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Characterization of Benthic Habitats and Contaminant Assessment in Kenai Peninsula Fjords and Bays

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List of Acronyms

AAS	atomic absorption spectroscopy
ADEC	Alaska Department of Environmental Conservation
ADF&G	Alaska Department of Fish & Game
Ag	silver
Al	aluminum
AKMAP	Alaska Monitoring & Assessment Program
AOOS	Alaska Ocean Observation System
APHA	American Public Health Association
As	arsenic
ASTM	American Society of Testing and Materials
Cd	cadmium
CFR	Code of Federal Regulations
CIRCAC	Cook Inlet Regional Citizens Advisory Council
Cr	chromium
Cu	copper
DDT	dichlorodiphenyltrichloroethane
DO	dissolved oxygen
EMAP	Environmental Monitoring and Assessment Program
EPA	Environmental Protection Agency
ERL	Effects range - low
ERM	Effects range - median
EVOS	Exxon Valdez Oil Spill
Fe	iron
GC/ECD	gas chromatography/electron capture detector
GC/MS	gas chromatography/mass spectroscopy
gm	gram
GOA	Gulf of Alaska
H’	diversity (Shannon-Weiner)
HCH	hexachlorocyclohexane
Hg	mercury
ICP	inductively coupled plasma
KBNERR	Kachemak Bay National Estuarine Research Reserve
km	kilometer
L	liter
m	meter
MDL	method detection limit
mg	milligram
Mn	manganese
MS	matrix spike
MSD	Matrix spike duplicate
ng	nanogram
Ni	nickel
NIST	National Institute of Standards and Technology
NPRB	North Pacific Research Board
NOAA	National Oceanic and Atmospheric Administration
NS&T	National Status and Trends
P	Probability
PAH	polycyclic aromatic hydrocarbon
Pb	lead
PCA	principal component analysis

PCB	polychlorinated biphenyl
POP	persistent organic pollutant
POTW	publically owned treatment works
ppt	parts per thousand
PWSRCAC	Prince William Sounds Regional Citizens Advisory Council
QA/QC	quality assurance/quality control
Sb	antimony
Se	selenium
Si	silicon
Sn	tin
SQG	sediment quality guidelines
SQT	sediment quality triad
SRM	standard reference material
TBT	tributyltin
TIC	total Inorganic carbon
TOC	total oganic carbon
UAF	University of Alaska Fairbanks
ug	microgram
Zn	zinc

EXECUTIVE SUMMARY

A baseline environmental characterization of the embayments and fjords on the Kenai Peninsula, Alaska was conducted using a sediment quality approach based on sediment chemistry, and benthic invertebrate community structure. Sediment toxicity and resident fish body burdens were also assessed at one bay near an abandoned mine site. The study area was subdivided into seven distinct water bodies on the peninsula's north side, draining into Kachemak Bay, and two on the western tip of the peninsula, opening into Lower Cook Inlet. Sampling sites for water quality measurements, sediment, and benthic infauna were randomized within each embayment. Concentrations of 140 organic and elemental contaminants were analyzed. Habitat parameters (depth, salinity, temperature, dissolved oxygen, sediment grain size, and organic carbon content) that influence species and contaminant distribution were also measured at each sampling site. A detailed benthic community condition assessment was performed at each site.

Sediment characteristics varied widely between, and in some cases, within bays. Most sites in bays draining into Kachemak Bay had fine grained sediments. Bays further down the peninsula opening into lower Cook Inlet had coarser sediments. Fjords with submerged moraines exhibited some degree of stratification in the water column, which in turn affected water quality in the upper reaches of the bays. Concentrations of chromium and nickel were extremely high in Chrome Bay. Concentrations were several times higher than observed concentrations seen throughout other locations in south-central Alaska. Other elemental concentrations varied between and within bays, with several locations exceeding lower sediment quality guidelines. Concentrations of chlorinated pesticides and PCBs were uniformly low, with the exception of Seldovia Harbor, where total DDT and PCBs exceeded the lower sediment quality guidelines. Concentrations of PAHs were relatively low, except in Seldovia Harbor. Sediments in Seldovia Harbor exceeded lower sediment quality guidelines for PAHs, and in one location approached the upper limit. That concentration of PAHs exceeded all other measurements in the National Status & Trends database for the entire State of Alaska. Characteristics of the PAH compounds present indicate large contributions of pyrogenic sources (burned fuel and/or other organic matter). Seldovia Bay had much lower PAH concentrations than the harbor.

Infaunal assemblages were highly variable. More than 280 taxa were enumerated throughout the study area. Two dozen taxa were numerically dominant over all the rest. Some locations contained thousands of a particular taxon resulting in a very spotty pattern of abundance. The average number of organisms per grab (0.04 m^2) was 1,770 (range 15-7,350). Sadie Cove had a depauperate benthic community, with only 4 taxa and 15 organisms. This is likely due to hypoxic stress resulting from water circulation being impeded by glacial moraines. This has

been observed by other researchers in Sadie Cove. The next lowest site was in Seldovia Harbor, with 38 taxa and 150 organisms. Statistically, the benthic assemblages form five main groupings. Sadie Cove is unique. Seldovia Bay, Tutka Bay, Halibut Cove, Jakolof Bay and China Poot Bay have an overlapping species complex that split out into three subgroups. The third main group is from Dogfish and Chrome Bays, which share relatively few taxa with the other bays. Port Graham is also unique in that it shares some taxa with the bays draining into Kachemak Bay, but has a large number of species found nowhere else. The final main group constitutes sites located in the upstream portions of the other bays which had distinctly different assemblages from the lower bays.

Whole sediment amphipod toxicity bioassays were conducted with sediments from Chrome Bay. No sample exhibited significant mortality or sublethal effects. Also, body burdens of three species of fish captured in Chrome Bay did not exhibit elevated concentrations relative to other studies in Kachemak Bay or the Alaska Dept. of Environmental Conservation, Fish Monitoring Program. Despite the very high concentrations of Cr and Ni in the sediments, the metals do not appear to be bioavailable to resident biota.

1. INTRODUCTION

1.1 National Status and Trends Bioeffects Studies

As part of the National Status and Trends (NS&T) Program, NOAA conducts bioeffects studies to determine the spatial extent and severity of chemical contamination and associated adverse biological effects in coastal bays and estuaries of the United States. This program encompasses a broad spectrum of research and monitoring studies, including long-term, nationwide monitoring of contaminant concentrations in sediments and resident organisms, sediment toxicity assessments in specific coastal areas, evaluation and application of biomarkers; and the development of ecological indices (Turgeon *et al*. 1998, Hartwell and Claflin 2005). The National Status and Trends Program has conducted bioeffects assessment studies in coastal water bodies since 1991. Results from previous sediment bioeffects studies in over 20 coastal water bodies and estuaries have been published (Long *et al*. 1996, Turgeon *et al*. 1998, Long 2000, Hartwell *et al.* 2001, Hartwell and Hameedi 2006, Hartwell and Hameedi 2007, Pait *et al*. 2006, Hartwell *et al.* 2009).

The mission of the State of Alaska Department of Environmental Conservation (ADEC) Division of Water is to improve and protect the quality of all Alaskan waters and under the Clean Water Act (CWA) Sections 303(d) and 305(b), Alaska has the responsibility to report and identify causes and sources of water quality impairment. One way the division carries out this mission is to monitor and report on water quality.

Part of the NS&T goal is to expand its coastal contamination and benthic community database in Alaska. Sediment chemistry, toxicity, and benthos assessments were conducted on the north side of Kachemak Bay in 2007 and in the deep central portions of the Bay in 2008, in collaboration with the North Pacific Research Board (Hartwell *et al*. 2009) and the Cook Inlet Regional Citizens Advisory Council (CIRCAC). This report summarizes the results of a joint NOAA, ADEC and the University of Alaska Fairbanks (UAF) project to assess chemistry, benthic community, and limited sediment toxicity studies in the embayments on the south side of Kachemak Bay and bays on the Kenai Peninsula, including an abandoned mining site.

Sediment contamination in U.S. coastal areas is a major environmental issue because of potential toxic effects on biological resources and, often, indirectly on human health. A large variety of contaminants from industrial, agricultural, urban, and maritime activities are associated with bottom sediments, including synthetic organic chemicals, polycyclic aromatic hydrocarbons (PAHs), and trace elements. In many instances, fish consumption advisories are coincident with severely degraded sediments in coastal water bodies. Contaminants, particularly those that are lipophilic, can biomagnify in the coastal food chain with increasing

concentration in predatory wildlife and humans. Thus, characterizing and delineating areas of sediment contamination and toxicity are viewed as important goals of coastal resource management. This is particularly important in Alaska, where subsistence food contamination is an emerging health concern, especially in rural areas where large amounts of these foods are consumed as a primary source of protein (Wolfe 1996). Excessive levels of contaminants in the sediments, whether of natural or anthropogenic origin, can pose ecological and human-health risks. The presence of contaminants in coastal ecosystems can cause habitat degradation and loss of biodiversity through degraded habitats, loss of fauna, biomagnification of contaminants in the coastal ecosystem, and human consumption of contaminated fish and wildlife.

Macrobenthic organisms play an important role in the estuarine environment. Critical habitats and food chains supporting many fish and wildlife species involve the benthic environment. Benthic organisms are secondary consumers in the ecosystem, and represent an important link between primary producers and higher trophic levels for both planktonic and detritus-based food webs. They are composed of diverse taxa with a variety of reproductive modes and life history characteristics. They are a particularly important food source for juvenile fish and crustaceans. Furthermore, most benthic species have limited mobility and cannot physically avoid stressful environmental conditions. Benthic assemblages thus cannot evade, and must respond to, a variety of stressors, such as toxic contamination, eutrophication, sediment quality, habitat modification, and seasonal weather changes. Biological systems are able to integrate the complexity of natural habitat stressors and ambient pollutant mixtures, through physical contact with sediments, ingesting sediment, bioaccumulating contaminants in food webs, and expressing the synergetic effects of exposure to toxic chemicals.

Distributions of benthic organisms are predictable along estuarine gradients and are characterized by similar groups of species over broad latitudinal ranges. Benthic species composition, abundance, and biomass are influenced by habitat conditions, including salinity, sediment type, and environmental stressors, both natural and anthropogenic (Slim *et al.* 1997, Nanami *et al.* 2005). Information on changes in benthic population and community parameters due to habitat change can be useful for separating natural variation from changes associated with human activities. For that purpose, benthic community studies have a long history of use in regional estuarine monitoring programs and have been proven to serve as an effective indicator for describing the extent and magnitude of pollution impacts and habitat modification in estuarine ecosystems, as well as for assessing the effectiveness of management actions (Llanso *et al*. 2004, Long *et al.* 1995).

Several examples exist in which marine benthic communities' response to contaminant and physical stressors have been documented. Impacts of organic enrichment on marine benthos have shown that total biomass, relative proportion of deposit feeders, and abundance of species with 'opportunistic' life histories (e.g. high fecundity, short generation time, and rapid dispersal) increase. Some opportunistic taxonomic groups are known to be tolerant of chemical toxicants. Others are capable of thriving in physically disturbed habitats (e.g. high sedimentation, dredging operations, etc.) but not necessarily in contaminated areas. In areas impacted by excessive sedimentation from terrestrial runoff, dominant organisms tend toward surface suspension feeding modes and high reproductive potential regardless of taxonomic relationship, whereas away from the sedimentation stress, feeding modes shift to species that are deep deposit feeders and the emergence of filter feeders (Wlodarska-Kowalczuk *et al.* 2005, Pearson and Rosenberg 1978). Experimental manipulation of habitats has shown that specific taxonomic lines, with opportunistic life history strategies respond positively to organic enrichment (Lenihan *et al*. 2003). Other taxa respond negatively to both toxicants and excessive organic enrichment. The response of specific species to organic and toxic contamination is mediated by life history and feeding mode characteristics.

National Status and Trends Bioeffects studies also utilize measures of toxicity using bioassays that may evaluate different modes of contaminant exposure (bulk sediment, sediment porewater, and chemical extracts of contaminants from sediment) to a variety of species and different assessment end-points (i.e., mortality, impaired reproduction, physiological stress, and biomarker response). Since the test results are usually not necessarily axiomatic, and biological effects of contaminants occur at different levels of biological organization, i.e., from cells to ecosystems, results from a suite of toxicity tests are used in the "weight of evidence" context to infer the incidence and severity of environmental toxicity (Chapman 1996). Typically, the amphipod mortality bioassay, the sea urchin fertilization impairment bioassay, the Microtox test, and, in recent years, a Human Reporter Gene System (HRGS) P450 tests, are used in each study area. Other tests, based on promising new techniques, e.g. full life-cycle tests, and genotoxicity, have also been used in some areas for test evaluation or to meet a specific information need.

Taken together, all three assessments, sediment chemistry, sediment benthic assemblage, and sediment toxicity constitute what is referred to as the Sediment Quality Triad (SQT). The SQT is an important ecosystem based management tool widely used by coastal managers for coastal resource management.

1.2 Assessments in South Central Alaska

Although Alaska has an extensive coastline of 49,700 miles, greater than the contiguous US (U.S. EPA, 2005; Shorezone, 2016), and vast natural marine and coastal resources, due to a small population and lack of infrastructure, Alaska lacks adequate data to provide baseline information necessary to assess future trends. More environmental monitoring and research is needed to assess not only areas of known pollution impact, but also the whole Alaskan coastal region. Historically, assessment in Alaska has been either limited or focused on areas of known impairment. The National Status and Trends Program has analyzed contaminants in sediment and mussels collected from selected sites in the Gulf of Alaska (O'Connor 2002). The Alyeska Pipeline Service Company and the Prince William Sound Regional Citizens Advisory Council (PWSRCAC) has been assessing PAHs and other petroleum-related compounds in Prince William Sound since the Exxon Valdez Oil Spill in 1989 (EVOS) (Blanchard et al. 2011; Page et al. 2001; PWRCAC 2018). In collaboration with the U.S. EPA Environmental Monitoring and Assessment Program, ADEC undertook a state-wide coastal ecological condition study (AKMAP) that encompasses assessment of contaminants and benthic assemblage in sediment along the Gulf of Alaska and the Aleutian Islands (Saupe *et al.* 2005). The Cook Inlet Regional Citizens Advisory Council (CIRCAC) assesses the impacts of oil and gas operations in Cook Inlet, including chemical and benthic community assessment, and undertook a comprehensive sediment and water quality survey of Cook Inlet in 2008. The study reported here augments these efforts to provide detailed data on sediment quality on the Kenai Peninsula, where data is sparse. The goal of the project was to assess habitat conditions that influence biodiversity and distribution of the benthic infaunal community.

The resulting data of this project are georeferenced and could be integrated into the Alaska Ocean Observation System (AOOS) database. The data will help achieve the long-term goal of conducting research designed to address pressing fishery management or marine ecosystem information needs. The National Status and Trends Program has produced a relational web-portal database on contaminants, toxicity, and benthic infaunal species distribution in coastal United States. The data portal is an "Internet doorway" to data and information products of NS&T. Data of this study is incorporated into this database and available to local managers as well to concerned citizens nationally. The comprehensive georeferenced data base of this and previous studies are available online in downloadable format through our data portal at https://products.coastalscience.noaa.gov/nsandt_data/data.aspx

1.3 Site Background

Kachemak Bay is a 64 km long glacial fjord on the east side of lower Cook Inlet located in south central Alaska. At the mouth between Anchor Point in the north and Point Pogibshi to the south, Kachemak Bay is nearly 40 km wide, but narrows to 10-11 km at Homer spit (Figure

1), which bisects the Bay into inner and outer portions. The inner portion of the Bay behind the spit is approximately 32 km long. The north shore of Kachemak Bay is characterized by extensive tidal flats below sandy bluffs with numerous coal seams. The steep bluffs are vulnerable to landslides. The south shore is bounded by the Kenai Peninsula, which has numerous smaller fjords and embayments cut into steep terrain that rises to glaciated valleys and uplifted mountain peaks. Except for the Jakolof Trench running along its southern edge, inner Kachemak Bay has a relatively flat bottom and averages 46 m in depth. The outer Bay has a sill at the opening to Cook Inlet from 20-70 m deep and drops to more than 160 m deep in Jakolof Trench south of Homer Spit. Glaciers have covered and retreated from Kachemak Bay repeatedly over the past 25,000 years. Homer Spit and the Archimandritof Shoals to the west of it may be the result of terminal glacial moraines. An extensive description of the physiography of Kachemak Bay is presented by Alaska Department of Fish and Game, ADF&G (1998).

The relatively flat watershed to the north lies in the Kenai Lowlands of the Cook Inlet Basin. In contrast, the south side on the Kenai Peninsula is characterized by steep mountains that rise 1,000-2,000 m, composed of a jumble of volcanic rock and upthrusted marine sedimentary deposits. The Kenai Peninsula is a tectonic rupture zone and is subject to violent earthquakes, including the largest ever recorded in North America in modern times (Good Friday earthquake 1964). This caused a land subsidence of 4 ft. in the Kachemak Bay area. This sudden change in elevation has resulted in dynamic changes in local sedimentation and erosional patterns. There are five active volcanoes on the western side of Cook Inlet. These periodically contribute volcanic ash to the region, and have produced tsunamis that impact Kachemak Bay. Runoff from the northern rivers is from spring and fall precipitation and spring snowmelt. On the Kenai Peninsula, there are nine glaciers that contribute meltwater to the bay during the summer months. The volume of flow from glacial rivers can be much higher than from clear-water rivers. The summer glacial meltwater delivers large volumes of freshwater into the Bay. Glacial and clear-water streams are characteristically different with respect to turbidity. Glacial meltwater carries a large sediment load of clay and silt, and this is what gives them their color and opacity. As glaciers melt in the summer, the freshwater drains into the Bay, altering salinity and possibly the circulation patterns. Glaciers can also cause flooding and large mudslides when ice dams that hold back lakes fail and release huge amounts of silt and water downstream. The Fox and Bradley Rivers in the eastern end of the bay deliver large volumes of freshwater and silt to the bay from the Kachemak, Dinglestadt and Chernof Glaciers.

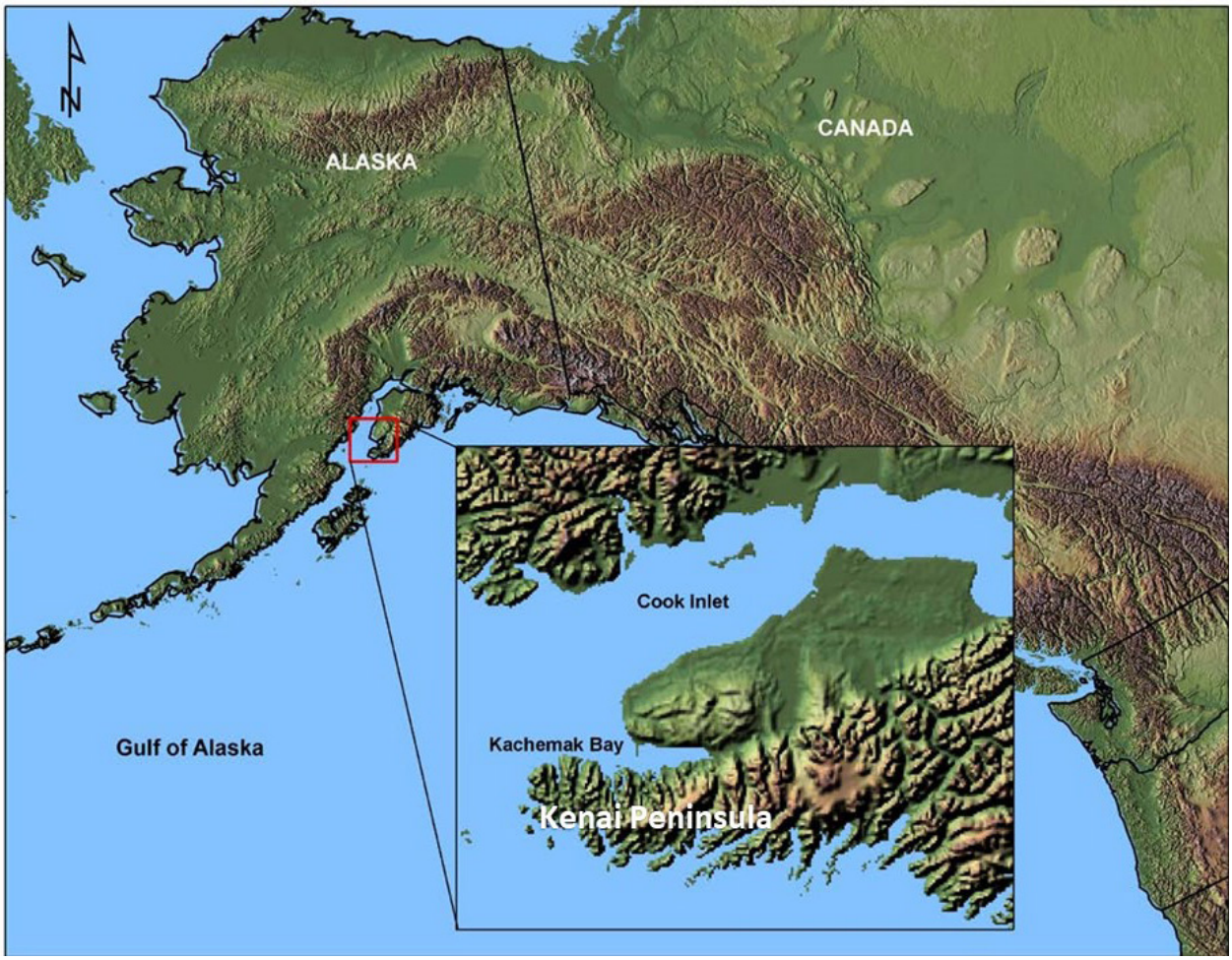

Figure 1. Map of Alaska and (inset) the Kenai Peninsula study area.

Kachemak Bay has a complex water circulation pattern (Burbank 1977, KBNERR 2001). The inner bay displays the characteristic features of a brackish water estuary resulting from the mixing of freshwater inflow at the head of the bay and saltwater coming from the outer bay. In addition to the main sources of freshwater input in the east, turbid glacial meltwater also enters from ice fields on the south side during the summer. The semi-diurnal tidal range in the inner bay is as high as 6 m. The tide and wind fuel the mixing of masses of fresh and saline waters in the inner bay that creates two counterclockwise tidal gyres that tend to deposit sediment in the northern portion of the bay (Burbank 1977). Seasonal winds and summer glacial melt causes the eastern gyre to periodically elongate and eliminate the western gyre, encompassing the entire inner bay. The net overall inner Bay circulation remains in a counterclockwise direction in spring, summer, and early fall, with inflow along the southern shore and outflow along the northern shore. This circulation pattern coupled with the tidal exchange help create diverse habitats, such as exposed tidal flats, kelp beds, marshes and eelgrass, and a relatively deep zone in the middle of the bay. In addition to these habitats, the brackish and low current water makes the inner bay an excellent spawning ground and for several marine organisms (KBNERR 2001).

The circulation pattern in the outer bay is characterized by the seawater influx from the Gulf of Alaska (GOA) via lower Cook Inlet, and input of low salinity brackish water from the inner bay. Both lower Cook Inlet and the outer Kachemak Bay are part of the general Gulf of Alaska circulation system (Figure 2). According to Burbank (1977), seawater transported northward by the Alaskan Current from the GOA enters lower Cook Inlet through the Kennedy entrance. The bulk of the seawater bypasses the outer Kachemak Bay. Because of upwelling along the tip of the Kenai Peninsula northwest of the Chugach Islands, the seawater is diverted offshore. The outer bay circulation is dominated by two semi-permanent gyres. The outer clockwise gyre is driven by wind and tidal currents and the predominant northward flowing current along the east side of Cook Inlet. The inner counterclockwise gyre is driven by the outer gyre and the surface outflow from the inner Kachemak Bay. The net exchange of water in and out of each gyre occurs primarily around the gyre perimeters, with water gain from the south and water loss to the north. The outflow of water from the outer bay is carried out along the northeast shoreline of Cook Inlet. (Burbank 1977). The introduction of GOA water and upwelled water delivers a rich supply of nutrients to Kachemak Bay and the Kenai Peninsula.

