

Baseline assessment of heavy metal concentrations in surficial sediment from Kachemak Bay, Alaska

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Abstract Heavy metal inputs to coastal Alaska ecosystems are driven by sediment loads from glacial meltwater and river outflows. This study characterized the spatial distribution of 16 major and trace metals in five strata in Kachemak Bay, as well as sediment total organic carbon content and grain size. Homer Harbor, a shallow harbor within the study area, contained elevated metal concentrations compared to the other strata. Outside the harbor, several metals, including Cr, Ni, Pb, and Zn, were significantly higher in the eastern strata than in the western portions of the bay. The opposite was true for a few other metals, such as Hg. However, most metal concentrations were below the National Oceanic and Atmospheric Administration's sediment quality guidelines for sediment toxicity to benthic communities.

Keywords Metals · Surficial sediment · Kachemak Bay · Grain size · Organic carbon

Introduction

Sediment contamination in US coastal areas is a major environmental issue because of potential toxic effects on

biological resources and often, indirectly, on human health. Heavy metals from land-based sources, both anthropogenic and natural, are often associated with bottom sediments, which constitute an environmental sink. The presence of contaminants in coastal ecosystems can cause habitat degradation, loss of biodiversity, and coastal food chain contamination. This contamination of food sources is a primary concern as it may affect human health. In many instances, fish consumption advisories are coincident with severely degraded sediments in coastal water bodies. Thus, characterizing bottom sediment and water quality in coastal areas is important management tools for assessing coastal ecosystem health. This is particularly important in Alaska, which has an extensive coastline of 33,000 miles, greater than the contiguous United States. Alaska also has vast natural marine and coastal resources, but lacks adequate data to provide baseline information necessary to assess coastal health (EPA 2005).

Located within the Kenai Peninsula in south-central Alaska, Kachemak Bay (Fig. 1) is a nutrient rich estuarine environment, with the Fox and Bradley Rivers in the eastern end of the bay delivering large volumes of freshwater. According to a 2010 ecological assessment by the Kachemak Bay National Estuarine Research Reserve (KBNERR), the bay sustains diverse marine wildlife of important economic value, such as dungeness crab, cockles, clams, salmon, and pacific halibut (KBNERR 2001). The bay supports significant subsistence and commercial fishery resources and is considered one of the most productive bays in the USA, although stocks have been reported to be

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declining in recent years (Szarzi et al. 2007; ADF&G 1998). 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). 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 (e.g., 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 changes in local sedimentation and erosional patterns. The bay is subject to atmospheric deposition of metals, as it sits downwind of five active volcanoes on the west side of Cook Inlet. Although there are no known industrial point sources of contamination, Kachemak Bay was impacted by the Exxon Valdez oil spill (EVOS) of 1989. Current sources of pollution to Kachemak Bay may include wastewater discharge, leaking septic tanks, marine activities associated with commercial and recreational fishing, commercial shipping, stormwater runoff, and long-range atmospheric transport. According to the Alaska Department of Environmental Conservation (ADEC), the deep-water anchorage of the bay is being proposed as one of several repair and safe refuge sites for distressed and disabled vessels for oil and cargo traffic (ADEC 2008), increasing the potential for unforeseen anthropogenic contamination.

Despite its ecological importance and vast natural marine and coastal resources, Kachemak Bay resource managers lack adequate data to provide baseline information necessary to assess future trends. Previous characterizations of sediment contamination in the Gulf of Alaska, including Kachemak Bay, are limited to areas of known pollution or special studies. The NOAA National Status and Trends Program (NS&T) has analyzed contaminants in sediment and mussels collected from a few selected sites in the Gulf of Alaska (O'Connor 2002; Kimbrough et al. 2008). In collaboration with the U.S. EPA Environmental Monitoring and Assessment Program (EMAP), the Alaska Department of Environmental Conservation undertook a state-wide coastal ecological condition study that encompassed assessment of contaminants and benthic assemblages in sediment along the Gulf of Alaska and the Aleutian Islands (Saupe et al. 2005). Additionally, as a result of the planned expansion of Homer Harbor, in 2007, the Alaska District of the Army Corps of Engineers (COE) conducted an

environmental assessment that included sediment contamination in the harbor proper.

As part of a collaborative effort with the North Pacific Research Board, the NS&T Program assessed the overall condition in Kachemak Bay by measuring a suite of heavy metals in surficial sediment. Sediment heavy metal content was evaluated in the context of assessing (1) the potential of anthropogenic enrichment using Al as a reference element (Schropp et al. 1990); (2) the magnitude of metal concentrations relative to other coastal areas, including comparison to long-term national data (NS&T data portal, <http://egisws02.nos.noaa.gov/nsandt/index.html#>); and (3) sediment quality by comparing measurements to NOAA's sediment quality guidelines (Long et al. 1996). The results of this study will serve as a baseline data for unforeseen events and future reference for sediment contamination in Kachemak Bay.

