

Trace metal dynamics in mangrove sediments within temperate estuaries

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Abstract

Mangrove sediments have a high capacity to retain organic matter because of the low mineralization processes induced by the waterlogged conditions around them. The accumulation of organic matter and deposition of fine particles within mangrove forests are favorable for anaerobic metabolic processes that produce inorganic sulphur, which has a high capacity to sequester trace metals. This means that mangrove sediments have the ability to protect surrounding environments from trace metal contamination. However, changes in redox conditions in mangrove sediments as a result of natural or anthropogenic activities may result in trace metals being released to overlying waters. The released metals from mangrove sediments are a serious environmental threat worldwide because of their persistent nature, and they tend to accumulate in estuarine food chains. Such complex dynamics of metal cycling within temperate mangroves and their effects on surrounding ecosystems require further investigation. Thus, a comprehensive field-based study on the factors influencing the redox conditions of mangrove sediments is needed to understand trace metal dynamics in these habitats, especially in temperate areas, such as New Zealand. Hence, this study aims to enhance our knowledge on the process involved in metal cycling induced by natural and anthropogenic factors in temperate mangrove sediments, which could be a useful benchmark for estuarine management in temperate regions, including New Zealand. Such estuarine management approach should consider several physical and ecological factors because the distribution of trace metals in mangrove sediments may exclusively vary on a site-by-site basis. Hence, in this study, four different mangrove stands at Mangawhai Harbour and two stands at Manukau Harbour, both located in northern New Zealand, were selected as study locations, which represent rural and urban temperate mangrove stands, respectively. The study aims to understand trace metal distributions up to 30 cm sediment depth, representing the majority of mangrove live root zone which may influence metal distribution patterns. Overall, the results indicate that organic matter highly controls trace metal cycling in mangrove sediments and the variation of organic matter within the system is influenced by several natural and anthropogenic factors. Especially, local weather pattern, fluctuations in anthropogenic inputs, and hydrographic condition are major factors controlling organic matter and trace metal distributions in these mangrove sediments. The results also revealed significant variations in trace metal levels between mangrove sediments and adjacent mudflats, which indicate that mangrove sediments have the inherent sequestering capacity. However, the results also indicate that there are possible impacts of trace metal contamination to surrounding environments during pre- and post-mangrove removal assessment. Hence, the study utilizes a unique and rare opportunity especially during the mangrove removal period to provide field-based scientific information that physical

disturbances in the mangrove ecosystem could change the habitat from a sink to a source of trace metals. In summary, the findings of the study show that mangrove sediments could act as both natural filters and secondary sources of trace metals depending on several factors influencing sediment redox conditions. Thus, mangrove ecosystems may be important agents to minimize trace metal contamination in estuarine and coastal ecosystems worldwide. Overall, the outcomes of the study provide essential scientific information on trace metal cycling in mangrove sediments, which is likely to assist with estuarine management and conservation strategies in New Zealand and worldwide. Also, the study highlights the necessity for periodic scientific assessments on trace metals in mangrove ecosystems, especially before making management decisions involving their removal in New Zealand and worldwide.

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Attestation of authorship

“I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person (except where explicitly defined in the acknowledgements), nor material which to a substantial extent has been submitted for the award of any other degree or diploma of a university or other institution of higher learning.”

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Co-author contributions

The total contribution (%) to each experimental manuscript (Chapter 2, 3, 4, 5) of this thesis are calculated based on the involvement of co-author during experimental design, field visit/ sample collection, laboratory analysis, data analysis/ interpretation, writing, and/or reviewing/ editing.

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	Laboratory analysis	
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	Laboratory analysis		
Cyril Marchand	Reviewing and editing	4	
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“Only One Earth, Care & Share”

Chapter 1. General introduction and literature review

1.1 Background

1.1.1 Global status of mangrove ecosystems

Mangroves are halophytic plants that grow in the coastal intertidal zone and predominantly found between latitude 30° N and 30° S. They also extend further north in Bermuda (32°20'N) and Japan (31°22'N) and south in Australia (38°45'S), New Zealand (38°03'S), and the east coast of South Africa (32°59'S) (Spalding et al., 1997; Giri et al., 2011). There are about 70 mangrove species worldwide within some 19 families (Spalding et al., 1997; FAO, 2007; Saint-Paul and Schneider, 2010) which inhabit a transition zone between terrestrial and coastal environments (Alongi, 2002) receiving both fresh and seawater inflows. Mangrove tree height and biomass decrease with increasing latitude and are highest in the tropics (Giri et al., 2011). Mangrove ecosystems provide vital economic and ecological benefits (Alongi, 2002) and are regarded as one of the most threatened natural habitats (Valiela et al., 2001; Gilman et al., 2006; Duke et al., 2007). Widespread recognition of this global ecological impact, and a growing appreciation of mangrove values in coastal protection, water quality, wildlife and fisheries habitats and tourism have led to increasing efforts to restore, conserve and sustainably manage mangrove areas in many countries (Field, 1999; Saenger, 2002; Lewis, 2005; Walton et al., 2006; Bosire et al., 2008).

There are few studies that have estimated the global mangrove area (Figure 1.1), and these studies are essential to understand the status of mangrove forests and their worldwide management practices. Giri et al. (2011) determined the status and distribution of global mangroves in 2000 using hybrid supervised and unsupervised digital image classification techniques. The study interpreted about 1000 archived Landsat data and estimated the global mangrove area as 137760 sq km in 118 countries and territories. The study further determined that 42% of the world's mangrove forests are located in Asia followed by Africa (20%), North and Central America (15%), Oceania (12%), and South America (11%). It has also been confirmed that 75% of mangroves are found in just 15 countries with the majority being

between 5° N and 5° S. Giri and the team’s estimation in total mangrove area was about 10% less than previously estimated by FAO (2007) for 2005. FAO (2007) made an indicative estimation in global mangrove area collecting approximately 2900 national and subnational data sets of mangrove ecosystems from 124 countries. The study used classified forest type data received from individual countries plus remote sensing data for countries that were not able to provide these details. The study estimated the global mangrove area for 2005 as 152000 sq km and concluded a loss of 20% of mangrove forests since 1980. The total area of mangroves in the world was estimated to be about 20% less than the estimation made by Spalding et al. (1997). An overall preview of global mangrove areas as reported by several authors has been illustrated in Figure 1.1 (FAO and UNEP, 1981; Saenger et al., 1983; FAO, 1994; Groombridge, 1992; Fisher and Spalding, 1993; Spalding et al., 1997; FAO, 2007; Giri et al., 2011).

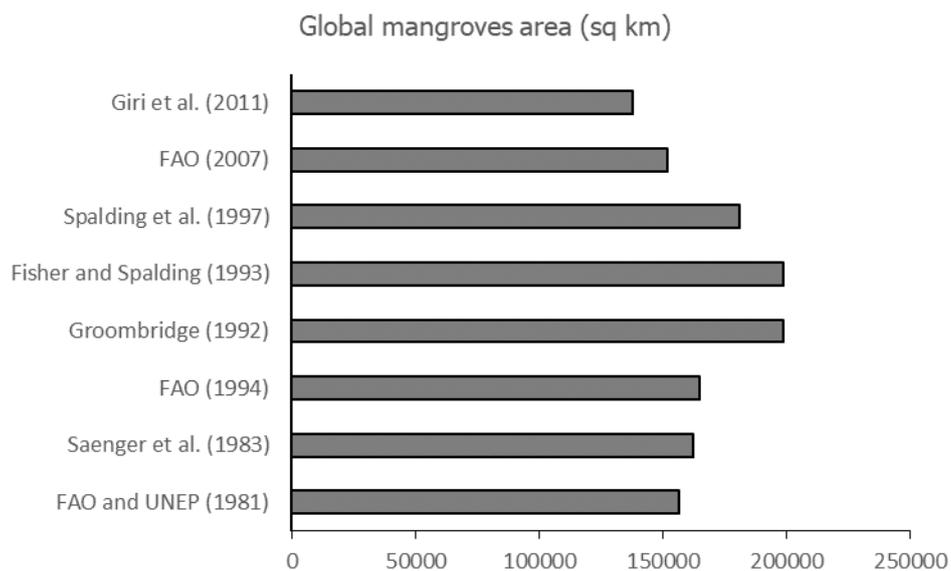


Figure 1.1. Estimated global mangrove area according to various studies.

1.1.2 Temperate mangroves

Temperate mangroves are different from tropical or subtropical mangroves in several ways, mostly due to the low number of mangrove species (Morrisey et al., 2010). In general, with increasing latitude, the number of mangrove species decreases (Giri et al., 2011). Temperate mangroves are found in parts of Australia, New Zealand, Japan, USA, Bermuda, and South

Africa. In contrast to the worldwide trend of loss of tropical mangrove forests, mangroves in several temperate regions are expanding. Such expansions of mangroves could be related to the high rate of sedimentation in temperate estuaries and their locations mostly in developed countries having effective mangrove management policies. Several studies have reported that New Zealand mangroves are expanding seawards, whereas, Australian and the US mangroves are expanding landwards (Morrisey et al., 2007; Giri and Long, 2016). The only mangrove sub-species found in New Zealand is *Avicennia marina subsp. australasica* (Walp.) J.Everett which is known locally as Manawa (Morrisey et al., 2007). They are confined to latitudinal limits of mangrove, north of about 38° S in the top half of the North Island and their rapid expansions have taken place since 1970s due to increased rates of sedimentation in the estuaries and harbours of New Zealand (Woodroffe, 1982; Morrisey et al., 2007). The local and regional councils protect mangrove habitats in New Zealand under the Resource Management Act, 1991 (Morrisey et al., 2007). However, their rapid expansion has led to concerns from local residents who call for their removal due to unpleasant odours from anoxic sediments, rodent abundances, loss of open water views and boating spaces (Harty, 2009). As a result, mangrove management approaches have increased focus on mangrove removal activities since the 1990s (Morrisey et al., 2007; Lundquist et al., 2017). Hence, a number of “Estuary Care” groups have been formed throughout the North Island of the country with a primary goal to clear mangrove habitats (Harty, 2009). Considering mangrove removal as a control measure, regional councils have been granting permission to these local groups to clear mangroves from selected areas. Contrasting these views, conservation groups maintain that removal of mangroves results in adverse impacts on estuarine and surrounding environments, including changes in sediment geochemistry (Alongi and de Carvalho, 2008; Tovilla et al., 2001). The impact assessment of such mangrove removal activities is not well-practiced in New Zealand (Morrisey et al., 2007). Hence, an in-depth study regarding the roles of mangrove to protect estuarine ecosystems is needed to address the ongoing mangrove management debates in New Zealand (Morrisey et al., 2007).

1.1.3 Organic matter in mangrove sediments

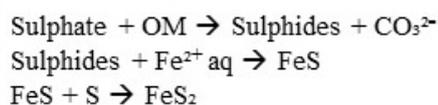
Mangroves are highly productive ecosystems having a high capacity to trap the coastal sedimentary carbon (10-15%, Alongi, 2014). Mangrove sediments are rich in organic matter because of the waterlogged condition and low mineralization processes within these estuarine and coastal habitats (Grellier et al., 2017). Mangrove litter contributes significant amounts of organic matter to the mangrove sediments and is considered a major source of organic matter in a mangrove ecosystem (Woodroffe, 1985; Ray et al., 2006). Allochthonous substances also enter the mangrove ecosystem during freshwater inputs and tidal cycles. Mangrove trees act as physical barriers to retain both autochthonous and allochthonous substances by reducing the velocity of water waves (Furukawa and Wolanski, 1996). The trees also trap fine sediments; hence organic matter rich mangrove sediments are composed of fine particles having lower sediment consolidation than surrounding estuarine sediments (Kathiresan, 2003; Avnimelech et al., 2001). Mangrove sediments are mostly inundated and anoxic. Anaerobic metabolism by fermenting and sulphate-reducing bacteria constitute a key organic matter decomposition process (Alongi, 2009). However, mangrove sediments may be occasionally oxidised due to the renewal of electron acceptors, as a result of physical disturbances during rainfall, oxygen diffusion by aerial roots and/or by infaunal borrowing and feeding activities (Clark et al., 1998). Hence, organic matter decomposition pathways in mangrove sediments are extremely complex processes, which depend upon sediment redox conditions, and either aerobic or anaerobic bacteria facilitate the degradation process (Kristensen et al., 2008).

1.1.4 Trace metals in mangrove sediments

The organic-rich mangrove sediments are mostly dominated by fine particles having a larger surface area, which creates a favourable condition to adsorb trace metals (Singh et al., 1999; Lewis et al., 2011). A close association between redox-sensitive metals, such as Iron (Fe) and Manganese (Mn), and organic matter (OM) decomposition pathways has played a crucial role in regulating trace metal cycling in mangrove ecosystems (Lacerda et al., 1999; Marchand et al., 2006). Specifically, the formation of reduced inorganic sulphur (FeS and FeS₂, Figure 1.2) during anaerobic metabolism process, enhances the capacity of mangrove sediments to sequester trace metals (Alongi, 2009). On the other hand, precipitation of Fe and Mn may occur as oxy-hydroxides in the oxic environment, which react with organic matter as electron donors, and trap trace metals (Marchand et al., 2006; Du Laing et al., 2009). In summary, organic mangrove sediments rich in iron sulphides or ferric oxy-hydroxides have inherent properties to trap several trace metals. Hence, mangrove sediments are considered sinks of trace metals (Harbison, 1986), and several studies have reported that mangrove sediments have higher levels of trace metal concentrations than adjacent estuarine sediments (Ramanathan et al., 1999; Ray et al., 2006; Jingchun et al., 2010). However, the trapped trace metals within mangrove sediments could be remobilized due to physical or biological disturbances, resulting in their dispersal into overlying waters in bioavailable forms (Du Laing et al., 2009; Lundquist et al., 2012). Such disturbances may also lead to increase sediment acidity due to sediment oxidation, and conversion of sulphides to sulphate compounds (Figure 1.2) that further dissolve to release sulphuric acid (Ponnamperuma, 1972; Clark et al., 1998; Saenger and McConchie, 2004; Marchand et al., 2012). Hence, sediment redox conditions highly control trace metal cycling in mangrove sediments. The redox cycling and association between Fe and other trace metals in marine sediments are comprehensively explained by various authors as summarized below. Marchand et al. (2006) reported that the dynamics of Fe and Mn cycling in mangrove sediments were influenced by redox conditions. Similarly, Thanh-Nho et al. (2019) concluded that the spatial variation of Fe partitioning in mangrove sediments could be a result of different redox

conditions influenced by rates of organic matter decomposition. A detailed study on pyritization in different anoxic marine sediments by Huerta-Diaz et al. (1992) found that the degree of trace metal pyritization (DTMP) of most analysed metals increased with increasing degree of pyritization (DOP). Noël et al. (2017) explained that anthropogenic pressure could create a favourable condition for oxidative dissolution of Ni-pyrite from mangrove sediments. However, the pyrite presence in the underlying anoxic layers of sediments could trap those released aqueous Ni⁺ and prevent further Ni dispersion. Hence, the input of effluent to mangrove stands could change redox conditions, which has been suggested by Marchand et al. (2011a), who stated that mangrove sediments receiving effluent inputs may act as sinks because trace metals are less mobile in this condition. Also, the findings regarding the transfer of oxide metal to organic and sulphide metal forms due to organic diagenesis processes have been reported by Marchand et al. (2012). A similar oxygenated phase of mangrove sediments was also analysed by Bourgeois et al. (2019), who found that the metal dispersion was a result of the dissolution of iron sulphides due to organic matter oxidation.

Anaerobic decomposition processes mediated by sulphate-reducing bacteria



Oxidation of sediments due to physical or biological disturbances

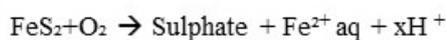


Figure 1.2. Sulphate reduction/ iron sulphides dissolution in mangrove sediments (adapted from Marchand et al., 2006).

Several other factors, such as the proportion of clay content in sediments, sediment pH, hydrographic condition, rate of effluent inputs, and/or local weather conditions directly or indirectly control the mobility and distribution trace metals in mangrove sediments (Harbison, 1986; Bruemmer et al., 1986; Lacerda et al., 1988; Tam and Wong, 1995; Gäbler, 1997).

Generally, mangrove stands near the sea (mouth of an estuary) have lower tendency to trap trace metals compared to those in upper estuary areas because of downstream dilution and energetic environments created by tidal waves (Nelson and Lamothe, 1993; Barreiro et al. 1994; Tam and Wong 1995). However, due to the presence of anthropogenic sources of contaminants at the mouth of the estuary, a complex trace metal distribution pattern may occur (Emmerson et al., 1997; Wright and Mason, 1999). Furthermore, trace metal distributions in mangrove sediments are also influenced by local weather conditions. Several studies have suggested that trace metal concentrations in mangrove sediments are lower in the summer than in the winter season (Wright and Mason, 1999). The higher atmospheric temperature in summer enhances microbial activities, and ultimately leach metals from sediments to overlying waters (Lau and Chu, 1999). On the other hand, high rainfall during the wet season enhances dispersal and dilution of surface sediments, resulting in low trace metal concentrations in mangrove sediments (Alagarsamy, 2006). Hence, the metal leaching could occur due to low sediment pH either as result of sulphide oxidation (Saenger and McConchie, 2004) or increases in organic matter decomposition rate during the summer season.

The sources of trace metals in any sedimentary environment could be either natural or anthropogenic (Förstner and Salomons, 1980; Duruibe et al., 2007). Specifically, the eroded sedimentary or igneous rocks are considered natural trace metal sources (Bianchi, 2007), which are transported to mangrove ecosystems during freshwater inputs or tidal events. On the other hand, several studies have highlighted that numerous anthropogenic sources, such as industries, mines, agriculture, urban areas, and sewage treatment plants tend to increase trace metal levels in mangrove ecosystems (Table 1.1).

Table 1.1. Studies reporting potential anthropogenic sources of trace metals in mangrove sediments.

Study location	Trace metals	Potential anthropogenic sources	Author/s
Australia	Cd, Ce, Cu, Pb, V, Mo, Ni, Zn, As	Industries, urban areas, sewage treatment plant	Mackey and Hodgkinson (1995)
Brazil	Cu, Hg, Zn	Landfill area	Machado et al. (2002)
China	Cu, Zn	Industries	Tam and Yao (1998)
China	Cd, Cu, Ni, Cr, Pb, Zn,	Industries, urban areas	Shi et al. (2019)
China	Cr, Cu, Pb, Ni, Zn	Industries	Chai et al. (2019)
Ecuador	Ag, Cd, Cu, Se, Pb	Industries	Fernández-Cadena et al. (2014)
Hong Kong	Cd, Cr, Cu, Ni, Pb, Zn	Industries, urban areas, agriculture	Tam and Wong (2000)
Iran	Al, Cd, Cu, Fe, Ni, Pb, V, Zn	Industries	Davari et al. (2010)
India	Cr, Ni, Pb, Zn	Industries, aquaculture	Singh et al. (2010)
India	Cd, Co, Cu Pb	Industries, urban areas, shipping activities	Banerjee et al. (2012)
Malaysia	Cu, Pb, Zn	Industries, agriculture, aquaculture	Praveena et al. (2010)
Senegal	Cd, Hg, Ni	Industries, urban areas	Bodin et al. (2013)

1.2 Thesis objectives and rationale

Few studies have been carried out to understand trace metal cycling in temperate mangroves, hence less local scientific data are available regarding metal dynamic in this region. As the role of a mangrove ecosystem to sequester trace metal is ubiquitous, a better understanding of several factors controlling complex trace metal dynamics in temperate mangrove sediments is needed. In light of the declining trend in global mangrove ecosystems due to permitted and non-permitted removal practices, this thesis provides a better understanding of possible consequences in sediment geochemistry due to habitat destruction or modification. Hence, the study is based on the hypothesis that a periodical scientific assessment on trace metals in mangrove ecosystems is necessary, especially before making management decisions involving their removal in New Zealand. The goals of such assessment for mangrove management are only achieved considering a range of factors (e.g. weather conditions, hydrodynamics, proximity to contaminant sources) that influence trace metal dynamics in mangrove sediments. Hence, the primary goal of the thesis is to explore the distribution patterns of trace metals in mangrove sediments and elucidate the possible site-specific physical and ecological factors controlling such distributions within a temperate region. Furthermore, the study aims to answer the following questions regarding trace metal dynamic in temperate mangrove sediments, which ultimately assist with the management and conservation strategies of temperate mangrove ecosystems.

- How does the level of organic matter (OM) in mangrove sediments influence trace metal levels?

The study aims to measure the levels of OM and trace metals in mangrove/mudflat's sedimentary profiles to understand these parameters and their interlinking.

- Is hydrodynamic condition of mangrove habitat controlling trace metal distributions in mangrove sediments?

The study aims to assess the sediment trace metal levels in different mangrove stands within an estuary having extremely different hydrodynamic conditions. The findings will elucidate how hydrodynamic conditions influence trace metal dynamic in mangrove sediments.

- Do trace metals in mangrove sediments vary seasonally?

The study aims to understand the seasonal pattern of trace metal levels in temperate mangrove sediments, especially the roles of atmospheric temperature, rainfall, and anthropogenic inputs in trace metal cycling.

- Are mangrove sediments trace metal sinks and/or sources?

The study aims to compare the trace metal levels between mangrove and adjacent mudflat sediments to understand the role of mangrove to sequester metals. Also, the study utilizes a unique and rare opportunity of before-after assessment on mangrove removal to understand whether any physical disturbances affect the sequestering capacity of mangrove sediments.

- How are trace metals distributed along sediment depths in mangrove stands?

The study aims to assess and compare the trace metal distribution in sedimentary profiles up to 30 cm depth representing the majority of mangrove (*Avicennia marina*) live root zone. This depth profile study helps to explain how several abiotic and biotic factors influence trace metal distribution in the sedimentary profiles.

- How are trace metals distributed in different mangrove stands within a harbour?

The study aims to understand the distribution pattern of trace metals in different mangrove stands located in the upper to the lower estuary. The study also aims to investigate key factors influencing trace metal variations between geographically separated urban and rural mangroves of a very contaminated harbour in New Zealand.

- Are urban mangroves playing crucial roles to protect estuarine ecosystems from metal contamination?

The study aims to elucidate whether urban mangroves protect surrounding ecosystems from metal contamination. The study also aims to highlight the need for comprehensive scientific assessments on trace metal cycling in mangrove sediments, especially before making mangrove management decisions, such as ongoing removal activities in many urban locations within northern New Zealand.

1.3 Material and methods

1.3.1 Study locations

The thesis is a collection of a series of experimental studies conducted in mangrove stands of Mangawhai Harbour (Chapter 2, 3, 4) and Manukau Harbour (Chapter 5), northern New Zealand (Figure 1.3). Detailed descriptions about study locations and sampling sites are given in the respective chapters.



Figure 1.3. Map of the northern Island of New Zealand showing study locations.

Mangawhai Harbour is located about 100 km north of Auckland City on the east coast of Kaipara District, Northland, New Zealand. The 4.6 km² estuary is surrounded by sparse

settlement and farmland, where the Tara Creek (northwest) and the Bob Creek (southeast) drain Tara volcanic and Waitemata sediments, respectively (Hulbert 2014; Valois 2017). Chapter 2 consists a study in four different mangrove stands from upper to lower estuary of Mangawhai Harbour (Jack Boyd, Molesworth, Insley, and Mangrove Island); whereas Chapter 3 and 4 are based at the Mangrove Island only. Mangrove stands at Mangawhai Harbour have been spreading in their distribution since the early 1950s and most of the expansion has taken place in the upper harbour. The aerial photograph of Mangawhai Harbour taken in 1963 indicates that the mangrove expansion at one of the study locations (Mangrove Island) started in the early 1960s (Figure 1.4). Since March 2014, mangrove removal activities at some parts of Mangawhai Harbour were started, including the mechanical removal of all trees and seedings of the 12-ha Mangrove Island (Figure 1.4) in June 2015.

Manukau Harbour is located in the south-western part of the Auckland region, which covers about 365 km² area at high tide. The main four channels (i.e. Waiuku, Papakura, Purakau, and Wairopa) drain both volcanic and sedimentary sediments to the harbour (Cromarty and Scott, 1995; Ballance, 2009). Chapter 5 consists of a study in two different mangrove stands at Manukau Harbour (Big Muddy Creek and Mangere Inlet), which represent less and most contaminated areas in the harbour, respectively. The north-east arm of the harbour is surrounded by urban areas and industries and has a long history of contamination since the 1920s (Kelly, 2008; Kelly, 2008a). The Mangere Wastewater Treatment Plant started operating since 1960 to minimise contamination to the harbour but the performance of the plant was not satisfactory as the discharges from the plant were still contaminating the waterbody (Kelly, 2008a). However, the technical improvements to the treatment plant in the late 1980s have largely helped to protect the harbour from further contaminations (Kelly, 2008a). Indeed, trace metals are persistent in nature and remain in the environment for a long time, hence their levels are still high in the Manukau Harbour as reported in several studies (Aggett and Simpson 1986; Glasby et al., 1988; Williamson and Wilcock, 1994; Reed and Gadd, 2009).



Figure 1.4. Photographs of Mangrove Island at Mangawhai Harbour. (A) Aerial photograph of Mangawhai Harbour taken on 11 October 1963 which shows small patches of mangroves at Mangrove Island (Tiaki Reference Number WA-60918-F, Whites Aviation Collection, Alexander Turnbull Library). (B) Photograph of Mangrove Island taken during the field visit on 05 June 2015 (before mangrove removal). (C) Photograph of Mangrove Island taken during the field visit on 14 June 2015 (during mangrove removal). (D) Photograph of the Island taken during the field visit on 05 September 2015 (after mangrove removal).

1.3.2 Sample collections and laboratory analyses

The detailed descriptions about sampling sites, sampling events, sampling methods, and laboratory analyses have been presented in each experimental study chapters.

In general, sediment samples were collected from four different mangrove stands and adjacent mudflats at Mangawhai Harbour from the year 2014 to 2018. Sediment samples from two different mangrove stands at Manukau Harbour were also collected in 2017 and 2018. All sediment cores were collected using a 30-cm stainless steel corer. Standard protocols and techniques were followed during sample collections, sample preservations, and laboratory analyses. A brief step-by-step preview on sample collection, sample processing, and instrumental analyses is illustrated in Figure 1.5.

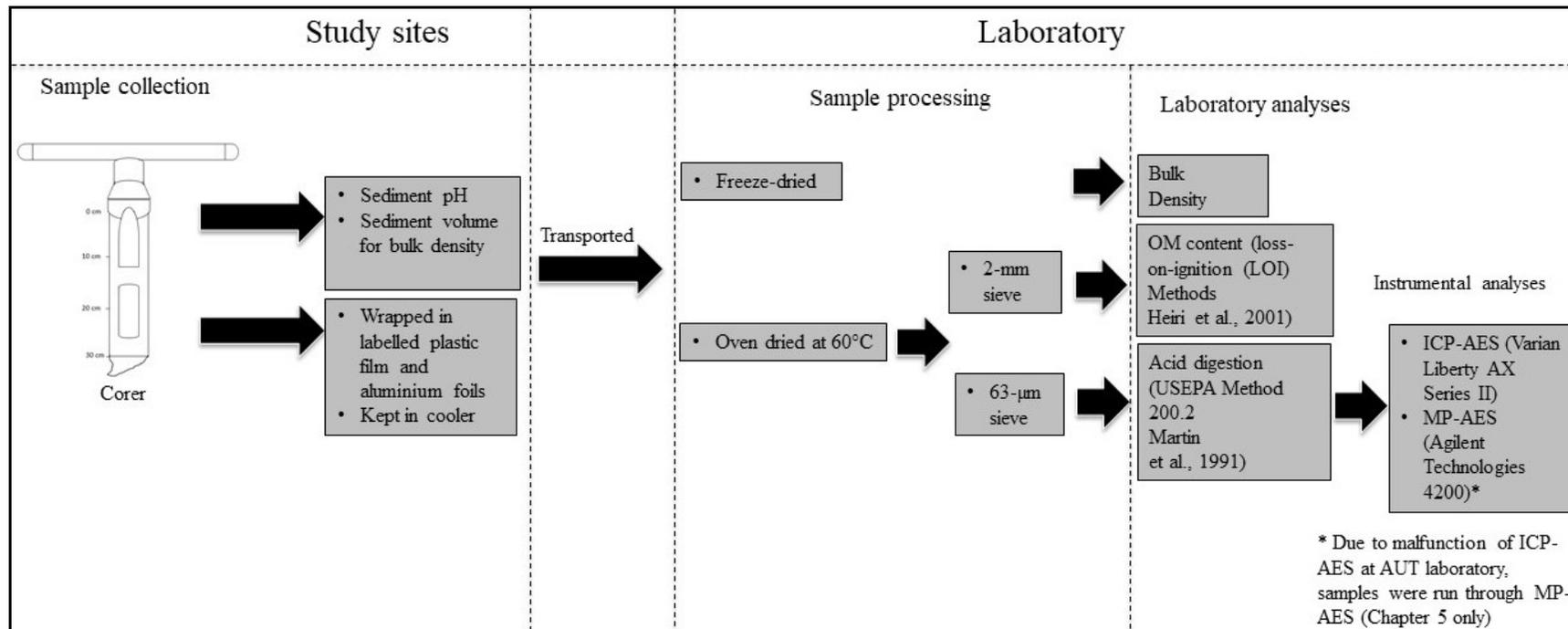


Figure 1.5. Flow chart showing a brief overview on sample collection, sample processing, and instrumental analyses.

1.4 Thesis structure

The thesis consists of six chapters, among which chapter 1 provides a general introduction and literature review on the research topics. Chapter 2, 4, and 5 are peer-reviewed published articles, whereas chapter 3 has been accepted in a peer-reviewed journal. Hence, chapter 2, 3, 4, and 5 are presented in the thesis according to their respective journal formats. Chapter 6 consists of an overall discussion, conclusion, and recommendations sections. The references of all chapters are listed at the end of the thesis following American Psychological Association (APA) format. The appendices consist of sheets of data in detail, which were used in the experimental studies of the thesis (chapter 2 to 5). An overview of the thesis structure is shown in Figure 1.6.

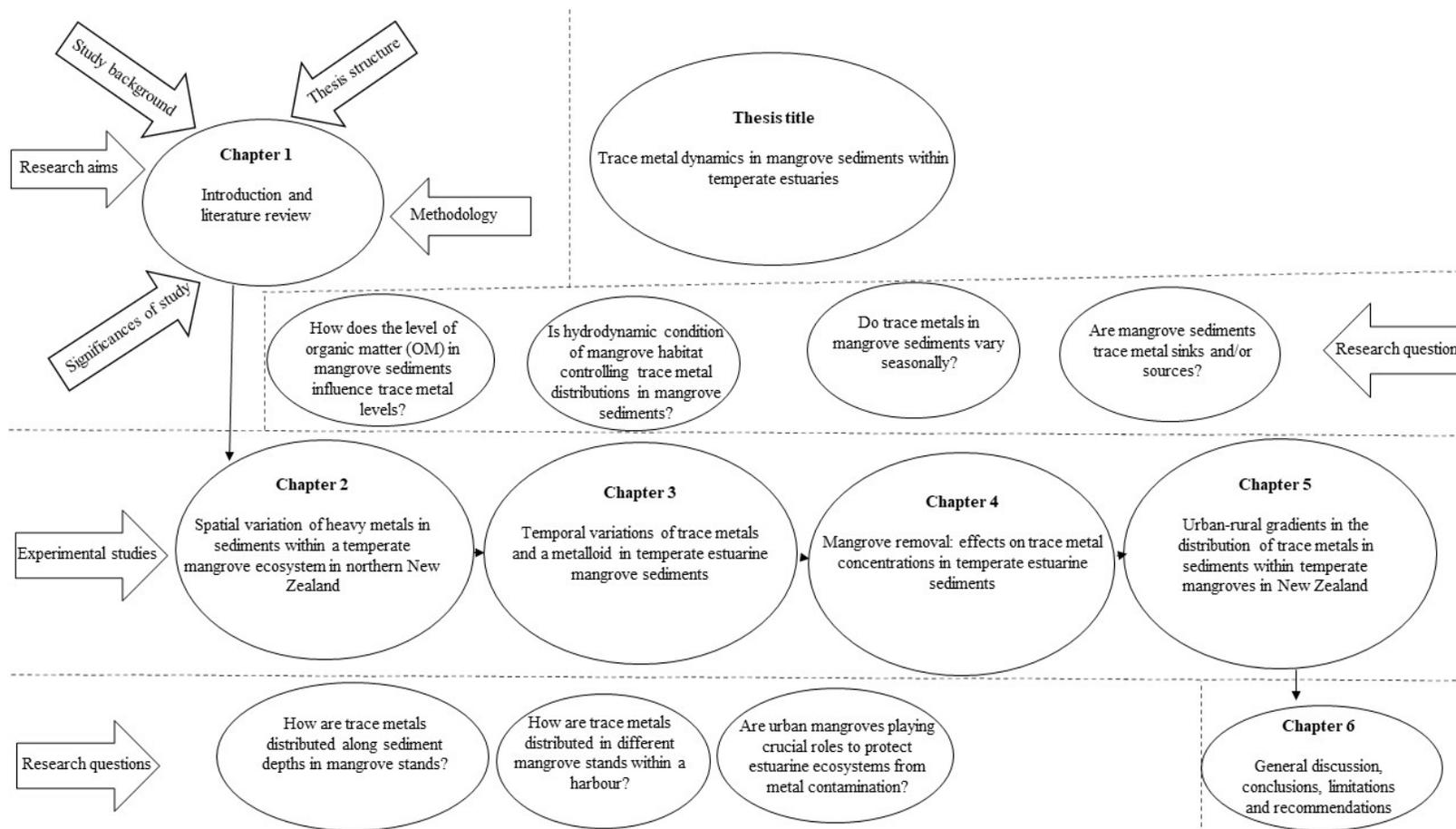


Figure 1.6. The structure of the thesis with research questions.

Chapter 2. Spatial variation of heavy metals in sediments within a temperate mangrove ecosystem in northern New Zealand

Prelude

The chapter aims to understand the patterns of the spatial distribution of trace metals in mangrove sediments from upper to lower parts of an estuary. The assessment on trace metal levels in mangrove sediments and adjacent mudflat sediments helps to elucidate the role of mangrove sediments to sequester trace metals. However, such sequestering capacity may vary from one mangrove stand to others due to several site-specific physical and ecological factors. Hence, this chapter helps to understand distribution patterns of trace metals in mangrove sediments in four different locations within an estuary, and the outcomes may assist local authorities to make mangrove management decisions on a site-by-site basis. All the contents of this chapter have been accepted and published in a peer-review journal as “Bastakoti, U., Robertson, J., & Alfaro, A. C. (2018). Spatial variation of heavy metals in sediments within a temperate mangrove ecosystem in northern New Zealand. *Marine Pollution Bulletin*, 135, 790-800.”

2.1 Abstract

Spatial dynamics of heavy metals (Cd, Cu, Fe, Pb, and Zn) and metalloid As were investigated along the sedimentary column, inside and outside mangrove stands, within the upper, middle, and lower Mangawhai Estuary, New Zealand. Organic matter contents (1.89 to 17.15%) were 10 times higher inside versus outside mangroves, and decreased sharply with depth to 30 cm. Cu, Fe, and Zn were highest in the upper estuary and Pb was highest close to a road (lower estuary), reflecting road run-off. A mangrove island (lower estuary; high energy) had lowest heavy metal and highest As concentrations (resulting from high absorption of As by the carbonate rich sediments). Most of the analysed sediment parameters were higher inside versus outside mangroves, suggesting the accumulation of organic matter and build-up capacity to buffer pollutants. Results show that mangrove stands tend to accumulate heavy metals and may act as natural filters of pollution of coastal waterways.

2.2 Introduction

Mangrove habitats are generally characterized by having fine grained sediments, high organic content and periodically inundated times, which promote high salinity and low oxygen concentrations (Lewis et al., 2011; Maiti and Chowdhury, 2013), as well as complex and active microbial fauna (Alongi, 2009). Depletion of oxygen below the upper surface sediment favours anaerobic metabolism by fermenting and sulphate-reducing bacteria, which mediate the decomposition of organic matter (Alongi, 2009). This anaerobic reduction results in most mangrove sediments having high concentrations of reduced inorganic sulphur, especially pyrite (FeS_2) and elemental sulphur (S), but negligible levels of iron monosulphide (FeS) and free sulphide (H_2S) (Alongi, 2009). The sulphide ions help trap metals, since most metal sulphides have a very low solubility. Thus, mangrove sediments may act as sinks for heavy metals by sequestering allochthonous organic matter from terrigenous sources (Lewis et al., 2011; Maiti and Chowdhury, 2013). The high adsorption capacity of mangrove sediments (Giblin et al., 1980) helps to retain organic and inorganic pollutants and stops them from infiltrating into the surrounding marine ecosystems (Maiti and Chowdhury, 2013). In turn, they also may serve as sources of heavy metals during metal remobilization. For an example, studies have shown that after mangrove removal, the physical disturbances of sulphidic sediments cause subsequent release of sulphide metals into adjacent aquatic environments (Du Laing et al., 2009; Lundquist et al., 2012). Furthermore, the oxidation of sulphides releases sulphuric acid, which leads to further leaching of metals from these disturbed sediments (Saenger and McConchie, 2004).

