The Vertical Distribution of Selected Trace Metals and Organic Compounds in Bottom Materials of the Proposed Lower Columbia River Export Channel, Oregon, 1984

By Gregory J. Fuhrer and Arthur J. Horowitz

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CONVERSION FACTORS, INCH-POUND TO METRIC

For readers who prefer to use metric (International System) units rather than the inch-pound terms used in this report, the following conversion factors may be used:

Multiply inch-pound units	By	To obtain SI units
	Length	
millimeter (mm)	25.4	inch (in.)
meter (m)	0.3048	foot (ft)
kilometer (km)	1.609	mile (mi)
	Area	
square kilometer (km^2)	2.590	square mile (mi^2)
	Volume	
cubic meter (m^3)	0.2832	cubic foot (ft^3)
cubic meter (m^3)	1233.	acre-foot (acre-ft)
	Flow	
cubic meter per second (m^3/s)	0.02832	cubic foot per second (ft^3/s)

SEA LEVEL: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929."

THE VERTICAL DISTRIBUTION OF SELECTED TRACE METALS AND ORGANIC COMPOUNDS IN BOTTOM MATERIALS OF THE PROPOSED LOWER COLUMBIA RIVER EXPORT CHANNEL, OREGON, 1984

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ABSTRACT

A proposal to deepen the lower Columbia River navigation channel prompted a study of the vertical distribution of selected trace metals and organic compounds in bottom materials, to evaluate the effects of dredging and disposal operations. Bottom-material core samples and native-mixing water samples were collected during September and October 1984. Bottom materials were cored to 6 meters, to coincide with proposed channel depths. Attempts to use lead-210 isotopic techniques to chronologically relate trace-metal concentrations to different core depths were severely hampered by a lack of fine grain-sized sediments. Instead, a deposition rate between 0.8 and 1.3 centimeters per year was estimated by using cesium-137 isotopic data. Elutriation testing of bottom material indicated chemical concentrations as large as 900 μg/L (micrograms per liter) for barium (from the midddle interval of the Skipanon River core), 6,500 μg/L for manganese (from the upper interval of the Cathlamet Bay core), and 14 μg/L for nickel (from the lower interval of the Skipanon River core). The amount of oxygen present during elutriation testing of reduced bottom material (middle interval of the Skipanon River core) was shown to have a negligible effect on manganese elutriate-test concentrations, but did affect barium and iron concentrations; barium concentrations were larger under reducing test conditions (900 μg/L) than under oxic test conditions (500 μg/L), and, conversely, iron concentrations were smaller under reducing test conditions (440 μg/L) than under oxic test conditions (800 μg/L).

Sediment-associated organochlorine compounds detected in Skipanon River (SR-S2)and Cathlamet Bay (CB-S6) core samples were as large as 0.1 μg/kg (micrograms per kilogram) for aldrin, 2.0 μg/kg for chlordane, 27 μg/kg for DDD (dichloro diphenyl dichloroethane), 5.0 μg/kg for DDE (dichloro diphenyl dichloroethylene), 0.2 μg/kg for DDT (dichloro diphenyl trichloroethane), 0.2 μg/kg for dieldrin, 37 μg/kg for PCB's (polychlorinated biphenyls), 0.1 μg/kg for PCN's (polychlorinated naphthalenes), and 0.1 μg/kg for heptachlor epoxide. Mathematical normalization of the data to grain size shows that organochlorine compounds are preferentially sorbed to fine-grained sediments rich in organic carbon. Small concentrations of phthalate esters (7 to 20 μg/kg) were detected in Skipanon River core samples and larger concentrations of polycyclic aromatics (8 to 278 μg/kg) were detected in Cathlamet Bay core samples.

Concentrations of cadmium, lead, and zinc in selected cores were found to exceed those of local basalt rocks. In the Columbia River core sample collected near Astoria, concentrations of cadmium as large as 3.6 μg/g were found in a portion of the core. In the Skipanon River core sample, concentrations of lead and zinc were as large as 26 μg/g and 210 μg/g, respectively, throughout the core.

In the Cathlamet Bay core sample, concentrations of cadmium, chromium, copper, iron, and zinc associated with the less-than-100-micrometer size fraction are larger than those associated with the greater-than-100-micrometer fraction. Within upper core depths of the same core, large concentrations of cadmium, mercury, and zinc correspond to a time when naval vessels were being maintained in the Cathlamet Bay area.

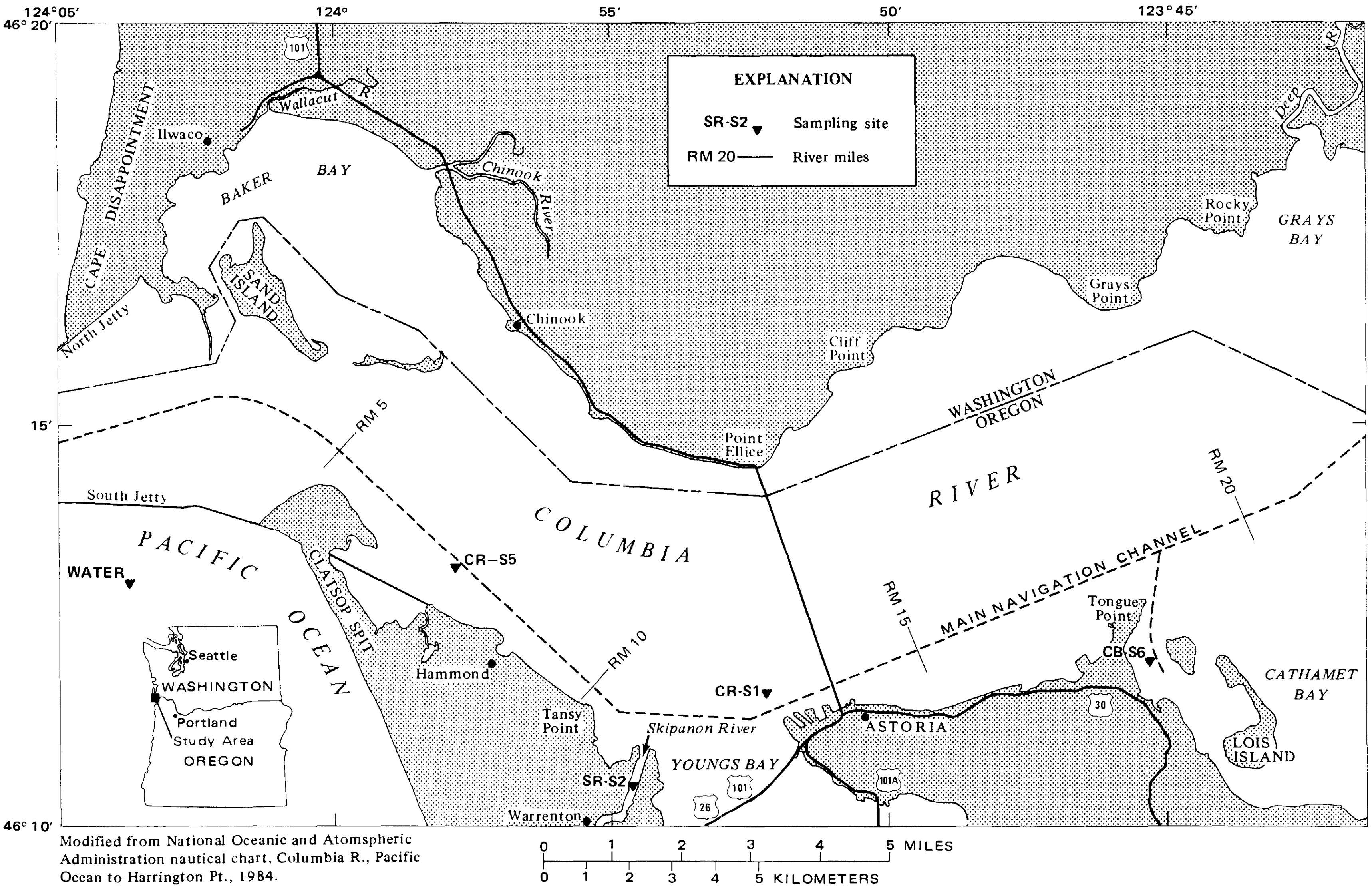
Results of differential extraction techniques indicate that much cadmium and lead is sorbed to particle surfaces in upper core intervals from Skipanon River, Cathlamet Bay, and the Columbia River near Hammond. Because cadmium is associated with large concentrations of total organic carbon, it is unlikely to adversely affect benthic organisms. Lead, however, may bioaccumulate in benthic organisms, although concentrations of lead in clam tissue from the study area are estimated to be slightly less than World Health Food Standards.

INTRODUCTION

Background and Statement of Problem

In response to a resolution by the U.S. Senate Committee on Public Works dated October 15, 1981, a study was begun to determine the feasibility of deepening the Lower Columbia River Deep Draft Navigation Channel from river mile (RM) 18, at Tongue Point, Oregon, to the mouth of the river (fig. 1). The resolution was passed in response to projected increases in exports, such as coal, that could improve the Pacific Northwest's regional economy if railways near large coal reserves in several western states were to be extended to link coal fields to the Columbia River estuary. Although at present there are no firm commitments for these activities, the Port of Astoria (fig. 1), located near RM 13, has been proposed for development of a large coal export facility, and construction operations in support of the oil and gas exploration industry have been proposed at Skipanon River near Columbia RM 11 (fig. 1). Also under consideration in Oregon is the development of a wood-products export facility in Cathlamet Bay near RM 18 (U.S. Army Corps of Engineers, Portland District, 1984). Export facilities would service vessels with drafts as great as 17 meters. Channels from RM minus 2 to RM 18 would require deepening to accommodate such vessels; present depths are 15 meters from RM minus 2 to RM 3 and 12 meters from RM 3 to RM 18. The proposed channel would increase present depths by 4.5 to 6 meters.

Prior Columbia River reconnaissance studies found that sediments in some areas of the proposed channel may, when mixed with native water, release dissolved Cd (cadmium), Cu (copper), Mn (manganese), and Ni (nickel) in concentrations exceeding U.S. Environmental Protection Agency (EPA) criteria for the protection of marine aquatic life (Fuhrer and Rinella, 1983; Fuhrer, 1984). Also identified in surficial bottom materials were organochlorine compounds, many of which are known to bioaccumulate (Fuhrer and Rinella, 1983; Fuhrer, 1984).



Modified from National Oceanic and Atomspheric Administration nautical chart, Columbia R., Pacific Ocean to Harrington Pt., 1984.

Figure 1.--Sampling-site locations.

Purpose and Scope

The proposed deepening of the Columbia River navigation channel poses questions concerning economic feasibility, technical feasibility, and environmental effects. This report focuses on environmental effects, specifically the chemical effect of dredging and disposal on estuarine water and bottom material. Trace metals and organic compounds in dredge-site bottom material can degrade ambient water quality as well as the chemical quality of disposal-site bottom material. Ultimately aquatic organisms are affected if trace metals or organic compounds from contaminated sediments or water are biologically accumulated. The objectives of this study are to

- assess the vertical distribution of chemical constituents in bottom-material core samples representing the proposed dredging depth,
- determine the potential contribution of dissolved chemicals from dredged sediments to native water,
- determine concentrations of trace metals in dredged sediments corresponding to grain sizes ingested by benthic organisms,
- assess the feasibility of making lead-210 determinations of bottom materials,
- determine the relations of trace metals with selected bottom-material phases, like particle size and total organic carbon (TOC),
- determine whether trace-metal concentrations are large relative to those in local soils and estimate if selected metals exist in biologically available forms.

On the basis of an earlier geophysical survey of the study area, four sites were selected for collection of bottom-material core samples. Native mixing water was collected from the vicinity of the proposed ocean disposal site.

Description of Study Area

The Columbia River estuary (fig. 1) has an area of 378 square kilometers, a drainage basin area of 671,000 square kilometers, and a mean annual freshwater input of 2.36×10^{11} m^3 [cubic meters] (Percy and others, 1974, p. 1). The estimated population of the drainage basin is greater than 3,000,000. The estuary has several industrial sites and receives municipal sewage discharge from the entire basin. From late fall to early spring, monthly-average river discharge fluctuates from about 2,830 m^3/s (cubic meters per second) to about 14,200 m^3/s and is affected primarily by runoff west of the Cascade mountain range. In late spring, discharge is influenced by snowmelt and averages about 12,700 m^3/s; from summer to early fall, discharge drops to 2,830 m^3/s, with little contribution from west of the Cascades. Since 1870, as a result of man's activities to stabilize the Columbia River navigation channel, 24 percent of the estuary surface area has been lost; 85 percent of this loss is attributed to dikes and 12 percent to accretion of sand at the mouth of the estuary (Fox and others, 1984, p. 1). Textural characteristics of sediment cores collected by Hubbell and Glenn (1973, p. 18) are considered marine from RM minus 2 to RM 8, transitional from RM 8 to RM 23, and fluvial above RM 23.

Acknowledgments

The authors would like to thank the U.S. Army Corps of Engineers, Tongue Point Field Headquarters, for providing a boat and crew for the timely transport of samples to the field laboratory.

APPROACH AND METHODS

Elutriate-test procedures are used to evaluate short-term chemical degradation caused by the disposal of dredge spoils of native water at disposal-sites. The elutriate test does not evaluate the long-term fate of chemicals associated with sediments. Elutriate tests simulate conditions that result in metal-dissolution when bottom material is dredged, transported, and deposited at in-water disposal sites. In this study, chemical analyses of elutriate test filtrates (ETF) for selected trace metals and organic compounds were used to identify those dredge-site locations and, where possible, those sediment-column depth intervals, in which chemicals in bottom material could impact disposal-site waters. Subsequently, the ETF concentrations were evaluated against EPA water-quality criteria (U.S. Environmental Protection Agency, 1976 and 1980). The standard elutriate test involves the mechanical stirring of one part bottom material from the proposed dredge-site into four parts native water from the disposal-site (volume/volume) for 30 minutes, followed by a 1-hour quiescent period and 0.45-micron filtration (Plumb, 1981). Oxic elutriate tests are identically mixed, but are oxygenated by passing air through the elutriate-test mixture.

Chemical concentrations in native water also were determined. These concentrations, subtracted from the concentrations in the ETF, permit determination of sediment-associated metal contributions, henceforth termed "release" or "ETF release." Chemical releases vary among metals during elutriate testing and are dependent on such physiochemical conditions as pH, Eh, dissolved-oxygen levels, and solid-to-liquid ratio that are maintained during the test and on how these conditions affect the partitioning of the metals between the solid and solution phases.

The standard elutriate test does not reflect field conditions in instances when DO (dissolved oxygen) is depleted during elutriate testing. The effect of DO on metal release was estimated by subjecting Skipanon River bottom material to both a standard elutriate test and an aerated test (oxic elutriate test). Measurable DO was maintained throughout the oxic test and DO was monitored during the elutriate test prior to filtration. For a detailed explanation of processing elutriate samples, see Fuhrer (1984).

