Use of Elutriate Tests and Bottom-Material Analyses in Simulating Dredging Effects on Water Quality of Selected Rivers and Estuaries in Oregon and Washington, 1980-1983

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CONTENTS

ILLUSTRATIONS

[Plate is in pocket]

TABLES

CONVERSION FACTORS AND ABBREVIATIONS

For the convenience of readers who may prefer to use metric (International System) units rather than inch-pound units used in this report, values may be converted by using the following factors:

Multiply inch-pound units	By	To obtain metric units
	Length	
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
	Area	
square mile (mi^2)	2.590	square kilometer (km^2)
	Volume	
cubic foot (ft^3)	0.02832	cubic meter (m^3)
	Flow	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
	Mass	
ounce, avoirdupois (oz)	0.03527	gram (g)
pound, avoirdupois (lb)	0.002205	gram (g)
	Specific Conductance	
microsiemen per centimeter at 25° Celsius (μS/cm at 25 °C)	1.000	micromho per centimeter at 25° Celsius (μmho/cm at 25 °C)
	Temperature	
degree Celsius (°C)	F= 9/5 °C + 32	degree Fahrenheit (°F)

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.

USE OF ELUTRIATE TESTS AND BOTTOM-MATERIAL ANALYSES IN SIMULATING DREDGING EFFECTS ON WATER QUALITY OF SELECTED RIVERS AND ESTUARIES IN OREGON AND WASHINGTON, 1980-83

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ABSTRACT

Native waters, elutriate-test filtrates, and bottom materials were analyzed for selected trace metals and organic compounds, listed in the U.S. Environmental Protection Agency (EPA) Priority Pollutant List, prior to dredging and disposal activities. A single reconnaissance sampling was made at several sites in 17 rivers and estuaries, from 1980 to 1983, in an area that extends south to the Coos River in western Oregon, north to Baker Bay in southwest Washington, east to the Willamette River near Portland, Oregon, and west to the Pacific Ocean.

Copper, iron, lead, manganese, and zinc were the only trace metals detected in about 50 percent of the native-water samples. In contrast, arsenic, cadmium, copper, iron, manganese, mercury, nickel, and zinc were detected in about 50 percent of the elutriate-test filtrates. Organochlorine compounds examined in elutriate-test filtrate generally were below analytical detection limits. The organochlorine compounds dieldrin, endosulfan, endrine, heptachlor, and lindane were detected in 25 percent of the bottom-material samples. Most of the maximum organochlorine concentrations occurred in bottom material from Willamette Harbor.

The salinity of the native water used for mixing in the elutriate test was found to affect the elutriate-test-filtrate trace-metal concentrations. In elutriate tests made with identical bottom material but different mixing water, concentrations of barium, iron, manganese, and zinc derived from mixing with saline water exceeded concentrations from tests with freshwater. Beryllium, cadmium, chromium, copper, mercury, and lead appear unaffected by mixing-water salinity.

Elutriate-test-filtrate concentrations of ammonia, beryllium, cadmium, copper, manganese, and mercury were found to exceed aquatic life criteria. Water-quality concentration exceeded EPA criterion most frequently for ammonia and manganese and less frequently for beryllium and copper. Beryllium concentrations exceeded EPA criterion in the Astoria-project area, and copper concentrations exceeded EPA criterion in the Skipanon-project area. Cadmium concentrations exceeding the EPA criterion occurred near the mouth of the Columbia River. Mercury concentrations for this study were problematic because the EPA criterion for mercury is much lower than present-day analytical detection limits.

INTRODUCTION

In the late 1960's, concern over the environmental impact of dredging increased substantially and led to the National Environmental Policy Act of 1969. This law required the U.S. Army Corps of Engineers (COE) to prepare an environmental impact statement whenever dredging activities might significantly affect the aquatic environment (Engler, 1980). Procedures currently used by COE for evaluating potential dredge material are listed in Federal Register 45 (U.S. Environmental Protection Agency, 1980). The Register specifies the use of bulk analyses, benthic bioassays, water column bioassays, and standard elutriate tests to indicate the effect from dredged sediments at disposal sites. Additionally, the COE and the U.S. Environmental Protection Agency (EPA) now suggest the use of the "oxic" elutriate test when dredged materials are to be disposed of under oxic conditions. Oxic tests use compressed air for elutriate-test mixing, but are not recommended when volatile-organic determinations are needed (Plumb, 1981).

This study investigated elutriate testing as a means of simulating the effect of dredging on local-water quality and identified areas where dredging might degrade water quality and so threaten aquatic biota. Water- and sediment-reconnaissance samples were collected from 17 Oregon and Washington project areas (fig. 1 and pl. 1). These areas were sampled once from 1980 to 1983 (Fuhrer and Rinella, 1983; Fuhrer, 1984, 1986). Analytical methods, field procedures, and other pertinent information are discussed in the above reports. Sampling areas extend south to the Coos River in western Oregon, north to Baker Bay in southwest Washington, east to the Willamette River near Portland, Oregon, and west to the Pacific Ocean.

The purpose of this report is to present results of a study whose objectives were to:

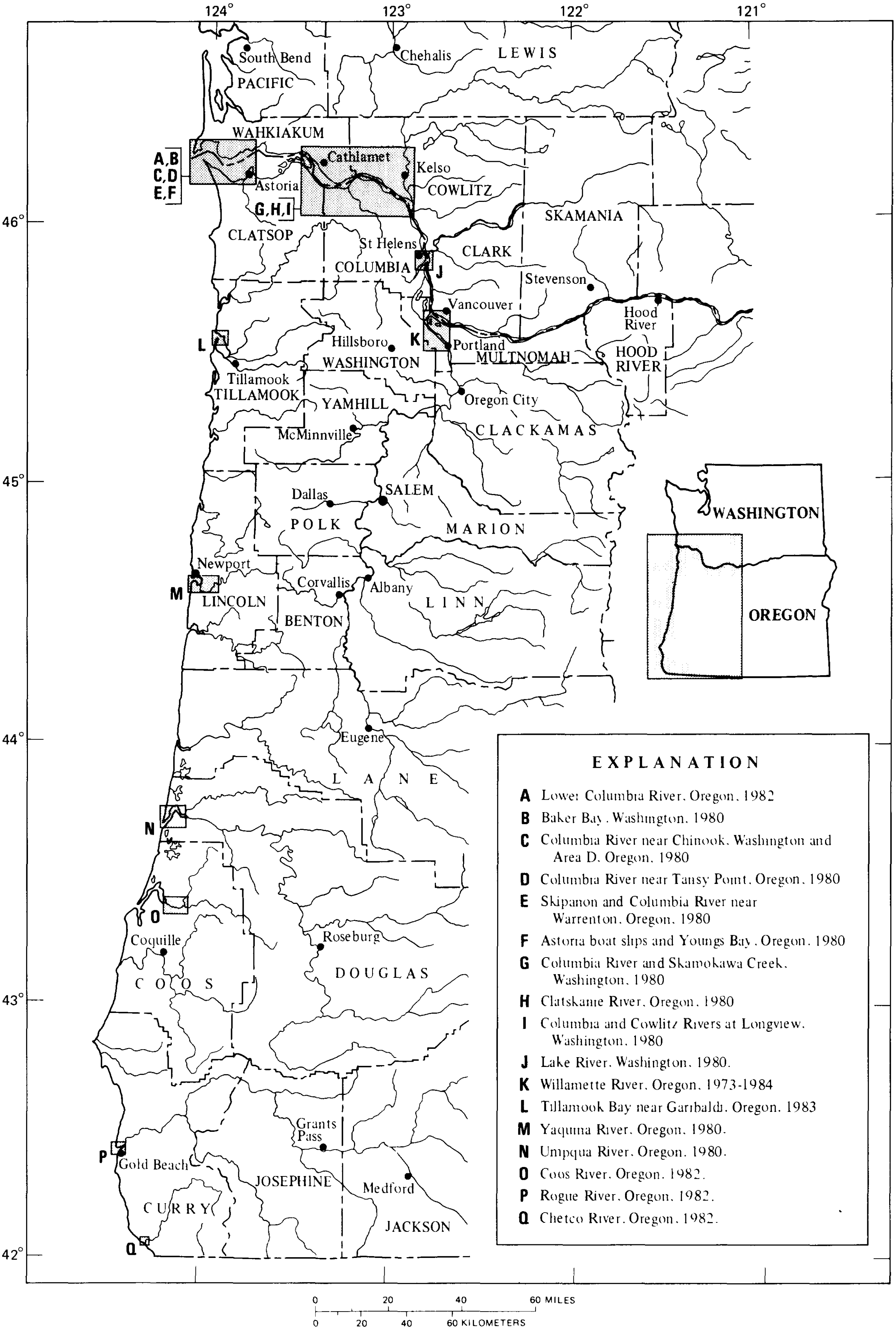
(1) identify sampling sites where elutriate-test filtrate (ETF) chemical concentrations increase substantially compared to concentrations in native water and where concentrations exceed EPA guidelines for fresh-water and saltwater aquatic life,

(2) relate chemical concentrations in bottom material to those in elutriate-test filtrate, and

(3) describe factors causing elutriate-test variability and identify the limitations of relating elutriate-test results to the effects of dredging on the aquatic environment.

APPROACH AND METHODS

Elutriate-test procedures are used to predict short-term chemical degradation of disposal-site native water by the disposal of dredge spoils. The elutriate test does not evaluate the long-term fate of chemicals associated with sediments. Instead, the test simulates conditions that result in chemical dissolution of sediment when bottom material is dredged, transported, and deposited at in-water disposal sites. Elutriate tests examined in this study are "standard" tests. The standard elutriate test involves the mixing of one part bottom material from a dredge site with four parts native water (volume per volume) from a disposal site for 30 minutes, followed by filtration through a 0.45-μm (micrometer) filter (Plumb, 1981). The inorganic



EXPLANATION

A	Lower Columbia River, Oregon, 1982
B	Baker Bay, Washington, 1980
C	Columbia River near Chinook, Washington and Area D, Oregon, 1980
D	Columbia River near Tansy Point, Oregon, 1980
E	Skipanon and Columbia River near Warrenton, Oregon, 1980
F	Astoria boat slips and Youngs Bay, Oregon, 1980
G	Columbia River and Skamokawa Creek, Washington, 1980
H	Clatskanie River, Oregon, 1980
I	Columbia and Cowlitz Rivers at Longview, Washington, 1980
J	Lake River, Washington, 1980.
K	Willamette River, Oregon, 1973-1984
L	Tillamook Bay near Garibaldi, Oregon, 1983
M	Yaquina River, Oregon, 1980.
N	Umpqua River, Oregon, 1980.
O	Coos River, Oregon, 1982.
P	Rogue River, Oregon, 1982.
Q	Chetco River, Oregon, 1982.

Figure 1.--Locations of 17 Oregon and Washington project areas.

dissolved constituents (trace metals, nutrients, and cyanide) were filtered through the 0.45-μm-pore-size filter, and dissolved-organic constituents (organic carbon, phenols, insecticides, and herbicides) were filtered through a nominal 10-μm-pore-size filter (Fuhrer and Rinella, 1983). The resultant filtrate--henceforth termed ETF--along with the native water was analyzed for the above dissolved constituents, which correspond to, but are not inclusive of constituents in the EPA Priority Pollutant List (Chapman and others, 1982). Bottom material was analyzed for selected trace metals and organic compounds included on the EPA Priority Pollutant List (Chapman and others, 1982). The term "chemical release," or "release," is used when ETF chemical concentrations exceed native-water chemical concentrations after considering the precision of the analytical method.

Analytical Methods

Native-water, elutriate, and bottom-material samples were analyzed as follows:

1. Dissolved trace metals, nitrogen, major ions, and all total recoverable constituents were analyzed by the U.S. Geological Survey using methods described by Skougstad and others (1979).

2. Dissolved cyanide, phosphorus, orthophosphate, and gross phenols were analyzed by the COE using methods described in "Standard Methods for the Examination of Water and Wastewater" (American Public Health Association and others, 1975).

3. Dissolved organic compounds, including insecticides and herbicides, were analyzed by the U.S. Geological Survey using methods described by Goerlitz and Brown (1972).

Immediately following filtration of selected samples, specific conductance and pH were measured at the U.S. Geological Survey's Portland laboratory using methods described by Skougstad and others (1979).

Phenolic determinations of ETF made using the 4-aminoantipyrene method (American Public Health Association, 1975) are not appropriate for determining gross-phenol content because many chlorinated phenols are weakly reactive or do not react at all (Faust and Lorentz, 1964). Ortho-cresol, meta-cresol, and chlorinated phenols are among the compounds detected using this method, whereas para-cresol, anisole, p-nitrophenol, and 2,4-dimethylphenol are among the compounds that are not (Faust and Lorentz, 1964). Therefore, phenol concentrations determined in the present study underestimate gross-phenol content.

Data Base

The data base contains results of chemical analyses of 19 native-water samples, 127 ETF samples, and 47 bulk bottom-material samples. The native water used for mixing in elutriate tests, henceforth termed native-mixing water or native water, was analyzed for constituents listed in tables 1 and 2. Chemical symbols or abbreviations for constituents used in this report also are listed in tables 1 and 2.

Table 1.--Chemical Constituents determined in native-water, elutriate, and bottom-material samples

[Native-water and elutriate samples were analyzed for dissolved constituents; bottom materials were analyzed for total-recoverable constituents; ( ) = chemical symbol or abbreviation, where applicable]

Cadmium (Cd)
Chromium (Cr)
Copper (Cu)
Iron (Fe)
Lead (Pb)
Manganese (Mn)
Mercury (Hg)
Zinc (Zn)
Total organic carbon (TOC)
Nitrogen, ammonia (NH_3)
Orthophosphate phosphorus
Gross phenols[1]

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[1] Determinations of water and particulate passing through a nominal 10-micrometer-pore size filter.

Table 2.--Chemical constituents determined for a limited number of native-water, elutriate, and bottom-material samples

[Native-water and elutriate samples were analyzed for dissolved constituents; ( ) = chemical symbol or abbreviation, where applicable]

Trace metals and nutrients

Arsenic (As)
Barium (Ba)
Beryllium (Be)
Cyanide (CN)
Nickel (Ni)
Nitrogen, ammonia + organic (NH_4+Org_N)
Phosphorus

Pesticides-organochlorine compounds

Aldrin
Chlordane
Dichloro diphenyl dichloroethane (DDD)
Dichloro diphenyl dichloroethylene (DDE)
Dichloro diphenyl trichloroethane (DDT)
Dieldrin
Endosulfan
Endrin
Heptachlor
Heptachlor epoxide
Lindane
Methoxychlor
Mirex
Perthane
Toxaphene
Polychlorinated biphenyls (PCB)
Polychlorinated naphthalenes (PCN)
2,4-DP (dimethylphenol)
2,4-D (2,4-dichlorophenoxyacetic acid)
2,4,5-T (2,4-trichlorophenoxyacetic acid)

The 127 elutriate tests were analyzed using the following scheme: 43 were analyzed for constituents shown in tables 1 and 2 and 84 were analyzed for chemicals in table 1. Bottom materials also were analyzed for constituents shown in tables 1 and 2 (except for phenols); in addition, bottom materials from the lower Columbia River were analyzed for acid/base neutral and organic priority pollutants, excluding volatile organics. In 1982, herbicide determinations in bottom material were discontinued because of their high solubility and their rare detection.

To facilitate chemical comparisons of elutriate tests, the data have been subdivided into estuarine, euryhaline, and fresh elutriate classifications. These classifications are based on salinity and specific conductance boundaries (fig. 2). For example, at a temperature of 25 °C (degrees Celsius), the respective salinity and specific conductance boundary between fresh- and euryhaline-elutriate tests is 0.22 g/kg (grams per kilogram) and 492 μS/cm (microsiemens per centimeter); between euryhaline- and estuarine-elutriate tests the boundary is 12.6 g/kg and 20,900 μS/cm. Subdividing elutriate-test results into classifications enables grouping of similar project areas for chemical comparisons. Of the original 127 elutriate tests, 64 were classified as estuarine, 30 as euryhaline, and 33 as freshwater. A similar classification of 47 chemical analyses of bottom materials, using geographical location (estuarine compared to riverine bottom materials), resulted in data sets too small to be of statistical value. Bottom materials consequently have been combined into a single data set for chemical comparisons.

Statistical Tests

Bottom-material samples collected in the reconnaissance study were not selected in a random manner; most samples were collected from such anthropogenically-influenced areas as navigation channels and sites adjacent to industries. In addition, the number and type of chemical analyses made at each sampling site depended on visual inspection of sediments and relative proximity of the sampling site to point sources of pollution. For example, consider two hypothetical sampling sites, the first located in coarse bottom material and removed from likely point sources and the second located in fine, organically-enriched bottom materials and adjacent to a point source. Typically, data from the first sampling site would consist of results of an elutriate test (without bulk sediment analysis) in which only a limited number of trace metals and nutrients were analyzed (table 1); from the second sampling site, both elutriate and bottom materials would be analyzed for a greater number of trace metals, pesticides, and frequently, priority organic pollutants (tables 1 and 2). This type of sampling design is biased positively toward sites more likely to contain elevated levels of chemical constituents.

Most reconnaissance data are not distributed normally or log normally and cannot be analyzed using parametrical statistics (mean, standard deviation, etc.). Reconnaissance data reviewed in this study are better represented by nonparametric statistics such as percentiles, analysis of variance (ANOVA), and Tukey's studentized range test (Byrkit, 1972; SAS, 1982). A special form of the ANOVA procedure, one designed to run on unbalanced data (inequality in the number of chemical constituents found in each classification), was used to test for significant differences ($\rho = 0.05$) between the mean ranks of chemical constituents common to fresh- and estuarine-elutriate classifications.

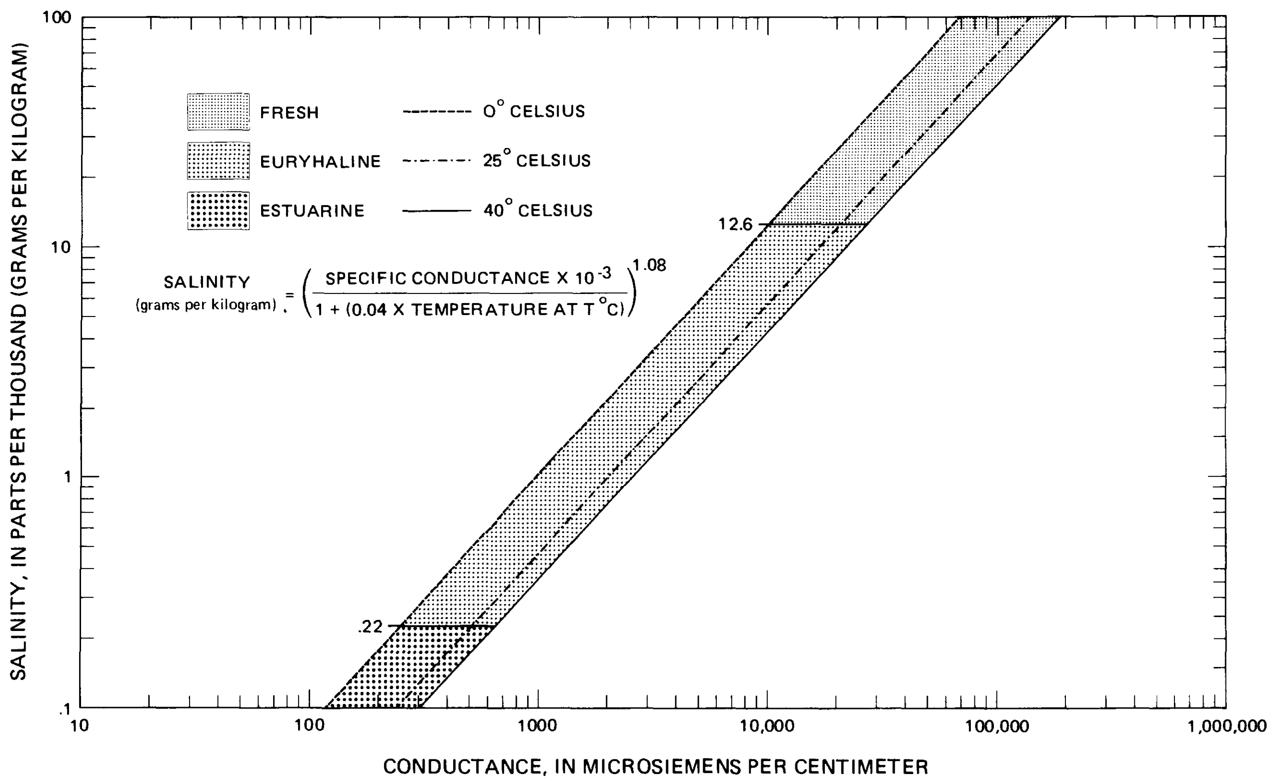


Figure 2.--Ranges of salinity and specific conductance for elutriate tests classified as fresh, euryhaline, and estuarine water.

