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Final

2024 Sediment Metals Report

A pilot study of the Long-Term Environmental Monitoring Program

PREPARED FOR

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Table of Contents

ACRONYMS AND ABBREVIATIONS

ADEC................	Alaska Department of Environmental Conservation
AMT..................	Alyeska Marine Terminal, site name for Valdez Marine Terminal
ANS	Alaska North Slope
APDES..............	Alaska Pollutant Discharge Elimination System
BWTF	Ballast Water Treatment Facility
EPA....................	U.S. Environmental Protection Agency
ERL....................	Effects Range Low
ERM..................	Effects Range Medium
EVOS	Exxon Valdez Oil Spill
GOC	Gold Creek Reference Site
LTEMP..............	Long-Term Environmental Monitoring Program
NOAA................	National Oceanic and Atmospheric Administration
PAHs	Polycyclic aromatic hydrocarbons
PPB	Parts Per Billion (ng/g [nanograms per gram] or µg/L [microgram/ liter])
PPM...................	Parts Per Million (mg/kg [milligram per kilogram])
PWSRCAC	Prince William Sound Regional Citizens' Advisory Council
SQG.................. .	Sediment Quality Guidelines

1. Abstract

Following the 1989 Exxon Valdez oil spill, concerned citizens and congressional legislation established the Prince William Sound Regional Citizens' Advisory Council (Council). The Council's mission is to promote the environmentally safe operation at the Valdez Marine Terminal and associated oil tanker activities within the spill-affected area. Since 1993, annual monitoring of marine sediments and intertidal blue mussels has been conducted, focusing on crude oil-specific hydrocarbons. However, concern over the accumulation of metals, specifically zinc, in sediments from the terminal and tanker operations spurred investigations into sediment metal concentrations.

In 2024, we analyzed 23 different metals in sediments at the Valdez Marine Terminal (terminal), close to the outfall from the Ballast Water Treatment Facility and the Port Valdez reference site at Gold Creek. Twenty-two metals were detected at each site, ranging from 40,000 mg/kg dry-weight Iron in terminal sediments to less than 0.1 mg/kg mercury at the terminal and Gold Creek. The terminal sediments had significantly higher metal concentrations overall, and for 10 specific metals, than Gold Creek. Both sites exceed NOAA's sediment quality guidelines for the protection of benthic life for eight metals. Several metals known to be in Ballast Water Treatment Facility effluent from recent Council work were also found in higher concentrations at the terminal compared to Gold Creek. Of these metals with a suggested effluent origin, four metals—aluminum, copper, iron, and vanadium—exceeded the effect range thresholds, suggesting that terminal and tanker operations may be eliciting adverse effects on benthic organisms. These findings warrant further investigation into the extent of the metal accumulation, the sensitivity of benthic organisms in the area, and the source of high metal concentrations locally.

2. Introduction

The Long-Term Environmental Monitoring Program (LTEMP), managed by the Prince William Sound Regional Citizens' Advisory Council (Council), is in its 31st year of monitoring hydrocarbons after the Exxon Valdez oil spill (EVOS) in 1989. Through LTEMP, we aim to determine the source of hydrocarbons and the potential adverse effects on the ecosystem from Alyeska Pipeline Service Company's Valdez Marine Terminal (terminal) and tanker activity. These data have been insightful in understanding the influence of terminal and non-terminal sources of hydrocarbons and environmental factors on hydrocarbon dynamics across Prince William Sound and the Gulf of Alaska.

The 2024 LTEMP campaign also collected sediment samples to assess the degree of metal accumulation. In Spring 2024, the Council's Scientific Advisory Committee decided to include a pilot sampling campaign on sediment metals as recent studies by the University of New Orleans detected metals in water samples collected at the Valdez Marine Terminal's Ballast Water Treatment Facility (BWTF) (Harsha & Podgorski, 2023). There is a potential ecological risk associated with the discharge of metals from the BWTF, as metals are generally stable and do not degrade; thus, there is a possibility that metals accumulate in sediment, reaching toxic levels (Long et al., 1995). While not a part of the core LTEMP campaign, this additional sampling benefitted from piggybacking on the sampling, analysis, and data visualization of LTEMP's hydrocarbon analysis. The 2024 LTEMP campaign collected sediment samples from two sites in Port Valdez (i.e., Gold Creek and the BWTF's outfall at the Valdez Marine Terminal).

