DEVELOPMENT AND APPLICATION OF A METHODOLOGY TO ESTIMATE REGIONAL NATURAL CONDITIONS FOR TRACE METALS IN MARINE SEDIMENTS OF SOUTHCENTRAL ALASKA'S COASTAL REGION

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A
THESIS

Presented to the Faculty
of the University of Alaska Fairbanks

in Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

By

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Fairbanks, Alaska

December 2010

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Abstract

Increasing levels of resource development and population growth along Alaska's relatively pristine coastline require responsible environmental stewardship that is based on scientifically defensible monitoring and assessment. This thesis develops a methodology to assess the spatial distribution of coastal sediment trace metals and estimate their natural condition along Alaska's coastline. Marine sediments provide a better integrated long-term signal for naturally occurring and anthropogenic chemicals than repeated water measurements. The first of three manuscripts reports on marine sediment trace metal concentrations from a probabilistic sampling survey of Alaska's Southcentral coastal region. Results are described on a proportional basis, i.e., percent of estuary area, for the distribution of As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, and Zn in the sediments. With the exception of naturally elevated Cr and Ni at a site bounded by a chromite ore body, sediment trace metal concentrations measured represent non-analmous levels. The second manuscript develops natural conditions for fluvial trace metal inputs from two major Southeast Alaska coastal watersheds: Cook Inlet and Copper River. The stream sediment trace metal natural conditions place levels in the adjacent coastal sediments into context. Two exploratory data analysis techniques, the Tukey Box plot and Median + 2 Median Absolute Deviation, combined with geochemical mapping are used to develop stream sediment trace metal natural conditions. The third manuscript builds on the first two to develop a methodology to estimate coastal sediment natural conditions. Population estimates for the cumulative area 90% UCB 95% sediment trace metal of interest obtained from the sampling survey methodology and screened reference sites is used to establishing an upper threshold value for regional natural conditions. While this work establishes natural condition marine sediment trace metal levels for this region, the significance of these levels from an ecotoxciological perspective remains to be established. Additional studies are needed along other sections of Alaska's coastline, coupled with biological assessments, if Alaska is to develop relevant sediment quality guidelines.

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Dedication

To my parents, who long ago taught me to challenge myself, and to my wife and daughter, who not only provided support, but made sacrifices, over the years as I worked on pursuing my educational goals.

A debt of gratitude is due Dr. John Kelley, Advisory Chair Committee Chair and long time friend, whose patience and guidance will forever be appreciated.

Chapter 1: General Introduction

Introduction

Alaska contains almost 75% of the total area of the United States' bays, sounds, estuaries, and offshore marine shelves, yet less than 1% of Alaska's coastal aquatic resources have been adequately surveyed in regard to U.S. Federal Clean Water Act assessment needs (ADEC, 2005). Section 305(b) of the Clean Water Act requires states to report on conditions of their waters biennially with a scope that provides:

- a description of the water quality of *all* navigable waters, accounting for seasonal, tidal, and other variations.
- an analysis of the extent to which *all* navigable waters allow for recreational activities on land and waters and provide for the protection and propagation of a balanced population of shellfish, fish, and wildlife.

While there have been many assessments of water quality in Alaska over the years by various federal, state, and local agencies, including non-governmental entities, most have been targeted surveys that address specific issues and do not address the status of all waters (ADEC, 2005).

Targeted assessments are by their nature focused, addressing specific environmental issues, but they cannot be used to make inferences about populations (all waters) distributed over space. Understanding large-scale environmental concerns (e.g., coastal sediment distribution changes due to climate change) requires measures characterizing the population of concern (Long et al., 1996; Cox et al., 1997; Stevens and Olsen, 1999). Survey sampling provides a scientifically rigorous methodology to sample a subset of the ecological resource of interest (e.g., coastal estuaries) to provide an estimate of the condition or status of the estuaries with a statement about uncertainty surrounding that estimate.

As part of the Alaska Department of Environmental Conservation (ADEC) Water Quality Monitoring and Assessment Strategy (2005), that agency started adapting the

U.S. Environmental Protection Agency (USEPA) National Aquatic Resource Survey methodology (USEPA, 2010), to large regions in Alaska. This methodology uses a probability survey design providing an estimate of the quality of all waters in the target population. This sampling survey methodology allows the Alaska Department of Environmental Conservation to obtain estimates of known precision and uncertainty in reporting on aquatic resource status (ADEC, 2005; USEPA, 2010). For example, one objective is to estimate the proportion of a resource—in this case estuary— above or below a water quality standard, such as dissolved oxygen. The ADEC Assessment and Monitoring Program (AKMAP) works with EPA and others in conducting these surveys.

One objective of the AKMAP work is the development of regional background or natural conditions for marine sediment trace metals ultimately for use in development of sediment quality guidelines. The ADEC Water Quality Standards Criteria (18 AAC 70.9904(41)) define natural conditions as "any physical, chemical, biological, or radiological condition existing in a water body before any human-caused [anthropogenic] or influence on, discharge to, or addition of material to, the water body" (ADEC, 2006). Natural conditions provide a background that provides a needed reference for agencies and organizations responsible for making environmental policy and management decisions.

Sediments provide an integrated long-term signal for naturally occurring and anthropogenically derived chemicals compared to "snapshot" variable and temporal water column measurements (Newman and Watling, 2007). Coastal sediments represent a sink for many particle-reactive trace metals and other chemicals of natural and anthropogenic origin, with concentrations generally exceeding those in the water column by several orders of magnitude (Förstner and Whittmann, 1979). Environmental monitoring programs use sediment because of its ability to concentrate contaminants of concern, linkage to the aquatic food web, and applicability to assessing the spatial and temporal extent of contaminant distributions (Summers et al., 1996)

No universal standard procedure for determination natural condition exists, and an approach that works in one region may not work elsewhere (Daskalakis and O'Connor, 1995; Rodríguez et al., 2006). Ultimately, environmental agencies responsible for managing coastal marine ecological resources require sediment guidance based on pragmatism, as well as science (GIPME, 2000). In contrast to the highly industrialized conterminous United States for most of Alaska's coastal waters, it is still possible to obtain pre-development reference status for many abiotic and biotic aquatic resources. Establishing status assists environmental resource managers in better understanding and protecting the integrity of coastal aquatic resources while managing for environmentally responsible development (NRC, 1990; Zedler, 1996; Tibbetts, 2000).

Dissertation Focus

This dissertation develops a methodology for establishing marine coastal sediment trace metal natural conditions for Alaska. This step supports a long-term effort to develop State of Alaska sediment quality guidelines in marine sediments. The focus of the research is on:

1. Developing and providing a robust estimate, with uncertainty, of the concentration of trace metals in all of Southcentral Alaska estuary marine sediments and of natural condition values for those trace metals.
2. Two specific hypotheses are evaluated based on results of the AKMAP Southcentral coastal sampling survey and natural conditions assessment. The hypotheses are as follows:
    - NOAA sediment quality guidelines, Effect Range Low and Effect Range Median, are exceeded in less than 10% of the cumulative estuary area.
    - Trace metal concentrations assessed in 2002 AKMAP Southcentral survey the coastal sediments reflect the natural local and regional geologic environments.

Sediment Data Sets Used

The principal marine data set used is from the ADEC Alaska Monitoring and Assessment Program (AKMAP) 2002, Alaska Southcentral Coastal 2002 field survey (Figure 1-1). For readers interested in additional details on the Southcentral 2002 survey and the data sets for water column, benthic invertebrates, trawl and fish histopathology, and sediment chemistry, this information can be downloaded from the U.S. Environmental Protection Agency National Coastal Assessment website (USEPA, 2009).

The freshwater stream sediment data set for the two principal Southcentral coastal watersheds of Cook Inlet and Copper River was obtained from the mid-1970 United States Atomic Energy Commission (AEC) National Uranium Resource Evaluation Program (NURE) surveys (USGS, 2009).

Manuscript Progression, Ch. 2–4

The next three chapters, comprising the manuscript portion of this dissertation, build upon each other and follow this progression:

Chapter 2

This chapter provides the background on the Alaska Southcentral 2002 survey methodology and presents the results, as cumulative distribution functions, for the sediment trace metal data collected. These data are used in Chapter 4 in the development of regional natural conditions for Southcentral marine sediments.

Chapter 3

From both a flow and mass sediment basis, this chapter assesses the fluvial input of trace metals from Cook Inlet and Copper River, the two principal drainages providing sediments into the Southcentral Region. Using U.S. Geological Survey (USGS) NURE data sets, stream sediment trace metal natural conditions are established on a regional basis for the trace metals of interest in both Cook Inlet and Copper River.

Chapter 4

This chapter integrates the preceding chapters' conclusions and data to develop and demonstrate a methodology for establishing Southcentral regional marine sediment natural conditions for As, Cr, Cu, Pb, Hg, Ni, and Zn.

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Figure

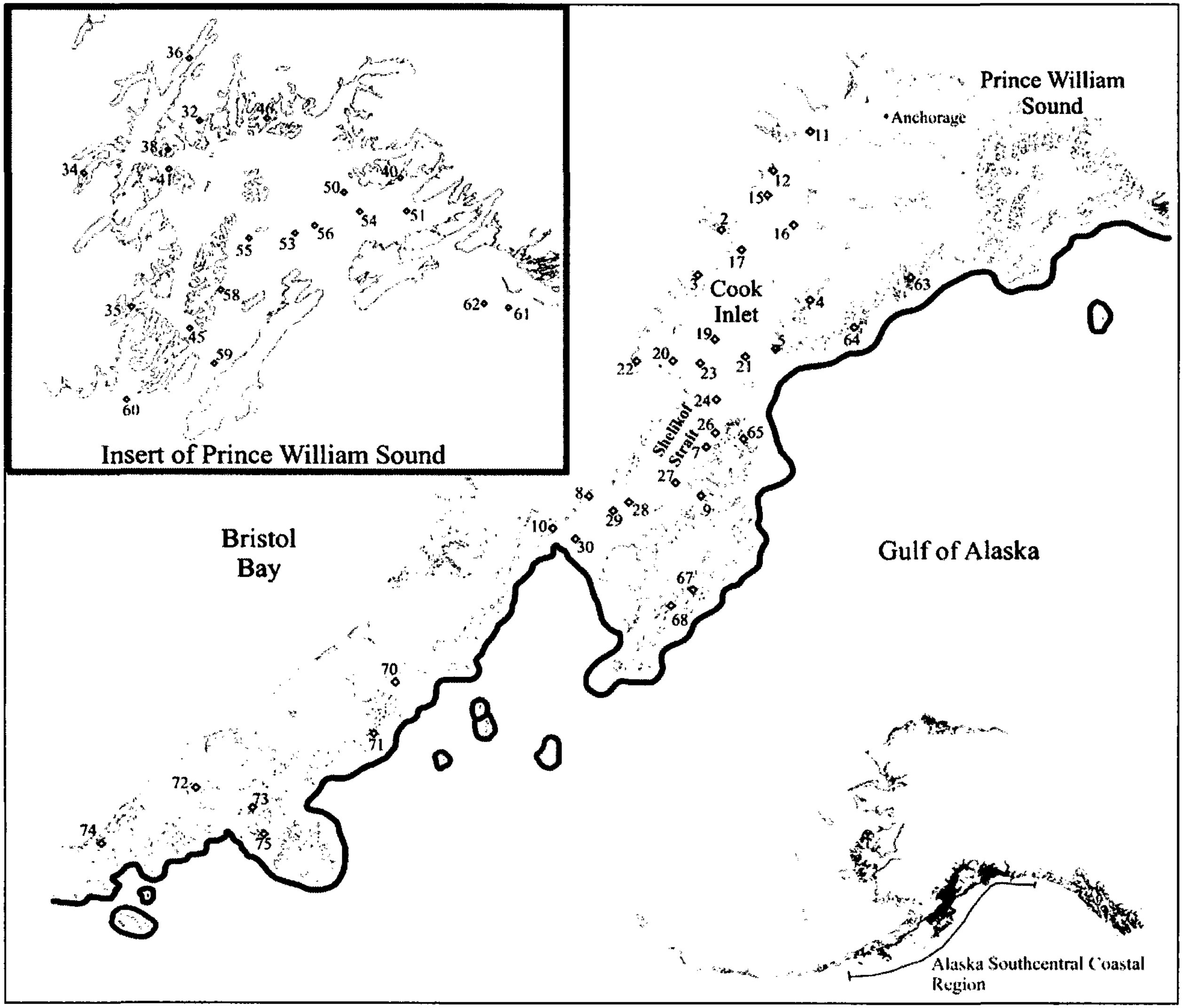

Figure 1-1: Alaska Southcentral Coastal Survey Region

Chapter 2: Alaska Monitoring and Assessment Program (AKMAP): Spatial Distribution of Nine Priority Pollutant Trace Metals in the Sediments of the Southcentral Alaska Coastal Biogeographical Province[1]

Abstract

Increasing resource development is projected for Alaska's coastal regions, and environmental management of this development requires an understanding of environmental conditions on a regional basis. Sediment trace metal concentrations collected for this purpose as part of a probabilistic survey are discussed. Percentage of estuary area relative to NOAA's Effect Range Low (ERL) and Effect Range Median (ERM) sediment quality guidelines is estimated. No estuary area exceeds ERLs for Pb or Ag: but Cd, Hg, and Zn exceed the ERL in 0.3%, 1.7% and 0.4%, respectively of the area. The elements of As, Cr, Cu, and Ni fall between ERL and ERM ranges in 58.2%, 23.8%, 43.1%, and 56.4%, respectively of the area. However, Cr and Ni exceed ERMs in 0.2% and 5.9%, respectively of the area. With the exception of elevated Cr and Ni at a site near a chromite ore body, sediment trace metal values represent non-anomalous levels without indication of anthropogenic influence.

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[1] Dasher, D.H. Alaska Monitoring and Assessment Program (AKMAP). Spatial Distribution of Nine Priority Pollutant Trace Metals in the Sediments of the Southcentral Alaska Coastal Biogeographical Province. Prepared for submission to Marine Pollution Bulletin, Baseline, Elsevier.

Introduction and Discussion

Alaska contains almost 75% of the total area of the United States' bays, sounds, estuaries, and offshore marine shelves (NRC, 1984; USEPA, 2006), yet less than 1% of Alaska's coastal aquatic resources have been adequately surveyed in regard to Clean Water Act assessment needs (ADEC, 2005). Aquatic resources encompass the aquatic ecosystem. Our case focuses on the relationship between water quality, which includes sediments, and the ecosystem biota (Texas State University, 2010). Alaska's coastal population increased 63% between 1980 and 2003 (Crossett et al., 2004), and oil and gas, mineral, and fisheries resource development activities are increasing with globally driven demands (State of Alaska, 2007). Major coastal monitoring efforts in Alaska are associated with pollution from point sources, such as domestic or industrial wastewater treatment facilities; targeted monitoring of specific areas of concern, such as off-shore oil and gas lease or production regions; or response to an environmental disaster, such as the Exxon Valdez oil spill. Other environmental concerns facing Alaska's coastal resources involve non-localized drivers, such as climate change and long-range transport of contaminants. Monitoring and assessment efforts, thus, have been spatially restricted and do not provide the public and the resource managers with a holistic understanding of the aquatic resource condition or status of the coastal regions of Alaska. Status here refers to a synoptic measure of a resource condition, which can be environmental contaminants or biological indices, at a certain time. This lack of understanding of the areal or spatial extent of environmental status at regional and larger scales limits the ability to place the results of localized monitoring within a broader regional perspective. The focus of this paper is on sediment trace metal concentrations relative to the proportion of the resource, in this case the estuary area in Southcentral Alaska. For readers interested in additional details on the Southcentral 2002 survey and the data sets for water column, benthic invertebrates, trawl and fish histopathology, and sediment chemistry, this information can be downloaded from the USEPA National Coastal Assessment website (USEPA, 2009a).

In contrast to the highly industrialized conterminous United States, it is still possible to obtain pre-development reference status for many abiotic and biotic aquatic resources for most of Alaska's coastal waters. Establishing status assists environmental resource managers in better understanding and protecting the integrity of coastal aquatic resources while managing environmentally responsible development (NRC, 1990; Zedler, 1996; Tibbetts, 2000). The Alaska Department of Environmental Conservation (ADEC) Alaska Monitoring and Assessment Program (AKMAP) is adapting the U. S. Environmental Protection Agency (USEPA) Environmental Monitoring and Assessment Program (EMAP) statistical sampling survey approach to help meet the challenge of assessing the water quality of Alaska's vast coastal waters. The EMAP sampling survey methodology allows ADEC to obtain estimates of known precision and uncertainty in estimating aquatic resource status (ADEC, 2005; USEPA, 2009b). For example, one objective is to estimate the proportion of a resource—in this case estuary area—above or below a water quality guideline. An understanding of the status of water quality over a regional context provides resource managers a consistent background for assessing the results of targeted sampling and patterns of contamination (Stein and Bernstein, 2008). Probability survey designs provide a scientifically rigorous way to sample a subset of a target population, such as all voters in Alaska, to infer how all the voters may vote, including the uncertainty surrounding that estimate. In this case the target population is the estuary area of Southcentral Alaska's coastal region. A clear difference exists between the Southcentral Alaska AKMAP sampling survey and previous sampling in this region, which were not designed to extrapolate from sample to a target population level (e.g., X% of the estuary area above a certain water quality guideline).

In survey sampling, a determination of sample size must be made to provide for an estimate of precision for statements made about the sampled data (Lohr, 1999). The primary goal of the AKMAP sampling is to estimate the proportion of the sampled population meeting an index, where precision can be approximated based on the proportion to be estimated (e.g., percent of resource meeting a water quality index confidence level as defined by a project's Measurement Quality Objectives (MQO), and number of samples) (Cochran, 1977).

$$Percent\ Precision, P = Z \times 100 \times \sqrt{[p \times (1-p) \div N]}$$

Z is a factor accounting for the desired level of confidence, p is the proportion to be estimated of the resource against some index, and N is the number of samples.

The desired MQO precision and uncertainty are established in the initial sampling design phase and then used to calculate the number of samples required. The EMAP national survey goal for precision is ±12% at 90% confidence for population proportion estimates (USEPA, 2007a). While post hoc variance of the proportion is not known at the design stage, a conservative approach is used to calculate N based on assuming a $p=0.5$, as this produces maximum variance for a simple random sample. Using the equation:

$$N = \left(\left(Z \times 100 \times \sqrt{p \times (1-p)}\right) \div P\right)^2$$

estimates of the sample size necessary to meet the precision requirement of ±12% with 90% confidence (USEPA, 2001a; USEPA, 2007a), are made. Fifty samples meet the EMAP precision requirement. Results for different sample numbers and proportions are shown in Table 2-1.

With federal, state, non-profit, and academic partners, AKMAP conducted its first sampling survey of Southcentral Alaska in 2002 as part of the Western States Coastal EMAP initiative under the National Coastal Assessment (NCA) program (Saupe et al., 2005). The Southcentral Alaska province is just one of five biogeographical provinces modified from the four originally proposed by Holland (1990). The Southcentral region includes Cook Inlet, a large, high-latitude macrotidal estuary; Prince William Sound, a large, semi-enclosed basin with restricted exchange of waters with the open ocean; and Central and Northwest Gulf of Alaska coastlines, including the shelf surrounding Kodiak Island. Estuaries are defined for the sampling design as transitional coastal regions of interaction between rivers and near-shore ocean waters, where tidal action and river flow mix fresh and salt water. Such areas include bays, inlets, mouths of rivers, salt marshes, and lagoons. For Southcentral Alaska, 55 sites were surveyed between June 14 and August 02, 2002, as detailed in Table 2-2 and Figure 2-1.

The extent of Alaska's coastline presents challenges to conducting representative environmental assessments of aquatic resources. Two basic options for obtaining this information are a complete census or a probability sampling survey strategy (Paulsen et al., 1998; Olsen et al., 1999; Stevens and Olsen, 1999). Fiscal and logistical constraints rule out taking a census of a state's water resource. Probabilistic sampling surveys of an extensive resource, such as coastal estuaries, allow valid scientific inferences of environmental condition to be extrapolated, based on a limited subset of samples, to the population of interest (Olsen et al. 1999; Stevens and Jensen 2007). Sampling surveys provide answers to environmental management questions, such as "What proportion of the areal extent of the estuaries in Southcentral Alaska exceed the sediment quality guideline for Cr?" Principal sampling survey design components are:

1. Clear statement of objectives.
2. Precise definition of the target population denoting the resource for which information is sought (e.g., all estuaries).
3. Construction of a sample frame, a list or map identifying every unit (e.g. estuaries) within the target population.
4. Selection of sampling survey design to meet objectives.
5. Selection of random sample sites using survey design.
6. Sampling with consistent measurement protocols at all sampled sites.
7. Use of survey analysis matched to survey design and objectives.

The EMAP design views offshore estuarine waters as an areal or a continuous population that does not contain distinct natural units, such as the surface area within Cook Inlet. Sample frame design was done by the US National Wetlands Research Center/Gulf Breeze Project Office in Gulf Breeze, Florida. The Southcentral Alaska coastal survey partitioned the estuarine population domain into polygons that define the individual estuary boundaries based on a geomorphological approach. The Cook Inlet polygons are shown in Figure 2-2. The target population is defined as all of the estuaries in the region, with the U.S. Geological Survey 1:100,000 Digital Line Graph representing the sample frame. Selection of the sampling sites utilized a random sampling program that runs in ARCView™. The program overlays the sampling frame with a hexagon grid, with the objective of randomly selecting hexagons with a single random sampling point placed in the hexagon. Hexagon sizes can vary for estuary polygon classes of differing size. For the Southcentral region, with target population estuary sizes ranging from approximately 1 km^2 to 15,935 km^2, six strata were selected, with a pre-determined number of sites to be randomly selected for each stratum. Stratum-specific hexagon grid sizes were used in the overlay. Table 2-1 shows the strata and hexagon size. The target population members, estuary polygons, have a probability of being included in the sample that is directly proportional to their area. Results of the program run produced 49 base sites, plus additional intensive or oversample sites (backup sampling sites in case a base site could not be sampled). The base sites are sampled in descending order if feasible. If a base site cannot be sampled, the next sequentially numbered oversample site is used (USEPA, 2001a). Due to the potentially large distances involved in Alaska this descending order is not practical, so if a base site cannot be sampled, the nearest oversample site is selected. At each sample station, core sets of ecological condition indicators, such as macroinvertebrates, and stressors, such as sediment trace metals, are sampled.

Historically, most surveys of sediments for trace elements in this region have been related to oil, gas and mining studies, assessment of the Exxon Valdez oil spill, or marine geology studies (Burrell, 1977; Klein, 1983; Naidu and Klein, 1988; ENRI, 1995; Boehm, 2001). The analysis was based on cumulative distribution functions (CDFs) that were used to estimate the areal extent or proportion of the total area falling within a given range of values of an indicator variable. Probabilistic sampling of the target population, with each sampling site having a weight based on proportional area, allows the use of Horvitz-Thompson ratio estimators to calculate estimated CDFs for each indicator variable against spatial area (Stevens and Olsen, 1999). Confidence bounds are calculated for the CDF using a Normal Distribution multiplier. The estimated CDF is also used to calculate specified percentiles for the indicator variables with confidence intervals for each percentile estimate. The mean, variance, and standard deviation are estimated for the population. The R statistical programming language with the USEPA "spsurvey" package is used to calculate the estimated population CDFs, mean, variance, standard deviation and percentile data for each indicator variable (e.g., trace metal) (Diaz-Ramos et al., 1996; USEPA, 2007b). Further information on EMAP sampling and methodology can be found at the USEPA Aquatic Resource Monitoring website (USEPA, 2007a).

The Southcentral Coastal AKMAP followed the National Coastal Assessment Quality Assurance Plan 2001–2004 (USEPA, 2001a). Depending upon the vessel platform used, sediment samples were collected with either a stainless steel single or double 0.1 m^2 Van Veen sampler. The Van Veen sampler, collection instruments and mixing bowl were thoroughly washed with LiquiNox™ detergent and rinsed with ambient seawater prior to use, though it was not washed between grab samples at the same location. Upon return to the surface, the sample was evaluated to determine if the sampling was successful (e.g., if sediment sample surface was level). If the grab sample passed the initial evaluation, any water overlying the sediment was carefully siphoned off with clean Teflon™ tubing. A complete 0.1 m^2 grab was collected first for the macroinvertebrate sample, with subsequent grabs composited for analyses of sediment organic chemicals, such as hydrocarbons and chlorinated pesticides and trace metals, total organic carbon, sediment toxicity, and sediment grain size. A pre-cleaned stainless steel spoon was used to collect the top 2-3 cm of the sediment and deposit it into a clean stainless steel bowl that was covered by clean (unused from the box) aluminum foil between samples. The composite sediments were well mixed. For trace metals approximately 200 ml of sediment was placed in a prelabeled, wide-mouth I-Chem glass jar certified to meet EPA performance specifications for metals, which were filled to no more than 75% capacity. Samples were sealed with electrical tape and immediately frozen at –20°C.

Sediment trace metal sample preparation and analysis varied depending upon the trace metal. All sediment trace metal analyses were run by the Washington Department of Ecology's Manchester Laboratory. Table 2-3 provides a list of the metals analyzed and their laboratory-reported Method Detection Limits (MDLs). The MDLs are defined to "represent the minimum occurrence of a concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte" (USEPA, 2001a).

Samples for total mercury were digested and analyzed following USEPA Method 245.5 Cold Vapor Atomic Absorption Spectrophotometry. For analysis of the rest of the trace metals except tin, the sediments were digested in a microwave oven, following USEPA Method SW-846-3052. Low-level Sn contamination problems, which were believed to be related to the digestion vessel used in USEPA Method 3052, occurred in the Sn blank. The problem with contamination of the Sn blank was solved by change of digestion vessel, following USEPA Method SW-846-3050. Analytical methods for Al and Fe followed USEPA Method SW-846-6010, using Inductively Coupled Plasma (ICP) – Atomic Emission Spectrometry, and for trace metals USEPA Method SW-846-6020, ICP – Mass Spectrometry was followed.

All analyses were performed within established USEPA holding times and met the QC performance requirements established in the Measurement Quality Objectives (MQO) for the West Coast USEPA Environmental Monitoring and Assessment Program (USEPA, 2001a). PriorityPollutnT^{TM} /CLP inorganic soils #247 from Environmental Resource Associates were used as the standard reference material (SRM) for determination of analytical accuracy of all the trace metals, except for Hg, where NIST SRM 2709 was used. The sediments' trace metal matrix spikes were within the MQO-required 50% to 120% recovery range, relative percent difference and coefficient of variation of the matrix spikes and reference materials met the MQO average of less than 30%, and 70% of the individual reference material trace metal values were within ±35% of the true value.

As the sediment samples represent the upper 2-3 cm it is important to understand the varying sediment mass accumulation rates within the region in regard to potential anthropogenic inputs. With strong tidal currents, Cook Inlet generally has low sediment mass accumulation rates, with a mean value estimate of 0.20 ± 0.09 g cm^{-2} yr^{-1} for five core samples collected from Outer Cook Inlet and Northern Shelikof Strait (Rember and Trefry, 2005). These authors also reported a sediment mass accumulation rate of 0.44±0.11 g cm^{2} yr^{-1}, more than double that of Outer Cook Inlet and Northern Shelikof Strait in lower Shelikof Strait area. Sediment mass accumulation rate for central Prince William Sound is estimated at 0.59 g cm^{2} yr^{-1} based on a rate of 0.37 cm yr^{-1} (Klein, 1983) and a sediment density of 1.6 g cm^{3}. The spatial scale of the current assessment is focused on the estuary area covering all of Southcentral Alaska, thus providing a range in sediment trace metal values for the full region. While a majority of the resulting values may remain within Southcentral regional CDF range, surveys of marine sediments at different regional scales will be influenced by focusing of fine grain sediments. Many anthropogenic contaminants are particle-reactive readily attaching to suspended sediments to ultimately be deposited in areas of high mass accumulation, such as Shelikof Strait. Prince William Sound and Shelikof Strait, both areas of high sediment mass accumulation, provide researchers with the opportunity to assess trace metal accumulation and concentration over time.

Cumulative distribution functions for the proportion of the area (expressed as a percentage)—in this case estuary area— is used to characterize the probability distribution of sediment trace metal concentration, along with 95% confidence bounds. In Figure 2-3 through 2-11, the probability distribution is presented for each sediment trace metal concentration on the (x-axis) versus the estuary cumulative area (y-axis). Estimated population mean, standard deviation, and median are shown in Table 2-4 with their 95% confidence bounds.

A basic use of the CDF results is to make estimates of the cumulative percentage of a resource class, such as estuary area, which is above or below some level of interest—for example, the percentage of estuaries with Cr above a biological effects level. ADEC

Water Quality Guidelines [18AAC70] do not have quantitative sediment quality guidelines for specific toxic inorganic or organic chemicals. Instead, the guidelines apply qualitative criteria stating that *"There may be no concentrations of toxic substances in water or in shoreline or bottom sediments, that, singly or in combination, cause, or reasonably can be expected to cause, adverse effects on aquatic life or produce undesirable or nuisance aquatic life, except as authorized by this chapter (*ADEC, 2007*)."* Sediment trace metal concentrations for the nine priority pollutant metals are evaluated with the U.S. National Oceanic and Atmospheric Administration (NOAA) Effect Range Low (ERL) and Effect Range Median (ERM) sediment quality screening guidelines (USEPA, 2001b; Buchman, 2008). These screening guidelines were derived from an ordered listing of sediment chemical concentrations from the scientific literature where some biological effect was observed, where the ERL and ERM represent the 10th and 50th percentiles of the list (Long et al., 1995). Sediment trace metal screening values are provided on a dry weight basis and are not adjusted for grain size, bioavailable metals, or total organic carbon. The ERL and ERM represent the potential probability of sediment toxicity, but they are, especially if used by themselves, not predictive of actual toxic biological effects in any particular sediment (O'Connor, 2004). NOAA principally used its United States Coastal National Status and Trends data set to develop ERL and ERM, which only contained a limited number of Alaska sites (NOAA, 2009). Relevance of ERL and ERM to site-specific Alaska marine sediment macroinvertebrates is yet to be determined. Southcentral Alaska's environmental conditions, such as cold, seasonal food constraints, high glacial sediment loading and the organism's physiological adaptation to these conditions, such as high-lipid content, slow growth rates, simple food chain webs, and antifreeze mechanisms, suggest possible differing sensitivity to contaminants compared with temperate organisms (King and Riddle, 2001; Chapman and Riddle, 2005a; Chapman and Riddle, 2005b; Olsen et al., 2007; and Konovalov et al., 2010). The current research base on potential differences between arctic, sub-arctic and temperate species response to contaminants remains small, and until further work is done, the magnitude of differences remains unclear. Looking at Fe, Mn, Zn, V, Ni, Cu, Cr, Co, and

Pb, a 1982 study within Prince William Sound found that these metals, except for Pb, were typically tightly bound within sediment clay crystal lattice (Naidu et al., 1983). Such tightly bound trace metals are not generally bioavailable, limiting their toxicity (Newman, 1998). Therefore ERL and ERM are used here as qualitative assessment tools to help focus future assessment research efforts.