This nutrient rich estuarine environment sustains a diverse marine wildlife of important economic value, such as shrimp, Dungeness crab, cockles, blue mussels, and clams (KBNERR 2001). Additionally, hundreds of plant and animal species inhabit the bay and its watershed, including thriving populations of sea otters, bald eagles, moose, black bears, trout, salmon, Pacific halibut and a large number of other marine organisms. The bay supports significant subsistence and commercial fishery resources and it is considered as one of the most productive bays in the U.S., although stocks have been reported to be declining in recent years (Szarzi *et al*. 2007, ADF&G 1998). Commercial harvests of herring, coonstripe shrimp, and king, Dungeness, and Tanner crabs have been closed due to depressed stock (ADF&G 1998). Other studies point to impacts of natural changes and anthropogenic activities that cause pollution as the overriding causes of the depressed stock (Exxon Valdez Oil Spill Trustee Council 2002).

With no known industrial point sources of contamination, current sources of pollution on the Kenai Peninsula may include wastewater discharge, marine activities associated with commercial and recreational fishing, commercial shipping, fuel tank leaks, storm water runoff, and long-range atmospheric transport. Historically, seafood canning operations and the mining and export of coal and minerals in the region have generated shoreline and watershed contaminant inputs in the region. Additionally, natural sources of pollution, particularly trace elements, may be associated with river runoff**.**

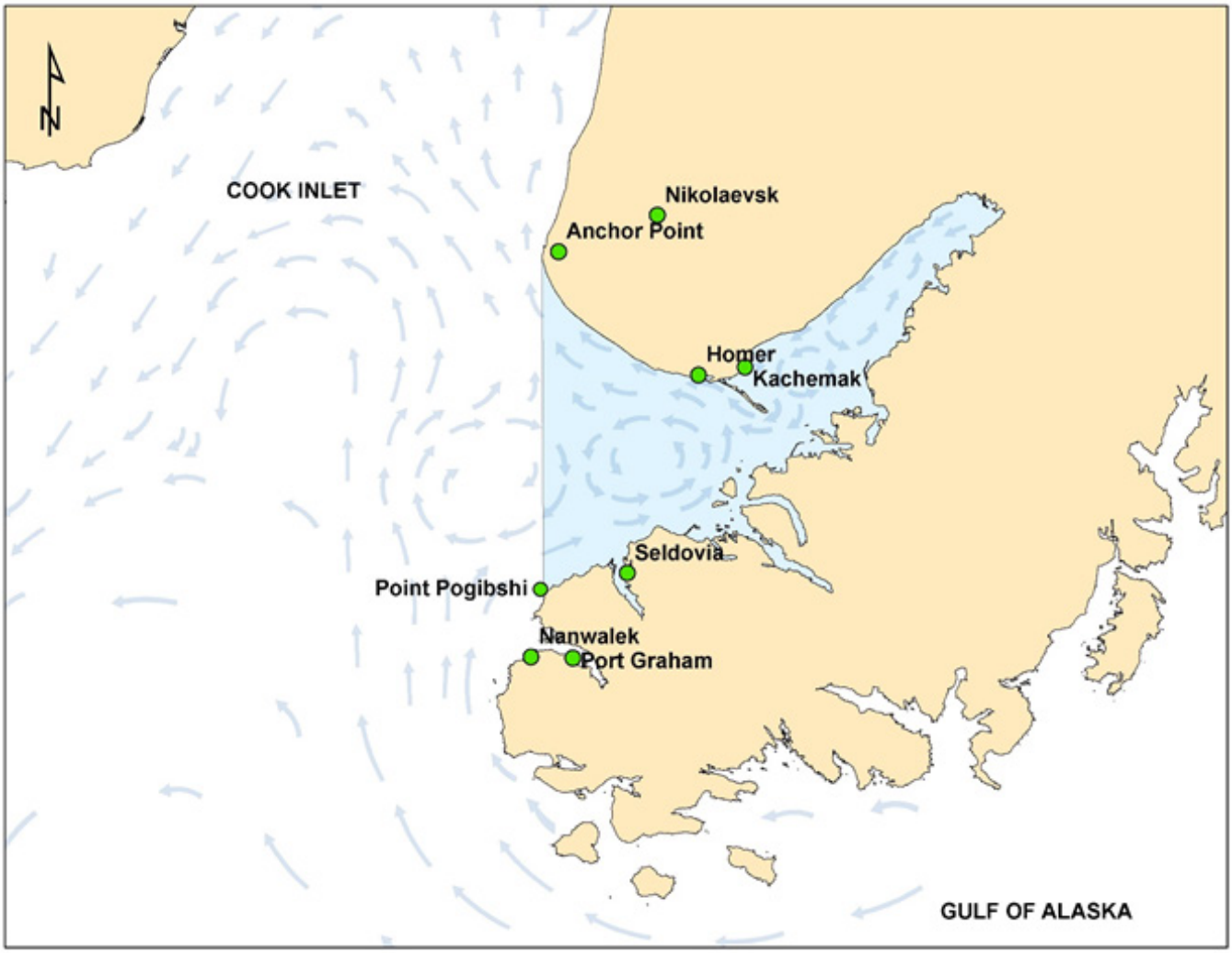

Figure 2. Map detailing Lower Cook Inlet and Kachemak Bay circulation pattern. Circulation in Kachemak Bay is driven by a complex interaction between the Alaskan Current, wind and tidal currents, and surface outflow from the inner bay.

Since Kachemak Bay lies between Cook Inlet and Prince William Sound oil operations traffic, its deep water anchorage is being proposed as one of several repair sites and safe refuges for distressed and disabled vessels (ADEC 2006). The risk of using the bay as shelter for vessels would be pollution from oil leaks and release of other hazardous substance that can impact marine resources. The bay was impacted by the Exxon Valdez Oil Spill (EVOS) of 1989. Fourteen days after the spill, the oil slick travelled westward then northward through the Kennedy Entrance to cover part of the lower Cook Inlet and Kenai Peninsula (www.evostc.state.ak.us/History/PWSmap.cfm). Kachemak Bay, being further removed from the spill epicenter in Prince William Sound, suffered relatively minimal ecological damages (Kuletz 1994), which nevertheless injured marine and coastal resources. It is anticipated that results of this study will serve as baseline data for unforeseen events and future reference.

1.4 Objectives

The objectives of this project were to:

1) identify natural and anthropogenic stressors that influence habitat quality and affect infaunal community spatial distribution;

2) provide chemical concentrations for a suite of metals and organic contaminants including metals and metalloids, PAHs and persistent organic pollutants (POPs);

3) produce a comprehensive taxonomic list and distribution patterns of infaunal species in each of the embayments on the Kenai Peninsula; and

4) assess potential chemical contamination from abandoned mining sites on habitats and biota.

Photo Credit: NOAA.

2. METHODS

The National Status and Trends Program and AKMAP use a stratified-random design for selection of sampling sites to determine the spatial extent of sediment toxicity in U.S. coastal waters. One of the design principles is to apply the same suite of tests synoptically to all areas so that comparisons can be made without the confounding interference of using different methods in different areas. Thus, comparison of spatial extent of impact between areas is possible even if the areas are not contiguous.

The choice of the study locations on the southern side of Kachemak Bay was to complement previous studies and to specifically address potential pollution in Chrome Bay from historical mining activities there. Dogfish and Chrome Bays were expected to contain substantially different biological communities than the fjords within Kachemak Bay due to physical factors. Dogfish Bay (also known as Koyuktolik Bay) was sampled as a control site for Chrome Bay. Chrome Bay is a small bay (0.7 km^2) off Port Chatham at the tip of the Kenai Peninsula, and connects to an even smaller bay (Clam Cove) that is mostly exposed at low tide. Chrome Bay and Port Chatham are somewhat protected by Elizabeth Island 3 km to the south, but are exposed to the open ocean conditions of Kennedy Entrance at the mouth of Cook Inlet. Dogfish Bay is 7 km northwest of Chrome Bay, also at the tip of the Kenai Peninsula. It is a 3 km long by 1.5-2 km wide bay with the mouth also open to the open ocean of Kennedy Entrance. Port Graham Bay is a 10 km bay/fjord that lies to the northeast of Dogfish Bay and opens into lower Cook Inlet. It was sampled by NS&T with the same methods presented here (Hartwell *et al*. 2009) and completes the data set for the peninsula. Seldovia Bay is a 1x6 km long bay/fjord northeast of Port Graham that opens into the mouth of Kachemak Bay. The City of Seldovia sits on the eastern side of the mouth of the bay. The Bay and the harbor at Seldovia were both sampled. Jakolof Bay is a smaller fjord (3.5 km) that opens into Kasitsna Bay. Sadie Cove and Tutka Bay are narrow fjords (9 and 15 km long, respectively) that are mostly less than 1 km wide, with multiple submerged moraines along their lengths. China Poot Bay is a much shallower embayment, protected by a low barrier island and with extensive sand/gravel flats behind it that are exposed at low tide. Halibut Cove Lagoon is a small (2 km long) but relatively deep lagoon (70+ m) surrounded by steep scarps that drop straight into the water. Access is through a narrow channel with extreme tidal currents. Sand flats adjacent to the channel are partially exposed at low tide. In addition to the bays described above, data collected in 2007 from Port Graham Bay are included in this report.

Three sampling sites were located on a random basis within each bay except Sadie Cove and Tutka Bay (Figure 3). This approach combines the strengths of a stratified design with the random-probabilistic selection of sampling locations, allowing the data generated within each

stratum to be attributed to the size of that stratum with a quantifiable degree of confidence (Heimbuch *et al*. 1995). Within each bay, two randomly selected alternate sites were also selected for each primary sampling site. In instances where the primary site could not be sampled due to non-accessibility or an unsuitable substratum, the next sequential alternate site was sampled. One extra sample was taken in Clam Cove, a shallow arm of Chrome Bay. Two locations on either side of the Homer POTW effluent on the north side of Kachemak Bay were also sampled, but the data are not addressed in this report because they were taken in open waters of Kachemak Bay, not embayments. Two of the sites in Halibut Cove were in the lagoon proper, while one was located outside the lagoon in Halibut Cove.

2.1 Sampling procedures

Two sediment samples were taken at each site in addition to water quality measurements with YSI meter readings at the surface and bottom of the water column. A total of 26 sites were sampled. Samples were collected with a Kynar-coated 0.1 m^2 Young-modified Van Veen grab sampler. The sampler was initially washed, rinsed with acetone and deionized water, followed by an acid wash with 10% HCl and again rinsed with deionized water. At each site, the sampler was rinsed with acetone and deionized water immediately prior to sampling. Only the upper 2-3 cm of the sediment was retained in order to assure collection of recently deposited materials. A sediment sample was discarded if the jaws of the grab were open, or the sample was partly washed out.

Sediments were removed with a Teflon coated stainless steel scoop. Sediment was composited from multiple grabs in a bucket with an acetone rinsed, high-density polyethylene (HDPE) liner. Between each deployment of the sampler, the bucket was covered with an HDPE lid to minimize sample oxidation and exposure to atmospheric contamination. Additional grab samples were taken, and the top layer of sediment was collected and composited until sufficient volume (~1 L) of sediment for all the chemical analyses was collected. Additional volume was collected at Chrome Bay for sediment bioassays.

The sediment samples were thoroughly homogenized in the field with an acetone-rinsed, stainless steel mixer attachment on an electric drill. This composite sample was subdivided for distribution to various testing laboratories. Subsamples were collected for grain size characterization. Samples for chemical analyses were stored in pre-cleaned glass jars with Teflon® liners and frozen. Samples for toxicity testing were stored in 1 L polyethylene jars with Teflon® coated lids and kept refrigerated. The bucket liners were not reused between sampling sites. A second sample was taken for benthic community analysis with a Kynar-coated 0.04 m^2 PONAR grab sampler. The entire contents of an acceptable sample (at least 5 cm deep) were sieved on site through 0.5 mm mesh. All organisms were retained in Nalgene bottles and preserved in buffered formalin containing Rose Bengal stain.

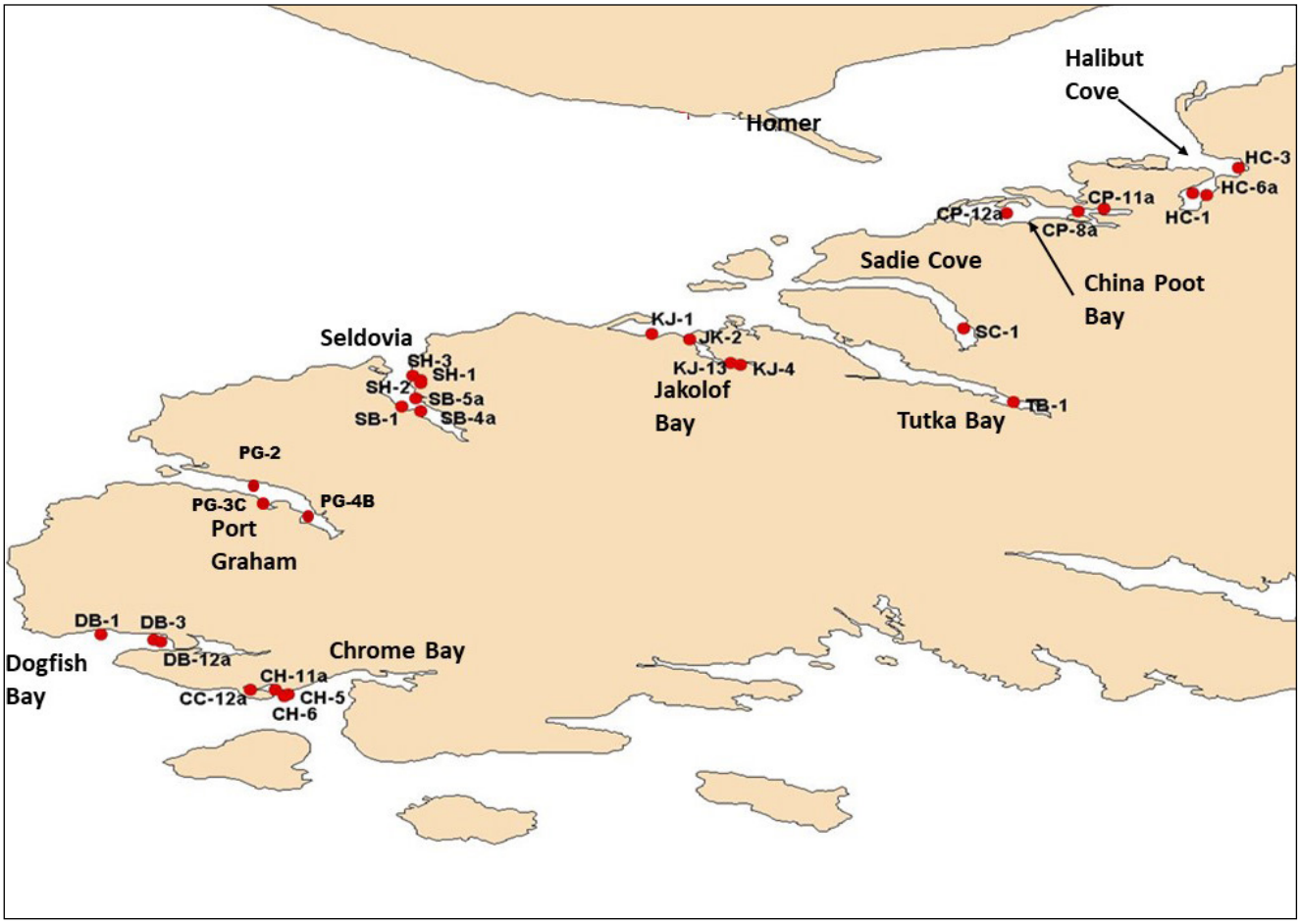

Figure 3. Map of the Kenai Peninsula showing sampling site locations. From right to left: Halibut Cove (HC), China Poot Bay (CP), Sadie Cove (SC), Tutka Bay (TB), Kasitsna/Jakolof Bay (K-J), Seldovia harbor (SH) & Seldovia Bay (SB), Dogfish Bay DB), Chrome Bay(CH), and Clam Cove (CC). Two locations on either side of the Homer sewage outfall (HO) on the north side of Kachemak Bay were also sampled. Three stations in Port Graham (PG) from a 2007 study are also included in the analyses.

Fish were collected by hook and line at Chrome Bay. All samples were frozen in double plastic zip lock bags and shipped to the Alaska Department of Environmental Health Laboratory for whole body analysis for As, Cd, Cr, Cu, Pb, Ni, Se, and Hg. Blue mussels (*Mytilus edulis*) were collected from Chrome Bay and at Tutka Bay for tissue analyses at the NS&T contract analytical lab also.

2.2 Chemical analysis

Chemical analyses followed procedures routinely used in the NOAA NS&T Program (Kimbrough and Lauenstein 2006a, 2006b; ASTM 2004). A broad suite of sediment contaminants were analyzed at each station, including 51 PAHs, 25 aliphatics from C_{10}-C_{34} plus pristane and phytane, 30 chlorinated pesticides, including DDT and its metabolites, 15 major and trace elements, and 54 polychlorinated biphenyls (PCBs), (Tables 1-4). Other parameters

included grain size analysis, total organic/inorganic carbon (TOC/TIC), and percent solids. Butyltins (Table 5) were analyzed in sediments collected in Seldovia Harbor.

2.2.1 Organics (PAHs, PCBs, chlorinated pesticides, aliphatics)

Samples were shipped frozen to the laboratory and stored at -20 °C until analysis. An aliquot of approximately 1 gm of sample was weighed and oven dried at 63 – 56 °C to constant weight to determine wet/dry weight. Homogenized sample aliquots were chemically dried with Hydromatix®. Sample/Hydromatix® mixtures were spiked with surrogates then extracted with 100% dichloromethane using an accelerated solvent extraction method. The extracts were then concentrated to 3 ml by evaporative solvent reduction. Silica gel/alumina column chromatography was utilized to concentrate and purify the samples before analysis. If sediment or other particulates were present in the sample extract, the extracts were filtered through a funnel containing glass wool and sodium sulfate. Quality control samples were processed with each batch of samples in a manner identical to the samples, including matrix spikes. Extracts were stored in the dark at or below 4°C. A method blank was run with every 20 samples, or with every sample set, whichever was more frequent. If blank levels for any component were above three times the method detection limit (MDL), samples analyzed in that sample set were re-extracted and reanalyzed. If insufficient sample was available for extraction, the data were reported and appropriately qualified. Matrix spike/matrix spike duplicate samples were run with every 20 samples, or with every sample set, whichever was more frequent. Surrogate standards were spiked into every sample and quality control sample.

Quantitation of PAHs and their alkylated homologues was performed by gas chromatography mass spectrometry (GC/MS) in the selected ion monitoring (SIM) mode. Target analytes are listed in Table 1. The compounds in the surrogate solution were deuterated naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}. The internal standards were fluorene-d_{10}, and benzo[a]pyrene-d_{12} at 4 µg/mL, and were prepared with a certified standard (NIST or equivalent). The GC conditions were set so that the internal standards were resolved, but would elute in close proximity to the analytes of interest.

Table 1. Polycyclic Aromatic Hydrocarbons (PAHs) measured in Kenai Peninsula samples.

Compound		
Naphthalene	Carbazole	Naphthobenzothiophene
C1-Naphthalenes	Anthracene	C1-Naphthobenzothiophenes
C2-Naphthalenes	Phenanthrene	C2-Naphthobenzothiophenes
C3-Naphthalenes	C1-Phenanthrene/Anthracenes	C3-Naphthobenzothiophenes
C4-Naphthalenes	C2-Phenanthrene/Anthracenes	Benz(a)anthracene
Benzothiophene	C3-Phenanthrene/Anthracenes	Chrysene
C1-Benzothiophenes	C4-Phenanthrene/Anthracenes	C1-Chrysenes
C2-Benzothiophenes	Dibenzothiophene	C2-Chrysenes
C3-Benzothiophenes	C1-Dibenzothiophene	C3-Chrysenes
Biphenyl	C2-Dibenzothiophene	C4-Chrysenes
Acenaphthylene	C3-Dibenzothiophene	Benzo(b)fluoranthene
Acenaphthene	Fluoranthene	Benzo(k)fluoranthene
Dibenzofuran	Pyrene	Benzo(e)pyrene
Fluorene	C1-Fluoranthenes/Pyrenes	Benzo(a)pyrene
C1-Fluorenes	C2-Fluoranthenes/Pyrenes	Perylene
C2-Fluorenes	C3-Fluoranthenes/Pyrenes	Indeno(1,2,3-c,d)pyrene
C3-Fluorenes		Dibenzo(a,h)anthracene
		Benzo(g,h,i)perylene

A solution containing 2- to 5-ring PAH compounds was used to fortify matrix spike samples. A certified solution (NIST SRM 2260) was diluted to the appropriate working concentration. Dibenzothiophene was not present in the SRM and was added to the solution by weighing neat material to make a concentration of 1.00 µg/L. The spiking solution was used to fortify samples to a final concentration of approximately ten times the MDL. A laboratory reference oil solution was analyzed as an instrument reference solution with each analytical batch. After every 8 - 10 samples, the mass spectrometer response for each PAH relative to the internal standard was determined using check standards. Daily response factors for each compound were compared to the initial calibration curve and recalibration was repeated when necessary. The standard reference oil was analyzed with all analytical batches.

Table 2. Chlorinated pesticides measured in Kenai Peninsula samples.

Compound Class	Compound	Compound Class	Compound
Cyclodienes	Aldrin	DDT and metabolites	2,4'-DDD
	Dieldrin		4,4'-DDD
	Endrin		2,4'-DDE
	Heptachlor		4,4'-DDE
	Heptachlor-Epoxide		2,4'-DDT
	Oxychlordane		4,4'-DDT
	Alpha-Chlordane	Chlorinated Benzenes	1,2,3,4-Tetrachlorobenzene
	Gamma-Chlordane		1,2,4,5-Tetrachlorobenzene
	Trans-Nonachlor		Hexachlorobenzene
	Cis-Nonachlor		Pentachloroanisole
Hexachlorocyclohexanes	Alpha-HCH		Pentachlorobenzene
	Beta-HCH	Other	Endosulfan II
	Delta-HCH		Endosulfan I
	Gamma-HCH		Endosulfan Sulfate
			Mirex
			Chlorpyrifos

Table 3. Major and trace elements measured in the Kenai Peninsula samples. For simplicity, the term metal is used without distinction between true metals and metalloids/nonmetals.

Symbol	Element	Symbol	Element	Symbol	Element
Al	Aluminum	Li	Lithium	Ni	Nickel
As	Arsenic	Fe	Iron	Se	Selenium
Cd	Cadmium	PB	Lead	Ag	Silver
Cr	Chromium	MG	Magnesium	Sn	Tin
Cu	Copper	Hg	Mercury	Zn	Zinc

When available, a standard reference material was extracted and analyzed with each batch of samples. Target concentrations were defined as the range of the certified value plus or minus the 95% confidence intervals found in the SRM certification. The measured concentration was within ±30% of the target concentration on average for all analytes either certified or non-certified with concentrations greater than 10 times the MDL. The actual analytical method detection limit (MDL) was determined following procedures outlined in CFR 40, part 136 (1999).

Table 4. Polychlorinated biphenyls (PCBs) measured in Kenai Peninsula samples (Co-eluting congeners are shown together).

