DISTRIBUTION OF MINE WASTE ALONG THE WAIHOU RIVER FLOOD PLAINS

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Abstract

Solid waste production, in the form of mine tailings, is the result of mining of natural mineral resources. The Ohinemuri River tributary of the Waihou River was designated as an official sludge channel during the period of mining operations in the catchment as an official sludge channel during the mining period for mining operations in the catchment in 1895. The 1910 Commission recommended it be revoked and only “slimes” be discharged under a range of restrictions. Essentially processing technology had changed by 1910 and it was no longer necessary to discharge most of the waste. However, the designation remained in place as an official sludge channel during the mining period for mining operations in the catchment. Mine waste included metals such as: copper (Cu), Zinc (Zn), Manganese (Mn), Lead (Pb) and Arsenic (As). Regular flooding of the Ohinemuri and Waihou Rivers resulted in the rivers overtopping their banks and dispersing mine waste into the floodplain areas. The result was dispersion of metal contaminants in the Waihou River catchment area. The effects of this regular flooding had an adverse effect on stocks. The flooding destroyed the crops, the slimes and sludge from flood damaged grass paddocks. The cyanide sludge destroyed the fish stock in the lower Ohinemuri River and upper Waihou River. This continued until stop-banks were installed to reduce the occurrence of overbank flooding, mostly long after any mining disposal had ceased. It was assumed that the heavy metals were migrating downstream. However, recent studies show no strong evidence of downstream migration of contaminated sediments in the Waihou River to the Firth of Thames. This research will investigate the heavy metal concentration along the Waihou River floodplain by mapping metal concentrations from mine waste.

Field sampling has found that the mine waste has not travelled far beyond Paeroa and is concentrated on the flood plains. Some sample sites have levels of contaminants that exceed the thresholds for chronic toxicity. These results are consistent with research limited to the immediate vicinity of the river channel.

Key words: Waihou River, Ohinemuri River, mine tailings, heavy metals, contaminated sediments.

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Chapter One

Introduction

1.1 Overview

This study follows previous research assessing the impact of historical mining activities, particularly the Martha and Tui mines, by tracking the dispersal of contaminants within sediments of the Ohinemuri River and lower Waihou River. Webster (1995) investigated the chemical processes that affect contaminant transport within fluvial systems, especially in the Waihou River. Her research was mainly focused on heavy metals such as Cu, Zn, Mn, Pb, As, Fe, Cr, Cd, and Hg. The results showed higher concentrations of contaminated sediments in the Ohinemuri River and the Tui Stream, which then discharged into the lower part of the Waihou River at Paeroa and Te Aroha respectively (Webster, 1995).

Therefore, it was inferred that there was a downstream (seaward) migration of contaminants in the lower Waihou River. Immediately downstream from Paeroa a high concentration of contaminants was identified in both in the river bed as well as the water column, but by Hikutaia the contaminant had dropped to essentially background or undetectable contamination. This suggested that the mining contamination could still be actively migrating downstream.

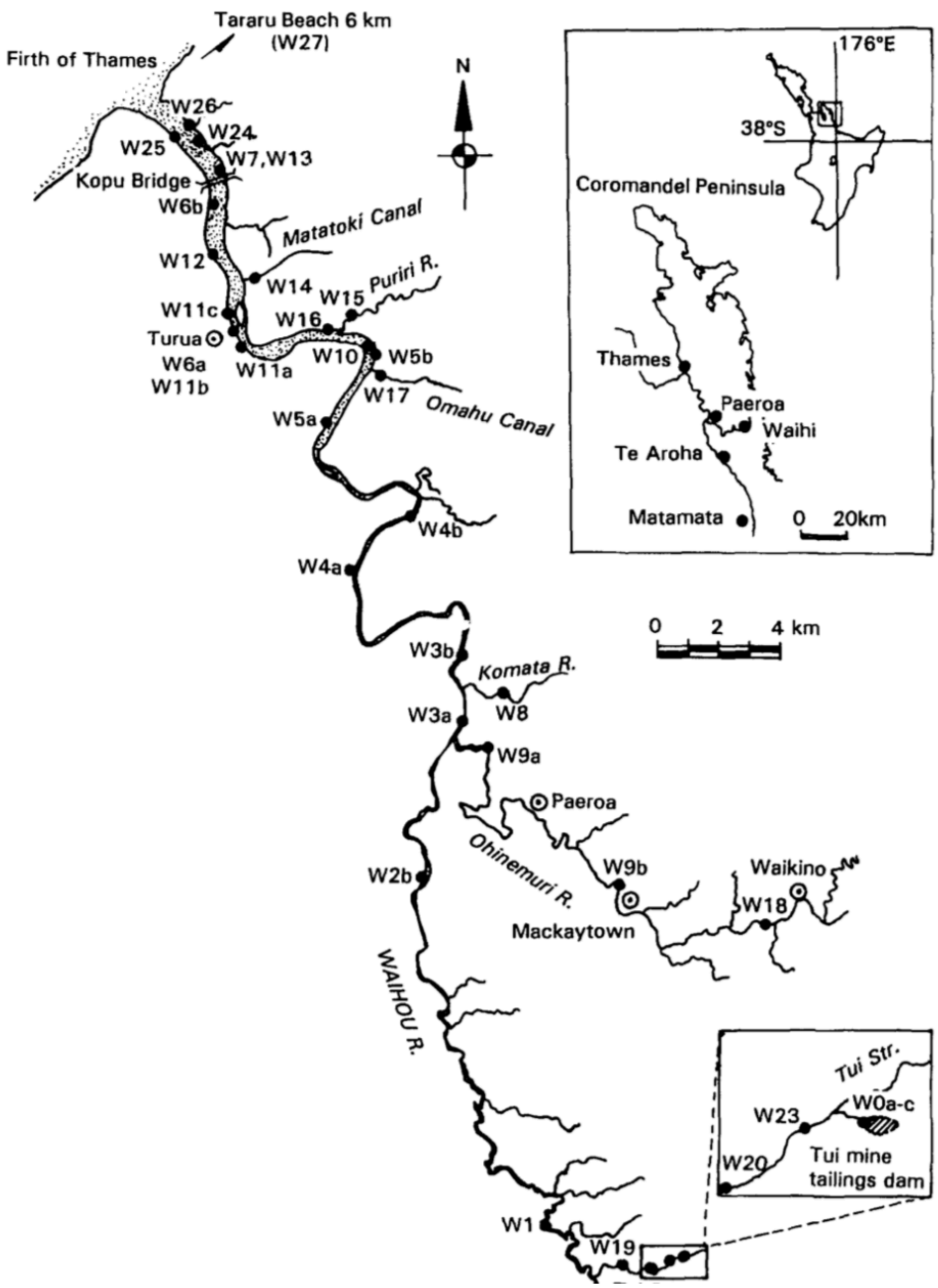

Figure 1 Webster sample location map outlining the Waihou River and its tributaries.

Upiap (2016) resampled the Ohinemuri River and the Paeroa to Kopu stretch of the lower Waihou River to assess the changes that may have occurred two decades after the Webster (1995) study. This included sampling from as many of the same area/sites as sampled by Webster as shown in figure 1. Upiap's study revealed that the overall contaminant concentrations have decreased since the earlier study. However, there wasn't any conclusive evidence of continuing downstream migration of contaminants, with the gap identified by Webster still present (Upiah, 2016). Upiap tested for additional metals (Ag, Fe, Mn & Cr), and the distribution of all contaminants suggested that there was upstream migration of sediments from the Firth of Thames, possibly associated with fluid muds, which affected the lower tidal reaches of the Waihou River to Paeroa, where it is strictly tidal. It was also inferred that from Firth of Thames to Paeroa upstream sediment migration was strictly tidal.

Clement et al (2017) examined floodplain deposits along the Ohinemuri River and identified a stratigraphic unit deposited by the 14 January 1907 flood of the Ohinemuri River. During this event, around 1.13 M m3 of gold mining tailings were deposit in the floodplains near Paeroa township in the form of a dirty yellow silt layer. This study found that the sediment rate increased from ~ 0.2 mm yr−1 in the Holocene ear to ~ 5.5–26.8 mm yr−1 after the flood event. This study indicates that it is possible that most of the contaminated waste from mines within the Ohinemuri catchment was dispersed on the flood plains upstream of Hikutaia. Clement et al (2017) also indicates that the mine waste and heavy metal contaminant doesn't show a downwards trend as mentioned in previous studies.

This study continues this research but focuses on the floodplain sediments that weren't sampled by Webster (1995), Upiap (2016), and Clement et al (2017). Samples were collected from near Te Aroha to Paeroa from the flood plains of the Ohinemuri and Waihou Rivers to determine the contaminant concentration and its distribution along the floodplain. In total, 30 sites were sampled and analysed using the portable XRF (X-ray fluorescence) and ICP-MS (Inductively couple plasma mass spectrometry). The samples were also analysed using the Mastersizer 3000 particle sizer to find out the clay percentage and assess if the grain size influences the distribution of contaminants.

This research will be helpful to identify the extent of the heavy metal pollution from previous mining activities. This may have implications on agriculture as a large percentage of the floodplain is now used for farming, specifically dairy farming. The result of this study will enable the regional council to manage the contaminated land accordingly.

1.2 Study site

The Coromandel Peninsula lies east of Auckland, in the North Island of New Zealand. This study focuses on areas including the Southern Coromandel Peninsula from Te Aroha to Paeroa, North Island, New Zealand. The Coromandel Peninsula contains various gold (Au) and silver (Ag) deposits. Since 1800, various mining operations extracted metals from these deposits. The mining activities produced mine waste as a by-product, which contained heavy metals harmful to the environment as well as to human beings. The study area follows two major rivers: Ohinemuri River and the Waihou River. The Waihou River, with a catchment area of 198,769 ha originates from the Kaimai Mamaku ranges and flows in the northerly direction through Te Aroha, then Paeroa, and through the Hauraki plains before it enters into the Firth of Thames (Baillie & Yao, 2018). The Ohinemuri River originates from the north-east of Waihi, following northerly through the steep Karangahake Gorge where it joins with the Waitawheta Stream. While running through the Karangahake Gorge, the three-historical battery stations, the Crown, the Woodstock and the Talisman, fall near its path (Conservancy, 2006). From there it then flows through Hauraki Plains and joins the Waihou river near Paeroa (Morgan, 1967).

1.3 Study Aim

The aim of this thesis is to determine the distribution of heavy metal concentrations associated with mine wastes along the lower Waihou River and part of Ohinemuri river floodplains. This was achieved by undertaking the following objectives:

1) General areas for sample sites were defined for the lower Waihou and Ohinemuri Rivers to complement research by Webster (1995), Upiap (2016) and Clement et al (2017).

2) Sample sites were specifically identified by developing flood maps of the Waihou River and Ohinemuri Rivers using ArcGIS.

3) Samples were collected and analysed by particle size analysis, portable XRF and ICP-MS.

4) The distribution of heavy metal contaminants throughout the study area was then mapped using ArcGIS.

1.4 Thesis structure

1.4.1 Chapter 1- Introduction

Chapter 1 provides the introduction into the thesis topic, a summary of the study area, thesis aim and objective. This chapter also outlines the various research objectives for the study. A summary of the implications of this research is also included in this chapter.

1.4.2 Chapter 2 - Literature Review

Mining of minerals produces mine waste as a by-product. This mine waste contains heavy metals which, without the proper disposal methods, end up in waterways. The previous study by Webster (1995) identified heavy metal contaminant in the Waihou River and its tributaries from mining activities. The waste from the Martha and Tui mines was being discharged into the Tui Stream and the Ohinemuri River which are two main tributaries for the Waihou River. Therefore, the sludge disposal of mine waste ended up in the Waihou River. This study will review the various mineral deposits in the Coromandel region and the mining history of the region. The various techniques used for mineral extraction and the mine waste discharge which contains the heavy metal contaminant used in the extraction process will also be reported on. The periodic flooding events resulted in these heavy metal contaminants being deposited in the floodplain. The dispersal of contaminant has an adverse effect on the environment and has implications on agriculture fields as much of the land in the floodplain zone is being used as a dairy farm.

1.4.3 Chapter 3 - Methods and descriptions

This chapter describes the various sampling method, GIS process and the laboratory methods used to achieve the thesis aim.

1.4.4 Chapter 4 - Results and interpretations

This chapter explains the results of various laboratory techniques used in this study such as grain size analysis. The results from XRF and ICP-MS analysis are also explained. These results are then interpreted and compared with the previous study in the same area.

1.4.5 Chapter 5 - Conclusions

This chapter summarises the results of the study. The results will help as a base template for the council to manage the agricultural land in the contaminated field.

1.4.6 Appendices

The appendices are attached at the end which summarise the results from grain size analysis, portable XRF and ICP-MS tests.

Chapter Two

Literature Review

2.1 Introduction

Mining activities produce unwanted processed waste in the form of mine tailings. These mine tailings are often produced in large volumes as a consequences of mining minerals such as gold, silver and zinc etc. During mining operations, the desired mineral can be <10 g/tonne of the ore, with the remainder discarded as mine tailings. Historically, mine tailings were often discharged into nearby rivers or streams, which acted as a sludge channel for mine waste. These rivers and streams may then become saturated with sediments and be chemically altered due to the presence of minerals such as pyrite, and heavy metal contaminants. Pyrite is a sulphide, which decomposes in the presence of oxygen (Salomons, 1995). Sediments containing mine waste may disperse on the floodplain during flooding events.

This research focuses on the heavy metal contaminants from the mining activities in the Coromandel region. The Coromandel Peninsula, North Island, New Zealand, has several mineral deposits and has been mined for various minerals extractions such as gold, silver, zinc and lead. The Tui Mine environment is the most polluted in New Zealand due to mining activities. During the operation period around 160,000 tonnes of ore were extracted through an underground network of shafts and adits. The mine waste from these mines is then deposited into sediments which gets dispersed in the floodplain during flooding events. This study investigates the heavy metal contaminant along the Waihou River floodplain.

The Waihou River begins in the Kaimai-Mamaku ranges and flows northwards into the Firth of Thames. The mining activities used the tributaries as a sludge channel for mine tailing. The Tui Stream, which starts from Te Aroha, and the Ohinemuri River, from Waikino, north-east of Waihi, act as main tributaries for the Waihou River. These tributaries have been contaminated from mining operations (Webster, 1995) and contain heavy metals such as Pb, Zn, Cd, Cr, Hg and As. These contaminants have then ended up in the Waihou River which resulted in a high contaminant concentration. Regular flooding in the Waihou River results in the contaminant depositing in the Waihou River floodplains. Regular flooding in 1901, 1907, 1910 and 1917 etc. resulted in large amounts of sediment depositing in the floodplain. The result of heavy rainfall in 1960 caused stop bank breach which then caused flooding in the Komata-Hikutaia basin (Monin, 2010a). The study carried out by Webster in 1995 compared data from a previous study by Livingstone (1987) and Tay (1980) which showed the seaward migration of contaminants. Another study completed by Joyce (2016) to investigate changes following Webster's study didn't show any conclusive evidence of downstream contaminant migration.

Historically, mining activities had poor mine tailing management and have used streams and rivers as sludge channels which resulted in the contamination of the river and stream. During flooding events these contaminants are then deposited into the floodplains. The flooding destroyed the crops, the slimes and sludge from flooding damaged grass paddocks. The cyanide sludge destroyed the fish stock in lower Ohinemuri River and upper Waihou River. This study gathers the contaminant concentration measurements along the floodplains and can assist in decision making when it comes to environmental monitoring.

The following sections review previous research done on the Waihou and Ohinemuri Rivers, their contaminant levels and the contaminant level in the floodplain. They also discuss the mineral resources in the Coromandel Peninsula, mining activities, mineral extraction processes, and production of processed rock in the form of mine tailings.

2.2 Study Area Geology - Mineral Resources in Coromandel Peninsula.

2.2.1 Tectonic Setting

The area of this study is in the Coromandel Peninsula in the North Island of New Zealand, particularly the southern end from Thames to Waihi. The Coromandel Peninsula forms a promontory separating the Firth of Thames from the Hauraki gulf in the west, and Pacific Ocean in the east. The Coromandel Peninsula in the southward direction continues in from the Kaimai ranges. The basement rock consists of greywacke rock of the Jurassic period of the Mesozoic era (around 140 million years old). This is then overlain by Miocene age andesite rock (around 15 million years old). The rhyolitic volcanic rock, Pliocene age overlays andesite volcanic rocks (around 3 million years ago)(LIVINGSTON *et al.*, 1987). The general geology of the Coromandel region is shown in figure 2.

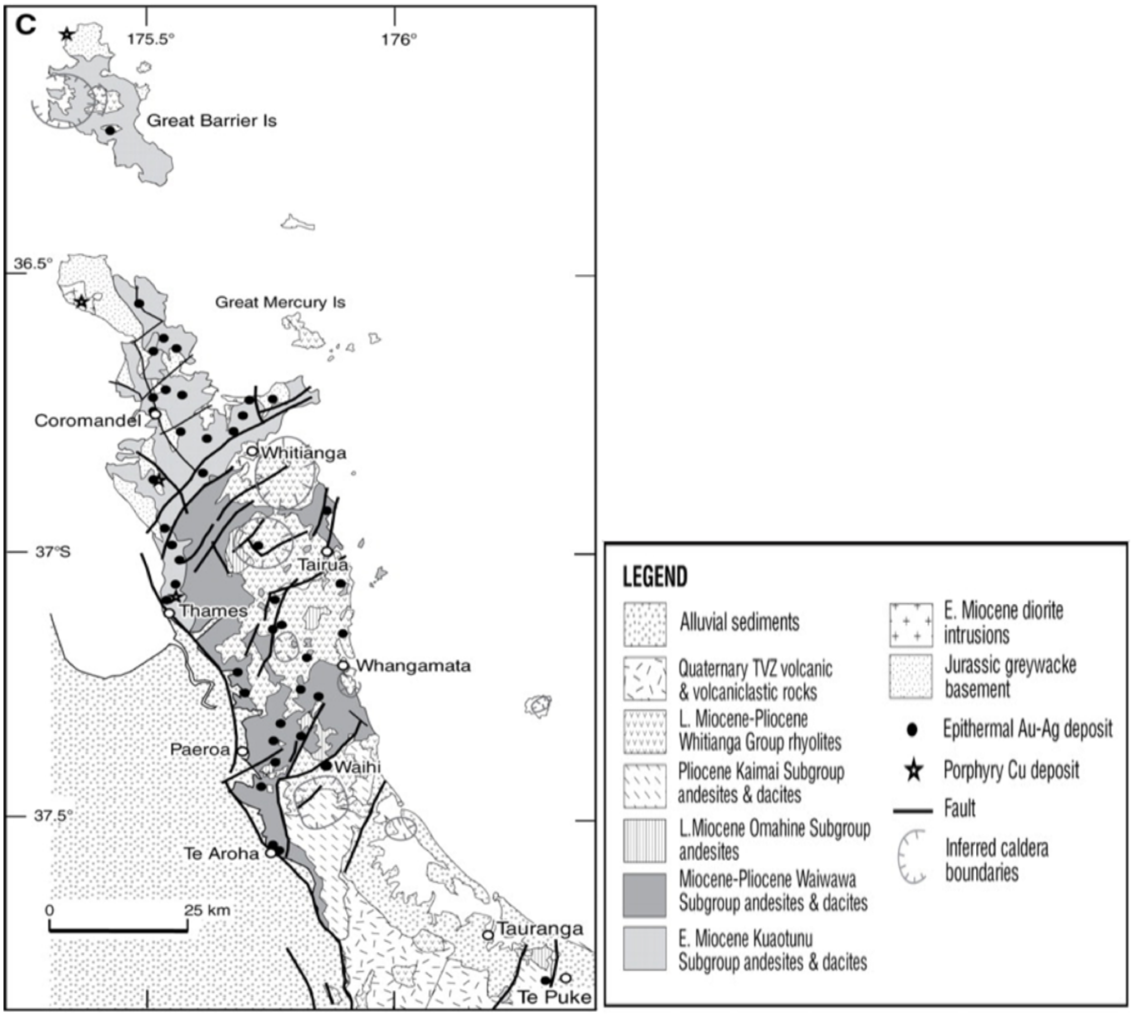

Figure 2: Geology of the Coromandel region (Phillips, 2000).

The Coromandel region overlaps the Hauraki plains on the west and the Taupo Volcanic zone in the south. The study area comes under the Coromandel volcanic zone. The Hauraki Plains is an alluvial plain built from the Waihou and Piako River sediment deposits. During the Miocene era the Hauraki plain developed a rift valley. The Hauraki rift contains two depressions which are separated by a median ridge. This rift valley, which extends from the Hauraki Gulf to the Firth of Thames, is approx. 25km wide and 200km long (Phillips, 2000). The still-active rift contains fault angle depressions which are surrounded by active faults. These active faults have a mean strike of 339 degrees which also indicates the Hauraki Rift access (Hochstein *et al.*, 1986). The eastern boundary of the Hauraki system terminates against the Coromandel Peninsula. The volcanic sequence overlies the protruding greywacke rock in the northern and western areas of the Coromandel Peninsula. The normal fault striking N-NNE, NW-NNW that formed in the peninsula in the Cretaceous period, cuts through the greywacke rock as well as the volcanic sequence (Begbie *et al.*, 2007). The greywacke basement in the Waihi area is overlain by the Waiwawa and Kaimai subgroup. The Waiwawa subgroup is around 6.3-7.9Ma and the Kaimai subgroup is around 3.5–5.6Ma years old (Smith *et al.*, 2006). The Kaimai subgroup contains the east and south parts of the Mangakino and Waihi faults whereas Waiwawa comprises of outcrop protruding in the west and north of these faults as shown in figure 3. The hot underground water, due to volcanic activity, circulates through the volcanic rocks, and also along the faults which results in hydrothermal alteration. The hydro thermic alteration results in mineral leaching and also converts silicon minerals (pyroxene) into other minerals which are stable at lower temperatures such as quartz and clay (LIVINGSTON *et al.*, 1987). These areas are of hydrothermal altered rocks and are scattered throughout the Coromandel peninsula.

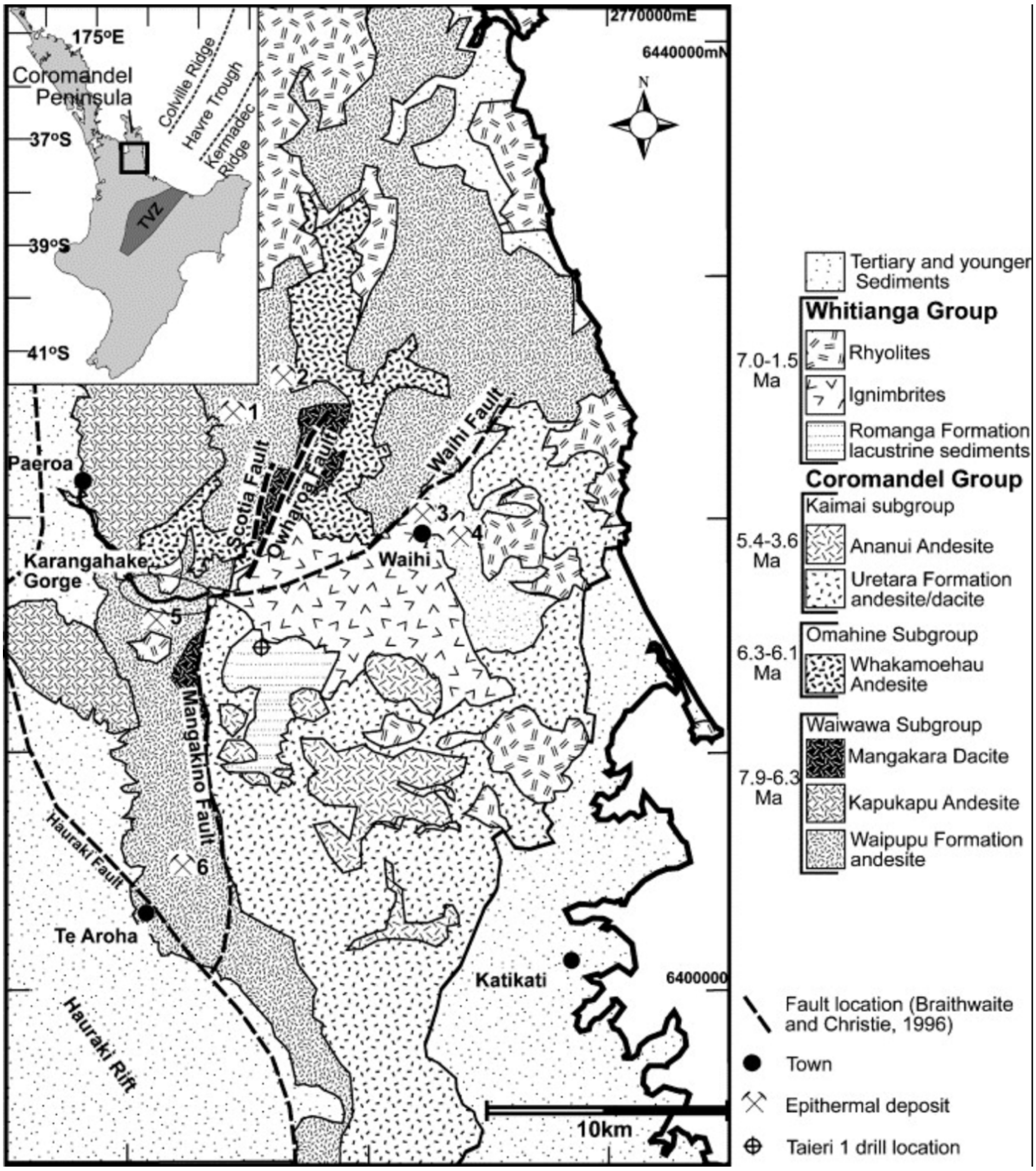

Figure 3: The Mangakino and Waihi fault as well as the regional geology of the Coromandel Peninsula (Phillips, 2000).

2.2.2 Mineralogy

The Coromandel Peninsula has several epithermal Au-Ag (Gold-Silver) deposits. Tui mine in the Hauraki goldfield, has base metal and epithermal gold-silver deposits. Tui mine contains two lobes i.e. Champion and Ruakaka lobes steeply dipping. These lobes brecciated quartz contains sulphides and quartz. It contains quartz, galena, pyrite, sphalerite and chalcopyrite minerals(Sabti *et al.*, 2000). The mineral deposit is restricted to a quartz vein, present mostly in the andesite and dacite volcanic rocks. Karangahake gorge, Martha Hill, Golden Cross and the Broken Hill kinematic data postulate that the extensional events (faults and fractures) are responsible for vein formation (Begbie *et al*., 2007). Dip slips are mainly responsible for vein formation. The mineral deposits were found in the andesite rock at Martha and Favona Hill. The Martha plain has a complex braided vein and fault system where the Martha lode dips southeast and the rest of the vein dips northeast which then merges at depth resulting in open pit mining to gold mining. The Favona vein dips northeast and extends vertically up to 400m. The Favona vein is surrounded by hydrothermal breccia in the hanging which results in the mining of minerals only through underground mining (Christie *et al*., 2007). In Thames, epithermal mineralization has minerals such as quartz, alunite, dickite and Kaolinite which can be identified by the presence of enargite in some epithermal veins. The bonanza style of mineralization is quite common in Thames where it contains high grade gold (Au) and has a higher gold/ silver ratio. In this area, the veins commonly have a diameter of 0.05-1.2m but it tends to pinch and swell up to 9m wide. The below figure 4 shows the various vein structure in different mines in Coromandel Peninsula.

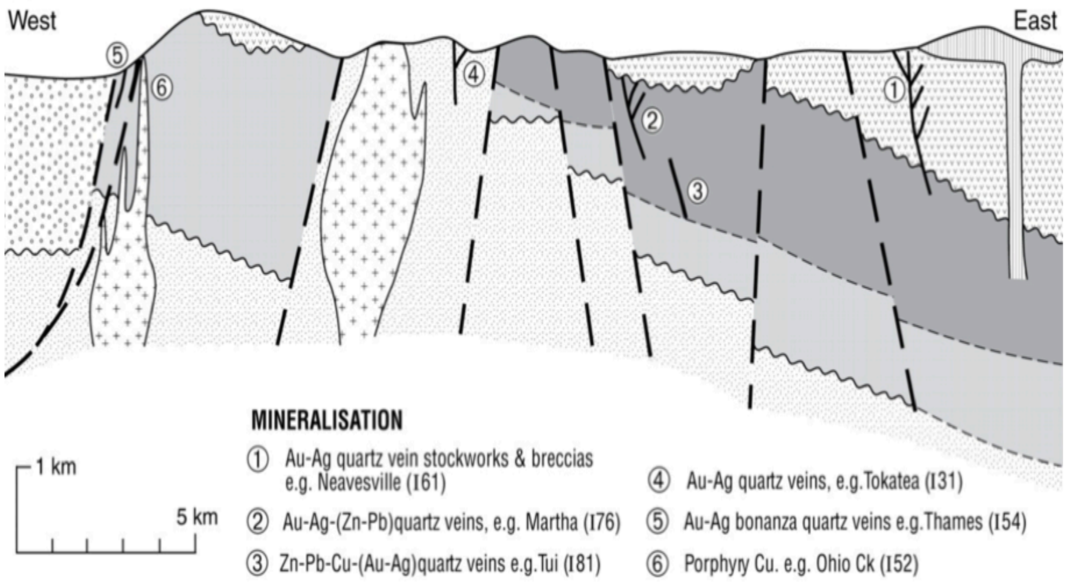

Figure 4: The different vein structures in the various mines in the Coromandel region (Begbie *et al*., 2007; Christie *et al*., 2007).

The Karangahake Gorge trends to N-NE in andesite rocks and has moderate to steep dips. In Mount Karangahake the andesite veins move into quartz veins which occur in the silicified rhyolite top. The gold-silver deposits at Karangahake gorge were discovered from of a metallogenic zone 200 km long that contains epithermal Au-Ag deposits and Cu-Au mineralization spread from the Great Barrier Reef to Te Aroha and Te Puke(TALISMAN).

The Golden Cross deposits are present in andesite and dacite rocks. The veins occur in the NE striking the empire fault zone and have continuous structure which extends over 500m. Figure 5 show the various mineral deposits in the Coromandel region as well as the vein structure present at the various deposit sites.

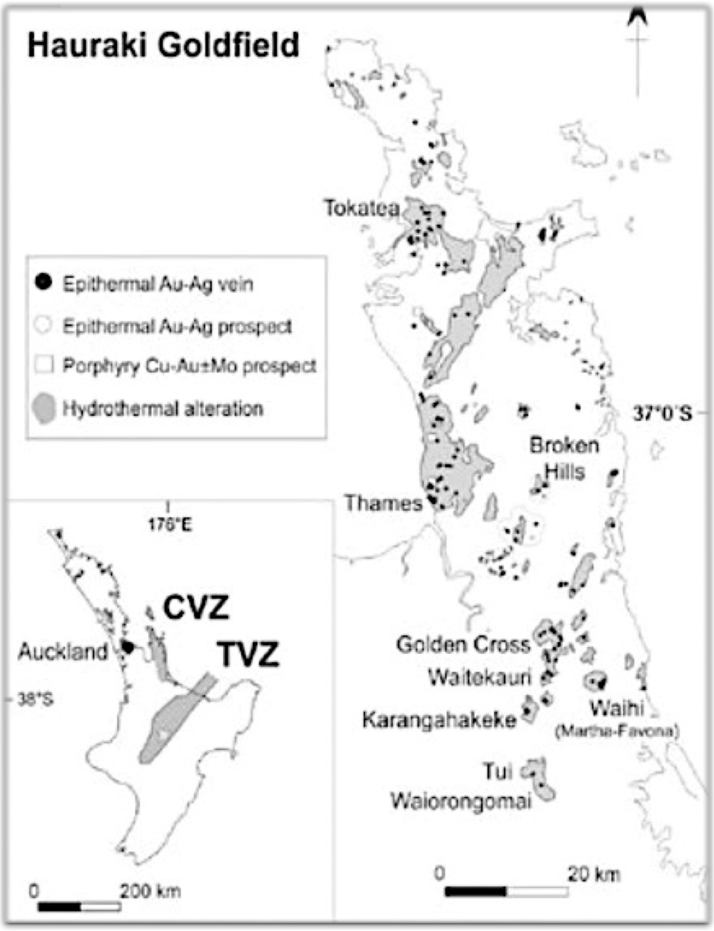

Figure 5: Various mining sites in the Coromandel Peninsula along with the deposit prospect (Christie *et al*., 2007).

2.3 Previous Research

Mine tailing and its effect on the environment have been studied in various published and unpublished work. Tay (1980) studied the impact of heavy metal discharge from Tui mine. Tay's study outlined that the Tui Stream and sediments have a higher concentration of Cd, Cu, Pb and an exceptionally higher Zn concentration. The Cd concentration was found to be 37 mg/l, Cu – 270 mg/l, Pb

– 80 mg/l, Zn – 10300 mg/l. These are the results of poor management of the mine tailing treatment and disposal (Tay, 1980). From findings in a survey for trace metal sediments of the streams and sediments of the Coromandel region, Livingston (1987) shows a high trace metal concentration in Tui and a couple of tributaries of Ohinemuri River. The survey also indicated that the higher concentration in the tailing dam and the areas nearby are because of higher acid solubility of heavy metals (LIVINGSTON *et al*., 1987). According to Tay and Livingston, a pH of 4.4 was obtained at Tui Stream as a result of heavy metal dissolution. Webster did a study in 1995 on the Waihou River to investigate how the various chemical events have affected the trace metal transportation in the river. The Waihou River receives trace metal from the Tui Stream and Ohinemuri River which resulted in an increased amount of dissolved metal and suspended metals such as Cu, Zn, Mn and As in the water column.

The Webster study indicated that the contaminants are migrating seawards. In the Waihou estuary, the suspended metal bounded sediments flocculates resulting in an increased metal concentration in the sediments (Webster, 1995). The Webster data also indicated that the neutral pH for the Tui Stream is due to groundwater and surface-water neutralizing the acidic pH found in previous studies. Joyce's study in 2016 was to fill out the time series gap from the Webster study. Joyce's thesis used samples taken from the same sites as in Webster's. The study revealed that there was an overall decrease in trace metal concentration and didn't find any evidence of downstream migration of trace metals. Instead, the study suggested that the metal distribution was affected by its surroundings such as mining upstream of the Waihou River, Thames mining etc. (Upiah, 2016). A study in 2017 looked at the environmental and geomorphological impact of gold mining activities in the Waihou and Ohinemuri River catchments. This study investigated the impact of the 1907 flood in the floodplains. The mine waste deposited in the form of yellow silt profiles have a thickness of 0.15-0.50m. The heavy metal concentration was also elevated in the floodplain, river channel and the overflow deposits with Pb of 200-570mg/kg, as 30-80mg/kg, and Ag-3mg/kg. (Clement *et al*., 2017). The mine deposits downstream trend and thickness are also affected by geomorphic factors, thickest at the straight downstream of Karangahake Gorge and lower floodplain. These findings do not show any downstream trend of contaminants however, the grain size decreases downstream. This thesis involves investigating mine tailing deposits in the floodplain of the Ohinemuri and Waihou Rivers. The tailing deposits in the floodplain will help to identify the extent of contamination during the past flooding events.

2.4 Mining History

New Zealand has a rich mining history. Mining has provided overseas revenue and contributed to New Zealand development during the 19^{th} century. Mining brought several towns such as Te Aroha into existence. In 1838, the first report of gold appears in Te Aroha. A local man George White reported the discovery of auriferous ore in the Hangawera Ranges opposite Te Aroha ranges (Morrell, 1997). The first record of gold discovery in New Zealand was found in small quantities in Driving Creek on the Coromandel Peninsula of the North Island in 1852 by Tasmanian Charles Ring (Walrond, 2006). However, the exploration of gold did not go far in the North Island and was more successful from 1861 in the South Island, particularly Otago and the West Coast (Monin, 2010b). In the North Island, minerals such as gold are present in the quartz reef whereas, in the South Island, gold was mostly alluvial which made gold mining initially more favourable in this region. The gold rush started in Otago in 1861 and 1865 in West Coast of the South Island. In the North Island, the first big gold discovery occurred in 1867 near Thames, in the form of gold bearing quartz reef. Subsequently, a gold bearing reef was discovered in Waihi (Martha Hill) in 1878 and in Karangahake mountain in 1882 (Clement *et al.*, 2017). The gold discovery in 1878 at Martha Hill was the start of major gold exploration known today as the "Martha Mine" (Monin, 2010b). This major discovery was made by John McCombie and Robert Lee and although it was considered the time of the gold rush it was a lengthy process with many hurdles, mainly due to limited equipment and poor techniques (Waihi Gold Company, 1985) . Martha Mine also had a large quantity of low-grade quartz ore bodies which also contributed to the length of time it took to mine the gold.

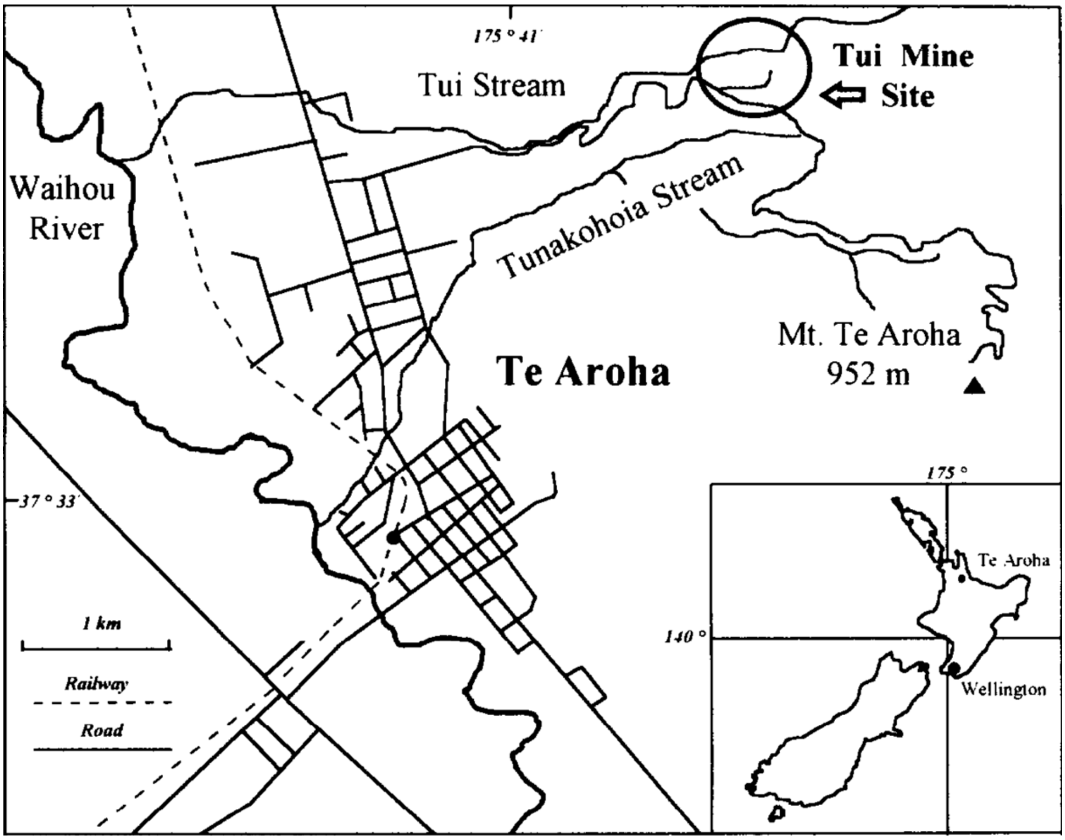

Figure 6: Tui Mine location (Simpson & Mauk, 2007).

In the early 1880's while production was slow, the discovery of gold and silver was also discovered at Mount Te Aroha (Tay, 1980). Waiorongomai valley was located in the foot of the Kaimai ranges in the southwest of Te Aroha. Gold was first discovered here in 1880. Upon investigating the valley for a sustainable supply of gold in 1881, gold was discovered in the reef which was easterly facing and runs around 2.5 miles north-south in the valley(Matheson, 1978). The mining activities declined considerably after 1884 but mining continued intermittently until 1912 with limited yield.

In the Te Aroha region, the discovery of the Champion lode in 1884 by A.C. Cornes laid the groundwork for mineral deposits. The Champion lode was discovered on the Karangahake range near Tui creek and was developed at the site which later had its name changed to Tui mine as shown in above figure 6. Tui mine was established with the first mining of Pb (lead) which was used as a flux for gold smelting. However, this later ceased due to a high content of Zn making it unfit for this purpose.

In 1875, a gold deposit at Karangahake was first mined. The introduction of a cyanide treatment process in 1890 resulted in increased gold recovery. This resulted in increased gold output. Three battery stations at Karangahake: Talisman, Woodstock and Crown were established to treat the gold ore from Karangahake gold mines. Figure 7 shows the various mining sites and battery stations located around these two rivers.

Figure 7: Various mining sites and battery station around the Ohinemuri and Waihou River (Eric, 2019).

In 1890, the Waihi Gold Mining Company purchased Martha Mine providing better sourced equipment and resources which then resulted in an increase in gold and silver extraction rates. The introduction of a cyanide extraction process in 1894 further increased production rates and the ability to extract 90% of minerals from the ore. Martha Mine operated for 24 years however, ore quantity began to decline rapidly after 1911, decreasing production until it eventually ceased all production in June 1952. Over the course of these years that the Martha Mine was operating, it extracted in total around 1,000,000kg in gold. The recent gold mining phase started in 1988 with open pit mining at Martha mine. This pen pit mine has produced around 55,584kg gold (Au), 381,513kg silver (Ag) until December 2016 (Christie *et al*., 2007). The Favona deposit was recently discovered, located 1.5km from the Martha open pit mine and has an estimate of resources of around 18,468 kg of gold (Torckler *et al*., 2006) and is shown in figure 8 below.

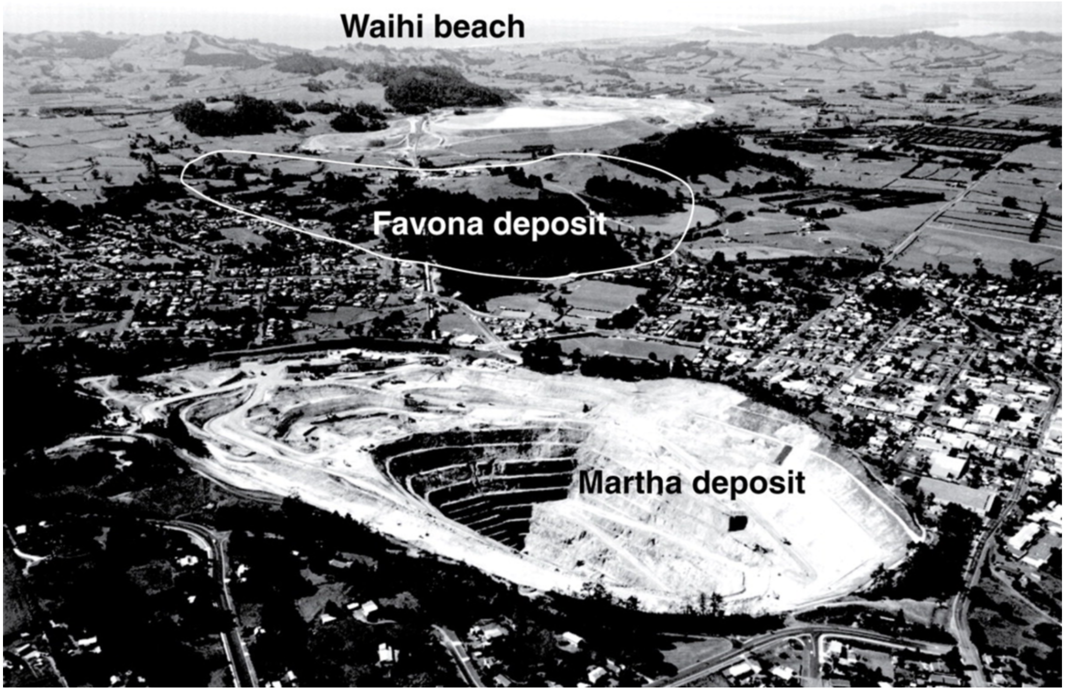

Figure 8: Arial view of Martha deposits in the form of an open pit mine and Favona deposits (Morrell, 1997).

Although Tui Mine ceased operation in the 1880's, it was reopened in 1966 and operated by Norpac Mining Limited. The mine was used to extract Pb, Zn and Cu which were transported to Japan for smelting. In 1973, the mine was closed due to the high levels of mercury found in the ore, deeming it unsuitable. Over the operating times a total of 25,000-27,000 tonnes of ore concentrate was produced from the Tui Mine (LIVINGSTON *et al*., 1987).

The Ohinemuri River channel was also dredged previously to extract gold from the coarse sediment at the bottom of river channel. Before the introduction of the cyanide process, processed ore from the mine was disposed using the river as a sludge channel. This resulted in the river bed containing coarse sediments in the form of processed ore. The Waihi dredging plant on the Ohinemuri River dredged the river channel. This was then processed at the battery station using a cyanide process to extract gold. The Waihi dredging plant operate from 1904 - 1914. In

1908 the Waihi plant was dismantled and the Waihi Paeroa Gold extraction plant was developed off Mill road, Paeroa. Dredged sediment from the Ohinemuri River was then transported to the Paeroa plant for processing. The Victoria battery at Waikino was used to processed ore until 1952.

2.5 Extraction of Minerals

The Coromandel has been explored for mining since 1867. Gold and silver were discovered in the Te Aroha area in 1880. Silver was found in the form of telluride, first found in the Moa Reef. At Champion Lobe in the Tui Mine, silver was found partially in the form of telluride and partially in the form of sulphide of antimony (Hart, 2016). Lead ore, galena, mercury and iron pyrite were also discovered at Mount Te Aroha. Initially, the mineral was extracted using explosives. At the Karangahake Mountain, miners used to explore a quartz vein with the likelihood of gold at the mountain rock face. A mine was created by tunnelling into the rock containing quartz vein. Then explosives were used to extract the rock containing minerals and then transported into rail trollies to the surface. The gold bearing quartz rubble was then processed in the Victoria battery or the Talisman battery site (Conservancy, 2006). These quartz rubbles had to be crushed and treated before any extraction process. The introduction of the McArthur-Forest cyanide process increased the gold recovery dramatically (Conservancy, 2006).

Martha Mine was considered a valuable site due to the quantities of gold and silver that were found to be contained in the large volume of low-grade quartz ore bodies. However, for the gold and silver to be extracted from the ore, a chemical process was needed. This process, called amalgamation, used mercury for extraction until 1894 but was found to be unsuccessful in extracting the full value from the ore resulting in a poor production rate. The aim was to get a full recovery of the valuable resources, increasing the production rate and value of the mine.

After the Waihi Gold Mining Company purchased the mine, a cyanide process was introduced. In 1894, due to this new process the recovery rate of valuable gold and silver from the ore rose to 90%. The Victoria Battery, Waikino processed the ore and extracted the gold and silver. The process involved primary and secondary crushers. It was during the secondary crushing that the ore was crushed into wet products. The ore was then passed through twin mercury plates where the gold and silver would attach to the plates because of amalgamation (Middleton, 1987). To ensure all valuable gold and silver were collected, water was added to the wet crushed ore producing a solution that would separate any sand from the slime. The cyanide treatment using sodium cyanide was then used to processed gold. This processed solution was then flushed out as tailing into the Ohinemuri River which was used as a sludge channel (Middleton, 1987). The gold was extracted from the river bed through dredging. The Ohinemuri River bed was dredged between 1903 - 1918 near Paeroa town and produced over 900,000 pounds of gold. During this dredging around 900,000 tonnes of tailing from mining activities were reprocessed(Tribunal, 2006).

Up until 1888, he Tui mine, was used to produce Pb which was used to extract gold from the Waiorongomai Valley. It was discovered later that the Pb ore from Tui mine contained an equal amount of Zn which made it unsuitable for the smelting process in gold extraction (Morrell, 1997). The Tui Mine, was then explored as a source of Zn, Pb and Cu. The Tui mine was mined using a 'shrinkage stopping' method of underground mining where the roof of the mine was selectively caved and worked on from the floor. The Tui mine, noted for its severe metal pollution, used a process of froth floatation to extract the main ore of Pb, Zn and Cu. The minerals were then sent to Japan for further mineral refinement. The froth floatation process separates the contaminants from the mineral ores which results in a high concentration collected in the tailings dam (Tay, 1980). During the mining period of 1966 - 1973 the total extraction of Pb, Zn and Cu ore was 27,000 tonnes which meant the equivalent of 100,000 tonnes of tailings were discharged into the Tui Stream. In 1971, heavy rainfall (230mm in 24 hours) resulted in thousands of tonnes of mine waste being discharged into the stream. The prolonged contamination of the stream, with significant levels of base metal sulphide, resulted in contaminated waterways in the stream and in the Waihou River.

