

Antifouling biocides in marinas: Measurement of copper concentrations and comparison to model predictions for eight Auckland sites

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Reviewed by	Approved for Auckland Council publication by
Marbine	Manes
Name: Megan Carbines	Name: Grant Barnes
Position: Senior Scientist	Position: Manager - Research, Investigations and
Organisation: Auckland Council	Monitoring
Date:12/10/2012	Organisation: Auckland Council
	Date: 15/10/2012

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Antifouling biocides in marinas: Measurement of copper concentrations and comparison to model predictions for eight Auckland sites

Jennifer Gadd Marcus Cameron

Prepared for Auckland Council

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National Institute of Water and Atmospheric Research Ltd., 41 Market Place, Auckland Central, Auckland 1010 Private Bag 99940, Newmarket, Auckland 1149, New Zealand

Executive Summary

The use of copper-based antifouling paints on vessel hulls in New Zealand has increased significantly since organotin based products were banned for use on recreational vessels in 1988. Copper is now found in almost all antifouling paints in New Zealand and these products therefore represent a potentially significant source of copper to the marine environment. A recent project for the New Zealand EPA (Environmental Protection Authority) modelling biocides released from antifouling paints applied to vessels suggested that in many New Zealand marinas, including several in Auckland, copper concentrations could be above guidelines for protection of marine aquatic life (Gadd et al. 2011). Given these high predictions, a study was designed to measure the copper concentrations in the water column of Auckland marinas to provide a preliminary validation of these model results and to investigate the likelihood for environmental effects on aquatic biota. A further aim of this study was to measure export of copper from a marina to the wider coastal environment (e.g., the Waitemata Harbour).

A survey was undertaken of eight marinas in Auckland, namely: Gulf Harbour, Westhaven, Westpark, Bayswater, Half Moon Bay, Pine Harbour, Milford and Orakei. At each marina three water samples were collected and analysed for dissolved and total copper, zinc, chromium, arsenic and iron; and a single sample from the middle of each marina was analysed for the co-biocide diuron. Water samples were also collected from the Waitemata Harbour as 'reference' samples. The flux of copper from Westpark Marina was examined by sampling hourly over a complete tidal cycle to provide an estimate of the copper inputs, outputs and net flux.

Dissolved and total copper were measured above the detection limit $(1 \ \mu g/L)$ in samples from all marinas. The highest concentrations were measured at Westpark (2.8-20 $\mu g/L$) and Milford marinas (5.4-9.5 $\mu g/L$), which are both also influenced by urban stormwater and hard-stand marina activities. The lowest concentrations were measured at Bayswater Marina (<1-1.8 $\mu g/L$), which has floating walls rather than the rock revetment walls primarily used at all other marinas. The results from the Waitemata Harbour indicated that dissolved and total copper concentrations are elevated in marina waters compared to ambient concentrations in the harbour. However, total copper was still detectable in the wider harbour at appreciable levels.

In most of the marinas, the concentrations exceeded ANZECC (2000) water quality guidelines for aquatic protection based on either 95% or 90% levels of protection. In four of the eight marinas, the concentrations also exceeded site-specific chronic water quality guidelines for aquatic protection derived from the concentration of Dissolved Organic Carbon (DOC) measured at each site. In two of the eight marinas (Westpark and Milford), the concentrations also exceeded site-specific acute water quality guidelines derived from the concentration of DOC at each site.

When the measured copper concentrations were compared to the predicted environmental concentrations (PECs) from the MAMPEC model, the concentrations were within the same order of magnitude for all marinas. For most marinas, there was overlap between the three measurements and

the range of the modelled results. Measured copper concentrations at Gulf Harbour Marina were well below all modelled concentrations for this marina. In contrast, measured copper concentrations at Westpark and Milford Marinas were about twice as high as modelled concentrations. Overall the predictions of total copper from the MAMPEC model, even based on the initial inputs from literature, are considered to be close enough to the measured concentrations to support the further use of this model in risk assessment, at least for these Auckland marinas.

Based on the comparison of modelled and measured results, leaching of antifouling paints on vessels appears to be the major source of the copper in the water column for the marinas studied. There are also likely to be additional sources of copper, including stormwater and runoff from hard-stand activities such as boat-washing, scraping and repainting. Although these sources were not investigated through sampling in the present study, some limited information is provided in this report about these additional sources.

Copper concentrations in the export analysis were lower than measured in the survey but were above detection for total copper in all samples and for dissolved copper in 9 out of 13 samples. Total zinc was above detection (4 μ g/L) for most samples however dissolved zinc was almost always below detection. Calculations of metal flux indicated that dissolved copper was exported at a rate of 67-180 g/tide, but total copper was exported at only 5-18 g/tide due to import of particulate copper. For dissolved copper this equates to around 5-12% of the total load from leaching and for total copper, around 0.3-1.2% of the total load. On an annual basis, this equates to around 47-127 kg/year of dissolved copper is due to the import of particulate copper, which is likely to be derived from stormwater from Henderson Creek. Stormwater-derived particulates are also thought to be the source of total zinc imported into Westpark Marina at a rate of ~620 kg/year.

Based on the results for Westpark Marina, and using predictions of fate from the MAMPEC model, an estimate of the total export of copper from Auckland marinas due to vessel leaching has been made. This equates to approximately 3100 kg/year, which is roughly double that predicted from stormwater for the entire Waitemata Harbour catchment.

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1.0 Introduction

1.1 Background

Antifouling coatings used to manage biofouling on the underwater hulls of vessels primarily function by continuous release of a biocide at a concentration that will kill or deter settling organisms. Organotin biocides were banned for use on recreational vessels in NZ in 1988 and since then the most commonly used biocide in antifouling coatings has been copper, typically in the form of cuprous oxide or cuprous thiocyanate (EPA 2012a). In fact almost all of the registered biocidal antifouling paints in New Zealand now contain copper (EPA 2012a). Many copper coatings also contain a secondary, or booster, organic co-biocide to broaden the spectrum of antifouling effectiveness to more-copper tolerant organisms, particularly diatoms and algae (Turner 2010). Zinc oxide is also used in some formulations but is included to control paint solubility, or as a paint stabilizer, modifier or pigment, rather than as a biocide (IPPIC 2012).

As copper released through leaching from antifouling paints is predominantly in dissolved form, it is readily bioavailable to aquatic biota. A recent project for EPA NZ modelling biocides from antifouling paints suggested that copper concentrations in many New Zealand marinas, including several in Auckland, could be above guidelines for protection of marine aquatic life (Gadd et al. 2011). In some marinas these water quality guidelines were markedly exceeded by the concentrations predicted using the MAMPEC (Marine Antifoulant Model to Predict Environmental Concentrations) model. Given the high model predictions, a study was designed to measure copper concentrations and compare these to the model predictions.

1.2 Project aims

The primary aims of the research project are as follows:

- To measure copper concentrations for marinas around the Auckland Region and compare these with the predicted environmental concentrations from the MAMPEC model to provide a preliminary validation of the model results for Auckland marinas;
- To investigate the likelihood for environmental effects on aquatic biota from copper in the water column of marinas; and
- To measure export of copper from marinas to the wider coastal environment (e.g., the Waitemata Harbour).

