Effects of antifouling paint and particle size on metal concentrations in Okahu Bay

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Abstract:

The aim of this study was to analyze the effect of antifouling paint from moored boats on sediment in Okahu Bay, in order to help understand decades of pollution in the bay. In addition, it included an analysis of particle size vs. depth, and discussed the influence of particle size on metal concentration in sediment. Sediment was taken using a piston corer, and sediment was analyzed at depths of 0-2 cm, 12-14 cm, and 22-24 cm. A Malvern Mastersizer was used to determine particle size, while a Flame Atomic Absorption Spectrometer was used for metal concentration. In general, mooring type did not control metal concentration, however, moorings with maintained boats had much higher metal concentration at surface depths than expected. This finding showed that, in general, something besides antifouling paint controls metal concentration, but over the past few years, maintained boats have been a potent heavy metal pollution source. Analysis of mud fraction vs. metal concentration showed a high correlation, suggesting that particle size is a significant factor on metal concentration. This study suggests that future work keeps particle size in mind, and uses it as a means of revealing metal sources.

Introduction:

Okahu Bay is situated in Waitemata Harbor in Auckland, New Zealand (Figure 1). It is a bay of immense value to the Ngâti Whâtua iwi, who once owned the bay and relied on its abundance of seafood as a protein source (Faaui 2012). A main pillar of Maori culture is the preservation of natural resources for future generations. Thus, the Ngâti Whâtua thrived off the bay in a sustainable fashion, until the 19th century, when the iwi began to gradually lose control of the bay to European colonists. As Auckland developed into the enormous urban center it is today, Okahu Bay changed as well. Today, it is a hub of recreational marine activity and a pollution dilution site. As a result, the bay is drastically altered by a marina, a hardstand, a breakwater, hundreds of moorings, a heavily trafficked road, and a pipe that deposits storm water catchment runoff directly into the bay.

Figure 1: Location of Okahu Bay (Google Maps)

Wary of these developments, many studies have analyzed pollution in Okahu Bay with mixed results. The most conclusive result was a drastic decrease in the bay's shellfish population and a decrease in shellfish reaching maturity (Hauraki Gulf Forum, 2010). It is reasonable to assume this effect is a result of development in and around the bay; however, further studies have failed to pinpoint a precise cause. For example, several studies analyzed metal concentrations throughout the bay. In 2011, Poynter Associates determined that copper levels in the bay are elevated, but not above standard acceptable levels (Poynter Associates 2011). Another more broad report, carried out by the National Institute of Water and Atmospheric Research (NIWA), Auckland Regional Council and Ngâti Whâtua o Orâkei, found that there was no evidence of 'elevated metal contamination (NIWA 2008). A student driven research project, by Elliot Hurst and supervised by Dr. Kepa Morgan, found somewhat different results. While most sites did not have metal concentrations above ARC standards, one muddy location on the western end of the beach had unacceptably high copper values, and in general, more muddy areas had higher concentrations of zinc (Hurst 2012).

The inconsistent range of results concerning metal contamination in the bay is perplexing, and as Hurst recommends, further study is necessary. The findings of moderately raised metal concentrations in muddy locations, in conjunction with one sampling point of high copper concentration suggest a potent metal pollution source. While this undetermined source has not caused concentrations exceeding standard levels yet, further understanding

the cause will help prevent metal concentrations from reaching dangerous levels in the future. Thus, this study will closely follow Hurst's methods in an attempt to expand on his conclusions on particle size and metal contamination of sediment in the bay. In addition, this study will attempt to quantify the effect of antifouling paint on metal concentrations. This study expected higher metal values near moorings with boats regularly recoated with antifouling paint. However, a lack of correlation between type of mooring and metal concentration revealed that antifouling paint is not nearly as influential to metal concentrations as particle size of sediment. Even so, surface concentrations from moorings with well-maintained boats were higher than trends would predict, indicating that antifouling paint may have a negative effect.

Background:

Study of Okahu Bay requires a comprehensive understanding of its many pollution sources and ecosystem altering structures (See Figure 2). For example, manmade structures have considerably decreased the energy of the bay. In order to create an ideal harbor for recreational boaters, Okahu Bay is, to a certain extent, disconnected from the rest of Waitemata Harbor. The hardstand and marina jut out to enclose Okahu Bay on one side. Directly across from the beach, a breakwater slows the flow of waves, although it is of course permeable. The shape of the coastline isolates two more sides naturally. As a result of this disconnectedness from the energy of Waitemata Harbor, the water is calm enough for more fine particles to deposit on the sea floor.