The level of heavy metal contamination in an ecosystem may be measured by analysing water, soil, sediment and/or biological samples. However, to determine the extent of anthropogenic impacts on a certain ecosystem, heavy metal analyses in sediments has become a standard method to elucidate this impact (Chatterjee et al., 2009). Analysis of pollutants in sediments may also provide critical information to identify anthropogenic water pollution (Senten, 1989;

Buajan and Pumijumnong, 2010), since some pollutants are absorbed by fine grained particles that may be continuously resuspended and deposited on the benthos.

Globally, mangrove ecosystems are regarded as one of the most threatened natural habitats (Gilman et al., 2006). Widespread recognition of this global ecological impact, and a growing appreciation of mangrove values in coastal protection, water quality, wildlife and fisheries habitats and tourism has led to increasing efforts to restore, conserve and sustainably manage mangrove areas in many countries (Field, 1999; Saenger, 2002; Lewis, 2005; Walton et al., 2006; Bosire et al., 2008). However, temperate mangroves may be significantly different to their tropical and sub-tropical counterparts. Indeed, recent research has found that temperate mono-specific mangrove stands in New Zealand appear to have lower species diversity and less importance in terms of breeding and nursery grounds as previously thought (Alfaro, 2006; Alfaro et al., 2006; Morrisey et al., 2007; Alfaro, 2010; Morrisey et al., 2010).

Mangrove ecosystems are often affected by anthropogenic activities, such as urban and agricultural runoff, solid waste disposal, and contaminants from effluent discharge (Wang et al., 2013). Following industrialization, unnatural quantities of metals, such as arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), lead (Pb), nickel (Ni) and zinc (Zn) have been released into the aquatic environment at various rates depending on the local conditions at a given site. Mangrove sediments are mostly fine and rich in organic matter which results in a unique capacity to accumulate heavy metals and other allochthonous materials (Harbison, 1986). Accumulated heavy metals may persist in mangrove sediments over time, resulting in bioaccumulation and biomagnification in estuarine food chains (Harbison, 1986; Burger and Gochfeld, 2003; Wang et al., 2013; Natesan et al., 2014). The level of heavy metals accumulated in mangrove sediments may vary spatially within the estuary depending on sediment characteristics, particularly organic matter content, grain size, mineral constituents or cation exchange capacity (Vertačnik et al., 1995; Tam and Wong, 2000). The understanding of these complex physico-chemical dynamics is critically important to the development of sound

conservation and management strategies of these boundary zones between land and ocean ecosystems. The aim of this research is to identify the spatial distribution of heavy metals (including the metalloid As) in sediments within Mangawhai Harbour Estuary, northern New Zealand, and to evaluate the role of mangrove habitats as sequesters of these inorganic pollutants. The contamination levels according to sediment depth profiles were assessed to determine mobility patterns of pollutants according to their vertical distribution. As, Cd, Cu, Pb, Fe, and Zn were selected for analysis in our study as these are common inorganic pollutants in the region. This information is likely to assist with coastal management and conservation strategies that require the assessment of mangroves as pollutant buffer zones.

2.3 Material and methods

2.3.1 Sampling sites

Mangawhai Harbour is located about 100 km north of Auckland, northern New Zealand (Figure 2.1). Mangroves in Mangawhai are composed of *Avicennia marina subsp. australasica* (Walp.) *J.Everett*, which is the only mangrove species found in New Zealand. Mangrove stands at Mangawhai Harbour have been spreading in their distribution since the early 1950s and most of the expansion has taken place in the upper harbour. In recent years, this expansion has been noticed in the middle and even lower reaches of the estuary, where the environment is sandy and high in energy exposure. There are two main streams in the area, including Tara Creek, which drains the Tara volcanic area west of the study area and Bob Creek located at the southern arm of the estuary and drains the Waitemata sediments. The Tara Creek is partly spring fed emerging from the basalt rocks north-west of Mangawhai.

Four different locations were selected at Mangawhai Harbour, including Mangrove Island, Jack Boyd, Insley, and Molesworth (Figure 2.1). Mangrove Island (IS) is located downstream in the middle of the lower estuary, and it has sandy sediments and mangroves of an average height of 1–2 m. Sediments were collected from five different sampling sites inside the IS mangrove stand and four outside the mangroves at this location. Jack Boyd (JB) has comparatively taller mangroves (4–5 m) with muddy sediments, and is located in the upper reaches of the estuary. At this location, there were three sampling sites inside the mangrove stand and one outside the mangroves. The Insley mangroves (IN) are located in the lower part of the estuary, where sediments are sandy in texture and mangroves are 1–2 m tall. Sediment samples were collected from nine different sampling sites inside mangroves in Insley only. Located in the mid-estuary, Molesworth (MW) has muddy to sandy sediments with an average mangrove height of 3 m. Sediments were collected from three different sampling sites inside mangroves in Molesworth. All the samples were targeted to be collected on the same day (one sampling event). However, due to time constraint and incoming tide, outside mangrove samples from Insley and

Molesworth were unable to be collected. Unfortunately, logistic constraints did not permit an even number of samples throughout the different locations.

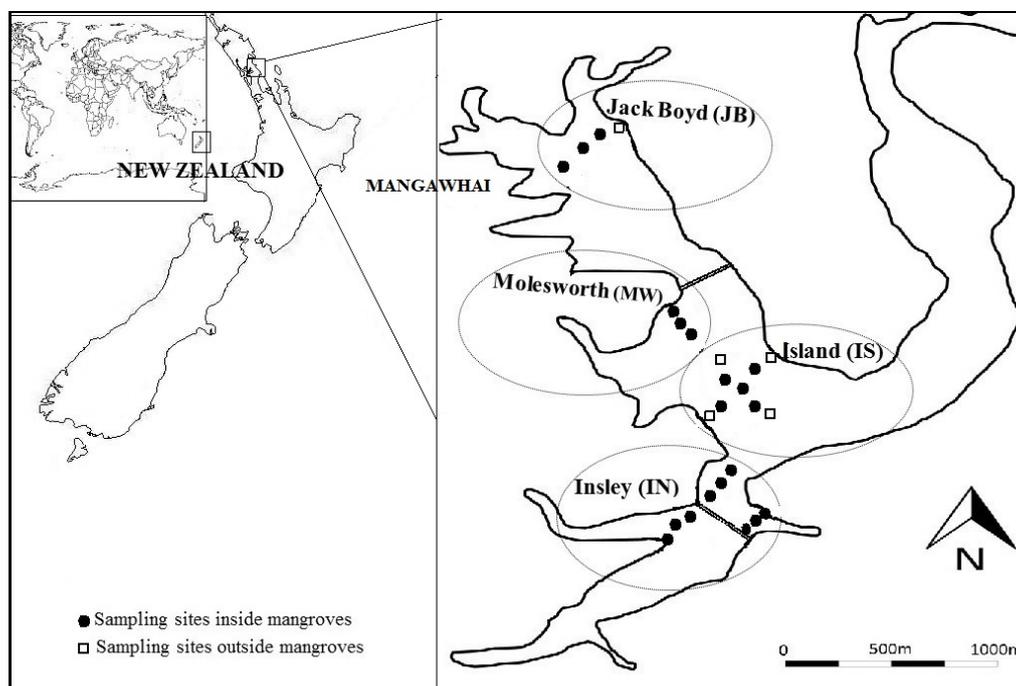


Figure 2.1. Map of the study area with all the sampling locations (IS = Mangrove Island, JB = Jack Boyd, MW = Molesworth, IN = Insley), including inside (circles) and outside (square) mangrove sites within each location at Mangawhai Harbour, New Zealand.

2.3.2 Sediment sampling

Sediment samples were collected from 3 depths, including surface (0–10 cm), middle (10–20 cm) and bottom (20–30 cm) in one sampling event (4th May 2015), except for samples from outside mangroves in IN and MW, which were not obtained. The sediments were collected using an acid washed stainless steel core sampler (30-cm long, 8-cm internal diameter). A series of core samples were collected at low tide from each sampling sites. The sediment samples were split according to the three depths in the field, and these were stored separately wrapped in labelled plastic film and aluminium foil in order to reduce gas exchange. All samples were oven dried (60 °C) and sieved (2 mm) before laboratory analyses.

Graduated syringes (50 ml) with tips cut off were used to collect sediment samples to calculate bulk density (BD). The volume of each sample from all depths was recorded. Then, the samples

were put in airtight labelled zip lock bags and transported to the laboratory to measure their fresh weights.

2.3.3 Laboratory analyses

A loss-on-ignition (LOI) method (Heiri et al., 2001) was used to determine the percentage of organic matter in the sediment samples. A 5 g scoop of soil from each sample was placed into a crucible and dried at 105 °C overnight. All samples were cooled in a desiccator, the weights were recorded and the samples were transferred to a muffle furnace and heated to 550 °C for at least 4 h. Then, the samples were cooled in a desiccator and weights were taken again. Organic matter content was calculated as the difference between the initial and final sample weights. To calculate the bulk density, sediment samples were freeze-dried for 3 days until constant weights were achieved. Then, bulk density was calculated using dry weights and volume of samples. The USEPA Method 200.2 was used for the digestion to determine the concentration of As, Cd, Cu, Fe, Pb, and Zn in sediment samples (Martin et al., 1991). All precautions were taken to avoid contamination during extraction. A total of 1.0 ± 0.01 g of dried sediment sample was placed in a beaker and 4 ml (1 + 1) HNO₃ and 10 ml of (1 + 4) HCl were added, followed by heating at about 95 °C for 30 min. The samples were allowed to cool and then transferred to a 100-ml volumetric flask and diluted with reagent water. These flasks were kept overnight for extraction so that the insoluble materials were separated. The extracted samples were measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) at the chemistry laboratory, Auckland University of Technology.

2.3.4 Statistical analyses

Individual three-way ANOVAs with Tukey tests were performed using the statistical program R to identify organic matter/heavy metal (including the metalloid As) concentration differences among habitats, locations, and depths. Also, correlation analyses were performed to determine the relationships among different sediment parameters. The correlation coefficient value (*r* value) gives a good indication of the origin of the particular metal of interest by their pairwise

comparisons. Generally, the metals accumulated in sediments from a common source are highly correlated and vice-versa (Acevedo-Figueroa et al., 2006; Desmond et al., 2012).

2.4 Results

2.4.1 Spatial variations along the estuary

Overall, OM and most of the measured elements varied significantly along different locations within the estuary ($p < 0.05$, Table 2.3), signalling the high spatial variability of these parameters. The average OM content in mangrove sediments at Mangawhai Harbour ranged from 1.89 to 17.15% (Table 2.1). The maximum values were found in the upper (JB, 17.15%) followed by lowest parts of the estuary (IN, 16.74%), where these locations receive direct effluents from the Tara and Bob creeks, respectively. Lower values were observed in the middle of the estuary (MW, 14.54%) and minimum values were observed in the Island (IS, 1.89%). Bulk density in mangrove sediments was found to be higher downstream of the estuary (IS, 1.48 g/cm³; IN, 0.84 g/cm³), lower at mid-estuary (MW, 0.75 g/cm³) and lowest at the upper reaches of the estuary (JB, 0.43 g/cm³).

Table 2.1. Average values for sediment parameters (OM = organic matter %, BD = bulk density g/cm³, As = arsenic mg/kg, Cd = cadmium mg/kg, Cu = copper mg/kg, Fe = iron mg/kg, Pb = lead mg/kg, Zn = zinc mg/kg) recorded from inside and outside of mangroves in IS, JB, IN, and MW. N/A: data not available.

	Inside						Outside					
	IS Avg	JB Avg	IN Avg	MW Avg	Min	Max	IS Avg	JB Avg	IN Avg	MW Avg	Min	Max
OM	1.89	17.15	16.74	14.54	1.89	17.15	0.88	1.30	NA	NA	0.88	1.30
BD	1.48	0.43	0.84	0.75	0.43	1.48	1.49	1.28	N/A	N/A	1.28	1.49
Fe	3573.12	11522.48	10720.92	9187.35	3573.12	11522.48	1726.88	14346.76	NA	NA	1726.88	14346.76
Cu	12.24	26.73	16.87	14.63	12.24	26.73	5.03	9.72	NA	NA	5.03	9.72
Zn	14.58	43.20	21.07	37.90	14.58	43.20	10.02	23.61	NA	NA	10.02	23.61
Pb	0.95	9.43	3.68	10.01	0.95	10.01	0.48	6.73	NA	NA	0.48	6.73
Cd	0.49	0.10	0.05	0.10	0.05	0.49	0.00	0.10	NA	NA	0.00	0.10
As	40.66	38.47	33.03	31.39	31.39	40.66	51.68	38.61	NA	NA	38.61	51.68

OM contents within the sedimentary column were highly correlated with the concentrations of Fe and Pb, whereas Cu, Zn, and Pb were highly correlated with Fe contents within the mangrove sediments (Table 2.2). Consequently, the same patterns were observed for those elements along the estuary, with higher concentrations found in the upper and lowest parts of the estuary, lower concentrations in the Middle (MW) and lowest within the Island mangrove

sediments. As and Cd concentrations were found in high concentrations in sediments poor in organic matter (Table 2.1), and were therefore present in high concentrations in the Island, with values up to 40.66 mg/kg and 0.49 mg/ kg, respectively. However, Cd concentrations were close to the limit of detection. A similar pattern was observed for bulk density, which was negatively correlated with OM.

Table 2.2. Correlation matrices of organic matter (OM), bulk density (BD) and heavy metals (including As) for inside and outside mangrove sediments in different locations at Mangawhai Harbour. Correlation values >0.7 indicate a high positive correlation and a high possibility of a common source (Acevedo-Figueroa et al., 2006; Desmond et al., 2012). Bold values indicate high positive correlations

	<i>OM</i>	<i>BD</i>	<i>Fe</i>	<i>Cu</i>	<i>Zn</i>	<i>Pb</i>	<i>Cd</i>	<i>As</i>
<i>Inside Mangroves</i>								
OM	1.0000							
BD	-0.8565	1.0000						
Fe	0.9308	-0.8501	1.0000					
Cu	0.6874	-0.7160	0.7433	1.0000				
Zn	0.6867	-0.7637	0.7059	0.7172	1.0000			
Pb	0.7039	-0.7814	0.7105	0.5953	0.9046	1.0000		
Cd	-0.8397	0.6931	-0.7609	-0.3369	-0.4908	-0.6215	1.0000	
As	-0.2099	0.0678	-0.0974	0.2790	-0.0674	-0.2130	0.5534	1.0000
<i>Outside Mangroves</i>								
OM	1.0000							
BD	-0.3798	1.0000						
Fe	0.6889	-0.5679	1.0000					
Cu	0.7565	-0.7866	0.8974	1.0000				
Zn	0.9107	-0.6466	0.7371	0.8534	1.0000			
Pb	0.9356	-0.6409	0.8263	0.9054	0.9831	1.0000		
Cd	0.7183	-0.7023	0.9824	0.9483	0.8052	0.8786	1.0000	
As	0.1301	0.2037	-0.5089	-0.2597	0.1461	-0.0059	-0.4501	1.0000

2.4.2 Spatial variations among habitats

Overall, the OM contents and associated elements measured within the sandy habitats outside mangroves indicate a similar pattern along the estuary as that observed for mangrove sediments, but the element concentrations were significantly lower (Table 2.2, Appendix 2.1). Most of the sediment parameters varied significantly along habitats (inside and outside mangroves) within

the estuary ($p < 0.05$, Table 2.3). OM contents dropped from an average of 12.58% within mangroves down to 1.09% in the border of mangrove habitats. Fe, Pb, Cu and Zn followed the same pattern and dropped from an average of 8750.97, 6.02, 17.62 and 29.19 mg/kg, respectively within mangrove sediments, down to 8036.82, 3.61, 7.37 and 16.82 mg/kg, respectively outside mangroves (Appendix 2.1). However, highest concentrations of Fe were found outside mangrove forests, with an average of 14,346.8 mg/kg within the sandy habitats in the upper part of the estuary (JB) and lowest value of 1726.88 mg/kg within Island sandy sediments (IS) compared to 11,522.48 and 3573.12 mg/kg within the same locations, but in mangrove sediments (Table 2.1). As was found in higher concentrations outside mangrove habitats (an average of 45.15 mg/kg) than inside mangroves (an average of 35.89 mg/kg), but showed the same pattern along the estuary as those observed within mangrove habitats. Bulk density of sediments showed the same pattern as higher average value of 1.39 g/cm³ was observed outside and lower average value of 0.88 g/cm³ inside mangroves. Concentrations of Cd were also found higher inside mangroves (an average of 0.19 mg/kg) than outside mangrove sediments (an average of 0.05 mg/kg) and were close to the limit of detection within all locations (Appendix 2.1).

Table 2.3. Statistical analyses (three-way ANOVAs) for all sediment characteristics (OM, As, Cd, Cu, Fe, Pb, and Zn) between two habitats (inside and outside mangroves), four locations (IS = Island; JB = Jack Boyd; IN = Insley; MW = Molesworth), and three depths (top, 0-10 cm; middle, 10-20 cm and bottom, 20-30 cm).

Source	d.f.	Mean Sq	F-value	p-value	d.f.	Mean Sq	F-value	p-value	
<i>Organic Matter (OM)</i>					<i>Iron (Fe)</i>				
Habitat (H)	1	1411.9	161.314	< 0.0012	Habitat (H)	1	208383442	36.939	0.001
Location (L)	3	650.7	74.342	< 0.001	Location (L)	3	303672324	53.831	0.001
Depth (D)	2	58.6	6.698	0.00284	Depth (D)	2	33206642	5.886	0.00536
H X S	1	369.8	42.248	0.001	H X S	1	36696117	6.505	0.01423
H X D	2	18.2	2.077	0.13715	H X D	2	6733652	1.194	0.31253
S X D	6	11.6	1.326	0.26528	S X D	6	14383608	2.55	0.03278
H X S X D	2	10	1.147	0.32672	H X S X D	2	3326780	0.59	0.55871
Residuals	45	8.8			Residuals	45	5641228		
<i>Arsenic (As)</i>					<i>Lead (Pb)</i>				
Habitat (H)	1	1865.4	16.32	0.000206	Habitat (H)	1	145.44	30.331	1.67E-06

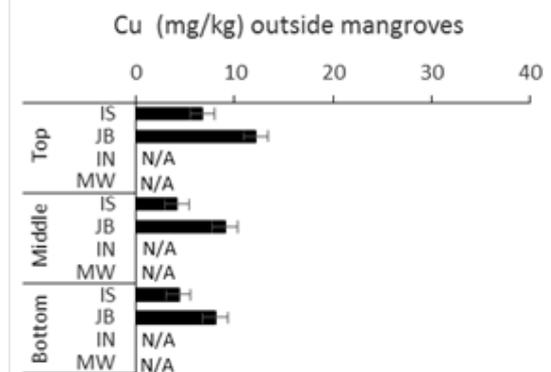
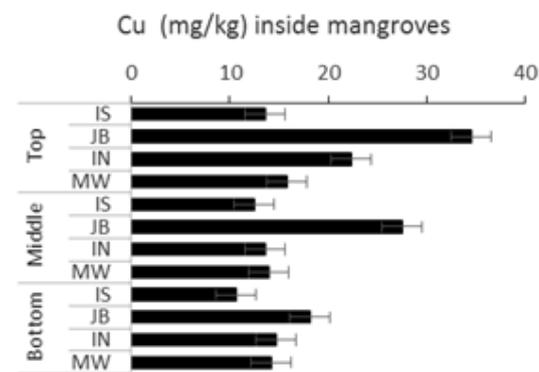
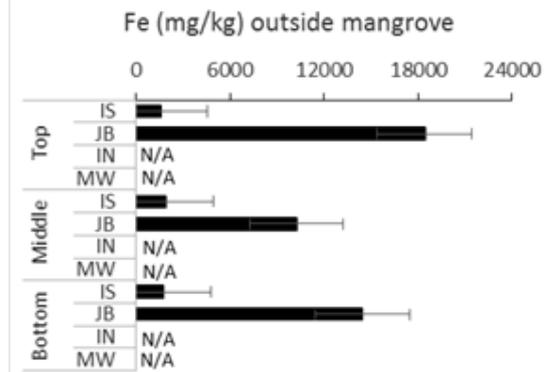
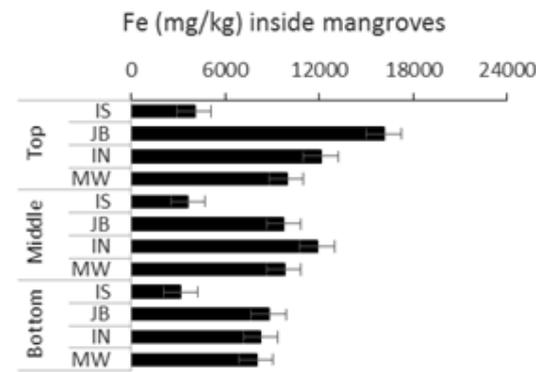
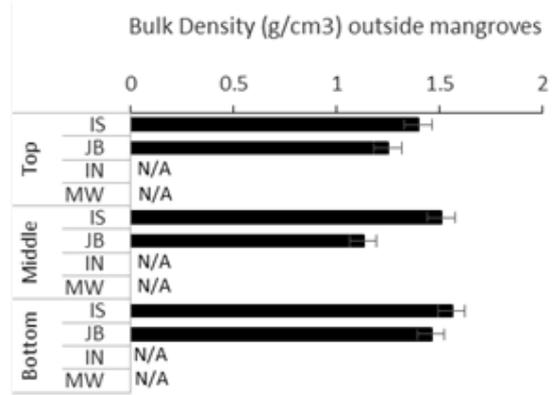
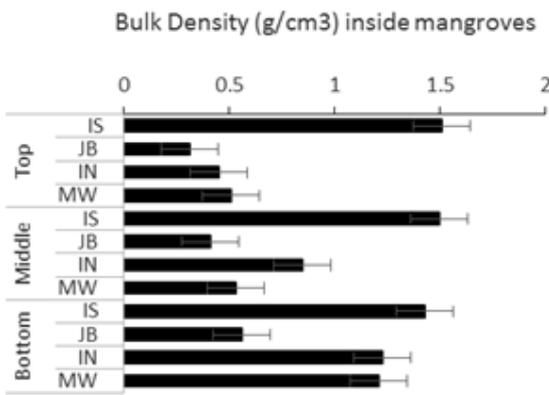
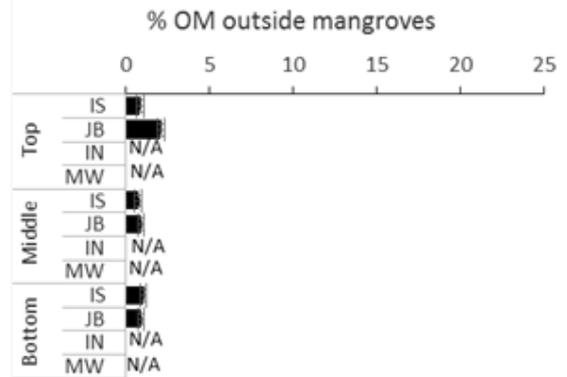
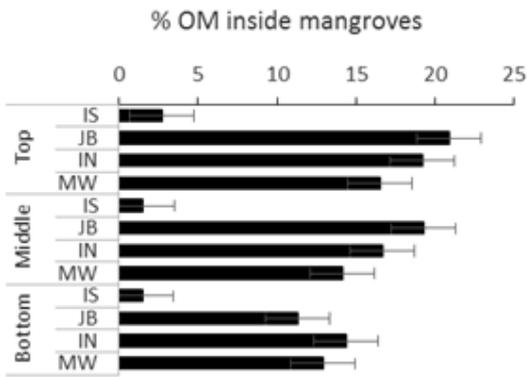
Location (L)	3	289.8	2.536	0.068616	Location (L)	3	245.54	51.208	1.49E-14
Depth (D)	2	695.6	6.086	0.004578	Depth (D)	2	21.5	4.483	0.0168
H X S	1	199	1.741	0.193658	H X S	1	8.41	1.755	0.192
H X D	2	2.6	0.023	0.977479	H X D	2	0.7	0.145	0.8654
S X D	6	47.1	0.412	0.867304	S X D	6	15.29	3.188	0.0108
H X S X					H X S X				
D	2	84.9	0.742	0.481706	D	2	4.34	0.905	0.4119
Residuals	45	114.3			Residuals	45	4.8		
<i>Cadmium (Cd)</i>					<i>Zinc (Zn)</i>				
Habitat (H)	1	0.3998	4.043	0.05037	Habitat (H)	1	2374.5	37.398	0.001
Location (L)	3	0.4531	4.581	0.00697	Location (L)	3	1992.7	31.385	0.001
Depth (D)	2	0.0125	0.127	0.88114	Depth (D)	2	482.2	7.595	0.00144
H X S	1	0.386	3.903	0.05436	H X S	1	379.7	5.981	0.01844
H X D	2	0.0026	0.026	0.97402	H X D	2	40	0.629	0.5375
S X D	6	0.0055	0.056	0.99923	S X D	6	191	3.009	0.01472
H X S X					H X S X				
D	2	0.0004	0.004	0.99597	D	2	9.6	0.151	0.86046
Residuals	45	0.0989			Residuals	45	63.5		
<i>Copper (Cu)</i>									
Habitat (H)	1	1528.6	38.434	0.001					
Location (L)	3	394.7	9.923	0.001					
Depth (D)	2	198.1	4.98	0.0111					
H X S	1	161.9	4.071	0.0496					
H X D	2	16.8	0.422	0.6583					
S X D	6	39.4	0.99	0.4434					
H X S X									
D	2	19.4	0.489	0.6166					
Residuals	45	39.8							

2.4.3 Variations along the sedimentary column

In all locations and habitats, OM and element contents tended to decrease along the sedimentary column ($p < 0.05$, Table 2.3), except for Cd which had concentrations that did not vary significantly with depth and were close to the limit of detection. Overall, the sediment bulk density (BD) inside and outside mangroves showed an increasing trend with increasing depth in most of the locations. However, its values were slightly higher on top of mangrove sediments at IS compared to the middle and bottom at same location.

Inside mangroves, the highest concentrations of OM, BD, Fe, Cu, and Zn were found on the top sediment (0–10 cm) in JB, located in the upper estuary (i.e. 20.87%, 1.51 g/cm³, 16,096.83 mg/kg, 34.53 mg/kg, and 55.23 mg/kg), whereas As was found to be highest on the top of the sediments in IS (48.52 mg/kg), and Cd was found in the intermediary horizon of IS (0.52 mg/kg). Outside mangroves, all the sediment parameters, except As and BD, were found to have higher concentrations in the top sediments (0–10 cm) of JB compared to intermediary (10–20 cm) and deepest horizons (20–30 cm) (i.e. OM: 2.1%, Fe: 18400 mg/kg, Cu: 12.12 mg/kg, Pb: 13.39 mg/kg, Zn: 41.65 mg/kg, and Cd: 0.13 mg/kg). Conversely, As and BD were found to be highest on intermediary (55.12 mg/kg) and bottom horizons (1.56 g/cm³) in the IS's sediments, respectively. In all locations and sedimentary columns, Cd concentrations did not vary significantly and were close to the limit of detection.

In all locations and habitats, OM was highest in the surface sediments and tended to decrease with increasing depth (Appendix 2.1 and Figure 2.2). All elements displayed the same decreasing gradient along the sedimentary column. The exception was Fe in the sandy habitats of the upper part of the estuary where this element was present in higher concentrations in the deepest horizon (20–30 cm) compared to the intermediary horizon (10–20 cm).



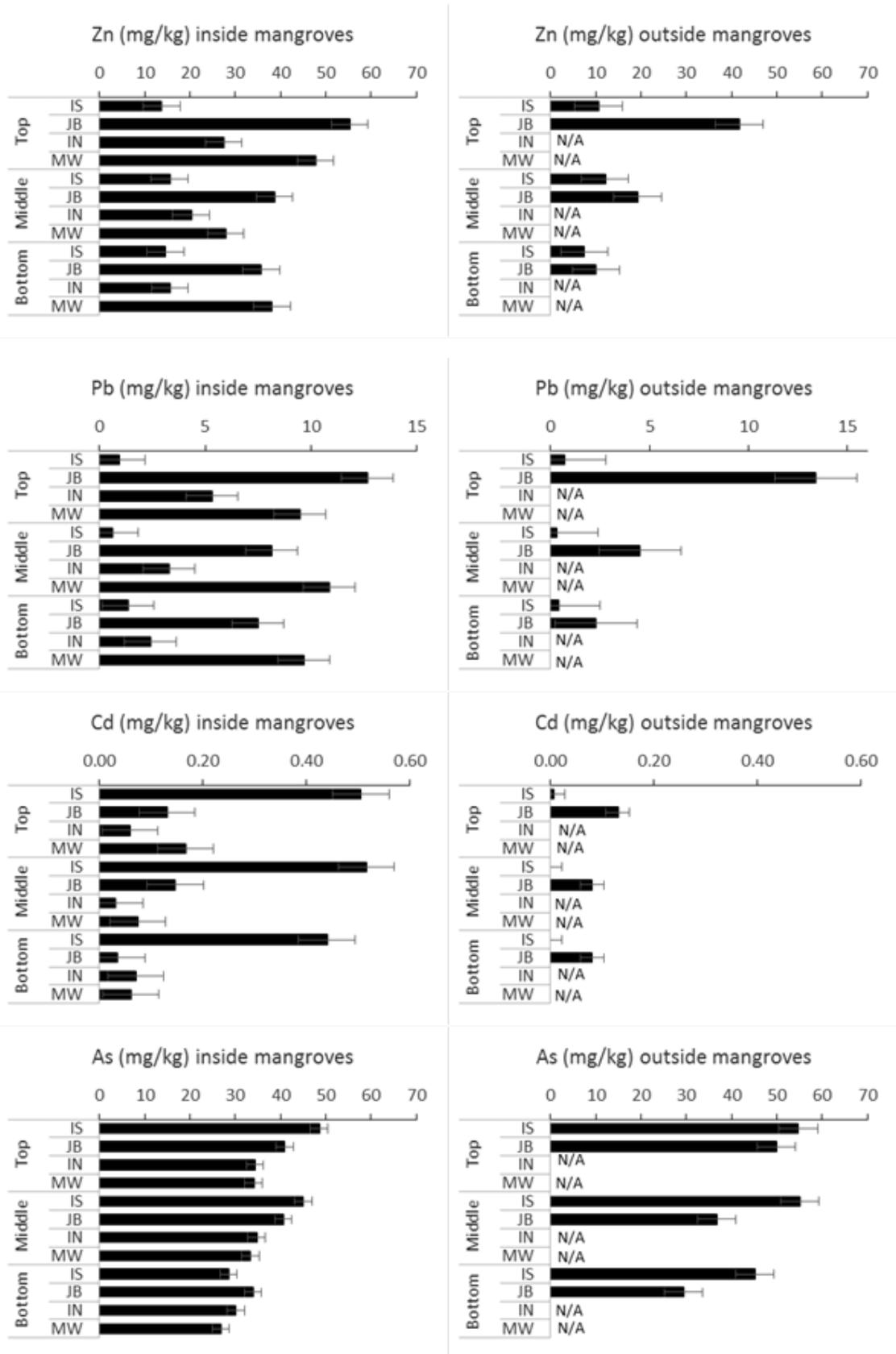


Figure 2.2. Percent organic matter (OM), Bulk Density (g/cm³) and concentrations (mg/kg) of Arsenic (As), Cadmium (Cd), Copper (Cu), Iron (Fe), Lead (Pb), and Zinc (Zn) inside (left) and outside (right) mangroves in May 2015 (Top = 0-10 cm, Middle = 10-20 cm, Bottom = 20-30 cm; IS = Mangrove Island, JB = Jack Boyd, IN = Insley, MW = Molesworth), N/A = data not available.

2.5 Discussion

The sources of OM in the estuary could be derived from creek inputs (sedimentary rock, farming activities, sewage effluents or autochthonous productions [trees, algae, benthos]) (Kristensen et al., 2008; Bouillon et al., 2008). Mangroves have very high OM storage capacity due to waterlogging conditions and low mineralization processes found in these environments. Both igneous and sedimentary rocks are natural sources of trace metals (Bianchi, 2007). Tara Creek flows through the Tara volcanic area, northwest of the estuary (Hulbert, 2014) and primarily passes through the low energy environment in the upper estuary (JB). The creek may play an important role by importing heavy metals into the estuary. The eroded rocks in its catchment area and agricultural wastes from nearby farmlands, especially pastures (Department of Land and Survey NZ, 1980), could be potential sources of heavy metals (Bianchi, 2007; Christophe et al., 2011). Furthermore, the sparse settlements in the Mangawhai area could have some contribution for heavy metal contamination in the estuary. It has been reported that Tara Creek has been contaminated by faecal matter (Valois, 2017), which indicates the existence of point source input of some pollutants into the creek due to anthropogenic activities (Bianchi, 2007). Comparatively, most of the heavy metals were found in high levels in the upper estuary, compared to other sampling locations within the estuary. This trend shows downstream dilution of heavy metals in the estuary (Nelson and Lamothe, 1993). Additionally, mangrove stands situated in the low energy environment in JB may provide favourable conditions to deposit heavy metals by trapping allochthonous substances carried by Tara Creek.

In general, organic matter is retained by trees which reduce the water wave velocity and facilitate sedimentation, whereas the outside habitats do not have this biological barrier. Also, the capacity of mangrove sediments to trap organic matter depends on their hydrographic conditions. In our study, locations such as IS (situated in the middle of the lower estuary) have coarse sediments with low organic matter. As a result of these high energy environments, the sedimentation rate is relatively low and flushing rate of autochthonous substances toward the

sea is relatively high. Conversely, low energy environments with low wave velocity, such as in JB promote the deposition and sedimentation of fine particles, leading to fine sediments with high organic content (Hulbert, 2014) and high storage capacity. Also, the capacity of sediments to trap metals by adsorption and organic matter by flocculation increases with decreased grain size (Keil et al., 1994; Haque et al., 1982; Tam and Wong, 2000; Buajan and Pumijumnong, 2010). Thus, fine particles are known to be an important substrate for metal attachment. As a result of fine sediments and high OM content in locations such as JB, the consolidation of sediments is normally low, resulting in low bulk density (Avnimelech et al., 2001). Furthermore, the age of the mangrove stand contributes to the organic matter inputs within a mangrove ecosystem. Comparative studies have found higher root biomass in the upper 40 cm of the sedimentary column in the upper part of this estuary (Tran, 2014). Several studies have reported high restitution of organic matter as dead roots and litter fall within mangrove forests (Bianchi, 2007; Kristensen et al., 2008; Bouillon et al., 2008), a characteristic that increases with the age of the mangrove stand.

Organic matter decomposition pathways and their interactions with some metals, such as Fe and Mn play an important role in trapping metals within sediments as these elements have highly redox sensitive characteristics (Lacerda et al., 1999; Marchand et al., 2006). In our study, Fe concentrations in sediments were found to be comparatively higher than other analysed elements likely due to the fact that natural Fe is more abundant in the Earth's crust than other elements (Gordon et al., 1982; Beard and Johnson, 2004; Hansel, 2017). The levels of Fe in mangrove sediments at Mangawhai are in the range of other tropical mangrove forests where total concentrations can reach up to 75,000 mg/kg in ultramafic soils (Alongi et al., 2000; Marchand et al., 2012). In general, the natural source of Fe in mangrove sediments could be due to erosion of rocks present in the coastal zone and catchments which feed the creeks that flow along the mangroves. The level of Fe concentration was found to be higher in locations fed by a creek in JB and lower in young mangrove stands and high energy environments in IS. This resulted in a very positive correlation between Fe and OM. Many studies have described the

interactions of OM and Fe and their role in decomposition pathways of organic matter and the availability of these elements in the ecosystem (Alongi et al., 1998; Alongi et al., 2000; Marchand et al., 2006; Marchand et al., 2011). In old mangrove stands exposed to low energy, the upper part of the sedimentary column is characterized by high organic content and fine particles. The *Avicennia* root system that develops in this upper horizon contributes to diffuse oxygen within the substrate, leading to a precipitation of this element as oxy-hydroxides. In the presence of high concentrations of organic matter, these oxy-hydroxides react with the organic matter as electron donors and enter the aqueous phase as dissolved Fe^{2+} . This cycle of dissolved phase within the upper profile of sediment column supports Fe to bind with other elements in refractory time frames (Marchand et al., 2006).

