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Central Waitemata Harbour Contaminant Study

Trace Metal Concentrations in Harbour Sediments

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Central Waitemata Contaminants Harbour Study. Trace Metal Concentrations in Harbour Sediments

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Preface

The Waitemata Harbour is comprised of tidal creeks, embayments and the central basin. The harbour receives sediment and stormwater chemical contaminant run-off from urban and rural land from a number of subcatchments, which can adversely affect the ecology. An earlier study examined long-term accumulation of sediment and stormwater chemical contaminants in the Upper Waitemata Harbour. However, previously little was known about the existing and long-term accumulation of sediment and stormwater chemical contaminants in the central harbour. The Central Waitemata Harbour Contaminant Study was commissioned to improve understanding of these issues. This study is part of the 10-year Stormwater Action Plan to increase knowledge and improve stormwater management outcomes in the region. The work was undertaken by the National Institute of Water and Atmospheric Research (NIWA).

The scope of the study entailed:

1) field investigation,

2) development of a suite of computer models for

    a. urban and rural catchment sediment and chemical contaminant loads,

    b. harbour hydrodynamics and

    c. harbour sediment and contaminant dispersion and accumulation,

3) application of the suite of computer models to project the likely fate of sediment, copper and zinc discharged into the central harbour over the 100-year period 2001 to 2100, and

4) conversion of the suite of computer models into a desktop tool that can be readily used to further assess the effects of different stormwater management interventions on sediment and stormwater chemical contaminant accumulation in the central harbour over the 100-year period.

The study is limited to assessment of long-term accumulation of sediment, copper and zinc in large-scale harbour depositional zones. The potential for adverse ecological effects from copper and zinc in the harbour sediments was assessed against sediment quality guidelines for chemical contaminants.

The study and tools developed address large-scale and long timeframes and consequently cannot be used to assess changes and impacts from small subcatchments or landuse developments, for example. Furthermore, the study does not assess ecological effects of discrete storm events or long-term chronic or sub-lethal ecological effects arising from the cocktail of urban contaminants and sediment.

The range of factors and contaminants influencing the ecology means that adverse ecological effects may occur at levels below contaminant guideline values for individual chemical contaminants (i.e., additive effects due to exposure to multiple contaminants may be occurring).

Existing data and data collected for the study were used to calibrate the individual computer models. The combined suite of models was calibrated against historic sedimentation and copper and zinc accumulation rates, derived from sediment cores collected from the harbour.

Four scenarios were modelled: a baseline scenario and three general stormwater management intervention scenarios.

The baseline scenario assumed current projections (at the time of the study) of

- future population growth,
- future landuse changes,
- expected changes in building roof materials,
- projected vehicle use, and
- existing stormwater treatment.

The three general stormwater management intervention scenarios evaluated were:

1) source control of zinc by painting existing unpainted and poorly painted galvanised steel industrial building roofs;
2) additional stormwater treatment, including:
    - raingardens on roads carrying more than 20,000 vehicles per day and on paved industrial sites,
    - silt fences and hay bales for residential infill building sites and
    - pond / wetland trains treating twenty per cent of catchment area; and
3) combinations of the two previous scenarios.

International Peer Review Panel

The study was subject to internal officer and international peer review. The review was undertaken in stages during the study, which allowed incorporation of feedback and completion of a robust study. The review found:

- a state-of-the-art study on par with similar international studies,
- uncertainties that remain about the sediment and contaminant dynamics within tidal creeks / estuaries, and
- inherent uncertainties when projecting out 100 years.

Key Findings of the Study

Several key findings can be ascertained from the results and consideration of the study within the context of the wider Stormwater Action Plan aim to improve stormwater outcomes:

- Henderson Creek (which drains the largest subcatchment and with the largest urban area, as well as substantial areas of rural land) contributes the largest loads of sediment, copper and zinc to the Central Waitemata Harbour. The second largest loads come from the Upper Waitemata Harbour.

- Substantial proportions of the subcatchment sediment, copper and zinc loads are accumulating in the Henderson, Whau, Meola and Motions tidal creeks and in the Shoal Bay, Hobson Bay and Waterview embayments.

- Central Waitemata Harbour bed sediment concentrations of copper and zinc are not expected to reach toxic levels based on current assumptions of future trends in urban landuse and activities.

- Zinc source control targeting industrial building roofs produced limited reduction of zinc accumulation rates in the harbour because industrial areas cover only a small proportion of the catchment area and most unpainted galvanised steel roofs are expected to be replaced with other materials within the next 25 to 50 years.

- Given that the modelling approach used large-scale depositional zones and long timeframes, differences can be expected from the modelling projections and stormwater management interventions contained within these reports versus consideration of smaller depositional areas and local interventions. (For example, whereas the study addresses the Whau River as a whole, differences exist within parts of the Whau River that may merit a different magnitude or type of intervention than may be inferred from considering the Whau River and its long-term contaminant trends as a whole.) As a consequence, these local situations may merit further investigation and assessment to determine the best manner in which to intervene and make improvements in the short and long terms.

Research and Investigation Questions

From consideration of the study and results, the following issues have been identified that require further research and investigation:

- Sediment and chemical contaminant dynamics within tidal creeks.

- The magnitude and particular locations of stormwater management interventions required to arrest sediment, copper and zinc accumulation in tidal creeks and embayments, including possible remediation / restoration opportunities.

- The fate of other contaminants derived from urban sources.

- The chronic / sub-lethal effects of marine animal exposure to the cocktail of urban contaminants and other stressors such sediment deposition, changing sediment particle size distribution and elevated suspended sediment loads.

- Ecosystem health and connectivity issues between tidal creeks and the central basin of the harbour, and the wider Hauraki Gulf.

Technical reports

The study has produced a series of technical reports:

Technical Report TR2008/032
Central Waitemata Harbour Contaminant Study. Landuse Scenarios.

Technical Report TR2008/033
Central Waitemata Harbour Contaminant Study. Background Metal Concentrations in Soils: Methods and Results.

Technical Report TR2008/034
Central Waitemata Harbour Contaminant Study. Harbour Sediments.

Technical Report TR2008/035
Central Waitemata Harbour Contaminant Study. Trace Metal Concentrations in Harbour Sediments.

Technical Report TR2008/036
Central Waitemata Harbour Contaminant Study. Hydrodynamics and Sediment Transport Fieldwork.

Technical Report TR2008/037
Central Waitemata Harbour Contaminant Study. Harbour Hydrodynamics, Wave and Sediment Transport Model Implementation and Calibration.

Technical Report TR2008/038
Central Waitemata Harbour Contaminant Study. Development of the Contaminant Load Model.

Technical Report TR2008/039
Central Waitemata Harbour Contaminant Study. Predictions of Stormwater Contaminant Loads.

Technical Report TR2008/040
Central Waitemata Harbour Contaminant Study. GLEAMS Model Structure, Setup and Data Requirements.

Technical Report TR2008/041
Central Waitemata Harbour Contaminant Study. GLEAMS Model Results for Rural and Earthworks Sediment Loads.

Technical Report TR2008/042
Central Waitemata Harbour Contaminant Study. USC-3 Model Description, Implementation and Calibration.

Technical Report TR2008/043
Central Waitemata Harbour Contaminant Study. Predictions of Sediment, Zinc and Copper Accumulation under Future Development Scenario 1.

Technical Report TR2008/044
Central Waitemata Harbour Contaminant Study. Predictions of Sediment, Zinc and Copper Accumulation under Future Development Scenarios 2, 3 and 4.

Technical Report TR2009/109
Central Waitemata Harbour Contaminant Study. Rainfall Analysis.

Contents

1 Executive Summary

The overall aim of the Central Waitemata Harbour (CWH) Conataminant Study is to model contaminant accumulation (sediment, zinc, copper) within the harbour for the purposes of, amongst other things, identifying significant contaminant sources, and testing efficacy of stormwater treatment and zinc source control of industrial roofs. The objective is to predict (using models) contaminant build-up and movement in the CWH.

This report presents results from a field survey, conducted in the summer of 2006, with the purpose of describing the physical and chemical characteristics of CWH sediments, in particular, concentrations of the trace metals copper and zinc. Results cover 33 surface sediment samples, as well as three downcore sediment profiles. Metal concentrations were determined for three size fractions: <25 μm (clay), 25–63 μm (silt), and 63–250 μm (sand). Information developed here was used to calibrate and validate the Urban Stormwater Contaminant (USC) model, which was used to predict sedimentation and heavy metal accumulation in bed sediments of the harbour.

Present-day surface sediments show spatially-variable concentrations of zinc and copper, with maximum concentrations occurring on intertidal flats near tidal creek outlets and stormwater drains, and in the south western embayment of the CWH. Zinc and copper were also found to be enriched in upper Shoal Bay.

Median zinc concentrations were 81 ppm (mg kg^{-1} dry weight), 74 ppm and 131 ppm for the sand, silt and clay fractions, respectively. Median copper concentrations were 6.5 ppm, 14 ppm and 25 ppm for the sand, silt and clay fractions, respectively. These results indicate a 2–3 times enrichment of zinc and 2–5 times enrichment of copper compared to reference sites outside the CWH and compared to deep sediment layers within the CWH.

Despite the large spatial variations in absolute metal concentrations for all particle sizes, the Zn/Cu ratio for the silt and clay fractions was practically invariant between sites and also in downcore profiles, indicating that copper and zinc were transported and distributed similarly for these particle size fractions. In contrast, the sand fraction had a 2 times higher Zn/Cu ratio and large variability, indicating a decoupling of the accumulation patterns for zinc and copper in the sand fraction.

Concentration profiles in dated sediment cores from three locations showed a similar pattern of 2–3 times elevated zinc and copper concentrations in surface layers compared to background levels (at 44 cm depth). Converting sediment depth to time of deposition using measured sediment accumulation rates indicates that marked increases of zinc and copper started around 1950, coinciding with the beginning of rapid urbanisation. The steepest increases in Zn and Cu concentrations compared to background levels appear to have occurred more than 20 years ago, corresponding to a depth of 10 to 30 cm in the sediment cores. Sediment layers above this zone of rapid concentration increase were characterised by more or less uniformly elevated copper and zinc concentrations.

2 Introduction

Modelling and empirical data indicate that stormwater contaminants are rapidly accumulating in the highly urbanised side branches of the Central Waitemata Harbour (CWH). However, there is limited information about the fate of contaminants exported from these side branches into the main body of the harbour, or that of contaminants discharged directly into the central harbour.

The main aim of the study is to model contaminant (zinc, copper) and sediment accumulation within the CWH for the purposes of, amongst other things, identifying significant contaminant sources, and testing efficacy of stormwater treatment and zinc source control of industrial roofs.

2.1 Aims of the study

The Central Waitemata Harbour Contaminant Study aims to:

- predict contaminant loads based on past, present and future land use and population growth for each sub-catchment discharging into the CWH, allowing for stormwater treatment and zinc source control of industrial roofs;
- predict dispersal and accumulation (or loss) of sediment and stormwater contaminants in the CWH;
- calibrate and validate the dispersal/accumulation model;
- apply the various models to predict catchment contaminant loads and accumulation of copper, zinc and sediment in the CWH under specific scenarios that depict various combinations of projected land use/population growth, stormwater treatment efficiency, and zinc source control of industrial roofs;
- determine from the model predictions the relative contributions of sediment and contaminant from individual sub-catchments and local authorities;
- provide an assessment of the environmental consequences of model outputs;
- provide technical reports on each component of the work; and
- provide a desktop application suitable.

2.2 Model suite

The study centres on the application of three models that are linked to each other in a single suite:

- The GLEAMS sediment-generation model, which predicts sediment erosion from the land and transport down the stream channel network. Predictions of sediment supply are necessary because, ultimately, sediment eroded from the land dilutes the concentration of contaminants in the bed sediments of the harbour, making them less harmful to biota[1].

- The CLM contaminant/sediment-generation model, which predicts sediment and contaminant concentrations (including zinc, copper) in stormwater at a point source, in urban streams, or at end-of-pipe where stormwater discharges into the receiving environment.
- The USC-3 (Urban Stormwater Contaminant) contaminant/sediment accumulation model, which predicts sedimentation and accumulation of contaminants (including zinc, copper) in the bed sediments of the estuary. Underlying the USC-3 model is yet another model: an estuarine sediment-transport model, which simulates the dispersal of contaminants/sediments by physical processes such as tidal currents and waves.

Underlying the USC model are three other models: an estuarine hydrodynamic model, a wave model, and a sediment-transport model. Together these simulate the dispersal of contaminants/sediments by physical processes such as tidal currents and waves.

2.3 This report

This report presents results from a field survey conducted in the summer of 2006 to measure sediment metal concentrations in the Central Waitemata Harbour. It constitutes one module of the Central Waitemata Harbour Contaminant Study, with the purpose of describing current concentrations of the stormwater-characteristic metals zinc and copper in CWH bed sediments. The survey encompassed the chemical analysis of 33 surface sediment samples, as well as three downcore sediment profiles, to a depth of 45 cm. Zinc and copper concentrations were determined for three sediment size fractions: <25 μm (clay), 25–63 μm (silt), and 63–250 μm (sand).

This report describes median concentrations of zinc and copper for the three particle size fractions as well as their spatial distribution throughout the CWH. This information contributes to a more detailed understanding of metal accumulation patterns in the CWH and can be related to known or presumed stormwater discharges into the CWH. It also provides a dataset suitable for the tuning and validation of the Urban Stormwater Contaminant (USC) model, described above.

2.4 Background

The Central Waitemata Harbour (CWH) covers an area of 50 km^2 between the Upper Harbour Bridge at Whenuapai and the Auckland Harbour Bridge (Figures 1 and 2). The urbanised catchments of the Whau River and Henderson Creek together account for 67 % of the CWH catchment and have been identified as major sources of fine sediment and trace metals to the harbour.

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[1] We use the term "contaminant" herein to mean chemical contaminants such as zinc and copper, and we refer to "sediments" separately.

The Waitemata Harbour is a drowned-valley estuary. It is the largest east coast estuary in the Auckland region, with a surface area of some 80 km^2 and a tidal prism of *c*. 216 million m^3. The 50 km^2 CWH remains substantially subtidal despite the sediment deposition that has occurred over the last several thousand years. Infilling is most advanced in the tidal creeks. The central subtidal basin, with water depths of 0–5 m below chart datum, is flanked by extensive intertidal flats east of Te Atatu Peninsula and Pollen Island. Te Tokaroa (Meola) Reef extends some 2 km from the shore into the harbour and largely constrains tidal flows to and from the CWH to the main tidal channel. Field measurements show that fine sediments in intertidal and subtidal areas are mainly resuspended by waves (Oldman et al. 2008).

Figure 1

Aerial photograph of the Central Waitemata Harbour and adjacent water bodies (source: LINZ).