2.6 Effects of Mining on Heavy Metal

The earliest study reported high concentrations of Cu, Zn, Cd and Pb in soils and streams near the mine and downslope of the tailing dam (Ward *et al*., 1977). The Tui Mine tailings were deposited in the tailing dam which was flanked by the Tui and Tunakohoia Streams which flow into the Waihou river These streams, either by being used as a sludge channel or through leaching contain elevated concentrations of heavy metals which made it an unsuitable source of potable water from upstream of the Te Aroha township (Sabti *et al*., 2000). The Tui Stream is almost lifeless due to the mine tailings. The alluvial fan ground water is also contaminated. The contaminated stream water is then recharged in the groundwater in the alluvial fan (Pang, 1995). In the Tunakohoia Stream, most of the contaminated water goes into the Tui Stream while some goes into the groundwater through a fractured andesite bedrock. The groundwater flow regime shows the contaminated plume originated from the tailing dam and is most likely limited to 1km downstream of the tailing dam (Pang, 1995).
Due to the discharging of mine tailings, the Waihou River shows evidence of heavy metal concentration. This is said to be contributed to by nearby town waste discharge, natural erosion in the environment and the past historic mining activities of the Tui and Martha Mines. Heavy metals such as Cu, Pb, As, Zn, Mn, Fe and Cd were found as suspension and particulates and in the bed sediments of the Waihou River (Webster, 1995). The historic mining activities used the Waihou River, Ohinemuri River and the Tui Stream as sludge channels and have been reported as the largest contributories to the contamination. Evidence of high heavy metal concentration has been reported in the upper Ohinemuri River and Tui Stream in form of characteristic bright orange floc because of ferric hydroxide deposition, elevated acidity and sulphate content near the tailing sites in which the mining waste was discharged (LIVINGSTON *et al*., 1987). The floodplains however, worked as sinks for the contaminants. The resident time of metal contaminant depends on the fluvial system capacity of sediment storage, flooding events, sediment transportation process and mine tailing disposal rates (Bradley, 1984; Black *et al*., 2004).

The Webster study reported that the Fe, Cu, Pb and Zn concentration in the Tui Stream and the Ohinemuri River were lower than in the 1985 recorded data.

However, the Tui tailings dam had higher metal concentration in the 1995 data than found in data reported in 1980 by Tay and in 1987 by Livingston. Metal concentrations in the two different locations are said to be affected by the acidity in tailing and water flow profile over the years as this affects the dissolution of metals in the area.

2.7 Metal Dissolution

Generally, naturally eroded metals from rock do not present harm to the environment. Sulphide minerals, such as pyrite, contained in these metals can react with oxygen, forming acids as shown in the below equation.

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \text{ ...... (1)}$$

(LIVINGSTON *et al*., 1987)

pyrite + water + oxygen $\longrightarrow$ metal + sulphate + acid

(Ferrous ion)

The greater the quantity of mineral ores the higher the chance of any reaction occurring and increasing the acidity levels. These acids, when in higher concentration, dissolve heavy metals. Therefore, increased oxidation of metal results in an increased acidity which in turn increases the heavy metal dissolution. The Middleton study reported that the cyanide treatment process used in the Victoria Battery for gold recovery resulted in sulphide minerals released in the form of mine tailings (Middleton, 1987). In addition to producing acids because of oxidation, it also releases heavy metals in the solution of:

$$2Fe^{3+} + 6H_2O \longrightarrow 2Fe(OH)_3 + 6H^+ \text{ .... (2)}$$

(LIVINGSTON *et al*., 1987)

Ferric ion water Ferric hydroxide Acid

Equation 1 and 2 show that the pyrite mineral oxidized and released ferrous ion and produced acid. The ferrous ion is then oxidized to ferric ion which is then oxidized and releases iron in form of ferric hydroxide.

Tailing dams contain the processed ore from the mineral extraction process. This is oxidized and releases acid which in turn releases heavy metals into the solution.

This results in a low pH level in the tailing dams. The Tui tailing dam had a high acidity level resulting in a low pH of 2.8 (Webster, 1995). Continuous weathering of the large volumes of finely ground tailings and the high abundance of heavy metal sulphide in the extracted ore resulted in a low pH 2.8 level in the Tui tailing dam compared to other sample sites.

The acidic nature of the tailing dam resulted in heavy metals dissolution and increased metal concentration. Where water bodies, i.e. streams and rivers were used as sludge channels the metal concentration fluctuates due to a change in flow and other environmental factors. The surface run off or the groundwater recharges the water bodies, resulting in a higher pH level compared to the tailing dam. The pH level of the Tui Stream was found to be 4.4 in both Tay and Livingston's data. However, the 1995 study found a neutral acidity for Tui Stream. This shows that there was a low heavy metal concentration in the 1995 data as compared to the Tay and Livingston data. This can be contributed to the surface water and groundwater neutralizing the acid, reducing the metal dissolution. This in turn decreased the acidity levels in the Ohinemuri River and Tui Stream.

2.8 Legislation Regarding Mining in the Coromandel Region and Safe Limits of Various Heavy Metals in Soils

The Coromandel region has been mined for gold and silver deposits. During mining processes the mine waste in the form of mine tailing wasn't managed properly. So the legislation was put in place to clarify the management of the mine waste. Initially in 1891 the Mining Act was passed. According to section 152 of the Mining Act 1981 a provision was passed under which any watercourse can be used for mine tailing, debris and any waste water discharged from a mine or any licensed holding. The watercourse term includes any river, stream, pool, creek or tributary. In 1985, a proclamation was passed under which the Waihou River, Ohinemuri River and its tributaries apart from Komata and Tarariki creek can be used as a sludge channel(Tribunal, 2006). This results in watercourses becoming polluted and unfit for drinking and agricultural purposes. In the beginning the mine waste was coarse sand but the water quality increased with improved machinery for grinding and crushing. This results in mine waste being discharged in form silt or slimes. The introduction of the cyanide process further increased the mine tailing output. In the wake of the siltation of Waihou and Ohinemuri Rivers and flooding in 1895 result the Crown passed the Waihou and the Ohinemuri River Improvement Act 1910 Waihou Valley Catchment Flood Protection and Erosion Control Scheme'(Tribunal, 2006). The main purpose of this Act was to remedy and prevent further siltation in the rivers. This Act is implemented to also consider the overflow of part of the Waihou and Ohinemuri Rivers and to improve the rivers for navigation purposes. The stop banks were built along the part of Waihou and Ohinemuri River. However, continuous periodic flooding of the rivers resulted in the Hauraki Catchment Board implementing the Waihou Valley Catchment Flood Protection and Erosion Control Scheme in 1971(Tribunal, 2006).

Water scarcity is a global issue. The historic mining activities resulted in heavy metal contaminants leaching into groundwater, rivers, streams and floodplains. The past flooding events in Waihou and Ohinemuri Rivers resulted in dispersal of contaminants in the floodplains. The cyanide process in mineral processing results in increase mine tailing. It is also responsible for killing fish stocks in the upper Ohinemuri River. The heavy metal contaminant poses a risk to the atmosphere and to the living organisms due to its toxic nature, resulting in a subject of interest in the scientific community. The heavy metal concentration in the drinking water, its sources and in the agricultural land is particularly of concern. The acceptable heavy metal limit in drinking water .according to the World Health Organization and the Ministry of Health, New Zealand is given in the table 1 below. For example, Arsenic (As) has an acceptable limit of 0.01 mg/l and Cr of 0.05. Anything above the acceptable limit poses a threat.

Table 1: WHO and NZ guidelines for drinking water standards (Organization, 2006; Health, 2008).

Contaminant	WHO provisional guideline value (mg/l)	Drinking Water Standard for NZ maximum acceptable value (mg/l)
Arsenic	0.01	0.01
Chromium	0.05	0.05
Cadmium	0.003	0.004
Copper	2.0	2.0
Nickel	0.07	0.08
Mercury	0.006	0.007
Zinc	3.0	NA
Lead	0.01	0.01
Iron	NA	0.2

The acceptable limit of heavy metals changes in the soils and as shown in the table 2 below. Here, heavy metal concentration differs depending on the different soil uses. For example,, the acceptable limit of As is 17 mg/kg in a lifestyle block with 25% production, whereas in a residential block with 10% produce, this limit is 20 mg/kg. because where the soil is used for farming or cropping there is more likely to be contaminant via ingesting plant/grass or soils entering the animals and then humans.

Table 2: Soil contaminant standards for inorganic substances (mg/kg)(Environment, 2011).

	Arsenic	Boron	Cadmium (pH 5)[1]	Chromium III	Chromium VI	Copper	Inorganic lead	Inorganic mercury
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Rural residential / lifestyle block 25% produce	17	>10,000	0.8	>10,000	290	>10,000	160	200
Residential 10% produce	20	>10,000	3	>10,000	460	>10,000	210	310
High-density residential	45	>10,000	230	>10,000	1,500	>10,000	500	1,000
Recreation	80	>10,000	400	>10,000	2,700	>10,000	880	1,800
Commercial / industrial outdoor worker (unpaved)	70	>10,000	1,300	>10,000	6,300	>10,000	3,300	4,200

The BioGro's standard for heavy metal contaminants are given in Table 3 below. This table shows the maximum accepted limit for As is 20 ppm, Cr is 150ppm, Mercury is 1ppm etc. Therefore, readings above these maximums poses a hazard to the environment and living organisms. This study looked into contaminants from past mining activities and its pathway into animals. It shows that the small proportion of this contaminant enters animals via grazing pasture plants on contaminant land. However, when animals' faeces were investigated it identified that the involuntarily ingested soil is the major pathway for contaminants into livestock. The grazing cattle involuntarily ingest up to 18% soil, of the total dry metal consumed. Therefore, around 9-80% of Pb, 30-90% of As enters into the livestock through soil ingestion (Thorton & Abrahams, 1983; Smith *et al*., 2009).

Table 3: Maximum acceptable limits for heavy metal concentration in soil (Biogro, 2009).

'Total' Metal	mg/kg (or ppm wt/wt)
Arsenic	20
Cadmium	2
Chromium	150
Copper	60
Lead	100
Mercury	1
Nickel	35
Zinc	300

Another study assessed the risk on human health from the heavy metal contaminant. This study investigated the area affected by flooding resulting in dispersal of contaminants on the floodplain. The human consumption of vegetables such as lettuce, wheat and cabbage growing on the floodplain risk an exposure of heavy metals such as Pb and Cd (Albering *et al.*, 1993-1994).

2.9 Contaminant Risk on Environment and Human Health

Mine tailings contains heavy metal contaminants. The mine tailing from the Martha Mine consists of aggregate, mostly silt sized particles (slimes) containing the contaminants. Mining produced heavy metals such as Pb, Zn, As, Cr, Cd, Hg and Ag. The dispersal of these heavy metals in water sources and soils is a hazard to the environment and a health risk to humans. The heavy metal contamination doesn't undergo biodegradation and has detrimental effects on the biological system. The cyanide sludge kills the fish stock, eels and whitebait in Waihou and Ohinemuri Rivers.. The sludge also destroys the grass paddock, green potatoes and other crops of native people. Heavy metals such as mercury can undergo methylation by anaerobic bacteria when leached into river, Mercury, in the form of methylmercury is toxic to pregnant women and can cross the placental barrier, decreasing walking, talking and learning abilities in the infant (Moreno *et al.*, 2005). Mercury also enters plants and can be passed on to humans. Crops grown on mercury laden soils are shown to have higher mercury concentration in the range of 0.05-0.13mg/kg (Qian *et al*., 2009). The mercury mining area of Lanmuchang, China has a total mercury concentration reaching to 18mg.kg in the green cabbage crop. The rice crop has methylmercury levels that can reach up to 174 microgram/kg. A study of mice which were fed with rice contaminated with mercury shows significant brain damage (Wang *et al*., 2012). Excessive concentration of the heavy metal copper can cause cellular and tissue damage and is also linked to Wilsons' disease. Lead can accumulate in the body tissue such as the liver, erythrocytes and kidneys and hinder enzyme functionality responsible for the formation of haem (pigment combines with goblin protein to form haemoglobin). In the bones, inorganic lead can replace calcium, and deposit there for long-term release in the body. In excessive concentrations this can cause brain damage in children (Ward, 1977). Arsenic exposure results in cardiovascular disease, neurological disorders and haematologic disorders. Elevated levels of As in the human body can cause arsenic poisoning. This affects all the organs and can cause bladder, skin and liver cancer (Tchounwou *et al*., 2012). Cadmium can cause gastrointestinal and pulmonary irritation, when ingested resulting in vomiting, muscle cramps, loss of consciousness, abdominal pain and vertigo. These heavy metals in soils can cause a decrease in soil production due to the process of bioaccumulation in plant roots and leaf and bio magnification in the crops (Rajeswari & Sailaja, 2014). The contaminants also impact the aquatic fauna due to their movement in the water sources especially on fish which serves as a food source for humans.

2.10 Data Comparison

Present day and historical mining activity possess a threat with contaminants present in the river system as well as in the floodplain. Webster's study suggested that the heavy metal contaminant is migrating seawards in Ohinemuri River, Waihou River and the Tui Stream. Higher metal concentration was found in the tailing dam. The pH level of the Tui Stream was recorded as 4.4 (Webster, 1995). This demonstrates an acidic nature, resulting in a higher metal dissolution. The data recorded by Tay (1980) and Livingston (1987) shows the higher metal concentration in the water bodies close to the source i.e. the upper reaches of Tui Stream, Ohinemuri River and the tailing dam. The sample sites with a neutral pH level in the Tui Stream and Ohinemuri River have demonstrated chemical processes such as adsorption and precipitation affected the metal dissolution. In these sites, heavy metals such as Cu, Pb, Zn and As are mostly bound by sediments which reduces metal dissolution. The 1995 study by Webster also states that these processes differ in salinity and affect the metal ions migration. The water column is removed of metals such as Fe, Mn, Pb, and Zn which are absorbed either in suspension or as precipitates. The heavy metals such as Cu and As are only partially absorbed in the column. Once absorbed into sediments the contaminants becoming stable. They do not migrate downstream, except with slow moving bedload sediments. The 2016 study to fill out the time series gap from the Webster study found that the overall contaminant concentration is decreasing with some sites having heavy metals such as Pb, Hg and Ag in exceedingly high concentration levels. However, this data from this study doesn't suggest any downstream migration since the 1990 data. The distribution of contaminant is suggested to be influenced by its surroundings. In the floodplains, the heavy metal concentration is controlled by geomorphological processes that are governed by the fluvial system and a disposal rate. Therefore, at present the contaminant posing a hazard is a result of geomorphic processes affecting the contaminant residence time coupled with weathering and erosion of mine tailing deposits. The study investigating the 1907 floods in the Waihou River and the Ohinemuri River shows the elevated concentration of Pb and As in the floodplain (Clement *et al*., 2017). Mine waste deposit is present in the form of dirty yellow silt in the floodplains and the core profile. The elevated concentration of Zn, Ag, Pb and Hg was also in the river channel sediment and overbank sediment. The geomorphic factor controls the thickness profile of mine waste and was mostly present in the upstream reaches.

2.11 Summary and Conclusion

- This chapter provides information on the mineral resources present in Coromandel Peninsula; the mining activities started in early 1880 with the major gold discovery of Champion lobe at the Karangahake George, Te Aroha; followed by gold mining at the Martha Mine.
- The mining activities produced processed ore in the form of mine tailing. Mine tailing contains heavy metals such as Pb, As, Cd, Cr, Zn, Hg. These mine tailings were stored in the form of the tailing dam where it ends up in the streams and rivers through leaching and weathering.
- The mine tailing from Tui Mine leached into the Tui Stream and Ohinemuri River which then enters the Waihou River. The heavy metal contaminated the river and streams.
- During the periodic flooding events in 1901 and1907 these contaminants then deposited in the floodplain resulting in elevated concentration of contaminant in the soil. Previous research has indicated the mine waste deposited in the form of a thick yellow silt layer.
- This study will investigate contaminant concentration along the floodplain of the Waihou River.

Chapter Three

Methods and Descriptions

3.1 Introduction

This study is targeted on the floodplains of Ohinemuri and the Waihou River. In this study the present heavy metal concentration on the floodplain will be examined. The methods involve both field work and laboratory work. Field work, the initial stage of the process, involves collecting the soil samples from the floodplains. Field work will involve firstly identifying the Global Positioning System (GPS) location for sample sites, site description, and sampling. These study sites were chosen based on the flood map created by ArcGIS. Therefore, sample sites were selected that will be on the river flood plains but will also coincide with the previously flooded area. Samples sites are located on the public land along the Ohinemuri River bank and the bank of the Waihou River. The laboratory work consists of processing the results, calculating the grain size, pXRF (Portable x-ray fluorescence) and ICP-MS (Inductively coupled plasma mass spectrometry) analyses of the field samples. All results will then be analysed and the heavy metal concentration will be populated in the form of a graph.

3.2 Fieldwork

Initially a flood map of the Waihou River was created using ArcGIS. The flood map outlines the low elevation areas which were affected by floods prior to stop banks being installed along the river bank. The samples sites were chosen based on the flood map along the floodplain. The samples were collected from the river floodplains. The samples sites were chosen based on accessibility and distance away from the flood bank. At each sample site, samples were collected from various depths to allow for the contamination factor as the sample sites are on close proximity to the road. Therefore, the deeper the sample taken the less chance of contamination from roading materials. The samples from different sites and various depths were collected and stored individually in labelled sealed bags.

3.3 Sample sites

The aim of this study is to analysis the soil in the Waihou and Ohinemuri River flood plains. The aim of the soil samples collected was for them to be from the area affected by either direct disposal of contaminant or by contaminant dispersal through flood water. The Waihou River was getting contaminant from the Tui Stream and Ohinemuri River which were used as a sludge channel for mine tailings. The river was periodically flooded in the past resulting in flood water containing heavy metal contaminant being dispersed in the river flood plains. Therefore, to identify the sites for sample collection a flood map for the Waihou River needed to be developed. The ArcGIS is a powerful tool which helps to visualise data spatially. The Geographic Information System (GIS) plays an important role in decision making when the natural hazard multi-dimensional phenomena contain spatial details for example, mapping the flood hazard prone area supports decision making in constructing stop banks(Coppock, 1995). The GIS application in hazard management brings some risk as well. The GIS model will have some uncertainty and it will be different for various models used. Input data can also produce some error which affects model outcomes. A study used GIS in storm surge modelling for Cairns, Australia. The spatial analysis helped to identify the urban area affected by storm surges based at various wave heights(Zerger, 2002).

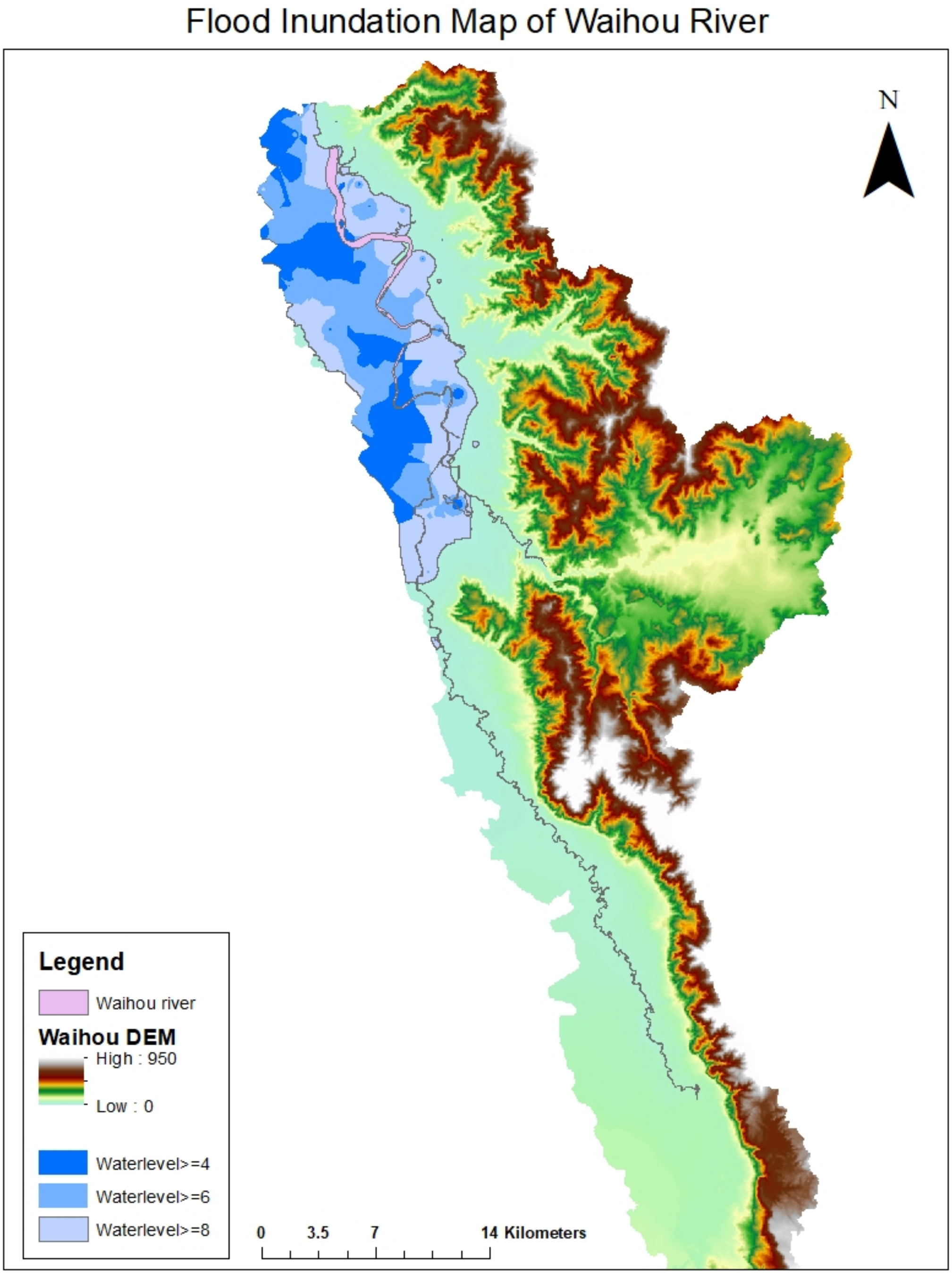

Figure 9: Flood inundation map of the Waihou river catchment.

Flood inundation map

For this study, ArcGIS software was used to create a flood inundation map or flood hazard map for the Waihou and Ohinemuri Rivers The Waihou River catchment area was the focus of this study. A river shape file was used from NZ Topo 250 to plot data in its flood plain and to verify the sample site locations. Firstly, a DEM (Digital Elevation Map) map of the catchment area was created A DEM 10m of the Waikato region was used and extracted out for the Waihou catchment using "Extract by Mask" tool. the DEM for areas less than 2, 4 and 6 was extracted using the Less Than Equal spatial analysis tool. Then a Raster to Polygon tool converted it into polygons. These methods provided information on the area around the river that are under DEM of 2, 4 and 6. These areas are flooded frequently. Therefore, these areas are most susceptible to dispersal of mine tailing through flood waters. The above figure 9 shows the flood inundation map of the Waihou River catchment area. This figure also shows the geomorphology of the floodplains area. Here, low points are the area where the contaminate can accumulate.

A flood hazard map from the Waikato Regional Council was used to cross reference the flood hazard for Te Aroha and Paeroa towns as shown in figure 10. Both towns were flooded frequently due to past flooding. The Waihou River flows through Te Aroha town where the previous flooding events would have resulted in heavy metal dispersal near the township. Paeroa town is in the flooding zone of the Ohinemuri River according to the Waikato Regional flood hazard map and has been affected by past flooding events. ArcGIS software was used to narrow down the study areas and locate the suitable sample sites.

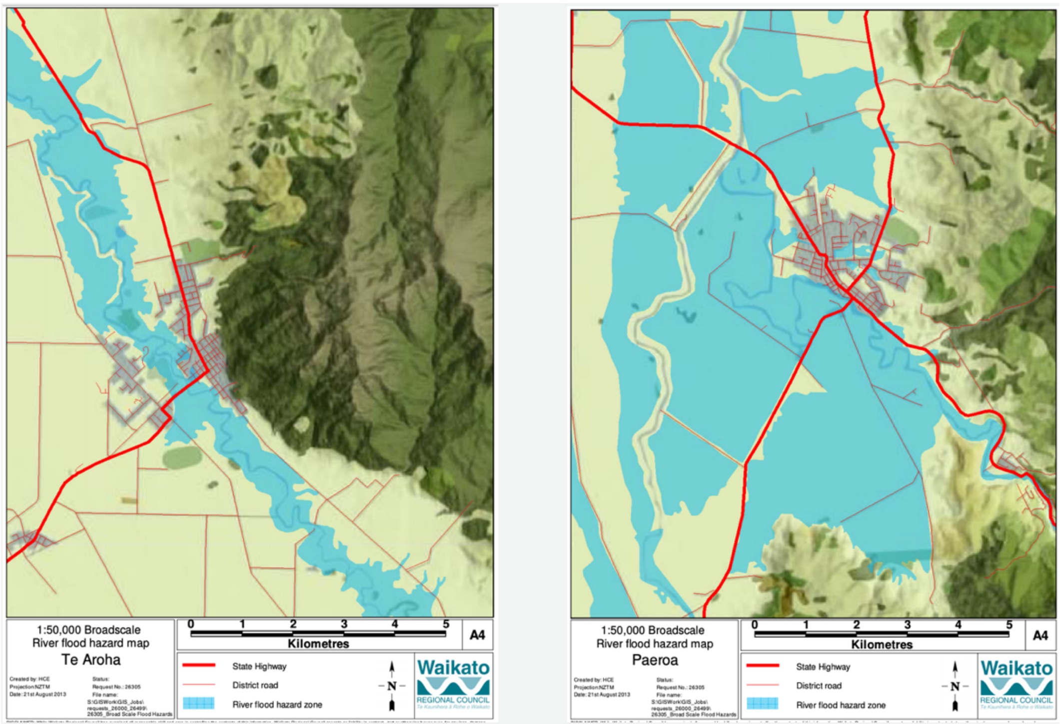

Figure 10 Flood hazard map of Te Aroha and Paeroa (Council, 2013).

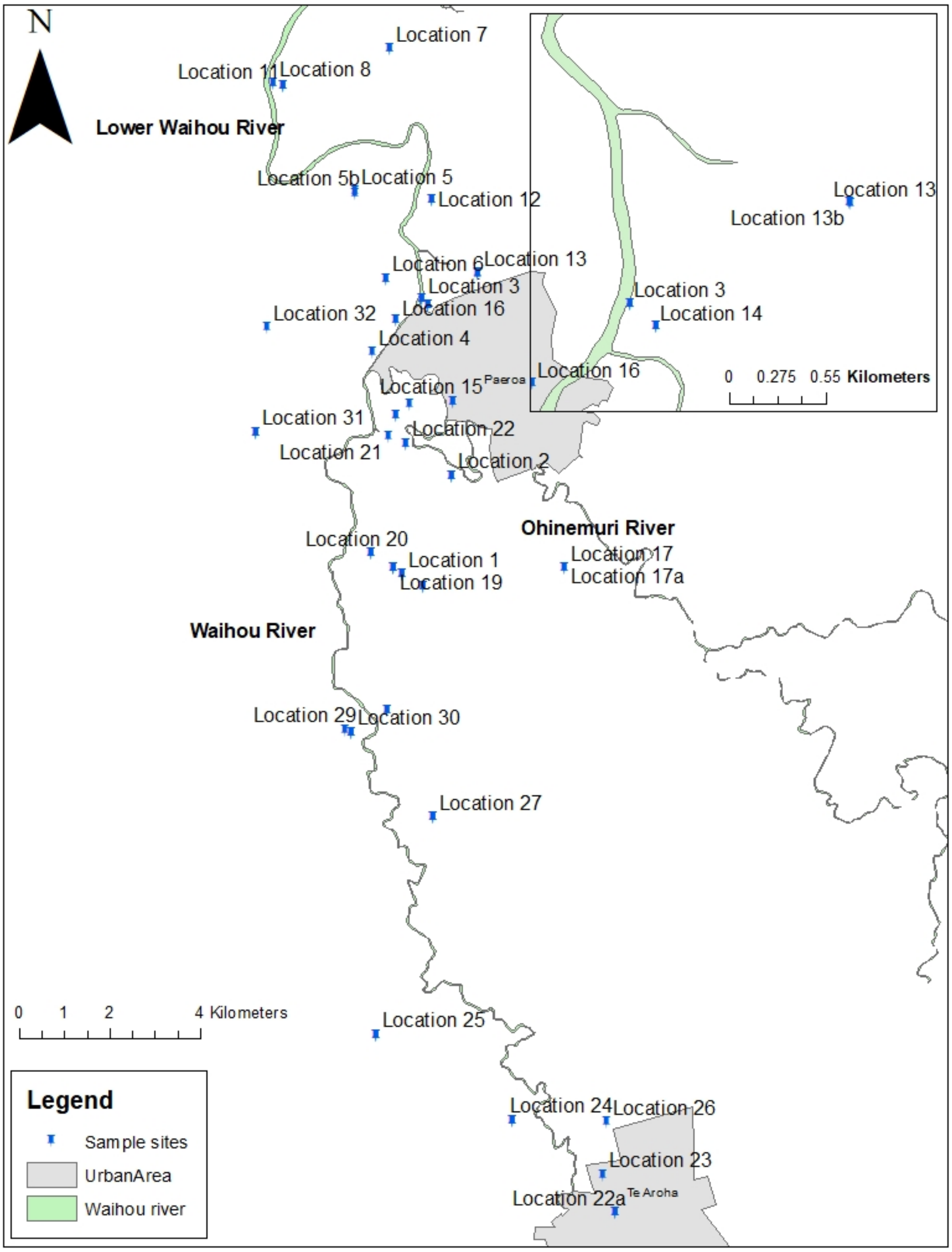

Figure 11: Sample sites used for this study.

Most of the samples were taken from the Waihou River flood plain apart from a few sample sites at the Ohinemuri River flood plain. Most of the samples were collected from river flood plains, however some sample sites such as locations 7, 32, 31, 18, 19 were located further away to measure the dispersion of heavy metals contaminants. The sample sites are shown in the above figure 11. The various sample locations, the coordinates and depths are given in Table 4 below.

Table 4: Sample location and collection at various depths.

Date	Depth	Sample location	Longitude	Latitude	Elevation (m)
19/04/2018	surface	Location 1	175.64593	-37.4105	7
19/04/2018	50 cm				
19/04/2018	120 cm				
19/04/2018	surface	Location 2	175.65734	-37.39065	4
19/04/2018	20 cm				
19/04/2018	40 cm				
19/04/2018	surface	Location 2a	175.64658	-37.3766	2
19/04/2018	surface	Location 2b	175.64313	-37.3789	3
19/04/2018	40 cm				
19/04/2018	surface	Location 3	175.64869	-37.35581	2
19/04/2018	40 cm				
19/04/2018	70 cm				
19/04/2018	surface	Location 4	175.63699	-37.3666	3
19/04/2018	surface	location 5	175.63138	-37.33476	3
19/04/2018	surface	Location 5b	175.63148	-37.33508	3
19/04/2018	surface	Location 6	175.63969	-37.35193	3
19/04/2018	40 cm				
19/04/2018	surface	Location 7	175.63893	-37.30619	2
19/04/2018	15 cm				
19/04/2018	surface	location 8	175.61045	-37.3138	8
19/04/2018	40 cm				
24/10/2018	surface	location 11	175.61292	-37.31414	9.2
24/10/2018	20 cm				
24/10/2018	40 cm				
24/10/2018	surface	location 12	175.65051	-37.33592	8.6
24/10/2018	20 cm				
24/10/2018	50 cm				
24/10/2018	surface	location 13	175.66263	-37.35031	12.3
24/10/2018	surface	location 13a	175.66267	-37.35034	12.2
24/10/2018	surface	location 13b	175.66263	-37.35031	12.3
24/10/2018	surface	location 14	175.65042	-37.35694	9.8
24/10/2018	30 cm				
24/10/2018	50 cm				
24/10/2018	surface	location 15	175.65729	-37.37588	9.9
24/10/2018	30 cm				
24/10/2018	surface	location 16	175.64258	-37.36004	8.3
24/10/2018	30 cm				
24/10/2018	surface	location 17	175.68623	-37.40833	5.6
24/10/2018	5 -7 cm	location 17a	175.6862	-37.40834	9.6
24/10/2018	surface	location 18	175.65102	-37.41286	9.9
24/10/2018	20 cm				
24/10/2018	40 cm				
24/10/2018	surface	location 19	175.64368	-37.40929	7
24/10/2018	20 cm				
24/10/2018	40 cm				
24/10/2018	60 cm				
24/10/2018	surface	location 20	175.63804	-37.40643	-5.2
24/10/2018	20 cm				
24/10/2018	40 cm				
24/10/2018	surface	location 21	175.64154	-37.38321	8.1
24/10/2018	surface	location 22	175.64574	-37.38456	9.1
24/10/2018	surface	location 22_PL	175.64574	-37.38456	9.1
15/11/2018	surface	location 22a	175.70339	-37.53604	18.6
15/11/2018	30 cm				
15/11/2018	50 cm				
15/11/2018	surface	location 23	175.69996	-37.52858	27.8
15/11/2018	surface	location 24	175.67703	-37.51826	15.4
15/11/2018	30 cm				
15/11/2018	50 cm				
15/11/2018	surface	location 25	175.64259	-37.502	11.4
15/11/2018	30 cm				
15/11/2018	50 cm				
15/11/2018	surface	location 26	175.70063	-37.51802	22.3
15/11/2018	surface	location 27	175.65522	-37.45855	16.2
15/11/2018	30 cm				
15/11/2018	50 cm				
15/11/2018	surface	location 28	175.64298	-37.43769	17.9
15/11/2018	20 cm				
15/11/2018	surface	location 29	175.63282	-37.44167	13.8
15/11/2018	surface	location 30	175.63415	-37.44218	13.8
15/11/2018	26 cm				
15/11/2018	40 cm				
15/11/2018	30 cm	location 31	175.60857	-37.38308	15.1
15/11/2018	25 cm				
15/11/2018	40 cm				
15/11/2018	10 cm	location 32	175.61061	-37.36228	8.6

3.4 Sample Collection

The sample sites were initially selected using the flood inundation/hazard map for reference and from previous research. In total 3 field trips were undertaken to collected samples. An Auger and spade were used to dig holes and collect soil samples from the various soil horizons at each sample site. The sample sites were chosen based on accessibility, on public land and located on the flood plains. This resulted in most of the sample sites being located by the road side. The surface soil near the road side was believed to be contaminated from previous road works. Therefore, by taking samples at various depths at almost each sample site insured capture of the true picture of the soil profile.

Samples were taken and stored in clean zip-loc bags to prevent loss and contamination. Each bag was labelled accordingly with the study site name, area and depth. These were then transported back to the laboratory. Figures 12 and 13 show the different sample sites. Thirty-two sites had samples taken, at various depths. During the first field trip samples were analysed using pXRF on the field itself using NIST 2711a as a soil standard as shown in figure 14. During the rest of the sample collection process the samples were analysed in the laboratory.

Figure 12: Various sample sites dug to different depths to collect different soil horizon samples. Sample site 28 (Left). Sample site 2 (Right)

Figure 13: Various sample sites dug to different depths to collect different soil horizon samples. Sample site 25 (left). Sample site 12 or 3/31 (Right).

GPS was used to record the sample locations. Etrex 10 Garmin GPS was used to record the elevation and location of sample sites. Once all the samples' location was recorded in GPS it was then exported into a csv file which was then plotted on a map using ArcGIS software. ArcGIS software used "GPX to feature" tool to convert into a feature layer showing the sample location along with elevation on the map.

Figure 14: Analysing soil samples in the field using pXRF machine.

At some sample sites such as at locations 27, 28, 12, 21 and 22 there were predominately yellow silt layer present below the A horizon as shown in figure 15. The clay, minerals and organic compounds leached down from the A horizon get stored in this horizon. The soils contaminated by mine tailing from past mining activities will store the minerals, clay and iron oxides in the B horizon as a result of the weathering process as shown in figures 12 and 13. In figure 13, the left image shows that the B horizon has clay rich minerals from 12 cm- 50cm, while in figure 12 the right image has a yellow silt layer from 15cm onwards. In figure 13, the right image shows the yellow red zone because of iron oxide present in the B horizon. The sampling process spans to different soils profiles. The Waihou River catchment has two different soil profile – Gley soils and Melanic soil profile. Here in figure 12 (left image) and in figure 13 the profiles represent Gley soils while Image B represents Melanic soils. Melanic soils are scattered around New Zealand but only make 1% of NZ soils(Research, 2019). Gley soils have waterlogging issues. During sample collection, quite a few sample sites had waterlogged soils characterised by reddish brown mottles. The samples collected from various sites were then analysed in the laboratory for heavy metals. The Location 4 was in the proximity to one of the sample locations in the Joyce Thesis and in the Webster study which helped to compare the heavy metals' concentration in various studies.

Figure 15: Yellow silt layer, silt-clay layer at Location 27 (Left) and Location 11 (Right).

Three main analytical techniques were used for the laboratory work needed to complete this study:

- Portable XRF - Determines trace/heavy metal composition,
- Grain size Analysis – This measures the particle size,
- ICP-MS – Measures trace metal concentrations contained in the flood plains.

Previous study by Webster utilised both grain size and XRF whereas the Joyce study utilised all three methods – grain size analysis, pXRF and ICP-MS.

3.5 Grain Size Analysis

Sample preparation

The soil samples contain organic-matter. The organic matter can decrease the efficiency when measuring the particle size. Therefore, soil samples needed to be acid digested before processing for grain size. The soil samples were digested using the hydrogen peroxide (H_2O_2). A study used different acid to digest the soil and sludge samples to compare the efficiency in removing organic matter. The study used hydrogen peroxide, Fenton's reagent, NaOH solution and 10% KOH solution. The soil samples were acid digested using 30% H_2O_2 at 70 °C. The study found that higher temperatures increase the efficiency of organic matter removal. The hydrogen peroxide can remove around 80 – 87% of organic matter in the sludge and 96 – 108% organic matter removal in soil samples(Hurley *et al.*, 2012). In this study, soil samples were pre-treated to remove any organic matter. The 2-5 gm of soil samples were measured and stored in separate containers. Then 10% of H_2O_2 were added to the samples. The samples were then placed on the heater overnight for around 50°C. The majority of reaction occurs in first 48 hours. Temperature was maintained at 50-degree C during the whole digestion process. Higher temperatures destroy peroxide. Most of the digestion occurs in first few days. Peroxide digest the organic matter in the soil samples.

The 10% hydrogen peroxide was added for 10 days to prevent the samples from drying out. Then the 30% hydrogen peroxide was added to the solution to digest any remaining organic matter. The pre-treated samples were then used for grain size analysis. 1 ml of 5% Calgon was added to a pre-treated sample. The Calgon is a surfactant containing 15.8 gm/2l of sodium carbonate and 71.4gm/2l of sodium polyphosphate. The Calgon acts as a catalyst to make soil particles more reactive. The samples were then heated in the ultrasonic bath for 15minutes to prevent re-agglomeration of particles. This acts as a catalyst and exercises the soil particles in the solution which helps in grain size analysis by Mastersizer.

Instrument

Figure 16: Malvern-2000 Mastersizer.

The Mastersizer 2000 was used for the grain size analysis and is a stand-alone computer system with its own standard operating procedures that outline the processes. Malvern software controls the optical system and sample dispersion units. Soil mode (soile.os) operating systems are set as the modes of measurement. On-screen data was displayed during the process. The Mastersizer 2000 is a laser diffraction particle size analyser that works on the principle of laser diffraction and is shown in figure 16. Mastersizer measures the distribution of the partial sizes in dry, wet, wet and dry dispersion types. This uses laser diffraction or low angle light scattered to measure particle size distribution. It can measure from 20nm or 0.02micron to 2000 micron or 2mm. It uses two different wavelengths of light (red and blue laser) which are used to compare the large particle size range. It also uses a combination of forward angle detection and a series of side angle and size scattered detectors which help to measure large size particle distribution with one system without needing to change optics. The Malvern hydro LV module is a wet feed system used to measure the particles in the suspension. The suspension is pumped, stirred and pumped through a measuring zone and circulated back for continuous measurement. The results are displayed on the computer in the form of particle size. A wet dispersion type was applied with an IWD (intensity weight distribution) in volume and the first measurement setting was run through the operating systems soil.os and sediment.os (Malvern, 2007).

Analytical procedures

Initially, the machine was switched on and left to warm up until it signalled that it was time to add in a sample. A small amount of the thoroughly mixed sample concentration was added. The sample was added into the dispersion unit, controlled by monitoring the obscuration of the laser beam, where it was wet sieved using plain water. The obscuration bar on the computer screen shows the amount of sample that had been added. If the obscuration range is red the concentration is out of range and therefore the process needs to be restarted. The obscuration range for each sample is shown below in Table 5.

Table 5: Obscuration percentage applied to each sample in during grains size analysis process by Mastersizer.

Sample	**Obscuration (%)**
Location 1 surface	15.36
Location 1 50 cm	16.04
Location 1 120cm	14.98
Location 2 surface	16.64
Location 2 20 cm	17.44
location 2 40 cm	16.81
Location 2a2 surface	15.74
Location 2b surface	17.19
Location 2b 40 cm	16.35
Location 3 surface	16.35
Location 3 40 cm	17.28
Location 3 70 cm	15.54
Location 4 surface	17.41
location 5 surface	14.94
Location 5b surface	15.84
Location 6 surface	15.33
Location 6 40 cm	17.16
Location 7 surface	18.59
Location 7 15 cm	17.26
location 8 surface	17.11
location 8 40 cm	16.37
location 11 surface	16.31
location 11 20 cm	17.24
location 11 40 cm	16.45
location 12 surface	17.5
location 12 20 cm	16.57

Sample	**Obscuration (%)**
location 12 50 cm	17.81
location 13 surface	14.85
location 13a surface	16.43
location 13b surface/90cm deep	17.49
location 14 surface	15.86
location 14 30 cm	21.09
location 14 50 cm	16.67
location 15 surface	15.55
location 15 30 cm	17.31
location 16 surface	17.6
location 16 30 cm	16.49
location 17 surface	15.22
location 17a 5-7cm	15.61
location 18 surface	16.44
location 18 20cm	15.68
location 18 40 cm	16.28
location 19 surface	15.86
location 19 20cm	16.91
location 19 40 cm	15.87
location 19 60 cm	16.18
location 20 surface	16.2
location 20 20 cm	16.98
location 20 40 cm	18.97
location 21 surface	16.63
location 22 surface	16.06
location 22a surface	17.33
location 22a 30cm	17.5
location 22a 50 cm	16.01
location 23 surface	16.65
location 24 surface	16.16
location 24 30 cm	18.09
location 24 50cm	16.44
location 25 surface	16.44
location 25 30 cm	18.67
location 25 50 cm	17.71
location 26 surface	18.09
location 27 surface	15.59
location 27 30 cm	18.49
location 27 50 cm	16.95
location 28 surface	17.8
location 28 20 cm	16.39
location 29 surface	15.55

Sample	Obscuration (%)
location 30 surface	16.29
location 30 26 cm	17.74
location 30 40 cm	19.78
location 31 surface	15.71
location 31 25 cm	16.37
location 31 40cm	16.16
location 32 10cm	17.25

The measurement was run once the obscuration reached a certain percentage with the result displayed on the screen. Results are then exported into Excel for later interpretation. Each new measurement or sample required the dispersion unit to be cleaned. The unit empties itself and washes any leftover particles away however in some cases this was done manually to ensure no cross-contamination.

Limitations

The limitations with this analysis are that irregular shapes of the particles from the samples can affect the results. The results are more accurate if the particles are rounder.

3.6 Portable XRF Analysis

Sample preparation

The soil samples are used to analyse heavy metals using the pXRF. The soil samples were removed of any road metal and visible organic matter such as leaves and plant root etc. Soil samples were not dried or treated before the analysis process

Instrument

The pXRF analysis used Olympus Delta handheld XRF. The machine was setup in the lab as shown in Figure 17. The soil mode setting was chosen on the machine and then it analysed the sample for 90 seconds.

Figure 17: pXRF set up in laboratory for sample analysis.

The previous study by Joyce uses XRF for contaminant concentration analysis. XRF has a lower error compared to the pXRF but it also depends on element LOD. So, for this study pXRF provides a precise element concentration in the sample. The Olympus Delta handheld XRF has a detection confidence of 99.7%.

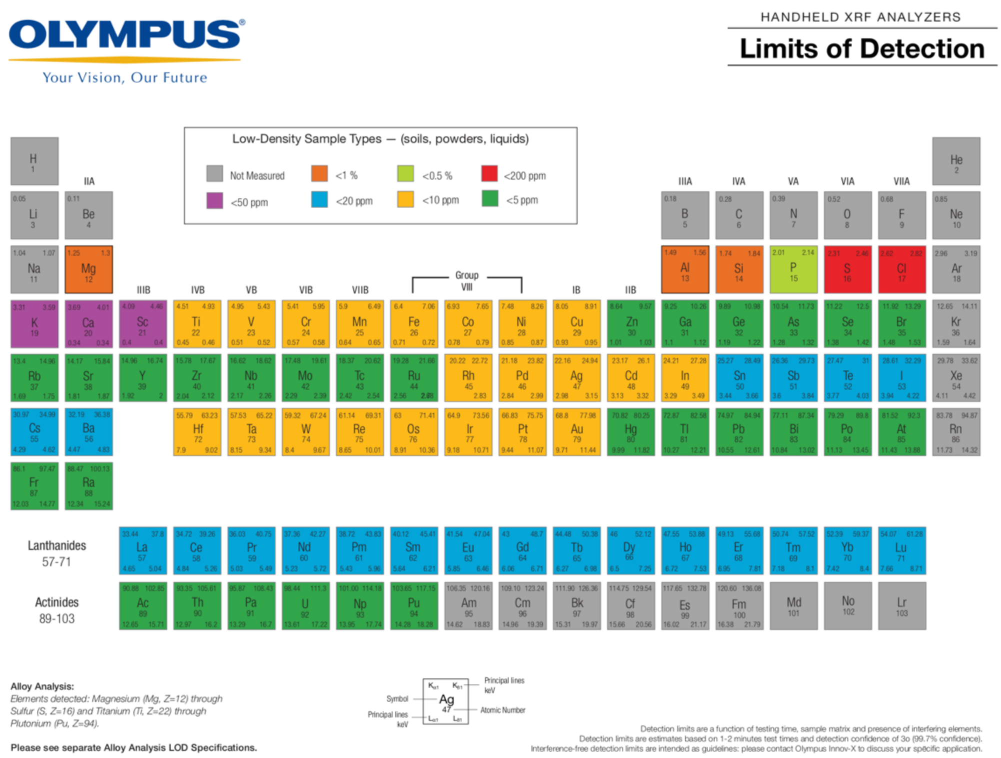

Figure 18: pXRF detection limit (Olympus Delta handheld XRF analyser) (Olympus).

Analytical procedure

The portable Delta XRF was used to analyse the soil samples. Soil was measured in one of three ways: in situ soil testing and bagged soil sample testing. During the first field trip soil was tested in the field using the in-situ soils testing method. In this method pXRF was placed directly on the soil sample after removing any plant growth, roots and foreign objects. In the later stage of sample collection samples were bagged and tested in the laboratory, A small amount of each sample was placed over the lens of the pXRF in Delta XRF Workstation.

Working principle

The pXRF works on the principle of x-ray diffraction. The X-rays from the pXRF (excitation source) are fired onto the soil samples. The interaction of x-rays with the test samples results in secondary fluorescence x-rays emission from the sample. These secondary x-rays have the energy which characterised the atoms present in the test samples(Thompson, 2009).

Heavy metal concentration was detected after calibrating the pXRF against two standards: NIST 2711a and 2710a. Each sample was analysed individually with the results exported to Excel for interpretation. The portable XRF machine indicates the different concentration of heavy metal contaminants in the soil samples. The resolution of the machine is in ppm (part per million). The lower limit of detection varies with different elements and is shown below in figure 18. Therefore, when the sample concentration is lower than this resolution the heavy metal concentration result will be displayed as less than detection (<LOD). Anything above will be given a value in PPM (part-per-million) concentration.

