Heavy Metal Pollution in Puget Sound Marinas and Shipyards

James Michael Scukas

JScukas@uw.edu

School of Oceanography, Box 357940

University of Washington, Seattle, WA

Abstract

As worldwide industrial activities continue to grow, concerns have risen over the varied and potentially harmful effects of heavy metal accumulation in the marine environment. While some of these elements may be necessary for life at small concentrations, most heavy metals are defined as such to denote some degree of toxicity, usually occurring as concentrations increase significantly (Ansari et al. 2004). In this study, marine surface sediment samples were taken at maritime-related sites in the Puget Sound to analyze for heavy metal content, in order to investigate trends in metal contamination between sites of varying activities and sizes. There were elevated metal concentrations, compared to average shale rock, at every site. The most contaminated sites were clearly maritime academy and shipyard sites, followed by marinas and the control site, indicating that anthropogenic sources for certain metals like Pb and Cu are present and partially dependent on local activities.

Introduction

Commonplace in the maritime industry, antifouling hull paint serves to prevent marine organisms, such as algae and barnacles, from growing on and negatively impacting the performance of boats. Unfortunately, these hull paints are often copper-based and resultantly toxic, having been found to exist in levels that are harmful to many marine organisms (Carson 2009). Further, lead-based paints were common up until tighter restrictions were set in 1976, with evidence of their use existing as early as 700 BC (Eklund 2014). This proves to be especially worrying when considering that estuarine ecosystems, such as the Puget Sound, are important hosts to a wide variety of plant and animal life (Beck 2001). As an area high in both population and shipping/boating activity, there are a number of maritime-related sites with the potential for chronic marine heavy metal pollution. While antifouling paint is a common source of marine copper pollution, other heavy metals like lead, zinc, selenium, and arsenic have been shown to exist in these environments at toxic levels (Ansari et al. 2004). Common sources of heavy metals are industrial pollutants and runoff, which can contain significant levels of, for example, lead and arsenic solutions (Turner 2009). Further, several similar areas to those chosen in this study have been the focus of government cleanup efforts, with notable locations like Harbor Island in Seattle even being declared a federal cleanup site through the EPA's Superfund program. While this may indicate that many past and current regulations and policies were insufficient, much could be learned by comparing the heavy metal concentrations present in the sediments adjacent to these sites.

While some studies have found that industrial shipyards and recreational marinas both contain elevated heavy metal levels, it should be noted that each serve notably different purposes (Carson 2009; Papamanolis 2018). Shipyards often carry out significant repairs to much larger vessels, compared to the primarily recreational vessels which are docked and cleaned at marinas. Regarding where in the marine environment heavy metal pollution is most prominent, a different study noted that metal concentrations in their sampling sites were primarily influenced by sediment grain size: higher metal concentrations were usually associated with finer grained sediments (Bloom 1987). Additionally, further studies demonstrate how sediments in these marine environments can provide a sink for heavy metals and other pollutants, as the metals are able to accumulate on many sediments without form-altering chemical interactions occurring (González-Fernández et al. 2011; Horowitz 1985).

Non-toxic alternatives to copper-based antifouling paint exist, but cost and inferior performance have often stood in the way of these eco-friendly versions finding widespread success (Ciriminna 2015; Carson 2009). In addition to worries about bioaccumulation, the close proximity to residential areas and the prevalence of aquatic activities around Puget Sound also drive concern over marine heavy metal pollution. As such, the goal of this project is not solely to examine the sediment metal analysis data and report back polluted sites. Rather, it is to combine these findings with existing research to investigate which metals pose the most concern, and discuss the potential effects of metal contamination.

Sampling data will be analyzed with regards to my hypothesis, which is that high heavy metal concentrations in marine sediments are positively correlated with the scale of maritime-related activity at that site: that is, large industrial shipyards will experience higher concentrations of

heavy metal pollution than smaller recreational marinas, and both more so than the control site. Evidence backing this hypothesis includes how toxic cleanup sites often originate from heavily pollutive industrial activity and the ineffective disposal of industrial waste, combined with how marine sediments act as sinks for these pollutants (González-Fernández et al. 2011; Ansari et al. 2004). Recreational marinas certainly deal with a variety of pollution sources like copper-based hull paint (Lagerström 2015). However, my hypothesis is that recreational sites will have lower marine sediment concentrations of toxic heavy metals compared to industrial sites, based on differences in the types of activities carried out, the scale of the site, and the types of vessels most commonly present.

