Metal concentrations within the sediments of Hawksbury Lagoon / Matainaka.

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Te Tiaki Mahinga Kai

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1. Introduction.

1.1 Importance of lagoon habitats and the threats posed to them.

Coastal lagoon and wetland ecosystems are dynamic and productive habitats (Danovaro and Pusceddu 2007) which support high biodiversity (Zedler and Kercher 2005, Danovaro and Pusceddu 2007). These ecosystems form the link between terrestrial and marine environments, facilitating the transfer of energy and nutrients between the two (Danovaro and Pusceddu 2007). Coastal lagoons and wetlands provide numerous ecosystem services including sediment and nutrient retention, flood control, coastal stabilisation, water quality improvement, biodiversity and biomass reservoirs, key breeding and juvenile habitat and as a result hold significant recreational, cultural and economic value (Danovaro and Pusceddu 2007).

Over recent decades a marked decline in the health of lagoon, and wetland habitat has been reported over a global scale (Callaway *et al* 1998, Bellucci *et al* 2002, Acevedo-Figueroa *et al* 2006, Accornero *et al* 2008). These changes are typically associated with anthropogenic activities and often result in decreased biodiversity, alteration of ecosystem function and an overall loss of habitat (Callaway *et al* 1998). Primary drivers for this decline include the modification of hydrological processes (Kim *et al* 2007), changing land use practices (Kim *et al* 2007, Accornero *et al* 2008), deforestation (Fuller *et al* 1988), intensified agriculture (Bramley and Roth 2002) and pollution from household and industrial waste (Callaway *et al* 1998, Bellucci *et al* 2002). Despite our understanding of the key role these ecosystems play the degradation of important lagoon and wetland habitats has occurred and continues to occur today (Accornero *et al* 2008).

The anthropogenic input of metals into lagoon habitats can significantly impact ecosystem functioning (Acevedo-Figueroa *et al* 2006). Lagoon ecosystems are particularly susceptible to metal pollution as they often act as drainage basins for farm and urban runoff and in some cases receive industrial discharge and wastewater (Feng *et al* 2004, Acevedo-Figueroa *et al* 2006). The source of these metals are often linked to practices such as agriculture, where metals are introduced to the soil through agrochemicals such as pesticides and fertilizers (Wong *et al* 2002); wastewater disposal, where metals accumulate from urban runoff and household wastes (Callaway *et al* 1998, Bellucci *et al* 2002, Karvelas *et al* 2003); deforestation, where metals are released from the soil at increased rates through accelerated weathering processes (Fuller *et al* 1988); landfills, where large amounts of waste breakdown,

releasing associated metals into the soil (Oygard *et al* 2004); and industrial activity, where through the production of metals, plastics and other metal bearing products large amounts of wastes and fumes are released into the environment (Callaway *et al* 1998, Bellucci *et al* 2002). Metals which have been transported to lagoon sediments often remain for years but bio-turbation, dredging and/or changing hydrological regimes can cause the release of metals, which affect water quality through toxicity and increased bioavailability of metals, which is the total amount of metal able to be utilized by organisms (Acevedo-Figueroa *et al* 2006). Toxic effects occur once metal concentrations reach a threshold where aquatic organisms can no longer process, excrete or utilize the metal (Chapman *et al* 1999).

Toxic effects of metals can be diverse and influence the entire ecosystem through bioaccumulation (Borgmann 2000, Askoy *et al* 2005). Metals are taken up from sediment by organisms from lower trophic levels either through direct absorption, or through consumption of sediment (Lopez and Liventon 1987). When higher trophic level species consume these organisms the accumulated metals are transferred to the predator. Although concentrations of metals within the environment may be sub-lethal, through accumulation lethal effects can occur (Mountouris *et al* 2002). The threshold of when a metal becomes toxic to an organism is highly dependent on factors such as prior exposure, natural background levels within the environment, the bioavailability of a metal (as this is not directly proportional to the total concentration within the sediment) and the specific biological requirement of the organism for a particular metal. Metal toxicity is therefore species specific (Borgmann 2000, Mountouris *et al* 2002). There are a variety of terms used for describing when a metal becomes toxic to an organism and these are usually split into two thresholds; one below which effects rarely occur and one above which effects are likely to occur (Burton 2002). A conservative approach is advised when testing for toxicity and therefore the lower threshold levels should be used to warn of possible toxic effects (Burton 2002). Effects are not only present within the aquatic habitat but often affect terrestrial plants which border such environments and take up metals through their root system (Askoy *et al* 2005, Rai 2008). Metals that are considered extremely toxic to aquatic organisms at high levels include arsenic cadmium, lead and mercury (Burton 2002). Other metals which can have toxic effects at high concentrations and are considered common pollutants include copper, chromium, manganese, nickel, tin and zinc (Burton 2002, Acevedo-Figueroa *et al* 2006). These metals occur naturally in the environment in varying concentrations but are also introduced through

anthropogenic sources and are considered to be toxic at different concentrations. (Table 1) (Bellucci *et al* 2002).

Table 1. Metals considered harmful anthropogenic pollutants to aquatic ecosystems. Common anthropogenic sources of metals, their effect on aquatic organisms and the lowest concentration at which these effects may occur, recognised as the threshold effect level (Burton 2002).

Metal	**Arsenic (As)**	**Cadmium (Cd)**	**Chromium (Cr)**	**Copper (Cu)**	**Manganese (Mn)**	**Nickel (Ni)**	**Lead (Pb)**	**Zinc (Zn)**
Source	Herbicides/pesticides, car batteries, wood preservative.	Batteries, stabiliser for plastics, electroplating.	Wood preservative, electroplating, dye, tanning agent.	Electronics and wiring, plumbing and roofing.	Batteries, fertilizers, steel manufacturing and as a disinfectant.	Plating to avoid corrosion, magnets, coins and batteries.	Batteries, bullets, weights, paints, water piping and fuel.	Plating and galvanising and batteries.
Effect on aquatic organisms	Inhibits growth, photosynthesis and reproduction.	DNA damage, infertility, damage to immune and nervous systems.	DNA damage, inhibits photosynthesis, and carcinogenic.	DNA damage, loose ability to regulate salt transport and damages gills.	Tumour development, disturbs division of water in plants.	DNA damage and mutation.	Affects nervous system and brain function.	Interferes with plants uptake of other metals.
Threshold effect level in sediment	5.9 mg kg^{-1}	0.6 mg kg^{-1}	37.3 mg kg^{-1}	35.7 mg kg^{-1}	460 mg kg^{-1}	18 mg kg^{-1}	35 mg kg^{-1}	123 mg kg^{-1}

1.2. Detecting metal contamination in aquatic environments.

If successful management and mitigation of the effects of metal contamination is to take place an understanding of the amount of metals bound within the sediment is necessary (Bellucci 2002). If sediments are disturbed and consequently the metals bound within them are released to the water column, serious negative effects are posed to the biota of the immediate habitat but also to biota in associated estuarine and coastal ecosystems (Acevedo-Figueroa *et al* 2006, Callaway *et al* 1998). Assessing the degree and effects of contaminants involves assessing the chemical, physical and biological characteristics of the sediment and also the surrounding environment (Chapman *et al* 1999).

Background or pristine concentrations of metals are needed in order to understand the significance of contamination, this can be achieved in a number of ways; (i) by determining metal concentrations of texturally equivalent sediments as reported in published literature; (ii) through a measurement taken from sediment deposited at a corresponding time in a relatively pristine environment; and (iii) through the concentrations of sections of sedimentary cores which predate significant anthropogenic affects (Belzunce *et al* 2004). Through the analysis of metal concentrations along sediment depth profiles, information on the temporal evolution of inputs of metal pollutants can be gained (Bellucci *et al* 2002). The analysis of sediment cores allows for estimates of the amount of metals bound within surface and deeper sections of the sediment profile (Bellucci *et al* 2002). If the rate of sediment deposition is found then the approximate timing of contamination may be estimated. This information can be linked to activities or processes occurring during that time period to pinpoint the most likely source of pollution.

In combination with understanding metal concentrations it is important to discern the origin of the particular metal of interest, whether it be of a natural/crustal or anthropogenic source (Acevedo-Figueroa *et al* 2006). This can be achieved by examining matrices, where pairwise comparisons of metal concentrations are made to assess how correlated one metal is to another. When metals that come from a common source accumulate in sediments their concentrations should be relative to one another and therefore correlate highly. A high correlation is considered >0.7 (1 being perfectly positively correlated and 0 being uncorrelated) (Acevedo-Figueroa *et al* 2006). If one metal does not correlate highly with the other metals this indicates differences in sources (Acevedo-Figueroa *et al* 2006). A high correlation (>0.7) with iron indicates that the metal is likely to be from a natural/ crustal

source (the weathering of rock) as iron is highly abundant in the earth's crust and is a major metal in clay sediments (Acevedo-Figueroa *et al* 2006). If a metal is not highly correlated with iron this indicates it is likely to be from an anthropogenic source (Acevedo-Figueroa *et al* 2006).

1.3.Hawksbury Lagoon History and management.