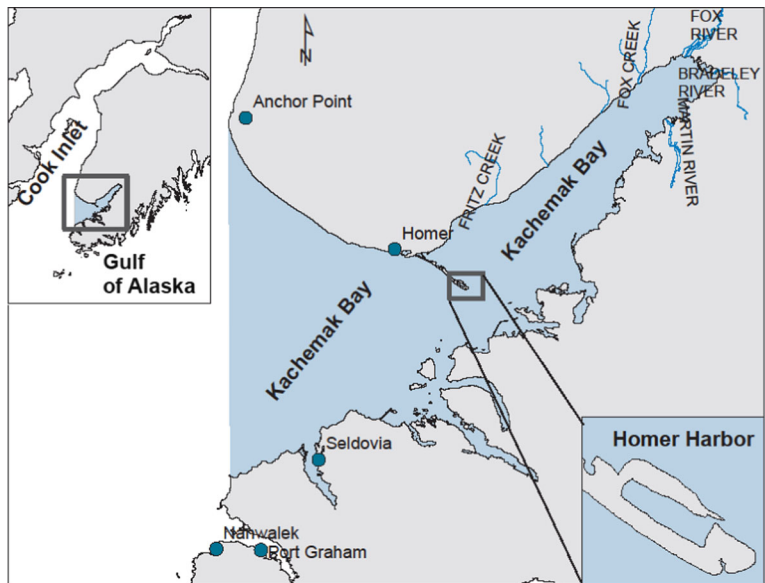
Methods

Study area

Kachemak Bay is a 64-km-long glacial fjord on the east side of lower Cook Inlet, located in south central Alaska (Fig. 1). An extensive description of the physiography of Kachemak Bay is presented by the Alaska Department of Fish and Game (ADF&G 1998). The most prominent feature of the bay is the Homer Spit, which bisects the bay into inner and outer portions. The inner portion of the bay behind the spit is approximately 32 km long, has a relatively flat bottom, and averages 46 m in depth. The north shore of Kachemak Bay is characterized by extensive tidal flats below sandy bluffs with numerous coal seams. The south shore has numerous smaller fjords and embayments cut into steep terrain that rises to glaciated valleys and mountain peaks on the Kenai Peninsula.

The study area was located in the northern half of the inner Kachemak Bay, where extensive soft bottom habitat and diverse assemblages of marine organisms were present. A stratified random sampling design divided the area into five strata, corresponding to different bottom habitats (Fig. 2a): Homer Harbor (HH), west intertidal mudflats (WF) and subtidal zones (WS), and east intertidal mudflats (EF) and subtidal zones (ES). Multiple sampling sites were located on a random basis within each stratum. Three sites were located in Homer Harbor;

Fig. 1 Map detailing Lower Cook Inlet and Kachemak Bay. Major rivers are also shown



six sites were located in the WS and WF strata, and seven sites were placed in the EF and ES strata (Fig. 2). 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 dimensions of that stratum with a quantifiable degree of confidence (Heimbuch et al. 1995).

In addition to the 29 sites sampled in the stratified random sampling scheme, three randomized sites were taken in Port Graham Bay to assess conditions in the vicinity of the Native village of Port Graham (Fig. 2b). Because it was not a part of the initial stratified design, data from the Port Graham sites were not included in the

statistical analyses of the designed study, but do offer informative contrasts to the data set.

Sampling procedures

Surficial sediments were collected at each station using Young-modified Van Veen grab sampler following NS&T protocols (Apeti et al. 2012). Equipment was scrubbed clean with site water, rinsed with acetone, and then distilled water at each site to reduce the possibility of cross contamination. From each grab, the top 3 cm of the sediment was sub-sampled with a Kynar-coated scoop and placed in pre-labeled 250 ml Ichem jars. Separate sediment samples were collected into

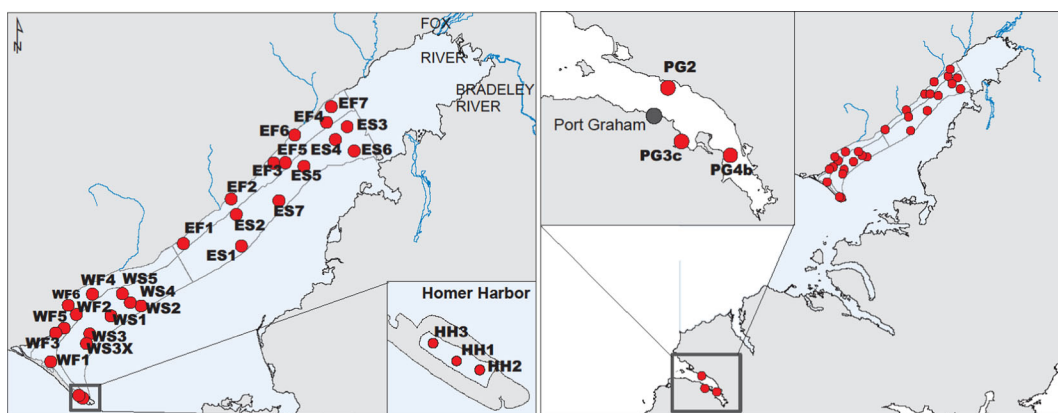


Fig. 2 Maps of Kachemak Bay showing strata and site locations. *Left* main study area in inner Kachemak Bay. The insert depicts the Homer Harbor stratum (HH). *Right* site location in Port Graham Bay

Ziploc bags for grain size and TOC analysis. Samples were stored on ice in the field and shipped to the laboratory where they were stored at -20°C until analyzed. Samples for grain size analysis were not frozen to avoid altering the grain structure as result of freezing.