Methods

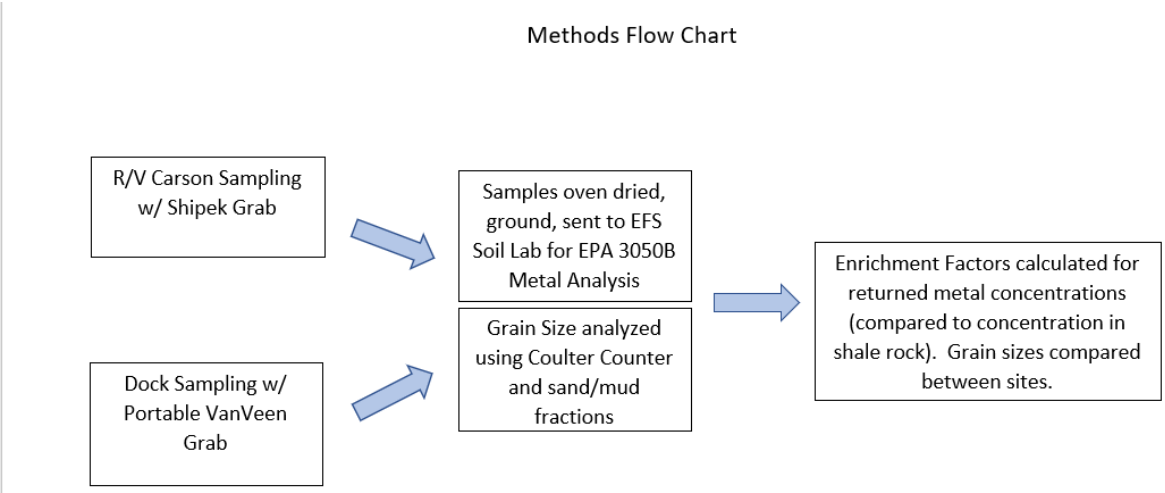

Chart 1: Order of procedures

The sediment samples for this study were taken using both Shipek and portable Van Veen grabs. Generally, the Shipek grab is viewed as most effective when sampling finer, sandy sediment, while the Van Veen grab is more suitable for coarser, muddier sediment (Romano 2017). On the *RV Rachel Carson*, a Shipek grab was used for one dry dock, one control, and two shipyard sites, while the portable Van Veen grab was used for one maritime academy and three

marina sites; an A/B attached to the sample ID represents two samples run at that same site (Table 1; Figure 1). With the portable grab, samples were taken at the edge of site docks adjacent to boat launch ramps, and as close to docked boats as possible. *Carson* sediment grabs were taken from aboard the vessel after moving close in proximity to the water-facing areas of the sites. Though the general locations for sampling were different between methods, both were taken in locations which see significant usage related to marine activities. On the *Carson*, samples were stored in Ziplock bags and placed inside the vessel's freezer. For portable sampling, samples were stored in Ziplock bags, placed in a cooler, and driven back to a walk-in freezer at the University of Washington.

Collection Date	Site Name	Sample ID	Lat/Long	Description
1/11/2019	Lake Union Dry Dock	JS03A/B	47.63382, -122.33216	12-acre full service shipyard, 90 year history
1/13/2019	Control	JS05	47.204238, -122.92479	Near Arcadia, WA away from industrial activity
1/11/2019	Foss Shipyard	JS06	47.655223, -22.366922	6-acre full service shipyard
1/11/2019	Stabbert Shipyard	JS07A/B	47.56818, -122.34759	Full service shipyard, 20,000 sqft covered structure
2/3/2019	Northlake Marina	JS10A/B	47.649967, -122.33074	60-slip dock, no live-aboards
2/3/2019	The Seattle Marina	JS11	47.648115, -122.34675	70+-slip dock, 10% live-aboards
2/3/2019	Seattle Maritime Academy	JS12A/B	47.660614, -122.37371	Opened 2016; maritime career training w/ machine shop, vessel docked at time of sample
2/3/2019	Shilshole Marina	JS13	47.686890, -122.40399	1,430 total capacity, sample taken at Northernmost boat launch ramp

Table 1: Site Descriptions

Figure 1: Map of Sites (control indicated with coordinates)

To begin metal analysis, the wet sediment samples were placed in acid-cleaned vials, and oven-dried at 60 deg C. Once dried, they were ground to a fine dust using a mortar and pestle, then submitted to the UW School of Forestry Soil Lab. Once received, samples were processed in accordance with EPA method 3050B, returning the respective concentrations (µg/g) of Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, S, Se, Si, and Zn. With this method, each sample is digested in acid, then analyzed for heavy metal content using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Additionally, grain size analysis was performed on samples from each site. First, samples were homogenized in their bag, then had both 1g and 4g of sediment removed and sonicated in dispersant solution (0.05% sodium hexametaphosphate). These samples were then sieved through a 63µm screen and rinsed into a previously-weighed glass jar with DI water. For the 1g samples, the resulting mud fraction jars were run through a Coulter Counter in UW's Ogsten lab to output silt and clay grain size distributions. For the 4g samples, a drying tin was additionally used to collect the sand fraction. Both the sand and mud fractions of the 4g samples were oven-dried then weighed, in order to calculate the mud and sand grain size distributions. In all, this analysis returned the 3-bin distributions for sand, silt, and clay in each sample. Clay is defined as 0-3.86 µm, silt as 4.24-63.4 µm, and sand as greater than 63.4 µm – the gap between clay and silt due to the Coulter Counter's intervals. Chart 1 illustrates an outline of the methods used.

Results

Metal data was received with each site's metal concentrations given in µg/g (parts per million [ppm]). To compare site concentrations with the typical concentrations found in nature, the initial values were converted to enrichment factors (EF) using the following equation:

$$EF = \left(\frac{element}{Al}\right)_{sample} / \left(\frac{element}{Al}\right)_{shale} \quad \textit{(Equation 1)}$$

Each metal concentration was ratioed in proportion to its corresponding aluminum concentration at each site, then compared to the same average elemental ratio found naturally in shale rock – used as an analogue for upper continental crust metal concentrations (Brumsack 2005; Taylor and McLennan 1985). The resulting enrichment factor indicates the relative depletion (EF<1) or enrichment (EF>1) for each metal, shown in Table 2 below. Another study cited an EF of above 1.5 to be indicative of anthropogenic inputs (Idris 2008). Table 3 shows actual concentrations of metal in ppm, with concentrations above Washington state marine sediment quality standards highlighted in red, and Table 4 indicates the detectable limits for each metal (Toxics Cleanup Program 2013 p.45; Leazer 2018).