The CDFs in Figures 2-3 through 2-11 show the cumulative-percent area versus trace metal concentration, upper and lower 95% confidence bounds, against ERL and ERM reference traces metal concentrations. Total coastal area for the survey-sampled population is 273,291 km^2. Some sample stations with nearby known ore bodies (Weaver, 1983; USGS, 1997) exhibited relatively high concentration values for Cr and Ni, which are also found in the adjacent ore bodies. For visual clarity of the CDFs, these high concentrations are referenced but not shown in Figures 2-4, 2-5, and 2-9.

Table 2-3 summarizes the trace metal ERL and ERM values used in this assessment and provides estimated cumulative-percent area in relation to the guideline values. None of the Southcentral area exceeded ERLs for Pb or Ag, whereas Cd, Hg, and Zn were above the ERL in 0.3%, 1.7%, and 0.4% of the cumulative area, respectively. Concentrations of As, Cr, Cu, and Ni fell between the ERL and ERM values in 58.2%, 23.8%, 43.1%, and 56.4% of the cumulative estuary area, respectively. Only Cr and Ni exceeded the ERMs in 0.2% and 5.9% of the Southcentral estuary area, respectively. A study conducted for the US Department of Interior Mineral Management Service, Sediment Quality in Depositional Areas of Shelikof Strait and Outermost Cook Inlet (Boehm, 2001) concluded that As, Cu, and Ni in regional sediments were generally comparable to local river suspended sediments and local rock values (MMS, 2000). Background levels of As, Cu, and Ni in the region's geological material suggest that concentrations of these trace metals in excess of the ERL are natural. However, the highest Cr and Ni values, which greatly exceed the ERM and occur at Chrome Bay are likely due more too technological enhancement from historic mining activities than natural erosion factors.

The concentrations of Cr and Ni sediment were highest at Chrome Bay (AK02-0005 or site 5 on Table 2-2) on the south end of the Kenai Peninsula. From 1916 to 1918, two thousand tons of chromite ore were mined at Claim Point, adjacent to Chrome Bay, where the ore was loaded on ships for transport to processing plants (Gill, 1922). The Cr sediment level of 1,320 µg/g dry weight (dw) at Chrome Bay was the only sample to exceed the Cr threshold guidelines. While Ni exceeded the ERM guideline of 51.6 µg/g for five sites, it was by no more than a factor of 1.3 at the higher four sites; at Chrome Bay it was higher by a factor of 16 with a value of 756 µg/g dw. The percentage area results apply to the overall study area and do not define the potential range of sediment Cr within Chrome Bay. A smaller targeted or small sample estimation survey is required to assess Cr and Ni sediment levels throughout Chrome Bay.

Acknowledgments

This study was supported by the U.S. Environmental Protection Agency Office of Research and Development through Cooperative Agreement # R-82911501. Walt Nelson, Dixon Landers, Tony Olsen and others with USEPA ORD enthusiastically supported our efforts and understood the importance of this pioneering effort in Alaska. Ms. Sue Saupe, scientific director with Cook Inlet Regional Citizens Advisory Council (CIRCAC), was instrumental in the implementation, field work, and reporting on the Southcentral Coastal survey. Thanks for the constructive comments and suggestions provided by Drs. John Kelley, Franz Mueter, Sathy Naidu, Larry Duffy and Robert Perkins and others of the University of Alaska Fairbanks.

This document has not been subjected to CIRCAC, ADEC or USEPA internal institutional peer review and/or administrative review and does not necessarily reflect these organizations' views, nor does any mention of trade names or commercial products constitute endorsement or recommendation.

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Tables

Table 2-1: Sample Size Estimates to Meet Precision Requirements

Assumed Proportion (percent)	Precision with 90% Confidence for Alternative Sample Sizes				
	25	50	100	400	1000
20%	±13	±9	±7	±3	±2
50%	±17	±12	±8	±4	±3

Table 2-2: Southcentral Alaska Estuary Sampling Design Information

Strata	Description	Hexagon Sizes, km^2
001	15 sites in Southcentral system (one remaining after strata 002-006)	1060.88
002	20 sites in large estuaries in Cook Inlet system[1].	1601.28
003	10 sites in mid-small estuaries of Cook Inlet system.	280.59
004	5 sites in small estuaries of Prince William Sound.	280.59
005	10 sites in mid-estuaries of Prince William Sound.	124.71
006	15 large estuaries of Prince William Sound.	419.16

1– Cook Inlet system includes Cook Inlet proper and Shelikof Strait.

Table 2-3: Sampled Stations Southcentral Alaska Sites

AKMAP Station ID[1]	Depth, Meters	Latitude Degrees[2] North	Latitude Minutes North	Longitude Degrees[2] West	Longitude Minutes West	Visual Descriptive Composition
AK02-0002	4.3	60	12.580	152.00	44.305	Silt/Clay
AK02-0003	3.9	59	49.752	153.00	7.701	Silt/Clay
AK02-0004	65.0	59	37.232	151.00	14.851	Silt/Clay
AK02-0005	4.5	59	12.579	151.00	49.343	Gravel
AK02-0007	72.0	58	23.301	152.00	58.886	Fine Sand
AK02-0008	24.0	57	58.581	154.00	57.378	Mixed
AK02-0009	102.0	57	58.851	153.00	4.258	Sand
AK02-0010	24.0	57	42.525	155.00	34.034	Silt/Clay
AK02-0011	9.2	61	1.954	151.00	14.259	Sand
AK02-0012	4.0	60	42.169	151.00	51.588	Sand
AK02-0015	5.2	60	29.976	151.00	57.831	Fine Sand with Silt
AK02-0016	12.0	60	14.971	151.00	31.653	Mixed
AK02-0017	39.0	60	2.504	152.00	24.008	Mixed
AK02-0019	87.0	59	17.379	152.00	50.526	Fine Sand
AK02-0020	30.0	59	6.482	153.00	33.131	Silt/Clay
AK02-0021	116.0	59	8.723	152.00	19.847	Coarse Sand
AK02-0022	8.0	59	6.251	154.00	9.753	Silt/Clay
AK02-0023	130.0	59	5.294	153.00	5.281	Silt/Clay
AK02-0024	168.0	58	47.094	152.00	49.042	Silt/Clay
AK02-0026	155.0	58	30.316	152.00	49.976	Silt/Clay
AK02-0027	182.0	58	5.412	153.00	30.145	Silt/Clay
AK02-0028	215.0	57	55.568	154.00	17.451	Silt/Clay
AK02-0029	232.0	57	51.151	154.00	33.132	Silt/Clay
AK02-0030	274.0	57	37.170	155.00	11.169	Silt/Clay
AK02-0032	25.9	60	54.930	147.00	48.460	Silt
AK02-0034	125.0	60	43.650	148.00	38.362	Silt/Clay
AK02-0035	148.0	60	14.696	148.00	17.708	Silt/Clay
AK02-0036	206.0	61	8.366	147.00	52.837	Mixed
AK02-0038	5.4	60	48.686	148.00	1.881	Mud
AK02-0040	19.0	60	42.699	146.00	21.684	Mixed
AK02-0041	232.0	60	44.467	148.00	1.510	Silt/Clay

Table 2-3: Sampled Stations Southcentral Alaska (Continued)

AKMAP Station ID[1]	Depth, Meters	Latitude Degrees[2] North	Latitude Minutes North	Longitude Degrees[2] West	Longitude Minutes West	Visual Descriptive Composition
AK02-0045	325.0	60	10.081	147.00	52.689	Silt/Clay
AK02-0046	23.9	60	55.491	147.00	19.252	Mixed
AK02-0050	282.0	60	39.511	146.00	46.194	Silt/Clay
AK02-0051	122.0	60	35.413	146.00	18.771	Silt/Clay
AK02-0053	219.0	60	30.647	147.00	7.220	Silt/Clay
AK02-0054	120.0	60	35.320	146.00	39.319	Silt/Clay
AK02-0055	158.0	60	29.552	147.00	27.052	Silt/Clay
AK02-0056	352.0	60	32.351	146.00	58.763	Silt/Clay
AK02-0058	138.0	60	18.383	147.00	39.258	Mixed
AK02-0059	181.0	60	2.454	147.00	42.030	Mixed
AK02-0060	72.0	59	54.667	148.00	19.902	Mixed
AK02-0061	30.0	60	14.614	145.00	34.028	Silt/Clay
AK02-0062	56.0	60	15.446	145.00	44.824	Silt
AK02-0063	117.0	59	48.546	149.00	32.924	Silt/Clay
AK02-0064	210.0	59	23.507	150.00	30.267	Silt
AK02-0065	129.0	58	27.442	152.00	21.762	Silt/Clay
AK02-0067	12.5	57	11.780	153.00	12.510	Mixed
AK02-0068	94.0	57	3.751	153.00	34.540	Silt/Clay
AK02-0070	132.0	56	25.245	158.00	13.515	Silt/Clay
AK02-0071	128.0	55	59.506	158.00	35.517	Silt/Clay
AK02-0072	32.0	55	32.259	161.00	34.324	Mud
AK02-0073	26.0	55	22.358	160.00	37.363	Fine Sand with Mud
AK02-0074	17.0	55	4.521	163.00	8.539	Sand
AK02-0075	62.0	55	9.064	160.00	25.995	Sand

[1] The AKMAP Station ID integers are the site locations numbers referred to in Figure 2–2.

[2] Latitude and Longitude are referenced to North American Datum 27.

Table 2-4: Washington Department of Ecology Method Detection Limits (MDL)

Trace Metal	MDL (μg/g dw)
Arsenic	0.032
Cadmium	0.016
Chromium	0.18
Copper	0.71
Lead	0.065
Mercury	0.001
Nickel	0.43
Silver	0.02
Zinc	1.3

Table 2-5: Southcentral Alaska Estuary Sediment Trace Metal Estimated Population Descriptive Statistics[1]

Trace Metal (µg/g dw)	N	Mean	LCB 95%	UBC 95%	Std. Dev.	LCB 95%	UCB 95%	Median	LCB 95%	UCB 95%
As	55	8.83	8.11	9.55	2.85	2.54	3.16	9.00	7.86	9.87
Cd	52	0.07	0.05	0.09	0.07	0.05	0.09	0.16	0.15	0.17
Cr	55	61.39	56.87	65.91	20.68	18.48	22.87	60.28	43.92	71.40
Cu	55	30.27	28.17	32.37	10.65	9.46	11.85	29.39	23.82	34.38
Pb	55	12.18	11.68	12.67	2.44	2.07	2.81	12.25	11.43	12.55
Hg	53	0.06	0.05	0.07	0.03	0.02	0.04	0.05	0.04	0.06
Ni	55	29.55	25.35	33.75	14.77	8.76	20.78	25.96	21.41	32.13
Ag	53	0.18	0.17	0.20	0.05	0.04	0.07	0.17	0.16	0.17
Zn	55	82.31	77.66	89.96	22.24	19.08	25.04	78.38	68.67	86.09

1–Number (N) is less than 55 when some samples were below minimum detection level. Lower confidence bounds (LCB). Upper confidence bounds (UBC). Dry weight (dw)

Table 2-6: Effects Range Low (ERL) and Effects Range Median (ERM) Sediment Quality Screening Guidelines versus Percentage of Southcentral Estuary Area within Specified Ranges

Trace Metal	ERL (µg/g dw)	ERM (µg/g dw)	% Area <ERL	% Area >ERL & <ERM	% Area >ERM
As	8.20	70.00	41.8%	58.2%	
Cd	1.20	9.60	99.7%	0.3%	
Cr	81.00	370.00	75.6%	23.8%	0.6%
Cu	34.00	270.00	56.9%	43.1%	
Pb	46.70	218.00	100%		
Hg	0.15	0.71	98.3%	1.7%	
Ni	20.90	51.60	37.7%	56.4%	5.9%
Ag	1.00	3.70	100%		
Zn	150.00	410.00	99.6%	0.4%	

Figures

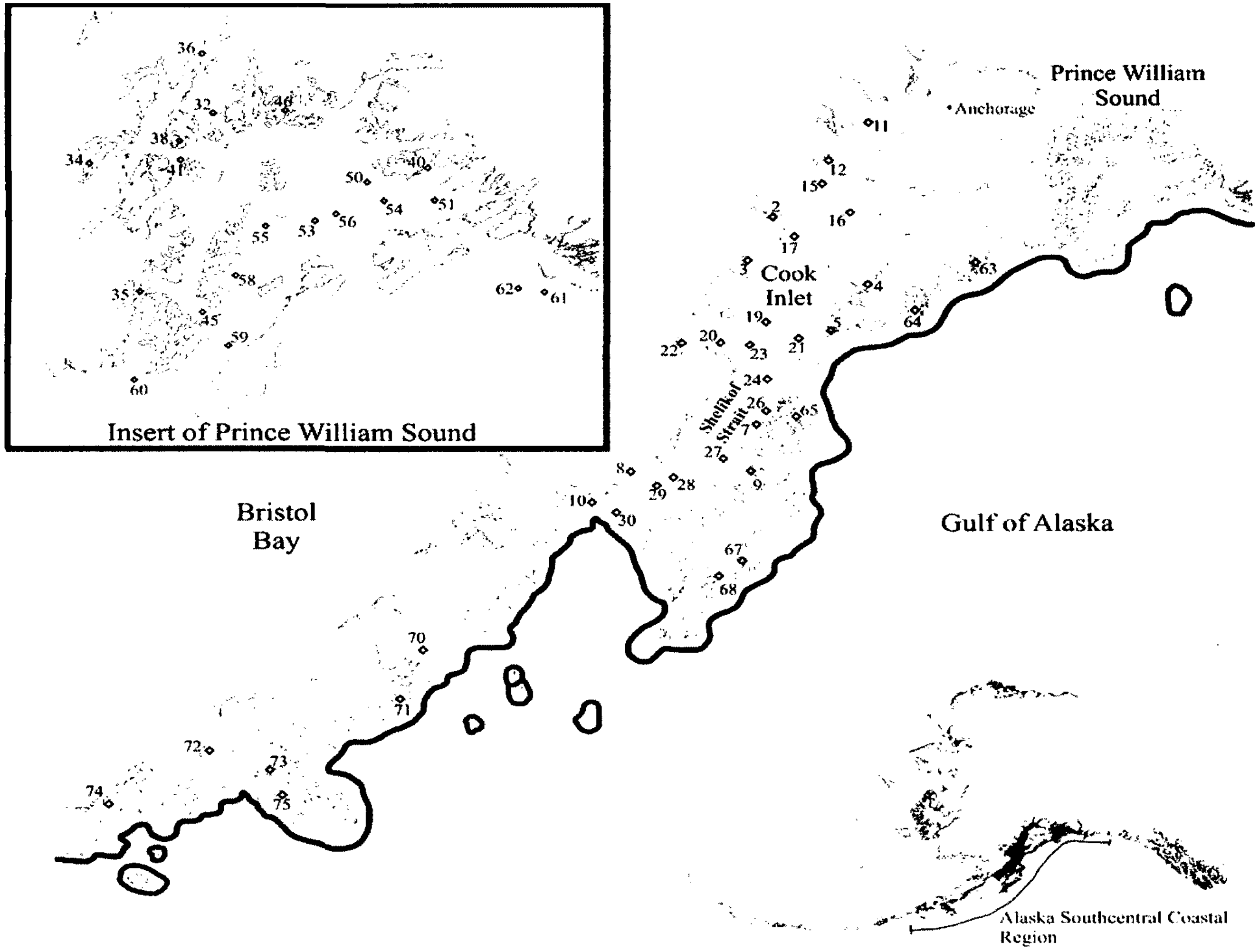


Figure 2-1: Alaska Monitoring and Assessment Program Southcentral Sampled Sites and Sample Frame

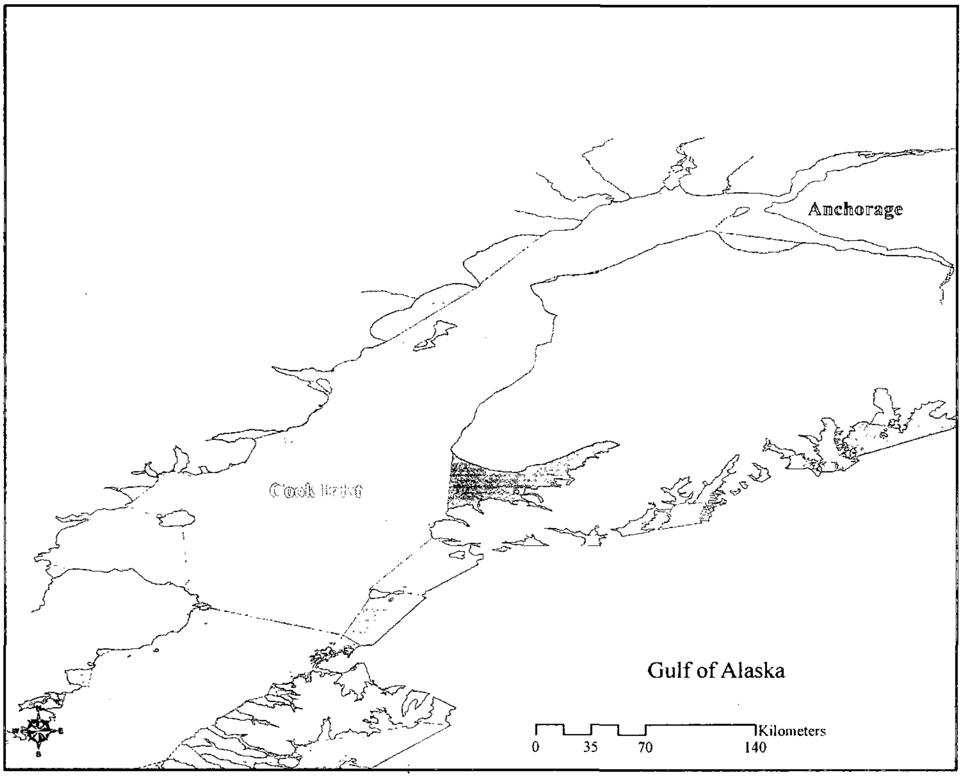


Figure 2-2: Section of Southcentral Alaska Sample Frame with Estuary Polygons in Gray

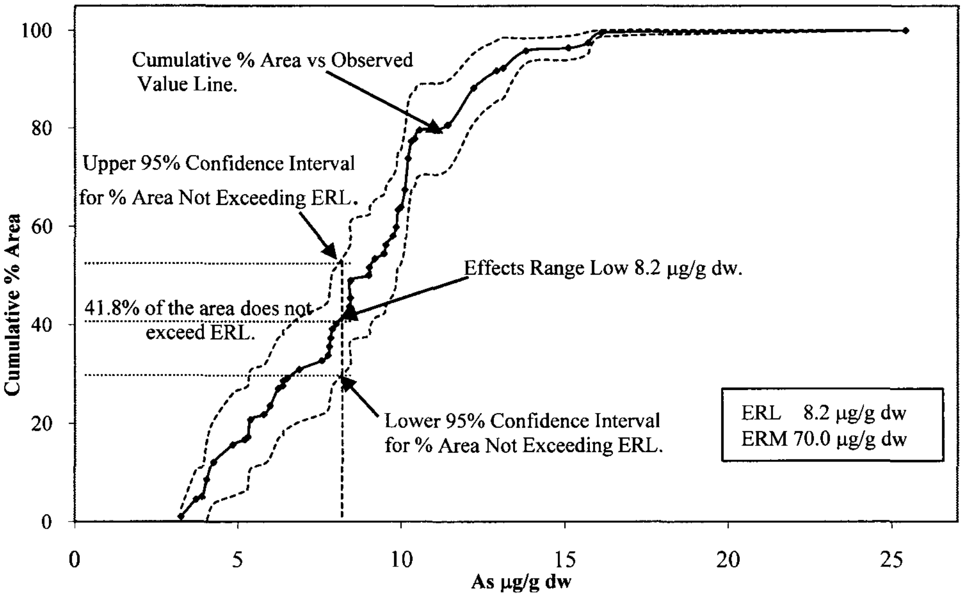
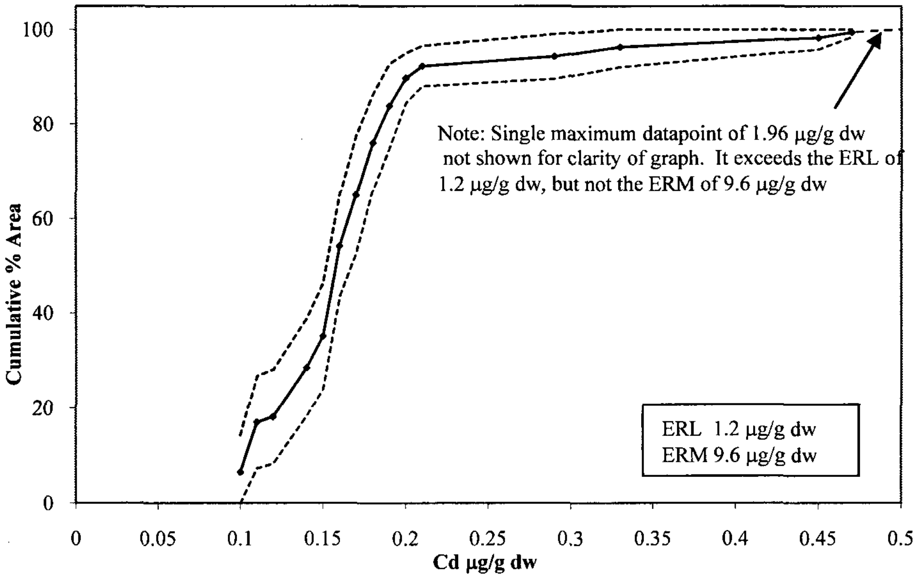
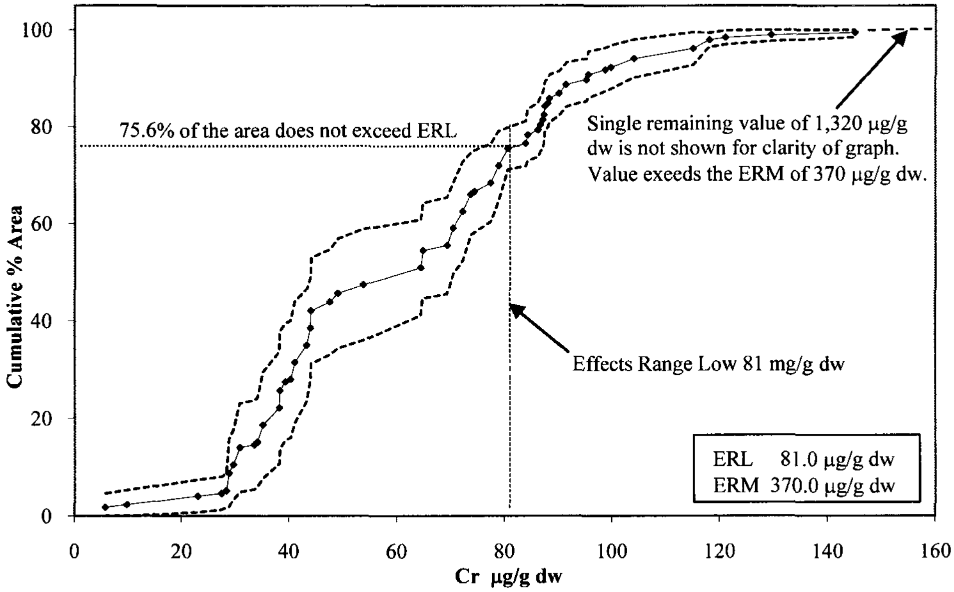


Figure 2-3: Arsenic Cumulative Distribution Function with 95% confidence interval. Effect Range Low (ERL) and Effect Range Median (ERM) are indicated. (Explanation applies to remaining figures.)



Note: Single maximum datapoint of 1.96 µg/g dw not shown for clarity of graph. It exceeds the ERL of 1.2 µg/g dw, but not the ERM of 9.6 µg/g dw

Figure 2-4: Cadmium CDF (For explanation see Fig. 3.)



75.6% of the area does not exceed ERL

Single remaining value of 1,320 µg/g dw is not shown for clarity of graph. Value exeeds the ERM of 370 µg/g dw.

Effects Range Low 81 mg/g dw

Figure 2-5: Chromium CDF

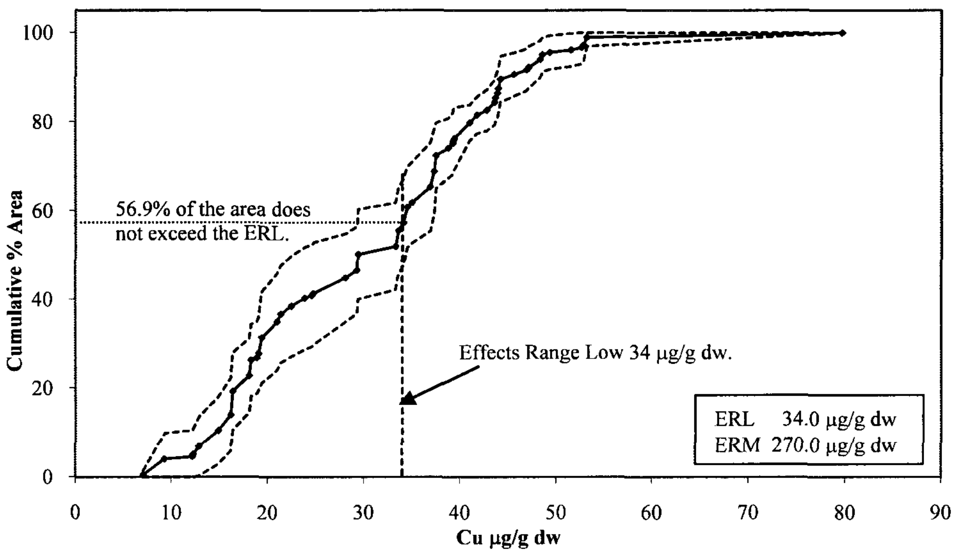


Figure 2-6: Copper CDF

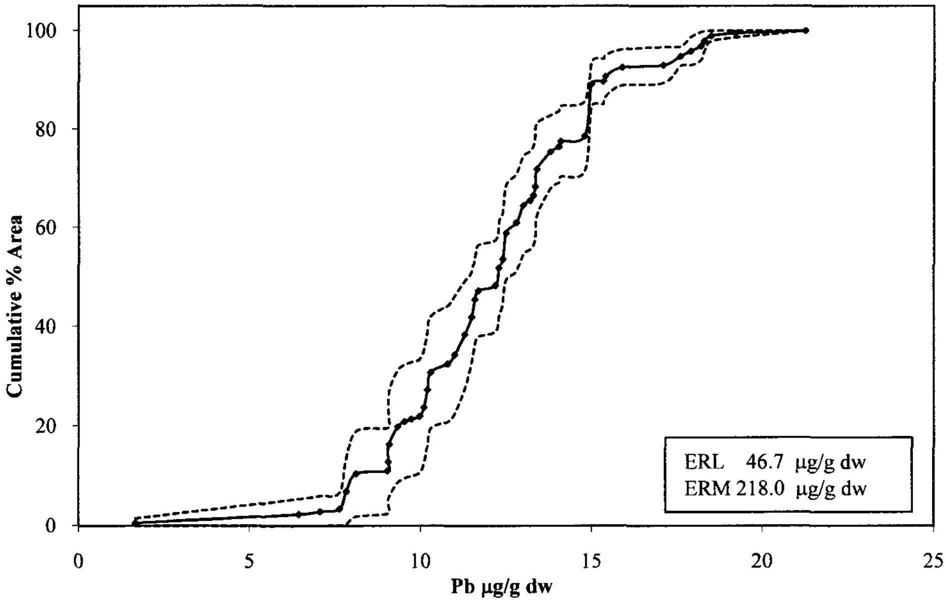


Figure 2-7: Lead CDF

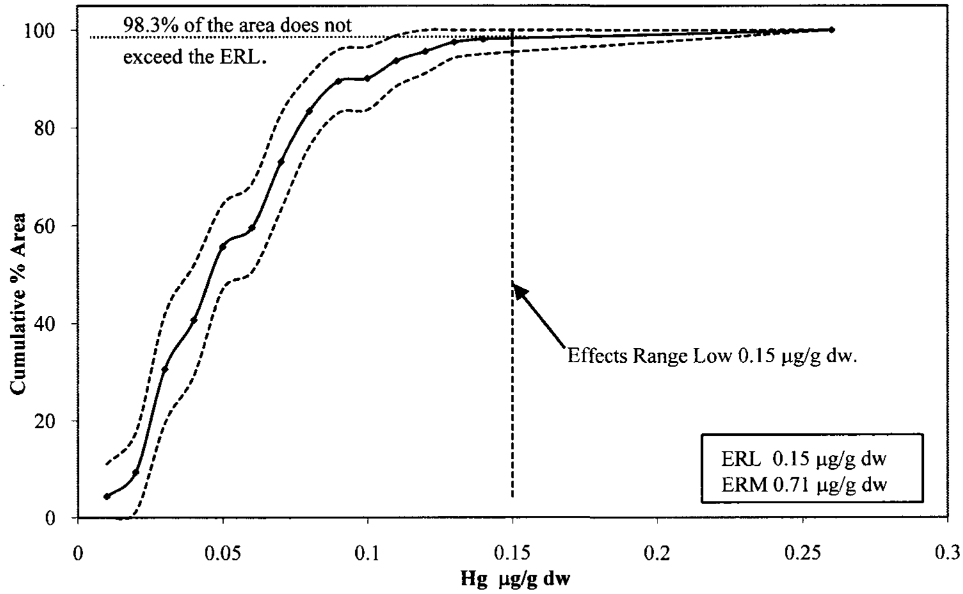


Figure 2-8: Mercury CDF

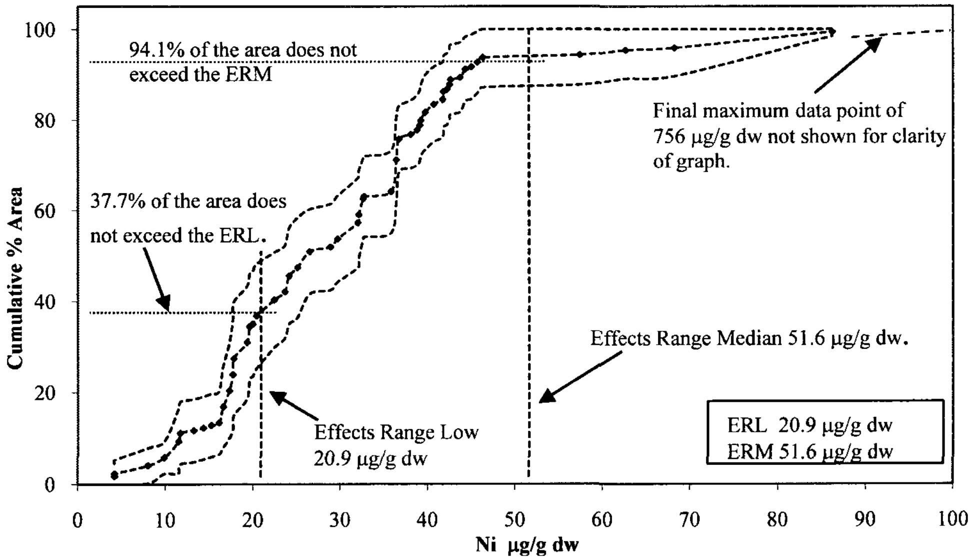


Figure 2-9: Nickel CDF

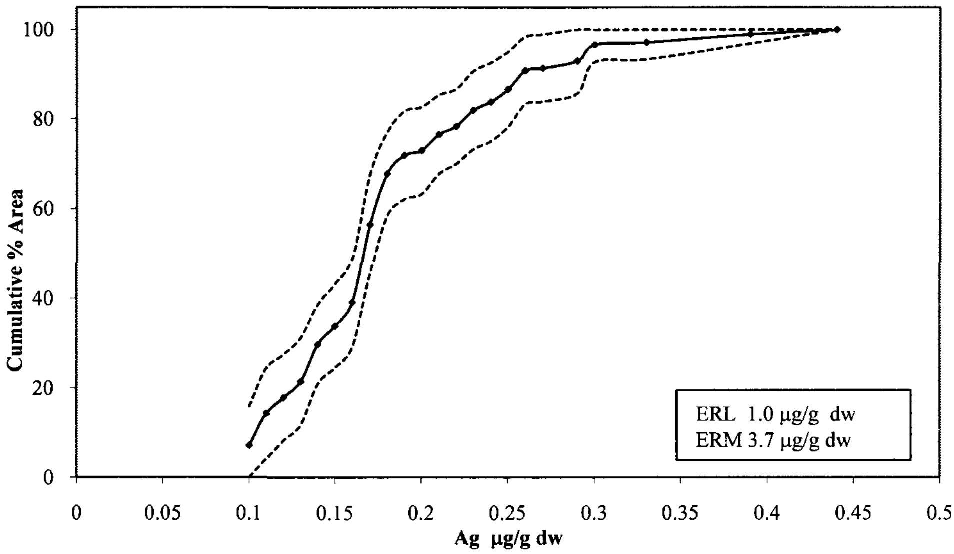


Figure 2-10: Silver CDF

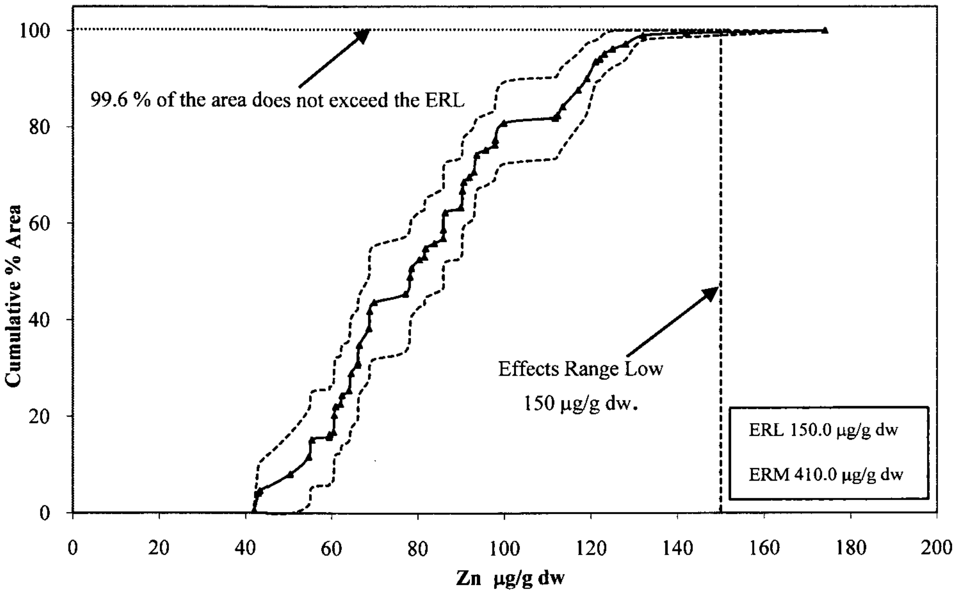


Figure 2-11: Zinc CDF

Chapter 3: Regional Natural Conditions for Select Priority Pollutant Trace Metals in Stream Sediments in the Cook Inlet and Copper River, Alaska, Watersheds[2]

