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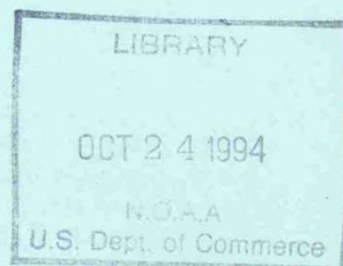
NOAA Technical Memorandum NMFS-NWFSC-16

National Status and Trends Program

National Benthic Surveillance Project: Pacific Coast

Analyses of Elements in Sediment and Tissue Cycles I to V (1984-88)

August 1994



U.S. DEPARTMENT OF COMMERCE
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National Marine Fisheries Service



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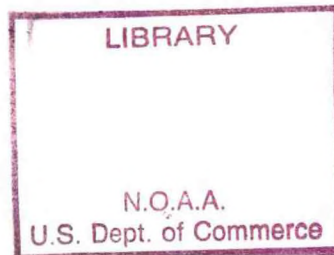
**National
Benthic Surveillance Project:
Pacific Coast**

**Analyses of Elements
in Sediment and Tissue
Cycles I to V (1984-88)**

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U.S. DEPARTMENT OF COMMERCE

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EXECUTIVE SUMMARY

This technical memorandum summarizes and interprets the results for the metal and metalloid (elements) contaminants for the first 5 years (1984-88) of the Pacific coast portion of the National Benthic Surveillance Project (NBSP). As a component of NOAA's National Status and Trends Program, the NBSP determines the levels of contaminant chemicals and prevalence of pathological lesions in bottom fish and relates them to contaminant levels in associated sediment. The levels of organic contaminants and the prevalence of presumptive pollution-related liver and kidney lesions are documented in other technical memorandums and publications.

Employing uniform sampling protocols and state-of-the-art analytical methods, an extensive database has been developed, which includes detailed information on the distribution of selected elemental contaminants. These include the toxic elements antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, tin, and zinc as well as the major elements aluminum, iron, manganese, and silicon in surficial sediments, liver tissues, and in stomach contents of selected fish. Of the 51 sites sampled in Washington, Oregon, California (West Coast), and Alaska, 27 were located in or near urban centers. (Pacific coast sites include all West Coast and Alaskan sites, even though three of the Alaskan sites are in the Arctic.) The locations of the sites in urban embayments were selected to be as representative as possible to assess inputs to the area from multiple sources; hence, the results from individual sites should not be viewed as representative of entire embayments because of limited sampling.

The overall findings from the NBSP for the years 1984-88 indicate that the highest concentrations of most sediment-associated toxic elements were present in the highly urbanized areas. Results of measured concentrations in sediment and analysis

of the nonurban sediment to derive natural background concentrations indicate that a number of urban sites contained elevated concentrations of metals and metalloids beyond what was expected for sediment that was relatively pristine. Based on the frequency of excess toxic element concentrations over background levels in sediment (excluding chromium and nickel), the sites most contaminated were Elliott Bay near Seattle; Oakland estuary in San Francisco Bay; San Pedro Outer Harbor, San Pedro Canyon, and west Santa Monica Bay in the Los Angeles area; and San Diego Bay (north and south), and National City in the San Diego area. Moderate contamination was found at Skagway (Alaska); Castro Creek, Oakland, Redwood City, and Hunters Point (all San Francisco Bay); and west Harbor Island (San Diego Bay). Often, sediment from a site that contained high concentrations of one toxic element also contained elevated concentrations of other toxic elements. The toxic elements found most often in excess of background concentrations in the sediments (>19 sites) were lead, nickel, and zinc. The next most frequent group of elevated metals consisted of copper, silver, and tin with excess values occurring for 11-13 of the sites. Another group of elements with less frequent overages (4-8 sites) consisted of antimony, arsenic, cadmium, chromium, mercury, and selenium. In terms of concentration, only copper, lead, nickel, and zinc were generally much higher (>2x) than their background or reference concentration. We conclude, by a weight of evidence argument, that those sites with concentrations of many elements elevated above background levels at all 3 stations for most years sampled are generally contaminated.

When correlations of elements in sediment were examined a few interesting patterns emerged. In West Coast urban sediments, copper, iron, lead, manganese, and zinc all correlated highly to each other. Iron and manganese are major components of sediment and their abundance is probably controlled in part by such factors as grain size and redox state. Copper, lead, and zinc were all correlated to each other probably due to common sources found in these industrialized areas. Based on correlations of

iron and manganese, it appears that the background geochemical makeup of the Alaskan sites is generally the same as the West Coast sites (Washington, Oregon, and California). One difference between the Alaskan sites and the West Coast urban sites is a weak correlation between copper and zinc at Alaskan sites, which may be due to differences in the source of these metals. Alaskan sites do however display a strong correlation between zinc and lead, indicating a common source, possibly mining operations.

An examination of a few sites for extractable metals with 1N hydrochloric acid was informative in that this study indicated some elements may be more labile, and hence probably more bioavailable than others. By subjecting a sediment to a weak acid extraction, labile metals will be released from the surface of sediment particles indicating which portion of the total concentration may be available for uptake by organisms. Some elements (cadmium, lead, nickel, and silver) exhibited high levels of extractability, even at some reference sites (particularly Bodega Bay). The results are preliminary, but high levels of extractability of these elements at reference sites may explain the observed high stomach contents and liver concentrations of these same elements in fish from some of these sites.

In general, total concentrations of elements in sediment did not correlate with those found in liver tissue of fish. One metal, mercury, did show some association that was strongest in flatfish (English sole, flathead sole, hornyhead turbot, and starry flounder). Mercury in fish generally occurs in the organic (methyl) form which will accumulate in tissues and may be abundant in liver, whereas other elements may be regulated by the fish and not accumulated. Correlations of concentrations of elements between sediment and stomach contents were stronger than the correlations between liver and sediment. This was especially evident for chromium, copper, lead, mercury, and nickel. The predominant prey for flatfish are sediment-dwelling invertebrates, which because of their close association with the benthos, probably better reflect

sediment concentrations than fish prey, especially if the predators were feeding recently in the area where sediment was collected.

The results of 5 years of monitoring the Pacific coast have demonstrated that concentrations of aromatic and chlorinated hydrocarbons in sediments were generally highly correlated with levels of these compounds or their derivatives in fish. This is generally not true for metals and metalloids for several reasons: 1) Most elements (essential and nonessential) are regulated by fish using various homeostatic control mechanisms; hence, even though in some cases these elements are taken up by the fish in proportion to their broad concentration range in the sediment, they may not accumulate in the tissues. 2) Many factors control the bioavailability of metals to organisms making determination of the form available for uptake difficult and correlations between tissue and sediment equivocal. Because sediments vary widely in these factors (e.g., grain size, organic (humic and fulvic acids) and inorganic (sulfides) ligands, redox state, cation exchange capacity, pH) and our understanding of their function is incomplete, it is not possible at this time to determine the portion of the total element concentration in sediment that is available for uptake. 3) Elements in sediment are commonly distributed in a nonhomogeneous fashion over small geographic areas, whereas fish are mobile over large areas; hence, accumulation of elements by fish within a site may be so variable that correlation analysis would be futile. 4) We examined only the liver, which may be the best single tissue to assess metal accumulation; however, other tissues such as kidney or brain may be more important for accumulation of certain elements. Future research will attempt to identify the various organismal compartments where metals and metalloids may accumulate.

We believe that some of the high concentrations of elements observed in the fish livers from reference areas may be due to the global spread of pollutants, especially at the West Coast sites. Because these reference sites are often sandy and

have low total organic carbon (TOC), low manganese and iron oxides, and other properties associated with metal accumulation in sediments, the contaminant metals found there are more concentrated on a unit weight basis when normalized to one of these properties (e.g., TOC or percent fine sediment). Because these characteristics may control bioavailability (or are correlated to the actual controlling parameter), these stations having sandy sediment may have a higher proportion of the element that is bioavailable, even when compared to stations with higher concentrations of that element and a greater percentage of fine particles. The extraction study with hydrochloric acid to assess labile (bioavailable) concentrations supports this observation for many elements. Also, the stomach contents of fish from these reference sites contained elevated concentrations of elements possibly due to the increased bioavailability to sediment-dwelling invertebrate prey. Additionally, we have noticed that for many fish species, the elements arsenic, cadmium, lead, mercury, nickel, and silver were higher in fish livers from reference sites along the West Coast (Washington, Oregon, and California), which was generally not true for flathead sole from the Alaskan reference site when compared to Alaskan urban sites. All of these incidental observations taken together point to possible increased contamination at our reference and nonurban areas.

When all fish species are considered together, several elements exhibit elevated concentrations in liver tissue. Elements such as copper, mercury, selenium, and silver display significant differences between various fish species and are often associated with high sediment concentrations. Most concentrations show a progression, decreasing from sediment to stomach contents to liver. The elements cadmium, mercury, and selenium show the opposite pattern in that the liver concentration is much higher than that found in sediment. Because selenium is an essential element and basically constant over all species, its high concentration in tissue in relation to sediment concentration is generally not of concern, although the levels that

distinguish normal from toxic are not well defined. Some elements (copper, silver, and zinc) show both patterns which may indicate inherent species differences or response to high sediment concentrations. Because cadmium and mercury are nonessential elements and they show a gradation of concentration, increasing from sediment to liver (with stomach contents intermediate in concentration), they appear to be bioaccumulated. Other nonessential elements which are lower in sediment than tissue, such as arsenic and silver, and which display species differences, may also be bioaccumulated.

Overall this survey has highlighted some important patterns of metal and metalloid abundance in sediment and fish along the Pacific Coast of the United States. Although this data set is relatively small for a monitoring program and covers only a few years, the results indicate some important trends which should be followed in subsequent studies. Many of the results, such as the association of mercury in flatfish, elevated sediment concentrations at urban sites, and the acid-extracted studies, generate new directions for research and testable hypotheses for clarification of mechanisms. Because of the inherent variability seen in sediment and tissue concentrations and the assumed complex nature of element speciation and control of bioavailability, future work highlighting the nature of chemical forms and their ability to be assimilated by organisms will go a long ways towards understanding the dynamic interactions between elements in water, sediment, and marine organisms.

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PREFACE

The National Benthic Surveillance Project (NBSP) was initiated in 1984 by NOAA as a component of the National Status and Trends Program, which was designed to assess and document the status of and long-term changes in the environmental quality of the Nation's coastal and estuarine waters. The NBSP is a cooperative effort between the National Marine Fisheries Service (NMFS) and the Coastal Monitoring and Bioeffects Assessment Division (CMBAD) of NOAA's National Ocean Services. The specific objectives of NBSP are

- Measurement of concentrations of chemical contaminants in sediment and in species of bottom-dwelling fish at selected sites in urban and nonurban embayments.
- Determination of the prevalence of diseases in these same fish species.
- Exploration of associations between contaminant concentrations in tissue and sediment and between tissue, sediment, and fish disease.
- Evaluation of spatial and temporal trends of contaminant concentrations and fish diseases.

During the early years, the NBSP involved the Northwest, Northeast, and Southeast Fisheries Science Centers of NMFS, using similar protocols and analytical instrumentation. Currently, the Northwest and Southeast Fisheries Science Centers conduct all investigations relating to toxic element contaminants. Sixty sites in embayments along the Atlantic, Gulf, and Pacific coasts, including Alaska, have been sampled on an annual basis since 1984, with each annual sampling referred to as a "cycle" (e.g., 1984 = Cycle I).

This technical memorandum summarizes the results of the toxic element contaminant analyses for the first 5 years of the Pacific coast portion of NBSP. It

reports on the concentrations measured in sediment (1984-88) and tissues of fish (1984-87) from sites along the Pacific coast of the United States. The sites are from various bays and estuaries in Alaska, Washington, Oregon, and California. Our intent was to report, compare, and evaluate concentrations of elements in sediment and tissue from these sites in order to determine the current status, and if any spatial and temporal trends existed. We performed statistical analyses with sediment concentrations from nonurban sites to determine natural background levels and evaluated each urban site's concentration with respect to these baseline levels. In our study we also performed correlations in order to search for spatial patterns of association between elements in a single matrix (e.g., in sediment between sites) and elements in two matrices (e.g., one element in sediment vs. tissue). We could not pursue temporal trend analysis because of the high variability found at sites and the limited number of time points for each site. Future reports may attempt to take subsequent data from this program, in addition to historical data, and attempt temporal trend analysis.

While this technical memorandum is an overview of findings as well as a detailed presentation and treatment of these data, it is not meant to comprehensively review the related marine pollution literature on this subject. However, pertinent references on the most significant aspects are included in discussions.

INTRODUCTION

The National Benthic Surveillance Project (NBSP) was designed to provide information on levels of chemical contaminants in surface sediments in coastal and estuarine areas, and the levels of these same contaminants in selected marine organisms. Information was also gathered on the prevalence of pollution-associated pathological conditions in representative bottom fish and the relationship of those abnormalities to environmental contaminants. Sediments serve as a repository for a large number of environmental contaminants, including those relatively water insoluble organic compounds and the many metals and metalloids that are released due to human activities (McCain et al. 1988, Flegal and Sañudo-Wilhelmy 1993, Hanson et al. 1993).

Among the goals of the NBSP are assessments of environmental quality of coastal areas in the United States. Such knowledge is essential for effective management of the Nation's highly productive coastal habitats and the resources they support. To date, the NBSP has been highly successful in generating an extensive overview of the present status of environmental quality in coastal waters. However, the variability of many of the measured parameters in urban areas points to the need for continued collection of chemical data to provide a sound statistical basis for the analyses of trends of pollutants in sediment and organisms.

Because of the broad geographical coverage of this study, it has been necessary to sample a limited number of sites in each location (e.g., a major embayment). Hence, the data from these individual sampling sites are not intended to describe the environmental status of entire embayments nor target "hot spots" of contamination. However, these data can be used to identify polluted sites in an embayment which can be investigated more intensively in the future. Included are descriptions of sampling

strategies and analytical methods, detailed presentations of the toxic element data, principal findings, and statistical evaluations.

High concentrations of elements in sediment are a potentially serious threat to organisms because of the possibility for uptake through diet or by respiratory exchange from water. Invertebrates, which serve as dietary sources to fish, have been shown to take up elements from sediment (Bryan 1985, Bryan and Langston 1992). High concentrations in invertebrate prey therefore have the potential to be a main route of exposure for fish. Other work has shown that sediments can be a source of dissolved elements to overlying water which facilitates exposure to water-column organisms (Flegal and Sañudo-Wilhelmy 1993). There are very few studies, if any, which examine the relative contribution of water, sediment, and diet to body burden accumulation in fish.

Levels of contaminants in bottom fish generally reflect chemical contamination over a wider geographical area than do levels in sediments or in sedentary organisms due to the mobility of the fish and their consequent ability to act as integrators of certain chemicals from a variety of sources. Bottom fish from a number of chemically contaminated coastal areas have been reported to have pathological conditions, including liver lesions such as neoplasms (McCain et al. 1977; Couch and Harshbarger 1985; Murchelano and Wolke 1985; Myers et al. 1987, 1993) and fin erosion (Wellings et al. 1976, Sherwood and Mearns 1977) which have been shown to be associated with chemical pollution. Thus, the presence of selected chemical contaminants and certain pathological conditions in fish have become useful indicators of environmental degradation. Cause-and-effect relationships between metal contaminants and biological function in various taxa have been inferred from field surveys (for a review see Langston 1990), and further substantiated by long-term laboratory studies (for a review of fish literature see Sorensen 1991).

This technical memorandum summarizes and interprets the results for the first 5 years of the Pacific coast portion of NBSP. It builds upon previous reports and technical memorandums (Varanasi et al. 1988, 1989a), and it complements similar reports on organic chemical contaminants (McCain et al. 1994) and fish pathology (Myers et al. 1993).

METHODS

Site Selection and Descriptions

The selection of sites for inclusion in the monitoring project was based on the following site characteristics:

- Availability of bottom-feeding fish
- Subtidal, sedimentary-depositional zone
- Site away from point sources or authorized dumpsites
- Site not subject to dredging, scouring, or slumping.

Each site consisted of three stations, generally less than 0.4 km apart, which were selected to represent the given site. However, the samples were not intended to characterize the entire embayment (e.g., San Diego Bay or Elliott Bay) in which the site was located.

Some sites were specifically located in areas that integrated inputs from multiple sources but were not directly adjacent to any known point sources. The reference and nonurban sites were in areas remote from known local inputs, although they may reflect a wider spread of regional background contamination (i.e., global spread).

Samples were collected from 51 Pacific coast sites, with complete sets of samples collected from 37 of these sites (Table 1). The 14 remaining sites were sampled for exploratory purposes only. The locations of these sampling sites, the

types of samples collected, the frequency of sampling, and the site abbreviations are presented in Table 1. In this technical memorandum, we consider the Pacific coast to include all sites, including Alaska, and the West Coast to include only those sites in Washington, Oregon, and California. (Three sites were actually from the Arctic but are considered with the Pacific coast sites for simplicity.) Figures 1 and 2 illustrate the location of the sampling sites. Of the 37 complete sites, 27 of these sites were in or near urban embayments, and the remaining 10 sites were in nonurban embayments, four of which served as reference (comparison) sites. The reference sites were selected for minimal contamination while having the same fish species as obtained at the urban sites. Examination of these reference area sediments and fish thus assisted in interpreting the significance of elevated concentrations that were observed in the respective sediments and fish from the urban sites.

Following is a brief description of each sampling site.

Alaska

The **Oliktok Point** site is in shallow water west of Oliktok Point which is the eastern edge of the Colville River delta and near one of the North Slope sealift barge staging areas in the Beaufort Sea.

The **Endicott Field** site is located west of an earthen causeway serving petroleum production facilities at Endeavor Island in the Beaufort Sea north of the Prudhoe Bay oil field.

The **Chukchi Sea** site is offshore of the location near Kotzebue where a major ore (lead and zinc) transshipment facility will be constructed for the world-class Red Dog Mine.

The **Port Moller** site is in western Bristol Bay just off the entrance to the community of Port Moller which has been recommended for development as a support base for southern Bering Sea petroleum exploration, development, and production.

The **Dutch Harbor** site is near a major support base for an international bottom-fish fleet which includes major container loading piers and small shipyards built on the site of a large World War II naval facility.

The **Kamishak Bay** site is located south of the active Augustine Island volcano and is an important commercial fishing and integration site for Cook Inlet, a major marine petroleum production area.

The **Port Valdez** site is along the northern side of a narrow fjord at the head of Prince William Sound which serves as the marine terminal for the Trans-Alaska Pipeline System and its associated ballast water treatment facility. The new town of Valdez on the north side has developed a small boat facility and receives commercial freight traffic.

The **Lutak Inlet** site (near Skagway) is a reference site for the Alaskan sites. It is located between the ports of Haines and Skagway in an arm off Lynn Canal.

The **Nahku Bay** site is in an embayment about 2 km north of the port of Skagway near the head of Taiya Inlet.

The **Skagway** site is in the harbor area at the port of Skagway adjacent to the ore loading docks which recently have seen a shift from mineral and commercial commerce to large cruiseship operations.

The **Boca de Quadra** site is in a deep fjord once selected as a potential location for submarine mine tailings discharge from the proposed world-class Quartz Hill molybdenum mine.

Washington

The **Elliott Bay** site is in a major commercial shipping harbor of the port of Seattle north of Harbor Island between the West and East Waterways that constitute the mouth of the Duwamish River.

The **Commencement Bay** site is in the major commercial shipping harbor of the Port of Tacoma located between the mouths of the heavily industrialized Hylebos and Blair Waterways.

The **Nisqually Reach** site is the reference site located off the mouth of the forest- and rural-bordered Nisqually River in southern Puget Sound.

The **Columbia River Estuary** site is north of the town of Astoria, Oregon between Desdemona Sands and the Washington shore representing a dynamic but depositional environment of the lower Columbia River.

Oregon

The **Youngs Bay** exploratory site is a small tidal estuary immediately west of Astoria impacted by earlier fish processing, lumbering, and coal gas processing facilities.

The **Coos Bay** site represents three stations along the estuarine portions of the Coos River from the shipping port of Coos Bay, with its lumber related industries and light manufacturing, to its northern reach off the town of North Bend.

California

The **Humboldt Bay** exploratory site covers the estuary from South Bay north to Arcata Bay, including the Mad River Slough and the Arcata and Eureka Channels.

The **Bodega Bay** reference site is in the bight between Bodega Rock and the Doran Beach shoreline. This rural area is experiencing an accelerated population growth; however, no known pollution point sources exist, except for residential inputs.

The **Farallon Islands** exploratory site is approximately 30 miles west of San Francisco Bay and just southwest of Southeast Farallon Island.

The **Islais Creek** exploratory site is a heavily industrialized, partially-dredged ship channel in southern San Francisco Bay which receives a combined sewer overflow discharge (Chapman et al. 1986).

The **Hunters Point** site is located along the edge of the tidal flats south of the site of the former San Francisco Naval Shipyard and east of Candlestick Park where it receives the shoreside discharges from the communities and industries along the west side of San Francisco Bay. Stations are located on both the tidal flats (less than 1.5 m depth) and in the undredged channel (greater than 6 m).

The **Redwood City** site is at the southern extremity of San Francisco Bay in the undredged channel off the mouth of Redwood Creek; this location integrates the surface discharges from the communities around San Jose and Silicon Valley.

The **Oakland Estuary** site, sampled in Cycles IV and V, is the restricted partially-dredged Inner Harbor channel between Oakland and Alameda near Coast Guard Island which represented the contaminant impacts from historical heavy and light industry, wharfs, docks, and marinas, and urban development.

The **Oakland** site, sampled in the first cycle, is immediately west of the Alameda Naval Air Station south of the Oakland Inner Harbor entrance.

The **Southampton Shoal** site is just east of the shipping channel to upper San Francisco and San Pablo Bays located about equidistant between the refinery town of Richmond and Angel Island. This location is influenced on the surface by outflowing fresh water from the Sacramento and San Joaquin River systems and at depth by upwelling of oceanic water entering through the Golden Gate.

The **Castro Creek** site is a shallow tidal estuary with known industrial and refinery contamination northwest of Point San Pablo on the southern entrance to San Pablo Bay.

The **San Pablo Bay** site is in eastern San Pablo Bay south of Mare Island Naval Shipyard where Carquinez Strait discharges the Sacramento and San Joaquin Rivers

and is locally impacted by agriculture, urbanization, shipping, and petroleum refining.

The **Moss Landing** exploratory site is at the head of the submarine Monterey Canyon off Moss Landing where the primary potential impacts are a power plant, a marina, and local agricultural runoff.

The **Monterey Bay** site is northeast of Monterey in open water with only modest localized residential and agricultural impacts now that the once-thriving sardine canneries have closed.

The **Estero Bay** exploratory site on the central California coast is offshore southwest of the entrance to Morro Bay beyond the 10 m depth contour. English (*Pleuronectes vetulus*) and petrale sole (*Eopsetta jordani*) were found here but no white croaker (*Genyonemus lineatus*). A limited sampling effort more inshore during Cycle I was unsuccessful.

The **San Luis Obispo** exploratory site is in open water at 50 m depths due south of Point San Luis. White croaker were found here but no English sole were caught. This and the previous site were investigated as potential central California reference sites.

The **Channel Islands** site, an exploratory site between Santa Cruz and Santa Rosa Islands south of Santa Barbara, was investigated as a possible reference site but was found to have insufficient target fish species.

The **West Santa Monica** site is in deep water (>50 m) north of the Hyperion sewage discharge.

The **East Santa Monica** site is off Manhattan Beach between the El Segundo power plants and the Redondo Beach marina.

The **San Pedro Canyon** site sampled during Cycle I is in open water south of the San Pedro breakwater.

The **San Pedro Outer Harbor** site is located in the undredged outer harbor between the San Pedro breakwater and the main section of Los Angeles Harbor and is impacted by heavy industry, shipbuilding and repair, fishing and recreational boating, shipping, petroleum production and refining, and urban runoff.

The **Long Beach** site is in the main undredged Long Beach Harbor approach (one of the largest ports on the West Coast) with similar types of contaminant inputs as for the San Pedro Outer Harbor site. The Long Beach Naval Shipyard and Naval Station is located between this and the previous site.

The **Cerritos Channel** site is located in the east basin turning area, which is just off the main channel in San Pedro Bay.

The **Seal Beach** site sampled in Cycle I is nearshore between the breakwater to Alamitos Bay and the Island Chaffe petroleum production platform.

The **Dana Point** reference site is in open water immediately off the Dana Point Marina breakwater. No local pollution point sources (besides occasional recreational boating discharges) are known for this area; however, the southward flowing longshore current may carry materials from the Los Angeles area.

The **Dana Point Inside** site is an exploratory site inside the breakwater at Dana Point and close to a large marina.

The **Oceanside** exploratory open-water site is 30 miles north of San Diego and was sampled in Cycle IV. This sampling was an unsuccessful attempt to obtain black croaker (*Cheilotrema saturnum*) for reference comparison to the San Diego sites.

The **Outside Mission Bay** site (Cycle V) offshore of Pacific Beach in the San Diego area was a more successful site for obtaining black croaker.

The **Outside San Diego** site is in open water west of Silver Strand Beach (Coronado) and was to represent an integration area immediately outside the San Diego Bay entrance; however, adequate numbers of target fish species were not available.

The **North San Diego** site is an urban site south of Lindbergh Field off the east end of Harbor Island in the northeast corner of north San Diego Bay.

The **South San Diego** site is outside and northeast of the main dredged channel, immediately adjacent to the piers largely devoted to shipbuilding and repair, between the Coronado Bridge and the 28th Street Pier (approximate northern boundary of the San Diego Naval Station).

The **National City** site is along the west edge of the channel in south San Diego Bay opposite the Seventh Street Channel. Stations included both tidal flats (<4 m) and channel (>10 m).

The **Shelter Island** site is north of the dredged channel adjacent to Shelter Island in northwestern San Diego Bay.

The **West Harbor Island** site is immediately adjacent to the western end of Shelter Island in north San Diego Bay in proximity to numerous recreational boating marinas.

Field Sampling

The sites along the coasts of Washington, Oregon, and California were sampled using the NOAA ship *McArthur* (S-330), the research vessel (R/V) *Harold W. Streeter* or the R/V *Sea Otter*. The NOAA ship *Miller Freeman* (R-223) and the U.S. Fish and Wildlife Service vessel *Curlew* were used in Alaska. To maximize comparability of data over space and time, standardized collection gear and sampling methods were used. All vessels were equipped with navigational equipment to determine the location (latitude/longitude) of all the sampling stations. Sampling was conducted during a May-September field season each year. We collected sediment and fish in each of the 5 years covered by this technical memorandum, but report fish tissue concentrations only for the first four years (1984 through 1987). Sediment

concentrations were determined for each year; however, fish tissues were not analyzed for cycle 5 (1988).

At each sampling site, surface sediments (top 2-3 cm) were collected with either a modified Van Veen grab sampler (0.1 m^2), Smith-McIntyre grab (0.1 m^2), or a box corer (0.3 m^2). Three grabs were taken at each of three stations and three cores (15 to 19 cm x 3 cm diameter plastic tubes) were taken from each grab (total of 27 core tubes per site). Cores were put on ice and frozen at -20°C within four hours for future analyses.

Bottom-dwelling fish were collected with an otter trawl (7.5 m opening, 10.8 m total length, 3.8 cm-mesh in the body of the net, and 0.64 cm-mesh in the liner at the cod end, none of which was chemically treated) using a trawl time of 5-15 minutes. Fish of a minimum size (generally $> 15 \text{ cm}$ in length) were randomly selected from each haul and assigned a unique identification number. These fish were kept alive (to prevent autolysis of tissues) until necropsies were performed. The necropsy procedure for each fish involved a) weighing, b) measuring, c) removing otoliths for age determination, and d) excision of the liver and stomach contents for elemental analysis. Approximately 30 fish per target species (Table 2a) were necropsied at each site. The liver tissue was placed in a separate, acid-rinsed plastic vial and frozen at -20°C for analyses at a later time. The remainder of the fish tissues were reserved for organic chemistry, histopathology, and bioindicator analyses. The total contents of stomachs from at least 10 fish per target species at several sites (Table 1) were removed and composited in an acid-rinsed glass jar and frozen for chemical analyses.

Laboratory Analyses

Analysis of Elements in Sediment and Tissue

The particle size characteristics and total organic carbon (TOC) content of sediment samples were determined by personnel of the Southeast Fisheries Science Center, National Marine Fisheries Service (NMFS).

For elemental analysis in sediment, one core tube from each grab was thawed at room temperature and the excess water drained from the bottom (ca. 30 min.). The top 2 cm of the sediment core was extruded with the outermost surface layer of sediment in contact with the plastic core tube being discarded and the wet sediment from each grab oven dried at 85° C. Equal weights of the three dried samples from replicate cores were composited into a single sample for each individual station. Hence, we analyzed three station composites (three grabs per station) for a total of three separate analyses per site. The sediment was subjected to a total acid digestion with 6 mL of hydrofluoric acid (HF) and 2 mL of aqua regia (hydrochloric acid (HCl): nitric acid (HNO₃) 3:1) (HF, HCl and HNO₃, ultrapure, Seastar Chemicals, Sidney, British Columbia). The sediment/acid mixture was sealed in a Teflon vial and heated in a stainless steel Parr bomb at 120° C for 36-48 hours. The digestate was quantitatively transferred to a 50 mL volumetric flask and brought to volume using saturated boric acid (H₃BO₃ (Puratronic), Aesar/Johnson Matthey, Ward Hill, Massachusetts).

Recent work has shown that fish length can have a strong influence on the concentration of some elements in tissues (Evans et al. 1993); therefore, we sampled the livers of the three largest female fish to give a total of three analyses per site (Table 2b). The fish lengths from most sites were relatively close to the mean with little variation; however, high variation occurred in starry flounder because occasionally we would catch a very large individual.

For analysis of elements in fish tissue, livers from three individual female fish were completely digested with HNO_3 (7 mL acid for ≈ 0.25 g of tissue, dry weight). The liver/acid mixture was sealed in a Teflon vial, placed on top of a drying oven set at 110°C and left overnight. After this initial digestion, the sealed Teflon vials were placed inside another container and were subjected to a three-step microwave digestion (1 min. at 50% power, short pause, 4 min. at 50% power, 15-30 min. pause, and finally 4 min. at 50% power). When the digestate had cooled, a total of 3 mL of hydrogen peroxide (H_2O_2) (ultrapure, Fluka Chemical, Ronkondoma, New York) was added in increments of 1 mL over three 1-hour time intervals. The final digestate was brought to 25 mL volume using Milli-Q water (Millipore Corporation, Bedford, Massachusetts).

Stomach contents samples for each site were obtained from a composite of 10 fish. Analysis of elements in stomach contents was performed with a protocol which combined the sediment and tissue digestion procedures. First, 0.25 g dry weight of stomach contents were digested according to the liver protocol. Then 6 mL of HF and 1 mL of HCl were added to each vial. The sealed vials were then placed in the stainless steel Parr bombs and heated at 120°C for 48 hours. After cooling the digestate was brought to 50 mL volume using saturated H_3BO_3 .

The analyses of all three sample types were conducted via the techniques of atomic absorption spectroscopy (AAS): flame, heated graphite atomization, hydride generation, and cold vapor for mercury (see Table 3). Initially a Perkin-Elmer Model 5000 atomic absorption spectrophotometer, equipped with deuterium background correction, was used. For later cycles, some elements were analyzed with a Perkin-Elmer Model 5100 atomic absorption spectrophotometer equipped with Zeeman background correction. Instrument calibration curves were made with a minimum of five concentrations using single-element standards prepared by diluting 10 mg/mL of certified standard solutions (National Institute of Standards and Technology (NIST)).

Computerized least squares linear or quadratic fit was determined for all samples falling within the end points of the calibration curves. All elemental concentrations in sediment and tissue have been reported based on a dry weight basis. Additional details on sample preparation and AAS analysis can be found in Robisch and Clark (1993).

Quantification was achieved by using solution blanks and certified reference materials (CRM) provided by the National Research Council of Canada (NRCC), Ottawa, Ontario, Canada; the U.S. Environmental Protection Agency (EPA), Cincinnati, Ohio; and the National Institute of Standards and Technology, Gaithersburg, Maryland. These materials are called standard reference materials (SRMs) by NIST. The CRMs included both marine sediments and various fish and invertebrate tissues and were processed in the laboratory alongside our field samples. These reference materials were used to correct our sample concentrations for loss or enhancement caused by sample preparation and digestion or instrument interferences. These corrections were accomplished by a response factor (RF) which was our measured concentration of the CRM divided by the published certified value. These RF were applied to all measured values.

For tissue, we analyzed the CRMs DORM-1, DOLT-1, and TORT-1 (NRCC), 1566 and Bovine liver (NIST), and "Trace Metals in Fish" (EPA). For sediments we analyzed the CRMs MESS-1, BCSS-1, and PACS-1 (NRCC), in addition to 1645 and 1646 (NIST).

Extractable Elements

A select number of sediments from the 1989 (Cycle VI) sampling effort for NBSP were subjected to acid leaching in order to assess the difference between total and labile concentrations. (These total concentrations were not part of other statistical analyses in this technical memorandum.) We attempted to test the hypothesis that the concentration of an element in the weak-acid extractable fraction, as a percentage of

the total concentration found in the bulk sediment, may indicate excess amounts due to urban inputs when compared to background concentrations. Katz and Kaplan (1981) propose that leachable metals may be an indication of anthropogenic input because the excess metal would be associated with the exterior of the sediment particle and would not be a part of the lattice structure which could be released only through harsh acid digestion. This is exclusive of metal particles from human activities which would not yield high concentrations of leachable metals because of their refractory nature. The amount associated with the exterior of sediment particles may be available for bioaccumulation either through uptake from water (of that portion in equilibrium with surrounding water (overlying or interstitial water)) or available to organisms from ingested sediment.

Sediment samples from all three stations (A, B, and C) at seven sites (plus two reference sites; Bodega Bay and Dana Point) were analyzed. We took about 5 g of wet sediment, added 50 mL of HCl to make the final solution of 1 N, agitated the slurry for 3 hours, and allowed it to stand for 24 hours. The pH was measured after 24 hours of standing and was always 0.3 to 0.9. Solutions were analyzed by AAS, corrected for matrix effects, and related to the sediment concentrations in micrograms per gram dry weight ($\mu\text{g/g}$ dry wt).

Statistical Analyses

A variety of statistical methods were used to analyze the data from the chemical analyses in order to present the large amount of data in a graphical format. This was done to facilitate interpretation and allow us a way to evaluate possible interrelationships among the concentrations of the elements in sediments and fish.

Screening of Chemical Data for Accuracy

In accordance with Little and Smith (1987), chemical data were initially examined using graphical methods for multivariate outlier detection. Outlying samples were located and identified using three-dimensional scatterplots (see Huber 1987), and the accuracy of their constituent values was confirmed by reference to original records. Where analytical errors were identified, original data were recalculated. Our data contained only a few values (2-3% of the total) below their respective detection limits; hence, we did not use any censored-data algorithms in estimation of statistical parameters. Those concentrations below their detection limit were treated as equal to the detection limit value.

Display Techniques

Calculation of comparison intervals in graphs—In order to compare the concentrations of elemental contaminants in sediment and fish tissues at sites along the entire Pacific coast, comparison interval graphs were constructed. For comparison of elements over sites and over species, we used GT2 plots and floating-bar plots which are modified GT2 plots (Landahl 1994). Below is a general discussion on GT2 plots followed by specific information for each type of plot.

While it is relatively easy to calculate 95% confidence intervals for mean concentrations based on the number of samples (n) and the variability for each mean, it is not as easy to infer whether two means from a group of means are the same or different by examining plots of confidence intervals. Instead, a statistical technique, similar to the confidence interval but more closely related to an analysis of variance, was employed for graphical comparisons. Therefore, we generated GT2 plots which involved calculating and plotting a "comparison interval" (Gabriel 1978, Sokal and Rohlf 1981) for each mean, based on:

- the number of samples for that mean,

- the variability about that mean, and
- the number of means being compared.

Hence, mean contaminant concentrations and comparison intervals for each site can be calculated and plotted in order of decreasing contamination. The advantageous property of these comparison intervals is that they overlap when the means are not significantly different. In the remainder of this report, significant differences among chemical concentrations were determined with a criterion of $\alpha \leq 0.05$, unless noted otherwise.

When sample sizes for the means of interest are unequal, it is desirable to use the GT2 method for calculating the comparison intervals. Also, the span of a comparison interval depends on the within-group variability in the entire data set and on the number of samples in each category. For a particular data set, categories with the same number of samples have identical comparison interval spans regardless of their individual means and standard deviations.

When data for only two stations at a site are available, the comparison interval will of necessity be quite large for the same reason that a confidence interval would be. That is, the value of the t-statistic is large, because of the uncertainty of variability about the mean when $n = 2$. When $n = 1$, the comparison interval is indeterminate. Thus, the method was used only when sample data were available for at least two stations at a site.

Floating-bar plots--Some of the data have been presented as a modified boxplot showing the arithmetic mean (thick horizontal bar) and one standard deviation (top and bottom of box). The horizontal bar on the vertical line ("whisker") represents the geometric mean of the data and the length of the whisker is the 95% comparison interval calculated by the GT2 method using $\ln(x+1)$ transformed data values (Landahl 1994). The position of the horizontal bar on the whisker gives some

indication of the distribution of the data around the geometric mean. The number of analyses are listed (usually above) for each site and the bottom of the horizontal gray line across most figures is the upper comparison interval (UCI) for the contiguous West Coast reference site (either Bodega Bay, Dana Point, or Nisqually Reach) having the highest concentration for the element plotted. On these plots, two sites are significantly different when their comparison intervals (whiskers) do not overlap. The numbers for these plots were back transformed to arithmetic values for plotting and hence have asymmetrical comparison whiskers.

GT2 plots—GT2 plots were constructed for the figures comparing tissue, sediment, and stomach contents. The top of each bar is the mean concentration for an element over all years and sites. The vertical whisker is the comparison interval. Nonoverlapping bars indicate significantly different means at $\alpha \leq 0.05$. For these GT2 plots we used \log_{10} values for calculation of the mean and comparison intervals and plotted them as log values. These plots were constructed with log values because we were mainly interested in comparisons, whereas in the floating-bar plots we were interested in showing the different concentrations for each site in addition to making comparisons. The symmetrical comparison interval whiskers about the mean also allowed easier judgment of variability among compartments. The left ordinate shows the plotted log values in parts per million ($\mu\text{g/g}$) and the right ordinate on each plot shows the arithmetic equivalent.

Data Analysis

Determining background sediment concentrations—To determine if an element's abundance was correlated with percent fine sediment we plotted each element from all reference sites (except Nisqually Reach) plus all nonurban sites and a few exploratory sites that were judged acceptable (11 sites total) against the percent fines (percent of clay plus silt; i.e., $< 63 \mu\text{m}$ particle diameter). This is similar to

Hanson et al. (1993) who used aluminum as a comparison variable; however, we tested every element separately with percent aluminum and found only one (antimony) was significantly correlated.

Many elements varied significantly with percent fines including iron and manganese. For those elements (copper, selenium, and zinc) that displayed a strong correlation to percent fines, a linear regression equation was developed with log concentrations in order to express the relationship and to characterize the amount of that element that would be expected given variable levels of percent fine sediment. For these elements a line was drawn above and parallel to the line given by the regression equation in order to include all reference sites. This line, extracted from the regression equation, was greater than two times the upper 95% confidence interval for the regression. For those elements which showed no correlation to percent fines, a horizontal line was drawn which was above all reference stations. If the concentration of an element from an urban station was found to be above this line, we considered that station to be contaminated, that is, above the background concentration that was expected for that element in a relatively pristine, nonurban area. If the concentration of an element was above this baseline concentration for a station in any given year, it was included in a table which lists sites by elements and their background concentration. If a site contained more than one station measurement above the baseline, its mean and standard deviation (sd) was reported, along with the number of measured values (3 stations analyzed/site/year). The total number of measurements is variable for each site and can be obtained from Figures 3-8.

Methods for correlations—Product-moment (Pearson) correlation coefficients between elements in the different matrices (sediment and tissue) over sites were determined in order to discover which elements, if any, were highly correlated. For example, correlation coefficients were determined for all pair combinations ($n=153$) of

the 16 elements measured in all sediment samples plus percent fines and TOC. These coefficients are displayed in tables and the significant correlations are highlighted bold. This information was used to assess sources of elements and geochemical associations. Significant correlations were determined by setting $\alpha = 0.05$ and then correcting for the number of comparisons to allow for comparisonwise error ($\alpha + \text{number of comparisons}$) (Milliken and Johnson 1984). For the example above of $n=153$, the α level for significance became 0.00033.

Cluster analysis was performed by the following method. First a product-moment correlation (r) matrix was calculated for all \log_{10} transformed elements of interest (usually 16 elements) and for selected cases (e.g., Alaska only or reference sites only). The few missing values were replaced by mean substitution, which had little or no effect on the correlations. This matrix was then used to calculate a similarity matrix based on $1 - r$, which was used as the distance metric in the clustering calculations. From this, a hierarchical tree was constructed using single linkage amalgamation. The clusters are groups of elements joined by nodes and the closer the node is to vertical axis (elements) the more closely related the elements are in that cluster. The horizontal axis is scaled in percentage of the maximum to minimum distance that the clusters are joined $(\text{link}/\text{max}) \cdot 100$. Groups of elements were made from the dendrogram based on similarity by selecting those which fell below the 40% value which generally corresponds to a similarity (r) of approximately 0.60.

Due to the large variability in concentration found at the stations within a site and the incomplete sampling scheme (few sampling years for a given site), trend analysis was not attempted. We felt that the incomplete database would not produce reliable patterns for determination of temporal trends. When additional data are collected, we may have enough data points to test hypotheses regarding such trends.

RESULTS AND DISCUSSION

The objectives of this section are to

- present in detail the results of element analyses in sediment and tissue and discuss the significance of the results with respect to similar studies,
- present an analysis of baseline and excess element concentrations in sediments along with correlations to highlight patterns of occurrence, and
- evaluate statistical relationships between concentrations of elements in sediment and those in fish liver and stomach contents.

Because many of the previous studies involved sampling and analytical techniques which were different from those used in the NBSP, only general comparisons are possible between this study and the previous studies. Also, we did not make extensive comparisons of our fish tissue data with other published literature because we felt very little information would be gained from such an exercise. Because the tissue concentrations are dependent on exposure concentration it would be futile to compare our data to those in studies without detailed information about exposure concentrations. Due to the high variability observed in fish tissues, reporting maximum and minimum tissue concentrations has little meaning without corresponding exposure concentrations. There are very few field studies such as this one which have a large database for both tissue and sediment.

Concentrations of Selected Elements in Sediments

Selected metal and metalloid contaminants are commonly used to assess impacts of human activities on urban embayments. Sediments serve as repositories for these contaminants and integrate variable amounts found in the water column. As stated in the Methods section, significant differences among means were determined

with a criterion of $\alpha \leq 0.05$; hence, on the floating-bar plots the range of the comparison intervals must be mutually exclusive for statistically significant differences. Where several reference sites are utilized, the statistical comparison is always made with the reference site with the highest concentration the analyte being discussed. Lutak Inlet (Alaska) was not used for reference comparison because it was not sampled every year as were the other reference sites. All element concentrations are based on dry weight measurements of the sediments and all means and standard deviations are reported as mean (sd).

Antimony, Arsenic, and Cadmium

Floating-bar plot presentations of the antimony (Sb), arsenic (As), and cadmium (Cd) in sediments are given in Figure 3.

Antimony—Mean antimony concentrations varied by about an order of magnitude between 0.18 and 1.5 $\mu\text{g/g}$, with all sites overlapping with the maximum reference site (Nisqually Reach UCI: 1.14 $\mu\text{g/g}$) (Fig. 3). If the next highest reference site (Dana Point) was used, only one site (Elliott Bay) would be significantly higher than the reference upper comparison interval. The exploratory sites with single determinations grouped towards the lower concentrations: Farallon Islands (0.61 $\mu\text{g/g}$), San Luis Obispo (0.49 $\mu\text{g/g}$), Dana Point Inside (0.44 $\mu\text{g/g}$), outside Mission Bay (0.42 $\mu\text{g/g}$), and Estero Bay (0.32 $\mu\text{g/g}$).

Although antimony is very toxic to mammals and is subject to controls to protect public health, very little is known about its abundance in most Pacific coast estuarine and coastal waters. One major anthropogenic source of antimony is lead smelting (Furness and Rainbow 1990). With a history of lead smelting in the Pacific Northwest, perhaps it is not surprising that the Elliott Bay and Commencement Bay sites have mean concentrations grouped in the highest five sites on Figure 3.

Chapman et al. (1986) reported a limit of detection (LOD) of 50 $\mu\text{g/g}$ which was considerably higher than our LOD of 0.1 $\mu\text{g/g}$ and any of the concentrations we determined for the San Francisco Bay region (maximum at Redwood City at 0.85 (0.11) $\mu\text{g/g}$ and minimum at Bodega Bay at 0.62 (0.32) $\mu\text{g/g}$).

Robertson and Abel (1990) found 0.72 $\mu\text{g/g}$ in Kamishak Bay whereas our mean (sd) was 0.43 (0.06) $\mu\text{g/g}$. Robertson and Abel also reported 0.69 $\mu\text{g/g}$ off Kotzebue vs. our Chukchi Sea NBSP mean of 0.18 (0.03) $\mu\text{g/g}$ and 0.74 $\mu\text{g/g}$ off Oliktok vs. our NBSP mean of 0.53 (0.23) $\mu\text{g/g}$. Additionally, Robertson and Abel (1990) found 0.70 $\mu\text{g/g}$ off Prudhoe Bay which was the same as our mean Endicott Field concentration of 0.70 (0.2) $\mu\text{g/g}$.

Arsenic—Arsenic values in surface sediments from most Pacific coast sites were similar (means range 0.63-13 $\mu\text{g/g}$) and did not vary significantly from the reference site (Dana Point UCI: 9.3 $\mu\text{g/g}$) (Fig. 3). However, the mean concentration of arsenic in sediment from the Oakland estuary was the highest (mean (sd): 13 (1.6) $\mu\text{g/g}$) and was significantly higher than the nearby reference site at Bodega Bay (4.3 (2.5) $\mu\text{g/g}$). The analytical results for single-sediment samples (not shown on Fig. 3) collected from Dana Point Inside (8.3 $\mu\text{g/g}$), outside Mission Bay (6.4 $\mu\text{g/g}$), Estero Bay (5.0 $\mu\text{g/g}$), San Luis Obispo (1.5 $\mu\text{g/g}$), and the Farallon Islands (<0.1 $\mu\text{g/g}$), ranged from the high end down to below detection.

Arsenic can exist in a variety of chemical forms in marine and estuarine ecosystems, including inorganic species, methylated forms, arseno-lipids, arseno-sugars, arsenobetaine, and arsenocholine (Phillips 1987). Arsenic chemistry in the aquatic environment is unusually complex and may be influenced by a host of interactions and processes, such as redox state, ligand exchange, precipitation, adsorption, and biological interactions (Sadiq 1990).

Crecelius et al. (1985) reported surface sediment concentrations of 15-20 $\mu\text{g/g}$ at locations surrounding our NBSP Commencement Bay site (3.8 (2.8) $\mu\text{g/g}$). They also

determined that preindustrial concentrations were near 7 $\mu\text{g/g}$. The study by Schults et al. (1987) reported a value from a site off the mouth of Blair Waterway of 24 $\mu\text{g/g}$, with concentrations as great as 288 $\mu\text{g/g}$ inside other local waterways.

Our Coos Bay mean value of 6.9 (4.0) $\mu\text{g/g}$ compares with a value around 5 $\mu\text{g/g}$ reported by Fuhrer and Rinella (1983). Chapman et al. (1986) reported high arsenic sediment concentration at their sites in San Francisco Bay: 44-70 $\mu\text{g/g}$ in southwestern San Pablo Bay (our NBSP mean (sd): 8.1 (3.7) $\mu\text{g/g}$), 49-64 $\mu\text{g/g}$ off Oakland (NBSP: 13 (0.3) $\mu\text{g/g}$), and 57-72 $\mu\text{g/g}$ in Islais Creek (NBSP: 9.4 (1.9) $\mu\text{g/g}$). Gunther et al. (1987) reported that the main source of arsenic to San Francisco Bay was riverine inputs and nonurban runoff.

In Southern California Jan and Hershelman (1980) reported a mean arsenic concentration of 3.7 $\mu\text{g/g}$ in the vicinity of the NBSP west Santa Monica Bay site (5.0 (1.8) $\mu\text{g/g}$). Ladd et al. (1984) reported arsenic sediment levels in north San Diego Bay of 6.5 $\mu\text{g/g}$, which was comparable to our NBSP mean of 7.7 (1.7) $\mu\text{g/g}$. They also reported values of 4.8-20 $\mu\text{g/g}$ (NBSP mean: 10 (3.0) $\mu\text{g/g}$) for south San Diego Bay and 5-13 $\mu\text{g/g}$ (NBSP mean: 9.4 (5.3) $\mu\text{g/g}$) for National City.

Robertson and Abel (1990) reported 8.1 $\mu\text{g/g}$ arsenic in Kamishak Bay sediments near our NBSP site where we found only 1.8 (0.7) $\mu\text{g/g}$. They also reported 8.4 $\mu\text{g/g}$ for Kotzebue vs. our mean (sd) Chukchi Sea site value of 6.4 (1.4) $\mu\text{g/g}$, and 25.7 $\mu\text{g/g}$ mean for five sites in the Beaufort Sea vs. our Endicott Field site mean of 1.3 (0.3) $\mu\text{g/g}$. Our Oliktok Point site contained 2.3 (2.0) $\mu\text{g/g}$ in sediment.

Cadmium—The only site with cadmium sediment mean values significantly greater than the highest reference site (Nisqually Reach UCI: 0.86 $\mu\text{g/g}$) was west Santa Monica Bay (2.1 $\mu\text{g/g}$) (Fig. 3). In the section on baseline metals and excess concentrations in urban sediments, we discuss the possibility that cadmium at Nisqually Reach was elevated beyond normal background concentrations; hence, this site was excluded in the determination of background cadmium concentrations. The

reference site with the next lowest concentration (Dana Point) was used instead; however, only one additional site (San Pedro Canyon) was significantly elevated above this reference site's upper comparison interval ($0.55 \mu\text{g/g}$).

The single-sediment sample collected from the outside Mission Bay site ($3.3 \mu\text{g/g}$) (not shown on Fig. 3) was one of the highest cadmium values found on the Pacific coast. The other single-sample sites were lower: Dana Point Inside ($1.2 \mu\text{g/g}$), San Luis Obispo ($0.39 \mu\text{g/g}$), the Farallon Islands ($0.14 \mu\text{g/g}$), and Estero Bay ($0.08 \mu\text{g/g}$).

Crecelius et al. (1985) reported recent surface sediment concentrations of cadmium of $0.17\text{--}0.38 \mu\text{g/g}$ at Commencement Bay (NBSP mean (sd): $0.64 (0.3) \mu\text{g/g}$) and determined that concentrations in sediment were below $0.17 \mu\text{g/g}$ before the area was industrialized. Schults et al. (1987) reported that their site near the mouth of Blair Waterway (Commencement Bay) contained $0.26 \mu\text{g/g}$ cadmium, with more elevated levels to $3.9 \mu\text{g/g}$ inside nearby waterways. Our mean (sd) values for the Columbia River estuary and Youngs Bay sediments ($0.58 (0.31)$ and $0.13 (0.02) \mu\text{g/g}$, respectively) were lower than those reported by Fuhrer and Rinella (1983) of 2 and $4 \mu\text{g/g}$. Their value of approximately $3 \mu\text{g/g}$ was also greater than the NBSP mean ($0.44 (0.22) \mu\text{g/g}$) at Coos Bay.

Available data for cadmium in San Francisco Bay sediments indicate little evidence of widespread or heavy enrichment (Phillips 1987) and that riverine input is probably the dominant local input source (Gunther et al. 1987). Chapman et al. (1986) found $1 \mu\text{g/g}$ or less at their San Pablo Bay, Outer Oakland, and Islais Creek sites which agrees with our mean (sd) NBSP data ($0.29 (0.22)$, $0.16 (0.006)$ and $0.51 (0.24) \mu\text{g/g}$, respectively).

Word and Mearns (1978) calculated that 28 control stations of their 71-station 60 m depth contour survey in southern California had a mean cadmium level of $0.39 \mu\text{g/g}$. Near the Hyperion sludge outfall, Jan and Hershelman (1980) reported

2.3 $\mu\text{g/g}$ (NBSP mean (sd) of 2.1 (2.5) $\mu\text{g/g}$). Off Palos Verdes, north of our San Pedro Canyon site (1.17 (0.54) $\mu\text{g/g}$) and San Pedro Outer Harbor site (0.82 (0.38) $\mu\text{g/g}$), Hershelman et al. (1981) reported 2.1 $\mu\text{g/g}$. These elevated levels at NBSP sites may have been due in part to the closeness of local sewer outfalls: 2.5 km from Hyperion and 8+ km from the Whites Point outfall for the Los Angeles County Sanitation District.

In San Diego Bay, Ladd et al. (1984) reported 0.5-1.0 $\mu\text{g/g}$ in sediment from north San Diego Bay (NBSP mean: 0.52 (0.17) $\mu\text{g/g}$), 0.5-2.0 at their south San Diego Bay site (0.68 (0.4) $\mu\text{g/g}$), and 1.5-12.5 $\mu\text{g/g}$ off National City (0.36 (0.16) $\mu\text{g/g}$). In Hecate Strait, south of Boca de Quadra (0.44 (0.01) $\mu\text{g/g}$), Harding and Goyette (1989) reported a mean (sd) cadmium concentration of 0.38 (0.08) $\mu\text{g/g}$.

Chromium, Copper, and Lead

Floating-bar plot presentations of the chromium (Cr), copper (Cu), and lead (Pb) in sediments are given in Figure 4.

Chromium—Bodega Bay, a reference site, had the highest mean value (490 $\mu\text{g/g}$) of any site and was, therefore, not useful as a reference site. We used the next highest reference site (Nisqually Reach UCI: 140 $\mu\text{g/g}$) and found that five sites were deemed significantly higher than reference. These were Bodega Bay, Humboldt Bay (453 (250) $\mu\text{g/g}$), San Pablo Bay (361 (215) $\mu\text{g/g}$), Hunters Point (234 (82) $\mu\text{g/g}$), and South Hampton Shoal (213 (56) $\mu\text{g/g}$).

Of the 13 sites with the highest sediment concentration, all were around the greater San Francisco Bay area, except for two (Chukchi Sea off Kotzebue and Port Valdez, both in Alaska). A single-sediment sample collected from Estero Bay (5770 $\mu\text{g/g}$) was the highest single concentration found on the Pacific coast (not shown on Fig. 4). The other single-sample values ranged from 210 $\mu\text{g/g}$ in the Farallon Islands

off San Francisco to 53 $\mu\text{g/g}$ at the outside Mission Bay site, with the others being intermediate: San Luis Obispo (130 $\mu\text{g/g}$) and Dana Point Inside (59 $\mu\text{g/g}$).

Chromium distribution in sediment is obviously related to geographical area and requires further investigation.

Chromium exists in nature in valence states ranging from Cr^{-2} to Cr^{+6} , the most common forms are the trivalent and hexavalent forms. Trivalent chromium, essential at low concentrations for mammals, is generally considered to be less toxic than hexavalent chromium. Human activities remobilize considerably more chromium than do natural processes, largely due to the element's use in the metallurgical and chemical industries. While most chromium is thought to enter through atmospheric pathways, direct sources to aquatic environments are from metal finishing industries and sewage treatment plants plus inputs from iron and steel works, tanneries, textile manufacturers, and urban runoff (Phillips 1987).

Crecelius et al. (1985) reported Commencement Bay surface sediment concentrations of 49-72 $\mu\text{g/g}$ around our NBSP site (61 (8) $\mu\text{g/g}$), which was similar to preindustrial sediment levels. In their study of this area, Schults et al. (1987) report their highest concentration at Blair Waterway (14.3 $\mu\text{g/g}$), which was far below our NBSP site.

Fuhrer and Rinella (1983) reported levels of chromium at 4 and 8 $\mu\text{g/g}$ for surface sediments from the Columbia River estuary. Our mean (sd) Columbia River estuary (40 (13) $\mu\text{g/g}$) and Youngs Bay (50 (3.2) $\mu\text{g/g}$) sites were much higher. They also report about 20 $\mu\text{g/g}$ for Coos Bay compared with our NBSP mean of 80 (57) $\mu\text{g/g}$.

Chapman found chromium concentrations of 72-93 $\mu\text{g/g}$ in their southern San Pablo Bay site (northeast San Pablo Bay NBSP mean (sd): 361 (215) $\mu\text{g/g}$), 85-95 $\mu\text{g/g}$ at their Outer Oakland Harbor site (NBSP: 196 (4) $\mu\text{g/g}$), and 110-146 $\mu\text{g/g}$ in Islais Creek Channel (NBSP: 145 (7) $\mu\text{g/g}$). Gunther et al. (1987) estimates that nonurban

runoff is the dominant input (62-83 %) to the San Francisco Bay area with riverine contributions next in importance. This suggests that the high chromium levels found in San Francisco Bay and Bodega Bay are not anthropogenic, but rather reflect crustal rock contributions.

In southern California, Word and Mearns (1978) calculated a control site concentration of chromium along the 60 m depth contour to be 23.1 $\mu\text{g/g}$. Near the Hyperion outfall, Jan and Hershelman (1980) found 69 $\mu\text{g/g}$ chromium compared to our NBSP mean (sd) of 101 (43) $\mu\text{g/g}$. Hershelman et al. (1981) reported a value of 77 $\mu\text{g/g}$ off of Palos Verdes, north of our San Pedro Canyon (106 (30) $\mu\text{g/g}$) and San Pedro Outer Harbor (80 (14) $\mu\text{g/g}$) sites. Our mean (sd) values for San Diego Bay (north: 62 (14) $\mu\text{g/g}$; south: 90 (48) $\mu\text{g/g}$; and National City: 60 (22) $\mu\text{g/g}$) generally agree with the values reported by Ladd et al. (1984) of 61-79, 80-158, and 83-140 $\mu\text{g/g}$ for these sites, respectively.

Sweeney and Naidu (1989) reported surface sediment chromium levels of 16-125 $\mu\text{g/g}$ for the area around Oliktok Point (NBSP mean (sd): 71 (16) $\mu\text{g/g}$) and 15-87 $\mu\text{g/g}$ in the Prudhoe Bay area (NBSP Endicott Field mean: 59 (16) $\mu\text{g/g}$), while Robertson and Abel (1990) reported 89 $\mu\text{g/g}$ off Oliktok Point and 85 $\mu\text{g/g}$ off Prudhoe Bay (Endicott Field). Robertson and Abel (1990) also found 65 $\mu\text{g/g}$ chromium near our NBSP site in Kamishak Bay (82 (6) $\mu\text{g/g}$) and 333 $\mu\text{g/g}$ off Kotzebue near our Chukchi Sea site for which we reported a mean (sd) of 200 (24) $\mu\text{g/g}$. In Hecate Strait, south of Boca de Quadra (NBSP: 53 (17) $\mu\text{g/g}$), Harding and Goyette (1989) reported chromium concentrations of 28.8 (14.5) $\mu\text{g/g}$.

Copper--Copper occurs in excess concentrations at many sites, particularly those associated with areas of urbanization or marine transportation and repair activities (Fig. 4). The mean (sd) copper concentration in Pacific coast sediments was significantly higher than the maximum reference site (Nisqually Reach upper comparison interval (UCI): 26 $\mu\text{g/g}$) in the urbanized areas of San Diego: north bay

(103 (23) $\mu\text{g/g}$), south bay (181 (46) $\mu\text{g/g}$) and National City (117 (73) $\mu\text{g/g}$); Los Angeles: San Pedro Outer Harbor (102 (31) $\mu\text{g/g}$), Long Beach (67 (16) $\mu\text{g/g}$), and west Santa Monica Bay (60 (34) $\mu\text{g/g}$); San Francisco: Oakland estuary (115 (22) $\mu\text{g/g}$), Oakland Outer Harbor (72 (5) $\mu\text{g/g}$), Redwood City (55 (4) $\mu\text{g/g}$), and Hunters Point (53 (10) $\mu\text{g/g}$); and central Puget Sound: Seattle's Elliott Bay (105 (36) $\mu\text{g/g}$) and Tacoma's Commencement Bay (48 (7) $\mu\text{g/g}$).

In the section on baseline metals and excess concentrations in urban sediments, we discuss the possibility that copper at Nisqually Reach was elevated beyond normal background concentrations; hence, this site was excluded in the determination of baseline copper concentrations. The reference site with the next lowest concentration (Dana Point) was used instead leading to 13 additional sites that have been determined to be significantly higher than the reference site's upper comparison interval (9 $\mu\text{g/g}$). In this section we also address the variability of copper concentrations as a function of sediment grain size. It should be kept in mind that copper concentrations vary widely with grain size making it difficult to determine contamination levels.

Copper is an essential element in vertebrates, being associated with numerous metalloenzymes and metalloproteins (Thompson 1990). Its mobilization by human activities is like that of lead; roughly 10-15 times nature's rate (Phillips 1987). After mercury and silver, copper is ranked as the third most toxic to aquatic biota of the more common metal contaminants (Waldichuk 1974), and the margin between its concentration in the marine environment and those concentrations known to be at least chronically toxic to marine biota is very small (Klapow and Lewis 1979).

The concentrations of copper in sediments found in Puget Sound were variable. Long and Chapman (1985) summarized data from several sources and reported copper concentrations at 34-206 $\mu\text{g/g}$ at various Elliott Bay sites (NBSP mean (sd): 105 (37) $\mu\text{g/g}$). Crecelius et al. (1985) reported copper contents of surficial sediments from

Commencement Bay ranging from 46 to 65 $\mu\text{g/g}$ (NBSP mean (sd): 48 (7) $\mu\text{g/g}$) and a preindustrial sediment concentration for copper to be in the range of 30-40 $\mu\text{g/g}$. Long and Chapman (1985) reported 51-581 $\mu\text{g/g}$ at Commencement Bay sites with high values associated with shallow inshore sites, especially in channels and waterways with restricted water circulation. Schults et al. (1987) reported 37 $\mu\text{g/g}$ off the mouth of the Blair Waterway with higher levels inside other waterways (to 581 $\mu\text{g/g}$) and lower at their reference site (11 $\mu\text{g/g}$). Dexter et al. (1985) discussed historical inputs to Puget Sound from such sources as the former ASARCO copper smelter on the western shore of Commencement Bay and Quinlan et al. (1985) concluded that up to one-third of the total anthropogenic copper to central Puget Sound was attributed to this source. This smelter discharged both liquid and atmospheric particulates enriched in copper, and smelter slag was used for sandblasting of ships, as rip rap, and for roadbed materials. In addition, copper can be contributed by other shipyard operations and the gradual dissolution of antifouling paints from vessels in industrial ports, such as Seattle's Harbor Island and Duwamish Waterway. Compared with other surface waters in the Puget Sound Basin, Paulson and Feely (1985) found elevated levels of copper in inner Commencement Bay. They also found surface waters with elevated dissolved copper concentrations in the vicinity of Harbor Island in Elliott Bay which suggested localized anthropogenic inputs (Paulson and Feely 1985).

Fuhrer and Rinella (1983) reported 4 $\mu\text{g/g}$ of copper just north of our NBSP Columbia River estuary site compared with our mean (sd) value of 16.8 (3.2) $\mu\text{g/g}$. Also, our Youngs Bay site was not as high (36 (9) $\mu\text{g/g}$) as their site (180 $\mu\text{g/g}$). The NBSP mean value for Coos Bay was 13 (12) $\mu\text{g/g}$ which was slightly less than their value of 25 $\mu\text{g/g}$.

Previous surveys of San Francisco Bay area sediments show an enrichment of copper (>50 $\mu\text{g/g}$) in nearshore stations of South Bay and in much of San Pablo Bay

(some sites $>100 \mu\text{g/g}$), with generally lower levels ($<25 \mu\text{g/g}$) in the sediments of Central Bay and the Golden Gate area (Phillips 1987). Oakland Outer Harbor has levels exceeding $75 \mu\text{g/g}$, compared with our value of $72 (5) \mu\text{g/g}$ and Oakland estuary values were reported exceeding $50 \mu\text{g/g}$ compared with our mean value of $115 (22) \mu\text{g/g}$ (Phillips 1987). Chapman et al. (1986) reported $30\text{-}53 \mu\text{g/g}$ for southern San Pablo Bay (our NBSP mean: $40 (18) \mu\text{g/g}$), south of Oakland Outer Harbor levels of $43\text{-}51 \mu\text{g/g}$, and high levels in Islais Creek Channel of $68\text{-}130 \mu\text{g/g}$ (NBSP mean (sd): $73 (16) \mu\text{g/g}$).

Word and Mearns (1978) reported coastal southern California baseline concentrations of copper to be 2.8 to $31 \mu\text{g/g}$. Jan and Hershelman (1980) reported $42 \mu\text{g/g}$, and Brown et al. (1986) found levels of $25 \mu\text{g/g}$ near the NBSP west Santa Monica Bay site, compared to our $60 (34) \mu\text{g/g}$. Young et al. (1980) showed levels of copper of $40\text{-}617 \mu\text{g/g}$ near our west Santa Monica Bay site with strong concentration gradients for copper and other metals in the immediate vicinity of the Hyperion sewage outfall. Hershelman et al. (1981) reported $45 \mu\text{g/g}$ at their closest site to our San Pedro Canyon ($31 \mu\text{g/g}$) and San Pedro Outer Harbor ($102 (32) \mu\text{g/g}$) sites.

Our north San Diego Bay NBSP site contained $103 (23) \mu\text{g/g}$ compared with Ladd et al. (1984) who reported values of 28.5 and $42.5 \mu\text{g/g}$ for nearby sites. Our south San Diego Bay site mean was $181 (46) \mu\text{g/g}$ compared to the Ladd et al. (1984) finding of $25\text{-}340 \mu\text{g/g}$. On the west side of the channel off National City we found $117 (73) \mu\text{g/g}$ whereas Ladd et al. (1984) reported $2,000$ and $19,000 \mu\text{g/g}$ closer to the pier heads. The high sediment concentrations in San Diego Bay may reflect the presence of a major copper ore shipping facility at the south end of the bay.

On Alaska's North Slope, Sweeney and Naidu (1989) reported copper values near Oliktok Point of $6.3\text{-}83 \mu\text{g/g}$ compared with our value of $18 (6) \mu\text{g/g}$. Our lower Endicott Field value of $12 (4) \mu\text{g/g}$ compared with Sweeney and Naidu's reduced range of $9\text{-}29 \mu\text{g/g}$ in the Stefansson Sound-Prudhoe Bay area. Likewise, our mean

copper sediment concentration of 60 (6) $\mu\text{g/g}$ compared favorably with the Feder et al. (1990) value of 59 for Port Valdez. The levels in Port Valdez could reflect natural inputs of river-borne suspended material. For example, Feely et al. (1981) found levels of 63 $\mu\text{g/g}$ in suspended particulate matter from the nearby Copper River, and nearshore northeast Gulf of Alaska suspended particulate matter contained 55-109 $\mu\text{g/g}$. In Hecate Strait, south of Boca de Quadra (NBSP mean (sd): 22 (5) $\mu\text{g/g}$), Harding and Goyette (1989) reported copper concentrations of 4.3 (0.8) $\mu\text{g/g}$. The copper in Dutch harbor sediments could reflect extensive fishing boat and shipping activities concentrated in this confined water body on Alaska's Aleutian Island chain. The more remote Port Moller had only 13 (1.5) $\mu\text{g/g}$ copper in surface sediments which is probably related to grain size.

Analytical results for copper in single-sediment samples (not shown on Fig. 4) collected from Farallon Islands (8 $\mu\text{g/g}$), San Luis Obispo (8 $\mu\text{g/g}$), Estero Bay (6 $\mu\text{g/g}$), and outside Mission Bay (2 $\mu\text{g/g}$), all ranged below the maximum reference site value (26 $\mu\text{g/g}$), except for the sample collected in the entry channel to the large Dana Point marina, Dana Point Inside (40 $\mu\text{g/g}$). Copper was not detected (<1.0 $\mu\text{g/g}$) in sediments collected from the Channel Islands site.

Lead—The mean (sd) lead concentrations in Pacific coast sediments were significantly higher than the reference site (Dana Point upper comparison interval; 22 $\mu\text{g/g}$ dry weight) at Long Beach (101 (36) $\mu\text{g/g}$), Oakland estuary (99 (10) $\mu\text{g/g}$), north (53 (10) $\mu\text{g/g}$) and south (80 (31) $\mu\text{g/g}$) San Diego Bay, and San Pedro Outer Harbor (41 (11) $\mu\text{g/g}$). The sites with the highest three lead values (Long Beach, Oakland estuary, and south San Diego Bay) were significantly higher than 28 of the sites (except Port Valdez) beginning with Commencement Bay (Fig. 4).

