

Legacy Tove Project Note No. 5

Trace Metals and Organic Compounds in Seabed Sediments 1978-2016

Hawk Inlet & Young's Bay, Admiralty Island, Alaska

Friends of Admiralty



SUMMARY: We sampled trace metals and organic compounds in marine sediment in Hawk Inlet and Young's Bay in 2015-2016. Analytical results are contrasted with monitoring data and *original* (1978-1981) baseline sediment values.

- METALS CONCENTRATION CHANGE OVER TIME: Eleven heavy metals have been analyzed from seabed sediments collected by researchers from Hawk Inlet from 1978 to 2016: Arsenic, Cadmium, Chromium, Copper, Lead, Manganese, Mercury, Nickel, Selenium, Silver and Zinc. Concentrations of all eleven metals increased substantially during the industrial mining period, from 1.2 (manganese) to 646 (lead) times the original baseline level. The highest reported mercury concentration during the mining period was 77 times the maximum original baseline level, and 287 times the mean inlet-wide baseline level. *The average increase for eleven metals was 73 times original baseline levels, and 183 times the inlet-wide <u>mean original baseline</u> levels. Whereas measured metal levels in sediment have 'fluctuated' over time and by area, peaks (or maxima), are compared to baseline levels here because heavy metals persist in the environment once released. Biota, pore water and habitats are affected by the cumulative effects of metals added over time and compounding impacts of multiple metals.*
- **ORGANIC SUBSTANCES**: Sediments in Hawk Inlet have detectable levels of diesel and motor oil; the head of Hawk Inlet sediments contain a broad range of aromatic hydrocarbons (*eg* naphthalene, benzo-x). A biologically harmful level of the banned bottom paint compound, Tributyltin, was detected in the ore dock vicinity subtidal sediment.
- **CHANGE COMPARED TO YOUNG'S BAY CONTROL SITE**: The designated control site in Young's Bay shows relatively little to no change in most of the eleven trace metals analyzed since 1981.
- **GEOGRAPHY OF METAL LOADING:** Highest levels of metals are concentrated near the ore dock; all Hawk Inlet sites tested have increases in heavy metals relative to original baseline studies reported in the 1983 EIS.
- CONCENTRATIONS OF METALS RELATIVE TO ENVIRONMENTAL HARM SCREENING VALUES: Hawk Inlet metal concentration maxima exceed every ADEC-referenced NOAA trace metal benchmark for protecting marine life.

This Legacy Cove Note provides an overview of the marine sediment component of FOA research to date.

INTRODUCTION

In order to explore the ecological status of the Hawk Inlet, Alaska marine ecosystem after over a quarter century of industrial mining, we conducted a multifaceted, interdisciplinary reconnaissance of features of the ecosystem in 2015-2016. This note serves as a summary report describing one aspect of "Legacy Cove" pilot research conducted by Oceanus Alaska, with funding from Friends of Admiralty, in Hawk Inlet marine waters adjacent to the Admiralty Island National Monument: trace metals and organic contaminants in marine sediment.

We sampled Hawk Inlet and Young's Bay seabed sediment in May 2015 through June 2016 and analyzed samples for trace metals and organic contaminants – specifically, petroleum range hydrocarbons and tributyltin. Results are compared to the *original* pre-mining baseline data prepared for the 1983 Environmental Impact Statement (USDA EIS 1983). Additionally, results are discussed in the context of trace metal concentrations reported annually by the mining company for ADEC-directed monitoring requirements to meet US EPA and State of Alaska environmental regulations.

BACKGROUND

Impetus for sampling

Seabed sediment is a dynamic and defining feature of the marine ecosystem which may retain organic and nonorganic substances, including contaminants, as surface layer and subsurface accumulation. Metals may enter marine waters from terrestrial and atmospheric sources, sub-seafloor or ocean current deposition, or from mining related activity. Compounds or elements like heavy metals may adhere to native sediment mineral and organic particles and reside in a dissolved state in pore water occupying interstitial spaces among rocks, granules, sand grains or sediment particles. Metals and some organic metal compounds tend to be very conservative – metals typically remain in ecosystems long after initial deposition, or may adsorbed, ingested or absorbed by living organisms that redistribute the metals in the marine environment. These metals may bioaccumulate in organisms and biomagnify in foodwebs, achieving concentrations far above the levels detected in seawater or sediments. Yet, the bioavailability of each metal varies. Regardless of the bioaccumulation factor (BAF) or biological concentration factor (BCF), organisms exposed to single metals or a blended "cocktail" of metals in pore water and sediments can experience adverse effects, reproductive impairment or death.

When contemplating the potential source of metals in marine sediments in this ecosystem, it is clear that the Hawk Inlet watershed on Admiralty Island contains rich natural ore bodies loaded with heavy metals. For this reason these rich deposits have been exploited by exploratory miners to industrial scale mining operations for decades. The marine environment has therefore likely been influenced by natural metal concentrations and some effect of small mines prior to development of the industrial mining complex in Hawk Inlet in the early 1980s. However, onset of the industrial mining phase was a significant inflection point in Hawk Inlet ecological history: fracturing, crushing and grinding minerals exposed the watershed to higher levels of heavy metals.

Adding to the natural leaching from ore deposits, mining techniques implemented at the Greens Creek Mine adjacent to Hawk Inlet in the early 1980s significantly accelerated the introduction of ore-laden soils and metal concentrate sediments to the atmosphere as dust, dissolved in process water, rain and seawater, and through direct contact with ore concentrate and tailings (Kline 1994). To quantify the scale of input, for example: in recent years the HGCMC reports extraction and transfer of over 686,026,239 pounds of tailings to impoundments on the land surface (USEPA ECHO 2016). The HGCMC toxic release inventory summarized that 1.3 million pounds of arsenic, 60,000 pounds of chromium, 5,207 pounds of copper, 9,446,357 pounds of lead and 12,685 pounds of mercury, plus 20 million pounds of zinc were released to surface during 2014 mining operations (See table in Discussion section; USEPA ECHO 2016).

In order to explore whether and to what degree metal and organic contaminant concentrations have changed in seabed sediment subsequent to the onset of industrial mining, we sampled at sites used as clean or "control sites" and sites inside Hawk Inlet, many of which were sampled prior to the industrial mining phase.

Unique Geomorphology

Hawk Inlet has a unique undersea geology and shape, or geomorphology, which affects ocean current flow, seawater circulation and biogeochemical processes. It is a glacially carved fjord comprised of three basins partially separated from one another by shallow, glacially deposited sills. Hawk Inlet should therefore be referred to as a silled fjord, rather than a simple inlet. This unique shape of Hawk Inlet was observed by scientists prior to permitting the mine, and raised concerns: "The mark of the glaciers is still evident in the inlet. The topography of the basin, in particular, greatly influences circulation in the inlet, and other ecological features related to glaciation are also evident. Hawk Inlet is a fjord. This type of estuarine topography offers unique problems and opportunities for industrial development ..." (IEC 1980). The figure below shows, in relief and cross-section, three prominent sills and basins, as well as broad intertidal deltas in the Hawk Inlet fjord:



The above view shows that Hawk Inlet is a narrow waterway chiseled into the western shoreline of Admiralty Island from Chatham Strait. Hawk Point and Pile Driver Cove are geographic features of the entrance that are separated from the inner inlet by Sill 1. Sill 1 is less than 10 meters deep at low tide, and lies at the western edge of the vast Greens Creek Delta. Intertidal sediment flats are known to harbor bacteria which can mediate biogeochemical processes like the methylation of mercury – affecting its mobility foodwebs (Hines *et al* 2012).

North of Sill 1 is Basin 1, which exceeds 90 meters in depth. Deeper seawater in the basin moves much differently than shallow waters flowing over the sill; deep water movement is likely restricted. Ocean current studies during original baseline research, plus fishermen and divers over the past 20 years, have documented that there is greatly reduced current at depth in Hawk Inlet. The 1983 EIS estimated deep water movement at less than ten percent of surface current flow rate at depths of greater than 30 meters (Ridgway, unpublished data, 2016, IEC 1980, USDA EIS 1983). In similar systems in the Gulf of Alaska, it has been demonstrated that deep basin seawater retention time and flushing are significantly reduced in silled fjords, at least on a seasonal basis (Nebert 1972, Niebauer 1980). This may influence retention of contaminants at depth.

