

AN ABSTRACT OF THE THESIS OF

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Title: SEDIMENT CHARACTERISTICS AS INDICATORS OF TOXIC CADMIUM AND
COPPER CONCENTRATIONS IN OREGON ESTUARIES.

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Dr. Danil R. Hancock

Several physical and chemical characteristics of sediments have been proposed for use in tiered testing plans to predict the presence of trace metals in estuarine sediments. Correlations often exist, but the mere presence of a trace metal does not indicate toxicity; a more thorough approach is needed.

Available information on natural background concentrations, bioavailability, and toxicity of Cd and Cu was used to determine concentrations likely to cause toxic effects in Oregon sediments.

Concentrations of Cd and Cu in 31 sediment samples from nine Columbia River sites were measured using atomic absorption spectrophotometry. Correlations between the Cd and Cu concentrations and the sediment characteristics of grain size, oil and grease, volatile solids, total organic carbon, pH, iron, manganese were calculated. The percent of volatile solids was the factor which most often correlated significantly with Cd, whereas median grain size was the factor which most often correlated significantly with Cu.

The characteristics best suited for predicting toxic concentrations of Cd and Cu--especially when data from other Oregon estuaries were considered--are, by weight, >5% volatile solids or

>35% silt-size or finer grains. Below these indicator values,
sediments with toxic concentrations of Cd or Cu are highly unlikely.

Sediment Characteristics as Indicators
of Toxic Cadmium and Copper Concentrations
in Oregon Estuaries

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SEDIMENT CHARACTERISTICS AS INDICATORS OF TOXIC CADMIUM AND
COPPER CONCENTRATIONS IN OREGON ESTUARIES

INTRODUCTION

The world's estuaries have often been used as dumps for wastes, where it is thought that they will be transported out to sea and diluted. The mixing of fresh and salt water that occurs in estuaries, however, causes many contaminants to precipitate out and be deposited in the sediments. The contaminants trapped in the sediments become quite concentrated and pose a toxic threat to estuarine organisms.

A major concern in estuaries is trace or heavy metal toxicity from both natural and anthropogenic sources. Trace metals causing toxicity include cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), and zinc (Zn) (Bryan, 1984). Trace metal pollution can be measured directly in the sediments, in the overlying water, and with bioassays. Each of these methods, in turn, is an improvement on the preceding one, as well as being more expensive in time and money. Each method also presents unique measurement problems.

The high costs of testing have led to the recent development of "tiered" testing plans by government agencies and research institutes. A typical plan has three or four "tiers" or levels of testing (Turner, in press; Dillon and Gibson, 1986). Failure of the sediment to meet any of the criteria of one tier leads to testing at the next, more complex tier. Effort is focused, thereby, on those

sediments most likely to present a toxicity problem. Bulk sediment characteristics should not be the sole criteria for deciding whether a sediment is toxic or not. The bulk characteristics merely indicate that the sediment should be tested more thoroughly.

The key to a tiered plan is deciding when to invoke the next level of testing. As the primary screening device, the first tier is crucial--too little sensitivity and toxic sediments are not identified, too much sensitivity and the costs of unnecessary testing escalate. To determine the appropriate sensitivity for a first tier consisting of physical sediment characteristics, at least four main questions need to be answered. First, what are the natural background concentrations of the trace metals of interest? Second, if background concentrations are exceeded, how much of the excess metal is bioavailable? Third, if bioavailable, what are the concentrations at which the metal becomes toxic? Fourth, what sediment characteristics are associated with these toxic concentrations?

The answers are different for each trace metal. In Oregon, however, two of the toxic metals of most concern are Cd and Cu. The two metals arise from different sources and have the opposite fate in estuaries. Copper pollution in estuaries is often caused by industrial effluent or anti-fouling compounds applied to boats. Its behavior in estuaries is typical of most metals, it precipitates out of the water column and deposited in the sediments. Cadmium pollution, on the other hand, is usually caused by runoff of municipal wastewater. In an estuary, Cd is released from the

sediments into the water column, unlike Cu and most other metals. Since Cd and Cu arise from different sources and exhibit the two extremes of metal behavior in estuaries, they were used in this study to determine the best characteristics for use in predicting sediments with toxic trace metal concentrations.

REVIEW OF LITERATURE

Estimated Background Concentrations

Background concentrations of trace metals may be established in two ways: estimation from sediment sources and measurement of sediment samples from pristine reference sites or depths.

Estimates of crustal averages, for instance, range from 0.1-0.2 ppm for Cd and 24-40 ppm for Cu (Cox, 1979; Nriagu, 1979; Nriagu, 1980; Thornton, 1986). In Oregon, the natural background concentrations in estuaries are different for each of the five major drainages, reflecting the different bedrock material, soil contents, heavy mineral assemblages, and sediment transport and deposition patterns (Kulm et al., 1968; Baldwin, 1976; Shacklette and Boerngen, 1984).

Elevated background concentrations of Cu (>40 ppm) occur in sediments formed from the weathering of basaltic parent rocks. Rivers along the north and south coasts of Oregon drain through extensive formations of basalt and so does the Columbia River. Cadmium background concentrations of >1 ppm are present in sediments derived from organic-laden, sedimentary bedrock (Nriagu, 1980) and this type of bedrock occurs only in the Yaquina and Rogue estuaries in Oregon. The Rogue River drains through black shales, a type of rock particularly enriched in Cd (Lund et al., 1981). Past mining activities in the Klamath Mountains (Pardee, 1930), may also have enriched Rogue River sediments.

Soil concentrations of Cd and Cu show a similar pattern of distribution. Soils from the North Coast, Columbia River, and Klamath basins are enriched in Cu and soils from the Klamath basin are enriched in Cd (Shacklette and Boerngen, 1984).

Sediments whose heavy mineral suites contain over 89% pyroxenes and amphiboles, are found in the Columbia, Tillamook, Umpqua, and Rogue estuaries (Kulm et al., 1968). Pyroxenes and amphiboles are usually rich in Cu, containing 128 and 78 ppm on the average (Wedepohl, 1978; Cox, 1979). Heavy minerals are present in varying amounts in different estuaries, however, and their total contribution to the sediment may be small, 15% or less in the Columbia River, for instance (White, 1970; Whetten et al., 1969).

Information on trace metal concentrations in the parent rock types, soils, and heavy mineral assemblages provides an estimate for the Columbia River of background concentrations of Cd and Cu derived from natural sources. In Columbia River sediments, background Cd concentrations should be near the average crustal abundance (<1 ppm) and Cu towards the high end of crustal abundance (30-40 ppm).

All of the above are estimates of the maximum, natural background concentrations since some of the sediment in the main channels of most Oregon estuaries is derived from oceanic beaches and headlands (Peterson, 1984). These littoral sediments are usually coarse sands lower in trace metal concentrations due to larger grain size, different parent rocks, or leaching of trace metals by saltwater.