Lead has no known biological function or requirement and is classified as nonessential (Thompson 1990). It is ubiquitous in terrestrial and aquatic environments due to numerous anthropogenic sources and its natural rate of

mobilization is exceeded by human contributions by a factor of 10-15 (Phillips 1980). Industrial effluents and urban runoff may contain large quantities of lead, the latter largely through the deposition of lead on pavement surfaces from its use as an antiknock agent in automotive fuels, an important nonpoint source discharge of lead to urban environments (Gunther et al. 1987). This element is unusual in that it exhibits only moderate toxicity in aquatic environments but is highly toxic to mammals (Phillips 1987).

Lead in Elliott Bay (Seattle) was high (47 (27) $\mu\text{g/g}$) possibly due to a lead smelter in Seattle which had historically contributed lead contamination to the area, although the discharges were significantly curtailed in the early 1980s (Dexter et al. 1985). Other anthropogenic sources of lead adjacent to the Duwamish Waterway also appear to have resulted in elevated dissolved lead concentrations in Elliott Bay surface waters (Paulson and Feely 1985).

Previous studies of metals in sediments (Malins et al. 1982, Long and Chapman 1985) in Puget Sound located in areas adjacent to NBSP sites found levels similar to those reported here. For example, Schults et al. (1987) reported a lead concentration of 19 $\mu\text{g/g}$ off the mouth of the Blair Waterway, slightly inshore from the Commencement Bay NBSP site where we found 26.8 (10.7) $\mu\text{g/g}$. The exhaustive study by Shults et al. routinely found much higher levels (to 790 $\mu\text{g/g}$) inside the waterways, intermediate levels in Commencement Bay, and lowest levels at their reference site (Browns Point; 9 $\mu\text{g/g}$). Crecelius et al. (1985) reported 25 $\mu\text{g/g}$ lead in sediment collected north of the NBSP site and a predevelopment (pre-1900) concentration in central Commencement Bay of less than 15 $\mu\text{g/g}$. A major local input of lead to the Tacoma area was from the now-closed ASARCO lead smelter established along the northwestern shore of Commencement Bay in 1889 and converted to copper smelting in 1902. Input has been as liquid wastes, shoreline deposition of smelter

slag, and as atmospheric particulates enriched in metals (as much as 23 metric tons of lead per year).

Our mean (sd) concentration of lead (9.9 (6.5) $\mu\text{g/g}$) in the Columbia River estuary compared favorably with a value of 10 $\mu\text{g/g}$ found by Fuhrer and Rinella (1983, as reported in Buchman 1989) and our Youngs Bay, Oregon site (17.8 (1.5) $\mu\text{g/g}$) was further inshore than the Fuhner and Rinella site which contained 10 $\mu\text{g/g}$. Their value for Coos Bay sediments in 1980 (approx. 13 $\mu\text{g/g}$) compared favorably with our 1984-88 mean of 10.8 (7.4) $\mu\text{g/g}$.

Lead concentrations have been reported to be fairly evenly distributed over the four basins of San Francisco Bay with no areas reaching 100 $\mu\text{g/g}$; however, several nearshore areas had higher levels (Phillips 1987). Risebrough et al. (1978) reported levels of 40-69 $\mu\text{g/g}$ for Oakland Outer Harbor near our NBSP site (44 (2) $\mu\text{g/g}$), 70-99 $\mu\text{g/g}$ for Hunters Point (NBSP mean (sd): 30 (15) $\mu\text{g/g}$), 40-69 $\mu\text{g/g}$ off Angel Island near our Southampton Shoal site (17 (11) $\mu\text{g/g}$), and 10-39 $\mu\text{g/g}$ from San Pablo Bay sediments (NBSP mean: 16 (10) $\mu\text{g/g}$). Luoma and Phillips (1988) reported 54 $\mu\text{g/g}$ at their Hunters Point location. Chapman et al. (1986) reported surface sediment lead levels from southern San Pablo Bay of 18-25 $\mu\text{g/g}$, south of the mouth of the Oakland estuary at 29-33 $\mu\text{g/g}$, and 49-223 $\mu\text{g/g}$ from the Islais Creek Channel (NBSP mean: 47 (17) $\mu\text{g/g}$).

Word and Mearns (1978) reported a mean sediment lead concentration of 6.6 $\mu\text{g/g}$ for their 28 "control" stations along the 60 m depth contour from Point Conception to the U.S.-Mexico border in southern California and Katz and Kaplan (1981) calculated a "pollution-free baseline" concentration for the area to be 10 $\mu\text{g/g}$. The majority of the NBSP sites were located more inshore of these control stations and contained up to three time higher concentrations at the NBSP open water and reference sites.

Young et al. (1980) reported levels of 20-50 $\mu\text{g/g}$ in the area of our west Santa Monica Bay site (27 (14) $\mu\text{g/g}$) and 20-30 $\mu\text{g/g}$ in the inshore area (NBSP mean 26 $\mu\text{g/g}$), while Jan and Hershelman (1980) reported a mean lead value of 17 $\mu\text{g/g}$ near the Hyperion sewage sludge discharge outfall. Our mean (sd) San Pedro Canyon sediment concentration (17 (3) $\mu\text{g/g}$) was similar to that found by Hershelman et al. (1981) at their closest Palos Verdes station (Sta. 10A: 15 $\mu\text{g/g}$) south of the Joint Water Pollution Control Plant's Palos Verdes outfall. Thompson et al. (1986) reported lead values (4-9 $\mu\text{g/g}$) in deeper-water sediments off the San Gabriel Canyon, south and west of our sites. The NBSP Long Beach site mean lead concentration was 3-4 times greater than nearby sites and probably reflects multiple urban inputs, including the large input of street runoff from the Los Angeles River drainage which enters San Pedro Bay near this site (Eganhouse and Kaplan 1982).

Ladd et al. (1984) reported levels of lead in San Diego Bay sediments from a 1982-83 nearshore survey ranging from 15 to 315 $\mu\text{g/g}$, with their south San Diego Bay sites having 15-150 $\mu\text{g/g}$ ($n = 3$) compared with our NBSP site's mean (sd) of 80 (31) $\mu\text{g/g}$; north San Diego Bay sites having 22-31 $\mu\text{g/g}$ ($n = 2$) compared with our 53 (10) $\mu\text{g/g}$; and National City (20-200 $\mu\text{g/g}$; $n = 2$) compared to our mean value of 44 (19) $\mu\text{g/g}$.

Our mean (sd) value for Port Valdez was 23 (5) $\mu\text{g/g}$ which compares well with a mean value of 30 $\mu\text{g/g}$ for a site slightly east of the NBSP site (Feder et al. 1990). For sites near Skagway (Skagway and Nakhu Bay), the loading of lead ores inside that harbor was a source of air-borne lead dust (Robinson-Wilson and Malinkay 1986). In Hecate Strait, south of Boca de Quadra (NBSP mean (sd) 18 (3) $\mu\text{g/g}$), Harding and Goyette (1989) reported a mean (sd) lead concentration of 11.8 (10.7) $\mu\text{g/g}$.

Analytical results for single-sediment samples (not shown on Fig. 4) collected from Dana Point Inside (26.2 $\mu\text{g/g}$), Farallon Islands (10.3 $\mu\text{g/g}$), San Luis Obispo

(4.9 $\mu\text{g/g}$), outside Mission Bay (4.9 $\mu\text{g/g}$), and Estero Bay (<0.3 $\mu\text{g/g}$) all ranged near or below the maximum reference site value (25 $\mu\text{g/g}$).

Mercury, Nickel, and Selenium

Floating-bar plot presentations of the mercury (Hg), nickel (Ni), and selenium (Se) in sediments are given in Figure 5.

Mercury—The total mercury concentration in Pacific coast sediments was quite variable at many sites but significantly higher than the maximum reference site (Nisqually Reach UCI: 0.31 $\mu\text{g/g}$) at three of the urban sites: Oakland estuary (1.07 (0.32) $\mu\text{g/g}$), south (0.72 (0.53) $\mu\text{g/g}$) and north San Diego Bay (0.61 (0.20) $\mu\text{g/g}$). Mercury was not detected (<0.01 $\mu\text{g/g}$) in sediments from Moss Landing, east Santa Monica Bay, or Oceanside. In the section on baseline metals and excess concentrations in urban sediments, we discuss the possibility that mercury at Nisqually Reach was elevated beyond normal background concentrations; hence, this site was excluded in the determination of baseline mercury concentrations. The reference site with the next lowest concentration (Dana Point; UCI: 0.2 $\mu\text{g/g}$) was used instead; however, this caused only two additional sites (Seal Beach and Elliott Bay) to become significantly elevated above the upper comparison interval of this reference site.

Mercury has no known biological function and can be classified as nonessential (Thompson 1990). Human activities tend to mobilize two to three times as much mercury as do natural global processes (Phillips 1987) and many inputs are concentrated along coastal margins. The element is highly toxic in the methylated form, which may be produced by microbial methylation of inorganic mercury in sediments and elsewhere. Industrial sources of mercury include mining and smelting, fossil fuel combustion, chlor-alkali plants, manufacturing of electrical equipment,

pulp and paper mills, antifouling or mildew-proofing activities, and fungicides in agriculture (Phillips 1987).

Published data for mercury in Puget Sound and San Francisco Bay sediments emphasize the ubiquity of this element which may correlate with atmospheric and runoff inputs (Dexter et al. 1985, Crecelius et al. 1985, Phillips 1987). Large quantities of mercury can enter an estuary attached to suspended river-borne particles that settle to the bottom surficial sediments. Natural (e.g., storms, flooding) and anthropogenic processes (e.g., dredging, dumping) undoubtedly contribute to the redistribution of this element throughout the estuaries (Phillips 1987). For example, San Francisco Bay may receive considerable quantities of mercury from the large San Joaquin-Sacramento Rivers drainage basin upstream of the delta. Mercury sources in the Central Valley include weathering from naturally rich deposits in the coast range and washdown of mercury used in historical gold mining activities (3,500 tons shipped into the area) in the Sierra Nevada Range. Our data show that mercury concentrations in sediments from San Francisco Bay and Puget Sound cause most of these sites to be ranked in the upper half of all sites (Fig. 5).

Dexter et al. (1985) reported the average surficial sediment mercury content in the Puget Sound central basin to be about 0.3 $\mu\text{g/g}$. Crecelius et al. (1985) found values of 0.04-0.15 $\mu\text{g/g}$ for sites in Commencement Bay (NBSP mean (sd): 0.14 (0.12) $\mu\text{g/g}$) and reported preindustrial concentrations less than 0.08 $\mu\text{g/g}$.

Our findings of concentrations of mercury in the Columbia River estuary (0.11 (0.11) $\mu\text{g/g}$) and Youngs Bay (0.02 (0.02) $\mu\text{g/g}$) sediments were considerably lower than those (10 and 30 $\mu\text{g/g}$, respectively) reported by Fuhrer and Rinella (1983). Their value for Coos Bay was also higher (0.24 $\mu\text{g/g}$) than the mean concentration (0.14 (0.16) $\mu\text{g/g}$) for our NBSP site, but probably not significantly higher.

Phillips (1987) and Long et al. (1988) reviewed knowledge about the mercury content of San Francisco Bay sediments. Long and coworkers calculated a mean value

of 0.43 (0.46) $\mu\text{g/g}$ from more than 1,000 analyses (1970-87). Risebrough et al. (1978) reported levels of 0.25-0.49 $\mu\text{g/g}$ off Treasure Island and Angel Island (NBSP mean (sd): 0.50 (0.6) $\mu\text{g/g}$ at Oakland and 0.13 (0.09) $\mu\text{g/g}$ at Southampton Shoal) and less than 0.25 $\mu\text{g/g}$ at San Pablo Bay (NBSP mean: 0.23 (0.54) $\mu\text{g/g}$) and Hunters Point (NBSP mean: 0.25 (0.18) $\mu\text{g/g}$). Our mean (sd) mercury concentration in sediments from Islais Creek Channel of 0.32 (0.09) $\mu\text{g/g}$ was at the low end of the range of 0.37-1.2 $\mu\text{g/g}$ found by Chapman et al. (1986), the source of which is thought to be runoff from the surrounding highly urbanized catchment (Phillips 1987).

In other areas, Hershelman et al. (1981) reported mercury in sediments collected midway between the Los Angeles County Sanitation District's Palos Verdes Peninsula outfall and our NBSP San Pedro Canyon site (NBSP mean (sd): 0.31 (0.28) $\mu\text{g/g}$) of 0.20-0.42 $\mu\text{g/g}$. Also, in Hecate Strait, Alaska, south of Boca de Quadra (0.04 $\mu\text{g/g}$), Harding and Goyette (1989) reported mean (sd) mercury concentrations of 0.05 (0.01) $\mu\text{g/g}$.

Analytical results for single-sediment samples (not shown on Fig. 5) collected from the Farallon Islands (0.09 $\mu\text{g/g}$), San Luis Obispo (0.08 $\mu\text{g/g}$), Estero Bay (0.08 $\mu\text{g/g}$), Dana Point Inside (0.04 $\mu\text{g/g}$), and outside Mission Bay (<0.01 $\mu\text{g/g}$) were all less than the reference sites.

Nickel—Only one site, Oakland estuary (125 (24) $\mu\text{g/g}$), contained a total nickel concentration that was significantly higher than the maximum reference site (Bodega Bay: upper comparison interval 59 $\mu\text{g/g}$) (Fig. 5). The Nisqually Reach site had a maximum interval of 55 $\mu\text{g/g}$ which suggests that the Bodega Bay value is not anomalously high, assuming the source for both is geological rather than anthropogenic. The San Francisco Bay-northern California area appears to have higher sediment nickel concentrations than the other major urban estuaries; for example, the 10 sites with the highest concentrations of nickel (>47 $\mu\text{g/g}$) were in this area, accounting for essentially all of the NBSP sites in the region. Interestingly, Moss

Landing (16 (3) $\mu\text{g/g}$) and Monterey Bay (7 (4) $\mu\text{g/g}$) to the south and Coos Bay (23 (16) $\mu\text{g/g}$) to the north were lower.

Nickel is considered only moderately toxic in aquatic environments; according to Phillips (1987) its rate of mobilization by human activities (metal finishing industries, urban runoff, battery manufacturing and disposal, municipal effluents) is only twice that of natural processes.

Crecelius et al. (1985) reported values of 31-37 $\mu\text{g/g}$ in Commencement Bay sediments surrounding the NBSP site (28 (3) $\mu\text{g/g}$) and their nickel profiles with depth to strata before urbanization were relatively constant at these levels.

Phillips (1987) summarized existing sediment results and concluded that there was little spatial variation of nickel in San Francisco Bay sediments and that the levels were generally close to 100 $\mu\text{g/g}$. This level can be compared to a naturally-weathered, average shale with a nickel content of 95 $\mu\text{g/g}$. Gunther et al. (1987) suggested that the major sources of nickel to the San Francisco Bay environment are riverine, not directly anthropogenic. However, data suggest there is a nickel source to the South Bay environs and to a lesser extent in the Sacramento/San Joaquin estuary (Phillips 1987). Risebrough et al. (1978) reported nickel concentrations from surface sediments at several comparable locations to our NBSP sites in San Francisco Bay. Their two San Pablo Bay sites (<74 $\mu\text{g/g}$ and 75-99 $\mu\text{g/g}$) were close to our San Pablo Bay site (71 (25) $\mu\text{g/g}$) and their Angel Island site (75-99 $\mu\text{g/g}$) was just west of our Southampton Shoal site (64 (17) $\mu\text{g/g}$). They also reported a concentration for Oakland Outer Harbor (125-149 $\mu\text{g/g}$) which was near our site of the same name (104 (4) $\mu\text{g/g}$), and their Bayview Park site (125-149 $\mu\text{g/g}$) was inshore of our Hunters Point site (81 (31) $\mu\text{g/g}$). Chapman et al. (1986) reported 76-85 $\mu\text{g/g}$ in southwestern San Pablo Bay, 72-84 $\mu\text{g/g}$ off Oakland, and 88-94 $\mu\text{g/g}$ in Islais Creek Channel (Islais Creek NBSP mean: 108 (35) $\mu\text{g/g}$).

In southern California, Word and Mearns (1978) established a mean of 12.2 $\mu\text{g/g}$ for nickel ($n = 28$; range 8.6-15.9 $\mu\text{g/g}$) at control locations along their 60 m depth contour survey from Point Conception to the U.S.-Mexico border. Katz and Kaplan (1981) suggested that an average background (nonpolluted) surface sediment concentration for southern California was about 15 $\mu\text{g/g}$ and a polluted peak mean was 107 $\mu\text{g/g}$. Our west and east Santa Monica Bay site means (sd) were 13 (3) and 14 (10) $\mu\text{g/g}$, respectively and our San Pedro Canyon and San Pedro Outer Harbor values were 23 (3) and 37 (20) $\mu\text{g/g}$, respectively. Jan and Hershelman (1980) reported a mean nickel sediment value of 10.5 $\mu\text{g/g}$ near the Hyperion outfall and Hershelman et al. (1981) found variable nickel concentrations ranging from 16 to 134 $\mu\text{g/g}$ off the Palos Verdes Peninsula.

Katz and Kaplan (1981) reported a total nickel content for the deep-water San Diego Trough surface sediments of 2-8 $\mu\text{g/g}$, compared with our outside San Diego Bay concentration of 6 (4) $\mu\text{g/g}$. Moving inshore, Ladd et al. (1984) found 8.5-11.5 $\mu\text{g/g}$ in north San Diego Bay (NBSP mean(sd): 14 (8) $\mu\text{g/g}$), 16-23 $\mu\text{g/g}$ in south San Diego Bay sediments (NBSP: 20 (8) $\mu\text{g/g}$), and 19-20 $\mu\text{g/g}$ off National City (our NBSP mean (sd): 23 (9) $\mu\text{g/g}$).

In Alaska, Sweeney and Naidu (1989) found 8.4-59 $\mu\text{g/g}$ nickel in the Oliktok Point (NBSP: 23 (18) $\mu\text{g/g}$) area of Alaska's Beaufort Sea and 15-43 $\mu\text{g/g}$ in the Prudhoe Bay area (Endicott Field: 18 $\mu\text{g/g}$). Feely et al. (1981) reported nickel levels in suspended particulate matter from the Copper River of 61 $\mu\text{g/g}$ and as high as 81 $\mu\text{g/g}$ in surface nearshore northeastern Gulf of Alaska waters. The highest central Gulf of Alaska NBSP value for nickel was found at Lutak Inlet (17 (8) $\mu\text{g/g}$) and the lowest was found a few miles to the north at Skagway (4.3 (1.6) $\mu\text{g/g}$), but the difference was not statistically significant. Feder et al. (1990) reported a value for a mudflat near our Port Valdez site which was considerably greater than our mean (sd) value (83 vs. 17 (0.5) $\mu\text{g/g}$).

The analytical results for nickel from single-sediment samples (not shown on Fig. 5) collected from the Estero Bay (49 $\mu\text{g/g}$), the Farallon Islands (42 $\mu\text{g/g}$), San Luis Obispo (30 $\mu\text{g/g}$), Dana Point Inside (29 $\mu\text{g/g}$), and outside Mission Bay (11 $\mu\text{g/g}$) were all lower than the reference site.

Selenium--Selenium showed some variation from 0.10 to 1.12 $\mu\text{g/g}$ in mean surface sediment concentrations between Pacific coast NBSP sites which is probably related to grain size or a parameter such as surface area which correlates to grain size. The total mean selenium concentration was significantly higher than the maximum reference site (Bodega Bay UCI: 0.5 $\mu\text{g/g}$) in only two Pacific coast sediments. These were San Pedro Outer Harbor (1.11 (0.45) $\mu\text{g/g}$) and Nakhu Bay (0.87 (0.39) $\mu\text{g/g}$). The single analysis (not shown) for Dana Point Inside was 0.53 $\mu\text{g/g}$ and for the Farallon Islands was 0.29 $\mu\text{g/g}$.

The biogeochemistry of selenium in the aquatic environment is highly complex in that this element can exist in nature in four oxidation states. Selenium is both an essential and a toxic element; the concentration window between required intake levels and those known to be damaging for this element is unusually small (Phillips 1988). It is required in small amounts by both plants and animals, based upon the specific incorporation into certain enzymes (e.g., glutathione peroxidase), as well as nonspecific incorporation into proteins (selenomethionine).

Selenium is used in pesticides, shampoos, and in the manufacture and production of glass, pigments, rubber, metals and their alloys, medical therapeutic agents, photographic emulsions, and petroleum. Selenium is present in the fossil fuels, petroleum and coal, as well as in natural seleniferous soils, including parts of the Rocky Mountains and High Central Plains and regions of the southeastern United States (Phillips 1987).

Crecelius et al. (1985) reported that selenium in Commencement Bay surface sediments did not exceed 0.8 $\mu\text{g/g}$ which agrees with our mean (sd) value of

0.34 (0.13) $\mu\text{g/g}$. Risebrough et al. (1978) reported values of 2.6-3.0 $\mu\text{g/g}$ in the Carquinez Straits upstream of the NBSP San Pablo Bay site (0.18 (0.13) $\mu\text{g/g}$), 1.1-1.5 $\mu\text{g/g}$ off Angel Island which exceeded our nearby Southampton Shoal site (0.19 (0.17) $\mu\text{g/g}$) and less than 1.0 $\mu\text{g/g}$ at Oakland Outer Harbor (NBSP: 0.37 (0.09) $\mu\text{g/g}$). According to Phillips (1988), San Francisco Bay exhibits widespread selenium enrichment. Phillips (1987, 1988) suggested that selenium inputs to the San Francisco Bay area were from at least three important sources: leaching of seleniferous soils (as selenate from irrigation by agricultural activities) in the San Joaquin catchment, industrial inputs in the Carquinez Straits area (mainly selenite from six major oil refineries), and an unidentified input from south San Francisco Bay. Phillips (1988) reports that some of the earlier data may list values higher than those determined by more sensitive analytical techniques.

Many Alaskan sites also had high mean selenium concentrations, including Dutch Harbor (0.70 (0.15) $\mu\text{g/g}$) and the remote Boca de Quadra site (0.74 (0.16) $\mu\text{g/g}$), which suggests a possible geological component. No selenium (<0.1 $\mu\text{g/g}$) was found in the sediments from the Chukchi Sea. Nakhu Bay produced the second highest mean value on the Pacific coast but this was not significantly different from the Alaskan reference site at Lutak Inlet (0.43 (0.25) $\mu\text{g/g}$).

Silver, Tin, and Zinc

Floating-bar plot presentations of the silver (Ag), tin (Sn), and zinc (Zn) in sediments are given in Figure 6.

Silver—The total silver concentration in Pacific coast sediments was significantly higher than the maximum reference site (Nisqually Reach UCI: 0.4 $\mu\text{g/g}$) at west Santa Monica Bay (5.6 $\mu\text{g/g}$), Moss Landing (1.8 $\mu\text{g/g}$), and three San Diego Bay sites: National City (1.4 $\mu\text{g/g}$), south bay (1.2 $\mu\text{g/g}$), and north bay (0.9 $\mu\text{g/g}$)

(Fig. 6). The west Santa Monica Bay silver concentration was significantly higher than all other Pacific coast sites. Moss Landing and National City values were also significantly higher than the lower 36 sites (Fig. 6). The high silver concentrations reported for Moss Landing are perplexing but consistent over the three stations sampled (1.6, 1.7, and 2.0 $\mu\text{g/g}$). Unfortunately, we sampled this site at only one time period (1986).

In the section on baseline metals and excess concentrations in urban sediments, we discuss the possibility that silver at Nisqually Reach was elevated beyond normal background concentrations; hence, this site was excluded in the determination of background silver concentrations. The reference site with the next lowest concentration (Dana Point) was used instead and only one additional site (San Pedro Outer Harbor) was significantly elevated above reference site upper comparison interval (0.33 $\mu\text{g/g}$).

Industries that have had potential for being sources of silver include jewelry, battery, porcelain, ink, antiseptic, and silverware manufacturing; photographic, ink, electroplating, and food processing, and cloud seeding and mining. About 40% of the U.S. supply of silver is for photographic film and chemicals (McComish and Ong 1988). Silver forms strong complexes with sulfides and will also complex with organic matter (McComish and Ong 1988).

One study has found variable concentrations of silver in surface sediment of Commencement Bay (0.07 to 0.34 $\mu\text{g/g}$) (Crecelius et al. 1985) which is similar to what we found at this site (0.28 (0.12) $\mu\text{g/g}$). Preindustrial silver concentrations in sediment for this area were found to be less than 0.05 $\mu\text{g/g}$ (Crecelius et al., 1985).

According to Phillips (1987), silver in sediments from northern San Francisco Bay and the Sacramento/San Joaquin River Delta exhibit concentrations similar to background levels (<0.2 $\mu\text{g/g}$), indicating little anthropogenic contamination from upriver sources. Our San Pablo Bay and Castro Creek sites had mean (sd) sediment

concentrations of 0.24 (0.20) and 0.16 (0.07) $\mu\text{g/g}$, respectively. However, within the central and southern reaches of the San Francisco Bay, silver is more abundant and concentrations in sediments are indicative of moderate enrichment in many areas with substantial enrichment in a few locations, such as Islais Creek (Phillips 1987). Our data fit this pattern with the highest silver levels from Islais Creek (0.59 (0.40) $\mu\text{g/g}$), followed by Oakland estuary (0.43 (0.14) $\mu\text{g/g}$), Hunters Point (0.42 (0.29) $\mu\text{g/g}$), and Redwood City (0.34 (0.07) $\mu\text{g/g}$).

Because municipal waste discharges are common sources of silver (Phillips 1987), the high sediment concentrations of silver at west Santa Monica Bay site may have been due in part to its location approximately 2.5 km north of the Seven-Mile Hyperion Sewer outfall. Even, one year after the Hyperion sludge discharge to the nearshore environment was terminated (November 1987), the silver levels in the immediate vicinity remained unchanged in the range of roughly 20 to 80 $\mu\text{g/g}$ (Konrad 1989). At sites off the Palos Verdes Peninsula sewage discharge site, located between our east Santa Monica Bay (0.36 (0.07) $\mu\text{g/g}$) and San Pedro Outer Harbor (0.64 (0.19) $\mu\text{g/g}$) sites, Hershelman et al. (1981) reported surficial levels of silver ranging from 1.4 to 27 $\mu\text{g/g}$. Word and Mearns (1978) reported baseline levels for silver in coastal southern California marine sediments ranging from 0.06 to 1.7 $\mu\text{g/g}$ (average: 0.2 $\mu\text{g/g}$), which are also similar to the values in our report.

Our mean (sd) for National City (1.4 (0.7) $\mu\text{g/g}$) was similar to those (2.0 and 4.0 $\mu\text{g/g}$) reported by Ladd et al. (1984), as well as those for south San Diego Bay (NBSP mean (sd): 1.2 (0.7) $\mu\text{g/g}$ vs. 0.5-2.5 $\mu\text{g/g}$) and north San Diego Bay (NBSP mean (sd): 0.95 (0.46) vs. 1.0 $\mu\text{g/g}$).

Caution is needed in interpreting absolute levels of silver in sediments because no certified reference sediment materials are currently available for establishing accuracy of analysis. We rely on NOAA interlaboratory comparison studies to gauge

our accuracy, which have shown our Pacific coast analyses to be comparable to silver analyses by other NBSP and Mussel Watch investigators.

Analytical results for single-sediment samples (not shown on Fig. 6) collected from the San Luis Obispo (0.6 $\mu\text{g/g}$), Estero Bay (0.5 $\mu\text{g/g}$), outside Mission Bay (0.4 $\mu\text{g/g}$), Dana Point Inside (0.11 $\mu\text{g/g}$), and the Farallon Islands (<0.01 $\mu\text{g/g}$) were grouped around the reference site.

Tin—The concentration of total tin in Pacific coast sediments was significantly higher than the reference site (Dana Point UCI: 3.2 $\mu\text{g/g}$) at only two sites: Oakland estuary (10 (6.1) $\mu\text{g/g}$) and south San Diego Bay (6.3 (3.2) $\mu\text{g/g}$) (Fig. 6). It is apparent that tin was elevated in some urban sites, possibly due to organotin release from antifouling paint on boats. It is possible that tin in Dana Point sediments was elevated beyond background levels and choosing the next reference site, Bodega Bay, would have caused many more sites (eight) to be significantly higher than the UCI of that reference site. This was not done because there was no clear pattern of elevated concentrations at Dana Point.

Analytical results for single-sediment samples (not shown on Fig. 6) collected from Dana Point Inside (3.1 $\mu\text{g/g}$), Farallon Islands (2.2 $\mu\text{g/g}$), outside Mission Bay (2.2 $\mu\text{g/g}$), San Luis Obispo (0.8 $\mu\text{g/g}$), and Estero Bay (<0.7 $\mu\text{g/g}$) were all below the maximum reference site value.

The activities of humans have radically increased the mobilization of tin from the earth's crust by a factor of more than 10 (Phillips 1980); however, the impact of tin on aquatic ecosystems has received little attention because of the low toxicity exhibited by the inorganic form (Phillips 1987). Due to difficulties in analyzing tin in marine samples and to the low toxicity of inorganic tin to aquatic systems, few large-scale monitoring efforts on the tin content in sediments are available for the Pacific coast. Concern about tin in the aquatic environment was altered dramatically during the 1970s with the widespread use of organotins as an antifouling agent for vessels.

Organotins have been used for stabilizing polyvinylchloride polymers and as bactericides, fungicides, and insecticides (Champ 1986). As an antifouling agent in hull bottom paints, the organotins proved highly effective, but unfortunately they also exerted toxic effects in the parts-per-trillion range on nontarget aquatic organisms. Before the U.S. Congress imposed restrictions on their use in 1988, organotins could be found at toxic levels in water bodies with limited circulation (e.g., marinas, channels, harbors, urban bays).

The present study has generated one of the largest collections of total tin data for surficial sediments for this region. As the interest in organometals, such as tributyltin in antifoulants, increases, more information will undoubtedly become available.

Zinc—The total zinc concentrations in Pacific coast sediments were significantly higher than the maximum reference site (Nisqually Reach UCI: 130 $\mu\text{g/g}$) at sites representing the four major urban areas of Oakland estuary (310 $\mu\text{g/g}$), south (282 $\mu\text{g/g}$) and north San Diego Bay (230 $\mu\text{g/g}$), Long Beach (189 $\mu\text{g/g}$) and San Pedro Outer Harbor (178 $\mu\text{g/g}$), and Elliott Bay (187 $\mu\text{g/g}$) off Seattle (Fig. 6).

In the section on baseline metals and excess concentrations in urban sediments, we discuss the possibility that zinc at Nisqually Reach was elevated beyond normal background concentrations, thus this site was excluded in the determination of baseline zinc concentrations. The reference site with the next lowest concentration (Dana Point) was used instead; hence, 23 additional sites have been determined to be significantly higher than this reference site's upper comparison interval (64 $\mu\text{g/g}$). Because the background concentration of zinc is strongly affected by grain size, determination of contaminant levels is difficult. We address grain size effects in the section on chemical correlations.

Zinc can be considered an essential element because it is a requirement of several metalloproteins, particularly metalloenzymes (Thompson 1990). Phillips

(1987) estimates a mobilization rate of zinc due to human activities of 10-15 times that of the natural rate, much like copper and silver, although the impact is considered to be significantly less.

High levels of zinc in Elliott Bay sediments are reflected in dissolved zinc distribution in this area. Paulson and Feely (1985) found low water concentrations of zinc in the Duwamish River upstream of most point sources and increasing surface water concentrations in Elliott Bay as they approached the mouth of the Duwamish Waterway downstream of the point sources. These findings strongly suggests that anthropogenic inputs injected by industrial and other sources along the Duwamish River and Duwamish Waterway on Harbor Island were responsible for an elevation in dissolved levels and ultimately in high sediment concentrations in underlying sediments. The mean value for our Elliott Bay NBSP site sediments of 187 (45) $\mu\text{g/g}$ was in the mid-range (86-319 $\mu\text{g/g}$) for values reported by Malins et al. (1980) from this area.

The mean (sd) NBSP site concentration (92 (8) $\mu\text{g/g}$) from Commencement Bay was higher than that reported by Schults et al. (1987) for a nearby site off Blair Waterway (50 $\mu\text{g/g}$), but less than that found elsewhere in local waterways (to 1190 $\mu\text{g/g}$). Crecelius et al. (1985) reported zinc values of 87-94 $\mu\text{g/g}$ from nearby sites and a preindustrial concentration of about 70 $\mu\text{g/g}$. While zinc inputs can occur from the pulp and paper industry (Dexter et al. 1985), Grieve and Fletcher (1977) showed that major river systems can contribute significant zinc to estuarine and coastal sediments.

Our mean (sd) zinc value (90 (15) $\mu\text{g/g}$) was higher than reported by Fuhrer and Rinella (1983) for the Columbia River estuary (22 $\mu\text{g/g}$) as was our Youngs Bay site (NBSP mean (sd): 132 (80) vs. 35 $\mu\text{g/g}$). Our Coos Bay value (64 (37) $\mu\text{g/g}$) was similar to that reported by Fuhrer and Rinella (1983).

Phillips (1987) concluded that the average San Francisco Bay zinc sediment concentration was about 100 $\mu\text{g/g}$ with relatively little variation from basin to basin, except in the immediate vicinity of sources which appeared largely to be rivers and sewage treatment plants. Risebrough et al. (1978) found levels ranging from 150 to 174 $\mu\text{g/g}$ near Treasure Island and Hunters Point, in agreement with our zinc values for nearby sites (Oakland NBSP mean: 172 (9) $\mu\text{g/g}$; and Hunters Point 136 (25) $\mu\text{g/g}$); however, Luoma and Phillips (1988) more recently reported 405 $\mu\text{g/g}$ in Oakland Outer Harbor near Treasure Island and 202 $\mu\text{g/g}$ at Hunters Point. It is not known whether these differences reflect local variability in sampling or temporal increases. Risebrough et al. (1978) also reported concentrations of 100-124 $\mu\text{g/g}$ near our Southampton Shoal site (104 (21) $\mu\text{g/g}$) and 100 $\mu\text{g/g}$ in southwest San Pablo Bay (116 (24) $\mu\text{g/g}$).

The east Santa Monica Bay site contained low zinc sediment concentrations (35 (9) $\mu\text{g/g}$) whereas the west Santa Monica site near the Hyperion sewage sludge outfall had considerably more zinc (102 (56) $\mu\text{g/g}$). Brown et al. (1986) reported levels of 54 $\mu\text{g/g}$ for a nearshore site and 70 $\mu\text{g/g}$ for a site near the Hyperion outfall. In their 71-station, 60 m depth contour survey between Point Conception and the U.S.-Mexico border, Word and Mearns (1978) found a background range of 37-47 (mean: 44) $\mu\text{g/g}$ zinc in surficial sediments. Our San Pedro Canyon (118 (11) $\mu\text{g/g}$) and Seal Beach (125 (30) $\mu\text{g/g}$) sites showed elevated concentrations above the background levels of Word and Mearns (1978). Higher yet, were the sites at nearby Long Beach (189 (23) $\mu\text{g/g}$) and San Pedro Outer Harbor (179 (35) $\mu\text{g/g}$) sites. Hershelman et al. (1981) reported that their southeasterly most transect off Palos Verdes had zinc sediment levels of 118-186 $\mu\text{g/g}$; this transect was between the Palos Verdes sewer outfall diffusers and our San Pedro Canyon site.

Our mean value for south San Diego Bay (281 (75) $\mu\text{g/g}$) was in the range (43-765 $\mu\text{g/g}$) reported by Ladd et al. (1984), although we found higher levels (NBSP

mean (sd): 230 (40) $\mu\text{g/g}$ vs. 89.5-120 $\mu\text{g/g}$) at our north San Diego Bay site and lower levels (NBSP mean (sd): 206 (109) vs. 490-4300 $\mu\text{g/g}$) at the National City site.

The values for zinc at the Oliktok Point and Endicott Field sites (81 (24) and 72 (12) $\mu\text{g/g}$, respectively) were in the range reported by Sweeney and Naidu (1989) for nearby sites (28-160 and 40-105 $\mu\text{g/g}$, respectively). Likewise, our mean (sd) concentration found at Port Valdez (150 (8) $\mu\text{g/g}$) was similar to that (128 $\mu\text{g/g}$) from inshore sediments off nearby Island Flats (Feder et al. 1990). Feely et al. (1981) found 133 $\mu\text{g/g}$ zinc in Copper River particulate matter and 210-292 $\mu\text{g/g}$ in surface nearshore suspended matter in the northeastern Gulf of Alaska which suggests that our central Alaskan values could represent geologically-derived zinc. In Hecate Strait, south of Boca de Quadra (104 (8) $\mu\text{g/g}$), Harding and Goyette (1989) reported zinc concentrations of 33.1 (7.6) $\mu\text{g/g}$.

Analytical results for single-sediment samples (not shown on Fig. 6) collected from the Dana Point Inside (118 $\mu\text{g/g}$), Farallon Islands (48 $\mu\text{g/g}$), outside Mission Bay (47 $\mu\text{g/g}$), San Luis Obispo (44 $\mu\text{g/g}$), and Estero Bay (38 $\mu\text{g/g}$) were all less than the reference site.

Aluminum and Iron

Floating-bar plot presentations of the major sediment (crustal) components aluminum (Al) and iron (Fe) in sediments are given in Figure 7. The maximum comparison interval value for the reference site is not included on the figures because these elements are considered as strictly geologically derived.

Aluminum—The mean aluminum concentrations group within the ranges for estuarine sediments (3.5-8.5%) and all comparison intervals overlap within the maximum (7.9%) and minimum (4.3%) reference site values, as do the exploratory site single determinations.

Sediment concentrations at our Puget Sound sites varied from 6.5 to 7.5%, which is in line with values cited by Crecelius et al. (1985) for Commencement Bay (5.1-6.6%) sediments. In California, Chapman et al. (1986) reported southwestern San Pablo Bay sediment concentrations of 7.5-7.9% (NBSP mean (sd): 6.4 (1.6) %), 7.2-9.9% for Oakland Outer Harbor (NBSP: 6.8 (0.15) %), and 7.5-8.0% in Islais Creek Channel (NBSP mean: 5.2 (0.3) %).

The mean (sd) aluminum concentrations ranged from high values along the margins of the Gulf of Alaska (8.5 (0.9) % at Port Moller, Skagway (8.3 (0.7) %, and Port Valdez (8.1 (0.3) %) to low values in the Chukchi (3.6 (0.4) %) and Beaufort Seas (Endicott: 3.5 (0.3) %). The aluminum concentrations at the three lowest Alaskan sites (Endicott Field, Chukchi Sea, and Oliktok Point) were significantly lower than at the three highest Alaskan sites. Robertson and Abel (1990) found 3.5% aluminum off Prudhoe Bay (NBSP Endicott Field mean 3.5%), 4.2 % at Kotzebue (NBSP Chukchi Sea mean 3.6%), 6.1% off Oliktok Point (NBSP mean 4.4 (1.1) %), and 7.7 % in Kamishak Bay sediments near our NBSP site (7.5 (0.4) %). Feder et al. (1990) reported even higher (16.9%) surficial sediment levels at their experimental mudflat site east of Port Valdez (NBSP mean: 8.2 (0.3) %). In Hecate Strait, south of Boca de Quadra (NBSP mean: 7.0 (1.0) %), Harding and Goyette (1989) reported a mean (sd) aluminum concentration of 7.2 (2.3%).

Iron—The mean (sd) iron concentrations fell between 6.4 (0.9) % at Port Moller and 0.8 (0.56) % at Monterey Bay (Fig. 7) and is probably related to grain size (see section on correlations). The comparison intervals for all sites overlap with the maximum (5.4%) and minimum (1.5%) intervals found for all reference site values (Nisqually Reach, Bodega Bay, and Dana Point) as do the exploratory single-site determinations (1.8-3.3%). No obvious geographic or anthropogenic patterns are apparent from the data (Fig. 7).

Crecelius et al. (1985) reported iron levels in Commencement Bay sediments of 3.8-4.2% compared with our NBSP value of 3.7 (0.1) %. Likewise, in southwestern San Pablo Bay, Chapman et al. (1986) found 4.6-5.1% vs. our NBSP site 4.4 (0.5) %. They also report at Oakland Outer Harbor values were 4.3-6.2% compared with 5.1 (0.2) %, and in Islais Creek Channel the values were 4.8-5.0% compared with NBSP mean of 4.9 (0.3) %. The NBSP sites in Santa Monica Bay were near the lower end of the range of values for the Pacific coast sites (2.1 and 1.5%) but were not as low as Jan and Hershelman (1980) reported for their Hyperion outfall site (1.0%).

In the Beaufort Sea, Sweeney and Naidu (1989) report Oliktok Point and Prudhoe Bay area concentrations range from 0.8-4.8% and 0.8-2.9%, respectively, and Robertson and Abel (1990) report 3.7% and 3.0%, respectively. This is compared with the corresponding NBSP site values of 2.5 (0.7) % and 2.0 (0.2) %. Robertson and Abel (1990) reported a surficial iron sediment concentration of 3.5 % near the Kamishak Bay NBSP site (3.5 (0.08) %) and 2.5% off Kotzebue near our NBSP Chukchi Sea site (NBSP mean: 2.5 (0.4) %). At Port Valdez, the NBSP mean value of 5.1 (0.3) % was less than what Feder et al. (1990) reported (7.4%).

Manganese and Silicon

Floating-bar plot presentations of the major sediment (crustal) components manganese (Mn) and iron (Fe) in sediments are given in Figure 8. The maximum comparison interval value for the reference site is not included on the figure for silicon because this element is considered as strictly geologically derived.

Manganese—Manganese is a crustal element and, although measured in hundreds of parts per million, is important in understanding the biogeochemistry of estuarine and coastal sediments (Fig. 8). The mean surface sediment concentrations for the Pacific coast varied by about an order of magnitude (110 to 1250 $\mu\text{g/g}$) and is

probably related to grain size. The reference site values (Nisqually Reach: comparison interval of 1117 $\mu\text{g/g}$) for manganese overlapped with all the urban sites and the single determination sites fell within the midrange of the remaining Pacific coast samples. The single analysis sites are outside Mission Bay (666 $\mu\text{g/g}$), Dana Point Inside (326 $\mu\text{g/g}$), Estero Bay (310 $\mu\text{g/g}$), Farallon Islands (263 $\mu\text{g/g}$), and San Luis Obispo (192 $\mu\text{g/g}$).

Crecelius et al. (1985) reported manganese levels in Commencement Bay surface sediments in the range of 470-570 $\mu\text{g/g}$ (NBSP mean (sd): 540 (86) $\mu\text{g/g}$) with little change in concentration over a vertical profile which covered the last 100 years. Schults et al. (1987) reported a lower concentration (111 $\mu\text{g/g}$) at their nearby Blair Waterway entrance station as well as all of their other Commencement Bay and Tacoma waterways sites (maximum: 368 $\mu\text{g/g}$) which is probably due to variable grain size.

Our manganese values in the San Francisco Bay area closely approximated those reported by Chapman et al. (1986) for southwestern San Pablo Bay at 640-790 $\mu\text{g/g}$ (NBSP mean (sd): 730 (129) $\mu\text{g/g}$), for Oakland Outer Harbor at 510-760 $\mu\text{g/g}$ (NBSP: 530 (55) $\mu\text{g/g}$), and for Islais Creek Channel at 380-450 $\mu\text{g/g}$ (NBSP: 410 (65) $\mu\text{g/g}$). Jan and Hershelman (1980) reported a mean manganese concentration of 89 $\mu\text{g/g}$ off the Hyperion outfall in Santa Monica Bay compared with 410 $\mu\text{g/g}$ at our nearby, but more northern site (west Santa Monica Bay).

Sweeney and Naidu (1989) reported ranges of manganese of 115-555 $\mu\text{g/g}$ and Robertson and Abel (1990) found 491 $\mu\text{g/g}$ for the Oliktok Point area (NBSP: 390 $\mu\text{g/g}$); likewise, the former reported 205-420 $\mu\text{g/g}$ and the latter 369 $\mu\text{g/g}$ for the Prudhoe Bay area (NBSP: 330 (109) $\mu\text{g/g}$). Robertson and Abel (1990) reported 698 $\mu\text{g/g}$ in surface sediments in Kamishak Bay near our NBSP site (766 (19) $\mu\text{g/g}$) and 405 $\mu\text{g/g}$ off Kotzebue compared with our Chukchi Sea mean of 460 (97) $\mu\text{g/g}$. Our

Port Valdez site's mean (sd) concentration of 1030 (73) $\mu\text{g/g}$ corresponded with Feder et al. (1990) value of 1140 $\mu\text{g/g}$ in a mudflat to the north of the Lowe River mouth.

Silicon—The mean (sd) silicon concentrations fell between 22.9 (0.7) % at Dutch Harbor and 42.9 (13.5) % at Humboldt Bay (Fig. 8) and is probably related to grain size (see section on correlations). The mean West Coast silicon values group within the ranges for estuarine sediments (23-33%), with the values for Humboldt Bay (42.9%), Monterey Bay (38.9%), and Chukchi Sea (35.8%) being higher. The comparison intervals overlap within the maximum (36%) and minimum (25%) reference site values, as do the exploratory site's single determinations (26-33%).

Chapman et al. (1986) reported silicon levels in southwestern San Pablo Bay of 26.9-31.2% compared with our value of 29.9%, Oakland Outer Harbor of 27.4-33.6% compared with 28.6%, and Islais Creek Channel of 23.3-24.4% compared with our 25.8%. Feder et al. (1990) reported a value of near 60% for his Port Valdez site compared with our value of only 26.9%.

General Discussion of Sediment Chemistry

Of the 16 elements routinely analyzed in Pacific coast sediments, copper, lead, mercury, nickel, tin, and zinc appear to be the most likely pollution-associated elements because they were found in the highest concentrations in one or more urban sites. When compared to one of the three West Coast reference sites (Nisqually Reach, Bodega Bay, or Dana Point), many urban sites had significantly higher concentrations of these elements. In the section on baseline metals and excess concentrations in urban sediments we will explore this subject in greater depth.

Although the concentrations of a variety of elements were significantly higher in the sediments from certain urban sites (e.g., south San Diego Bay, west Santa Monica Bay, Oakland estuary, and Elliott Bay) compared to the reference sites, the high degree of intrasite variability in chemical concentrations at many of the sites

frequently made it difficult to identify statistically significant intersite differences with the comparison intervals. For example, the mean cadmium concentration in sediment from Oceanside (Fig. 3) was up to 50 times less than at 32 other Pacific coast sites, yet these differences were not statistically significant.

A number of factors may have influenced this intrasite variability, including 1) heterogeneous spatial distribution of chemicals in sediment within a small geographical area due to variable sediment characteristics, and 2) temporal changes in the accumulation of contaminants in sediment, such as episodic releases. Clearly, Factor 1 is well documented and may have had a strong influence on the observed variability, and Factor 2 can be evaluated using trend analyses, even though it is difficult to distinguish spatial variability from temporal variability. Additional years of sampling and sample analyses should provide sufficiently large sample sizes to reduce the intrasite variability, permit more realistic trend analyses, and thus allow more accurate estimates of intersite differences.

Concentrations of Elements in Fish Livers

In order to assess the general health of the coastal and estuarine environments, fish were also analyzed for selected elements to determine if elements deposited in sediments from human activities would be transferred to biota. Livers and, in a limited number of cases, stomach contents of bottom-dwelling or bottom-feeding fish were analyzed for the first four cycles of Pacific coast sampling. As mentioned earlier, we made few comparisons of liver concentrations to published values because the data are sparse for the Pacific coast, and such information is less useful without information on exposure concentrations for comparison.

Ideally, in order to avoid species-specific differences, individuals of the same fish species should be compared when evaluating the exposure of fish to contaminants at different sites. However, because the same fish species do not inhabit all of the

Pacific coast sampling sites, a total of eight target species were sampled for comparative purposes. Each target species (except black croaker) was sampled at a minimum of one urban (human-impacted) and one nonurban site. The target species and the geographical areas from which they were captured are given in Table 2a.

Interspecies differences in the uptake and fate of toxic chemicals by fish have been demonstrated by Varanasi et al. (1986, 1987, 1989b). For example, although both English sole and starry flounder (*Platichthys stellatus*) metabolized benzo[a]pyrene at similar rates, the two species showed differences in the detoxification of certain metabolites. Due to possible species-specific differences in uptake and metabolism of toxic elements, comparisons of tissue chemistry between species has not been strongly emphasized, however some interspecies comparisons are presented because we felt they highlighted potentially important patterns. In general, we will make intraspecies comparisons to indicate the degree to which fish were being exposed to contaminants at different sites.

The data on liver concentrations for each species and site (mean of three largest female specimens) are displayed graphically in Figures 9 through 43. In the section on correlations in liver, stomach contents, and sediment, we present pooled data from all individuals of a species over all geographic locations collected and compare liver concentrations to other compartments (stomach contents and sediment) in order to search for patterns of contamination. In all but a few cases, the concentrations of toxic elements in the livers of fish from urban sites were similar to, and occasionally lower than, those in livers from nonurban sites. There were few significant differences between populations at these different sites, but trends are evident and we believe that as comparison-sample sizes increase, significant differences will become more apparent. In the section on the relationship between chemical parameters (tissue and sediment) we propose a hypothesis which may explain the counterintuitive nature of high concentrations in reference site fish.

Fourhorn Sculpin, Spotted Sand Bass, Spotted Turbot, and Black Croaker

Floating-bar plot presentations for elements in liver tissue from fourhorn sculpin (*Myoxocephalus quadricornis*) from the Beaufort Sea and spotted sand bass (*Paralabrax maculatofasciatus*), spotted turbot (*Pleuronichthys ritteri*), and black croaker from southern California are combined in Figures 9-13 because of the limited amount of data available for each species. The plots of antimony (Sb), arsenic (As), and cadmium (Cd) are shown in Figure 9; chromium (Cr), copper (Cu), iron (Fe) are shown in Figure 10; lead (Pb), manganese (Mn), and mercury (Hg) in Figure 11; nickel (Ni), selenium (Se), and silver (Ag) in Figure 12; and tin (Sn) and zinc (Zn) in Figure 13. In comparing the Alaskan sites, the overlap of comparison intervals for the Endicott Field site (human impacted) with the Oliktok Point site (nonurban) was complete for all 14 elements in the fourhorn sculpin, except for zinc and arsenic which were significantly higher at the former site. Arsenic in another species from Alaska (flathead sole (*Hippoglossoides elassodon*)) was also high and is presented next. Black croaker, spotted sand bass, and spotted turbot were all taken in the San Diego area and are shown not for comparison but for informational purposes only. It is noteworthy that concentrations of mercury and cadmium were very high in spotted sand bass, and black croaker contained elevated concentrations of several elements, including tin.

Flathead Sole

Floating-bar plot presentations of antimony (Sb), arsenic (As), and cadmium (Cd) in liver tissue from flathead sole from Alaskan sites are given in Figure 14. The plots of chromium (Cr), copper (Cu), iron (Fe) are shown in Figure 15; lead (Pb), manganese (Mn), and mercury (Hg) in Figure 16; nickel (Ni), selenium (Se), and silver (Ag) in Figure 17; and tin (Sn) and zinc (Zn) in Figure 18. Lutak Inlet was used as the reference site for this Alaskan species. The concentration of arsenic in the flathead

sole livers from Boca de Quadra (85 (26) $\mu\text{g/g}$) was significantly higher than the reference site (UCI: 34 $\mu\text{g/g}$), as well as for fish from Dutch Harbor and Skagway. Lead in liver of fish from Skagway (4.2 (5.0) $\mu\text{g/g}$) was significantly higher than from the reference site (Lutak Inlet upper comparison interval (UCI): 0.44 $\mu\text{g/g}$) and all other Alaskan sites except Dutch Harbor. The concentration of mercury in fish caught at the Dutch Harbor (0.42 (0.06) $\mu\text{g/g}$) and Kamishak Bay (0.27 (0.18) $\mu\text{g/g}$) sites was significantly higher than the reference site (UCI: 0.10 $\mu\text{g/g}$). Likewise, chromium (1.0 $\mu\text{g/g}$) and manganese (10.4 $\mu\text{g/g}$) concentrations in flathead sole from Dutch Harbor were significantly above the reference site UCI (0.32 $\mu\text{g/g}$ and 4.7 $\mu\text{g/g}$, respectively). Manganese displayed a strong pattern with high levels in fish from Dutch Harbor to over an order of magnitude lower concentration in fish from Skagway. Other elements (arsenic, iron, and selenium) were also low in fish from Skagway, which may be related to the high levels of lead observed.

English Sole

Floating-bar plot presentations of antimony (Sb), arsenic (As), and cadmium (Cd) in liver tissue from English sole are given in Figure 19. The plots of chromium (Cr), copper (Cu), iron (Fe) are shown in Figure 20; lead (Pb), manganese (Mn), and mercury (Hg) in Figure 21; nickel (Ni), selenium (Se), and silver (Ag) in Figure 22; and tin (Sn) and zinc (Zn) in Figure 23. Only tin in livers from English sole caught from Elliott Bay (1.8 (2.7) $\mu\text{g/g}$) was significantly higher than the UCI for the reference site Nisqually Reach (0.72 $\mu\text{g/g}$). For English sole, there were two reference sites to choose from, Nisqually Reach or Bodega Bay. When all sites were considered, liver tissue from the reference site Nisqually Reach, often contained the first or second highest mean concentration of the selected element (copper, silver, nickel, chromium, arsenic, cadmium, iron, manganese, and antimony), but the concentration was generally not significantly different from other sites. For example, the nickel

concentration in liver from Nisqually Reach and Commencement Bay was significantly higher than concentrations in livers from Elliott Bay and Bodega Bay. Livers from English sole in Commencement Bay contained more iron and manganese than livers from English sole in Monterey Bay and more iron than in English sole livers from Bodega Bay. As mentioned earlier, Nisqually Reach may have contained elevated concentrations of some elements in the sediment. In comparing the different sites for English sole, only copper, nickel, zinc, and iron would be affected if the alternate reference site (Bodega Bay) was chosen for the benchmark.

Starry Flounder

Floating-bar plot presentations of antimony (Sb), arsenic (As), and cadmium (Cd) in liver tissue from starry flounder are given in Figure 24. The plots of chromium (Cr), copper (Cu), iron (Fe) are shown in Figure 25; lead (Pb), manganese (Mn), and mercury (Hg) in Figure 26; nickel (Ni), selenium (Se), and silver (Ag) in Figure 27; and tin (Sn) and zinc (Zn) in Figure 28. Only three means were significantly higher than their reference site UCI; chromium in liver of fish from Coos Bay (0.73 (0.66) $\mu\text{g/g}$) and the Columbia River estuary (0.63 (0.44) $\mu\text{g/g}$) and tin in fish from Coos Bay (2.8 (4.2) $\mu\text{g/g}$). The UCI for chromium and tin at Bodega Bay was 0.35 and 0.63 $\mu\text{g/g}$, respectively. Silver in fish liver from the Bodega Bay reference site was significantly higher than silver in fish from the San Francisco Bay sites of San Pablo Bay, Southampton Shoal, and Castro Creek and from the Columbia River estuary and nearby Youngs Bay sites. Arsenic in liver of starry flounder from San Pablo Bay was significantly lower than from fish caught in the Columbia River estuary and zinc in liver of fish from Bodega Bay was significantly higher than in fish from San Pablo Bay.

White Croaker

Floating-bar plot presentations of antimony (Sb), arsenic (As), and cadmium (Cd) in liver tissue from white croaker are given in Figure 29. The plots of chromium (Cr), copper (Cu), iron (Fe) are shown in Figure 30; lead (Pb), manganese (Mn), and mercury (Hg) in Figure 31; nickel (Ni), selenium (Se), and silver (Ag) in Figure 32; and tin (Sn) and zinc (Zn) in Figure 33. Several elements (lead, mercury, selenium, and cadmium) show strong trends; however, none were significantly different. For this species, there was a strong trend in mercury levels in liver; however, none were significant. The levels of cadmium, iron, silver, selenium, and zinc in one or both of the reference sites were the first or second highest mean value determined for white croaker livers. Interestingly, cadmium in liver of fish from San Pedro Outer Harbor and Long Beach was significantly lower than in fish from the reference site which was unexpected. Even though the range between minimum and maximum mean concentrations for some elements (lead, antimony, and tin) was 10 to 15 times, the large variability within sites precluded statistically significant differences.

Hornyhead Turbot

Floating-bar plot presentations of antimony (Sb), arsenic (As), and cadmium (Cd) in liver tissue from hornyhead turbot (*Pleuronichthys verticalis*) are given in Figure 34. The plots of chromium (Cr), copper (Cu), iron (Fe) are shown in Figure 35; lead (Pb), manganese (Mn), and mercury (Hg) in Figure 36; nickel (Ni), selenium (Se), and silver (Ag) in Figure 37; and tin (Sn) and zinc (Zn) in Figure 38. No site produced a significantly higher concentration of any element in hornyhead turbot liver when compared to the reference site (Dana Point) concentration (horizontal line) although a few were close. However, when comparing all sites to each other, copper in fish caught in San Pedro Canyon was significantly higher than that for fish from west

Santa Monica Bay and outer San Diego Bay. This observation might be explained by sewage effluents from the Palos Verdes sewer outfall (Brown et al. 1986).

The mean (sd) concentration of silver in west Santa Monica Bay (1.9 (1.0) $\mu\text{g/g}$) hornyhead turbot liver was significantly higher in individuals from outer San Diego Bay (0.5 (0.3) $\mu\text{g/g}$). This pattern was reversed for zinc with outer San Diego Bay having a higher concentration. East Santa Monica Bay (11 (7) $\mu\text{g/g}$) and west Santa Monica Bay (9 (2) $\mu\text{g/g}$) fish liver contained significantly higher selenium concentrations than individuals from San Pedro Canyon (1.5 (0.4) $\mu\text{g/g}$) and outer San Diego Bay (2.0 (0.9) $\mu\text{g/g}$). Also, fish liver from San Pedro Canyon (7.2 (3.4) $\mu\text{g/g}$) and outside San Diego Bay (6.1 (1.5) $\mu\text{g/g}$) contained significantly higher concentrations of manganese than fish liver from west Santa Monica Bay (1.8 (2.1) $\mu\text{g/g}$) and east Santa Monica Bay (2.8 (0.8) $\mu\text{g/g}$).

Barred Sand Bass

Floating-bar plot presentations of antimony (Sb), arsenic (As), and cadmium (Cd) in liver tissue from barred sand bass (*Paralabrax nebulifer*) are given in Figure 39. The plots of chromium (Cr), copper (Cu), iron (Fe) are shown in Figure 40; lead (Pb), manganese (Mn), and mercury (Hg) in Figure 41; nickel (Ni), selenium (Se), and silver (Ag) in Figure 42; and tin (Sn) and zinc (Zn) in Figure 43. Mean (sd) lead 1.3 (0.06) $\mu\text{g/g}$ and silver (0.12 (0.02) $\mu\text{g/g}$) in Mission Bay fish were significantly higher than their respective reference site concentration (Dana Point UCI: 0.53 and 0.07 $\mu\text{g/g}$, respectively). Lead was also significantly higher in Mission Bay fish than in fish from south San Diego Bay (0.5 (0.3) $\mu\text{g/g}$) and National City (0.4 (0.1) $\mu\text{g/g}$). Zinc in Dana Point barred sand bass livers (lower comparison interval (LCI): 82 $\mu\text{g/g}$) was significantly higher than in fish from south San Diego Bay (72 (17) $\mu\text{g/g}$) and National City (54 (23) $\mu\text{g/g}$). These values were unexpected because Mission Bay is not an industrialized area; however, this bay can receive substantial amounts of surface

water runoff which may contain contaminants (Cole et al. 1984), including lead from automobiles.

Concentrations of Elements in Fish Stomachs

We are not including figures for stomach contents because so few sites and years were selected for analysis which made the sample sizes for a given species small. Due to these small sample sizes, comparison intervals were generally very large and hence, differences were difficult to detect. For elements such as tin, chromium, selenium, arsenic, and antimony there were no real differences between species and location. Several of the elements showed a trend with higher means generally occurring in the more urbanized locations, but none were significantly higher than reference areas.

In several species there was a trend for the concentration of elements in stomach contents to be higher than the liver concentration; however, none were significantly different. In hornyhead turbot and barred sand bass, several elements (silver, mercury, chromium, lead, zinc) displayed a trend of higher means at the more urban sites (e.g., south San Diego) vs. a reference site (e.g., Dana Point). The same is true for silver, copper, lead, zinc in white croaker. In the section on correlations in liver, stomach contents, and sediment, we pooled stomach contents chemistry for all individuals of a species for comparisons between species and for comparisons to sediment and liver within a species.

Relationships Between Chemical Parameters

Sediment

Baseline metals and excess concentrations in urban sediments—The concentrations of each element at reference (Bodega Bay, Dana Point, Lutak Inlet) and many nonurban sites (e.g., Kamishak, Oliktok, San Luis Obispo, Channel Islands) were plotted against the percent fine sediment and a determination of background concentration was made. Any urban station which displayed an element concentration elevated above this background concentration was considered "contaminated". From the determinations for each element, a list was devised which highlights those stations with concentrations measured above the background level.

We chose percent fine sediment (silt plus clay; $<63\ \mu\text{m}$) for plotting because we believed that naturally and anthropogenically occurring elements would associate mechanistically with some closely allied property of grain size (e.g., TOC or surface area). Both surface area and TOC are physicochemical factors which may control the abundance of some elements. Usually, as the sediment particles become smaller, sediment surface area increases as does organic carbon content because of additional sites for association. Also, iron and manganese, which were positively correlated with decreasing grain size (increasing percentage fines), can control metal concentrations by providing a surface for adsorption via iron and manganese oxides.

Because several parameters are correlated with grain size and this is a property that is easy to measure, we chose it for our independent variable by which we assessed the variation in background element concentration. The correlation of element abundance and grain size has been discussed by Klammer et al. (1990) and reviewed by Horowitz (1991). In our study we analyzed the bulk sediment for total metal concentration instead of separating the sediment into discrete grain size fractions for analysis, as was done by Klammer et al. (1990). Hence, the results may be similar, but excessive dilution by sediment particles greater than $63\ \mu\text{m}$ may skew the

results and lead to poorer correlation coefficients than found in other studies. In general, our approach to baseline metal concentrations is rudimentary and readers should consult Luoma (1990) for a more detailed discussion on this subject.

Element regression on aluminum concentration in sediment from the East Coast of the United States was done by Hanson et al. (1993) to determine background or reference concentrations. Because Hanson et al. (1993) found high correlations for most elements with aluminum, we can only conclude that the geochemical makeup or geological histories between the areas (East Coast vs. West Coast) must be different or that our sample size was insufficient to determine such trends. One difference between our study and Hanson et al. (1993) is that they reported many aluminum concentrations below 4%, whereas in our study we had very few values (none of the reference sites) below this level. In our study, aluminum from clean sites moderately correlated with the percent fine sediment particles ($r = 0.41$) which was less than that found ($r = 0.75$) by Hanson et al. (1993). Our study does agree with Hanson et al. (1993) in that our strongest respective correlations (%aluminum or %fines) were with copper, iron, lead, and zinc.

The correlations for the Pacific coast reference and nonurban sites are listed in Table 4. Although Port Moller and Nahku Bay are categorized as nonurban, we did not include them in this group because we felt that zinc and lead were elevated at Nahku Bay, and zinc and tin were elevated in Port Moller sediments. The Nisqually Reach reference site was also excluded because several elements exhibited elevated concentrations. Elements which increase in sediments as percent fines increase may do so naturally or because of anthropogenic input. We could not separate natural from anthropogenic accumulation because we did not have a situation where the type of input was known and constant over variable grain size. At this time we cannot separate the natural from anthropogenic inputs but can expect that the reference areas will generally contain lower concentrations of contaminants than the urban sites. For

some elements we may assume that contaminated areas with a higher frequency of smaller particles will be expected to accumulate more of the contaminant elements than sites with a sediment containing a lower percent of fine particles. Also, we can not rule out the possibility that even some of the reference sites may contain elevated concentrations due to the global spread (i.e., widespread dissemination from urban areas) of contaminants. Because of this possible global spread, some elements (e.g., cadmium and lead) may be elevated at our nonurban and reference sites which may obscure any relationship between grain size and sediment concentration.

Percentage fine sediment ($<63\ \mu\text{m}$) may be a good measure, or a surrogate, of the variation observed for the concentration of some elements in sediment; however, correlation with grain size determined in more size categories (e.g., $1\text{--}2\ \mu\text{m}$, $2\text{--}4\ \mu\text{m}$, $4\text{--}8\ \mu\text{m}$, etc.) may be more appropriate. In this study, both percent iron and TOC were correlated to percent fines when all Pacific coast sites were considered together ($r = 0.57$ for iron and $r = 0.55$ for TOC) (data not shown). At Pacific coast reference sites, iron was still significantly correlated with percent fines ($r = 0.67$) and TOC less so ($r = 0.35$) (Table 4). For some of the other data subsets (e.g., West Coast reference sites) the percent fines correlated poorly to iron and TOC, possibly due to low sample sizes. Surfaces such as iron oxides can control metal concentrations by providing a surface for adsorption. Organic carbon can also serve as ligand for some elements; hence, those sediments with higher TOC may contain higher concentrations of certain elements. The mean (sd) percent fine sediment for each site is shown in Figure 44 and the mean (sd) percent TOC for each site is shown in Figure 45, along with the frequency distribution for TOC in Figure 46. One can see that there were many sites with highly variable TOC or percent fines and many of the outliers (high TOC with low percent fines and low TOC with high percent fines) are Alaskan sites.

Each element in reference and nonurban sediments was plotted against percent fine sediment. Two elements (copper and zinc) were strongly correlated and two

others (lead and selenium) were moderately correlated with percent fine sediment and therefore varied naturally as a consequence of grain size (Fig. 47) (see Table 4 for correlations). The differences in geochemical makeup may include variable iron and manganese oxides due to differences in sediment grain size and redox state. These oxides can scavenge dissolved metals which may lead to variable sediment concentrations. It is also possible that these nonurban areas experience elevated dissolved concentrations of certain elements which may lead to a slight increase in bulk concentrations and hence a correlation to grain size. The predictive regression equation for each of these elements as a function of percent fine sediment is also shown in Figure 47. The similarity in slope for these equations indicates that a similar process of association of element with sediment may be occurring. Even though the linear correlation for lead was relatively high ($r = 0.63$), it was not treated like copper, selenium, and zinc because its association with percent fines was curvilinear (Fig. 47c). The baseline concentration of lead was determined, like all the other uncorrelated elements, with a horizontal line above all reference and nonurban concentrations to determine contaminant concentrations.

In most cases, it appeared that elements were randomly distributed over the percentage fine material for all reference sites. In a few cases, it seemed that some reference sites contained excess concentrations of a particular element. For example, chromium and nickel concentrations (Figs. 48a and 48b) at the reference site Bodega Bay were far above those measured at all other reference sites (but not elevated at all Bodega Bay stations) which may indicate a degree of contamination from a local anthropogenic source. Conversely, there may be some natural geological source in this area which explains the elevated concentrations of these two metals because both metals were high at most San Francisco area sites. At this point it is difficult to determine why Bodega Bay contains elevated levels of chromium and nickel without a more thorough investigation of local sources.

Another metal, mercury (Fig. 48c) was elevated in two of the Dana Point samples which may be due to a local source. These mercury concentrations are 4 to 7 times higher than mercury concentrations in most other reference sites. Nisqually Reach (mean (sd): 0.16 (0.3) $\mu\text{g/g}$) was excluded in baseline determination of mercury because of elevated concentrations. Tin was also elevated at Dana Point (compared to other reference sites) which may be due to a nearby marina and contamination from organotins (Fig. 48d). The data show that 1988 and 1987 levels were higher than those found in samples for 1985 and 1986, indicating an increasing trend. Elevated levels of tin occurred in other urban sites (e.g., San Diego Bay) and may be related to boating activity. Also shown is cadmium for reference sites (Fig. 48e) which is elevated at Dana Point.

Nisqually Reach, Washington has been one of our reference sites, but was excluded in background determination because some elements (e.g., copper, mercury, and zinc) were elevated beyond normal reference-station background concentrations for its low percent of fine sediment. Figures 47a and 47b show the elevated values for copper and zinc at Nisqually Reach. Also because the Bodega Bay reference site contained elevated concentrations of nickel and chromium, it was excluded in determination of background concentrations for only these elements. We left Bodega Bay in the plots for all other elements because these concentrations were below the calculated background concentrations and because the large number of sites added to our discriminatory power for such background determinations. If Bodega Bay was left in for chromium, the background concentration would have been 1100 (vs. 300) $\mu\text{g/g}$ (dry wt.), and the background concentration for nickel would have been 80 (vs. 30) $\mu\text{g/g}$ (dry wt.). Overall it seems that some of our nonurban sites that we have designated as "reference areas" may in fact receive contaminants from local sources or from the global spread (mobilization) of elements. Because both nickel and chromium have been shown to be highly correlated with percent fine sediment (clay

plus silt; particles $< 63 \mu\text{m}$) (Horowitz and Elrick 1987), our lack of correlation could be due to these elevated concentrations at Bodega Bay which would cloud the underlying association. Without Bodega Bay, the correlation of nickel and fine sediment in Pacific coast reference sites improves from $r = -0.32$ to $r = 0.48$ and chromium improves from $r = -0.59$ to $r = 0.29$.

