Extractable Cadmium, Mercury, Copper, Lead, and Zinc in the Lower Columbia River Estuary, Oregon and Washington

By Gregory J. Fuhrer

U. S. Geological Survey
Water-Resources Investigations Report 86-4088

Prepared in cooperation with the
U. S. Army Corps of Engineers

Portland, Oregon
1986

UNITED STATES DEPARTMENT OF THE INTERIOR

DONALD HODEL, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director

For additional information
write to:

Oregon Office Chief
U.S. Geological Survey
847 N.E. 19th Ave., Suite 300
Portland, Oregon 97232

Copies of this report can
be purchased from:

U.S. Geological Survey
Books and Open-File Reports
Federal Center, Building 41
Box 25425
Denver, CO 80225

CONTENTS

ILLUSTRATIONS

TABLES

DEFINITION OF TERMS

Anthropogenic	Occurring as a result of human activity.
Carbon, Inorganic	Inorganic forms of carbon associated with bulk bottom material.
Elutriation	The mixing of bottom material from a potential dredge site with native water (collected from either a dredge or disposal site). The liquid part of the mixture is removed, filtered, and chemically analyzed. Elutriation tests were designed to simulate interactions between native water and bottom material when dredged and transported as a mixture.
Extractable Cadmium	Soft digestion (1N HCl) of bottom material finer than 100 microns in diameter per gram bottom material finer than 100 microns.
Extractable Chromium	Soft digestion (1N HCl) of bottom material finer than 100 microns in diameter per gram bottom material finer than 100 microns.
Extractable Copper	Soft digestion (1N HCl) of bottom material finer than 100 microns in diameter per gram bottom material finer than 100 microns.
Extractable Iron	Soft digestion (1N HCl) of bottom material finer than 100 microns in diameter per gram bottom material finer than 100 microns.
Extractable Lead	Soft digestion (1N HCl) of bottom material finer than 100 microns in diameter per gram bottom material finer than 100 microns.
Extractable Manganese	Soft digestion (1N HCl) of bottom material finer than 100 microns in diameter per gram bottom material finer than 100 microns.
Extractable Nickel	Soft digestion (1N HCl) of bottom material finer than 100 microns in diameter per gram bottom material finer than 100 microns.
Extractable Zinc	Soft digestion (1N HCl) of bottom material finer than 100 microns in diameter per gram bottom material finer than 100 microns.
Percent Clays	Percent bottom material less than 4 microns in diameter.
Percent <100 um	Percent bottom material finer than 100 microns in diameter.

Percent Silts	Percent bottom material ranging from 4 to 63 microns in diameter.
Percent TVS	Percent total volatile solids in bottom material finer than 100 microns.
TOC, Bulk	Total organic carbon associated with bulk bottom material.
TOC, <100 um	Total organic carbon associated with bottom material finer than 100 microns in diameter per kilogram bottom material finer than 100 microns.
Total Mercury	Harsh digestion (HCl, HNO_3, $KMnO_4$) of bottom material finer than 100 microns in diameter.

CONVERSION FACTORS

Multiply inch-pound units	By	To obtain SI units
	Length	
inch (in.)	25.40	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	Flow	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)

Multiply SI units	By	To obtain inch-pound units
	Length	
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
	Volume	
liter (L)	0.2642	gallon (gal)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
gram (g)	0.002205	pound, avoirdupois (lb)
	Temperature	
degree Celsius (° C)	F= 9/5°C + 32	degree Fahrenheit (° F)
	Specific Conductance	
microsiemen per centimeter at 25° Celsius (μs/cm at 25° C)	1	micromho per centimer at 25° Celsius (μmho/cm at 25°)

EXTRACTABLE CADMIUM, MERCURY, COPPER, LEAD, AND ZINC IN THE LOWER COLUMBIA RIVER ESTUARY, OREGON

--

By Gregory J. Fuhrer

--

ABSTRACT

In July of 1983 the U.S. Geological Survey, in cooperation with the U.S. Army Corps of Engineers, collected and analyzed bottom-material samples from the Columbia River estuary in order to investigate trace metals associated with the bottom material that is expected to accumulate at the sediment/water interface of in-water disposal sites and thus impact benthic deposit feeders. The interaction between bottom material and water during dredging was simulated by volumetrically mixing bulk bottom materials with native water. The association of trace metals with bottom material at the disposal site was simulated by sieving the native water and bottom material slurry to less than 100 microns in diameter--those grain sizes frequently ingested by benthic deposit feeders--and chemically extracting with 1N HCl. The 1N-HCl extraction of bottom material finer than 100 microns is a non-specific extraction that has been shown in other studies to correlate well with concentrations of metals found in the tissues of many estuarine organisms. Concentrations of trace metals in estuarine organisms were not determined in this study.

Concentrations of copper, mercury, lead, and zinc in bottom material processed under the simulated dredging/disposal procedure are not elevated, either in the high energy areas of the main navigation channel or in the low energy areas of the Ilwaco boat channel. Furthermore, these metals are not elevated relative to concentrations found in local soils, in earlier reconnaissance studies, or observed in other anthropogenically influenced estuaries.

Concentrations of cadmium from the high energy area of the main navigation channel, processed under the simulated dredging/disposal procedure, are elevated, when compared to concentrations found in lower energy areas of the Ilwaco boat channel and are similar to concentrations observed in other, anthropogenically contaminated estuaries. Bottom material in the main navigation channel has small concentrations of substrate-binding constituents like iron, manganese, and organic material. The bioavailability of cadmium to deposit feeders under these circumstances may be of concern.

Other studies have shown that the bioavailability of mercury is inversely related to total volatile solids, a measurement of organic carbon. Areas sampled in the Ilwaco boat channel contained large concentrations of total volatile solids. Thus bottom materials from these areas are not likely to contain mercury in bioavailable forms.

INTRODUCTION

Background and Statement of Problem

The U.S. Geological Survey, Water Resources Division, is a scientific agency with a mission to provide the hydrologic information and understanding needed for the best use and management of the Nation's water resources. The U.S. Army Corps of Engineers has the management responsibility for maintaining navigation channels and, under section 404 of the Clean Water Act and section 103 of the Marine Protection of Sanctuaries Act, is required to evaluate bottom materials prior to dredging. The U.S. Environmental Protection Agency examines study findings, with respect to environmental considerations, and approves the Corps of Engineers selection of a physical location for disposal of dredged materials. In cooperation with the Corps of Engineers, the Geological Survey is studying the sediment chemistry of the Columbia River estuary to provide needed information on chemicals associated with bottom material in or near authorized navigational channels. Identifying these chemicals and their respective concentrations will assist in determining potential impacts of dredged materials that may reform the sediment-water interface.

Metals bound to bottom material can be present in various physical and chemical forms, with each form capable of having a different biological availability (Bryan, Langston, and Hummerstone, 1980). In the past, elutriation tests have been used in an attempt to assess short-term impacts of dissolved chemicals in the water column. Elutriation tests, however, do not define how trace metals associate with bottom material; nor do they indicate the biological significance of sediment bound metals for deposit-feeding organisms.

The Geological Survey, in cooperation with the Corps of Engineers, collected native-water and bottom-material samples and processed elutriate samples in reconnaissance studies between May and December of 1980 (Fuhrer and Rinella, 1983) and in August of 1982 (Fuhrer, 1984).

As a result of these two earlier reconnaissance studies in the Columbia River estuary, a two-stage interpretative study was begun. The first stage (Fuhrer, unpublished data, 1985) deals with (1) assumptions and limitations of using elutriate-test data relative to dredging effects on water quality, (2) effects of dissolved constituents released from bottom material based on elutriation data, (3) identification of sampling sites where elutriate-test concentrations are elevated relative to U.S. Environmental Protection Agency criteria (U.S. Environmental Protection Agency, 1976), and (4) identification of relations between physical and chemical properties of bottom material and other water-quality characteristics. Results of the first stage indicate that some navigation-channel bottom materials contain trace-metal concentrations that are potentially toxic to benthic organisms. This potential toxicity could occur either in bottom materials re-deposited at the dredged channel or at depositional areas associated with in-water disposal sites. The second stage of the study deals with trace metals associated with bottom material and is presented in this report.

Purpose and Scope

The objectives of this study are as follows:

- determine concentrations of trace metals associated with bottom material finer than 100 microns (those grain sizes frequently ingested by deposit feeders) that have been mixed with native water and maintained in an oxygenated environment (to simulate metals that remain associated with bottom material after being dredged, transported, and disposed of in-water at an oxic disposal site),
- examine the relations of these trace metals with selected bottom-material phases,
- compare concentrations of these trace metals in bottom material with: (1) concentrations observed in other estuaries, (2) levels observed in Lower Columbia River basin soil samples, and (3) where possible, with concentrations observed in both bottom material and deposit-feeding organisms from other studies,
- review literature describing the association of trace metals with bottom-material phases.

Eight sampling sites were selected, based on the elevated trace-metal concentrations in bottom material and on the total phenol concentrations in elutriate-test filtrate that were observed in earlier reconnaissance studies (Fuhrer and Rinella, 1983; Fuhrer, 1984); results of the phenol study will be presented in a separate document. All samples were collected within approximately 13 miles of one another.

This paper does not address the speciation of trace metals in the dissolved state in the water column.

Description of Study Area

In July of 1983, bottom-material and water samples were collected in the Columbia River estuary--from the Ilwaco boat channel in Washington, from the main nagivation channel, and from a docking facility at the Port of Astoria in Oregon (fig. 1 and table 1).

According to Percy and others (1974), the Columbia River estuary is characterized by the following: (1) area of estuary equals 146 mi^2, (2) area of drainage basin equals 259,000 mi^2, (3) mean annual freshwater input equals 1.91 x 108 acre-ft, (4) estimated population of the drainage basin is greater than 3,000,000, (5) estuary has the highest degree of industrialization of any in Oregon, and (6) estuary receives municipal sewage discharge. From late fall to early spring, monthly-average river discharge fluctuates from about 100,000 ft^3/s to about 500,000 ft^3/s and is primarily affected by runoff west of the Cascade mountain range; in late spring, discharge is influenced by snowmelt and averages about 450,000 ft^3/s; from summer to early fall, discharge drops to 100,000 ft^3/s, with little contribution west of the Cascades.

Table 1.--Location of sampling sites in Baker Bay, Washington and Astoria, Oregon

Site number	Site designation	Collection date	Site location		Remarks
			Latitude	Longitude	
1	Baker Bay	07-11-83	46°15'36"	124°02'46"	Main navigation channel.
2	do.	07-11-83	46°17'31"	124°02'47"	Ilwaco boat channel.
3	do.	07-11-83	46°17'44"	124°02'31"	Do.
4	do.	07-12-83	46°17'57"	124°02'21"	Do.
5	do.	07-12-83	46°18'08"	124°02'27"	Do.
6	do.	07-12-83	46°18'18"	124°02'30"	Do.
7	Astoria	07-11-83	46°11'20"	123°51'19"	Ship pier
8	do.	07-11-83	46°11'25"	123°51'21"	Do.

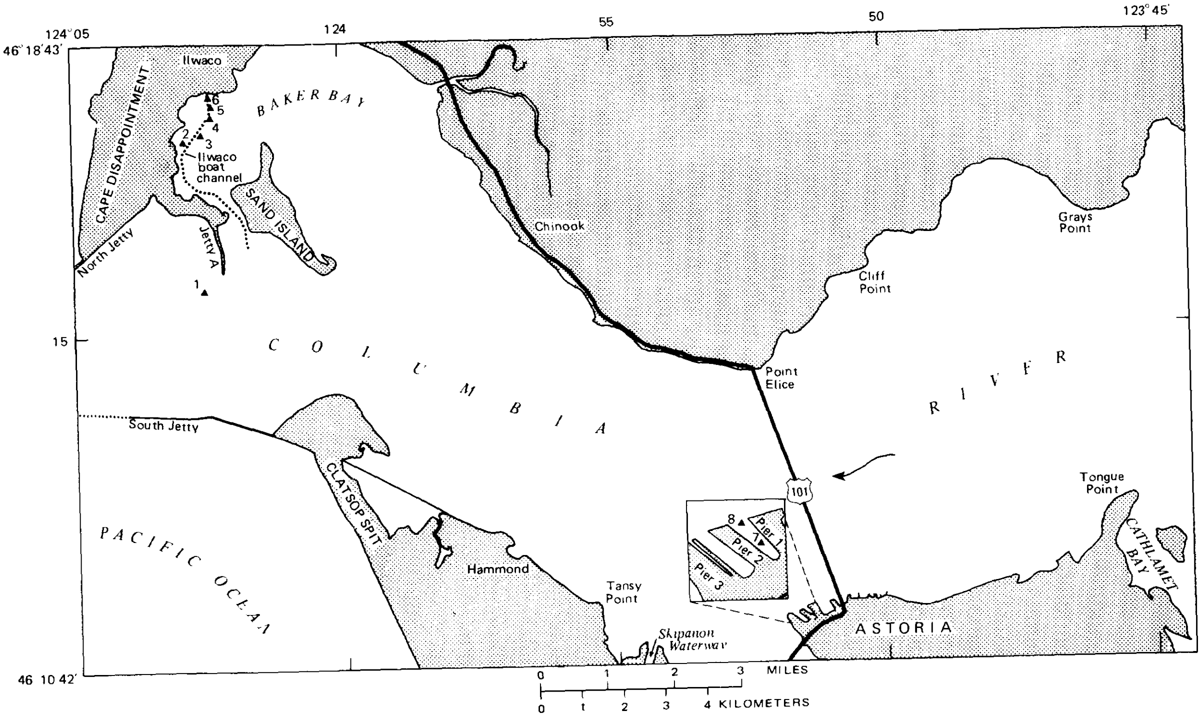

Figure 1. – Sampling site locations for Baker Bay, Washington and Astoria, Oregon.

Since 1870, as a result of man's activities to stabilize the Columbia River navigation channel, 24 percent of the estuary has been lost; 85 percent of this loss is attributed to dikes, 12 percent to disposal of dredged material, and 3 percent to accretion of sand at the mouth of the estuary (Fox and others, 1984). The aquatic environment is basically marine from Columbia River mile 8 to the mouth of the estuary; the environment between river mile 8 and 23 is a transitional zone between fluvial and marine influences (Hubbell and Glenn, 1973); and the environment above Columbia River mile 23 is fluvial.

Acknowledgements

I would like to thank Samuel N. Luoma for advice on 1N-HCl extractions of bottom material and for providing numerous journal articles relevant to this study. I would like to thank Arthur J. Horowitz for an exceptionally thorough colleague review. I would also like to thank the National Marine Fisheries Service, Hammond Field Office, for providing a sampling vessel and crew.

TRACE METALS IN THE ESTUARINE ENVIRONMENT--A REVIEW

Transformations of Trace Metals in Bottom Material

In estuarine environments, bottom sediments exist in two different states, oxic and anoxic. The oxic (oxidized zone) sediments are often a surficial layer having the greatest contact with the water column above and may overlay anoxic (reduced zone) sediments (Luoma and Bryan, 1981). Reduced solutes migrating upward from anoxic sediments interact with oxygen and other chemicals at the oxic sediment/water interface. The oxidized surface layer of bottom material acts like a diffusion zone for reduced chemical solutes. In the oxic sediment layer, the exchange of trace metals between bottom material and water is usually controlled by the precipitation of hydrous iron and manganese oxides or hydroxides (Jenne, 1968). If other trace metals are available, they may likewise be coprecipitated during this exchange. Further solute controls include organic carbon in bottom material, bioturbation of the surfacial sediment layer, and the availability of surfaces for reactions (such as clay minerals).

As the oxic sediment layer becomes buried beneath the oxic/anoxic boundary, hydrous iron and manganese oxides are exposed to reducing conditions. When a reduction of hydrous iron and manganese oxides occurs in anerobic sediments, the trace metals that are coprecipitated or sorbed onto these forms may become solubilized (Forstner and Wittman, 1979). In the presence of trace concentrations of sulfides the mobility of these trace metals may be reduced. Based only on solubility products for sulfide formation, elements like zinc, cadmium, copper, lead, and mercury are likely to be immobile in the presence of iron sulfides characterized by trace concentrations of free sulfides (Bella, 1975). There are some exceptions; Elderfield and Hepworth (1975), in Forstner and Wittman (1979), found (in interstitial pore waters) concentrations of copper, lead, and zinc that greatly exceeded those predicted from sulfide solubilities. Apparently, in some instances, other factors are responsible for soluble trace metals, even in the presence of sulfide.

Trace metals associated with bottom material are considerably less available to organisms than are dissolved metals; however, concentrations of trace metals associated with bottom material are usually orders of magnitude larger than concentrations in the dissolved phase (Luoma and Bryan, 1979; Oakley, Williamson, and Nelson, 1980) and, as such, may be a significant source to deposit-feeding organisms. Organisms living in the contact zone between sediment and water are exposed directly to metals in the oxic sediment water interface (Luoma, written commun., 1982). Most deposit feeders acquire their food--and consequently trace metals--by ingestion of certain particle-size classes of material within this important oxic zone. Particle-size selectivity may vary between species; for example, the deposit-feeding clam *Macoma balthica* ingests bottom materials finer in size than 80 microns (Luoma, 1983).

In biological organisms, the cellular membrane is considered a hydrophobic structure capable of regulating group A ions (Na^+ and Mg^{+2}), which are hydrophilic and, as such, penetrate cellular membranes in a regulated manner (Simkiss, 1983). In contrast, group B ions are considerably more complex and not as easily regulated. Some group B ions (copper, iron, manganese, nickel, and zinc) are important micronutrients for cellular activities and are primarily involved in enzymatic processes. However, some of the micronutrients, along with other group B ions (cadmium, chromium, mercury, nickel, and zinc), can be toxic when present in sufficient concentration (Engel, Sunda, and Fowler, 1981). Many organisms have a very low tolerance for increased group B metal concentrations, even in environments without anthropogenic influences (Luoma, 1983). In some instances certain organisms, like the polychaete worm Nereis, can regulate their body burden of trace metals such as zinc (Luoma and Bryan, 1978). In cases where the organism is capable of homeostatic regulation of trace-metal concentrations, it is difficult--if not impossible--using chemical extraction techniques, to assess trace metal bioavailability for that organism.

Shown in figure 2 is a simplified illustration of hypothetical trace-metal interactions with water and bottom material that would result from the disposal of dredged materials. The disposal of dredged material may affect filter feeders in the water column and (or) deposit feeders that ingest trace metals associated with resettled sediments that have become oxidized. Dissolved trace metals in the water column may chemically partition to bottom material. Gibbs (1977) describes several mechanisms for this chemical partitioning, as follows:

- Adsorption on fine grained material (clays)
- Precipitation of metal compounds
- Coprecipitation with hydrous iron/manganese oxides and carbonate
- Association by adsorption and (or) chemical bonding with organic matter
- Incorporation in crystalline minerals

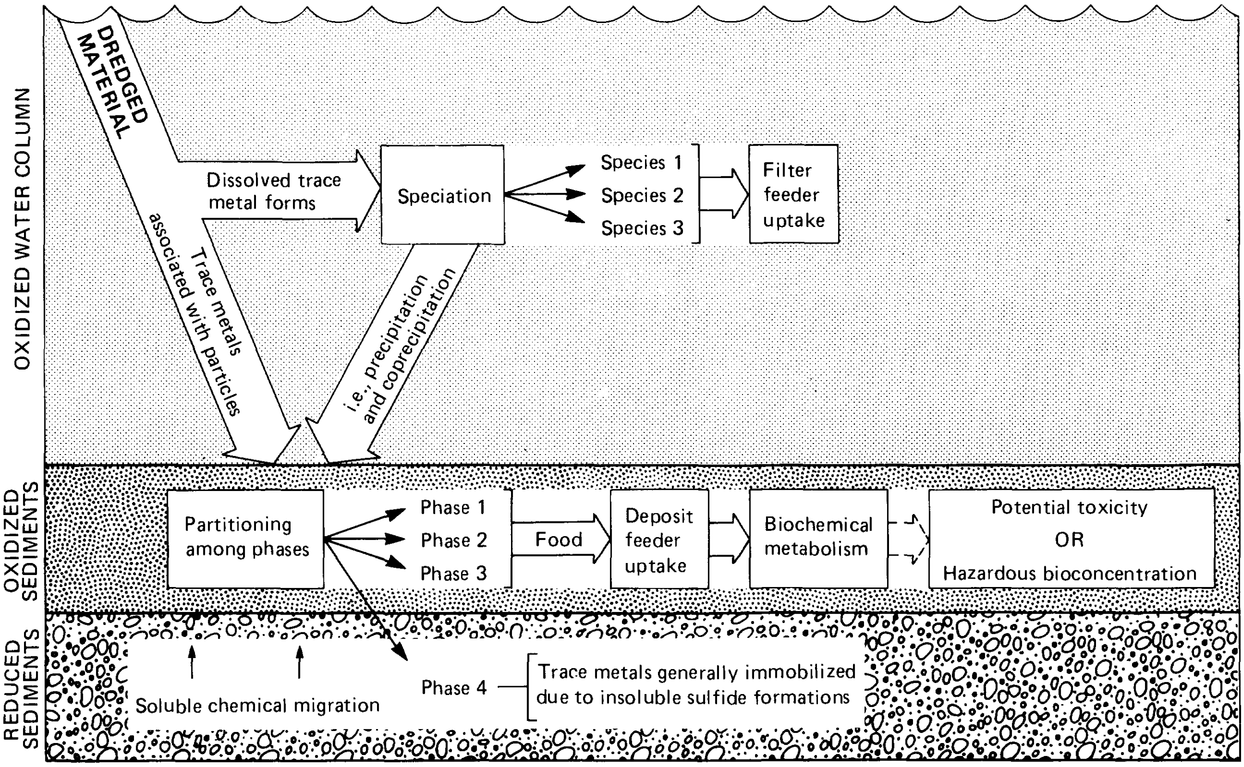

Figure 2. – Hypothetical trace-metal transformations in dredged material disposed in the aquatic environment where oxidized and reduced zones are established.