Site	As	B	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg
Lake Union Dry Dock	34.98	3.40	9.81	1.87	TR	5.45	83.93	4.31	0.29	3.36
Lake Union Dry Dock	14.79	3.21	9.87	1.81	TR	5.11	77.25	3.90	0.29	3.40
Control (Arcadia)	40.72	4.44	2.41	14.56	ND	4.65	4.01	4.25	0.44	4.90
Foss Shipyard	37.66	4.66	12.57	4.05	ND	7.19	29.09	5.36	0.33	4.50
Stabbert Shipyard	176.56	5.76	26.75	3.89	TR	9.39	146.58	6.51	0.32	4.08
Stabbert Shipyard	166.51	6.03	36.17	4.75	TR	9.68	111.46	7.63	0.34	4.93
Northlake Marina	ND	2.54	12.62	5.71	ND	4.67	24.83	3.22	0.20	3.31
Northlake Marina	41.95	2.80	13.45	5.48	ND	4.48	25.95	3.00	0.20	3.50
Shilshole Marina	ND	5.11	4.80	16.11	ND	5.34	32.29	3.41	0.57	6.43
Seattle Maritime Academy	16.49	5.16	16.62	3.61	ND	7.27	85.08	4.88	0.33	3.96
Seattle Maritime Academy	ND	4.53	14.50	3.06	ND	5.97	68.88	5.28	0.20	3.30
The Seattle Marina	ND	3.52	7.03	2.25	ND	3.48	18.38	4.57	0.14	3.43

Site	Mn	Mo	Na	Ni	P	Pb	S	Se	Zn	Si	Ag
Lake Union Dry Dock	0.00	173.85	0.47	7.33	9.35	206.71	29.17	2774.35	43.17	250.49	450.44
Lake Union Dry Dock	0.00	161.26	0.44	7.01	9.27	160.66	21.26	2688.79	36.26	210.42	TR
Control (Arcadia)	0.00	154.03	3.90	6.95	9.99	37.38	2.84	2990.43	4.79	196.05	ND
Foss Shipyard	0.00	195.44	0.41	9.33	11.85	101.87	3.15	3639.64	35.81	211.71	ND
Stabbert Shipyard	0.00	370.90	0.72	8.81	13.33	200.87	15.96	3708.32	111.16	219.18	ND
Stabbert Shipyard	0.00	362.48	0.72	9.49	14.16	191.21	14.38	4186.85	114.19	242.43	ND
Northlake Marina	0.00	133.13	0.30	6.74	10.06	77.51	3.67	2393.19	21.23	215.41	ND
Northlake Marina	0.00	140.99	0.29	7.05	11.41	80.64	4.07	2588.89	21.95	254.66	ND
Shilshole Marina	0.00	179.62	9.50	9.04	14.18	52.70	17.49	2851.26	12.40	265.07	ND
Seattle Maritime Academy	0.00	209.46	0.97	9.88	17.75	104.48	17.37	3611.27	91.86	218.16	ND
Seattle Maritime Academy	0.00	206.77	0.77	8.22	12.42	87.07	13.88	3239.62	77.32	269.25	ND
The Seattle Marina	0.00	135.74	0.34	6.46	7.08	55.85	1.21	2586.33	15.97	173.50	ND

Table 2: Metal Enrichment Factors (EFs) - Mn has positive EFs ranging from 0.000314 to 0.00102

ND=not detected (ND<Detection Limit). TR=trace (Detection Limit < TR < Quantitative Limit [Table 4])

	sample site	µg/g Al	µg/g As	µg/g B	µg/g Ba	µg/g Ca	µg/g Cd	µg/g Cr	µg/g Cu	µg/g Fe	µg/g K	µg/g Mg
Lake Union Dry Dock	JS03A	12847.91	49.44	54.62	83.21	4315.43	TR	71.37	549.97	30468.06	1277.70	7760.83
Lake Union Dry Dock	JS03B	12021.66	19.56	48.27	78.34	3921.18	TR	62.60	473.60	25792.52	1194.14	7363.64
Control (Arcadia)	JS05	5662.50	25.36	31.43	8.99	14843.22	ND	26.85	11.59	13248.14	843.91	4997.14
Foss Shipyard	JS06	6778.77	28.08	39.49	56.24	4935.69	ND	49.68	100.57	19966.21	760.87	5487.46
Stabbert Shipyard	JS07A	7054.66	137.01	50.81	124.56	4940.68	TR	67.54	527.39	25260.96	770.96	5186.03
Stabbert Shipyard	JSO7B	7620.60	139.58	57.48	181.93	6512.73	TR	75.20	433.21	31986.20	871.50	6766.94
Northlake Marina	JS10A	7743.74	ND	24.54	64.48	7963.39	ND	36.86	98.04	13730.13	533.31	4619.06
Northlake Marina	JS10B	7790.35	35.95	27.27	69.18	7679.63	ND	35.63	103.09	12843.98	540.53	4905.11
Shilshole Marina	JS13	5601.74	ND	35.79	17.73	16239.51	ND	30.52	92.24	10501.42	1084.72	6478.65
Seattle Maritime Acad	JS12B	7351.56	13.34	47.43	80.62	4776.37	ND	54.49	318.99	19746.34	822.28	5237.57
Seattle Maritime Acad	JS12A	8507.87	ND	48.19	81.45	4690.06	ND	51.80	298.87	24711.57	577.77	5047.12
The Seattle Marina	JS11	6257.24	ND	27.52	29.04	2539.31	ND	22.22	58.67	15733.39	288.50	3865.88