1.3 Scope

The scope of the study included the following components:

- A survey of eight marinas in Auckland including the larger marinas, namely: Gulf Harbour, Westhaven, Westpark, Bayswater, Half Moon Bay and Pine Harbour; and, two of the following smaller marinas: Milford, Orakei, Outboard Boating Club or Bucklands Beach Yacht Club.
- Collection of water samples from three locations (inner, mid and outer) in each marina and analysis for dissolved and total copper, zinc, chromium, arsenic and iron; and a single sample from the middle of each marina analysed for the co-biocide diuron.
- An examination of the export of copper from one marina by sampling hourly over a complete tidal cycle (12 hours), measuring change in water depth and using these to calculate the mass load of copper exiting the marina each hour, and the total export per tide.

Analysis of chromium, arsenic, iron and diuron were added to the scope to provide further information on potential sources of any copper found in the marinas. The presence of iron is also known to affect the bioavailability of some metals, including arsenic (Lamie, 2012).

The scope of this study did not include examining the contribution of discharges from hard-stand areas or urban stormwater, although it is noted that these may be significant additional sources in some locations. Where possible, existing data and information on these additional sources of copper are used to provide further context for the results of this study.

1.4 Report outline

This report has five sections following this brief introduction:

- Section 2 (Background) reviews existing knowledge of antifouling biocides in marinas internationally and in New Zealand, including data collected by marina operators as part of consent conditions.
- Section 3 (Methods) describes the sites, sampling and analytical methods used in this study, including quality control procedures. The MAMPEC model is briefly described and the model inputs reported for the two marinas that had not previously been modelled. This section also includes a discussion of water quality guidelines used in this report.
- Section 4 (Results) describes the results of the marina survey, the export analysis and the predictions from the MAMPEC model.
- Section 5 (Discussion) discusses these results in greater detail including discussion of vessel leaching as a source of copper, potential for adverse environmental effects in the marinas, and the implications of copper release on the wider coastal environment.
- Section 6 (Conclusions and recommendations) provides the conclusions of the report, recommendations based on its findings and recommendations for further work.

2.0 Background

2.1 Existing data for copper and diuron in marina water and sediment

Concern was raised about the increasing use of copper in antifouling paints and its potential effect on the Auckland aquatic environment in the early 1990s and resulted in a study by NIWA for Auckland Regional Council (Williamson et al. 1995). The focus of that investigation was the fate and potential effects of copper-based paint debris from boat maintenance, including wash-off from hard-stand areas and tidal grids.

The study found that paint flakes from boat washing and scraping contained 2-30% copper by weight (Williamson et al. 1995). These flakes are not readily removed from washwater due to their small size and low density (similar to clay to medium silt). They therefore have potential to disperse in receiving environments and continue to leach copper for up to a few weeks (Williamson et al. 1995). Extremely elevated concentrations of copper were measured in benthic sediments, particularly inter-tidal mudflats, around stormwater outfalls from marina hard stand yards. Leachable copper concentrations (using a solution specially developed to extract copper oxide, see Williamson et al. 1995 for further details) were often ~300-400 mg/kg immediately adjacent to outfalls, but rapidly decreased with distance from the outfall. Immediately outside of marinas the sediment concentrations were typically below guidelines thought to protect aquatic organisms (Williamson et al. 1995). This study did not include any measurements of copper in the water column.

Several of the marinas in Auckland are required by resource consent to monitor the concentrations of copper in their sediment. This is also a typical requirement prior to disposal of any dredged sediment. Indicative concentrations from recent monitoring are shown in Table 2-1 below and a table of results for other metals, along with other details such as dates of sampling, is given in Appendix A. These copper concentrations from the wider marina are much lower than those adjacent to stormwater outfalls from hardstand areas (Williamson et al. 1995) but are elevated when compared to concentrations for reference sites and those in the Upper Waitemata Harbour (UWH), away from urban sources of copper (see Mills and Williamson 2012). None of the marinas are required to monitor copper in the water column.

Although there have been no measurements of copper in the water column of Auckland marinas, as mentioned previously there have been modelled predictions of copper concentrations due to vessel leaching for marinas around New Zealand, including six in the Auckland Region (Gadd et al. 2011). The predicted median dissolved copper concentrations in all of these marinas ranged from ~1.4 μ g/L for Bayswater marina to ~7.5 μ g/L in Half Moon Bay marina (see Figure 2-1). Importantly, the median concentrations for all marinas were predicted to exceed the Australian and New Zealand Environment and Conservation Council (ANZECC) 95% trigger value of 1.3 μ g/L and at five of these marinas, the predicted dissolved copper concentrations also exceed the ANZECC 90% trigger value of 3 μ g/L.

	Total Recoverable copper (mg/kg)		Years since		
	Median	Minimum	Maximum	previous	Reference
				dredging	
Half Moon Bay	62	47	112	11	Golder (2010)
Milford	107	71	161	1-2	Kingett Mitchell Ltd (2006)
Orakei	25	17	32	5-6	Poynter (2011)
Pine Harbour	78	41	150	Unknown	Bioresearches (2009)
Westhaven	26	8.2	131	Unknown	Bioresearches (1998)
Westpark	25	11.9	90	1	Bioresearches (2010)
UWH	19	14	24	n/a	Mills & Williamson 2012

Table 2-1 Copper in sediment measured by marina operators as part of consent conditions



Figure 2-1 Comparison of predicted median dissolved and particulate copper concentrations with the ANZECC 95 and 90% trigger value.

Diuron concentrations were also modelled for the same marinas. This suggested that concentrations in all marinas except Bayswater would be at or above the water quality guideline for diuron of 1800 ng/L (ANZECC 2000; ERMA 2003; see Section 3.6.3). However the modelling was to estimate worst-case concentrations and therefore used an estimate of diuron-containing antifouling paints on

90% of vessels. This is not a realistic estimate for New Zealand vessels. Although the actual percentage is unknown, an estimate of use on 5-10% of vessels was suggested by Gadd et al. (2011) by comparison to measured data, well below the worst-case percentage of 90%. The EPA (2012b) in its preliminary risk assessment of antifouling paints used an estimate of 20%, based on an assumption of the market share. National surveys of co-biocides in marinas, ports and estuarine waters (Stewart 2003, 2006) found that diuron was widespread and present at concentrations of <10 – 830 ng/L, which although elevated, is substantially less than the modelled predictions.

No local studies have been undertaken to date which could verify the modelled copper concentrations in the water column of NZ marinas. However, studies internationally indicate that copper concentrations in marinas are elevated due to leaching from antifouling paints. For example, in UK marinas and ports, dissolved copper was measured at 0.30 to 6.7 μ g/L (Jones and Bolam 2007). Somewhat higher concentrations were measured in San Diego marinas, with a mean of 8.5 μ g/L (range 1.1 to 21 μ g/L; Schiff et al. 2007) and in San Francisco Bay marinas (range 0.1 to 18 μ g/L; Singhasemanon et al. 2009). Thirty saltwater marinas were sampled in the latter study, and median dissolved copper concentrations in these marinas ranged from 0.5 μ g/L to 14 μ g/L, with an overall median of 3.3 μ g/L. In many of these marinas, the dissolved copper concentrations exceeded the water quality guidelines or criteria relevant to that area.