Metals associated with bottom material may partition among these various phases. Metals tend to partition into phases with the lowest bioavailability (Luoma and Jenne, 1977). Common estuarine phases may include iron and manganese oxides or hydroxides, organic materials, and, to a lesser extent, clays and carbonates. Most silt-clay particles in surficial estuarine sediments occur as organic mineral aggregates (Luoma, 1983). For a complete review of trace-metal interactions see Luoma (1983) and Horowitz (1984).

Role of Bottom-Material Phases

"Phase," as used in this report, describes a substance capable of binding trace metals to bottom materials. Commonly identified phases in estuarine environments are hydrous iron and manganese oxides, carbonates, and organic materials. Generally, trace metals are selectively sorbed to phases with the greatest bonding strength--primary phases such as hydrous iron and manganese oxides; consequently, other metals associated with these phases probably have small bioavailability.

Phase associations that leave metals in bioavailable form may occur when primary phases are insufficient in concentration to bond all trace metals; under these circumstances, trace metals may bond to secondary phases having lower bonding strength (such as manganese carbonates) and thus the metals have greater bioavailability (Luoma and Jenne, 1977; Luoma and Bryan, 1981; and Luoma, 1983).

Clays are generally a relatively minor phase for the adsorption of trace metals; however, they may serve as a mechanical substrate for the precipitation and flocculation of organic material and of primary phases such as hydrous iron and manganese oxides, which under oxidizing conditions play an important role as sinks for trace metals (Jenne, 1976). Curtis (1966), in Forstner and Wittman (1979), describes different associations between metal ions and dissolved organic material that may ultimately lead to metal-ion adsorption on clay particles. In some cases metal ions that interact in solution with dissolved organic matter are more readily adsorbed on clay minerals, whereas in other cases metal ions and dissolved organic material may compete for adsorption or bonding sites (Johansson, 1977).

To broaden the scope from trace-metal/clay associations to trace-metal concentration dependency on sediment grain size and organic carbon content, Horowitz (written commun., 1985) states:

> Most trace-metal and total organic carbon concentrations increase with decreasing grain size; whether this effect is between grain size and trace metals or grain size and total organic carbon, or dependent on all three, is not absolutely known. However, it is assumed that all three interact to produce the effect.

Hydrous iron oxide phases can exist in several different forms of varying extractability. They may occur as layers on particle surfaces or as discrete particles of mineralogic iron (usually cryptocrystalline). Further, freshly precipitated amorphous iron oxides can adsorb trace metals to a greater degree than can older, more crystalline forms (Luoma and Bryan, 1981). Large concentrations of complexing organics may inhibit the formation of the less reactive crystalline forms, such as lepidocrocite, a hydrous ferric hydroxide prominent on the overturn and oxidation of iron in estuarine bottom material (Schwertmann and Fischer, 1973). Iron in most estuarine bottom materials (which are calcareous, organic rich, near neutral pH, and have a high partial pressure of carbon dioxide) will be found as poorly ordered (amorphous) iron containing appreciable amounts of organic matter (Aston and Chester, 1976).

Manganese may occur in estuarine bottom material as several phases, including manganese oxides of varying structure, manganese carbonate, or manganese bound to other substrates (Luoma and Bryan, 1981). More than 30 hydrous oxides of manganese exist. Manganese dioxide has been identified as the most stable phase in bottom material under a wide range of pH in an oxidizing environment (Forstner and Wittmann, 1979).

However, in the natural environment a poorly ordered hydrous manganese oxide of variable stoichiometry, termed "metastable birnessite," is more common (Davies and others, 1982). These manganese phases may also occur as discrete particles or as coatings on clay minerals (Burton and Liss, 1976). Extractions with 1N HCl appear to dissolve manganese from manganese carbonate and manganese oxide, as well as manganese bound to other substrates (Luoma and Bryan, 1981).
Many naturally occurring particulate materials are complex, interlayered, intermeshed mixtures of iron oxide coatings, organic coatings, and minute but discrete manganese oxide particles, often adsorbed on the surfaces of clay particles (Jenne, 1976).

Estuarine organic matter is capable of binding most heavy metals, especially nickel, copper, and iron. It is humified (present in organic acid forms) to varying degrees and may originate in the estuary from algae, saltmarsh flora, and fecal deposits from estuarine organisms. Estuarine organic matter includes soil humic material that is derived from the surrounding land and often coflocculated with iron and aluminum (Davies and others, 1982). Humic materials (weak-alkali-extractable organic matter) in soils and estuarine bottom material can constitute 40 to 70 percent (or more) of estuarine organic matter. These humic materials are characterized by a hydrophobic "aromatic core" which can bond--either chemically or physically--polysaccharides, proteins, simple phenols, and trace metals; however, their overall character is hydrophilic, probably resulting from the surface orientation of functional groups in such compounds as proteins.

Fulvic and humic acids are two important fractions of organic substances; both are operationally defined and have an affinity for trace metals. The fulvic acid fraction--molecular weight less than 10,000--has a higher water solubility and assumes a more important role in transporting trace metals in water than it does in incorporating them into bottom material. The less soluble humic acid fraction--molecular weight greater than 200,000--is more important in trace metal transport and sorption by bottom material (Head, 1976; and Jenne, 1976), most likely a result of the greater abundance of this fraction (Jenne, 1976). Metal ions may be attached to particulate humic substances by weak bonding, such as physical adsorption, that allows the metal ions to be easily replaced. They may also be attached by strong chemical bonds, as in chelation, where a metallic ion is combined into a ring by unshared electrons in the chelating organic material (Forstner and Wittmann, 1979).

APPROACH AND METHODS

To simulate oxic conditions that would likely be encountered by dredged material at in-water disposal sites in the Columbia River, bottom material was mechanically mixed with native water (four parts native water to one part bottom material) for 30 minutes while under continuous aeration (aerated elutriation mixing). The steps involved in the preparation of bottom material for chemical and physical analyses are shown in figure 3.

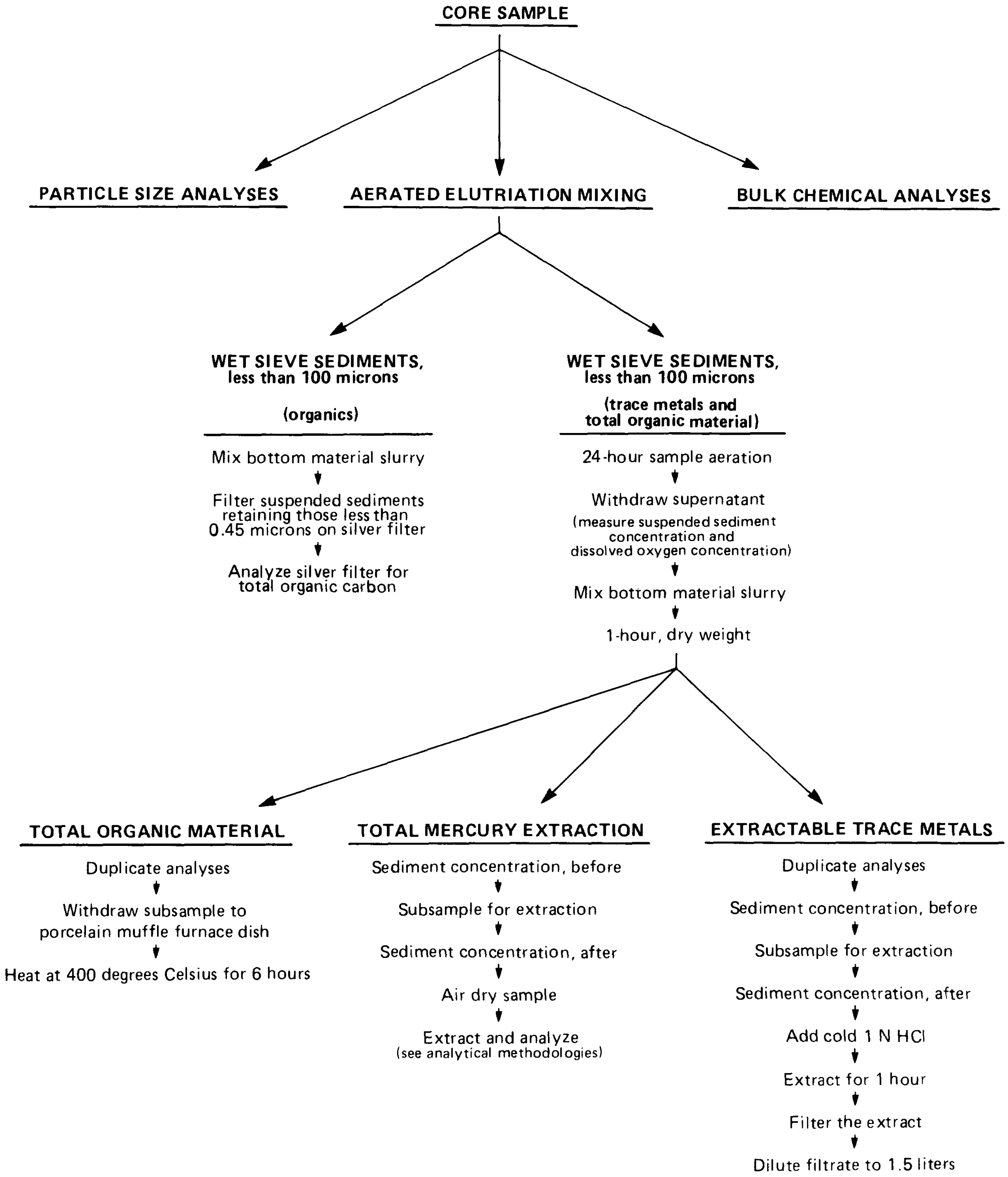

Figure 3. – Procedure for chemical and physical analyses of bottom material.

The mixture was then sieved, with filtered native water, to obtain the less-than-100-micron fraction, and the resultant slurry was maintained in an oxygenated environment for 24 hours while the suspended sediments settled. The dilution and mixing were an attempt to simulate conditions that may occur when bottom materials are dredged, transported, and then deposited at an in-water disposal site. Bottom materials that are dredged and (or) transported often remain in or quickly revert back to the reduced state; those accumulating at the sediment/water interface within the disposal site become primarily oxidized.

Luoma (written commun., 1982) states that organisms living in the contact zone between bottom material and water are exposed directly to metals in the environment of the oxic sediment/water interface. For this reason, chemical extraction procedures were made on oxidized bottom materials. The less-than-100-micron size break was selected for trace-metal extractions because of the likelihood of ingestion by deposit-feeding benthic organisms and subsequent trace-metal exposure. The assumption was made that benthic organisms, feeding on selective particle sizes (for example, less than 100 microns in diameter), are more impacted by trace metals within their size class than by those in larger particle sizes that are excluded from ingestion. In addition, Horowitz (oral commun., 1985) has used a broad geographical data base to determine that total trace metal concentrations in bulk bottom material correlate with the percentage of bottom material finer than the 63- and 125-micron size fractions.

Chemical extraction procedures are used to extract trace metals that remain associated with bottom materials after mixing with native water under simulated-oxic disposal site conditions. During this mixing period, some trace metals associated with reduced sulfides in bottom materials may oxidize and dissolve into the native mixing water. Trace metals removed from bottom materials in this manner are measured in the elutriate-test filtrate and are distinct from those determined by the chemical extraction procedure, unless, during the mixing and settling periods, they are reincorporated into the bottom material by an adsorption mechanism, such as coprecipitation with hydrous iron/manganese oxides.

In preparation for determination of organic carbon, a subsample of bottom material finer than 100 microns is placed in a stainless-steel filtering unit where material between 0.45 and 100 microns is retained on a silver filter for analysis. For analyses of trace metals, the native-water supernatent is withdrawn after 24 hours and the remaining slurry is mechanically mixed and subsampled into an Erlenmeyer flask using a 1-ml Eppendorf pipet[1].

---

[1] Use of brand names in this report is for identification purposes only and does not constitute an endorsement by the U.S. Geological Survey.

An approximate sediment concentration of the slurry is determined to ensure that sufficient bottom material is extracted to yield trace-metal concentrations above analytical detection limits. Results of the 1N-HCl extraction of trace metals are reported on a dry weight, salt-free basis, in micrograms metal per gram sediment; representative 1-ml subsamples of the bottom material are placed in 1 liter of distilled deionized water, filtered, and dried in order to determine the salt-free dry weight of bottom material used in each chemical extraction (Thomson and others, 1980). Chemical extractions of trace metals were made using cold 1N HCl, except for the extraction of mercury, where both cold 1N-HCl extractions and hot nitric, hydrochloric-acid extractions were made. For a complete discussion of sample processing see Appendix I.

The 1N HCl used for extractable trace-metal determinations contains sufficient acidity to neutralize the carbonate buffering capacity of native estuarine water (Luoma and Bryan, 1981). The 1N-HCL extraction procedure is not designed to extract metals from a single bottom-material phase; instead, it is commonly used to operationally define an "extractable phase" of trace metals most representative of the bioavailable fraction. Luoma and Bryan (1982) concluded that extraction with 1N HCl appears to be the best method for generally identifying the "extractable" portions of silver, cadmium, cobalt, copper, and lead that are bioavailable in bottom material. Although it is not a phase-specific extraction, the results correlate well with concentrations of metals found in the tissues of many estuarine deposit-feeding organisms.

Partial extractions with 1N HCl are not a good method for estimating biologically available mercury in estuarine sediments, probably because the stable bond formed between mercury and organic matter is resistant to 1N-HCl extractions but susceptible to enzymatic decomposition in the gut of aquatic organisms. Langston (1982) reported that the percentage of total mercury extracted by 1N HCl was small (mean value of 6.5 percent for the five British estuaries studied) and did not serve as a meaningful indicator of biologically available mercury. Therefore, 1N-HCl extractions will not always define biologically available trace metals in bottom material.

To test for correlation between constituent concentrations determined in 1N-HCl extracts, Kendall's tau correlation coefficients were computed. Because correlations do not necessarily define cause and effect relations, but are simply mathematical relations, a statistically significant correlation between two or more constituent concentrations may not be of scientific significance, if the relation does not represent a physical or chemical process. The Kendall's tau test is similar to parametric correlation tests in that it derives a measure of correlation between -1 and +1 at a particular significance level. The test differs from parametric correlations tests in that it will accept chemical data that are not normally distributed; because it is a nonparametric test it works with ranks and not actual values (Conover, 1980). Kendall tau correlation coefficients were computed at the 0.1 significance level unless otherwise indicated.

Sampling Procedures

Bottom-material samples were collected by using a 200-pound gravity corer operated with a boom winch. The depth of sediment penetration ranged from 1.5 to 2 ft, with the exception of sites in Baker Bay (site 1) in the Columbia River navigation channel, where the coring depth was 0.75 ft. The core barrel was lined with a removable transparent butyrate-acetate cylinder (2-5/8 inches diameter by 24 inches length), prerinsed with acid and distilled water. Native-mixing water samples were collected using a 4-liter Van Dorn bottle and were placed into 5-gallon collapsible polyethylene containers; water samples were collected approximately 1 foot above the channel bottom. Native-water and bottom-material samples were iced in the field and refrigerated at 4 °C in the Geological Survey laboratory (Portland, Oregon) until processing.

Analytical Methods

Determinations of selected trace metals from 1N-HCl extracts were made by the U.S. Geological Survey, Water Resources Division, Central laboratory in Arvada, Colorado. The 1N-HCl extracts were diluted with distilled dionized water (see Appendix I) and analyzed, using methods described by Skougstad and others (1979). Table 2 shows U.S. Geological Survey method numbers, detection limits, and precision data. Total mercury analyses of bottom material finer than 100 microns were made by the Geological Survey, Geologic Division, Mineral Resources Laboratory in Lakewood, Colorado, using a flameless atomic absorption spectrometer. The total mercury analysis is a harsh extraction procedure using concentrated nitric and hydrochloric acids, with recoveries ranging from 90 to 105 percent (Huffman and others, 1972).

Chemical determinations of total organic carbon in both bulk and finer-than-100-micron bottom material were made by the Geological Survey, Water Resources Division, Central Laboratory in Arvada, Colorado. The concentration of total organic carbon in bulk bottom material is calculated by determining the difference in concentrations between inorganic-plus-organic carbon (method number Q-5101-83) and inorganic carbon (method number Q-5102-83), Wershaw and others (1983). Determination of total organic carbon in finer-than-100-micron bottom material was made using a technique for suspended organic carbon, method number Q-7100-83, (Wershaw and others, 1983).

Particle-size analyses were made by the Geological Survey, Water Resources Division, Oregon Office Laboratory in Portland, Oregon. Representative bulk bottom-material subsamples for particle size were analyzed by two methods: (1) a visual-accumulation tube for bottom material between 53 and 2,000 microns in diameter, and (2) a pipet method used for bottom material finer than 53 microns in diameter (Guy, 1969). Both methods determine particle-size distribution in terms of fall diameter in quiescent distilled water (Stokes Law).

Table 2.--Geological Survey analytical method numbers, detection limits, and precision data expressed in terms of relative deviation for small, medium, and large concentration ranges

[All concentrations are in the dissolved state and are reported in units of micrograms per liter]

				Relative deviation for the following analytical concentration ranges								
				Small			Medium			Large		
Chemical	Method number[1]	Detection limit	Analytical concentration range[2]	Number of labs	Mean concentration	Relative standard deviation (percent)[3]	Number of labs	Mean concentration	Relative standard deviation (percent)[3]	Number of labs	Mean concentration	Relative standard deviation (percent)[3]
Cadmium	I-1472-79	0.01	0.01-17	--	--	--	--	--	--	--	--	--
Chromium	I-1238-78	1	1-25	3	8	25	--	--	--	12	23	82
Copper	I-1271-78	10	1-75	5	25	23	--	--	--	--	--	--
Iron	I-1381-78	10	10-3000	17	100	31	13	445	49	--	--	--
Lead	I-1400-78	1	1-100	7	4	38	--	--	--	7	45.6	10
Mercury	I-2462-78	.1	.1-10	1	0.72	11	1	2.17	5	1	7.51	4
Manganese	I-1454-78	10	10-2000	23	70	20	34	256	9	--	--	--
Nickel	I-1500-78	1	1-100	8	5.9	37	4	12.2	31	13	23.2	23
Zinc	I-1901-78	.2	.2-15	--	--	--	--	--	--	--	--	--

[1] Method numbers are from Skougstad, 1979.

[2] The analytical concentration range represents the range of chemical concentrations on which precision data has been determined.

[3] Relative standard deviation is the ratio of standard deviation to the mean, multiplied by 100.

RESULTS OF CHEMICAL EXTRACTIONS

Results of 1N-HCl extractions on bottom material finer than 100 microns will be referred to as "extractable trace metals," and results of the concentrated nitric and hydrochloric-acid extraction on bottom material finer than 100 microns will be referred to as "total trace metals;" both extractions will be reported as a dry weight unless otherwise indicated. In the results section, iron, manganese, and total organic carbon are considered as "chemical phases" or substrates and are presented in a combined format; mercury, cadmium, copper, lead, and zinc are discussed individually. Each constituent in the latter group will be discussed in two sections: the first will provide specific information about each metal and will reference specific case studies; the second will discuss results of chemical extractions in this study and compare them to those of other related studies.

Reviewing the quality-assurance program for this study will be helpful in evaluating results of chemical extractions. This information is provided in Appendix II.