The potential for chemical degradation of disposal site bottom material was assessed by analysis of dredge-site bottom material for selected trace metals and for organic compounds included in the EPA organic-priority pollutant list (Chapman and others, 1982). Metal concentrations were compared to those of Columbia River basalts to determine if dredge-site bottom material is metal-enriched. Lead-210 (^{210}Pb), radium-226 (^{226}Ra), and cesium-137 (^{137}Cs) determinations were made to equate metal-enriched sediments with core depth, although these efforts were limited by a lack of fine-grained size sediments. Radon-222 (^{222}Rn) diffuses into the atmosphere from soil containing ^{226}Ra.

Radium-226 rapidly decays to Pb^{210}, which falls to earth and is preferentially adsorbed to fine-grained sediments (Martin and Rice, 1981, p. 2). Lead-210 is assumed to be in constant flux and to be immobilized once adsorbed to sediment. The ^{210}Pb in excess of the amount in equilibrium with ^{226}Ra (excess ^{210}Pb) is used to date the deposited layers.

As a result of a dredging and disposal operation, dredge-site sediment may reform an oxic sediment/water interface at an in-water disposal site. Organisms living in the contact zone between sediment and water are exposed directly to metals in the oxic sediment/water interface (Sam Luoma, U.S. Geological Survey, written commun., 1982); for this reason trace-metal determinations were made on oxidized bottom materials from the dredge site. The <100-μm (less-than 100-micrometer) size fraction was selected for metal determinations because of the likelihood of its ingestion by deposit-feeding organisms and their subsequent trace-metal exposure. Metal determinations were made in two ways on sediment intervals of core samples corresponding to those used for elutriate testing. The first determination, a weak extraction, involves the mixing of dredge-site sediment with disposal-site water under oxic elutriate-test conditions. Instead of the filtration step used in the elutriate test, the sediment/water mixture (slurry) is concentrated by removing the supernatant. The concentrated slurry is subsampled and extracted with cold 1-normal hydrochloric acid (1N-HCl). Metal concentrations are reported on a dry weight, salt-free basis, in micrograms metal per gram sediment (μg/g). For a detailed description of the 1N-HCl extraction procedure, see Fuhrer (1986).

The second determination, a harsh extraction, involves treating the <100-μm size fraction with concentrated $HF/HClO_4/HNO_3$ (hydrofluoric acid/perchloric acid/nitric acid) and heat, which completely destabilizes the sediment matrix, and is referred to in this report as total-metal extraction. By comparing the results from both extractions, it is possible to identify sediment intervals of the core where significant portions of the metals are environmentally "available." Where this availability occurs, the relations between extractable metal and Fe (iron), TOC, and clay content were examined and compared to those relations developed by others for estimating potential metal "bioavailability" to benthic fauna (Luoma and Bryan, 1978; Luoma and Jenne, 1976,). Relations between total Hg (mercury) and TVS (total volatile solids) are compared to those developed by Langston (1982) for estimating Hg bioavailability.

Kendall's tau correlation coefficients were computed to examine relations of grain size and organic carbon with 1N-HCl extractable metals. Data need not be normalized for Kendall's tau, since computations are based on ranks (Conover, 1980, p. 256). Where data are likely to be normally distributed, Pearson correlation coefficients (r) are computed. Levels of significance for both types of correlation coefficients are less than or equal to 0.05 (ρ <0.05) unless otherwise indicated. Though both techniques compute coefficients between minus 1 and plus 1, coefficients from different techniques cannot be compared to one another. Further, Kendall's tau cannot be mathematically squared like an "r" to determine the amount of variation explained by the independent variable.

Sampling Site Selection

A marine geophysical survey was conducted in August 1983 by Northern Technical Services of Kirkland, Washington, for the U.S. Army Corps of Engineers (COE). Geologic information was obtained by "seismic reflection subbottom profiling" (Robert Chesney, U.S. Army Corps of Engineers, written commun., August 1983). This information was used to determine river-bottom characteristics that could affect the operation of a dredge. Results of the geophysical survey indicate that potential dredge material consists of clays, muds, silts, and of fine, medium, and coarse sands. Chart recordings in nineteen areas had subsurface high amplitude reflections (HAR) indicating the presence of semiconsolidated sands or indurated marine clays. The 19 HAR areas would require further investigation by subsurface sampling (vibra-coring) to determine the feasibility of dredging these subbottom materials (Robert Flanagan, U.S. Army Corps of Engineers, written commun., July 1983). Four of these HAR areas were selected for chemical testing; selection was based on earlier reconnaissance studies in which large surficial concentrations of trace-metals or organic compounds were determined (Fuhrer and Rinella, 1983; Fuhrer, 1984). Two areas were located in the main navigation channel near Hammond and Astoria, one in the Skipanon River near Warrenton, and one in Cathlamet Bay near Tongue Point (fig. 1 and table 1). Native mixing water was collected near the proposed ocean disposal sites near the south entrance jetty of the Columbia River.

Table 1.--Location of sampling sites

Site number	Site designation	Collection date	Site location		Remarks
			Latitude	Longitude	
CB-S6a	Cathlamet Bay	09-27-84	46°11'13"	123°54'20"	Vibra-core sample
CR-S1	Columbia River	09-26-84	46°09'36"	123°51'20"	Vibra-core sample
CR-S5	Columbia River	10-01-84	46°13'19"	123°57'40"	Vibra-core sample
SR-S2	Skipanon River	09-25-84	46°10'53"	123°54'09"	Vibra-core sample
Water	Pacific Ocean	09-24-84	46°13'00"	124°03'40"	Water sample

Sampling Procedures

Bottom-material samples were obtained from the above sites by vibra-coring. Vibra-coring involves the pneumatic placement of a 20-foot transparent butyrate-acetate core liner, 2-5/8 inches in diameter, into the proposed channel sediments. The resulting core was cut into 5-foot lengths, sealed, and transported vertically and under refrigeration to the field lab. Native mixing water samples were collected 5 feet below water surface using a 4-liter Van Dorn bottle, placed in 5-gallon glass carboys, and then refrigerated and transported to the field lab. Prior to the sampling, core liners and carboys were washed with Liqui-nox, acid-rinsed with 6.5-percent hydrochloric acid, and rinsed numerous times with distilled-deionized water.

At the field lab, Eh measurements (Wood, 1976, p. 18) were made every 12 inches along the core by placing an Eh probe through a drilled opening in the core liner. The cores then were longitudinally cut into halves by scoring the exterior with a router and by drawing a stainless steel blade along the core. Once sectioned, the cores were visually inspected, and variations in color, grain size, and moisture were noted. Core contents were subsampled, either longitudinally over two or three depth intervals or by the removal of several discrete intervals, depending upon the type of chemical test to be conducted.

Analytical Methods

Determinations of selected trace metals from 1N-HCl (1-normal hydrochloric acid) extracts and elutriate tests were made by the U.S. Geological Survey Central Laboratory in Arvada, Colorado. The 1N-HCl extracts were diluted with distilled-deionized water and analyzed, using methods described by Fishman and Friedman (1985). Determinations of TOC, organochlorine compounds, and acid and base/neutral organic compounds were made at the Central Laboratory, using methods described by Wershaw and others (1983). Gamma analyses of ^{210}Pb and ^{137}Cs were made at the Central Laboratory, using methods described by Thatcher and others (1977). Total Hg determinations of bottom material were made by the Geological Survey Mineral Resources Laboratory in Lakewood, Colorado, using a flameless atomic absorption spectrometer. The total Hg analysis is a complete extraction procedure using concentrated HNO_3 and HCl acids, with recoveries ranging from 90 to 105 percent (Huffman and others, 1972). Total metal analyses of sediment samples were made at the Geological Survey Research Laboratory in Doraville, Georgia; these analyses were carried out by digesting the samples with a combination of $HF/HClO_4/HNO_3$ acids in Teflon beakers at 200 °C, with quantitation by flame atomic absorption spectroscopy (Horowitz and Elrick, 1985).

Analyses for total volatile solids and particle-size were made at the Geological Survey Oregon Office Laboratory in Portland, Oregon. Total volatile solids were determined by igniting bottom material at 400 °C (Fuhrer, 1986, p. 56). 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 μm in diameter and (2) a pipet method for bottom material <53 μm in diameter (Guy, 1969). Both methods determine particle size in terms of fall diameter in quiescent distilled water (Stokes Law).

DISTRIBUTION OF TRACE METALS AND ORGANIC COMPOUNDS

Lead-210 Dating of Cathlamet Bay Bottom Material

Attempts to estimate sedimentation rates in Cathlamet Bay, using both ^{210}Pb and ^{137}Cs, were severely hampered by a lack of sufficient fine-grained sediment (60 grams of dry <100-μm sediment is needed per determination). This deficiency necessitated compositing from fairly large depth intervals of the core. Of the five preliminary samples submitted for analysis (intervals 2-20, 92-98, 176-182, 251-257, and 432-442 centimeters), only the 2- to 20-cm (centimeter) interval contained excess ^{210}Pb (table 2) after comparison with the values for ^{226}Ra. Below 74 cm, ^{210}Pb concentrations were at or near background. In addition, ^{137}Cs was detected only in the 2- to 20-cm interval. After this preliminary analysis, further investigations were confined to the upper 92 cm of the core. This additional work indicated that excess ^{210}Pb, as well as the presence of ^{137}Cs, was confined to the upper 50 cm of the core.

Table 2.--Lead-210 and radon-226 activities in Cathlamet Bay bottom material

[cm = centimeters; dpm/g = disintegrations per minute per gram. Total lead-210 and radon-226 standard deviations are ±0.2 and ±0.04 dpm/g respectively]

Interval number	Depth interval (cm)	Normalized[1] average depth (cm)	Lead-210 (dpm/g)	Radon-226 (dpm/g)	Excess lead-210 (dpm/g)
1	2-20	12.2	2.62	2.15	0.47
2	20-50	41.2	4.34	3.55	.79
3	50-56	62.3	2.15	2.15	0
4	56-62	66.9	2.13	1.98	.15
5	62-68	69	2.26	2.04	.22
6	68-74	73.7	2.62	3.29	0
7	80-92	85.2	2.40	2.62	0
8	92-98	91.6	1.82	2.22	0
9	176-182	175.5	1.98	1.82	.16
10	251-257	249.9	1.95	1.89	.07
11	432-442	434.2	1.95	2.00	0

[1] Depths are normalized to an average percent moisture of 30.8 percent.

Excess ^{210}Pb activity compared to depth is plotted in figure 2 in addition to depth intervals where ^{137}Cs was detected. Depths were normalized to the average percent moisture (30.8 percent) for the entire core. Normalizing prevents variations in amounts of interstitial water from masking the amount of sediment deposited each year. Sediment deposition rates are normally calculated using a least-squares technique through intervals of constant slope on the curve of excess ^{210}Pb compared to depth (Martin and Rice, 1981). However, too few data points are available to make such a calculation meaningful.

In some instances, the first occurrence of ^{137}Cs can be used to estimate sedimentation rates (Jerry Glenn, U.S. Geological Survey, written commun., 1985). In the present study, the first occurrence of this isotope is in the 2- to 20-cm interval, but it was also found in the 20- to 50-cm interval (fig. 2). Since ^{137}Cs has a 1-year residence time between its introduction to the atmosphere and incorporation in bottom materials (Yang and Ambats, 1982) and since its first introduction to the atmosphere could not have occurred before 1952, the earliest date that can be assigned to the 0- to 50-cm interval is 1953.

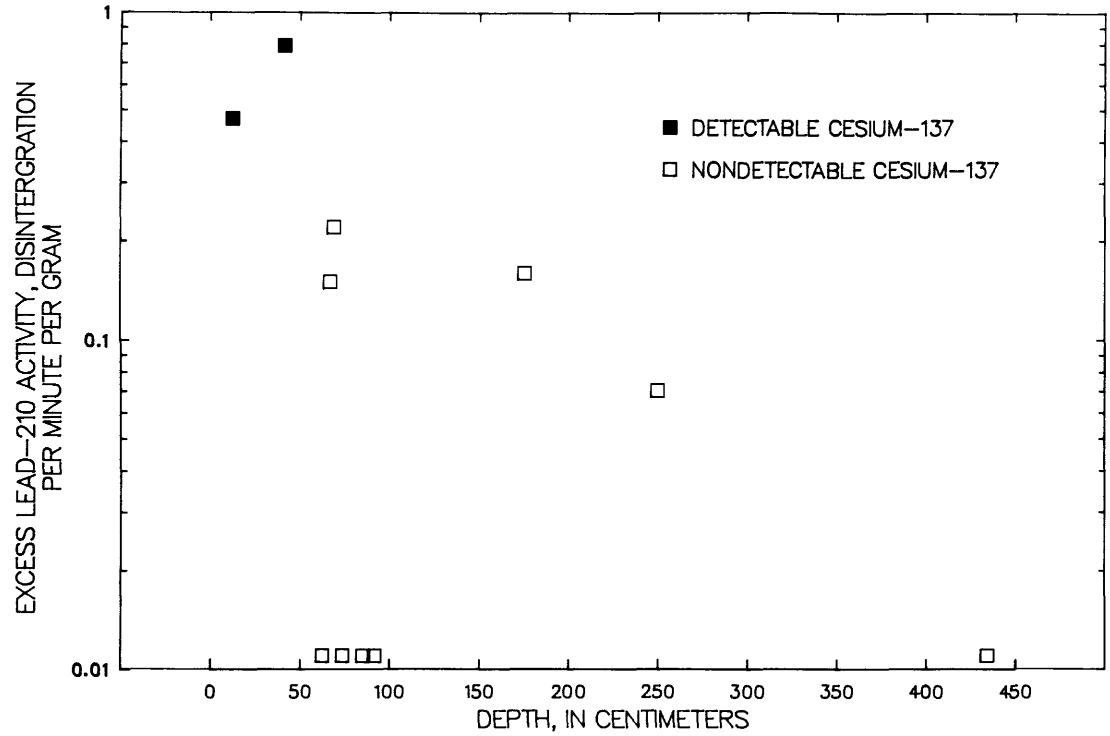


Figure 2.--Excess lead-210 activity and occurrences of cesium-137 compared to depth in Cathlamet Bay bottom material (lead-210 activities below limits of detection are reported as 0.01).

