RELATIONSHIP BETWEEN SEDIMENT CHARACTERISTICS AND
CONTAMINANT CONCENTRATIONS ON OʻAHU AND KAUAʻI

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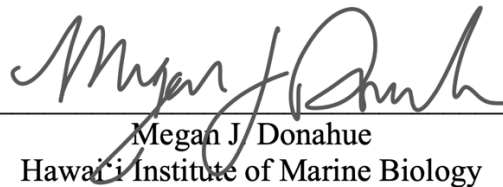Thesis Advisors

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We certify that we have read this thesis and that, in our opinion, it is satisfactory in scope and quality as a thesis for the degree of Bachelor of Science in Global Environmental Science.

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For my mother and father, Yuko and Yuichi Katayama, who have supported me through every step of my endeavors.

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ABSTRACT

Land-based pollution in coastal ecosystems occurs when harmful substances originating from activities occurring on the land are transported, along with water and sediments, through watersheds into the nearshore environment. Heavy metals are found in the coastal ecosystem of Hawaiʻi, often associated with land-based sediment. Sediment characteristics can provide insight to better understand metal contamination, because sediments can retain pollutants from the surrounding water via processes such as hydrolysis and absorption. Percent organic matter (POM) and grain size analysis are two fundamental sediment characteristics. This study analyzes these two sediment characteristics in samples taken from 22 locations throughout Oʻahu and Kauaʻi in Hawaiʻi, and it examines their relationship with metal concentrations. The highest POM was found at Kāneʻohe Bay (5.65%), which was also the site with the greatest fraction of sediment in the smallest grain size class (5.76% in <53 um) and in the largest size class (47.16% in >4000 μm). In contrast, Haleʻiwa Harbor had the lowest POM (2.75%). One-way ANOVA and linear regression were used to analyze the relationships between POM, grain size distribution, and metal concentrations. Significant relationships were found between the variables for some locations. In addition to the sediment characteristics, the results also revealed that sediment type and contaminant concentrations can have significant relationships with geography, land-use, and the presence of harbors. This study demonstrated the importance of sediment characteristics in future toxicology research that aim to understand the presence, behaviors, origins, and effects of pollutants in coastal ecosystems.

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1.0 INTRODUCTION

In ancient Hawaiʻi, each island, or moku, was divided into ahupuaʻa, or land divisions (Delevaux et al., 2018). To achieve the most effective resource and community management, most ahupuaʻa extend from mountain to the sea, often encompassing watersheds (Delevaux et al., 2018), and the design of this land-management system acknowledged that what happens on land affects the sea and vice versa (Delevaux et al., 2018). This connection between land and sea remains, and we can see this connection in the LBSP used on land that impact the aquatic. Today, the land-based pollutants of the modern industrial past and present are impacting the aquatic environment, especially in coastal ecosystems (Kong et al. 2018). These land-based pollutants pose negative impacts to the environment and increase the risk of major health issues and cancers in humans (Yi et al., 2001; Sojka et al., 2018).

Land-based pollution is a result of the introduction of harmful substances into coastal ecosystems that originate from activities occurring on the land (Diamante et al., 1991). Two major categories of land-based pollution sources are agricultural and industrial. Agricultural sources include fertilizers and pesticides (Maloku, 2015). These pollutants often enter the streams, estuaries and coastal waters via run-off and soil erosion. Industrial sources include organic and inorganic pollutants, which are produced from industrial and mining processes (Maloku, 2015). These pollutants enter the streams, estuaries and coastal waters via erosion and leaching into groundwater from disposal sites (Diamante et al., 1991). Once in the coastal waters, these land-based pollutants may spread to the deeper and broader oceans via the oceanic circulation systems.

The United States Environmental Protection Agency (EPA) has compiled a priority pollutant list for the chemical pollutants of major concern (EPA, 2014). Each pollutant group is regulated with testing methods developed by the EPA. There are currently 126 pollutants on the list, which includes heavy metals. In this study, I will specifically focus on six heavy metals: arsenic, lead, copper, nickel, thallium, and zinc.

1.1 Broader research context

The University of Hawaiʻi Sea Grant College Program has an ongoing research project addressing land-based pollutants in Hawaiian coral reef ecosystems. The project works closely with communities to examine contamination at sites along the coasts of Oʻahu and Kauaʻi. The objectives of the project are to (1) determine the presence of specific land-based pollutants, (2) compile data on the health of significant coastal ecosystems of Hawaiʻi, and (3) examine the transport of pollutants from land to sea. The project is providing useful information for resource managers and community organizations that will aid in future management plans. To support the ongoing work, the objectives of this thesis specifically are to: (1) analyze the percent organic matter (POM) of the sediments, and (2) to compare the POM to the grain size distribution and pollutant concentrations across sites.

1.2 Heavy metals

Heavy metals are an important group of aquatic pollutants. Some heavy metals, such as arsenic and mercury, can be highly toxic, abundant, and persistent (Tajam and Kamal, 2013; Sojka et al., 2018). There are both natural and anthropogenic sources of heavy metals (Bastami et al., 2015; Sojka et al., 2018; Tajam and Kamal, 2013). Heavy

metals can naturally occur from processes such as atmospheric deposition, erosion, acidification and weathering. Anthropogenic sources of heavy metals include industrial, agricultural, and aquacultural processes. In recent years, heavy metals from anthropogenic sources have become one of the major pollutants in the aquatic environment, especially in developing nations (Tajam and Kamal, 2013; Maloku et al., 2015).

Table 1. Heavy metals with sources and human health effects

Heavy metals	Sources	Human health effects
Arsenic	Wood preservatives, agriculture, pesticides	Skin, liver, bladder, and lung cancer
Copper	Boat and harbor paint, volcanic activity, mining, agriculture, pesticides	Liver and kidney damage
Lead	Leaded gasoline and paint, ceramics, batteries, cosmetics, pipes and plumbing material, solder, ammunition	Cardiovascular, kidney, and reproductive problems
Nickel	Volcanic soil, fossil fuel combustion, manufacturing facilities	Lung and nasal cancer
Thallium	Rat poisoning, pesticides, fossil fuel combustion, smelting, cement production	Liver and kidney damage, alopecia
Zinc	Wood preservatives, catalysts, smelting, mining, brass production, paint production	Decreasing cholesterol levels

Some major concerns of heavy metal are the possibilities of the sub-lethal or lethal effects on the fish and other marine organisms, as well as the human populations that consume these fish (Yi et al., 2001; Kong et al. 2018). Pollutants are transported from their sources on-land and into aquatic environments (Han et al., 2021), and coastal

areas adjacent to large human populations or industrial activities are most likely to be contaminated. Once they enter the aquatic environments through water and sediment, pathways into fish and other marine organisms depend on their specific characteristics. Pollutants may bioaccumulate in organisms, the process of toxins from the environment building up in an individual organism (Yi et al., 2001; Sojka et al., 2018). Starting from the bottom of the food chain, pollutants may also biomagnify, the process of toxins traveling up a food web and increase concentration levels as it increases trophic levels (Yi et al., 2001). The organisms in the higher trophic level marine organisms such as fish and shellfish that humans consume. As shown in Table 1, human exposure to these contaminants through consumption increase the risk of serious health issues such as liver and kidney damage, or bladder and skin cancer (EPA, 2007).