3.7 ICP-MS analysis

Sample preparation

Inductively Coupled Plasma Mass Spectrometry is used for analysis element concentration in the samples. It is an industry accepted method due to its low concentration detection (ppb – part per billion) and ability to detect rare earth elements. The ICP-MS process combines the high temperature Inductively coupled plasma with the mass spectrometry. The ICP source initially converts the elements in the samples into ions which in turn get separated and identified by the mass spectrometer(Wolf, 2005). Most ICP-MS use Argon gas (inert gas) as a source.

To prepare the samples, the sediments must be dried prior to the analysis. Ten grams of each sample of sediment was spread in an aluminium tray and dried in the Contherm Digital Series Oven at 60°C for 24 hours. Once dried, each sample was manually ground into a fine powder using a mortar and pestle. The samples were then transferred to clean, sealable zip-loc bags and re-labelled. The mortar and pestle were cleaned between each sample using ethanol to reduce the risk of contamination between sample sites. 1gm of this sample was weighed and placed in a clean, zip-loc bag, sealed and labelled. Each sample was analysed using the ICP-MS machine in C Block of the University of Waikato.

1 gm of the sample is added in to 50ml falcon tube. Then soil is digested by adding 3ml of HNO_3 and 1ml of HCL. The samples were then left overnight to predigest. Next day the samples were heated on a graphite digestion block at °C

for an hour. Once digestion is finished then the samples could cool down. The next step was to add 40 ml of ASTM Type I water in the falcon tube containing the pre-digested samples. The samples were then centrifuged for 10 minutes at 4000rpm. The centrifuged sample was then filtered using the 0.45micron syringe filter. Around 15ml of samples were filtered and stored in separate 15ml falcon tubes and re-labelled. Out of 15ml of filtered sample, 9.9ml of the sample is then transferred into separate 15ml falcon tubes and 0.1 ml of concentrated nitric acid (HNO_3)(Martin *et al*., 1994). The process was repeated for all the samples. Once completed and re-labelled the samples were then submitted to ICP-MS suite in the C-block for analysis.

Analytical procedures

The method applied in this analysis is called ME-MS41L (ASL code) and is described as "Lowest Detection Limit Super Trace Analysis for Soils and Sediments". In the ICP-MS process the lower the mass the more difficult to analyse. Therefore, it had a slightly higher detection limit. The elements such as silica (Si) were analysed using the triple clawed method. During the process oxygen was added to Si therefore, it is analysing silicon at a mass of 44 instead of a mass of 28. This removes some of the interferences. The elements such as silica, arsenic and selenium were analysed based on this method. The standard used in this process was a multi element standard: IV71a inorganic ventures. Hg, Sb and Mo used a single element standard. The multi element standard uses 2% by volume of nitric acid to calibrate it. Mercury used 1% of HCL and 1% of nitric acid to calibrate.

The digested solution once analysed using the ICP-MS that produced concentration results for 53 elements shown in Appendix E. The results were exported as Excel files for interpretation.

In the 1995 study (Webster, 1995), the sediments were dry-sieved through 85 microns nylon mesh. In the Joyce study the samples were sieved through 90 microns nylon mesh. For this study samples were not sieved. They were ground when dried and the sample was pre-digested straight away without the need of sieving.

All three analytical methods were then analysed for results (heavy metal concentration and grain size) and heavy metal concentration at various sample sites were compared.

Advantages and disadvantages

The ICP-MS method has several advantages over other methods which includes ability to get isotopic information, superior detection limit, detection limit is equal or better than Graphite Furnace Atomic Absorption Spectroscopy (GFAAS). ICP-MS sampler orifices and skimmer cones have small diameters which results in some limitations. For ICP-MS analysis the samples shouldn't have more than 0.2% of total dissolved solids

Chapter Four

Results

4.1 Introduction

This chapter summarises the results obtained from sample analysis. The samples were obtained from the flood plain of Ohinemuri River and Waihou River. The samples were processed using analytical processes such as the grain size analysis, pXRF analysis and ICP-MS. The grain size analysis was used to calculate the majority of the samples' grain size. The pXRF (portable XRF) was used to initially identify the heavy metal concentration in the soil samples. The soil samples were then analysed using ICP-MS to obtain a higher resolution (in ppb or ug/L) of heavy metal concentration. The pXRF and ICP-MS data was then compared to obtain a precise result in identifying the distribution of heavy metals along the flood plains.

4.2 Samples Analysis: Physical Examination

The soils samples were collected from 32 different locations at various depths. Since sample sites were present predominantly at the road side, in some sites the top soil surface was contaminated by road metals. Some sample sites such as location 5 have a significant amount of metal contaminating the sample sites. Therefore, a sub site 5b was used to collect another set of samples to compare the results and to remove any interference in the results. Location 6 has some road metal contamination at 30cm depth which was eliminated by digging to a depth of 40cm to obtain a clear picture of the soil profile at those sample sites. At some sample sites there was a clear yellow silt layer present below the A horizon. At location 2, soil contained calcified shells at a depth of 20cm. This suggested that the soil originated in the form of alluvial sediment deposits on flood plains. Due to the stop bank installation alluvial sedimentation declined in the river catchment area and therefore shell was only observed at some depths in the soil profile.. Sample at location 30 was collected from a farm, where the soil was waterlogged and had shallow soil profile. All the samples were carefully labelled and stored and analysed further in the lab using the analytical processes.

4.3 pXRF

The handheld Olympus Delta portable XRF was used to analyse the soil samples. The sample' concentration was detected in part per million and the samples' concentration below the detection level is displayed as <LOD. The LOD for pXRF differs with various elements. The pXRF provides a concentration of various elements present in the soil samples. The results are given in the table 6 and 7. The raw data is given in the appendix A. The heavy metal concentration is also give in the table 6 below.

4.3.1 Heavy Metal Concentration (Toxic Metals)

During this study each sample site was analysed for heavy metal contaminants from previous mining activities such as Fe, Pb, Cr, Cu, As, Ag and Hg. Previous studies by Webster and Joyce used the XRF analysis to identify the river bed chemistry and to determine the concentration of heavy metals in the sediments. The pXRF error margin depends on the element detection limit. In the river catchment heavy metals were dispersed during the flooding events Therefore, the larger the flooding event the greater the chances of wide spread dispersal of the contaminant. The contaminant concentration is given in the figures 19 -26 below.

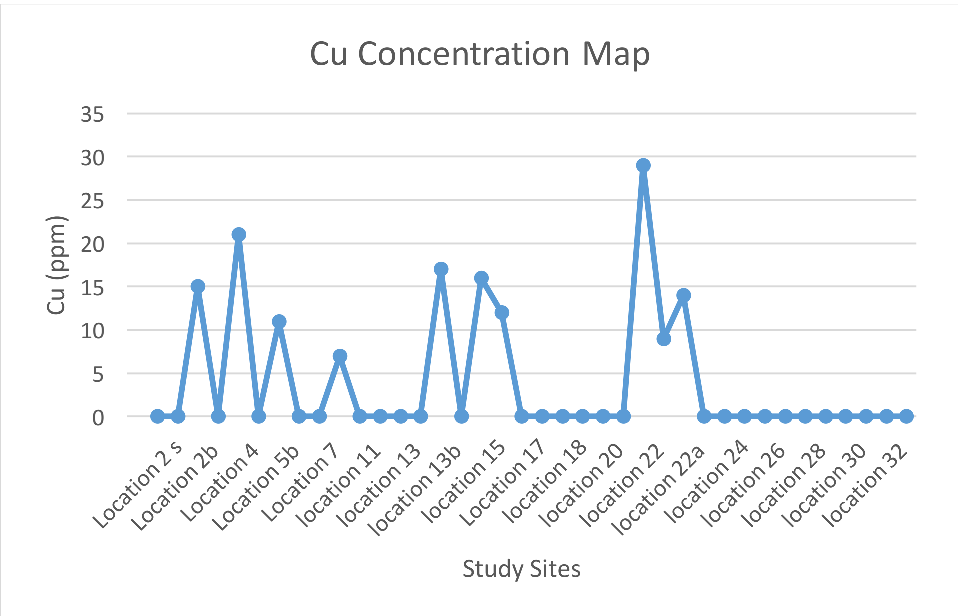

Figure 19 : Cu concentration map based on pXRF results from various sites.

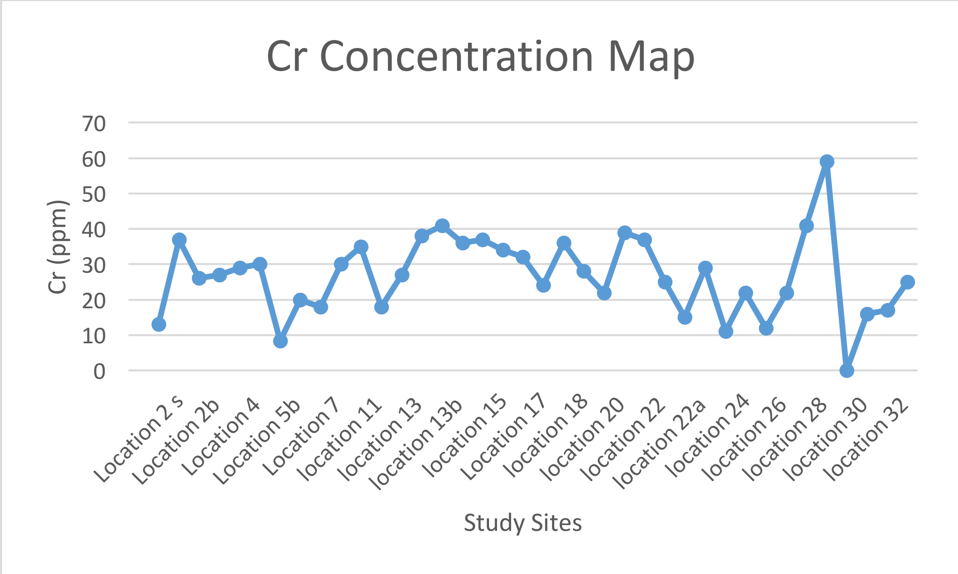

Figure 20: Cr concentration map based on pXRF results for various sample sites.

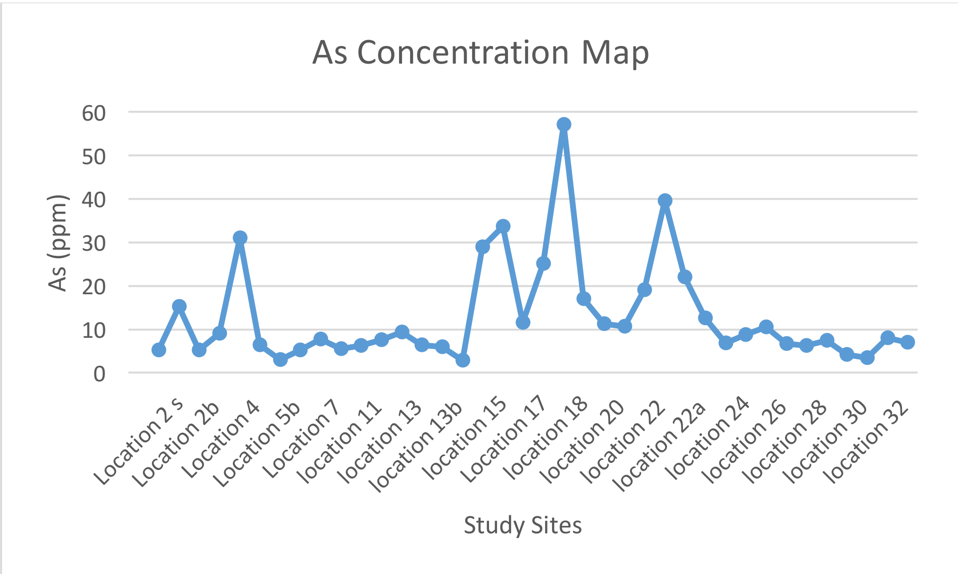

Figure 21: AS concentration map based on pXRF results for various sample sites.

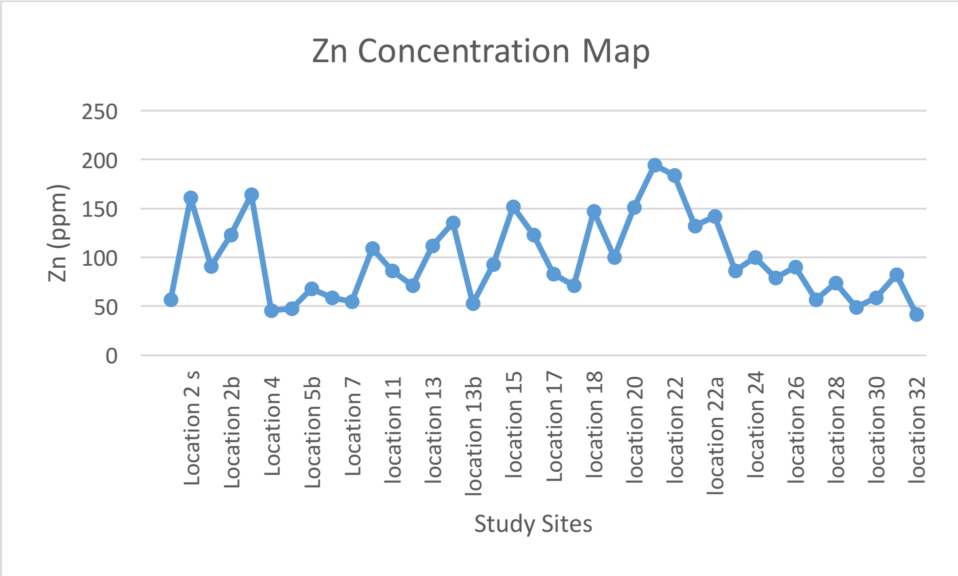

Figure 22: Zn concentration map based on pXRF results for various sample

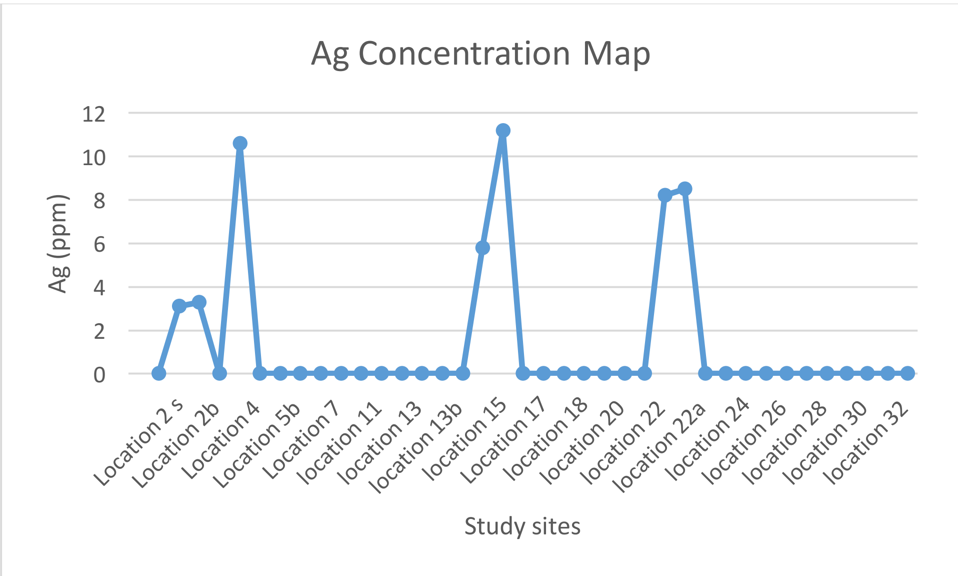

Figure 23: Ag concentration map based on pXRF results for various sample sites.

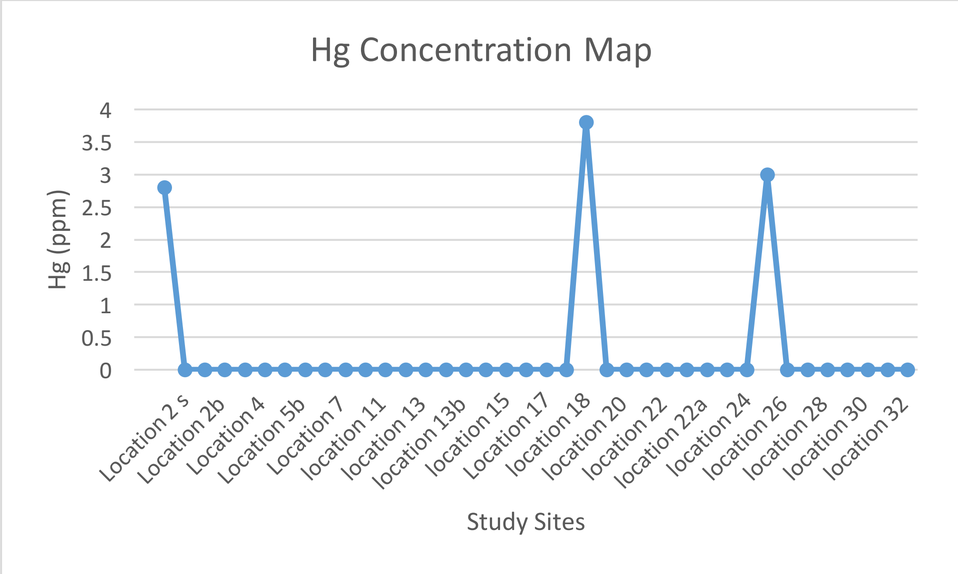

Figure 24: Hg concentration map based on pXRF results for various sample sites

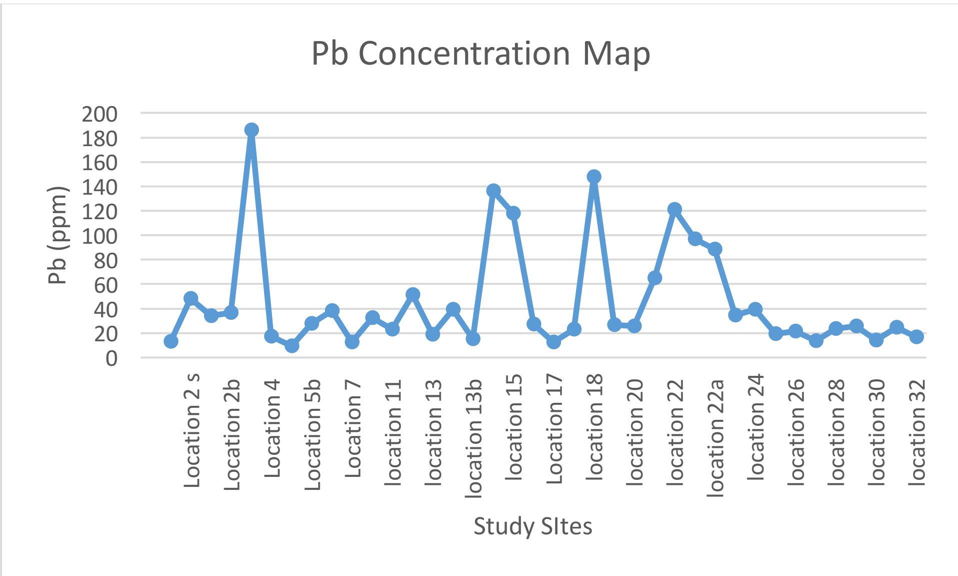

Figure 25: Pb concentration map based on pXRF results for various sample sites

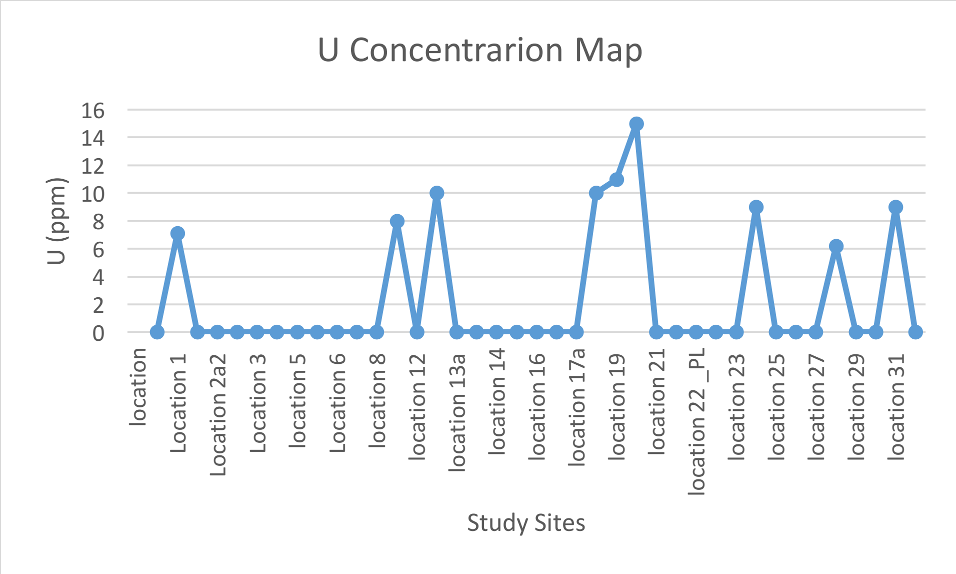

Figure 26: U concentration map based on pXRF results for various sample sites

The metals such as Zinc (Zn) and Copper (Cu) have the highest concentration detected at location 21. Higher zinc levels were detected near the end of the Ohinemuri River flood plain (Location 21) which indicates an accumulation of Martha Mine tailings from past flooding events. The amount decreases downstream until location 4 where the Ohinemuri River merges into the Waihou River and then decreases in the flood plains further down. This indicates that the flooding results in Zn contaminant dispersion into the floodplains and is the result of flooding in either or both rivers. Zinc reduces in concertation when moved further away from this convergence zone. The silver (Ag) was found in samples from location 2, 2a, 3, 14, 15, 22 and 22a. Silver metal shows the similar trend as Zn with the highest concentration at location 15 where the Martha Mine tailing mixes into the Ohinemuri River. Its concentration falls below the detection limits when it moves further away from the Ohinemuri River flood plain. Mercury (Hg) was detected in samples from locations 1, 18 and 25. High As concentration was found in locations 3, 14, 15, 17a and 22.

Uranium was found in locations 1, 11, 13, 18, 19, 20, 24, 28 and 31. This may be linked with cadmium which is used as a fertiliser. Lead (Pb) was concentrated near the Waihou and Ohinemuri convergence. Lead was also found in higher concentration in the flood plains where flood plains of the Ohinemuri River and the Waihou River overlap. Locations 7, 8, 11 and 5 shows a low concentration of contaminants in the flood plains. This shows that the contaminants didn't travel further up and the flooding didn't result in contaminate dispersal in these locations. The As concentration was found above the threshold limit in location 3, 14, 15, 17, 17a and 22. Higher As levels were detected at those locations mainly concentrated near Paeroa township and the convergence area of both rivers. Apart from these locations the As concentration decreases in the catchment downstream of the Waihou River. Arsenic concentration also reduces in the floodplains around lower Waihou River.

4.3.2 Other Element Concentration in the Flood Plains

The pXRF analysis also identified another important element in the samples. The elements are grouped together into toxic and non-element as shown in the table 7. The elements such as Phosphorus (P), Titanium (Ti), Vanadium (V), Cobalt (Co), Nickel (Ni), Selenium (Se), Barium (Ba), Bismuth (Bi), Thorium (Th) and Tin (Sn) are grouped together as toxic elements. The other elements such as Gold (Au), Calcium (Ca), Potassium (K), Manganese (Mn), Iron (Fe), Sulphur (S), Lanthanum (La) etc. are grouped as non-toxic elements. The toxic elements such as Co and Se were identified in the samples but their concentration was below the detection limit. Nickel was present in higher concentration at locations 2 and 3. Location 2 was located in the flood plain between both rivers where the flooding in any of these two rivers resulted in contaminant dispersal. The Ohinemuri River is bringing contaminant from the Martha Mine in the form of tailings from the Waikino battery station, Karangahake Gorge. The Waihou River brings contaminant from the Tui Mine tailings. Nickel concentration decreases in the catchment downstream and upstream of Waihou River. Thorium was present in higher concentration at locations 19, 20, 22a, 31, 17 a. The higher concentration was noticed in the Waihou River flood plains apart from at location 17a where Th was reported in higher concentration. The Th concentration decreases in the flood plains downstream from the Waihou River. Bismuth was present in higher concentration at locations 2 and 3 while at the remaining locations it was below the detection limit. This could be result of contaminant from the Martha Mine, Karangahake mining and the Komata battery station. Tin was below the detection limit at the majority of places apart from locations 2, 3, 14, 21, 22, 26 and 31. Tin is mostly concentrated in the Waihou River flood plains. Its concentration also decreasesd in the floodplains upstream from the Waihou River. Overall the concentration of toxic elements was present in low levels to below the detection limit.

The non-toxic elements such as gold were identified using pXRF but its concentration was reported below the detection level. Mn was reported in higher concentration at locations 2, 2a, 8 and 21. These higher concentrations were reported near the old rivers Waihou River channel, the floodplains around Lower Waihou River. High Fe concentration was reported in location 12, 20 and 28. The concentration reduces further downstream of the Waihou River. Cerium (Ce) and Lanthanum (La) were also detected in the samples but were present mostly in low concentration to be detected by pXRF. Ce however, was detected in location 2, 3 and 25. Chlorine(Cl) was detected in higher concentration at location 18 and 19. The concentration reduces in the floodplains downstream of Waihou River. In the flood plains at upstream of the Waihou River its concentration fluctuates but remains in the lower level. Calcium (Ca) was identified in higher concentration at locations 13, 17 and 18. At location 2, shells were also located around 50cm deep Location 2 was in the old river channel. Dredging of Waihou and Ohinemuri River in the past resulted in sediment deposit from the river bed into these old channels. It was present in higher concentration in floodplains around the Paeroa town. However, its concentration decreased upstream and fluctuated at first then decreased in the flood plains downstream of the Waihou River.

Molybdenum (Mo) and Antimony (Sb) were identified in the samples but were below the detection at the majority of the sample locations apart from a few locations where their concentration was still in lower concentration but was detected by pXRF. Potassium (K) was present in higher concentration at locations18, 19, 22a and 25. The higher concentration was reported near Paeroa and the convergence point whereas the concentration decreases in the lower Waihou River flood plains. Strontium (Sr) has higher concentration at locations 13 and 18. Its concentration slowly increases and peaks at the flood plains downstream of the lower Waihou River and continues to decrease to the coast. Sulphur (S) concentration peaks at locations 17 and 18. Its higher concentration in the floodplains of the lower Ohinemuri River is a result of mining activities around the Ohinemuri river. Its concentration reduces upstream and downstream of Ohinemuri and Waihou River flood plains. Overall the non-toxic elements were identified in the concentration range of High to Less than detection limit for pXRF at the various sample locations.

Table 6: Concentration of heavy metal detected on the floodplain by pXRF.

Sample locations	Trace(Heavy) Metals							
	Cu	Cr	Zn	As	Ag	Hg	Pb	U
Location 1 surface	<LOD	13	57	4.1	<LOD	2.8	13	<LOD
Location 1 50 cm	<LOD	6	46.8	5	<LOD	<LOD	12.6	<LOD
Location 1 120cm	<LOD	<LOD	36.8	5.2	<LOD	<LOD	11.4	7.1
Location 2 surface	<LOD	22	124	13.7	<LOD	<LOD	48.4	<LOD
Location 2 20 cm	<LOD	37	161	15.3	3.1	<LOD	37.6	<LOD
location 2 40 cm	<LOD	36	47.9	5.4	<LOD	<LOD	11	<LOD
Location 2a2 surface	15	26	91	5.2	3.3	<LOD	34	<LOD
Location 2b surface	<LOD	19	123	9.1	<LOD	<LOD	36.5	<LOD
Location 2b 40 cm	<LOD	27	66	6.8	<LOD	<LOD	9.2	<LOD
Location 3 surface	14	26	140	18.4	4.6	<LOD	59.7	<LOD
Location 3 40 cm	21	29	164	31	10.6	<LOD	186	<LOD
Location 3 70 cm	17	23	135	16.6	6.4	<LOD	80	<LOD
Location 4 surface	<LOD	30	45.9	6.4	<LOD	<LOD	17.5	<LOD
location 5 surface	11	8.4	47.8	3	<LOD	<LOD	9.4	<LOD
Location 5b surface	<LOD	20	68	5.3	<LOD	<LOD	27.8	<LOD
Location 6 surface	<LOD	10	59	7.7	<LOD	<LOD	38.4	<LOD
Location 6 40 cm	<LOD	18	31.2	4.8	<LOD	<LOD	11.1	<LOD
Location 7 surface	7	<LOD	54.8	4.9	<LOD	<LOD	12.4	<LOD
Location 7 15 cm	<LOD	30	37.8	5.5	<LOD	<LOD	10.8	<LOD
location 8 surface	<LOD	22	84	6.3	<LOD	<LOD	32.4	<LOD
location 8 40 cm	<LOD	35	109	6	<LOD	<LOD	27.9	<LOD
location 11 surface	<LOD	10	86	5.1	<LOD	<LOD	15.1	<LOD
location 11 20 cm	<LOD	18	66	7.6	<LOD	<LOD	17.2	8
location 11 40 cm	<LOD	18	41.1	<LOD	<LOD	<LOD	22.9	<LOD
location 12 surface	<LOD	27	71	9.4	<LOD	<LOD	51.3	<LOD
location 12 20 cm	<LOD	26	57	7.1	<LOD	<LOD	13	<LOD
location 12 50 cm	<LOD	19	51	7.4	<LOD	<LOD	18.8	<LOD
location 13 surface	<LOD	38	112	6.4	<LOD	<LOD	18.7	10
location 13/3a surface	17	41	135	6	<LOD	<LOD	39.2	<LOD
location 13b surface	<LOD	36	53.1	2.8	<LOD	<LOD	15.3	<LOD
location 14 surface	<LOD	14	82	7.7	<LOD	<LOD	20.2	<LOD
location 14 30 cm	13	37	87	24.3	4	<LOD	93	<LOD
location 14 50 cm	16	18	93	28.9	5.8	<LOD	136	<LOD
location 15 surface	9	34	152	29	8.1	<LOD	89	<LOD
location 15 30 cm	12	31	129	33.6	11.2	<LOD	118	<LOD
location 16 surface	<LOD	30	123	11.5	<LOD	<LOD	27.4	<LOD
location 16 30 cm	<LOD	32	63	11.1	<LOD	<LOD	26.4	<LOD
location 17 surface	<LOD	24	83	25.1	<LOD	<LOD	12.7	<LOD
location 17a 5-7cm	<LOD	36	71	57.1	<LOD	<LOD	23.2	<LOD
location 18 surface	<LOD	28	147	7.3	<LOD	<LOD	35.2	10
location 18 20cm	<LOD	21	74	8.1	<LOD	<LOD	41.8	<LOD
location 18 40 cm	<LOD	25	85	17	<LOD	3.8	148	<LOD
location 19 surface	<LOD	22	76	8.5	<LOD	<LOD	26.9	11
location 19 20cm	<LOD	19	90	8.7	<LOD	<LOD	20.5	<LOD
location 19 40 cm	<LOD	16	100	11.2	<LOD	<LOD	21.3	<LOD
location 19 60 cm	<LOD	15	74	11.2	<LOD	<LOD	21.3	<LOD
location 20 surface	<LOD	39	151	8.2	<LOD	<LOD	24.9	15
location 20 20 cm	<LOD	31	84	7.8	<LOD	<LOD	24.3	<LOD
location 20 40 cm	<LOD	29	66	10.7	<LOD	<LOD	25.8	<LOD
location 21 surface	29	37	194	19.1	<LOD	<LOD	65	<LOD
location 22 surface	9	25	184	39.5	8.2	<LOD	121	<LOD
location 22 surface_PL	14	15	132	22	8.5	<LOD	97	<LOD
location 22a surface	<LOD	22	142	9.7	<LOD	<LOD	88.4	<LOD
location 22a 30cm	<LOD	23	137	12.6	<LOD	<LOD	88	<LOD
location 22a 50 cm	<LOD	29	111	6.9	<LOD	<LOD	61.9	<LOD
location 23 surface	<LOD	11	86	6.9	<LOD	<LOD	34.7	<LOD
location 24 surface	<LOD	14	71	6.1	<LOD	<LOD	39.3	<LOD
location 24 30 cm	<LOD	22	100	8.7	<LOD	<LOD	27.6	<LOD
location 24 50cm	<LOD	15	58	8	<LOD	<LOD	23.1	9
location 25 surface	<LOD	7	79	6.1	<LOD	<LOD	19.6	<LOD
location 25 30 cm	<LOD	11	59	10.5	<LOD	<LOD	16	<LOD
location 25 50 cm	<LOD	12	42.9	7	<LOD	3	13.1	<LOD
location 26 surface	<LOD	22	90	6.7	<LOD	<LOD	21.7	<LOD
location 27 surface	<LOD	13	44.1	2.8	<LOD	<LOD	10.9	<LOD
location 27 30 cm	<LOD	30	57	6.3	<LOD	<LOD	13.7	<LOD
location 27 50 cm	<LOD	41	38.4	4.8	<LOD	<LOD	11.5	<LOD
location 28 surface	<LOD	20	74	6.4	<LOD	<LOD	23.5	<LOD
location 28 20 cm	<LOD	59	47	7.4	<LOD	<LOD	11	6.2
location 29 surface	<LOD	<LOD	49	4.2	<LOD	<LOD	25.6	<LOD
location 30 surface	<LOD	<LOD	52.6	3.5	<LOD	<LOD	14.3	<LOD
location 30 26 cm	<LOD	<LOD	59	3.5	<LOD	<LOD	12.6	<LOD
location 30 40 cm	<LOD	16	32.3	<LOD	<LOD	<LOD	12	<LOD
location 31 surface	<LOD	16	82	8	<LOD	<LOD	24.6	<LOD
location 31 25 cm	<LOD	17	54	7.6	<LOD	<LOD	21.7	9
location 31 40cm	<LOD	17	63	7.8	<LOD	<LOD	14.2	<LOD
location 32 10cm	<LOD	25	41.5	7	<LOD	<LOD	17	<LOD

Table 7: Concentration of other toxic and non-toxic metal detected along floodplain by pXRF.

Sample locations	Toxic and Non toxic Metals																													
	Nd	Pr	Ce	La	Ba	Y	P	S	Cl	K	Ca	Ti	V	Mn	Fe	Co	Ni	Se	Rb	Sr	Zr	Nb	Mo	Sn	Sb	Ta	W	Au	Bi	Th
Location 1 surface	<LOD	<LOD	<LOD	<LOD	317	24.7	<LOD	<LOD	218	4673	3638	1347	29.4	653	14816	<LOD	<LOD	<LOD	44	92	170	11.8	<LOD	<LOD	<LOD	9.4	<LOD	<LOD	<LOD	4.4
Location 1 50 cm	<LOD	<LOD	<LOD	<LOD	293	38.7	<LOD	159	147	3480	935	1036	26.7	189	6768	<LOD	<LOD	<LOD	38.7	66.3	203	11.8	<LOD	<LOD	<LOD	9.8	<LOD	<LOD	<LOD	8.2
Location 1 120cm	<LOD	<LOD	<LOD	<LOD	368	27.8	<LOD	<LOD	105	4473	1448	1102	28.7	79	5368	<LOD	<LOD	<LOD	46	122	208	5.1	<LOD	<LOD	<LOD	7.3	<LOD	<LOD	<LOD	9.8
Location 2 surface	<LOD	<LOD	<LOD	<LOD	282	16.1	<LOD	<LOD	<LOD	3609	3209	1503	34	648	16994	<LOD	<LOD	<LOD	38.6	54.2	90.3	5.5	<LOD	<LOD	<LOD	6.5	<LOD	<LOD	<LOD	4.7
Location 2 20 cm	<LOD	<LOD	<LOD	<LOD	417	21.5	<LOD	<LOD	<LOD	4836	4597	2281	51	1022	23511	<LOD	34	<LOD	49.8	67.8	126.1	5.1	<LOD	11	<LOD	9.4	<LOD	<LOD	<LOD	7.1
location 2 40 cm	<LOD	<LOD	68	<LOD	400	21.8	<LOD	<LOD	<LOD	3999	2591	2448	47	584	18667	<LOD	39	<LOD	39.5	52.3	139.3	<LOD	<LOD	10	<LOD	6.9	<LOD	<LOD	41	5
Location 2a2 surface	<LOD	<LOD	<LOD	<LOD	320	19.7	<LOD	<LOD	<LOD	4384	5560	1840	32	590	19606	<LOD	34	<LOD	50.2	94.8	97.8	<LOD	<LOD	11	<LOD	6.4	<LOD	<LOD	31	5.6
Location 2b surface	<LOD	<LOD	<LOD	<LOD	264	14.6	<LOD	<LOD	<LOD	4088	2888	1664	30	1156	14391	<LOD	<LOD	<LOD	47.8	53	99.6	7.2	<LOD	<LOD	<LOD	7.2	<LOD	<LOD	<LOD	4.7
Location 2b 40 cm	<LOD	<LOD	<LOD	<LOD	305	13.3	<LOD	<LOD	<LOD	4411	824	2303	39	408	18199	<LOD	12	<LOD	51.1	52.9	155	4.8	<LOD	<LOD	<LOD	10.3	<LOD	<LOD	<LOD	8.6
Location 3 surface	<LOD	<LOD	<LOD	<LOD	214	22	<LOD	<LOD	<LOD	4250	1782	1530	29	466	20837	<LOD	<LOD	<LOD	38.1	41.3	127.5	8.3	<LOD	<LOD	7	6	<LOD	<LOD	<LOD	5.1
Location 3 40 cm	<LOD	<LOD	<LOD	<LOD	325	19.9	<LOD	<LOD	<LOD	5925	1669	1400	28.5	438	18305	<LOD	41	<LOD	49.3	55.3	104.9	<LOD	<LOD	12	9	5	<LOD	<LOD	24	6
Location 3 70 cm	<LOD	<LOD	68	<LOD	280	23.1	<LOD	177	<LOD	5105	1744	1393	28.4	328	16778	<LOD	18	<LOD	47.7	56.9	123.9	3.1	<LOD	<LOD	9	5.5	<LOD	<LOD	20	7
Location 4 surface	<LOD	<LOD	<LOD	<LOD	211	13.7	<LOD	<LOD	<LOD	4190	652	2103	35	204	27349	<LOD	<LOD	<LOD	52.9	43.3	96.7	6.4	<LOD	<LOD	<LOD	7.8	<LOD	<LOD	<LOD	3.4
location 5 surface	<LOD	<LOD	<LOD	<LOD	184	16.1	<LOD	232	<LOD	3082	7024	1249	25.1	531	17697	<LOD	<LOD	<LOD	31.8	130	71	<LOD	<LOD	<LOD	<LOD	3.8	<LOD	<LOD	<LOD	<LOD
Location 5b surface	<LOD	<LOD	<LOD	<LOD	252	12.9	<LOD	<LOD	<LOD	3766	5075	1670	26	459	18284	<LOD	13	<LOD	43.7	112	87.7	2.6	<LOD	<LOD	<LOD	6.5	<LOD	<LOD	<LOD	4.9
Location 6 surface	<LOD	<LOD	<LOD	<LOD	148	14	<LOD	184	173	2493	762	1435	26.8	168	10932	<LOD	<LOD	<LOD	30	34.1	77.8	4.8	<LOD	<LOD	<LOD	6.3	<LOD	<LOD	<LOD	5.7
Location 6 40 cm	<LOD	<LOD	<LOD	<LOD	183	21.3	<LOD	122	<LOD	3975	101	1979	27.3	55	12553	<LOD	<LOD	<LOD	44.2	47.7	119.1	3.5	2.1	<LOD	<LOD	7.3	<LOD	<LOD	<LOD	6.1
Location 7 surface	<LOD	<LOD	<LOD	<LOD	153	10.7	<LOD	296	223	3136	2368	719	17.8	756	8775	<LOD	<LOD	<LOD	30.9	43.7	60.4	6.6	<LOD	<LOD	<LOD	2.9	<LOD	<LOD	<LOD	4.3
Location 7 15 cm	<LOD	<LOD	<LOD	<LOD	245	16.3	<LOD	<LOD	<LOD	4688	443	1751	36.2	111	14733	<LOD	16	<LOD	57	40.4	117.8	4.6	<LOD	<LOD	<LOD	9.1	<LOD	<LOD	<LOD	6.2
location 8 surface	<LOD	<LOD	<LOD	<LOD	213	13	<LOD	<LOD	<LOD	3750	2400	1509	31	779	16586	<LOD	<LOD	<LOD	34.8	65.1	76.9	3.8	<LOD	<LOD	<LOD	5.8	<LOD	<LOD	<LOD	6.4
location 8 40 cm	<LOD	<LOD	<LOD	<LOD	227	15.8	<LOD	<LOD	<LOD	4437	1889	1699	31	1777	24107	<LOD	<LOD	<LOD	35.1	65.5	69.6	<LOD	<LOD	<LOD	<LOD	4.7	<LOD	<LOD	<LOD	6.2
location 11 surface	<LOD	<LOD	<LOD	<LOD	144	17.9	<LOD	<LOD	<LOD	2475	4526	1182	20.9	838	18074	<LOD	<LOD	<LOD	31.7	110	85	16.5	<LOD	<LOD	<LOD	6.4	<LOD	<LOD	<LOD	5
location 11 20 cm	<LOD	<LOD	<LOD	<LOD	167	15.6	<LOD	184	<LOD	3189	3968	1644	25	659	25063	<LOD	<LOD	<LOD	42.8	100	130	12.6	<LOD	<LOD	<LOD	7.6	<LOD	<LOD	<LOD	5.7
location 11 40 cm	<LOD	<LOD	<LOD	<LOD	167	15.6	<LOD	184	<LOD	3189	3968	1644	25	659	25063	<LOD	<LOD	<LOD	42.8	100	130	12.6	<LOD	<LOD	<LOD	7.6	<LOD	<LOD	<LOD	5.7
location 12 surface	<LOD	<LOD	<LOD	<LOD	226	24	<LOD	<LOD	211	5167	3234	2297	34	417	26411	<LOD	<LOD	<LOD	67.9	117	175	16.8	<LOD	<LOD	<LOD	11.4	<LOD	<LOD	<LOD	10.9
location 12 20 cm	<LOD	<LOD	<LOD	<LOD	238	24.2	<LOD	<LOD	<LOD	2944	1792	3566	45	436	42166	<LOD	<LOD	<LOD	43.4	96	270	11.7	<LOD	<LOD	<LOD	12.2	<LOD	<LOD	<LOD	9.5
location 12 50 cm	<LOD	<LOD	<LOD	<LOD	227	26	<LOD	<LOD	<LOD	3628	675	2213	40	212	28441	<LOD	<LOD	<LOD	58.5	84	183	14.2	<LOD	<LOD	<LOD	10.3	<LOD	<LOD	<LOD	10.6
location 13 surface	<LOD	<LOD	<LOD	<LOD	331	31	<LOD	<LOD	<LOD	6246	17267	5110	62	961	42750	<LOD	<LOD	<LOD	54.7	376	172	13.8	<LOD	<LOD	<LOD	11.6	<LOD	<LOD	<LOD	7
location 13/3a surface	<LOD	<LOD	<LOD	<LOD	256	38	<LOD	281	<LOD	3710	5562	2107	44	524	29762	<LOD	<LOD	<LOD	44.3	122	174	16.4	<LOD	<LOD	<LOD	10.1	<LOD	<LOD	<LOD	11.3
location 13b surface	<LOD	<LOD	<LOD	<LOD	141	20.9	<LOD	<LOD	182	1652	2332	1866	33	427	17970	<LOD	<LOD	<LOD	18.8	44.8	104.9	7	<LOD	<LOD	<LOD	6.6	<LOD	<LOD	<LOD	3.5
location 14 surface	<LOD	<LOD	<LOD	<LOD	160	20.6	<LOD	<LOD	201	2734	933	1347	20.2	528	17871	<LOD	<LOD	<LOD	38.5	59.1	114	10.9	<LOD	<LOD	<LOD	6.4	<LOD	<LOD	<LOD	6.3
location 14 30 cm	<LOD	<LOD	<LOD	<LOD	233	18.5	<LOD	<LOD	<LOD	5441	1928	1778	39	670	34044	<LOD	<LOD	<LOD	47.7	82	134	3.2	<LOD	4	<LOD	4.2	<LOD	<LOD	<LOD	8.6
location 14 50 cm	<LOD	<LOD	<LOD	<LOD	268	21.9	<LOD	<LOD	<LOD	6417	1554	1259	26	661	16896	<LOD	<LOD	<LOD	54.3	98	128	5.9	<LOD	5.8	<LOD	6.2	<LOD	<LOD	<LOD	8.6
location 15 surface	<LOD	<LOD	<LOD	<LOD	257	33	<LOD	<LOD	<LOD	5384	3352	1917	36	669	31068	<LOD	<LOD	<LOD	66.7	123	207	23.3	<LOD	8.1	<LOD	12.8	<LOD	<LOD	<LOD	8
location 15 30 cm	<LOD	<LOD	<LOD	<LOD	308	30	<LOD	<LOD	<LOD	5576	1536	1650	25	849	29372	<LOD	<LOD	<LOD	58.4	94	172	13	<LOD	11.2	<LOD	8.6	<LOD	<LOD	<LOD	10.1
location 16 surface	<LOD	<LOD	<LOD	<LOD	188	25	<LOD	247	<LOD	5377	2183	2481	40	405	33103	<LOD	<LOD	<LOD	74.1	96	179	16.5	<LOD	<LOD	<LOD	15	<LOD	<LOD	<LOD	12.1
location 16 30 cm	<LOD	<LOD	<LOD	<LOD	184	30	<LOD	<LOD	<LOD	5270	540	2590	43	197	33504	<LOD	<LOD	<LOD	68.7	83	195	15.7	<LOD	<LOD	<LOD	12	<LOD	<LOD	<LOD	11.3
location 17 surface	<LOD	<LOD	<LOD	<LOD	260	29	<LOD	616	<LOD	4166	17984	1938	39	922	35769	<LOD	<LOD	<LOD	45.1	274	135	17	<LOD	<LOD	<LOD	12.3	<LOD	<LOD	<LOD	<LOD
location 17a 5-7cm	<LOD	<LOD	<LOD	<LOD	270	29	<LOD	<LOD	<LOD	4130	7193	2306	45	874	37762	<LOD	<LOD	<LOD	55	187	183	15.1	<LOD	<LOD	<LOD	13.3	<LOD	<LOD	<LOD	13
location 18 surface	<LOD	<LOD	<LOD	<LOD	365	40	<LOD	546	196	5540	11534	1845	45	716	32148	<LOD	<LOD	<LOD	52.9	276	231	21.1	<LOD	<LOD	<LOD	12.6	<LOD	<LOD	<LOD	11
location 18 20cm	<LOD	<LOD	<LOD	<LOD	422	36	<LOD	<LOD	204	6803	7369	2021	32	428	22557	<LOD	<LOD	<LOD	60.5	360	318	20.9	<LOD	<LOD	<LOD	13.9	<LOD	<LOD	<LOD	14
location 18 40 cm	<LOD	<LOD	<LOD	<LOD	432	39	<LOD	<LOD	354	6892	13364	2540	45	838	35070	<LOD	<LOD	<LOD	61.7	325	236	14.5	<LOD	<LOD	<LOD	16.1	<LOD	<LOD	<LOD	8
location 19 surface	<LOD	<LOD	<LOD	<LOD	476	62	<LOD	<LOD	527	7691	4608	1552	43	228	23257	<LOD	<LOD	<LOD	70.2	248	327	22.3	<LOD	<LOD	<LOD	15.3	<LOD	<LOD	<LOD	19
location 19 20cm	<LOD	<LOD	<LOD	<LOD	496	57	<LOD	<LOD	249	6146	2288	1516	39	343	19106	<LOD	<LOD	<LOD	63.3	162	403	28.1	<LOD	<LOD	<LOD	14.1	<LOD	<LOD	<LOD	19
location 19 40 cm	<LOD	<LOD	<LOD	<LOD	493	60	<LOD	<LOD	176	5580	1656	1525	40	271	18524	<LOD	<LOD	<LOD	60.9	138	482	31.1	<LOD	<LOD	<LOD	15.5	<LOD	<LOD	<LOD	21
location 19 60 cm	<LOD	<LOD	<LOD	<LOD	477	81	<LOD	<LOD	212	4666	1213	1528	47	253	17435	<LOD	<LOD	<LOD	53.9	123	456	29.5	<LOD	<LOD	<LOD	18.5	<LOD	<LOD	<LOD	23
location 20 surface	<LOD	<LOD	<LOD	<LOD	338	44	<LOD	267	<LOD	6182	8670	2641	42	645	40098	<LOD	<LOD	<LOD	81.9	260	315	23.8	<LOD	<LOD	<LOD	17.4	<LOD	<LOD	<LOD	14
location 20 20 cm	<LOD	<LOD	<LOD	<LOD	279	38	<LOD	184	<LOD	5643	4022	2271	41	389	27695	<LOD	<LOD	<LOD	69.7	135	215	16.2	<LOD	<LOD	<LOD	11.9	<LOD	<LOD	<LOD	15
location 20 40 cm	<LOD	<LOD	<LOD	<LOD	246	31	<LOD	<LOD	<LOD	5741	2717	2173	36	258	26061	<LOD	<LOD	<LOD	69	116	237	17.1	<LOD	<LOD	<LOD	13.6	<LOD	<LOD	<LOD	13.6
location 21 surface	<LOD	<LOD	<LOD	<LOD	279	38	<LOD	264	<LOD	6135	9627	2277	40	1023	38424	<LOD	<LOD	<LOD	70.5	203	185	18.5	<LOD	<LOD	<LOD	12.9	<LOD	<LOD	<LOD	13
location 22 surface	<LOD	<LOD	<LOD	<LOD	228	22	<LOD	<LOD	<LOD	5168	3619	1523	31	635	25071	<LOD	<LOD	<LOD	63.3	98	143	14	<LOD	8.2	11	9.1	<LOD	<LOD	<LOD	7.2
location 22 surface_PL	<LOD	<LOD	<LOD	<LOD	230	14.3	<LOD	<LOD	179	3205	2300	1095	24	445	16508	<LOD	<LOD	<LOD	48.4	60.9	86	7.6	<LOD	8.5	10	5.8	<LOD	<LOD	<LOD	<LOD
location 22a surface	<LOD	<LOD	<LOD	<LOD	325	16.3	<LOD	<LOD	<LOD	4829	1970	1586	30.6	463	13875	<LOD	<LOD	<LOD	54.7	83.7	169	12.1	<LOD	<LOD	<LOD	5.8	<LOD	<LOD	<LOD	6.3
location 22a 30cm	<LOD	<LOD	<LOD	<LOD	560	20	<LOD	<LOD	<LOD	7075	1813	2133	43	667	25160	<LOD	<LOD	<LOD	85.4	152	194	11.4	<LOD	<LOD	<LOD	9.3	<LOD	<LOD	<LOD	8.3
location 22a 50 cm	<LOD	<LOD	<LOD	<LOD	412	42	<LOD	<LOD	243	7228	1398	997	28.2	299	20643	<LOD	<LOD	<LOD	63.1	89	380	23.2	<LOD	<LOD	<LOD	11	<LOD	<LOD	<LOD	13.8
location 23 surface	<LOD	<LOD	<LOD	<LOD	223	21	<LOD	238	178	3876	6629	1442	27	649	19495	<LOD	<LOD	<LOD	45.7	198	189	17.8	<LOD	<LOD	<LOD	7.5	<LOD	<LOD	<LOD	8.3
location 24 surface	<LOD	<LOD	<LOD	<LOD	289	30	<LOD	<LOD	<LOD	4226	5660	1215	28.3	467	19690	<LOD	<LOD	<LOD	46.7	240	205	16.8	<LOD	<LOD	<LOD	8.5	<LOD	<LOD	<LOD	8.6
location 24 30 cm	<LOD	<LOD	<LOD	<LOD	434	65	<LOD	<LOD	185	6733	4974	1457	41	521	25086	<LOD	<LOD	<LOD	59.6	227	350	22.4	<LOD	<LOD	<LOD	13.7	<LOD	<LOD	<LOD	15
location 24 50cm	<LOD	<LOD	<LOD	<LOD	471	43	<LOD	<LOD	234	5480	3041	1415	36	259	19950	<LOD	<LOD	<LOD	56	196	331	19.4	<LOD	<LOD	<LOD	12.9	<LOD	<LOD	<LOD	16
location 25 surface	<LOD	<LOD	<LOD	<LOD	258	38	<LOD	<LOD	<LOD	4727	1695	856	21.9	491	18754	<LOD	<LOD	<LOD	43.5	123	258	17.4	<LOD	<LOD	<LOD	10	<LOD	<LOD	<LOD	10
location 25 30 cm	<LOD	<LOD	<LOD	<LOD	412	42	<LOD	<LOD	243	7228	1398	997	28.2	299	20643	<LOD	<LOD	<LOD	63.1	89	380	23.2	<LOD	<LOD	<LOD	11	<LOD	<LOD	<LOD	13.8
location 25 50 cm	<LOD	<LOD	69	<LOD	417	33.8	<LOD	<LOD	178	8007	1084	976	32	219	19941	<LOD	<LOD	<LOD	59.9	51.4	283	17.4	<LOD	<LOD	<LOD	10.1	<LOD	<LOD	<LOD	10.8
location 26 surface	<LOD	<LOD	<LOD	<LOD	286	24	<LOD	<LOD	196	5262	6880	1649	36	542	20262	<LOD	<LOD	<LOD	43.5	156	122	9.1	<LOD	10	<LOD	8.3	<LOD	<LOD	<LOD	4.7
location 27 surface	<LOD	<LOD	<LOD	<LOD	317	24.4	<LOD	<LOD	200	5005	1659	1420	28.4	206	12931	<LOD	<LOD	<LOD	45.5	67.8	214	16.3	<LOD	<LOD	<LOD	7.6	<LOD	<LOD	<LOD	9.2
location 27 30 cm	<LOD	<LOD	<LOD	<LOD	317	34	<LOD	<LOD	<LOD	5937	1491	2369	37	179	26395	<LOD	<LOD	<LOD	58.1	82	365	22.2	<LOD	<LOD	<LOD	13.4	<LOD	<LOD	<LOD	10.9
location 27 50 cm	<LOD	<LOD	<LOD	<LOD	230	22.5	<LOD	<LOD	<LOD	4409	881	2583	36	97	28251	<LOD	<LOD	<LOD	50.9	62	277	14.7	<LOD	<LOD	<LOD	10.4	<LOD	<LOD	<LOD	9.4
location 28 surface	<LOD	<LOD	<LOD	<LOD	284	24.8	<LOD	<LOD	<LOD	3448	2058	2456	43	746	25346	<LOD	<LOD	<LOD	38.6	75	319	14.5	<LOD	<LOD	<LOD	11.2	<LOD	<LOD	<LOD	11.6
location 28 20 cm	<LOD	<LOD	<LOD	<LOD	185	15.4	<LOD	<LOD	<LOD	<LOD	282	3534	56	235	59140	<LOD	<LOD	<LOD	11.2	18.7	226	10.1	<LOD	<LOD	<LOD	14.5	<LOD	<LOD	<LOD	11.6
location 29 surface	<LOD	<LOD	<LOD	<LOD	368	37	<LOD	<LOD	171	4833	2915	1369	28.2	435	14631	<LOD	<LOD	<LOD	62.5	187	439	20.9	<LOD	<LOD	<LOD	11.7	<LOD	<LOD	<LOD	14
location 30 surface	<LOD	<LOD	<LOD	<LOD	286	21.1	<LOD	<LOD	192	3799	2850	1330	25	168	12985	<LOD	<LOD	<LOD	56.3	138	321	19.4	<LOD	<LOD	<LOD	11.7	<LOD	<LOD	<LOD	9.7
location 30 26 cm	<LOD	<LOD	<LOD	<LOD	253	18.3	<LOD	178	<LOD	3213	2925	1167	16.6	170	11286	<LOD	<LOD	<LOD	49.2	141	250	17.4	<LOD	<LOD	<LOD	10	<LOD	<LOD	<LOD	10.1
location 30 40 cm	<LOD	<LOD	<LOD	<LOD	324	14.5	<LOD	<LOD	155	4925	2260	1837	29.3	86	13871	<LOD	<LOD	<LOD	55.7	96.9	223	10.1	<LOD	<LOD	<LOD	9.2	<LOD	<LOD	<LOD	6.2
location 31 surface	<LOD	<LOD	<LOD	<LOD	313	44	<LOD	<LOD	293	5637	1766	1262	33	318	34348	<LOD	<LOD	<LOD	55.5	104	337	27.3	<LOD	12	<LOD	13.7	<LOD	<LOD	<LOD	9
location 31 25 cm	<LOD	<LOD	<LOD	<LOD	395	63	<LOD	<LOD	186	4916	1973	1528	38	181	24872	<LOD	<LOD	<LOD	54.5	127	344	25.7	<LOD	<LOD	<LOD	14.7	<LOD	<LOD	<LOD	12
location 31 40cm	<LOD	<LOD	<LOD	<LOD	328	51	<LOD	<LOD	<LOD	5329	1602	1397	32	277	30864	<LOD	<LOD	<LOD	50.7	100	401	24	<LOD	<LOD	<LOD	13.2	<LOD	<LOD	<LOD	15
location 32 10cm	<LOD	<LOD	<LOD	<LOD	194	27.2	<LOD	238	<LOD	2863	980	1315	27	99	27684	<LOD	<LOD	<LOD	39.3	80	108	9	<LOD	<LOD	<LOD	6.5	<LOD	<LOD	<LOD	8.8