When fresh-, euryhaline-, and estuarine-elutriate classifications were tested, a more powerful nonparametric procedure (Tukey's studentized range test) was used to determine whether the mean rank of a chemical constituent from one classification was significantly different (ρ = 0.05) from the mean rank of a chemical constituent in either of the other two remaining classifications.

To test for correlation between concentrations of chemical constituents, Kendall's Tau correlation coefficients were computed. Kendall's Tau test is similar to others in computing a measure of correlation between -1 and +1 at a particular significance level. The test differs from others in that it can be run on chemical data that are non-normally distributed, because the test is made on ranked data rather than actual data values (Conover, 1980). Kendall Tau correlations are generated to show the significance level, type of correlation (+ or -), and in some instances the number of observations used to determine specific correlations. The actual value of the Kendall Tau correlation is not reported; only its significance level is shown. It is not the intent of the authors to discuss all significant Kendall Tau correlations; rather, included for discussion are correlations that relate directly to water-quality concerns and for which possible explanations exist.

ELUTRIATE TESTING: A REVIEW

The following section summarizes the evolution, variability, and limitations of elutriate testing.

Test Rationale

Elutriate-test procedures are based on dredging methods. Jones and Lee (1978) state that the sediment-to-water ratio for the elutriate test is based on the generally accepted hydraulic-dredge pumping ratio of one part sediment to four parts dredging-site water. This method of dredging is the one used most commonly by the COE in the Pacific Northwest. The 30-minute mixing time is specified to represent the mixing of the bottom material and dredging-site water from the time of entry into the suction head of the dredge until the mixture enters the water at the disposal site. The 1-hour settling period allows for any additional chemical release from the sediment into the turbid plume. How closely the elutriate-test procedures simulate actual conditions depends on the dredging method (hopper, clamshell, or agitation); elutriate testing simulates hopper dredging most closely.

The mixture entering the suction head rarely is maintained at 20-percent bottom material. Suction-head depth is adjusted to achieve maximum bottom-material removal without clogging the intake. Bottom-material concentrations common to Pacific Northwest dredging operations usually range from 20 to 50 percent (Bob Ellard, U.S. Army Corps of Engineers, oral commun., 1981). The amount of material contained in the hopper generally is greater than 20 percent, because overflowing the hopper concentrates bottom material in the hopper dredge. During the dredging of Isthmus Slough near Coos Bay, Oregon, bottom material made up 20 to 25 percent of the inflow, 18 to 20 percent of the overflow by volume, and 30 to 35 percent of the hopper contents by weight. Rinella and McKenzie (1977) reported up to 45-percent sediment in the hopper while monitoring water quality during a pilot dredging study in the Willamette River. Larger concentrations of bottom material in the hopper are likely as dredged material becomes coarser.

Test Variability

Elutriate-test reliability in simulating contaminant release is influenced by variation in test procedures and by the ability to collect representative bottom-material samples. Test conditions known to affect contaminant release are sediment-water ratio, method of agitation, sample storage, variations of sample temperature or dissolved oxygen concentrations, and settling time. An important component of any sampling effort--and one not always easily achieved--is the collection of a representative bottom-material sample. Surficial bottom-material samplers (ponar-type samplers) remove only the top several inches of bottom material. With these samplers, it is difficult to avoid atmospheric exposure when transferring material from sampler to storage container. Atmospheric exposure of bottom material can result in the volatilization of chemicals with high vapor pressures in addition to the introduction of airborne contaminants. Gravity core samplers, under ideal conditions, remove up to 3 feet of bottom material; however, under non-ideal conditions (such as the presence of coarse or fiberous bottom material), these samplers may obtain less than 1 foot of sample. Where bottom materials are stratified, differences in sampler penetration could produce large variations in analytical results (Plumb, 1981). Where stratification occurs, as often commonly is the case in depositional areas (Plumb, 1981), these analytical differences can be eliminated by sampling from top to bottom of the channel, coincident with the proposed channel depth. This sampling is accomplished best by vibratory coring, in which a core liner is drilled pneumatically into the bottom material.

Temperature, pH, specific conductance, and DO (dissolved oxygen) concentrations in the water column will vary seasonally and with tidal fluctuations. In elutriate testing, the release of chemicals associated with bottom material to ETF is dependent on the aforementioned conditions. To eliminate variability in test procedures, the temperature of elutriate-test water and the native water should be the same. This may require a warming of the native water, normally refrigerated to 4 °C, prior to elutriate testing. Dissolved oxygen and pH should be monitored at regular intervals during the 1-hour quiescent period of the elutriate test; specific conductance should be determined on the elutriate-test filtrate. These measurements will aid in evaluating test results by allowing investigators to determine if test conditions are similar to actual disposal-site conditions.

Elutriate-test results vary when samples of native water or bottom material--or both--are stored for extended periods. However, when these samples are stored less than 77 days, ETF trace-metal and orthophosphate concentrations are unaffected (Wyeth and Sweeney, 1978). Unlike ETF trace-metal concentrations, concentrations of dissolved-trace metals in native-mixing water vary when storage times are less than about 75 days. Of the trace metals examined, Fe and Mn concentrations decreased, Zn and Cu increased; and Cd, Cr, and Ni were unaffected (Wyeth and Sweeney, 1978). Decreases in concentrations of Fe and Mn probably result from oxidation and subsequent precipitation of Fe and Mn to sample-container walls. Increases in dissolved Cu and Zn probably result from decomposition of organic material or, in the case of Zn, desorption from the polyethylene sample bottles (Zn is a catalyst in polyethylene synthesis). U.S. Army Corps of Engineers and EPA procedures (Plumb, 1981) call for completion of the test within 1 week of sample collection. To minimize changes in sample composition resulting from photo-oxidation, biological activity, and redox conditions, samples are to be sealed and stored in the dark at 4 °C.

Studies by Lee and others (1975), O'Conner (1975), and Jones and Lee (1978) evaluated the effects of varying sediment-to-water ratios on chemical concentrations in ETF. These authors reported that ETF concentrations of Cu, Cd, Ni, Cr, Hg, and As generally were unaffected by sediment-water ratios and did not differ significantly from concentrations found in the native-mixing water. However, the sediment-water ratio may affect significantly the release of Mn, ammonia (NH_3), and orthophosphate (Lee and others, 1975; and Jones and Lee, 1978). As mentioned earlier, the sediment-water ratio may affect ETF NH_3 concentrations. Elutriate-test-filtrate NH_3 concentrations have been shown to increase linearly as the elutriate-test sediment-water ratio is increased (Lee and others, 1975). Jones and Lee (1978) reported that ETF NH_3 concentrations resulting from 20-percent bottom material in the elutriate-test mixture ranged from 1.4 to 4 times greater than concentrations resulting from 5-percent bottom material. Lee and others (1975) found that Mn release in tests using 20-percent bottom material were twice that of tests using 5-percent bottom material. They found no difference in Mn release among tests using 10-, 15-, and 20-percent bottom material. Using a data base much larger than that incorporated in the above studies, Jones and Lee (1978) show that for 65 percent of the bottom materials tested, Mn releases correspond to increasing sediment-water ratios. Manganese releases are three times larger when bottom material comprises 20 percent, rather than 5 percent, of the elutriate-test mixture. Although relations between Mn release and sediment-water ratios have been reported, they are rarely linear.

Bottom materials that affect ETF, DO, and pH levels, do so in a manner that is dependent on the sediment-water ratio. Elutriate-test-filtrate chemical concentrations ultimately are affected by shifting DO and pH levels. O'Conner (1975) monitored pH and DO levels while bottom material and water were mixed in a closed container. Tests using sediment-water ratios of 1:4 or greater became anoxic within a few minutes of mixing, and the pH dropped from 7.8 to 6.4. For sediment-water ratios of 1:12, the mixture did not become anoxic; but pH dropped from 7.8 to 6.9. Elutriate-test-filtrate chemical concentrations may deviate significantly from actual chemical concentrations in the hopper dredge as the ratio changes and shifts in pH and DO levels occur.

Elutriate-test mixing times are not nearly as significant as sediment-water ratios in affecting ETF chemical concentrations (Lee and others, 1975; and Jones and Lee, 1978). Concentrations of trace metals in all elutriate tests were similar for 15-, 30-, 60-, and 90-minute mixing periods. The test results for trace metals tended to be more consistent, however, for the 30-minute period than for the 15-, 60-, or 90-minute periods. Lee and others (1975) reported that the release of NH_3 occurred only in the first 15 minutes, and likely is explained by the rapid release of NH_3 from the bottom material (Windom, 1973). O'Conner (1975) observed that in tests made with marine-mixing water, ETF Zn concentrations were greater following longer mixing periods than short ones. He concludes that for Zn the test usually does not represent an equilibrium between bottom material and water.

Lee and others (1975) conducted tests that compared the effects on trace-metal release by stirring or shaking. Trace-metal releases were similar, regardless of the method used to agitate the elutriate mixture, except in the case of iron. More iron was released with stirring, and concentrations varied as much as 100-fold with different test methods.

Redox conditions can have a substantial effect on ETF chemical concentrations (Lee and others, 1975; O'Conner, 1975; Jones and Lee, 1978). Tests to measure the effects of redox conditions on ETF chemical concentrations were accomplished by bubbling air or oxygen-free nitrogen gas through the sediment-water mixture (Lee and others, 1975). Results of those tests generally were more reproducible than those for standard elutriate tests. Under standard test conditions, whether the elutriate mixture becomes oxic or anoxic depends on the redox conditions of the bottom material. These redox conditions (or more specifically, the presence or absence of oxygen during the test) can affect the magnitude of the chemical release. In the absence of oxygen (anoxic test), Mn releases were smaller than those found in the oxic test. In contrast, the anoxic-test release of Fe was approximately 175 times greater than the oxic-test release of Fe. Knowing whether DO is present or absent in disposal-site water can aid in selecting the most appropriate elutriate test.

Test Limitations

The elutriate test is designed to measure the short-term release of chemicals that may occur during dredging and disposal operations. Because chronic and acute toxicity criteria are established by 48-hour, 96-hour, or longer-duration bioassays, they may not be appropriate for comparison with chemical concentrations in ETF. Most dissolved trace metals released from dredging return to ambient concentrations within 1 hour; non-metals such as NH_3 and orthophosphate persist longer (Wyeth and Sweeney, 1978; Jones and Lee, 1978).

It is difficult to determine test reliability by monitoring dredging operations, except in very simple one-directional laminar-flow systems. It is difficult to know the correct time and place to sample a plume that results from dredging or in-stream disposal. Most harbor areas plumes are affected by currents, which often cause the plumes to move in different directions.

Jones and Lee (1978) compared chemical concentrations in ETF with chemical concentrations measured while monitoring disposal operations. They reported that trace-metal release patterns within the turbid plumes and elutriate tests were similar. Whether or not the elutriate test accurately predicted release or uptake at specific sampling sites was not reported. No single elutriate-test procedure consistently predicted the magnitude or directions of release and uptake of orthophosphate, as measured by field monitoring studies during dredged-material disposal. Elutriate-test-filtrate concentrations of NH_3 were approximately one order of magnitude greater than those measured in the turbid plumes. Lower concentrations in the turbid plume were attributed to dilution.

Wyeth and Sweeney (1978) concluded that the elutriate test may characterize conditions within the hopper dredge; chemicals released in ETF were usually detected when monitoring the disposal of dredged material. However, elevated concentrations of chemicals such as orthophosphate and Hg measured during disposal operations were often not measured during corresponding elutriate tests.

SEDIMENT-CHEMISTRY CONCEPTS: A REVIEW

Bottom materials commonly are regarded as permanent sinks for nutrients, organics, and trace metals; however, the chemistry of sediments involves many dynamic exchanges between dissolved and solid states at sediment-water interfaces. Trace metals in hydrologic environments are, on a weight basis, at least three orders of magnitude more concentrated in the solid phase than in the aqueous phase (Jenne and others, 1980). The rate and direction of the sediment-water exchange of chemicals are dependent on sediment-surface characteristics, chemical properties of dissolved constituents, and the chemistry of surrounding waters.

Trace metals originally in dissolved form may associate with bottom material by (1) direct adsorption on inorganic particles (clays), (2) adsorption onto hydrous iron and manganese oxides, (3) adsorption or complexation with organic substances, and (4) direct precipitation (Forstner and Wittmann, 1979, p. 207-217).

Trace metals can be transported and deposited in the mineral substances of natural rock debris, frequently in inert lattice positions. Silicate minerals usually have low trace-metal concentrations, whereas clay minerals contain substantially higher trace-metal concentrations and commonly are correlated to specific sources of trace metals (Forstner and Wittmann, 1979). Unbalanced charges on clay surfaces commonly are balanced by the adsorption of divalent trace-metal cations. This balancing is most pronounced along broken bonds, which occur on the vertical planes of clay particles. The amount of cation adsorption is related to the number of broken bonds and increases with decreasing particle size.

At low pH values, hydronium ions are the principal agent responsible for displacing trace-metal cations from clay minerals as they compete for exchange sites with the trace-metal cations. Treatment of radioisotope-labeled marine sediments with acetic acid/ammonium acetate solution at pH = 5.4 caused 100 percent of the Cd, 50 percent of the Mn and Pb, and 33 percent of the Zn to be leached; no Fe or Cu was extracted. The difference in extractability has been attributed to the diffusion of certain trace metals into fixed intercrystalline positions while other trace metals are adsorbed only at exchangeable positions (Duursma, 1976).

The most significant role played by clay-size minerals (relative to trace metals) is that of a mechanical substrate for surface coatings of hydrous Mn and Fe oxides, sulfides, carbonates, and organic matter (Jenne, 1976). Under oxidizing conditions, Fe and Mn oxides and hydroxides on clay size minerals constitute significant "sinks" of trace metals and nutrients in aquatic systems (Cutshall, 1967; Gibbs, 1973; and Forstner and Wittmann, 1979, p. 213). These oxides and hydroxides readily sorb or coprecipitate with cations, so that even small concentrations of Fe and Mn can influence trace-metal distributions (Forstner and Wittmann, 1979).

Under anoxic conditions (as in many elutriate tests), trace metals associated with hydrous Fe/Mn oxides will dissolve (Hem, 1970). Dissolution of these oxides can act as a source of dissolved trace metals in natural waters (Jenne, 1976). The mobility of newly dissolved trace metals can be significantly decreased, however, by small amounts of sulfide ions (Forstner and Wittmann, 1979). For example, under reducing conditions and in the presence of sulfide, Cd, Hg, and Pb form insoluble sulfide complexes.

When reduced bottom materials are exposed to oxygenated waters, Mn^{+2}, Fe^{+2}, and sulfides will be oxidized, resulting in (1) precipitation of manganese dioxide and ferric hydroxide, (2) release and coprecipitation of trace metals, (3) formation of sulfate ion and elemental sulfur, and (4) a decrease in DO and pH (Bella, 1975, p. 18; O'Conner, 1975; Forstner and Wittmann, 1979). The rate of Fe and Mn oxidation is dependent on the DO concentration and pH of the surrounding water, as well as on the form of the trace metals. At a pH of 7, the formation of ferric hydroxide from Fe^{+2} will occur within minutes, while the oxidation of Mn^{+2} is much slower; consequently, Mn^{+2} is likely to persist much longer at the same pH.

Organic detritus and inorganic particles with natural organic coatings exhibit moderate to strong binding energies (Dexter and Pavlou, 1978). For example, analysis of Tama River bottom material in Japan indicates that Cd accumulation is related mainly to organic material (Suzuki and others, 1979). In New Jersey streams, concentrations of Pb, Zn, Cu, Ni, and Cd have been found to be related closely to the distribution of organic matter in bottom materials (Baker, 1980, p. 271). Humic and fulvic acid, important components of organic material, will bond trace-metal ions at both exchangeable and complexation sites (Rashid, 1971). Both acids play an important role in bonding trace metals; however, the humic fraction is more important in trace-metal transport because of the greater quantity found (Jenne, 1976). Trace-metal ions associated with organic material may be removed from the water column at the estuary-river interface by flocculation of organic material in the presence of salt water (Sholkovitz, 1978; Forstner and Wittmann, 1979). When these trace metals are complexed with humic acids in freshwater systems, they are unavailable for the formation of insoluble salts such as sulfides, carbonates, and hydroxides (Rashid and Leonard, 1973), but, in the presence of hydrous iron/manganese oxides, these trace metals are coprecipitated. In earlier studies (Forstner and Wittmann, 1979), Cu was found to be coprecipitated almost completely in the presences of humic acids, and coprecipitation of Zn was increased substantially compared with coprecipitation in distilled water. Organic material also is important in bottom materials because its oxidation will result in the depletion of DO, followed by the sequential reduction of nitrates and nitrites to NH_3, reduction of sulfates to sulfides, and reduction of carbonates to methane.

STATISTICAL ANALYSIS OF ELUTRIATE TESTING AND CHEMICAL DETERMINATIONS OF BOTTOM MATERIAL

Percentiles of Chemical Concentrations in Native-water, Elutriate, and Bottom-material Samples

Chemical analyses of dissolved chemicals in native water and ETF, and total-recoverable chemicals in bottom-material samples were summarized statistically by reporting the maximum, 75-percentile, median, 25-percentile, and minimum chemical concentrations (tables 3, 4, 5, 6, 7, and 8). Of the trace metals examined, concentrations of Cu, Fe, Pb, Mn, and Zn were the only trace metals detected in at least 50 percent of the native-water samples (table 3). Concentrations of As and Be were below analytical detection limits of <1 μg/L (micrograms per liter) and <10 μg/L in all water samples, respectively. Likewise, with the exception of 2,4-D and 2,4-DP gross phenols and heptachlor, organochlorine compounds were below analytical detection limits in all water samples (table 3).

Chemical analyses of ETF samples, partitioned into classifications of fresh, euryhaline and estuarine waters, were summarized statistically (tables 5, 6, and 7). Trace metals were detected in varying frequencies, depending on the trace metal and the classification. For example, Hg was detected in at least 3 percent of the fresh ETF's, 50 percent of the euryhaline ETF's, and 25 percent of the estuarine ETF's.