The Deep Basin 1 site, called HI-3 by pre-mining baseline researchers in 1978, lies in the deepest reach of the largest of three basins in Hawk Inlet. Early research documents describe a "large eddy" that rotates seawater within the basin (IEC 1980, USDA EIS 1983). This location was a priority sediment sampling site in 2015 for several reasons: it is the inlet's greatest depth, the presence of a documented eddy (or gyre), its separation from Chatham Strait by the shallow sill, and its proximity to both the mine operations area and undersea outfalls. Sediment samples were collected in this deep basin in 1978, 1980 and then in 2015 for comparison.

Establishing Baseline Sediment Conditions Prior to Industrial Mining

At least three studies were conducted from 1978-1981 to document heavy metal concentrations in Hawk Inlet marine sediment for the 1983 Environmental Impact Statement for the proposed (then) Noranda Mining Project (VTN 1978, IEC 1980, Martin Marietta 1981). Collectively, data from these studies were the foundation for the pre-mining baseline status of sediment. Researchers characterized their findings as follows: "The concentrations observed were comparable to levels reported for "pristine" and "unpolluted" marine areas of the northeast Pacific coast and were orders of magnitude lower than levels reported for "polluted" or "semi-polluted" environmentsThese data were quantitatively similar to data previously collected from Hawk Inlet by VTN, indicating that year to year variability in sediment metals is small (IEC 1980, Martin Marietta 1981).

The three charts below show historical to present day sediment sample location maps used by research and monitoring teams in 1978 (VTN), 1980 (IEC),1981 (Martin Marietta) and 2015 FOA (red sites) & HECLA (green):



In the final EIS (USDA EIS 1983), however, baseline metal concentration values reported from two of the three studies were reduced to two entries for each metal as inlet-wide average or ranges (Table 3-1 in USDA EIS 1983). Then, subsequent to development of the baseline for the FEIS, a new concept regarding baseline emerged – it was proposed that, as a new monitoring program began, data could be collected that may further "build" the baseline database, by incorporating annual monitoring values. In correspondence with the USDA Forest Service, Federal Agencies concerned about fish and their habitat strongly opposed this concept (USDA EIS 1982).

Once the mine was in production phase, ADEC-directed annual reports on Hawk Inlet monitoring include "baseline values" which do not reflect original baseline concentrations of metals, but rather reflect average levels derived from various combinations of stations located from Pile Driver Cove to the Head of Hawk Inlet sampled during the mine development and production period: 1984 – 1989: *not the pre-mining period*. Records indicate that there was significant exploratory, mining and construction activity during this period, therefore it is likely that the data collected during these years may not exclude effects of the modern industrial mining era. That is to say, it is likely that values for metals in sediments are different (higher) than the *original* baseline.

The table below shows all values known at the time of this writing from the three studies cited above. The baseline table provides summary statistics for describing the range and variation of values, and provides mean values for each metal. We propose using this mean pre-mining baseline value for each metal concentration as the *Original Baseline* value for sediments, to serve as the pre-*industrial* mining status of the Hawk Inlet seabed.

			AL OPERATI	IONS AT THE	GREENS CRI	EEK MINE.	VINE. DATA COLLECTED 1978-1981					
							тот	AL TRACE N	IETAL CON	CENTRATI	ONS ug/kg	(ppm) dı
Study Source of Data and Sampling Dates	Sample Site Reported	Station Description	Zone	No of Samples (n)	Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel
FEIS 1983 Table 3-1 based on VTN79	ALL	INLETWIDE	ALL	4	9.7-12.6	0.25	83.8- 130	21.8- 31.3	22.5- 90.3	na	0.02- 0.04	18-58.5
FEIS 1983 Table 3-1 based on IEC80	ALL	INLETWIDE	ALL	4	13-24	0.15- 1.0	14-60	17-39	4.8- 19.0	240- 370	0.049- 0.35	17-43
	HI-3	Cannery	ST	1	0.48	0.92	35	39	19	nd	0.09	26
VTN 1979 aka Noranda 1979, as reported in IEC	HI-3	Cannery	ST	1	1.5	0.65	29	34	19.7	nd	0.24	31
1980 pg B4 -40. Samples collected September	HI-7	GC Delta	IT	1	0.41	0.37	15	23	9.2	nd	0.01	20
1978	HI-7	GC Delta	IT	1	2.1	0.15	28	31	14	nd	0.09	36
	HI-3	Cannery	ST	1	9.7	0.25	116	21.8	37	nd	0.02	18
IEC 1980 as reported in IEC 1980 page B4-40.	HI-3	Cannery	ST	1	12.6	0.25	83.8	22.4	22.5	nd	0.02	23.8
Samples collected 30 May 1980	HI-7	GC Delta	IT	1	11.9	0.25	115	31.3	90.3	nd	0.04	58.5
	HI-7	GC Delta	IT	1	12.6	0.25	130	28.3	55	nd	0.04	53
	2	GC Delta	ST	5	20	0.24	43	18	11	nd	0.078	26
Holland <i>et al</i> 1981 aka Martin Marietta	1	GC Delta	IT	5	22	<0.15	57	17	8.4	nd	0.35	43
Environmental. Table 3, Page III-7 (values based	4	Cannery	ST	5	24	1	60	39	19	nd	0.15	39
on average of n=5 samples*) collected 8-14	3	Cannery	IT	5	13	0.22	14	18	4.8	nd	0.049	17
July, 1981	5	Head HI	IT	5	18	1.3	35	27	8.7	nd	0.11	23
	6	Head HI	ST	5	17	0.48	55	16	7.4	nd	0.034	42
				n*	38	38	38	38	38	2	38	38
			m	iean	11.81	0.49	58.27	26.13	23.29	305.00	0.09	32.59
Summary Descriptive Statistics for All Original B	aseline Data /	Available by	me	edian	12.60	0.25	49.00	25.00	16.50	na	0.06	28.50
June 2016 from references	cited	tranciste sy	m	ode	12.60	0.25	35.00	39.00	19.00	na	0.09	26.00
			max	(imum	24	1.3	130	39	90.3	370	0.35	58.5
			min	imum	0.41	0.15	14	16	4.8	240	0.01	17
			standard	d deviation	8.09	0.37	38.52	7.89	23.53	na	0.10	13.04
Compilation of data sets & collection	records availa	ble by June 201	L6 by Miche	elle Ridgway	, Oceanus Al	aska. Raw	field repo	rts and ana	lytical reco	ords may ir	nprove da	ta resolut

ORIGINAL BASELINE CONDITIONS FOR HAWK INLET TRACE METAL CONCENTRATIONS IN SEDIMENT: ESTABLISHING STATUS OF HAWK INLET SEABED SEDIMENT FOLLOWING CANNERY & INDUSTRIAL OPERATIONS AT THE GREENS CREEK MINE. DATA COLLECTED 1978-1981

METHODS FOR 2015-2016 Sediment Study

Sample Collection

Sediment samples were collected at 18 intertidal and subtidal sites in Hawk Inlet and Young's Bay between 16 May 2015 and 09 May 2016, during four sampling events. Eight sites corresponded to original pre-mining baseline sites sampled from 1978-1981 (VTN 1979, IEC 1980, Martin Marietta 1981, and USDA FEIS 1983), and five stations monitored intermittently by HECLA mining company, while several stations were exploratory.

Sample location data were collected using a global positioning system (GPS), Garmin model GPS*map*76CS*x* at intertidal and subtidal stations. Subtidal station depth and redundant latitude and longitude were also recorded from the shipboard Furuno NavNet TZ integrated GPS and depth sounder system, model TZT14.

Samples were collected in Young's Bay at intertidal and subtidal reference sites near the 1981 stations, on May 16, 2015 during or immediately following a -2.7 foot low tide. Details on Hawk Inlet stations are provided in the following section. Samples were collected in habitats across the marine waters depth range accessible within Hawk Inlet: from the mid-low intertidal zone (elevation approximately -1 to -2.5 feet below mean lower low water, or "0") to very low intertidal (elevation approximately -2.5 to -4.3 feet below mean lower low water, or "0"), to a maximum depth of -247 feet in Basin 1. Sample areas, weather and tidal conditions during sampling are described in the table below.