Hawksbury Lagoon, also known by the Māori name Matainaka, is located within the East Otago township of Waikouaiti, it is a shallow, coastal lagoon/hapua with a surface area of 40 hectares and a mean depth of 0.4 meters (Irricon and Kunzea Consultants 2010). Matainaka was named after its important role as a major breeding ground for whitebait/inānga, the young of several galaxiid species (Prebble and Mules 2004). Hawksbury Lagoon has been identified in the Ngāi Tahu Claims Settlement Act 1998 as a customary fishery due to its key role in supporting local iwi in the past. Historically the lagoon provided habitat to significant eel/tuna (*Anguilla dieffenbachia*) populations and many migratory and non migratory water fowl species (Prebble and Mules 2004). After over 100 years of environmental degradation Hawksbury lagoon now supports limited flora and fauna species and a number of migratory bird species (Rate *et al* 2009, Prebble and Mules 2004). The once abundant populations of inānga and tuna are now gone and fishing on the lagoon is not possible. Ironically, a fishing easement is present to allow access for members of the local Rūnaka Kāti Huirapa ki Puketeraki to fisheries in Hawksbury Lagoon(Prebble and Mules 2004). Hawksbury Lagoon forms part of the East Otago Taiāpure established in 1999 (a customary fishery management area).

Prior to 1860 Hawksbury Lagoon covered a large part of what is now the Waikouaiti township. During the 1860's extensive drainage of the area took place in order to convert the fertile lagoon into farmland. A number of causeways were constructed from 1881 to 1883 as a precursor to further drainage; however this did not go ahead as the local community opposed the drainage and in 1912 the lagoon became a wildlife reserve.

The lagoon acts as a drainage basin for a catchment area of approximately 1600 ha which is predominantly farmland. The majority of native vegetation has been removed in order to convert this area, which is likely to have changed the hydrology and rate of runoff from the catchment area (Rate 2009, Irricon and Kunzea Consultants 2010). Hawksbury Lagoon is situated in close vicinity to a current and a disused land-fill site and is bordered by significant urban development (Irricon and Kunzea Consultants 2010, www.hawksburylagoon.org.nz).

Other possible sources of pollutants within the drainage basin of Hawksbury lagoon include construction yards where timber, metals, concrete and fertiliser are stored, and where stock trucks are often washed, a battery hen farm (approximately 500,000 hens) and the Main South Line Railway track, which passes over Post Office Creek at the northern end of Hawksbury Lagoon. Hawksbury Lagoon is periodically opened to the ocean in times of heavy rainfall when either the sandbank controlling outflow is washed away or manually excavated (S. McKewen, pers comm, 2012).

There is evidence to suggest water quality has declined over the past century, water levels and dissolved oxygen concentrations have decreased and leaching from surrounding soils has occurred (Irricon and Kunzea Consultants 2010). Preliminary results have shown that the lagoon is in a eutrophic state with the major cause being increased levels of nitrogen entering the lagoon (Irricon and Kunzea Consultants 2010). Active measures by the Hawksbury Lagoon Trust have been taken to improve water quality within the lagoon through extensive planting in areas around the lagoon edge. Restoration of vegetation had the aim of decreasing sedimentation, stabilising soils as well as promoting the uptake of excess nutrients (S. McKewen, pers comm, 2012). High plant mortality, shortly after planting, has limited the success of the restoration project. In 2010 3000 plants, including seven different species, were planted back from the lagoon edge in the Northern end of Hawksbury Lagoon and approximately 1500 to 2000 of these have survived. Along the lagoon edge three species of sedge (760 individuals) were planted with almost 100% mortality occurring. 500 *Carex secta* were planted at the northwest end of the lagoon with only a few surviving. 2500 *Carex secta* were planted midway along the west edge of the lagoon with almost 100% mortality occurring (S. McKewen, pers comm., 2012). In the past Hawksbury Lagoon was a key fishery but is now an example of a highly modified and degraded coastal lagoon that highlights the loss of biodiversity as a result of habitat degradation.

1.4. Aims and scope of research.

This study was conducted in response to concerns by the Hawksbury Lagoon Trust that there may be issues surrounding sediment toxicity within Hawksbury Lagoon after high mortality was observed in recent plantings around the lagoon edge from 2010 onwards. Understanding what contaminants may be present and their concentrations within sediments is also of importance in assessing current proposals to modify hydrological regimes and reconnect the lagoon with the sea. Significant changes in water movement within the lagoon may have the

potential to re-suspend contaminated sediments, releasing pollutants to the water column making them more bioavailable (Mountouris *et al* 2002). It may also cause contamination of less polluted areas of the lagoon and connected habitats, such as terrestrial and open coast ecosystems (Eggleton and Thomas 2004). The present study aimed to determine the concentration of a range of metals within the sediment of Hawksbury Lagoon. Metal concentrations were determined for surface sediment samples taken from the three major arms of the lagoon and from the major inflow to the lagoon (Figure 1). Sediment core samples were also taken from the three arms to determine how metal concentrations differed over depth. The extent of contamination was determined through comparison of metal concentrations with two other lagoons in the East Otago area. To the best of our knowledge this is the first quantitative analysis of metal concentrations within Hawksbury Lagoon, therefore the baseline information provided in this study is essential in the successful management of such an area, which has been influenced by significant anthropogenic activities.

2. Methods.

2.1. Study site.

Hawksbury Lagoon (45^{o} 36' 12.6" S, 170^{o} 40' 25.1" E) (Figure 1) is divided into three separate arms by causeways. The water level of two of the three arms is controlled by two manually operated flood gates which open into Post Office Creek, the main tributary of Hawksbury Lagoon. A land fill operates approximately 200 metres to the east of the lagoon while the western and southern sides of the lagoon are bordered by residential properties. The Mainland poultry hen farm is located approximately 1km southeast of the lagoon. Approximately 50 meters to the north of the lagoon is the site of a disused landfill and approximately 650 meters to the northeast, and in close proximity to Post Office Creek, there is a construction yard. The position of these sites is indicated on Figure 1.

The two comparative study sites of Stony Creek Lagoon (otherwise known as Andersons Lagoon) and the upper Waikouaiti River were selected for the analysis of metal concentrations. Stony Creek Lagoon (45^{o} 30' 24.9" S, 170^{o} 46' 30.1" E) has an approximate mean depth of 0.6 meters. Stony Creek Lagoon is surrounded by agricultural land and is periodically open to the ocean. The upper Waikouaiti River (45^{o} 37' 19.9" S, 170^{o} 38' 20.3" E) is a tidal estuary which branches away from the main river. Water level fluctuates with both tidal cycles and rainfall but is predominantly <0.3 meters at high tide in the area

sampled. It is bordered primarily by agricultural land but includes the extensive grounds of a disused psychiatric hospital.

2.2. Sampling Design.

Hawksbury Lagoon was divided into four sub-sites through the presence of the causeways, those being the North, East and South Arms and Post Office Creek (Figure 1). The sampling design aimed to estimate metal concentrations in each of the four sub-sites, as well as pin point possible gradient effects associated with areas of inflow and connectivity between arms. Through the use of satellite images each sampling area was divided into 25m by 25m grids and each grid square assigned a number. Random numbers were used to select five surface sampling locations in each sub-site. The same technique was used to select three sediment core sampling sites within each of the North, East and South Arms (Figure 1). Within the sites of Stony Creek Lagoon and Waikouaiti River, five surface and three core sediment samples were taken using the same randomisation procedure as that used for Hawksbury Lagoon.

2.3. Sample collection.

Sediment samples were collected from Hawksbury Lagoon on the 29th of March 2012 and from Stony Creek Lagoon and Waikouaiti River on the 12th of April 2012. Surface sediment samples were manually collected from the top 5cm of sediment using 500ml, sterile, plastic jars. Core samples were collected manually by driving a 50mm diameter PVC corer down to a depth of approximately 20 cm, at this depth there was hard clay which meant coring was not possible at greater depths. The top 5cm and bottom 5cm of core sample was collected from Hawksbury Lagoon while only the bottom 5 cm of core sample was collected from Stony Creek Lagoon and upper Waikouaiti River. Sediment samples were sealed in 500mL, sterile, plastic jars and refrigerated at 4^{o}C until analysis.

2.4. Sample digestion and analysis.

Approximately 10 grams of sediment from each sample was placed in a 50ml falcon tube which was topped up with Milli-Q ultra pure water. Samples were washed by centrifuging at 3500rpm for 15 minutes, the solution was decanted and the process repeated. This had the purpose of removing excess salt ions and also to avoid artificial cementing during the drying process. After the second wash the solution was decanted and each sediment sample was left to dry at ambient room temperature for 96 hours.

Approximately 0.3g of dried sediment was transferred to a digestion tube, 4ml of concentrated nitric acid (HNO_3) and 10ml of 1+4 hydrochloric acid (HCl) was added. Samples were left to digest for two hours at a temp of 104^{o}C. Samples were then topped up to 50ml with ultra pure water and left to settle. 0.5ml of digested sample was then diluted with 4.5ml 2%HNO_3 and 0.1ml of reference solution was added, this follows the Standardised method of EPA 200.8 used for determining trace elements in water and wastes. Blanks were prepared to test for contamination during the preparation period, blanks were subject to all conditions that samples were including exposure during drying and acid digestion. Samples and blanks were analysed by an Agilent 7500ce ICP-MS analyser. Inductively Coupled Plasma Mass Spectrometry is an extremely useful tool in the rapid concentration analysis of a wide range of metals and some non metals. ICP-MS offers high detection power, low sample consumption and a very wide dynamic range of over 7 orders of magnitude (Falciani *et al* 2000).

2.5. Metals.

A total of 44 metals were analysed, 9 metals, identified in the scientific literature as common anthropogenic pollutants, were selected for indepth statistical analysis, these were Mn (Manganese), Zn (Zinc), Pb (Lead), Cr (Chromium), Ni (Nickel), Cu (Copper), As (Arsenic), Sn (Tin) and Cd (Cadmium) (Feng *et al* 2004, Acevedo-Figueroa *et al* 2006). Fe (Iron) and Al (Aluminium) were also analysed as they are recognised as reference metals when comparing relative concentrations to other sites and studies, as well as for assessing anthropogenic input (Feng *et al* 2004, Acevedo-Figueroa *et al* 2006).