Congener (s)	
PCB8/5	PCB128
PCB18	PCB138/160
PCB28	PCB146
PCB29	PCB149/123
PCB31	PCB151
PCB44	PCB153/132
PCB45	PCB156/171/202
PCB49	PCB158
PCB52	PCB170/190
PCB56/60	PCB174
PCB66	PCB180
PCB70	PCB183
PCB74/61	PCB187
PCB87/115	PCB194
PCB95	PCB195/208
PCB99	PCB199
PCB101/90	PCB201/157/173
PCB105	PCB206
PCB110/77	PCB209
PCB118	

Table 5. Butyltins measured in Kenai Peninsula samples.

Symbol	Compound
MBT	Monobutyltin trichloride
DBT	Ditbutyltin dichloride
TBT	Triobutyltin trichloride

Quantitation of aliphatic alkanes of C-10 through C-34 plus pristane and phytane was performed by high resolution, capillary gas chromatography with flame ionization detection (GC/FID). Quality control procedures (blanks, duplicates, matrix spikes) were identical to the PAH procedures, except there are no certified SRMs for these materials. The compounds in the surrogate solution were deuterated n-dodecane-d26, n-eisocane-d42, and n-triacontane-d62. The internal standards were 5α-androstane and n-hexadecane-d34.

Chlorinated hydrocarbons (chlorinated pesticides and PCBs, Tables 2, 4) were quantitatively determined by capillary gas chromatography with an electron capture detector (ECD). If the response for any peak exceeded the highest calibration solution, the extract was diluted, a known amount of surrogate and tetrachloro-m-xylene (TCMX) solution added, and the sample

reanalyzed for those analytes that exceeded the calibration range. Analyte concentrations in the samples were based on calculations using the PCB 103 surrogate. The internal standard (TCMX) was used to calculate surrogate recoveries. 4,4'-dibromooctafluorobiphenyl (DBOFB) or PCB 198 was used to calculate selected analytes concentrations, if it was demonstrated that they produced more reliable data (i.e., if matrix interference occurs with PCB 103) based on percent recoveries in spiked blanks, matrix spikes, or reference materials. The calibration solutions that were analyzed as part of the analytical GC/ECD run were preceded by no more than six samples, and no more than six samples were run between calibration mixtures.

An acceptable method blank contained no more than two target compounds at concentrations three times greater than the MDL. All samples and quality control samples were spiked with DBOFB, PCB 103 and PCB 198. The surrogate standard solution was spiked into the samples prior to extraction in an attempt to minimize individual sample matrix effects associated with sample preparation and analysis. A matrix spike and a duplicate were analyzed with each sample set or every 20 field samples, whichever was more frequent. The acceptable matrix spike recovery criteria were 50 - 125% recovery for at least 80% of the analytes. Criterion for duplicates was ≤30% relative percent difference (RPD). The method detection limit was determined following the procedures outlined in CFR 40, part 136 (1999). Most target compounds, surrogates and internal standards were resolved from one another and from interfering compounds. When they were not, coelutions were documented. A standard reference material sample was analyzed per batch of samples or every 20 samples, whichever was more frequent.

2.2.2 Trace and major elements

Samples were shipped frozen to the laboratory and stored at -20 °C until analysis. Samples were prepared for inductively coupled plasma/mass spectrometry analysis (ICP-MS) for major metals, while atomic fluorescence spectrometry was utilized to measure arsenic and selenium, and atomic absorption spectrometry was used for mercury analysis. In general, samples were homogenized, freeze dried, weighed and digested in a sequence of heating steps with metal grade HNO_3, HF and boric acid. For analysis of Hg, sediment samples were digested based on a modified version of U.S. EPA (1991) method 245.5, using a concentrated H_2SO_4 and HNO_3 digestion, followed by addition of $KMnO_4$, and $K_2S_2O_8$, and then the samples were again digested. Before analysis, 5 mL of 10% (w/w) $NH_2OH \cdot HCl$ were added to reduce excess permanganate and the volume brought to 40 mL with distilled water.

Quality control samples were processed in a manner identical to actual samples. A method blank was run with every 20 samples, or with every sample batch, whichever was more frequent. If corrected blank concentrations for any component were above three times the

method detection limit (MDL), the whole sample set was re-extracted and reanalyzed. If insufficient sample was available for re-extraction, the data was reported and appropriately qualified. Matrix spike/matrix spike duplicate (MS/MSD) samples were run with every 20 samples, or with every sample set, whichever was more frequent. Recalibration standards were also run every 12 samples, and matrix modifiers were used as necessary. The appropriate spiking level was ten times the MDL. Reference materials were extracted with each set of sample and were analyzed when available. The MDLs were determined following the procedures outlined in CFR 40, part 136 (1999).

For analysis of Hg, sediment samples were digested using a modified version of EPA method 245.5, using a concentrated H_2SO_4 and HNO_3 digestion, followed by addition of $KMnO_4$, and $K_2S_2O_8$, and then the samples were again digested. Before analysis, 5 mL of 10% (w/w) $NH_2OH \cdot HCl$ were added to reduce excess permanganate and the volume brought to 40 mL with distilled water.

2.2.3 Butyltins

An aliquot of freeze dried sediment was weighed and appropriate amounts of surrogate standards (approximately 10 times the method detection limit, MDL) were added to all samples, matrix spikes, and blanks. Samples were extracted three times by agitation with tropolone in dichloromethane. The sample extract was concentrated in a hot water bath, and the extract was centrifuged and further concentrated. The solvent was exchanged to hexane and concentrated to a final volume of about 10 – 20 mL, at which point only hexane remained. Hexylmagnesium bromide (2 M; Grignard reagent) was added to the sample extract under nitrogen and heated to hexylate the sample. After separation from the organic phase, pentane:CH_2Cl_2 (3/1, v/v) was added to the aqueous phase and the sample shaken vigorously. The pentane:CH_2Cl_2 extraction was done twice. The hexylated extract was dried by addition of anhydrous Na_2SO_4 and then concentrated. The extract was purified using silica gel/alumina column chromatography. The eluent was collected and concentrated on a water bath.

The quantitative method was based on high resolution, capillary gas chromatography using flame photometric detection (GC/FPD). This method quantitatively determined tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT).

Quality control samples were processed in a manner identical to actual samples. A method blank was run with every 20 samples, or with every sample batch, whichever was more frequent. If corrected blank concentrations for any component were above three times MDL, the whole sample set was re-extracted and reanalyzed. If insufficient sample was available for re-extraction, the data was reported and appropriately qualified. Matrix spike/matrix spike

duplicate (MS/MSD) samples were run with every 20 samples, or with every sample batch, whichever was more frequent. The appropriate spiking level was ten times the MDL. Reference materials were extracted with each set of sample and were analyzed when available. The method detection limit was determined following the procedures outlined in CFR 40, part 136 (1999).

2.3 Benthic community characterization

In the laboratory, samples were inventoried, rinsed gently through a 0.5 mm mesh sieve to remove formalin and residual sediment, stained with Rose Bengal, and stored in 70% isopropanol solution until processing. Sample material (sediment, detritus, and organisms) were placed in white enamel trays for sorting under Wild M5A dissecting microscopes. All macroinvertebrates were carefully segregated into major taxonomic groups (e.g. Polychaeta, Mollusca, and Arthropoda). The macroinvertebrates were then identified to the lowest practical identification level, which in most cases is to species level unless the specimen is a juvenile, damaged, or otherwise unidentifiable. The number of individuals of each taxon, excluding fragments was recorded. Data were synthesized into a data summary report for each site, which includes a taxonomic species list and benthic community parameters list. At a minimum, 10 percent of all samples were resorted and recounted on a regular basis. Also, 10 percent of samples were randomly selected and re-identified. The minimum acceptable sorting and taxonomic efficiency was 95%. A voucher collection composed of representative individuals of each species encountered in the project was accumulated and retained.

Taxa are distributed along environmental gradients, so there are generally no distinct boundaries between communities. However, the relationships between habitats and species assemblages reflect the interactions of physical and biological factors and can indicate major ecological trends. Quantitatively, the benthic communities were characterized as enumeration by abundance, species richness, evenness, and diversity, followed by pattern and classification analysis for delineation of taxa assemblages. Abundance was calculated as the total number of individuals per square meter; taxa richness as the total number of taxa represented at a given site; and taxa diversity was calculated with the Shannon-Weiner Index (Shannon and Weaver, 1949), using the following formula:

Eqn1 $$H' = -\sum_{i=1}^{S} p_i (\ln p_i)$$

where, S = is the number of taxa in the sample, i is the i_{th} taxa in the sample, and p_i is the number of individuals of the i_{th} taxa divided by the total number of individuals in the sample.

2.4 Sediment toxicity bioassays

Amphipod mortality bioassays were carried out on the sediment samples collected at Chrome Bay only. All methods are based on standard methods promulgated by ASTM (2004). The whole sediment toxicity bioassay test is commonly used in North America for assessing sediment quality, in part because the test integrates the effects of complex contaminant mixtures in relatively unaltered sediment, and also because amphipods are fairly common and ecologically important species in coastal waters. The organisms are standard test species with known ranges of sensitivity and their presence or absence in a particular habitat is not relevant because they are tested under standardized conditions. The amphipod *Eohaustorius estuarius* is found in shallow subtidal water along the Pacific coast. *E. estuarius* is a free burrowing deposit feeder found in medium-fine sand with some organic content. It is routinely collected in areas where pore-water salinity ranges from 1 to 25‰.

The tests were performed in accordance with a standard guide for conducting 10-day static sediment toxicity tests with amphipods (ASTM 2004), and additional guidance developed for testing four different amphipod species (U.S. EPA 1994). Briefly, amphipods were exposed to test and control sediments for 10 days under static conditions. The bioassays included 5 replicates, with 20 animals per replicate. During the test, the animals were exposed to constant light in filtered, aerated seawater at 28 ppt salinity. The test chambers were 1L glass vessels, containing 200 mL of sediment. The vessels were monitored daily for water temperature and condition of test organisms. Measurements for salinity, dissolved oxygen, ammonia, and pH were made at least twice during the course of the bioassay. Hydrogen sulfide in sediment pore water was also measured periodically.

A positive control, or reference toxicant test, was used to document the sensitivity the batch of test organisms. A commonly used industrial chemical, sodium dodecyl sulfide, also known as sodium lauryl sulfide, was used in 96-hour water-only exposure bioassay as a control test. The LC_{50} results were recorded in a control chart, and were expected to be within 2 standard deviations of the mean of the previous 20 positive control tests.

2.5 Statistical contrasts

2.5.1 Contaminants

Because trace elements and other compounds naturally vary in concentration by several orders of magnitude, normalized values were calculated for the purpose of summarizing contaminant data in consistent units. Data were normalized to the overall mean for each chemical. This was applied to each element. Thus, all metals can be contrasted against each other, or metals against organics in consistent units. Spearman rank correlations

were calculated to assess the degree of association between sediment characteristics, the concentration of trace metals and organic compounds, and benthic community metrics.

2.5.2 Sediment quality guidelines

Numerical sediment quality guidelines (SQG) developed by Long and Morgan (1990) and Long *et al*. (1995) known as ERM and ERL (effects range-median, effects range-low), (Appendix A) express statistically derived levels of contamination, above which toxic effects would be expected to be observed with at least a 50% frequency (ERM), and below which effects were rarely (<10 %) expected (ERL). The mean ERM quotient (Long *et al*. 1998) is the average of the ratio of ERM value to sediment concentration for each chemical. The mean quotient of the ERMs and observed contaminant concentrations were calculated on a site by site basis. The calculation included all the individual metals, low weight PAHs, high weight PAHs, total PCBs, and total DDT and its metabolites.

2.5.3 Benthic community analysis

Multivariate cluster analysis was employed to group site and species data. The objective was to produce a coherent pattern of association between sites and species. Cluster analysis is a two-step process including; 1) creation of a resemblance data matrix from the raw data, and 2) clustering the resemblance coefficients in the matrix. The input resemblance (similarity or dissimilarity) matrix can be created by a number of methods. Input data may or may not be standardized or transformed depending on the requirements of the method (e.g. Bray Curtis). Based on previous research (Hartwell and Claflin 2005), the Jaccard method (Goodall 1973) was used to generate the similarity matrix.

The Jaccard method is a binary method based only on presence/absence data, and thus ignores abundance values. Cluster analyses were calculated from the matrices using the Unweighted Pair-Group Method Using Arithmetic Averages procedure, which clusters coefficients based on arithmetic mean distance calculations (Sneath and Sokal 1973). To optimize the cluster analysis results, several manipulations of the input data were performed to remove confounding effects and bias.

1- Epiphytic species such as sea anemones and tunicates were eliminated from the data set as they are not truly infauna.

2- Artificial species (resulting from failure to identify some specimens all the way down to species) were identified as a data bias. For example, if specimens of 2-3 species were identified in genus A, and other specimens were identified only to genus A, this tends to artificially increase species richness and diversity of the sample when in fact that diversity

is an artifact of imperfect taxonomic identification. In some instances, specimens were only identifiable to family, order or class. To address this problem, specimens not identified to species level were eliminated, unless they were identified to a taxonomic level below which no other specimens in the collection belonged. That is, even though they were not identified to species, they were the only representative of that taxonomic line and did represent a non-redundant taxon. In other cases, where a specimen was identified to genus and there was only one species identified in that genus, they were combined at the genus level.

3- Rare and unique taxa were defined as those species that were found at no more than two stations. Although they do contribute to the overall assessment of biodiversity, they were eliminated from the cluster analysis data set. Because of their limited distribution, by definition, they do not provide information on the impact of contaminant or other stressors gradients in the environment because they do not occur across the entire gradient.

The site and species clusters were also characterized by physicochemical habitat parameters, contaminant concentrations, and other site-specific data (Figure 4). For each species, the parameters were normalized to their abundance at each site. For example, if 100 specimens of species A were found at a site with a TOC value of 1.5% and 10 were found at a site where TOC was 2%, the abundance normalized TOC preference for species A would be [(100*1.5)+(10*2)]/110=1.55.

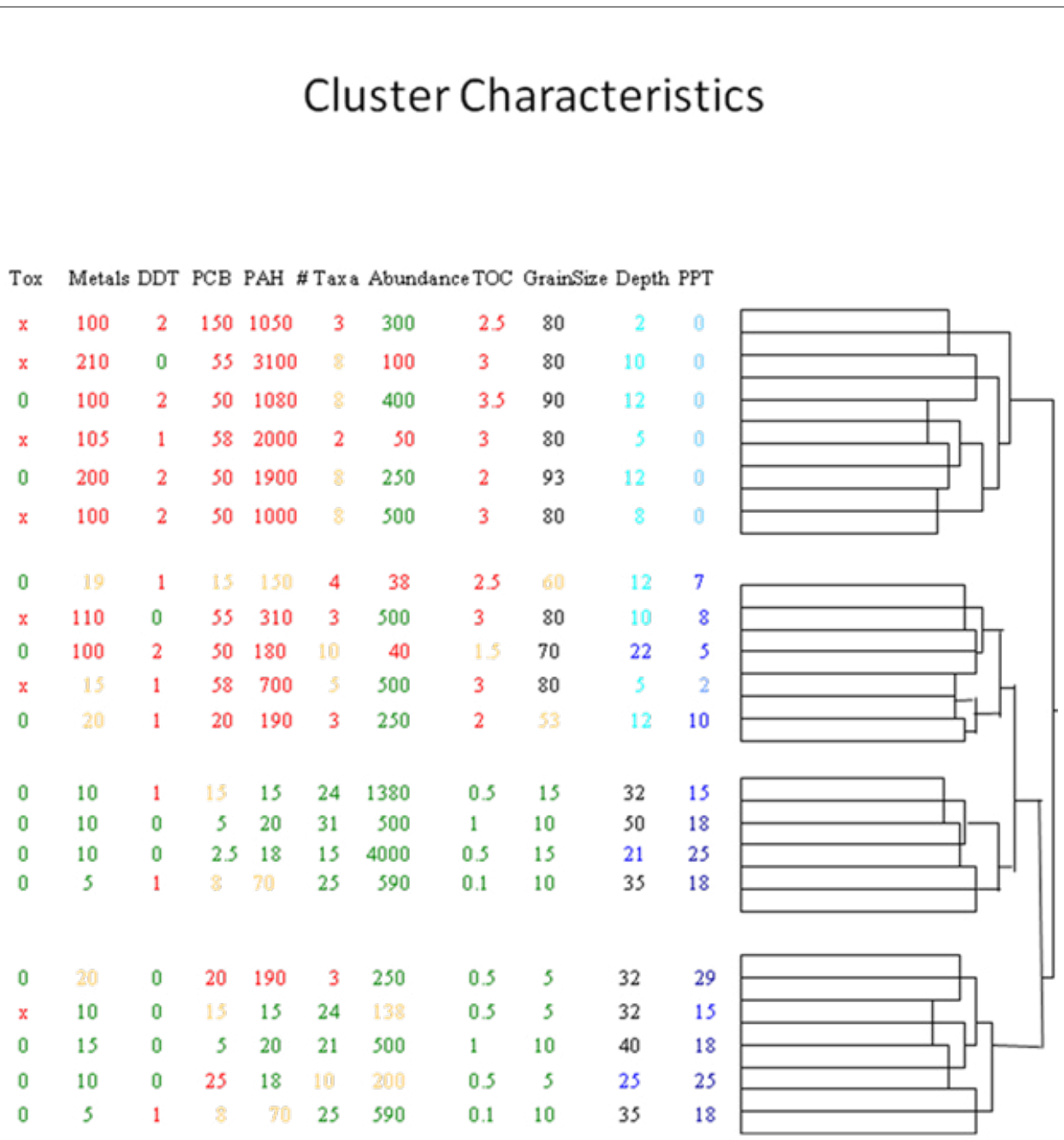

Figure 4. Conceptual representation of the distribution of physicochemical habitat parameters, contaminant concentrations, and other site-specific data used to characterize site and species clusters.

3. RESULTS AND DISCUSSION

3.1 Habitat Conditions

None of the sampled areas receive drainage from existing glaciers. All water input is from rain, snowmelt, and groundwater. Water clarity as measured by Secchi disk averaged nearly 4 meters (Figure 5). In contrast, the eastern portion of Kachemak Bay water clarity averages only one meter due to glacial runoff from the Fox and Bradley Rivers (Hartwell *et al*. 2009). China Poot Bay and Clam Cove were so shallow, water clarity extended to the bottom. Water clarity was slightly greater than the other bays in Dogfish and Chrome Bays, which open through wide mouths to coastal water masses.

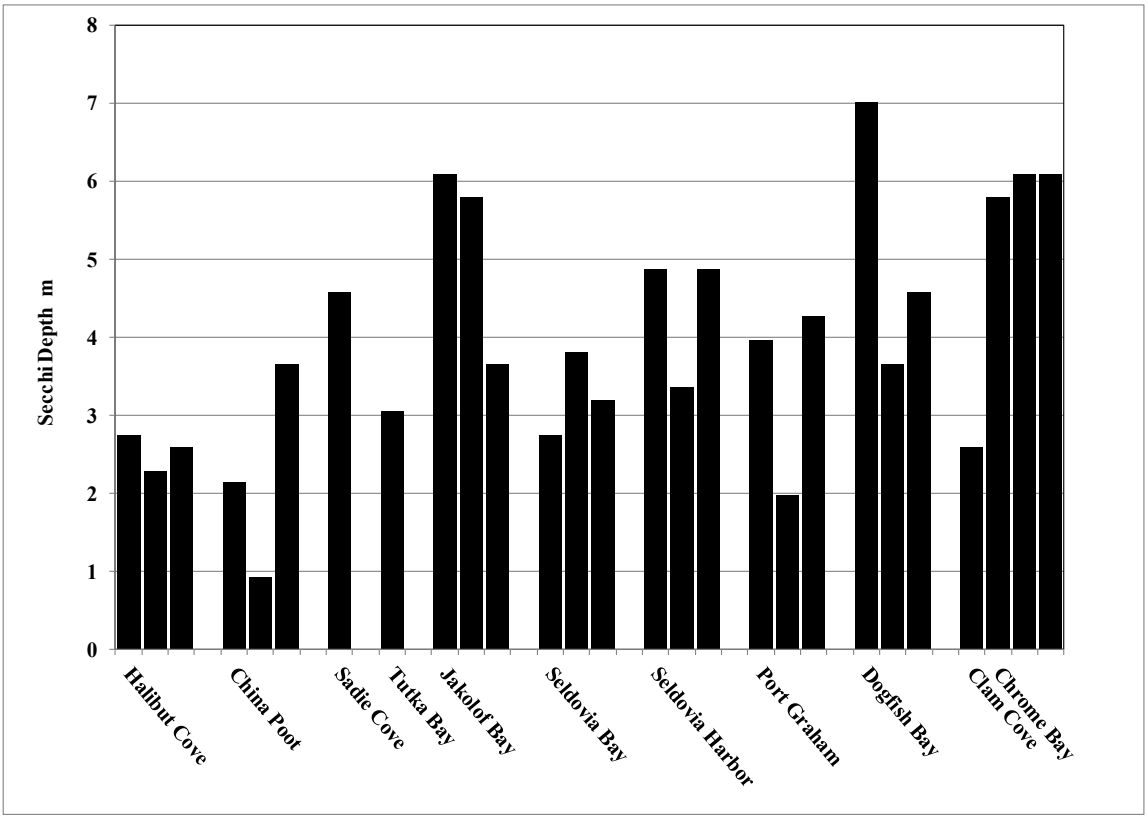

Figure 5. Water clarity in fjords and bays on the Kenai Peninsula.

Halibut Cove Lagoon, Tutka Bay and Sadie Cove were relatively deep, although the tidal range varies by 6+ meters, so the measured depths are approximate (Figure 6). The latter two had submerged glacial moraines in the mid-sections which affects water circulation in the upper portions of the fjords. The deep bays and the deeper areas in Seldovia Bay tended to have finer grained sediment (Figure 7). The water column was well mixed in all places except Halibut Cove Lagoon and Sadie Cove based on temperature, salinity and dissolved oxygen levels (Figures 8-10). Halibut Cove Lagoon appears to have been stratified at the time of sampling. The bottom of the water column in the upper Sadie cove had relatively low oxygen

concentrations, with large differences in temperature and salinity between surface and bottom, indicating that the moraine restricts water circulation in the upper portion of the fjord. This has been observed by other researchers (K. Holderied, personal communication). Sediment in Sadie Cove was 96% fine grained material, and was anoxic.