	FOAS	Sediment Sa	mpling in H	awk Inlet, 20	015-2016	·
	Sedime	nt Sample		Max Lo	ow Tide in Ha	wk Inlet
Location	Depth zone	Date	Weather	Time	Ht (ft)	Ebb - Flood - Slack
Head of Hawk	IT	5/17/2015	Sunny, clear	0717	-3.03	slack low
Near S3 Head	IT	5/17/2015	Sunny, clear	0717	-3.03	flood
Near S3 Head	IT	5/17/2015	Sunny, clear	0717	-3.03	flood
East Head	IT	5/17/2015	Sunny, clear	0717	-3.03	flood
Near Empire mine	IT	5/17/2015	Sunny, clear	0717	-3.03	flood
GCD near S2	IT	5/18/2015	Sunny, clear	0802	-3.38	slack low
GCD near S2	IT	5/18/2015	Sunny, clear	0802	-3.38	slack low
Near S4-S5	ST	5/19/2015	Sunny, clear	0846	-3.22	slack high
Near S4-S5	ST	5/19/2015	Sunny, clear	0846	-3.22	slack high
Near S4-S5	ST	5/18/2015	Clear	0802	-3.38	flood
Near HI-1	ST	5/19/2015	Sunny, clear	0846	-3.22	slack low
Near HI-1	ST	5/19/2015	Sunny, clear	0846	-3.22	slack low
Outfall 002	ST	5/19/2015	Sunny, clear	0846	-3.22	flood
Outfall 002	ST	5/19/2015	Sunny, clear	0846	-3.22	flood
Near S2	IT	5/20/2015	Sunny, clear	0928	-2.61	flood
Near HI-3	ST	5/19/2015	Sunny, clear	2053	1.86	ebb
Butch Beach	IT	5/9/2016	Overcast	0950	-3.31	flood
Butch Beach	IT	5/9/2016	Overcast	0950	-3.31	flood
Near S3 Head	IT	5/17/2015	Sunny, clear	0717	-3.03	flood
Basin 2 Grn FltHs	ST	7/20/2015	Overcast	1032	0.23	flood

Tidal Data Source: Hawk Inlet Entrance Station 9452294 (NOAA 2016)

Legacy Gove Freject Note No. 5Trace Metals in Hawk Inlet & Young's Bay Marine SedimentsFriends of AdmiraltySediments for off-site analysis were collected in the intertidal zone from pits dug by shovel to a depth of 12 to15 cm. Additional samples were collected from the subtidal zone by research vessel using a van Veen bottomgrab. Sediment aliquots were taken directly from exposed pit walls, or from the center of a sediment masssampled by shovel scoop or van Veen grab. Aliquots were taken using dedicated synthetic spoons and placeddirectly into laboratory-prepared sample jars. Care was taken to sample sediment with grain size smaller thanapproximately 0.5 cm, typically mud, sand or fine gravel. Where possible, sampled material was photographedfor recording color and texture. Photos below show sampling tools and texture of some intertidal sediments.



Shovels and the van Veen grab were prepared for sampling sediments for metals prior to every sampling event using the following protocol:

Rinse in saltwater, rinse in freshwater, wash with Dawn soap, fresh water rinse. Wash with Alconox laboratory grade metal-free (anionic) detergent. Rinse 3 x with ample volume of double distilled, deionized water.

Dedicated, new synthetic scoops and spades were prepared in the same manner in the laboratory and sealed in metal free synthetic bags for use at each sample station, then bagged per project IDW protocol. Sediments for organic contaminant analysis were sampled using lab-prepared, sealed stainless steel instruments.

Sample Processing/Handling

Individual sediment samples were sealed, labeled with date, time and unique alpha-numeric sample identifiers corresponding to site code, then placed in coolers with ice. Field duplicates were labelled sequentially, following the same convention, providing for "blind" laboratory analysis of duplicate samples. Samples were logged into field data logbooks and chain of custody forms. Samples remained chilled on ice or frozen in freezers in sampler possession until shipped to analytical laboratories. Chain of custody records remained with samples from the time of collection and during shipping and transfers. Chilled samples remained sealed in coolers and were shipped via express overnight Alaska Airlines Goldstreak service to a certified commercial laboratory in Seattle. Sealed coolers were inspected and sample status documented at transfer and cataloguing of samples at the lab.

Sample Analysis

Samples underwent preparation, extraction and analysis for eleven trace metals, total petroleum range hydrocarbons (TPH), and polycyclic aromatic hydrocarbons (PAH), plus targeted tributyltin (TBT) compound analysis. US EPA Method 8270 with addition of Select Ion Monitoring (SIM), Gas Chromatography and Mass Spectrometry (GC/MS) provided low detection levels and specificity for analytes of interest. Laboratory analytical methods for each metal or compound of interest are detailed in the table below. Analytical method parameters for metals are provided in the second table below (page 8).

 Legacy Gove Project Note No. 5
 Trace Metals in Hawk Inlet & Young's Bay Marine Sediments
 Friends of Admiralty

 Lab Extraction Methods, Analytical Methods and Method Parameters for Hawk Inlet sediment Analyses

Г

	Laboratory Analytical Metho	ds	
Analyte(s)	Analytical Method	Extraction Method	Minimum Detection Level (MDL)
Metals in Solid for As, Cd, Cr, Cu, Pb,	Metals in Solid 200.8 / 6020A	Dry, then	See MDL, RPD and % Spike
Mn, Ni, Se, Ag, Zn		Acid	Recovery Standards in Table
Mercury in Solid	Hg in solid / USEPA 7471B	Digestion	below
Total Petroleum Hydrocarbon	AK102/AK103 TPHD	NWTPH-	Diesel AK 1.98 mg/kg
	TPH (Extractables) in Solid	Dx	Motor Oil AK 3.42 mg/kg
Semivolatile Organic Compounds	SW8270 D-SIM PAH	SW3546	0.65 – 3.5 ug/kg
Polynuclear Aromatic Hydrocarbons	(EPA 8270D-SIM)		Range for compounds
(Tri)butyltin Compounds (TBT)	8270 D-SIM Butyltins in solid	SW3546	TBT 1.52 ug/kg
	(EPA8720D-SIM)		

		Trace Metals in S For Method	Sediment An I 200.8 in So	alytical M lid (EPA 20	ethod Paran)0.8) — 6020/	neters A		
	Minimum	Reporting	Surro Dupl	ogate icate	Matrix	Spike	Blank Spi	ke / LCS
Analyte	Level (MDL)	Level	% Rec	RPD	%Rec	RP D	% Rec	RPD
Arsenic-75a	0.0480	0.200	75-125	20	75-125	20	80-120	20
Arsenic-75b	0.0920	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Cadmium-111	0.0100	0.100 mg/kg	75-125	20	75-125	20	80-120	20
Cadmium-114	0.00500	0.100 mg/kg	75-125	20	75-125	20	80-120	20
Chromium-52	0.0450	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Chromium-53	0.118	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Copper-63	0.158	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Copper-65	0.236	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Lead-208	0.0460	0.100 mg/kg	75-125	20	75-125	20	80-120	20
Manganese-55	0.0220	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Nickel-60	0.0790	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Nickel-62	0.0890	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Selenium-82	0.127	0.500 mg/kg	75-125	20	75-125	20	80-120	20
Selenium-78	0.324	2.00 mg/kg	75-125	20	75-125	20	80-120	20
Silver-107	0.00800	0.200	75-125	20	75-125	20	80-120	20
Zinc-66	0.497	4.00 mg/kg	75-125	20	75-125	20	80-120	20
Zinc-67	0.531	4.00 mg/kg	75-125	20	75-125	20	80-120	20
Zinc-68	0.524	4.00 mg/kg	75-125	20	75-125	20	80-120	20

Legacy Gove Project Note No. 5 Trace Metals in Hawk Inlet & Young's Bay Marine Sediments Approach for assessing potential environmental effects

Seabed sediment habitat supports benthic productivity and nutrient cycling critical to marine ecological functions. Macroinfauna, microfauna inhabiting interstitial spaces, sessile epifauna and motile organisms interacting with seafloor habitats are directly and indirectly affected by contaminants associated with organic and inorganic components of the sediment environment. Yet, sediment metal concentration limits to protect seabed habitats have not been established in the State of Alaska. The Alaska Department of Environmental Conservation instead *references* the NOAA Screening Quick Reference Tables (SQuiRTs) threshold effects level (TEL) and the probable effects level (PEL) values, "for screening purposes only" (ADEC 2013). The TEL represents the concentration below which adverse effects are expected to *occur rarely* in bottom-feeding aquatic organisms. The PEL represents the concentration above which adverse effects are expected to *occur frequently* in bottom-feeding aquatic organisms.