1.3 Relationship between pollutants and sediments

Sediments are key to the transport and fate of marine pollutants and, therefore, can help us understand their distribution (Uluturhan, 2010; Tajam and Kamal, 2013). The history of the human activities and pollution of an area can be represented in sediments (He et al., 2016). Pollutants can be retained in sediment from the water via adsorption, hydrolysis and co-precipitation of metal ions (Ding et al., 2016; Bastami et al., 2015). Therefore, sediments can be used to analyze the history of pollution in the area (Tajam and Kamal, 2013). Overall, the majority of free metal ions are retained in the sediment with a small fraction of the ions left in the water column, so water sampling alone would not be sufficient data for analysis of heavy metals of an area (Bastami et al., 2015).

Heavy metals tend to remain in the sediment once retained (Yi et al., 2001). However, sediments can release the retained pollutants back into the water, triggered by

changes in chemical and hydrological conditions (Ding et al., 2016), and act as an additional source of pollution in an area (Tajam and Kamal, 2013). In addition, bottom sediments are a major habitat and food source for benthic fauna, such as microorganisms and invertebrates. Therefore, the pollutants may spread to the surrounding flora and fauna, directly or indirectly (Yi et al., 2001).

1.4 Data being analyzed: POM and grain size distribution

To support the ongoing research, two fundamental sediment characteristics of toxicology research will be analyzed: POM and grain size. POM is an important indicator of sediment characteristics, it is simple to measure, and is a common part of environmental toxicology studies (Kimble et al., 2001). While sediment is made up of organic and inorganic matter, heavy metals are more likely to bind to organic matter and is carried throughout the watershed by organic matter (Anawar, 2013). Grain size distribution is another informative indicator of potential contaminant loads. Grain size is often used in geochemistry to study the affinities of small grain sizes and surface area to contaminants (Poppe et al., 2000). Previous studies suggest that percent organic matter is higher in smaller grain sizes, hence higher contaminant concentrations (Bastami, 2015). The goal of this study is to understand the relationship between the POM and grain size distribution. These sediment characteristics will then be compared to known pollutant concentrations to better understand how sediment type and composition relate to the introduction of metals into the marine environment, the trophic transfer of pollutants, and consequences for ecosystem health.

2.0 METHODS

2.1 Sampling locations

Sediment samples were collected from 22 locations along the coast of Oʻahu and Kauaʻi, Hawaiʻi between May 26, 2018 and February 1, 2020 as part of ongoing surveys of trophic transfer of contaminants in coastal environments (Figure 1). The samples were taken from two different efforts. The locations of the first round of sampling were chosen to be adjacent to areas that are potentially contaminated due to their land-use, such as landfills and agriculture. This round had three replicates per location of 10 cm depth. The second round of sampling were location in Maunalua Bay, where a more targeted effort was taken to look at sites where runoff occurs. This round had multi-increment with three replicates per location, where 25 small sediment cores of 10 cm depth in a 10 by 5 meter square were combined, homogenized, and subsampled.

Figure 1.   Sample locations along the coasts of (a) Oʻahu (b) Kauaʻi, and (c) Maunalua Bay on the south shore of Oʻahu.

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Table 2. Locations and descriptions of sample sites.

Island	Location	Description
Oʻahu	Kahala	Residential & golf course, channelized stream
Oʻahu	Niu Stream	Residential, channelized stream
Oʻahu	Wailupe Stream	Residential
Oʻahu	Wailupe	Residential, channelized stream
Oʻahu	Paikō	Residential, stream outflow from wetland
Oʻahu	Kuliouou Near Shore	Residential, near harbor - near shore
Oʻahu	Kuliouou Far Shore	Residential, near harbor - far from shore
Oʻahu	MBBP	Residential, near harbor
Oʻahu	Hawaiʻi Kai Harbor	Residential, near harbor
Oʻahu	Kewalo	Near the Kewalo Marine Lab, former landfill site
Oʻahu	Ala Wai	Near the Ala Wai canal outflow (by Magic Island) on sandy reef
Oʻahu	Sand Island	Sandy beach area near the harbor entrance
Oʻahu	Kāneʻohe Bay	Near the YWCA near the Marine Corps Base & Yacht Club
Oʻahu	Waimanalo Gulch	Near the outflow pipe in the cove, sandy well mixed area
Oʻahu	Haleʻiwa Harbor	Outside of harbor area in rocky reef area, well mixed
Kauaʻi	Hāʻena Manoa Stream	Has road running through stream, dry when sampled
Kauaʻi	Hāʻena Manoa Beach	Beach w/ high wave action, road running through stream, dry when sampled
Kauaʻi	Hāʻena Limahuli	Perennial stream
Kauaʻi	Anini	Near large stream outflow area on the reef
Kauaʻi	Hanapēpē Harbor	Industrial harbor with calm water, harbor near former landfill
Kauaʻi	Nāwiliwili Kalapaki	Stream area near the harbor with low water motion
Kauaʻi	Kekaha	Beach area

2.2 Sample pre-processing prior to study

Sediment samples were stored at -20 °C until processing. The samples were
analyzed for grain size distribution prior to the start of this study. Each location had three
replicates except for Kuliouou Near Shore and Hāʻena Manoa Beach which had two
replicates, while Haleʻiwa Harbor and Hāʻena Manoa Stream had one replicate.
Sediments were passed through 7 sieves that separate the sediment into eight categories
of grain size: <53 μm, 53-125 μm, 125-250 μm, 250-500 μm, 500-1000 μm, 1000-2000
μm, 2000-4000 μm, and >4000 μm. For the purposes of this study, the grain size will be
referred to by the lower end of the range (for example, 53-125 μm will be labeled as 53
μm). As shown in Table 3, each category of grain size is associated with different
sediment characteristics (Blair and McPherson, 1999). Sediments were sent to
collaborators at the Geochemical and Environmental Research Group at Texas A&M
University in College Station, Texas for dissolved pollutant analysis using gas
chromatography-mass spectrometry.

Table 3. Grain size distribution and sediment descriptions. Grain size classes will be
used to refer to the ranges throughout the study.

Grain size class (μm)	Grain size range (μm)	Sediment description
<53	<53	Mud
53	53-125	Very fine sand grain
125	125-250	Fine sand grain
250	250-500	Medium sand grain
500	500-1000	Coarse sand grain
1000	1000-2000	Very coarse sand grain
2000	2000-4000	Granule
4000	>4000	Pebble

2.3 Sample processing

68 mm aluminum trays were labeled with sample ID and weighed. Each sample was added into its respective tray and weighed. Then, the samples were placed into the drying oven at 60°C for at least 48 hours to evaporate water out of the sample. The samples were removed from the drying oven and weighed again before combustion: this is the dry weight of the sample (w_d). Next, the samples were placed into the muffle furnace at 500 °C for 4 hours to remove organic matter from the sample. The samples were removed from the muffle furnace, and a final weight was taken. This is the ash-free dry weight of the sample (w_{db}). Lastly, the POM was calculated for each sample as shown in Equation 1.

2.4 Data organization

2.4.1 Calculating POM

To calculate the POM the mass lost to burning (m_b) was found as follows:

$$m_b = w_d - w_{db} \tag{1}$$

where w_d is the sample weight after drying and w_{bd} is the sample weight after drying and burning. POM was found by dividing the mass lost to burning (m_b) by the sample weight after drying (w_d) and multiplying by 100 to convert it to a percentage:

$$POM = \frac{m_b}{w_d} \times 100 \tag{2}$$

2.4.2 Filtering

Most sites had three replicates of samples used for POM analysis. At some locations, the entire sample was consumed in the processing for heavy metal and grain size analysis. Therefore, Kuliouou Near Shore and Hāʻena Manoa Beach had two replicates. Hāʻena Manoa Stream and Haleʻiwa Harbor both had one replicate.

Table 4. Location and categories in the geographic, land-use, and harbor groupings.