The stations (each site consists of 3 station measurements for each year analyzed) above the baseline for all years (listed by site) are included in Table 5 which shows the mean (sd) concentration of each element for all overages. If a site had more than one measurement above the baseline, the mean (sd) of all overages were reported, along with the number of overages. The total number of measurements is variable for each station and can be obtained from Figures 3-8. Our assessment of background concentrations of elements in sediment (Table 5) agrees favorably with those devised by Katz and Kaplan (1981) except for chromium, and those elements in our study requiring grain size adjustment (copper, selenium, and zinc). Our background concentrations for some elements also agree closely with values derived from NBSP sites on the East Coast of the United States (Hanson et al. 1993).

Mean values in Table 5 and Figures 3-8 may not agree in every case because only those stations which were above the background concentration were included in the mean for Table 5, whereas all values were used to generate the means for Figures 3-8. Also, chromium and nickel background concentrations were calculated without Bodega Bay and all background calculations were done without Nisqually Reach as a reference site because of elevated concentrations of many elements. There is no statistical significance to these overage concentrations; the background concentration is an absolute value determined from all reference sites. If the concentration of an element from an urban site was higher than this reference concentration, it was included in Table 5. Overage concentrations that are close to the background

concentrations should not be given as much importance as those several times higher than background.

An examination of Table 5 shows some interesting patterns. It can be seen that certain sites, such as Oakland estuary, south San Diego Bay, west Santa Monica Bay, and others, exceeded background levels for several elements. By a weight of evidence argument, it can be concluded that these sites are severely contaminated. In some cases an element's background concentration was exceeded at a site many times, essentially at each station (A, B, and C) for all years. For example, sites such as south and north San Diego Bay, and Hunter's Point show that some elements exceeded background concentrations routinely.

Looking vertically on Table 5, one can see that copper, lead, nickel, and zinc are elevated beyond expected natural concentrations at many sites. Additionally, a number of sites displayed overages with mercury, silver, and tin. Elements such as cadmium, antimony, and selenium do not appear to be elevated at most sites because of single overages and close to background concentrations. Other sites displayed overages for only a few elements but are also considered contaminated, depending on the amount above background. Sites such as Long Beach were slightly over background for some elements (e.g., cadmium) but were very high for others (e.g., lead). These excess concentrations in sediment are very important because sediments can act as a source of elements to the overlying water and enhance dissolved concentrations far above those observed in nonurban areas (Flegal and Sañudo-Wilhelmy 1993). The consequences of this include the potential for increased deleterious effects to water-column organisms, especially those migrating in from outside the estuary that are not adapted to the higher dissolved metal concentrations.

Extractable metals--Shokes and Mankiewicz (1979) and Katz and Kaplan (1981) discuss the hypothesis that most of the acid-extractable metal is that associated with

the outside of the sediment particle and hence related to excess additions as a consequence of anthropogenic activity. Therefore, lattice bound elements are part of the particle's natural geochemical structure and are considered as background or baseline. To test this hypothesis, we subjected selected sediments from Cycle VI (1989; not reported in this technical memorandum) to a 1 N HCl acid extraction. Although these sediment samples were not from the years reported in this technical memorandum, the samples were from the same sites and were expected to be essentially the same as those sampled in cycles I - V. We hypothesized that reference areas (e.g., Bodega Bay, Dana Point, etc.) would produce very little acid-extractable metal because most of the total metal would be lattice bound. As a result, sites with a high acid-extractable concentration to total sediment concentration ratio (HCl:Tot) would be expected to contain excess amounts of that particular element on the outside of the particle. This excess accumulation could be due to ligands, such as organic carbon coatings and manganese and iron oxides, complexing metals from the water column where concentrations may be elevated due to natural or anthropogenic processes. Acid at a 1N concentration would release elements complexed to surface ligands but not those associated with the mineral lattices.

The concentration of the total element in sediment (Tot), the concentration of the element in the HCl-extractable fraction (expressed as total μg extracted normalized to sediment weight), and the ratio of total to extractable for each are shown in Figures 49a-k. For elements such as silver, cadmium, lead, and nickel, the ratio of HCl:Tot was high at most sites, especially those urban sites identified as contaminated (Table 5).

Commencement Bay produced the highest levels of extractable arsenic and the highest HCl:Tot ratio (Fig. 49a), which may be related to a nearby copper smelter which operated in the area for decades and released large amounts of arsenic. Other

sites also produced high concentrations of HCl-extractable arsenic, and the lowest levels were found in reference sites (Bodega Bay and Dana Point).

The concentrations of total and HCl-extractable cadmium and the HCl:Tot ratio were generally highest at urban sites and relatively low at the reference sites (Fig. 49b) although the ratio at Bodega Bay was high. This is a strong indication that some of the cadmium in sediments may be due to water-borne or enriched particle input (possibly due to anthropogenic sources) leading to accumulation in sediment. Hence, the level of labile cadmium is high, as evidenced by the acid extractable concentrations. The relatively high ratio at Bodega Bay also indicates some accumulation in the sediments and Figure 48e shows possible enrichment of total cadmium at this reference site. Because some of the Bodega Bay sediments containing a very low percentage of fine particles have total cadmium concentrations less than $0.1 \mu\text{g/g}$, other Bodega Bay stations in the range of 0.3 to $0.5 \mu\text{g/g}$ may be due to excess accumulation.

Extractable chromium at some urban sites like San Diego (both north and south), indicate possible enrichment of the sediment as shown by the HCl:Tot ratios (Fig. 49c). Bodega Bay, even with its very high total chromium concentrations, produced relatively low concentrations of acid-extractable metal indicating that these high concentrations are probably a natural geological component and not contaminant related.

Although acid-extractable copper was very high at some sites, it was surprising that the acid-extractable concentrations for some of the more heavily copper-contaminated sites like San Pedro and San Diego Bays, were relatively low (Fig. 49d). Even when copper concentrations were adjusted for grain size, sites such as south San Diego Bay with very high total copper, produced only a small amount of labile copper. Even though copper may accumulate in sediments, it may be poorly released by acid extraction (Allen et al. 1993) because of strong associations with factors such as

iron or manganese oxides, organic carbon, or mineralization. Even if sediment concentrations are much higher than background levels, the low HCl:Tot ratio may indicate low bioavailability; however, these low concentrations may be sufficient to cause toxicity. Sites with total copper concentrations much higher than background levels need to be examined in more detail in order to make conclusions about excess amounts and bioavailability.

Lead was quite labile (and probably available) at the urban sites and less so at the reference sites (Fig. 49e). One exception is the Bodega Bay site with its low total mean (sd) concentration (1.7 (1.2) $\mu\text{g/g}$) for which a very high HCl:Tot ratio was observed, indicating that a large percentage of the total amount may be due to anthropogenic input. These results are consistent with the high lead concentrations found in white croaker liver from this site (Fig. 31).

Manganese (Fig. 49f) levels were relatively constant in all sites which is not surprising since it is considered to be not a contaminant, but a natural component of the sediment which occurs at high concentration. The slight variation observed may be related to grain size differences found at the various sites.

Nickel also displayed high HCl:Tot ratios at urban sites and less at one reference site, Dana Point (Fig. 49g). Unlike chromium, the HCl:Tot ratio for nickel at Bodega Bay was very high, indicating that the high sediment concentrations of this metal may be due to external complexation on sediment particles. This situation could arise if nickel were high in the water because of some process (natural or human caused) in the river systems, causing this metal to accumulate in nearby coastal sediments.

Selenium, although high at some sites, showed virtually no extractable concentrations (Fig. 49h). The highest HCl:Tot ratios occurred at the sites with relatively low total concentrations which were mainly at urban sites. Even if selenium occurs at excess concentrations in the water column and associates with the

exterior of sediment particles, it is possible that the 1N HCl extraction is not the best method to assess the labile portion because of some strong controlling variable that is not affected by the acid. Conversely, selenium may not occur in excess concentrations in the water which would indicate that the variation in sediment concentrations seen in Figure 5 is due to natural geochemical enrichment.

Most sites studied displayed very high HCl:Tot ratios for silver except at Dana Point and Coos Bay, two sites with low total silver (Fig. 49i). Bodega Bay also contained low total silver, but a high extractable to total concentration ratio (HCl:Tot) which may be related to the low TOC and percent fines associated with this site. Even though the total silver concentration at Bodega Bay may be low, this total concentration was relatively high considering its sandy nature. Though the background concentration for silver is listed at 0.5 $\mu\text{g/g}$ (Table 5), it appears that some sites with concentrations below this level have very high HCl:Tot ratios, which may be due to anthropogenic or natural accumulation.

Tin in sediment, although very high at some sites, especially those which may contain high levels of butyltins, did not produce high extractable concentrations (Fig. 49j). Because butyltins are unaffected by 1N HCl and have no affinity for the acidified matrix, we would not expect organotins to be mobilized into the extractable phase. However, an urban site (e.g., Hunters Point) which may contain organotins, could exhibit elevated concentrations of inorganic tin (which is mobilized by 1N HCl) as a consequence of bacterial degradation of butyltins (tributyltin, dibutyltin, and monobutyltin) (TBT \rightarrow DBT \rightarrow MBT \rightarrow inorganic tin).

Zinc was high at many of the urban sites and the highest concentrations produced the highest levels of extractable metal (Fig. 49k). Of the four highest total concentrations, only Oakland had a total zinc concentration at the expected value, given its percentage of fine-grain sediment particles (Table 5, Fig. 47b). The total zinc concentration at the other sites, north and south San Diego Bays and San Pedro Outer

Harbor, exceeded their expected concentrations by 25 to 60 $\mu\text{g/g}$. In comparing the HCl:Tot ratio for Oakland and the other high total-concentration sites, no correlation to HCl:Tot ratios could be found. The only discernible pattern was with Dana Point and Bodega Bay which contained the lowest total concentrations and produced the lowest HCl:Tot ratios. One possibility is that zinc, like copper, is too strongly bound to one or more controlling ligands to be released by 1N HCl.

In summary, it appears that acid-extraction of elements from sediments may be a useful way to determine which locations contain excess amounts of metals and metalloids of concern. However, while this technique may work for many elements, some elements, while associated with sediment because of excess concentrations, may not be released by this technique. In several cases (cadmium, lead, nickel, and silver) the high ratios of extractable metals to total metals were from urban sites that are suspected of being contaminated by excess metals; however, some metals, such as copper and zinc, may not be amenable to such extraction due to undefined complexing properties of the sediment.

Correlations of elements in sediment—A correlation matrix of \log_{10} concentrations was used to form a dendrogram in cluster analysis in order to search for groups of elements that cooccur. We examined several subsets of the data, including Pacific coast urban sites, West Coast urban sites, Pacific coast nonurban sites (including reference sites), West Coast nonurban sites, all West Coast sites, and all Alaskan sites. Based on the metric of $1 - r$ (r is the product-moment (Pearson) correlation coefficient), we grouped elements with similar distributions over sites. From the dendrogram we chose 40 as the value for forming groups because it corresponded to a correlation coefficient of around 60 and because there were natural groupings below this value and few in the 40 to 50 range. When all Pacific coast urban sites (excluding reference and nonurban sites) were clustered ($n = 250$), one group

emerged which included copper, iron, lead, manganese, and zinc (Table 6; Fig. 50a). The high correlation of copper and lead has been noted before by Meador (1990) in sediments from Puget Sound, Washington and Rice et al. (in press) in sediments from the Hudson-Raritan estuary, New York. The cause of such association of elements in sediment is due to either a natural geochemical association or common pollutant sources. It is tempting to speculate that copper, lead, and zinc might generally cooccur in urban areas due to common inputs (i.e., urban areas have high inputs of these metals and nonurban areas have low inputs). Conversely, manganese and iron, which are known to act as ligands which control the sediment concentration of some metals, cooccur in such high concentrations that their association is probably due to a natural geological process which varies with grain size.

An examination of the cluster dendrogram for West Coast reference and nonurban sites (Fig. 50b, Table 7) and only Alaskan sites (Fig. 50c, Table 8) shows an interesting pattern. In the West Coast nonurban sites, copper and zinc were weakly correlated ($r = 0.50$) compared to all Pacific coast urban sites ($r = 0.87$). Lead was also less strongly correlated with copper and zinc in the reference sites when compared to urban sites but was weakly correlated with cadmium. For the Alaskan sites, the copper and zinc correlation was weak and the strong correlations consisted of a group containing aluminum, antimony, iron, lead, manganese, and zinc. For all Pacific coast urban sites, zinc and lead correlated at $r = 0.67$ (Table 6), which was much stronger than in West Coast reference and nonurban sites ($r = 0.26$) but essentially the same at Alaskan sites (0.74). Also, chromium and nickel, were highly associated in all urban sites and West Coast reference and nonurban sites, but less so at Alaskan sites (Table 8). For the West Coast reference sites, there was a weak correlation of elements to fine sediment which may be due to the limited range in grain size for these sites as compared to that observed for all reference (including Alaska) and nonurban sites (Table 4). Conversely, the correlation of elements and grain size may occur only

under conditions where excess elements occur in solution and can associate with sediment. If we assume that the native concentration of an element in sediment is a function of the whole particle, then the a priori assumption that surface area (as approximated by grain size) would control element concentration may not be appropriate because concentration would be a function of particle weight.

By plotting iron and manganese, two nonpollutant associated metals, separately for all West Coast (non-Alaskan) sites ($r = 0.77$) and all Alaskan sites ($r = 0.96$), it can be seen that both display a similar pattern of high correlation (Figs. 51a and 51b) leading us to believe that the natural geochemical makeup of the Alaskan sites is basically the same or very similar to that found at West Coast sites. Robertson and Able (1990) also found a good correlation ($r = 0.60$ to 0.72) between iron and manganese in their samples from the Gulf of Alaska. They also found a high correlation between aluminum and iron at these sites as we did in our Alaskan sites; however, we did not see a high correlation for our West Coast sites.

Figures 52a and 52b show the strong correlation between copper and zinc in all West Coast urban sites ($r = 0.92$) (no table shown) and weakly correlated in West Coast reference and nonurban sites ($r = 0.50$) and Alaskan sites ($r = 0.40$) (Fig. 52c). (If Nisqually Reach is included with West Coast nonurban sites, the correlation of copper and zinc increases to $r = 0.69$.) Notice also that the association between copper and zinc was very strong at high (contaminant) concentrations (Fig. 52a) which were in excess of those seen in Figure 52b (> 1.3 log ppm). Due to the natural geochemical similarity between Alaskan and West Coast sediments and the described pattern for copper and zinc, we conclude that these two elements have a common source in West Coast urban sites that is only weakly present in West Coast nonurban and Alaskan sites.

Lead and copper were also highly associated for all Pacific coast ($r = 0.71$, Table 6) and West Coast urban sites ($r = 0.75$), especially at high concentrations

(Fig. 53a) but only weakly correlated at Alaskan (Fig. 53b) and West Coast reference sites (Fig. 53c). We conclude from this that copper and lead are associated because of common urban sources which are only weakly present in nonurban West Coast and Alaskan sites. The basic pattern of association is present in Alaskan sites, but is weak because of a few sites (e.g., Skagway and Nakhu Bay) which are elevated with lead only. Although not high by site standards, the Alaskan sites, Skagway and Nakhu Bay, appear to be contaminated with lead, possibly from mining operations which are known to occur in the area. Lead and zinc are also highly correlated ($r = 0.74$) in all Alaskan sites which seems to be driven by the sites Skagway and Nakhu Bay and may be due to a common source, such as mining (Figure 54).

It is interesting to note that the most highly correlated elements (copper, zinc, selenium and lead) are also correlated with grain size, which occurs singly for each element (Fig. 47 and Table 4). Examination of urban sites indicates a correlation of percent fine sediment with either copper, lead, or zinc leading us to the conclusion that when elevated above background concentrations, these metals cooccur due to their accumulation in fine sediment of urban sites. This is in addition to the association of these metals to each other and sediment fines in reference and nonurban sites which may be due to either natural geochemical associations or accumulations from distant anthropogenic sources. It is possible that there is a global spread of certain elements which can cause elevations in concentrations at remote sites (e.g., our reference and nonurban sites) which would lead to similar, but weaker, correlations observed for urban sites. It is possible that some property associated with small grain size (e.g., surface area, manganese or iron coatings, or TOC) allows these elements to accumulate when they occur together from a common source (e.g., an urban area). One can readily see that urban areas with high concentrations of copper, zinc, and lead, could lead to high correlation coefficients for these elements.

Tissue and Sediment

Liver tissue and stomach contents—The concentration of each element in liver and stomach contents was plotted vs. total organic carbon content of the sediment in order to highlight those sites that contained fish with elevated tissue concentrations (Figs. 55a-k). Total organic carbon was chosen for the abscissa because it is one physical-chemical factor which may control the bioavailability of metals to individual fish.

Few correlations were found between mean liver and stomach contents concentration (Table 9), possibly due to greater temporal variation in the concentration of elements in stomach contents than that which may occur for liver. However, Figures 55 a-k show that at some sites, high liver concentration (upper figure) corresponds to high stomach contents concentration (lower figure). For several elements a site producing high concentrations in fish liver can also be found to have fish with that element at high concentration in stomach contents. Unfortunately, there were only a few samples for stomach contents and not every stomach contents concentration had a corresponding liver concentration, although we present data for most species and sites (Table 1 shows which species and sites have stomach contents data). These figures also help to explain the contradictory occurrence of high element concentrations in reference site (Bodega Bay, Dana Point, and Nisqually Reach) fish livers. It appears that the prey items in the stomachs of some fish can have high concentrations of certain elements which may in turn produce high liver concentrations. This is further supported by the high lability for some elements at reference sites as seen in the extractable-metals study (Fig. 49a-k).

Another interesting pattern is that some of the highest concentrations for the elements antimony, cadmium, mercury, and silver in liver occur at sites with the lowest TOC levels (0 - 0.5%). This leads to the hypothesis that elements at sites with lower sediment TOC may have greater bioavailability to fish than elements at sites

with high TOC. No such pattern occurs for the metals copper, lead, tin, and zinc. For the essential metals copper, selenium, and zinc, regulation by the animals may occur which would mask any such uptake patterns. For the nonessential metals lead and tin, it may be that the levels are not sufficiently high to produce such a pattern of high liver concentration at low TOC content. Additionally, there may be relatively few sites that are contaminated with these metals, or the bioavailability of these metals is very low due to strong complexation by the sediment. It should be kept in mind that essential elements such as copper, selenium, and zinc are regulated by fish and there may be a fine line between normal and toxic concentrations.

For many of the elements (antimony, arsenic, cadmium, copper, lead, mercury, nickel, selenium, silver, and zinc) it is obvious that some of the highest liver concentrations are found at the reference sites in Washington and California. This is generally not true for elements in flathead sole liver from Alaska when the reference site (Lutak Inlet) is compared to the urban sites. In general, the stomach contents concentrations, which is one measure of exposure, supports the high liver concentrations. For the elements antimony, arsenic, cadmium, lead, mercury, nickel, selenium, and silver, high liver concentrations have a correspondingly high stomach concentration at some of the West Coast reference sites. For example, silver (Fig. 55i) was very high in the liver of many fish from Dana Point and Bodega Bay. Although we had only a few measurements of stomach contents from these sites, we did find very high levels in one Dana Point fish, indicating at least the possibility that high concentrations can exist in the stomach contents. This would imply that the prey items, which were generally sediment dwelling invertebrates, were accumulating high concentrations of these elements that may then pass to the fish predators. It should also be kept in mind that while the mean concentration for most elements in reference sediments was low, there were often a few stations from these sites which

contained high concentrations. While these results are not conclusive, the data allow us to see the possibilities and formulate hypotheses for future work.

This pattern of increased liver concentration at low TOC sites may explain the observation that for some elements, fish livers from reference sites are often as high or higher than some urban sites. Most of our reference sites are characterized by low TOC content (Fig. 45). Any increase above natural background geochemical concentrations at these low TOC sites may allow an element to be more available on a unit weight basis compared to those sites with finer sediments and higher TOC content. This may be highly relevant for the sediment-dwelling invertebrates which selectively feed on the organic-carbon rich fine fraction of these coarse-grained sediments. This is a simplistic observation which ignores many controlling ligands for metals, such as acid volatile sulfides (AVS), oxides of manganese and iron, and other inorganic phases. It is possible that TOC correlates to one or several of these other ligands and may explain the observed pattern without being the causal factor. Acid volatile sulfides may have been a better variable to use for the abscissa, but we have no measurements for this parameter. Total organic carbon may be correlated to AVS content because sediments high in TOC are often anoxic, and AVS is associated with only anoxic sediments. The reference sites generally contain coarse sediment particles (sand) which contain little TOC and are hence probably fully oxidic. Sediments with low levels of AVS and TOC, in addition to coarse particles which contain low levels of iron and manganese oxides, may produce higher bioavailability on a per gram basis when compared to finer-grained sediment.

Significant correlations were observed between sediment and stomach contents for several elements when all species were considered as a group (Table 9). When individual species or species-groups were considered, some of these associations became stronger, suggesting that these species were more likely than others to take up and accumulate elements from dietary sources. For example, mercury in all

species correlated at $r = 0.57$, but when only English sole was considered, the correlation was even stronger ($r = 0.92$) (however the sample size was small: $n = 6$ site-year occurrences). Similar patterns can be seen for other elements and a few for stomach contents and sediment are shown in Figs. 56a-c. The general pattern of mercury in all species (Fig. 56a) shows a moderate but significant trend ($r = 0.57$) with several of the fish displaying high stomach contents concentrations at those sites with high sediment concentrations. Chromium (Fig. 56b) displayed a highly significant association ($r = 0.84$) which appears to indicate that prey of sand bass and white croakers contain high levels of this metal. This pattern was also strong in English sole and white croaker (Table 9) but weak in all other species. Lead in sand bass and croakers (Fig. 56c) showed a similar trend ($r = 0.65$) between the concentration in stomach contents and that found in sediment.

The correlation of sediment and stomach contents is always suspect because of the possibility that sediment may contaminate the sample and lead to erroneous conclusions about the source. We visually inspected our samples and determined that they were essentially free of sediment; hence, we believe that the dietary source to fish was mainly animal prey and not sediment. If sediment had contaminated our samples, we believe that many elements, not just a few, would have shown high correlation coefficients. Additionally, for elements such as mercury, the stomach contents concentration is often the same or higher than the sediment concentration which means that large quantities of sediment would be required to contaminate a sample in order to achieve these observed concentrations. Although small amounts of sediment in the samples may have eluded our detection, their presence would be acceptable because sediment is a possible dietary source of elements for these species and its contribution would be important.

Correlations of elements in liver tissue, stomach contents, and sediment--

Correlation analysis of the sediment and liver tissue data was performed in order to determine if any associations existed. Our main hypothesis was that high concentrations of elements in sediment would be reflected in the concentrations measured in the liver tissue of fish from the different sites.

We examined the association between elements in fish liver and sediment with all available data. The results presented in Table 10 are the correlations of all mean \log_{10} concentrations of elements in liver and sediment for each site over years. Each sediment and liver concentration was matched by location (site), species, and year. Some of the correlations in Table 10 were deemed spurious because a few points determined the high correlation coefficient which was not representative of the entire sample. Two of these correlations are shown in Figures 57a and b. We also tried correlating liver concentration with sediment concentration that had been normalized to organic carbon and found no improvement in describing relationships.

A few elements showed a consistent pattern over species. Mercury in liver and sediment was significantly correlated for all species which appears to be primarily due to the flatfish (English sole, flathead sole, hornyhead turbot, and starry flounder (minus two individual outliers) (Fig. 58a). This relationship can be improved when certain species combinations are chosen. In Figure 58b, the correlation of mercury in liver and sediment was 0.67 when we plotted species from predominantly low mercury sites (all flathead sole) and species from sites which were predominantly high in mercury (all white croaker). We were not able to assess the prey composition of each species; hence, we cannot derive any conclusions about dietary input to elucidate this particular association. Another example is zinc in flatfish which appears to have inversely correlated liver and sediment concentrations (Fig. 58c).

One reason for the lack of correlation for most elements may be due to the high variability between tissue samples from a given species. It is not uncommon to find

that the concentration of an element in three independent tissue or sediment samples from a site vary by a factor of 2 to 5. Even for one species at a given site in a given year, the coefficient of variation can exceed 50-100% or more. For example, in 1986 English sole from Bodega Bay (a reference site) exhibited a mean and standard deviation (sd) concentration in liver of silver, mercury, and cadmium of 1.3 (1.2), 1.0 (0.6) and 2.3 (1.8) $\mu\text{g/g}$, respectively. An example of the variation for both liver and sediment concentrations at various sites for one element and species can be seen in Figure 59.

Because of such large variability, attempting to correlate sediment and tissue concentrations is usually futile. Due to the fact that concentrations of elements in sediments are patchy and localized and because fish are usually very mobile, we would expect such variation to be normal. In the future, we recommend analysis of infaunal invertebrates which are generally much less mobile than fish and may reflect the elevated levels of metals and elements found in urban areas of our coastline. These data, in conjunction with concentrations in fish and stomach contents, may help to pinpoint areas of contamination. Assessment of infaunal invertebrates and their bioaccumulation of toxic elements will help us to determine food-chain transfer from prey organisms to fish and possible human consumers.

We also explored the concentrations of elements in liver, stomach contents, and sediment from all available data. The results are presented in GT2 plots (Figs. 60 a-l). The data are \log_{10} means of all liver, stomach contents, and sediment concentrations for a species at all sites where it occurs, over all years collected. Each bar in the GT2 plot is the mean concentration of that element in its respective compartment (e.g., BSLV is barred sand bass liver) and the vertical whiskers are the comparison interval. (In the floating bar-plots of Figures 3 through 43, the box is the standard deviation.) Nonoverlapping whiskers indicate significantly different means at the $\alpha = 0.05$ level. Numbers above the bars are sample sizes. The concentration of

elements from each sediment station (A, B, and C) and individual fish analyzed at a given site were used to construct the GT2 plots. With these GT2 plots, comparisons can be made between like or dissimilar compartments within a figure (e.g., liver between different species or stomach contents vs. liver for one species).

Unfortunately, there was no one-to-one correspondence between liver and stomach contents samples (e.g., stomach contents were composited and livers were from individuals). Also, because we have very little information regarding the nature of the stomach contents from these samples, we cannot make any inferences about trophic transfer. Some species (e.g., English sole) feed predominantly on invertebrates and others ingest fish. Some species (e.g., white croaker) will take both kinds of prey which may lead to highly variable stomach contents concentrations. Another cause of variability is the mobility of the fish which allows them to feed over a large area that may have a patchy distribution of sediment contaminants. On a temporal scale, stomach contents concentrations can be much more variable than liver concentrations because fish feed over a wide area with known chemical heterogeneity, whereas the liver integrates over the whole exposure area.

In general, by looking at the concentrations in all individuals of a species we are ignoring some geographical patterns, including urban vs. reference sites, but we are increasing the sample size over that seen in Figures 9 through 43 which gives us more power to discriminate patterns. Also, by looking at a species, we are integrating some geographical patterns; for example, all flathead sole samples were from Alaska and barred sand bass were generally from southern California (San Diego).

When individual elements are considered, some interesting trends can be seen. One clear trend for many elements (e.g., antimony, chromium, lead, nickel) is that the liver concentration is lowest of the three compartments, followed by stomach contents, and then sediment concentration which is the highest of the three. Other elements (copper and zinc) show basically no pattern, although a few (e.g., copper in

starry flounder and zinc in hornyhead turbot and starry flounder) show a trend of increasing concentration from sediment to stomach contents to liver. Still other elements (arsenic, cadmium, mercury, selenium, and silver) were quite low in sediment and displayed an increasing trend in tissue (stomach contents to liver), indicating bioaccumulation.

Antimony. When all samples for antimony are considered, white croaker and barred sand bass liver were generally lower (not significantly) than the other species (Fig. 60a) and sediment was generally uniform. However, white croaker liver was significantly lower in concentration than English sole, but only slightly. None of the stomach contents concentrations were significantly different when compared among species, and there was a strong tendency for antimony to decrease from sediment to liver.

Arsenic. Arsenic, a nonessential element, exhibited few patterns (Fig. 60b). The most noteworthy is that flathead sole had significantly higher concentrations of arsenic in their liver than all other species except English sole, even though the sediment concentration associated with flathead sole was not particularly high. Interestingly, all flathead sole samples were from Alaska, which is noted for high arsenic levels in fish (Fig. 14) although sediment concentrations were not elevated (Fig. 3). There seems to be a trend of increasing concentration (significantly higher) from sediment to liver for flathead sole and English sole for arsenic which may indicate biomagnification, (assuming two or more trophic levels are involved).

Cadmium. The data for cadmium are highly variable and few patterns can be discerned (Fig. 60c). When means are examined, it appears that there was a general increase of concentration from sediment to liver for all species. This pattern is strongest for English sole, starry flounder, and white croaker, and there was a significant difference between liver and sediment concentrations for four of the species (English sole, hornyhead turbot, starry flounder, and white croaker) indicating

bioaccumulation. When all species are compared, none show significant differences in liver cadmium.

Chromium. The data for chromium are relatively consistent for liver, stomach contents, and sediment concentrations (Fig. 60d). Examination of sediment and liver concentrations shows no difference among species. Because chromium is considered to be an uncommon contaminant, it is not surprising to find such uniformity.

Copper. Copper concentrations are generally uniform but show some pattern of increasing from sediment to tissue in starry flounder and white croaker (Fig. 60e). Also noteworthy is barred sand bass which exhibited significantly reduced copper concentrations in the liver, a possible species specific characteristic. This is supported by the low concentrations in fish from urban and nonurban sites. Interestingly, barred sand bass occurred at sites with the highest sediment copper. This observation is counterintuitive and will be pursued further. White croaker and starry flounder liver also seems to be higher in copper than that found in the other species, especially English sole and flathead sole, which appears to correlate with sediment concentrations.

Lead. Lead was always lower in liver tissue than stomach contents or sediment (Fig. 60f). For most species there was a strong pattern of decreasing concentration from sediment to stomach contents and liver; however, none of the species were significantly different. The concentration in liver appears uniform across all species with the highest variability in flathead sole, which were all from Alaska. Alaskan sites display some of the highest and lowest lead concentrations in both fish liver and sediment concentration (Figs. 4 and 16).

Mercury. The concentration of mercury in liver, stomach contents, and sediment was relatively uniform across sediment samples, but significantly elevated for some sites (Fig. 60g). Mercury was considerably (and significantly) higher in barred sand bass and white croaker liver than in flathead sole, English sole, and starry

flounder, which seems to be associated with sites that have high sediment concentration. Barred sand bass and white croaker are species collected from sites (such as Long-Beach, San Diego, Hunter's Point) that are considered contaminated with mercury (Table 5). Flathead sole, from the Alaskan sites which contained very little mercury in the sediment, displayed the lowest mercury concentrations in liver. Barred sand bass, which may prey on fish, are found at sites with high mercury concentrations in the sediment and are therefore more likely to bioaccumulate mercury than species which prey predominantly on organisms lower in the food web (e.g., invertebrates). The other species listed above are all flatfish and feed predominantly on invertebrates. It is interesting to note that mercury in fish and invertebrates is predominantly in the organic form (Bloom 1992), which allows it to be bioaccumulated to a greater extent than the inorganic forms.

Nickel. Nickel concentrations were always lower in fish liver and considerably higher in sediment (Fig. 60h). There appears to be no difference among species except that English sole and white croaker liver show slightly higher levels of nickel than the other four species. The sediment concentrations for nickel were not greatly different among sites and the lowest nickel concentrations in liver are associated with the lowest sediment concentrations.

Selenium. There was a very strong gradient of selenium concentration from the sediment to stomach contents and liver (Fig. 60i). There was essentially no difference among sediment concentrations as seen by the comparison intervals except at sites for flathead sole which were significantly higher than sediment found at sites where English sole and barred sand bass were collected. Also, concentrations of selenium in white croaker were significantly higher than those found in starry flounder and hornyhead turbot, although the sediment concentration for sites where these species were collected was not high. Because selenium is an essential element, and the concentrations measured in liver were in the normal range for fish livers,

there appears to be no contaminant-related concentrations. However, the range in selenium concentration that determines healthy from toxic may be narrow and, of course, if levels were high enough to be toxic, those individuals may not have been collected.

Silver. This metal was significantly lower in the liver of barred sand bass and almost so for flathead sole when compared to sediment (Fig. 60j). Conversely, when hornyhead turbot and white croaker were examined, silver concentrations in their livers were higher (but not significantly) than that found in sediment. Silver in English sole and starry flounder liver was essentially the same as in sediment. There was high variability in silver concentrations found in fish liver, ranging almost tenfold between barred sand bass and hornyhead turbot. Silver in liver of white croaker and hornyhead turbot was significantly higher than that found in barred sand bass, English sole, flathead sole, and starry flounder. Both flathead sole and English sole had low liver concentrations which corresponded to low sediment concentrations. Conversely, barred sand bass liver silver content was low but the sediment concentration was higher than most other sediment groups.

Tin. There was no pattern among liver or sediment tin concentrations, although English sole and starry flounder displayed a slight elevation in concentration over white croaker and barred sand bass (Fig. 60k). The significantly lower tin concentration in stomach contents of flathead sole from Alaska may reflect lower levels of organotins, which we suspect are very low in invertebrate prey at these sites. Because organotins (particularly TBT) can bioaccumulate in tissue, sites with slight differences in total tin, but large differences in organotins, may contain invertebrates with widely different body burdens of tin.

Zinc. When all sites are considered, it appears that sediment zinc concentrations varied only slightly among sites (Fig. 60l). The same is true for zinc in liver; however, hornyhead turbot were significantly higher than barred sand bass.

Because zinc is an essential element and regulated by fish, we are not sure if the differences seen in liver were due to exposure differences or inherent species variability.

CONCLUSIONS

Some metals and metalloids in sediment from urban sites were elevated to concentrations higher than natural geochemical levels. The sites that were most contaminated contained many elements over background concentration, but the elements found most often in excess were lead, nickel, and zinc. Other elements such as copper, silver, and tin were also found to frequently exceed background concentrations, whereas elements such as arsenic, cadmium, mercury, and selenium were found less frequently at elevated concentrations.

Correlation analysis revealed that copper, lead, and zinc from Pacific coast urban sites were associated with each other, suggesting that they may be from a common source. This pattern was generally weak at nonurban West Coast sites suggesting that copper, lead, and zinc were highly associated mainly in urban areas, possibly due to anthropogenic inputs to coastal waters, but that a global spread (widespread dissemination) of these elements to nonurban sites may be producing weak associations. In addition, a moderately strong association was found between lead and zinc at all Alaskan sites that was also present in Pacific coast urban sites but weak at West Coast nonurban sites. We conclude from these patterns that some Alaskan sites have elevated concentrations of these metals which may be due to a common source, such as mining.

The study on extractable metals revealed interesting patterns which may help elucidate the patterns of excess accumulation. Because dissolved concentrations of elements may be elevated in contaminated areas, accumulations may result by

association with external coatings of sediment particles. The natural geochemical makeup of sediment particles consists of all the elements under consideration, but most are integrated within the matrix of the particle. Release of these elements is accomplished only through total acid digestion, whereas the surface associated elements may be released with a weak acid extraction. By comparing the total amount of an element to the amount leached off the sediment particles with weak acid, we attempted to assess the amount of contaminant accumulation in sediment due to elevated concentrations of waterborne elements. Several elements displayed high extractable to total concentration ratios in sediment from urban sites indicating that a large proportion of the total element was easily displaced from the sediment surface. This pattern is consistent with the theory of excess accumulation of certain elements in sediment.

In all but a few cases, the concentrations of toxic elements in the livers of fish from urban sites were similar to those in livers from nonurban sites. In general, there was no strong correlation between element concentrations in fish liver and sediment with the one exception of mercury in flatfish. Several factors may contribute to the lack of correlation, including 1) the fact that sediments and tissues exhibit high variation at a given site within a given year; 2) insufficient assessment of other biological compartments (e.g., other tissues besides liver) that are involved in bioaccumulation; and 3) the lack of determination of the bioavailable fraction of the total concentration found in sediment. Although there were few significant differences between populations at these different sites, trends were evident and we believe that as comparison-sample sizes increase, significant differences will become more apparent.

When all individuals of a fish species are examined, some species show elevated concentrations of elements in liver, such as arsenic in flathead sole and mercury in barred sand bass and white croaker which is probably due to higher

sediment concentrations at the sites where these species are found. Reduced levels of mercury in flathead sole (taken only in Alaskan waters) compared to other West Coast flatfish correlates with variable sediment concentration and is an indication of urban related bioaccumulation.

Concentrations of elements in stomach contents show much greater correlation to sediment concentrations than do those in fish liver which may be due to the relative immobility of the invertebrate prey and their closer reflection of the ambient conditions. Of course these differences could also be attributed to different abilities of the invertebrate prey and the fish to regulate accumulate elements. Although our database is small and incomplete, it appears that many elements in liver were very high in fish from reference sites which may be caused by elevated concentrations in prey. One explanation for this considers the bioavailability of metals from sediments at these reference sites, which often have very low amounts of fine sediment particles ($<63\ \mu\text{m}$). Because some elements may concentrate in the fine fraction of these coarse-grain (sandy) sediments leading to high concentrations in this fraction and many sediment dwelling invertebrates select the fine fraction for ingestion, element concentrations may be higher in these species when compared to species from sediments with a higher percentage of fine particles and less element per gram of fine material. The relatively small amount of fine particles of these coarse-grained sediments contain most of the organic carbon and surfaces for element adsorption and accumulation.

Differences in element concentrations in fish liver may be due to either increased bioaccumulation at some sites over others or because of inherent species differences unrelated to contaminant exposure. In general, we assume that accumulations of nonessential elements were attributed to contaminant exposure, whereas variations for essential elements could be caused by differences in species physiology. Analysis of tissue concentrations in relation to sediment concentrations

revealed that some nonessential elements (arsenic, cadmium, and mercury) displayed a strong pattern of increasing concentration in some species from sediment, to stomach contents, to liver and, therefore, were probably bioaccumulated. Others elements (copper, silver, and zinc) displayed a weak trend in some species indicating possible bioaccumulation at some locations. For the essential elements (copper and zinc) it is not possible to tell if the species differences were due to bioaccumulation from contaminated sediments or were just inherent species differences. The remainder of the elements (antimony, chromium, lead, nickel, and selenium) displayed no pattern over sediments and species indicating no bioaccumulation or species differences were found.

While this report represents 5 years of data, and a seemingly large database, many more years of sampling will be needed before definite trends can be identified. Because of the large variability observed in sediment and tissue concentrations, associations between tissues and sediments are general trends with little statistical confidence. It is encouraging to see emerging patterns of element abundance in a data set such as this with its inherent uncertainty due to spatial and temporal variability, myriad geochemical factors, and physiological mechanisms.

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TABLES

Table 1. Pacific coast sites sampled in Cycles I-V (1984-1988) as part of the National Benthic Surveillance Project.

State	Site name	Site abbrev.	Location Lat. (N) Long. (W)	Years 84 85 86 87 88	Type of site	Fish species
AK	Oliktok Point	OlktPt	70°30.4' 149°53.4'	• •	N	FH, AF
AK	Endicott Field	EnFl	70°20.8' 147°58.0'	• •	U	FH
AK	Chukchi Sea	ChkS	67°29.5' 164°02.8'	•	N	Ø
AK	Port Moller	PtMl	56°06.4' 160°41.0'	•	N	FS
AK	Dutch Harbor	DuHb	53°54.0' 166°29.9'	• •	U	FS
AK	Kamishak Bay	KmBy	59°11.7' 153°39.6'	• •	N	FS
AK	Port Valdez	PtVz	61°06.5' 146°15.5'	• •	U	FS
AK	Lutak Inlet	LtIn	59°18.7' 135°31.5'	• •	R	FS
AK	Nakhu Bay	NkBy	59°28.1' 135°20.3'	• •	N	FS
AK	Skagway	Skag	59°26.6' 135°19.7'	• •	E/U	FS
AK	Boca de Quadra	BdQd	55°16.5' 130°32.5'	• •	N	FS
WA	Elliott Bay	ElBy	47°35.5' 122°21.4'	• •	U	ES
WA	Commencement Bay	CmBy	47°16.7' 122°25.0'	• •	U	ES
WA	Nisqually Reach	NsRh	47°06.7' 122°41.9'	• •	R	ES
OR	Columbia River	CIRes	46°13.2' 123°55.6'	• •	U	SF
OR	Youngs Bay	YnBy	46°10.2' 123°50.1'	• •	E/U	SF
OR	Coos Bay	CsBy	43°22.6' 124°12.5'	• •	U	SF, ES
CA	Humboldt Bay	HmBy	40°48.7' 124°09.8'	• •	E/U	SF
CA	Farallon Islands	FrIs	37°39.4' 123°03.5'	• •	E/N	Ø
CA	Bodega Bay	BdBy	39°18.3' 123°02.5'	• •	R	ES, WC, SF
CA	Islais Creek	IsCk	37°44.9' 122°22.7'	• •	E/U	WC
CA	Hunters Point	HnPt	37°42.0' 122°21.5'	• •	U	WC, SF
CA	Redwood City	RdCy	37°33.4' 122°11.2'	• •	U	WC
CA	Oakland Estuary	OkEs	37°46.8' 122°15.0'	• •	U	WC
CA	Oakland	Oakl	37°47.5' 122°20.3'	• •	U	WC
CA	Southampton Shoal	SoSh	37°53.2' 122°24.4'	• •	U	SF
CA	Castro Creek	CsCk	37°58.9' 122°24.8'	• •	U	SF
CA	San Pablo Bay	SPbBy	38°02.9' 122°17.6'	• •	U	SF
CA	Moss Landing	MsLg	36°48.1' 121°47.6'	• •	E/U	ES
CA	Monterey Bay	MtBy	36°37.6' 121°52.3'	• •	U	ES
CA	Estero Bay	EBY	35°21.5' 121°53.2'	•	E/N	Ø

Table 1. Continued.

State	Site name	Site abbrev.	Location		Years				Type of site	Fish species
			Lat. (N)	Long. (W)	84	85	86	87	88	
CA	San Luis Obispo	SLO	35°06.0'	120°45.9'					•	♂
CA	Channel Islands	ChnIs	34°00.9'	120°01.7'			•			♂
CA	West Santa Monica	wSMBY	33°56.5'	118°33.3'			•		•	HT
CA	East Santa Monica	eSMBY	33°53.2'	118°25.8'	•	•				HT
CA	San Pedro Canyon	SPCn	33°42.0'	118°15.7'	•					HT
CA	San Pedro Outer Harb	SPOHb	33°42.6'	118°15.4'		•	•	•		WC
CA	Long Beach	LnBh	33°44.6'	118°10.6'		•	•	•		WC
CA	Cerritos Channel	CrCh	33°45.8'	118°15.3'						WC*
CA	Seal Beach	SlBh	33°44.1'	118°08.8'	•					WC
CA	Dana Point Inside	DnPti	33°26.6'	117°40.5'				•		♂
CA	Dana Point	DnPt	33°26.7'	117°41.4'	•	•	•	•	•	HT, BS, WC, SF, ST
CA	Oceanside	Ocn	33°12.6'	117°24.8'				•		♂
CA	Mission Bay	MsBy	32°47.3'	117°14.7'			•			BS*
CA	outside Mission Bay	oMsBy	32°47.1'	117°15.8'					•	♂
CA	Outside San Diego	oSDBY	32°39.2'	117°11.5'	•	•				HT, ES, ST
CA	North San Diego	nSDBY	32°43.2'	117°11.3'	•	•	•	•	•	WC, BS, ST
CA	South San Diego	sSDBY	32°41.0'	117°08.2'	•	•	•	•	•	BS, SB, DT
CA	National City	NtCy	32°39.9'	117°07.6'				•		BS
CA	Shelter Island	ShIs	32°42.5'	117°13.6'				•		BC
CA	West Harbor Island	wHIs	32°43.3'	117°12.7'				•		WC

Type of site: U = urban; N = nonurban; R = reference; E = exploratory. Fish species: AF = arctic flounder, BC = black croaker, BS = barred sand bass, DT = diamond turbot, ES = English sole, FH = fourhorn sculpin, FS = flathead sole, HT = hornyhead turbot, SB = spotted sand bass, SF = starry flounder, ST = spotted turbot, WC = white croaker. * Fish only (no sediment), ♂ sediment only (no fish). Bold site names are reference sites. Bold species abbreviations are those with liver and stomach contents data; italics denote stomach contents only. Years sampled shows when sediment and fish collected and analyzed (sediment only in 1988).

Table 2a. Target and exploratory fish species and the sites where collected for elemental analysis.

Species	Abbr	Sites of capture
Arctic flounder (<i>Liopsetta glacialis</i>)	AF	Oliktok Point, AK.
Barred sand bass (<i>Paralabrax nebulifer</i>)	BS	Dana Point, Mission Bay, National City, and north and south San Diego Bay, CA.
Black croaker (<i>Cheilotrema saturnum</i>)	BC	Shelter Island, CA.
Diamond turbot (<i>Hysopsetta guttulata</i>)	DT	south San Diego Bay, CA.
English sole (<i>Parophrys vetulus</i>)	ES	Elliott Bay, Commencement Bay, and Nisqually Reach, WA; Coos Bay, OR; Bodega Bay, Moss Landing, Monterey Bay, and outer San Diego Bay, CA.
Flathead sole (<i>Hippoglossoides elassodon</i>)	FS	Port Moller, Dutch Harbor, Port Valdez, Kamishak Bay, Boca de Quadra, Nakhu Bay, Skagway, and Lutak Inlet, AK
Fourhorn sculpin (<i>Myoxocephalus quadricornis</i>)	FH	Oliktok Point and Endicott Field, AK.
Hornyhead turbot (<i>Pleuronichthys verticalis</i>)	HT	East and west Santa Monica Bay; Dana Point; San Pedro Canyon; and outside San Diego Bay, CA.
Spotted sand bass (<i>Paralabrax maculatofasciatus</i>)	SB	south San Diego Bay, CA.
Spotted turbot (<i>Pleuronichthys ritteri</i>)	ST	Dana Point, north and outer San Diego Bay, CA.
Starry flounder (<i>Platichthys stellatus</i>)	SF	Columbia River estuary, Youngs Bay and Coos Bay, OR; Bodega Bay, Humboldt Bay, San Pablo Bay, Southampton Shoal, Hunters Point, and Dana Point, CA.
White croaker (<i>Genyonemus lineatus</i>)	WC	Bodega Bay, Hunters Pt, Oakland, Oakland est, Islais Cr, Redwood City, San Pedro Outer Harb, Seal Beach, Cerritos Channel, Long Beach, Dana Point, west Harbor Is, and north San Diego Bay, CA.

Bold names are target species. Stomach contents only for AF and DT. Black croaker at only one site. Spotted sand bass and spotted turbot were secondary species at their respective sites.

Table 2b. Fish lengths. Mean and standard deviation (sd) fish lengths in millimeters for all years collected.

Site	mean	sd	Species	Site	mean	sd	Species
BdBy	432	119	Starry flounder	MtBy	351	49	English sole
BdBy	284	41	English sole	NkBy	262	10	Flathead sole
CIREs	259	83	Starry flounder	nSDBy	221	26	spotted turbot
BdQd	321	19	Flathead sole	nSDBy	285	20	White croaker
CmBy	314	33	English sole	NsRh	308	41	English sole
BdBy	265	27	White croaker	NtCy	251	5	Barred sand bass
CrCh	231	6	White croaker	Oakl	202	36	White croaker
CsBy	197	48	Starry flounder	OkEs	188	11	White croaker
CsCk	299	89	Starry flounder	OikPt	163	41	Fourhorn sculpin
DnPt	238	24	White croaker	oSDBy	226	13	Hornyhead turbot
DnPt	256	38	Hornyhead turbot	PtMI	318	17	Flathead sole
ElBy	289	37	English sole	PtVz	311	25	Flathead sole
DuHb	203	6	Flathead sole	RdCy	241	44	White croaker
DnPt	270	29	Barred sand bass	ShIs	250	0.6	Black croaker
EnFl	195	46	Fourhorn sculpin	SkG	267	15	Flathead sole
eSMBY	235	23	Hornyhead turbot	SlBh	202	7	White croaker
HmBy	323	205	Starry flounder	SoSh	492	46	Starry flounder
HnPt	289	32	White croaker	SPbBy	293	31	Starry flounder
HnPt	430	66	Starry flounder	SPCn	234	23	Hornyhead turbot
KmBy	328	12	Flathead sole	SPOHb	244	12	White croaker
IsCk	266	40	White croaker	sSDBy	221	46	Spotted sand bass
LnBh	238	18	White croaker	sSDBy	233	41	Barred sand bass
LtIn	321	45	Flathead sole	wHIs	264	5	White croaker
MsLg	378	48	English sole	wSMBY	225	26	Hornyhead turbot
MsBy	235	10	Barred sand bass	YnBy	223	24	Starry flounder

Site abbreviations in Table 1. See Figures 9-43 for sample sizes.

Table 3. Elements analyzed in sediment, liver, and stomach contents.

Element	Symbol	<u>Limit of detection</u>		<u>Method</u>	
		Sediment	Tissue	Sediment	Tissue
Aluminum	Al	500	nd	N ₂ O-F	nd
Antimony	Sb	0.1	0.1	GF	GF
Arsenic	As	0.1	0.1	ZGF	ZGF
Cadmium	Cd	0.01	0.01	ZGF	ZGF
Chromium	Cr	1.0	0.1	F	GF
Copper	Cu	1.0	0.1	F	GF
Iron	Fe	500	4.0	F	F
Lead	Pb	0.1	0.1	GF	GF
Manganese	Mn	5.0	0.5	F	F
Mercury	Hg	0.01	0.01	CV	CV
Nickel	Ni	0.1	0.1	GF	GF
Selenium	Se	0.1	0.1	ZGF	ZGF
Silver	Ag	0.01	0.01	GF	GF
Tin	Sn	0.1	0.1	GF	HGF
Zinc	Zn	5.0	1.0	F	F

Limit of detection in $\mu\text{g/g}$ dry weight for 0.3 g dry weight samples and method used to analyze prepared digests. N₂O-F: nitrous oxide flame atomic absorption spectroscopy (AAS); F: air-acetylene flame AAS; GF: graphite furnace AAS; ZGF: Zeeman-corrected graphite furnace AAS; CV: cold vapor AAS; HGF: hydride generation AAS; nd means not determined.

Table 4. Product-moment correlations in sediment for Pacific coast reference and nonurban sites. Correlations of log₁₀ element concentrations for all reference and non-urban sites, including some exploratory sites. Sites include Bodega Bay, Boca de Quadra, Chukchi Sea, Channel Islands, Dana Point, Estero Bay, Farallon Islands, Kamishak Bay, Lutak Inlet, Oliktok Point, and San Luis Obispo. Number of measurements between 39 and 57 for stations over years for each element. Bold entries are significant at $\alpha = 0.00033$.

	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Si	Sn	Zn	Fine	TOC	
Ag	0.43	-0.35	-0.26	0.25	0.26	0.34	-0.01	0.36	0.11	-0.18	0.33	0.11	-0.35	0.30	0.19	0.01	0.25	Ag
Al		-0.01	0.29	-0.33	0.22	0.33	-0.16	0.46	-0.43	0.37	0.54	0.13	-0.44	0.22	0.34	0.41	0.34	Al
As			-0.07	0.03	-0.54	-0.13	0.07	-0.17	0.08	-0.03	-0.12	-0.11	0.60	-0.01	-0.22	-0.27	-0.41	As
Cd				-0.45	0.29	0.23	-0.01	0.19	-0.24	0.60	0.24	0.49	-0.27	-0.12	0.30	0.51	0.23	Cd
Cr					-0.23	0.01	0.10	-0.14	0.76	-0.69	-0.23	-0.45	0.28	0.14	-0.25	-0.59	-0.25	Cr
Cu						0.77	-0.23	0.60	-0.11	0.50	0.22	0.53	-0.58	0.13	0.81	0.76	0.44	Cu
Fe							-0.06	0.86	0.14	0.35	0.38	0.52	-0.43	0.05	0.90	0.67	0.29	Fe
Hg								-0.14	0.26	-0.07	0.20	-0.08	0.23	-0.30	-0.11	-0.21	-0.02	Hg
Mn									-0.11	0.38	0.37	0.48	-0.45	0.09	0.78	0.60	0.24	Mn
Ni										-0.57	-0.13	-0.13	0.19	-0.10	-0.08	-0.32	0.12	Ni
Pb											0.34	0.59	-0.24	-0.04	0.47	0.63	0.24	Pb
Sb												0.33	-0.38	-0.10	0.43	0.31	0.18	Sb
Se													-0.42	-0.10	0.63	0.66	0.64	Se
Si														-0.10	-0.53	-0.61	-0.54	Si
Sn															-0.01	-0.10	0.26	Sn
Zn																0.86	0.38	Zn
Fine																	0.35	Fine

Element abbreviations are defined in Table 3. TOC is total organic carbon and Fine is fine sediment particles (< 63 μm).

Table 5. Mean concentrations measured in bulk sediment for stations considered contaminated. Values are mean, standard deviation (sd) ($\mu\text{g/g}$ dry wt.), and number of samples for all concentrations that exceeded the baseline concentration for that element. Single values are concentrations of single station overages. Total number of possible samples in Figures 3-8. Most sites sampled at three stations.

St	Site	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Se	Sn	Zn
		0.5	12	1.3	300	16-95*	0.7	30	27	1.4	0.4-2.5*	4.6	56-263*
AK	Boca de Quadra												
AK	Chukchi Sea												
AK	Dutch Harbor												
AK	Endicott Field												
AK	Kamishak Bay												
AK	Lutak Inlet												
AK	Nakhu Bay			1.3					43 (9) 3		1.3		180
AK	Oliktok Point							45 (1) 2					
AK	Port Moller												101 (11) 3
AK	Port Valdez								29				
AK	Skagway								52 (13) 3				171 (58) 2
WA	Commencement								37 (7) 4				
WA	Elliott Bay			1.3		105 (37) 9	0.8 (0.1) 2	37 (3) 8	67 (22) 5	2.5 (1) 2			187 (45) 9
WA	Nisqually Reach						0.9	35 (5) 8		1.6			99 (13) 9
OR	Columbia River												92 (14) 8
OR	Coos Bay					24		39 (9) 5			0.6		116
OR	Youngs Bay	0.75 (0.2) 2											
CA	Bodega Bay				570 (215) 12			61 (12) 10					
CA	Castro Creek					51.4 (7.6) 2		83 (7) 6	39 (19) 3	2		5 (0.4) 3	118 (23) 3
CA	Channel Islands												
CA	Dana Point												
CA	Estero Bay				5770			49					
CA	Farallon Is.			3.3				42					
CA	Humboldt Bay				597 (177) 2			60 (13) 3		1.8			

Table 5. Continued.

Element	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Sb	Se	Sn	Zn
Baseline Conc.	0.5	12	1.3	300	16-95*	0.7	30	27	1.4	0.4-2.5*	4.6	56-263*
CA Hunters Point	0.62 (0.17) 8	25 (20) 4		371 (40) 3			81 (30) 15	39 (11) 9			6 (0.3) 4	139
CA Islais Creek	0.87						108 (35) 2	47 (17) 2				
CA Long Beach			1.3				39 (5) 6	101 (32) 9			5	226
CA Mission Bay out												
CA Monterey Bay												
CA Moss Landing	1.8 (0.1) 3											
CA National City	1.9 (0.2) 4	14 (1.5) 3			114 (50) 4		36	56 (7) 4			6 (2) 3	237 (90) 5
CA Oakland		13 (0.3) 3				1.2	104 (4) 3	44 (2) 3				
CA Oakland Est	0.55 (0.2) 3	14 (0.8) 4			129 (23) 3	1.1 (0.3) 6	125 (24) 6	99 (10) 6			11 (6) 5	310 (34) 6
CA Oceanside												
CA Redwood City							92 (4) 6	30 (3) 6			9 (5) 3	
CA San Luis Obispo	0.6											
CA San Pablo Bay		13 (0.4) 3		597 (129) 6	51 (6) 2	2.2	79 (17) 13	33 (5) 3				115 (20) 7
CA San Pedro Cany			1.5 (0.1) 2		40					0.8 (0.1) 2	5.2	118 (11) 3
CA San Pedro OH	0.66 (0.17) 9		1.3		102 (32) 9		47 (12) 6	44 (10) 7		2.1	6.7	166 (40) 4
CA E. Santa Monica								33 (2) 3				
CA W. Santa Monica	5.6 (4.1) 6		4.6 (3.6) 2		67 (34) 5			43 (20) 2		0.9	8 (4) 2	145 (50) 3
CA Seal Beach						0.9		31 (5) 2				
CA Shelter Island					46						11 (6) 2	108
CA N. San Diego	1.3 (0.1) 6				103 (23) 9	0.8 (0.1) 4		51 (13) 10		1.0	8 (4) 5	230 (40) 9
CA O. San Diego												
CA S. San Diego	1.8 (0.4) 12	13 (1.2) 5	1.6		181 (46) 15	1.2 (0.4) 7		73 (32) 15			7 (3) 13	281 (72) 15
CA Southampton		14 (1.2) 5		323 (8) 2			64 (17) 15	34 (7) 3				89 (8) 8
CA West Harbor Is					48 (5) 2			29 (2) 3			13 (10) 2	126 (20) 5
Hanson et al. 1993	0.14-0.2	6 - 24	0.3 - 0.4	40-140	5-26	0.1-0.2	11-50	12 - 47		0.4 - 0.9		40 - 175
Katz and Kaplan 1981	0.4		0.4	25	9		15	10				44

* Regression equation used to determine baseline concentration as it varied over percent fine sediment. Hanson et al. and Katz and Kaplan published background sediment concentrations from other areas which are listed here for comparison. See text and Figure 47 for additional details. Element abbreviations in Table 3. Reference sites are in bold.

Table 6. Product-moment correlations in sediment for Pacific coast urban sites. Correlations of \log_{10} element concentrations for all West Coast and Alaskan urban sites. Number of measurements between 184 and 250 for stations over all years for each element. Bold entries are significant at $\alpha = 0.00033$.

	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Si	Sn	Zn	Fine	TOC	
Ag	0.27	0.25	0.25	0.08	0.56	0.31	0.40	0.16	0.04	0.57	0.02	0.03	-0.26	0.39	0.52	0.31	0.19	Ag
Al		0.21	0.22	-0.01	0.38	0.44	0.12	0.41	0.07	0.43	0.38	0.08	-0.22	0.36	0.38	0.23	0.01	Al
As			0.08	0.37	0.35	0.17	0.27	-0.06	0.32	0.29	0.04	-0.01	0.01	0.22	0.23	0.29	-0.01	As
Cd				-0.22	0.39	0.18	0.31	0.12	-0.03	0.33	0.26	0.30	-0.29	0.25	0.33	0.19	0.31	Cd
Cr					0.12	0.30	0.07	0.22	0.67	-0.04	0.03	0.07	0.04	0.06	0.13	0.17	-0.08	Cr
Cu						0.68	0.68	0.38	0.31	0.71	0.21	0.29	-0.53	0.55	0.87	0.62	0.45	Cu
Fe							0.35	0.79	0.53	0.42	0.35	0.29	-0.51	0.31	0.84	0.61	0.33	Fe
Hg								-0.01	0.26	0.58	0.19	0.15	-0.35	0.44	0.62	0.36	0.34	Hg
Mn									0.27	0.16	0.34	0.27	-0.36	0.19	0.58	0.28	0.10	Mn
Ni										0.12	0.18	0.23	-0.15	0.06	0.35	0.38	0.14	Ni
Pb											0.12	0.26	-0.38	0.56	0.67	0.56	0.37	Pb
Sb												0.21	-0.35	0.06	0.31	0.22	0.15	Sb
Se													-0.38	0.18	0.33	0.46	0.55	Se
Si														-0.19	-0.56	-0.58	-0.52	Si
Sn															0.52	0.26	0.22	Sn
Zn																0.65	0.44	Zn
Fine																	0.53	Fine

Sites listed in Table 1 and element abbreviations are defined in Table 3. TOC is total organic carbon and Fine is fine sediment particles ($< 63 \mu\text{m}$).

Table 7. Product-moment correlations in sediment for West Coast reference and nonurban sites. Correlations of log₁₀ element concentrations for all reference and nonurban sites. Sites include Bodega Bay, Channel Islands, Dana Point, Estero Bay, Farallon Islands, and San Luis Obispo. Number of measurements between 24 and 38 for stations over all years for each element. Bold entries are significant at $\alpha = 0.00033$.

	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Si	Sn	Zn	Fine	TOC
Ag	0.24	-0.26	-0.37	0.40	0.03	0.29	0.18	0.28	0.36	-0.37	0.19	-0.05	-0.22	0.10	-0.21	-0.41	0.20
Al		0.36	0.43	-0.54	0.16	0.32	0.06	0.50	-0.46	0.55	0.33	0.32	-0.13	0.13	0.42	0.63	0.02
As			0.09	-0.20	-0.09	0.46	0.29	0.41	-0.11	0.24	0.22	0.42	0.52	-0.13	0.51	0.49	0.03
Cd				-0.41	0.11	-0.03	0.01	-0.06	-0.35	0.58	0.12	0.41	-0.04	0.02	0.01	0.41	0.05
Cr					-0.04	0.38	0.11	0.04	0.84	-0.71	-0.15	-0.39	0.20	0.13	-0.03	-0.74	-0.11
Cu						0.36	0.07	0.03	-0.11	0.32	-0.05	-0.05	0.02	0.07	0.50	0.30	0.47
Fe							0.31	0.67	0.36	0.05	0.37	0.07	0.26	0.20	0.77	0.08	0.24
Hg								0.15	0.11	0.06	0.51	0.22	0.34	-0.40	0.18	-0.20	0.20
Mn									-0.05	0.20	0.29	0.03	0.20	0.33	0.57	0.12	-0.07
Ni										-0.75	-0.03	-0.22	0.17	0.16	-0.02	-0.59	-0.09
Pb											0.32	0.52	0.13	-0.05	0.26	0.59	0.13
Sb												0.46	0.15	-0.11	0.39	0.03	0.17
Se													0.19	-0.13	0.29	0.36	0.32
Si														-0.21	0.21	-0.10	0.14
Sn															0.17	0.04	0.26
Zn																0.55	0.24
Fine																	0.27

Sites listed in Table 1 and element abbreviations are defined in Table 3. TOC is total organic carbon and Fine is fine sediment particles (< 63 μm). West Coast sites are those from California, Oregon, and Washington.

Table 8. Product-moment correlations in sediment for all Alaska sites. Correlations of \log_{10} element concentrations for all sites in Alaska. Number of measurements between 40 and 43 for stations over all years for each element. Bold entries are significant at $\alpha = 0.00033$.

	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Si	Sn	Zn	Fine	TOC	
Ag	0.51	-0.01	-0.08	-0.05	0.29	0.22	-0.12	0.23	-0.28	0.60	0.52	0.20	-0.23	0.28	0.58	0.57	-0.03	Ag
Al		0.01	0.14	-0.04	0.48	0.81	-0.24	0.83	-0.47	0.61	0.59	-0.16	-0.47	0.28	0.68	0.35	-0.16	Al
As			-0.25	0.51	0.21	0.03	-0.11	0.07	0.20	0.15	-0.18	-0.05	0.42	0.26	-0.09	0.00	-0.16	As
Cd				-0.55	0.02	0.45	0.37	0.43	-0.05	0.37	0.39	0.43	-0.58	-0.52	0.52	0.21	0.24	Cd
Cr					0.17	-0.04	-0.30	-0.01	0.46	-0.30	-0.36	-0.35	0.40	0.21	-0.30	-0.04	-0.28	Cr
Cu						0.51	0.06	0.54	-0.15	0.27	0.48	0.31	-0.46	0.20	0.40	0.66	0.18	Cu
Fe							-0.10	0.96	-0.23	0.48	0.60	-0.02	-0.59	0.00	0.74	0.39	-0.18	Fe
Hg								-0.15	0.15	0.04	0.02	0.30	-0.13	-0.17	0.02	0.06	0.32	Hg
Mn									-0.27	0.48	0.55	-0.01	-0.56	0.07	0.67	0.37	-0.14	Mn
Ni										-0.38	-0.34	0.20	0.30	-0.46	-0.21	0.08	-0.11	Ni
Pb											0.48	0.24	-0.28	-0.14	0.74	0.57	0.02	Pb
Sb												0.30	-0.73	0.05	0.77	0.57	0.04	Sb
Se													-0.41	-0.36	0.25	0.55	0.60	Se
Si														-0.07	-0.57	-0.44	-0.39	Si
Sn															-0.19	-0.26	0.11	Sn
Zn																0.68	-0.10	Zn
Fine																	0.08	Fine

Sites listed in Table 1 and element abbreviations are defined in Table 3. TOC is total organic carbon and Fine is fine sediment particles ($< 63 \mu\text{m}$).

Table 9. Element correlations. Correlations of mean \log_{10} concentrations for stomach contents and sediment and stomach contents and liver matched by site and year. For all correlations, $p \leq 0.05$ and significant at $\alpha = 0.003$ (shown in bold).

Species	<u>Stomach and sediment</u>						<u>Stomach and liver</u>		
	r	element	n	r	element	n	r	element	n
All species	-0.42	Cd	48	0.53	Ni	48			
	0.58	Cr*	47	0.54	Pb	39			
	0.50	Cu	48	0.29	Zn*	48			
	0.57	Hg	38						
English sole	-0.72	As	8	0.82	Cu	8			
	-0.81	Cd	8	0.92	Hg	6			
	0.88	Cr	8	0.91	Mn	8			
Flathead sole	0.80	Ni	7	0.72	As	7	0.71	Sn	7
	-0.80	Sn	7	0.75	Se	7			
Starry flounder							-0.71	Pb	11
White croaker	0.82	Cr	9				-0.67	Se	10
	0.67	Pb	9						
Sand bass & white croakers	-0.64	Cd	15	0.54	Zn	15	-0.72	Sb*	13
	0.84	Cr	14	0.49	Cu	15			
	0.54	Mn	15	0.55	Hg	14			
	0.65	Pb	14						
All flatfish (ES, FS, HT, SF)	0.45	Cr*	32	0.37	Ag*	32	0.38	Ag*	32
	0.42	Cu	32	0.42	Pb*	32	0.41	Ni*	32
	0.49	Hg	25	-0.48	Sn*	32			
	0.55	Ni	32						

* Spurious correlation is a significant correlation that is unduly influenced by a few points. Number of correlations made for each species and compartment pair (liver, stomach, or sediment) was 15 (e.g., stomach contents and sediment for 15 elements in English sole), hence the significance level (α) for pearson correlation was $0.05 \div 15 = 0.003$. Abbreviations for elements are in Table 3 and fish species are in Table 2.

Table 10. Correlations of elements in liver and sediment. Correlations of mean \log_{10} concentrations for liver and sediment matched by site and year. For all correlations, $p \leq 0.05$ and significant at $\alpha = 0.003$ (shown in bold).

Species	Correlations			
	r	element	n	Spurious
All species	0.41	Hg	81	
	-0.28	Sn	80	
	-0.40	Zn	101	
English sole	-0.59	Cd	15	*
	0.65	Fe	15	*
Flathead sole	-0.92	Sn	8	*
Hornyhead turbot	0.85	As	9	*
	-0.76	Sn	8	*
Starry flounder	-0.47	Cd	24	*
	-0.49	Sn	17	*
	-0.45	Zn	24	*
White croaker	0.47	Se	25	
All flatfish (ES, FS, HT, SF)	-0.44	Sn	42	*
	-0.49	Zn	58	
	0.41	Hg	40	
	-0.28	Cd	57	*
Sand bass and white croaker	0.50	Se	37	
	-0.39	Zn	39	

* Spurious correlation is a significant correlation that is unduly influenced by a few points. Number of correlations made for each species and compartment pair was 15 (e.g., liver and sediment for 15 elements in English sole), hence the significance level (α) for pearson correlation was $0.05 \div 15 = 0.003$. Abbreviations for elements are in Table 3 and fish species are in Table 2.