2.6. Origin of metals.

Pairwise correlation matrices were constructed in Microsoft Excel 2007 to investigate the likely origin of each metal, natural/crustal or anthropogenic. The level of correlation between metals within the sites of North, East and South Arm and Post Office Creek were compared. A high correlation value of >0.7 indicates a common source for the two metals being compared, a high correlation with iron, a major component of clay minerals, indicates a high probability of a natural origin (Feng *et al* 2004, Acevedo-Figueroa *et al* 2006).

2.7. Statistical analysis.

Analysis of variance (ANOVA) was carried out on the nine metals mentioned above using the statistical programme SigmaStat 2.03. One-way ANOVA was used to test for differences

in surficial and 15-20cm deep metal concentrations among sites. It was also used to test for a difference between 0-5cm (top of the core sample) and 15-20cm deep metal concentrations within sites. A post hoc Tukey Test was used to discern which sites differed in concentration when there was a significant difference. All data was tested for normality before undertaking ANOVA using a Kolmogorov-Smirnov test.

Permutational analysis of variance (PERMANOVA) and plotting of multidimensional scaling (MDS) plots was carried out using the statistical programme PRIMER 6 with PERMANOVA+ 1.0.2 (Plymouth, UK). If metals were below or close to (<3 times the detection limit) the detection limit they were omitted from statistical analysis. Draftsman plots were constructed to distinguish which of the 44 metals analysed were highly correlated with each other. When the correlation (r^2 value) between two metals was greater than 0.98 one of the pair was omitted. This was done essentially as they show the same trend and introduce redundancy to the model if both are kept (Clarke and Ainsworth 1993). After this procedure the remaining 23 of the 44 metals were used in further fingerprinting analysis. Data were square-root or Log-transformed to improve the normality of their distribution (Clarke and Ainsworth 1993). Data were then normalised to account for differences of scale among variables (Clarke and Ainsworth 1993). A resemblance matrix based on the Euclidean distance measure was constructed and from this, two MDS plots were made using 25 restarts. The first compared surface metal concentrations of the 23 metals from all sites sampled while the second compared surface concentrations of those metals within the North, East and South Arms of Hawksbury Lagoon. A one-way PERMANOVA, using the unrestricted raw data and up to 9999 permutations, was carried out to compare differences in metal concentrations of the 23 metals between regions (random factor), with the North, East and South Arms representing Hawksbury Lagoon as a whole. Significant results in the main tests were followed by pair wise analyses by region. A one-way PERMANOVA, using the unrestricted raw data and 9999 permutations, was also carried out to compare differences in metal concentration for the 23 metals within the arms of Hawksbury Lagoon (random factor). Monte Carlo P values were used as sample sizes were small.

Top Left: Core sample being taken from the East Arm of Hawksbury Lagoon. Top right: Core sample sectioned into 0-5cm and 15-20cm depths. Bottom left: Surficial sample taken from Post Office Creek. Bottom right: Stony Creek Lagoon looking out to the coast.

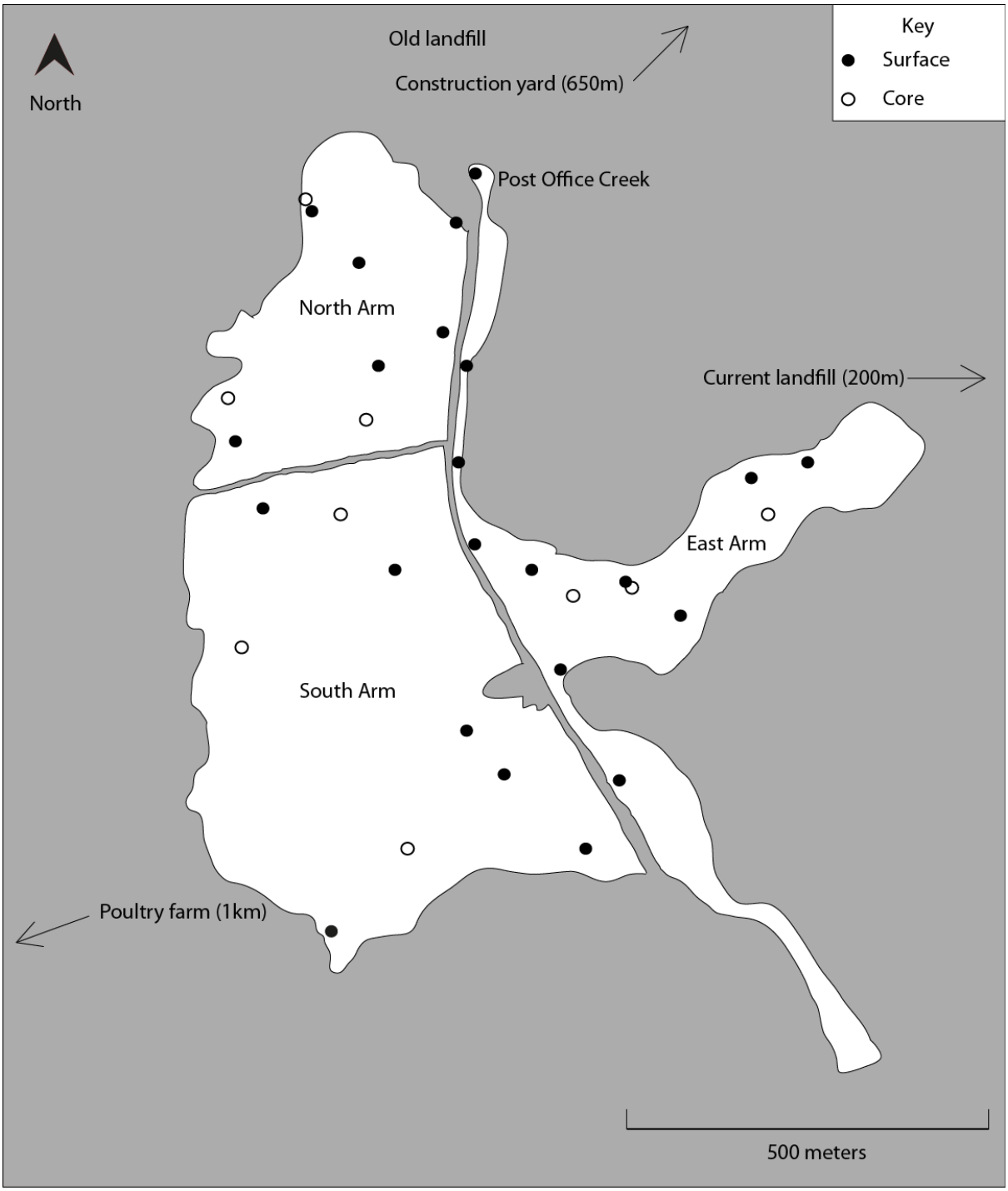


Figure 1. Sampling sites within Hawksbury Lagoon showing surface and core sampling sites. Arrows indicate possible sources of contamination and their approximate distance from Hawksbury Lagoon.

3. Results.

3.1. Sediment finger-printing.

A multivariate fingerprint of metal concentrations within the sediment of each sample site was constructed through the MDS plots shown in figure 2a and b. This analysis considers the concentrations of 23 metals in all samples simultaneously. Each point on the plot represents an individual sample, and the similarity of the metal composition in each sample is indicated by the proximity of each point. Points that are closer together have more similar metal compositions than points that are further apart. Stress factors were low for both plots (0.049, 0.029) meaning that the MDS plots are an accurate representation of the multidimentional variation in two dimensional space. Large variation in metal concentration was present within the sites of Hawksbury Lagoon compared to Waikouaiti River and Stony Creek Lagoon (Figure 2a). Stony Creek Lagoon showed a relatively tight grouping of samples with the exception of one site, indicating high similarity between metal concentrations within the lagoon. Similarly, samples from Post Office Creek were not as variable as those from the Arm's within Hawksbury Lagoon. A permutaional analysis of variance showed Hawksbury Lagoon, as a whole, was not significantly different from the Waikouaiti River or Stony Creek Lagoon in the concentration array of the 23 metals analysed (Appendix 2a). There was also no significant difference the concentration array found among the arms of Hawksbury Lagoon (Figure 2a,b, Appendix 2b).

3.2. Surface sediment metal concentrations.

Due to the high variability of metal concentrations within sites, differences in surface metal concentrations of 8 of the 9 common metal pollutants were not statistically significant among sites. Cadmium was present only within the East and South Arms of Hawksbury Lagoon and was confined to localised areas (Figure 3). Cadmium showed low correlations with all 10 (including Fe and Al) metals in the East Arm and with Mn, Zn, Pb, As and Sn in the South Arm, indicating an anthropogenic origin of cadmium in these areas (Table 2) (Acevedo-Figueroa *et al* 2006). The concentrations of cadmium fell within the contaminated range (Table 4) and were above the threshold effect level for aquatic organisms, meaning negative effects may be likely (Table 1). Low correlations with other metals suggest the anthropogenic contribution of nickel and manganese in the South Arm and arsenic and manganese in Post Office Creek (Table 2). However the concentrations of these metals are well below the levels of contamination (Table 4) and the threshold effect level (Table 1). Arsenic (One-way

ANOVA $F_{1,4}$= 8.141 P=0.046) and copper (One-way ANOVA $F_{1,4}$= 16.255 P=0.016) concentrations in the East Arm were significantly higher in surface sediment compared to sediment at 15-20cm depth (Figure 3, appendix 1a).However these concentrations were well below contamination (Table 4) and threshold effect levels (Table 1).