In addition to this fundamental altering of the bay, several sources expose the bay to pollutants. One such source is the hardstand, where boats are washed, maintained and launched into the water. A filtration system installed in the last few years treats byproducts from these activities before it reaches the bay. However, prior to the filtration, the byproducts flowed directly into the bay. Based on an estimate of depositional rate of 7 mm per year in Okahu Bay, this filtration system only influences a few centimeters of sediment on the surface of the sea floor (Raukivi 2003). Such byproducts include heavy metals from paints, and organotins from pesticides used in the cleaning of boats (Capital Regional District). In certain concentrations, these byproducts are toxic. In particular, heavy metals harm marine biota by decreasing the dissolved oxygen content of water (Ellis 1996). Proximity to this hardstand is certainly an important factor in any metal concentration analysis of Okahu Bay.

Another pollution source is a pipe that deposits storm water into the bay. This water is a non-point source, therefore it could have picked up a wide variety of pollutants in its journey from the atmosphere to Okahu Bay. Considering the urban setting, such pollutants include a range of chemicals from vehicle emissions and asphalt, polycyclic aromatic hydrocarbons, and heavy metals, to name a few (Capital Regional District). In a smaller scale, these pollutants may reach the bay from direct runoff from Tamaki drive. A weakness of this study is its narrow scope; by only analyzing metal concentrations, this study ignores many other pollutants.
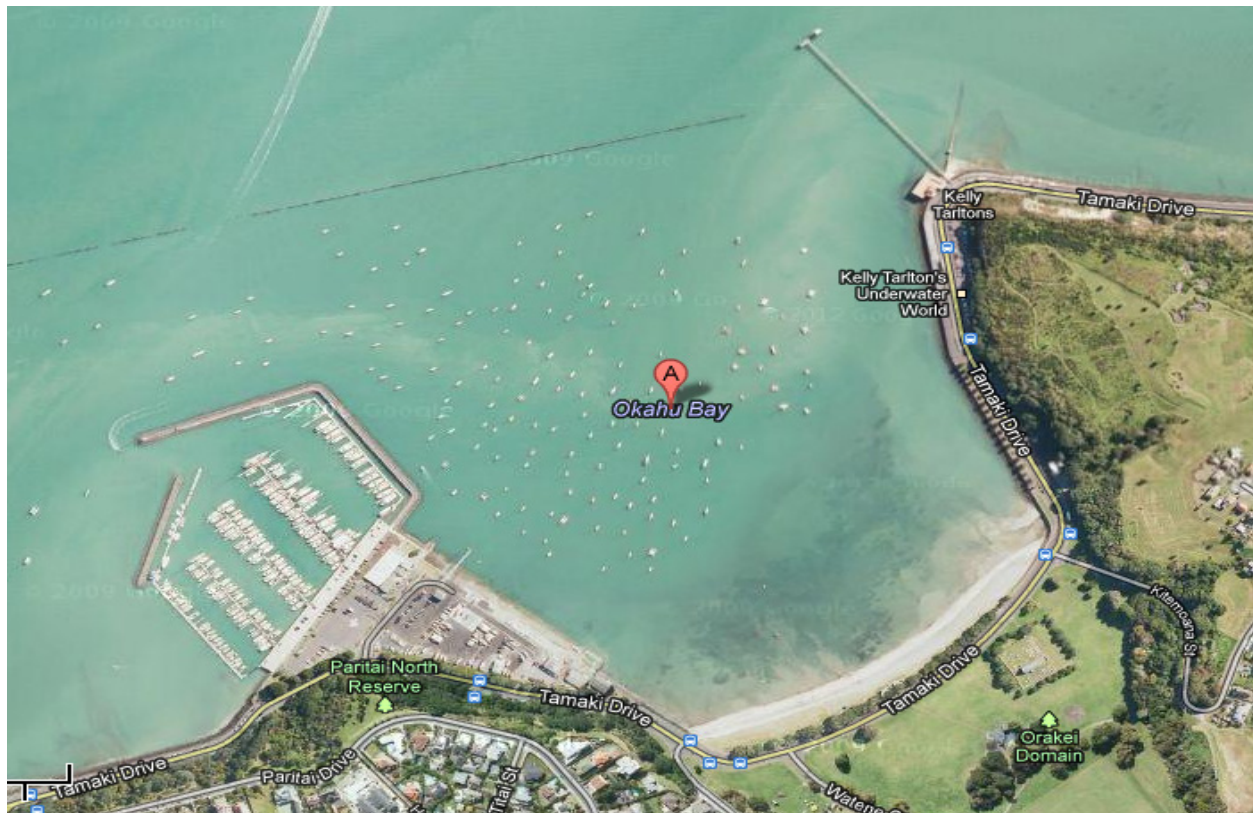

Figure 2: Okahu Bay (Google Maps)

A third pollution source, and a focus of this study, is the leeching of copper and zinc (Cu and Zn) from antifouling paint on boats on moorings. A 2010 study by Ytreberg, et al analyzed rates that Cu and Zn leech from antifouling paint, and concluded that Cu and Zn leech at rates fast enough to be a pollution concern (Ytreberg 2010). One assumption of this study is that these leeched metals are deposited in the sediment almost directly beneath the boat. Since the bay is a low energy environment, the metals likely settle before moving far, however, at depths of about five meters, it is worthwhile to keep this assumption in mind.