Location	Geographic groups	Land-use groups	Harbor groups
Kahala	Maunalua Bay, Oʻahu	Residential	Non-harbor
Niu Stream	Maunalua Bay, Oʻahu	Residential	Non-harbor
Wailupe Stream	Maunalua Bay, Oʻahu	Residential	Non-harbor
Wailupe	Maunalua Bay, Oʻahu	Residential	Non-harbor
Paikō	Maunalua Bay, Oʻahu	Residential	Non-harbor
Kuliouou Near Shore	Maunalua Bay, Oʻahu	Residential	Harbor
Kuliouou Far Shore	Maunalua Bay, Oʻahu	Residential	Harbor
MBBP	Maunalua Bay, Oʻahu	Residential	Harbor
Hawaiʻi Kai Harbor	Maunalua Bay, Oʻahu	Residential	Harbor
Kewalo	Rest of Oʻahu	Industrial	Harbor
Ala Wai	Rest of Oʻahu	Industrial	Harbor
Sand Island	Rest of Oʻahu	Industrial	Harbor
Kāneʻohe Bay	Rest of Oʻahu	Residential	Harbor
Waimanalo Gulch	Rest of Oʻahu	Industrial	Non-harbor
Haleʻiwa Harbor	Rest of Oʻahu	Industrial	Harbor
Hāʻena Manoa Stream	Hāʻena, Kauaʻi	Semi-rural	Non-harbor
Hāʻena Manoa Beach	Hāʻena, Kauaʻi	Semi-rural	Non-harbor
Hāʻena Limahuli	Hāʻena, Kauaʻi	Semi-rural	Non-harbor
Anini	Rest of Kauaʻi	Semi-rural	Non-harbor
Hanapēpē Harbor	Rest of Kauaʻi	Industrial	Harbor
Nāwiliwili Kalapaki	Rest of Kauaʻi	Industrial	Harbor
Kekaha	Rest of Kauaʻi	Semi-rural	Beach area

As shown in Table 4, there were three different groupings made for analysis purposes: geographic, land-use, and harbor groups. The geographic groups were organized into four categories. The first group of sites are all located in Maunalua Bay, Oʻahu at the stream outflow areas throughout the bay. The rest of sites on Oʻahu comprise the second. The third group of sites are all in Hāʻena, Kauaʻi. The fourth group includes the rest of the Kauaʻi sites. The land-use groups were seperated into three categories: residential, industrial, and semi-rural. Harbor groups were separated into harbor versus non-harbor locations to analyze harbors as an independent variable.

2.5 Data analysis

The mean and standard deviation of POM, grain size distribution, and metal concentrations were calculated for each location. First, to examine spatial patterns of sediment characteristics, grain size and POM were compared between locations using analysis of variance (ANOVA). Note that because the grain sizes are fractions of a whole, the comparisons of each grain size across sites are not independent of one another. In addition, POM was modeled as a function of grain size using linear regression. Second, to examine spatial patterns of heavy metals contamination, the concentration of metals was compared across sites and groupings using ANOVA. Additionally, to evaluate the relationship between sediment and metals, the concentration of metals was related to POM and grain size using linear regression.

3.0 RESULTS

3.1 POM

POM differed between locations (ANOVA, $F(21, 36) = 5.07$, $P < 0.0001$, Figure 2), but there were no significant differences in POM between geographic or land-use groupings (ANOVA, $P > 0.05$, see Appendix 1). The average POM of all locations was 2.75%. Kāneʻohe Bay had the highest mean POM (5.65%). Hanapēpē Harbor had the second highest POM, followed by Anini (4.77% and 4.18%, respectively). The location with the lowest mean POM was Haleʻiwa Harbor (1.40%).
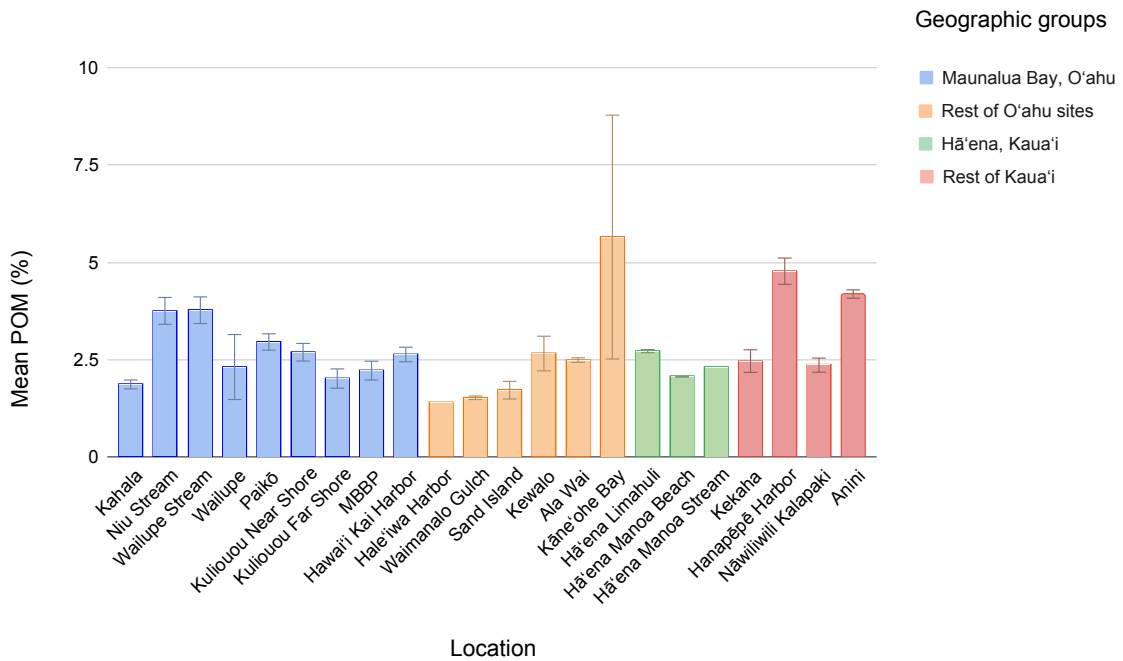

Figure 2. Mean POM at each location. Error bars represent the standard deviation. The locations are categorized into the geographic groups by color.