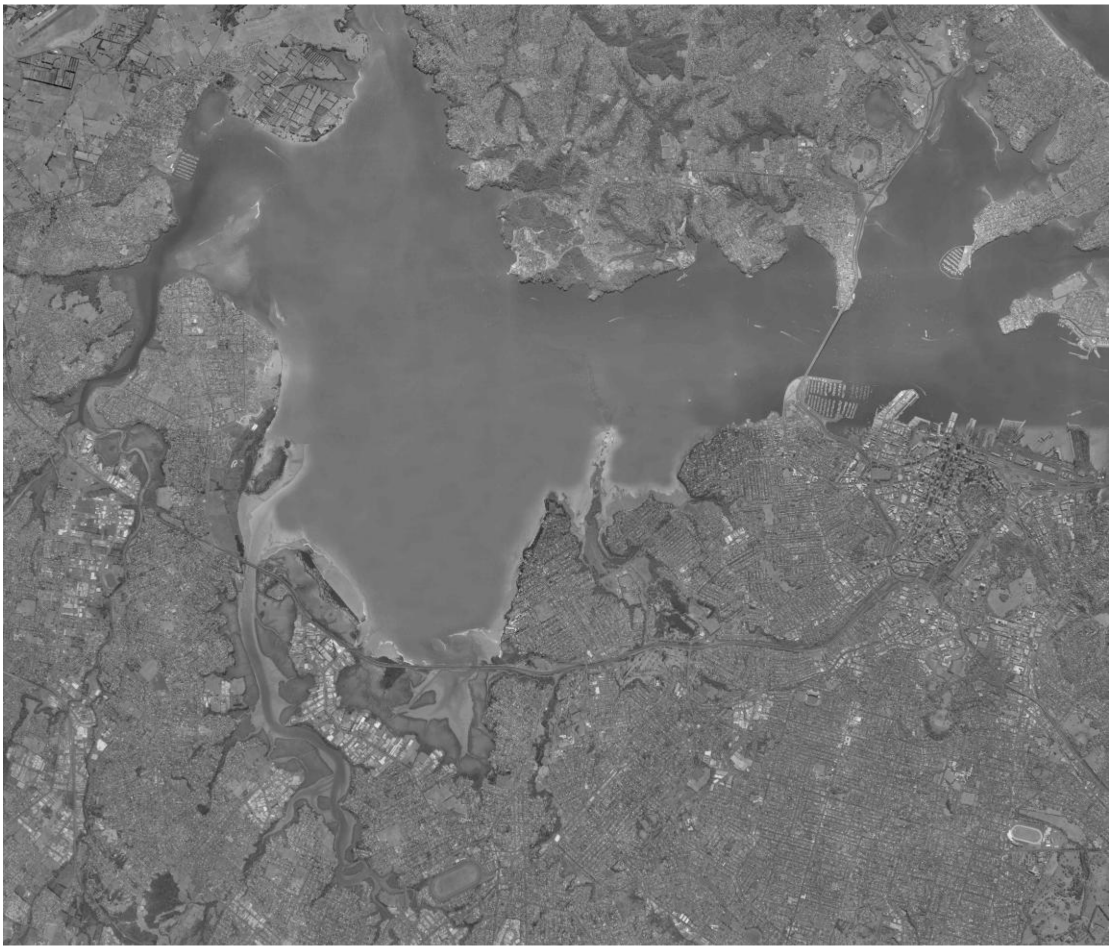
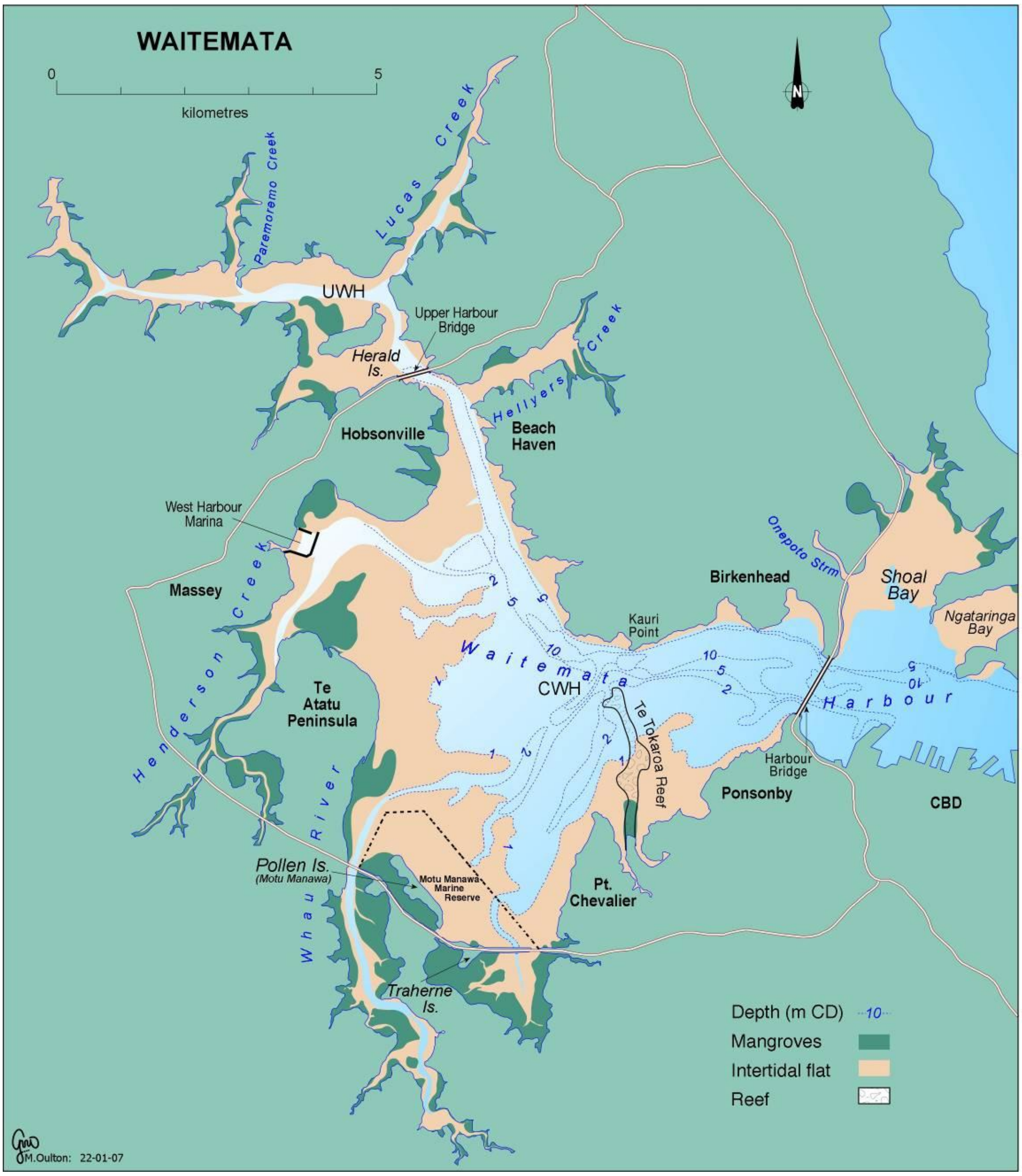


Figure 2

Map showing the Upper Waitemata Harbour (UWH), Central Waitemata Harbour (CWH) and Shoal Bay. The CWH and Shoal Bay are the focus of the present study. Extent of intertidal flat and mangrove habitats is also shown. Water depths in terms of chart datum (CD).



The CWH receives run-off from a 205 km^2 land catchment, 50 % of which discharges to the Harbour via Henderson Creek. The Henderson Creek catchment drains the eastern Waitakere ranges, with landcover consisting of regenerating conifer–hardwood forest dominated by kauri, rata, totara and rimu. The lower flanks of the ranges include low-density urban land use. Large-scale catchment deforestation began in the late 1840s and was largely complete by the late 1860s. Establishment of pasture involved scrub clearance by fire, which was often uncontrolled, and it is likely that soil erosion increased during this period. Viticulture and orcharding were established in the lower catchment from the 1890s, and at this time Henderson Township was expanding.

Farming had virtually ceased by the 1920s due to soil infertility. Large-scale urbanisation at Henderson, Massey and Te Atatu began in the 1960s following construction of the Northwestern Motorway (Denyer et al. 1993; Swales et al. 2002a).

Auckland City developed from the 1840s onwards and by the early 1900s land fringing the southern shore of the CWH at Avondale, Point Chevalier and Herne Bay had been urbanised. On the North Shore, settlements developed from the mid-1800s at Birkenhead, Northcote, Takapuna and Devonport, which could be serviced by ferries. However, most of the North Shore remained rural (pasture and native scrub). Large-scale urbanisation followed the construction of the Auckland Harbour Bridge in the early 1950s. For example, the Hellyers Creek catchment was completely urbanised by the early 1970s (Williamson and Morrisey, 2000).

Trace metals such as zinc, copper and lead are typically enriched in urban stormwater and road run-off (Lee et al. 2005; Brown and Peake, 2006), with common sources being building materials (roofs, paint, spouting), vehicles (tyres, brakes, body), boats and marine structures (paint) as well as corrosion of pipes (Davis et al. 2001; van Metre and Mahler, 2003). In addition to these anthropogenic sources, zinc and copper, among other metals, tend to be enriched in certain natural soils, such as volcanic soils (ARC, 2001; Reed, 2008), which can have concentrations 10 times higher than non-volcanic soils such as loams.

So far, most studies of sediment trace metal concentrations have focussed on the nearshore settling zones and tidal creeks feeding into the Waitemata Harbour. The ongoing ARC long-term marine sediment monitoring programme has measured trace metal concentrations in the <500 μm and <63 μm particle size fractions at 27 locations around Auckland; eight of which fall into the CWH proper (Motions, Meola, Te Tokaroa, Oakley, Whau-Upper, Whau-Lower, Wairau, Henderson) and three of which fall into the Upper Waitemata Harbour (Lucas, Kaipatiki Creek, Paremoremo). Metal concentrations (<63 μm, cold 2 M HCl extraction) at these sites range from less than 50 ppm to over 350 ppm for zinc and 5–50 ppm for copper (McHugh and Reed, 2006).

Results from the ARC sediment monitoring programme, now into its tenth year, have detected a steady increase of sediment metal concentrations at many locations from 1998 to 2005. Increased zinc and copper concentrations have also been found at other locations analysed for the ARC Regional Discharges Project (Williamson and Kelly, 2003). In contrast, few data on metal concentrations in subtidal sediments in the CWH exist.

The most comprehensive study to date of intertidal and subtidal sediment metal concentrations in the Waitemata Harbour has been that of Glasby et al. (1988), who carried out a comprehensive analysis of 29 cores and 104 grab samples. The study analysed, among other metals, zinc and copper in the <20 μm size fraction in surface (0–4 cm) and subsurface (20–24 cm) sediments, and ranked regions using a 6-grade geoaccumulation index (I_{geo}), ranging from 0 ("uncontaminated" = background), to 6 ("extremely contaminated" = 96x background). Stations were grouped into areas named "Upper Harbour", "Avondale" (Waterview-Whau), "Point Chevalier" (Motions-Meola), "City" (Central Business District), "Orakei" (Hobson) and "Outer Harbour" (Hauraki Gulf).

Mean background concentrations in the Outer Harbour (<20 μm particle size) were 109 ppm for zinc (range 92–146 ppm) and 21 ppm for copper (range 16–50 ppm). The

Upper Harbour region included a 6-station transect from Te Atatu to Kauri Point, as well as a number of nearshore stations in the tidal channel between Chelsea and Northcote Point. Mean surface sediment concentrations in this region were 130 ppm for zinc (range 83–183 ppm) and 31 ppm for copper (range 21–42 ppm). These concentrations corresponded to an I_{geo} rank of 1 for both metals ("uncontaminated to moderately contaminated" ≈ 3x background).

For more nearshore regions, such as Avondale (Whau) and Pt Chevalier (Motions-Meola), considerably higher zinc concentrations were reported: 65–310 ppm for Avondale (mean 171 ppm) and 234–879 ppm for Pt Chevalier (mean 465 ppm), corresponding to enrichment factors of 3–6 times for Avondale and 6–24 times for Pt Chevalier. Copper concentrations ranged from 18–104 ppm for Avondale (mean 57 ppm) and 46–90 ppm for Pt Chevalier (mean 63 ppm).

City stations, located roughly between the Harbour Bridge, Central Business District, Port and Shoal Bay, had mean surface concentrations of 162 ppm for zinc (range 42–368 ppm) and 36 ppm for copper (range 13–79 ppm), corresponding to 3–6 times enrichment for zinc and generally 3 times enrichment for copper.

Glasby et al. (1988) concluded that the three near-city areas (Avondale, Pt Chevalier and City) showed evidence of moderate to strong metal pollution by zinc and copper (and lead), "suggesting a possible anthropogenic influence". Analysis of subsurface sediments led to the same conclusion, with the Avondale, Pt Chevalier and City regions showing the largest enrichment in surface sediments compared to subsurface sediments. As main sources of zinc, Glasby et al. (1988) suspected corrosion and vehicle tyres. For copper, pipe reticulation corrosion was suspected as the dominant source, due to the very low or non-existent buffer capacity of Auckland's freshwater supply. No further, systematic analysis of subtidal sediments has been carried out in the Central Waitemata Harbour since this 1988 study.

2.5 Specific study aims

The goal of the trace metal analysis component of the Central Waitemata Harbour Contaminant Study was to address the following questions:

- What are the typical present day concentrations of zinc and copper in surface sediments of the CWH and Shoal Bay?
- What is the variation of zinc and copper concentrations between different sediment particle size fractions?
- How much do zinc and copper concentrations vary between locations? Are there notable spatial gradients? Do the three different particle size fractions show similar spatial patterns, and how similar are spatial distribution patterns for copper and zinc to each other?
- How do currently measured surface metal levels compare to historic background levels, as inferred from downcore metal profiles? Have zinc and copper concentrations increased significantly in recent decades? Are zinc and copper accumulation rates similar among particle size fractions?

3 Methodology

3.1 Surface and subsurface sediment sampling

Total zinc (Zn) and copper (Cu) concentrations were determined for 33 surface sediment samples (0–3 cm), from a set of 138 sites sampled within the CWH and Shoal Bay as part of a comprehensive sedimentological survey to describe sediment physical characteristics, such as particle settling velocities, particle size and density, and sediment accumulation rates (Swales et al. 2007). At 33 sites, zinc and copper were analysed in three particle size fractions, defined as clay (<25 μm), silt (25–62.5 μm) and fine sand (62.5–250 μm).