3.3. Core metal concentrations.

At 15-20cm depth lead was significantly higher in the North Arm compared to the South Arm (One-way ANOVA $F_{4,10}$= 5.867 P=0.002), Stony Creek Lagoon (One-way ANOVA $F_{4,10}$= 5.867 P=0.018) and Waikouaiti River (One-way ANOVA $F_{4,10}$= 5.867 P=0.022). The North Arm had a significantly higher concentration of chromium than the South Arm (One-way ANOVA $F_{4,10}$= 3.726 P=0.03). There was no evidence to suggest that these differences were from an anthropogenic source (Table 3) and they were well below contamination (Table 4) and threshold effect levels (Table 1).

Low correlation with other metals suggest past anthropogenic contributions of lead and manganese in the East Arm and arsenic in the South and North Arms (Table 3). Concentrations for all three metals are however well below contamination (Table 4) and threshold effect levels (Table 1).

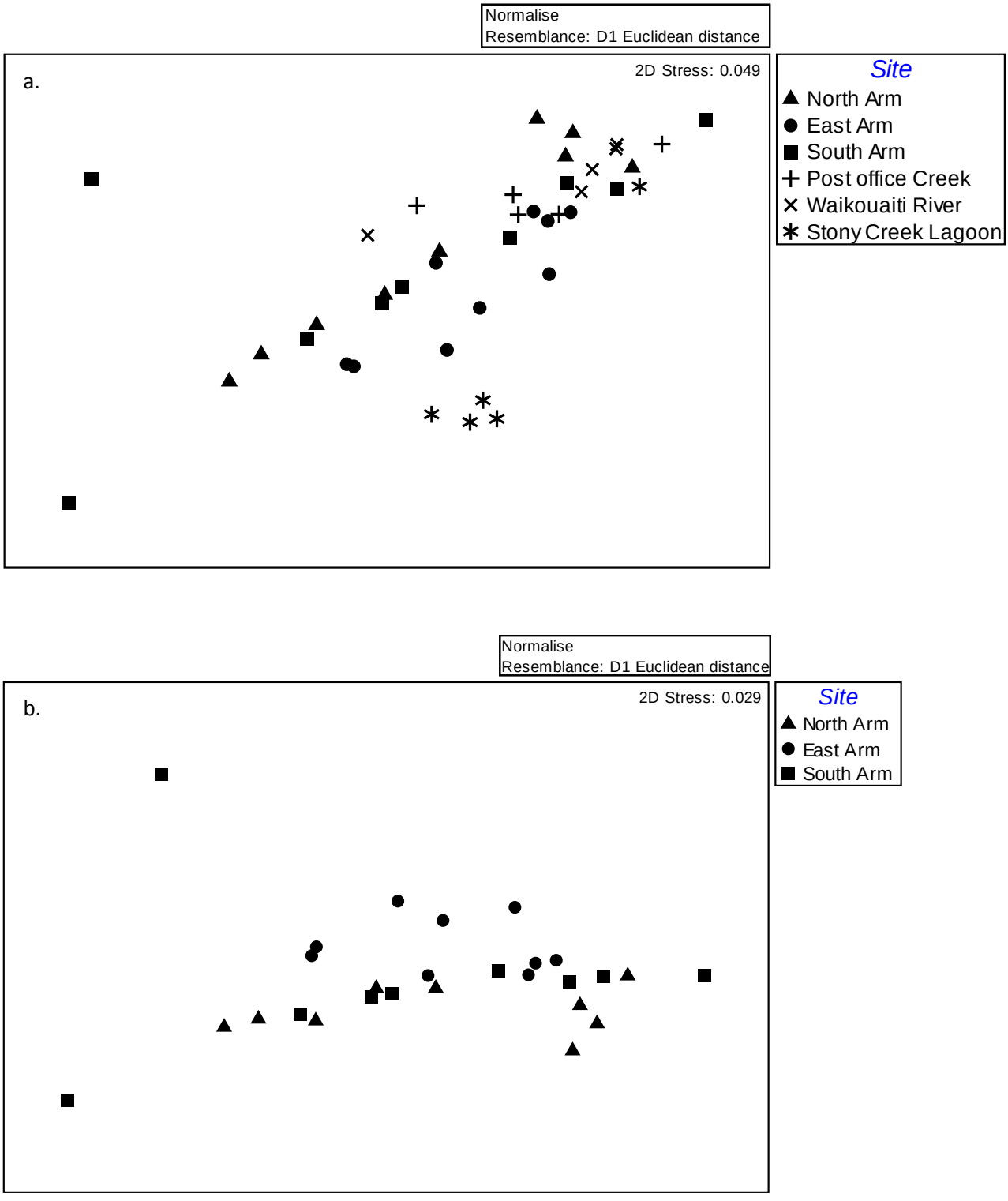
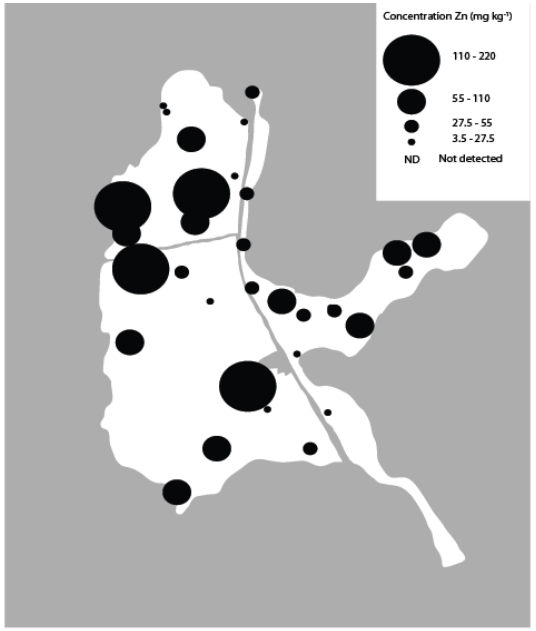
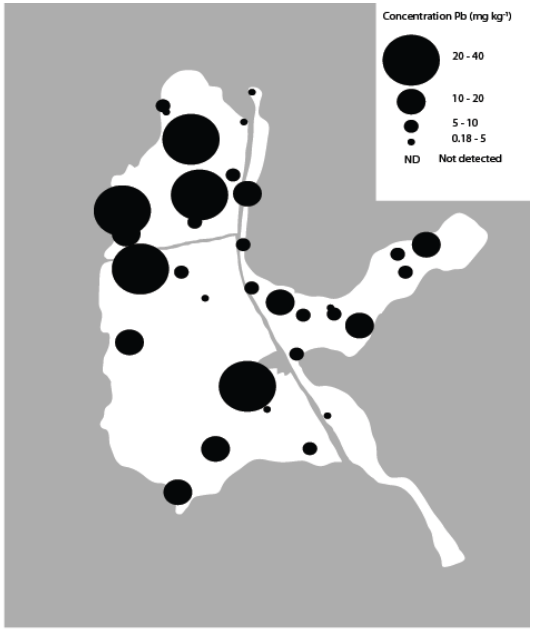
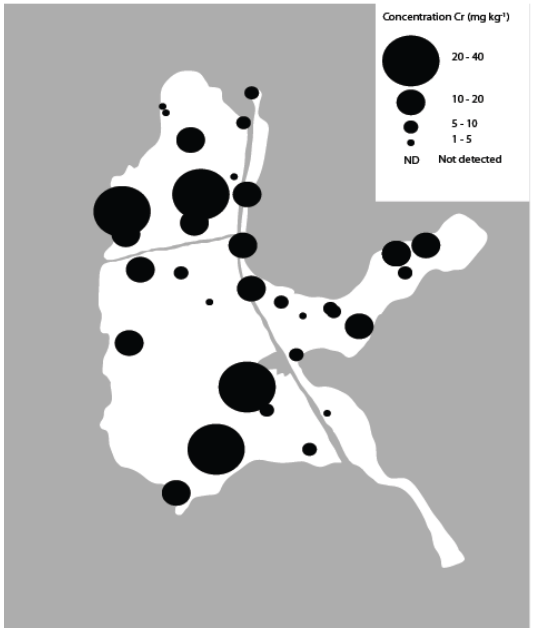


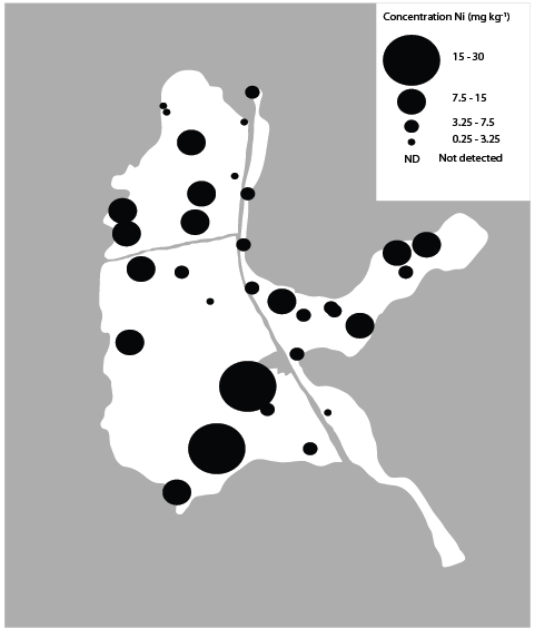
Figure 2a,b. Multidimentional scaling plots for 23 metals a. All sample sites and b. North, East and South Arms of Hawksbury Lagoon.