FIGURES

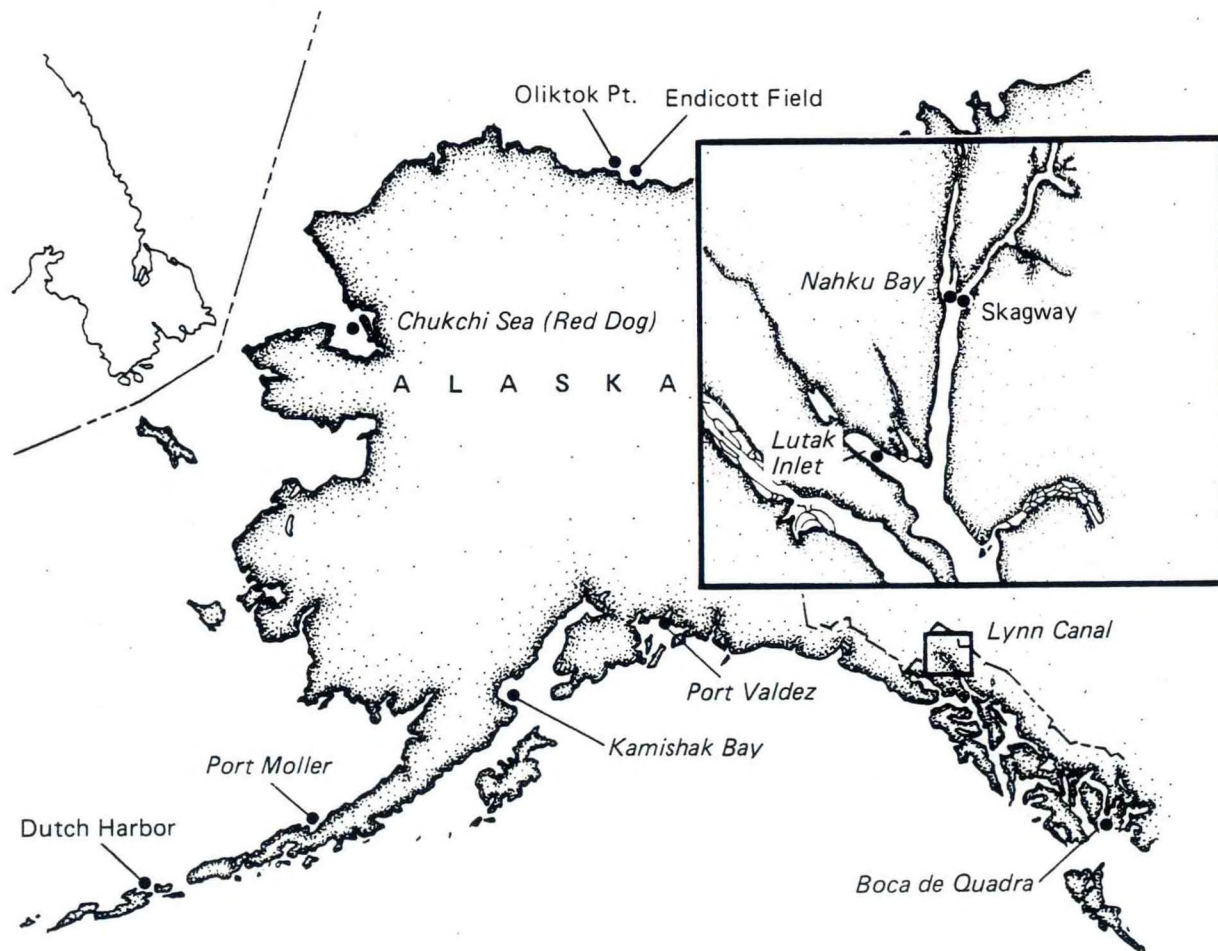


Figure 1. Location of sampling sites in Alaska.

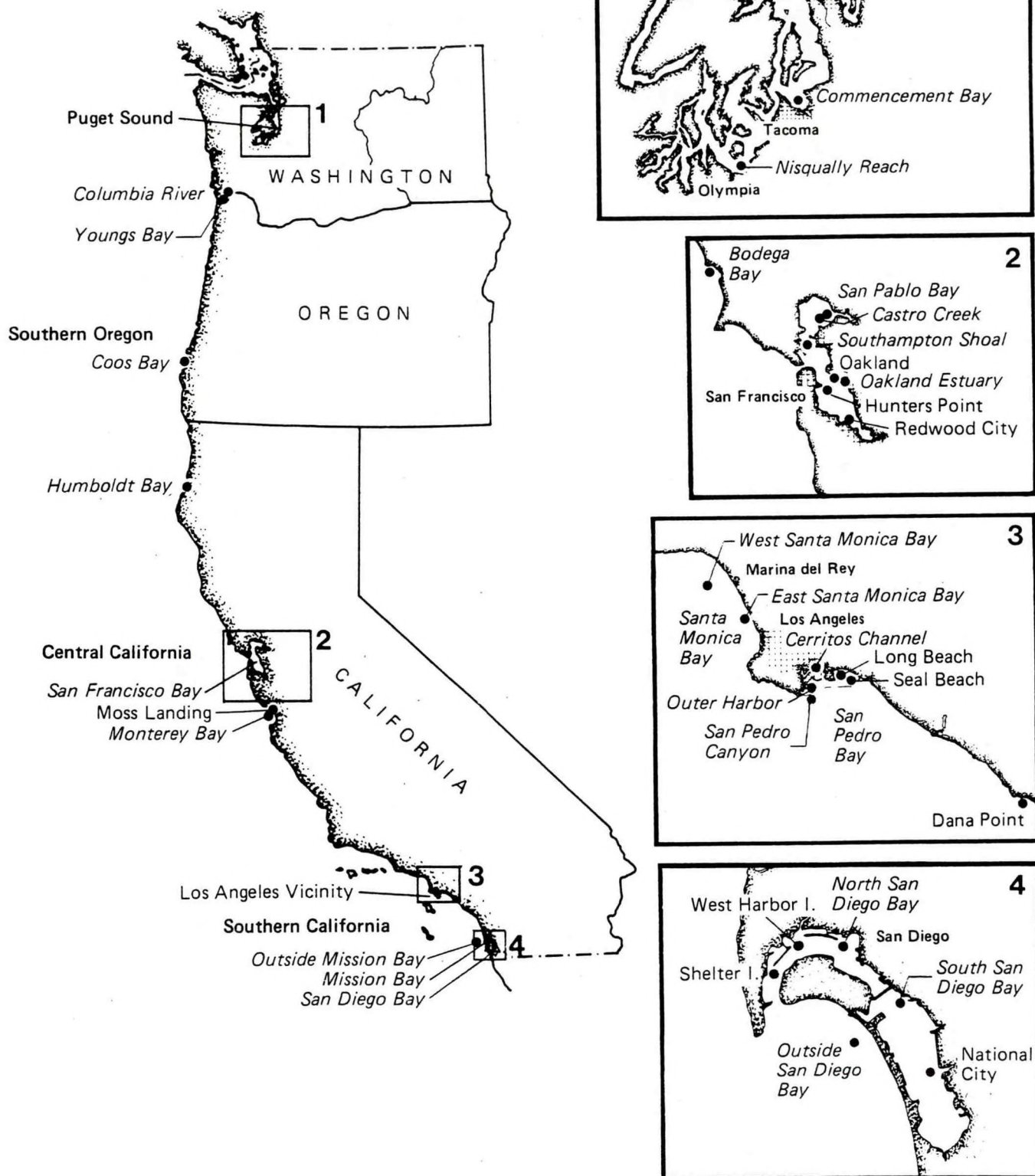


Figure 2. Location of sampling sites on the West Coast of the United States. Pacific coast sites include West Coast and Alaskan sites.

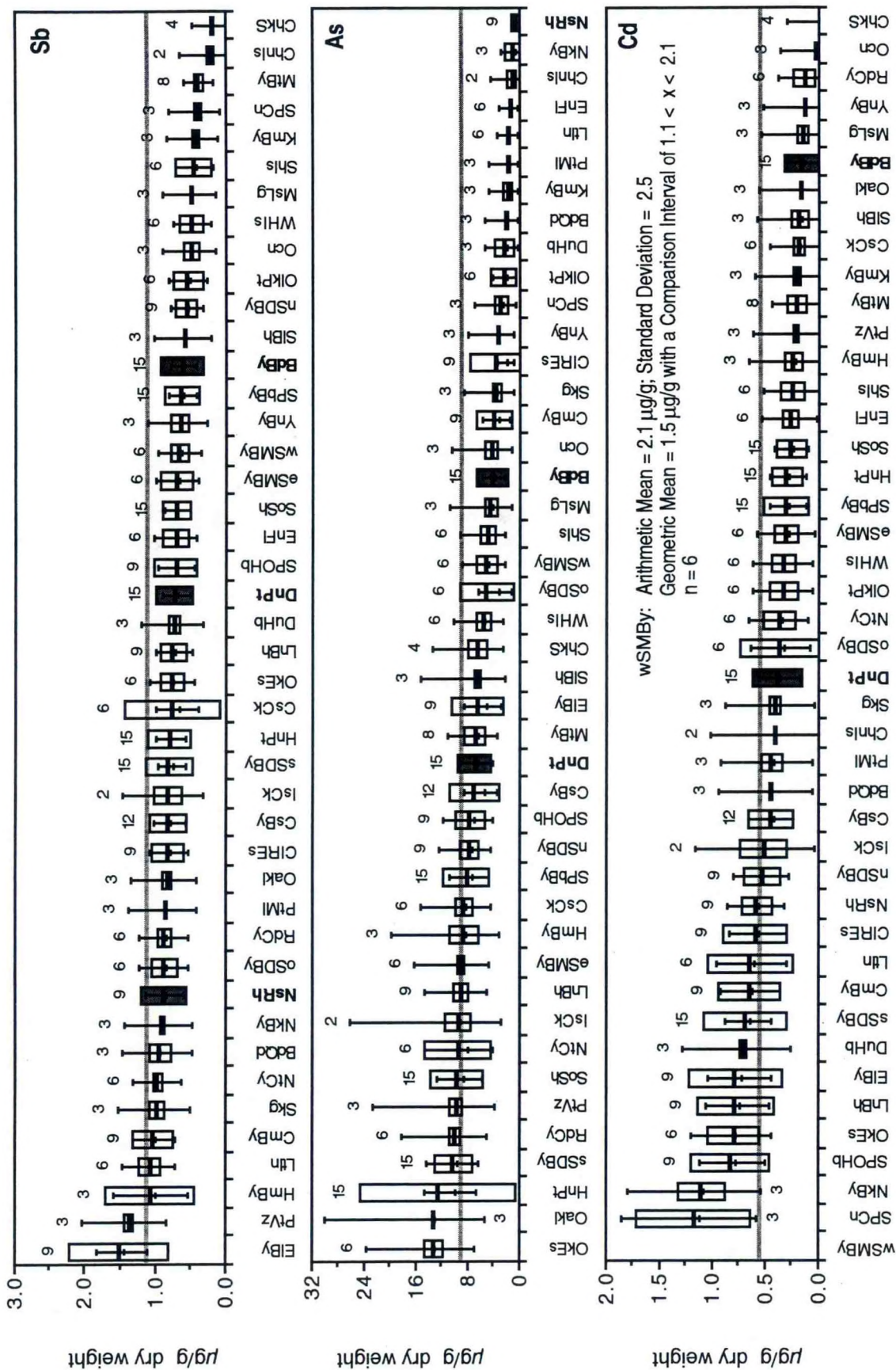


Figure 3. Floating-bar plots of elements in sediment for the years 1984-88. Plot components are arithmetic mean concentration [—], one standard deviation [---], geometric mean [---], comparison interval [I], and maximum comparison interval value [III] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

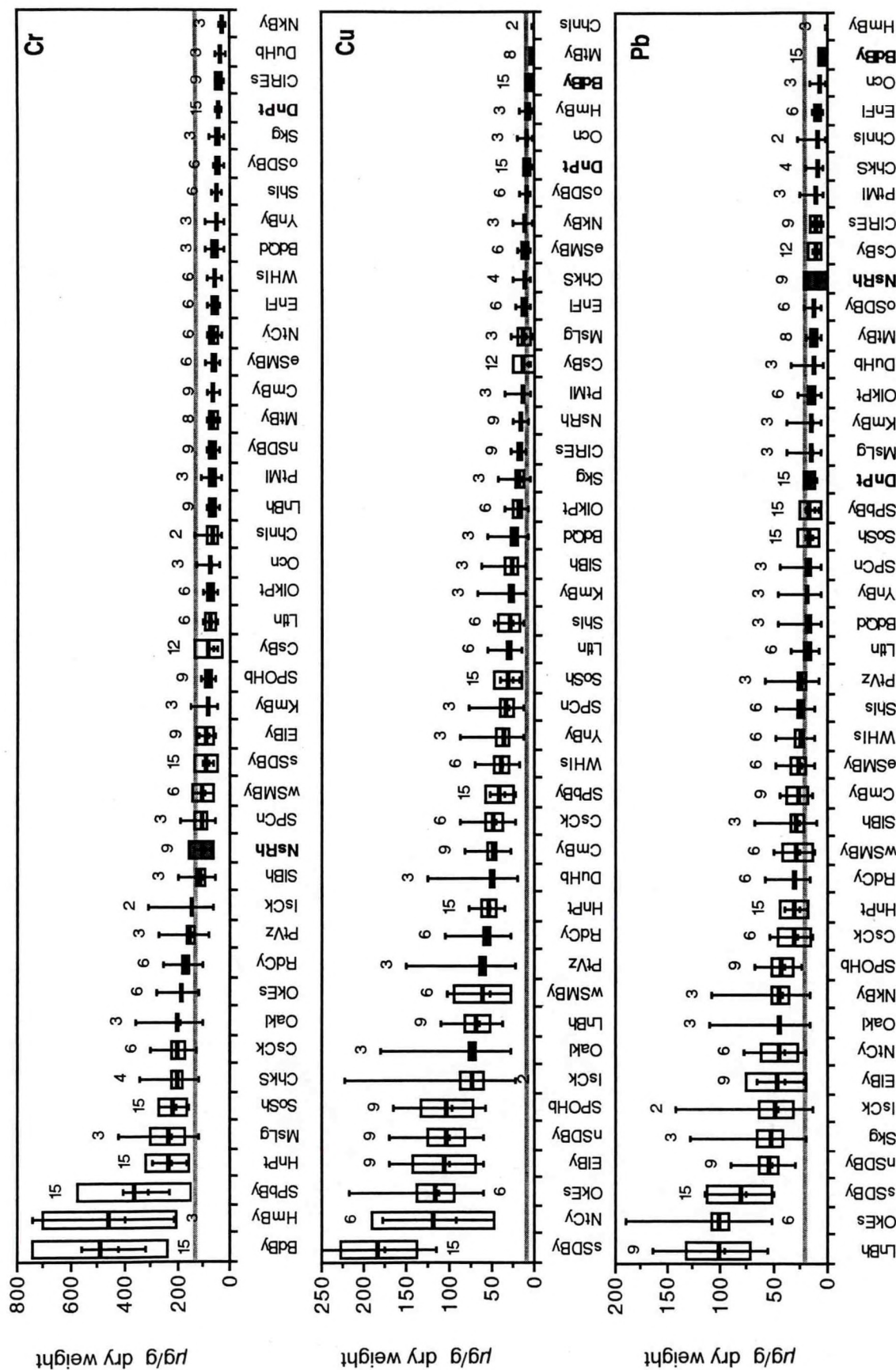


Figure 4. Floating-bar plots of elements in sediment for the years 1984-88. Plot components are arithmetic mean concentration [—], one standard deviation [---], geometric mean [—], comparison interval [I], and maximum comparison interval value [·····] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

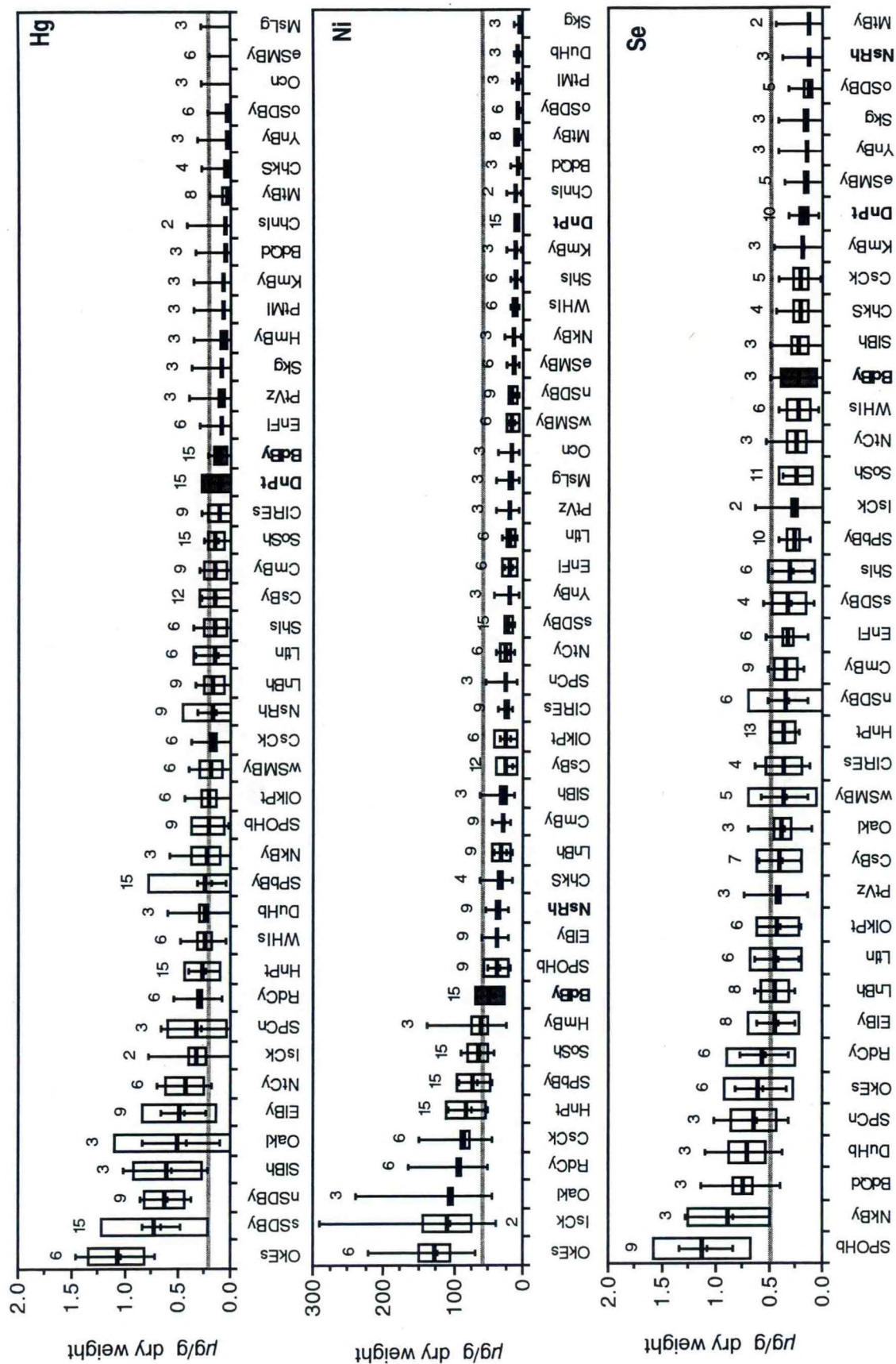


Figure 5. Floating-bar plots of elements in sediment for the years 1984-88. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [....] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

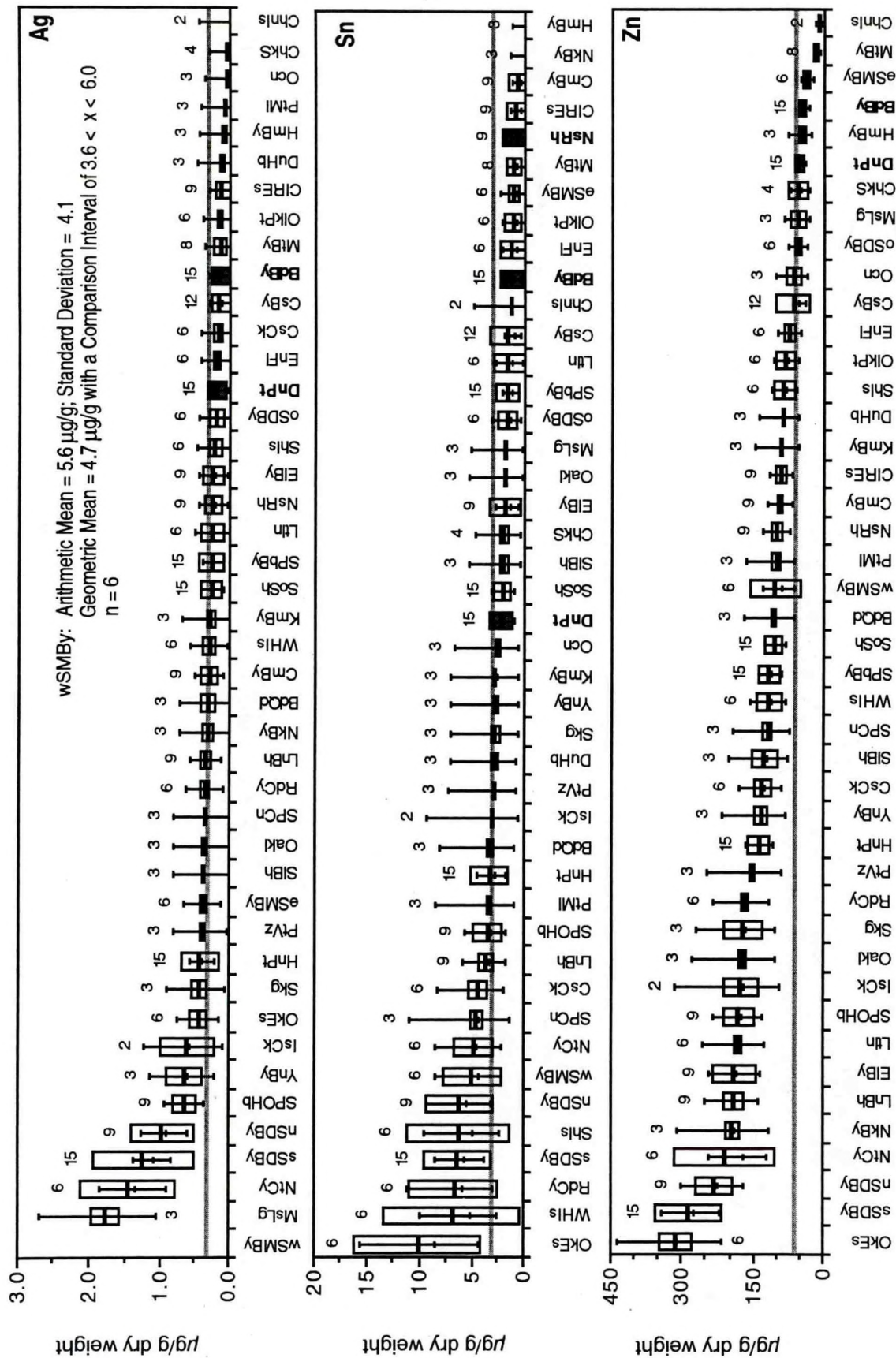


Figure 6. Floating-bar plots of elements in sediment for the years 1984-88. Plot components are arithmetic mean concentration [—], one standard deviation [---], geometric mean [---], comparison interval [I], and maximum comparison interval value [] for the reference site [wSMBY]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

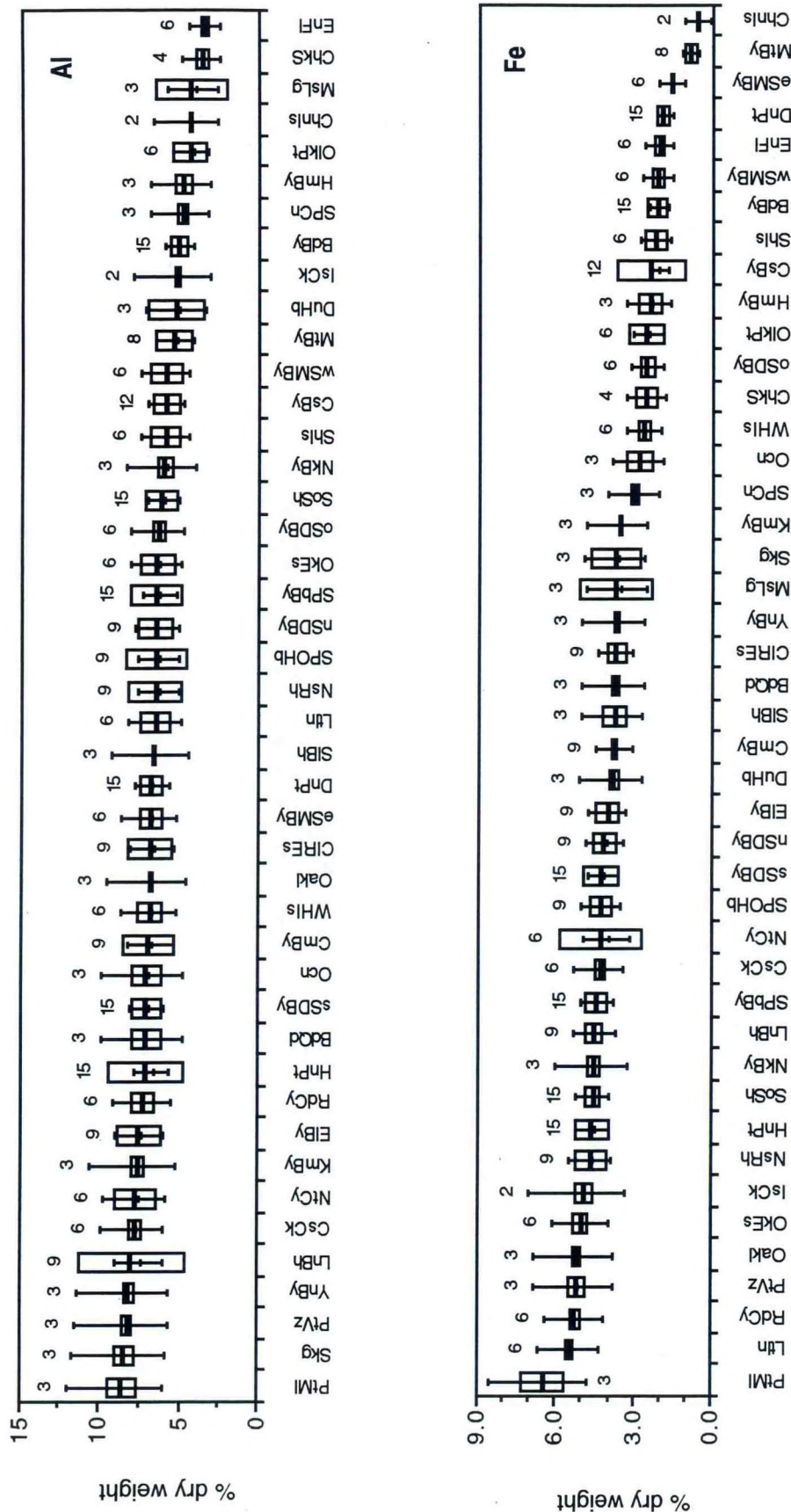


Figure 7. Floating-bar plots of elements in sediment for the years 1984-88. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

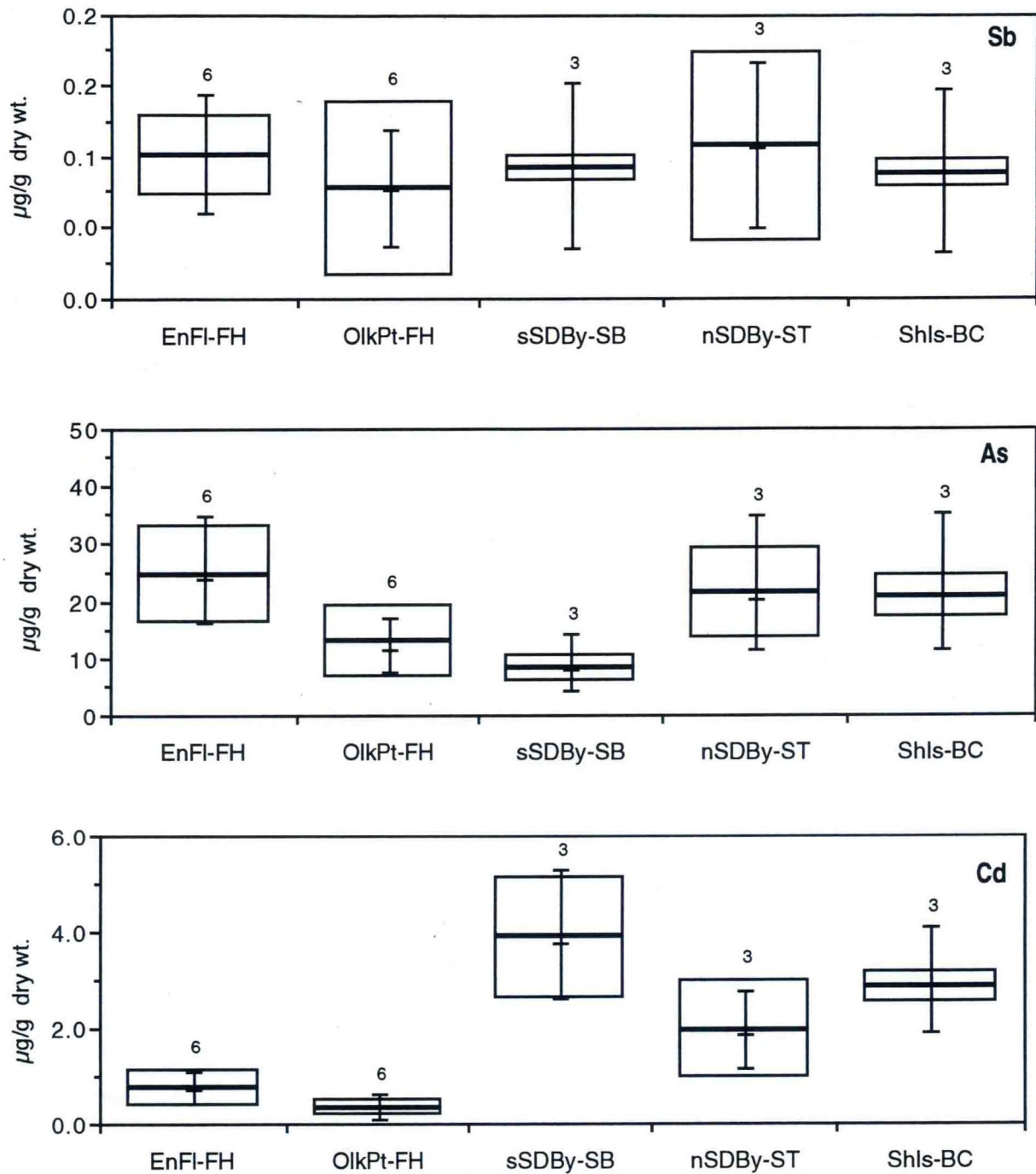


Figure 9. Floating-bar plots of elements in fish livers for the years 1984-87. Species are fourhorn sculpin, spotted sand bass, spotted turbot, and black croaker. Components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], and comparison interval [I]. See Tables 1, 2, and 3 for site, species, and element abbreviations. Numbers for each site-species category indicate sample size.

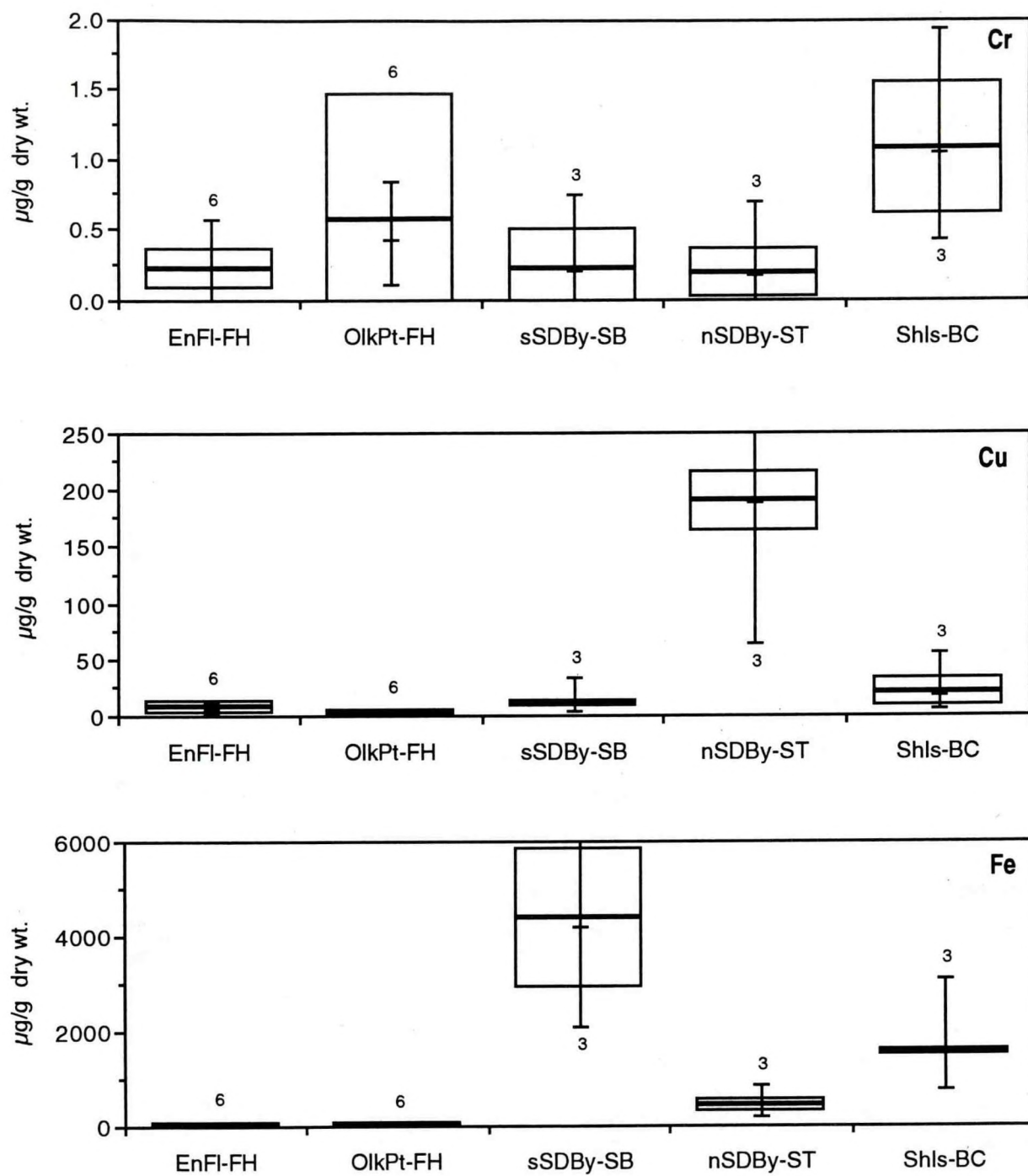


Figure 10. Floating-bar plots of elements in fish livers for the years 1984-87. Species are fourhorn sculpin, spotted sand bass, spotted turbot, and black croaker. Components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], and comparison interval [I]. See Tables 1, 2, and 3 for site, species, and element abbreviations. Numbers for each site-species category indicate sample size.

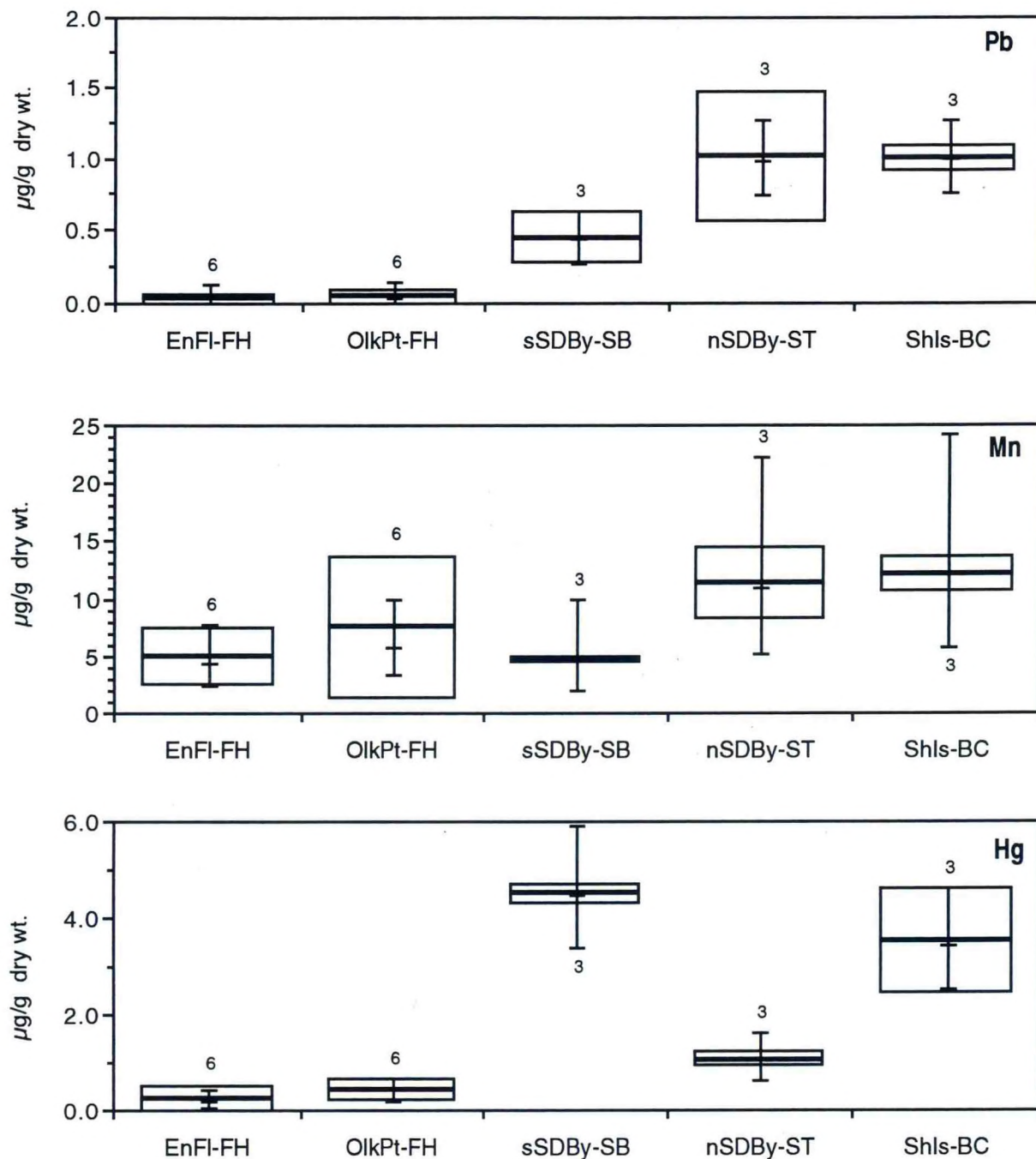


Figure 11. Floating-bar plots of elements in fish livers for the years 1984-87. Species are fourhorn sculpin, spotted sand bass, spotted turbot, and black croaker. Components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], and comparison interval [I]. See Tables 1, 2, and 3 for site, species, and element abbreviations. Numbers for each site-species category indicate sample size.

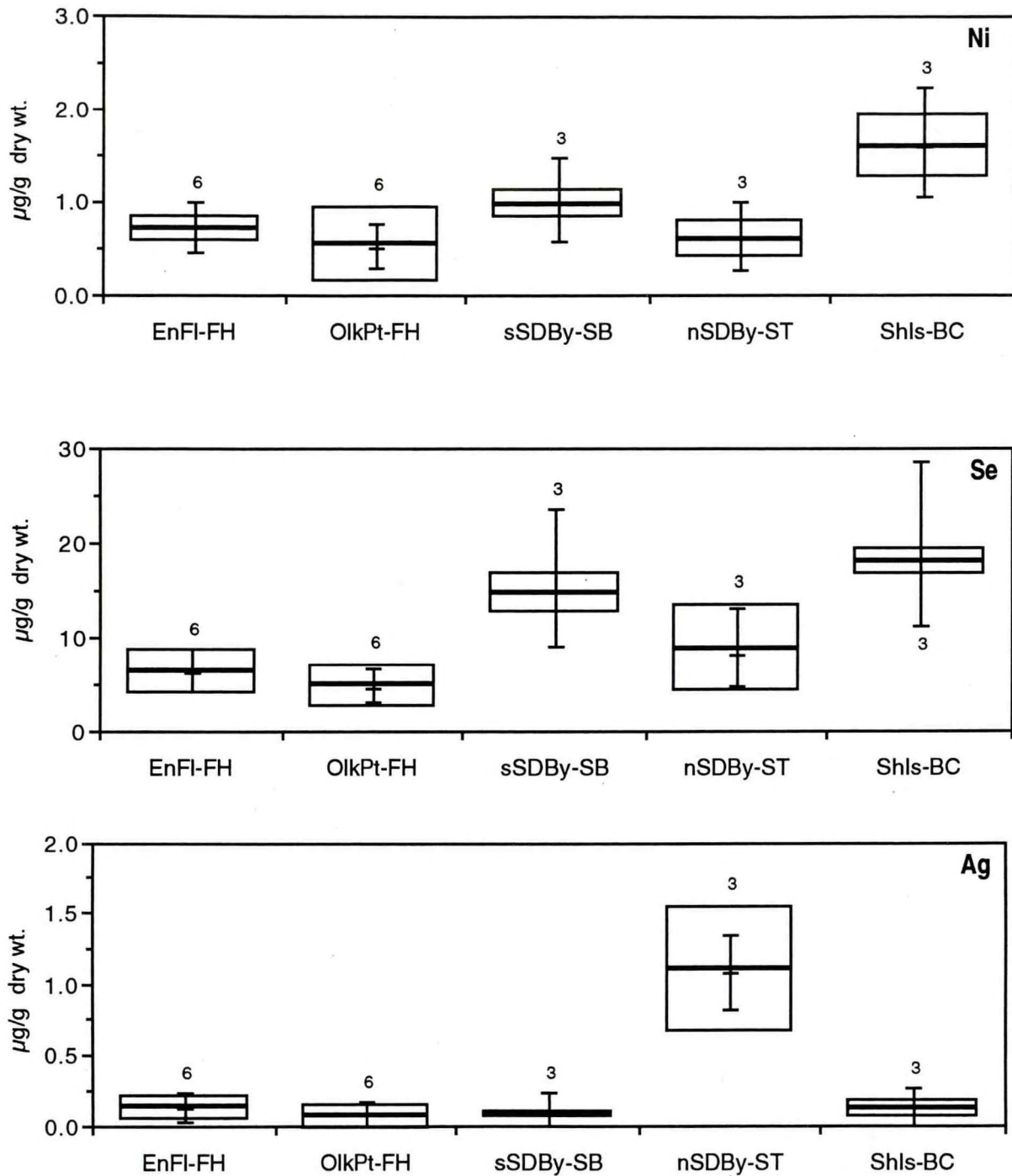


Figure 12. Floating-bar plots of elements in fish livers for the years 1984-87. Species are fourhorn sculpin, spotted sand bass, spotted turbot, and black croaker. Components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], and comparison interval [I]. See Tables 1, 2, and 3 for site, species, and element abbreviations. Numbers for each site-species category indicate sample size.

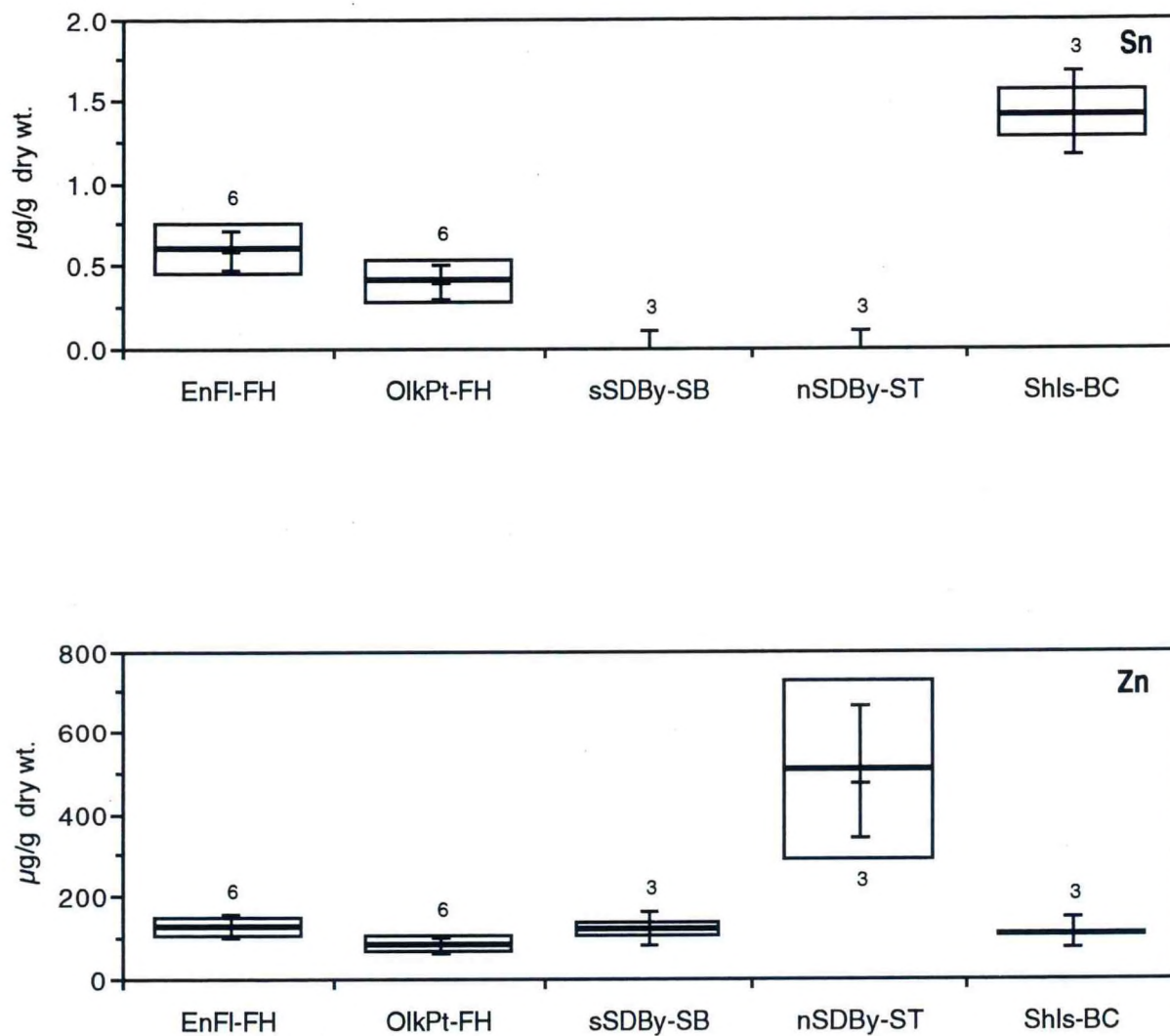


Figure 13. Floating-bar plots of elements in fish livers for the years 1984-87. Species are fourhorn sculpin, spotted sand bass, spotted turbot, and black croaker. Components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], and comparison interval [I]. See Tables 1, 2, and 3 for site, species, and element abbreviations. Numbers for each site-species category indicate sample size.

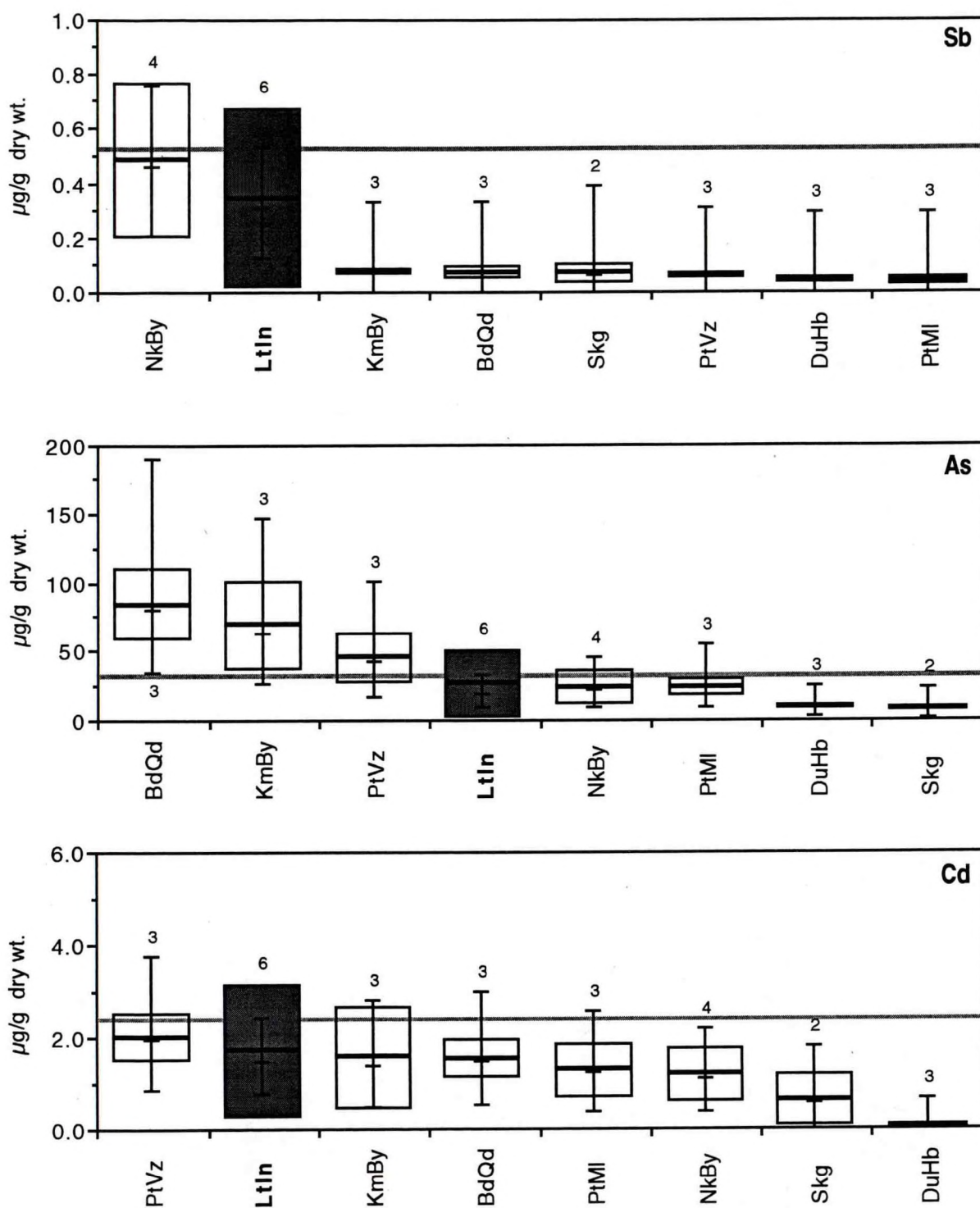


Figure 14. Floating-bar plots of elements in fish livers for the years 1984-87. Species is flathead sole. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

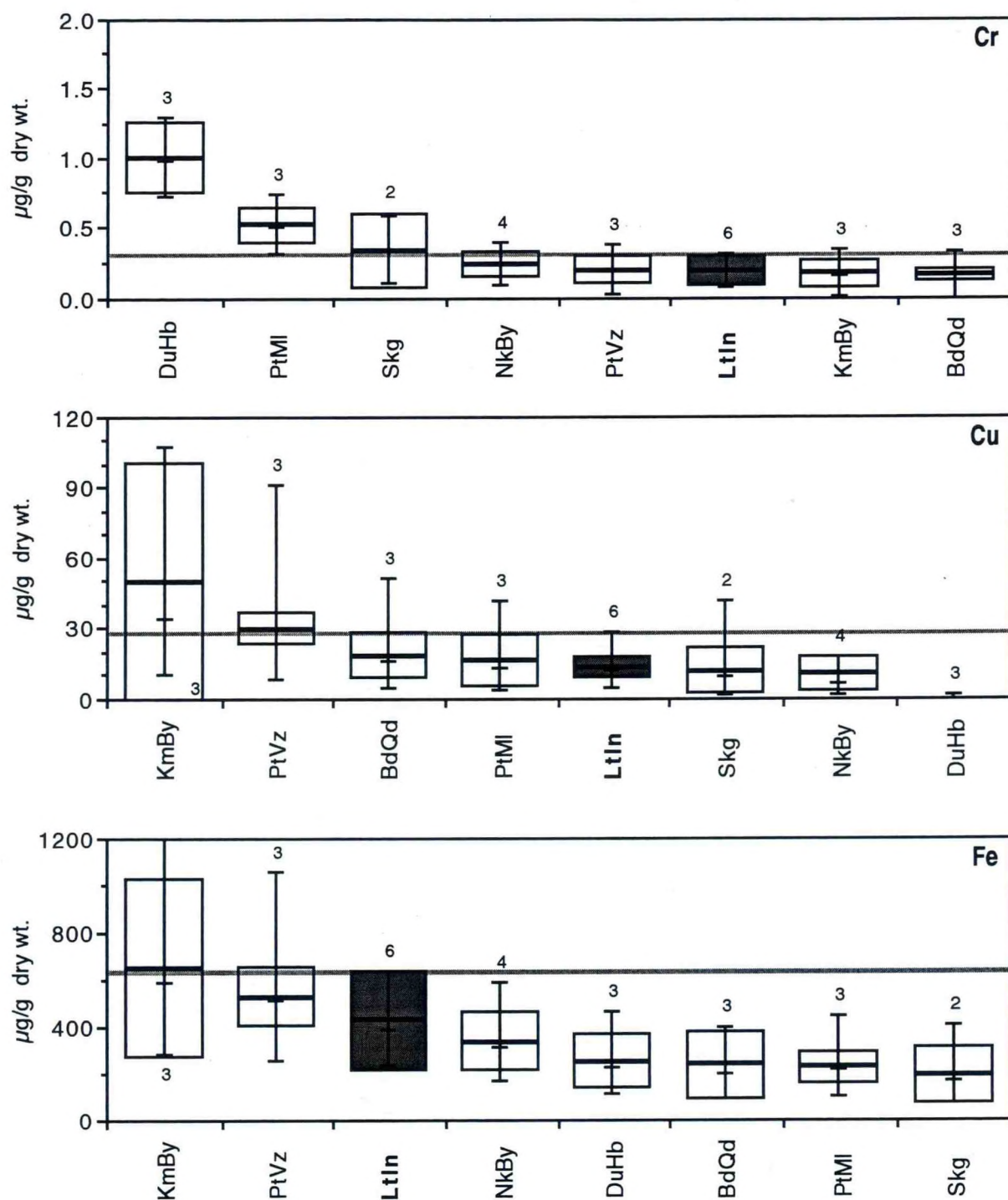


Figure 15. Floating-bar plots of elements in fish livers for the years 1984-87. Species is flathead sole. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

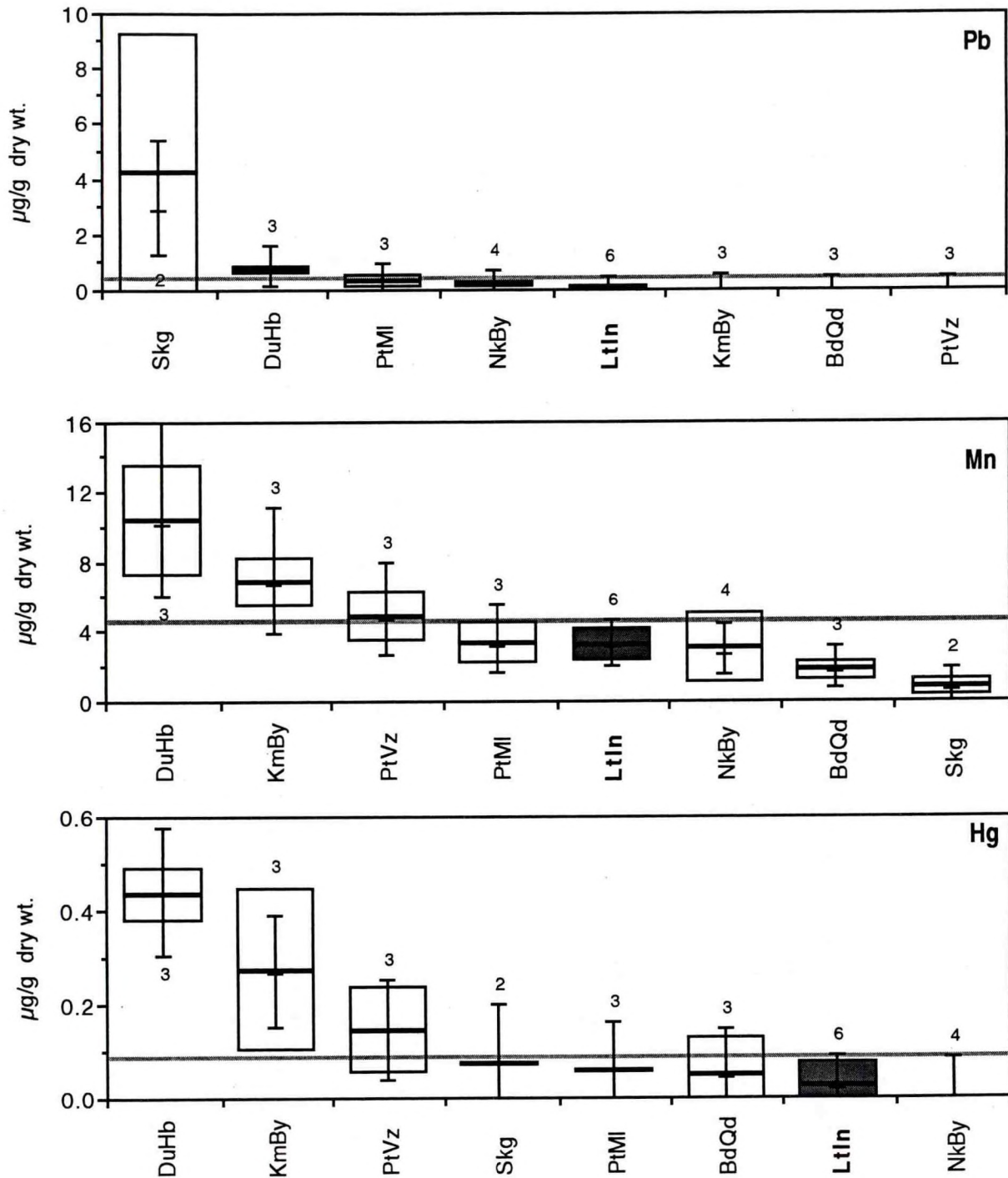


Figure 16. Floating-bar plots of elements in fish livers for the years 1984-87. Species is flathead sole. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

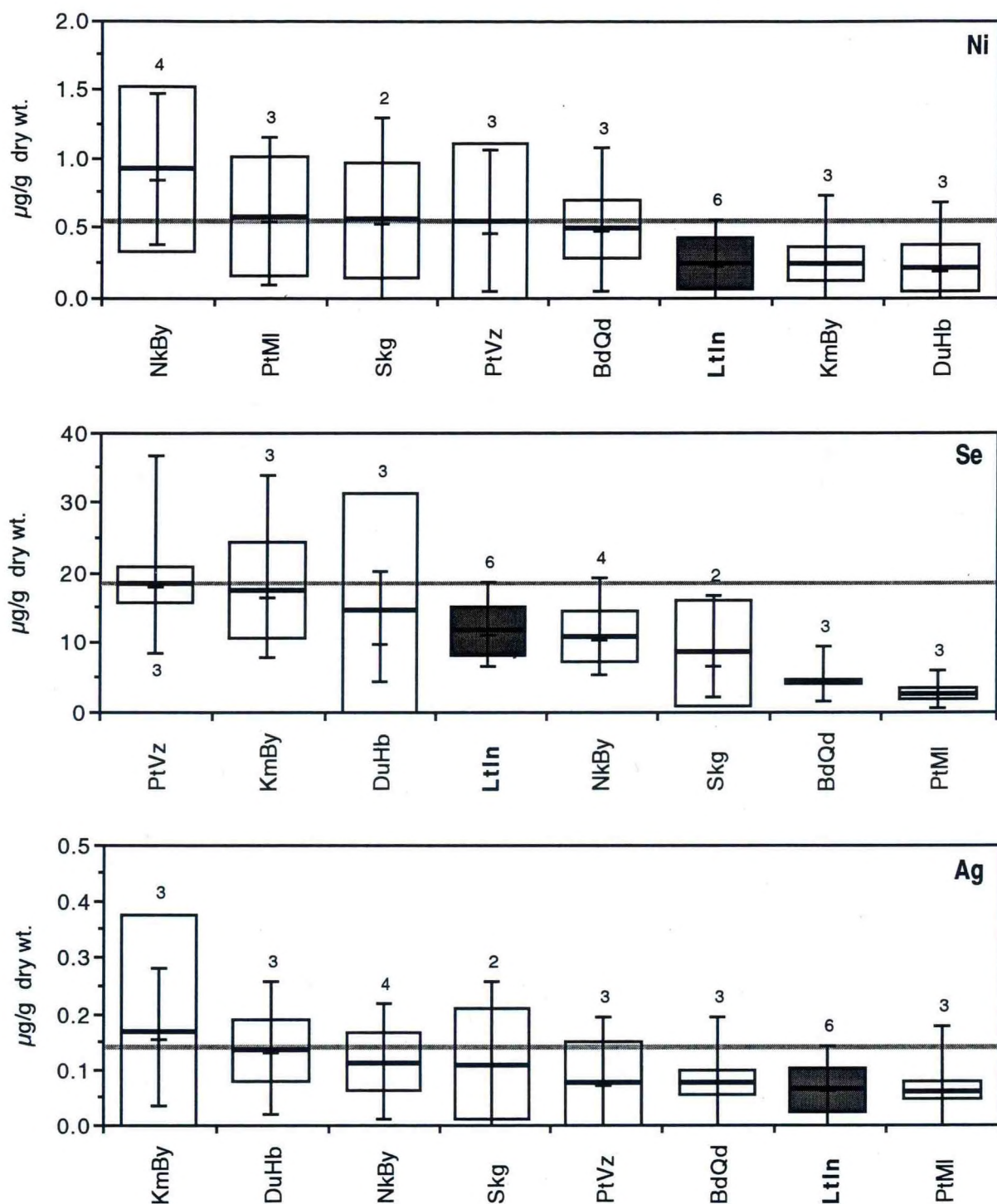


Figure 17. Floating-bar plots of elements in fish livers for the years 1984-87. Species is flathead sole. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

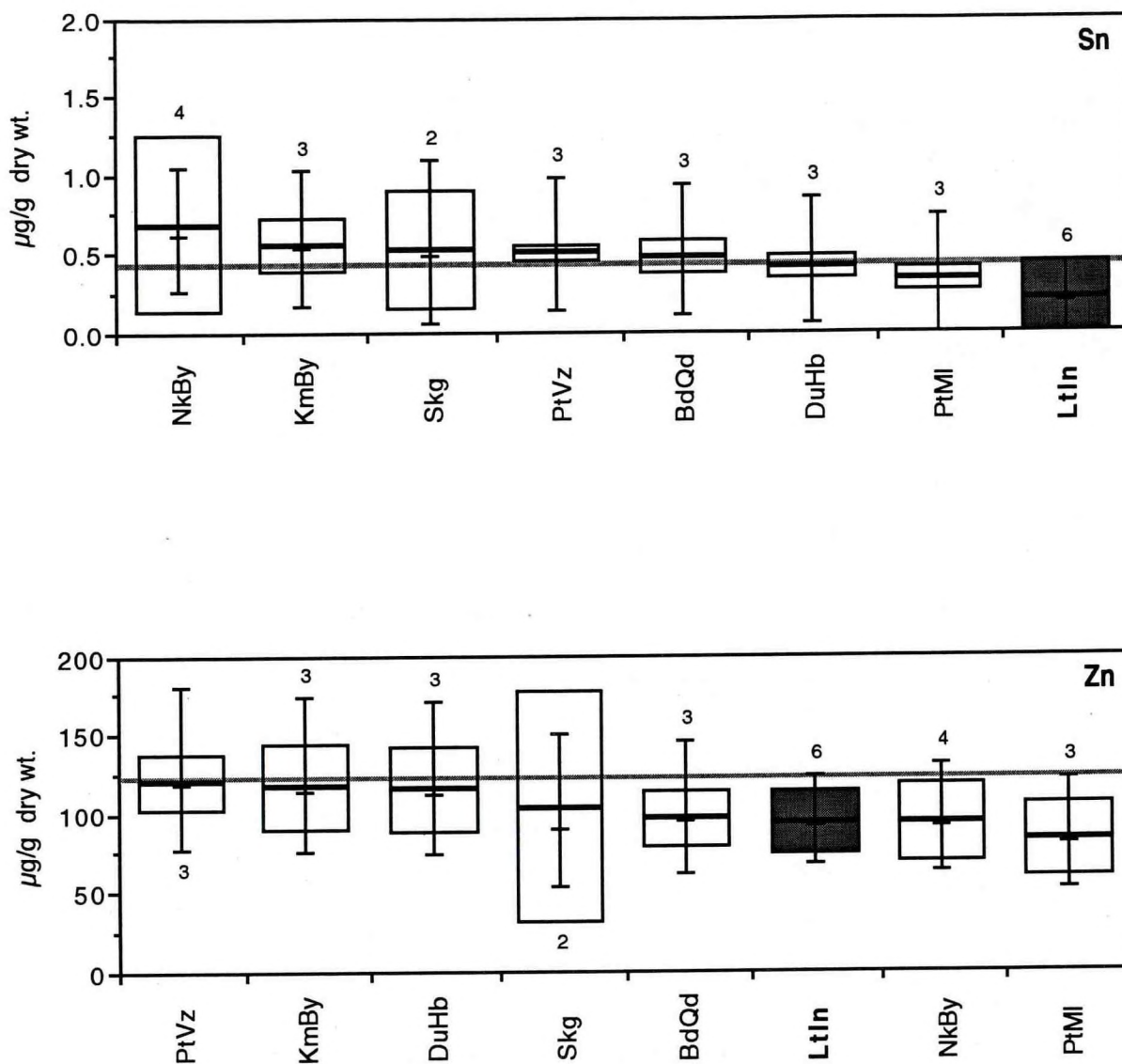


Figure 18. Floating-bar plots of elements in fish livers for the years 1984-87. Species is flathead sole. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [---], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

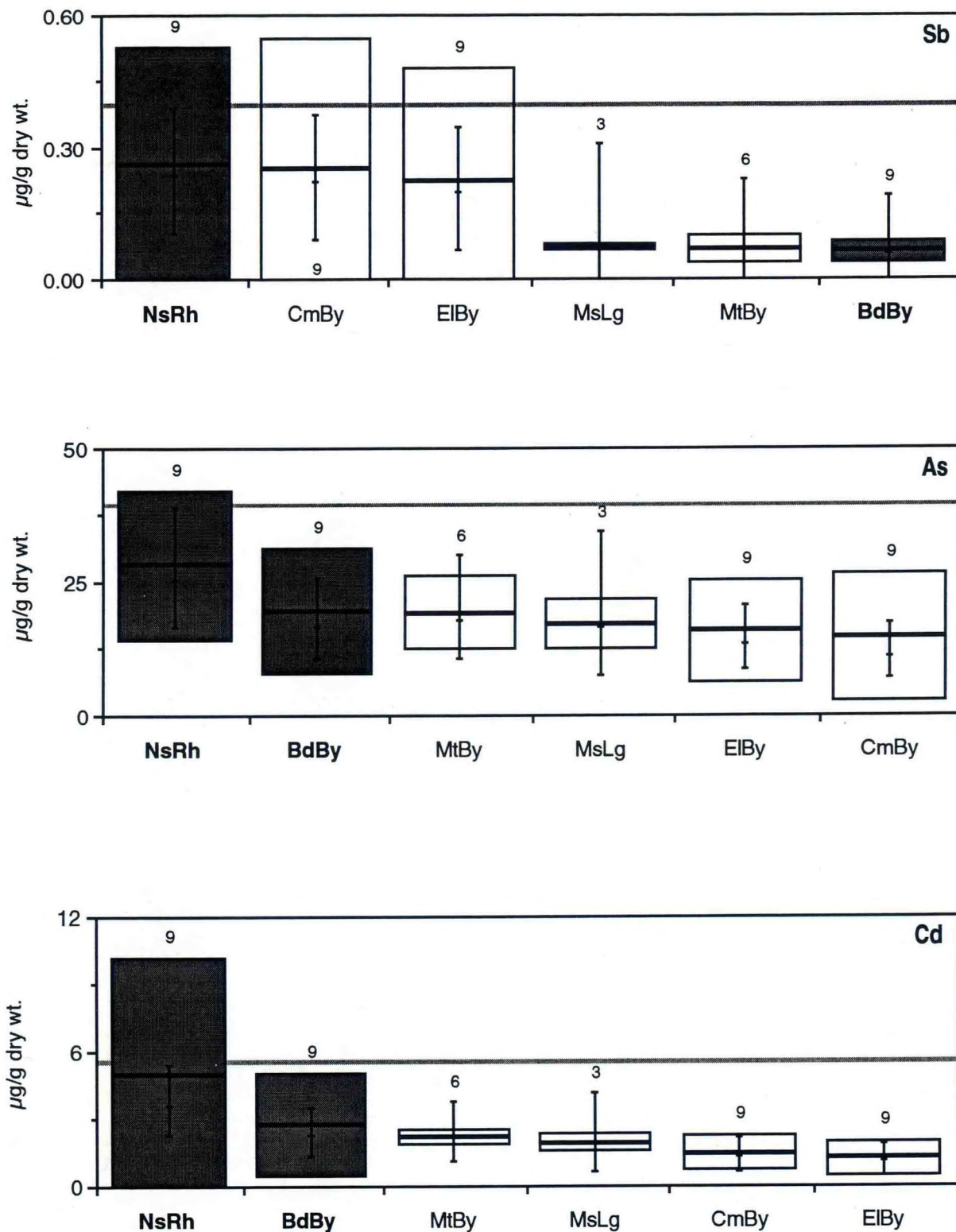


Figure 19. Floating-bar plots of elements in fish livers for the years 1984-87. Species is English sole. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [---], comparison interval [I], and maximum comparison interval value [.....] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