Bioavailability

The most bioavailable and toxic forms of Cd and Cu in estuaries are the dissolved cations Cd^{2+} and Cu^{2+} (Sunda et al., 1978; Magnuson et al., 1979; Borgmann, 1983; Nebeker et al., 1986). Cadmium and Cu bound to the sediments are much less toxic, but occur in much greater concentrations--about 10^3 times the Cd and 10^5 times the Cu in the overlying water (Phillips, 1980; Bryan, 1985).

The sediment fraction that the metal is associated with determines how easily it is released and thus, its availability to organisms. Sequential chemical extractions have shown most of the sediment-bound Cd in estuaries to be associated with the bioavailable fractions of the sediment--the exchangeable and reducible fractions. Most of the Cu, on the other hand, is associated with the bioresistant organic and residual fractions (Calmano and Forstner, 1983; Brannon et al., 1976).

Only one published study has included chemical extraction data from Oregon sediment fractions. Brannon et al. (1980) analyzed 32 sediment samples from across the United States. The five samples from the Columbia River showed Cd to be more associated with the residual fraction than Cu.

Unfortunately, none of the existing sequential extraction schemes specifically delineates a sediment fraction and none of them allow the prediction of metal bioavailability to a wide variety of organisms (Luoma, 1983). Avoiding contamination while handling the samples is also difficult (Rapin et al., 1986).

Another method to determine the amounts of trace metals released from sediments is to centrifuge the sediments and remove the interstitial water. If the metals in interstitial water are in equilibrium with those in the sediment, measuring the metals in solution indicates their bioavailability from the sediment.

A more elegant approach to measuring trace metal release is to conduct an elutriate test. An elutriate test simulates the mixing between the sediments and water that occurs during processes such as dredging and waste disposal. Brannon et al. (1976), found that net mass release of Cu during elutriate tests significantly ($p < 0.01$) correlated with long-term release of Cu in four-month ($r^2 = 0.695$) and eight-month ($r^2 = 0.561$) leaching tests. Cadmium concentrations in elutriates were weakly correlated with four-month leachates ($p < 0.05$, $r^2 = 0.203$).

Although there are positive correlations between elutriate releases of metals and long-term leaching, the relationship is qualitative rather than quantitative. Not surprisingly, elutriate tests, which are designed to mimic conditions during dredging, are better at predicting short-term than long-term releases.

Field studies have shown only transitory releases of metals other than Mn from dredged sediments. Cadmium, however, is one of these easily released metals. Concentrations of 0.08 to 2.5 ppb have been observed for a few minutes in the water column after disposal of dredged material (Brannon et al., 1976).

Toxicity

Concentrations of Cd²⁺ and Cu²⁺ causing acute toxicity have been determined for many organisms. Toxicity varies with pH, salinity, temperature, redox conditions, and other environmental factors, as well as from organism to organism. Some general figures have been published (Table 1).

Table 1. Marine 96 hr LC₅₀ (milligrams/L).

	Cd	Cu
Fish	22-55	2.5-3.2
Crustaceans	.015-47	.170-100
Mollusks	2.2-35	.140-2.3
Polychaetes	2.5-12	.16-.5
Echinoderms	.820	-----

from Connell and Miller (1984)

Most of the LC₅₀ values are in the 1000 ppm range for Cd and an order of magnitude less for Cu. Sublethal concentrations are smaller yet. Eisler (1979) gives the following values in milligrams/L (ppm), for sublethal Cu effects in some marine organisms: Algae - .05, mussels and oysters - .025-.027, clams - .025, other mollusks - .01-.012, and a sensitive flatfish - .01. Mysid spp. are chronically affected by Cd concentrations of .007-.008 ppm--they are one of the most sensitive saltwater organisms that is usually tested (Gentile, 1984). Bryan (1985) and Lussier et al. (1985) give .001 to .01 ppm as the threshold for toxic effects of both Cd and Cu, which is 10-100 times greater than most background dissolved concentrations (Coombs, 1979; Phillips, 1980; Bryan, 1985).

An approximate value for toxic amounts of trace metals in

sediments can be calculated using these data. If Cd is toxic at .001 milligrams/L (ppm) or more in solution, then a concentration greater than 1 ppm (micrograms/g) in the sediment presents a danger to estuarine biota. This is a conservative estimate, for most dissolved Cd in estuaries, such as the Columbia is complexed with chloride ions. For example, when the salinity is only 5 ppt less than 20% of the dissolved Cd is present as the free cation (Mantoura et al., 1978; Raspor, 1980). Even allowing for seasonal variation, bottom water in the Columbia River should be more saline than this through at least river mile 18 (Army Corps of Engineers, Portland District, 1987). Thus, the actual concentration at which a sediment is denoted as toxic may need to be modified by location, depending on salinity or other factors such as organic content.

The equivalent toxic concentration of Cu in the sediment is 100 ppm (microgram/g). These values, 1 ppm Cd and 100 ppm Cu, are similar to those that Tetra Tech (1986) determined in their studies of sediments from Puget Sound, Washington. They found the lowest values for an apparent effects threshold (concentration above which statistically significant biological effects would always be predicted) to be 3.4 ppm Cd and 160 ppm Cu.

Correlated sediment characteristics

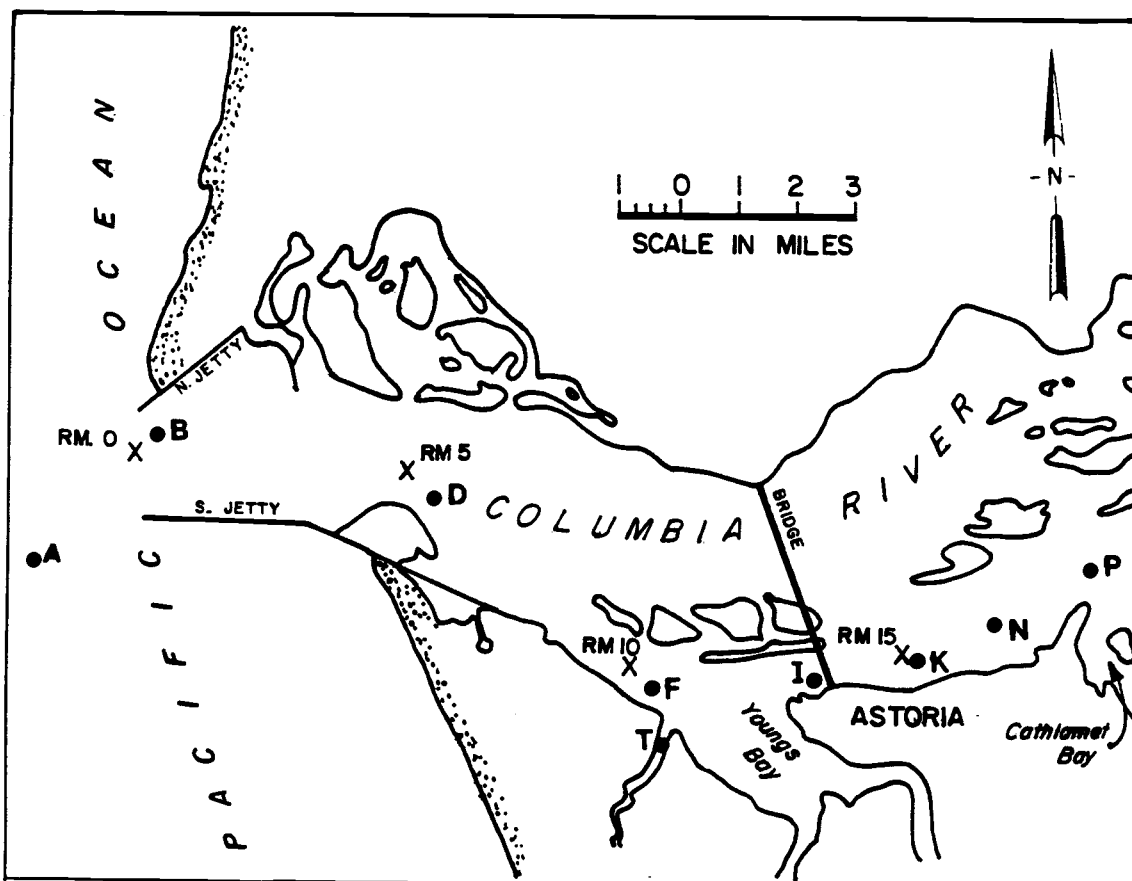
Previous researchers have found that grain size, oil and grease content, volatile solids and total organic carbon are physical characteristics that are associated with trace metal concentrations