To develop a framework within which to evaluate environmental status of Hawk Inlet sediment, one would ideally address bioavailability of metals to specific biota and pathways through which organisms and their foodweb may be affected by those metals singly or synergistically - in combination. As we have no such research construct at present, we will compare Hawk Inlet sediment sample results to federally established sediment screening levels: the TEL, ERM and PEL from the NOAA SQuiRTs tables. ERM is the Effects Range Median; the range above which effects are *generally or always* observed (Long *et al* 1995).

For providing further context for readers, sediment values are also contrasted with the AET – the Apparent Effects Threshhold values which are based upon bioassay effects to species groups (amphipods, bivalves, echinoderms, infauna, etc, per SQUIRT card NOAA Chapter 173-204 WAC, 1991/95 as supplemented by WA Department of Ecology Staff with unpublished data). The AET is the contaminant concentration above which adverse effects are *always expected* for a particular biological indicator (Barrick *et al* 1989). Values for these screening levels are summarized in the table below, to provide a framework for evaluating the relative biological effects that trace metal concentrations in Hawk Inlet sediments may have on resident and migratory, larval and adult species.

Reference Level	Ag	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn
Threshold Effect Level	0.73	7.24	0.68	52.3	18.7	0.13	260 b	15.9	30.24	1.0	124
Effects Range	1.0	8.2	1.2	81	34	0.15	260 b	20.9	46.7	1.0	150
Level ₂₀₀₈											
Probable Effects Level	1.77	41.6	4.21	160	108	0.7	0.7	42.8	112		271
Apparent Effects	3.1B	35B	3N	62N	390MO	0.41M	260N	110EL	400B	1.0A	4101
Threshold											

NOAA – NMFS – US EPA SQUIRT CARD SEDIMENT SCREENING LEVELS: TEL, ERL, PEL, AET (NOAA ORR 2016) AND ADEC-RECOMMENDED EVALUATION LEVELS: TEL, PEL (ADEC 2013)

The Apparent Effects Threshold (AET) Bioassay endpoints: M – Microtox; B – Bivalve; E – Echinoderm Larvae; O – Oyster Larvae; A – Amphipod; N – Neanthes; L – larval bioassay; I – Infaunal larvae

It is important to note that sampling in the Legacy Cove research program has included sampling of Hawk Inlet seabed sediment and seawater *above* the seabed (seawater column data is reported in Legacy Cove Project Note No.7). However, pore water in the sediment bears higher concentrations of sediment leachate, influences movement of metals at the sediment-seawater interface, and affects benthic aquatic life directly (Zhu *et al* 2016). Measuring the concentration and flux of metals in seabed porewater was beyond the scope of this reconnaissance. Results of all sediment sampling and analyses area presented in the next section.

Friends of Admiralty

Legacy Gove Project Note NO. 5 **RESULTS**

Sediment samples were collected from the intertidal and subtidal locations indicated in red on the chart shown here. Stations shown in green are HGCMC annual monitoring sites, but station S-3 data is no longer reported for monitoring.

The analytical laboratory indicated that one sample jar was broken upon retrieval from coolers, and the sample was immediately transferred to appropriate glassware. Laboratory analysis for metals and organic contaminants proceeded without incident. The lab supervisor reported that all analyses were within method calibration, surrogate and spike recovery and RPDs were within control ranges unless specifically noted.



Results of organic compound analysis

A summary of organic compounds detected in nine Hawk Inlet sediment samples is shown in the table below.

Petroleum Range Hydrocarbons and Semi Volatile Organic Compounds in Hawk Inlet Sediments Intertidal (IT) and Subtidal (ST) Stations May 2015

Location	Depth	Latitude	Map	Analytical	Compound	Value	Unit
	Zone		No.	& Extraction	·		Dry
		Longitude		Methods			wt
Basin 3	IT	N 58.1865	12	AK102/AK103 TPHD	Diesel Range Hydrocarbons	30	mg/kg
Head of HI		W -134.7432		Extract: NWTPH-Dx	Motor Oil	24	mg/kg
Basin 3	IT	N 58.1865	13	SW8270 D-SIM GC/MS	Naphthalene	2.4	µg/kg J
Head of HI		W -134.7431		Extract: SW3546	Phenanthrene	2.7	µg/kg J
					2-Methylnaphthalene	5.1	µg/kg
					Phenanthrene	3.5	µg/kg J
Basin 3		N 58.1793		SW8270 D-SIM GC/MS	Fluoranthene	2.7	µg/kg J
	IT	W -134.7456	14B		Pyrene	2.4	µg/kg J
Head of				Extract: SW3546	Benzo(a)pyrene	3.2	µg/kg J
Hawk Inlet					Dibenz(a,h)anthracene	2.5	µg/kg J
					Benzo(g,h,i)perylene	3.2	µg/kg J
					Total Benzofluoranthenes	9.1	µg/kg
Sill 1	IT	N 58.1038	21	SW8270 D-SIM GC/MS	No tributyltin detected	<3.4	µg/kg
GC Delta		W -134.7726		Extract: SW3546			
Sill 1	IT	N 58.1031	23	AK102/AK103 TPHD	No Diesel detected	<6	mg/kg
GC Delta		W -134.7728		Extract: NWTPH-Dx	No Motor Oil detected	<12	
Basin 1	ST	N 58.1265	39	SW8270 D-SIM GC/MS	Tributyltin Ion	19	µg/kg
Ore Dock		W -134.7576		Extract: SW3546			
Basin 2	ST	N 58.1649	41	AK102/AK103 TPHD	Diesel Range Hydrocarbons	20	mg/kg
		W -134.7653		Extract: NWTPH-Dx	Motor Oil	20	mg/kg
PileDriver	IT	N 58.0854	48	AK102/AK103 TPHD	Diesel Range Hydrocarbons	12	mg/kg
Cove		W-134.7740		Extract: NWTPH-Dx	No Motor Oil Detected	<13	mg/kg
PileDriver	IT	N 58.0854	49	AK102/AK103 TPHD	Diesel Range Hydrocarbons	66	mg/kg
Cove		W -134.7740		Extract: NWTPH-Dx	Motor Oil	23	mg/kg
		<u>X</u> –exce	eds TEL	X -exceeds ERL2008	X* –exceeds PEL		

LMRidgway *Oceanus Alaska* July 2016 www.friendsofadmiralty.org Page 10 The Legacy Cove Project Note Series provide updates on research activities by Friends of Admiralty, an Alaskan 501 (c)3

Friends of Admiralty

Lab results indicate that sediments in Hawk Inlet have low to modest levels of diesel and motor oil at most stations sampled. Basin 3, the northern end, or "head" of Hawk Inlet sediments contain a broader range of detectable aromatic hydrocarbons compared to all other stations.

One of two sites sampled for the anti-fouling paint additive, tributyltin, had a detectable level of TBT ion. 19 μ g/kg is above levels known to have biological effects and will be discussed further in the following section.

Organic compound results by sample are provided on the Hawk Inlet chart below. Low to moderate levels of diesel range hydrocarbons and motor oil were detected from outside sill 1 at Pile Driver Cove throughout the inlet to Basin 3 at the head of Hawk Inlet. Both intertidal sites, and deeper subtidal areas like sample site 41 in basin 2 contained detectable levels of petroleum hydrocarbons. Note that no samples from near the ore loading facility nor the floatplane dock area were analyzed for petroleum range hydrocarbons. This is a very active area for vessels, aircraft and vehicles and characterizing petroleum in this areas was not the focus of this research. No human or natural *source* of petroleum hydrocarbons in Hawk Inlet were identified, nor are they implied.



LMRidgway *Oceanus Alaska* July 2016 www.friendsofadmiralty.org Page 11 The Legacy Cove Project Note Series provide updates on research activities by Friends of Admiralty, an Alaskan 501 (c)3

Legacy Gove Freject Note NO. 5 Results for Trace Metals

Laboratory results for eleven trace metals in five sediment samples from Young's Bay and 19 samples from Hawk Inlet indicate that Manganese and Zinc are the most highly concentrated metals at both sites. In terms of total concentration hierarchy, the mean values pattern for metal concentrations in sediment are very similar:

Young's Bay: Mn > Zn > Cr > Ni > Cu > As > Pb > Se > Cd > Hg > Ag

Hawk Inlet: Mn > Zn > Cr > Ni > Cu > Pb > As > Se > Cd > Hg > Ag

The maximum values for each metal from this study in Hawk Inlet are roughly double to triple the maximum concentrations in Young's Bay, except lead – which is about 13 times greater than the Young's Bay level, and Manganese is at a similar level to Young's Bay. Silver was below method quantification levels in every sample. The total – *additive* – eleven metal concentrations combined was highest at the Greens Creek Sill (729 mg/kg), near the ore loading dock at 698 mg/kg and at the Greens Creek Delta near outfall 002 (675 mg/kg). Intertidal basin 2 and Pile Driver Cove samples were lowest in total metal concentration, at 385 and 393 mg/kg, respectively. Note that this "total metal" metric is heavily influenced by variable manganese and zinc values.

