HMSC   jµ   75-7

School of

OCEANOGRAPHY

O S U

OREGON STATE UNIVERSITY

FINAL REPORT

**Geochemical Baseline Data
Youngs Bay, Oregon, 1974**

by
Vernon G. Johnson
and
Norman H. Cutshall

Submitted to
Alumax Pacific Aluminum Corporation

Contract Period:
1 November 1973 through 30 April 1975

Reference 75-7

Geochemical Baseline Data
Youngs Bay, Oregon, 1974

FINAL REPORT

1 November 1973 through 30 April 1975

Submitted to

Alumax Pacific Aluminum Corporation

By

Vernon G. Johnson

and

Norman H. Cutshall

Edited by

Karla J. McMechan

School of Oceanography
Oregon State University
Corvallis, Oregon 97331

Reference 75-7

April 1975

John V. Byrne

Dean

ACKNOWLEDGMENT

Participating Staff
(listed alphabetically)

Norman H. Cutshall, Ph.D.	Research Associate
Vernon G. Johnson, M.S.	Research Assistant
Ingvar L. Larsen, M.S.	Research Associate
David R. TenHulzen, B.S.	Research Assistant
Jerome J. Wagner, B.A.	Research Assistant

Student Part-time Employees

Keith L. Anderson, B.S.	CWSP
Alan K. Bingham, B.S.	CWSP
James W. Carter, B.S.	CWSP
Clayton D. Gosmeyer	CWSP
Kristi S. Stewart	CWSP

TABLE OF CONTENTS

LIST OF TABLES

DATA

APPENDIX

LIST OF FIGURES

TEXT

DATA

APPENDIX

INTRODUCTION

This report comprises one part of a final report to the Alumax Pacific Aluminum Corporation on the "Physical, Chemical and Biological Studies of Youngs Bay". The data reported herein are the product of the geochemical baseline section of the project.

The primary objectives of the geochemical study were:

1) to provide a baseline record of fluoride and selected trace metal levels in Youngs Bay bottom sediment,
2) to identify areas that might function as heavy metal traps,
3) to attempt to determine the recent depositional history of sediment in the bay. (Research Proposal Addendum, November 1973)

In addition to these primary objectives, a number of secondary tasks were undertaken during the study: 1) estimating the solubility of fluoride in aluminum plant particulate effluent, 2) estimating the limit of fluoride solubility in estuarine water, 3) determining the variation of sediment fluoride with particle size and mineralogy, and 4) attempting to determine "reactive" and non-reactive sediment fluoride.

While time did not allow these additional studies to be carried to completion, preliminary results are included herein because of their potential usefulness in assessing the impact of environmental releases of fluoride to aquatic systems in the vicinity of Youngs Bay or elsewhere.

This report is made up of two major sections. In the first, a description of sample collection and analytical procedures is followed by a discussion of the baseline results. Obvious vertical and horizontal patterns of elemental distribution are identified and their origins considered. Problems needing further research are also discussed. In the second section, the data are presented in interpretive, graphical form, as well as in tables.

SAMPLE COLLECTION

Methods

Surface sediment samples were collected with a small dredge (Farrow and Larsen, 1974) which skims the top 1 to 6 centimeters (cm), depending upon substrate texture. The R/V SACAJAWEA was used at all stations in the bay proper and canoes were used for sample collection in the relatively shallow reaches of the upper Skipanon River. The samples were placed in polyethylene bags and stored in a freezer chest with dry ice for return to the laboratory. They were kept frozen in the laboratory until processing was begun.

Large diameter sediment cores were required to minimize distortion of the sediment column and to obtain sufficient sample material for all of the analyses required. Cores were obtained with a hand-operated, six-inch diameter coring device (described in Appendix A) at all shallow water locations and with a box corer (Bouma and Marshall, 1964) operated from the R/V CAYUSE at the deeper water stations. The cores were kept in a vertical position at all times and were extruded and sectioned in the field immediately after collection. The outer 1 cm of each section was trimmed off with a plastic knife and discarded. The trimmed sections were stored in polyethylene bags as above.

Site Selection

Sampling sites for surface sediment in the bay proper were located at approximately equally spaced intervals along five transects which lie perpendicular to the bay axis. Other samples were taken in mid-channel at various upstream locations in each of the rivers flowing into the bay. A special sampling effort was made along the Skipanon River because of its proximity to the proposed plant site. A few samples from locations outside the study area were collected for comparative purposes.

1

Coring stations were selected in areas where either active deposition was known to occur or where potential reducing conditions were suspected. A total of ten cores was collected.

Site locations and their relationship to bottom topography are shown in the Data Section.

Station positions were documented by sightings on landmarks.

SAMPLE PREPARATION AND ANALYTICAL PROCEDURES

Sediment samples were air-dried, mixed thoroughly and divided into subsamples for trace metal, fluoride, sulfide, radionuclide, particle size and mineralogical analysis. The remaining sediment was stored for future reference. The various subsamples were then processed according to the following procedures for each type of analysis.

Trace Metal Analytical Procedure

Ten gram (g) portions were digested in 50 milliliters (ml) of a hydrochloric acid/hydroxylamine hydrochloride solution (1 N HC1/0.25 N NH$_2$OH•-HCl) for two hours at 50°C. The suspension was centrifuged and the supernate transferred to a 100 ml volumetric flask. The centrifugate was rinsed twice with a total volume of 25 ml of one Normal ammonium chloride, and the rinse solution was combined with the extracts. This solution was brought to volume with deionized distilled water. The samples processed in this manner were all stored in linear polyethylene bottles until analysis.

Trace metal levels in the extracts were determined by atomic absorption spectrophotometry (AAS) using a Varian-Techtron model AA-5R. Standards were prepared in the same solution mixture used for extraction of the sediment samples. The AAS operating parameters used for each metal were those recommended by the manufacturer (Varian, 1971). Output from the AAS was recorded on punched paper tape and typed simultaneously. The punched paper tape record served as the data file for computer processing using a Digital Equipment Corporation model PDP 11/05 computer. A complete description of the overall system has been described elsewhere (Cutshall, 1975). The instrument precision obtained during the analysis of extracts from Youngs Bay sediment samples was better than 1% for Zn, Cu, Fe, Mn, and Co and better than 10% for Cd, Ni, Pb, and Cr.[1]

Fluoride Analytical Procedure

For the baseline study it was considered important to determine total fluoride in the sediment first and to develop selective extraction

[1] Precision is defined as the relative standard deviation expressed in percent of the mean.

procedures for various components later. The method used for determining total fluoride is described in this section. The preliminary efforts directed toward determining selective extraction procedures will be covered in the discussion section.

Most methods of estimating fluoride concentrations are sensitive to interferences from sample matrix and, therefore, require a separation step prior to analysis. This is especially true where soil and mineral analysis is involved. The standard method for fluorine separation has been the Willard-Winter type distillation, a tedious and time consuming procedure that is of questionable reliability for mineral-type samples (Fleischer and Robinson, 1963). The pyrohydrolytic method selected for this study is described in Newman (1968) and Clements et al. (1971). Details of the pyrohydrolytic apparatus and operating conditions used in this study are described in Appendix A.

Separation. The dried sediment samples were first ground in a mechanical mortar and pestle to pass through a 63 micrometer (μm) screen. The ground samples were stored in a vacuum dessicator for a minimum of one week before analysis. Just prior to the separation step, 0.5 g quantities of sample powders were mixed with 1 g of flux material consisting of bismuth trioxide, sodium tungstate, and vanadium pentoxide prepared as described in Clements et al. (1971). The sample-flux mixture was transferred to a polyethylene vial and mixed vigorously with a Vari-Whirl® vibratory mixer.

Nominal half-gram portions of the sample-flux mixture were then weighed into nickel boats. All weighings were made on a Mettler analytical balance and weights were recorded to the nearest 0.1 milligram (mg). The samples were then subjected to the pyrohydrolytic separation procedure. (In this procedure fluorine is liberated from the sample flux mixture upon heating and carried by steam flow into the bottle of scrubber solution). The alkaline scrubber solutions, 5 ml of 0.2 molar (M) sodium hydroxide plus 20 ml of deionized distilled water, were buffered to pH 5 with a sodium acetate/acetic acid solution (Clements et al., 1971). The buffered solutions were then stored in conventional polyethylene bottles until they were analyzed. Just prior to analysis the solutions were transferred to 50 ml volumetric flasks and diluted to volume with double distilled water. The contents were then transferred to a polypropylene beaker for the analytical step. Reagent blanks and subsamples of a Youngs Bay composite sediment mixture (secondary standard) were processed with each batch of samples to maintain quality control and to monitor system performance.

Analysis. Fluoride concentrations in the solutions from the separation step were determined with an Orion Specific Ion Electrode System consisting of the following components: 1) a model 90-01 single junction reference electrode, 2) model 94-09 fluoride electrode, and 3) an Orion 801 digital electrometer. Instrument response for samples and standards was recorded on a strip chart recorder to monitor the approach to steady-state cell potentials. The steady-state digital electrode potentials were recorded and the millivolt values so

obtained were converted to concentration by calibration curve method. Data reduction was accomplished on the aforementioned PDP 11/05 computer. Standards were prepared in the same solution mixture used for samples. Instrument variability for replicate determinations of a single test solution was less than 0.5%. Overall process precision was 2%, based on 23 replicate determinations of the composite sediment sample. Typical sample solution concentrations were 1.5 parts per million (ppm). The limit of detection for the system was approximately 0.02 ppm with a practical limit of detection of approximately 0.1 ppm. (The long response time required to reach steady-state cell potentials at the lower concentrations makes the practical limit higher than the actual).

Comparison of our results for determination of fluoride levels in geochemical reference standards and other materials of known fluoride level showed good agreement (Appendix B). Taking these comparisons and all other variables into consideration, we judge the values reported herein to be within 10% of the true total fluoride present in the sediment.

Sulfide Analytical Procedure

A limited number of samples from selected sections of three cores used in this study were subjected to total sulfide analysis. The samples selected for this treatment were from locations where reducing conditions were known or suspected to prevail.

Samples were taken by inserting a plastic syringe (with the end removed) into freshly exposed core sections and withdrawing approximately 10 cubic centimeters (cc) of wet sediment. The syringe was removed and the end quickly wrapped with Saran Wrap® and secured with rubber bands. The syringe-sediment sample was then immediately frozen with dry ice and stored frozen until analysis. The APHA (1971) iodometric method was used to determine the total sulfide present in the thawed samples. Replicate analyses of subsamples of a well mixed portion of sediment from one of the cores analyzed yielded an estimate of precision of 2%. Limit of detection was six milligrams per kilogram (mg/kg).

Radionuclide Analytical Procedure

All of the radionuclide measurements were made by direct counting techniques with no sample preparation other than drying and loading into counting tubes. Gamma-ray spectrometric methods were used for all radionuclide analyses. Methods used are described below.

Subsamples of the dried sediments were packed in 12 cc counting tubes and analyzed in the well of a lead-shielded 5 x 5 inch (12.7 x 12.7 cm) NaI (Tl) well detector coupled to a Nuclear Data ND-130 AT 512-channel analyzer. Samples were counted for 200 minutes each. Punched paper tape output was

used as data file for batch processing on the OSU CDC 3300 computer. The gamma-ray spectra were resolved using a least-squares computer program (Schonfeld, 1966) adapted for use on the OSU computer.

Weekly analysis of a Columbia River sediment sample was made during the period of investigation as a check on precision and analyzer reliability. Evaluation of these replicate analyses yielded precisions of 5% for cobalt-60 (^{60}Co), europium-152 (^{152}Eu) and cesium-137 (^{137}Cs), and 10 to 15% for the natural radionuclides, potassium-40 (^{40}K), uranium-238 (^{238}U) and thorium-232 (^{232}Th). The lower levels of detection (LLD)[1] estimated by the method of Pasternack and Harley (1971) were approximately 0.1 picocuries per gram (pCi/g) for ^{60}Co and ^{137}Cs and 0.2 pCi/g for ^{152}Eu.

All of the numerical radionuclide data listed in this report were obtained with the above described system. However, in addition to analyses made with the NaI(Tl) system, selected samples were analyzed with a high resolution counting system which utilizes a solid-state Ge(Li) detector combined with state-of-the-art electronic and computer data processing interfaces. (A complete description of this system is included in Cutshall, 1975). The newer system has greatly improved resolution as well as lower levels of detection. Results from Ge(Li) analysis of selected samples were used to verify radionuclide ratios for age-dating of cores and to extend the depth of radionuclide detection. The lower levels of detection for this system under the conditions used for the Youngs Bay study were as follows: ^{60}Co, 0.03 to 0.007 pCi/g; ^{137}Cs and ^{152}Eu, 0.04 to 0.01 pCi/g. (The range results from the use of 125 ml and 500 ml sample containers). The LLD values were calculated by the methods of Pasternack and Harley (1971).

Particle Size Determination

Ten gram portions of air-dried sample were weighed and then presoaked in distilled water for approximately one hour. The slurry was then stirred vigorously and washed through a 1000 μm screen onto a 63 μm screen with a jet of tap water. The sediment retained on each screen was then washed into beakers and the supernate siphoned off. These two fractions were then dried and weighed. The percent of fine material was calculated from the difference between the initial weight and the weight of sample retained by the 63 μm screen. The sand fractions were saved for possible further size separations. For special samples the sieve and settling column/pipet method (Royse, 1970) was used for complete particle size analysis.

---

[1] LLD: The minimum amount of radionuclide which must be present in order that a value greater than zero will be reported approximately 95% of the time.

Mineralogical Identification

Complete mineral analysis involves both petrographic analysis for the sand fraction and X-ray diffraction analysis for the fine fraction. Time limitations restricted this phase of investigation to petrographic analysis of the sand fraction.

Selected samples were disaggregated and wet-sieved to isolate the sand-size fraction. The entire sand-size fraction was then separated into heavy and light fractions by density separation (Royse, 1970), and these two fractions were mounted on glass slides for petrographic examination. Percentage estimates of mineral groups and mineral constituents were made by point count and visual estimate techniques.

RESULTS AND DISCUSSION

Sediment Texture

The textural analysis of bottom sediments was made because this variable may influence the concentration of trace elements. A complete particle size analysis for geological interpretation, however, was considered unnecessary for this purpose. Rather, only "percent fines" (or percent passing through a 63 um sieve) was measured. The areal distribution of this parameter is related to the morphology of the bay. Very little fine sediment was found in the main channel where tidal and current velocities are great enough to prevent fine sediment from accumulating. In general the shallow southwest side of the bay contains finer textured material than the north side. Pockets of very fine sediment occur in protected areas, such as behind the Highway 101 causeway, in the Skipanon Waterway, in the Lewis and Clark River area, and to the west of Pier 3. The presence of fine sediment in the Pier 3 area might reflect disposal of harbor dredged material.

The vertical distribution of percent fines shows numerous discontinuities. There are some cases, for example Profile I, Data Figure I-1 where coarse sand overlies a rather thick layer of fine sediment with yet another layer of coarse sand near the bottom. In other cores the reverse was noted; a sand layer is interbedded within an otherwise continuous profile of fine sediment (Profile G, Data Figure I-1). The greatest variability was seen in the Daggett Point core which ranged from poorly sorted mixtures of sand, mud and gravel near the surface to uniformly fine sediment below the 25 cm level. The transition from sand to mud at the 40 cm level in Profile E (on Data Figure I-1) can be attributed to construction of the causeway, at least the filled portion, in 1963-64.

The many extreme textural variations observed in the depth profiles supports the conclusions of Hubbell and Glenn (1971) for the Columbia River estuary, that alternating periods of scour and deposition occur. The time scale for these events is not entirely clear, although some light is shed on this subject for Youngs Bay by the radionuclide-dating effort.

Mineralogy

Samples (12) selected for sand grain mineral analysis came from eight sites selected arbitrarily from around the bay so as to represent geomorphic classes, i.e. channels, slopes, and flats (Hubbell and Glenn, 1971), plus four sections of the core taken at Daggett Point (Station 72, Data Figure II-1). In general, the sand fraction mineralogy closely resembles the mineralogy described by Glenn (1971) for lower Columbia River sediment.

A most striking feature is the change in mineralogy with depth in the Daggett Point core. There is an abrupt decrease of hematite near the bottom of the core, as well as a dramatic change from volcanic rock fragments to sedimentary rock fragments. The disappearance of the hematite indicates a more highly weathered (older) sediment from a source different than that of the overlying sediments. It is also noteworthy that pebbles 2 to 3 cm in diameter were found in the upper strata of the core. These mudstone and siltstone pebbles apparently eroded from the Youngs River basin. The lower radionuclide concentrations in the Daggett Point core indicate significant sediment dilution from Youngs River drainage as compared to the bay in general.

Heavy Metal Distribution

In general the heavy metals distribution pattern paralled the sediment texture. Where there were deposits of very fine sediment, heavy metals were high and where the sediment was primarily sand, they were low. An exception to this generalization was the distribution of manganese in which surface enrichments in some cores were not necessarily related to sediment texture. In these cases it appears that the manganese distribution is more related to chemical redox conditions in the sediment column. Near the surface of the core where conditions are presumably well oxygenated, manganese is high and it decreases with increasing depth in the core. Comparison of total sulfide distribution to manganese distribution supports this view (Profile J, Data Figure I-10).

At depth in the core it appears that reducing conditions prevail and manganese is easily converted from the insoluble oxide form to divalent, soluble manganese. The soluble species is then free to migrate upward in the core by diffusion. Near the sediment surface, oxygen penetration reoxidizes the manganese so that the manganese concentration is enriched. Such a manganese distribution is well known for many lakes and has been well documented at other locations (Gorham and Swaine, 1965).

In addition to the general pattern of heavy metals showing a direct relationship to fines, certain zones appear to be slightly enriched in some metals. For example, zinc, copper and cadmium concentrations in the Port of Astoria docks and in the Skipanon Waterway are 1.5 to 2 times higher than a control sediment. Sediment in the Skipanon and Astoria dock areas is fine textured and must be compared to similarly fine-textured control sediment. The apparent enrichment of these metals

might be related to harbor activities (hull main-tenance, painting, net treatment, etc.). Copper is a primary constituent of many anti-fouling boat paints (Young *et al.*, 1974) and copper sulfate is commonly used in treatment of nets. Alternatively, these areas might be chemically reducing zones where the generation of hydrogen sulfide leads to precipitation and accumulation of the heavy metals. Perhaps both factors are at work. Whether the apparent enrichment of these metals is due to human activities or to the reducing potential of these sediments has not been absolutely resolved at present. The correspondence between known uses and observed high concentrations of zinc, copper and cadmium, however, is presumptive evidence of contamination. More detailed statistical analysis of the data will help to identify anomalous areas of enrichment and to differentiate high concentra-tions due to contamination from naturally elevated levels due to fine sediment content.

Another area deserves special mention here. The deepwater zone in the main channel of the Youngs River off Daggett Point (Station 72, Data Figure II-1) is an unusual geologic, hydrologic and geochemical feature in Youngs Bay. It had been suggested in previous radioactivity studies that this area was a reducing zone (Jennings, 1966). The core data suggest that a chemically reducing sediment does indeed underlie the oxidized surface layers. Precipitated sulfide content of the sedi-ment increases dramatically just below the surface. In addition, manganese is relatively depleted in the deeper layers and relatively enriched near the surface. This structure, coupled with the textural variations described earlier and the bathymetry, suggest that the deep zone may be alternately scoured and buried. This extreme activity may be related to seasonal flow patterns, although we have no evidence of the frequency or periodicity of the variations.

Radionuclide Distribution

Radionuclides from three sources are present in Youngs Bay. These sources are naturally radio-active rocks and minerals, and artificial radio-nuclides from fallout from atmospheric nuclear detonations and byproducts of the use of Columbia River water to cool reactors at Hanford, Washing-ton. Radionuclides identified in the Youngs Bay samples included the following:

Radionuclide	Half life (years)	Predominant Source
Potassium-40	1.3 billion	natural
Thorium-232	14 billion	natural
Uranium-238	4.5 billion	natural
Cobalt-60	5.25	Hanford
Cesium-137	30.0	Hanford and fallout
Europium-152	12.7	Hanford
Europium-154	16.0	Hanford
Europium-155	1.8	Hanford

The artificial radionuclides, ^{60}Co, ^{152}Eu and ^{137}Cs, were detectable with the NaI(Tl) system used for most of the radioanalyses. The presence of ^{154}Eu and ^{155}Eu was detected in a few select sam-ples using a high resolution Ge(Li) system.

The surface distribution of ^{60}Co, ^{152}Eu, and ^{137}Cs follows the distribution of fine sediment. Concentrations in the Youngs Bay surface samples are not unlike levels found in surface sediment in the upper part of the Columbia River estuary (Stations 50 and 52, Data Figure II-3). Since the closure of the last plutonium production reactor in 1971, the only new radionuclides entering the river have been small amounts from N reactor (Robertson *et al.*, 1973). These are probably undetectable in the lower river. Therefore, the major source of these nuclides has been transport of residual radioactivity with the bed sediment of the Columbia River. Thus only particulate ^{60}Co, ^{152}Eu and ^{137}Cs has been introduced into Youngs Bay by the river. This point, together with the fact that radionuclide concentrations for sediment of like texture in the Columbia River estuary and in the bay are very similar, suggests that a signifi-cant portion of the sediment accumulation in the bay is of Columbia River origin.

The depth distribution of the Hanford radio-nuclides reflects not only the operating history of the reactors, but also reflects decreases due to radioactive decay and to changes related to sediment texture. History of the Hanford plant operation has been discussed by Foster (1972). Radionuclide introduction into the river was roughly related to the number of reactors operating at a given time. An abrupt change in operation occurred in early-to-mid 1965 when three of the eight reac-tors were phased out. A strike shut down the reac-tors for six weeks in mid-1966. Two more reactors were shutdown in mid-1967 and early 1968. The upper portion of at least two of the profiles seem to reflect the declining number of reactors. However, a second peak at a deeper level in E profile (Data Figures I-2 and I-5) is not readily explainable sim-ply from operating history.

Another point of interest in the depth profiles for artificial radionuclides (Data Figures I-2, I-4 and I-5) is the apparent discontinuities which coincide with textural breaks in the profiles (Data Figure I-1). This occurs most notably where sandy layers overlie dense clay layers (Profiles C, I and J). This also occurs, however, in profile G at the position where the layer of sandy textured mud occurs in an otherwise uniformly fine textured profile.