Abstract

Natural conditions provide a needed reference for agencies and organizations responsible for making environmental policy and management decisions. This information helps place the ecosystem stresses resulting from increasing human population, resource extraction activities, and climate change in the context of the variability of natural conditions. Development of marine sediment natural conditions benefits from an understanding of fluvial trace metal input from major drainages in the coastal provinces of interest. This paper focuses on the Southcentral Alaska coastal region that contains two large watersheds, Cook Inlet and Copper River. A large stream sediment trace metal data set for Alaska from the mid-1970 United States Atomic Energy Commission (AEC) National Uranium Resource Evaluation Program (NURE) surveys is used to examine stream sediment trace metal concentrations in the Cook Inlet and Copper River watersheds. The U.S. Geological Survey (USGS) National Geochemical Survey (NGS) re-sampled many of the archived NURE stream sediments, thus providing a high quality data set from which to infer regional natural conditions for Cook Inlet and Copper River watersheds. Using two exploratory data analysis techniques, the Tukey Box plot and Median ± 2 Median Absolute Deviations, combined with geochemical mapping, a range for natural conditions of trace metals in stream sediments for these two watersheds is developed.

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[2] Dasher, D.H. Regional Natural Conditions for Select Priority Pollutant Trace Metals in Stream Sediments in the Cook Inlet and Copper River, Alaska, Watersheds. Prepared for submission in Environmental Earth Sciences, International Journal of Geosciences, Springer.

Introduction

Alaska's coastal marine ecosystems, while considered pristine relative to developed regions, are seeing increased resource development pressure (e.g., oil and gas exploration and extraction) (AMAP 1998). Trans-boundary transport of mercury and other pollutants to Alaska's remote coastal regions is occurring and is typically coupled to atmospheric and oceanic currents (Sunderland et al. 2009; Landers et al. 2010). Development of appropriate environmental policy and management actions to address the impacts of these stresses requires knowledge of existing baseline or "natural conditions" (Parr et al. 2003; Durell et al. 2005). The Alaska Department of Environmental Conservation (ADEC) Water Quality Standards Criteria (18 AAC 70.9904(41)) define natural conditions as "any physical, chemical, biological, or radiological condition existing in a water body before any human-caused [anthropogenic] or influence on, discharge to, or addition of material to, the water body" (ADEC 2006). Biogeochemical processes control in part these natural conditions, which are characterized by variability over spatial and temporal frames and are represented by mixed populations on the larger regional, statewide and continental scale (Matschullat et al. 2000).

Alaska has five general biogeographical coastal regions that were established in early 2000 as part of the planning for the US Environmental Protection Agency (USEPA) Environmental Monitoring and Assessment program's West Coast pilot project (Holland 1990; Saupe et al. 2005). The ADEC Alaska Monitoring and Assessment Program (AKMAP) has undertaken a long-term effort to conduct initial natural condition surveys of Alaska's coastal regions with one objective being the development of regional natural conditions for marine sediment trace metals. The focus of this paper is to estimate the regional natural conditions for trace metals in stream sediments in two principal watersheds, Cook Inlet and Copper River, which provide sediments to the Southcentral Province (Figure 3–1). Assessment of the spatial variability of trace metals in stream sediments helps place contaminant data in a context that is helpful to those making management decisions necessary to protect or remediate the environment (Birch et al.

2001). This assessment also provides a range for estimates of trace metal input into the marine environment from coastal watersheds.

Development of marine sediment trace metal natural conditions requires an understanding of the influence of fluvial sediment trace metal input from major drainages in the coastal province of interest (Ridgway et al. 2003; Perry and Taylor 2007). Weathering and erosion of crustal rock and volcanic activity account for about 80% of natural trace metal emissions to the environment, with forest fires and biogenic sources accounting for the other 20% (Nriagu 1990; Callender 2005). Geochemical assessments of coastal watershed streams and adjacent marine sediments found similar compositions of metals, though the physical and chemical factors controlling deposition may result in disconnected spatial distributions (Ohta et al. 2007).

Human activities, such as mining, oil and gas development, domestic sewage discharge, and nonpoint source pollution contribute an anthropogenic signature on top of the naturally occurring trace metals. Separating natural condition from anthropogenic metal concentrations in sediments is often accomplished by "normalizing" the data against a conservative element or other values, such as grain size, that is insensitive to anthropogenic input, co-varies with the other natural metals, and remain stable under different physical and chemical conditions (Loring 1991). Granulometric normalization reduces the effects of "dilution" from the coarser grain fraction and is an option for normalizing regional stream sediment data sets (Rice 1999; Szava-Kovats 2008). The most widely analyzed sediment fraction for normalization is <63 μm, but other fractions, such as sand (63–2000 μm), silt (2–63 μm), and clay (<2 μm) have been used (Sutherland 2000). Trace metal analysis of the NURE stream sediments occurred on the <100 mesh (<149 μm) fraction (Sharp and Aamodt 1978) and provided a normalized data set.

Combined, Cook Inlet and Copper River watersheds annually contribute more than $115\text{x}10^6$metric tones (t) of sediments to the Gulf of Alaska (Milliman and Meade 1983; Brabets 1997; Brabets et al. 1999). Marine sediment trace metals of interest that were sampled during the AKMAP Southcentral Coastal Province survey in 2002 are As, Cd, Cr, Cu, Ni, Pb, Sb, Se, Sn, and Zn. These trace metals are part of the listed USEPA priority pollutants (USEPA 1994).

Streambed sediments provide an integrated composition of the soils and underlying bedrock above the sampling site, natural or anthropogenic point sources, and non-point source anthropogenic input (Klein et al. 2000). This study uses Alaska data sets from the U.S. Geological Survey (USGS) National Geochemical Survey (NGS) recent re-sampling of archived stream sediments collected in mid-1970 under the United States Atomic Energy Commission (AEC) National Uranium Resource Evaluation Program (NURE) (Smith 2006). The NURE Hydrogeochemical and Stream Sediment Reconnaissance Program (HURE) collected stream, pond, and spring sediments in Alaska.

The NURE program sampling density was approximately one sample per 10 km^2 for Cook Inlet and one sample per 23 km^2 for Copper River watersheds. No sampling was conducted in the Prince William Sound watersheds. The 1970 NURE focus was on uranium where analytical method detection levels were not adequate to assess natural background levels of trace metal concentrations (Xuejing and Hangxin 2001).

In 2000, the USGS National Geochemical Survey analyzed a random selection of archived NURE stream and pond sediment samples, including those from Alaska (USGS, 2009a). The NURE 2000 Alaska Cook Inlet and Copper River watersheds streambed trace metal concentrations for Cd and Sn were all below detection level, Se had >30% non-detects, and Sb was not analyzed. Using data sets containing non-detect values in excess of 20–25% is not recommended, even with the newer statistical tests (ADEC 2006; Singh et al. 2007). Application of these guidelines limits the trace metal assessments in this paper to As, Cr, Cu, Hg, Ni, Pb, and Zn.

Environmental Setting

Cook Inlet and Copper River, two principal watersheds contributing significant sediments to the Southcentral Alaska Province, are within the Pacific Rim "belt" ring of fire. These watersheds consist of various geological terranes, transported here from regions farther south by tectonic plate movement (Brabets 1997; Brabets et al. 1999; Richter et al. 2006). Periods of glaciations have occurred, along with current and historic volcanic activity. Bedrock mountain outcrops and those underlying the basins are of sedimentary, intrusive igneous, and volcanic origins. Unconsolidated deposits present in much of the lowland area consist primarily of alluvium and glacial deposits, with some aeolian and beach deposits. The Copper River has the greatest discharge and the largest watershed of any single river draining into the Gulf of Alaska (Sharma 1979; Brabets 1997). The Susitna River, within Cook Inlet Watershed, is the second largest river draining into the Gulf of Alaska, with the second largest discharge. The NURE stream sediment sample sites within the two watersheds are shown in Figure 3–2. Estimates of the percentage cover of major rock types, including coverage of these types by stream sample site (Table 3-1) are derived from overlaying the sampling sites with a USGS digital (USGS 1997a) Beikman 1980 Geological Alaska Map. Major rock types and coverage from the Beikman digital version are shown for Cook Inlet (Figure 3-3) and Copper River (Figure 3-4) watersheds. This map is useful for providing a conceptual overview but does suffer from serious attribution and accuracy problems (AGDC 2009).

Cook Inlet

Four principal geological terranes consisting of consolidated rock and unconsolidated deposits make up the Cook Inlet watershed. These terranes are the Chugach, Peninsular, Kahiltna and Wrangellia (Brabets et al. 1999). The Alaska-Aleutian Range felsic plutonic batholiths occupy a large portion of the west side of Cook Inlet and some of the upper reaches of the Matanuska Valley (Weaver 1983).

This watershed basin covers approximately 101,851 km^2 and has an average annual surface water discharge to Cook Inlet of approximately 3,248 m^3 s^{-1} with 47% of the annual discharge coming from the Susitna River basin (Brabets et al. 1999). The Anchorage/Matanuska, Kenai Peninsula, and Western Cook inlet drainages contribute 14, 16, and 22 % of the discharge, respectively. The flows are controlled by climatic conditions, with the largest inflow occurring during the summer period (May through

September) and lowest flow in late winter around March. In the lower part of the inlet, the Kenai and Drift Rivers are the major freshwater contributors (Sharma 1979). Estimated annual suspended sediment loads into Cook Inlet from the major watersheds are:

Susitna River Basin ~ 29,668,770 t - annually.
Anchorage/Matanuska ~ 6,705,954 t - annually.
Kenai Peninsula ~ 7,620,402 t - annually.
Western Cook Inlet ~ 1,023,166 t - annually.

This annual estimated discharge of more the 45,018,290 t of suspended sediments, principally the result of glacial erosion, occurs during peak flow periods of May through September, with dramatic reductions in flow and suspended sediments in the other months (Brabets et al. 1999).

Copper River

Seven principal geologic terranes of consolidated rock and unconsolidated deposits make up the Copper River watershed (Winkler 2000). The Copper River watershed covers approximately 62,160 km^2 and drains large, glaciated watersheds contributing approximately $77.2x10^6$ t to $117.9x10^6$ t $year^{-1}$of fine-grained sediments and silts to the Gulf of Alaska (Feely et al. 1981; Milliman and Meade 1983).

Methods

Original 1970 NURE Sample Collection

NURE field teams collected composite samples of fine-grained, organic-rich sediments of sufficient volume after processing to fill a pre-cleaned 25 ml vial (Sharp and Aamodt 1978). A polyethylene scoop was used to collect stream sediments. Samples of equal volume were composited from three locations within 30 meters of the designated sample site. Collected water was drained from the scoop by tilting it with coarse gravel removed by hand before the sample was transferred to a polyethylene bag. Back in the laboratory, the samples were dried at 100°C or less and dry-sieved through 100 mesh (149 µm) stainless steel sieves. If more material than necessary to fill the 25 ml vial was present, it was split and quartered. One quartered section was placed into the vial. This method was repeated until the vial was full. USGS retains the NURE sediments in an archive.

Spatial Sampling Design – National-Scale Geochemistry

The USGS NGS relies in part on NURE samples collected throughout the United States. The USGS, with consistent analytical methods and good quality control and assurance, periodically reanalyzes subsets from the NURE sediment archive (USGS 2009a). In 2000, the USGS reanalyzed a randomly selected subset of NURE samples, including those from Alaska. For the western United States, the samples were stored in boxes corresponding to USGS 1:250,000 scale quadrangles. The quadrangles were divided into approximately 17 km x 17 km (289 km^2) grids, with samples selected at random from each cell. The Alaska NURE 2000 data set includes stream, spring, and pond sediments. Only stream sediment data are used in this study, as differing physical and chemical processes occurring in ponds and springs may alter the distribution of trace metals in comparison to stream sediments (Davenport 1990).

This coverage does not diminish the robustness of the assessment for natural conditions on a large regional scale for stream sediments in the majority of the Cook Inlet basin, nor for comparison of coastal marine sediments and stream sediments. The NURE stream sediments integrate the geologic composition of the respective surrounding watershed area (Klein et al. 2000). Of the four major drainage areas in Cook Inlet, the Susitna Basin and the Anchorage/Matanuska area provide 89% of the suspended sediment load to Cook Inlet (Brabets et al. 1999). The NURE stream sediment sample site breakdown has 43% or 52 sites within the Susitna Basin and 26% or 32 sites in the Anchorage/Matanuska basin. Though sampling density is low, each point must be viewed as representing its upstream watershed area, and represents geological processes occurring on the larger regional scale. A recent assessment of low density geochemical mapping found low density surveys to be quite robust at delineating geochemical patterns (Smith and Reimann 2008). The lack of spatial distribution of the NURE sample locations within the Kenai Peninsula and Western Cook Inlet basins does limit the application in these regions' lower basins.

NGS NURE 2000 Analytical Technique

Stream sediment samples were used "as is" from a selected group from the original 25 ml vials. For the trace metals of interest in this paper, ICP Acid Dissolution results were used for Cr, Cu, Ni, Pb, and Zn. A sample aliquot size of 200 mg was digested at low temperatures in a mix of hydrochloric, nitric, perchloric, and hydrofluoric acids to achieve complete dissolution. The resulting digestate was then aspirated into the Inductively Coupled Plasma-Atomic Emission Spectrometery (ICP-AES) instrument. Arsenic was analyzed by Hydride-Generation Atomic Absorption spectrometry. Mercury (Hg) sample aliquots of 100 mg were digested with a mixture of sulfuric acid, 5% potassium permanganate, and 5% potassium peroxydisulfate in a one-hour water bath for Hg analysis. Cold Vapor Atomic Absorption Spectrometry was used for this analysis. Additional details on laboratory methods and QA/QC are found at Briggs (2001) and USGS (2009a). A breakdown on methods used and detection limits for the elements of interest are shown in Table 3-2.

NURE-archived samples were not originally collected with appropriate Hg protocols or stored under proper storage conditions for Hg. Some NURE samples are believed to have been contaminated with Hg during original handling, though that has not been documented for Alaska samples (USGS 2009b). Drying the samples at 100°C may also result in the loss of some of the Hg, especially any organic Hg present. The Alaska NURE Hg values were compared to other Alaska studies (Frenzel 2000; Frenzel 2002) with no observable indications of gross contamination or unusually low levels noted.

Mapping for Adjacent Ore Deposits

Stream sediment sites are mapped against a digital data set that contains significant Alaskan metalliferous mines, prospects, deposits, or occurrences based on size and geological importance (ADNR 2009a). As metal anomalies representing sites highly enriched in metals rarely have dispersion trains detectable more than 10–20 km downstream (Helgen and Moore 1996), a 20 km search radius search was established around each metalliferous load site of documented significance. Using ArcGIS™ Near Analysis, any NURE stream sample sites within this 20 km radius were identified.

Data Analysis

In the assessment of natural conditions, the objective is to use statistics coupled with expert judgment to establish the central tendency of the dominant, in this case regional, background population (Singh et al. 2007). This assessment consists of a careful review of spatial geological information, summary statistics, exploratory data analysis, and statistical methods to estimate natural condition limits.

Geochemical data, especially on the regional or larger scale covering multiple watersheds and lithologies, have characteristics that limit or require carefully considered applications of classical statistical techniques. The data sets reflect individual site environmental processes (climate, local geology, organic material, anthropogenic influences), usually are spatially dependent, represent multiple populations, and have uncertainties associated with sampling, handling, and analysis. It is rare, at least on a regional or larger scale, that geochemical data follow a normal distribution even if transformed (Lepeltier 1969; Reimann and Filzmoser 1999; Stanley 2006; Szava-Kovats 2006). Geochemical data, such as trace element data reported in parts per million, are considered a closed array as they sum up to a constant; thus, the variables are not independent of each other (e.g., as one changes, another element concentration must compensate) (Pawlowsky-Glahn and Egozcue 2006; Reimann et al.2008).

Many classical statistical techniques are based upon assumptions of a normal distribution, equality of variances between sampled populations, spatial independence, and unconstrained random variables. If raw (untransformed) data do not meet these assumptions, especially if they exhibit positive skewness, steps are frequently taken to mathematically transform the data, most often by taking the natural logarithm, to obtain a normal distribution. Positive skewness may represent biased sampling (Power 1992), analytical error or bias, closed data, and multiple populations with potential outliers, rather than a true log normal distribution coming from a single population (Singh et al. 1997; Reimann and Filzmoser 1999). Using simulated and actual USEPA Superfund site data, it has been demonstrated that when log transformation data sets are statistically analyzed, the lognormal assumption can hide outliers and polypopulational data sets (Lepeltier 1969; Singh et al. 1997). The geological mapping for this region identifies multiple lithological units, including mineralized zones related to higher grade ore bodies (USGS 1997a). No attempt was made to transform the NURE 2000 data sets to meet assumptions of normality in this assessment of natural condition.

Exploratory data analysis, applying two techniques resistant to the data set distributional characteristics and outliers, combined with careful examination of geochemical distribution maps is used to determine outliers (Lepeltier 1969; Matschullat et al. 2000; Salminen and Gregorauskiene 2000; Reimann 2005; Reimann et al. 2005; Singh et al. 2007). This work proceeds only after a careful quality assessment screening of the laboratory data is done and remove any obvious errors. Three general steps are used in the assessment of the data sets:

1. Creation of a combined set of two plots with equal y-axis trace metal scales against a box plot and a plot of the cumulative frequency distribution or cfd plot.
2. Determination of Median ± 2 Median Absolute Deviation (MAD) values.
3. Plotting of the trace metal data, including outliers identified in the above steps, on maps with geologic, population density, and mining information helps assess potential factors contributing to any data outliers. If no underlying

relationship is identified between the outlier(s) and population density or mining activity, the raw data set is accepted for natural background estimation. If outliers are observed that represent mining or human-related activities, their impact on natural conditions will be assessed as follows:

i. Without the outlier(s), steps 1–3 above are re-run to assess the influence of the outlier on the background estimate.
ii. If the estimated background level is significantly inflated by retaining the outlier, it is dropped from the data set since the objective is to represent the majority of the data set's dominant population(s).

Statistica^{TM}, Version 8, by StatSoft (2008) and ProUCL 4.0 (Singh et al. 2007) were used for the statistical calculations.

Box plots are a non-parametric, graphical depiction of the data, and are robust to the presence of outliers (Tukey 1977; Hoaglin et al. 1983). The data are summarized using five statistics: the minimum value, the lower quartile (Q1), the median (Q2), the upper quartile (Q3), and the interquartile range (IQR) upper limit (Tukey 1977). Outliers are those values exceeding the IQR upper limit, which is defined as:

$$\text{IQR Upper Limit} = Q3 + 1.5 * \text{IQR} \ (Q3 - Q1)$$

Though this MAD value remains non-parametric and is not adjusted to a normal distribution, the median ±2MAD is analogous to the often used mean±2SD procedure to select outliers in geochemical data sets, but it is less influenced by data distribution and is robust against extreme values (Hoaglin et al. 1983; Reimann et al. 2005). This is the case for the median, which is considered more suitable for determining the critical value of measurements that have distributions of different shape and contain extreme values, compared to the arithmetic mean (Reimann et al. 2008). Since we are interested in the upper limits for the sediment trace metals, the median+2MAD is used. The MAD is taken as the median of the absolute values of the residuals or deviations from the data median. For a sample set $X_1, \ldots\ldots X_n$:

$$\text{MAD} = \text{median}_i \left(|X_i - \text{median}_j (X_j)| \right)$$

The performances of both box plots and median+2 MAD were evaluated on simulated normal and log normal data sets that included simulated outliers (Reimann et al. 2005). Box plots performed well in dealing with up to 15% outliers, where median±2MAD functions best above 15%, but below 50% outliers.

Results

Trace Metals in Stream Sediments

That sample locations covered complex mixed populations of lithological units and mineralized ore bodies is reflected in the lack of concordance between mean, median, standard deviation, and MAD in Table 3-3. The NURE 2000 stream sediment data set for the basins contained duplicate analyses at six sampling locations for which relative percent differences (RPD) were calculated. For an RPD ≤ 30%, the average of the two values was used; for RPD >30%, the values were not included in the analyses. None of the original or duplicate values represented extreme outliers in the box plot, with the exception of Copper River Hg where the original value was 0.03 and the duplicate measure was 0.79 µg/g (RPD 44%).

In Cook Inlet, 13 sites were flagged and trace metal concentrations were evaluated. Only one Cook Inlet site had an outlier maximum data set value for Cu of 142 µg/g dry weight (dw), with the second highest level for Hg of 0.66 µg/g dw. Seven sites were flagged in Copper River basin, but only one outlier value for Cu of 102 µg/g dw was observed. The sites exhibiting these higher data values were converted to Keyhold Markup Language (KML) files for further assessment within Goggle Map™. Neither site was within the same drainage as the metalliferous load site, thus all Cu and Hg values were retained for analysis. No outliers were removed from either the Cook Inlet or Copper River stream sediment database in the analysis.

Trace metal concentrations were mapped using four box plot classes against geologic base map coverage. This type of geological mapping is useful in assessing stream sediment results against average crustal values for various rock types and the earth's crust (Reimann et al. 2005). As the detailed geological maps become too crowded, for illustrative purposes, Figure 3-5 shows trace metal concentrations for As in Cook Inlet plotted against coverage of Late Cretaceous and Cenozoic magmatic (igneous) geological units (USGS 1997b).

In Figures 3-6 through 3-12 (Cook Inlet) and 3-13 through 3-19 (Copper River), the raw data, combined box, and cfd plots are shown for each trace metal of concern. The IQR upper limit value, hereafter referred to as IQR and other features of the box plot are examined against a cfd plot. Table 3-4 presents the IQR values breakdown for each trace metal and watershed, along with the median+2MAD value.

Results of Table 3-3 and 3-4 are compared with crustal trace element concentrations (Wedephol 1995) and 1970s NURE Alaska mean values in Table 3-5 and USGS National Water Quality Assessment (NAWQA) contiguous United States baseline sites (Horowitz and Stephens 2008), hereafter referred to as NAWQA U.S. in Table 3-6.

Arsenic

Cook Inlet and Copper River watersheds stream sediment As mean values are about two times higher than those observed in the NAWQA U.S., but they do not differ greatly from the Alaska 1970 NURE statewide results. The maximum values of 240 μg/g dw for Copper River were four times higher than the NAWQA U.S. maximum value of 60 μg/g. Approximately 7% of the Cook Inlet and 5% of the Copper River values exceed the NAWQA maximum.

A review of As spatial distribution, shown in Figure 3-5, with concentration classes within the box plot percentiles found outliers (44.8–64.1) and extremes (69–224) within or close to mapped magmatic rock areas. No distinct clumping was observed, nor was there any association with known population or industrial areas. The box plot IQR threshold value for As is 39 μg/g for Cook Inlet and 55 μg/g for Copper River watersheds.

Chromium and Nickel

As they are closely correlated in rocks, soils, and sediments, Cr and Ni are discussed together (Alloway 1990). Cook Inlet and Copper River watershed basins Cr results are in close agreement with the NAWQA U.S., with the highest Cr value of 260 µg/g dw observed for Copper River bracketed by the NAWQA U.S. range of 6.3–270 µg/g. Mean and median Ni values for Cook Inlet and Copper River basins were slightly higher than NAWQA U.S., but the ranges fell within the NAWQA U.S. brackets. The box plot IRQ threshold value for Cr is 139 µg/g for Cook Inlet and 133 µg/g for Copper River. The box plot IQR threshold value for Ni is 73 µg/g for both Cook Inlet and Copper River.

Copper

Cook Inlet and Copper River watershed basins Cu results are in close agreement with the Alaska mean value of 37µg/g, with the mean and median values slightly higher than the NAWQA U.S. values. The box plot IQR threshold value for Cu is 101 µg/g for Cook Inlet and 92 µg/g for Copper River.

Lead

Mean and median results of Pb for both watersheds were slightly lower, but in close agreement with the NAWQA U.S. baseline in Table 3-6. The mean values were higher than the Alaska NURE 1970 mean of 12 µg/g. The box plot IQR threshold value for Pb is 46 µg/g for Cook Inlet and 30 µg/g for Copper River.

Mercury

Mean and median Hg results for Cook Inlet and Copper River watershed basins are in close agreement with NAWQA U.S. values. The maximum observed NAWQA U.S. Hg value of 3.1 µg/g is about two times higher than the Copper River watershed maximum Hg value of 1.95 µg/g. The box plot IQR threshold value for Hg is 0.31 µg/g for Cook Inlet and 0.25 μg/g for Copper River. The Hg value of 1.95 μg/g (location 63.144 -145.1597 NAD 27) occurred in the northern part of the Copper River watershed in a remote area distant from any mining activity identified on the ADNR (2009a) significant metalliferous mining digital data set.

Zinc

Mean and median results for Zn in both watersheds were slightly lower but in close agreement with the national NAWQA U.S. baseline values in Table 3-5. The observed maximum values for Cook Inlet and Copper River basins are about half of the maximum NAWQA U.S. Zn value of 430 μg/g. The Cook Inlet and Copper River Zn mean values are lower than the Alaska NURE 1970s mean of 157 μg/g. The box plot IQR threshold value for Zn is 166 μg/g for Cook Inlet and 156 μg/g for Copper River. These natural condition levels are slightly lower than the value of a Cook Inlet NAWQA study (Frenzel 2002) estimate of 190 μg/g.

Finally, for the NURE mean values between the Cook Inlet and Copper River watersheds, overall Cr, Cu, Ni and Zn showed small relative percent differences of 4.4%, 9.3%, 0%, and 6.2 % respectively. Between the two watersheds, As, Pb and Hg showed higher relative percent differences of 34%, 42% and 21% respectively.

Discussion

Natural Condition Assessment

Based on simulation modeling conducted on theoretical data sets (Reimann et al., 2005), the results for box plots perform best when outlier proportions are ≤ 15%, whereas the median+2MAD performs best in the outlier ranges >15% and ≤50%. Examination of the combined box and cfd plots suggests that less than 10 to 15% of the data are outliers. As a result, the IQR values in Table 3-4 are recommended as natural background threshold trace metal levels for Cook Inlet and Copper River watersheds.

In any discussion of natural condition, the selected values, while providing insight and direction in assessing conditions, are not "true" values. Natural variability, sample design, laboratory errors, and non-detect results will still likely end in errors of a factor of two or more, even in the best geological surveys (Matschullat et al. 2000).

The elevated As mean value for Cook Inlet and Copper River watersheds, relative to the NAWQA U.S. mean of As, may be associated to the fact that arsenopyrite is not uncommon in these watersheds considering the regions' gold deposits and related sulfide mineralogy (USGS 1996; Frenzel 2002). Global means for As in soil are between 1 and 40 µg/g, but substantially higher levels (900 µg/g) are seen in minerals like arsenopyrite (Alloway 1990). Volcanic ash, which has frequently dusted this region, can contain As, but little information exists as to concentrations in recent Alaskan ash falls or historic events (Glass and Frenzel 2001). A study of two ash fall samples from the Copahue volcano in Neuguén, Argentina, found the material enriched in As and depleted in Cr, Hg, and Ni (Smichowski et al. 2003).