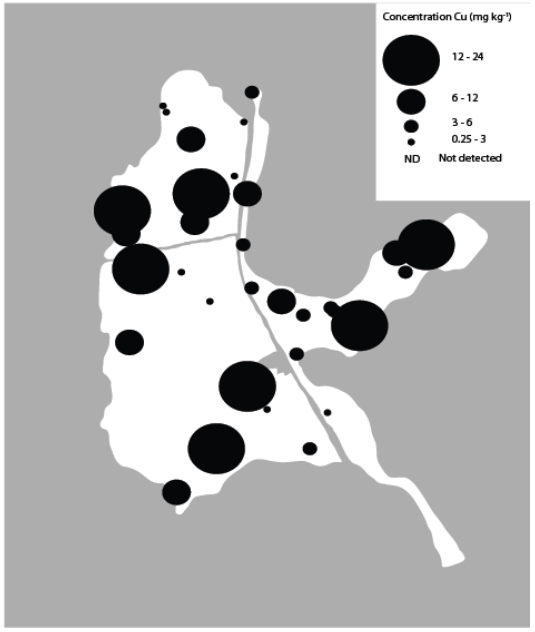

Concentration Mn (mg kg-1)
600 - 1200
300 - 600
150 - 300
1 - 150
ND
Not detected


Concentration Zn (mg kg-1)
110 - 220
55 - 110
27.5 - 55
3.5 - 27.5
ND
Not detected


Concentration Pb (mg kg-1)
20 - 40
10 - 20
5 - 10
0.18 - 5
ND
Not detected


Concentration Cr (mg kg-1)
20 - 40
10 - 20
5 - 10
1 - 5
ND
Not detected


Concentration Ni (mg kg-1)
15 - 30
7.5 - 15
3.25 - 7.5
0.25 - 3.25
ND
Not detected


Concentration Cu (mg kg-1)
12 - 24
6 - 12
3 - 6
0.25 - 3
ND
Not detected

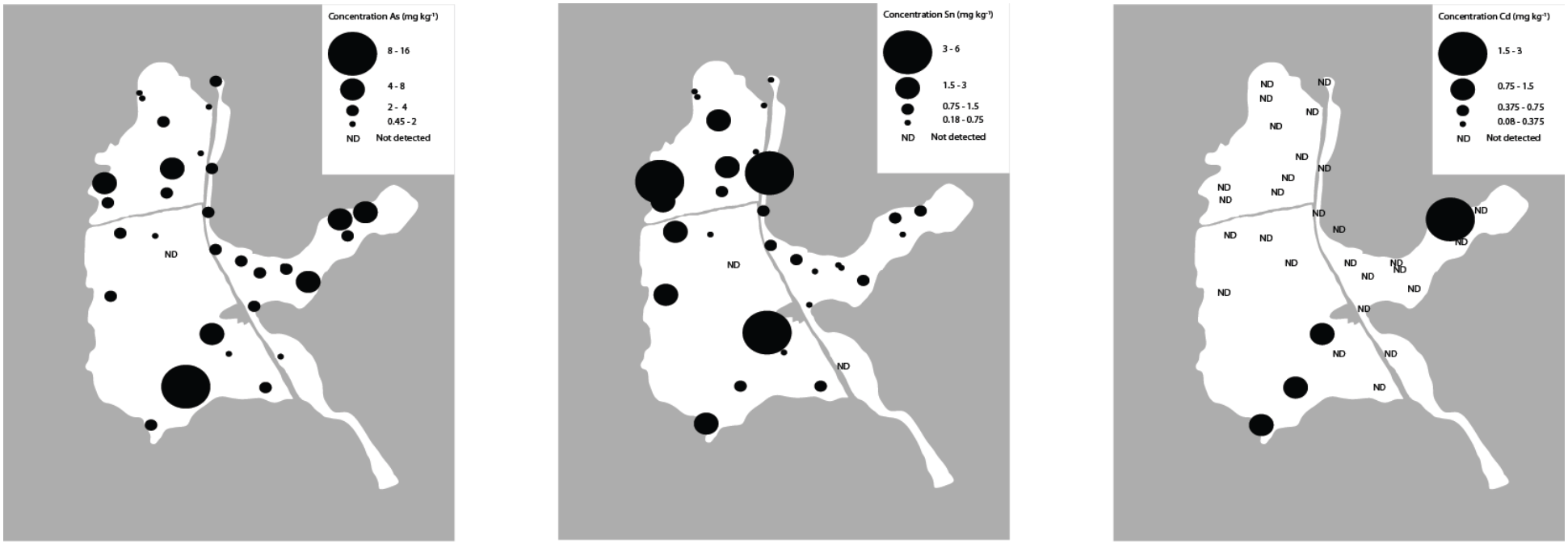


Figure 3. Surface sediment concentration ranges of nine metals within the North, East and South Arms and Post Office Creek. Concentration ranges represent the range of metal concentrations found within Hawksbury Lagoon, with the lowest value being the detection limit of the specific metal analysed. Each dot represents one surface sample taken from that specific area of the lagoon, with the centre of the dot being the exact location of the sample. Nd: not detected.

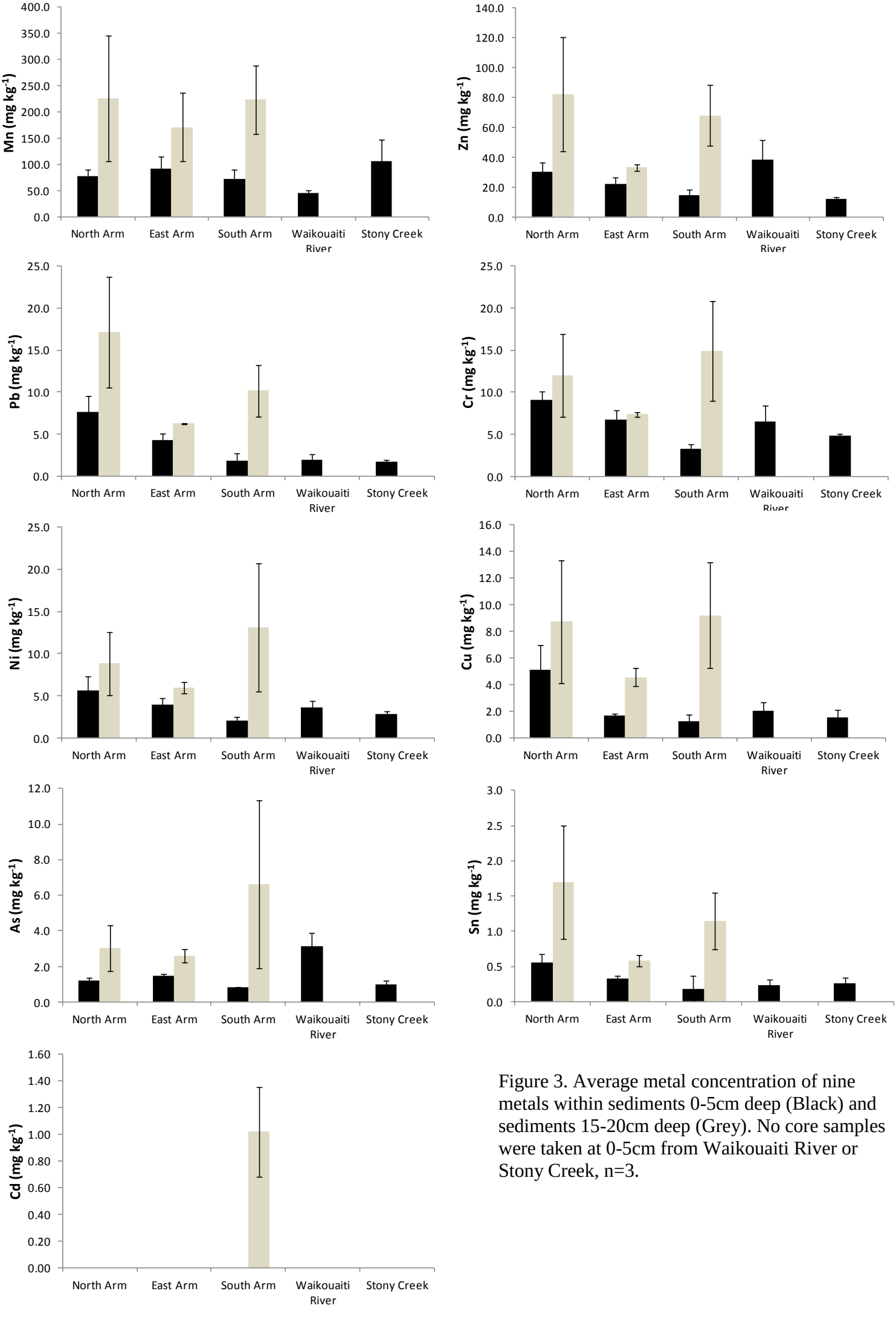


Figure 3. Average metal concentration of nine metals within sediments 0-5cm deep (Black) and sediments 15-20cm deep (Grey). No core samples were taken at 0-5cm from Waikouaiti River or Stony Creek, n=3.

Table 2. Concentration correlation matrices for surficial sediments of the North, East and South Arms and Post Office Creek. Correlation of >0.7 indicates a strong positive correlation and a high probability of a common source. Bold values indicate possible anthropogenic contamination using methods of Acevedo-Figueroa *et al* (2006).