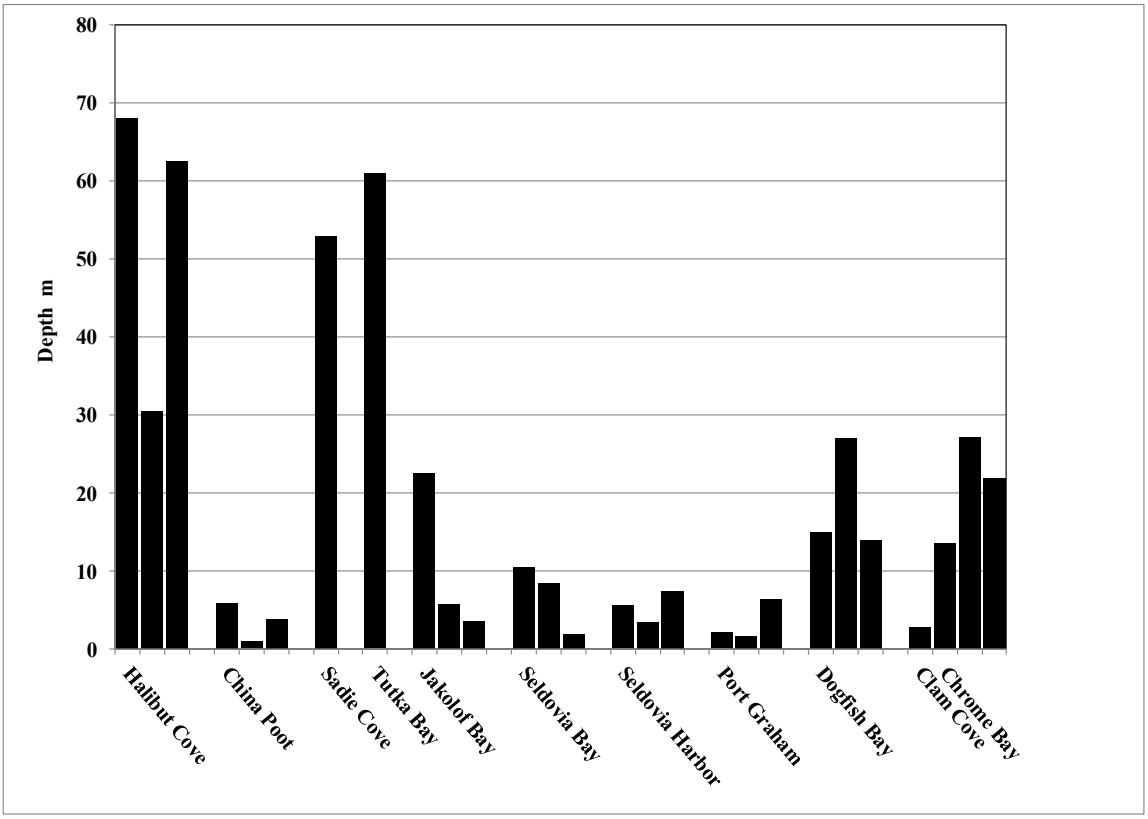

Figure 6. Measured depths in fjords and bays on the Kenai Peninsula.

Sediment physical characteristics are one of the overriding environmental parameters that influence the distribution of both contaminants and benthic species. Sediment type (e.g. mud vs. sand) and associated levels of organic matter content also influences the capacity of the sediment to sequester contaminants, and hence the potential to be toxic to organisms. The percent composition of fine grained sediment was strongly correlated with organic carbon content (Spearman's rho = 0.7919, $p < 0.0001$), as shown in Figure 11.

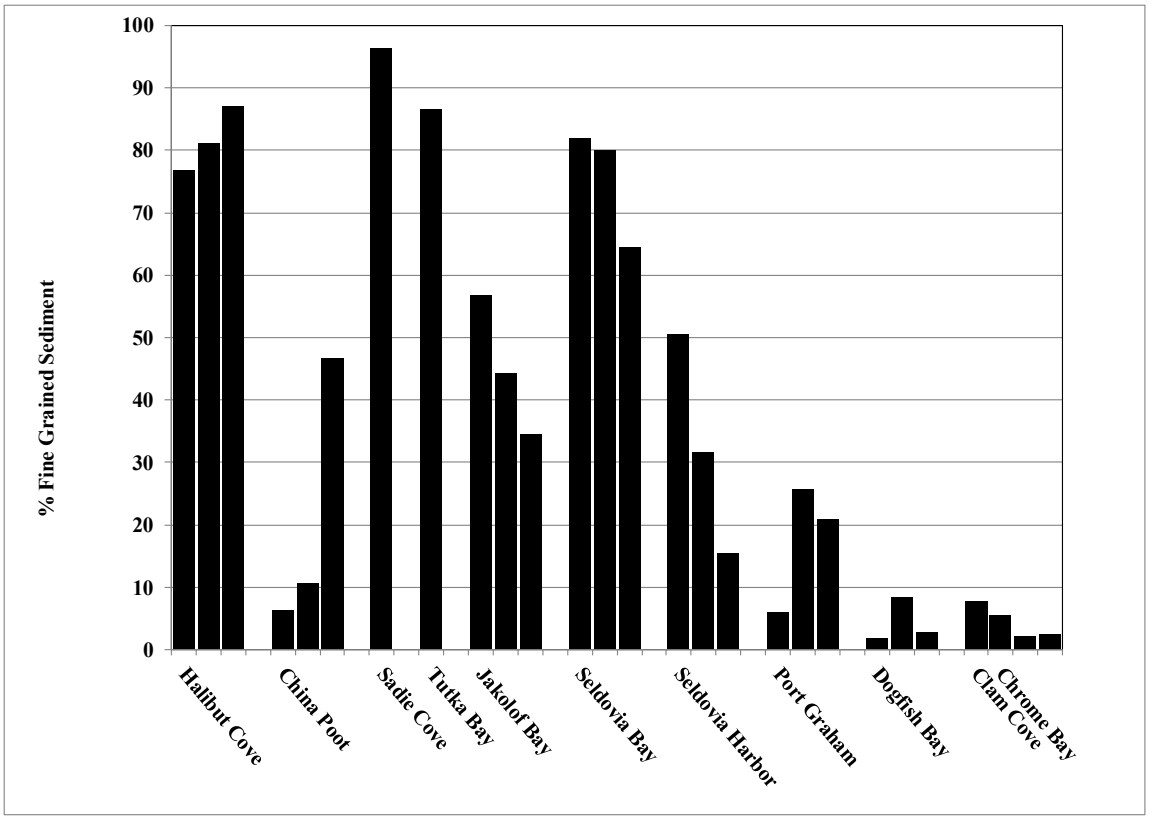

Figure 7. Percent fine-grained sediment (silt + clay) in fjords and bays on the Kenai Peninsula.

Halibut Cove Lagoon, Sadie Cove, and Tutka Bay are stratified to varying degrees, so the bottom water layer is less disturbed than would otherwise be the case. This allows fine grained material to settle and accumulate. The central portion of Seldovia Bay does not appear stratified, but is a deeper basin than the surrounding bay, where fine grained material has accumulated (Figure 7). Total organic carbon content in the sediments was highly variable between the bays (Figure 12). Halibut Lagoon had surprisingly little TOC. China Poot Bay is relatively shallow and tidal currents do not allow settlement of fine grained material where TOC could accumulate, unlike the other bays. Dogfish and Chrome Bays also have very low TOC. They have wide mouths open to the Kennedy Entrance that allow thorough tidal flushing.

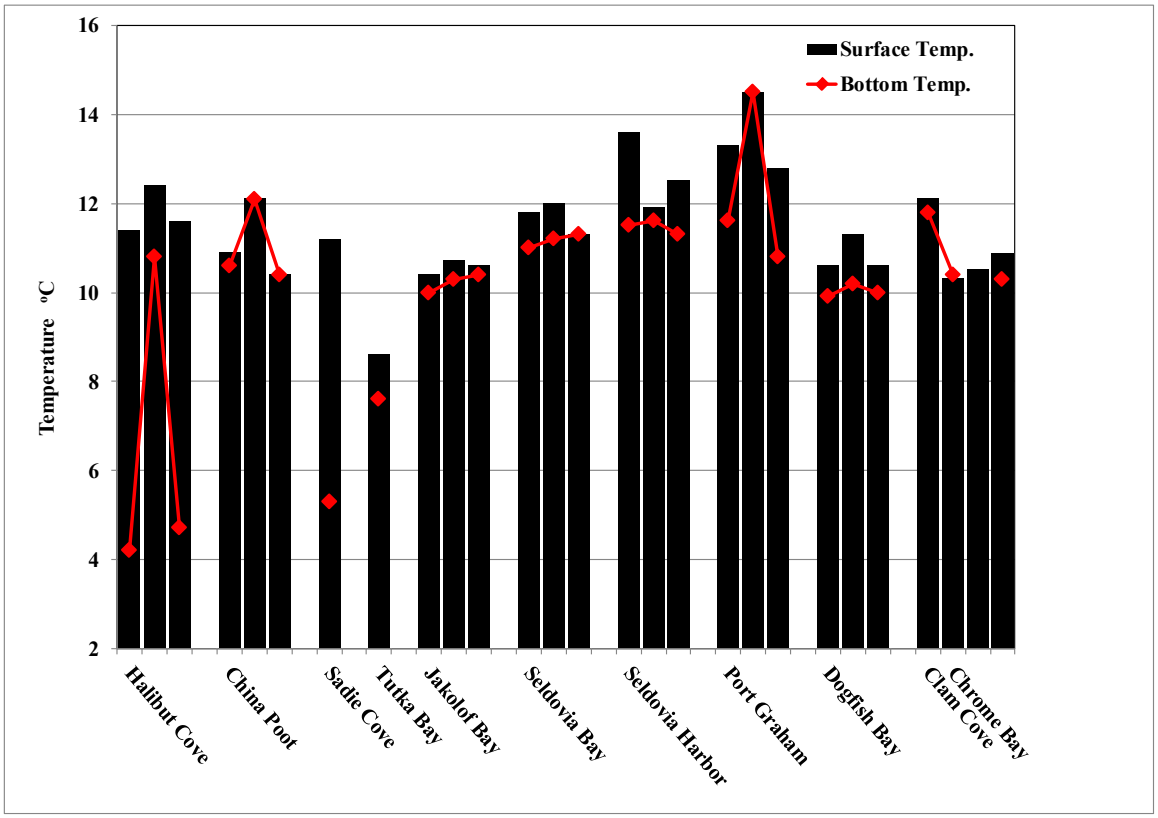

Figure 8. Surface and bottom water temperatures in fjords and bays on the Kenai Peninsula.

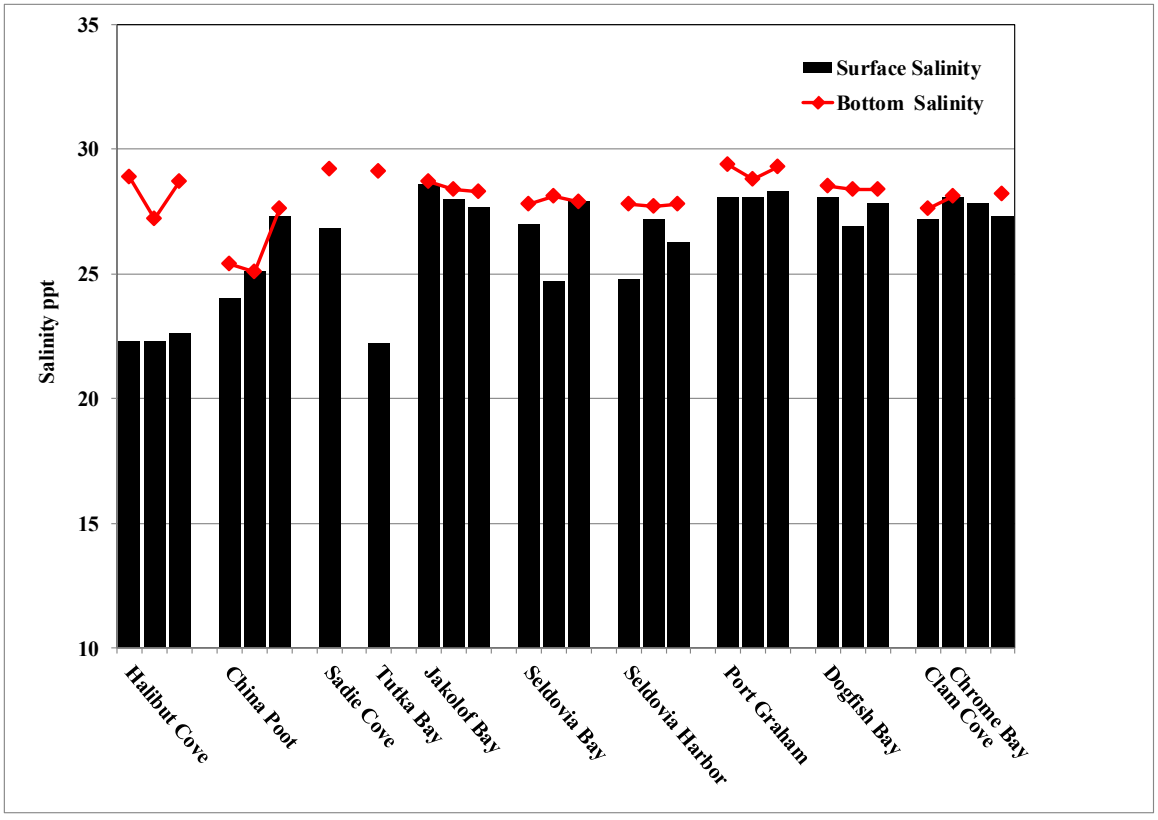

Figure 9. Surface and bottom water salinity in fjords and bays on the Kenai Peninsula.

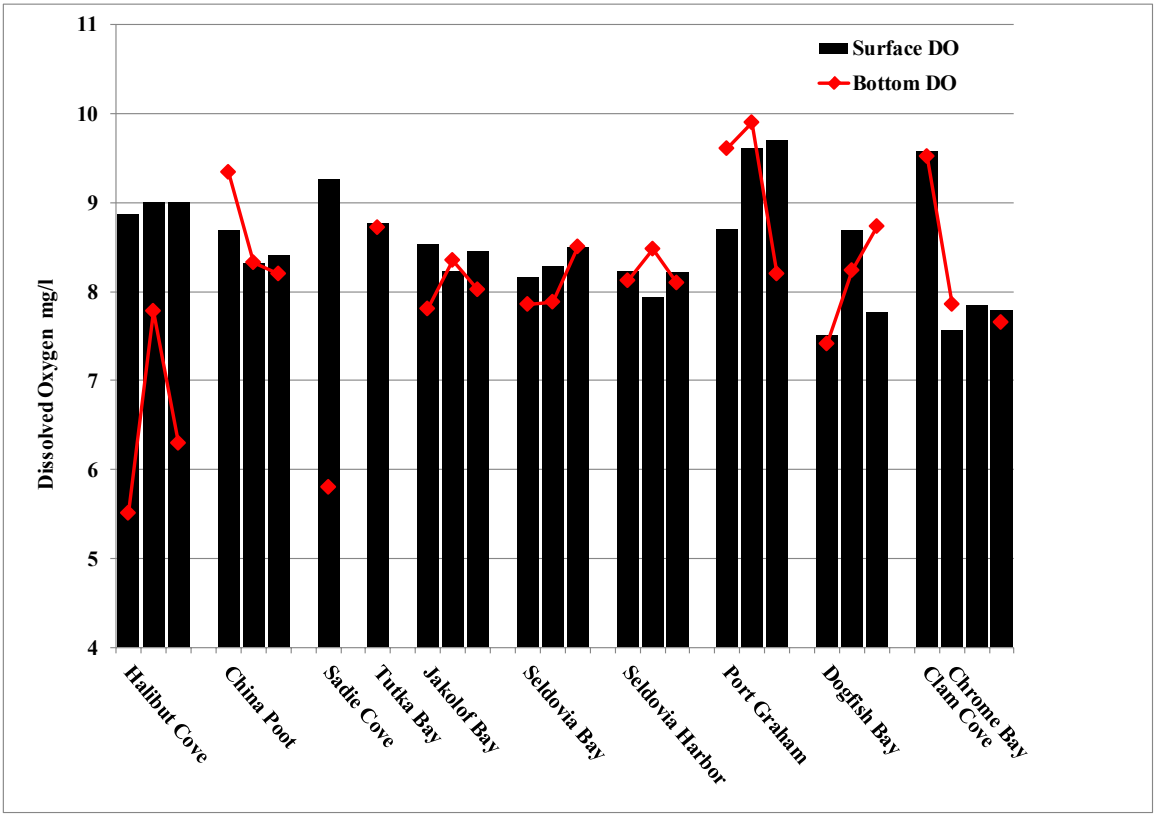

Figure 10. Surface and bottom water dissolved oxygen in fjords and bays on the Kenai Peninsula.

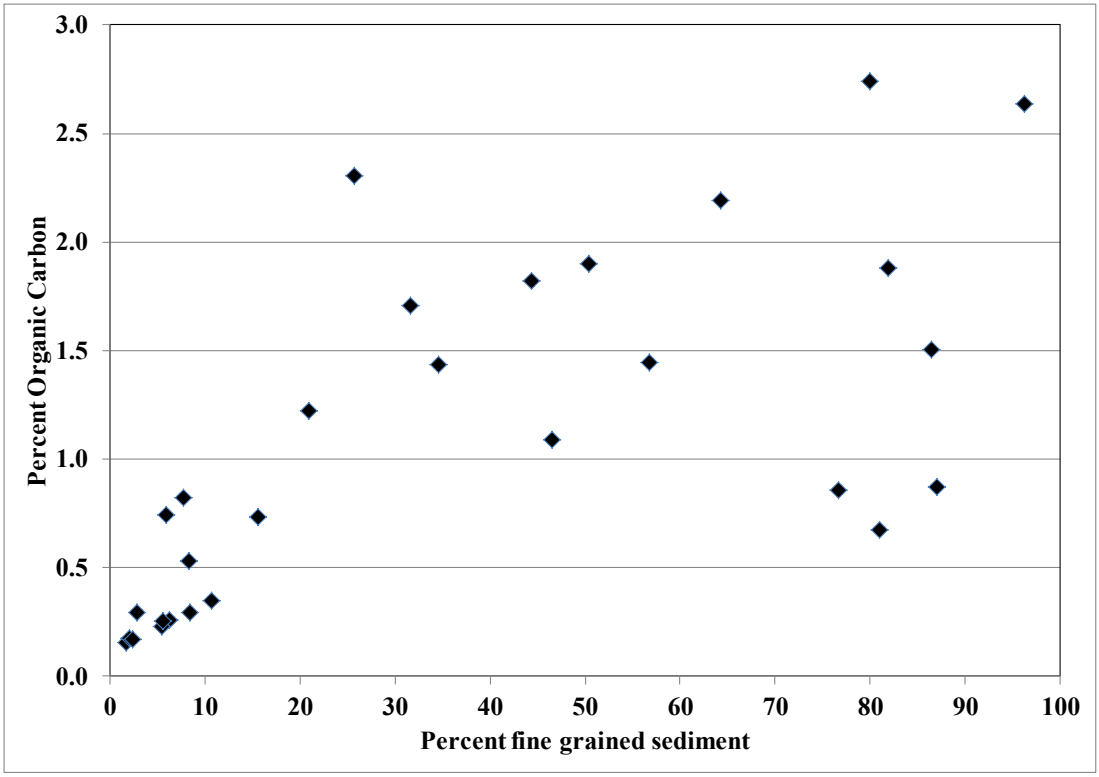

Figure 11. Relationship between fine grained sediment and organic carbon content.

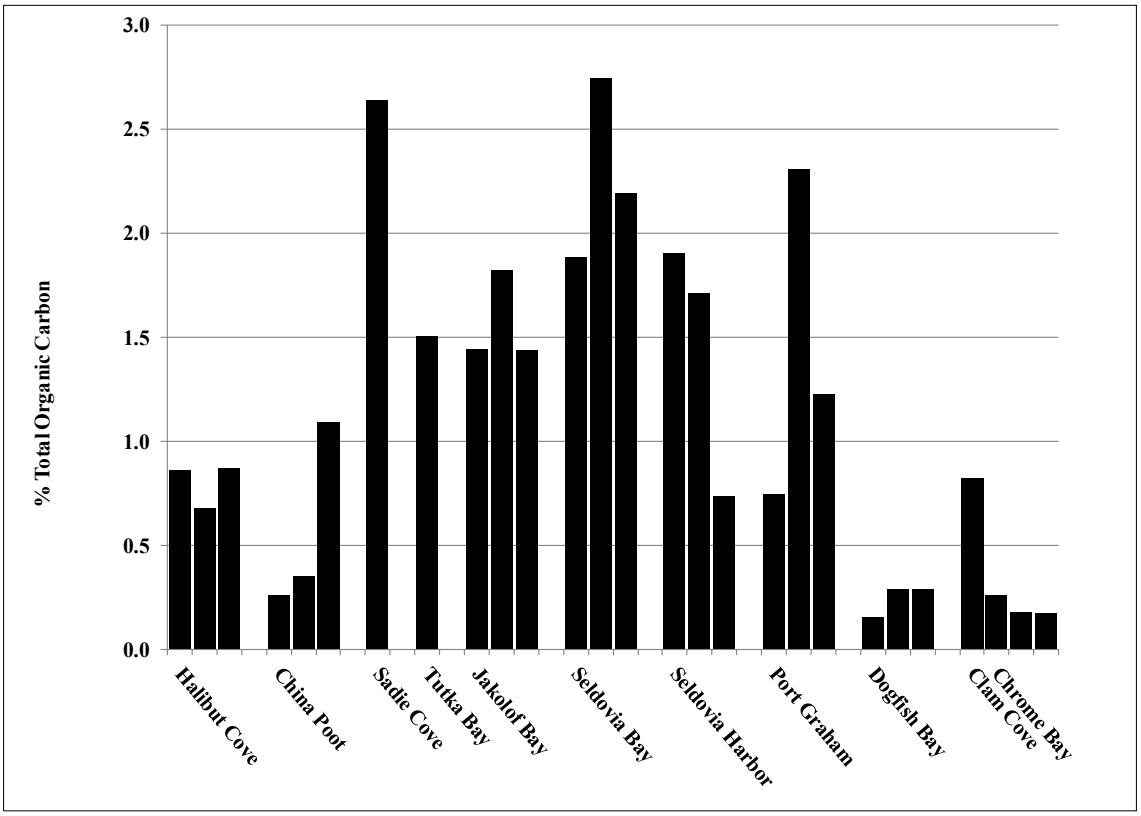

Figure 12. Total organic carbon content of sediment oxygen in fjords and bays on the Kenai Peninsula.

3.2 Trace element and organic chemical concentrations

3.2.1 Metals and metalloids

Arsenic, Cr, Cu, Hg, and Ni exceeded the ERL concentrations at multiple sites (Table 6). Nickel exceeded the ERL at all sites except in Dogfish Bay. Nickel and chromium concentrations far exceeded the ERMs in Chrome Bay (Figure 13, 14). Each of the embayments has its own unique mix of trace elements, reflecting differences in the geology/physical processes of the specific locations. Normalizing each element to its mean value in the entire data set allows comparison between different elements.

Table 6. Sediment concentrations (ug/g) of As, Cr, Cu, Hg, and Ni in fjords and bays on the Kenai Peninsula. The ERM and ERL values are listed at the bottom. ERL exceedances are highlighted and ERM exceedances are in bold.