4.4 Grain Size Analysis

The soil samples for all the sample location sites were analysed by Mastersizer. Mastersizer helps to identify the various grains size of soil samples. The grain size of each sample was analysed using the Mastersizer. The soil samples were initially acid digested with hydrogen peroxide to remove any organic matter. This assisted in determining if there is any correlation between the grain size and the metal concentration in the soil sample. The grain size is given in the table 8 below. The raw data is given in the appendix B. In a sample grain size below the 0.0039mm this was classified as clay, between 0.0039 to 0.0625mm was classified as silt, from 0.0625mm to 2mm was classified as soil. Anything above 2mm was classified as gravel. The texture of the soil samples was analysed based on the sorting, mean (Hz), kurtosis and skewness. The mean grain size for each sample was also converted from phi to millimetres. The grain size is described in the form of sand proportion, clay proportion and silt proportion. The mean grain size, sorting and skewness are also discussed below and shown in the table 9.

Table 8: Grain Size Distribution table(Wentworth, 1922)

Millimeters (mm)		Micrometers (µm)	Phi (φ)	Wentworth size class	
	4096		-12.0	Boulder	Gravel
	256		-8.0	Cobble	
	64		-6.0	Pebble	
	4		-2.0	Granule	
	2.00		-1.0	Very coarse sand	Sand
	1.00		0.0	Coarse sand	
1/2	0.50	500	1.0	Medium sand	
1/4	0.25	250	2.0	Fine sand	
1/8	0.125	125	3.0	Very fine sand	
1/16	0.0625	63	4.0	Coarse silt	Silt
1/32	0.031	31	5.0	Medium silt	
1/64	0.0156	15.6	6.0	Fine silt	
1/128	0.0078	7.8	7.0	Very fine silt	
1/256	0.0039	3.9	8.0	Clay	Mud
	0.00006	0.06	14.0		

4.4.1 Sand Distribution

The soil texture across all the different sample sites revealed that locations 18, 19 were dominated by sand fraction. The soil samples were taken at various depths. Therefore, the grain size composition varies with the depth. The grain size distribution of various samples are shown below in Figure 27. Location 18 at 40 cm is dominated by sand whereas the surface of location 19 is dominated by a proportion of sand. The flood plains between the Ohinemuri and the Waihou Rivers, west of State Highway 26 were dominated by a proportion of sand. Location 15 at 30 cm has a slightly higher sand proportion than the silt proportion. Overall, the silt and clay proportions dominate the flood plains at lower and upper Waihou and Ohinemuri Rivers. The location 16 at 30cm depth has 0.22% gravel. The study by Tay (1980) identified that the distribution of grain size at various locations was controlled by deposition location and the physical processes controlling transportation of sediments. The 1995 study by Webster also supported that theory. Webster mentioned that when there is a transition from fast flowing rivers to a wide spread slow-moving estuary environment, the consistent fining of sediments occurs. The study found that there was consistent fining of sediments occurring towards Firth of Thames.

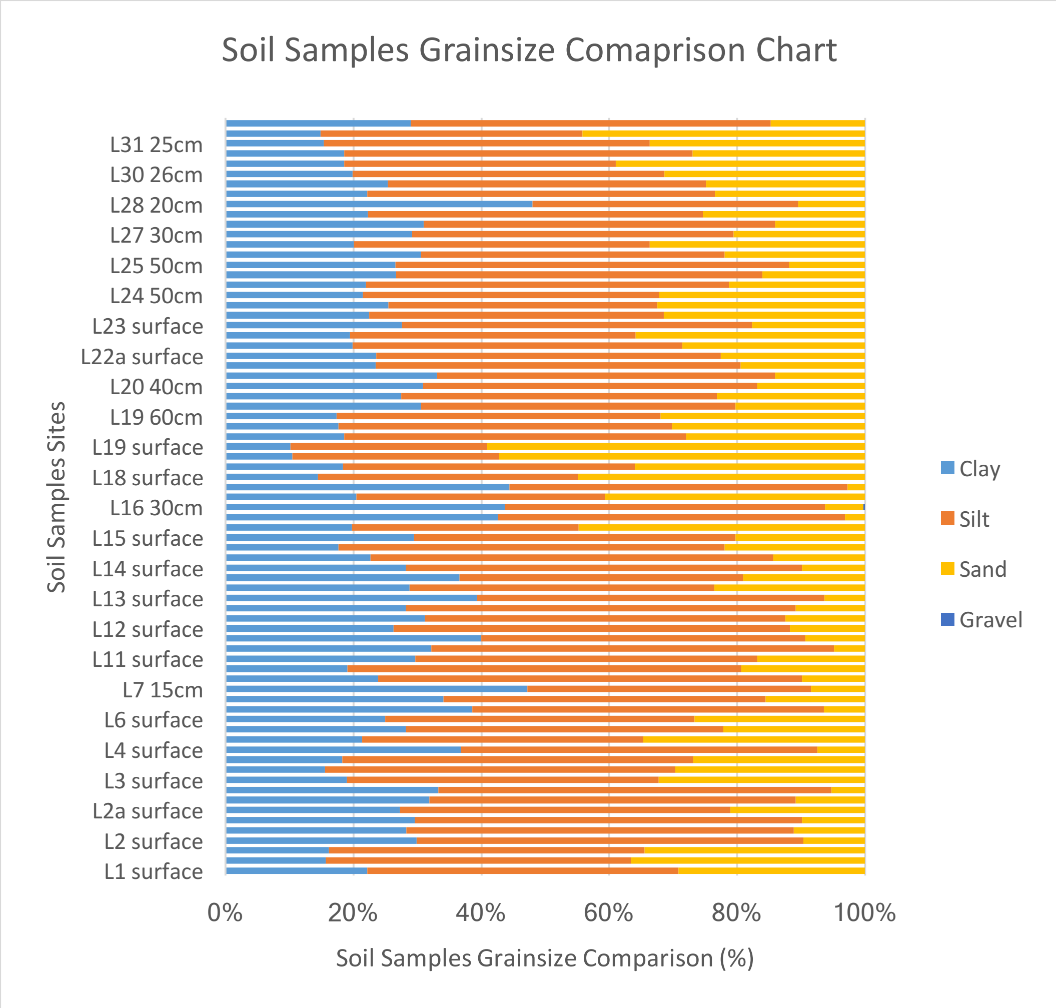

Figure 27: Soil samples grain size comparison chart.

At Locations 18 and 19, soil samples were dominated by sand. Location 18 at 40cm depth had 57.19% of sand fraction and at location 19 the surface is dominated by sand at 59.10% of sand fraction. At location 15at 30 cm depth the soil proportion is marginally higher than the silt proportion with sand proportion of 44.76% compared to 43.96% o of silt proportion. The grain size started fining in the flood plains as identified at locations 5, 5b, 8, 11 and 12 as shown in the table 8. Here locations 5 and 5b have higher proportions of sand fraction i.e. 34.68%, 22.15% compared to sand samples at locations 8, 11 and 12 with respectively a sand fraction of 9.79, 16.82 and 11.73 at surface. Here in these sites sand fraction slightly fluctuates. Overall these sites contain the lowest sand fraction in a sample as compared to other sites apart from poor sand proportion at locations 2, 17a and16. The factors affecting the sand proportion in the flood plains at these areas includes tidal mixing zones, floods and winds. which affects the mix of the sediment Thus during flooding events there is a less proportion of sand deposited at these locations which are primarily dominated by silt fraction. Soil fraction fluctuates upstream of the Waihou River at locations 22a, 23, 24, 25 and 26 but remains in at a lower level. The sand proportion also fluctuates at the upstream of the Ohinemuri River flood plain. Here low sand fraction of around 2.72% was measured at location 17a which then increased to 40% at location 17 and then again dropped around 10% for location 2 and then increased around 20% at location 15 in the surface soil sample sites. Location 2 had shells deposits at 20-40cm depth which affected the soil fraction.

4.4.2 Silt Distribution

Most of the sample sites were dominated by a silt fraction which indicates that most of the flood plains around the Waihou and the Ohinemuri Rivers are silt dominated. Sample sites at location 15 at 30cm depth, location 18 at 40cm depth and location 19 surface are the only sample sites where the silt was present in lower fraction as shown in the table 9. At location 31 at 40cm depth the silt fraction is marginally higher with fraction of 47.24% than the soil fraction of 44.21%. The highest silt fraction was measured at location 8 surface with silt fraction of 77.15% followed by 76.96% at location 11 at 20cm depth. The silt fractions were over 70% at locations 2, 2b, 4, 6, 12, 13, 14, 16 and 25. Downstream of the Waihou River the silt fraction increases with some fluctuation. Location 12 has 74.68% being the highest silt fraction, then locations 5 and 5b have lower silt fractions of 52.84% and 61.16% respectively. The silt fraction increases again at locations 8 and 11 with the highest silt fraction of 771.5% and 76.96% respectively. Location 7 has a slighter lower silt fraction of 65.60% due to being located further away from the river. This indicates that the less flood water that reaches that location results in lower silt size grain deposition.

4.4.3 Clay Distribution

The sample collected from the floodplain of the Ohinemuri and the Waihou River sat various locations has a lower fraction of clay size sediments. The highest fraction of clay in the soil samples was obtained from location 28 at 20cm depth with the clay fraction of 30.03% as shown in the table 9. At this location the clay fraction was almost triple that of the sand fraction of 10.43%. The other locations that had a clay fraction of around 25% or more than 25% were obtained from location 7 at 15cm depth with the clay fraction of 26.12%, at location 16 at 30cm depth it was 26.52% and at location 17a of 25.56%. The lowest clay fraction was obtained at location 19 surface with clay fraction of 5.52%. The less than 10% of clay fraction was obtained at locations 1, 3, 14, 18, and 31. The clay fraction increased downstream of the Waihou River with the locations 5 and 5b having the highest clay fraction of 12.48% and 16.69% respectively. There was an increase with slight fluctuation at location 8.The highest clay fraction was 13.06% which increased at location 11 which had a clay fraction of 24.01%. Location 7 was the furthest away from the Waihou River and still had a high clay fraction of 26.12%. The upstream of the Waihou River had clay in slightly lower but fluctuating clay concentration with highest clay concentration staying around 17%.

Table 9: Grain size distribution table obtained from Mastersizer grain size analysis.

Sample	Sand	Silt	Clay	Fines	Mean (Mz)	Sorting (SI)	Skewness (SkI)	Kurtosis (KG)	Mean (mm)
L1 surface	29.21	58.68	12.11	70.79	6.05	2.89	-0.22	0.78	0.015
L1 50cm	36.53	55.76	7.71	63.47	5.60	2.90	-0.08	0.78	0.021
L1 120cm	34.51	56.74	8.75	65.49	5.66	2.89	-0.09	0.80	0.020
L2 surface	9.60	73.16	17.24	90.40	7.47	2.47	-0.17	1.22	0.006
L2 20cm	11.14	72.84	16.02	88.86	7.37	2.59	-0.20	1.31	0.006
L2 40cm	9.88	73.35	16.77	90.12	7.47	2.56	-0.21	1.36	0.006
L2a surface	21.06	64.17	14.77	78.94	6.64	2.69	-0.42	0.87	0.010
L2b surface	10.87	70.97	18.16	89.13	7.56	2.60	-0.26	1.44	0.005
L2b 40cm	5.23	76.49	18.28	94.77	8.16	1.95	-0.07	1.47	0.003
L3 surface	32.28	57.18	10.54	67.72	6.01	2.65	-0.08	0.70	0.015
L3 40cm	29.64	61.58	8.78	70.36	6.03	2.47	0.01	0.80	0.015
L3 70cm	26.90	62.97	10.13	73.10	6.18	2.50	-0.06	0.78	0.014
L4 surface	7.42	71.94	20.64	92.58	8.20	2.10	-0.14	1.62	0.003
L5 surface	34.68	52.84	12.48	65.32	5.86	2.96	-0.15	0.76	0.017
L5b	22.15	61.16	16.69	77.85	6.98	3.03	-0.28	0.85	0.008
L6 surface	26.65	58.80	14.55	73.35	6.20	2.97	-0.33	0.82	0.014
L6 40cm	6.43	70.64	22.93	93.57	8.33	2.07	-0.11	1.70	0.003
L7 surface	15.59	65.60	18.81	84.41	7.44	2.77	-0.34	1.34	0.006
L7 15cm	8.44	65.44	26.12	91.56	8.31	2.16	-0.21	1.10	0.003
L8 surface	9.79	77.15	13.06	90.21	7.25	2.06	-0.30	1.46	0.007
L8 40cm	19.38	70.53	10.09	80.62	6.30	2.98	-0.49	1.67	0.013
L11 surface	16.82	67.10	16.08	83.18	7.32	2.75	-0.33	1.40	0.006
L11 20cm	4.82	76.96	18.22	95.18	8.23	1.90	-0.05	1.60	0.003
L11 40cm	9.37	66.62	24.01	90.63	8.33	2.29	-0.19	2.02	0.003
L12 surface	11.73	74.68	13.59	88.27	7.07	2.25	-0.39	1.39	0.007
L12 20cm	12.41	69.24	18.35	87.59	7.48	2.63	-0.25	1.34	0.006
L12 50cm	10.84	73.07	16.09	89.16	7.51	2.54	-0.24	1.48	0.005
L13 surface	6.28	71.53	22.19	93.72	8.35	2.02	-0.12	1.79	0.003
L13a surface	23.51	60.24	16.25	76.49	6.92	2.92	-0.20	0.77	0.008
L13b surface - 90cm depression	19.03	59.92	21.05	80.97	7.32	2.89	-0.33	0.79	0.006
L14 surface	9.88	74.62	15.50	90.12	7.15	2.16	-0.35	1.31	0.007
L14 30cm	14.35	72.82	12.83	85.65	6.80	2.35	-0.28	1.04	0.009
L14 50cm	21.94	68.17	9.89	78.06	6.33	2.44	-0.13	0.79	0.012
L15 surface	20.22	63.53	16.25	79.78	7.07	2.89	-0.30	0.84	0.007
L15 30 cm	44.76	43.96	11.28	55.24	5.22	2.89	0.36	0.67	0.027
L16 surface	3.17	72.35	24.48	96.83	8.50	1.79	-0.03	1.61	0.003
L16 30cm	6.22	67.26	26.52	93.78	8.46	2.06	-0.12	1.10	0.003
L17 surface	40.70	47.67	11.63	59.30	5.77	2.91	-0.09	0.64	0.018
L17 5-7cm	2.72	71.72	25.56	97.28	8.53	1.80	-0.04	0.97	0.003
L18 surface	44.91	46.48	8.61	55.09	5.03	2.88	0.34	0.75	0.031
L18 20cm	35.96	53.32	10.72	64.04	5.74	2.89	-0.08	0.77	0.019
L18 40cm	57.19	36.78	6.03	42.81	4.30	3.05	0.40	0.79	0.051
L19 surface	59.10	35.38	5.52	40.90	4.25	3.04	0.41	0.79	0.052
L19 20cm	27.98	61.59	10.43	72.02	6.11	2.62	-0.09	0.84	0.014
L19 40cm	30.13	59.80	10.07	69.87	5.90	2.78	-0.12	0.79	0.017
L19 60cm	31.92	59.32	8.76	68.08	5.82	2.84	-0.13	0.79	0.018
L20 surface	20.28	62.36	17.36	79.72	7.09	2.91	-0.30	0.83	0.007
L20 20cm	23.13	61.29	15.58	76.87	6.57	2.65	-0.32	0.78	0.011
L20 40cm	16.89	65.34	17.77	83.11	7.30	2.92	-0.31	1.43	0.006
L21 surface	14.03	66.94	19.03	85.97	7.42	2.70	-0.28	1.24	0.006
L22 surface	19.42	66.92	13.66	80.58	6.57	2.43	-0.13	0.80	0.010
L22a surface	22.57	62.87	14.56	77.43	6.38	2.59	-0.12	0.79	0.012
L22a 30cm	28.52	59.43	12.05	71.48	6.12	2.60	-0.05	0.80	0.014
L22a 50 cm	35.87	52.01	12.12	64.13	5.68	3.07	-0.12	0.80	0.020
L23 surface	17.63	65.33	17.04	82.37	7.13	2.73	-0.12	0.82	0.007
L24 surface	31.50	55.06	13.44	68.50	6.04	2.79	-0.10	0.74	0.015
L24 30 cm	32.50	52.81	14.69	67.50	6.11	2.85	-0.18	0.71	0.014
L24 50cm	32.13	56.28	11.59	67.87	5.97	2.76	-0.08	0.73	0.016
L25 surface	21.21	66.42	12.37	78.79	6.41	2.48	-0.14	0.78	0.012
L25 30cm	16.05	68.90	15.05	83.95	6.76	2.36	-0.21	0.79	0.009
L25 50cm	11.81	73.73	14.46	88.19	6.87	2.24	-0.23	0.98	0.009
L26 surface	21.98	60.13	17.89	78.02	6.99	2.97	-0.23	0.80	0.008
L27 surface	33.69	54.05	12.26	66.31	5.81	2.92	-0.10	0.77	0.018
L27 30cm	20.51	61.83	17.66	79.49	6.98	2.85	-0.14	0.78	0.008
L27 50cm	14.07	68.30	17.63	85.93	7.31	2.64	-0.20	1.06	0.006
L28 surface	25.38	61.46	13.16	74.62	6.30	2.62	-0.15	0.79	0.013
L28 20cm	10.43	59.54	30.03	89.57	8.33	2.33	-0.23	1.13	0.003
L29 surface	23.48	63.25	13.27	76.52	6.32	2.68	-0.18	0.85	0.012
L30 surface	24.89	59.27	15.84	75.11	6.40	2.65	-0.15	0.77	0.012
L30 26cm	31.37	56.29	12.34	68.63	5.98	2.75	-0.06	0.76	0.016
L30 40cm	38.96	49.47	11.57	61.04	5.29	2.90	0.30	0.77	0.026
L31 surface	26.94	62.14	10.92	73.06	6.14	2.67	-0.13	0.86	0.014
L31 25cm	33.68	58.51	7.81	66.32	5.72	2.83	-0.11	0.80	0.019
L31 40cm	44.21	47.24	8.55	55.79	4.95	3.05	0.26	0.78	0.032
L32 10cm	14.72	69.12	16.16	85.28	7.32	2.70	-0.26	1.34	0.006

4.4.4 Mean Grain Size

The samples taken from various locations vary in the mean grain size. The grain size varies from 4.25 phi to 8.53 phi. i.e. the grain size varies from fine sand – coarse silt to very fine silt. The coarse silt or fine sand with mean grain size of 4.25 phi was obtained from location 19 surface with the very fine silt with mean grain size of 8.53 phi obtained from location 17a. The mean gain size chart for each location is given in the figure 28 below. The majority of the samples collected from various locations in the flood plains varies between fine silt to medium silt with very few having a mean grain size of coarse silt.

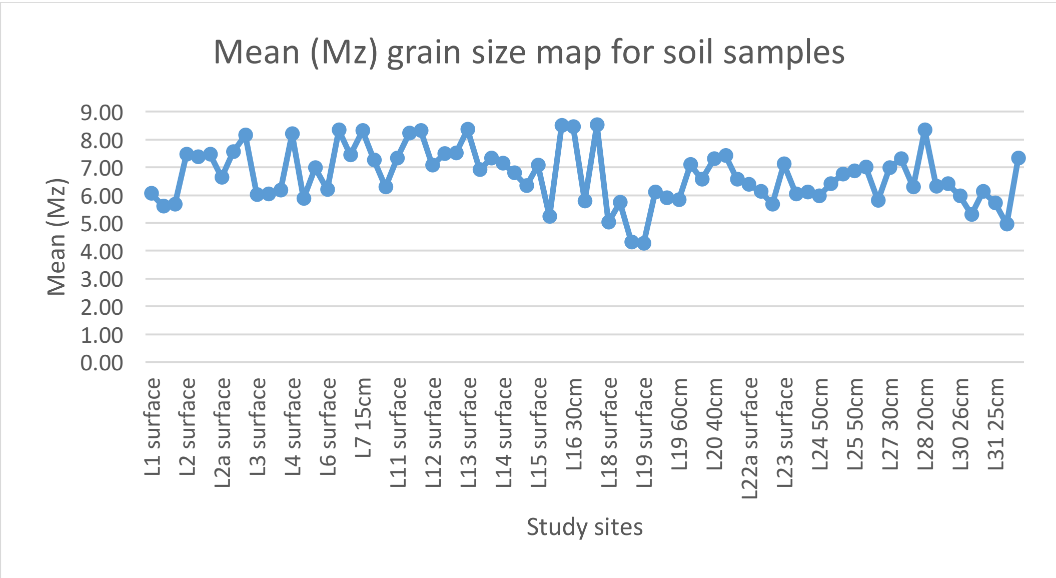

Figure 28 Mean gain size of samples taken from various locations.

4.4.5 Sorting

All the samples were analysed for sorting as a part of grain size analysis by Mastersizer. Sorting is described as a distribution of grain size in a soil sample. Soil samples can be classified in the form of poorly sorted or well sorted soil samples. The poorly sorted soil samples will have grains with various grain sizes and high variables and would look like a mixture of different grain sizes. Well sorted soil samples or deposits have low variables with similar grain sizes and soil deposits appear uniform. In the soil samples sorting varied from poorly sorted 1-2 phi to very poorly sorted 2-4phi as shown in the figure 29 below. The poorly sorted soil samples were obtained from location 16 surface, Location 17a, location 11 at 20cm depth and location 2b at 20cm depth. Overall in the flood plain downstream of the Waihou River soil sample sorting was relatively better with sorting varying from between 1.9 phi – 2.25phi apart from location 5 and 5b. The very poorly sorted soil sample was obtained from location 22a at 50cm depth with the sorting value of 3.07phi. overall the sorting was getting poor with some fluctuation in the floodplains upstream of the Waihou River. At location 25 sorting was better than upstream samples sites. The soring was relatively better in the middle of the Waihou River where the Ohinemuri and Waihou Rivers converges. Here at locations 4 and 16 sorting varied at around 2.10. At location 31 the sorting was 3.05 phi with location 32 sorting value of 2.70 due to samples were taken further away from the river in the flood plains.

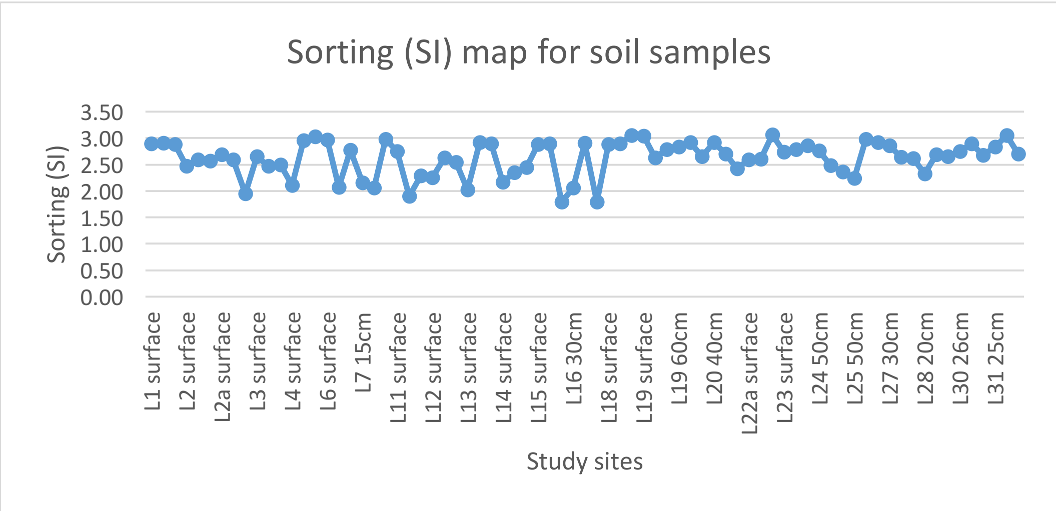

Figure 29 – Sorting map for soil samples collected from various sample sites.

4.4.6 Skewness in the Soil Samples

Skewness can be defined as the asymmetry of soil samples. The grain size asymmetry at various sample sites were measured in skewness. The skewness values are recorded in the form of negative and positive phi value. The soil samples for this study varied in skewness in the range of -0.49phi to 0.41phi and shown in the figure 30 below. The negative skewness i.e. -0.49 phi shows that soil samples are more symmetric and have low coarse material and a higher proportion of fine materials. Here the location 8 the skewness of -0.49 with a sand proportion of only 19.38% and fines (silt and clay) of around 80.62%. The positive skewness value i.e. 0.41 shows that the soil sample is more asymmetric with a higher proportion of coarse material and a low proportion of fine materials. At location 19 surface the sample has a skewness value of 0.41 with the coarse proportion of 59.10% and fines (silt and clay) proportion of 40.90%. In this study most of the sample sites had a negative skewness value with a higher proportion of fines as compared to the coarse materials.

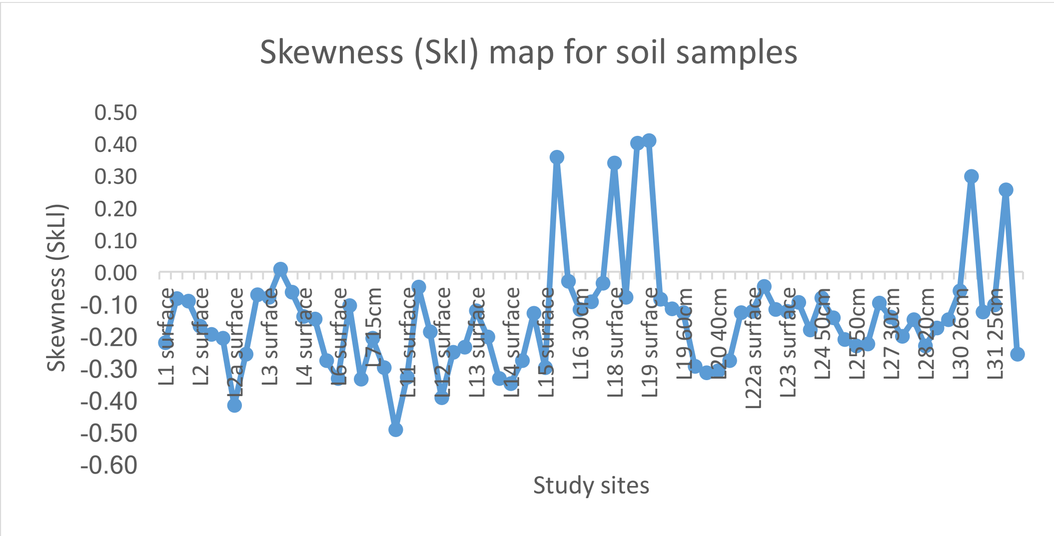

Figure 30 – Skewness of soil samples collected from various sample sites.

4.5 ICP-MS Analysis:

4.5.1 Heavy (Trace) Metal Concentration –

The soil samples were analysed to identify the accurate concentration of various heavy metals and other toxic and non-toxic elements through ICP-MS analysis. The ICP-MS analysis process resulted in a soil sample analysis of a very low detection limit of 1-10 ppt (part per trillion). The detection limit varies with elements. The heavy (trace) metals concentration through ICP-MS analysis is given in the table 10 below. The raw data is given in the appendix C.

Table 10: Concentration of various heavy (trace) elements using the ICP-MS analysis

Sample Name	Cr (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Ag (ppm)	Hg (ppm)	Pb (ppm)	U (ppm)
L1 surface	4.48	7.71	18.20	1.72	0.09	0.11	9.29	0.73
Location 1 50 cm	3.37	6.44	12.45	1.39	0.08	0.15	9.29	1.45
Location 1 120cm	4.13	2.52	8.12	1.82	0.04	0.12	8.57	1.31
Location 2 surface	10.48	16.60	130.45	9.83	4.60	0.51	63.46	0.67
Location 2 20 cm	11.16	16.76	148.35	5.50	3.83	0.51	49.08	0.65
location 2 40 cm	9.89	8.22	32.38	2.84	0.45	0.33	13.28	1.00
Location 2a2 surface	6.33	15.96	63.27	3.11	2.81	0.58	26.01	0.43
Location 2b surface	9.09	12.57	97.66	5.61	2.31	0.39	46.34	0.85
Location 2b 40 cm	6.13	4.30	21.14	2.64	0.21	0.29	9.29	0.76
Location 3 surface	10.14	17.55	96.24	6.94	6.30	0.67	59.96	0.75
Location 3 40 cm	8.97	19.84	118.82	7.75	6.97	0.65	83.58	0.70
Location 3 70 cm	8.28	18.08	84.28	10.39	6.21	0.49	76.11	0.50
Location 4 surface	5.02	7.48	22.67	1.70	0.18	0.11	13.44	0.79
Location 5b surface	5.42	9.91	35.68	1.80	0.19	0.06	20.82	0.39
Location 6 surface	8.61	10.41	32.12	4.48	1.06	0.25	30.79	0.99
Location 6 40 cm	6.78	4.89	9.17	1.14	0.13	0.10	10.24	1.01
Location 7 surface	8.49	13.94	34.37	4.73	0.14	0.15	15.78	0.51
Location 7 15 cm	10.61	8.78	10.46	4.84	0.24	0.31	7.67	0.63
location 8 surface	9.38	10.04	71.64	3.61	1.57	0.24	39.20	0.56
location 8 40 cm	7.78	10.45	62.82	4.36	1.90	0.21	50.01	0.49
location 11 surface	6.11	13.33	69.95	3.05	0.18	0.12	11.88	0.44
location 11 20 cm	5.41	5.46	21.55	2.78	0.12	0.08	10.50	0.50
location 12 surface	4.80	6.79	18.68	1.26	0.17	0.08	10.35	0.57
location 12 20 cm	6.56	4.29	12.61	0.92	0.06	0.06	9.62	0.50
location 12 50 cm	3.93	4.47	10.95	1.63	0.23	0.10	10.14	0.67
location 13 surface	5.41	10.12	38.16	1.93	0.09	0.05	7.74	0.19
location 13a surface	10.22	17.20	52.22	2.48	0.52	0.21	289.26	0.43
location 14 surface	5.97	9.18	52.50	3.99	1.17	0.16	21.11	0.65
location 14 30 cm	5.02	13.30	38.54	9.13	3.16	0.26	66.74	0.48
location 14 50 cm	4.54	19.26	45.86	12.92	4.87	0.30	113.52	0.44
location 15 surface	7.94	13.02	60.91	10.05	6.01	0.30	55.37	0.46
location 15 30 cm	7.01	14.73	51.33	11.71	6.23	0.36	81.04	0.52
location 16 surface	4.98	5.67	33.67	2.35	0.65	0.14	14.53	0.64
location 16 30 cm	4.84	5.39	17.04	1.75	0.80	0.17	15.74	0.74
location 17 surface	4.96	9.59	27.93	9.49	0.10	0.05	8.71	0.26
location 17a 5-7cm	6.53	7.16	21.60	21.56	0.14	0.09	13.01	0.46
location 18 surface	4.45	8.59	44.59	1.09	0.08	0.04	18.40	0.78
location 18 20cm	2.89	4.26	13.75	0.97	0.05	0.04	17.24	0.48
location 18 40 cm	3.66	7.72	17.47	1.06	0.04	0.03	98.88	0.40
location 19 surface	2.82	5.68	11.05	1.28	0.06	0.07	9.27	0.80
location 19 20cm	2.19	3.44	12.41	0.90	0.08	0.11	8.45	0.91
location 19 40 cm	1.98	1.75	10.54	1.01	0.06	0.14	8.32	1.11
location 19 60 cm	0.09	0.07	0.31	0.04	0.00	0.01	0.38	0.06
location 20 surface	5.50	6.70	31.73	0.75	0.04	0.05	8.11	0.45
location 20 20 cm	5.36	6.74	22.33	1.59	0.07	0.08	11.92	0.75
location 20 40 cm	4.92	5.44	17.85	1.97	0.08	0.08	13.48	0.80
location 21 surface	6.28	21.80	72.99	5.01	2.80	0.20	37.43	0.52
location 22 surface	7.14	15.77	93.34	12.61	9.67	0.56	86.52	0.43
location 22a surface	11.13	10.19	113.56	3.95	0.50	0.20	102.46	0.47
location 22a 30cm	13.16	8.73	60.24	3.51	0.39	0.17	98.24	0.31
location 22a 50 cm	9.94	10.53	60.50	3.05	0.67	0.15	61.13	0.39
location 23 surface	8.41	11.50	46.44	3.69	0.14	0.05	24.86	0.46
location 24 surface	6.09	11.98	44.71	1.97	0.05	0.05	31.52	0.59
location 24 30 cm	4.87	10.06	36.43	2.31	0.05	0.06	18.25	0.89
location 24 50cm	2.79	4.98	20.65	1.30	0.04	0.04	13.48	1.32
location 25 surface	3.72	11.05	48.38	4.38	0.06	0.07	10.46	0.93
location 25 30 cm	1.10	2.34	11.06	4.13	0.04	0.08	6.38	0.75
location 25 50 cm	0.56	1.43	6.23	2.27	0.02	0.06	6.04	0.72
location 26 surface	11.53	14.63	79.30	3.37	0.07	0.05	18.34	0.43
location 27 30 cm	6.91	2.33	13.02	2.44	0.02	0.14	11.66	0.64
location 28 surface	7.56	9.72	30.92	1.26	0.05	0.12	20.01	1.30
location 28 20 cm	8.81	8.46	13.01	0.60	0.02	0.11	16.35	1.68
location 31 surface	4.13	4.25	18.49	1.68	0.06	0.10	11.26	0.88
location 31 25 cm	3.44	1.91	7.55	1.91	0.04	0.10	8.24	1.38
location 31 40cm	4.28	1.95	8.84	5.27	0.04	0.10	9.36	1.02
location 32 10cm	5.29	8.97	22.97	2.40	0.15	0.08	24.99	1.24

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Most of the trace metals such as arsenic, chromium, copper, zinc and silver show the similar concentration pattern as XRF analysis. Metals such as mercury, lead and uranium show a slightly different concentration pattern as compared to the XRF. In general, the heavy metal concentration analysed by ICP-MS is in the lower level as compared to the XRF results.

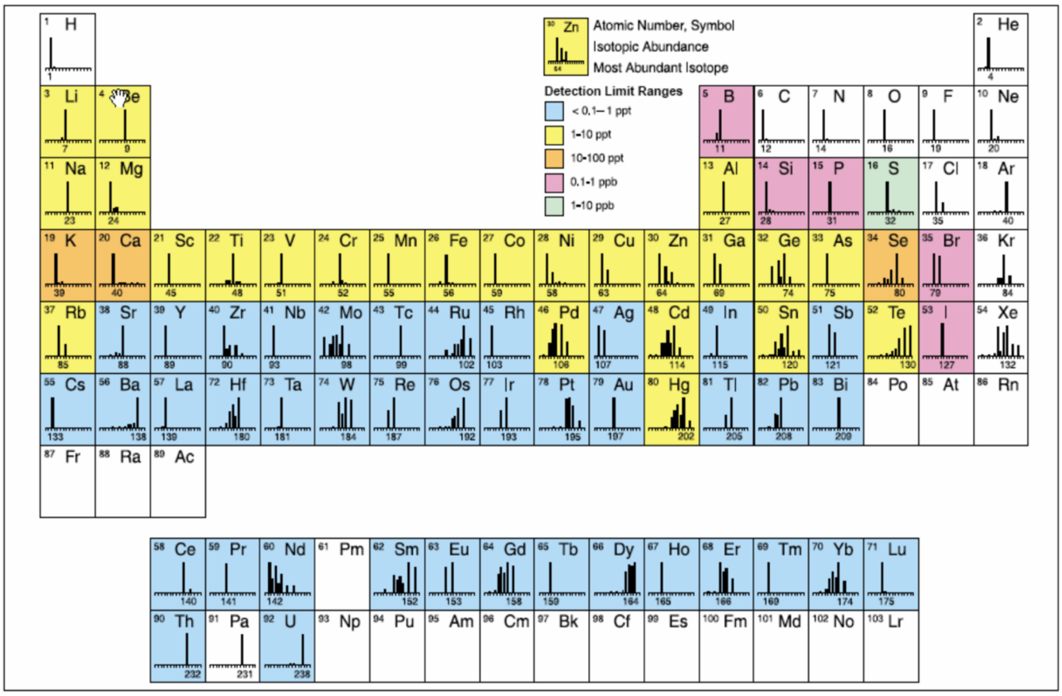


Figure 31: Approximate detection limit of ICP-MS for various elements(Banerjee).

The detection limit for various samples using ICP-MS is given in figure 31. Here for As detection limit is 1-10ppt, for Ag it drops down to <0.1 – 1 ppt. The silver detected in the samples were below then the detection limit. The figure 36 shows that highest Ag concentration was reported at location 22. The higher concentrations were also reported at location 3 and 15. All three locations were located near Paeroa and where the Ohinemuri River merges into the Waihou River. In the past, Ohinemuri River was dredged to process ore using cyanide process which is then transported to Paeroa for processing. This might be a contributing factor to high silver concentration in these locations.

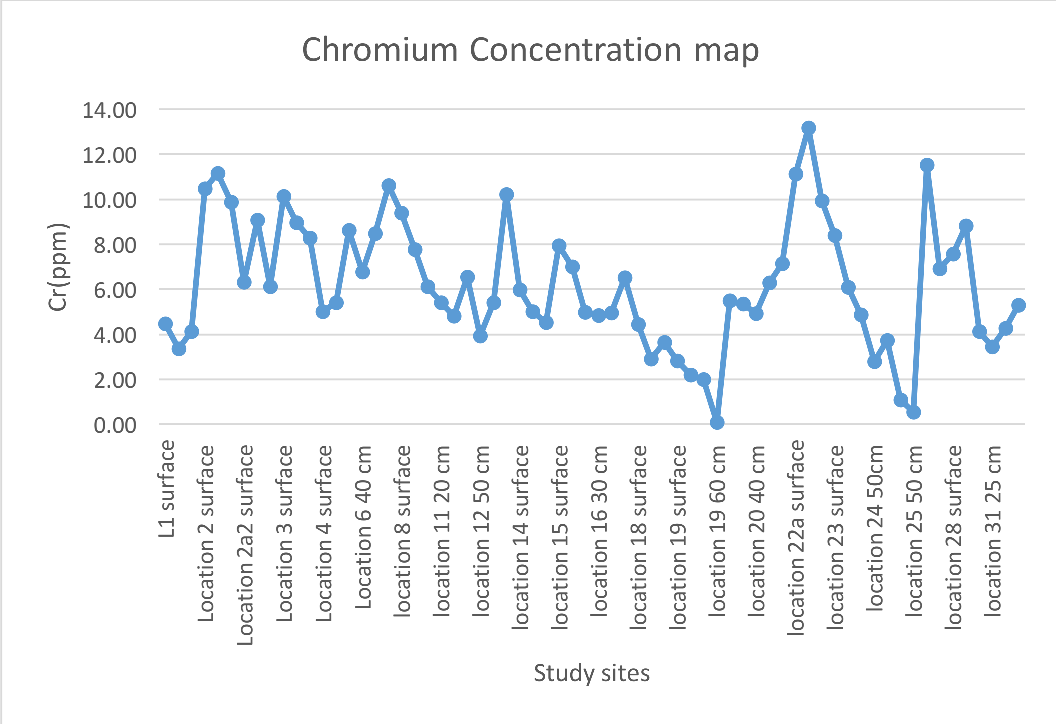


Figure 32: Chromium (Cr) concentration map based on ICP-MS results from various sites.