North Arm

	Fe	*Al*	*Mn*	*Zn*	*Pb*	*Cr*	*Ni*	*Cu*	*As*	*Sn*	*Cd*
Fe	1										
Al	0.986939	1									
Mn	0.947715	0.917307	1								
Zn	0.985004	0.997596	0.90558	1							
Pb	0.988931	0.974393	0.913065	0.976767	1						
Cr	0.985001	0.992111	0.906733	0.986587	0.97636	1					
Ni	0.982554	0.997627	0.90704	0.998375	0.97484	0.986324	1				
Cu	0.989656	0.991688	0.917804	0.996084	0.981217	0.976539	0.993044	1			
As	0.969762	0.974079	0.844526	0.980666	0.981289	0.978635	0.977334	0.976569	1		
Sn	0.991164	0.992237	0.927406	0.994429	0.981024	0.980738	0.989025	0.996379	0.971364	1	
Cd	No value	No value	No value	No value	No value	No value	No value	No value	No value	No value	1

East Arm

Fe	1										
Al	0.987254	1									
Mn	0.791113	0.841486	1								
Zn	0.994884	0.994866	0.81845	1							
Pb	0.879485	0.87934	**0.536367**	0.885657	1						
Cr	0.996286	0.987334	0.770026	0.995318	0.900142	1					
Ni	0.966151	0.991747	0.84686	0.982139	0.891861	0.969515	1				
Cu	0.951268	0.9808	0.834698	0.971708	0.906966	0.958428	0.995388	1			
As	0.954577	0.95718	0.864466	0.962569	0.785587	0.93886	0.942569	0.91975	1		
Sn	0.976499	0.991463	0.849337	0.989117	0.887959	0.974759	0.993183	0.985757	0.967825	1	
Cd	**0.24423**	**0.246066**	**0.522947**	**0.2366**	**-0.22003**	**0.210698**	**0.172073**	**0.113513**	**0.340882**	**0.19012**	1

South Arm

Fe	1										
Al	0.985289	1									
Mn	0.828981	0.906493	1								
Zn	0.954702	0.987399	0.949513	1							
Pb	0.834268	0.908116	0.961123	0.954367	1						
Cr	0.999269	0.983128	0.817883	0.948486	0.826563	1					
Ni	0.906922	0.823241	**0.526109**	0.744211	**0.531926**	0.911841	1				
Cu	0.996895	0.984122	0.833552	0.961764	0.852371	0.995013	0.895103	1			
As	**0.643905**	**0.508705**	**0.118186**	**0.390626**	**0.133845**	**0.655215**	0.903472	**0.624489**	1		
Sn	0.812231	0.896851	0.988353	0.946735	0.988307	0.802689	**0.492135**	0.824478	**0.078598**	1	
Cd	0.799162	0.772103	**0.592417**	**0.699033**	**0.530725**	0.805578	0.79931	0.768839	**0.62973**	**0.548396**	1

Post Office Creek

Fe	1										
Al	0.973279	1									
Mn	0.800265	**0.644683**	1								
Zn	0.906186	0.936389	**0.571977**	1							
Pb	0.852976	0.835516	**0.655878**	0.959562	1						
Cr	0.956174	0.944281	0.709848	0.977953	0.956066	1					
Ni	0.979322	0.994168	**0.670248**	0.959382	0.880282	0.973557	1				
Cu	0.975394	0.999073	**0.659179**	0.935423	0.840066	0.942826	0.992188	1			
As	0.844168	0.765538	0.794589	**0.578907**	**0.504543**	0.712252	0.765432	0.757737	1		
Sn	0.753528	0.823037	**0.425669**	0.856882	0.804085	0.775286	0.806761	0.839159	**0.310119**	1	
Cd	No value	No value	No value	No value	No value	No value	No value	No value	No value	No value	1

Table 3. Concentration correlation matrices for 15-20cm deep sediments of the North, East and South Arms. Correlation of >0.7 indicates a strong positive correlation and a high probability of a common source. Bold values indicate possible anthropogenic contamination using methods of Acevedo-Figueroa *et al* (2006).

North Arm

	Fe	*Al*	*Mn*	*Zn*	*Pb*	*Cr*	*Ni*	*Cu*	*As*	*Sn*	*Cd*
Fe	1										
Al	0.999822	1									
Mn	0.975991	0.971707	1								
Zn	0.896913	0.905097	0.77906	1							
Pb	0.981934	0.98533	0.917144	0.964385	1						
Cr	0.999874	0.999996	0.972403	0.903832	0.984819	1					
Ni	0.912443	0.920002	0.801406	0.999335	0.973389	0.918835	1				
Cu	0.991468	0.993751	0.939271	0.946903	0.998222	0.993415	0.957998	1			
As	**-0.99984**	**-1**	**-0.97188**	**-0.90478**	**-0.9852**	**-1**	**-0.91971**	**-0.99367**	1		
Sn	0.996938	0.998236	0.955971	0.928743	0.993723	0.998056	0.941645	0.998625	**-0.99819**	1	
Cd	No value	No value	No value	No value	No value	No value	No value	No value	No value	No value	1

East Arm

Fe	1										
Al	0.995083	1									
Mn	**0.259217**	**0.353603**	1								
Zn	0.999748	0.997055	**0.280823**	1							
Pb	**0.299109**	**0.203126**	**-0.84407**	**0.277622**	1						
Cr	0.998986	0.998534	**0.302446**	0.999744	**0.255835**	1					
Ni	0.994474	0.999982	**0.359181**	0.996579	**0.197277**	0.998193	1				
Cu	0.768299	0.701122	**-0.41906**	0.753743	0.840592	0.738695	**0.696853**	1			
As	0.993524	0.977385	**0.1478**	0.990724	**0.405592**	0.9874	0.976105	0.836052	1		
Sn	0.999095	0.998395	**0.300062**	0.999798	**0.258251**	0.999997	0.998039	0.740378	0.987792	1	
Cd	No Value	No Value	No Value	No Value	No Value	No Value	No Value	No Value	No Value	No Value	1

South Arm

Fe	1										
Al	0.859177	1									
Mn	0.976558	0.949178	1								
Zn	0.998404	0.828909	0.962843	1							
Pb	0.988041	0.927798	0.99807	0.977756	1						
Cr	0.815267	0.996764	0.920807	0.781263	0.894807	1					
Ni	0.994076	0.9097	0.994168	0.986351	0.998946	0.873377	1				
Cu	0.966852	0.961347	0.99915	0.950889	0.99466	0.936105	0.988876	1			
As	0.716275	**0.258349**	**0.549274**	0.754541	**0.600112**	**0.17986**	**0.636188**	**0.514354**	1		
Sn	0.965414	0.962867	0.998904	0.949149	0.99407	0.93805	0.988032	0.999984	**0.509566**	1	
Cd	No value	No value	No value	No value	No value	No value	No value	No value	No value	No value	1

4.Discussion.

4.1. Concentrations of metals within Hawksbury Lagoon.

The presence of cadmium within the East and South Arms combined with the low correlation shown with other metals in these areas is indicative of an anthropogenic contribution (Acevedo-Figueroa *et al* 2006). This contamination is not evident at 15-20cm deep so is therefore likely to have recently occurred and may still be occurring (Feng *et al* 2004). Due to the spatial separation of sites where contamination was present it is most likely that there are two contamination sources, one in the East Arm originating in the northeast reaches and one in the South Arm which affects the centre and northeast edge of the arm (Figure 3). The level of contamination is relatively high in comparison to other studies (Table 4) and is also above the threshold effect level for aquatic organisms at each of the four locations, meaning that cadmium is likely having a negative effect on organisms within these areas (Table 1). It is difficult to attribute this contamination to a source as the affected sites show little spatial connectivity. It is possible that contamination is entering the South Arm at the eastern edge and spreading westward as concentrations decrease in this direction (1.14mg kg^{-1}, 1.02mg kg^{-1} and 0.87mg kg^{-1}). The most likely source for this contamination is the Waikouaiti landfill site located approximately 800m from the eastern edge of the South Arm, however more extensive sampling would be required to pinpoint if and how the contaminant is reaching the East and South Arms.

Although there were statistically significant differences in concentrations of some metals within and among sites, few of these were attributed to an anthropogenic contribution shown by the correlation matrices (Table 2 and 3). Low correlations shown by the matrices (Table 2 and 3) indicated anthropogenic contributions, of arsenic in the surface and 15-20cm deep sediment of the South Arm, lead, manganese and chromium in 15-20cm deep sediment in the East Arm, and arsenic in 15-20cm deep sediment in the North Arm. Although evidence suggests there may be an anthropogenic contribution the concentrations of these metals were not statistically different from other arms within Hawksbury Lagoon, and for arsenic, lead and chromium the concentrations present fell within the uncontaminated range (Table 4). Manganese however did fall within the contaminated range in localised areas of the East Arm but was just below the threshold effect level for aquatic organisms (Table 1). This contamination was only present in the top end of the East Arm, indicating that again the

Waikouaiti land fill may be a likely source of contaminants but more extensive sampling is required to pinpoint the source.

Apart from a few areas of localised contamination, the high variability observed within and among the three arms of Hawksbury Lagoon and Post Office Creek could be due to differences in sediment grain size. These size differences affect the way metals bind to each particle, for example clay minerals are naturally metal bearing as they have a high sorptive process, therefore areas of sediment which have a high proportion of smaller grain sizes are likely to have relatively higher metal concentrations (Kersten and Smedes 2002, Feng *et al* 2004). Other factors contributing to variability in concentration may be differing hydrological regimes in each arm affecting oxidative processes, this would influence the rate of re-suspension of anoxic sediment into the oxic water column, altering the chemical properties in different ways depending on hydrology (Petersen and Williamowski 1997). The origin of the sediment may also play a role in the variability observed; Hawksbury Lagoon is fed by multiple tributaries and receives sediment from localised soil weathering, each of which may contribute soil with differing metal concentrations (Chatterjee *et al* 2007).

