples. This may reflect the effect of the larger source of trace metals in the larger sediment samples which, if desorption and/or dissolution mechanisms slightly predominate over sorption mechanisms, would be expected to show a larger release.
- The release of trace metals (Cd, Cu, Pb and Zn) under oxygen rich conditions in general increased the water column concentration 30-200 percent. Ratios of elutriate to original water concentrations in general ranged from 1.3 to 2.0 for samples which originally had trace metal concentrations similar to values found in the Bay. The iron release was

substantial under reducing conditions with ratios of elutriate to original waters ranging from 50 to 3000. This phenomenon should be very uncommon in San Francisco Bay because the water column is not normally oxygen deficient. Under the usual oxygen rich conditions in the Bay, iron ratios of elutriate to original water concentrations were 2 to 4.

- Further study will be necessary to determine whether the metals released under oxygen rich conditions cause any environmental harm.

Predictor Relationships

- Multiple regression predictor relationships for the final elutriate concentration of cadmium, copper, iron, lead and zinc were developed for each sediment utilizing the independent variables of the sorption-desorption experiment. The equations in general predict 20 to 60 percent of the variability of the data. The lack of precision in trace metal analysis techniques in the sub and low parts per billion range and other variables not monitored probably contribute to the mediocre predictive values.
- Predictor equations incorporating sediment bulk parameters such as cation-exchange-capacity, clay content, organic carbon content, total sulfide and total heavy metal content show a small improvement over equations derived considering only the independent variables of the sorption-desorption results. In all cases the bulk sediment properties were of lesser

importance in explaining the variability of the data than the variables such as dissolved oxygen, salinity, agitation time and solids content. More work is necessary to determine whether the lesser importance of sediment characteristics is valid or only an artifact of the small number and similarity of sediments utilized.

PRELIMINARY CHARACTERIZATION OF METAL SPECIES IN SOLUTION

- Sediment interstitial waters, boiling water extracts, and ammonium acetate extracts were selected for detailed studies of chemical form on the assumption that they contained materials which were less likely to have been chemically modified. These solutions contained less than five percent of the total quantity of metals in the sediments, and the quantity of metal in the solutions differed with metal type and sediment location.
- Copper, selected for detailed chemical characterization because of its relatively high concentration in interstitial waters and boiling water and ammonium acetate extracts, was largely associated with soluble materials of less than 10,000 molecular weight.
- Of the soluble materials in the less than 10,000 molecular weight fractions, copper in the interstitial waters was evenly distributed between the 500-10,000 molecular weight fraction and the less than 500 molecular weight fraction, whereas copper in the boiling water and ammonium acetate

extracts was present primarily in the less than 500 molecular weight fraction.

- Several distinct, and apparently organic, components containing most of the copper were separated on application of Sephadex chromatography to molecular weight fractions from the boiling water extracts of Oakland Inner Harbor sediments.
- Application of thin-layer electrophoretic techniques to a Sephadex fraction which exhibited chemical properties characteristic of aromatic and carboxylic acid materials resulted in the separation of three components differing in charge and electrophoretic mobility.

RELATIONSHIP OF RESULTS TO THE ENVIRONMENTAL EFFECTS OF DREDGING AND DISPOSAL IN SAN FRANCISCO BAY AND RECOMMENDATIONS

The fine silts and clays found in the shipping channels of areas such as Oakland Inner Harbor, Oakland Outer Harbor Turning Basin, and Mare Island Straits contain large quantities of sulfides and, in general, constitute an oxygen deficient environment. From the semi selective extraction data it appears that a portion of the heavy metals present in the sediment may be bound in the sulfide or organic phases. From the sorption-desorption experiments performed, it appears that when the reduced Bay sediments are allowed to oxidize for periods of 1 to 144 hours, the trace metal concentrations of the water column may increase.

More studies are needed to determine whether the actual dredging and disposal operations would release trace metals through the apparent mechanism of oxidation as found in this laboratory study. The long-term fate of trace metals in disposal spoils should also be investigated to compare with the relatively short time scale utilized in this laboratory study.

It is possible that the potential for release of trace metals back to the water column may be largest after the disposal. The much shorter time involved in dredging in comparison with the long exposure after disposal is the basis for this hypothesis. The high solids-to-solution ratio of the removed spoils during dredging and short time of dredging probably does not allow complete oxidation of the total volume of dredge spoils.

From literature studies,[90,95] the disposal operation in open waters usually occurs over a time period of minutes. In most cases the whole barge load should slump to the bottom as one cohesive mass and thus oxidation would be minimal. The disposed sediment forms a new interface with the water column until covered by new spoils, natural sediment or dispersed by current, wind or tidal induced forces.

The oxygen rich water column will start to interact with the reduced surface spoils and an oxidized layer will be formed. During this oxidation it is possible that as in the laboratory studies cadmium, copper, lead, zinc, and probably other heavy metals will be mobilized. In high energy disposal sites which are common in San Francisco Bay continual agitation and transport may increase the oxidation of dredge spoils as the top layer is displaced and deeper spoils contact the water column.

A similar release of trace metals could be expected from reduced sewage and industrial wastes as they mix and contact the oxygen rich waters of the Bay.

Assuming that the mechanisms presented to explain the laboratory studies apply to San Francisco Bay, two options come to mind for the disposal of dredged spoils. One alternative which would result in lower concentration increases, but higher masses of metals released would be to dispose in regions of high scouring potential. The high currents through the region would increase the mass of sediment oxidized by continually disturbing the sediment-water interface. The large volumes of water which could move through the region would probably dilute any concentration increases in heavy metals despite the potentially high mass of metals that could be mobilized.

The second alternative of disposal would be to find a quiescent region in which spoils would not be disturbed after disposal. Under these conditions only the thin interface of the spoils would oxidize and a small quantity of metals would potentially be released. The small volume of water that might move through the quiescent region would have less chance to dilute the resultant concentration of trace metals.

The biological uptake mechanisms of biota in the disposal regions would have to be evaluated to determine which spoiling alternative would cause the least effect on the organisms.

Another environmental parameter which was found to effect the elutriate concentration of heavy metals was salinity. For zinc, cadmium and for one sediment copper, significantly higher concentrations of these metals were found in solution as the salinity increased from $1^{\circ}/_{\circ\circ}$ to $15^{\circ}/_{\circ\circ}$ and $29^{\circ}/_{\circ\circ}$. Besides influencing the release of trace metals during dredging, salinity could potentially be an important mobilization factor during its natural seasonal changes in the northern section of San Francisco Bay and this merits study. During periods of high freshwater runoff, the northern part of San Francisco Bay has low salinities. At these times it is also probable that currents are higher than normal and turbulent scouring could aid the oxidation process. As the drier seasons commence, the salinity of the northern reaches increases and currents may subside. Even if the oxidized thin surface layer is not disturbed, further metal mobilization may occur at the higher salinities.

If the magnitude of the release of trace metals under oxidizing conditions in the laboratory studies represents the actual releases in the Bay, these concentrations, 1.3-3.4 times the ambient concentrations, should be investigated in biological uptake and availability studies. It must be determined whether increases of the observed magnitude cause deterimental effects on the biota found in the Bay to fully assess the effects of dredging and disposal.

The predominance of fine grained sediment in the channels could lead to a potential turbidity problem which should be assessed. The samples for which total Kjeldahl nitrogen determinations were run all exceeded the 0.1 percent by dry weight allowable limit for open water disposal.

REFERENCES

1. Sustar, J. F. "Dredge Material Disposal Study, San Francisco Bay and Estuary," presented at the Fifth World Dredging Conference at Hamburg, Germany, June 12-15, 1973.

2. U. S. Army Engineer District, Corps of Engineers - San Francisco District. "Plan of Study - Dredge Disposal Study for San Francisco Bay and Estuary," September 1973.

3. Bender, M. L., and C. Shultz. "The Distribution of Trace Metals in Cores From a Traverse Across the Indian Ocean," Geochim. Cosmochim. Acta, Vol. 33, pp. 292-297, 1969.

4. Bopp, F., III, and R. B. Biggs. "Trace Metal Environments Near Shell Banks in Delaware Bay," University of Delaware College of Marine Studies, Report DEL-SG-9-72, 1972.

5. Butterworth, J., P. Lester and G. Nickless. "Distribution of Heavy Metals in Severn Estuary," J. Marine Pollution, Vol. 3, No. 5, pp. 72-74, 1973.

6. Cranston, R. E., and D. E. Buckley. "Mercury Pathways in a River and Estuary," Environ. Science & Tech., Vol. 6, No. 3, pp. 274-278, March 1972.

7. Crecelius, E. A., and D. Piper. "Particulate Lead Contamination Recorded in Sedimentary Cores From Lake Washington," Environ. Science & Tech., Vol. 7, No. 11, pp. 1053-55, November 1973.

8. Cronan, D. S. "Average Abundance of Mn, Fe, Ni, Co, Cu, Pb, Mo, V, Cr, Ti, and P in Pacific Pelagic Clays," Geochim. Cosmochim. Acta, Vol. 33, pp. 1562-65, 1969.

9. Drago, E. A. "Baseline Environmental Investigation of Dredging Activities, Mobile Bay, Alabama," Manuscript, 1973.

10. Hann, R. W., Jr., and J. F. Slowey. "Sediment Analysis - Galveston Bay," Texas A&M University, Estuarine Systems Project Tech. Report No. 24, 1972.

11. Holmes, C. W., E. A. Slade and C. J. McLerran. "Migration and Redistribution of Zinc and Cadmium in a Marine Estuarine System," Environ. Science & Tech., Vol. 8, No. 3, pp. 255-59, March 1974.

12. Mackay, D. W., W. Halcrow and I. Thornton. "Sludge Dumping in the Firth of Clyde," J. Marine Pollution, Vol. 3, No. 2, pp. 7-11, 1973.

13. Saila, S. B., S. D. Pratt and T. T. Polgar. "Dredge Spoil Disposal in Rhode Island Sound," University of Rhode Island, Marine Technical Report No. 2, 1972.

14. Salazar, M. H. "Effects of Lead and Chromium From NARF, San Diego, on the Marine Environment," Manuscript, undated.

15. Villa, O., Jr., and P. G. Johnson. "Distribution of Metals in Baltimore Harbor Sediments," Environmental Protection Agency, Baltimore, MD. NTIS PB 229-258, January 1974.

16. Chen, K. Y., and C. C. Wang. "Physicochemical Results of Elutriate Tests of Sediments From the Proposed LNG Route," report submitted to the Board of Harbor Commissioners of the City of Los Angeles, June 1974.

17. Anderlini, V. C., J. W. Chapman, D. G. Girvin, A. S. Newton and R. W. Risebrough. "Dredging Impact - Heavy Metals Uptake Study," Draft Final Report to U. S. Army Corps of Engineers, San Francisco District by Lawrence Berkeley Laboratories, September 1974.

18. Harlin, C. C. "Control of Mercury Pollution in Sediments," Robert S. Kerr Water Research Center, Ada, Oklahoma, EPA Technical Series No. EPA-R2-72-043, 1972.

19. Haupert, T. J. "An Investigation of Concentration Profiles and the Biological Activity of Heavy Metals in Estuarine Muds and Benthic Invertebrates," Final Report, California State College, Sacramento, CA, October 24, 1972.

20. Moyer, B. R., and T. F. Budinger. "Cadmium Levels in the Shoreline Sediments of San Francisco Bay," Lawrence Berkeley Laboratories, Report 2642, April 1974.

21. U. S. Army Corps of Engineers. "Preliminary Report on the Main Ship Channel, San Francisco Bar," San Francisco District, San Francisco, CA, June 1971.