Chemical Phases in Columbia River Bottom Material

Chemical phases have been defined as substances capable of binding trace metals to bottom material. In Columbia River bottom material, concentrations of extractable manganese range from 53 to 314 $\mu g/g$, with a median concentration of 128 $\mu g/g$ (table 3). Extractable manganese is significantly correlated ($\alpha \leq 0.1$) with total organic carbon ($r = 0.62$), extractable copper ($r = 0.62$), iron ($r = 0.62$), lead ($r = 0.52$), and zinc ($r = 0.68$), as shown in table 4. Concentrations of extractable iron range from 990 to 11,000 $\mu g/g$, with a median concentration of 7,330 $\mu g/g$. Extractable iron is significantly correlated with bulk inorganic carbon ($r = 0.55$), total mercury ($r = 0.64$), total volatile solids ($r = 0.60$) in less-than-100-micron bottom material, extractable chromium ($r = 0.68$), lead ($r = 0.71$), manganese ($r = 0.62$), and zinc ($r = 0.68$).

Table 3.--Results of trace metal and organic carbon determinations on bottom materials

[Analyses of bottom material finer than 100 microns; concentration reported per gram or kilogram finer-than-100-micron bottom material, unless otherwise designated as "bulk"; TVS = total volatile solids; see "definition of terms," p. vi-vii for heading notations and abbreviations]

									Extraction									Particle-size summary		
Site name	Site no.	Date	TOC <100 -µm, g/kg	TOC, bulk, g/kg	TVS, pct.	Carbon, in-organic, bulk, g/kg	Total mercury µg/g	Total mercury divided by pct TVS, µg/g	Cadmium µg/g	Chromium µg/g	Copper µg/g	Iron µg/g	Lead µg/g	Mercury µg/g	Manganese µg/g	Nickel µg/g	Zinc µg/g	<100-µm diameter pct.	Silt pct.	Clay pct.
Baker Bay	1	7-11-83	3.1	0.4	--	0.1	--	--	2.2	0.6	2.6	990	2.6	<.08	53	3.2	15	0.8	--	--
Baker Bay	2	7-11-83	8.0	12	5.6	.9	0.17	0.030	1.9	5.9	26.7	11,000	31.8	<.08	314	5.1	131	64	41	20
Baker Bay	3	7-11-83	6.0	12	4.9	.3	.13	.027	0.92	6.0	17.5	7,750	10.5	<.08	128	6.6	93	99.5	73	24
Baker Bay	4	7-12-83	4.7	10	4.6	.5	.14	.030	.68	3.2	20.6	6,670	12.6	<.08	112	5.0	62	99	75	21
Baker Bay	5	7-12-83	6.6	16	5.2	.4	.14	.027	.60	5.8	19.4	7,330	13.3	<.08	116	4.3	62	100	73	25
Baker Bay	6	7-12-83	5.5	15	6.0	.4	.17	.028	.87	5.8	22.8	9,040	16.7	<.08	170	2.2	90	100	69.5	30
Astoria	7	7-11-83	6.2	14	4.7	.3	.09	.019	.91	3.6	21.0	6,630	11.2	<.08	276	5.1	80	100	75	23
Astoria	8	7-11-83	4.6	8.3	3.4	.2	.07	.021	--	--	--	--	--	--	--	--	--	91	66	14

Both iron and manganese hydroxides and oxides can, under oxidizing conditions and at even relatively small concentrations, sorb or coprecipitate trace metals; consequently, these phases can be significant trace-metal sinks. The processes of sorption or coprecipitation may account for the trace-metal correlations with iron and manganese. It is not surprising to see manganese associated with organic carbon, because both manganese and organic carbon are capable of forming coatings on particulate matter; in addition, organic matter--primarily humic substances--can physically or chemically bond trace metals. Concentrations of total organic carbon in finer-than-100-micron bottom material ranged from 3.1 to 8.0 g/kg, with a median concentration of 5.5 g/kg. Total organic carbon is significantly correlated ($\alpha \leq 0.1$) with bulk total organic carbon (r = 0.62), inorganic carbon (r = 0.52), total volatile solids (r = 0.52), and extractable chromium (r = 0.58), lead (r = 0.52), and manganese (r = 0.62).

Table 4.--Kendall's tau correlation coefficients for selected constituents with a significance level greater than or equal to 90 percent

[Correlations are derived from trace metals and organics associated with bottom materials finer than 100 microns in diameter, unless otherwise specified; P is less than or equal to 0.1]

									Extractable trace metals							
	TOC	TOC, bulk	Pct. TVS	Carbon, inorganic	Pct. <100-µm	Pct. silts	Pct. clays	Total mercury	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Nickel	Zinc
TOC	--	0.62	0.52	0.52	--	--	--	--	--	0.58	--	--	0.52	0.62	--	--
TOC, bulk	0.62	--	.58	--	0.59	--	0.76	--	-0.58	--	--	--	--	--	--	--
Percent TVS	.52	.58	--	--	--	--	--	0.75	--	--	--	0.60	--	--	--	--
Carbon, inorganic	.51	--	--	--	--	--	--	.79	--	--	0.65	.55	.79	--	--	--
Percent <100-µm	--	.60	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Percent silts	--	--	--	--	--	--	--	--	-.55	--	--	--	--	--	--	--
Percent clays	--	.76	.62	--	.84	--	--	--	-.52	--	--	--	--	--	--	--
Total mercury	--	--	.75	.79	--	--	--	--	--	--	--	.64	.79	--	--	--
Extractable cadmium	--	-.58	--	--	--	-.55	-.52	--	--	--	--	--	--	--	--	--
Extractable chromium	.58	--	--	--	--	--	--	--	--	--	--	.68	--	--	--	0.75
Extractable copper	--	--	--	.65	--	--	--	--	--	--	--	--	.71	.62	--	.58
Extractable iron	--	--	.60	.55	--	--	--	.64	--	.68	--	--	.71	.62	--	.68
Extractable lead	.52	--	--	.75	--	--	--	.79	--	--	.71	.71	--	.52	--	--
Extractable manganese	.62	--	--	--	--	--	--	--	--	--	.62	.62	.52	--	--	.68
Extractable nickel	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Extractable zinc	--	--	--	--	--	--	--	--	--	.75	.58	.68	--	.68	--	--

All Columbia River sampling sites have a greater proportion of total organic carbon associated with bottom material coarser than 100 microns than with bottom material finer than 100 microns (table 5). This relation may be attributed to the presence of discrete fragments of organic detritus observed in the greater-than-100-micron fraction, which is, on a weight basis, significantly greater than the thickest organic coating on particles finer than 100 microns. Total organic carbon in bulk bottom material is significantly correlated with the following: (1) percent bottom material finer than 100 microns ($r = 0.59$), (2) percent clay-sized bottom material, ($r = 0.76$), and (3) total volatile solids ($r = 0.58$). The value and significance level of the correlation coefficients increase with decreasing particle-size diameter (figs. 4 and 5), suggesting that the amount of total organic carbon in finer-than-100-micron bottom material increases as the overall percentage of fine material increases. Both total organic carbon in finer-than-100-micron bottom material and that in bulk bottom material are significantly correlated ($r = 0.52$ and $r = 0.58$ respectively) with total volatile solids.

Table 5.--Total organic carbon concentrations in bottom materials of diameter greater than 100 microns and less than 100 microns

Total organic carbon (TOC) in both size fractions is calculated assuming that TOC in a bulk bottom material sample = TOC in bottom material finer than 100 microns plus total organic carbon in bottom material coarser than 100 microns. Concentrations for both size fractions are in units of grams total organic carbon in bottom material finer or coarser than 100 microns per kilogram of bulk sediment

Site description	Site number	Date	TOC in less than 100 μm material g/kg	TOC in greater than 100 μm material g/kg
Baker Bay	1	7-11-83	<0.1	0.4
Baker Bay	2	7-11-83	5.1	6.9
Baker Bay	3	7-11-83	5.9	6.1
Baker Bay	4	7-12-83	4.5	5.5
Baker Bay	5	7-12-83	6.5	9.5
Baker Bay	6	7-12-83	5.5	9.5
Astoria	7	7-11-83	6.1	7.9
Astoria	8	7-11-83	3.7	4.6

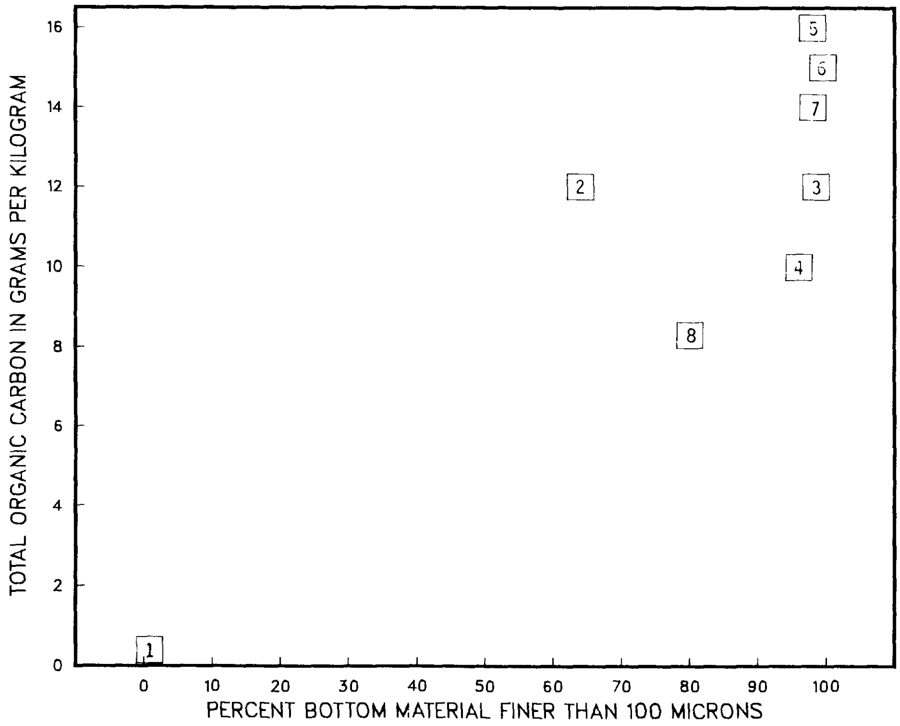

Figure 4.--Total organic carbon in bulk bottom material versus the percent of bottom material finer than 100 microns (numbers inside plotting symbols represent sampling site locations; 4 = 0.59 and α = 0.05).

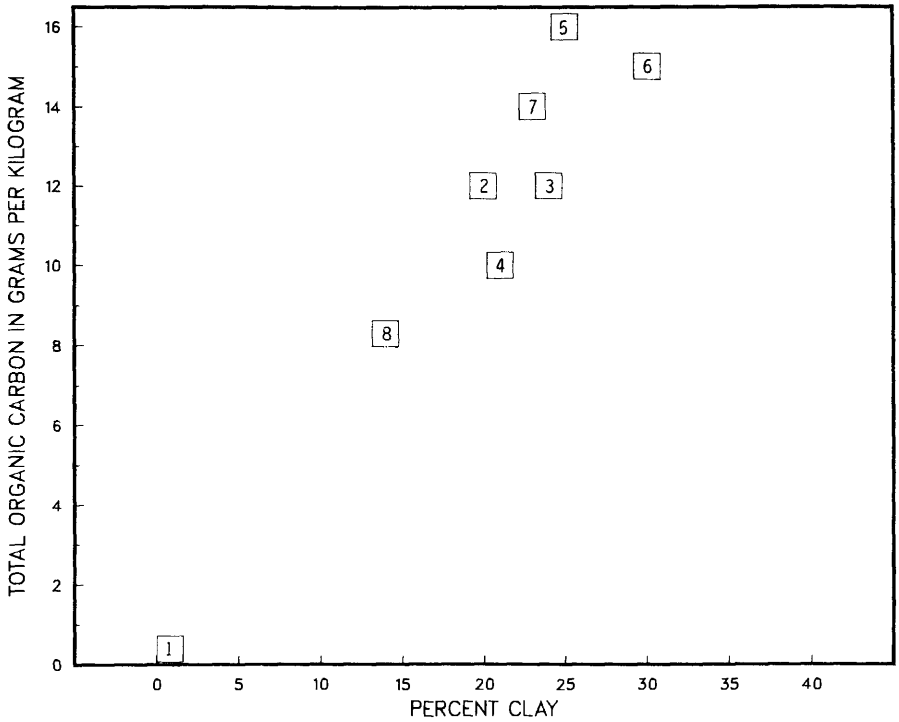

Figure 5.--Total organic carbon in bulk bottom material versus the percent of clays (numbers inside plotting symbols represent sampling site locations; r = 0.76 and α = 0.01).

Chemistry of Mercury Combined with Selected Case Studies in Aquatic Environments

Several studies suggest that suspended sediments contain significantly more mercury than bottom material, on a weight/weight basis. For example, in the Mersey Estuary (Great Britain), suspended sediments contain 10 $\mu g/g$ total mercury compared to 0.5 $\mu g/g$ in bottom material (Burton and Liss, 1976). This type of data is unavailable for the Columbia River; however, Borthner and Carpenter (1973), have determined that 52 percent of the total mercury in water (suspended plus dissolved forms) is associated with suspended bottom materials. An explanation for this occurrence may be the affinity of mercury for sorption on very fine suspended sediments of relatively high surface area and associated sorptive capacity (Aston and Chester, 1976).

A small proportion of mercury associated with bottom material can be converted by microorganisms to methylmercury, as a detoxification measure (Burton and Liss, 1976). This small proportion, as measured by Bisogni and Lawrence (1975), can account for the synthesis of methylmercury at rates approaching 1 percent per year of the inorganic mercury present in bottom material. Under oxidizing conditions, mercury-demethylation processes can occur as described by Wood (1983). These processes may produce mercuric ion (Hg^{2+}), butane (C_2H_6), methane (CH_4), and dimethylmercury ($(CH_3)_2Hg$), all of which may be volatilized to the atmosphere (Wood, 1983). Bartlett and Craig (1981) showed that, under mildly reducing conditions (100 to 150 mV), demethylating processes diminish and the microbial production of methylmercury increases. In addition, under these redox conditions, sulfate reducing bacteria (Desulfovibra) produce sulfides, which further decreases bottom-material redox conditions. Under these lower redox conditions cinnabar forms, making inorganic mercury unavailable for methylmercury formation; as additional sulfides are produced, an important conversion route of methyl mercury to dimethylmercury occurs, whereby methylmercury is volatilized from bottom material (Bartlett, 1981). Columbia River bottom material in this study was maintained under oxidizing conditions; it is assumed that methylmercury, if present, is volatilized from bottom materials and that cinnabar, if present, is lost to the aqueous phase as Hg^{2+} prior to total or 1N-HCl extraction.

In bottom material, mercury has been classified as a "chalcophilic element," or an element which tends to concentrate in insoluble sulfides, principally cinnabar (Fleischer, 1970). Based upon Eh and pH equilibrium conditions (likely to occur with mercury under oxic or anoxic conditions), elemental mercury (liquid) and cinnabar (solid) are likely to enter into an equilibrium association affecting the solubility of mercury. Even mildly reducing conditions can drive this equilibrium toward the formation of mercury sulfide, which will remain relatively insoluble as long as reducing conditions exist (Cadigan, 1970).

The important effect of oxidizing conditions on most sulfide solids, including cinnabar, is dissolution; mercury shows a pattern of oxidation from the mercuric sulfide solid (HgS) to the metallic liquid (Hg (1)) to dissolved mercuric ion (Hg^{2+}), according to Morel and others (1975). In an estuarine environment, the solubility of mercury under oxidizing conditions is increased by formation of the very soluble (69 g/L) mercuric chloride ($HgCl_2$), when chloride ion concentrations are large (Hem, 1970).

In British estuaries, concentrations of total mercury ranged from 0.07 µg/g in uncontaminated estuaries to 6.2 µg/g in industrially contaminated estuaries (Langston, 1982). The Columbia River and its tributaries are located on the landward extention of the east Pacific Rise, the location of major mercury deposits (cinnabar) in the Western Hemisphere. Thus, there are also naturally occurring sources of mercury near the estuary (May and McKinney, 1981). Concentrations of mercury determined in earlier Columbia River reconnaissance samplings (table 6) range from <0.01 to 0.28 µg/g, with a median concentration of 0.03 µg/g (Fuhrer, 1984). Soil samples collected throughout the conterminous United States--at a depth of 8 inches to avoid anthropogenic contamination--yielded 912 total mercury samples (table 7) with a geometric mean of 0.07 µg/g and a geometric deviation of 0.003 µg/g. Two soil samples, collected within 8 miles of one another (near Columbia River mile 39), have identical total mercury concentrations of 0.09 µg/g. A third sample collected 30 miles north of the estuary, in B horizon soil (a zone of accumulation of leachate from upper soils) had a total mercury concentration of 1.2 µg/g (Skacklette and others, 1971b; Boerngen and Shacklette, 1981).

There is strong evidence to suggest that mercury is associated with organic matter in estuarine bottom material. There is also an association between dissolved organic carbon and dissolved mercury in fresh, estuarine, and interstitial pore waters (Lindberg and Harris, 1974). In addition, high molecular weight dissolved organic carbon rapidly flocculates in a saline-dependent manner during estuarine mixing, when trace metal adsorption can occur on the organic carbon flocculant (Boyle and others, 1978). Total mercury in both contaminated and uncontaminated bottom materials, in Puget Sound (Washington), is associated with organic material in oxidized surface sediments (Sherbin, 1979 and JRB Associates, 1984). In soil samples, mercury has been shown to be associated with organically stained sands, suggesting that mercury was enriched in the organic materials present (Fleischer, 1970; Shacklette and others, 1971b). Jenne (1970) reported that the amount of mercury associated with five surficial soil samples from Sweden varied directly with the organic matter content.

Table 6.--Concentrations of trace metals in Columbia River bottom material from earlier reconnaissance studies using a two-step extraction procedure (Fuhrer and Rinella, 1983 and Fuhrer, 1984)

[Soft digestion procedures were used on bulk samples. Some samples were anerobic. The digestion procedure uses a preliminary extraction of trace metals associated with organic matter by oxidation with a 30 percent hydrogen-peroxide solution, followed a second-step extraction of all sorbed metals with a hot 0.3 molar HCl solution. River miles enclosed in parenthesis are for the river shown under site description, not Columbia River miles. Concentrations reported in micrograms per gram]

				Extraction										
Site description	River mile no.	Date	Latitude Longitude	Cadmium µg/g	Chromium µg/g	Copper µg/g	Iron µg/g	Lead µg/g	Manganese µg/g	Mercury µg/g	Nickel µg/g	Zinc µg/g	Particle size percent <125-µm	Comments
Pacific Ocean	--	8/03/82	46°11'27" 124°02'48"	10	1	1	1,800	<100	40	0.01	--	8	20	Off Columbia River, south jetty.
Columbia River	1	8/03/82	46°15'30" 124°03'32"	<10	--	--	3,400	--	60	--	--	--	3	
Columbia River	3	8/03/82	46°13'33" 124°01'45"	<10	--	--	3,600	--	90	--	--	--	--	
Baker Bay	--	7/23/80	46°17'51" 124°02'43"	1	7	17	6,900	20	130	.06	10	52	--	Near site #3, Ilwaco boat channel.
Baker Bay	--	7/23/80	46°17'46" 124°02'29"	2	15	37	22,000	30	230	.17	10	160	--	Adjacent to Ilwaco boat channel.
Baker Bay	--	7/23/80	46°17'50" 124°02'20"	2	24	43	17,000	40	280	.28	30	190	--	Adjacent to Ilwaco boat channel.
Baker Bay	--	7/23/80	46°18'03" 124°01'37"	<1	5	5	4,000	10	54	.01	10	21	--	Tidal flat in Baker Bay.
Baker Bay	--	7/23/80	46°17'05" 124°01'13"	<1	5	5	3,100	10	52	.01	10	19	--	East of Sand Island in Baker Bay.
Columbia River	6	8/03/82	46°13'33" 123°58'15"	<10	2	2	4,100	<100	55	<.01	--	15	20	
Chinook	--	8/20/80	46°15'58" 123°57'24"	8	18	44	17,000	30	420	.07	20	135	--	Near Columbia River Mile 5.
Columbia River area D	6	8/19/80	46°14'29" 123°56'50"	2	4	4	4,700	10	150	.01	10	22	--	
Columbia River Tansey Point	8	8/19/80	46°11'32" 123°55'17"	2	6	5	4,500	10	87	.02	10	40	--	
Skipanon	(2)	7/22/80	46°09'59" 123°55'11"	7	12	50	19,000	30	160	.0	20	300	--	Confluence at Columbia River Mile 10.7.
Columbia River	11	8/03/82	46°11'32" 123°54'08"	<10	--	--	4,800	--	65	--	--	--	8	
Columbia River	13	8/02/82	46°12'15" 123°51'39"	<10	--	--	4,300	--	65	--	--	--	3	
Astoria Boat Basin	13	12/02/80	46°11'24" 123°51'21"	5	14	31	11,000	10	190	0.09	20	110	--	
Youngs Bay	--	7/22/80	46°10'07" 123°50'44"	4	8	180	11,000	10	140	0.03	20	35	--	Confluence at Columbia River Mile 12.0
Columbia River	16	8/02/82	46°12'15" 123°48'00"	<10	--	--	3,500	--	80	--	--	--	2	
Columbia River	18	8/02/82	46°13'05" 123°45'50"	<10	2	2	2,600	<100	70	0.02	--	22	2	
Columbia River	18	8/02/82	46°12'34" 123°45'15"	10	--	--	6,000	--	350	--	--	--	80	
Columbia River	18	8/02/82	46°12'14" 123°45'21"	<10	3	19	4,300	<100	160	0.06	--	40	95	
Columbia River	18	8/02/82	46°11'53" 123°45'09"	<10	--	--	4,600	--	140	--	--	--	93	
Columbia River	32.7	5/15/80	46°16'01" 123°28'57"	1	2	5	5,900	10	150	<0.01	10	25	--	
Skamokawa	(0.15)	5/15/80	46°16'09" 123°27'13"	1	10	22	21,000	10	400	0.03	30	60	--	Confluence at Mile 33.3.