Water Body	Station	Arsenic	Chromium	Copper	Mercury	Nickel
Halibut Cove	HC-1	19.6	87.9	66.2	0.20	46.9
Halibut Cove	HC-3	18.7	88.8	71.0	0.20	47.4
Halibut Cove	HC-6a	19.8	90.5	68.4	0.21	47.3
China Poot	CP-11a	6.8	51.0	32.8	0.08	23.9
China Poot	CP-12a	6.0	65.3	34.4	0.10	29.5
China Poot	CP-8a	6.1	58.3	44.1	0.14	31.6
Sadie Cove	SC-1	4.4	38.3	29.8	0.15	20.9
Tutka Bay	TB-1	8.7	67.9	52.2	0.18	37.0
Jakalof Bay	KJ-1	5.8	52.3	16.7	0.10	22.6
Jakalof Bay	KJ-13a	9.0	62.8	24.6	0.14	39.2
Jakalof Bay	KJ-4	9.0	62.1	28.8	0.23	40.8
Seldovia Harbor	SH-1	7.7	130.2	56.0	0.10	40.2
Seldovia Harbor	SH-2	8.9	139.9	32.1	0.09	47.9
Seldovia Harbor	SH-3	4.4	71.9	26.0	0.05	33.1
Seldovia Bay	SB-1	6.4	92.7	32.3	0.13	**55.2**
Seldovia Bay	SB-4a	7.1	194.5	33.6	0.13	**220.1**
Seldovia Bay	SB-5a	7.8	116.4	32.6	0.11	48.8
Port Graham	PG-2	8.0	55.2	19.3	0.12	23.0
Port Graham	PG-3c	10.2	50.9	26.3	0.35	25.2
Port Graham	PG-4b	8.6	334.0	23.1	0.14	37.4
Dogfish Bay	DB-1	4.6	7.3	36.9	0.05	5.4
Dogfish Bay	DB-12a	6.1	23.1	33.5	0.11	9.0
Dogfish Bay	DB-3	5.5	12.5	52.6	0.05	7.5
Clam Cove	CC-12a	12.6	**856.7**	11.9	0.04	**497.3**
Chrome Bay	CH-11a	5.0	**420.0**	20.6	0.06	**204.7**
Chrome Bay	CH-5	4.0	**602.1**	17.0	0.33	**179.3**
Chrome Bay	CH-6	3.2	**275.7**	18.9	0.04	**141.8**
ERM		**70**	**370**	**270**	**0.71**	**51.6**
ERL		8.2	81	34	0.15	20.9

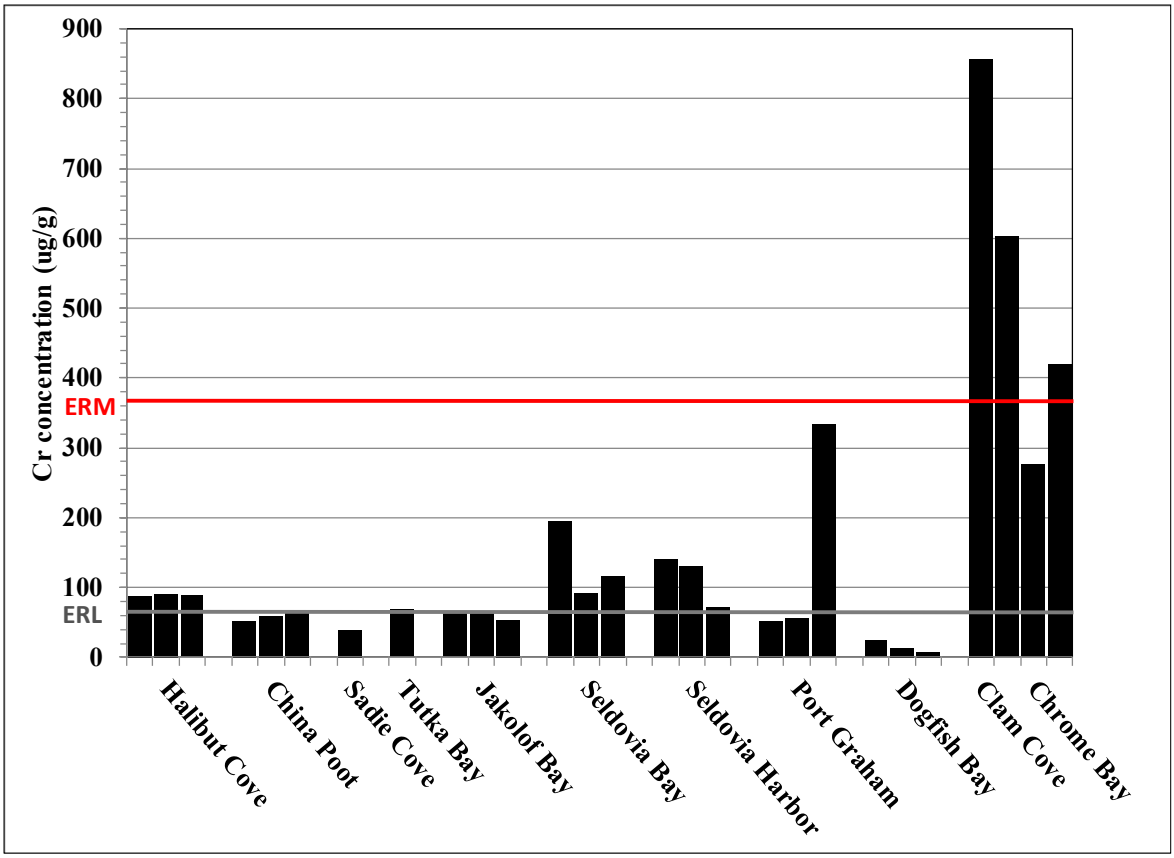

Figure 13. Concentrations of Cr in sediments in fjords and bays on the Kenai Peninsula and the ERL and ERM.

Figure 15 shows the normalized values for As, Cr, Cu, Ni, Pb, and Zn. Chrome Bay and Clam Cove have much higher concentrations of chromium and nickel than all other locations, but relatively low copper concentrations. Clam Cove is a very shallow embayment connected to Chrome Bay by a narrow channel (Figure 16). It is protected on all sides by mountains and gravel bars, but has very coarse grained sediment (Figure 7). Elements eroded off the chromite intrusion (Figure 17) on the shore of Chrome Bay settle in Clam Cove. Dogfish Bay is adjacent to Chrome Bay on the peninsula, but exhibits a very different mix of elements, with very little nickel or chromium. Zinc is more or less evenly distributed throughout the study area. Normalized values for the trace elements Ag, Cd, Hg, and Se are shown in Figure 18. Again, there is no obvious spatial pattern to the values. Sadie Cove had a concentration of cadmium that was over 500x the mean concentration, but the adjacent bays did not. In fact, Tutka Bay had zero measurable cadmium.

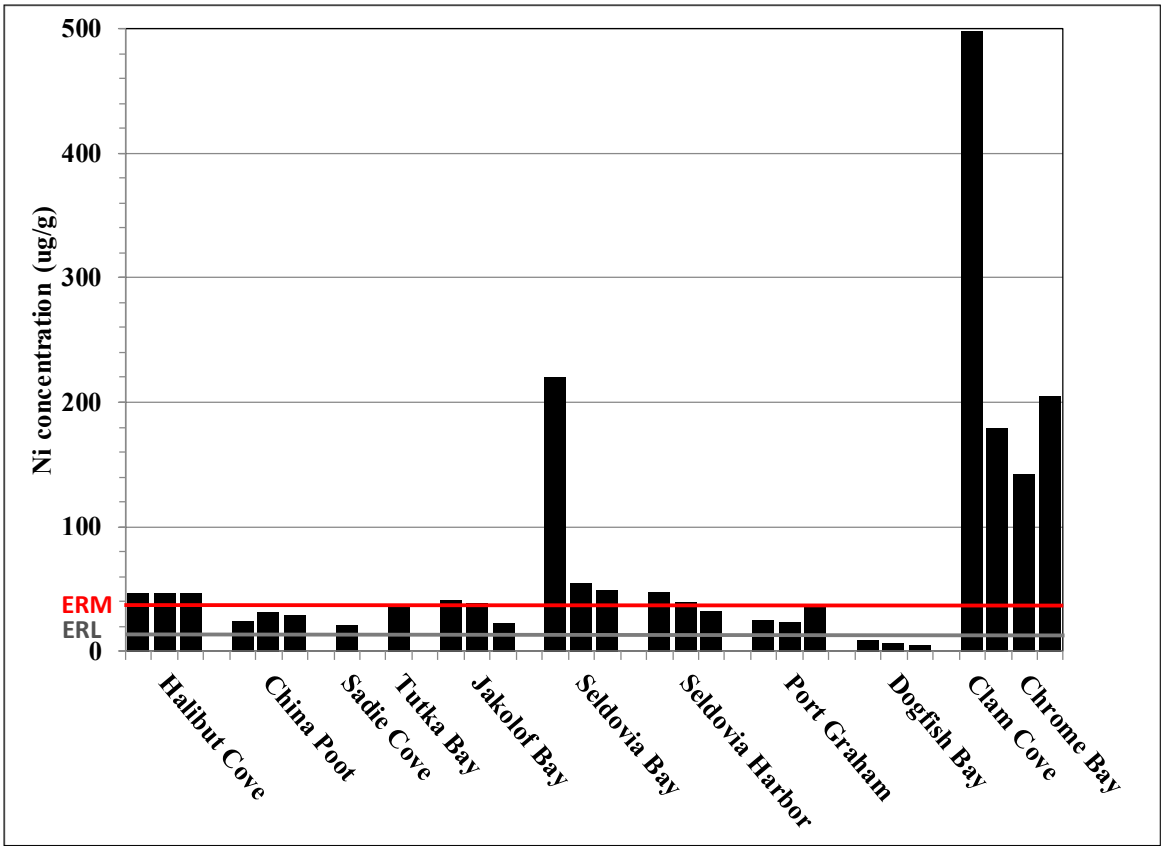

Figure 14. Concentrations of Ni in sediments in fjords and bays on the Kenai Peninsula and the ERL and ERM.

The major constituents of sediments are Al and Fe, or Si, depending on the watershed geology and depositional environment (e.g. sand vs mud). Normally, there is a relationship between trace elements the major elements, either negative or positive. Plots of elements vs Al can be used to identify locations where outliers indicate anthropogenic pollution inputs or naturally occurring localities with unusual geologic inputs. In the case of the Kenai Bays, few of the trace elements were correlated with the major metals in any consistent pattern. Even without the outlier at Clam Cove, where Al concentration was only 1.9%, the relationship between Al and Fe was very weak (Figure 19), with an R^2 correlation coefficient of only 0.1335. This is another indication that the geology of the individual bays and fjords is quite different, which results in unique combinations of elemental content. In contrast, in the larger Kachemak Bay system where all inputs are well mixed with multiple sources on all sides of the bay, the relationship between Al and most elements was relatively tight, with Port Graham sites showing up as outliers (Hartwell *et al.* 2009).

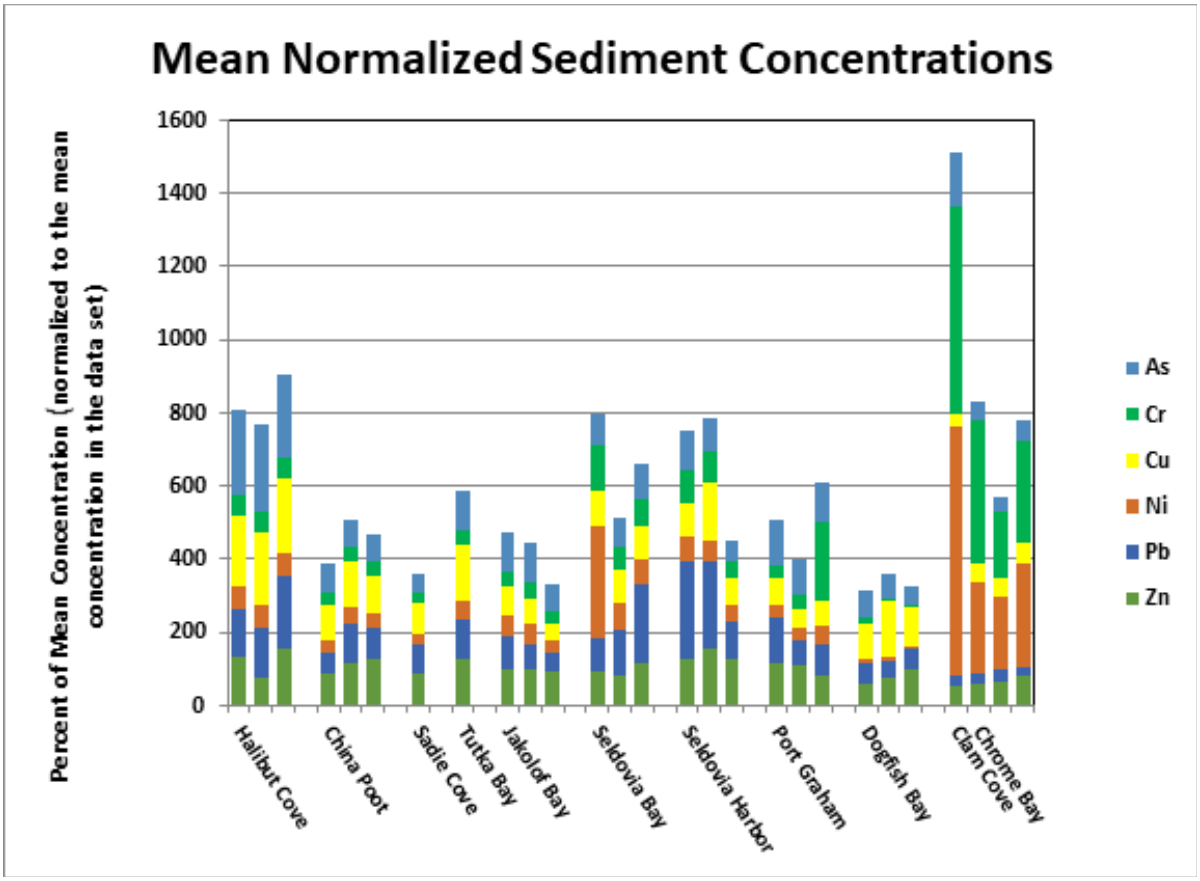

Figure 15. Mean normalized values for As, Cr, Cu, Ni, Pb, and Zn.

Figure 16. Clam Cove at low tide.

Figure 17. Chromite intrusion on the shoreline at Chrome Bay. Note the climber in the white circle for scale.

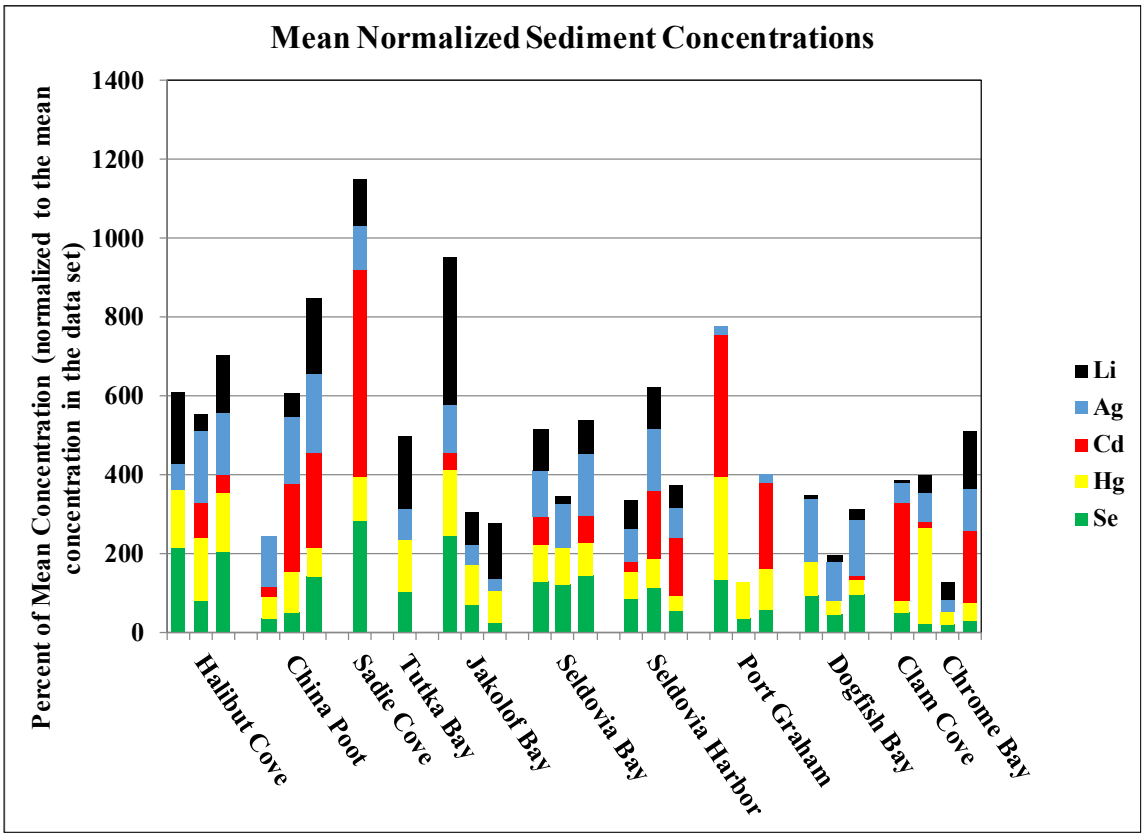

Figure 18. Mean normalized concentration values for Li, Ag, Cd, Hg, and Se.

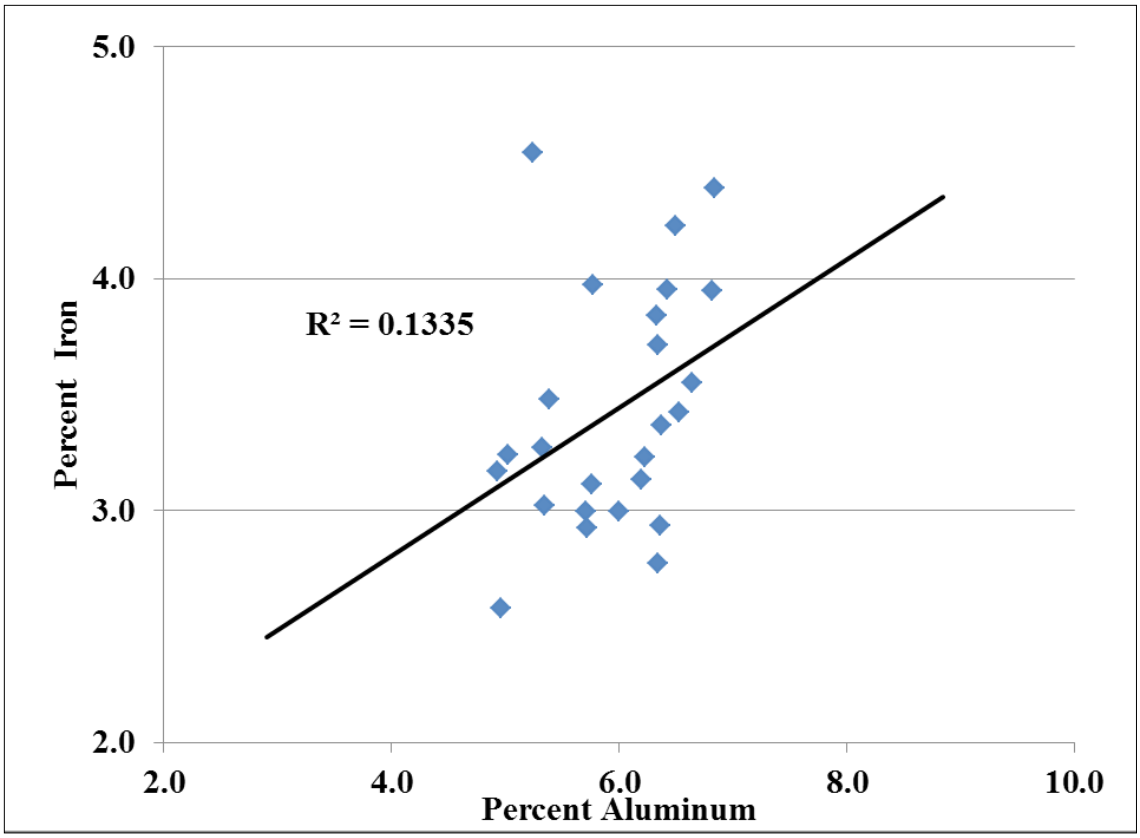

Figure 19. Relationship between sediment concentrations of Al and Fe.

Spearman rank correlations among all metals are shown in Table 7. Few elemental combinations showed significant correlation. Fewer still had Rho values of 0.707 or higher, indicating strong correlation (e.g. Cr & Ni). However, other studies have reported significant correlations between Al, Fe, and Mn in Alaska (Burrell, 1979; Robertson and Able, 1990) in open water habitats.

Only a few of the trace elements were significantly correlated with grain size (Table 8). As expected, the correlations were generally negative with % sand and positive with % fine grained sediment. This is consistent with the observation that elemental concentrations are elevated in finer sediments due to adsorption onto particle surfaces.

Table 7. Spearman Rank correlation coefficients, Rho (above) and probabilities, p(below) between elements. (MtERMq = mean ERMq).

Variable	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Selenium	Silver	Tin	Zinc	Mercury	MtERMq
Aluminum	0.43176	-0.25728	-0.41673	0.46252	0.42264	0.39533	-0.34102	0.3746	0.11693	-0.28148	0.38101	0.38265	-0.03597
	0.0245	0.1951	0.0306	0.0151	0.0315	0.0413	0.0817	0.0542	0.5614	0.1549	0.0499	0.0488	0.8706
Arsenic		0.0644	0.13006	0.294	0.08172	0.54879	0.23477	0.4149	-0.02931	-0.34315	0.31446	0.45732	0.46540
		0.7496	0.5179	0.1366	0.6915	0.003	0.2385	0.0314	0.8846	0.0797	0.1102	0.0165	0.0252
Cadmium			0.20498	-0.02955	-0.21471	0.16304	0.12597	0.25475	0.24355	-0.06936	0.10576	0.05974	0.34492
			0.3051	0.8837	0.2922	0.4165	0.5312	0.1997	0.2209	0.731	0.5996	0.7672	0.1070
Chromium				-0.27473	-0.29231	0.07237	0.91331	-0.17155	-0.163	0.20513	-0.13736	-0.04702	0.82937
				0.1655	0.1473	0.7198	<.0001	0.3922	0.4166	0.3047	0.4945	0.8158	<0.0001
Copper					0.18291	0.59359	-0.1917	0.51404	0.68437	0.15507	0.43956	0.19511	0.03125
					0.3711	0.0011	0.3381	0.0061	<.0001	0.4399	0.0218	0.3294	0.8874
Iron						0.03249	-0.3265	-0.11726	-0.20479	-0.08855	0.04684	0.11286	-0.15481
						0.8748	0.1035	0.5683	0.3156	0.6671	0.8203	0.5831	0.4915
Lead							0.12947	0.64153	0.3374	-0.22534	0.71176	0.39554	0.17544
							0.5198	0.0003	0.0852	0.2584	<.0001	0.0411	0.4233
Nickel								-0.02198	-0.06166	0.30525	-0.13492	0.05252	0.81399
								0.9134	0.76	0.1216	0.5022	0.7947	<0.0001
Selenium									0.37912	-0.21734	0.49512	0.4516	0.05506
									0.0511	0.2762	0.0086	0.018	0.8030
Silver										0.46215	0.13858	-0.00672	-0.07540
										0.0152	0.4906	0.9735	0.7324
Tin											-0.58669	-0.38412	0.04266
											0.0013	0.0479	0.8468
Zinc												0.19298	0.03571
												0.3348	0.8715
Mercury													0.31266
													0.1464

Total organic carbon (TOC) ranged from 0.15 – 2.74% and was only weakly correlated with individual elements (Table 8). The pattern of correlation generally followed that of the % fines, as TOC and %fines would be expected to be confounded.

The concentrations of metals measured in this study were comparable to previously published data by the U.S. Corps of Engineers Alaska District, (U.S. CEAD 2007) and EMAP (Saupe *et al*. 2005). The Corps characterized dredged materials from Homer Harbor and found arsenic and chromium at concentrations ranging from 6 - 14.9 µg/g and 16.7 - 56.7 µg/g respectively. These concentrations were in exceedance of the State of ADEC bench standard for soil (ADEC 2008). Relatively higher concentrations of arsenic and mercury were recorded in

Kachemak Bay, with values of 44 µg/g for arsenic and 0.17 µg/gm for mercury (Hartwell *et al.* 2009). These results agree with the EMAP findings. Data published by Saupe *et al*. (2005) also indicated that concentrations of antimony, arsenic, chromium, copper, mercury and zinc were relatively elevated in the inner Kachemak Bay. The NS&T Program has had monitoring sites in the Gulf of Alaska since the 1990s. Selected results are shown in Figure 20 a & b. Chrome Bay and Clam Cove far exceed any other location for chromium and nickel. Kachemak Bay has higher concentrations of mercury and arsenic but the source(s) is not known. Mercury was below detection limits in Seldovia Harbor.