22. McCulloch, D. S., et al. "Distribution of Mercury in Surface Sediments in San Francisco Bay Estuary, California," San Francisco Bay Region Environment and Resource Planning Study by U. S. Department of the Interior/Geological Survey and U. S. Department of Housing and Urban Development/Research and Technology, 1971.

23. Peterson, D. H., et al. "Distribution of Lead and Copper in Surface Sediments in the San Francisco Bay Estuary, California," San Francisco Bay Regional Environment and Resource Planning Study by U. S. Department of the Interior/Geological Survey and U. S. Department of Housing and Urban Development/Research and Technology, 1972.

24. Burrell, D. C. Atomic Spectrometric Analysis of Heavy Metal Pollutants in Water, Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 331 pp., 1974.

25. Brooks, R. R., B. J. Presley and I. R. Kaplan. "Trace Elements in the Interstitial Waters of Marine Sediments," Geochim. Cosmochim. Acta, Vol. 32, pp. 397-414, 1968.

26. Cutshall, N. H. "Heavy Metals in Estuaries and the Coastal Zone," Oregon State University School of Oceanography, Corvallis, Oregon, paper presented October 5, 1972.

27. Dehlinger, P., W. F. Fitzgerald, S. Y. Feng, D. F. Paskanskay, R. W. Garvine and W. F. Bohlen. "Determinations of Budgets of Heavy Metal Wastes in Long Island Sound," Annual Report, University of Connecticut Marine Sciences Institute, June 1973.

28. Duchart, P., S. E. Calvert and N. B. Price. "Distribution of Trace Metals in the Pore Waters of Shallow Marine Sediments," J. Limn. and Ocean., Vol. 18, No. 4, pp. 605-610, July 1973.

29. Knauer, G. A., and J. H. Martin. "Seasonal Variations of Cadmium, Copper, Manganese, Lead and Zinc in Water and Phytoplankton in Monterey Bay, California," J. Limn. and Ocean., Vol. 18, No. 4, pp. 597-604, July 1973.

30. Schell, W. R., and R. S. Barnes. "Lead and Mercury in the Aquatic Environment of Western Washington State," in Aqueous-Environmental Chemistry of Metals, A. J. Rubin, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1974.

31. Windom, H. L. "Processes Responsible for Water Quality Changes During Pipeline Dredging in Marine Environments," paper presented at World Dredging Conference, Hamburg, Germany, June 1973.

32. Zirino, A., and M. L. Healy. "Voltametric Measurement of Zinc in the Northeast Tropical Pacific Ocean," J. Limn. and Ocean., Vol. 16, No. 5, pp. 773-78, September 1971.

33. Lee, G. F., and R. H. Plumb. "Literature Review on Research Study for the Development of Dredged Material Disposal Criteria," U. S. Army Corps of Engineers, Vicksburg, MS, Contract No. DACW-39-74-C-0024, 1974.

34. Chester, R., and M. J. Hughes. "The Distribution of Manganese, Iron, and Nickel in a North Pacific Deep Sea Clay Core," Deep Sea Res., Vol. 13, pp. 627-34, 1966.

35. Chester, R., and M. J. Hughes. "The Trace Element Geochemistry of a North Pacific Pelagic Clay Core," Deep Sea Res., Vol. 16, pp. 639-654, 1969.

36. Chester, R., and M. J. Hughes. "A Chemical Technique for the Separation of Ferro-manganese Minerals, Carbonate Minerals, and Absorbed Trace Elements From Pelagic Sediments," Chem. Geol., Vol. 2, pp. 249-262, 1967.

37. Nissenbaum, A., B. J. Presley and I. R. Kaplan. "Early Diagenesis in a Reducing Fjord, Saanich Inlet, British Columbia. I - Chemical and Isotopic Changes in Major Components of Interstitial Water," Geochim. Cosmochim. Acta, Vol. 36, pp. 1007-1027, 1972.

38. Nissenbaum, A. "Distribution of Several Metals in Chemical Fractions of a Sediment Core From the Sea of Okhotsk," Israel J. of Earth Sciences, Vol. 21, pp. 143-54, 1972.

39. Engler, R. M., J. M. Brannon, J. Rose and G. Bigham. "A Practical Selective Extraction Procedure for Sediment Characterization," U. S. Army Corps of Engineers, Vicksburg, MS, Manuscript, 1974.

40. Gibbs, R. J. "Mechanisms of Trace Metal Transport in Rivers," Science, Vol. 180, p. 72, April 6, 1970.

41. Turekian, K. K., and M. R. Scott. "Concentrations of Cr, Ag, Mo, Ni, Co, and Mn in Suspended Material in Streams," Environ. Science & Tech., Vol. 1, p. 940, November 1967.

42. Presley, B. J., Y. Kolodny, A. Nissenbaum and I. R. Kaplan. "Early Diagenesis in a Reducing Fjord, Saanich Inlet, British Columbia. II - Trace Element Distribution in Interstitial Water and Sediment," Geochim. Cosmochim. Acta, Vol. 36, pp. 1073-1090, 1972.

43. Hirst, D. M. "The Geochemistry of Modern Sediments From the Gulf of Paria. II - Trace Elements," Geochim. Cosmochim. Acta, Vol. 26, pp. 1147-1187, 1962.

44. Gross, M. G., et al. "Survey of Marine Waste Deposits, New York Metropolitan Region," Technical Report No. 8, Marine Sciences Research Center, State University of New York, Stony Brook, NY, April 1971.

45. Mattraw, H. C. "Cation Exchange Capacity and Exchangeable Metals in Soils and Sediments of a South Florida Watershed," Florida State University for U. S. Department of the Interior, NTIS PB 233-526, 1973.

46. Walters, L. J., Jr., and T. J. Wolery. "Transfer of Heavy Metal Pollutants From Lake Erie Bottom Sediments to the Overlying Water," State of Ohio Water Resources Center, Ohio State University, January 1974.

47. Syers, J. K., I. K. Iskandar and D. R. Keeney. "Distribution and Background Levels of Mercury in Sediment Cores From Selected Wisconsin Lakes," J. Water, Air & Soil Pollution, Vol. 2, p. 105, 1973.

48. Stumm, W., and J. J. Morgan. Aquatic Chemistry, Wiley-Interscience, Inc., New York, NY, 1970.

49. Garrells, R. M., and C. L. Christ. Solutions, Minerals and Equilibria, Harper and Row, New York, NY, 1965.

50. Leckie, J. O., and R. O. James. "Control Mechanisms for Trace Metals in Natural Waters," in Aqueous-Environmental Chemistry of Metals, A. J. Rubin, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1974.

51. Jenne, E. A. "Controls on Mn, Fe, Co, Ni, Cr and Zn Concentrations in Soils and Water," in Trace Inorganics in Water, Advances in Chemistry Series No. 73, American Chemical Society, Washington, DC, 1968.

52. Zirino, A., and S. Yamamoto. "A pH-Dependent Model for the Chemical Speciation of Copper, Zinc, Cadmium and Lead in Seawater," J. Limn. and Ocean., Vol. 17, No. 5, pp. 661-71, September 1972.

53. Zirino, A., and M. L. Healy. "Inorganic Zinc Complexes in Seawater," J. Limn. and Ocean., Vol. 15, No. 6, pp. 956-58, November 1970.

54. Gardiner, J. "The Chemistry of Cadmium in Natural Water, I: A Study of Cadmium Complex Formation Using the Cadmium Specific Ion Electrode," Water Research, Vol. 8, pp. 23-30, 1974.

55. Krenkel, P. A., R. S. Reimers and W. D. Burrows. "Mechanisms of Mercury Transformation in Bottom Sediments, Part I," Technical Report No. 31, Environmental and Water Resources Engineering, Vanderbilt University, Nashville, TN, May 1973.

56. Feick, G., R. A. Horne and D. Yeaple. "Release of Mercury From Contaminated Freshwater Sediments by Runoff of Road Deicing Salt," Science, Vol. 175, p. 1142, March 1972.

57. Bothner, M. H., and R. Carpenter. "Sorption-Desorption Reactions of Mercury With Suspended Matter in the Columbia River," IAEA/SM-158/5, International Atomic Energy Agency, Vienna, Austria.

58. Stumm, W., and H. Bilinski. "Trace Metals in Waters: Difficulties of Interpretation Arising From Our Ignorance on Their Speciation," Proceedings of the Sixth International Conference on Advances in Water Pollution Research, p. 42, Pergamon Press, New York, NY, 1971.

59. Matson, W. R. "Trace Metals, Equilibrium and Kinetics of Trace Metal Complexes in Natural Media," Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, January 1968.

60. Fitzgerald, W. F. "A Study of Certain Trace Metals in Sea Water Using Anodic Stripping Voltammetry," Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, January 1970.

61. Barcia, J., M. P. Stainton and A. L. Hamilton. "Mobilization of Some Metals in Water and Animal Tissues by NTA, EDTA and TPP," Water Research, Vol. 7, pp. 1791-1804, 1973.

62. Siegel, A. "Equilibrium Binding Studies of Zinc-Glycine Complexes to Ion Exchange Resins and Clays," Geochim. Cosmochim. Acta, Vol. 30, p. 757, 1966.

63. Gardiner, J. "The Chemistry of Cadmium in Natural Water, II. The Adsorption of Cadmium on River Muds and Naturally Occurring Solids," Water Research, Vol. 8, pp. 157-164, 1974.

64. Kharker, D. P., K. K. Turekian and K. K. Bertine. "Stream Supply of Dissolved Silver, Molybdenum, Antimony, Selenium, Chromium, Cobalt, Rubidium, and Cesium to the Oceans," Geochim. Cosmochim. Acta, Vol. 32, p. 285, 1968.

65. Johnson, V., N. Cutshall and C. Osterberg. "Retention of ^{65}Zn by Columbia River Sediments," Water Resources Research, Vol. 3, p. 99, 1967.

66. Robertson, D. E., W. B. Silker and J. C. Langford, Jr. "Transport and Depletion of Radionuclides in the Columbia River," in Radioactive Contamination of the Marine Environment, International Atomic Energy Agency, Vienna, Austria, pp. 141-158, 1973.

67. Anderson, B. J., E. A. Jenne and T. T. Chao. "The Sorption of Silver by Poorly Crystallized Manganese Oxides," Geochim. Cosmochim. Acta, Vol. 37, pp. 611-622, 1973.

68. Bondietti, E. A., R. M. Perhac, F. H. Sweeton and T. Tamura. "4.4. Toxic Metals in Lake and River Sediments," ORNL-NSF Environmental Program Progress Report, June 30, 1973.

69. Jenne, E. A., and J. S. Wahlberg. "Role of Certain Stream-Sediment Components in Radioion Sorption," Geological Survey Professional Paper 433-F, F1-16, 1968.

70. Loganathan, P., and R. G. Burau. "Sorption of Heavy Metal Ions by a Hydrous Manganese Oxide," Geochim. Cosmochim. Acta, Vol. 37, pp. 1277-1293, 1973.

71. Lockwood, R. A., and K. Y. Chen. "Adsorption of Hg(II) by Hydrous Manganese Oxides," Environ. Science & Tech., Vol. 7, No. 11, pp. 1028-1034, November 1973.

72. Parks, G. A. "Trace Metals in Water: Origin, Fate, and Control. Vol. I - Mercury," Report of Progress - March 1, 1972 to February 1, 1973; NSF Grant GI-32943, Stanford University, Palo Alto, CA, 1973.

73. Williams, S. L., D. B. Aulenbach and N. L. Clesceri. "Sources and Distribution of Trace Metals in Aquatic Environments," in Aqueous-Environmental Chemistry of Metals, A. J. Rubin, ed., Ann Arbor Science Publishers, Inc., Ann Arbor, MI, 1974.