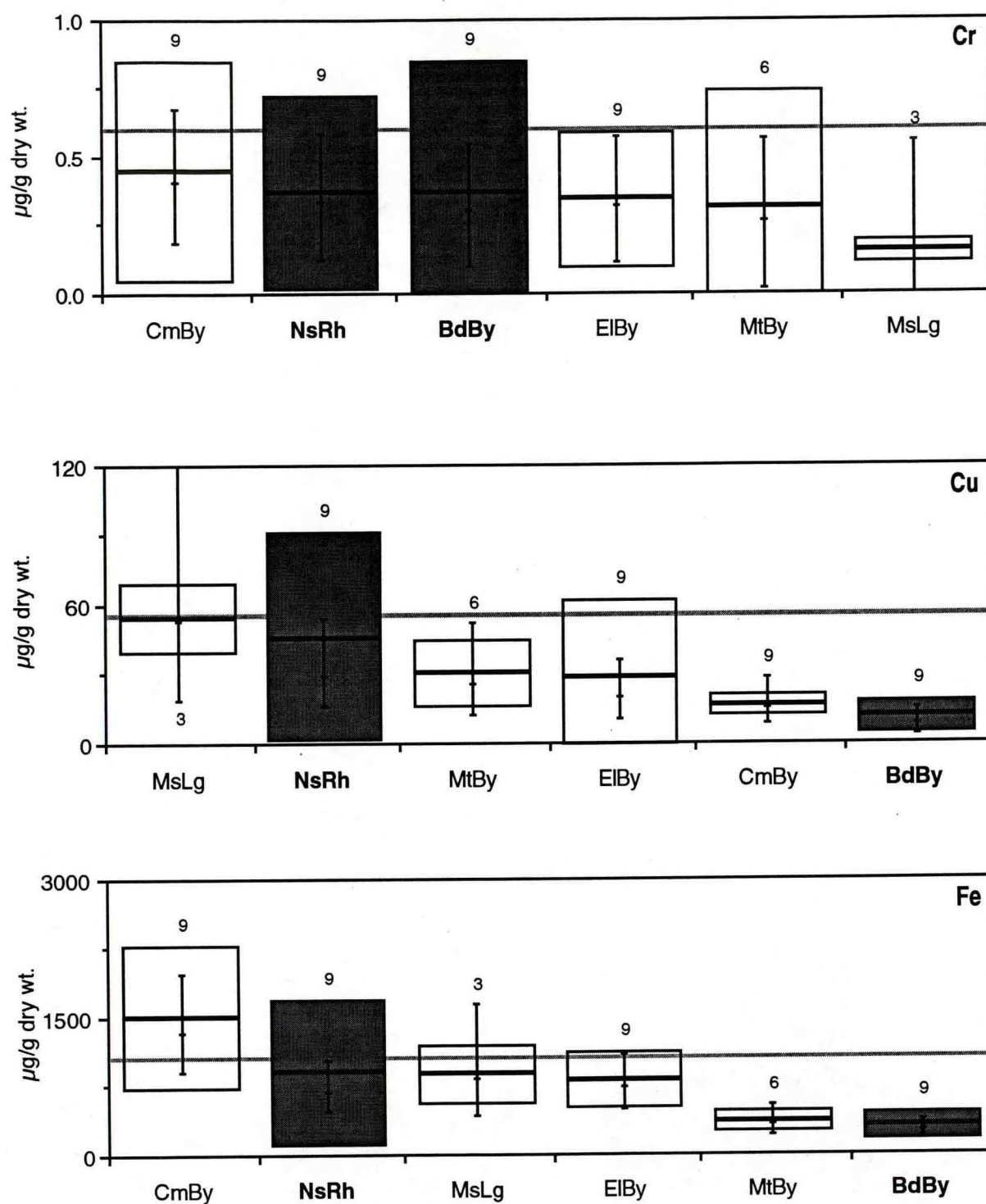


Figure 20. Floating-bar plots of elements in fish livers for the years 1984-87. Species is English sole. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [---], comparison interval [I], and maximum comparison interval value [...]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

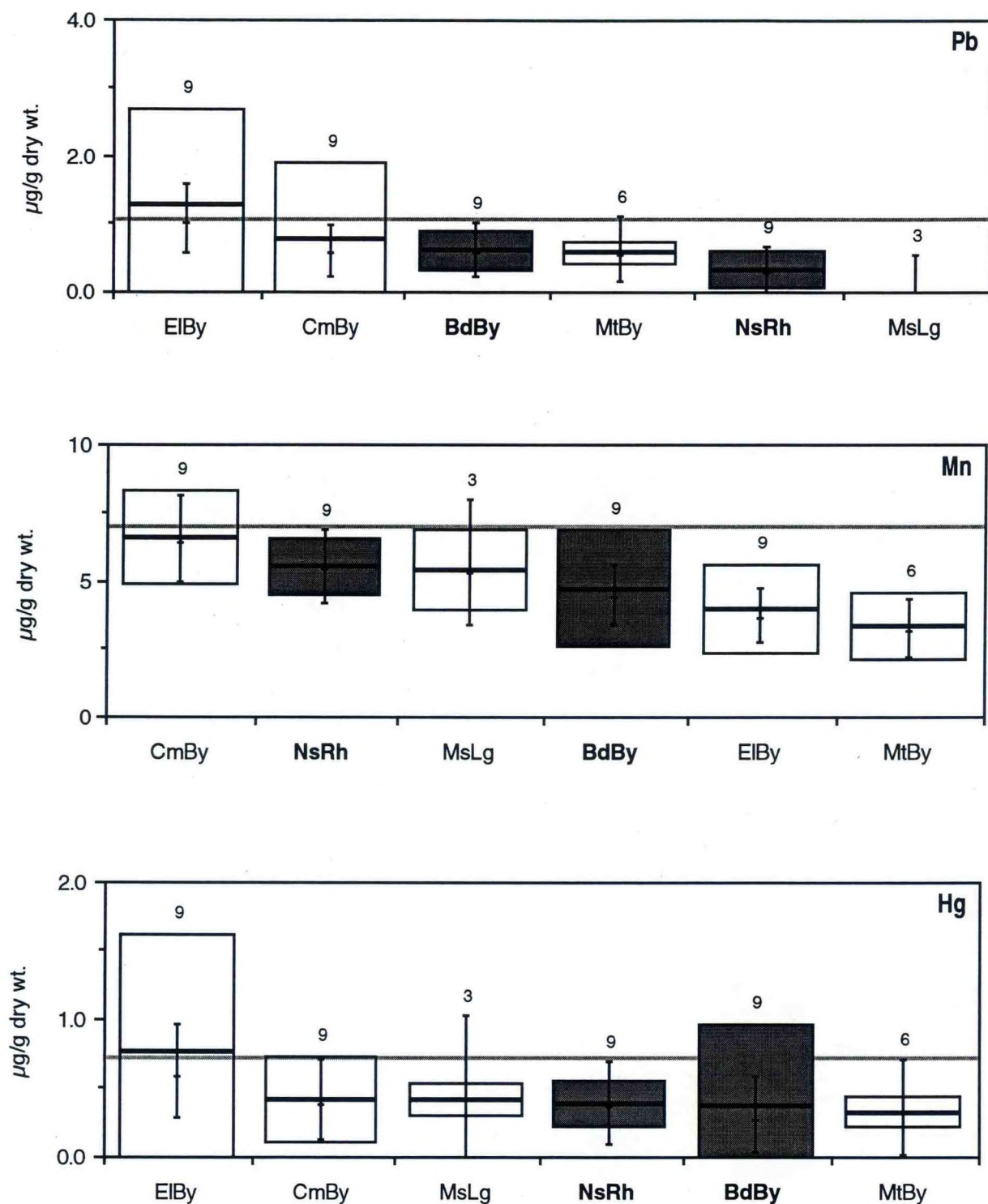


Figure 21. Floating-bar plots of elements in fish livers for the years 1984-87. Species is English sole. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [...] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

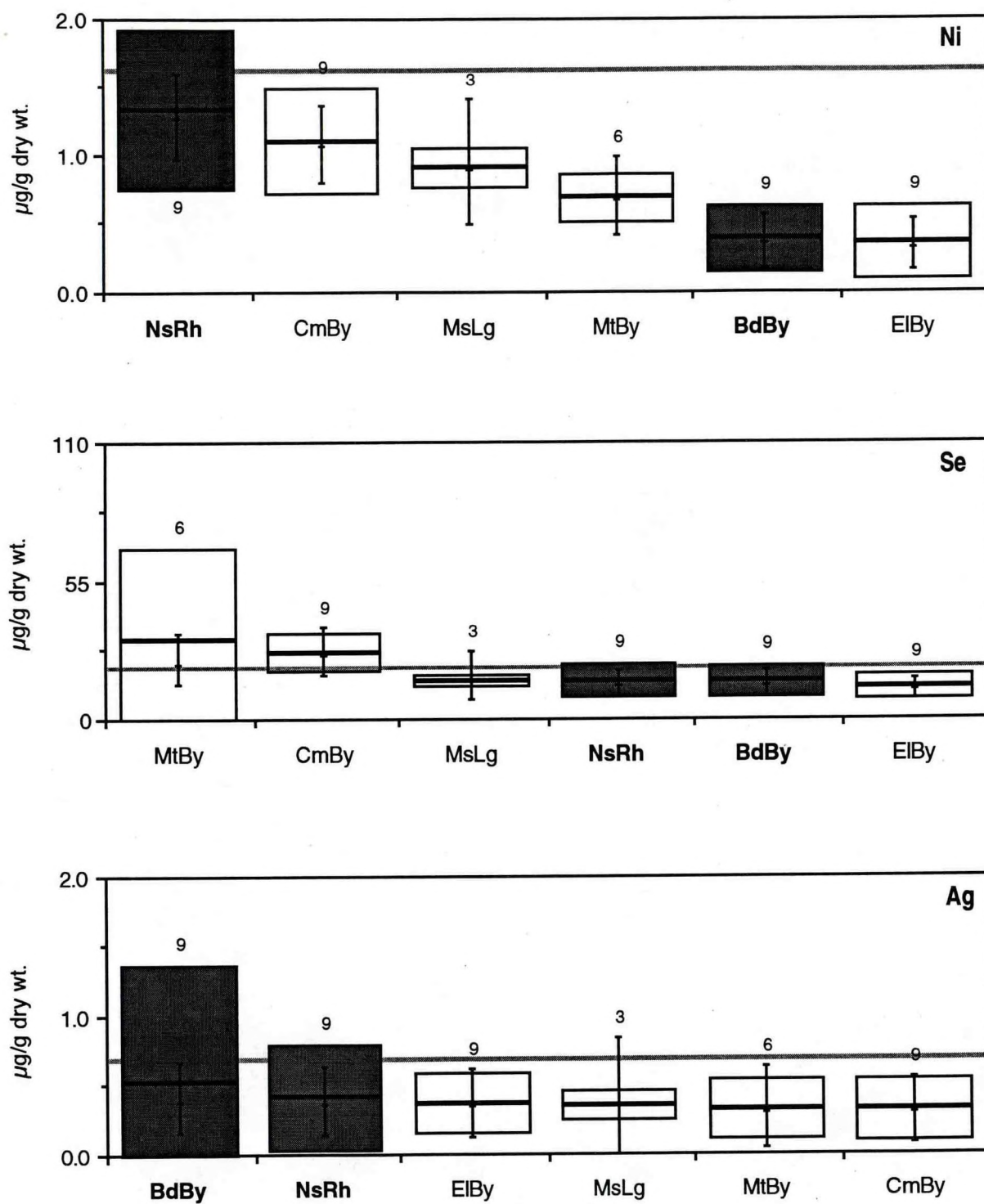


Figure 22. Floating-bar plots of elements in fish livers for the years 1984-87. Species is English sole. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

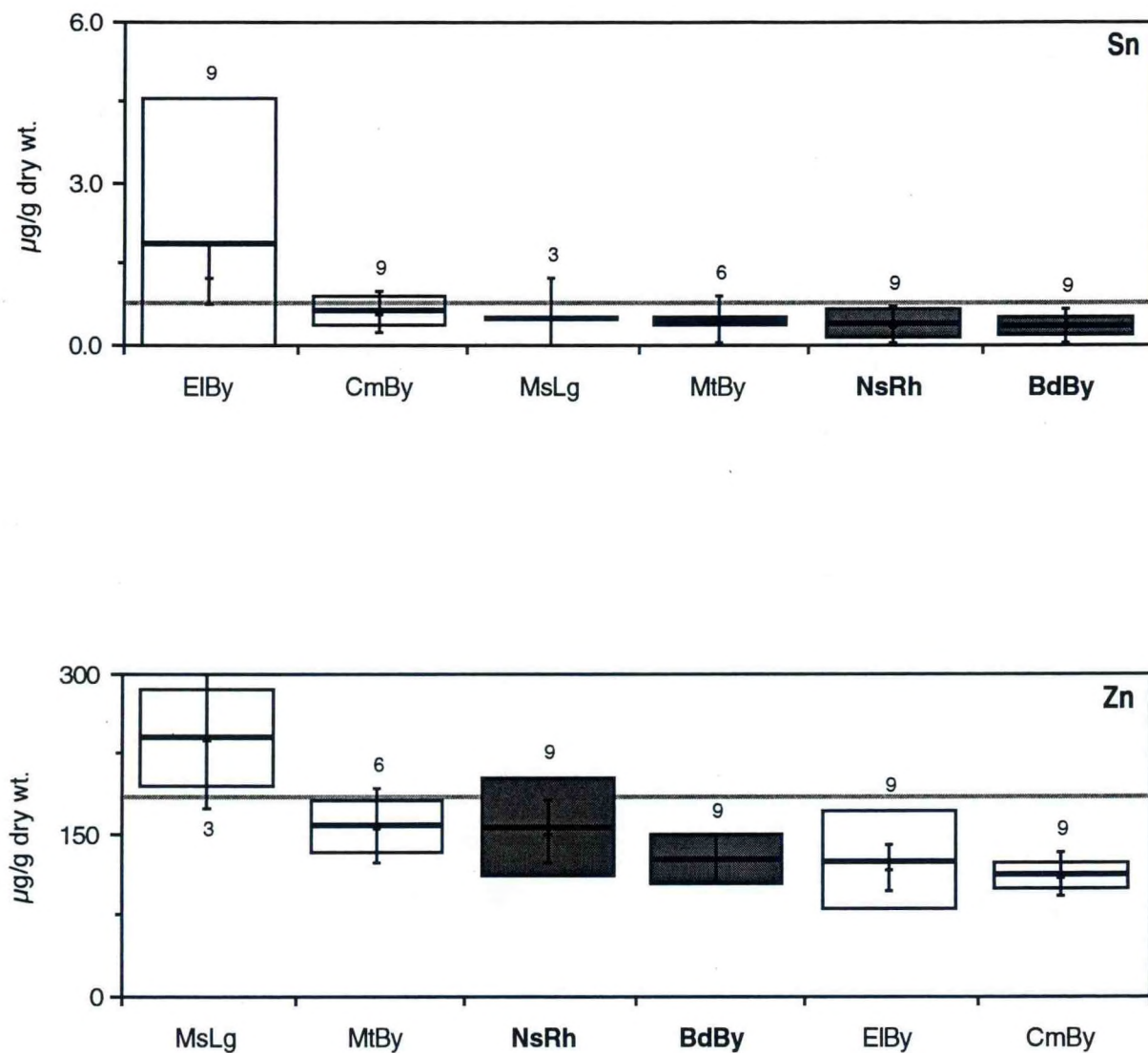


Figure 23. Floating-bar plots of elements in fish livers for the years 1984-87. Species is English sole. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [...] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

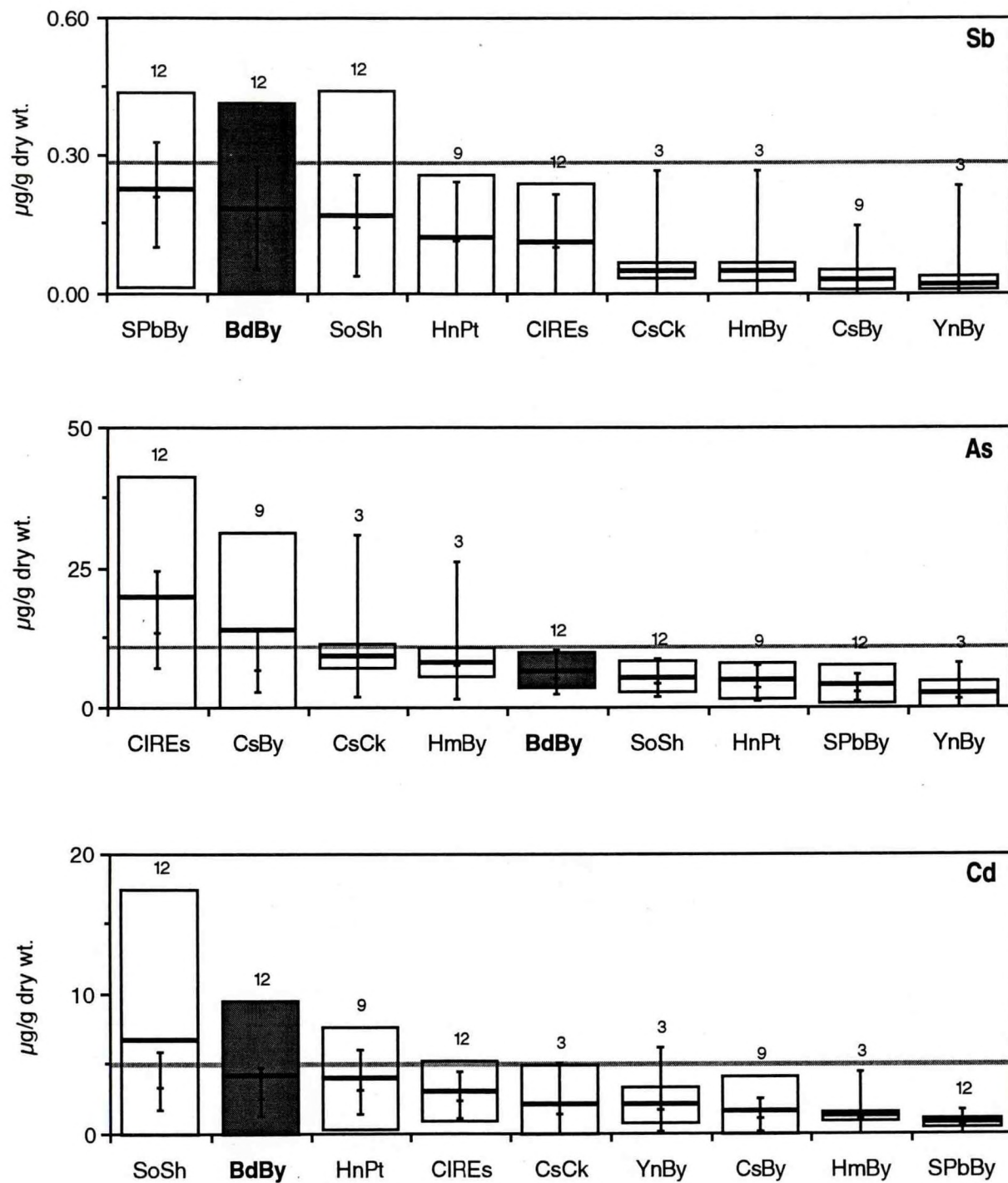


Figure 24. Floating-bar plots of elements in fish livers for the years 1984-87. Species is starry flounder. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

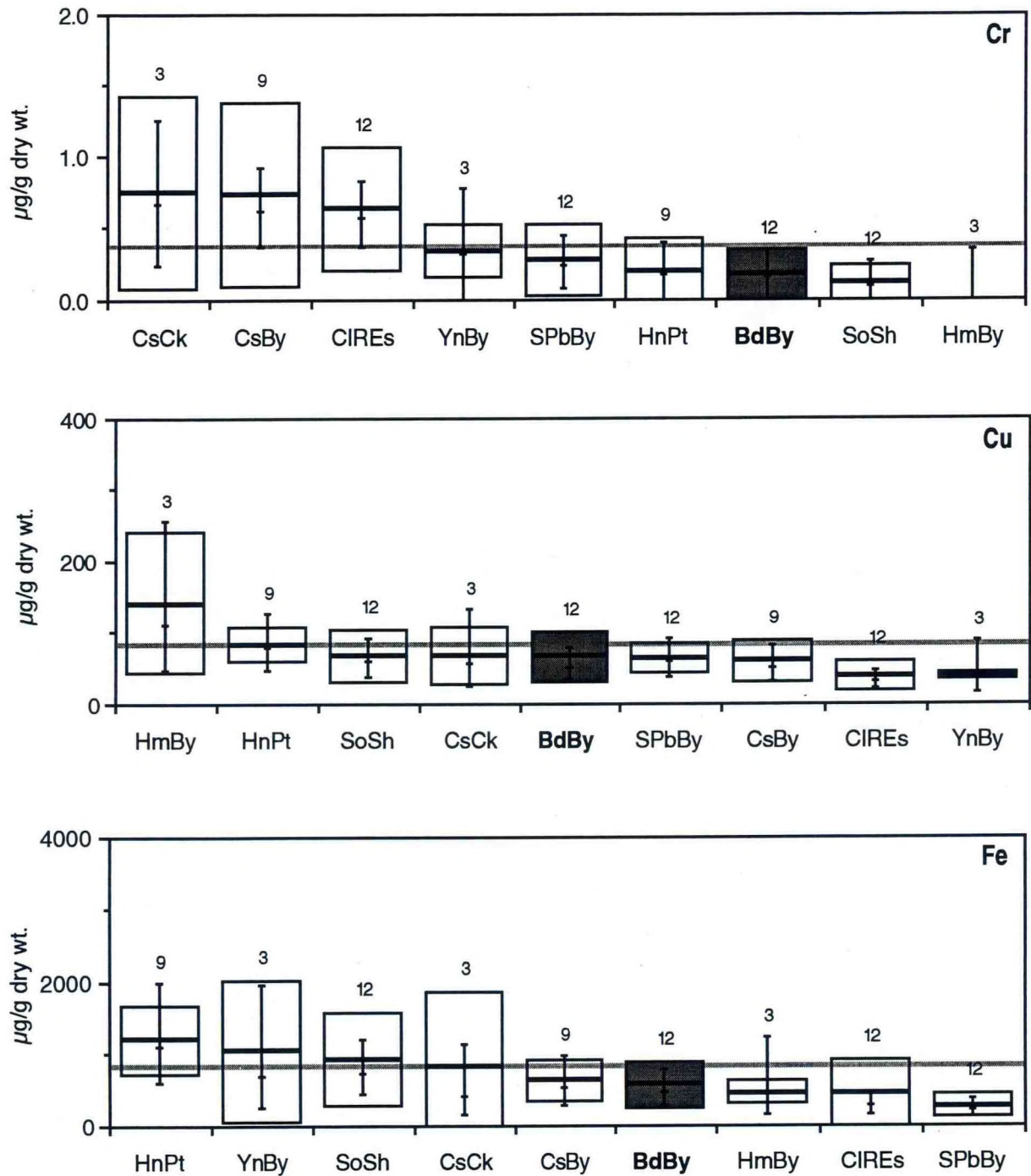


Figure 25. Floating-bar plots of elements in fish livers for the years 1984-87. Species is starry flounder. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

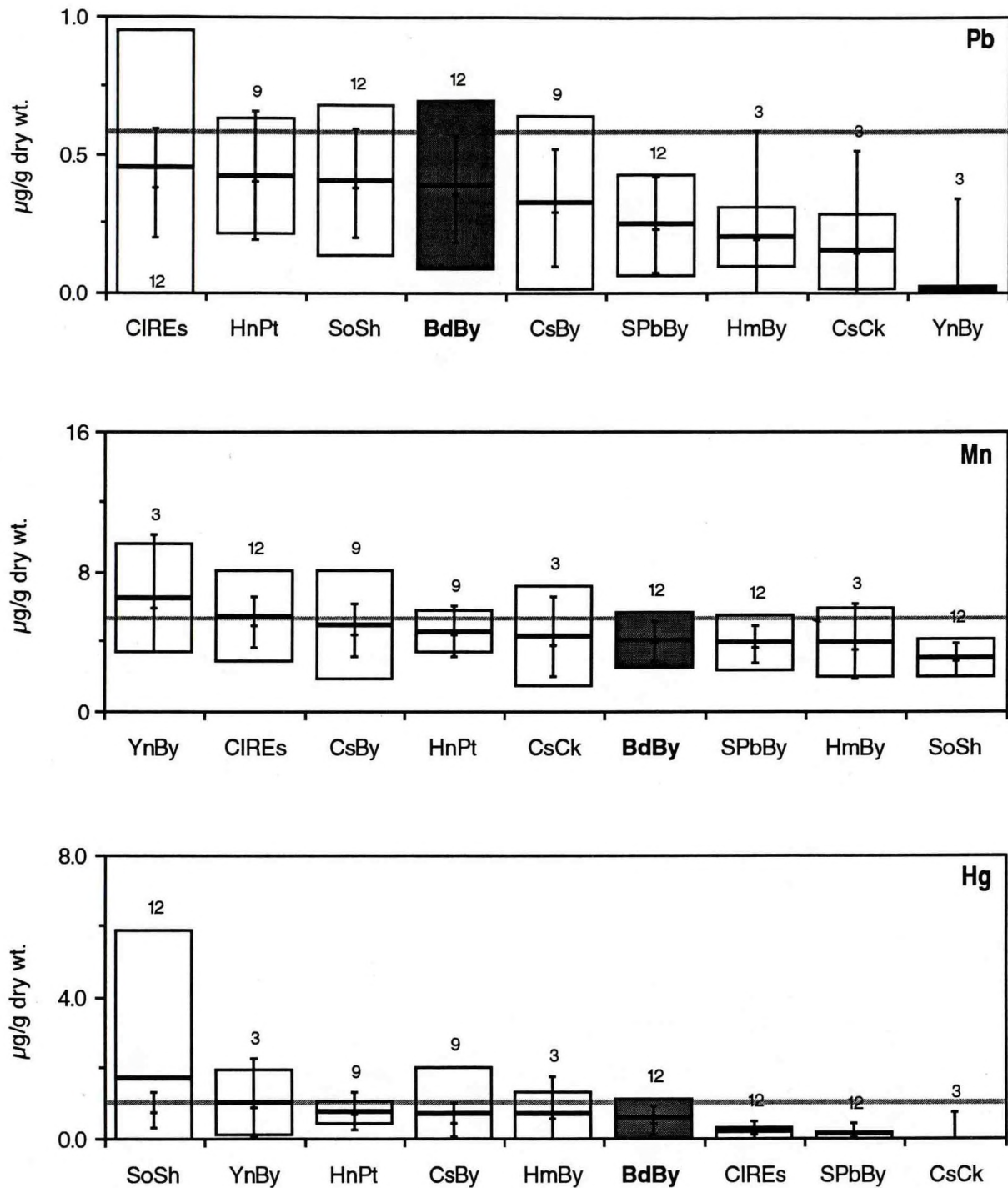


Figure 26. Floating-bar plots of elements in fish livers for the years 1984-87. Species is starry flounder. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

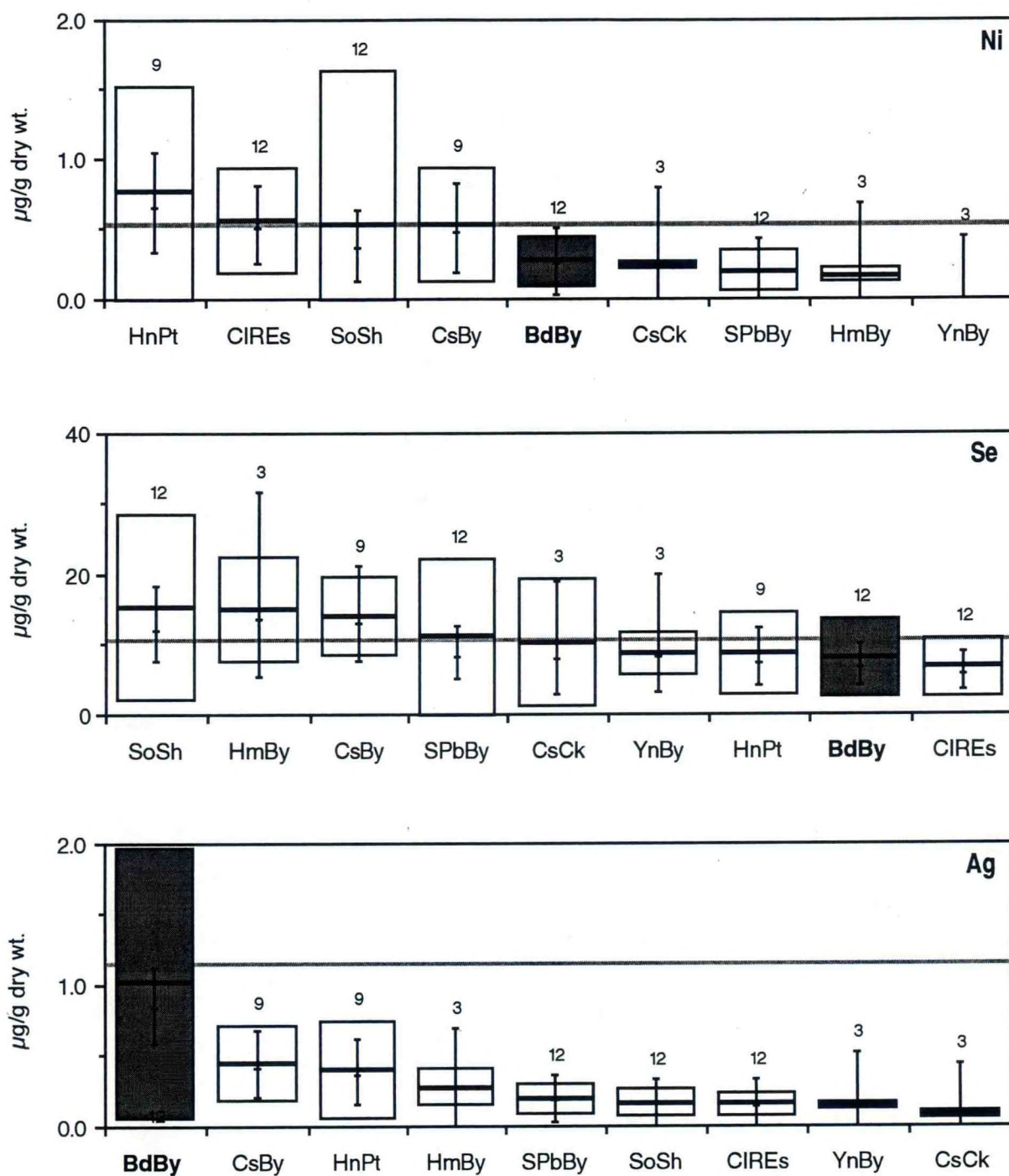


Figure 27. Floating-bar plots of elements in fish livers for the years 1984-87. Species is starry flounder. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

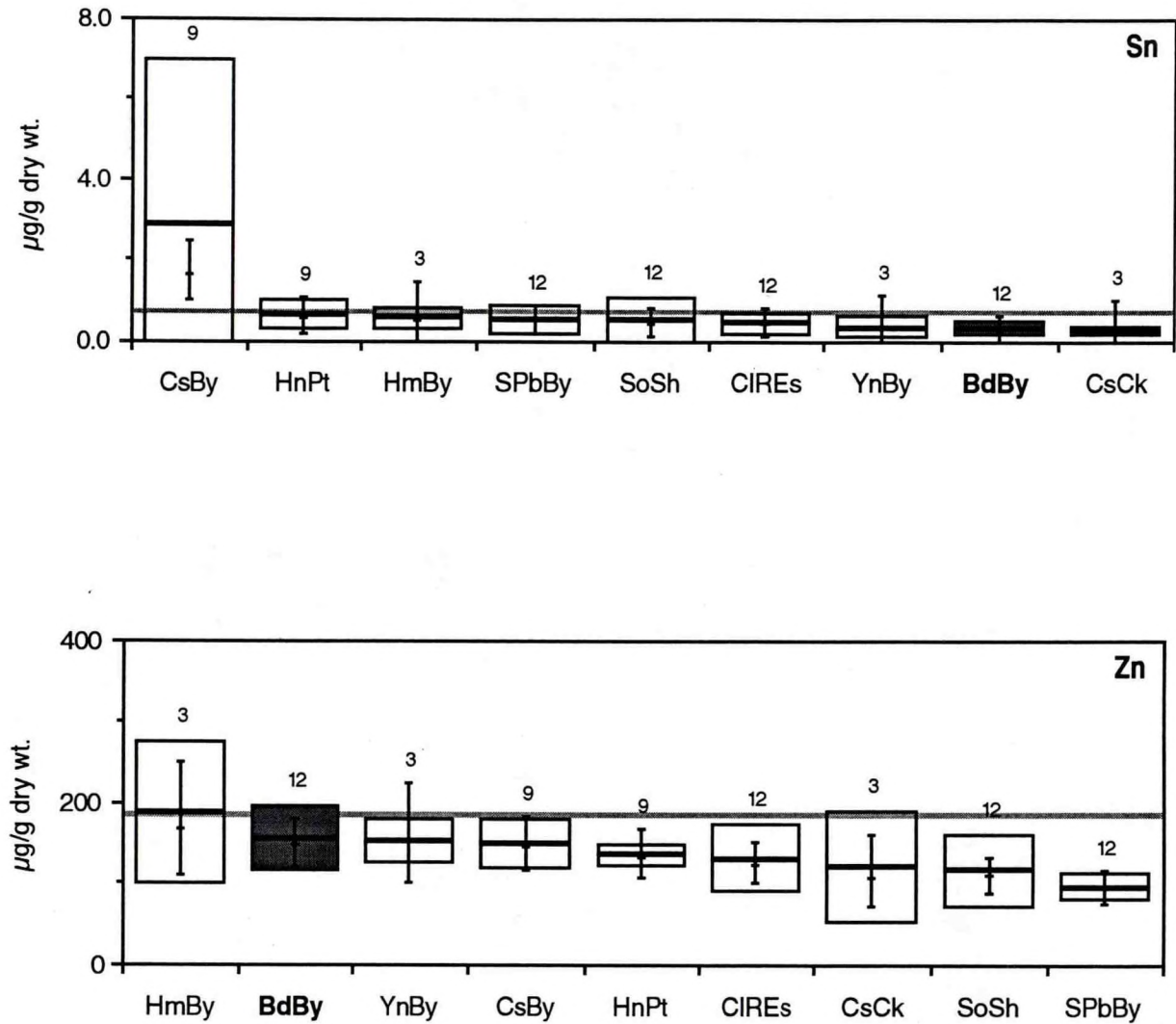


Figure 28. Floating-bar plots of elements in fish livers for the years 1984-87. Species is starry flounder. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ■ ...] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

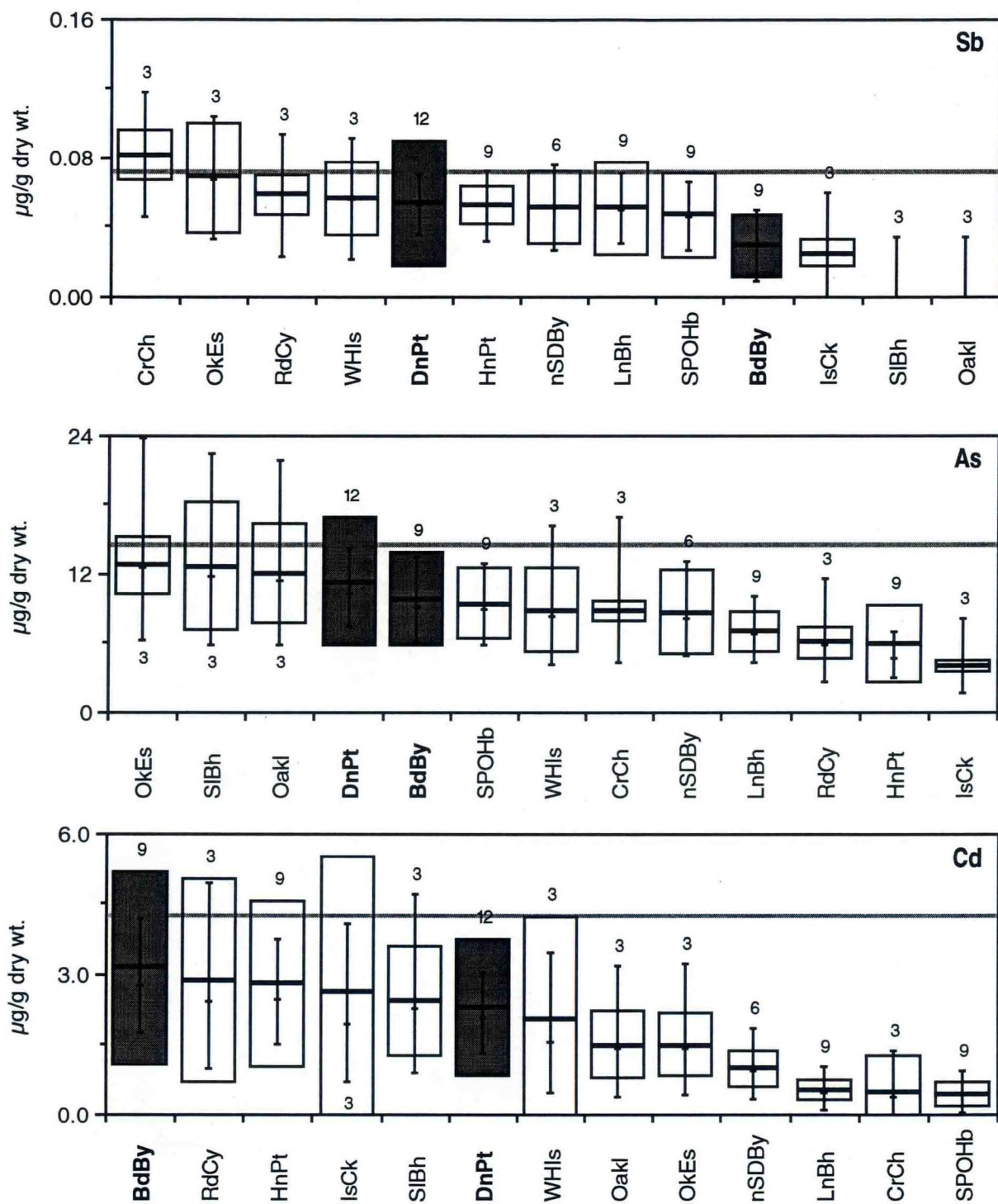


Figure 29. Floating-bar plots of elements in fish livers for the years 1984-87. Species is white croaker. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [...]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

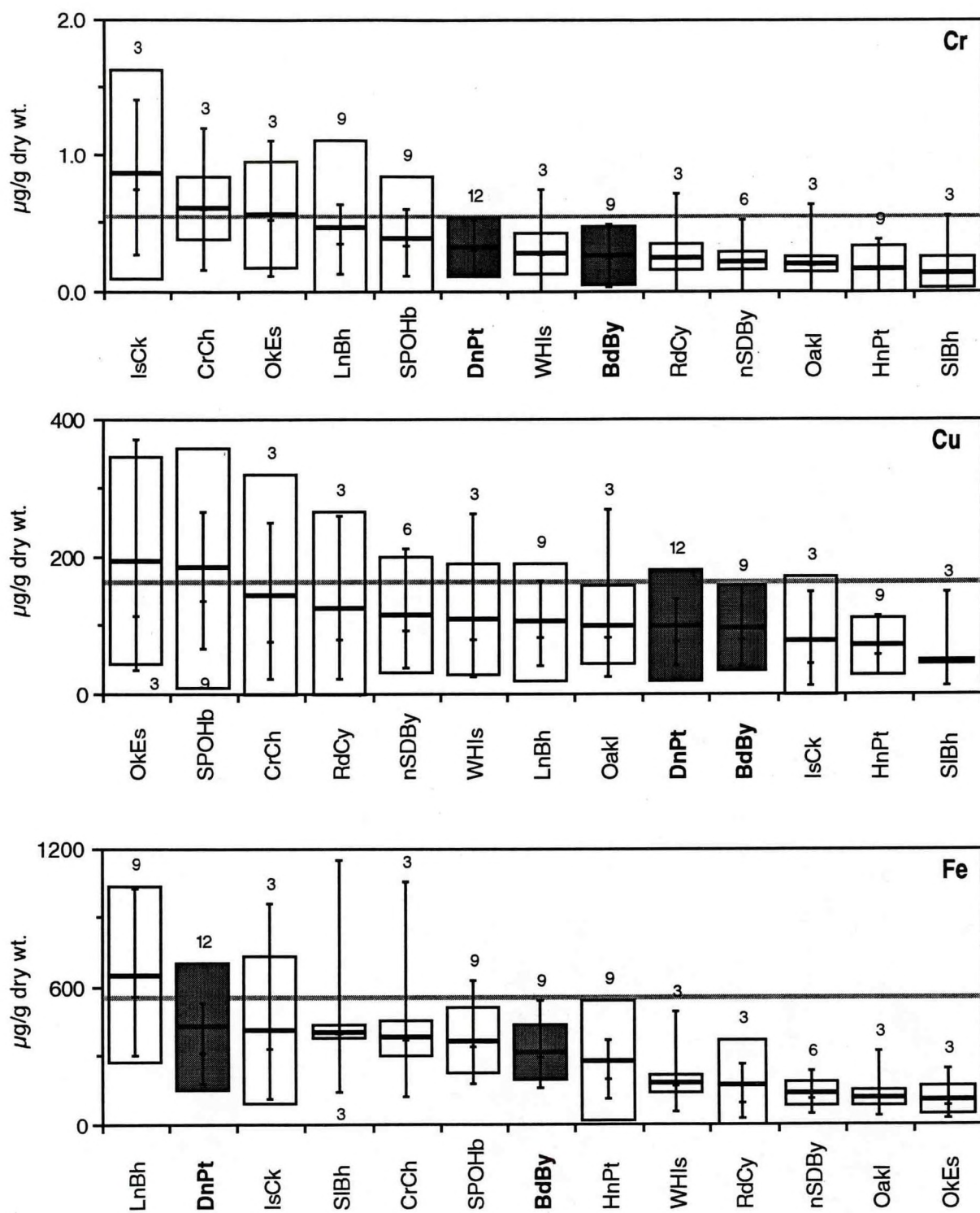


Figure 30. Floating-bar plots of elements in fish livers for the years 1984-87. Species is white croaker. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [...] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

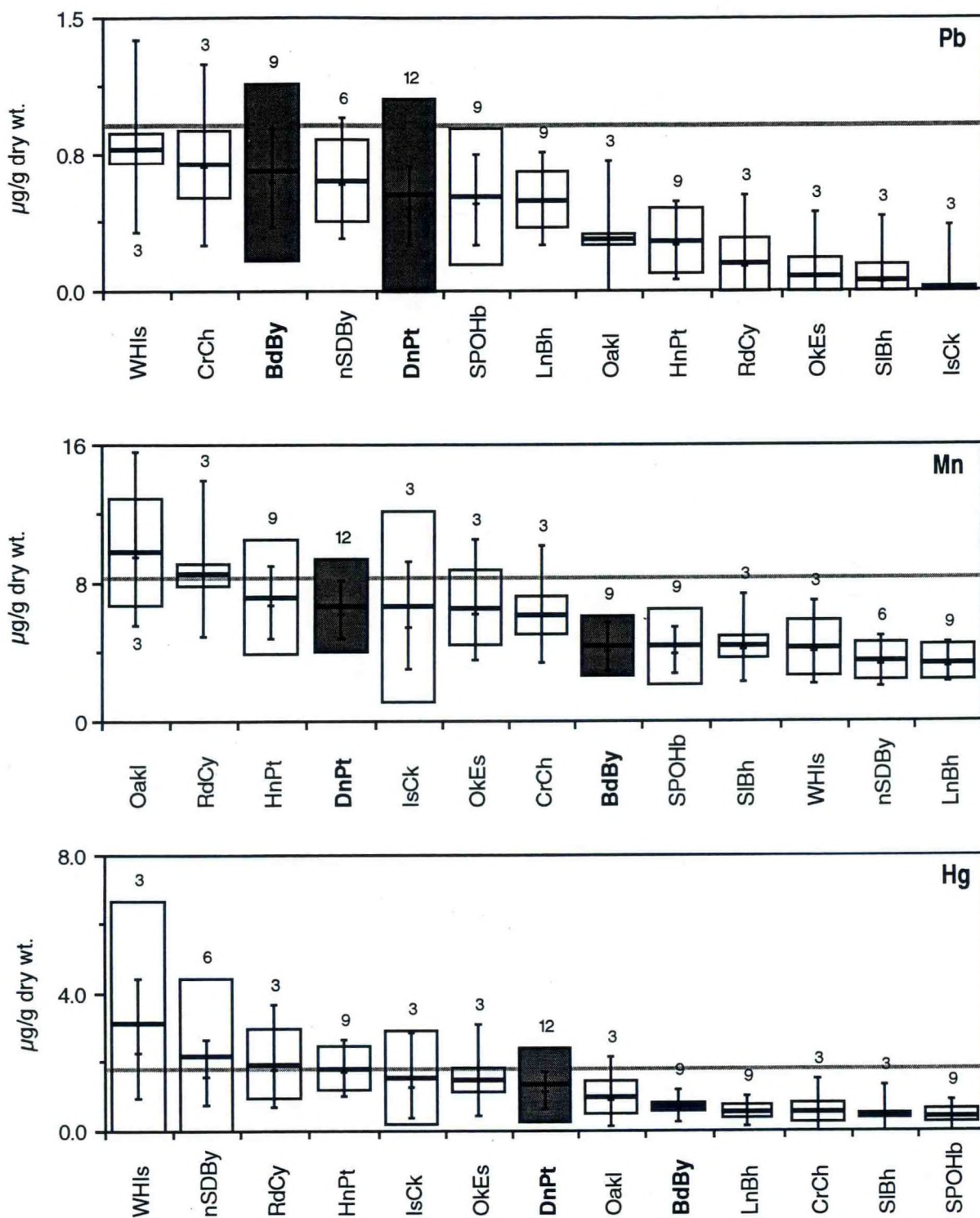


Figure 31. Floating-bar plots of elements in fish livers for the years 1984-87. Species is white croaker. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [...]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

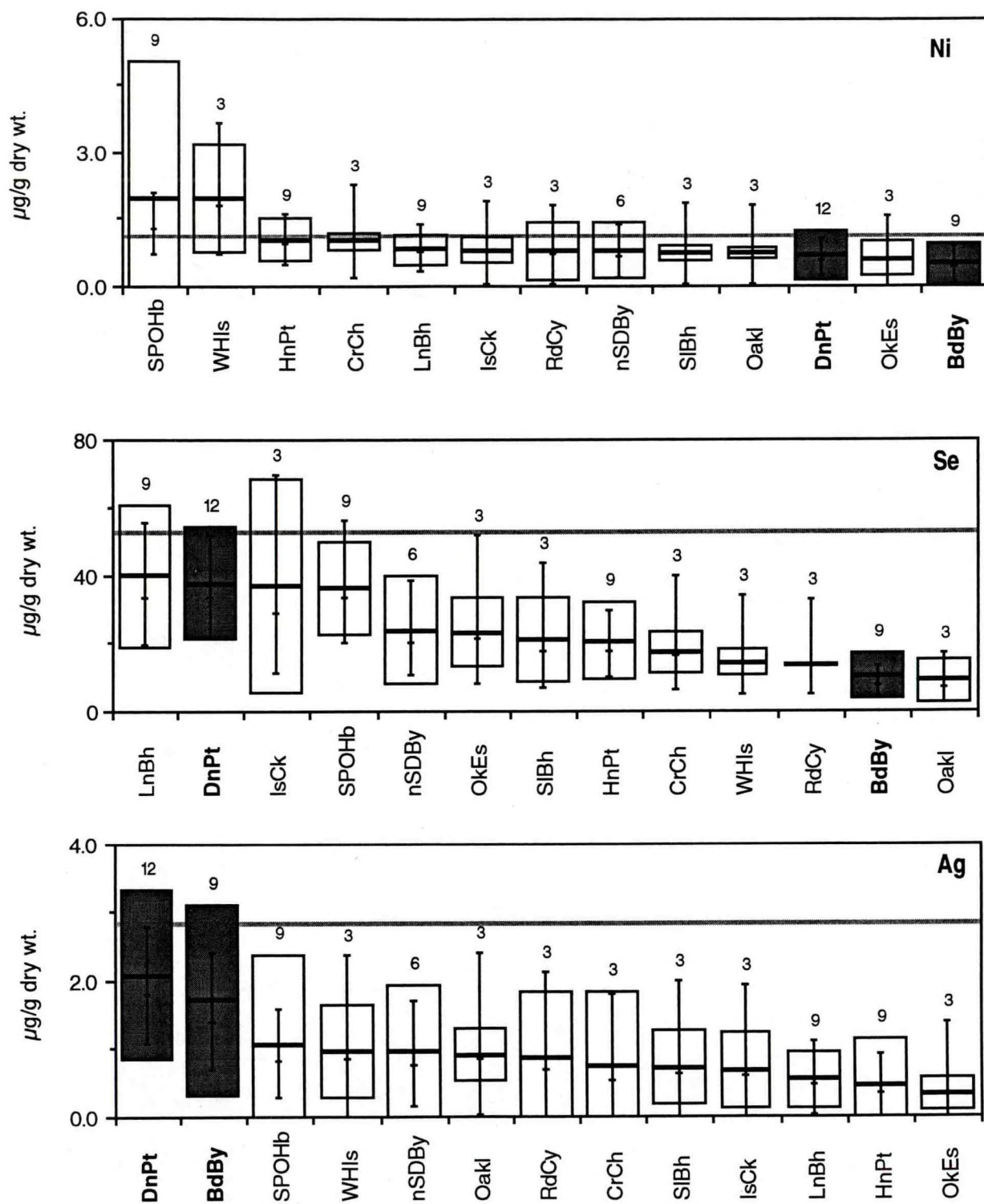


Figure 32. Floating-bar plots of elements in fish livers for the years 1984-87. Species is white croaker. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

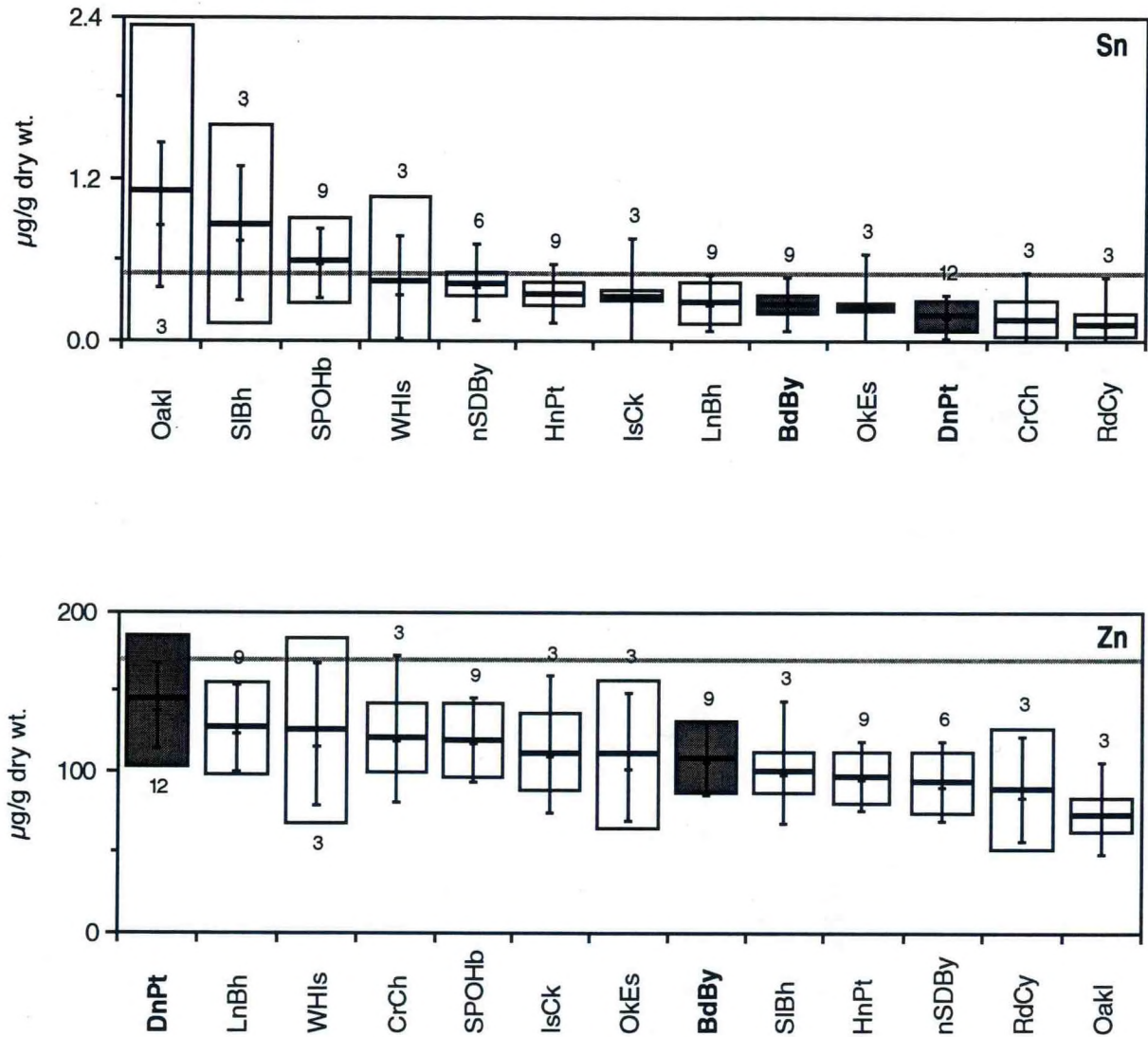


Figure 33. Floating-bar plots of elements in fish livers for the years 1984-87. Species is white croaker. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

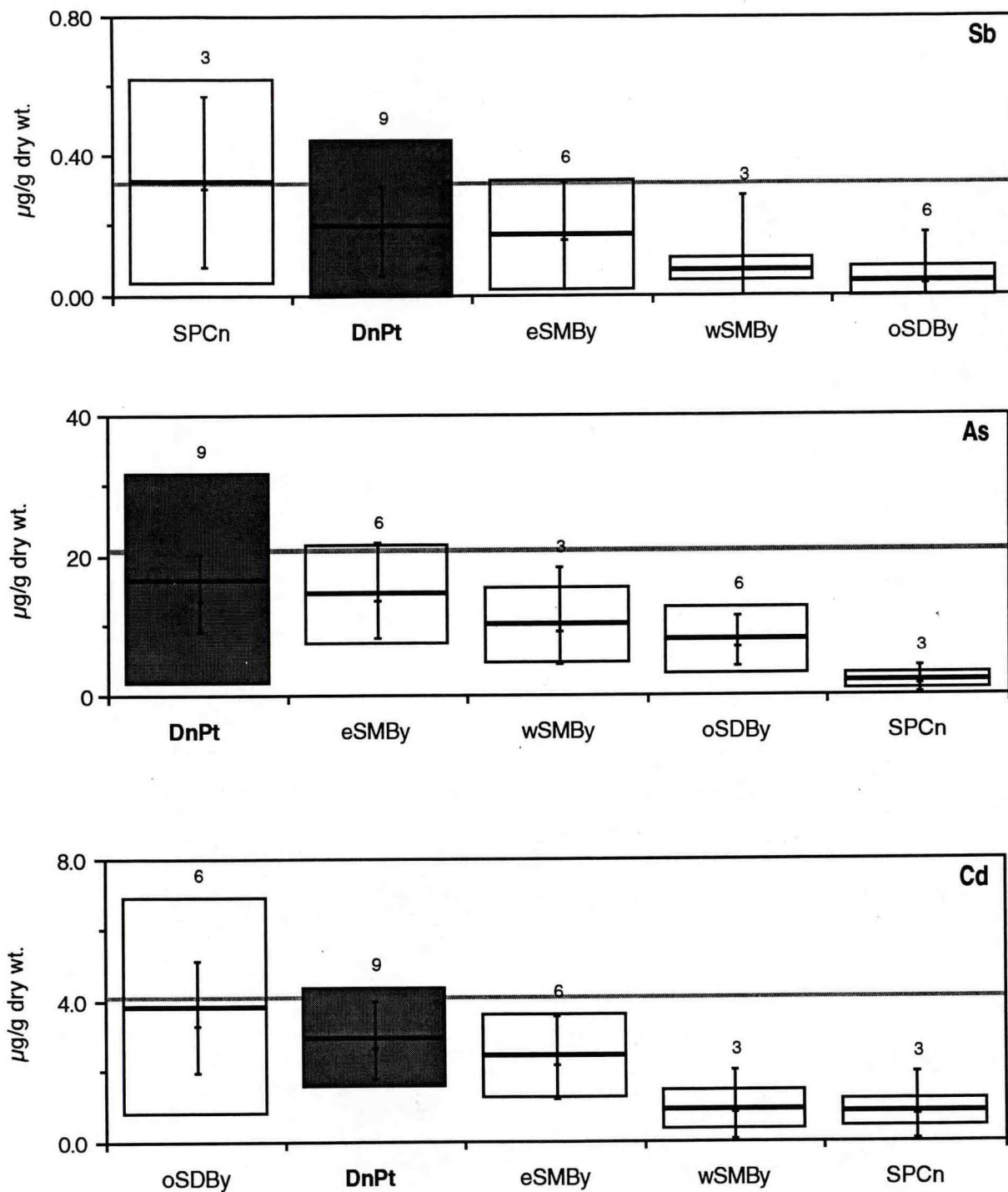


Figure 34. Floating-bar plots of elements in fish livers for the years 1984-87. Species is hornyhead turbot. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

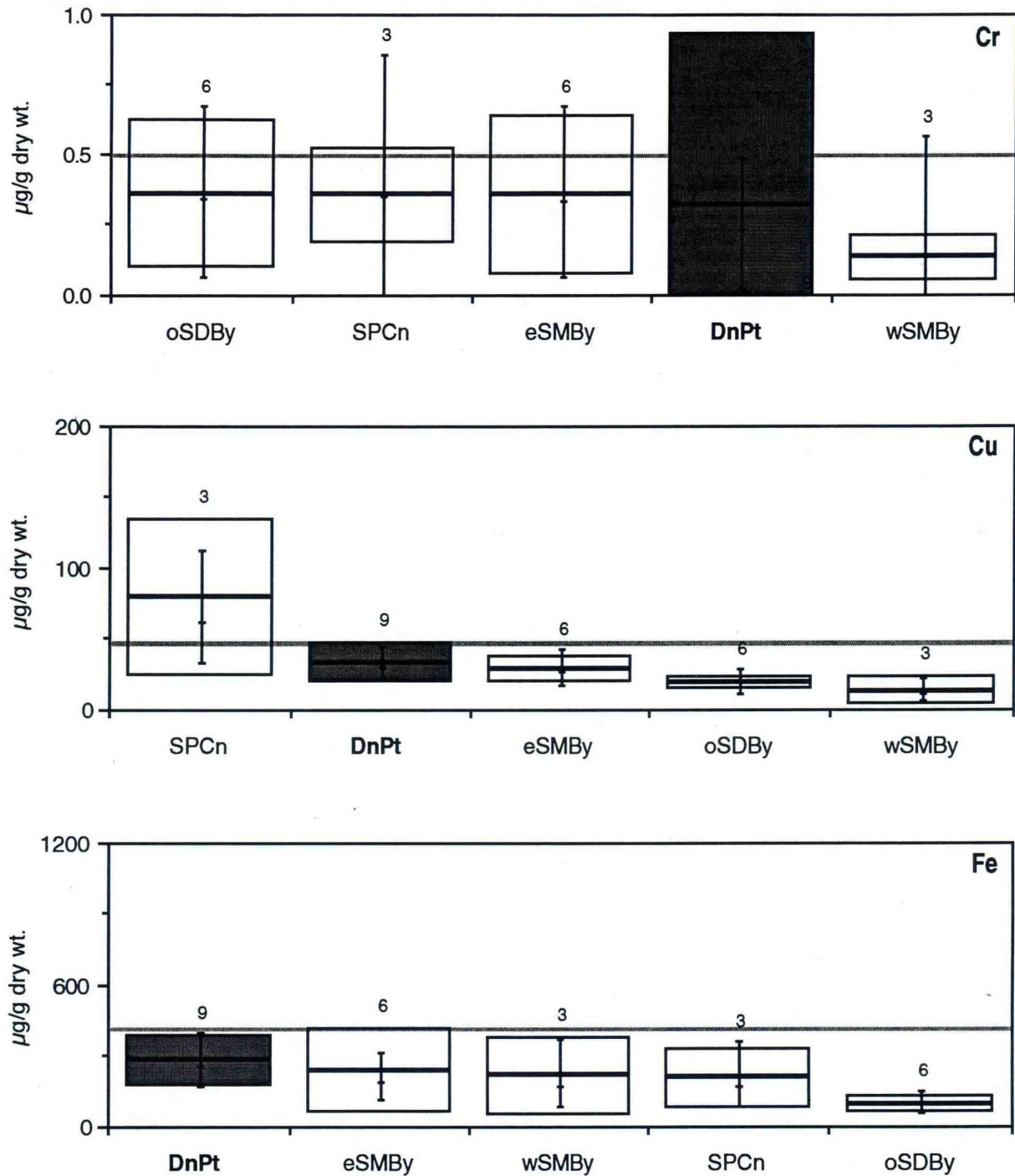


Figure 35. Floating-bar plots of elements in fish livers for the years 1984-87. Species is hornyhead turbot. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

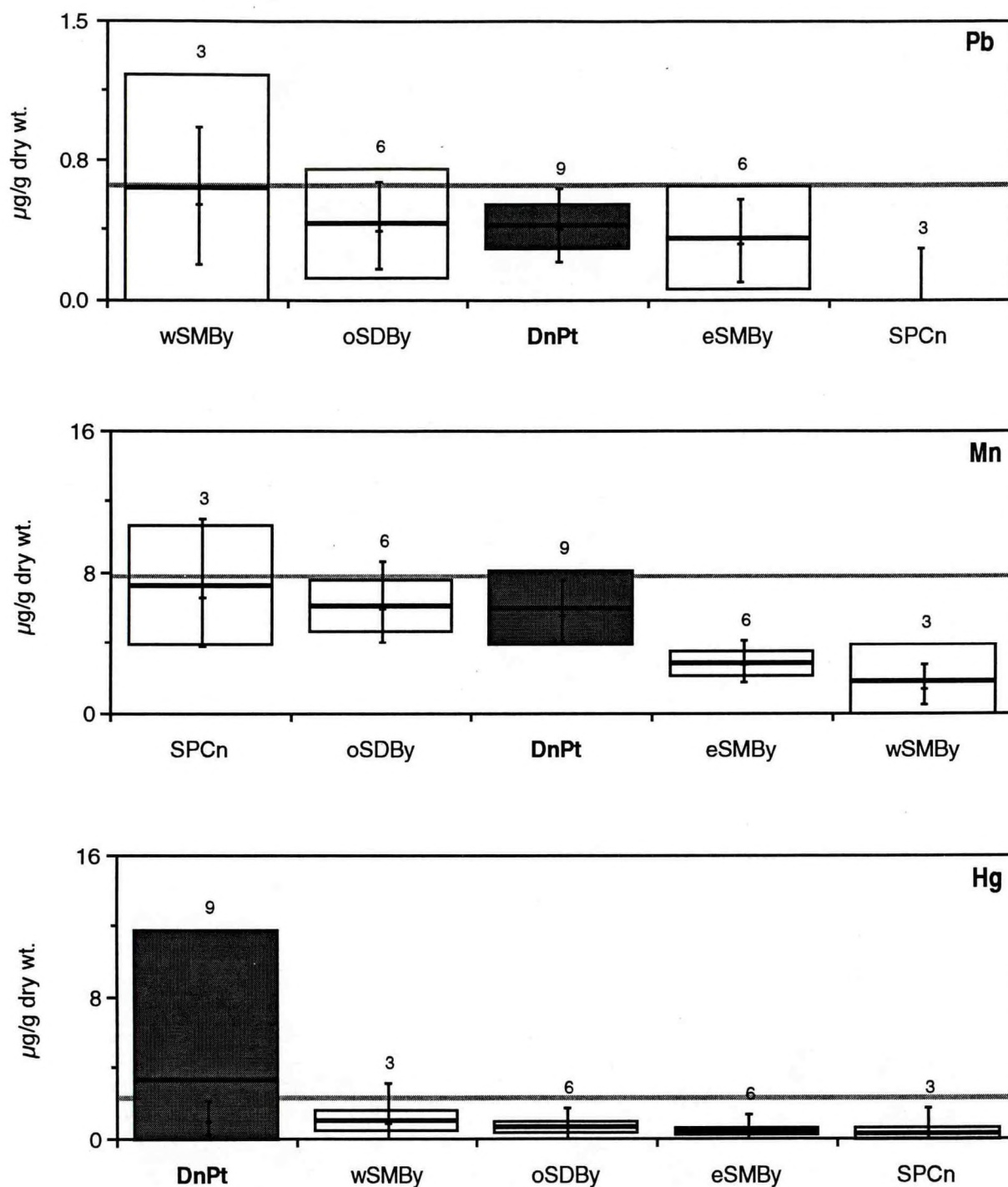


Figure 36. Floating-bar plots of elements in fish livers for the years 1984-87. Species is hornyhead turbot. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ■ ...] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