While no anomalous Cr or Ni values were observed when compared with NAWQA U.S. results, there are known high grade Cr with related elevated Ni deposits within the Cook Inlet watershed on the lower Kenai Peninsula at Red Mountain and Chrome Bay (Gill 1922).

The elevated mean Cu value compared to the NAWQA U.S. result is not unexpected. Historically, a large Cu mine at Kennicott, Alaska, operated from 1911 to 1938 in the Copper River watershed (Miller 1946). A large copper-gold-molybdenum porphyry deposit is located in southwest Alaska adjacent to the upper boundary of the Cook Inlet watershed (ADNR 2009b). Igneous rock and sedimentary deposits of shale and sandstone present in these watersheds generally contain elevated levels of Cu, as shown in Table 3-5.

Mercury values were comparable or even exhibited a lower maximum value than observed levels in the NAWQA U.S. study. Known mercury-rich mineral deposits are documented in other regions of Alaska, principally Southwestern Alaska outside of the

Cook Inlet watershed, and stream sediment samples near some cinnabar mines contain total Hg in excess of 5,000 µg/g (USGS 1996).

The mean Pb values in the Cook and Copper River watersheds compared to the Alaska NURE 1970s mean for Pb may be reflective of the presence of the higher Pb in younger volcanic rocks and sedimentary sandstone and shale (Table 3-5) in the Cook and Copper River watersheds. The 1970s NURE study did not conduct extensive sampling around the massive silver-lead-zinc sulfide deposits (USGS 1996) in the northwestern Brooks Range, where Pb stream sediment mean values in some regions are as high as 480 µg/g (Graham et al. 2009).

One phenomenon noticeable in a review of the main section within the cfd plot (Figure 3-20) is extensive discretisation of the values reported by the laboratory. Only 32% of the Pb values for Cook Inlet and 26% of the values for Copper River were unique. This artificial data structure creates difficulty in the application of many statistical tests (Reimann et al. 2008). Still, the structure does provide a range for estimating a reasonable upper natural background IQR value with the box plot method.

The NURE Cook Inlet IQR natural condition Pb value is higher than the Cook Inlet NAWQA study (Frenzel 2002) background level for Pb of 21 µg/g, which was based on a visually observing a sharp break in a cumulative frequency plot line. Applying the combined box and cfd plotting method to the Cook Inlet NAWQA data set produced an IQR threshold value of 27 µg/g for Pb (Figure 3-21). The relative percent difference between the two approaches is 25%, which is considered a reasonable agreement. The USGS NAWQA U.S. and Cook Inlet studies analyzed the <63 µm sediment fraction, and the USGS NURE 2000 used the <149 µm sediment fraction. Analytical methods were similar and run at the USGS National Water Quality Laboratory following similar protocols. Regional coverage was different (Figure 3-22), with the Cook Inlet NAWQA study including the more urbanized Anchorage area but not providing the sample number or density of the NURE 2000 work. Comparing the NURE 2000 Cook Inlet Pb cfd plot (Figure 3-21) with the Cook Inlet NAWQA Pb cfd (Figure 3-

9) study it is clear that the range of the main body of the Pb data does not reflect a sharp break until the higher outlier value of 41 ug/g is reached.

The difference between the Pb threshold values determined in the two studies exemplifies how differing background values can be obtained in regional surveys of differing scale and scope. This difference emphasizes the importance of understanding study values in the context of the survey design, scale, sampling density, and analytical methods when applying the results to decision making (Salminen and Gregorauskiene 2000; Reimann et al. 2009).

The Cook Inlet and Copper River watersheds Zn mean values are slightly lower than the 1970's NURE Zn, but this is not unexpected in that other NURE sampled regions of Alaska, have areas of sulfide deposits exhibiting higher values of Zn in stream sediments (Graham et al. 2009).

Conclusions

Natural condition trace element concentrations in stream sediments are best represented by a justifiable data set representing the dominant background, while retaining only those outliers that cannot be associated with direct anthropogenic activities or high-grade ore bodies. This natural condition remains at best an approximation, closely linked to the size of the region, density of sampling, sampling methods, and analytical techniques. The stream sediment data sets and estimated natural condition concentrations from the Cook Inlet and Copper River watersheds provide a large-scale regional characterization. At this scale they are useful for screening stream sediment trace metal concentrations for anomalous values, but they do not replace careful characterization of locally elevated sites.

Methods for estimating background remain varied, and there is no universal agreement on appropriate statistical techniques (Covelli and Fontolan 1997; Reimann and Filzmoser 1999; Nakić et al. 2007). Multiple robust statistical techniques coupled with an examination of geochemical sources, industrial activities, and human population density provide for a reasonable background estimate. Attempts to quantify a "true" natural background, especially at a regional or larger scale, are not feasible given the numerous variables and level of effort required (Matschullat et al. 2000). The methods described in this paper provide a reasonable approach to setting a regional natural background range that will help flag anomalous concentrations for further assessment.

The results of this work provide natural condition levels of trace elements in stream sediments in these two watersheds that place the findings of more targeted contamination studies into a regional context. These results also provide a background for future investigations of the trace metal composition of coastal marine sediments.

Acknowledgments

The U.S. Environmental Protection Agency Office of Research and Development supported this study through Cooperative Agreement # R-82911501. Walt Nelson, Dixon Landers, Tony Olsen, and others with USEPA ORD enthusiastically supported our efforts and understood the importance of this pioneering endeavor in Alaska. Ms. Sue Saupe, scientific director with Cook Inlet Regional Citizens Advisory Council (CIRCAC) was instrumental in the implementation, field work, and reporting on the Southcentral Coastal survey. Thanks for the constructive comments and suggestions provided by Drs. John Kelley, Franz Mueter, Sathy Naidu, Larry Duffy and Robert Perkins and others of the University of Alaska Fairbanks.

This document has not been subjected to CIRCAC, ADEC, or USEPA internal institutional peer review and/or administrative review and does not necessarily reflect these organizations' views, nor does any mention of trade names or commercial products constitute endorsement or recommendation.

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Tables

Table 3-1: Estimates of Percentage Coverage of Rock Type[1] and Stream Sites

Major Rock Types	% in Cook Inlet Watershed	% Cook Inlet Watershed Stream Sites	% in Copper River Watershed	% Copper River Watershed Stream Sites[2]
Continental Deposits	7.2%	4.8%	0.5%	0.0%
Glaciers	10.2%	2.4%	30.4%	2.7%
Intrusive Rocks	10.9%	29.8%	2.6%	5.5%
Large Lakes	0.2%	0.0%	0.2%	
Metamorphic Rock	1.1%	3.2%	0.1%	0.0%
Stratified Sedimentary Sequence	64.9%	54.0%	55.3%	75.5%
Ultramafic Rocks	0.1%	2.4%	0.1%	0.0%
Volcanic Rock	5.5%	3.2%	10.8%	15.5%

1– ADGC 2009. 2– One site was not located within any known coverage rock type on the Bekiman Geologic Map.

Table 3-2: Method Detection Level[1]

Analysis Technique	Element	Unit	Lower Detection Limit	Upper Detection Limit
ICP-MS	As	ppm	10	50000
	Cr	ppm	2	25000
	Cu	ppm	2	15000
	Ni	ppm	3	50000
	Pb	ppm	4	50000
	Zn	ppm	2	15000
Hydride-generation AAS	As	ppm	0.06	20
Cold Vapor AAS	Hg	ppm	0.02	>1.8 require dilution

1– Briggs 2001.

Table 3-3: Summary Statistics for National Uranium Resource Survey 2000 Stream Sediment Trace Metals

				Raw Statistics using Detected Observations (µg/g dw)					
Variable	**Num Ds**	**NumNDs**	**% NDs**	**Minimum**	**Maximum**	**Mean**	**Median**	**SD**	**MAD**
As (Cook Inlet)	119	0	0.0%	1.0	224.0	19.6	11.2	28.6	6.3
As (Copper River)	105	3	2.8%	1.1	240.0	18.6	9.6	28.0	7.1
Cr (Cook Inlet)	119	0	0.0%	6.0	159.0	52.8	47.0	32.9	21.0
Cr (Copper River)	107	0	0.0%	11.0	260.0	65.7	59.0	39.0	23.0
Cu (Cook Inlet)	120	0	0.0%	2.0	142.0	37.7	34.0	22.4	13.5
Cu (Copper River)	107	0	0.0%	7.0	162.0	41.7	38.0	25.2	14.0
Pb (Cook Inlet)	118	0	0.0%	7.0	157.0	22.8	19.0	16.5	5.0
Pb (Copper River)	108	0	0.0%	7.0	71.5	19.6	18.0	8.5	3.0
Hg (Cook Inlet)	112	8	6.7%	0.02	1.21	0.1	0.07	0.1	0.09
Hg (Copper River)	87	20	18.7%	0.02	1.95	0.1	0.06	0.2	0.06
Ni (Cook Inlet)	116	4	3.3%	5.0	110.0	33.8	28.5	21.3	13.5
Ni (Copper River)	108	0	0.0%	11.0	101.0	42.2	38.5	18.7	10.5
Zn (Cook Inlet)	120	0	0.0%	24.0	277.0	97.5	91.5	40.2	17.5
Zn (Copper River)	108	0	0.0%	23.0	185.0	81.7	77.0	30.7	19.5

Table 3-4: Inter-Quartile Range (IQR) and Median+2 Median Absolute Deviation (MAD) Results

Watershed	IQR - Box Plot Upper Whisker	Median+2MAD
Cook Inlet (µg/g dw)		
As	39	24
Cr	139	89
Cu	101	61
Pb	46	29
Hg	0.31	0.15
Ni	73	56
Zn	166	127
Copper River (µg/g dw)		
As	55	24
Cr	133	105
Cu	92	66
Pb	30	24
Hg	0.25	0.12
Ni	73	60
Zn	156	116

Table 3-5: Earth Crust Trace Metal Values (μg/g)

	Igneous Rock[1]			Sedimentary Rock[1]			
Trace Metal	Ultramafic	Mafic	Granitie	Limestone	Sandstone	Shales	Earth's Crust[2]
As	1	1.5	1.5	1	1	13 (1-900)	2.0
Cr	2980	200	4	11	35	90	35
Cu	42	90	13	5.5	30	39	14.3
Hg	0.004	0.01	0.08	0.16	0.29	0.18	0.056
Ni	2000	150	0.5	7	9	68	18.6
Pb	14	3	24	5.7	10	23	17
Zn	58	100	52	20	30	120	52

1– Alloway 1990. 2– Upper crust concentrations (Wedephol 1995).

Table 3-6: United States Geological Survey Continental National Water Quality Assessment Program (NAWQA) Baseline and Alaska National Uranium Resource Evaluation (NURE) Survey Sediment Trace Metals Levels

		NAWQA Fluvial Sediments Contiguous Continental U.S. Baseline Sites[2] (μg/g dw)			
Trace Element	Alaska NURE[1] Mean	Mean	Median	MAD	Range
As	17	8.1	6.6	2.2	0.1 - 60
Cr	115	66	58	13	6.3 -270
Cu	37	24	20	6	1 - 150
Hg	-	0.08	0.04	0.02	0.01–3.1
Ni	37	28	23	7	1 - 160
Pb	12	24	20	6	2 - 200
Zn	157	100	91	20	5.2 - 430

1– Weaver 1983. 2–Horwitz and Stephens 2008.

Figures

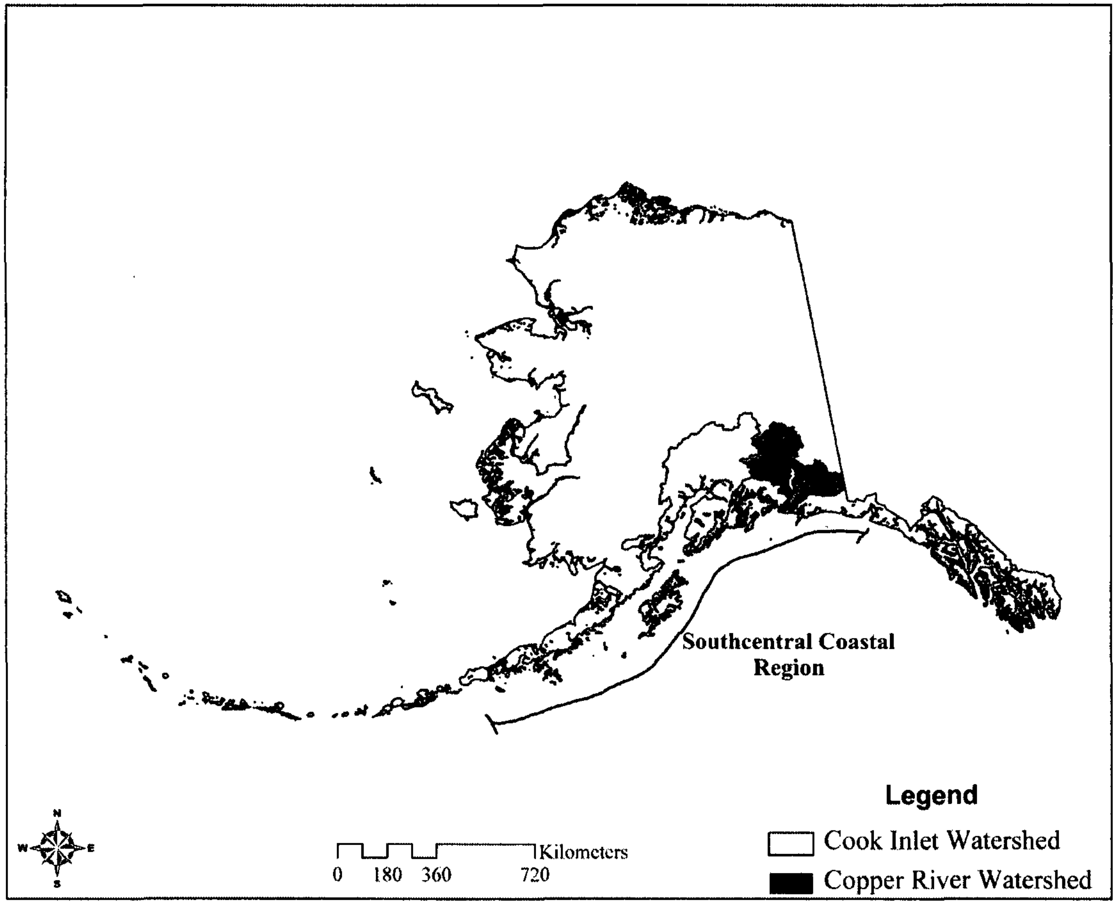


Figure 3-1: Location of Watersheds and Coastal Alaska Monitoring and Assessment Program Region

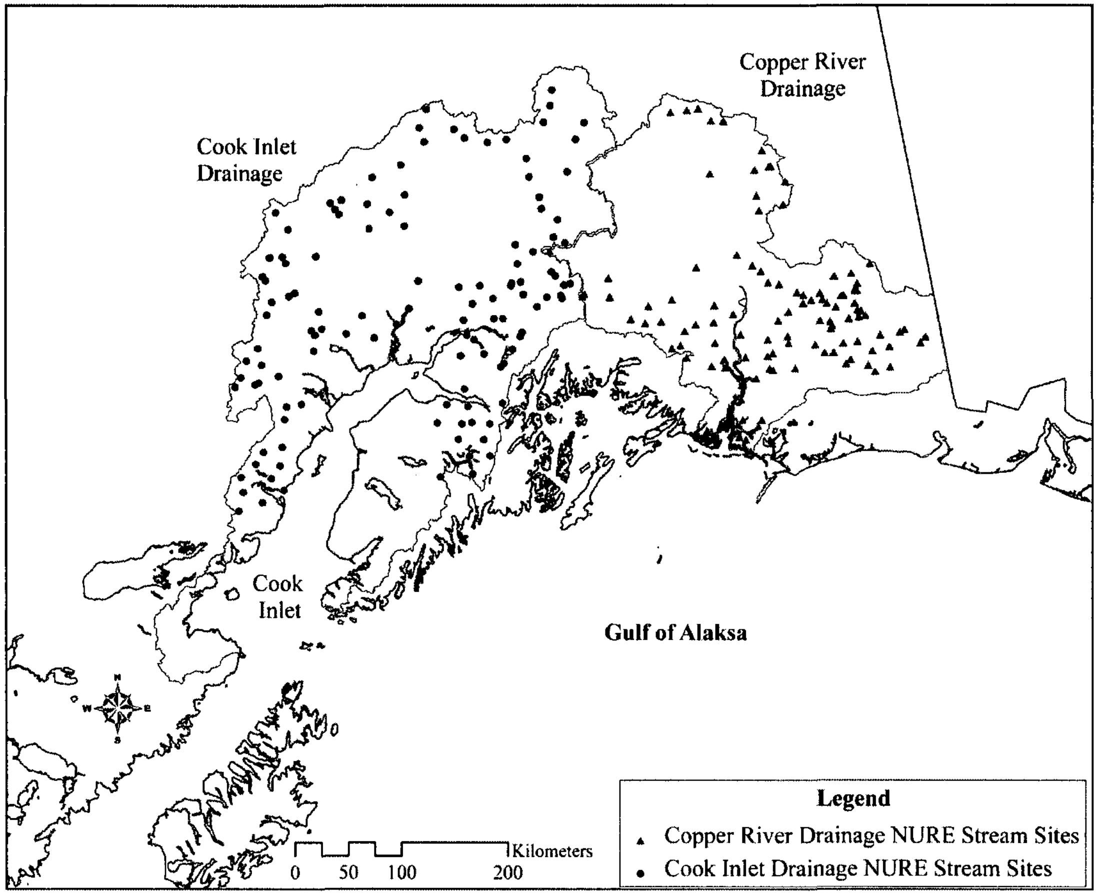


Figure 3-2: National Uranium Resource Survey 2000 Stream Sediment Sample Sites

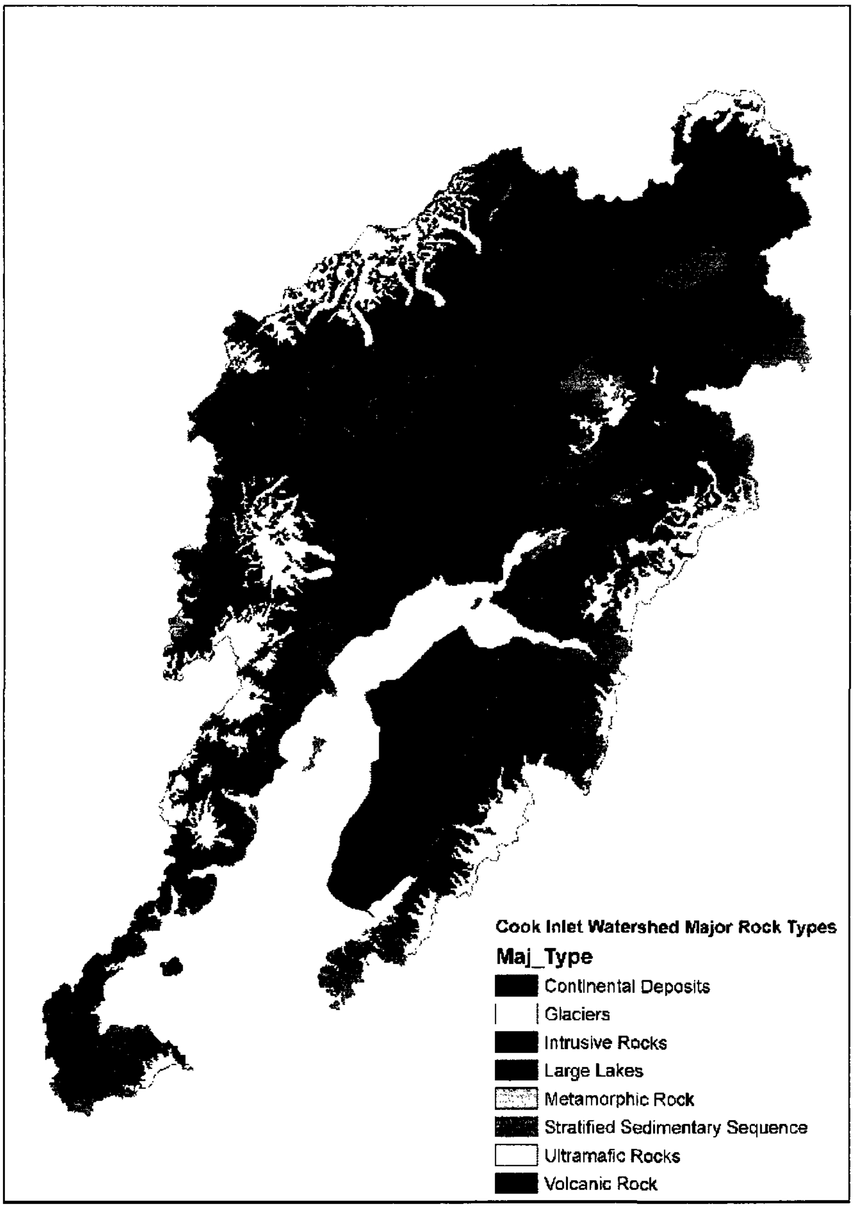


Figure 3-3: Cook Inlet Geological Map (USGS, 1997a)

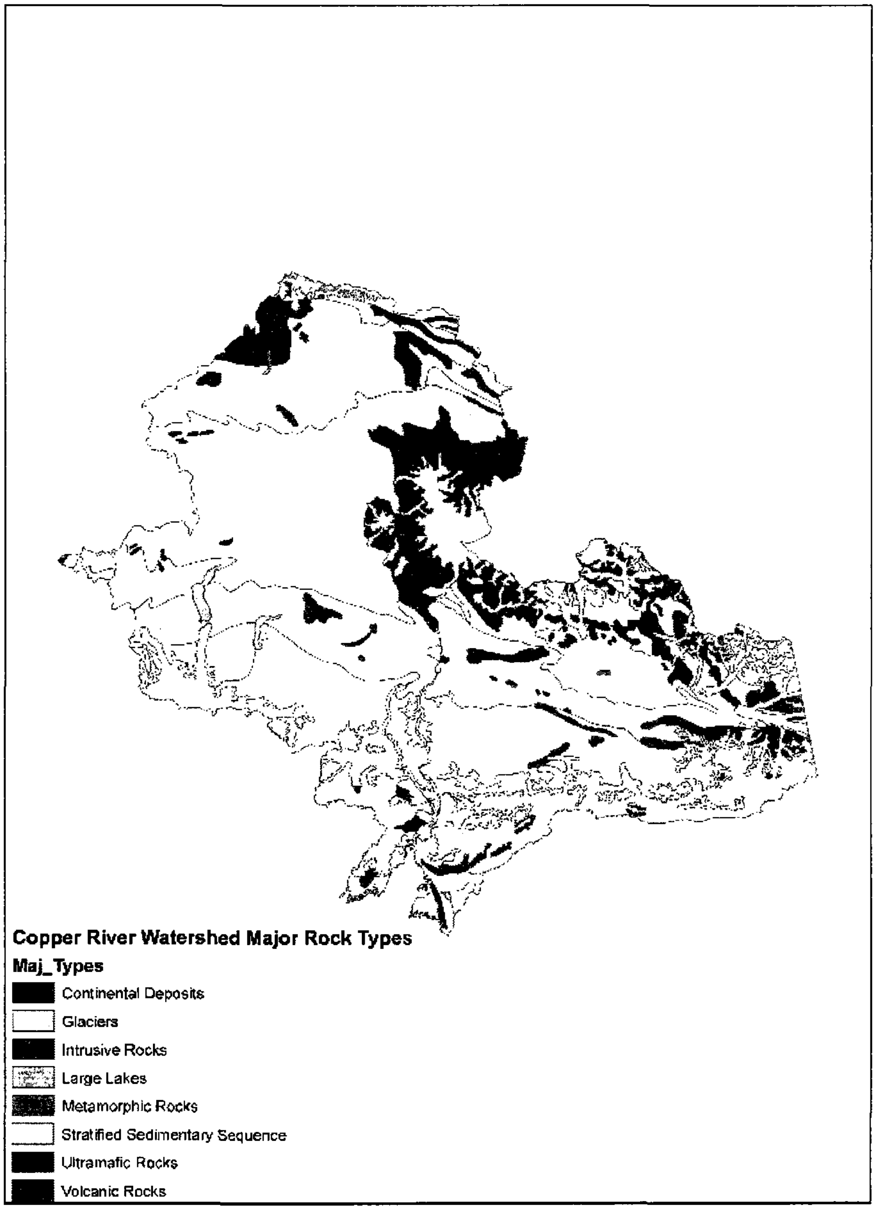


Figure 3-4: Copper River Geological Map (USGS, 1997a)

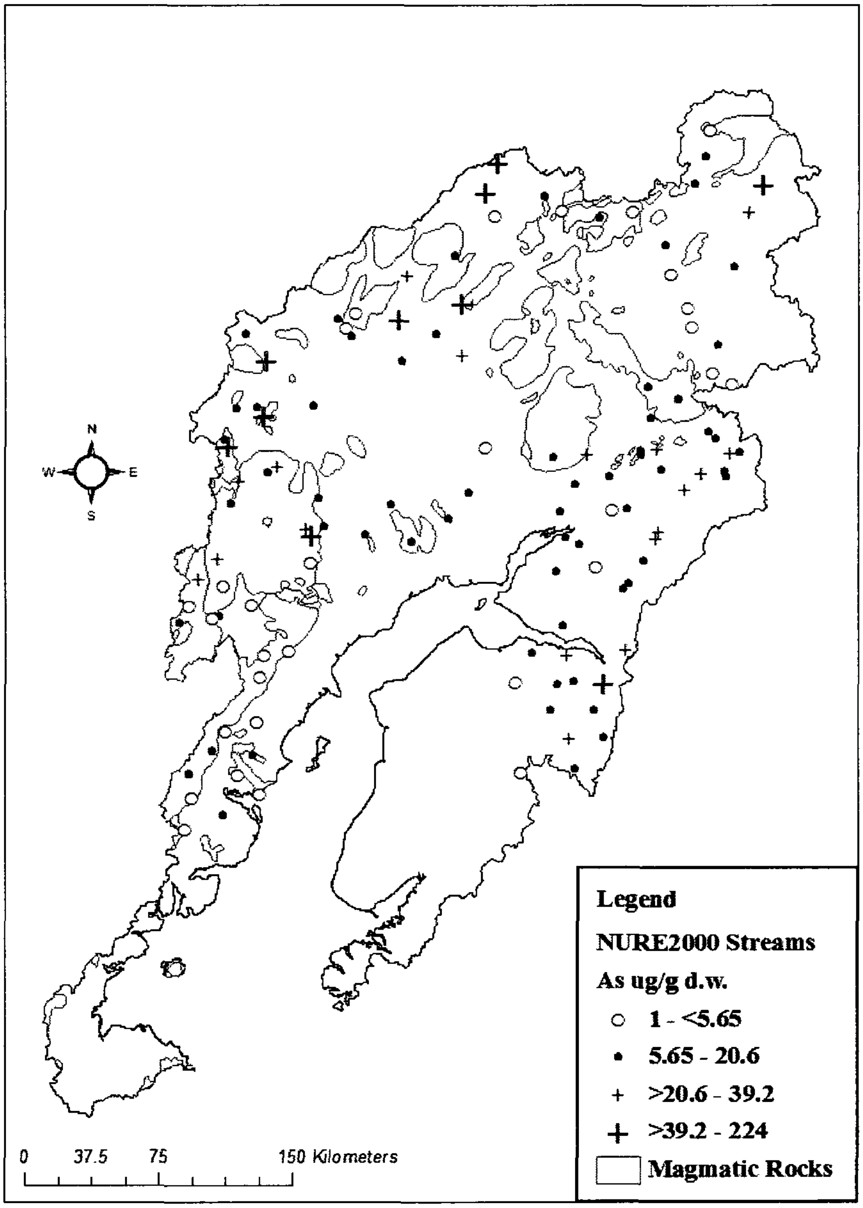


Figure 3-5: Cook Inlet As (µg/g dw) with Box Plot Concentration Classes

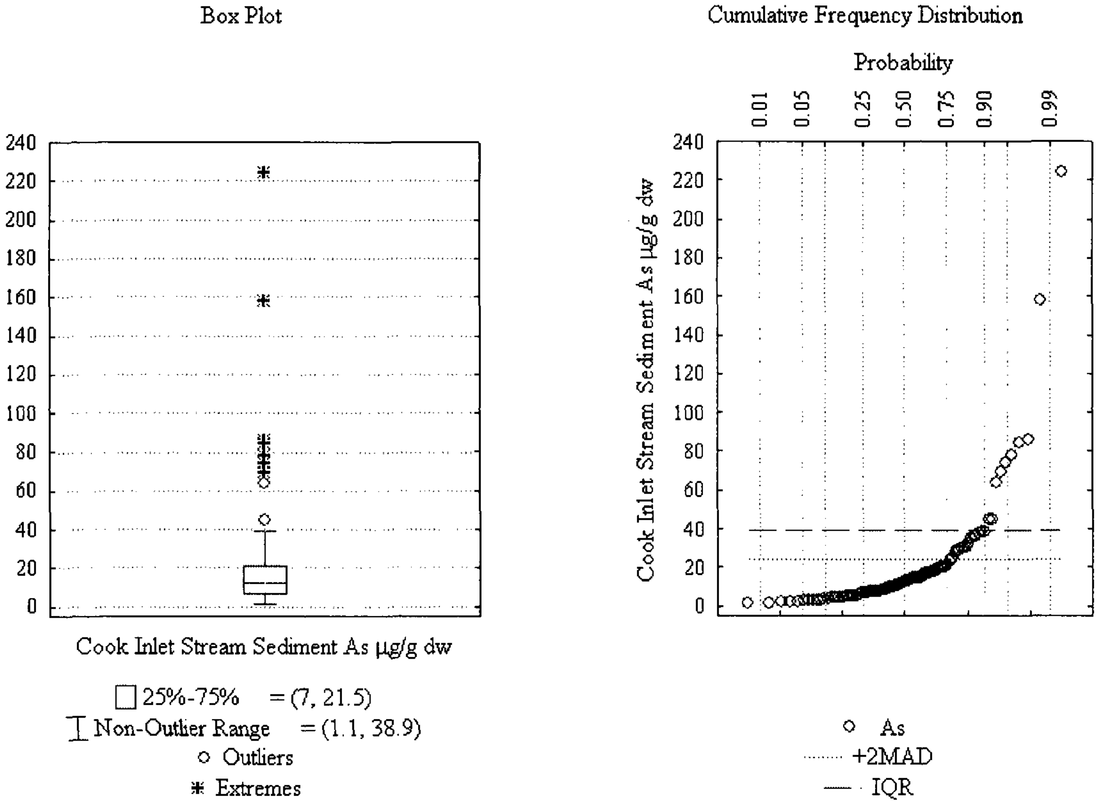


Figure 3-6: Cook Inlet Stream Sediment As (µg/g dw)