The following study presents the 2024 sediment metals results from the LTEMP pilot study and aims to determine the following:

- The sediment metal concentrations and the level of variability at the Valdez Marine Terminal and the Gold Creek reference site.
- The potential bioavailability and ecotoxicological risk posed by the measured metal concentrations using protective sediment quality guidelines.
- The influence and potential effects of metals originating from the terminal and tanker activities.
- Recommendations for future monitoring of sediment metals at the terminal and in Prince William Sound.

3. Methods

Sediment samples were collected in early June of 2024, at LTEMP monitoring stations in Port Valdez, Alyeska's Valdez Marine Terminal, and Gold Creek (Figure 1). Sediment sampling was performed using a modified Van Veen grab deployed from a local fishing vessel, Equinox. The top 5 cm of undisturbed sediment was scooped using a clean metal spoon and placed in a glass sampling jar. Triplicate grab samples were collected at each site. Samples were frozen until shipped to Pace Analytical Services in Mansfield, Massachusetts.

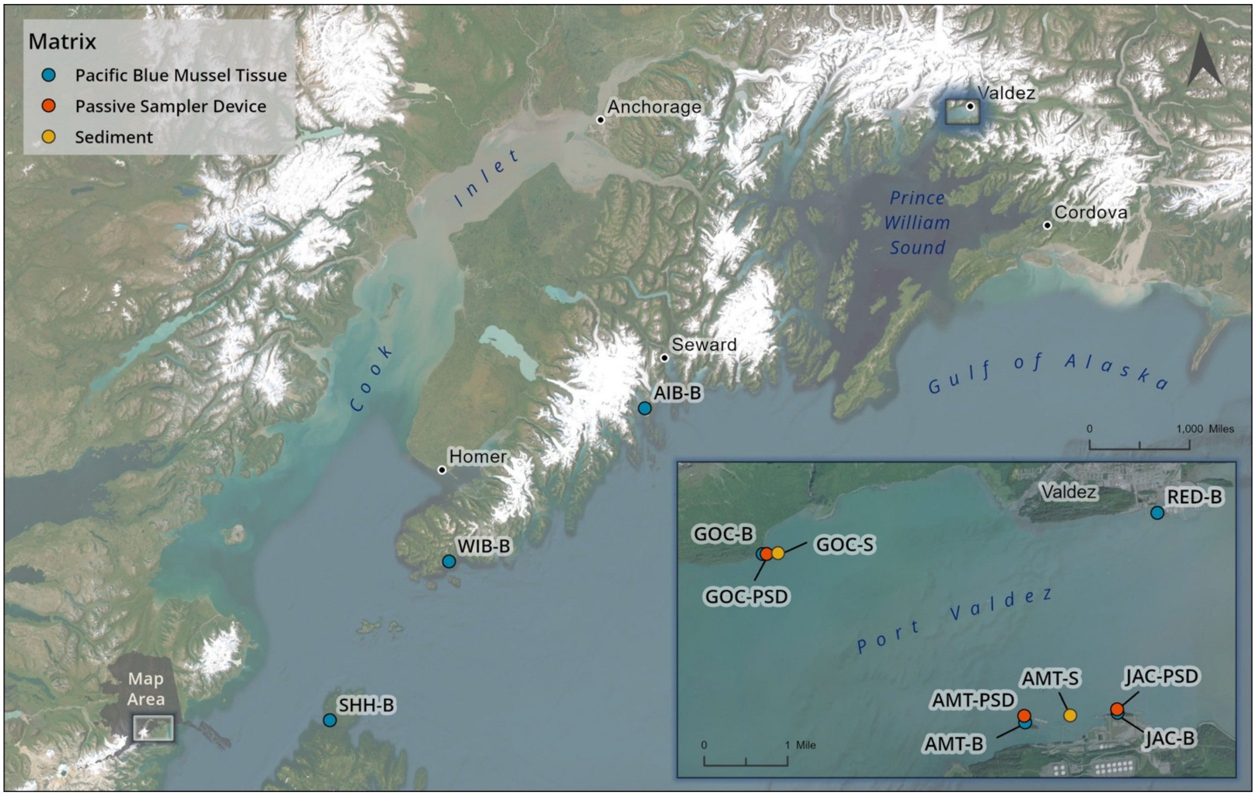

Figure 1. 2024 sampling sites for the Long-Term Environmental Monitoring Program in Port Valdez and the North Gulf of Alaska. The color of the points and labels represent differences in sampling matrices. Sediment metals samples were collected from the yellow-colored (S) sites only.