2.2 Predictions of copper loadings

The total environmental loading of copper to the marine environment from leaching was also estimated for the marinas in Figure 2-1, and for the Ports of Auckland and Onehunga (Gadd et al. 2011). This suggested that the total copper emissions from leaching from vessels within these marinas and ports are approximately 9,800 kg/yr, of which approximately 7,600 kg/yr (78%) is from the marinas (Gadd et al. 2011). This estimate for marinas is about half the value of 16,000 kg/yr calculated by Williamson et al. (1995) for the Auckland Region, assuming 8000 vessels. The estimate of 8000 vessels included those in all marinas in Auckland, as well as vessels moored in yacht clubs and mooring areas; and is just under double the number of vessels included in the EPA modelling estimates (Gadd et al. 2011). If the estimate by Gadd et al. (2011) is scaled for the total number of vessels in the Auckland Region, this suggests total copper emissions for the region are ~14,000 kg/yr similar to that estimated by Williamson et al. (1995). Beca Infrastructure (2012) estimated that there were 11,000 yachts and launches in Auckland in 2011. The total copper emissions based on this would be around 20,000 to 22,000 kg/yr.

Differences in the estimated loads based on the information from Gadd et al. (2011) and Williamson et al. (1995) are due to differences in the values used for vessel surface areas and the rate of copper release from antifouling paints. Williamson et al. (1995) used an average vessel surface area of 25 m², whereas the surface area of vessels varied in the calculations by Gadd et al. (2011). Williamson et al. (1995) used a substantially higher estimate of copper release at 22 μ g/cm²/day, compared to

8.2 μ g/cm²/day used by Gadd et al. (2011). There is considerable range in the leaching rate estimates that can be used in risk assessments (see EPA 2012b). EPA (2012b) recently used 18 μ g/cm²/day in their preliminary risk assessment, suggesting that 8.2 μ g/cm²/day may be an underestimate. Although the lower leaching rate used by Gadd et al. (2011) is below a value recommended for antifouling control of 10 μ g/cm²/day, this rate accounts for the many vessels that have biofilm growths, have not recently been repainted or are not adequately maintained. Use of the lower leaching rate from Gadd et al. (2011) is therefore likely to be conservative in the estimation of the total load released from antifouling and may result in predicted environmental concentrations that are lower than reality.

Additional copper and co-biocides are expected to be released to the marine environment during vessel maintenance and repair, such as high-pressure washing, scraping and sanding. Williamson et al. (1995) estimated a loss of 7,300 kg/yr of copper on hard stands in the Auckland Region from maintenance and repair. Of this, the total copper input from high-pressure washing was estimated as 280 kg/yr, indicating that the majority of the input would be from scraping and sanding (Williamson 1995). Estimates by Gadd et al. (2011) based on a marina hard stand area dealing with 600 vessels per year suggest copper release of ~360 kg/yr. A comparison of this estimate from the hard stand area to that expected from leaching within a single marina of similar size indicates that leaching is still the major source at ~730 kg/yr. No estimate was provided for the entire Auckland region, but if scaled to 6700 boats (as used by Williamson et al. 1995) this would suggest 4020 kg/yr, similar to that estimated by Williamson et al. (1995); and somewhat lower than the total estimated load from vessel leaching for the region of 14-16,000 kg/yr.

These estimated copper loads from antifouling paints can also be compared to the estimated loads from stormwater. Stormwater runoff is a major source of copper to the Auckland marine environment, primarily due to the presence of copper at high concentrations in vehicle brake pads, but also due to sources such as copper roofing and spouting and industrial processes (Kennedy and Sutherland 2008). Copper loading to the Waitemata Harbour was estimated at ~1500 kg/yr from stormwater (Timperley and Reed 2008). This compares with ~6300 kg/yr estimated from vessel leaching in the port and marinas in the Waitemata Harbour.

3.0 Methods

3.1 Marina survey

3.1.1 Sampling sites

Eight marinas in the Auckland Region were selected for the survey as follows:

- Gulf Harbour
- Westpark
- Westhaven
- Bayswater
- Half Moon Bay
- Pine Harbour
- Orakei
- Milford Marina

These marinas were selected to cover a wide range of characteristics, including largest in the region (Westhaven), newest in the region (Orakei), a marina with floating walls (Bayswater), and a marina within a tidal creek (Milford). Locations of the marinas sampled in this study are shown in Figure 3-1.

Three locations were sampled within each marina which aimed to represent the inner marina, middle marina and outer marina (near to the marina mouth). For some marinas, due to their configuration, the distinction between these three locations was somewhat arbitrary. The sample locations, codes, dates and times of sampling are provided in Table 3-1. The sampling locations within each marina are also shown in figures in Appendix B.

'Reference' samples were also collected from three locations within the Waitemata Harbour. These were from the outer harbour close to Bean Rock; for the central harbour close to the Chelsea saline water quality site used by Auckland Council in their state of the environment monitoring programme; and in the upper harbour near the confluence of the main flows from Henderson Creek and Upper Waitemata Harbour. The approximate locations of these sites are also shown in Figure 3-1.

3.1.2 Timing of sampling

Samples were collected from marinas and the harbour around low tide as previous studies (e.g. Stewart 2003) had suggested that highest concentrations would be found then. This approach thus represents a 'worst-case' scenario, in terms of time, for each site. Sampling was undertaken within a period between 2 hours prior to low tide and one hour following low tide, with the exception of Milford Marina. Milford Marina has a sill which holds water in the marina during low tide to retain a suitable depth for mooring. This sill prevents the incoming tide from entering the marina until approximately two

hours after low tide when the sill is lowered. This marina was sampled between 1 and 2 hours after low tide to achieve a worst-case scenario.

Marina	Site	Site code	Berth No.	Date sampled	Time sampled	Low tide time ^a
Westhaven	Inner	WHN-IN	B26	17-Feb-12	07:50	09:54
	Mid	WHN-MID	P42		09:00	
	Outer	WHN-OUT	A17		08:35	
Orakei	Inner	OKA-IN	B14	17-Feb-12	10:25	09:54
	Mid	OKA-MID	C pier end		09:50	
	Outer	OKA-OUT	D27		10:10	
Half Moon Bay	Inner	HMB-IN	D33	27-Feb-12	16:50	18:00
	Mid	HMB-MID	F pier end		16:30	
	Outer	HMB-OUT	H69		16:00	
Pine Harbour	Inner	PHB-IN	B22	27-Feb-12	18:45	18:00
	Mid	PHB-MID	E35		18:20	
	Outer	PHB-OUT	H44		17:55	
Westpark	Inner	WPK-IN	A28	16-Mar-12	08:45	08:35
	Mid	WPK-MID	D42		08:25	
	Outer	WPK-OUT	G58		07:55	
Gulf Harbour	Inner	GHB-IN	K24	28-Mar-12	18:00	18:04
	Mid	GHB-MID	E42		17:30	
	Outer	GHB-OUT	Z33		17:00	
Bayswater	Inner	BSW-IN	B11	5-Apr-12	11:14	11:44
	Mid	BSW-MID	E21		10:55	
	Outer	BSW-OUT	H2		10:28	
Milford	Inner	MFD-IN	B5	5-Apr-12	13:21	11:44
	Mid	MFD-MID	Halfway down Pier C		13:00	
	Outer	MFD-OUT	End of E pier		12:33	
	Upstream	MFD-UPPER	U/s Inga Rd bridge		13:50	
Waitemata	Upper	WHB-Upper	n/a	19-Apr-12	11:50	11:58
Harbour	Central	WHB-Central			11:10	
	Outer	WHB-Outer			10:25	

Table 3-1 Details of sampling dates, times and locations for each marina in the survey and the harbour sites

Notes: ^a From Land Information New Zealand tide predictions for Auckland. All times in NZ daylight savings time



Figure 3-1 Location of marinas sampled in this study and 'ambient' water sampling sites in the Waitemata Harbour

Sampling was undertaken during dry weather and with at least 48 hours antecedent dry period. This was to increase the likelihood that the marina waters primarily reflected copper inputs from passive leaching rather than discharges of urban stormwater or discharges from marina hard-stand areas. It began to rain lightly during sampling at Pine Harbour Marina, however this was not considered to greatly affect results due to the minor stormwater input at the time of sampling. There was also potential for discharges from hard-stand areas due to boat wash-down, however no discharges from this source were observed at the time of sampling in any marina.