If the midpoint (25 cm) of this interval is used and constant sedimentation rates are assumed, deposition at this station in Cathlamet Bay has not exceeded 0.8 cm/yr (centimeters per year) since 1953. If the ^{137}Cs was incorporated after 1962, when atmospheric testing was at maximum (Yang and Ambats, 1982), then deposition in the Bay has probably not exceeded 1.3 cm/yr. These sedimentation rates are less than the net deposition rate computed by Hubbell and Glenn (1973, p. 47) at a site located 2 miles east of Cathlamet Bay Site 6b (CB-S6b). Using relative rates of decay of zinc-65 (^{65}Zn) and cobalt-60 (^{60}Co), the authors determined a net deposition rate of 8.2 cm/yr for a core containing comparatively fine bottom material from an area where continuous deposition probably has been occurring. Too few data presently exist to determine if differences between sedimentation in the present study and in the study by Hubbell and Glenn (1973) are attributable to spatial variations or to use of different radiometric techniques.

Chemical Analyses of Standard Elutriate-test Filtrate

During the standard test the mixture is not oxygenated, and by test completion some mixtures contain DO, whereas others do not (table 3). Standard tests were made on upper and lower intervals of four cores; in one of these--the core for Skipanon River Site 2 (SR-S2)--three intervals were tested (table 3). Of the metals examined in the four cores, ETF releases of As (arsenic), Be (beryllium), Cd (cadmium), Cr (chromium), Cu (copper), Pb (lead), and Hg (mercury) were small (table 3) relative to concentrations observed in earlier reconnaissance studies (Fuhrer and Rinella, 1983; Fuhrer, 1984). The disposal of dredge spoils would not appear to affect the local concentrations of these metals.

Table 3.--Chemical analyses of elutriate-test filtrate and native mixing water

[Concentrations are in micrograms per liter except where otherwise noted; mg/L = milligrams per liter; pct = percent; min = minute]

Site name	Site no.	Depth interval (meters)	Arsenic	Barium	Beryllium	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Zinc	Ammonia as nitrogen (mg/L)	Ammonia plus organic nitrogen (mg/L)	Moisture (pct)	Dissolved organic carbon (mg/L)	Dissolved oxygen		
																			1-min (mg/L)	30-min (mg/L)	60-min (mg/L)
Cathlamet Bay	6a	0-0.9	1	100	<10	0.1	<1	<1	150	1	6500	<0.1	9	3.0			23	5	11.1	10	9.4
Cathlamet Bay	6a	0.9-3.7	1	<100	20	<.1	4	<1	200	2	510	.2	2	1	50	48	28	5	8.4	2	1.4
Columbia River	1	0-.9	2	600	<10	.1	<1	1	160	2	80	.1	4	<0.5	66	66	35	24	8.6	5.9	0.6
Columbia River	1	1.9-6.1	1	400	20	<.1	<1	<1	170	2	70	.3	2	.5	39	38	27	9	9.6	6.3	6.3
Columbia River	5	0.08-1	<1	<100	20	<.1	<1	<1	170	<1	1000	<.1	6	.5	3.0	3.2	21	0.6	9.5	6.1	3.6
Columbia River	5	1.8-3.8	<1	<100	20	<.1	6	<1	130	2	430	.1	4	<.5	3.6	3.8	18	.7	8.9	7.9	7.2
Skipanon River	2	0-0.9	2	500	10	.1	<1	1	1300	<1	1700	.4	5	8.0	33	36	53	13	0.6	<0.1	<0.1
Skipenon River	2	0.9-4.1	2	900	<10	<.1	8	<1	440	3	330	.2	4	4.4	59	58	47	30	2.7	<.1	<0.1
Skipanon River[1/]	2	0.9-4.1	1	500	10	<.1	<1	3	800	3	220	.2	4	4.0	56	56	47	30	6.5	0.5	4.4
Skipanon River	2	4.1-5.7	<1	<100	<10	.5	2	<1	130	<1	240	.2	14	<.5	2.2	3.1	17	8	10.8	11.0	11.2
Pacific Ocean Water[2/]			<1	<100	<10	1	<1	1	150	4	30	.2	4	3.6	0.005	0.2		2			

[1/] Oxic elutriate test; air is passed through the sediment-water mixture during the 30-minute mixing and 1-hour quiescent period.

[2/] Native mixing water used in elutriate tests and the wet sieving of bottom material for chemical extractions.

However, releases of Ba (barium) and Mn (manganese) were large. Barium releases were as large as 900 μg/L (see middle interval of core SR-S2). Manganese releases were as large as 6,500 μg/L (see upper interval of core from CB-S6a (Cathlamet Bay Site 6a) in table 3), and Ni releases were as large as 14 μg/L (see lower interval of core SR-S2). Although quantities of Mn were released by all the sediment samples regardless of depth in the sediment column, contributions were greatest from the upper levels, specifically depths of 1 m (meter) or less. The concentrations of Mn in the ETF exceed the EPA criteria of 50 μg/L for domestic water supplies (table 3).

The large releases of Mn, particularly from CB-S6a, appear anomalous. In aquatic systems under oxidizing conditions, as existed for the upper interval of CB-S6a (table 3), sediment-associated Mn normally occurs as an oxide; this form would not be expected to solubilize during elutriate testing unless reducing conditions occurred during some period of the test. Dissolved oxygen measurements during the test indicated a well oxygenated elutriate mixture (table 3) in which reducing conditions did not occur. The large Mn releases may be due to ion exchange between the sediment and native water or to passage of colloidal Mn through the 0.45-μm filter. Ion exchange (essentially desorption) could occur if there was a difference in the conductivity of the interstitial water in the sediment column when compared with that of the native water. This process is similar to the ion exchange that occurs when lower conductance river water mixes with higher conductance estuarine water (Van Der Weijden and others, 1977). Because colloidal Mn does not normally form in native ocean water, another source or sources of colloidal Mn must be sought (John Hem, U.S. Geological Survey, oral commun., 1986). Two possible sources are ship maintenance and the artifacts of elutriate testing. During the 1940's and 50's the armor plate of ships was sandblasted at the Tongue Point Naval Facility in Cathlamet Bay. The slag used for sand-blasting and the armor plate are both potential sources of finely divided Mn. Another potential source is the elutriate test itself. Some of the Mn present as surface coatings could have been physically separated from sediment surfaces due to the mechanical mixing required during the elutriate test. Confirmation of the presence of colloidal Mn would require additional testing, which would entail an additional filtration step through a 0.10-μm filter after initial filtration through a 0.45-μm filter. Future elutriate tests should include this step.

Barium and and Ni (nickel) were also released during the elutriate tests. Although no EPA aquatic life criteria exist for Ba, ETF concentrations are well below the 50-mg/L concentration considered toxic to marine aquatic life (Thurston and others, 1979, p. 35). If sulfate concentrations present during the test were similar to average concentrations (10.8 mg/L) at RM 38.9 (Frank Rinella, U.S. Geological Survey, written commun., 1985), Ba releases at Columbia River Site 1 (CR-S1) and SR-S2 (middle and upper intervals) are larger than the 120 μg/L attributable to the dissolution of the mineral barite ($BaSO_4$). In this case, releases could also occur from two sources: barite dissolution and Ba desorption from clay-size particles. For Ni, ETF concentrations from both the 0- to 0.9-m interval of CB-S6a (9 μg/L) and the 4.1- to 5.7-m interval of SR-S2 (14 μg/L) exceed the EPA criteria for marine life of 7.1 μg/L (tables 3 and 4). None of the other sediment samples tested exceeded the EPA criteria, and there did not appear to be substantial release differences between the upper and lower portions of the sediment column. Native water contains only 4 μg/L Ni.

Therefore, if Ni releases are limited to no more than those found during the elutriate tests, the disposal of dredge spoils will not raise Ni concentrations above the EPA criteria.

Chemical Analysis of Oxic Elutriate-test Filtrate

Jones and Lee (1978) report that ETF metal concentrations may be dependent on DO levels maintained during elutriate tests. This dependency on DO has led to the development of the oxic elutriate test, in which the system is constantly aerated (Jones and Lee, 1978). The differences in metal releases determined by the two tests need to be investigated to evaluate potential environmental impacts. These differences are especially important because some of the sediments in the study area appear to be reducing, and proposed disposal sites are well oxygenated. Under these circumstances, DO would be consumed in a standard test, while during an actual disposal, the reduced dredge-spoil mixture would rapidly become oxygenated; thus the standard test would inadequately simulate field conditions. Evaluation of the tests required a sediment sample from a reduced environment; the middle interval of core SR-S2 (0.9- to 4.1-m) was found suitable for this comparison. Eh values were sufficiently small (fig. 3) to indicate reducing conditions; reducing conditions were further substantiated when all measurable DO in the native mixing water was consumed during the standard test (table 3). It should be borne in mind that because the reproducibility of standard elutriate tests can be poor (Jones and Lee, 1978), only substantial differences between the two tests need to be addressed.

Because the standard ETF Mn concentrations (reducing conditions) increased only slightly over the oxic test concentration (table 3), sediments were likely reducing prior to coring and subsequent testing. Any Mn oxides present at the time of initial deposition would have dissolved and migrated upward through the sediment column through diffusion processes (Forstner and Wittman, 1979, p. 80). Therefore, little Mn oxide would be present in the sediment, and redox conditions of the elutriate test would have little or no effect on ETF Mn concentrations.

Reducing conditions prevalent during the standard test coincided with larger Ba and Cr ETF concentrations than were found in the oxic test. Ba concentrations for standard and oxic tests were 900 and 500 μg/L respectively; Cr concentrations were small, 8 and <1 μg/L respectively. In most sediments Cr is found either in substitution sites in mineral lattices or as chromite, and, in either case, desorption is unlikely (Burton and Liss, 1976, p. 41; Forstner and Wittmann, 1979). The Ba results are likely problematic, both because of the relatively large concentrations found and because of the substantial differences between the two tests. Barium usually occurs in sediments in association with Mn oxide coatings or as barite ($BaSO_4$), which is highly insoluble. If, as suspected, the concentration of Mn oxide is small in SR-S2 (reducing conditions), Ba previously associated with the oxide would now likely occur in interstitial water.

Table 4.--Selected U.S. Environmental Protection Agency guidelines for various water uses, including freshwater and marine aquatic life

[Guidelines are based on total concentrations (dissolved and suspended chemical forms); welfare = to control for undesirable taste and odor quality; LC50 = concentraction lethal to 50 percent of the test organisms. ND = not determined; µg/L = microgram per liter; hr = hour]

Constituent	Maximum concentration (µg/L)	Water use (U.S. Environmental Protection Agency, 1976)	Maximum concentration (µg/L)	Aquatic life (U.S. Environmental Protection Agency, 1980)
Arsenic	50	Domestic water supply (health)	440	Freshwater aquatic life
	100	Irrigation of crops	508	Marine aquatic life
Barium	1,000	Domestic water supply (health)		
Beryllium	11	Aquatic life in soft fresh water (0-75 mg/L $CaCO_3$)	130 5.3	Freshwater, acute Freshwater, chronic
	1,100	Aqautic life in hard fresh water (150-300 mg/L $CaCO_3$)		
	100	Continuous irrigation		
	500	Irrigation on neutral to alkaline fine textured soils		
Cadmium	10	Domestic water supply (health)	0.012	Freshwater 24-hr average at 50 mg/L $CaCO_3$, not to exceed 1.5 µg/L at any time
	0.4	Soft fresh--cladocerans, salmonid fishes		
	4.0	--less sensitive organisms	4.5	Marine 24-hr average, not to exceed 59 µg/L at any time
	1.2	Hard fresh--cladocerans, salmonid fishes		
	12.0	--less sensitive organisms		
Chromium	50	Domestic water supply (health)	0.29	Freshwater 24-hr average, not to exceed 21 µg/L at any time (hexavalent)
	100	Freshwater aquatic life		
			2,200	Freshwater at 50 mg/L $CaCO_3$
			18	Marine 24-hr avg, not to exceed 1,260 µg/L at any time (hexavalent)
			10,300	Marine, acute (trivalent)
Copper	1,000	Domestic water supply (welfare)	5.6	Freshwater 24-hr average, not to exceed 12 µg/L at 50 mg/L $CaCO_3$
	0.1 times 96 hr LC50	Aquatic resident species	4.0	Marine 24-hr average, not to exceed 23 µg/L at any time

Table 4.--Selected U.S. Environmental Protection Agency guidelines for various water uses including freshwater and marine aquatic life--Continued

Constituent	Maximum concentration (µg/L)	Water use (U.S. Environmental Protection Agency, 1976)	Maximum concentration (µg/L)	Aquatic life (U.S. Environmental Protection Agency, 1980)
Iron	300	Domestic water supply (welfare)		
	1,000	Freshwater aquatic life		
Lead	50	Domestic water supply (health)	0.75	Freshwater 24-hr avg, not to exceed 74 at 50 mg/L $CaCO_3$
	0.01 times 96 hr LC50	Freshwater resident		
			668	Marine, acute
			25	Marine, chronic
Manganese	50	Domestic water supply (welfare)		
	100	Consumers of marine mollusks		
Mercury	2	Domestic water supply (health)	.00057	Freshwater 24-hr average, not to exceed 0.0017
			0.025	Marine 24-hr average, not to exceed 3.7 µg/L at any time
Nickel	0.01 times 96hr LC50	Freshwater and marine aquatic life	56	Freshwater 24-hr average at 50 mg/L $CaCO_3$, not to exceed 1,100 µg/L
			7.1	Marine 24-hr average at 50 mg/L $CaCO_3$, not to exceed 140 µg/L
Zinc	5,000	Domestic water supply (welfare)	47	Freshwater 24-hr average at 50 mg/L $CaCO_3$, not to exceed 180 µg/L at any time
	0.01 times 96 hr LC50	Sensitive resident species		
	1	Chinook salmon (1 month old)	58	Marine 24-hr average, not to exceed 170 µg/L at any time
pH	5-9	Domestic		
	5-9.0	Freshwater aquatic		
	5-8.5	Marine aquatic life (not more than 0.2 units outside normally occurring range)		

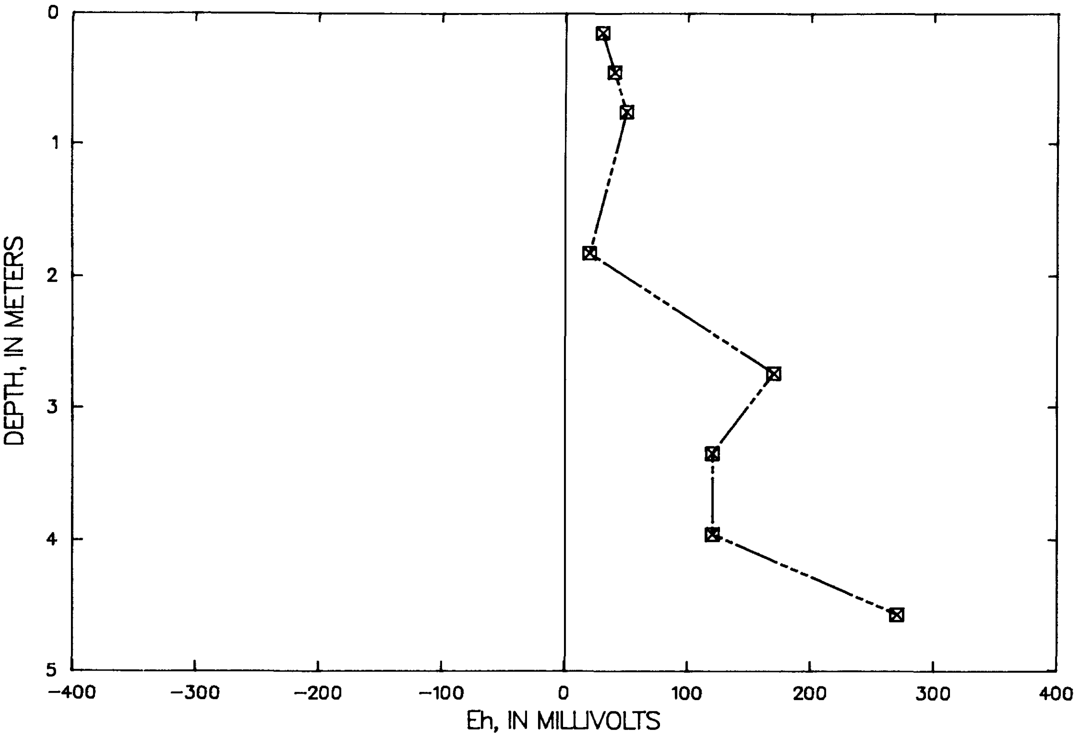


Figure 3.--Measurements of Eh compared to depth in bottom material from Skipanon River, Site 2, near Columbia River mile 1.3.

