Characterization of metal/metalloid concentrations in fjords and bays on the Kenai Peninsula, Alaska

S. Ian Hartwell **D** · Doug Dasher · Terri Lomax

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Abstract A baseline environmental characterization of Chrome and Dogfish bays on the Kenai Peninsula, Alaska, was conducted using a sediment quality triad approach. Resident fish and blue mussel body burdens were also assessed. The data was derived from a larger study that assessed seven distinct water bodies on the Kenai Peninsula's north side, draining into Kachemak Bay. Sampling sites for water quality measurements and sediment 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 elemental distribution were also measured at each sampling site. Chrome Bay and Dogfish Bay open into lower Cook Inlet and had coarser sediments than the other bays studied. 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

S. I. Hartwell $(\boxtimes) \cdot$ D. Dasher \cdot T. Lomax

D. Dasher e-mail: dhdasher@alaska.edu

T. Lomax e-mail: terri.lomax@alaska.gov quality guidelines. Whole sediment amphipod toxicity bioassays were conducted with sediments from Chrome Bay. No sample exhibited significant mortality or sublethal effects. Body burdens of three species of fish and mussels collected 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.

Keywords Kenai Peninsula, AK · Metal contaminants · Chromium . Nickel . Toxicity. Body burden

Introduction

Alaska has an extensive coastline of 49,700 miles, greater than the contiguous USA (U.S. EPA [2005;](#page-11-0) Shorezone [2016](#page-11-0)), and vast natural marine and coastal resources. However, due to a small population and lack of infrastructure, Alaska lacks adequate data to provide baseline information necessary to assess future trends. Historically, assessment in Alaska has been either limited or focused on areas of known impairment. Contaminants 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

Center for Coastal Monitoring and Assessment, NOAA/NOS, 1305 E. W. Hwy., N/SCI-1, Silver Spring, MD 20910, USA e-mail: ian.hartwell@noaa.gov

areas where large amounts of these foods are consumed as a primary source of protein (Wolfe [1996\)](#page-11-0).

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 USA. Results from previous sediment bioeffects studies in over 20 coastal water bodies and estuaries have been published (Long et al. [1996;](#page-11-0) Turgeon et al. [1998](#page-11-0); Long [2000](#page-11-0); Hartwell et al. [2001](#page-11-0); Hartwell and Hameedi [2006;](#page-10-0) Hartwell and Hameedi [2007;](#page-10-0) Pait et al. [2006;](#page-11-0) Hartwell et al. [2009,](#page-11-0) [2016](#page-11-0)).

The NS&T Program has analyzed contaminants in sediment and mussels collected from selected sites in the Gulf of Alaska (O'Connor [2002](#page-11-0)). In collaboration with the US EPA Environmental Monitoring and Assessment Program, the Alaska Dept. of Environmental Conservation (ADEC) undertook a coastal ecological condition study (Alaska Monitoring and Assessment Program, AKMAP) that encompassed assessment of contaminants and benthic assemblage in sediment along the Gulf of Alaska and the Aleutian Islands (Saupe et al. [2005](#page-11-0)). Anomalously high concentrations of chromium were found on the Kenai Peninsula in Chrome Bay sediments. The study reported here augments these efforts to provide detailed data on sediment quality on the Kenai Peninsula, where data is sparse.

Cook Inlet is a major estuary in South Central Alaska. The watershed covers $102,000 \text{ km}^2$ and is home to 482,166 people or 65% of Alaska's population, including the State's largest city, Anchorage (Brabets et al. [1999](#page-10-0); Alaska Department of Labor [2019\)](#page-10-0). Pollutants from human activities within the watershed are delivered to the estuary from both non-point and point sources. These sources may include wastewater discharge, marine activities associated with commercial and recreational fishing, commercial shipping, oil rig maintenance, stormwater runoff, and short- and longrange atmospheric transport (Saupe et al. [2005](#page-11-0); Norman [2011](#page-11-0)). 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. Oil from the Exxon Valdez oil spill was carried by currents from the Prince William Sound into the lower Cook Inlet, including into the Kachemak Bay (Saupe et al. [2005](#page-11-0)). The Cook Inlet estuary hosts a major salmon fishery, an endangered beluga whale population, and provides a major recreational/subsistence resource to Alaskans.