When analyzing the deposition of heavy metals, particle size of its sediment substrate is an essential factor to consider. Considering equal volumes of sediment, a sample made up of

smaller particle sizes will have a greater surface area than a sample made up of larger particles. Greater surface area allows for more sites that metal cations can bind to, and thus sediment with smaller sediment size will be able to more efficiently bind metal cations from the water (Sadeghi 2012). In order to quantify particle size, this study will determine what percentage of a sediment sample is made up of grain sizes below 63 mcg. This will hereafter be referred to as mud fraction.

Materials and Methods:

Sampling Procedure

Samples were taken from Okahu Bay during low tide over a few hours in the late morning of February, 22nd, 2013. 18 cores of sediment were obtained using a piston corer. These cores were taken from 6 different moorings, two with no boats attached, two with poorly maintained boats, and two with a well maintained boat (See Figure 3). A long-employed, knowledgeable skipper helped make these qualitative distinctions. At each of moorings, three cores were taken, each roughly 120 degrees apart and within 5 m of the mooring. Analysis of sediment in lab did not occur until late May. Until then, sediment was stored in halves of PVC pipes. This analysis followed the same procedure as Elliot Hurst (Hurst 2012).
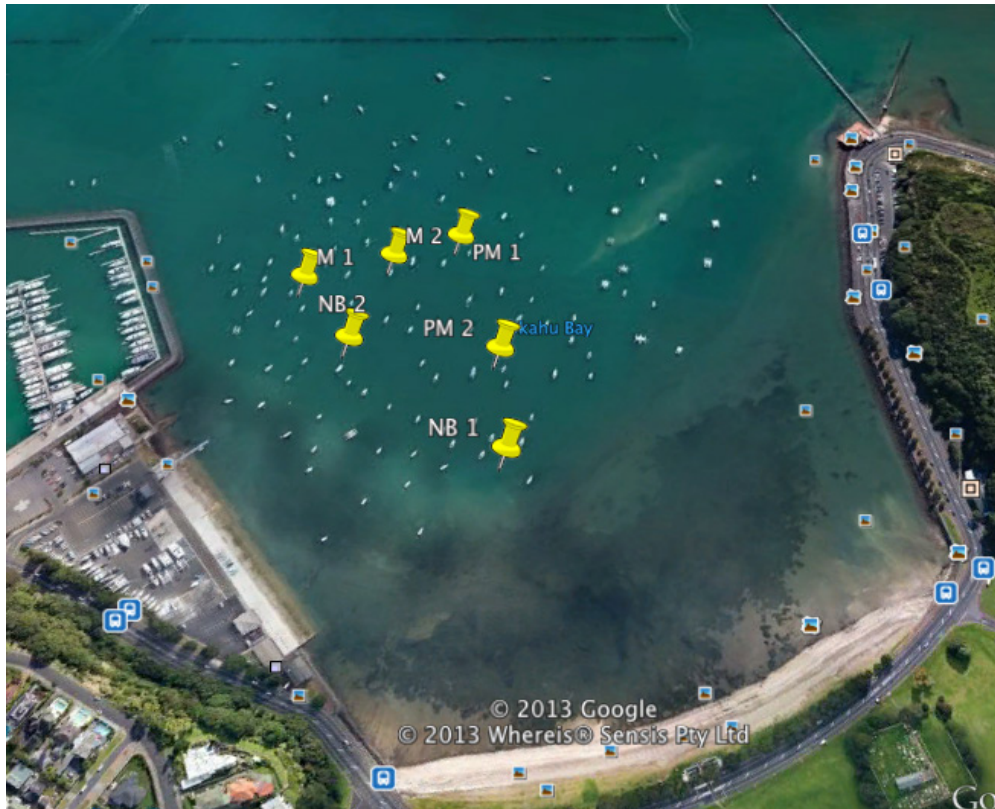

Figure 3: Piston core sites (Google Maps)

Particle Size Analysis

For each core, about 5 ml of sediment were taken from depths of 1 cm, 13 cm, and 23 cm, and placed in separate centrifuge tubes. The goal of the particle size analysis was to determine percentages of each range on the Wentworth grain size scale. This was achieved with the use of a Malvern Mastersizer, which determines each particle's size by observing how much each grain of sediment refracts a laser. In order to ensure the assortment of grains was suspended in solution and evenly distributed, several steps were taken. 20 mL of .55% Calgon solution was added to the sediment, which was then shaken until all sediment dispersed into solution and allowed to sit for 24 hours. Next, each tube was shaken, and set in an ultrasonic bath for 10 minutes. The Malvern Mastersizer requires only a few mL of suspended solution, which was extracted from the tubes with a bulb pipette. Before extraction, each tube was shaken once more, and sediment drawn out of the tube while spinning in a Vortex device. It is important to extract the solution slowly, with the pipette starting from the bottom and steadily drawing in solution as it is pulled out. In addition, all of the solution from the pipette must be expelled into the Mastersizer. When done properly, these precautions will ensure the mixture tested by the Mastersizer reflects the mixture of sediment accurately.