Chemical analysis

Fifteen major and trace metals (Ag, Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Si, Sn, and Zn) were analyzed following procedures routinely used in the NOAA NS&T program (Kimbrough and Lauenstein 2006). For most trace and major elements, samples were analyzed using inductively coupled plasma/mass spectrometry analysis (ICP-MS). Atomic fluorescence spectrometry was utilized to measure arsenic and selenium, while cold vapor atomic absorption spectrometry was used for mercury analysis. In general, samples were homogenized and freeze dried. Aliquots of 0.10–0.45 g dried sediment were 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 EPA method 245.5, using concentrated H_2SO_4 and HNO_3 , followed by addition of KMnO_4 and $\text{K}_2\text{S}_2\text{O}_8$, and a second acid digestion. Before analysis, 5 ml of 10 % (w/w) NH_2OH HCl was added to reduce excess permanganate and the volume was brought to 40 ml with distilled water.

Quality control samples were processed in a manner identical to field samples. A method blank was run with every 20 samples, or with every sample set, whichever was more frequent. Matrix spike/matrix spike duplicate samples were run with every 20 samples or with every sample set. National Institute of Standard and Technology (NIST) reference materials were analyzed with each set of samples. Metals can exist in the environment in several forms, but the analytical methods used by the NS&T do not distinguish between these various forms. Instead, analytical results are reported as total metal concentration (aggregation of all species of a metal) in microgram per milligram ($\mu\text{g g}^{-1}$) for dry sediment weight (dw).

Other ancillary parameters included grain size and total organic carbon (TOC). Total organic carbon was determined using combustion/NDIR detection. Grain size determination utilized wet sieving and pipetting techniques following EPA methods (EPA 1995). Grain size and TOC measurements are reported as percentages of the total sample weight.

Statistical analysis

Primary statistical analyses were conducted using JMP-5.1TM system statistical package. The data were tested for normality using Shapiro–Wilk “goodness of fit test.” Box-plot statistics were used to assess the concentration variations among strata for metals. The approach uses the range of concentration distribution in each stratum based on quartiles and Chi-square approximation for inter-stratum concentration comparison. The plots show the median, the 25th and 75th percentile (bottom and top of the box), and the whiskers above and below the box represent the 10th and 90th percentiles. Multivariate cluster analyses were conducted to determine natural breaks within the concentration range of each metal. Wilcoxon rank-sum or Kruskal–Wallis rank tests was used to assess differences between inter-strata comparison. ArcGIS data classification based on the Jenks’ grouping was used to assess the spatial distribution of sediment grain size. Relationships between variables (e.g., inter-metal correlations) were assessed using Spearman rank correlation.

Results

Sediment grain size and TOC

Sediments collected were virtually gravel-free, thus sediment grain size composition was assessed based on the relative percentages of fine grain mud (silt + clay). In the study area, sediment grain size composition was fairly broad (Fig. 3). Percent fine grain sediment varied from low 9.5 % at the ES6 site to high 97 % at the HH3 site. At the three sites within Homer Harbor, sediment was finer, with more than 80 % fine grained material. Outside the harbor, there was no difference between eastern and western strata for sediment grain size content ($p=0.47$). However, within the western strata, grain size distribution showed a strong onshore-offshore gradient with finer materials (mud) found at sites closer to shore while no real discernable pattern was observed in the eastern strata (Fig. 3).

Total organic carbon ranged from low 0.31 % to high 4.02 % (Fig. 3) in the study area. The distribution of TOC in sediment exhibited a distinct east to west gradient with Wilcoxon test indicating a significantly higher TOC content in the western strata compared to the eastern strata ($p=0.0001$). Like fine grain sediment,

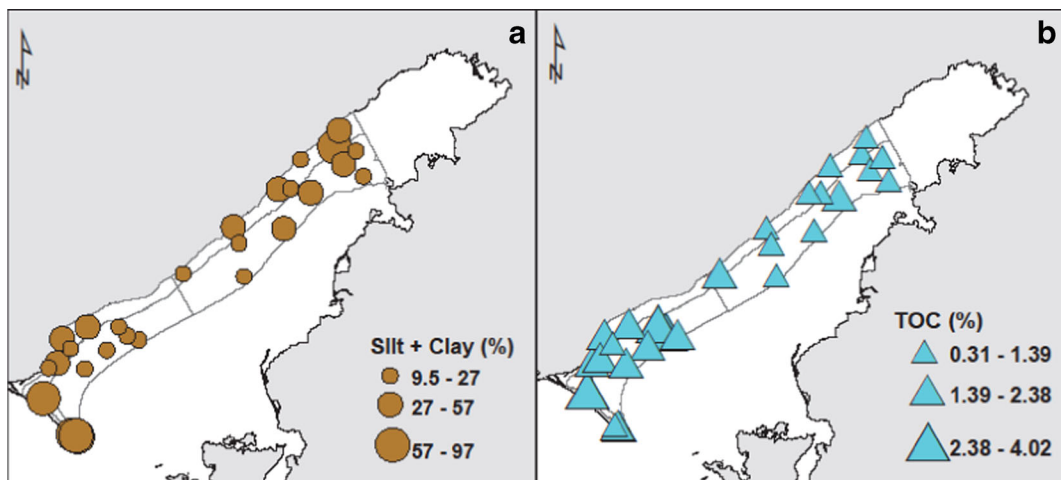


Fig. 3 Spatial distribution of fine sediment (% silt + clay) (a) and total organic carbon (TOC %) (b) in the Kachemak Bay study sites

the distribution of TOC showed a discernable pattern onshore-offshore gradient in the western strata (Fig. 3).