During the standard test (reducing conditions), Ba would likely remain in interstitial water and contribute to the larger standard-test release of Ba. The smaller oxic-test release of Ba could occur if the Ba in interstitial water were precipitated as $BaSO_4$, under the oxidizing conditions of the oxic test. This precipitation would certainly not be expected to remove all the Ba from solution, as sulfate concentrations in Columbia River water are limiting. It is unlikely that Ba was removed during the oxic test by reincorporation with Mn oxides because there was little difference between ETF Mn concentrations for the standard and oxic tests (see table 3, and discussion above).

Concentrations of iron (Fe) in ETF standard and oxic tests were 440 and 800 μg/L respectively (table 3). If, as suspected, the sediments were reducing, the Fe was likely to be in the form of sulfides, and the observed differences in ETF Fe concentrations may be explained on the basis of Fe sulfide dissolution. The initial DO concentration in the native water in the standard test was sufficient to release 440 μg/L Fe through the dissolution of some of these sulfides. Once the initial oxygen was exhausted, no further dissolution occurred. During the oxic test, where a constant supply of DO was maintained, Fe sulfides continued to dissolve and released more Fe, hence the higher ETF Fe concentrations from the oxic test. If the time between elutriate test mixing and settling were increased, ferric ion (Fe^{3+}) from the dissolution of Fe sulfides would react with hydroxide ions and begin precipitating as ferric hydroxide ($Fe(OH)_3$). Iron contained in this hydroxide, though in solid form, would be considered as ETF Fe (dissolved) because of the ability of $Fe(OH)_3$ colloids to pass through a 0.45-μm filter (Forstner and Wittman, 1979, p. 82 and p. 215). Accurate ETF Fe determinations for extended settling times would require 0.1-μm filtration of the test mixture.

As can be seen from the comparisons of oxic and standard elutriate tests, substantial differences in metal releases can occur depending upon the redox conditions. Thus oxic tests may provide more realistic indications of potential metal releases from dredge spoils when reduced sediments are placed in oxygenated disposal-site waters (for example, if the sediments from the mid-level of core SR-S2 were placed in an oxygenated open water disposal site). However, if the sediments were placed in an adjacent upland site, where the mixture would be poorly oxygenated, potential metal releases are more likely to follow the results of the standard elutriate test.

Organic Compounds in Bottom Material at Various Depth Intervals

Organochlorine Compounds

Organochlorine compounds [pesticides, polychlorinated naphthalenes (PCN's), and polychlorinated biphenyls (PCB's)] can be divided into two groups: hydrophobes (compounds with no affinity for water), which are concentrated in sediments and biota, and quasi-hydrophobes, which also have a hydrophilic character--having an affinity for water (Chapman and others, 1982). The hydrophobe group includes chlordane, dichloro diphenyl dichloroethane (DDD), dichloro diphenyl dichloroethylene (DDE), dichloro diphenyl trichloroethane (DDT), dieldrin, endosulfan, toxaphene, mirex, heptachlor, methoxychlor, PCN's, and PCB's. The quasi-hydrophobe group includes aldrin, heptachlor epoxide, and endrin. Organic-coated minerals or organic particles adsorb hydrophobes by partitioning the hydrocarbonaceous portion of the organochlorine compound to their surfaces (Thurman, 1985). These adsorbed hydrophobes may degrade environmental quality in two ways. First, these compounds can be removed from the sediment by deposit and filter feeders, who concentrate them in their tissues (Menzie, 1981, p. 4). This removal can lead to biomagnification and concentration up the food chain. Secondly, although these compounds are essentially hydrophobic, very small quantities may be released into the water column. Although the concentrations are extremely low, fish and other organisms can concentrate them because of the extremely high volumes of water contacted during feeding or respiration. The quasi-hydrophobes have the same effect on environmental quality as the hydrophobes, but are released to the water column in larger quantities.

Organochlorine-compound determinations were made on cores collected from sites CR-S1, SR-S2, and CB-S6 (table 5). The intervals analyzed correspond to those used in the elutriate tests. Two cores (CB-S6a and CB-S6b) were collected to examine organochlorine distribution in more detail, particularly the relation between grain-size distribution and TOC content.

Table 5.--Organochlorine and organic carbon determinations at various depth intervals in bottom material

[Concentrations in micrograms per kilogram (µg/kg), except where otherwise indicated; g/kg = grams per kilogram; < = less than; > = greater than; "--" = analysis not made; DDD = dichloro diphenyl dichloroethane; DDE = dichloro diphenyl dichloroethylene; DDT = dichloro diphenyl trichloroethane; PCB = polychlorinated biphenyls; PCN = polychlorinated naphthalenes]

																			Total organic carbon		
Site name	Site No.	Depth interval (meters)	Aldrin	Chlordane	DDD	DDE	DDT	Dieldrin	Endosulfan	Endrin	Gross PCB	Gross PCN	Hept-epox	Heptachlor	Lindane	Methoxychlor	Mirex	Perthane	Toxaphene	<100µm (g/kg)	>100µm (g/kg)	Bulk (g/kg)
Cathlamet Bay	6a	0-0.9	<0.1	<1	1.3	0.4	<0.1	<0.1	<0.1	<0.1	2.0	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<1	<10	2.1	2.2	2.2
Cathlamet Bay	6a	0.9-3.7	.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	--	3.2	--
Columbia River	1	0-1.9	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	2.6	10.5	3.8
Columbia River	1	1.9-6.1	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	2.9	4.5	3.4
Skipanon River	2	0.-.9	<.1	2.0	23	5.0	<.1	.2	<.1	<.1	37	--	.1	<.1	<.1	<.1	<.1	<1	<10	5.8	159.4	7.4
Skipanon River	2	.9-4.1	<.1	2.0	27	2.9	<.1	<.1	<.1	<.1	9.0	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	5.4	108	5.4
Skipanon River	2	4.1-5.7	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	1.8	<.2	<.2
Cathlamet Bay	6b	.56-.76	<.1	<1	8.9	.9	.2	<.1	<.1	<.1	15	1	<.1	<.1	<.1	<.1	<.1	<1	<10	10.7	8.2	10.6
Cathlamet Bay	6b	1.17-1.40	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	9.7	19.8	10.9
Cathlamet Bay	6b	1.78-1.98	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	12.2	18.9	13.3
Cathlamet Bay	6b	2.58-2.76	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	6.4	2.5	6.0
Cathlamet Bay	6b	3.10-3.20	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	8.4	1.2	3.2
Cathlamet Bay	6b	3.23-3.44	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	8.8	1.5	3.4
Cathlamet Bay	6b	2.64-3.82	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	66.8	4.6	11.2
Cathlamet Bay	6b	4.22-4.42	<.1	<1	<.1	<.1	<.1	<.1	<.1	<.1	<1	<1	<.1	<.1	<.1	<.1	<.1	<1	<10	7.6	1.4	3.2

Although the suite of compounds varied, at least some organochlorine compounds were detected in all the cores except CR-S1. Organochlorines in the upper (0- to 0.9-m) and middle (0.9- to 4.1-m) intervals of SR-S2 represent concentration maxima for all cores. However, no organochlorines were detected in the lower interval (4.1 to 5.7 m of SR-S2). Smaller but detectable concentrations were also found in CB-S6b (0.56 to 0.76 m) and in the upper interval of CB-S6a (0 to 0.9 m). Compounds detected and quantified in at least one of the three cores analyzed include aldrin, chlordane, DDD, DDE, DDT, dieldrin, PCB's, PCN's, and heptachlor epoxide (table 5). Endosulfan, endrin, heptachlor, lindane, methoxychlor, mirex, perthane, and toxaphene were below analytical detection limits for these intervals (table 5).

Grain-size distributions (table 6) and TOC content (table 5) are directly related to the presence and concentration of organochlorine compounds. CB-S6b was subsampled at eight "discrete intervals", each about 20 cm in length. The upper interval, (0.56 to 0.76 m), that is within the upper-depth interval of core CB-S6a, (0 to 0.9 m), contained larger concentrations of DDD, DDE, and DDT than CB-S6a (table 5). Thus, larger organochlorine concentrations were found in the shorter interval of core CB-S6b than were found in the larger interval of CB-S6a. It may be that the smaller interval simply contains more organochlorines than the larger one. However, the smaller interval has both a higher silt-clay and a higher TOC content (tables 5 and 6) than the larger interval--68 percent and 10.6 g/kg and 13 percent and 2.2 g/kg, respectively. Previous work has shown that organochlorines tend to preferentially sorb to fine-grained sediment over coarser sediment; in addition, organic content plays an important role (Frink and others, 1982, p. 14). Therefore, it seems likely that the organochlorine enrichment in the smaller interval is due to the larger concentration of silt-clay and TOC.

Additional evidence supporting the relations between organochlorine concentrations and grain size and TOC can be obtained by normalizing organochlorine concentrations with respect to grain size and TOC. If silt-clay is the concentrator, normalizing should reduce or eliminate its influence; normalized concentrations should then be similar in both intervals. Normalized concentrations of DDD, DDE, and PCB's are 10, 3, and 15 μg/kg in the larger interval and 13, 1.3, and 22 μg/kg in the smaller interval. Similar results were obtained when the organochlorine concentrations were normalized to TOC content. The normalized organochlorine concentrations are essentially the same for both intervals (considering analytical precision and accuracy), supporting the hypothesis that organochlorines are preferentially sorbed to fine-grained, TOC-rich sediments.

If bottom material from the 0.56- to 0.76-m interval formed a new sediment surface at the disposal-site sediment-water interface, one of the primary concerns would be the effect of organochlorine compounds on the food chain. Although no biological samples were collected in this study, EPA determined that organochlorine concentrations in crayfish sampled from the nearby Willamette River, where bottom material contained DDD, DDE, and PCB's in amounts similar to SR-S2 and CB-S6b, contained no detectable DDD, DDE, or PCB's (Bruce Cleland, U.S. Environmental Protection Agency, written commun., 1984). Crayfish consume benthic invertebrates and other organic forms (living or dead) and are therefore an indicator species for anthropogenic (influenced by man) organic compounds entering the food chain. The EPA results indicate that organochlorine compounds did not bioaccumulate in crayfish, but until local biota are sampled and analyzed, no conclusions can be made for the present study area.

Table 6.--Analyses of particle size in percent finer than a specified particle-size diameter, in micrometers (μm)

Site name	Site no.	Depth interval (meters)	Percent sands							Percent silts				Percent clays	
			1000μm	500μm	350μm	250μm	175μm	125μm	88μm	62μm	31μm	16μm	8μm	4μm	2μm
Cathlamet Bay	6a	0-0.9	100	100	100	100	87	52	23	13	7	4	3	2	2
Cathlamet Bay	6a	0.9-3.7	100	100	100	98	80	56	42	35	23	16	11	8	6
Cathlamet Bay	6b	.025-.203	100	100	100	98	80	32	19	13	6	4	3	2	1
Cathlamet Bay	6b	.38-.56	100	100	100	100	94	63	23	15	9	6	4	3	2
Cathlamet Bay	6b	.56-.76	100	100	100	100	99	94	80	68	39	24	15	9	9
Cathlamet Bay	6b	.81-.91	100	100	100	100	96	76	40	22	11	7	5	3	3
Cathlamet Bay	6b	1.57-1.78	100	100	100	100	97	85	49	24	8	5	3	2	2
Cathlamet Bay	6b	2.41-2.59	100	100	100	100	97	86	66	51	33	21	15	11	2
Cathlamet Bay	6b	4.22-4.42	100	100	100	93	62	29	23	21	14	10	7	5	3
Columbia River	1	0-1.9	100	100	100	99	97	92	81	68	48	33	24	14	11
Columbia River	1	1.9-6.1	100	100	100	99	84	61	34	24	16	11	8	6	4
Columbia River	5	.08-1	100	100	98	76	29	13	10	9	8	6	4	3	2
Columbia River	5	1.8-3.8	100	100	100	87	49	19	16	16	10	6	4	3	3
Skipanon River	2	0-0.9	100	100	100	100	100	99	99	99	88	70	47	35	26
Skipanon River	2	0.9-4.1	100	100	100	100	100	100	100	100	90	69	49	33	23
Skipanon River	2	4.1-5.7	100	100	100	97	68	2	0	0	0	0	0	0	0

Gas Chromatograph/Mass Spectrometric Determinations

Acid and base-neutral extractable organic compounds, corresponding to EPA's organic priority pollutant list, were determined by gas chromatograph/mass spectrometric (GC/MS) analyses of core sediments collected from CB-S6b, SR-S2, and CR-S1 (table 7). These compounds were divided into nine groupings, according to chemical type (table 7). Only organic compounds in the phthalate esters (PE) and polycyclic aromatics (PA) groupings were detected. Small concentrations of some PE's were detected at SR-S2, but none were detected at other sites.

PA's are of environmental significance because of their persistence in sediment, movement up the food chain, and identification as carcinogens (Baker, 1980, p. 26; Siftig, 1981, p. 563). Ten of 16 PA determinations in CB-S6b (0.56 to 0.76 m) tested positive; concentrations ranged from 8 μg/kg for napthalene to 278 μg/kg for fluoranthene (table 7). There are two probable sources for PA's in CB-S6b. The first and most direct source would be petroleum spills, which may have occurred while naval vessels were maintained in Cathlamet Bay during the late 1940's and early 1950's. A second and somewhat indirect source might be combustion processes, especially the incomplete combustion of fossil fuels, which result in atmospheric deposition of PA's in aquatic systems (Baker, 1980, p. 16). Defining the exact sources of PA's to the lower estuary must await further study.