Fluoride Distribution

The dominant feature in the fluoride data is the correlation between fluoride concentration and the sediment texture. This feature is strikingly illustrated in Figure 1. The same high, positive correlation is also found for surficial sediment results, illustrated in Figure 2. Fleischer and Robinson (1963) observed that fluoride distribu-tion in the lithosphere tends to follow the dis-tribution of hydroxyl groups. Since fluoride and hydroxide (OH) have similar ionic radii (1.36 and

6
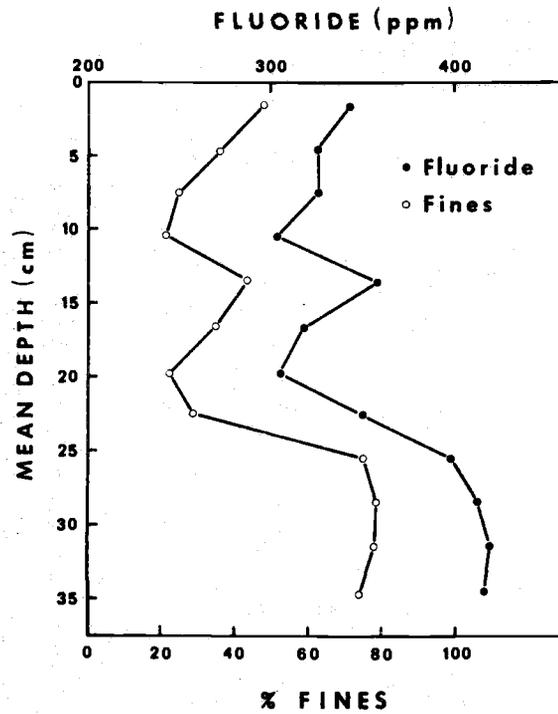
FLUORIDE (ppm)

Figure 1. Depth distribution of fluoride concentration and sediment texture in a Youngs Bay core. Fines shown as percent <63 µm.

r = 0.863
slope = 1.60 ± 0.11
intercept = 240 ppm
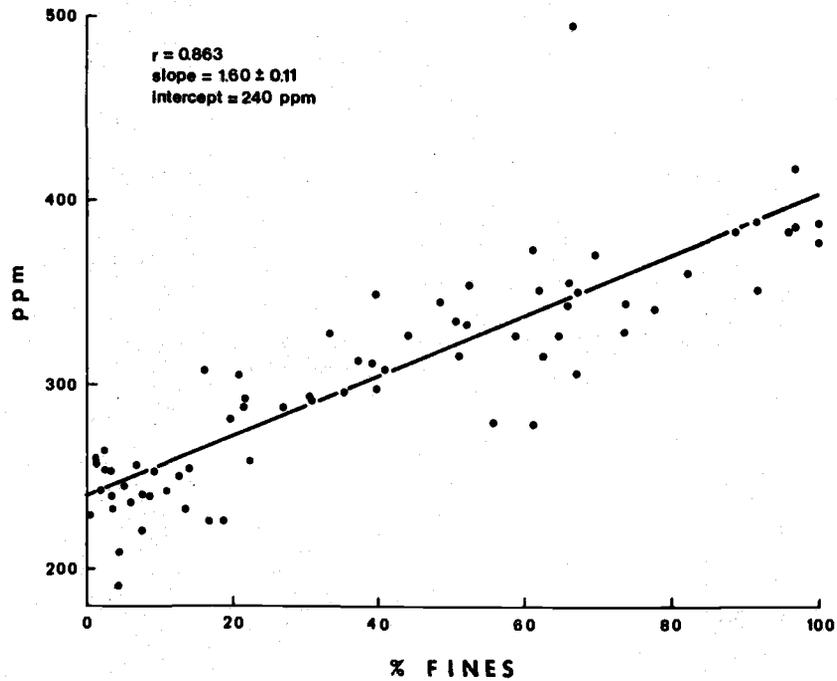
Figure 2. Total fluoride concentration (ppm) versus percent fines (<63 µm) for Youngs Bay surface sediment samples, 1974.

1.40 angstrom) and charges, they may be isomorphously substituted. Clay minerals are typically strongly enriched in OH and are themselves more abundant in the fine fraction of sedimentary deposits. These factors may combine to produce an indirect dependence of fluoride concentration on particle size. Mineralogy of various size classes of lower Columbia River sediment is summarized in Figure 3. Clay mineral content increases with decreasing particle size fraction, as would be expected. It is also interesting to note the relative OH concentration in the various mineral groups shown in the following table.

Average Hydroxide Concentration of Major Mineral Groups

Mineral Group	Weight (%)
Amphiboles	3.8
Pyroxenes	none
Feldspars	none
Quartz/Silica	none
Clay minerals	26

This possibility was examined further by fractionating a sediment sample from near the main channel of the Columbia River upstream from Astoria and measuring fluoride concentrations in each size fraction. (This site was chosen so that results could be compared with the mineralogical data summarized in Figure 3). Results are summarized in Figure 4. Fluoride levels do in fact increase with decreasing particle size. As much as 650 ppm was found in the <2 μm fraction. Clay mineral content of the same size classes shows the same trend. Since many trace constituents increase with decreasing particle size because of surface area considerations, this alternate explanation was also considered. If the increase in clay mineral content were dependent on surface area, then the fluoride concentration should increase with decreasing particle size in proportion to surface area.

Figure 5 shows the observed fluoride concentration as a function of mean particle diameter. The theoretical line is based on a simple model which assumes that all of the particles are spherical in shape. This relationship has been found to exist in other situations, even though sediment particles are not spherical (Fenchel, 1971). However, there is such a wide departure of the observed fluoride concentrations from the theoretical (Figure 5) that it seems certain that fluoride in the sediment fractions is not dependent upon surface area. This in turn suggests it is present as a bulk property of the sediment. Most of the sediment fluoride is, therefore, present as a constituent of various mineral groups and is most likely nonreactive, that is, unavailable for interaction with other components of the ecosystem.
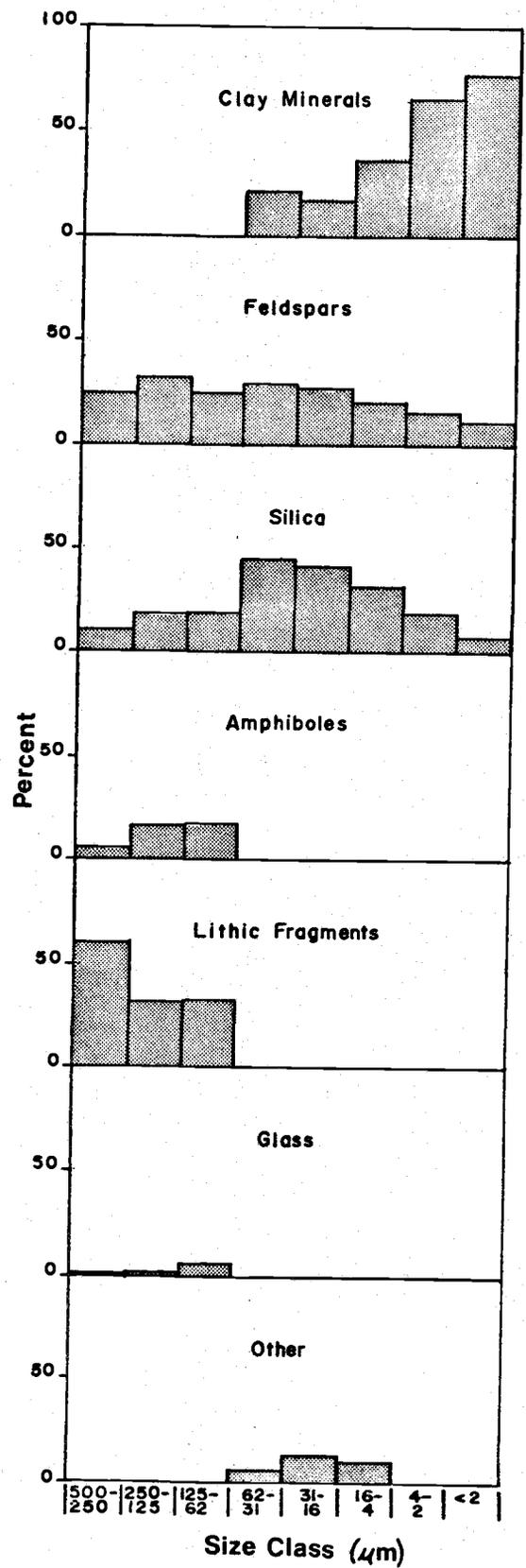
Figure 3. Distribution of major mineral groups among size classes of lower Columbia River sediment. Percentages in each size class sum to 100%. (Summarized from Glenn, 1971).
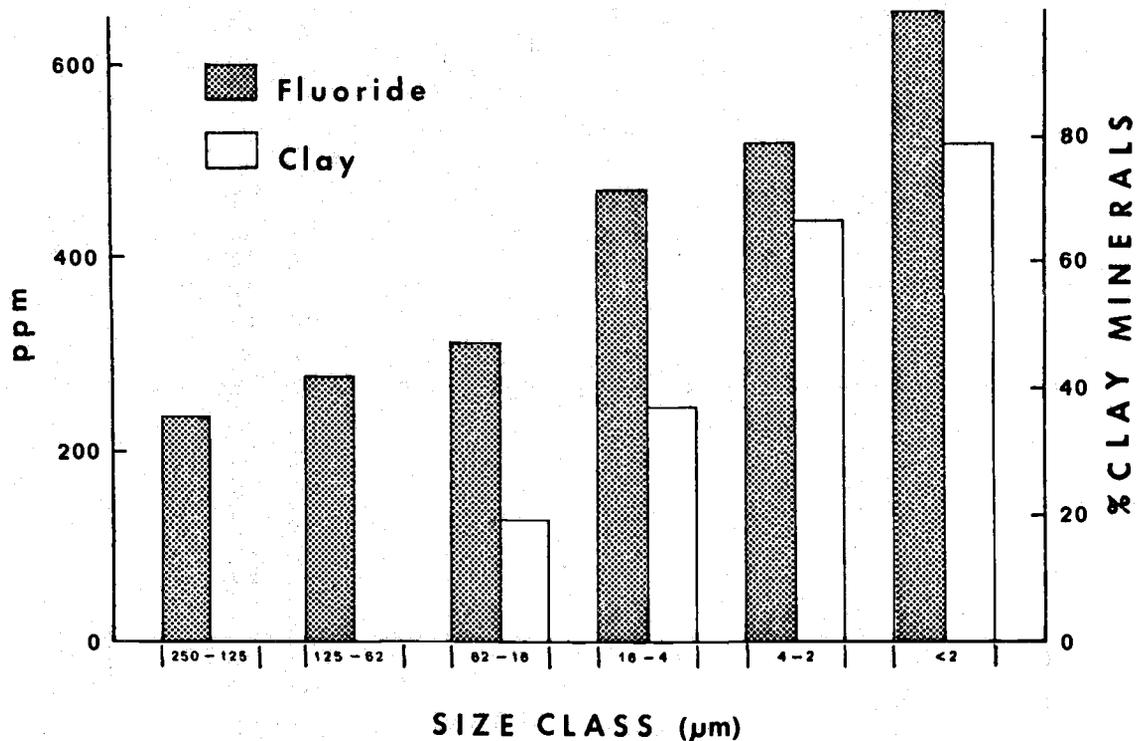
Figure 4. Fluoride and clay mineral content versus size class for Columbia River sediment.
Fluoride data is for sediment collected near Tongue Point (Station 54); clay
mineral data is from Glenn (1971). (Station Location: Data Figure II-3)
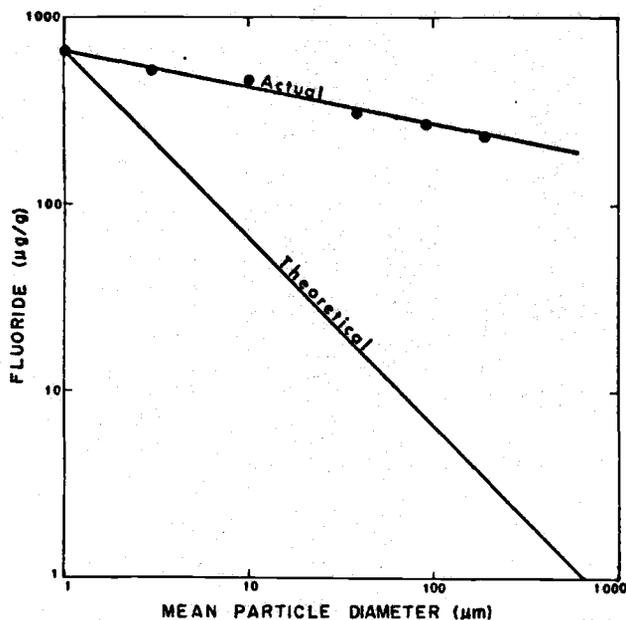
Figure 5. Fluoride concentration as a function of
mean particle diameter. The theoretical line shows
the relationship between content and particle diam-
eter that would prevail, if surface area were the
controlling parameter.

This conclusion is further supported by the
observation that little if any fluoride could be
removed from sediment samples by various chemical
treatments. These treatments included acid extrac-
tion, reducing extraction, oxidizing extraction
and a dilute caustic extraction. Only two to five
percent of the total fluoride present was removed
by all these treatments combined. This was es-
pecially surprising for a sample from the Skipanon
Waterway since this appears to be a highly reducing
sedimentary environment. As noted by Beak Consult-
ants (1974), Kullenberg and Sen Gupta (1973) proposed
that under anoxic conditions fluoride precipitates
from sea water to bottom sediment. This process
would presumably be accelerated when a large amount
of suspended sediment is present. Both these con-
ditions prevail at least part of the time in the
Skipanon Waterway. The sample used for the chemi-
cal treatments mentioned above was collected in
October, a time well into the minimum flow of the
Columbia River when maximum intrusion of salt water
would be occurring. Therefore, conditions were
theoretically optimal for precipitation to have
occurred. The lack of a significant amount of
fluoride in the extracts makes it seem that either
precipitation is not a quantitatively important
process for Youngs Bay and vicinity, or that once
precipitation has occurred, redissolution does not
occur. The fact that Skipanon fluoride levels are
no higher than those in other fine-grained samples
makes the former alternative more likely. Total
fluoride levels in the surface sediments and with
depth in the Skipanon core showed no significant
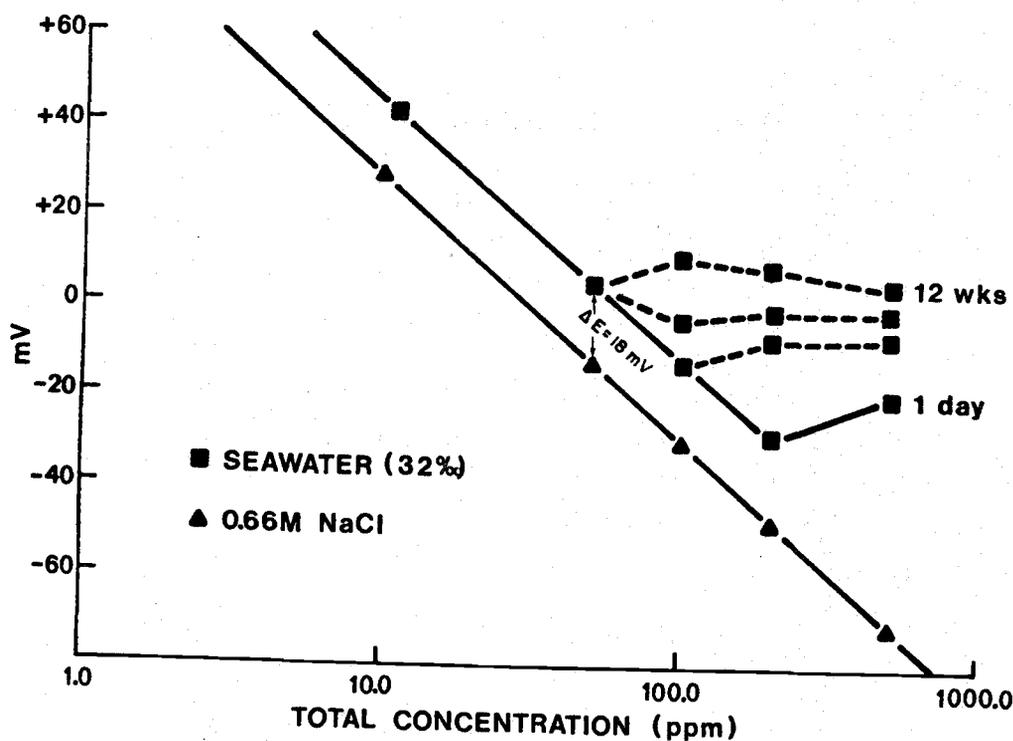
Figure 6. Fluoride electrode potentials versus total fluoride concentration in 0.66 M sodium chloride (NaCl) and 32‰ seawater. Deviations from the linear portion of the seawater curve at the higher concentrations show precipitation has occurred. The 18 mV difference between NaCl and seawater curves is due to the formation of complexes between the constituents of seawater and fluoride.

departure from the percent fines/fluoride regression line in Figure 2, further indicating that longer term fluoride chemical processes are also inconsequential to the total fluoride budget. In terms of a reactive fluoride fraction, however, the special chemical environment in a reducing mud does merit further research. This subject is further discussed below.

Special Studies

Solubility of Fluoride. As support to the biological effects portion of this study (Holton, Ulbricht and Morgan, In Preparation) the limits of solubility of sodium fluoride added to seawater media were explored and the expected maximum solubility of fluoride associated with stack particulate material from aluminum reduction facilities was determined. These investigations yielded chemically interesting results.

The solubility of fluoride added to seawater was tested by first preparing a sodium chloride (NaCl) solution of the same ionic strength as the seawater test media. Output of the fluoride electrode (which responds only to free fluoride) in the NaCl solution was compared to the output of the same fluoride concentrations in seawater, in order to determine the effect of complexing. Solutions were made ranging from 10 to 500 ppm of fluoride, added as sodium fluoride (NaF) in solution. At the time of preparation, only the 500 ppm solution indicated incomplete solubility. This is evidenced by

the linear calibration curve shown on Figure 6. However, as the fluoride concentrations were followed in time (see Figure 7 for example), solutions as low as 50 ppm in seawater deviated from a linear curve, indicating that precipitation occurred in these samples. The time required for the precipitate to form was somewhat surprising. At the 50 ppm level the solution was approximately five times higher than theoretical solubility considerations for equilibrium with calcium fluoride (CaF_2) would allow. These solubility considerations must be considered in planning experiments on biological effects or interpreting results therefrom, if fluoride levels exceed 50 ppm.
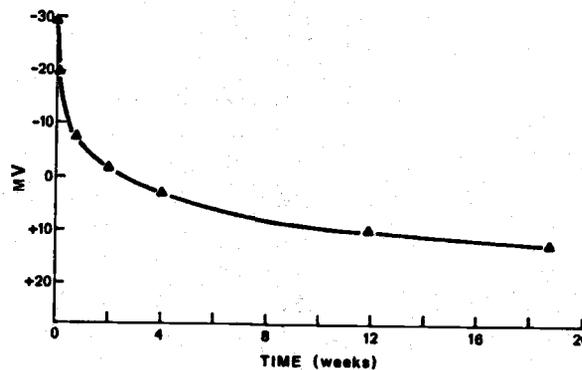
Figure 7. Fluoride electrode potentials versus time for the seawater solution initially containing 200 ppm fluoride shown in Figure 6. (More positive values indicated lower concentrations in solution.)

Another important point is the difference between the linear portions of the two curves shown in Figure 6. The curves indicate an 18 millivolt (mV) difference for the same quantity of added fluoride in NaCl solutions versus seawater. (More positive readings indicate a lower free fluoride ion concentration.) The 18 mV difference corresponds to 49% free fluoride in the samples up to 50 ppm. This agrees quite well with determinations of the fraction of free fluoride present at natural levels in seawater for similar salinities and temperature (Brewer, Spencer and Wilkniss, 1970) and Warner (1969). Thus it appears that seawater is able to complex fluoride to the same degree over the full range of its apparent solubility in seawater. This complexing has been theoretically attributed to ion pair formation with Mg^{++} ions to form MgF^+. Experimental verification has been made by Brewer, Spencer and Wilkniss (1970). Fluoride complex formation may reduce the effective concentration available for active uptake by organisms.

In summary, it appears that certain constituents of seawater limit the solubility of fluoride to a level not greater than 50 ppm. Below this level, approximately one-half of the total fluoride is present as free fluoride (F^-).

Stack-Particulate Fluoride Solubility. Since the majority of the fluoride projected to be released from the proposed aluminum reduction facility was estimated to be particulate material released through stacks, the solubility of this fraction was evaluated. Need for this evaluation arose during consideration of the biological effects of particulate fluoride, since it is presumed that only soluble forms are involved in biological uptake (Holton, Ulbricht and Morgan, In Preparation).

Stack particulate material was obtained from the INTALCO aluminum reduction facilities located in Ferndale, Washington. The material was obtained from 0.45 μm membrane filters in the stack monitoring system on the dry scrubber. Since only small amounts of stack particulate material were obtainable, a grab sample from the "baghouse" was also obtained. Presumably, solubility of the baghouse sample is representative of the material released from the stack, although the former has a larger average particle size.

The first solubility test involved successive extraction of 0.5 g of stack particulates (collected as above) with distilled water. The extractions were carried out by continuously mixing the particulates with 50 ml portions of water for 20 minutes using a magnetic stirrer. After equilibration, the slurry was centrifuged and the supernate decanted. The decanted fraction was then analyzed for fluoride. This process was repeated sequentially until 10 successive extractions had been made. Total fluoride in the particulates was determined by the pyrohydrolysis technique described earlier. The percentages of fluoride removed in each successive fraction was computed and added to produce the curve shown in Figure 8. These results follow a relationship of the form:

$$\frac{Y}{X} = \frac{1}{A + BX} ,$$

where Y is the cumulative percent removed and X is fraction number. A and B are constants determined

by regressing X/Y on X. A plot of X/Y versus X is linear, with A being the intercept and B the slope. Using constants thus determined and increasing X infinitely, the maximum removal or ultimate percent soluble can be estimated. That value is 59%.
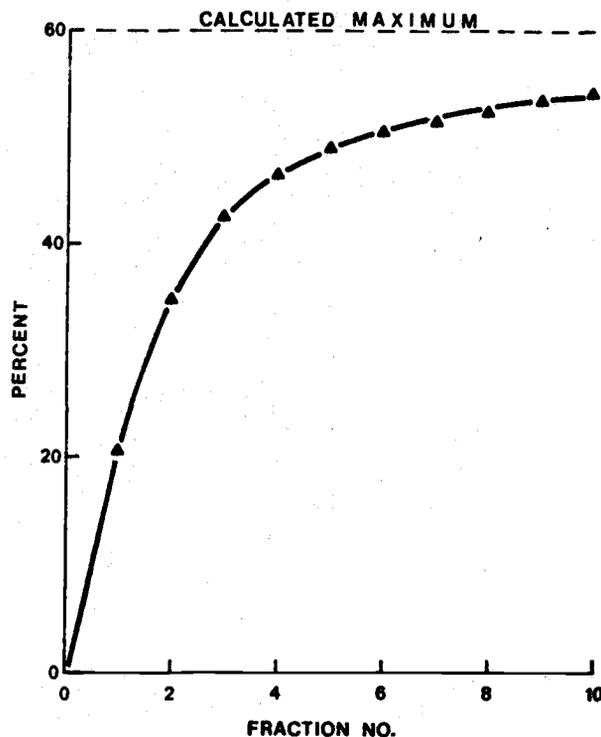
Figure 8. Extraction of fluoride from stack particulates with successive fractions of distilled water.

Similar extraction tests using the baghouse material at salinities of 1‰ and 15‰ showed that smaller portions would be removed with the same number of extractions up to 10. This appeared to be a rate effect rather than a solubility limitation. That is, the extent of removal of fluoride from stack particulate material in any given fraction appears to be less for seawater than for distilled water. Given enough fractions or infinite dilution, removal in seawater would probably be the same as in distilled water. Although runs were made to determine rates of removal in seawater and in distilled water, mathematical treatment of the data remains to be accomplished. However, it appears from cursory inspection that the slower removal rate in seawater is a complex function involving interactions of fluoride with chemical constituents of seawater as well as simple dissolutions of the fluoride from the particulate phase. Further analysis of the data and more elaborate kinetic experiments would be helpful.

Forms of Sediment Fluoride. Carpenter (1969) indicated that fluoride can be incorporated into estuarine and marine bottom sediment by chemical precipitation and by biogenic deposition (skeletal

carbonate/apatite, etc.). Wiklander [1964] has suggested that fluoride might be associated with iron oxide coatings. Other suggestions include the possibility that interstitial waters may be slightly enriched because of decomposition of organic material and release of tissue fluoride. Each of these mechanisms could produce fluoride fractions in natural sediment which are more reactive than fluoride in the mineral fragments. Because of this possibility the size of these potential reservoirs in the sediment was investigated.