This study characterizes sediment habitat and metal concentrations for the Kachemak Bay part of the Cook Inlet estuarine system and Chrome Bay, which lies along the southeastern Kenai Peninsula at the Cook Inlet entrance (Fig. [1](#page-2-0)). Sediment chemistry, toxicity, and benthos assessments were conducted by NS&T on the north side of the 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](#page-11-0)) and the Cook Inlet Regional Citizens Advisory Council (CIRCAC), respectively. This paper summarizes the concentrations of major and trace element results of a joint NOAA, ADEC, and University of Alaska Fairbanks (UAF) project to assess chemistry, benthic community, and sediment toxicity studies in the embayments on the south side of the Kachemak Bay and bays on the Kenai Peninsula, including an abandoned chromite (Cr_2O_3) ore mining site (Hartwell et al. [2017](#page-11-0)). A companion paper summarizes the results of organic (PAHs, chlorinated organics, butyl-tins) contaminant results.

Kachemak Bay is a 64-km-long glacial fjord on the east side of lower Cook Inlet in south-central Alaska (Fig. [1\)](#page-2-0). The south shore is bounded by the Kenai Peninsula, which has numerous smaller fjords and embayments cut into steep terrain that rise to glaciated valleys and uplifted mountain peaks 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.

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 at the tip of the Kenai Peninsula. Between 1916 and 1918, approximately 2000 tons of chromite ore was surface mined from the land adjacent to Chrome Bay (Gill [1922](#page-10-0); Guild [1941](#page-10-0)). 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 is exposed to open ocean conditions of Kennedy

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

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. The Dogfish and Chrome bays were expected to contain substantially different habitats and biological communities than the fjords within Kachemak Bay due to physical factors. Other bays/fjords that were sampled included Port Graham Bay, Seldovia Bay and the harbor at Seldovia, Jakolof Bay, Sadie Cove, Tutka Bay, China Poot Bay, and Halibut Cove Lagoon (Fig. [2\)](#page-3-0) (Hartwell et al. [2017\)](#page-11-0).

Methods

The National Status and Trends Program and AKMAP use a stratified-random design for the selection of sampling sites to determine the spatial extent of sediment toxicity in US coastal waters. Three sampling sites were located on a random basis within each bay (Fig. [2\)](#page-3-0). This approach combines the strengths of a stratified design with the random-probabilistic selection of sampling locations. One extra sample was taken in Clam Cove.

Two sediment samples were taken at each site in addition to water quality measurements with YSI (Yellow Springs Instruments) meter readings at the surface and bottom of the water column. Samples were collected with a stainless steel PONAR 0.04 m² sampler. Sampling methods followed standard NS&T field methods (Apeti et al. [2012\)](#page-10-0) that ensure QA/QC and minimize cross contamination. Only the upper 2–3 cm of the sediment was retained in order to assure collection of recently deposited materials. Additional sediment was collected at Chrome Bay for sediment bioassays.

Fig. 2 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) and Seldovia Bay (SB), Port Graham (PG),

Dogfish Bay (DB), Chrome Bay (CH), and Clam Cove (CC). Inset shows Kenai Peninsula in relation to Cook Inlet and Prince William Sound in the Gulf of Alaska

The sediment samples were thoroughly homogenized in the field with an acetone-rinsed, stainless steel mixer attached 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.

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. Mussel beds were not found near sampling sites at the other locations.

Chemical analyses followed procedures routinely used in the NOAA NS&T Program (Kimbrough and Lauenstein [2006](#page-11-0); ASTM [2004](#page-10-0)). In addition to 15 major and trace elements (Table [1\)](#page-4-0), a broad suite of sediment contaminants was analyzed, including 51 PAHs; 30 chlorinated pesticides, including DDT and its metabolites; 54 polychlorinated biphenyls (PCBs); and butyl tins, which are reported elsewhere (Hartwell et al. [2017\)](#page-11-0). Other parameters included grain size analysis, total organic/inorganic carbon (TOC/TIC), and percent solids.

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. For analysis of Hg, sediment samples were digested based on a modified version of the US EPA ([1991](#page-11-0)) method 245.5, using a concentrated $H₂SO₄$ and HNO₃ digestion, followed by addition of $KMnO₄$, and $K₂S₂O₈$, and then the samples were again digested. QA/QC controls included standard reference Table 1 Major and trace elements measured in the Kenai Peninsula samples. For simplicity, the term metal is used without distinction between true metals and metalloids/non-metals

materials, matrix spikes, duplicate analyses, internal standards, and blanks. The actual analytical method detection limit (MDL) was determined following procedures outlined in CFR 40, part 136 (1999).

Amphipod mortality bioassays were carried out on the sediment samples collected at Chrome Bay. All methods are based on standard methods promulgated by ASTM [\(2004\)](#page-10-0) and additional guidance developed for

Table 2 Sediment concentrations (μg/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 italicized and ERM exceedances are in bold

Fig. 3 Concentrations of Cr in sediments in fjords and bays on the Kenai Peninsula and the ERL and ERM

testing four different amphipod species (U.S. EPA [1994\)](#page-11-0) using the amphipod Eohaustorius estuarius as the test species.