Metals concentration and distribution

Metal concentrations were variable across the study area. Summary statistics of concentration range and mean values for each trace and major element are shown

in Table 1. Box-plot statistics and chi-square approximation tests indicated significant differences ($P < 0.05$) between strata for nearly all measured metals, except Sb and Si (Fig. 4a, b). Homer Harbor stratum was shown to have elevated concentrations for most metals. Among the other strata, elemental concentrations were fairly broad, except for a few site spikes. The most noticeable of these spikes was recorded for the site EF4, where

Table 1 Mean metal concentrations ($\mu\text{g g}^{-1}$ dry weight) in sediment from the Kachemak Bay study area and Port Graham Bay

Element	Homer Harbor	Western Flat	Western Subtidal	Eastern Flat	Eastern Subtidal	Port Graham	ERL	ERM
Ag	0.12–0.15 (0.130)	0.08–0.11 (0.10)	0–0.07 (0.05)	0.07–0.14 (0.09)	0.04–0.11 (0.08)	0.05	1	3.7
As	14.1–17.9 (15.4)	13.7–21.4 (17.7)	18–48.6 (31.2)	10.7–26 (16.7)	15.2–43.4 (24.6)	8.93	8.2	70
Cd	0.19–0.22 (0.20)	0.10–0.17 (0.14)	0–0.097 (0.05)	0.11–0.171 (0.13)	0–0.14 (0.07)	0.24	1.2	9.6
Cr	94.3–96.2 (95.2)	59.3–73.5 (66.8)	61.8–68.1 (65.0)	67.3–110 (78.0)	74.7–109 (84.8)	147	81	370
Cu	60.2–69.4 (64.8)	20.1–40.3 (30.3)	21.8–27.9 (25.1)	27.5–65.6 (38.0)	23.5–39.7 (33.1)	23	34	270
Hg	0.11–0.12 (0.12)	0.09–0.12 (0.11)	0.09–0.11 (0.10)	0.06–0.10 (0.07)	0.05–1.07 (0.07)	0.21	0.15	0.71
Mn	650–703 (685)	467–635 (519)	500–1,080 (688)	507–863 (632)	592–989 (734)	668	–	–
Ni	45.5–45.9 (45.7)	32.0–37.7 (35.0)	33.4–43.7 (37)	33.7–56.5 (40.3)	33.5–43.6 (39.5)	28.5	20.9	51.6
Pb	13.9–14.9 (14.2)	8.29–11.6 (9.89)	8.33–9.82 (8.97)	9.22–15.2 (11.6)	8.56–13.6 (11.4)	4.73	46.7	218
Sb	1.26–1.34 (1.30)	0.93–1.33 (1.16)	0.93–1.79 (1.20)	1.01–2.04 (1.27)	0.94–1.76 (1.38)	0.23	–	–
Se	0.30–0.33 (0.32)	0.15–0.30 (0.20)	0.0–0.27 (0.14)	0.11–0.26 (0.18)	0.0–0.22 (0.10)	0.57	–	–
Sn	1.82–2.02 (1.95)	1.33–1.69 (1.46)	1.13–1.72 (1.34)	1.35–1.98 (1.58)	1.48–1.76 (1.57)	1.15	–	–
Zn	144–158 (151)	74.5–92.6 (83.1)	74–83.4 (80.2)	82.4–139 (96.3)	78.4–97.3 (90.6)	81.5	150	410
Al	76.8–85.5 (79.7)	62.5–72.1 (65.2)	65.6–71.9 (68.4)	72.6–84 (76.8)	65.7–74.8 (70.9)	62.4	–	–
Si	257–288 (267.6)	250–299 (280.)	275–325 (303.2)	266–311 (291.7)	261–305 (290.7)	255	–	–
Fe	46.6–49 (47.9)	31.9–39.2 (358.)	35.7–61 (44.4)	33.3–52.5 (38.9)	35.3–43.5 (41.1)	40.3	–	–

Kachemak Bay values are minimum and maximum with the stratum mean in parenthesis. ERL and ERM values are provided