	sample site	µg/g Mn	µg/g Mo	µg/g Na	µg/g Ni	µg/g P	µg/g Pb	µg/g S	µg/g Se	µg/g Zn	µg/g Si	µg/g Ag
Lake Union Dry Dock	JS03A	314.09	33.50	777.98	72.51	961.07	663.95	11244.27	267.33	610.16	1000.89	4.63
Lake Union Dry Dock	JS03B	293.68	29.08	688.76	64.89	891.30	482.84	7667.79	242.43	479.47	786.70	TR
Control (Arcadia)	JS05	555.65	13.08	2868.49	30.32	452.46	52.91	482.66	127.00	29.86	345.26	ND
Foss Shipyard	JS06	346.94	19.87	363.35	48.72	642.62	172.63	640.44	185.04	267.01	446.33	ND
Stabbert Shipyard	JS07A	283.94	39.25	659.69	47.85	752.45	354.26	3376.97	196.21	862.60	480.89	ND
Stabbert Shipyard	JSO7B	347.29	41.43	716.74	55.69	863.41	364.29	3286.52	239.30	957.25	574.56	ND
Northlake Marina	JS10A	215.92	15.46	304.96	40.20	623.22	150.06	852.29	138.99	180.85	518.78	ND
Northlake Marina	JS10B	225.41	16.48	297.05	42.30	711.39	157.05	950.04	151.26	188.07	616.98	ND
Shilshole Marina	JS13	156.27	15.09	6915.54	39.00	635.40	73.80	2939.84	119.79	76.38	461.80	ND
Seattle Maritime Acad	JS12B	301.13	23.10	923.11	55.93	1044.09	192.01	3830.20	199.11	742.88	498.79	ND
Seattle Maritime Acad	JS12A	299.05	26.39	848.39	53.87	845.53	185.19	3543.04	206.72	723.59	712.42	ND
The Seattle Marina	JS11	189.20	12.74	278.81	31.13	354.51	87.37	227.63	121.37	109.90	337.64	ND

Table 3: Metal ppm concentrations; highlighted red if over WA state sediment quality standards

	Detection Limit	Quantitative Limit	PCA TR value
Al	0.039	0.130	0.084
As	0.083	0.277	0.180
B	0.009	0.030	0.019
Ba	0.006	0.020	0.013
Ca	0.056	0.187	0.121
Cd	0.046	0.153	0.100
Cr	0.042	0.140	0.091
Cu	0.019	0.063	0.041
Fe	0.019	0.063	0.041
K	0.395	1.317	0.856
Mg	0.109	0.363	0.236
Mn	0.003	0.010	0.006
Mo	0.018	0.060	0.039
Na	0.10	0.34	0.219
Ni	0.008	0.027	0.017
P	0.085	0.283	0.184
Pb	0.070	0.233	0.152
S	0.075	0.250	0.162
Se	0.147	0.490	0.318
Zn	0.029	0.097	0.063
Si	0.092	0.307	0.199
Ag	0.005	0.017	0.011

Table 4: SEFS metal analysis detection limits (ppm); the PCA TR is the midpoint between the two limits (Leazer 2018).

For As, Cu, Pb, and Zn, four metals of particular interest to this study, calculated enrichment factors were significantly above 1 in all but four cases (where As was not detected). Pb was found to be more enriched at every shipyard and marina site compared to the control site, and concentrations were particularly high at Stabbert Shipyard and Lake Union Drydock. Foss Shipyard and Seattle Maritime Academy additionally had higher Pb enrichments than each marina and the control site. This pattern generally held true for other metals, with the more industrial of sites (shipyards, drydock, maritime academy) tending to be more enriched in heavy metals than marina and control sites. Further, marina sites were more enriched in Cu, Pb, and

Zn than the control site. The control site did however have a high arsenic enrichment. Additionally, Se was found to have EFs well above any other metal analyzed. And, while generally lower in value than the maritime sites, it should be noted that the control site had an EF>1 in 17/21 metals.

Derived from 3-bin Coulter counter data, grain size distributions of sand, silt, and clay (listed in order of decreasing size) were compared to enrichment factors at each site. Grain sizes appeared to have some correlation to metal enrichment levels, primarily for the maritime academy and marina sites, with smaller grain size distributions tending to have higher metal enrichments. However, Stabbert Shipyard had the third highest distributions of sand, while also having the highest combined enrichment, and some locations with similar distributions (Shilshole, Northlake, and Stabbert) had notable differences in enrichment factors. Figures 2 and 3 compare the arsenic, copper, lead, and zinc enrichments to grain size distributions at each site, respectively. Other studies have found elevated heavy metal concentrations primarily in grain sizes of silt or smaller (<63 μm) (Hosseini and Sajjadi 2018). It should be noted that Figure 2 uses averaged EF values for the following sites where two samples were taken for reproducibility: Lake Union Dry Dock, Stabbert Shipyard, Seattle Maritime Academy, and Northlake Marina.