Table 7.--Gas chromatographic/mass spectrometric determinations of acid/base-neutral extractable organic compounds in bottom material

[Units are in micrograms per kilogram, µg/kg; m = meters; < = less than; "--" = analysis not made]

	Cathlamet Bay	Skipanon River			Columbia River	
Compound	Site-6b, depth interval 0.56-0.76 m	Site-2 depth interval 0-0.9 m	Site-2 depth interval 0.9-4.1 m	Site-2 depth interval 4.1-5.7 m	Site-1 depth interval 0-1.9 m	Site-1 depth interval 1.9-6.1 m
Halogenated Aliphatics						
bis(2-Chloroethoxy)methane	<16	<15	<16	<16	<24	<16
Hexachlorobutadiene	<40	<38	<40	<41	<60	<41
Hexachlorocyclopentadiene	<53	<50	<52	<54	<79	<54
Hexachloroethane	<59	<56	<58	<60	<88	<60
Ethers						
4-Bromophenyl phenyl ether	<19	<40	<38	<36	<62	<36
bis(2-Chloroethyl)ether	<10	<18	<19	<20	<29	<20
bis(2-Chloroisopropyl)ether	<100	<95	<98	<102	<148	<101
4-Chlorophenyl phenyl ether	<15	<25	<24	<22	<39	<22
Phthalate Esters						
Butyl benzyl phthalate	<9	<31	<30	<20	<46	<22
Diethyl phthalate	<7	13	<8	<8	<14	<8
Dimethyl phthalate	<5	7	<7	<8	<11	<8
Di-n-butyl phthalate	<4	--	<6	--	--	--
Di-n-octylphthalate	<8	<30	<29	20	<43	<22
bis(2-Ethylhexyl)phthalate	<8	<28	<26	--	<39	<1
Polycyclic Aromatics						
Acenaphthene	<7	<12	<11	<11	<18	<11
Acenaphthylene	<6	<6	<6	<6	<9	<6
Anthracene	<20	<24	<15	9	<16	<9
Benz(a)anthracene	159	<26	<25	17	<38	<19
Benzo(b)fluoranthene	127	<31	<30	<20	<45	<22
Benzo(k)fluoranthene	134	<38	<36	<25	<55	<27
Benzo(g,h,i)perylene	173	<55	<52	<36	<79	<39
Benzo(a)pyrene	223	<48	<46	<31	<70	<34
Chrysene	76	<27	<26	18	<39	<19
Dibenzo(a,h)anthracene	<200	<60	<58	39	<87	<43
Fluoranthene	278	32	78	<10	<17	<10
Fluorene	<6	<11	<10	<10	<17	<10
Indeno(1,2,3-cd)pyrene	<132	<52	<50	<3	<75	<37
Naphthalene	8	26	41	<8	<11	<8
Phenanthrene	72	<22	65	<8	<14	<8
Pyrene	260	49	146	<11	<24	<12

Table 7.--Gas chromatographic/mass spectrometric determinations of acid/base-neutral extractable organic compounds in bottom material--Continued

	Cathlamet Bay	Skipanon River			Columbia River	
Compound	Site-6B, depth interval 0.56-0.76 m	Site-2 depth interval 0-0.9 m	Site-2 depth interval 0.9-4.1 m	Site-2 depth interval 4.1-5.7 m	Site-1 depth interval 0-1.9 m	Site-1 depth interval 1.9-6.1 m
Monocyclic Aromatics						
1,2-Dichlorobenzene	<22	<21	<22	<23	<33	<22
1,3-Dichlorobenzene	<22	<21	<22	<22	<33	<22
1,4-Dichlorobenzene	<20	<19	<20	<21	<30	<20
2,4-Dinitrotoluene	<44	<73	<70	<66	<114	<66
2,6-Dinitrotoluene	<32	<53	<51	<48	<83	<48
Hexachlorobenzene	<25	<42	<40	<38	<65	<38
Nitrobenzene	<19	<18	<18	<19	<28	<19
1,2,4-Trichlorobenzene	<24	<23	<24	<25	<36	<25
Compound Related to Polychlorinated Biphenyls						
2-Chloronaphthalene	<10	<10	<10	<11	<16	<11
Nitrosamines and Other Compounds						
n-Nitrosodimethylamine	<56	<53	<55	<57	<82	<56
n-Nitrosodiphenylamine	<17	<28	<27	<25	<44	<25
n-Nitrosodi-n-propylamine	<93	<89	<92	<95	<139	<94
Pesticides						
Isophorone	<9	<8	<9	<9	<13	<9
Phenols and Cresols						
4-Chloro-3-methylphenol	<27	<26	<27	<28	<40	<28
2-Chlorophenol	<27	<26	<27	<28	<40	<27
2,4,-Dichlorophenol	<35	<33	<35	<36	<52	<35
2,4,-Dimethylphenol	<29	<27	<28	<29	<43	<29
4,6-Dinitro-2-methylphenol	<118	<194	<185	<175	<303	<175
2,4,-Dinitrophenol	<180	<286	<284	<267	<463	<268
2-Nitrophenol	<72	<68	<71	<73	<106	<73
4-Nitrophenol	<51	<85	<81	<76	<132	<77
Pentachlorophenol	<67	<111	<106	<110	<173	<100
Phenol	<22	<21	<22	<22	<32	<22
2,4,6-Trichlorophenol	<42	<40	<42	<43	<62	<43

Of the 16 PA determinations made in upper (0 to 0.9 m), middle (0.9 to 4.1 m), and lower (4.1 to 5.7 m) intervals of SR-S2, three to four PA's were detected in each interval; concentrations ranged from 9 μg/kg for anthracene to 146 μg/kg for pyrene (table 7). The largest concentrations (upper and middle intervals) correspond to sediments composed of silt-clay (table 6), which contain up to 7.4 g/kg TOC; sediments in these intervals were probably deposited after the 1939 dredging of Skipanon River (Rudd Turner, U.S. Army Corps of Engineers, written commun., 1986). PA compounds were likely emitted from the operation of a wigwam burner (incinerator) adjacent to SR-S2; combustion-produced PA-associated particles have probably combined with sediment in upper and middle intervals near the combustion source. The facility was operated by a lumber company until 1982 (Tom Lucas, Oregon Department of Environmental Quality, oral commun., 1986).

If, during disposal, the PA-concentrated silt-clay were to settle last, it would reform at the disposal-site sediment-water interface. PA concentrations expected within interface sediments are similar to those determined by the U.S. Environmental Protection Agency in Willamette Harbor sediment (Bruce Cleland, U.S. Environmental Protection Agency, written commun., 1984). As with organochlorine compounds, crayfish were used as an indicator species. EPA results indicate that PA compounds did not bioaccumulate, but until local biota from the present study sites are sampled and analyzed, no conclusions can be made.

Total Metals in Bottom Material

One of the most significant factors controlling sediment capacity for collecting and concentrating trace metals, and possibly the most important factor causing variability of sediment metal concentrations through space or time, is grain size (Forstner and Wittmann, 1979; Horowitz, 1984). There is a strong positive correlation between decreasing grain size and increasing metal concentration. This correlation is the result of numerous factors related to the chemical and physical nature of sediments, including, but not limited to: (1) surface area, (2) cation exchange capacity, (3) surface charge, and (4) composition (for example, Fe and Mn oxides and hydroxides, organic matter, clay mineralogy). The influence (or concentration) of these factors increases with decreasing grain size and probably accounts for the increased capacity of fine-grained sediments to retain trace metals.

Critical Bands

On the basis of visual examination, fine-grained bulk sediment bands ranging in length from 0.5 to 10 cm were excised from cores collected at sites CB-S6a, CR-S1, and SR-S2. These "critical bands" were removed immediately after the cores were split and analyzed for total metals (table 8). To determine if metals were enriched in critical bands, the chemical data from these bands were compared with total-metal concentrations for both Columbia River basalts (CR-basalts) and the <100-μm fraction of sediments in the larger depth intervals (table 9) which include the bands. CR-basalts were used because they represent the local geology; the <100-μm fraction was used because it is similar in particle size to the critical bands.

Table 8.--Total-metal analyses of bulk bottom material at selected critical bands

[pct = percent; µg/g = micrograms per gram; < = less than]

Site Name	Site no.	Depth (meters)	Aluminum (pct)	Cadmium (µg/g)	Chromium (µg/g)	Copper (µg/g)	Iron (pct)	Lead (µg/g)	Manganese (pct)	Nickel (µg/g)	Selenium (µg/g)	Zinc (µg/g)	Comments
Cathlamet Bay	6a	2.1-2.2	6.8	<0.5	55	28	4.1	8	0.06	27	0.1	81	Medium silts to very fine sands.
Columbia River	1	0.5-.6	6.1	3.6	53	37	4.6	8	.07	35	.2	118	Clay with some intermixed silts, very dry.
Columbia River	1	4.7	5.8	<.5	45	23	3.6	3	.06	22	.1	73	Fragmented clay lens, interspersed with organic detritus.
Skipanon River	2	1.1-1.15	6.2	.5	54	49	4.5	22	.04	27	.2	210	Coarse to fine clays, light colored, contains shell fragments.
Skipanon River	2	2.7-2.78	6.8	<.5	72	53	4.8	26	.05	44	.2	203	Coarse to fine clays, dark black in color.

The critical band of the core from Columbia River Site 1 (CR-S1, 0.5 to 0.6 m) contained 3.6 µg/g Cd (table 8). This concentration is considerably larger than the 0.08 to 0.2 µg/g found in CR basalts (Wedepohl, 1970a, p. 48-E-4) and also exceeds the <0.5 µg/g in the larger depth interval (0 to 1.9 m) of CR-S1 (table 9), which appears to reflect local geological sources. Therefore, Cd is enriched within the critical band, but not throughout the larger depth interval. During dredging and disposal, the effect of critical-band Cd enrichment would be unmeasurable due to the small thickness of the critical band relative to the much larger interval dredged. This Cd dilution is evidenced in the larger depth interval (0. to 1.9 m) where the concentration is below analytical detection.

Two critical bands in SR-S2 (1.10 to 1.15 and 2.70 to 2.78 m) contain Pb and Zn concentrations that are elevated when compared to those found in CR basalts. Pb levels in the upper and lower bands are 22 and 26 µg/g and Zn levels in the upper and lower bands are 210 and 203 µg/g (table 8); all are higher than the 1.2- to 8.5-µg/g Pb levels and the 119-µg/g Zn levels reported for CR-basalts (Wedepohl and others, 1970b; Wedepohl and other, 1970c, p. 82-E-4). Concentrations of Pb and Zn in the larger depth interval of SR-S2 (0.9 to 4.1 m) are similar to those within the critical bands (table 9). Thus Pb and Zn enrichment is evident throughout the entire core depth.

Table 9.--Trace-metal extraction of bottom materials less than 100 micrometers (<100 μm) with 1-normal hydrochloric acid (1N-HCl) compared to total-metal extraction procedures

[μg/g = micrograms per gram; pct = percent]

Site name	Site no.	Depth interval (meters)	Cadmium 1N-HCl (μg/g)	Cadmium Total (μg/g)	Chromium 1N-HCl (μg/g)	Chromium Total (μg/g)	Copper 1N-HCl (μg/g)	Copper Total (μg/g)	Iron 1N-HCl (pct)	Iron Total (pct)	Lead 1N-HCl (μg/g)	Lead Total (μg/g)	Manganese 1N-HCl (μg/g)	Manganese Total (μg/g)
Cathlamet Bay	6a	0-0.9	0.6	<0.5	4	78	10	31	0.6	5.1	12	11	180	900
Cathlamet Bay	6a	0.9-3.7	.2	1.2	3	66	16	32	.9	4.7	5	5	310	800
Columbia River	1	0-1.9	.2	<.5	3.0	62	19	49	.9	4.9	3	9	320	900
Columbia River	1	1.9-6.1	.2	1.0	2.0	75	18	34	.9	5.1	4	6	350	800
Columbia River	5	.08-1	.9	<.5	4	63	18	43	.9	5.2	17	17	180	700
Columbia River	5	1.8-3.8	<.1	<.5	80	164	17	27	1.0	5.6	4	9	200	800
Skipanon River	2	0-0.9	1.7	2.2	11	72	26	60	1.1	4.6	22	33	200	700
Skipanon River	2	0.9-4.1	1.3	<.5	6	64	27	57	1.1	4.9	22	29	310	700
Skipanon River	2	4.7-5.7	.2	<.5	8	121	10	26	.9	11.1	13	40	100	1,100

Site name	Site no.	Depth interval (meters)	Mercury 1N-HCl (μg/g)	Mercury Total (μg/g)	Nickel 1N-HCl (μg/g)	Nickel Total (μg/g)	Zinc 1N-HCl (μg/g)	Zinc Total (μg/g)	Total organic carbon <100μm (μg/g)	Total organic carbon >100μm (μg/g)	Total volatile solids <100μm (percent)
Cathlamet Bay	6a	0-0.9	<0.1	0.10	5	31	55	141	2.1	2.2	8.4
Cathlamet Bay	6a	0.9-3.7	<.1	.08	6	35	23	93	--	3.2	6.0
Columbia River	1	0-1.9	<.1	.40	6	34	31	105	2.6	10.5	4.0
Columbia River	1	1.9-6.1	<.1	.06	6	30	24	98	2.9	4.5	4.0
Columbia River	5	.08-1	<.1	.21	7	22	87	170	3.6	1.8	5.7
Columbia River	5	1.8-3.8	<.1	.08	30	70	22	96	1.1	1.9	6.5
Skipanon River	2	0-0.9	<.1	.52	5	34	104	225	5.8	159.4	9.2
Skipanon River	2	.9-4.1	<.1	.25	6	32	110	170	5.4	108	9.3
Skipanon River	2	4.7-5.7	<.1	.09	7	43	31	150	1.8	<.2	10.8

Total Metal Analysis of Less-than 100-micrometer Compared to Greater-than 100-micrometer Bottom Material

For five depth intervals of CB-S6b, bottom material passing through a 100-μm sieve and bottom material retained in the sieve were independently analyzed for total metals (table 10). These analyses show if metal concentrations vary with depth and between size fractions. The 100-μm size break was selected because sediments and associated trace metals passing through the sieve are similar to those ingested by many benthic deposit feeders. For example, the deposit feeding clam Macoma balthica ingests sediments <88 μm in diameter (Luoma, 1983).