4.2. Comparison of Hawksbury Lagoon with Waikouaiti River, Stony Creek and other similar studies.

Although surface sediment concentrations of metals appeared to be higher in Hawksbury Lagoon compared to both the Waikouaiti River and Stony Creek Lagoon, high variability within these sites meant that these differences were not statistically significant. An exception to this was cadmium, found only in detectable concentrations within the East and South Arms of Hawksbury Lagoon. Metal concentrations in sediment 15-20cm deep were also variable among sites and there was no clear trend that showed Hawksbury Lagoon to have higher concentrations compared with Waikouaiti River and Stony Creek Lagoon. This variability is most likely due to the reasons explained in Section 4.1. The use of sediment finger printing confirmed these findings showing that the array of metal concentrations within Hawksbury Lagoon as a whole were not significantly different compared to Waikouaiti River and Stony Creek Lagoon when 23 metals were analysed (Figure 2a).

A review of 10 similar studies from around the world showed Hawksbury Lagoon to have relatively low concentrations of most metals and that it appeared most similar to sites which were considered uncontaminated (Table 4) (Gonzalez and Brugmann 1991, Absil and van Scheppingen 1996, Bradley-Moran and Wood 1997, Bothner *et al* 1998, Leivouri 1998,

Bahena-Manjarrez *et al* 2002, DelValls 2002, Arambarri *et al* 2003, Mora *et al* 2004, Acevedo-Figueroa *et al* 2006). Levels of cadmium in the East and South Arms of Hawksbury Lagoon however were similar to studies conducted in locations contaminated by cadmium (Table 4) (Gonzalez and Brugmann 1991, Absil and van Scheppingen 1996, Leivouri 1998, Bahena-Manjarrez *et al* 2002, Mora *et al* 2004, Acevedo-Figueroa *et al* 2006). Concentrations of manganese within surface sediment samples in the North, East and South Arms and Stony Creek Lagoon also fell within what the scientific literature suggest is a contaminated range (Gonzalez and Brugmann 1991, Absil and van Scheppingen 1996, Leivouri 1998, Bahena-Manjarrez *et al* 2002, Mora *et al* 2004, Acevedo-Figueroa *et al* 2006). It is most likely that these high concentrations of manganese are attributed to redox related diagenetic recycling of manganese in the surface sediments, as the high concentrations are only present in areas where a deep anoxic layer was observed (Boyle *et al* 1998).

Table 4. Sediment metal concentration ranges (mg kg^{-1}) from this study compared to 10 similar studies of sediment metal concentrations found in freshwater and estuarine environments from different regions of the world. These ranges were from areas which were either considered contaminated or uncontaminated, with the lower and upper values being the lowest and highest concentration found from the range of the 10 studies and this study. Only two similar studies included concentrations of tin. Bold values indicate sites which fall within the contaminated range. (Gonzalez and Brugmann 1991, Absil and van Scheppingen 1996, Bradley-Moran and Wood 1997, Bothner *et al* 1998, Leivouri 1998, Bahena-Manjarrez *et al* 2002, Del Valls *et al* 2002, Arambarri *et al* 2003, Mora *et al* 2004, Acevedo-Figueroa *et al* 2006).

	Mn	Zn	Pb	Cr	Ni	Cu	As	Sn	Cd
"Contaminated" Range	253 - 1169	83.2 - 531	18 - 340	59.6 - 343	50.1 - 332	31.9 - 297	12.5 - 239	8.1 - 113	0.14 - 2.85
"Uncontaminated" Range	3.5 - 200	4.2 - 86	2.3 - 54.9	0.06 - 85	0.8 - 53	2.2 - 23	1.8 - 18	1.1 - 8.1	0.05 - 0.2
North Arm	**63 - 532**	**16.2 - 152.4**	4.2 - 29.8	3.1 - 22.2	2.3 - 15.5	0.9 - 17.5	0.8 - 5.4	0.34 - 3.26	<0.83
East Arm	**98 - 451**	**23.8 - 88.1**	4.3 - 15.4	5.8 - 17.5	4 - 14.4	3 - 14.4	1.6 - 5.3	0.35 - 1.47	**<0.83 - 2.8**
South Arm	**45 - 1105**	**5.9 - 212.3**	0.6 - 36.3	1.2 - 32.7	0.95 - 28	0.38 - 22.2	<0.45 - 16	<0.18 - 5.62	**<0.83 - 1.14**
Post Office Creek	59 - 125	9 - 51.5	0.91 - 10.9	2.3 - 13	1.7 - 8.4	0.7 - 6	1 - 3.9	<0.18 - 3.75	<0.83
Waikouaiti River	41 - 152	**13 - 153.2**	1.4 - 7.4	2.8 - 17.5	2.3 - 8.6	1.2 - 5.6	2 - 9.9	<0.18 - 0.6	<0.83
Stony Creek	**108 - 631**	9 - 55.2	1.5 - 10.8	3.2 - 11	2.3 - 10.5	1.1 - 8.6	1.2 - 4.4	<0.18 - 0.76	<0.83

5. Conclusion and recommendations.

Cadmium contamination in localised areas of the East and South Arms may be causing negative effects on aquatic and terrestrial organisms which inhabit these areas. Further sediment metal analysis is required intensively around these localised areas. A sampling design which will pinpoint the location that contaminants are entering Hawksbury Lagoon is needed. This will require radial sampling around the contaminated sites, focusing on any inflow entering Hawksbury lagoon close to these areas. Remediation procedures are not recommended in this case as the contamination is fairly localised. If sediment was manually removed from these areas it would pose risks to less contaminated areas of the lagoon through the re-suspension of sediments and the liberation of metals from within it (Petersen and Williamowski 1997).

Hawksbury Lagoon shows only minor localised levels of sediment metal contamination and therefore this cannot be the sole cause of plant mortality and the current eutrophic state of the Lagoon. The only significant contamination was restricted to the East and South Arms but the majority of plant mortalities occurred in and around the North Arm. Further research into sedimentation rate within Hawksbury Lagoon may help pinpoint the time that this contaminant was deposited and therefore attribute them to a likely source. Other contaminants that may be negatively influencing the sediment and water column of Hawksbury Lagoon could include, organophosphates, which are common pesticides and insecticides used in agriculture and horticulture. Organophosphates can cause wide spread mortality among aquatic organisms, they are relatively soluble in water and have a high potential to enter aquatic ecosystems through runoff (Tse *et al* 2004). Polycyclic aromatic hydrocarbons (PAHs) may also pose a contamination threat within Hawksbury Lagoon. PAHs come from the burning of fossil fuels and biomass, they tend to accumulate in soils and sediment and are one of the most widespread global organic pollutants (Budzinski *et al* 1997). It is recommended that further research should focus on the anoxic state of the Hawksbury Lagoon sediments as well as the inputs of nutrients to the lagoon, which is the most likely cause of the current eutrophic state. A sampling design should focus on quantifying the inputs of nutrients, namely nitrogen and phosphorus which are entering the lagoon at major inflow points. It would be beneficial to also understand the hydrodynamics of the lagoon in order to model re-suspension of sediments at various water flows, this is essential information required if the hydrological regime of the lagoon is ever to be modified as the threat to coastal ecosystems would be great if sediments were flushed from the lagoon.

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Appendix:

1a. Analysis of Variance of metal concentration 0-5cm vs. 15-20cm deep within sites.

Copper (Cu) *East Arm*

Factor	DF	F	P
Between Groups	1	16.255	0.016
Residual	4		
Total	5		

Arsenic (As) *East Arm*

Factor	DF	F	P
Between Groups	1	8.141	0.046
Residual	4		
Total	5		

1b. Analysis of Variance of metal concentration 15-20cm deep between sites.

Aluminium (Al)

Factor	DF	F	P
Between Groups	4	5.171	0.016
Residual	10		
Total	14		

Tukey Test	P
North Arm Vs. Waikouaiti River	0.017
North Arm Vs. South Arm	0.031

Lead (Pb)

Factor	DF	F	P
Between Groups	4	5.867	0.011
Residual	10		
Total	14		

Tukey Test	P
North Arm Vs. Stony Creek	0.018
North Arm Vs. South Arm	0.02
North Arm Vs. Waikouaiti River	0.022

Chromium (Cr)			
Factor	DF	F	P
Between Groups	4	3.726	0.042
Residual	10		
Total	14		

Tukey Test	P
North Arm Vs. South Arm	0.03

Arsenic (As)			
Factor	DF	F	P
Between Groups	4	6.405	0.008
Residual	10		
Total	14		

Tukey Test	P
Waikouaiti River Vs. South Arm	0.006
Waikouaiti River Vs. Stony Creek	0.02
Waikouaiti River Vs. North Arm	0.034

2a. Permutational analysis of variance of surface metal concentrations between region with Hawksbury Lagoon representing the North, East and South Arms.

