Heavy metal contamination within Okahu Bay of Auckland, New Zealand

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This study attempts to determine the extent to which the intertidal zone of Okahu Bay; located within Auckland, New Zealand; has been impacted by anthropogenic heavy metal contamination, specifically along its western shoreline. Potential sources of anthropogenic contamination include both point and nonpoint sources, such as a storm water drainage outlet and runoff from the surrounding impervious surfaces. In this study, 18 surface sediment samples were taken from the western corner of the intertidal zone and analyzed for copper and zinc concentrations. This was then compared to the guidelines for zinc and copper concentrations for urban receiving environments as outlined by the Auckland Regional Council and the relative impact of the area was quantitatively and qualitatively accessed. This study found that within this area of concern sediment samples contained elevated copper concentrations; however zinc concentrations never exceeded moderate impact values. While zinc concentrations did not exceed acceptable limits, a positive correlation between zinc and copper was determined with an R^2 value of 0.51 suggesting that elevated zinc concentrations could potentially be used as an indicator of other heavy metal species within the bay, but cannot be used to predict the concentrations of these metals .

Introduction

Okahu Bay located within the Waitemata harbor of Auckland, New Zealand is a culturally significant area for the local Maori population. Within the Orakei Catchment, Okahu Bay historically was the home of the Ngati Whatua O Orakei Iwi (tribe) and was a source of many local resources (Faaui 2012). Currently the Maori population has become concerned with the state of the bay and questions to what extent the Mauri, or essential life force, of the bay has been impacted by changes in land use and development around the bay over the past century.

Due to this concern, several studies in the past year have been conducted to begin to identify how Okahu Bay has been affected by human development resulting in a preliminary understanding of the bay's environmental state.

Specifically this preliminary research has identified that the western coast Okahu Bay may contain elevated levels of copper and zinc (Hurst and Morgan, 2012). This study will examine the extent to which the western coast of the bay has been impacted by these heavy metals, and attempt to identify the source of heavy metal contamination. Specifically we will examine surface sediments located within the area of concern to determine the concentration of zinc and copper in the sediment.

Objective

The main objective of research includes determining the extent of potential sediment contamination within Okahu Bay as identified by Hurst and Morgan, to a finer resolution.

Background

Study Location

Okahu bay is located inside Waitemata harbor (Fig.1) within the Orakei catchment basin. Historically the bay provided abundant natural resources to the Ngati Whatua Iwi, specifically shellfish which the Ngati Whatua regularly harvested (Fauui, 2012). These resources were then threatened by land development beginning in the late 19^{th} century up to the present, resulting in a trend of increasing impermeable surfaces surrounding the bay. Consequently runoff into the bay has increased while also decreasing the amount of eroded material from the headlands into the bay.

Fig. 1 Location of Okahu Bay. Image Source: Google Maps

The bay also was effected by the development of the Auckland and Suburbs Drainage Scheme in 1909, from which untreated wastewater was released directly into the bay at Bastion Point. This led to increased nutrient loading in the bay, increasing the amount of organic material in sediments located near the outlet. Further development which threatened the state of the bay includes the construction of Orakei Marina in 2005, which is enclosed on three sides by solid break waters (Fauui 2012).   Construction of the marina (Fig.2) also involved the dredging of 140,000m^3 of sand from the ocean floor (Fauui 2012). Construction of Orakei Marina has therefore significantly affected hydrologic patterns and trends in sedimentation (Hurst 2012).

Fig. 2 Okahu Maina and Tamaki Drive. Image Source: Google Maps

With members of the Ngati Whatua Iwi acting as kaitiaki, or guardians and environmental stewards of the region, the development that has occurred within and around the bay has become a significant concern. According to the kaitiaki of the bay, shellfish populations have significantly decreased and sediment composition has been drastically altered (Hurst 2012 and Dromgoole 1983). Additionally a potential sediment contaminant plume of heavy metals poses a considerable threat to the Mauri of the bay. This contamination threatens human health as heavy metals could potentially bioaccumulate within shellfish which continue to be harvested by local Maori. Additionally these contaminants have the potential to become resuspended within the water column increasing the scope of concern. Therefore, further understanding the scope of this environmental hazard will allow for proper remediation techniques to begin in order to restore the Mauri of the Bay.