in other estuaries (Donazzolo et al., 1981; Luoma and Bryan, 1981; Cosma et al., 1982; Luoma, 1983; Carruesco and Lapaquellerie, 1985; and Krom et al., 1985). A few studies of Oregon sediments have shown similar correlations. Hancock et al. (1984) found mean grain size to be the physical characteristic most highly correlated with Cd in Coos Bay. When other metals were considered as well, they found organic content to be the best predictor of contamination. Fuhrer (1986) found extractable Cd negatively associated with silt and clay while extractable Cu was positively associated with inorganic carbon ($P < .10$) in eight samples from the lower Columbia River. Results from a more recent study (Fuhrer and Horowitz, in press) indicate the opposite, that Cd is positively associated with silt and clay and that both Cd and Cu are associated with organic carbon ($P < .10$).

MATERIALS AND METHODS

Nine sediment cores were taken from the main navigation channel in the Columbia River (Figure 1), in conjunction with a channel-deepening study done by the U.S. Army Corps of Engineers, Portland District (1987). The samples were taken using a pneumatically driven, vibrating corer, 3.5 inches in diameter. Each 6- to 9-meter core was cut into 2-meter sections, capped, and put on ice before shipment to the laboratory. Core sections were stored in a freezer at the laboratory until tested. All sediment samples were tested within twelve weeks. (Although some shifting of metal between different sediment fractions may have occurred during storage due to changing redox conditions (Rapin et al., 1986), the amount of metal extracted during the acid digestion would not since it does not, distinguish between the different fractions.)

Each core section was split lengthwise and one of the halves was archived. A series of subsamples was taken from the remaining half. The first subsample was material from approximately the first meter of depth. The second was material from the next meter. The third subsample was from the bottom meter of the core, which was below past-dredging depths. A fourth subsample, when taken, was a composite of dark, fine-grained bands of material between the depths of the second and third samples. The subsamples were sent to the Army Corps of Engineers' Materials Testing Laboratory, in Troutdale, Oregon, for physical and chemical analysis.



<u>SITE</u>	<u>RIVER MILE</u>
A	-3.0
B	0.5
D	5.5
F	10.5
I	13
K	15
N	16.5
P	18.5
T	11 (1 mile up Skipanon)

Figure 1. Map of Columbia River sample sites

One half of each sediment subsample was used to determine grain size and percentage of volatile solids by settling velocity and weight loss upon ignition at 550 C (Methods D421-58, D422-63, D2487-69, American Society for Testing and Materials). The other half was refrozen until chemically analyzed.

For trace metal analysis, the subsamples were digested with nitric acid and hydrogen peroxide, followed by HCl as the final reflux agent. During addition of each reagent, the subsample was heated to 95 C. This same procedure was used to prepare the samples for both flame and graphite furnace atomic absorption spectrophotometry (AA) to determine trace metal concentrations (Method 3050, U.S. Environmental Protection Agency SW-846, 1982). Flame AA was used for both Cu and Cd, but Cd was also analyzed with graphite furnace AA, since its concentration often falls below the detection limits of flame AA.

Standard elutriate tests were run on samples F2, I2, and P2 (Methods according to U.S. Army Engineer Waterways Experiment Station, 1981). Aerated elutriate tests were run on T1 and T2 (Methods according to U.S. Army Engineer Waterways Experiment Station, 1985).

Spearman rank correlations (Scheffler, 1980) were calculated between the physical sediment characteristics and Cd and Cu concentrations using the SYSTAT computer statistics program. This nonparametric correlation test was used because the Cd data were markedly skewed towards the detection limit of the analytical equipment.

RESULTS and DISCUSSION

Trace Metal Concentrations

Concentrations of Cd and Cu in the 31 Columbia River sediment subsamples analyzed with flame AA (Table 3) were comparable to those in other studies of the Columbia River (Fuhrer, 1982; Fuhrer, 1986) and Coos Bay estuaries (Hancock et al., 1984; Sollitt et al., 1984).

Background concentrations were calculated by averaging the metal concentrations in the subsamples taken from the deepest part of each of the 9 cores. The background concentrations of Cd were 1.3 ± 0.04 ppm. Background Cu concentrations were 15.8 ± 6.35 ppm. The Cd values are higher than expected from the sediment sources of the Columbia River, and the Cu values, lower (Table 5). Analysis of samples from Yaquina Bay (Appendix B) also showed the same pattern of higher than expected Cd and lower than expected Cu.

The elevated Cd concentrations in the Columbia River are particularly surprising since these samples are taken at depths below any likely anthropogenic input and they do not decrease in pH enough from the surface to expect much formation of sulfides (Forstner, 1980; Horowitz, 1985)). The explanation apparently lies in the analytical methods used.