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 element. Thus, all metals can be contrasted against each other in consistent units.

Numerical sediment quality guidelines (SQG), developed by Long and Morgan ([1990\)](#page-11-0) and Long et al. ([1995](#page-11-0)) known as ERM and ERL (effects range-median, effects range-low), 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).

Results and discussion

Neither 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 5.5 m. In contrast, the eastern portion of

and ERM

Fig. 5 Mean normalized values for As, Cr, Cu, Ni, Pb, and Zn

the Kachemak Bay water clarity averages only 1 m due to glacial runoff from the Fox and Bradley Rivers (Hartwell et al. [2009](#page-11-0)). Dogfish and Chrome bays open through wide mouths to open coastal water masses.

Depths varied from 3 m in Clam Cove to 27 m in Dogfish and Chrome bays (ave. 20 m without Clam Cove). The water column was well mixed based on temperature (bottom 10.4 °C vs surface 10.9 °C), salinity (28.2 ppt vs 27.6 ppt), and dissolved oxygen (8.2 mg/ L vs 8.1 mg/L .

Arsenic, Cr, Cu, Hg, and Ni exceeded the ERL concentrations at multiple sites (Table [2](#page-4-0)). Values from the other bays on the peninsula are shown for comparison. Nickel exceeded the ERL at all sites except in Dogfish Bay. Nickel and chromium concentrations far exceeded the ERMs in Chrome Bay (Figs. [3](#page-5-0) and [4\)](#page-5-0). 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.

Figure 5 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 protected on all sides by mountains and gravel bars, but has very coarse-grained sediment (27% gravel, 66% sand). Trace elements eroded off the chromite intrusion (Fig. 6) on the shore of Chrome Bay and mining activities settle in Clam Cove.

Fig. 6 Chromite intrusion on the shoreline at Chrome Bay. Note the climber in the white circle for scale

Fig. 7 Relationship between sediment concentrations of Al and Fe in ten bay/fjords on the Kenai Peninsula

Fig. 8 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

Fig. 9 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

| Sample | E mergence ^{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 | |

Table 3 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

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

Table 4 Whole body tissue concentrations (μg/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 | < 0.2 | < 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 |

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.

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 and 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 an outlier at Clam Cove, where Al concentration was only 1.9%, the relationship between Al and Fe was very weak (Fig. [7\)](#page-6-0), 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 (Al vs Fe; R^2 = .3013), with glacially influenced sites showing up as outliers (Hartwell et al. [2009\)](#page-11-0). Other studies have reported significant correlations between Al, Fe, and Mn in Alaska (Burrel [1979;](#page-10-0) Robertson and Abel [1990](#page-11-0)) in open water habitats.

The concentrations of metals measured in this study were comparable to previously published data by the US Corps of Engineers Alaska District, (U.S. CEAD [2007](#page-10-0)) and EMAP (Saupe et al. [2005](#page-11-0)). The Corps characterized

Table 5 Composite soft tissue concentrations (μg/g dry wt) of mussels collected at Chrome Bay and Tutka Bay. The average of 13 other mussel samples from the NS&T database for the Kenai Peninsula and western Prince William Sound are also shown

| | As | C _d | Сr | ∪u | 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 | l.53 | 22.02 | 0.93 | 4.16 | 3.52 | 0.113 |

dredged materials from Homer Harbor and found arsenic and chromium at concentrations ranging from 6 to 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/g for mercury (Hartwell et al. [2009\)](#page-11-0). These results agree with the EMAP findings. Data published by Saupe et al. ([2005\)](#page-11-0) 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 Figs. [8](#page-7-0) and [9.](#page-8-0) 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. Potential arsenic sources in the region are volcanic ash, coal-, and gold-bearing deposits, which may contain arsenopyrite (Walsh et al. [1979](#page-11-0); Matschullat [2000\)](#page-11-0).

Mercury concentration, and particularly its biomagnification in the aquatic food chain, is a concern in Alaska and elsewhere. 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 (Obrist et al. [2017](#page-11-0)).

Sediment toxicity testing did not reveal any acute (mortality) or sub-acute toxicity (reburial) in any test (Table [3](#page-9-0)). These results are consistent with the results of body burden analyses of fish and mussels (Tables [4](#page-9-0) and [5\)](#page-9-0). 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 bays (Hartwell et al. [2016](#page-11-0)), and for salmon from Kachemak Bay (Apeti et al. 2013) and the Alaska DEC Fish Monitoring Program. Blue mussels' body burdens of metals were at or below concentrations seen on the Kenai Peninsula and Prince William Sound in the NS&T database dating back to 1990. 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](#page-11-0)).

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