74. Feick, G., E. E. Johanson and D. S. Yeaple. "Control of Mercury Contamination in Freshwater Sediments," EPA Document EPA-R2-72-077, October 1972.

75. Windom, H. L. "Transport, Fate and Geochemical Interactions of Mercury, Cadmium and Other Inorganic Pollutants in the Coastal Littoral-Salt Marsh Environment of the Southeastern United States," EPA report, NTIS PB 227-035, May 1973.

76. Sverdrup, H. U., M. W. Johnson and R. H. Fleming. The Oceans, Prentice Hall, Inc., Englewood Cliffs, NJ, pp. 1008-1017, 1942.

77. Windom, H. L. "Environmental Aspects of Dredging in Estuaries," J. of Waterways, Harbors and Coastal Engrg., pp. 475-487, November 1972.

78. Lopez-Diaz, J. M. "Aqueous Environmental Chemistry of Copper and Other Heavy Metals in Torch Lake and Selected Waters of the Keweenaw Peninsula Area of Lake Superior," M.S. Thesis, University of Wisconsin, Madison, WI, 1973.

79. Lu, J. C. S., and K. Y. Chen. "Transport of Trace Metals From Nearshore Sediments," presented at 168th ACS National Meeting, Atlantic City, NJ, Symposium on Chemistry of Marine Sediments, September 1974.

80. Rohatgi, N., and K. Y. Chen. "Transport of Trace Metals by Suspended Particles Upon Mixing With Seawater," presented at 47th Annual Conference of the Water Pollution Control Federation, Denver, CO, October 6-11, 1974.

81. Hendricks, T. J., and D. R. Young. "Modeling the Fates of Metals in Ocean Discharged Wastewaters," Southern California Coastal Water Research Project, TM 208, January 1974.

82. Interdepartmental Task Force on PCB's. "Polychlorinated Biphenyls and the Environment," Departments of Agriculture; Commerce; Health, Education and Welfare; Interior; and Environmental Protection Agency; plus other participating agencies. NTIS Report No. COM-72-10419, 1972.

83. Goldberg, E. D. "Baseline Studies of Heavy Metal, Halogenated Hydrocarbon, and Petroleum Hydrocarbon Pollutants in the Marine Environment and Research Recommendations," National Science Foundation, NTIS PB-233 959, 1972.

84. Harvey, G. R., W. G. Steinhauer and J. M. Teal. "Polychlorobiphenyls in North Atlantic Ocean Water," *Science*, Vol. 180, pp. 643-44, May 11, 1973.

85. Servizi, J. A., R. W. Gordon and D. W. Martens. "Marine Disposal of Sediments From Bellingham Harbor as Related to Sockeye and Pink Salmon Fisheries," International Pacific Salmon Fisheries Commission Progress Report No. 23, New Westminster, B. C., Canada, 1969.

86. Kneip, T. J., G. Re and T. Hernandez. "Cadmium in an Aquatic Ecosystem: Distribution and Effects," presented at 8th Annual Conference of Trace Substances in Environmental Health, University of Missouri, June 1974.

87. NAVOCEANO, Physical Oceanography Division. "Environmental Investigation of a Dredge Spoil Disposal Site Near Mayport, Florida," Technical Note No. 6110-4-73, July 1973.

88. Slotta, L. S., C. K. Sollitt, D. A. Bella, D. R. Hancock, J. E. McCauley and R. Parr. "Effects of Hopper Dredging and In-Channel Spoiling in Coos Bay, Oregon," report for U. S. Army Corps of Engineers, Portland District, Portland, OR, July 1973.

89. Westley, R. E., E. Finn, M. I. Carr, M. A. Tarr, A. J. Scholz, L. Goodwin, R. W. Sternberg and E. E. Collias. "Evaluation of Effects of Channel Maintenance Dredging and Disposal on the Marine Environment in Southern Puget Sound, Washington," State of Washington Department of Fisheries, Management and Research Division, Olympia, WA, December 1973.

90. May, E. B. "Environmental Effects of Hydraulic Dredging in Estuaries," *Alabama Marine Resources Bulletin*, No. 9, pp. 1-85, April 1973.

91. May, E. B. "Effects on Water Quality When Dredging a Polluted Harbor Using Confined Spoil Disposal," Alabama Marine Resources Bulletin, No. 10, pp. 1-8, May 1974.

92. Windom, H. L., and R. R. Stickney. "Research to Determine the Environmental Response to the Deposition of Spoil on Salt Marshes Using Diked and Undiked Techniques," NTIS No. AD-757 717, April 1972.

93. Boyd, M. B., R. T. Saucier, J. W. Keeley, R. L. Montgomery, R. D. Brown, D. B. Mathis and C. J. Guice. "Disposal of Dredge Spoil - Problem Identification and Assessment and Research Program Development," U. S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MI, Technical Report H-72-8, November 1972.

94. U. S. Fish and Wildlife Service. "Effects on Fish Resources of Dredging and Spoil Disposal in San Francisco and San Pablo Bays, California," Washington, DC, November 1970.

95. Brown and Caldwell. "Effects of Dredged Materials on Dissolved Oxygen in Receiving Water," report for U. S. Army Corps of Engineers, San Francisco District, San Francisco, CA, March 1973.

96. Moodie, C. D., H. W. Smith and R. L. Hansenbuiller. Laboratory Manual for Soil Fertility, pp. 31-40, 1963.

97. Patrick, W. H., Jr. "Modification of Method of Particle Size Analysis," Proc. Soil Science Soc. of America, Vol. 22, No. 4, pp. 366-67, 1958.

98. Kittrick, J. A., and E. W. Hope. "A Procedure for the Particle Size Separation of Soils for X-ray Diffraction Analysis," Soil Science, Vol. 96, No. 5, pp. 319-325, 1963.

99. Routson, R. C., R. E. Wildung and R. J. Serne. "A Column Cation-Exchange-Capacity Procedure for Low Exchange-Capacity Sands," Soil Science, Vol. 115, p. 107, 1973.

100. Standard Methods, American Public Health Association, Inc., 13th ed., pp. 551-559, 1971.

101. Hajek, B. F., and R. E. Wildung. "Chemical Characterization of Pond Sediments," Northwest Science, Vol. 43, No. 2, pp. 30-130, 1969.

102. Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside, NY 11377.

103. Black, C. A., ed. Methods of Soil Analysis, Part 2, American Society of Agronomy, No. 9, pp. 1389-1392, 1965.

104. Smith, R. G., and H. L. Windom. "Analytical Handbook for the Determination of Arsenic, Cadmium, Cobalt, Copper, Iron, Lead, Manganese, Mercury, Nickel, Silver, and Zinc in the Marine and Estuarine Environments," Georgia Marine Science Center, Technical Report Series No. 72-6, September 1972.

105. Ramirez-Munoz, J. Atomic Absorption Spectroscopy, Elsevier Publishing Company, 1968.

106. Kalb, G. W. "The Determination of Mercury in Water and Sediment Samples by Flameless Atomic Absorption," A. A. News, Vol. 9, No. 4, pp. 84-87, 1970.

107. Wisconsin Alumnae Research Foundation, P.O. Box 2599, Madison, WI 53701.

108. Pesticide Analytical Manual, Vol. I, 2nd ed., revised July 1970, Section 212 and 320.

109. Knudsen, M. The Determination of Chlorinity by the Knudsen Method, G. M. Manufacturing Company, New York, NY, 1962.

110. Brooks, R. R., B. J. Presley and I. R. Kaplan. "APDC-MIBK Extraction System for the Determination of Trace Elements in Saline Waters by Atomic Absorption Spectrophotometry," Talanta, Vol. 14, pp. 809-816, 1967.

111. Segar, D. A., and J. G. Gonzalez. "Evaluation of Atomic Absorption With Graphite Atomizer for the Direct Determination of Trace Transition Metals in Sea Water," Anal. Chim. Acta, Vol. 58, pp. 7-14, 1972.

112. Chen, K. Y., University of Southern California, Department of Environmental Engineering. Personal communication, July 1974.

113. Gotoh, S., and W. H. Patrick, Jr. "Transformation of Manganese in a Water-logged Soil as Affected by Redox Potential and pH," Proc. Soil Science Soc. of America, Vol. 36, No. 5, pp. 738-742, 1972.

114. Gotoh, S., and W. H. Patrick, Jr. "Transformation of Iron in a Water-logged Soil as Influenced by Redox Potential and pH," Proc. Soil Science Soc. of America, Vol. 38, No. 1, pp. 66-71, 1974.

115. Engler, R. M., and W. H. Patrick, Jr. "Sulfate Reduction and Sulfide Oxidation in Flooded Soil as Affected by Chemical Oxidants," Proc. Soil Science Soc. of America, Vol. 37, No. 5, pp. 685-688, 1973.

116. Pearson, E. A., P. N. Storrs and R. E. Selleck. "Final Report: A Comprehensive Study of San Francisco Bay. Volume VIII - Summary, Conclusions and Recommendations," SERL Report No. 67-5, July 1970.

117. Wakeman, T. H., U. S. Army Corps of Engineers, San Francisco District. Personal communication, 1974.

118. Kuenen, P. H. "Geological Conditions of Sedimentation," in *Chemical Oceanography, Vol. 2*, J. P. Riley and G. Skirrow, eds., Academic Press, pp. 1-20, 1965.

119. Berner, R. A. "Kinetic Models for the Early Diagenesis of Nitrogen, Sulfur, Phosphorus, and Silicon in Anoxic Marine Sediments," in *The Sea, Volume 5: Marine Chemistry*, E. D. Goldberg, ed., John Wiley and Sons, New York, NY, pp. 427-450, 1974.

120. Wakeman, T. H., U. S. Army Corps of Engineers, San Francisco District. Personal communication, July 2, 1973.

121. Chen, K. Y., University of Southern California, Department of Environmental Engineering, Los Angeles, CA. Personal communication, 1974.

122. Brannon, J. M., U. S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MS. Personal communication, 1974.

123. VanLoon, J. C., J. Lichwa, D. Ruttan and J. Kinrade. "The Determination of Heavy Metals in Domestic Sewage Treatment Plant Wastes," *J. Water, Air and Soil Pollution*, Vol. 2, pp. 473-482, 1973.

124. Peterson, J. O. "A Study of Lead in Lake Sediments," Ph.D. Thesis, University of Wisconsin, Madison, WI, 1973.

125. Barnard, W. M., and M. J. Fishman. "Evaluation of the Use of the Heated Graphite Atomizer for the Routine Determination of Trace Metals in Water," *A. A. News*, Vol. 12, No. 5, September-October 1973.

126. Keeley, J. W., and R. M. Engler. "Discussion of Regulatory Criteria for Ocean Disposal of Dredged Materials: Elutriate Test Rationale and Implementation Guidelines," Misc. Paper D-74-14, U. S. Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MS, March 1974.

APPENDIX A

NEUTRON ACTIVATION, X-RAY FLUORESCENCE DATA AND SELECTED CORRELATIONS

APPENDIX A

NEUTRON ACTIVATION, X-RAY FLUORESCENCE DATA AND SELECTED CORRELATIONS

Analytical results by neutron activation and X-ray fluorescence on San Francisco Bay sediment samples are given in Table A-I. The sediment samples were dried, ground, and well-mixed prior to subsampling for analysis. The elements were determined directly without further pretreatment or post-treatment to separate and purify constituents in the sediments. Twenty-eight elements were determined by neutron activation and twenty-one elements were determined by X-ray fluorescence. Eleven elements were determined by both methods giving a total of thirty-eight different elements. The methods agreed within a standard deviation for the elements aluminum, chlorine, chromium, iron, and arsenic. Both analytical techniques employed NBS geological standards AGV-1 and BCR-1 for calibration.