The first approach was to use chemical extraction procedures commonly used to prepare sediment samples for mineralogical analysis (Jackson, 1958). Such treatments include a reducing extraction step to remove oxide coatings; acid extraction to remove carbonates, shell tests, etc.; treatment with a dilute base to remove alumina; and digestion with peroxide to remove organic matter. In addition to these treatments, water soluble and exchangeable fractions were determined. The sequential flow sheet was:

Step	Chemical Treatment	Expected Form of Fluoride
1	distilled water extraction	water soluble
2	1 N sodium acetate	exchangeable
3	Hydrogen peroxide digestion	oxidizable organic fraction
4	Acetic acid, pH 5	carbonate fraction
5	Sodium citrate/dithionite extraction	iron and manganese oxide fraction
6	Sodium carbonate digestion	free or amorphous alumina fraction

When the above treatments were performed on the dried Youngs Bay composite sample (referred to previously), it was found that all of the treatments combined removed only two percent of the total fluoride. (Analyses were made by method of known additions with the fluoride probe in TISAB III buffer/decomplexing agent. It was necessary to adjust the pH in some of the extracting solutions prior to fluoride determination and to correct for reagent blanks.) When the same treatments were made on a sample from the Skipanon Waterway, a larger fraction of total fluoride could be dissolved. While this fraction only amounted to 5% of the total fluoride, it is noteworthy that half of the removal occurred with destruction of organic matter by peroxide. It appears that sediment with high organic content may contain a higher reactive fluoride component than sediment low in organic matter. Furthermore, reducing zones are typically related to high organic loading so that there may be correspondence with the observation made by Kullenberg and Sen Gupta (1973) in Youngs Bay. If these preliminary results are representative, virtually all of the fluoride inventory in bottom sediment is nonreactive or inert. While this may be so, it cannot be concluded that the reactive reservoirs, however small, are necessarily unimportant

in an aquatic system exposed to elevated fluoride levels. More research on this point needs to be done. Indeed, from a monitoring point of view it would be important to determine extractable as well as total fluoride, since a small increase could be obscured in the presence of the relatively high natural levels.

Deposition Rate

Rates of sediment deposition were estimated for some of the cores using the radioisotope ratio technique described previously (Forster, 1972; Hubbell and Glenn, 1971). Co-60/Eu-152 ratios were used for this purpose in the Youngs Bay study. Figure 9 shows a plot of this ratio versus depth in a core from behind the causeway (Station 61) where active deposition of fine sediment has apparently occurred since its construction in 1964. From the slope of the linear regression line an estimate of the overall or average rate of sediment accumulation can be made. Deposition rate over the entire profile is computed at 4.1 cm/year. Examination of the stratigraphic distribution of texture for this core reveals a sharp break from very fine sediment to sandy layers at approximately the 40 cm level. Thus, if we consider that the sharp textural transition occurred upon completion of the causeway, we have an historical date assignment of approximately 1964 to the 40 cm level, or an average accumulation rate of 4 cm/year. Thus, there appears to be concordance between the two methods of estimating sedimentation rate.

The same technique applied to the core taken near the Lewis and Clark bridge (Station 69), another zone of fine sediment, yields a sedimentation rate of 2 cm/year for the upper 18 cm of
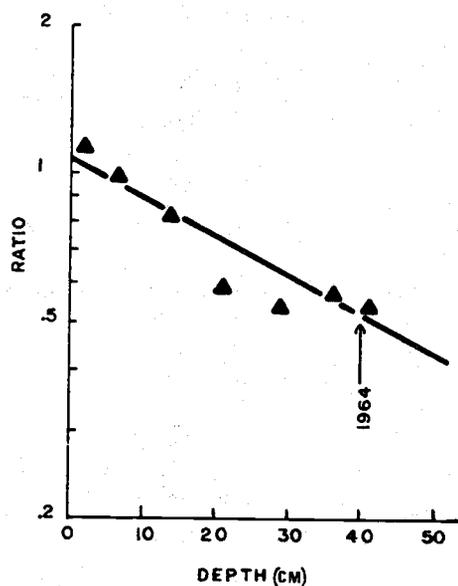
Figure 9. Co-60/Eu-152 ratios versus depth in causeway core (Station 61). The line represents results of a linear regression of ln (ratio) on depth; r = 0.926, slope ± 0.189 ± 0.00346. All data based on results from Ge(Li) radioanalysis.

sediment. Below this level there is no radionuclide record, even though the ratio (^{60}Co/^{152}Eu) suggests an age of only approximately 8 to 10 years at the 18 cm level. It is interesting that this sharp break in the radionuclide record coincides with the appearance of a layer of sandy mud, whereas the profile above and below exhibits uniformily fine sediment. The appearance of sand in an otherwise fine-textured stratigraphic distribution suggests that a temporary high energy environment, such as a flood, existed in an otherwise quiescent zone. Jennings (1966) found that a 1964 flood caused extensive movement of surface sediments and radionuclides. Erosion and deposition both occurred in different parts of the estuary. This might explain the deposition pattern and rate observed at Station 69. (See also Forster, 1972 and Schubel, 1973). Another interesting feature of this core is the disappearance of bark at the same level as the sand layer and the break in radioactivity. The bark is undoubtedly from log-rafting activities and may be another useful dating indicator if its incidence can be calibrated independently.

Deposition rates calculated from the slope of regression lines (as illustrated in Figure 9) for 5 of the 10 cores range from 1.8 to 4.7 cm/year. (In the other cores either the radionuclide profile was obviously mixed, as in the main channel, or the record was missing.) While these rates cannot be considered as an overall average for the bay, they can be considered as representative. Forster (1972) estimated similar rates for Alder Slough (3 cm/year). Alder Slough is a semi-protected inlet just northwest of the entrance to the Skipanon Waterway.

It is clear that erosion and deposition are both occurring in the bay at the present time. It is also clear that some sites where deposition is now dominant have been areas of net erosion in the past. This shifting pattern of sediment movements is not particularly surprising and presumably results from variations in water circulation owing to natural seasonal cycles, to construction of piers, bridges, etc., as well as to maintenance of the navigation channel. It is noteworthy that an area where sand wave migration produces vertical homogeneity would appear to have virtually infinite deposition rates based on radionuclide data alone, even though no net deposition whatsoever might be occurring. Interpretations of rates must utilize all possible sources of knowledge. It does not seem appropriate to characterize the entire Youngs Bay area as a zone of deposition or a zone of erosion but rather as a dynamic system in which both processes interact. Nonetheless within selected areas of deposition some history can be inferred. Age assignments are indicated in Figure I-1. These assignments were made by relating the observed ^{60}Co/^{152}Eu ratio at each location to the ratio in the causeway core (Station 61).

Fluoride Inventory for Youngs Bay Sediment

To estimate the present inventory of fluoride we use an area of 2870 acres for the Youngs Bay and vicinity, an average fluoride concentration of 325 ppm and a sediment density of 1 g/cc. This

yields a reservoir size of 38 metric tons (or 83,000 pounds) per centimeter of depth.

While this amount of fluoride may seem impressively large, it must be recognized that this quantity is almost entirely inert, being tightly bound in the crystal structure of the various mineral constituents of the sediment. Where the focus of concern is a total fluoride budget, the mineral-bound fluoride must, of course, be considered. On the other hand, where the focus of concern is biological effects or where the baseline against which additions of soluble fluoride are to be referenced is estimated, the total fluoride values are clearly inappropriate. Soluble and reactive fluoride reservoirs should be the reference in those cases.

Areas of Concern and Suggested Further Research

Several zones within the study area have clear signs of contamination by man's activities. Bottom sediments from the Astoria Port Docks area and from the Skipanon Waterway have elevated levels of metals which can be associated with ship operations. The zone directly west of Astoria Pier 3 is badly cluttered with debris and has apparently been used as a dump. The lower Youngs River and Lewis and Clark River have substantial areas of bark accumulations, presumably the byproducts of log rafting. These zones of contamination merit continued attention if the ecological impact of man on them is to be accurately seen. The Skipanon Waterway, because of its semi-enclosed nature and slow flushing, is an area of special concern. Addition of further insult to the Skipanon system should be weighed very carefully.

Complete analysis of the data from this study will require at least several months. Mathematical manipulation to remove the effects of particle size on the elemental distribution patterns will reveal any residual structure that may be a more sensitive indicator of sources of the elements. The distribution of metals in sediments, particularly Mn/Fe ratios, are so clearly related to redox status of the sediment that their use for locating oxygen sinks is suggested.

The special focus on fluoride in this study has uncovered some scientifically interesting and ecologically significant questions: Why do interstitial waters appear to be enriched in fluoride? Is the enrichment related to oxidation-reduction chemistry? Are reducing areas likely to accumulate fluoride, as suggested by Kullenberg and Sen Gupta (1973)?

It is clear that the bulk of the fluoride contained in sediment does not react with water or the biosphere short of geological-scale times. What fraction of the fluoride does react? What is the nature of the solid phases which are potentially soluble under environmental conditions? The chemistry of precipitation of fluoride added to estuarine waters is a complicated matter which apparently involves salinity, initial level of added fluoride and probably more than a single solid phase. Reaction times may span several weeks in the laboratory. Are reactions more or less rapid in the natural system? What effect would sediments

have on the rate? What is the solid phase formed when fluoride is added to estuarine waters?

These are not questions to be answered glibly, but rather they are questions intended to demonstrate areas of potentially significant future research. Substantial effort would be required to answer them. The present research serves mainly to focus clearly upon such questions by defining present-day baseline conditions. The effort already expended has been productive. Recognition of new questions is indicative of an increased level of perception. Continued efforts will be required if further insight is to be developed.

DATA

I

AREAL AND VERTICAL DISTRIBUTION OF SEDIMENT

MEASUREMENTS OF YOUNGS BAY SAMPLES

Table I-1. Core sample collection data. Station locations are shown on Data Figures II-1 and II-2.
Grab station data is given on Table II-1.

Core Label*	Station Number	Date Collected (day/mo/yr)	Coring Device	Core Length (cm)	Approximate Water Depth (feet) (MLLW)
A	75	10/10/74	box corer	56	15
B	70	29/09/74	box corer	24	31
C	71	29/09/74	box corer	30	31
D	74	10/10/74	box corer	17	10
E	61	18/06/74	Large diameter corer (LDC)	58	0
F	60	18/06/74	LDC	57	+1
G	69	04/08/74	LDC	58	0
H	73	10/10/74	box corer	26	11
I	68	04/08/74	LDC	55	+1
J	72	10/10/74	box corer	36	40

* Core label is used in Figures I-1 through I-17 to relate depth profile plots to station location.
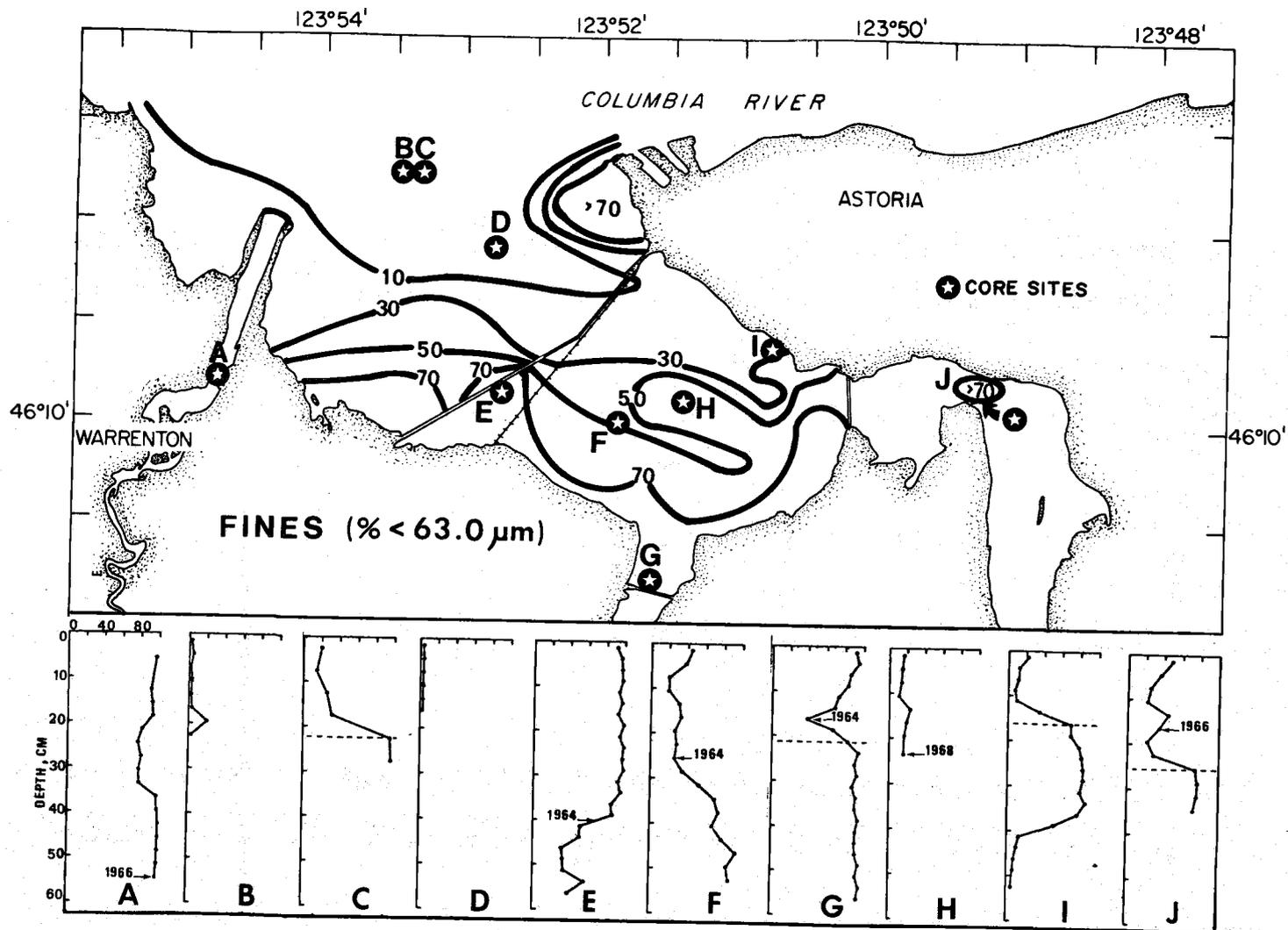
Figure I-1. Sediment texture with age assignments on depth profiles. The dotted horizontal lines on the profiles mark the top of the pre-Hanford (1944) strata. Dates shown were assigned on the basis of radioactivity ratios discussed in text.