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3.2 Grain size distribution

All grain size classes except 53 μm differed between locations (P < 0.0001) (see
Appendix 2). The greatest variation between locations were in the 250, 1000, and 125 μm
size classes with (F(21, 39) = 77.86, 30.27 and 23.97, respectively). The <53 μm size
fraction had the lowest variation between locations (F(21, 39) = 2.22), followed by 4000,
2000, and 500 μm size fractions (F(21, 39) = 5.42, 8.33 and 16.65, respectively).
Kāneʻohe Bay had the highest percentage of sediment in the two lowest grain size
classes: <53 and 53 μm (5.76% and 21%, respectively) (Figure 3). It also had the highest
percentage in the largest size class, 4000 μm (47.16%). Nāwiliwili had fine-grained
sediment and had the highest percentage in the 125 μm size class (51.21%). Kekaha and
Waimanalo Gulch both had high percentages of sediment in the sand size fraction (250
and 500 μm). Anini and Wailupe, which both receive stream runoff, had the highest
percentages of sediment in the 1000 (very coarse sand grain) and 2000 μm size classes
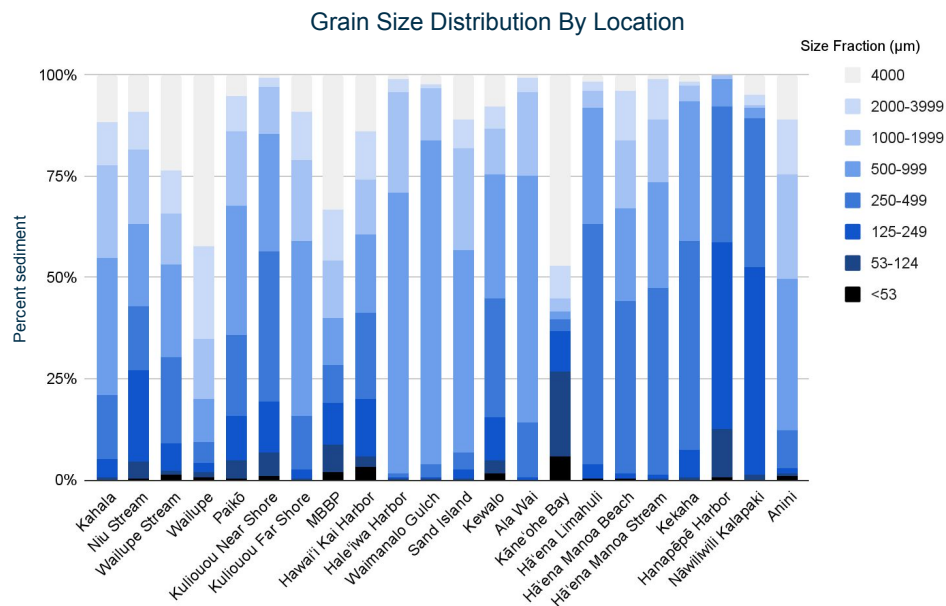(granule), respectively (26.02% and 2.99%) (Appendix 2).

Figure 3. Grain size distribution at each location.

Table 5. Mean percent of sediment for each grain size class (µm) at each location. The highest concentration for each grain size class is bolded. The highest concentration for each location is italicized.

| Location	<53	53	125	250	500	1000	2000	4000
Kahala	0.13	0.39	4.61	15.77	*33.81*	23.06	10.53	11.69
Niu Stream	0.41	4.16	*22.41*	15.84	20.28	18.42	9.36	9.12
Wailupe Stream	1.17	1.18	6.82	21.29	22.90	12.32	10.85	*23.47*
Wailupe	0.59	1.37	2.11	5.41	10.42	14.87	**22.99**	*42.24*
Paikō	0.33	4.61	10.76	20.07	*32.08*	18.19	8.66	5.29
Kuliouou Near Shore	0.83	5.92	12.48	*37.19*	29.03	11.47	2.50	0.58
Kuliouou Far Shore	0.03	0.41	2.21	13.18	*43.05*	20.24	11.73	9.16
MBBP	1.86	6.99	10.31	9.16	11.80	14.02	12.72	*33.15*
Hawaiʻi Kai Harbor	3.14	2.76	14.24	*21.24*	19.12	13.65	12.08	13.78
Haleʻiwa Harbor	0.00	0.30	0.30	0.90	*69.30*	24.90	3.25	1.06
Waimanalo Gulch	0.00	0.27	0.27	3.34	**79.88**	13.00	0.95	2.28
Sand Island	0.12	0.14	2.30	4.18	*50.12*	25.07	7.04	11.03
Kewalo	1.64	3.12	10.57	29.52	*30.77*	10.99	5.67	7.72
Ala Wai	0.01	0.04	0.50	13.49	*61.15*	20.75	3.45	0.61
Kāneʻohe Bay	**5.76**	**21.00**	9.95	2.85	2.03	3.38	7.78	***47.16***
Hāʻena Limahuli	0.25	0.21	3.53	*59.16*	28.82	4.23	2.14	1.65
Hāʻena Manoa Beach	0.17	0.09	1.22	*42.74*	22.99	16.66	12.34	3.79
Hāʻena Manoa Stream	0.12	0.10	1.09	*45.94*	26.16	15.50	10.21	0.87
Kekaha	0.15	0.38	6.84	***51.58***	34.71	3.70	1.11	1.53
Hanapēpē Harbor	0.52	12.09	*46.14*	33.59	6.75	0.73	0.11	0.07
Nāwiliwili Kalapaki	0.08	1.15	***51.21***	36.92	2.44	0.88	2.57	4.74
Anini	0.95	0.68	1.20	9.42	*37.26*	**26.02**	13.62	10.86

3.3 POM and grain size
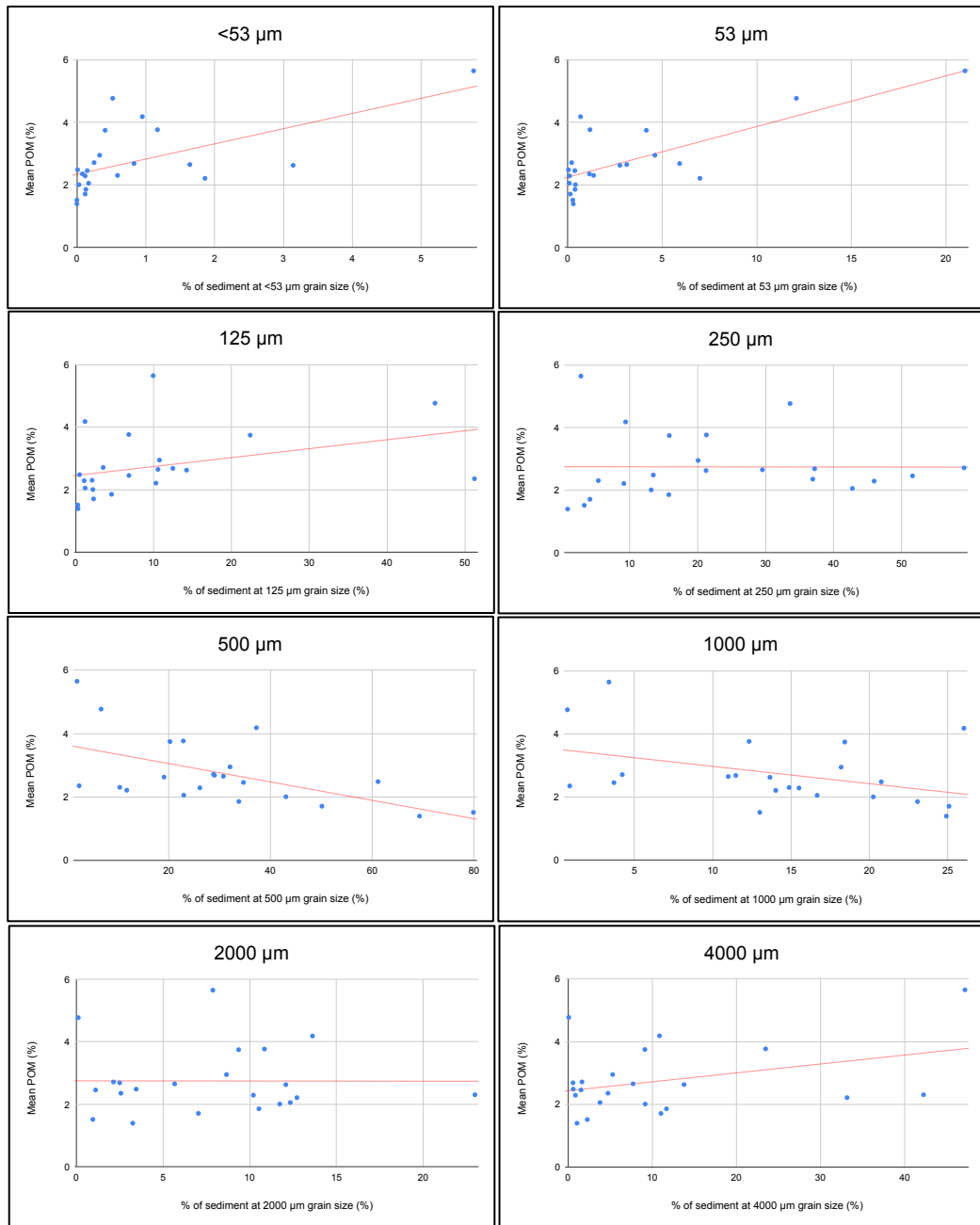
Figure 4. Comparison of relationships between POM and percent sediment in different grain size classes at each location.