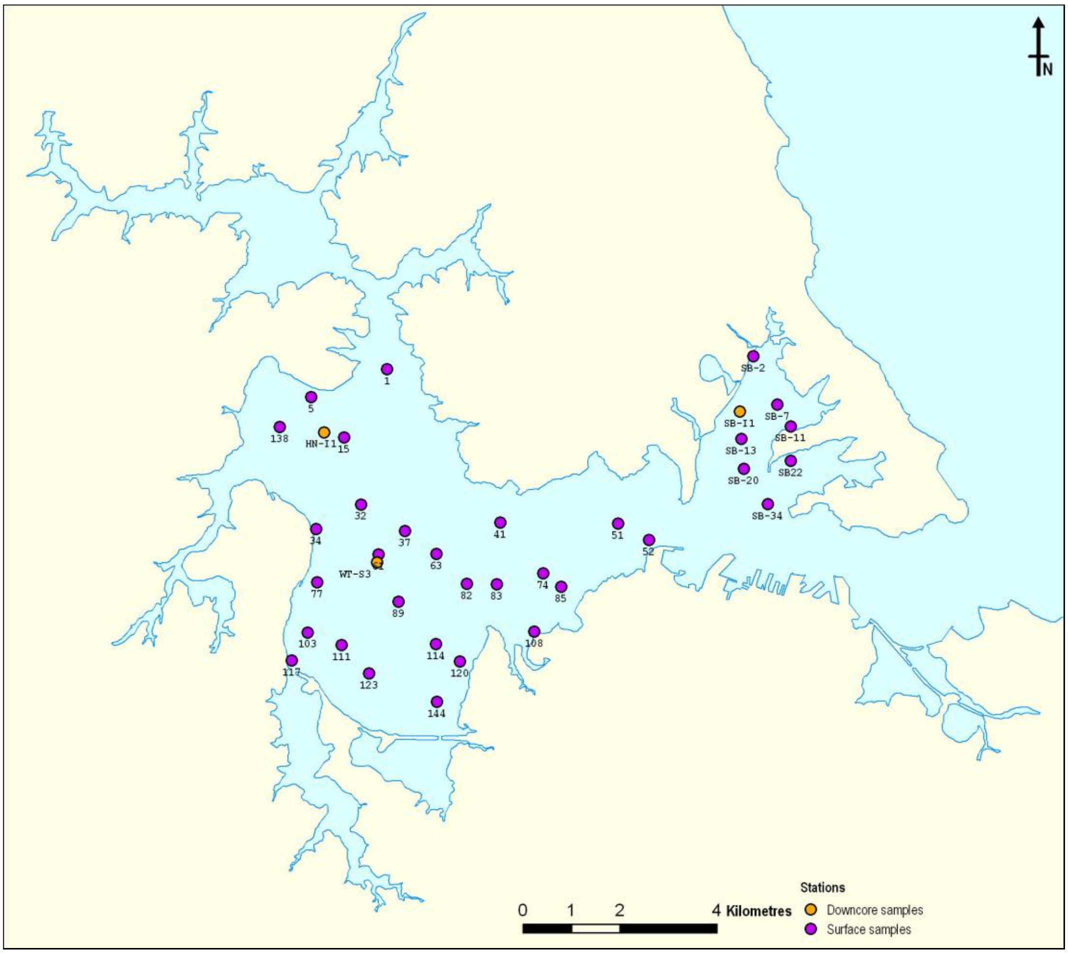
Figure 3 shows the locations of the 33 sites. In addition to the surface samples, subsurface sediments were collected at 21 sites to a depth of 0.5 m. Of these, three cores were subsequently selected for analysis of zinc and copper: SB-I1 (Shoal Bay – intertidal), WT-S3 (CWH - subtidal basin) and HN-I1 (Henderson Creek mouth – intertidal).

The field survey was designed to sample surface sediments within intertidal and subtidal subenvironments at sufficient density to identify spatial patterns and gradients in particle size. Duplicate sediment samples were collected on a semi-regular 0.5 km grid during 19–20 January and 20–21 March 2006. SCUBA divers inserted 20 cm long by 5 cm diameter clear-PVC push cores into the sediment. The co-ordinates of all metal sediment-sampling sites are listed in Appendix 1. One core from each duplicate set was refrigerated and the other frozen immediately after collection and stored at NIWA Hamilton.

Sediment cores were collected during February–March 2006. Sampling locations were selected to be depositional environments, based on previous studies undertaken in the Waitemata Harbour and expert judgement. Accordingly, it was anticipated that downcore sediment layers would preserve the history of environmental changes that have occurred in the CWH. In this regard, it needs to be noted that post-depositional mixing resulting from feeding and burrowing activities of benthic fauna and/or remobilisation by waves and currents can complicate the interpretation of sediment profiles.

To determine mixing depths, sediment cores were analysed for the short-lived tracer beryllium-7 (^{7}Be). To date downcore sediment layers, and from that infer sediment accumulation rates, the radioisotope tracers caesium-137 (^{137}Cs) and lead-210 (^{210}Pb) were measured. Further details on the radioisotope dating can be found in Swales et al. (2007). Metal profiles have also been used to delineate the onset of urban development (eg, Valette-Silver, 1993; Abrahim and Parker, 2002; Swales et al. 2002a; 2002b; 2005).

Figure 3
Location of surface and downcore samples collected for metals analyses in the Central Waitemata Harbour and Shoal Bay, Auckland, during January – March 2006.



3.1.1 Definition of sediment layers

Surface sediments in this report are defined as the top 3 cm of the sediment column. The thickness of the surface sediment layer was defined based on the vertical distribution of ^{7}Be in sediment cores (Swales et al. 2007). Downcore sediment horizons were analysed in three cores, to a depth of 44 cm, in 1 cm-thick layers, spaced 1–3 cm apart.

3.1.2 Wet sieving

Sediment samples were processed for metal analysis as follows: frozen sediment samples were allowed to thaw before wet sieving through stainless-steel sieves to yield the <25 µm, 25–63 µm, 63–250 µm and >250 µm size fractions. Sediment was washed through the sieves using nanopure de-ionised water. The sediment fractions were dried at 60°C for 48 hours.

3.1.3 Metal analyses

Total recoverable Fe, Cu and Zn were analysed by Hill Laboratories for the <25 μm ("clay"), 25–63 μm ("silt"), and 63–250 μm ("sand") size fractions, following U.S. EPA 200.2 method for environmental analyses of soils and sediments. Specifically, 1 g of powdered dry sediment sample was placed into a 50 mL polypropylene centrifuge tube and digested for 30 min at 95 °C in dilute nitric/hydrochloric acid (2 mL $HNO_{3,}$ 2 mL HCl, 10 mL distilled water). Samples were subsequently diluted 10x with 1 % nitric acid prior to analysis to reduce acid strength and centrifuged at 2500 rpm for 10 minutes to remove suspended solids. This digestion method was selected in consultation with the ARC. The extracts were decanted into clean plastic tubes and analysed for metals by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) according to APHA method 3125B. Detection limits were 0.2 ppm (mg kg^{-1}) for copper and 0.4 ppm (mg kg^{-1}) for zinc. Results were analysed using Excel, and SigmaPlot. Distribution maps were created with ArcGIS.

Original metal concentration data are reported in units of mg kg^{-1} dry weight (Appendices 2 and 3). However, for ease of reading, the non-SI unit ppm has been adopted for the discussion of results.

4 Results and Discussion

4.1 Surface sediments

This section describes present-day (2006) concentrations of zinc and copper in Central Waitemata Harbour surface sediments. Historic metal concentrations, inferred from downcore profiles in three dated sediment cores, are described in Section 4.2.

4.1.1 Particle size

To provide a general physical characterisation of surface sediments, a contour map of mean particle size is shown in Figure 4, taken from Swales et al. (2007). Further details of the geostatistical analysis of surface sediments are provided in Swales et al. (2007).

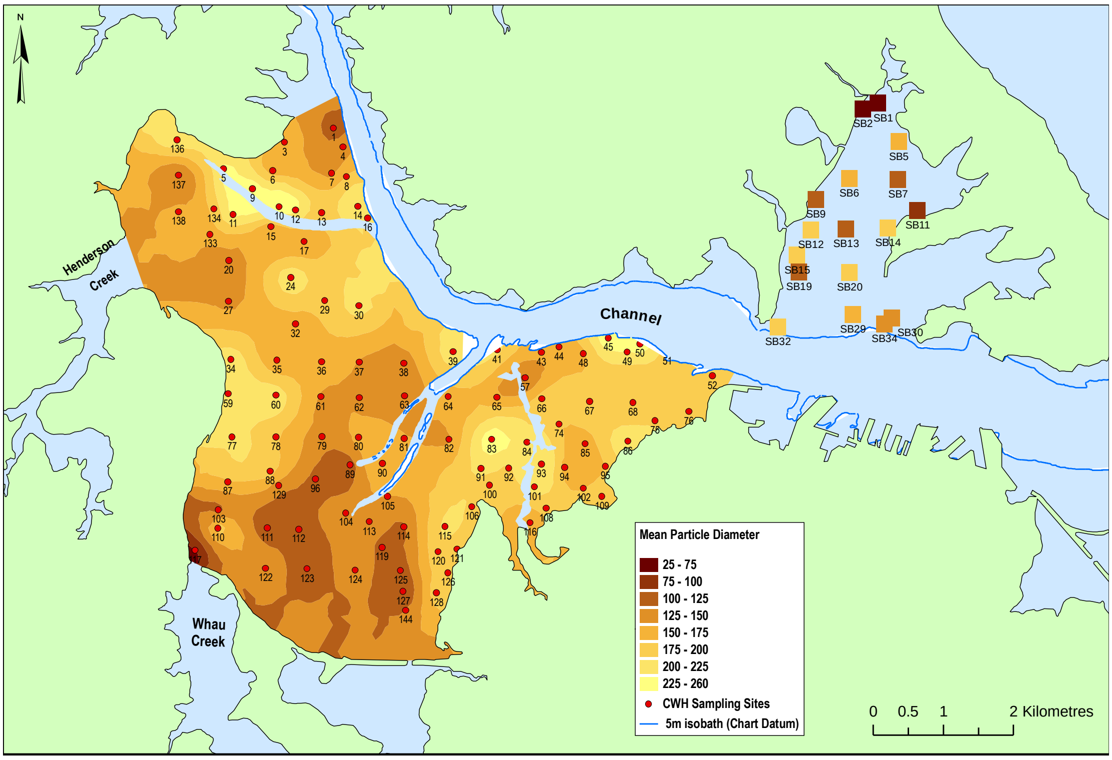
The contour map of mean particle size shows that the finest sediments, composed primarily of silts and very fine sands (≤ 100 µm), occur on intertidal and subtidal flats between Waterview and the Whau embayment. The intertidal flats off Hobsonville and the Te Atatu Peninsula are characterised by coarser sediments in the fine sand range. Similarly, the surface sediments of the central subtidal basin near the main tidal channel are mostly composed of sandier sediment, except along the border with the Upper Waitemata Harbour.

Surface sediments in Shoal Bay are generally finer than in the CWH. This is likely to be due to Shoal Bay having a smaller fetch (~2.5 km) than the CWH (~5 km) and being partly sheltered from the prevailing southwesterly winds. It should be noted that variations in mean particle size are considerable at most locations, indicating poor sorting.

Surface sediments in the Whau embayment and central basin are better sorted than sediments elsewhere in the CWH. The most poorly sorted sediments occur on the intertidal flats off Hobsonville and the subtidal flats fringing the main tidal channels. The mud (<63 µm) content of surface sediments is typically <16 % by volume over most of the CWH and Shoal Bay (Swales et al. 2007). Sediments in the Whau embayment contain >16 % mud with the mud content increasing towards the Whau Creek mouth (>64 % mud). The upper Shoal Bay is also a mud sink. The Te Atatu and Meola–Motions intertidal flats and the flats flanking the main channel have the lowest mud content, being <2 %. Sediments of the central basin have an 8–16 % (by volume) mud content.

Figure 4

Mean particle diameter (micrometres) of surface sediments in the Central Waitemata Harbour and Shoal Bay, December 2005 – March 2006 (from Swales et al. 2007).



4.1.2 Zn and Cu concentrations in surface sediments

Concentrations of zinc and copper in 33 surface sediment samples were analysed separately for three size fractions and are summarised in Table 1. Complete analytical results for each sample are listed in Appendix 2.

Table 1

Present-day (2006) zinc and copper concentrations in surface sediments.

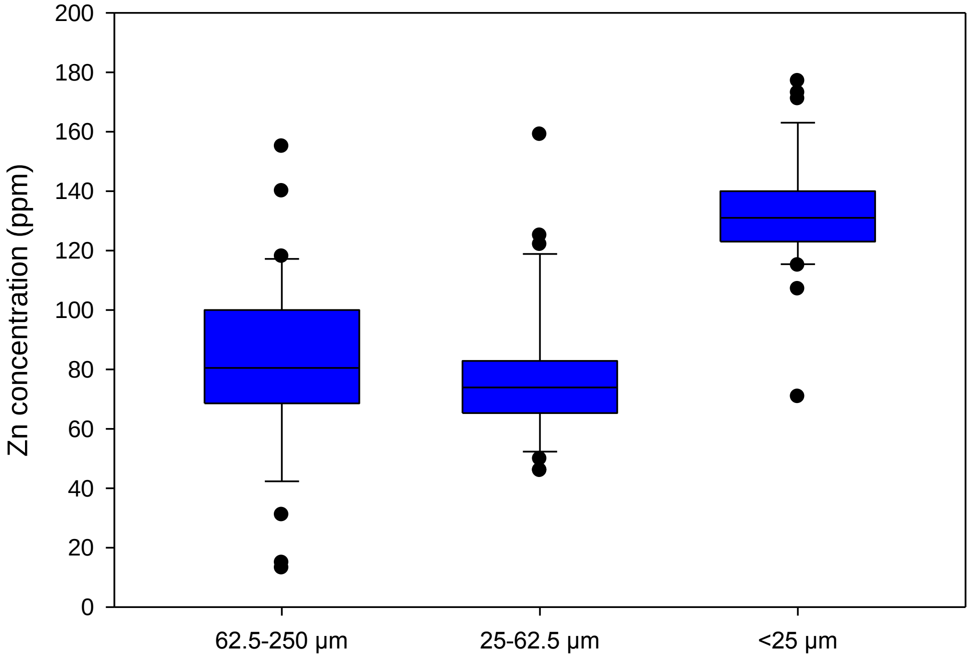
Size fraction (µm)	**Zn (ppm = mg kg^{-1})**			**Cu (ppm = mg kg^{-1})**		
	Min	**Max**	**Median**	**Min**	**Max**	**Median**
62.5-250 (sand)	13.1	155.0	80.5	1.4	27.2	6.5
25-62.5 (silt)	45.9	159.0	73.9	2.9	29.4	13.8
<25 (clay)	70.8	177.0	131.0	12.9	32.9	25.2

4.1.2.1 Zinc

Present-day zinc concentrations in surface sediments ranged between 13–177 ppm (Table 1 and Figure 5). In the sand fraction (62.5–250 µm) the median zinc concentration was 81 ppm; in the silt fraction (25–62.5 µm) it was 74 ppm; and in the clay fraction (25–62.5 µm) it was 131 ppm. Zinc concentrations in the sand fraction were the most variable, with a 12-fold difference between minimum and maximum concentrations. In the silt fraction there was a 3.5-fold difference, and in the clay fraction there was a 2.5-fold difference. Compared to an estimated background concentration of 35–37 ppm, Zn on particles <63 μm (ARC, 2004), results show widespread, moderate zinc contamination in the CWH, of 2–3 times over background.