Table 7.--Trace-metal concentrations in soil samples collected near the Columbia River estuary and geometric mean and deviation of soil samples collected throughout the conterminous United States[1]

[Concentrations in micrograms per gram dry weight, unless otherwise noted]

	Concentration at location[2]			Geometric	Geometric[3]	
	A	B	C	mean,	deviation,	
Element	Columbia River estuary			United States	United States	n
Chromium	100	100	70	37	2.32	863
Copper	20	70	50	18	2.28	855
Iron	5 pct.	5 pct.	3 pct.	1.8 pct.	2.30	861
Lead	15	15	20	16	1.91	863
Manganese	700	700	300	340	2.7	861
Mercury	0.09	0.09	1.2	0.07	0.003	912
Nickel	10	50	20	14	2.26	862
Zinc	93	85	40	44	1.86	863

[1] From Shacklette and others, 1971a and b, and Boerngen and Shacklette, 1981.

[2] Locations A and B are within 8 miles of one another, near Columbia River mile 39; site C samples were collected 30 miles north of the estuary, in B horizon soil (a zone of accumulation of leachate from upper soils).

[3] The range from the geometric mean multiplied by the geometric deviation to the geometric mean includes about two-thirds of the analytical values.

Using both total and partial mercury-extraction procedures, Baldi and Bargagli (1982) concluded that mercury in bottom material is stably bound to organic material and occurs to a lesser extent as fine-grained cinnabar; in fact, mercury is stably complexed by proteins with R-SH groups and the humic acid fraction of organic material. In estuaries and estuarine salt-water marshes, total mercury has been shown to correlate well with organic matter in bottom material. The only exception to this relation appears in the presence of fibrous organic matter containing smaller mercury concentrations, such as decaying plant matter (Breteler and others, 1981). Bartlett and Craig (1981) concluded that total mercury was associated with organic rich silt/clay-sized bottom material (<62 μm) in the Mersey Estuary, Great Britain. By oxidizing organic material with hydrogen peroxide, Langston (1982) has shown that within British estuaries 41 to 61.6 percent of the total mercury is associated with organic matter in oxidized bottom materials. In an estuarine environment it appears unlikely that any significant amount of mercury will be sorbed onto hydrous manganese oxide phases, due to the inhibiting effect of chloride ions at ambient concentrations (DeGroot and others, 1976).

Concentrations of mercury in organisms are not necessarily related to total mercury concentrations in bottom material, but rather to the manner in which mercury is associated with bottom material (Breteler and others, 1981). Much of the literature suggests that moderate concentrations of mercury associated with bottom material having low concentrations of organic matter may result in significantly high concentrations of mercury in the tissues of deposit-feeding organisms. The inverse of this relation is also true; bottom material with elevated concentrations of mercury associated with high concentrations of organic matter may result in significantly lower concentrations of mercury in tissues of deposit-feeding organisms (Bretler and others, 1981; Baldi and Bargagli, 1982). Mercury bound to highly organic estuarine bottom material (Luoma, 1974) was bioaccumulated in small amounts by the polychaete worm _Nereis succina_ and the deposit-feeding shrimp _Palemon debilis_. The sand worm _Nereis virens_ was exposed to mercury in New York harbor bottom material that contained as much as 38 μg/g of mercury, but it showed no measurable uptake. These bottom materials also contained large amounts of total organic carbon, which could account for the lack of bioavailable mercury in anthropogenically contaminated bottom materials (Rubinstein and others, 1983).

To illustrate the critical role of organic material in controlling concentrations of biologically available mercury to deposit feeders, Langston (1982) studied English estuaries having small concentrations of TVS (total volatile solids), a measurement of organic carbon content. Oxidized estuarine bottom material with a TVS of 0.24 percent and a mercury concentration of 0.08 μg/g was linked to a relatively large tissue concentration of 0.51 μg/g mercury in the deposit-feeding clam _Macoma balthica_. Langston showed that ratios of mercury to TVS more realistically estimate anthropogenic inputs of sediment-bound mercury than total mercury concentrations; in fact, these ratios produce significant correlations ($\alpha < 0.001$) with tissue concentrations in _Macoma balthica_ (fig. 6). Figure 6 illustrates three important concepts, developed by Langston (1982), concerning mercury associated with bottom material, TVS, and concentrations in tissues:

- Small concentrations of mercury (0.08 μg/g) associated with bottom material having small concentrations of total volatile solids result in relatively large tissue concentrations of mercury.

- Small concentrations of mercury associated with bottom material having large concentrations of total volatile solids result in relatively small tissue concentrations of mercury.

- Large concentrations of mercury associated with bottom material having large concentrations of total volatile solids result in relatively small tissue concentrations of mercury.

The conclusions of Langston's study, relative to the importance of total volatile solids, are applicable to the present study, because the present study is based on the use of chemical extractions and did not include analyses of deposit feeders for mercury.

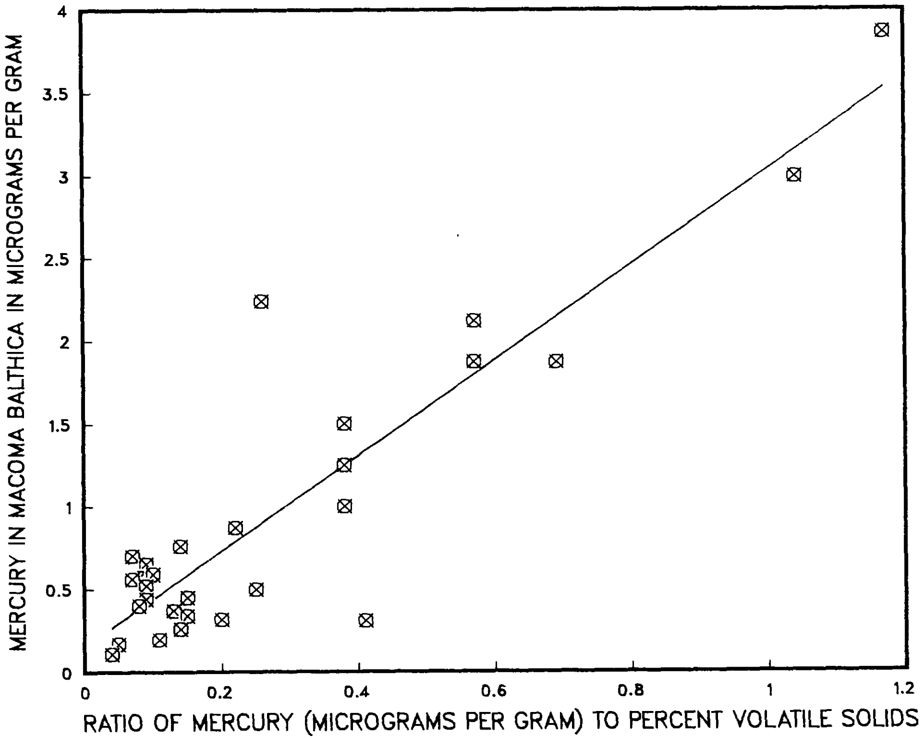

Figure 6.--Relation between mercury in Macoma balthica and total mercury in bottom material, normalized to percent total volatile solids, in an English estuary (modified from Langston, 1982).

In addition, the same species of clam used by Langston (Macoma balthica) was the principle species identified by Durkin and Emmett (1980) in surficial sediments at two sites in Baker Bay, Washington, corresponding to areas sampled in this study. The mean annual numbers of Macoma balthica in the two sites sampled by Durkin and Emmett are 1,000 and 1,600 per square meter.

Concentrations of mercury in filter-feeding northern squawfish at upstream Columbia River sites are elevated relative to concentrations observed in benthic deposit feeders in the Columbia River estuary. Mercury observed in northern squawfish in the Columbia River at Bonneville Dam (river mile 145) exceeds the 85th nationwide percentile (0.010 μg/g wet weight from 98 monitoring stations). Mercury concentrations in whole fish samples from the 98 monitoring stations nationwide range from 0.01 to 0.84 and average 0.11 μg/g wet weight; northern squawfish monitored on the Columbia River at Bonneville Dam average 0.23 μg/g wet weight mercury (May and McKinney, 1981). Results of a study of mercury in Columbia River estuarine shellfish indicate that concentrations in the bivalve mollusk Corbicula fluminea and in the Anodonta species range from 0.016 to 0.033 and 0.016 to 0.019 μg/g wet weight respectively (Caldwell and Buhler, 1983). The U.S. Food and Drug Administration's upper limit for mercury is 1 μg/g wet weight; the concentrations observed by Caldwell are among the lowest reported in the literature.

Total Mercury Determinations in Columbia River Bottom Material

Concentrations of total mercury in estuarine bottom material ranged from 0.07 to 0.17 μg/g, with a median of 0.14 μg/g, indicating a relatively narrow range of mercury concentrations within the areas sampled in the Columbia River estuary. During sample aeration, sulfide forms of mercury may be solubilized. Only those soluble mercury forms reincorporated on oxic bottom-material phases during sample aeration--or those originally present in oxic bottom materials--will be extracted in the total mercury procedure. There is a significant correlation (r = 0.64) between total mercury and extractable iron in Columbia River estuary bottom material. This relation has a lower Kendall's tau correlation coefficient than that between total mercury and TVS and indicates that a small portion of total mercury may be associated with hydrous iron oxide/hydroxide phases. The proportion of total mercury associated with iron phases is probably small, since concentrations of extractable mercury are reported as less than the detection limit of 0.08 μg/g. Also, because mercury forms a stable bond with organic matter and this bond is resistant to the 1N-HCl extraction, it is not surprising to see concentrations of extractable mercury reported less than the detection limit.

There is a significant correlation (r = 0.75) between TVS and total mercury in Columbia River estuarine bottom material. They form a fairly linear distribution (fig. 7) where no sampling sites contain large concentrations of total mercury relative to TVS.

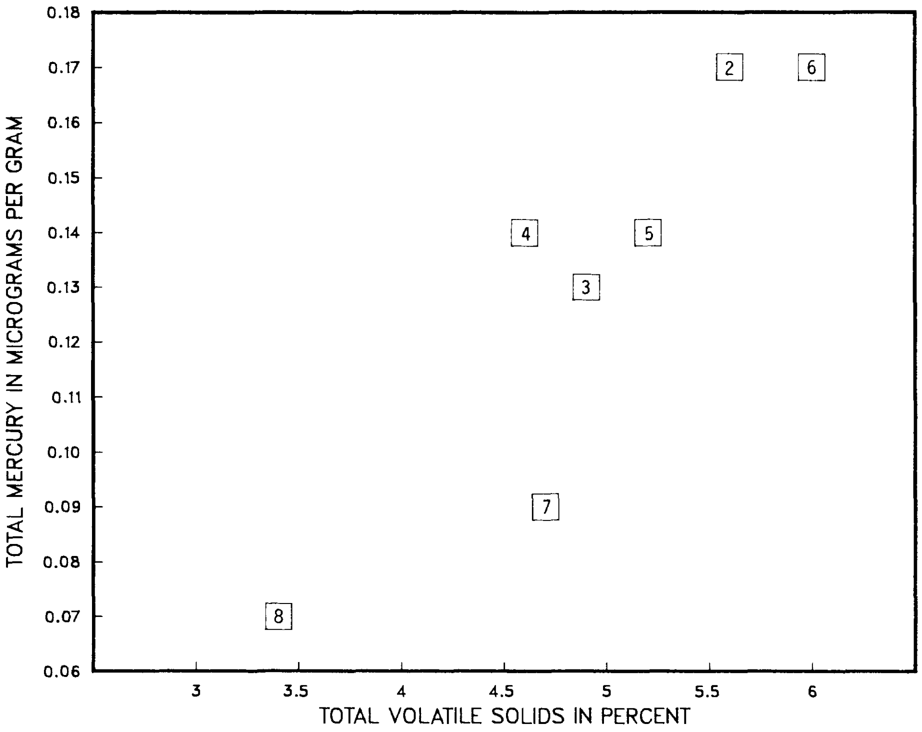

Figure 7.--Total mercury versus total volatile solids in bottom materials finer than 100 microns (numbers inside plotting symbols represent sampling site locations; r = 0.75 and α = 0.02).

Langston (1982) has shown that ratios of total mercury to total volatile solids in bottom material finer than 100 microns reflect the degree of contamination to which an estuary is subjected. Total volatile solids from the Columbia River estuary ranged in percent from 3.4 to 6.0, with a median of 4.9. These concentrations of total volatile solids are large in comparison to other estuaries, where anthropogenic inputs of mercury are of concern for benthic organisms. Areas sampled within the Columbia River estuary indicate that mercury concentrations are not significantly elevated in comparison to total volatile soilds; in fact, ratios of mercury/TVS range from 0.019 to 0.030, with a median value of 0.026. Contaminated English estuaries with mercury in bioavailable form have shown ratios of mercury/TVS approaching 1.2 (Langston, 1982).

If the deposit-feeding clam Macoma balthica, present in the Columbia River estuary (Durkin and Emmett, 1980), accumulates mercury similarly to Macoma balthica in English estuaries (Langston, 1982; fig. 6, p. 24) and the conclusions of Langston (1982) regarding TVS and mercury are valid, then tissue concentrations should be well within the limits set by the U.S. Food and Drug Administration. Concentrations of total mercury in Columbia River estuarine bottom material are similar to those observed in soils (Shacklette and others, 1971b; Boerngen and Shacklette, 1981), to concentrations of total recoverable mercury in earlier Columbia River reconnaissance studies (Fuhrer and Rinella, 1983; Fuhrer, 1984), and are far below concentrations observed in anthropogenically contaminated estuaries (Langston, 1982).

Chemistry of Cadmium Combined with Selected Case Studies in Aquatic Environments

The availability of cadmium from bottom material is difficult to determine when the physicochemical form of cadmium is unknown or when phases responsible for cadmium adsorption are undefined. The uptake of labeled cadmium from solution to bottom-material phases decreases with increasing salinity, mainly because of the complexation of cadmium by chloride. Cadmium has no known biological function in marine mollusks but is strongly accumulated by organisms because of its chemical similarity to zinc; cadmium may displace zinc in certain enzymes, consequently disrupting metabolic function. High concentrations of cadmium have been reported in soft tissues of deposit-feeding organisms existing near urbanized areas, especially areas associated with electroplating industries (Callahan and others, 1979). Cadmium also occurs as a natural contaminant of zinc compounds, in which case any corrosion of zinc-plated fittings can result in cadmium mobilization to dissolved forms and its eventual incorporation into bottom material (Sittig, 1981). Generally, cadmium is not biologically magnified in the food chain, and deposit-feeding organisms receive their body burden of cadmium from direct ingestion of contaminated bottom material (Davies and others, 1982). Cadmium is highly toxic to man; the National Health and Medical Research Council of Australia has set maximum concentration limits for human consumption at 2.0 $\mu g/g$, wet weight (Caldwell and Buhler, 1983).

In a study of 100 surficial bottom material samples from 30 estuaries in England, Bryan and others (1980) concluded that total cadmium ranges from 0.2 μg/g in uncontaminated estuaries to 3.6 μg/g in contaminated estuaries receiving mining wastes. In a contaminated estuary where total cadmium ranged from 1.8 to 3.6 μg/g, concentrations of cadmium in the soft parts of the deposit-feeding clam <u>Scrobicularia plana</u> ranged from 6.0 to 31.5 μg/g (Bryan and others, 1980). In the Columbia River estuary, concentrations of cadmium in the Anodonta species of fresh-water clam range seasonally from 0.042 to 0.148 μg/g wet weight and, in the freshwater clam <u>Corbicula flummea</u> of the upper Columbia River estuary, from 0.009 to 0.103 μg/g wet weight (Caldwell and Buhler, 1983). Organism dry weights may be estimated as 20 percent of the reported wet weight; this will allow comparisons between organisms where tissue-metal concentrations are reported in wet and dry weights. As an example, the tissue concentration of 0.21 μg/g cadmium (dry weight) was estimated from a wet weight concentration of 0.042 μg/g cadmium in the Anodonta species of clam. The 0.21 μg/g concentration may now be used for comparison with cadmium concentrations in mussels. Cadmium in the mussel <u>Mytilus californianus</u>, collected from Columbia River mile 3 in 1977, was reported at 1.4 μg/g dry weight (Goldberg and others, 1978).

In an attempt to determine the bioavailability of trace metals associated with various sedimentary phases, investigators have used laboratory-prepared trace-metal phases labeled with radioactive tracers. Even though this method does not consider the effect of more than one phase competing for a trace metal at a given time, it provides valuable information on the availability of trace metals from a particular phase. Luoma and Jenne (1976) used laboratory prepared hydrous-iron oxides and organic detritus, coprecipitated with labeled cadmium, to determine the uptake of cadmium to the deposit-feeding clam <u>Macoma balthica</u>. They reported the following:

- no detectable uptake from ingestion of labeled organic detritus,
- no detectable uptake from ingestion of particulate hydrous-iron oxide labeled with the nuclide and coated with organic material (using labeled cadmium concentrations of 1.9 to 30.6 μg/g),
- detectable uptake from ingestion of particulate hydrous-iron oxide labeled with the nuclide but not coated with organic material (using labeled cadmium concentrations of 2.3 and 34.0 μg/g),
- detectable uptake from natural sediment.

Hydrous iron oxides are an important control on the adsorption of cadmium to bottom material (Jenne, 1968; Callahan and others, 1979; and Davies and others, 1982). In a unique study by Luoma and Bryan, 1978, covering a broad geographical range (19 estuaries) in Southern England, extractable cadmium was shown to significantly correlate--among all samples--with amorphous iron, determined by extraction with 1N HCl.

A model of metal partitioning among competing phases by Davies and others (1982) predicts cadmium partitioning in estuarine sediments to be dominated by hydrous-iron oxide (approximately 80 percent or more of bottom material capacity for cadmium) while other phases, such as manganese oxides and organic matter, are of lesser importance. Cadmium may be in a bioavailable form when associated with hydrous-iron oxides; however, if cadmium is associated with organic detritus or organic coatings on hydrous-iron oxides, the availability is diminished (Davies and others, 1982).