POM was higher at sites with a higher proportion of sediment in the <53um size class ($P = 0.002$, $R^2 = 0.38$, $F(1, 20) = 12.01$) and the 53 μm size class ($P < 0.0001$, $R^2 = 0.58$, $F(1, 20) = 27.29$). POM was lower at sites with a higher proportion of 500 μm sediments ($P = 0.007$, $R^2 = 0.31$, $F(1, 20) = 8.97$). There was no relationship between POM and other grain size classes (all $P > 0.05$).

3.4 Heavy metal concentrations

As shown in Table 7, arsenic was found at the highest concentrations at MBBP (64.14 mg/kg). Wailupe Stream had the highest concentration of copper (26.00 mg/kg), and Manoa Steam in Hāʻena had the highest concentrations of nickel (346.67 mg/kg). This was notably higher than the concentration of nickel at other locations, which ranged from 10.37 to 146.67 mg/kg. Lead was found at the highest concentrations at Kewalo (75.99 mg/kg). Concentrations of thallium were relatively low throughout all sampled locations, with MBBP having the highest concentrations (1.11 mg/kg). Zinc concentrations were highest at Hanapēpē Harbor (282.93 mg/kg), which were nearly double the concentration of the next highest location, Kāneʻohe Bay (142.50 mg/kg).

Metal concentrations differed by location. Copper varied significantly between locations ($P < 0.0001$, $F(17, 34) = 28.82$). Because copper is associated with paints used on boats, we grouped locations into harbors versus non-harbor and found that copper concentrations higher in harbor locations ($P < 0.0001$, $F(1, 50) = 3.95$).

Lead varied by location ($P < 0.0001$, $F(16, 29) = 6.90$), although the ratio of between site to within site variability was less than copper; it also varied between land-use groups ($P < 0.0001$, $F(2, 43) = 6.88$).
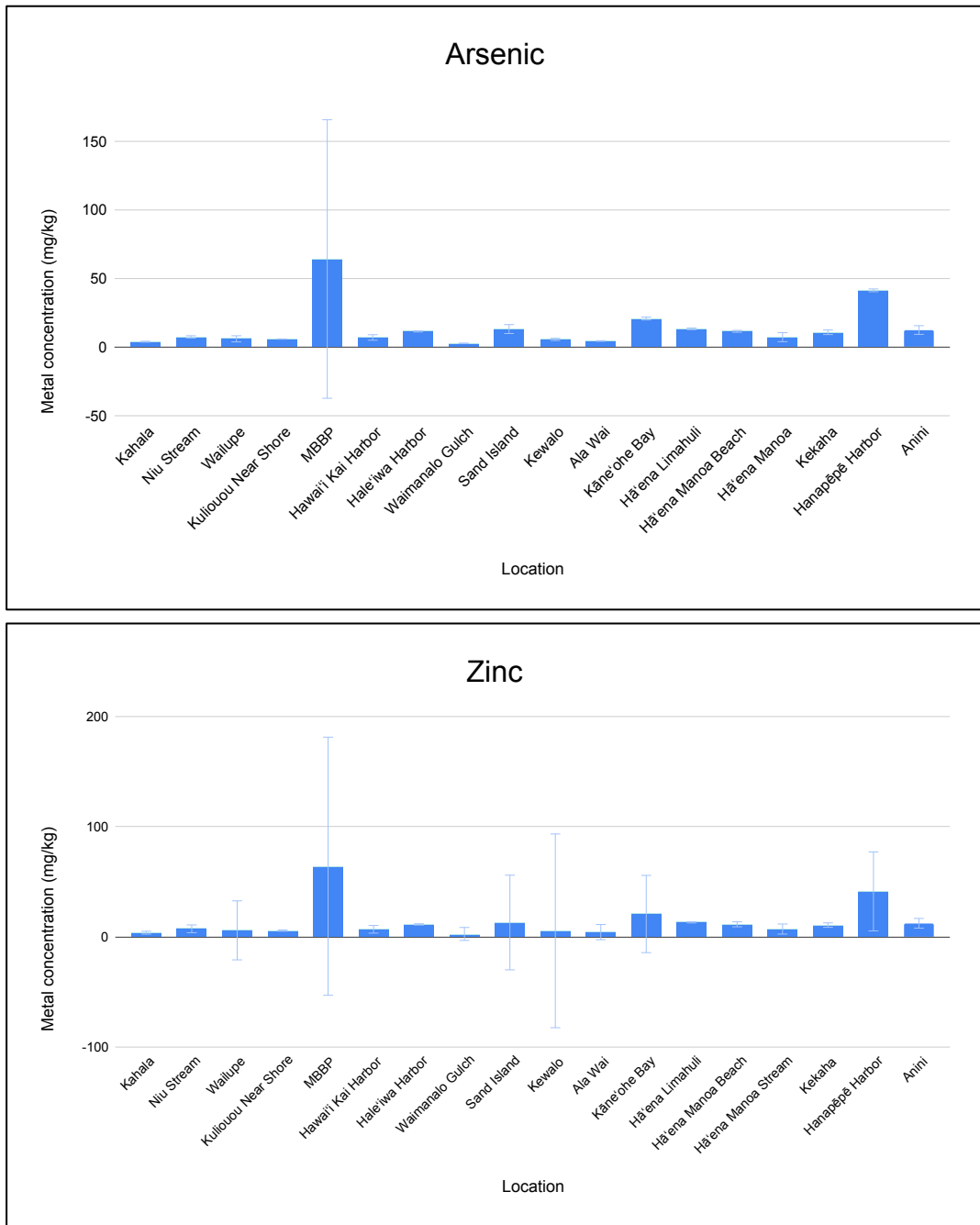
Figure 5. Metal concentration of arsenic and zinc at each location. Error bars represent the standard deviation.

Table 6. Mean metal concentrations at each location. The highest concentration for each metal is bolded. ND indicated that data was not available for that location.

Locations	Arsenic	Copper	Lead	Nickel	Thallium	Zinc
Kahala	3.93	3.73	5.53	10.37	ND	8.50
Niu Stream	7.45	12.00	1.45	46.50	ND	18.00
Wailupe Stream	6.03	**37.00**	12.00	87.00	ND	64.33
Kuliouou Near Shore	5.83	6.30	0.97	18.00	0.04	9.43
MBBP	**64.14**	3.25	1.16	22.34	**1.11**	82.09
Hawai'i Kai Harbor	7.00	4.07	1.37	72.67	0.04	12.10
Hale'iwa Harbor	11.44	1.04	0.03	21.12	0.02	3.04
Waimanalo Gulch	2.78	3.53	5.00	43.67	0.01	17.13
Sand Island	13.15	2.52	4.68	21.82	0.01	47.93
Kewalo	5.60	11.81	**75.99**	40.86	0.02	115.54
Ala Wai	4.45	8.79	4.86	12.27	0.02	37.61
Kāne'ohe Bay	20.83	7.35	18.94	21.21	0.03	142.50
Hā'ena Limahuli	13.33	6.37	0.29	146.67	ND	12.33
Hā'ena Manoa Beach	11.50	2.25	0.23	96.00	ND	6.30
Hā'ena Manoa Stream	7.23	26.00	0.64	**346.67**	ND	37.00
Kekaha	10.79	2.97	ND	54.25	0.01	13.36
Hanapēpē Harbor	41.33	10.15	53.80	70.10	0.02	**282.93**
Anini	12.44	4.91	0.55	21.40	0.02	26.77

Nickel concentration differed between locations ($P < 0.0001$, $F(17,35) = 48.66$) and had the highest ratio of between site to within site variability. Land-use groups were also tested, and significant differences were found in nickel concentrations between them ($P < 0.0001$, $F(2, 50) = 10.65$). Zinc had a relatively low variance between locations, but the differences were significant ($P < 0.0001$, $F(17, 34) = 9.17$). There was also a significant difference in zinc concentrations between harbor and non-harbor locations (P

< 0.0001, $F_{(1, 50)} = 14.57$), as well as between residential, industrial, and semi-rural locations ($P = 0.04$, $F_{(2, 49)} = 3.53$).