19
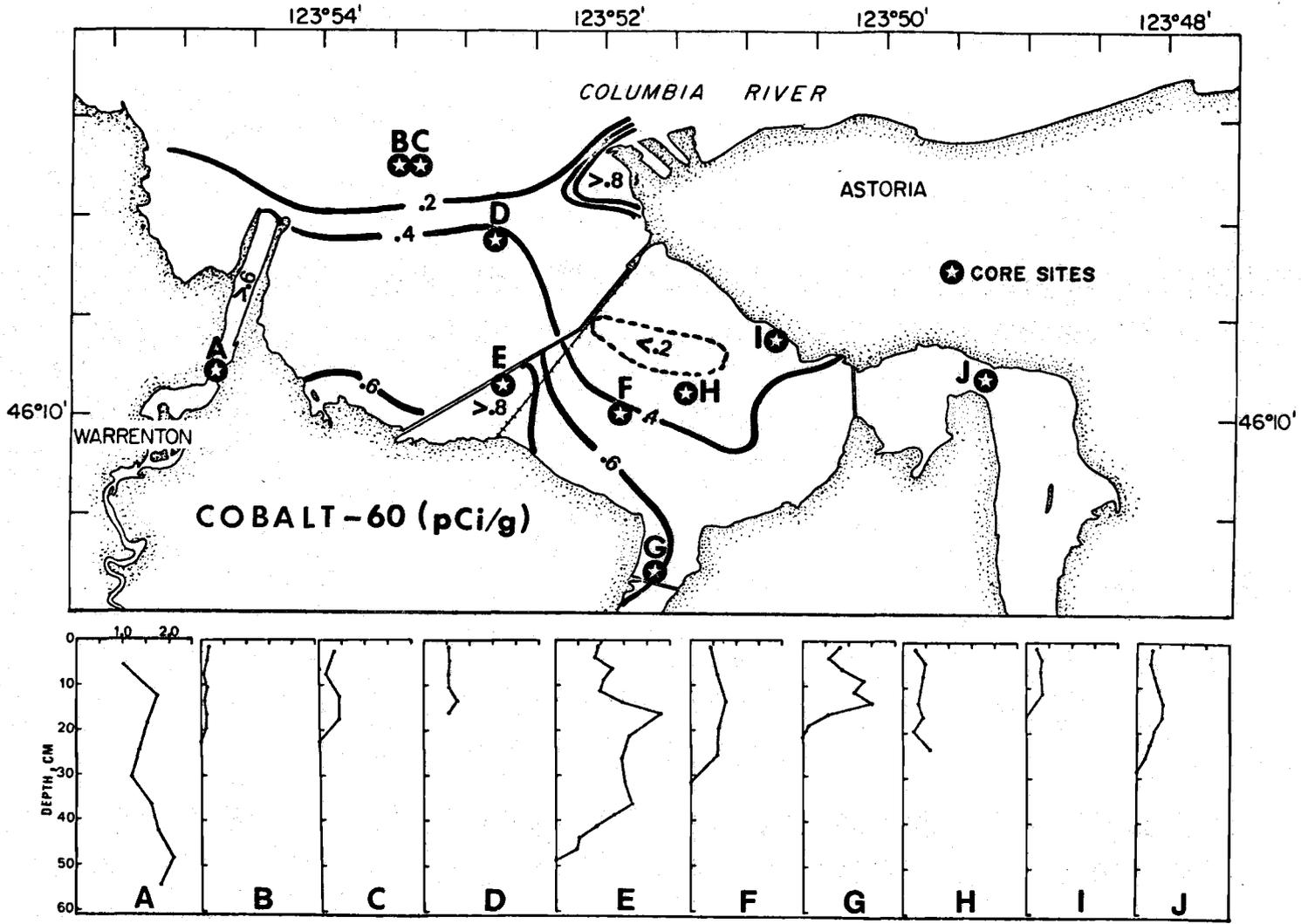
Figure I-2. Cobalt-60.
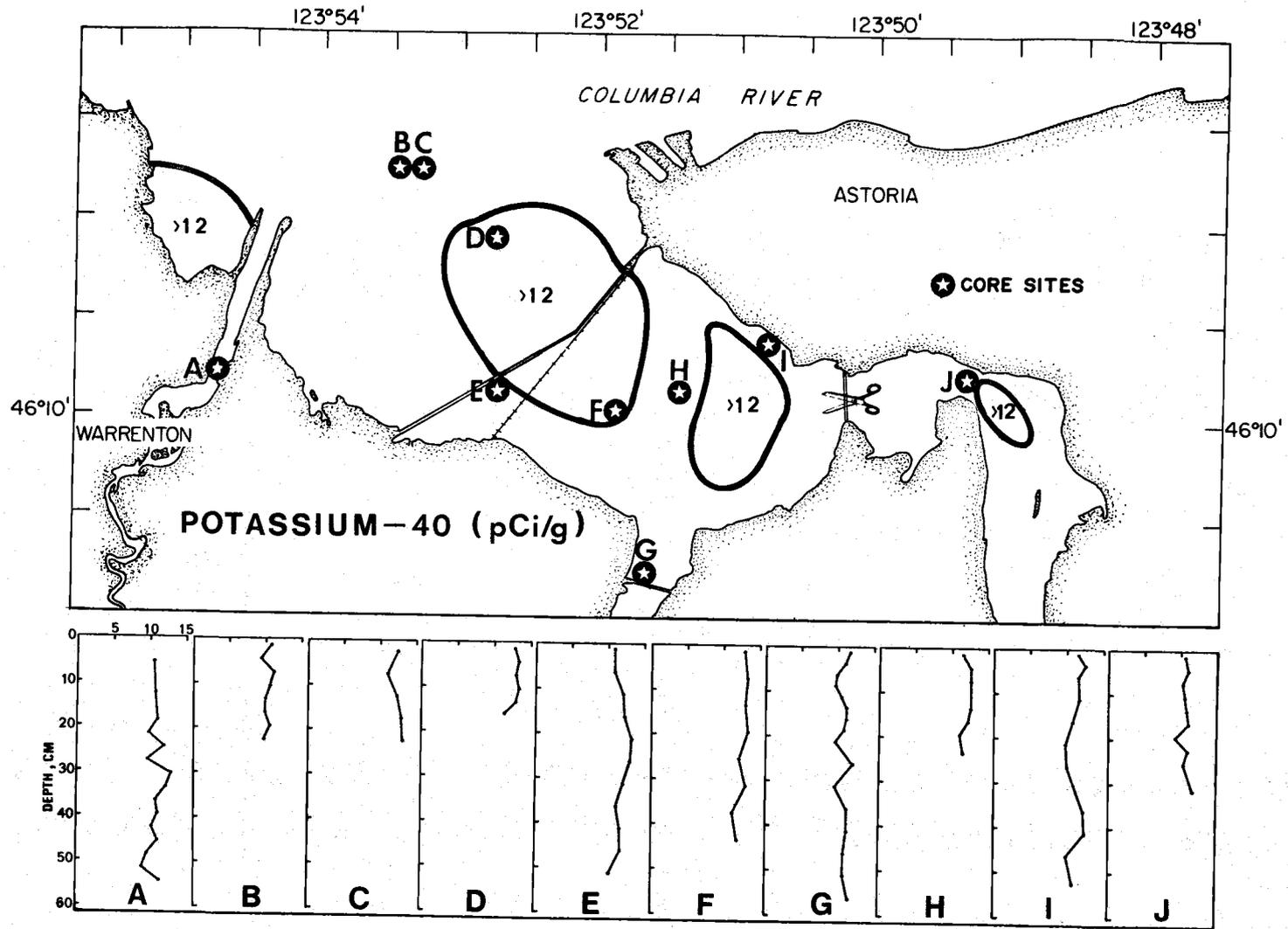
Figure 1-3. Potassium-40.
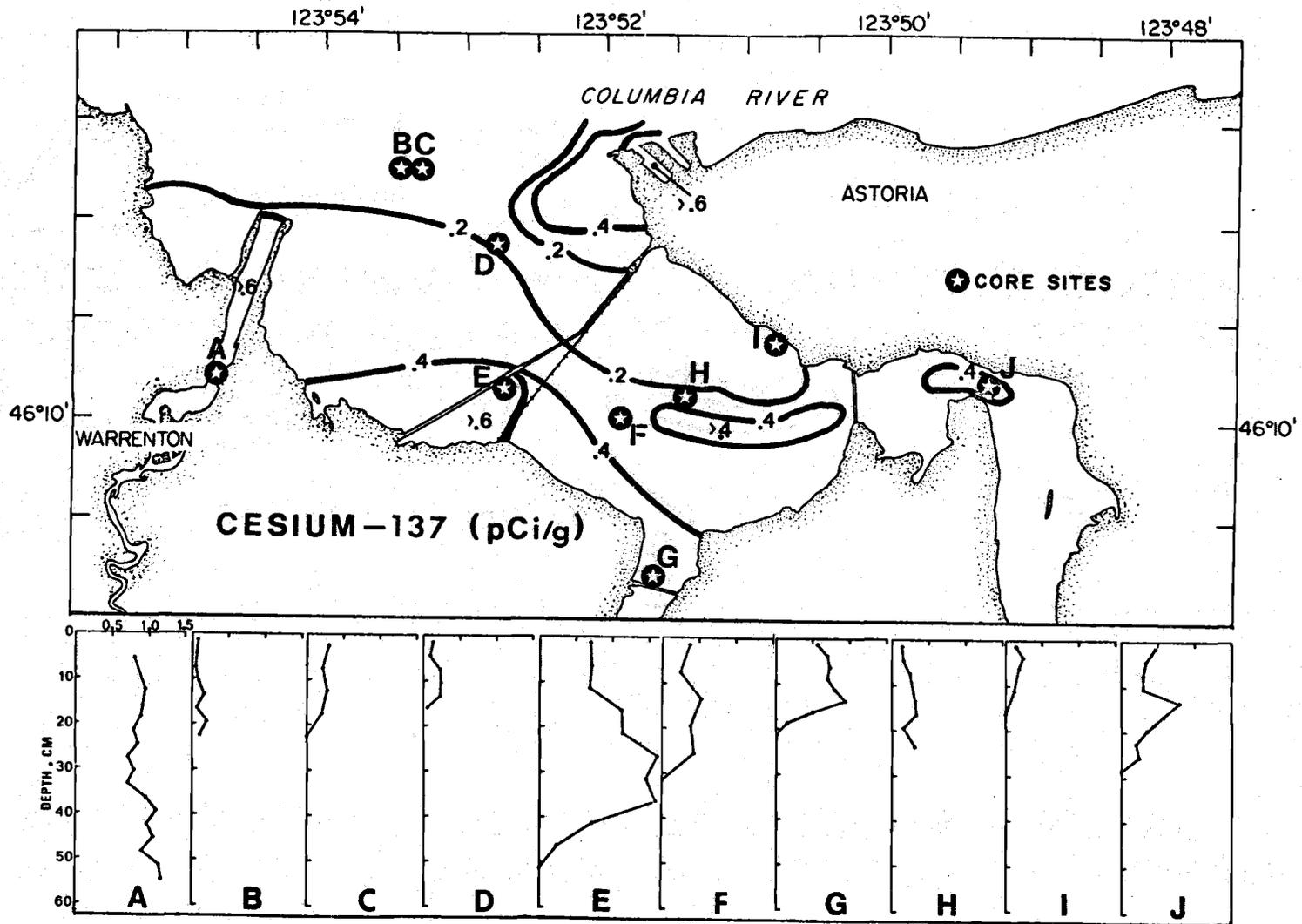
Figure I-4. Cesium-137.
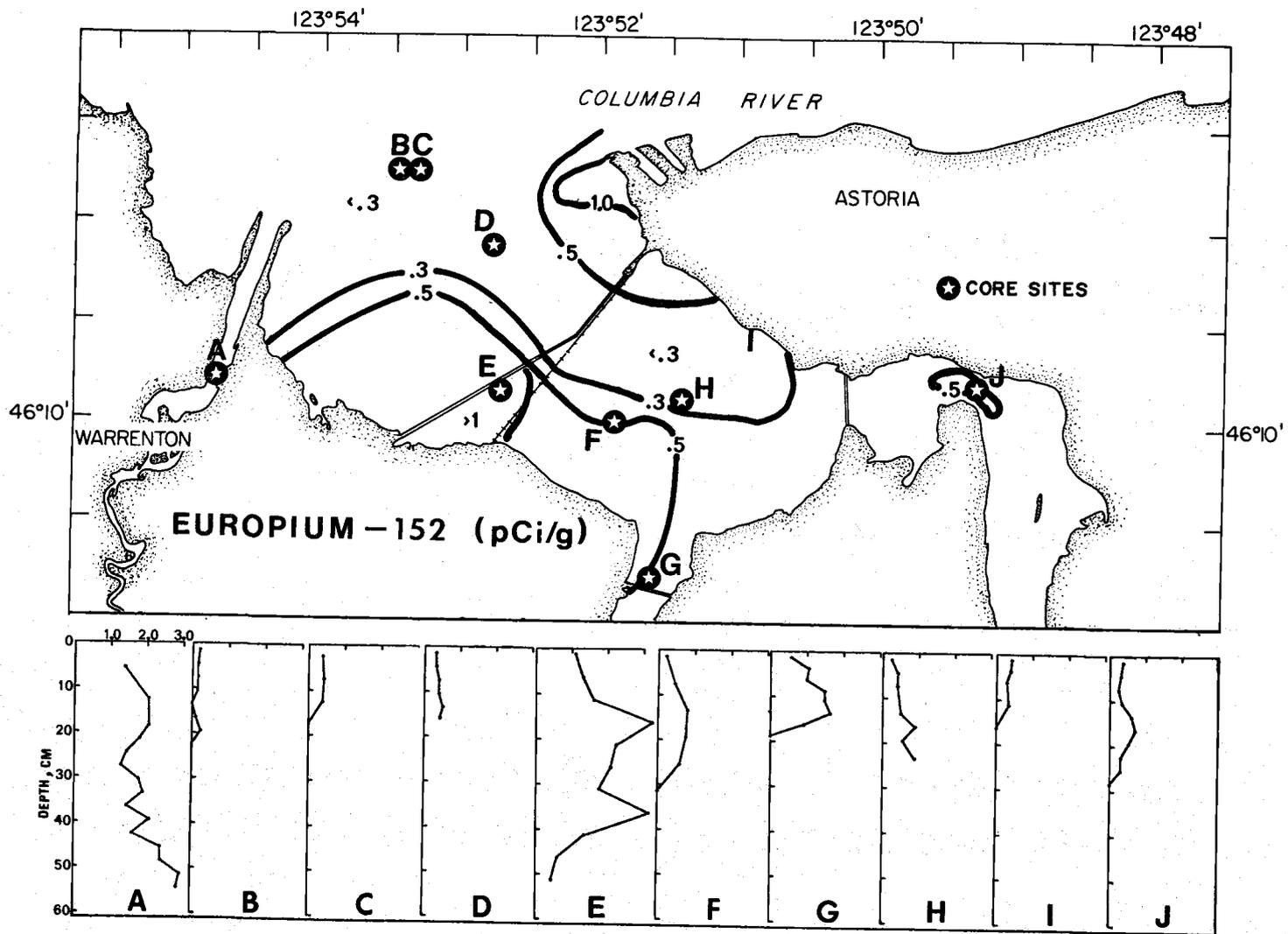
Figure I-5. Europium-152.
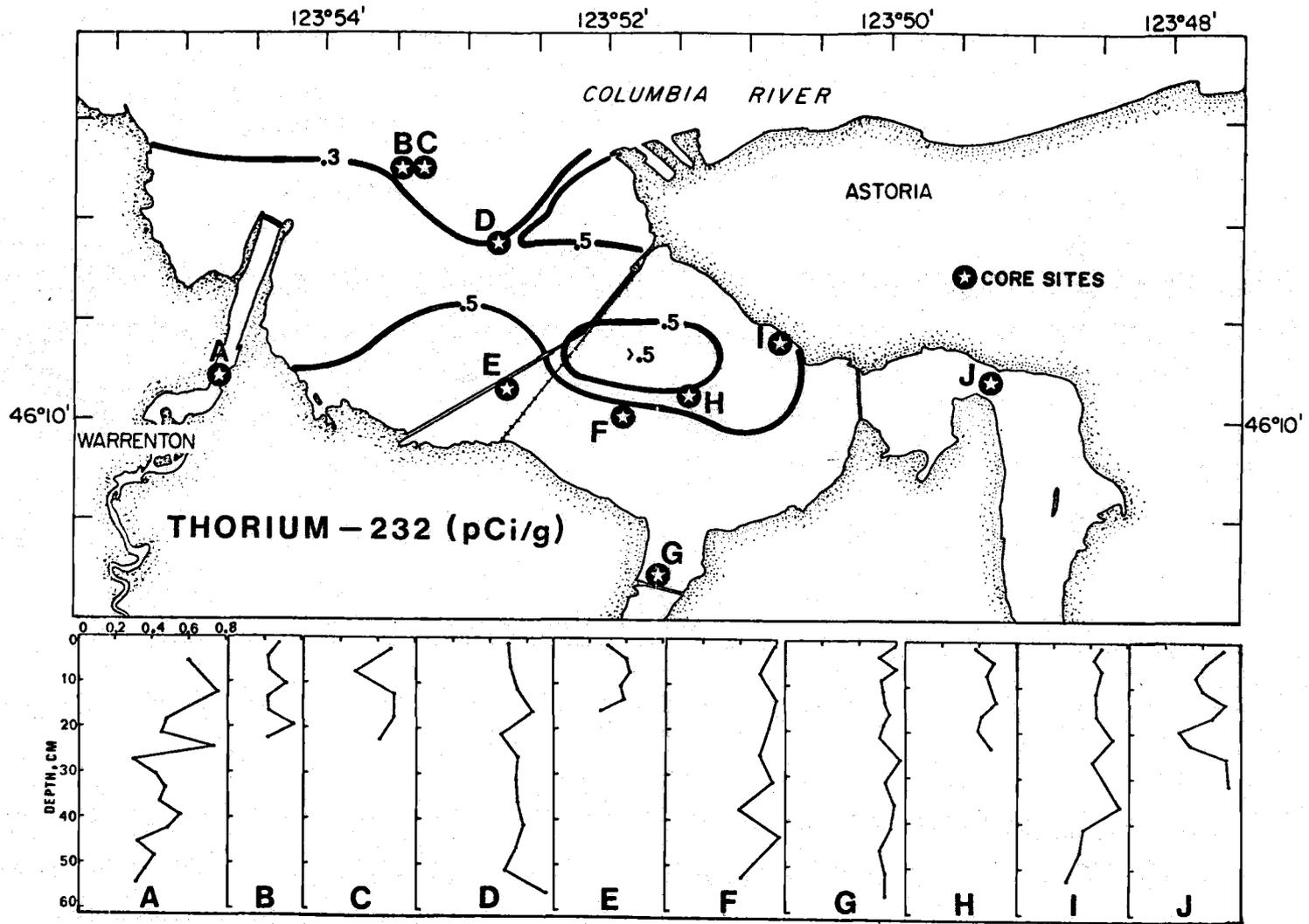
Figure I-6. Thorium-232.
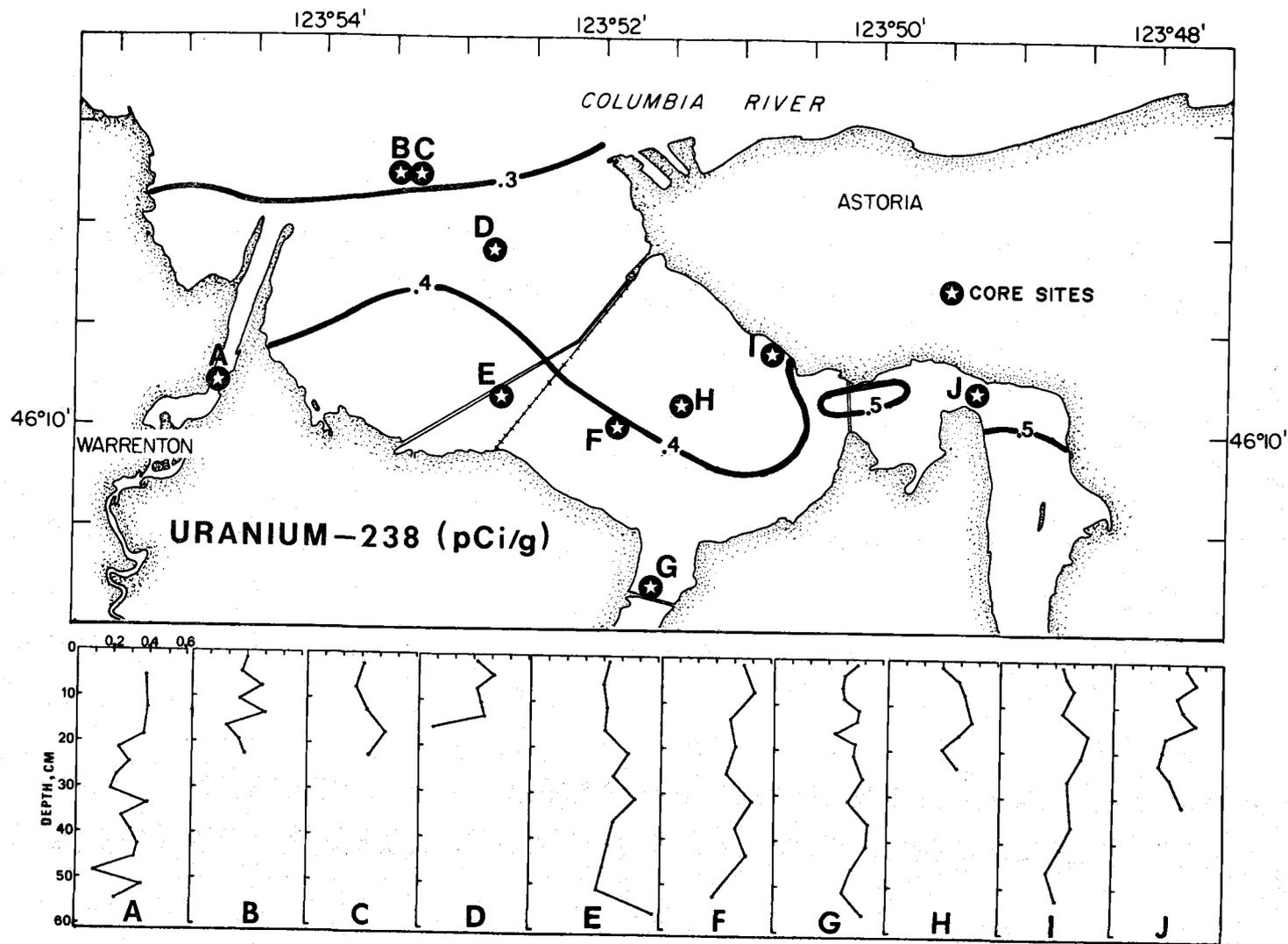
Figure I-7. Uranium-238.
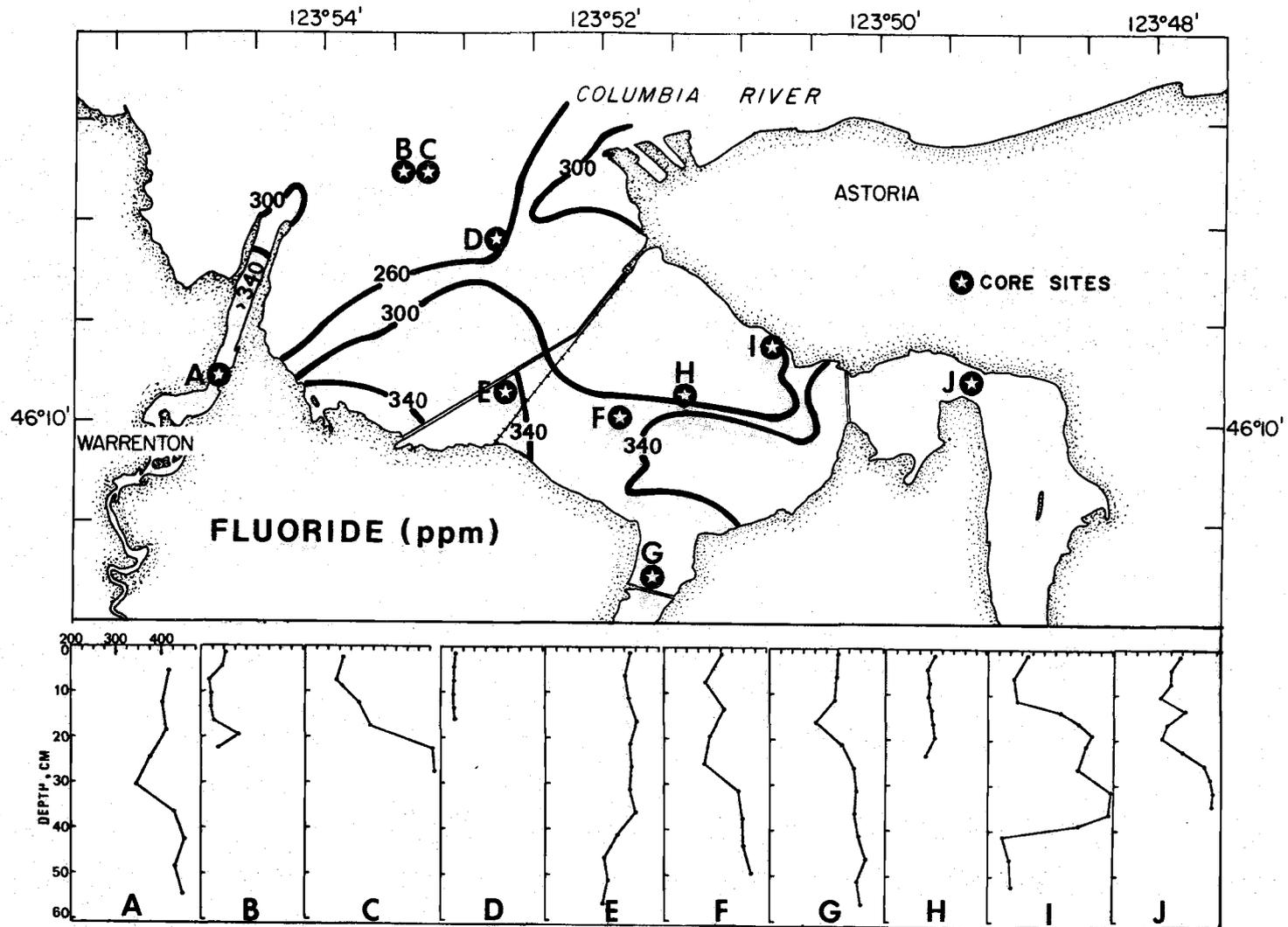
Figure I-8. Fluoride.
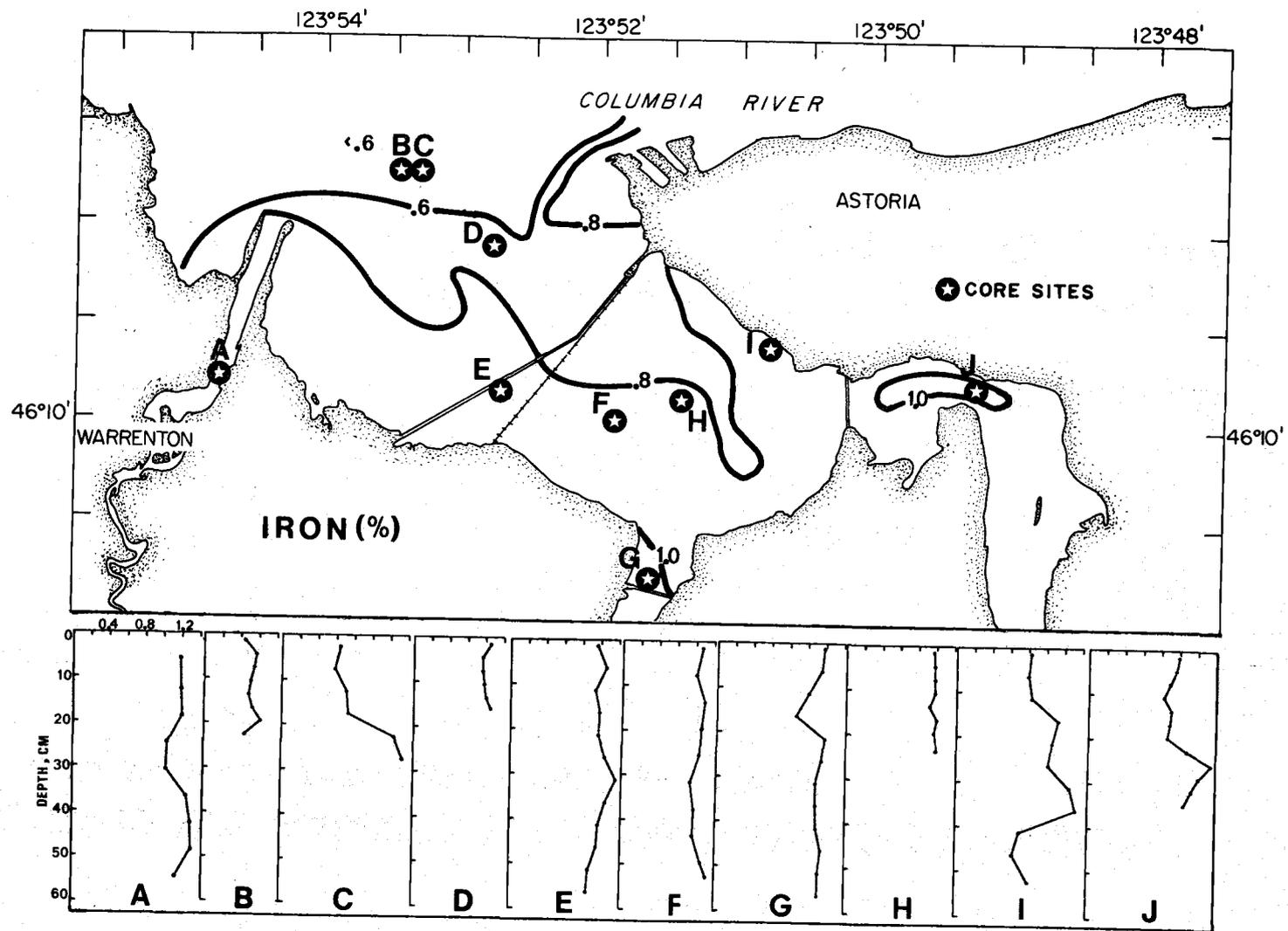
Figure I-9. Iron.
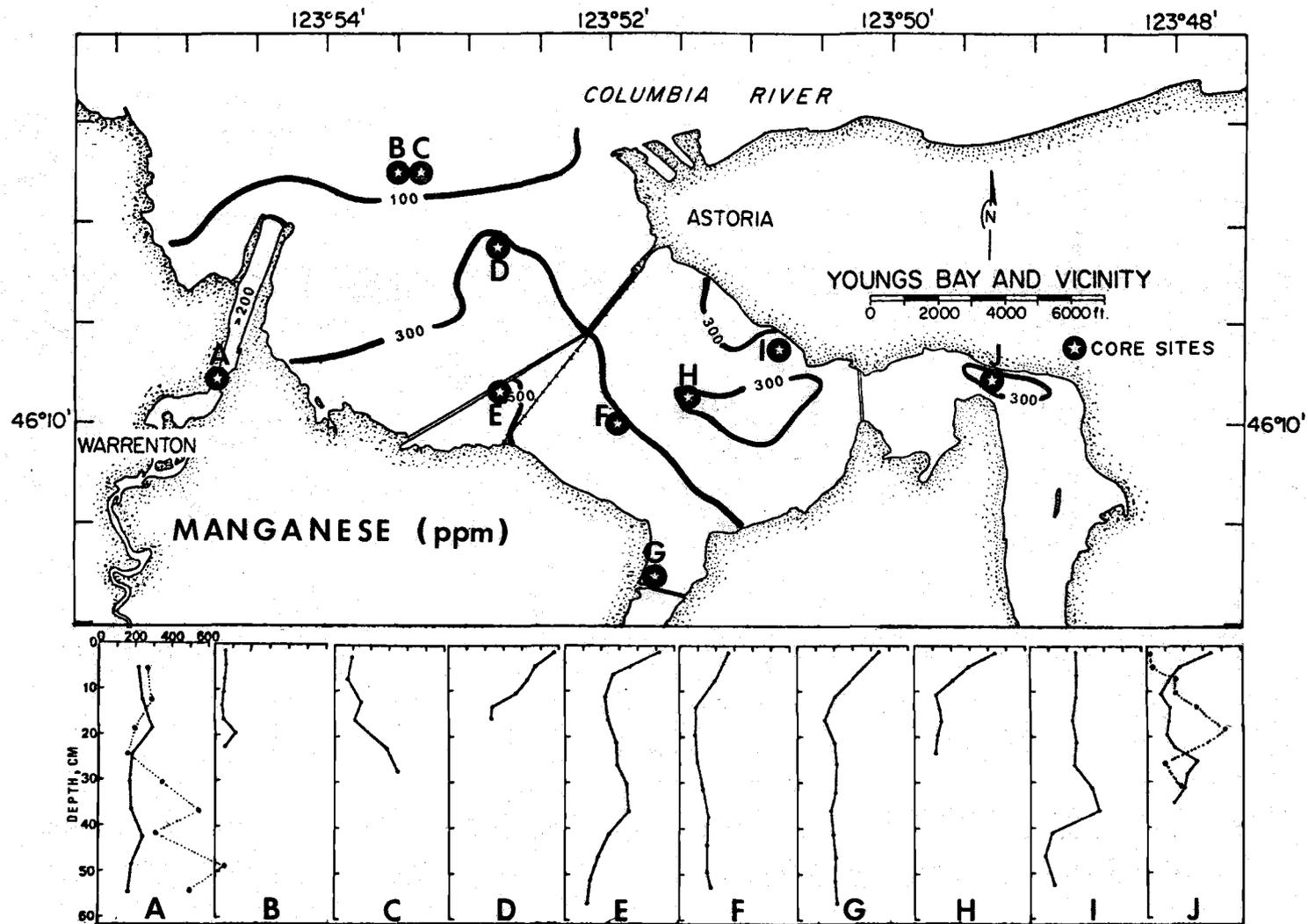
Figure I-10. Manganese. The dotted lines are depth profiles of total sulfide measured in the same core (each division on the horizontal scale corresponds to 200 ppm). Note the enrichment of manganese in the upper strata of cores D, E, F, G, H, and J.