Figure 5

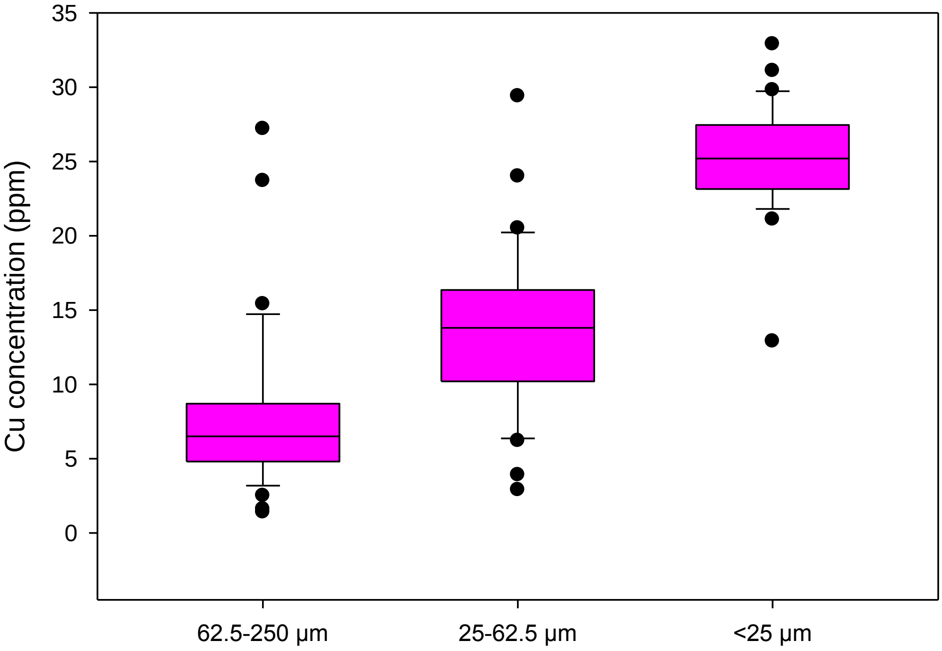
Present-day zinc concentrations (ppm) in CWH surface sediments. Box marks 25th, 50th and 75th percentiles; top and bottom whiskers denote 10th and 90th percentiles, respectively.



4.1.2.2 Copper

Present-day copper concentrations range between 1.4–33 ppm (Table 1 and Figure 6). In the sand fraction the median copper concentration was 6.5 ppm; in the silt fraction it was 14 ppm; and in the clay fraction it was 25 ppm. Copper concentrations in the sand fraction were the most variable, with a 19-fold difference between minimum and maximum concentrations; in the silt fraction there was a five-fold difference, and in the clay fraction there was a 2.5-fold difference. Compared to an estimated background concentration of 1.5–5 ppm, Cu on particles <63 μm (ARC, 2004), there is widespread, moderate copper contamination in the CWH, of 2–5 times over background.

Figure 6
Present-day copper concentrations (ppm) in CWH surface sediments. Box marks 25th, 50th and 75th percentiles; top and bottom whiskers denote 10th and 90th percentiles, respectively.



4.1.3 Spatial distributions

4.1.3.1 Zinc

The following comments relate to the distribution of zinc (Figures 7 to 9). The colour-concentration scale for each figure is adjusted to accentuate relative differences in metal concentrations for a given particle size fraction. Thus "red" always denotes sediment with the highest metal concentration and "blue" always corresponds to sediment with the lowest metal concentration. The same colours might correspond to different absolute metal concentrations for different particle size fractions.

- Highest zinc concentrations in all three size fractions occurred at shallower stations, closest to shore and close to known sources of contaminated stormwater, such as the mouth of the Whau River (stn #103 and stn #117), Motions Creek (stn #108), Westhaven (stn #52) and Hillcrest Creek (stn #SB2 (see Figures 7, 8 and 9).
- Zinc concentrations in sand and silt reached lower values on the subtidal flats of the Whau embayment (near Te Atatu peninsula), and increased towards main tidal channels.
- Zinc concentrations in the clay fraction were universally high (125–150 ppm) throughout the main basin (with the exception of stations #32 and #37), as well as along the western shoreline, indicative of uniform dispersal of fine sediment particles throughout the CWH.

- Spatial variability was strongest for the sand fraction, indicative of less efficient spatial dispersal. Very low zinc concentrations occurred off the Te Atatu peninsula and highest concentrations occurred at the discharge point of the Whau River, Hillcrest (#SB2) and Motions Creek (#108), and also within the greater discharge plume of Henderson Creek (stations #15, #32, #37, and #61).
- Zinc concentrations in Shoal Bay were generally lower than in the CWH, with the exception of Hillcrest Creek (station #SB2), which had concentrations on all size fractions exceeding 100 ppm.

Figure 7

Zinc concentrations in CWH surface sediments, in "sand" fraction (62.5–250 µm). Colour spectrum was chosen to accentuate relative differences in metal concentrations for a given particle size fraction. Lowest concentrations correspond to blue, whereas highest concentrations correspond to red. Note: different colour scale applies to different particle size fractions.

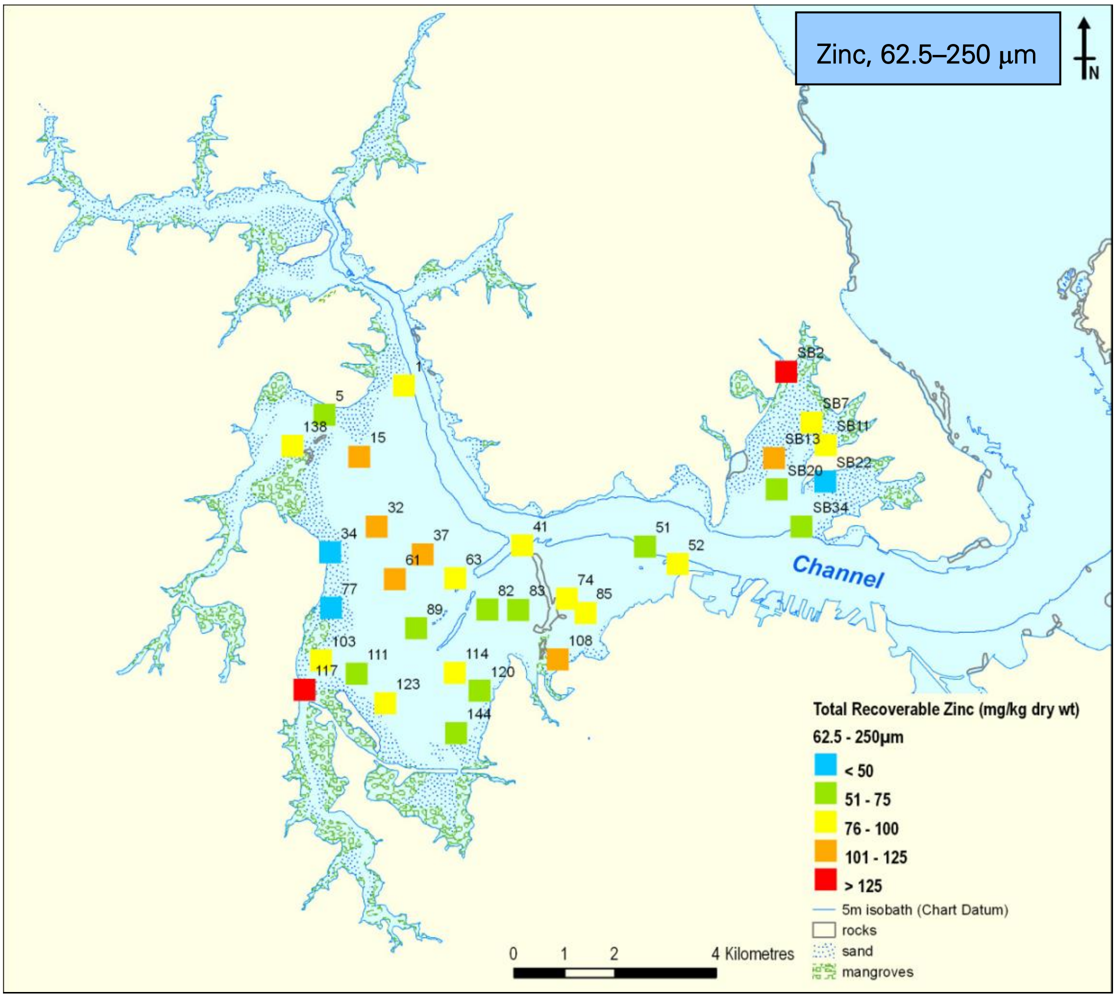


Figure 8

Zinc concentrations in CWH surface sediments, in “silt” fraction (25-62.5 µm). Note: different colour scale compared to previous figure.

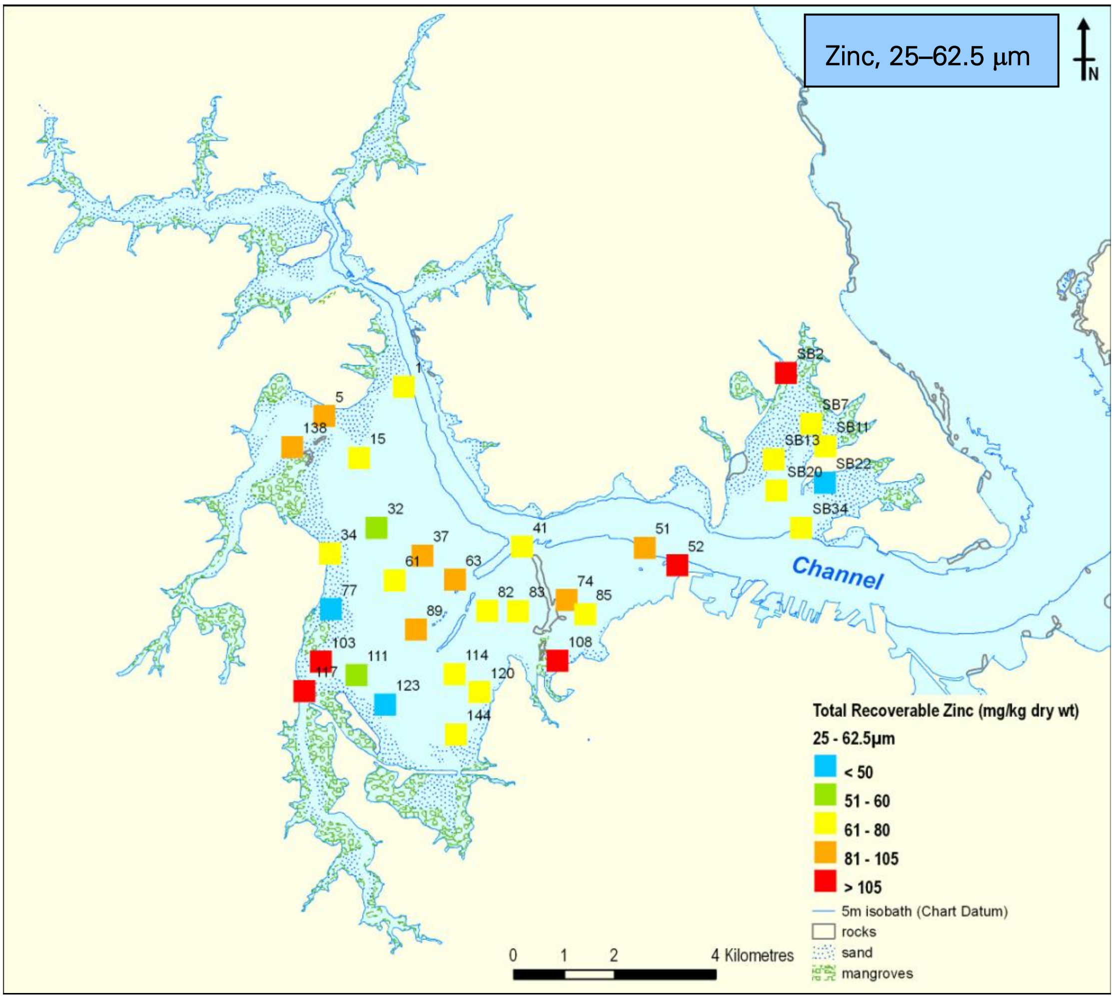
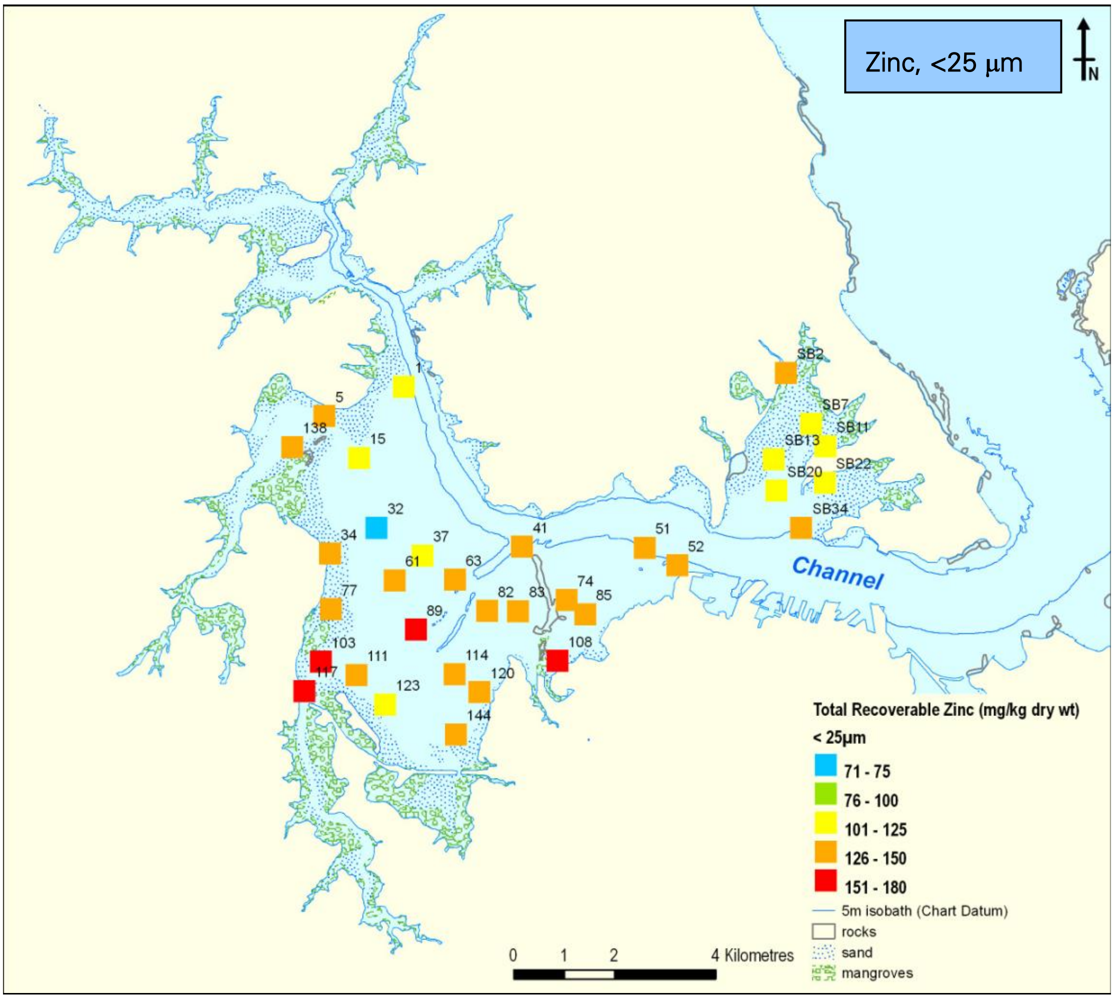


Figure 9

Zinc concentrations in CWH surface sediments, in "clay" fraction (<25 µm). Note: different colour scale compared to previous figure.