Several of the sediment samples analyzed by the neutron activation studies were both freeze dried and oven dried. Analyses showed no definite differences in the concentrations of elements in the sediments by these drying techniques. Three subsamples, Oakland Outer Harbor Channel PVC 2, Richmond Harbor Channel PVC 1, and Mare Island Strait Channel PVC 2, were washed with distilled water before freeze-drying. These samples are marked with an asterisk in Table A-I. The other freeze-dried samples were not washed and were dried in an instrument which inadvertently allowed mercury from a manometer to contaminate

TABLE A-I

NEUTRON ACTIVATION AND X-RAY FLUORESCENCE DATA

		Elements in Sediment as % or ppm Dry Weight												
		Na (%)	Mg (%)	Al (%)	Si (%)	S (%)	Cl (%)	K (%)	Ca (%)	Sc ppm	Ti (%)	V ppm	Cr ppm	Mn ppm
Oakland Outer Harbor Channel														
PVC1 Oven Dry	XRF			5.68	27.1	.22	1.40	1.13	1.17		.30	185	238	376
PVC1 Oven Dry	NAA	2.06								14			330	
PVC2 Oven Dry	XRF			7.05	28.4	.28	1.47	1.33	1.10		.38	218	327	460
PVC2 Oven Dry	NAA		1.0	6.12			1.70				.31	110		590
PVC2 Freeze Dry*	NAA	2.46	1.6	5.99			2.00			16	.33	110	270	380
Oakland Outer Harbor Turning Basin														
PVC1 Oven Dry	XRF			8.33	26.4	.44	1.91	1.71	.85		.46	207	198	463
PVC1 Oven Dry	NAA	2.23	1.3	7.25			1.90			21	.30	130	190	390
PVC1 Freeze Dry	NAA	2.36	1.1	7.47			2.70			21	.35	130	180	400
PVC2 Oven Dry	XRF			10.69	27.0	.39	2.31	1.72	.85		.45	170	290	350
Oakland Inner Harbor Channel														
PVC1 Oven Dry	XRF			6.81	21.8	.43	2.59	1.41	.98		.36	241	311	493
PVC1 Oven Dry	NAA	2.80	1.4	6.49			2.90			19	.25	110	270	430
PVC1 Freeze Dry	NAA	2.27	3.3	6.18			1.80			18	.29	120	270	380
PVC2 Oven Dry	XRF			7.78	23.8	.45	1.46	1.43	1.06		.38	187	263	449
Islais Creek Shoal														
PVC1 Oven Dry	XRF			9.26	28.9	.62	2.34	1.59	.96		.46	343	290	540
PVC1 Freeze Dry	NAA	2.77	1.3	7.02			3.3			20	.24	110	200	410
PVC1 Oven Dry	NAA	2.36	1.1	6.43			2.2			18	.24	110	220	380
PVC2 Oven Dry	XRF							1.73	1.07		.44	271	298	534
Richmond Harbor Channel														
PVC1 Oven Dry	XRF			10.25	30.22	.57	2.17	1.68	.96		.48	228	171	488
PVC1 Oven Dry	NAA	2.35	1.8	8.18			2.80			19	.46		170	430
PVC1 Freeze Dry*	NAA	2.61	1.4	6.89			3.1			19	.48	150	170	370
PVC2 Oven Dry	XRF			9.41	28.74	.47	2.67	1.72	.92		.47	247	255	460
Average Standard Deviation (in %)	NAA	5	30	5			10			5	20	5	5	5
	XRF			14	11	15	11	11	11		12	35	24	14

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*Sample was rinsed with distilled water prior to freeze drying.

TABLE A-I (Cont'd.)

		Elements in Sediment as % or ppm Dry Weight												
		Fe (%)	Co ppm	Ni ppm	Cu ppm	Zn ppm	As ppm	Se ppm	Br ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Sb ppm
Oakland Outer Harbor Channel														
PVC1 Oven Dry	XRF	3.40		73	106	106	12		50	44	199	21	121	
PVC1 Oven Dry	NAA	3.32	13				6.3	2.2	70	48	390			.74
PVC2 Oven Dry	XRF	4.24		84	99	136	5.0		66	46	168	22	145	
PVC2 Oven Dry	NAA													
PVC2 Freeze Dry*	NAA	4.01	14				7.8	2.2	110	62	<100			1.0
Oakland Outer Harbor Turning Basin														
PVC1 Oven Dry	XRF	6.19		120	170	213	11		101	66	122	27	143	
PVC1 Oven Dry	NAA	5.61	18				14	4.2	130	106	106			1.6
PVC1 Freeze Dry	NAA	5.54	18				15	4.3	140	86	150			1.4
PVC2 Oven Dry	XRF	5.53		120	150	190	10		85	57	102	24	116	
Oakland Inner Harbor Channel														
PVC1 Oven Dry	XPF	5.15		78	178	256	3		116	59	142	26	144	
PVC1 Oven Dry	NAA	5.22	17				15	<1	160	87	390			1.7
PVC1 Freeze Dry	NAA	4.70	16				11	3.7	97	69	300			1.5
PVC2 Oven Dry	XRF	4.96		114	156	231	11		75	53	155	25	141	
Islais Creek Shoal														
PVC1 Oven Dry	XRF	5.60		109	165	218	3		104	60	139	25	145	
PVC1 Freeze Dry	NAA	5.37	18				13	<1	180	88	170			1.2
PVC1 Oven Dry	NAA	4.90	16				13	1.4	140	80	<100			2.0
PVC2 Oven Dry	XRF	5.97		98	156	248	11		101	71	158	28	172	
Richmond Harbor Channel														
PVC1 Oven Dry	XRF	5.14		105	144	196	6		84	54	116	23	133	
PVC1 Oven Dry	NAA	5.14	17				13	2.0	120	89	390			2.1
PVC1 Freeze Dry*	NAA	5.02	17				13	2.5	170	91	<100			1.9
PVC2 Oven Dry	XRF	5.90		125	158	235	13		121	71	155	29	174	
Average Standard Deviation (%)	NAA	5	5				10	10	10	10	20			10
	XRF	12		19	17	14	56		14	14	11	15	11	

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*Sample was rinsed with distilled water prior to freeze drying.

TABLE A-I (Cont'd.)

		Elements in Sediment as % or ppm Dry Weight											
		Cs ppm	Ba ppm	La ppm	Sm ppm	Eu ppm	Tb ppm	Yb ppm	Hf ppm	Ta ppm	Hg ppm	Pb ppm	Th ppm
Oakland Outer Harbor Channel													
PVC1 Oven Dry	XRF											30	
PVC1 Oven Dry	NAA	2.2	630	14	2.8	.72	.64	3.6	4.5	.50	.30		28
PVC2 Oven Dry	XRF											32	
PVC2 Oven Dry	NAA												
PVC2 Freeze Dry*	NAA	2.9	310	18	3.1	.8	.65	3.7	3.6	1.1	1.6		6.1
Oakland Outer Harbor Turning Basin													
PVC1 Oven Dry	XRF											90	
PVC1 Oven Dry	NAA	5.5	680	23	3.9	.91	.93	3.5	3.3	1.0	1.1		7.4
PVC1 Freeze Dry	NAA	5.5	690	21	3.6	.91	.71	3.0	3.2	.8	29.0		7.6
PVC2 Oven Dry	XRF											69	
Oakland Inner Harbor Channel													
PVC1 Oven Dry	XRF											117	
PVC1 Oven Dry	NAA	4.7	650	20	3.5	.90	.69	4.1	3.6	.85	2.5		6.8
PVC1 Freeze Dry	NAA	3.5	750	20	3.3	.87	.70	2.5	3.4	.50	61		6.0
PVC2 Oven Dry	XRF											93	
Islais Creek Shoal													
PVC1 Oven Dry	XRF											86	
PVC1 Freeze Dry	NAA	4.7	560	21	3.5	1.0	.68	2.8	3.2	.20	56		6.1
PVC1 Oven Dry	NAA	4.7	640	20	3.4	.85	.80	3.5	3.3	1.1	3.2		7.3
PVC2 Oven Dry	XRF											90	
Richmond Harbor Channel													
PVC1 Oven Dry	XRF											64	
PVC1 Oven Dry	NAA	4.7	610	21	3.6	.89	.54	3.6	3.3	.91	1.5		7.6
PVC1 Freeze Dry*	NAA	4.3	650	22	3.5	.86	.89	2.7	3.9	1.0	1.4		7.6
PVC2 Oven Dry	XRF											72	
Average Standard Deviation (%)	NAA	10	20	5	5	5	10	10	5	10	20		5
	XRF											20	

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*Sample was rinsed with distilled water prior to freeze drying.

TABLE A-I (Cont'd.)

		Elements in Sediment as % or ppm Dry Weight												
		Na (%)	Mg (%)	Al (%)	Si (%)	S (%)	Cl (%)	K (%)	Ca (%)	Sc ppm	Ti (%)	V ppm	Cr ppm	Mn ppm
Southampton Shoal Channel														
PVC1 Oven Dry	XRF			3.07	21.87	.05	.72	.88	1.87		.26	187	309	609
PVC1 Oven Dry	NAA	2.01								19			450	
PVC2 Oven Dry	XRF			4.92	25.74	.05	.52	1.01	2.07		.31	260	531	790
PVC2 Oven Dry	NAA	2.27	2.6	5.89						16	.34	140	240	820
PVC2 Freeze Dry	NAA		.7	6.18			1.3							520
Pinole Shoal Channel														
PVC1 Oven Dry	XRF			9.86	26.58	.32	1.11	1.73	1.00		.46	268	243	851
PVC1 Oven Dry	NAA	2.09	1.7	7.60						22	.32	150	220	710
PVC1 Freeze Dry	NAA	1.94	2.3	8.66						22	.36	150	160	
PVC2 Oven Dry	XRF							1.46	.82		.44	336	218	624
Mare Island Straits Channel														
PVC1 Oven Dry	XRF			10.37	27.55	.22	1.03	1.44	.89		.50	307	236	814
PVC1 Oven Dry	NAA	1.69								21			190	
PVC2 Oven Dry	XRF							1.44	1.03		.50	212	271	837
PVC2 Oven Dry	NAA		2.0	6.17			1.0				.31	120		620
PVC2 Freeze Dry*	NAA	1.83	1.7	7.60			1.5			21	.30	120	200	640
Redwood Creek Channel at Mouth														
PVC1 Oven Dry	XRF			8.26	26.51	.45	2.41	1.72	1.34		.45	224	251	902
PVC1 Oven Dry	NAA	2.44	.3	6.85			2.8			17	.33	110	180	610
PVC1 Freeze Dry	NAA	4.25	2.8	6.13			6.9			17	.23	84	160	540
AL3 Oven Dry	XRF			8.34	26.50	.49	1.68	1.73	1.26		.45	224	172	750
Redwood Creek Channel near Corkscrew Slough														
PVC1 Oven Dry	XRF			7.11	23.06	.53	2.07	1.64	4.69		.37	208	255	790
PVC1 Oven Dry	NAA	1.97	2.2	6.0			2.5			16	.28	93	160	590
Average Standard Deviation (in %)	NAA	5	30	5			10			5	20	5	5	5
	XRF			14	11	15	11	11	11		12	35	24	14

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*Sample was rinsed with distilled water prior to freeze drying.

TABLE A-I (Cont'd.)