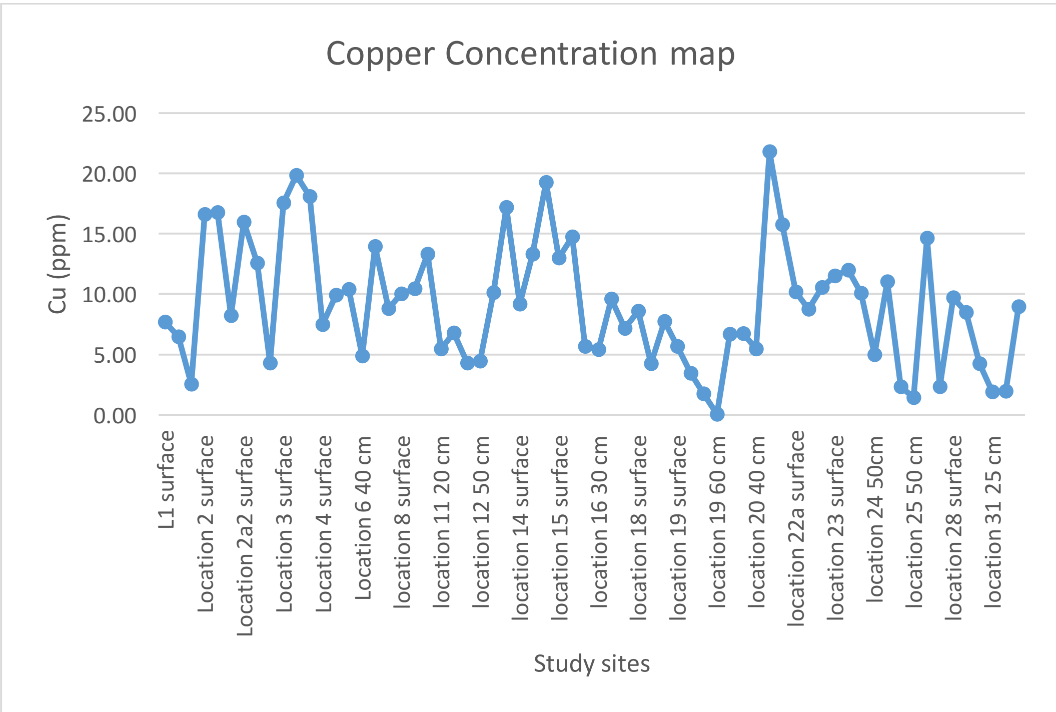


Figure 33: Copper (Cu) concentration map based on ICP-MS results from various sites

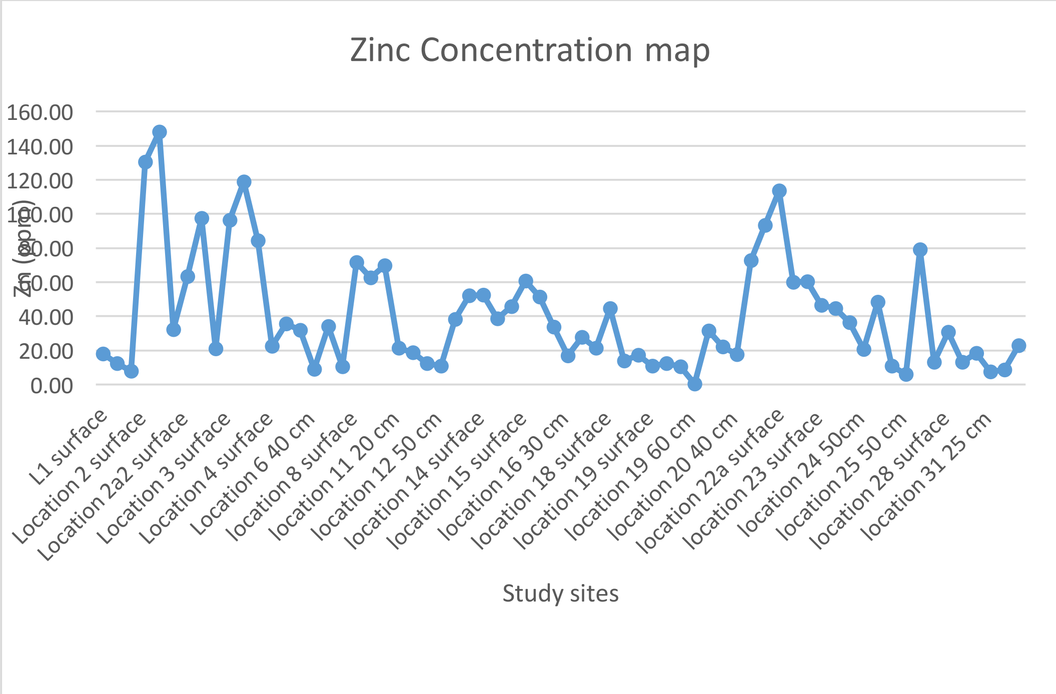


Figure 34: Zinc (Zn) concentration map based on ICP-MS results from various sites.

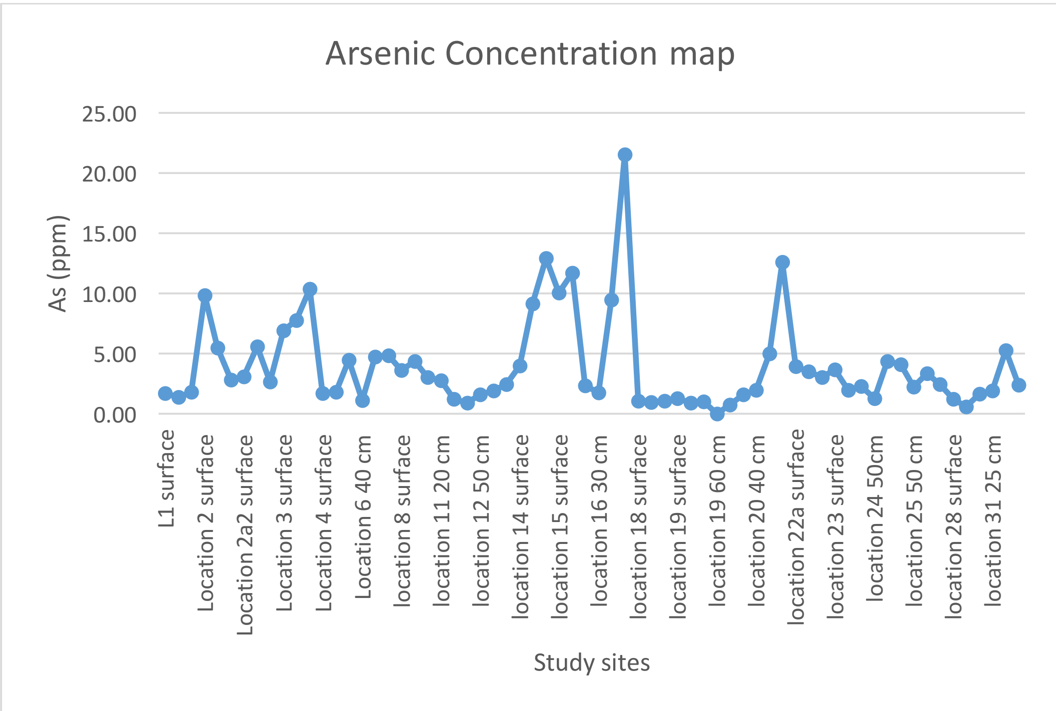


Figure 35: Arsenic (As) concentration map based on ICP-MS results from various sites

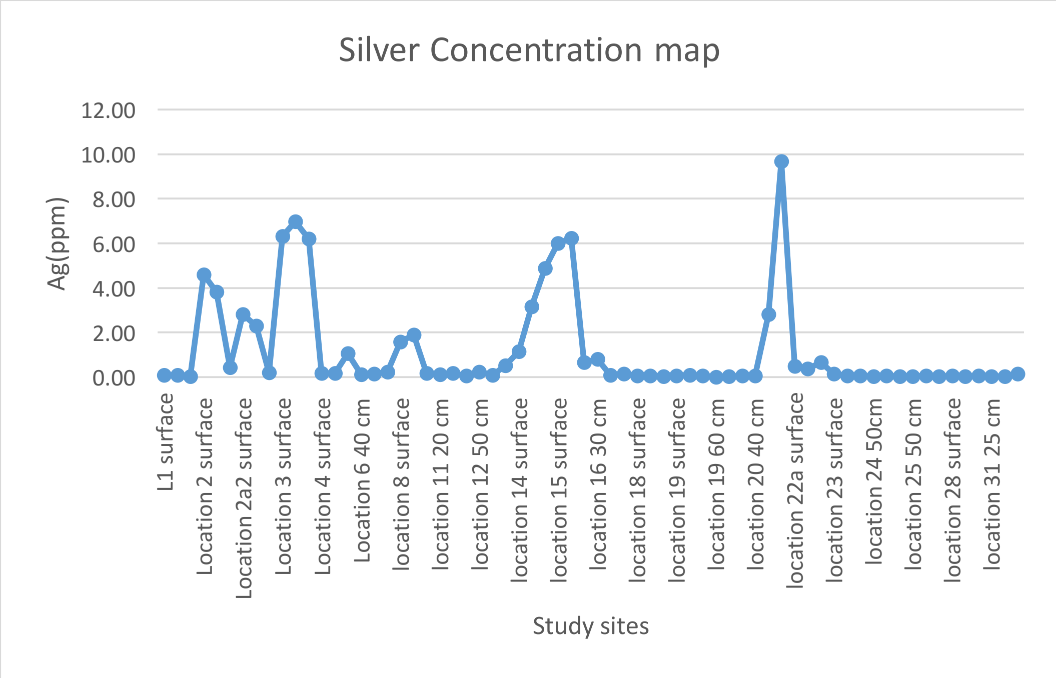


Figure 36: Silver (Ag) concentration map based on ICP-MS results from various sites.

According to table 12 showing the guideline values, heavy metals such as mercury concentration in figure 37 remains below the guideline value at all sample sites. The highest mercury concentration of 0.67ppm was however found at location 3. The chromium and copper concentration from figure 32, 33 remains well below the guideline values. Zinc concentration follows the same path. However, Arsenic at location 17a have higher concentration of 21.56 ppm which is higher than the guideline value as shown in figure 35. The figure 32 -39 shows metal concentration.

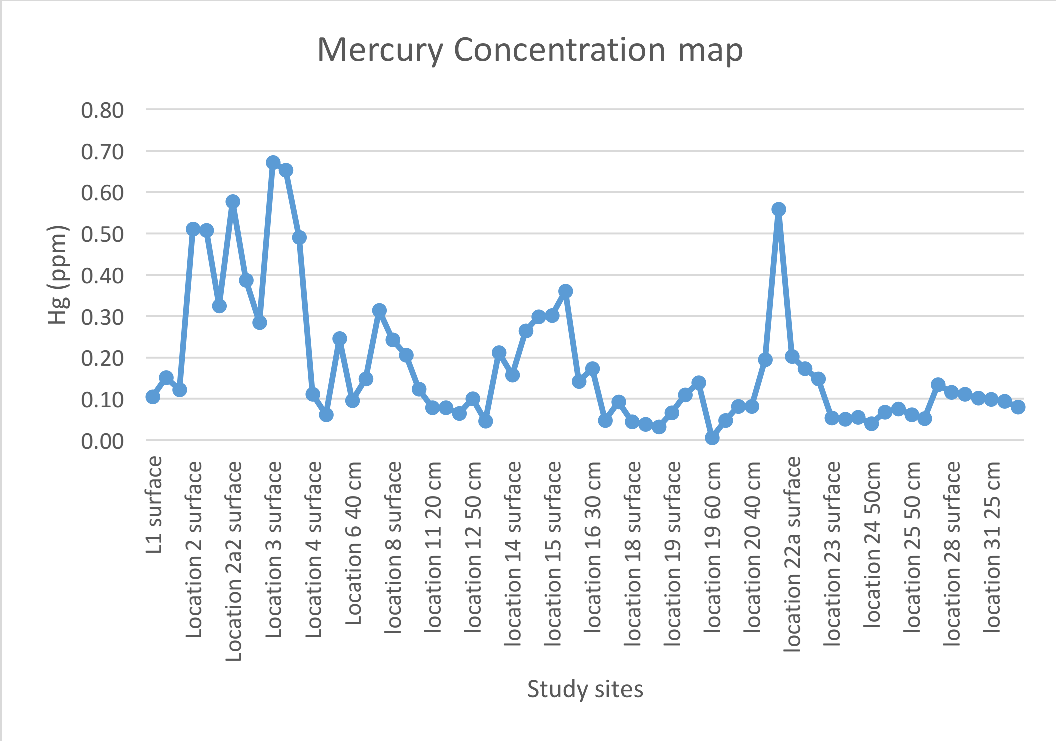


Figure 37: Mercury (Hg) concentration map based on ICP-MS results from various sites.

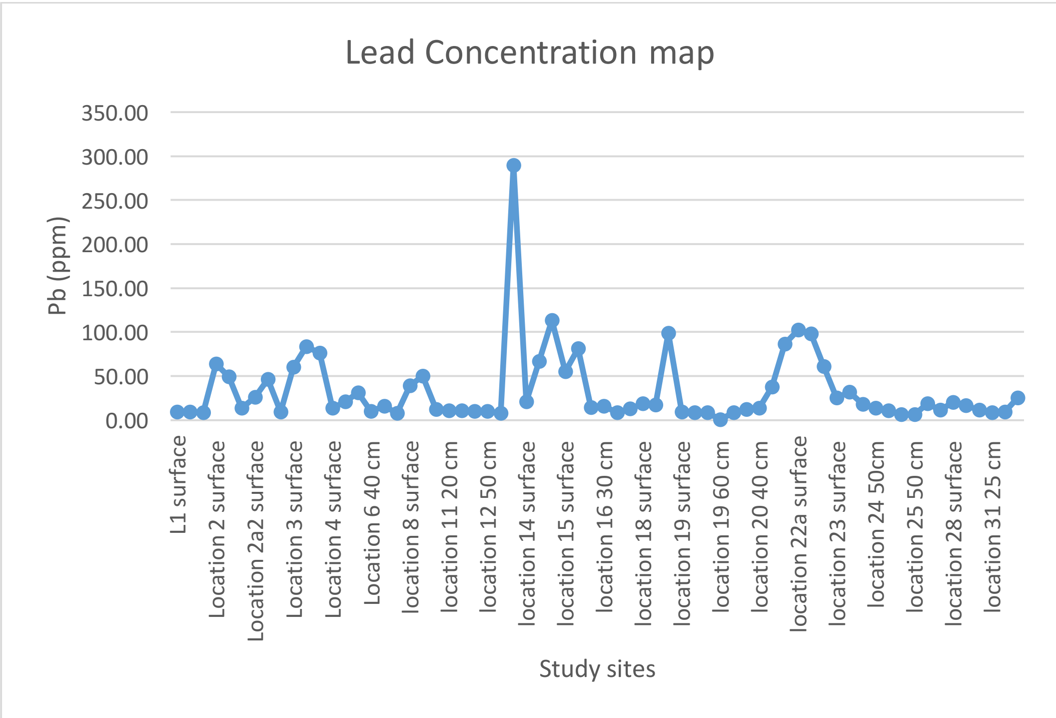


Figure 38: Lead (Pb) concentration map based on ICP-MS results from various sites.

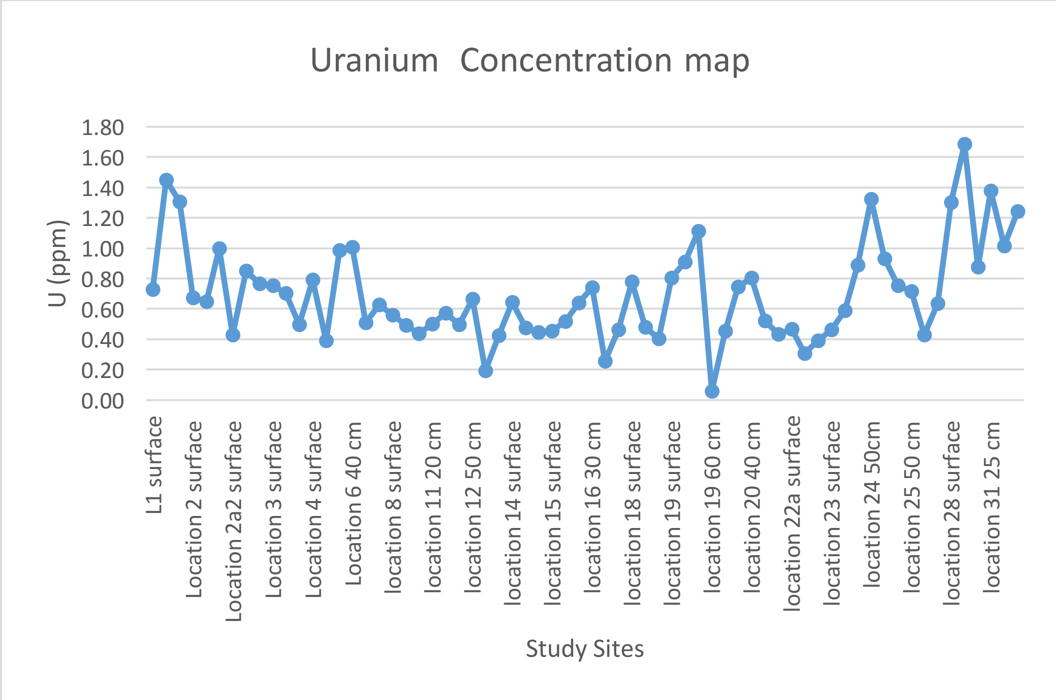


Figure 39: Uranium (U) concentration map based on ICP-MS results from various sites.

The heavy elements comparison between Zn and Pb shows that mine tailings from pervious mining activities were rich in lead as compared to zinc. Due to this a higher lead concentration was found as compared to zinc in the floodplains at various sample sites. Higher lead concentration was noticed at location 13 where the Ohinemuri River merged into the Waihou River resulting in a spike in lead concentration figure 36. The Uranium concentration was found over 1ppm at several sample sites such as location 1, 6, 19, 24, 28 and 31 from figure 39.

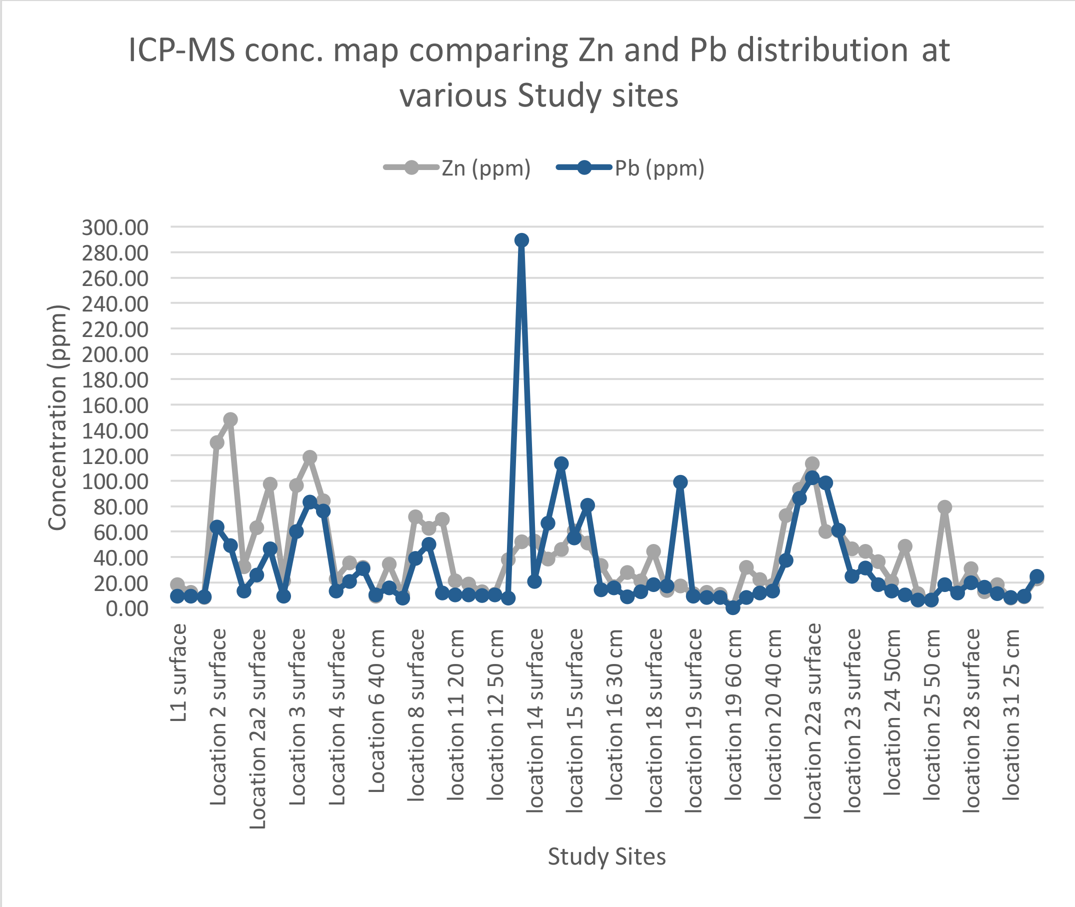


Figure 40 – ICP-MS concentration map comparing Zn and Pb at various sample sites.

The figure 40 and 41 compares different metal concentration obtained from ICP-MS analysis. The other heavy metals such as chromium and copper stay in the lower level with copper have a slightly higher concentration. Arsenic which was released during gold and copper ore mining is also released in the mine tailings of the Martha Mine, mining at Karangahake Gorge and at the Tui Mine. Arsenic was also released during the process of dredging the sediment at Paeroa. Oxidation or weathering of sulphide minerals such as pyrite, arsenopyrite released arsenic in the soil. Due to this significant amount of arsenic was found at locations 3, 14, 15, 17 and 22. Here apart from location 17, the rest of the sampled sites have an arsenic concentration in ppm that stays below the threshold value. A slightly higher copper concentration occurring in the flood plains is the result of mine tailings dispersal from the Ohinemuri and Waihou River flooding.

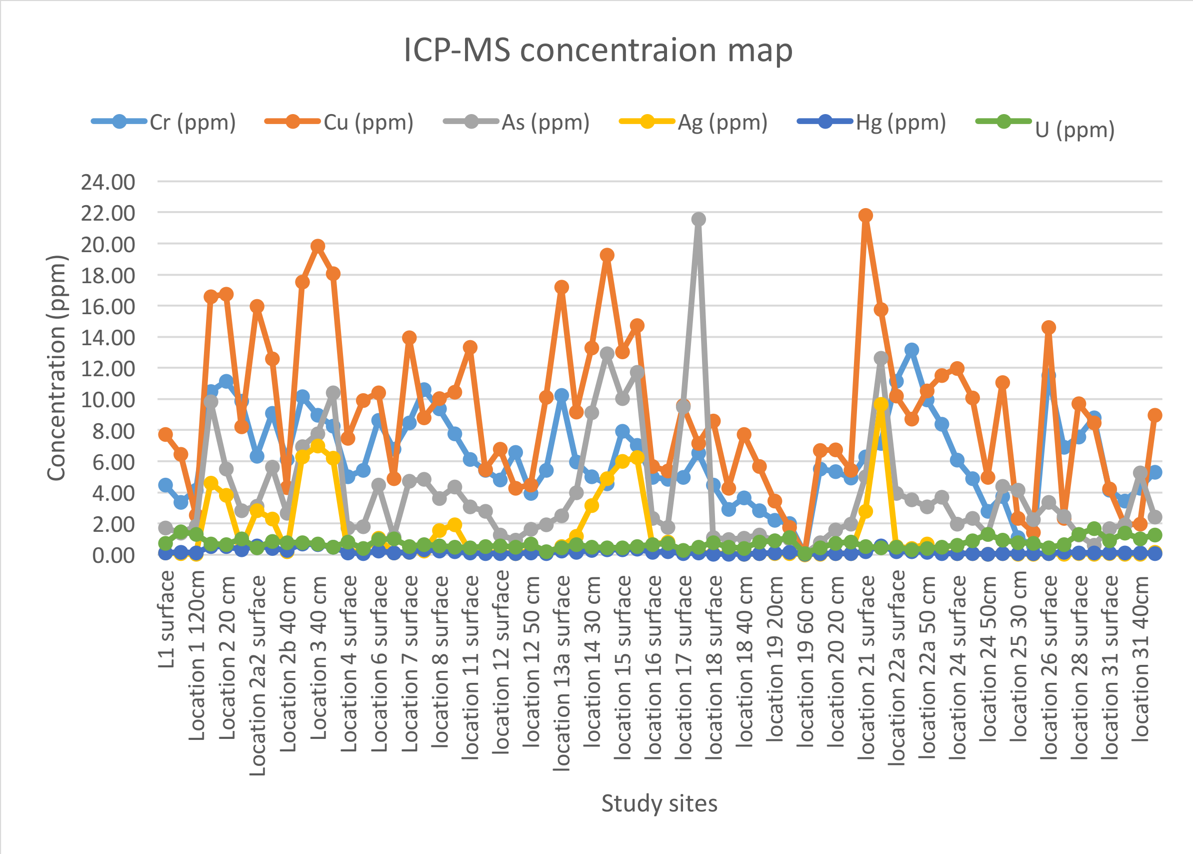


Figure 41 – ICP-MS concentration map comparing trace (heavy) metals such as Cr, Cu, As, Ag, Hg and U.

4.5.2 Other Metal Concentration –

ICP-MS revealed that the most of toxic and non-toxic metals follow the same pattern as the XRF. The non-toxic metals such as gold were not detected by ICP-MS analysis. Other metals such as Sb and Cd were identified as below the detection level by ICP-MS as shown in table 11. The highest Mo concentration of 0.72 ppm was recorded at location 27 at 30cm depth. At the majority of sites its concentration stays below 0.50ppm. The locations 2, 4, 6, 8, 11 were detected below the detection limit. The highest concentration of 11.04 ppm was recorded for toxic metal nickel at location 26. Nickel was found to have a slightly fluctuating level of lower concentration downstream of the Waihou River. Fe was found in higher concentration at location 2, 3 12, 22, 22a, 26 and 31. The highest iron concentration in the soil detected at location 31.The phosphorus concentration varies markedly ranging from as low as 0.53 at location 19 at 60cm depth to highest value of 939.33ppm at location 11. Cobalt was recorded in lower concentration levels in the floodplains at various sample sites. However at location 12 at 20 cm depth cobalt concentration increased markedly to 34.32ppm.

Table 11: Concentration of various toxic and non-toxic element using ICP-MS analysis.

Sample Name	B (ppm)	Na (ppm)	Mg (ppm)	Al (ppm)	Si (ppm)	P (ppm)	S (ppm)	K (ppm)	Ca (ppm)	V (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Se (ppm)	Sr (ppm)	Mo (ppm)	Cd (ppm)	Sb (ppm)	Ba (ppm)
L1 surface	0.42	90.04	322.08	8660.55	5069.93	141.84	82.72	374.94	860.63	18.09	532.85	4822.03	6.28	2.40	0.23	7.08	0.64	0.11	0.14	109.01
Location 1 50 cm	0.27	39.18	119.36	14950.20	3291.82	97.31	75.44	179.24	204.17	15.45	52.36	2022.86	1.31	0.95	0.48	2.27	0.51	0.09	0.09	93.31
Location 1 120cm	0.16	38.35	99.91	10988.03	4518.18	28.10	33.47	154.96	56.33	18.27	10.60	1461.81	0.94	0.64	0.27	1.20	0.32	0.07	0.10	101.97
Location 2 surface	0.37	90.54	1130.01	5601.13	3389.21	436.60	93.44	183.38	2468.60	29.28	1217.39	12821.24	9.38	5.63	0.49	20.30	0.36	0.62	0.77	167.78
Location 2 20 cm	0.31	75.53	1040.43	5332.92	1544.00	291.07	52.73	145.98	3081.08	30.54	1309.35	13123.71	10.08	6.41	0.39	26.42	0.31	0.64	0.68	224.11
location 2 40 cm	0.12	53.32	849.15	3953.82	1200.97	75.72	<0.00	128.98	1594.39	31.00	571.79	12972.59	11.46	3.96	0.19	19.46	0.37	0.10	0.32	169.37
Location 2a2 surface	0.48	175.05	674.85	3582.10	1657.73	689.45	79.31	575.76	2407.74	19.73	606.27	7306.08	5.83	3.20	0.23	20.03	0.29	0.35	0.27	90.21
Location 2b surface	0.21	95.11	951.47	4988.47	1436.90	252.74	54.91	331.42	1616.29	18.86	1429.75	8459.73	6.25	4.35	0.38	13.39	0.30	0.53	0.40	112.09
Location 2b 40 cm	0.05	40.21	616.16	3684.69	2325.47	71.45	<0.00	249.37	767.67	17.09	777.34	8989.20	11.74	2.03	0.19	10.30	0.24	0.06	0.16	120.33
Location 3 surface	0.33	49.78	1024.32	5033.33	1130.20	298.44	90.04	173.25	1002.65	22.90	415.47	11743.99	7.45	6.13	0.92	9.00	0.43	0.49	1.01	99.07
Location 3 40 cm	0.24	62.88	901.50	3562.40	1103.96	283.53	34.02	161.43	1044.34	19.85	641.54	11762.60	9.88	6.23	0.34	9.04	0.36	0.72	1.09	104.33
Location 3 70 cm	0.17	50.58	779.73	2979.07	1755.51	148.58	21.72	134.48	1111.40	17.48	438.83	9893.35	5.84	4.30	0.34	7.61	0.30	0.29	1.01	82.14
Location 4 surface	0.21	47.10	752.69	3055.67	1658.11	272.24	62.41	395.11	1063.05	10.82	218.61	7068.65	4.04	2.59	0.20	11.37	0.24	0.08	0.07	45.10
Location 5b surface	0.61	137.13	661.23	3160.36	2707.43	437.80	80.64	418.96	2396.98	16.24	409.65	6643.06	4.22	3.65	0.11	17.75	0.34	0.14	0.12	56.26
Location 6 surface	0.22	55.41	263.54	9137.09	2710.78	606.62	160.20	114.36	567.22	15.69	102.35	6685.97	3.19	5.72	0.98	4.78	0.38	0.16	0.23	24.68
Location 6 40 cm	0.16	46.43	162.85	3706.30	2876.70	76.11	33.36	206.88	240.23	9.49	16.43	2995.98	0.92	1.36	0.30	5.78	0.18	0.03	0.09	17.74
Location 7 surface	0.35	84.11	480.55	3545.40	2846.69	798.03	232.95	939.52	1174.58	15.41	556.15	6755.73	5.36	4.41	0.67	8.68	0.53	0.17	0.10	47.11
Location 7 15 cm	0.11	49.91	183.84	4179.06	2295.53	242.04	79.71	405.01	509.08	14.12	95.53	7623.22	1.65	2.20	1.02	4.86	0.33	0.07	0.18	62.23
location 8 surface	0.81	164.04	1434.41	3263.98	2340.89	367.56	75.91	423.12	1407.28	16.71	692.63	10209.44	6.43	5.33	0.16	14.92	0.23	0.26	0.25	65.76
location 8 40 cm	0.33	70.99	1003.77	2351.39	2350.20	156.43	3.79	428.18	957.88	10.74	579.37	9649.65	5.60	3.69	0.12	11.03	0.17	0.16	0.30	43.52
location 11 surface	2.49	171.62	1104.43	2916.61	2445.77	939.33	207.51	611.69	4992.25	19.22	1125.88	9335.54	7.24	4.06	0.14	29.35	0.25	0.19	0.26	70.53
location 11 20 cm	0.37	98.92	726.40	2780.46	2101.47	226.85	27.68	515.26	1922.14	12.70	256.56	8157.11	3.43	2.02	0.15	14.61	0.16	0.06	0.10	36.82
location 12 surface	0.15	92.05	580.96	2596.31	533.31	367.56	158.70	757.38	1554.40	12.45	350.91	5218.34	4.14	2.37	0.14	13.11	0.20	0.14	0.06	40.98
location 12 20 cm	0.11	31.45	208.38	1758.23	739.83	56.43	<0.00	179.85	528.04	31.43	1451.14	15040.99	34.32	1.40	0.12	5.57	0.34	0.06	0.08	155.74
location 12 50 cm	0.14	46.94	432.33	2530.51	1063.64	110.46	12.84	281.94	759.20	10.31	143.38	6582.11	3.53	1.57	0.19	8.51	0.16	0.06	0.07	38.59
location 13 surface	2.31	168.80	1421.78	3579.44	2451.57	422.68	101.45	302.92	3258.99	21.92	525.47	8637.30	6.49	4.25	0.08	38.61	0.23	0.15	0.09	51.80
location 13a surface	0.42	119.39	1001.19	3712.56	3033.56	440.57	66.07	1359.93	2284.43	30.75	536.08	9339.77	8.01	5.24	0.28	18.39	0.29	0.24	0.42	130.75
location 14 surface	0.23	77.39	814.20	2758.39	1371.19	845.38	164.91	727.36	1401.66	12.81	600.11	8247.70	9.52	4.90	0.25	13.46	0.34	0.40	0.19	58.11
location 14 30 cm	0.13	55.55	721.49	1871.08	878.48	104.10	11.98	270.33	983.29	12.22	350.72	8056.36	5.84	2.83	0.20	9.38	0.25	0.13	0.69	69.30
location 14 50 cm	0.11	57.40	696.91	1756.59	732.93	112.22	8.71	186.44	792.67	11.72	434.22	7372.90	5.09	2.76	0.24	7.48	0.25	0.18	1.11	55.77
location 15 surface	0.21	62.17	950.27	3020.02	1694.47	384.09	72.47	236.16	1284.49	20.82	542.97	9331.86	5.53	4.39	0.29	10.28	0.33	0.23	0.87	70.39
location 15 30 cm	0.02	38.98	745.90	2482.80	813.50	131.47	5.70	148.99	870.75	20.14	783.01	11374.96	9.25	3.58	0.23	8.22	0.39	0.21	1.29	70.83
location 16 surface	0.09	51.41	683.69	3187.17	482.85	275.99	98.98	564.37	1372.97	11.26	174.67	8694.89	2.60	2.04	0.27	11.96	0.27	0.11	0.15	30.19
location 16 30 cm	0.05	50.15	421.63	3254.67	466.93	137.63	36.89	478.14	625.25	10.63	119.62	8553.36	2.59	1.47	0.26	8.66	0.23	0.04	0.20	24.44
location 17 surface	1.13	298.52	678.77	3766.60	1754.23	563.18	150.34	622.73	5754.40	18.65	667.52	5536.33	5.81	5.02	0.07	29.69	0.30	0.17	0.15	78.73
location 17a 5-7cm	0.08	170.96	496.86	3828.09	1656.98	253.10	32.65	175.78	1140.13	25.23	511.94	7387.54	7.53	3.34	0.15	9.10	0.40	0.11	0.36	56.94
location 18 surface	0.51	169.31	390.81	4038.46	850.25	817.93	92.79	339.45	2651.29	12.77	460.06	4876.88	4.43	3.79	0.12	14.42	0.38	0.34	0.17	92.42
location 18 20cm	0.63	76.79	222.66	2055.71	2915.90	156.75	18.61	166.56	1363.07	9.12	157.56	3182.70	2.70	1.68	0.07	6.56	0.21	0.08	0.07	40.10
location 18 40 cm	0.13	135.35	335.50	2169.06	834.30	182.53	<0.00	136.55	1313.66	13.72	316.05	4452.99	5.04	3.17	0.05	9.36	0.31	0.12	0.10	43.01
location 19 surface	0.07	40.06	150.63	3395.72	1521.22	105.18	43.39	244.46	368.65	11.41	60.03	4794.80	1.66	1.34	0.21	2.71	0.27	0.09	0.16	69.48
location 19 20cm	0.05	36.12	95.87	4502.37	525.69	46.04	40.72	221.23	163.04	10.26	156.43	6581.58	2.70	1.04	0.23	1.91	0.38	0.07	0.11	131.53
location 19 40 cm	0.03	36.93	82.50	5482.03	832.12	23.70	19.35	185.74	126.64	9.61	133.18	4834.33	2.60	0.78	0.11	3.28	0.37	0.05	0.08	175.85
location 19 60 cm	<0.00	1.37	3.11	263.27	18.53	0.53	0.10	7.10	7.23	0.55	3.02	156.04	0.08	0.02	0.00	0.36	0.02	0.01	0.00	8.68
location 20 surface	0.21	201.69	483.66	3101.55	930.87	538.35	94.51	238.80	1834.96	14.53	239.53	4870.63	3.25	3.14	0.10	12.37	0.27	0.16	0.05	53.57
location 20 20 cm	0.32	118.68	412.58	3844.73	3133.43	320.36	57.01	241.11	1378.52	14.16	210.22	5696.09	3.81	2.29	0.15	9.55	0.30	0.12	0.06	51.22
location 20 40 cm	0.52	85.09	419.65	3449.90	2522.04	137.29	20.66	286.63	1238.08	11.65	142.42	5244.66	3.67	1.95	0.13	9.13	0.40	0.06	0.09	46.11
location 21 surface	0.50	160.21	802.96	3865.47	3117.82	591.33	131.82	486.59	3297.65	19.75	707.75	8898.78	6.69	4.20	0.20	22.62	0.26	0.28	0.29	79.85
location 22 surface	0.20	86.09	873.36	3457.20	2719.00	429.60	96.89	311.96	1911.28	20.48	621.71	9566.59	4.86	3.40	0.42	13.72	0.29	0.38	1.09	72.09
location 22a surface	0.46	46.39	1327.15	4367.32	2088.69	310.61	81.18	409.28	1764.25	21.01	792.26	13742.53	8.21	4.90	0.31	16.64	0.49	0.51	0.27	119.48
location 22a 30cm	0.24	28.50	1648.14	4118.96	1786.29	201.99	18.80	295.30	853.20	25.08	831.48	17102.81	12.57	6.31	0.23	7.58	0.51	0.29	0.33	73.32
location 22a 50 cm	0.82	61.21	1231.43	6739.45	1874.44	176.80	42.89	411.20	716.09	22.78	1238.26	14238.39	11.84	5.01	0.36	7.30	0.56	0.40	0.29	87.47
location 23 surface	1.30	217.22	1167.60	6570.72	5110.24	497.43	148.56	492.02	2938.22	20.73	747.33	9450.17	7.79	5.23	0.18	17.54	0.47	0.31	0.14	58.57
location 24 surface	1.53	469.99	1930.98	10454.48	5122.06	592.58	181.58	578.32	1888.18	18.04	328.33	9061.61	4.51	6.72	0.14	19.50	0.52	0.27	0.08	70.05
location 24 30 cm	1.15	110.09	1054.10	11876.10	4912.04	241.86	58.18	284.60	1276.10	14.36	328.26	8549.13	4.05	3.94	0.12	13.93	0.48	0.18	0.09	83.76
location 24 50cm	0.95	115.82	405.34	11372.21	2698.40	38.49	10.21	208.06	707.77	12.82	131.17	7295.32	2.62	1.67	0.06	15.10	0.41	0.08	0.10	135.58
location 25 surface	0.96	96.06	786.97	8164.54	6046.23	399.60	175.52	138.95	1130.42	13.82	360.39	9285.82	4.12	2.64	0.35	9.39	0.49	0.28	0.07	77.04
location 25 30 cm	0.73	92.89	220.61	4038.81	5644.80	50.28	17.44	110.07	389.98	5.77	140.23	6554.91	1.86	0.70	0.19	4.80	0.25	0.05	0.04	68.59
location 25 50 cm	0.76	92.48	138.58	3043.63	3227.71	29.66	<0.00	116.87	351.72	3.86	126.84	6230.30	1.43	0.35	0.14	5.31	0.14	0.04	0.04	74.85
location 26 surface	0.83	271.93	2101.13	6699.78	4714.57	410.30	36.68	429.51	1710.73	22.50	414.51	10108.37	8.72	11.04	0.10	17.35	0.29	0.39	0.20	61.75
location 27 30 cm	0.76	89.11	502.10	5744.95	4321.11	37.96	3.61	181.45	837.49	38.02	248.59	28093.90	3.60	0.66	0.23	13.55	0.72	0.03	0.09	72.02
location 28 surface	0.83	46.22	225.09	5622.31	4601.07	116.92	54.02	279.60	933.11	30.96	849.77	11549.70	8.70	1.38	0.21	10.61	0.67	0.21	0.15	148.77
location 28 20 cm	0.64	27.65	125.48	3745.96	4170.56	11.13	<0.00	116.19	417.22	27.67	189.90	12334.40	5.66	0.65	0.05	9.48	0.48	0.06	0.15	149.46
location 31 surface	0.85	81.06	201.15	10389.29	2525.61	361.48	134.12	157.09	318.71	15.53	277.75	17351.84	1.25	0.98	0.24	4.54	0.49	0.15	0.06	85.86
location 31 25 cm	0.88	211.22	152.05	12586.60	1857.68	58.80	12.42	79.95	382.09	32.19	98.17	22883.94	1.27	0.46	0.11	11.65	0.34	0.05	0.05	172.72
location 31 40cm	0.79	90.39	136.84	10502.96	1781.05	254.86	49.36	87.15	293.29	35.81	360.53	70089.77	1.42	0.33	0.09	6.99	0.49	0.10	0.03	100.05
location 32 10cm	1.77	69.69	374.27	7189.40	3630.12	699.06	253.29	398.62	497.28	11.42	38.02	15596.12	2.01	1.68	0.10	12.90	0.30	0.04	0.08	94.82

Chapter Five

Discussion

The gold rush resulted in mining activities in the Coromandel region. This mining produces the mine tailing which contains processed ore as an ore waste from mining. The mine tailings were disposed using rivers, streams or any other watercourse as a sludge channel. The Ohinemuri River was used as a sludge channel for the Martha Mine whereas the Waihou River was used as a sludge channel for the Tui Mine. Flooding events resulted in mine tailings being dispersed in the flood plains. The 1907 floods in the Ohinemuri River resulted in the dispersal of mine tailings in form of a yellow-brown silt layer in the flood plain (Clement *et al*., 2017).

The Ohinemuri River received mine tailings rich in Zn, Mn, Cu and As from the Martha Mine. The flooding resulted in the dispersal of these mine tailings. Waihou River received mine tailings from the Tui Mine and from the Ohinemuri River when the latter merged into the former and become part of the Waihou River. The Waihou River has flooded periodically in the past in 1901, 1910 and 1927 which resulted in mining contaminant being dispersed in the flood plains.

This study focuses on the mine tailings in the Waihou River. The Tui Mine has been studied extensively resulting in contaminant concentration being measured in various studies. In New Zealand, the Tui Mine environment is the most polluted mining site. Around 160,000 tonnes of ore were extracted and during this process mine tailing was disposed in Tui Stream as a sludge channel which then entered the Waihou river. The Livingston, Tay, Webster, Joyce and several other studies concentrated on the mining effect on the Waihou River. There was no conclusive evidence of mining contaminants travelling downstream. Therefore, this study was chosen to study the dispersion of contaminants in the floodplains because of the flooding in the Waihou River. The Ohinemuri River, Tui Stream feeds into the Waihou River, therefore, flooding in these rivers also contribute to the contaminant's dispersal.

The samples were taken from the flood plain at various depths. The samples taken at locations 27 and 28 have a dirty yellow silt layer present below the A horizon.

The sample site at location 27 has a yellow silt layer between 28-38 cm (from the bottom) and at location 28 the yellow silt layer was present between a depth of 15-23cm. These locations were present in the zone of overflow identified in the Clement study in 2017 as shown in the figure 42 below.

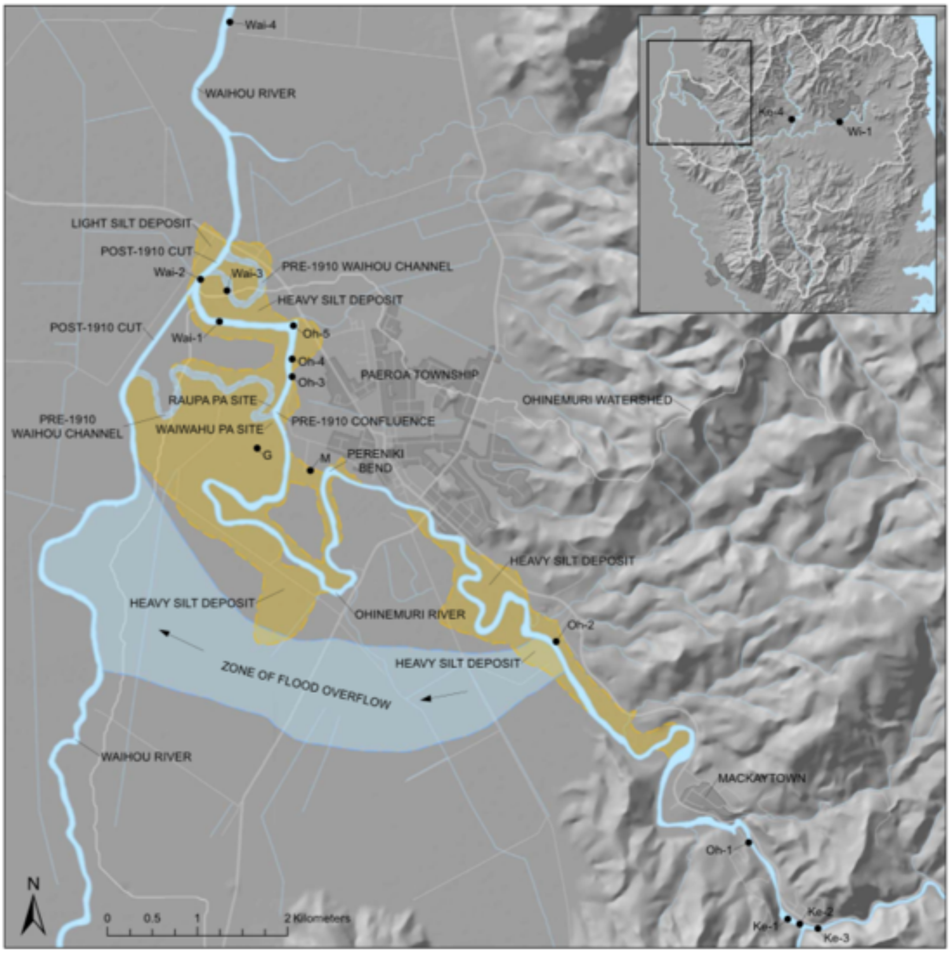


Figure 42: The Ohinemuri –Waihou River convergence, zone of overflow and silt deposits in the floodplains.

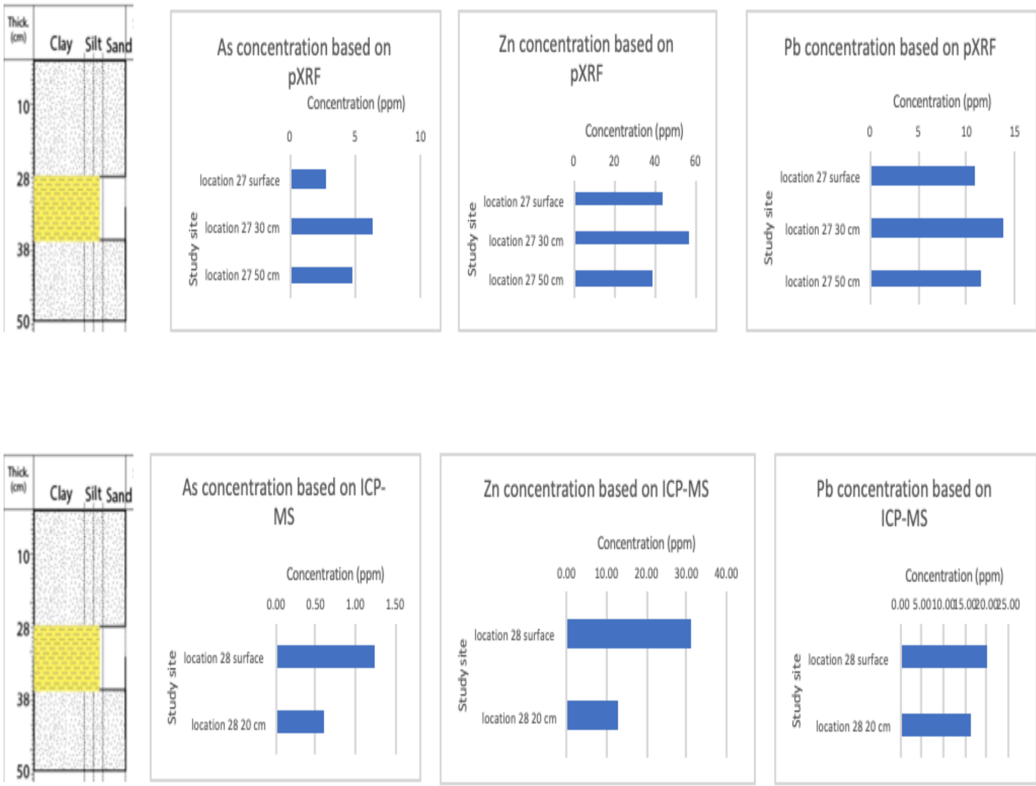


Figure 43 : Stratigraphic column of Location 27 soil profile and metal concentration based on pXRF analysis and ICP-MS analysis.