		Ма	rine Sedi	ment Sa	npling Lo	ocations,	Depth Z	one and	Total Tra	ace Meta	I Concer	trations	from 201	5-2016			
									٦	TOTAL TRAC	E METAL CO	NCENTRATIO	NS ug/kg (pp	m) dry weigh	nt		
Vicinity of Subarea or Station	Closest Traditional Station Description	Zone	Longitude	Latitude	Sample ID n=1	Sample Date	Arsenic	Cadmium	Chromium	Copper	Lead	Manganese	Mercury	Nickel	Selenium	Silver	Zinc
Young's Bay	YB S REF	п	-134.7	58.168	1	5/16/2015	3.8	0.2	41.1	10	2.3	511	0.03	36.2	0.6 u	0.3 u	56
Young's Bay	YB S DOCK	π	-134.699	58.172	2	5/16/2015	2.9	0.2	40.2	17.3	3.3	311	0.02 u	34.1	0.6 u	0.3 u	38
Youngs Bay	YB N REF	Π	-134.698	58.175	3	5/16/2015	4.2	0.2	41	17.8	1.7	304	0.03 u	31.4	0.6 u	0.2 u	33
Young's Bay	YB S REF	ST	-134.699	58.168	4	5/16/2015	6.5	0.4	43.2	13.8	4.4	341	0.04	38.5	0.8 u	0.3 u	55
Young's Bay	YB N REF	ST	-134.698	58.175	5	5/16/2015	5.3	0.2	41	11.1	3.9	311	0.03	42.8	0.7 u	0.3 u	42
Head of Hawk	Basin 3	IT	-134.743	58.187	11	5/17/2015	12.6	0.4	44.5	25.7	5.3	445	0.05	28.6	0.7 u	0.3 u	79
Near S3 Head	Basin 3	п	-134.746	58.179	14	5/17/2015	10.9	0.7	36.9	22	6.5	419	0.08	24.3	0.8	0.3 u	82
East Head	Basin 3	IT	-134.73	58.178	15	5/17/2015	7.6	0.5	27.4	15.6	4.5	307	0.08	22.3	0.6 u	0.3 u	54
Near Empire min	ne Basin 2	п	-134.756	58.17	17	5/17/2015	5.3	0.3	27	21.6	3.2	341	0.03 u	19.7	0.6 u	0.2 u	55
GCD near S1	GCD Sill 1	IT	-134.773	58.103	20	5/18/2015	7.8	0.5	81.7	27.2	10.4	399	0.05	60.7	0.9	0.2 u	141
GCD near S1	GCD Sill 1	п	-134.773	58.103	22	5/18/2015	6.2	0.4	70.2	27.4	9.8	302	0.07	52.7	0.8	0.2 u	127
Near S4-S5	Basin 1	ST	-134.758	58.127	37	5/18/2015	5.2	0.5	26.7	58	53.5	247	0.1	18.7	0.7 u	0.4	124
Near S4-S5	Basin 1	ST	-134.758	58.127	38	5/19/2015	6.6	0.5	32.9	60.9	61.6	340	0.1	24	0.7 u	0.4	171
Near S4-S5	Basin 1	ST	-134.758	58.126	40	5/19/2015	9.5	0.4	29.5	19.8	25.3	373	0.05	22.2	0.6 u	0.3 u	92
Near HI-1	Basin 2	ST	-134.765	58.165	42	5/19/2015	7.2	0.4	39.5	23	9.4	266	0.09	24.2	1	0.3 u	78
Near HI-1	Basin 2	ST	-134.765	58.165	43	5/19/2015	8.7	0.4	40	24	10.5	267	0.09	25.9	0.9	0.3 u	82
Outfall 002	Sill 1	ST	-134.775	58.102	44	5/18/2015	5	0.2	58.7	13.5	4.7	446	0.03	53.8	0.5 u	0.2 u	93
Outfall 002	Sill 1	ST	-134.775	58.102	45	5/19/2015	5	0.1	59.4	16.5	6.7	375	0.04	43.8	0.5 u	0.2 u	85
Near S2	Piledriver	п	-134.774	58.085	47	5/20/2015	2.9	0.3	30	10	1.8	276	0.03	22.2	0.6 u	0.3 u	50
Near HI-3	Basin 1	ST	-134.764	58.122	77	5/19/2015	9.8	0.9	57	23	11.1	284	0.13	38	2 u	0.6 u	130
Butch Beach	Basin 2	п	-134.771	58.154	107	5/9/2016	7	0.5	33.5	15.6	5.2	247	0.03	22.8	1.3	0.11J	71
Butch Beach	Basin 2	IT	-134.771	58.154	108	5/9/2016	7.5	0.5	28.5	10.5	3.9	246	0.02	20.9	1.1	0.09J	66
Near S3 Head	Basin 3	п	-134.749	58.179	109	5/9/2016	7	0.2	29.4	16.2	20.6	311	0.0197J	21.4	1.1	0.07J	59
Mid Inlet Grn Flt	H Basin 2	ST	-134.77	58.164	118	7/20/2015	10.1	0.6	49	28	14	304	0.09	31	2	0.33J	104
	FC	DA MEAN VA	LUES Young's	Bay n=5			4.54	0.24	41.3	14	3.12	355.6	0.03	36.6	0.66	0.28 u	44.8
	F	OA MAX VAL	UES Young's	Bay n=5			6.5	0.4	43.2	17.8	4.4	511	0.04	42.8	0.8	0.3 u	56
	FC	DA MEAN VA	LUES Hawk Ir	nlet n=19			7.47	0.44	42.2	24.13	14.11	326.05	0.06	30.38	0.92	0.27 u	91.74
	F	oa max vai	LUES Hawk Inl	et n=19			12.6	0.9	81.7	60.9	61.6	446	0.13	60.7	2	0.6 u	171
	MAX	ALUES repo	rted by HGCM	in Hawk Inlet			14	33	256	450	2,270	nd	27.05	92	15,050	14	34,800

LMRidgway *Oceanus Alaska* July 2016 www.friendsofadmiralty.org Page 12 The Legacy Cove Project Note Series provide updates on research activities by Friends of Admiralty, an Alaskan 501 (c)3 Some sample locations and data from 2015-2016 are shown in the figure below, representative of each region in the Inlet. Data shows that elevated trace metal concentrations occur not only at the ore dock and near outfall 002, but throughout Hawk Inlet, both in the intertidal and subtidal zones, and in all three basins.



Legacy Gove Froject Note No. 5 DISCUSSION

Researchers for Martin Marietta indicated that "Hydrocarbon burdens in sediment were high. However, gas chromatography demonstrated that the high values near the delta and head of the inlet were of natural origin, while those at the cannery were a result of chronic petroleum contamination" (Martin Marietta 1981). Here are results of their analysis. Note that both the units and type of analyses reported differ from FOA results. Aliphatics refer to open chain hydrocarbons and aromatics are ring-based compounds.

	Baseline Petr in Hawk Inlet Sed	oleum Range Hydro iments 1981 (Marti mg/g dry weight	carbon Data n Marietta 1981)	
Location	Depth Zone	Oil & Grease	Aliphatics F1	Aromatics F2
Greens Creek	Intertidal	630	0.029	0.023
Delta Sill 1	Subtidal	270	0.003	0.004
Cannery/Dock	Intertidal	2300	0.052	0.95
Basin 1	Subtidal	930	0.007	0.013
Head of Inlet	Intertidal	820	0.30	0.099
Basin 3	Subtidal	1100	0.002	0.004

Sources of petroleum based compounds in Hawk Inlet may include historical cannery operations, sport, charter and commercial fisheries activities, mining activities and other input. Hydrocarbons were relatively high during the pre-mining baseline study period, and are lower decades later. This may be due to improved fuel handling protocols, fewer vessels or degradation of hydrocarbon sources present in sediment in the early 1980s.

Other organic contaminants may enter Hawk Inlet through accidental releases upland or from vessels. Process water and wastewater from mining operations, for example, is a likely source and vector for movement of a range of organic contaminants from mining and tailings sites into the surrounding environment (Kline 1994).