		Elements in Sediment as % or ppm Dry Weight												
		Fe (%)	Co ppm	Ni ppm	Cu ppm	Zn ppm	As ppm	Se ppm	Br ppm	Rb ppm	Sr ppm	Y ppm	Zr ppm	Sb ppm
Southampton Shoal Channel														
PVC1 Oven Dry	XRF	4.11		69	56	93	14		20	29	242	17	84	
PVC1 Oven Dry	NAA	5.13	23				6.3	<1.0	25	44	470			.71
PVC2 Oven Dry	XRF	4.56		46	78	90	14		13	32	249	19	86	
PVC2 Oven Dry	NAA	4.8	21				9.5	<1.0	53	49	470			.72
PVC2 Freeze Dry	NAA													
Pinole Shoal Channel														
PVC1 Oven Dry	XRF	5.82		141	124	141	13		48	59	150	25	211	
PVC1 Oven Dry	NAA	5.52	23				12	4.1	70	64	340			1.4
PVC1 Freeze Dry	NAA	5.55	20				8.1	<1.0	69	83	290			1.0
PVC2 Oven Dry	XRF	5.69		129	136	161	9.0		54	53	119	27	156	
Mare Island Straits Channel														
PVC1 Oven Dry	XRF	5.96		128	142	184	16		51	63	147	30	182	
PVC1 Oven Dry	NAA	5.24	22				14	2.6	62	81	220			1.9
PVC2 Oven Dry	XRF	5.78		93	147	187	9		42	56	150	28	175	
PVC2 Oven Dry	NAA													
PVC2 Freeze Dry*	NAA	5.34	22				13	.7	80	84	290			2.3
Redwood Creek Channel at Mouth														
PVC1 Oven Dry	XRF	5.47		122	122	175	8		102	63	155	27	150	
PVC1 Oven Dry	NAA	4.81	18				11	3.6	130	91	300			1.1
PVC1 Freeze Dry	NAA	4.62	16				7.8	<1.0	290	84	200			1.1
AL3 Oven Dry	XRF	5.51		137	104	177	9		70	65	141	28	148	
Redwood Creek Channel near Corkscrew Slough														
PVC1 Oven Dry	XRF	5.13		115	173	266	9		94	63	229	24	128	
PVC1 Oven Dry	NAA	4.59	16				10	3.8	110	82	270			.83
Average Standard Deviation (in %)	NAA	5	5				10	10	10	10	20			10
	XRF	12		19	17	14	56		14	14	11	15	11	

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*Sample was rinsed with distilled water prior to freeze drying.

TABLE A-I (Cont'd.)

		Elements in Sediment as % or ppm Dry Weight											
		Cs ppm	Ba ppm	La ppm	Sm ppm	Eu ppm	Tb ppm	Yb ppm	Hf ppm	Ta ppm	Hg ppm	Pb ppm	Th ppm
Southampton Shoal Channel													
PVC1 Oven Dry	XRF											13	
PVC1 Oven Dry	NAA	1.8	550	24	3.5	.90	.70	3.6	3.2	.78	<1.0		7.8
PVC2 Oven Dry	XRF											6	
PVC2 Oven Dry	NAA	3.1	710	24	4.2	1.0	.62	2.7	2.6	1.2	1.1		4.9
PVC2 Freeze Dry	NAA												
Pinole Shoal Channel													
PVC1 Oven Dry	XRF											16	
PVC1 Oven Dry	NAA	5.2	450	22	3.9	.94	.84	3.5	3.4	1.2	1.1		7.0
PVC1 Freeze Dry	NAA	5.2	430	25	4.9	1.2	1.2	3.2	3.4	1.0	11		5.9
PVC2 Oven Dry	XRF											38	
Mare Island Straits Channel													
PVC1 Oven Dry	XRF											51	
PVC1 Oven Dry	NAA	4.8	370	24	4.0	1.1	1.1	3.5	3.8	1.3	0.8		6.2
PVC2 Oven Dry	XRF											47	
PVC2 Oven Dry	NAA												
PVC2 Freeze Dry*	NAA	4.4	650	24	4.0	.82	.82	4.2	4.4	1.3	2.7		6.7
Redwood Creek Channel at Mouth													
PVC1 Oven Dry	XRF											51	
PVC1 Oven Dry	NAA	4.8	470	21	3.4	.87	.86	2.8	3.6	1.1	<1.0		7.4
PVC1 Freeze Dry	NAA	4.8	750	18	3.0	.82	1.0	3.0	2.8	.6	22		5.5
AL3 Oven Dry	XRF											56	
Redwood Creek Channel near Corkscrew Slough													
PVC1 Oven Dry	XRF											85	
PVC1 Oven Dry	NAA	4.4	150	20	3.3	.8	.66	3.3	2.8	1.0	1.1		6.8
Average Standard Deviation (in %)	NAA	10	20	5	5	5	10	10	5	10	20		5
	XRF											20	

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*Sample was rinsed with distilled water prior to freeze drying.

the samples. Besides the large mercury values caused by this contamination, several of these samples show that salts left in the drying process can give erroneously high chlorine, sodium, and magnesium values as shown by Islais Creek Shoal PVC 1 and Redwood Creek Channel PVC 1.

The average differences between the other elements measured by both techniques are presented in Table A-II. The average difference for each element was calculated using the formula:

$$\% \text{ Difference} = \frac{\Sigma(\text{XRF} - \text{NAA})\ 100}{\Sigma \text{ XRF}}$$

where XRF is the value measured by X-ray fluorescence

NAA is the value measured by neutron activation.

TABLE A-II

AVERAGE DIFFERENCES BETWEEN THE VALUES OBTAINED BY X-RAY FLUORESCENCE AND NEUTRON ACTIVATION

Element	Average Difference (%)
Ti	+28
V	+49
Mn	+16
Rb	-39
Br	-39
Sr	-83

The V and Ti measurements by X-ray fluorescence were probably high due to an interference by barium. Barium was not determined by X-ray fluorescence and therefore a correction was not applied.

The Sr data obtained by neutron activation was not as accurate as the X-ray fluorescence data. Strontium values were near the detection limit for neutron activation. The cause for differences in the Rb and Br data are unknown.

In an attempt to evaluate the analytical values obtained by the two techniques, these results were compared to reported values obtained on similar sediments.

Figure A-1 is a plot of the ratio of vanadium to aluminum using both the X-ray fluorescence and neutron activation data. For comparison, the ratio V/Al of nearshore sediment, sands and pelagic clays are included.[1-4] Compared to the referenced literature values it appears that the neutron activation data agree more favorably than the X-ray fluorescence data. The Bay sediments also appear to be slightly enriched in vanadium.

A similar plot of the Sr/Ca ratio in the sediments would show the X-ray fluorescence data for strontium to compare more favorably than the neutron activation data to average values in the literature.

Deep sea pelagic clays have an average chromium content of 102 ppm and nearshore sediments have an average chromium content of 93 ppm.[2,3,4,6,7] The Bay sediment were all enriched over these values. The highest chromium values, Southampton Shoal Channel and Oakland Outer Harbor Channel, were areas of high sand content.

Nickel concentrations in the Bay sediment fell between the nearshore average (60 ppm) and the deep sea pelagic clay average (120-160 ppm). Low nickel contents were found in the sand sediments

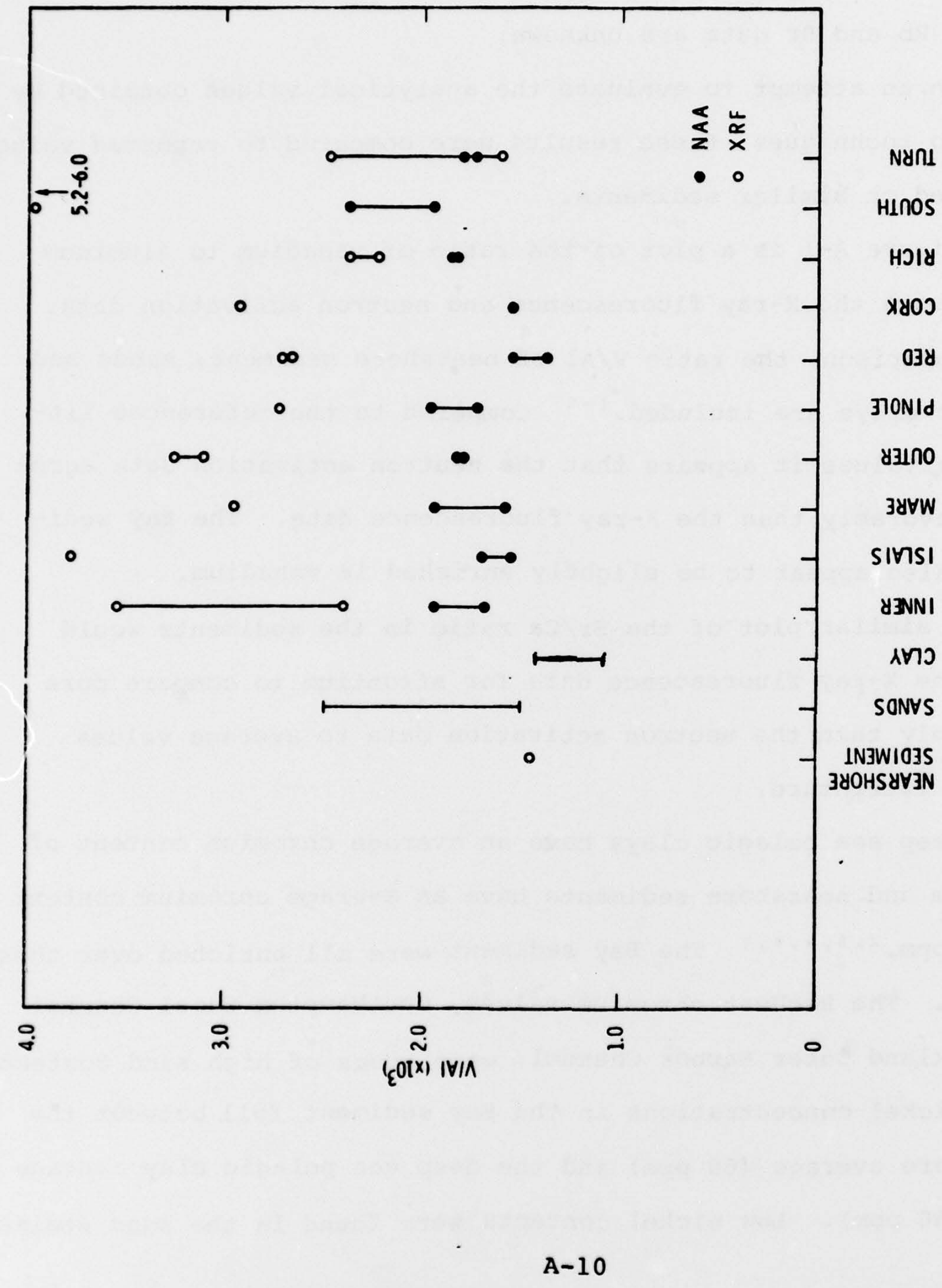

FIGURE A-1. COMPARISON OF VANADIUM RESULTS of Southampton Shoal Channel and Oakland Outer Harbor Channel. Pinole Shoal Channel appeared to have the highest nickel content.

The zinc concentrations in the Bay sediments were much higher than the nearshore average value of 80 ppm and most of the Bay sediments were higher than deep sea pelagic clays which average 144-164 ppm. Low zinc concentrations were found in the sandy sediments, Southampton Shoal Channel and Oakland Outer Harbor Channel, and in the open region of Pinole Shoal Channel. The highest zinc contents were found in regions of high industrialization, Oakland Inner Harbor Channel, Islais Creek Shoal and Richmond Harbor Channel. The highest zinc content was found near Corkscrew Slough in Redwood Creek Channel which might have been caused by the nearby sewage outfall.