Samples were analyzed for 23 metals (Table 1) and the standard suite of LTEMP analytes (i.e., PAHs, saturated hydrocarbons, and geochemical petroleum biomarkers; Fjord & Fish, 2024). Sediment physical analyses included particle size (not reported herein) and total organic carbon content. Metals except mercury were quantified using the analytical method Environmental Protection Agency (EPA) 6020B (i.e., inductively coupled plasma). Mercury was quantified using EPA method 7474 to detect low-level mercury in ppb and ppm ranges. The results were of acceptable precision and accuracy based on laboratory quality control and quality assurance data.

Sediment quality guidelines (SQG) are numerical chemical concentrations intended to be either protective of biological resources, predictive of adverse effects on those resources, or both (Hübner et al., 2009). Here, we use the NOAA's SQGs for metals, expressed as effect ranges. Effect Range Low (ERL) is a threshold concentration below which effects should rarely be observed (i.e., in less than 10% exposure incidences; Long et al., 1995). It can be considered an appropriate sediment quality guideline that protects benthic organisms as it is based on the consensus value from 100s of rigorous exposure experiments conducted across multiple laboratories and benthic taxa (Long et al., 1995). Effect Range Medium (ERM) was also used, indicating that adverse effects would frequently occur above this threshold (i.e., up to 95% of exposure incidences; Long et al., 1995). These SQGs are found to perform well at predicting primarily acute effects of contaminants in sediments on benthic organisms (Hübner et al., 2009).

Using R (R Core Team, 2024), metal concentrations were plotted as bar charts with mean concentrations and standard deviation across the three replicates. Statistical analysis between sites was done using a Two-Sample t-test for samples with equal variance (i.e., variance is less than an order of magnitude different between sites) and a Welch Two-Sample T-Test when variance was unequal. Statistical significance was set at alpha <0.05. Statistical parameters are presented (Table 2).

4. Results & Discussion

Twenty-two metals were detected at each site, with 21 found at both sites (Figure 2). Concentrations ranged from 40,000 mg iron /kg dry weight in terminal sediments to less than 0.1 mg mercury /kg at the terminal and Gold Creek. Iron, aluminum, magnesium, sodium, calcium, potassium, and magnesium exceeded 1000 mg/kg in the terminal and Gold Creek sediments. Meanwhile, antimony, beryllium, silver, cadmium, selenium, and thallium were estimated as concentrations under the reporting detection limit at both sites.