There were no significant differences in arsenic and thallium concentrations between locations ($P = 0.32$ and $P = 0.54$, respectively) (see Appendix 3). For arsenic, one of the concentration values at Kāneʻohe Bay was notably higher than the rest of the data set (181.2 mg/kg versus the range of concentrations of other locations being 2.71 to 42.45 mg/kg) which could have been inaccurately increasing the variability in the data. Therefore, a second ANOVA test was conducted without the outlier value. Significant differences were seen between the other locations ($P < 0.0001$, $F_{(16, 33)} = 84.66$), but there were no significant differences between land-use groups.

3.5 Metals and sediment characteristics

3.5.1 Metals and POM

Linear regression was performed to test if heavy metal concentrations were significantly correlated to POM. Zinc was the only metal that had a significant positive relationship with POM ($P = 0.005$, $R^2 = 0.39$, $F_{(1, 16)} = 10.22$, b = 3824.18). None of the other metals had a statistically significant relationship with POM (all $P > 0.05$).
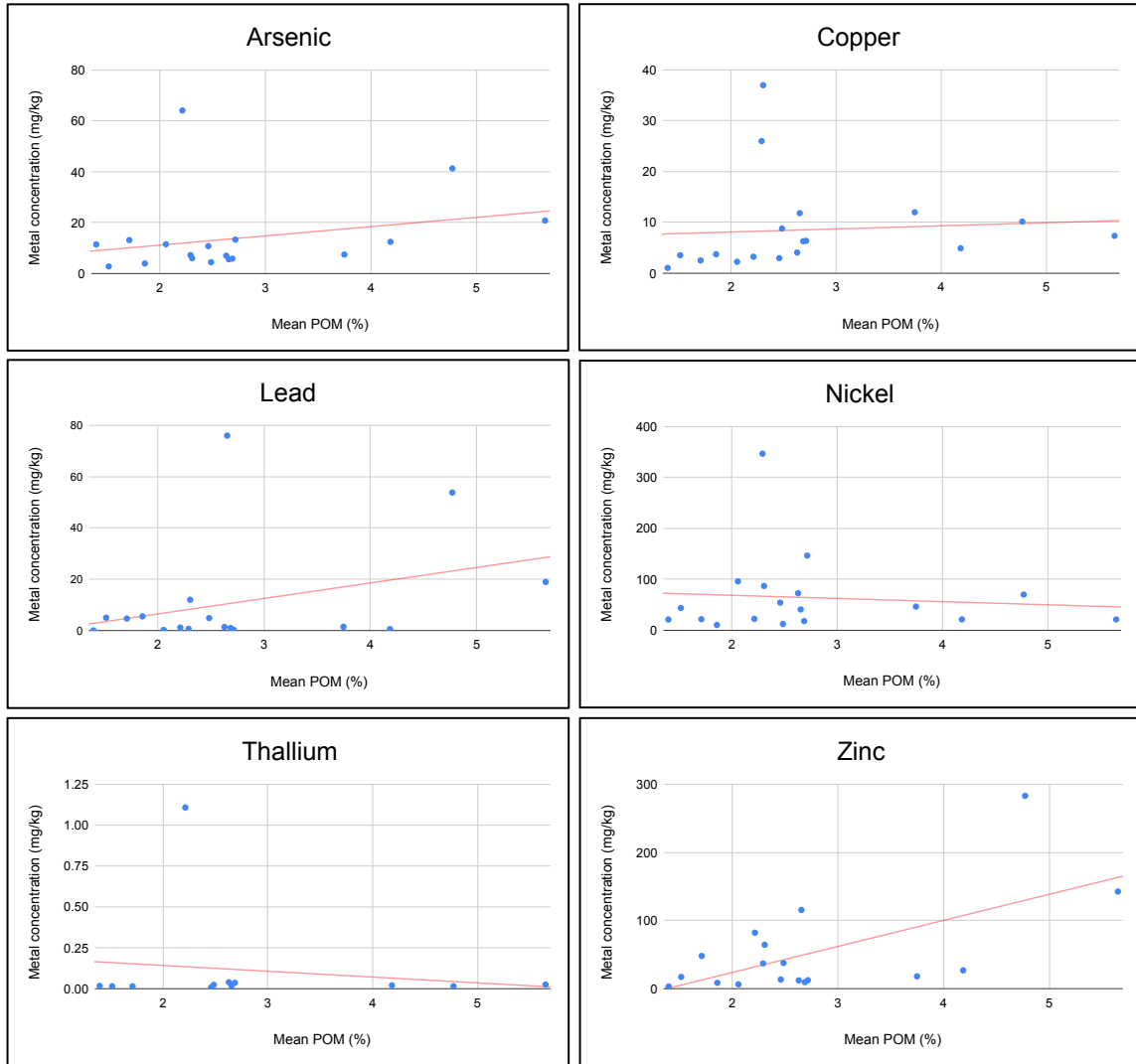
Figure 6. Concentrations of metals versus POM for (a) arsenic, (b) copper, (c) lead, (d) nickel, (e) thallium, (f) zinc. Comparison of relationships between metal concentrations and POM at each location.