All sampling was conducted during the week and as such all marinas were observed to have a high proportion of berths occupied at the time of sampling.

3.1.3 Sampling methods

For all marinas with the exception of Milford Marina, samples were collected from the floating berths. At Milford Marina, the berths do not float and a small unpowered inflatable vessel was used to collect the samples.

Water samples were collected directly from the marina waters into cleaned laboratory bottles, sampling at elbow length depth (approximately 20-30 cm). Previous studies internationally indicated that surface waters have the highest concentrations of antifouling contaminants (Jones and Bolam 2007; Schiff et al. 2007), presumably due to the presence of vessel hulls (and thus leaching) in surface waters. This sampling depth therefore represents a worst-case scenario.

At each location within each marina (inner, middle and outer), and in the Waitemata Harbour (upper, central, outer), multiple water samples of differing volumes (100 to 1000 ml) were collected as follows:

- Spare bottle for metal analysis
- Bottle for total metal analysis at Hill Laboratories
- Bottle for dissolved metal analysis at Hill Laboratories
- Bottle for Dissolved Organic Carbon (DOC) analysis at NIWA laboratories
- Bottle for organonitrogen and organophosphorus pesticides analysis at Hill Laboratories (N.B. only collected at the middle site in marinas and at the central site in the Waitemata Harbour)
- Bottle for Total Suspended Solids (TSS) analysis at NIWA laboratories.

Additional dissolved and total metals samples were also collected at a single location in Wairau Creek, upstream of Milford marina, to estimate the ambient concentration of metals entering this marina.

For metal analysis, double-bagged pre-labelled bottles were prepared in a clean laboratory workroom. All other sampling bottles prepared either by Hill laboratories (for pesticides) or by NIWA (for DOC and TSS) were placed into a large zip-lock bag along with the double-bagged bottles for metals.

In the field, clean hands procedures were used to collect the samples for metal analysis. Briefly, one member of the field team (dirty hands) would don wrist-length gloves and the other member (clean hands) would don these and elbow length gloves on top. 'Dirty hands' would open the outer bag of the

double-bagged bottles. 'Clean hands' would open the inner bag and remove the clean sample bottle. 'Dirty hands' would then closer the outer bag while samples were collected. At no point would 'clean hands' touch any surface other than the inner bag, the sample bottle or the water to be sampled.

Spare bottles prepared by NIWA for future potential metal analysis were filled with laboratory grade deionised water from a Milli-Q system (hereafter referred to as MQ water). This was discarded into a container on the berth and the lid replaced. The sample bottle was then plunged into the marina and the lid opened below the surface. A small volume of sample was allowed to enter the bottle and the lid replaced. On bringing the bottle to the surface, the bottle was shaken and then the water discarded. This was repeated twice and then the bottle was filled to the neck using the same procedure. For metal analysis at Hill Laboratories, sample bottles were not filled with MQ water. Samples were collected directly into the bottle after removing the cap underwater and allowing the bottle to fill. For both bottle types, the bottles were then replaced into the inner bag and this was sealed by 'clean hands', and then 'dirty hands' resealed the outer bag.

Following collection of the metal samples, 'clean hands' would continue to fill the remaining bottles, using the same procedure of opening the bottle underwater at elbow length depth, allowing it to fill and then replacing the lid underwater.

Field measurements were also made of salinity, conductivity, temperature, pH and dissolved oxygen using a WTW Multi 340i instrument with TetraCon 325 probe (salinity, conductivity, temperature) and SenTix 41 probe (pH) and a Hach HQ40 with an LDO probe (dissolved oxygen and temperature). After water samples were collected, the probes were placed directly into the marina water at a depth of approximately 20 cm. Readings were taken from the instruments after allowing a few minutes for the values to stabilize. Observations such as the presence of waves and scums were also recorded at each site.

3.2 Marina export

3.2.1 Sampling sites

Westpark Marina was selected for further investigation into the export of copper and zinc in the water column. This marina was selected for the following reasons:

- Solid wall surrounding the marina (with the exception of a small area to the north west where there is some exchange near high tide only)
- Single entry and exit point
- Detectable copper concentrations in the marina survey
- Simple hydrodynamics at exit point from marina (i.e., no strong back current or eddies).

Water samples were collected from the mouth of the marina from a 4.3 m powered rigid inflatable boat at a location slightly to the left of the main channel to allow incoming and outgoing boat traffic to proceed through the entrance (see Figure 3-2).

A pressure transducer (Greenspan PS200, 0 to 5 m range) was installed on the marina bed adjacent to the start of the E pier. The pressure transducer was housed in a pipe to prevent silt deposition onto the instrument which could affect the readings. The PT was set to log water depth every 5 minutes and was installed from 19th to 22nd April 2012.

Water samp

Figure 3-2 Location of water sampling and pressure transducer installation at Westpark Marina

3.2.2 Timing of sampling

Water samples were collected on 20th April 2012. Samples were collected approximately hourly over a full tidal cycle, from approximately high tide, through low tide and back to high tide. Because of safety concerns in working from a boat in a marina during darkness, samples were collected during daylight hours only. Thirteen samples were collected in total (Table 3-2), starting at 6.50 am and finishing at approximately 6.00 pm.

Approximate sampling time	Sample code
6:50	T1
7:45	T2
8:45	Т3
9:45	T4
10:40	T5
11:30	T6
12:25	T7
13:25	T8
14:20	Т9
15:15	T10
16:10	T11
17:05	T12
18:05	T13

Table 3-2 Codes for samples collected during the marina export analysis

3.2.3 Sampling methods

Samples were collected using a different protocol to the marina survey. Samples were all collected at the same location. First water depth was measured using a hand held portable depth sounder (Depthmate®). Based on the depth reading water was then pumped from the middle of the water column (in an attempt to estimate the 'average' concentration entering or exiting the marina) using a peristaltic pump and a 7 m long tygon tubing hose attached to a PVC pole. The hosing was flushed with seawater prior to samples being collected.

Again, clean hands / dirty hands procedures as described in Section 3.1.3 were used to collect the water samples for metal analysis. Samples for total metals samples were collected by discharging the sample hose directly into bottles. Samples for dissolved metal water samples were collected after attaching a capsule filter to the end of the sample hose and pumping water through for approximately 1 minute before sample capture.