Most of the time, mangrove sediments are inundated, which results in sulphide ions highly influencing the binding of trace metals (e.g. Fe) in sediments (Alongi, 2009; Bianchi, 2007). In turn, Fe is known to influence the concentrations of other trace metals, such as Cu and Zn, which precipitate with iron oxy-hydroxides in suboxic sediments. Several studies have reported the precipitation of other metals (Pb) with Mn oxy-hydroxides (Lienemann et al., 1997; Zwolsman and Van Eck, 1999; Dong et al., 2000; Marchand et al., 2006; Marchand et al., 2012; Marchand et al., 2016).

Cd concentrations were close to the limit of detection and Zn followed more or less similar trends as Fe in all locations. The average concentrations of Pb were slightly higher in the mid-estuary (MW). Roads are considered to be line sources of lead pollution, even in areas away from cities (Ward et al., 1975; Collins, 1984; Stewart, 1989). A main road (Molesworth Drive) passes through the causeway in MW, which could be a line source of Pb pollution, especially in the past when gasoline used to contain Pb. Insley Street also passes through the causeway in IN. However, IN has a comparatively high energy environment, which may lead to dispersal of pollutants, resulting in comparatively lower Pb levels than MW. We can conclude that the

elevated concentrations of Pb outside mangroves in JB (upper estuary) could be due to the sampling location being close to the road where vehicles are parked.

Similar to heavy metals, the sources of As could be either natural or anthropogenic (Mandal and Suzuki, 2002). Naturally, As is present in both sedimentary and igneous rocks with average concentrations of 2 mg/kg (Mandal and Suzuki, 2002). Various researchers have reported that natural processes could be the main reason for elevated As in uncontaminated marine sediments (Reimann et al., 2009; Mirlean et al., 2011; Mirlean et al., 2013). Naturally, carbonate materials also play an important role in retaining As in marine sediments (Mirlean et al., 2013). Many marine algae, especially brown macroalgae accumulate huge amounts of As, especially during their growth stages, and this could result in elevated As in marine sediments (Fariás et al., 2007; Mirlean et al., 2011). Algae may contain arsenic at concentrations of 2000–5000 times greater than that of seawater (Nair et al., 2003). During our field work, sediment samples collected from outside mangrove stands, and especially in the Island, were rich in carbonate materials. These carbonate residues of dead calcareous organisms were mainly present on surface sediments which have the tendency to absorb more As released from algal decay (Mirlean et al., 2011). Also, the vertical dispersion of As across sediment profiles may be due to water exchange within sediment depths (Mirlean et al., 2011). The Arsenates, As (V) are the most common As species found in marine environments (Francesconi and Edmonds, 1996). In an oxidising state and low-alkalinity condition in shallow marine water, sorption of these arsenates by Fe (III) hydroxides takes place (Whalley et al., 1999; Mirlean et al., 2011). When Fe (III) hydroxides are reduced, As are released into pore water and diffuse upward to surface sediments (Mirlean et al., 2011), resulting in elevated amounts in upper sediment layers. Generally, the mobility of trace elements in sediment profiles depend on the organic matter availability, clay content, redox potential, and pH (Bruemmer et al., 1986; Gäbler, 1997). They bind strongly to organic matter, so their levels are generally found higher in organic sediments (Burone et al., 2003; Saenger and McConchie, 2004). Most of our sediment samples from inside mangrove stands and top sediment profiles were comparatively rich in OM compared to samples from outside

mangrove stands and lower sediment profile, respectively. This could have resulted in the samples from inside mangrove stands and surface sediment to enhance their tendency to attach heavy metals (Bruemmer et al., 1986) and lower migration tendency and mobility within the sediment depth. Generally, inside mangrove habitats experience low energy environments compared to outside mangroves because of the mangrove trees themselves and including pneumatophores and prop roots which attenuate energy of water flows, resulting in comparatively higher organic matter deposition and fine sediment deposition. These fine textured sediments with high organic matter content are effective sinks for heavy metals (Burone et al., 2003; Saenger and McConchie, 2004).

Overall, our study on spatial variation of heavy metals in mangrove sediments indicates that mangrove stands have a very important role in sequestering pollutants. Mangrove forests experiencing low energy environments, especially those located in upper estuary, may tend to sequester significantly higher levels of heavy metals compared to those located in the lower estuary with high energy environments. Also, significant spatial variations of heavy metals along the habitats (inside and outside mangroves) support mangroves acting as heavy metal sinks because of various sediment characteristics. Among them, sediment texture is the most important since the fine sediments of mangrove habitats have a tendency to adsorb higher amounts of heavy metals compared to coarser sediments. This is because the former has more surface area than the latter, and also due to the surface properties of clay minerals in fine sediments (Singh et al., 1999). The results in this contribution also suggest that mangrove ecosystems within Mangawhai Harbour estuary are comparatively less contaminated with heavy metals than other New Zealand estuaries, such as the Manukau Harbour (Aggett and Simpson, 1986; Glasby et al., 1988), Waitemata Harbour (Glasby et al., 1988) and Hawksbury Lagoon (Desmond et al., 2012). Mangawhai has very sparse settlements and only few small industries so the influence of anthropogenic activities to pollute the estuary may be relatively low. However, extensively settled areas, industries and heavy traffic close to other locations, such as

Manukau/Waitemata Harbours and Hawksbury Lagoon have a high likelihood to contaminate these estuaries.

Contrary to the worldwide trends of loss of mangrove forests, the expansion in New Zealand is interrelated with increased sedimentation rates in many estuaries (Morrisey et al., 2007). Expansion of mangroves along Mangawhai Harbour Estuary has been observed since the early 1950s, based on aerial photographs (Hulbert, 2014). “Mangrove management” approaches in New Zealand are basically focused on control measures by removal (Morrisey et al., 2007). Likewise in other estuaries in New Zealand, some patches of mangroves in Mangawhai Harbour have been removed. To minimise circumstances such as potential loss of biodiversity, increases in soil erosion or leaching of heavy metals from disturbed mangrove sediments, detail scientific research focusing on mangrove ecosystems, including water/sediment chemistry and geology is essential.

2.6 Conclusions

Most of the heavy metals analysed in the sediment samples were found in elevated amounts in fine textured organic sediments. Distinct spatial variations were observed along the estuary, where higher levels of heavy metals were found in the upper estuary in JB, which consisted of fine organic sediments, compared to the middle and lower estuary locations. Outside mangrove locations were mostly influenced by high energy environment due to lack of biological barriers resulting in sandy and poor organic matter sediments with low capacity to sequester heavy metals compared to inside mangrove sediments. Variation along the sedimentary column was also observed as the upper fine and rich in organic matter sediments had developed a prominent characteristic to sequester most of the heavy metals and discourage migration and mobility within the sediment depth. Contrasting the heavy metals, the metalloid, As was found in higher amounts in sediments rich in calcareous substances having high As accumulation tendency in the middle of the lower estuary (IS) and outside the mangrove sediments compared to those in the upper estuary (JB) and inside mangrove sediments, respectively. Overall, it can be concluded from our study that mangrove sediments have a unique capacity to accumulate allochthonous and autochthonous materials and can also be considered as a sink of heavy metals. Any disturbances including mangrove removal activities could change mangrove ecosystem from sink to source of heavy metals and adversely impact surrounding ecosystems.

Chapter 3. Temporal variations of trace metals and a metalloid in temperate estuarine mangrove sediments

Prelude

The chapter aims to investigate the influence of variations in weather patterns and anthropogenic inputs on trace metal concentrations in mangrove sediments. The previous experimental chapter discussed the spatial variations of trace metals between four different mangrove stands situated in upper to lower estuary, whereas this chapter provides extensive information on temporal variations of trace metals in sediments of a mangrove stand located in the middle of an estuary with unique hydrographic conditions. The findings on how weather patterns and anthropogenic inputs influence trace metal distributions are useful with the development of estuarine management and conservation strategies in New Zealand and worldwide. All the contents of this chapter have been accepted in a peer-review journal (Environmental Monitoring and Assessment) as “Bastakoti, U., Robertson, J., Bourgeois, C., Marchand, C., & Alfaro, A.C. (Accepted). Temporal variations of trace metals and a metalloid in temperate estuarine mangrove sediments.”

3.1 Abstract

Mangrove sediments are strong modulators of organic matter (OM) content and pollutant dynamics, acting both as sinks and sources of these components in estuarine and coastal areas throughout the world. In this study, we investigated the temporal dynamics of OM within temperate mangrove sediments, and their ability to sequester pollutants. Specifically, trace metals (Fe, Cu, Zn, Pb, Cd), and a metalloid (As) were measured within mangrove and mudflat sediments located in a high energy environment in Mangawhai Harbour Estuary, Northern New Zealand. Sediment cores were collected from a mangrove stand and adjacent mudflats at three depths within the sedimentary columns during different months over a year. Variations in OM and elements were compared to rainfall and temperature patterns observed during the sampling period. All element concentrations, except for those of As, were significantly higher in mangrove compared to mudflat sediments during the entire sampling period. This is consistent with the well-reported ability of mangroves to trap suspended particles and OM. In addition, we

observed a decreasing trend in trace metal concentrations with increasing sediment depth within mangrove habitats, which correlated well with decreasing OM content. Our results also suggest that most elements had different, but significant, temporal variations throughout the year, especially in mangrove sediments. Overall, the concentrations of Cu, Zn, Pb, Cd, and As in mangrove sediments increased during summer, whereas maximum concentrations of Fe and OM were observed in winter. This temporal pattern was determined to be related to OM and redox cycling as a result of changes in effluent input rates and physical/chemical environments during different seasonal temperature and rainfall patterns.

3.2 Introduction

Mangrove stands are important boundaries between terrestrial and oceanic environments, where they modulate the transport and accumulation of organic matter (OM) and pollutants through complex physicochemical and biological processes. Generally, the sediments within these habitats tend to have high OM contents and have the ability to sequester trace metals (Harbison 1986; Tam and Wong 1996; Tam and Wong 2000; Thanh-Nho et al. 2019). Indeed, most mangrove ecosystems are considered to be long-term sinks of metal contaminants (Harbison 1986; Clark et al. 1998; Alongi 2009; Noël et al. 2015; Noël et al. 2017). However, any disturbance due to natural or anthropogenic activities could release trace metals from mangrove sediments (Eggleton and Thomas 2004). Specifically, as a result of mangrove deforestation, trace metals could potentially be released to overlying waters and significantly impact surrounding organisms and ecosystems as reported in several studies (Lacerda 1998; Sandilyan and Kathiresan 2012; Sandilyan and Kathiresan 2014; Li et al. 2019). Although, the net global rate of mangrove deforestation has been significantly reduced since 2000, the deforestation rate in several regions, especially in Southeast Asia is still ongoing at an alarming rate (Spalding et al. 2010; Hamilton and Casey 2016; Feller et al. 2017), which possess high metal contamination threats.

The level of trace metal concentrations in estuarine sediments may vary spatially from the upper to the lower estuary. Many studies have reported a seaward decrease in trace metal concentrations, and such lower levels could be a result of downstream dilution of contaminants (Nelson and Lamothe 1993; Barreiro et al. 1994; Tam and Wong 1995). Such spatial variations were also observed in a previous study at Mangawhai Estuary, where low levels of trace metal concentrations were observed within mangrove stands in the lower estuary (Bastakoti et al. 2018).

Generally, temporal variations in trace metal levels in mangrove sediments are associated with both local weather pattern and rate of anthropogenic inputs. The redox cycling in estuarine

sediments could be highly influenced by atmospheric temperature and rainfall pattern, which may ultimately result the variations in trace metal levels as reported in various studies (Marchand et al. 2006; Nóbrega et al. 2013). Particularly, during the wet season, the high release of trace metal and organic carbon loads into the estuary due to surface runoff could be a potential pollution threat (Sanders et al. 2015; Thanh-Nho et al. 2018). In addition, the estuarine sediments themselves may release trace metals to overlying waters during the wet season. As a result, the levels of some trace metals in estuarine sediments during wet seasons tend to be lower than during the rest of the year (Alagarsamy 2006). Following this, the level of contamination in estuarine sediments may sharply increase in the dry season due to the continuous accumulation of trace metals from the overlying waters (Sundaramanickam et al. 2016). Several studies in estuarine sediments have suggested that trace metal concentrations increase during the dry winter season (Nwadinigwe et al., 2014; Feng et al., 2017). On the other hand, atmospheric temperature could also be associated with seasonal variations in trace metals in estuarine sediments. During the summer season, increases in atmospheric temperature may enhance the release of contaminants from sediments to overlying waters, hence lowering the sediment contamination levels (Lau and Chu 1999).

Compared to the tropical and sub-tropical mangroves, few studies have been carried out on the capacity of temperate estuarine mangrove sediments to sequester pollutants or how these processes may change among seasons (Silva et al. 1990; Bernini et al. 2010; Bastakoti et al. 2018; Bourgeois et al. 2019a). Although, some studies have investigated trace metal concentrations in New Zealand mangroves and estuaries (Glasby et al. 1988; Webster et al. 2000; Desmond et al. 2012; Abraham and Parker 2008), there is still a lack of local scientific knowledge and adequate data available regarding metal concentrations and seasonal cycling of such elements in these areas. Such comprehensive studies of trace metal cycling are solely needed in New Zealand, as the country has only one mangrove species *Avicennia marina subsp. australasica* (Walp.) J.Everett, which grows close to the latitudinal limits of their global distribution (Woodroffe 1982; Morrisey et al. 2007). Also, such studies are essential in light of

ongoing permitted and non-permitted mangrove removal practices currently taking place in New Zealand, which tend to significantly alter the sediment geochemistry of these sites (Alfaro 2010).

Thus, the aim of this study is to investigate the temporal dynamics of OM and elemental composition (Fe, Cu, Zn, Pb, Cd, and As) of sediments within depth profiles of a mangrove stand and adjacent mudflats in a temperate northern New Zealand estuary. In this study, our hypothesis is that the temporal dynamics of trace metals in mangrove and adjacent mudflat sediments are influenced by seasonal changes in effluent input, temperature, and rainfall patterns.

3.3 Methods and material

3.3.1 Study sites

The study was conducted in Mangawhai Harbour, a 4.6 km² estuary located about 100 km north of Auckland city, on the east coast of the North Island, New Zealand (Figure 3.1). Surrounded by a sparse settlement, the estuary consists of an 11-km long shallow channel with strong tidal currents (McCabe et al. 1985; Lindsay 2014; Valois 2017). The major sources of freshwater to the estuary are the Tara Creek (northwest) and the Bob Creek (southeast). These creeks drain the Tara volcanic and Waitemata sediments, respectively (Hulbert 2014; Valois 2017). The study area consists of a 12-ha island located in the middle of the lower estuary (S36° 07.001', E174° 34.829'), which is exposed to strong tidal currents. This island is colonized by *Avicennia marina* trees of 1 to 2 m in height and bordered by mudflats hosting gastropods and bivalves (Hulbert 2014). Previous studies in the estuary showed that this mangrove stand developed after 1960 on a tidal sandflat that included a calcareous layer that now lays at 25 cm depth (Hulbert 2014; Lindsay 2014). Furthermore, previous stratigraphic analyses indicate that the mangrove island and peripheral mudflats are dominated by medium-grain sediments that coarsen in the upper 10 cm, and that have the lowest OM contents of the estuary (Hulbert 2014).

In New Zealand, the warmest months are December, January, and February; whereas June, July, and August are the coldest. Mangawhai Harbour located in northern New Zealand is under a sub-tropical climate zone and experiences warm humid summers and mild wet winters (Chappell 2013; NIWA 2019). The average annual rainfall in Mangawhai area is around 1203 mm (Lindsay 2014).

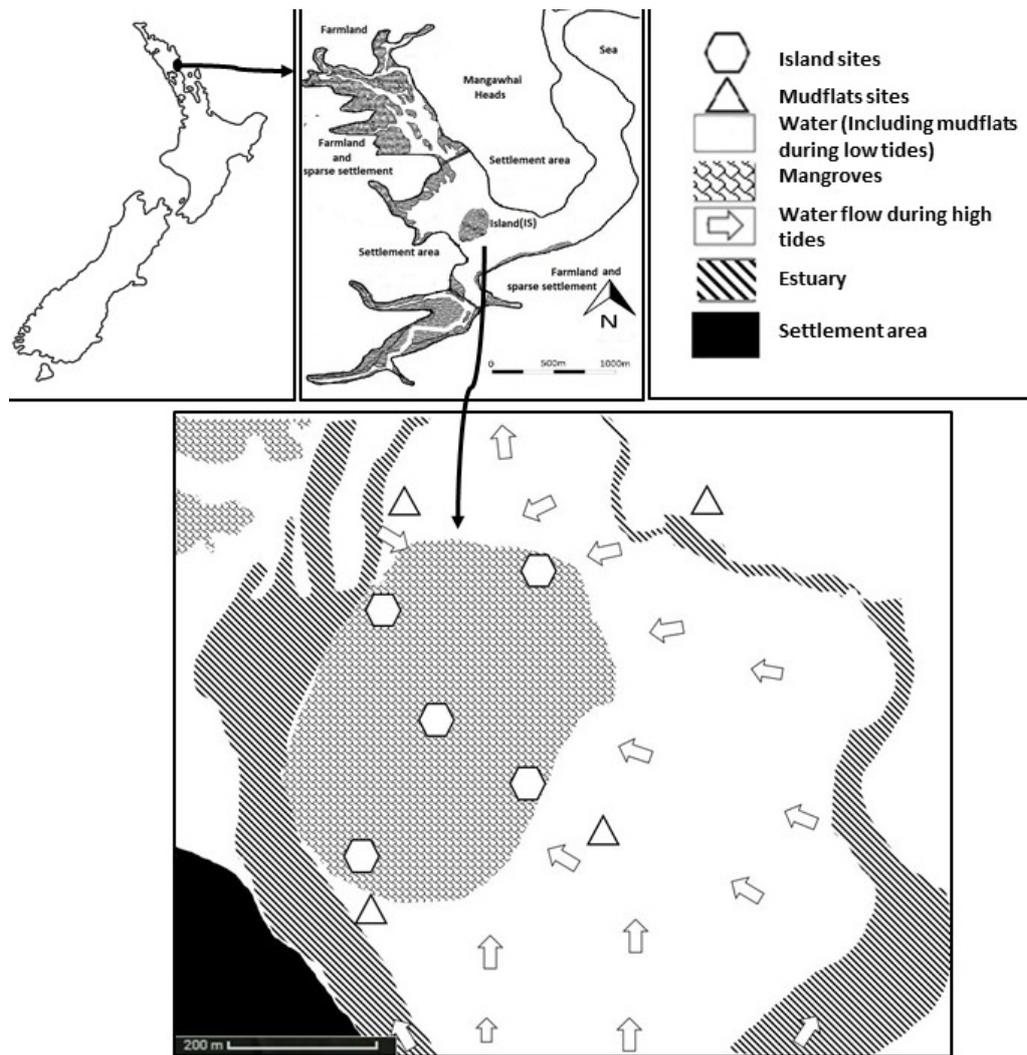


Figure 3.1. Map of the study area indicating sampling sites.

3.3.2 Sediment sampling

Sediment samples were collected from five different sites within the mangrove island and four sites outside the mangrove stand within mudflats during low tide (Figure 3.1) in post-winter (September 2014), summer (December 2014, February 2015), pre-winter (May 2015), and winter (June 2015). Visible ribbons were tied to trees at each site located inside the mangrove stand and GPS coordinates were recorded at all sites inside and outside the mangrove stand to identify the exact locations for subsequent sampling. At each sampling period and in each of the 9 locations, 30-cm core samples representing the majority of mangrove live root zone (Tran 2014) were collected in triplicates with a stainless-steel corer (30 cm long × 8 cm internal

diameter) in a circular plot of 2-m radius. Immediately after collection, the sediment samples were divided into 3 sections (surface 0-10 cm, middle 10-20 cm, and bottom 20-30 cm), labelled, wrapped in plastic film and aluminium foil and transported to the laboratory in a cooler. The samples were stored in the laboratory in the dark at -18°C until further analyses.

3.3.3 Laboratory analyses

All analyses were performed at the chemistry laboratory of the School of Science, Auckland University of Technology, Auckland, New Zealand. Prior to the analyses, all sediment samples were dried in the oven at 60°C until a constant weight was achieved. Then, the dried samples were sieved through a 2-mm stainless sieve, grounded, and split into two sub-samples. One set of sub-samples was used to measure the OM content by the loss-on-ignition (LOI) method (Heiri et al. 2001). Five grams of dry sediment were placed into a crucible and further dried at 105°C overnight. After the dried samples were cooled in a desiccator, weights were recorded again, and the samples were transferred to a muffle furnace and heated to 550°C for at least four hours. OM contents in sediment samples were calculated as the difference between dried and final furnace weights. The second set of sub-samples were sieved through a 63-µm stainless sieve prior to elemental analyses. Total recoverable elemental concentrations (Fe, Cu, Zn, Pb, Cd, As) were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Varian Liberty AX Series II, USA) after sediment digestion in 4 ml (1+1) HNO₃ and 10 mL of (1+4) HCl, following the USEPA Method 200.2 (Martin et al. 1991). For the precision of data, certified reference material (NRC-Canada HISS-1, Appendix 3.1) and several blank samples were also analysed.

3.3.4 Rainfall and temperature

Total weekly rainfall and daily average air temperature data for the sampling period were collected from Mangawhai Heads Weather Station (www.mangawhaiweather.co.nz). The weather station is close to the Mangawhai Estuary. The data were further analysed to calculate total monthly rainfall and average monthly temperature.

3.3.5 Statistical analyses

Temporal and spatial variations of OM and elements across the habitats and the depth profiles were analysed by performing three-way repeated ANOVAs (5 sampling months \times 2 habitats \times 3 depths) after testing for normality. Further comparisons were investigated using post-hoc Tukey's HSD tests. Pearson correlation coefficients (r) were used to assess the relationships between the sediment parameters themselves, and between sediment parameters and rainfall/temperature data. All tests were performed using the statistical programme R software version 3.2.1 (R Development Core Team 2017; www.r-project.org).

3.4 Results

3.4.1 Variations across habitats

Throughout the sampling period, higher mean OM content and concentrations of Fe, Cu, Zn, Pb, Cd were measured in sediment samples collected from inside the mangrove stand than in the mudflats. Overall, the mean OM content and Fe concentrations inside the mangrove sediments were about two-fold higher than in the mudflats during all sampling events (OM: 1.83 % and 0.89 %, Fe: 3561.57 mg kg⁻¹ and 1816.29 mg kg⁻¹, respectively; Appendix 3.1). Furthermore, the mean Cu and Pb concentrations in sediments inside the mangrove stand were about two-fold to three-fold higher than outside the mangrove stand (Cu: 10.15 mg kg⁻¹ and 4.24 mg kg⁻¹, Pb: 1.11 mg kg⁻¹ and 0.38 mg kg⁻¹, respectively; Appendix 3.1). Sediments inside the mangrove stand had 30% higher Zn concentrations than in the mudflats (14.64 mg kg⁻¹ and 10.15 mg kg⁻¹, respectively; Appendix 3.1). During all sampling events, Cd concentrations in mudflats were not detectable or close to the limit of detection, whereas the mean Cd concentrations inside the mangrove stand were below 1 mg kg⁻¹ (Appendix 3.1). Conversely, the mean total concentration of As in the mudflats was about 25% higher than in the mangrove stand (49.70 mg kg⁻¹ and 36.94 mg kg⁻¹, respectively; Appendix 3.1). Accordingly, all the analysed trace metals, except for Cd, were significantly positively correlated with sediments rich in OM ($r > 0.28$, $p < 0.05$; Table 3.1), whereas the concentrations of As were significantly negatively correlated with Fe, Cu, Zn, and Cd over all sampling events, depths, and habitats ($r < -0.17$, $p < 0.05$; Table 3.1). The correlations between analysed sediment parameters and temperature/rainfall data were only significant for Zn, Pb, and Cd. According to our observations, Zn was significantly positively correlated with both total monthly rainfall and average monthly temperature ($r > 0.12$, $p < 0.05$; Table 3.1), whereas, Pb and Cd were significantly positively correlated only with the average monthly temperature ($r > 0.23$, $p < 0.05$; Table 3.1).

Table 3.1. Correlation matrices with Pearson coefficient and p values of organic matter (OM) and trace metals and As for sediments from inside the mangrove stand and adjacent mudflats.

	<i>OM</i>	<i>Fe</i>	<i>Cu</i>	<i>Zn</i>	<i>Pb</i>	<i>Cd</i>	<i>As</i>	<i>Rainfall</i>	<i>Temperature</i>
OM	1								
Fe	0.778 (0.0001)	1							
Cu	0.288 (0.0001)	0.4227 (0.0001)	1						
Zn	0.434 (0.0001)	0.5548 (0.0001)	0.5323 (0.0001)	1					
Pb	0.359 (0.0001)	0.4232 (0.0001)	0.4676 (0.0001)	0.5976 (0.0001)	1				
Cd	0.062 (0.099)	0.0973 (0.0557)	0.3477 (0.0001)	0.2974 (0.0003)	0.2161 (0.0021)	1			
As	-0.032 (0.14)	-0.1811 (0.0071)	-0.1951 (0.0045)	-0.1719 (0.0097)	-0.0248 (0.159)	-0.2809 (0.0003)	1		
<i>Rainfall</i>	-0.017 (0.1695)	0.018 (0.1622)	-0.0308 (0.1404)	0.12816 (0.0274)	0.01105 (0.1792)	-0.0725 (0.0796)	-0.0673 (0.0919)	1	
<i>Temperature</i>	-0.0419 (0.1231)	-0.0408 (0.1292)	0.07816 (0.0736)	0.20278 (0.004)	0.23062 (0.0004)	0.25071 (0.0008)	0.0374 (0.1307)	0.0715 (0.0777)	1

3.4.2 Variations across depth profiles

The OM contents and concentrations of Fe, Zn, and As depicted different trends across the depth profiles inside and outside the mangrove stand over the sampling period (Figure 3.2). Indeed, the OM, Fe, Cu, Zn, and As values measured in the mangrove stand sediments varied significantly with depths (Tukey's test, $p < 0.05$), where OM, Fe, and As were higher at the surface sediments during all sampling months (Figure 3.2). A similar pattern was observed for the concentrations of Zn in the mudflats during all sampling months, except May 2015. However, the OM content and concentration of Fe remained constant across the entire depth profiles in this habitat (Tukey tests, $p > 0.05$; Figure 3.2). The values of As were recorded in the surface and intermediate sediments of mudflats were similar, and the lowest concentrations were observed in the bottom sediments during all sampling months. The other trace metals (Pb and Cd) did not show any significant variations in their concentrations across the depth profiles in either habitat (ANOVA depth tests, $p > 0.05$; Table 3.2).

3.4.3 Temporal variations

Most of the sediment parameters showed different temporal variations throughout the year. However, most of the observed significant temporal variations were much more noticeable in

the surface sediments than other depths, and in the sediment samples from inside the mangrove stand than samples collected from the mudflats. During the study period, there were non-significant seasonal variations in sediment OM content in either habitat (repeated 3-way ANOVA test, $p > 0.05$; Table 3.2). However, the mean OM concentration inside the mangrove stand was lowest in summer (December: $1.63 \pm 0.31 \text{ mg kg}^{-1}$) with an increasing trend after winter (Appendix 3.1). Specifically, in the mangrove surface sediments, the minimum mean value of OM was observed in early summer (December: $2.24 \pm 0.32 \%$), followed by a steady increase until the beginning of winter (May: $2.7 \pm 0.3 \%$), a slight decrease in early winter (June: $2.46 \pm 0.43 \%$), and a maximum value at the end of winter (September: $2.98 \pm 0.3 \%$) (Figure 3.2, Appendix 3.2).

Similar to OM, there were non-significant seasonal variations in sediment Fe concentration (repeated 3-way ANOVA test, $p > 0.05$; Table 3.2), however the mean Fe concentration inside the mangrove stand showed an increasing trend after winter (Appendix 3.1). Specifically, the mean concentration of Fe in the surface sediments of the mangrove stand decreased in early summer (December: $4054.42 \pm 316.64 \text{ mg kg}^{-1}$), with maximum concentrations throughout winter (June: $4493.71 \pm 247.03 \text{ mg kg}^{-1}$; September: $4362.73 \pm 81.13 \text{ mg kg}^{-1}$) (Figure 3.2, Appendix 3.2). However, a post-summer increase was observed in May for OM and for Fe in June. No significant seasonal trends were observed in Fe in mudflats or in any sediment depth layer in either habitat (repeated 3-way ANOVA test, $p > 0.05$; Table 3.2).

The mean Cu concentrations showed temporal variations throughout the year at all depths in mangrove sediments (repeated 3-way ANOVA test, $p < 0.05$; Table 3.2), with a general increasing trend in concentrations during the summer ($5.16 \pm 0.82 \text{ mg kg}^{-1}$ (September) to $11.01 \pm 1.32 \text{ mg kg}^{-1}$ (December) and $11.28 \pm 0.54 \text{ mg kg}^{-1}$ (February); Appendix 3.1). However, in the adjacent mudflats, the mean Cu concentrations showed a decreasing trend during the summer ($3.99 \pm 0.78 \text{ mg kg}^{-1}$ (September) to $3.85 \pm 0.53 \text{ mg kg}^{-1}$ (December) and $3.94 \pm 0.88 \text{ mg kg}^{-1}$ (February); Appendix 3.1). Such temporal variations were significant between Cu

concentrations observed in September and May during the sampling period (Tukey's test, $p < 0.05$), but the Cu values did not correlate with either temperature or rainfall ($P > 0.05$, Table 3.3).

Zn concentrations in all sediments within depths, inside and outside the mangrove stand varied significantly among months (repeated 3-way ANOVA test, $p < 0.05$; Table 3.2), but such variations were not the same in both habitats. Specifically, inside the mangrove stand, the mean Zn concentration was highest in early summer (December: $18.78 \pm 1.44 \text{ mg kg}^{-1}$) and lowest at the end of winter (September: $11.34 \pm 0.85 \text{ mg kg}^{-1}$) (Figure 3.2, Appendix 3.1). However, seasonal variations were not observed in any sediment depth profile of adjacent mudflats (Figure 3.2, Appendix 3.2). A significant positive correlation was found between Zn concentrations of all depths and atmospheric temperature in mangrove sediments ($r > 0.253$, $p < 0.05$; Table 3.3).

Table 3.2. Statistical analyses (three-way repeated ANOVAs after data transformation) for all sediment parameters (OM, As, Cd, Cu, Fe, Pb, and Zn) between two habitats (inside and outside mangrove stands), three depths (top, 0-10 cm; middle, 10-20 cm and bottom, 20-30 cm), and five months between September 2014 to June 2015.

Source	df	Sum Sq	Mean Sq	F-value	p-value	Source	df	Sum Sq	Mean Sq	F-value	p-value
<i>Organic matter (OM)</i>						<i>Iron (Fe)</i>					
Habitat (H)	1	13.79	13.79	85.62	<0.001	Habitat (H)	1	14.95	14.95	228.78	<0.001
Depth (D)	2	2.49	1.25	7.74	<0.001	Depth (D)	2	0.94	0.47	7.17	0.001
Month (M)	4	0.32	0.08	0.49	0.7384	Month (M)	4	0.29	0.07	1.11	0.3567
H X D	2	4.73	2.37	14.71	<0.001	H X D	2	0.45	0.22	3.42	0.0363
H X M	4	0.31	0.08	0.48	0.7507	H X M	4	0.28	0.07	1.09	0.3653
D X M	8	0.38	0.05	0.29	0.9664	D X M	8	0.3	0.4	0.57	0.7976
H X D X M	8	0.07	0.008	0.05	0.9999	H X D X M	8	0.15	0.02	0.28	0.9716
Residuals	105	16.91	0.16			Residuals	105	6.86	0.06		
<i>Copper (Cu)</i>						<i>Zinc (Zn)</i>					
Habitat (H)	1	19.26	19.26	35.43	<0.001	Habitat (H)	1	3.55	3.55	64.5	<0.001
Depth (D)	2	3.86	1.93	3.55	0.0322	Depth (D)	2	0.98	0.49	8.88	<0.001
Month (M)	4	6.31	1.58	2.9	0.0254	Month (M)	4	0.9	0.23	4.11	0.0039
H X D	2	0.21	0.11	0.2	0.821	H X D	2	0.23	0.11	2.1	0.1281
H X M	4	3.58	0.89	1.65	0.168	H X M	4	1.35	0.34	6.12	<0.001
D X M	8	1.17	0.14	0.27	0.9759	D X M	8	0.67	0.08	1.51	0.161
H X D X M	8	0.48	0.06	0.11	0.9988	H X D X M	8	0.34	0.04	0.76	0.6351
Residuals	105	57.08	0.54			Residuals	105	5.78	0.05		
<i>Lead (Pb)</i>						<i>Cadmium (Cd)</i>					
Habitat (H)	1	17.58	17.58	22.35	<0.001	Habitat (H)	1	1.9	1.9	20.04	<0.001
Depth (D)	2	4.63	2.32	2.94	0.057	Depth (D)	2	0.03	0.01	0.16	0.8493
Month (M)	4	9.63	2.42	3.08	0.0193	Month (M)	4	2.37	0.59	6.23	<0.001
H X D	2	4.68	2.34	2.96	0.0553	H X D	2	0.02	0.008	0.82	0.9212
H X M	4	7.81	1.95	2.49	0.0482	H X M	4	1.79	0.45	4.72	0.0015
D X M	8	4.01	0.5	0.64	0.7455	D X M	8	0.07	0.008	0.09	0.9994
H X D X M	8	6.16	0.77	0.98	0.4571	H X D X M	8	0.04	0.005	0.05	0.9999
Residuals	105	82.6	0.79			Residuals	105	9.97	0.95		
<i>Arsenic (As)</i>											
Habitat (H)	1	5424	5424	68.97	<0.001						
Depth (D)	2	5512	2756	35.04	<0.001						
Month (M)	4	924	231	2.94	0.024						

H X D	2	1807	904	11.49	<0.001
H X M	4	309	77	0.98	0.421
D X M	8	126	16	0.2	0.99
H X D X M	8	373	47	0.59	0.782
Residuals	105	8258	79		

The observed values of Pb showed significant temporal variations over the year (repeated 3-way ANOVA test, $p = 0.0193$; Table 3.2). However, such variations were significant only inside the mangrove stand (Tukey test, $p < 0.05$), and not in the adjacent mudflats (Tukey test, $p > 0.05$). Inside the mangrove stand, the mean Pb concentration was highest in summer (December: $1.65 \pm 0.25 \text{ mg kg}^{-1}$ and February: $1.65 \pm 0.57 \text{ mg kg}^{-1}$) which steadily decreased after the arrival of winter (May: $0.95 \pm 0.22 \text{ mg kg}^{-1}$, June: $0.86 \pm 0.3 \text{ mg kg}^{-1}$ and September: $0.43 \pm 0.24 \text{ mg kg}^{-1}$; Appendix 3.1). During this time, a significant positive correlation was found between Pb concentration and atmospheric temperature ($r > 0.2828$, $p < 0.05$; Table 3.3).