123°54' 123°52' 123°50' 123°48'

COLUMBIA RIVER

BC

ASTORIA

50

D

CORE SITES

75

100

A

I

E

H

46°10'

100

F

46°10'

WARRENTON

75

ZINC (ppm)

G

0 100 200

DEPTH, CM

A   B   C   D   E   F   G   H   I   J
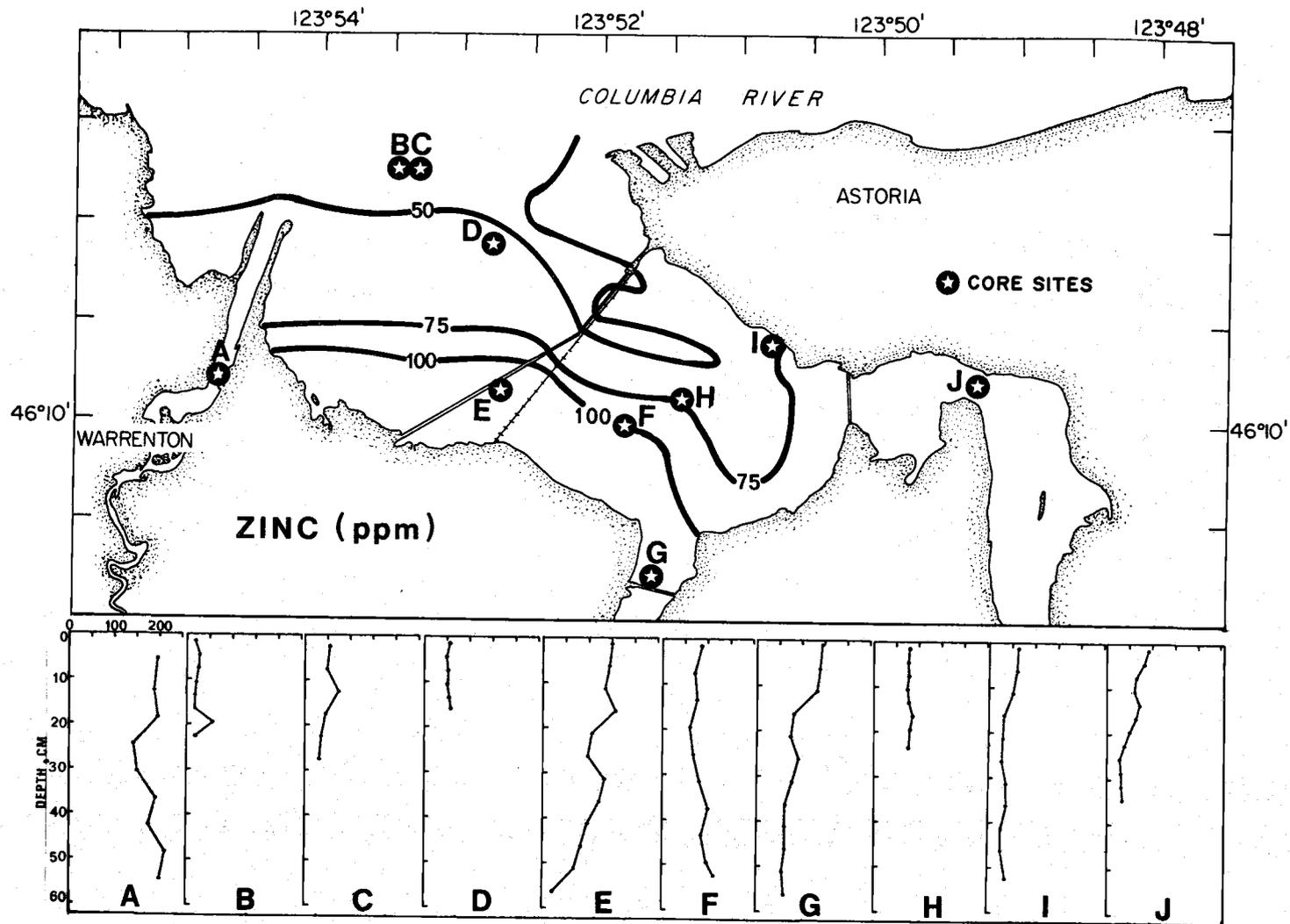
Figure I-11. Zinc.
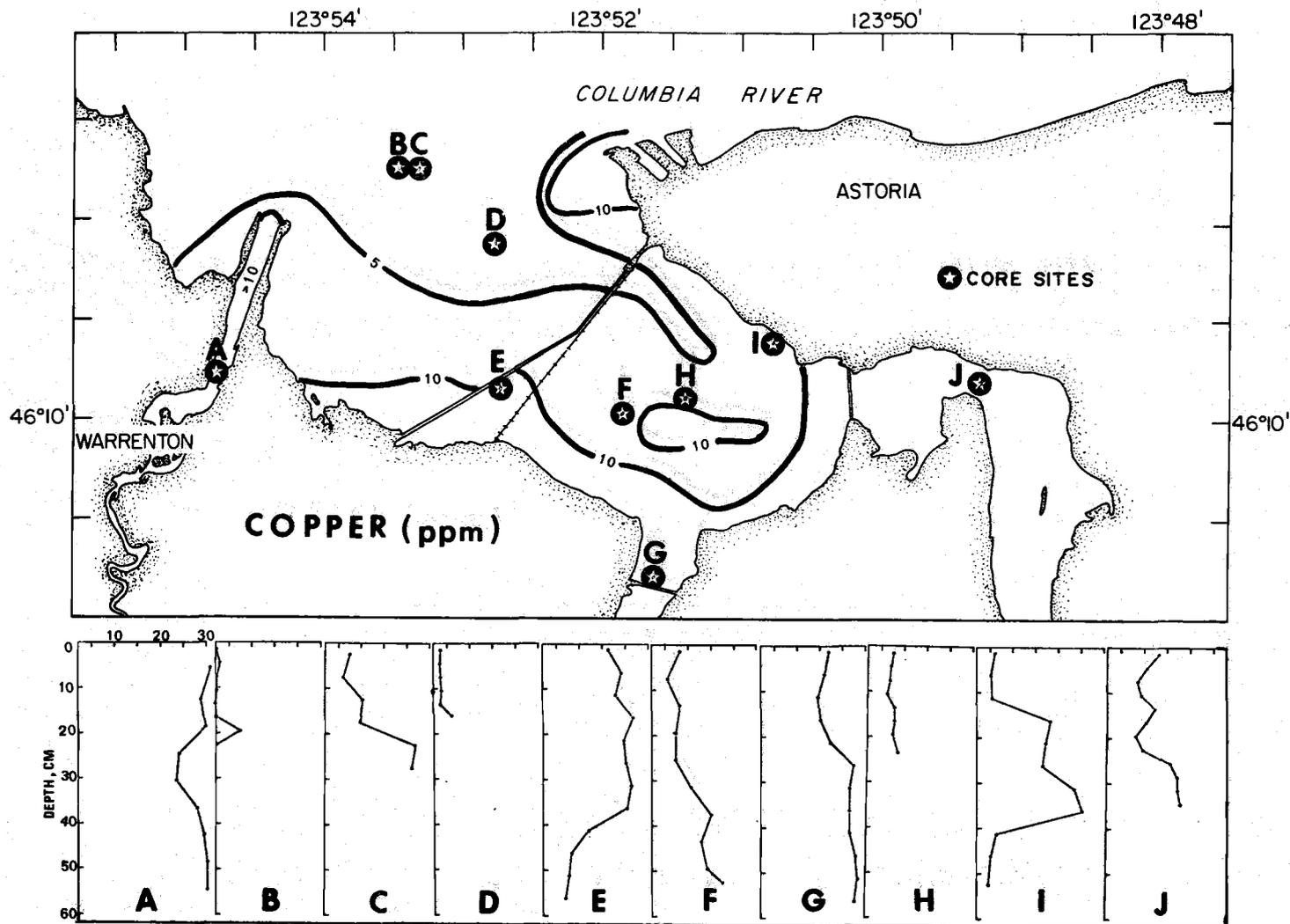
Figure I-12. Copper.
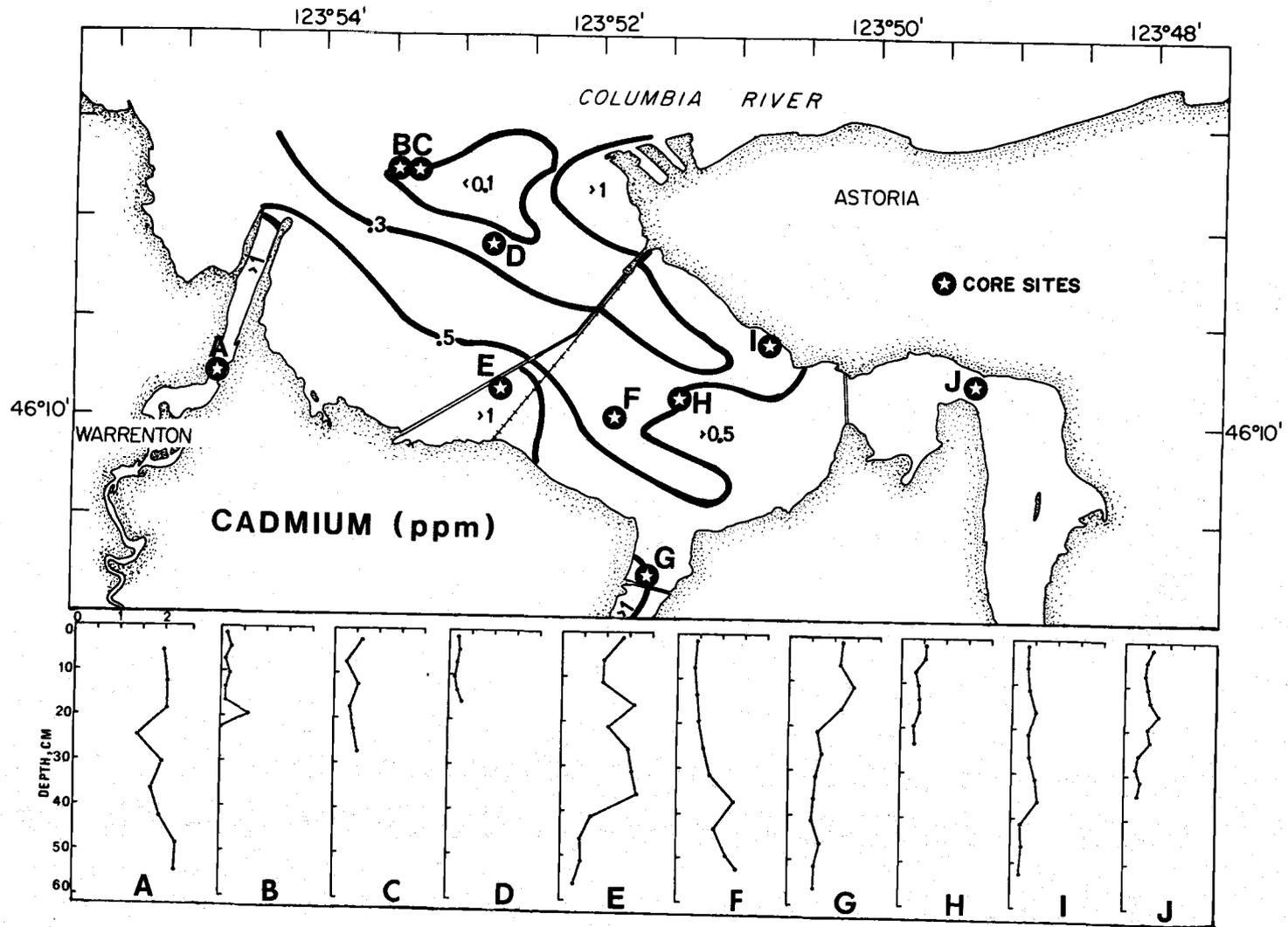
Figure I-13. Cadmium.
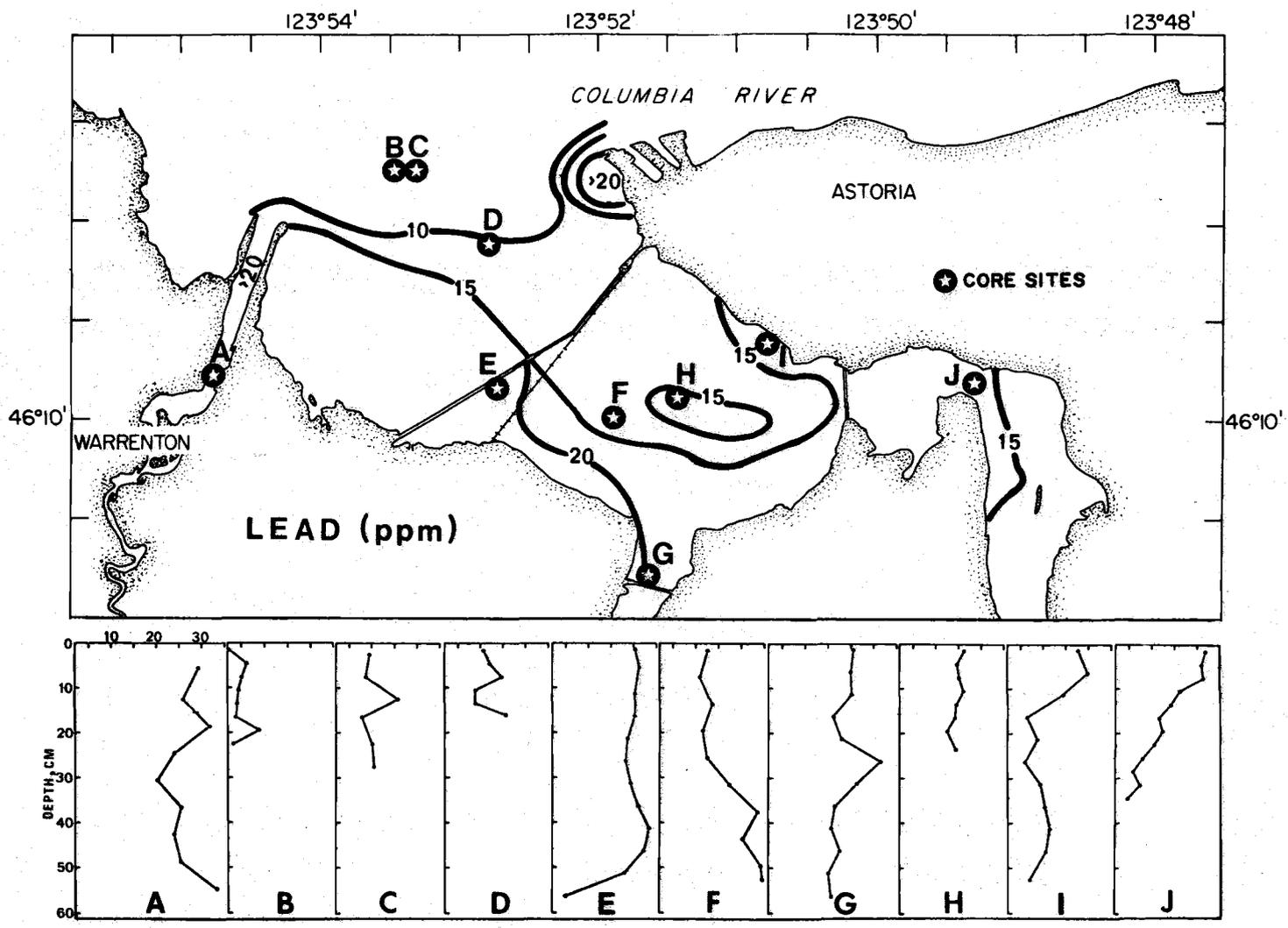
Figure I-14. Lead.
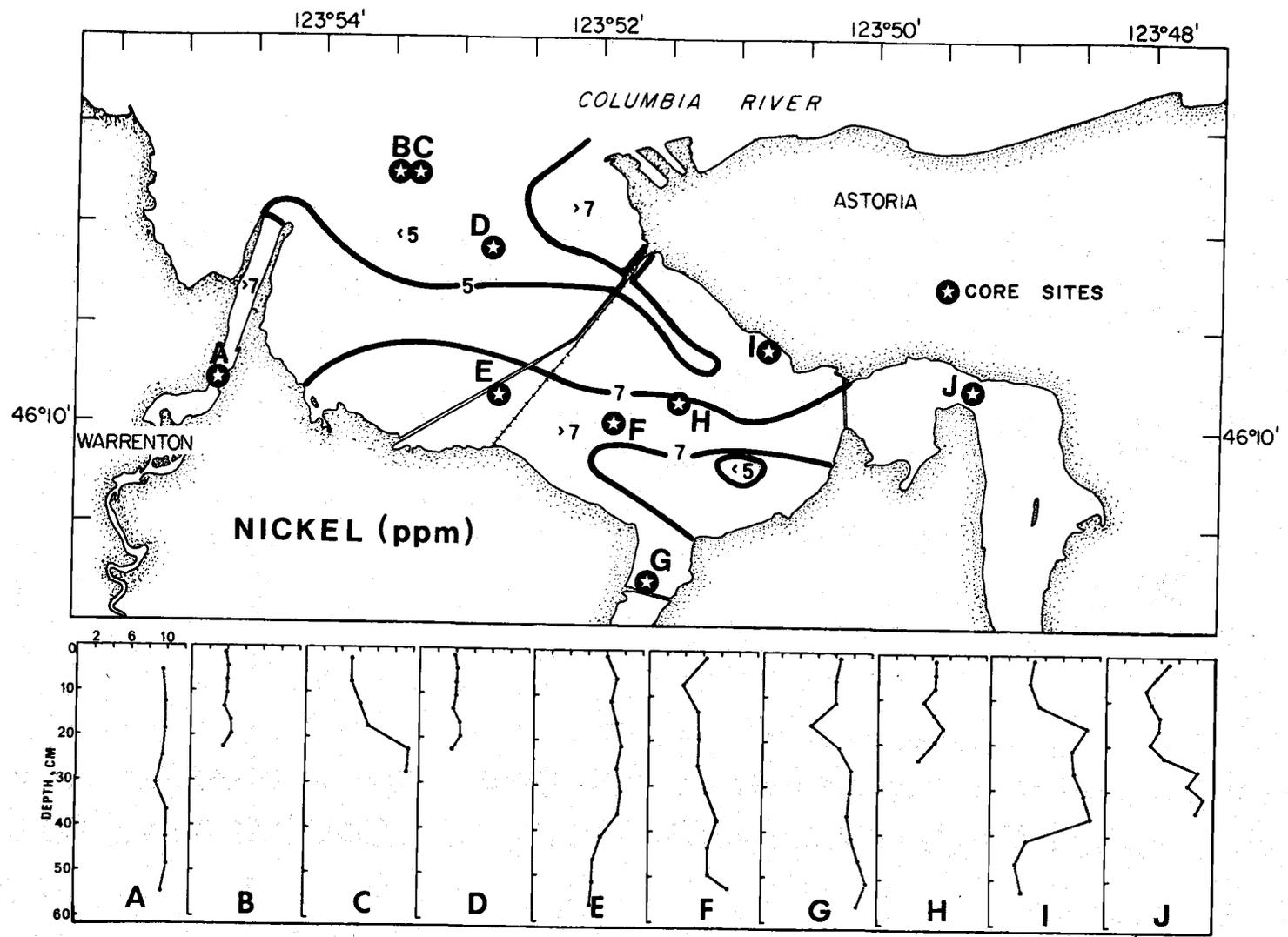
Figure I-15. Nickel.
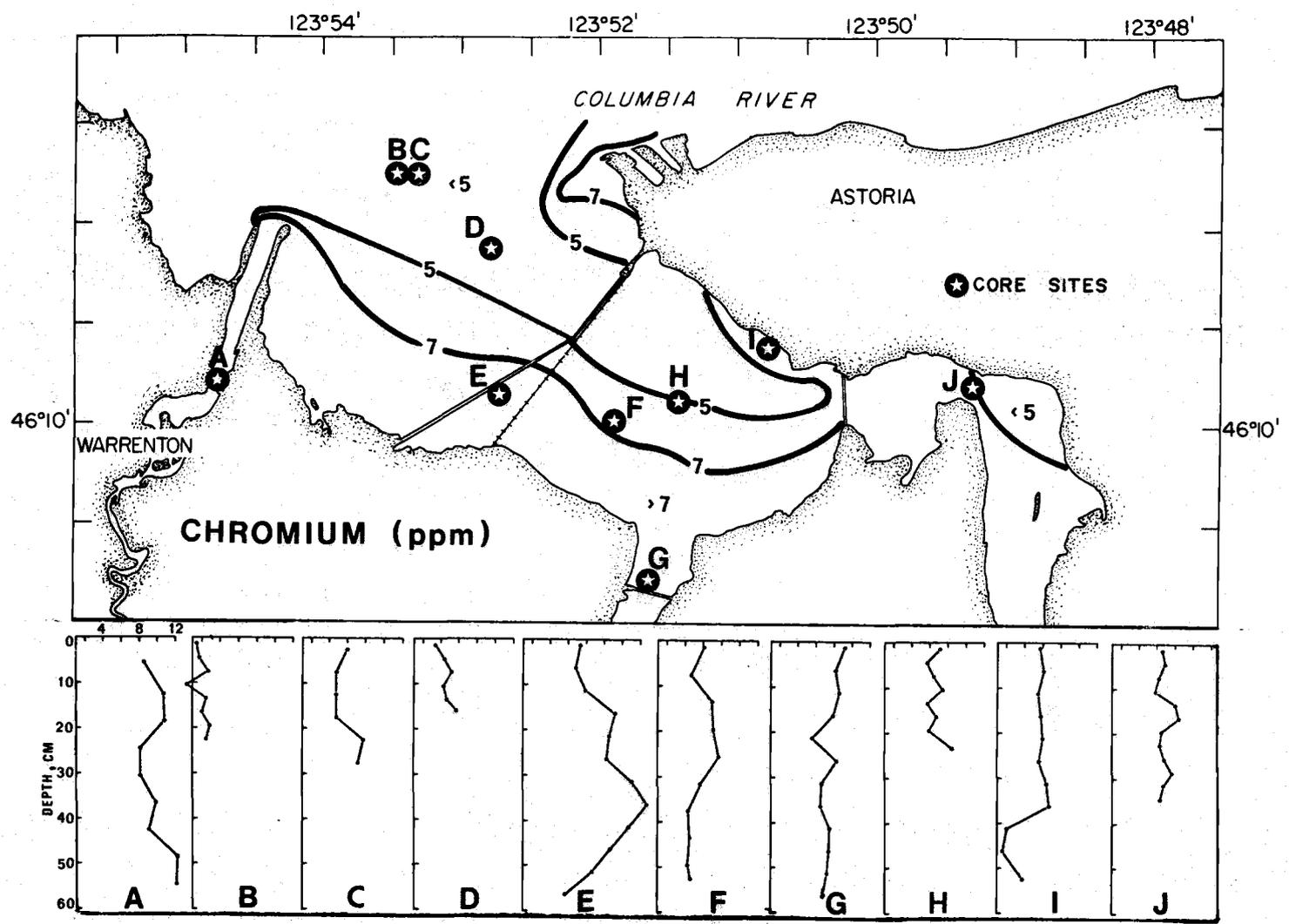
Figure I-16. Chromium.
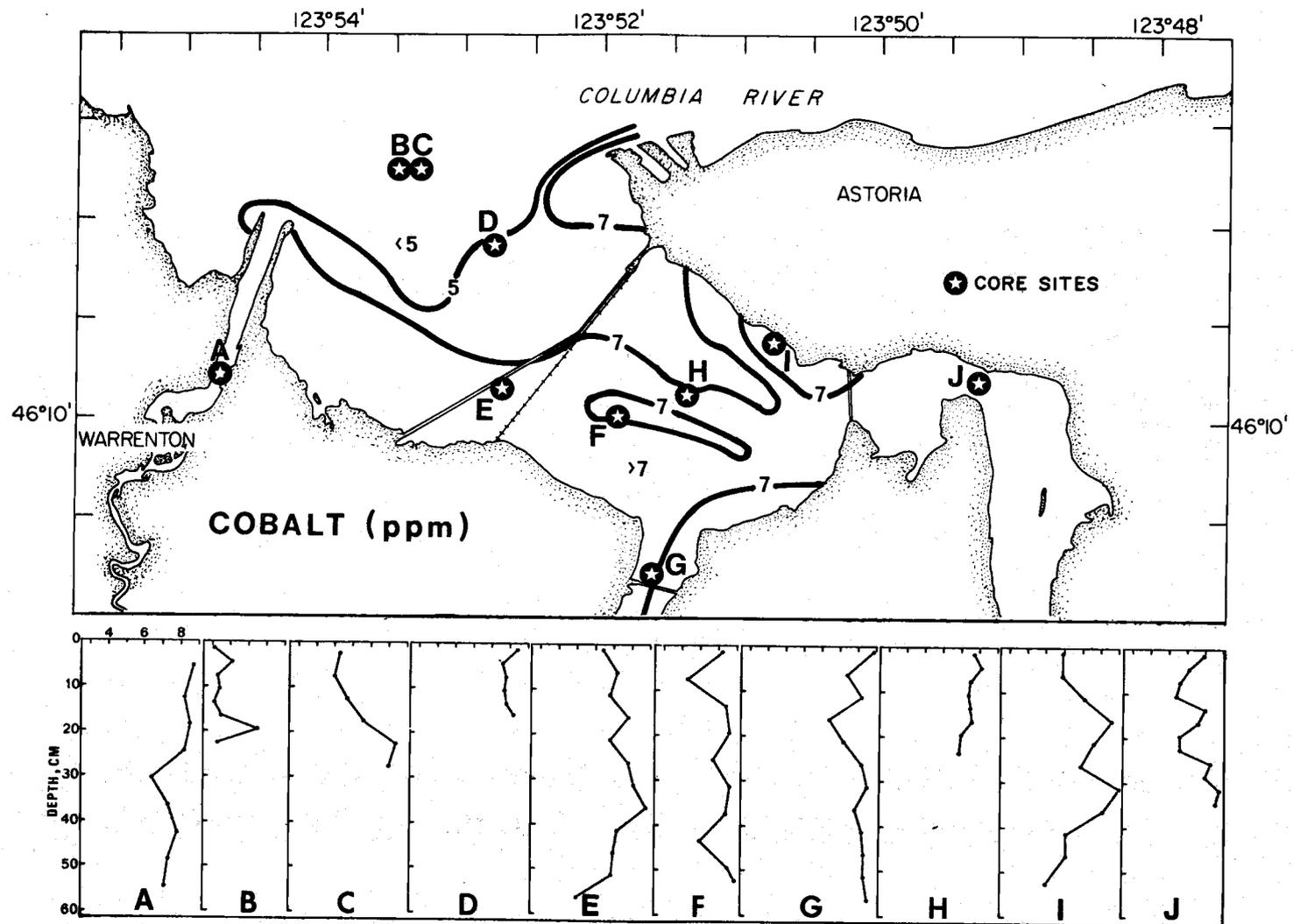
Figure I-17. Cobalt.