Duplicate samples were collected at each time, and all were stored double-bagged in a chilly bin. One set of samples (one for total and one for dissolved) was shipped to Hill Laboratories in Hamilton for copper and zinc analysis. The remaining set was stored in the refrigerator at NIWA Auckland for future potential analyses.

Prior to sampling, all hosing and connectors used for metals sampling were soaked in the laboratory for at least 24 hours in 10% hydrochloric acid. Filters were rinsed by pumping 10% hydrochloric acid through the hosing and filters for at least 20 minutes. MQ water was then flushed through the hosing and connectors and then pumped through the filters for at least 20 minutes to remove any residual acid. All bottles were labelled and double-bagged in a clean laboratory environment. During sampling,

filters were monitored for flow rate and colour change due to suspended-sediment build-up. Filters were changed after sampling four times.

Once water sampling was complete at each station a YSI 556 hand-held water quality meter was used to measure salinity, conductivity, temperature, dissolved oxygen and ORP. These measurements were made at the same depth as the samples were collected from (i.e., mid-water column).

Event sampling times were noted, as well as any general site observations such as winds, currents, sediment plumes or flotsam.

3.2.4 Calculation of discharge, metal flux and net export

Measurements of water depth downloaded from the pressure transducer were used to calculate the change in water depth at each 5 minute interval. The total area of the marina was calculated from an aerial photograph and was $114,774 \text{ m}^2$. At low tide an area of rock shelf on the north-west side of the marina was exposed resulting in a smaller area of $106,242 \text{ m}^2$. A mean of $110,508 \text{ m}^2$ was used for the calculations.

Although field notes were taken to establish when this rock wall became exposed, use of a differing area in the flux calculations resulted in a net export of water over the tidal cycle. This would influence the net copper flux and it was considered that using a standard area would provide more certainty in the calculations.

The discharge from the marina in (m^3/s) was calculated for each 5 minute period from the mean area and the change in water depth, with an adjustment for the 5 minute period between water depth measurements.

As metal concentrations were measured approximately hourly and discharge calculated on a 5-minute basis, some approximation was required to provide metal concentrations on a 5-minute basis. Two methods were investigated:

Firstly metal concentrations measured at one time point were carried forward to a point halfway to the next measurement point. That is, if a measurement was made at 14:00 and the next at 14:50, the first measurement would apply until 14:25, and at 14:30 the value would change to the second measurement. This approach was called projected concentrations.

Secondly a linear interpolation was used to approximate the metals at every 5 minute interval based on the preceding and following measurements. This approach was called interpolated concentrations.

The metal concentrations were then combined with the discharge for every 5-minute period to calculate a metal flux in g/s.

The net export of metals was calculated by summing across a complete tidal cycle. The length of the tidal cycle was established by the water depth, i.e., the water depth was the same at the start and the end of the tidal cycle. This was cross-checked by summing the discharge values across the tidal cycle which resulted in a net discharge of zero.

3.3 Laboratory analysis methods

Samples for the marina survey were analysed for the following parameters:

- Total Suspended Solids (TSS)
- Dissolved Organic Carbon (DOC)
- Total metals (arsenic, chromium, copper, iron, zinc)
- Dissolved metals (arsenic, chromium, copper, iron, zinc)
- Organonitrogen and organophosphorus pesticides, including diuron.

Samples for the export survey were analysed for the following parameters:

- Total copper and zinc
- Dissolved copper and zinc

Analysis of TSS and DOC was undertaken by the NIWA Water Quality Laboratory in Hamilton. TSS was measured by gravimetric determination at filtration and drying at 104°C (APHA 2540D). DOC (low level) was measured (after filtration at NIWA Auckland through pre-combusted GF/F filters) by high temperature catalytic oxidation then infra-red detection using a total organic carbon (TOC) analyser (APHA 5310B).

Analysis of metals and pesticides was undertaken by Hill Laboratories in Hamilton. Samples collected in the marina survey for dissolved metals were filtered by Hill Laboratories through a 0.45 µm membrane filter and preserved with nitric acid (APHA 3030B 21st ed. 2005). Samples collected in the export survey were field filtered and did not require this step. Samples for total metals were digested with nitric acid (APHA 3030E 21st ed. 2005). All metals were analysed by ICP-MS with dynamic reaction cell, ultratrace mode. Samples for pesticides were extracted using liquid/liquid extraction then GPC (if required) followed by GC-MS analysis in SIM mode.

Detection limits for key parameters analysed are shown in Table 3-3.

Parameter	Detection limit (µg/L unless stated)
TSS (mg/L)	0.5
DOC (mg/L)	0.1-0.2 (batch dependent)
Dissolved Arsenic	4
Total Arsenic	4.2
Dissolved Chromium	1
Total Chromium	1.1
Dissolved Copper	1
Total Copper	1.1

Table 3-3 Detection limits for key parameters analysed

Parameter	Detection limit (µg/L unless stated)
Dissolved Iron	4
Total Iron	4.2
Dissolved Zinc	4
Total Zinc	4.2
Diuron (ng/L)	40

Notes: ^a The organonitrogen and organophosphorus pesticide suite contains 90 compounds. Diuron was the only compound detected.

3.4 Quality Control (QC) and Quality Assurance (QA)

3.4.1 Laboratory QA/QC

Hill Laboratories

Hill Laboratories quality control procedures for the methods used for this project include: procedural blanks for both metals and organics; analysis of an in-house seawater QC sample; duplicate sample analysis; sample spikes for metals; and surrogate compound recoveries, matrix and laboratory control spikes for organics.

Laboratory QC results related to the samples in this study are presented in Section 4.1.1.

NIWA Water Quality Laboratory

The NIWA Water Quality Laboratory's QA/QC procedures for the methods used for this project include duplicate sample analysis and analysis of CRMs (Certified reference materials).

For TSS analysis, 10% of all samples in the batch are analysed in duplicate. The analytical balance used for suspended solids weighing is calibrated externally annually and internally with repeatability testing done monthly (single readings for 3 different weights) and 3 monthly (10 readings for 2 different weights).

The Shimadzu TOC analyser is calibrated using 8 standards covering the range from 0-5 mg/L DOC. Independent check standards of Urea (0.5 and 2 mg/L) and Proline (1 and 4 mg/L) are also included in each run, as well as the CRMs. CRMs are analysed with each batch of samples for DOC. These CRMs were supplied by the Rosenstiel School of Marine and Atmospheric Science at the University of Florida (http://www.rsmas.miami.edu/).

The salinity meter is calibrated against an Atlantic seawater standard each time it is used and the seawater standard is measured periodically throughout the batch being measured.

Laboratory QC results related to the samples in this study are presented in Section 4.1.2.

3.4.2 Sampling QA/QC

Field blanks were collected for the marina survey and for the export analysis. These comprised Milli-Q water from the laboratory dispensed into sampling bottles in the field. For the marina survey, sampling bottles were submerged in a vessel containing the Milli-Q water, following the procedures used for real samples. For the export analysis blank, the Milli-Q water was pumped into the sampling bottles through the tubing used to sample. As with marina water samples, the tubing was initially flushed with the 'sample water', in this case Milli-Q, before a sample was collected. Two field blanks for dissolved metals were collected by pumping Milli-Q water through a filter and, after an initial flushing period, blanks were collected in sample bottles.

