Heavy Metal Absorption in Okahu Bay Sediment

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6/21/2013

Abstract

The Orakei Domain landscape and land usage have been drastically changed by development in Auckland since European settlement beginning in the 1850s. Urban and business development, roads, and railways have introduced various sorts of pollution into the surrounding waters, particularly heavy metals such as copper, lead, and zinc. Heavy metals in sediments pose a significant threat to the ecological health of the bay as well as human health. Previous research has identified the southern region of Okahu Bay as having unusually high levels of heavy metal contamination. This project aims to identify the stormwater drainage pipe on the southeast corner of Okahu Bay as a direct source of pollution and examine why pollutants in this particular area settle into the sediment instead of being washed out of the bay. Metal concentrations of Copper and Zinc were measured in this region. Samples of the top 0-3cm of sediment were collected at low tide and analyzed following Auckland Regional Council (ARC) Technical Project 168 guidelines. Sediment testing showed consistent results to previous research; levels of contamination of copper were significantly above allowed values, and zinc concentrations were very low. Most significantly, both metals were highest in concentration not directly below the drain, but twenty meters west of it along the concrete wall that lines the southern coast of the bay.

1.0 Introduction

Okahu Bay is located in the Waitmata Harbour in Auckland, New Zealand, and is on the north-western edge of the Orakei Peninsula (Fig. 1), which has historically been the land of Ngati Whatua o Orakei Iwi. In the past century, the Auckland Council has assumed management and responsibility for the bay and surrounding lands which has resulted in high levels of urban development and harmful environmental management practices. The first damage to the bay began about 160 years ago, when rights to the Orakei region surrounding the Okahu Bay were given to the Crown. About twenty families from the tribe were able to maintain ownership of "Boot Hill," (Fig. 2) but the rest of the land was developed by the city. In 1908, strained but untreated sewage from about 100,000 Auckland residents began being directly added into the bay at Okahu Point (Fig. 2) (Watercare Service 2011), and four years later, the sewage system was linked to hospitals and industries, resulting in toxic poisons and chemicals, hospital waste, and raw diseases such as typhoid and cholera being discarded into the water and ultimately into the bay (Kahui-McConnell, 2013). This continued into the 1950s, when the sewage water was redirected to the Managere shoreline in the upper Manukau Harbor. In 1960, the Managere Treatment Plant opened, and sewage was finally treated before release into Manukau Harbor (Watercare Service 2011). Besides contaminating surrounding receiving waters, development on land and within the bay altered the natural shape and coastal features,

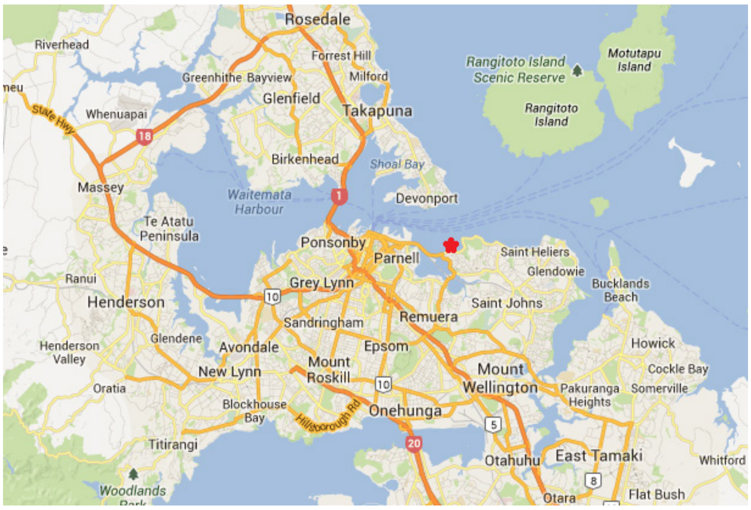


Figure 1 Okahu Bay in South East of Waitemata Harbour. Google Maps.