The organic compound, Tributyltin, is a highly toxic biocide used extensively in the maritime industry as an additive to antifouling paint from the late 1960s through 2000s. Use of TBT is prohibited for most Alaskan vessels, but exemptions exist for some exclusive vessel types. TBT is of concern because it is highly toxic to most aquatic life and is an endocrine-disrupting chemical that causes severe reproductive effects in aquatic organisms. TBT can affect marine creatures' growth and survival – particularly that of snails and clams. TBT is extremely stable and resistant to natural degradation in water, lasting over 30 years in some environments. A biologically harmful level of Tributyltin was detected in ore dock subtidal sediment, at 19 ug/kg.

TBT became available for commercial use in the 1960s, and largely banned in most countries by 1990. TBT in Hawk Inlet subtidal sediments may be from anti-foulant paint on historic fish trap structures, cannery structures, or fishing vessels, or from mining ore ships, mining service vessels or other vessels. That it was detected in a single, random sediment sample suggests that it may be more widespread and could be at higher concentrations in Hawk Inlet sediment. Further sampling would be required to assess TBT distribution in the Hawk Inlet seabed.

Trace metals

Comparing data from this study and that of other studies to the original baseline is informative to evaluate change in Hawk Inlet sediments over time, area and depth. In order to answer the broader question regarding whether geomorphology or oceanography affect metals accumulation in Hawk Inlet, samples were taken at several subtidal sites that are not sampled by monitoring efforts. One example is a deep sample collected in

LMRidgway *Oceanus Alaska* July 2016 www.friendsofadmiralty.org Page 14 The Legacy Cove Project Note Series provide updates on research activities by Friends of Admiralty, an Alaskan 501 (c)3 *Legacy Geve Freject Note* No. 5 Trace Metals in Hawk Inlet & Young's Bay Marine Sediments Friends of Admiralty basin one. Seafloor sediment was collected deep in this same basin during the original baseline research, but no monitoring or other sampling has been reported since that time. The results of the baseline and 2015 analysis are summarized in the table below. Data shows that eight of the metals analyzed are higher in concentration in 2015 compared to 1980, arsenic is lower in concentration than in 1980, copper is close to the same level as in 1980, and silver and selenium were below detection limits. Cadmium, chromium, mercury, nickel, lead and zinc doubled or tripled in concentration in the deeper reaches of basin one at the sample depths of 63 and 66 meters during this 35 year time period. As described in the background section of this report, oceanographers and other scientists observed that Hawk Inlet was a silled fjord with deep basins and an eddy in basin one. It was predicted that metals may accumulate at such deep-water fish and crab benthic habitats, yet ADEC-directed monitoring efforts focused elsewhere.

(Qua	antitativ	ve Cha Ba	nge (ased up	(Δ) in N pon Two	Metals	in Dee dent Sam	e p Basiı pling Ever	n from ^{hts}	1980	-2016		
Location	n	Source	Ag	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn
Deep Basin	1	BASE	<0.14	<u>13</u>	0.22	14	18	0.049	240	17	4.8	0.3	50
Hawk 63m/66m	1	FOA	0.6u	<u>9.8</u>	<u>0.9</u>	<u>57</u>	<u>23</u>	<u>0.13</u>	<u>284</u>	<u>38</u>	11.1	2 u	<u>130</u>
	0	HGCMC				No De	ep Basin	Data Repo	orted by	HGCMC			
Quantitative Cl Metals in Deep 1980-20	hang Bas 016	ge∆in in from	n/a	-3.2	+0.68	+43	+5	+0.081	+44	+21	+6.3	n/a	+120
Compare to NOAA	sta	ndards: <u>X</u>	-exceeds	5 TEL	X –excee	eds ERL20	₀8 <u>X</u> * –€	exceeds PE	L 201	6 values	rounded	to two	digits

Trace metal concentrations in Hawk Inlet and the original Young's Bay control site from the 1978-1981 baseline research, the HGCM annual monitoring program and this (2015-2016) study are presented in the table on the next page. Data are summarized under each of the most commonly recognized site names, using the best available sample location data from baseline studies, HGCMC station coordinates and coordinates from this study to cluster samples at sites based on proximity. Because ADEC directed HGCMC to stop reporting data for seven metals in 1999, and for station S-3 entirely, comparisons for the metals arsenic, silver, nickel, chromium, manganese, nickel and selenium by site were made using data collected at stations between 1984 and 1999.

All Hawk Inlet sediment sites tested have increases in heavy metals relative to original baseline studies developed for the 1983 EIS. Although highest concentrations of metals are near the ore dock, elevated metals are found in each of the three basins. No baseline data were located for Pile Driver Cove; metal levels at that site are similar to the Greens Creek Delta and basin 3, at the Head of Hawk Inlet. HGCMC monitoring reports indicate that metal levels at Pile Driver Cove have exhibited similar trends to increases in metals at sites closer to the mine. Because oceanographic currents flow from the outfall 002 location directly toward Pile Driver Cove, it is likely that this site has been influenced by dissolved metals from the outfall, ore concentrate dust carried by currents and movement of metals bound to organic material in the water column.

Both HGCMC monitoring data and data from this study show that zinc, cadmium, chromium, copper, nickel and lead concentrations increased substantially in almost all cases over time at Greens Creek Delta intertidal and subtidal stations, in Basin 1 ore dock to deep site, and in Basin 3 – the Head of Hawk Inlet. The degree of increase is very high in basin 1, likely rendering significant harm to benthic habitat ecological function.

	Comp HECLA	oarison of d Monitorir	ata from	Trace M origina AC, all r	letal Cor al baseli netal pe	ncentra ne stud aks 198	tions in y (1978 34-1999)	Hawk Inl -1981), Fo : Cd. Cu.	et DA Stud Hg. Pb. J	y (2015- Zn only 2	2016), and	d 5)	
					Units:	ppm d	ry weig	ht					
Location	Zone	Source	Ag	As	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Se	Zn
	Intertidal	BASE	<0.22	20	0.24	43	18	0.35	320	26	11	0.03	59
ek k		FOA	0.2	7.8	0.5	81.7	27.2	0.05	399	60.7	10.4	0.9	141
Cre		HGCMC	0.14	32	0.89	450	39.5	0.14		88	23.7	14*	188
ens Del	Subtidal	BASE	<0.2	22	<0.15	57	17	0.35	370	43	8.4	0.55	110
Gre		FOA	0.2	5	0.2	59.4	16.5	0.04	446	53.8	6.7	0.5	93
-		HGCMC	0.14	32	0.89	450	39.5	0.14		88	23.7	14	188
	Intertidal	BASE	0.39	24	1.0	60	39	0.15	250	39	19	1.7	110
		FOA	<0.211	7.03	0.17	29.4	16.19	0.02	311.2	21.42	20.59	1.11	59.14
ery ock		HGCMC	4.15	21	4.23	153	286	3.7		53	658		920
ann e D	Subtidal	BASE	<0.14	13	0.22	14	18	0.049	240	17	4.8	0.3	50
وَ ت ۩		FOA	0.4	6.6	0.5	32.9	60.9	0.10	340	24	61.6	<0.7	171
		HGCMC	16.9	64	256	200	2,270	27.05		92	15,050	6.8	34,800
	Intertidal	BASE	<0.22	18	1.3	35	27	0.11	250	23	8.7	0.79	57
let 3		FOA	0.3u	10.9	0.7	36.9	22	0.08	419	24.3	6.5	0.8	82
sin ∷ ad c ≮ In		HGCMC*	0.6	33	2.76	110	105	0.21		54	34.4	9	310
Bas Hea awl	Subtidal	BASE	<0.15	17	0.48	55	16	0.034	320	42	7.4	0.38	110
Т		HGCMC			NO	DAI	FARE	PORT	ED B	YHG	СМС		
	Subtidal	BASE					N	D DATA LO	CATED				
isin 2 npire cinity	Subtidal	FOA	0.3u	8.7	0.4	40	24	0.09	267	25.7	10.5	0.9	82
Ba En Vii	Intertidal	FOA	0.2	5.3	0.3	27	21.6	0.03u	341	19.7	3.2	0.2	55
<u>د</u> م	Intertidal	BASE					N	D DATA LO	CATED				
ove		FOA	0.3	2.9	0.3	30	10	0.03	276	22.2	1.8	0.6	50
		HGCMC	0.15	8.5	0.42	185	29.5	0.09		78	8.3	2	93.4
مد	Deep	BASE _{63m}	<0.14	13	0.22	14	18	0.049	240	17	4.8	0.3	50
beel asii 1	Subtidal	FOA77	<0.6	9.8	0.9	57	23	0.13	284	38	11.1	<2	130
		HGCMC	1C NO DATA REPORTED BY HGCMC										
MEAN IN B	ASELINE 197	78-81	0.26	11.8	0.49	58.3	26.1	0.09	305	32.6	23.3	0.63	95.6
MAX IN BA	SELINE 1978	8-81	0.39	24	1.3	130	39	0.35	370	58.5	90.3	1.7	140
MAX PEAK	VALUES 197	8-2016	16.9	33	256	450	2,270	27.05	446	92	15,050	14	34,800
PEAK VALU	IE vs BASELIN	NE	43x	1.4x	197x	7.5x	58x	77x	1.2x	2.1x	792x	8.3x	316x
MAX AT CO	ONTROL SITE	2016	0.3	6.5	0.4	43.2	17.8	0.4	511	42.8	4.4	0.8	56
ENVIRONN	IENTAL HAR	M GUIDELIN	E LEVELS	(ADFG 2	013, NOA	A 2008)						
Thres	hold Effects	Level (TEL)	0.73	7.24	0.68	52.3	18.7	0.13	260 b	15.9	30.24	1.0 ^a	124
Prob	able Effects	Level (PEL)	1.77	41.6	4.21	160	108	0.7	0.7	42.8	112		271