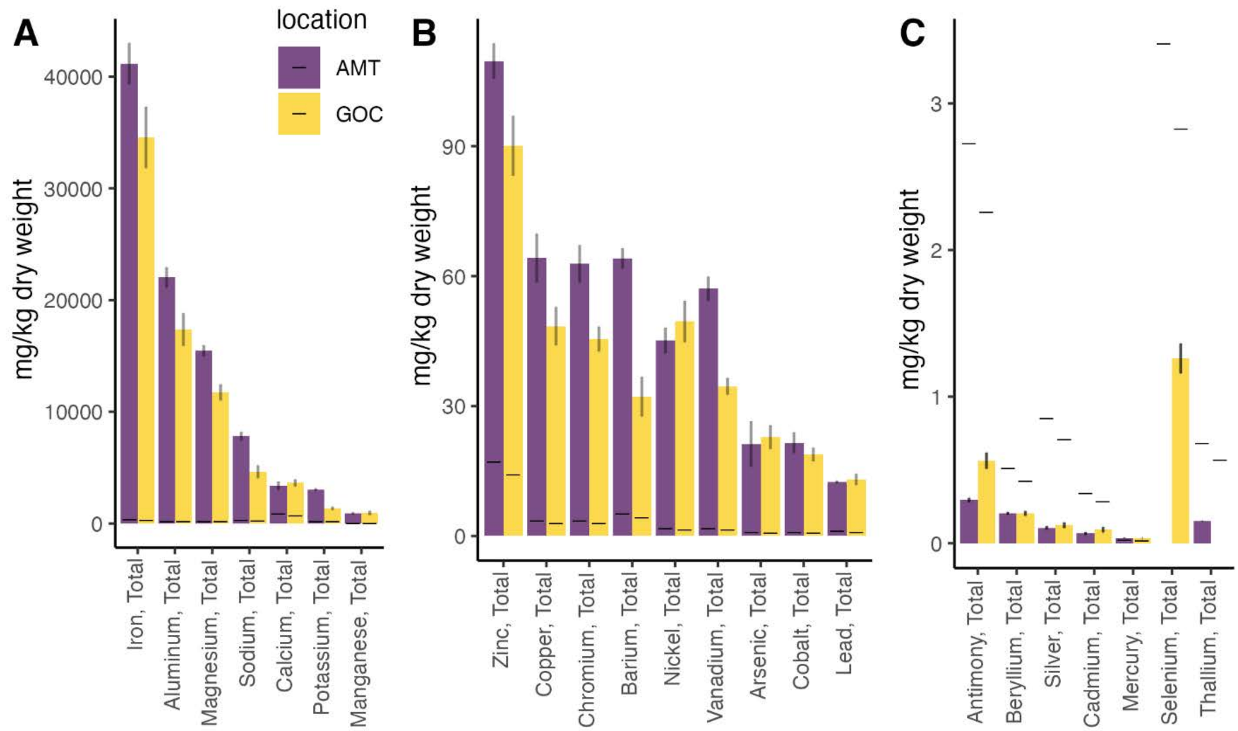

Figure 2. Sediment metal concentrations are displayed as a bar plot with mean ± standard deviation for Valdez Marine Terminal (AMT) in purple and Gold Creek (GOC) in yellow. Dashes represent the mean metal-specific reporting limit. Note that each panel has a different scale.

Were there differences between sites?

The terminal sediments had higher metal concentrations than Gold Creek, with statistically significantly higher concentrations of aluminum, barium, chromium, copper, iron, magnesium, potassium, sodium, vanadium, and zinc (Tables 1 and A1). Gold Creek had significantly higher concentrations of antimony compared to the terminal. Estimated selenium concentrations were detected at Gold Creek, while thallium was estimated at the terminal. The total organic carbon percentage was similar across both sites (0.50-0.52%), indicating similar metal bioavailability (Zhang et al., 2020).

Are these metal levels of concern for the ecosystem/biota?

Using the most protective empirically based sediment quality guidelines (e.g., Long et al. 1995), the ERL was exceeded at one or both stations for iron, vanadium, aluminum, arsenic, nickel, cobalt, copper, and selenium (Figure 3). The ERM was exceeded at in one replicate at Gold Creek for nickel (i.e. Nickel ERM set at 50 mg/kg and nickel values were 54.5, 49.1, and 45.0 mg/kg).

Zinc was one metal identified explicitly in the Harsha and Podgorski work, and Alaska Department of Environmental Conservation (ADEC) 2019 Alaska Pollutant Discharge Elimination System (APDES) permit renewal that is thought to be driving effluent toxicity. Here, we see that sediment zinc levels are, in fact, significantly higher at the terminal than at Gold Creek; however, these levels do not exceed the NOAA's protective effect thresholds for benthic life (i.e., ERM-L; Long et al., 1995). No other sediment toxicity thresholds were investigated in this pilot study.