Al, Fe, and Si are in mg g^{-1}

ERL effect rang-low, ERM effect range-median, – not available

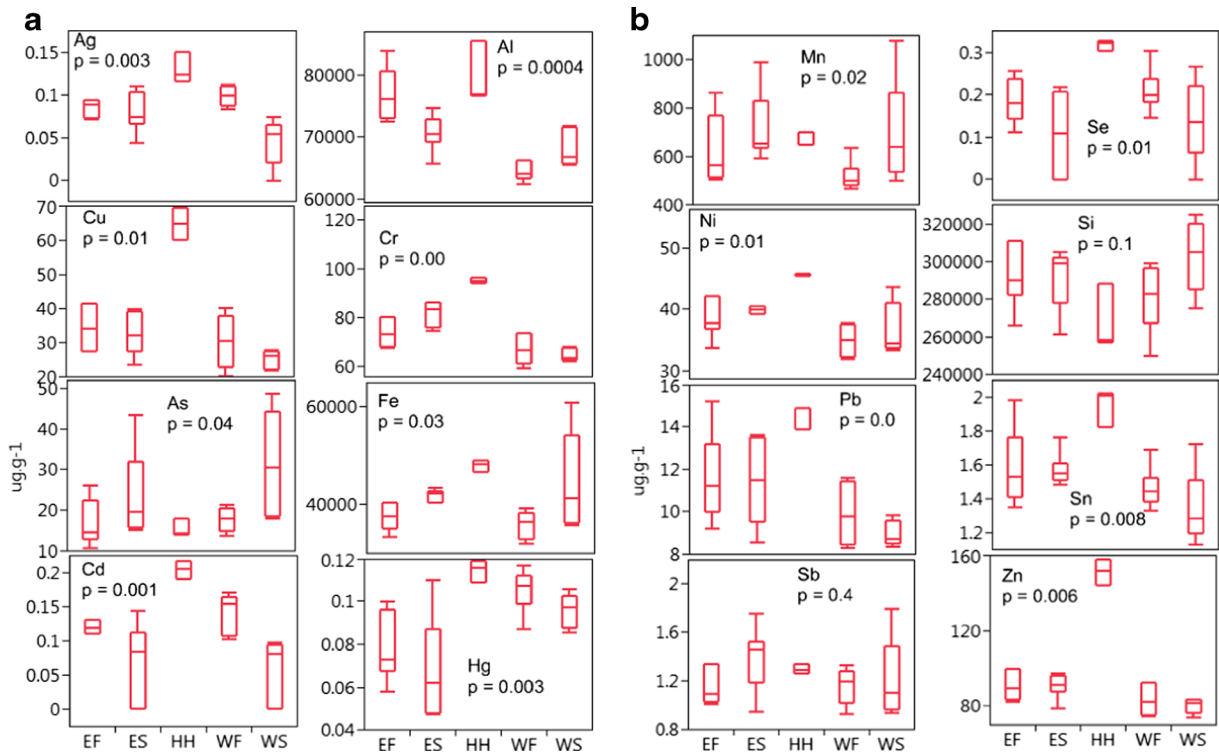


Fig. 4 **a** Box-plot statistics illustrating metal distribution in each stratum. The p value indicates the significance of nonparametric inter-stratum comparison based on the Wilcoxon rank-sum test. **b**

Box-plot statistics illustrating metal distribution in each stratum. The p value indicates the significant of nonparametric inter-stratum comparison based on the Wilcoxon rank-sum test

virtually all measured elements were relatively elevated (Table 1). However, site WF6 in the western flats stratum also showed spikes in the concentration of Ag, Cr, Cu, Ni, Hg, Se, Sb, and Zn. Excluding Homer Harbor, Wilcoxon tests revealed significant differences between the western and the eastern strata. Concentrations of Al, Cu, Cr, Mn, Ni, Pb, Sb, and Zn were found to be significantly elevated in the eastern strata compared to the western strata ($P < 0.05$). Mercury was higher in the western strata relative to the eastern ($p = 0.002$), while concentrations of Ag, As, Cd, Fe, and Si were not different.

Metal concentrations from the three Port Graham Bay sites were also variable. While the PG-2 site located directly across the bay from the village of Port Graham has the lowest metal concentrations, PG-4b site, located toward the head of Port Graham, was elevated in Cr ($334 \mu\text{g g}^{-1}$) and Cd ($0.27 \mu\text{g g}^{-1}$) compared to the sites in the study area (Table 1). Additionally, mean values of Cd, Hg, and Se were statistically higher in Port Graham than in the Kachemak Bay. Conversely, As, Sb, and Pb at all three Port Graham sites were approximately half the concentrations seen in the main study area.

Summary results illustrated in Table 2 showed that relative to regional sediment assessment data from EMAP (Saupe et al. 2005), U.S. Army Corp of Engineer (COE 2007), and the NS&T Mussel Watch monitoring program (1995–1997), metal concentrations in Kachemak Bay were generally within the regional averages. However, at the Mussel Watch monitoring site of Port Valdez Mineral Creek located in Prince William Sounds, concentrations of metals, including As, Cr, Ni, and Pb, were elevated relative to Kachemak Bay (Table 2). The corps characterized dredged materials from Homer Harbor and found arsenic and chromium at concentrations ranging from 7 to $17 \mu\text{g g}^{-1}$ and 18 to $24 \mu\text{g g}^{-1}$, respectively (COE 2007). The concentrations the corps found were in exceedance of the ADEC bench standard for soil (ADEC 2008). This study found even higher concentrations for these two contaminants, perhaps resulting from difference in sediment digestion method (COE 2009; Kimbrough and Lauenstein 2006), with mean values of $21.4 \pm 1.8 \mu\text{g g}^{-1}$ for arsenic and $76.7 \pm 2.6 \mu\text{g g}^{-1}$ for chromium. Saupe et al. (2005) have also reported similar concentration levels for As and Cr in the

inner Kachemak Bay. It is noteworthy to highlight that Hg appeared to be relatively elevated in sediment from Kachemak Bay compared to the Prince William Sound (Table 2).

Levels of metal concentrations in Kachemak Bay sediment were compared to the NOAA numerical sediment quality guidelines (SQG) developed by Long and Morgan (1990) and Long et al. (1995), known as ERM and ERL (effects range-median and effects range-low) shown in Table 1. The ERM and ERL values 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). When concentrations of most of the trace metals were below the ERM values, Ni was found to be higher than the ERM in the eastern mudflat stratum (Table 1). Several metals, however, had concentrations at or above the ERL values. Arsenic and Cu had sediment concentrations that were above the ERL in all the strata; Cr was above the ERL in Homer Harbor and the eastern strata; and Zn was higher than the ERL value in Homer Harbor.