Figure 2. Orakei Domain and 'Boot Hill.' Source: Google Maps

which changed the flow of water into the bay. This has resulted in frequent flooding of the Ngati Whatua cemetery, a serious insult to Maori culture (Kahui-McConnell 2013).

Okahu Bay is now a public recreational water zone, home to a marina and a kayaking club. Tamaki Drive follows the coastline around the bay, in some places within a few meters of the water, and other major roads cut through the area as well. In general, the Orakei Domain is full of urban and business development, with the northern-most embankment being the sole undeveloped region (Fig. 2). The marina moorings and bridge that cuts through the Hobson and Orakei bays create a low-energy zone in the water, which prevents proper water flow in and out of the bay, effectively trapping water and its contaminants in the area (Kahui-McConnell 2013). Historically, the sediment in the bay was pure sand, but now it is mostly black silt sediment, which is indicative of an unhealthy ecosystem (Kahui-McConnell 2013). Urban intensification accelerates contaminant accumulation, and with the region's continuous development, the problem can only be expected to get worse. Contaminants are accumulating quickly in receiving environments across Auckland's numerous harbors and concentrations in some areas are rapidly approaching levels where substantial changes in ecological health are likely to be seen (ARC, 2004). Urban environment contaminants typically include toxic metals (such as copper, lead, and zinc), hydrocarbons, nutrients from detergents and other home products, and pesticides, all of which have harmful effects on the environment (Hall and Anderson 1986).

Stormwater runoff is a non-point source pollutant, which means it comes from many diffuse sources, and is composed of rainwater that has run over paved surfaces and through the ground, collecting natural and anthropogenic contaminants along the way (EPA 1994). The majority of contaminants enter the receiving water from treated sewage plants or stormwater runoff, but pollution from non-point sources can account for over half the contaminant load entering waterways (Hall and Anderson 1986). Although metal and other pollutant concentrations of stormwater runoff are comparatively lower than concentrations in sewer system discharge, there is a much higher volume of water regularly discharged from stormwater (Ellis 1996). Vehicle emissions, oil and petroleum products, vehicle tire wear, and chemicals from the asphalt and composition of the paved surfaces are all diffuse sources of chemical contaminants from non-point sources, and during rainfall they enter into the stormwater system and receiving waters (Brown and Peake 2004).

This research measures the concentrations of two heavy metals, copper and zinc, because these are the most prominent toxic trace metals and are of particular concern due to their typically high concentrations surrounding industrial and commercial land use areas (Hall and Anderson 1986), and their high level impacts on ecological aquatic health (Brown and Peake 2004). Polycyclic aromatic hydrocarbons (PAHs) are also contained in urban runoff and are of particular concern for similar reasons, but this study was not able to include this analysis. In urban areas, the main sources of PAHs are the incomplete combustion of fossil fuels or wood and split petroleum products, and typically accumulate on paved surfaces (Brown and Peake, 2004).

These chemicals pose threats to the environment and human health when concentrations reach high enough levels, particularly in conjunction with each other. In general, materials accumulating in the sediment layers of receiving waters provide poor habitats for most plant and animal species and pose a threat to ecological marine life by depleting dissolved oxygen in the sediment which reduces plant growth (Ellis 1996). This polluted water also contains a variety and concentrated number of pathogenic bacteria and viruses, such as *e.coli*, *fecal coli*, and *fecal streptococci*, which settle quickly and remain for extended time periods in polluted sediment (Ellis 1996). *E.coli* poisoning can lead to intestinal infection and hemolytic uremic syndrome, particularly in children and elderly (EPA 2013). Three *e.coli* tests are done in the bay each year, and each one yields results that are above levels acceptable for public usage (Kahui-McConnel 2013).

This project is a follow-up on similar research completed in early 2012 by Andrea Mikol and Elliot Hurst (University of Auckland undergraduates) and aims to measure the levels of copper and zinc in the sediment surrounding the stormwater runoff drain, to determine whether this source is directly impacting the health of the bay, and to compare concentrations of metals with previous data. Understanding the exact anthropogenic impacts on Okahu Bay is an important step to restoring the original environmental health of the bay and towards effective and responsible resource management on the watershed from which the stormwater runoff flows.