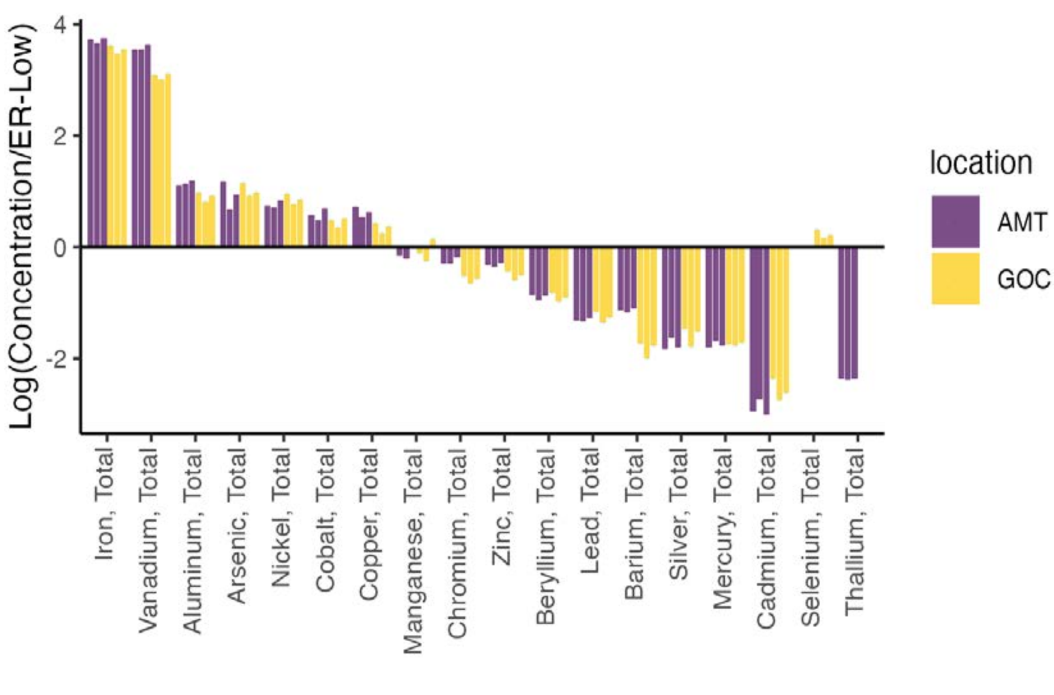

Figure 3. Sediment metal concentrations normalized to the Effect Range Low (ERL) value, shown on a log scale and organized by the degree of ERL threshold exceedance. Each sample replicate is displayed individually. Bar colors represent location. Metals that do not surpass the ERL threshold have negative values due to the log scale. Metals without an ERL threshold are excluded from the plot.

Are metals at the terminal likely related to terminal and tanker activity?

Of the metals found at concentrations > 1 µg/L in the BWTF effluent by Harsha and Podgorski (2023) (i.e., barium, zinc, magnesium, nickel, aluminum, mercury, arsenic, iron, copper), only nickel, mercury, and arsenic were not significantly enriched in the terminal sediments compared to Gold Creek. While found in low concentrations (i.e., < 1 µg/L) in the BWTF effluent, vanadium and potassium were significantly higher in the terminal sediments compared to Gold Creek.

Are metals likely contributed by terminal and tanker activity of environmental concern?

Four metals—aluminum, copper, iron, and vanadium—exceeded the effect range thresholds and are significantly elevated in the terminal sediments compared to Gold Creek. However, all of these metals exceed the effect range threshold at Gold Creek. No metal was found to only exceed the effect threshold at the terminal. This is most clearly seen in Figure 3.

Previous work by the EPA in Port Valdez conducted before and during the construction of the Valdez Marine Terminal and the Trans-Alaska Pipeline found widespread and comparable concentrations of metals, including vanadium, nickel, iron, chromium, and cobalt (EPA, 1976). Vanadium, for example, is a common naturally occurring element in the lithosphere but is also used intensely as an additive in the steel industry, with its rust-resistant properties making it highly valuable in shipbuilding and an emerging marine pollution concern (Tambat et al 2024). Other potential sources of metals are contemporary metal-based biocides used in antifouling paints, which contain copper and zinc (Torres and De-la-Torre, 2021).

5. Conclusion

The 2024 LTEMP sampling for hydrocarbons was complimented by sediment sampling for trace metals. The recent 2019 ADEC report cites that the principal water quality concerns from the terminal BWTF effluent are zinc, total aromatic hydrocarbons, and whole effluent toxicity (ADEC 2019). Aqueous input of metals, such as from the BWTF effluent, does not completely explain the presence and concentrations of the metals found in the terminal sediment; rather, the physical and chemical properties of individual metals and of the sediments themselves influence sediment metal concentrations (Zang et al 2020).