Heavy Metals and Trends in Sedimentation

Heavy metals undergo complex interactions at the soil-water interface. These interactions can result in the retardation of free heavy metal cations through the soil column dependent on the inorganic and organic components which make up the soil. Typically soils which contain high levels of clay minerals or organic material have the potential to hold higher concentrations of heavy metals due to a high cation exchange capacity (CEC) which represents the quantity of cations that can be reversibly adsorbed to a soil particle surface (Sparks 1995). For this reason soil composition will be significant when determining areas of concern.

Methods

Sampling Procedure

Surface sediment samples were collected near the point of concern as identified by Hurst and Morgan (2012) on May 23, 2012. Samples were collected in a radiating pattern from an identified storm water outlet, and then the locations of these points were identified using a total station. Despite intentions of mapping sampling points to conduct a spatial analysis, the total station data collected was insufficient for mapping purposes and sampling points could only be roughly plotted (Fig 1). These samples were taken with a spade to a depth of 5cm, and stored in plastic bags until further testing.

Fig. 3. Rough schematic of sampling sites. Red points represent sites 1 through 11, with site 1 on the left; and blue point represent sites 12 through 18, with point 12 furthest from the shoreline. Image source: Google Maps

Sediment Analysis

After collection, sediment samples were divided into two lots for analysis. Sediment samples were analyzed for metal content using the metal extraction procedure, TP168 (ARC, 2004) outlined by Hurst and Morgan (2012). To perform the extraction, between 100 and 200 grams of ea ;round with a mort e gram of the each sample was transferred into a 250 mL beaker and 4mL (1:1) nitric acid (HNO_3) and 10mL (1:4) hydrochloric acid (HCl) were added to each for acid extraction. The samples were then refluxed at 95˚C for 30 minutes, and then diluted to 100mL and centrifuged. Total zinc and copper concentration were then determined using Flame Atomic Adsorption Spectroscopy.

Results

Field Observations

At the site location, observations were made regarding the surrounding built environment and the sediment composition of the coastline. Features of the built environment at the immediate area include a retention wall that defined the western coast of the bay, and a storm water outlet from which a steady stream was flowing. At the site, fine grey-brown sediment was deposited in the western corner of the bay which was sitting on top of level bedrock, and along the southern coast there was mix of fine to coarse grain sand and broken shells. It was also noticed that the deposition of fine grained sediment correlated to the flow of effluent from the outlet.

Sediment Analysis

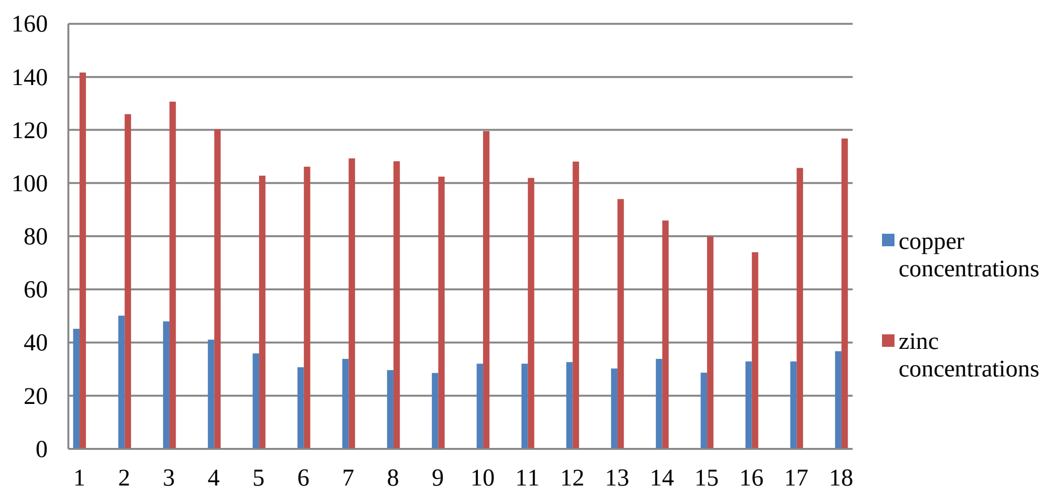
Below is a table outlining the data collected using the Flame Atomic Adsorption Spectroscopy (table 1). This table includes measured aqueous metal concentrations, which were then converted into solid phase concentrations by multiplying the measured aqueous concentrations by the conversion factor of 100mL/gram of soil, due to the dilution during metal extraction. The deviations in concentrations for each sample are also represented by the high and low aqueous concentrations which were used to statistically derive the measured concentration. Low variance in the high and low concentrations indicates higher statistical significance, while a high variance reduces the significance of each measured concentration. The average variance in copper concentrations was significantly higher than that of the zinc concentrations, which is most likely due to the low aqueous copper concentration.