2.0 Background

2.1 Okahu Bay

Hundreds of years before European settlement occurred in New Zealand, the Orakei Peninsula was occupied by Ngati Whatua and was used as a *Pa*, a fortified defensive settlement. The whole peninsula region was acquired by the Crown in 1854, but was not significantly changed until the early 1900s. By 1926 the land was fairly developed by homes and businesses (Fig. 3), and by 1929 the land had been extremely modified by construction of the railroad and station (ARC 2002) which are still in use today, over 75 years later. Maori reclamation of the land occurred between 1940 and 1960, but further development of all but the north embankment continues to occur (Kahui-McConnell 2013).

Figure 3 Orakei Domain 1920, Sir George Grey Special Collections, Auckland Libraries, 4-8368

The Ngati Whatua tribe has recently been given back thirty three hectares of land, and restoration projects are already underway in this space and in the other eighty hectares that compose the Maori land around Auckland city (Kahui-McConnell 2013). Irrespective of the absence of physical remains, Ngati Whatua o Orakei is mana whenua (caretaker with territorial rights) of the area and it's Maori Heritage (Kahui-McConnel 2013). In 2007, the entire sewage system in the Orakei Domain was updated, leading to reduce sewage overflow into stormwater runoff systems and therefore lower health risk (Fletcher 2007).

2.2 Previous Research

The Auckland Regional Council (ARC) has done significant monitoring work through the Regional Discharges Project (RDP) over the past decade on water and sediment quality in many bays and harbours surrounding Auckland, but not specifically Okahu Bay. The Council has developed a guide of indication levels for zinc, copper, lead, and PAHs in marine sediment (Fig, 4). Red levels indicate there is a high level of impact where significant degradation has already occurred and remedial opportunities are limited. The amber parameter indicates sites that show levels of contamination and potentially apparent adverse effects on ecology. Further evaluation is required to assess biological and chemical impacts, but restoration is possible. Green levels reflect minimal impact with slight to no degradation and do not need reassessment in less than five years.

A. Primary contaminants (mg/kg)

Parameter	Red[1,2]	Amber[1,2]	Green[1,2]	Source of Red – Amber Threshold	Source of Amber-Green Threshold[3]
Zinc	>150	124-150	<124	ER-L	ISQG (CCME)
Copper	>34	19-34	<19	ER-L	ISQG (CCME)
Lead	>50	30-50	<30	ISQG-Low (ANZECC)	ISQG (CCME)
HMW-PAH[4]	>1.7	0.66-1.7	<0.66	ISQG-Low (ANZECC)	TEL

Figure 4 Contaminant Level Guidelines. ARC 2012.

In 2012, University of Auckland student Elliot Hurst followed Auckland Regional Council (ARC) guidelines for monitoring sediment quality in bays but focused on particle size and copper and zinc levels across the entire Okahu Bay. Hurst found that the central parts of Okahu Bay were 51% mud, whilst the eastern areas were only 5.5%. In addition, he noted that sites on the eastern end of the bay had lower levels of contamination than the middle. Zinc concentration varied between 34 and 102 micrograms/gram, which are considered safe by ARC guidelines and do not impact environmental standards, (Hurst 2012). In general, copper had lower levels of concentration than zinc except for one data point collected near the middle of the bay, which measured 44 micrograms/gram, which was defined as a hazardous level of toxicity by ARC. According to his research, Okahu Bay does not have significant metal contamination (Hurst, 2012).

Most recently, Andrea Mikol studied copper and zinc concentrations in sediment around the drainage pipe in the Southeast corner of the bay. Her results indicated copper levels in most the samples were above acceptable levels and zinc levels were all within Auckland limits. She also referenced geological historical data, which indicated that volcanic soils in Auckland have high levels of zinc and copper. Her results were overall inconclusive about the source of contaminants, but she suggests that the contamination in the bay does not come from anthropogenic sources (Mikol, 2012).