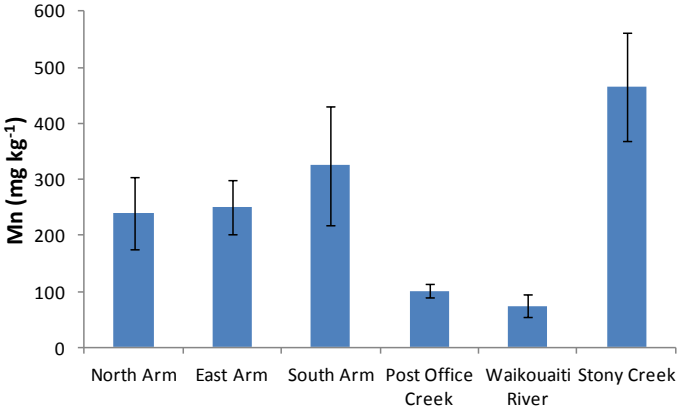
Factor	DF	Pseudo-F	P	Unique Perms
Region	3	2.5714	0.04	9938
Residual	38			
Total	41			

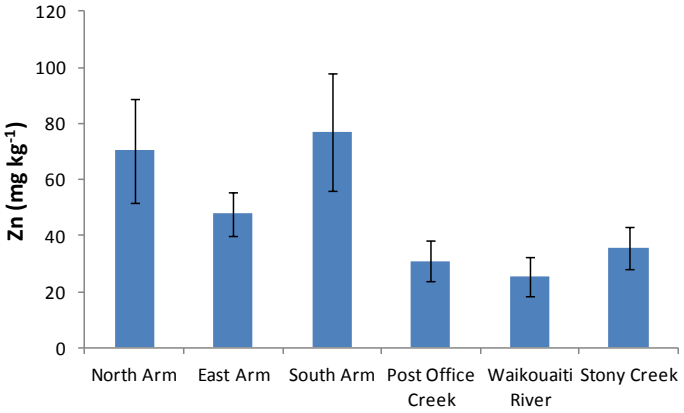
Pair wise tests	t	P(MC)	Unique Perms
Hawksbury Lagoon Vs. Post Office Creek	1.3983	0.1514	9725
Hawksbury Lagoon Vs. Waikouaiti River	1.7733	0.0591	9661
Hawksbury Lagoon Vs. Stony Creek	1.4303	0.1305	9712
Post Office Creek Vs. Waikouaiti River	0.75635	0.5282	126
Post Office Creek Vs. Stony Creek	2.256	0.0254	126
Waikouaiti River Vs. Stony Creek	2.4835	0.0197	126

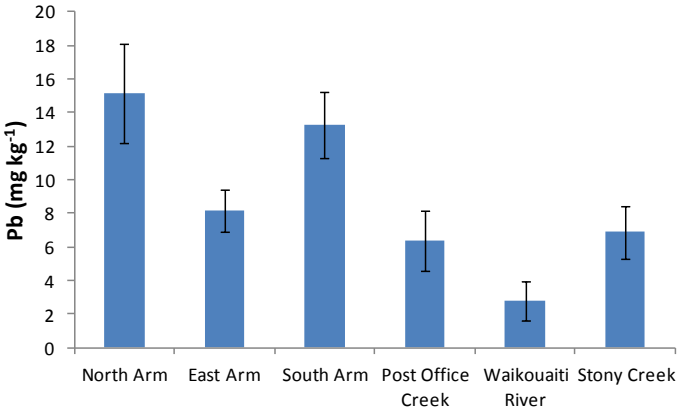
2b. Permutational analysis of variance of surface metal concentrations between the North, East and South Arms of Hawksbury Lagoon

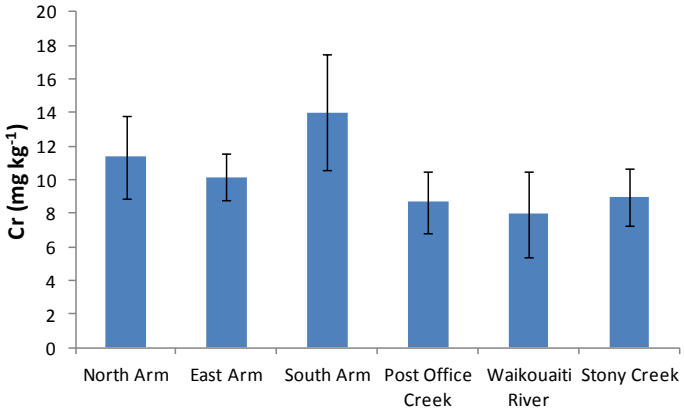
Factor	DF	Pseudo-F	P	Unique Perms
Sites	2	0.6462	0.5832	9951
Residual	24			
Total	26			

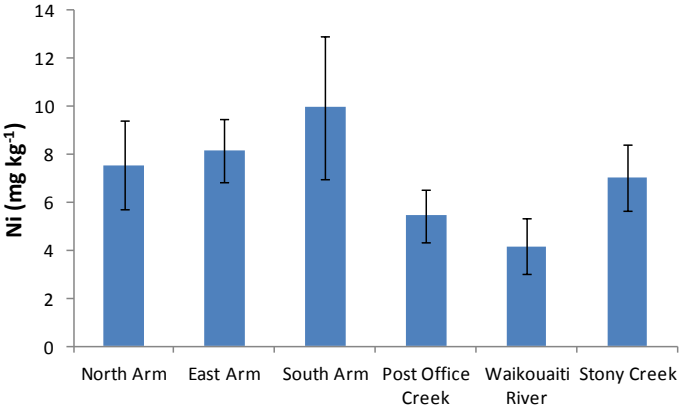
3. Average surface sediment metal concentrations of nine metals within Hawksbury Lagoon, Waikouaiti River and Stony Creek Lagoon. North, East and South Arms N=9, Post Office Creek, Waikouaiti and Stony Creek N=5.

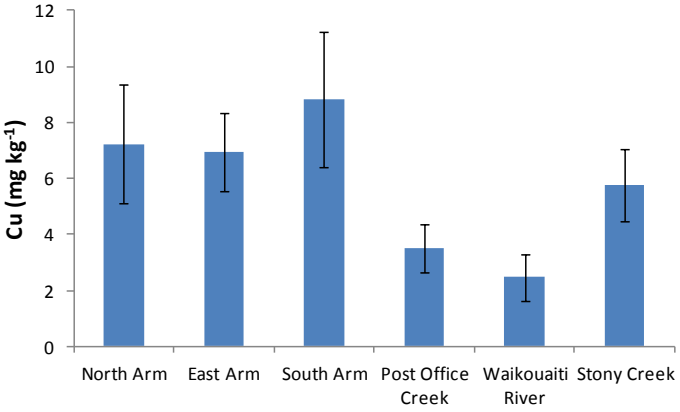


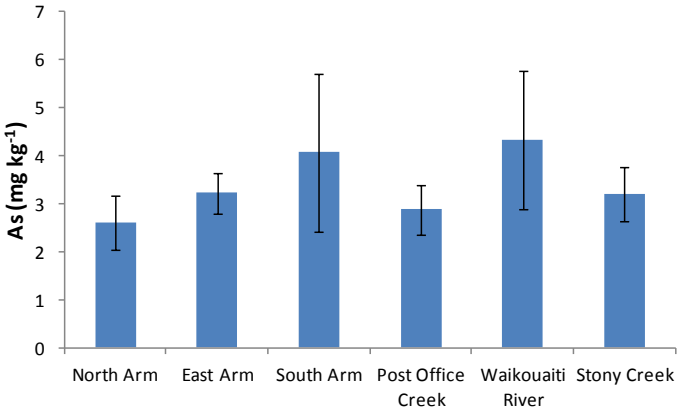


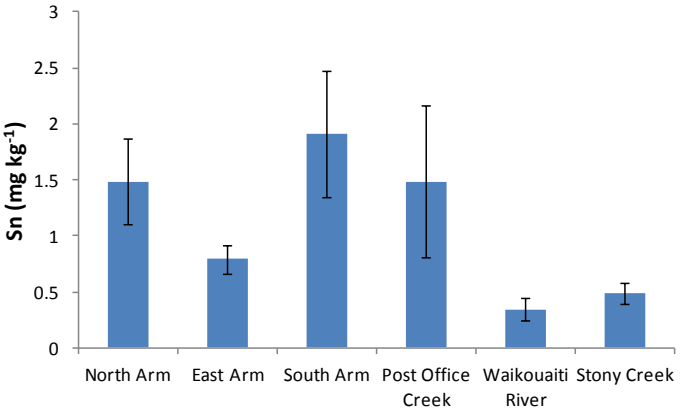


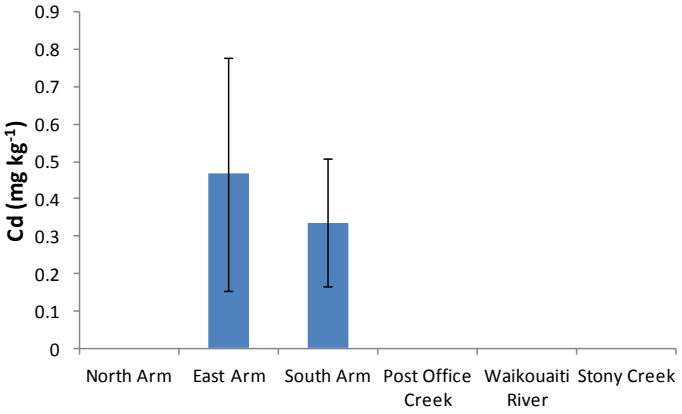



Ni (mg kg-1)
0
2
4
6
8
10
12
14
North Arm
East Arm
South Arm
Post Office Creek
Waikouaiti River
Stony Creek


Cu (mg kg-1)
0
2
4
6
8
10
12
North Arm
East Arm
South Arm
Post Office Creek
Waikouaiti River
Stony Creek


As (mg kg-1)
0
1
2
3
4
5
6
7
North Arm
East Arm
South Arm
Post Office Creek
Waikouaiti River
Stony Creek


Sn (mg kg-1)
0
0.5
1
1.5
2
2.5
3
North Arm
East Arm
South Arm
Post Office Creek
Waikouaiti River
Stony Creek


Cd (mg kg-1)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
North Arm
East Arm
South Arm
Post Office Creek
Waikouaiti River
Stony Creek