Extractable Cadmium Determinations in Columbia River Bottom Material

Extractable cadmium in Columbia River estuarine sediments ranged from 0.60 to 2.2 μg/g, with a median concentration of 0.91 μg/g. Sampling sites 1 and 2 have more than twice the cadmium found in sites 3 through 7. Site 1 has the smallest concentration of extractable iron and total organic carbon in bottom material finer than 100 microns; site 2 has the largest concentration of extractable iron. Unlike other studies, this one demonstrates no significant correlations between 1N-HCl extractable cadmium and extractable iron. Site 1 is located in the Columbia River navigation channel (fig. 1, p. 4), adjacent to the Ilwaco boat channel and is characterized by predominantly coarse material, in which less than 1 percent is finer than 100 microns in diameter (table 3, p. 15). Sampling sites 2 through 6 are located in the Ilwaco boat channel and sites 7 and 8 in Astoria boat slips, where 65 to 100 percent of the bottom materials are finer than 100 microns. It is quite apparent that the larger concentrations of extractable cadmium are associated with less than 1 percent of the bulk bottom material at site 1. Concentrations of extractable cadmium are significantly ($\alpha \leq 0.1$) negatively correlated with percent silts ($r = -0.55$) and clays ($r = -0.52$), indicating that concentrations of extractable cadmium increase as the percentage of fine material decreases. The percent silts and clays has been determined for bulk bottom material. It is interesting that the concentration of cadmium extracted from the less-than-100-micron bottom material at site 1 is larger than that extracted from all other sampling sites, with some sites containing as much as 100 times more fine material than site 1. Earlier reconnaissance data (Fuhrer, 1984) show a concentration of 10 μg/g cadmium in bulk bottom material collected off the Columbia River south jetty, using a stronger partial extraction procedure (table 6, p. 21); in terms of large diameter particles this site is similar to site 1. At this reconnaissance study sampling site, 5 percent of the cadmium (by weight) associated with bottom material (sediments and interstitial water) was subsequently released (dissolved) into elutriate-test native mixing water. In this elutriation test--in which one part bottom material was mixed (volume/volume) with four parts native water and the filtrate analyzed--the concentration of cadmium in the elutriate-test filtrate was 210 μg/L; median cadmium concentrations normally observed are <1 μg/L.

In brief, the present study shows large concentrations of extractable cadmium associated with the small proportion of bottom material finer than 100 microns (at site 1); past reconnaissance sampling (near site 1) shows larger concentrations of total recoverable cadmium in predominantly coarse bulk bottom material, similar to that found at site 1. Thus, present and past reconnaissance studies have isolated cadmium in bottom materials finer than 100 microns and in predominantly coarse bulk bottom material. Therefore, it may not be accurate to conclude that cadmium is only associated with the small percentage of bottom material finer than 100 microns in the main navigation channel; cadmium could well be distributed among both bottom materials less than 100 microns and those greater than 100 microns in diameter.

The relation between extractable iron and extractable cadmium is illustrated in figure 8; site 1 is distinct in this distribution, with the smallest iron concentration (990 µg/g) and the largest cadmium concentration (2.2 µg/g). The largest observed range (4.9 g/kg) of organic carbon between sites 1 and 2, where cadmium concentrations are quite similar (2.2 and 1.9 µg/g respectively) is illustrated in figure 9. As a result of the large concentration of total organic carbon and iron associated with the less-than-100-micron bottom material at site 2, the literature suggests (Luoma and Jenne, 1976) that cadmium is probably unavailable to benthic organisms in the type of bottom material encountered at site 2.

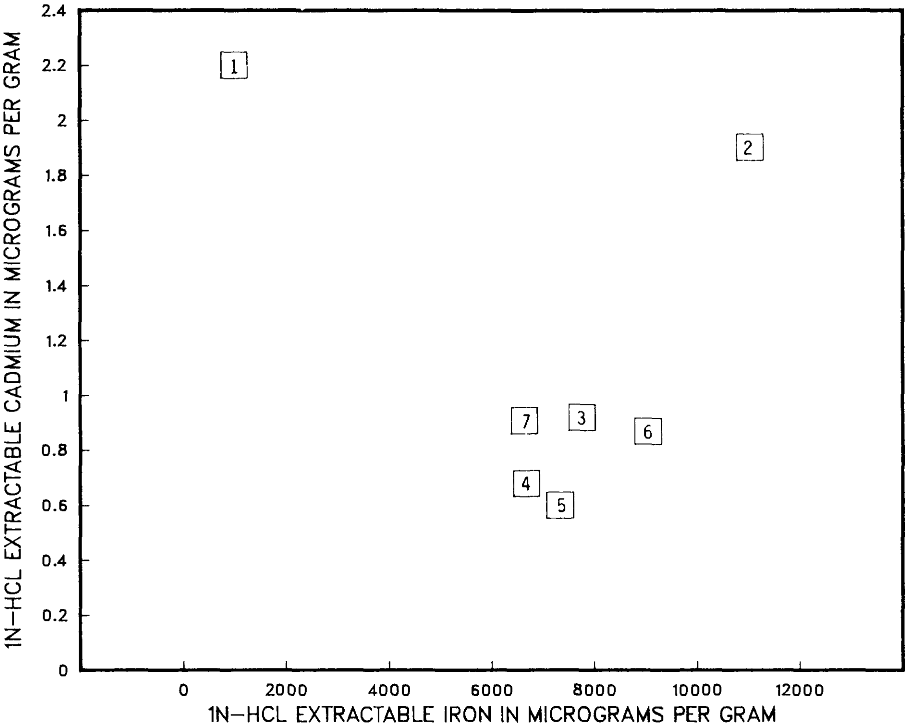

Figure 8.--1N-HCl extractable iron versus extractable cadmium in bottom materials finer than 100 microns (numbers inside plotting symbols represent sampling site locations).

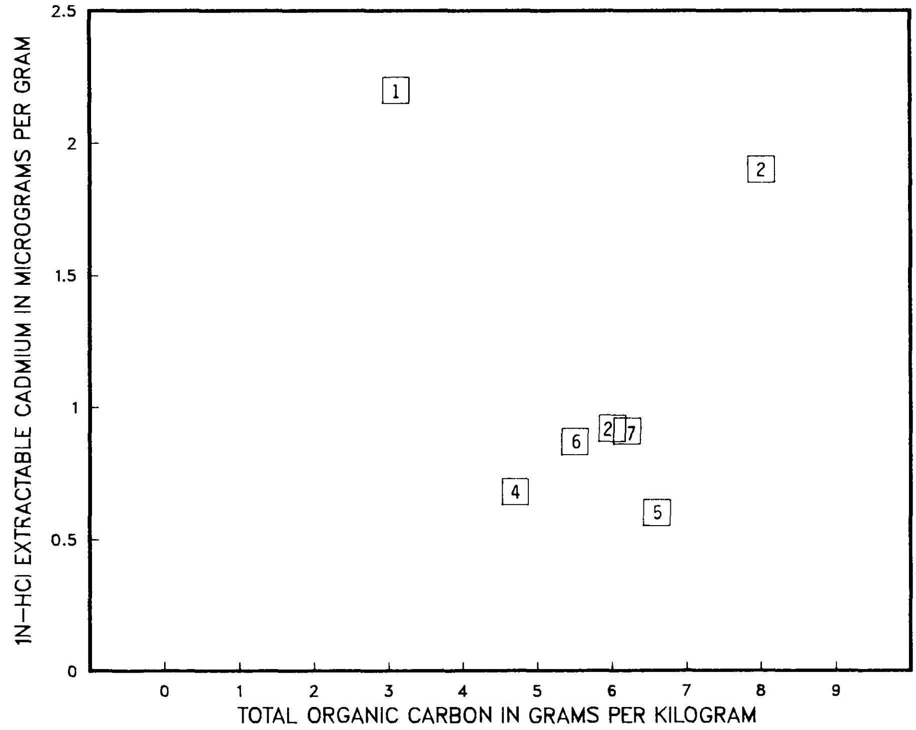

Figure 9.--1N-HCl extractable cadmium versus total organic carbon in bottom materials finer than 100 microns (numbers inside plotting symbols represent sampling site locations).

What may be of concern is the large concentration of cadmium at site 1. At this site, concentrations of total organic carbon and iron are small; thus cadmium may be in a form available to benthic organisms.

There is a possibility that cadmium associated with less-than-100-micron bottom materials at site 1 may not be entirely associated with the hydrous-iron oxide phases. Under these circumstances it is possible that some cadmium could be associated with a secondary or minor phase; metals with the greatest influence on bioavailability could be the small fraction which "spills over" from a major phase to a minor phase (Luoma and Bryan, 1982).

Hem (1972) has studied the stability fields of heavy metals by use of Eh-pH diagrams that describe the dominant form of heavy metal. Assuming equilibrium exists for site 1, where Eh is positive and pH is 8.2, cadmium could exist as the solid cadmium carbonate. In a study on the Rhine and Meuse Rivers in Germany, carbonates were found to occur in the coarser grained fractions of bottom material (DeGroot and others, 1976; and Callahan and others, 1979). In addition, cadmium bound to biogenic calcium carbonate (crushed clam shells) was readily available to the deposit-feeding bivalve Cerstoderma edule, but cadmium bound to precipitated calcium carbonates was of significantly lower bioavailability (Eisler, 1981). Bottom material at site 1 in the Columbia River is characterized as predominately coarse, with more than 99 percent sands larger than 125 microns in diameter (table 8).

Table 8.--Analyses of particle size in percent finer than a specified particle-size diameter in microns

[Sites number 2 and 4 represent duplicate analyses]

Site	Site		Sands								Silts			Clays	
number	name	Date	700	500	350	250	175	125	88	62.5	31	16	8	4	2
1	Baker Bay	7-11-83	--	98	84	38	5	1	0.8	--	--	--	--	--	--
2	Baker Bay	7-11-83	--	--	100	97	76	66	65	63	56	44	30	20	16
2	Baker Bay	7-11-83	--	--	100	96.5	75.5	64.5	63.5	62	56	44	30	21	15
3	Baker Bay	7-11-83	--	--	--	--	--	100	99.5	98.5	79	55	36	24	17
4	Baker Bay	7-12-83	--	--	--	--	100	99	99	98	76	55	32	20	15
4	Baker Bay	7-12-83	--	--	--	--	100	99.5	98.5	95	77	57	33	22	16
5	Baker Bay	7-12-83	--	--	--	--	--	100	99.5	98	83	60	38	25	18
6	Baker Bay	7-12-83	--	--	--	--	--	--	100	99.5	92	72	49	30	22
7	Astoria	7-11-83	--	--	--	--	--	100	99.5	98	82	57	35	23	18
8	Astoria	7-11-83	--	--	100	99.5	98	94	88.5	80	53	33	20	14	10

Carbonates found in estuarine bottom material are mostly from shell fragments (Davies and others, 1982). In unpolluted waters, the exchange of cadmium for calcium in the lattice structure of carbonate minerals can remove cadmium from solution (Callahan and others, 1979). In this study, the occurrence of cadmium carbonate at site 1 is unknown. Favorable conditions do exist for cadmium carbonate formation, but conclusions pertaining to available forms of cadmium at site 1 have not been confirmed by chemical testing.

What is important to note at site 1 is that, regardless of the phase (hydrous-iron oxides and (or) biogenic calcium carbonates) with which cadmium is associated, the concentrations of extractable cadmium associated with dredged materials characteristic of this site may be in a form available to deposit-feeding benthic organisms and deserves further study. The present study and earlier reconnaissance studies indicate that bottom materials sampled in the navigation channel at the mouth of the estuary appear to have elevated concentrations of cadmium that are released by chemical extractions and elutriation of bottom material.

Chemistry of Copper Combined with Selected Case Studies in Aquatic Environments

Copper is an essential micronutrient for aquatic organisms and is one of the more soluble trace metals (Callahan and others, 1979). Concentrations in organisms that exceed natural concentrations and thereby inhibit enzymatic processes may be of concern (Bryan and others, 1980; Davies and others, 1982). Copper can be metabolically regulated in tissues of some organisms (fish); however, the accumulation of copper in marine organisms is not totally uncoupled from exposure (Luoma, 1983). Concentrations of copper are not biologically magnified in the food chain (Davies and others, 1982). Anthropogenic inputs of copper into the estuary may include copper associated with the application of pesticides and copper contained in marine paints used on metallic surfaces of ships and bridges and in electroplating (Callahan, 1979; Sittig, 1981); copper may also be leached from metallic fittings and mining wastes.

In a study of 100 surficial bottom-material samples from 30 estuaries in England, Bryan and others (1980) concluded that total copper concentrations ranged from 13 µg/g in uncontaminated estuaries to 2,540 µg/g in estuaries contaminated with mining wastes. Concentrations of copper in the soft parts of *Scrobicularia plana* and *Nereis diversicolor* range from 9 and 10 µg/g in uncontaminated estuaries to 752 and 1,430 µg/g in contaminated estuaries. Elevated concentrations of copper in bottom material do not necessarily correspond to elevated concentrations in the deposit feeder *Scrobicularia plana*. *Scrobicularia plana* in bottom material with less than 50 µg/g total copper contained 619 µg/g copper; in contrast, *Scrobicularia plana* in bottom material with greater than 3,000 µg/g total copper contained 102 µg/g copper (Bryan and others, 1980). In the lower Columbia River, at river mile 3, the concentration of copper in the mussel *Mytilus californianus* (a filter feeder) was reported as 5.8 µg/g. The guideline for copper set by the National Health and Medical Research Council of Australia is 30 µg/g wet weight (Caldwell and Buhler, 1983).

Soil samples (table 7, p. 22) collected throughout the conterminous United States--at a depth of 8 inches to avoid anthropogenic contamination--yielded 855 total copper samples with a geometric mean of 18 µg/g and a geometric deviation of 2.28 (Shacklette and others, 1971b; Boerngen and Shacklette, 1981); two-thirds of the copper values from soil samples ranged from 8.0 µg/g to 41 µg/g. Two soil samples, collected within 8 miles of one another (near Columbia River mile 39), had total copper concentrations of 20 and 70 µg/g, and a third sample collected 30 miles north of the estuary in B horizon soil had a total copper concentration of 50 µg/g (Boerngen and Shacklette, 1981).

Chemical extractions of bottom material with 1N HCl appear to desorb copper associated with secondary manganese phases like manganese carbonates and (or) sorbed manganese; in addition, 1N HCl can desorb organically bound copper (Luoma and Bryan, 1981).

Relations of extractable copper with extractable iron are dependent on the amount of humic substances, manganese, and total organic carbon present in estuarine bottom material. Where concentrations of humic substances, manganese, and total carbon are small, extractable copper relates strongly to extractable iron. Under these conditions iron would appear to dominate the partioning of copper. Conversely, when concentrations of humic substances are large, the iron phase is subservient to humic substances in partitioning copper (Luoma and Bryan, 1981). The bonding interactions between metals and humic substances are extremely stable (Luoma, 1983) and have the following order of decreasing stability:

$$Pb^{2+} > Cu^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Fe^{2+} > Mn^{2+} > Mg^{2+}$$

(DeGroot and others, 1976). Jenne (1968), in a literature review on the sorption of copper in soils and bottom material, concluded that--with the exception of those containing large concentrations of organic matter--hydrous iron and manganese oxides are important phases for the adsorption of copper. It is important to understand that other phases--such as clays, carbonates, and so forth--may also be responsible for the adsorption of copper, but the identification of a primary phase for the adsorption of copper is currently unresolved. Recent studies suggest that, in oxidized estuarine bottom material, the sorption of copper appears to be dominated by amorphous iron oxides and estuarine humic substances.

In a study by Luoma and Bryan (1982), extractable copper in oxic bottom material was not indicative of tissue concentrations in the deposit-feeding bivalve Scrobicularia plana; in fact, tissue concentrations appeared unrelated to concentrations of total organic carbon, humic substances, carbonates, iron, manganese, and the influence of particle size. In contrast to the study results for the Scrobicularia plana, concentrations of copper in the polychaete worm Nereis diversicolor were predicted from concentrations of 1N-HCl extractable copper in bottom material. The authors concluded that large concentrations of the iron oxide phase in bottom material result in the reduced bioavailability of copper; however, the inverse--small concentrations of iron oxide resulting in the large copper content in Scrobicularia plana--is not true. Bryan and others (1980) indicate that concentrations of copper in Nereis diversicolor relate to chemically extractable copper in bottom material and that no relation exists between chemically extractable copper in bottom material and concentrations observed in Scrobicularia plana; therefore copper associated with bottom material may be available at markedly different degrees in Scrobicularia plana and Nereis diversicolor.

In a laboratory study using a partial extraction procedure on a single sediment type--0.1 N hydroxylamine hydrochoride in 0.01 N nitric acid at pH 2--to relate copper associated with bottom material to concentrations observed in deposit-feeding tubificid worms, Diks and Allen (1983) concluded that copper associated with the easily reducible phases (manganese oxides and amorphous iron oxides) is significantly correlated ($\alpha \leq 0.5$) to concentrations in the worm.

Tubificid worms receive their body burden of trace metals from the solid state in suspended particulate matter and bottom material. The "easily reducible phase" is a commonly used acid extraction to solubilize copper associated with manganese oxides and amorphous iron oxides.

Extractable Copper Determinations in Columbia River Bottom Material

Concentrations of extractable copper in Columbia River bottom material range from 2.6 to 26.7 μg/g, with a median concentration of 20.6 μg/g. Concentrations of extractable copper in estuarine bottom material are similar to concentrations of total copper observed in bulk soils near the estuary (Shacklette and others, 1971b and Boerngen and Shacklette, 1981) and are similar to total copper in Columbia River bulk estuarine sediments (Fuhrer, unpublished data, 1985). The concentrations of extractable copper are also similar to those observed in uncontaminated English estuaries (Bryan and others, 1980). Extractable copper is significantly correlated with inorganic carbon ($r = 0.65$), extractable lead ($r = 0.71$), manganese ($r = 0.62$), and zinc ($r = 0.58$). In contrast to results from other studies, no significant correlations were found between extractable copper and (1) total organic carbon and (2) extractable iron in Columbia River bottom material. The lack of a significant correlation between extractable copper and total organic carbon suggests that carbon concentration does little to control concentrations of extractable copper in Columbia River bottom materials.

Even though extractions with 1N HCl may not desorb all copper associated with all manganese phases, and particularly manganese oxides (Luoma and Bryan, 1981), a significant relation is apparent between extractable copper and manganese in Columbia River bottom material (fig. 10). This relation may be explained by examining the role of carbonates relative to manganese and copper. Carbonates occur in large concentrations in estuarine environments, increasing from head to mouth in most estuaries (Luoma and Bryan, 1981). In estuarine environments and in highly calcareous lakes, dissolved cupric ions incorporate themselves into the crystaline structure of these carbonate mineral forms (Callahan, 1979). Inorganic carbon is primarily a measurement of carbonate, and in Columbia River bottom material the correlation between inorganic carbon and extractable copper may indicate an association of copper with carbonate mineral forms.

It is not possible to determine the bioavailability of copper to benthic organisms in general by using chemical extractions of bottom material; copper bioavailability appears to be specific to the particular deposit feeder. As an example, tissue concentrations of copper in the deposit-feeding clam *Scrobicularia plana* appear unrelated to phase concentrations (Luoma and Bryan, 1982); however, tissue concentrations of copper in the polychaete worm *Nereis diversicolor* were related to the concentration of extractable copper in bottom material.

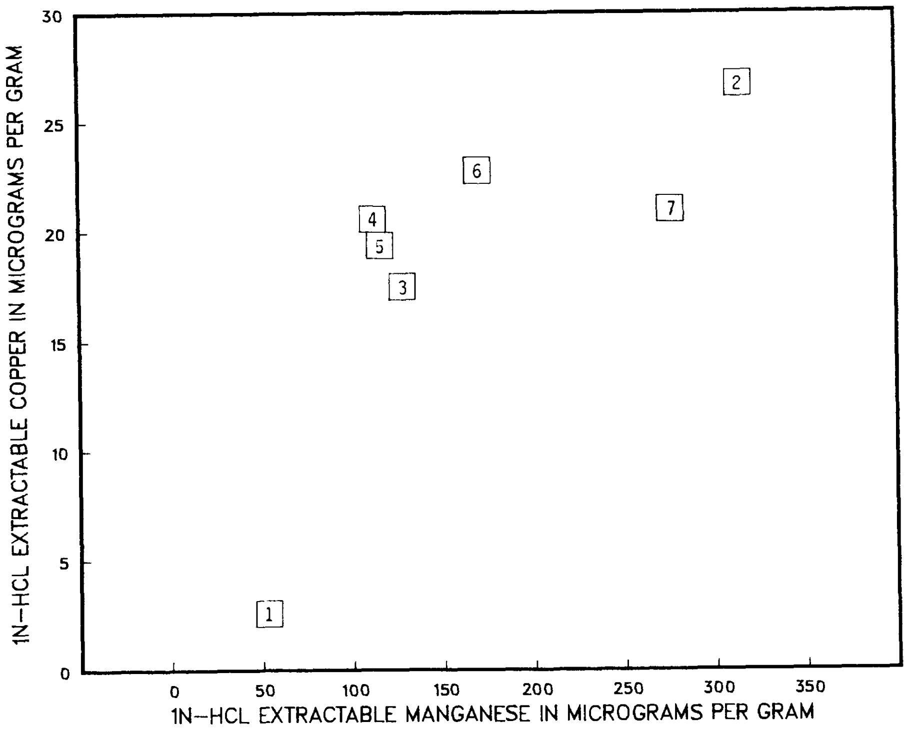

Figure 10.--1N-HCl extractable manganese versus extractable copper in bottom materials finer than 100 microns (numbers inside plotting symbols represent sampling site locations; $r = 0.62$ and $\alpha = 0.05$).