Linear regression statistics were performed on the total copper, lead, zinc and mercury concentrations versus the total iron, aluminum and sulfur contents of the sediments. The sixteen sediment samples shown in Table A-III were used because they were the only samples for which data were available for all the elements listed above. X-ray fluorescence data were used for all values but mercury which was determined by flameless atomic absorption.

Figure A-2 is a plot of the lead content versus total iron content of the Bay sediments. The lead contents like zinc were higher than average nearshore sediments reported in the literature[3-7] for natural nearshore sediments. Again the sandy and open Bay region sediments showed the lowest lead contents and nearshore industrialized regions had the largest lead content.

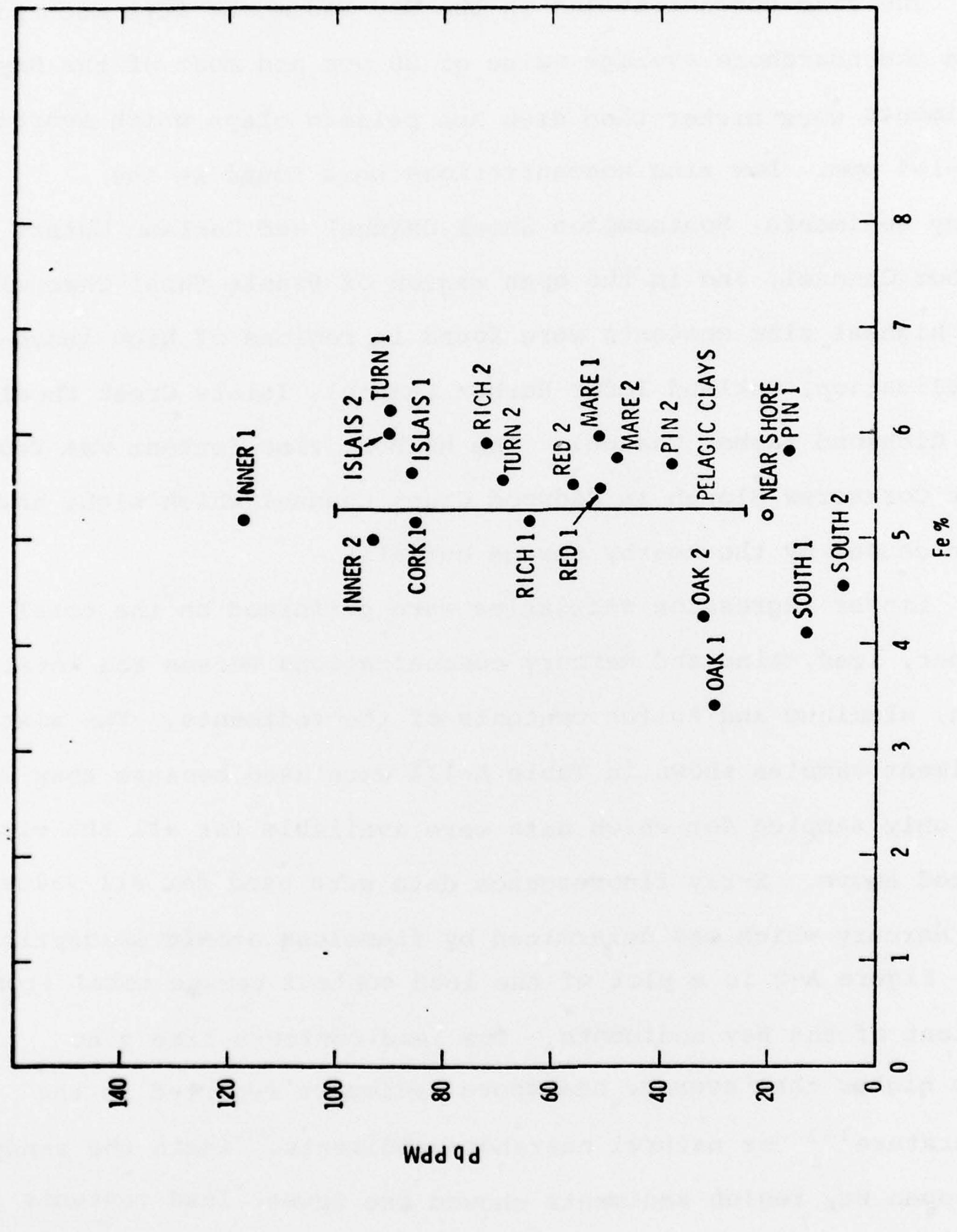

FIGURE A-2. LEAD CONTENT VS IRON IN SEDIMENT

TABLE A-III

SAMPLES USED FOR REGRESSION ANALYSES

1	Oakland Outer Harbor	PVC 1
2	Oakland Outer Harbor	PVC 2
3	Oakland Turning Basin	PVC 1
4	Oakland Turning Basin	PVC 2
5	Oakland Inner Harbor	PVC 1
6	Oakland Inner Harbor	PVC 2
7	Islais Creek	PVC 1
8	Richmond Harbor	PVC 1
9	Richmond Harbor	PVC 2
10	Southampton Shoals	PVC 1
11	Southampton Shoals	PVC 2
12	Pinole Shoals	PVC 1
13	Mare Island	PVC 1
14	Redwood Creek	PVC 1
15	Redwood Creek	Al 3
16	Corkscrew Slough	PVC 1

Figure A-3 contains the copper content of the sediments plotted versus total iron content. The copper content of the Bay sediments were higher than nearshore sediments reported in the literature.[3-7] As with other trace metals the high copper values were found in the finer sediments near industrialized areas.

Figures A-4 and A-5 are plots of the lead and copper contents of the sediments versus the total aluminum contents. As with iron data there was a general positive correlation of heavy metals with aluminum content.