Table 1. Determination of heavy metal concentrations of sediment samples collected from Okahu Bay

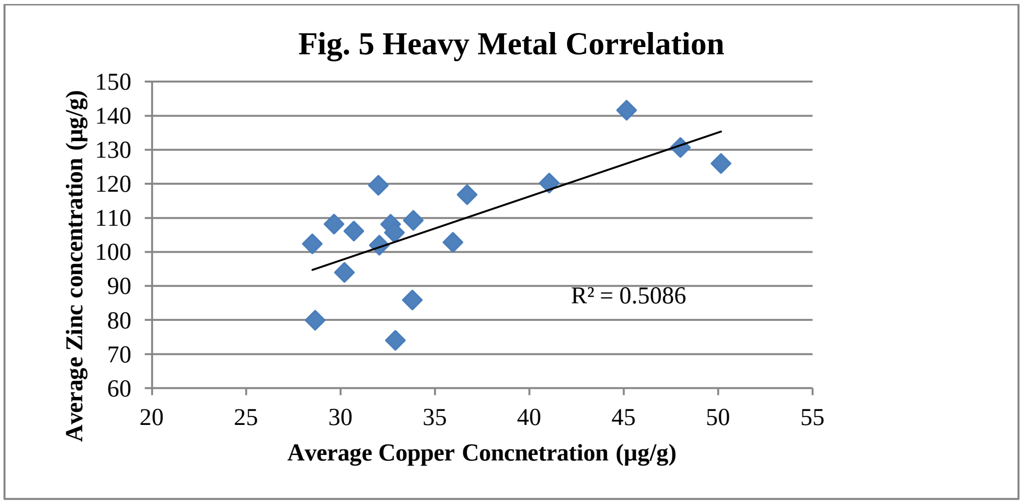
Sample	Aqueous Copper Conc. (µg/ml)	High Conc.	Low Conc.	Variance	Solid Phase Copper Conc. (µg/g)	Average Conc.	Aqueous Zinc Conc. (µg/ml)	High Conc.	Low Conc.	Variance	Solid Phase Zinc Conc. (µg/g)	Average Conc.
1a	0.371	6.95	0.0204	6.9296	37.1		1.463	1.84	0.1462	1.6938	146.3	
1b	0.532	2.29	0.0291	2.2609	53.2	45.15	1.37	0.66	0.138	0.522	137	141.65
2a	0.505	2.57	0.0276	2.5424	50.5		1.293	0.51	0.1312	0.3788	129.3	
2b	0.498	1.61	0.0273	1.5827	49.8	50.15	1.227	1.31	0.1253	1.1847	122.7	126
3a	0.45	1.8	0.0247	1.7753	45		1.271	0.4	0.1292	0.2708	127.1	
3b	0.51	1.07	0.0279	1.0421	51	48	1.343	0.7	0.1357	0.5643	134.3	130.7
4a	0.412	3.84	0.0226	3.8174	41.2		1.241	0.4	0.1265	0.2735	124.1	
4b	0.409	1.19	0.0224	1.1676	40.9	41.05	1.164	1.46	0.1196	1.3404	116.4	120.25
5a	0.354	2.03	0.0194	2.0106	35.4		1.015	0.87	0.1057	0.7643	101.5	
5b	0.365	1.81	0.0201	1.7899	36.5	35.95	1.042	0.81	0.1083	0.7017	104.2	102.85
6a	0.293	1.53	0.0161	1.5139	29.3		1.061	1.8	0.11	1.69	106.1	
6b	0.321	4.55	0.0176	4.5324	32.1	30.7	1.062	0.38	0.1101	0.2699	106.2	106.15
7a	0.372	0.66	0.0204	0.6396	37.2		1.145	0.03	0.1178	-0.0878	114.5	
7b	0.305	0.64	0.0168	0.6232	30.5	33.85	1.041	0.98	0.1081	0.8719	104.1	109.3
8a	0.293	1.98	0.0161	1.9639	29.3		1.083	1.21	0.1121	1.0979	108.3	
8b	0.3	3.78	0.0165	3.7635	30	29.65	1.081	0.72	0.1118	0.6082	108.1	108.2
9a	0.289	3.15	0.0159	3.1341	28.9		1.052	1.69	0.1091	1.5809	105.2	
9b	0.281	5.01	0.0154	4.9946	28.1	28.5	0.996	0.5	0.1039	0.3961	99.6	102.4
10a	0.29	2.73	0.0159	2.7141	29		1.065	0.59	0.1104	0.4796	106.5	
10b	0.35	2.28	0.0192	2.2608	35	32	1.327	0.75	0.1342	0.6158	132.7	119.6
11a	0.35	1.9	0.0192	1.8808	35		1.032	0.3	0.1073	0.1927	103.2	
11b	0.291	3.14	0.016	3.124	29.1	32.05	1.008	0.44	0.1051	0.3349	100.8	102
12a	0.318	3.42	0.0175	3.4025	31.8		1.126	0.93	0.1161	0.8139	112.6	
12b	0.335	3.33	0.0184	3.3116	33.5	32.65	1.037	0.76	0.1077	0.6523	103.7	108.15
13a	0.286	3.92	0.0157	3.9043	28.6		0.901	3.82	0.0949	3.7251	90.1	
13b	0.318	2.66	0.0175	2.6425	31.8	30.2	0.979	2.08	0.1023	1.9777	97.9	94
14a	0.348	4.78	0.0191	4.7609	34.8		0.944	0.92	0.099	0.821	94.4	
14b	0.328	3.48	0.018	3.462	32.8	33.8	0.774	4.06	0.0825	3.9775	77.4	85.9
15a	0.287	1.25	0.0158	1.2342	28.7		0.757	0.28	0.0808	0.1992	75.7	
15b	0.286	8.97	0.0157	8.9543	28.6	28.65	0.842	0.3	0.0891	0.2109	84.2	79.95
16a	0.334	4.72	0.0183	4.7017	33.4		0.808	1.08	0.0858	0.9942	80.8	
16b	0.324	1.83	0.0178	1.8122	32.4	32.9	0.673	1.6	0.0724	1.5276	67.3	74.05
17a	0.326	2.68	0.0179	2.6621	32.6		1.04	0.24	0.108	0.132	104	
17b	0.331	5.23	0.0182	5.2118	33.1	32.85	1.074	1.29	0.1113	1.1787	107.4	105.7
18a	0.376	2.88	0.0206	2.8594	37.6		1.255	1.38	0.1278	1.2522	125.5	
18b	0.358	3.02	0.0197	3.0003	35.8	36.7	1.082	1.65	0.112	1.538	108.2	116.85
Average				2.9995	35.3					0.9651	107.4	