Of the following ETF trace metals examined, at least 50 percent were detected: As, Cd, Cu, Fe, Mn, Ni, and Zn in fresh ETF (table 5); As, Fe, Mn, Hg, and Ni in euryhaline ETF (table 6); and Ba, Cu, Fe, Mn, Ni, and Zn in estuarine ETF (table 7). Each percentile concentration of Fe, Mn, and Zn in estuarine ETF exceeds those of fresh and euryhaline ETF. Larger estuarine Mn ETF concentrations may occur because the rate of Mn^{+2} oxidation and precipitation is diminished in the presence of sulfate and bicarbonate ions in estuarine waters (Hem, 1963). Native-mixing waters used in estuarine-elutriate tests are likely to contain larger concentrations of sulfate and bicarbonate ions than are found in euryhaline and fresh elutriate tests.

Both euryhaline and estuarine nitrogen as NH_3 median-percentile concentrations are five times greater than corresponding fresh ETF concentrations. Large concentrations of Cd occur with greater frequency in fresh ETF; however, estuarine ETF has a maximum value of 210 μg/L, 24 times greater than the fresh ETF maximum.

Table 3.--Statistical summary of dissolved chemicals in native water

[If greater than 20 percent of the data are below detection limits, they will be reported as such; if less than 20 percent are below detection limits, the detection limit will be divided by 2 and reported; concentrations are reported in micrograms per liter, except where otherwise indicated. mg/L = milligrams per liter, µS/cm = microsiemens per centimeter. Other organic compounds analyzed for, but not detected, are: atratone, atrizine, cyanazine, cyprazine, heptachlor epoxide (total), prometone, prometryne, propazine, simazine, simetone, simetryne. DDD = dichloro diphenyl dichloroethane, DDE = dichloro diphenyl dichloroethylene, DDT = dichloro diphenyl trichloroethane, PCB = polychlorinated biphenyls, and PCN = polychlorinated naphthalenes; 2,4-D = 2,4-dichlorophenoxyacetic acid; 2,4-DP = 2,4-D-dimethylphenol; 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid; < = less than]

		Concentrations, by percentile					
Number of samples	Constituent analyzed	Maximum	75-percentile	Median 50-percentile	25-percentile	Minimum	Project area with highest value
18	Arsenic	<1	<1	<1	<1	<1	
18	Barium	300	<100	<100	<100	<100	Umpqua
18	Beryllium	<10	<10	<10	<10	<10	
17	Cadmium	3	1.2	<1	<1	<1	Umpqua
17	Chromium	4	1.2	<1	<1	<1	Chetco
19	Copper	6	3.5	2	<1	<1	Columbia/Pacific Ocean
19	Iron	280	150	100	20	10	Clatskanie
19	Lead	32	4	2	<1	<1	Cowlitz
19	Manganese	130	40	30	<10	<10	Cowlitz
18	Mercury	.2	<.1	<.1	<.1	<.1	Coos Bay
17	Nickel	5	3	<1	<1	<1	Umpqua
19	Zinc	60	30	11	<10	<10	Coos Bay
18	Organic carbon (mg/L)	6.4	3.8	2.7	2.2	.7	Yaquina/Pacific Ocean
15	Orthophosphate, as P (mg/L)	.08	.06	.05	.02	.01	Coos Bay
18	pH (units)	8.2	8.1	7.9	7.6	6.9	Yaquina/Pacific Ocean
15	Nitrogen, ammonia plus organic, as N (mg/L)	1.8	.6	.45	.33	.05	Skamokawa
15	Nitrogen, ammonia, as N (mg/L)	.12	.06	.04	<0.01	<.01	Coos Bay
12	Cyanide	4	3	1	1	<.5	Skamokawa
19	Specific conductance (µS/cm)	56,000	42,900	183	133	83	Yaquina/Pacific Ocean
14	Aldrin	<.01	<.01	<.01	<.01	<.01	
14	Chlordane	<.1	<.1	<.1	<.1	<.1	
14	DDD	<.01	<.01	<.01	<.01	<.01	
14	DDE	<.01	<.01	<.01	<.01	<.01	
14	DDT	<.01	<.01	<.01	<.01	<.01	
14	Dieldrin	<.01	<.01	<.01	<.01	<.01	
14	Endosulfan	<.01	<.01	<.01	<.01	<.01	
14	Endrine	<.01	<.01	<.01	<.01	<.01	
14	Lindane	<.01	<.01	<.01	<.01	<.01	
12	Methoxychlor	<.01	<.01	<.01	<.01	<.01	
14	Mirex	<.01	<.01	<.01	<.01	<.01	
14	PCB	<.1	<.1	<.1	<.1	<.1	
14	PCN	<1	<1	<1	<1	<1	
14	Perthane	<1	<1	<1	<1	<1	
14	Silvex	<.01	<.01	<.01	<.01	<.01	
14	Toxaphene	<.1	<.1	<.1	<.1	<.1	
13	2,4-D	.04	<.01	<.01	<.01	<.01	Columbia, RM 70.8
14	2,4-DP	.04	<.01	<.01	<.01	<.01	Columbia, RM 70.8
14	2,4,5-T	<.01	<.01	<.01	<.01	<.01	
15	Phenols (gross)	12	9	4	2	<1	Cowlitz
14	Heptachlor (total)	.02	<.01	<.01	<.01	<.01	

Table 4.--Statistical summary of dissolved chemicals in fresh-, euryhaline-, and estuarine-elutriate classifications

[If greater than 20 percent of the data are below detection limits, they are reported as such; if less than 20 percent are below detection limits, the detection limit is divided by 2 and reported. Concentrations are reported in micrograms per liter, except where otherwise indicated. Other organic compounds analyzed for, but not detected, are atratone, atrizine, cyanazine, cyprazine, prometone, prometryne, propazine, simazine, simetone, simetryne. DDD = dichloro diphenyl dichloroethane, DDE = dichloro diphenyl dichloroethylene, DDT = dichloro diphenyl trichloroethane, PCB = polychlorinated biphenyls, and PCN = polychlorinated naphthalens; 2,4-D = 2,4-dichlorophenoxyacetic acid; 2,4-DP = 2,4-D-dimethylphenol; 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid; < = less than; mg/L = millgrams per liter; * = constituent used in analysis of variance is from the euryhaline elutriate data set]

Number of samples	Constituent analyzed	Concentrations, by percentile					Project area with highest value	Analysis of variance
		Maximum	75-percentile	Median 50-percentile	25-percentile	Minimum		
42	Arsenic	15	3	2	<1	<1	Rogue	Yes
41	Barium	1,500	300	<100	<100	<100	Astoria	
41	Beryllium	20	<10	<10	<10	<10	Astoria	
118	Cadmium	210	<1	<1	<1	<1	Lower Columbia	
118	Chromium	40	<1	<1	<1	<1	Umpqua	
123	Copper	19	3	2	<1	<1	Skipanon	
123	Iron	4,300	170	110	50	10	Astoria	Yes
123	Lead	5	2	<1	<1	<1	Baker Bay	
123	Manganese	15,000	670	200	80	<10	Lower Columbia	Yes
123	Mercury	.7	.1	<.1	<.1	<.1	Chinook	
42	Nickel	18	7	4	2	.5	Chetco	Yes
123	Zinc	90	40	20	<10	<10	Chinook	Yes
120	Organic carbon (mg/L)	48	12.8	6.6	3.6	.5	Willamette	Yes
110	Orthophosphate, as P (mg/L)	.21	.05	.03	.02	<.01	Baker Bay	Yes
47	pH (units)	9.1	7.9	7.7	7	6.2	Baker Bay	Yes
37	Nitrogen, ammonia plus organic, as N (mg/L)	36	7.6	3.2	1.3	.21	Chinook	Yes
117	Nitrogen, ammonia, as N (mg/L)	46	3.9	1.3	.23	<.01	Astoria	Yes*
30	Aldrin	<.01	<.01	<.01	<.01	<.01		
30	Chlordane	.1	<.1	<.1	<.1	<.1		
30	DDD	<.01	<.01	<.01	<.01	<.01		
30	DDE	<.01	<.01	<.01	<.01	<.01		
30	DDT	<.01	<.01	<.01	<.01	<.01		
30	Dieldrin	<.01	<.01	<.01	<.01	<.01		
30	Endosulfan	<.01	<.01	<.01	<.01	<.01		
30	Endrine	<.01	<.01	<.01	<.01	<.01		
30	Heptachlor	.07	<.01	<.01	<.01	<.01		
30	Lindane	<.01	<.01	<.01	<.01	<.01		
26	Methoxychlor	<.01	<.01	<.01	<.01	<.01		
30	Mirex	<.01	<.01	<.01	<.01	<.01		
30	PCB	.1	<.1	<.1	<.1	<.1		
28	PCN	.1	<.1	<.1	<.1	<.1		
30	Perthane	.1	<.1	<.1	<.1	<.1		
30	Silvex	<.01	<.01	<.01	<.01	<.01		
30	Toxaphene	<1	<1	<1	<1	<1		
30	2,4-D	.04	<.01	<.01	<.01	<.01	Skamokawa	
25	2,4-DP	.02	<.01	<.01	<.01	<.01	Cowlitz	
30	2,4,5-T	.03	<.01	<.01	<.01	<.01	Chinook	
12	Phenols (gross)	419	117	32	10	<1	Baker Bay	
30	Heptachlor (total)	.07	<.01	<.01	<.01	<.01	Skamokawa	

Table 5.--Statistical summary of dissolved chemicals in the fresh-elutriate classification

[If greater than 20 percent of the data are below detection limits, they are reported as such; if less than 20 percent are below detection limits, the detection limit is divided by 2 and reported. Concentrations are reported in micrograms per liter, except where otherwise indicated. Other organic compounds analyzed for, but not detected, are atratone, atrizine, cyanazine, cyprazine, heptachlor epoxide (total), prometone, prometryne, propazine, simazine, simetone, simetryne. DDD = dichloro diphenyl dichloroethane, DDE = dichloro diphenyl dichloroethylene, DDT = dichloro diphenyl trichloroethane, PCB = polychlorinated biphenyls, and PCN = polychlorinated naphthalens; 2,4-D = 2,4-dichlorophenoxyacetic acid; 2,4-DP = 2,4-D-dimethylphenol; 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid; < = less than; mg/L = milligrams per liter; * = Constituents used in analysis of variance are from the freshwater elutriate data set]

		Concentrations, by percentile						
Number of samples	Constituent analyzed	Maximum	75-percentile	Median 50-percentile	25-percentile	Minimum	Project area with highest value	Analysis of variance*
13	Arsenic	3	3	2	<1	<1	Clatskanie	
13	Barium	<100	<100	<100	<100	<100		Yes
13	Beryllium	<10	<10	<10	<10	<10		
28	Cadmium[1]	8.6	1	.4	.1	<.1	Cowlitz	Yes
30	Chromium	24	<1	<1	<1	<1	Skamokawa	
30	Copper	9	3	2	<1	<1	Rogue	
30	Iron	580	150	70	30	10	Rogue	Yes
30	Lead	4	2	<1	<1	<1	Cowlitz	
30	Manganese	820	290	160	81	5	Skamokawa	Yes
30	Mercury	.1	<.1	<.1	<.1	<.1		
13	Nickel	8	5	3	2	5	Willamette	Yes
30	Zinc	70	23	10	6	.5	Cowlitz	Yes
27	Organic carbon (mg/L)	48	6.9	5.2	3.3	1.3	Willamette	Yes
27	Orthophosphate, as P (mg/L)	.048	.03	.018	.009	<.001	Clatskanie	Yes
18	pH (units)	8.1	7.8	7.1	6.7	6.2	Rogue	Yes
14	Nitrogen ammonia plus organic as N (mg/L)	9.9	7.9	2.9	1.1	.21	Willamette	Yes
29	Nitrogen, ammonia, as N (mg/L)	8.6	2.6	.28	.03	<.01	Willamette	Yes
7	Aldrin	<.01	<.01	<.01	<.01	<.01		
7	Chlordane	<.1	<.1	<.1	<.1	<.1		
7	DDD	<.01	<.01	<.01	<.01	<.01		
7	DDE	<.01	<.01	<.01	<.01	<.01		
7	DDT	<.01	<.01	<.01	<.01	<.01		
7	Dieldrin	<.01	<.01	<.01	<.01	<.01		
7	Endosulfan	<.01	<.01	<.01	<.01	<.01		
7	Endrine	<.01	<.01	<.01	<.01	<.01		
7	Heptachlor	.07	<.01	<.01	<.01	<.01	Skamokawa	
7	Lindane	<.01	<.01	<.01	<.01	<.01		
7	Methoxychlor	<.01	<.01	<.01	<.01	<.01		
7	Mirex	<.01	<.01	<.01	<.01	<.01		
7	PCB	.1	<.1	<.1	<.1	<.1		
7	PCN	<.1	<.1	<.1	<.1	<.1		
7	Perthane	<.1	<.1	<.1	<.1	<.1		
7	Silvex	<.1	<.1	<.1	<.1	<.1		
7	Toxaphene	<1	<1	<1	<1	<1		
7	2,4-D	.04	.03	<.01	<.01	<.01	Skamokawa	
7	2,4-DP	.02	.013	<.01	<.01	<.01	Cowlitz	
7	2,4,5-T	<.01	<.01	<.01	<.01	<.01		
25	Phenols (gross)	210	124	56	11.5	4		Yes

[1] The detection limit for cadmium is 0.1 μg/L.

Table 6.--Statistical summary of dissolved chemicals in the euryhaline elutriate classification data from 1980, 1982, and 1983 reconnaissance studies

[If greater than 20 percent of the data are below detection limits, they are reported as such; if less than 20 percent are below detection limits, the detection limit is divided by 2 and reported. Concentrations are in micrograms per liter, except where otherwise indicated. Other organic compounds analyzed for, but not detected, are atratone, atrizine, cyanazine, cyprazine, heptachlor epoxide (total), prometone, prometryne, propazine, simazine, simetone, simetryne. DDD = dichloro diphenyl dichloroethane, DDE = dichloro diphenyl dichloroethylene, DDT = dichloro diphenyl trichloroethane, PCB = polychlorinated biphenyls, and PCN = polychlorinated naphthalenes; 2,4-D = 2,4-dichlorophenoxyacetic acid; 2,4-DP = 2,4-D- dimethylphenol; 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid; < = less than; mg/L = milligrams per liter; * = Constituents used in analysis of variance are from the euryhaline elutriate data set]

		Concentrations, by percentile						
Number of samples	Constituent analyzed	Maximum	75-percentile	Median 50-percentile	25-percentile	Minimum	Project area with highest value	Analysis of variance*
10	Arsenic	15	6	3.5	2	2	Rogue	Yes
10	Barium	400	<100	<100	<100	<100	Chetco	Yes
9	Beryllium	<10	<10	<10	<10	<10		
32	Cadmium	<1	<1	<1	<1	<1		
30	Chromium	5	<1	<1	<1	<1	Rogue	
33	Copper	19	3	<1	<1	<1		
33	Iron	840	75	40	30	10	Rogue	Yes
33	Lead	5	<1	<1	<1	<1	Baker Bay	
33	Manganese	5,300	212	80	40	5	Chetco	Yes
33	Mercury	.6	.2	.1	<.1	<.1	Skipanon	
10	Nickel	18	8	2	<1	<1	Chetco	
33	Zinc	61	12.5	<10	<10	<10	Rogue	Yes
33	Organic carbon (mg/L)	35	22	13	8.6	3.4	Baker	Yes
29	Orthophosphate, as P (mg/L)	.21	.07	.04	.02	.01	Baker	Yes
10	pH (units)	9.1	8.6	8.1	7.8	7.4	Baker	Yes
8	Nitrogen, ammonia plus organic, as N (mg/L)	11	6.8	4.9	3.1	1.5	Yaquina	Yes
33	Nitrogen, ammonia, as N (mg/L)	19	7.2	1.4	.84	.04	Skipanon	Yes
10	Aldrin	<.01	<.01	<.01	<.01	<.01		
10	Chlordane	.1	.1	<.1	<.1	<.1		
10	DDD	<.01	<.01	<.01	<.01	<.01		
10	DDE	<.01	<.01	<.01	<.01	<.01		
10	DDT	<.01	<.01	<.01	<.01	<.01		
10	Dieldrin	<.01	<.01	<.01	<.01	<.01		
10	Endosulfan	<.01	<.01	<.01	<.01	<.01		
10	Endrine	<.01	<.01	<.01	<.01	<.01		
10	Heptachlor	<.01	<.01	<.01	<.01	<.01		
10	Lindane	<.01	<.01	<.01	<.01	<.01		
10	Methoxychlor	<.01	<.01	<.01	<.01	<.01		
10	Mirex	<.01	<.01	<.01	<.01	<.01		
10	PCB	.1	.1	<.1	<.1	<.1		
10	PCN	.1	.1	<.1	<.1	<.1		
10	Perthane	.1	.1	<.1	<.1	<.1		
9	Silvex	<.01	<.01	<.01	<.01	<.01		
10	Toxaphene	<1	<1	<1	<1	<1		
9	2,4-D	.04	<.01	<.01	<.01	<.01	Yaquina	
8	2,4-DP	.01	.01	<.01	<.01	<.01	Rogue	
9	2,4,5-T	<.01	<.01	<.01	<.01	<.01	Baker Bay	
28	Phenols (gross)	382	165	40	17	<1	Baker Bay	Yes

Table 7.--Statistical summary of dissolved chemicals in the estuarine-elutriate classification

[If greater than 20 percent of the data are below detection limits, they are reported as such; if less than 20 percent are below detection limits, the detection limit is divided by 2 and reported. Concentrations are in micrograms per liter, except where otherwise indicated. Other organic compounds analyzed for, but not detected, are atratone, atrizine, cyanazine, cyprazine, heptachlor epoxide (total), prometone, prometryne, propazine, simazine, simetone, simetryne. DDD = dichloro diphenyl dichloroethane, DDE = dichloro diphenyl dichloroethylene, DDT = dichloro diphenyl trichloroethane, and PCN = polychlorinated naphthalenes; PCB = polychlorinated biphenyls; 2,4-D = 2,4-dichlorophenoxyacetic acid; 2,4-DP = 2,4-D- dimethylphenol; 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid; < = less than; mg/L = milligrams per liter; * = constituents used in analysis of variance from the estuarine water elutriate data set]

		Concentrations, by percentile						Analysis
Number of samples	Constituents analyzed	Maximum	75-percentile	Median 50-percentile	25-percentile	Minimum	Project area with highest value	of variance*
19	Arsenic	4	2	<1	<1	<1	Chinook	Yes
18	Barium	1,500	500	300	<100	<100	Astoria	Yes
19	Beryllium	20	20	<10	<10	<10	Astoria	
58	Cadmium	210	<1	<1	<1	<1	Lower Columbia	
58	Chromium	40	<1	<1	<1	<1	Umpqua	
60	Copper	13	3	1.2	<1	<1	Lower Columbia	
60	Iron	4,300	180	150	110	50	Astoria	Yes
60	Lead	4	<1	<1	<1	<1	Umpqua	
60	Manganese	15,000	1,500	480	160	20	Lower Columbia	Yes
60	Mercury	.7	.1	<.1	<.1	<.1	Chinook	
19	Nickel	16	10	4	3	.5	Lower Columbia	Yes
60	Zinc	90	40	30	20	5	Chinook	Yes
60	Organic carbon (mg/L)	20	10.8	5.4	3.3	.5	Baker Bay	Yes
54	Orthophosphate, as P (mg/L)	.085	.054	.038	.028	.002	Tillamook	Yes
58	pH (units)	8	7.8	7.7	7.5	6.7	Baker Bay	Yes
15	Nitrogen, ammonia plus organic, as N (mg/L)	36	14	2.1	1.1	.46	Chinook	Yes
55	Nitrogen, ammonia, as N (mg/L)	46	4.5	1.4	.36	.03	Astoria	Yes
13	Aldrin	<.01	<.01	<.01	<.01	<.01		
13	Chlordane	<.1	<.1	<.1	<.1	<.1		
13	DDD	<.01	<.01	<.01	<.01	<.01		
13	DDE	<.01	<.01	<.01	<.01	<.01		
13	DDT	<.01	<.01	<.01	<.01	<.01		
13	Dieldrin	<.01	<.01	<.01	<.01	<.01		
13	Endosulfan	<.01	<.01	<.01	<.01	<.01		
13	Endrine	<.01	<.01	<.01	<.01	<.01		
13	Heptachlor	<.01	<.01	<.01	<.01	<.01		
13	Lindane	<.01	<.01	<.01	<.01	<.01		
13	Methoxychlor	<.01	<.01	<.01	<.01	<.01		
13	Mirex	<.01	<.01	<.01	<.01	<.01		
13	PCB	<.1	<.1	<.1	<.1	<.1		
13	PCN	<.1	<.1	<.1	<.1	<.1		
13	Perthane	<.1	<.1	<.1	<.1	<.1		
14	Silvex	<.01	<.01	<.01	<.01	<.01		
13	Toxaphene	<.1	<.1	<.1	<.1	<.1		
14	2,4-D	<.01	<.01	<.01	<.01	<.01		
11	2,4-DP	<.01	<.01	<.01	<.01	<.01		
14	2,4,5-T	<.03	<.01	<.01	<.01	<.01		
59	Phenols (gross)	419	86	25	8	<1	Baker Bay	Yes

Organochlorine determinations of ETF generally are below analytical detection limits; only gross phenols exceeded detection levels (tables 5, 6, and 7). The maximum concentration of gross phenols occurred in estuarine ETF (419 μg/L); however, the highest median concentration, 56 μg/L, occurred in fresh ETF. The gross phenols contribution from native-mixing water to ETF is negligible.