3.0 Methods

3.1 Research Design

This quantitative project was chosen from a list of environmentally focused earth system projects at the University of Auckland. A literature review was completed on background information on Okahu Bay, Auckland city's historical relationship with the bay, and previous sediment research done in Okahu Bay. Finally, samples were collected, stored, and later analyzed in the School of the Environment geography laboratories. Sediment samples were taken by hand and without environmental impact.

3.2 Collecting Samples

Samples were collected February 22, 2013 in the Eastern corner of Okahu Bay (Fig. 3) at low tide. The samples were collected over three hours. No rain had occurred in the area over one week prior to collection, but a small amount of clear water was flowing out of the drainage pipe consistently.

Figure 4 Southeast Corner of Okahu Bay and rough schematic of collection points. Google maps.

The top 0-3 cm of sediment was collected in a 5-8cm diameter circle using a hand spade. Contents were placed in plastic bags, sealed, labelled, and their location recorded using GPS. Certain areas, such as sample location 13, had very little sediment on top of the bedrock (0-1 cm). One 30-meter transect extended perpendicular to the drainage pipe, and three 20-meter transects stemmed from the first transect every 10 meters (Fig. 2). Sixteen samples were collected at 10-meter intervals along transects.

Sampling was targeted toward recently deposited, surficial sediments in order to detect changes in contaminants that can be linked, as closely as possible, to existing stormwater quality. The top 2 cm contains sediments over a 0.2 – 7 year period, so taking samples from the top two cm balanced out very shallow, recently impacting events only, with older, diluted sediments that could have accumulated over the timeframe of 5-30 years (ARC 2004). In general, sites being tested for sediment quality should be remote from clear sources of pollution, such as pipes. However, this particular area was noted of interest in 2012 by Hurst to have possibly particularly high levels of heavy metals.

3.3 Sample Analysis

Due to time restrictions and available laboratory space, sample analysis did not begin until May. Until that point, the samples were stored at room temperature indoors in clear plastic bags.

The method was based off the ARC TP168 procedure for producing consistent and reliable data, and followed Mikol's (2012) procedure almost exactly. Two-hundred grams of each sample were weighed and placed in aluminum dishes using a small spade. The samples were then heated at 60°C for 24 hours in an oven. Each sample was then ground using a mortar and pestle, and sieved using a 500 micrometer sieve. Two grams of each sample were weighed and mixed with 25mL Nitric Acid, then distilled over hot plates for thirty minutes. Samples were centrifuged and the liquid layer was separated into new test tubes and measured for copper and zinc levels using an Atomic Absorption Flame Spectrometer.