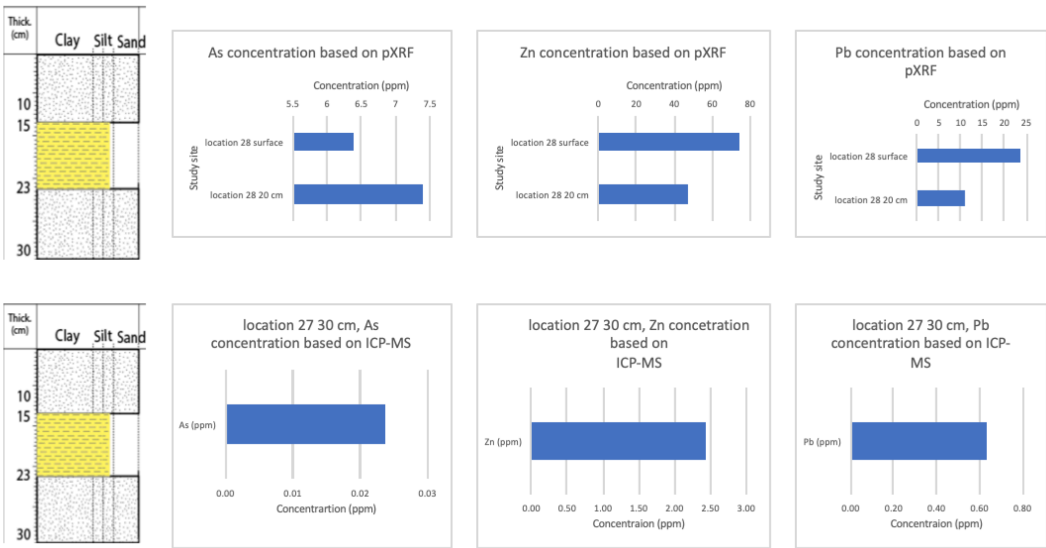


Figure 44 : Stratigraphic column of Location 28 soil profile and metal concentration based on pXRF analysis and ICP-MS analysis.

The yellow silt layer which is believed to be result of 1907 flood and doesn't seem to have higher concentrations of lead, arsenic and zinc. Here a hand held XRF identified that at 27 at 30cm depths the As level is 6.3ppm with a lead level of 13.7

ppm and at locations 28 at 20 cm. The As level is 7.4 ppm and the lead level is 11 ppm. The stratigraphic column at these two locations are shown in figure 43 and 44 which correlates the contaminant concentration in that particular depth. These recordings might be a result of a small-scale flood or the flooding in Waihou River. At location 28 at 20cm 6.2ppm of uranium was also identified. Uranium enters the soil from fertilizers. Fertilizers such as rock phosphate when added to the field as a phosphorus source, resulted in a release of uranium in the soils. In New Zealand, overall uranium is present in the level of 1.1 – 2.3 ppm(Selvarajah, 2000). The highest concentration of 15ppm was identified in the study sites at location 20 surface.

The handheld XRF was initially used to analyse the sample. There is an increase in concentration of Pb, Zn and As in the flood plains. A small amount of mercury was also firstly identified at locations 1, 18 and 25. Upon analysing the sample sites using ICP-MS, relatively higher mercury concentrations were obtained at locations 2, 3 and 22a. At location 2 the mercury concentration was recorded at 12.77 whereas at location 3 it was slightly higher with concentration recorded at 16.79 ppm and at location 22a mercury concentration was recorded at 13.96ppm. Location 22a was in the vicinity of the Tui Stream where it enters the Waihou River. Location 2 was located in the Ohinemuri River flood plains where 1907 flooding resulted in dispersal of mine waste rich in Pb, Zn, As and Hg. The Clement study in 2017 found an elevated mercury level with a concentration of 0.4 mg/kg in the overbank deposits. The higher concentration at location 3 was a result of the merging of the Ohinemuri River into the Waihou River.

The soil structure in the floodplains also affects the retention capability of various elements. The soil contains 3 types of inorganic particles i.e. sand, silt and clay. The clay particles are smallest in size with size range of less than 0.002 mm as shown in the Wentworth table. The clay particles, due to smaller size but a very large surface area, can retain elements such as calcium, potassium, magnesium, trace elements and phosphorus. The clay particle has a net negative charge resulting in retaining positively charge particles. The silt particles have a size between 0.002 to 0.05. The silt particles have limited ability to retain plant nutrients and have a more spherical shape. In this study most of the study sites have low silt particles. The silt deposit is a result of flooding and was identified in the zone of overflow between Ohinemuri and the Waihou River. mentioned by past studies. The soil portion was made of coarser material and has a particle size of 0.0625 to 2mm. The locations 18 and 19 are dominated by sand and have more of a silty sand texture. Sand particle doesn't retain nutrients and elements, as the element doesn't tend to stick with soil particles and the rain can flush the sediment or the sediment can be leached into the groundwater. This is evident in the ICP-MS results as both of these sites are low in the trace (heavy) metals and other toxic and non-toxic metals. Location 15 at 30cm depth has a marginally higher sand portion which means that this site is still poor to hold the elements. Apart from high iron metal other elements were also present in the low level.

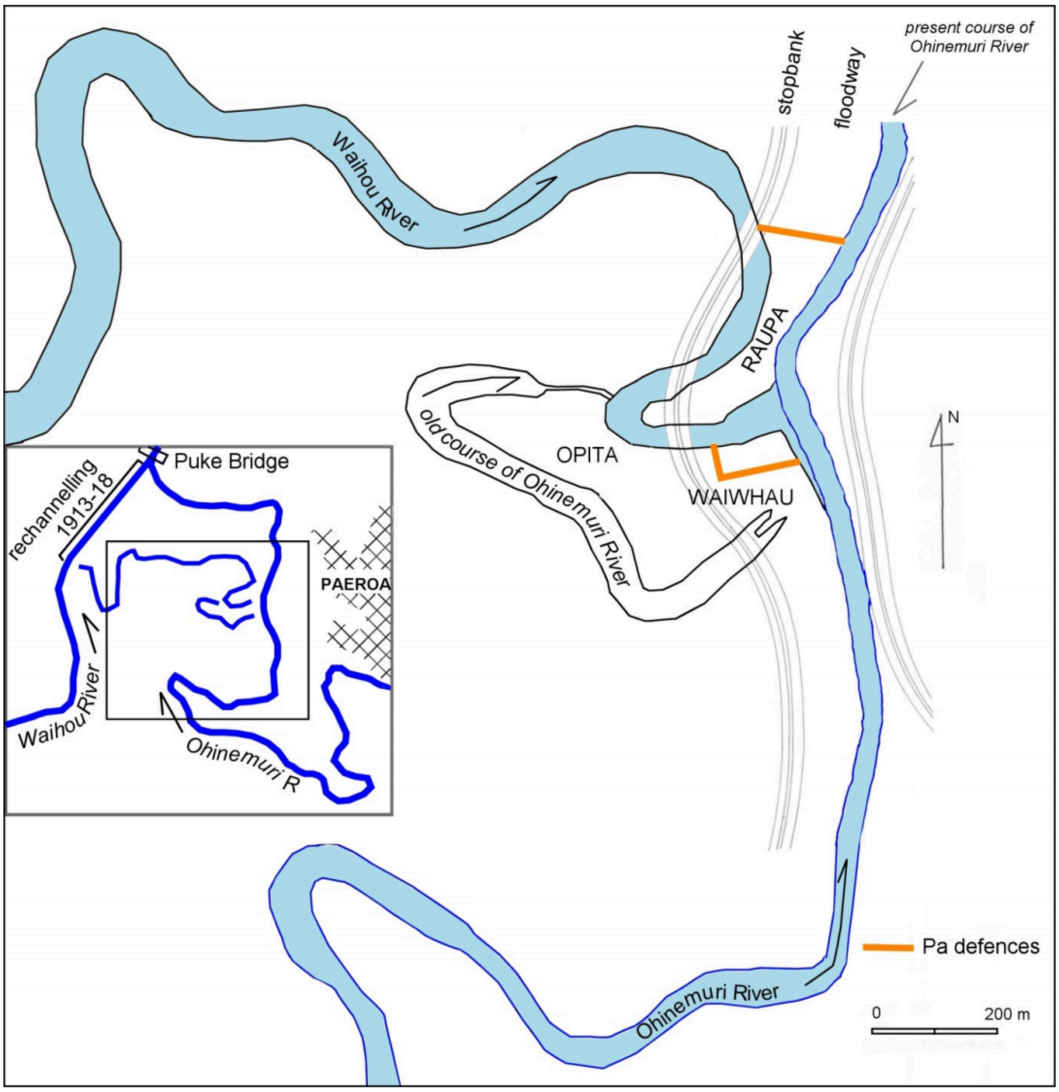
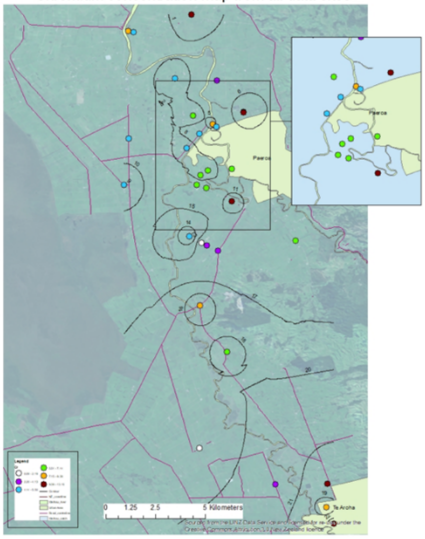


Figure 45 – Changing River courses for the Ohinemuri River and the Waihou River and former river junction (Phillips & Allen, 2013).

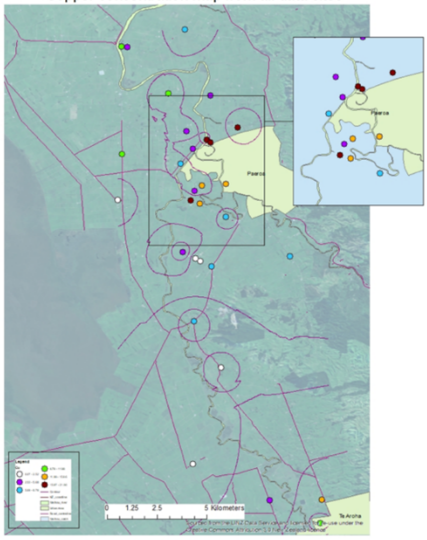
Both rivers have been rechannelled in the past for a remedy of frequent flooding in Paeroa township as shown in figure 45. The major bend near Opita in the Waihou River, the narrow bend of Ohinemuri River, old Waihou-Ohinemuri River junction was then turned into swampy land which was filled with silt deposit from mine tailing with frequent floods. The flooding event of 1954, 1981 resulted in Paeroa region being covered in yellow-brown silt. This has been identified with this study. The mine waste hasn't spread much beyond Paeroa apart from higher contaminant concentration near the Komata River floodplains which is a combined result of the flooding event in the Waihou River and the mining at Komata Reef.

Channel straightening of the Waihou and the Ohinemuri Rivers resulted in the old river channel having higher metal concentrations. The locations 2, 2b, 21 and 22 present near the old river channel. This old channel harbours the mine tailings in the form of silt deposits in the old river basin. Broken shell was noticed at location 2 and 20cm depth which it was buried due to past flooding. The old river channel also causes the higher concentration of trace/heavy metals. The chromium has its highest concentration at location 22a of 13.16ppm

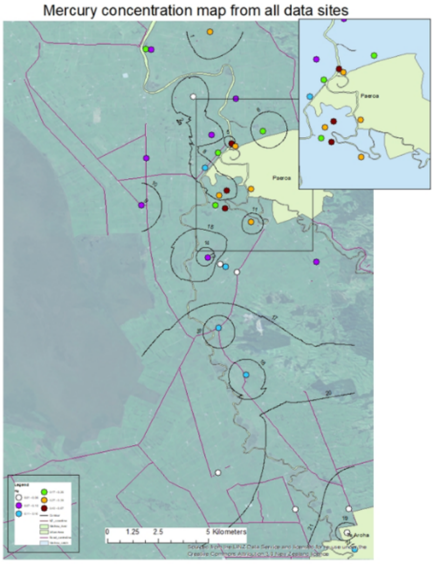
Chromium concentration map from all data sites



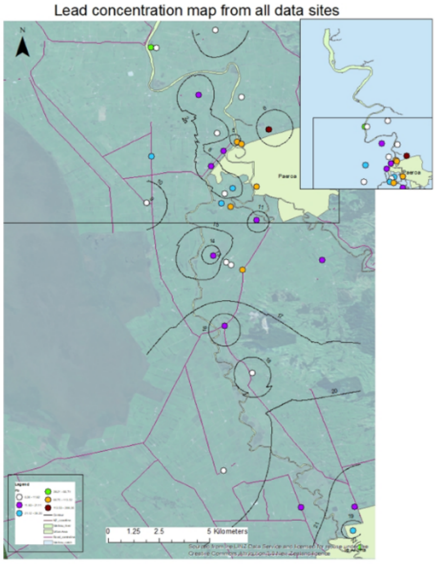
Copper concentration map from all data sites



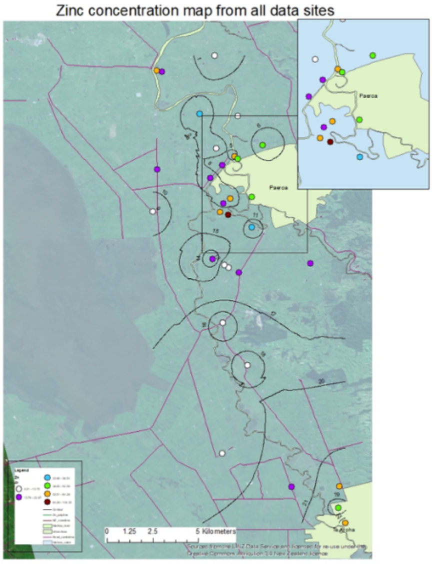
Mercury concentration map from all data sites



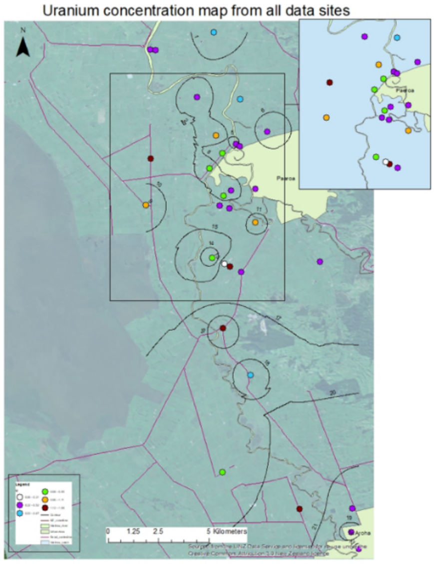
Lead concentration map from all data sites



Zinc concentration map from all data sites



Uranium concentration map from all data sites



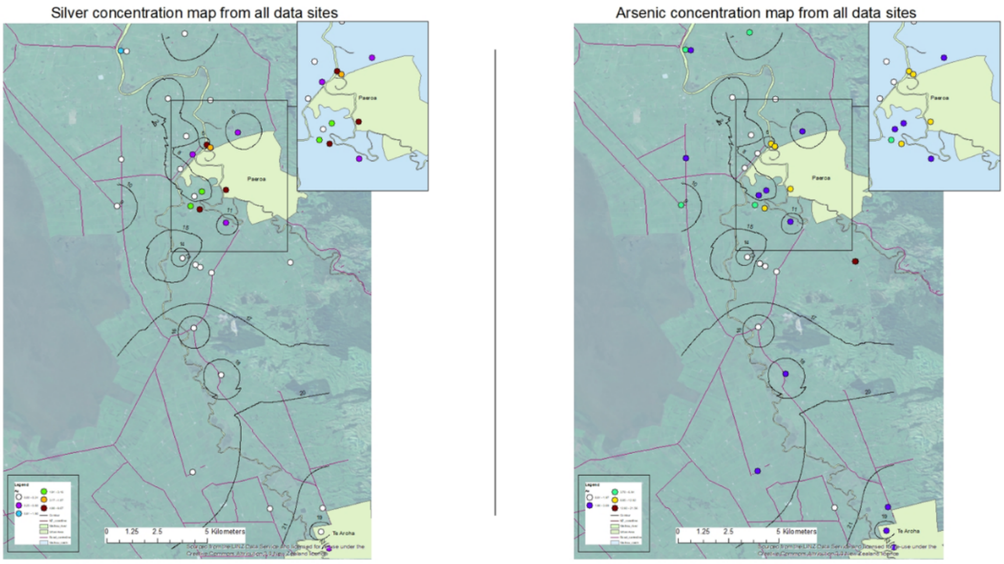


Figure 46: Map of heavy metal contaminant concentration in the floodplains by ICP-MS analysis.

The above is the geomorphology map of the study area. Here, the zoomed version shows that this study focused on the Paeroa area and north of Paeroa area for mining contaminant in the floodplains. The ICP-MS results from the above figure 46 shows lead has its highest concentration of 289.26 reported at location 13a. Location 13a is located in the flood plains of the Komata River. The Komata Reef has been mined for gold and silver from 1891- 1930. This resulted in Komata River being used as a sludge channel with mine tailings rich in zinc, lead, mercury etc. The surface sample shows lead in higher concentration with chromium identified with a relatively higher concentration then the rest of sample sites. The higher concentration of chromium in the floodplains at location 22a is a result of mine tailing from Tui Mine and mining at Waiorongomai Valley, Te Aroha. This resulted in higher concentration of contaminants in Waihou River near Te Aroha which in flooding events spread in nearby areas and the floodplains. Near the Paeroa wharf contaminant was brought after dredging of the river and process at Paeroa plant. This resulted in relatively higher contaminants such as chromium, copper, mercury, silver and arsenic etc. concentration around the Paeroa township. Therefore, this study confirms that the contaminant associated with mining hasn't spread much beyond Paeroa. The flooding caused dispersion of contaminant on the floodplains. The contamination associated with mining hasn't contributed to the contamination at the Firth of Thames. This study does shows that the farmland on the floodplains might be at risk as could potentially be sitting on the contaminated flood deposits.

5.1 Comparison with soil quality guidelines

Table 12: Guideline values for various contaminant (Organization, 2006; Biogro, 2009; Environment, 2011).

Contaminant	WHO provisional guideline value (mg/l)	Drinking Water Standard for NZ maximum acceptable value (mg/l)	Rural residential /lifestyle block 25% produce (mg/kg)	Residential 10% produce (mg/kg)	High density residential (mg/kg)	Recreation (mg/kg)	Commercial/ industrail outdoor worker (mg/kg)	Maximum acceptable level in the soil (mg.kg)
Arsenic	0.01	0.01	17	20	45	80	70	20
Chromium (VI)	0.05	0.05	290	460	1500	2700	6300	150
Cadmium (pH5)	0.003	0.004	0.8	3	230	400	1300	2
Copper	2	2	>10,000	>10,000	>10,000	>10,000	>10,000	60
Nickel	0.07	0.08						35
Mercury	0.006	0.007	200	310	1000	1800	4200	1
Zinc	3	NA						300
Lead	0.01	0.01	160	210	500	880	3300	100
Iron	NA	0.2						
Boron	NA	NA	>10,000	>10,000	>10,000	>10,000	>10,000	

The guideline values for various heavy metal contaminants are shown in the above table 12. Some sample sites in this study have contaminant concentration above the threshold concentration as shown in figure 47. According to the above table, location 17a is not suitable for a lifestyle block or residential area with over 10% production as arsenic can be absorbed by plants and enter the animals. Similarly, location 13a sample site, is also unsuitable as a farm land due to lead concentration higher than the threshold value. The Cadmium value at location 3 at 40 cm depth was close to the threshold value which make that site less favourable to be used as agricultural land.

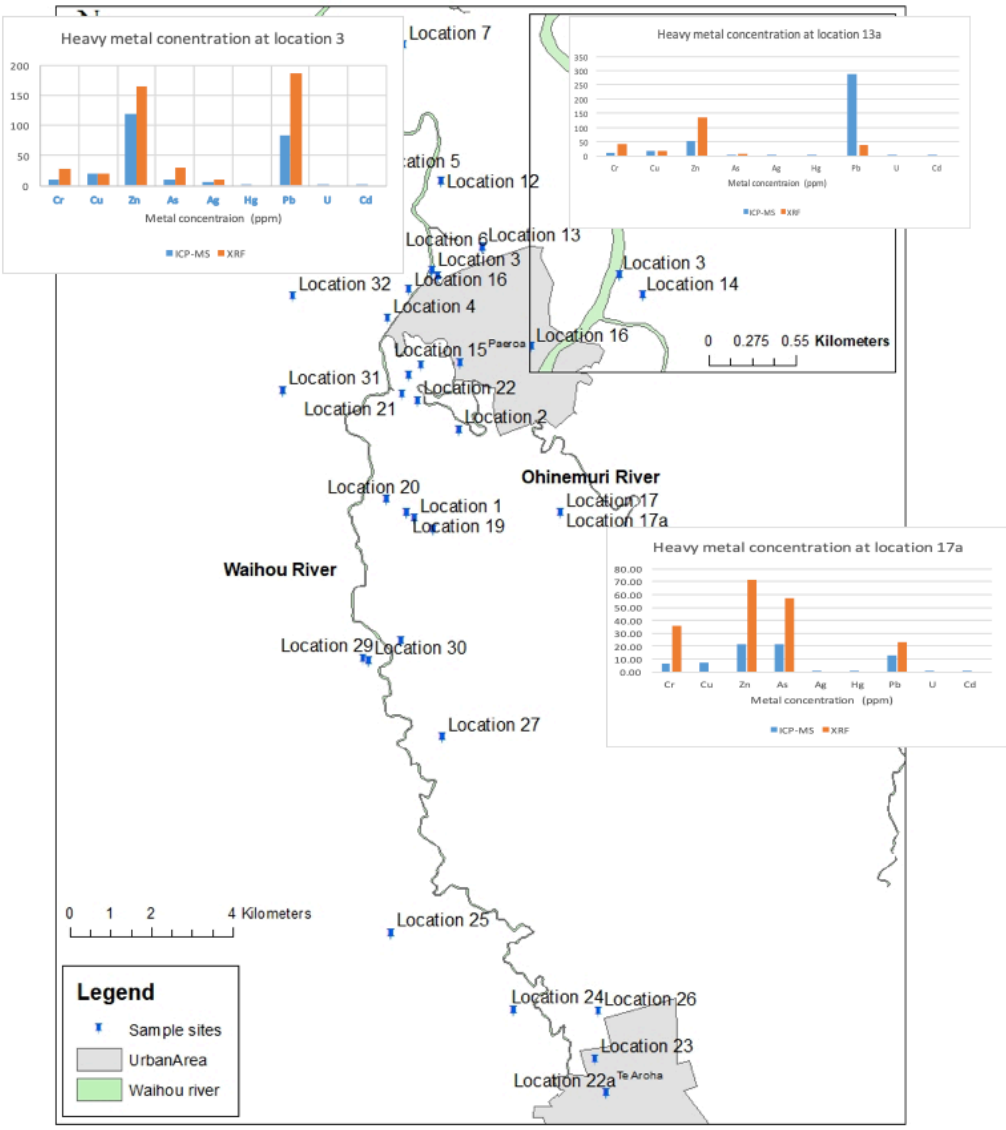


Figure 47: Map of locations with heavy metal concentrations above the threshold limits.

The limitations to this study mainly focus around the fact that the study sites are on public land when the results would have been more conclusive had they been taken from the surrounding private farm land. Unfortunately, samples were unable to be taken from the private land apart from location 30. Therefore, the sample sites mainly consist of areas along the roadside. These samples have been carefully taken to ensure limited contamination from the road metal etc. however, at certain sites the road metal was too close to the where the sample needed to be taken. Without being able to access the private land this meant certain samples that were initially planned could not be taken from some sites.

Chapter Six

Conclusion and Recommendations

6.1 Conclusions

It was initially assumed that the mine waste from the Ohinemuri River and the Waihou River washed out to the Firth of Thames. But previous studies indicate no downstream migration of contaminant. Therefore, this study looked at the contaminant concentration in the floodplains. The flooding in the Waihou River, which gets the mine tailing from the Tui Stream and Ohinemuri River, results in dispersal of mining contaminant containing trace (heavy) metals along the floodplains. The concertation of contaminant in the floodplains was determined using the XRF and ICP-MS analysis. The study was primarily focused on trace metal contaminants such as Cu, Zn, Pb, Mn, Cd, Cr, Ag, Hg and As but all detectable toxic and non-toxic elements were measured. The contaminant concentration at the sample sites mostly fall below or just below the guidelines apart from As and Pb. The As was present above threshold limits at one location and Pb was present above the threshold limit at one sample sites. The higher silver concentration was found in the floodplains near Paeroa and near the old river channel. The cadmium concentration was also noted close to the threshold limit at another sample sites.

The XRF and ICP-MS analysis of soil samples from various study sites gives the similar distribution pattern of Cr, Cu, As, Zn and Ag apart from minor differences in Hg, Pb, U distribution pattern. In general, the contaminant concentration decreases downstream of the Waihou River floodplains. The resemblance in the results of XRF and ICP-MS analysis signifies the accuracy of the analysis processes. The slight increase in Cr, Cu and Pb concentration at location 7 which is located downstream in the floodplains is a result of mine tailing from gold mining at Komata Reef. The mine tailing was processed at the Komata battery station resulting in increased contaminant concentration in that particular location.

The Tui Mine influence in the floodplains was identifies at location 26, 22a with a higher concentration of Cr, Cu and Zn. When Ohinemuri River merges into the Waihou River higher concentration of Cd, As, Pb, Hg, Cu and Cr was found. The higher concentration of As, Pb, Cu, Ag and Cr was identified in the Ohinemuri floodplains occupied between both rivers. These study sites location 2, 21, 22, 2b, 15 and 17 floodplains were getting flooded from flooding in either or both rivers.

The study has found that the contaminant was present in high concentration in the floodplains where the Tui Stream enters the Waihou River because of Tui Mine and other mining activities in the Waihou River. The high contaminant concentration near the Ohinemuri River floodplains as a results of mining activities in the Martha Mine and at Karangahake George. Most of the contaminant were present in higher concentration where the Ohinemuri River merges into the Waihou River. The old Waihou River channel and past frequent flooding resulted in higher trace element concentration in the floodplains near Paeroa. This study found that the similar concentration of contaminant was noticed to what was reported in the river which means the mine waste has spread in the floodplains. The contaminant concentration reduces in the floodplains downstream of the Waihou River which shows minimum downstream migration of contaminant towards Firth of Thames.

6.2 Recommendations

Samples for this study were taken from the public areas of the floodplains. Therefore, further study with samples taken from the private land areas would be beneficial as this could then give the complete picture of the contaminant in Waihou River floodplains from the mining activities. Continual research and monitoring are important to monitor the dispersal of contaminants in the floodplains over time. This study used pXRF to initially analyse the sample, using XRF could improve the accuracy of the result further. Some sample sites found to have elevated concentration of contaminants above the threshold level. The farm lands near these sites potentially have higher than recommended contaminant levels which can potentially affects the health standard. Further studies into this is recommended.

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Appendices

Appendix A: pXRF raw data

Date	Locations	Nd	Nd +/-	Pr	Pr +/-	Ce	Ce +/-	La	La +/-	Ba	Ba +/-	Y	Y +/-	P	P +/-	S	S +/-	Cl	Cl +/-	K	K +/-	Ca	Ca +/-	Ti	Ti +/-
19/04/2018																									
19/04/2018	NIST 2711a	<LOD	253	<LOD	138	<LOD	80	<LOD	62	697	15	56	3	<LOD	4572	443	77	<LOD	213	19530	225	19205	196	2376	34
19/04/2018																									
19/04/2018		<LOD	270	<LOD	148	<LOD	86	<LOD	68	307	15	22.4	1.7	<LOD	2817	<LOD	141	191	56	4586	88	3661	63	1283	22
19/04/2018	Location 1 120cm	<LOD	231	<LOD	127	<LOD	74	<LOD	58	317	13	24.7	1.5	<LOD	2730	<LOD	127	218	53	4673	85	3638	60	1347	22
19/04/2018	Location 1 50 cm	<LOD	185	<LOD	102	<LOD	60	<LOD	47	293	10	38.7	1.4	<LOD	1599	159	31	147	32	3480	53	935	27	1036	14
19/04/2018	Location 1 120cm	<LOD	209	<LOD	115	<LOD	67	<LOD	53	368	12	27.8	1.5	<LOD	1608	<LOD	86	105	35	4473	67	1448	34	1102	16
19/04/2018	Location 2 surface	<LOD	212	<LOD	116	<LOD	67	<LOD	53	282	12	16.1	1.2	<LOD	2569	<LOD	135	<LOD	142	3609	71	3209	54	1503	22
19/04/2018	Location 2 20 cm	<LOD	194	<LOD	106	<LOD	61	<LOD	48	417	11	21.5	1.2	<LOD	2755	<LOD	141	<LOD	147	4836	78	4597	61	2281	27
19/04/2018	location 2 40 cm	<LOD	206	<LOD	112	68	22	<LOD	50	400	11	21.8	1.2	<LOD	2923	<LOD	143	<LOD	164	3999	82	2591	53	2448	32
19/04/2018	Location 2a surface	<LOD	213	<LOD	116	<LOD	67	<LOD	52	320	11	19.7	1.2	<LOD	2989	<LOD	145	<LOD	144	4384	80	5560	73	1840	25
19/04/2018	Location 2b surface	<LOD	219	<LOD	120	<LOD	70	<LOD	55	264	12	14.6	1.2	<LOD	2365	<LOD	136	<LOD	151	4088	77	2888	52	1664	24
19/04/2018	Location 2b 40 cm	<LOD	211	<LOD	115	<LOD	67	<LOD	52	305	12	13.3	1.2	<LOD	2264	<LOD	131	<LOD	154	4411	80	824	35	2303	29
19/04/2018	Location 3 surface	<LOD	214	<LOD	117	<LOD	68	<LOD	54	214	12	22	1.3	<LOD	2442	<LOD	136	<LOD	141	4250	77	1782	42	1530	22
19/04/2018	Location 3 40 cm	<LOD	200	<LOD	109	<LOD	63	<LOD	49	325	11	19.9	1.3	<LOD	2470	<LOD	132	<LOD	130	5925	86	1669	40	1400	20
19/04/2018	Location 3 70 cm	<LOD	203	<LOD	111	68	21	<LOD	50	280	11	23.1	1.3	<LOD	2296	177	45	<LOD	133	5105	79	1744	40	1393	20
19/04/2018	Location 4 surface	<LOD	226	<LOD	123	<LOD	72	<LOD	56	211	12	13.7	1.3	<LOD	3135	<LOD	178	<LOD	194	4190	90	652	38	2103	31
19/04/2018	location 5 surface	<LOD	206	<LOD	113	<LOD	66	<LOD	52	184	11	16.1	1.1	<LOD	2607	232	46	<LOD	122	3082	59	7024	74	1249	18
19/04/2018	Location 5b surface	<LOD	204	<LOD	112	<LOD	65	<LOD	51	252	11	12.9	1.1	<LOD	2448	<LOD	123	<LOD	132	3766	68	5075	64	1670	22
19/04/2018	Location - no sample	<LOD	243	<LOD	133	<LOD	78	<LOD	61	219	13	13.7	1.3	<LOD	3330	<LOD	182	<LOD	215	4421	102	1762	54	2111	34
19/04/2018	Location 6 surface	<LOD	204	<LOD	111	<LOD	66	<LOD	52	148	11	14	1.1	<LOD	1962	184	42	173	44	2493	55	762	30	1435	20
19/04/2018	Location 6 40 cm	<LOD	202	<LOD	110	<LOD	65	<LOD	51	183	11	21.3	1.2	<LOD	1941	122	39	<LOD	126	3975	67	101	24	1979	24
19/04/2018	Location 7 surface	<LOD	236	<LOD	131	<LOD	77	<LOD	61	153	13	10.7	1.2	<LOD	2368	296	50	223	50	3136	68	2368	48	719	15
19/04/2018	Location 7 15 cm	<LOD	198	<LOD	108	<LOD	63	<LOD	50	245	11	16.3	1.2	<LOD	2272	<LOD	120	<LOD	124	4688	74	443	28	1751	22
19/04/2018	location 8 surface	<LOD	214	<LOD	117	<LOD	68	<LOD	53	213	12	13	1.1	<LOD	2664	<LOD	141	<LOD	149	3750	75	2400	49	1509	23
19/04/2018	location 8 40 cm	<LOD	201	<LOD	110	<LOD	64	<LOD	50	227	11	15.8	1.1	<LOD	2591	<LOD	138	<LOD	152	4437	77	1889	42	1699	24

Locations	V	V +/-	Cr	Cr +/-	Mn	Mn +/-	Fe	Fe +/-	Co	Co +/-	Ni	Ni +/-	Cu	Cu +/-	Zn	Zn +/-	As	As +/-	Se	Se +/-	Rb	Rb +/-	Sr	Sr +/-	Zr	Zr +/-
NIST 2711a	68	3	46	3	510	8	23872	132	<LOD	72	<LOD	12	100	5	348	5	94	6	2.8	0.8	111.8	1.5	249	4	309	4
	31	2	9	2	646	9	14380	82	<LOD	52	<LOD	10	<LOD	7	52	2	4.4	0.9	<LOD	1.3	44	0.9	90	2	158	3
Location 1 120cm	29.4	2	13	2	653	9	14816	80	<LOD	51	<LOD	10	<LOD	7	57	2	4.1	0.9	<LOD	1.2	44	0.9	92	2	170	3
Location 1 50 cm	26.7	1.3	6	1.5	189	4	6768	44	<LOD	34	<LOD	10	<LOD	7	46.8	1.8	5	0.8	<LOD	1.2	38.7	0.8	66.3	1.5	203	2
Location 1 120cm	28.7	1.5	<LOD	4.9	79	3	5368	37	<LOD	30	<LOD	9	<LOD	6	36.8	1.7	5.2	0.8	<LOD	1.1	46	0.8	122	2	208	3
Location 2 surface	34	2	22	2	648	8	16994	85	<LOD	51	<LOD	9	<LOD	7	124	3	13.7	1.2	<LOD	1.2	38.6	0.8	54.2	1.5	90.3	1.6
Location 2 20 cm	51	2	37	3	1022	10	23511	122	<LOD	67	34	4	<LOD	8	161	3	15.3	1.2	<LOD	1.4	49.8	0.9	67.8	1.5	126.1	1.8
location 2 40 cm	47	3	36	3	584	8	18667	97	<LOD	57	39	4	<LOD	7	47.9	1.9	5.4	0.9	<LOD	1.3	39.5	0.8	52.3	1.4	139.3	1.9
Location 2a surface	32	2	26	3	590	8	19606	106	<LOD	61	34	4	15	3	91	3	5.2	1.1	<LOD	1.3	50.2	1	94.8	1.9	97.8	1.7
Location 2b surface	30	2	19	2	1156	12	14391	76	<LOD	48	<LOD	9	<LOD	7	123	3	9.1	1.1	<LOD	1.2	47.8	0.9	53	1.5	99.6	1.8
Location 2b 40 cm	39	2	27	3	408	7	18199	90	<LOD	53	12	3	<LOD	7	66	2	6.8	0.8	<LOD	1.2	51.1	0.9	52.9	1.4	155	2
Location 3 surface	29	2	26	2	466	7	20837	102	<LOD	57	<LOD	10	14	2	140	3	18.4	1.3	<LOD	1.3	38.1	0.8	41.3	1.3	127.5	2
Location 3 40 cm	28.5	1.9	29	2	438	6	18305	99	<LOD	59	41	4	21	3	164	3	31	2	<LOD	1.4	49.3	0.9	55.3	1.4	104.9	1.6
Location 3 70 cm	28.4	1.8	23	2	328	5	16778	90	<LOD	55	18	4	17	3	135	3	16.6	1.5	<LOD	1.3	47.7	0.9	56.9	1.4	123.9	1.9
Location 4 surface	35	3	30	3	204	6	27349	135	<LOD	69	<LOD	10	<LOD	7	45.9	1.9	6.4	1	<LOD	1.2	52.9	0.9	43.3	1.4	96.7	1.8
location 5 surface	25.1	1.7	8.4	1.9	531	7	17697	90	<LOD	54	<LOD	10	11	2	47.8	1.9	3	0.8	<LOD	1.1	31.8	0.7	130	2	71	1.5
Location 5b surface	26	1.9	20	2	459	6	18284	95	<LOD	56	13	3	<LOD	7	68	2	5.3	1	<LOD	1.2	43.7	0.9	112	2	87.7	1.6
Location - no sample	35	3	24	3	190	6	21998	122	<LOD	68	<LOD	11	<LOD	8	46	2	4.3	1	<LOD	1.4	49.6	1	51.3	1.6	96.9	2
Location 6 surface	26.8	1.8	10	2	168	4	10932	57	<LOD	39	<LOD	8	<LOD	6	59	1.8	7.7	1	<LOD	1.1	30	0.7	34.1	1.2	77.8	1.5
Location 6 40 cm	27.3	1.9	18	2	55	3	12553	70	<LOD	47	<LOD	10	<LOD	7	31.2	1.6	4.8	0.8	<LOD	1.2	44.2	0.9	47.7	1.3	119.1	1.8
Location 7 surface	17.8	1.6	<LOD	6	756	9	8775	52	<LOD	38	<LOD	9	7	2	54.8	1.9	4.9	0.8	<LOD	1.1	30.9	0.7	43.7	1.5	60.4	1.6
Location 7 15 cm	36.2	1.9	30	2	111	4	14733	79	<LOD	50	16	3	<LOD	7	37.8	1.7	5.5	0.8	<LOD	1.2	57	0.9	40.4	1.2	117.8	1.8
location 8 surface	31	2	22	3	779	10	16586	85	<LOD	51	<LOD	9	<LOD	7	84	2	6.3	1	<LOD	1.1	34.8	0.8	65.1	1.6	76.9	1.6
location 8 40 cm	31	2	35	3	1777	16	24107	120	<LOD	64	<LOD	10	<LOD	7	109	3	6	1	<LOD	1.2	35.1	0.8	65.5	1.5	69.6	1.4

Locations	Nb	Nb +/-	Mo	Mo +/-	Ag	Ag +/-	Cd	Cd +/-	Sn	Sn +/-	Sb	Sb +/-	Ta	Ta +/-	W	W +/-	Au	Au +/-	Hg	Hg +/-	Pb	Pb +/-	Bi	Bi +/-	Th	Th +/-	U	U +/-
NIST 2711a	15.8	1.1	<LOD	3.6	7.3	1.2	47.5	1.7	11	3	28	3	11.3	1.5	<LOD	19	<LOD	9	8.3	1.5	1327	10	<LOD	18	17.1	1.9	<LOD	7
	12	1	<LOD	3	<LOD	3.7	<LOD	4.5	<LOD	9	<LOD	9	9.1	0.9	<LOD	10	<LOD	4.6	<LOD	2.6	14.3	1.3	<LOD	15	6	1.5	<LOD	6
Location 1 120cm	11.8	0.9	<LOD	2.6	<LOD	3.2	<LOD	3.8	<LOD	8	<LOD	8	9.4	0.8	<LOD	10	<LOD	4.7	2.8	0.9	13	1.2	<LOD	14	4.4	1.3	<LOD	5.3
Location 1 50 cm	11.8	0.9	<LOD	2.2	<LOD	2.5	<LOD	3.1	<LOD	7	<LOD	7	9.8	0.8	<LOD	10	<LOD	4.6	<LOD	2.5	12.6	1.2	<LOD	14	8.2	1.1	<LOD	4.1
Location 1 120cm	5.1	0.8	<LOD	2.6	<LOD	2.9	<LOD	3.7	<LOD	8	<LOD	8	7.3	0.8	<LOD	9	<LOD	4.4	<LOD	2.3	11.4	1.1	<LOD	14	9.8	1.4	7.1	1.8
Location 2 surface	5.5	0.8	<LOD	1.9	<LOD	2.8	<LOD	3.4	<LOD	7	<LOD	7	6.5	0.8	<LOD	11	<LOD	4.5	<LOD	2.5	48.4	1.6	<LOD	13	4.7	1.1	<LOD	4.5
Location 2 20 cm	5.1	0.9	<LOD	1.9	3.1	0.8	<LOD	2.9	11	2	<LOD	6	9.4	1	<LOD	13	<LOD	5.2	<LOD	2.9	37.6	1.6	<LOD	14	7.1	1	<LOD	4.1
location 2 40 cm	<LOD	2.5	<LOD	2	<LOD	2.4	<LOD	3	10	2	<LOD	7	6.9	0.8	<LOD	11	<LOD	5.1	<LOD	2.6	11	1.2	41	4	5	1	<LOD	4.3
Location 2a surface	<LOD	2.7	<LOD	2	3.3	0.9	<LOD	3.2	11	2	<LOD	7	6.4	0.9	<LOD	12	<LOD	5.1	<LOD	2.8	34	1.6	31	5	5.6	1.1	<LOD	4.8
Location 2b surface	7.2	0.9	<LOD	2	<LOD	2.9	<LOD	3.5	<LOD	8	<LOD	7	7.2	0.8	<LOD	11	<LOD	4.6	<LOD	2.6	36.5	1.5	<LOD	14	4.7	1.1	<LOD	4.6
Location 2b 40 cm	4.8	0.8	<LOD	2.2	<LOD	2.6	<LOD	3.3	<LOD	7	<LOD	7	10.3	0.8	<LOD	10	<LOD	4.5	<LOD	2.5	9.2	1.1	<LOD	13	8.6	1.2	<LOD	4.6
Location 3 surface	8.3	0.9	<LOD	2.1	4.6	1	<LOD	3.5	<LOD	7	7	2	6	0.8	<LOD	11	<LOD	4.7	<LOD	2.5	59.7	1.7	<LOD	14	5.1	1.1	<LOD	4.5
Location 3 40 cm	<LOD	2.6	<LOD	1.9	10.6	0.9	<LOD	3	12	2	9	2	5	0.9	<LOD	13	<LOD	5.5	<LOD	3	186	3	24	5	6	1	<LOD	4.3
Location 3 70 cm	3.1	0.9	<LOD	2	6.4	0.9	<LOD	3.2	<LOD	7	9	2	5.5	0.9	<LOD	12	<LOD	5.1	<LOD	2.9	80	2	20	5	7	1.1	<LOD	4.5
Location 4 surface	6.4	0.9	<LOD	2.1	<LOD	2.9	<LOD	3.5	<LOD	8	<LOD	8	7.8	0.8	<LOD	10	<LOD	4.9	<LOD	2.5	17.5	1.3	<LOD	14	3.4	1.1	<LOD	5
location 5 surface	<LOD	2.5	<LOD	1.8	<LOD	2.8	<LOD	3.4	<LOD	7	<LOD	7	3.8	0.7	<LOD	10	<LOD	4.4	<LOD	2.4	9.4	1.1	<LOD	13	<LOD	3.2	<LOD	4.9
Location 5b surface	2.6	0.9	<LOD	1.9	<LOD	2.7	<LOD	3.4	<LOD	7	<LOD	7	6.5	0.8	<LOD	10	<LOD	4.7	<LOD	2.5	27.8	1.4	<LOD	14	4.9	1.1	<LOD	4.7
Location - no sample	7.4	1	<LOD	2.2	<LOD	3.2	<LOD	3.9	<LOD	8	<LOD	8	7.6	0.9	<LOD	11	<LOD	5.2	<LOD	2.9	18.9	1.5	<LOD	16	7.8	1.3	<LOD	5.3
Location 6 surface	4.8	0.8	<LOD	1.8	<LOD	2.8	<LOD	3.5	<LOD	7	<LOD	7	6.3	0.7	<LOD	9	<LOD	4.1	<LOD	2.2	38.4	1.4	<LOD	13	5.7	1	<LOD	4.2
Location 6 40 cm	3.5	0.9	2.1	0.7	<LOD	2.7	<LOD	3.3	<LOD	7	<LOD	7	7.3	0.8	<LOD	10	<LOD	4.6	<LOD	2.4	11.1	1.2	<LOD	14	6.1	1.1	<LOD	4.1
Location 7 surface	6.6	0.9	<LOD	2	<LOD	3.5	<LOD	4.2	<LOD	9	<LOD	9	2.9	0.6	<LOD	9	<LOD	4.1	<LOD	2.2	12.4	1.2	<LOD	14	4.3	1.2	<LOD	4.9
Location 7 15 cm	4.6	0.9	<LOD	2	<LOD	2.6	<LOD	3.3	<LOD	7	<LOD	7	9.1	0.8	<LOD	10	<LOD	4.7	<LOD	2.5	10.8	1.2	<LOD	14	6.2	1	<LOD	4.3
location 8 surface	3.8	0.8	<LOD	1.9	<LOD	2.8	<LOD	3.4	<LOD	7	<LOD	7	5.8	0.8	<LOD	10	<LOD	4.4	<LOD	2.4	32.4	1.4	<LOD	13	6.4	1.1	<LOD	4.4
location 8 40 cm	<LOD	2.6	<LOD	1.7	<LOD	2.5	<LOD	3.2	<LOD	7	<LOD	7	4.7	0.8	<LOD	11	<LOD	4.7	<LOD	2.6	27.9	1.4	<LOD	14	6.2	1	<LOD	4.1