Acid-soluble herbicides, unlike many organochlorine compounds, are water soluble. These herbicides were detected in a few instances in native-mixing water and rarely in bottom material. Acid herbicides like 2,4-D and 2,4-DP were detected in a few fresh and euryhaline ETF's (tables 5 and 6). However, most elutriate tests with detectable 2,4-D and 2,4-DP concentrations contained similar dissolved herbicide concentrations in the native-mixing water. For example, Columbia River native water--collected at RM (river mile) 70.8--contained 2,4-D and 2,4-DP concentrations of 0.04 μg/L (Fuhrer and Rinella, 1983). Elutriate tests made with this mixing water and Cowlitz River bottom material also contained similar concentrations. In these instances herbicides probably are not being solubilized from bottom material, but rather come from native-mixing water.

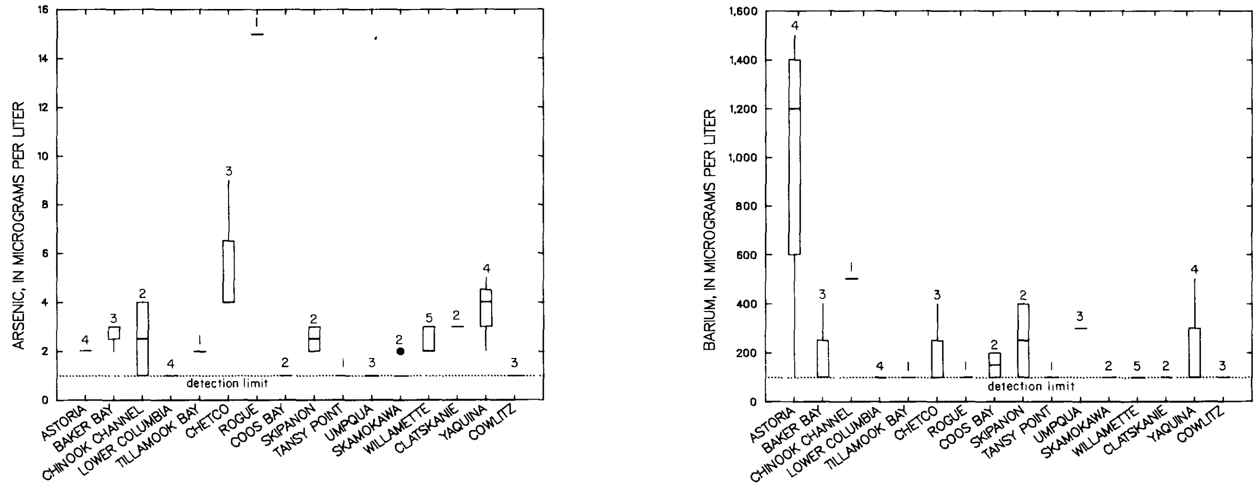
Although many organochlorine compounds are no longer in use, their persistence in bottom material and their potentially hazardous metabolites provide justification for their determination. Most of the maximum organochlorine concentrations occur in Willamette River bottom material. Agricultural practices in the Willamette Valley, combined with suspended-sediment transport and deposition, probably account for these organochlorine concentrations. Organochlorine compounds that are nearly insoluble in water (hydrophobic compounds) commonly partition to bottom material (Chapman and others, 1982). These compounds include insecticides such as chlordane, DDD, DDE, DDT, dieldrin, endosulfan, heptachlor, lindane, and the compounds PCB and PCN (Chapman and others, 1982). As would be expected, organochlorine compounds were detected with greater frequency in bottom material than in ETF (tables 4 and 8). Even so, percentile concentrations of many organochlorine bottom-material determinations are below analytical detection limits (table 8); median concentrations of all organochlorine compounds with the exception of PCB compounds and DDE are less than analytical detection limits. Of the organochlorine compounds in the 75th percentile (table 8), aldrin, chlordane, DDD, DDE, DDT, dieldrin, endosulfan, endrine, heptachlor, lindane, methoxychlor, and PCB were detected in bottom material. Polychlorinated biphenyl, normally associated with bottom material, was detected (0.1 μg/L) in Clatskanie River ETF. Polychlorinated biphenyls in Clatskanie ETF may be associated with fine organic material or organic coated colloids capable of passing through the nominal 10-micrometer pore-size fiberglass filter used before chemical analysis. Though not defined as dissolved (<0.45 μm), PCB compounds in a filtered sample would be reported as dissolved.

Project areas containing relatively large chemical concentrations are easily identified by comparison of box plots. These box plots illustrate percentile concentrations, by project area, for chemicals determined in ETF and bottom material (figs. 3a to 3o and 4a to 4o). For example, ETF Cd concentrations (median, 75-percentile, and maximum) in the lower Columbia River (fig. 3d) are greater than those of other project areas. Box plots simplify the identification of project areas comprising any given percentile class. For example, Astoria Bay, Skipanon River, Lower Columbia River, Tillamook Bay, and Chetco River (fig. 4d) are project areas containing bottom-material concentrations of Cd which exceed the 75th percentile (2.3 micrograms per gram) [table 8].

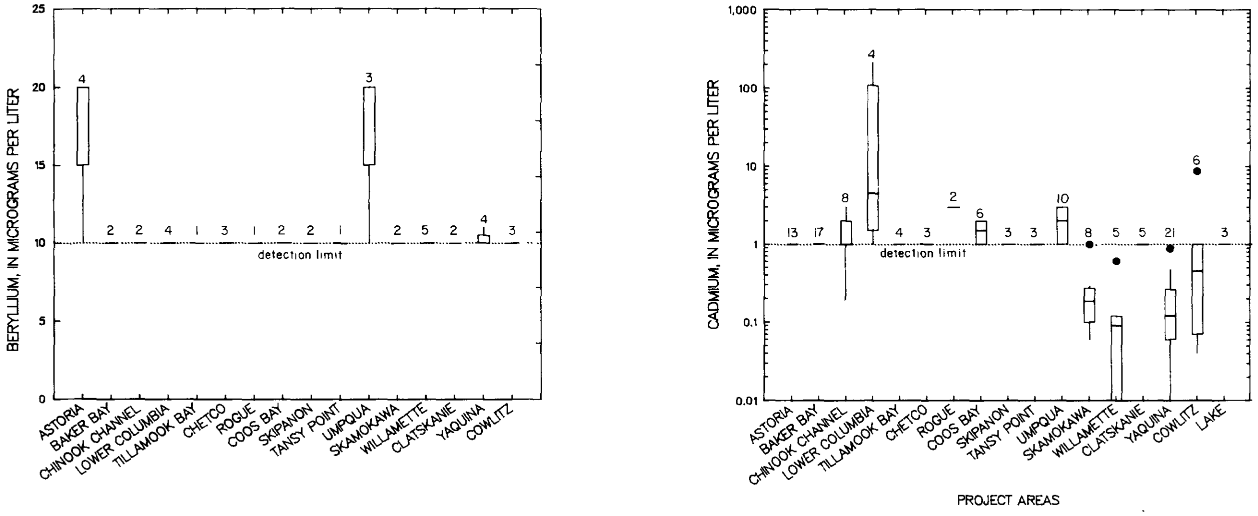
Table 8.--Statistical summary of total-recoverable chemicals in bottom material

[If greater than 20 percent of the data are below detection limits they, are reported as such; if less than 20 percent are below detection limits, the detection limit is divided by 2 and reported. Concentrations are in micrograms per gram, except where otherwise indicated. DDD = dichloro diphenyl dichloroethane, DDE = dichloro diphenyl dichloroethylene, DDT = dichloro diphenyl trichloroethane, PCB = polychlorinated biphenyls, and PCN = polychlorinated naphthalenes; 2,4-D = 2,4-dichlorophenoxyacetic acid; 2,4-DP = 2,4-D- dimethylphenol; 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid; < = less than; g/kg = grams per kilogram; mg/L = milligrams per liter]

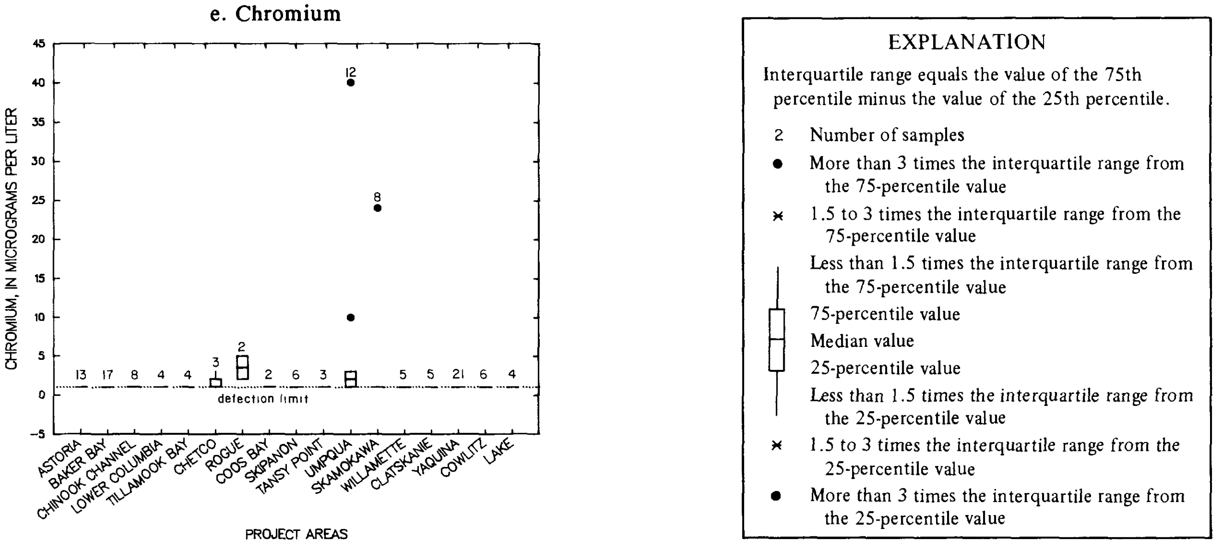
Number of samples	Constituent analyzed	Concentrations, by percentile					Project area with highest value
		Maximum	75-percentile	Median 50-percentile	25-percentile	Minimum	
47	Arsenic	12	7	4	2	<1	Yaquina
33	Barium	400	90	30	5	<5	Baker Bay
33	Beryllium	5	<.5	<.5	<.5	<.5	Willamette
38	Cadmium	29	2.3	<1	<1	<1	Tillamook
40	Chromium	30	15	10	5	<1	Yaquina
40	Copper	180	34	17.5	7	<1	Youngs
47	Iron	31,000	12,000	7,600	4,300	1,400	Yaquina
36	Lead	40	20	<5	<5	<5	Baker Bay
47	Manganese	500	270	140	70	32	Willamette
38	Mercury	.28	.08	.04	.01	.01	Baker Bay
33	Nickel	40	20	20	10	<10	Willamette
40	Zinc	300	88.7	40	22	4	Skipanon
33	Total organic carbon (g/kg)	133	20	7.8	1.6	.6	Skamokawa
33	Nitrogen, ammonia plus organic, as N (mg/L)	2,280	1,300	320	124	29	Skipanon
33	Nitrogen, ammonia, as N (mg/L)	330	150	20	4.1	<.4	Willamette
33	Cyanide	<1	<1	<1	<1	<1	
37	Aldrin	.1	.1	<.1	<.1	<.1	Willamette
39	Chlordane	10	3	<.1	<.1	<.1	Willamette
39	DDD	14	2.5	<.1	<.1	<.1	Willamette
38	DDE	6.8	2	.1	<.1	<.1	Skipanon
38	DDT	1.3	.1	<.1	<.1	<.1	Willamette
39	Dieldrin	.5	.1	<.1	<.1	<.1	Yaquina
37	Endosulfan	.1	.1	<.1	<.1	<.1	Willamette
39	Endrine	.1	.1	<.1	<.1	<.1	Willamette
39	Heptachlor	.4	.1	<.1	<.1	<.1	Willamette
39	Lindane	.4	.1	<.1	<.1	<.1	Chinook
38	Methoxychlor	1.5	.8	<.1	<.1	<.1	Chetco
37	Mirex	<1	<1	<1	<1	<1	
38	PCB	170	28	4	<1	<1	Willamette
14	PCN	<1	<1	<1	<1	<1	
36	Perthane	<1	<1	<1	<1	<1	
30	Silvex	.1	<.1	<.1	<.1	<.1	Willamette
39	Toxaphene	<10	<10	<10	<10	<10	
31	2,4-D	.1	<.1	<.1	<.1	<.1	Willamette
9	2,4-DP	<.1	<.1	<.1	<.1	<.1	
29	2,4,5-T	.1	<.1	<.1	<.1	<.1	Willamette
21	Total volatile solids	17.5	4.8	1.6	.94	.13	Yaquina


a. Arsenic

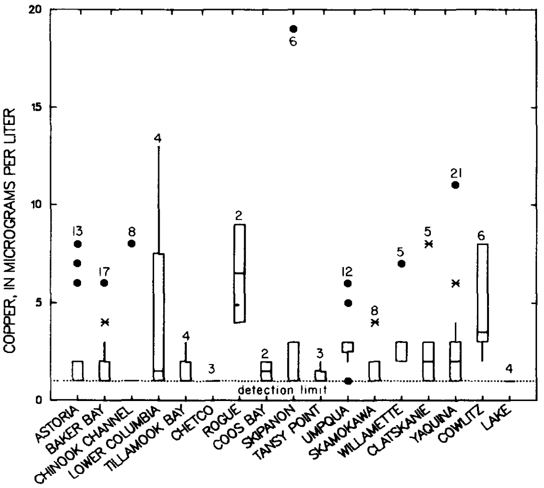
b. Barium


c. Beryllium

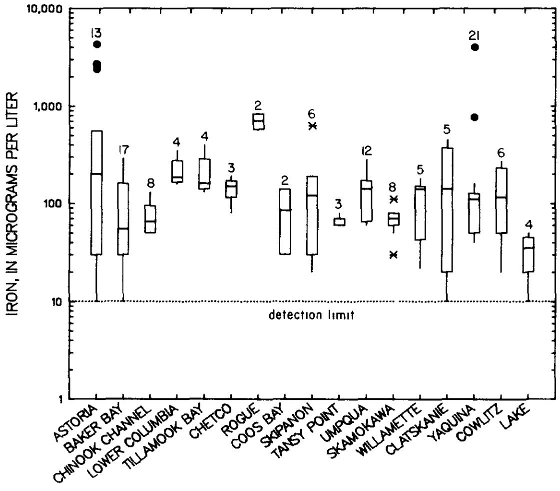
d. Cadmium


e. Chromium

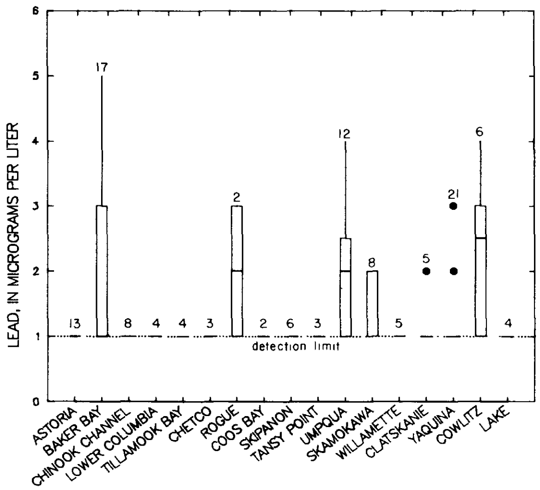
Figures 3a-o.--Comparisons of percentile distributions in elutriate-test filtrate at reconnaissance study project areas for selected elements and constituents. The analytical detection limit for cadmium is 0.01 micrograms per liter for Chinook Channel, Skamokawa, Willamette, Yaquina, and Cowlitz project areas. The analytical detection limit for zinc is 0.12 micrograms per liter for Willamette, Yaquina, Cowlitz, and Lake project areas.