Discussion

Sediment physical characteristics are one of the overriding environmental parameters that influence the distribution of contaminants. Within the eastern subtidal stratum, sediment composition varied from a coarser sandy type to a finer sandy mud according to sediment nomenclature based on the sand-silt-clay composition (Shepard 1954). In the Homer Harbor stratum, the bottom sediment was mainly composed of mud with high contents of clay and silt. The high finer mud content of sediment in the harbor is an indication of a low-energy depositional area. Both eastern and western subtidal areas of the inner bay have similar sediment composition of sand to sandy mud as indicated by the Jenks' grouping. Sediment composition in the intertidal mudflats varied from sandy silt to clayey silt in the eastern flat, and from sandy mud to silty sand in the waster flat. Sediment type (e.g., mud vs. sand) and associated levels of organic matter content influence the capacity of the sediment to sequester contaminants, and hence the potential to be toxic to organisms.

Table 2 Mean metals concentrations from the present study compared to average Mussel Watch data from southern Alaska (Cook Inlet Homer Spit (CIHS), Port Valdez Mineral Creek (PVMC), and

PWS = average of five sites in Prince William Sound, and AKMAP (Saupe et al. 2005) and US Army Corp of Engineer (COE 2007)

Element	Mean	MW CIHS1997	MW PVMC	MW PWS	AKMAP (Saupe et al. 2005)	US Army Corp (COE 2007)
Ag	0.09±0.01	0.1	0.13	0.08	0.20±0.08	
As	21.4±1.8	16.26	24.67	12.8	8.94±3.97	7.3
Cd	0.11±0.01	0.06	0.12	0.08	0.22±0.25	
Cr	76.7±2.6	93.29	146.67	144	74.95±71.82	17.3
Cu	35.6±2.6	27.16	65.67	30.5	35.51±14.60	
Hg	0.09±0	0.06	0.01	0.03	0.07±0.04	
Mn	649±29	775	2167	982	738.0±145.64	
Ni	38.9±1.01	43.13	60.33	53.7	32.35±99.03	
Pb	11±0.4	10.94	17.33	11	13.23±3.02	
Sb	1.26±0.05	0.88	2	1.2	0.91±0.45	
Se	0.17±0.02	0.16	0.43	0.22	0.14±0.30	
Sn	1.55±0.04	1.16	1.03	0.93	0.64±0.27	
Zn	95.1±4.4	82.78	150	92.2	90.08±28.11	
Al	71.7±1.5	74.9	88.7	75.2	47.44±15.47	
Fe	40.8±1.2	35.8	60.10	42.6	42.79±1030	
Si	288.6±3.6	248.3				
Fine grain	36.6±5.1	26.32	100			
%TOC	1.58±0.2					

Al, Fe, and Si are in mg g⁻¹

Metal concentrations varied broadly in the study area. Relative to the other strata, most of the metals were elevated in Homer Harbor, although some spikes were recorded at isolated sites in the mudflats (Table 1). Compared to the NOAA sediment quality guideline, concentrations of several metals were found to be above ERL values (Table 1). Most notably, Ni concentrations were above the ERL value at all sites, and at the EF4 site, nickel's concentration was above the ERM value. Station EF4 had a much higher percentage of fine grained sediment than the surrounding stations (Fig. 3). Cadmium, while high at EF4 relative to the rest of the system, is nevertheless well below the ERM and ERL. Mercury exceeds the ERL, but the high concentration at the Port Graham PG3c site was half of the ERM while chromium is nearly at the ERM level. Given the well documented harmful biological consequences of Cd, Cr, Hg, and Se, a follow-up study to assess

bioavailability and bioaccumulation in local biota may be warranted. Several metals do not have ERL or ERM values, (Sb, Mn, Se, and Sn), or State guideline criteria for comparison.

Elevated concentrations of As and Cr, which exceeded the State of Alaska Department of Environmental Conservation bench standard for soil (ADEC 2008), were recorded in Kachemak Bay. In general, mean concentration values in Kachemak Bay were within the regional average for most metals. However, Hg was found to be relatively elevated in the bay compared to published data in the region (Table 2). Mercury concentration, and particularly its biomagnification in aquatic food chains, is a concern in Alaska. In Kachemak Bay, the source of Hg 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.

Table 3 Spearman rank correlations between metals, grain size (silt + clay), and TOC, only significant correlations are presented (n=29)