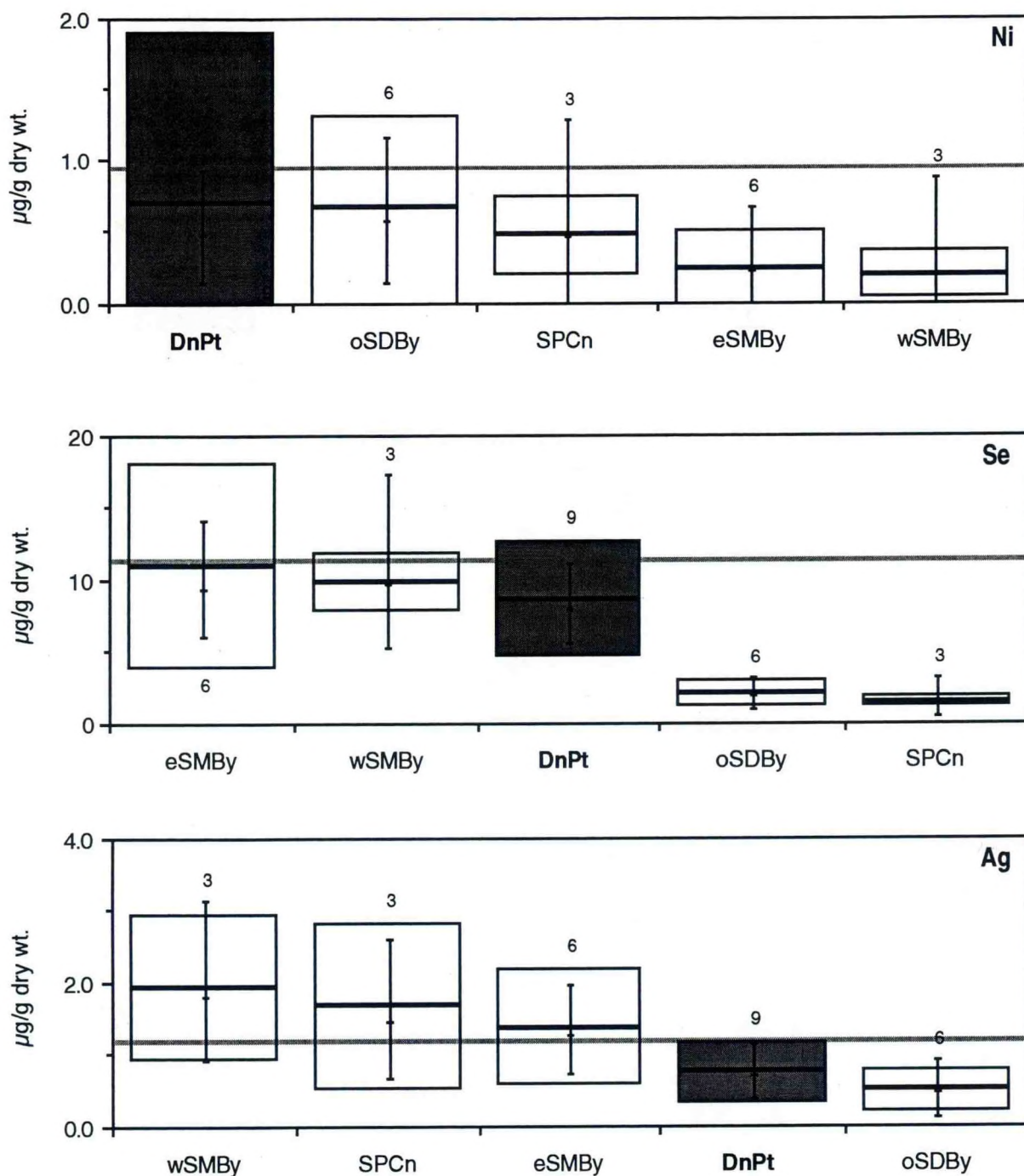


Figure 37. Floating-bar plots of elements in fish livers for the years 1984-87. Species is hornyhead turbot. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

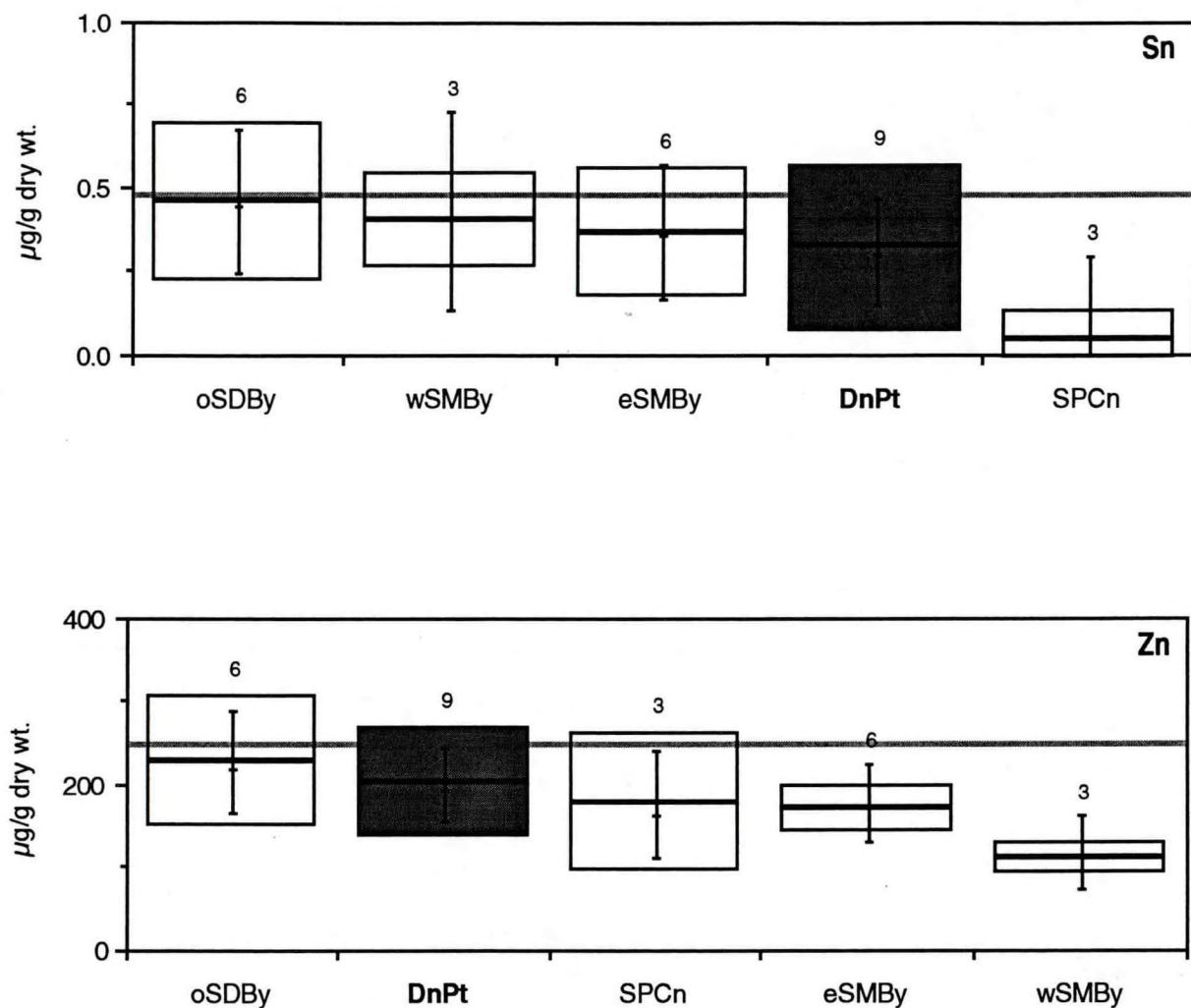


Figure 38. Floating-bar plots of elements in fish livers for the years 1984-87. Species is hornyhead turbot. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

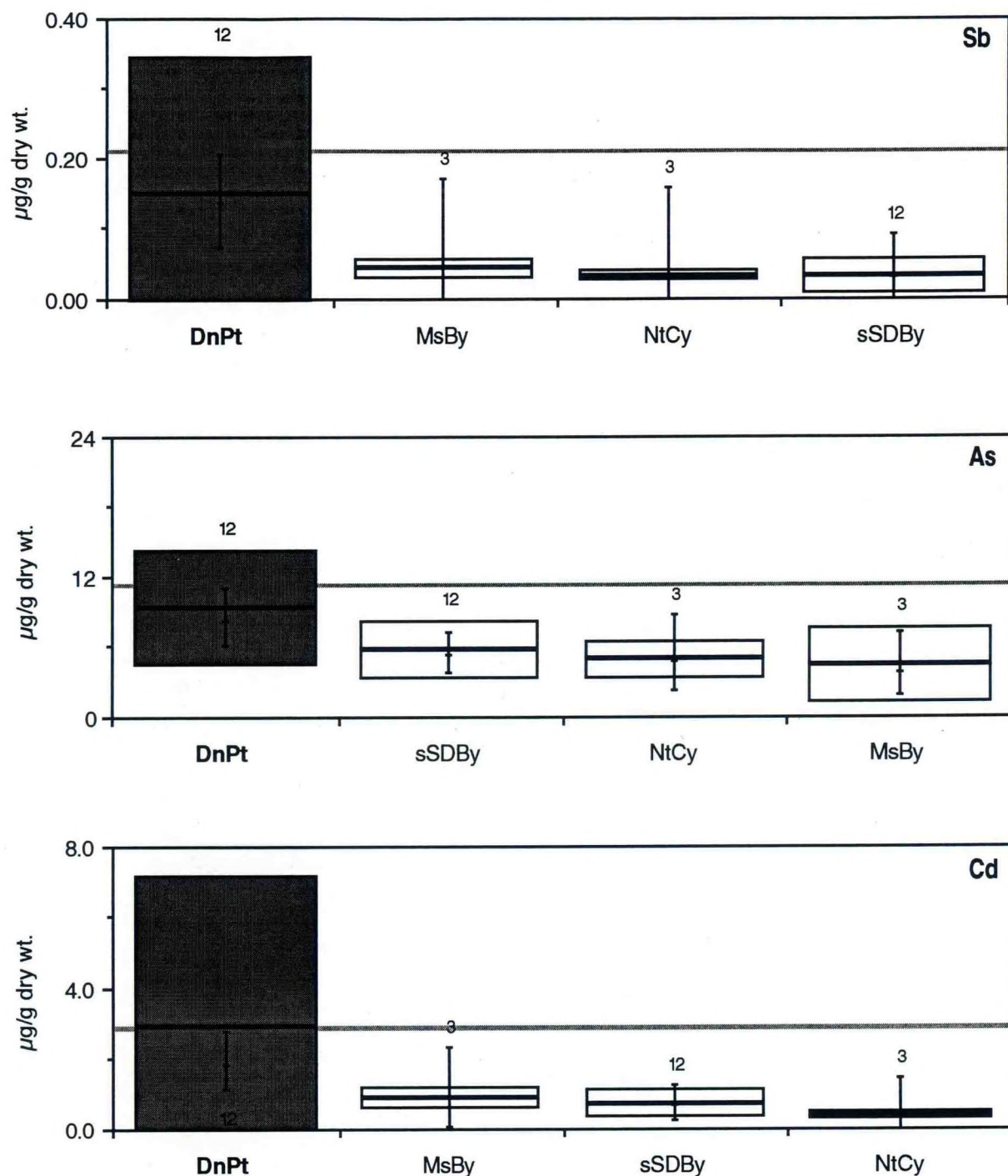


Figure 39. Floating-bar plots of elements in fish livers for the years 1984-87. Species is barred sand bass. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [⋮] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

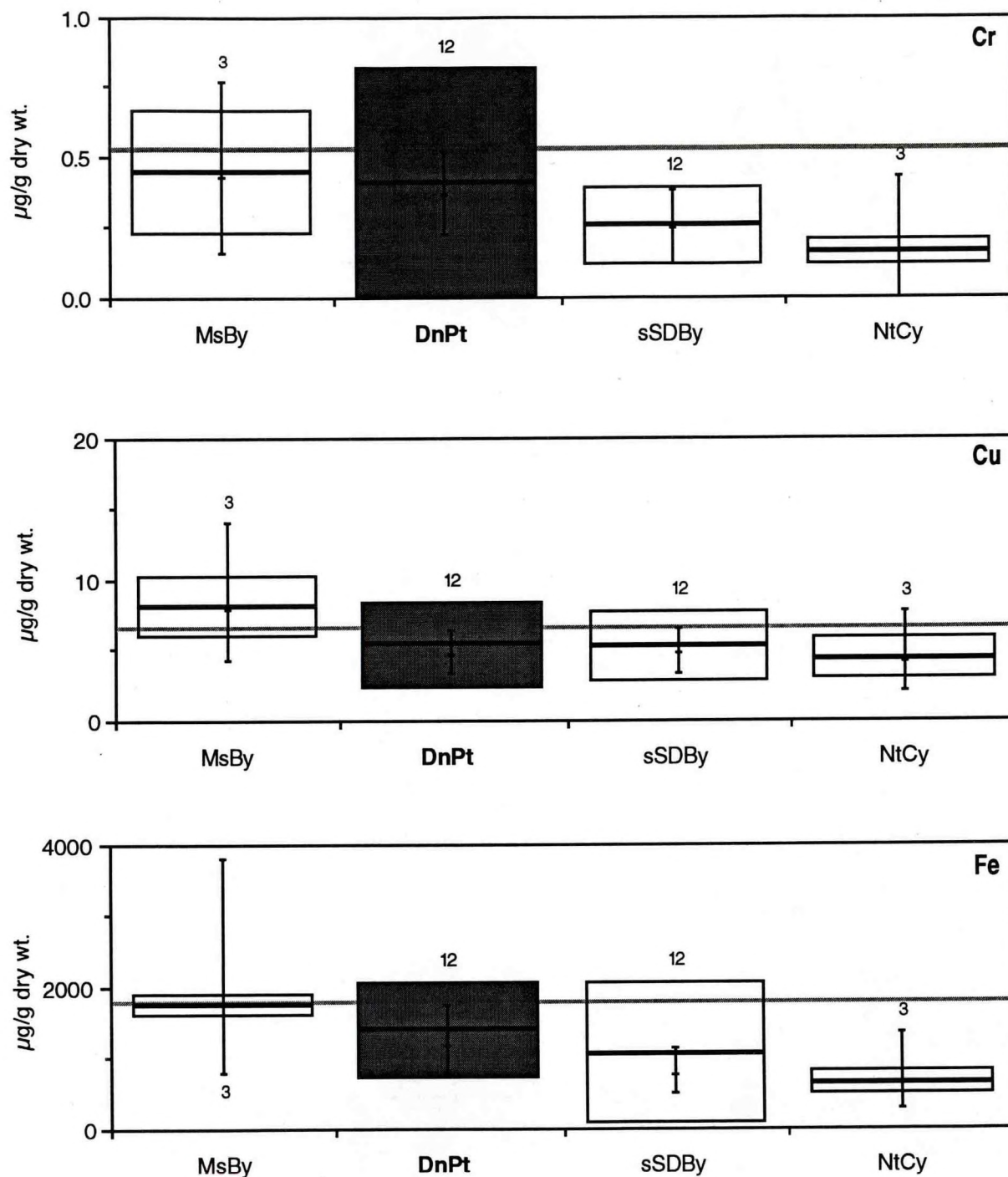


Figure 40. Floating-bar plots of elements in fish livers for the years 1984-87. Species is barred sand bass. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [⋯] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

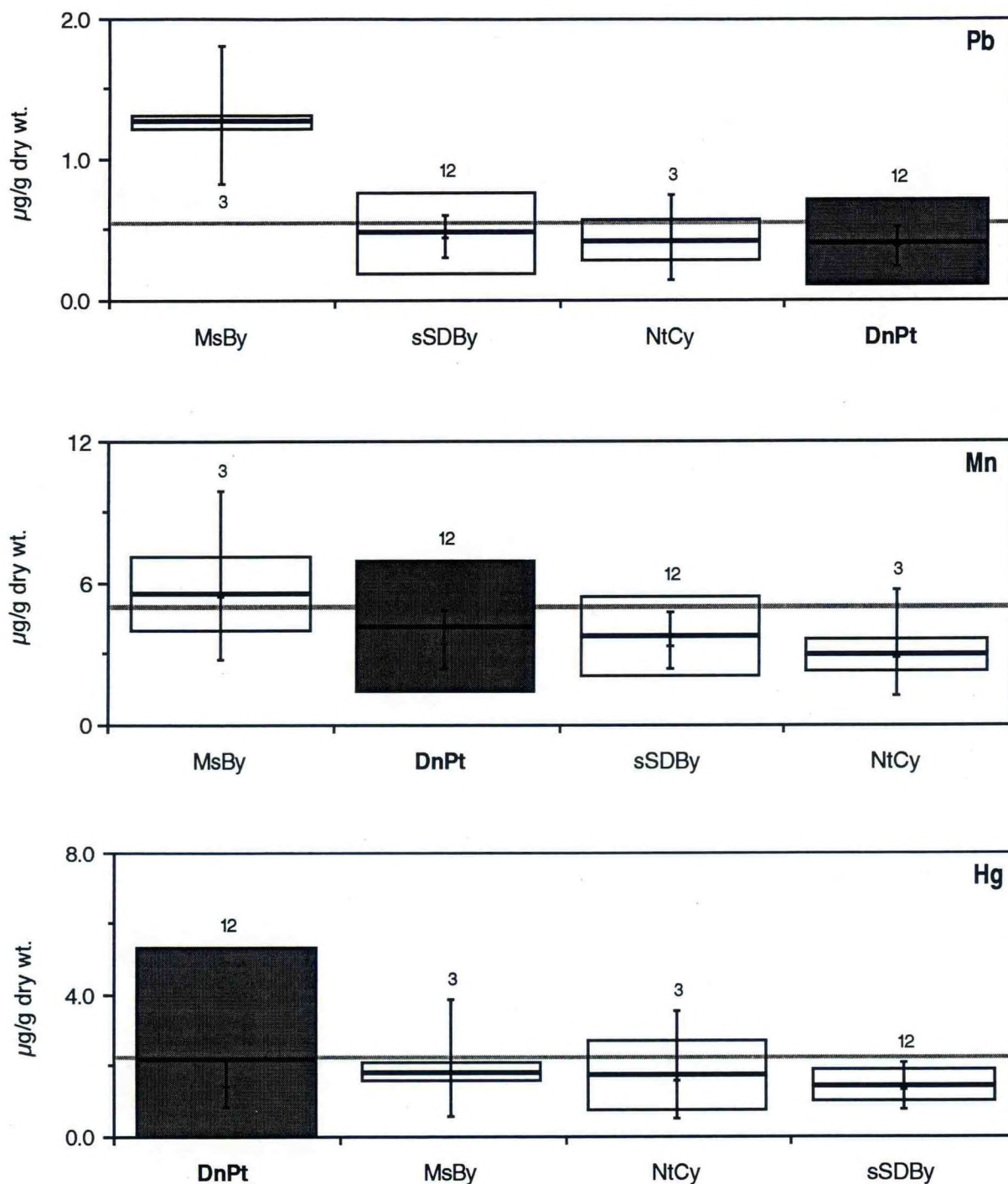


Figure 41. Floating-bar plots of elements in fish livers for the years 1984-87. Species is barred sand bass. Plot components are arithmetic mean concentration [■], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval [---] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

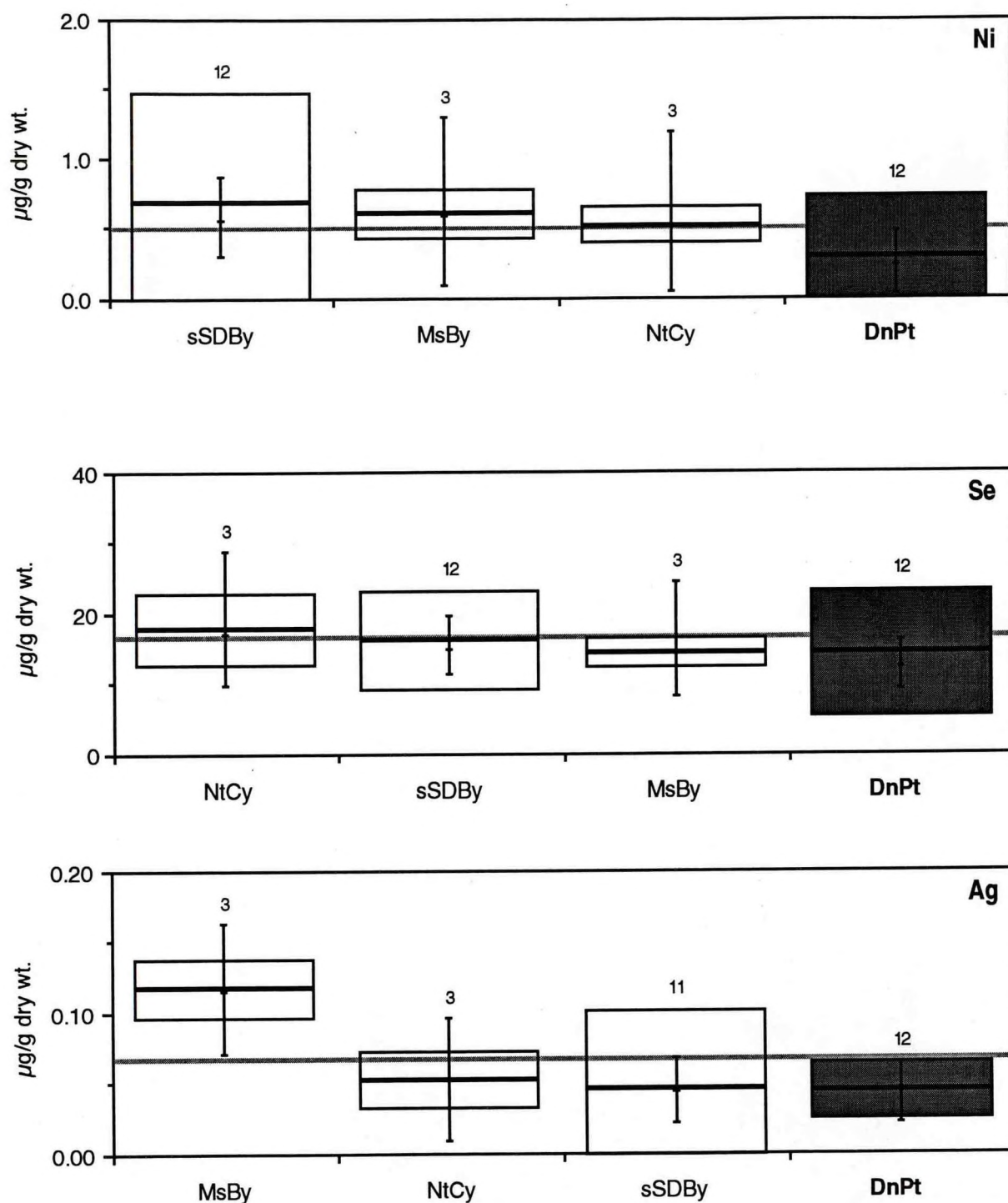


Figure 42. Floating-bar plots of elements in fish livers for the years 1984-87. Species is barred sand bass. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

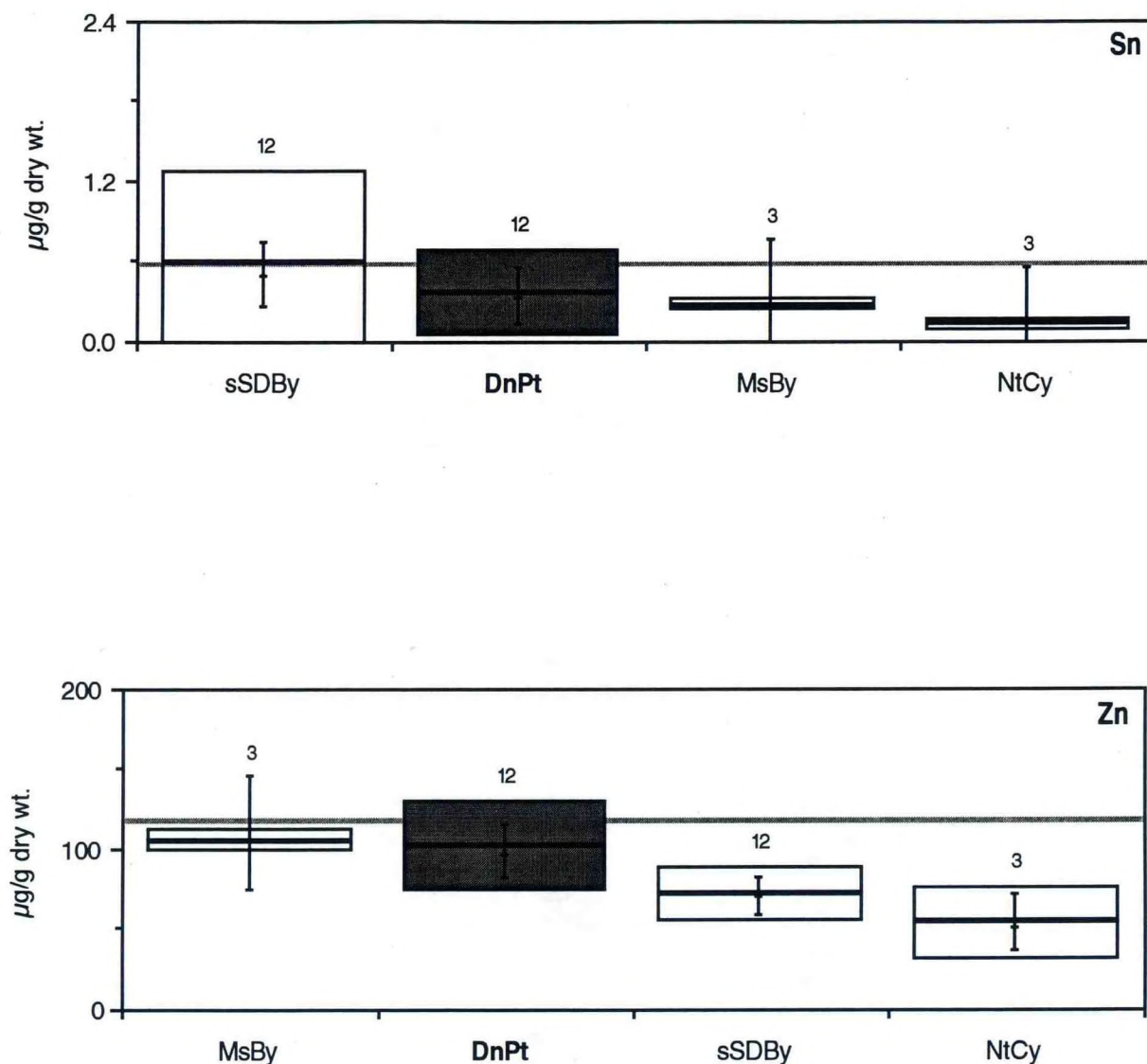


Figure 43. Floating-bar plots of elements in fish livers for the years 1984-87. Species is barred sand bass. Plot components are arithmetic mean concentration [—], one standard deviation [□], geometric mean [—], comparison interval [I], and maximum comparison interval value [... ..] for the reference site [■]. Sites are ranked in order of arithmetic mean concentration along the x-axis. See Tables 1 and 3 for abbreviations. Numbers for each site indicate sample size.

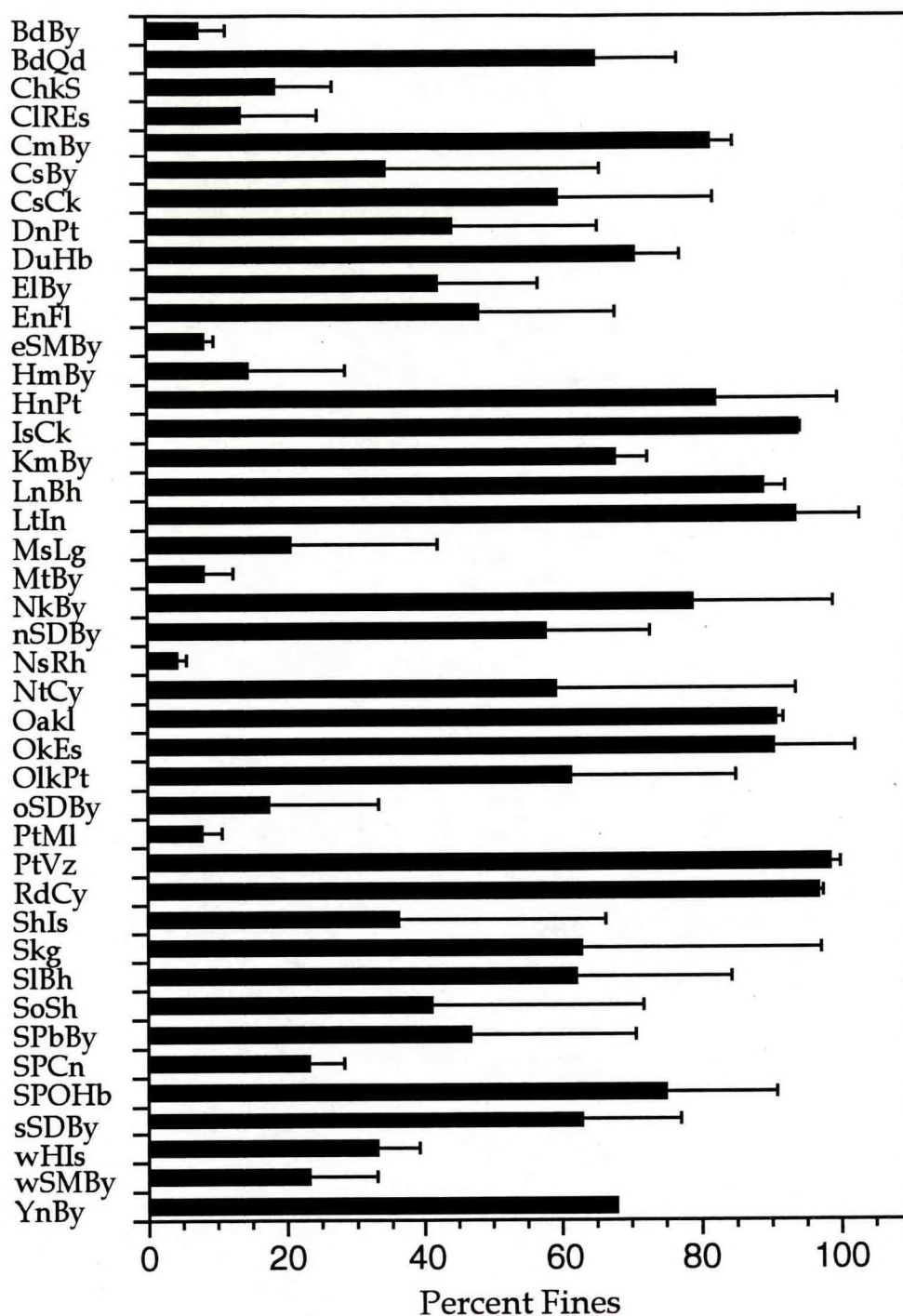


Figure 44. Percent fine particles in sediment. Percent of particles, by dry weight, that are less than $63 \mu\text{m}$. Each site value is the mean and standard deviation of all measurements made at each station (A, B, C) over all years sampled (1984-88). Sample sizes can be seen on Figure 3. Site location abbreviations in Table 1.

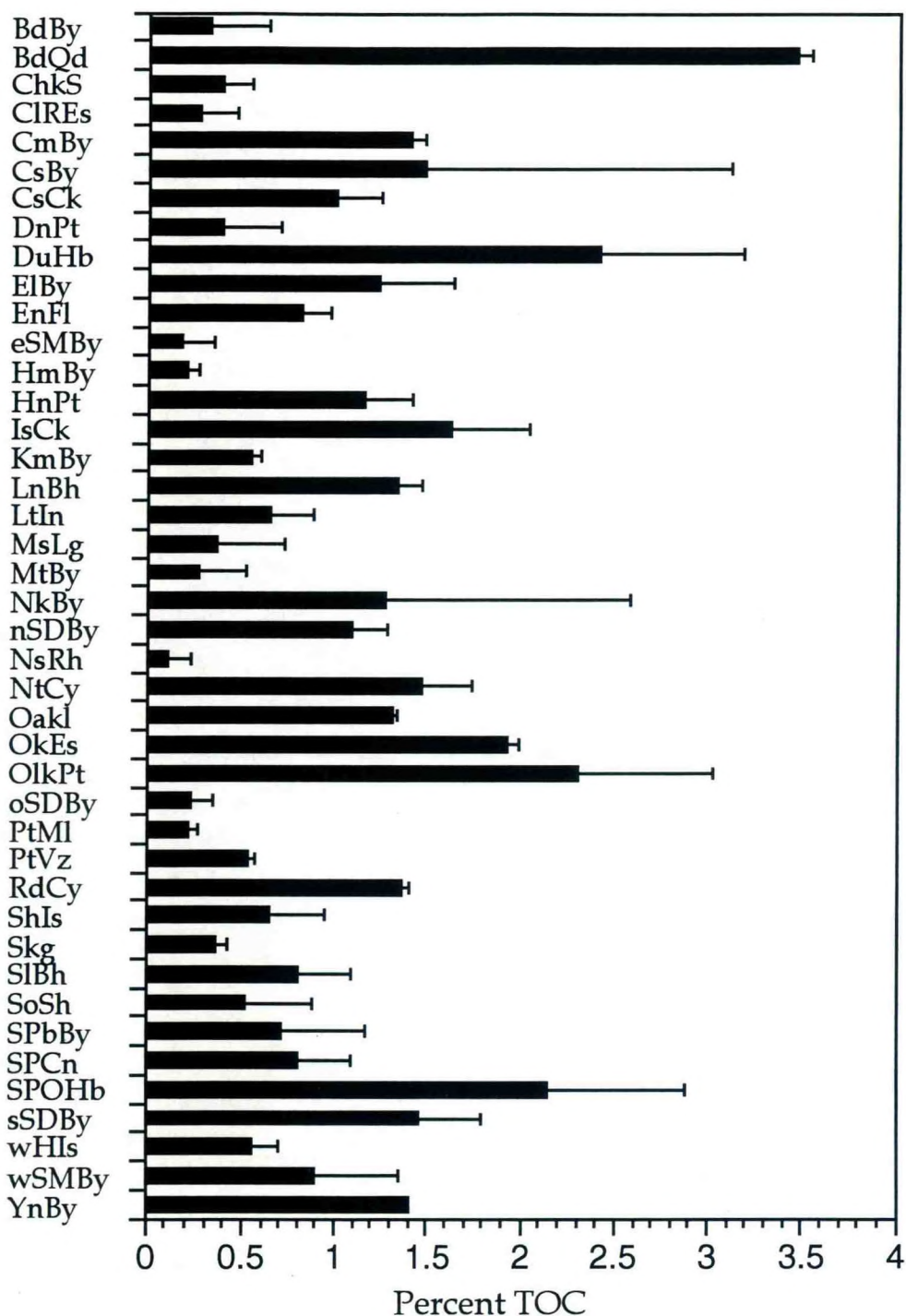


Figure 45. Percent total organic carbon (TOC) in sediment. Each site value is the mean and standard deviation of all measurements made at each station (A, B, C) over all years sampled (1984-1988). TOC is percent of sediment by dry weight. Sample sizes can be seen on Figure 3. Site location abbreviations in Table 1.

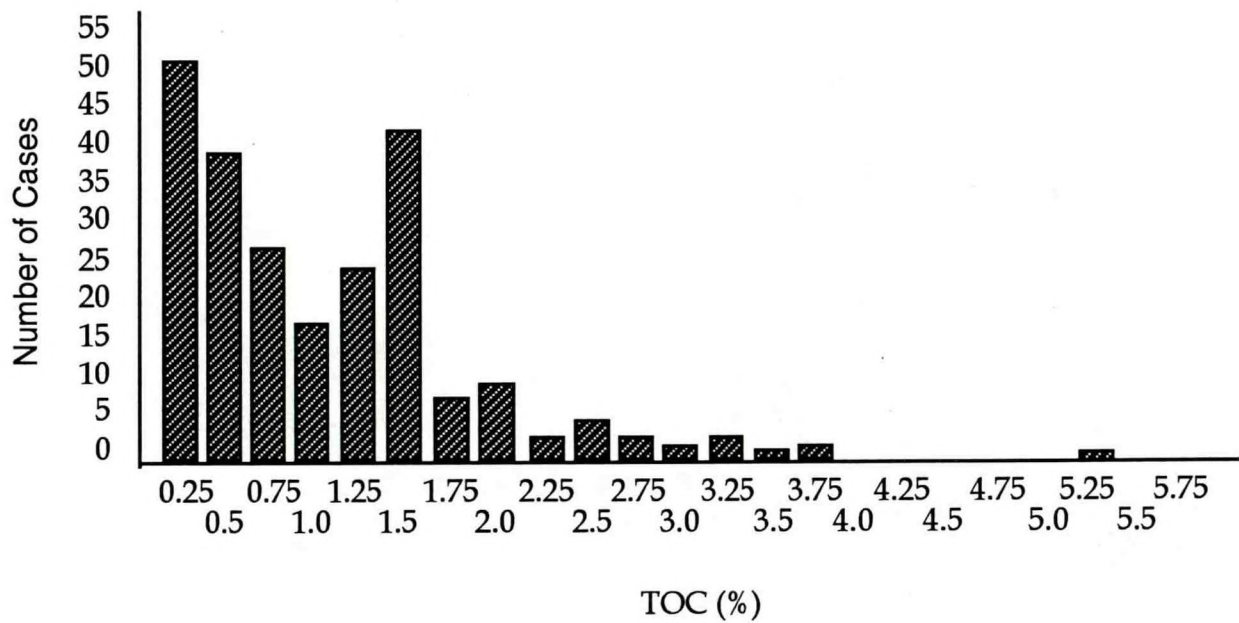


Figure 46. Frequency histogram of total organic carbon (TOC) in sediment. Frequency occurrence of mean TOC measurements made in bulk sediment from stations (A, B, C) at each site. See Figure 45 for additional details.

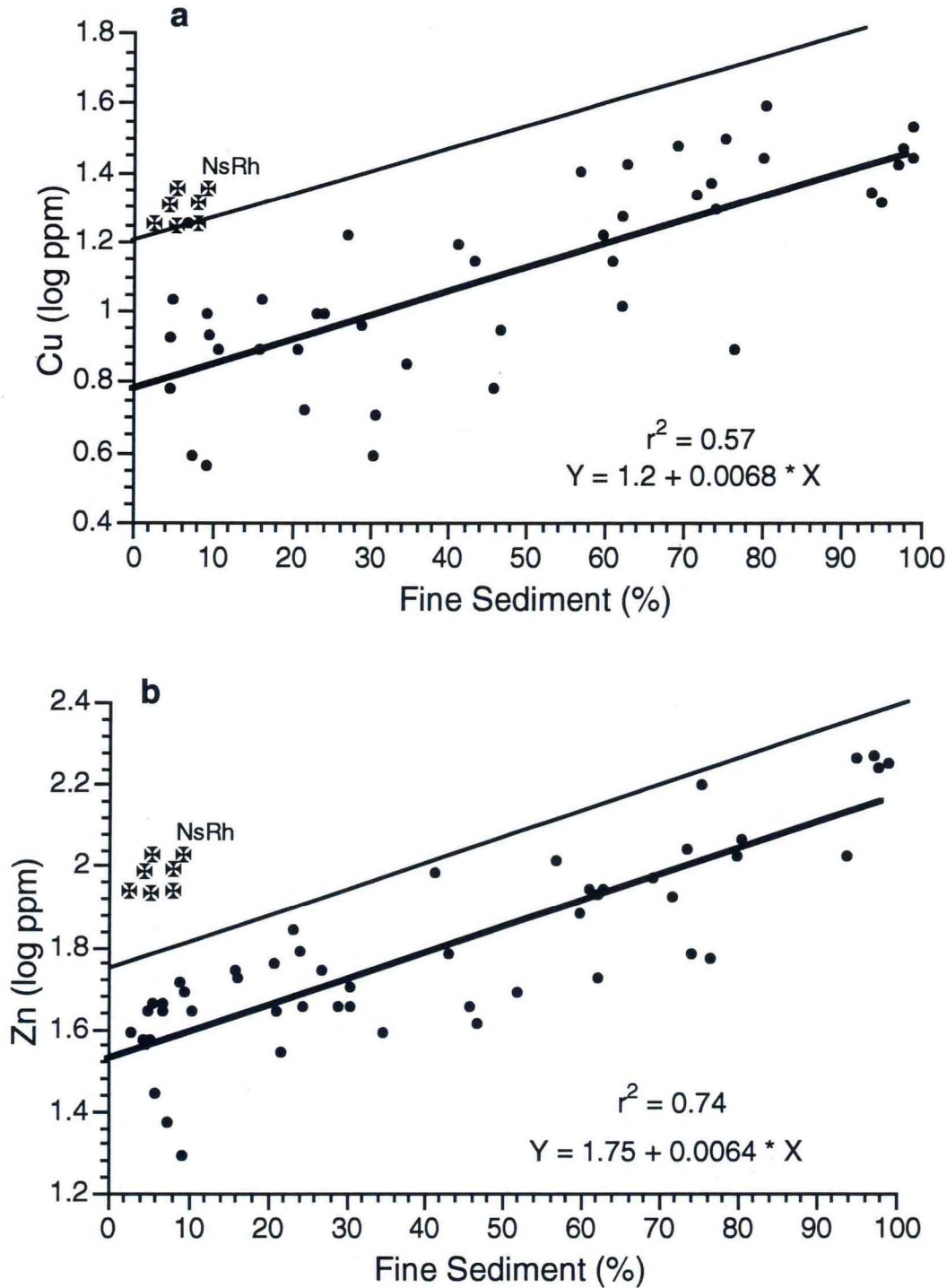


Figure 47. Plot of metal concentrations and percent fine sediment. Plots show $\log_{10} \mu\text{g/g}$ concentrations (dry weight) from reference and nonurban sites that were used to develop relationships for determination of background concentrations. Equation shows upper confidence band and r^2 is the amount of variation in the dependent variable that is explained by the independent variable. Nisqually Reach (x) not included in calculation of regression. a. Copper. b. Zinc.

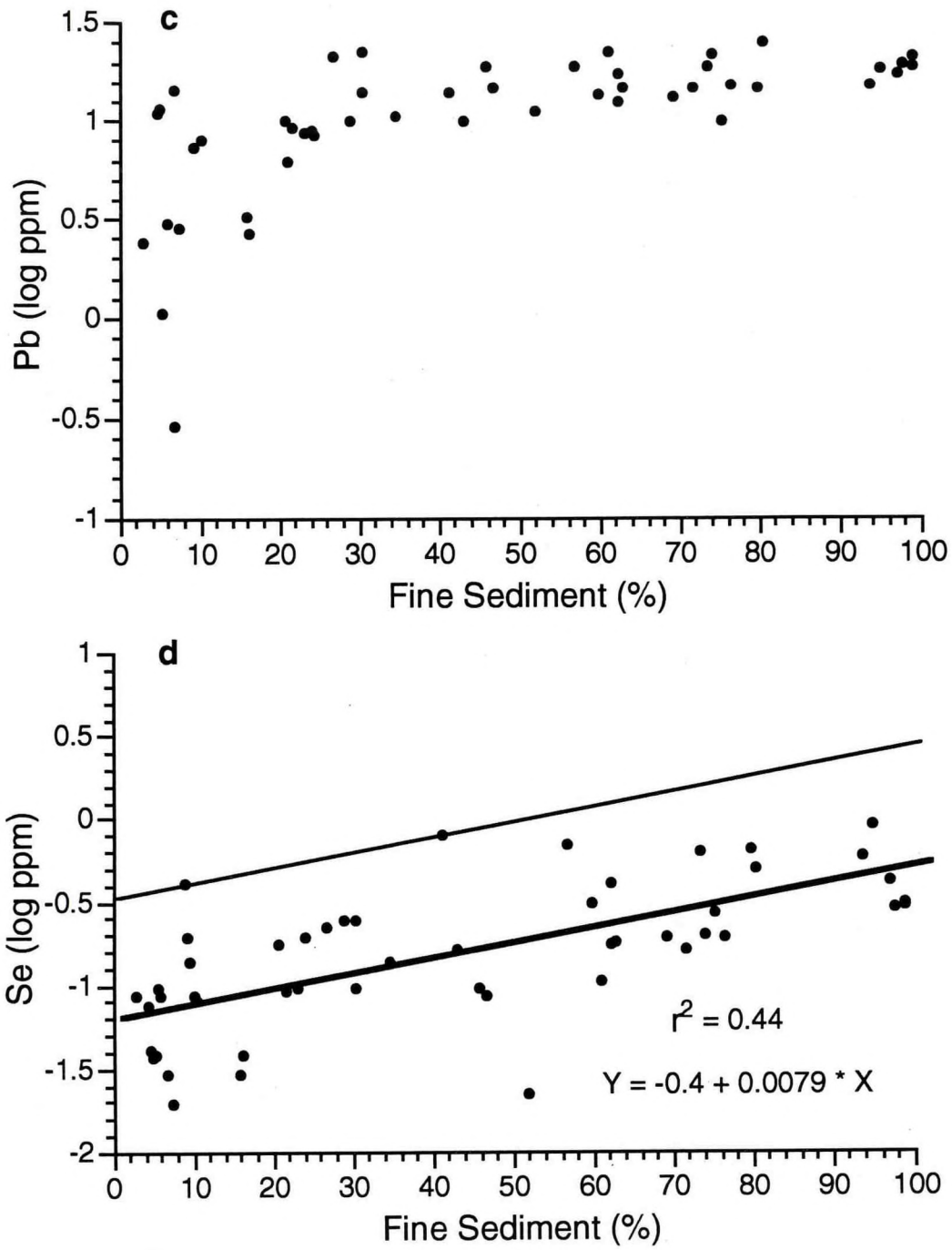


Figure 47. Continued. c. Lead. d. Selenium.

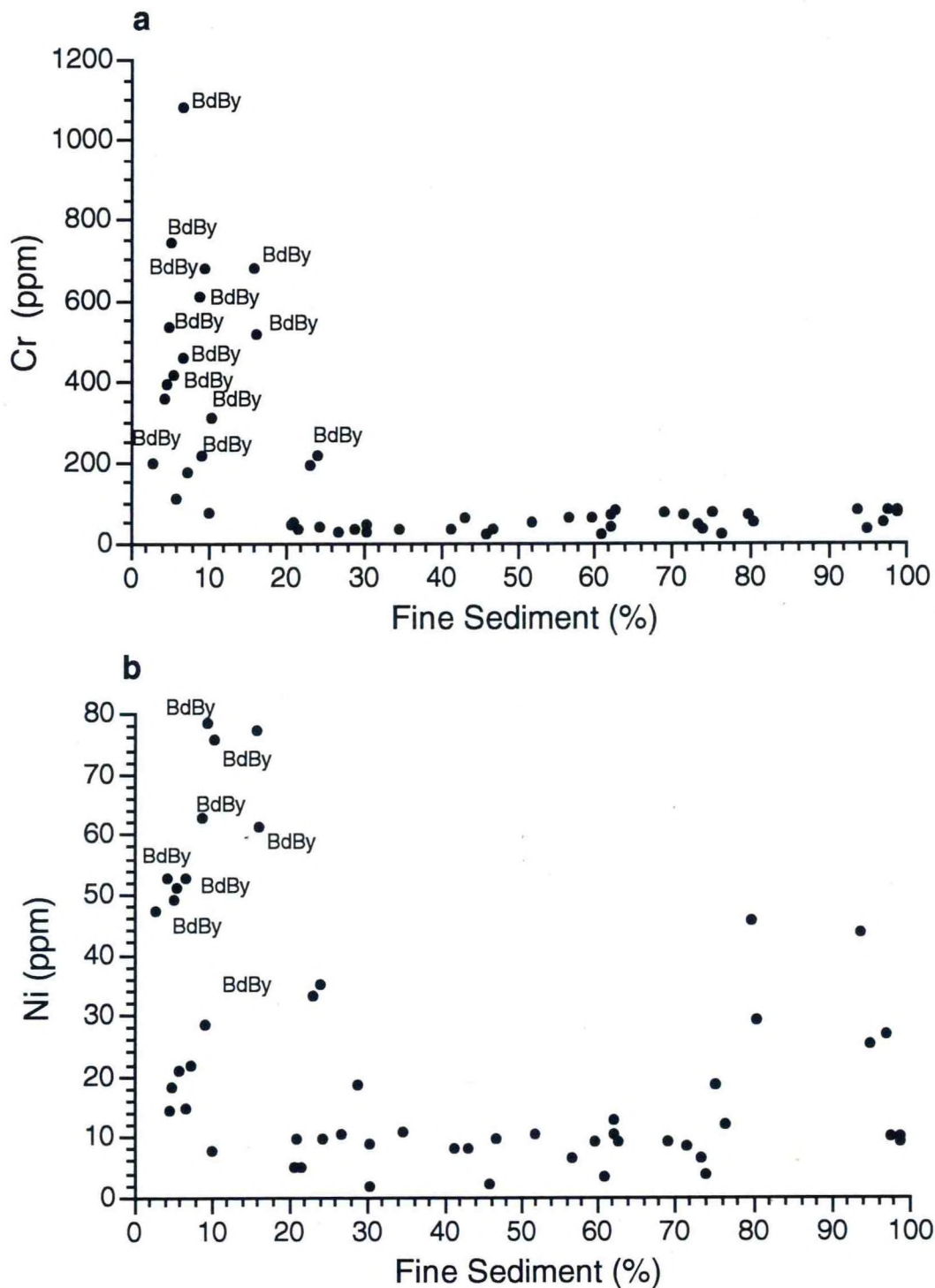


Figure 48. Plot of metal concentrations and percent fine sediment. Plots show $\mu\text{g/g}$ (ppm) concentrations (dry weight) from reference and nonurban sites that were used for determination of background concentrations. Names by data points are sites. See Table 1 for abbreviations. a. Chromium. b. Nickel.

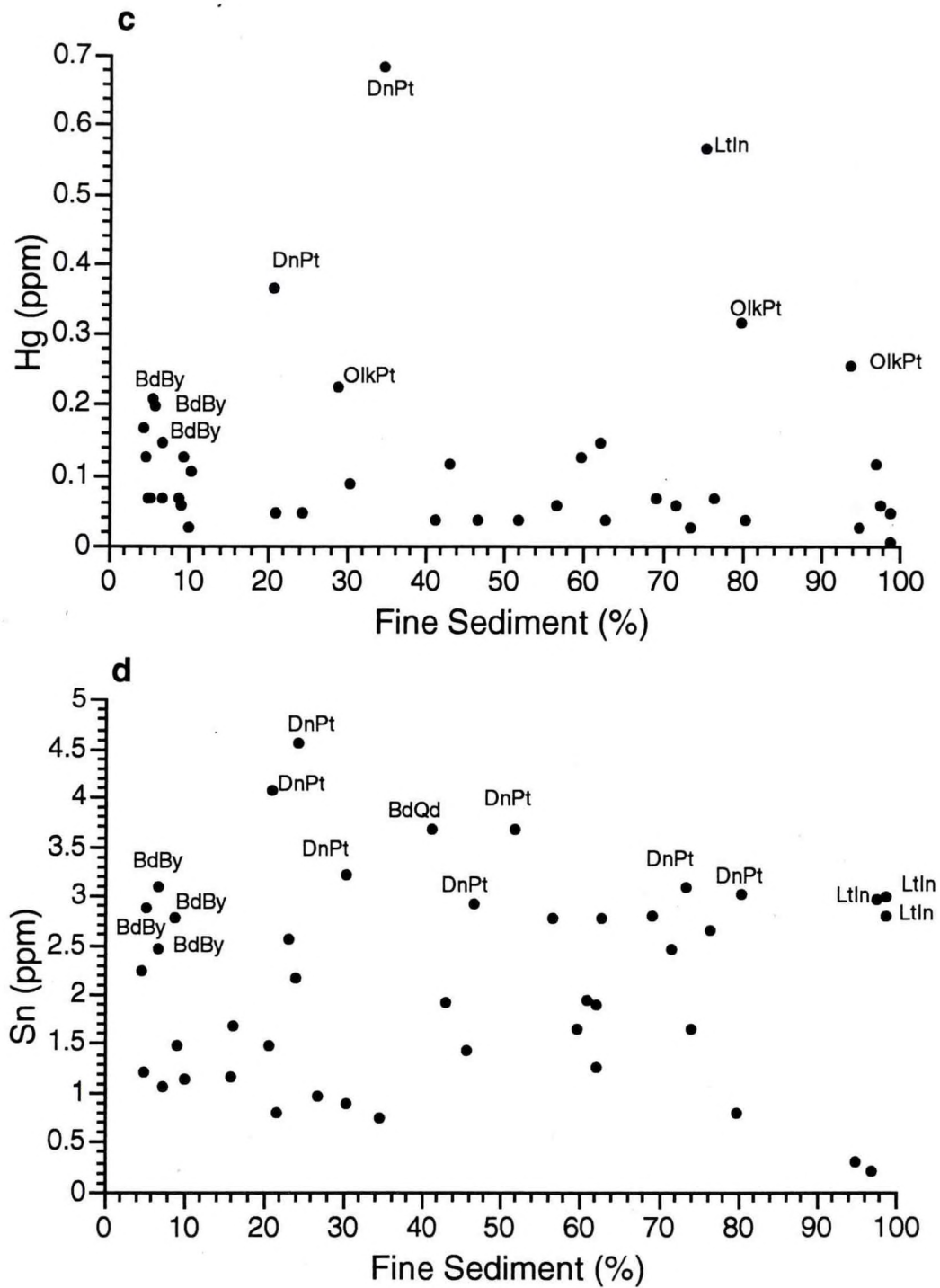


Figure 48. Continued. c. Mercury. d. Tin.

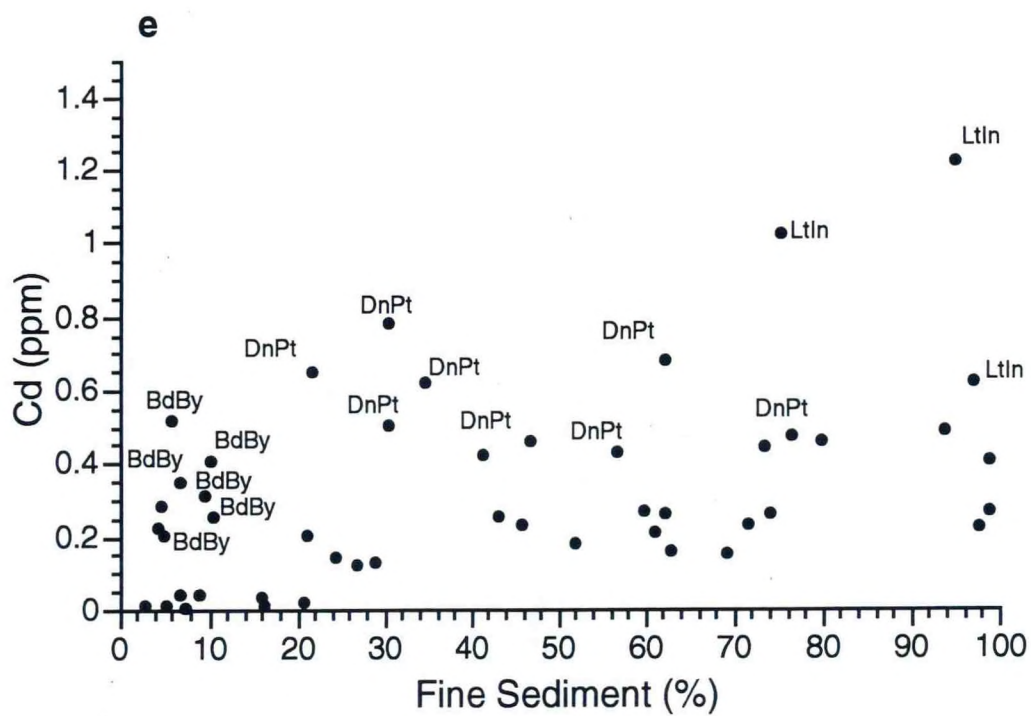


Figure 48. Continued. e. Cadmium

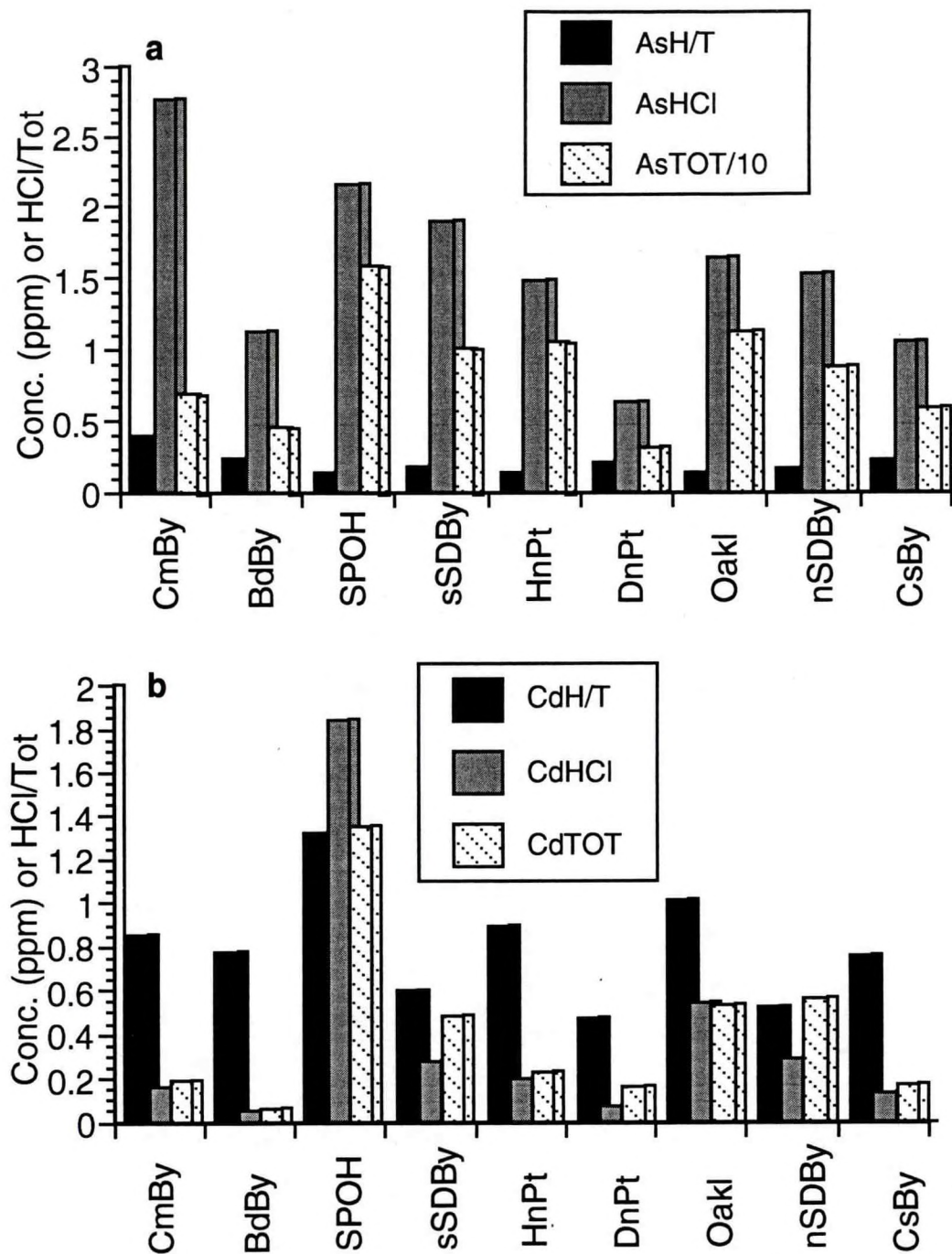


Figure 49. Acid extractable elements. Concentration of elements extracted in 1N HCl (=HCl) (based on total μg extracted normalized to sediment weight), bulk sediment concentration (=TOT), and the ratio of the two (H/T). Abscissa is site sampled in 1989; ordinate is the concentration in ppm ($\mu\text{g/g}$) of HCl or TOT or H/T ratio. Some of the concentrations are scaled ($\times 10$ or $\times 100$) for graphing. See Table 1 for site abbreviations. a. Arsenic. b. Cadmium.

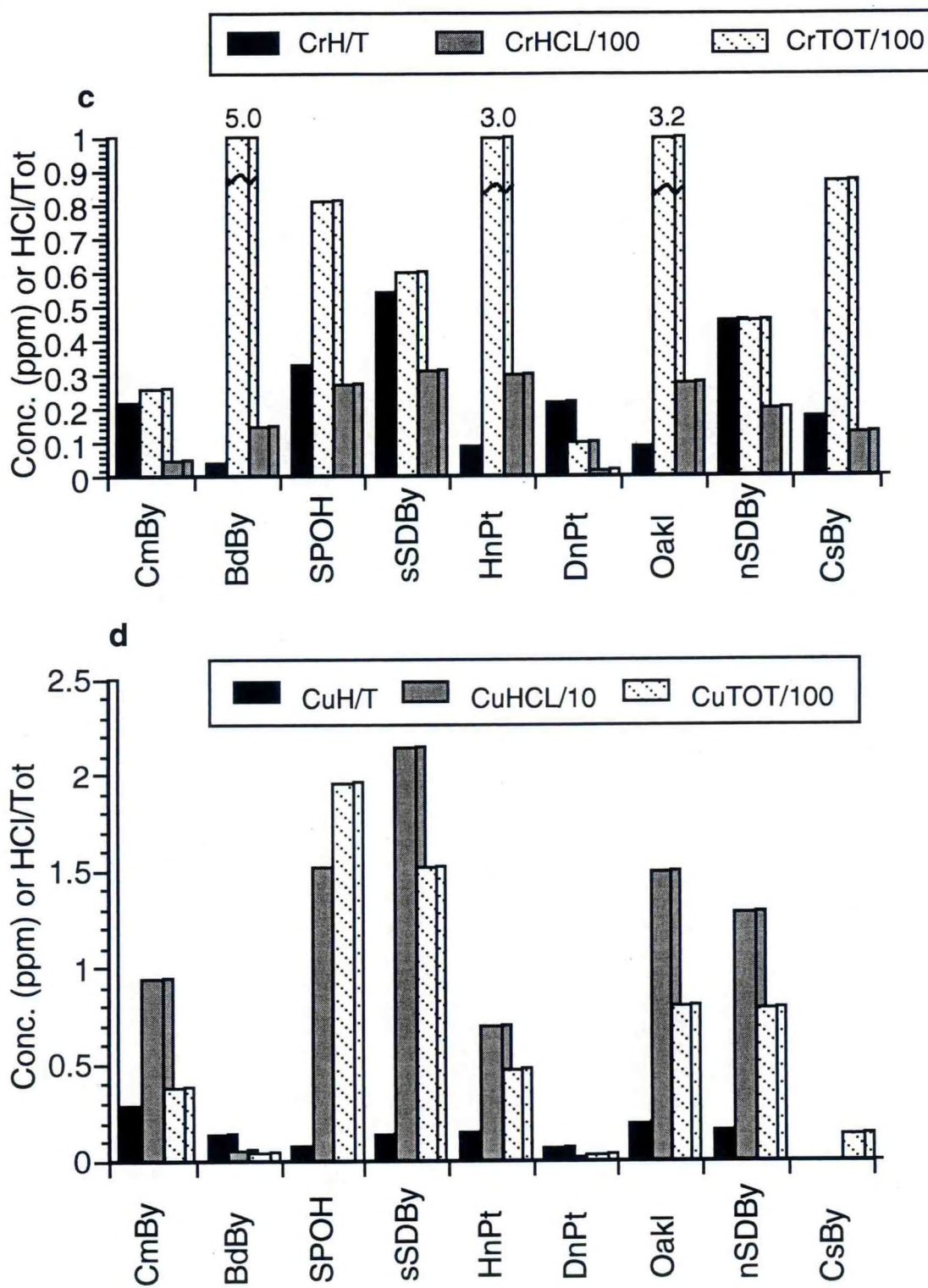


Figure 49. Continued. c. Chromium. d. Copper

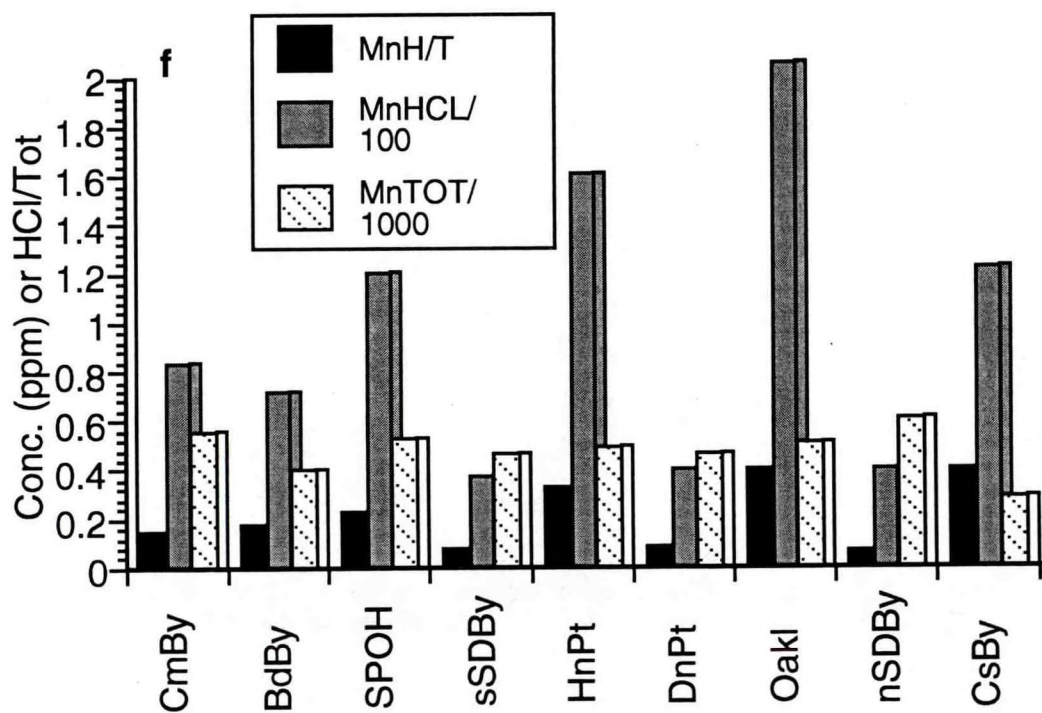
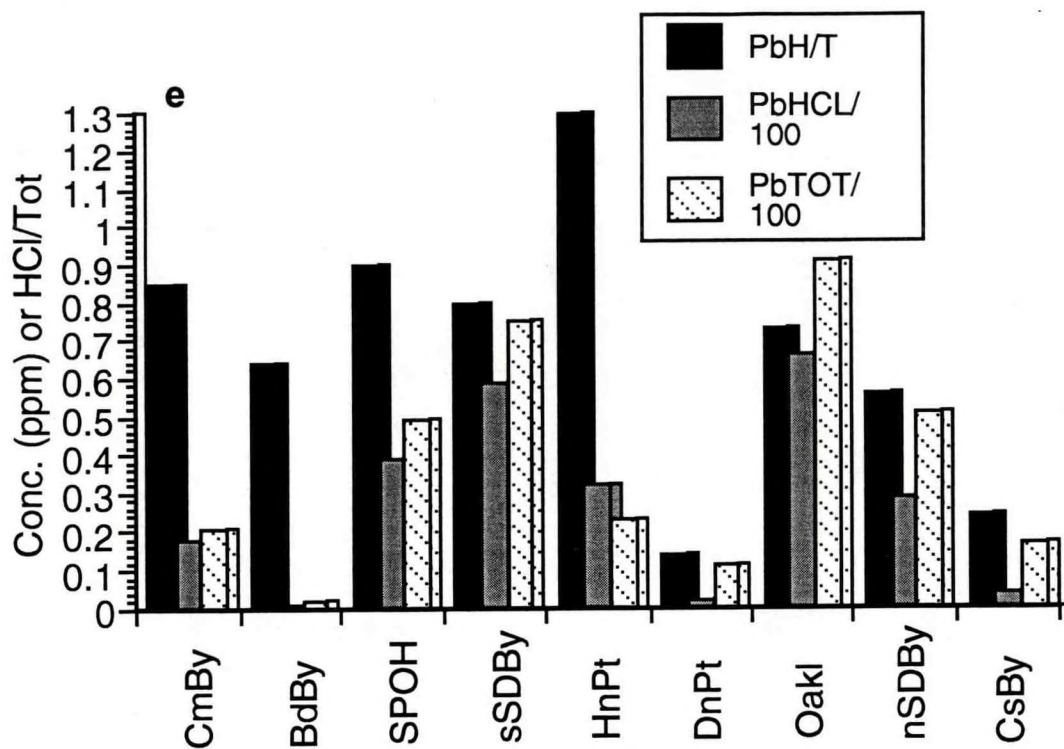


Figure 49. Continued. e. Lead. f. Manganese.