Mercury concentration, and particularly its biomagnification in aquatic food chain, is a concern in Alaska and elsewhere. In Kachemak Bay the source of mercury may be linked to both geological and anthropogenic sources. The Cook Inlet basin that encompasses Kachemak Bay and its watershed lies on top of large coal deposits (Flores *et al.* 2004). Coal has been mined for export and burned for electricity in the Homer region. Coal-fired power plants emit mercury, but its presence in Kenai sediments may be of atmospheric and/or geological source.

Table 8. Spearman Rank correlation coefficients, Rho (above) and probabilities, p (below) between elements and sediment characteristics. (MtERMq = mean ERMq).

Variable	Aluminum	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Selenium	Silver	Tin	Zinc	Mercury	MtERMq
%Sand	-0.08006	-0.56931	-0.09372	-0.05138	-0.29447	0.21965	-0.5912	-0.16304	-0.56719	-0.08399	0.26877	-0.29249	-0.5393	-0.23158
	0.7165	0.0046	0.6706	0.8159	0.1726	0.326	0.003	0.4573	0.0048	0.7032	0.2149	0.1756	0.0079	0.2451
%Fines	0.22189	0.52928	0.1288	-0.01581	0.37846	-0.19029	0.67227	0.06917	0.61957	0.19763	-0.29545	0.38735	0.60059	0.17951
	0.3089	0.0094	0.5581	0.9429	0.075	0.3963	0.0004	0.7538	0.0016	0.366	0.1711	0.0678	0.0024	0.3703
%TOC	-0.00692	0.41395	0.22695	0.11422	0.10284	-0.44011	0.62404	0.15377	0.55575	0.07911	-0.22695	0.37132	0.33737	0.11922
	0.975	0.0496	0.2977	0.6038	0.6405	0.0404	0.0015	0.4836	0.0059	0.7197	0.2977	0.0811	0.1154	0.5537

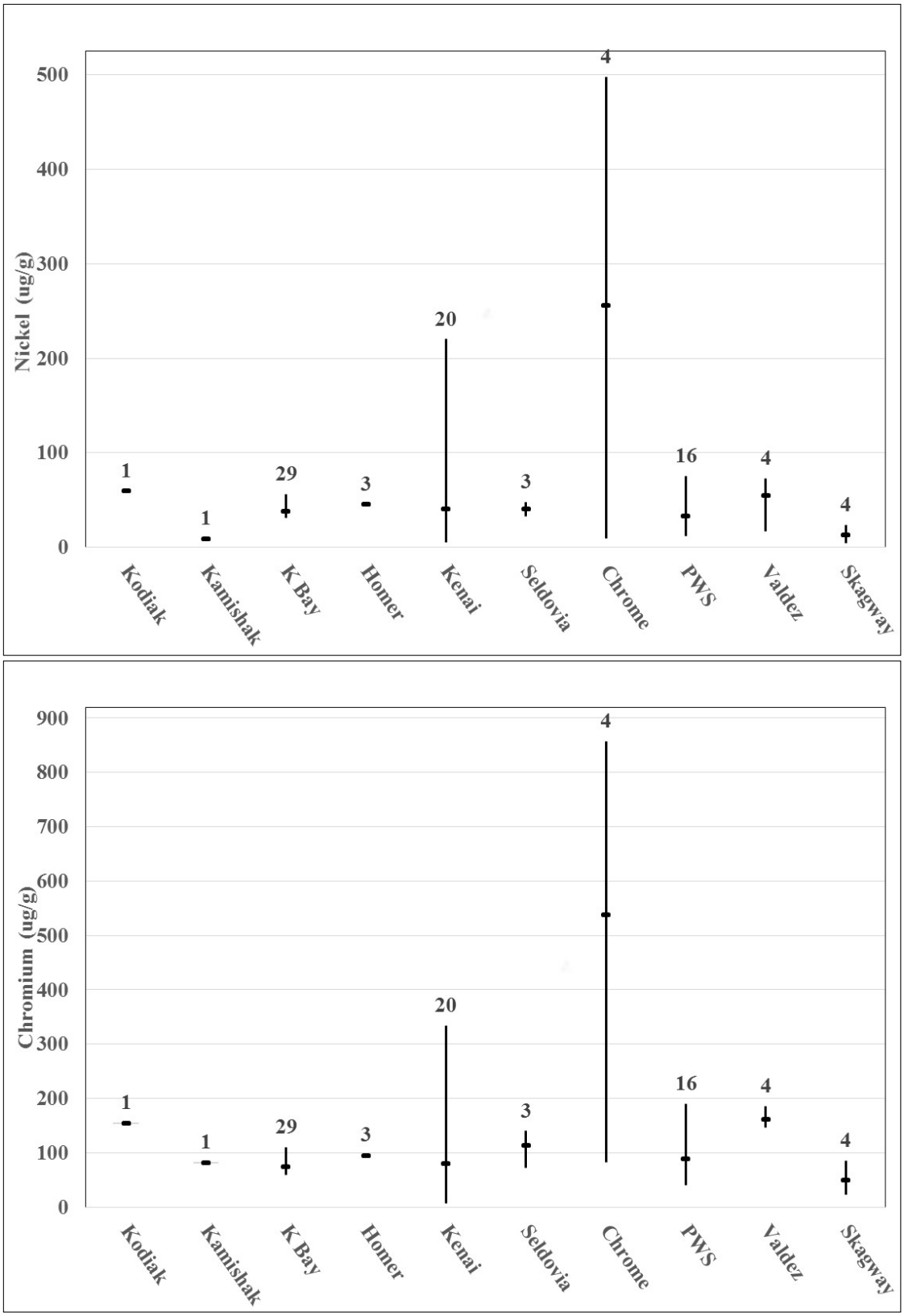

Figure 20a. Mean, high and low sediment concentrations of chromium, and nickel from various locations in the Gulf of Alaska. (K Bay=Kachemak Bay; PWS=Prince William Sound; Kenai Bays=all the bays in this study except Chrome Bay/Clam Cove and Seldovia Harbor). Numbers indicate the number of samples.

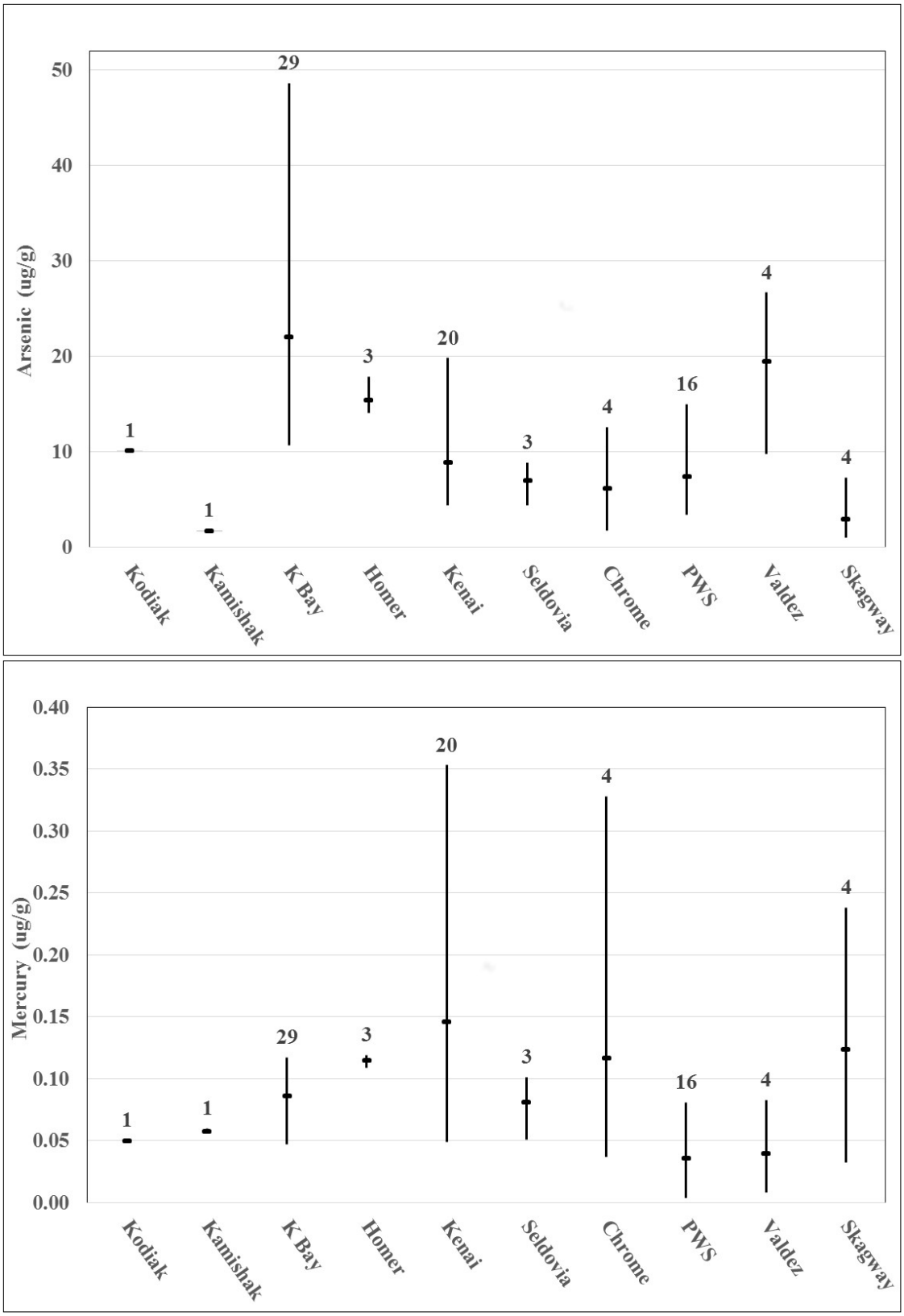

Figure 20b. Mean, high and low sediment concentrations of mercury and arsenic from various locations in the Gulf of Alaska. (K Bay=Kachemak Bay; PWS=Prince William Sound; Kenai Bays=all the bays in this study except Chrome Bay/Clam Cove and Seldovia Harbor). Numbers indicate the number of samples.

3.2.2 Organic contaminants

Mirex and chlorpyrifos were below detection limits at all stations. Endosulfan sulfate was found in Halibut Cove and Seldovia Harbor and Bay, but the highest concentration was only 5 ng/g (parts per billion). The EPA water quality criteria for human consumption of drinking water and fish consumption is 62 ug/l. There are no sediment standards. Endosulfan I and II were below detection limits at all stations. Hexachlorohexane was detected in several locations, but always less than 1 ppb. The gamma isomer (lindane) was not detected at any station. Chlorinated benzenes were also detected in most bays, but the highest concentration was 0.46 ppb. DDT and its breakdown products were found at isolated stations in Chrome Bay, China Poot Bay and in Seldovia Harbor and Bay (Figure 21). For comparative purposes, Homer Harbor is included in this graph from data collected in 2007 (Hartwell *et al*. 2009). One station in Seldovia Harbor (SH-3) and one in Seldovia Bay (SB-1) had total concentrations of 9.75 and 4.09 ppb, respectively, which exceeds the ERL for total DDTs of 1.58 ppb. No other station exceeded the ERL. The ERM for total DDTs is 46.1 ng/g. Chlordanes and related cyclodienes (e.g. Aldrin) were found everywhere except Dogfish Bay and Chrome Bay. The cis- isomer was almost ubiquitous. Only 2 stations in Seldovia Harbor exceeded 1.0 ppb.

There are no reliable records of pesticide use in the Kachemak Bay area and it is unknown if DDT and the other pesticides detected there were of local origin or not. The presence of these chemicals at concentrations above detection limits in a relatively remote and sparsely populated area like the Kenai Peninsula highlight their environmental persistence and the possible contribution of long range atmospheric transports (AMAP 2005). Chlordane and the related cyclodienes, and DDT have accumulated in the fine grained, organically enriched sediments in Seldovia, but not in Halibut Cove, Sadie Cove or Tutka Bay.

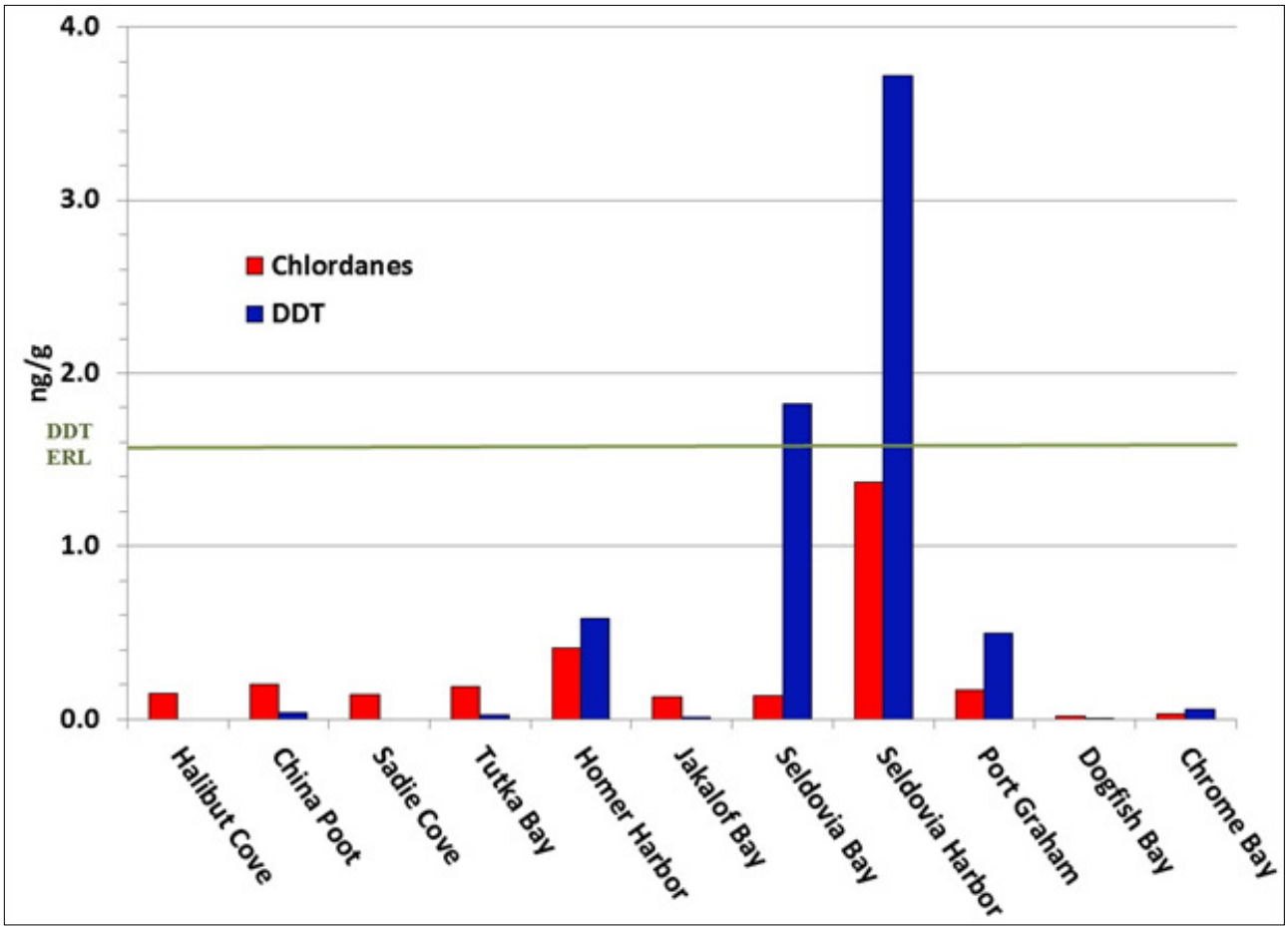

Figure 21. Average sediment concentrations of total DDTs and chlordanes and related cyclodienes in fjords and bays on the Kenai Peninsula.

Total PAH concentrations were highly variable between embayments. Seldovia harbor had the highest concentrations by far (Figure 22). All three stations exceeded the ERL for total PAHs, and one approaches the ERM (note the log scale). Seldovia Bay did not exhibit such high concentrations, but were still on the same order of magnitude as inside Homer Harbor, which is also included in this graph from data collected in 2007 (Hartwell *et al*. 2009). Perylene is a natural by-product of the breakdown of terrestrial plant material (NRC 1985). Perylene concentrations varied from negligible to 24% of total PAHs (0-400 ppb) (Figure 23), and removing this compound from the total PAH values did not alter the overall PAH pattern. The Seldovia harbor watershed is very small and includes the town of Seldovia. Outside of the harbor areas, the watersheds of the bays are sparsely populated and forest covered. It is unclear why there is such a wide spread in the perylene concentrations.

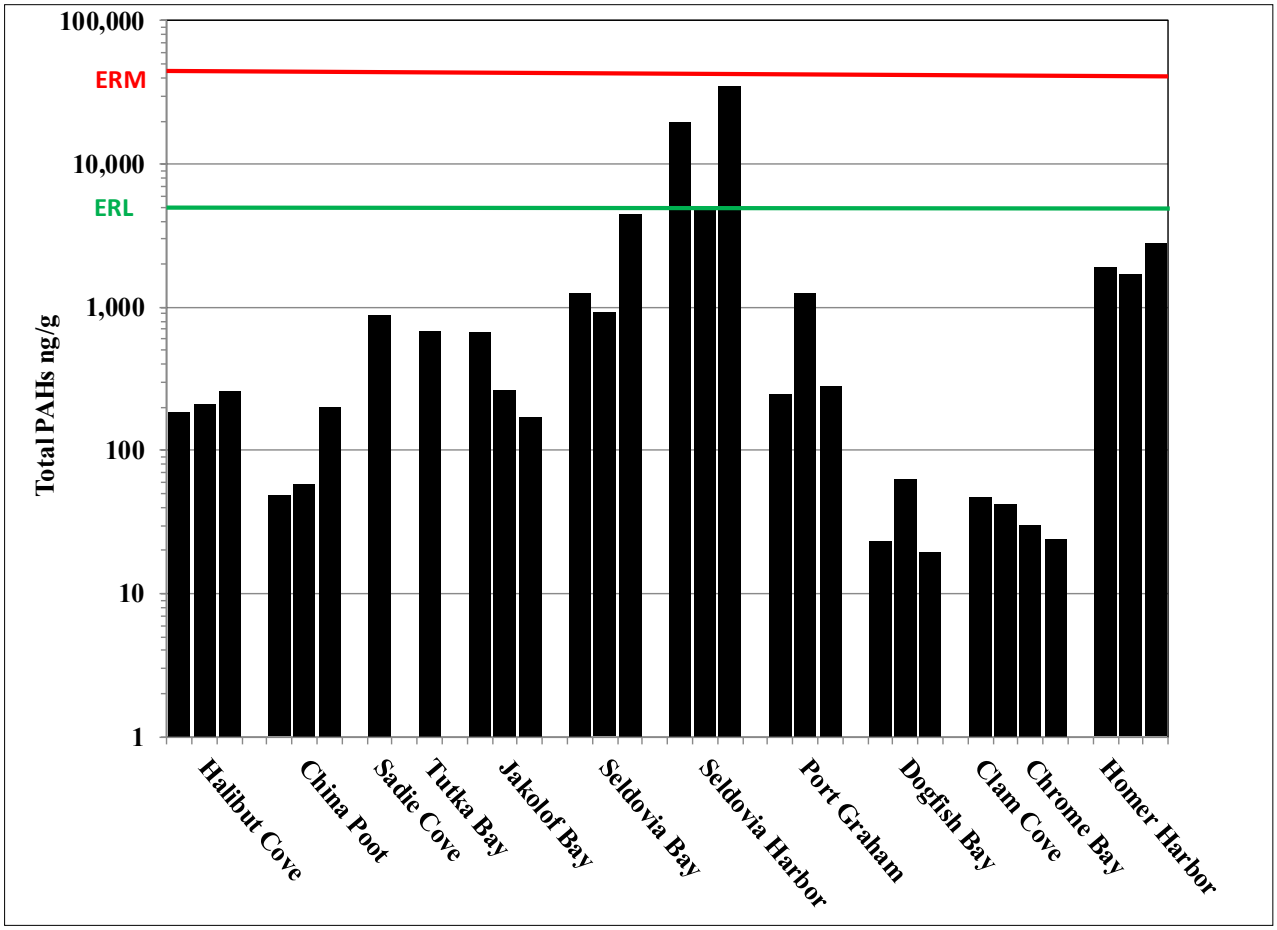

Figure 22. Sediment concentration of total PAHs in fjords and bays on the Kenai Peninsula.

Comparing the current PAH data to sediment concentrations throughout the rest of Alaska in the NS&T data base, Seldovia Harbor has higher concentrations than anywhere else. Figure 24 shows the mean and range of PAH concentrations on all three Alaskan coasts, in harbors and open water, excluding Seldovia Harbor. The lowest Seldovia Harbor concentration (5,221.8 ng/g) is greater than all other locations.

The Arctic estuary concentrations are higher than most locations. This is the result of abundant natural coal and peat deposited in the estuarine sediments. For example, Figure 25 shows the pattern of individual PAH concentrations in sediment from Wainwright Inlet and coal chips collected in the same vicinity in the Chukchi Sea. Note the large peak for perylene. In contrast, PAH concentrations in sediments from Seldovia Harbor demonstrate an entirely different pattern (Figure 26). In this case there are few low molecular weight compounds, and few alkylated homologues of the higher weight compounds. This would not indicate a fuel spill or a natural source, but more likely highly weathered oil, or a burned fuel source. Also note that station SH-3 has higher concentrations of all constituents, particularly fluoranthene and pyrene, typical of combustion products. The specific locations of the Seldovia Harbor sampling

stations are shown in Figure 27. Stations SH-1 and SH-2 were located in the boat slip area while SH-3 is behind the ferry dock. The history of spills and/or disposal or other potential sources, possibly going back to the 1964 Good Friday earthquake when Seldovia was a much larger industrial center, has not been documented. The PAH pattern in the Seldovia Bay samples mirrored the harbor samples, but at lower concentrations.