The average soil concentration for each site was determined by averaging samples A and B from each site, and soil concentrations were characterized as high, moderate or low impact using the guidelines for zinc and copper concentrations for urban receiving environments as outlined by the Auckland Regional Council (ARC 2004). In the above table samples highlighted in green represent low impact, samples in amber represent moderate impact, and samples in red represent high impact. Average copper and zinc concentrations were then graphed against each other for a visual representation of these values (Fig. 4). Overall, the average solid phase copper concentration of all collected samples was approximately 35µg/g which is above the threshold concentration for high impact; and that of zinc was 107µg/g, which is below the threshold concentration for low impact.

Fig. 4 Average Concentration of Heavy Metals



The concentrations of copper and zinc were then plotted against each other on a 1:1 scale, and the correlation between zinc and copper concentrations was observed. The R^2 value for this positive linear regression was determined to be approximately 0.51 (Fig. 5).



Discussion

Overall, it can be confirmed that the region of Okahu Bay identified by Hurst and Morgan (2012) has been impacted by some heavy metal contamination. Copper levels on average were above the acceptable threshold, indicating that the site has been impacted even though zinc concentrations fell within the acceptable limits. While quantitative spatial analysis was made impossible without the proper data for mapping purposes, a rough understanding of concentration at each site and the sites relative position to key features along the bay can offer some insight to potential sources of the copper contamination.

Metal Contamination

Using the criteria outline by the Auckland Regional Council (ARC), this site can be considered impacted by heavy metals, specifically copper; confirming the concerns presented by Hurst and Morgan in their initial study of the bay. These concentrations are consistent with copper and zinc levels found in their preliminary study. The soil sampled by Hurst and Morgan contained approximately 44µg/g of copper and 102 µg/g of zinc (2012). Despite a higher net zinc concentration, the threshold level of copper eco-toxicity is significantly lower than that of zinc and therefore even minimal copper contamination is of concern (ARC 2004).