Table 10.--Total-metal and organic carbon concentrations in bottom material from Cathlamet Bay, Site 6b

[pct = percent; μg/g = micrograms per gram; < = less than; > = greater than cm = centimeter; g/kg = grams per kilogram; "--" = analysis not made]

Depth interval (cm)	Aluminum (pct)	Cadmium (μg/g)	Chromium (μg/g)	Copper (μg/g)	Mercury (μg/g)	Iron (pct)	Lead (μg/g)	Manganese (pct)	Nickel (μg/g)	Zinc (μg/g)	Total organic carbon (g/kg)
Chemical analyses of bottom material less than 100 micrometers (<100μm)											
2.5-20.3	8.4	2.3	56	31	0.12	4.9	8	0.11	21	121	4.8
20.3-38.1	--	1.1	--	--	.16	--	--	--	--	158	--
38.1-55.9	--	1.1	--	--	.17	--	--	--	--	137	--
55.9-76.2	--	1.0	--	--	.12	--	--	--	--	134	--
81.3-99.1	7.7	.6	70	25	.15	4.6	12	.08	27	132	5.5
99.1-116.8	--	--	--	--	.06	--	--	--	--	--	--
116.8-140	--	--	--	--	.10	--	--	--	--	--	--
140-157	--	--	--	--	.05	--	--	--	--	--	--
157-178	7.8	<.5	77	26	.05	4.9	5	.08	29	88	4.8
241-259	7.6	<.5	82	30	.08	4.9	10	.09	36	89	8.2
422-442	7.9	<.5	61	39	.06	5.0	9	.07	30	98	7.6
Chemical analyses of bottom material greater than 100 micrometers (>100μm)											
2.5-20.3	7.7	<.5	34	13	--	2.9	10	.07	22	78	1.1
81.3-99.1	7.3	<.5	37	14	--	2.9	6	.08	23	79	2.0
157-178	7.8	<.5	37	15	--	2.9	6	.05	22	57	4.0
241-259	7.5	<.5	36	14	--	2.9	10	.05	22	54	2.3
422-442	8.1	<.5	30	12	--	3.1	2	.06	20	53	1.4

Of the metals examined, Cd, Hg, and Zn concentrations in the <100-µm fraction vary with depth (fig. 4); none of the metals in the >100-µm fraction vary significantly with depth. In addition, Cd, Cr, Cu, Fe, and Zn are substantially larger in the <100-µm fraction; Ni, Mn, and Pb show no concentration differences in either size fraction.

Before further discussing variations in metal concentrations with depth it is useful to review (1) how the element Al (aluminum) was used to determine if metal concentrations vary with depth intervals and (2) the role of aluminosilicate clay minerals as trace-metal concentrators.

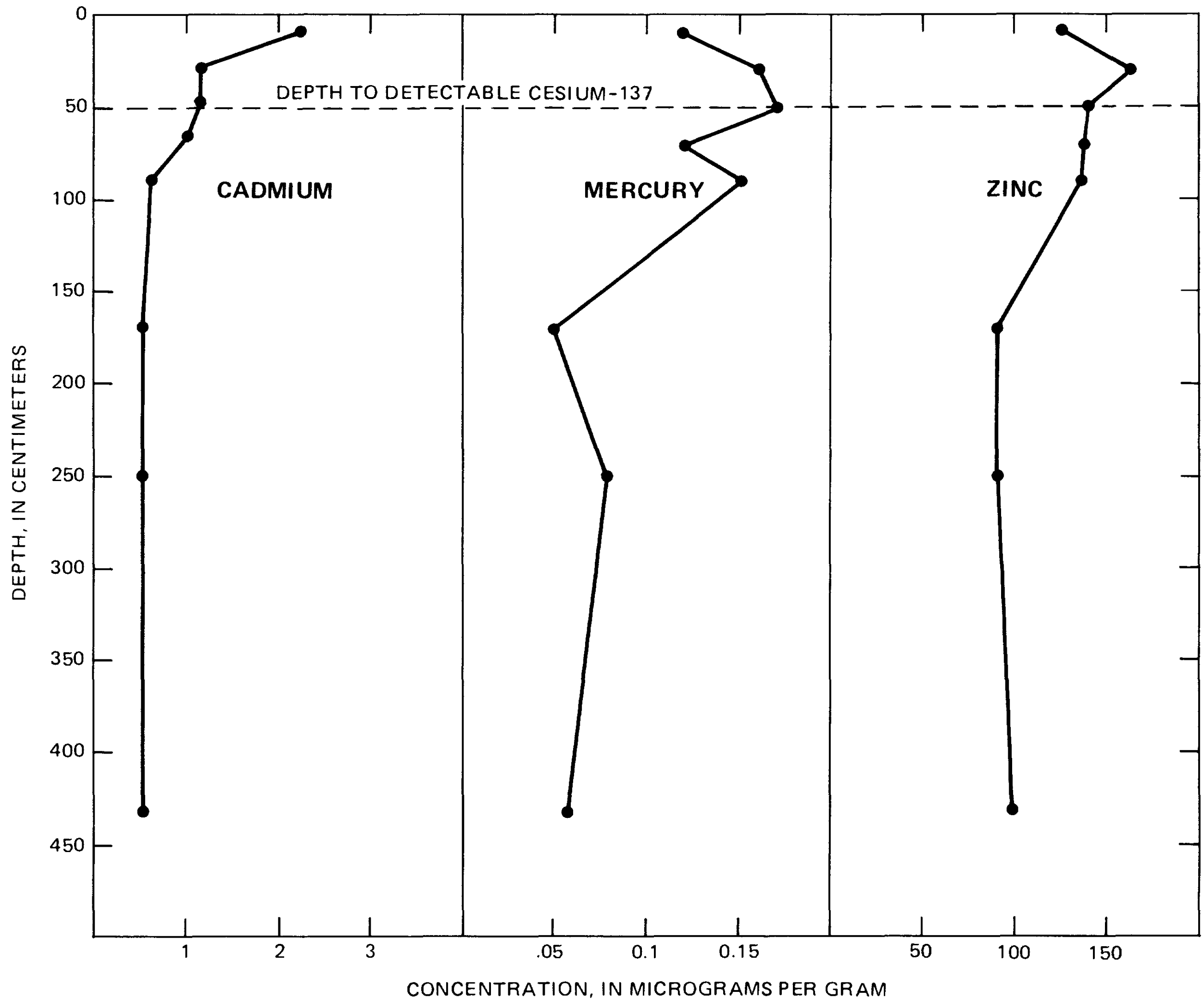


Figure 4.--Total cadmium, mercury, and zinc compared to depth in bottom material less than 100 micrometers in diameter from Cathlamet Bay, Site 6b.

Aluminium is assumed to have had a uniform flux to bottom material over the past century from the weathering of crustal rock (Forstner and Wittman, 1979). With this assumption in mind--and considering that Al concentrations in the present study are generally constant with core depth (table 10)--inputs of Al and associated metals from the weathering of CR-basalts are assumed to be constant with core depth. Metal concentrations exceeding those of CR-basalts are attributed to either anthropogenic or diagenetic (chemical alteration of sediment after deposition) metal-concentrating effects.

Aluminium is present in the form of aluminosilicate minerals that include clays (hydrated aluminosilicates). The clay minerals chlorite, daplinite, illite, montmorillonite, and vermiculite are common in Columbia River sediments (Glenn and Van Atta, 1973). Montmorillonite, chlorite, and illite are important because they can adsorb metal ions (Forstner and Wittmann, 1979). Several mechanisms have been proposed for the adsorption of metal ions; adsorption occurs either directly on mineral surfaces or indirectly where clay minerals serve as metal concentrators by acting as mechanical substrates for the precipitation and flocculation of organic matter and secondary minerals like hydrous Fe and Mn oxides (Jenne, 1976; Forstner and Wittmann, 1979). In the present study, because clays (particles <4 μm) are included in the <100-μm fraction, the presence of larger concentrations of Cd, Cr, Cu, Fe, and Zn in the fraction containing clays would be expected.

As mentioned earlier, upper intervals contain relatively large concentrations of Cd, Hg, and Zn. Between 2.5 and 99.1 cm, concentrations of Cd, Hg, and Zn are as large as 2.3, 0.17, and 158 μg/g; below 99.1 cm the concentrations are as small as <0.5, 0.05, and 88 μg/g respectively (table 10 and fig. 4). The Cd concentration in the upper interval (2.5 to 20.3 cm) is at least four times larger than those found below 81.3 cm; Hg and Zn in the upper interval (81.3 to 99.1 cm) are an average of 2.5 and 1.4 times larger, respectively, than those below 99.1 cm. Additional determinations between 2.5 and 99.1 cm (table 10) show large concentrations to depths of 76.2 cm (for Cd), 140 cm (for Hg), and 99.1 cm (for Zn). These metals are clearly concentrated in upper intervals, and it is suspected that Cd, Hg, and Zn enrichment in the upper interval reflects anthropogenic processes. This is suggested because no evidence of an oxic/anoxic boundary (fig. 5) or of large Fe and Mn concentrations (table 10) exists in the upper interval. If such a boundary had existed, Fe and Mn in the lower levels (reducing conditions) would be expected to migrate to upper intervals along with other metal ions (for example, Cd, Hg, and Zn) and concentrate by precipitating at an oxic/anoxic boundary (Burton and Liss, 1976, p. 47; Forstner and Wittmann, 1979, p. 214). Eh measurements at the time of sampling (and elutriate-test DO measurements as well) show the upper core to be slightly oxic and lacking a well defined oxic/anoxic boundary (fig. 5). Since there is no evidence of an oxic/anoxic boundary or of large Fe and Mn concentrations in upper intervals, it appears doubtful that considerable migration of metal ions occurred in the past or at the time of sampling. Thus larger Cd, Hg, and Zn concentrations in upper intervals most likely result from anthropogenic processes. Because metal enrichment in the upper intervals corresponds to the occurrence of ^{137}Cs (fig. 4), metal enrichment could have occurred as early as 1953, a time when naval vessels were being maintained in Cathlamet Bay.

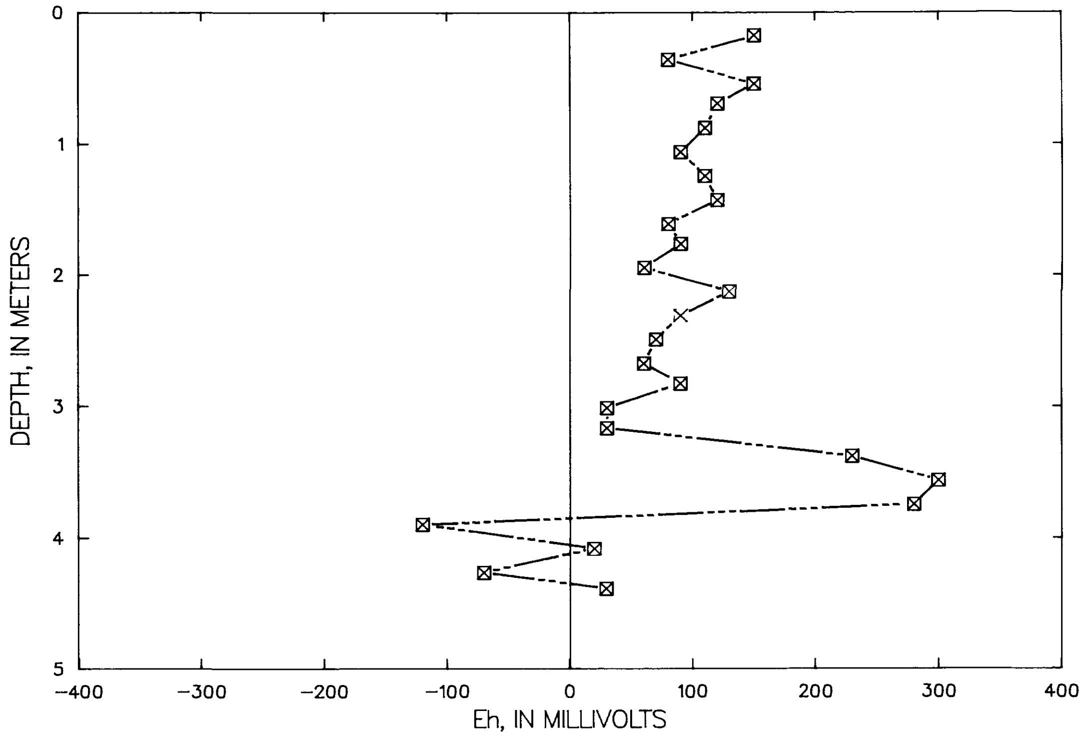


Figure 5.--Measurements of Eh compared to depth in bottom material from Cathlamet Bay, Site 6, near Columbia River mile 18, September 1984.

Trace-metal Extraction of Bottom Material with 1N-HCl Compared to Total-metal Extraction Procedures

On sediment intervals corresponding to those used for the elutriate tests, trace-metal concentrations associated with the <100-μm fraction were determined in two ways (table 9, p. 25). Weak extractions entailed treatment with cold 1N HCl and are assumed to represent readily available metals sorbed to sediment surfaces (extractable metal). Strong extractions entailed treatment with concentrated $HF/HClO_4/HNO_3$ and heat, which completely solubilizes the sediment matrix. These extractions provide data on the total-metal content of the sample. In a few instances, extractable metal concentrations exceeded those of total metal--a result of analytical errors, sample inhomogeneity, or both. The potential for this type of occurrence increases with decreasing metal concentrations in the leachate.

Of the metals examined, extractable Cd and Pb in the upper intervals of SR-S2, CR-S5, and CB-6a represent substantial parts of the total Pb and Cd (table 9, p. 25 and figs. 6 and 7). With the exception of Cr and Ni in the lower interval (1.8 to 3.8 m) of CR-S5, extractable Cr, Hg, Fe, Mn, and Ni represent only small parts of the total metal present for all sites and depth intervals (table 9, p. 25 and figs. 8-12). In addition, these metals exhibit little variation in concentration (extractable or total) between intervals. The large proportion of extractable Ni and Cr within the lower interval of CR-S5 is not associated with larger concentrations of TOC or silt/clay (table 6, p. 20 and table 9, p. 25) nor with a significant shift in mineralogy. The cause of this phenomenon is unknown.