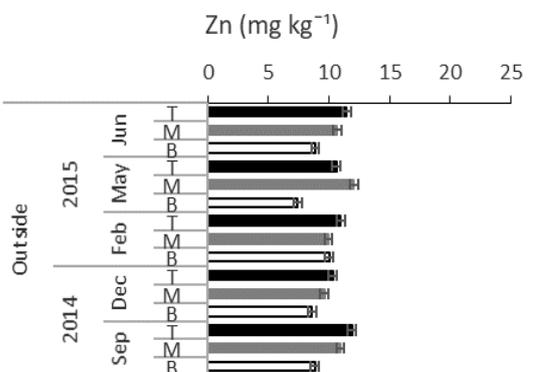
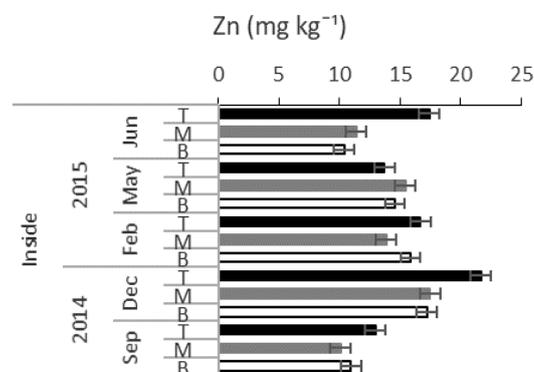
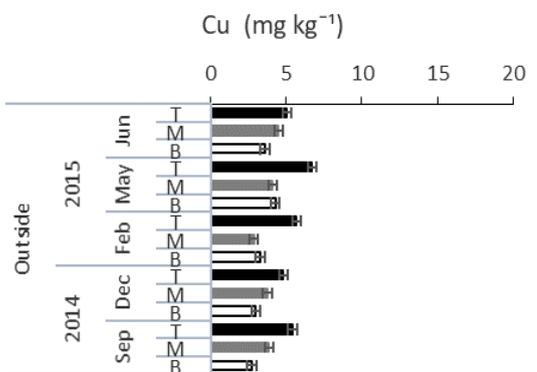
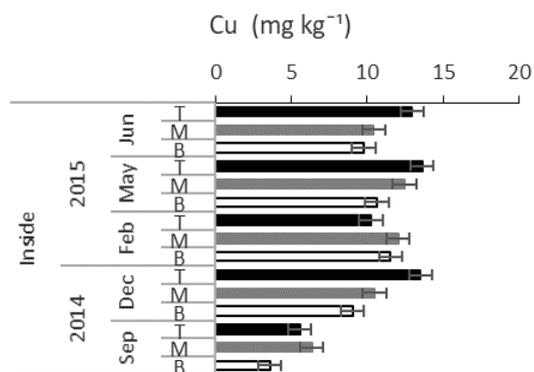
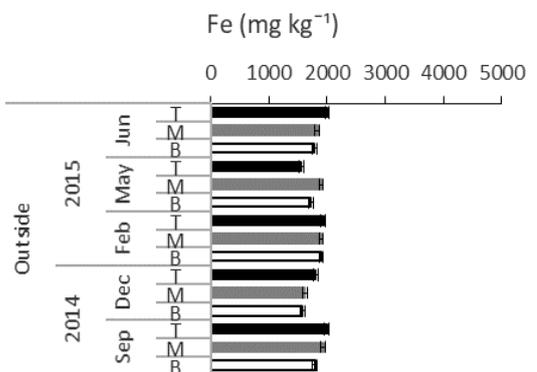
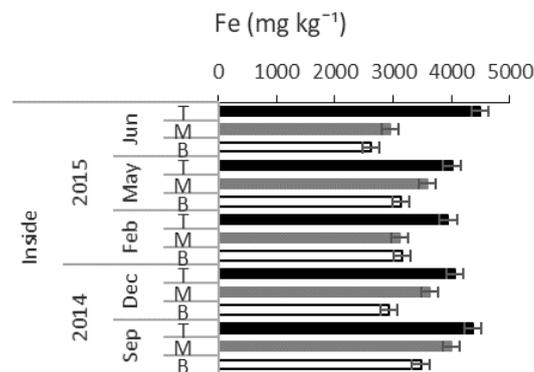
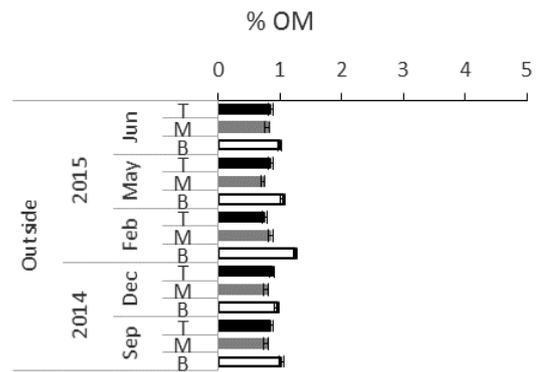
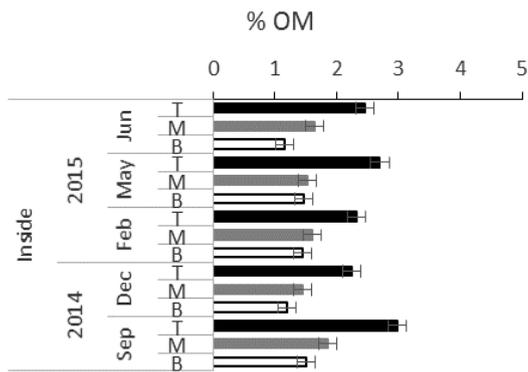
Similarly, significant temporal variations in sediment Cd concentrations were observed inside the mangrove stand at all depths (repeated 3-way ANOVA test, $p < 0.05$; Table 3.2), with Cd concentrations increasing positively and significantly with increasing atmospheric temperatures over the year ($r > 0.28$, $p < 0.05$; Table 3.3). Thus, minimum values were observed during winter (June: $0.01 \pm 0.01 \text{ mg kg}^{-1}$), while a clear increase was observed in summer (December: $0.10 \pm 0.02 \text{ mg kg}^{-1}$ and February: $0.57 \pm 0.06 \text{ mg kg}^{-1}$; Figure 3.2, Appendix 3.1). Conversely, the Cd contents measured in mudflat sediments were close to the limit of detection throughout the year, without any significant variation among depths (Figure 3.2 and Appendix 3.2).

Sediment As concentrations at all depths within both sites did not vary significantly among most of the sampling months (Tukey test, $p > 0.05$). However, the mean As concentrations inside the mangrove stand showed an increasing trend in summer (December: $34.81 \pm 7.73 \text{ mg kg}^{-1}$ and February: $40.21 \pm 6.94 \text{ mg kg}^{-1}$) and decreased in winter (September: $31.01 \pm 5.20 \text{ mg kg}^{-1}$; Appendix 3.1). However, such a season variation was not apparent in adjacent mudflats. We

did not observe any significant correlation of As with rainfall and atmospheric temperature ($p > 0.05$; Table 3.1).

Table 3.3. Correlation of sediment parameters with temperature and rainfall.

		Inside mangroves						
		OM	Fe	Cu	Zn	Pb	Cd	As
Surface								
rainfall	cor coef	0.0195	-0.098	0.0488	0.154	-0.132	-0.163	-0.104
	p-value	0.186	0.13037	0.164	0.0977	0.1023	0.0895	0.125
temp	cor coef	-0.214	-0.258	0.0706	0.253	0.489	0.4011	0.206
	p-value	0.06	0.0415	0.148	0.0441	0.00359928	0.0091	0.065
Middle								
rainfall	cor coef	-0.0779	0.32326	-0.0488	0.3479	0.2744	-0.0782	-0.285
	p-value	0.14277	0.02419	0.16296	0.017196	0.03919	0.14577	0.03339
temp	cor coef	0.1146	-0.07806	0.1406	0.3518	0.2828	0.33778	0.036
	p-value	0.11897	0.1351	0.1	0.0159	0.03499	0.02039	0.1751
Bottom								
rainfall	cor coef	0.0036	0.1122	-0.1424	0.286	0.09406	-0.049	0.06027
	p-value	0.198	0.1193	0.09878	0.03359	0.1323	0.1625	0.1565
temp	cor coef	0.0276	0.0462	0.2389	0.5007	0.4063	0.31568	0.153
	p-value	0.1769	0.1687	0.05018	0.002199	0.008598	0.02459	0.0919
Surface								
		Mudflats						
		OM	Fe	Cu	Zn	Pb	Cd	As
rainfall	cor coef	0.1436	-0.1906	-0.0088	-0.244	-0.04676	-0.334	0.07932
	p-value	0.0995	0.09138	0.1945	0.0595	0.16996	0.0315	0.14617
temp	cor coef	-0.145	-0.05	0.0036	-0.2789	-0.346	0.4178	-0.199
	p-value	0.1019	0.1657	0.1977	0.0491	0.0299	0.01319	0.08518
Middle								
rainfall	cor coef	-0.0856	-0.1557	0.01674	-0.01016	-0.02509	-0.2329	0.00346
	p-value	0.14517	0.1013	0.1887	0.19356	0.1833	0.11717	0.19836
temp	cor coef	0.06995	-0.06627	-0.2155	-0.2473	0.05488	0.3617	0.00275
	p-value	0.16116	0.15116	0.06958	0.05918	0.16276	0.03699	0.19856
Bottom								
rainfall	cor coef	-0.2314	-0.2344	-0.0716	-0.39717	-0.1196	NA	-0.0383
	p-value	0.0695	0.06378	0.15096	0.014597	0.1287	NA	0.17696
temp	cor coef	0.2513	0.02855	-0.0431	0.3714	0.18006	NA	-0.0961
	p-value	0.0581	0.18056	0.17036	0.024195	0.09058	NA	0.13477



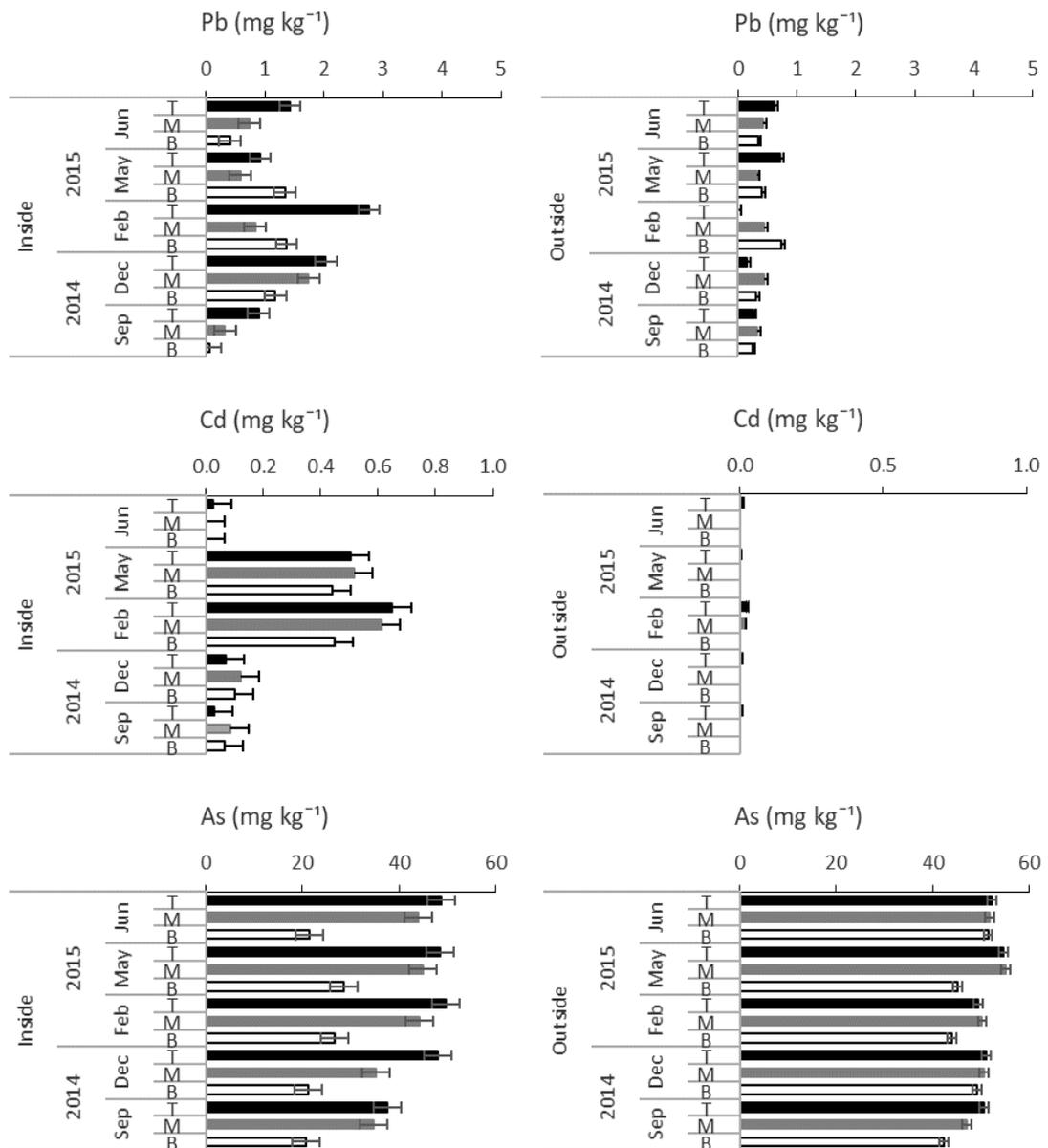


Figure 3.2. Mean (\pm SE) percent organic matter (OM) and concentrations (mg kg^{-1}) of Iron (Fe), Copper (Cu), Zinc (Zn), Lead (Pb), Cadmium (Cd), and Arsenic (As) inside (left) and outside (right) mangroves in 2014 and 2015 at Mangrove Island. Top (T) = 0-10 cm, Middle (M) = 10-20 cm, Bottom (B) = 20-30 cm.

Figure 3.3 shows the monthly and average monthly temperatures at Mangawhai during the sampling months (www.mangawhaiweather.co.nz). Throughout the sampling period, the maximum average monthly air temperature was observed in February 2015 (21.46°C) and minimum in June 2015 (14.19°C). The monthly rainfall was highest in December 2014 (143.9 mm) and lowest in June 2015 (33.6 mm). In this region, the June 2015 rainfall was below

normal, and there was an El Niño event during most of 2015, which was officially declared in June (NIWA 2014; NIWA 2015).

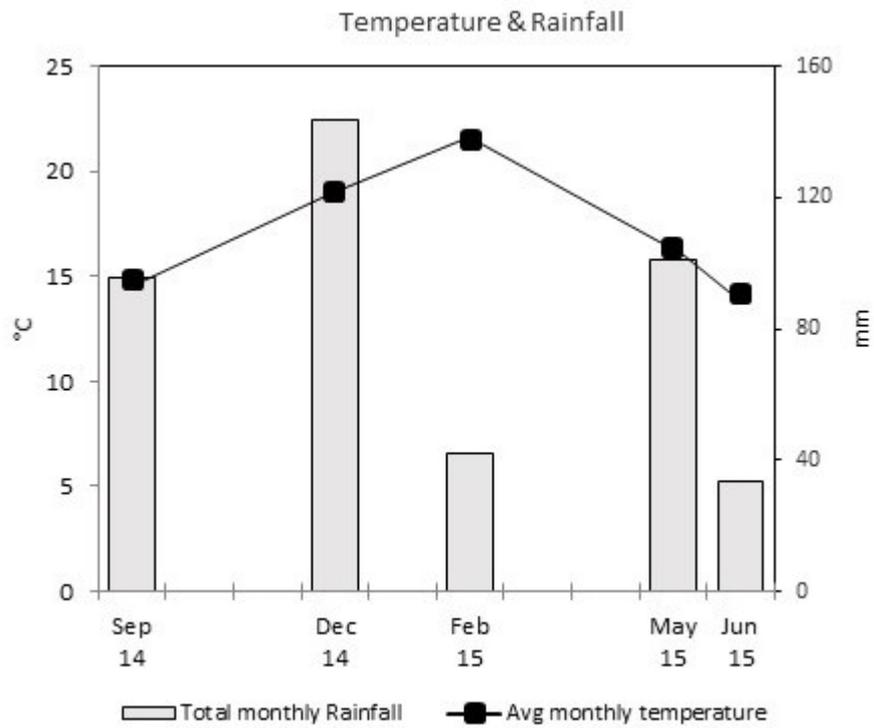


Figure 3.3. Total Monthly rainfall (mm) and average monthly air temperature (°C) between September 2014 and June 2015.

3.5 Discussion

In this study, the observed OM and trace metal levels appeared to be highly influenced by the hydrodynamic conditions of the sampling area and rate of input of contaminants into the estuary. Several authors have reported high levels of trace metal concentrations in estuarine and mangrove sediments as a result of anthropogenic pressure (Tam and Yao 1998; Tam and Wong 2000; Birch et al. 2015; Thanh-Nho et al. 2018). Indeed, trace metal contaminations in coastal environments, particularly in mangrove ecosystems, has become a serious threat worldwide due to industrialisation and urbanisation (Tam and Yao 1998). Generally, the observed levels of OM and trace metal in this study could be associated with the high hydrodynamic conditions of the Mangrove Island study area, which is situated in the middle of the lower estuary and mostly inundated during high tides. As a result, flushing and dispersal of fine particles induced by this high energy environment would have limited the accumulation of sediments. Such effects of high energy environment are noticeable throughout the island as top sediments of up to 30 cm depth are dominated by medium grained sands (Hulbert 2014). Hence, the findings of the present research indicate that the Mangrove Island study area has relatively low levels of trace metals, and this could also be associated with the relatively low anthropogenic pressure it receives from the nearby sparse settlement area having a population of only 1,329 people (Stats NZ 2013). Hence, the levels of most trace metals within Mangawhai Estuary are comparatively lower than other New Zealand estuaries (Aggett and Simpson 1986; Glasby et al. 1988; Abraham and Parker 2008; Desmond et al. 2012). In addition, the sediments at the Mangrove Island site have lower amounts of OM and trace metals compared to other mangrove stands within the estuary (Bastakoti et al. 2018), which could be a result of several factors like hydrodynamic conditions, young mangrove stand, sandy sediments, and downstream dilution.

3.5.1 Variations across habitats and depth profiles

Among the two sampling habitats in the present study, sediment OM levels inside the mangrove stand were comparatively higher than in the mudflats. In mangrove stand, mangrove trees and

pneumatophores would have not only produced OM themselves, acting as autochthonous sources (Woodroffe 1985) but also reduced flushing and dispersal of fine particles in some extent being as physical barriers (Furukawa and Wolanski 1996). However, adjacent mudflats habitat lacked such autochthonous sources and physical barriers. Likewise, sediment OM contents, we also observed higher trace metal concentrations inside the mangrove stand than the adjacent mudflats. Indeed, high organic sediments normally have high consolidation capacity to bind trace metals (Avnimelech et al. 2001; Ray et al. 2006) due to their sorptive nature (Singh et al. 1999; Burone et al. 2003; Eggleton and Thomas 2004; Förstner and Wittmann 2012). In addition, organic sediments, which are oxygen deficient are considered to provide favourable conditions for anaerobic metabolism (Alongi 2009), which leads to the formation of reduced inorganic sulphur (e.g. pyrite), which has high ability to sorb other metals (Marchand et al. 2012; Marchand et al. 2016). However, adjacent mudflats lacked such favourable conditions to sorb metals due to lower sediment OM contents and possible (sub)oxic conditions due to tidal current and a larger aerial extent than mangrove stand.

Higher levels of As concentrations in the mudflats and surface sediments versus mangrove stand and subsurface sediments are associated with carbonate materials, which have a high tendency to absorb As (Mirlean et al. 2011). A layer of calcareous substances along the eastern edge of the mangrove stand (Hulbert 2014) and their observed presence in mudflats and surface mangrove samples throughout our sampling periods would have resulted in such variations.

In our present study, sediment OM contents at Mangrove Island were found to be higher on the top layer, which could be associated with the deposition of fresh organic materials on top of the sediments. The trend of decreased OM content with increasing depth along the sedimentary column related well with the sharp decrease in concentration of some elements inside the mangrove stand. However, a similar trend was not observed in the mudflats, which appears to be related to the lower OM content within these sites. Also, due to the (sub)oxic conditions, Fe/Mn oxy(hydroxide) could be a primary binding fraction of trace metals in the mudflats (Du

Laing et al. 2009). The relatively low sediment OM concentrations at the study site are likely to be related to the young age of the mangrove stand (< 60 years old; Hulbert 2014), which has resulted in a low OM accumulation within the sediment depth profiles and a similar trend has been reported by Marchand et al. (2006) and Bourgeois et al. (2019) in young *Avicennia* forests. Additionally, the dissolution of iron oxides and/or sulphides at the redox boundary beneath the surface of the sediments could have induced an export of elements from the underlying system by the tidal action or an uptake by mangrove plants, which could have resulted in a decrease of total element concentrations in these sediments (Marchand et al. 2016; Noël et al. 2017). Sanders et al. (2015) suggested that a significant amount of trace metals, especially dissolved Fe originating from coastal wetlands (mangrove stands) could be exported to the ocean by small tidal estuaries. Beside trace metals, carbon export due to tidal pumping from mangrove sediment is also a common process as reported by Maher et al. (2013). We recommend future studies on trace metal levels in mangrove plant tissue to find bioconcentration factors, which may help to understand whether tidal action or plant uptake are major factors for trace metal export.

3.5.2 Temporal variations

Temporal trace metal dynamics at Mangawhai Estuary may result from both natural parameters and anthropogenic activities within the catchment area. The creeks, which are the main sources of freshwater to the estuary likely transport trace metals to the estuary via agricultural runoff from pasture lands (Department of Land and Survey NZ 1980; Mangawhai Community Wastewater Scheme 2015), eroded volcanic or Waitemata sediments from the catchment (Hulbert 2014; Valois 2017), and urban runoff from point or non-point sources (Valois 2007). Gray et al. (2003) and Marx et al. (2008) reported atmospheric deposition as a source of trace metals in rural areas in New Zealand. Indeed, atmospheric deposition from both intra-regional and inter-regional transports (Marx et al. 2008) could have also contributed to increase trace metal levels in Mangawhai Harbour, but future studies are needed to clarify this point. The local

weather pattern and fluctuation in effluents to the estuary could highly influence the trace metal levels in the estuarine ecosystem. Particularly, changes in local weather could have higher influences in sediment geochemistry resulting in significant temporal variations in trace metal concentrations. During our study period, the average monthly temperature ranged approximately from 14 to 22°C in Mangawhai. Interestingly, during this period, the monthly rainfall in early summer (December) and early winter (June) were above and below the normal, respectively, which is uncommon as New Zealand has dry summers and wet winters. Although several studies have suggested that concentrations of trace metals in estuarine sediments are higher during dry periods of the year (Nwadinigwe et al. 2014), lack of such a trend of temporal variations in our study could be explained by the complexity in weather patterns during the sampling events.

In our study, the observed significant temporal variations in sediment parameters were mostly apparent in surface sediments inside the mangrove stand. Such temporal variations could be a result of changes in sediment geochemistry due to diagenetic processes, and notably organic matter decomposition, influenced by rainfall, temperature, and/or changes in pollutant inputs due to human activities. Any physical disturbance, such as heavy precipitation could have significantly changed the chemical properties of the sediments (Eggleton and Thomas 2004), whereas high temperature could have enhanced the microbial activity (Alongi 1988). Both of these processes could subsequently reduce sediment pH and provide favourable conditions for the release of metals from the system. Several authors have reported similar findings regarding the release of contaminants from sediments during wet season or high temperature condition (Lau and Chu 1999; Alagarsamy 2006; Thanh-Nho et al. 2018). Specifically, during the wet season, rainfall may create oxic conditions in mangrove sediments due to the renewal of electron acceptor and this may result in the dissolution of sulphur minerals, releasing metals into porewaters. Hence, sediment remobilising activities could enhance the release of trace metals from estuarine sediments (Vidal-Durà et al. 2018). Furthermore, metals may also be released as

a result of higher water levels in the estuary during rainfall, which eventually increase the intensity of tidal flushing due to a higher energy environment.

Overall, the mean OM content in mangrove sediments was lowest in summer with an increasing trend after winter, but such a variation was not statistically significant. Specifically, temporal variations in OM in the surface sediments of the mangrove stand were much more noticeable throughout the sampling months with low levels in summer and a sharp increase in winter. Such variations could be associated with both local weather patterns and anthropogenic activities. During the early summer, particularly in December, the monthly rainfall in Mangawhai Harbour was comparatively high, which would have highly disturbed surface sediments inside the mangrove stand and further dilution and dispersal of autochthonous debris would have resulted in lower OM contents at the sediment surface. In addition, the higher mangrove litter production in late summer in Mangawhai Harbour (Tran 2014) could have resulted in the winter elevated OM levels. However, seasonal litterfall patterns of mangrove forests in Mangawhai Harbour have not been shown to be influenced by monthly rainfall (Tran 2014), since such patterns are more related to mangrove productivity and wind speed. Usually, the level of OM in mangrove sediments can be influenced by mangrove litter themselves and allochthonous substances, such as sewage or agricultural discharge carried by tidal water (Tam and Wong 1998; Kristensen et al. 2008; Bouillon et al. 2008; Gritcan et al. 2016). Evidence of faecal contamination, high nutrient levels, and low dissolved oxygen in Mangawhai Estuary have been reported by Valois (2017) and Mangawhai Community Wastewater Scheme (2015). Hence, the increase of visitors to Mangawhai Harbour during summer is likely to result in increases sewage enriched in OM and nutrients into the estuary (Mangawhai Community Wastewater Scheme 2015), which indicated possible point and non-point sources of OM and trace metals due to anthropogenic activities. As, these municipal wastes have low anaerobic decomposition rate (Bilgili et al. 2007), the effect of such contamination in mangrove sediments could be noticeable later during post-summer after the contaminants settle and get deposited in the surface sediments. OM decomposition rate is also correlated with temperature (Alongi et al. 2000), so the higher and

lower levels of OM contents could be associated with the winter and summer temperatures, respectively.

Similar to OM, Fe concentrations in the surface sediments of the mangrove stand demonstrated the same trend with low levels in summer and high levels in winter, which supports the notion that OM tends to trap Fe (Lacerda et al. 1988; Marchand et al. 2006) due to the high interrelationship between these elements along the decomposition pathways (Alongi et al. 2000; Marchand et al. 2006; Marchand et al. 2011). Although, the level of OM elevated in May, such post-summer elevation in Fe concentrations was observed a month later in June, which could have resulted from activation of anaerobic pathways of OM and fixation of Fe in sediments (Alongi 2009). Hence, the elevation in Fe level in June could be associated with the cumulative accumulation of Fe during pyritization in a favourable anaerobic condition.

In contrast to OM and Fe, a general increasing trend of Cu, Zn, Pb, Cd, and As in mangrove sediments during summer could be associated with Fe-cycling as a result of heavy rainfall in December. During rainfall events, these surface sandy sediments have high permeability and allow water to pass quickly, resulting in sediment oxidation followed by Fe oxy-hydroxides precipitation (Du Laing et al. 2009). As, Fe concentration was several times higher than other elements, a portion of Fe oxy-hydroxides created during the oxic environment would have reacted with available OM and entered the aqueous phase as dissolved Fe_2^+ and ultimately trapped other elements (Marchand et al. 2006) and increased their concentrations. However, such a trend was not observed in adjacent mudflats due to less OM availability and (sub)oxic conditions induced by hydrodynamic pattern. The continuous sediment dispersal by semi-diurnal tides due to the lack of any physical barrier makes the redox cycling process in mudflats habitat much more complicated compared to the nearby mangrove stand.

Overall, findings of our present study suggested that hydrodynamic condition of a habitat plays a vital role in OM and trace metal distributions. The study also highlighted a close association of OM with trace metal cycling in estuarine sediments. Additionally, we suggest that a change

in sediment oxidation state driven by local weather patterns and some anthropogenic activities could influence Fe-cycling, and ultimately affect the distribution of other trace metals in estuarine sediments.

3.6 Conclusions

The findings of this study indicate that trace metal contaminations at Mangrove Island, Mangawhai Harbour, are relatively low compared to other mangrove stands within the harbour and among other sites in northern New Zealand. Such low levels of trace metal concentrations may be related to the hydrodynamic conditions as our study site is located in a middle of the lower estuary, where high energy environment enhances flushing and dispersal of fine particles. Compared to the adjacent mudflats, the mangrove sediments within the Mangrove Island hold higher amounts of OM and a similar trend with trace metals has been observed. During anaerobic conditions, sulphate-reducing bacteria decompose OM resulting in high levels of reduced inorganic sulphur, which have a high capacity to trap metals. We suggest that the observed decrease of trace metal concentrations with increasing depths in mangrove sediments is associated with low OM content at depths and dissolution of oxides and/or sulphides at the redox boundary within sediment depths. In such a condition, the metals could be exported from the sedimentary column due to tidal pumping. However, metal cycling may occur in a mangrove ecosystem as a result of re-adsorption by pyrite within anoxic layers or accumulation by mangrove plants. We have observed significant temporal variations in surface mangrove sediments and conclude that these variations could be a result of diagenetic processes induced by rainfall, temperature, and/or change in contaminate levels. Usually, sediments get disturbed during high rainfall creating an oxic environment, whereas high temperature could enhance microbial activities and both conditions are favourable for metal release from sediments. A similar trend of seasonal variations was not observed in the adjacent mudflats because the habitat is highly dominated by tidal flushing due to the lack of any physical barrier. Hence, we can conclude that the hydrodynamic environment of a system plays a crucial role in metal cycling due to the change in sediment redox conditions. In summary, our present study suggested that seasonal variations in trace metal levels at Mangrove Island of Mangawhai estuary were driven by natural and anthropogenic factors. Our findings also alerted about the effects of ongoing mangrove removal activities in New Zealand, as any physical disturbances

could alter sediment geochemistry and ultimately reduce the retention capacity of mangrove sediments. We suggest that such a study on the magnitude of seasonal fluctuations of trace metals in estuarine sediments is an essential tool for environmental risk assessment, especially before mangrove removal. Furthermore, we recommend that future studies should focus on metal cycling in porewater and their accumulation by mangrove plants to further elucidate the complex geochemical dynamics in estuarine sediments within temperate mangrove ecosystems.

Chapter 4. Mangrove removal: effects on trace metal concentrations in temperate estuarine sediments

Prelude

The chapter aims to understand the influences of mangrove removal on trace metal concentrations in estuarine sediments. Such a pre- and post-mangrove removal study is a unique approach to investigate the inherent capacity of mangrove sediments to sequester trace metals. The previous two experimental chapters comprehensively explained the sequestering capacity of mangrove sediments and several factors controlling the spatio-temporal dynamics of trace metals in estuarine sediments, whereas this chapter elucidates the impacts of mangrove removal in the sequestering capacity of mangrove sediments. This field-based practical experiment provides a baseline for estuarine management in New Zealand, where ongoing mangrove removal activities lack comprehensive scientific assessments. All the contents of this chapter have been accepted and published in a peer-reviewed journal as “Bastakoti, U., Robertson, J., Marchand, C., & Alfaro, A. C. (2019). Mangrove removal: Effects on trace metal concentrations in temperate estuarine sediments. *Marine Chemistry*, 216, 103688.”

4.1 Abstract

Trace metal accumulation in mangrove sediments is of increasing global concern, as contaminants can easily remobilise to surrounding environments through a range of sediment geochemistry processes. Such processes are driven by various physical or biological disturbances, which tend to remobilise metals profligately. The present study aimed to investigate the effects of mangrove removal activities on trace metal concentrations in temperate mangrove sediments and adjacent mudflats. To understand patterns of trace metal mobilization due to the removal of mangroves, we measured levels of Fe, Cu, Zn, Pb, and Cd along with other sediment parameters (organic matter, pH, bulk density) during pre- and post-mangrove removal activities. Sediment cores from three different depths down to 30 cm were collected from the mangrove removal location and adjacent mudflats at Mangawhai Harbour Estuary, New Zealand, during pre/post-removal sampling events over a four-year period. Results indicate that levels of OM and trace metals were higher in mangrove sediments than adjacent mudflats,

which is consistent with the inherent capacity of mangrove sediments to sequester trace metals. However, after the removal of mangroves, the levels of OM and trace metals decreased in removal sites. During this period, we observed lower sediment pH levels, indicating an increase in sediment acidity which is associated with a lower sequestering capacity. We also observed increases in trace metal concentrations in adjacent mudflats during the post-removal period. Hence, our findings highlight the far-reaching effects of mangrove removal activities and provide important information to assist with future management strategies of temperate mangrove ecosystems.

4.2 Introduction

Mangrove forests are highly productive and dynamic ecosystems, which are often exposed to contaminants from both tidal and fresh water due to their location in a transition zone between terrestrial and marine environments. Indeed, increases in trace metal contaminations in mangrove sediments has become a global concern, as these inorganic contaminants are persistent in nature and tend to accumulate in estuarine food chains (Kulkarni, et al., 2018). As mangrove sediments tend to be anaerobic and rich in organic matter (OM) and sulphides, the sediments have high tendency to sequester trace metals (Harbison, 1986). However, sediment disturbances due to natural (bioturbation, fluvial erosion) or anthropogenic activities can oxidise sulphides to form sulphuric acid, which tend to reduce sediment pH (Bubb and Lester, 1994; Preda and Cox, 2002). As a result, metals are leached from mangrove sediments to overlying waters (Caetano et al., 2003; Saenger and McConchie, 2004; Eggleton and Thomas, 2004) in dissolved and bioavailable phases (Ankley et al., 1996). The release of metals from sediments due to physical disturbances is considered to be a faster process compared to disturbances caused by normal ecological processes (Atkinson et al., 2007).

Several studies have highlighted the impacts of disturbances on sediment properties and trace metal levels (Eggleton and Thomas, 2004; Atkinson et al., 2007; Blanco et al., 2012). Release of metals to overlying waters due to physical and biological disturbances followed by sediment oxidation was investigated by Atkinson et al. (2007), who suggested that metal release was mostly influenced by Fe and Mn redox cycling. Specifically, removal of mangrove trees would not only cause sediment disturbances but also loss of autochthonous sources and biological barriers leading to a decrease in sediment OM contents as reported by Grellier et al. (2017), Ngole-Jeme et al. (2016), and Alongi et al (1998). Indeed, trace metal mobility depends on the OM content in the sediments (Du Laing et al., 2009), and a decrease in OM levels could eventually lower the sequestering capacity of sediments and transform the mangrove habitat from a sink to a secondary source of trace metals (Harbison, 1986). Several past studies have

suggested that disturbed and oxidised estuarine sediments could release trace metals to surrounding environments (Salomons et al., 1987; Kalnejais et al., 2010; Fernandes and Nayak, 2012; Vidal-Durà et al., 2018; Thanh-Nho et al., 2019). Indeed, Sandilyan and Kathiresan (2014) noted that the decline in mangrove forests in Asia also presents a threat to the surrounding environments due to the release of metals from these habitats. Other consequences from sediment disturbances include nutrient releases, low sedimentation rates, increase in water turbidity, CO₂ emissions, and loss of fine-textured sediments (Granek and Ruttenberg, 2008; Lundquist et al., 2012; Sabeel et al., 2015; Stokes and Harris, 2015; Bulmer et al., 2017).

The adverse impact of contaminants released from disturbed sediments to surrounding environments can be minimised by implementing suitable remediation measures (Peng et al., 2009). Previous studies have suggested several physical, chemical, and biological remediation techniques (e.g. biochar, washing, floatation, chemical leaching, biostimulation, bioaugmentation, phytoremediation) to minimise ecological risk of co-contamination of sediments (Yao et al., 2012; Khalid et al., 2017; Liu et al., 2018; Ye et al., 2019). As the selection of a suitable remediation method depends on the environmental condition of the site and the qualitative or quantitative properties of the contaminants (Critto et al., 2006; Ye et al., 2017, Peng et al., 2009), a comprehensive scientific study is necessary to implement any remediation technique in mangrove removal sites.

In contrast to the global declining trend of mangrove habitats, rapid expansion of mangrove forests in New Zealand since the 1970s (Morrisey et al., 2007) has led to concerns from local residents who call for their removal due to unpleasant odours from anoxic sediments, rodent abundances, loss of open water views and boating spaces (Harty, 2009). As a result, mangrove management approaches have increased focus on mangrove removal activities since the 1990s (Morrisey et al., 2007; Lundquist et al., 2017). Hence, a number of “Estuary Care” groups have been formed throughout the North Island of the country with a primary goal to clear mangrove trees (Harty, 2009). Considering mangrove removal as a control measure, regional councils

have been granting permission to these local groups to clear mangroves from selected areas. Contrasting these views, conservation groups maintain that removal of mangroves results in adverse impacts on estuarine and surrounding environments, including changes in sediment geochemistry (Alongi and de Carvalho, 2008; Tovilla et al., 2001). Thus, as a first step to scientifically evaluate the ecological effects of mangrove removal on the sequestering capacity of the sediments, we assessed the level of trace metals (Fe, Cu, Zn, Pb, and Cd) along with other sediment parameters (organic matter, pH, bulk density) at Mangawhai Harbour Estuary during pre- and post-mangrove removal activities. Our aims were to determine variations between pre- and post-removal levels of trace metals and other sediment parameters in a mangrove habitat (removal location) and adjacent mudflats. We measured pH levels and OM content in sediments as key sediment characteristics, which control trace metal distributions (Peng et al., 2009). For elemental analyses, we selected the most common metals (Fe, Cu, Zn, Pb, and Cd), which represent inorganic pollution in estuarine sediments. We hypothesized that removal of mangroves could lead to decrease in sediment pH and lessen the capacity of sediments to sequester trace metals. It was envisaged that this study could provide a better understanding of the impacts of mangrove removal activities on trace metal dynamics for future management strategies, as well as advancing our knowledge of mangrove ecosystem dynamics globally.