Our findings show that several metals in sediments at the terminal exceed protective sediment quality guidelines, possibly causing adverse effects in benthic organisms. Port Valdez is a metal-rich system with a history of copper and gold mining and several large, glacially-fed rivers entering within miles of the sampling locations. These local sources may explain regional patterns such as high iron concentration. This may also call into question the utility of the NOAA's Sediment Quality Guidelines for benthic organisms residing in Port Valdez. More effort could be put into framing these metal concentrations in the local and regional background levels (e.g., values published in EPA's 1976 report titled The Sediment Environment of Port Valdez, Alaska), inputs from rivers and streams, LTEMP Hydrocarbon concentrations, or other areas with human activity and oil and gas transport.

Several metals are significantly elevated at the terminal, can be tied to BWTF effluent, and exceed protective guidelines. These metals accumulated in sediments near the terminal warrant further investigation, including understanding the specific sensitivity of local benthic organisms and the origin of metals detected using source identification techniques.

Table 1. A summary of sediment metal concentrations, analytical detection limits, sediment quality guidelines (Effect Range Low and Medium), exceedance of effect ranges, source of those effect ranges, and statistical test results of difference between stations.

Analysis	Valdez Marine Terminal (AMT)	Gold Creek (GOC)	Reporting Limit	Effects Range Low (ERL)	Effects Range Medium (ERM)	>ERL?	>ERM?	Source	Sign diff betwn sites?**
	Mean ± STD (mg/kg dry weight)			(mg/kg dry weight)					
Aluminum, Total	22033.33 ± 907.38	17366.67 ± 1464.01	141.33	7,000.00	-	yes	-	U.S. EPA, 2004	*
Antimony, Total	0.29 ± 0.02	0.56 ± 0.06	2.26	-	-	-	-		*
Arsenic, Total	21.27 ± 5.26	22.83 ± 2.75	0.71	8.2	70	yes	no	U.S. EPA, 2004	-
Barium, Total	64.1 ± 2.35	32.17 ± 4.57	4.24	200	-	no	-	Long et al., 1995	***
Beryllium, Total	0.2 ± 0.01	0.2 ± 0.02	0.42	0.5	3	no	no	Long et al., 1995	-
Cadmium, Total	0.07 ± 0.01	0.09 ± 0.02	0.28	1.2	4.2	no	no	Long et al., 1995	-
Calcium, Total	3386.67 ± 380.18	3643.33 ± 317.86	706	-	-	-	-		-
Chromium, Total	62.83 ± 4.3	45.47 ± 2.87	2.82	81	370	no	no	Long et al., 1995	**
Cobalt, Total	21.53 ± 2.38	18.8 ± 1.59	0.71	12	68	yes	no	Long et al., 1995	-
Copper, Total	64.2 ± 5.6	48.47 ± 4.41	2.82	34	197	yes	no	Long et al., 1995	*
Iron, Total	41166.67 ± 1858.31	34566.67 ± 2750.15	282.33	1,000.00	-	yes	-	U.S. EPA, 2004	*
Lead, Total	12.47 ± 0.31	13.07 ± 1.3	0.85	46	218	no	no	Long et al., 1995	-
Magnesium, Total	15466.67 ± 503.32	11733.33 ± 723.42	141.33	-	-	-	-		**
Manganese, Total	894.67 ± 110.75	947.33 ± 193.7	2.82	1,000.00	-	no	-	U.S. EPA, 2004	-
Mercury, Total	0.03 ± 0	0.04 ± 0	0.02	0.2	1	no	no	U.S. EPA, 2004	-
Nickel, Total	45.13 ± 2.99	49.53 ± 4.76	1.41	20.9	50	yes	some	Long et al., 1995	-
Potassium, Total	3043.33 ± 118.46	1360 ± 149.33	141.33	-	-	-	-		**
Selenium, Total	-	1.26 ± 0.1	2.82	1	9	yes	no	Long et al., 1995	
Silver, Total	0.1 ± 0.01	0.12 ± 0.02	0.71	0.6	7	no	no	Long et al., 1995	-
Sodium, Total	7836.67 ± 380.83	4623.33 ± 571.78	211.67	-	-	-	-		**
Thallium, Total	0.15 ± 0	-	0.57	1.6	-	no	-	U.S. EPA, 2004	
Vanadium, Total	57.07 ± 2.8	34.57 ± 1.93	1.41	1.6	-	yes	-	US EPA, 2004	***
Zinc, Total	109.67 ± 4.04	90.07 ± 6.92	14.13	150	410	no	no	Long et al 1995	*
Solids, Total (%)	56.4 ± 0.79	68.4 ± 2.69	0.1						
Total Organic Carbon (%)	0.52 ± 0.04	0.50 ± 0.03							
Total Metal Concentration	94343.52 ± 3033.14	74666.31 ± 5704.19							
Total Heavy Metals*	72446.47 ± 2522.56	57929.4 ± 4571.07							
*Total Heavy Metals (THM) by Harsha & Podgorski - Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, and Zn									
**P-value conversion	"-" = Not Significant; * , α= 0.05-0.01; **, α = 0.01-0.001; ***, α <0.001								

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Table A1. A summary of the statistical test results for tests between sites for each metal.