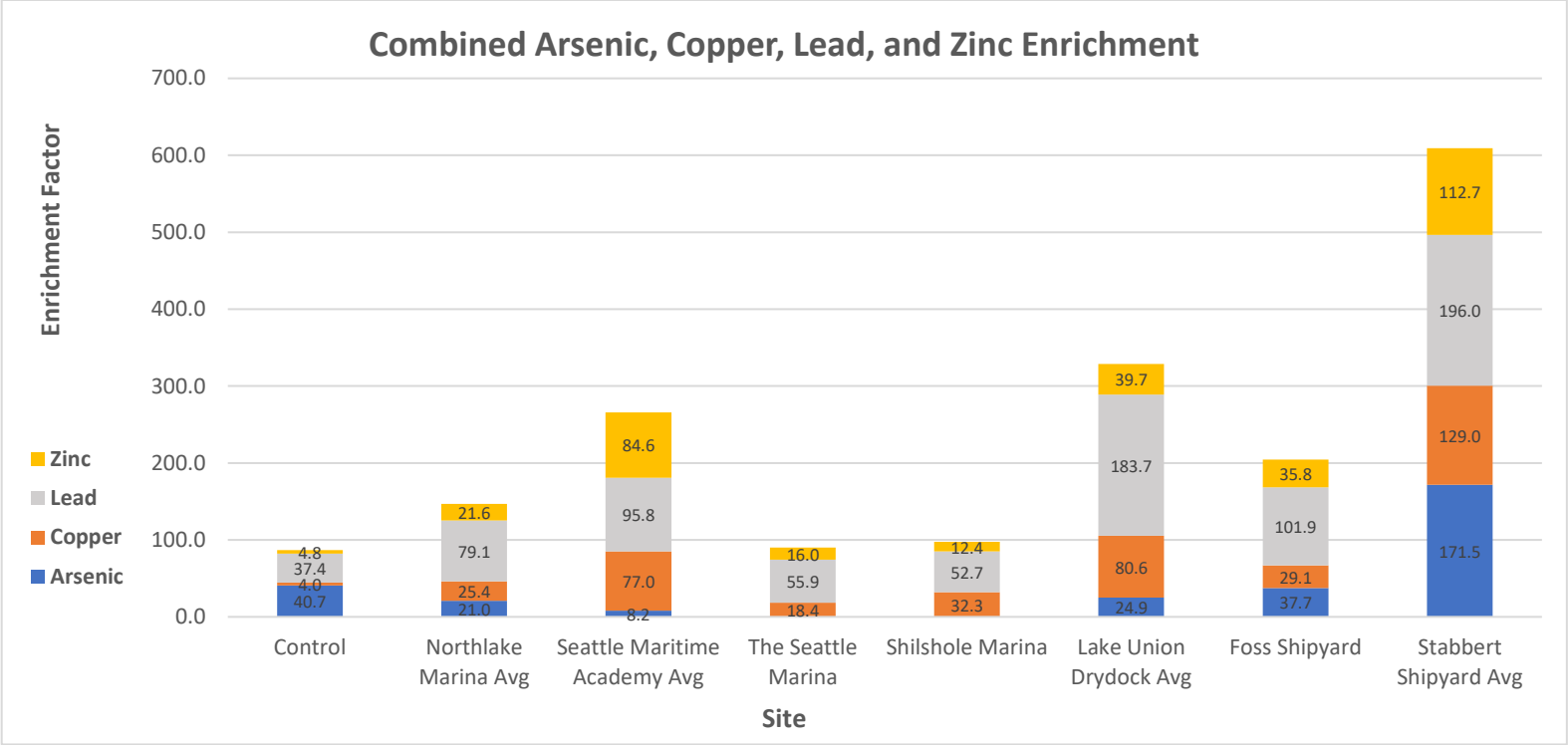

Figure 2: Combined enrichment factors for As, Cu, Pb, and Zn

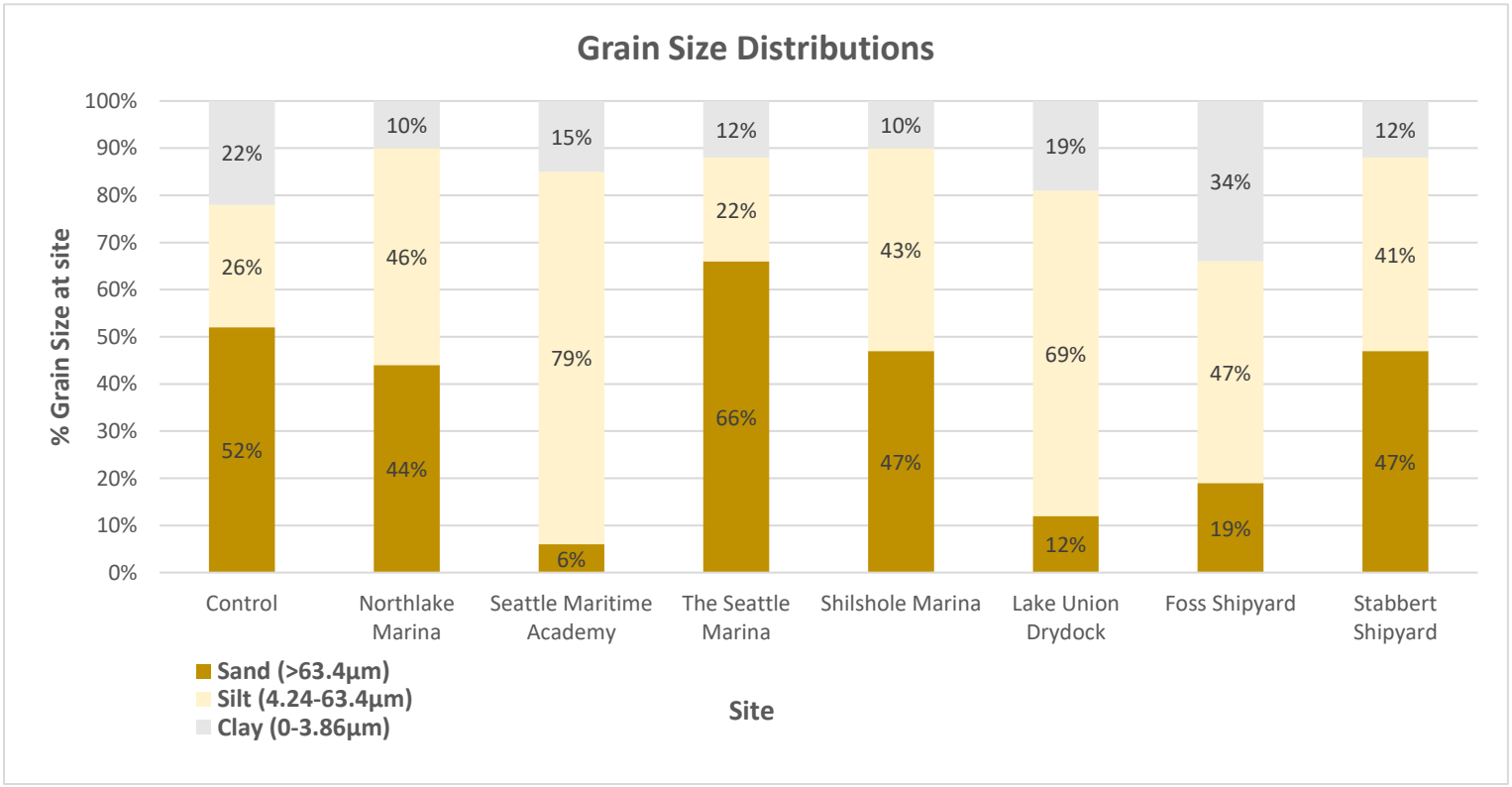

Figure 3: Grain size distribution percentages between sites

Discussion

Sediment Metal Enrichment

This study's initial hypothesis put forth that heavy metal concentrations in marine sediments would be elevated at the most industrial of maritime-related sites. This assessment was supported, with results indicating that the highest levels of heavy metal contamination were at the maritime academy and shipyards compared to the marina sites, namely Pb, Cu, Zn, and Se. Marina sites were largely more contaminated than the control site, excluding a few metals like As. An additional hypothesis that marina sites would experience elevated Cu contamination compared to the control was also supported, with every marina site returning a Cu enrichment factor between 4.5-8 times larger than the control (Figure 2). These findings held consistent with existing literature, which has found marine sediments to act as sinks for heavy metal contamination, and found this contamination to be elevated at maritime-related structures (Li et al. 2010; Turner 2009). Of further support is Seattle's status as a large seaport, with constant maritime activity. Locations like these are associated with chronic metal inputs, commonly from shipbuilding activities, industrial runoff, and other local anthropogenic sources (Ansari et al. 2004). Finally, calculated Enrichment Factors (EF's) based on shale rock were often well above the natural EF threshold of around 1–1.5, which suggests anthropogenic sources according to multiple studies, and most metals returned higher-than-natural enrichments across sites, strongly suggesting heavy metal inputs outside of natural sources (Brumsack 2005; Idris 2008; Hosseini and Sajjadi 2018).

Bioaccumulation and Uptake

One of the more complex aspects of heavy metal contamination are the processes which lead to bioaccumulation in marine organisms. Heavy metals in sediments often exist at concentrations 3-5 orders of magnitude greater than heavy metals in the overlying waters (Ansari et al. 2004). So, it is unproductive to make sweeping statements about