4.3 Material and methods

4.3.1 Site description

Mangawhai Estuary is about 100 km north of Auckland City in the Kaipara District Northland, New Zealand. The Mangawhai Estuary covers an area of 4.6 km², which consists of shallow channels, saltmarshes, mangroves, intertidal flats, and a sand spit (Lindsay, 2014). Several small creeks drain fresh water into the estuary, with the most notable ones being the Tara and Bob Creeks. Tara Creek drains the Tara volcanic sediments and Bob Creek drains the Waitemata sediments from the north-western and southern arms of the estuary, respectively. The study site is a 12-ha island (S36° 07.001', E174° 34.829') located in the middle of lower Mangawhai Estuary. The island consisted of a mangrove stand of *Avicennia marina* trees before their removal in June 2015. Inundation of mangrove sediments within the island by tidal water resulted a high energy environment in the area. The island is surrounded by mudflats which accommodate mostly two molluscan classes (i.e. Gastropoda and Bivalvia; Hulbert, 2014).

New Zealand's Northland Region experiences a warm humid summer, while the winters are mild and wet. The region is a narrow peninsula which causes moist wind and results in abundant rainfall (Chappell, 2013). Mangawhai receives an average annual rainfall of around 1203 mm (Lindsay, 2014). Mangawhai township has a sparse population, which increases and decreases seasonally depending on the number of visitors.

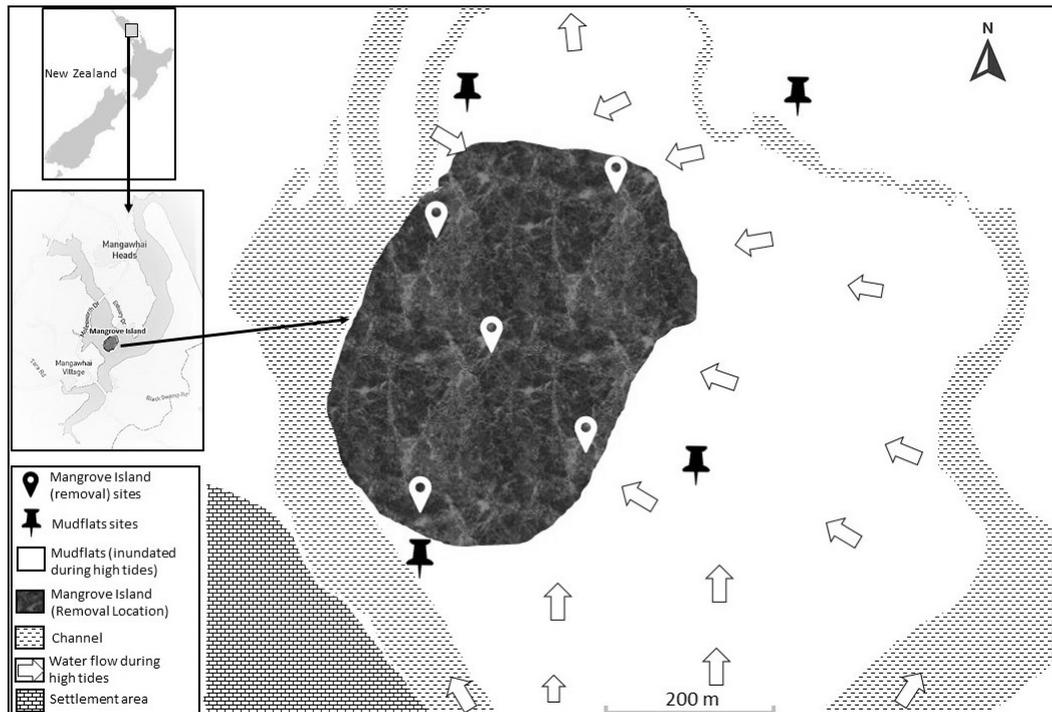


Figure 4.1. Map of the study area.

4.3.2 Mangrove removal at Mangawhai Harbour

Mangrove removal activities at some parts of Mangawhai Harbour started in March 2014, after a final decision made by the Environment Court of New Zealand in early December 2013 (Environment Court of New Zealand, 2013. Decision No. [2013] NZEnvC 284). In June 2015, mangrove removal works started at Mangrove Island (Figure 4.1), which ended two months later in August.

4.3.3 Sediment sampling

Sampling sites were selected during a preliminary survey with five sites inside the island and four sites within mudflats (outside the island). The mangrove site selection reflected a good spread and representation of the entire 12-ha area of mangrove stand. Hence, one site was in the middle of the island and the remaining four sites were close to the edges of the stand. The adjacent mudflat sites were selected to represent the immediate surroundings of the island. GPS coordinates were recorded at all sampling sites to re-locate them during all sampling events. Triplicate sediment samples were collected at each site using a 30-cm stainless steel corer (8 cm

internal diameter) in a circular plot of a 2-m radius, which incorporated a representative sample of the mangrove live root zone. All sediment samples were collected during low tides. Immediately after sampling, each of the core samples were divided into three segments up to a depth of 30 cm (surface 0-10 cm, middle 10-20 cm, and bottom 20-30 cm).

The sediment pH of each sub-sample was measured using a pH probe (pH meter, EUTECH Instruments), which was calibrated using buffer solutions of pH 4, 7, and 10. To measure bulk density (BD), sediment samples from each sub-sample were collected separately using graduated syringes (50 ml), and their respective volumes were recorded before putting them in airtight zip lock plastic bags. The subsamples from all sites were wrapped in plastic film and aluminium foil, individually labelled, and brought to the laboratory in a cooler. The samples were kept in the dark at -18°C until they could be analysed.

4.3.4 Sampling events

Sediment samples were collected from all sites within Mangrove Island and mudflats during five different sampling events from 2014 to 2018. Sediment samples were collected in September 2014, May 2015, September 2015, May 2017, and May 2018. As the removal occurred from June to August 2015, the former two sampling months represented pre-removal and later three months represented post-removal periods.

4.3.5 Laboratory analyses

All the laboratory analyses were performed at the chemistry laboratory of Auckland University of Technology. For the measurements of bulk density (BD), sediment samples were freeze-dried for at least 3 days until constant weights (dry weights) were achieved. BD of each sample was calculated as the sediment dry weight divided by sample volume (recorded in the field). All other wet sediment samples were oven-dried at 60°C until constant weights were achieved. The dried samples were sieved through a 2-mm stainless sieve and grounded. Five grams of dried sediment were further dried at 105°C overnight to measure OM contents by loss-in ignition (LOI) method (Heiri et al., 2001). After drying overnight, the sediment samples were cooled in

a desiccator and weights were again recorded. Then, the samples were transferred to a muffle furnace and heated at least 4 hours at 550°C. After cooling the samples in a desiccator, final weights were recorded, and OM contents were calculated as the difference in weights between samples dried overnight (105°C) and heated in the muffle furnace (550°C).

The oven-dried (60°C), sieved (2 mm), and grounded sediment samples were further sieved through a 63- μ m stainless sieve prior to elemental analyses. The elemental concentrations (Fe, Cu, Zn, Pb, and Cd) were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Varian Liberty AX Series II, USA) following USEPA Method 200.2 for sediment digestion with conc HNO₃ and HCl (Martin et al., 1991). Additionally, batches of blanks and references (NRC-Canada HISS-1, Marine Sediment Certified Reference Material) were prepared using the same digestion method, and analysed after every batch of 10 sediment samples for data accuracy. The results of reference material are presented in Appendix 4.1.

4.3.6 Statistical analyses

Data from the sediment parameters were analysed using the statistical programme R software version 3.2.1 (R Development Core Team, 2017; www.r-project.org). Repeated three-way ANOVAs (before and after mangrove removal \times 2 habitats \times 3 sediment depths) and Tukey's HSD tests were performed to determine the differences of sediment parameters along the time period. Additionally, correlation analyses were performed between all parameters to determine Pearson correlation coefficients (r) values and understand their interrelationship.

4.4 Results

During the entire sampling period (pre- and post-removal sampling events), significant positive correlations were observed between OM contents and Fe concentrations in both the island and mudflats ($r = 0.45$, $p < 0.01$, Figure 4.2). In addition, the majority of the analysed trace metals were positively correlated with one another. However, such correlations were not significant between Fe & Cd ($r = 0.1$, $p > 0.05$) and Cu & Cd ($r = 0.16$, $p > 0.05$) (Figure 4.2). pH values were negatively correlated with Fe ($r = -0.37$, $p < 0.05$) and Cd ($r = -0.23$, $p < 0.05$), whereas a positive correlation between BD and Pb was observed ($r = 0.18$, $p < 0.05$) (Figure 4.2).

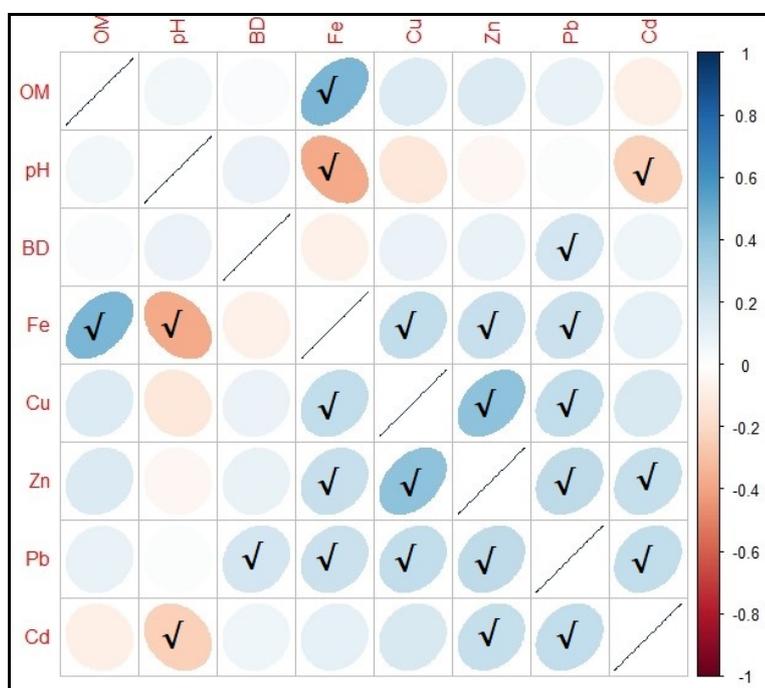


Figure 4.2. Pearson's correlation coefficients between sediment parameters represented by dark red (-1) to dark blue (+1). Colour index on right side of the figure ($r = -1$ to $+1$). Left and right oriented ovals represent negative and positive correlations, respectively. Tick marks (✓) indicates significant correlation values ($p < 0.05$).

4.4.1 Variability among habitats

During the entire sampling period (pre- and post-removal sampling events), pH values and Fe concentrations in sediment samples significantly varied between the island and mudflats (Figure 4.3, Tukey's test, $p < 0.05$). Significant variations in OM contents and Cu, Zn, and Cd concentrations were observed between mangrove sediments and mudflats during pre-removal sampling events (Figure 4.3, Tukey's test, $p < 0.05$). Additionally, variations in BD and Pb between the island and mudflats were significant during post-removal sampling events (Figure 4.3, Tukey's test, $p < 0.05$).

4.4.1.1 Variability among habitats before mangrove removal

During pre-removal sampling events, the mean OM content was found to be higher in mangrove sediments than adjacent mudflats, and a similar trend was followed by trace metals (Fe, Cu, Zn, Pb, and Cd) (Appendix 4.1 and 4.2). The mean concentrations of Fe, Cu, and Pb were approximately two-fold higher in mangrove sediments than in adjacent mudflats (Appendix 4.1 and 4.2). Similarly, the mean Zn concentrations were 25% higher in mangrove sediments than in mudflats (Appendix 4.1 and 4.2). Cd was not detectable or close to the detection limit in mudflats sediments. However, a mean value of $2.44 \pm 2.1 \text{ nmol g}^{-1}$ was observed in mangrove sediments (Appendix 4.1 and 4.2). On the other hand, mean pH and BD values were slightly higher in mudflats than in mangrove sediments (Appendix 4.1 and 4.2).

4.4.1.2 Variability among habitats after mangrove removal

During post-removal sampling events, mean values of pH, BD, and Pb were higher in mudflats than in the island (i.e. mangrove removal sites), which resulted in significant differences between these two locations (Appendix 4.1 and 4.2, Figure 4.3, Tukey's test, $p < 0.05$). A similar trend was observed for Cd concentrations, as the mean concentration was higher in mudflats than in the island (Appendix 4.1 and 4.2). However, an opposite trend was observed for Fe, which had a mean concentration of about 20% higher in the removal sites than in mudflats (Appendix 4.1 and 4.2). Similarly, the mean OM content and Zn concentration were

slightly higher in the removal sites than in mudflats (Appendix 4.1 and 4.2). However, mean Cu concentrations did not vary in two locations during post-removal sampling events (Appendix 4.1 and 4.2).

4.4.2 Variability along sediment depth profiles

During pre-removal sampling events, the mean values of most sediment parameters within the mangrove stand were higher on top sediments and had a decreasing trend with increasing sediment depth (Figure 4.3, Appendix 4.1). However, such a variation along the sedimentary column was significant only for OM and BD (Tukey's test, $p < 0.05$). As a result, significant variations along sediment depth profiles within the mangrove stand were observed for OM (top versus middle and bottom sediment depths) and BD (top versus bottom sediment depth) (Figure 4.3, Tukey's test, $p < 0.05$). Similarly, in mudflats sediments, BD varied significantly between top versus middle and bottom sediment depths during pre-removal sampling events (Figure 4.3, Tukey's test, $p < 0.05$).

During post-removal sampling events, a specific trend of variation in sediment parameters was not observed in mudflats and mangrove removal sites (Figure 4.3, Tukey's test, $p > 0.05$), except for BD, which significantly varied along all sediment depths in mangrove removal sites (Figure 4.3, Tukey's test, $p < 0.05$).

4.4.3 Variability due to mangrove removal

Overall, the mean values of OM and most of the trace metals were higher during pre-removal than post-removal sampling events. After removal of mangroves, the mean OM content plummeted more than 50% in the island, dropping from 2 ± 0.67 to $0.94 \pm 0.18\%$ (Appendix 4.1 and 4.2). Such a temporal variation in OM content after mangrove removal was highly significant in all depths (three-way ANOVAs, Table 4.1, Figure 4.3, Tukey's test, $p < 0.05$). A month after mangrove removal, in September 2015, the mean OM content in the island was $1.02 \pm 0.16\%$, which further decreased to $0.88 \pm 0.28\%$ in May 2017, and was slightly elevated to $0.90 \pm 0.08\%$ in May 2018 (Appendix 4.2). Although the mean OM content on top sediments of

mudflats slightly increased after removal of mangroves from the island (Appendix 4.1), a significant depth variation in OM in mudflats was not observed (Tukey's test, $p > 0.05$).

After mangrove removal, the mean pH values dropped about 7% in both the island and in mudflats (Appendix 4.1 and 4.2), but such a decrease in sediment pH levels was not statistically significant (Tukey's test, $p > 0.05$). Specifically in the island, the mean pH values showed a decreasing temporal trend during the post-removal sampling period, but such a temporal post-removal trend was not apparent in mudflats (Appendix 4.2).

The mean BD values in both island and mudflats increased from 1.41 ± 0.1 to 1.43 ± 0.11 g cm^{-3} and 1.43 ± 0.1 to 1.48 ± 0.07 g cm^{-3} , respectively after removal of mangroves (Appendix 4.1 and 4.2), and such a trend was mostly significant on top sediments (Figure 4.3, Tukey's test, $p < 0.05$). Specifically, the mean BD values on top sediments increased from 1.47 ± 0.06 g cm^{-3} (pre-removal) to 1.56 ± 0.03 g cm^{-3} (post-removal) in the island and 1.33 ± 0.08 g cm^{-3} (pre-removal) to 1.45 ± 0.08 (post-removal) g cm^{-3} in mudflats (Figure 4.3, Appendix 4.1).

In island sediments, the mean Fe concentration was higher during pre-removal than post-removal sampling events (Appendix 4.1 and 4.2), but such a variation was not significant (Tukey's test, $p > 0.05$). Such a decreasing trend of mean Fe concentration after mangrove removal was observed only within the top and middle sedimentary columns of the island, where the values dropped from 74.93 ± 4.50 to 60.63 ± 7.02 $\mu\text{mol g}^{-1}$ and 67.85 ± 5.20 to 62.29 ± 6.97 $\mu\text{mol g}^{-1}$, respectively (Figure 4.3, Appendix 4.1). However, after removal of mangroves from the island, an increase of over 50% in mean Fe concentration was observed in mudflat sediments and this variation was significant, especially within the bottom sedimentary column (Appendix 4.1 and 4.2, Figure 4.3, Tukey's test, $p < 0.05$).

The mean Cu concentration dropped from 0.14 ± 0.06 $\mu\text{mol g}^{-1}$ to 0.11 ± 0.02 $\mu\text{mol g}^{-1}$ in the island after removal of mangroves (Appendix 4.1 and 4.2). The decreasing level of mean Cu concentration after mangrove removal was over 20% in the island, particularly on the top and middle sedimentary columns (Figure 4.3, Appendix 4.1). Conversely, in mudflats, an increased

level of mean Cu concentration was observed in all sediment depths, where the mean value increased from $0.07 \pm 0.02 \mu\text{mol g}^{-1}$ (pre-removal) to $0.11 \pm 0.05 \mu\text{mol g}^{-1}$ (post-removal) (Appendix 4.1 and 4.2). However, such variations in Cu concentrations between pre- and post-removal sampling events were not significant in any sediment depths, neither in the island nor in mudflats (three-way ANOVAs, Table 4.1, Tukey's test, $p > 0.05$).

There was no significant pre- and post-removal variation in Zn concentrations along any sedimentary columns of both island and mudflats (Figure 4.3, three-way ANOVAs, Table 4.1, Tukey's test, $p > 0.05$). However, in September 2015, a month after mangrove removal, the mean Zn concentration in the island decreased about 10% compared to the value observed a month prior of removal in May 2015 (Appendix 4.2). Conversely, an increase in mean Zn concentration after mangrove removal was observed in mudflats and such a trend was apparent mostly in the top and bottom sediments (Appendix 4.1, Figure 4.3).

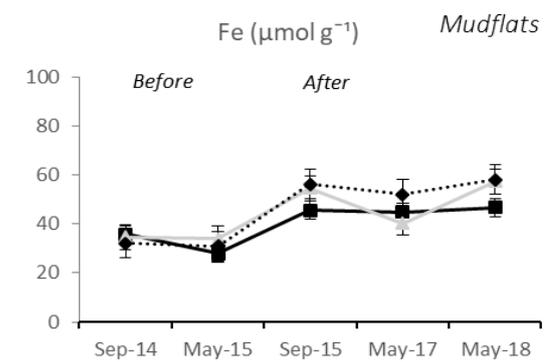
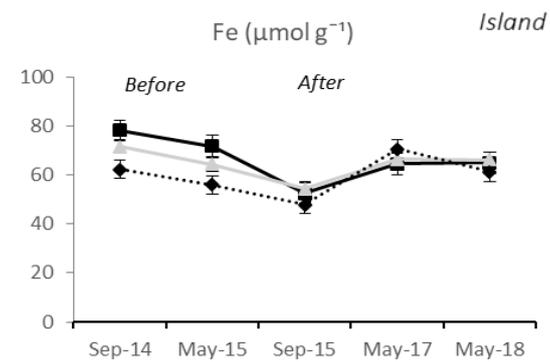
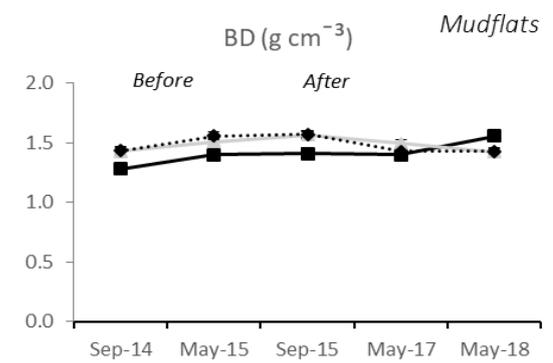
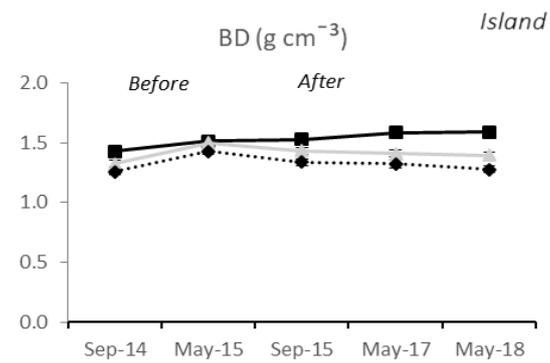
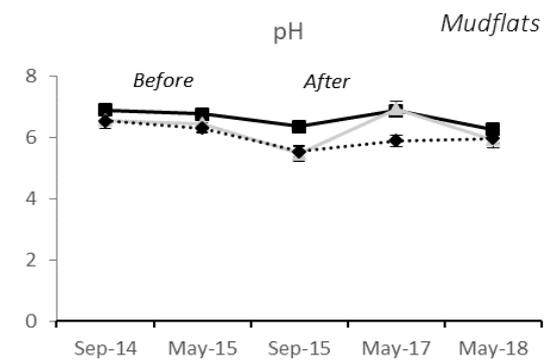
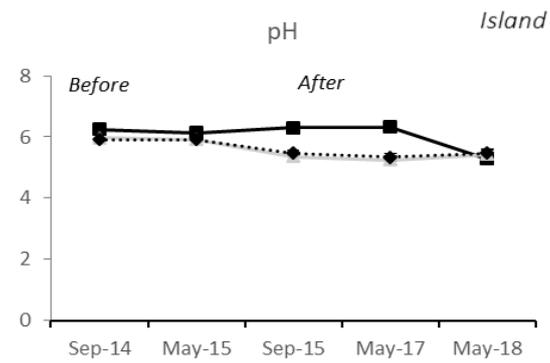
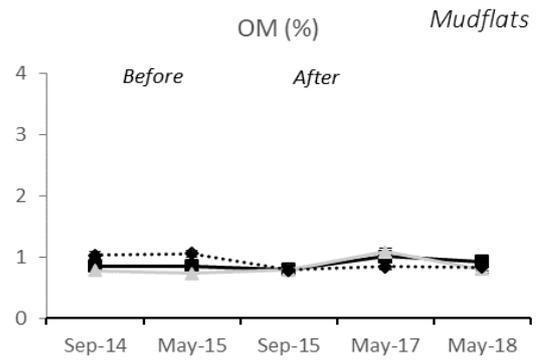
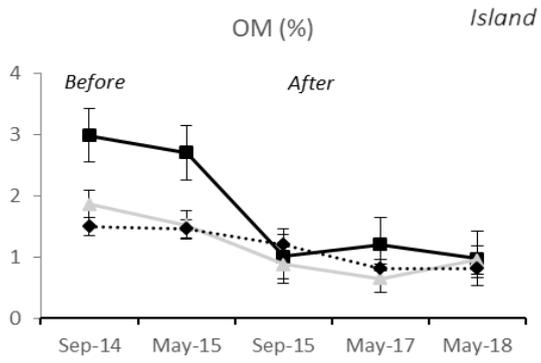
The mean Pb concentration in the island was $3.33 \pm 2.2 \text{ nmol g}^{-1}$ during pre-removal sampling events, which sharply dropped to $2.77 \pm 0.84 \text{ nmol g}^{-1}$ during post-removal sampling events, but this variation was not significant in any sedimentary columns (Figure 4.3, three-way ANOVAs, Table 4.1, Tukey's test, $p > 0.05$, Appendix 4.1). In September 2015, a month after mangrove removal, the mean Pb concentration decreased by nearly 50% compared to the value observed a month prior to removal in May 2015 (Appendix 4.2). Then, during the consecutive sampling events of the post-removal period, the mean Pb concentrations in the island showed an increasing trend (Appendix 4.2). In mudflats, a three-fold increase in mean Pb concentration was observed after removal of mangroves from the island (Appendix 4.1 and 4.2). However, such a variation was mostly significant in the bottom of the sedimentary column (Figure 4.3, Tukey's test, $p < 0.05$).

There was no significant variation in Cd concentration in the island between pre- and post-removal sampling events (Tukey's test, $p > 0.05$). In May 2015, a month prior to mangrove removal, the mean Cd concentration was $4.33 \pm 0.36 \text{ nmol g}^{-1}$ in the Island, and decreased during

the post-removal period to 2.60 ± 0.10 nmol g⁻¹ and 2.60 ± 1.38 nmol g⁻¹ in September 2015 and May 2017, respectively, but increased to 4.63 ± 0.27 nmol g⁻¹ in May 2018. In mudflats, although Cd was mostly not detected or close to the limit of detection during the pre-removal period, the mean concentration was 4.04 ± 1.77 nmol g⁻¹ during post-removal sampling events (Appendix 4.1 and 4.2), and this variation was significant mostly in bottom sediments (Figure 4.3, Tukey's test, $p < 0.05$).

Table 4.1. Three-way ANOVAs for sediment parameters (OM, pH, BD, Fe, Cu, Zn, Pb, and Cd) between mangrove removal status (before and after removal), two habitats (Mangrove Island and Mudflats), and three sediment depths (top, 0-10 cm; middle, 10-20 cm; and bottom, 20-30 cm).

Source	d.f.	Mean Sq	F-value	p-value	Source	d.f.	Mean Sq	F-value	p-value
Organic Matter (OM)					pH				
<i>Removal (R)</i>	1	10.809	75.064	<0.001	<i>Removal (R)</i>	1	7.104	13.923	<0.001
<i>Habitat (H)</i>	1	8.4	58.333	<0.001	<i>Habitat (H)</i>	1	9.757	19.123	<0.001
<i>Depth (D)</i>	2	1.985	13.783	<0.001	<i>Depth (D)</i>	2	3.019	5.916	0.003
<i>R X H</i>	1	8.513	59.119	<0.001	<i>R X H</i>	1	0.001	0.002	0.966
<i>R X D</i>	2	0.977	6.786	0.001	<i>R X D</i>	2	0.235	0.461	0.631
<i>H X D</i>	2	1.424	9.886	<0.001	<i>H X D</i>	2	0.148	0.29	0.748
<i>R X H X D</i>	2	1.432	9.941	<0.001	<i>R X H X D</i>	2	0.112	0.22	0.802
<i>Residuals</i>	117	0.144			<i>Residuals</i>	117	0.51		
Bulk Density (BD)					Iron (Fe)				
<i>Removal (R)</i>	1	0.022	6.687	0.01	<i>Removal (R)</i>	1	1023	7.602	0.006
<i>Habitat (H)</i>	1	0.034	10.434	0.001	<i>Habitat (H)</i>	1	13580	100.951	<0.001
<i>Depth (D)</i>	2	0.105	31.763	<0.001	<i>Depth (D)</i>	2	65	0.481	0.62
<i>R X H</i>	1	0.001	0.335	0.563	<i>R X H</i>	1	4440	33.01	<0.001
<i>R X D</i>	2	0.080	24.204	<0.001	<i>R X D</i>	2	398	2.959	0.055
<i>H X D</i>	2	0.180	54.684	<0.001	<i>H X D</i>	2	400	2.974	0.055
<i>R X H X D</i>	2	0.001	0.245	0.782	<i>R X H X D</i>	2	27	0.198	0.821
<i>Residuals</i>	117	0.003			<i>Residuals</i>	117	135		
Copper (Cu)					Zinc (Zn)				
<i>Removal (R)</i>	1	0.000	0.01	0.919	<i>Removal (R)</i>	1	0.002	0.644	0.424
<i>Habitat (H)</i>	1	0.037	6.445	0.0121	<i>Habitat (H)</i>	1	0.037	13.928	<0.001
<i>Depth (D)</i>	2	0.003	0.509	0.602	<i>Depth (D)</i>	2	0.005	1.953	0.146
<i>R X H</i>	1	0.023	4.051	0.046	<i>R X H</i>	1	0.001	0.348	0.556
<i>R X D</i>	2	0.006	1.079	0.343	<i>R X D</i>	2	0.002	0.869	0.422
<i>H X D</i>	2	0.000	0.043	0.958	<i>H X D</i>	2	0.000	0.109	0.897
<i>R X H X D</i>	2	0.002	0.423	0.656	<i>R X H X D</i>	2	0.004	1.502	0.227
<i>Residuals</i>	117	0.006			<i>Residuals</i>	117	0.003		
Lead (Pb)					Cadmium (Cd)				
<i>Removal (R)</i>	1	40.06	3.777	0.054	<i>Removal (R)</i>	1	159.73	25.435	<0.001
<i>Habitat (H)</i>	1	25.88	2.44	0.121	<i>Habitat (H)</i>	1	6.69	1.066	0.304
<i>Depth (D)</i>	2	10.69	1.007	0.368	<i>Depth (D)</i>	2	6.81	1.084	0.342
<i>R X H</i>	1	139.27	13.128	<0.001	<i>R X H</i>	1	89.96	14.324	<0.001
<i>R X D</i>	2	7.37	0.694	0.501	<i>R X D</i>	2	6.31	1.005	0.369
<i>H X D</i>	2	16.14	1.522	0.223	<i>H X D</i>	2	5.91	0.941	0.393
<i>R X H X D</i>	2	11.41	1.075	0.345	<i>R X H X D</i>	2	2.38	0.379	0.686
<i>Residuals</i>	117	10.61			<i>Residuals</i>	117	6.28		



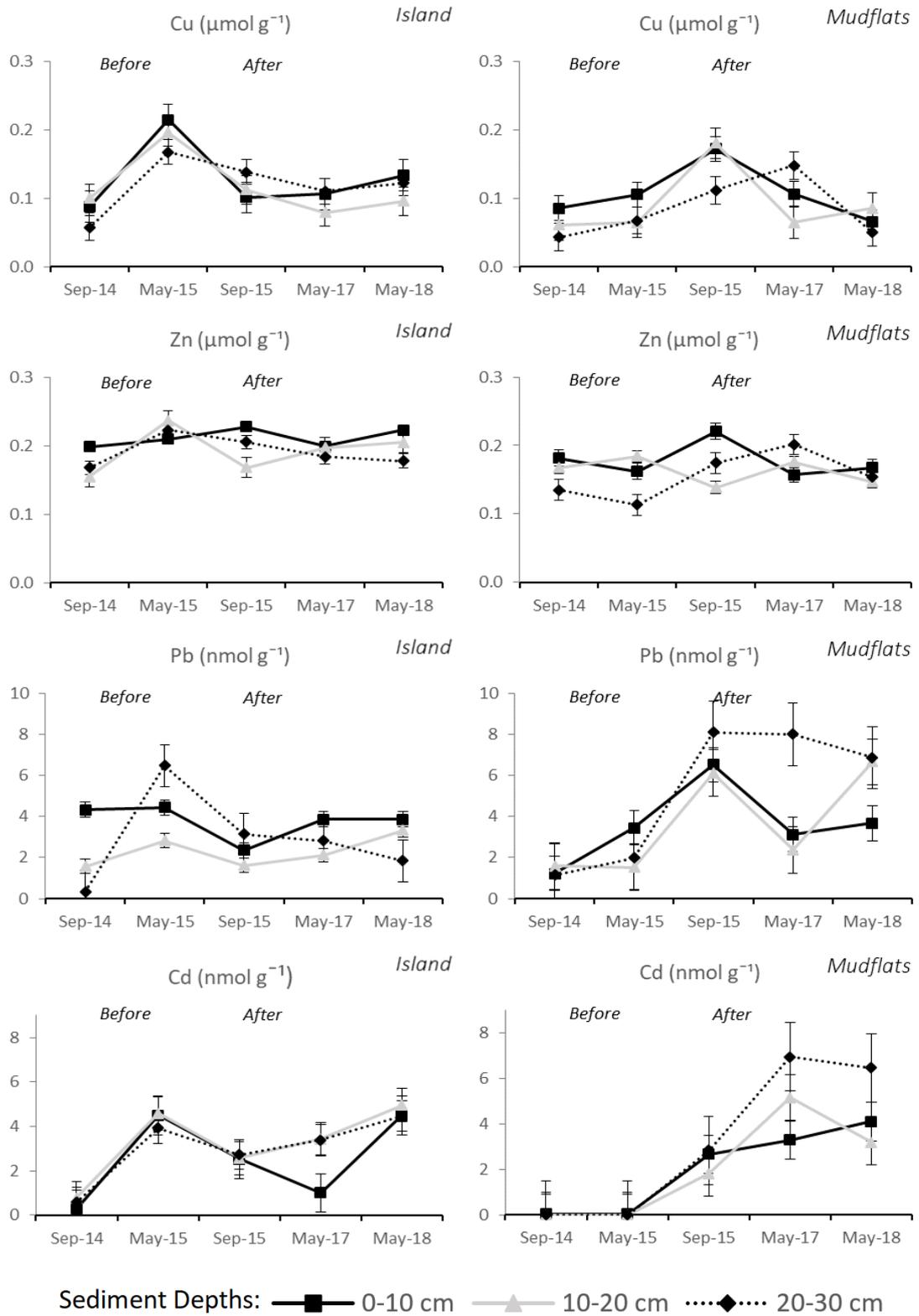


Figure 4.3. Percent organic matter (OM), pH, bulk density (g/cm^3) and concentrations of iron (Fe, $\mu\text{mol g}^{-1}$), copper (Cu, $\mu\text{mol g}^{-1}$), zinc (Zn, $\mu\text{mol g}^{-1}$), lead (Pb, nmol g^{-1}), and cadmium (Cd, nmol g^{-1}) in island (left) and mudflat (right) habitats before mangrove removal (Sep-14 and May-15) and after mangrove removal (Sep-15, May-17, and May-18) at three sediment depths (top=0–10 cm, middle=10–20 cm, bottom=20–30 cm).

4.5 Discussion

The inherent properties of mangrove sediments to sequester trace metals have been documented by several authors (Harbison, 1986; Clark et al., 1998; Marchand et al., 2016; Noël et al., 2017). Such high tendency to trap trace metals is associated with the formation of Fe-sulphides as a result of anoxic conditions in OM rich sediments (Berner, 1984; Clark et al., 1998; Noël et al., 2017). Specifically, available free irons in sediments precipitate to inorganic sulphur (FeS and FeS₂), which have high tendency to sorb other trace metals (Marchand et al., 2012; Marchand et al., 2016). Hence, trace metal concentrations in mangrove sediments are mostly dependent on levels of OM (Ray et al., 2006; Marchand et al., 2011).

4.5.1 Variations of trace metals and other sediment parameters among habitats

Our findings during the pre-removal period showed higher OM contents in mangrove sediments in the island than in mudflats, and this could be associated with mangrove trees, which not only produce organic detritus themselves, but also act as biological barriers to retain and minimise dispersal and dilution of allochthonous and autochthonous substances (Harbison, 1986, Sabeel et al., 2015). Additionally, low mineralization processes and waterlogging environments in mangrove habitats are ideal conditions to accumulate OM (Grellier et al., 2017). Conversely, mudflats lack biological barriers, have very low autochthonous productivity, and experience higher tidal influences compared to mangrove habitats, which makes them less favourable for OM accumulation. Generally, the majority of OM in mangrove sediments is deposited as a result of decomposition of mangrove litters, dead roots, and algae (Woodroffe, 1985; Ray et al., 2006). However, some proportions are transported from terrestrial or estuarine ecosystems during freshwater inputs and/or tidal events (Bouillon et al., 2003). This process of OM trapping in mangrove habitats could lead to reduce sediment consolidation, which eventually reduces sediment BD (Chen and Twilley, 1999; Lovelock et al., 2014). Hence, the observed lower BD values in mangrove sediments compared to mudflats could be associated with OM deposition and sedimentation processes, as OM has lower BD than minerals (Hossain et al., 2015).

Generally, the OM content in sediments is not only associated with BD, but also with sediment pH level, as such a level is related to rates of microbial decomposition and sulphate reducing conditions (Tam and Wong, 2000; Marchand et al., 2003). In other words, both sedimentary OM contents and dissolved sulphate availability make an ideal condition for bacterial sulphate reduction (Berner, 1984). The availability of sulphate is high in both mangrove and mudflat habitats because seawater is generally rich in dissolved sulphate (Berner, 1984), and its diffusion in sediments is a common process (Salomons et al., 1987). Since, mangrove sediments in this study were richer in OM content compared to adjacent mudflats, it is likely that there was increased microbial activity in the island and subsequently lowered sediment pH (Lacerda et al., 1995; Middelburg et al., 1996; Marchand et al., 2003). In addition, microbial decomposition of OM under reducing conditions produces organic acids (Sigel, 1985; Adeleke et al., 2017), which helps reduce sediment pH. Furthermore, acidification in mangrove sediments also results from OM decomposition and sulphide oxidation in suboxic conditions (Marchand et al., 2004). These conditions tend to be enhanced in the mangrove sediments due to their higher OM content. Conversely, coupled with low OM content, prolonged inundation conditions in mudflat habitats would have resulted in higher pH than in mangrove habitat because seawater has high buffering capacity due to its richness in carbonates and bicarbonates.