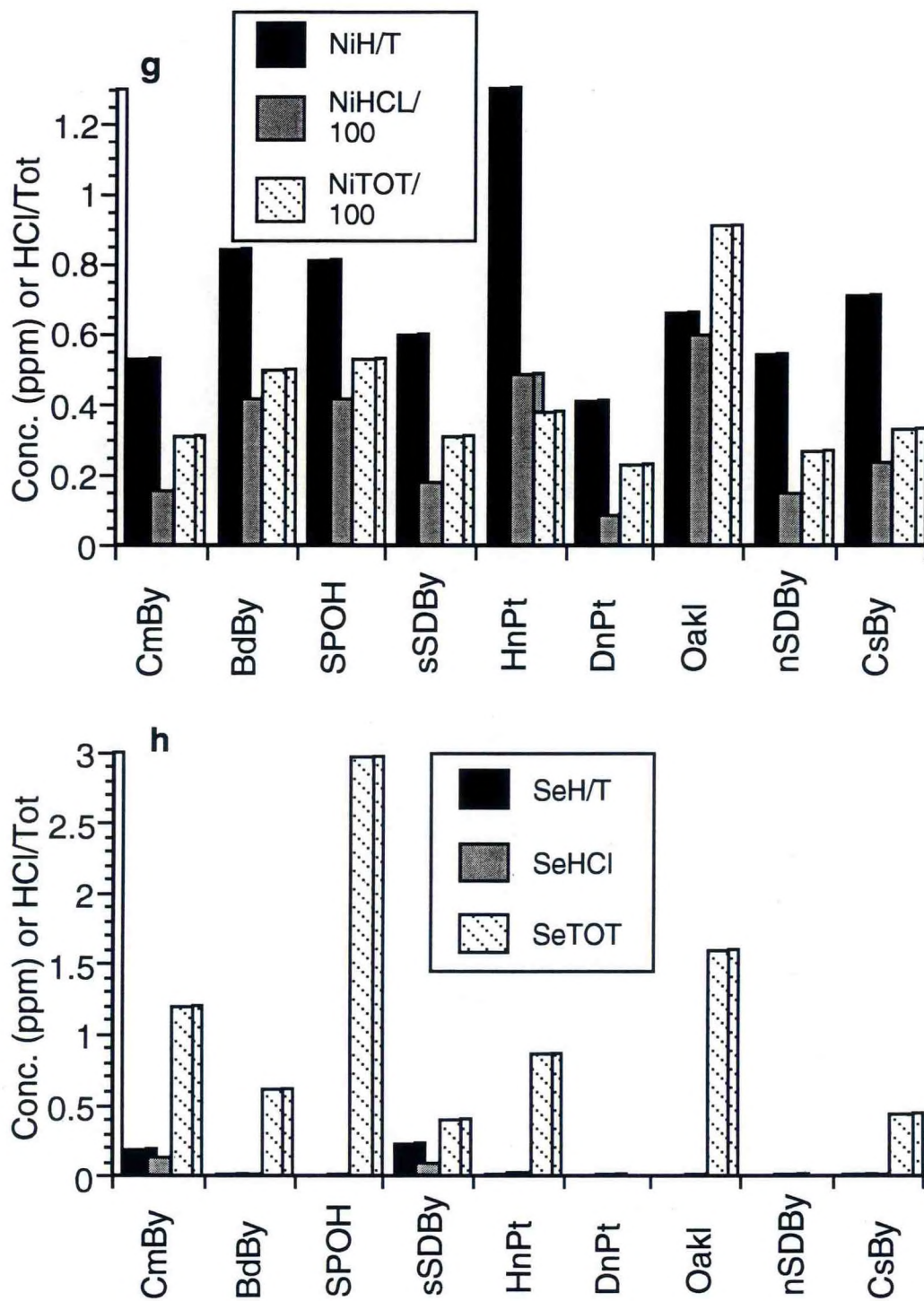


Figure 49. Continued. g. Nickel. h. Selenium

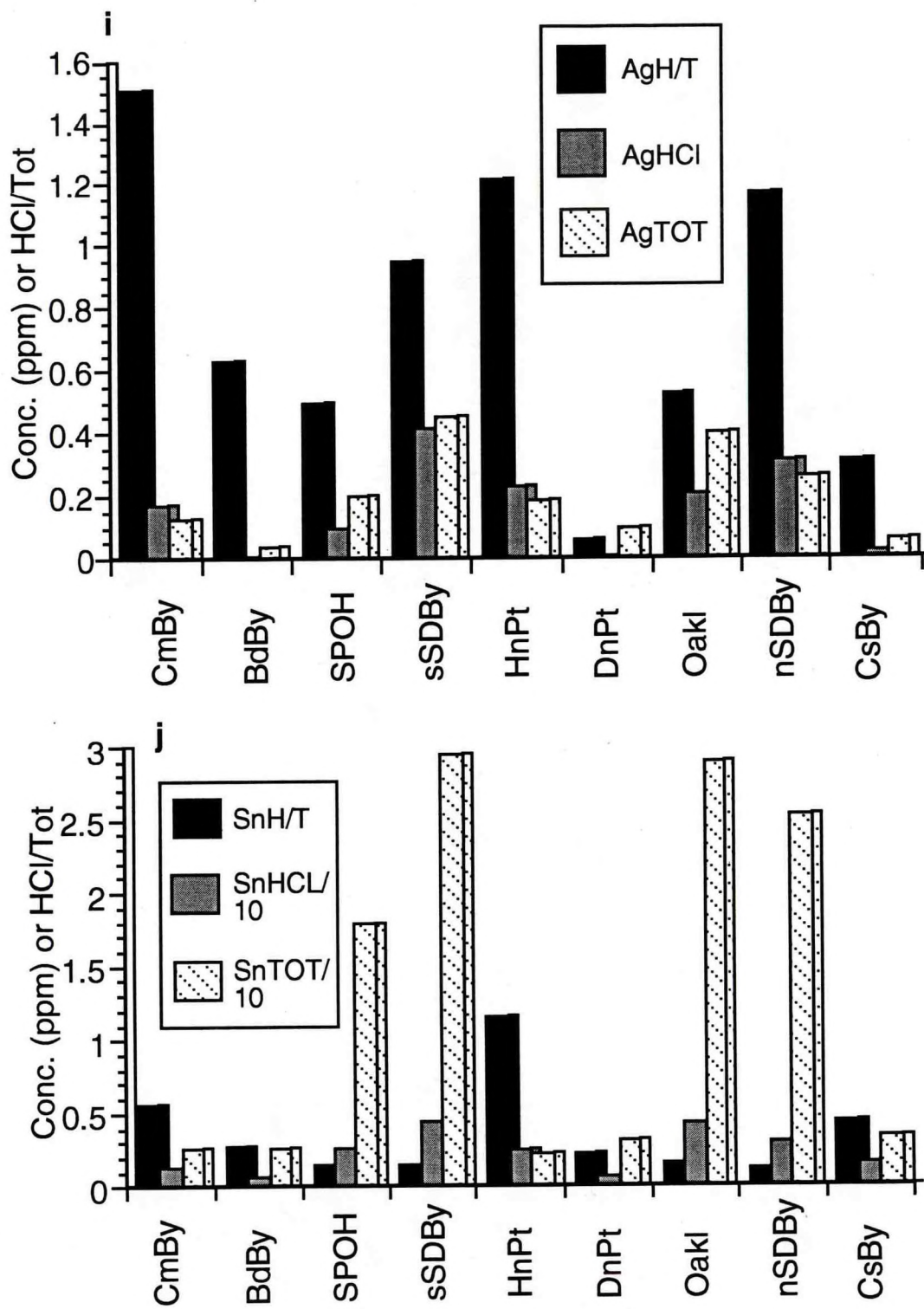


Figure 49. Continued. i. Silver. j. Tin.

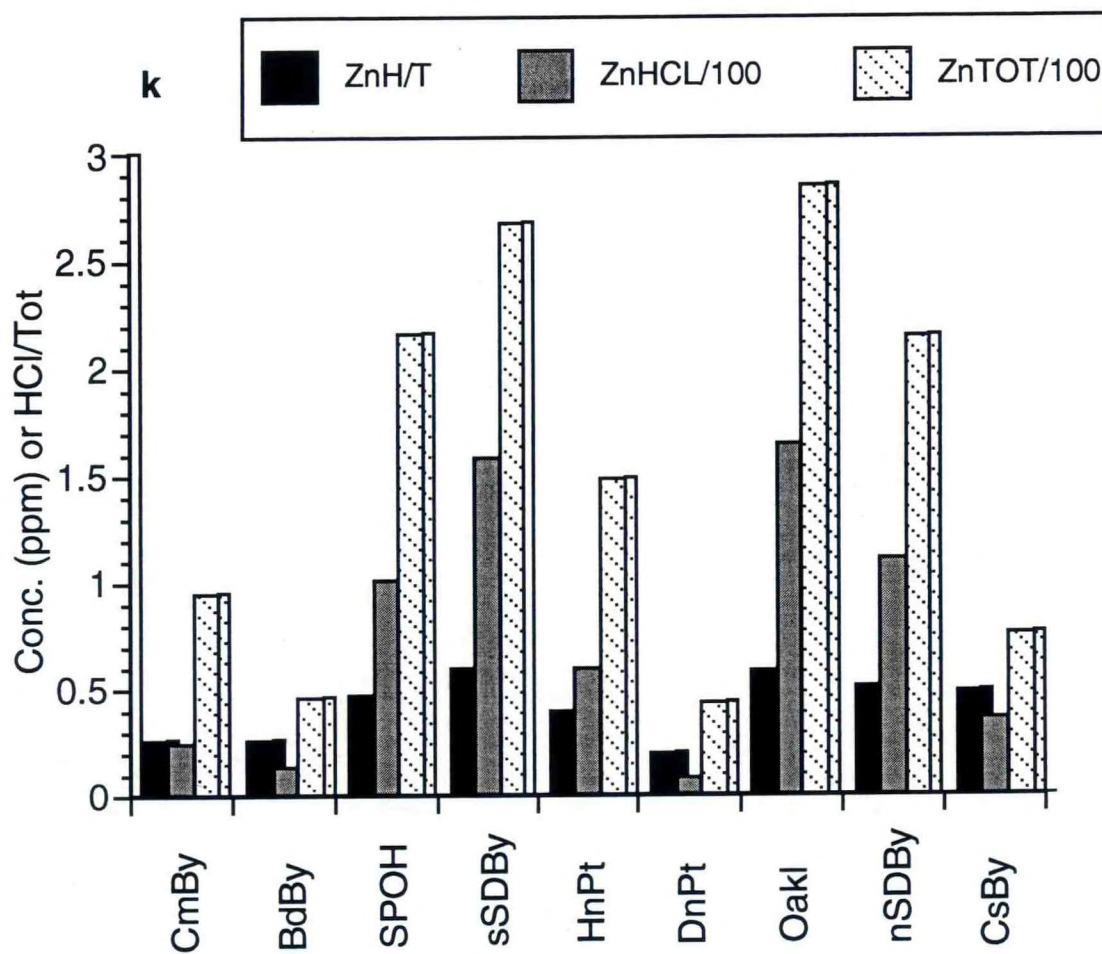


Figure 49. Continued. k. Zinc.

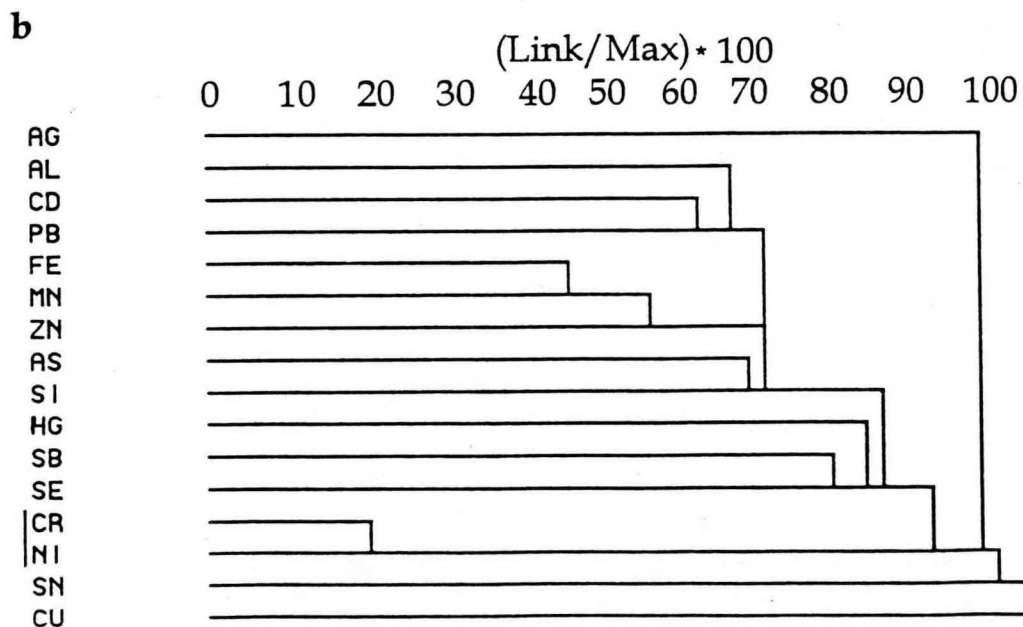
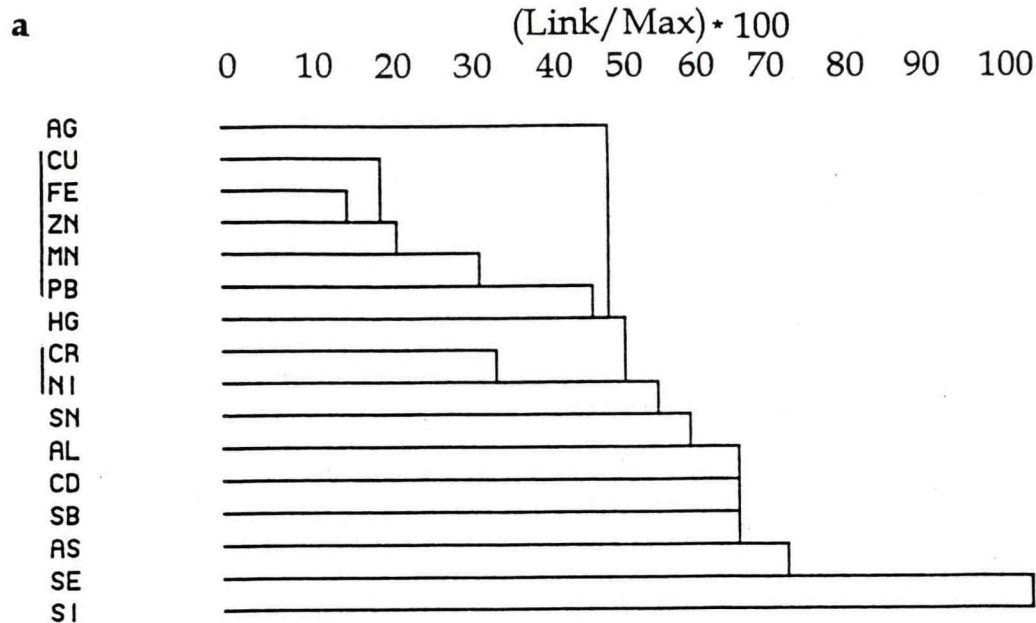


Figure 50. Dendrogram of cluster analysis for concentrations of elements in sediments. The horizontal axis (link/ max) is the percentage of the range from the maximum to minimum distance in the data. Vertical bars by elements denote groups which were determined for links < 40 percentage units of link/max. a. All Pacific coast urban sites (n = 250). b. West Coast reference and nonurban sites (n = 38). See Table 3 for element abbreviations.

c

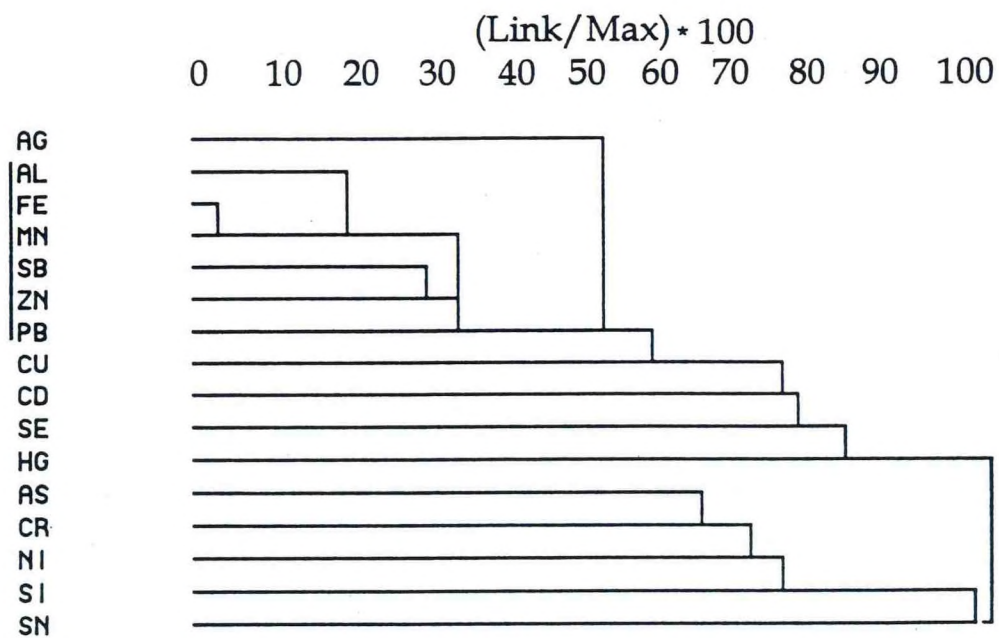


Figure 50. Continued. c. All Alaskan sites n = 43.

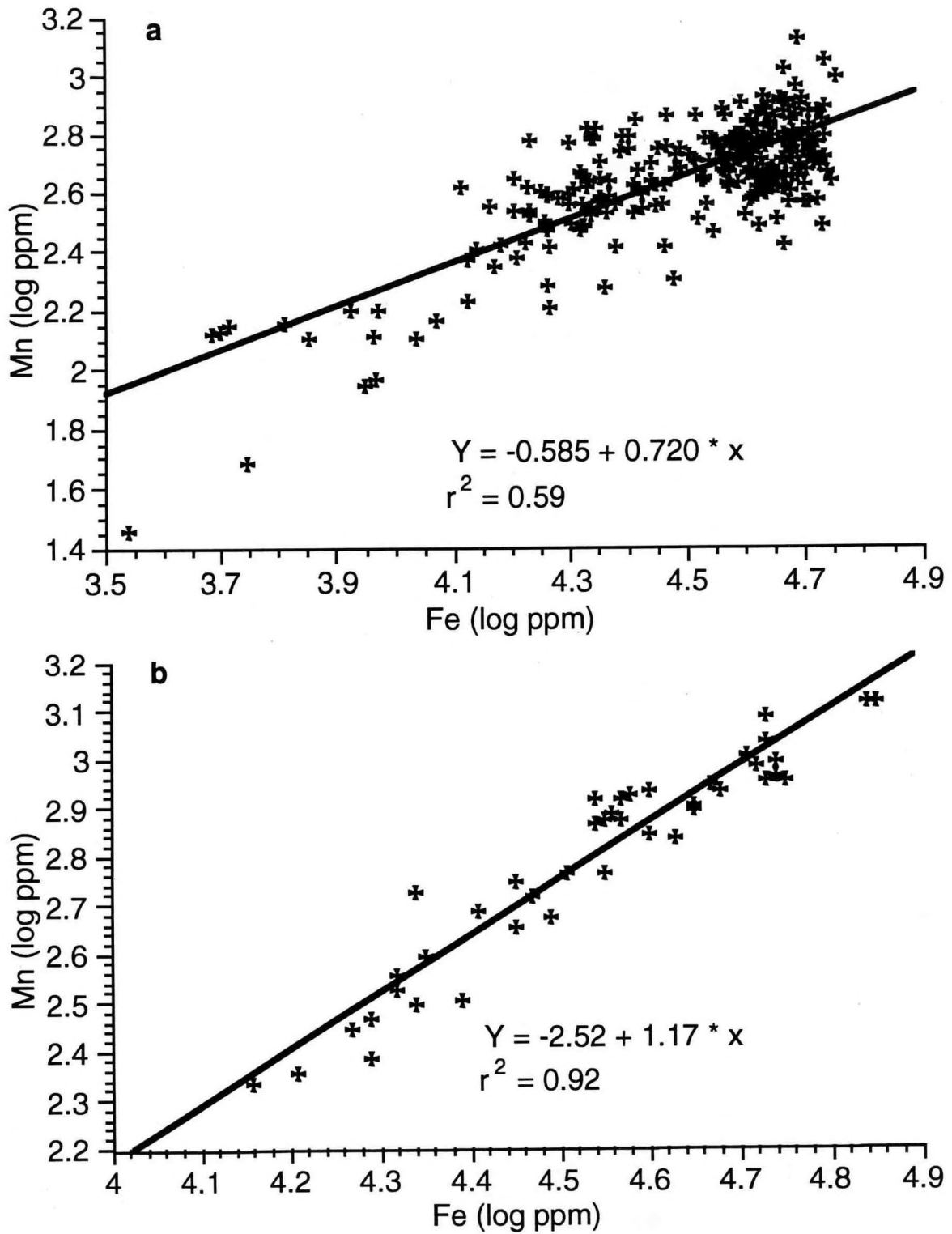


Figure 51. Plot of manganese and iron sediment concentrations. Plot shows correlation of manganese and iron $\log_{10} \mu\text{g/g}$ concentrations in sediment samples from different sites. a. All West Coast sites
 b. All Alaskan sites.

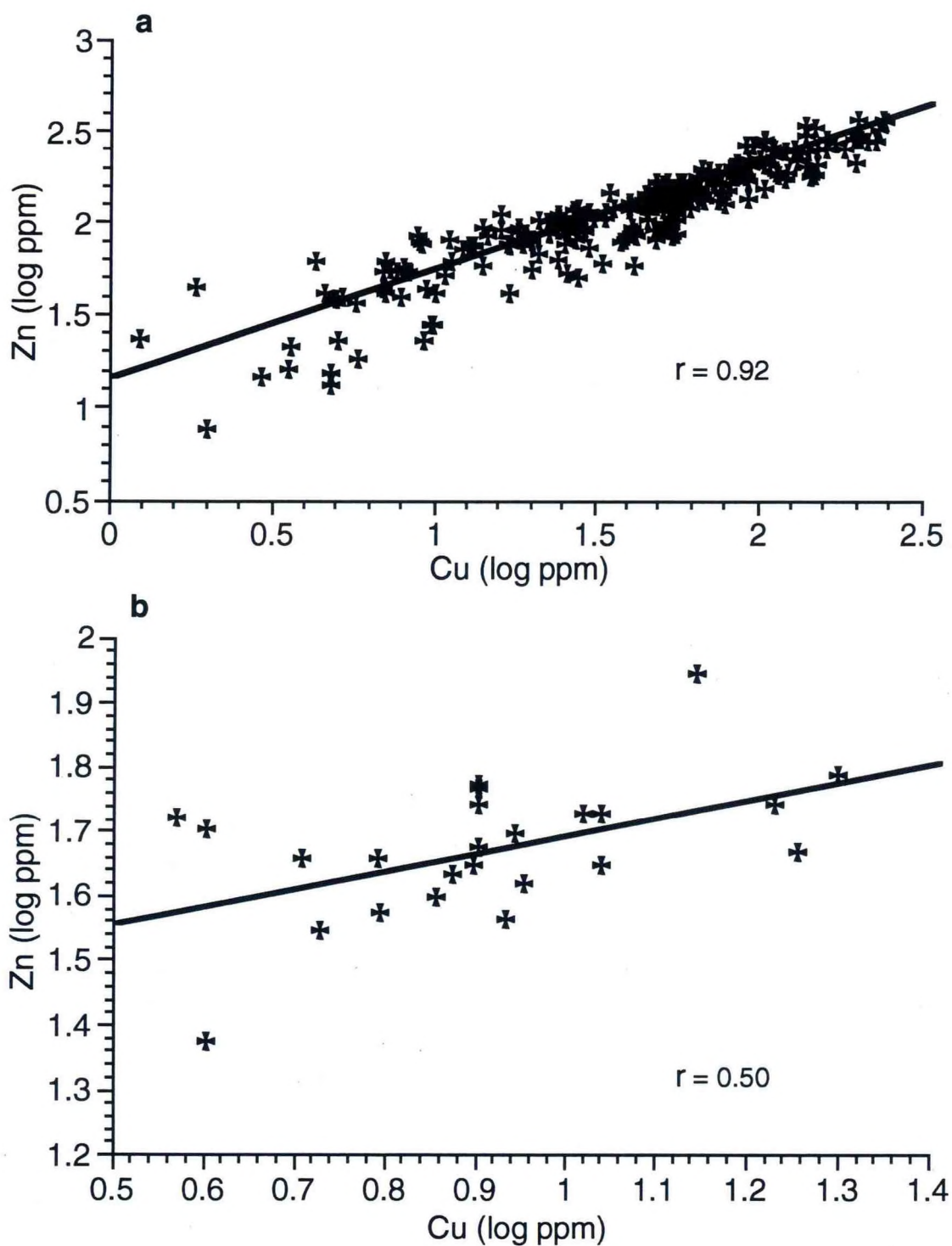


Figure 52. Plot of copper and zinc sediment concentrations. Plot shows correlation of copper and zinc log₁₀ $\mu\text{g/g}$ concentrations in sediment samples from different sites. See Table 1 for site abbreviations. a. All West Coast urban sites. b. All West Coast reference and nonurban sites.

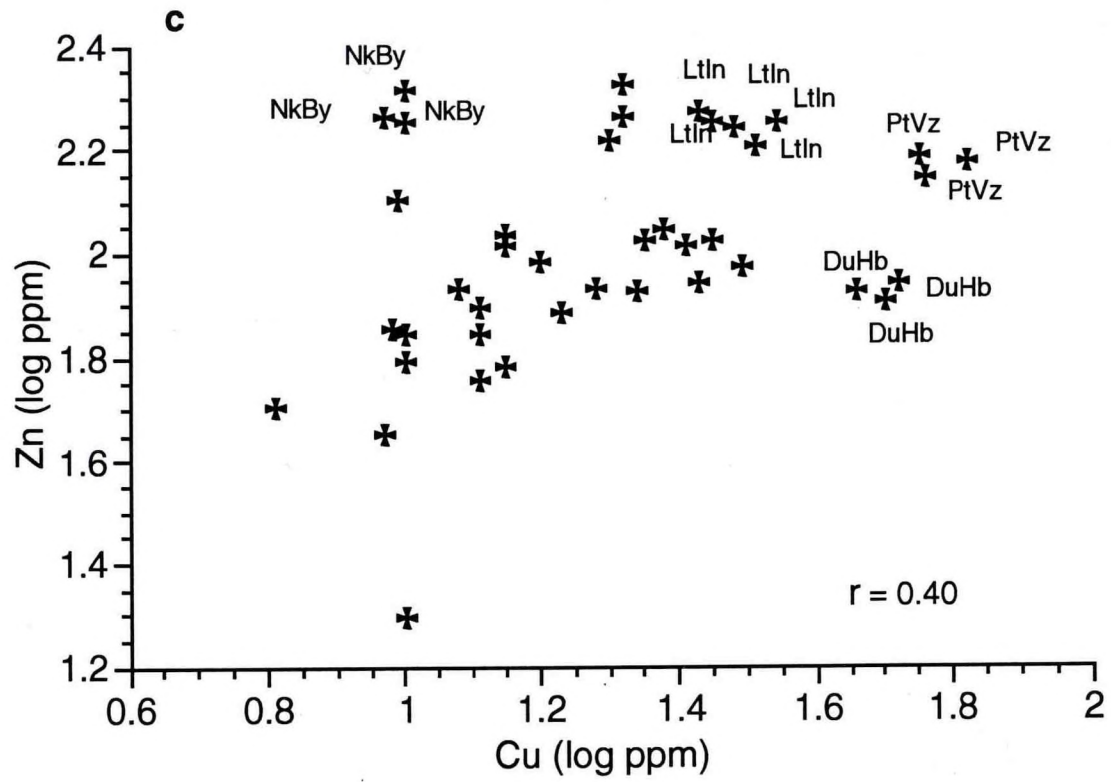


Figure 52. Continued. c. All Alaskan sites.

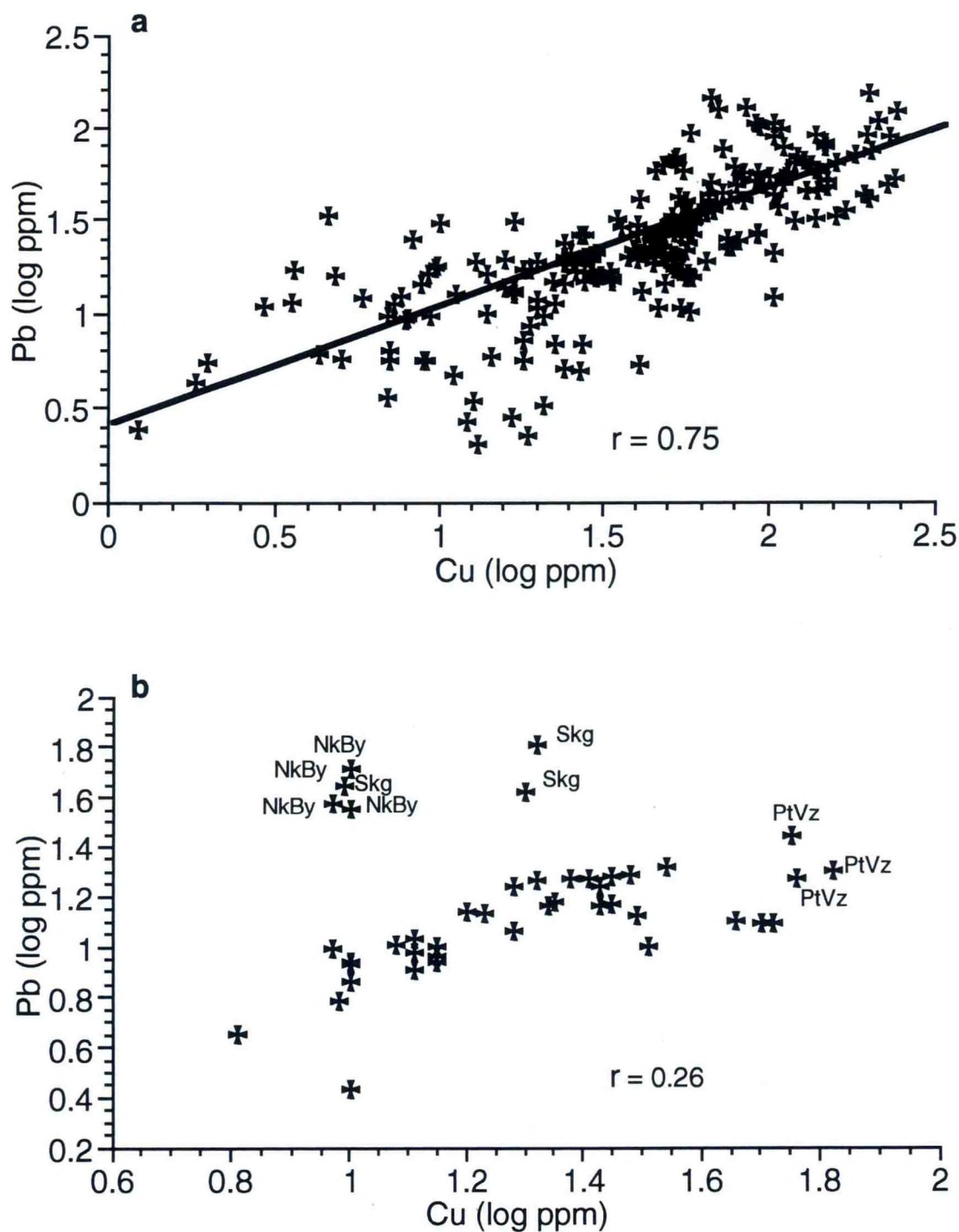


Figure 53. Plot of copper and lead sediment concentrations. Plot shows correlation of copper and lead log₁₀ µg/g concentrations in sediment samples from different sites. Site abbreviations in Table 1. a. All West Coast urban sites. b. Alaskan sites only.

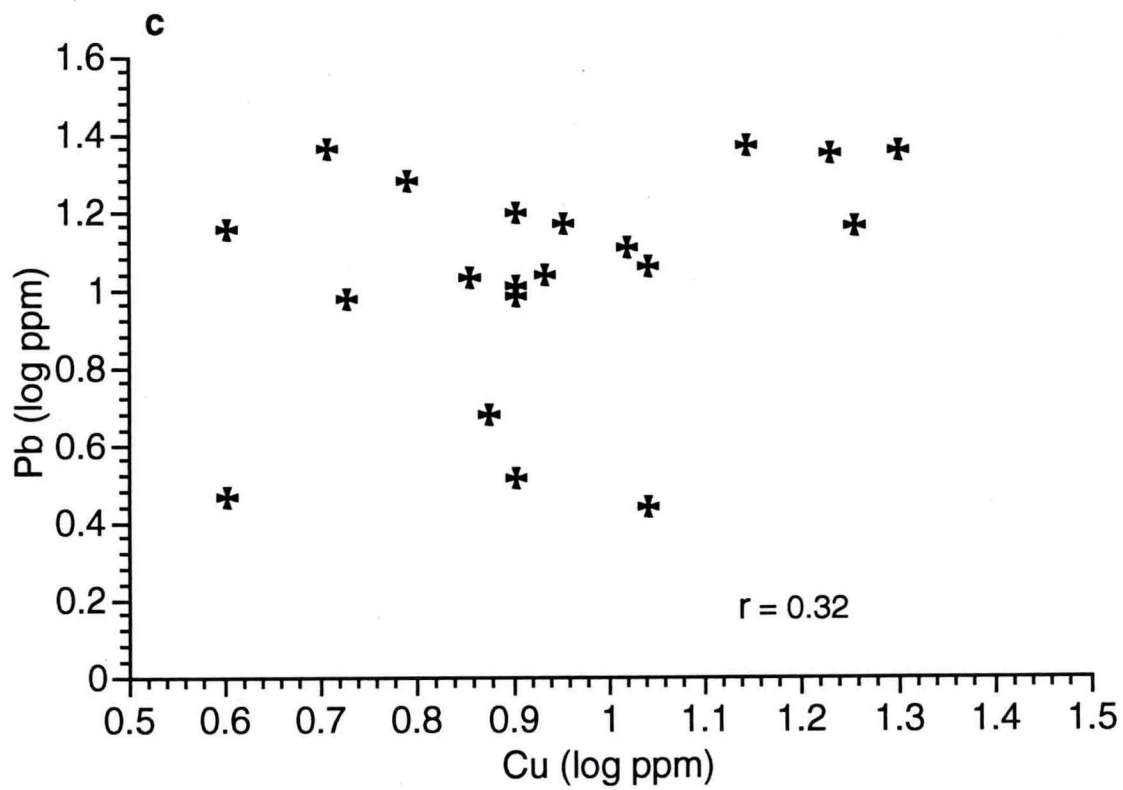


Figure 53. Continued. c. West Coast reference and nonurban sites.

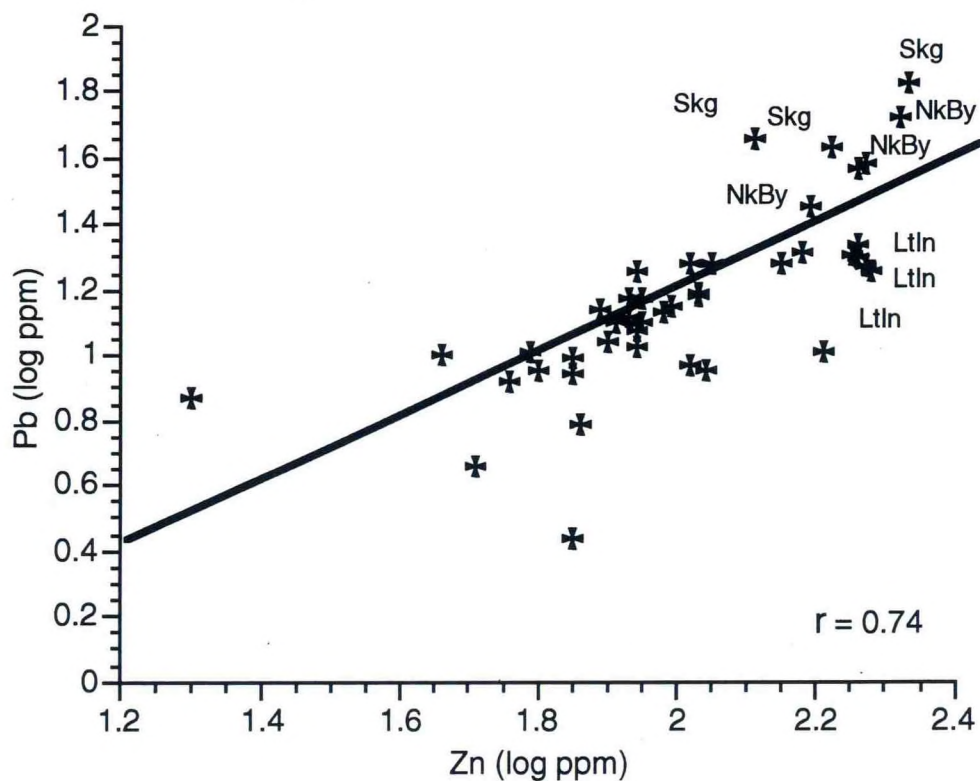


Figure 54. Plot of zinc and lead sediment concentrations. Plot shows correlation of zinc and lead $\log_{10} \mu\text{g/g}$ concentrations in sediment samples from all Alaskan sites. Site abbreviations in Table 1.

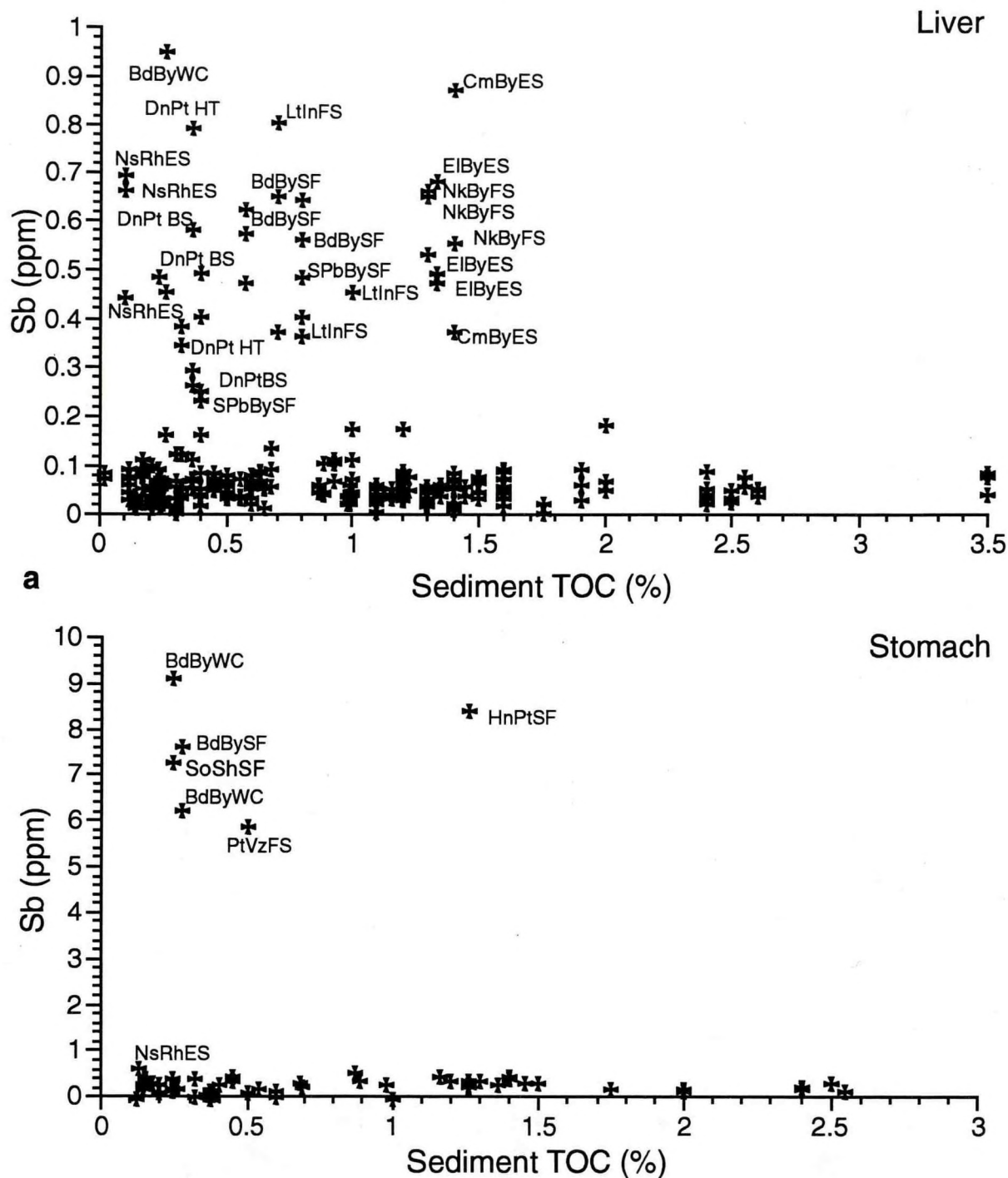


Figure 55. Concentration of elements in liver and stomach contents of fish for the years 1984-87. Concentrations of elements plotted against percent total organic carbon (TOC) found in sediment from the site where fish were collected. Only the highest concentrations are labeled. Liver is mean of three largest females and stomach contents is mean of 10 fish per site. $n = 311$ for liver and $n = 60$ for stomach contents. See Tables 1 and 2 for abbreviations of sites and species. a. Antimony.

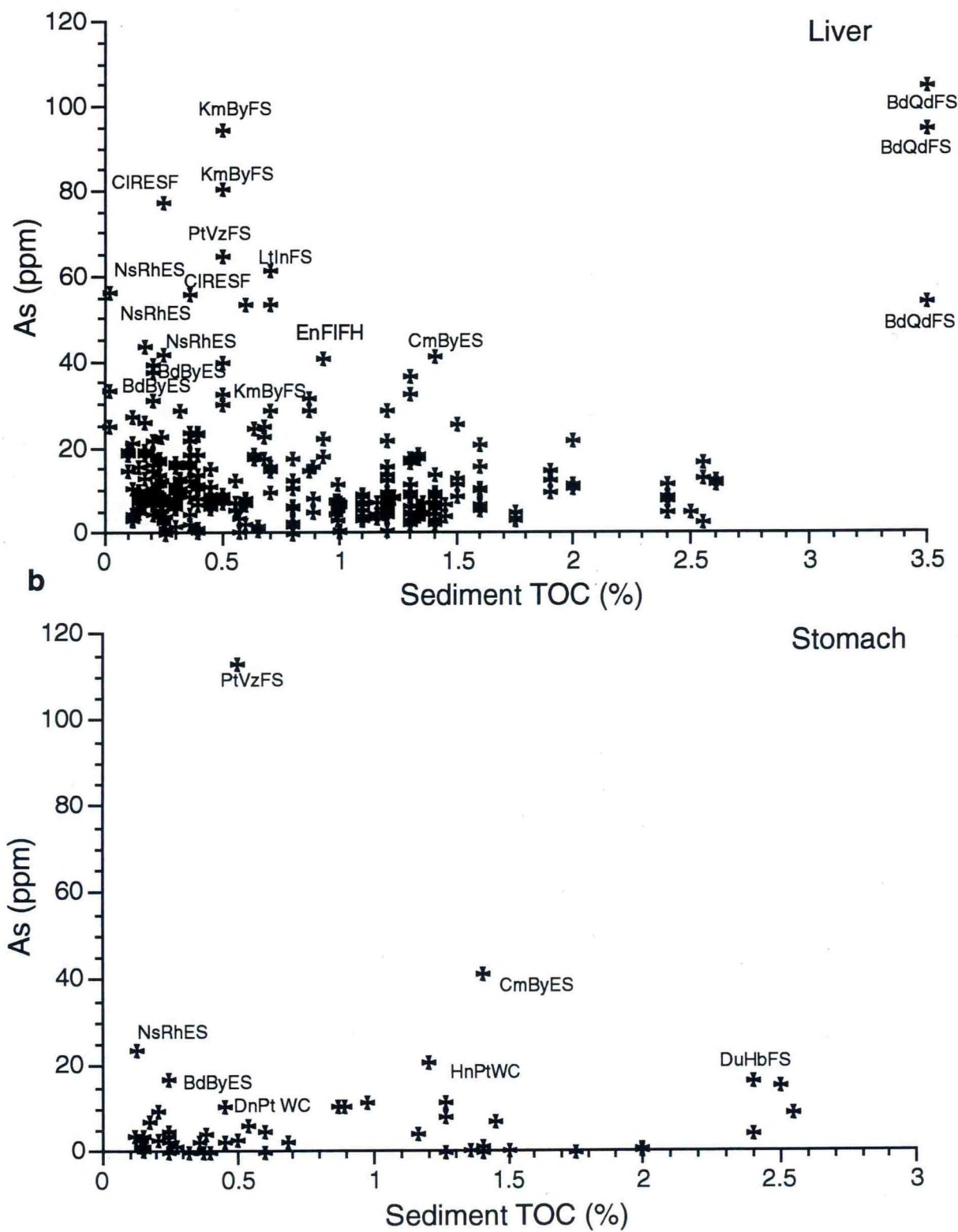


Figure. 55. Continued. b. Arsenic.

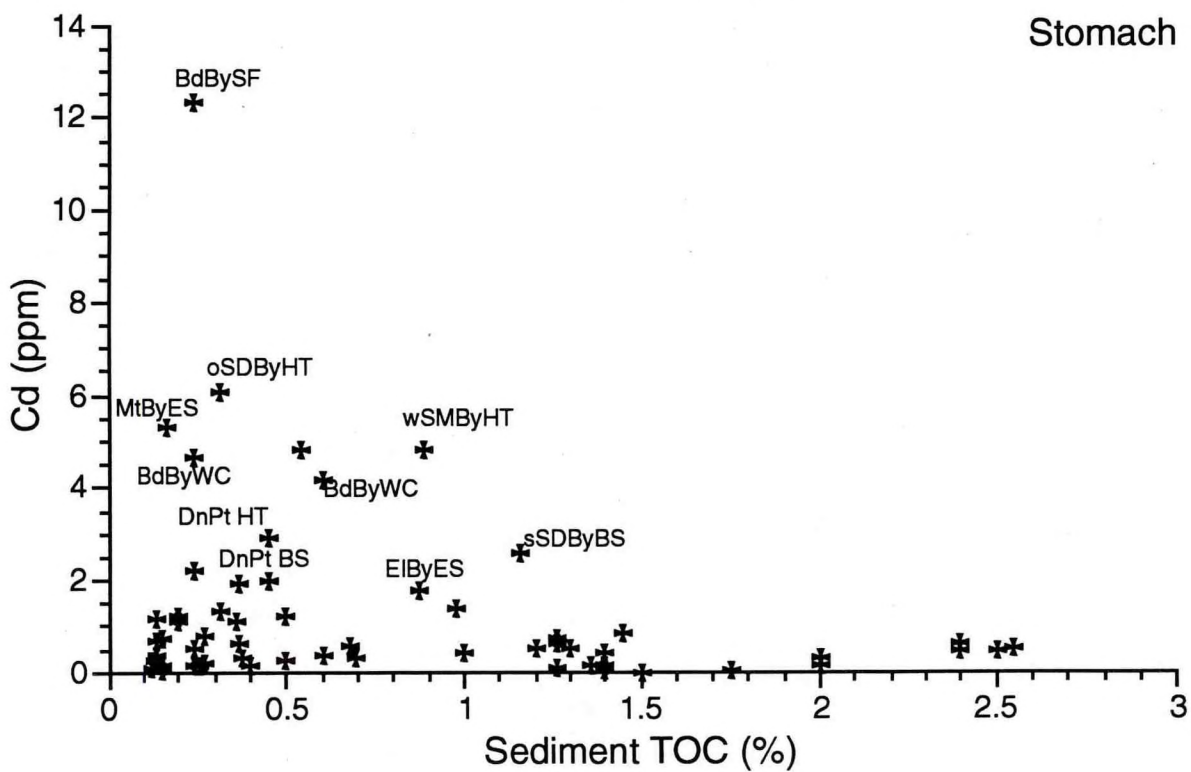
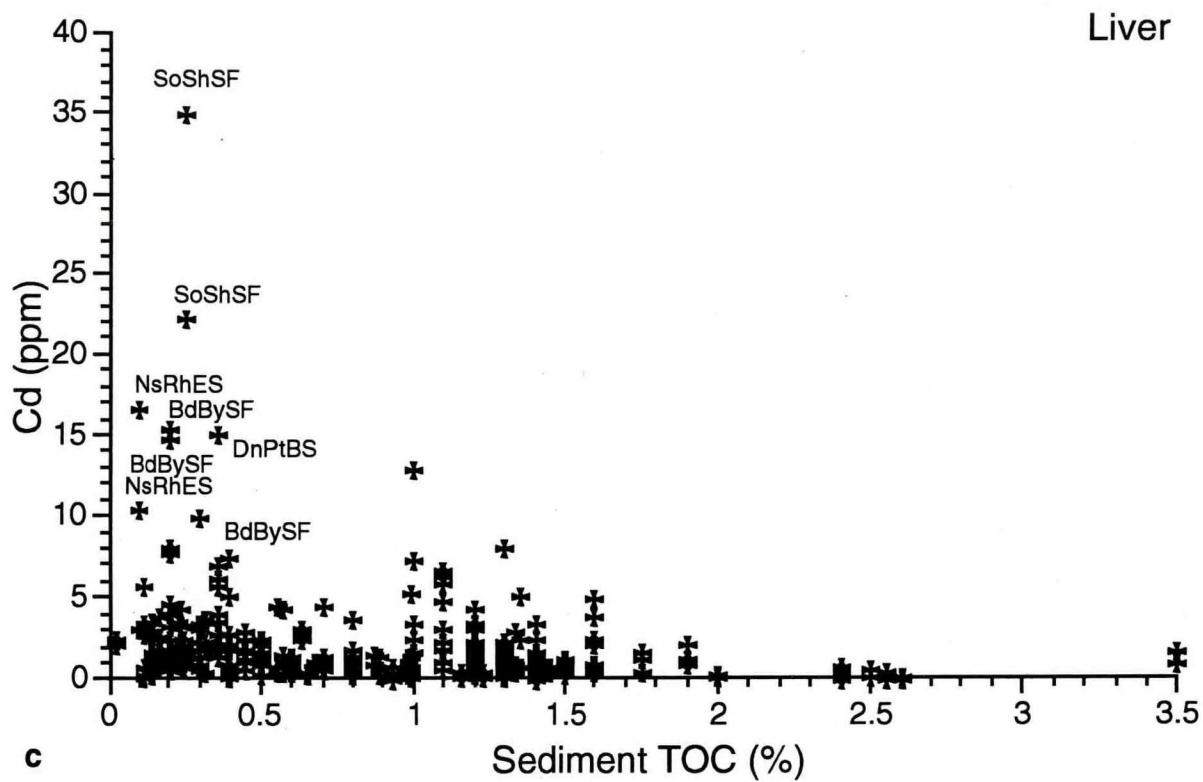


Figure 55. Continued. c. Cadmium

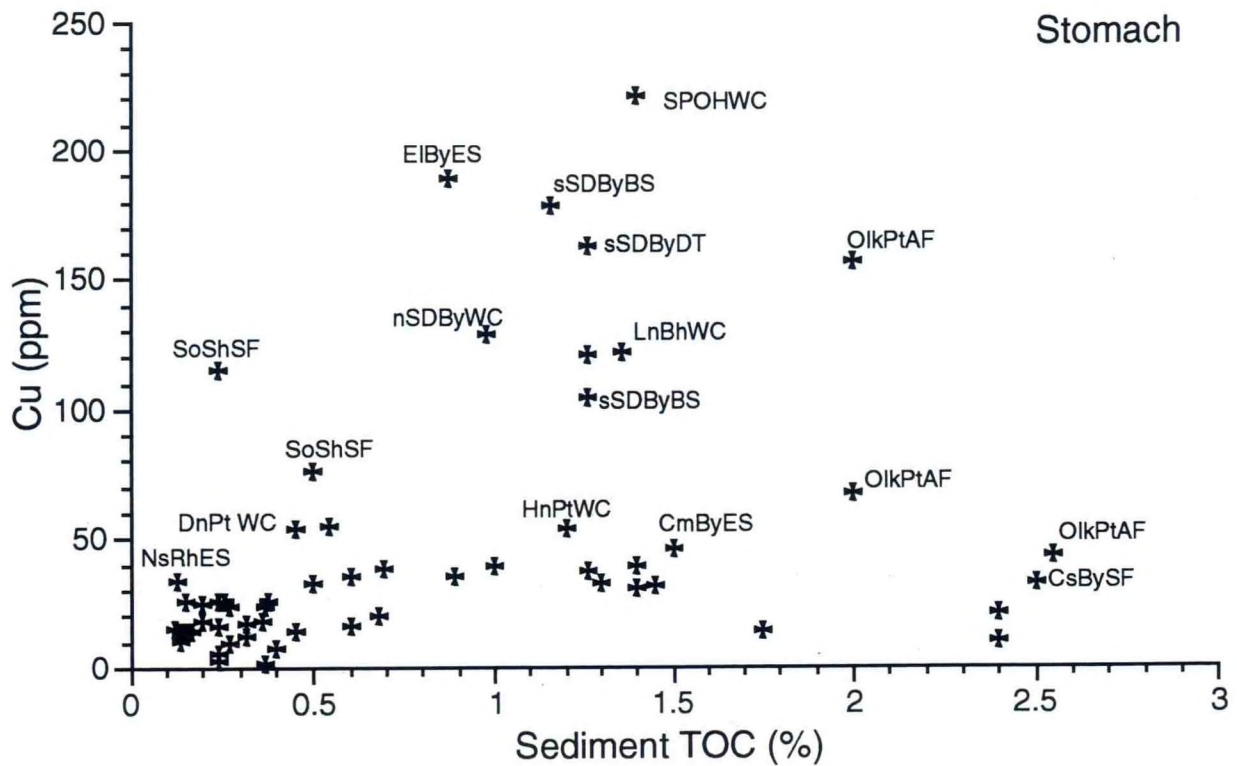
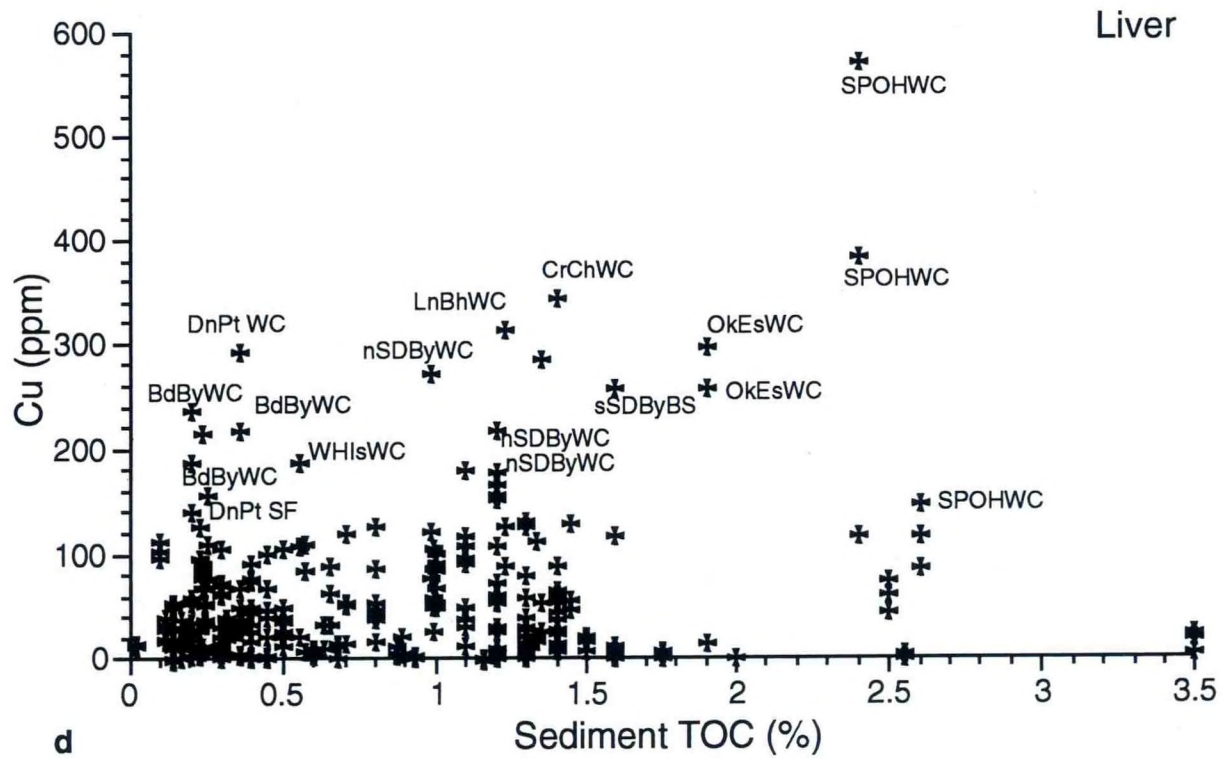


Figure 55. Continued. d. Copper.

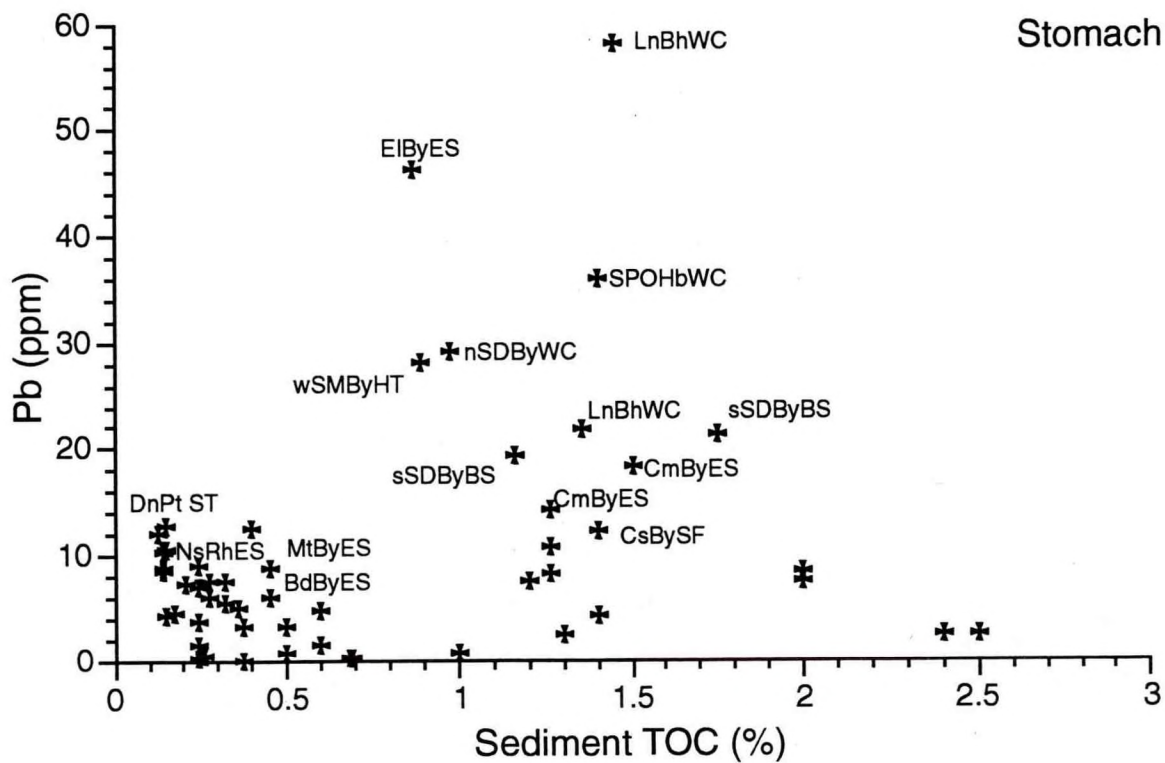
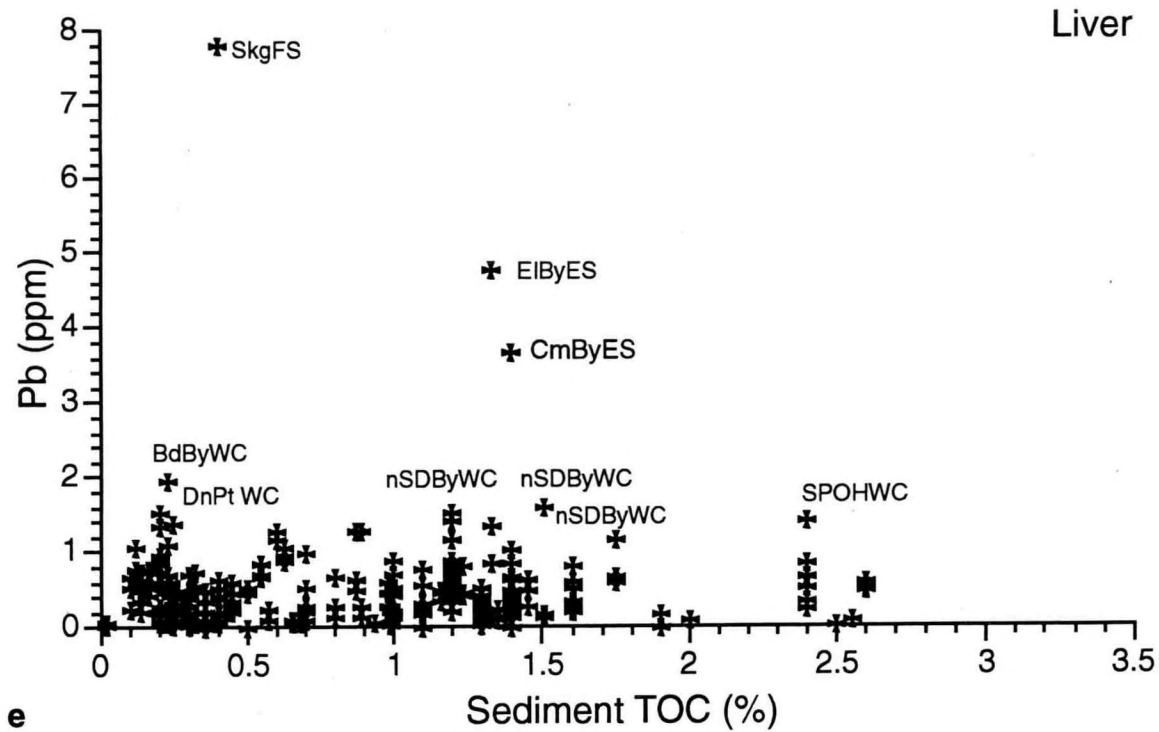


Figure 55. Continued. e. Lead.

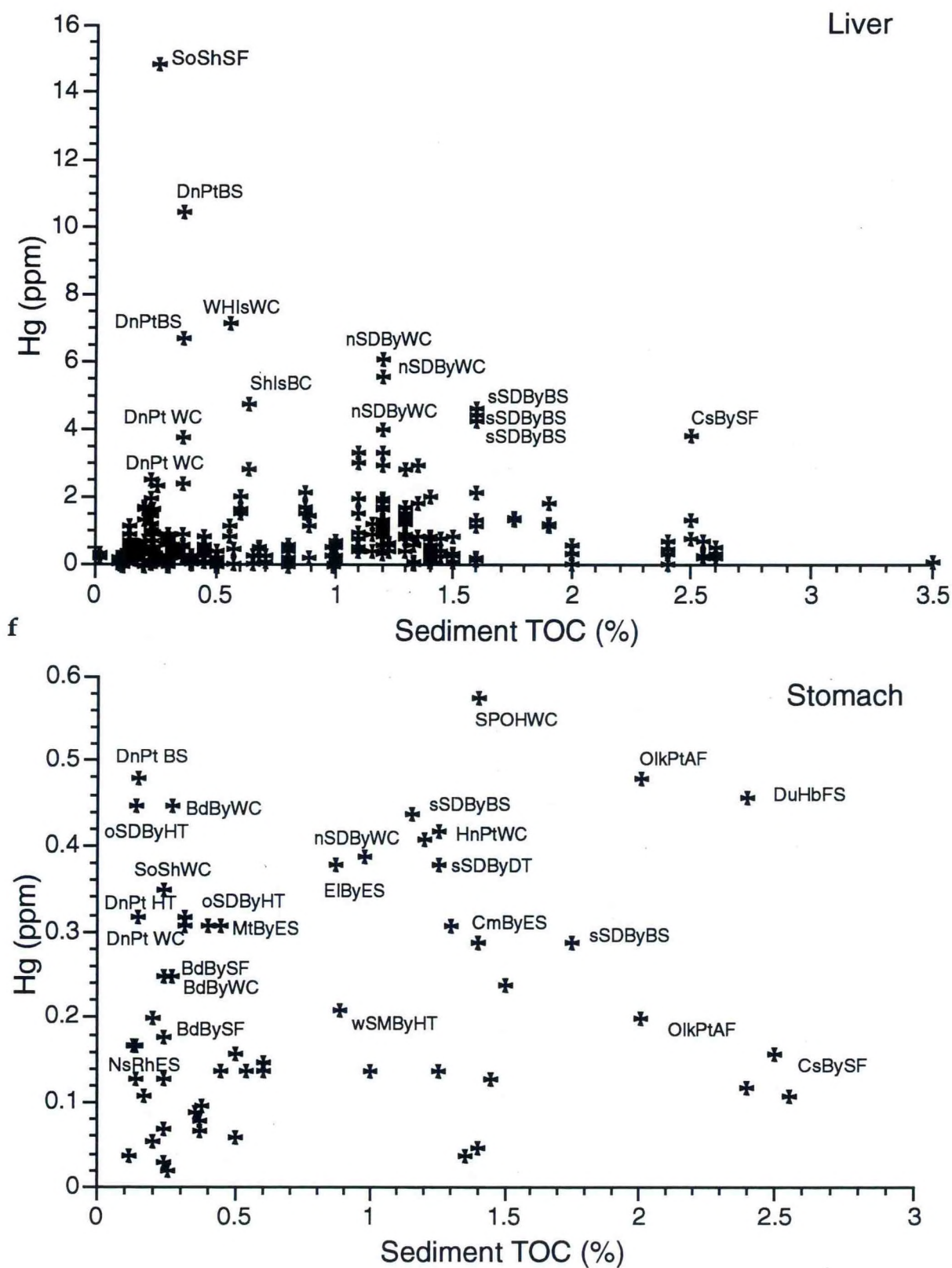


Figure 55. Continued. f. Mercury

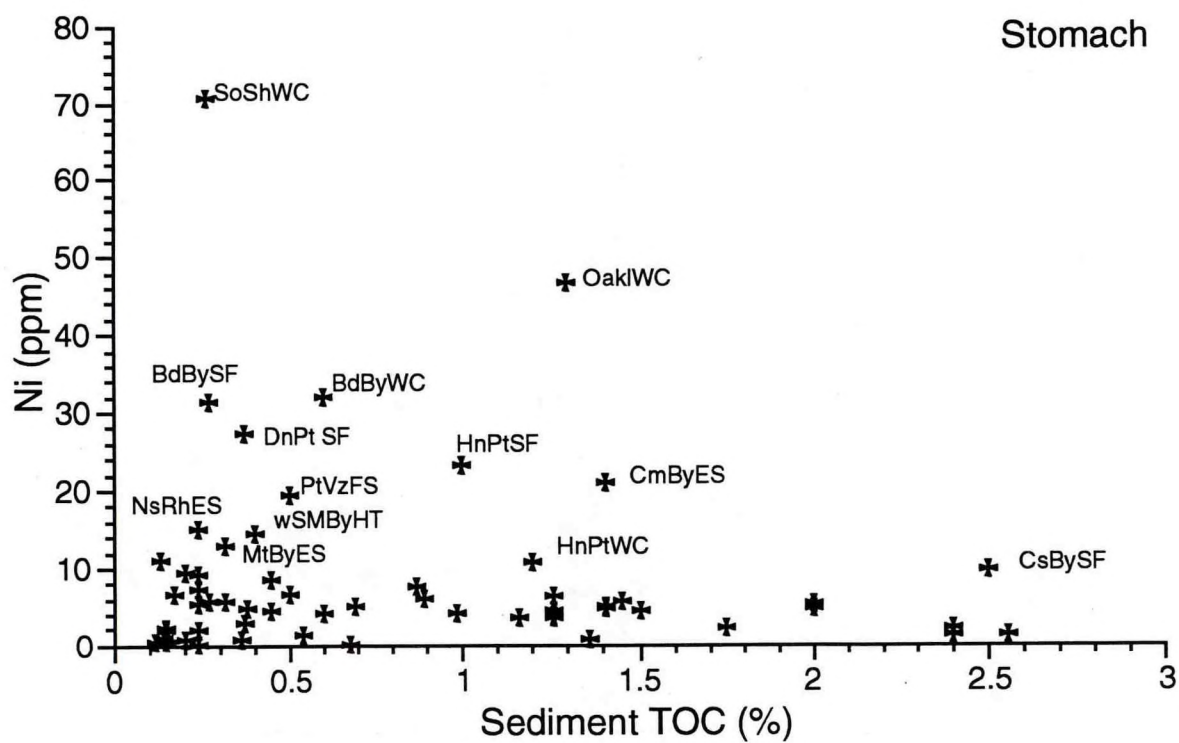
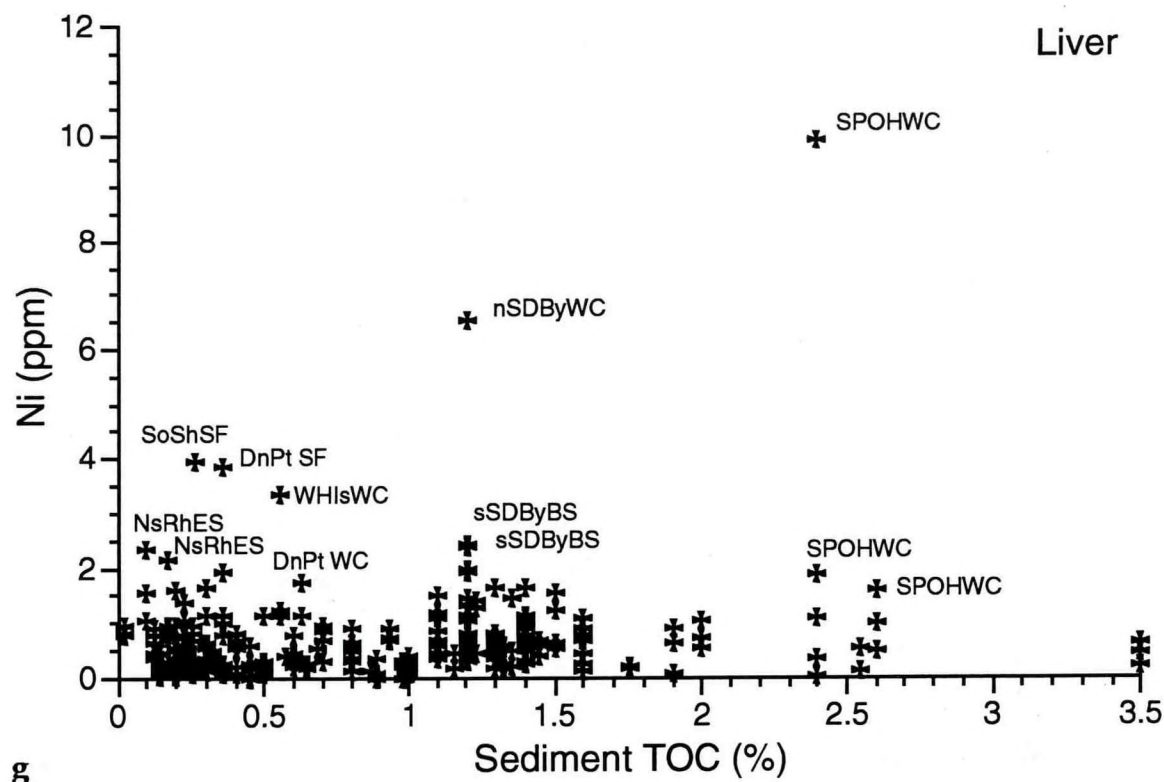
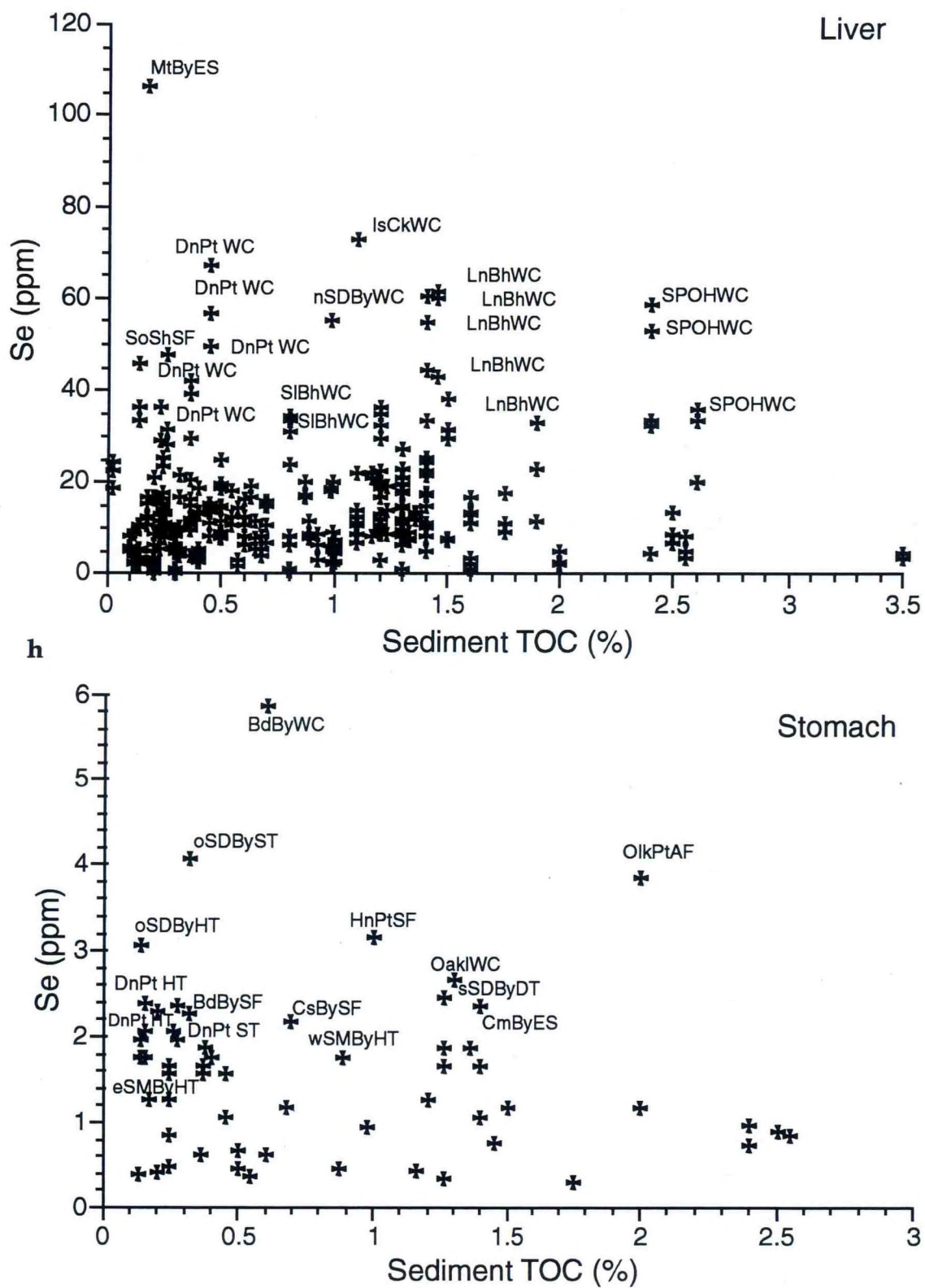


Figure 55. Continued. g. Nickel.