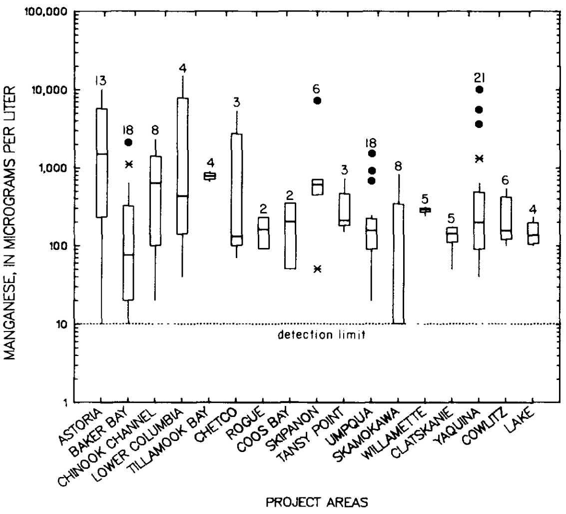
f. Copper



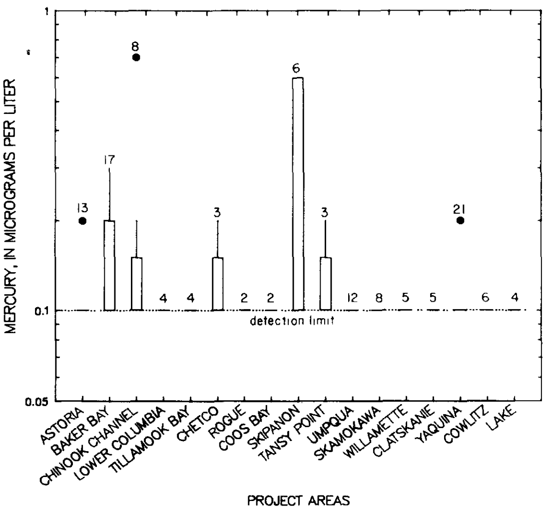
g. Iron



h. Lead



i. Manganese



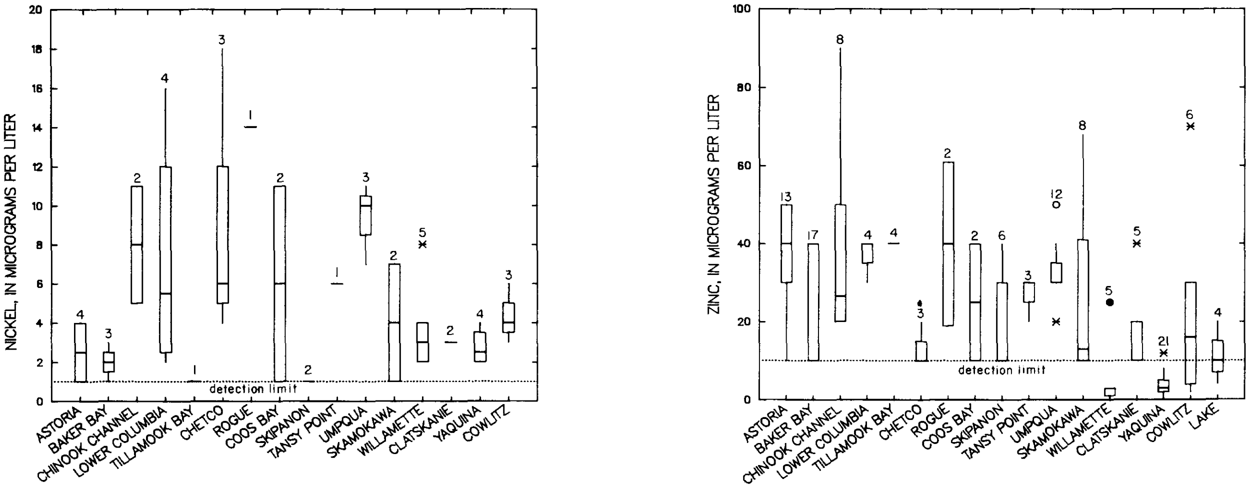
j. Mercury

EXPLANATION

Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

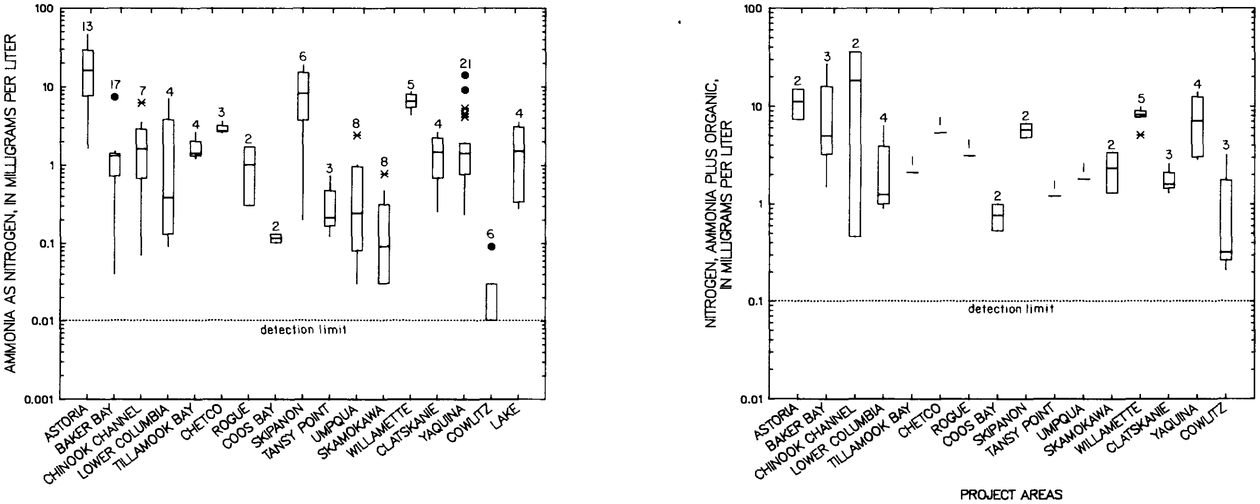
2	Number of samples
●	More than 3 times the interquartile range from the 75-percentile value
⨯	1.5 to 3 times the interquartile range from the 75-percentile value
	Less than 1.5 times the interquartile range from the 75-percentile value
	75-percentile value
	Median value
	25-percentile value
	Less than 1.5 times the interquartile range from the 25-percentile value
⨯	1.5 to 3 times the interquartile range from the 25-percentile value
●	More than 3 times the interquartile range from the 25-percentile value

Figures 3a-o.--Comparisons of percentile distributions in elutriate-test filtrate at reconnaissance study project areas for selected elements and constituents. The analytical detection limit for cadmium is 0.01 micrograms per liter for Chinook Channel, Skamokawa, Willamette, Yaquina, and Cowlitz project areas. The analytical detection limit for zinc is 0.12 micrograms per liter for Willamette, Yaquina, Cowlitz, and Lake project areas--Continued.



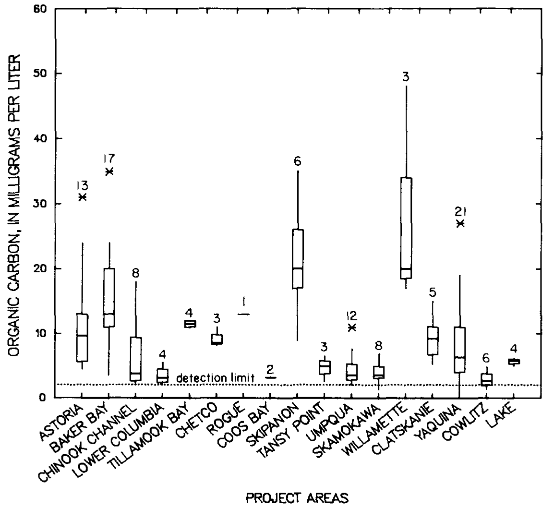
k. Nickel

l. Zinc



m. Ammonia

n. Nitrogen, ammonia plus organic



o. Organic carbon

EXPLANATION

Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

2 Number of samples

● More than 3 times the interquartile range from the 75-percentile value

⁎ 1.5 to 3 times the interquartile range from the 75-percentile value

Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

Median value

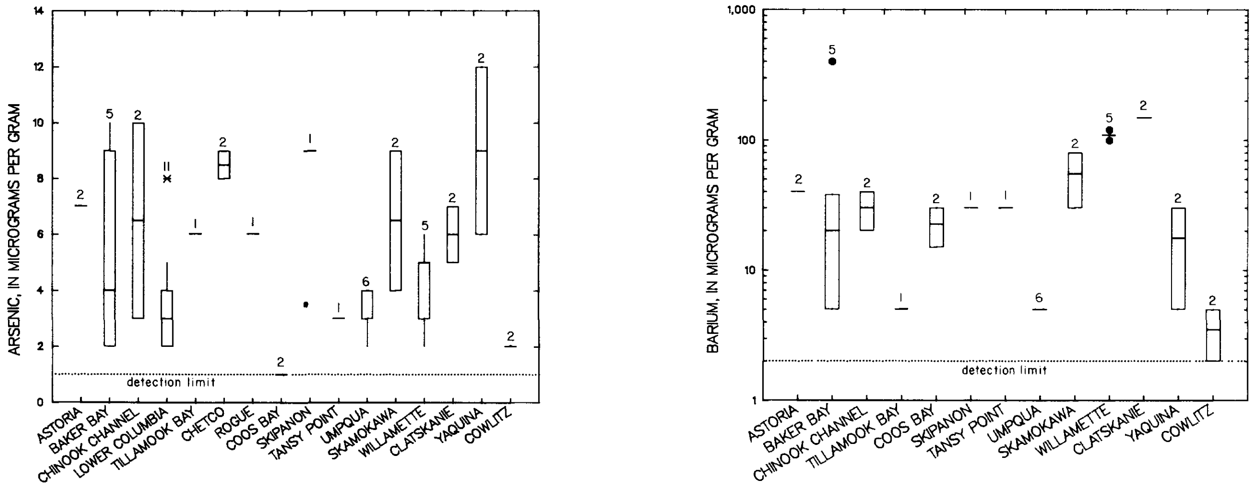
25-percentile value

Less than 1.5 times the interquartile range from the 25-percentile value

⁎ 1.5 to 3 times the interquartile range from the 25-percentile value

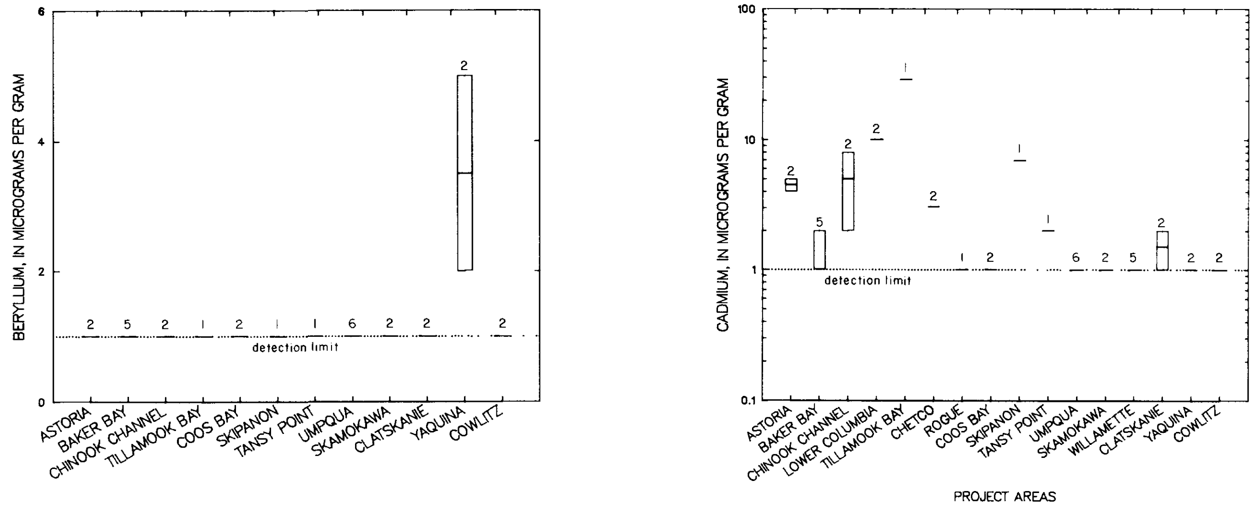
● More than 3 times the interquartile range from the 25-percentile value

Figures 3a-o.--Comparisons of percentile distributions in elutriate-test filtrate at reconnaissance study project areas for selected elements and constituents. The analytical detection limit for cadmium is 0.01 micrograms per liter for Chinook Channel, Skamokawa, Willamette, Yaquina, and Cowlitz project areas. The analytical detection limit for zinc is 0.12 micrograms per liter for Willamette, Yaquina, Cowlitz, and Lake project areas--Continued.



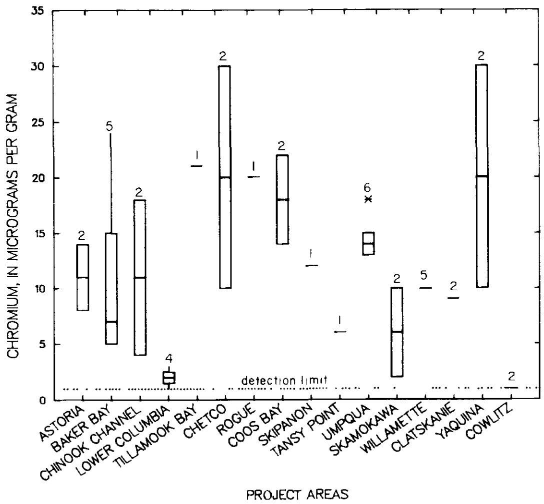
a. Arsenic

b. Barium



c. Beryllium

d. Cadmium



e. Chromium

EXPLANATION

Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

2 Number of samples

● More than 3 times the interquartile range from the 75-percentile value

⁎ 1.5 to 3 times the interquartile range from the 75-percentile value

Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

Median value

25-percentile value

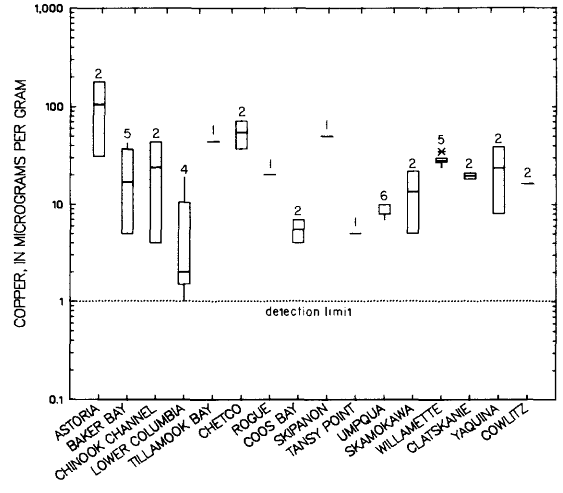
Less than 1.5 times the interquartile range from the 25-percentile value

⁎ 1.5 to 3 times the interquartile range from the 25-percentile value

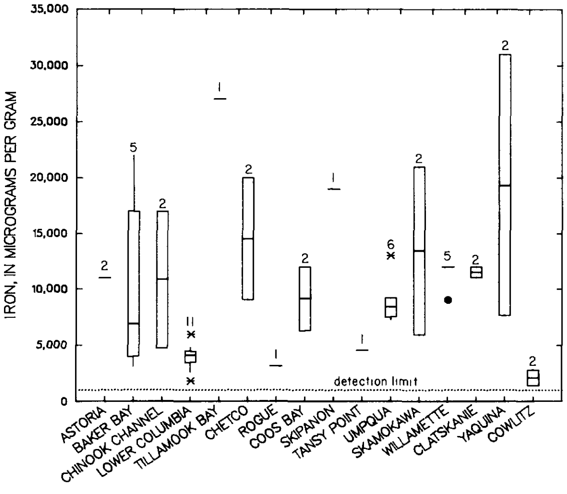
● More than 3 times the interquartile range from the 25-percentile value

Figures 4a-o.--Comparisons of percentile distributions in bottom material at reconnaissance study project areas for selected elements and constituents. The analytical detection limit for nickel is 2.5 micrograms per gram for the Cowlitz project area.

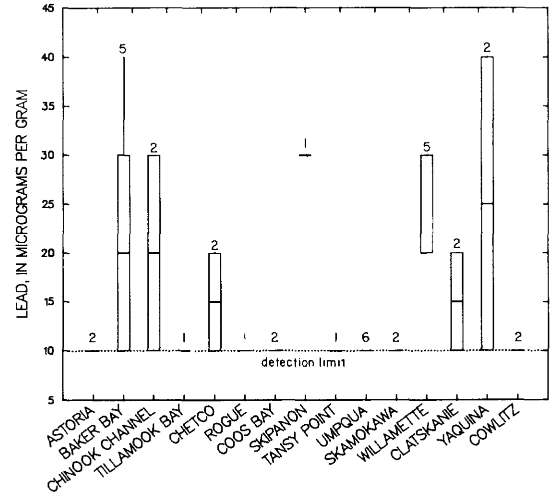
f. Copper



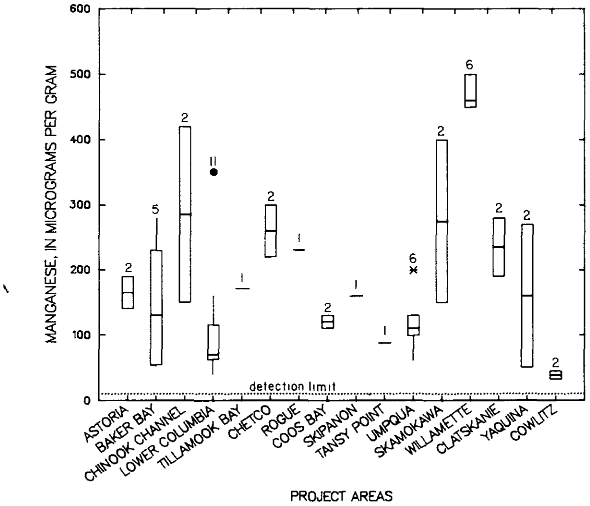
g. Iron



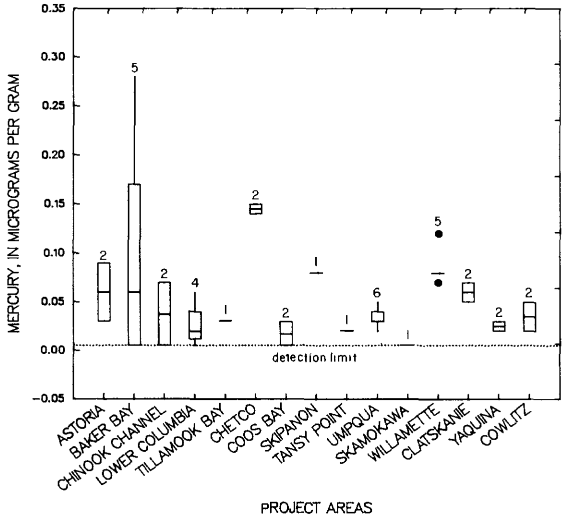
h. Lead



i. Manganese



j. Mercury



EXPLANATION

Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

2 Number of samples

● More than 3 times the interquartile range from the 75-percentile value

× 1.5 to 3 times the interquartile range from the 75-percentile value

Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

Median value

25-percentile value

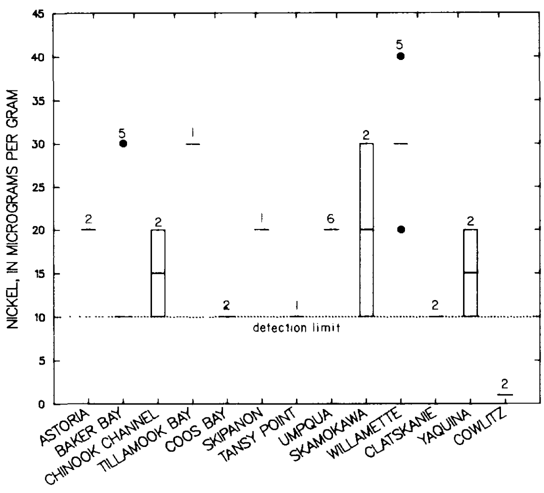
Less than 1.5 times the interquartile range from the 25-percentile value

× 1.5 to 3 times the interquartile range from the 25-percentile value

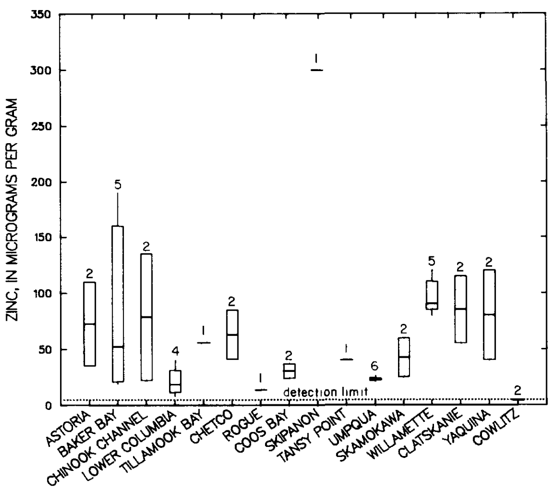
● More than 3 times the interquartile range from the 25-percentile value

Figures 4a-o.--Comparisons of percentile distributions in bottom material at reconnaissance study project areas for selected elements and constituents. The analytical detection limit for nickel is 2.5 micrograms per gram for the Cowlitz project area--Continued.