4.0 Results

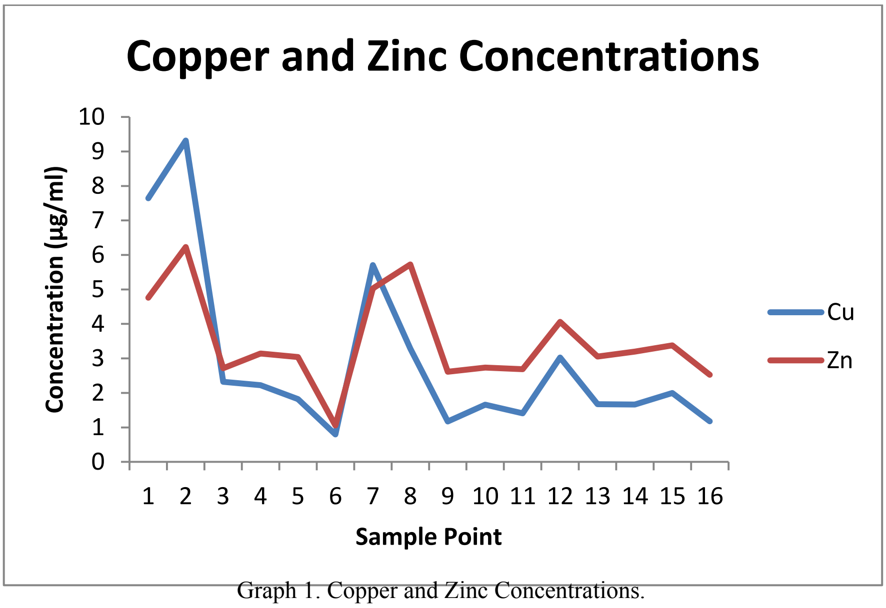
4.1 Heavy Metals

Copper and zinc concentrations were consistent with previous measurements in the region and increased and decreased with the other, which could indicate correlation with distance from the pollutant source. The highest concentration for each metal was at the second point of collection, which was 20 meters west of the drainage pipe, directly against the concrete wall that borders the south of the bay. Table 1 shows the quantitative results from testing, with green, amber, or red ARC indication levels included. Graph 1 indicates the relationship between copper and zinc at each sample site.

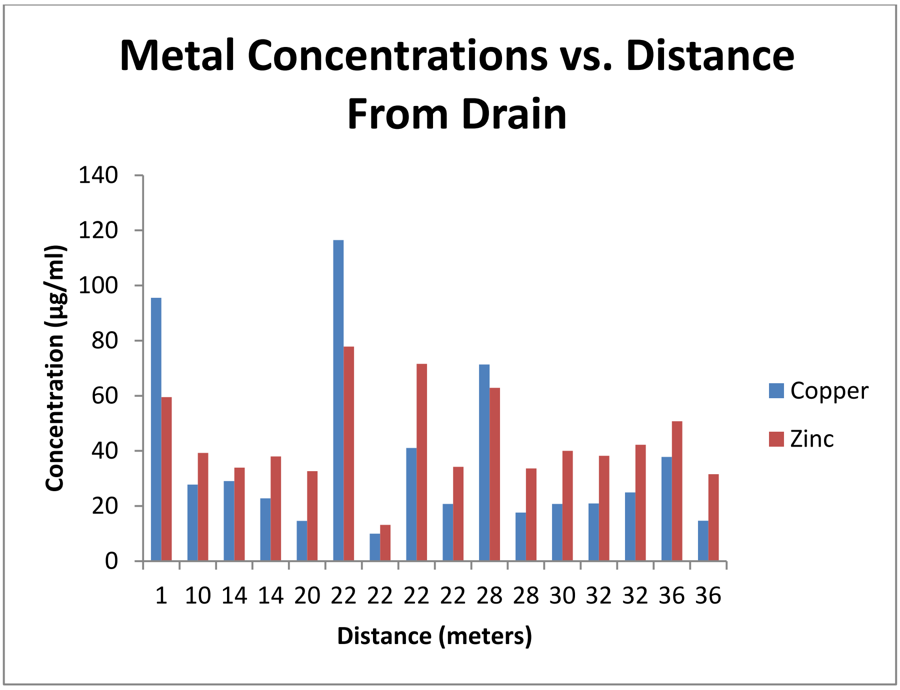
Table 1. Copper and Zinc Concentrations in Sediment Samples

	Copper			**Zinc**	
Sample	Conc. (µg/ml)	Conc. (µg/g)	Distance from Drain (m)	Conc. (µg/ml)	Conc. (µg/g)
1	7.644	95.55	1	4.759	59.4875
2	9.318	116.475	22	6.229	77.8625
3	2.322	29.025	14	2.716	33.95

4	2.223	27.7875	10	3.143	39.2875
5	1.821	22.7625	14	3.04	38
6	0.795	9.9375	22	1.054	13.175
7	5.706	71.325	28	5.031	62.8875
8	3.285	41.0625	22	5.724	71.55
9	1.17	14.625	20	2.613	32.6625
10	1.659	20.7375	22	2.736	34.2
11	1.408	17.6	28	2.69	33.625
12	3.026	37.825	36	4.06	50.75
13	1.673	20.9125	32	3.056	38.2
14	1.661	20.7625	30	3.199	39.9875
15	1.995	24.9375	32	3.377	42.2125
16	1.174	14.675	36	2.525	31.5625
Average		36.625			43.7125



Graph 1. Copper and Zinc Concentrations.