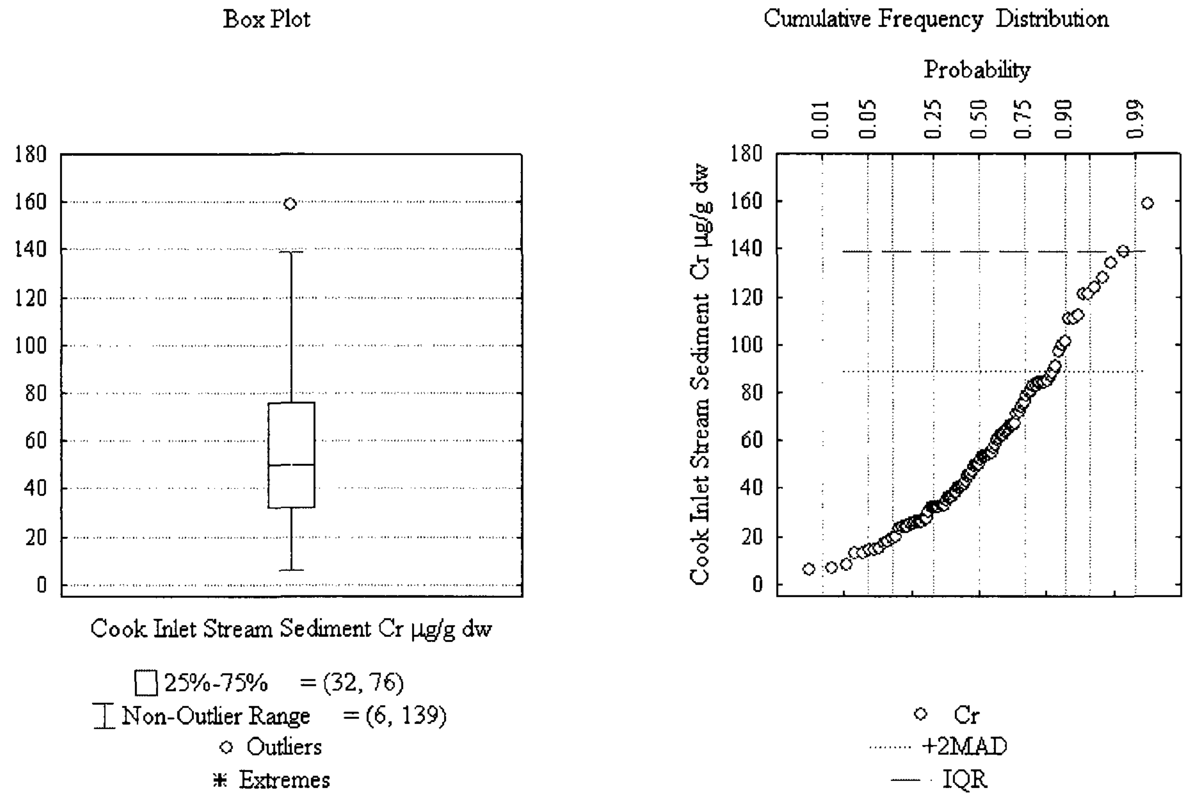


Figure 3-7: Cook Inlet Stream Sediment Cr (µg/g dw)

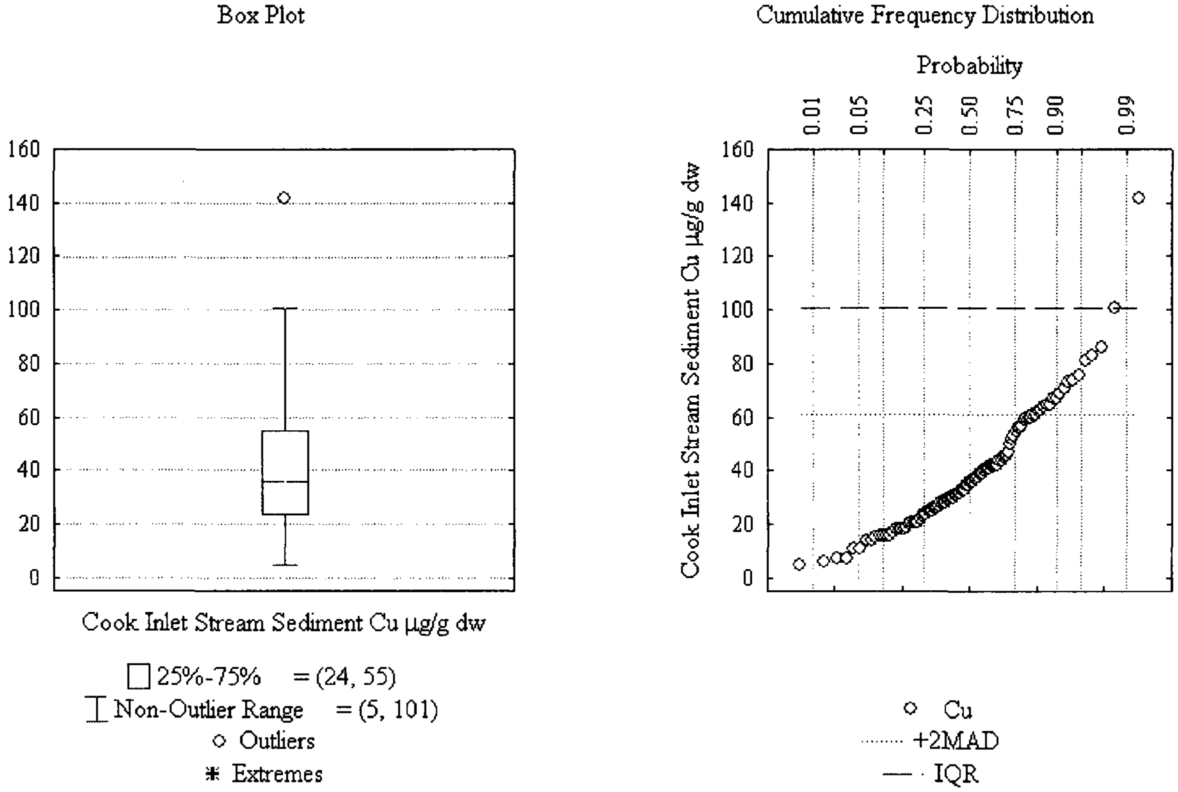


Figure 3-8: Cook Inlet Stream Sediment Cu (µg/g dw)

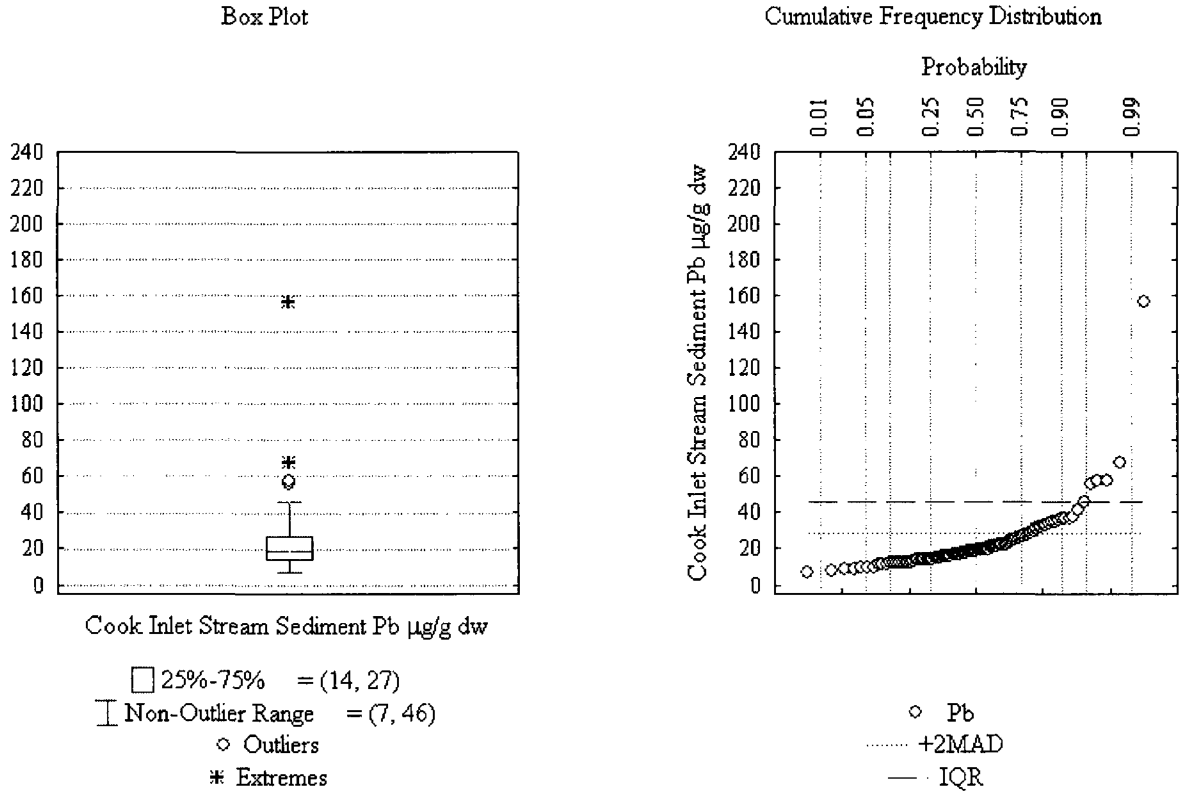


Figure 3-9: Cook Inlet Stream Sediment Pb (µg/g dw)

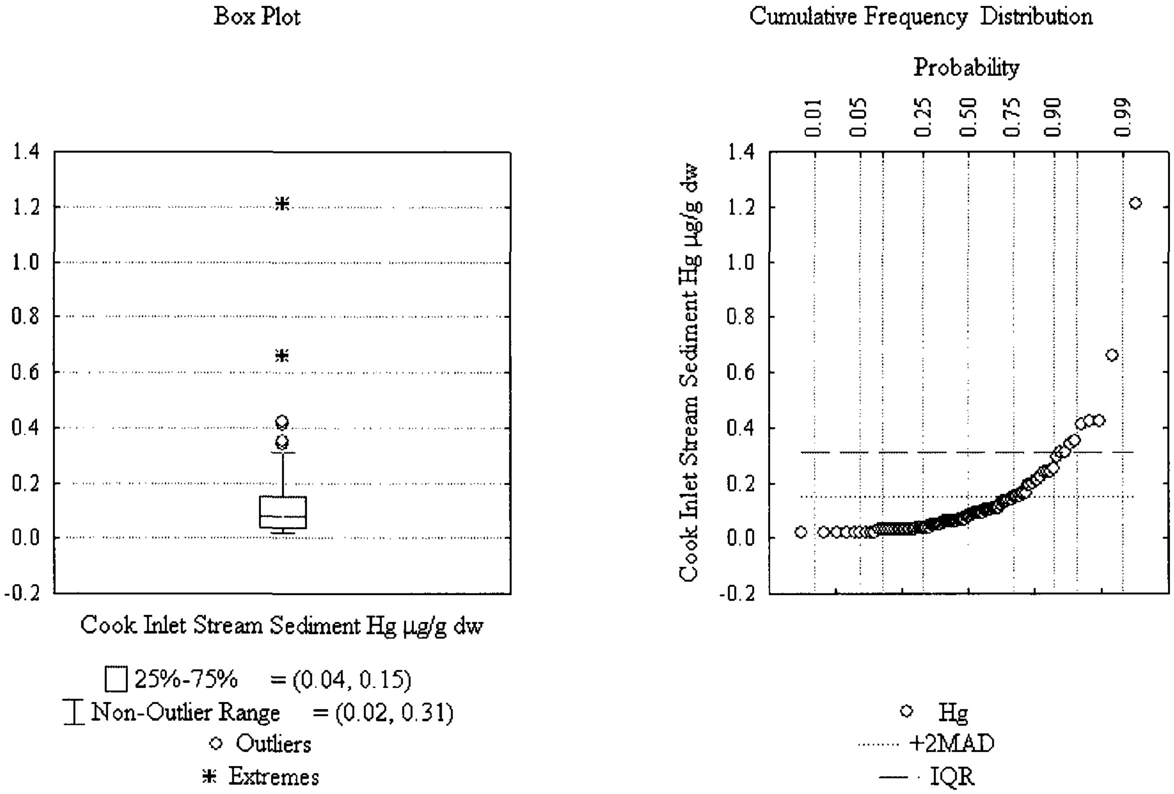


Figure 3-10: Cook Inlet Stream Sediment Hg (µg/g dw)

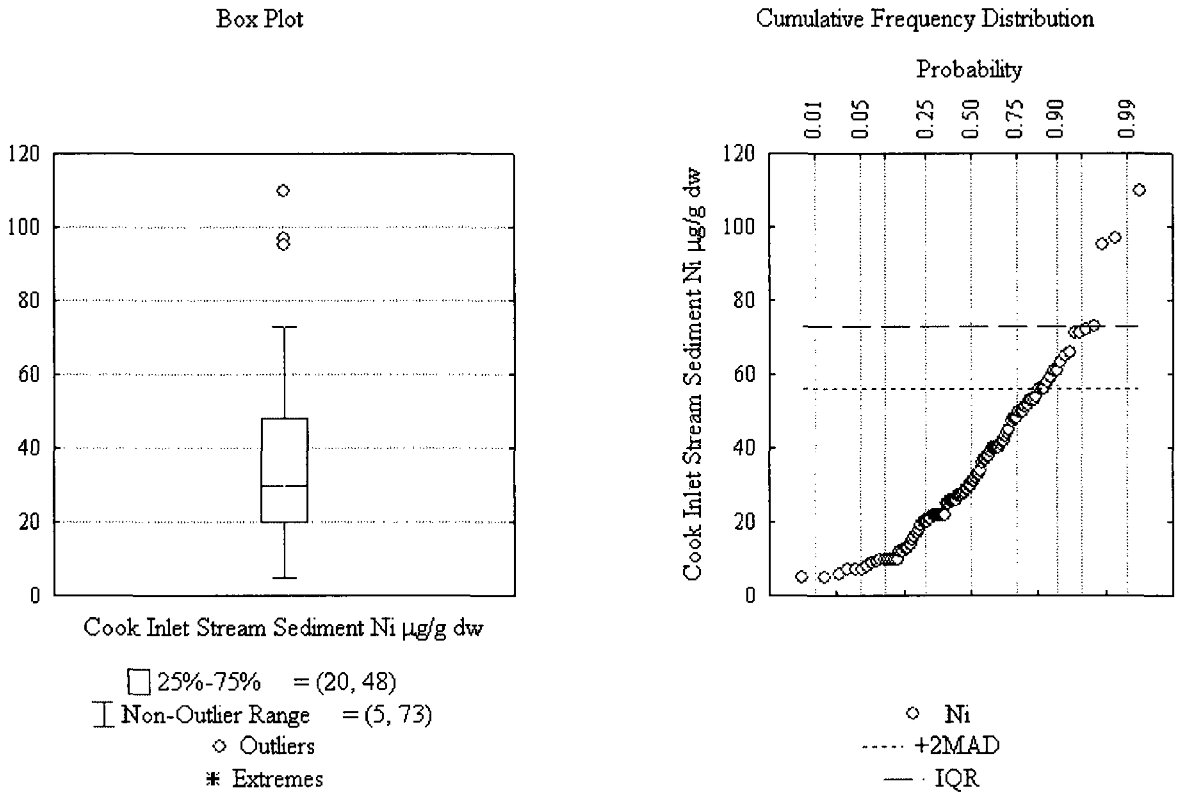
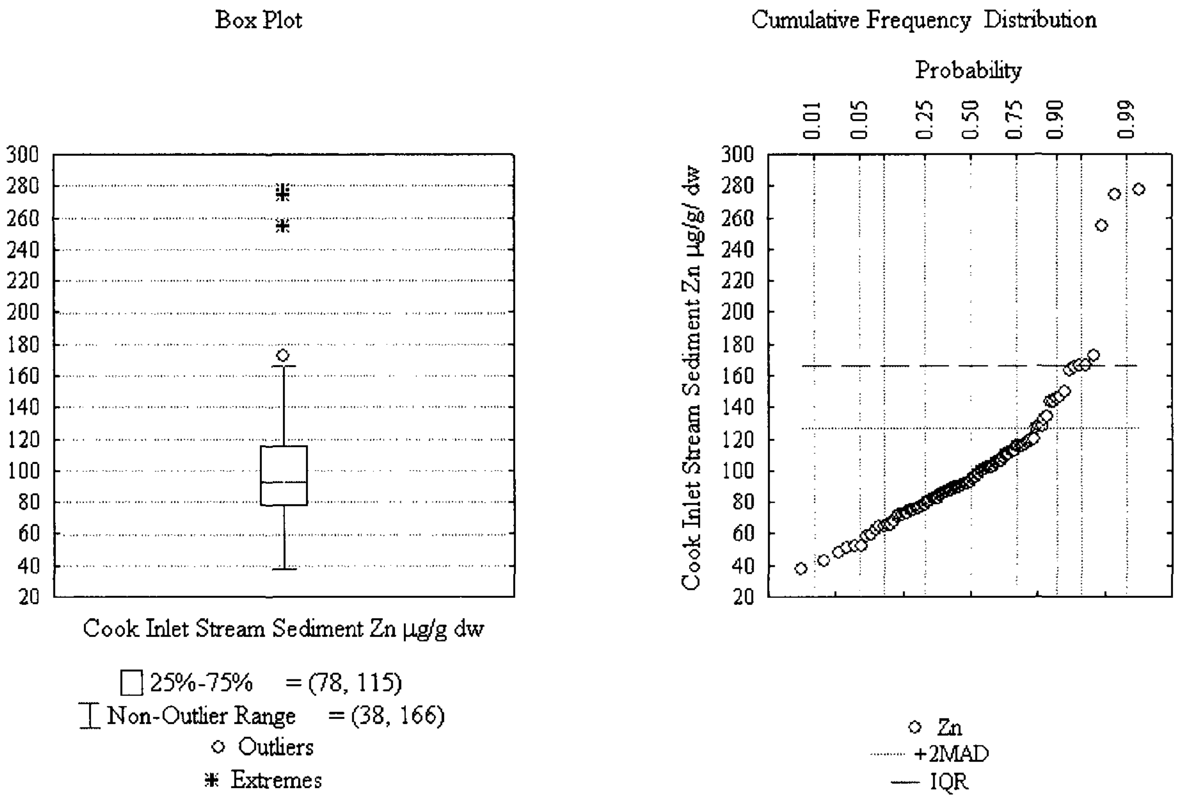
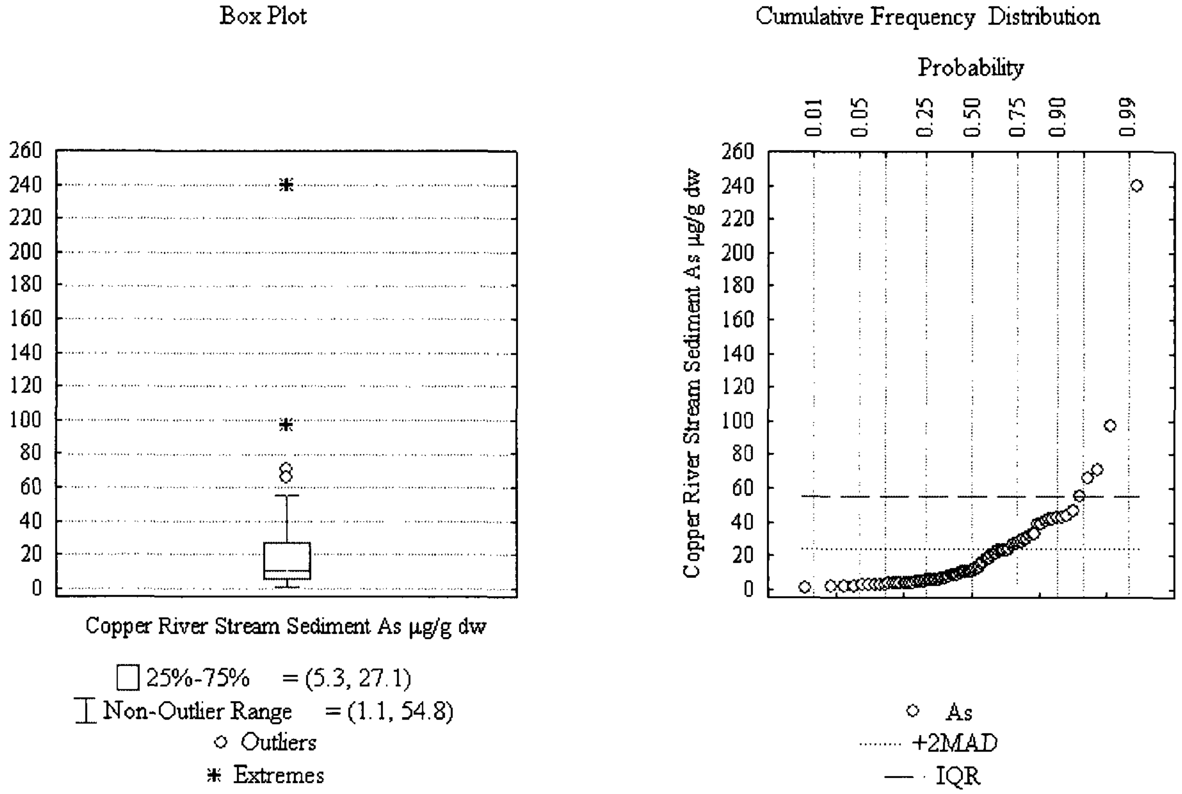


Figure 3-11: Cook Inlet Stream Sediment Ni (µg/g dw)


Box Plot

Cumulative Frequency Distribution

Figure 3-12: Cook Inlet Stream Sediment Zn (µg/g dw)


Box Plot

Cumulative Frequency Distribution

Figure 3-13: Copper River Stream Sediment As (µg/g dw)

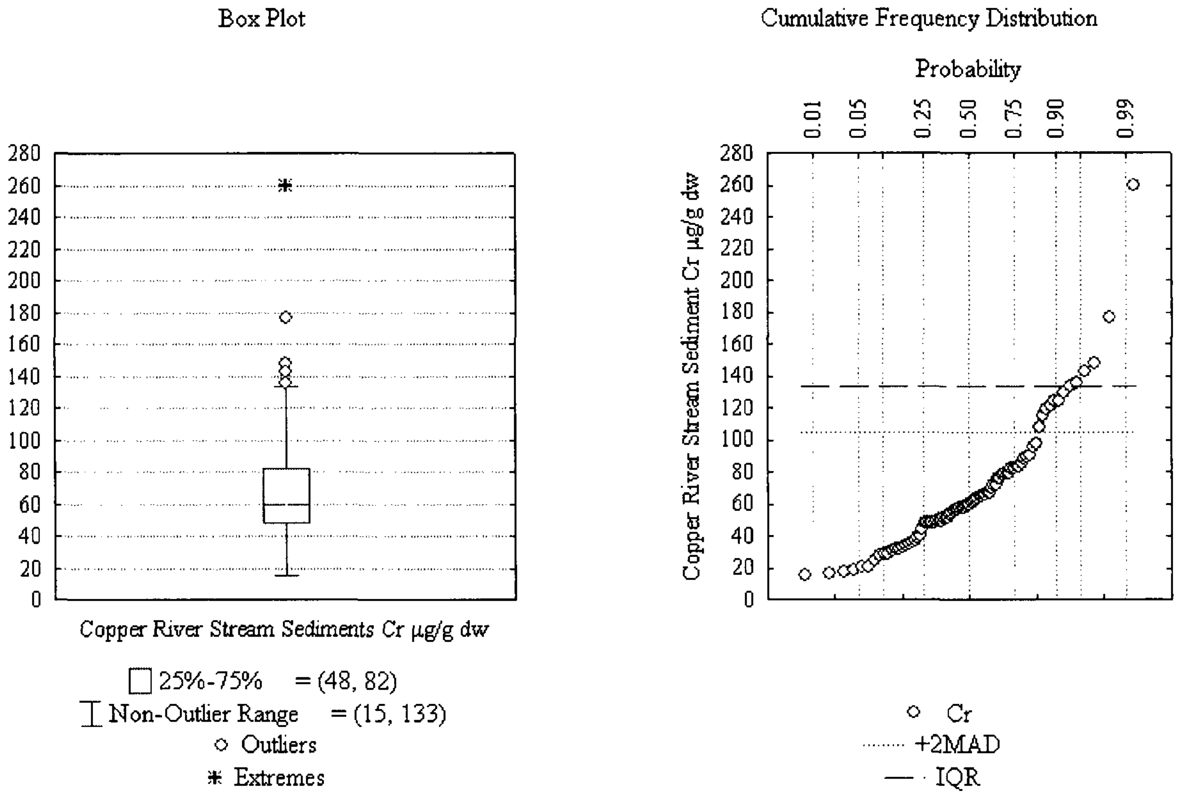


Figure 3-14: Copper River Stream Sediment Cr (µg/g dw)

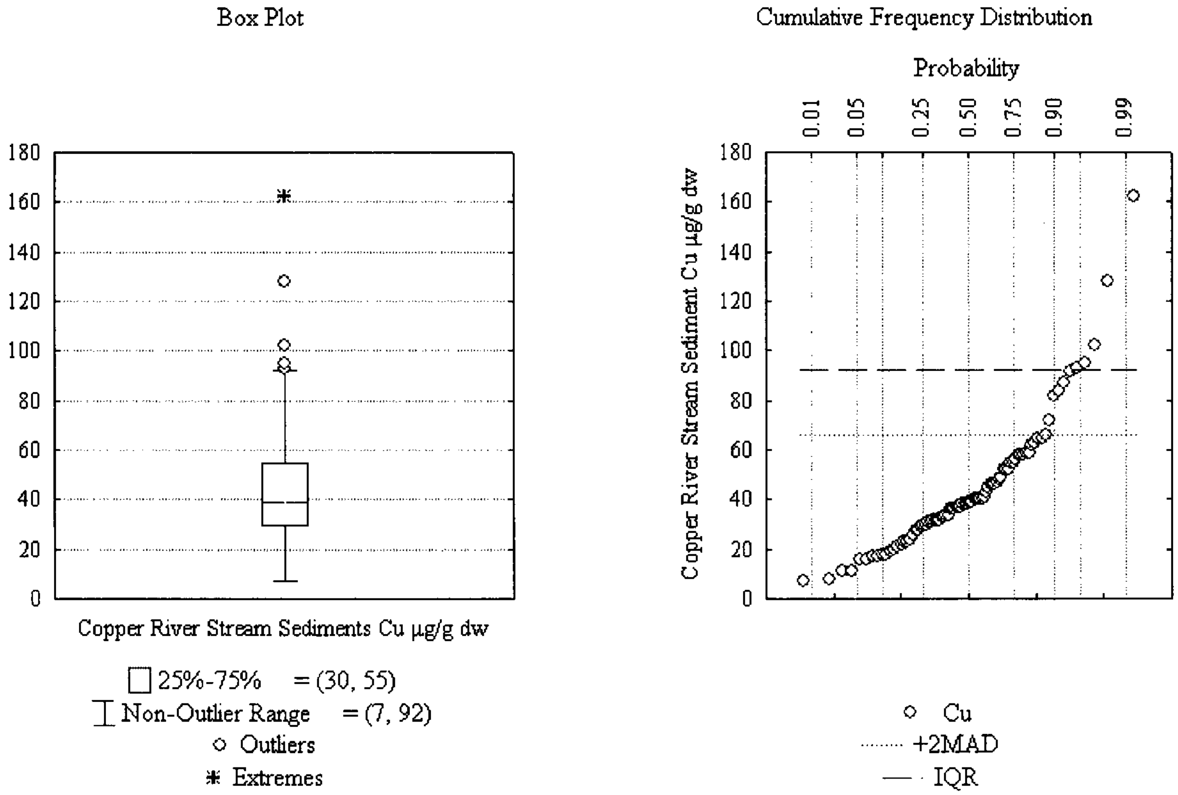


Figure 3-15: Copper River Stream Sediment Cu (µg/g dw)

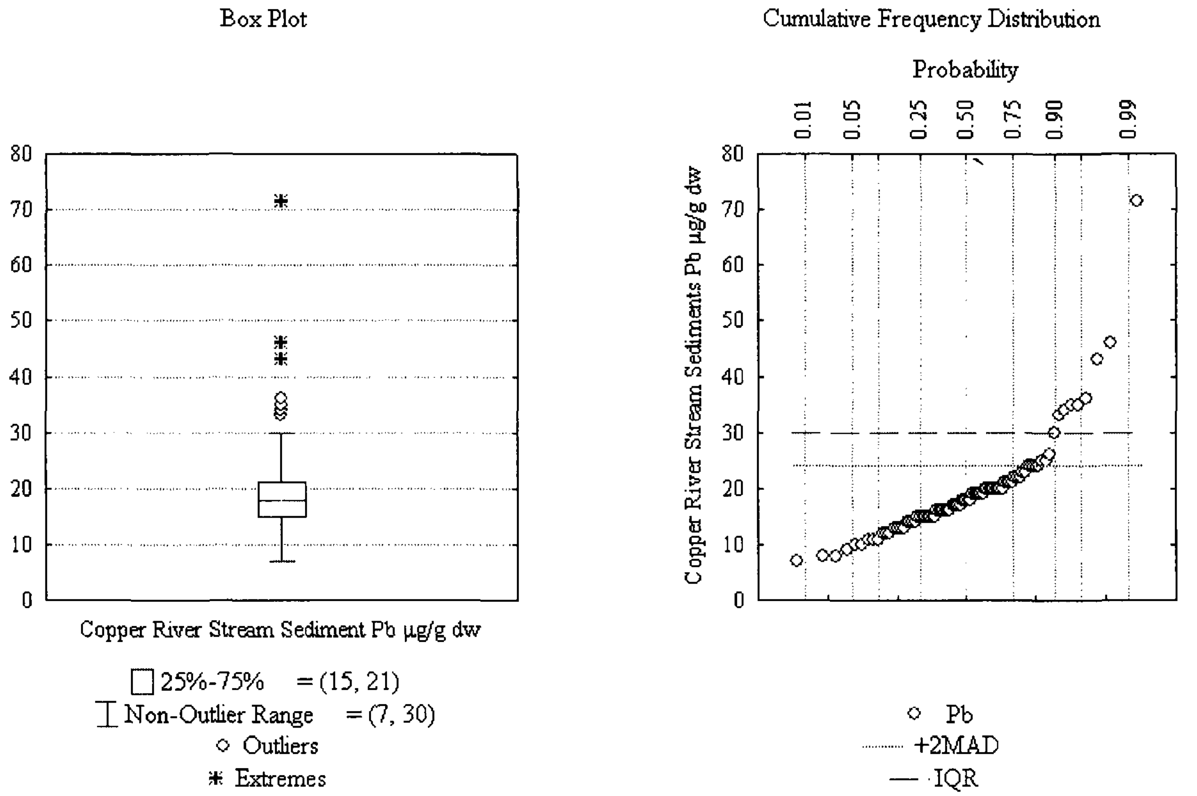


Figure 3-16: Copper River Stream Sediment Pb (µg/g dw)