Analysis	Valdez Marine Terminal (AMT)	Gold Creek (GOC)	Statistical Test	t Value	degrees of freedom	p-value
	Mean ± STD (mg/kg dry weight)					
Aluminum, Total	22033.33 ± 907.38	17366.67 ± 1464.01	Welch 2 sample t test	4.69280	3.339	0.01435
Antimony, Total	0.29 ± 0.02	0.56 ± 0.06	Welch 2 sample t test	-8.01800	2.2907	0.01009
Arsenic, Total	21.27 ± 5.26	22.83 ± 2.75	Two Sample t-test	-0.45732	4	0.6712
Barium, Total	64.1 ± 2.35	32.17 ± 4.57	Two Sample t-test	10.75400	4	0.0004239
Beryllium, Total	0.2 ± 0.01	0.2 ± 0.02	Two Sample t-test	0.03049	4	0.9771
Cadmium, Total	0.07 ± 0.01	0.09 ± 0.02	Two Sample t-test	-2.10580	4	0.103
Calcium, Total	3386.67 ± 380.18	3643.33 ± 317.86	Two Sample t-test	-0.89711	4	0.4204
Chromium, Total	62.83 ± 4.3	45.47 ± 2.87	Two Sample t-test	5.81620	4	0.00435
Cobalt, Total	21.53 ± 2.38	18.8 ± 1.59	Two Sample t-test	1.65500	4	0.1733
Copper, Total	64.2 ± 5.6	48.47 ± 4.41	Two Sample t-test	3.82180	4	0.01875
Iron, Total	41166.67 ± 1858.31	34566.67 ± 2750.15	Two Sample t-test	3.44410	4	0.02619
Lead, Total	12.47 ± 0.31	13.07 ± 1.3	Two Sample t-test	-0.77748	4	0.4803
Magnesium, Total	15466.67 ± 503.32	11733.33 ± 723.42	Two Sample t-test	7.33740	4	0.001837
Manganese, Total	894.67 ± 110.75	947.33 ± 193.7	Two Sample t-test	-0.40883	4	0.7036
Mercury, Total	0.03 ± 0	0.04 ± 0	Two Sample t-test	-0.25000	4	0.8149
Nickel, Total	45.13 ± 2.99	49.53 ± 4.76	Two Sample t-test	-1.35510	4	0.2468
Potassium, Total	3043.33 ± 118.46	1360 ± 149.33	Two Sample t-test	15.29600	4	0.0001066
Selenium, Total	-	1.26 ± 0.1				
Silver, Total	0.1 ± 0.01	0.12 ± 0.02	Two Sample t-test	-1.35590	4	0.2466
Sodium, Total	7836.67 ± 380.83	4623.33 ± 571.78	Two Sample t-test	8.10140	4	0.001262
Thallium, Total	0.15 ± 0	-				
Vanadium, Total	57.07 ± 2.8	34.57 ± 1.93	Two Sample t-test	11.45900	4	0.000331
Zinc, Total	109.67 ± 4.04	90.07 ± 6.92	Two Sample t-test	4.23830	4	0.01328
Solids, Total (%)	56.4 ± 0.79	68.4 ± 2.69				
Total Organic Carbon (%)	0.52 ± 0.04	0.50 ± 0.03				
Total Metal Concentration	94343.52 ± 3033.14	74666.31 ± 5704.19				
Total Heavy Metals*	72446.47 ± 2522.56	57929.4 ± 4571.07				
*Total Heavy Metals (THM) by Harsha & Podgorski - Ag, Al, As, Ba, Cd, Co, Cr, C						
**P-value conversion	"-" = Not Significant; * , α= 0.05-0.01; **, α = 0.01					