Graph 2. Concentrations and Sample Distance from Drain.

Sample	Average Cu Conc. (µg/ml)	Average Zn Conc. (µg/ml)
Beckwith (2013)	36.6	43.7
Mikol (2012)	35.3	107.1
Hurst (2012)	44.4	100

Table 2. Average Copper and Zinc Concentrations from Different Testing in Okahu Bay.

4.1.1 Copper

Copper levels were consistent with research done in the area in 2012; the average concentration exceeded the ARC red level by less than one percent, but five of the sixteen samples showed copper concentrations exceeding the red zone significantly. The two highest points, samples 1 and 2, were over three times the red level. Sample 1 was taken closest to the drain, about a meter away, and sample 2 was taken against the concrete wall, twenty meters west of the drain.

4.1.2 Zinc

Zinc levels from this study were significantly lower than measurements taken in 2012 by Hurst and Mikol, and also were safely below levels of environmental response concern as stated by ARC. Concentrations varied between 13 µg/g and 77 µg/g. The highest concentration was roughly half of the green level, and all other measurements were significantly below that.

4.2 Field Observations

Samples were collected 22 February, 2013, at the end of summer, and there had been no rain for at least one week prior to collection. Along the southern edge of the bay, Tamaki Drive, a 2-lane road, is within a few meters of the waterfront, and is separated by a concrete wall is approximately 2 meters above the water and slants from the sidewalk level down into the water. The beach width at high tide is approximately 25 meters, and at low tide 50 meters, and is composed of light sand and coarse shells.

5.0 Discussion

5.1 Metal Contamination

Copper levels were measured significantly above the red indicator level of contamination and have been at this level since the beginning of 2012 at the earliest. Auckland Regional Council has not identified Okahu Bay as a region of high contamination and is therefore not responding to the red zone levels as it should.

Zinc concentrations were significantly below previous measurements and ARC green indicator levels. This could be due to the lack of rainfall in the area prior to testing; copper may be retained in sediment for longer periods of time than zinc if copper levels were consistent with levels measured last year. To address this issue, testing should also have been taken after a rain event. In addition, metal concentrations cannot be compared to a perfectly clean standard. Local geology must be taken into account. For instance, pre-urbanized sediment in the Auckland region contained levels of zinc around 20 micrograms/gram (ARC 2002), which could be attributed to volcanic soil.

5.2 Other Factors

Concentrations of contaminants experienced in marine receiving systems depend on many factors, such as the mixing of fresh and salt waters, salinity gradients, water flow in and out of enclosed areas, and reactions between dissolved metals and sediment matter (ARC 2002). Of particular interest is the flow of the water in and out of the bay, as this is aspect has been most influenced by human construction of the marina, roads, boat moorings, and the wave-break in and around Okahu Bay.

Previous research in Okahu Bay has shown a possible correlation between metal contamination levels and particle size of sediment (Hurst 2012). It is acknowledged that contaminants tend to be absorbed more readily in muddier sediments due to high surface areas (Hurst 2012), but only historical information from locals can give indication of the change from pure sand that Okahu Bay has experienced (Kahui-McConnell 2013). In this study, however, all the samples were collected from such a small area comparatively that they were composed of very similar sediment size and particle size was not measured.