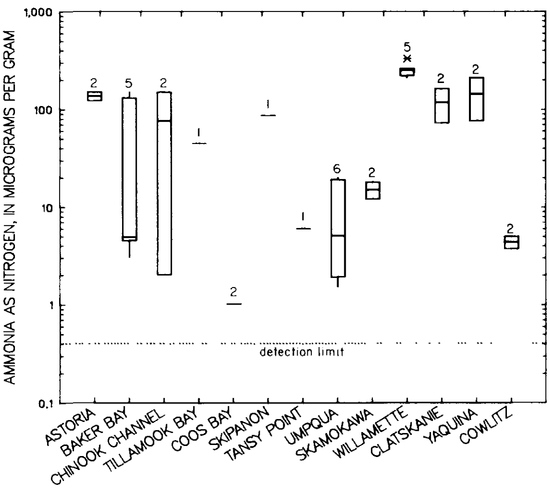
k. Nickel



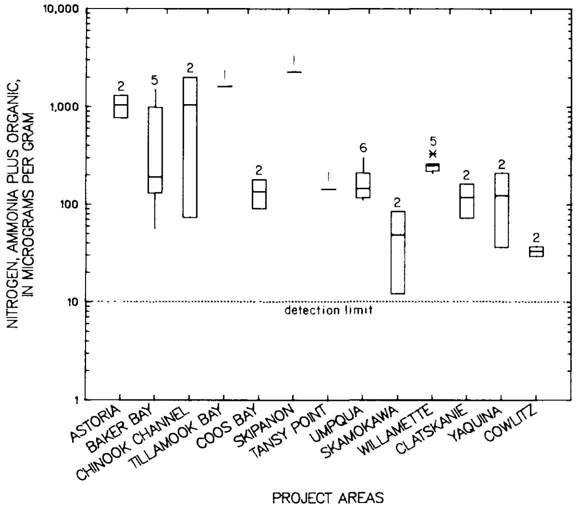
l. Zinc



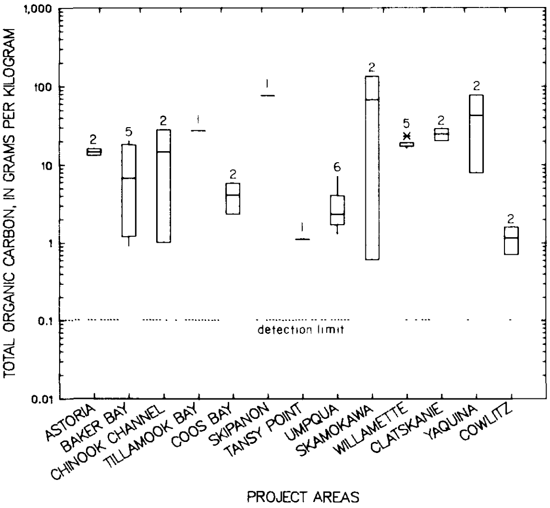
m. Ammonia



n. Nitrogen, ammonia plus organic



o. Organic carbon



EXPLANATION

Interquartile range equals the value of the 75th percentile minus the value of the 25th percentile.

2 Number of samples

● More than 3 times the interquartile range from the 75-percentile value

× 1.5 to 3 times the interquartile range from the 75-percentile value

Less than 1.5 times the interquartile range from the 75-percentile value

75-percentile value

Median value

25-percentile value

Less than 1.5 times the interquartile range from the 25-percentile value

× 1.5 to 3 times the interquartile range from the 25-percentile value

● More than 3 times the interquartile range from the 25-percentile value

Figures 4a-o.--Comparisons of percentile distributions in bottom material at reconnaissance study project areas for selected elements and constituents. The analytical detection limit for nickel is 2.5 micrograms per gram for the Cowlitz project area--Continued.

The Portland Harbor reach of the Willamette River is highly industrialized and urbanized. Of the chemicals examined in Portland Harbor sediments,. concentrations of Ba, Cu, Fe, Pb, Mn, Hg, Ni, Zn, NH_3, NH_4+Org_N (ammonia plus organic nitrogen as N), and TOC exceed the median concentration (table 8) of the other project areas (figs. 4b and 4f-4o). Chemical concentrations of Mn, Ni, and NH_3 in Willamette project bottom material are the maximum concentrations observed.

Analysis of Variance for Constituents within Elutriates Classified as Fresh, Euryhaline, and Estuarine

Analysis of variance and Tukey's studentized range test were used to test the statistical validity of partitioning elutriate data into fresh, euryhaline, and estuarine classifications based on salinity and specific conductance (fig. 2, p. 7). The procedure, unless otherwise indicated by a asterisk in table 9, was used on variables where at least 75 percent of the data were greater than or equal to the analytical-detection limit. Analysis of variance was used on unbalanced data to test the null hypothesis that mean ranks of constituents within one elutriate classification are equal to those of another. Rejection of the null hypothesis ($\rho = 0.05$) indicates that mean ranks for at least two elutriate classifications, for a given constituent, are significantly different. Analysis of variance determines if mean-rank chemical concentrations of fresh, euryhaline, and estuarine classifications are statistically different; it does not show which mean ranks are statistically different. Tukey's studentized range test is used on output generated from ANOVA to show specific elutriate classifications where mean ranks, for a given constituent, are similar or dissimilar to one another. Where mean-ranks differ from one another, the symbol (A, B, or C in tables 9 and 10) will differ for each classification; classifications where mean ranks are not significantly different will be assigned the same symbol.

Tukey's studentized range test indicates that, with the exception of specific conductance (the measurement originally used to partition the data set), no parameters have mean ranks that are significantly different for all three classifications (table 9). As an example, consider mean ranks derived from elutriate concentrations of Fe, Mn, and Zn. These constituents are different populations in tests classified as fresh and estuarine or euryhaline and estuarine, but are not different populations in fresh and euryhaline water. Some constituents, like gross phenols, NH_4+Org_N, and Ni have mean ranks in all three classifications that are not significantly different. In many instances, the partitioning of elutriate data cannot be supported statistically, yet intuitively some mechanism is sought to differentiate between elutriate tests of varying salinities and specific conductances.

Tukey's studentized range test can determine if mean ranks are significantly different, even though some mean ranks used in the ANOVA procedure are generated from chemical data below analytical detection limits (Ba, Be, Cd, Cr, Cu, Hg, and Pb; table 9). Mean ranks of Ba, Be, Cd, and Hg differ for two of the three elutriate classifications. No chemical constituent has mean ranks that are significantly different for all three classifications. Concentrations of Hg in the euryhaline classification have the highest mean rank, compared with fresh and estuarine groupings. The mean rank of Hg in the fresh classification is significantly different from those of euryhaline and estuarine classifications. Differences between mean ranks for Hg are not unexpected, since Hg in fresh classifications was detected less frequently and in smaller concentrations than it was in euryhaline and estuarine groupings.

Table 9.--Results of Tukey's studentized range test on analysis of variance on elutriates classified as fresh, euryhaline, and estuarine

[A, B, and C = classification designations; classifications with the same letter are not significantly different (ρ = 0.05). Values are the order of mean ranks for the units; 1, 2, 3 = rank of the highest to lowest mean, respectively; * = constituents assigned the same letter which may or may not have significantly different mean ranks (ρ = 0.1), because greater than 25 percent of data are below limits of detection]

	Fresh		Euryhaline		Estuarine	
Element	Classification	Rank	Classification	Rank	Classification	Rank
Arsenic	B*	2	A	1	B*	3
Iron	B	2	B	3	A	1
Manganese	B	2	B	3	A	1
Nickel	A	2	A	1	A	3
Zinc	B	2	B	3	A	1
Ammonia	B	3	A	1	A	2
Nitrogen, ammonia plus organic	A	3	A	1	A	2
Orthophosphate	B	3	A	2	A	1
pH	B	3	A	1	B	2
Total organic carbon	B	3	A	1	B	2
Gross phenols	A	2	A	1	A	3
Barium	B*	3	B*	2	A	1
Beryllium	B*	2	A*	3	A*	1
Cadmium	B*	2	B*	3	A	1
Chromium	A*	3	A*	2	A*	1
Copper	A*	1	A*	2	A*	3
Lead	A*	1	A*	3	A*	2
Mercury	B	3	A*	1	A*	2
Specific conductance	C	3	B	2	A	1

Table 10.--Results of Tukey's studentized range test on analysis of variance on elutriate tests made with estuarine and fresh native-mixing water on the same bottom material

[A and B = classification designations; classifications with the same letter are not significantly different ($\alpha = 0.05$). Values are the order of mean ranks for the units, 1 and 2 = rank of the highest and lowest mean, respectively. * = constituents assigned the same letter which may or may not have significantly different mean ranks ($\rho = 0.1$), because greater than 25 percent of data are below limits of detection]

Element	Estuarine mixing water		Fresh-mixing water	
	Classification	Rank	Classification	Rank
Arsenic	A	1	A	2
Iron	A	1	B	2
Manganese	A	1	B	2
Nickel	A	1	A	2
Zinc	A	1	B	2
Ammonia	A	1	A	2
Nitrogen, ammonia plus organic	A	1	A	2
Orthophosphate	A	2	A	1
pH	A	2	A	1
Total organic carbon	B	2	A	1
Gross phenols	A	1	A	2
Barium	A	1	B	2
Beryllium	A*	1	A*	2
Cadmium	A*	1	A*	2
Chromium	A*	1	A*	2
Copper	A*	2	A*	1
Lead	A*	1	A*	2
Mercury	A*	2	A*	1

Analysis of Variance for Elutriate Tests Made with Estuarine Water in Comparison to Fresh-native Water

The source of native-mixing water can affect chemical concentrations in ETF. When native-mixing water and interstitial pore water differ in conductance, ion-exchange reactions occur (Van Der Weijden and others, 1977). The end result of ion exchange (desorption) is an increase of dissolved trace metals in ETF. Generally, larger chemical concentrations occur in elutriate tests made with higher salinity mixing water (euryhaline and estuarine elutriates). As an example, the largest mean ranks (ranks = 1, table 9) for most of the parameters occur in euryhaline and estuarine elutriates.

Duplicate elutriate tests were made to better examine the role of mixing-water salinity on chemicals determined in ETF. Each test used identical bottom materials, but different mixing waters; estuarine mixing water was used in one test and fresh-mixing water was used in the other. Analysis of variance, combined with Tukey's studentized range test, was used to determine if mixing-water salinity affects ETF chemical concentrations.

Mean ranks of Fe, Mn, Zn, TOC, and Ba are significantly different in elutriate tests with the same bottom material but different mixing waters (table 10). Mean ranks of Fe, Mn, Zn, and Ba were greater with estuarine mixing water than with fresh (non-saline) water. In contrast, the mean rank of TOC is lower with saline mixing water than with riverine water. The removal of freshwater associated with dissolved organic carbon is not unusual during estuarine mixing (Burton and Liss, 1976). Chemical concentrations of As, NH_4+Org_N, orthophosphate, and gross phenols are unaffected (no significant difference between mean ranks) by mixing-water salinity. Likewise, Be, Cd, Cr, Cu, Hg, and Pb appear unaffected by mixing-water salinity, but, because greater than 25 percent of these data are below analytical detection limits, significant differences between mean ranks could be masked.

Kendall's Tau Correlation Tests of Single and Combined Elutriate Classifications

Selection of constituents for Kendall's Tau correlation tests varied according to elutriate classifications. Constituents were grouped for correlation testing based on whether or not their mean-rank chemical concentration significantly differed ($\rho = 0.05$) between elutriate classifications. When mean ranks differed, correlations were made independently on chemicals within each single classification. Conversely, when mean ranks did not significantly differ, chemical data were placed into a combined classification (fresh, euryhaline, and estuarine elutriates) for correlation testing.

Of the correlations made within the single-estuarine classification, Fe and Mn are negatively correlated with pH (table 11). The release of Fe and Mn appears to be directly related to the increased H^+ concentration during the test. The newly formed H^+ ions compete with heavy trace-metal cations, thereby releasing trace metals, like Fe and Mn, associated with bottom material (Forstner and Wittmann, 1979).

Table 11.--Levels of significance for Kendall's Tau correlations of elutriates classified as single and combined

[Significance levels determined for constituents in elutriate classifications (determined by Tukey's studentized range test) that have mean ranks significantly different from those in other classifications. Parentheses define significance levels in which 25 percent of data are below detection limits. * indicates that correlations were not made because more than 25 percent of the data are below detection limits]

	Single classifications										
	Fresh			Euryhaline			Estuarine				
Constituent	Ammonia	Mercury	Orthophosphate	Arsenic	pH	Organic carbon	Barium	Cadmium	Iron	Manganese	Zinc
Arsenic	0.001	*			-0.05		(0.1)	*			
Barium	*	*	*	*	*	*	*	*	*	*	*
Beryllium	*	*	*	*	*	*	*	*	*	*	*
Cadmium	*	*	*	*	*	*	*	*	*	*	*
Chromium	*	*	*	*	*	*	*	*	*	*	*
Copper		*	(-0.05)			(0.05)		*			
Iron		*			-.05			*		0.001	0.001
Lead	*	*	*	*	*	*	*	*	*	*	*
Manganese		*			-.1			*	0.001		.01
Mercury	*	*	*	*	*	*	*	*	*	*	*
Nickel		*		0.05		-.01		*		-.05	
Zinc		*		(.1)				*	(.001)	(.01)	
Ammonia		*				.001	(.05)	*	.001	.001	
Nitrogen, ammonia plus organic	.001	*	-.1					*		.01	
Orthophosphate		*					(-.01)	*	-.01	-.01	
Organic carbon		*					(.1)	*	.001	.001	
Gross phenols		*				.001		*	.05	.001	.01
pH	-.05	*	-.05	-.05					-.001	-.05	

	Combined classifications												
								Fresh, euryhaline, and estuarine					
	Fresh and estuarine			Euryhaline and estuarine									
Constituent	Arsenic	Organic carbon	pH	Ammonia	Beryllium	Mercury	Orthophosphate	Chromium	Copper	Nitrogen ammonia plus organic	Lead	Nickel	Gross phenols
Arsenic	*	0.001		0.05	*	*		*	*	0.001	*		0.05
Barium	*	*	*	*	*	*	*	*	*	*	*	*	*
Beryllium	*	*	*	*	*	*	*	*	*	*	*	*	*
Cadmium	*	*	*	*	*	*	*	*	*	*	*	*	*
Chromium	*	*	*	*	*	*	*	*	*	*	*	*	*
Copper	*					*		*	*		*		
Iron	*	.001		.05	*	*	-0.01	*	*		*		
Lead	*	*	*	*	*	*	*	*	*	*	*	*	*
Manganese	*	.001		.001	*	*	-.05	*	*	.05	*		.01
Mercury	*	*	*	*	*	*	*	*	*	*	*	*	*
Nickel	*	-.05		-.1	*	*	-.05	*	*		*		-.05
Zinc	*				*	*		*	*		*	(0.05)	
Ammonia	*	.001			*	*		*	*	.001	*		.01
Nitrogen, ammonia plus organic	*	.001		.001	*	*	-.05	*	*		*		.05
Orthophosphate	*				*	*		*	*	-.1	*		.001
Organic carbon	*			.001	*	*		*	*		*	-.01	.001
Gross phenols	*	.01		.001	*	*		*	*	.05	*	-.05	
pH	*				*	*		*	*				

Relations between Ni and organic carbon are more problematic. Ni correlated negatively with carbon in the euryhaline classification and in the combined fresh and estuarine classification (table 11). Because organic carbon determinations were made on ETF passing through a nominal 10-μm filter, carbon probably exists in two forms--dissolved organic carbon (DOC) and particulate organic carbon (POC). Particulate organic carbon can sorb trace-metal ions (including Ni) from solution (Forstner and Wittmann, 1979). If increases in DOC represent increased POC concentrations, the negative relation (between organic carbon and Ni) may result from sorption of Ni by POC during the test.

In the combined elutriate classification (fresh, euryhaline, and estuarine), gross phenols are significantly correlated with As, organic carbon, Mn, orthophosphate, as well as with NH_3 and NH_4+Org_N (table 11). Some phenols dissociate at ambient pH's found in the pore water of estuarine sediments. Sorption of these dissociated forms are significant in sediments enriched in organic carbon (Schellenberg and others, 1984). Because elutriate samples analyzed for gross phenols and organic carbon likely contain POC (particulate organic carbon passing through the nominal 10-μm pore-size filter), increases in gross-phenol concentration may result from the sorption of dissociated phenols to POC. Furthermore, the relations between gross phenols, NH_3, and NH_4+Org_N suggest that larger concentrations of gross phenols occur in anerobic sediments. Anerobic sediments are known to produce reduced nitrogen forms like NH_3 via the bacterial oxidation of organic matter (Wetzel, 1975).

Kendall's Tau Correlation Tests of Chemical Constituents in Bottom Material and Elutriates

Generally, the occurrence of large chemical concentrations in bottom material does not coincide with large chemical concentrations in ETF. Trace metals in bottom material commonly are isolated from the aqueous phase by inclusion in mineral lattices or by the coating of sediment particles by carbonates, POC, and oxides of silica and Fe (Jenne, 1976). Of the chemical relations examined, only correlations between NH_3 in bottom material and NH_3 in ETF are significant and common to each elutriate classification (tables 12, 13, and 14). Common to individual classifications are significant correlations between As, in fresh elutriates (table 12); Mn, in euryhaline elutriates (table 13); and Ba, Mn, Ni, TOC, and NH_4+Org_N, in estuarine elutriates (table 14). Because many factors (such as pH, Eh, DO, solid-to-liquid ratio, etc.) affect ETF chemical concentrations, bottom-material chemical concentrations--with the exception of NH_3--are not a reliable estimator of ETF chemical concentrations.

The negative relations between Cd ETF concentrations and Cu, Fe, Pb, Ni, and Zn in bottom material (tables 12 and 14) indicate that Cd release occurs in instances where trace-metal concentrations in elutriate-test sediments are small. The largest Cd ETF concentrations occur in estuarine elutriates made with predominantly coarse-grained, oxic sediments (Fuhrer, 1984). Why Cd--and not other trace metals--would be released in elutriation of coarse-grained sediment is unknown, although concentrations in coarse-grained sediments have been reported as large as 10 μg/g (Fuhrer, 1984). The ease of Cd dissolution in coarse-grained sediment may simply reflect the lack of substrates (hydrous Fe and Mn oxides, organic coatings, etc.) on coarse-grained sediments; however, further study of Cd releases in coarse-grained sediment is required.