Various trace metals, especially Fe, are strongly interlinked with OM decomposition pathways (Lacerda et al., 1999; Marchand et al., 2006). Generally, the decomposition of OM under anaerobic pathways mainly use Fe (III), Mn (IV), SO_4^{2-} , CO_2 , and NO_3^- as electron acceptors (Ponnamperuma, 1972; Kristensen, 2000) because of oxygen unavailability (Otero et al., 2009). This process mostly results in pyrite formation, which helps enhance the capacity of sediments to trap other trace metals (Noël et al., 2017). As a result, concentrations of Fe and other trace metals were found to be higher in mangrove sediments than in adjacent mudflats, which had lower OM content. Indeed, the fate of trace metal concentrations in estuarine sediments is highly associated with Fe reduction cycling (Burdige, 1993). The presence of basaltic rock within the catchment of Mangawhai Estuary (Department of Land and Survey NZ, 1980) could

be a major source of Fe in the estuary since basalts are rich in Fe (Bianchi, 2007; Thompson et al., 2011), and iron oxides are formed during weathering processes (Schwertmann and Cornell, 2000).

4.5.2 Variations of trace metals and other sediment parameters along the sedimentary column

In the present study, the decreasing trend of OM contents with increasing sediment depth in mangrove sediments could be related to the young age of the mangrove stand (Hulbert, 2014), since young mangrove stands tend to have low productivity and accumulate less sedimentary OM than mature stands (Marchand et al., 2003; Black and Shimmiel, 2003). Thus, this particular mangrove stand probably had less deposition and low migration of OM from the surface to sub-surface sediments. Indeed, the low trace metals in the sub-surface sediments of the mangrove stand could be a result of low OM contents. Additionally, such a low concentration of trace metals in sub-surface sediments could be a result of the aerial root system developed in the upper sediments of the mangrove stand. These cable roots diffuse oxygen to the sub-surface sediments, which could create a favourable condition for the dissolution of sulphide minerals that increase sediment acidity and thus release trace metals in porewater (Clark et al., 1998; Otero et al., 2009; Marchand et al., 2011). Also, the presence of calcareous layers up to 25 cm in depth at the eastern edge of the island (Hulbert, 2014) would have also led to lower trace metal concentrations in sub-surface sediments. Generally, pyrite concentrations are low in sediments dominated by CaCO_3 (Berner, 1984) and most trace metals are trapped within pyrites in mangrove sediments. Our findings of low trace metal concentrations in sub-surface mangrove sediments at the island sites are in agreement with the findings of other studies (Tam and Wong, 1993; Tam and Wong, 1996). Conversely, mudflats lacked a specific trend in OM and trace metal concentrations in sedimentary columns, which could be related to the high rate of dispersal and dilution of fine particles due to prolonged tidal inundation and absence of mechanisms to diffuse oxygen in sub-surface sediments.

4.5.3 Effect of mangrove removal on sediment properties

Mangrove removal is very likely to result in a significant impact on sediment geochemistry, such as changes in the oxidising state from anoxic to suboxic or oxic condition. Moreover, this transformation in sediment redox state could influence OM contents, pH, bulk density, and eventually the capacity of sediments to sequester nutrients and metals (Salomons et al., 1987; Förstner et al., 1994; Keller and Reiners, 1994; Caetano et al., 2003; Vidal-Durà et al., 2018; Grellier et al., 2017). In the present study, we identified significant changes in some sediment parameters, including levels of trace metals after removal of mangroves. Our findings suggest that sediment OM content and pH level had a strong connection with trace metal cycling.

4.5.3.1 Effect of mangrove removal on OM, BD, and pH levels

After removal of mangroves, lack of biological barriers in the island could have enhanced flushing rate, resulting in dispersal and dilution of organic substances, which would have increased dissolution of fine particles and reduced sedimentation and OM accumulation. In the present study, the removal of the mangrove trees (biological barrier) resulted in the removal of the chemical trapping mechanism of the site, loss of the source of litter production, and a resulting 50% decline in sediment OM content. Several studies have reported a similar trend of low OM content in sediments where mangroves have been removed (Granek and Ruttenberg, 2008; Lundquist et al., 2014; Sabeel et al., 2015; Grellier et al., 2017). On the other hand, mudflat sediments did not show such distinct variation, except for a slight increase in OM content on the top sediment layer and this increasing trend could be a result of OM dispersal from the removal area. However, accumulation and deposition of such transported substances were negligible in mudflats due to the prolonged inundation period and lack of any trapping mechanisms or biological barriers. Hence, despite the removal of mangroves, we observed slightly higher OM contents in the island than in adjacent mudflats. This could be associated not only with the low deposition rate in mudflats, but also with the remaining fine roots in the island sediments (Lundquist et al., 2014). These roots may still trap fine sediment particles by

enhancing particle aggregation, until the roots decompose and breakdown completely, which is a slow process (Robertson and Alongi, 2016). As the fine roots started to decompose and breakdown after mangrove removal, OM content also decreased steadily during post-removal period. This declining trend in OM content would have led to increasing sediment consolidation in the island, reducing sediment pore space and increasing BD (Avnimelech et al., 2001; Cahoon et al., 2003; Chaudhari et al., 2013). Similar results of decreased OM and increased BD after deforestation have been reported in several studies (Keller and Reiners, 1994; Hajabbasi et al., 1997). For instance, a recent study in a mangrove removal site in Brazil reported an increase in sediment BD over a period of three decades (Pérez et al., 2018). As the fine particles are easily flushed away due to the high energy environment of our study area, we also suggest a similar long-term increasing trend in sediment BD values at Mangawhai Estuary. From this standpoint, the transformation of mangrove removal sites to mud/sandflat habitat is inevitable. Another finding of this study was the decrease in sediment pH level in mangrove removal sites. Indeed, physical disturbances as a result of mangrove removal could oxidise sediments, and convert sulphides and pyrite to sulphate compounds, which further dissolve releasing sulphuric acid, and eventually reduce sediment pH (Ponnamperuma, 1972; Clark et al., 1998; Saenger and McConchie, 2004; Marchand et al., 2012). The high rate of OM decomposition due to the less anoxic environment after mangrove removal would have also lowered sediment pH in removal sites (Marchand et al., 2004; Noel et al., 2014). A series of past studies have reported an increase in sediment acidity due to the oxidation of sulphides (Holmer et al., 1994; Tam and Wong, 1998; Preda and Cox, 2002). Interestingly, much lower pH levels in sediment depths within mangrove removal sites were observed during the post-removal period and this could be a consequence of disturbances in sub-surface sediments, diffusion of oxygen through the holes created by the decayed root system, and aeration by remaining live roots themselves. Likewise, we observed a slight decrease in pH values in adjacent mudflat sediments after removal of mangroves from the island. This decrease in sediment pH could be associated with both

sediment disturbances of mudflats during mechanical removal activities and dispersal of acidic sediments from mangrove removal sites.

4.5.3.2 Effect of mangrove removal on trace metal concentrations

In mangrove sediments, anaerobic decomposition pathways are a major process involved in trace metal cycling, as most trace metals are trapped within pyrites in this anoxic environment. However, any physical disturbances could change the redox condition of mangrove sediments to an oxidative phase due to sediment resuspension and mixing with overlying waters (Atkinson et al., 2007). As a result, pyrites are oxidized and dissolved, and trace metals are released in porewaters and exported to adjacent ecosystems by tides creating a favourable condition for biological uptake (Bubb and Lester, 1994; Preda and Cox, 2002; Eggleton and Thomas, 2004). This process of pyrite oxidation could also drop sediment pH levels and create a competitive environment between H^+ and dissolved metals to bind with ligands. Such a competition between H^+ and metals could further diminish the adsorption capacity of sediments and ultimately remobilise trace metals. Such an effect of physical disturbances during mangrove removal activities was observed in mangrove removal sites in the present study, where most of the post-removal trace metal concentrations were lower than pre-removal concentrations. Hence, the present study highlights the fact that oxidation of mangrove sediments could lead to a release of trace metals from mangrove habitats, as a result of an increase in sediment acidity. Similar associations between oxidised sediments, pH, and metal release have been comprehensively explained by other authors (Gambrell et al., 1991; Calmano et al., 1993).

In the present study, we observed a decrease in Fe concentrations in island sediments after removal of mangroves. This decrease in Fe concentrations in mangrove removal sites could be associated with changes in the redox state of sediments due to physical disturbances, leading to oxidation of Fe sulphides and release of Fe to overlying waters in the soluble phase (Marchand et al., 2006; Otero et al., 2009; Noël et al., 2017). Several studies have reported similar findings of the release Fe from oxidised sediments (Saulnier and Mucci, 2000; Caetano et al., 2003).

Indeed, mobility of Fe could be interlinked with decreases in sediment pH after removal of mangroves (de Souza Machado et al., 2018). As a result, Fe concentrations on the top sediment layers of removal sites dropped significantly. However, despite the lower pH within sub-surface sediments, a slight fluctuation in Fe concentration was observed. This could be explained by the hydrodynamic condition above the sediment layers, as free Fe from surface sediments would have been easily exported by tidal water (Sanders et al., 2015; Holloway et al., 2016).

During the post-removal period, a temporal trend of Fe concentrations in mangrove removal sites was observed showing a sharp decline after one month of removal activities. However, the concentrations slightly increased after one and two years. Indeed, the effects of mechanical removal of mangrove trees could be more intense during removal periods, resulting in oxidation of sediments and release of soluble Fe to overlying waters. However, a slight increase in Fe concentrations after one and two years could be associated with newly precipitated Fe oxy(hydroxide) as a result of exposure of the habitat (loss of canopy and biological barriers).

In mudflats, the higher Fe concentrations during post-removal than pre-removal sampling events could be a result of the dispersal of Fe from island to mudflats habitats. Nevertheless, natural and anthropogenic inputs during a period of time would have also contributed to some extent to spike Fe concentrations during the post-removal period. Unlike in the island, we did not observe any specific post-removal temporal trend in Fe concentrations in mudflats sediments, probably due to the much higher energy environment and prolonged inundation conditions in this habitat.

After mangrove removal, other trace metals (Cu, Zn, Pb) in island sediments were also found in lower concentrations compared to their pre-removal levels. Such a decrease in trace metal concentrations after removal of mangroves could be explained by the impact of sediment disturbances, which tend to oxidise anaerobic sediments and remobilize trace metals to overlying waters (Saulnier and Mucci, 2000). As reported by de Souza Machado et al. (2018) in controlled conditions, the mobilisation of Fe could influence trace metal cycling. A similar trend

of strong interrelationship between Fe and trace metal concentrations was observed in the present study. Generally, these trace metals are interlinked with the levels of Fe sulphides in anoxic mangrove sediments, which after sediment oxidation are also released to overlying waters along with soluble Fe. A similar oxygenated phase of mangrove sediments was analysed by Bourgeois et al. (2019) who found that the metal dispersion was a result of the dissolution of iron sulphides due to sediment oxidation. On the other hand, as a result of the low pH of oxidised sediments, any coexisting metal with Fe/Mn oxy(hydroxide) could be released to overlying waters during a metal leaching process (Sigel, 1985; Saenger and McConchie, 2004).

During the post-removal period, Pb and Cd showed an increasing temporal trend in their concentrations, which was similar to that of Fe and a strong interrelationship between Pb/Cd and Fe-cycling was established. Similarly, the observed increased concentrations of most trace metals in adjacent mudflats during the post-removal period was associated with Fe-cycling. Likewise, sulphides in anoxic estuarine sediments, Fe/Mn oxy(hydroxide) in sub(oxic) estuarine sediments have a high capacity to sorb trace metals (Burdige, 1993; Du Laing et al., 2009). Hence, the released trace metals from removal sites would have been scavenged by Fe/Mn oxy(hydroxide) in mudflats to some extent, which would have resulted in increased trace metal concentrations during the post-removal period. Other anthropogenic sources such as agricultural and urban runoff, as reported in past studies (Northland Regional Council, 2002; Mangawhai Community Wastewater Scheme, 2015; Valois, 2017) could have contributed to increased trace metal concentrations during the post-removal period. Especially, a slightly increased level of Cd concentration in both island and mudflats was observed during the post-removal period and could be associated with chemical fertilizers and sewage sludge which contain high Cd concentrations. However, most trace metal concentrations observed in the present study during pre- and post-removal periods were lower than those reported in previous studies conducted in different locations within the same and other estuaries of New Zealand (Glasby et al., 1988; Roper et al., 1988; Bastakoti et al., 2018; Bourgeois et al., 2019a).

In summary, the present study indicates that removal of trees alters sediment geochemistry in a mangrove ecosystem, which eventually affects OM and trace metal cycling. Generally, trace metals could be in soluble, sorbed, or co-precipitated forms, and iron sulphides mainly control trace metal mobility and distribution in an anaerobic condition (Salomons et al., 1987). As a result of physical disturbances, such as mangrove removal activities, trace metals would be highly mobilized and exported from oxidised mangrove sediments to overlying waters in bioavailable forms (Ankley et al., 1996; Caetano et al., 2003; Eggleton and Thomas, 2004). Broadly interpreting our findings, and in light of the hydrodynamic conditions of the study area, the mangrove removal sites are likely to maintain their recent muddy/sandy character in terms of their physical and geochemical properties.

4.6 Conclusions

Based on our findings, we conclude that mangrove sediments have an inherent capacity to sequester trace metals due to their OM richness and anoxic conditions. Our findings support the notion that mangrove trees play a key role in the balance of OM and trace metal dynamics. Indeed, their removal could change the sediment geochemistry and ultimately diminish the capacity of sediments to sequester OM and trace metals. We suggest that the removal of mangroves could induce acidification of sediments and create a favourable condition to release trace metals from sediments to overlying waters. Hence, it is possible that the removal of mangrove trees from their natural habitat could result in the potential trace metal contamination of surrounding environments. Despite the low trace metal concentrations in mangrove sediments in the present study, we observed an increase in trace metal levels in adjacent mudflats during the post-removal period. Hence, our findings indicate the effects of trace metal dispersal due to mangrove removal could be exacerbated in contaminated mangrove ecosystems, especially in urban regions. We suggest the implementation of suitable eco-friendly remediation technique to minimise dispersal of contaminants to surrounding environments. Further studies that investigate levels of bioavailable trace metals in porewater, along with their levels in mangrove plant tissues may help to further explain the effects of mangrove removal on trophic levels within these estuarine ecosystems.

Chapter 5. Urban-rural gradients in the distribution of trace metals in sediments within temperate mangroves in New Zealand

Prelude

The chapter aims to explore the knowledge on trace metal distributions in mangrove sediments which are under anthropogenic pressure. The previous three experimental chapters were conducted at mangrove stands located in a rural area of New Zealand having less nearby anthropogenic sources, whereas this chapter further explains the dynamics of trace metals in mangrove sediments within a harbour located in an urban area of New Zealand. Hence, the results of this chapter help to identify key factors controlling trace metal concentrations in a mangrove stand located within an estuary having a long history of anthropogenic contamination. Furthermore, the chapter investigates trace metal variations between geographically separated urban and rural mangroves of a very contaminated harbour, hence the outcomes are very helpful with making any mangrove management decisions, such as ongoing removal activities in many urban locations within northern New Zealand. All the contents of this chapter are accepted and published in a peer-review journal as “Bastakoti, U., Bourgeois, C., Marchand, C., & Alfaro, A. C. (2019). Urban-rural gradients in the distribution of trace metals in sediments within temperate mangroves (New Zealand). *Marine Pollution Bulletin*, 149, 110614.”

5.1 Abstract

We investigated the sequestering capacity of mangrove sediments through better understanding of trace metal distributions within a temperate estuary. We selected two mangrove stands within Manukau Harbour, New Zealand, based on proximity to contaminant sources. Organic matter (OM), pH, and metal (Cd, Co, Cr, Cu, Fe, Mn, Pb, Zn) concentrations in sediments were analysed. Positive correlations between OM and most trace metals, and metals themselves suggest common contamination sources and sequestering capacity of organic sediments. Higher trace metals in urban versus rural mangrove sediments indicate that contamination source is a major factor controlling metal distribution in these temperate intertidal ecosystems. Specific seasonal trends in metal distributions were not observed due to complex weather patterns and possible fluctuations in anthropogenic inputs. Overall, we suggest that metal dynamics in

mangrove sediments are controlled by interacting factors, and that mangroves modulate the ultimate distribution and magnitude of these inputs within temperate estuaries.

5.2 Introduction

Globally, mangrove forests are often exposed to pollutants derived from various anthropogenic activities (Machado et al., 2002; Kulkarni et al., 2018). Several studies have reported on human-induced trace metal contamination in mangrove sediments (Mackey and Hodgkinson, 1995; Tam and Wong, 2000; Machado et al., 2002; Shi et al., 2019; Chai et al., 2019). Industrial effluents, domestic sewage, and agricultural discharge are major anthropogenic sources of trace metal contamination in mangrove forests (Tam and Wong, 2000; Tam, 2006; Branoff, 2017). Generally, these trace metals enter mangrove ecosystems via associations with Fe/Mn oxyhydroxides and precipitate as sulphides in oxygen-deficient sediments (Lacerda et al., 1993). Hence, mangrove sediments are rich in sulphides due to anaerobic decomposition processes mediated by sulphate-reducing bacteria, and this helps to enhance the capacity of sediments to sequester trace metals (Harbison, 1986; Alongi, 2009). The sequestration capacity of mangrove sediments appears to be associated with richness in organic matter (OM) due to low mineralization processes induced by waterlogged conditions (Harbison, 1986; Kristensen et al., 2008a; Grellier et al., 2017). Hence, mangroves may act as a prominent barrier to trap trace metals and minimize transport and distribution of contaminants to surrounding environments (Machado et al., 2002). However, an alarming decreasing trend of mangrove forests worldwide (Valiela et al., 2001; Duke et al., 2007) could lead to an inevitable release of trace metals due to loss of sediment sequestering capacity.

Trace metal concentrations in mangrove sediments vary from one geographical location to another (Ward and Young, 1981; Harbison, 1984; Tam and Wong, 1995; Tam and Wong, 2000; Chai et al., 2019). Such spatial variations in mangrove stands are the result of the complex and dynamic environmental condition of intertidal habitats, where the physical and chemical characteristics of sediments and pore-water are modulated by constantly changing terrestrial and oceanic influences (Harbison, 1986; Lacerda et al., 1988; Tam and Wong, 1995). Furthermore,

proximity to sources of contaminants may dramatically control trace metal distributions in mangrove stands (Ward and Young, 1981; Harbison, 1984; Chai et al., 2019).

In New Zealand, mangroves are found in the northern coastlines of the North Island; and contrasting global trend, they have been rapidly expanding since the late 1970s (Morrissey et al., 2007). Local and scientific studies on mangrove habitats are essential to assess the status of these ecosystems for coastal management purposes. Hence, in the present study, we identified and quantified the spatial distribution of dominant trace metals within Manukau Harbour, Auckland, as a first step to evaluate the ability of mangrove stands with different demographic characteristics to sequester major contaminants (Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn) in sediments within a temperate New Zealand estuary. We based this study on the hypothesis that the proximity to a contaminant source could be a major factor controlling trace metal distribution in these estuarine ecosystems and that mangrove stands would strongly modulate their distribution and magnitude.

5.3 Material and Methods

5.3.1 Study area

Manukau Harbour (37°02' S, 174°42' E) is located in the south-western part of the Auckland region, and is the second largest harbour in New Zealand. The harbour covers approximately 365-km² area at high tide and extends to a 460-km coastline of the Tasman Sea (Cromarty and Scott, 1995; Bell et al., 1998; Davis et al., 2018). The harbour is a shallow inlet dominated by a mixture of habitats consisting of intertidal mudflats, mangrove stands, and saltmarshes (Glasby et al., 1988; Cromarty and Scott, 1995). The catchment of the Manukau Harbour consists of both volcanic and sedimentary rocks (Cromarty and Scott, 1995; Ballance, 2009) and is drained by four main channels (Waiuku, Papakura, Purakau, and Wairopa) (Glasby et al., 1988; Bell et al., 1998).

Big Muddy Creek (BMC) and Mangere Inlet (MI) were selected as two study locations in the Manukau Harbour (Figure 5.1). BMC is located in the western part of Manukau Harbour, which is about 22 km west of Auckland City, south of Lower Nihotupu Dam in the Waitakere Region. Core samples were collected from a mangrove stand located east of the Nihotupu stream, which represented a less contaminated site within the Manukau Harbour, due to its remoteness from anthropogenic sources (Figure 5.1). The second study location (MI) is in the upper reaches of the north-eastern arm of the harbour, about 15 km south of Auckland City. Core samples were collected from a mangrove stand close to Ann's Creek in the northern shore of MI (Figure 5.1). These sampling sites were selected to represent the most contaminated area in the Manukau Harbour due to their proximity to urban areas and several industries.

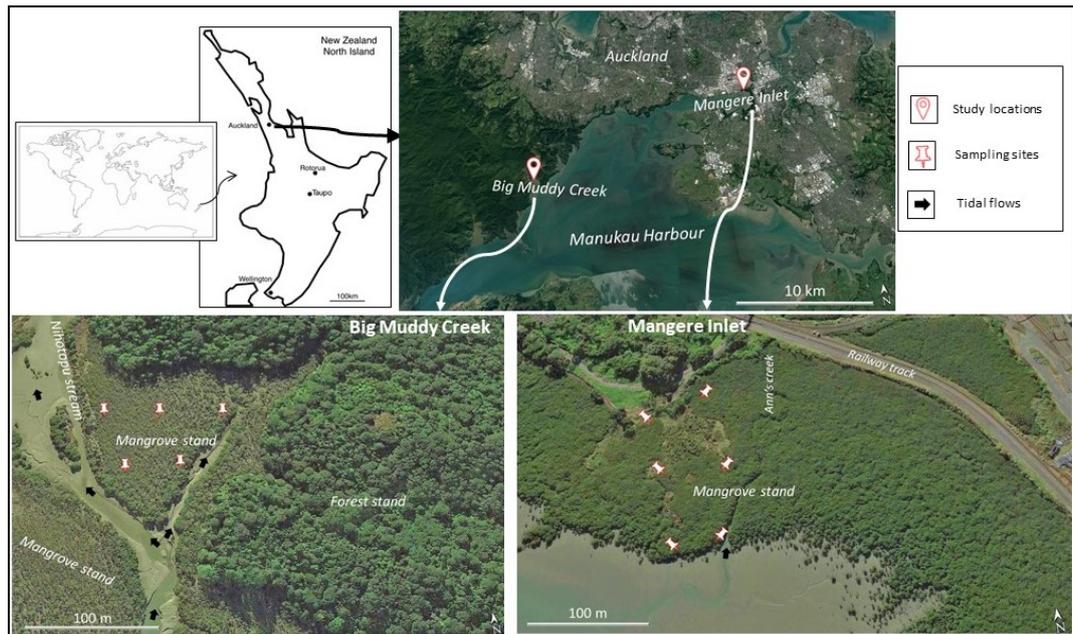


Figure 5.1. Map of Manukau Harbour, New Zealand, showing two study locations (Big Muddy Creek and Mangere Inlet) and sampling sites within mangrove stands.

5.3.2 Sediment sampling

Sediment samples were collected during low tide from mangrove stands of BMC and MI in May 2017 (Winter) and February 2018 (Summer). During a preliminary survey, sampling sites were selected in both locations. GPS coordinates were recorded and visible ribbons were tied to mangrove trees to identify sampling sites during all sampling events. Triplicate sediment cores were collected using a 30-cm stainless steel corer from five sampling sites within BMC and six sampling sites within MI (Figure 5.1). Each sediment core sample was further sub-divided into three sub-samples representing 0-10 cm, 10-20 cm, and 20-30 cm layers within the sedimentary column. The pH of each sub-sample was immediately measured in the field with a pH meter (EUTECH Instruments). Then, the subsamples were individually wrapped in labelled plastic film and aluminium foil, put in a cooler and transported to the laboratory, where they were stored in a freezer at -18°C before laboratory analysis.

5.3.3 Analytical methods

All the sediment samples collected from both sampling locations were analysed at the Chemistry Laboratory, Auckland University of Technology, Auckland. Wet sediment samples

were oven-dried at 60°C for at least 3 days until they had constant weights. The OM content of sediments was determined using a loss-on-ignition (LOI) method as suggested by Heiri et al. (2001). According to the method, five grams of dried sediment sample were sieved through a 2-mm stainless sieve and further oven-dried at 105°C for 24 hours, then heated in a muffle furnace (HDTP-S6-55, Canadian Instrumentation Company) for at least 4 hours at 550°C. The final weights of samples coming out of the muffle furnace and weights of oven-dried (105°C) samples were used to calculate OM contents.

To analyse trace metal concentrations in sediments, the oven-dried (60°C, 2-mm sieved) samples were further sieved through a 63- μ m stainless sieve. Then, a USEPA method 200.2 was followed for acid digestion (conc HNO₃ and HCl, Martin et al., 1991). The digested samples were filtered through Whatman ashless filter papers and the filtrates were run through a Microwave Plasma-Atomic Emission Spectrometer (Agilent Technologies 4200 MP-AES) to determine elemental concentrations. For quality check and data accuracy purposes, certified reference material (NRC-Canada HISS-1, Marine Sediment Certified Reference Material) and blank samples were prepared using the same digestion method and analysed by MP-AES (Appendix 5.1).

5.3.4 Rainfall and air temperature

Weather data were obtained from a MetService station at the Auckland Airport, which is located about 9 and 15 km aerial distance away from the study sites of Mangere Inlet and Nihotopu, respectively. The total monthly rainfall at the Auckland Airport in May 2017 and February 2018 were 111 and 149 mm, respectively. The monthly average air temperature ranged from 2 to 21°C in May 2017 and 15 to 28°C in February 2018 (MetService, 2017; MetService, 2018).

5.3.5 Data analyses

Statistical analyses were performed using R software, version 3.5.3 (R Development Core Team, 2019; www.r-project.org). Data variability among the two sampling locations, two sampling periods, and three sedimentary column depths were analysed with three-way

ANOVAs followed by post-hoc Tukey's HSD tests. Pearson correlation coefficients (r) along with respective significant values ($p < 0.05$) were calculated to assess relationships between sediment parameters.

5.4 Results

In the present study, most of the analysed trace metals in mangrove sediments showed a positive correlation between one another. Specifically, the correlation analyses between Co, Cr, Cu, Mn, Pb, and Zn resulted in positive correlation co-efficient values ($r > 0.52$, Figure 5.2), and they were highly significant ($p < 0.05$, Figure 5.2). Moreover, OM content was also positively correlated with most trace metals ($p < 0.05$, Figure 5.2). Furthermore, pH values in mangrove sediments were positively correlated with most trace metals, but such positive correlations were significant only with Pb and Zn concentrations ($R > 0.39$, $p < 0.05$, Figure 5.2).

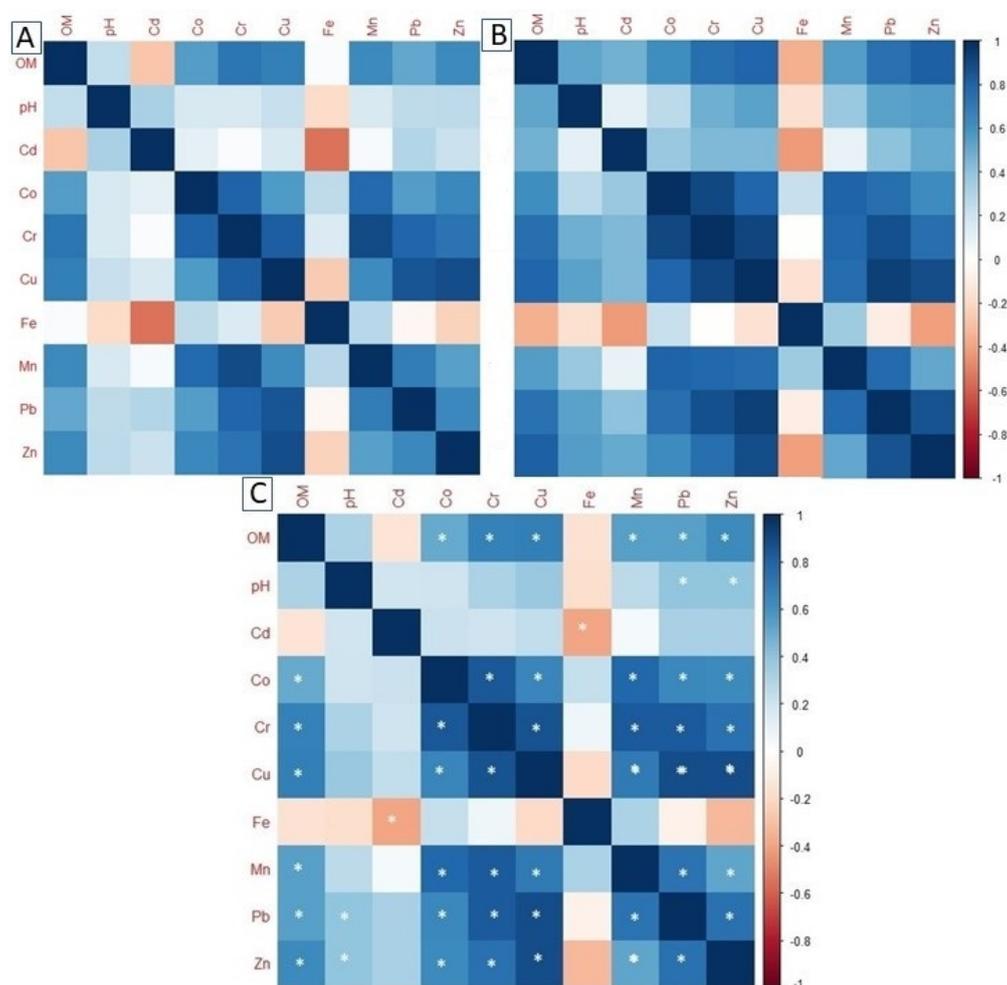


Figure 5.2. Pearson's correlation coefficients between OM, pH, Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn with colour index on right-side of the figure. Dark blue represents highly positive correlations (+1) and dark red represents highly negatively correlations (-1). Asterisks (*) indicate significant correlation values ($p < 0.05$). A = Winter (May 2017), B = Summer (February 2018), and C = Both seasons (May 2017 and February 2018).

5.4.1 Spatial variation in sediment parameters

Significant spatial variations were observed for most sediment parameters between mangrove sediments of BMC and MI (three-way ANOVAs, $p < 0.05$, Table 5.1, Figure 5.3). However, Fe concentrations did not vary significantly between these two locations (three-way ANOVAs, $p > 0.05$, Table 5.1, Figure 5.3). The average Fe concentration was slightly higher at BMC (24845 ± 1044 mg/kg in 2017 and 25678 ± 983 mg/kg in 2018) than at MI (23397 ± 1203 mg/kg in 2017 and 22258 ± 1616 mg/kg in 2018) during both sampling events (Figure 5.3, Appendix 5.1). Conversely, the average concentration of most trace metals (Cd, Co, Cr, Cu, Mn, Pb, and Zn) along with OM content and pH values in mangrove sediments of MI were higher than at BMC during both sampling events (Figure 5.3, Appendix 5.1).

5.4.2 Variations of sediment parameters along the sedimentary column

The average OM contents, pH values, and trace metal concentrations observed along three sedimentary depths (top: 0-10 cm, middle: 10-20 cm, bottom: 20-30 cm) in May 2017 and February 2018 are presented in Figure 5.3. While most sediment parameters were not significantly different along the sedimentary columns in both BMC and MI (three-way ANOVAs, Table 5.1, $p > 0.05$), most sediment parameters were higher on top than middle or bottom sediment layers in May 2017 and no specific trend was observed in both locations in February 2018 (Figure 5.3, Appendix 5.1).

The mean OM content, pH value, and most trace metal (Cd, Co, Cu, Mn, Pb) concentrations were higher on the top layer in May 2017 at the BMC location (Figure 5.3, Appendix 5.1). However, the mean Cr and Zn concentrations were higher in the middle, whereas average Fe concentration was higher in the bottom layer (Figure 5.3, Appendix 5.1). In February 2018, most mangrove sediment parameters were lower on top sediments at BMC (Figure 5.3, Appendix 5.1).

At the MI location, the mean OM content, pH value, and some trace metal (Co, Mn, and Zn) concentrations were higher on top sediments in May 2017 (Figure 5.3, Appendix 5.1). Other

trace metal concentrations were either higher in the middle (Cd, Cr, Cu, Pb) or bottom (Fe) sediment layers (Figure 5.3, Appendix 5.1). In February 2018, the mean pH value and some trace metal (Fe, Mn, and Pb) concentrations were higher on top sediments, whereas OM contents and other trace metals (Cd, Cr, Cu, Zn) were higher in middle sediments (Figure 5.3, Appendix 5.1).

5.4.3 Temporal variations of trace metals and other sediment parameters

5.4.3.1 Temporal variations in Big Muddy Creek

Most sediment parameters of the mangrove stand at BMC showed no significant temporal variation (three-way ANOVAs, Table 5.1, $p > 0.05$), except for OM content (three-way ANOVAs, Table 5.1, Tukey's test, $p < 0.05$). In this location, the average OM content was about 50% higher in May 2017 ($4.5 \pm 0.4\%$) than in February 2018 ($3.0 \pm 0.3\%$) (Appendix 5.1). Similarly, the average pH value, Cu, and Mn concentrations were slightly higher in May 2017 (pH: 6.4 ± 0.3 , Cu: 9.0 ± 0.7 mg/kg, Mn: 148.2 ± 5.9 mg/kg) than in February 2018 (pH: 6.4 ± 0.2 , Cu: 7.8 ± 0.3 mg/kg, Mn: 143.9 ± 4.2) (Appendix 5.1). However, other trace metals (Cd, Co, Cr, Fe, Pb, and Zn) showed the opposite temporal trend, as the average concentrations in mangrove sediments of BMC were higher in February 2018 than in May 2017 (Appendix 5.1).

5.4.3.2 Temporal variations in Mangere Inlet

The temporal variations in pH values, and most trace metal concentrations were not significant in mangrove sediments of MI (three-way ANOVAs, Table 5.1, Tukey's test, $p > 0.05$). However, significant temporal variations were observed only for OM and Cd concentrations (three-way ANOVAs, Table 5.1, Tukey's test, $p < 0.05$). The average OM content was about 20% higher in May 2017 ($6.8 \pm 0.1\%$) than in February 2018 ($5.4 \pm 0.1\%$), whereas the average Cd concentration was about three-fold higher in February 2018 (0.3 ± 0.0 mg/kg) than in May 2017 (0.1 ± 0.0 mg/kg). The pH value and concentrations of Co, Pb, and Zn also followed Cd temporal trend, as they were slightly higher in February 2018 than in May 2017 (Appendix 5.1).

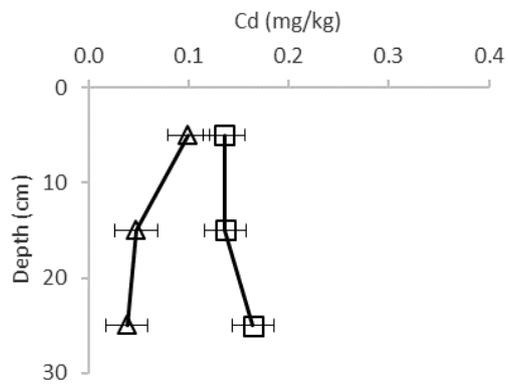
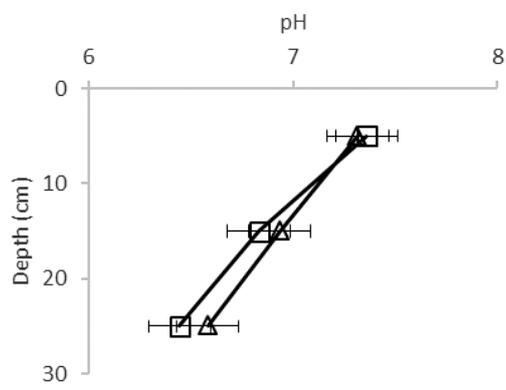
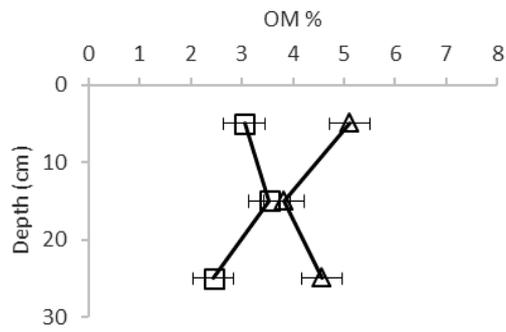
Conversely, the average concentrations of other trace metals (Cr, Cu, Fe, and Mn) were higher in May 2017 than in February 2018 (Appendix 5.1).