Variable	Ag	Al	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Sb	Se	Si	Sn	Zn	%Fine	%TOC	
Ag				$\rho = .873$ $p = .000$	$\rho = .392$ $p = .039$	$\rho = .780$ $p = .000$		$\rho = .571$ $p = .002$			$\rho = .653$ $p = .000$	$\rho = .539$ $p = .003$	$\rho = .717$ $p = 0.000$	$\rho = -.682$ $p = .000$	$\rho = .534$ $p = .003$	$\rho = .584$ $p = .001$	$\rho = .850$ $p = .000$		
Al					$\rho = .612$ $p = 0.001$	$\rho = .596$ $p = .001$	$\rho = .411$ $p = .030$	$\rho = .404$ $p = .033$	$\rho = .616$ $p = .000$	$\rho = .615$ $p = .000$					$\rho = .587$ $p = .001$	$\rho = .700$ $p = .000$	$\rho = .420$ $p = .026$		
As						$\rho = .432$ $p = .022$		$\rho = .378$ $p = .047$				$\rho = .473$ $p = .011$							
Cd						$\rho = .740$ $p = .000$		$\rho = .515$ $p = .005$			$\rho = .583$ $p = .001$		$\rho = .663$ $p = .000$	$\rho = -.643$ $p = .000$	$\rho = .460$ $p = .014$	$\rho = .550$ $p = .002$	$\rho = .894$ $p = .000$		
Cr						$\rho = .686$ $p = .000$	$\rho = .459$ $p = .007$	$\rho = .546$ $p = .003$	$\rho = .757$ $p = .000$	$\rho = .697$ $p = .000$	$\rho = .492$ $p = .008$				$\rho = .683$ $p = .000$	$\rho = .771$ $p = .000$	$\rho = .426$ $p = .024$	$\rho = .572$ $p = .001$	
Cu							$\rho = .496$ $p = .007$	$\rho = .437$ $p = .020$	$\rho = .705$ $p = .000$	$\rho = .785$ $p = .000$	$\rho = .720$ $p = .000$	$\rho = .594$ $p = .001$	$\rho = -.656$ $p = .000$	$\rho = .684$ $p = .000$	$\rho = .865$ $p = .000$	$\rho = .838$ $p = .000$			
Fe								$\rho = .820$ $p = .000$	$\rho = .684$ $p = .000$		$\rho = .695$ $p = .000$	$\rho = .381$ $p = .046$			$\rho = .542$ $p = .003$	$\rho = .602$ $p = .001$			
Hg											$\rho = .396$ $p = .037$	$\rho = .634$ $p = .000$	$\rho = -.597$ $p = .001$				$\rho = .477$ $p = .010$	$\rho = .559$ $p = .002$	
Mn										$\rho = .610$ $p = .001$		$\rho = .279$ $p = .003$			$\rho = .627$ $p = .000$	$\rho = .486$ $p = .009$	$\rho = .459$ $p = .014$		
Ni											$\rho = .656$ $p = .000$	$\rho = .553$ $p = .002$			$\rho = .555$ $p = .002$	$\rho = .827$ $p = .000$	$\rho = .464$ $p = .013$		
Pb												$\rho = .532$ $p = .004$		$\rho = -.554$ $p = .002$	$\rho = .717$ $p = .000$	$\rho = .833$ $p = .000$	$\rho = .768$ $p = .000$		
Sb													$\rho = .458$ $p = .014$	$\rho = -.633$ $p = .000$	$\rho = .542$ $p = .003$	$\rho = .623$ $p = .000$	$\rho = .428$ $p = .023$		
Se														$\rho = -.518$ $p = .005$		$\rho = .446$ $p = .017$	$\rho = .626$ $p = .000$	$\rho = .427$ $p = .024$	
Si																$\rho = -.509$ $p = .006$	$\rho = .489$ $p = .012$	$\rho = -.724$ $p = .000$	
Sn																	$\rho = .743$ $p = .000$	$\rho = .551$ $p = .002$	$\rho = .445$ $p = .018$
Zn																		$\rho = .692$ $p = .000$	

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 Kachemak Bay sediments may be of an atmospheric and/or geological source.

Differences in spatial distribution of metals between Homer Harbor and the eastern and western strata in the bay (Fig. 4a, b) may be the result of physical dynamics of benthic sediment distribution and water movement in the bay. Fine-grained sediment has a high surface to volume ratio. Thus, it has the ability to sequester higher concentrations of particle reactive metals through adsorption. Homer Harbor is a depositional environment with a high percentage of fine grain sediment. It is also a center of concentrated vessel activity and maintenance, which undoubtedly is a source of metal contamination. Outside the harbor, strata comparisons revealed that concentrations of most trace metals and some major elements, including Al, were relatively higher in the eastern strata near the head of the bay than the western strata. Sediment grain size tended to be finer in the eastern end of the bay, but grain size characteristics were also affected by proximity to shore and river discharge. Aside from the Fox and Bradley Rivers, which deliver large volume of freshwater at the head of the bay, a

system of nine glaciers also drain into the bay (ADF&G 1998). Levels of metal concentration in the eastern strata demonstrated the influence of river transport, which brings eroded materials to the head of the bay, as indicated by the presence of sediment types that varied from a coarser sandy type to a finer sandy mud. Thus, metal distribution in Kachemak Bay may not only be influenced by the physiographic characteristics of the sediment, but also by proximity to freshwater discharge in the bay.

In natural coastal waters, trace metals co-precipitate with the oxide/hydroxides of Al, Fe, and Mn, usually into the fine-grained fraction (clay or aluminosilicate) of sediments (Schropp et al. 1990). Since aluminosilicates are the metal-rich phase of bottom sediment, many approaches to delineate anthropogenic versus natural sources are based on grain size, using Al and Fe for normalization (Forstner and Wittmann 1981; Windom et al. 1989). That is, without anthropogenic inputs, metal concentrations are expected to co-vary among each other and with Al, Fe, and Mn, given that factors such as precipitation or diagenesis are very small. Deviations from direct metal-Al/Fe or metal-grain size correlations are interpreted as anthropogenic enrichment (Windom et al. 1989; MacDonald 1994). Significant inter-metal