A laboratory blank for DOC was also prepared to check for potential contamination of water samples while filtering in the laboratory. This blank was prepared by filtering an aliquot of Milli-Q water through pre-combusted GF/F filters alongside a batch of marina samples. This laboratory blank was analysed with the samples.

Field duplicate samples were collected during the marina survey to provide an indication of the variation due to sampling. These duplicates were collected at the inner site at Westpark marina. The field duplicate water samples were collected in the same manner as for the original water samples and at the same location. The duplicate samples were collected after the in-water measurements of salinity, temperature, pH etc.

Results for sampling QA/QC samples are given in Sections 4.1.3 and 4.1.4.

No duplicate samples were collected during the export analysis, however spare samples were collected at each sampling time to provide a back-up in case further analyses were required. These cannot be considered true duplicates as the bottles used were of a different kind and prepared in a different laboratory.

3.5 MAMPEC predictions

3.5.1 Model inputs

As mentioned previously, Gadd et al. (2011) predicted copper concentrations in marinas around NZ. This was undertaken using the MAMPEC (Marine Antifoulant Model to Predict Environmental Concentrations) model, for predicting concentrations of antifouling compounds within marinas, harbours and shipping lanes based on antifoulants emitted in, or discharged into the water body. For the 'service life' of vessels, MAMPEC first calculates emissions (in kg/d or kg/yr) to the marina based on a leaching rate specified by the user, the number of vessels, and the surface area of those vessels. The model then calculates environmental concentrations (in μ g/L) at steady-state using the physical characteristics (including harbour depth and tidal ranges) of each marina; water quality and sediment

characteristics; and chemical characteristics of the antifouling compound. For further information on the MAMPEC model, refer to van Hattum et al. (2002; 2011).

Predicted environmental concentrations (PECs) were already available for six of the eight marinas surveyed in this current project but not for Orakei or Milford marinas. The required input parameters for the model for Orakei and Milford marinas were therefore gathered for this study and include dimensions, water quality, hydrodynamics and flushing characteristics for the environment and the number of vessels in the various size classes. These data are provided in Table 3-4 and Table 3-5. To calculate the total daily emissions to the marina, MAMPEC also requires an antifouling application rate and leaching rate for the vessels within each marina. For the application rate, the default value of 95% of vessels was used (as used in Gadd et al. 2011). A leaching rate of 8.2 μ g/cm²/day was used based on studies by Valkirs et al. (2003) for both recreational and commercial vessels, regardless of paint type, as previously used for MAMPEC modelling (Gadd et al. 2011).

These data were input into MAMPEC 3.0 and the PECs modelled for each of these two marinas. Input data for all marinas is provided in Appendix C.

	5 – 11 m	11 - 20 m	21 – 30 m	31 – 40 m	Total no. vessels
Orakei Marina	23	129	23	3	178
Milford Marina	170	31	0	0	201

Table 3-4 Input data for vessel numbers in Orakei and Milford marinas

Table 3-5 Input data for Orakei and Milford marinas

	Orakei Marina			Milford Marina
	Value	Source	Value	Source
x2: Nominal length (m)	300	Measured from aerial	270	Measured from aerial
		pictures		pictures
x1: Distance from mouth (m)	450	1.5 x length	405	1.5 x length
y1: Nominal width (m)	205	Measured from aerial	90	Measured from aerial
	205	pictures	80	pictures
y2: Width of estuary mouth (m)	205	1 x length	80	1 x length
Depth (m)	57	Marina AEE roport	35	Based on information from
	5.7		5.5	Milford Cruising Club
Mouth width (x3, m)	18	Measured from aerial	33	Measured from aerial
	40	pictures	55	pictures

		Orakei Marina		Milford Marina
	Value	Source	Value	Source
Flow velocity (m/s ¹)	0.14	Same as Bayswater	0.1	Default value, also used for Gulf Harbour
Tidal period (h)	12.41	Default value used for all marinas	12.41	Default value used for all marinas
Silt / SS conc. (mg/L)	6.6		8.5	NSCC (undated)
Chlorophyll (µg/L)				No data available for Wairau
	2.3	Median data for 2002- 06, Chelsea (ARC 2008), also used for	2.3	Creek, median data for 2002- 06 at Browns Bay (ARC 2008), also used for Gulf Harbour
Salinity (ppt)	33	Bayswater & Westhaven	28	Professional judgement based on tidal streams
Temp. (ºC)	17		17	Same as other Auckland marinas
рН	8.1		8.0	Professional judgement based on tidal streams
POC conc. (mg/L)	0.9	Based on POC = 14% SPM, see Gadd et al. (2011)	1.2	Based on POC = 14% SPM, see Gadd et al. (2011)
DOC conc. (mg/L)	1.4	Default used for all marinas	1.4	Default used for all marinas
Tidal difference (m)	3	Same as Bayswater	2.1	Based on information from Milford Cruising Club
Density difference of tide (kg/m ³)	0.1	Default value used for marine marinas	0.1	Default value used for marine marinas
Nontidal daily water level change (m)	0	Not applicable to Orakei Marina	0	Not applicable to Milford Marina
Discharges into harbour (m ³ /s)	0	Not applicable to Orakei Marina	0.2	From Freshwater Environments NZ database
Density diff. of discharges (kg/m ³)	N/A	Not applicable to Orakei Marina	0.035	Based on difference in freshwater and saline waters
Depth in harbour entrance (m)	5.7	Marina AEE report	2.5	Based on information from Milford Cruising Club
Height of submerged dam (m)	0	Not applicable to Orakei Marina	1	Based on information from Milford Cruising Club
Width of submerged dam (m)	0	Not applicable to Orakei Marina	33	Based on mouth width, measured from aerials

		Orakei Marina		Milford Marina		
	Value	Source	Value	Source		
Exchange volume (m ³ /tide)	1.8 x 10⁵	Calculated	5.7 x 10⁴	Calculated		
Volume exchanged per tide (%)	53	Calculated	75	Calculated		
Depth sediment mixed layer (m)	0.1	Default suggested by van Hattum et al. (2011)	0.1	Default suggested by van Hattum et al. (2011)		
Sediment density (kg/m ³)	1000	Default for mixed sediment suggested by van Hattum et al. (2011)	500	Default for silts suggested by van Hattum et al. (2011)		
Degradation organic carbon in sediment (1/d)	0	Default (van Hattum et al. 2011)	0	Default (van Hattum et al. 2011)		
Nett sedimentation velocity (m/d)	0.5	Default suggested by MAMPEC v2.5, used by Gadd et al. (2011)	0.5	Default suggested by MAMPEC v2.5, used by Gadd et al. (2011)		

3.5.2 Model results comparison

The water column predictions of minimum, mean and maximum copper concentrations from MAMPEC were compared with the minimum, mean and maximum of the three values measured in each marina.

Quantitative validation was not considered to be appropriate for this study as the number of samples collected in each marina was low (three only) and the range in concentrations predicted by the model was relatively wide for within each marina, compared to the range between marinas.

3.5.3 Model revision

The original model inputs (from Gadd et al. 2011) relied on literature values for many of the water quality parameters required. These were typically not site-specific for each marina. As part of the marina survey, measurements of suspended solids, pH, temperature, salinity and dissolved organic carbon were made at each of the three locations in each marina. These data were used to update the model inputs with site-specific data with the aim of improving the modelled PECs.