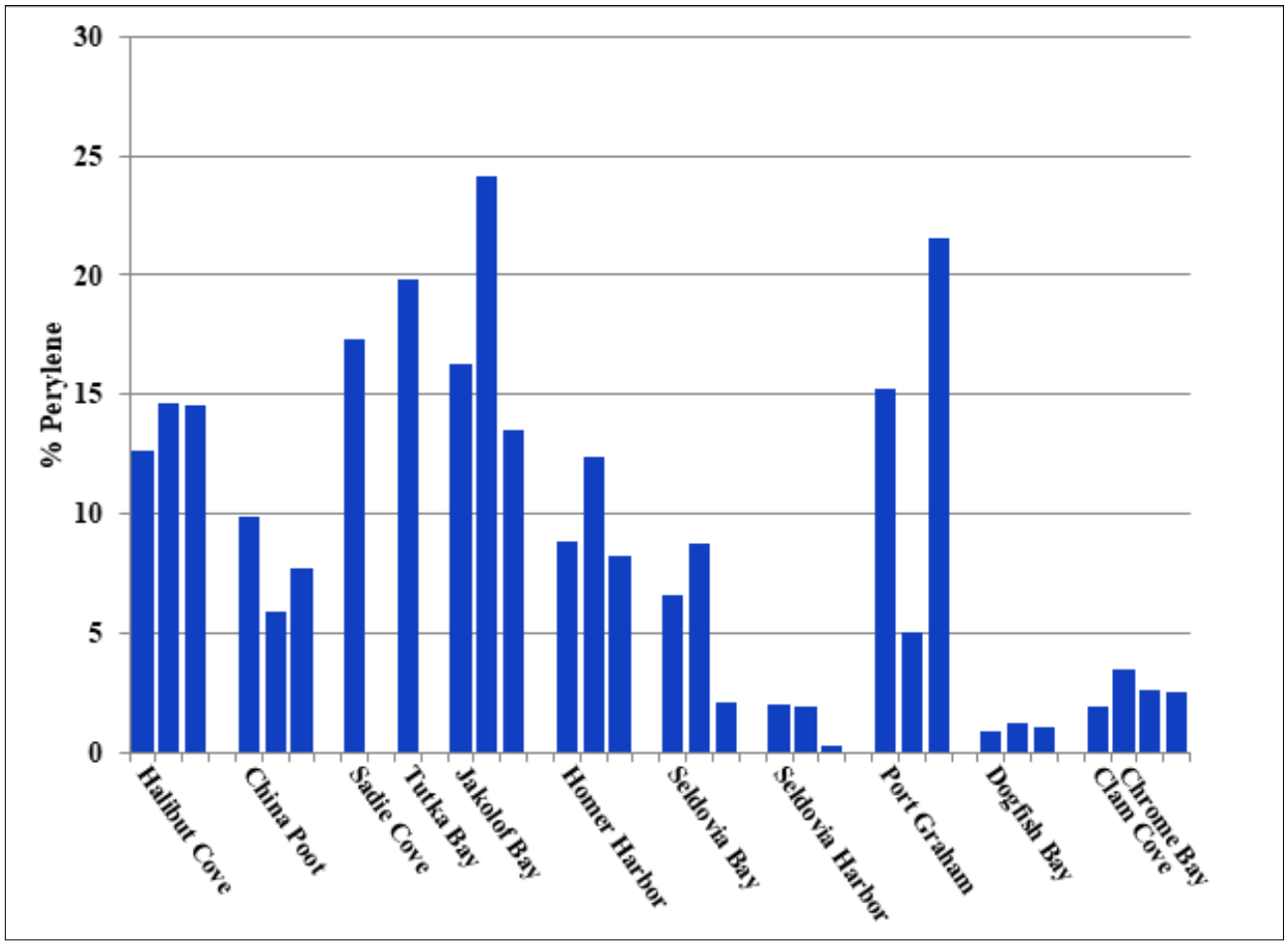

Figure 23. Sediment concentration of perylene in fjords and bays on the Kenai Peninsula.

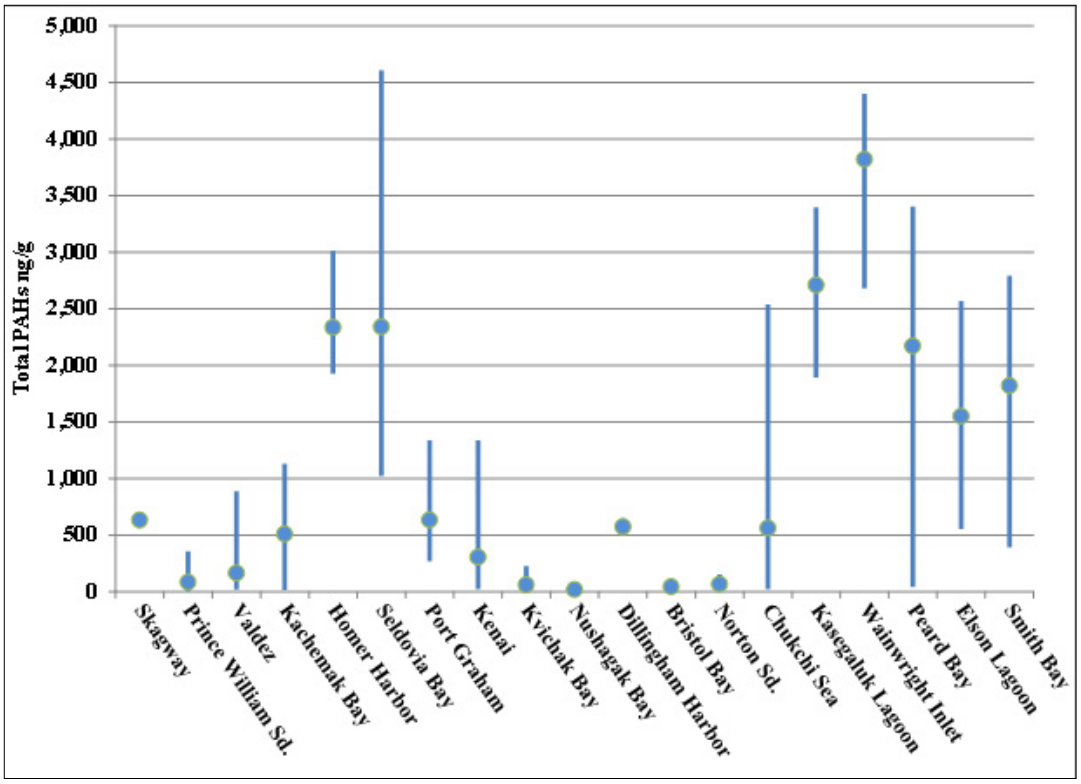

Figure 24. Mean, high, and low concentrations of PAHs from locations around Alaska, without Seldovia Harbor. (Data from NS&T).

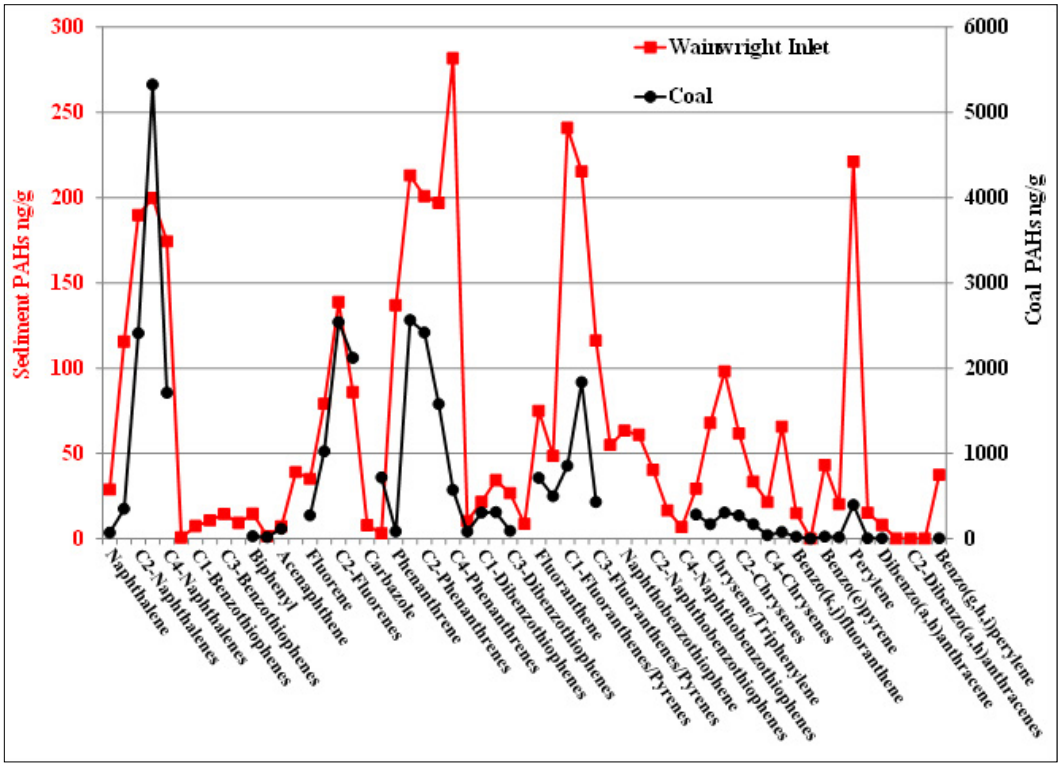

Figure 25. Individual PAH concentrations in sediment from Wainwright Inlet and coal chips in the Chukchi Sea. (For clarity, every other PAH compound is listed on the X axis.).

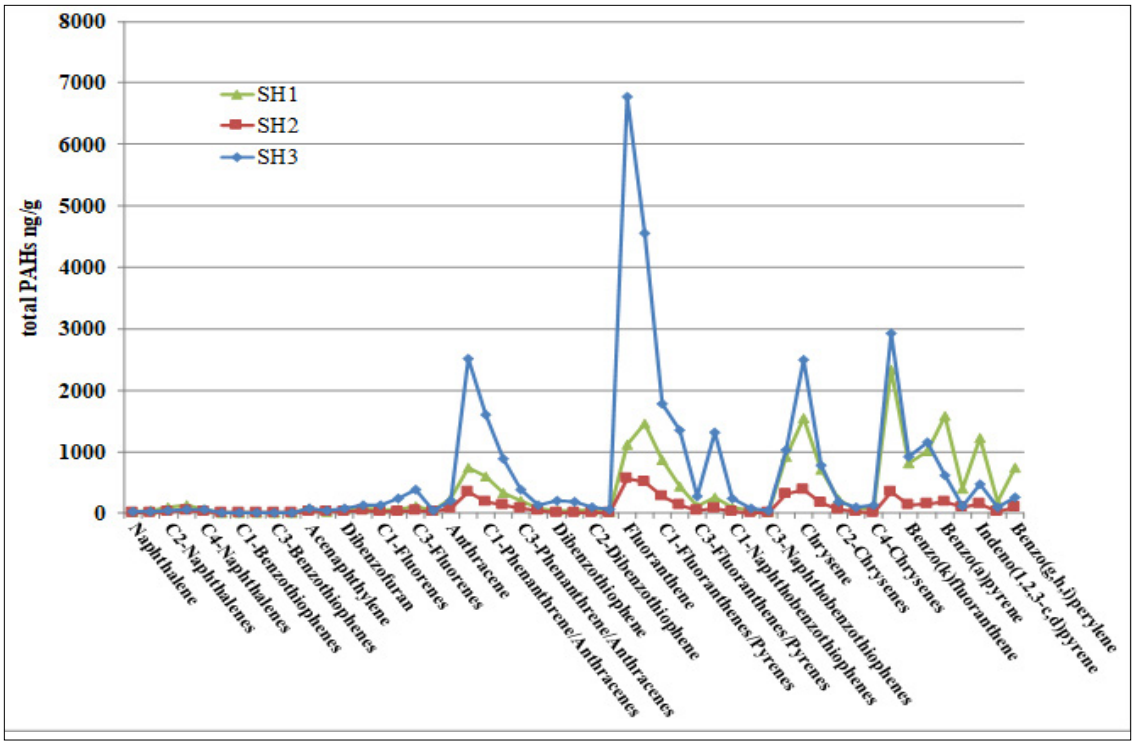

Figure 26. Individual PAH concentrations in sediment samples from Seldovia Harbor. (For clarity, every other PAH compound is listed on the X axis.).

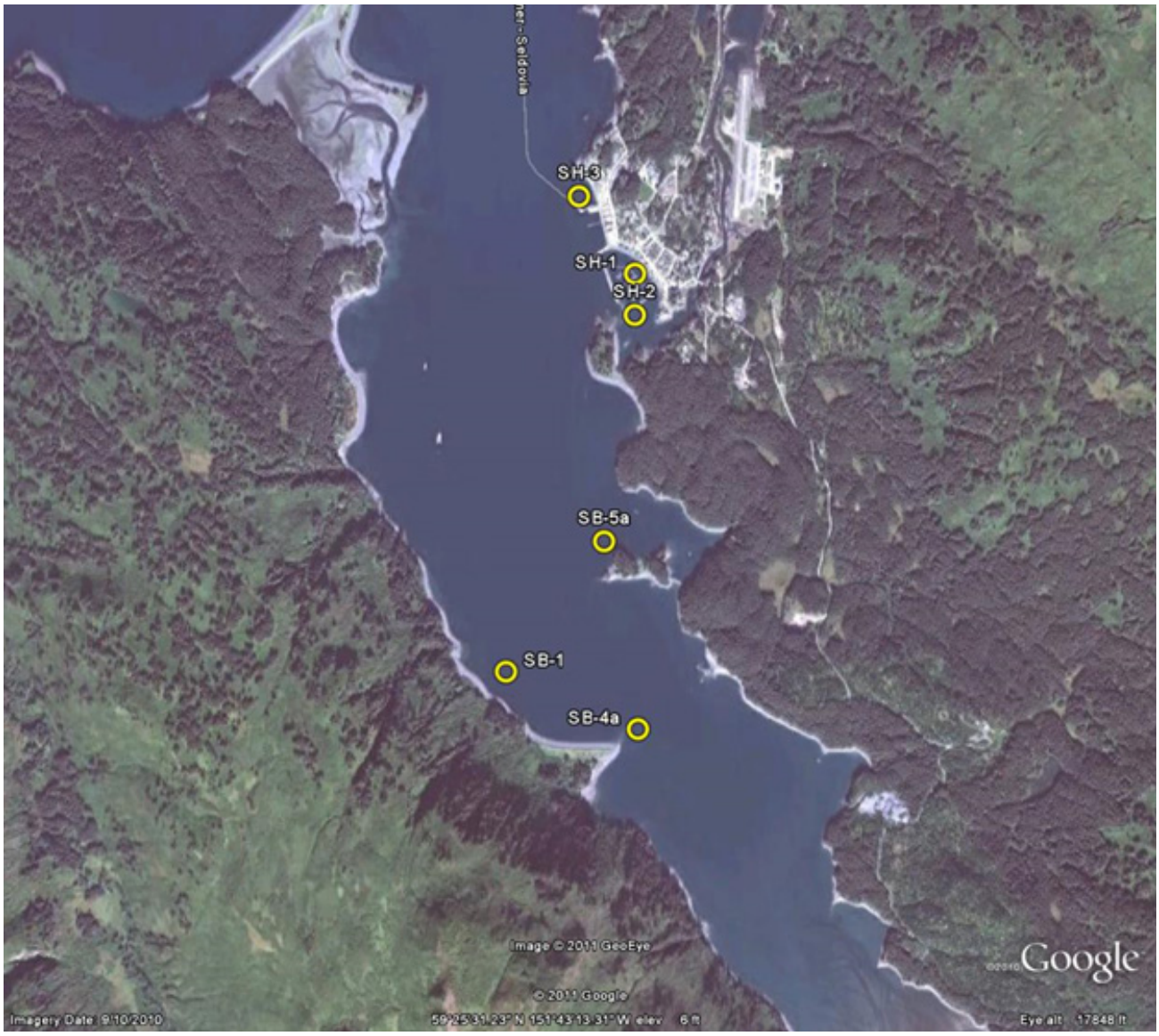

Figure 27. Specific sampling locations in Seldovia Harbor and Bay.

Distribution of measured PCBs in the study area is illustrated in Figure 28. PCBs were detected throughout the study area and their spatial distributions were similar to those of PAHs. Seldovia Harbor and Bay, and Homer Harbor had elevated PCB concentrations relative to other areas. Two sites in Seldovia Harbor exceeded the ERL, but no site approached the ERM (180 ng/g). In this case, the two highest values were in the boat slip area as opposed to the ferry dock.

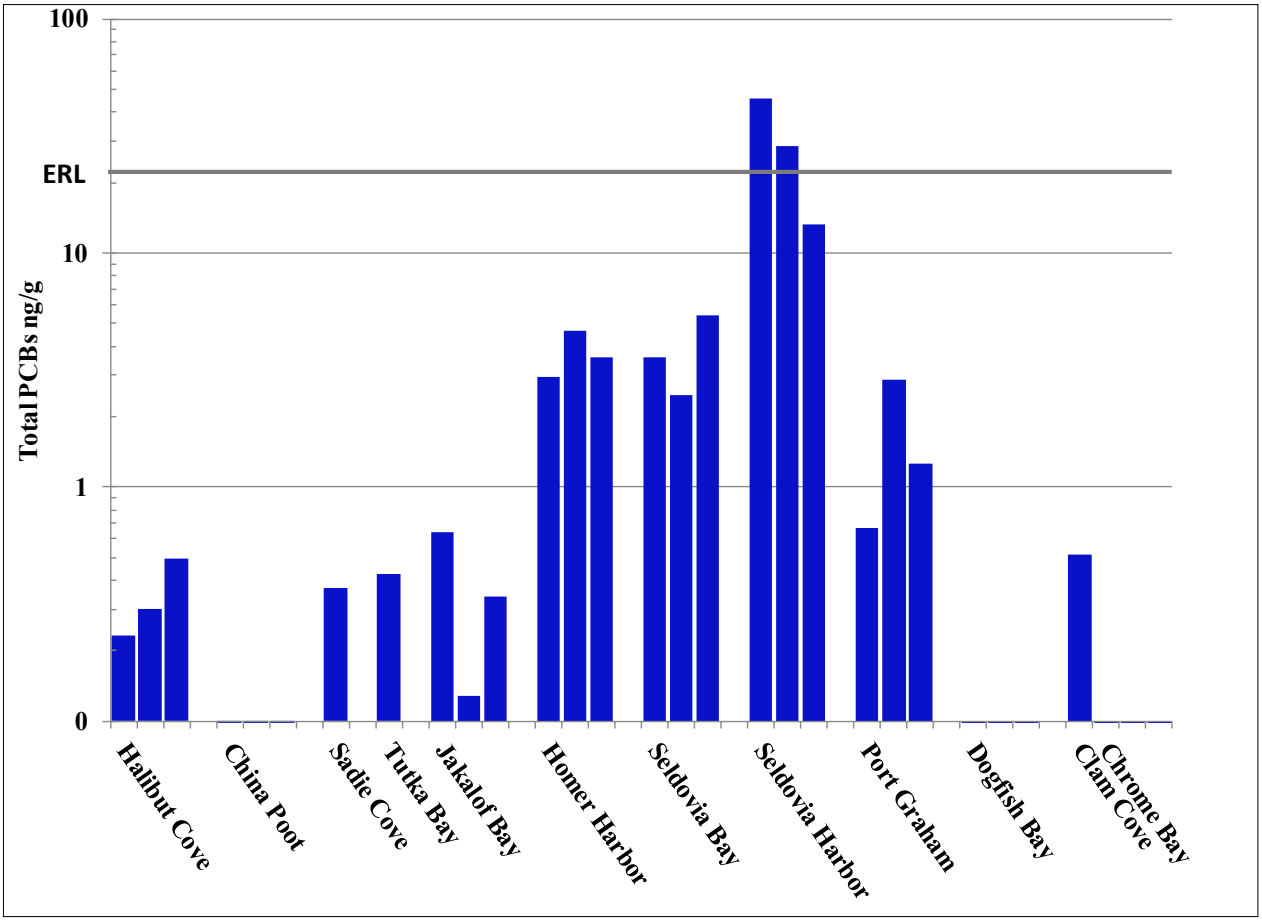

Figure 28. Sediment concentration of total PCBs in fjords and bays on the Kenai Peninsula.

Spearman rank correlations between physical factors and organic contaminants are shown in Table 9. As expected, most organic contaminants were significantly positively correlated with fine grained sediment and percent TOC and negatively correlated with coarse grained sediment. Total DDTs, which were rarely found at elevated levels, did not correlate with any physical parameter. These relationships did not change when the extreme values from Seldovia Harbor were excluded from the data set.

Aliphatic and total petroleum hydrocarbon concentrations are shown in Table 10, along with descriptive ratios. Consistent with the PAH data, Seldovia Harbor had the highest petroleum hydrocarbon concentrations among the other Kenai locations. Homer Harbor did have higher concentrations than Seldovia however. Concentrations of all constituents in Chrome and Dogfish Bays were relatively low in comparison. The ratio of odd to even alkanes was greater than 1 in almost all cases. The carbon chains from biogenic sources tend to have more odd numbered alkanes. Long term degradation tends to increase the number of even numbered alkanes as the chains break down, and the ratio approaches 1. Degradation also produces increasingly higher proportions of lower weight alkanes. The ratio of low weight (n-C≤20)

to high weight (n-C≥21) alkanes is also an indicator of biogenic vs petroleum sources. In all cases, this ratio is less than 1. Both of these ratios indicate primarily biogenic sources predominate, even in Seldovia Harbor.

Table 9. Spearman Rank correlation coefficients (above) and probabilities (below) between organic constituents and sediment characteristics. (totCyclo = total chlordanes and cyclodienes) .

Variable	% Fines	TOC	TotalPAH	TotalPCB	TotalCyclo	Total DDT
% Sand	-0.95726	-0.69171	-0.54151	-0.57802	-0.35469	0.0718
	<.0001	<.0001	0.0035	0.0016	0.0695	0.7219
% Fines		0.7537	0.65934	0.64374	0.47424	0.02372
		<.0001	0.0002	0.0003	0.0124	0.9065
% TOC			0.82119	0.70122	0.51422	0.33892
			<.0001	<.0001	0.0061	0.0837
TotalPAH				0.79933	0.70387	0.60826
				<.0001	<.0001	0.0008
TotalPCB					0.52939	0.42697
					0.0045	0.0263
totCyclo						0.34393
						0.0790

The values in Dogfish Bay are contradictory. However, the overall concentrations of alkanes in this location were so low, with many zero values, the ratios may be meaningless. The dominant alkane at most sites was n-C 27 or 29, which is typically associated with vascular plant sources (Colombo *et al*. 1989). The major alkane at Seldovia Harbor site SH-3 was 21, which is much closer to typical petroleum values. The carbon preference index (CPI=2(C27 + C29)/(C26 + 2C28 +C30)) (Boehm *et al*. 1984) was greater than 3 in all cases, except Seldovia Harbor site SH-3, which is another indicator of biogenic sources. Again, the values in Chrome and Dogfish Bays are unreliable due to so many zero values. A ratio of pristane + phytane /n-C17 much greater than 1 indicates contamination by degraded oil (Gill and Robotham 1989). The two highest values of this ratio were seen at Seldovia and Homer Harbors.

3.2.3 Butyltins

Butyltins were analyzed only in samples from Seldovia Harbor to contrast with the data from Homer Harbor. Tributyltin was the active ingredient in a popular boat bottom paint, which has been banned in most countries due to side effects on non-target organisms,

especially mollusks. Homer Harbor was the only location where butyltins were detected in all of Kachemak Bay in 2007 (Hartwell *et al*. 2009). In Seldovia Harbor only one sample had detectable dibutyltin (a breakdown product of the original tributyltin) at a relatively low level of 4 ng/g Sn. Homer Harbor concentrations ranged between 7 and 11 ng/g Sn.

Table 10. Alkane and petroleum hydrocarbon concentrations (ug/g) in sediments embayments on the Kenai Peninsula. (N/A – cannot calculate due to zeros).