4.1.3.2 Copper

The following comments relate to the distribution of copper (Figures 6 to 12):

- Highest concentrations occurred in the vicinity of contaminated stormwater inputs (eg, Whau River, #117; Motions Creek, #108; and Hillcrest Creek, #SB2).
- Concentrations were commonly lower further from shore, but with some local high values.
- Copper concentration in the sand fraction showed the highest spatial variability, with maximum concentrations measured near river mouths. Additional localised high concentrations were found in several shallow subtidal locations (Meola Reef station #74, and station #41, off Kendall Bay). Very low concentrations occurred near the Te Atatu peninsula, similar to what was observed for zinc.

- The silt fraction had more uniform copper concentrations throughout most of the CWH and Shoal Bay, generally varying less than three-fold. High concentrations were found only in shallow, nearshore locations close to presumed stormwater sources.
- Copper concentrations in the clay fraction showed the most uniform spatial distribution, and varied by less than a factor of 2.5. Concentrations were highest at the mouths of the Whau River (#117) and Motions Creek (#108). High concentrations were also found along the Te Atatu shoreline (stations #103, #77, and #34) up to the discharge point of Henderson Creek (#138, and #5), and at stations bordering Meola Reef (stations #41, #83, #74 and #85) and the subtidal channel between Kendall Bay and Pt Chevalier. Lowest concentrations occurred at more offshore intertidal stations, away from river mouths and the channels.
- As was the case for zinc, the entire western CWH shoreline was characterised by elevated copper concentrations in the clay fraction.
- Concentrations in Shoal Bay were generally lower than in the CWH, with the exception of Hillcrest Creek (station #SB2).

Figure 10

Copper concentrations in CWH surface sediments, in "sand" fraction (62.5–250 μm). Note: different colour scale for different particle size fractions.

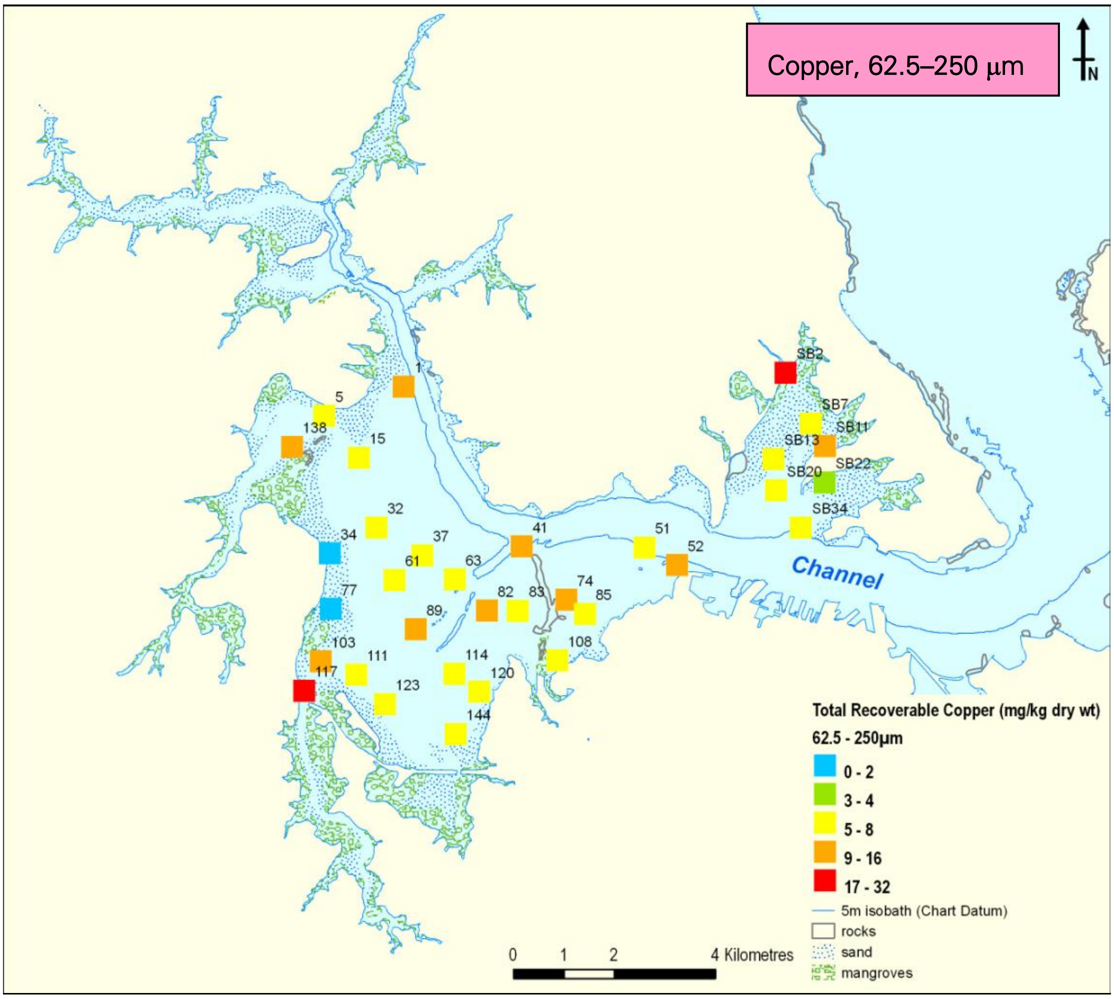


Figure 11

Copper concentrations in CWH surface sediments, in “silt” fraction (25-62.5 µm). Note: different colour scale compared to previous figure.

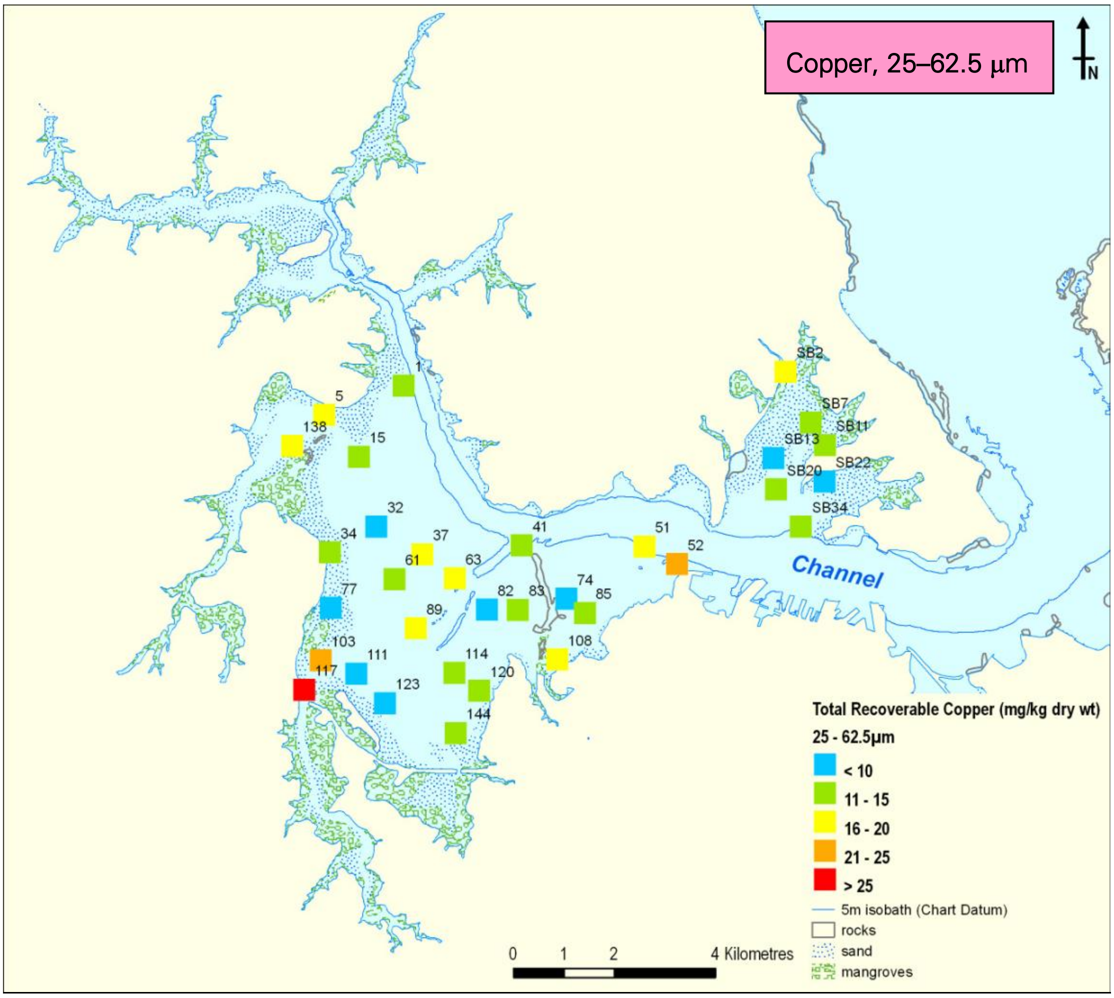
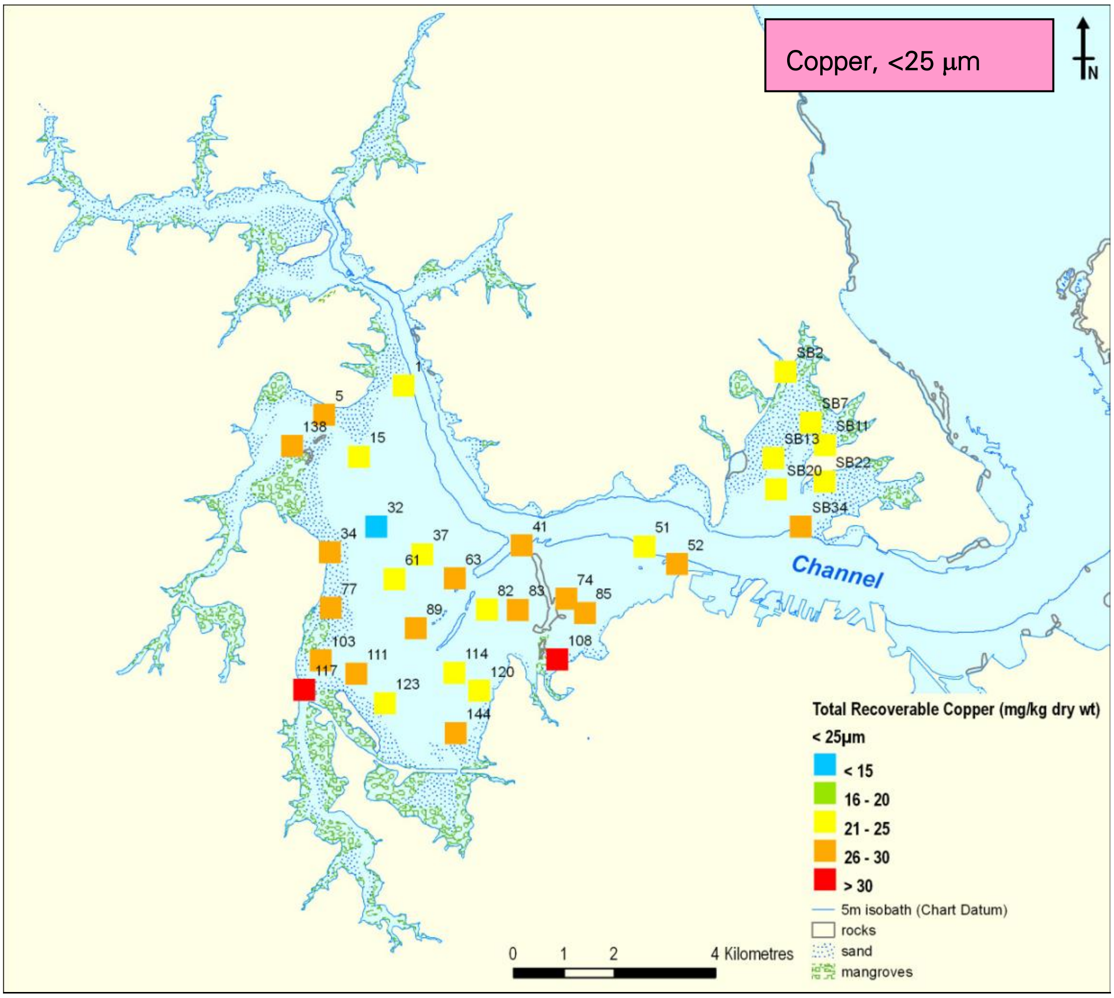


Figure 12

Copper concentrations in CWH surface sediments, in "clay" fraction (<25 µm). Note: different colour scale compared to previous figure.



4.1.4 Comparison of zinc and copper concentration patterns

The primary source of elevated zinc and copper concentrations in Auckland's estuaries is believed to be urban stormwater discharges from land (Williamson and Morrisey, 2000). If it is assumed that zinc and copper enter estuaries via the same route (eg, rivers and stormwater outfalls) and subsequently bind to particles to a comparable extent, then it would be reasonable to expect a close correlation between the Zn and Cu datasets and a similar distribution pattern of both metals throughout the CWH.

As shown in Figure 13, Zn and Cu concentrations in surface sediments, indeed showed a reasonable degree of correlation for both silt (r^2=0.58) and clay fractions (r^2=0.74), but were only weakly correlated (r^2=0.39) in the sand fraction. This suggests that zinc and copper in clay and silt-sized particles are transported and deposited similarly throughout the harbour, whereas they are decoupled for sand-sized particles.

An alternative way of illustrating the Zn/Cu relationship is by using the Zn/Cu ratio. As shown in Figure 14, the median Zn/Cu ratio was 5.4 and 5.2 for the silt and clay fractions, respectively, with remarkable constancy (except for two outliers, stations #74 and #82 that had exceptionally low Cu levels in the silt fraction). In contrast, the median Zn/Cu ratio for the sand fraction (62.5–250 µm) was significantly higher (12) and showed a high degree of variability, indicating a decoupling of zinc and copper in this size fraction at numerous sites.

Figure 13

Relationship between Zn and Cu concentrations, plotted separately for the three particle size fractions (sand, silt and clay).