Precision of the flame AA was better. The two duplicate samples run for quality control showed 7% and 0% relative differences for flame AA, versus 88% and 45% relative differences for furnace AA. Recovery of two Cd-spiked samples was 100% for both

Table 2. Columbia River physical sediment analysis

Site	Depth(m)	%Sand	%VFSand	%Silt	%Clay	Median(mm)
A1	1.50	84.80	12.10	0.70	0.00	0.180
A2	5.64	98.20	87.20	68.80	12.00	0.038
A3	7.65	96.50	37.60	3.50	0.00	0.150
B1	0.81	91.60	38.20	13.70	2.00	0.150
B2	2.31	99.80	97.60	96.80	0.00	0.056
B3	5.55	94.90	29.00	4.90	0.00	0.170
D1	0.90	88.70	2.90	0.60	0.00	0.180
D2	7.08	87.10	71.40	54.40	8.00	0.050
D3	9.00	68.30	13.00	7.10	0.00	0.200
F1	1.80	80.00	58.20	50.80	10.00	0.060
F2	1.80	61.10	7.50	3.90	0.00	0.200
F3	5.28	91.80	12.70	5.90	0.00	0.170
F4	8.70	99.70	88.20	0.30	12.00	0.043
I1	0.63	18.10	8.70	5.80	0.00	0.400
I2	1.53	92.90	64.90	40.90	13.00	0.080
I3	5.16	90.70	11.30	2.70	0.00	0.180
I4	6.09	96.50	71.20	43.30	8.00	0.075
K1	0.90	40.80	23.50	18.00	2.00	0.300
K2	4.35	99.00	54.20	26.40	5.00	0.120
K3	8.10	98.00	36.50	15.40	2.00	0.150
N1	1.20	24.00	4.80	1.90	0.00	0.330
N2	5.19	51.90	13.70	6.30	0.00	0.230
N3	8.46	98.90	85.60	59.80	11.00	0.043
P1	1.02	31.20	6.40	3.00	0.00	0.300
P2	1.92	99.00	72.30	33.90	6.00	0.080
P3	5.10	98.50	84.80	49.10	8.00	0.060
P4	8.70	98.30	87.90	62.50	16.00	0.025
T1	1.62	98.10	90.30	82.20	14.00	0.019
T2	2.88	97.00	88.40	80.40	16.00	0.022
T3	4.17	27.80	4.90	2.20	0.00	0.300
T4	8.70	93.90	25.60	18.20	5.00	0.170

Sand=<0.250 mm, very fine sand=<0.125mm, silt=<0.062mm,
clay=<0.004mm, median=median grain size.

Table 3. Columbia River chemical sediment analyses

Site	pH	Oil	%Vol	TOC	Fe	Mn	Cd*	Cd**	Cu
A1	8.1	700	0.80	1.0	13000	130	0.18	0.70	8.3
A2	8.1	2800	4.60	31.0	21000	110	0.43	0.69	4.0
A3	8.5	-	1.10	19.0	18000	160	0.15	1.2	7.9
B1	8.3	780	1.20	17.0	20000	220	0.25	1.5	15.0
B2	8.5	-	0.80	-	18000	170	0.20	1.3	8.3
B3	8.5	-	0.90	-	20000	200	0.28	1.5	9.2
D1	7.6	-	0.70	2.0	17000	160	0.25	1.4	91.0
D2	8.0	-	3.80	-	21000	370	0.25	1.4	23.0
D3	8.5	-	1.60	-	20000	220	0.11	1.5	2.0
F1	7.9	2000	4.10	11.0	21000	220	0.58	2.0	32.0
F2	7.3	1900	0.60	2.0	15000	140	0.11	0.37	5.0
F3	8.7	970	0.80	2.0	14000	160	0.11	1.2	7.0
F4	8.6	-	3.10	5.0	21000	470	0.24	1.5	28.0
I1	7.6	980	0.80	1.0	16000	200	0.19	1.2	16.0
I2	7.9	2200	3.10	11.0	20000	430	0.23	2.3	1.5
I3	8.2	-	0.70	1.0	15000	150	0.21	1.4	5.0
I4	8.2	-	3.10	23.0	20000	230	0.24	1.0	18.0
K1	7.8	-	1.50	-	16000	210	0.22	1.3	6.9
K2	8.4	1200	2.20	15.0	20000	300	0.22	1.3	16.0
K3	8.4	-	1.40	-	19000	160	0.20	1.0	11.0
N1	8.0	-	0.50	-	16000	200	0.15	1.3	11.0
N2	7.8	-	0.80	-	18000	180	0.43	1.4	17.0
N3	8.1	-	3.50	11.0	22000	510	0.25	1.5	32.0
P1	7.2	730	0.50	10.0	15000	190	0.15	1.1	11.0
P2	7.8	2800	2.50	11.0	20000	300	0.21	0.67	15.0
P3	7.9	1500	4.10	15.0	21000	430	0.25	1.1	23.0
P4	7.9	-	4.30	12.0	21000	390	0.24	1.5	20.0
T1	7.6	1700	4.60	25.0	21000	340	0.63	1.6	34.0
T2	7.8	1500	4.70	33.0	20000	300	1.83	1.5	31.0
T3	8.6	510	1.00	1.0	14000	160	0.12	1.2	9.0
T4	9.1	620	1.30	12.0	20000	190	0.15	1.0	14.0

Cd* determined by furnace AA, Cd** determined by flame AA,
 toc=total organic carbon, vol=volatile solids, oil=oil & grease
 "-="not tested

with flame AA, and 109% and 92% with furnace AA.

The concentrations of Cd measured by flame AA, although more precise, were usually 2-6 times higher than those for the same Columbia River sample measured by furnace AA. Furnace AA gives lower concentrations because of its greater sensitivity. Furnace AA is better for measuring trace metals which are present in low concentrations, such as Cd.

There were, however, some obvious problems with precision in our study. Possible reasons for the lack of precision with furnace AA are noted by Raspor (1980) and in ASTM's commentary on graphite atomic absorption spectrophotometry (Method D3919-80, American Society for Testing and Materials). Those most applicable to this study are volatilization, matrix interferences, and sensitivity to contamination through handling such small samples. The ramped technique used (carefully increasing the temperature in stepped intervals) normally controls the problem of volatilization, but with seawater samples, the salts and organic materials volatilize at low enough temperatures to interfere with the determination of Cd, one of the most volatile metals (Van Loon, 1982).

The concentrations indicated by furnace AA are probably closer to true Cd concentrations in sediments. Background Cd concentrations for Columbia River sediments using furnace AA values were 0.21 ± 0.04 ppm. This agrees with concentrations in sediment sources, less than 1 ppm. (Table 5). Fuhrer and Horowitz's recent study (in press) of other Columbia River sites also found similar background concentrations (0.5 ppm).

My results seem to show that previous measurements of elevated cadmium concentrations in Oregon may have been due to analytical problems, rather than contaminated sediments, since Cd concentrations were close to flame AA detection limits of 1 ppm. The dilution required for processing adds another source of error. The additional handling while diluting may have introduced small amounts of trace metals. Or a minute difference between samples, when multiplied by the dilution factor, may also have caused higher readings.

More studies should be done with furnace AA, but in order to compare my results with previous analyses of Oregon sediments, flame AA-determined concentrations were used for calculating the correlation coefficients shown in Table 4. The possibility that Cd values determined by flame AA are somewhat high should be kept in mind.

Measured concentrations of Cu, on the other hand, were surprisingly low in most Oregon estuaries considering the sediment sources (Table 5). However, Cu concentrations were within anticipated concentrations. For example, the Columbia River had higher Cu concentrations than mid-coast estuaries, such as Yaquina. The most enriched sediments, with an average of over 50 ppm Cu, occurred in Tillamook Bay (unpublished data). This enrichment is due to the low input of sands from ocean beaches (Peterson, 1984) and surrounding parent rocks of basalt.

The wide variation in Cu concentrations between samples in a single estuary was puzzling. Perhaps the occurrence of Cu tends to

fluctuate because Cu is more tightly bound to certain sediment components. Concentrations of Cu may be more dependent on local variations in sediment constituents than Cd.