Further revisions to the MAMPEC inputs were required for this project to enable an assessment of predicted sediment quality with measured sediment quality. In the original modelling (Gadd et al. 2011) default values were used for the four parameters required to predict sediment quality (depth sediment mixed layer, sediment density, degradation organic carbon in sediment, nett sedimentation

velocity). These values were the same for all marinas. However, site-specific data was required to predict the sediment quality data more accurately. Data on the nett sedimentation velocity was gathered from information on the sedimentation and dredging at each marina as recommended by van Hattum et al. (2011); and from fall velocity information reviewed by Auckland Regional Council (Semadeni-Davies 2009).

3.6 Water quality guidelines

3.6.1 Introduction

Water quality guidelines have been used in this report to provide an indication of the likelihood of risk to aquatic biota from the metals, metalloids and co-biocides measured in the marinas.

3.6.2 Metals and metalloids

Chronic guidelines are most appropriate for the average biocide concentrations in the marinas. ANZECC (2000) provides statistically derived chronic 'trigger values' and uses New Zealand species in their derivation, and as such these values are the most applicable to New Zealand marine waters. The trigger values are based on various levels of protection, that is, nominally protecting 99%, 95%, 90% or 80% of species. The trigger values for the parameters measured in the marina survey are shown in Table 3-6. Typically the dissolved fraction is compared to these trigger values as the dissolved phase is the most bioavailable.

For chromium, trigger values are provided for two oxidation states: chromium (III) and chromium (VI). As can be seen by comparing the trigger values, chromium (VI) compounds are more toxic than chromium (III). Chromium (VI) is also the predominant form in oxic seawater (Boughriet et al. 1994; Gardner and Ravenscroft 1996), though it can be reduced to chromium (III) by hydrogen sulphide in the presence of sulphate-reducing bacteria (Smillie et al., 1981). Iron would not be expected to be toxic unless very high concentrations were present.

	ANZECC trigger values for level of protection (µg/L)						
	99%	95%	90%	80%			
Arsenic	ID	ID	ID	ID			
Chromium (III)	7.7	27.4	48.6	90.6			
Chromium (VI)	0.14	4.4	20	85			
Copper	0.3	1.3	3	8			
Iron	ID	ID	ID	ID			
Zinc	7	15	23	43			

Table 3-6 ANZECC (2000) trigger values for various nominal protection levels in marine waters.

ID = insufficient data for guideline derivation

The 95% level of protection is the default for "slightly to moderately disturbed ecosystems", which could be considered to include the modified environments of marinas. However the 90% level of protection is considered to be more appropriate for these environments which are in many cases highly modified and for which some adverse effects are anticipated.

Exceedance of the ANZECC (2000) trigger values does not automatically mean that there is a high risk to aquatic species. Site-specific factors need to be considered, which can include chemical or water quality modifiers. These modifiers can greatly affect chemical bioavailability and toxicity and therefore the guidelines can be adjusted accordingly. Internationally, modifications to marine copper guidelines have been suggested based on complexation of copper to organic ligands, which lowers bioavailability and toxicity. No modifications have yet been developed for the ANZECC (2000) guidelines.

Arnold et al. (2006) proposed equations for calculating site-specific criteria for copper based on the concentration of dissolved organic carbon (DOC) in the water body. These equations were derived from toxicity of copper to *Mytilus galloprovincialis,* the blue or Mediterranean mussel, and incorporated toxicity testing in laboratory water and water collected from estuarine environments. These equations were:

Chronic criterion (μ g/L) = 3.59 * DOC ^{0.60}

Acute criterion (μ g/L) = 5.61 * DOC ^{0.60}

The European Copper Institute (2008) has recently undertaken a voluntary risk assessment for copper which included deriving a Proposed No Effect Concentration (PNEC) for copper in marine waters. This PNEC incorporated the influence of DOC by normalising toxicity data to a standard DOC concentration prior to PNEC calculation. The calculated PNEC for dissolved copper was 5.2 μ g/L, for a water body with DOC of 2 mg/L. This is very similar to Arnold's chronic criterion of 5.4 μ g/L for DOC of 2 mg/L. The European Copper Institute's risk assessment has been adopted by the European Commission, 2009).

Data for DOC in New Zealand coastal waters is limited in its extent and range (see Gadd et al. 2011) but the available data suggests that DOC is generally lower than 2 mg/L and is more likely closer to 1.4 mg/L. A chronic criterion using Arnold's equation and based on this DOC would be 4.4 μ g/L. This is slightly higher than the ANZECC 90% protection trigger value, and three-fold higher than the 95% protection trigger value, which are both also used for chronic effects. An acute criterion using Arnold's equation and based on this DOC would be 6.9 μ g/L. This is slightly lower than the ANZECC 80% protection trigger value.

Measurements of DOC in each of the marinas surveyed in this project will enable the calculation of site-specific guidelines for each marina. Site-specific guidelines could be either based on the equation by Arnold (2006) or by normalizing the toxicity data set used by the European Copper Institute to different DOC concentrations prior to calculating the PNEC. As the chronic criteria suggested by Arnold is very similar to that adopted by the European Commission (see Table 3-7), the Arnold equation is used for this project.

Table 3-7 Comparison of PNECs derived by European Copper Institute with chronic criteria based on Arnold et al. (2006).

	Copper concentration (µg/L)					
	PNEC	Chronic criteria				
DOC (mg/L)	(European Copper Institute 2008)	(Arnold et al. 2006)				
0.2	1.3	1.4				
0.5	2.2	2.4				
2	5.2	5.4				

3.6.3 Diuron

ANZECC (2000) does not provide robust trigger values for diuron due to insufficient toxicity data. It does however report a low reliability trigger value of 1800 ng/L for marine water, by applying an adjustment factor of 1000 to the EC_{50} for acute effects on growth of a marine mollusc (ANZECC 2000). This value was used by ERMA as an Environmental Exposure Limit (EEL) for diuron as part of the approval process (ERMA 2003). For the recent reassessment of diuron as an antifouling co-biocide, the EPA derived a Proposed No Effect Concentration (PNEC) of 5.48 ng/L (see EPA 2012b). Internationally, Netherlands use a Maximum Permissible Concentration of 430 ng/L as reported in Van Wezel and van Vlaardinger (2001) and Lamoree et al. (2002). The European Chemicals Agency (ECHA) uses a PNEC of 32 ng/L (ECHA 2012).

3.6.4 Summary

In this report a range of water quality guidelines are used for comparison to measured concentrations. These include the ANZECC guidelines (both 95% and 90% trigger values) for initial screening. For copper, chronic and acute site-specific guidelines are also derived for each marina on the basis of the equations from Arnold (2006). For diuron, the range of guidelines described above are used.

4.0 Results

4.1 QA/QC data

4.1.1 Hill Laboratories QA/QC results

Laboratory QC data for dissolved metals is tabulated in Table 4-1. All procedural blanks were below the detection limits with one exception for dissolved iron. In this situation, the dissolved iron concentration in the blank would normally be subtracted from each sample before reporting. However, all samples assigned to that blank were below the detection limit so subtraction was unnecessary.