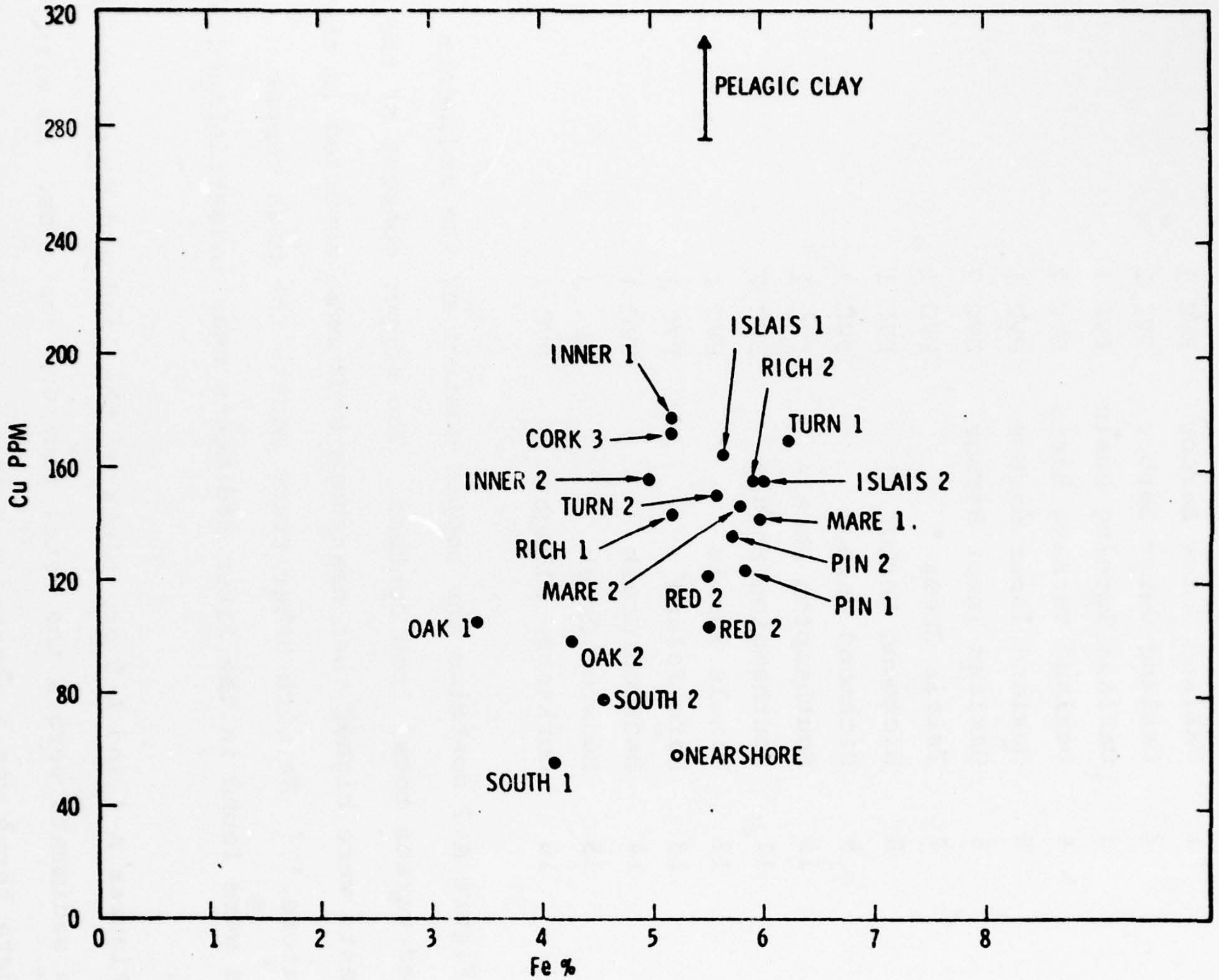

FIGURE A-3. COPPER CONTENT VS TOTAL IRON IN SEDIMENT

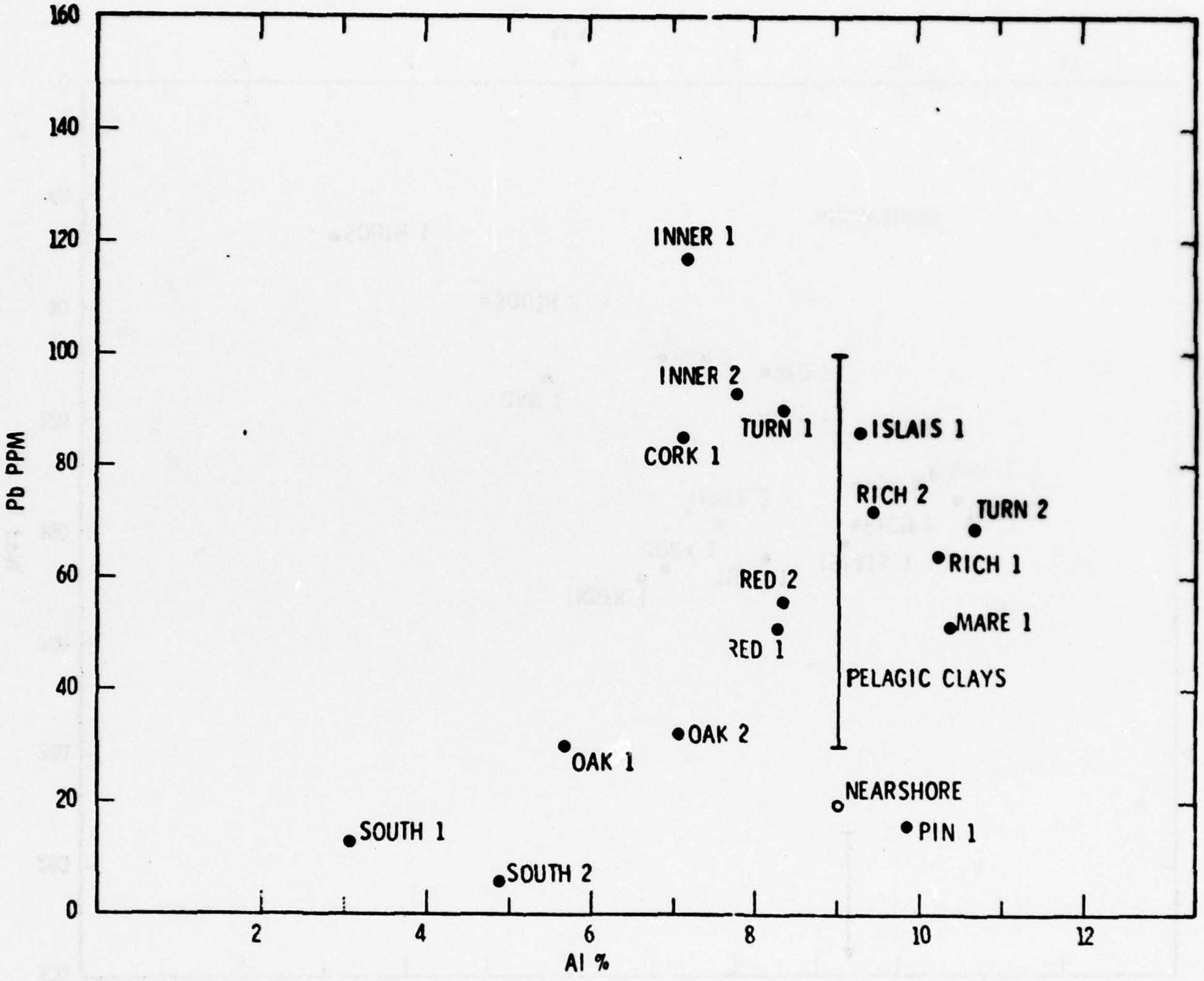

FIGURE A-4. LEAD CONTENT VS TOTAL ALUMINUM IN SEDIMENT

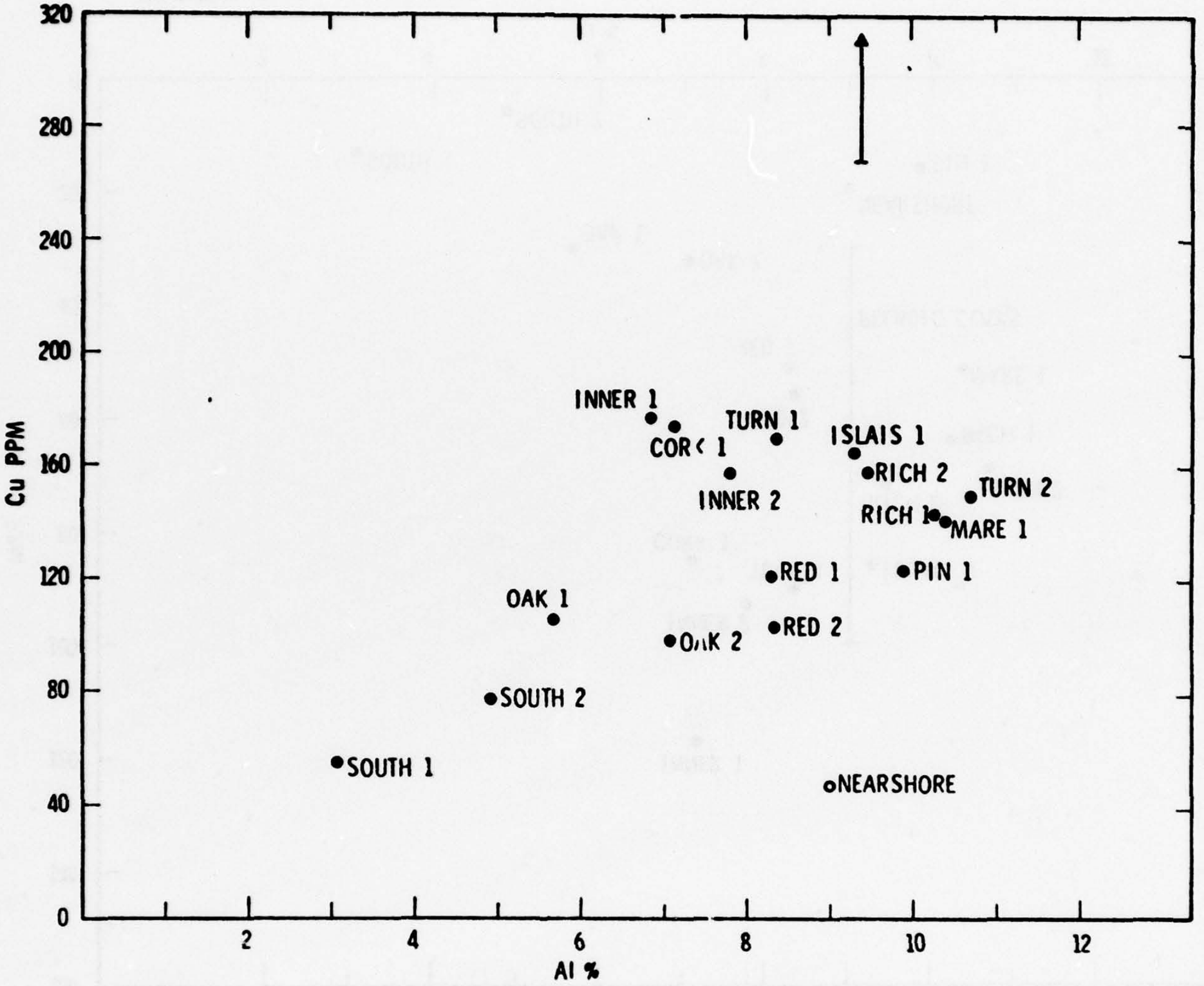

FIGURE A-5. COPPER CONTENT VS TOTAL ALUMINUM IN SEDIMENT

Figures A-6 and A-7 show plots of lead and copper contents of the sediments versus total sulfur content. The positive correlation of heavy metals with increasing sulfur content of the sediment is apparent. Similar plots of zinc and mercury would show the same trends.

Table A-IV presents the linear regression and correlation coefficients of the heavy metals with total iron, aluminum and sulfur.

TABLE A-IV

CORRELATIONS AND LINEAR REGRESSION EQUATIONS

Y vx X	r	Y = mX+b
Pb vs Fe	.40	Pb (ppm) = 19.41 Fe(%)-91.02
Cu vs Fe	.61*	Cu (ppm) = 28.84 Fe(%)-16.29
Zn vs Fe	.58*	Zn (ppm) = 42.42 Fe(%)-37.63
Hg vs Fe	.35	Hg (ppm) = 0.14 Fe(%)- 0.19
Pb vs Al	.37	Pb (ppm) = 5.65 Al(%)+ 5.85
Cu vs Al	.61*	Cu (ppm) = 10.36 Al(%)+50.45
Zn vs Al	.50	Zn (ppm) = 12.98 Al(%)+78.51
Hg vs Al	.47	Hg (ppm) = 0.06 Al(%)- 0.01
Pb vs S	.76**	Pb (ppm) = 144.2 S(%)+ 4.48
Cu vs S	.77**	Cu (ppm) = 162.2 S(%)+72.40
Zn vs S	.83**	Zn (ppm) = 273.0 S(%)+80.01
Hg vs S	.58*	Hg (ppm) = 1.0 S(%)+ 0.14

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*Significant at 5% level
**Significant at 1% level

The total iron content and total aluminum contents do not appear to significantly explain the variation in lead and mercury concentrations and only weakly explain copper and zinc. No conclusions about the geochemical distributions of the heavy metals can be drawn from this data. The total iron and total