II

RESULTS OF YOUNGS BAY SEDIMENT ANALYSES FOR SEDIMENT TEXTURE

RADIONUCLIDES, FLUORIDE, AND TRACE METALS

Table II-1. Surface sediment collection data.

Station/Sample Number	Date Collected (day/mo/yr)	Sampling Device	Comments (general location, etc.)
1	03/03/74	mini dredge	lower Youngs River
2	03/03/74	mini dredge	lower Youngs River
3	03/03/74	mini dredge	lower Youngs River
4	no sample		
5	03/03/74	mini dredge	near Youngs River
6	03/03/74	mini dredge	inner bay
7	03/03/74	mini dredge	inner bay
8	03/03/74	mini dredge	inner bay
9	03/03/74	mini dredge	inner bay
10	03/03/74	mini dredge	inner bay
11	03/03/74	mini dredge	inner bay
12	03/03/74	mini dredge	inner bay
13	03/03/74	mini dredge	inner bay
14	03/03/74	mini dredge	inner bay
15	03/03/74	mini dredge	inner bay
16	03/03/74	mini dredge	inner bay
17	03/03/74	mini dredge	inner bay
18	03/03/74	mini dredge	inner bay
19	03/03/74	mini dredge	inner bay
20	03/03/74	mini dredge	inner bay
21	03/03/74	mini dredge	inner bay
22	03/03/74	mini dredge	inner bay
23	03/03/74	mini dredge	inner bay
24	03/03/74	mini dredge	inner bay
25	03/03/74	mini dredge	inner bay
26	03/03/74	mini dredge	inner bay
27	03/03/74	mini dredge	inner bay
28	03/03/74	mini dredge	inner bay
29	03/03/74	mini dredge	inner bay
30	03/03/74	mini dredge	inner bay
31	no sample		

Table II-1. (Continued)

Station/Sample Number	Date Collected (day/mo/yr)	Sampling Device	Comments (general location, etc.)
32	03/03/74	mini dredge	outer bay
33	03/03/74	mini dredge	outer bay
34	03/03/74	mini dredge	outer bay
35	03/03/74	mini dredge	outer bay
36	03/03/74	mini dredge	outer bay
37	03/03/74	mini dredge	outer bay
38	03/03/74	mini dredge	outer bay
39	03/03/74	mini dredge	outer bay
40	03/03/74	mini dredge	outer bay
41	03/03/74	mini dredge	outer bay
42	03/03/74	mini dredge	outer bay
43	03/03/74	mini dredge	outer bay
44	03/03/74	mini dredge	outer bay
45	03/03/74	mini dredge	outer bay
46	03/03/74	mini dredge	outer bay
47	03/03/74	mini dredge	outer bay
48	03/03/74	mini dredge	outer bay
49	03/03/74	mini dredge	at entrance to Skipanon Waterway
50	29/08/73	hand scoop	tide flats near channel marker 10, Cathlamet Bay
51	14/06/73	mini dredge	between Pier 2 and 3, Astoria docks
52	25/09/73	hand scoop	tide flats at North Island, Columbia River estuary
53	14/06/73	mini dredge	between Pier 2 and 3, Astoria docks
54	29/08/73	hand scoop	tide flats near channel marker 10, Cathlamet Bay
55	19/12/73	mini dredge	near Lewis and Clark River bridge
56	18/04/74	Smith-McIntyre grab	outer bay
57	18/04/74	Smith-McIntyre grab	outer bay
58	19/12/73	mini dredge	lower Lewis and Clark River
59	18/06/74	mini dredge	lower Youngs River
60	18/06/74	corer	inner bay, top 3 cm section
61	18/06/74	corer	inner bay, top 2.5 cm section
62	19/06/74	hand scoop	at base of Youngs River Falls
63	19/06/74	hand scoop	from bank on upper Lewis and Clark River
64	19/06/74	hand scoop	approximately 1/3 mile downstream from Youngs River Falls

Table II-1. (Continued)

Station/Sample Number	Date Collected (day/mo/yr)	Sampling Device	Comments (general location, etc.)
65	09/07/74	Smith-McIntyre grab	outer bay
66	09/07/74	Smith-McIntyre grab	inner bay
67	09/07/74	Smith-McIntyre grab	outer bay
68	04/08/74	corer	inner bay, top 2.5 cm section
69	04/08/74	corer	inner bay, top 2.5 cm section
70	29/09/74	corer	outer bay, top 3 cm section
71	29/09/74	corer	outer bay, top 5 cm section
72	10/10/74	corer	Daggett Point, (Youngs River), top 3 cm section
73	10/10/74	corer	inner bay, top 3 cm section
74	10/10/74	corer	outer bay, top 3 cm section
75	10/10/74		
76	24/10/74	mini dredge	near bridge crossing of S.E. Dolphin Ave. on upper Skipanon River
77	24/10/74	mini dredge	upper Skipanon River
78	24/10/74	mini dredge	upper Skipanon River
79	24/10/74	mini dredge	upper Skipanon River
80	24/10/74	mini dredge	Skipanon River near Warrenton High School fish hatchery
81	24/10/74	mini dredge	Skipanon River near Highway 101 bridge
82	24/10/74	mini dredge	lower Skipanon River
83	24/10/74	mini dredge	lower Skipanon River near tide gate
84	24/10/74	mini dredge	lower Skipanon River approximately 1/2 mile above railroad bridge.
85	24/10/74	mini dredge	turning basin, Skipanon Waterway
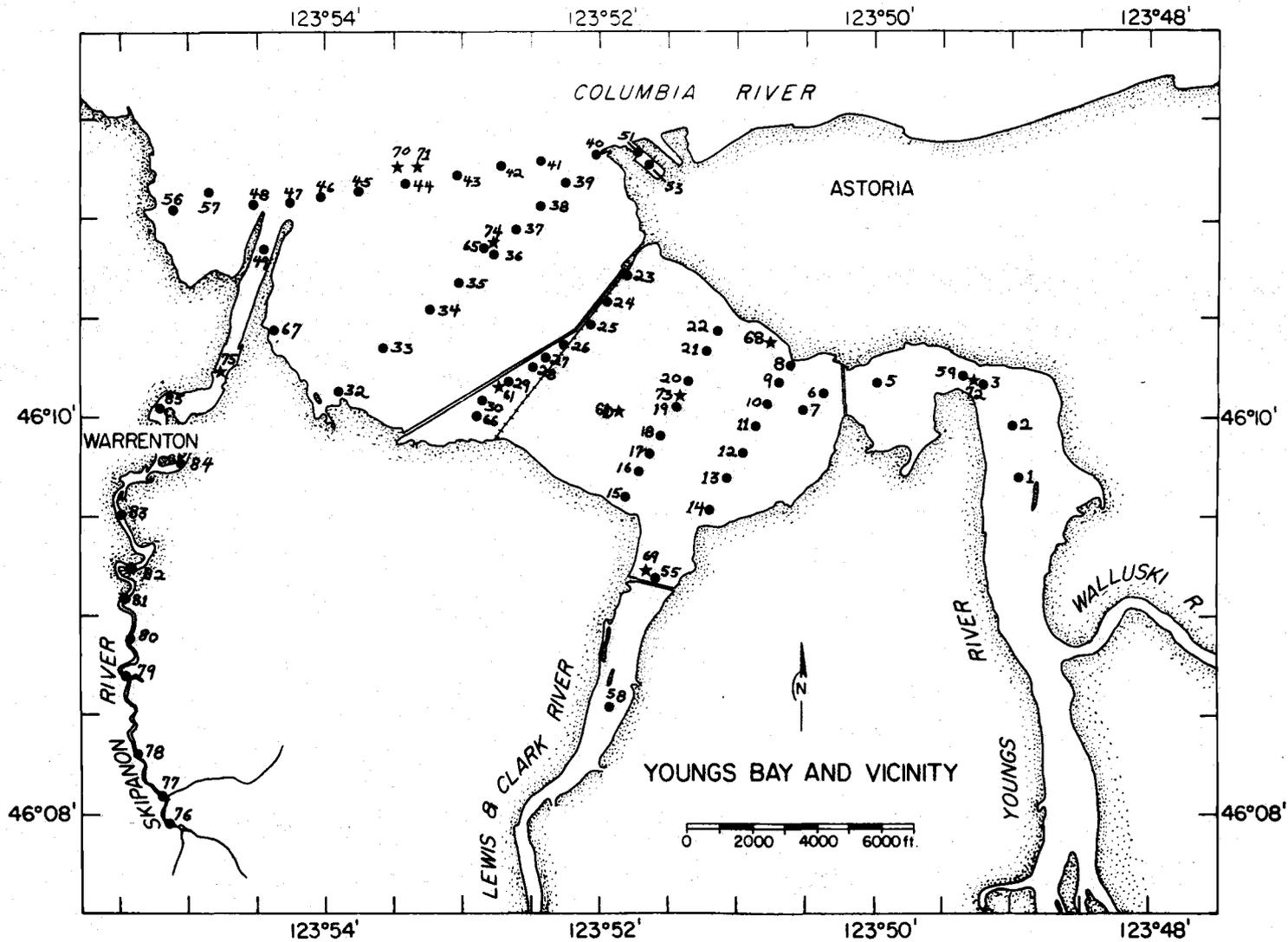
Figure II-1. Sample site locations and station numbers for Youngs Bay. Stars denote core stations; dots denote grab stations.
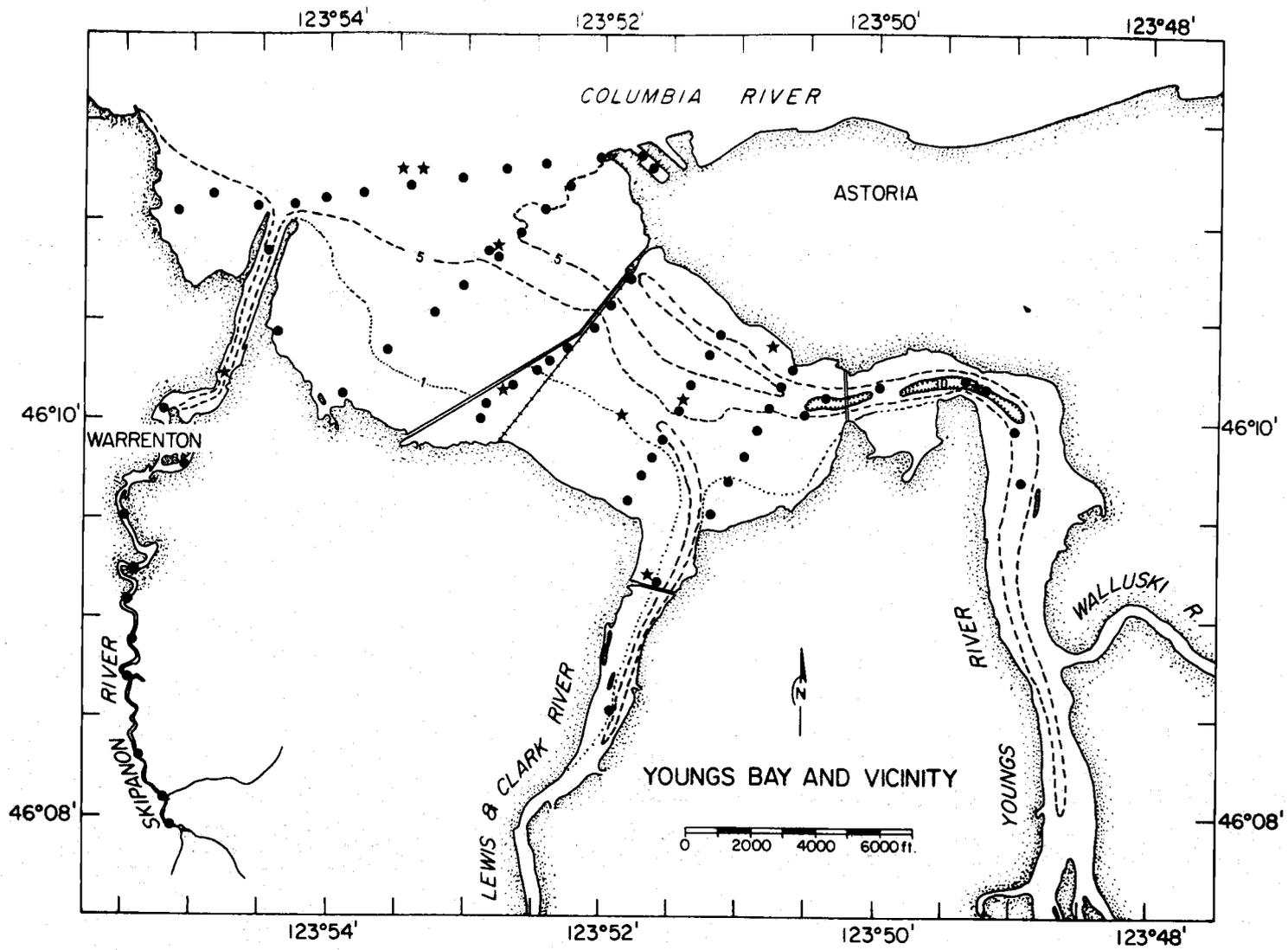
Figure II-2. Bathymetry and sample site locations for Youngs Bay. Depth contours are given in feet at mean lower low water.
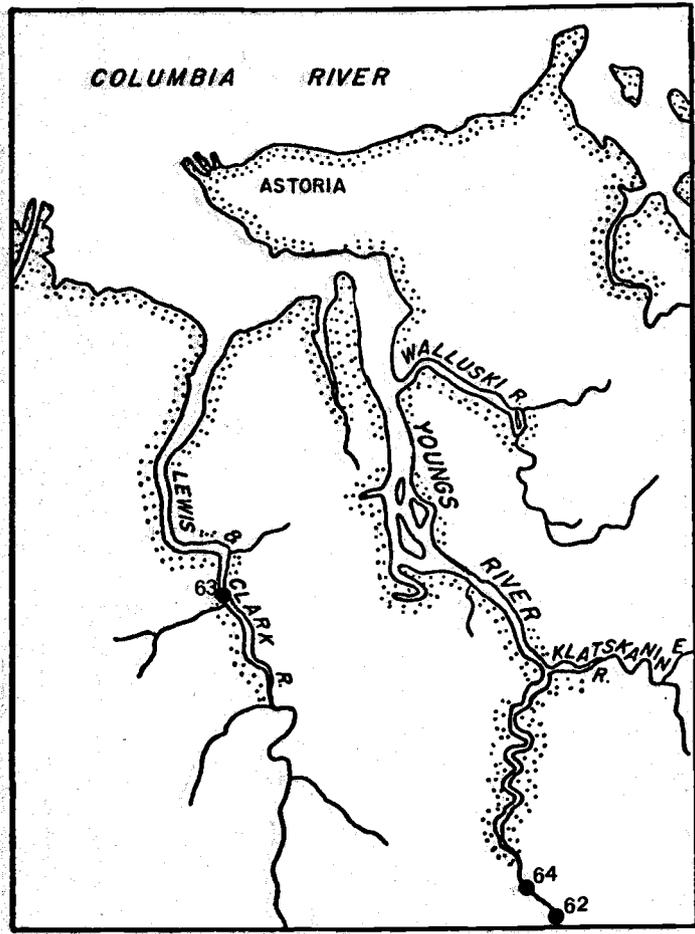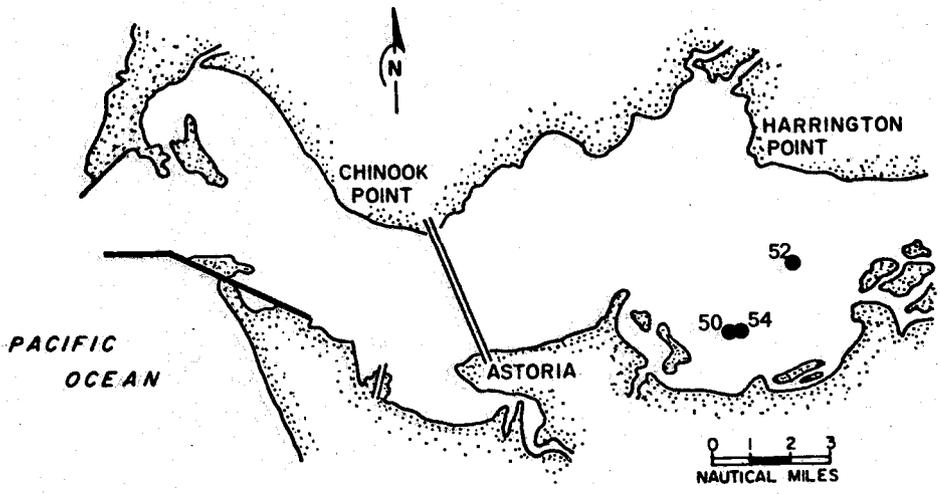
Figure II-3. Sample site locations and station locations outside the Youngs Bay area.

Table II-2. Mean, minimum, and maximum values for grab and core samples.

	Fines	^{60}Co	^{40}K	^{137}Cs	^{152}Eu	^{232}Th	^{238}U	F	Fe	Mn	Zn	Cu	Cd	Pb	Ni	Cr	Co
Units	%	pCi/g	pCi/g	pCi/g	pCi/g	pCi/g	pCi/g	µg/g	%	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Mean	46.3	0.53	11.5	0.48	0.79	0.50	0.40	325	0.929	233	76.6	11.3	0.61	14.0	7.4	6.2	6.7
Minimum	0	0	8.61	0	0	0.22	0.10	191	0.417	41.5	12.2	1.1	0.02	2.0	2.1	0.69	2.2
Maximum	99.9	2.30	14.5	1.61	3.24	0.98	0.94	494	1.91	575	211	31.0	2.27	33.3	12.6	14.7	11.6

Table II-3. Grab station analytical results.