However despite the fact that this study uses the guidelines developed by the ARC to identify impacted zones of contamination, it is necessary to consider both anthropogenic and natural sources of these heavy metals within the Orakei catchment. For example a study of background heavy metal concentrations conducted within the Greater Auckland Region; found that volcanic soils have higher naturally occurring concentrations of heavy metals (ARC 2001). This study found that background levels of copper in Auckland were between 51 and 60 mg/kg (µg/g), and found zinc levels up to 250 mg/kg (ARC 2001). While the ARC guidelines for impacted receiving environments are useful in identifying zones which may have a negative impact on the biology of the bay, the sources used to develop these guidelines were not New Zealand specific. In both cases the observed metal concentrations fell below the background levels identified in the 1999 study and therefore it is not conclusive that elevated concentration of heavy metals within the bay have an anthropogenic source.

While it is inconclusive whether the source of these metals is anthropogenic in nature, an analysis of the distribution of these metals across the study location is useful for understanding the modes of sediment deposition and its relationship with metal accumulation within the bay. Generally there are two ways metals are transported into the receiving environment into the sediment column. The first is through deposition of fine sediments containing sorbed metal cations, and the second is through the precipitation of aqueous metals out of the water column. Looking at table 1, one can see that sites 1 though 5 and site 18 have the highest copper concentrations, and sites 1 through 3 have the highest zinc concentrations. These are the sites located furthest from the sandy shoreline and closest to Tamiki Drive. These sites therefore are likely to have the lowest sand to silt ratio because they are located furthest from the sandy coastline. As a result of this they are also most likely to have the highest cation exchange capacity for the reasons discussed earlier. Because of their proximity to Tamiki Drive, it can be hypothesized that runoff into the bay could be contributing to the elevated metal concentrations. Site 18 which had a high copper concentration is also the closest site to the storm water drainage outlet, meaning this may also be a source of copper in the marine environment. This outlet could likely be depositing fine sediments into the bay or it may contain aqueous metals which precipitate out into the bay due to the change in salinity. While this can be hypothesized, the information gathered in this study was not extensive enough to be conclusive.

Correlation between Zinc and Copper

Looking at figure 5, there is a positive correlation between copper and zinc concentrations. While this correlation does exist, it is only a weak correlation. This is most likely related to the CEC of each soil sample rather than a connection between zinc and copper. Soils with a higher CEC have a higher capacity to adsorb metal cations, however the concentration of one metal cation is not directly proportional to the other. In all cases zinc concentrations were higher than that of copper, and this could be a combined the result of higher net concentrations of zinc within the catchment, and a higher selectivity of zinc on the particle surface.

Conclusion

Overall, the concentrations of zinc and copper within the area sampled are similar to the values measured by the previous study conducted by Hurst and Morgan. According to the guidelines suggested by the Auckland Region Council, copper concentrations in this zone indicate that the western end of the bay has been impacted in a negative way. Potential sources of contamination include urban runoff into the bay and storm water outflow into the bay through a drainage pipe located on the western shore of the bay, though a detailed spatial analysis could not be conducted.

Despite this classification it is necessary to consider both natural sources of these metals as well as the anthropogenic. According to the earlier studies conducted within the Auckland region, Auckland volcanic soils naturally contain elevated concentrations of heavy metals, and background concentrations in this study have actually exceeded the concentrations observed in Okahu Bay. This calls into question the validity of the guidelines used for monitoring heavy metals in Auckland's receiving environments which has been modeled off of guidelines not specific to Auckland or even New Zealand.

While these metals are naturally occurring in Auckland soils, changes in sediment deposition could be having a negative effect on the bay. Urban runoff, an increase in impervious surfaces, and the construction of the marina can alter sediment deposition patterns by increasing the load of fine sediments into the bay and by altering the hydrologic patterns within the bay. Finer sediments by nature have a higher capacity to retain heavy metal cations to the soil particle surface, and therefore are a greater threat to the biota of the bay. It is therefore necessary, to study the historic trends in fine sediment deposition within the bay to gain an understanding of how it has been impacted. Overall, trends in sediment deposition are likely to be a more useful indicator of the health of the bay than to the concentrations of heavy metals.

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