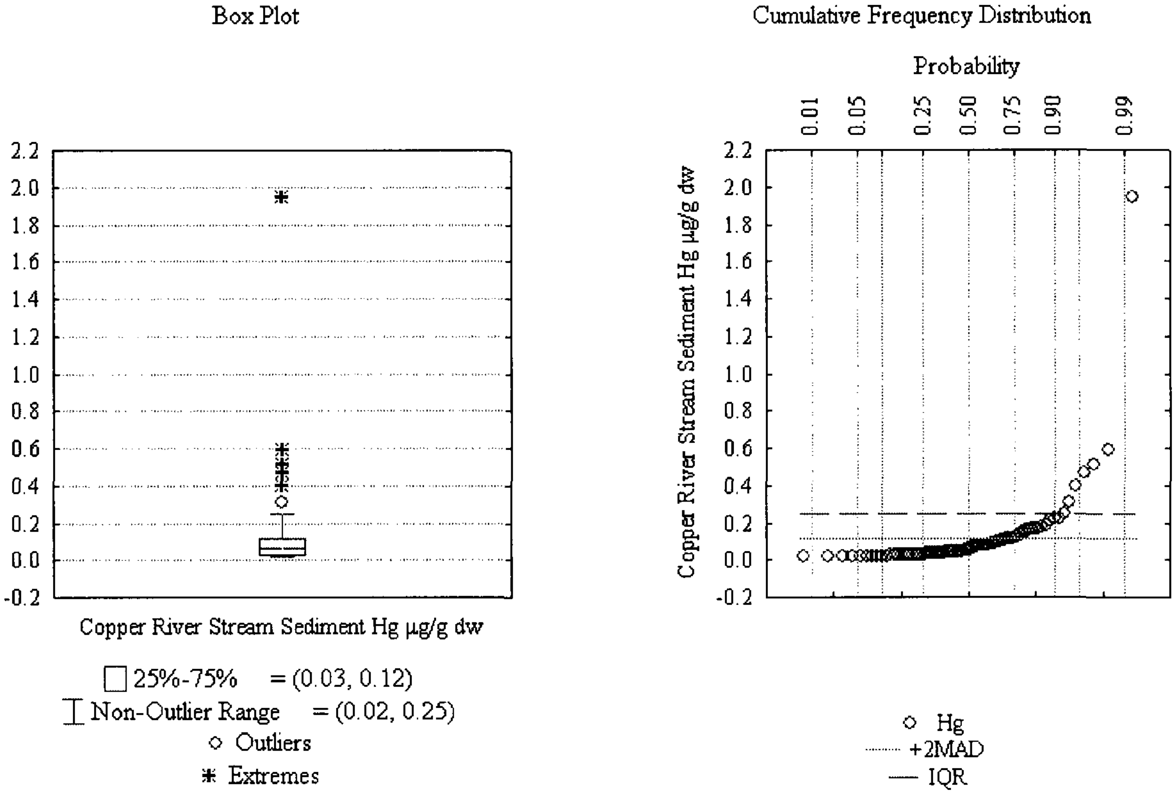
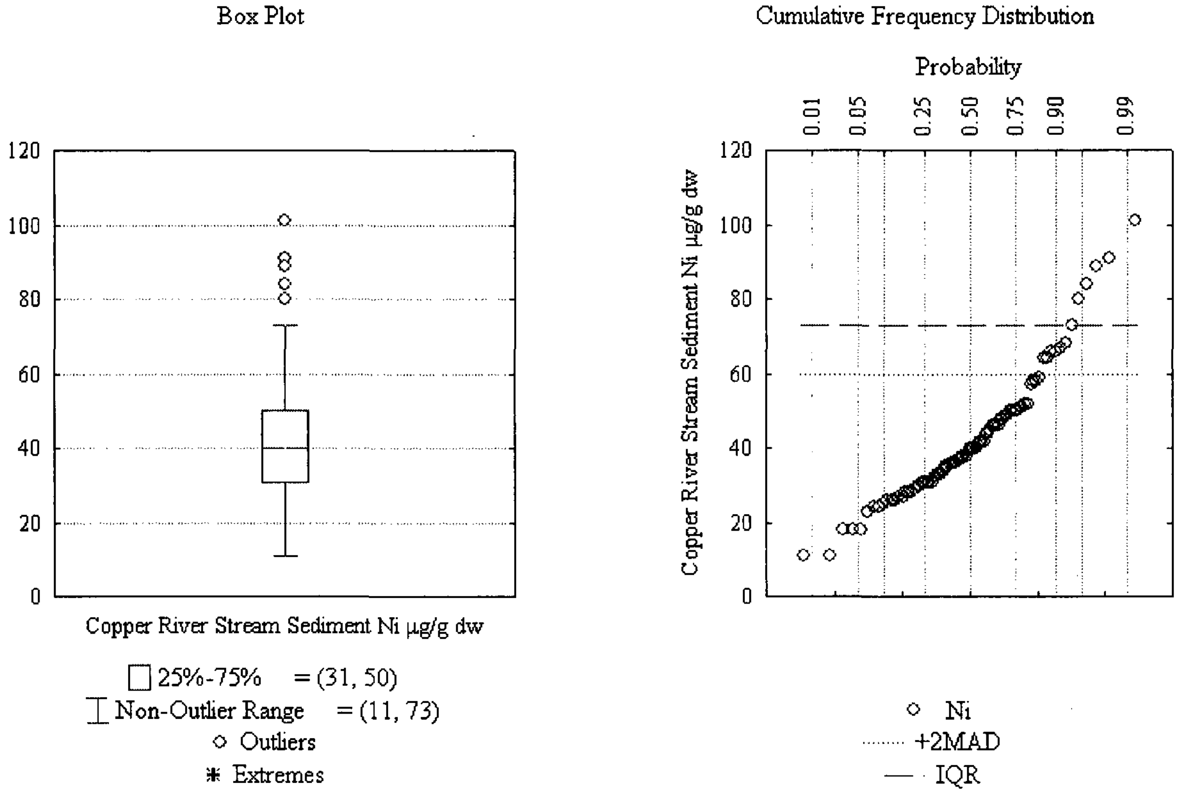


Figure 3-17: Copper River Stream Sediment Hg (µg/g dw)



Box Plot

Cumulative Frequency Distribution

Figure 3-18: Copper River Stream Sediment Ni (µg/g dw)

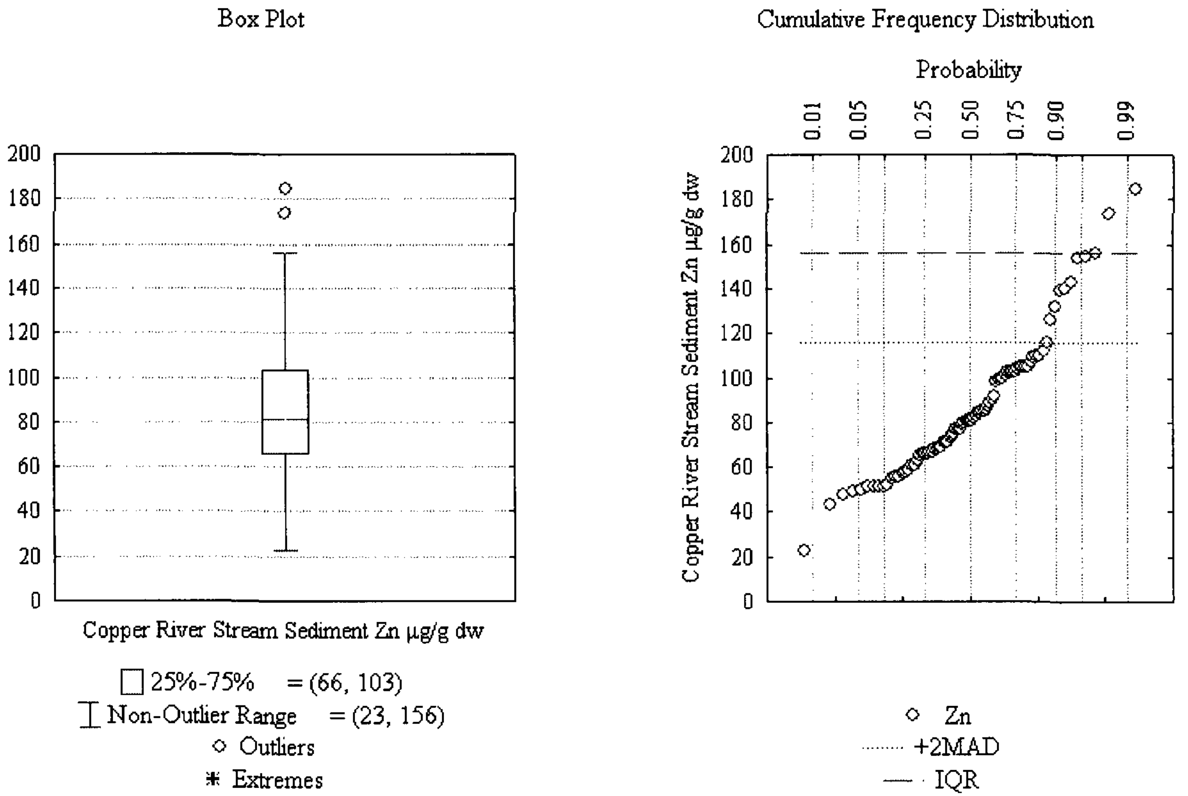


Figure 3-19: Copper River Stream Sediment Zn (µg/g dw)

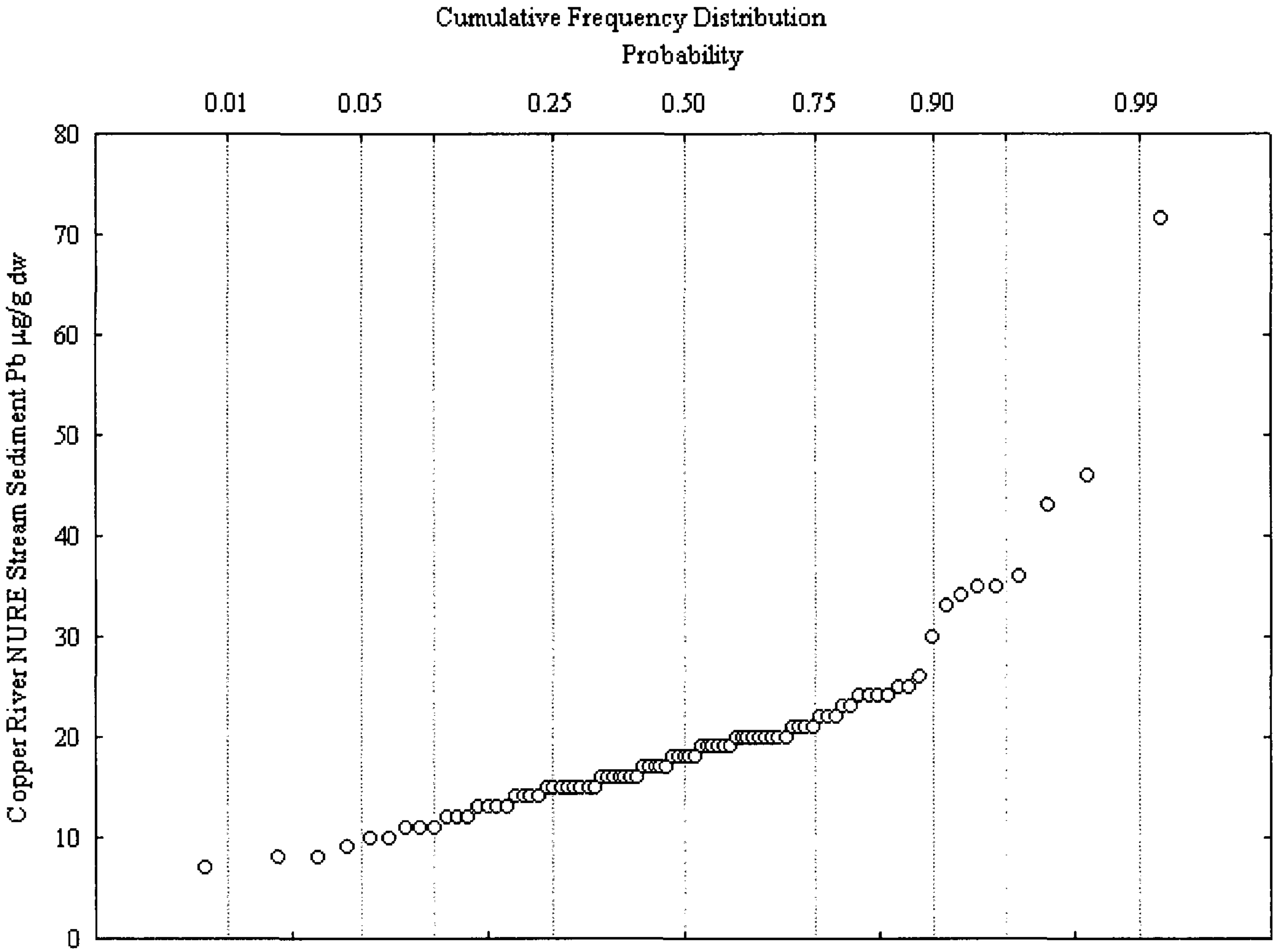


Figure 3-20: Copper River Stream Sediment Pb (µg/g dw)

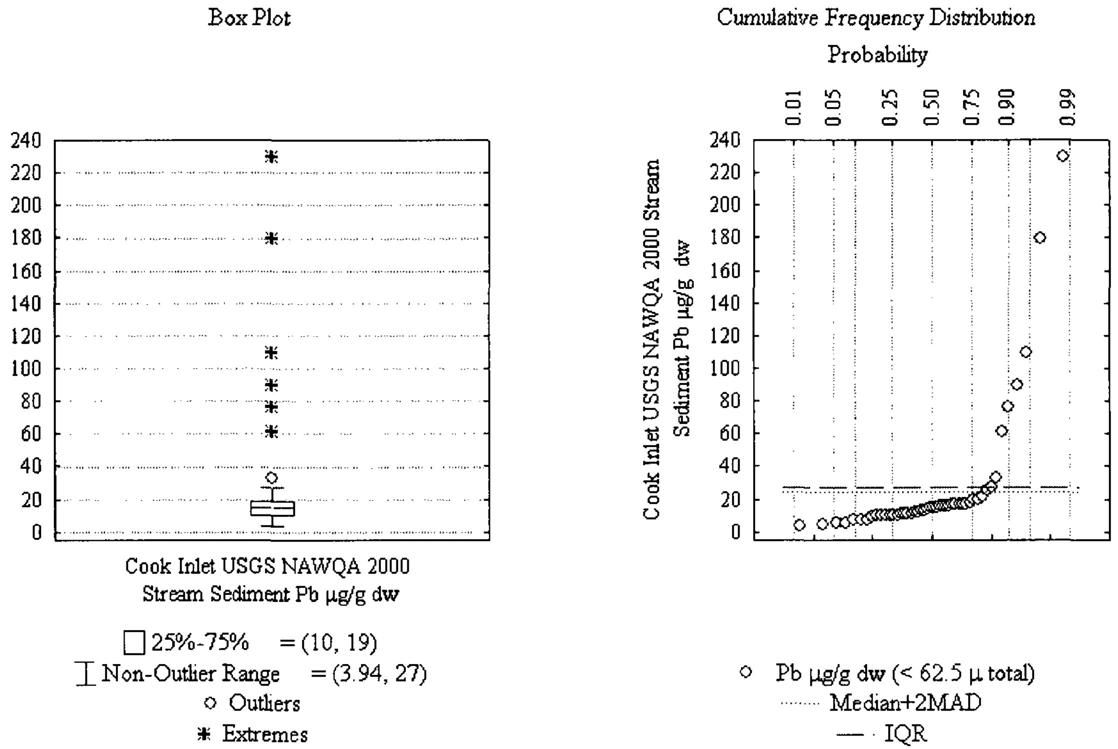


Figure 3-21: Box and cfd plots of 2000 United States Geological Survey National Water Quality Assessment Cook Inlet Stream Sediment Pb (µg/g dw)

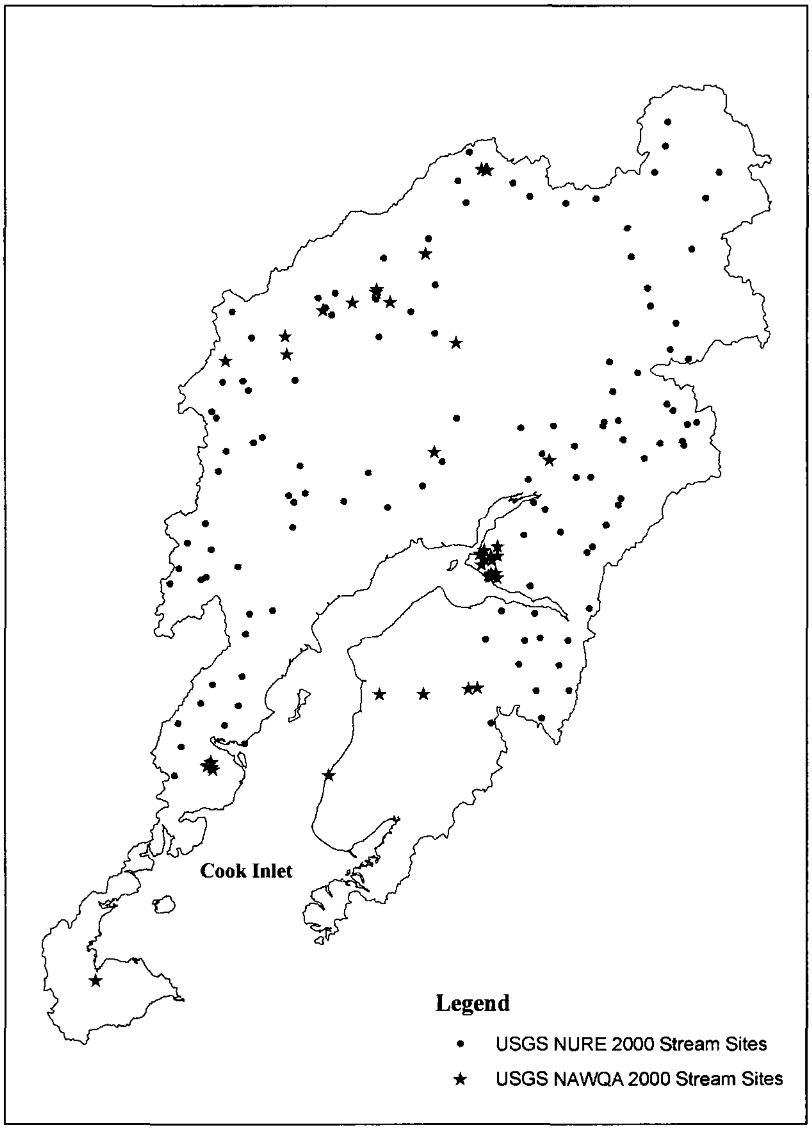


Figure 3-22: Cook Inlet United States Geological Survey National Uranium Resource Evaluation 2000 and National Water Quality Assessment Stream Stations

Chapter 4: A Method to Estimate Regional Natural Conditions for Trace Metals in Marine Sediments of Southcentral Alaska's Coastal Regions[3]

Abstract

Alaska's 40,000 km coastline remains relatively untouched by direct pollution, although hydrocarbon and mineral resource extraction and vessel wastewater discharges are increasing along the coastline. Sediments provide an integrated long-term signal for naturally occurring and anthropogenic chemicals—in this case, trace metals—in contrast to repeated water measurements, which can be highly variable. Establishment of sediment chemical, in this case trace metals, natural conditions is critical to detecting, understanding, and managing future environmental changes. Knowledge of natural conditions helps identify and place in context regional patterns of contamination. Natural condition values for sediment trace metals are assessed against risk-effects-based screening Effects Range Low and Effects Range Median values. Alaska can use its coastline's almost pristine condition to establish regional natural conditions for sediment trace metals. Natural conditions are based on the population distribution of the trace metals, which incorporates variations in grain size, trace and major elements, and total organic carbon. For As, Cr, Cu, Pb, Hg, Ni, and Zn, regional Southcentral Alaska sediment trace metal natural conditions based on probabilistic survey population estimates are developed.

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[3] Dasher, D.H. Regional Natural Conditions for Select Priority Pollutant Trace Metals in Stream Sediments in the Cook Inlet and Copper River, Alaska, Watersheds. Prepared for submission in Marine Pollution Bulletin, Elsevier.

1.0 Introduction

Alaska's 40,000 km of coastline remains relatively untouched by direct point or non-point sources of pollution, although hydrocarbon and mineral resource extraction, as well as vessel wastewater discharges, increasingly occur along the coastline. Indirectly, through anthropogenic greenhouse gas contributions or trans-boundary pollutants, human activities can impact Alaska's remote coastline (AMAP, 1998; State of Alaska, 2009; Sunderland et al., 2009; Landers et al., 2010). Coastal marine sediments represent a sink for many particle reactive dissolved and particulate trace metals and other chemicals of natural and anthropogenic origin, with concentrations generally exceeding those in the water column by several orders of magnitude (Förstner and Whittmann, 1979). Sediments provide an integrated long-term signal for naturally occurring and anthropogenically derived chemicals in contrast to highly variable "snapshot" water column measurements (Newman and Watling, 2007). Environmental monitoring programs use sediment because of its ability to concentrate contaminants of concern, linkage to the aquatic food web, and applicability to assessment of the spatial and temporal extent of contaminants distribution (Summers et al., 1996).

Assessment of the source of trace metals in sediments, either natural or anthropogenic, requires an understanding of the range of natural background variability. No standard procedure for determination of background exists, and an approach that works in one region may not work elsewhere (Daskalakis and O'Connor, 1995; Rodríguez et al., 2006). Ultimately, environmental agencies responsible for managing coastal marine ecological resources require sediment guidance based on pragmatism, as well as science (GIPME, 2000).

In regards to trace metals, the coastal regions of Alaska, remain generally pristine, with metal accumulation in the sediment from anthropogenic atmospheric, or oceanic transport typically too low to interfere with assessments of the natural variability of sediment trace metals (Boehm, 2001; Naidu et al., 2001). It is possible to identify localized point sources that may contribute significant anthropogenic trace metal sediment accumulation. Alaska has the opportunity to use the present almost pristine condition of the coastal resources to establish regional background levels for its resources. The State of Alaska Department of Environmental Conservation (ADEC) Water Quality Standards Criteria (18 AAC 70.9904(41)) define natural conditions as "any physical, chemical, biological, or radiological condition existing in a water body before any human-caused influence on, discharge to, or addition of material to, the water body" (ADEC, 2006). Establishment of natural conditions, combined with long-term trend assessment, is critical to detecting, understanding, and managing future environmental changes (Parr et al., 2003).

The Alaska Department of Environmental Conservation (ADEC) Water Quality Standards narrative criteria for the protection of the *Growth and Propagation of Fish, Shellfish, Other Aquatic Life, and Wildlife* states "There may be no concentrations of toxic substances in water or in shoreline or *bottom sediments*, that, singly or in combination, cause, or reasonably can be expected to cause, adverse effects on aquatic life….." (ADEC, 2007). Numerical sediment criteria are not addressed in the ADEC Water Quality Standards, which is consistent with the general scientific understanding that assessment of sediment toxicity must integrate biological, chemical, and physical factors (Newman, 1998; GIPME, 2000; Anderson et al., 2007; Newman and Watling, 2007). Sediment quality guidelines (SQGs) typically have been developed from correlations between total sediment metals concentrations and biological effects based on field observations or laboratory toxicity testing. A wide range of SQGs have been developed spanning several orders of magnitude for the same contaminant (Chapman et al., 1999; Buchman, 2008). One potential important limitation for Alaska, especially for the Arctic and sub-arctic regions, is the lack of data on benthic community responses to contaminants in sediments. Arctic environmental conditions, such as cold temperature, seasonal food constraints and the organism's physiological adaptation to these conditions, such as high-lipid content, slow growth rates, simple food chain webs, and antifreeze mechanisms, suggest possible differing sensitivity to contaminants compared with temperate organisms (King and Riddle, 2001; Chapman and Riddle, 2005a; Chapman and Riddle, 2005b; Olsen et al., 2007; Konovalov et al., 2010).

This paper establishes the groundwork for the development of a set of integrated sediment quality guidelines that are applicable to Alaska marine waters. The focus of this paper is on demonstrating a method for utilizing background reference conditions to establish sediment trace metal levels representative of natural conditions. Understanding sediment trace metal natural conditions helps regulators place natural condition and sediment quality guidelines in context, especially where natural conditions may exceed SQGs developed elsewhere (Vosnakis and Perry, 2009).

Alaska's first ADEC Alaska Monitoring and Assessment Program (AKMAP) sampling survey of its coastal regions began in 2002 as part of the United States Environmental Protection Agency (USEPA) National Coastal Assessment (NCA) (ADEC, 2005). Using a probabilistic design and a common core set of analyses and indicators to assess current aquatic resource status and trends, the NCA program seeks to establish the condition of coastal resources. The core set of parameters includes oceanographic and water quality parameters, sediment toxicity analyses, sediment chemistry, tissue chemistry, fish pathology, benthic community analyses, and fish community analyses (ADEC, 2005). Fiscal and logistical constraints required that the NCA for Alaska's 40,000 km of coastline be divided into five biogeographical provinces to be surveyed individually over time (Figure 4-1).

Sediment trace metal results from the 2002 AKMAP Coastal Southcentral survey (Saupe et al., 2005; Dasher, 2010a) and terrestrial stream sediment studies done in Cook Inlet and Copper River watersheds (Dasher, 2010b) provide the data sets used to develop regional sediment trace level natural conditions in the Southcentral coastal region. Specific trace metals assessed are As, Cr, Cu, Pb, Hg, Ni, and Zn, which are listed USEPA priority pollutants (USEPA, 2010) and have comparable regional background stream sediment trace metal concentrations developed from the United States Geological NURE 2000 study (Dasher, 2010b).

2.0 Southcentral Coastal Environmental Setting

The AKMAP Coastal Southcentral Alaska study area extends from Unimak Pass at the southwest extent of the Alaska Peninsula, to just east of Prince William Sound (Figure 4-2). Numerous inlets, fjords, bays, and estuaries adjacent to a steep mountainous topography characterize Alaska's Southcentral coastline. Two major estuaries are Cook Inlet, a large high-latitude tidal estuary, and Prince William Sound, a large semi-enclosed basin with restricted exchange of waters with the open ocean (Sharma, 1979).

Cook Inlet estuary covers more than 26×10^3 km^2 and is about 370 km long and 80 km wide (Sharma, 1979). It includes Kamishak and Kachemak Bays and Turnagain and Knik Arms. Tides combine with the bathymetry to create powerful currents in excess of 3 knots, which provide for robust water column mixing and sediment bed load movement. Prince William Sound, a nearly enclosed glacially carved embayment, covers over 3.6×10^3 km^2 with many tidewater glaciers, some of which produce large plumes of glacial sediments in the receiving fjords (Sharma, 1979). Prince William Sound is bordered on the west, north, and east by mountains, including the Chugach Mountains, which are the highest coastal range in the world. Bathymetry resembles the adjacent topography of the coastal mountains with a narrow, often rocky shelf nearshore and a shoreline that drops rapidly to considerable depths (Saupe et al., 2005).

Two major fluvial sediment inputs into the coastal region of Southcentral Alaska occur from the Cook Inlet and Copper River watersheds. In Cook Inlet the freshwater inputs create density-driven currents resulting in a net flow of water toward the mouth of Cook Inlet along the west side, introducing large amounts of glacial silt into the coastal Gulf of Alaska (Saupe et al., 2005). The input of annual suspended sediments into Cook Inlet exceeds 45.0×10^6 tonnes (t), principally the result of glacial erosion. Peak flow periods are May through September, with dramatic reductions in flow and suspended sediments in the other months (Brabets et al., 1999). The Copper River watershed covers approximately 62,160 km^2, and its numerous glaciers contribute approximately 77.2×10^6

t to $117.9\text{x}10^6$ t year^{-1}of fine-grained sediments and silts to the Gulf of Alaska (Feely et al., 1981; Milliman and Meade, 1983).

These riverine sediment inputs can be seen in Figure 4-3: a September 2002, true-color Terra/MODIS satellite image (NASA, 2010). The major riverine sediment plumes from the main Cook Inlet rivers and the Copper River are distinctly visible. The counterclockwise Alaska Coastal Current transports sediments from Copper River and Cook Inlet westward along the Gulf of Alaska shelf (Hood and Zimmerman, 1986). Carried northward on the Alaska Current from the Bering Glacier and others glaciers to the south, sediment input can be seen east of Kayak Island. A significant amount of sediment introduced by upper Cook Inlet rivers and the Copper River are transported and deposited hundreds of miles downstream into lower Cook Inlet and Shelikof Strait (Hein et al., 1977; Rember and Trefry, 2005).

2.1 Anthropogenic Inputs

The Cook Inlet watershed drains an area of $1.0\text{x}10^6$ km^2 (about the size of the state of Virginia) and includes the largest urban area in Alaska with a population of about 419,000, approximately two thirds of the entire population of the state (ADCRA, 2009; USCB, 2009), During the summer season this basin has a transient visitor population of about 900,000 (USFS, 2008). The potential for nonpoint pollution runoff is greatest in this watershed. Other potential sources of water quality stressors in this watershed include onshore and offshore oil and gas exploration and production, municipal discharges, mining waste, vessel traffic, fish processing discharges, as well as numerous smaller industries.

Prince William Sound receives low quantities of year-round wastewater discharge from small communities bordering the sound. Mining activities are few, though several Fe, Cu, and Zn sulfide mineral deposits have the potential to leach trace metals to the region (USGS, 1996). The principal anthropogenic impact to this region was the Exxon Valdez oil spill in 1989.

3.0 Materials and Methods

3.1 Sampling

The U.S. EPA's Office of Research and Development in conjunction with the Alaska Department of Environmental Conservation developed the Southcentral Alaska sampling design in 2001. The objective was to estimate with known uncertainties the condition of the coastal resources within the area of interest (target population). This was accomplished through a probability sampling design that uses a relatively small number of samples to make inferences about a large population (Lohr, 1999). All coastal bays and estuaries in the defined region (Figure 4-2) encompassed the target population, and a probabilistic sampling methodology was used to locate stations. Sampling sites were generated by overlaying the region with six classified hexagon grid sizes that provided each coastal bay and estuary an equal chance of being selected. A GIS data layer for the target population, which is the aquatic resource (estuaries) projected for surveying, was developed, and a series of programs running under ARCView© was used to randomly select base sites and alternative sites (Stevens and Olsen, 1999). Further information on EMAP sampling and methodology can be found at the USEPA Aquatic Resource Monitoring website (USEPA, 2009) and in Dasher (2010a).

Fifty-five (55) stations in the Southcentral region were surveyed between June 14 and August 02, 2002 (Figure 4-2). The latitude, longitude, and the visually descriptive sediment texture are listed for each sample station in Table 4-1. The areal coverage of the sampled estuary population, a subset of the Target Population excluding the portion that could not be sampled due to weather or other conditions, is approximately $67.8\text{x}10^3$ km^2. A single sample was collected at each station during the summer sampling period. All samples were collected and analyzed in a consistent manner, creating spatial estimates of condition with a known level of uncertainty, and the results can be compared across the United States to create a "snapshot" of coastal conditions (USEPA, 2001a). Results were statistically summarized using the estimated population mean, standard deviation, median, and cumulative-area-based 95% lower and upper confidence bounds for the selected sediment trace metals (Table 4-2).