BOLD = value > PEL *HGCMC data reported for years 1984 -2002 only. ** from HGCMC data in Ridgway 2003

LMRidgway *Oceanus Alaska* July 2016 www.friendsofadmiralty.org Page 16 The Legacy Cove Project Note Series provide updates on research activities by Friends of Admiralty, an Alaskan 501 (c)3 *Logacy Teve Project Nete* No. 5 Trace Metals in Hawk Inlet & Young's Bay Marine Sediments Friends of Admiralty **Environmental harm:** Hawk Inlet metal concentration maxima measured in research projects or monitoring efforts exceed every ADEC-referenced NOAA trace metal benchmark for protecting marine life. In addition, the maximum, or peak values reported for metal concentrations since 1984 show exceedences of the Apparent Effects Threshold (AET) for every metal except arsenic and nickel – though Hawk Inlet levels were only slightly below the AET. As described in the background section in this report, Apparent Effects Threshold values are based upon bioassay effects to species groups (amphipods, bivalves, echinoderms, infauna, etc, per SQUIRT card NOAA Chapter 173-204 WAC, 1991/95 as supplemented by WA Department of Ecology Staff with unpublished data). The AET is the contaminant concentration above which adverse effects are *always expected* for a particular biological indicator (Barrick *et al* 1989).

Because sediment values for individual metals have also exceeded these higher benchmark levels reported in research literature to cause reproductive harm, death or impact populations of specific organisms, it appears that the widespread elevation of metals and the concentrations near the ore dock, in particular, will have enduring negative impact on Hawk Inlet seabed sediment as viable habitat for infauna, epifauna and other associated organisms. Whether concentrations were consistently or intermittently spiking above AET levels, impacts of reducing biodiversity or reduction of a yearclass or population of taxonomically related groups of organisms such as crustaceans, molluscs, etc, can cause ecosystem shifts that lead to unraveling of the integrity of Hawk Inlet marine system and reduce habitat value for species that rely upon that system.

Potential sources of metals in Hawk Inlet sediments

Sources of trace metals in Hawk Inlet likely includes natural sources in the rich ore bodies in the watershed. Sources of metal increases observed in sediment in the fjord likely include anthropogenic activity – mining, tailings leachate, effluent, fugitive dust carried by rain from on-land transport in the Hawk Inlet watershed, plus the known sources of spilled ore, ore dust and the frequent occurrence of "little spills" of ore concentrate from the ore loading procedures. Direct observations over several years of mining at the Greens Creek site has shown that ore concentrate billows out of cargo vessel holds during loading – where it lands on dock structures, loading vessel decks, and the seawater surface. Surface tension of seawater and tidal action may serve as a horizontal conveyor belt for ore concentrate dust to be transported into Hawk Inlet, where it may be deposited onto intertidal beaches during falling tides, fall out of the water column into the subtidal zone, dissolve in seawater, or bind to organic material. Observers have also reported that ore concentrate adhering to conveyor belts during loading operations resulted in concentrate dropping off into the nearshore environment. Containment of the conveyor belt years after the mine began operating may serve to reduce this occurrence, thereby saving more of the profitable concentrate product being loaded for export.

There may be other sources of metals input at Hawk Inlet, but there are neither data nor observations to which it may be linked. Atmospheric dust transports metals, and is suspected to carry mercury from coal burning facilities in Asia toward the eastern Pacific. Cruise ship effluent is documented to contain metals from human waste and other inputs onboard ships. Hawk Inlet is adjacent to a heavily traveled route cruise ship route and near formerly used blackwater discharge area ("donut hole"). Quantifying sources of metals in Hawk Inlet is beyond the scope of this note discussion. However, the aforementioned documented releases and transfers of metals in the US EPA ECHO report table below quantifies heavy metals and organic contaminants generated by HGCMC activities: in recent years the HGCMC reports extraction and transfer of over 686,026,239 pounds of tailings to impoundments on the land surface (USEPA ECHO 2016). The HGCMC toxic release inventory summarized that 1.3 million pounds of arsenic, 60,000 pounds of chromium, 5,207 pounds of copper, 9,446,357 pounds of lead and 12,685 pounds of mercury, plus 20 million pounds of zinc were released to surface during 2014 mining operations (USEPA ECHO 2016).

LMRidgway *Oceanus Alaska* July 2016 www.friendsofadmiralty.org Page 17 The Legacy Cove Project Note Series provide updates on research activities by Friends of Admiralty, an Alaskan 501 (c)3

🔹 🛈 🔒 🛛 https://echo.epa.gov/d	etailed-facility-rep	ort?fid=11003288	2735		C	Q, Search		☆ 自 ♥	🔶 🧍 😕
Toxics Release Inventory Tota	al Releases and	Transfers in Pou	nds by Chemical	and Year 🛈					
Chemical Name	2015 📍	2014 •	2013 📍	2012 📍	2011	2010	2009	2008 •	2007
1,2,4-TRIMETHYLBENZENE									
ANTIMONY COMPOUNDS			3	3	4	3	2	5	5
ARSENIC COMPOUNDS	1,400,244	1,300,244	2,700,511	2,600,501	2,500,501	2,500,501	2,500,481	2,300,481	2,300,481
BARIUM COMPOUNDS		10,300,112							
CADMIUM COMPOUNDS	1	1	1	1	1	0	0		0
CHROMIUM	50,000	60,000	54,000	67,000	48,000	50,000	51,000	52,000	47,000
CHROMIUM COMPOUNDS(EXCEPT CHROMITE ORE MINED IN THE TRANSVAAL REGION)									
COBALT COMPOUNDS									
COPPER COMPOUNDS	4,807	5,207	5,411	5,912	6,216	6,916	6,812	7,927	6,624
CYANIDE COMPOUNDS									0
ETHYLENE GLYCOL									0
LEAD COMPOUNDS	8,455,193	9,446,357	16,822,044	16,048,284	15,456,422	15,595,284	15,652,693	14,562,362	14,705,475
MANGANESE	15,006	17,005							
MANGANESE COMPOUNDS									
MERCURY COMPOUNDS	11,332	12,685	14,243	13,611	13,068	13,192	13,231	12,323	12,668
NAPHTHALENE									
NICKEL COMPOUNDS									
SILVER COMPOUNDS									
XYLENE (MIXED ISOMERS)									

USEPA ECHO 2016. Enforcement and Compliance History Online Detailed Facility Report for Greens Creek Mine: FRS ID: 110032882735. Online at https://echo.epa.gov/detailed-facility-report?fid=110032882735

Closing Remarks / Recommendations

Concentrations of all eleven metals increased substantially during the industrial mining period, from 1.2 (manganese) to 646 (lead) times the original baseline level. The highest reported mercury concentration during the mining period was 77 times the maximum original baseline level, and 287 times the mean inlet-wide baseline level. *The average increase for eleven metals was 73 times original baseline maximum levels, and 183 times the inlet-wide <u>mean original baseline</u> levels. Whereas measured metal levels in sediment have 'fluctuated' over time and by area, peaks (or maxima), are compared to baseline levels here because heavy metals persist in the environment once released. Biota, pore water and habitats are affected by the cumulative effects of metals added over time and compounding impacts of multiple metals. USFWS long-term research on sediment, blue mussels and eagle blood in Hawk Inlet provides some insight on these effects and also contributes to our understanding of bioavailability of some of the metals in the Hawk Inlet ecosystem (Rudis et al 2010).*

It should be noted that it is likely that the metal values in the 2015-2016 samples *under represent* maximum metal concentrations at the sites sampled. Future assessments would benefit from analysis of grain size, total organic carbon, and pore water. Because sampling was designed to emulate the original baseline sampling, sediment aliquots were collected *below* the sediment surface (10-15 cm). It is likely that inclusion of the surface sediment would have captured higher metal concentrations from recent deposition.