6.0 Conclusion

6.1 Overview

Marine environments surrounding developed regions can be significantly impacted by urban development. Contaminants in the form of chemicals, heavy metals, and bacteria enter waterways most often in the form of run-off stormwater pollution, which collects these toxins from paved surfaces and ushers them, without treatment, directly into large bodies of water. These contaminants negatively impact the marine health of the receiving water ecosystem and pose human-health risks. The southeastern corner of Okahu Bay, which is part of the easternmost Waitemata Harbor and under management of Auckland Regional Council and Ngati Whatua, contains a stormwater runoff drain, and has been noted by previous research to have particularly higher levels of heavy metal contamination than the rest of the bay.

This study showed that the storm water runoff pipe could have an impact on copper and zinc concentrations, especially given a rain event. A stronger correlation was found between metal concentrations and the role of the concrete wall and the flow of water in the bay than the distance between the sediment samples and the drain. This research successfully measured copper and zinc concentrations surrounding the drain and did not find a correlation between the distance of the sediment location and the drain, but did find that the metals increased and decreased proportionally to each other. Due to the lack of rainfall prior to testing but the high levels of copper present, this data supports the unlikeliness that the copper and zinc levels measured in this study are directly impacted by the stormwater runoff.

The land has historically been maintained by Ngati Whatua, and it is hoped that collaboration between the tribe and the Auckland Regional Council can address the high levels of copper that are retained in the sediment surrounding the stormwater drain and the rest of the bay.

6.2 Recommended Future Research

Future research could be completed in Okahu Bay examining how the concrete wall and marina change the flow of the water around the bay. This could be achieved by testing for sediment metal concentrations around the edges of the entire bay, and comparing to sediment quality of less confined waters, such as those in Mission Beach. In order to fully understand the health of the bay and the role that human development plays, many more studies must be undertaken and should examine sediment and water contamination, marine life health, and historical changes to the area. This study looks at identifying sources of pollution entering from stormwater drains, historical land usage and water treatment in the area, measures copper and zinc contamination levels, and can serve as a point of reference for further research.

7.0 References

Auckland Libraries, Sir George Grey Special Collections, 4-8368. 2013.
http://tinyurl.com/lbx79d3

Auckland Regional Council, (2004), Blueprint for Monitoring Urban Receiving Environments, Technical Publication 168.

Auckland Regional Council, (2012), Marine Sediment Contaminants: Status and Trends 1998-2010, Technical Report TR2012/041.

Auckland Regional Council, (2002), Environmental Targets for the Urban Coastal Marine Area

Environmental Protection Agency, (2013), Basic e.coli Information EPA
<http://water.epa.gov/drink/contaminants/basicinformation/ecoli.cfm>

Environmental Protection Agency, (1994), What is Nonpoint Source Pollution? EPA-841-F-94-005
< http://www.epa.gov/owow/nps/qa.html>

Ellis, J.B., and Hvitved-Jacobsen, T. (1996) Urban Drainage Impacts on Receiving Waters, Journal of Hydraulic Research, 34:6, 771-783

Fletcher Construction (2007) Orakei Basin Sewer Separation. Online Resource.
< http://www.fletcherconstruction.co.nz/projects.php?id=319&action=search>

Gordon, Steve, The Ohio State University (2001), Measures of Toxic Metals in Water.
< http://tycho.knowlton.ohio-state.edu/heavyinfo.html>

Hurst, Elliot (2012): Okahu Bay Restoration Project, the University of Auckland.

Kahui-McConnell, R., (2013), Interview.

Mikol, Andrea (2012), Heavy Metal Contamination within Okahu Bay of Auckland, New Zealand, the University of Auckland.

National Oceanographic and Atmospheric Administration. Ecological Impacts to Stormwater. 22 February, 2013.

Saeed, Samir M., Shaker, Ibrahim M., (2008). Assessment of Heavy Metals Pollution in

Water and Sediments and Their Effect on Oreochromis Niloticus in the Northern

Delta Lakes, Egypt.

<http://ag.arizona.edu/azaqua/ista/ISTA8/FinalPapers/PDF%20Files/37%20SAMIR%20M.%20SAEED.pdf>