Heavy Metal Analysis

The metals tested were Cu and Zn, by a Flame Atomic Absorption Spectrometer. Similarly to the particle size analysis, sediment was taken from three different places on each core. In this case, however, all of the sediment was taken from the ranges 0-2 cm, 12-14 cm, and 22-24 cm. These samples were dried in an oven at 60 degrees Celsius, ground by mortar and pestle, then put through a 500 mcg sieve. Roughly 2 g of sediment was weighed out, and boiled in 70% nitric acid for 30 minutes. 25 mL of this solution was poured off into a centrifuge tube, which was then centrifuged at 3000 rpm for 5 minutes. 15 mL of solution was drawn off from each tube, to remove any particles. This solution was tested using the spectrometer for Zn and Cu.

Data and Results:

Particle Size vs. Depth:
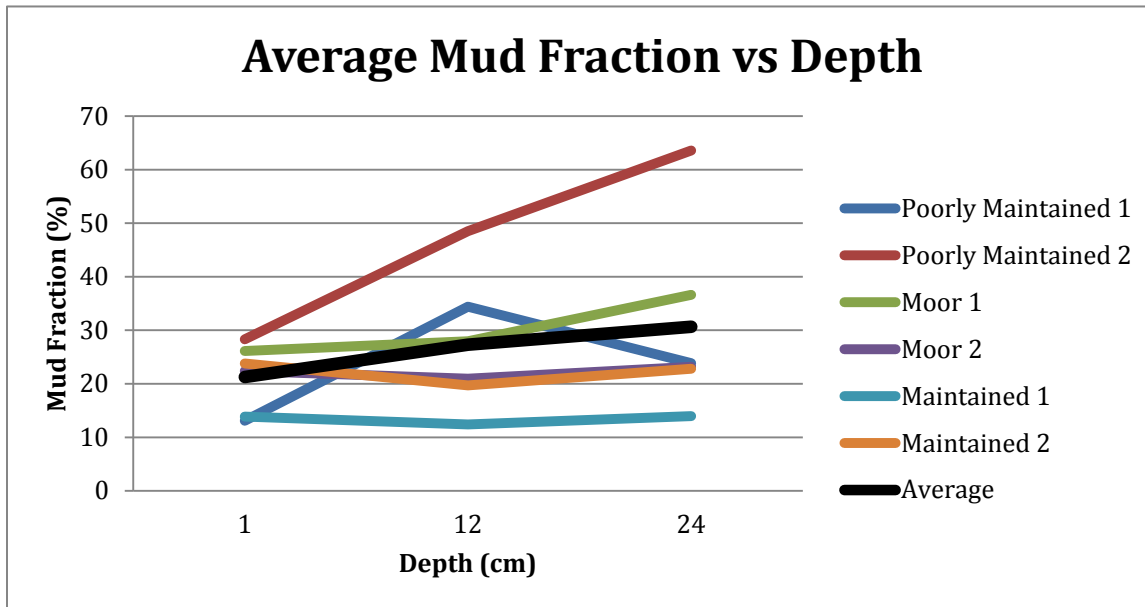
The chart above plots mud fraction vs. depth, averaged for each mooring, in order to give a rough history of sediment deposition. These results show a slight increase in mud fraction as depth increases. However, looking at each core individually reveals that this is an unreliable correlation. Cores show a variety of trends, as some increase at each interval, while others peak at 12 cm and drop at 24 cm, and many keep a constant mud fraction.