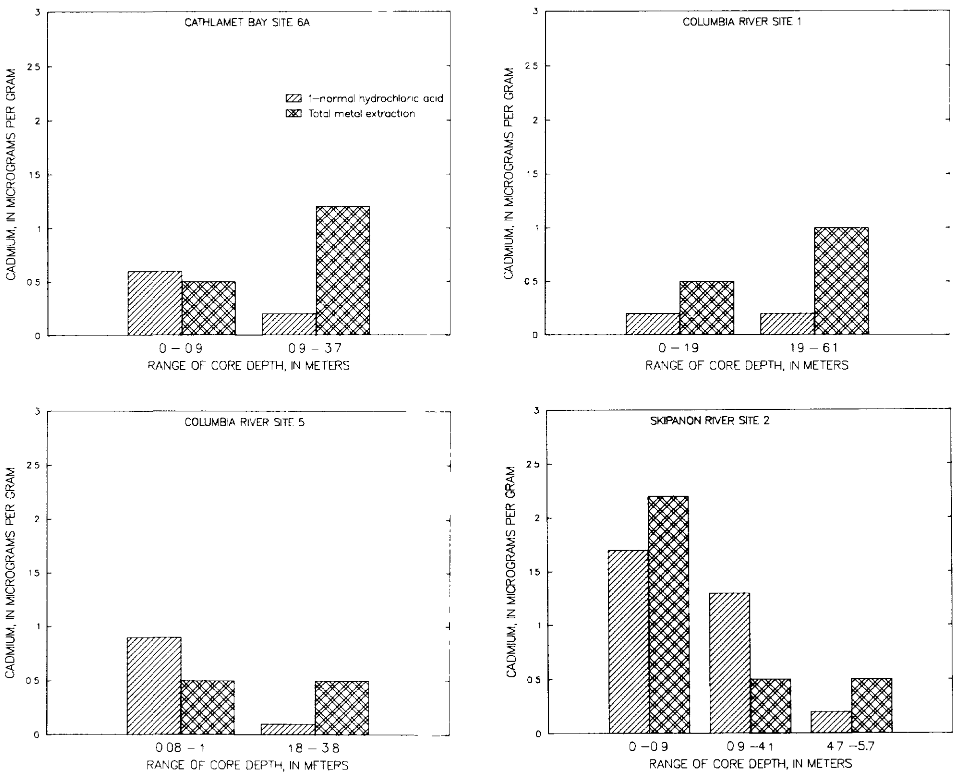


Figure 6.--Comparison of cadmium concentrations extracted from core samples using 1-normal hydrochloric acid and total-metal extraction procedures (total-metal extraction concentrations less than 0.5 micrograms per gram are set equal to 0.5 micrograms per gram; total-metal extraction is complete sediment dissolution using concentration hydrofluoric, oerchloric, and nitric acids.

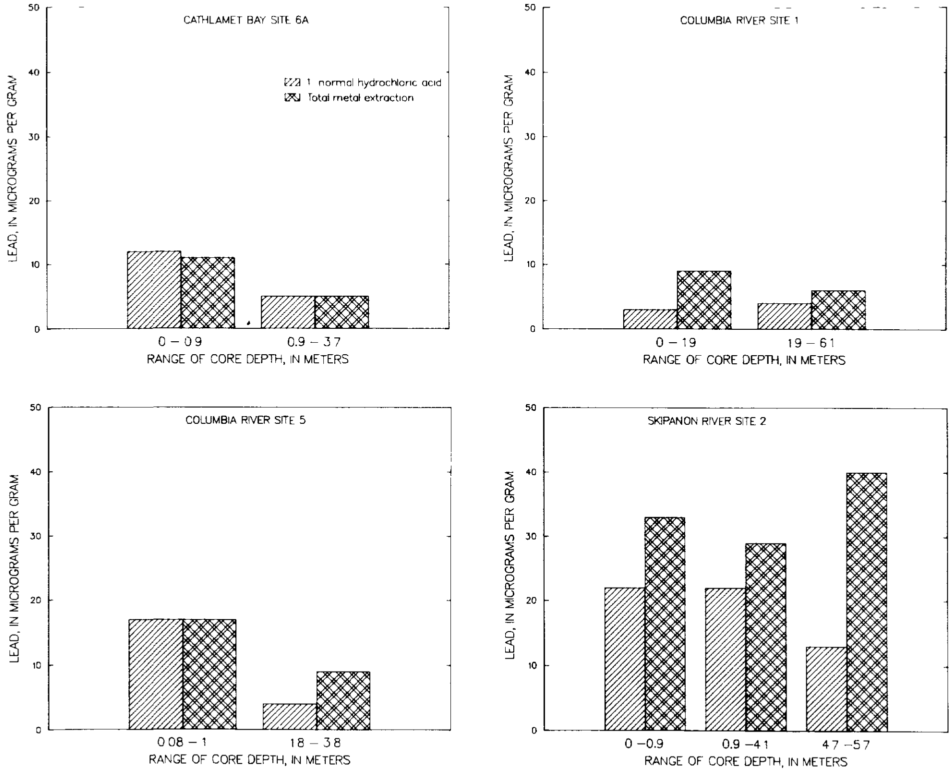


Figure 7.--Comparison of lead concentrations extracted from core samples using 1-normal hydrochloric acid and total-metal extraction procedures.

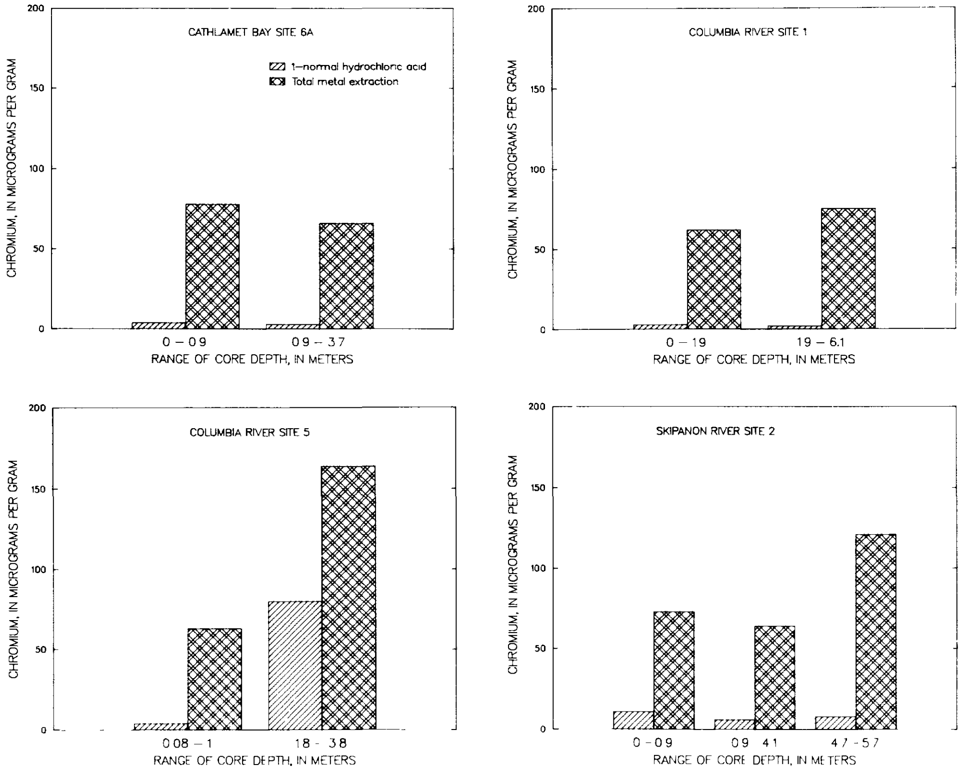


Figure 8.--Comparison of chromium concentrations extracted from core samples using 1-normal hydrochloric acid and total-metal extraction procedures.

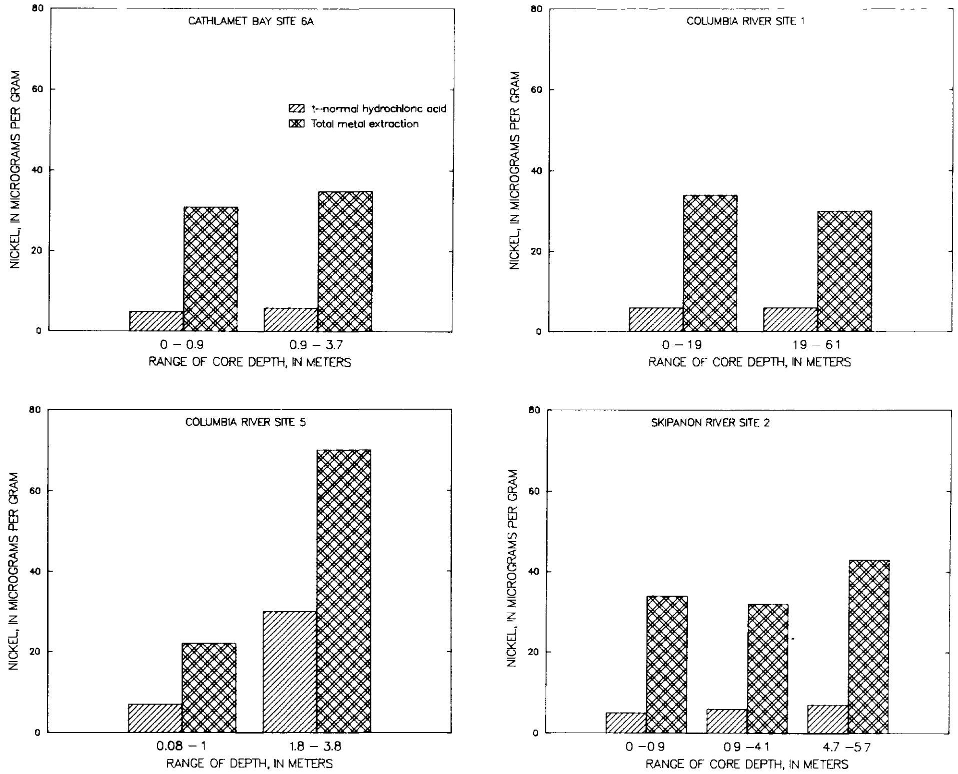


Figure 9.--Comparison of nickel concentrations extracted from core samples using 1-normal hydrochloric acid and total-metal extraction procedures.

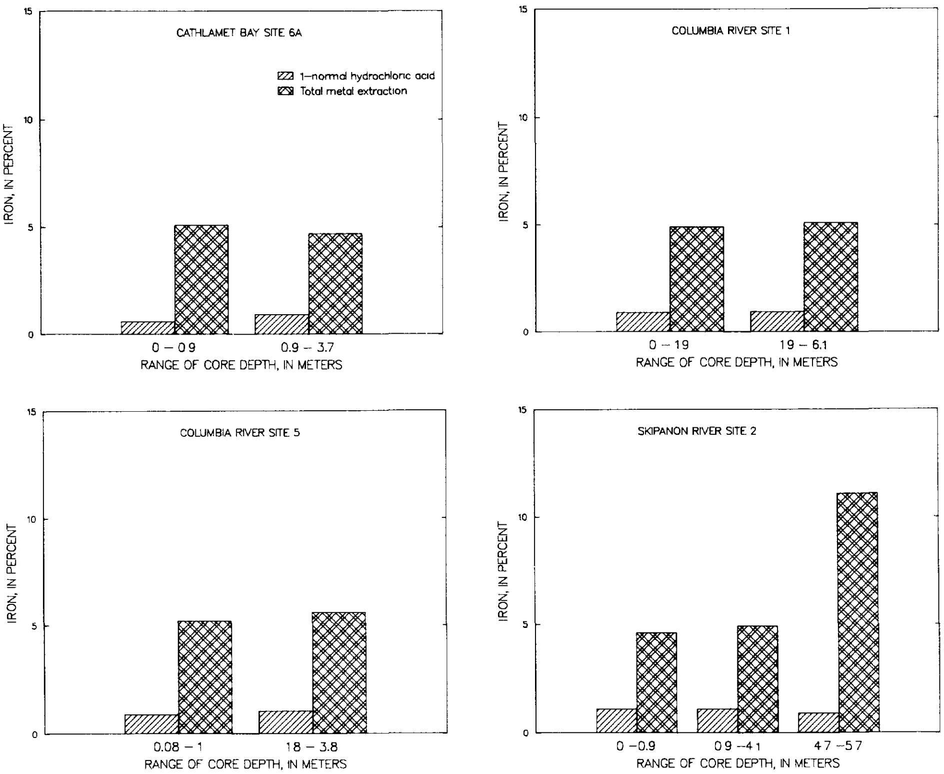


Figure 10.--Comparison of iron concentrations extracted from core samples using 1-normal hydrochloric acid and total-metal extraction procedures.

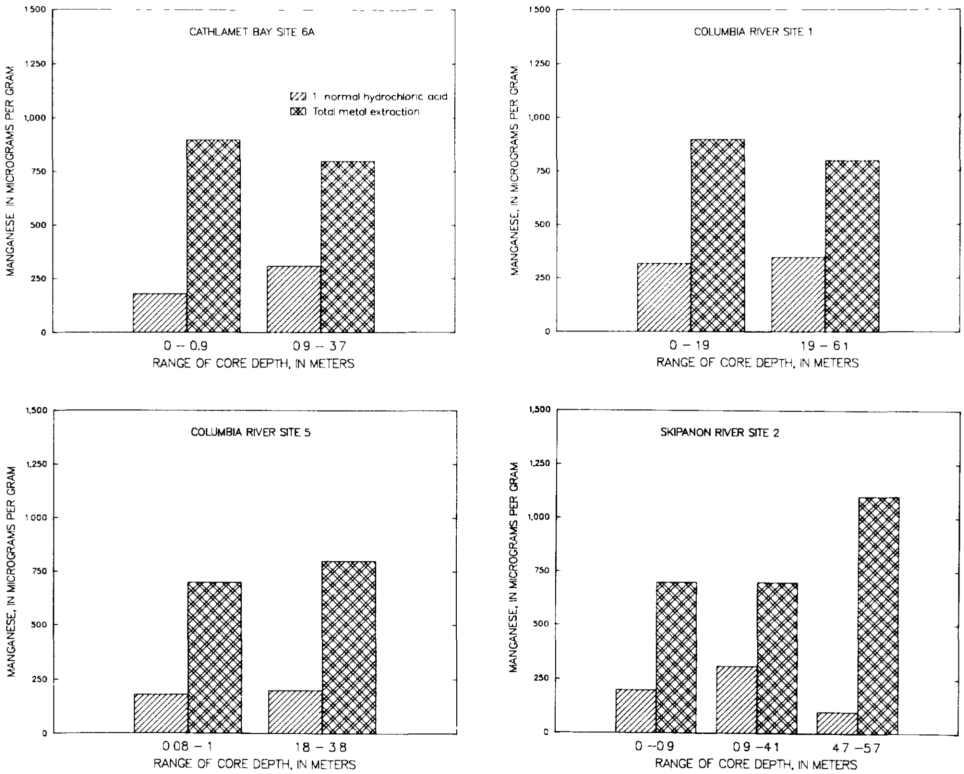


Figure 11.--Comparison of manganese concentrations extracted from core samples using 1-normal hydrochloric acid and total-metal extraction procedures.