Examination of the literature provides little definitive information for assessing the biological availability of extractable copper from chemical extractions to the general benthic community. What can be emphasized about extractable copper in the Columbia River estuary is that concentrations of copper do not appear to be elevated, falling within the range observed in uncontaminated estuaries.

Chemisty of Lead Combined with Selected Case Studies in Aquatic Environments

Lead can be found in lead-based marine paints, fuel additives, storage batteries and alloyed to other metals. Anthropogenic lead can enter the estuary in runoff from regions of heavy vehicular traffic or directly through emissions from boat traffic. Lead can also be dissolved from naturally occurring mineral forms in which it may be adsorbed to hydrous ferric oxides or hydroxides, combined with carbonates or may react with sulfate to form insoluble compounds (Callahan and others, 1979).

In a study of 100 surficial samples of bottom material from 30 estuaries in England, Bryan and others (1980), concluded that total lead ranged from 30 μg/g in uncontaminated estuaries to 2,175 μg/g in estuaries receiving drainage from old lead mines.

Concentrations of total recoverable lead in estuarine bottom material, collected in earlier Columbia River reconnaissance studies (Fuhrer and Rinella, 1983 and Fuhrer, 1984), ranged from 10 to 40 μg/g with a median concentration of 10 μg/g (table 6, p. 21). Some total-recoverable lead concentration data from the 1982 Columbia River reconnaissance studies are reported as "less than 100 μg/g." These values indicate the minimumum detection limits of the analytical method; furthermore, these values do not reflect anything other than that the lead concentration was below the analytical detection limit. Concentrations of total lead in Columbia River estuarine bulk bottom material range from 3 to 26 μg/g (Fuhrer, in review, 1986).

Soil samples (table 7, p. 22) collected throughout the conterminous United States--at a depth of 8 inches to avoid anthropogenic contamination--yielded 863 total-lead samples with a geometric mean of 16 μg/g and a geometric deviation of 1.91 (Shacklette and others, 1971b); two-thirds of the lead values range from 8 μg/g to 30 μg/g. Two soil samples, collected within 8 miles of one another (near Columbia River mile 39) have identical total-lead concentrations of 15 μg/g; a third sample, collected 30 miles north of the estuary in B horizon soil, had a total-lead concentration of 20 μg/g dry weight (Boerngen and Shacklette, 1981).

Lead can be incorporated into the hydroxide structure of iron oxides and exhibits a strong affinity for the hydroxyl group of the FeO(OH) crystal (Forstner and Wittman, 1979). The ability of hydrous iron oxides to sorb lead increases with increasing pH, and studies of lead sorption show 91 percent of the added lead was sorbed at pH 8.1 (Callahan and others, 1979). Luoma and Bryan (1978, 1982) have shown that the extractable fraction of iron in bottom material has a stronger association with extractable forms of lead than does total iron; this finding has been attributed to the higher density of sorption sites available in amorphous forms of iron. Luoma and Bryan (1981) found that concentrations of extractable lead correlated weakly ($r = 0.46$), but very significantly ($\alpha = 0.001$), with extractable iron in 19 English estuaries. They noted a strong correlation where either manganese or organic carbon were present in small concentration. Lead can be adsorbed by colloidal or particulate organic matter (especially under alkaline pH conditions) and can form either weak bonds, leaving metal ions easily replaceable (physical adsorption), or strong bonds similar to chemical bonding (metal chelation by organic material). In addition, certain components of organic matter such as humic and fulvic acids are especially efficient at complexing lead. Lead may also be associated with clay particles and has been empirically determined to have a greater affinity for adsorption onto clay surfaces, relative to other metals, as follows: lead > nickel > copper > zinc (Forstner and Wittman, 1979). In the presence of carbonates, lead forms insoluble lead carbonate under oxidizing conditions at pH's less than 11.5; even small concentrations of carbonate (due to the dissolution of atmospheric carbon dioxide) are sufficient to rapidly precipitate dissolved forms of lead (Callahan and others, 1979).

In a study of 20 English estuaries with varying physicochemical characteristics (Luoma and Bryan, 1978), concentrations of lead in the deposit-feeding bivalve Scrobicularia plana are related to physicochemical characteristics in bottom material. The log-scale ratio of extractable lead to extractable iron in the 20 English estuaries formed a highly significant correlation with lead in Scrobicularia plana (Luoma and Bryan, 1978). The explanation favored by Luoma and Bryan (1978) for the control of amorphous iron oxides over bioavailable lead is the strong binding capacity of the insoluble iron oxides. The bioavailability of iron-oxide bound lead is low relative to lead associated with other phases. Subsequent increases in iron-oxide bound lead could result in further decreases of bioavailable lead. To test the predictive capability of these findings they formulated the following equation:

$$\log Y = 1.071 \log X + 0.496$$

where X is equal to the ratio of extractable lead ($\mu g/g$) divided by the concentration of extractable iron (mg/g) and Y is the predicted concentration of lead ($\mu g/g$) in Scrobicularia plana. To test this equation, four estuaries were selected, representing both contaminated and uncontaminated bottom materials. The predicted lead concentrations in Scrobicularia plana agreed reasonably with actual measured concentrations. Similar tests were conducted to determine the predictive value of this equation relative to seasonal changes; predicted concentrations of lead agreed reasonably with seasonally measured concentrations of lead in Scrobicularia plana. Thus, concentrations of extractable lead can be used to estimate the concentration of bioavailable lead to the deposit feeder Scrobicularia plana. For example, when extractable concentrations of iron in bottom material are large compared to those of extractable lead, concentrations of lead in Scrobicularia plana are small. In addition, concentrations of extractable iron in bottom material correlated negatively with concentrations of lead in the polychaete worm Nereis diversicolor (Luoma and Bryan, 1982). Anthropogenically enriched concentrations of lead associated with coarser grained bottom material can have high bioavailability in bottom material that is low in either organic matter or amorphous iron phases.

In the deposit-feeding clam Scrobicularia plana, lead originates primarily from the ingestion of bottom material as a food source, as opposed to uptake from dissolved forms of lead (Davies and others, 1982). Concentrations of lead in the deposit-feeding clam Scrobicularia plana range from 5 $\mu g/g$ in uncontaminated English estuaries to 1,080 $\mu g/g$ in estuaries contaminated by lead wastes; concentrations in the polychaete worm Nereis diversicolor range from 0.2 $\mu g/g$ in uncontaminated estuaries to 1,190 $\mu g/g$ in contaminated estuaries (Bryan and others, 1980). In the lower Columbia River, at river mile 3, the concentration of lead in the mussel Mytilus californianus (a filter feeder) was 3.1 $\mu g/g$ dry weight (Goldberg and others, 1978). World Health Food Standards for lead have been set at 10 $\mu g/g$ (Callahan and others, 1979).

Extractable Lead Determinations in Columbia River Bottom Material

Extractable lead in Columbia River bottom material ranged from 2.6 to 31.8 μg/g, with a median concentration of 12.6 μg/g. Extractable lead is significantly correlated with total organic carbon (r = 0.52), bulk inorganic carbon, (r = 0.79), total mercury (r = 0.79), extractable copper (r = 0.71), extractable iron (r = 0.71), and extractable manganese (r = 0.52).

Concentrations of extractable lead increase with total organic carbon in bottom material (fig. 11). Concentrations of extractable lead also increase with increased concentrations of extractable iron in bottom material (fig. 12) and behave similarly to extractable manganese. Many studies (Callahan and others, 1979; Luoma and Bryan, 1981; and Forstner and Wittmann, 1979) have suggested that sorption of lead by iron and manganese oxides is a major sorption process in bottom material. Concentrations of extractable iron and extractable lead from Ilwaco channel and Astoria boat slips are very similar, even though the sampling sites are approximately 10 miles apart. In a 1982 reconnaissance study, concentrations of lead (using a different partial extraction procedure) from two sites near Ilwaco boat channel and one site in the Astoria boat basin were 30, 40, and 10 μg/g, respectively.

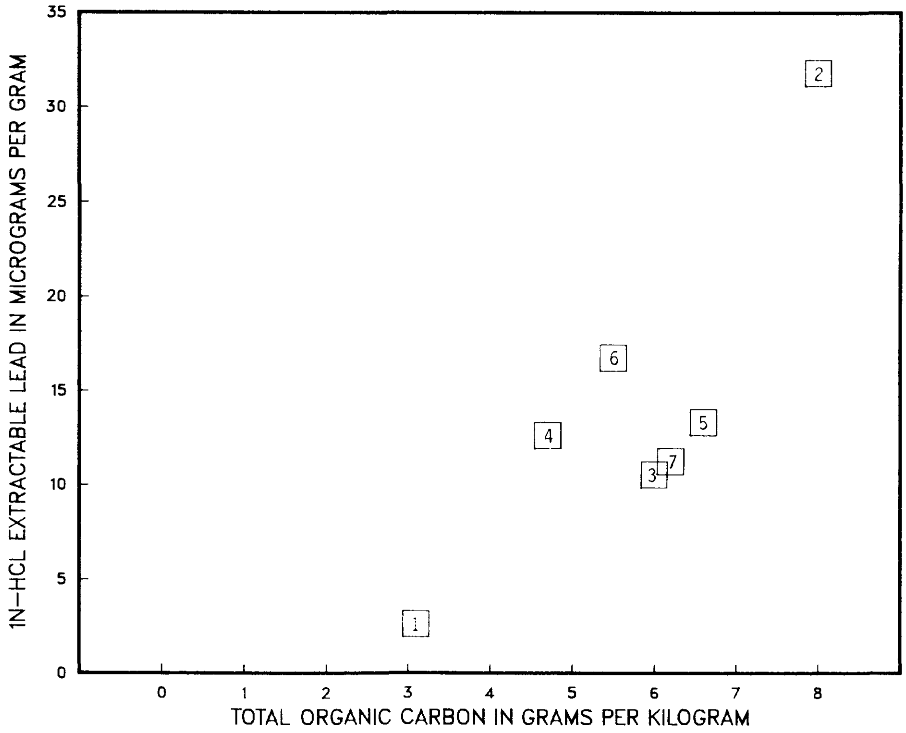

Figure 11.--Total organic carbon versus 1N-HCl extractable lead in bottom materials finer than 100 microns (numbers inside plotting symbols represent sampling site locations; r = 0.52 and α = 0.09).

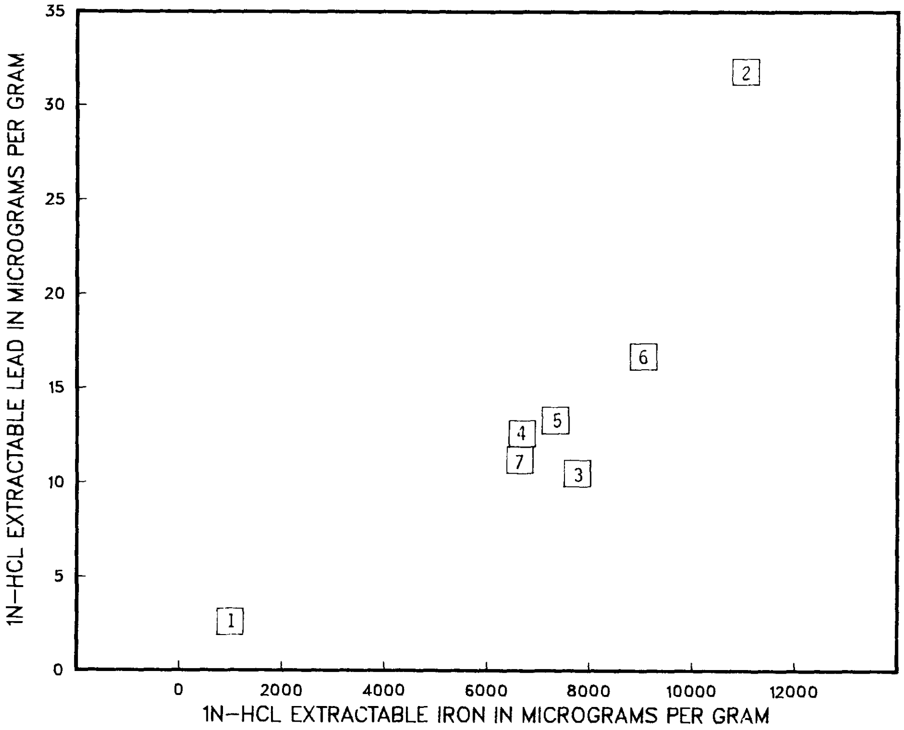

Figure 12.--1N-HCl extractable iron versus extractable lead in bottom materials finer than 100 microns (numbers inside plotting symbols represent sampling site locations; $r = 0.71$ and $\alpha = 0.02$).

These concentrations are similar to concentrations of extractable lead observed in the current study. Phase concentrations at site 1 are small relative to sites 2 through 7; consequently, extractable lead concentrations at site 1 are small. The significant correlation between extractable lead and inorganic carbon may be explained by the presence of carbonates (an inorganic carbon form capable of forming insoluble lead carbonate).

Using ratios of extractable lead/extractable iron from Columbia River bottom materials as input data in a relation developed by Luoma (1978), estimated concentrations of lead in Scrobicularia plana were calculated and are shown in table 9. This relation may be a useful indicator of bioavailable forms of lead in Baker Bay or Astoria bottom-material samples. The estimated concentrations of lead in Scrobicularia plana range from 4 to 10 μg/g dry weight, with a median concentration of 6 μg/g dry weight. The estimated median lead concentration in Scrobicularia plana is below the World Health Food Standard of 10 μg/g dry weight. Concentrations of extractable lead in Columbia River bottom material are not elevated relative to concentrations found in soils from the surrounding area (Boerngen and Shacklette, 1981), concentrations found in earlier reconnaissance studies (Fuhrer and Rinella, 1983; Fuhrer, 1984), or concentrations observed in anthropogenically contaminated estuaries (Bryan and others, 1980). Estimated concentrations of lead in Scrobicularia plana for Columbia River bottom material are similar to actual concentrations observed in Scrobicularia plana in uncontaminated English estuaries (Bryan and others, 1980).

Table 9.--Estimated concentrations of lead in the soft tissues of the deposit-feeding bivalve Scrobicularia plana

[From a relation developed by Luoma (1978) and the ratio of extractable lead to extractable iron in Columbia River bottom material. Concentrations are reported in micrograms or milligrams per gram]

Site description	Site number	Extractable lead µg/g	Extractable iron mg/g	Ratio of lead/iron	Estimated concentration in Scrobicularia plana[1] µg/g (dry weight)
Baker Bay	1	2.6	1.0	2.6	9
Baker Bay	2	31.8	11.0	2.9	10
Baker Bay	3	10.5	7.8	1.4	4
Baker Bay	4	12.6	6.7	1.8	6
Baker Bay	5	13.3	7.3	1.9	6
Baker Bay	6	16.7	9.0	1.9	6
Astoria	7	11.2	6.6	1.7	5

[1] Equation to describe the concentration of lead in Scrobicularia plana is $\log Y = 1.071 \log X + 0.496$, where Y is the lead concentration in µg/g (dry weight) in the deposit feeder, and X is the ratio of extractable lead (µg/g)/extractable iron (mg/g).

Chemistry of Zinc Combined with Selected Case Studies in Aquatic Environments

In most estuarine bottom materials, extractable phases of iron appear to dominate the partitioning of zinc. In addition, the extractable fraction of iron shows a stronger association with zinc than does total iron (Luoma and Bryan, 1981 and Luoma and Bryan, 1982). This is likely a result of the higher density of sorption sites associated with 1N-HCl extractable forms of iron (amorphous forms) as opposed to older more crystalline forms that are only solubilized in the total extraction procedure (Luoma and Bryan, 1981).

Under reducing conditions in bottom material, iron may become immobilized due to the formation of insoluble iron sulfides; however, under the same reducing conditions, when sulfides are low in concentration, iron may be mobilized in interstitial waters. Reduced soluble forms of iron or manganese that migrate upward through bottom material may encounter an oxic/anoxic interface zone. Under oxidizing conditions the reduced soluble forms can precipitate as a coating or discrete particles of hydrous iron or manganese oxides/hydroxides (Forstner and Wittman, 1979). These precipitates can be negatively charged and are capable of coprecipitating zinc (Callahan and others, 1979), thereby serving as an effective phase for the removal of dissolved zinc forms.

The availability of zinc associated with bottom material declines as the strength of the binding increases between zinc and a given phase (Luoma and Jenne, 1977). Some deposit feeders, like the polychaete worm *Nereis diversicolor*, can physiologically regulate their zinc concentration (Luoma and Bryan, 1982 and Luoma, 1983).

In a study of 100 surficial bottom-material samples, from 30 estuaries in England, Bryan and others (1980) concluded that total zinc concentrations in most estuarine bottom materials are less than 200 µg/g and, in estuaries draining old mining areas, are as much as 3,000 µg/g. Concentrations of zinc associated with the soft parts of the estuarine bivalve *Scrobicularia plana* range from 500 µg/g in uncontaminated areas to 3,300 µg/g in contaminated English estuaries. In the upper Columbia River estuary, concentrations of zinc in the Anodonta species of freshwater clam ranges seasonally from 25.5 to 51.7 µg/g wet weight and from 12.0 to 26.3 µg/g wet weight for the freshwater clam *Corbicula fluminea* (Caldwell and Buhler, 1983). In the lower Columbia River estuary, at river mile 3, concentrations of zinc in the mussel *Mytilus californianus*, a filter feeder, are 100 µg/g dry weight (Goldberg and others, 1978). No detectable accumulation of radionuclide zinc-65 was observed from ingestion of Columbia River sediments in tubificids, a deposit-feeding oligochaete worm living in surficial bottom material (Jenne and Luoma, 1977). The National Health Medical Research Council of Australia has set maximum tissue concentration limits of zinc for human consumption at 1,000 µg/g wet weight (Caldwell and Buhler, 1983).

Soil samples (table 7, p. 22) collected throughout the conterminous United States--at a depth of 8 inches to avoid anthropogenic contamination--yielded 863 total zinc samples, with a geometric mean of 44 µg/g and a geometric deviation of 1.86 (Shacklette and others, 1971b; and Boerngen and Shacklette, 1981); two-thirds of the zinc values range from 24 to 82 µg/g. Two soil samples, each collected within 8 miles of one another (near Columbia River mile 39), have total zinc concentrations of 93 and 85 µg/g. A third sample collected 30 miles north of the estuary in B horizon soil had a total zinc concentration of 40 µg/g. Concentrations of total recoverable zinc shown in table 6 (p. 21) are from earlier reconnaissance samples (Fuhrer and Rinella, 1983, and Fuhrer, 1984) collected in the lower Columbia River from sites in the main channel, in adjacent bays, or in contributing streams. The samples ranged in concentration from 8 µg/g (in coarse material, from the Columbia River off the south jetty) to 300 µg/g (in fine material fed into the lower estuary from Skipanon River). Median concentration was 40 µg/g.

In 50 bottom-material samples collected from 19 English estuaries, a very strong correlation between acid extractable iron and zinc occurred among bottom-material samples low in the binding phases of manganese, total organic carbon, or humic substances (Luoma and Bryan, 1981). This correlation suggests that extractable iron may not compete as efficiently for zinc as do other phases present at higher concentrations.

To determine the availability of zinc to the deposit-feeding bivalve Macoma balthica, Luoma and Jenne (1977) used individual laboratory-prepared phases that coprecipitated with labeled zinc as a tracer. They noted little bioaccumulation of labeled zinc when Macoma balthica was associated with either hydrous iron or manganese oxide phases; however, labeled zinc associated with detrital-organic material was accumulated by the deposit-feeding clam. Macoma balthica accumulated labeled zinc at a higher rate from biogenic carbonates, a relatively minor phase, than from other phases (Luoma and Jenne, 1977). The authors concluded that, in any system where hydrous iron or manganese oxides dominate the adsorption of trace metals within bottom material, the availability of sediment-bound zinc to deposit feeders should be minimal. However, where zinc complexation with organic material dominates zinc sorption to bottom sediments, significant zinc uptake may occur.