Table 5.1. Three-way ANOVAs for OM, pH, Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn levels between two months/seasons (May 2017 - Winter; February 2018 - Summer), two locations (Big Muddy Creek, Mangere Inlet), and three sedimentary column layers (top, 0-10 cm; middle, 10-20 cm; and bottom, 20-30 cm).

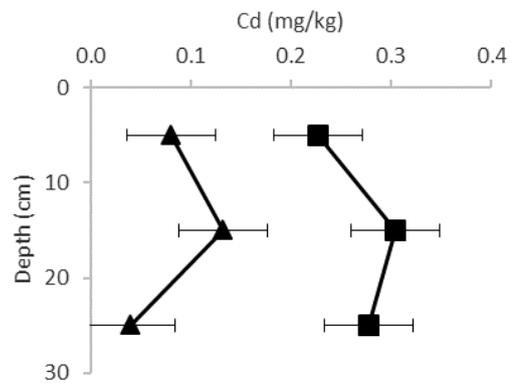
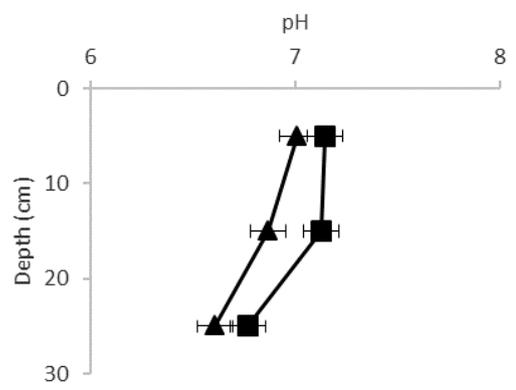
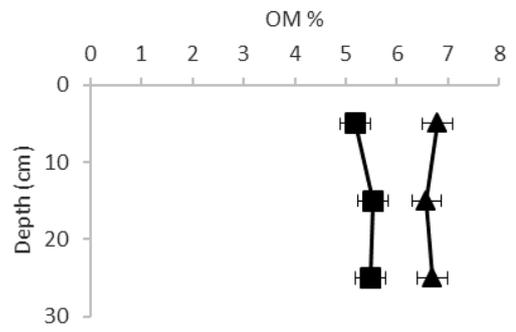
Source	d.f.	Mean Sq	F-value	p-value	Source	d.f.	Mean Sq	F-value	p-value
Organic Matter (OM)					pH				
Month (M)	1	17.37	18.38	<0.01	Month (M)	1	0.03	0.06	0.80
Location (L)	1	47.17	49.92	<0.01	Location (L)	1	2.34	4.71	0.04
Depth (D)	2	0.18	0.19	0.829	Depth (D)	2	1.10	2.22	0.13
M X L	1	0.08	0.08	0.773	M X L	1	0.14	0.29	0.60
M X D	2	1.19	1.26	0.301	M X D	2	0.005	0.01	0.99
L X D	2	0.34	0.36	0.700	L X D	2	0.17	0.34	0.72
M X L X D	2	0.55	0.58	0.565	M X L X D	2	0.01	0.03	0.97
Residuals	24	0.94			Residuals	24	0.49		
Cadmium (Cd)					Cobalt (Co)				
Month (M)	1	0.16	16.95	<0.01	Month (M)	1	0.16	0.07	0.79
Location (L)	1	0.05	5.03	0.03	Location (L)	1	39.09	17.57	<0.01
Depth (D)	2	0.002	0.22	0.80	Depth (D)	2	0.15	0.07	0.93
M X L	1	0.02	2.44	0.13	M X L	1	0.05	0.02	0.88
M X D	2	0.006	0.64	0.53	M X D	2	1.81	0.81	0.45
L X D	2	0.007	0.70	0.50	L X D	2	0.12	0.06	0.94
M X L X D	2	0.001	0.02	0.98	M X L X D	2	0.29	0.13	0.88
Residuals	24	0.01			Residuals	24	2.23		
Chromium (Cr)					Copper (Cu)				
Month (M)	1	3	0.02	0.89	Month (M)	1	8.4	0.68	0.42
Location (L)	1	8877	52.84	<0.01	Location (L)	1	2915.8	235.21	<0.01
Depth (D)	2	73	0.43	0.65	Depth (D)	2	5.5	0.45	0.64
M X L	1	11	0.07	0.8	M X L	1	0.6	0.05	0.82
M X D	2	3	0.02	0.98	M X D	2	0.2	0.01	0.98
L X D	2	57	0.34	0.71	L X D	2	1.6	0.13	0.88
M X L X D	2	3	0.02	0.98	M X L X D	2	3.8	0.30	0.74
Residuals	24	168			Residuals	24	12.4		
Iron (Fe)					Manganese (Mn)				
Month (M)	1	210506	0.01	0.91	Month (M)	1	149	0.01	0.92
Location (L)	1	53345518	2.91	0.10	Location (L)	1	217132	16.08	<0.01

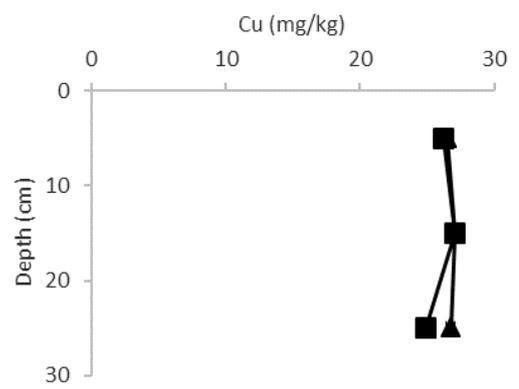
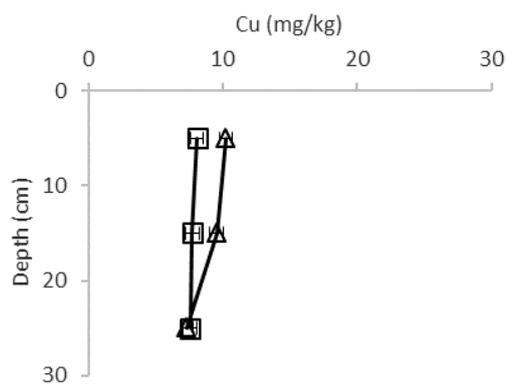
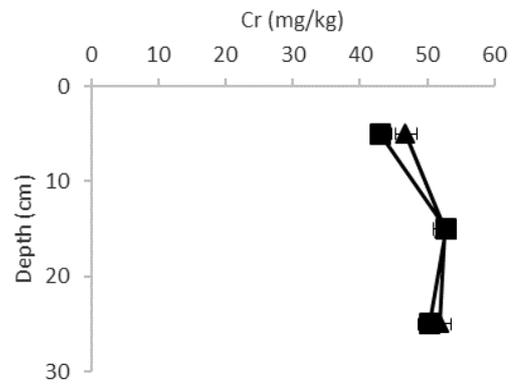
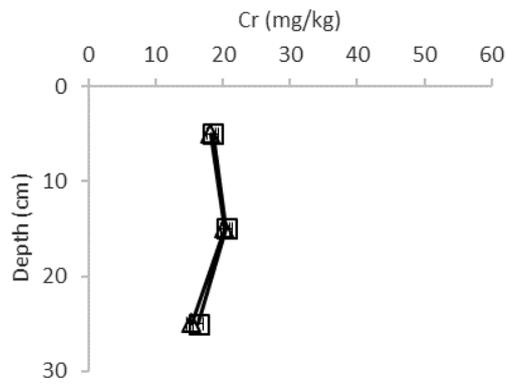
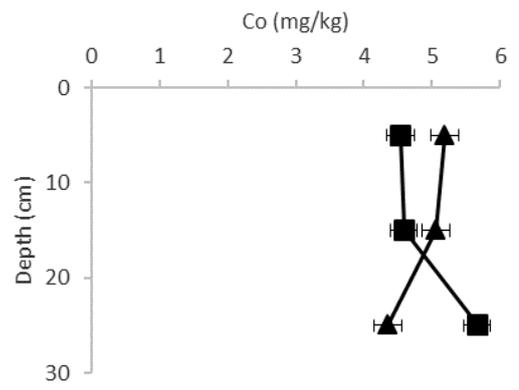
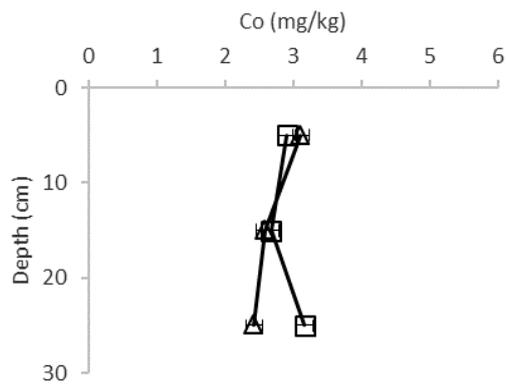
Depth (D)	2	9117112	0.50	0.61	Depth (D)	2	5326	0.39	0.68
M X L	1	8750894	0.48	0.50	M X L	1	0	0	0.99
M X D	2	19250323	1.05	0.36	M X D	2	134	0.01	0.99
L X D	2	7594481	0.41	0.66	L X D	2	2848	0.21	0.81
M X L X D	2	1263175	0.07	0.93	M X L X D	2	46	0.003	0.99
Residuals	24	18331317			Residuals	24	13500		
Lead (Pb)					Zinc (Zn)				
Month (M)	1	10.6	0.37	0.55	Month (M)	1	88	0.30	0.59
Location (L)	1	2561.5	89.01	<0.01	Location (L)	1	55397	188.91	<0.01
Depth (D)	2	14.5	0.50	0.61	Depth (D)	2	172	0.59	0.56
M X L	1	2.6	0.09	0.77	M X L	1	10	0.04	0.85
M X D	2	20.6	0.71	0.50	M X D	2	127	0.43	0.65
L X D	2	9.2	0.32	0.73	L X D	2	80	0.27	0.76
M X L X D	2	55.6	1.93	0.17	M X L X D	2	381	1.3	0.29
Residuals	24	28.8			Residuals	24	293		

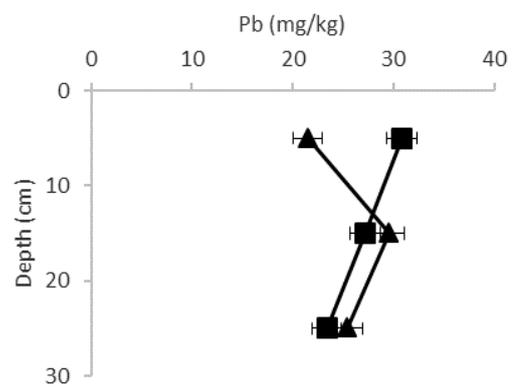
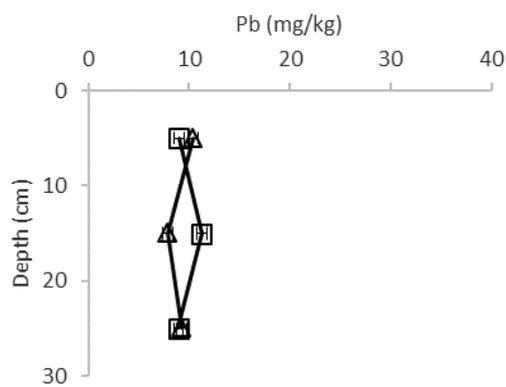
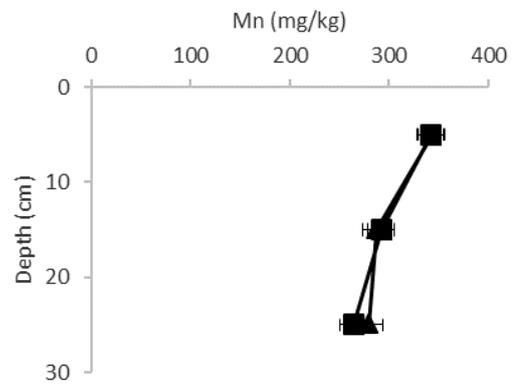
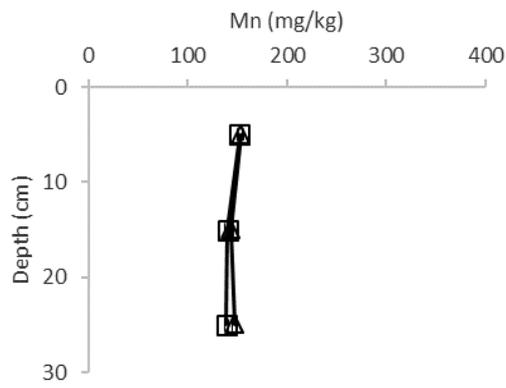
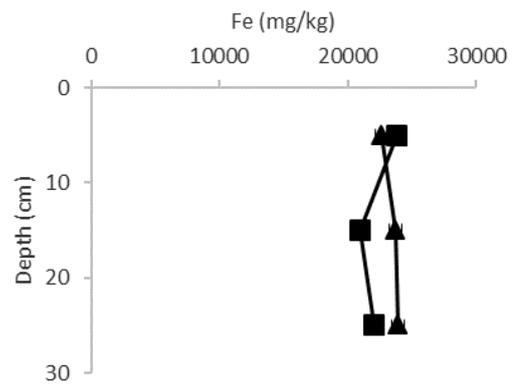
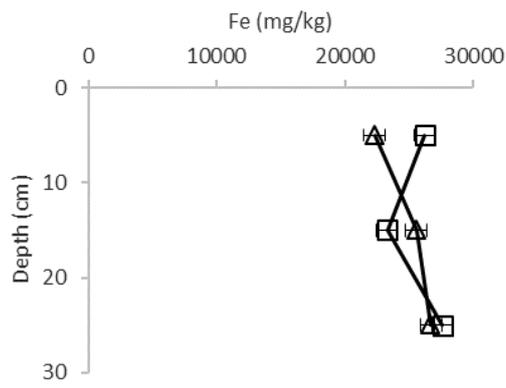
Big Muddy Creek



Mangere Inlet







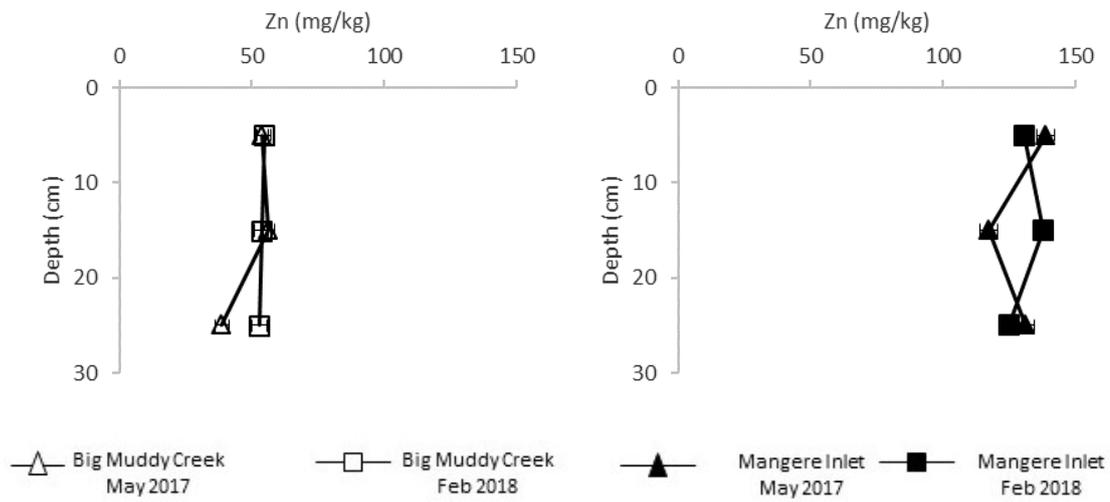


Figure 5.3. Organic matter (OM, %), pH, and concentrations (mg/kg) of Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper(Cu), Iron (Fe), Manganese (Mn), Lead (Pb), and Zinc (Zn) in two locations (Big Muddy Creek, Mangere Inlet) at three sediment depths (top, 0-10 cm; middle, 10-20 cm; and bottom, 20-30 cm) in May 2017 (Winter) and February 2018 (Summer).

5.5 Discussion

Like other urban estuaries worldwide, the concentrations of trace metal contamination in the Manukau Harbour are associated with historical urbanization and industrialization activities in the Auckland region (Cromarty and Scott, 1995). The higher trace metal levels in Manukau Harbour, as reported by several authors (Aggett and Simpson 1986; Glasby et al., 1988; Williamson and Wilcock, 1994; Reed and Gadd, 2009) could be the result of proximity to the various sources of anthropogenic contaminants. Specifically, the MI location has been heavily contaminated by trace metals due to intense urban and industrial discharges and is considered to be the most polluted area of the Manukau Harbour (Glasby et al., 1988; Williamson and Wilcock, 1994; Kelly, 2008). Indeed, the presence of mangrove stands at MI has been suggested to serve as the main pollutant sequestration mechanisms in the estuary (Harbison, 1986). The findings of the present study support this assertion and we further identified factors controlling trace metal distribution in sediments of mangrove stands at two locations in the estuary.

5.5.1 Spatial variations of trace metals and other sediment parameters

In the present study, the concentrations of most trace metals were higher than those measured in other New Zealand estuaries (Desmond et al., 2012; Bastakoti et al., 2018; Bourgeois et al., 2019a). Among the two study locations within the Manukau Harbour, the levels of OM and most trace metals in mangrove sediments were higher in Ann's Creek at MI than at BMC and the findings were consistent with the results of several past studies in the same harbour (Williamson et al., 1999; Mills et al., 2000; Mathieson et al., 2002; Reed and Gadd, 2009). Indeed, urban mangrove stands within MI receive comparatively more anthropogenic contaminants than rural mangrove stands at BMC. We observed that the concentrations of most of these trace metals were positively correlated with one another, which indicates a common source of contamination (Tam and Wong, 1995; Acevedo-Figueroa et al., 2006; Desmond et al., 2012).

The observed trend of OM contents within the two mangrove stands suggests that both autochthonous and allochthonous substances significantly contribute to fluctuating levels of OM content in mangrove sediments. Most importantly, mangrove litter provides a major contribution to the OM content in a mangrove forest, but allochthonous substance inputs from catchment areas also play a dynamic role (Woodroffe, 1985; Tam and Wong, 1998; Bouillon et al., 2003; Kristensen et al., 2008). Especially, in our urban mangrove site, the input of anthropogenic contaminants from surrounding urban areas during high freshwater inputs and/or tidal cycles would have contributed to a greater extent to the elevated sediment OM contents. Also, the prolonged tidal inundation in this urban mangrove stand due to proximity to the estuary would have lowered mineralization processes and enhanced OM accumulation in mangrove sediments (Harbison, 1986; Kristensen et al. 2008a; Grellier et al., 2017). On the other hand, the major sources of OM in the rural mangrove site could be the input of plant litters from mangrove stands and adjacent coastal forests (Pohutukawa, Puriri, Kanuka; Davis et al., 2018). The OM contribution from autochthonous sources is likely to be higher in the rural mangrove stand since this stand has the tallest and biggest mangrove trees in the Auckland region (Hayward and Morley, 2004). However, the OM content in the rural mangrove site was found to be lower than at MI, which suggested that proximity to the anthropogenic sources is a major factor controlling OM distribution in mangrove sediments.

In fact, the decomposition of OM and oxidation of sulphides in suboxic conditions commonly found in mangrove forests tend to increase sediment acidity (Sigel, 1985; Lacerda et al., 1995; Marchand et al., 2004; Adeleke et al., 2017). Despite the higher OM content, mangrove sediments of the urban site were slightly less acidic than those in the rural site, which could be due to differences in the length of tidal inundation periods between these two locations. The reducible condition induced by prolonged tidal inundation would have resulted higher sediment pH in mangrove sediments in the urban site (Tam and Wong, 1998; Li et al., 2007). Notably, seawater helps to neutralize sediment pH because the seawater is rich in carbonates and bicarbonates and has a high buffering capacity (Thompson and Bonnar, 1931; Pytkowicz,

1967). Such capacity of seawater to neutralize sediment pH was also found in the sedimentary column, as pH levels were comparatively higher on top sediments in both locations during the study period.

In the present study, Fe concentrations were slightly higher in the rural than in the urban mangrove stand, which is probably due to the natural abundance of this element in the Earth's crust and rock types within this catchment areas. Specifically, the higher concentration of Fe in the rural mangrove site could be a result of easily erodible volcanoclastic sandstones and siltstones present within the nearby Waitakere Ranges (Reid et al., 2008). On the other hand, the basaltic volcanic field of the Auckland region (Reid et al., 2008) would have also contributed to enrich Fe concentrations in both locations in the study area. During anaerobic reduction process, these iron-enriched eroded materials from the catchment are buried in the mangrove sediments as Fe sulphides (FeS_2 and FeS). Generally, anoxic sediments rich in sulphides have a high capacity to sequester trace metals (Alongi, 2009), whereas, in oxic or suboxic conditions, metals are trapped by Fe and Mn oxy(hydroxides) (Du Laing et al., 2009). In the present study, we did not observe a close association between Fe and other trace metals due to possible dissimilarity in their major input sources. The enrichment in Fe concentration was likely from eroded catchment rocks, whereas trace metals would have been derived from anthropogenic sources. The observed positive correlation between OM and most trace metals (Co, Cr, Cu, Mn, Pb, and Zn) suggests that the metal distribution was influenced by OM content in the sediments because OM is another key binding phase for trace metals in sediments (Ankley et al., 1996; Yu et al., 2001). As a result, these trace metals were higher in mangrove sediments of the urban site than in the rural site. Indeed, sediments rich in OM content and clay minerals (larger surface area; Singh et al., 1999) have a high capacity to sequester trace metals (Marchand et al., 2011). Several previous studies have reported on the great capacity of OM to sequester trace metals in mangrove sediments (Marchand et al., 2011; Thanh-Nho et al., 2018; Bastakoti et al., 2019). Generally, this trapping mechanism is associated with an inherent capacity of OM to form complexes with metals (Clark et al., 1998). The negatively charged surface of OM and fine

sediments retain cations (metal ions) and such process is facilitated by the higher proportion of humic compounds found in OM (Rashid, 1974; Evan, 1989). Additionally, these humic substances help to bind the metal ions within OM as a result of the complexation or chelation process (Evan, 1989). Coupled with organic-rich fine sediments, the mangrove stand at MI is located near an urban area that has a history of contamination since the 1920s (Kelly, 2008; Kelly, 2008a). Also, the higher sediment pH observed in this urban mangrove stand presents favourable condition to retain trace metals since metal leaching is common in acidic sediments (Saenger and McConchie, 2004). Hence, we suggest that higher concentrations of trace metals in mangrove sediments of the urban site were the result of OM richness and nearby anthropogenic sources. Conversely, BMC has very few nearby anthropogenic sources of potential contaminants and the sediments were relatively coarser, organic poorer, and more acidic compared to MI sediments (Reed and Gadd, 2009), which had lowered trace metal concentrations. Hence, our results support the findings of several past studies, that mangrove sediments in the proximity of contaminant sources sequester high amounts of these pollutants (Ward and Young, 1981; Harbison, 1984; Chai et al., 2019).

5.5.2 Temporal variations in trace metals and other sediment parameters

Temporal variation in trace metal concentrations in mangrove sediments could have resulted in significant changes in sediment geochemistry due to local weather patterns and/or fluctuations in effluent inputs. In general, low atmospheric temperatures during the winter season are favourable conditions to accumulate contaminants in sediments. However, the warm temperature during the summer season may enhance microbial decomposition and organic acid formation, which help to leach trace metals from the sediments (Alongi, 1988). Most importantly, the changes in redox conditions during the wet season may also help to modulate trace metal concentrations in sediments. Especially, physical disturbances due to rainfall may create oxic or sub-oxic environments in mangrove sediments resulting in oxidation of sulphides into sulphates and releasing the trapped metals to overlying waters (Eggleton and Thomas,

2004; Atkinson et al., 2007). Hence, both atmospheric temperature and rainfall are key meteorological factors that regulate redox cycling, which then leads to fluctuating trace metal concentrations in mangrove sediments (Marchand et al., 2006; Nóbrega et al., 2013). Several studies have reported high trace metal concentrations in estuarine sediments during the dry winter season of tropical and sub-tropical regions (Nwadinigwe et al., 2014; Feng et al., 2017). However, New Zealand has dry summers and wet winters, which makes temporal/seasonal trace metal dynamics highly complex in this region. Due to the complex weather patterns in New Zealand and possible fluctuations in anthropogenic inputs, it was difficult to identify specific temporal/seasonal trends in trace metal concentrations in this study. Despite the dry summers in New Zealand, the total monthly rainfall was higher in February 2018 (summer) than in May 2017 (winter) (Metservice, 2017; Metservice, 2018). As a result, the OM content in mangrove sediments at both locations within the harbour was lower in the summer than in the winter months. Indeed, a long duration of tidal immersion during high rainfall in February 2018 would have created a higher energy environment and flushing of fine particles along with OM away from the mangrove stands. Such prolonged inundation periods could also lower trace metal, as observed with some trace metals at the top of the sedimentary column. On the other hand, rainfall may also mobilise top sediments, and enhance sulphide oxidation leading to dispersion of trace metals to overlying waters (Eggleton and Thomas, 2004; Atkinson et al., 2007). As a result, we observed OM levels and most trace metal concentrations to be higher on top sediments during the low rainfall period in winter, and such a trend did not exist, when the rainfall was higher in the summer. Furthermore, a higher level of OM and trace metals on top sediments during winter could also be associated with the low rate of anaerobic consumption of OM due to low rainfall and temperature. In addition, higher summer temperatures are often associated with high microbial decomposition on top sediments, which leads to increased sediment acidity and trace metal releases to overlying waters (Lau and Chu, 1999; Alagarsamy, 2006; Thanh-Nho et al., 2018). Hence, our findings suggest that the effects of rainfall and temperature were mostly apparent on top sediment layers. Since the mangrove stand in our rural

site had a dense canopy (tall mangrove trees; Hayward and Morley, 2004), we expect that the physical impact of rainfall on sediments would have been less than at MI (Brandt, 1988). This physical barrier may have been responsible for the fact that most trace metals on top sediments did not decrease in concentration in the rural mangrove site as they did in the urban mangrove site. Furthermore, the lack of specific trends in the sedimentary column between the urban and rural mangrove stands could also be associated with the history of metal contamination in these locations. Several studies have reported that sites with a long history of contamination generally have a higher level of trace metal concentrations in sub-surface than surface sediments (Osher et al., 2006; Nguyen et al., 2009; Dias-Ferreira et al., 2016). Likewise, in the present study, most trace metals were at a higher level either in the middle or bottom sediment profiles in the urban sites. Conversely, a higher level of most trace metals was observed on the top sediments in the rural sites. Such a trend in the urban sites could be associated with the long-term strong mixing of sediment layers and facilitated by the tidal currents during inundation periods. Especially, the higher concentrations of Cd, Cr, and Cu were observed in sub-surface sediment profiles of the urban sites during both seasons, which could represent historical metal signatures.

In general, we did observe an increase in average concentration values of some trace metals (Cd, Co, Pb, and Zn) during high rainfall periods in the summer, and such a trend could be associated with anthropogenic effluent inputs during excessive surface runoff. Several studies have reported that these trace metals are the most common contaminants derived from industries, farmlands, transportation, and domestic sewage (Erlenkeuser et al., 1974; Nriagu and Pacyna, 1988; Tariq et al., 2005). The increase in effluent inputs would have changed the sediment redox condition and decreased the mobility of trace metals within mangrove sediments (Marchand et al., 2011a).

Besides, the effects of anthropogenic inputs and weather patterns, the trace metal cycling in mangrove sediments in this study would have been influenced by biological activities, such as the distribution of aerial root systems of *Avicennia* forests and infaunal borrowing and feeding activities (Glasby et al., 1988; Williamson et al., 1995). Generally, bioturbation enhances the

diffusion of oxygen in sediments at depth, where sulphides at the redox boundary are oxidised and metals are released to pore waters in the bioavailable phase (Clark et al., 1998; Otero et al., 2009; Marchand et al., 2011). Thus, it is likely that trace metal cycling in mangrove sediments of the Manukau Harbour also reflect complex biological processes mediated by the mobility and distributions of the organisms inhabiting this ecosystem. Particularly, as a result of bio-accumulation process, metals could also enter the food chain, and such effects have been highlighted in several studies in estuarine sediments (Abdullah, 2007; Castiglioni et al., 2018; Chen et al., 2019; Thanh-Nho et al., 2019a).

5.6 Conclusions

The higher trace metal concentrations in mangrove sediments of the urban sites compared to the rural site in the present study indicate that proximity to the source of contaminants significantly regulates trace metal distributions in estuarine ecosystems. Hence, the influence of anthropogenic sources appeared to have a greater effect on diagenetic processes with regards to the distribution of most trace metals in the Manukau Harbour. Our findings also highlight associations between trace metal concentrations and OM levels, as organic rich sediments were found to be favourable for trace metal retention. It is well known that mangrove sediments have an inherent capacity to sequester trace metals, and the urban mangrove stand in our present study may indeed have a high sequestering capacity for trace metals and may help to reduce contamination threats to surrounding environments. However, several factors such as rainfall, atmospheric temperature, and/or bioturbation may influence trace metal cycling in mangrove sediments. As a result, mangrove sediments could act as secondary sources of contaminants when these trace metals are released to overlying waters in bioavailable forms. Thus, future studies may investigate the level of bioavailable trace metals in porewater and metal concentrations in mangrove tissues to more comprehensively understand the processes involved in metal dynamics within temperate estuaries. Our data did not conclusively detect seasonal variations in trace metal concentrations within mangrove sediments in the Manukau Harbour, which may require longer-term experiments to elucidate these complex patterns with the changeable weather conditions commonly observed in New Zealand and possible fluctuations in anthropogenic inputs in these temperate ecosystems.

Chapter 6. General discussion, conclusions, limitations and recommendations

6.1 Discussion

This chapter summarizes the major outcomes of the thesis and their scientific contribution. The comprehensive explanations and justifications on the findings are presented in discussion sections of the individual chapters (Chapter 2, 3, 4, 5). In this section of the chapter, I have also outlined the practical application of the outcomes of all experimental chapters to develop a better understanding of trace metal dynamics in context to the management and conservation of temperate mangrove ecosystems. Most importantly, chapter 2, 3, and 4 outline the role of mangroves to sequester trace metals and highlight the major factors controlling trace metal distribution in a less contaminated estuary of a temperate region. On the other hand, chapter 5 aims to further elaborate such understandings by assessing trace metal dynamics in mangrove sediments within an area under anthropogenic pressure. Overall, the outcomes of the thesis provide a solid recommendation with scientific justifications for the necessity of extensive scientific assessments on trace metals in mangrove ecosystems, especially before making management decisions involving their removal in New Zealand.

6.1.1 Factors controlling trace metal distributions in mangrove sediments

It is well known that several factors regulate trace metal cycling in mangrove sediments (Alongi et al., 2004; Marchand et al., 2016). Among them, the results of my experimental studies suggest that organic matter content in sediments is a key factor controlling trace metal distributions in mangrove sediments. During the entire study period, I observed a strong association between organic matter and trace metals. As a result, sediments having higher organic matter contents have higher metal sequestering capacity than poor-organic sediments (Ray et al., 2006; Marchand et al., 2011). The results of my study indicate that the mangrove stands within the upper estuary of Mangawhai Harbour have higher organic matter contents and trace metal concentrations in their sediments (Chapter 2). A similar positive correlation was observed during both temporal and spatial studies at Mangawhai and Manukau Harbours (Chapter 3, 4, 5). Generally, mangrove sediments are waterlogged and anoxic, so organic matter

decomposition pathways mostly use Fe (III) as an electron acceptor (Ponnamperuma, 1972; Kristensen, 2000; Otero et al., 2009). The formation of inorganic sulphur (FeS_2) during the anaerobic decomposition process induced by sulphate-reducing bacteria create a favourable condition to adsorb trace metals. However, changes in sediment redox conditions could influence the sequestering capacity of mangrove sediments. Such a change in sediment redox condition could be a result of any physical or biological disturbances. The effects of such disturbances on trace metal distributions have been observed in my study (Chapter 3, 4, and 5). During high rainfall events, the mangrove sediments are oxidised due to the renewal of electron acceptor, and this could lead to sulphur dissolution and trace metal release to porewaters (Eggleton and Thomas, 2004; Atkinson et al., 2007). The physical impacts during mangrove removal activities are extensive, and release of trace metals from sediments could be in a large scale. As a result, trace metal concentrations in mangrove removal sites of my study area sharply declined. On the other hand, bioturbation due to infaunal and root activities could also change sediment redox conditions and trace metals may be released to porewater due to the diffusion of oxygen in sediments (Clark et al., 1998). Metal releases from mangrove sediments in bioavailable forms may cause adverse impacts on surrounding ecosystems due to contaminant dispersals. Similar results were observed in my study, as trace metal concentrations in adjacent mudflat sediments were increased after mangrove removal. Sediment oxidation and sulphate formation as a result of physical disturbances could also lead to decreases in sediment pH and further leaching of trace metals to overlying waters may occur (Saenger and McConchie, 2004).

The hydrographic conditions of mangrove stands also influence sediment trace metal distribution. In the study, locations like Mangrove Island of Mangawhai Harbour had a high energy environment because it was situated in the middle of the estuary. As the high energy environment enhances dissolution and dispersal of fine particles, the organic matter content and trace metal concentrations in the island were very low compared to other mangrove stands within the same estuary.

Indeed, proximity to the sources of contaminants is another key factor influencing the trace metal distribution in mangrove sediments (Ward and Young, 1981; Harbison, 1984; Chai et al., 2019). In the study, such influences of anthropogenic sources were widely observed both in Mangawhai and Manukau Harbours. In chapter 2, it was reported that higher Pb concentration in sediments of mangrove stands close to Molesworth Drive (the main road) was a result of proximity to the line source of contamination. Similarly, in chapter 6, the level of trace metal concentrations in an urban mangrove stand (Mangere Inlet) was found to be several times higher than in a rural mangrove stand (Big Muddy Creek).

Overall, the findings on several factors influencing trace metal distributions in mangrove sediments suggest that effective mangrove management is only possible if it includes comprehensive local information on a site-by-site basis.

6.1.2 Distribution of trace metals along the sedimentary column

The findings of the thesis suggest that organic matter and most trace metals decreased with increasing sediment depth in mangrove habitats, especially in Mangawhai Harbour. However, a specific trend was not observed in highly contaminated Manukau Harbour because of possible fluctuation in contaminant inputs and a long history of contamination. Generally, due to the changes in redox condition induced by waterlogging after effluent inputs, trace metals are less mobile in the mangrove stands when effluents are received (Marchand et al., 2011a). Moreover, the trend of trace metal concentration in sedimentary columns was highly associated with the levels of organic matter in mangrove sediments. For an example, organic matter contents along with most trace metals on top sediments were higher in most mangrove stands of Mangawhai Harbour. On the other hand, due to lower organic matter contents on top sediments of mudflat, most trace metals were also in lower concentrations in this habitat. Hence, it can be concluded that high organic matter in top mangrove sediments has developed a prominent characteristic to trap trace metals and discourage downward migration and mobility. Overall, such findings on depth variations highlight that the implementation of decisions on mangrove management

including mangrove removal should be eco-friendly, so that sediment perturbation is minimised to avoid further metal leaching from sediment depths.

6.1.3 Seasonal variations of trace metals in mangrove sediments

In my study, seasonal variations of trace metals were found to be more or less controlled by local weather patterns and the rate of contaminant inputs. However, due to the complex weather conditions of this temperate region and possible fluctuations in anthropogenic inputs, a specific trend on seasonal variation of trace metals in mangrove sediments was difficult to identify. Especially, in the less contaminated mangrove stands of Mangawhai Harbour, seasonal variations in atmospheric temperature and rainfall were found to be key factors regulating temporal variations in trace metals. Indeed, high temperature enhances microbial activities, whereas high rainfall physically disturbs sediments and also tends to increase tidal immersion in mangrove stands. As a result, trace metals are released to overlying waters and similar results have been observed in Mangawhai Harbour. However, in urban mangrove stands of Manukau Harbour, a more complex scenario might have been created because of the higher rates of urban runoff entering these mangrove stands during rainfall events. Indeed, the influences of high temperature and physical disturbances created by rainfall have been observed in the top sediments of Manukau Harbour, as well. As a result, most trace metals decreased during rainfall events during the summer season. Overall, my study suggests that both weather patterns and anthropogenic inputs control temporal trace metal variations in mangrove sediments, but the degree of influence depends on the geographical location of the mangrove stand.