Date	Sample	Nd	Nd +/-	Pr	Pr +/-	Ce	Ce +/-	La	La +/-	Ba	Ba +/-	Y	Y +/-	P	P +/-	S	S +/-	Cl	Cl +/-	K	K +/-	Ca	Ca +/-	Ti	Ti +/-	V	V +/-
24/10/2018	NIST 2711a	<LOD	250	<LOD	137	<LOD	79	<LOD	62	684	15	53	3	<LOD	4592	449	78	269	74	19374	223	19579	198	2447	34	70	3
24/10/2018	NIST 2710a	<LOD	275	<LOD	150	<LOD	86	<LOD	66	807	17	77	4	<LOD	4901	4868	181	772	102	19079	244	7197	111	2813	42	84	4
24/10/2018	location 22a surface	<LOD	279	<LOD	154	<LOD	90	<LOD	71	228	16	22	2	<LOD	2948	<LOD	158	<LOD	166	5168	92	3619	62	1523	24	31	2
24/10/2018	location 22a surface_PL	<LOD	231	<LOD	127	<LOD	74	<LOD	58	230	13	14.3	1.4	<LOD	2188	<LOD	122	179	50	3205	68	2300	47	1095	19	24	1.8
24/10/2018	location 19 20cm	<LOD	297	<LOD	163	<LOD	96	<LOD	75	496	18	57	3	<LOD	2359	<LOD	132	249	54	6146	96	2288	49	1516	23	39	2
24/10/2018	location 18 20cm	<LOD	324	<LOD	176	<LOD	103	<LOD	82	422	19	36	3	<LOD	3361	<LOD	156	204	60	6803	109	7369	94	2021	29	32	2
24/10/2018	location 21 surface	<LOD	330	<LOD	181	<LOD	106	<LOD	84	279	19	38	3	<LOD	3959	264	68	<LOD	198	6135	108	9627	115	2277	32	40	3
24/10/2018	location 18 surface	<LOD	331	<LOD	181	<LOD	106	<LOD	83	365	19	40	3	<LOD	3962	546	74	196	65	5540	102	11534	131	1845	28	45	3
24/10/2018	location 12 surface	<LOD	278	<LOD	153	<LOD	89	<LOD	71	226	16	24	2	<LOD	2813	<LOD	160	211	59	5167	91	3234	58	2297	30	34	2
24/10/2018	location 11 surface	<LOD	285	<LOD	157	<LOD	93	<LOD	73	144	16	17.9	1.8	<LOD	2510	<LOD	134	<LOD	136	2475	58	4526	62	1182	19	20.9	1.7
24/10/2018	location 20 surface	<LOD	365	<LOD	199	<LOD	116	<LOD	92	338	21	44	3	<LOD	3852	267	65	<LOD	196	6182	106	8670	106	2641	35	42	3
24/10/2018	location 15 surface	<LOD	341	<LOD	186	<LOD	110	<LOD	86	257	19	33	3	<LOD	3037	<LOD	165	<LOD	169	5384	95	3352	60	1917	28	36	2
24/10/2018	location 11 40 cm	<LOD	264	<LOD	144	<LOD	85	<LOD	67	236	15	22.6	2	<LOD	2270	<LOD	124	<LOD	158	4478	81	652	33	2520	31	31	2
24/10/2018	location 19 40 cm	<LOD	311	<LOD	170	<LOD	100	<LOD	79	493	19	60	3	<LOD	2443	<LOD	133	176	53	5580	93	1656	44	1525	23	40	2
24/10/2018	location 19 surface	<LOD	321	<LOD	176	<LOD	103	<LOD	81	476	19	62	3	<LOD	3007	<LOD	146	527	66	7691	115	4608	71	1552	24	43	2
24/10/2018	location 14 30 cm	<LOD	274	<LOD	149	<LOD	87	<LOD	69	233	15	18.5	1.8	<LOD	3876	<LOD	203	<LOD	240	5441	123	1928	60	1778	34	39	3
24/10/2018	location 12 50 cm	<LOD	284	<LOD	156	<LOD	92	<LOD	72	227	16	26	2	<LOD	2483	<LOD	150	<LOD	176	3628	81	675	36	2213	31	40	3
24/10/2018	location 12 20 cm	<LOD	291	<LOD	158	<LOD	93	<LOD	73	238	16	24.2	2	<LOD	3317	<LOD	178	<LOD	222	2944	86	1792	53	3566	47	45	3
24/10/2018	location 13a surface	<LOD	285	<LOD	157	<LOD	91	<LOD	72	256	16	38	2	<LOD	3235	281	60	<LOD	176	3710	79	5562	78	2107	29	44	3
24/10/2018	location 20 40 cm	<LOD	277	<LOD	151	<LOD	89	<LOD	71	246	16	31	2	<LOD	2887	<LOD	152	<LOD	173	5741	97	2717	54	2173	29	36	2
24/10/2018	location 14 surface	<LOD	232	<LOD	127	<LOD	75	<LOD	59	160	13	20.6	1.5	<LOD	2082	<LOD	122	201	47	2734	59	933	32	1347	20	20.2	1.7
24/10/2018	location 11 20 cm	<LOD	275	<LOD	151	<LOD	89	<LOD	70	167	15	15.6	1.7	<LOD	3105	184	55	<LOD	168	3189	74	3968	65	1644	25	25	2
24/10/2018	location 13 surface	<LOD	207	<LOD	114	<LOD	67	<LOD	53	141	11	20.9	1.2	<LOD	2207	<LOD	118	182	48	1652	49	2332	44	1866	24	33	2
24/10/2018	location 13b surface	<LOD	309	<LOD	170	<LOD	99	<LOD	78	331	18	31	2	<LOD	4772	<LOD	226	<LOD	234	6246	116	17267	186	5110	58	62	4
24/10/2018	location 19 60 cm	<LOD	303	<LOD	164	<LOD	98	<LOD	77	477	18	81	3	<LOD	2230	<LOD	114	212	52	4666	83	1213	38	1528	23	47	2
24/10/2018	location 20 20 cm	<LOD	276	<LOD	152	<LOD	89	<LOD	70	279	16	38	2	<LOD	3003	184	56	<LOD	176	5643	97	4022	65	2271	30	41	3
24/10/2018	location 16 30 cm	<LOD	283	<LOD	155	<LOD	91	<LOD	73	184	16	30	2	<LOD	2835	<LOD	160	<LOD	181	5270	96	540	36	2590	34	43	3
24/10/2018	location 16 surface	<LOD	294	<LOD	161	<LOD	95	<LOD	75	188	16	25	2	<LOD	3212	247	60	<LOD	181	5377	95	2183	50	2481	32	40	3
24/10/2018	location 15 30 cm	<LOD	300	<LOD	165	<LOD	96	<LOD	76	308	17	30	2	<LOD	3026	<LOD	163	<LOD	179	5576	103	1536	47	1650	27	25	2
24/10/2018	location 14 50 cm	<LOD	264	<LOD	145	<LOD	85	<LOD	66	268	15	21.9	1.9	<LOD	2767	<LOD	145	<LOD	170	6417	109	1554	47	1259	23	26	2
24/10/2018	location 17a 5-7cm	<LOD	293	<LOD	161	<LOD	94	<LOD	74	270	16	29	2	<LOD	3689	<LOD	187	<LOD	193	4130	89	7193	95	2306	33	45	3
24/10/2018	location 17 surface	<LOD	334	<LOD	182	<LOD	107	<LOD	84	260	19	29	2	<LOD	4174	616	78	<LOD	196	4166	88	17984	180	1938	29	39	3
24/10/2018	location 18 40 cm	<LOD	308	<LOD	168	<LOD	98	<LOD	77	432	18	39	3	<LOD	4222	<LOD	198	354	77	6892	122	13364	154	2540	36	45	3
24/10/2018	NIST 2710a	<LOD	278	<LOD	151	93	29	<LOD	67	802	17	86	5	<LOD	5169	4727	181	612	101	19222	248	7401	114	2898	43	81	4

Date	Sample	Cr	Cr +/-	Mn	Mn +/-	Fe	Fe +/-	Co	Co +/-	Ni	Ni +/-	Cu	Cu +/-	Zn	Zn +/-	As	As +/-	Se	Se +/-	Rb	Rb +/-	Sr	Sr +/-	Zr	Zr +/-
24/10/2018	NIST 2711a	53	3	515	8	25117	138	<LOD	73	21	4	93	5	370	5	99	6	<LOD	2.2	116.6	1.5	246	4	314	4
24/10/2018	NIST 2710a	50	4	1853	21	48594	275	<LOD	113	<LOD	16	3299	26	4166	28	1503	16	<LOD	4.3	111.7	1.7	273	4	220	4
24/10/2018	location 22a surface	25	3	635	9	25071	128	<LOD	68	<LOD	10	9	3	184	3	39.5	1.9	<LOD	1.4	63.3	1	98	3	143	3
24/10/2018	location 22a surface_PL	15	2	445	7	16508	84	<LOD	52	<LOD	9	14	2	132	3	22	1.6	<LOD	1.2	48.4	0.9	60.9	1.7	86	1.8
24/10/2018	location 19 20cm	19	2	343	6	19106	102	<LOD	59	<LOD	11	<LOD	7	90	3	8.7	1	<LOD	1.4	63.3	1	162	4	403	6
24/10/2018	location 18 20cm	21	3	428	7	22557	125	<LOD	68	<LOD	11	<LOD	8	74	2	8.1	1.3	<LOD	1.5	60.5	1.1	360	6	318	5
24/10/2018	location 21 surface	37	3	1023	13	38424	205	<LOD	92	<LOD	12	29	3	194	4	19.1	1.6	<LOD	1.5	70.5	1.2	203	5	185	4
24/10/2018	location 18 surface	28	3	716	10	32148	177	<LOD	85	<LOD	12	<LOD	9	147	3	7.3	1.3	<LOD	1.5	52.9	1.1	276	6	231	5
24/10/2018	location 12 surface	27	3	417	7	26411	133	<LOD	69	<LOD	10	<LOD	7	71	2	9.4	1.3	<LOD	1.3	67.9	1.1	117	3	175	3
24/10/2018	location 11 surface	10	2	838	9	18074	94	<LOD	55	<LOD	9	<LOD	7	86	2	5.1	0.9	<LOD	1.1	31.7	0.8	110	3	85	2
24/10/2018	location 20 surface	39	3	645	9	40098	220	<LOD	97	<LOD	12	<LOD	10	151	4	8.2	1.2	<LOD	1.6	81.9	1.3	260	6	315	6
24/10/2018	location 15 surface	34	3	669	9	31068	166	<LOD	81	<LOD	11	9	3	152	3	29	1.8	<LOD	1.5	66.7	1.2	123	4	207	4
24/10/2018	location 11 40 cm	16	2	164	5	18062	94	<LOD	55	<LOD	9	<LOD	7	41.1	1.8	<LOD	2.8	<LOD	1.2	67.2	1	82	2	163	3
24/10/2018	location 19 40 cm	16	2	271	6	18524	102	<LOD	60	<LOD	10	<LOD	8	100	3	11.2	1.1	<LOD	1.4	60.9	1.1	138	4	482	7
24/10/2018	location 19 surface	22	3	228	5	23257	127	<LOD	69	<LOD	11	<LOD	8	76	2	8.5	1.1	<LOD	1.4	70.2	1.2	248	5	327	5
24/10/2018	location 14 30 cm	37	4	670	12	34044	189	<LOD	92	<LOD	13	13	3	87	3	24.3	1.9	<LOD	1.5	47.7	1.1	82	2	134	3
24/10/2018	location 12 50 cm	19	3	212	6	28441	144	<LOD	73	<LOD	10	<LOD	7	51	2	7.4	1	<LOD	1.3	58.5	1	84	3	183	3
24/10/2018	location 12 20 cm	26	3	436	8	42166	217	<LOD	95	<LOD	12	<LOD	8	57	2	7.1	1	<LOD	1.4	43.4	1	96	3	270	4
24/10/2018	location 13a surface	41	3	524	8	29762	150	<LOD	75	<LOD	11	17	3	135	3	6	1.2	<LOD	1.4	44.3	0.9	122	3	174	3
24/10/2018	location 20 40 cm	29	3	258	6	26061	130	<LOD	68	<LOD	10	<LOD	7	66	2	10.7	1.1	<LOD	1.3	69	1.1	116	3	237	4
24/10/2018	location 14 surface	14	2	528	7	17871	85	<LOD	51	<LOD	9	<LOD	6	82	2	7.7	0.9	<LOD	1	38.5	0.7	59.1	1.8	114	2
24/10/2018	location 11 20 cm	18	3	659	9	25063	127	<LOD	67	<LOD	10	<LOD	7	66	2	7.6	1	<LOD	1.2	42.8	0.9	100	3	130	3
24/10/2018	location 13 surface	36	2	427	6	17970	82	<LOD	49	<LOD	8	<LOD	5.9	53.1	1.7	2.8	0.7	<LOD	1.1	18.8	0.6	44.8	1.4	104.9	1.8
24/10/2018	location 13b surface	38	4	961	13	42750	226	<LOD	97	<LOD	12	<LOD	9	112	3	6.4	1.1	<LOD	1.5	54.7	1.1	376	6	172	4
24/10/2018	location 19 60 cm	15	2	253	5	17435	99	<LOD	59	<LOD	11	<LOD	8	74	2	11.2	1.1	<LOD	1.4	53.9	1	123	3	456	6
24/10/2018	location 20 20 cm	31	3	389	7	27695	138	<LOD	71	<LOD	10	<LOD	8	84	2	7.8	1	<LOD	1.3	69.7	1.1	135	3	215	4
24/10/2018	location 16 30 cm	32	3	197	5	33504	162	<LOD	78	<LOD	10	<LOD	7	63	2	11.1	1.1	<LOD	1.3	68.7	1.1	83	3	195	3
24/10/2018	location 16 surface	30	3	405	7	33103	167	<LOD	79	<LOD	10	<LOD	8	123	3	11.5	1.1	<LOD	1.4	74.1	1.2	96	3	179	3
24/10/2018	location 15 30 cm	31	3	849	11	29372	154	<LOD	76	<LOD	11	12	3	129	3	33.6	2	<LOD	1.5	58.4	1.1	94	3	172	3
24/10/2018	location 14 50 cm	18	3	661	10	16896	93	<LOD	56	<LOD	10	16	3	93	3	28.9	1.9	<LOD	1.3	54.3	1	98	3	128	3
24/10/2018	location 17a 5-7cm	36	3	874	11	37762	193	<LOD	87	<LOD	11	<LOD	9	71	2	57.1	1.6	<LOD	1.3	55	1	187	4	183	4
24/10/2018	location 17 surface	24	3	922	12	35769	194	<LOD	89	<LOD	12	<LOD	9	83	3	25.1	1.2	<LOD	1.4	45.1	1	274	6	135	4
24/10/2018	location 18 40 cm	25	3	838	12	35070	194	<LOD	91	<LOD	13	<LOD	10	85	3	17	2	<LOD	1.5	61.7	1.2	325	6	236	4
24/10/2018	NIST 2710a	56	4	1888	22	48810	274	<LOD	113	<LOD	15	3329	26	4095	28	1500	16	<LOD	4.2	113.2	1.7	280	4	225	4

Date	Sample	Nb	Nb +/-	Mo	Mo +/-	Ag	Ag +/-	Cd	Cd +/-	Sn	Sn +/-	Sb	Sb +/-	Ta	Ta +/-	W	W +/-	Au	Au +/-	Hg	Hg +/-	Pb	Pb +/-	Bi	Bi +/-	Th	Th +/-	U	U +/-
24/10/2018	NIST 2711a	18	1.1	<LOD	3.6	7.7	1.2	52	1.7	12	3	29	3	15.4	1.6	<LOD	19	<LOD	8	7.2	1.5	1404	10	<LOD	19	15.7	1.9	<LOD	7
24/10/2018	NIST 2710a	7	1.2	5.9	1.3	39.1	1.5	12.2	1.5	25	3	45	3	28	4	126	19	<LOD	20	15	4	5410	33	62	8	17	2	14	3
24/10/2018	location 22a surface	14	1	<LOD	3.1	8.2	1.5	<LOD	5.3	<LOD	11	11	4	9.1	1	<LOD	13	<LOD	5.1	<LOD	2.9	121	2	<LOD	16	7.2	1.7	<LOD	7
24/10/2018	location 22a surface_PL	7.6	0.9	<LOD	2.1	8.5	1.2	<LOD	4	<LOD	8	10	3	5.8	0.8	<LOD	11	<LOD	4.6	<LOD	2.6	97	2	<LOD	14	<LOD	3.3	<LOD	5.2
24/10/2018	location 19 20cm	28.1	1	<LOD	4.8	<LOD	4.7	<LOD	5.8	<LOD	11	<LOD	11	14.1	1	<LOD	11	<LOD	4.8	<LOD	2.8	20.5	1.4	<LOD	16	19	2	<LOD	9
24/10/2018	location 18 20cm	20.9	1.1	<LOD	4.7	<LOD	5.2	<LOD	6	<LOD	13	<LOD	12	13.9	1	<LOD	12	<LOD	5.3	<LOD	3	41.8	1.8	<LOD	17	14	3	<LOD	10
24/10/2018	location 21 surface	18.5	1.1	<LOD	4	<LOD	5.2	<LOD	6	<LOD	13	<LOD	13	12.9	1.1	<LOD	14	<LOD	5.6	<LOD	3.3	65	2	<LOD	18	13	2	<LOD	10
24/10/2018	location 18 surface	21.1	1.1	<LOD	4.5	<LOD	5.2	<LOD	6	<LOD	13	<LOD	13	12.6	1.1	<LOD	14	<LOD	5.8	<LOD	3.1	35.2	1.8	<LOD	18	11	2	10	3
24/10/2018	location 12 surface	16.8	1	<LOD	3.3	<LOD	4.3	<LOD	5.3	<LOD	11	<LOD	11	11.4	0.9	<LOD	11	<LOD	4.8	<LOD	2.7	51.3	1.8	<LOD	16	10.9	1.8	<LOD	8
24/10/2018	location 11 surface	16.5	0.9	<LOD	2.8	<LOD	4.6	<LOD	5.8	<LOD	11	<LOD	11	6.4	0.7	<LOD	10	<LOD	4.4	<LOD	2.4	15.1	1.3	<LOD	15	5	1.6	<LOD	7
24/10/2018	location 20 surface	23.8	1.2	<LOD	5.4	<LOD	6	<LOD	7	<LOD	14	<LOD	14	17.4	1.2	<LOD	14	<LOD	5.5	<LOD	3.3	24.9	1.8	<LOD	19	14	3	15	4
24/10/2018	location 15 surface	23.3	1.1	<LOD	4.2	8.1	2	<LOD	7	<LOD	13	<LOD	13	12.8	1.1	<LOD	13	<LOD	5.7	<LOD	3.1	89	2	<LOD	18	8	2	<LOD	9
24/10/2018	location 11 40 cm	15	0.9	<LOD	3.1	<LOD	4.1	<LOD	5	<LOD	10	<LOD	10	11.8	0.9	<LOD	10	<LOD	4.6	<LOD	2.5	22.9	1.4	<LOD	15	8.1	1.6	<LOD	7
24/10/2018	location 19 40 cm	31.1	1.1	<LOD	5.3	<LOD	4.9	<LOD	6	<LOD	12	<LOD	12	15.5	1	<LOD	12	<LOD	5.1	<LOD	2.9	21.3	1.5	<LOD	17	21	3	<LOD	9
24/10/2018	location 19 surface	22.3	1.1	<LOD	4.9	<LOD	5.1	<LOD	6	<LOD	13	<LOD	12	15.3	1	<LOD	12	<LOD	5.1	<LOD	2.9	26.9	1.6	<LOD	17	19	3	11	3
24/10/2018	location 14 30 cm	3.2	1	<LOD	3	4	1.3	<LOD	4.6	<LOD	10	<LOD	10	4.2	0.9	<LOD	13	<LOD	5.9	<LOD	3.2	93	3	<LOD	17	8.6	1.6	<LOD	7
24/10/2018	location 12 50 cm	14.2	1	<LOD	3.4	<LOD	4.4	<LOD	5.4	<LOD	11	<LOD	11	10.3	0.9	<LOD	10	<LOD	4.7	<LOD	2.6	18.8	1.4	<LOD	16	10.6	1.8	<LOD	7
24/10/2018	location 12 20 cm	11.7	1	<LOD	3.9	<LOD	4.3	<LOD	5.2	<LOD	11	<LOD	11	12.2	1	<LOD	11	<LOD	5	<LOD	2.9	13	1.4	<LOD	16	9.5	1.9	<LOD	7
24/10/2018	location 13a surface	16.4	1	<LOD	3.4	<LOD	4.4	<LOD	5.5	19	4	<LOD	11	10.1	0.9	<LOD	11	<LOD	5	<LOD	2.8	39.2	1.7	<LOD	16	11.3	1.9	<LOD	7
24/10/2018	location 20 40 cm	17.1	1	<LOD	3.7	<LOD	4.2	<LOD	5.3	<LOD	11	<LOD	11	13.6	0.9	<LOD	11	<LOD	4.8	<LOD	2.6	25.8	1.5	<LOD	16	13.6	1.9	<LOD	7
24/10/2018	location 14 surface	10.9	0.8	<LOD	2.4	<LOD	3.5	<LOD	4.3	<LOD	9	<LOD	9	6.4	0.7	<LOD	9	<LOD	4.2	<LOD	2.2	20.2	1.2	<LOD	13	6.3	1.3	<LOD	5.3
24/10/2018	location 11 20 cm	12.6	0.9	<LOD	3	<LOD	4.2	<LOD	5.2	<LOD	11	<LOD	10	7.6	0.8	<LOD	10	<LOD	4.5	<LOD	2.5	17.2	1.4	<LOD	15	5.7	1.6	8	2
24/10/2018	location 13 surface	7	0.8	<LOD	2	<LOD	3	<LOD	3.8	<LOD	8	<LOD	8	6.6	0.7	<LOD	8	<LOD	4	<LOD	2.1	15.3	1.1	<LOD	13	3.5	1	<LOD	4.5
24/10/2018	location 13b surface	13.8	1.1	<LOD	3.8	<LOD	4.6	<LOD	5.7	<LOD	12	<LOD	11	11.6	1	<LOD	13	<LOD	5.5	<LOD	3.2	18.7	1.6	<LOD	18	7	2	10	3
24/10/2018	location 19 60 cm	29.5	1.1	<LOD	4.9	<LOD	4.6	<LOD	5.9	<LOD	12	<LOD	12	18.5	1.1	<LOD	12	<LOD	5.1	<LOD	2.9	21.3	1.5	<LOD	17	23	3	<LOD	8
24/10/2018	location 20 20 cm	16.2	1	<LOD	3.6	<LOD	4.2	<LOD	5.2	<LOD	11	<LOD	11	11.9	0.9	<LOD	11	<LOD	4.8	<LOD	2.7	24.3	1.5	<LOD	16	15	2	<LOD	7
24/10/2018	location 16 30 cm	15.7	1	<LOD	3.5	<LOD	4.4	<LOD	5.4	<LOD	11	<LOD	11	12	0.9	<LOD	11	<LOD	4.8	<LOD	2.7	26.4	1.5	<LOD	15	11.3	1.8	<LOD	8
24/10/2018	location 16 surface	16.5	1	<LOD	3.5	<LOD	4.5	<LOD	5.6	<LOD	11	<LOD	11	15	1	<LOD	12	<LOD	5.2	<LOD	2.9	27.4	1.6	<LOD	16	12.1	1.9	<LOD	8
24/10/2018	location 15 30 cm	13	1	<LOD	3.5	11.2	1.7	<LOD	5.8	<LOD	12	<LOD	12	8.6	1	<LOD	13	<LOD	5.6	<LOD	3	118	3	<LOD	16	10.1	1.9	<LOD	8
24/10/2018	location 14 50 cm	5.9	0.9	<LOD	2.9	5.8	1.3	<LOD	4.7	<LOD	10	<LOD	10	6.2	0.9	<LOD	12	<LOD	5.2	<LOD	2.8	136	3	<LOD	15	8.6	1.6	<LOD	7
24/10/2018	location 17a 5-7cm	15.1	1	<LOD	3.6	<LOD	4.5	<LOD	5.4	<LOD	11	<LOD	11	13.3	1	<LOD	12	<LOD	5.5	<LOD	3	23.2	1.6	<LOD	17	13	2	<LOD	8
24/10/2018	location 17 surface	17	1.1	<LOD	3.8	<LOD	5.3	<LOD	6	<LOD	13	<LOD	13	12.3	1	<LOD	12	<LOD	5.6	<LOD	3	12.7	1.5	<LOD	18	<LOD	6	<LOD	9
24/10/2018	location 18 40 cm	14.5	1.1	<LOD	4.1	<LOD	4.6	<LOD	5.5	<LOD	11	<LOD	11	16.1	1.2	<LOD	13	<LOD	6	3.8	1.1	148	3	<LOD	18	8	2	<LOD	9
24/10/2018	NIST 2710a	7.3	1.2	6.4	1.3	41	1.6	13.4	1.5	22	3	48	3	27	4	189	19	<LOD	19	<LOD	11	5395	32	68	8	18	2	14	3

Date	locations	Nd	Nd +/-	Pr	Pr +/-	Ce	Ce +/-	La	La +/-	Ba	Ba +/-	Y	Y +/-	P	P +/-	S	S +/-	Cl	Cl +/-	K	K +/-	Ca	Ca +/-
15/11/2018																							
15/11/2018	location 32 10cm	<LOD	244	<LOD	134	<LOD	79	<LOD	62	194	14	27.2	1.7	<LOD	2571	238	58	<LOD	165	2863	72	980	38
15/11/2018	location 24 50cm	<LOD	297	<LOD	163	<LOD	96	<LOD	75	471	18	43	3	<LOD	2626	<LOD	129	234	55	5480	93	3041	56
15/11/2018	location 31 surface	<LOD	298	<LOD	164	<LOD	96	<LOD	76	313	17	44	3	<LOD	2468	<LOD	141	293	58	5637	95	1766	46
15/11/2018	location 31 40cm	<LOD	277	<LOD	152	<LOD	89	<LOD	70	328	16	51	2	<LOD	2875	<LOD	149	<LOD	172	5329	94	1602	45
15/11/2018	location 22a 30cm	<LOD	289	<LOD	159	<LOD	92	<LOD	73	560	17	20	2	<LOD	2946	<LOD	158	<LOD	192	7075	121	1813	52
15/11/2018	location 25 surface	<LOD	303	<LOD	167	<LOD	98	<LOD	78	258	17	38	2	<LOD	2570	<LOD	147	<LOD	163	4727	90	1695	46
15/11/2018	location 30 40 cm	<LOD	197	<LOD	107	<LOD	63	<LOD	49	324	11	14.5	1.1	<LOD	2269	<LOD	124	155	47	4925	78	2260	44
15/11/2018	location 25 50 cm	<LOD	211	<LOD	115	69	22	<LOD	53	417	12	33.8	1.6	<LOD	2486	<LOD	124	178	52	8007	111	1084	39
15/11/2018	location 31 25 cm	<LOD	315	<LOD	172	<LOD	101	<LOD	80	395	18	63	3	<LOD	2444	<LOD	135	186	55	4916	89	1973	47
15/11/2018	location 24 30 cm	<LOD	302	<LOD	166	<LOD	97	<LOD	76	434	18	65	3	<LOD	3094	<LOD	156	185	59	6733	109	4974	75
15/11/2018	location 27 surface	<LOD	212	<LOD	117	<LOD	68	<LOD	54	317	12	24.4	1.4	<LOD	2166	<LOD	116	200	48	5005	82	1659	41
15/11/2018	location 30 surface	<LOD	267	<LOD	147	<LOD	87	<LOD	69	286	15	21.1	1.9	<LOD	2319	<LOD	125	192	48	3799	72	2850	51
15/11/2018	location 26 surface	<LOD	229	<LOD	126	<LOD	74	<LOD	58	286	13	24	1.5	<LOD	3048	<LOD	147	196	56	5262	90	6880	85
15/11/2018	location 24 surface	<LOD	276	<LOD	151	<LOD	88	<LOD	70	289	16	30	2	<LOD	2859	<LOD	151	<LOD	150	4226	81	5660	77
15/11/2018	location 22 surface	<LOD	217	<LOD	119	<LOD	69	<LOD	55	325	12	16.3	1.4	<LOD	2326	<LOD	131	<LOD	141	4829	80	1970	43
15/11/2018	location 28 surface	<LOD	246	<LOD	135	<LOD	79	<LOD	62	284	14	24.8	1.7	<LOD	2775	<LOD	160	<LOD	182	3448	81	2058	50
15/11/2018	location 23 surface	<LOD	300	<LOD	164	<LOD	97	<LOD	77	223	17	21	2	<LOD	3091	238	55	178	55	3876	79	6629	86
15/11/2018	location 22a 50 cm	<LOD	263	<LOD	144	<LOD	85	<LOD	67	385	15	22	1.9	<LOD	2723	<LOD	137	213	65	6526	114	1283	46
15/11/2018	location 25 30 cm	<LOD	274	<LOD	150	<LOD	88	<LOD	69	412	16	42	2	<LOD	2714	<LOD	150	243	57	7228	112	1398	44
15/11/2018	location 28 20 cm	<LOD	248	<LOD	135	<LOD	79	<LOD	62	185	13	15.4	1.3	<LOD	3578	<LOD	208	<LOD	234	<LOD	147	282	34
15/11/2018	location 27 30 cm	<LOD	271	<LOD	148	<LOD	86	<LOD	68	317	15	34	2	<LOD	2673	<LOD	134	<LOD	182	5937	102	1491	45
15/11/2018	location 27 50 cm	<LOD	272	<LOD	150	<LOD	87	<LOD	69	230	15	22.5	1.9	<LOD	2627	<LOD	135	<LOD	184	4409	89	881	39
15/11/2018	location 30 26 cm	<LOD	287	<LOD	158	<LOD	93	<LOD	74	253	16	18.3	2	<LOD	2566	178	44	<LOD	135	3213	67	2925	52
15/11/2018	location 29 surface	<LOD	311	<LOD	171	<LOD	100	<LOD	80	368	18	37	3	<LOD	2643	<LOD	134	171	52	4833	87	2915	55

Date	locations	Ti	Ti +/-	V	V +/-	Cr	Cr +/-	Mn	Mn +/-	Fe	Fe +/-	Co	Co +/-	Ni	Ni +/-	Cu	Cu +/-	Zn	Zn +/-	As	As +/-	Se	Se +/-
15/11/2018																							
15/11/2018	location 32 10cm	1315	23	27	2	25	3	99	4	27684	133	<LOD	68	<LOD	10	<LOD	6	41.5	1.8	7	0.9	<LOD	1.2
15/11/2018	location 24 50cm	1415	23	36	2	15	2	259	6	19950	106	<LOD	60	<LOD	10	<LOD	7	58	2	8	1	<LOD	1.2
15/11/2018	location 31 surface	1262	22	33	2	16	3	318	6	34348	174	<LOD	83	<LOD	10	<LOD	8	82	3	8	1.1	<LOD	1.4
15/11/2018	location 31 40cm	1397	23	32	2	17	3	277	6	30864	152	<LOD	75	<LOD	10	<LOD	7	63	2	7.8	1	<LOD	1.3
15/11/2018	location 22a 30cm	2133	32	43	3	23	3	667	10	25160	136	<LOD	72	<LOD	11	<LOD	8	137	3	12.6	1.6	<LOD	1.4
15/11/2018	location 25 surface	856	18	21.9	1.9	7	2	491	8	18754	105	<LOD	61	<LOD	10	<LOD	7	79	2	6.1	1	<LOD	1.3
15/11/2018	location 30 40 cm	1837	23	29.3	2	16	2	86	4	13871	77	<LOD	50	<LOD	10	<LOD	7	32.3	1.7	<LOD	2.5	<LOD	1.3
15/11/2018	location 25 50 cm	976	19	32	1.9	12	2	219	5	19941	96	<LOD	55	<LOD	9	<LOD	6	42.9	1.7	7	0.8	<LOD	1.2
15/11/2018	location 31 25 cm	1528	24	38	2	17	3	181	5	24872	132	<LOD	70	<LOD	10	<LOD	8	54	2	7.6	1.1	<LOD	1.3
15/11/2018	location 24 30 cm	1457	24	41	2	22	3	521	8	25086	132	<LOD	69	<LOD	10	<LOD	8	100	3	8.7	1.1	<LOD	1.4
15/11/2018	location 27 surface	1420	21	28.4	1.9	13	2	206	5	12931	68	<LOD	44	<LOD	9	<LOD	6	44.1	1.7	2.8	0.8	<LOD	1.1
15/11/2018	location 30 surface	1330	20	25	1.8	<LOD	6	168	4	12985	72	<LOD	47	<LOD	9	<LOD	7	52.6	1.9	3.5	0.8	<LOD	1.2
15/11/2018	location 26 surface	1649	24	36	2	22	3	542	8	20262	99	<LOD	57	<LOD	9	<LOD	7	90	2	6.7	0.9	<LOD	1.2
15/11/2018	location 24 surface	1215	21	28.3	2	14	2	467	7	19690	102	<LOD	59	<LOD	10	<LOD	7	71	2	6.1	1.1	<LOD	1.2
15/11/2018	location 22 surface	1586	22	30.6	2	22	2	463	7	13875	72	<LOD	46	<LOD	9	<LOD	7	142	3	9.7	1.4	<LOD	1.2
15/11/2018	location 28 surface	2456	34	43	3	20	3	746	10	25346	124	<LOD	66	<LOD	9	<LOD	7	74	2	6.4	1	<LOD	1.2
15/11/2018	location 23 surface	1442	23	27	2	11	2	649	9	19495	107	<LOD	62	<LOD	10	<LOD	7	86	3	6.9	1.1	<LOD	1.3
15/11/2018	location 22a 50 cm	2022	31	42	3	29	3	952	12	18056	100	<LOD	59	<LOD	10	<LOD	7	111	3	6.9	1.4	<LOD	1.3
15/11/2018	location 25 30 cm	997	20	28.2	2	11	2	299	6	20643	108	<LOD	61	<LOD	10	<LOD	7	59	2	10.5	1	<LOD	1.3
15/11/2018	location 28 20 cm	3534	46	56	4	59	4	235	7	59140	275	<LOD	105	<LOD	11	<LOD	8	47	2	7.4	1	<LOD	1.3
15/11/2018	location 27 30 cm	2369	32	37	3	30	3	179	5	26395	136	<LOD	71	<LOD	11	<LOD	7	57	2	6.3	1	<LOD	1.3
15/11/2018	location 27 50 cm	2583	34	36	3	41	3	97	4	28251	143	<LOD	73	<LOD	11	<LOD	7	38.4	1.9	4.8	0.9	<LOD	1.3
15/11/2018	location 30 26 cm	1167	19	16.6	1.7	<LOD	5.9	170	4	11286	66	<LOD	44	<LOD	9	<LOD	7	59	2	3.5	0.8	<LOD	1.3
15/11/2018	location 29 surface	1369	22	28.2	2	<LOD	7	435	7	14631	85	<LOD	53	<LOD	10	<LOD	7	49	2	4.2	1	<LOD	1.3

Date	locations	Rb	Rb +/-	Sr	Sr +/-	Zr	Zr +/-	Nb	Nb +/-	Mo	Mo +/-	Ag	Ag +/-	Cd	Cd +/-	Sn	Sn +/-	Sb	Sb +/-	Ta	Ta +/-	W	W +/-	Au	Au +/-
15/11/2018																									
15/11/2018	location 32 10cm	39.3	0.8	80	2	108	2	9	0.9	<LOD	2.6	<LOD	3.5	<LOD	4.6	<LOD	9	<LOD	9	6.5	0.7	<LOD	10	<LOD	4.4
15/11/2018	location 24 50cm	56	1	196	4	331	5	19.4	1	<LOD	4.4	<LOD	4.7	<LOD	5.8	<LOD	12	<LOD	11	12.9	0.9	<LOD	10	<LOD	4.8
15/11/2018	location 31 surface	55.5	1	104	3	337	5	27.3	1.1	<LOD	4.6	<LOD	4.7	<LOD	5.8	12	4	<LOD	11	13.7	1	<LOD	12	<LOD	5.1
15/11/2018	location 31 40cm	50.7	1	100	3	401	5	24	1	<LOD	4.2	<LOD	4.2	<LOD	5.2	<LOD	11	<LOD	10	13.2	0.9	<LOD	11	<LOD	4.7
15/11/2018	location 22a 30cm	85.4	1.3	152	3	194	3	11.4	1	<LOD	3.5	<LOD	4.1	<LOD	5.1	<LOD	11	<LOD	11	9.3	1	<LOD	12	<LOD	5.2
15/11/2018	location 25 surface	43.5	0.9	123	3	258	4	17.4	1	<LOD	3.9	<LOD	4.7	<LOD	6	<LOD	12	<LOD	12	10	0.9	<LOD	11	<LOD	4.8
15/11/2018	location 30 40 cm	55.7	1	96.9	1.8	223	2	10.1	0.9	<LOD	2.4	<LOD	2.5	<LOD	3.1	<LOD	7	<LOD	7	9.2	0.8	<LOD	10	<LOD	4.9
15/11/2018	location 25 50 cm	59.9	0.9	51.4	1.5	283	3	17.4	0.9	<LOD	2.8	<LOD	2.8	<LOD	3.4	<LOD	7	<LOD	7	10.1	0.8	<LOD	9	<LOD	4.4
15/11/2018	location 31 25 cm	54.5	1	127	3	344	5	25.7	1.1	<LOD	4.7	<LOD	5	<LOD	6	<LOD	12	<LOD	12	14.7	1	<LOD	11	<LOD	4.9
15/11/2018	location 24 30 cm	59.6	1.1	227	5	350	5	22.4	1.1	<LOD	4.7	<LOD	4.7	<LOD	5.8	<LOD	12	<LOD	12	13.7	1	<LOD	11	<LOD	4.9
15/11/2018	location 27 surface	45.5	0.8	67.8	1.7	214	3	16.3	0.9	<LOD	2.7	<LOD	2.9	<LOD	3.6	<LOD	8	<LOD	8	7.6	0.7	<LOD	9	<LOD	4.3
15/11/2018	location 30 surface	56.3	0.9	138	3	321	4	19.4	0.9	<LOD	3.9	<LOD	4.1	<LOD	5.2	<LOD	10	<LOD	10	11.7	0.8	<LOD	10	<LOD	4.3
15/11/2018	location 26 surface	43.5	0.8	156	3	122	2	9.1	0.9	<LOD	2.4	<LOD	3.1	<LOD	3.9	10	3	<LOD	8	8.3	0.8	<LOD	10	<LOD	4.6
15/11/2018	location 24 surface	46.7	0.9	240	4	205	4	16.8	1	<LOD	3.4	<LOD	4.2	<LOD	5.2	<LOD	10	<LOD	10	8.5	0.8	<LOD	10	<LOD	4.7
15/11/2018	location 22 surface	54.7	0.9	83.7	1.9	169	2	12.1	0.9	<LOD	2.4	<LOD	2.9	<LOD	3.7	<LOD	8	<LOD	8	5.8	0.8	<LOD	11	<LOD	4.5
15/11/2018	location 28 surface	38.6	0.8	75	2	319	4	14.5	0.9	<LOD	3.6	<LOD	3.4	<LOD	4.3	<LOD	9	<LOD	9	11.2	0.9	<LOD	10	<LOD	4.7
15/11/2018	location 23 surface	45.7	0.9	198	4	189	4	17.8	1	<LOD	3.6	<LOD	4.8	<LOD	5.8	<LOD	12	<LOD	12	7.5	0.8	<LOD	11	<LOD	4.7
15/11/2018	location 22a 50 cm	70	1.1	91	2	184	3	9.6	1	<LOD	3.1	<LOD	3.8	<LOD	4.7	<LOD	10	<LOD	10	7.1	0.9	<LOD	12	<LOD	5
15/11/2018	location 25 30 cm	63.1	1	89	3	380	5	23.2	1	<LOD	4.3	<LOD	4.1	<LOD	5.1	<LOD	10	<LOD	10	11	0.9	<LOD	11	<LOD	5
15/11/2018	location 28 20 cm	11.2	0.6	18.7	1.1	226	3	10.1	0.9	<LOD	3.1	<LOD	3.3	<LOD	4.3	<LOD	9	<LOD	9	14.5	1	<LOD	11	<LOD	5
15/11/2018	location 27 30 cm	58.1	1	82	2	365	5	22.2	1	<LOD	4.1	<LOD	3.9	<LOD	4.8	<LOD	10	<LOD	10	13.4	1	<LOD	11	<LOD	4.9
15/11/2018	location 27 50 cm	50.9	1	62	2	277	4	14.7	1	<LOD	3.7	<LOD	3.9	<LOD	4.9	<LOD	10	<LOD	10	10.4	0.9	<LOD	11	<LOD	4.9
15/11/2018	location 30 26 cm	49.2	0.9	141	3	250	4	17.4	1	<LOD	3.9	<LOD	4.5	<LOD	5.7	<LOD	11	<LOD	11	10	0.8	<LOD	10	<LOD	4.5
15/11/2018	location 29 surface	62.5	1.1	187	4	439	6	20.9	1	<LOD	5.1	<LOD	5	<LOD	6	<LOD	12	<LOD	12	11.7	0.9	<LOD	10	<LOD	4.8

Date	locations	Hg	Hg +/-	Pb	Pb +/-	Bi	Bi +/-	Th	Th +/-	U	U +/-
15/11/2018											
15/11/2018	location 32 10cm	<LOD	2.4	17	1.3	<LOD	14	8.8	1.5	<LOD	6
15/11/2018	location 24 50cm	<LOD	2.6	23.1	1.5	<LOD	16	16	2	9	3
15/11/2018	location 31 surface	<LOD	2.8	24.6	1.6	<LOD	17	9	2	<LOD	8
15/11/2018	location 31 40cm	<LOD	2.6	14.2	1.3	<LOD	16	15	2	<LOD	7
15/11/2018	location 22a 30cm	<LOD	3	88	2	<LOD	16	8.3	1.8	<LOD	8
15/11/2018	location 25 surface	<LOD	2.6	19.6	1.5	<LOD	16	10	2	<LOD	8
15/11/2018	location 30 40 cm	<LOD	2.6	12	1.2	<LOD	14	6.2	1.1	<LOD	4.5
15/11/2018	location 25 50 cm	3	0.9	13.1	1.2	<LOD	14	10.8	1.3	<LOD	4.8
15/11/2018	location 31 25 cm	<LOD	2.8	21.7	1.5	<LOD	17	12	2	9	3
15/11/2018	location 24 30 cm	<LOD	2.8	27.6	1.6	<LOD	17	15	2	<LOD	9
15/11/2018	location 27 surface	<LOD	2.3	10.9	1.1	<LOD	13	9.2	1.3	<LOD	4.8
15/11/2018	location 30 surface	<LOD	2.5	14.3	1.3	<LOD	15	9.7	1.9	<LOD	7
15/11/2018	location 26 surface	<LOD	2.5	21.7	1.3	<LOD	14	4.7	1.3	<LOD	5.5
15/11/2018	location 24 surface	<LOD	2.6	39.3	1.6	<LOD	15	8.6	1.9	<LOD	8
15/11/2018	location 22 surface	<LOD	2.4	88.4	1.9	<LOD	14	6.3	1.2	<LOD	5
15/11/2018	location 28 surface	<LOD	2.5	23.5	1.4	<LOD	15	11.6	1.7	<LOD	6
15/11/2018	location 23 surface	<LOD	2.7	34.7	1.6	<LOD	16	8.3	2	<LOD	8
15/11/2018	location 22a 50 cm	<LOD	2.9	61.9	1.9	<LOD	15	6.5	1.6	<LOD	7
15/11/2018	location 25 30 cm	<LOD	2.7	16	1.4	<LOD	16	13.8	2	<LOD	7
15/11/2018	location 28 20 cm	<LOD	2.8	11	1.4	<LOD	15	11.6	1.5	6.2	1.8
15/11/2018	location 27 30 cm	<LOD	2.9	13.7	1.4	<LOD	16	10.9	1.8	<LOD	7
15/11/2018	location 27 50 cm	<LOD	2.6	11.5	1.3	<LOD	15	9.4	1.7	<LOD	7
15/11/2018	location 30 26 cm	<LOD	2.5	12.6	1.3	<LOD	15	10.1	2	<LOD	8
15/11/2018	location 29 surface	<LOD	2.7	25.6	1.5	<LOD	17	14	2	<LOD	9

Appendix B: Grain Size Raw Data

								Clay
Sample Name	0.05	0.06	0.12	0.24	0.49	0.98	2	3.9
L1 surface	0	0	0	0	0.06	5.21	12.11	22.12
L1 50cm	0	0	0	0	0	3.15	7.71	15.65
L1 120cm	0	0	0	0	0.04	3.8	8.75	16.2
L2 surface	0	0	0	0	0.12	7.93	17.24	29.84
L2 20cm	0	0	0	0	0.09	7.03	16.02	28.3
L2 40cm	0	0	0	0	0.09	7.31	16.77	29.53
L2a surface	0	0	0	0	0.06	6.11	14.77	27.26
L2b surface	0	0	0	0	0.11	8.17	18.16	31.83
L2b 40cm	0	0	0	0	0.08	7.7	18.28	33.32
L3 surface	0	0	0	0	0.06	4.74	10.54	18.99
L3 40cm	0	0	0	0	0.04	3.87	8.78	15.54
L3 70cm	0	0	0	0	0.04	4.35	10.13	18.21
L4 surface	0	0	0	0	0.1	8.97	20.64	36.74
L5 surface	0	0	0	0	0.09	5.78	12.48	21.33
L5b	0	0	0	0	0.14	8.28	16.69	28.21
L6 surface	0	0	0	0	0.15	7.39	14.55	24.96
L6 40cm	0	0	0	0	0.23	11.78	22.93	38.55
L7 surface	0	0	0	0	0.13	8.59	18.81	34.12
L7 15cm	0	0	0	0	0.2	11.94	26.12	47.16
L8 surface	0	0	0	0	0.05	5.64	13.06	23.83
L8 40cm	0	0	0	0	0	4.2	10.09	19.01
L11 surface	0	0	0	0	0.08	7.11	16.08	29.63
L11 20cm	0	0	0	0	0.13	8.78	18.22	32.14
L11 40cm	0	0	0	0	0.24	12.44	24.01	39.96
L12 surface	0	0	0	0	0	5.26	13.59	26.3
L12 20cm	0	0	0	0	0.15	8.93	18.35	31.13
L12 50cm	0	0	0	0	0.11	7.68	16.09	28.16
L13 surface	0	0	0	0	0.13	9.9	22.19	39.3
L13a surface	0	0	0	0	0.11	7.36	16.25	28.81
L13b surface	0	0	0	0	0.22	10.26	21.05	36.54
L14 surface	0	0	0	0	0.08	6.92	15.5	28.21
L14 30cm	0	0	0	0	0.06	5.68	12.83	22.66
L14 50cm	0	0	0	0	0.04	4.26	9.89	17.68
L15 surface	0	0	0	0	0.08	6.86	16.25	29.43
L15 30 cm	0	0	0	0	0.09	5.2	11.28	19.79
L16 surface	0	0	0	0	0.16	11.13	24.48	42.62
L16 30cm	0	0	0	0	0.39	13.67	26.52	43.71
L17 surface	0	0	0	0	0.08	5.28	11.63	20.49
L17 5-7cm	0	0	0	0	0.24	12.27	25.56	44.44
L18 surface	0	0	0	0	0.06	4.01	8.61	14.44
L18 20cm	0	0	0	0	0.06	4.81	10.72	18.31
L18 40cm	0	0	0	0	0	2.57	6.03	10.44
L19 surface	0	0	0	0	0	2.33	5.52	10.18
L19 20cm	0	0	0	0	0.05	4.53	10.43	18.57
L19 40cm	0	0	0	0	0.08	4.82	10.07	17.62
L19 60cm	0	0	0	0	0.04	3.73	8.76	17.37
L20 surface	0	0	0	0	0.11	7.84	17.36	30.6
L20 20cm	0	0	0	0	0.1	7	15.58	27.42
L20 40cm	0	0	0	0	0.13	8.42	17.77	30.92
L21 surface	0	0	0	0	0.14	8.66	19.03	33.11
L22 surface	0	0	0	0	0.1	6.36	13.66	23.44
L22a surface	0	0	0	0	0.11	6.88	14.56	23.55
L22a 30cm	0	0	0	0	0.08	5.48	12.05	19.81
L22a 50 cm	0	0	0	0	0.1	5.85	12.12	19.45
L23 surface	0	0	0	0	0.15	8.37	17.04	27.54
L24 surface	0	0	0	0	0.08	6.05	13.44	22.51
L24 30 cm	0	0	0	0	0.07	6.19	14.69	25.49
L24 50cm	0	0	0	0	0.08	5.24	11.59	21.5
L25 surface	0	0	0	0	0.05	5.21	12.37	21.92
L25 30cm	0	0	0	0	0.07	6.35	15.05	26.65
L25 50cm	0	0	0	0	0.04	5.76	14.46	26.58
L26 surface	0	0	0	0	0.11	7.89	17.89	30.54
L27 surface	0	0	0	0	0.07	5.51	12.26	20.05
L27 30cm	0	0	0	0	0.08	7.54	17.66	29.17
L27 50cm	0	0	0	0	0.05	7.1	17.63	31.02
L28 surface	0	0	0	0	0.07	5.61	13.16	22.29
L28 20cm	0	0	0	0	0.82	16.39	30.03	48.02
L29 surface	0	0	0	0	0.09	6.21	13.27	22.13
L30 surface	0	0	0	0	0.19	8.4	15.84	25.35
L30 26cm	0	0	0	0	0.14	6.44	12.34	19.87
L30 40cm	0	0	0	0	0.13	6.07	11.57	18.56
L31 surface	0	0	0	0	0.07	5.12	10.92	18.58
L31 25cm	0	0	0	0	0.03	3.35	7.81	15.4
L31 40cm	0	0	0	0	0.06	4.03	8.55	14.84
L32 10cm	0	0	0	0	0.1	7.36	16.16	28.94