Cadmium concentrations released from Columbia River sediments to the water during elutriate tests were 10^{-1} to 10^{-2} times that of the sediments. Copper elutriates were 10^{-3} the concentration of the Cu in the sediments. Both of these releases were 10-100 times higher than expected under long-term equilibrium conditions. The elutriate concentrations, however, were similar to those in the receiving water (23 ppb Cd and 25 ppb Cu) and did not appear to be a significant increase over background dissolved concentrations.

Correlations

Spearman rank correlations showed no correspondence between physical characteristics and Cd concentrations in the Columbia River sediments analyzed by flame AA (Table 4). When data from other estuaries, including Yaquina, Tillamook, Umpqua, Coos (Fuhrer, 1983; Fuhrer, 1984; Hancock et al., 1984) and earlier Columbia studies (Fuhrer, 1986; Fuhrer, in press) were included, however, the percentage of volatile solids was the physical characteristic that most consistently showed high correlations with Cd (Appendix B).

Median grain size was the characteristic most often significantly related to Cu in the Columbia and other estuaries (Table 5). Other physical factors varied in correlation strengths from estuary to estuary.

Concentrations of Cd determined by furnace AA, unlike those determined by flame AA, closely corresponded to many physical sediment characteristics, especially median grain size (Table 4).

The only other obvious correlation trend was that the two measures of organic content, volatile solids and TOC, were significantly correlated with smaller grain sizes ($P < .01$).

Table 4. Cadmium correlations

	P<.01	P<.05	Not significant
Col flame	none	Cu(.409)	sand, vfsand silt, clay median, oil volatile solids TOC, pH
Col furn	Cu (.757) median (-.710) vfsand (.702) clay (.694) silt (.674) Fe (.671) volso1 (.512)	Mn (.434) sand (.415)	oil TOC pH
Coos	oil (.751) volso1 (.555) mean (-.544) Cu (.519) median (-.516)	none	none
All Est	volso1 (.476) TOC (-.405)	none	sand, vfsand silt, clay Fe, Mn median

Table 5. Copper correlations

	P<.01	P<.05	Not significant
Col	median (-.596) vfsand (.571) silt (.546) Mn (.544) Fe (.520)	clay (.575) sand (.413) Cd (.409)	oil volso1 TOC pH
Coos	volso1 (.880) median (-.863) mean (-.817) oil (.658) Cd (.519)	none	none
All Est	median (-.688) Mn (.673) Fe (.535)	clay (.329) TOC (.305)	sand, vfsand silt, oil volso1

Management Strategies for Oregon sediments

Jenne et al. (1986) outline four basic approaches to managing chemical contamination of sediments: background, nondegradation, water quality, and equilibrium partitioning.

The background approach allows trace metal concentrations to be equal to natural background concentrations or a certain percentage above them, such as 150%. Defining the background concentrations is difficult, since few places on earth have not been influenced at least to some degree by humans. "Permissible" concentrations above background are arbitrary and do not represent the actual biological hazard.

Nondegradation is not a worthwhile approach for Oregon, for, unlike sites along the Gulf Coast or East Coast of the U.S. or in Europe, Oregon does not have trace metal concentrations consistently and significantly elevated above natural background. Some elevation of contamination above background can occur without being toxic.

Jenne et al. (1986) mention several problems with the water quality approach. Basically, low, fluctuating concentrations of dissolved metals are difficult to evaluate. If used, however, the water quality approach calls for identifying samples that cause dissolved concentrations to exceed standards set by the Environmental Protection Agency (EPA, 1980). The EPA set 4.5 micrograms/L for Cd and 4 micrograms/L for Cu as a 24-hour average concentration causing acute toxicity in marine life. This means sediment concentrations of 4 ppm Cd and 400 ppm Cu are toxic,

assuming a $1:10^3$ water to sediment ratio (Phillips, 1980; Bryan, 1985).

Recognizing that trace metal concentrations in the sediment are the best long-term indicators of toxic effects, Jenne et al. (1986) proposed the establishment of equilibrium models for management decisions rather than the background, nondegradation, or water quality approaches. Equilibrium models require accurate field measurements and understanding of all of the physical, chemical, and biological interactions with metallic species in the sediment and water. Although clearly the best management approach, a complete understanding of the complexities involved in equilibrium partitioning does not yet exist. The best management approach for Oregon sediments at present, appears to be a hybrid of the background and water quality approaches. This approach accomplishes two things. First, it allows concentrations to exceed the background concentrations by margins that avoid most false positives, and takes into account small variations in background concentrations caused by changes in parent rocks, salinity, or other factors from estuary to estuary. Second, it allows permissible concentrations to be set low enough to encompass all sediment concentrations that may release toxic amounts of Cd^{2+} and Cu^{2+} into the water column. This last should include some margin for error since release of trace metals from sediments is influenced by many different factors.

Following the guidelines above, the concentrations of Cd in Oregon sediments that indicate a need for more extensive testing at

the next tier, are those that exceed 2 ppm. A similar value for Cu is 40 ppm.

SUMMARY

One possibility currently being considered for the first tier of a tiered testing plan for Oregon, the "20-1000-5 plan," includes three physical parameters: >20% silt (<.062mm grain size), >1000ppm oil and grease, and >5% volatile solids (Turner, in press). These parameters detected 71.8% of samples with Cd or Cu concentrations greater than permissible levels when our flame AA data was combined with that from other studies. The frequency of "false positives," where an excessive concentration was indicated but did not exist, was 57.4%.

One of the biggest drawbacks of the 20-1000-5 plan is that every time oil and grease exceeded 1000 ppm or volatile solids exceeded 5%, the sediment was already identified by a silt content of greater than 20%. Thus, the silt content was the only essential parameter of the three; oil and grease and volatile solids were superfluous.

A second plan, the "5-08 plan," uses volatile solids > 5% and median grain size < 0.08mm to indicate the need for further testing. It is a simpler alternative based on the calculated correlations. The 5-08 plan has a detection rate of 63%, slightly worse than the 20-1000-5 plan. Its false positive rate of 50% is slightly better. The only substantial improvement the 5-08 plan represents is in simplicity because it does not require a separate oil and grease analysis.

The third plan, the "35-5 plan," is simpler yet as well as more

accurate. Parameters of 35% or more silt and 5% or more volatile solids detected 71.8% of the sediments with excessive Cd and Cu, giving only 26% false readings. Keeping the 5% volatile solids criteria allows detection of high organic content while making the grain size criteria more exclusive and thereby cutting down on the number of false positives.

All three of the plans predict the sediment concentrations that would exceed the EPA's water quality criteria (Cd > 4.5 ppm and Cu > 4 ppm) at greater than 80% accuracy, missing only 1 of 7 sediments with those concentrations. The 1 unidentified sediment was taken from site E4 in Coos Bay (Appendix B). It was a sandy sediment with low organic content and it could not have been spotted except by lowering the physical parameters to such a degree that virtually all the sediment samples would have been identified as toxic. Also the percentage of silt was not available for this site and, if calculated, may have indicated toxicity.