Table 12.--Levels of significance for Kendall's Tau correlations of bottom material with elutriates classified as fresh water

[Parenthesis define significance levels determined where 25 percent of the data are below analytical detection limits; negative correlations are indicated preceding the significance level, all others are positive. N = the number of elutriate and bottom-material samples correlated. * = correlations not made because more than 25 percent of data were below detection limits]

		Elutriates classified as fresh water																
Bottom material	N	Arsenic	Barium	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Zinc	Ammonia	Organic carbon	Total volatile solids	Phosphorus	Gross phenols	Beryllium
Arsenic	11	(0.05)	*		*	(-0.1)		*		*								*
Barium	11	(.001)	*		*			*		*			0.01	0.05				*
Cadmium	11	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
Chromium	11		*		*			*	-0.01	*		-0.01	.05					*
Copper	11	(.05)	*	-0.05	*			*		*			.001	.05		-0.05		*
Iron	11		*		*	(-.05)		*	.01	*			.1					*
Lead	11	(.1)	*	(-.05)	*			*		*		(-.05)	(.01)	(.05)	(0.05)			*
Manganese	11	(.05)	*	.05	*			*		*		-.05	.001	.05	.05	-.05		*
Mercury	10	(.05)	*		*			*	.05	*		-.1	.05	.05		-.1		*
Nickel	11		*	-.05	*			*	.05	*		-.05	.001		.01			*
Zinc	11	(.01)	*		*			*		*			.001		.1			*
Ammonia	11	(.05)	*	-.05	*			*		*			.001	.001	.001	-.05		*
Total organic carbon	7		*		*			*		*			.1					*
Nitrogen, ammonia plus organic	11	(.001)	*	.1	*			*		*		-.05	.001	.05				*
Phosphorus	11	(.01)	*		*			*		*		-.05	.001	.05	.05			*
Total volatile solids	7	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*

Table 13.--Levels of significance for Kendall's Tau correlations of bottom material with elutriates classified as euryhaline water

[Parenthesis define significance levels determined where 25 percent of the data are below analytical detection limits; negative correlations are indicated preceding the significance level, all others are positive; N = the number of elutriate and bottom-material samples correlated. * = correlations not made because more than 25 percent of data were below detection limits]

Bottom material	N	Barium	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Zinc	Ammonia	Nitrogen, ammonia plus organic	Phosphorus	Gross phenols	Beryllium
		Elutriates classified as euryhaline water														
Arsenic	12	*	*	*	*		*				*	0.001	0.01	-0.05		*
Barium	9	*	*	*	*		*			(-0.1)	*				0.1	*
Cadmium	12	*	*	*	*		*		(0.05)		*	.05				*
Chromium	12	*	*	*	*	0.05	*	0.05			*	.05			.05	*
Copper	12	*	*	*	*		*				*	.001	.1			*
Iron	12	*	*	*	*		*				*	.01	.01		.01	*
Lead	12	*	*	*	*		*				*	.1				*
Manganese	12	*	*	*	*		*	.001			*					*
Mercury	11	*	*	*	*		*	.1			*					*
Nickel	9	*	*	*	*		*				*	.05				*
Zinc	12	*	*	*	*		*				*				.05	*
Ammonia	9	*	*	*	*		*	.05			*	.01	.01	-.1	.01	*
Total organic carbon	9	*	*	*	*	.05	*				*	.001	.1		.1	*
Nitrogen, ammonia plus organic	9	*	*	*	*		*				*	.01			.01	*
Phosphorus	9	*	*	*	*		*	.05			*				.1	*
Total volatile solids	9	*	*	*	*		*				*	.05				*

Table 14.--Levels of significance for Kendall's Tau correlations of bottom material with elutriates classified as estuarine water

[Parentheses define significance levels determined where 25 percent of the data are below analytical detection limits; negative correlations are indicated preceding the significance level, all others are positive. N = the number of elutriate and bottom material samples correlated; * = correlations not made because greater than 25 percent of data were below detection limits]

		Elutriates classified as estuarine water																
Bottom material	N	Arsenic	Barium	Cadmium	Chromium	Copper	Iron	Lead	Manganese	Mercury	Nickel	Zinc	Ammonia	Organic carbon	Nitrogen, ammonia plus organic	Phosphorus	Gross phenols	Beryllium
Arsenic	23	*	0.01		*			*	0.01	*	0.01	0.1	0.001	0.001	0.001	-0.05		*
Barium	19	*	(.05)		*	(-0.1)		*	.05	*			.05	.01	.05	-.01	0.05	*
Cadmium	23	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*		*
Chromium	23	*	(.1)		*			*	.05	*				.01	.1		.05	*
Copper	23	*	(.01)	-0.01	*			*	.01	*	.001		.01	.001	.001		.05	*
Iron	23	*	(.01)	-.05	*			*	.01	*	-.01		.05	.001	.01		.1	*
Lead	23	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*		*
Manganese	23	*	(.01)		*			*	.001	*			.05	.01	.1		.01	*
Mercury	23	*	.05		*			*	.001	*			.05	.01	.01		.1	*
Nickel	19	*			*			*		*	-.1							*
Zinc	23	*		-.1	*			*	.01	*	-.01		.01	.001	.01		.01	*
Ammonia	19	*	(.1)	-.1	*		0.05	*	.001	*	-.01		.001	.001	.001		.01	*
Total organic carbon	19	*			*		.01	*	.01	*	-.01		.01	.001	.05		.05	*
Nitrogen, ammonia plus organic	19	*		-.1	*		.05	*	.001	*	-.001		.01	.001	.05		.05	*
Phosphorus	19	*			*			*	.01	*	-.01			.001		-.05	.01	*
Total volatile solids	17	*			*			*	.01	*	-.1		.05	.05				

In the present study, total-volatile-solids (solids, volatile on ignition, in bottom material) or grain-size criteria are of limited value for characterizing sediments likely to release chemicals into ETF. As an example, consider total phenols detected in estuarine elutriate tests. In 50 percent of these tests, the total-phenol concentration exceeded 55 µg/L and bottom material contained less than 4-percent volatile solids. If volatile solids exceeding 4 percent were used as a guide for omitting testing, these bottom materials would have been excluded. More specifically, bottom material from the Columbia River near RM 32.2 contained only 2-percent volatile solids and no measurable concentration of particles less than 62 micrometers in diameter; yet, concentrations of total phenols were 210 µg/L. Conversely, 21 percent of the bottom materials in which volatile solids exceeded 4 percent corresponded to tests in which concentrations of total phenols were less than 55 µg/L. Characterizing bottom materials likely to release chemicals into ETF based on total volatile-solids or grain-size criteria is of limited value for this study.

POTENTIAL WATER-QUALITY CONCERNS

Median ETF concentrations, representing the combined-elutriate classification (table 4), were selected as reference points for the discussion of water-quality concerns. Median ETF concentrations of Mn, NH_3, and phenols were the only concentrations that exceed EPA criteria established to protect aquatic organisms (tables 4 and 15). Whether or not ETF chemical concentrations persist for time periods corresponding to those used for EPA toxicity tests is not known. Trace constituents generally are present in native water in two basic states: sorbed to suspended-sediment particles and dissolved in native water. The latter state, measured in the present study, reflects directly on water quality because dissolved-trace constituents are readily available to the biota. The sorbed state, not measured in the present study, reflects indirectly on water quality because suspended-trace constituents are ingested and bioaccumulated by many benthic organisms. Water-quality concerns discussed in the present study focus solely on dissolved-trace constituents and should be evaluated accordingly.

Manganese

The toxicity of Mn to aquatic organisms is less severe than indicated by the 100-µg/L guideline (U.S. Environmental Protection Agency, 1977). The 48-hour LC50 (that concentration lethal to 50 percent of the organisms tested) for embryos of the American oyster, *Crassostrea Virginica*, and the 96-hour LC50 for young rainbow trout, *Salmo gairdneri* (England and Cummings, 1971), are reported to be as large as 16,000 µg/L, 160 times the EPA guideline maximum (Calabrese and others, 1973). A 29-day exposure to 370 to 4,000 µg/L Mn (as aqueous manganese sulphate, 4 to 40 times the EPA guideline maximum, resulted in a 5- to 23-percent increase in mortality of developing rainbow trout eggs (Lewis, 1976).

Manganese toxicity probably is of greater concern in saline water systems than in fresh waters. As mentioned earlier, mean-rank Mn ETF concentrations are larger in tests made with saline mixing water than in tests made with non-saline water. The largest ETF concentration of Mn (15,000 µg/L) occurred when anoxic sediments were mixed with native ocean water (Fuhrer, 1984). If dredge spoils containing similar Mn concentrations are placed in ocean disposal waters, the sulfate and bicarbonate complexes that are likely to form with Mn^{+2} in ocean water

Table 15.--U.S. Environmental Protection Agency guidelines for various water uses including fresh and marine water aquatic life

[Guidelines are based on total concentrations (dissolved and suspended chemical forms); welfare = to control for undesirable taste and odor quality; LC50 = the concentration lethal to 50 percent of the test organisms; ND = not determined; concentrations are in micrograms per liter (µg/L), unless otherwise stated; mg/L = milligrams per liter; aquatic-life criteria are derived for hardness of 50 milligrams per liter, as $CaCO_3$ (calcium carbonate). DDD = dichloro diphenyl dichloroethane, DDE = dichloro diphenyl dichloroethylene, DDT = dichloro diphenyl trichloroethane, PCB = polychlorinated biphenyls, and PCN = polychlorinated naphthalenes; 2,4-D = 2,4-dichlorophenoxyacetic acid; 2,4-DP = 2,4-D-dimethylphenol; 2,4,5-T = 2,4,5-trichlorophenoxyacetic acid; < = less than]

Constituent	Maximum concentration	Water use (U.S. Environmental Protection Agency, 1977)	Maximum concentration	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	Aquatic 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)	.012	Freshwater 24-hour average. not to exceed 1.5 µg/L at any time
	.4	Soft fresh--cladocerans, salmonid fishes		
	4.0	--less sensitive organisms	4.5	Marine 24-hour 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)	.29	Freshwater 24-hour average, not to exceed 21 µg/L at any time (hexavalent)
	100	Freshwater aquatic life		
			2,200	Freshwater at (trivalent)
			18	Marine 24-hour average, not to exceed 1,260 at any time (hexavalent)
			10,300	Marine, acute (trivalent)

Table 15.--U.S. Environmental Protection Agency guidelines for various water uses including fresh and marine water aquatic life--Continued

Constituent	Maximum concentration	Water use (U.S. Environmental Protection Agency, 1977)	Maximum concentration	Aquatic life (U.S. Environmental Protection Agency, 1980)
Copper	1,000	Domestic water supply (welfare)	5.6	Freshwater 24-hour average, not to exceed 12 μg/L at any time
	.1 times 96 hour LC50	Aquatic resident species	4.0	Marine 24-hour average, not to exceed 23 μg/L
Iron	300	Domestic water supply (welfare)		
	1,000	Freshwater aquatic life		
Lead	50	Domestic water supply (health)	0.75	Freshwater 24-hour average, not to exceed 74 μg/L at any time
	.01 times 96 hour 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-hour average, not to exceed 0.0017 μg/L at any time
			0.025	Marine 24-hour average, not to exceed 3.7
Nickel	.01 times 96 hour LC50	Freshwater and marine aquatic life	56	Freshwater 24-hour average not to exceed 1,100 μg/L at any time
			7.1	Marine 24-hour average not to exceed 140 μg/L at any time
Zinc	5,000	Domestic water supply (welfare)	47	Freshwater 24-hour average not to exceed 180 μg/L at any time
	.01 times 96 hour LC50	Sensitive resident species		
	1	Chinook salmon (1 month old)	58	Marine 24-hour average, not to exceed 170 μg/L at any time
Total Phosphate Phosphorus	50	Streams		
	25	Lakes or reservoirs		
	100	Desired goal for streams or flowing waters not discharging directly to lakes or impoundments		

Table 15.--U.S. Environmental Protection Agency guidelines for various water uses including fresh and marine water aquatic life--Continued

Constituent	Maximum concentration	Water use (U.S. Environmental Protection Agency, 1977)	Maximum concentration	Aquatic life (U.S. Environmental Protection Agency, 1980)
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)		
Aldrin	.003	Freshwater and marine aquatic life	3	Freshwater
			1.3	Marine
Chlordane	.01	Freshwater aquatic life	.0043	Freshwater 24-hour average, not to exceed 2.4 μg/L at any time
	.004	Marine aquatic life		
DDD	ND			
DDE			1050	Freshwater aquatic life
			14	Marine aquatic life
DDT	.001	Freshwater and marine aquatic life	.0010	Freshwater 24-hour average, not to exceed 1.1
			.0010	Marine 24-hour average, not to exceed 0.13 μg/L at any time
Dieldrin	.003	Freshwater and marine aquatic life	.0019	Freshwater 24-hour average, not to exceed 2.5 μg/L at any time
			.0019	Marine 24-hour average, not to exceed 0.71 μg/L at any time
Endosulfan	.003	Freshwater aquatic life	.056	Freshwater 24-hour average, not to exceed 0.22 μg/L at any time
	.001	Marine aquatic life	.0087	Marine 24-hour average, not to exceed 0.034 μg/L at any time
Endrine	.2	Domestic water supply (health)	.0023	Freshwater 24-hour average, not to exceed 0.18 μg/L at any time
	.004	Freshwater and marine aquatic life	.0023	Marine 24-hour average, not to exceed 0.037 μg/L at any time
Heptachlor	.001	Freshwater and marine aquatic life	.0038	Freshwater 24-hour average, not to exceed 0.52 μg/L at any time
			.0036	Marine 24-hour average, not to exceed 0.053 μg/L at any time

Table 15.--U.S. Environmental Protection Agency guidelines for various water uses including fresh and marine water aquatic life--Continued

Constituent	Maximum concentration	Water use (U.S. Environmental Protection Agency, 1977)	Maximum concentration	Aquatic life (U.S. Environmental Protection Agency, 1980)
Lindane	4	Domestic water supply	0.08	Freshwater 24-hour average, not to exceed 2.0 μg/L at any time
	.01	Freshwater aquatic life		
	.004	Marine aquatic life	.16	Marine
Methoxychlor	100	Domestic water supply (health)		
	.03	Freshwater and marine aquatic life		
Mirex	.001	Freshwater and marine aquatic life		
PCB	.001	Freshwater and marine aquatic life	.014	Freshwater 24-hour average, not to exceed 2.0 μg/L at any time
			.03	Marine 24 hour average, not to exceed 10.0 μg/L at any time
PCN	ND			
Perthane	ND			
Silvex (2,4,5-TP)	10	Domestic water supply (health)		
Toxaphene	5	Domestic water supply (health)	.013	Freshwater 24-hour average, not to exceed 1.6 μg/L at any time
			.070	Marine
2,4-D	100	Domestic water supply (health)		
2,4-DP			2,020	Freshwater, acute
			365	Freshwater, chronic
2,4,5-T	ND			
Phenols	1	Domestic water supply (welfare) and for the protection against fish flesh tainting	10,200	Freshwater, acute
			2,560	Freshwater, chronic
			5,800	Marine
			3.5 mg/L	Public health
			.3 mg/L	Controlling undesirable taste and odor quality of ambient water

will inhibit oxidation and subsequent precipitation of Mn. Such Mn complexes are readily soluble and, depending on the rate of dilution at the disposal site, may be toxic to marine mollusks (Thurston and others, 1979). The rate of dilution is dependent on the hydrologic regime at the disposal site and will likely vary at different depths. Manganese probably is less toxic in freshwater systems because these systems contain small sulfate and bicarbonate ion concentrations, which limit Mn complexation and make the oxidation and subsequent precipitation of Mn more likely.

Ammonia

When ammonia gas is dissolved in water, an equilibrium is established between the un-ionized ammonia/water complex ($NH_3 \cdot H_2O$) and ionized ammonia (NH_4^+) in solution with hydroxide ions (OH^-). The equilibrium for these chemical species is represented as follows:

$$(1) \quad NH_{3(g)} + H_2O_{(\ell)} \rightleftharpoons NH_3 \cdot H_2O_{(aq)} \rightleftharpoons NH_4^{+}{}_{(aq)} + OH^{-}{}_{(aq)} .$$

Increasing salinity will cause the equilibrium to shift to the right, increasing the concentration of NH_4^+ (Skarheim, 1973; Thurston and others, 1977). Increasing pH and temperature will drive the equilibrium to the left and increase the $NH_3 \cdot H_2O$ concentration. At pH values usually associated with surface waters, ionized-ammonia species are more prevalent than un-ionized ammonia species.

The toxicity of NH_3 in water has been attributed to un-ionized ammonia complexed with water; EPA criterion for un-ionized ammonia in freshwater has been set at 0.02 mg/L as NH_3 (U.S. Environmental Protection Agency, 1977), based on reports that 0.2 mg/L NH_3 is lethal to rainbow trout fry, Salmo gairdners, and a safety factor of 0.1 (Liebmann, 1960; U.S. Environmental Protection Agency, 1977). Recomputation (Thurston and others, 1979) of Liebman's original data (Wuhrman and Woker, 1948), using more accurate aqueous ammonia equilibrium tables, resulted in a level of 0.32 mg/L NH_3.

A study by Brown and others (1969) indicated that fluctuating NH_3 concentrations increase toxicity to rainbow trout. Large and small ammonia-concentration fluctuations at 2-hour intervals resulted in higher mortality rates than fluctuations between the same concentrations at 1-hour intervals or constant exposure to the larger concentrations. Because the release of NH_3 during hopper dredging also will fluctuate, NH_3 toxicity may be significant.

Salmonid species are likely to be found in most of the project areas (U.S. Department of Commerce, National Marine Fisheries Service, 1980). In areas where salinity is low, the 0.02-mg/L NH_3 criterion, based on bioassays using salmonid species, is applicable. In most of the study areas, the salinity values range from 11 to 35 g/kg, but there is no EPA criterion for marine and estuary aquatic life.

If concentrations of NH_3 released during elutriate testing represent those released during dredging operations, disposal of dredged material probably will be deleterious to aquatic organisms. Ammonia ETF concentrations ranged from <0.001 to 46 mg/L and releases of NH_3 occurred in 90 percent of the samples. Ammonia also was detected frequently during elutriate testing and disposal operations by other investigators (Wyeth and Sweeney, 1978; Jones and Lee, 1978). As mentioned earlier, results of Tukey's studentized range test suggest that NH_3 release is unaffected by the salinity of the native-mixing water. Ammonia releases probably are related to the redox state of the sediment, as evidenced in the present study, where TOC-enriched anoxic sediments correspond to large ETF NH_3 concentrations. Oxidation of TOC probably made the sediment anoxic and produced large amounts of ETF NH_3 through denitrification.

To evaluate NH_3 ETF concentrations, the temperature, salinity, and pH of disposal-site waters must be known before NH_3 can be determined from the available tables (Skarheim, 1973; Thurston and others, 1977). Un-ionized ammonia concentrations for one ETF at various pH, salinity, and temperature values are shown in table 16. As is evident from the table, NH_3 concentrations at sites with low pH and temperature values will remain at or near the EPA criterion (0.02 mg/L); and concentrations at sites with little mixing and high pH and temperature values are likely to exceed the EPA criterion. It also is evident that, relative to temperature and pH, salinity will have an insignificant effect on NH_3 concentrations.