GRAB NO	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
1	65.6	0.43	11.2	0.46	0.47	0.70	0.56	344	1.005	287	83.3	11.5	0.71	15.3	7.8	6.3	7.2
2	52.2	0.33	12.4	0.23	0.00	0.67	0.52	355	0.882	296	70.8	9.3	0.52	12.0	7.2	4.8	7.2
3	65.8	0.25	12.2	0.39	0.24	0.62	0.46	356	0.968	352	74.8	12.0	0.60	11.7	7.8	4.8	7.9
4																	
5	56.2	0.44	12.4	0.37	0.29	0.62	0.50		1.014	278	98.5	10.8	0.62	15.0	8.3	6.9	8.0
6	66.3	0.30	10.6	0.33	0.67	0.66	0.51	494	0.873	298	81.5	13.2	0.58	13.7	6.8	4.6	6.4
7	73.4	0.35	11.2	0.44	0.42	0.53	0.46	329	0.896	241	91.3	10.2	0.51	13.2	7.3	5.3	7.2
8	39.0	0.26	11.7	0.18	0.29	0.50	0.44	312	0.831	226	79.9	8.3	0.38	17.3	6.0	6.5	5.0
9	22.1	0.41	12.9	0.17	0.20	0.52	0.28	259	0.849	660	66.9	6.3	0.36	8.8	6.6	4.5	8.9
10	39.5	0.46	12.2	0.20	0.17	0.48	0.44	298	0.824	342	70.5	8.1	0.49	12.0	5.9	3.4	6.5
11	61.7	0.55	12.8	0.45	0.42	0.51	0.35	352	0.954	351	92.3	11.4	0.64	16.8	7.7	6.0	8.0
12	13.7	0.40	12.3	0.18	0.44	0.44	0.31	255	0.682	284	59.0	5.9	0.52	11.4	5.9	4.7	5.7
13	39.4	0.41	12.0	0.35	0.26	0.57	0.49	350	0.931	257	90.1	9.1	0.42	18.1	6.6	8.5	7.4
14	50.8	0.52	11.6	0.29	0.34	0.63	0.36	316	0.959	311	86.0	10.1	0.52	18.9	6.6	8.2	6.5
15	64.6	0.66	9.6	0.46	1.07	0.52	0.38	327	1.161	444	121.7	12.4	0.89	21.8	7.5	9.7	10.3
16	73.5	0.38	10.4	0.35	0.63	0.55	0.46	344	0.972	321	102.7	11.1	0.63	17.3	6.9	8.6	7.2
17	58.4	0.47	11.7	0.38	0.60	0.56	0.41	327	0.969	315	94.9	9.6	0.35	22.7	6.8	7.4	8.1
18	69.3	0.64	11.1	0.39	0.70	0.64	0.40	371	1.056	289	103.6	13.0	0.63	13.7	7.5	6.6	7.6
19	67.0	0.34	11.8	0.43	0.33	0.52	0.40	351	0.863	339	89.0	12.0	0.48	15.7	7.2	5.0	7.0
20	55.5	0.30	11.4	0.40	0.37	0.59	0.46	280	0.800	279	69.9	9.3	0.49	11.1	6.4	4.1	6.9
21	1.1	0.14	11.2	0.26	0.00	0.48	0.33	258	0.607	164	34.2	1.9	0.04	5.2	3.7	1.9	5.1
22	21.4	0.25	12.7	0.14	0.24	0.48	0.34	293	0.854	478	64.1	6.1	0.41	11.8	6.3	3.7	8.5
23	8.5	0.26	12.2	0.17	0.56	0.51	0.37	240	0.647	251	50.1	4.0	0.17	9.7	5.0	3.9	5.6
24	33.1	0.28	13.3	0.25	0.00	0.47	0.44	328	0.746	278	71.3	6.4	0.23	12.3	5.6	5.0	6.8
25	26.7	0.14	11.2	0.15	0.36	0.61	0.27	288	0.655	146	46.7	7.9	0.40	5.5	5.7	3.2	5.3
26	30.3	0.32	12.2	0.17	0.19	0.56	0.38	294	0.849	335	68.3	7.0	0.48	12.2	6.2	5.5	7.6
27	30.6	0.29	11.6	0.36	0.27	0.47	0.36	292	0.771	234	62.4	5.8	0.25	8.1	6.1	4.1	6.0
28	40.7	0.46	12.9	0.29	0.50	0.50	0.40	309	0.996	426	104.1	7.8	0.57	15.0	7.8	7.1	8.7
29	99.6	1.61	12.5	0.83	1.73	0.54	0.38	387	0.970	205	136.5	16.7	1.00	23.5	8.6	10.6	8.4
30	99.7	1.14	11.8	0.79	1.11	0.66	0.35	377	1.221	729	165.4	20.3	1.28	23.4	11.0	9.5	11.6
31																	
32	81.8	0.81	11.0	0.42	0.84	0.72	0.52	360	0.889	470	104.3	10.1	0.54	16.8	8.3	8.8	7.8
33	50.4	0.58	11.9	0.39	0.85	0.55	0.39	335	0.871	367	97.3	8.6	0.54	18.6	7.1	8.0	7.7
34	37.0	0.42	10.5	0.29	0.47	0.68	0.45	314	0.700	213	66.2	6.1	0.45	10.3	5.1	5.1	4.6
35	20.6	0.48	13.1	0.24	0.31	0.41	0.37	306	0.850	317	73.2	4.5	0.43	15.4	5.6	5.5	6.5

Table II-3. (Continued)

GRAB NO	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
36	6.6	0.48	13.5	0.19	0.18	0.41	0.32	257	0.733	366	64.1	3.2	0.23	8.6	6.4	4.0	6.4
37	1.0	0.28	11.1	0.06	0.15	0.84	0.44	261	0.490	187	29.0	1.9	0.04	6.1	4.2	3.6	4.8
38	51.8	0.26	12.0	0.31	0.26	0.50	0.38	333	0.808	280	83.8	8.4	0.70	10.3	7.3	4.6	7.3
39	62.5	0.89	11.5	0.52	1.38	0.52	0.39		0.926	201	116.1	16.5	1.38	27.4	8.7	7.1	7.8
40	60.8	0.32	10.7	0.30	0.17	0.51	0.39	374	1.060	311	80.5	13.4	0.37	12.9	7.0	10.2	6.4
41	2.2	0.18	10.3	0.10	0.20	0.28	0.19	265	0.436	49	22.0	2.6	0.09	2.5	4.4	0.7	2.7
42	3.1	0.12	10.7	0.00	0.00	0.26	0.29	240	0.491	63	27.4	3.2	0.10	4.1	4.5	4.5	3.3
43	1.1	0.16	9.4	0.10	0.29	0.32	0.19	259	0.420	48	18.4	2.3	0.01	3.4	3.9	3.9	3.4
44	1.7	0.14	11.7	0.00	0.00	0.28	0.29	243	0.417	69	27.4	1.8	0.02	3.4	4.4	4.4	3.7
45	3.1	0.11	12.9	0.06	0.24	0.34	0.21	254	0.515	85	26.9	3.1	0.19	3.8	3.7	3.7	3.9
46	9.0	0.18	11.2	0.14	0.43	0.42	0.24	253	0.614	156	41.1	4.9	0.28	6.5	4.2	4.2	3.6
47	35.0	0.16	12.3	0.23	0.00	0.48	0.45	296	0.613	183	62.8	6.9	0.42	9.6	5.5	5.5	3.8
48	10.7	0.24	11.6	0.08	0.18	0.44	0.23	243	0.544	200	40.8	4.9	0.26	6.1	4.1	4.1	4.6
49	95.6	0.60	11.0	0.63	0.00	0.57	0.41	383	1.013	280	129.3	20.8	1.07	19.6	7.7	7.7	7.6
50		0.70	10.4	0.43	0.35	0.55	0.62	361	0.970	253	140.0	17.5	0.92	13.7	8.2	5.7	7.1
51		1.16	9.9	0.68	0.84	0.36	0.29	379	0.967	260	205.0	22.3	1.42	21.6	8.7	6.8	5.3
52		0.58	10.5	0.48	0.57	0.52	0.46	353	0.848	383	114.0	13.3	0.61	14.5	7.7	6.6	6.6
53								369	0.963	237	194.0	21.8	1.47	21.3	7.9	7.2	5.3
54		0.62	10.3	0.27	0.45	0.60	0.59	358	0.926	216	116.0	15.0	0.52	14.2	8.5	6.1	7.0
55	77.5	0.47	11.0	0.36	0.43	0.58	0.50	341	0.963	320	89.1	9.9	0.56	10.8	7.2	5.8	5.3
56	12.5	0.25	12.0	0.20	0.36	0.56	0.28	250	0.465	77	35.9	3.7	0.15	6.0	3.6	3.5	3.5
57	13.3	0.23	12.9	0.22	0.13	0.38	0.36		0.516	102	43.3	4.0	0.30	5.3	3.3	3.4	3.3
58	66.9	0.42	11.4	0.46	0.90	0.62	0.44	306	1.744	546	110.4	10.5	0.70	15.2	9.0	5.8	8.7
59	74.6	0.28	10.5	0.43	0.49	0.58	0.43		1.109	429	90.9	14.5	0.78	15.3	9.5	5.9	8.0
60*	43.9	0.44	12.9	0.37	0.22	0.59	0.45	327	0.864	268	87.2	8.2	0.43	12.6	7.3	6.1	6.2
61*	91.3	0.93	10.8	0.70	1.10	0.50	0.43	368	0.959	517	150.6	16.3	1.15	20.3	9.0	7.3	6.4
62	3.3	0.00	9.5	0.47	0.00	0.55	0.30										
63	33.6	0.05	12.3	0.32	0.00	0.45	0.32										
64	85.4	0.14	11.8	0.10	0.16	0.70	0.51										
65	7.6	0.62	14.5	0.35	0.40	0.33	0.39	241									
66	88.3	0.71	11.4	0.63	0.80	0.56	0.41	383									
67	5.0	0.47	13.7	0.21	0.10	0.33	0.30	245									
68*	21.4	0.23	11.6	0.14	0.42	0.46	0.34	288	0.825	247	62.7	6.1	0.34	17.7	5.8	5.7	5.9
69*	91.5	0.81	11.7	0.62	0.57	0.59	0.46	351	1.180	443	144.0	17.0	1.17	20.4	9.5	9.2	9.8
70*	2.4							254	0.447	59	18.1	2.1	0.12	2.3	4.8	1.4	3.1

Table II-3. (Continued)

GRAB NO	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
71*	19.7	0.33	12.4	0.30	0.38	0.47	0.31	282	0.639	95	55.1	7.5	0.60	9.5	6.1	6.0	5.3
72*	48.3	0.33	10.6	0.47	0.36	0.51	0.40	345	0.991	339	91.8	13.1	0.61	21.8	7.9	6.6	6.9
73*	16.0	0.27	11.5	0.16	0.24	0.38	0.30	308	0.965	440	78.7	7.6	0.55	16.2	7.4	7.1	7.7
74*	3.4	0.54	12.8	0.13	0.31	0.32		233	0.851	575	56.1	3.5	0.19	10.6	4.8	3.4	8.4
75*	96.5	1.02	10.6	0.80	1.38	0.60	0.38	416	1.180	217	195.0	31.0	1.96	29.3	10.6	8.5	8.7
76	4.4	0.08	12.9	1.10	0.00	0.28	0.23	209	0.757	132	18.8	1.5	0.41	3.6	3.3	4.3	2.5
77	4.1							191	1.270	57	12.2	1.1	0.09	2.0	2.1	3.0	2.2
78	16.6	0.00	11.6	1.37	0.00	0.34	0.23	226	1.600	261	23.0	3.0	0.02	3.4	4.7	2.2	4.7
79	18.6							226	1.500	140	25.4	2.5	0.19	5.5	4.1	3.2	3.6
80	7.4	0.00	14.5	1.52	0.00	0.38	0.20	221	1.910	195	43.8	8.0	0.46	6.8	6.4	5.1	7.3
81	61.0							279	1.240	86	22.4	1.8	0.16	2.4	3.0	3.3	3.2
82	13.3	0.09	13.1	1.03	0.00	0.50	0.23	232	1.300	68	25.7	3.5	0.18	7.2	3.4	4.3	3.4
83	6.0	0.00	12.8	0.31	0.00	0.37	0.19	236	0.758	143	18.6	3.4	0.19	3.0	3.1	3.4	3.2
84	62.4	0.38	10.4	0.89	0.41	0.50	0.28	316	1.740	239	102.1	14.8	0.80	18.2	8.3	7.3	8.0
85	96.7	1.25	9.2	0.96	0.32	0.60	0.42	385	1.440	162	179.0	31.0	1.79	28.2	8.5	9.9	7.0

Table II-4. Core station analytical results, Station 60.

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
60	1.50	43.9	0.44	12.9	0.37	0.22	0.59	0.45	327	0.864	268	87.2	8.2	0.43	12.6	7.3	6.1	6.2
60	4.50	37.6																
60	7.50	19.5	0.58	13.2	0.25	0.47	0.51	0.43	291	0.804	196	72.1	5.4	0.38	10.9	4.7	4.7	4.3
60	10.50	19.0																
60	13.50	30.9	0.77	13.0	0.53	0.81	0.60	0.38	333	0.902	89	77.1	8.1	0.43	13.6	6.4	7.0	6.4
60	16.50	32.9																
60	19.50	26.3	0.61	13.4	0.39	0.77	0.56	0.41	300	0.863	85	60.8	7.2	0.48	11.5	6.5	7.1	6.6
60	22.50	28.3																
60	25.50	25.9	0.57	12.2	0.43	0.60	0.51	0.36	288	0.846	95	68.3	7.1	0.59	12.5	6.4	7.7	5.7
60	28.50	34.9																
60	31.50	53.1	0.19	13.1	0.15	0.00	0.58	0.50	363	0.750	131	80.5	10.5	0.73	17.4	7.4	5.7	6.6
60	34.50	70.0																
60	37.50	74.8	0.27	11.3	0.00	0.00	0.40	0.41	372	0.791	158	101.7	14.9	1.26	23.6	8.6	4.3	6.4
60	40.50	68.4																
60	43.50	78.5	0.00	11.9	0.00	0.00	0.62	0.47	374	0.783	152	86.3	12.7	0.83	20.3	7.6	4.5	5.0
60	46.50	94.0																
60	49.50	84.3							391	0.880	152	98.6	13.9	1.10	24.3	7.6	4.3	6.5
60	52.50	87.0	0.00	8.6	0.00	0.00	0.41	0.29		0.936	170	114.4	17.2	1.33	24.6	9.8	4.6	6.9

Table II-5. Core station analytical results, Station 61.

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
61	1.25	91.3	0.93	10.8	0.70	1.10	0.50	0.43	388	0.959	517	151.0	16.3	1.15	20.3	9.0	7.3	6.4
61	3.75	96.1																
61	6.25	97.0	1.24	10.9	0.71	1.32	0.51	0.40	377	1.057	262	145.2	19.2	0.93	21.2	10.1	6.8	7.2
61	8.75	97.1																
61	11.25	94.1	0.98	12.1	0.69	1.64	0.55	0.42	385	0.936	221	135.1	17.9	0.91	20.3	9.5	7.9	6.8
61	13.75	97.4																
61	16.25	93.1	2.30	12.3	1.13	3.24	0.63	0.41	403	0.988	236	158.6	21.7	1.61	20.2	10.1	11.2	7.8
61	18.75	99.2																
61	21.25	95.0	1.61	13.3	1.14	2.23	0.46	0.54	398	0.970	280	106.9	19.6	1.05	18.6	10.6	10.6	6.8
61	23.75	99.2																
61	26.25	97.7	1.43	13.1	1.61	2.08	0.55	0.46	391	1.048	287	97.9	20.1	1.49	18.2	10.1	10.3	7.8
61	28.75	99.2																
61	31.25	93.1	1.50	12.1	1.46	1.77	0.54	0.58	388	1.117	338	134.7	21.3	1.57	19.3	10.6	13.1	8.8
61	33.75	96.5																
61	36.25	86.4	1.67	11.2	1.58	3.13	0.55	0.46	400	1.057	348	123.4	20.3	1.68	21.0	10.3	14.7	8.8
61	38.75	87.6																
61	41.25	52.1	0.89	11.7	0.72	1.35	0.58	0.43	360	0.980	240	96.8	11.9	0.68	23.4	8.4	12.7	7.2
61	43.75	51.2																
61	46.25	32.1	0.46	11.8	0.24	0.60	0.54	0.40	331	0.967	180	83.5	8.1	0.44	22.2	7.6	10.7	7.0
61	48.75	32.9																
61	51.25	33.9	0.18	10.3	0.22	0.43	0.48	0.37	339	0.879	138	68.6	7.6	0.46	18.0	7.5	8.7	6.9
61	53.75	56.5																
61	56.25	38.6	0.22	10.1	0.00	0.00	0.65	0.68	328	0.859	123	21.9	6.8	0.30	4.9	7.3	5.7	5.0

Table II-6. Core station analytical results, Station 68.

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
68	1.25	21.4	0.23	11.6	0.14	0.42	0.46	0.34	288	0.825	247	62.7	6.1	0.34	17.7	5.8	5.7	5.9
68	3.75	12.3	0.34	12.5	0.24	0.38	0.42	0.36										
68	6.25	11.1	0.31	11.6	0.18	0.28	0.46	0.40	258	0.794	249	60.2	5.1	0.33	19.8	5.3	6.1	5.9
68	8.75	7.5																
68	11.25	9.5	0.35	11.8	0.12	0.33	0.43	0.34	266	0.831	249	52.0	5.4	0.38	14.3	6.3	5.5	7.1
68	13.75	34.7							362									
68	16.25	69.9	0.16	10.8	0.00	0.00	0.43	0.48	401	1.130	227	33.4	18.1	0.52	6.3	11.6	5.8	8.6
68	18.75	69.9							430									
68	21.25	78.5	0.00	9.8	0.00	0.29	0.52	0.44	417	1.060	247	31.2	17.1	0.37	8.6	10.0	6.0	7.6
68	23.75	81.3																
68	26.25	82.9	0.00	10.0	0.13	0.00	0.41	0.37	400	1.020	237	28.9	16.4	0.39	5.8	10.2	5.6	6.9
68	28.75	83.3																
68	31.25	79.9							472	1.260	332	38.4	23.4	0.52	9.3	11.3	6.4	9.0
68	33.75	85.7																
68	36.25	77.3	0.23	12.2	0.00	0.00	0.56	0.39	467	1.330	370	39.6	25.1	0.58	10.3	12.1	6.7	8.1
68	38.75	51.6							400									
68	41.25	13.5	0.11	12.4	0.00	0.00	0.36	0.33	232	0.704	114	29.2	6.3	0.21	11.4	5.0	2.1	6.1
68	43.75	10.3																
68	46.25	7.9	0.00	9.9	0.00	0.00	0.34	0.26	247	0.633	79	28.4	5.1	0.24	10.5	3.8	1.6	6.1
68	48.75	6.9																
68	52.50	5.2	0.09	10.7	0.00	0.00	0.27	0.31	251	0.805	129	30.9	4.5	0.19	6.9	4.5	3.8	5.0

Table II-7. Core station analytical results, Station 69.

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
69	1.25	91.5	0.81	11.7	0.62	0.57	0.59	0.46	351	1.180	443	144.0	17.0	1.17	20.4	9.5	9.2	9.8
69	3.75	94.4	0.57	11.1	0.70	1.09	0.51	0.39										
69	6.25	85.9	0.86	9.9	0.73	0.99	0.60	0.38	348	1.150	321	139.0	16.0	1.12	19.9	9.0	8.2	8.4
69	8.75	83.2	1.33	9.7	0.71	1.48	0.52	0.39										
69	11.25	72.9	1.12	10.5	0.80	1.45	0.53	0.47	344	1.010	205	133.0	14.6	1.42	20.2	9.0	8.6	9.2
69	13.75	69.0	1.51	11.2	0.94	1.63	0.54	0.46										
69	16.25	39.4	0.55	11.2	0.51	0.92	0.56	0.34	301	0.861	146	81.8	15.1	1.14	16.1	6.3	7.9	7.4
69	18.75	67.1	0.13	10.8	0.16	0.00	0.53	0.45										
69	21.25	80.3	0.06	9.7	0.09	0.00	0.51	0.44	359	1.190	202	74.4	17.4	0.64	17.9	9.4	5.6	8.2
69	23.75	94.6																
69	26.25	90.8	0.19	12.1	0.18	0.00	0.62	0.49	384	1.160	214	93.1	22.3	0.73	26.5	10.8	8.3	9.2
69	28.75	93.2																
69	31.25	88.8	0.16	9.6	0.08	0.00	0.54	0.41	390	1.100	206	78.8	21.5	0.60	21.3	10.6	6.6	9.5
69	33.75	92.4																
69	36.25	91.6	0.10	11.2	0.13	0.00	0.59	0.52	386	1.100	183	63.5	21.5	0.56	16.5	10.4	6.5	8.8
69	38.75	95.1																
69	41.25	92.6	0.06	11.2	0.13	0.00	0.57	0.51	394	1.110	193	62.6	21.5	0.52	15.7	10.9	7.5	9.2
69	43.75	92.1																
69	46.25	92.5	0.18	10.8	0.00	0.00	0.51	0.43	410	1.170	207	62.7	22.8	0.70	17.6	11.7	7.4	9.3
69	48.75	95.5																
69	51.25	93.5	0.20	10.8	0.18	0.00	0.54	0.38	391	1.140	204	56.8	23.2	0.58	15.1	12.6	7.2	9.3
69	53.75	97.2																
69	56.25	94.7	0.14	11.5	0.10	0.00	0.54	0.49	400	1.140	214	61.7	22.5	0.57	15.7	11.6	6.7	9.5

Table II-8. Core station analytical results, Stations 70 and 71.

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
70	1.50	2.4	0.16	10.8	0.19	0.19	0.28	0.30	254	0.447	59	18.1	2.1	0.12	2.3	4.8	1.4	3.1
70	4.50	4.3	0.12	9.4	0.07	0.15	0.22	0.27	247	0.569	63	27.9	2.9	0.21	6.2	5.1	1.7	4.1
70	7.50	1.7	0.05	11.1	0.05	0.15	0.23	0.38	218	0.549	55	25.8	2.2	0.09	5.1	5.0	2.7	3.3
70	10.50	2.6	0.13	10.6	0.09	0.15	0.32	0.26	222	0.509	48	20.4	2.3	0.19	4.4	5.0	0.3	3.4
70	13.50	2.4	0.07	10.0	0.17	0.00	0.22	0.40	222	0.488	42	17.9	1.8	0.10	4.1	4.7	2.5	3.1
70	16.50	3.2	0.12	9.9	0.07	0.10	0.22	0.19	229	0.524	48	17.4	2.3	0.10	3.7	5.4	2.0	3.5
70	19.50	19.6	0.11	10.6	0.21	0.24	0.36	0.26	263	0.618	110	58.2	7.4	0.60	8.8	5.5	2.9	5.5
70	22.50	3.0							238	0.443	53	18.9	2.3	0.02	3.2	4.6	2.5	3.3

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
71	2.50	19.7	0.33	12.4	0.30	0.38	0.47	0.31	282	0.639	95	55.1	7.5	0.60	9.5	6.1	6.0	5.3
71	7.50	14.7	0.15	11.0	0.22	0.42	0.28	0.27	268	0.580	71	49.4	6.0	0.26	8.7	6.1	4.2	5.0
71	12.50	26.1	0.44	12.3	0.28	0.38	0.49	0.33	318	0.710	146	74.4	10.4	0.53	15.8	7.1	4.8	5.7
71	17.50	31.7	0.43	12.9	0.21	0.00	0.49	0.43	344	0.732	109	46.1	9.8	0.34	7.9	8.0	4.8	6.6
71	22.50	95.3	0.15	13.1	0.08	0.00	0.61	0.52	481	1.240	283	36.1	21.8	0.43	10.1	12.5	7.8	8.4
71	27.50	96.4							485	1.340	343	31.9	21.0	0.53	10.5	12.3	7.2	8.0

51

Table II-9. Core station analytical results, Stations 72 and 73.

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
72	1.50	48.3	0.33	10.6	0.47	0.36	0.51	0.40	345	0.991	339	91.8	13.1	0.61	21.8	7.9	6.6	6.9
72	4.50	36.2	0.30	11.0	0.34	0.30	0.42	0.45	326	0.958	178	83.1	10.5	0.47	21.0	6.6	6.9	6.1
72	7.50	25.3	0.38	10.2	0.30	0.24	0.36	0.35	325	0.895	116	65.3	8.6	0.44	21.4	5.4	6.2	5.6
72	10.50	21.6	0.47	10.5	0.30	0.33	0.40	0.38	303	0.824	98	61.0	9.4	0.50	16.1	6.0	5.8	5.4
72	13.50	44.6	0.57	10.7	0.79	0.65	0.52	0.45	358	0.913	122	72.4	12.3	0.55	14.1	6.9	8.0	7.0
72	16.50	35.0	0.56	11.0	0.63	0.70	0.45	0.29	319	0.895	114	64.2	10.4	0.74	11.6	6.8	8.4	6.6
72	19.50	21.9	0.39	9.2	0.35	0.52	0.27	0.27	306	0.864	106	50.0	8.2	0.50	12.4	5.9	6.5	5.6
72	22.50	28.9	0.28	10.9	0.20	0.30	0.33	0.25	351	1.080	147	38.4	9.8	0.56	10.6	7.4	6.3	5.6
72	25.50	74.9	0.18	10.3	0.24	0.28	0.52	0.31	406	1.360	267	28.3	15.8	0.31	8.0	11.1	6.8	7.3
72	28.50	77.8							413	1.220	212	31.0	17.3	0.25	6.0	10.0	7.6	7.0
72	31.50	76.7	0.00	11.6	0.00	0.17	0.54	0.38	419	1.140	198	31.7	17.4	0.35	7.5	11.8	6.6	7.8
72	34.50	73.4							417	1.060	147	33.8	18.0	0.29	4.8	11.0	6.3	7.6

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
73	1.50	16.0	0.27	11.5	0.16	0.24	0.38	0.30	308	0.965	440	78.7	7.6	0.55	16.2	7.4	7.1	7.7
73	4.50	14.4	0.49	12.6	0.17	0.42	0.48	0.39	293	0.974	294	76.7	7.1	0.53	14.7	7.4	5.7	8.1
73	7.50	13.4	0.44	12.6	0.25	0.41	0.44	0.42	298	0.978	208	77.3	6.9	0.32	15.1	7.3	6.4	7.5
73	10.50	10.7							295	0.982	117	73.9	6.3	0.39	16.1	6.1	7.4	7.4
73	13.50	20.3	0.34	12.6	0.32	0.50	0.49	0.46	302	0.921	129	77.5	7.9	0.41	14.5	7.2	5.7	7.5
73	16.50	18.1	0.44	12.2	0.34	0.91	0.41	0.39	304	1.000	144	85.2	7.9	0.41	14.2	8.2	6.7	7.6
73	19.50	16.5	0.24	11.1	0.16	0.60	0.39	0.30	308	0.967	124	79.4	7.5	0.30	12.4	7.3	5.9	7.8
73	23.50	15.8	0.59	11.5	0.31	0.89	0.46	0.38	288	0.997	115	76.1	8.7	0.32	14.4	5.5	8.4	6.9

Table II-10. Core station analytical results, Stations 74 and 75.