Other trace metals also appear to be even more strongly correlated with the same sediment characteristics as Cd and Cu (Tables A-2 and B-3). Concentrations of As, Cr, Pb, Hg, and Zn that exceed the average concentrations are detected in at least 40% of the cases and the false values are less than 81% in the 3 proposed tier testing plans (Table B-4). (Expected natural background concentrations of these other metals in Oregon estuaries have not been determined yet. For the calculations of detection and false positives, sediments containing above average concentrations of metals were the ones identified.) Thus, the use of sediment

characteristics in the first tier of a tiered testing plan works reasonably well for most toxic trace metals.

Each of these approaches to predicting toxic concentrations of trace metals by using sediment characteristics, the 20-1000-5, the 5-08, and the 35-5 plans, should be evaluated further. Background concentrations need to be determined for estuaries other than the Columbia River. Metals other than Cd and Cu need to be examined along with organic contaminants. (Oil and grease content, for example, may be a good predictor of organic contaminants, such as PCB's or pesticides.) Bioavailable and toxic concentrations should be determined on a wider range of sediments and organisms. Interactions between different metals and organics also need to be examined. Many such interactions are synergistic. All of these considerations need to be incorporated into a single comprehensive management plan. Ideally, with enough data, a separate management strategy can be designed for each estuary, just as Oregon has divided the state's waters into 19 separate basins with rules for water quality standards in each (Oregon Administrative Rules 340-41). Such an approach would acknowledge the inherent differences in background concentrations, bioavailability, and correlations between estuaries.

As further study better determines how physical characteristics and trace metals interact in sediments, more accurate parameters for predicting contaminated sediments can be developed. This study just examined two trace metals, Cd and Cu, and for those two, a silt content exceeding 35% and a volatile solid percentage of greater

than 5% appear to be the most effective sediment characteristics for the first tier of a tiered testing plan for Oregon sediments.

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APPENDICES

APPENDIX A

Other Columbia River Data

Table A-1. Columbia River sediment analyses of other trace metals.

Site	As	Cr	Fe	Pb	Mn	Hg	Zn
A1	6.0	12	13,000	13	130	0.135	150
A2	35	23	21,000	24	110	0.058	130
A3	5.7	13	18,000	10	160	0.008	45
B1	9.0	15	20,000	13	220	0.011	68
B2	6.0	10	18,000	7.8	170	0.006	56
B3	5.3	14	20,000	11	200	0.009	50
D1	6.0	3	17,000	12	160	0.012	49
D2	15	15	21,000	13	370	0.014	72
D3	5.5	1.7	20,000	10	220	0.006	43
F1	15	20	21,000	25	220	0.125	120
F2	6.0	18	15,000	2.3	140	0.029	53
F3	4.8	8	14,000	13	160	0.006	43
F4	15	25	21,000	14	470	0.002	78
I1	7.5	8	16,000	13	200	0.007	57
I2	16	10	20,000	14	430	0.023	78
I3	15	8	15,000	10	150	0.005	62
I4	14	13	20,000	12	230	0.013	66
K1	7.0	12	16,000	12	210	0.009	55
K2	13	22	20,000	15	300	0.020	66
K3	6.0	12	19,000	9	160	0.034	45
N1	5.1	11	16,000	9	200	0.011	51
N2	3.4	13	18,000	12	180	0.010	61
N3	12.2	35	22,000	16	510	0.023	85
P1	4.4	14	15,000	9	190	0.011	66
P2	2.5	17	20,000	7	300	0.018	100
P3	8.6	21	21,000	10	430	0.022	86
P4	10.8	26	21,000	14	390	0.016	69
T1	2.9	13	21,000	11	340	0.042	140
T2	-	18	20,000	14	300	0.081	240
T3	3.2	13	14,000	12	160	0.001	42
T4	6.7	20	20,000	13	190	0.003	54

**Table A-2. Matrix of correlation coefficients for other metals
in Columbia River sediments.**

	Sand	VFSand	Silt	Clay	As	Fe	Mn	Pb	Hg
Sand	1.000								
VFSand	0.815	1.000							
Silt	0.683	0.944	1.000						
Clay	0.566	0.796	0.825	1.000					
As	0.208	0.263	0.307	0.399*	1.000				
Fe	0.609	0.789	0.792	0.816	0.426	1.000			
Mn	0.398	0.599	0.608	0.697*	0.226	0.727	1.000		
Pb	0.163	0.330	0.391	0.573*	0.535	0.459	0.333	1.000	
Hg	0.205	0.334	0.318	0.507*	0.120	0.347	0.154	0.243	1.000

	Median	TOC	Vol	As	Fe	Mn	Pb	Hg
Median	1.000							
TOC	-0.589	1.000						
Vol	-0.825	0.568	1.000					
As	-0.317	0.165	0.322	1.000				
Fe	-0.804	0.458	0.848*	0.426	1.000			
Mn	-0.528	0.285	0.647	0.226	0.727	1.000		
Pb	-0.422	0.396	0.543	0.535	0.459	0.333	1.000	
Hg	-0.453	0.393	0.462	0.120	0.347	0.154	0.243	1.000

d.f. = 29, $P < .05 = 0.355$, $P < .01 = 0.456$

* = best correlation for that metal

APPENDIX B

Data from Other Estuaries

Table B-1. Data from other Oregon estuaries.