metal toxicity on marine life, as opposed to analyzing metal toxicity based on species or phyla, given the different levels of pollution experienced between, e.g., a shellfish and a marine mammal. In addition, bioaccumulation is dependent on marine biogeochemical aspects involving speciation, organic matter, and pH, among others (Elder and Collins 1991). As a result, looking solely at the total concentration of an element can be an inaccurate metric for determining toxicity, an issue which this study has attempted to address by including Enrichment Factors, site analyses, and specific toxicity discussion for the primary metals of focus (Mamindy-Pajany et al. 2013). Efforts to sieve sediment for invertebrate samples failed to unearth sufficient volumes of invertebrate tissue, but collecting such samples in future studies could provide further information regarding the bioavailability and toxicity of heavy metals. Analyzing samples for speciation would also be productive, but requires complex and varied methods out of budget for this study.

Existing literature does, however, indicate that heavy metal contamination generally leads to toxic marine conditions and negative health impacts on local organisms, and that increasing concentrations can amplify these effects (Boening 1999; Peterson 1986). As these metals accumulate they tend to travel up the food chain, eventually gaining the potential to impact humans. Both environmental events and anthropogenic activity can mobilize pollutants from

the sediments, and lead to increased bioavailability to local marine organisms (Mamindy-Pajany et al. 2013). So, while metal concentrations and EFs may not be sufficient to determine the specific toxicities of these heavy metals to marine organisms, areas which return insignificant levels of metal contamination are less likely to be of interest to studies on chronic heavy metal toxicity. Total concentrations in ppm are still commonly used to set sediment quality standards. And, these values do appear to be sufficient in determining areas that experience high levels of chronic heavy metal inputs, where concerns outside of bioaccumulation could be present considering the populous locations of the sample sites.