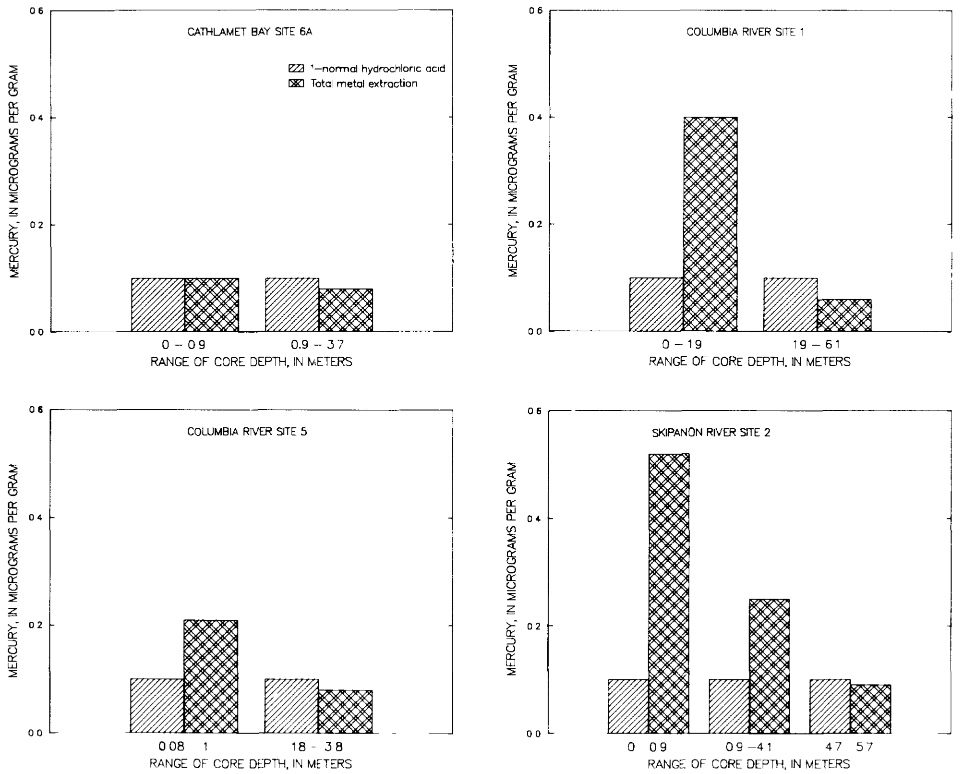


Figure 12.--Comparison of mercury concentrations extracted from core samples using 1-normal hydrochloric acid and total-metal extraction procedures.

Of the extractable metals examined, concentrations of Cd, Cu, Pb, and Zn are significantly correlated with decreasing grain size, as evidenced by their relation with percent clay-size sediments (table 11). In addition, concentrations of Cr, Cu, Pb, and Zn are significantly correlated with extractable iron, and Cd, Cu, and Pb are significantly correlated with TOC (table 11). Thus decreasing grain size or increasing concentrations of TOC and extractable Fe (or both) are conditions favoring the adsorption of Cd, Cu, Pb, and Zn.

Extractable Cd in the upper intervals of CB-S6a, CR-S5, and SR-S2 represents a significant part of the total Cd in the samples and implies that much of the Cd is sorbed to surfaces and could be readily available to benthic fauna. However, if this Cd also is associated with large concentrations of TOC, it is unlikely to be available to these organisms (Luoma and Jenne, 1976). To explore the relation between TOC and extractable Cd, data from the present study have been combined with data from an earlier study (fig. 13) of the lower Columbia Estuary (Fuhrer, 1986). Using the combined data set, concentrations of extractable Cd were found to be significantly correlated with TOC (r = 0.79). Lower depth intervals are characterized by small concentrations of both TOC and extractable Cd and form a distinct group. Upper depth intervals have generally larger extractable Cd concentrations and correspondingly larger TOC concentrations. Baker Bay site 1 is the only site where Cd may be bioavailable (Fuhrer, 1986) as indicated by the large quantity of extractable Cd and small TOC concentration. Because none of the sites sampled in the present study were like Baker Bay Site 1 (fig. 13), Cd may be unavailable to organisms at the disposal site.

Table 11.--Kendall's tau correlation coefficients for selected bottom material constituents with a significance level greater than or equal to 90 percent (ρ less than or equal to 0.1)

[Correlations are derived from trace metal and organics associations with bottom materials less than 100 micrometers (<100 µm) in diameter; TOC = total-organic carbon; TVS = total volatile solids]

	Extractable trace metals								Percent				
	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Nickel	Zinc	TOC	TVS	Clay	Silt	<100µm
Extractable:													
Cadmium			0.36		0.41		-0.35	0.62	0.48		0.33		
Chromium				0.41	.44			.45					
Copper				.39	.49			.65	.47		.68	0.66	0.59
Iron					.41			.36					
Lead								.66	.36		.38		.36
Manganese													
Nickel													
Zinc											.52	.46	.50
Percent:													
TOC											.54	.47	.45
TVS													
Clay												.82	.88
Silt													.81
<100µm													

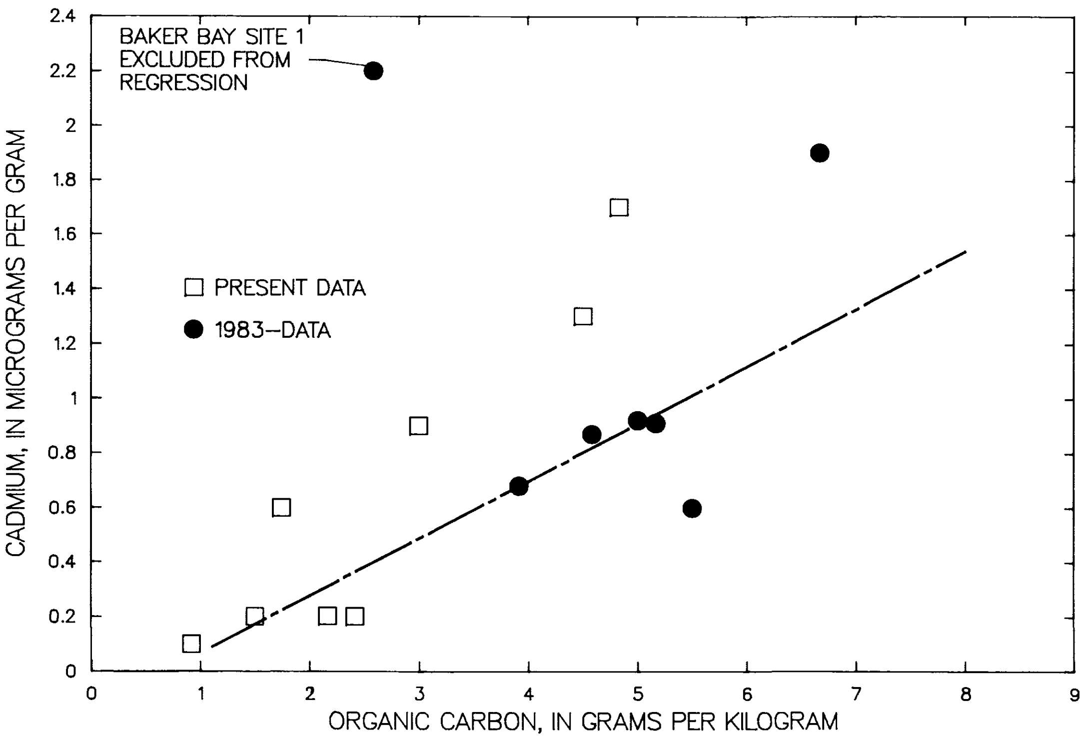


Figure 13.--Relation between 1-normal hydrochloric acid, extractable cadmium, and total organic carbon in bottom material less than 100 micrometers in diameter (correlation coefficient = 0.79; Y = 0.21 x -0.14, where Y = cadmium in micrograms per gram and X = organic carbon in grams per kilogram).

The extractable Pb in upper intervals of CB-S6a, CR-S5, and SR-S2 represents from 67 to 100 percent of the total Pb in the samples, suggesting that much of the Pb is sorbed to surfaces and could be readily available to benthic fauna. The availability of Pb is inversely related to the concentration of extractable Fe in bottom material (Luoma and Bryan, 1978). The explanation favored for this relation is the strong binding capacity of the insoluble iron oxides (Luoma and Bryan, 1978). Using ratios of extractable Pb to extractable Fe from the present study as input to the relation developed by Luoma and Bryan (1978) for predicting Pb in clam tissue indicates that Pb in clams ingesting sediments similar to upper intervals of CB-S6, CR-S5, and SR-S2 would be approximately 7 $\mu g/g$ (dry weight). This concentration is close to the World Health Food Standard, 10 $\mu g/g$, (Callahan and others, 1979).

The ratio of total Hg to TVS reflects the degree of contamination to which an estuary is subjected and also relates to the availability of Hg to the deposit-feeding clams (Langston, 1982, p. 676). Even small total Hg concentrations can become biologically available when TVS is small. If Macoma balthica, present in the Columbia River estuary (Durkin and Emmett, 1980), accumulate Hg in a similar manner to those in English estuaries (Langston, 1982, p. 678) and if the conclusions of Langston (1982) are valid, tissue concentrations would be expected to range from 0.3 to 0.6 $\mu g/g$, well within the limits (1 $\mu g/g$ wet weight) set by the U.S. Food and Drug Administration (Caldwell and Buhler, 1983, p. 22). In fact, ratios Hg/TVS in the present study range from 0.008 to 0.100, with a median value of 0.015. These values are considerably smaller than those of contaminated English estuaries, where ratios approach 1.2 (Langston, 1982, p. 678).

SUMMARY

A proposal to deepen the lower Columbia River navigational channel prompted a study of vertical distribution of selected trace metals and organic compounds in bottom material to evaluate the effects of dredging and disposal operations. On the basis of earlier studies, four sites were selected for collection of bottom-material core samples; native mixing water was collected from the proposed disposal site. Core samples (and mixing water) were collected in September and October 1984.

Estimates of sediment deposition rates using ^{137}Cs in core CB-S6 range from 0.8 to 1.3 cm/yr. Although ^{210}Pb and ^{137}Cs were detected in the upper 50 cm of the core, excess ^{210}Pb data points were too few to calculate sediment deposition rates.

Significant concentrations of Ba and Mn occurred in elutriate-test filtrate (ETF). Concentrations were as high as 900 $\mu g/L$ for Ba (middle interval of core SR-S2) and 6,500 $\mu g/L$ for Mn (upper interval of core CB-S6a). Barium may be released from the dissolution of Ba adsorbed to clay-size particles. Colloidal Mn may be a source of the Mn concentrations.

Standard and oxic elutriate tests were made on sediments in the middle interval of core SR-S2 (0.9 to 4.1 m). Elutriate-test filtrate Mn concentrations are virtually unaffected by the presence or absence of oxygen during these tests. On the other hand, the ETF Ba concentration is larger in the standard test (reducing conditions) than in the oxic test. The smaller concentration in the oxic test probably results from the formation of insoluble $BaSO_4$, and the larger concentration in the standard test likely represents dissolved Ba in interstitial water. In contrast, ETF Fe concentrations in the standard test (440 $\mu g/L$) are smaller than in oxic tests (800 $\mu g/L$). These differences may be attributed to iron sulfides, which consume available oxygen (O_2) in the process of releasing dissolved Fe. Thus oxic ETF Fe concentrations would be expected to exceed standard ETF Fe concentrations because oxic-test O_2 is abundant in comparison to standard-test O_2.

Sediment-associated organochlorine compounds were detected in cores SR-S2 and CB-S6. Compounds detected and quantified include aldrin, chlordane, DDD, DDE, DDT, dieldrin, PCB's, PCN's and heptachlor epoxide. Compounds in the upper (0 to 0.9 m) and middle (0.9 to 4.1 m) intervals of SR-S2 represent concentration maxima for the study. Organochlorine compounds appear confined to specific areas of core CB-S6, where large concentrations of silt-clay and TOC exist. In general, organochlorine compounds are preferentially sorbed to fine grained TOC-rich sediments.

Of the nine groups of acid/base-neutral extractable compounds on the EPA organic priority pollutant list, only phthalate esters (PE) and polycyclic aromatics (PA) were detected in bottom material. PE compounds were detected in small concentrations (7 to 20 μg/kg) and PA compounds in larger concentrations. Of 16 PA determinations in CB-S6b (0.56 to 0.76 m), 10 were detected; concentrations ranged from 8 to 278 μg/kg. Of 16 PA determinations made at upper (0 to 0.9 m), middle (0.9 to 4.1 m), and lower (4.1 to 5.7 m) intervals of SR-S2, only three or four PA's were detected in each interval. PA's in core CB-S6b probably occurred because of petroleum spills associated with maintaining naval vessels during the late 1940's and early 1950's. PA compounds in core SR-S2 were likely emitted from a nearby incinerator.

Critical-band metal concentration determinations were made on bulk sediment excised from cores CB-S6a, CR-S1, and SR-S2. Critical-band Cd concentrations in CR-S1 (0.5 to 0.6 m) were considerably larger than those in Columbia River basalts. However, the critical-band Cd concentrations are not representative of concentrations throughout core CR-S1 and are not likely to degrade the chemical quality at a disposal site. Conversely, critical-band concentrations of Pb and Zn in core SR-S2 (1.10 to 1.15 and 2.70 to 2.78 m) are large in comparison to those in CR basalts. These SR-S2 concentrations are not confined to critical bands, but are distributed throughout core SR-S2 (0.9 to 4.1 m).

Of the metals examined in five depth intervals of core CB-S6b, Cd, Hg, and Zn concentrations differ with depth in the <100-μm fraction; none vary with depth in the >100-μm fraction. In addition, concentrations of Cd, Cr, Cu, Fe, and Zn are substantially larger in the <100-μm fraction; Ni, Mn, and Pb show no differences in either size fraction. Cesium-137 determinations and redox conditions suggest that large Cd, Hg, and Zn concentrations in upper depth intervals result from human processes that occurred during the 1950's when naval vessels were being maintained near core site CB-S6b.

Results of two different techniques to chemically extract metals from bottom material imply that much Cd and Pb is sorbed to particle surfaces in upper intervals of cores SR-S2, CR-S5, and CB-S6a. However, because Cd is associated with relatively large TOC concentrations, it may be unavailable to benthic organisms at the disposal site. The fate of Pb is not as certain; concentrations of extractable Fe, which decrease the bioavailability of sorbed Pb, are not large enough to ensure that Pb exists in non-bioavailable form. In fact, estimated concentrations in clam tissue are close to the World Health Food Standard. Chemical extractions suggest that only small amounts of Hg are sorbed to particle surfaces, but even these concentrations can be bioavailable when the concentration of total volatile solids is small. However, the total volatile solids concentrations are large and estimated concentrations of Hg in clam tissue are expected to fall within limits set by the U.S. Food and Drug Administration.

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