Location	Site	%Sand	%VFSand	%Silt	%Clay	Median (mm)	Oil/ Grease	Volsol	TOC
Ast	7	99.00	99.00	93.00	15.00	0.015	-	3.10	15.70
Bak B	4	70.00	12.00	10.00	3.00	0.200	-	1.29	6.70
Bak B	6	99.00	99.00	93.00	13.00	0.018	-	5.53	18.00
Bak B	8	99.00	98.00	92.00	12.50	0.075	-	-	19.70
Bak B	12	80.00	2.00	0.01	0.00	0.200	-	0.81	0.90
Bak B	14	85.00	5.00	2.50	0.00	0.175	-	0.86	1.00
Cath B	6a	98.00	56.00	35.00	8.00	0.120	-	-	2.20
Cath B	6b	99.00	63.00	32.00	4.67	0.000	-	-	5.90
Cath B	6b	100.00	76.00	22.00	3.00	0.000	-	-	3.75
Cath B	6b	100.00	85.00	24.00	2.00	0.000	-	-	4.40
Cath B	6b	100.00	86.00	51.00	11.00	0.000	-	-	5.25
Cath B	6b	93.00	29.00	21.00	5.00	0.000	-	-	4.50
Chet R	2	99.00	97.00	89.00	23.00	0.009	-	6.10	-
Chet R	4	94.00	70.00	38.00	7.00	0.080	-	-	-
Chnk J	5	23.00	7.50	6.00	2.50	0.410	-	0.70	-
Chnk J	8	99.00	97.50	91.00	25.00	0.011	-	6.18	26.60
Col R	1	4.00	0.01	0.00	0.00	0.000	-	0.67	1.00
Col R	1	99.00	97.00	68.00	14.00	0.000	-	-	2.80
Col R	1	99.00	61.00	24.00	6.00	0.000	-	-	3.07
Coos B	E1	-	-	-	-	0.590	<50	0.51	-
Coos B	E2	-	-	-	-	0.200	<50	-	-
Coos B	E3	-	-	-	-	0.260	<50	0.73	-
Coos B	E4	-	-	-	-	0.200	<50	1.34	-
Coos B	E4	-	-	-	-	0.260	<50	-	-
Coos B	E4	-	-	-	-	0.260	<50	0.32	-
Coos B	E4	-	-	-	-	0.260	<50	-	-
Coos B	E4	-	-	-	-	0.270	<50	0.20	-
Coos B	E4	-	-	-	-	0.240	<50	0.20	-
Coos B	E5	-	-	-	-	0.024	440	7.35	-
Coos B	E5	-	-	-	-	0.210	370	1.84	-
Coos B	E5	-	-	-	-	0.040	490	5.50	-
Coos B	E5	-	-	-	-	0.090	300	4.30	-
Coos B	E6	-	-	-	-	0.043	540	6.55	-
Coos B	E6	-	-	-	-	0.150	385	-	-
Coos B	E6	-	-	-	-	0.046	370	6.97	-
Coos B	E6	-	-	-	-	0.150	510	4.33	-
Coos B	E6	-	-	-	-	0.026	670	7.80	-
Coos B	E6	-	-	-	-	0.045	410	5.70	-
Coos B	E7	-	-	-	-	0.007	-	11.80	-
Coos B	E7	-	-	-	-	-	1020	-	-
Coos B	E7	-	-	-	-	0.015	920	11.00	-
Coos B	E7	-	-	-	-	-	900	-	-
Coos B	E7	-	-	-	-	0.013	1050	9.20	-
Coos B	E7	-	-	-	-	0.013	970	12.90	-
Coos B	E8	-	-	-	-	0.120	500	3.70	-

Coos B	E8	-	-	-	-	0.130	680	4.70	-
Coos B	E8	-	-	-	-	0.140	320	4.20	-
Coos B	E8	-	-	-	-	0.100	490	5.20	-
Coos B	E9	-	-	-	-	0.012	1600	10.60	-
Coos B	E9	-	-	-	-	-	2000	-	-
Coos B	E9	-	-	-	-	0.017	2800	21.60	-
Coos B	E9	-	-	-	-	0.016	1840	17.90	-
Coos R	1	12.00	0.01	0.01	0.00	0.420	-	1.45	2.00
Coos R	2	26.00	10.00	7.50	2.00	0.380	-	8.79	6.00
Dpt S	10	91.00	85.00	77.50	18.00	0.018	-	17.48	76.60
Rog R	2	97.00	92.00	85.00	10.00	0.019	-	6.60	-
Skip C	6	93.00	88.00	83.00	20.00	0.012	-	13.79	74.90
Skip C	2	100.00	99.00	99.00	35.00	0.009	-	-	0.17
Skip C	2	100.00	100.00	100.00	33.00	0.008	-	-	0.11
Tans P	4	27.00	8.00	7.00	2.50	0.400	-	2.89	1.00
TilGar	2	96.00	90.00	81.00	14.00	0.023	-	11.02	26.40
Umpq R	6	40.00	1.00	0.01	0.00	0.290	-	1.62	2.00
Umpq R	8	14.00	4.00	3.50	0.00	0.380	-	1.01	1.90
Umpq R	9	80.00	17.00	6.00	2.50	0.190	-	1.18	7.00
Umpq R	11	55.00	5.00	4.00	0.00	0.220	-	1.54	3.00
Umpq R	12	50.00	6.00	4.00	0.00	0.230	-	1.40	4.00
Umpq R	15	32.00	3.00	2.00	0.00	0.310	-	1.14	1.00
Yaq B	1	55.40	0.80	0.10	0.00	0.210	-	1.00	-
Yaq B	2,3	40.00	0.20	0.20	0.00	0.280	-	0.60	-
Yaq B	4	90.00	5.00	0.01	0.00	0.170	-	0.60	6.80
Yaq B	7	96.70	7.70	0.50	0.00	0.180	-	1.40	-
Yaq B	8	97.00	15.90	1.00	0.00	0.180	-	2.80	-
Yaq B	9	92.30	32.20	5.20	0.00	0.170	-	5.50	-
Yaq B	10	33.20	2.20	0.50	0.00	0.300	-	1.30	-

Table B-2. Chemical data from other Oregon estuaries.

Site	As	Cd	Cr	Cu	Fe	Pb	Mn	Hg	Zn	Study
7	7.0	5.0	14.0	31.0	11000	10.0	190.0	0.0900	110.0	A
4	4.0	1.0	7.0	17.0	6900	20.0	130.0	0.0600	52.0	A
6	9.0	2.0	15.0	37.0	22000	30.0	230.0	0.1700	160.0	A
8	10.0	2.0	24.0	43.0	17000	40.0	280.0	0.2600	190.0	A
12	2.0	1.0	5.0	5.0	4000	10.0	54.0	0.0100	21.0	A
14	2.0	1.0	5.0	5.0	3100	10.0	52.0	0.0100	19.0	A
6a	-	0.5	55.0	28.0	41000	8.0	600.0	-	81.0	B
6b	-	1.2	45.0	22.0	39000	9.0	900.0	0.1100	126.0	B
6b	-	0.55	53.5	19.5	37500	9.0	800.0	0.7200	105.5	B
6b	-	0.5	57.0	20.5	39000	5.5	650.0	0.0500	72.5	B
6b	-	0.5	59.0	22.0	39000	10.0	700.0	0.0800	71.5	B
6b	-	0.5	45.5	25.5	40500	5.5	650.0	0.0600	75.5	B
2	9.0	3.0	10.0	37.0	9000	10.0	300.0	0.1400	41.0	C
4	8.0	3.0	30.0	72.0	20000	20.0	220.0	0.1500	85.0	C
5	3.0	2.0	4.0	4.0	4700	10.0	150.0	0.0100	22.0	A
8	10.0	8.0	18.0	44.0	17000	30.0	420.0	0.0700	135.0	A
1	4.0	1.0	2.0	5.0	5900	10.0	150.0	0.0100	25.0	A
1	-	3.6	53.0	37.0	46000	8.0	700.0	-	118.0	B
1	-	0.5	45.0	23.0	36000	3.0	600.0	-	73.0	B
E1	-	1.2	-	2.1	5000	14.0	45.0	-	99.0	D
E2	-	1.7	-	1.8	4600	12.0	56.0	-	20.0	D
E3	-	2.3	-	2.3	5600	14.0	44.0	-	45.0	D
E4	-	9.1	-	2.6	5500	12.0	33.0	-	71.0	D
E4	-	2.0	-	3.3	5800	14.0	46.0	-	65.0	D
E4	1.2	0.3	-	2.1	4590	5.2	35.0	0.0085	12.0	D
E4	2.0	1.3	-	2.3	3950	5.1	36.0	0.0125	8.4	D
E4	1.3	0.8	-	1.0	5000	3.4	31.0	0.0030	12.0	D
E4	1.2	1.8	-	2.8	5400	13.0	45.0	0.0090	13.0	D
E5	2.8	1.4	-	14.0	21600	21.0	105.0	0.0110	69.0	D
E5	3.4	1.7	-	17.0	24600	24.0	150.0	0.0120	70.0	D
E5	3.6	1.6	-	14.0	8500	19.0	131.0	0.0150	77.0	D
E5	2.4	1.1	-	5.4	10000	7.5	58.0	0.0040	29.0	D
E6	-	4.6	-	13.0	19500	25.0	200.0	-	540.0	D
E6	-	1.6	-	7.5	14100	15.0	190.0	-	67.0	D
E6	3.1	1.6	-	14.0	22300	21.0	117.0	0.0970	70.0	D
E6	2.9	1.8	-	23.0	29500	27.0	365.0	0.0200	85.0	D
E6	3.5	1.8	-	18.0	26900	25.0	150.0	0.0200	110.0	D
E6	6.1	1.7	-	18.0	24500	22.0	263.0	0.0390	87.0	D
E7	-	2.6	-	26.0	35300	32.0	330.0	-	290.0	D
E7	-	2.6	-	5.1	25400	26.0	240.0	-	180.0	D
E7	4.1	3.0	-	31.0	29600	40.0	142.0	0.0770	121.0	D
E7	7.7	2.5	-	33.0	36800	39.0	166.0	0.3300	154.0	D
E7	6.3	2.6	-	32.0	33900	37.0	209.0	0.0210	124.0	D
E7	9.5	2.4	-	29.0	35000	33.0	172.0	0.0450	121.0	D
E8	1.8	1.5	-	11.0	17000	16.0	89.0	0.0630	64.0	D
E8	3.0	1.4	-	12.0	21000	22.0	125.0	0.0450	61.0	D
E8	3.0	1.3	-	12.0	18600	16.0	102.0	0.0150	67.0	D