In another study Luoma and Bryan (1979) collected the deposit-feeding bivalve Scrobicularia plana from 17 English estuaries and Macoma balthica from San Franciso Bay. No significant correlations were determined between any single acid extractable form of zinc and zinc in either of the deposit-feeding bivalves. However, the ratio of hydroxylamine hydrochloride extractable iron to ammonium acetate extractable manganese correlated strongly with the bioavailability ratio, defined as the concentration of zinc in the organism (μg/g) divided by the concentration of zinc in the bottom material (μg/g). As a result of this relation, the concentration of ammonium acetate extractable manganese declined as the sampling stations approached the head of the estuary, while the bioavailability ratio of Macoma balthica increased, suggesting that, as the concentration of extractable manganese decreases relative to extractable iron, the concentration of zinc in the organism increases. In addition, this study found that, when total organic carbon in bottom material exceeded 1 percent (10 g/kg), the predicted bioavailability ratio exceeded the observed bioavailability ratio. This observation prompted investigators to conclude that organic materials may decrease the bioavailability of zinc to deposit-feeding organisms. In the 17 English estuaries studied, the most significant correlations were between concentrations of zinc in Scrobicularia plana and the product of ammonium acetate extractable zinc multiplied by the ratio of humic substances to organic carbon. The statistical evidence indicates that increasing concentrations of humic substances (an extractable fraction of organic material) enhanced the bioavailability of zinc in bottom material (Luoma and Bryan, 1982 and Luoma and Bryan, 1979).

In the aforementioned studies there are some apparent ambiguities relative to the availability of zinc associated with such phases as amorphous iron oxides and (or) organic carbon. From these earlier studies it is not entirely clear whether organic carbon may act to reduce or promote the availability of zinc to benthic deposit feeders.

The same is true for zinc associated with amorphous iron oxide forms; in the above studies, using laboratory prepared phases and labeled zinc, no significant uptake of labeled zinc from hydrous iron oxide phases was observed in the deposit-feeding bivalve Macoma balthica. In contrast, in San Francisco Bay bottom material, statistical correlations indicate that the availability of zinc to the bivalve Macoma balthica is increased when concentrations of amorphous iron oxides (hydroxylamine hydrochloride extractable iron) are increased in sediments (Luoma and Bryan, 1979).

Extractable Zinc Determinations in Columbia River Bottom Material

Extractable zinc in Columbia River bottom material ranges from 15 to 131 μg/g, with a median concentration of 80 μg/g. Zinc concentrations were compared with: (1) total zinc in bulk bottom material from soil samples near the estuary (Shacklette and others, 1971b; Boerngen and Shacklette, 1981), (2) total zinc in Columbia River estuarine bulk bottom material (Fuhrer, unpublished data, 1985), (3) total zinc in bulk bottom material from uncontaminated English estuaries (Bryan and others, 1980), and (4) total recoverable zinc in Columbia River estuarine bulk bottom material. These comparisons clearly indicate that concentrations of extractable zinc fall well within concentrations observed in other uncontaminated estuaries and within concentrations observed both temporally and spatially in the Columbia River estuary, for a range of particle-size and sediment types.

Examining the relation between concentrations of extractable zinc and potential primary phases, such as extractable iron, manganese, and organic carbon, can provide useful information on the distribution of zinc in Columbia River estuarine bottom material. Extractable zinc in Columbia River bottom material is significantly correlated with extractable chromium ($r = 0.75$), copper ($r = 0.58$), iron ($r = 0.68$), and manganese ($r = 0.68$). The relation between extractable zinc and the iron and manganese phases is illustrated in figure 13. Both correlation coefficients and levels of significance for these two relations are identical, suggesting that both phases are equally important in the adsorption of zinc. It is not statistically possible to separate extractable iron and extractable manganese in terms of acting as primary phases. There are no significant relations between total organic carbon in bottom material finer than 100 microns and concentrations of extractable zinc; it appears that, in Columbia River estuarine bottom material, the iron and manganese phases compete more effectively for extractable zinc than does total organic carbon. Total organic carbon, particularly humic substances, can be an important phase for complexing zinc (Luoma and Bryan, 1982 and Luoma and Bryan, 1979); however, in sampled Columbia River bottom material, concentrations of iron and manganese are the only chemical phases relating to extractable zinc.

It is not possible to use the relation between extractable zinc and iron and manganese phases to estimate the biological availability of zinc to the general benthic community or even to a single deposit feeder like Macoma balthica, found in Ilwaco boat channel (Durkin and Emmette, 1980).

The reason given by Luoma and Bryan, (1982) is that the uptake of zinc by deposit feeders will not be entirely dependent on the concentration of hydrous iron and manganese oxides in bottom material, but rather upon the characteristics of the oxides themselves, as is evidenced by the varying solubilities of zinc in different chemical extracts.

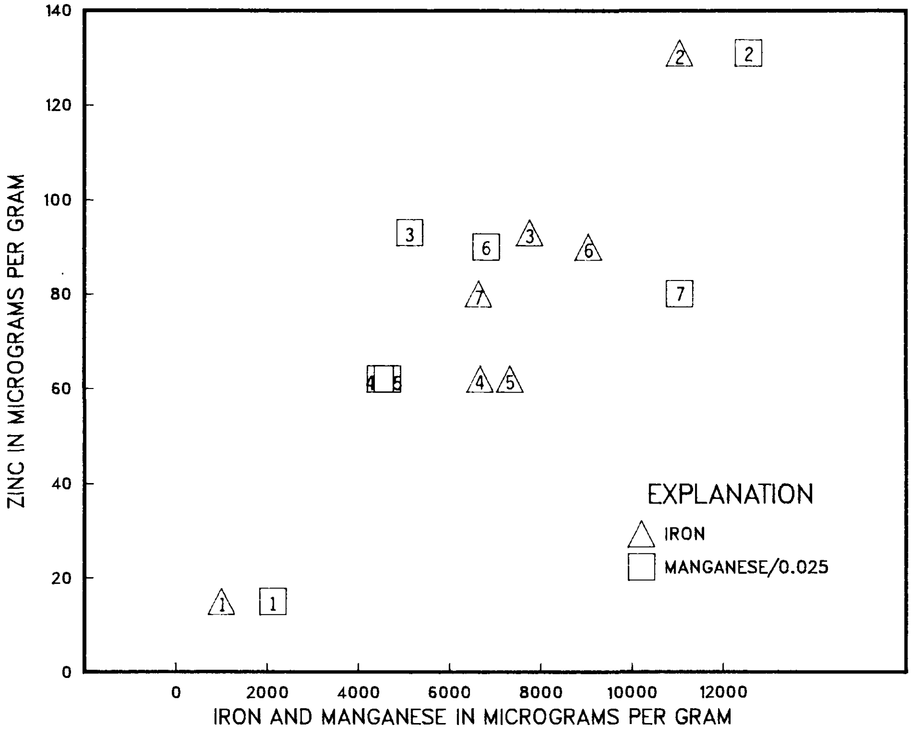

Figure 13.--1N-HCl extractable iron and manganese versus extractable zinc in bottom materials finer than 100 microns (numbers inside plotting symbols represent sampling site locations; for extractable iron, r = 0.68 and α = 0.03; for extractable manganese, r = 0.68 and α = 0.03).

SUMMARY

Trace metals will be partitioned to phases with the greatest metal binding capability. Common phases in estuarine environments are organic materials, carbonates, hydrous iron and manganese oxides, hydroxides and clay minerals. Carbonate phases may play a significant role in binding certain trace metals, such as zinc and cadmium. This mechanism appears to be most effective under alkaline pH conditions and occurs as a result of precipitation of carbonate minerals. The humic fraction of organic material is also an important phase. It is capable of binding trace metals and constitutes 40 to 70 percent or more of estuarine organic material.

Concentrations of total mercury associated with Columbia River bottom material ranged from 0.07 to 0.17 μg/g, with a median of 0.14 μg/g. This is a relatively narrow range of mercury concentrations and is in general agreement with those determined in soils in the lower Columbia River estuary and those observed in earlier Columbia River estuary reconnaissance studies. Concentrations of total mercury similar to those observed in Columbia River bottom material have been shown, by other investigators in different hydrologic environments, to accumulate in deposit-feeding benthic organisms; yet concentrations reported for bivalve mollusks in the Columbia River estuary are extremely low. The key difference in these findings appears to be the percentage of total volatile solids in Columbia River bottom material and their strong association with mercury. Bottom materials found in depositional areas sampled in the present study have a high percentage of total volatile solids associated with them, compared to those in other estuaries where anthropogenic inputs of mercury are sufficient to cause concern for deposit-feeding organisms. These large percentages of total volatile solids may result in less biologically available forms of mercury associating with Columbia River bottom material.

Extractable cadmium ranged from 0.60 to 2.2 μg/g, with a median concentration of 0.91 μg/g. Extractable cadmium is significantly correlated ($\alpha \leq 0.1$) negatively with percent silts and percent clays; as a result, concentrations of cadmium in bottom material finer than 100 microns increase as the percentage of bottom material finer than silt and (or) clay size decreases. The largest extractable cadmium concentration occurred at site 1 in the Columbia River navigation channel (where less than 1 percent of the bottom material is finer than 100 microns). Generally, it appears that, as the less-than-100-micron fraction of bulk bottom material decreases--which occurs as sampling sites in the Ilwaco boat channel approach the main navigation channel of the Columbia River--the respective concentration of cadmium associated with this size fraction increases. The mechanism for this phenomenon is not currently known.

Elutriation tests from earlier reconnaissance studies show that the greatest releases of cadmium, from bottom material to native mixing water, occurred in predominantly coarse material collected near the entrance to the Columbia River navigation channel, where only 20 percent of the bottom material is finer than 125 microns. There appears to be no strong relation between extractable cadmium and extractable iron, suggesting that iron may not be acting as an important phase for the adsorption of cadmium, especially at site 1 in the Columbia River navigation channel. Though other investigators have shown relations between 1N-HCl extractable iron and extractable cadmium, such relations are not evident in this study. Concentrations of extractable cadmium are elevated relative to extractable iron at site 1; thus some phase other than iron may be responsible for controlling concentrations of cadmium. In addition, concentrations of total-recoverable cadmium in bulk bottom material and cadmium released from bulk bottom material to elutriate-test filtrates are also elevated at a nearby sampling site. Reconnaissance data show that cadmium from the vicinity of site 1 is easily desorbed from bulk sediments by mixing these with native water (via elutriate tests). Cadmium is also easily desorbed from bulk sediments by a sequential chemical extraction using hydrogen peroxide and hot HCl. In addition, data from the current study show that cadmium in bottom material finer than 100 microns from site 1 can be extracted, using cold HCl, at concentrations similar to those found in anthropogenically influenced estuaries. Further study of cadmium in the vicinity of site 1 would be necessary to determine its association with other bottom material phases and to assess the potential impact of these associations on bioavailable forms of cadmium.

Extractable copper in Columbia River bottom material ranged from 2.6 to 26.7 μg/g, with a median concentration of 20.6 μg/g. Extractable copper is significantly correlated with inorganic carbon, extractable lead, manganese and zinc. Concentrations of extractable copper do not exceed concentrations observed in soils and are generally similar to background concentrations found in other estuaries. Other studies have shown associations between extractable copper and such primary phases as iron and manganese oxides and organic carbon, particularly the humic acid component. The significant correlation between extractable copper and inorganic carbon may indicate an association of copper with carbonate mineral forms in estuarine bottom material.

Extractable lead in Columbia River bottom material ranged from 2.6 to 31.8 μg/g, with a median concentration of 12.6 μg/g. Extractable lead is significantly correlated with total organic carbon, bulk inorganic carbon, total mercury, 1N-HCl extractable copper, iron and manganese. Concentrations of 1N-HCl extractable lead are small in the Columbia River main navigation channel relative to sites in the Ilwaco boat channel and Astoria boat slips. Concentrations also increase as the chemical phases of extractable iron and manganese increase; this relation is in agreement with findings in other investigations and suggests that sorption of lead by iron and manganese oxides is a major concentrating process in bottom material. Concentrations of lead in Scrobicularia plana, estimated for the Columbia River using a relation developed by Luoma (1978), are below the World Health Food Standards.

Concentrations of 1N-HCl extractable zinc in Columbia River bottom material range from 15 to 131 μg/g, with a median concentration of 80 μg/g. They are not elevated relative to total zinc concentrations in industrialized estuaries. In a study of 30 English estuaries, concentrations of total zinc in less industrialized areas are less than 200 μg/g. In this study extractable zinc is significantly correlated with extractable chromium, copper, iron, and manganese. Total organic carbon, humic substances in particular, can be an important phase for complexing zinc; however, in sampled Columbia River bottom material, sediment concentrations of iron and manganese are the only chemical phases relating to extractable zinc.

SELECTED REFERENCES

Aston, S. R., and Chester, R., 1976, Estuarine sedimentary processes, in: Estuarine chemistry, Burton, J. D., and Liss, P. S., eds.: Academic Press, p. 37-52.

Baldi, F., and Bargagli, R., 1982, Chemical leaching and specific surface area measurements of marine sediments in the evaluation of mercury contamination near cinnabar deposits: Marine Environmental Research, v. 6, p. 69-82.

Bartlett, P. D., and Craig, P. J., 1981, Total mercury and methyl mercury levels in British estuarine sediments - II: Water Research, Pergamon Press, Great Britain, v. 15, p. 37-47.

Bella, D. A., 1975, Tidal flats in estuarine water quality analyses: U.S. Environmental Protection Agency, EPA-660/3-75-025, 186 p.

Bisogni, J. J., and Lawrence, A. W., 1975, Kenetics of mercury methylation in aerobic and anerobic environments: Journal of Water Pollution Federation, v. 47, p. 135-152.

Boerngen, J. G., and Shacklette, H. T., 1981, Chemical analyses of soils and other surficial materials of the conterminous United States: U.S. Geological Survey Open-File Report 81-197, p. 1-133.

Bothner, M. H., and Carpenter, R., 1973, Sorption-desorption reactions of mercury with suspended matter in the Columbia River, in Radioactive contamination of the marine environment, Proceeding of a symposium, Seattle, Washington, 1972, p. 73-87. Vienna: International Atomic Energy Agency, Report no. IAE-SM-15815.

Boyle, E. A., Edmond, J. M., and Sholkoyitz, E. R., 1978, The mechanism of iron removal in estuaries: Geochim. Cosmochim. Acta, Great Britain, v. 41, p. 1313-1324.

Breteler, R. J., Ivan, V., and Teal, J. M., 1981, Bioavailability of mercury in several northeastern United States spartina ecosystems: Estuarine, Coastal and Shelf Science, Academic Press, London, v. 12, p. 155-166.

Bryan, G. W., Langston, W. J., and Hummerstone, L. G., 1980, The use of biological indicators of heavy-metal contamination in estuaries: Marine Biological Association of the United Kingdom, Occasional Publication number 1.

Burton, J. D., and Liss, P. S., 1976, Estuarine chemistry: Great Britain, Academic Press, 229 p.

Cadigan, R. A., 1970, Mercury in sedimentary rocks of the Colorado Plateau, in Mercury in the environment: U.S. Geological Survey Professional Paper 713, p. 17-18.

Caldwell, R. S., and Buhler, D. R., 1983, Heavy metals in estuarine shellfish from Oregon: Archives of Environmental Contamination and Toxicology, v. 12, p. 15-23.

Callahan, M. A., Slimak, M. W., Gabel, N. W., May, I. P., Fowler, C. F., Freed, J. R., Jennings, P., Durfee, R. L., Witmore, F. C., Maestri, B., Mabey, W. R., Holt, B. R., and Gould, C., 1979, Water related fate of 129 priority pollutants. Volume I: Introduction and technical background, metals and inorganics, pesticides and PCBs: PB80-204373, National Technical Information Service, Springfield, Virginia, p. 1-1-31-7.

Conover, W. J., 1980, Practical nonparametric statistics, (2d ed.): John Wiley & Sons, New York, p. 256-257.

Curtis, C. D., 1966, The incorporation of soluble organic matter into sediments and its effect on trace element assemblages, in Forstner, U., and Wittman, T. T. W., 1979, Metal pollution in the aquatic environment: New York, Springer-Verlag Berline Heidleberg, p. 224.

Davies, R. J., Nelson, P. O., Williamson, K. J., 1982, Estuarine sediment controls on trace metal distributions: PB83-175208, National Technical Information Service, Springfield, Virginia, 224 p.

DeGroot, A. J., Salomons, W., and Allersma, E., 1976, Processes affecting heavy metals in estuarine sediments, in Estuarine chemistry, Burton J. D., and Liss, P. S., eds.: Academic Press, p. 131-157.

Diks, D. M., and Allen, H. E., 1983, Correlation of copper distribution in a freshwater-sediment system to bioavailability: Bulletin of Environmental Contamination Toxicology, v. 30, p. 37-43.

Durkin, J. T., and Emmett, R. L., 1980, Benthic invertebrates, water quality, and substrate texture in Baker Bay, Youngs Bay, and adjacent areas of the Columbia River Estuary: Coastal zone and estuarine studies: National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Seattle, Washington, 44 p.

Eisler, R., 1981, Trace metal concentrations in marine organisms: New York, Pergaman Press, p. 154.

Elderfield, H., and Hepworth, A., 1975, Diagenesis, metals and pollution in estuaries: Marine Pollution Bulletin, V. 6, p. 85-87.

Engel, E. W., Sunda, W. G., and Fowler, B. A., 1981, Factors affecting trace metal uptake and toxicity to estuarine organisms. Part I. Environmental parameters: in Biological monitoring of marine pollutants, Calabrese, A., Thurberg, F. P., and Vernberg, J., eds.: Academic Press, New York, New York, p. 127-163.

Fleisher, M., 1970, Summary of the literature on the inorganic geochemistry of mercury in Mercury in the environment: U.S. Geological Survey Professional Paper 713, p. 6-13.

Forstner, U., and Wittmann, T. T. W., 1979, Metal pollution in the aquatic environment: New York, Springer-Verlag Berlin Heidelberg, 486 p.

Fox, D. S., Bell, S., Nehlsen, W., and Damron, J., 1984, The Columbia River Estuary - Atlas of physical and biological characteristics: Seattle, Washington, Graphic Color, 87 p.

Fuhrer, G. J., 1984, Analyses of elutriates, native water, and bottom material from the Chetco, Rogue, and Columbia Rivers in western Oregon: U.S. Geological Survey Open-File Report 84-133, Portland, Oregon, 57 p.

Fuhrer, G. J., and Rinella, F. A., 1983, Analyses of elutriates, native water, and bottom material in selected river and estuaries in western Oregon and Washington: U.S. Geological Survey Open-File Report 82-923, 147 p.

Gibbs, R., 1977, Transport phases of transition metals in the Amazon and Yukon Rivers: Geological Society of America Bulletin, v. 88, p. 829-843.

Goldberg, E. D., Bowen, V. T., Farrington, J. W., Harvey, G., Martin, J. H., Parker, P. L., Risebrough, R. W., Robertson, W., Schneider, E., and Gamble E., 1978, The mussel watch: Environmental Conservation, Switzerland, v. 5, no. 2, p. 101-125.

Guy, H. P., 1979, Laboratory theory and methods for sediment analyses: U.S. Geological Survey Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, chap. Cl, 58 p.

Head, P.C., 1976, Organic processes in estuaries, in Estuarine chemistry, Burton, J. D., and Liss, P. S., eds., Academic Press, p. 53-91.

Hem, J. D., 1970, Chemical behavior of mercury in aqueous media, in Mercury in the environment: U.S. Geological Survey Professional Paper 713, p. 19-23.

______ 1972, Chemistry and occurrence of cadmium and zinc in surface water and ground water: Water Resources Research, v. 8, p. 661-679.

Horowitz, A. J., 1984, A primer on trace-sediment chemistry: U.S. Geological Survey Open-File Report 84-709, Doraville, Georgia, 81 p.

Hubbell, D. W., and Glenn, J. L., 1973, Distribution of radionuclides in bottom sediments of the Columbia River Estuary: U.S. Geological Survey Professional Paper 433-L, p. 63.

Huffman, C., Rahill, R. L. Shaw, V. E., and Norton, D. R., 1972, Determination of mercury in geologic materials by flameless atomic absorption spectrometry: U.S. Geological Survey Professional Paper 800C, p. C203-C207.

Jenne, E. A., 1968, Controls on manganese, iron, cobalt, nickel, copper, and zinc concentration in soils and water: The significant role of hydrous manganese and iron oxides, in Trace inorganics water: ASCE Symposium Series 73, American Chemical Society, p. 337-387.

______ 1970, Atmospheric and fluvial transport of mercury, in Mercury in the environment: U.S. Geological Survey Professional Paper 744, p. 40-45.

______ 1976, Trace element sorption by sediments and soil-sites and processes, in Symposium on molybdenum in the environment, Chappel, W., and Peterson K., eds.: M. Kekker, Inc., New York, p. 425-511.

Jenne, E. A., and Luoma, S. N., 1977, Forms of trace elements in soils, sediments, and associated waters: An overview of their determination and biological availability, in Biological implications of metals in the environment: CONF-750929, National Technical Information Service, Springfield, Virginia, p. 110-143.