3.5.2 Metals and grain size

The relationship between heavy metal concentrations and grain size was tested with a linear regression. The percent of sediment in the 53 μm grain size class also had a significant positive relationship with zinc ($P = 0.001$, $R^2 = 0.49$, $F(1, 16) = 15.08$) and arsenic ($P = 0.04$, $R^2 = 0.23$, $F(1, 16) = 4.90$). None of the other grain size classes had a statistically significant relationship with any of the other metals examined (all $P > 0.05$).
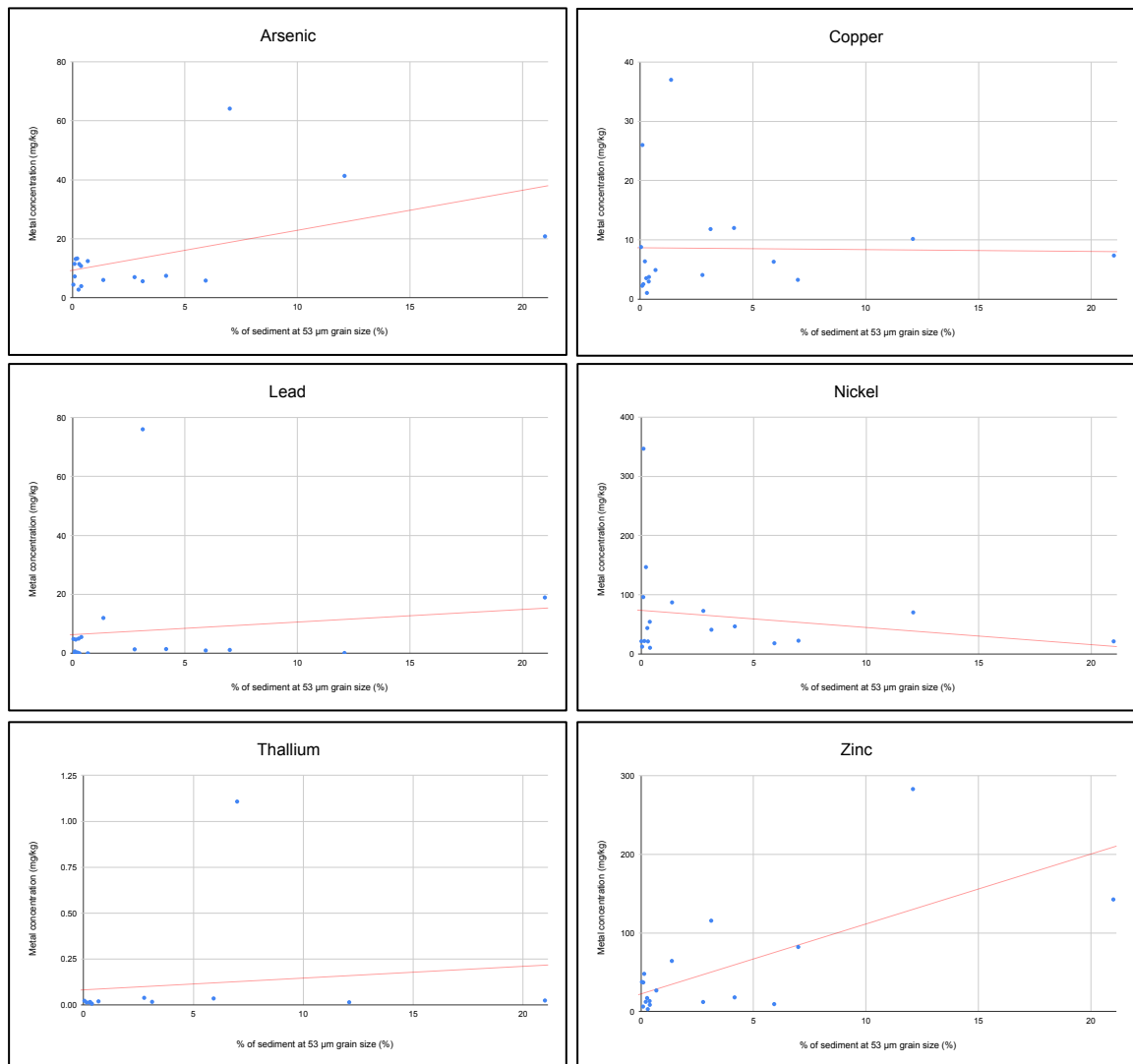
Figure 7. Comparison of the relationship between metal concentrations to percent sediment in the 53 μm grain size class at each location.

4.0 DISCUSSION

High POM was positively related to small grain sizes, and these two characteristics were associated with stream mouths. Kāneʻohe Bay, Hanapepe, and Anini sites were all near a stream mouth, and these sites had the highest POM. Kāneʻohe Bay had the highest percent of sediment in the two smallest grain size classes. This grain size distribution is

aligned with its POM results and can be explained by the stream mouth location, which had small mud particles that can adhere to POM (<53 and 53 μm). Hanapēpē Harbor sediments were concentrated in the lower grain sizes with very fine, fine, and medium sand grains. In contrast, Anini had the highest percent of sediment in the 1000 μm grain size class but also had high POM. The sample site was located near a large stream outflow area on the reef. Although it is very coarse sand and not smaller grains, the area may receive suspended sediment from the stream outflow and wave action, which could contribute to the high POM.

Nāwiliwili had fine grain sand with the highest percent of sediment in the 125 μm class. A possible reason why the highest percent was not in a smaller grain size class is that the samples were not taken directly from the stream mouth, but rather in a calm area within the harbor. This reflects the relatively low POM value. The percentage of sediment in the 250 μm grain size fraction was highest at Kekaha, which was sampled in a well-mixed beach area with medium sand grains. Similarly, Waimanalo Gulch was sampled in a well-mixed sandy cove. It had a high percentage of sediment in the 500 μm coarse sand grain size class and had the second to lowest POM, after Haleʻiwa Harbor. Wailupe had the highest percent of sediment in the 2000 μm grain size class. The granule grain size can be explained by the channelized stream which was built to reduce erosion of the shore and may be preventing mud from traveling to the coast.

The low POM at Haleʻiwa Harbor was expected because although it is near a stream mouth, the samples were taken off the reef of Kawailoa Beach located north of the harbor. The highest percent of sediment at Haleʻiwa Harbor was in the 500 μm size fraction with coarse sand grain, which also aligns the characteristics of a well-mixed,

rocky reef area. Hale'iwa Harbor also had no sediment in the smallest grain size class, which would typically be correlated with higher POM. The regression between POM and grain size was significant in <53 and 53 μm, and negatively significant in the 500 μm grain size classes. This reflects Kāne'ohe Bay having both the highest POM and the highest percent of sediment in the <53 and 53 μm grain size class, while Hale'iwa Harbor had both the lowest POM and the highest percent of sediment in 500 μm. A possible limiting factor for Hale'iwa Harbor is that there was only one replicate processed for grain size analysis.

Some metal concentrations showed a significant relationship with the sediment characteristics, while some presented stronger relationships with spatial patterns. Arsenic had the highest concentrations at MBBP, followed by Hanapēpē Harbor and Kāne'ohe Bay. The three locations with the highest arsenic concentrations are harbor locations which may receive contaminants via run-off and leaching. Arsenic is known to be associated with wood preservatives that were used in the past before being banned for residential use, such as copper chromated arsenate (CCA) (EPA, 2007). MBBP and Kāne'ohe Bay are categorized in the residential land-use groups, which could still have remains of CCA. CCA is still used for industrial uses, which corresponds to Hanapēpē Harbor's industrial land use grouping. Another possible source of arsenic is agricultural pesticides used in the surrounding neighborhoods. Hanapēpē Harbor and Kāne'ohe Bay both had high POM and small grain sizes, which arsenic may adhere to.

At MBBP, the POM was close to the average POM of all locations, and it did not have a high percent of sediment in the smaller grain size classes. However, natural sources of arsenic could have been high due to the high sedimentation at MBBP. The

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regression by location showed a significant positive relationship between arsenic concentrations and grain size. This does not reflect the results of the three locations with the highest concentrations of arsenic, which showed a negative correlation between small grain sizes and high arsenic concentrations. This could be explained by these three sites being outliers. The rest of the locations can be found with low grain size and low arsenic concentrations (Figure 6).

Concentrations of copper were high at Wailupe stream, Hāʻena Manoa Stream, and Niu Stream. Copper is associated with boat paints and can often be found in high concentrations at harbors (EPA, 2007). These results do not support this relationship because all top three locations are not near harbors. However, all three locations are sampled at streams, which may have received concentrations of copper via run-off. No consistent relationships between sediment characteristics and copper concentrations were found.

Lead was found at the highest concentrations at Kewalo, and at the second highest concentrations at Hanapēpē Harbor. Both locations are categorized as industrial and are near harbors. Sources of lead are closely associated with industrial land-uses, including pipes, plumping materials, solder, and ammunition (EPA, 2007). Residues of leaded gasoline and leaded paint that were used for industrial purposes in the past could be contributing to the lead concentrations found in these locations (EPA, 2007). Neither sediment characteristic had a significant relationship with lead concentrations.