E8	3.7	1.6	-	17.0	23600	22.0	103.0	0.0120	87.0	D
E9	5.1	2.3	-	25.0	25300	31.0	108.0	0.0450	101.0	D
E9	6.8	2.9	-	34.0	32100	45.0	164.0	0.0270	128.0	D
E9	9.0	2.3	-	32.0	34100	38.0	203.0	0.0240	123.0	D
E9	10.6	3.1	-	34.0	38700	45.0	247.0	0.0390	129.0	D
1	1.0	1.0	14.0	4.0	6300	10.0	130.0	0.0300	24.0	A
2	1.0	1.0	22.0	7.0	12000	10.0	110.0	0.0100	37.0	A
10	12.0	1.0	30.0	39.0	31000	40.0	270.0	0.0300	120.0	A
2	6.0	1.0	20.0	20.0	3100	10.0	230.0	0.1000	13.0	C
6	9.0	7.0	12.0	50.0	19000	30.0	160.0	0.0800	300.0	A
2	-	0.5	54.0	49.0	45000	22.0	400.0	-	210.0	B
2	-	0.5	72.0	53.0	48000	26.0	500.0	-	203.0	B
4	3.0	2.0	6.0	5.0	4500	10.0	87.0	0.0200	40.0	A
2	6.0	29.0	21.0	44.0	27000	10.0	170.0	0.0300	56.0	A
6	4.0	1.0	13.0	7.0	7700	10.0	110.0	0.0500	22.0	A
8	4.0	1.0	15.0	8.0	9100	10.0	99.0	0.0200	23.0	A
9	3.0	1.0	13.0	8.0	7500	10.0	61.0	0.0300	22.0	A
11	2.0	1.0	18.0	10.0	13000	10.0	110.0	0.0300	26.0	A
12	4.0	1.0	15.0	8.0	9200	10.0	200.0	0.0400	24.0	A
15	4.0	1.0	13.0	10.0	7300	10.0	130.0	0.0300	21.0	A
1	1.3	3.1	-	3.3	-	21.0	-	0.0520	7.5	E
2,3	0.5	2.7	-	1.0	-	21.0	-	0.0420	6.1	E
4	6.0	1.0	10.0	8.0	7600	10.0	50.0	0.0200	40.0	E
7	0.55	3.3	-	2.2	-	24.0	-	0.0380	13.0	E
8	-	2.2	-	4.0	-	24.0	-	0.0510	20.0	E
9	0.83	4.0	-	8.9	-	24.0	-	0.0470	27.0	E
10	0.26	3.6	-	2.2	-	24.0	-	0.0780	12.0	E

A=(Fuhrer and Rinella,1982) digestion: 30% H₂O₂ followed by hot 0.3 M HCl

B=(Fuhrer and Horowitz,1986) digestion: HF/HClO₄/HNO₃ at 200 C

C=(Fuhrer,1984) digestion: 30% H₂O₂ followed by hot 0.3 M HCl

D=(Hancock et al., 1984) digestion: HNO₃ followed by 6 N HCl

E=(unpublished) digestion: HNO₃,H₂O₂, followed by HCl

Table B-3. Matrix of correlations between sediment characteristics and trace metals in other Oregon estuaries.

	Sand	VFSand	Silt	Clay	As	Fe	Mn	Pb	Hg
Sand	1.000								
VFSand	0.823	1.000							
Silt	0.633	0.907	1.000						
Clay	0.605	0.851	0.871	1.000					
As	-0.049	0.195	0.286	0.215	1.000				
Fe	0.575	0.657*	0.629	0.614	0.072	1.000			
Mn	0.598	0.685*	0.661	0.659	0.060	0.840	1.000		
Pb	0.103	0.221	0.211	0.299	0.362	-0.037	-0.103	1.000	
Hg	0.152	0.175	0.167	0.221	0.059	-0.127	-0.030	0.225	1.000

d.f. = 59, $P < .05 = 0.232$, $P < .01 = 0.303$

	Median	TOC	Vol	As	Fe	Mn	Pb	Hg
Median	1.000							
TOC	-0.188	1.000						
Vol	0.003	0.022	1.000					
As	-0.214	0.336*	0.278	1.000				
Fe	-0.517	0.171	0.223	0.112	1.000			
Mn	-0.633	0.402	-0.100	0.335	0.609	1.000		
Pb	-0.142	-0.146	0.503*	0.186	0.351	-0.023	1.000	
Hg	-0.314	0.248	0.251*	0.349	0.101	0.182	0.213	1.000

d.f. = 49, $P < .05 = 0.278$, $P < .01 = 0.361$

* = best correlation for that metal

Table B-4. % detection / % false positives for all estuaries

<u>Plan</u>	<u>>4 ppm Arsenic</u>	<u>>12 ppm Chromium</u>	<u>>14 ppm Lead</u>	<u>>0.05 ppm Mercury</u>	<u>>67 ppm Zinc</u>
20-1000-5	93 / 76	100 / 81	93 / 76	65 / 69	92 / 78
5-08	79 / 81	90 / 72	100 / 75	73 / 67	92 / 79
35-5	86 / 71	40 / 90	86 / 71	50 / 69	85 / 74