The Field Operations Manual (USEPA, 2001b) and the National Coastal Assessment Quality Assurance Plan 2001 – 2004 (USEPA, 2001c), with exceptions noted in the specific regional scope of work, were followed (Saupe et al., 2005; Dasher, 2010a). Sediment samples were collected with a 0.1 m^2 Van Veen sampler thoroughly washed with LiquiNox™ detergent and rinsed with ambient seawater prior to use, though not between grab samples at the same location. The macroinvertebrate sample was taken from the first acceptable grab, with subsequent grabs composited for sediment chemistry, including trace metals, total organic carbon, sediment toxicity, and sediment grain size. The well-mixed composited sediment samples were placed in appropriately clean containers and either frozen or refrigerated.

3.2 Analytical Techniques

Analysis of the sediments for trace metals, grain size, and total organic carbon (TOC) was done by the State of Washington Department of Ecology's Manchester Laboratory. Grain size analysis was done by wet and dry sieving, with a pipet technique used for the silt-clay fraction (USEPA, 2003). TOC was analyzed by USEPA Standard Method 415.1. Samples for total mercury underwent digestion and were analyzed following USEPA Method 245.5 Cold Vapor Atomic Absorption. Remaining sediments for trace metal analysis were digested following USEPA Method SW-846-3052 (microwave) total digestion, except for tin, which was digested following SW-846-3050 partial digestion. The digestion vessel used for Method 3052 leached low levels of tin into the blank, but this problem was resolved by using Method 3051. USEPA Method SW-846-6010, Inductively Coupled Plasma (ICP)–Atomic Emission Spectrometry, and USEPA Method SW-846-6020, ICP–Mass Spectrometry, were used for the trace metal analysis. All analyses were performed within established USEPA holding times and met the QC performance requirements established in the Data Quality Objectives (DQO) for the West Coast USEPA Environmental Monitoring and Assessment Program (USEPA, 2001c).

3.3 Regional Natural Condition Methodology

Large areas of the Southcentral coastal region have little in the way of disturbance measures, such as population density, domestic and industrial discharges, or physical habitat alteration in relation to significant anthropogenic trace metal inputs (Boehm, 2001). A large part of the coastal region contains reference sites for sediment trace metals, thus allowing for inferences of natural condition from probabilistic survey sampling.

First, cluster analysis was used to assess if similarities or groupings existed between sampling stations, and correlation analysis was conducted on the variables to assess potential associations. These results were later evaluated along with Enrichment Factors (EF) used to screen the sediment trace metal results for anomalous levels. Then anomalous findings were assessed further by overlaying the corresponding sites on geochemical and population maps to evaluate potential anthropogenic sources of contamination. Only anomalous values based on existing GIS information indicating human influence or nearby ore bodies were removed.

Second, the probabilistic survey sampling design provided estimates with uncertainty, of the spatial extent of the resource—in this case estuarine area (km^2)—against a continuous variable, such as trace elements (Diaz-Ramos et al., 1996). With the anomalous values removed and the sampled population size readjusted, the population distribution of sediment trace metal concentrations in Southcentral estuaries was statistically summarized. These summaries included cumulative percent area estimates of trace metal concentrations in the sediment samples with 95% lower (LCB) and upper confidence bounds (UCB).

3.3.1 Cluster and Spearman Rank Correlation Analysis

With hierarchical cluster analysis, using Ward's method with Euclidean distances, the Southcentral Coastal Alaska standardized sediment trace metal results were examined to evaluate if similarities existed between the sampled station locations and trace metals (Romesburg, 2004). The As, Cr, Cu, Hg, Ni, Pb, and Zn concentration values were standardized to equalize the weight between values, such as Zn and Hg, so that they all contributed more equally to similarities of the trace metals. Standardization was accomplished by applying the following equation (Romesburg, 2004):

$$Z_{\mathrm{mj}}=(X_{\mathrm{mj}} - X_{\mathrm{M}}) \div S_{\mathrm{M}}$$

In this equation, Z_{mj} is the standardized unitless value for the attribute, X_{mj} is the attribute, X_{M} is the attribute mean, and S_{M} is the attribute standard deviation. The resulting station clusters (i.e., groups of stations with similar trace metal concentrations) were examined for potential relationships with sources of anthropogenic or high-grade ore bodies.

In addition, relationships among trace metal concentrations, TOC, and %clay were examined using pairwise non-parametric Spearman rank correlations (Sparks, 2000). Statistica™, Version 8, by StatSoft (2008) was used for the statistical calculations.

3.3.2 Enrichment Factors

Enrichment factors (EF) are frequently used to distinguish between natural and anthropogenically enriched elements in air, sediments, and water (Zoller et al., 1974; Blaser et al., 2000; Zhou et al., 2007). Conceptually this has been expressed for sediments as (GIPME, 2000):

$$\mathrm{EF} = (\mathrm{M/N})\ \mathrm{obs} / (\mathrm{M/N})\ \mathrm{nat}$$

(M/N) obs: metal to normalizer ratio for sediment sample.

(M/N) nat: metal to normalizer ratio for natural conditions.

Lacking regional data, the background (M/N) nat ratio is based generally on crustal element values (Wedephol, 1995; Blaser., 2000). Global crustal values vary between reference sources used, vary in uncertainty, may differ greatly from regional lithological rock values, and do not represent surficial materials modified by biogeochemical cycles (Salminen and Gregorauskienė, 2000; Reimann and Carita, 2005 ; Galuszka, 2007). If natural conditions are available for the region, they are preferred to the use of crustal values (Blaser et al., 2000) In this study regional natural condition stream sediment trace metal values based on upper estimates of the natural condition range were obtained from an assessment (Dasher, 2010b) of the 1970s National Uranium Resource Evaluation (NURE) (Table 4-3). The NURE stream sediment trace metal values were *a prior* normalized by sampling only the ≤ 149 µm grain size. The Southcentral marine sediment closest reported grain size to the ≤ 149 µm grain size was ≤ 125 µm. Southcentral AKMAP sediment trace metal values were normalized for calculating EF values by dividing by the ≤ 125 µm sediment grain size percentage. Enrichment Factors were calculated only for the trace metals Cr, Cu, Pb, Ni and Zn, which showed strong correlation with the ≤ 125 µm sediment grain size.

Cook Inlet natural condition stream sediment trace metal concentrations from Table 4-3 were used for all sites within the inlet; Copper River values were used for Prince William Sound and the south side of the Kenai Peninsula. For Shelikof Straits and the lower Southcentral Alaska Peninsula, Cook Inlet and Copper River natural condition values were weighted averages. The weighted averages were based on an estimated sediment deposition mix to Shelikof Strait: 80% Cook Inlet and 20% Copper River (Boehm, 2001). These stream sediment natural conditions represent box plot upper inter-quartile range (IQR) values based on regional samples with no significant anthropogenic sources. The IQR value represents an upper limit that takes into account the variation of trace elements in the stream sediment materials. Using the IQR value is more appropriate in representing natural conditions, which are a range of common values, rather than means, which should only be applied to normally distributed populations, or median values (Salminen and Gregorauskienė, 2000). This rationale is frequently applied in environmental remediation, where background threshold values computed on a range of values are applied to determine if remediation site concentrations are comparable to background (Singh et al., 2007).

Variation in biogeochemical processes, use of average crustal values versus other types (soil) or local values, and large variation in normalizing element equal to or larger than the observed element of interest contribute to significant variation in EF values, even with little or no anthropogenic influences (Reimann and Carita, 2005). In practice, Enrichment Factor cutoff values are arbitrary, ranging from 1 to 500 (Reimann and Carita, 2005), depending upon the professional judgment. In this paper the EF method is applied as a qualitative or comparison reference not as an inference to differentiate anthropogenic or natural element sources. An EF value of five was chosen to identify anomalous metal concentrations because such a small enrichment may occur easily from field sampling or measurement errors, or from local variations in mineralogy and biogeochemical processes. Levels exceeding an EF of 5 are evaluated by mapping the results against known geological and anthropogenic sources. Figure 4-9 presents graphs for the locations where the EF values were > 5.

3.3.3 Geochemical Mapping

ARCView© was used to map the sample stations and trace element data for comparison with known geologically enriched sites and potential anthropogenic sources. An example is the region around site AK02-005 (Figure 4-4), which was identified as hosting ultramafic plutonic rock, rich in chromite (Wilson et al., 2009).

3.3.4 Natural Condition Threshold Estimates

Development of defensible and representative natural conditions requires a careful assessment and removal of any anomalous values that are the result of anthropogenic input or extremely high natural anomalous values. Removal of potentially anomalous values that cannot be associated with anthropogenic inputs or high (ore body related) values is discouraged to keep subjective decisions to a minimum (Grant and Middleton, 1998).

Once anomalous values are removed, cumulative distribution functions (CDFs) are calculated for each of the trace metals to assess the cumulative percentage of the overall area with concentrations below a given value (Diaz-Ramos et al., 1996).

Percentile estimates, with lower and upper confidence bounds, of trace metal concentrations in the sampled population are also calculated. Calculations were done utilizing the R: Programming Environment for Data Analysis and Graphics and the U.S. USEPA spatial survey design and analysis R package (USEPA, 2009).

Grain size had strongest correlation with Cr, Cu, Pb, Ni, and Zn. The population estimate of the distribution of grain size and 95% upper and lower confidence bounds (the fit has been smoothed using a least-squared-distance method in Statistica™ statistical software) and a scatter plot of Cu and percentage fines is shown in Figure 4-5.

Background threshold values (BTV) for contaminants of potential concern or not-to-exceed values are often estimated from reference site data, with these upper limit values used for point-by-point versus natural condition (Singh et al., 2007). One method used by USEPA to estimate background levels is to estimate an upper threshold level, generally a 95% confidence limit of the 95% percentile of the distribution of the contaminant of concern (Singh et al., 2007). R-package "spsurvey" can provide a table output containing percentile estimates of the trace metal concentrations with estimated population values and lower and upper confidence bounds.

3.3.5 Sediment Quality Guidelines

The development of natural conditions does not address potential biological effects of the sediment trace metals. As ecosystems co-exist with sediment trace metal concentrations they may adapt to elevated natural sediment trace metal concentrations (Klerks and Weis, 1987), but it is informative to compare the estimated values for natural condition against NOAA Effects Range Low (ERL), Effects Range Median (ERM), and Apparent Effects Thresholds (AET) sediment quality guidelines.

The ERL and ERM screening guidelines are based on scientific literature reports correlating sediment chemical concentrations with observed biological effects (Long et al., 1995). Resulting sediment chemical concentrations—for the sediment contaminant of interest— are placed in rank order, with the ERL and ERM represented respectively, by the 10th and 50th percentile. Correlation does provide some indication of potential toxicity, but it cannot provide a cause effect basis for actual toxic effect of the contaminant at the measured concentration (Borgmann, 2003). Bioavailabilty of the trace metal, which may be tightly bound to the sediment clay or organic portion, also influences whether the observed concentration will exhibit toxicity (Presley, 1997). The ERL and ERM both represent potential sediment toxicity, but they are not predictive of actual toxic biological effects in any particular sediment, especially if used by themselves (O'Connor, 2004). The ERL and ERM are used here as qualitative assessment points to help focus future assessment or toxicity research efforts.

Apparent Effects Thresholds are another benchmark based upon empirical relationships between sediment concentrations and observed toxicity bioassay results or observed benthic community impacts (Buchman, 2008). For each contaminant, paired observations are ranked in increasing concentrations. The highest concentration associated with a nontoxic sample then sets the AET value, so only toxic samples are observed at higher concentrations. Note, however, that toxic samples may also have been observed at values below the AET. AETs are applied as a set, so that a single analyte exceeding its AET would be predictive of adverse impacts. Separate AETs have been developed for specific bioassay endpoints (species) and for benthic community impacts. AETs were originally developed using marine data; however, freshwater values have subsequently been calculated as well.

4.0 Results and Discussion

4.1 Anomalous values

The sediment trace metal cluster analysis tree, also known as a denogram, is shown in Figure 4-6. Because the focus is on determining clusters over a broad region the resulting denogram after a visual examination was cut at a linkage distance of ten (Romesburg, 2004). Two primary cluster groups I and II are present, with a third, Station AK02-005, a single isolated station with Cr and Ni sediment concentrations approximately 10 times greater than any other station. For AK02-005 no other cluster grouping when plotted on regional geochemical, mining, and population maps was associated with direct anthropogenic inputs or known ore bodies.

Only Spearman correlations with $p \leq 0.05$ are shown; those ranked as strong for this study ($p \leq 0.05$ and $r > 0.7070$) are shown bold in Table 4-4. The resulting strong correlations between percentage clay (< 3.9 μm) and Cr, Cu, Pb, Ni, and Zn, support the importance of clay size particles role in partitioning these trace metals in the sediment matrix. Total organic carbon did not exhibit any strong correlations with trace metals, suggesting that it plays a minor role in the sequestration of metals. Neither As nor Hg exhibited strong correlations with percentage clay or TOC, a finding similarly noted in other regions of Alaska (Naidu et al., 1997).

The sites with EF > 5 are shown in Table 4-5. For AK02-005, As, Cr, Ni have EF values > 5, with As having the lowest value of 8. For this site, Cr and Ni had high EF values of 186 and 202, respectively. This site is bounded by a chromite deposit (Figure 4-4) within the Kenai Peninsula region noted for other rich chromite deposits, such as Red Mountain (Gill, 1922). Previous mining of this chromite ore at Chrome Bay in the 1920s may have provided some waste ore to the bay, but natural outcroppings of chromite ore exist on land and are also likely submerged. These outcroppings and submerged material suggest that Cr and Ni enriched sediment is natural, though likely enhanced by mining activity. In the cluster analysis, this site was clearly separated from all the other sites, indicating a unique trace metal composition. Site AK02-0021 has EF values > 5 for Cr, Pb, Hg, Ni, and Zn, but no value exceeds 12. This site represents an anomaly in that it has the lowest percentage material less than 125 μm, but these fines appear to provide a proportionally higher Cr, Pb, Ni, and Zn contribution to the sediment trace metal loading than do other samples. No known anthropogenic source for these trace metals exists in the region around this site, though it is possible that subsea ore bodies may exist in this region adjacent to the Kenai Peninsula chromite deposits. The values are low and lack defined anthropogenic or high grade ore body confirmation. In the Shelikof Strait, Kodiak Island, and lower Western Alaska Peninsula regions, only site AK02-009 within the Kodiak Island group had EF values > 5 for Pb and Zn, which did not exceed 6. No nearby anthropogenic or ore body sources were documented. Finally, within the Prince William Sound sample no EF values exceeded 2.

Site AK02-005 is the only site at which documented, significantly elevated levels of Cr and Ni could be directly related to a high-grade ore body. No other sites had documented, nearby anthropogenic sources or high-grade ore bodies. This site was removed as anomalous from further analysis, and the remaining sites are retained as reference sites for further assessment. The Chrome Bay polygon in the sample design only covers a little over 1 km^2, and the adjusted estuary sampled population area with Chrome Bay removed is almost unchanged at 67,825 km^2.

4.2 Regional Natural Conditions Threshold

The remaining sample stations' sediment trace metal concentrations are considered to represent reference sites suitable for development of a regional natural condition. Population estimates of sediment trace metal concentration values and confidence bounds for the cumulative area 25%, 50%, 75%, and 90% quartiles are shown in Table 4-6. The sampled estuary population cumulative area 90% Upper Confidence Bound (UCB) 95% values, hereafter referred to as 90% UCB 95%, are the proposed regional natural condition threshold values for use by environmental managers determining if further assessment effort is warranted. One caveat is that the 90% UCB 95% sediment trace metal values must be compared to samples taken with similar field sampling and analytical procedures. The sediment samples taken in our work are processed for analysis with a total digestion method and cannot be directly compared with methods using partial digestions (Loring et al., 1991).

4.3 Sediment Quality Guidelines

The median value (50%) and the 90% UCB 95% values for reference site trace metal data sets, with an anomalous site removed for Cr and Ni, are compared with the widely used sediment quality guidelines ERL and ERM and the AET in Table 4-7. The 90% UCB 95% concentrations for As, Cr, and Cu exceeded their ERL values by 89%, 28%, and 43%, respectively. Nickel 90% UCB 95% concentration exceeded both the ERL and ERM. Nickel in suspended sediments of the Copper and Susitna Rivers is reported with a range of 35 – 77 µg/g (Boehm, 2001), and 83 µg/g was observed in mudflat sediments in Port Valdez (Feder et al., 1990). Other regions along the US West Coast have also reported elevated levels of Ni occurring naturally (Meador et al., 1998). Stream sediment means for As and Cu in both Cook Inlet and Copper River watersheds exceeded the ERLs. This is consistent with Frenzel (2000), who found elevated concentrations of As, Cr, Cu, and Ni in the Cook Inlet watershed. Regions of Cook Inlet contain areas with ultramafic rock containing chrome ores that are also rich in Ni (Gill, 1922). Prince William Sound and Copper River watersheds contain rich deposits of Fe, Cu, and Zn sulfide minerals in and near plutonic rocks (USGS, 1996). Elevated As levels can be related to arsenopyrite, which is usually associated with gold-bearing quartz veins in this region. Volcanic ash can also contribute to elevated levels of As (Smichowski et al., 2003).

4.4 Application - Kachemak Bay Sediment Trace Metals

The 90% UCB 95% trace metal concentrations are applied to the results of a recent NOAA NS&T 2007 study in Kachemak Bay (Hartwell et al., 2009, Figure 4-7). Arsenic exceeds the 15.5 µg/g dw 90% UCB 95% in 21 of the 34 sampled sites (Table 4-8). Only one of the three sites within Homer Harbor, an area defined as stressed because of physical sedimentation and chemical contamination, exceeds the 90% UCB 95% for As. In the Cook Inlet region, As is commonly found in stream sediments at levels exceeding the ERL and at times the ERM with a mean of 19.6±28 µg/g dw (Dasher, 2010b). Arsenic distribution and concentration appear to be related to numerous mineral resources, such as arsenopyrite typically located with gold bearing deposits, volcanic activity, associations with clay particulates and other factors common to the Cook Inlet Region (USGS, 2001). Neither percentage fines nor total organic carbon showed significant Spearman rank correlations within the larger AKMAP Southcentral or the NS&T Kachemak Bay study. It is hypothesized that As was present as the mineral arsenopyrite and that its distribution was dependent upon distance from the source, but further work was not done to test this hypothesis. Nothing suggests a significant source of anthropogenic As for Kachemak Bay.

Copper exceeds the 48.6 µg/g dw 90% UCB 95% level at all three Homer Harbor sites (HH-1, HH-2, HH-3) and at the Eastern Flat (EF-4) site. Copper is above the SQG ERL and is 23% of the ERM value. Zinc also exceeds the 129 µg/g dw 90% UCB 95% level for the same sample set, with Zn exceeding the SQG ERL and representing 37% of the ERM value. Homer Harbor and site EF-4 have the higher- percentage fines (>80%) compared to the other Kachemak Bay sites. The similarities in Cr, Cu, Pb, and Ni levels among these sites are likely partially related to the percentage fines.

The NS&T study noted that site HH-3 appeared stressed and had a paucity of invertebrate species found in the sediments. Cirratulids, a marine worm tolerant of physical disturbances, is the principal macroinvertebrate in Homer Harbor, with densities as high as 12,625 per square meter at site HH-3 (Hartwell et al., 2009). Copper and Zn have significant anthropogenic sources within boat harbors from the antifouling paint used on boats and many marine structures (Turner, 2010). While the individual toxicity of Cu is low, there is evidence that added Zn can increase Cu toxicity (Watermann et al., 2005). In the future, Cu and Zn in Homer Harbor sediments should be sampled periodically to see if the level responds to actions taken under Alaska Best Management Practices for Harbor, Marina, and Boat Operations guidance (ADNR, 2010).

5.0 Conclusion and Recommendations

Alaska and other similar regions around the world have a pristine or at least a minimally human-disturbed environment at the present time, but they face increased population growth and resource extraction activities. A short period of time remains to obtain a baseline of natural condition for sediment trace metals, other contaminants, and biodiversity. The approach in this paper is to use the fact that a large proportion of the marine coastline remains pristine coupled with a probabilistic sampling survey method to provide population estimates of the measured variables.

The proposed methodology consists basically of three steps: (1) develop and implement a well-thought-out probabilistic sampling survey of a target population with 50 or more target sites; (2) analyze data using a combination of Enrichment Factors with environmental and geochemical mapping to assess and remove anomalous values representing anthropogenic and nearby ore body origin; (3) utilize the remaining reference sites, assuming at least 60% of the sites remain as reference sites, and calculate population estimates for the cumulative area 90% UCB 95% sediment trace metal of concern to establish an upper threshold value for regional natural conditions.

Before applying any derived estimate of a threshold natural condition, environmental managers must understand the survey design, scale, analytical methods and statistical analysis used (Reimann et al., 2005; Reimann et al., 2008). The survey presented in this paper provides a context for comparison of smaller scale probabilistic or targeted survey scale studies. It is important to determine the analytical techniques employed as the resultant threshold natural condition generally will not be valid when different techniques have been utilized. No matter what methodology is used, resulting values are only qualitative in nature and not "true" values, even with statistical estimates of variability (Matschullat et al., 2000).

This study has established natural condition marine sediment trace metal levels for the Alaska Southcentral region. The significance of these levels from an ecotoxicological perspective remains to be established. Bioavailability of the trace metals in the sediments has not been determined. In addition, while some sediment trace metals are naturally elevated relative to a SQG, such as ERL and ERM, these levels have been present in the ecosystem for a long time; it is likely that the resident biological populations have adapted to the observed trace metal concentrations (Klerks and Weis, 1987; Bahrndorff et al., 2006). If no retrospective studies can be utilized, future studies are imperative if Alaska is to have relevant SQGs for arctic and subarctic conditions.

Finally, while this work provides a regional population based estimate of natural for sediment trace metals, it is cautioned that a rapidly evolving climate may be presenting us with an ecosystem already in a state of flux.

Acknowledgments

This study was supported by the U.S. Environmental Protection Agency Office of Research and Development through Cooperative Agreement # R-82911501. Walt Nelson, Dixon Landers, Tony Olsen and others with USEPA ORD enthusiastically supported our efforts and understood the importance of this pioneering endeavor in Alaska. Ms. Sue Saupe, scientific director with Cook Inlet Regional Citizens Advisory Council (CIRCAC) was instrumental in the implementation, field work, and reporting on the Southcentral Coastal survey. Thanks for the constructive comments and suggestions provided by Drs. John Kelley, Franz Mueter, Sathy Naidu, Larry Duffy and Robert Perkins and others of the University of Alaska Fairbanks.

This document has not been subjected to CIRCAC, ADEC, or USEPA internal institutional peer review and/or administrative review and does not necessarily reflect these organizations' views, nor does any mention of trade names or commercial products constitute endorsement or recommendation.

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Tables

Table 4-1: Sample Station Locations and Sediment Description

AKMAP Station ID[1]	Sample Depth, Meters	Latitude Degrees[2] North	Latitude Minutes North	Longitude Degrees[2] North	Longitude Minutes North	Visual Descriptive Composition
AK02-0002	4.3	60	12.580	152.00	44.305	Silt/Clay
AK02-0003	3.9	59	49.752	153.00	7.701	Silt/Clay
AK02-0004	65.0	59	37.232	151.00	14.851	Silt/clay
AK02-0005	4.5	59	12.579	151.00	49.343	Gravel
AK02-0007	72.0	58	23.301	152.00	58.886	Fine sand
AK02-0008	24.0	57	58.581	154.00	57.378	Mixed
AK02-0009	102.0	57	58.851	153.00	4.258	Sand
AK02-0010	24.0	57	42.525	155.00	34.034	Silt/Clay
AK02-0011	9.2	61	1.954	151.00	14.259	Sand
AK02-0012	4.0	60	42.169	151.00	51.588	Sand
AK02-0015	5.2	60	29.976	151.00	57.831	Fine Sand with Silt
AK02-0016	12.0	60	14.971	151.00	31.653	Mixed
AK02-0017	39.0	60	2.504	152.00	24.008	Mixed
AK02-0019	87.0	59	17.379	152.00	50.526	Fine Sand
AK02-0020	30.0	59	6.482	153.00	33.131	Silt/Clay
AK02-0021	116.0	59	8.723	152.00	19.847	Coarse Sand
AK02-0022	8.0	59	6.251	154.00	9.753	Silt/Clay
AK02-0023	130.0	59	5.294	153.00	5.281	Silt/Clay
AK02-0024	168.0	58	47.094	152.00	49.042	Silt/Clay
AK02-0026	155.0	58	30.316	152.00	49.976	Silt/Clay
AK02-0027	182.0	58	5.412	153.00	30.145	Silt/Clay
AK02-0028	215.0	57	55.568	154.00	17.451	Silt/Clay
AK02-0029	232.0	57	51.151	154.00	33.132	Silt/Clay
AK02-0030	274.0	57	37.170	155.00	11.169	Silt/Clay
AK02-0032	25.9	60	54.930	147.00	48.460	Silt
AK02-0034	125.0	60	43.650	148.00	38.362	Silt/Clay
AK02-0035	148.0	60	14.696	148.00	17.708	Silt/Clay
AK02-0036	206.0	61	8.366	147.00	52.837	Mixed
AK02-0038	5.4	60	48.686	148.00	1.881	Mud

Table 4-1: Sample Station Locations and Sediment Descriptions (Continued)

AKMAP Station ID[1]	Sample Depth, Meters	Latitude Degrees[2] North	Latitude Minutes North	Longitude Degrees[2] North	Longitude Minutes North	Visual Descriptive Composition
AK02-0040	19.0	60	42.699	146.00	21.684	Mixed
AK02-0041	232.0	60	44.467	148.00	1.510	Silt/Clay
AK02-0045	325.0	60	10.081	147.00	52.689	Silt/Clay
AK02-0046	23.9	60	55.491	147.00	19.252	Mixed
AK02-0050	282.0	60	39.511	146.00	46.194	Silt/Clay
AK02-0051	122.0	60	35.413	146.00	18.771	Silt/Clay
AK02-0053	219.0	60	30.647	147.00	7.220	Silt/Clay
AK02-0054	120.0	60	35.320	146.00	39.319	Silt/Clay
AK02-0055	158.0	60	29.552	147.00	27.052	Silt/Clay
AK02-0056	352.0	60	32.351	146.00	58.763	Silt/Clay
AK02-0058	138.0	60	18.383	147.00	39.258	Mixed
AK02-0059	181.0	60	2.454	147.00	42.030	Mixed
AK02-0060	72.0	59	54.667	148.00	19.902	Mixed
AK02-0061	30.0	60	14.614	145.00	34.028	Silt/Clay
AK02-0062	56.0	60	15.446	145.00	44.824	Silt
AK02-0063	117.0	59	48.546	149.00	32.924	Silt/Clay
AK02-0064	210.0	59	23.507	150.00	30.267	Silt
AK02-0065	129.0	58	27.442	152.00	21.762	Silt/Clay
AK02-0067	12.5	57	11.780	153.00	12.510	Mixed
AK02-0068	94.0	57	3.751	153.00	34.540	Silt/Clay
AK02-0070	132.0	56	25.245	158.00	13.515	Silt/Clay
AK02-0071	128.0	55	59.506	158.00	35.517	Silt/Clay
AK02-0072	32.0	55	32.259	161.00	34.324	Mud
AK02-0073	26.0	55	22.358	160.00	37.363	Fine Sand with mud
AK02-0074	17.0	55	4.521	163.00	8.539	Sand
AK02-0075	62.0	55	9.064	160.00	25.995	Sand

1–The AKMAP Station ID integers are the site locations numbers referred to in Figure 4-2.

2–Latitude and Longitude are referenced to North American Datum 27.

Table 4-2: Estimated Population Mean, Standard Deviation, Median, and their 95% Lower Confidence Bounds (LCB) and Upper Confidence Bounds (UBC) (µg/g dw)

Trace Metal µg/g dw	N	Mean	Mean		Std. Deviation	Std. Deviation		Median	Median	
			LCB95%	UCB95%		LCB95%	UCB95%		LCB95%	UCB95%
As	55	8.83	8.11	9.55	2.85	2.54	3.16	9.00	7.86	9.87
Cr	55	61.39	56.87	65.91	20.68	18.48	22.87	60.28	43.92	71.40
Cu	55	30.27	28.17	32.37	10.65	9.46	11.85	29.39	23.82	34.38
Pb	55	12.18	11.68	12.67	2.44	2.07	2.81	12.25	11.43	12.55
Hg	53	0.06	0.05	0.07	0.03	0.02	0.04	0.05	0.04	0.06
Ni	55	29.55	25.35	33.75	14.77	8.76	20.78	25.96	21.41	32.13
Zn	55	82.31	77.66	89.96	22.24	19.08	25.04	78.38	68.67	86.09

Table 4-3: Cook Inlet and Copper River Watersheds Stream Sediment Regional Natural Background Condition (μg/g dw) Inter-Quartile Range (IQR)

Cook Inlet	IQR	Copper River	IQR
As	39	As	55
Cr	139	Cr	133
Cu	101	Cu	92
Pb	46	Pb	30
Hg	0.31	Hg	0.25
Ni	73	Ni	73
Zn	166	Zn	156

Table 4-4: Spearman Rank Correlation Analysis

Analyte	**As**	**Cr**	**Cu**	**Pb**	**Hg**	**Ni**	**Zn**
As	1.0						
Cr		1.0					
Cu	0.268	**0.716**	1.0				
Pb		0.699	**0.791**	1.0			
Hg		0.471	0.578	0.549	1.0		
Ni		**0.890**	**0.740**	0.672	0.432	1.0	
Zn		**0.710**	**0.890**	**0.821**	0.612	**0.735**	1.0
TOC %		0.499	0.418	0.393	0.435	0.365	0.403
% Clay ($\leq 3.9\ \mu m$)		**0.754**	**0.855**	**0.796**	0.576	**0.744**	**0.898**

Only correlations with $p \leq 0.05$ are show. Those of high significance for this study ($p \leq 0.05$ and $r > 0.7070$) are shown here in bold.