Metals vs. Mooring Type:

Zn Concentration vs Mooring Type
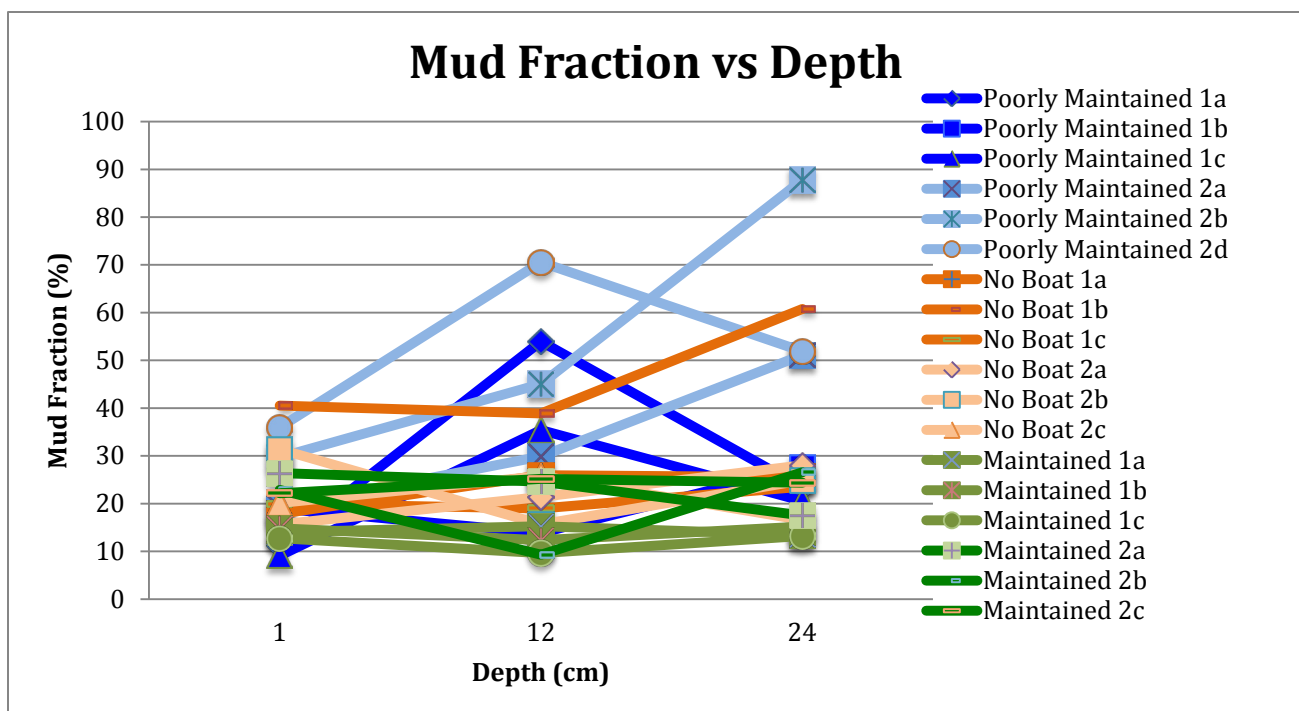
Cu Concentration vs Mooring Type
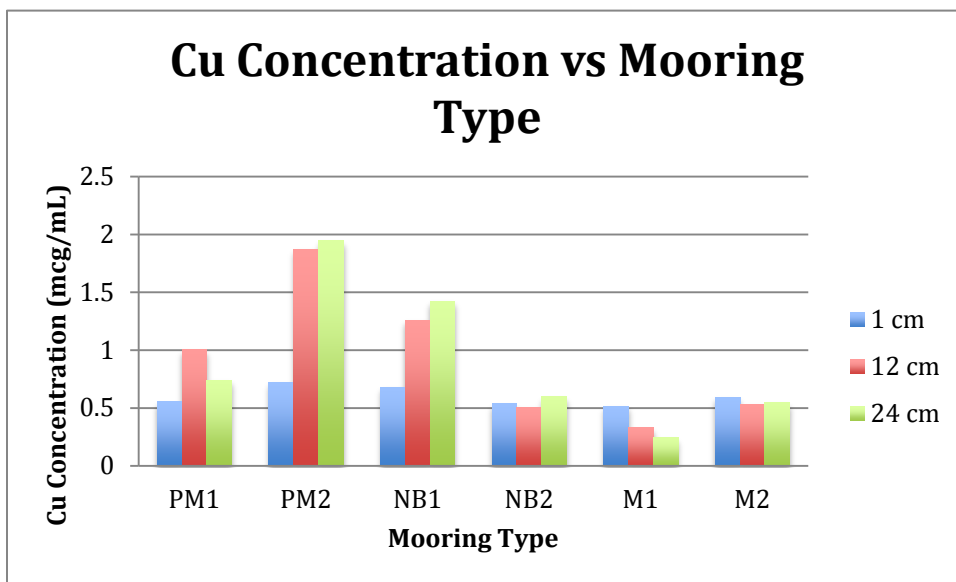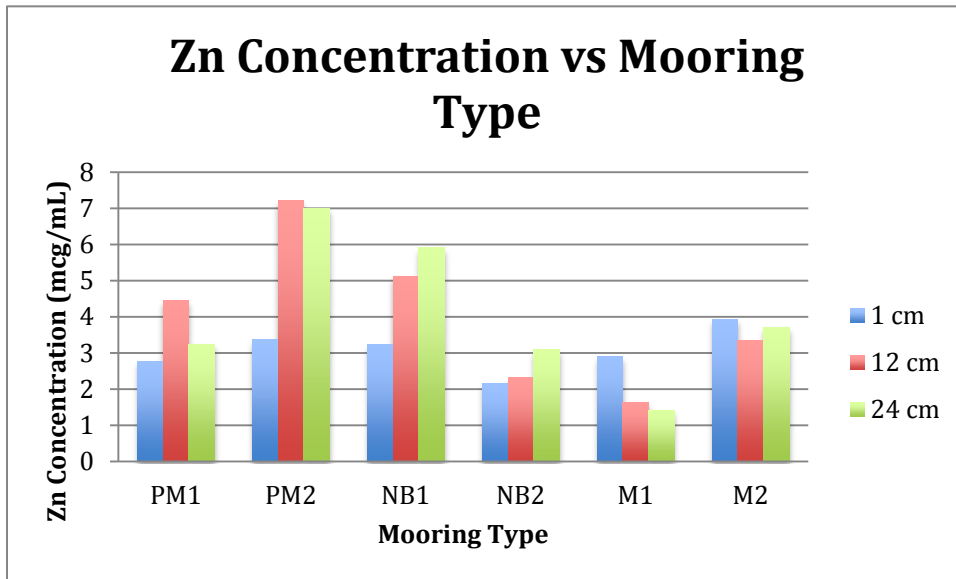
These results show no correlation between metal concentrations and mooring type. If a correlation did exist, each pair of moorings with similar boat types would need to have similar metal concentrations. In general, this is not the case for any of the pairs.