The three locations with the highest concentrations of nickel were all in Hāʻena, Kauaʻi: Hāʻena Manoa Stream, Hāʻena Limahuli, and Hāʻena Manoa Beach. Nickel is known to be associated with industrial activities such as fossil fuel combustion and

manufacturing facilities (EPA, 2007). However, Hāʻena is categorized as a semi-rural land-use area. Nickel can also be found in high concentrations in volcanic soil (EPA, 2007). Since nickel concentrations did not have a significant relationship with POM or grain size, this result could be reflecting the geographical location and the presence of volcanic soil in Hāʻena, Kauaʻi.

Thallium was found in high concentrations at MBBP, followed by Kuliouou Near Shore and Hawaiʻi Kai Harbor. Similar to nickel, a source of thallium is industrial activities such as fossil fuel combustion, smelting, and cement production (EPA, 2007). Other sources include the production of thermometers, electronic devices, and fireworks (EPA, 2007). However, all top three locations are residential and near harbors, not industrial. Although these sources could be contributing some to the thallium concentrations at these locations, a more likely source may be rodenticides for rat poisoning used in residential areas (EPA, 2007). All three sampling sites are near drainage areas that could be carrying run-off into the surrounding coastal waters. No significant relationships were found between the sediment characteristics and thallium concentrations, further supporting the likely relationship with the pesticides, residential land-use, and drainage at these locations.

The three locations with the highest zinc concentrations were Hanapēpē Harbor, Kāneʻohe Bay, and Kewalo. Zinc is associated with smelting and mining (EPA, 2007). It can also be found in paint, wood preservatives, catalysts, ceramics, fertilizers, batteries, and supplements (EPA, 2007). All three locations are located near harbors, which could be receiving concentrations of zinc through run-off and leaching. More importantly, zinc was the only metal to have significant relationships with both POM and grain size. Zinc

concentrations had a significant positive relationship with POM, suggesting that locations with higher POM would have higher zinc concentrations. Zinc concentrations also had a positive correlation to grain size. Hanapēpē Harbor and Kāneʻohe Bay, which had the two highest POM values of all sampled locations, follow the trend of high POM equating to high zinc concentrations. Kewalo, which has sediment in higher grain size classes, follows the trend of larger grain size and high POM. Zinc had a stronger relationship with POM, more than four times greater than that of grain size.

These result supports those of previous studies, which found that the grain size and POM of sediment had significant relationships with the heavy metal concentrations (Bastami, 2015). One limitation of this study was the insufficient supply of sample sediment from some locations. The lack of sediment replicates resulted in some locations having fewer samples to test. The next steps of this study would be to compare the sediment characteristics and heavy metals to organic pollutants such as polychlorinated biphenyls (PCBs), which have been banned in the U.S., and pesticides (Markowitx, 2018). Like heavy metals, PCBs and pesticides continue to be a major health concern related to coastal environments (Markowitz, 2018).

5.0 CONCLUSION

In this study, significant relationships between POM, grain size distribution, and metal concentrations were found throughout the coasts of Oʻahu and Kauaʻi, Hawaiʻi. The analysis of the relationship between the two sediment characteristics found that there was a significant relationship between POM and grain size in the grain size classes <53, 53, and 500 μm. Overall, the data followed the trend identified by previous studies, where POM was more likely to adhere to smaller grain sizes (Bastami, 2015). Arsenic had a

significant relationship with grain size, and zinc had a significant relationship with both POM and grain size. Other factors such as geography, land-use, and harbors also influenced POM, grain size, and metal concentrations. This study demonstrated the importance of analyzing sediment characteristics to better understand the distribution of land-based pollutants. As future studies of land-based pollutants expand throughout the unique geography and ecosystems of Hawaiʻi, POM and grain size distribution will be two fundamental variables to successfully analyze the presence, behaviors, origins, and effects of pollutants in the coastal ecosystems.

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APPENDIX

APPENDIX 1

One-way analysis of POM by location, geographical groups and land-use groups

Table 7.   ANOVA analysis of POM by location

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	0.00668529	21	0.00031835	5.07052585	1.04737E-05
Within Groups	0.00226022	36	6.2784E-05		
Total	0.00894551	57			

Table 8.   ANOVA analysis of POM by geographical groups

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	0.00065846	3	0.00021949	1.43022305	**0.24404501**
Within Groups	0.00828705	54	0.00015346		
Total	0.00768488	51			

Table 9.   ANOVA analysis of POM by land-use groups

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	0.00082663	2	0.00041331	2.9530013	**0.06153444**
Within Groups	0.00685825	49	0.00013996		
Total	0.00768488	51			

APPENDIX 2

Analysis of grain size distribution by location

Table 10. ANOVA analysis of <53 μm

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	0.01117244	21	0.00053202	2.21512671	0.0155563
Within Groups	0.00936688	39	0.00024018		
Total	0.02053932	60			

Table 11. ANOVA analysis of 53 μm

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	0.01117244	21	0.00053202	2.21512671	0.05005728
Within Groups	0.00936688	39	0.00024018		
Total	0.30951561	60			

Table 12. ANOVA analysis of 125 μm

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	1.1515991	21	0.05483805	23.9709595	3.749E-16
Within Groups	0.08921979	39	0.00228769		
Total	1.24081889	60			

Table 13. ANOVA analysis of 250 μm

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	1.62365983	21	0.07731713	77.8634718	1.6933E-25
Within Groups	0.03872635	39	0.00099298		
Total	1.66238618	60			

Table 14. ANOVA analysis of 500 μm

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	2.36360449	21	0.11255259	16.6483211	1.6933E-25
Within Groups	0.2636633	39	0.0067606		
Total	2.62726779	60			

Table 15. ANOVA analysis of 1000 μm

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	0.37098313	21	0.01766586	30.265205	1.6933E-25
Within Groups	0.02276438	39	0.0005837		
Total	0.39374752	60			

Table 16. ANOVA analysis of 2000 μm

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	0.18550615	21	0.00883363	8.33471087	1.6933E-25
Within Groups	0.04133454	39	0.00105986		
Total	0.22684069	60			

Table 17. ANOVA analysis of 4000 μm

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	2.36360449	21	0.11255259	16.6483211	1.6933E-25
Within Groups	0.2636633	39	0.0067606		
Total	2.62726779	60			

APPENDIX 3

Analysis of metal concentrations by location

Table 18.   ANOVA analysis of arsenic

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	11947.4946	17	702.793802	1.19111078	0.32040649
Within Groups	20651.1295	35	590.032273		
Total	32598.6242	52			

Table 19.   ANOVA analysis of copper

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	4220.00117	17	248.235363	28.8183019	2.47E-15
Within Groups	292.869523	34	8.61380949		
Total	4512.87069	51			

Table 20.   ANOVA analysis of lead

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	21134.9639	16	1320.93524	6.89959067	4.04947E-06
Within Groups	5552.08619	29	191.451248		
Total	26687.0501	45			

Table 21.   ANOVA analysis of nickel

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	317949.295	17	18702.8997	48.6624379	2.44225E-19
Within Groups	13451.8844	35	384.339554		
Total	331401.179	52			

Table 22. ANOVA analysis of thallium

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	3.23902244	11	0.29445659	0.91662562	0.541697978
Within Groups	7.0672745	22	0.32123975		
Total	10.3062969	33			

Table 23. ANOVA analysis of zinc

	Sum of Squares	df	Mean Square	F	P-value
Between Groups	243743.507	17	14337.8534	9.16661025	3.10381E-08
Within Groups	53180.7289	34	1564.13909		
Total	296924.236	51			