Table 4-5: Locations and Sediment Trace Metals with Enrichment Factor > 5

Site Id	Group	As	Cr	Pb	Ni	Zn
AK02-0005	Cook Inlet	8	186		203	
AK02-0021	Cook Inlet		10	9	11	12
AK02-0009	Shelikof Strait			6		6

Table 4-6: Estimated Cumulative Area Population Percentiles and their Lower Confidence and Upper Confidence Bounds Sediment Trace Metals (µg/g dw)

Trace Metal	25%	LCB 95%	UCB 95%	50%	LCB 95%	UCB 95%	75%	LCB 95%	UCB 95%	90%	LCB 95%	UCB 95%
Raw data with no anomalous values												
As	6.1	4.7	7.8	9.0	7.9	9.9	10.2	10.0	12.0	12.6	11.6	15.5
Cu	18.2	16.3	20.3	29.4	23.8	34.4	39.1	37.3	41.9	44.7	43.6	48.6
Pb	10.1	9.1	11.2	12.2	11.4	12.5	13.7	13.2	14.9	15.4	14.9	17.5
Hg	0.027	0.023	0.032	0.146	0.037	0.061	0.071	0.064	0.082	0.098	0.080	0.124
Zn	63.3	55.3	66.7	78.4	68.7	86.1	95.3	90.4	112.3	119.0	112.3	129.0
Raw Data with anomalous values (AK02-005) removed												
Cr	39.1	34.2	44.0	64.4	44.1	71.3	80.2	75.9	87.2	94.3	88.1	103.7
Ni	17.8	15.5	21.1	26.6	23.2	32.3	36.6	35.9	41.7	43.8	39.8	76.5

Table 4-7: Sediment Quality Guidelines (μg/g dw)

Analyte	90% UCB 95%	ERL	ERM	AET
As	**15.5**	8.2	70.0	35.0 B
Cr	**103.7**	81.0	370.0	62.0 N
Cu	**48.6**	34.0	270.0	390.0 MO
Pb	17.5	46.7	218.0	400.0 B
Hg	0.124	0.150	0.710	0.410 M
Ni	**76.5**	20.9	51.6	110.0 EL
Zn	129.0	150.0	410.0	410.0 I

AET Bioassay Endpoints: B – Bivalve, E – Echinoderm larvae, I – Infaunal Community Impacts, L – Larval Bioassay, M – Microtox, N – Neanthes.

Note: The 90% UCB 95% values in bold are those that exceed the ERL or ERM values.

Table 4-8: National Oceanic and Atmospheric Administration National Status and Trends Program Kachemak Bay and Homer Boat Harbor Sediment Trace Metal Results (µg/g dw)

Station	%Fines	As	Cr	Cu	Pb	Hg	Ni	Zn
EF-1	17.6	14.2	74.2	35.6	9.22	0.1000	37.2	88.4
EF-2	38.7	13.0	73.2	34.2	10.00	0.0688	37.7	91.7
EF-3	36.8	10.7	72.7	31.9	11.20	0.0793	36.9	89.6
EF-4	93.4	**26.0**	110	65.6	15.20	0.0965	56.5	**139.0**
EF-5	21.3	14.5	67.3	27.5	11.40	0.0673	33.7	82.4
EF-6	25.6	**16.2**	68.1	27.6	10.90	0.0579	37.9	83.5
EF-7	43.8	**22.4**	80.0	41.5	13.20	0.0729	42.2	99.5
ES-1	26.6	**43.4**	75.8	31.5	12.40	0.0870	39.3	93.9
ES-2	12.9	**15.7**	109.0	23.5	10.40	0.0619	33.5	78.4
ES-3	17.3	**19.7**	86.2	32.2	11.50	0.0497	40.6	95.8
ES-4	31.6	**31.9**	83.2	39.0	9.53	0.0470	43.6	87.4
ES-5	32.6	**27.3**	74.7	39.7	13.60	0.1100	39.9	90.6
ES-6	9.5	15.2	84.7	27.6	8.56	0.0477	39.9	91.1
ES-7	34.0	**19.0**	79.9	37.9	13.50	0.0865	39.7	97.3
HH-1	84.2	14.1	96.2	**64.7**	13.90	0.1090	45.5	**158.0**
HH-2	93.1	14.3	95.1	**60.2**	13.90	0.1160	45.9	**144.0**
HH-3	96.9	**17.9**	94.3	**69.4**	14.90	0.1190	45.7	**152.0**
OH-1	68.1	11.0	87.1	45.6	11.50	0.1030	42.4	109.0
OH-2	50.5	12.6	77	38.4	10.60	0.0923	39.1	98.1
WF-1	65.9	**17.0**	73.5	40.3	11.40	0.1090	37.5	92.6
WF-2	16.6	**20.1**	61.6	20.1	8.29	0.0870	32.4	74.9
WF-3	38.9	**18.7**	62.7	28.2	9.83	0.1170	33.4	82.1
WF-4	36.1	**21.4**	70.2	32.6	9.73	0.1110	36.8	82.2
WF-5	23.2	13.7	59.3	23.8	8.49	0.1060	32.0	74.5
WF-6	57.3	15.4	73.5	36.8	11.60	0.1030	37.7	92.1
WS-1	11.8	**19.1**	63.1	21.8	9.37	0.0896	34.1	78.6

Table 4-8: National Oceanic and Atmospheric Administration National Status and Trends Program Kachemak Bay and Homer Boat Harbor Sediment Trace Metal Results µg/g dw (Continued)

Station	%Fines	As	Cr	Cu	Pb	Hg	Ni	Zn
WS-2	21.2	**40.0**	68.1	27.1	9.82	0.0993	43.7	83.4
WS-3	10.9	**18.0**	63.0	22.7	8.33	0.0856	34.5	74.0
WS-3X	15.8	**20.6**	61.0	25.1	10.20	0.0924	31.3	75.6
WS-4	16.4	**48.6**	61.8	27.9	8.70	0.1060	33.4	81.6
WS-5	10.5	**30.5**	67.3	26.0	8.64	0.0971	38.6	83.3

Data from report by Hartwell et al. (2009). Note: Values in bold exceed the Effects Range Low (ERL). HH-1 to HH-3 are in Homer Harbor, Alaska.

Figures

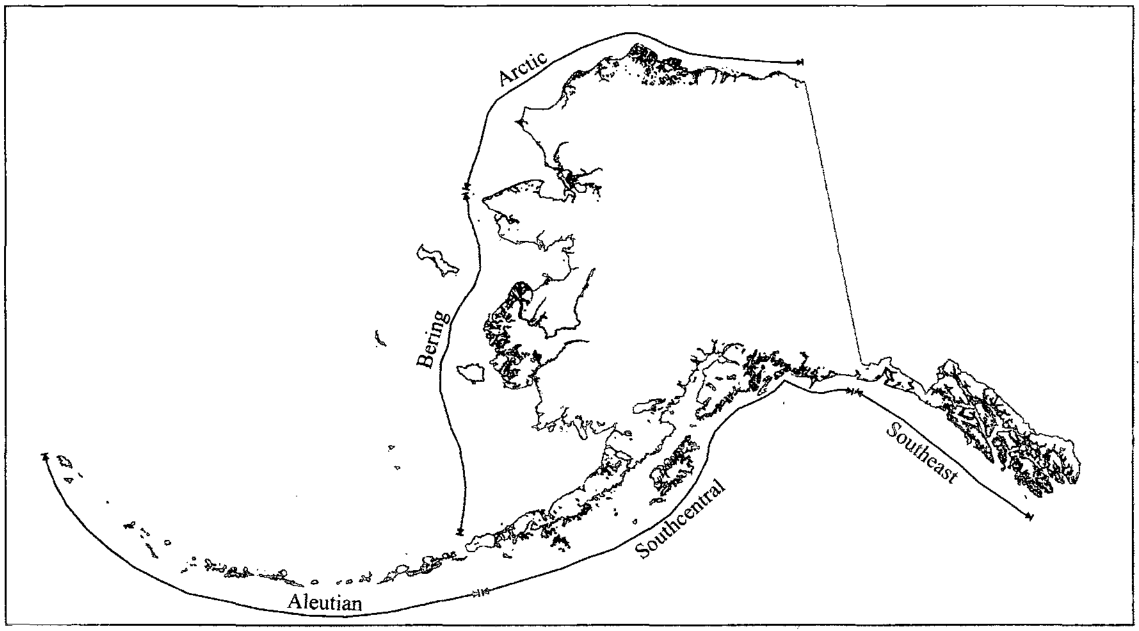


Figure 4-1: Five Alaska Coastal Biogeographical Provinces

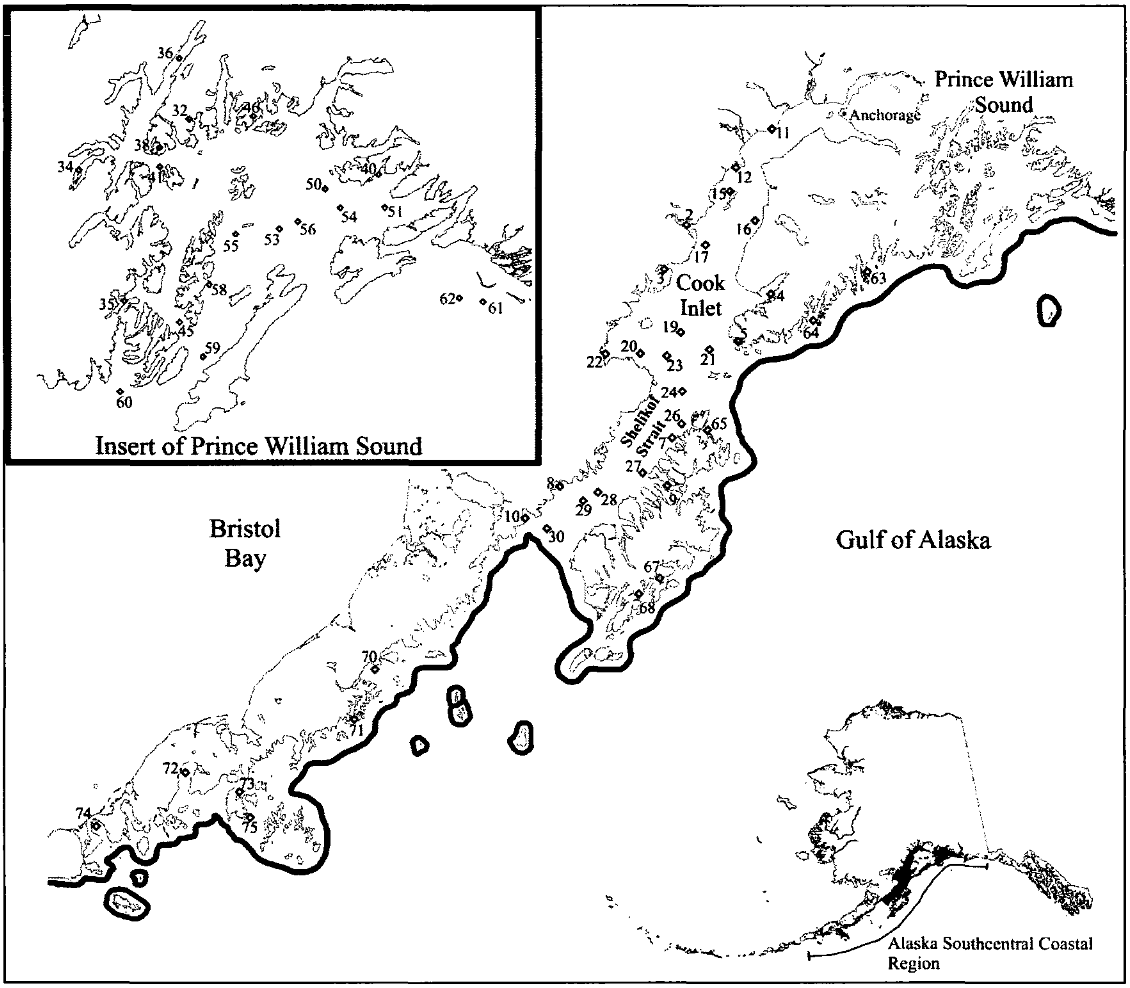


Figure 4-2: Alaska Southcentral Coastal Study Area

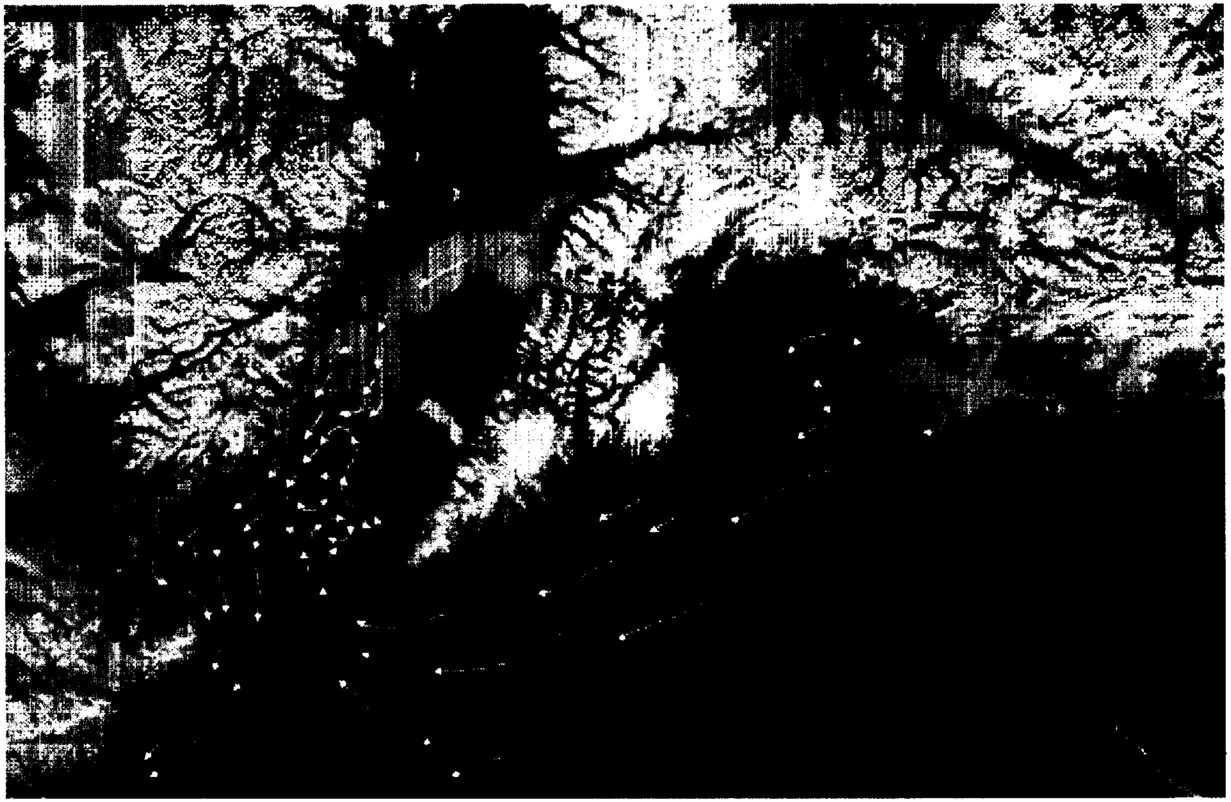
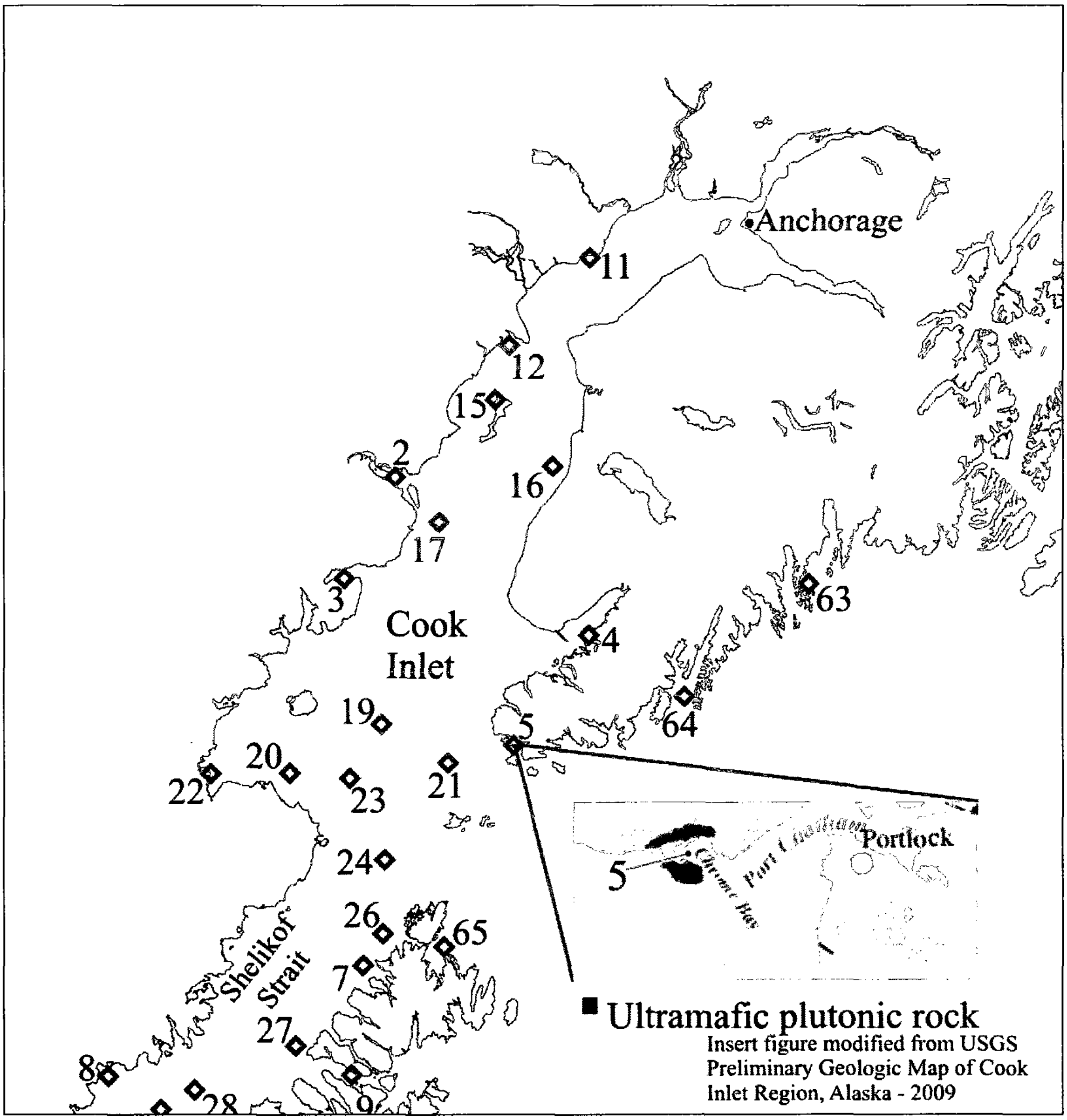


Figure 4-3: Southcentral Alaska National Atmospheric and Space Administration Terra Moderate Resolution Imaging Spectroradiometer Image of Coastal Currents



Insert figure modified from USGS Preliminary Geologic Map of Cook Inlet Region, Alaska - 2009

Figure 4-4: AK02-005 Chrome Bay Chromite Deposit

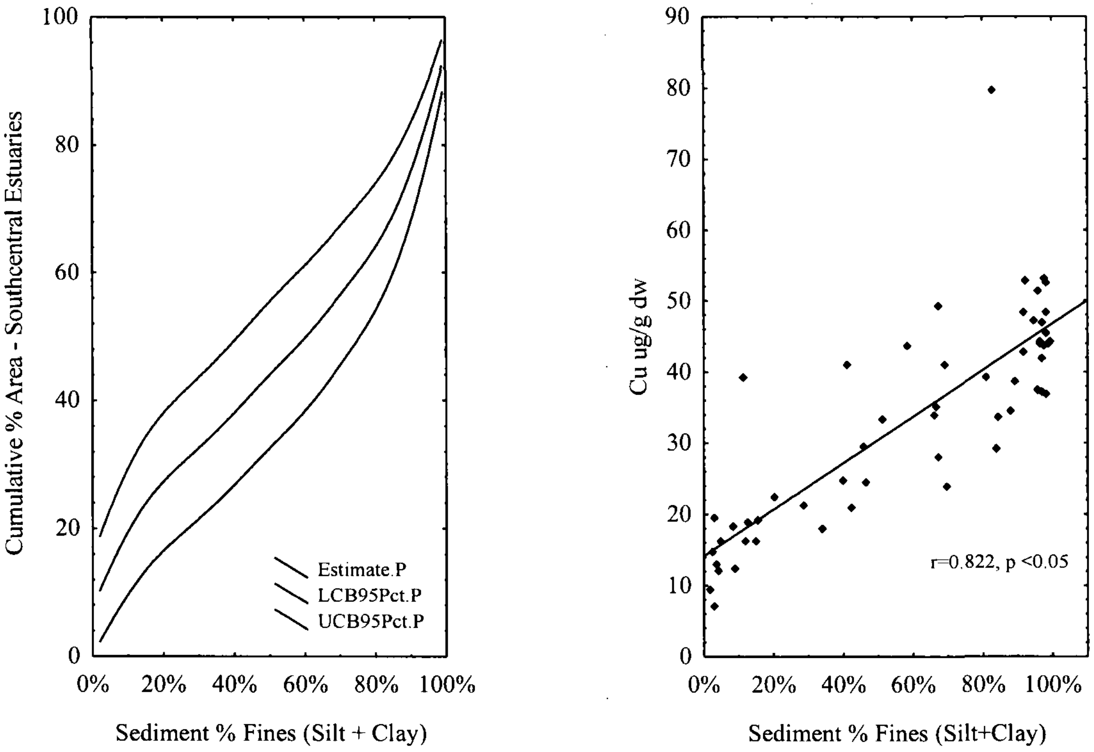


Figure 4-5: Cumulative Distribution Function of Cumulative % Area against Sediment Fines and a Scatterplot of Fines and Cu

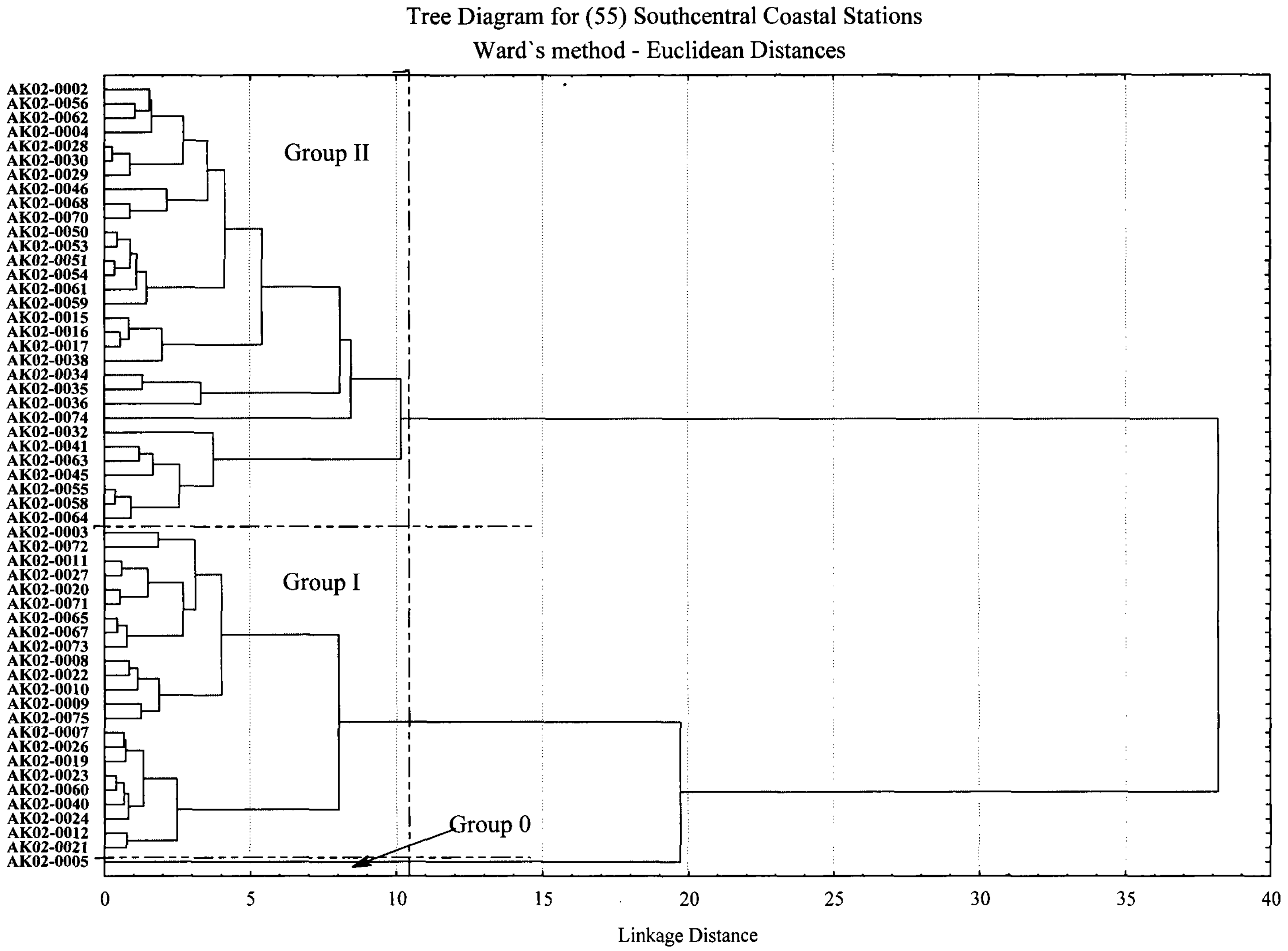


Figure 4-1: Dendrogram of Standardized Sediment Trace Metals, As, Cr, Cu, Hg, Ni, Pb, and Zn for Station Locations

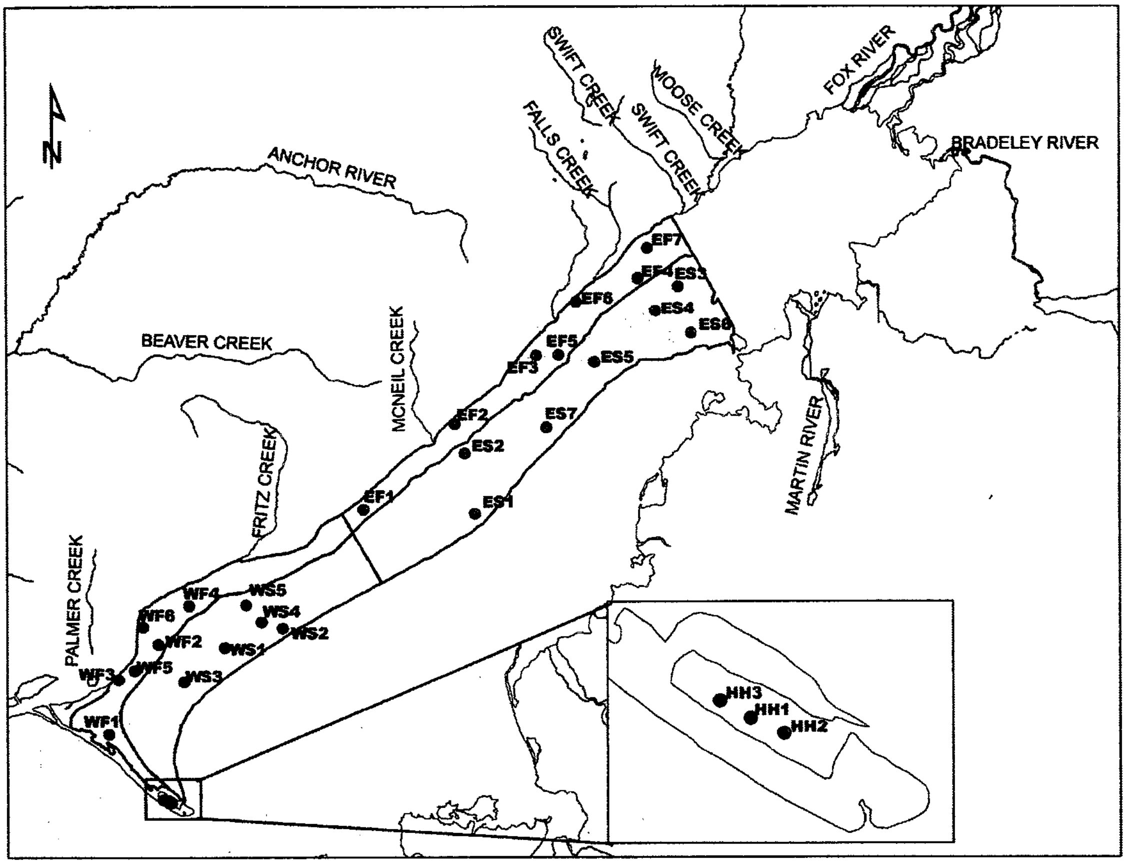


Figure 4-7: Kachemak Bay and Homer Boat Harbor (Insert in Map) Sample Stations (Hartwell et al., 2009)

Chapter 5: Conclusion

Conclusion

Our understanding of natural conditions in various environmental media (e.g., water, sediments, and biota) in an aquatic resource is essential to providing a sound scientific basis for environmental protection (NRC, 1990; Zedler, 1996; Tibbetts, 2000). This information is necessary for determining wastewater discharge limitations into aquatic resources, assessing environmental effects of contaminants, and determining appropriate and achievable contaminated site remediation cleanup goals.

In establishing natural conditions, the lack of suitable reference or non-anthropogenically affected sites can constrain the development of natural conditions. For Alaska and similar regions around the world, at the moment there are relatively large reference areas that remain minimally disturbed. These provide the opportunity to establish a natural condition data set for helping establish good water quality guidelines or other environmental standards. In the future, though, increasing population and resource development pressure will affect these remaining areas. If natural conditions are to be established, there is realistically a limited time to do so.

The previous three chapters developed and demonstrated a pragmatic methodology that can apply to the development of natural conditions for trace metals in both streambed sediments and coastal marine waters. The proposed methodology consists basically of three steps: (1) develop and implement a well-thought-out probabilistic sampling survey of a target population with 50 or more target sites; (2) analyze data using a combination of Enrichment Factors with environmental and geochemical mapping to assess and remove anomalous values representing anthropogenic and nearby ore body origin; (3) utilize the remaining reference sites, assuming at least 60% of the sites remain as reference sites, and calculate population estimates for the cumulative area 90% UCB 95% sediment trace metal of concern establishing an upper threshold value for regional natural conditions.

Before applying any derived estimate of a threshold natural condition, environmental managers must understand the survey design, scale, analytical methods and statistical analyses used (Reimann et al., 2005; Reimann et al., 2008). No matter what methodology is used, resulting values are only qualitative in nature and not "true" values, even with statistical estimates of variability (Matschullat et al., 2000).

This study has established natural condition marine sediment trace metal levels for the Alaska Southcentral region. Based on the results of the probabilistic sample survey design and the natural condition assessment methodology, the evidence supports the two hypotheses proposed in the introduction that:

1) NOAA sediment quality guidelines Effect Range Low and Effect Range Median are exceeded in less than 10% of the cumulative percent estuary area.
2) Trace metal concentrations assessed in 2002 AKMAP Southcentral survey of the coastal sediments reflect the natural local and regional geologic environments.

It is important to note that the significance of these levels from an ecotoxicological perspective remains to be established. Bioavailability of the trace metals in the sediments has not been determined. In addition, while some sediment trace metals are naturally elevated relative to a SQG, such as ERL and ERM, these levels have been present in the ecosystem for a long time, and it is likely that the resident biological populations have adapted to the observed trace metal concentrations (Klerks and Weis, 1987; Bahrndorff et al., 2006). Future studies, if no retrospective studies can be utilized, are imperative if Alaska is to have relevant SQGs for arctic and subarctic conditions.

Finally, while this work provides a regional population based estimate of natural for sediment trace metals, it is cautioned that a rapidly evolving climate may be presenting us with an ecosystem already in a state of flux (Wang et al., 2010)

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