Metal Concentration vs. Mud Fraction:
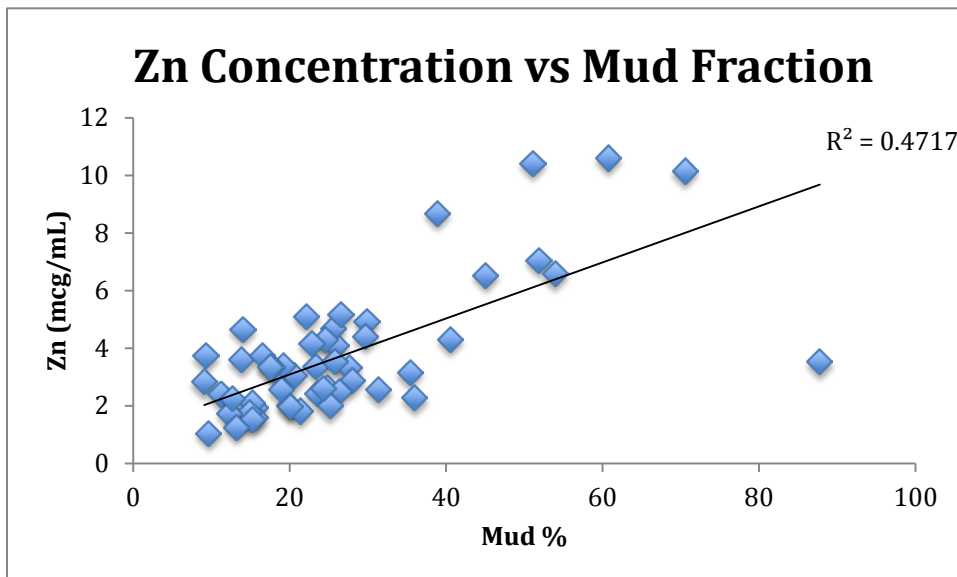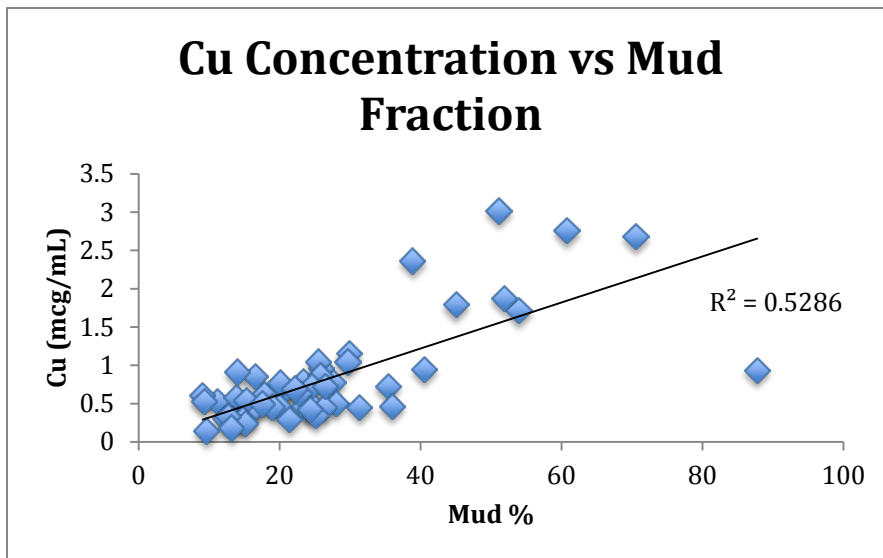
This study found a correlation between mud fraction and metal concentration for both Cu and Zn. The charts above show that as mud fraction increases, metal concentration increases. This is only somewhat supported by R^2 values of .529 for Cu and .4718 for Zn. These R^2 values are deflated, however, by an outlier of extremely high mud fraction and average metal concentration (87.766% with .935mcg/mL Cu and 3.535 mcg/mL Zn). If this point is disregarded, R^2 values jump to .73 for Cu and .67 for Zn.