Due to potential synergistic effects of multiple metals accumulating in sediments, a full assessment or future monitoring should include at least the eleven metals analyzed here. Values for tin (Sn) can be used to estimate organotin concentrations. Since tributyltin appears to be in the sediment system and can contribute to ecosystem harm by other contaminants and disturbances, it is recommended that this suite of compounds be assessed in Hawk Inlet.

Additional sampling of sediments in the deep basins in necessary to more fully assess the distribution of trace metals in sediment at depth. A sampling strategy which includes transects or a grid pattern from known metal sources such as the ore dock may yield valuable data on movement of metals, and refine maps of apparent

LMRidgway *Oceanus Alaska* July 2016 www.friendsofadmiralty.org Page 18 The Legacy Cove Project Note Series provide updates on research activities by Friends of Admiralty, an Alaskan 501 (c)3 $\mathcal{I}_{egacy} \mathcal{G}_{ove} \mathcal{F}_{reject} \mathcal{N}_{ote} \text{ No. 5}$ Trace Metals in Hawk Inlet & Young's Bay Marine Sediments Friends of Admiralty highly concentrated sediment "hotspots". Visual characterization of sediment *in situ* by diving, ROV imagery or other means may aid to delineating hotspots through extrapolation of analytical results and sediment type.

Sediments in Hawk Inlet have detectable levels of diesel and motor oil; the head of Hawk Inlet sediments contain a broad range of aromatic hydrocarbons (*eg* naphthalene, benzo-x). A biologically harmful level of the banned bottom paint compound, Tributyltin, was detected in the ore dock vicinity subtidal sediment.

The few samples collected in 2015 indicates that the designated control site in Young's Bay shows relatively little to no change in most of the eleven trace metals analyzed since 1981. Analysis of further samples is essential to draw conclusions regarding sediment conditions in Hawk Inlet. Because Young's Bay is exposed to a great deal of mining activity, plus tourism, cruise ship and public vessel traffic, and due to its location and geomorphology, it does not seem to be an ideal control site. A similar fjord-like inlet with less exposure to potential contaminants may serve as a better site for comparison of natural conditions to those inside Hawk Inlet.

Recognizing the intimate connection between organic and inorganic components of the sedimentary seabed habitat is essential for developing a reasonable suite of metrics by which to evaluate status of sediments for screening levels for metals. Absent a site-based study on effects of metals in sediment on local biota, site-based species data may be used to inform selective use of existing federal sediment reference levels (TEL. ERM, PEL, AET, etc.) to evaluate the potential effects of observed metal concentrations in sediment on Hawk Inlet.

The ecological status of Hawk Inlet sediments should be determined in order to assess habitat quality for organisms that reside or migrate through this fjord habitat. Obtaining the best available scientific data will inform the public and agencies on the status of this fjord/inlet marine habitat after thirty years of industrial mining. This may enlighten future risk assessments for future potential mines in marine watersheds across Alaska. And, for the present time, the abundant migratory waterfowl, salmon, crab, halibut and threatened and endangered creatures, plus mammals such as harbor seal, harbor porpoise, humans, bear and deer that interact with the dynamic benthic sediment habitats of Hawk Inlet through direct contact and food web linkages merit in-depth, strategic assessment.

This project note is intended to provide an update on results of study and analysis of marine sediment from Hawk Inlet and Young's Bay, and to provide some context for interpreting the level of trace metals and organic compounds found in sediment analyzed. Additional results, discussion and data appendices are published in reports for the Legacy Cove Project by Michelle Ridgway, Oceanus Alaska for Friends of Admiralty.

REFERENCES

ADEC 2013. Alaska Department of Environmental Conservation: Technical Memorandum Sediment Quality Guidelines, January, 2013. Juneau, Alaska

Barrick, R., Beller, H., S. Becker and T. Ginn 1989. Use of the Apparent Effects Threshold Approach (AET) in Classifying Contaminated Sediments. Chapter in Contaminated Marine Sediments: Assessment and Remediation. National Research Council. 508 pp

Hines, M., E. Poitras, S. Covelli, J. Faganeli, A. Emili, S. Zizek, M. Horvat 2012. Mercury methylation and demethylation in Hg-contaminated lagoon sediments (Marano and Grado Lagoon, Italy) Estuarine, Coastal and Shelf Science. Vol 11385–95, 10 November 2012

International Ecological Consultants (IEC) 1980. Marine Ecology Baseline Studies for the Greens Creek Project Admiralty Island, Alaska. For Noranda Explorations, Inc. by IEC, INC Project 4705.2

Kline, E. 1994. Potential Biological Consequences of Submarine Marine-Tailings Disposal: A Literature Synthesis. Prepared for US Department of Interior, Bureau of Mines by Edward Kline, University of Alaska School of Fisheries and Ocean Sciences. March, 1994. OFR- 36 – 94. 66 pp

Long, E., D. McDonald, S. Smith, and F. Calder 1995. "Incidence of Adverse Biological Effects Within Range of Chemical Concentrations in Marine and Estuarine Sediments." Environmental Management 19.1 (1995): 81-97

Oregon Institute of Oceanography 1984-2002. Laboratory results of semi-Annual NPDES sediment and mussel tissue sampling in Hawk Inlet, Alaska. Columbia Analytical Lab Data for years 1984-2002.

Martin Marietta 1981. By Holland, A., M. Hiegel and W. Richkus: Final Results of the 1981 Field Program for the Greens Creek Project. Part I: Hawk Inlet and Young's Bay and Part II: Chatham Strait. Martin Marietta Corp. Environmental Center Baltimore, MD.

Nebert, D. 1972. A Proposed Circulation Model for Endicott Arm, an Alaskan Fjord. MSc Thesis, University of Alaska Fairbanks. 90 pp.

Niebauer, H. 1980. A Numerical Model of Circulation of Continental Shelf – Silled Fjord Coupled System. Estuarine and Coastal Marine Science 10 (5): 502-521

NOAA ORR 2016. NOAA Office of Response and Restoration website. Screening Quick Reference Table for Inorganics in ("SQUIRTs tables") http://response.restoration.noaa.gov/sites/default/files/SQuiRTs.pdf

NOAA Tide Tables 2016. https://tidesandcurrents.noaa.gov/noaatidepredictions/viewDailyPredictions.jsp

Rudis, D., P. Schempf and M. Jacobson 2001. Bald Eagle, Blue Mussel and Sediment Contamination Concentrations from Hawk Inlet, Admiralty Island, Alaska. Poster presentation for bird conference.

VTN 1978. Data reported in Table B.4 – 13, Marine Ecology Baseline Studies for the Greens Creek Project, Admiralty Island, Alaska, Prepared for Noranda Exploration, Inc. by International Environmental Consultants, Inc. Denver, Colorado. Project 4705.2 October, 1980.

USEPA ECHO 2016. Enforcement and Compliance History Online Detailed Facility Report for Greens Creek Mine: FRS ID: 110032882735. Online at https://echo.epa.gov/detailed-facility-report?fid=110032882735

USDA EIS 1983. Greens Creek Final Environmental Impact Statement, Admiralty Island National Monument,

Legacy Cove Freject Note No. 5Trace Metals in Hawk Inlet & Young's Bay Marine SedimentsFriends of AdmiraltyAlaska. Proposed Noranda Mining, Inc. Project. US Dept of Agriculture, Forest Service, Alaska Region, AdminDoc. Number 115. January 1983 USEPA 1998. Response to Comments: Kennecott Greens Creek MiningCompany (Greens Creek Mine) NPDES Permit No. AK-004320-6 October 1998

Zhu, X., Shan, B., Tang, W. et al. Environ Sci Pollut Res (2016) 23: 5516. doi:10.1007/s11356-015-5709-7