Johansson, K., 1977, The Fundamental chemical and physical characteristics of Swedish lakes; heavy metal content in lake sediment from some lakes on the Swedish west coast and its connection with the atmospheric supply, in Forstner, U., and Wittman, T. T. W., 1979, Metal pollution in the aquatic enviroment: New York, Springer-Verlag Berlin Heidelberg, p. 224.

JRB Associates, 1984, Initial evaluation of alternatives for development of sediment related criteria for toxic contaminants in marine water (Puget Sound): U.S. Environmental Protection Agency, Washington, D.C., EPA Contract no. 68-01-6388, Work Assignment 42.

Langston, W. J., 1982, The distribution of mercury in British estuarine sediments and its availability to deposit-feeding bivalves: Journal of the Marine Biological Association of the United Kingdom, Plymouth: v. 62, p. 667-684.

Lindberg, S. E., and Harris, R. C., 1974, Mercury-organic matter association in estuarine sediments and interstitial water, Environmental Science and Technology: v. 8, no. 5, p. 459-462.

Luoma, S. N., 1974, Mercury cycling in an Hawaiian estuary: Water Resources Research Center Technical Memorandum no. 42, University of Hawaii, Honolulu.

______ 1977, The dynamics of biologically available mercury in a small estuary: Estuarine and Coastal Marine Science, v. 5, p. 643-652.

______ 1983, Bioavailability of trace metals to aquatic organisms - A review: The Science of the Total Environment, v. 28, p. 1-22.

Luoma, S. N., and Bryan, G. W., 1978, Factors controlling the availability of sediment-bound lead to the estuarine bivalve scrobicularia plana: Journal of the Marine Biological Association of the United Kingdom, Plymouth, v. 58 p. 793-802.

______ 1979, Trace metal bioavailability: Modeling chemical and biological interactions of sediment-bound zinc, <u>in</u> Chemical modeling - speciation, sorption, solubility, and kinetics in aqueous systems, Jenne, E. A., ed.: American Chemical Society, p. 577-611.

______ 1981, A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants: The Science of the Total Environment, v. 17, p. 165-196.

______ 1982, A statistical study of environmental factors controlling concentrations of heavy metals in the burrowing bivalve, Scrobicularia plana, and the polychaete worm Nereis diversicolor: Estuarine, Coastal and Shelf Science, v. 15, p. 95-108.

Luoma, S. N., and Jenne, E. A., 1976, Factors affecting the availability of sediment-bound cadmium to the estuarine deposit-feeding clam, Macoma balthica, <u>in</u> Radioecology and energy resources: Proceedings of the Fourth National Symposium on Radioecology, Dowden, Hutchinson, and Ross, Inc., Stroudsburg, Pennsylvania, p. 283-291.

______ 1977, The availability of sediment-bound cobalt, silver and zinc to a deposit-feeding clam, <u>in</u> Biological implication of metals in the environment: CONF-750929, National Technical Information Service, Springfield, Virginia, p. 213-230.

May, T. W., and McKinney, G. L., 1981, Cadmium, lead, mercury, arsenic, and selenium concentrations in freshwater fish, 1976-77 National Pesticide Monitoring Program: Pesticides Monitoring Journal, v. 15, no. 1, p. 14-38.

Morel, F. M. M., Westall, J. C., O'Melia, C. R., and Morgan, J. J., 1975, Fate of trace metals in Los Angeles County wastewater discharge: Environmental Science and Technology, v. 9, no. 8, p. 756-761.

Oakley, S. M., Williamson, K. J., and Nelson, P. O., 1980, The geochemical partitioning of trace metals in marine sediments: Oregon State University, Water Resources Research Institute, WRRI-68, 83 p.

Peart, D. B., and Thomas, N. A., 1984, Quality assurance data for routine water analysis in laboratories of the U.S. Geological Survey for water-year 1983: U.S. Geological Survey Open-File Report 84-4234, Denver Colorado, 112 p.

Percy, K. L., Bella, D. A., Sutterlin, C., and Klingeman, P. C., 1974, Descriptions and information sources for Oregon estuaries: Oregon State University, Sea Grant College Program, 221 p.

Schwertmann, U., and Fischer, W. R., 1973, Natural "Amorphous" ferric hydroxide, Geoderma, v. 10, p. 237-247.

Shacklette, H. T., Boerngen, J. G., and Turner, R. L., 1971a, Mercury in the environment - surficial materials of the conterminous United States: U.S. Geological Survey circular 644, p. 1-5.

Shacklette, H. T., Hamilton, J. C., Boerngen, J. G., and Bowles, J. M., 1971b, Elemental composition of surficial materials in the conterminous United States: U.S. Geological Survey Professional Paper 574-D, p. D1-D71.

Sherbin, G., 1979, Mercury in the Canadian environment: Canadian Environmental Protection Service, Economic and Technical Review Report EPS 3-EC-79-6, 359 p.

Simkiss, K., 1983, Lipid solubility of heavy metals in saline solutions: Journal of the Marine Biological Association of the United Kingdom, v. 63, no. 1, p. 1-7.

Sittig, M., 1981, Handbook of toxic and hazardous chemicals: Noyes Publication, Park Ridge, New Jersey, 729 p.

Skougstad, M. W., Fishman, M. J., Friedman, L. D., Erdmann, D. E., and Duncan, S. S., eds., 1979, Methods for the determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chap. A1, 625 p.

Thomson, E. A., Luoma, S. N., Cain, C. J., and Johansson, C., 1980, The effect of sample storage on the extraction of Copper, zinc, iron, manganese, and organic material from oxidized estuarine sediments: Water, Air, and Soil Pollution, v. 14, p. 215-233.

U.S. Environmental Protection Agency, 1976, Quality criteria for water: Washington, D.C., EPA-440/9-76-023, 501 p.

Weshaw, R. L., Fishman, M. J. Grabbe, R. R., and Lowe, L. E., eds., 1983, Methods for the determination of organic substances in water and fluvial sediments: U.S. Geological Survey, Open-File Report 82-1004, 173 p.

Wood, J. M., 1983, Microbial resistance to heavy metals: Environmental Science and Technology, v. 17, no. 12, p. 582A-590A.

APPENDIX I

SAMPLE PROCESSING AND HYDROCHLORIC-ACID EXTRACTION PROCEDURE

Preparation for 1N Hydrochloric-Acid Extraction

All glassware and polyethylene materials were washed and rinsed with distilled-deionized water (ddw), soaked overnight in 50 percent HCl, rinsed three times with ddw, soaked again in 50 percent HCl for three hours, soaked in ddw for three hours, and rinsed six times with ddw.

Bottom material for extractable trace metals (cold 1N HCl) and total mercury (hot H_2SO_4 and HNO_3) analyses were transferred from the sampling cores to a tared polyethylene pan. Bottom materials were thoroughly mixed in the polyethylene pan until the sample appeared homogeneous; a representative subsample was removed for analyses of particle size and percent moisture. Another representative subsample was removed from the polyethylene pan and mixed, one part sediment with four parts native water, volume/volume (approximately 800 grams wet weight of bottom material with 2 liters of native mixing water). The bottom-material slurry was mixed for 30 minutes in a 4-liter glass beaker using a polyethylene stirring paddle attached to a mechanical mixer (rotational speed approximately 750 revolutions per minute). While the sample was mixing, the bottom-material slurry was aerated with a peristaltic pump attached to a silicon aeration tube immersed in the 4-liter glass beaker. The bottom material was continuously aerated for 1 hour after mixing, to ensure oxic conditions. During this time dissolved oxygen was monitored using a Yellow Springs Instrument Model 57 oxygen meter.

The contents of the 4-liter beaker were then wet sieved using filtered native water to avoid introducing any suspended sediment to the sample. Bottom materials for trace-metal extractions were sieved through a 100-micron polyethylene mesh sieve into a polyethylene pan. The sieved contents of the polyethylene pan were transferred to a specially treated 4-liter glass beaker and aeration was continued, (15 minutes per hour for 24 hours, under refrigeration at 4 °C). The sample was monitored for dissolved oxygen during the first 4 to 6 hours to ensure that aeration was adequate.

In the 25th hour, aeration was discontinued for 1 hour prior to removal of the supernate. A peristaltic pump attached to a glass J-tube was used to withdraw the supernate from the 4-liter glass beaker with a minimal amount of resuspension of bottom materials. The supernate was transferred to a 2-liter graduated cylinder, where dissolved oxygen was measured to ensure that the sample remained oxic during the 1-hour quiescent period. To determine the percentage of bottom material lost in the supernate, a suspended-sediment sample was removed by attaching a 100-ml pipet (with an enlarged orifice) to a peristaltic pump and placing the pipet parallel to a churn in the 2-liter graduated cylinder while withdrawing a sample. At the end of the 25th hour the median percentage of bottom materials lost in the supernate was 0.7 percent.

The 24-hour aeration period provided adequate time for settlement of suspended sediments. Sample aeration introduced negligible sediment resuspension, as verified by analyses of suspended sediments.

When the supernate was withdrawn from the 4-liter beaker, the remaining bottom-material slurry in the 4-liter beaker was mixed, using the polyethylene stirring paddle attached to the mechanical mixer. To evenly suspend the settled material during mixing, the 4-liter beaker was repeatedly rotated, 1 minute in a clockwise direction and 1 minute in a counterclockwise direction, prior to and during withdrawals from the bottom-material slurry. Withdrawals were made with an Eppendorf pipet (model 3130) capable of withdrawing accurate and precise 1-ml aliquots.

Preparation for Total Mercury Analysis

The total mercury extraction procedure is a standard method, described and referenced in the analytical methodology section. The following information describes the preparation of the total mercury sample for chemical analyses. The volume of sample withdrawn from the 4-liter beaker for total mercury analysis was dependent upon the concentration of bottom material in the slurry; approximately 5 grams dry weight of bottom material were required for the mercury analyses. A 1-ml withdrawal was made from the bottom-material slurry and dried at 105 °C as an approximation to the concentration of bottom material in the slurry. Once an approximate dry weight of sample was established, an appropriate number of Eppendorf pipet withdrawals was made into 100-ml evaporating dishes, providing approximately 5 grams dry weight of sample. The samples were air dried at room temperature and placed in polyethylene bags prior to chemical analyses.

Preparation for Organic Carbon and Volatile Solids Analyses

All stainless steel and glassware used for organic analyses were washed and rinsed with ddw, then rinsed with acetone, followed by three ddw rinsings. Bottom materials for analyses of organic carbon were sieved through a brass 100-micron mesh sieve into a stainless-steel pan. The contents of the stainless-steel pan were then transferred to a 400-ml beaker, thoroughly mixed using a magnetic stirrer, and representatively subsampled using an Eppendorf pipet. The subsamples were placed in a stainless-steel filtering unit, where bottom material between 0.45 microns and 100 microns were retained on a silver filter for analyses of organic carbon associated with bottom material finer than 100 microns.

Analyses of total volatile solids were made on an appropriate number of 1-ml withdrawals from the bottom-material slurry to yield approximately 1.2 grams dry weight; subsamples were dried at 105 °C overnight, cooled for 1.5 hours, and weighed. This procedure was repeated until a uniform sample weight was obtained. The dried samples were placed in a muffle furnace for six hours, ignited at 400 °C, cooled for 1.5 hours, and weighed. The loss of weight on ignition at this temperature represents the amount of volatile solids in bottom materials finer than 100 microns and is related to the concentration of organic carbon.

Hydrochloric Acid Extraction Procedure for Metals

The volume of 1N HCl used to extract trace metals from bottom material is dependent upon the mass of bottom material present. For every 0.2 grams (dry weight) of bottom material, 10 ml of 1N HCl were used for the extraction procedure. The first 1-ml withdrawal was analyzed to determine an approximate sediment concentration of the bottom-material slurry in the 4-liter beaker. Once an approximate sediment concentration was established, an appropriate number of Eppendorf pipet withdrawals were placed into an Erlenmeyer flask for chemical extraction. In this study, 2.5 grams dry weight provided adequate sample for the chemical extraction. One-milliliter withdrawals were made from the slurry and separately placed in 1-liter volumes of ddw prior to and after the withdrawal of the bottom-material slurry for chemical extraction. These mixtures were filtered through a tared Gooch crucible, washed with an additional liter of ddw, and dried at 105 °C to determine the salt-free dry weight of the bottom-material slurry.

Extraction procedures were replicated, producing three separate 1N-HCl extraction samples; two of the three were chemically analysed, providing duplicate analyses at each sampling site (the third provided an extra sample). The 1N HCl was added volumetrically to bottom materials in the Erlenmeyer flask; a rubber stopper covered with a polyethylene sheet was fitted on the Erlenmeyer flask and the sample was shaken 1 minute every 10 minutes for 2 hours. The sample was not shaken during the last 10-minute period to allow adequate settling prior to filtration. A 2-liter Erlenmeyer flask was tared to the nearest 0.1 gram, and the extract was filtered through a 0.45-micron (Millipore Swinnex-47) filtration unit into the tared volumetric flask. The volume of filtered extract was noted (assuming a density of 1 gram per milliliter), and the extract was diluted with 1.5 liters of ddw. The filtered extract was transferred to both polyethylene and Teflon bottles prior to shipping samples to the Central Laboratory.

Laboratory analyses of the 1N-HCl extractions are reported in µg/L and with the information provided, can be calculated to a concentration in µg/g. The following example illustrates this procedure:

Given

A. Volume of pipet withdrawals of slurry used for extraction = 18 ml.
B. Average salt-free sediment concentration in slurry = 0.1241 g/ml.
C. Weight of dried sediment in 18 ml of slurry, 18 ml x 0.1241 g/ml = 2.2356 gm.
D. Volume of dried sediment in 18 ml of slurry assuming sediment density of 2.65 gm/ml, (1 ml/2.65 gm) x 2.2356 gm = 0.8 ml.
E. Volume of water in 18 ml of slurry, 18 ml - 0.8 ml = 17.2 ml.
F. Volume of 1N HCl used in extraction = 127.5 ml.
G. Volume of filtrate = 136.6 ml.
H. Volume of ddw added to dilute the filtrate = 1,363.4 ml.
I. Dissolved cadmium concentration in diluted filtrate = 0.94 µg/L.

Determine the extractable cadmium concentration using the following equation:

$$\frac{(0.94\ \mu g/1000\ ml) \times (136.6\ ml + 1363.4\ ml)}{2.2356\ g \times (136.6\ ml/(17.2\ ml + 127.5\ ml))} = 0.67\ \mu g\ Cd/g \text{ of dry sediment}$$

APPENDIX II

QUALITY-ASSURANCE PROGRAM

An essential component of any data-collection and analysis program is a good quality-assurance program to determine the degree of confidence in a given data base. A quality assurance program should include (1) a sample blank (to determine if a sought-for consitituent is introduced during sample processing), (2) a blind sample (to determine the accuracy of the analytical methodology), and (3) a replicate sample (to determine the precision of the analytical methodology). For the present study, blind samples were assigned station identification numbers and submitted to the Geological Survey Central Laboratory in the same manner as other extractable trace-metal samples.

Detection limits, analytical concentration ranges, and analytical precision data in terms of relative standard deviation are shown in table 2; these data will aid in evaluating results of blind quality-assurance samples and sample blanks. Chemical analyses of distilled and deionized water used for making the 1N-HCl extraction acid, for diluting 1N-HCl extracts (table 3), and for diluting quality-assurance standards are shown in table 10. Detection limits for analyses in table 10 are different from detection limits in table 2, as a result of using different analytical method numbers for distilled deionized dilution water analyses A, B, and C. All analyses of distilled deionized dilution water used to prepare 1N-HCl acid were below analytical detection limits, as denoted by the less-than sign preceding the concentration in table 10. Distilled deionized dilution water sample B represents water removed from the same polycarbonate storage container as sample A, but not filtered. The concentrations in samples A and B are similar, with the exception of the zinc concentration, which is slightly higher in sample B, as opposed to the <3 μg/L in sample A; however, this slight zinc contribution to extracts from site numbers 1 through 5 will have negligible contribution to the concentration of extractable trace metals. Distilled deionized water sample C represents a refilling of the polycarbonate storage container with a second batch of dilution water; trace-metal concentrations in sample C are at or near detection limits.

Table 10.--Analyses of distilled deionized dilution water used for chemical extractions, dilution of quality-assurance standards, and trace-metal leaching

[Units are in micrograms per liter; DDDW = distilled deionized dilution water; DDW = distilled deionized water. All analyses made by U.S. Geological Survey, Water Resources Division Central Laboratory, Arvada, Colorado]

Chemical	DDDW-A[1]	DDDW-B[2]	DDDW-C[3]
Cadmium	<1	1	<1
Chromium	--	--	--
Copper	<10	<10	<10
Iron	<3	<3	4
Lead	<10	<10	<10
Mercury	--	--	--
Manganese	<1	<1	<1
Nickle	--	--	--
Zinc	<3	6	<3

[1] Analyses of distilled deionized water passed through a 0.45-micron millipore filter soaked in 50 percent HCl and rinsed with DDW; this DDW was used to dilute concentrated ultra-pure HCl to 1N HCl for chemical extractions.

[2] Analyses of distilled deionized dilution water (unfiltered) used for dilution of extracts from site number 1 through 5.

[3] Analyses of distilled deionized dilution water (unfiltered) used for dilution of extracts from site numbers 6 and 7, quality control samples A and B, and sample blank C.

Results of Environmental Protection Agency standard concentrations diluted with distilled deionized dilution water (C in table 10) are shown in table 11. Laboratory results and standard concentrates A and B are in close agreement (table 11) with the exception of zinc and iron. Zinc in standard concentrates A and B has a positive bias, somewhat more pronounced at the lower end in standard concentrate A. Concentrations of zinc in 1N-HCl extracts, prior to back calculating concentrations associated with bottom material, range from 82 to 175 μg/L; the increased positive bias at the lower concentration range may affect the precision of extractable zinc concentrations in table 3.

Table 11.--Chemical determinations of trace metals in two varying standard concentrates and in a sample blank

[Units are in micrograms per liter; SC = standard concentrates; DDDW = distilled deionized dilution water]

	SC-A[1]			SC-B			Sample blank - C[2]	
Chemical	SC	Lab results	Rerun	SC	Lab results	Rerun	Lab results	Rerun
Cadmium	2.5	2.6	--	70	67	--	<0.01	--
Chromium	10	20	--	250	250	--	<1	--
Copper	11	10	--	350	380	--	<1	--
Iron	20	50	60	900	900	--	30	--
Lead	24	22	--	380	400	--	2	--
Mercury	.75	0.7	--	8.0	7.0	--	<.1	--
Manganese	15	10	--	500	460	--	<10	--
Nickel	30	32	--	300	280	--	<1	--
Zinc	16	75	[3]	400	480	490	2.5	2.8

---

[1] Standard concentrates A and B were diluted with DDDW-C (see table 10).

[2] The sample blank was made with DDDW-C (see table 10) placed in a polyethelene cubitainer 2 days prior to processing; the sample blank was processed in the same manner as all extraction samples, including the addition of 129.5 ml of 1N HCl (made with DDDW-A) to 25 ml of DDDW-C.

[3] A rerun was requested; however, sample volume was insufficient for a rerun.

In a quality-assurance report published by the Geological Survey (Peart and Thomas, 1984) zinc is characterized as having a positive bias but no lack of precision. In 48 zinc determinations over an analytical concentration range of 28 to 489 µg/L, 6.2 percent of the values exceeded 2 units of standard deviation. All chemical extractions in this study were analyzed in duplicate, and extractable zinc concentrations exhibited no lack of precision; however, even if a positive zinc bias exists, extractable zinc data may still provide valuable information in describing relations with other extractable trace metals.

Concentrations of iron in table 11 appear to have a positive bias at the lower concentration ranges; accuracy was not improved by a rerun analysis. Iron analyses have a relative standard deviation of 31 percent where mean concentrations are 100 μg/L, as shown in table 2. Iron in sample concentrate B has acceptable accuracy and, in duplicate extractions, exhibited no lack of precision; in addition, concentrations of iron, prior to back-calculating concentrations associated with bottom material, range from 7,700 to 14,000 μg/L and are certainly out of the lower concentration range, where iron values may be affected by a positive bias.

A sample blank was run using distilled deionized dilution water, C in table 10. Water sample C was collected from a polycarbonate carboy (used to store all dilution water) and was placed in a 5-gallon polyethylene cubitainer, as were all native water samples collected in the field. After 2 days a subsample was withdrawn from the cubitainer and processed in the same manner as bottom material samples for 1N-HCl extractions, described in the methods section of this report. Lab results for sample blank C (table 11) are below detection limits, with the exceptions of iron, lead, and zinc; these trace metals in sample blank C are not of sufficient concentration to measurably contribute to the extractable trace-metal concentrations.

☆U S GOVERNMENT PRINTING OFFICE 1986-791-326/60008