Discussion:

Particle size vs. depth

The patterns, and lack thereof, of particle size vs. depth is interesting when compared to previous research. Hurst's analysis differed in that his averaged data showed a decrease of particle size as depth increased. His study found average mud fraction around 30% at surface level, and around 20% at depths of 22-24 cm. This is almost exactly the opposite of the results found in this study. This might seem to be a strange finding, considering Hurst collected his data just one year prior to this study, in the same bay, where sediment deposits at about 7 mm per year. However, two factors justify this difference. The first is a simple matter of geography. Hurst's samples were all taken close to shore, while this study took samples from further out in the bay. Within Hurst's study, particle size changed significantly by location, with more mud on the western side. Still, location doesn't fully explain the difference between this study and Hurst's trends. Looking at Hurst's data with closest proximity to this study's points, the findings still contradict each other.
While both Hurst's study and this study found a small trend while looking at averages, analysis of individual samples was far less conclusive. Several cores keep a constant particle size, while others even peak at middle depths and drop at the deepest points. This lack of correlation in both studies invalidates the correlation found from average values. There is either no relation between depth and particle size, or the methods carried out in this study and Hurst's are unreliable.

Metal Concentration vs. Mooring Type
There is a surprising lack of correlation between mooring type and metal concentration. As stated above, similar mooring types do not always have similar metal concentrations. This is most apparent with the poorly maintained boats. Another finding that diminishes the importance of antifouling paint is the fact that moorings with no boats have significantly higher metal concentrations than moorings with well-maintained boats. In fact, the mooring with the second highest metal concentrations had no boat at all. It is crucial to note that the lack of mooring correlation does not prove antifouling paint has no effect. Rather, it just means something else is a much greater factor. A better analysis of antifouling effects could be found if such a factor could be identified, and controlled in future experiments. This discussion proposes that particle size is this controlling factor.

Before moving on to particle size, there is one interesting correlation in the data to consider. For both Cu and Zn, in most moorings, surface values are much lower than at greater depths. This study could not find any explanation for this correlation. However, an exception to this trend may have great importance. Moorings with well-maintained boats always had their highest metal concentrations at the surface. This exception is particularly

strong in M1, whose surface metal concentration is twice the value of its 12-14 cm value. In contrast, the surface metal concentration of PM2 is half the value of its 12-14 cm value. Furthermore, the highest surface value of Zn is found from M2, although its deeper metal concentrations are lower than PM2 and NB1, and comparable to PM1.

This exception is fascinating. One explanation is that these two boats had an application of antifouling paint in the past two years, leading to an increase of metal concentration in comparison to older, deeper sediment. This could not be verified, since this study failed to attain any records of maintenance from the harbormaster. This analysis could be greatly improved if such records could tell exactly how long these boats had been at their moorings, and when they were last painted. Although far from perfect, this interpretation does suggest that in the past few years, maintained boats have been a source of metal contamination.

Particle size:

The data shows a correlation between particle size and metal concentration. In particular, when an outlier is removed, R^2 values are .73 for Cu and .67 for Zn. This high correlation is reinforced when moorings are ranked by mud fraction and Zn concentration (Table 1).

Table 1: Mud Fraction vs. Zn Concentration

Mooring	Mud Fraction Ranking	Metal Concentration Ranking
PM1	3	3
PM2	1	1
NB1	2	2
NB2	4.5	5
M1	6	6
M2	4.5	4

This table strongly reinforces the idea that mud fraction, rather than mooring type, controls metal concentration. This correlation is so strong that it demands a new methodology for analyzing metal concentration. A study must ask: are metal concentrations at the level they are *due to* particle size, or *despite* particle size? If results indicate the former, you should determine what source is influencing particle size. If the latter is true, it indicates the presence of a potent metal source. Most of the data in this

study suggests that metal concentrations are at certain levels due to particle size. The exceptions, again, are the surface values for maintained boats. To be specific, the surface of M1 had the lowest mud fraction, but Cu and Zn values close to the average for surface concentrations. Meanwhile, M2 had the third highest mud fraction, but the highest Zn concentration. Moorings with maintained boats have high values despite their low mud fraction. Thus the maintained boats seem to be a potent metal source that compensates for the sediment's inherent tendency to absorb less metal cations. This conclusion is suggestive, however, the study would be more conclusive if moorings could be found with the same mud fraction.