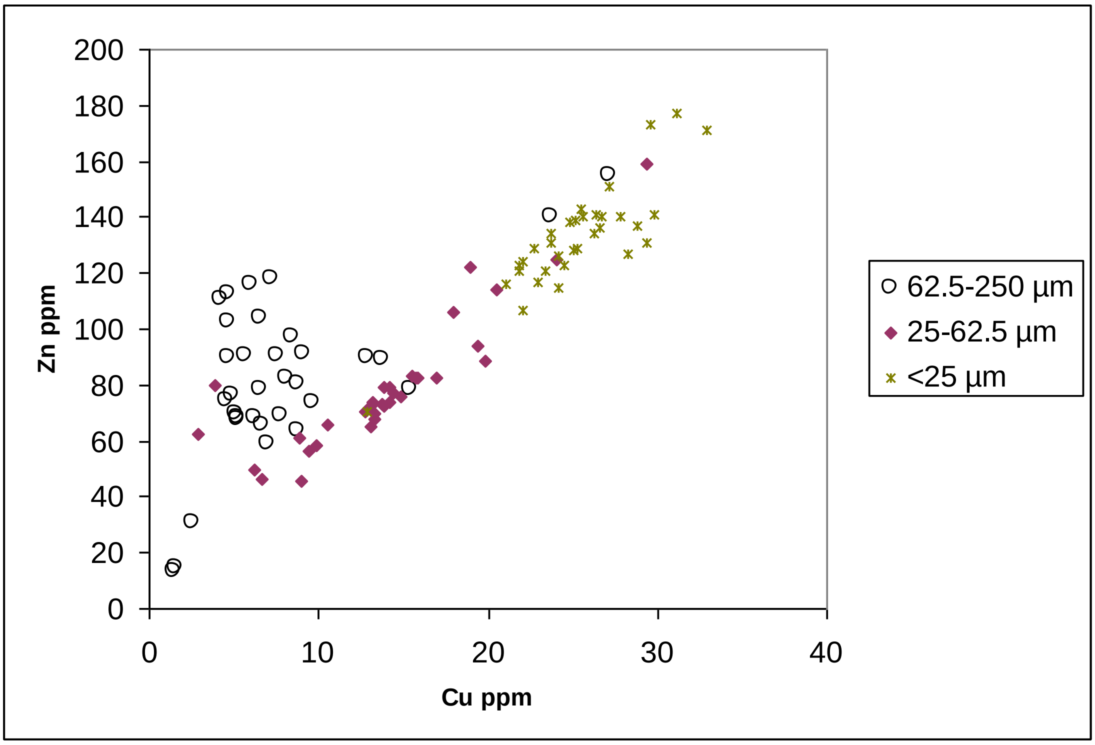
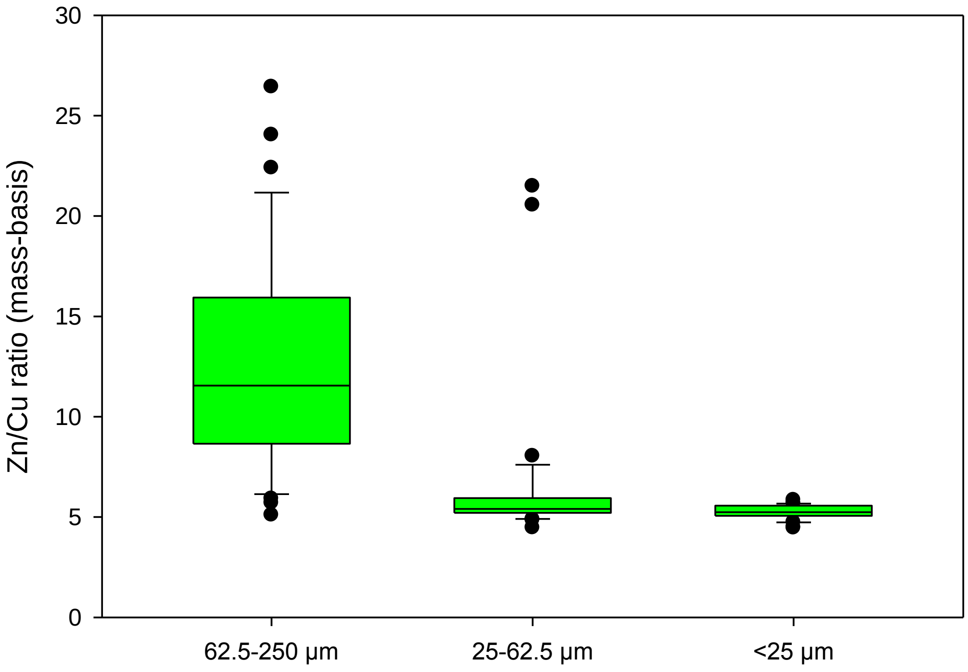


Figure 14

Median Zn/Cu ratio in surface sediments, for the three particle size fractions investigated (box marks 25th, 50th and 75th percentiles, top and bottom whiskers denote 10th and 90th percentiles, respectively).



4.2 Subsurface sediments

4.2.1 Zinc and copper concentrations in subsurface sediments

Downcore metal profiles were analysed in three 44 cm long sediment cores, taken from Henderson (HN-I1), Shoal Bay (SB-I1) and the Central Basin of the CWH (WT-S3; Figure 3). The same cores were also analysed for radioisotope dating, to calculate sediment accumulation rates (Swales et al. 2007). The downcore metal profiles provide a valuable dataset for reconstructing likely surface sediment Zn and Cu concentrations in the Central Waitemata Harbour over the last 100 years. The following statements apply to Figures 15 to 17:

- Downcore zinc concentration profiles of all particle size fractions showed a prominent decrease towards deeper (older) sediment layers. Copper concentrations also decreased by about 2-fold in most samples and size fractions.
- Average zinc concentrations in the deepest sediment layer (43–44 cm) were 25 ppm, 31 ppm and 57 ppm in the sand, silt and clay fractions, respectively. Corresponding surface zinc concentrations (average of three cores) were higher by a factor of 3.7 (sand), 2.0 (silt), and 2.2 (clay).
- Average copper concentrations in the deepest sediment layer (43–44 cm) were 4 ppm, 6 ppm and 13 ppm, in the sand, silt and clay fractions, respectively.

Corresponding surface copper concentrations (average of three cores) were higher by a factor of 1.6 (sand), 1.8 (silt), and 1.8 (clay).

- The core with the greatest downcore decrease in zinc and copper concentrations was Shoal Bay (SB-I1): surface zinc concentrations in Shoal Bay were 9x, 3x and 2.5x over background (ie, concentration at 43–44 cm depth), for sand, silt and clay, respectively. Surface copper concentrations at Shoal Bay were 3.5x, 2.6x and 2.4x over background for sand, silt and clay, respectively.
- The Central Waitemata Harbour core (WT-S3) had moderate changes in zinc and copper concentrations with depth: surface zinc concentrations in this core were 2.7x, 2.1x and 2.5x over background (ie, 43–44 cm depth), for sand, silt and clay, respectively. Copper concentrations were 0.9x, 2.1x and 1.7x compared to background for sand, silt and clay, respectively. Note that copper concentrations in the sand fraction were lower than background copper concentrations.
- The core with the smallest difference in downcore zinc and copper concentration profiles was the Henderson core (HN-I1): surface zinc concentrations for Henderson were 2.5x, 1.4x and 1.8x over background (ie, 43–44 cm depth), for sand, silt and clay, respectively. Surface copper concentrations were 1.3x, 1.2x and 1.5x over background for sand, silt and clay, respectively.
- The observed patterns confirm the hypothesis that present-day surface concentrations of Zn and Cu are, on average, 2–3 times higher than historic background concentrations. Based on estimates that sediments at 43–44 cm depth were deposited roughly 100 years ago (Swales et al. 2007), the prominent increases in zinc and copper are seen to coincide with Auckland's rapid urbanisation over the last century.
- Downcore profiles for zinc and copper were similar, resulting in a relatively uniform Zn/Cu ratio with depth. Sand-sized particles showed the greatest variation of the Zn/Cu ratio with depth, with a notable decline below approximately 25 cm.

Figure 15

Vertical concentration profiles of Zn, Cu and the Zn/Cu ratio from an intertidal sediment core taken off Henderson (HN-I1) for three particle size fractions, a. sand (62.5–250 µm), b. silt (25–62.5 µm), and c. clay (<25 µm).

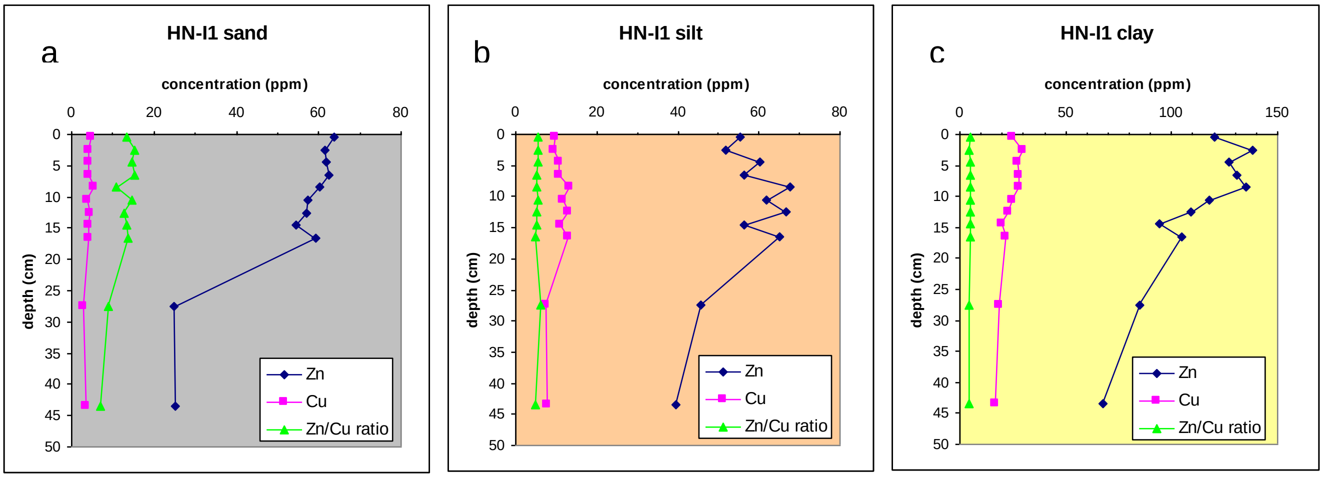


Figure 16

Vertical concentration profiles of Zn, Cu and the Zn/Cu ratio from an intertidal sediment core taken in Shoal Bay (HN-I1) for three particle size fractions , a. sand (62.5–250 µm), b. silt (25–62.5 µm), and c. clay (<25 µm).

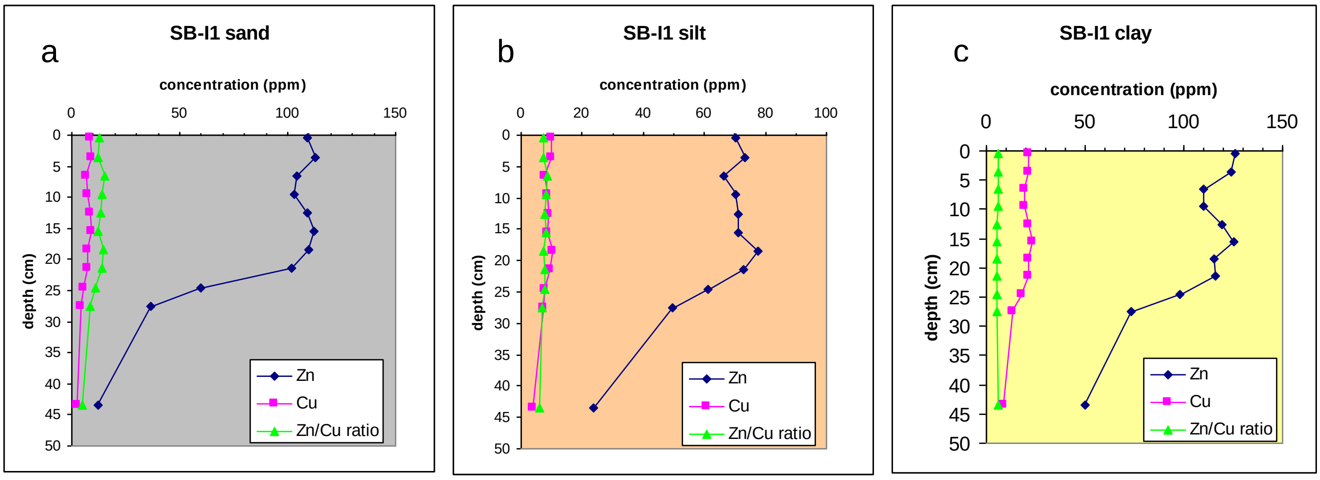
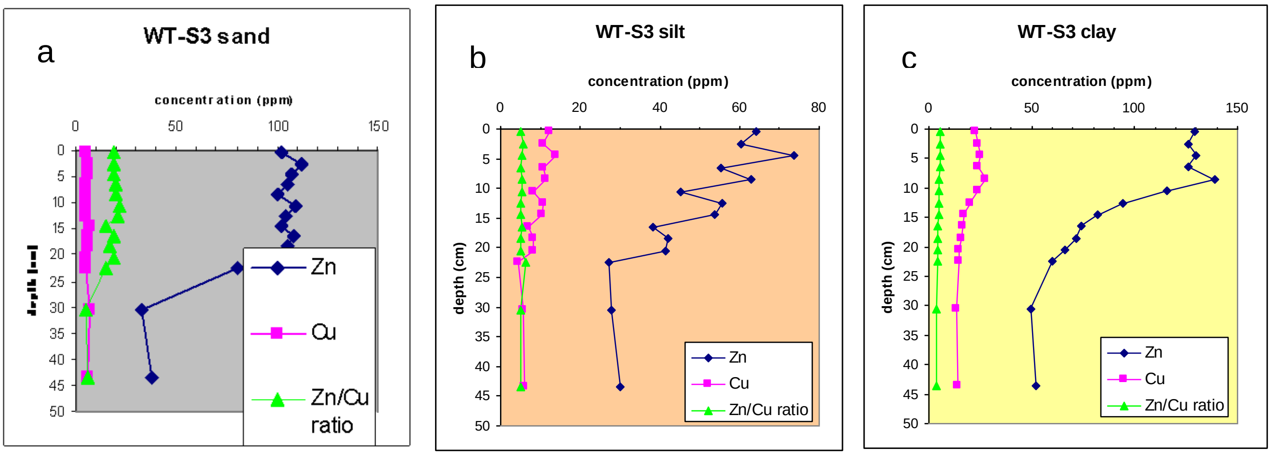


Figure 17

Vertical concentration profiles of Zn, Cu and the Zn/Cu ratio from a subtidal sediment core taken in the CWH, central basin (WT-S3), for three particle size fractions , a. sand (62.5–250 µm), b. silt (25–62.5 µm), and c. clay (<25 µm).