Copper

Cu is toxic to marine organisms above certain limits, though it is crucial to marine life at levels around 5-20ppm, and multiple forms of Cu can enter and contaminate marine sediments (US EPA 2016a). A wide variety of industrial activities utilize Cu, and though it is an important micronutrient, sufficiently high levels at certain bioavailabilities can negatively impact marine species diversity (Flemming and Trevors 1989). Though Cu at higher levels is among the most toxic heavy metals to marine organisms, it is also much less toxic to humans compared to other metals in this study like Pb (Solomon 2009). Cu EF's were greater than 1.5 for every site in this study, indicating concentrations of Cu in excess of natural levels defined as average shale rock (Idris 2008). Seattle Maritime Academy, Lake Union Drydock, and Stabbert Shipyard all had significantly higher Cu enrichments than other sites, and all work with or utilize larger-sized maritime vessels. Indeed, the Lake Union and Stabbert sites both had ppm concentrations exceeding Washington State marine sediment quality standards (390 ppm for Cu): the highest samples from each contained 549.9 ppm and 527.4 ppm of Cu, respectively (Tables 1 & 2;

Toxics Cleanup Program 2013 p.45). These notably high concentrations may indicate industrial sources aside from Cu-based antifouling paint, which is likely a main source of Cu contamination in the marina sites (Turner 2009).

To consider potential impacts on marine life, one study found the difference in invertebrate populations between areas with an average Cu sediment concentration of 589 ppm and 33 ppm to be 4.3 times larger in favor of the 33-ppm location, and that many organisms were not present in sites over 200 ppm (Rygg 1985). At the same time, other literature has stressed the importance of considering the chemical form of the metal and the presence of organic matter in determining the extent to which contaminated sediments are toxic. The chemical presence of many negatively charged groups in organic matter allow it to more easily adsorb cations and bind with metals, as indicated by how higher concentrations of organic matter have a positive relation to heavy metal content (Baran and Tarnawski 2015).

Lead

Pb, on the other hand, plays no essential biological role (Ansari et al. 2004). Perhaps one of the more worrying results of this study are the heavily enriched Pb values returned in Figure 2, with averaged Lake Union values of 573.4 ppm and an averaged EF of 183.7, considering Pb's potential to accumulate in both marine and human life (Hosseini and Sajjadi 2018). Though sediment toxicity involves more than just the metal concentrations, there have been studies indicating higher Pb uptake rates in sediment than water. Factors like higher amounts of extractable Fe may have a positive influence on Pb bioavailability, resulting in an increase in

their potential to enter and accumulate in marine organisms (Fe is another metal with uniformly positive EF's in this study) (Warren 1981).

Pb concentrations and EF's were significantly higher in this study than in both similar and different locations – samples from one study in the greater Puget Sound area did not detect Pb, with a detection limit of 0.07 ppm, and another study on Persian Gulf estuaries returned mean value between 0.32-4.37 ppm of Pb (Leazer 2018; Hosseini and Sajjadi 2018). The authors of the Persian Gulf study also calculated EF's using shale rock, and had their most contaminated site return a value of 3.21, before concluding that metal sources for all of their sites were anthropogenic (Hosseini and Sajjadi 2018). With non-control averaged lead concentration values between 73.80-573.4 ppm, and EF's between 52.70-196.0, this study concludes that Pb contamination at these sites originates primarily from anthropogenic sources.

Selenium

Like Cu, Se is a trace element required by numerous organisms, but can become toxic in high enough quantities in part due to its potential to bioaccumulate (Santos et al. 2015). A variety of agricultural and industrial sources for Se exist, including sources both historically and presently common around the Puget Sound, such as mining (Navarro-Alarcon and Cabrera-Vique 2008). While further research is still necessary to understand the extent and mechanisms of Se toxicity, and other biological interactions, Se contamination is thought to be on the rise and the element has grown in prominence as a significant pollutant (Lemly 2004).

A previous Puget Sound study found notably elevated Se contamination at their sample sites, three of which being near historical mines, with EF's ranging from 5,002 to 17,244 (Leazer

2018). While these values seem strikingly high compared to other metal EF's, mining is often cited as a source of Se contamination (Lemly 2004). Though the Puget Sound study looked mainly at copper mines, coal mining in particular produces waste which is almost always enriched in Se, and even the burning of coal produces an Se-enriched ash (Lemly 2004). This study found elevated levels of Se at every sample site, with an EF range between 2,393-4,186 – by far the highest average EF's out of the metals analyzed and indicative of anthropogenic Se sources near maritime sites. Two concurrent studies to this also examining heavy metals in Puget Sound found similarly high enrichments of Se. One returned sediment EFs ranging from 1,955-4,876, along with a control invertebrate sample returning a trace amount of Se compared to a site of interest invertebrate returning an EF of 844.7; the other found sediment EFs ranging from 2,385-4,241, with trace amounts in one invertebrate sample and no Se detected in the other invertebrate (Mandovi 2019; Bell 2019). While it is difficult to draw firm conclusions given the uncertainties around Se toxicity, especially considering the relative dearth of studies on Se in marine sediments, multiple instances of Se contamination affecting wildlife have been documented (Hamilton 2004; Lemly 2013; Santos et al. 2015).

Another study takes the stance that Se contamination has the potential to pose a significant hazard to the long-term health of aquatic ecosystems, and strongly criticizes oversights in Se pollution management and the absence of Se in many screening programs (Lemly 2004). The same author published an additional study which linked deformities commonly seen as a result of Se toxicity in fish to elevated levels of Se in fish tissues, with samples taken from a NC lake which sees inputs of coal waste from a nearby energy plant (Lemly 2013). Sediment Se concentrations were assessed to be 21-28 ppm in the lake, compared to concentrations

between 119-267 ppm in the Puget Sound in this study (Lemly 2013). While it should be noted that these concentrations are compared between significantly different bodies of water, this study concludes that these consistently elevated levels of Se present in Puget Sound are cause for further research. While it's possible the Puget Sound may have naturally elevated levels of Se, further support from this study includes how sites with higher industrial activity like Foss Shipyard, Stabbert Shipyard, and Seattle Maritime Academy all had notably larger enrichment factors than the control site, with the possibility that there exist both high natural Se levels and Se pollution from anthropogenic sources.