	Site	total Alkanes	Pristane	Phytane	Petroleum Hydrocarbons	Odd/Even	CPI	Dominant n-C	Low wt/ High wt	pris+phyt /n-C17
Halibut Cove	**HC 1**	3.43	0.01	0.00	23.51	3.81	11.83	27	0.25	0.11
	HC 3	2.33	0.00	0.00	14.16	4.14	14.77	27	0.17	N/A
	HC 6a	3.01	0.02	0.00	21.84	2.76	7.98	27	0.27	0.19
China Poot	**CP 11a**	0.33	0.00	0.00	5.32	1.81	N/A	27	0.84	0.00
	CP 12a	0.44	0.00	0.00	6.82	3.02	N/A	27	0.53	0.00
	CP 8a	2.18	0.01	0.03	22.81	2.44	5.85	27	0.52	0.27
Sadie Cove	**SC 1**	8.95	0.13	0.19	89.36	4.88	9.35	27	0.17	1.08
Tutka Bay	**TB 1**	6.03	0.03	0.02	43.64	3.99	8.31	27	0.14	0.41
Jakolof Bay	**KJ 1**	3.54	0.04	0.02	33.60	2.47	4.14	27	0.18	0.80
	KJ 13a	7.10	0.01	0.01	53.65	4.99	8.43	27	0.09	0.32
	KJ 4	4.18	0.02	0.01	46.77	3.52	4.70	27	0.11	0.73
Homer	**HH-3**	10.67	0.32	0.18	212.85	3.59	7.22	29	0.23	1.74
Seldovia Harbor	**SH 1**	6.40	0.09	0.06	113.68	3.49	13.83	27	0.21	1.07
	SH 2	5.83	0.04	0.02	76.92	4.62	11.89	27	0.16	0.48
	SH 3	3.81	0.08	0.05	93.90	1.94	2.87	21	0.44	1.65
Seldovia Bay	**SB 1**	7.67	0.07	0.02	59.78	3.63	8.35	27	0.18	0.69
	SB 4a	9.72	0.05	0.02	71.42	4.11	9.88	27	0.14	0.46
	SB 5a	6.29	0.06	0.02	72.03	3.01	7.06	27	0.18	0.53
Port Graham	**PG-3c**	4.12	0.03	0.02	67.72	3.36	5.85	29	0.25	0.63
Dogfish Bay	**DB 1**	0.06	0.00	0.00	1.43	0.28	N/A	16	3.64	N/A
	DB 12a	0.71	0.00	0.00	5.41	1.40	N/A	27	1.27	0.00
	DB 3	0.18	0.00	0.00	9.01	0.43	N/A	18	3.82	0.00
Clam Cove	**CC 12a**	0.91	0.02	0.00	12.10	4.53	N/A	27	0.33	1.23
Chrome Bay	**CH 11a**	0.39	0.00	0.00	5.18	1.16	2.42	multiple	0.51	0.00
	CH 5	0.26	0.00	0.00	3.23	0.71	1.59	multiple	0.60	N/A
	CH 6	0.22	0.00	0.00	7.52	0.75	1.95	16	0.78	0.00

3.3 Sediment Toxicity and Tissue Body Burdens

Sediment toxicity testing did not reveal any acute (mortality) or sub-acute toxicity (reburial) in any test (Table 11). These results are consistent with the results of body burden analyses of fish and mussels (Table 12a & b). Despite the very high concentrations of Cr and Ni in the sediments, the metals do not appear to be bioavailable to higher trophic levels. All three fish species are predators feeding on benthic epifauna and infauna. For starry flounder, the tissue values are at or below those reported (after conversion to wet weight) for starry flounder in Nushagak and Kvichak Bay (Hartwell *et al*., 2016), and for salmon from Kachemak Bay (Apeti *et al*., 2013) and the Alaska DEC Fish Monitoring Program. The mineral intrusion along the shoreline at Chrome Bay is chromite which is insoluble in water. The deposit is also rich in Ni, but the mineral form is not available (USGS, 1999).

Table 11. Means and standard deviations (n=5) of sediment emergence, percent mortality, percent of survivors failing to rebury, and percent total effective mortality of *Eohaustorius estuarius* exposed to sediments from Chrome Bay.

Sample	Emergence [1] (no./replicate)	Percent mortality	Percent Survivors Failing to Rebury	Percent Total Effective Mortality
Control	0.0 ± 0.0	2.0 ± 2.7	0.0 ± 0.0	2.0 ± 2.7
CB-5	1.2 ± 2.2	3.0 ± 2.7	0.0 ± 0.0	3.0 ± 2.7
CB-6	0.0 ± 0.0	2.0 ± 4.5	0.0 ± 0.0	2.0 ± 4.5
CB-11a	1.2 ± 2.7	3.0 ± 2.7	0.0 ± 0.0	3.0 ± 2.7

[1] *Daily emergence counts include all amphipods observed on or above the sediment surface, whether living or dead*

Table 12a. Whole body tissue concentrations (ug/g wet wt) of three species of fish collected at Chrome Bay.

Species	Length (cm)	Weight (kg)	As	Cd	Cr	Cu	Pb	Ni	Se	Hg
Southern Rock Sole	22.30	0.13	1.8	<0.01	0.35	<0.2	<0.05	0.23	0.21	< 0.01
Kelp Greenling	22.00	0.11	0.5	<0.01	0.34	0.42	<0.05	< 0.2	0.25	0.01
Kelp Greenling	33.30	0.62	0.72	<0.01	0.46	<0.2	<0.05	< 0.2	0.18	0.053
Kelp Greenling	42.50	1.60	1.1	<0.01	0.38	<0.2	<0.05	< 0.2	0.18	0.11
Kelp Greenling	40.90	1.20	0.81	<0.01	0.65	<0.2	<0.05	< 0.2	0.3	0.078
Kelp Greenling	38.50	0.90	1.3	<0.01	0.47	<0.2	<0.05	< 0.2	0.27	0.068
Starry Flounder	61.50	2.70	3.1	<0.01	0.44	<0.2	<0.05	< 0.2	0.27	0.062

Table 12b. Composite soft tissue concentrations (ug/g dry wt) of mussels collected at Chrome Bay and Tutka Bay. The average of 13 other mussel samples from the NS&T data base for the Kenai Peninsula and western Prince William Sound are also shown.

	As	Cd	Cr	Cu	Pb	Ni	Se	Hg
Chrome Bay	6.77	3.36	0.74	6.93	0.32	3.99	2.84	0.038
Tutka Bay	7.34	4.42	0.93	7.41	0.23	1.40	3.33	0.063
Kenai/PWS	10.70	3.90	1.53	22.02	0.93	4.16	3.52	0.113

3.4 Benthic Community Characterization

A total of 46,085 organisms, representing 315 taxa were enumerated, including epiphytic species. Following elimination of the 'artificial' species (see methods), there were 282 taxa and 46,017 organisms. The dominant taxa were polychaetes, malacostracans, bivalves and gastropods. Polychaete worms had the highest number of taxa and abundance at most stations. However, the individual stations, even within the same embayment, were highly variable due to site-specific conditions. The vast majority of malacostracans were amphipods (other taxa included decapod crabs and shrimp, isopods, harpacticoids, and cumaceans). The dominant taxa groups are listed in Table 13. At sites where bivalves were numerically among the dominant species, they were generally characterized by a large number of animals representing only one of a few species. Not included in the table are some noteworthy extremes. The upstream station in Jakolof Bay had 2,450 ticks (Acarida). Seldovia Harbor site #2 (at the mouth of Seldovia slough) had 2,500 Oligochaete worms, although the salinity was 27.7 ppt. China Poot Bay site #8A had 1,862 Harpacticoid copepods. The most numerous taxa were a tiny bivalve, *Turtonia minuta* (4,667), Oligochaeta sp. (4,381), Harpacticoida sp. (2,719), and Acarida sp. (2,534). Species distributions were dominated by two dozen taxa with very high abundances, and the vast majority with 500 or fewer individuals (Figure 29). Ninety-three taxa had five or fewer individuals.

Species richness, abundance, and calculated diversity are shown in Table 14. There were no obvious patterns between or within different embayments. Sadie Cove was noteworthy with consistently low species richness, abundance, and diversity. As noted above (Figures 8-10), the water column in Sadie Cove is stratified above the moraines and experiences hypoxic stress, at least in the upper reaches of the fjord.

Trace element concentrations had almost no significant relationships to benthic community metrics (Table 15). No significant correlations were seen between abundance and trace elements. Only Se was negatively correlated to diversity and number of taxa. This relationship is likely confounded by the positive relationship of selenium and % TOC (Table 8). Also, the

data distributions are confounded by locations such as Sadie Cove, with sediments that were very fine grained, high TOC, and anoxic (Figures 7 & 10), containing few organisms.

Spearman rank correlations between benthic community metrics, sediment characteristics and the organic contaminants are shown in Table 16. Abundance, diversity, and number of taxa were negatively correlated with percent fine grained sediment and the organic contaminants. Only the number of taxa was consistently statistically significant. These results are the consequence of the confounded relationships between the organic constituents and grain size. All but total DDTs were strongly negatively correlated with percent sand, and positively correlated with percent fine grained sediment.

The cluster analysis identified five major site groups (Figure 30). The Sadie Cove site was in a class by itself with only 4 species and 11 of the 15 organisms were the polychaete *Nephtys cornuta.* Seldovia Bay and Harbor, Tutka Bay, Halibut Cove, Jakolof Bay and China Poot Bay all shared a large number of species in common but each of the three groups also had a smaller number of species not found in the other clusters. Port Graham had some of the species in common with those bays, but also had a group of two dozen species found nowhere else in the entire sampling area. Dogfish Bay and Chrome Bay shared a dozen species with the other bays, but the bulk of their species did not overlap with the other bays. Both Dogfish and Chrome Bays had very coarse sandy sediment relative to the other areas. Finally, there was a group of sites that were shallow, upstream locations in Clam Cove, China Poot Bay, Jakolof Bay and Seldovia Harbor that clustered together. These sites had only a few of the species common to the lower reaches of their respective bays and contained a group of species not found in the other bays.

Table 13. Dominant taxa at each station (abundance numbers are actual counts in the sample, not number per square meter).

		Polychaetes			Malacostraca			Gastropods			Bivalves	
	Site	**Taxa**	**Abund.**		**Taxa**	**Abund.**		**Taxa**	**Abund.**		**Taxa**	**Abund.**
Clam Cove	CC-12A	20	6064.4		6	95.9		1	40		6	223.8
Chrome Bay	CH-11A	13	534.6		14	612.9		4	17.2		9	87.4
	CH-5	17	108		10	24		4	9		1	13
	CH-6	42	234		17	85		7	12		3	25
Dogfish Bay	DB-1	26	963		12	62		2	4		11	223
	DB-12A	37	782		12	174		5	11		12	208
	DB-3	33	1882		14	94		5	142		11	217
Port Graham	PG-2	36	476		10	105		6	16		9	705
	PG-3C	13	49		0	0		5	249		4	89
	PG-4B	37	1035		10	39		2	4		8	167
Seldovia Harbor	SH-1	21	81		10	48		1	3		5	17
	SH-2	8	215.2		6	85.2		1	21.3		2	2286.6
	SH-3	18	400.4		4	27.6		1	9		7	88.3
Seldovia Bay	SB-1	24	473		4	91		0	0		2	14
	SB-4A	16	500.9		6	78.2		1	5.3		1	26.7
	SB-5A	20	46		9	245		0	0		5	11
Jackalof Bay	KJ1	50	524		17	367		6	22		6	17
	KJ13A	24	549.7		2	16		4	128		9	176.8
	KJ4	3	15		5	918		3	26		4	250
Tutka	TB-1	13	171		2	3		0	0		4	4
Sadie	SC-1	4	15		0	0		0	0		0	0
China Poot	CP-11A	31	1055		10	66		2	45		7	40
	CP-12A	9	145		1	8		1	2		5	400
	CP-8A	23	3209		2	557		6	1939		6	2322
Halibut Cove	HC-1	23	1260.9		1	2.7		1	2.7		2	86.4
	HC-3	33	298		5	8		2	5		6	122
	HC-6A	26	238		0	0		1	1		0	0

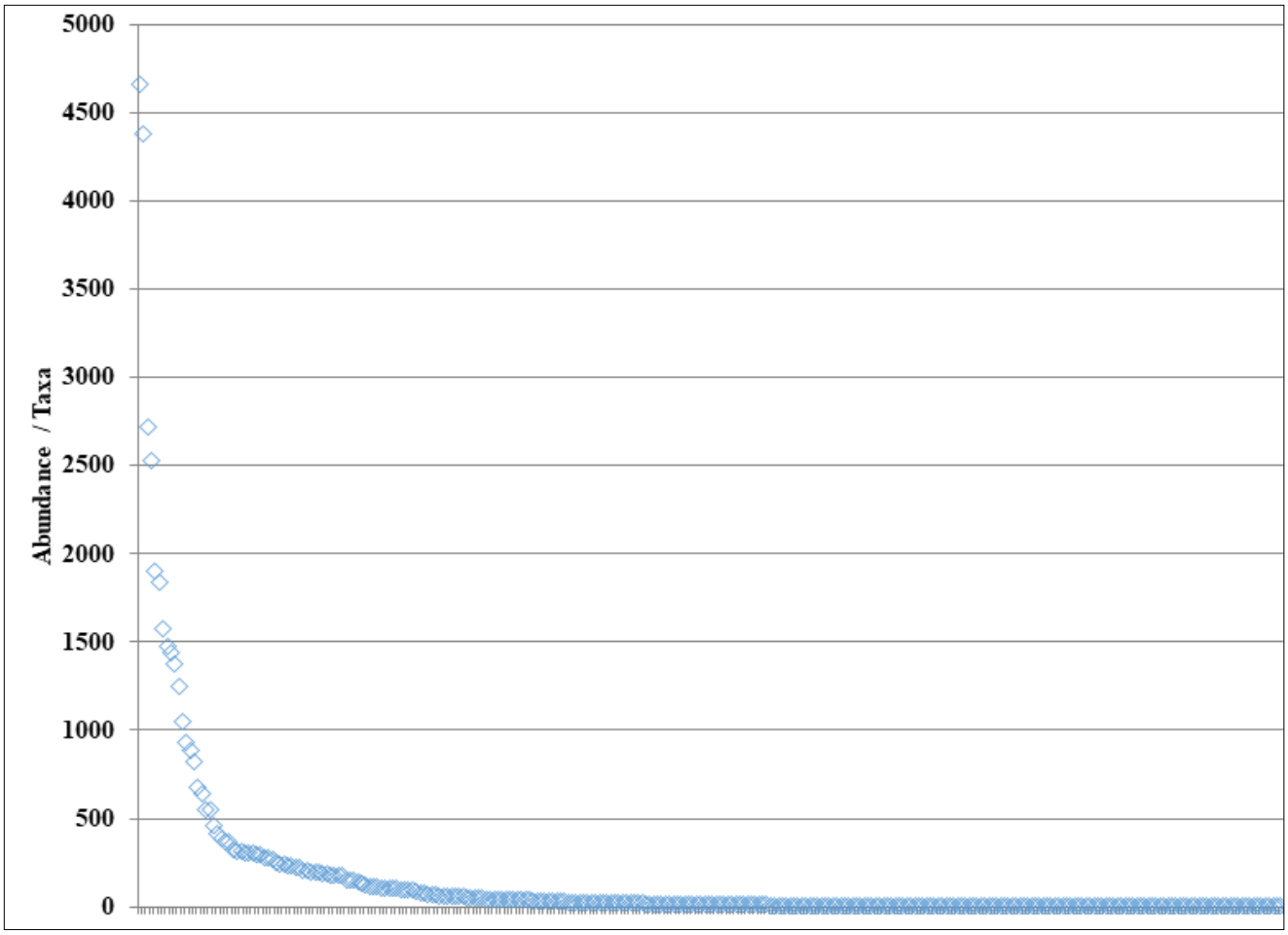

Figure 29. Total abundance of each taxon collected. Species are arranged on the X axis by abundance. Each diamond represents the total number of individuals of a taxon collected at all sites in Kenai Peninsula Bays. The abundance of all species is dominated by a small group of species.

Table 14. Species richness, diversity and total abundance (number/0.04 m^2 grab) of benthic infauna in Kenai Peninsula embayments.

	Site	# Taxa	Diversity	Abundance
Clam Cove	CC-12A	37	2.66	7351
Chrome Bay	CH-11A	42	2.63	1266
	CH-5	32	2.36	225
	CH-6	75	3.77	385
Dogfish Bay	DB-1	58	2.73	1529
	DB-12A	70	3.21	1187
	DB-3	72	2.84	2829
Port Graham	PG2	74	2.73	1342
	PG3C	24	1.99	390
	PG4B	70	1.83	1267
Seldovia Harbor	SH-1	38	3.12	150
	SH-2	20	1.14	5216
	SH-3	33	2.78	563
Seldovia Bay	SB-1	30	2.08	580
	SB-4A	23	1.77	606
	SB-5A	34	1.60	302
Jackalof Bay	KJ1	87	3.33	996
	KJ13A	44	3.27	981
	KJ4	23	1.77	5175
Tutka	TB-1	20	2.01	179
Sadie	SC-1	4	0.86	15
China Poot	CP-11A	55	2.33	1349
	CP-12A	18	1.49	578
	CP-8A	42	2.47	10921
Halibut Cove	HC-1	29	2.24	1477
	HC-3	48	3.10	475
	HC-6A	29	2.79	293

Table 15. Spearman Rank correlation coefficients (above) and probabilities (below) between elements and biological measures.

Variable	Aluminum	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Selenium	Silver	Tin	Zinc	Mercury	MtERMq
Abund.	0.08846	0.17593	-0.07468	-0.18182	-0.10375	0.14512	-0.21552	-0.07609	-0.1749	-0.05435	0.13043	-0.0751	-0.32032	-0.19574
	0.6881	0.4220	0.7349	0.4064	0.6376	0.5194	0.3233	0.7301	0.4248	0.8055	0.5530	0.7334	0.1362	0.3278
Diversity	-0.05487	-0.18685	-0.30078	-0.05584	0.04695	0.2553	-0.28999	-0.14826	-0.54312	-0.09933	0.255	-0.24463	-0.29221	-0.2099
	0.8036	0.3933	0.1631	0.8002	0.8315	0.2515	0.1795	0.4996	0.0074	0.6520	0.2403	0.2606	0.1761	0.2933
Taxa	-0.15063	-0.31462	-0.36296	-0.19733	-0.08457	0.13567	-0.42726	-0.22651	-0.60237	-0.09693	0.29674	-0.30069	-0.46388	-0.33201
	0.4927	0.1437	0.0887	0.3668	0.7012	0.5472	0.0420	0.2987	0.0024	0.6599	0.1692	0.1633	0.0258	0.0907

Table 16. Spearman Rank correlation coefficients (above) and probabilities (below) between sediment characteristics, organic contaminants, and biological metrics. (totCyclo = total chlordanes and cyclodienes).

Variable	% Fines	TOC	TotalPAH	TotalPCB	TotalCyclo	Total DDT	Abund	Diver	Taxa
% Sand	-0.95726	-0.69171	-0.54151	-0.57802	-0.35469	0.0718	0.33028	0.24489	0.42982
	<.0001	<.0001	0.0035	0.0016	0.0695	0.7219	0.0925	0.2183	0.0252
% Fines		0.7537	0.65934	0.64374	0.47424	0.02372	-0.38462	-0.26992	-0.50099
		<.0001	0.0002	0.0003	0.0124	0.9065	0.0476	0.1733	0.0078
% TOC			0.82119	0.70122	0.51422	0.33892	-0.26661	-0.4289	-0.49175
			<.0001	<.0001	0.0061	0.0837	0.1789	0.0256	0.0092
TotalPAH				0.79933	0.70387	0.60826	-0.36935	-0.30443	-0.41118
				<.0001	<.0001	0.0008	0.0580	0.1226	0.0331
TotalPCB					0.52939	0.42697	-0.33838	-0.26036	-0.54543
					0.0045	0.0263	0.0843	0.1897	0.0033
totCyclo						0.34393	-0.12781	-0.36336	-0.48883
						0.0790	0.5252	0.0625	0.0097
totDDT							-0.35616	-0.24758	-0.17996
							0.0682	0.2131	0.3691

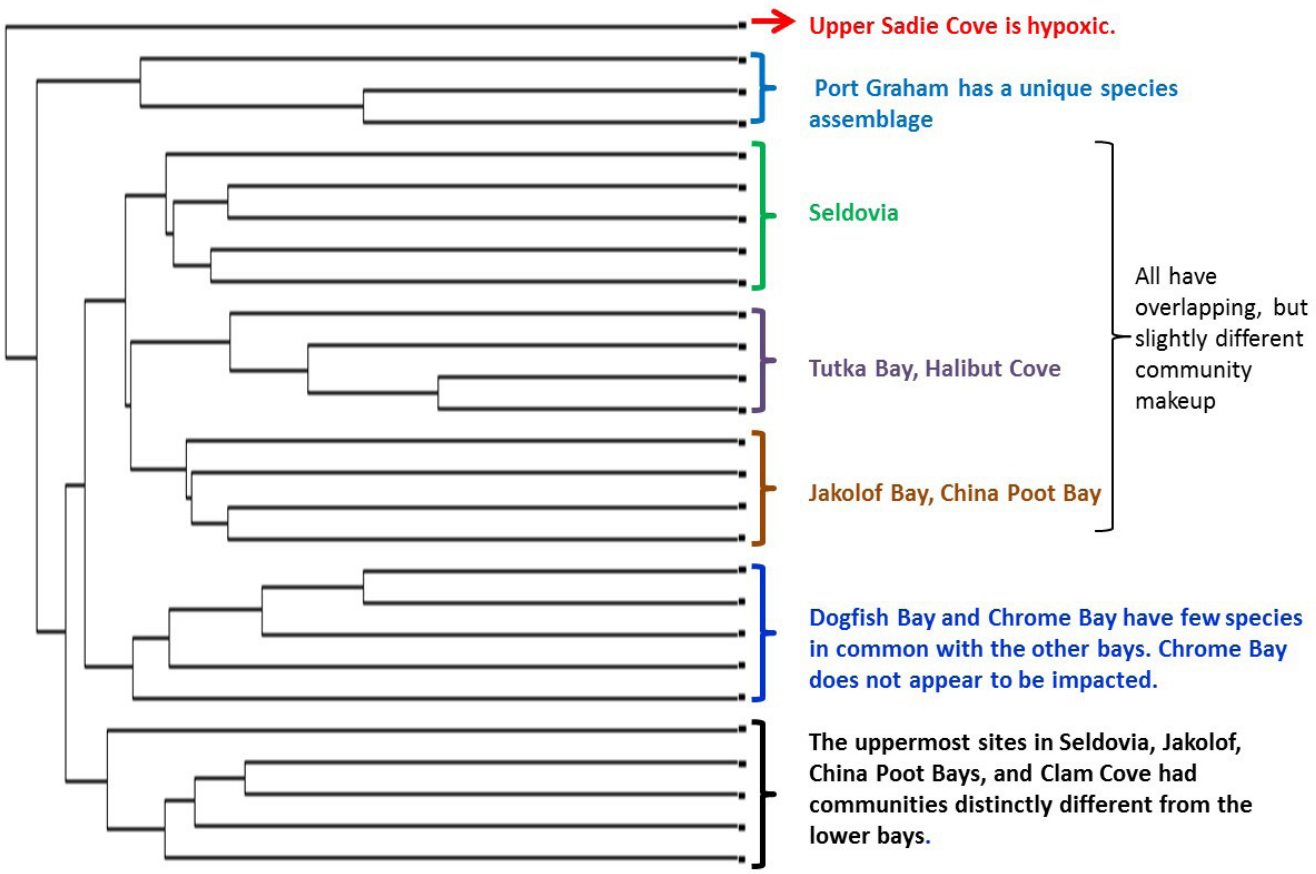

Figure 30. Cluster analysis for benthic species community found in embayments on the Kenai Peninsula.

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APPENDIX

Chemicals and chemical groups for which ERLs and ERMs have been derived (organics ppb, metals ppm, dry weight).

	ERL	ERM
Total DDT	1.58	46.1
pp'-DDE	2.2	27
Total PCBs	22.7	180
Total PAHs	4022	44792
High weight PAHs (≥ 4 rings)	1700	9600
Low weight PAHs (≤ 3 rings)	552	3160
Acenaphthene	16	500
Acenaphthylene	44	640
Anthracene	85.3	1100
Flourene	19	540
2-Methyl Naphthalene	70	670
Naphthalene	160	2100
Phenanthrene	240	1500
Benzo-a-anthracene	261	1600
Benzo-a-pyrene	430	1600
Chrysene	384	2800
Dibenzo(a,h)anthracene	63.4	260
Fluoranthene	600	5100
Pyrene	665	2600
Ag	1.0	3.7
As	8.2	70
Cd	1.2	9.6
Cr	81	370
Cu	34	270
Hg	0.15	0.71
Pb	46.7	218
Ni	20.9	51.6
Zn	150	410

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