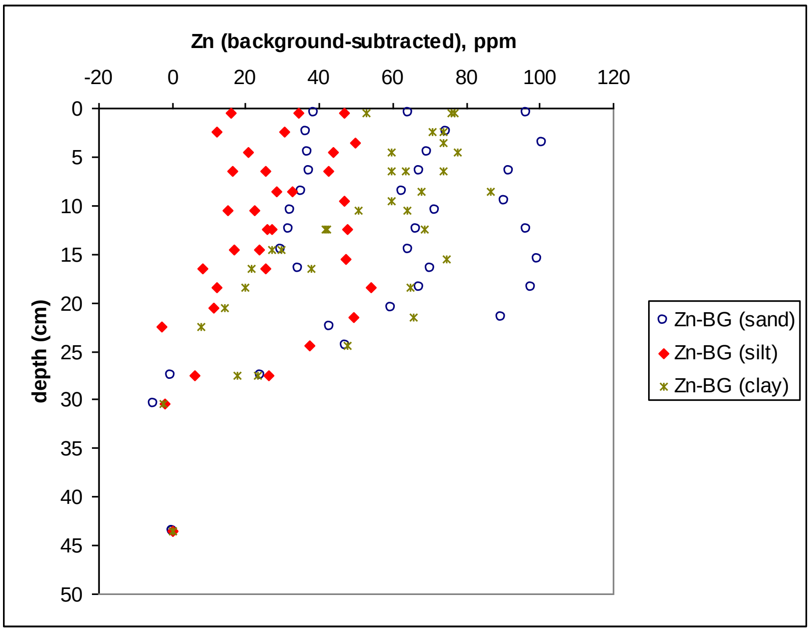
4.2.1.1 Estimating historic trends in metal accumulation

As shown in Figures 15 to 17, depth-profiles of zinc and copper show a decline of concentration with sediment depth in all three cores. Despite differences in absolute values between particle size fractions, this decline is seen for all three size fractions. In nearly all profiles, a pronounced drop in Zn and Cu concentrations was apparent at a depth of approximately 25 to 30 cm.

To facilitate comparison of metal accumulation trends of different cores and particle size fractions, data were standardised by subtracting from each metal profile the concentration in the deepest layer (43–44 cm) as the "background". This data transformation allows comparing the trends in different cores and particle size fractions in one plot, which is shown in Figure 18.

Figure 18

Downcore zinc profiles for three particle size fractions (in three cores), with respective background concentrations (ie, value at 43-44 cm) subtracted.



The following statements apply to zinc concentration profiles, comparing the deepest (43–44 cm) layer with surface concentrations:

- Zn concentrations increased by 40–100 ppm in the sand fraction. Greatest differences (9-fold change) were observed in Shoal Bay.
- Zn concentrations increased by 20–50 ppm in the silt fraction.
- Zn concentrations increased by 50–80 ppm in the clay fraction.
- The sand fraction showed the greatest change in zinc concentration with depth.
- Most increases in zinc concentration occurred over the depth interval 20–30 cm, with little further increases in layers closer to the surface.
- Zinc concentration profiles from all three cores had a similar shape, with a subsurface maximum occurring at a depth of 15–22 cm and an intermediate minimum around 10 cm for the sand fraction.

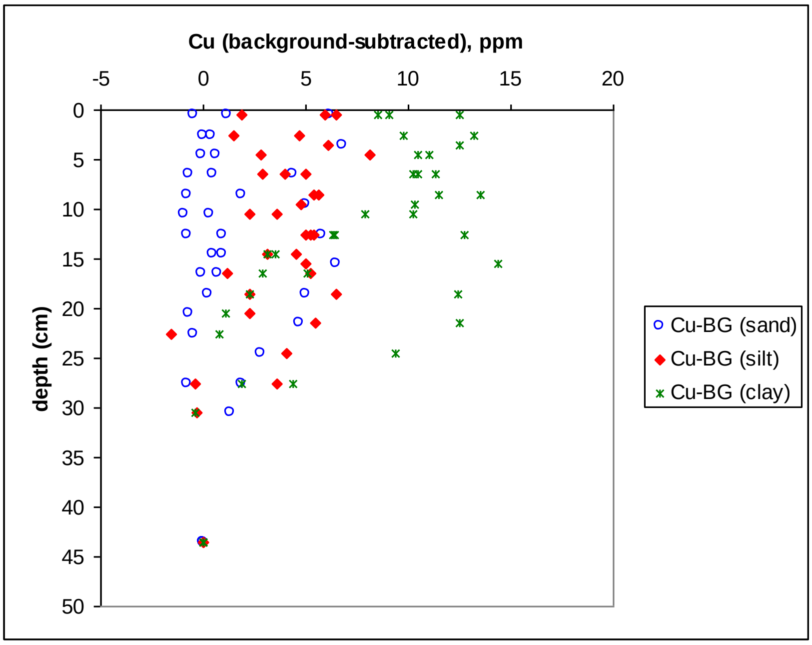
Figure 19 presents background-subtracted depth profiles for copper. The following statements apply to copper concentration profiles, comparing the deepest (43–44 cm) layer with surface concentrations:

- Cu concentrations increased by 0–6 ppm in the sand fraction. Greatest differences (3.5-fold change) were observed in Shoal Bay.
- Cu concentrations increased by 2–7 ppm in the silt fraction.
- Cu concentrations increased by 8–13 ppm in the clay fraction.
- The clay fraction showed the greatest absolute change in copper concentration with depth.

- Similar to zinc, most of the increases in copper concentrations occurred in the depth interval 20–30 cm, with little further increases in surface layers.

Figure 19

Downcore copper profiles for three particle size fractions (in three cores), with respective background concentrations (ie, value at 43-44 cm) subtracted.



4.2.2 Dating downcore metal profiles

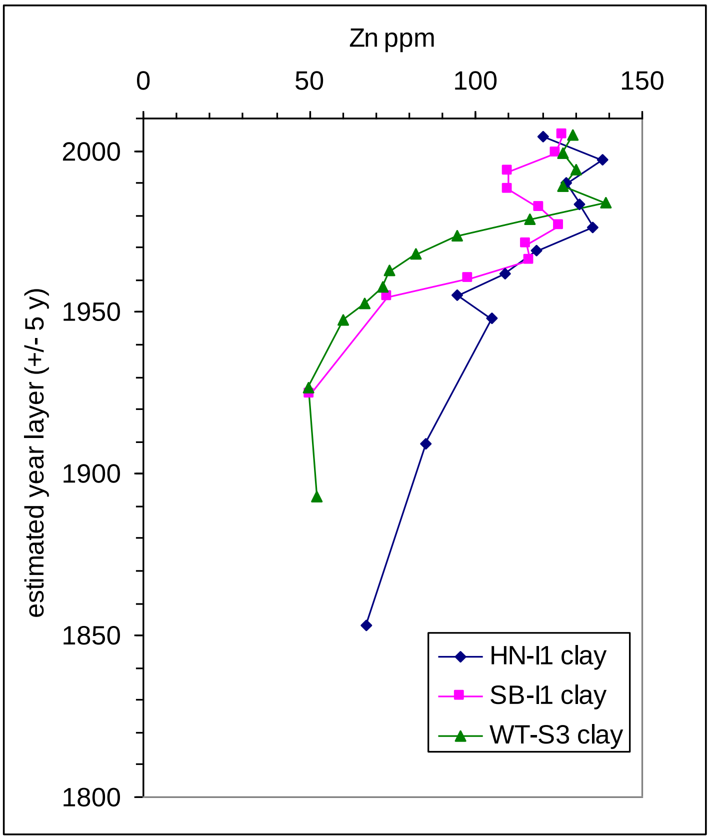
Whereas the vertical Zn and Cu concentration profiles, as presented above, indicate that metal concentrations have increased in more recent times, the concentration data by themselves do not provide information over which timescale these increases may have occurred.

Knowledge of the sediment accumulation rate (SAR) for a specific core makes it possible to estimate a likely year (or decade) during which a given depth layer was deposited. Based on SARs calculated from lead-210 (^{210}Pb) and caesium-137 (^{137}Cs) profiles, Swales et al. (2007) estimated annual-average sedimentation rates in the top 25 cm to be 2.9, 5.4 and 3.9 mm yr^{-1} for cores HN-I1, SB-I1 and WT-S3, respectively. Using these sedimentation rates, approximate time horizons were assigned to measured depth layers, noting a depth resolution of about 10 years, based on beryllium-7 (^{7}Be) mixing depths of 30–50 mm (Swales et al. 2007).

Figure 20 shows Zn concentrations in the clay fraction for the three cores versus estimated year. Largest increases in Zn levels were observed in the time period 1950 onwards (corresponding to the top 25 cm). For simplicity, SARs were assumed to be uniform to a depth of 50 cm, even though they may have been lower in pre-1950's sediment layers (>25 cm depth).

Figure 20

Downcore concentration profile of zinc in the clay fraction (<25 µm), with sediment depth converted to approximate depositional year, as estimated from average ^{210}Pb and ^{137}Cs sediment accumulation rates reported by Swales (2007). Time resolution approximately 10 years (±5 y), based on ^{7}Be mixing depths.



4.3 Comparison with previous surveys

This study found zinc and copper surface sediment concentrations in outer zones of the Central Waitemata Harbour to be approximately 2–3 times above natural background concentrations. Concentrations of zinc and copper in the clay fraction (<25 µm) measured in this study (131 and 25 ppm, respectively) agree closely with results from Glasby et al. (1988), who found mean concentrations of 130 ppm for Zn and 30 ppm for Cu in subtidal sediments (<20 µm particle size) in the region encompassing Te Atatu, Kauri Point and Northcote.

The spatial trend of increasing zinc and copper concentrations towards shore, especially near outflows of tidal creeks and stormwater discharges, corroborates observations from previous monitoring studies that have found metal concentrations in nearshore settling zones (eg, in tidal creeks) to be elevated, especially in the Whau–Wairau, Henderson, Motions–Meola and Shoal Bay areas. Present-day metal concentrations in the outer zones of the CWH are currently about half to a third of those fond in the most contaminated tidal creeks (eg, Whau and Motions; McHugh and Reed, 2006).

The finding that metal concentrations rapidly diminish from tidal creeks towards the open harbour suggests vigorous dilution and redistribution by waves and currents beyond the tidal creeks.

Contrary to trends seen in nearshore settling zones, where metal concentrations have been steadily increasing in the last 10 years (McHugh and Reed, 2006), no obvious increases of zinc and copper concentrations in the last two decades were observed in the three cores from the outer harbour zones, where most increases appear to have occurred more than 20 years ago.

5 Conclusions

The main conclusions of the metal analysis component of the CWH Study are:

- Zinc and copper concentrations in CWH surface sediments are 2–3 times elevated over background concentrations.
- Median zinc concentrations are approximately 80 ppm in sand (62.5–250 μm), 75 ppm in silt (25–62.5 μm), and 130 ppm in clay-sized (<62.5 μm) particles.
- Median copper concentrations are 6.5 ppm for sand, 14 ppm for silt and 25 ppm for clay.
- Metal concentrations for all particle size fractions are variable, with greatest variability found in the sand fraction.
- Copper and zinc concentrations in the CWH and Shoal Bay show highly variable spatial distributions. Highest concentrations tend to occur on the intertidal flats of the southwestern CWH and upper Shoal Bay, close to shore, and in the vicinity of tidal creeks. This demonstrates the importance of tidal creeks as depositional environments for metal-contaminated sediments, and their likely role as a secondary source of metal-contaminated particles for the wider harbour.
- The Zn/Cu ratio in silt and clay fractions is relatively invariant among sites as well as with depth, with a mean value of about 5.5. This suggests that zinc and copper in silt and clay sized particles are transported and deposited similarly throughout the harbour. It further suggests that post-depositional Zn solubilisation in the open harbour is not a major process in CWH fine sediments (corroborating the conclusion by Williamson, in ARC 2004), and points to a greater importance of physical particle dispersal for distributing Zn and Cu throughout the harbour.
- The Zn/Cu ratio for the sand fraction (62.5–250 μm) is significantly higher (12–14) and considerably more variable than the silt and clay fraction, indicating a decoupling of zinc and copper distribution patterns in the sand fraction.
- Based on data from three shallow cores (44 cm depth), zinc and copper concentrations appear to have increased 2–3 times over background levels over the last 50–60 years. Zn and Cu show similar downcore profiles, resulting in an almost invariant Zn/Cu ratio down to 40 cm depth. Based on information from radioisotope dating, most increases in zinc and copper appear to have happened more than 20 years ago, and changes in the most recent 10–20 cm have been moderate.

6 Acknowledgements

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8 Appendix 1: Sampling Locations of Surface and Substance Cores

Table 2

Location of surface sediment samples in the Central Waitemata Harbour and Shoal Bay New Zealand Map Grid (NZMG) co-ordinates.

Sample site	Date sampled	NZMG Easting	NZMG Northing
1	19 January 2006	2660208.9	6487336.6
5	19 January 2006	2658637.5	6486759.0
15	19 January 2006	2659318.3	6485928.8
32	19 January 2006	2659669.7	6484545.6
34	19 January 2006	2658747.0	6484038.6
37	19 January 2006	2660578.0	6483998.4
41	19 January 2006	2662544.3	6484172.6
51	19 January 2006	2664970.0	6484152.9
52	19 January 2006	2665614.3	6483806.9
61	19 January 2006	2660027.7	6483507.5
63	19 January 2006	2661219.9	6483520.7
74	20 January 2006	2663427.1	6483119.4
77	20 January 2006	2658762.2	6482938.3
82	20 January 2006	2661855.3	6482902.1
83	20 January 2006	2662468.1	6482897.7
85	20 January 2006	2663797.1	6482840.1
89	20 January 2006	2660444.9	6482535.8
103	20 January 2006	2658567.3	6481899.9
108	20 January 2006	2663241.6	6481915.5
111	20 January 2006	2659266.8	6481636.5
114	20 January 2006	2661211.6	6481655.0
117	20 January 2006	2658237.2	6481318.3
120	20 January 2006	2661704.1	6481299.0
123	20 January 2006	2659835.1	6481053.8
138	20 January 2006	2657997.2	6486143.4
144	20 January 2006	2661237.2	6480463.4
SB-2	19 January 2006	2667762.2	6487611.4
SB-7	19 January 2006	2668259.3	6486607.8
SB-11	19 January 2006	2668537.5	6486161.4
SB-13	19 January 2006	2667516.6	6485902.6
SB-20	19 January 2006	2667569.0	6485281.1
SB-22	19 January 2006	2668530.8	6485441.2

Sample site	Date sampled	NZMG Easting	NZMG Northing
SB-34	21 March 2006	2668063.5	6484546.2

Table 3

Location and sampling details of subsurface cores collected in the Central Waitemata Harbour and Shoal Bay. New Zealand Map Grid (NZMG) co-ordinates.

Core site	Date	Time (NZST)	Water depth (m)	NZMG Northing	NZMG Easting
Intertidal					
HN-I1	8-Feb-2006	1437	2.2	6486038	2658904
SB-I1	20-Mar-2006	1135	2.0	6487042	2667910
Subtidal					
WT-S3	9-Feb-2006	1115	1.8	6483344	2659995

9 Appendix 2: Surface Metal Concentrations

Table 4

Total recoverable copper and zinc concentrations of CWH surface sediments (0-3 cm depth), analysed separately for three particle size fractions.