Conclusion:

This goal of this study was to determine the effect of antifouling paint from moored boats, while adding to Hurst's analysis of sediment deposition by particle size. The analysis of particle size yielded an inconclusive result. The difference in location of samples likely led to different trends, however, the unpredictable nature of individual samples from both studies suggests that new methods and methodology may be required. Analyzing mooring type vs. metal concentration yielded no correlation at first, but by considering depth of samples, it was shown that well-maintained boats have higher metal content than expected at the depth of 0-2 cm. This exception suggests that over the past few years at these moorings, antifouling paint has been a significant factor. Still, the lack of records on the moorings detracts from the credibility of this conclusion. Future research should pursue these record. After finding that at most depths mooring type did not control metal concentration, this study analyzed and concluded that particle size is this controlling factor. Given this finding, any future research must consider particle size when analyzing metal concentration. As found in this study, outliers of the mud fraction vs. metal concentration trend point to a strong pollution source. This is applicable to many more studies than mooring locations. Future studies should test this conclusion, and perhaps attempt to find a controlling factor more important than paricle size, such as proximity to other pollution sources. Another path for future research would be to compare more moorings with equal mud fraction. This study's analysis has shed a little more light on the pollution of Okahu Bay, and further studies could make much more progress with a focus comparing pollution sources to mud fraction.

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Appendix

Raw Data: Note, 1s, 1m, and 1d refer to 1 shallow, medium, and deep, and so on.

Boat	Type	Core		Depth	Cu mcg/mL	Zn mgc/mL	Mud Percentage %
"Breakaway"	Old		1	1s	0.529	0.483	11.23201
			1	1m	1.713	1.318	53.977408
			1	1d	0.785	0.675	23.372085
			2	2s	0.525	0.611	18.985356

		2	2m	0.575	0.721	13.862192
		2	2d	0.778	0.666	27.624129
		3	3s	0.611	0.569	9.093277
		3	3m	0.725	0.634	35.419245
		3	3d	0.66	0.609	20.565775
"Ali Can"	Old	4	4s	0.657	0.684	19.265993
		4	4m	1.15	0.986	29.888577
		4	4d	3.016	2.083	51.102111
		5	5s	1.044	0.882	29.716064
		5	5m	1.79	1.307	45.059667
		5	5d	0.935	0.707	87.766171
		6	6s	0.467	0.457	35.983875
		6	6m	2.678	2.032	70.558497
		6	6d	1.878	1.411	51.879155
		7	7s	0.624	0.671	17.857607
0Q21	No Boat	7	7m	0.954	0.823	25.949547
		7	7d	1.044	0.936	25.554656
		8	8s	0.944	0.864	40.545807
		8	8m	2.363	1.736	38.88665
		8	8d	2.757	2.122	60.751941
		9	9s	0.466	0.406	19.97636
		9	9m	0.456	0.513	19.001329
		9	9d	0.465	0.489	23.556893
		10	10s	0.383	0.392	15.63786
OM23	No Boat	10	10m	0.289	0.365	21.39123
		10	10d	0.499	0.579	28.02267
		11	11s	0.451	0.512	31.38103
		11	11m	0.373	0.323	15.65499
		11	11d	0.449	0.527	24.88879
		12	12s	0.771	0.396	20.12451
		12	12m	0.86	0.706	25.79062
		12	12d	0.85	0.75	16.5617
		13	13s	0.912	0.933	14.02033
"Wanea"	Clean	13	13m	0.536	0.421	15.265

		13	13d	0.298	0.293	13.42098
		14	14s	0.296	0.358	14.82062
		14	14m	0.311	0.349	12.34381
		14	14d	0.242	0.303	15.21152
		15	15s	0.332	0.451	12.74383
		15	15m	0.144	0.212	9.643505
		15	15d	0.184	0.253	13.21152
		16	16s	0.452	0.503	26.383
"Sneaker"	Clean	16	16m	0.729	0.86	24.60129
		16	16d	0.495	0.671	17.52455
		17	17s	0.632	0.836	22.86838
		17	17m	0.526	0.749	9.306863
		17	17d	0.726	1.037	26.55895
		18	18s	0.691	1.024	22.17661
		18	18m	0.341	0.402	25.17661
		18	18d	0.419	0.523	24.36372

Feel free to email John Stockman with any questions