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
74	1.50	3.4	0.54	12.8	0.13	0.31	0.30	0.32	233	0.851	575	56.1	3.5	0.19	10.6	4.8	3.4	8.4
74	4.50	3.3	0.56	13.3	0.09	0.33	0.40	0.41	230	0.762	471	48.9	3.4	0.22	12.0	4.7	4.4	7.6
74	7.50	3.3	0.54	13.0	0.23	0.41	0.42	0.32	230	0.763	428	52.2	3.5	0.17	14.7	5.6	5.2	7.8
74	10.50	3.4	0.55	13.4	0.24	0.41	0.37	0.34	229	0.776	367	51.0	3.7	0.12	8.9	6.1	4.3	7.7
74	13.50	3.2	0.73	12.9	0.23	0.52	0.39	0.36	230	0.798	235	54.4	3.5	0.18	8.8	5.3	4.7	7.8
74	16.00	3.0	0.55	11.4	0.06	0.43	0.26	0.08	232	0.853	230	58.3	5.9	0.28	15.5	10.6	5.8	8.2

CORE NO	DEPTH CM	FINES %	CO-60 PC/G	K-40 PC/G	CS-137 PC/G	EU-152 PC/G	TH-232 PC/G	U-238 PC/G	F UG/G	FE %	MN UG/G	ZN UG/G	CU UG/G	CD UG/G	PB UG/G	NI UG/G	CR UG/G	CO UG/G
75	5.50	96.5	1.02	10.6	0.80	1.38	0.60	0.38	416	1.180	217	195.0	31.0	1.96	29.3	10.6	8.5	8.7
75	12.50	91.0	1.74	10.8	0.95	2.04	0.76	0.39	403	1.190	237	188.0	28.8	2.05	25.9	10.9	10.7	8.2
75	15.50	92.7																
75	18.50	93.1	1.54	11.1	0.89	2.05	0.48	0.37	411	1.200	290	196.0	29.9	2.04	31.6	10.9	10.8	8.5
75	21.50	81.6	0.91	10.9	0.79	1.79	0.45	0.23										
75	24.50	77.0	1.37	12.0	0.85	1.44	0.73	0.29	375	1.040	230	142.0	24.0	1.40	23.9	10.6	8.1	8.2
75	27.50	80.4	1.35	9.8	0.71	1.28	0.30	0.22										
75	30.50	78.3	1.19	13.0	0.79	1.77	0.42	0.19	345	1.030	168	150.0	23.4	1.95	20.1	9.9	8.1	6.4
75	33.50	78.3	1.66	12.3	0.79	1.89	0.47	0.39										
75	36.50	97.7	1.61	10.9	0.96	1.45	0.44	0.25	427	1.250	177	191.0	28.0	1.71	25.4	11.2	9.8	7.3
75	39.50	98.8	1.68	11.2	1.10	2.07	0.55	0.30										
75	42.50	99.6	1.76	10.4	0.97	1.60	0.48	0.34	449	1.300	240	175.0	29.5	1.90	23.8	11.1	9.0	7.8
75	45.50	99.6	2.43	11.2	1.06	2.38	0.32	0.32										
75	48.50	99.2	2.08	9.8	0.98	2.39	0.41	0.10	429	1.310	179	211.0	30.4	2.27	25.3	11.2	12.2	7.3
75	51.50	98.8	1.95	9.1	1.14	2.92	0.36	0.36										
75	54.50	97.4	1.81	11.5	1.17	2.83	0.31	0.22	445	1.140	162	199.0	30.3	2.25	33.3	10.6	12.1	7.1

III

MINERALOGICAL IDENTIFICATION AND TOTAL SULFIDE ANALYSIS

OF SELECTED YOUNGS BAY SEDIMENT SAMPLES

Table III-1. Mineralogy of sand fraction for selected surface sediment samples. Heavy mineral analyses were made by point counting grain mounds of sand size fractions between 2.5 Φ and 3.5 Φ. Total analyses were made by point counting whole sand fraction between 0 and 4 Φ.

Minerals	Station/Sample Number						
	1	7	15	28	37	46	56
SILICA GROUP	30%	28%	32%	40%	48%	54%	40%
FELDSPARS	20%	27%	24%	23%	19%	18%	15%
Plagioclase	72	65	71	65	60	72	76
K-Feldspars	28	35	29	35	40	28	24
GLASS	2%	4%	3%	5%	-	-	6%
ROCK FRAGMENTS	10%	15%	12%	20%	11%	12%	15%
Basaltic	80	62	50	55	79	62	60
Metamorphic	5	8	15	20	4	8	14
Sedimentary	15	28	35	25	15	19	10
Acid Igneous	-	2	-	-	2	11	16
HEAVY MINERALS	15%	11%	9%	10%	20%	14%	23%
Magnetite	12	18	15	18	12	20	24
Hematite	14	10	11	5	4	1	2
Ilmenite	4	6	15	8	20	12	8
Leucoxene	8	4	7	6	2	8	10
Hornblende	14	20	21	22	18	20	16
Clinopyroxene	14	8	4	8	8	10	6
Enstatite	-	2	-	4	2	-	6
Hypersthene	20	22	18	16	20	18	12
Garnet	2	2	4	4	10	8	10
Zircon	4	4	8	4	4	2	4
Glauconite	-	-	-	2	-	-	1
Staurolite	4	2	1	3	-	1	1
Sphene	2	-	-	-	-	-	-
ORGANICS	23%	15%	20%	2%	2%	2%	1%

Total Analyses

Constituent	1	7	15	28	37	46	56
QUARTZ GROUP	15%	25%	25%	40%	75%	70%	75%
FELDSPARS	5%	5%	15%	20%	15%	15%	15%
MICAS	35%	30%	30%	15%	5%	<5%	<5%
HEAVIES	5%	10%	15%	15%	5%	>5%	>5%
SEDIMENTARY ROCK FRAGMENTS	10%	10%	5%	5%	-	5%	-
ORGANICS	30%	20%	10%	5%	-	-	-

APPENDICES

APPENDIX A

EQUIPMENT AND APPARATUS

PART I

A large-diameter corer was specially designed and fabricated for collecting samples for the Youngs Bay study. Requirements for the corer were:

1. The corer should provide large samples even over a small increment of depth.

2. Potential sources of contamination should not contact the samples.

3. Vertical distortion of the sediment section should be eliminated.

4. The corer should be operable either remotely from a vessel or by hand on tidal flats in both soft and sandy substrates.

The corer which satisfied these requirements is illustrated in Figure A-1. The barrel is made from standard six-inch aluminum irrigation pipe. Interchangeable barrels of any desired length are simply and inexpensively fabricated. When used with only the barrel and collar, the corer is readily operated by hand, much like a "clam gun" used by razor clam diggers. Cores up to 75 cm in length have been taken in this mode, although two fairly strong persons are needed to retract the loaded corer.

Alternatively, with the yoke attached, the corer can be lowered on a wire from a ship or small boat. Lead rings are placed on the long yoke shaft to provide weight when operated in this manner. The valve and O-ring seal after the corer is lowered and prevent the core from being lost. In muddy areas cores have been successfully retrieved from depths of 20 meters with no other core retainer. Sandy cores have not been collected successfully.

A third mode of operation is being developed within the School of Oceanography. Ms. Kathy Jefferts and Mr. Danil Hancock, who provided helpful advice and assistance in developing the corer, have adapted it for use by SCUBA divers. The normal valve is replaced by a "tee" fitted valve to which a riser line and a compressed air line are plumbed. Compressed air is introduced into the riser line via this tee and allowed to escape. The resultant "pumping" of water out of the core barrel causes the corer to be forced into the sediment by the external pressure. Retrieval is then accomplished from a winch-equipped boat.

Yoke

Valve   "o" ring
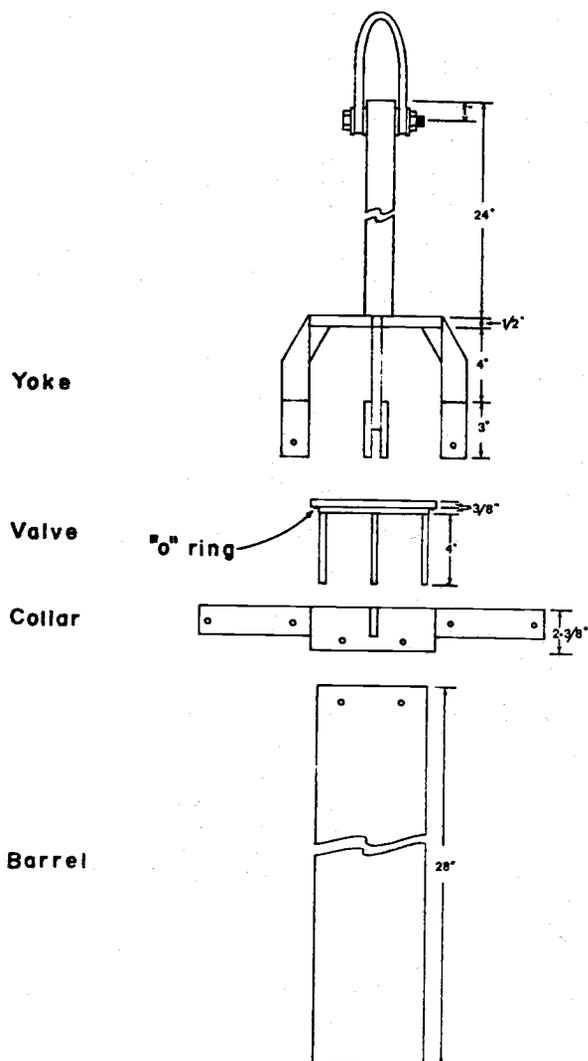
Collar

Barrel

Figure A-1.   Large-diameter coring device.

Once the core has been obtained the barrel, with core inside, and collar portion are situated on a vertical extruder and forced downward. As sections emerge from the top of the barrel they are trimmed to remove portions contaminated by the core barrel or particles carried downward as the barrel enters the sediment. Sections of desired thinknesses are sliced off and packaged.

Tests in both sandy and muddy substrates show that overall vertical distortion in taking cores is less than one centimeter for cores of 50-75 cm overall length. Examination of the corer before retraction reveals that this distortion is largely due to slumping during retraction rather than compression when the corer is forced into the sediment.

PART II

The pyrohydrolytic method of separating fluorine from minerals, or chemical compounds in general, is based on the thermodynamic principle which drives the following reaction to the right at high temperatures:

$$MF_{2n} + n\ H_2O \rightleftharpoons MO_n + 2nHF$$
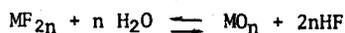
The position of equilibrium is shifted to the right because the standard entropy of two moles of hydrogen fluoride is about twice that of one mole of water (Newman, 1968). The rate of the above reaction is accelerated in the presence of oxides of vanadium, tungsten and bismuth which apparently act as catalysts. At temperatures of around 700°C the oxides melt and serve as a flux for the powdered sample.

The apparatus used for separation of fluorine from Youngs Bay sediment samples is shown in Appendix Figure A-2. This arrangement combines the methods described by Newman (1968) and Clements, Sergeant and Webb (1971). In the apparatus shown, compressed air passes first through a flow meter and then into a flask of heated water via a gas dispersion tube. The dispersion tube smooths the flow of air/steam through the system and prevents bumping from occurring in the steam generator. The air stream with entrained steam then passes through the reaction tube, over the sample boat and into the alkaline scrubber solution where the hydrogen fluoride from the sample is quantitatively removed from the air stream.

The condensate drain shown in Figure A-2 is a feature which was added to allow continuous, automatic removal of steam condensate which collects in the vertical rise of tubing and around the ball joint. The make-up water injection port allows additions of make-up water without opening the flask. These features substantially decrease the time required for sample processing.

The operating conditions used for the Youngs Bay samples were as follows:

air flow rate	40-50 ml/minute
still temperature	98-99°C
furnace temperature	700-710°C
reaction time	15 minutes

Recovery for the process was determined by analyzing known quantities of reagent grade sodium and calcium fluoride. Amounts recovered for these reagents were 97 ± 1% and 98 ± 1% respectively for triplicate determinations.
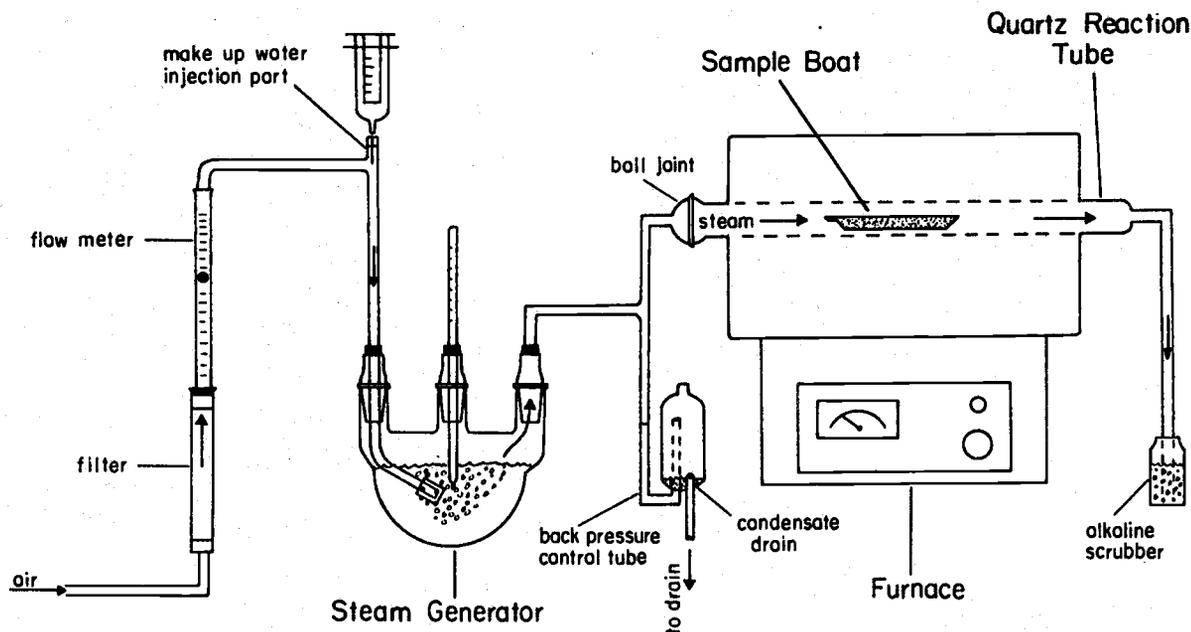
Figure A-2. Pyrohydrolytic apparatus.

Once the system was made operational a single technician could process and analyze 8-12 samples per day. A greater number of pyrohydrolytic trains would increase the throughput rate. The procedure is readily usable on samples having fluoride contents above 50 μg/g with precision of 1-2% and overall accuracy within 5-10% of the true value.

APPENDIX B

FLUORIDE REFERENCE STANDARDS

Table B-1. Results of analyses of known materials for total fluoride.

Material Analyzed	Amount Expected	Amount Found $(\overline{X} \pm S.E.M.)$	Reference
Geochemical Reference Standards		ppm	
Granite (G-2)	1290	1300 ± 10 (n = 3)	1
Diabase Basalt (W-1)	250	221 ± 7 (n = 3)	1
	222		2
Columbia River Basalt (CRB)	470	442 ± 3 (n = 3)	1, 3
Other Materials		percent	
NaF/Al$_2$O$_3$ mixture	0.441	0.431 ± .003 (n = 3)	4
CaF$_2$/Al$_2$O$_3$mixture	0.135	0.130 ± .001 (n = 4)	4
INTALCO Baghouse Composite (19 June 1974)	1.10	1.08 (n = 2)	5

1 Flanagan (1973)

2 Clements, Sergeant and Webb (1971)

3 Laul (1974), (OSU Radiation Center, secondary rock standard referenced to USGS BCR-1)

4 Known mixtures prepared from reagent grade sodium and calcium fluoride and pure aluminum oxide.

5 From INTALCO Analytical Lab, Mr. B.D. Rayborn, Supervisor.

REFERENCES

American Public Health Association. 1971. *Standard Methods for the Examination of Water and Wastewater*, 13th ed. APHA, Washington, D.C. 874 pp.

Beak Consultants, Inc. 1974. A Literature Review on the Effects of Fluorides on Aquatic Organisms and on the Biogeochemical Cycling of Fluorides in the Environment and a Theoretical Model of Fluoride Cycling in Youngs Bay Including the Impact due to AMAX Operations. Author, 1336 S.W. Second Avenue, Portland, Oregon 97201.

Bouma, Arnold H. and Niel F. Marshall. 1964. A method for obtaining and analyzing undisturbed oceanic sediment samples. *Marine Geol.* 2:81-99.

Brewer, P.G., D.W. Spencer and P.E. Wilkniss. 1970. Anomolous fluoride concentrations in the North Atlantic. *Deep-Sea Res.* 17:1-7.

Carpenter, Roy. 1969. Factors controlling the marine geochemistry of fluorine. *Geochimica et Cosmochimica Acta* 33:1153-1167.

Clements. R.L., G.A. Sergeant and P.J. Webb. 1971. The determination of fluorine in rocks and minerals by a pyrohydrolytic method. *Analyst* (London) 96:51-54.

Cutshall, N.H. 1975. Ecological Studies of Radioactivity in the Columbia River Estuary and Adjacent Pacific Ocean: Progress Report, 1 April 1974 through 31 March 1975 (RLO-2227-T12-54). School of Oceanography, Oregon State University, Corvallis, Oregon. 175 pp.

Farrow, N.D. and I.L. Larsen. 1974. A shallow water "mini-dredge." *Exposure: A Newsletter for Ocean Technologists* 2(5):10-11.

Fenchel, Tom. 1971. Studies on the decomposition of organic detritus derived from the turtle grass *Thalassia testudinum*. *Limnol. Oceanog.* 15(1):14-20.

Flanagan. F.J. 1973. 1972 values for international geochemical reference samples. *Geochimica et Cosmochimica Acta* 37:1189-1200.

Fleischer, Michael and W.O. Robinson. 1963. Some problems of the geochemistry of fluorine. Pp. 58-75 in D.M. Shaw, ed., *Studies in Analytical Geochemistry*, The Royal Soc. of Canada Special Publication #6. U.Toronto Press.

Forster, W.O. 1972. Radionuclide distribution in Columbia River and Adjacent Pacific Shelf sediments. Pp. 701-735 in A.T. Pruter and D.L. Alverson, eds., *The Columbia River Estuary and Adjacent Ocean Waters: Bioenvironmental Studies*. University of Washington Press, Seattle, Washington.

Foster, R.F. 1972. The history of Hanford and its contribution of radionuclides to the Columbia River. Pp. 3-18 in A.T. Pruter and D.L. Alverson, eds., *The Columbia River Estuary and Adjacent Ocean Waters: Bioenvironmental Studies*. University of Washington Press, Seattle, Washington.

Glenn, J.L. 1971. Relations Among Radionuclide Content and Physical, Chemical, and Mineral Characteristics of Columbia River Sediments. U.S. Geol. Surv., Water Resources Div., Open-file Report, Portland, Oregon.

Gorham, Eville and Dalway J. Swaine. 1965. The influence of oxidizing and reducing conditions upon the distribution of some elements in lake sediments. *Limnol. Oceanog.* 10(2):268-279.

Holton, R.L., R. Ulbricht and J. Morgan. (In Preparation) Biological Effects Data: Fluoride and Sulfur Dioxide. Final Report to Alumax Pacific Aluminum Corporation. School of Oceanography Reference 75-8. Oregon State University, Corvallis, Oregon.

Hubbell, D.W. and J.L. Glenn. 1971. Distribution of Radionuclides in Bottom Sediments of the Columbia River Estuary. U.S. Geol. Surv , Open-file Report, Portland, Oregon

INTALCO Analytical Lab. 1974. Personal Communication from Mr. B.D. Rayborn, Supervisor. Ferndale, Washington 98248.

Jackson, M.L. 1958. *Soil Chemical Analysis*. Prentice-Hall, Inc., Englewood Cliffs, N.J. 498 pp.

Jefferts, Katharine and Danil Hancock. 1975. Personal communication. School of Oceanography, Oregon State University, Corvallis, Oregon.

Jennings, C. David. 1966. Radioactivity of Sediments in the Columbia River Estuary. M.S. Thesis, Oregon State University. Corvallis, Oregon.

Kullenberg, B. and R. Sen Gupta. 1973. Fluoride in the Baltic. *Geochimica et Cosmochimica Acta* 37:1327-1337.

Laul, J.C. 1974. Personal communication. Radiation Center, Oregon State University, Corvallis, Oregon.

Mortimer, C.H. 1971. Chemical exchanges between sediments and water in the Great Lakes-speculations on probable regulatory mechanisms. *Limnol. Oceanog.* 16(2):387-404.

66

Newman, A.C.D. 1968. A simple apparatus for separating fluorine from alumino-silicates by pyrohydrolysis. *Analyst* (London) 93:827.

Pasternack, B.S. and N.H. Harley. 1971. Detection limits for radionuclides in the analysis of multi-component gamma-ray spectrometer data. *Nuclear Instruments and Methods* 91(3):533-540.

Robertson, D.E., W.B. Silker, J.C. Langford, M.R. Petersen and R.W. Perkins. 1973. Transport and depletion of radionuclides in the Columbia River. Pp. 141-155 in International Atomic Energy Agency, *Radioactive Contamination of the Environment*. (IAEA-SM-158) IAEA, Vienna.

Royse, Chester F. 1970. An Introduction to Sediment Analysis. Published by Author, Arizona State University, Tempe, Arizona. 180 numbered leaves.

Schonfeld, E. 1966. ALPHA: A computer program for the determination of radioisotopes by least squares resolution of the gamma-ray spectra, *Nuclear Instruments and Methods* 42:213-218.

Schonfeld, E., A.H. Kibbey and W. Davis, Jr. 1966. Determination of nuclide concentrations in solutions containing low levels of radioactivity by least squares resolution of the gamma-ray spectra. *Nuclear Instruments and Methods* 45:1-21.

Schubel, J.R. 1973. Geological sections in A.M. Andersen *et al.*, comp. and ed., Effects of Hurricane Agnes on the Environment and Organisms of Chesapeake Bay: Early Findings and Recommendations. A report for the U.S. Army Corps of Engineers, Philadelphia District. Chesapeake Bay Research Council, Chesapeake Bay Institute contribution 187, Johns Hopkins University, Baltimore, Maryland.

Varian Techtron Pty Limited. 1971. Instruction Manual for Varian Techtron Model AA-5 Atomic Absorption Spectrophotometer.

Warner, T.B. 1969. Fluoride in seawater: Measurement with lanthanum fluoride electrode. *Science* 165(3889):178-180.

Wiklander, Lambert. [1964] Cation and anion exchange phenomena. Pp. 163-205 in F.E. Bear, ed., *Chemistry of the Soil*. 2d ed. Reinhold Publishing Corporation, New York. (American Chemical Society Monograph Series, no. 160).

Young David R., Theodore C. Heesen, Deidre J. McDermott and Paul E. Smokler. 1974. Marine inputs of polychlorinated biphenyls and copper from vessel antifouling paints. TM 212, Southern California Coastal Water Research Project, El Segundo, California.