							Silt
Sample Name	7.8	15.6	31	37	44	53	63
L1 surface	33.56	45.57	58.02	61.29	64.47	67.8	70.79
L1 50cm	25.95	37.44	49.63	52.99	56.37	60.04	63.47
L1 120cm	25.24	36.38	49.91	53.8	57.66	61.78	65.49
L2 surface	45.18	62.55	78.78	82.26	85.33	88.18	90.4
L2 20cm	43.52	60.89	77.2	80.71	83.79	86.66	88.86
L2 40cm	45.06	62.84	79.42	82.82	85.7	88.26	90.12
L2a surface	43.36	60.12	71.68	73.73	75.53	77.33	78.94
L2b surface	48.38	66.57	80.78	83.34	85.51	87.52	89.13
L2b 40cm	52.49	73.94	88.65	90.79	92.43	93.79	94.77
L3 surface	29.62	41.88	54.34	57.51	60.67	64.21	67.72
L3 40cm	25.05	37.8	52.01	56.11	60.41	65.41	70.36
L3 70cm	29	42.26	55.81	59.62	63.65	68.38	73.1
L4 surface	55.77	74.59	87.17	89.04	90.48	91.69	92.58
L5 surface	31.71	42.94	53.45	56.14	58.9	62.08	65.32
L5b	42.99	58.6	69.67	71.82	73.82	75.92	77.85
L6 surface	37.63	51.78	64.25	66.85	69.18	71.44	73.35
L6 40cm	57.68	77.47	89.85	91.32	92.31	93.04	93.57
L7 surface	51.35	66.72	77.11	79.12	80.95	82.79	84.41
L7 15cm	66.41	78.2	85.43	87.05	88.6	90.18	91.56
L8 surface	42.46	66.33	81.98	84.49	86.62	88.61	90.21
L8 40cm	37.92	63.12	76.46	77.86	78.91	79.83	80.62
L11 surface	48.71	67.48	77.89	79.45	80.78	82.07	83.18
L11 20cm	53.46	77.1	90.32	92.06	93.39	94.47	95.18
L11 40cm	60.52	78.66	87.04	88.11	88.99	89.86	90.63
L12 surface	45.6	66.65	79.74	82.09	84.22	86.38	88.27
L12 20cm	47.74	66.31	78.96	81.32	83.47	85.66	87.59
L12 50cm	46.29	67.55	81.33	83.63	85.63	87.56	89.16
L13 surface	60.4	79.44	89.64	91.01	92.07	92.99	93.72
L13a surface	42.06	54.17	65.35	68.12	70.83	73.75	76.49
L13b surface	50.61	60.69	70.07	72.7	75.34	78.25	80.97
L14 surface	46.39	66.64	80.69	83.31	85.69	88.06	90.12
L14 30cm	37.69	57.14	72.96	76.35	79.54	82.81	85.65
L14 50cm	29.53	45.17	60.61	64.77	69	73.69	78.06
L15 surface	45.58	61.45	72.31	74.32	76.13	78.01	79.78
L15 30 cm	29.26	38.39	46.07	47.95	49.94	52.42	55.24
L16 surface	63.41	82.5	93.24	94.56	95.51	96.27	96.83
L16 30cm	62.86	80.43	90.3	91.53	92.44	93.19	93.78
L17 surface	31.37	42.42	51.43	53.48	55.43	57.45	59.3
L17 5-7cm	65.01	82.51	93.15	94.63	95.73	96.62	97.28
L18 surface	21.51	30.59	41.46	44.6	47.83	51.49	55.09
L18 20cm	27.1	38.04	50.54	53.87	57.15	60.7	64.04
L18 40cm	15.85	22.83	31.55	34.12	36.77	39.81	42.81
L19 surface	15.64	21.98	29.92	32.36	34.92	37.91	40.9
L19 20cm	27.96	40.05	55.21	59.43	63.58	68.01	72.02
L19 40cm	26.77	38.74	54	58.24	62.29	66.38	69.87
L19 60cm	27.66	39.15	52.58	56.39	60.2	64.31	68.08
L20 surface	46.08	60.92	71.6	73.75	75.75	77.82	79.72
L20 20cm	40.91	54.71	66.33	68.91	71.42	74.19	76.87
L20 40cm	46.64	63.04	75.63	77.87	79.77	81.58	83.11
L21 surface	48.59	63.81	76.25	78.88	81.31	83.79	85.97
L22 surface	34.62	48.02	63.54	67.82	72.05	76.56	80.58
L22a surface	33.23	45.82	61.48	65.62	69.59	73.74	77.43
L22a 30cm	28.26	39.68	54.92	59.11	63.19	67.53	71.48
L22a 50 cm	27.22	37.44	50.71	54.23	57.59	61.05	64.13
L23 surface	39.63	54.4	69.42	72.91	76.16	79.47	82.37
L24 surface	31.78	42.44	54.31	57.6	60.97	64.79	68.5
L24 30 cm	36.31	46.66	56.27	58.79	61.4	64.43	67.5
L24 50cm	31.95	41.78	53.15	56.58	60.12	64.08	67.87
L25 surface	33.09	47	62.6	66.67	70.66	74.92	78.79
L25 30cm	39.26	53.43	68.72	72.63	76.42	80.4	83.95
L25 50cm	40.42	56.22	73.23	77.38	81.23	85.03	88.19
L26 surface	43.37	55	66.34	69.29	72.17	75.23	78.02
L27 surface	28.72	39.39	51.84	55.31	58.82	62.68	66.31
L27 30cm	40.65	52.84	65.83	69.25	72.61	76.2	79.49
L27 50cm	44.68	59.68	74.01	77.21	80.2	83.26	85.93
L28 surface	32.97	45.83	60.04	63.78	67.41	71.22	74.62
L28 20cm	65.67	77.98	84.52	85.78	86.99	88.3	89.57
L29 surface	32.53	45.88	61.53	65.54	69.32	73.18	76.52
L30 surface	35.57	47.59	61.08	64.6	68.04	71.72	75.11
L30 26cm	28.59	39.81	53.17	56.9	60.64	64.76	68.63
L30 40cm	25.95	34.68	45.91	49.37	52.97	57.08	61.04
L31 surface	28.12	41.37	57.18	61.36	65.36	69.48	73.06
L31 25cm	25.15	36.58	50.56	54.52	58.42	62.57	66.32
L31 40cm	22.09	31.06	42.16	45.38	48.64	52.28	55.79
L32 10cm	45.34	63.1	76.91	79.44	81.6	83.62	85.28

								Fines sand												Sand			Gravel
Sample Name	74	88	105	125	149	177	210	250	300	350	420	500	590	710	840	1000	1190	1410	1680	2000	2380	2830	3360
L1 surface	73.48	76.25	78.92	81.42	83.76	85.93	87.99	90.05	92.22	94.05	96.09	97.79	99.01	99.74	99.98	100	100	100	100	100	100	100	100
L1 50cm	66.63	69.95	73.19	76.22	79.02	81.55	83.9	86.21	88.68	90.85	93.46	95.83	97.74	99.18	99.88	100	100	100	100	100	100	100	100
L1 120cm	68.79	72.12	75.26	78.14	80.79	83.22	85.51	87.78	90.15	92.17	94.53	96.62	98.25	99.44	99.95	100	100	100	100	100	100	100	100
L2 surface	92.13	93.6	94.75	95.64	96.33	96.92	97.48	98.06	98.68	99.16	99.61	99.88	100	100	100	100	100	100	100	100	100	100	100
L2 20cm	90.55	91.98	93.08	93.95	94.67	95.32	95.97	96.7	97.53	98.24	99	99.56	99.89	100	100	100	100	100	100	100	100	100	100
L2 40cm	91.49	92.6	93.44	94.1	94.67	95.22	95.81	96.48	97.24	97.89	98.59	99.16	99.58	99.87	99.99	100	100	100	100	100	100	100	100
L2a surface	80.46	82.16	84	85.95	88.08	90.27	92.49	94.69	96.75	98.16	99.26	99.82	100	100	100	100	100	100	100	100	100	100	100
L2b surface	90.44	91.67	92.72	93.6	94.34	94.97	95.58	96.29	97.14	97.92	98.79	99.45	99.86	100	100	100	100	100	100	100	100	100	100
L2b 40cm	95.51	96.16	96.69	97.14	97.51	97.8	98.05	98.3	98.58	98.85	99.2	99.53	99.79	99.96	100	100	100	100	100	100	100	100	100
L3 surface	71.2	75.2	79.53	83.93	88.27	92.21	95.56	98.01	99.53	99.99	100	100	100	100	100	100	100	100	100	100	100	100	100
L3 40cm	75.1	80.17	85.03	89.38	93.03	95.86	97.95	99.24	99.92	100	100	100	100	100	100	100	100	100	100	100	100	100	100
L3 70cm	77.61	82.35	86.75	90.46	93.31	95.32	96.72	97.7	98.52	99.11	99.65	99.96	100	100	100	100	100	100	100	100	100	100	100
L4 surface	93.3	94	94.67	95.31	95.93	96.52	97.09	97.67	98.26	98.73	99.21	99.57	99.82	99.97	100	100	100	100	100	100	100	100	100
L5 surface	68.55	72.14	75.69	78.83	81.41	83.52	85.53	87.91	90.9	93.69	96.76	98.9	99.92	100	100	100	100	100	100	100	100	100	100
L5b	79.65	81.61	83.63	85.63	87.65	89.59	91.46	93.28	95.05	96.42	97.79	98.83	99.53	99.92	100	100	100	100	100	100	100	100	100
L6 surface	75.02	76.73	78.46	80.26	82.27	84.52	87.05	89.93	93.01	95.44	97.73	99.21	99.92	100	100	100	100	100	100	100	100	100	100
L6 40cm	94.03	94.56	95.17	95.79	96.37	96.85	97.21	97.51	97.82	98.15	98.62	99.07	99.43	99.7	99.85	99.95	100	100	100	100	100	100	100
L7 surface	85.85	87.33	88.79	90.18	91.52	92.8	94.04	95.3	96.61	97.68	98.75	99.5	99.89	100	100	100	100	100	100	100	100	100	100
L7 15cm	92.77	93.95	95.01	95.87	96.48	96.83	97	97.11	97.34	97.7	98.32	98.97	99.49	99.84	99.98	100	100	100	100	100	100	100	100
L8 surface	91.53	92.77	93.88	94.88	95.82	96.7	97.51	98.24	98.88	99.29	99.61	99.81	99.94	100	100	100	100	100	100	100	100	100	100
L8 40cm	81.32	82.04	82.71	83.3	83.78	84.2	84.65	85.38	86.6	88.12	90.55	93.2	95.69	97.93	99.32	99.96	100	100	100	100	100	100	100
L11 surface	84.21	85.37	86.74	88.34	90.26	92.35	94.46	96.42	98.08	99.08	99.71	99.97	100	100	100	100	100	100	100	100	100	100	100
L11 20cm	95.67	96.03	96.31	96.56	96.81	97.06	97.32	97.57	97.8	97.98	98.21	98.51	98.88	99.33	99.69	99.92	100	100	100	100	100	100	100
L11 40cm	91.34	92.08	92.78	93.4	93.88	94.25	94.58	95.01	95.67	96.43	97.52	98.54	99.32	99.8	99.98	100	100	100	100	100	100	100	100
L12 surface	89.92	91.54	93.01	94.31	95.45	96.42	97.27	98.02	98.7	99.17	99.59	99.86	100	100	100	100	100	100	100	100	100	100	100
L12 20cm	89.27	90.95	92.48	93.82	94.95	95.89	96.7	97.43	98.14	98.71	99.27	99.69	99.92	100	100	100	100	100	100	100	100	100	100
L12 50cm	90.5	91.78	92.91	93.88	94.71	95.43	96.08	96.74	97.45	98.07	98.77	99.34	99.73	99.95	100	100	100	100	100	100	100	100	100
L13 surface	94.33	94.98	95.64	96.32	97.02	97.68	98.3	98.86	99.36	99.68	99.93	100	100	100	100	100	100	100	100	100	100	100	100
L13a surface	79.04	81.74	84.39	86.88	89.22	91.37	93.39	95.29	97.08	98.32	99.31	99.83	100	100	100	100	100	100	100	100	100	100	100
L13b surface	83.46	86.05	88.52	90.77	92.75	94.43	95.84	97.02	98.04	98.73	99.34	99.73	99.94	100	100	100	100	100	100	100	100	100	100
L14 surface	91.89	93.61	95.13	96.39	97.39	98.15	98.73	99.18	99.55	99.79	99.95	100	100	100	100	100	100	100	100	100	100	100	100
L14 30cm	88.08	90.36	92.28	93.81	94.95	95.79	96.46	97.08	97.75	98.34	99.02	99.56	99.89	100	100	100	100	100	100	100	100	100	100
L14 50cm	81.98	85.85	89.25	92.04	94.2	95.82	97.08	98.09	98.95	99.51	99.9	100	100	100	100	100	100	100	100	100	100	100	100
L15 surface	81.5	83.49	85.68	87.95	90.29	92.53	94.61	96.44	98	98.98	99.66	99.96	100	100	100	100	100	100	100	100	100	100	100
L15 30 cm	58.37	62.35	67.02	72.01	77.2	82.22	86.95	91.25	95.04	97.5	99.25	99.94	100	100	100	100	100	100	100	100	100	100	100
L16 surface	97.29	97.75	98.22	98.69	99.12	99.48	99.76	99.94	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
L16 30cm	94.26	94.75	95.24	95.71	96.15	96.53	96.85	97.09	97.28	97.4	97.55	97.73	97.96	98.28	98.58	98.87	99.14	99.38	99.6	99.78	99.92	100	100
L17 surface	61.11	63.35	66.26	69.93	74.65	80.03	85.7	91.12	95.73	98.39	99.79	100	100	100	100	100	100	100	100	100	100	100	100
L17 5-7cm	97.81	98.35	98.88	99.34	99.68	99.89	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
L18 surface	58.57	62.44	66.47	70.48	74.49	78.37	82.19	86	89.84	92.85	95.85	98.05	99.39	99.95	100	100	100	100	100	100	100	100	100
L18 20cm	67.19	70.61	74.13	77.59	81.01	84.26	87.32	90.21	92.96	95.03	97.05	98.55	99.5	99.94	100	100	100	100	100	100	100	100	100
L18 40cm	45.78	49.17	52.86	56.7	60.76	64.88	69.07	73.4	77.9	81.64	85.87	89.67	92.94	95.96	98.06	99.42	99.94	100	100	100	100	100	100
L19 surface	43.86	47.24	50.88	54.62	58.57	62.61	66.81	71.3	76.11	80.18	84.8	88.91	92.4	95.57	97.76	99.22	99.89	100	100	100	100	100	100
L19 20cm	75.64	79.31	82.76	85.83	88.5	90.75	92.73	94.52	96.24	97.55	98.77	99.56	99.93	100	100	100	100	100	100	100	100	100	100
L19 40cm	72.88	75.91	78.88	81.78	84.67	87.43	90.03	92.44	94.71	96.42	98.08	99.24	99.87	100	100	100	100	100	100	100	100	100	100
L19 60cm	71.47	74.91	78.11	80.92	83.34	85.42	87.34	89.31	91.51	93.5	95.82	97.77	99.13	99.87	100	100	100	100	100	100	100	100	100
L20 surface	81.52	83.51	85.65	87.83	90.06	92.18	94.15	95.91	97.43	98.44	99.23	99.7	99.93	100	100	100	100	100	100	100	100	100	100
L20 20cm	79.45	82.27	85.07	87.66	89.99	91.99	93.74	95.32	96.83	97.95	98.98	99.64	99.94	100	100	100	100	100	100	100	100	100	100
L20 40cm	84.48	85.92	87.36	88.75	90.04	91.17	92.13	92.92	93.62	94.2	95.01	95.98	97.08	98.34	99.27	99.84	100	100	100	100	100	100	100
L21 surface	87.9	89.83	91.6	93.16	94.5	95.61	96.54	97.31	97.97	98.41	98.83	99.2	99.53	99.83	99.98	100	100	100	100	100	100	100	100
L22 surface	84.06	87.38	90.19	92.45	94.21	95.61	96.8	97.87	98.84	99.48	99.9	100	100	100	100	100	100	100	100	100	100	100	100
L22a surface	80.7	83.99	87.03	89.74	92.12	94.16	95.95	97.47	98.74	99.49	99.91	100	100	100	100	100	100	100	100	100	100	100	100
L22a 30cm	75.06	78.78	82.34	85.6	88.57	91.21	93.59	95.74	97.65	98.89	99.73	99.99	100	100	100	100	100	100	100	100	100	100	100
L22a 50 cm	66.89	69.77	72.58	75.22	77.68	79.89	81.97	84.11	86.53	88.82	91.82	94.72	97.19	99.07	99.92	100	100	100	100	100	100	100	100
L23 surface	84.94	87.52	89.92	92.07	93.94	95.54	96.91	98.06	99.02	99.59	99.92	100	100	100	100	100	100	100	100	100	100	100	100
L24 surface	72.03	75.79	79.48	82.92	86.11	89.03	91.75	94.3	96.65	98.24	99.42	99.94	100	100	100	100	100	100	100	100	100	100	100
L24 30 cm	70.55	73.98	77.55	81.03	84.43	87.64	90.71	93.62	96.3	98.1	99.41	99.95	100	100	100	100	100	100	100	100	100	100	100
L24 50cm	71.43	75.21	78.94	82.48	85.87	89.05	92.07	94.85	97.31	98.83	99.78	100	100	100	100	100	100	100	100	100	100	100	100
L25 surface	82.26	85.77	89.01	91.88	94.32	96.31	97.9	99.02	99.72	99.99	100	100	100	100	100	100	100	100	100	100	100	100	100
L25 30cm	87.06	90.09	92.73	94.86	96.45	97.56	98.35	98.9	99.36	99.68	99.93	100	100	100	100	100	100	100	100	100	100	100	100
L25 50cm	90.79	93.2	95.21	96.82	98.04	98.91	99.49	99.82	99.98	100	100	100	100	100	100	100	100	100	100	100	100	100	100
L26 surface	80.56	83.19	85.73	88.07	90.17	91.97	93.53	94.89	96.19	97.19	98.25	99.09	99.65	99.94	100	100	100	100	100	100	100	100	100
L27 surface	69.65	73.12	76.4	79.35	81.98	84.34	86.64	89.14	91.98	94.46	97.09	98.94	99.87	100	100	100	100	100	100	100	100	100	100
L27 30cm	82.47	85.52	88.37	90.85	92.92	94.53	95.81	96.83	97.74	98.44	99.14	99.64	99.92	100	100	100	100	100	100	100	100	100	100
L27 50cm	88.25	90.52	92.55	94.3	95.75	96.91	97.87	98.64	99.27	99.66	99.93	100	100	100	100	100	100	100	100	100	100	100	100
L28 surface	77.64	80.68	83.54	86.19	88.7	91.08	93.38	95.6	97.62	98.93	99.79	100	100	100	100	100	100	100	100	100	100	100	100
L28 20cm	90.78	92.07	93.29	94.32	95.05	95.45	95.64	95.76	96.06	96.57	97.49	98.47	99.27	99.81	99.99	100	100	100	100	100	100	100	100
L29 surface	79.38	82.16	84.61	86.7	88.5	90.13	91.76	93.58	95.6	97.27	98.82	99.73	100	100	100	100	100	100	100	100	100	100	100
L30 surface	78.23	81.51	84.73	87.74	90.54	93.04	95.26	97.14	98.65	99.49	99.92	100	100	100	100	100	100	100	100	100	100	100	100
L30 26cm	72.24	76.05	79.79	83.29	86.58	89.59	92.4	94.99	97.31	98.8	99.77	100	100	100	100	100	100	100	100	100	100	100	100
L30 40cm	64.77	68.76	72.7	76.45	80.09	83.6	87.1	90.65	94.16	96.71	98.8	99.86	100	100	100	100	100	100	100	100	100	100	100
L31 surface	76.16	79.19	81.97	84.45	86.74	88.87	90.97	93.13	95.35	97.07	98.63	99.59	100	100	100	100	100	100	100	100	100	100	100
L31 25cm	69.71	73.2	76.56	79.68	82.56	85.12	87.42	89.5	91.5	93.1	94.92	96.58	97.99	99.16	99.8	100	100	100	100	100	100	100	100
L31 40cm	59.17	62.94	66.91	70.86	74.71	78.21	81.3	83.96	86.41	88.35	90.72	93.12	95.41	97.65	99.13	99.88	100	100	100	100	100	100	100
L32 10cm	86.71	88.18	89.65	91.09	92.51	93.85	95.13	96.34	97.5	98.35	99.12	99.64	99.91	100	100	100	100	100	100	100	100	100	100

Appendix C – ICP-MS Raw Data

	DL	32.4	135	30.8	194	421	35.7	706	138	85	8.5
Sample Name	**Comment**	**11 B [He]**	**23 Na [He]**	**24 Mg [He]**	**27 Al [He]**	**28 -> 44 Si [N2O]**	**31 P [He]**	**34 S [He]**	**39 K [He]**	**44 Ca [He]**	**51 V [He]**
Location 1 surface	19/04/2018	10.6	2251.0	8051.9	216513.8	126748.3	3546.1	2067.9	9373.6	21515.7	452.4
Location 1 50 cm	19/04/2018	6.66	979.41	2984.08	373755.00	82295.46	2432.82	1886.04	4480.95	5104.20	386.29
Location 1 120cm	19/04/2018	4.07	958.67	2497.82	274700.86	112954.43	702.40	836.75	3873.90	1408.23	456.76
Location 2 surface	19/04/2018	9.37	2263.54	28250.18	140028.35	84730.18	10915.10	2335.88	4584.41	61714.98	732.10
Location 2 20 cm	19/04/2018	7.70	1888.26	26010.83	133323.06	38599.96	7276.69	1318.36	3649.53	77027.11	763.54
location 2 40 cm	19/04/2018	2.99	1332.92	21228.82	98845.38	30024.22	1892.94	<0.000	3224.57	39859.82	774.99
Location 2a2 surface	19/04/2018	12.0	4376.3	16871.3	89552.5	41443.4	17236.2	1982.8	14394.1	60193.6	493.1
Location 2b surface	19/04/2018	5.36	2377.78	23786.71	124711.69	35922.58	6318.46	1372.70	8285.50	40407.37	471.54
Location 2b 40 cm	19/04/2018	1.32	1005.17	15403.96	92117.16	58136.72	1786.18	<0.000	6234.30	19191.76	427.14
Location 3 surface	19/04/2018	8.26	1244.62	25608.09	125833.24	28255.01	7460.89	2251.01	4331.22	25066.24	572.51
Location 3 40 cm	19/04/2018	6.01	1572.10	22537.47	89060.04	27598.95	7088.26	850.41	4035.72	26108.61	496.28
Location 3 70 cm	19/04/2018	4.24	1264.39	19493.22	74476.73	43887.74	3714.57	543.05	3361.99	27784.95	436.93
Location 4 surface	19/04/2018	5.23	1177.39	18817.20	76391.76	41452.64	6806.05	1560.37	9877.82	26576.36	270.51
Location 5b surface	19/04/2018	15.28	3428.36	16530.66	79009.04	67685.67	10945.04	2016.00	10474.02	59924.61	406.05
Location 6 surface	19/04/2018	5.39	1385.30	6588.50	228427.35	67769.60	15165.42	4005.02	2859.08	14180.42	392.24
Location 6 40 cm	19/04/2018	4.03	1160.63	4071.25	92657.51	71917.51	1902.76	834.12	5172.02	6005.68	237.14
Location 7 surface	19/04/2018	8.76	2102.72	12013.73	88635.04	71167.23	19950.86	5823.78	23487.94	29364.39	385.29
Location 7 15 cm	19/04/2018	2.77	1247.69	4596.06	104476.54	57388.22	6050.91	1992.63	10125.28	12727.05	352.94
location 8 surface	19/04/2018	20.3	4100.9	35860.2	81599.6	58522.2	9188.9	1897.7	10577.9	35182.0	417.7
location 8 40 cm	19/04/2018	8.32	1774.66	25094.22	58784.74	58754.95	3910.70	94.77	10704.51	23947.08	268.47
location 11/35 surface	24/10/2018	62.3	4290.5	27610.8	72915.3	61144.1	23483.3	5187.8	15292.4	124806.3	480.4
location 11/35 20 cm	24/10/2018	9.29	2472.97	18160.07	69511.61	52536.73	5671.30	691.97	12881.59	48053.62	317.43
location 12/31 surface	24/10/2018	3.87	2301.24	14524.07	64907.68	13332.79	9189.00	3967.59	18934.50	38860.05	311.26
location 12/31 20 cm	24/10/2018	2.79	786.13	5209.53	43955.72	18495.86	1410.70	<0.000	4496.20	13200.99	785.87
location 12/31 50 cm	24/10/2018	3.45	1173.43	10808.21	63262.83	26591.12	2761.52	320.97	7048.41	18980.11	257.63
location 13/29 surface	24/10/2018	57.7	4220.0	35544.5	89486.0	61289.2	10566.9	2536.3	7573.0	81474.8	548.1
location 13/3a/29 surface	24/10/2018	10.5	2984.6	25029.6	92813.9	75839.1	11014.2	1651.7	33998.2	57110.8	768.7
location 14/28 surface	24/10/2018	5.78	1934.74	20355.04	68959.82	34279.70	21134.60	4122.77	18183.88	35041.44	320.26
location 14/28 30 cm	24/10/2018	3.16	1388.86	18037.32	46776.91	21962.06	2602.41	299.46	6758.13	24582.16	305.57
location 14/28 50 cm	24/10/2018	2.80	1435.05	17422.74	43914.81	18323.26	2805.52	217.68	4661.00	19816.79	292.99
location 15/23 surface	24/10/2018	5.23	1554.31	23756.86	75500.48	42361.82	9602.14	1811.81	5903.88	32112.18	520.41
location 15/23 30 cm	24/10/2018	0.56	974.43	18647.54	62070.05	20337.56	3286.82	142.57	3724.65	21768.70	503.46
location 16/27 surface	24/10/2018	2.29	1285.24	17092.19	79679.30	12071.21	6899.78	2474.54	14109.21	34324.20	281.50
location 16/27 30 cm	24/10/2018	1.33	1253.71	10540.82	81366.82	11673.35	3440.72	922.19	11953.60	15631.19	265.70
location 17 surface	24/10/2018	28.1	7462.9	16969.3	94165.1	43855.9	14079.4	3758.6	15568.2	143859.9	466.3
location 17a 5-7cm	24/10/2018	2.10	4274.00	12421.58	95702.17	41424.50	6327.62	816.28	4394.44	28503.20	630.83
location 18 surface	24/10/2018	12.8	4232.8	9770.2	100961.4	21256.2	20448.3	2319.8	8486.2	66282.2	319.3
location 18 20cm	24/10/2018	15.7	1919.8	5566.5	51392.8	72897.4	3918.7	465.2	4164.0	34076.6	228.0
location 18 40 cm	24/10/2018	3.27	3383.66	8387.57	54226.56	20857.38	4563.30	<0.000	3413.77	32841.47	343.05
location 19/13 surface	24/10/2018	1.64	1001.41	3765.63	84892.97	38030.43	2629.38	1084.68	6111.61	9216.14	285.32
location 19/13 20cm	24/10/2018	1.24	903.07	2396.75	112559.14	13142.25	1151.08	1018.02	5530.65	4076.08	256.49
location 19/13 40 cm	24/10/2018	0.76	923.33	2062.62	137050.69	20803.05	592.39	483.71	4643.50	3165.95	240.13
location 19/13 60 cm	24/10/2018	<0.000	857.81	1946.89	164595.58	11582.35	333.64	63.49	4435.94	4518.09	340.78
location 20/17 surface	24/10/2018	5.37	5042.30	12091.57	77538.72	23271.68	13458.76	2362.63	5970.04	45874.07	363.26
location 20/17 20 cm	24/10/2018	8.08	2966.95	10314.45	96118.37	78335.76	8009.02	1425.20	6027.64	34462.92	353.95
location 20/17 40 cm	24/10/2018	13.0	2127.1	10491.3	86247.4	63051.0	3432.2	516.6	7165.8	30951.9	291.3
location 21/15 surface	24/10/2018	12.6	4005.2	20074.0	96636.9	77945.4	14783.3	3295.4	12164.6	82441.4	493.7
location 22 surface	24/10/2018	4.98	2152.27	21834.11	86429.89	67974.98	10740.04	2422.14	7798.99	47781.96	512.08
location 22a surface	15/11/2018	11.4	1159.8	33178.8	109183.0	52217.2	7765.4	2029.5	10231.9	44106.2	525.3
location 22a 30cm	15/11/2018	6.00	712.60	41203.55	102973.94	44657.26	5049.70	470.09	7382.60	21329.95	627.04
location 22a 50 cm	15/11/2018	20.4	1530.2	30785.7	168486.3	46860.9	4420.0	1072.3	10279.9	17902.3	569.4
location 23 surface	15/11/2018	32.5	5430.6	29189.9	164268.0	127756.1	12435.7	3714.1	12300.6	73455.4	518.3
location 24 surface	15/11/2018	38.3	11749.9	48274.5	261362.0	128051.6	14814.5	4539.6	14458.0	47204.5	451.1
location 24 30 cm	15/11/2018	28.6	2752.1	26352.5	296902.4	122801.1	6046.6	1454.5	7115.1	31902.4	359.1
location 24 50cm	15/11/2018	23.6	2895.4	10133.4	284305.3	67460.1	962.2	255.3	5201.5	17694.3	320.5
location 25 surface	15/11/2018	23.9	2401.4	19674.1	204113.4	151155.7	9990.1	4388.1	3473.7	28260.6	345.5
location 25 30 cm	15/11/2018	18.1	2322.1	5515.4	100970.3	141120.0	1256.9	436.0	2751.7	9749.5	144.2
location 25 50 cm	15/11/2018	18.9	2312.1	3464.4	76090.6	80692.8	741.5	<0.000	2921.8	8792.9	96.6
location 26 surface	15/11/2018	20.8	6798.3	52528.2	167494.5	117864.3	10257.5	917.0	10737.6	42768.3	562.5
location 27 30 cm	15/11/2018	19.1	2227.8	12552.4	143623.8	108027.8	949.1	90.4	4536.1	20937.2	950.5
location 28 surface	15/11/2018	20.8	1155.5	5627.2	140557.7	115026.6	2923.1	1350.5	6990.0	23327.7	774.1
location 28 20 cm	15/11/2018	16.1	691.2	3137.0	93649.0	104264.1	278.2	<0.000	2904.7	10430.5	691.8
location 31 surface	15/11/2018	21.2	2026.6	5028.7	259732.3	63140.3	9037.1	3353.1	3927.1	7967.8	388.2
location 31 25 cm	15/11/2018	22.0	5280.6	3801.1	314665.0	46442.0	1470.0	310.6	1998.8	9552.1	804.7
location 31 40cm	15/11/2018	19.8	2259.9	3421.0	262574.1	44526.3	6371.5	1233.9	2178.8	7332.4	895.3
location 32 10cm	15/11/2018	44.3	1742.2	9356.8	179734.9	90753.0	17476.4	6332.2	9965.6	12431.9	285.5
Method Blank	190122_Tofeeq	19.5	171.2	15.6	67.9	260.9	38.7	179.9	83.9	46.7	0.2

Here,

DL - Detection Limit

ND (<0.000) - Non-detect

[He] - analysis performed in He mode

[N2O] analysis performed in triple-quad using N2O as the reaction gas; '->' indicates the mass shift for the element of interest

RED - samples that are < DL

All concentrations reported in ppb (μg/L)

	DL	8.2	23	388	9.5	9.3	9.1	10	6.8	7.5	7.8
Sample Name	**Comment**	**52 Cr [He]**	**55 Mn [He]**	**56 Fe [He]**	**59 Co [He]**	**60 Ni [He]**	**65 Cu [He]**	**66 Zn [He]**	**75 -> 91 As [N2O]**	**82 -> 98 Se [N2O]**	**88 Sr [He]**
Location 1 surface	19/04/2018	112.1	13321.3	120550.8	157.0	60.0	192.7	455.1	43.1	5.8	176.9
Location 1 50 cm	19/04/2018	84.15	1309.03	50571.56	32.84	23.82	161.02	311.24	34.63	12.05	56.83
Location 1 120cm	19/04/2018	103.22	265.09	36545.23	23.53	15.91	63.07	203.06	45.46	6.83	29.94
Location 2 surface	19/04/2018	261.94	30434.83	320530.93	234.41	140.85	415.01	3261.24	245.84	12.25	507.45
Location 2 20 cm	19/04/2018	278.92	32733.84	328092.87	251.95	160.18	419.09	3708.69	137.44	9.80	660.61
location 2 40 cm	19/04/2018	247.20	14294.63	324314.64	286.61	98.88	205.56	809.57	70.89	4.67	486.44
Location 2a2 surface	19/04/2018	158.3	15156.6	182652.1	145.8	80.0	399.0	1581.7	77.8	5.8	500.8
Location 2b surface	19/04/2018	227.16	35743.80	211493.16	156.30	108.86	314.36	2441.39	140.37	9.56	334.74
Location 2b 40 cm	19/04/2018	153.29	19433.41	224729.92	293.50	50.64	107.62	528.60	66.09	4.84	257.45
Location 3 surface	19/04/2018	253.50	10386.63	293599.80	186.27	153.34	438.63	2406.00	173.52	23.04	224.98
Location 3 40 cm	19/04/2018	224.30	16038.61	294065.09	247.05	155.77	496.07	2970.38	193.73	8.52	226.00
Location 3 70 cm	19/04/2018	206.94	10970.75	247333.83	145.97	107.46	452.00	2107.09	259.79	8.60	190.34
Location 4 surface	19/04/2018	125.39	5465.13	176716.21	100.90	64.85	186.97	566.77	42.62	5.06	284.18
Location 5b surface	19/04/2018	135.54	10241.24	166076.42	105.62	91.22	247.69	892.08	45.07	2.73	443.84
Location 6 surface	19/04/2018	215.35	2558.80	167149.14	79.64	142.96	260.24	802.92	111.90	24.43	119.55
Location 6 40 cm	19/04/2018	169.38	410.73	74899.59	23.12	34.08	122.15	229.23	28.45	7.61	144.46
Location 7 surface	19/04/2018	212.21	13903.86	168893.21	134.01	110.31	348.54	859.29	118.32	16.72	216.93
Location 7 15 cm	19/04/2018	265.35	2388.25	190580.46	41.31	54.92	219.57	261.51	120.90	25.42	121.50
location 8 surface	19/04/2018	234.5	17315.7	255235.9	160.6	133.2	250.9	1790.9	90.2	4.0	373.1
location 8 40 cm	19/04/2018	194.56	14484.28	241241.24	139.90	92.18	261.26	1570.51	109.12	3.11	275.80
location 11/35 surface	24/10/2018	152.7	28146.9	233388.6	181.1	101.6	333.2	1748.7	76.4	3.5	733.7
location 11/35 20 cm	24/10/2018	135.31	6414.11	203927.86	85.83	50.54	136.41	538.76	69.61	3.65	365.30
location 12/31 surface	24/10/2018	120.06	8772.82	130458.50	103.62	59.18	169.73	466.89	31.51	3.53	327.71
location 12/31 20 cm	24/10/2018	163.95	36278.43	376024.82	858.10	35.07	107.16	315.13	22.89	2.90	139.37
location 12/31 50 cm	24/10/2018	98.36	3584.57	164552.77	88.27	39.35	111.81	273.74	40.72	4.69	212.79
location 13/29 surface	24/10/2018	135.3	13136.9	215932.5	162.1	106.3	253.0	953.9	48.3	1.9	965.2
location 13/3a/29 surface	24/10/2018	255.5	13402.0	233494.2	200.3	131.0	430.0	1305.4	62.0	7.0	459.8
location 14/28 surface	24/10/2018	149.36	15002.65	206192.60	238.05	122.44	229.38	1312.58	99.69	6.23	336.47
location 14/28 30 cm	24/10/2018	125.46	8768.09	201409.00	145.94	70.81	332.49	963.62	228.33	5.05	234.46
location 14/28 50 cm	24/10/2018	113.47	10855.56	184322.61	127.27	69.12	481.42	1146.54	323.01	5.91	186.93
location 15/23 surface	24/10/2018	198.54	13574.33	233296.43	138.31	109.71	325.53	1522.79	251.37	7.26	256.89
location 15/23 30 cm	24/10/2018	175.34	19575.27	284374.08	231.29	89.40	368.26	1283.29	292.79	5.76	205.40
location 16/27 surface	24/10/2018	124.54	4366.73	217372.19	64.99	51.05	141.68	841.66	58.75	6.74	298.96
location 16/27 30 cm	24/10/2018	121.00	2990.39	213833.93	64.79	36.71	134.77	425.99	43.81	6.58	216.46
location 17 surface	24/10/2018	123.9	16688.0	138408.1	145.2	125.4	239.7	698.4	237.2	1.8	742.2
location 17a 5-7cm	24/10/2018	163.16	12798.59	184688.47	188.27	83.55	178.96	539.88	538.91	3.80	227.42
location 18 surface	24/10/2018	111.3	11501.6	121921.9	110.7	94.9	214.6	1114.8	27.4	3.0	360.4
location 18 20cm	24/10/2018	72.3	3938.9	79567.4	67.5	41.9	106.5	343.9	24.3	1.8	164.0
location 18 40 cm	24/10/2018	91.41	7901.30	111324.78	125.91	79.18	192.95	436.71	26.38	1.16	234.01
location 19/13 surface	24/10/2018	70.49	1500.84	119869.91	41.46	33.56	142.01	276.18	31.94	5.32	67.65
location 19/13 20cm	24/10/2018	54.87	3910.86	164539.56	67.59	25.99	85.95	310.35	22.53	5.71	47.66
location 19/13 40 cm	24/10/2018	49.59	3329.51	120858.36	65.09	19.55	43.86	263.46	25.23	2.69	82.09
location 19/13 60 cm	24/10/2018	54.58	1889.90	97557.33	52.85	13.32	41.33	193.03	22.11	1.37	222.94
location 20/17 surface	24/10/2018	137.62	5988.26	121765.83	81.24	78.51	167.59	793.25	18.78	2.43	309.28
location 20/17 20 cm	24/10/2018	133.94	5255.45	142402.37	95.37	57.27	168.58	558.34	39.71	3.80	238.73
location 20/17 40 cm	24/10/2018	123.0	3560.5	131116.5	91.8	48.8	136.0	446.3	49.2	3.2	228.1
location 21/15 surface	24/10/2018	157.1	17693.6	222469.5	167.3	104.9	544.9	1824.8	125.2	5.0	565.4
location 22 surface	24/10/2018	178.55	15542.73	239164.78	121.62	85.05	394.28	2333.61	315.28	10.48	342.95
location 22a surface	15/11/2018	278.2	19806.4	343563.2	205.1	122.6	254.8	2839.0	98.8	7.9	415.9
location 22a 30cm	15/11/2018	329.03	20786.94	427570.17	314.15	157.76	218.16	1506.09	87.71	5.87	189.58
location 22a 50 cm	15/11/2018	248.5	30956.5	355959.8	296.0	125.2	263.3	1512.5	76.3	9.0	182.4
location 23 surface	15/11/2018	210.1	18683.3	236254.2	194.7	130.8	287.6	1160.9	92.2	4.6	438.4
location 24 surface	15/11/2018	152.1	8208.3	226540.1	112.8	167.9	299.4	1117.7	49.2	3.4	487.4
location 24 30 cm	15/11/2018	121.7	8206.5	213728.3	101.2	98.4	251.4	910.8	57.8	2.9	348.2
location 24 50cm	15/11/2018	69.9	3279.2	182383.0	65.6	41.8	124.5	516.2	32.6	1.6	377.6
location 25 surface	15/11/2018	92.9	9009.8	232145.5	103.1	66.1	276.1	1209.6	109.5	8.7	234.8
location 25 30 cm	15/11/2018	27.4	3505.8	163872.7	46.6	17.5	58.5	276.5	103.3	4.8	120.1
location 25 50 cm	15/11/2018	13.9	3170.9	155757.6	35.7	8.7	35.9	155.8	56.7	3.4	132.6
location 26 surface	15/11/2018	288.3	10362.8	252709.1	218.0	276.1	365.6	1982.4	84.2	2.4	433.8
location 27 30 cm	15/11/2018	172.9	6214.7	702347.6	90.0	16.6	58.2	325.5	60.9	5.8	338.7
location 28 surface	15/11/2018	189.0	21244.3	288742.5	217.5	34.4	242.9	773.1	31.4	5.2	265.3
location 28 20 cm	15/11/2018	220.3	4747.4	308360.1	141.6	16.1	211.6	325.3	15.0	1.2	237.0
location 31 surface	15/11/2018	103.3	6943.8	433796.0	31.2	24.5	106.2	462.3	42.1	5.9	113.5
location 31 25 cm	15/11/2018	85.9	2454.3	572098.4	31.8	11.5	47.6	188.8	47.8	2.6	291.2
location 31 40cm	15/11/2018	106.9	9013.2	1752244.4	35.5	8.3	48.6	221.0	131.8	2.2	174.8
location 32 10cm	15/11/2018	132.3	950.5	389903.1	50.2	42.1	224.2	574.2	59.9	2.4	322.5
Method Blank	190122_Tofeeq	0.4	<0.000	199.4	0.1	0.9	1.8	9.0	<0.000	<0.000	0.5

Here,

DL - Detection Limit

ND (<0.000) - Non-detect

[He] - analysis performed in He mode

[N2O] analysis performed in triple-quad using N2O as the reaction gas; '->' indicates the mass shift for the element of interest

RED - samples that are < DL

All concentrations reported in ppb (μg/L)

	DL	6.7	7.7	7.4	6.5	8.7	1.1	2.9	1.3
Sample Name	**Comment**	**95 Mo [He]**	**107 Ag [He]**	**111 Cd [He]**	**121 Sb [He]**	**137 Ba [He]**	**201 Hg [He]**	**207 Pb [He]**	**238 U [He]**
Location 1 surface	19/04/2018	16.1	2.3	2.9	3.5	2725.3	2.6	232.2	18.2
Location 1 50 cm	19/04/2018	12.63	1.94	2.17	2.29	2332.82	3.80	232.27	36.19
Location 1 120cm	19/04/2018	8.09	1.10	1.63	2.40	2549.13	3.05	214.20	32.63
Location 2 surface	19/04/2018	9.07	114.90	15.55	19.31	4194.50	12.77	1586.58	16.79
Location 2 20 cm	19/04/2018	7.68	95.80	16.04	17.05	5602.69	12.69	1226.91	16.18
location 2 40 cm	19/04/2018	9.20	11.13	2.55	8.04	4234.17	8.13	331.96	24.93
Location 2a2 surface	19/04/2018	7.2	70.3	8.7	6.8	2255.4	14.4	650.2	10.7
Location 2b surface	19/04/2018	7.57	57.65	13.28	10.12	2802.26	9.66	1158.41	21.31
Location 2b 40 cm	19/04/2018	6.12	5.13	1.43	3.88	3008.23	7.13	232.28	19.12
Location 3 surface	19/04/2018	10.83	157.62	12.30	25.23	2476.82	16.79	1499.02	18.80
Location 3 40 cm	19/04/2018	9.09	174.17	17.90	27.35	2608.30	16.34	2089.42	17.56
Location 3 70 cm	19/04/2018	7.40	155.21	7.34	25.36	2053.39	12.25	1902.70	12.44
Location 4 surface	19/04/2018	5.88	4.48	2.08	1.73	1127.43	2.77	335.95	19.82
Location 5b surface	19/04/2018	8.44	4.66	3.41	2.95	1406.49	1.56	520.46	9.77
Location 6 surface	19/04/2018	9.49	26.46	4.05	5.83	616.89	6.14	769.73	24.66
Location 6 40 cm	19/04/2018	4.51	3.22	0.70	2.17	443.46	2.40	255.92	25.13
Location 7 surface	19/04/2018	13.19	3.38	4.30	2.40	1177.84	3.70	394.61	12.76
Location 7 15 cm	19/04/2018	8.37	6.01	1.63	4.48	1555.69	7.85	191.82	15.68
location 8 surface	19/04/2018	5.7	39.2	6.4	6.4	1644.1	6.1	980.0	14.0
location 8 40 cm	19/04/2018	4.27	47.52	4.01	7.39	1088.12	5.16	1250.29	12.28
location 11/35 surface	24/10/2018	6.3	4.5	4.9	6.6	1763.3	3.1	297.1	11.0
location 11/35 20 cm	24/10/2018	3.88	3.03	1.44	2.46	920.40	1.96	262.47	12.53
location 12/31 surface	24/10/2018	4.96	4.24	3.57	1.39	1024.58	1.97	258.71	14.33
location 12/31 20 cm	24/10/2018	8.57	1.53	1.62	1.92	3893.47	1.61	240.56	12.41
location 12/31 50 cm	24/10/2018	4.02	5.86	1.39	1.67	964.76	2.53	253.60	16.66
location 13/29 surface	24/10/2018	5.8	2.3	3.9	2.2	1294.9	1.2	193.6	4.9
location 13/3a/29 surface	24/10/2018	7.2	13.1	6.1	10.5	3268.8	5.3	7231.6	10.7
location 14/28 surface	24/10/2018	8.39	29.16	9.94	4.80	1452.69	3.94	527.69	16.14
location 14/28 30 cm	24/10/2018	6.18	79.06	3.26	17.14	1732.46	6.62	1668.55	11.94
location 14/28 50 cm	24/10/2018	6.25	121.83	4.50	27.72	1394.32	7.45	2838.07	11.10
location 15/23 surface	24/10/2018	8.29	150.20	5.83	21.85	1759.80	7.56	1384.13	11.40
location 15/23 30 cm	24/10/2018	9.82	155.75	5.24	32.25	1770.64	9.00	2025.95	12.92
location 16/27 surface	24/10/2018	6.67	16.31	2.68	3.75	754.76	3.57	363.30	16.04
location 16/27 30 cm	24/10/2018	5.86	20.02	0.96	5.11	611.06	4.35	393.60	18.48
location 17 surface	24/10/2018	7.5	2.4	4.3	3.7	1968.3	1.2	217.7	6.4
location 17a 5-7cm	24/10/2018	10.11	3.41	2.69	8.97	1423.49	2.33	325.13	11.58
location 18 surface	24/10/2018	9.5	1.9	8.5	4.3	2310.5	1.1	460.0	19.5
location 18 20cm	24/10/2018	5.2	1.3	2.1	1.6	1002.4	1.0	430.9	12.0
location 18 40 cm	24/10/2018	7.70	0.95	3.08	2.52	1075.29	0.80	2471.88	10.08
location 19/13 surface	24/10/2018	6.73	1.41	2.23	4.11	1736.97	1.68	231.68	20.10
location 19/13 20cm	24/10/2018	9.49	2.04	1.66	2.66	3288.14	2.76	211.15	22.75
location 19/13 40 cm	24/10/2018	9.29	1.52	1.13	2.12	4396.31	3.50	208.05	27.77
location 19/13 60 cm	24/10/2018	10.68	1.07	4.46	2.05	5426.41	4.27	236.58	37.54
location 20/17 surface	24/10/2018	6.82	1.09	4.11	1.17	1339.30	1.21	202.65	11.37
location 20/17 20 cm	24/10/2018	7.45	1.84	3.03	1.49	1280.39	2.04	297.95	18.65
location 20/17 40 cm	24/10/2018	10.0	1.9	1.6	2.3	1152.6	2.1	336.9	20.1
location 21/15 surface	24/10/2018	6.4	70.1	7.1	7.2	1996.2	4.9	935.7	13.0
location 22 surface	24/10/2018	7.14	241.67	9.47	27.32	1802.31	13.96	2163.10	10.85
location 22a surface	15/11/2018	12.2	12.6	12.7	6.7	2987.1	5.1	2561.4	11.7
location 22a 30cm	15/11/2018	12.82	9.71	7.33	8.30	1832.90	4.36	2455.95	7.66
location 22a 50 cm	15/11/2018	13.9	16.7	9.9	7.2	2186.6	3.7	1528.2	9.8
location 23 surface	15/11/2018	11.7	3.5	7.7	3.5	1464.3	1.4	621.6	11.6
location 24 surface	15/11/2018	12.9	1.2	6.8	2.0	1751.2	1.3	787.9	14.7
location 24 30 cm	15/11/2018	12.0	1.3	4.6	2.3	2094.1	1.4	456.2	22.2
location 24 50cm	15/11/2018	10.2	1.0	2.0	2.6	3389.4	1.0	337.0	33.1
location 25 surface	15/11/2018	12.3	1.4	6.9	1.6	1925.9	1.7	261.5	23.3
location 25 30 cm	15/11/2018	6.1	1.0	1.2	1.0	1714.8	1.9	159.6	18.8
location 25 50 cm	15/11/2018	3.5	0.5	1.0	0.9	1871.3	1.5	150.9	17.9
location 26 surface	15/11/2018	7.3	1.9	9.8	5.1	1543.7	1.3	458.5	10.7
location 27 30 cm	15/11/2018	17.9	0.6	0.8	2.3	1800.6	3.4	291.6	15.9
location 28 surface	15/11/2018	16.8	1.3	5.2	3.8	3719.2	2.9	500.3	32.6
location 28 20 cm	15/11/2018	11.9	0.6	1.5	3.8	3736.6	2.8	408.8	42.1
location 31 surface	15/11/2018	12.3	1.5	3.7	1.4	2146.4	2.6	281.4	21.9
location 31 25 cm	15/11/2018	8.6	1.0	1.1	1.2	4318.0	2.5	206.1	34.4
location 31 40cm	15/11/2018	12.3	1.1	2.6	0.7	2501.3	2.4	234.1	25.4
location 32 10cm	15/11/2018	7.4	3.7	1.0	1.9	2370.6	2.0	624.8	31.1
Method Blank	190122_Tofeeq	0.1	<0.000	0.1	0.0	1.8	<0.000	<0.000	<0.000

Here,

DL - Detection Limit

ND (<0.000) - Non-detect

[He] - analysis performed in He mode

[N2O] analysis performed in triple-quad using N2O as the reaction gas; '->' indicates the mass shift for the element of interest

RED - samples that are < DL

All concentrations reported in ppb (μg/L)