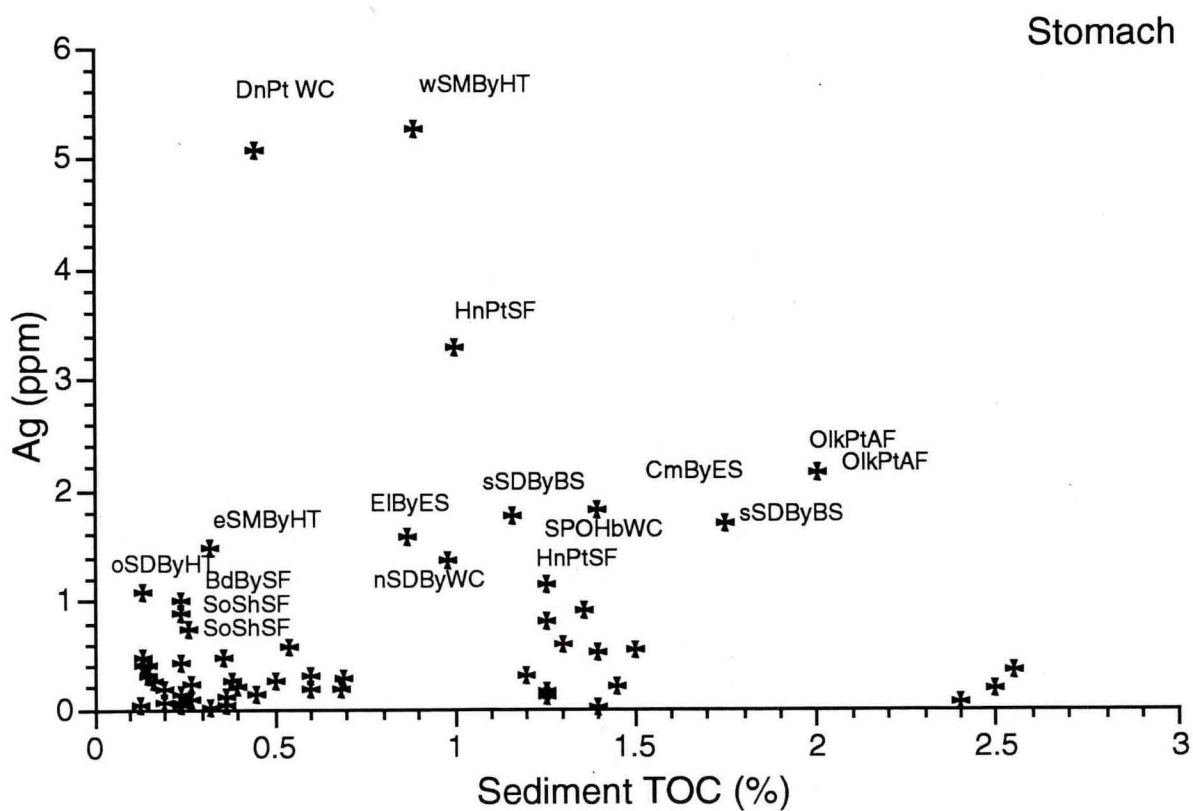
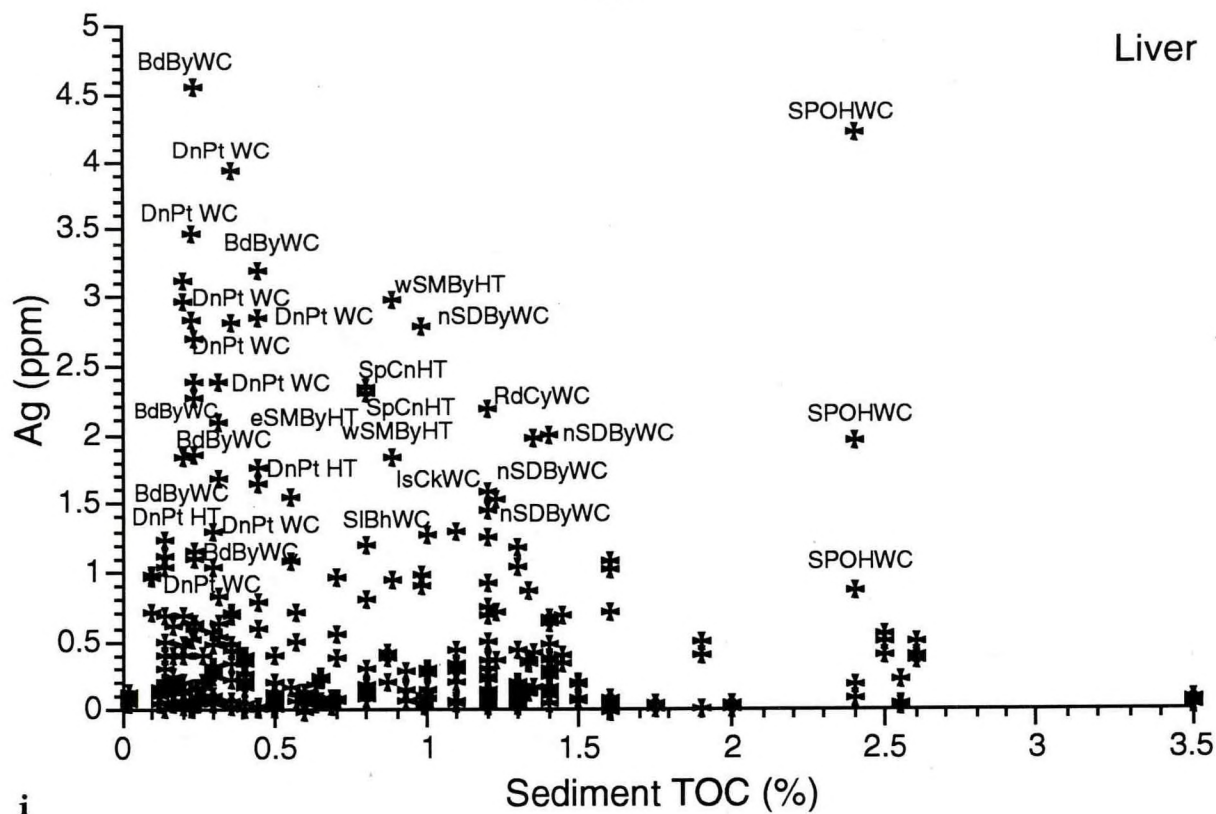


Figure 55. Continued. i. Silver

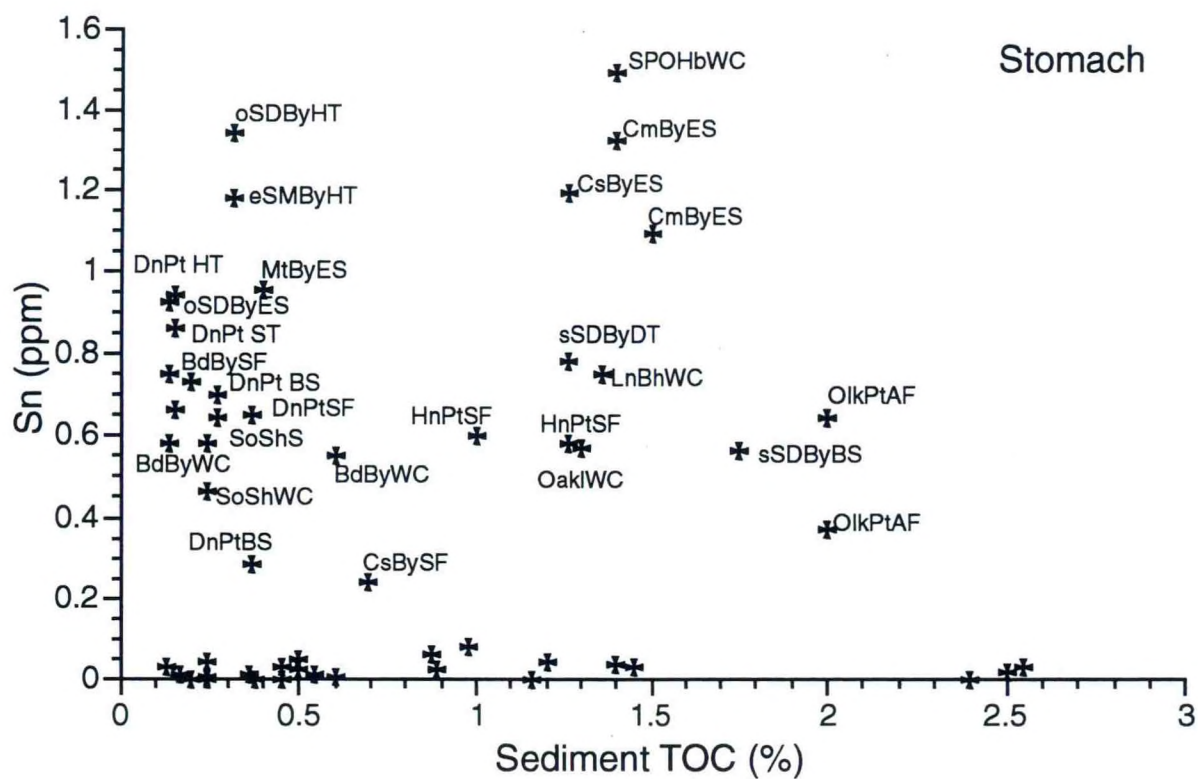
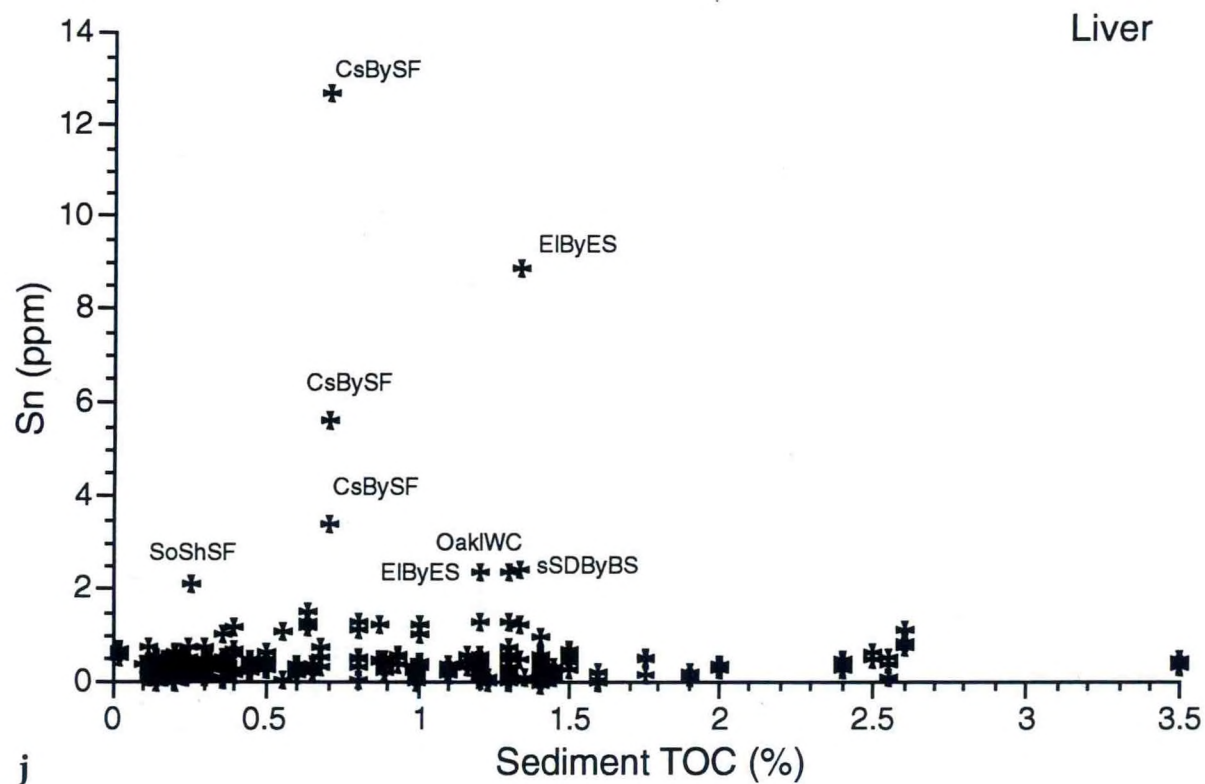


Figure 55. Continued. j. Tin.

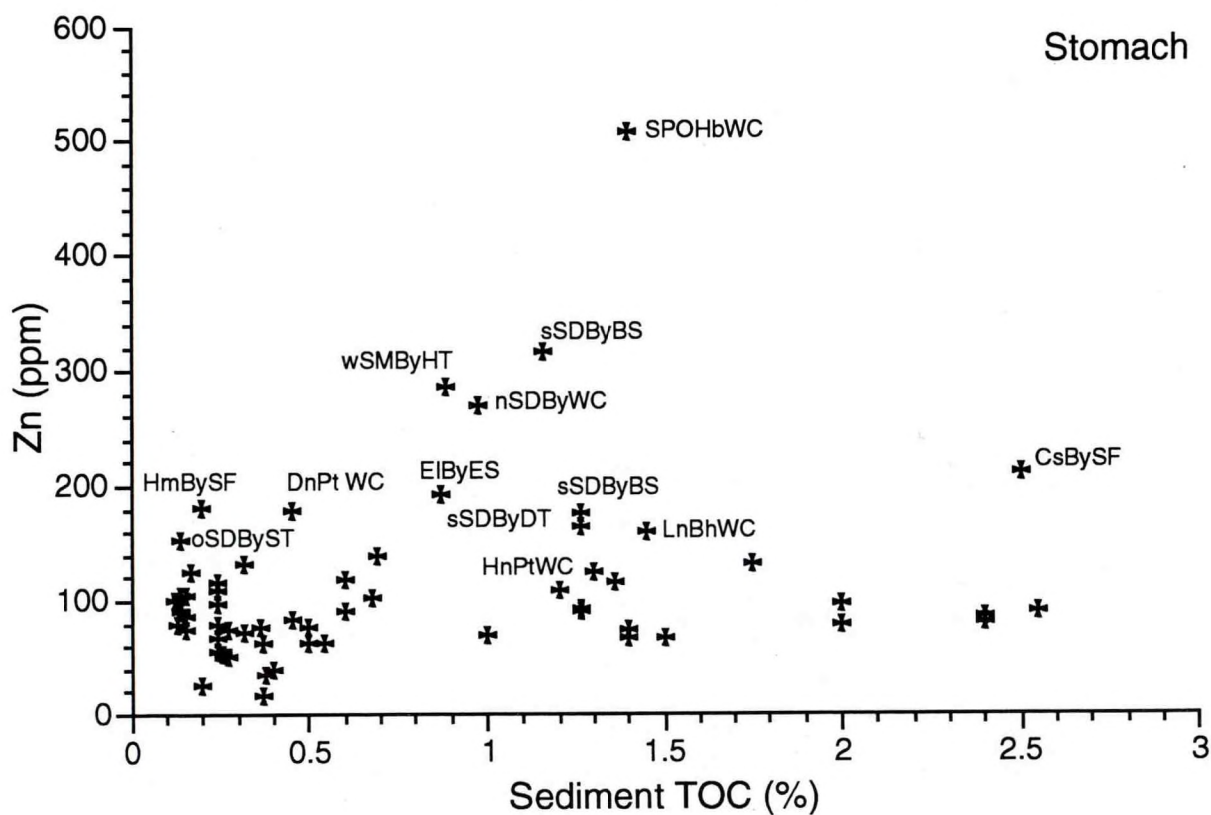
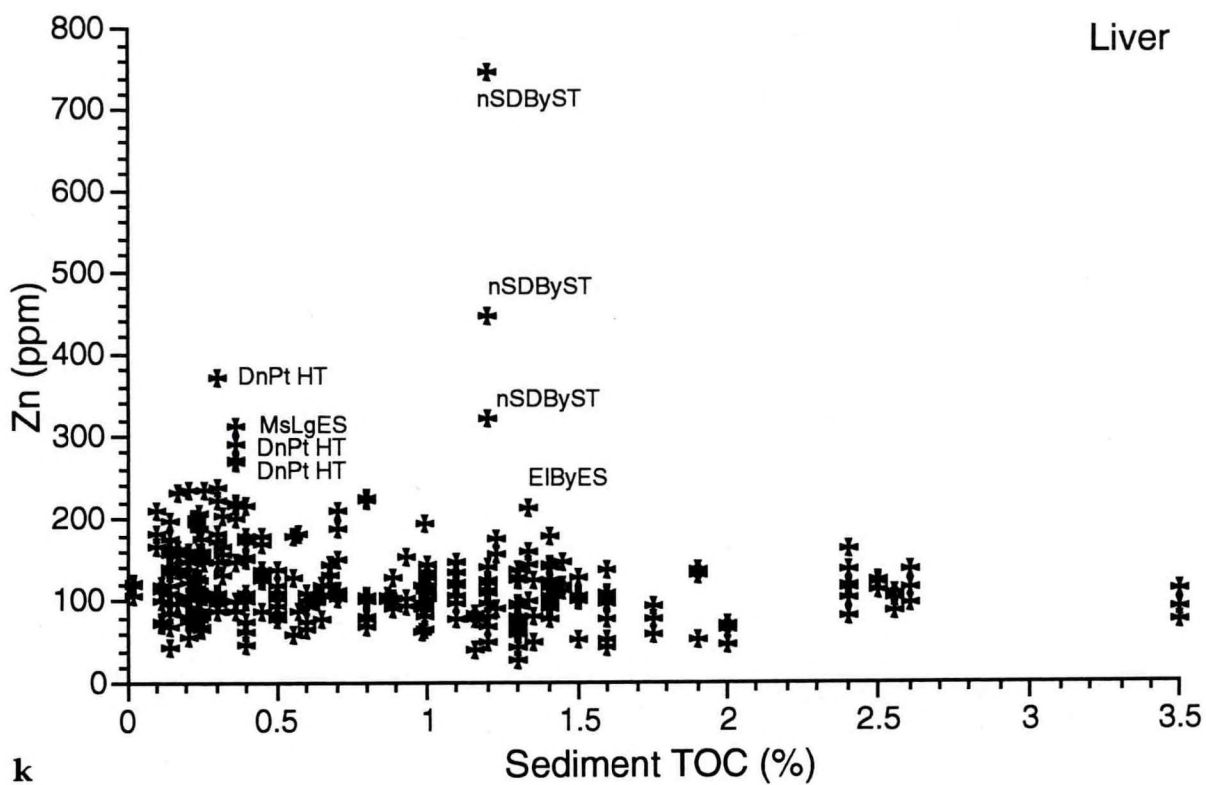


Figure 55. Continued. k. Zinc

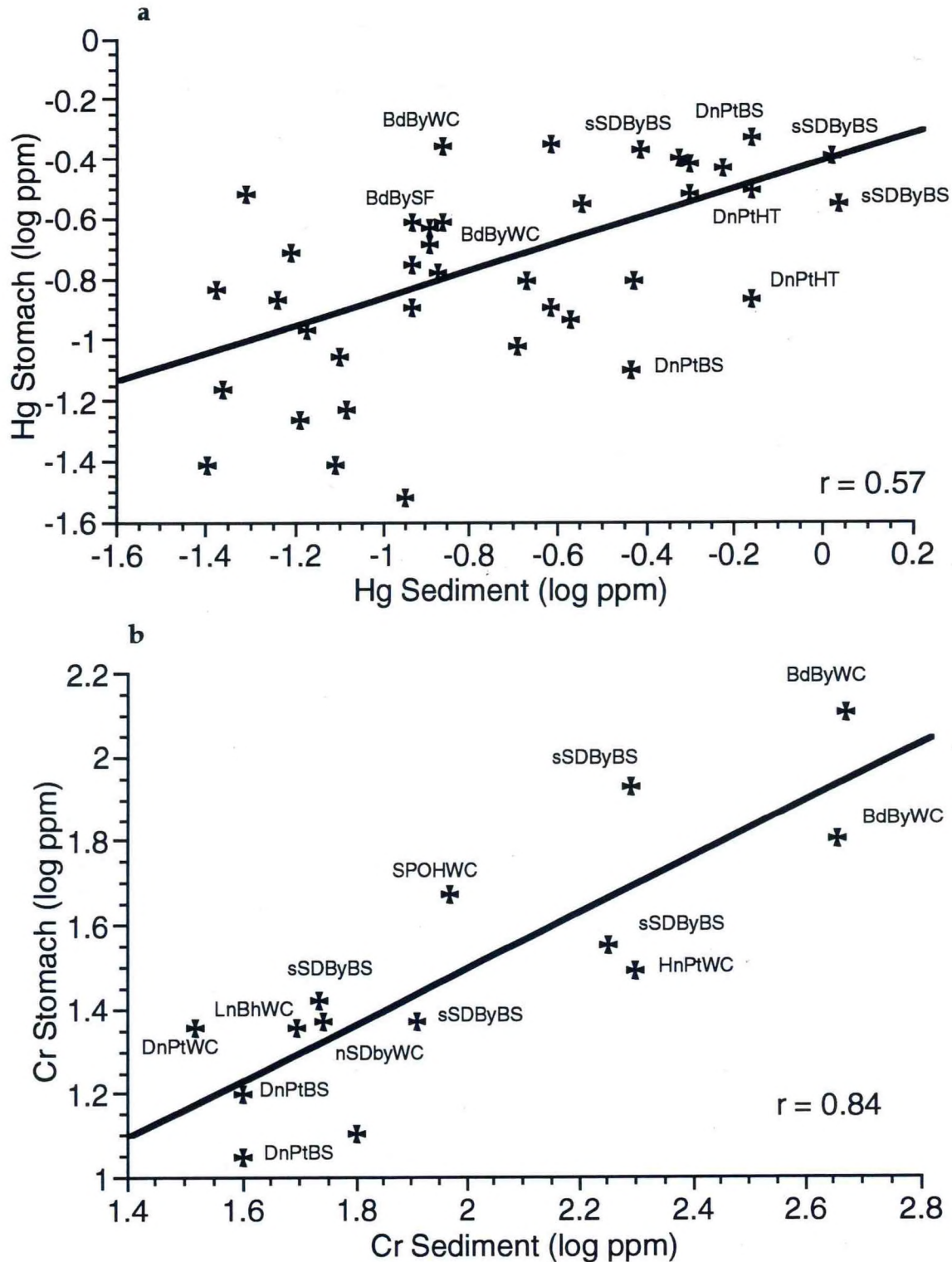


Figure 56. Correlation of element concentrations in stomach contents and sediment. Concentrations in $\log_{10} \mu\text{g/g}$. All sites and years plotted. See Tables 1 and 2 for abbreviations of sites and fish species. a. Mercury in all species. b. Chromium in sand bass and white croakers.

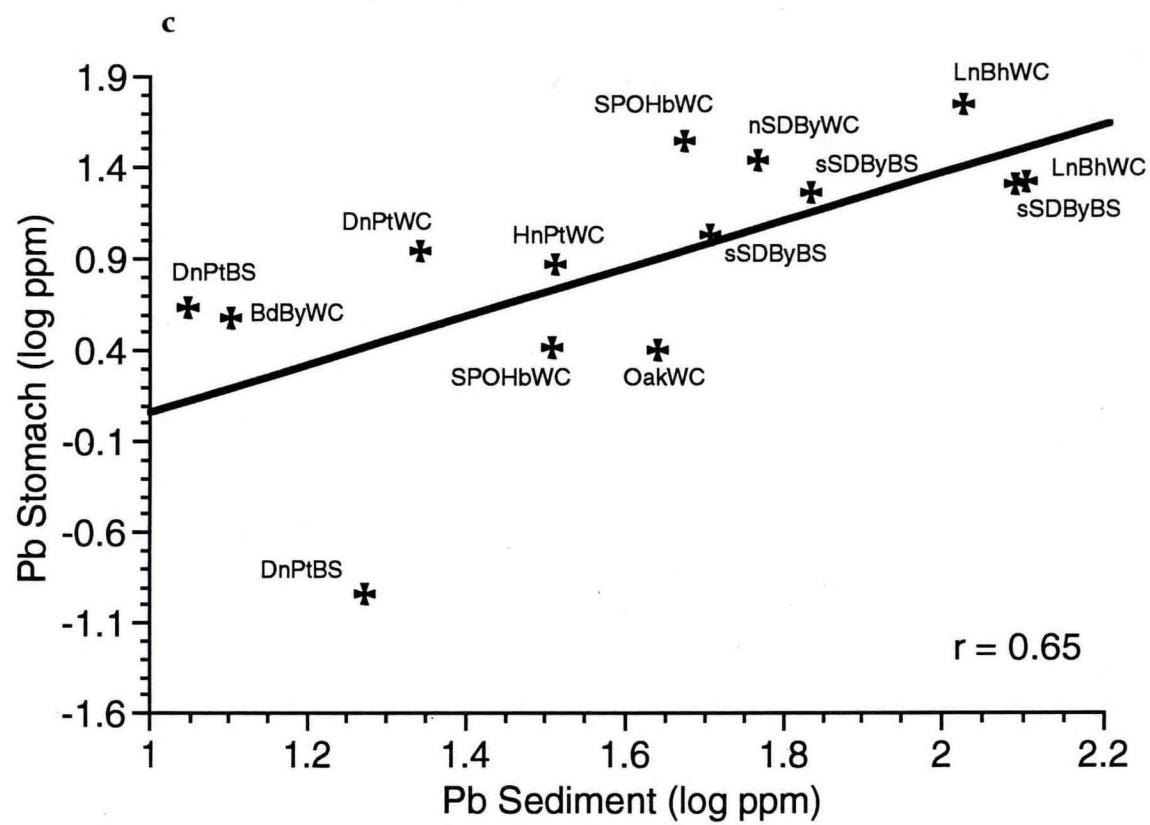


Figure 56. Continued. c. Lead in sand bass and white croaker.

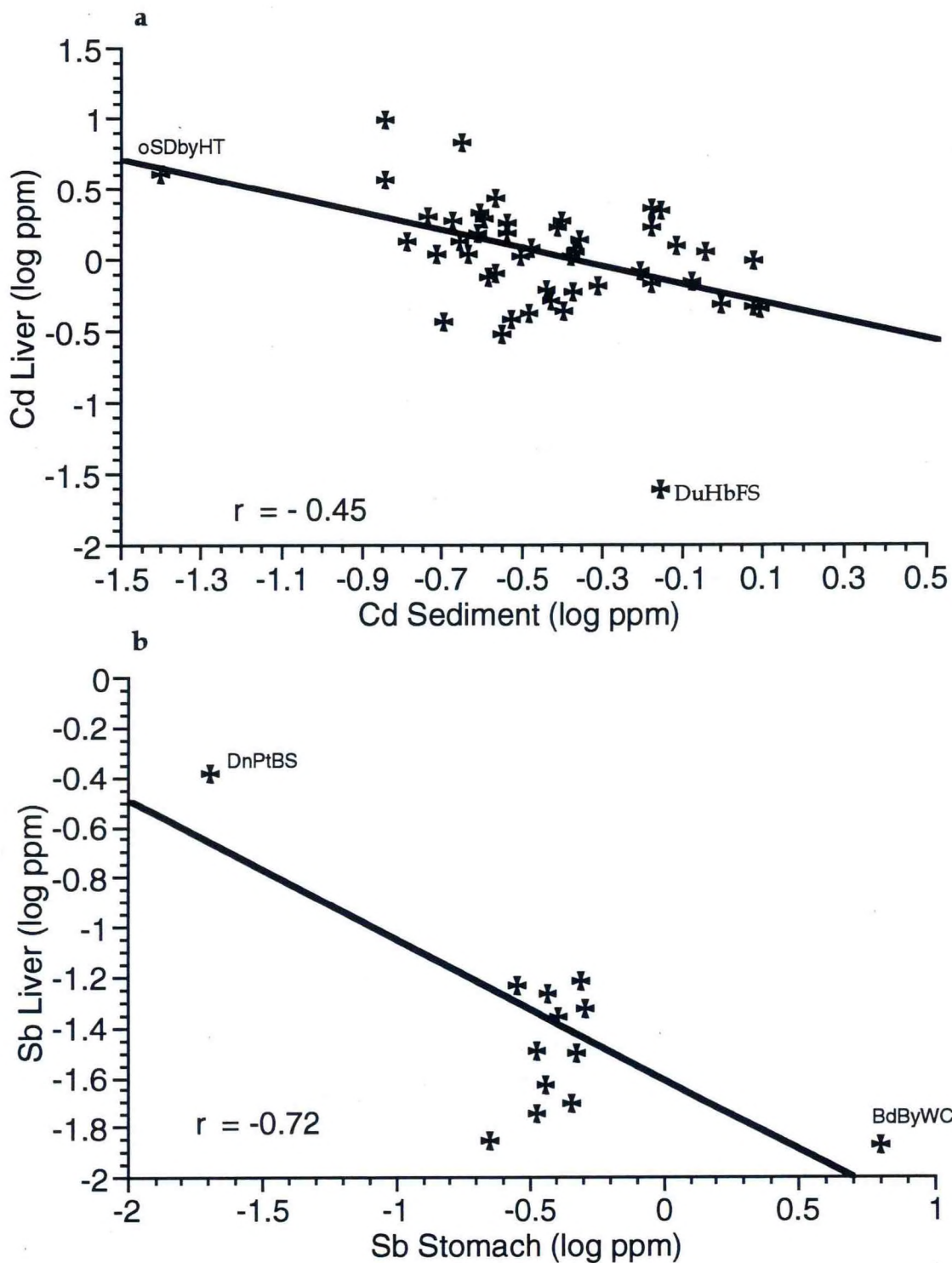


Figure 57. Plot of spurious correlations of element concentrations in liver and stomach contents. Concentrations in $\log_{10} \mu\text{g/g}$. All sites and years plotted. See Tables 1 and 2 for abbreviations of sites and fish species. a. Cadmium in all species. b. Antimony in sand bass and white croaker.

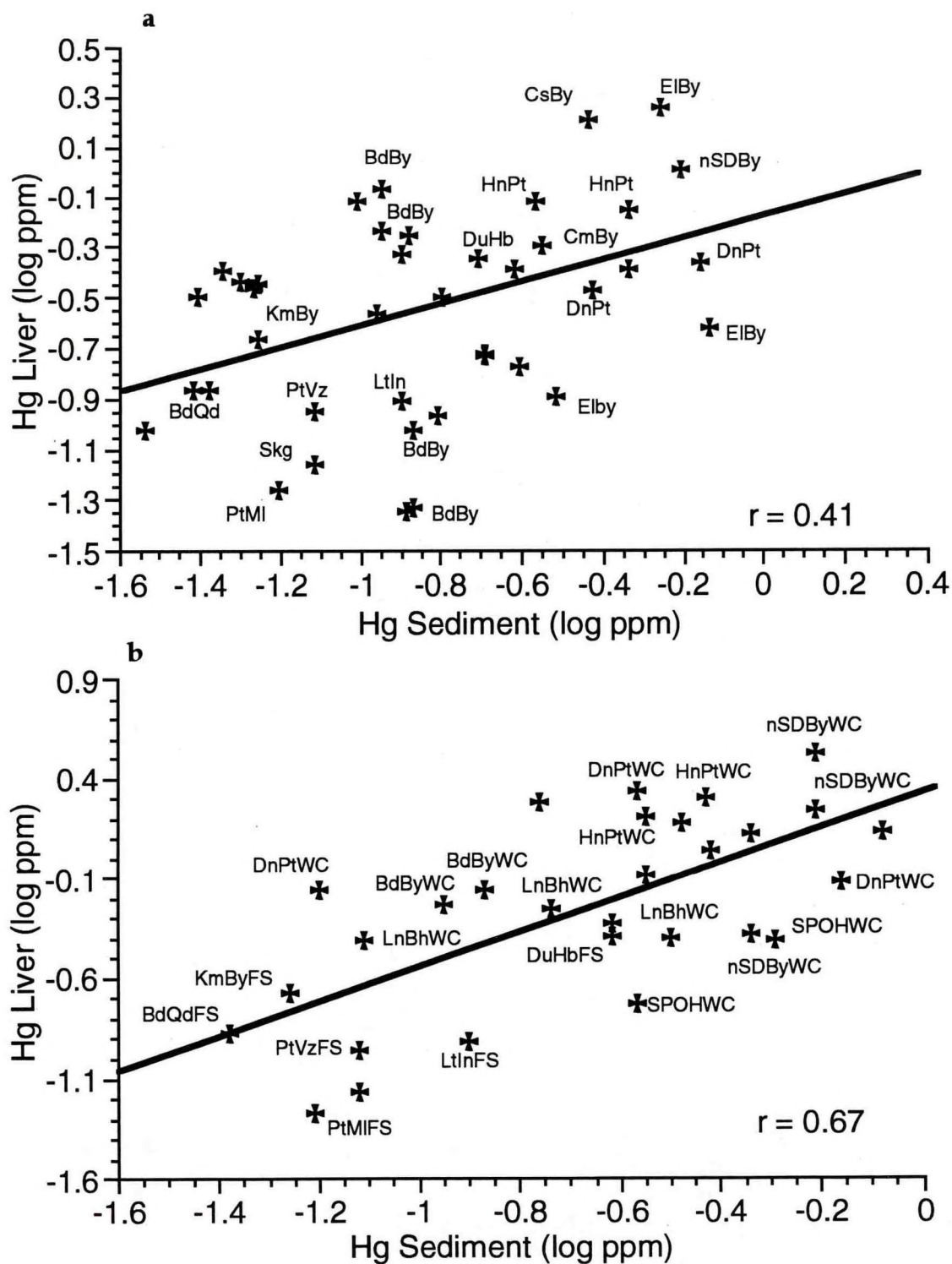
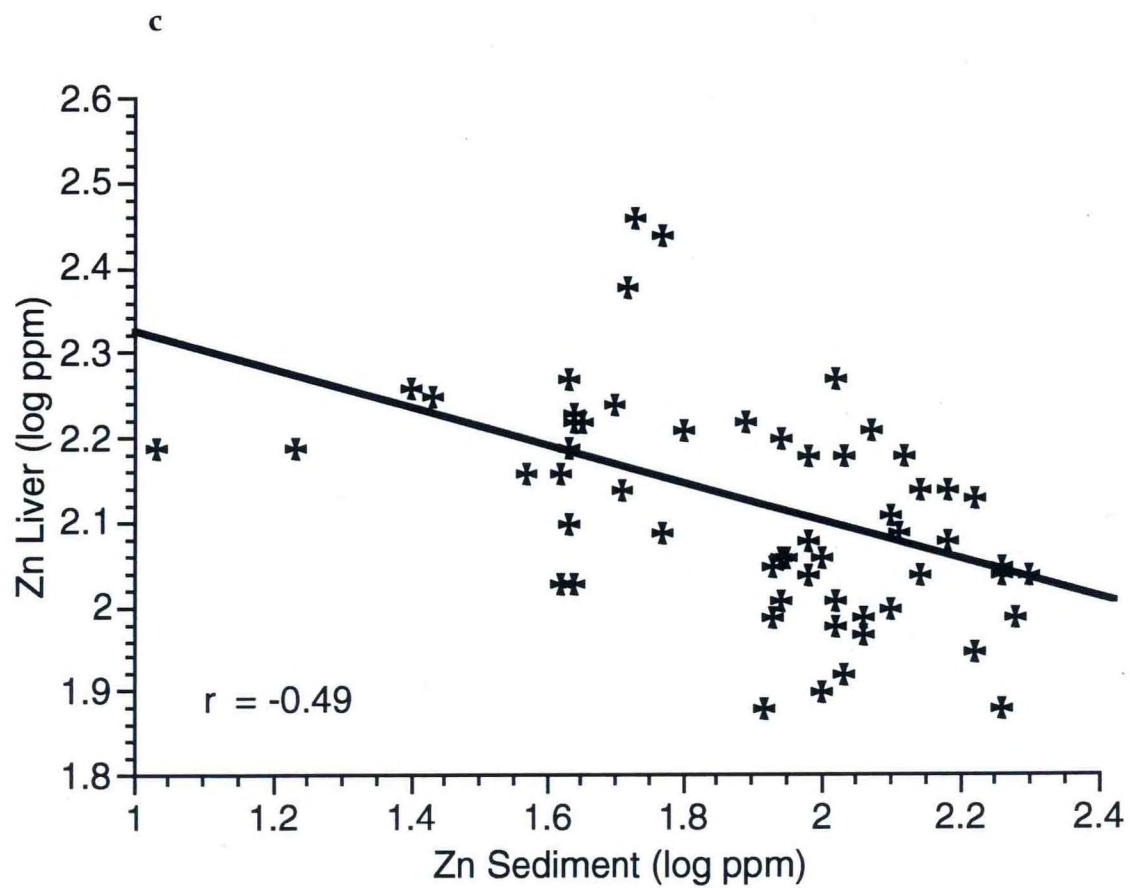


Figure 58. Plot of correlation of element concentrations in liver of fish and sediment. All sites and years plotted. Concentrations in log₁₀ µg/g. See Tables 1 and 2 for abbreviations of sites and fish species.
 a. Mercury in flatfish. b. Mercury in flathead sole and white croaker.



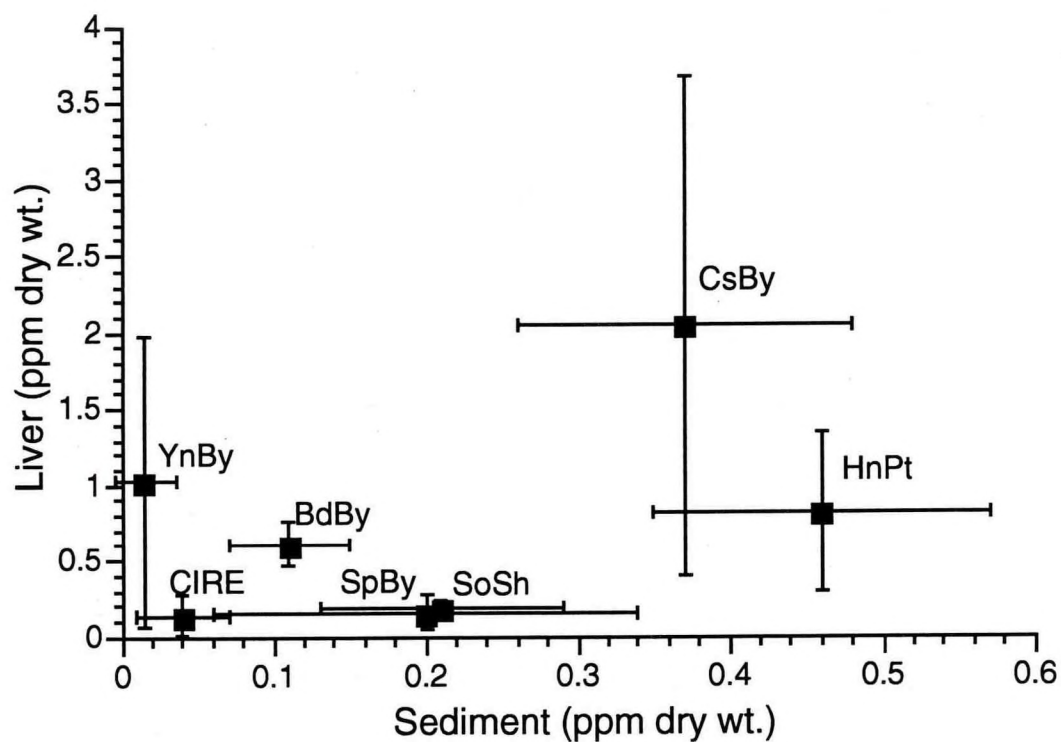


Figure 59. Variation in silver concentrations. Mean and standard deviation concentrations in $\mu\text{g/g}$ of three adult starry flounder livers and three sediment stations at each site for the one sampling period. Selected sites for 1986 are plotted. See Table 1 for abbreviations of sites.

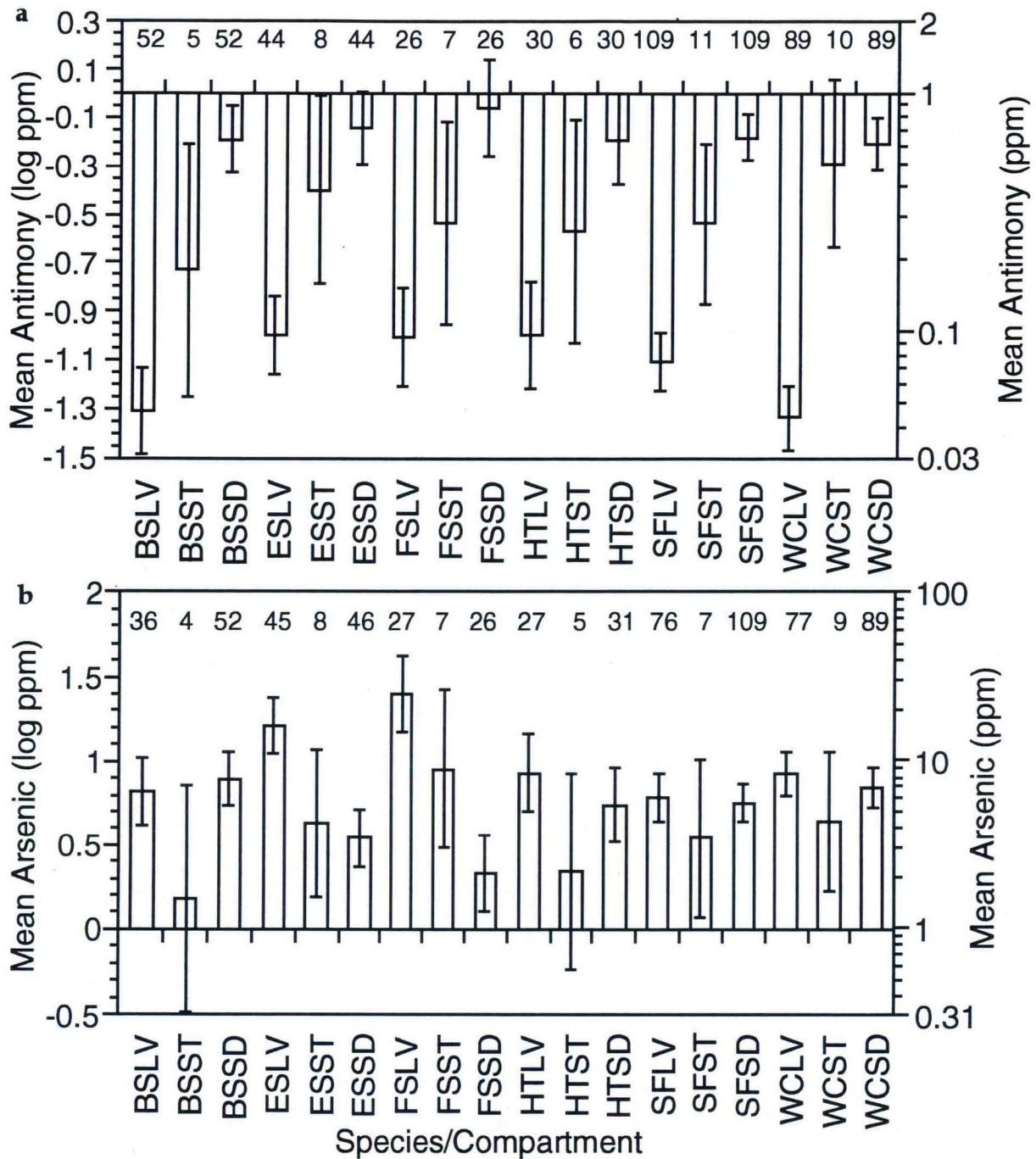


Figure 60. GT2 Plots of concentrations in liver, stomach contents, and sediment. Bar is mean \log_{10} concentration in $\mu\text{g/g}$ dry weight. Vertical whisker is comparison interval; nonoverlapping whiskers are significantly different at $\alpha = 0.05$. Right ordinate is concentration in $\mu\text{g/g}$. Samples sizes are shown by bars. Bars are in groups of three: liver (LV), stomach contents (ST), and sediment (SD). For example BSLV is barred sand bass liver. See Table 2 for species abbreviations. a. Antimony. b. Arsenic.

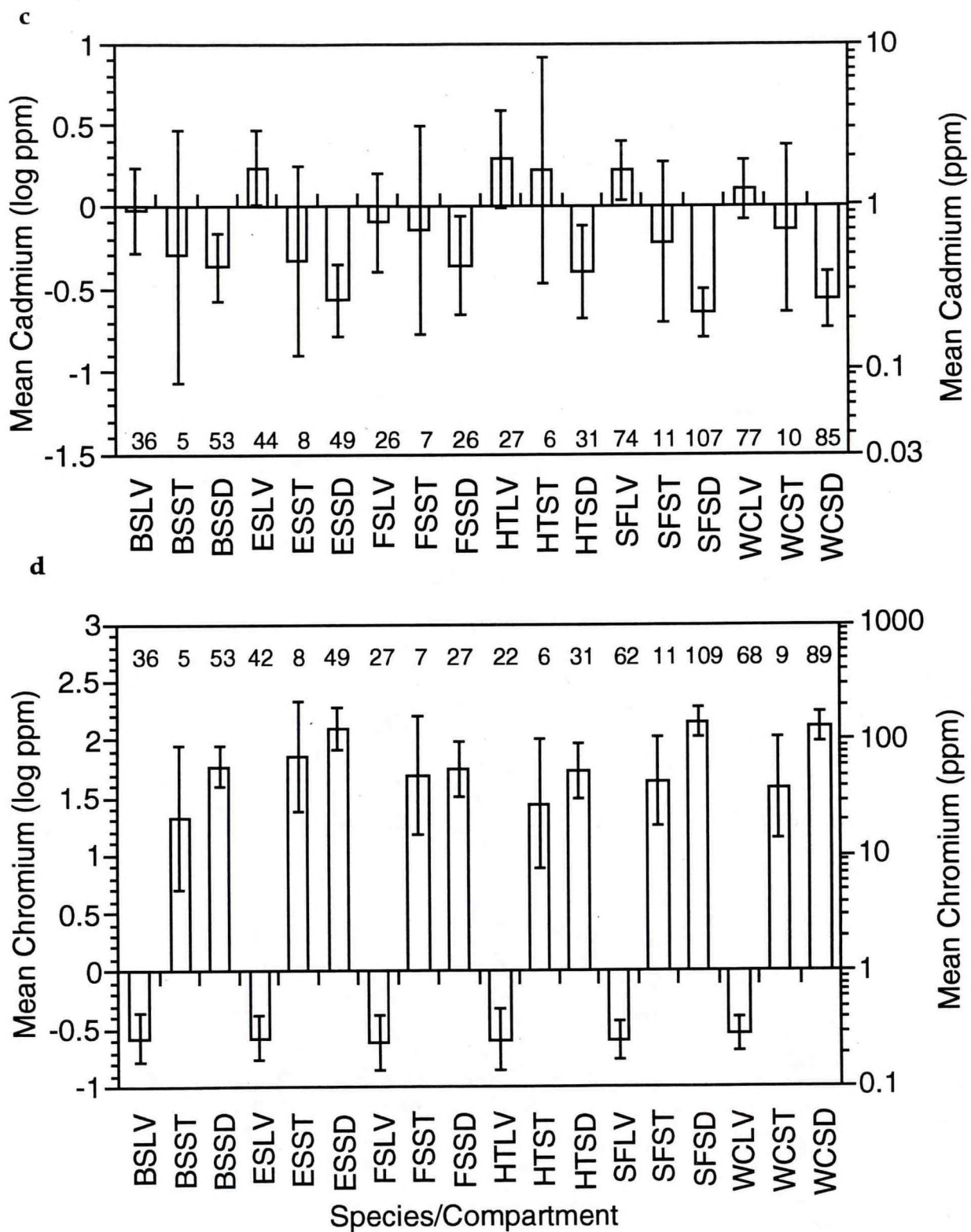


Figure 60. Continued. c. Cadmium. d. Chromium.

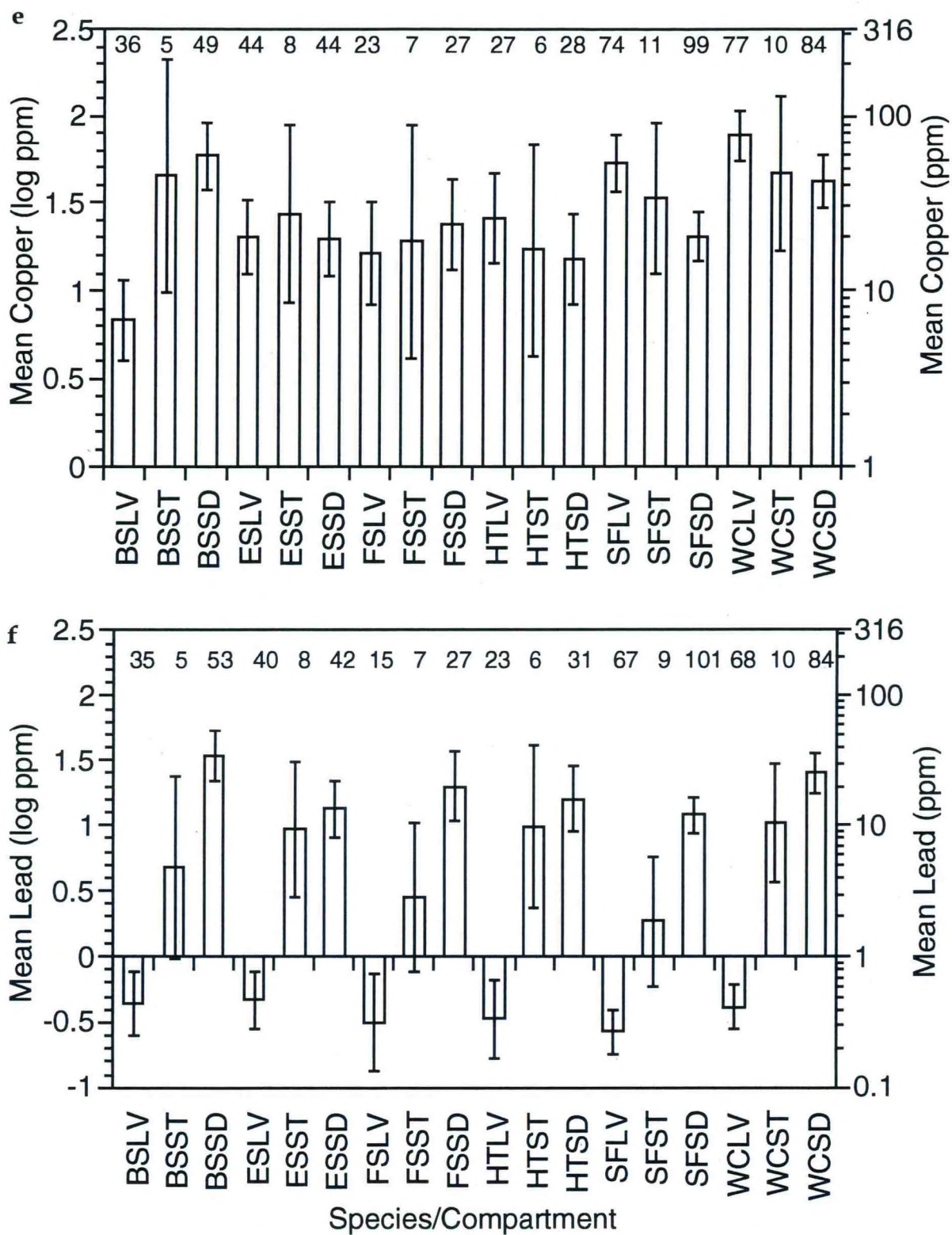


Figure 60. Continued. e. Copper. f. Lead.

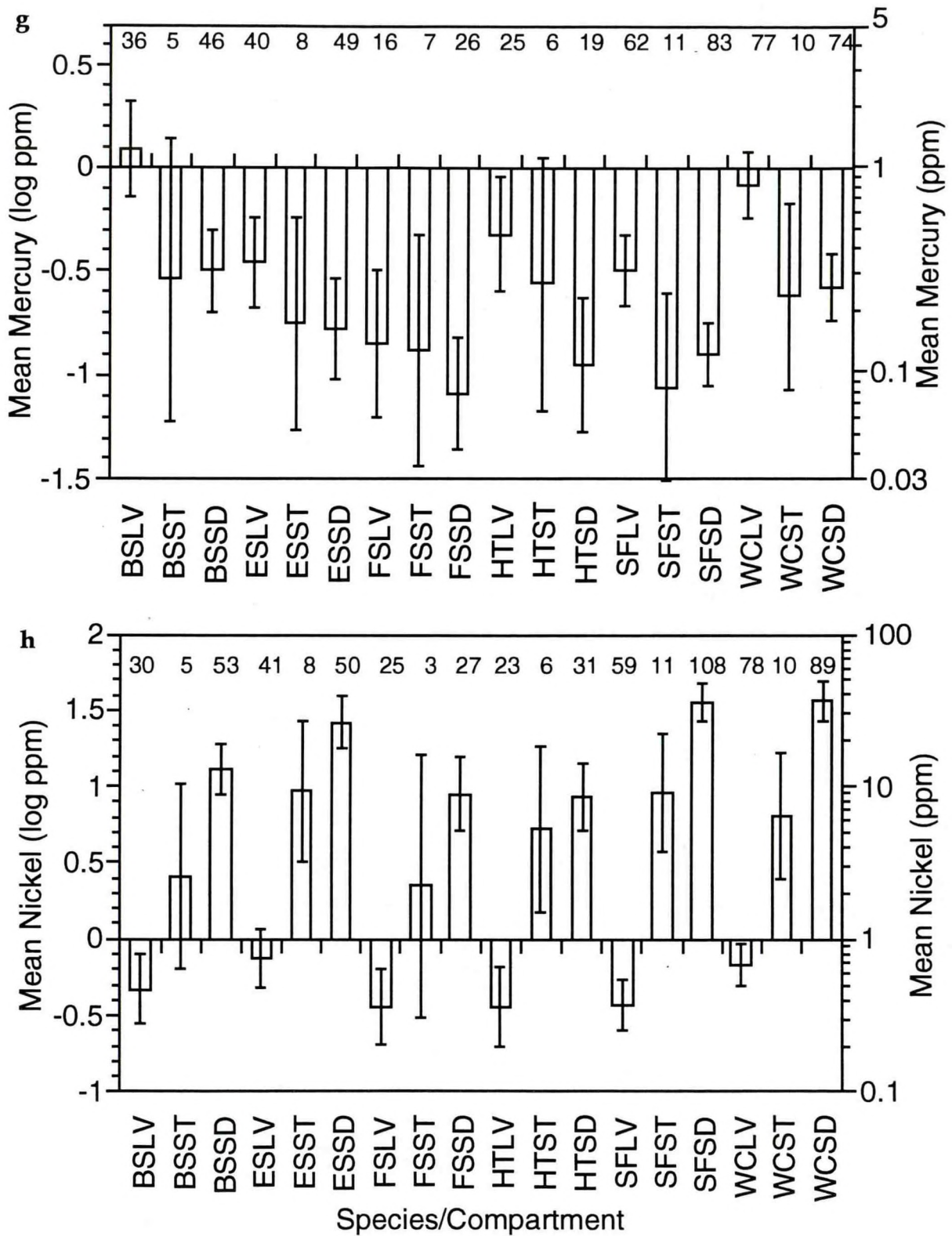


Figure 60. Continued. g. Mercury. h. Nickel.

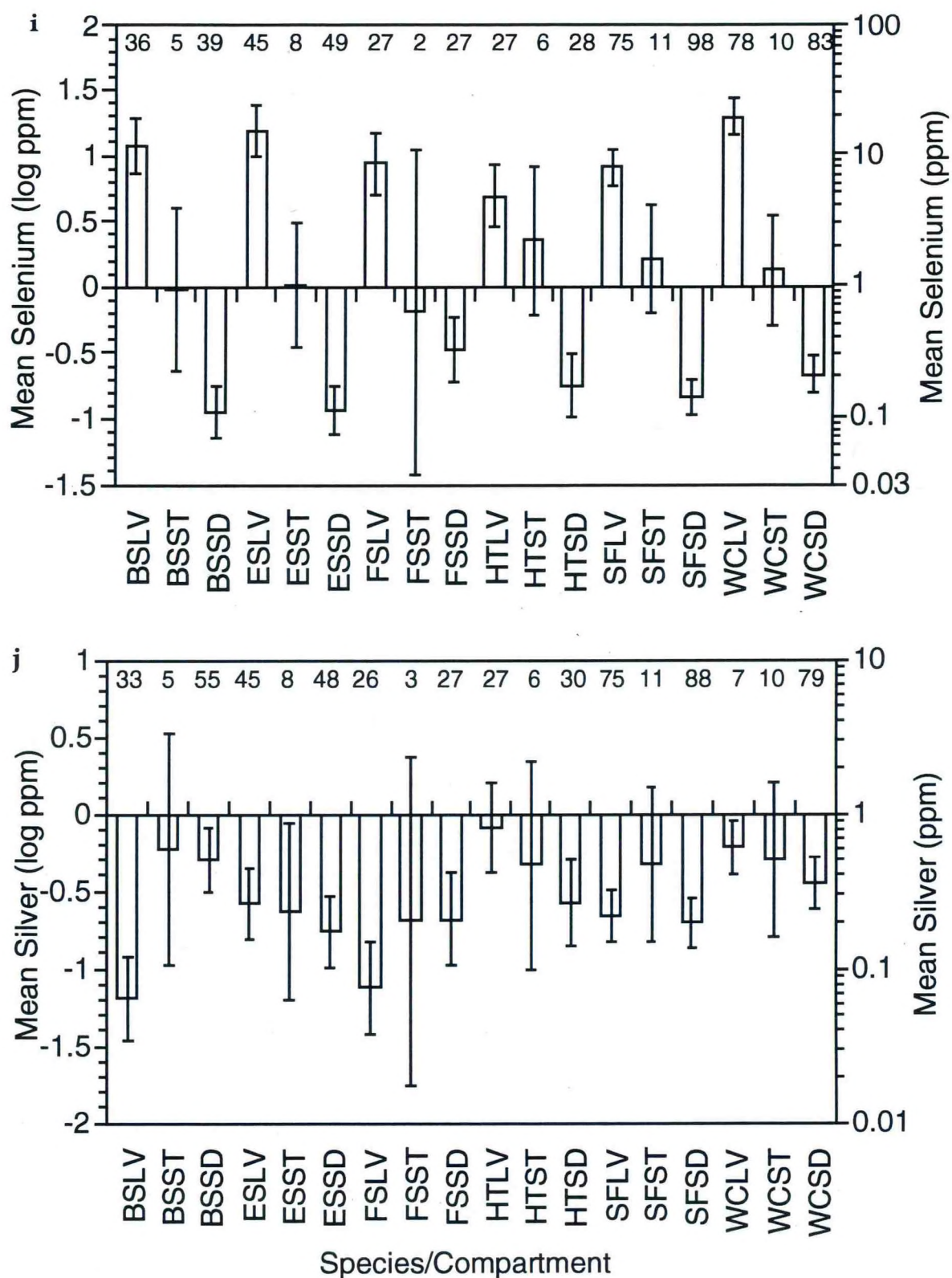


Figure 60. Continued. i. Selenium. j. Silver

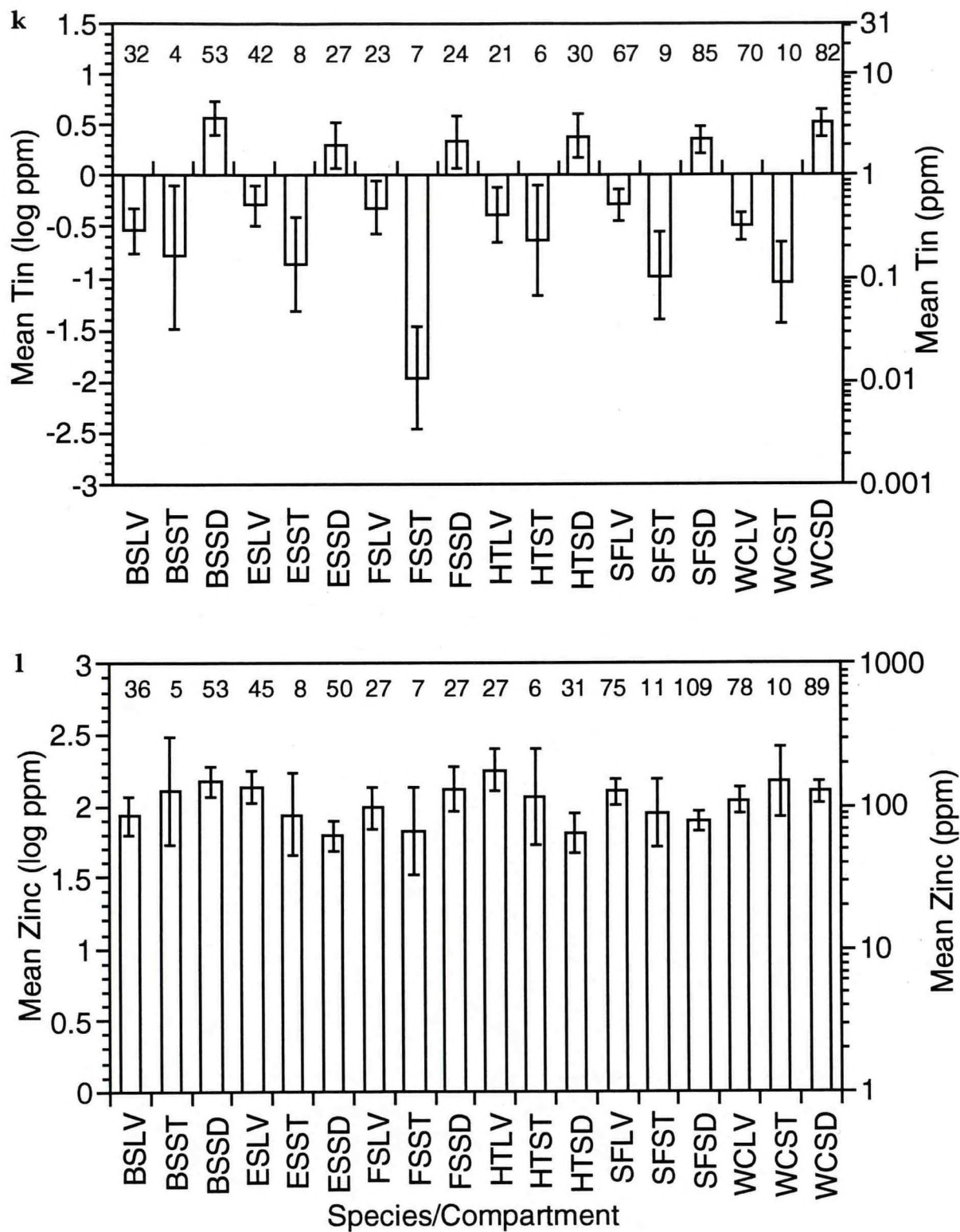


Figure 60. Continued. k. Tin. 1. Zinc.

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