6.1.4 Spatial variations of trace metals along the estuary

Similar to the organic matter content, trace metal concentrations in mangrove sediments of Mangawhai Harbour were higher in the upper estuary and this could be a result of low tidal mixing in this location (Chapter 2). The higher energy environment in mangrove stands located in the lower estuary would have enhanced dispersal of fine particles and downstream dilution of trace metal concentrations in mangrove sediments (Nelson and Lamothe, 1993). On the other

hand, trace metal concentrations were higher in an urban mangrove stand than in a rural mangrove stand within Manukau Harbour (Chapter 5). In this case, my study suggests that proximity to the source of contaminants would have played a key role to regulate trace metal distributions in mangrove sediments. Especially, in the context of the ongoing mangrove removal activities in several urban areas of northern New Zealand, this study highlights the need for comprehensive scientific assessments on trace metals that could address possible impacts and suggest mitigation measures to protect estuarine ecosystems.

6.1.5 Spatial variations of trace metals among habitats

The variations of trace metal concentrations between mangrove sediments and mudflat sediments were highly significant (Chapter 2, 3, and 4) because of the entirely different hydrographic conditions in these two habitats. Mangrove stands experienced comparatively low energy environments to mudflats due to the presence of mangrove trees, prop roots, and pneumatophores, which act as biological barriers against the energy of tidal water or freshwater flows. This would have resulted in a higher fine particle deposition and organic matter accumulation within mangrove stands. Indeed, such fine organic sediments of mangrove sediments have a high capacity to sequester trace metals (Burone et al., 2003; Saenger and McConchie, 2004). On the other hand, mudflats lack any physical or biological barriers resulting in a comparatively high energy environment than mangrove stands, which leads to dispersion and dilution of fine particles. Hence, due to the low fine particle deposition and organic matter accumulation, mudflat sediments lacked trace metal sequestering capacity. Such variations in organic matter contents and trace metal concentrations between mangrove sediments and mudflat sediments indicated that mangrove forests are natural sinks of trace metals.

6.2 Limitations of thesis and recommendations

The major limitation of the thesis is that my study did not assess the levels of trace metal concentrations in mangrove tissues, which could help to understand further metal cycling in estuarine ecosystems because trace metals are persistent in nature and tend to accumulate in estuarine food chains. My study focused on analysing trace metal concentrations in sediments as it is a standard method to evaluate the extent of contaminations in an estuarine ecosystem. However, the analyses of trace metals in mangrove tissues could be a good approach to understand their effects on trophic levels because my study suggests that any physical disturbances such as mangrove removal could facilitate the release of metals in bioavailable form. Hence, for a better understanding of trace metal cycling processes in mangrove ecosystems, I suggest future researchers to investigate the trace metal levels in trophic levels within these estuarine ecosystems. Especially, the analyses of trace metal levels in mangrove roots, leaves, and stems could be a useful tool to identify the pathways of trace metal exports. Trace metal exports could also be determined by analysing bioavailable trace metal concentrations in porewater. On the other hand, a study on total inputs of suspended sediments to a mangrove ecosystem could be helpful to estimate trace metal imports. Additionally, future works on metal speciation in mangrove sediments might extend the knowledge on trace metal mobility and distribution occurring in different carrying phases.

There was a lack of a “true” control site similar to the Mangrove Island at Mangawhai Harbour, hence it was not possible to perform a Before-After-Control-Impact (BACI) design during the before-after mangrove removal study. Another limitation of my study is that I had only one sampling event in Manukau Harbour for each season (Summer and Winter) to assess seasonal variations on trace metal concentrations in mangrove sediments. Due to the time limitation and my thesis timeline, I was unable to conduct a long-term temporal variation experiment, which may comprehensively explain the seasonal patterns on trace metal concentrations in mangrove sediments.

6.3 Conclusions

My study aims to understand the dynamics of trace metals on mangrove sediments and elaborate on the scientific knowledge on several factors controlling their distributions in temperate estuaries. The thesis provides additional information regarding the sequestering capacity of mangrove sediments through a comprehensive assessment of major factors controlling the distribution of trace metals in mangrove sediments within a temperate region. Overall, the results of this study demonstrate a strong influence of organic matter to trace metal distribution in estuarine sediments. Indeed, mangrove sediments are mostly in oxygen-deficient conditions due to waterlogging environments, which results in low mineralization and high organic matter accumulation. My study suggests that such condition in mangrove sediments is favourable for bacterial sulphate reduction and formation of iron sulphides, which mainly control mobility and distribution of trace metals in anoxic phases. Moreover, due to the influences of anthropogenic inputs of contaminants to mangrove forests, trace metal concentrations may increase dramatically as observed during the study. However, mangrove sediments experiencing physical or biological disturbances may lack the inherent capacity to sequester trace metals because of the oxidation of sulphides. Especially, my study on pre- and post-mangrove removal provides insights onto the effects of such sediment disturbances in sediment geochemistry of estuarine ecosystems. My study further suggests that the hydrographic condition of mangrove stands also plays a key role in trace metal distributions, as lower trace metal levels were observed in mangrove stands experiencing higher energy environments. Generally, local weather, especially rainfall and atmospheric temperature patterns of an area highly influence trace metal distributions in mangrove sediments and has been reported in this thesis. However, my findings could not identify a specific seasonal trend for all trace metals, especially in the mangrove stands influenced by anthropogenic inputs. Such lack of a specific trend in seasonal variation of trace metals could be a result of possible fluctuations in anthropogenic inputs, complex weather patterns in New Zealand, and/or a result of the short-term experimental study.

In summary, my study suggests that mangrove sediments are trace metal sinks and redox condition plays a key role to control their distributions in mangrove ecosystems. Hence, mangroves may protect estuarine and coastal ecosystems from land-based derived contamination. The study also highlights that mangrove sediments could act as potential trace metal sources after being influenced by natural or anthropogenic factors. The findings of my thesis provide a better understanding on trace metal dynamics and likely to assist with estuarine management and conservation strategies of temperate mangrove ecosystems in New Zealand and globally. Also, the outcomes of this field-based scientific investigation highlight the need for comprehensive scientific assessments on trace metals in mangrove ecosystems, especially before making management decisions involving their removal in New Zealand. Indeed, the study provides scientific information to local communities regarding the importance of mangrove habitats to protect and balance estuarine environments.

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Appendices

Appendix 2.1

Mean (\pm SE) values for sediment parameters recorded from inside and outside of mangroves in IS, JB, IN, and MW. N/A: Data Not Available.

Habitat	Depth	Location	% OM	Bulk Density (g/cm ³)	Fe mg/kg	Cu mg/kg	Zn mg/kg	Pb mg/kg	Cd mg/kg	As mg/kg
Inside Mangrove	Top	IS	2.7 \pm 0.3	1.51 \pm 0.14	4006.72 \pm 364	13.62 \pm 2.98	13.71 \pm 3.25	0.92 \pm 0.4	0.51 \pm 0.29	48.52 \pm 5.56
		JB	20.87 \pm 0.96	0.31 \pm 0.19	16096.83 \pm 3200	34.53 \pm 3.07	55.23 \pm 2.62	12.66 \pm 0.74	0.13 \pm 0.03	40.91 \pm 11.37
		IN	19.22 \pm 1.66	0.45 \pm 0.05	12088.52 \pm 907	22.33 \pm 2.94	27.48 \pm 4.53	5.33 \pm 0.93	0.06 \pm 0.03	34.32 \pm 3.72
		MW	16.53 \pm 1.52	0.51 \pm 0.03	9893.47 \pm 1156	15.76 \pm 1.62	47.78 \pm 6.08	9.49 \pm 1.84	0.17 \pm 0.09	34.08 \pm 4.6
	Middle	IS	1.52 \pm 0.29	1.50 \pm 0.14	3584.12 \pm 551	12.45 \pm 4.36	15.45 \pm 2.42	0.59 \pm 0.41	0.52 \pm 0.24	44.97 \pm 5.85
		JB	19.3 \pm 2.72	0.41 \pm 0.08	9715.96 \pm 2722	27.54 \pm 4.56	38.65 \pm 1.48	8.13 \pm 2.07	0.15 \pm 0.11	40.63 \pm 5.84
		IN	16.67 \pm 2.19	0.85 \pm 0.14	11842.65 \pm 2587	13.6 \pm 1.67	20.22 \pm 5.76	3.29 \pm 1.59	0.03 \pm 0.03	34.71 \pm 1.92
		MW	14.17 \pm 2.28	0.53 \pm 0.04	9725.15 \pm 783	13.92 \pm 3.91	27.83 \pm 6.08	10.86 \pm 1.24	0.07 \pm 0.07	33.33 \pm 6.22
	Bottom	IS	1.46 \pm 0.28	1.43 \pm 0.16	3128.53 \pm 491	10.64 \pm 2.51	14.58 \pm 2.20	1.34 \pm 0.62	0.44 \pm 0.25	28.5 \pm 5.44
		JB	11.27 \pm 0.13	0.56 \pm 0.10	8754.64 \pm 1085	18.12 \pm 0.91	35.73 \pm 4.31	7.51 \pm 2.96	0.03 \pm 0.03	33.88 \pm 6.97
		IN	14.33 \pm 3.18	1.23 \pm 0.16	8231.58 \pm 819	14.67 \pm 2.83	15.51 \pm 2.84	2.41 \pm 1.01	0.07 \pm 0.07	30.07 \pm 4.24
		MW	12.93 \pm 0.97	1.21 \pm 0.11	7943.43 \pm 1212	14.21 \pm 1.48	38.08 \pm 3.39	9.68 \pm 0.31	0.06 \pm 0.06	26.76 \pm 1.9
		Max	20.87\pm0.96	1.51\pm0.14	16096.83\pm3200	34.53\pm3.07	55.23\pm2.62	12.66\pm0.74	0.52\pm0.24	48.52\pm5.56
		Min	1.46\pm0.28	0.31\pm0.19	3128.53\pm491	10.64\pm2.51	13.71\pm3.25	0.59\pm0.41	0.03\pm0.03	26.76\pm1.9
	Avg	12.58\pm1.37	0.88\pm0.11	8750.97\pm1323.47	17.62\pm2.74	29.19\pm3.75	6.02\pm1.18	0.19\pm0.11	35.89\pm5.3	
Outside Mangrove	Top	IS	0.85 \pm 0.13	1.40 \pm 0.12	1557.7 \pm 298	6.71 \pm 2.36	10.6 \pm 0.85	0.72 \pm 0.45	0.01 \pm 0.01	54.74 \pm 1.96
		JB	2.1 \pm 0	1.25 \pm 0.05	18400 \pm 0	12.12 \pm 0	41.65 \pm 0	13.39 \pm 0	0.13 \pm 0	49.84 \pm 0
		IN	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

	MW	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Middle	IS	0.73±0.17	1.51±0.12	1899.57±341	4.1±1.58	12.04±1.23	0.32±0.32	0±0	55.12±3.31
	JB	0.9±0	1.13±0.04	10226.41±0	9.01±0	19.19±0	4.51±0	0.08±0	36.68±0
	IN	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	MW	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Bottom	IS	1.05±0.19	1.56±0.18	1723.36±253.98	4.28±1.07	7.41±0.33	0.41±0.41	0±0	45.18±4.94
	JB	0.9±0	1.46±0.06	14413.87±0	8.02±0	10±0	2.29±0	0.08±0	29.32±0
	IN	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	MW	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Max	2.1±0	1.56±0.18	18400±0	12.12±0	41.65±0	13.39±0	0.13±0	55.12±3.31
	Min	0.73±0.17	1.13±0.04	1557.7±298	4.1±1.58	7.41±0.33	0.32±0.32	0±0	29.32±0
	Avg	1.09±0.16	1.39±0.14	8036.82±297.85	7.37±1.67	16.81±0.8	3.61±0.39	0.05±0	45.15±3.40

Appendix 3.1

Mean values (\pm SE) for sediment parameters (OM = Organic Matter %, Fe = Iron mg kg⁻¹, Cu = Copper mg kg⁻¹, Zn = Zinc mg kg⁻¹, Pb = Lead mg kg⁻¹, Cd = Cadmium mg kg⁻¹, As = Arsenic mg kg⁻¹) recorded from inside and outside of mangroves in different months and total monthly rainfall mm and average monthly air temperature °C.

		% OM	Fe mg kg ⁻¹	Cu mg kg ⁻¹	Zn mg kg ⁻¹	Pb mg kg ⁻¹	Cd mg kg ⁻¹	As mg kg ⁻¹	Monthly Rainfall mm	Temp °C
Inside (Mangrove)	Sep-14	2.11±0.45	3942.85±258.83	5.16±0.82	11.34±0.85	0.43±0.24	0.06±0.02	31.01±5.20	95.8	14.83
	Dec-14	1.63±0.31	3538.87±327.26	11.01±1.32	18.78±1.44	1.65±0.25	0.10±0.02	34.81±7.73	143.9	19.03
	Feb-15	1.79±0.27	3403.43±269.7	11.28±0.54	15.46±0.83	1.65±0.57	0.57±0.06	40.21±6.94	41.8	21.46
	May-15	1.89±0.4	3573.12±253.57	12.23±0.87	14.58±0.5	0.95±0.22	0.49±0.02	40.66±6.17	101.3	16.4
	Jun-15	1.75±0.38	3349.59±579.66	11.06±0.97	13.06±2.2	0.86±0.3	0.01±0.01	38.03±8.43	33.6	14.19
	Min	1.63±0.31	3349.59±579.66	5.16±0.82	11.34±0.85	0.43±0.24	0.01±0.01	31.01±5.20	33.6	14.19
	Max	2.11±0.45	3942.85±258.83	12.23±0.87	18.78±1.44	1.65±0.57	0.57±0.06	40.66±6.17	143.9	21.46
	Mean	1.83	3561.57	10.15	14.64	1.11	0.24	36.94		
Outside (Mudflat)	Sep-14	0.88±0.07	1905.345±61.11	3.99±0.78	10.55±0.90	0.28±0.03	0	46.74±2.41	95.8	14.83
	Dec-14	0.87±0.05	1665.12±70.44	3.85±0.53	9.52±0.51	0.30±0.08	0	50.35±0.62	143.9	19.03
	Feb-15	0.95±0.15	1911.45±11.15	3.94±0.88	10.32±0.33	0.40±0.22	0.02±0.1	47.90±1.97	41.8	21.46
	May-15	0.88±0.09	1726.88±98.71	5.03±0.84	10.01±1.37	0.48±0.12	0	51.68±3.25	101.3	16.4
	Jun-15	0.88±0.06	1872.85±67.63	4.38±0.42	10.33±0.77	0.46±0.09	0	51.83±0.23	33.6	14.19
	Min	0.87±0.05	1665.12±70.44	3.85±0.53	9.52±0.51	0.28±0.03	0	46.74±2.41	33.6	14.19
	Max	0.95±0.15	1911.45±11.5	5.03±0.84	10.55±0.90	0.48±0.12	0.02±0.1	51.83±0.23	143.9	21.46
	Mean	0.89	1816.29	4.24	10.15	0.38	0.01	49.70		
HISS-1 certified values (\pm SD)			2460±90	2.29±0.37	4.94±0.79	3.13±0.4	0.024±0.009	0.801±0.0999		
HISS-1 observed values (\pm SD)			2262.796±74.96	2.09±0.149	5.41±0.40	2.802±0.17	0.0219±0.002	0.892±0.0972		

Appendix 3.2

Mean values (\pm SE) for sediment parameters (OM = Organic Matter %, Fe = Iron mg kg⁻¹, Cu = Copper mg kg⁻¹, Zn = Zinc mg kg⁻¹, Pb = Lead mg kg⁻¹, Cd = Cadmium mg kg⁻¹, As = Arsenic mg kg⁻¹) recorded on Top (T), Middle (M), and Bottom (B) from inside and outside of mangroves in different months.

		Site	% OM	Fe (mg kg ⁻¹)	Cu (mg kg ⁻¹)	Zn (mg kg ⁻¹)	Pb (mg kg ⁻¹)	Cd (mg kg ⁻¹)	As (mg kg ⁻¹)	
Inside (Mangrove)	2015	Jun	T	2.46 \pm 0.43	4493.71 \pm 247.03	12.97 \pm 3.39	17.42 \pm 2.08	1.42 \pm 0.54	0.02 \pm 0.02	48.68 \pm 4.63
		M	1.64 \pm 0.28	2939.58 \pm 204.68	10.43 \pm 3.04	11.37 \pm 1.23	0.74 \pm 0.25	0 \pm 0	44.03 \pm 4.67	
		B	1.16 \pm 0.19	2615.47 \pm 216.29	9.77 \pm 2.64	10.4 \pm 1.38	0.41 \pm 0.17	0 \pm 0	21.38 \pm 1.78	
	May	T	2.7 \pm 0.3	4006.72 \pm 364.66	13.62 \pm 2.98	13.71 \pm 3.25	0.92 \pm 0.4	0.51 \pm 0.29	48.52 \pm 5.55	
		M	1.52 \pm 0.28	3584.12 \pm 551.23	12.45 \pm 4.36	15.45 \pm 2.42	0.59 \pm 0.41	0.52 \pm 0.24	44.97 \pm 5.84	
		B	1.46 \pm 0.28	3128.53 \pm 491.46	10.64 \pm 2.51	14.58 \pm 2.2	1.34 \pm 0.62	0.44 \pm 0.25	28.5 \pm 5.43	
	Feb	T	2.32 \pm 0.53	3942.48 \pm 516.22	10.24 \pm 2.68	16.66 \pm 1.58	2.76 \pm 0.89	0.65 \pm 0.25	49.74 \pm 5.27	
		M	1.6 \pm 0.38	3116.84 \pm 523.07	12.04 \pm 5.36	13.87 \pm 2.82	0.83 \pm 0.63	0.61 \pm 0.4	44.18 \pm 4.88	
		B	1.44 \pm 0.38	3150.97 \pm 378.91	11.55 \pm 3.92	15.85 \pm 2.43	1.37 \pm 0.6	0.45 \pm 0.25	26.71 \pm 6.16	
	2014	Dec	T	2.24 \pm 0.32	4054.42 \pm 316.64	13.5 \pm 3.05	21.65 \pm 1.93	2.03 \pm 0.24	0.07 \pm 0.02	48.02 \pm 4.85
			M	1.44 \pm 0.19	3630.3 \pm 242.77	10.48 \pm 2.96	17.47 \pm 1.07	1.74 \pm 0.12	0.12 \pm 0.04	35.17 \pm 5.8
			B	1.2 \pm 0.27	2931.88 \pm 187.94	9.03 \pm 2.67	17.22 \pm 2.03	1.18 \pm 0.4	0.1 \pm 0.06	21.24 \pm 2.3
Sep		T	2.98 \pm 0.3	4362.73 \pm 81.13	5.56 \pm 1.99	12.95 \pm 1.04	0.9 \pm 0.33	0.03 \pm 0.03	37.55 \pm 3.17	
		M	1.86 \pm 0.31	3995.12 \pm 389.45	6.33 \pm 2.5	10.09 \pm 0.79	0.33 \pm 0.15	0.09 \pm 0.04	34.74 \pm 3.32	
		B	1.5 \pm 0.36	3470.7 \pm 339.32	3.59 \pm 1.57	10.96 \pm 0.91	0.07 \pm 0.05	0.06 \pm 0.03	20.74 \pm 3.09	
Outside (Mudflat)	2015	Jun	T	0.85 \pm 0.08	2004.96 \pm 242.15	5.04 \pm 1.32	11.46 \pm 0.53	0.63 \pm 0.39	0.01 \pm 0.01	52.28 \pm 1.56
		M	0.8 \pm 0.04	1831.97 \pm 191.95	4.5 \pm 1.28	10.66 \pm 0.83	0.43 \pm 0.26	0 \pm 0	51.73 \pm 2.09	
		B	1 \pm 0.04	1781.64 \pm 181.35	3.6 \pm 0.98	8.86 \pm 0.24	0.34 \pm 0.19	0 \pm 0	51.49 \pm 2.29	
	May	T	0.85 \pm 0.13	1557.7 \pm 298.29	6.71 \pm 2.36	10.6 \pm 0.85	0.72 \pm 0.45	0.01 \pm 0.01	54.74 \pm 1.96	
		M	0.73 \pm 0.16	1899.57 \pm 341.29	4.1 \pm 1.58	12.04 \pm 1.23	0.32 \pm 0.32	0 \pm 0	55.12 \pm 3.3	
		B	1.05 \pm 0.18	1723.36 \pm 253.98	4.28 \pm 1.07	7.41 \pm 0.33	0.41 \pm 0.41	0 \pm 0	45.18 \pm 4.93	

Feb	T	0.75±0.09	1933.66±201.14	5.68±1.59	10.98±0.54	0±0	0.03±0.01	49.41±3.49
	M	0.85±0.32	1902.11±200.44	2.85±0.91	9.95±0.82	0.45±0.45	0.02±0.02	50.3±1.28
	B	1.25±0.18	1898.6±171.72	3.29±0.63	10.02±0.45	0.74±0.74	0±0	44±5
Dec	T	0.88±0.12	1804.17±221.36	4.82±1.32	10.33±0.49	0.16±0.16	0.01±0.01	51.15±2.77
	M	0.78±0.06	1615.25±207.38	3.75±1.12	9.64±1.03	0.45±0.26	0±0	50.76±3.09
	B	0.95±0.05	1575.95±224.33	2.98±0.96	8.59±0.35	0.31±0.31	0±0	49.14±3.89
2014	T	0.85±0.10	1996.54±219.66	5.41±1.52	11.89±0.5	0.26±0.26	0.01±0.01	50.70±2.08
	M	0.78±0.11	1930.22±214.58	3.85±1.32	10.93±1.17	0.33±0.33	0±0	47.14±3.38
	B	1.03±0.13	1789.28±216.65	2.72±0.57	8.83±0.68	0.24±0.24	0±0	42.37±3.06

Appendix 4.1

Mean values (\pm SD) for sediment parameters (OM = Organic Matter in %, pH, BD = Bulk Density in g cm^{-3} , Fe = Iron in $\mu\text{mol g}^{-1}$, Cu = Copper in $\mu\text{mol g}^{-1}$, Zn = Zinc in $\mu\text{mol g}^{-1}$, Pb = Lead in nmol g^{-1} , Cd = nmol g^{-1}) on Top (0-10 cm) = T, Middle (10-20 cm) = M, and Bottom (20-30 cm) = B in the island and mudflats during pre- and post-mangrove removal periods.

Habitat	Status	Depth	OM (%)	pH	BD (g cm^{-3})	Fe ($\mu\text{mol g}^{-1}$)	Cu ($\mu\text{mol g}^{-1}$)	Zn ($\mu\text{mol g}^{-1}$)	Pb (nmol g^{-1})	Cd (nmol g^{-1})	
Island	Before Mangrove Removal	T	2.84 \pm 0.19	6.19 \pm 0.08	1.47 \pm 0.06	74.93 \pm 4.50	0.15 \pm 0.08	0.20 \pm 0.01	4.38 \pm 0.07	2.38 \pm 2.99	
		M	1.69 \pm 0.24	5.94 \pm 0.04	1.41 \pm 0.12	67.85 \pm 5.20	0.14 \pm 0.06	0.19 \pm 0.05	2.20 \pm 0.88	2.68 \pm 2.69	
		B	1.48 \pm 0.02	5.92 \pm 0	1.34 \pm 0.12	59.08 \pm 4.33	0.11 \pm 0.07	0.19 \pm 0.03	3.40 \pm 4.32	2.24 \pm 2.36	
		Mean	2\pm0.67	6.02\pm0.14	1.41\pm0.1	67.29\pm7.98	0.14\pm0.06	0.2\pm0.03	3.33\pm2.2	2.44\pm2.1	
	After Mangrove Removal	T	1.06 \pm 0.12	5.97 \pm 0.59	1.56 \pm 0.03	60.63 \pm 7.02	0.11 \pm 0.01	0.21 \pm 0.01	3.36 \pm 0.86	2.67 \pm 1.75	
		M	0.82 \pm 0.15	5.35 \pm 0.09	1.41 \pm 0.01	62.29 \pm 6.97	0.09 \pm 0.01	0.18 \pm 0.01	2.34 \pm 0.88	3.64 \pm 1.21	
		B	0.94 \pm 0.22	5.42 \pm 0.07	1.31 \pm 0.03	59.86 \pm 11.4	0.12 \pm 0.01	0.18 \pm 0.01	2.59 \pm 0.67	3.52 \pm 0.87	
		Mean	0.94\pm0.18	5.58\pm0.42	1.43\pm0.11	60.93\pm7.63	0.11\pm0.02	0.2\pm0.02	2.77\pm0.84	3.28\pm1.24	
	Mudflats	Before Mangrove Removal	T	0.85 \pm 0	6.82 \pm 0.09	1.33 \pm 0.08	31.82 \pm 5.55	0.09 \pm 0.01	0.17 \pm 0.01	2.34 \pm 1.56	0.04 \pm 0
			M	0.75 \pm 0.03	6.49 \pm 0.07	1.46 \pm 0.05	34.28 \pm 0.38	0.06 \pm 0.00	0.17 \pm 0.01	1.55 \pm 0.05	0 \pm 0
B			1.03 \pm 0.01	6.41 \pm 0.17	1.49 \pm 0.08	31.44 \pm 0.83	0.05 \pm 0.01	0.12 \pm 0.01	1.56 \pm 0.58	0 \pm 0	
Mean			0.88\pm0.13	6.58\pm0.22	1.43\pm0.1	32.52\pm2.87	0.07\pm0.02	0.16\pm0.03	1.82\pm0.85	0.01\pm0.02	
After Mangrove Removal		T	0.90 \pm 0.10	6.48 \pm 0.33	1.45 \pm 0.08	45.65 \pm 0.95	0.11 \pm 0.05	0.18 \pm 0.03	4.43 \pm 1.82	3.34 \pm 0.71	
		M	0.88 \pm 0.16	6.09 \pm 0.74	1.49 \pm 0.07	50.72 \pm 9.11	0.11 \pm 0.06	0.15 \pm 0.01	5.04 \pm 2.32	3.38 \pm 1.67	
		B	0.82 \pm 0.02	5.79 \pm 0.22	1.47 \pm 0.08	55.47 \pm 3.10	0.10 \pm 0.04	0.17 \pm 0.02	7.64 \pm 0.68	5.40 \pm 2.24	
		Mean	0.87\pm0.11	6.13\pm0.52	1.48\pm0.07	50.62\pm6.44	0.11\pm0.05	0.17\pm0.03	5.71\pm2.12	4.04\pm1.77	
HISS-1		Certified Values				44.05\pm1.61	0.036\pm0.006	0.0755\pm0.012	15.11\pm1.93	0.213\pm0.08	
		Observed Values				40.56\pm1.32	0.033\pm0.002	0.083\pm0.007	13.26\pm0.83	0.198\pm0.018	

Appendix 4.2

Mean values (\pm SD) for sediment parameters (OM = Organic Matter in %, pH, BD = Bulk Density in g cm^{-3} , Fe = Iron in $\mu\text{mol g}^{-1}$, Cu = Copper in $\mu\text{mol g}^{-1}$, Zn = Zinc in $\mu\text{mol g}^{-1}$, Pb = Lead in nmol g^{-1} , Cd = nmol g^{-1}) in the island and mudflats during pre- and post-mangrove removal periods including certified and observed values of Marine Sediment Certified Reference Material (HISS-1).

Habitat		Month	OM (%)	pH	BD (g cm^{-3})	Fe ($\mu\text{mol g}^{-1}$)	Cu ($\mu\text{mol g}^{-1}$)	Zn ($\mu\text{mol g}^{-1}$)	Pb (nmol g^{-1})	Cd (nmol g^{-1})
Island	Before Mangrove Removal	Sep14	2.11 \pm 0.77	6.05 \pm 0.17	1.33 \pm 0.08	70.6 \pm 8.02	0.08 \pm 0.02	0.17 \pm 0.02	2.08 \pm 2.03	0.53 \pm 0.25
		May15	1.89 \pm 0.69	5.98 \pm 0.12	1.48 \pm 0.04	63.98 \pm 7.86	0.19 \pm 0.02	0.22 \pm 0.01	4.57 \pm 1.82	4.33 \pm 0.36
		Mean	2\pm0.67	6.02\pm0.14	1.41\pm0.1	67.29\pm7.98	0.14\pm0.06	0.2\pm0.03	3.33\pm2.2	2.44\pm2.1
	After Mangrove Removal	Sep15	1.02 \pm 0.16	5.71 \pm 0.52	1.43 \pm 0.09	51.54 \pm 3.30	0.11 \pm 0.01	0.20 \pm 0.02	2.37 \pm 0.76	2.60 \pm 0.10
		May17	0.88 \pm 0.28	5.63 \pm 0.59	1.44 \pm 0.13	67.12 \pm 3.14	0.09 \pm 0.01	0.19 \pm 0.00	2.92 \pm 0.87	2.60 \pm 1.38
		May18	0.90 \pm 0.08	5.39 \pm 0.10	1.42 \pm 0.15	64.13 \pm 2.63	0.11 \pm 0.01	0.20 \pm 0.02	3.01 \pm 1.05	4.63 \pm 0.27
Mean	0.94\pm0.18	5.58\pm0.42	1.43\pm0.11	60.93\pm7.63	0.11\pm0.02	0.2\pm0.02	2.77\pm0.84	3.28\pm1.24		
Mudflats	Before Mangrove Removal	Sep14	0.88 \pm 0.12	6.66 \pm 0.19	1.38 \pm 0.08	34.1 \pm 1.89	0.06 \pm 0.02	0.16 \pm 0.02	1.32 \pm 0.23	0.01 \pm 0.02
		May15	0.87 \pm 0.16	6.49 \pm 0.23	1.50 \pm 0.09	30.9 \pm 3.06	0.07 \pm 0.02	0.15 \pm 0.03	2.31 \pm 1.00	0.01 \pm 0.02
		Mean	0.88\pm0.13	6.58\pm0.22	1.43\pm1	32.52\pm2.87	0.07\pm0.02	0.16\pm0.03	1.82\pm0.85	0.01\pm0.02
	After Mangrove Removal	Sep15	0.78 \pm 0.00	5.78 \pm 0.49	1.51 \pm 0.09	52.09 \pm 5.73	0.15 \pm 0.03	0.17 \pm 0.04	6.90 \pm 1.04	2.43 \pm 0.54
		May17	0.97 \pm 0.11	6.55 \pm 0.58	1.44 \pm 0.04	45.72 \pm 5.93	0.10 \pm 0.04	0.17 \pm 0.02	4.50 \pm 3.04	5.12 \pm 1.82
		May18	0.85 \pm 0.06	6.04 \pm 0.18	1.46 \pm 0.07	54.04 \pm 6.40	0.06 \pm 0.01	0.15 \pm 0.01	5.72 \pm 1.78	4.57 \pm 1.69
Mean	0.87\pm0.11	6.13\pm0.52	1.48\pm0.07	50.62\pm6.44	0.11\pm0.05	0.17\pm0.03	5.71\pm2.12	4.04\pm1.77		

Appendix 5.1

Mean values (\pm SE) for sediment parameters- Organic matter (OM, %), pH, and concentrations (mg/kg) of Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Lead (Pb), and Zinc (Zn) in two locations (Big Muddy Creek, Mangere Inlet) at three sediment depths (top, 0-10 cm; middle, 10-20 cm; and bottom, 20-30 cm) in May 2017 (Summer) and February 2018 (Summer).

		OM (%)	pH	Cd (mg/kg)	Co(mg/kg)	Cr (mg/kg)	Cu(mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Pb (mg/kg)	Zn (mg/kg)
Big Muddy Creek											
	T	5.10 \pm 1.07	6.81 \pm 0.19	0.1 \pm 0.10	3.11 \pm 0.33	18.1 \pm 2.34	10.24 \pm 0.93	22304.59 \pm 3291.82	153.68 \pm 9.45	10.42 \pm 2.97	53.8 \pm 3.86
May 2017	M	3.82 \pm 0.40	6.43 \pm 0.44	0.05 \pm 0.05	2.59 \pm 0.18	20.26 \pm 0.72	9.54 \pm 0.97	25549.69 \pm 392.69	143.63 \pm 10.08	7.90 \pm 1.06	56.17 \pm 6.88
	B	4.57 \pm 0.85	6.08 \pm 0.98	0.04 \pm 0.04	2.43 \pm 1.15	15.41 \pm 4.11	7.31 \pm 1.87	26683.28 \pm 467.63	147.24 \pm 17.32	9.22 \pm 2.25	38.67 \pm 3.65
	Avg	4.50\pm0.40	6.45\pm0.30	0.06\pm0.03	2.71\pm0.33	17.95\pm1.39	9.03\pm0.71	24845.86\pm1044.79	148.18\pm5.87	9.18\pm1.05	49.57\pm3.33
	T	3.05 \pm 0.95	6.86 \pm 0.01	0.14 \pm 0.05	2.91 \pm 0.16	18.53 \pm 2.53	8.09 \pm 0.55	26197.93 \pm 2024.38	152.30 \pm 7.48	9 \pm 0.80	54.74 \pm 0.8
Feb 2018	M	3.54 \pm 0.66	6.33 \pm 0.45	0.14 \pm 0.05	2.68 \pm 0.32	20.48 \pm 1.40	7.74 \pm 0.75	23287.11 \pm 2324.90	140.30 \pm 4.56	11.24 \pm 0.31	53.67 \pm 1.97
	B	2.45 \pm 0.15	5.94 \pm 0.66	0.16 \pm 0.01	3.17 \pm 0.13	16.34 \pm 4.10	7.57 \pm 0.58	27551.91 \pm 500.11	139.23 \pm 11.64	8.95 \pm 1.61	52.92 \pm 8.35
	Avg	3.02\pm0.33	6.38\pm0.24	0.15\pm0.02	2.92\pm0.12	18.45\pm1.40	7.80\pm0.27	25678.98\pm983.19	143.94\pm4.20	9.73\pm0.58	53.78\pm2.24
Mangere Inlet											
	T	6.80 \pm 0.11	7.01 \pm 0.17	0.08 \pm 0.05	5.18 \pm 1.19	46.8 \pm 8.88	26.49 \pm 1.28	22615.32 \pm 3063.04	342.85 \pm 100.37	21.50 \pm 7.03	138 \pm 13.85
May 2017	M	6.58 \pm 0.37	6.87 \pm 0.13	0.13 \pm 0.01	5.06 \pm 1.42	52.59 \pm 10.54	27.08 \pm 0.17	23705.19 \pm 1445.66	287.22 \pm 84.49	29.55 \pm 1.93	117.21 \pm 14.73
	B	6.70 \pm 0.25	6.61 \pm 0.08	0.03 \pm 0.02	4.36 \pm 1.10	51.9 \pm 10.99	26.72 \pm 0.11	23871.44 \pm 2762.47	279.93 \pm 82.24	25.48 \pm 2.12	131.11 \pm 16.86
	Avg	6.80\pm0.05	6.83\pm0.08	0.08\pm0.02	4.87\pm0.60	50.46\pm4.87	26.77\pm0.36	23397.32\pm1203.97	303.34\pm43.17	25.52\pm2.34	129.10\pm7.77
	T	5.19 \pm 0.06	7.15 \pm 0.18	0.23 \pm 0.11	4.54 \pm 1.19	43.11 \pm 11.56	26.16 \pm 4.31	23787.43 \pm 3014.60	341.56 \pm 86.20	30.84 \pm 2.43	130.48 \pm 5.74
Feb 2018	M	5.53 \pm 0.08	7.13 \pm 0.19	0.30 \pm 0.06	4.59 \pm 0.56	52.84 \pm 6.61	27.09 \pm 3.20	20969.04 \pm 2924.85	292.19 \pm 99.29	27.17 \pm 1.94	137.84 \pm 17.10
	B	5.48 \pm 0.21	6.77 \pm 0.21	0.28 \pm 0.03	5.66 \pm 0.95	50.30 \pm 11.35	24.93 \pm 3.60	22018.49 \pm 3952.15	264.57 \pm 109.69	23.41 \pm 5.43	125.15 \pm 2.11
	Avg	5.40\pm0.09	7.02\pm0.11	0.27\pm0.04	4.93\pm0.47	48.75\pm5.01	26.06\pm1.78	22258.32\pm1616.83	299.44\pm47.80	27.14\pm1.98	131.16\pm5.24
CRM (HISS-1)		Certified values (\pm SD)		0.024 \pm 0.009	0.65	30 \pm 6.8	2.29 \pm 0.37	2460 \pm 90	66.1 \pm 4.2	3.13 \pm 0.4	4.94 \pm 0.79
		Observed values (\pm SD)		0.0211 \pm 0.002	0.6 \pm 0.012	34.093 \pm 1.884	2.077 \pm 0.138	2255.769 \pm 89.066	70.809 \pm 0.48	2.938 \pm 0.072	5.361 \pm 0.139