Station #	**Size fraction (µm)**	**Hill lab sample code**	**Total recoverable copper (mg kg^{-1} dry wt)**	**Total recoverable zinc (mg kg^{-1} dry wt)**
1	62.5-250	439742/1	9.1	91.0
5	62.5-250	439742/1	7.8	68.9
15	62.5-250	439742/3	6	116
32	62.5-250	439742/4	4.7	113
34	62.5-250	439742/5	1.6	14.9
37	62.5-250	439742/6	7.2	118
41	62.5-250	439742/7	8.1	82.5
51	62.5-250	439742/8	4.5	74.7
52	62.5-250	439742/9	13.7	89.0
61	62.5-250	439742/10	4.6	103
63	62.5-250	439742/11	4.7	90.2
74	62.5-250	439742/12	15.4	78.5
77	62.5-250	439742/13	1.4	13.1
82	62.5-250	439742/14	8.7	64.0
83	62.5-250	439742/15	5.2	68.7
85	62.5-250	439742/16	4.9	76.7
89	62.5-250	439742/17	9.6	73.7
103	62.5-250	439742/18	12.8	90.2
108	62.5-250	439742/19	4.2	111
108	62.5-250	439742/19 dup 1&2	dup1=3.91 dup2=4.11	-
111	62.5-250	439742/20	5.2	67.9
114	62.5-250	439742/21	5.7	90.5
117	62.5-250	439742/22	27.2	155
120	62.5-250	439742/23	5.1	70.0
123	62.5-250	439742/24	6.5	78.2
138	62.5-250	439742/25	8.7	80.5
144	62.5-250	439742/26	7	59.3
SB2	62.5-250	439742/27	23.7	140
SB7	62.5-250	439742/28	7.5	90.8
SB11	62.5-250	439742/29	8.4	97.0
SB13	62.5-250	439742/30	6.5	104
SB20	62.5-250	439742/31	6.2	68.4
SB22	62.5-250	439742/32	2.5	31.0

Station #	**Size fraction (µm)**	**Hill lab sample code**	**Total recoverable copper** **(mg kg^{-1} dry wt)**	**Total recoverable zinc** **(mg kg^{-1} dry wt)**
SB34	62.5-250	439742/33	6.6	65.7
1	25-62.5	439742/34	14.9	75.8
5	25-62.5	439742/35	19.8	88.3
15	25-62.5	439742/36	14.2	73.9
32	25-62.5	439742/37	9.9	58.6
32	25-62.5	439742/37 dup1	9.23	-
34	25-62.5	439742/38	13.3	68.0
37	25-62.5	439742/39	15.5	82.9
41	25-62.5	439742/40	13.2	73.9
51	25-62.5	439742/41	16.9	82.5
52	25-62.5	439742/42	24	125
61	25-62.5	439742/43	12.7	70.4
63	25-62.5	439742/44	19.4	94.0
74	25-62.5	439742/45	3.9	80.1
74	25-62.5	439742/45 dup1&2	dup1=3.94 dup2=3.97	-
77	25-62.5	439742/46	9	45.9
82	25-62.5	439742/47	2.9	62.3
82	25-62.5	439742/47 dup1&2	dup1=2.88 dup2=2.77	-
83	25-62.5	439742/48	14.4	77.0
85	25-62.5	439742/49	14.2	79.1
89	25-62.5	439742/50	15.7	82.8
103	25-62.5	439742/51	20.5	114
108	25-62.5	439742/52	19.0	122
111	25-62.5	439742/53	9.4	56.1
114	25-62.5	439742/54	13.7	73.2
117	25-62.5	439742/55	29.4	159
120	25-62.5	439742/56	13.8	78.9
123	25-62.5	439742/57	6.6	46.0
138	25-62.5	439742/58	15.8	82.3
144	25-62.5	439742/59	13.9	72.8
SB2	25-62.5	439742/60	17.9	106
SB7	25-62.5	439742/61	10.5	65.7
SB11	25-62.5	439742/62	13.1	72.7
SB13	25-62.5	439742/63	8.9	61.2
SB20	25-62.5	439742/64	13.3	70.1
SB22	25-62.5	439742/65	6.2	49.8
SB34	25-62.5	439742/66	13.1	64.9
1	<25	439742/67	24.5	123
5	<25	439742/68	29.8	141

Station #	Size fraction (µm)	Hill lab sample code	Total recoverable copper (mg kg^{-1} dry wt)	Total recoverable zinc (mg kg^{-1} dry wt)
15	<25	439742/69	22.9	117
32	<25	439742/70	12.9	70.8
34	<25	439742/71	28.3	127
37	<25	439742/72	21.8	123
41	<25	439742/73	26.6	136
51	<25	439742/74	24.1	126
52	<25	439742/75	26.3	134
61	<25	439742/76	24.8	138
63	<25	439742/77	25.5	143
74	<25	439742/78	29.4	131
77	<25	439742/79	27.8	140
82	<25	439742/80	25.0	128
83	<25	439742/81	25.2	139
85	<25	439742/82	28.8	137
89	<25	439742/83	27.1	151
103	<25	439742/84	29.6	173
108	<25	439742/85	32.9	171
111	<25	439742/86	25.6	140
114	<25	439742/87	22.7	129
117	<25	439742/88	31.1	177
120	<25	439742/89	23.7	131
123	<25	439742/90	21.8	121
138	<25	439742/91	26.7	140
144	<25	439742/92	26.4	141
SB2	<25	439742/93	23.7	134
SB7	<25	439742/94	21.1	116
SB11	<25	439742/95	24.2	115
SB13	<25	439742/96	22.0	124
SB20	<25	439742/97	22.0	107
SB22	<25	439742/98	23.4	121
SB34	<25	439742/99	25.3	129

10 Appendix 3: Downcore Metal Concentrations

Table 5
Total recoverable copper and zinc concentrations in three sediment cores from the CWH, analysed for three particle size fractions.

Core	**Hills code**	**Fraction (µm)**	**Depth layer (cm)**	**Mean depth (cm)**	**Total recoverable copper (mg kg^{-1} dry wt)**	**Total recoverable zinc (mg kg^{-1} dry wt)**
HN-I1	442166/1	Sand (63-250)	0-1	0.5	4.8	63.8
HN-I1	442166/4	Sand (63-250)	2-3	2.5	4.0	61.6
HN-I1	442166/7	Sand (63-250)	4-5	4.5	4.2	61.9
HN-I1	442166/10	Sand (63-250)	6-7	6.5	4.1	62.6
HN-I1	442166/13	Sand (63-250)	8-9	8.5	5.5	60.3
HN-I1	442166/16	Sand (63-250)	10-11	10.5	3.9	57.3
HN-I1	442166/19	Sand (63-250)	12-13	12.5	4.5	56.9
HN-I1	442166/2/2	Sand (63-250)	14-15	14.5	4.1	54.6
HN-I1	442166/25	Sand (63-250)	16-17	16.5	4.3	59.3
HN-I1	442166/28	Sand (63-250)	27-28	27.5	2.8	25.0
HN-I1	442166/31	Sand (63-250)	43-44	43.5	3.6	25.1
HN-I1	442166/2	Silt (25-63.5)	0-1	0.5	9.8	55.5
HN-I1	442166/5	Silt (25-63.5)	2-3	2.5	9.4	51.9
HN-I1	442166/8	Silt (25-63.5)	4-5	4.5	10.7	60.2
HN-I1	442166/11	Silt (25-63.5)	6-7	6.5	10.8	56.2
HN-I1	442166/14	Silt (25-63.5)	8-9	8.5	13.3	67.8
HN-I1	442166/17	Silt (25-63.5)	10-11	10.5	11.5	62.0
HN-I1	442166/20	Silt 5-63.5)	12-13	12.5	13.1	66.6
HN-I1	442166/23	Silt (25-63.5)	14-15	14.5	11.0	56.5
HN-I1	442166/26	Silt (25-63.5)	16-17	16.5	13.1	65.0
HN-I1	442166/29	Silt (25-63.5)	27-28	27.5	7.5	45.6
HN-I1	442166/32	Silt (25-63.5)	43-44	43.5	7.9	39.6
HN-I1	442166/3	Clay (<25)	0-1	0.5	25.1	120
HN-I1	442166/6	Clay (<25)	2-3	2.5	29.8	138
HN-I1	442166/9	Clay (<25)	4-5	4.5	27.1	127
HN-I1	442166/12	Clay (<25)	6-7	6.5	27.9	131
HN-I1	442166/15	Clay (<25)	8-9	8.5	28.1	135
HN-I1	442166/18	Clay (<25)	10-11	10.5	24.5	118
HN-I1	442166/21	Clay (<25)	12-13	12.5	23.0	109
HN-I1	442166/24	Clay (<25)	14-15	14.5	19.7	94.3

Core	Hills code	Fraction (µm)	Depth layer (cm)	Mean depth (cm)	Total recoverable copper (mg kg^{-1} dry wt)	Total recoverable zinc (mg kg^{-1} dry wt)
HN-I1	442166/27	Clay (<25)	16-17	16.5	21.7	105
HN-I1	442166/30	Clay (<25)	27-28	27.5	18.5	85.1
HN-I1	442166/33	Clay (<25)	43-44	43.5	16.6	67.3
SB-I1	442166/34	Sand (63-250)	0-1	0.5	8.7	109
SB-I1	442166/37	Sand (63-250)	3-4	3.5	9.3	113
SB-I1	442166/40	Sand (63-250)	6-7	6.5	6.9	104
SB-I1	442166/43	Sand (63-250)	9-10	9.5	7.5	103
SB-I1	442166/46	Sand (63-250)	12-13	12.5	8.3	109
SB-I1	442166/49	Sand (63-250)	15-16	15.5	9.0	112
SB-I1	442166/52	Sand (63-250)	18-19	18.5	7.5	110
SB-I1	442166/55	Sand (63-250)	21-22	21.5	7.2	102
SB-I1	442166/58	Sand (63-250)	24-25	24.5	5.3	59.5
SB-I1	442166/61	Sand (63-250)	27-28	27.5	4.4	36.7
SB-I1	442166/64	Sand (63-250)	43-44	43.5	2.5	12.4
SB-I1	442166/35	Silt (25-63.5)	0-1	0.5	9.7	70.3
SB-I1	442166/38	Silt (25-63.5)	3-4	3.5	9.9	73.4
SB-I1	442166/41	Silt (25-63.5)	6-7	6.5	7.8	66.2
SB-I1	442166/44	Silt (25-63.5)	9-10	9.5	8.6	70.3
SB-I1	442166/47	Silt (25-63.5)	12-13	12.5	9.2	71.3
SB-I1	442166/50	Silt (25-63.5)	15-16	15.5	8.8	71.0
SB-I1	442166/53	Silt (25-63.5)	18-19	18.5	10.3	77.5
SB-I1	442166/56	Silt (25-63.5)	21-22	21.5	9.3	72.8
SB-I1	442166/59	Silt (25-63.5)	24-25	24.5	7.9	61.1
SB-I1	442166/62	Silt (25-63.5)	27-28	27.5	7.4	49.7
SB-I1	442166/65	Silt (25-63.5)	43-44	43.5	3.8	23.6
SB-I1	442166/36	Clay (<25)	0-1	0.5	21.2	126
SB-I1	442166/39	Clay (<25)	3-4	3.5	21.2	124
SB-I1	442166/42	Clay (<25)	6-7	6.5	19.2	110
SB-I1	442166/45	Clay (<25)	9-10	9.5	19.0	110
SB-I1	442166/48	Clay (<25)	12-13	12.5	21.4	119
SB-I1	442166/51	Clay (<25)	15-16	15.5	23.1	125
SB-I1	442166/54	Clay (<25)	18-19	18.5	21.1	115
SB-I1	442166/57	Clay (<25)	21-22	21.5	21.2	116
SB-I1	442166/60	Clay (<25)	24-25	24.5	18.1	98.0
SB-I1	442166/63	Clay (<25)	27-28	27.5	13.1	73.5
SB-I1	442166/66	Clay (<25)	43-44	43.5	8.7	50.2
WT-S3	442166/67	Sand (63-250)	0-1	0.5	5.4	102
WT-S3	442166/70	Sand (63-250)	2-3	2.5	5.9	112
WT-S3	442166/73	Sand (63-250)	4-5	4.5	5.8	107
WT-S3	442166/76	Sand (63-250)	6-7	6.5	5.2	105
WT-S3	442166/79	Sand (63-250)	8-9	8.5	5.1	100

Core	Hills code	Fraction (µm)	Depth layer (cm)	Mean depth (cm)	Total recoverable copper (mg kg^{-1} dry wt)	Total recoverable zinc (mg kg^{-1} dry wt)
WT-S3	442166/82	Sand (63-250)	10-11	10.5	5.0	109
WT-S3	442166/85	Sand (63-250)	12-13	12.5	5.1	104
WT-S3	442166/88	Sand (63-250)	14-15	14.5	6.8	102
WT-S3	442166/91	Sand (63-250)	16-17	16.5	5.8	108
WT-S3	442166/94	Sand (63-250)	18-19	18.5	6.1	105
WT-S3	442166/97	Sand (63-250)	20-21	20.5	5.2	97.1
WT-S3	442166/100	Sand (63-250)	22-23	22.5	5.4	80.6
WT-S3	442166/103	Sand (63-250)	30-31	30.5	7.2	32.3
WT-S3	442166/106	Sand (63-250)	43-44	43.5	5.9	37.5
WT-S3	442166/68	Silt (25-63.5)	0-1	0.5	12.4	64.3
WT-S3	442166/71	Silt (25-63.5)	2-3	2.5	10.6	60.5
WT-S3	442166/74	Silt (25-63.5)	4-5	4.5	14.0	73.8
WT-S3	442166/77	Silt (25-63.5)	6-7	6.5	10.9	55.4
WT-S3	442166/80	Silt (25-63.5)	8-9	8.5	11.5	62.8
WT-S3	442166/83	Silt (25-63.5)	10-11	10.5	8.2	45.2
WT-S3	442166/86	Silt (25-63.5)	12-13	12.5	10.9	55.6
WT-S3	442166/89	Silt (25-63.5)	14-15	14.5	10.4	53.8
WT-S3	442166/92	Silt (25-63.5)	16-17	16.5	7.1	38.4
WT-S3	442166/95	Silt (25-63.5)	18-19	18.5	8.2	42.2
WT-S3	442166/98	Silt (25-63.5)	20-21	20.5	8.2	41.4
WT-S3	442166/101	Silt (25-63.5)	22-23	22.5	4.3	27.3
WT-S3	442166/104	Silt (25-63.5)	30-31	30.5	5.6	27.8
WT-S3	442166/107	Silt (25-63.5)	43-44	43.5	5.9	30.0
WT-S3	442166/69	Clay (<25)	0-1	0.5	22.9	129
WT-S3	442166/72	Clay (<25)	2-3	2.5	23.6	126
WT-S3	442166/75	Clay (<25)	4-5	4.5	24.8	130
WT-S3	442166/78	Clay (<25)	6-7	6.5	24.0	126
WT-S3	442166/81	Clay (<25)	8-9	8.5	27.3	139
WT-S3	442166/84	Clay (<25)	10-11	10.5	24.0	116
WT-S3	442166/87	Clay (<25)	12-13	12.5	20.1	94.3
WT-S3	442166/90	Clay (<25)	14-15	14.5	17.3	81.8
WT-S3	442166/93	Clay (<25)	16-17	16.5	16.7	73.9
WT-S3	442166/96	Clay (<25)	18-19	18.5	16.1	71.9
WT-S3	442166/99	Clay (<25)	20-21	20.5	14.9	66.4
WT-S3	442166/102	Clay (<25)	22-23	22.5	14.6	60.0
WT-S3	442166/105	Clay (<25)	30-31	30.5	13.4	49.8
WT-S3	442166/108	Clay (<25)	43-44	43.5	13.8	52.2