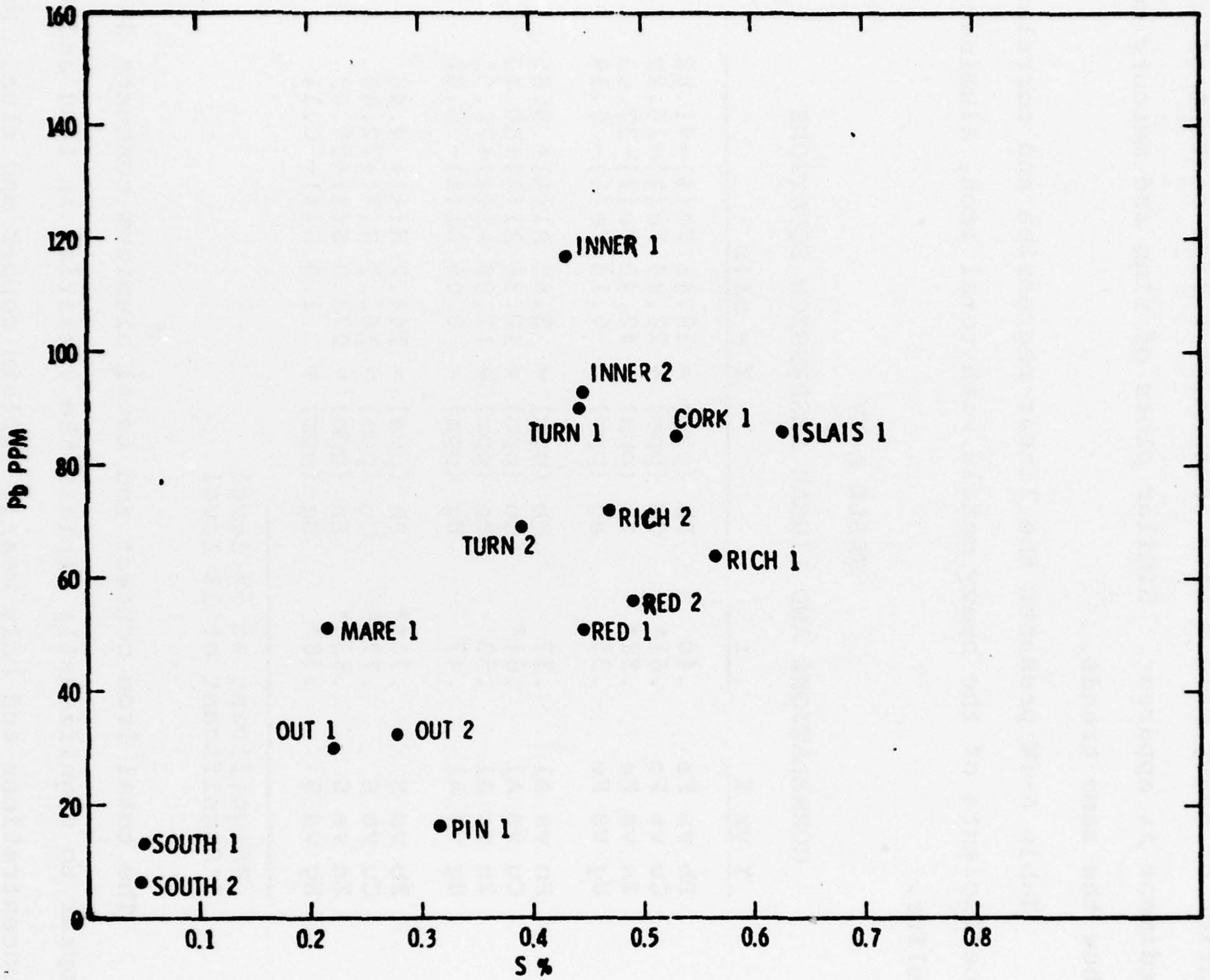

FIGURE A-6. LEAD CONCENTRATION VS TOTAL SULFUR IN SEDIMENTS

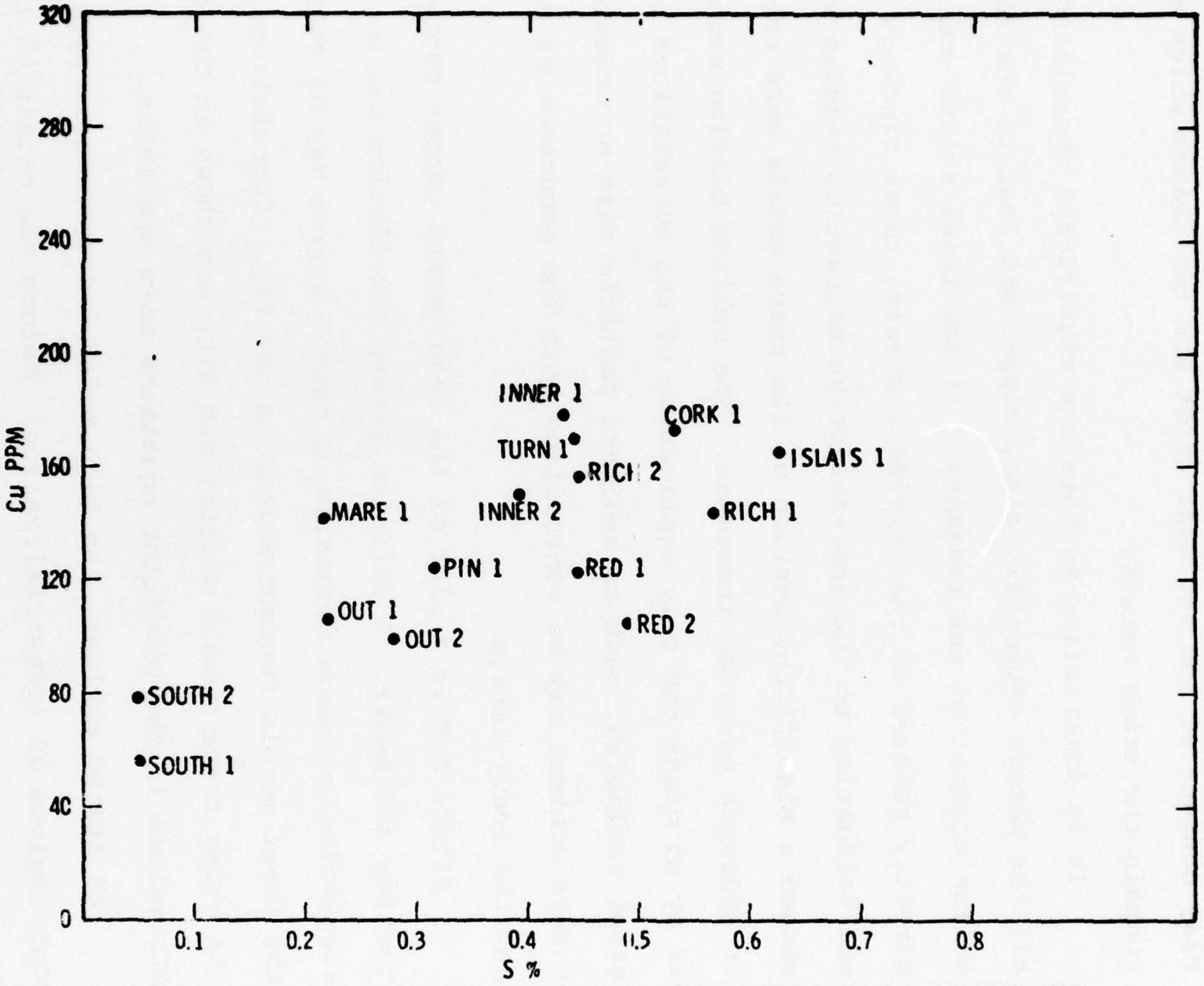

FIGURE A-7. COPPER CONCENTRATION VS TOTAL SULFUR IN SEDIMENTS aluminum may be only weakly related to the hydrous oxide and clay content of the sediment which are two phases which may contain the trace metals.

It is interesting to note the significant correlations of all the metals especially zinc, copper and lead to the total sulfur content of the sediment. If the total sulfur content is directly related to the sulfide contents, these findings may add validation to the semi-selective extraction results which showed a significant portion of the trace metals were released on hydrogen peroxide treatment. The sulfide binding mechanism is by no means the only explanation of the correlations because other variables, such as sediment particle size or organic carbon content may be controlling both the occurence of sulfur and the heavy metals.

Figure A-8 is a plot of the lead versus copper content of the Bay sediments. A definite linear correlation can be seen suggesting a common mechanism or common source may be controlling the trace metals concentrations in the Bay. Correlations with the other trace metals mercury and zinc are shown in Table A-V. All values in the predictor equations have ppm units.

As stated earlier, the high metal concentrations appeared near regions of industrialization. Before the origin of the metals can be attributed to man's activities, the source material of the Bay's sediments should be characterized to determine that the natural sediments are not inherently enriched in heavy metals. This enrichment may occur because of the significant mining which

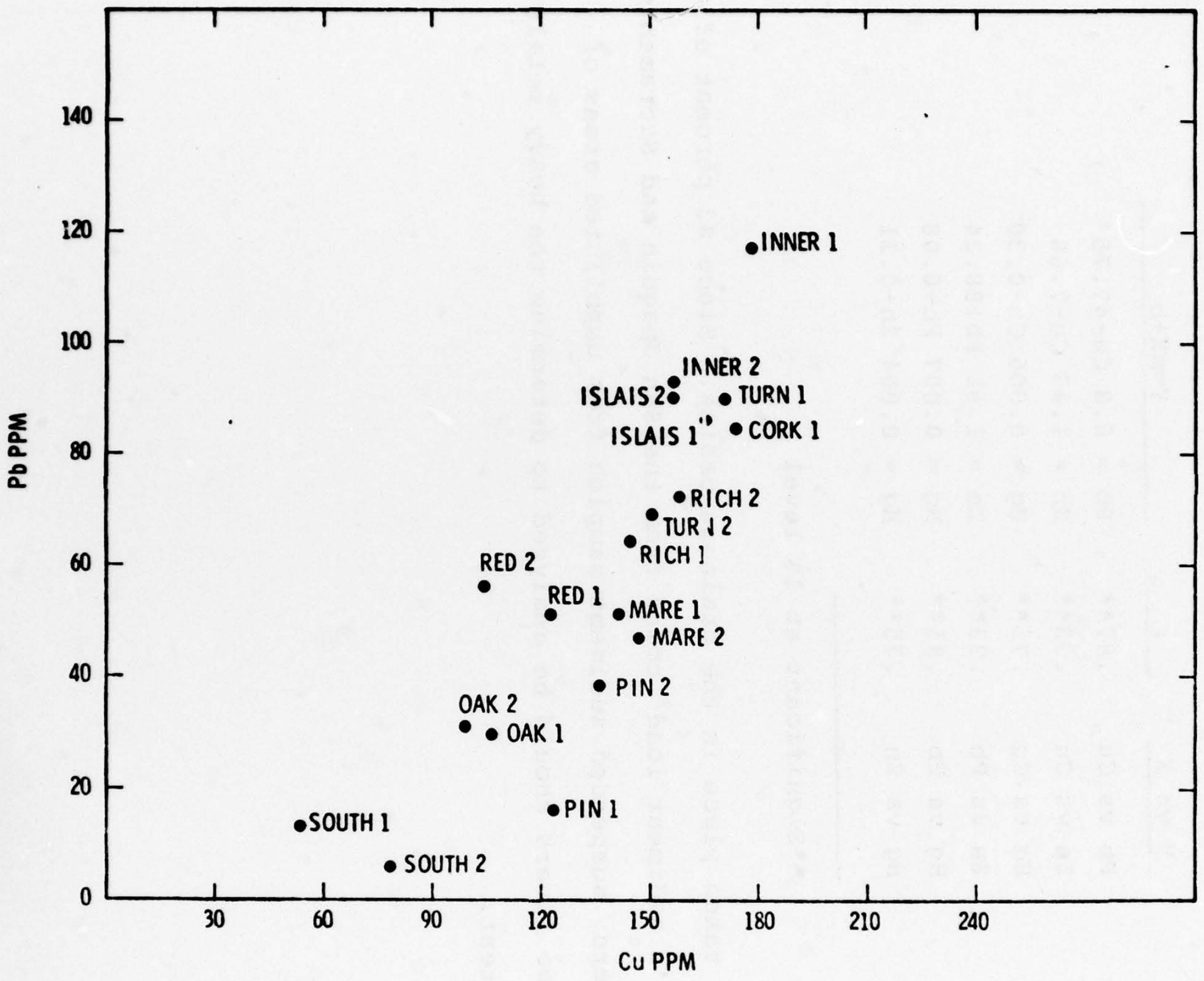

FIGURE A-8. LEAD CONCENTRATION VS COPPER CONCENTRATION IN SEDIMENT

TABLE A-V

METAL CORRELATIONS

Y vs X	r	Y=mX+b
Pb vs Cu	.87**	Pb = 0.8 Cu-49.75
Zn vs Cu	.93**	Zn = 1.43 Cu-7.68
Hg vs Cu	.75**	Hg = 0.006 Cu-0.30
Zn vs Pb	.93**	Zn = 1.61 Pb+88.24
Hg vs Pb	.81**	Hg = 0.007 Pb+0.08
Hg vs Zn	.75**	Hg = 0.004 Zn-0.21

**Significant at 1% level

has taken place in the drainage basins. Since 83 percent of the Bay's sediment load[9] comes from the San Joaquin and Sacramento Rivers, suspended sediment samples from unpolluted areas of these rivers should be analyzed to determine the heavy metals content.

APPENDIX A
REFERENCES

1. Chester, R. "Elemental Geochemistry of Marine Sediments," Chemical Oceanography, Vol. 2, J. P. Riley and G. Skirrow editors, Academic Press, New York, pp. 23-80, 1965.

2. Hirst, D. M. "The Geochemistry of Modern Sediments from the Gulf of Paria - I. Major Elements," Geochim. Cosmochim. Acta, Vol. 26, pp. 309-334, 1962.

3. Hirst, D. M. "The Geochemistry of Modern Sediments from the Gulf of Paria. II - Trace Elements," Geochim. Cosmochim. Acta, Vol. 26, pp. 1147-1187, 1962.

4. Cronan, D. S. "Average Abundances of Mn, Fe, Ni, Co, Cu, Pb, Mo, V, Cr, Ti and P in Pacific Pelagic Clays," Geochim. Cosmochim. Acta, Vol. 33, pp. 1562-1565, 1969.

5. Krauskopf, K. Introduction to Geochemistry, McGraw Hill Co., New York, pp. 639-640, 1967.

6. Chester, R. and M. J. Hughes. "The Distribution of Manganese, Iron, and Nickel in a North Pacific Deep Sea Clay Core," Deep Sea Res., Vol. 13, pp. 627-634, 1966.

7. Chester, R. and M. J. Hughes. "The Trace Element Geochemistry of a North Pacific Pelagic Clay Core," Deep Sea Res., Vol. 16, pp. 639-654, 1969.

8. Snedecor, G. W. and W. G. Cochran. Statistical Methods, 6th Ed., The Iowa State University Press, pp. 172-198, 1967.

9. Folger, D. W. "Characteristics of Estuarine Sediments of the United States," Geol. Sur. Prof. Paper 742, U. S. Government Printing Office, Washington DC, pp. 67-69, 1972.