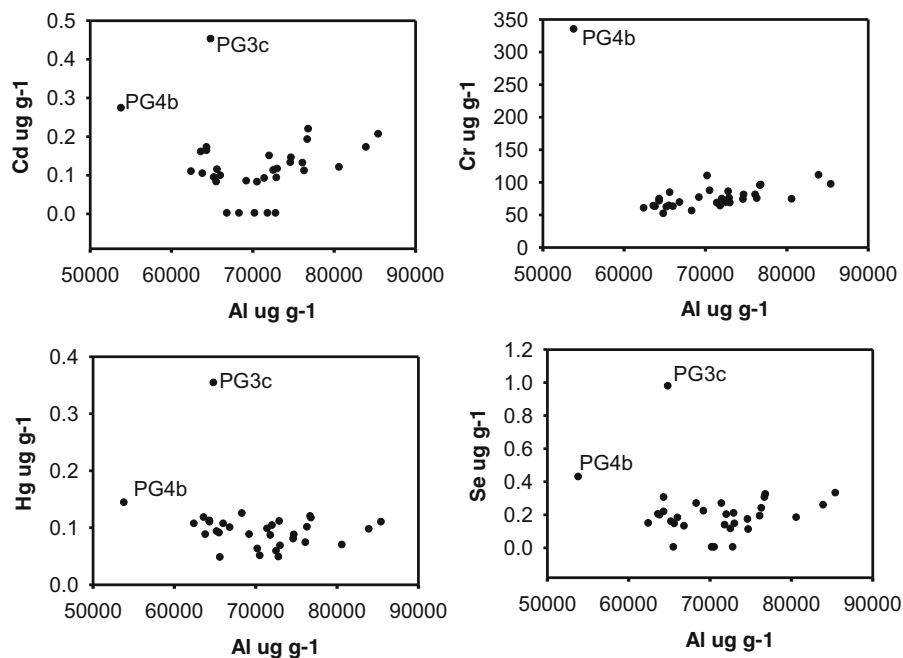


Fig. 5 Plots of chromium, cadmium, mercury, and selenium (ug g^{-1}) as a function of aluminum concentration in Kachemak Bay sediments. Selected stations in Port Graham are denoted with station numbers

correlations, as well as results of the correlation between metals and sediment parameters, (grains size and %TOC) are illustrated in Table 3.

Significant associations were found among several groups of metals. For example, significant correlations were found among the group Ag, Cd, and Cu. Zinc was correlated with Cr, Cu, Ni, Pb, and Sn. Nickel correlated with Cr and Cu. Arsenic is relatively elevated, but does not appear to correlate with Al in Kachemak Bay. EMAP sediment assessment in south central Alaska found similar correlations, especially among Cr, Cu, Sn, and Zn (Saupe et al. 2005). Among the major metals, correlations between Al, Mn, and Fe were positive ($p < 0.03$). Comparable results have been reported by Saupe et al. (2005), Burrell (1979), and Robertson and Abel (1990) for similar habitats. Silicon was not correlated with reference elements, such as Al or Fe, and was negatively correlated with virtually all trace metals. High silicon concentrations would be expected in sandy sediment, where there is low accumulation of metals. Additionally, plotting trace metals concentrations against major elements, such as Al, to normalize for the relative background input of minerals from the watershed can reveal associations between specific locations and contaminant input. For example, outliers in the relative distribution of Cd, Cr, and Hg in Chesapeake Bay (Hartwell and Hameedi 2007) have been used to identify anthropogenic contamination in harbors and industrial zones in Baltimore and Norfolk. Some metals (e.g., Hg and Se) are less predictable based on elemental ratios because they are subject to more complex fate and transport dynamics due to particle reactivity, valence states under varying redox conditions, biological uptake, cycling, and so on. Plots of selected metals were used to exemplify this phenomenon (Fig. 5). Except for Port Graham, Cd is generally low in Kachemak Bay. The fact that Cd, Cr, Hg, and Se are found at much higher concentrations in Port Graham than in Kachemak Bay (Table 1 and Fig. 5) may be an indication of significant differences in geologic composition of the watershed as much as anthropogenic contamination. Similarly, the relatively low levels of arsenic, antimony, and lead may be the result of local geology.

Grain size (% fine) was found to be significantly correlated with metals. This is consistent with the observation that elemental concentrations are elevated in finer sediment due to adsorption onto particle surfaces.

The depositional zone in Homer Harbor had metal concentrations greater than the other strata (Table 1), likely due to grain size and proximity to metal sources.

In addition to the grain size, inter-metal positive correlations, including those between Fe and Mn and several elements (Table 3), were clear indications of natural sources. In Alaska, positive correlations between metals and the fine fraction of sediments are usually linked to materials transported by glacial melt (Saupe et al. 2005). Thus, likely sources of metals in Kachemak Bay are natural bedrock weathering and terrigenous material transported from mountains by rivers and streams of glacial melt water. Outside of the harbor, anthropogenic inputs are negligible, as the human population density is low and no large scale industrial activities exist in the region. However, long range atmospheric transport is generally considered as a nonpoint source of air-borne contaminants in the arctic environment (Arctic Monitoring and Assessment Program, AMAP 2005). Thus, transboundary air pollution may contribute to the overall metals concentration in the region to some extent.

Conclusion

Heavy metal concentrations in Kachemak Bay varied broadly, but levels were generally within the regional averages. Metal distribution in the bay is likely influenced by river input at the head of the bay and sediments from glacial meltwater. Depositional areas in Homer Harbor and Port Graham do accumulate relatively elevated levels of heavy metals. While concentrations of some metals were at or above the ERL, overall sediment quality demonstrates that Kachemak Bay is a fairly pristine environment, with the likely source being from eroding geologic formations, or “terrigenous.” The results of this study would serve as a baseline data for unforeseen events and future reference for sediment contamination in Kachemak Bay.

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