Arsenic

While As in marine sediments has been recognized to have toxic effects on organisms, its mobility and bioavailability are important in determining the extent to which As contamination will harm marine life (Mamindy-Pajany et al. 2013). Still, the two most common forms of As in marine environments (As(III) and As(V)) have both been shown to harm marine organisms, with their exact toxicity depending on species and environment (Neff 1996).

As was detected in eight of the twelve samples analyzed, and was positively enriched in each of the eight. Excluding Seattle Maritime Academy, which detected As in one sample but not the other, averaged EFs for sites with detected As ranged from 24.89-171.5. Stabbert Shipyard returned the highest EFs, and additionally exceeded WA state marine sediment quality standards for As, with its averaged concentration of 138.3 ppm well above the 57-ppm limit.

One irregularity to note was the high level of As at the control site. The site was chosen to be away from industrial activity and shipping lanes, but with an enrichment factor of 40.71 has the

second largest averaged As enrichment. However, one study considers concentrations between 5 and 40 ppm of As in marine sediments as uncontaminated, and the control site fell within this threshold at 25.36 ppm; Lake Union sample A and Stabbert samples A and B all exceeded the contamination threshold, at 49.44, 137.0 and 139.6 ppm, respectively (Neff 1996). While As samples were generally less enriched than Cu, Pb, and Se, industrial sites still returned more consistent and highly enriched As values. Each marina or maritime academy site returned at least one sample with concentrations below the detection limit, while shipyards detected positively enriched As values for every sample – perhaps indicating that As contamination was more uniformly present at sites with higher levels of industrial activity.

Grain size

Heavy metal contaminates tend to be associated with smaller grain sizes due to their larger surface-to-volume ratios which increase adsorption area (Ansari et al. 2004). This study found reasonable correlations between grain size and metal enrichment, where sites with the highest EF's tended to have smaller average grain sizes (Figure 3). At the same time, sites with the smallest overall grain size did not always have the most elevated EF's. This non-uniformity is supported by studies which indicate that anthropogenic heavy metal inputs can supersede other factors like grain size and organic content, essentially resulting in a higher than expected levels of metal contamination (Rygg 1985).

Sites Factors

Exact details on some sites were unavailable at times, but most sites had a number of public details on their website. The less industrial marina sites, in rough order of smallest to largest, are Northlake Marina, The Seattle Marina, and Shilshole Marina. Northlake and The Seattle

Marina are much smaller than Shilshole, with approximately similar sizes around 60-70 slips, whereas Shilshole maintains a capacity of 1430 slips. Shilshole did have higher Cu enrichment than the other marinas, but had less As, Pb, and Zn enrichment than Northlake. This could suggest that while the scale of the site matters to an extent, like where a higher boat capacity is associated with higher Cu enrichment, the types of activities carried out at the site (and other factors) have a significant impact as well. For example, Seattle Maritime Academy likely sees much less boat traffic than a large marina like Shilshole, but had higher metal concentrations in As, Cu, Pb, Se, and Zn. Instead of many smaller recreational vessels, the maritime academy had one larger vessel docked at time of sampling, has a machine shop on the premises, and was fairly recently constructed.

A similar pattern follows when comparing industrial sites, where metal concentrations seem to be impacted by a combination of factors including scale and services offered. The biggest commonality between industrial sites were the high levels of Pb and As at shipyards compared to marinas, supporting the hypothesis that industrial sites may contribute to metal contamination via waste runoff or other anthropogenic sources. Lake Union, Foss, and Stabbert are all listed as full-service shipyards, and common activities include welding, machining, carpentry, painting, and other repairs. Lake Union specifically had total metal concentrations in excess of WA state marine sediment quality standards for Cu, Pb, and Zn, while Stabbert exceeded these standards for As and Cu, and Seattle Maritime Academy for Zn.

Conclusion

This study's analysis of heavy metal concentrations around Puget Sound maritime sites demonstrated that contamination becomes elevated as industrial activities increase in scale

and/or prevalence. While each metal poses a varying level of risk, the metals of most interest to this study tended to accumulate in the sediments of marina and shipyard sites at levels far exceeding natural crustal and weathering inputs. Cu, Pb, and Se were found at levels generally associated with toxicity or anthropogenic inputs, and other metals like As and Zn contaminated numerous sites as well. Se was of notable concern, given the relative lack of consensus around its toxicity threshold and health effects, and the consistently elevated concentrations and EF's in multiple Puget Sound studies. Resultantly, this study's initial hypothesis was supported, with metal enrichment data trending higher as the industrial nature of sites increased. And, recreational marina sites still experienced elevated levels of Cu compared to the control, supporting the presence of copper-based anti-fouling paint pollution. In all, metal contamination in the Puget Sound appears to exist at levels indicating widespread anthropogenic inputs, likely from industrial runoff and other sources of waste, and should be closely monitored in the future to safeguard against negative health effects on both marine and human life.

Additional Figures

Marine Sediment Quality Standards--Chemical Criteria

Chemical Parameter	mg/kg Dry Weight (Parts per Million (ppm) Dry)
Arsenic	57
Cadmium	5.1
Chromium	260
Copper	390
Lead	450
Mercury	0.41
Silver	6.1
Zinc	410

Table 5: WA State Marine Sediment Standards (Toxics Cleanup Program 2013 p.45)

Site Photos

Photo 1: Near Foss Shipyard site

Photo 2: Northlake Marina

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