Table 16.--Concentrations of un-ionized ammonia under various pH, temperature, and salinity conditions for an estuarine elutriate test

[Bottom material was collected from Astoria Boat Basin, site 7 (Fuhrer and Rinella, 1983). Ammonia as nitrogen concentration is 54 mg/L. g/kg = grams per kilogram; mg/L = milligrams per liter. Data for salinity = 0 are from Thurston and others (1977), and data for salinity = 15 and 35 are from Skarheim (1973)]

Salinity (g/kg)	pH (units)	Un-ionized ammonia nitrogen (mg/L)				
		Temperature (degrees Celsius)				
		5	10	15	20	25.5
0	6.5	0.02	0.03	0.05	0.07	0.10
0	7.0	.07	.10	.15	.21	.31
0	7.5	.21	.31	.46	.66	.98
0	8.0	.67	.99	1.5	2.0	3.0
0	8.5	2.0	3.0	4.3	6.0	8.4
15	6.5	.02	.02	.03	.05	.07
15	7.0	.05	.07	.10	.15	.22
15	7.5	.15	.22	.33	.48	.70
15	8.0	.47	.71	1.0	1.5	1.5
15	8.5	1.5	2.2	3.1	4.5	6.2
35	6.5	.01	.02	.03	.04	.06
35	7.0	.04	.07	.09	.16	.20
35	7.5	.14	.21	.31	.45	.64
35	8.0	.44	.65	.96	1.4	2.0
35	8.5	1.1	2.0	2.9	4.2	5.8

Ammonia concentrations of NH_3 at 0.02 mg/L are given for various pH and temperature values in table 17. Although values in the table are based on zero salinity, salinity effects are negligible; and an NH_3 concentration of 0.87 mg/L would correspond to the 0.02 mg/L criterion for water with a pH of 8 and a temperature of 13 °C. Typical summer pH and temperature values are 8.0 and 13 °C, for estuary and ocean waters along the Oregon Coast. If dredge spoils were to be disposed of under these temperature and pH conditions, NH_3 concentrations within the spoils should not exceed 0.87 mg/L, to ensure that NH_3 remains less than 0.02 mg/L.

Adverse impacts of high NH_3 release during disposal of dredged material can be minimized by disposing of material in ocean water when temperatures are low and rapid dilution is likely to occur.

Table 17.--Concentrations of ammonia containing an un-ionized ammonia concentration of 0.02 milligrams per liter (from Thurston and others, 1974)

pH (units)	Ammonia nitrogen, in milligrams per liter				
	Temperature, in degree Celsius				
	4.0	9.0	13.0	17.0	20.0
7.2	11.0	7.4	5.4	3.9	3.2
7.4	6.9	4.6	3.4	2.7	2.0
7.6	4.4	2.9	2.2	1.6	1.3
7.8	2.8	1.9	1.4	1.0	.82
8.0	1.8	1.2	.87	.65	.49
8.2	1.1	.75	.56	.42	.34
8.4	.71	.48	.36	.27	.22

Chlorophenols

Phenols, if present as chlorophenols, are of particular concern in the Pacific Northwest. Chlorophenols have had widespread use as a wood preservative. The toxicity of chlorophenols varies with the type, position, and number of substitutions on the parent molecule. For example, acute toxicity of unsubstituted phenol is as large as 10,200 μg/L, whereas that of the substituted phenol 2,3,5,6-tetrachlorophenol is as low as 440 μg/L (U.S. Environmental Protection Agency, 1980). However, a survey of toxicity data indicates that the position(s) of chlorination, the pH, and the octanol/water partition coefficient of the compound may affect the toxicity of chlorophenols as well (Rao and others, 1981).

Pentachlorophenol (PCP) and its sodium salt, sodium pentachlorphenate (Na-PCP), are the second most commonly used pesticides in the United States (Rao, 1978). Pentachlorophenol is available commercially as a bactericide, fungicide, and slimicide. As a chlorinated hydrocarbon, it is used as a herbicide, insecticide, and molluscicide (Sittig, 1981). In addition to being manufactured by man, chlorophenol compounds also are produced naturally by the decay of terrestrial and aquatic organisms into humic material, which contains large amounts of polyphenols.

Of the chlorophenols on the EPA Priority Pollutant List, phenol, 2-chlorophenol, and dichlorophenol appear to remain in the water column, whereas 2,4,6-trichlorophenol; pentachlorophenol; 2-nitrophenol; 4-nitrophenol; 2,4-dinitrophenol; 2,4-dimethylphenol; p-chloro-m-cresol; and 4,6-dinitro-p-cresol accumulate in bottom material (Chapman and others, 1982). Highly chlorinated phenols like PCP also are more resistant to degradation and are more likely to accumulate in the biota (Pierce and others, 1977; Pierce and others, 1980; and Chapman and others, 1982). Degradation occurs slowly and is mediated by chemical, microbiological, and photochemical processes (Bevenue and Beckman, 1967; Kaufman, 1978). Degradation of PCP in soils is primarily by reductive halogenation to simpler tetra-, tri-, and dichlorophenols (Kaufman, 1978). Pentachlorophenol also can be methylated to pentachloroanisole (PCA) (Kaufman, 1978; Pierce and others, 1980).

Large gross-phenol ETF concentrations were detected at sites with potential PCP point-source contamination (table 18). In the Skipanon River, gross-phenol ETF concentrations decrease progressively in downstream order from Warrenton, where a wood products mill using PCP as a preservative was located. Large ETF gross-phenol concentrations exist in Depot Slough, Lake River, Yaquina River, and Clatskanie River, where PCP wood preservative techniques are used, or have been used, in the past.

In tests with saline and non-saline mixing waters, ETF gross-phenol concentrations in the Yaquina River (RM 6.3) were 200 μg/L and 195 μg/L, respectively. Two lumber mills near RM 13 have used PCP as a wood preservative; however, determining whether phenols originated from either of the mills is difficult, because the analytical procedure used is nonspecific for PCP. Gross-phenol concentrations immediately below the lumber mills (RM 8.6 and 9.0) were no more than 10 percent of those detected at RM 6.3. Differences in ETF gross-phenol concentrations between RM 6.3 and those concentrations near the mill probably are related to differences in sediment-organic content. Total-volatile-solids determinations were used to estimate sediment-organic content; the concentration of total volatile solids measured in river sediments from RM 6.3 was greater than those measured at the three sites between RM 6.3 and 13. Thus, larger concentrations of gross phenols, whether naturally occurring or anthropogenic, may occur in association with sediments near RM 6.3 because of large organic-material concentrations.

If gross-phenol ETF concentrations at RM 6.3 represent PCP, oyster beds in this area could be affected adversely by dredging operations. Oysters exposed for 28 days to PCP concentrations of 2.5 and 25 μg/L had average tissue accumulations of 41 and 78 times background, respectively (Schimmel and others, 1978). Pentachlorophenol concentrations in oyster tissues reached an equilibrium during the first 4 days of exposure and returned to zero after 4 days in PCP-free water.

Large gross-phenol concentrations also have been detected in ETF from sites where potential point sources are less obvious (Fuhrer and Rinella, 1983). These sites include Baker Bay, Chinook Channel, Astoria Boat Basin, and Astoria Boat Slips. Possible sources include treated pilings and docks, marine-paint additives, and fuel spills.

Table 18.--Potential point sources of gross-phenol compounds detected in the reconnaissance study

[All concentrations are in micrograms per liter; PCP = pentachlorophenol, Na-PCP = pentachlorophenate]

Project area/sites	Phenol concentration	Possible source
Baker Bay:		Ilwaco Boat Basin: treated pilings, additives to dock and boat paints
Site No. 6	419	
Site No. 8	324	
Site No. 5	154	
Site No. 9	103	
Chinook Channel:		Chinook, Washington: treated pilings, paints and preservatives used on boats and docks
Site No. 8	231	
Site No. 9	185	
Skipanon:		Lumber mill at Warrenton: dip tank using Na-PCP, and Boat Basin near Site No. 6
Site No. 3	206	
Site No. 4	245	
Site No. 5	331	
Clatskanie:		Lumber mill in Clatskanie: (PCP)
Site No. 4	131	
Lake River:		Work treatment plant at Ridgefield (PCP)
Site No. 3	105	
Yaquina:		Two lumber mills at Toledo: using dip tanks; one has been using enclosed system since October 1981 (PCP)
Site No. 6	200	
Site No. 9	172	
Site No. 10	188	
Umpqua:		Pulp mill and lumber mill at Gardner: (PCP)
Site No. 13	86	

DISPOSAL OF DREDGED MATERIALS

U.S. Environmental Protection Agency water-quality guidelines stipulate that ETF chemical concentrations are not to exceed EPA water-quality guidelines outside disposal-site boundaries at any time or exceed guidelines at any point after allowing for initial mixing (U.S. Environmental Protection Agency, 1977; 1980). Initial mixing is defined as that dispersion or diffusion of liquid, suspended particulate, and solid phases of material that occurs within 4 hours after disposal (U.S. Environmental Protection Agency, 1980).

Initial mixing could not be determined for this study by an appropriate model. The U.S. Army Corps of Engineers procedures suggest a method of calculating the dilution volume necessary to dilute released chemicals (as represented by ETF concentrations) to concentrations allowable within EPA guidelines (U.S. Environmental Protection Agency and U.S. Army Corps of Engineers, 1977). The volume of dilution water required to bring ETF concentrations into compliance with EPA guidelines is computed using the following equation:

$$Vm = \frac{Vd(C1 - C2)}{C3 - C2}, \qquad (2)$$

where

Vm = volume of native-mixing water,
Vd = volume of dredge,
C1 = concentration in ETF,
C2 = concentration of receiving water, and
C3 = EPA concentration guideline.

By using the dilution-water volume equation (2), Vm was computed for chemicals considered to be potential water-quality concerns (table 19). The required dilution volumes range from 4,850 to 949,000 cubic yards. The smaller dilution volume is equivalent to an area approximately 10-yards deep, 100-yards wide, and 5-yards long; the larger dilution volume is equivalent to an area approximately 10-yards deep, 100-yards wide, and 880-yards long.

U.S. Environmental Protection Agency water-quality guidelines have been developed for the protection of domestic water supplies and aquatic life (see table 15). Some EPA guidelines require that 24-hour average concentrations not exceed an EPA-specified maximum (U.S. Environmental Protection Agency, 1980). Generally, use of aquatic guidelines requires a water-hardness (calcium carbonate, or $CaCO_3$) determination, because increasing water hardness decreases trace-metal bioavailability and ultimately lowers the EPA maximum. Lower hardness concentrations are a conservative choice, because these concentrations correspond to more stringent chemical-concentration guidelines. These guidelines are applied conservatively to ETF chemical concentrations; conservative application assumes ETF concentrations are equal to hopper dredge concentrations. Furthermore, ETF concentrations are not adjusted for the anticipated volume of disposal-site dilution water.

Of the trace metals examined, concentrations of Be, Cd, Cu, Mn, and Hg exceed EPA aquatic life criteria (see table 15). The exceedance of Hg is problematic because the EPA criterion (0.00057 μg/L) is far lower than the analytical detection limit (0.1 μg/L). Potential concerns with Be and Cu appear to be localized in the Astoria and Skipanon project areas, respectively. Cadmium is of concern near the mouth of the Columbia River in predominantly coarse-grained bottom material that is low in organic carbon.

Future testing should include Cd determinations at sampling sites near the mouth of the Columbia River. U.S. Army Corps of Engineers guidelines would have excluded these sampling sites from chemical and biological testing because of their coarse sand composition (U.S. Army Corps of Engineers Waterways Experiment Station, 1976). Furthermore, EPA Region V sediment criteria would classify these sites as "nonpolluted" because they contain no more than 5-percent total volatile solids (Bowden, 1977).

Table 19.--Volumes of native-receiving water required for dilution of elutriate-test concentrations of ammonia, manganese, and phenols to acceptable levels

[Units are in micrograms per liter (µg/L) unless otherwise noted; phenol calculations assume 100 percent pentachlorophenol; ammonia calculations assume a pH of 8.5 and temperature of 20 degrees Celsius; dredge volume of 3,060 cubic yards is size of U.S. Army Corps of Engineers hopper dredge; RM = river mile; # = number; mg/L = milligrams per liter; < = less than. * = assumes complete mixing, no further chemical release during dilution, and hopper concentrations equal elutriate concentrations]

Project	Parameter of concern	Elutriate concentration	U.S. Environmental Protection Agency, 1980 guidelines	Receiving water concentration	Dilution volume* (in cubic yards)
Coos RM 7.5	phenols	118	55	3	6,770
Umpqua RM 5.2	manganese	240	100	30	9,200
Umpqua RM 9.1	ammonia	.27 mg/L	.02 mg/L	0 mg/L	41,300
Umpqua RM 9.1	phenols	86	55	2	4,850
Umpqua RM 7.8	manganese	910 mg/L	100 mg/L	30	38,500
Yaquina RM 6.3	ammonia	.46 mg/L	.02 mg/L	$6.7\text{x}10^{-3}$ mg/L	104,000
Yaquina RM 6.3	phenols	200	55	<.01	11,100
Yaquina RM 13.4	manganese	10,000	100	30	436,000
Depot Sl RM .25	ammonia	1.02 mg/L	.02 mg/L	$6.7\text{x}10^{-3}$ mg/L	233,000
Tillamook Bay #1	manganese	890 mg/L	100 mg/L	40 mg/L	43,400
Lake RM 2.0	phenols	105	55	3	6,000
Lake RM 0.32	ammonia	.39 mg/L	.02 mg/L	<.01 mg/L	59,700
Clatskanie RM .67	ammonia	.29 mg/L	.02 mg/L	<.01 mg/L	44,400
Clatskania RM .67	phenols	131	55	3	7,530
Skipanon RM .5	manganese	7,200	100	60	546,000
Skipanon RM 1.5	phenols	331	55	8	21,000
Skipanon RM 1.5	ammonia	2.13 mg/L	.02 mg/L	<.01 mg/L	326,000
Astoria #12	phenols	169	55	3	9,770
Astoria #9	ammonia	5.15 mg/L	.02 mg/L	$3.4\text{x}10^{-3}$ mg/L	949,000
Astoria #7	manganese	10,000 mg/L	100 mg/L	50	609,000
Chinook #7	ammonia	.71 mg/L	.02 mg/L	.01 mg/L	214,000
Chinook #8	phenols	231	55	5	13,800
Skamokawa RM .15	ammonia	.09 mg/L	.02 mg/L	$4.5\text{x}10^{-3}$ mg/L	16,900
Columbia RM 33.20	phenols	210	55	4	12,400
Baker Bay #6	phenols	419	53	9	28,500
Baker Bay #6	manganese	2,100	100	60	156,500
Baker Bay #7	ammonia	.83 mg/L	.02 mg/L	<.01 mg/L	127,000

Although several organic compounds were detected in ETF, EPA criteria for organic compounds are in many instances orders of magnitude lower than analytical detection limits. As an example, chlordane was detected in ETF at a concentration of 0.1 μg/L. The EPA chlordane guidelines for freshwater and marine aquatic life are, respectively, 10 and 25 times lower than the analytical detection limit and, therefore, is not of practical use for evaluating this ETF organic concentration. Thus, some organic concentrations determined in the reconnaissance study may exceed EPA guidelines; but until analytical methodologies improve, these occurrences cannot be verified.

SUMMARY

The elutriate test attempts to simulate conditions that affect bottom material and water during hopper dredging, but may not always reflect these conditions accurately. For instance, the sediment-to-water mixing ratio in the hopper dredge is not a constant, as implied by the elutriate-test procedure, but rather varies with the physical properties of the bottom material. Some test releases, like those of Mn and NH_3, are affected significantly by the mixing ratio. Failure to collect bottom-material samples that are representative of the vertical depth to be dredged may also further compromise the elutriate-test results. This problem can be remedied by vibratory coring, which ensures sampler penetration to proposed channel depths.

Specific conductance, pH, DO, temperature, and salinity affect the elutriate-test release of chemicals. These parameters need to be monitored during testing and compared with those of disposal-site waters. For example, oxic disposal-site waters may substantially decrease concentrations of chemicals mobilized under reduced conditions in the hopper dredge.

In the present study, chemical analyses of native-mixing water, ETF, and bulk bottom material were made for selected trace metals and organic compounds. Elutriate-test results are subdivided into fresh, euryhaline, and estuarine classifications for data analyses. Of the trace metals examined, concentrations of Cu, Fe, Pb, Mn, and Zn were detected in about 50 percent of the native-water samples. In about 50 percent of the elutriate samples the following trace metals were detected (in their respective elutriate classifications): As, Cd, Cu, Fe, Mn, Ni, and Zn in the fresh classification; As, Fe, Mn, Hg, and Ni in the euryhaline classification; and Ba, Cu, Fe, Mn, Ni, and Zn in the estuarine classification. The 25-, 50-, and 75-percentile concentrations of Fe, Mn, and Zn in the estuarine classification exceed those of fresh and euryhaline classifications; percentile concentrations of NH_3 are greater in estuarine and euryhaline elutriates than in freshwater elutriates. Organochlorine compounds in ETF generally are below analytical detection limits, except in a few instances where the compounds also were found in the native-mixing water.

Median concentrations of all organochlorine compounds in bottom material, except PCB compounds and DDE, are below analytical detection limits. Of organochlorine compounds in the 75th percentile, aldrin, chlordane, DDD, DDE, DDT, dieldrin, endosulfan, endrine, heptachlor, lindane, methoxychlor, and PCB were detected in bottom material. Most of the maximum organochlorine concentrations occur in Willamette River bottom material. Willamette River sediments also contain concentrations of Ba, Cu, Fe, Pb, Mn, Hg, Ni, Zn, NH_3, NH_3+Org_N, and TOC that exceed median concentrations from all project areas.

On the basis of intersite comparisons, the results of Tukey's studentized range test indicate a lack of significant difference ($\rho = 0.05$) between elutriate classifications of fresh, euryhaline, and estuarine for some chemical constituents. In these instances, the physicochemical composition of the bottom material, rather than the specific conductance of the elutriate-test filtrate, may be the most important factor in controlling elutriate-test release.

The results of ANOVA indicate that a significant relation exists between the type of native-mixing water--fresh-native water as compared to estuarine-native water--and the elutriate-test release of chemicals for some chemicals. Tests made with identical bottom material, but different mixing water, indicate that mean ranks of Ba, Fe, Mn, and Zn are greater in tests with estuarine-mixing water than in those with fresh-mixing water. Thus, disposal of dredge spoils in fresh disposal-site water may limit the release of Ba, Fe, Mn, and Zn.

The organic carbon and NH_3 ETF concentration are directly related to ETF gross-phenol concentrations. Relations of organic carbon and NH_3 with gross-phenol concentrations suggest that gross-phenol enrichment occurs in anoxic organic-rich sediments, where denitrificating bacteria are producing large quantities of reduced nitrogen during the oxidation of organic matter. If, as indicated, gross phenols are associated with anoxic organic-rich sediment, dredging areas like Skipanon River, Yaquina River, and Baker Bay likely may result in the release of phenols to disposal-site waters.

The pH of the elutriate-test mixture affects the elutriate-test release of Fe and Mn in estuarine-elutriate tests. Mixtures in which pH values are low release larger ETF concentrations of Fe and Mn than mixtures in which pH values are high.

Chemical concentrations in bottom material generally are not a reliable estimator of elutriate-test chemical release. When evaluating bulk-sediment chemistry, care needs to be taken to avoid speculating on its effects on the water column. The use of total-volatile-solids and particle-size criteria as a basis for conducting elutriate testing will, in some cases, fail to consider bottom materials that could release deleterious chemical concentrations. For example, Cd was released from large grain-size particles that would have been excluded under present testing criteria.

Of the ETF chemicals examined, median concentrations of Mn, NH_3, and phenols exceed EPA criteria. If chemical concentrations released during elutriate testing represent those initially present in disposal-site waters, Mn and NH_3 may adversely affect aquatic life. Manganese release may pose more of a problem in saline disposal waters than in freshwaters. Ammonia release is probable when TOC-enriched anoxic sediments are disposed of in warm waters with low pH. To avoid adversely affecting resident aquatic biota at the disposal-site, disposal needs to be made in cool waters with high pH. Phenols released during elutriate testing could move up the food chain if they occur as chlorinated phenols. Placement of dredged material suspected of containing chlorinated phenols in a confined upland-disposal site, instead of open water, will lessen the likelihood of deleterious effects to marine-aquatic life. The ultimate effect of Mn, NH_3, and phenols to disposal-site water is dependent on the volume of disposal-site dilution water.

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