	Dissolved arsenic	Dissolved chromium	Dissolved copper	Dissolved iron	Dissolved zinc
Procedural blanks					
Batch 1 (WHN, OKA)	< 4	< 1	< 1	< 4	< 4
Batch 2 (HMB, PHB)	< 4	< 1	< 1	< 4	< 4
Batch 3 (WPK)	< 4	< 1	< 1	< 4	< 4
Batch 4 (GHB)	< 4	< 1	< 1	< 4	< 4
Batch 5 (BSW, MFD) - 1	< 4	< 1	< 1	< 4	No data
Batch 5 (BSW, MFD) - 2	< 4	< 1	< 1	< 4	< 4
Batch 6 (WHB)	< 4	< 1	< 1	16.9 ^a	< 4
Batch 7 (Export study) - 1	N/A	N/A	< 1	N/A	< 4
Batch 7 (Export study) - 2	N/A	N/A	< 1	N/A	< 4
In-house seawater QC					
In house seawater QC limits	10.9 – 79.4	7.5 – 11.3	12.9 – 19.6	371 – 497	-1.5 – 16.7
Batch 1 (WHN, OKA)	-70 ^b	9.3	15.8	420	5.8
Batch 2 (HMB, PHB)	35.8	9.6	16.3	451	7.8
Batch 3 (WPK)	39.6	10.6	17.4	454	5.8
Batch 4 (GHB)	34.9	9.7	15.7	434	6.7
Batch 5 (BSW, MFD) – 1	41.1	9.9	16.7	460	N/A
Batch 5 (BSW, MFD) – 2	40.4	10.7	18.8	502 ^b	7.0
Batch 6 (WHB)	40.1	10.3	16.3	420	5.9
Batch 7 (Export study) - 1	N/A	N/A	16.3	N/A	5.9
Batch 7 (Export study) - 2	N/A	N/A	15.7	N/A	15.8
Mean	23.1	10.1	16.6	449	7.6
CV	178%	5%	6%	6%	45%
Sample spike recovery (%)		·	I		
MFD-IN spike	101	104	86	101	-
T2 spike	N/A	N/A	84	N/A	85

Table 4-1 Quality control data for dissolved metals (all μ g/L).

Notes: ^a It has been noted that the blank for iron is greater than the detection limit. The samples assigned to that blank were all < detection limit. ^b Outside QC limit. Results accepted due to other QC data.

The in-house seawater QC sample was within the specified limits for each metal each time it was analysed, except for dissolved iron which was higher than the specified limit on one occasion. However, it must be pointed out that the acceptable limits for dissolved arsenic and zinc are extremely broad, varying 7-fold for dissolved arsenic. For dissolved zinc the range is from approximately zero to 16.7 μ g/L. For most of the QC samples analysed, the concentrations were very similar and the coefficient of variation (CV) for dissolved chromium, copper and iron were 5-6%. Outliers for dissolved arsenic and zinc resulted in much higher CVs, of 178% and 45% respectively. Without the outliers, the CVs were 7% and 12% respectively.

Some variation was also demonstrated in the analysis of samples analysed in duplicate by the laboratory (Table 4-2). These duplicate analyses were made from the same sample bottle. For most of these samples, one of the duplicates was below the detection limit and as such a Relative Percent Difference (RPD) between the results could not be reliably calculated. There was only one sample where both duplicates measured above the detection limit and the RPD was 9% for dissolved copper in this sample, which is an acceptable RPD.

All samples had recovery within the acceptable range of 80-120%.

Duplicate samples	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved
	arsenic	chromium	copper	iron	zinc
BSW-MID - 1	< 4	< 1	< 1	< 4	-
BSW-MID - 2	5.1	< 1	1.4	< 4	-
Mean	3.6 ^a	< 1	1 ^a	< 4	-
Relative Percent Difference	NC ^b	NC	NC	NC	-
Export study T1 - 1	N/A	N/A	1.2	N/A	< 4
Export study T1 - 2	N/A	N/A	1.1	N/A	< 4
Mean	-	-	1.2	-	< 4
Relative Percent Difference	-	-	9	-	NC
Export study T11 - 1	N/A	N/A	< 1	N/A	< 4
Export study T11 - 2	N/A	N/A	1	N/A	< 4
Mean	-	-	0.8 ^ª	-	< 4
Relative Percent Difference	-	-	NC	-	NC

Table 4-2 Results of duplicate analyses from the same bottle for dissolved metals (all µg/L).

Notes: ^a Based on substituting half the limit of detection where concentration reported as below detection limit. ^b NC Not calculated as sample below detection limit.

QC data for total metals is tabulated in Table 4.3. Procedural blanks were generally below the detection limits with one exception for copper and three exceptions for iron. In these cases, the total copper and iron concentrations in the blank were subtracted from each sample before reporting.

The in-house seawater QC sample was within the specified limits at all times. However, similar to the dissolved metals, the acceptable limits for total zinc are extremely broad, from approximately zero to 147 μ g/L. Total zinc concentrations in the QC samples analysed ranged from 9.1 to 99 μ g/L, a factor of 10 different (but still within the acceptable range). The CV for total zinc was 109%, above generally accepted values for precise measurements. This QC data suggests that total zinc concentrations in saline water samples are of fairly low reliability even at these moderate concentrations, which are well above the limit of detection. Precision for total arsenic, chromium, copper and iron were much better at 2-12%.

	Total	Total	Total	Total iron	Total zinc
	arsenic	chromium	copper		
Procedural blanks					
Batch 1 (WHN, OKA)	< 4	< 1.1	< 1.1	5.5 ^a	< 4.2
Batch 2 (HMB, PHB)	< 4	< 1.1	< 1.1	< 5	< 4.2
Batch 3 (WPK)	< 4	< 1.1	1 ^a	9 ^a	< 4.2
Batch 4 (GHB)	< 4	< 1.1	< 1.1	5.6 ^a	< 4
Batch 5 (BSW, MFD) - 1	< 4.2	< 1.1	< 1.1	< 5	< 4.2
Batch 5 (BSW, MFD) - 2	< 4.2	< 1.1	< 1.1	< 5	< 4.2
Batch 6 (WHB)	< 4	< 1.1	< 1.1	< 5	< 4
Batch 7 (Export study) - 1	N/A	N/A	< 1.1	N/A	< 4
Batch 7 (Export study) - 2	N/A	N/A	N/A	N/A	< 4
In-house seawater QC					
In house seawater QC limits	18 – 65.5	5.7 – 12.8	9.2 – 22.5	247.5 –	-143 – 147
				601.6	
Batch 1 (WHN, OKA)	28.4	9.9	18.7	470	9.9
Batch 2 (HMB, PHB)	29.2	9.6	16.0	433	99
Batch 3 (WPK)	34.6	10.2	18	448	9.1
Batch 4 (GHB)	31.4	9.6	15.9	454	10.5
Batch 5 (BSW, MFD) - 1	31.8	9.9	16.5	462	9.9
Batch 5 (BSW, MFD) - 2	36.6	9.8	16.9	469	9.1
Batch 6 (WHB)	26.5	9.9	18	463	66
Batch 7 (Export study) - 1	N/A	N/A	18	N/A	66
Batch 7 (Export study) - 2	N/A	N/A	N/A	N/A	9.8
Mean	31.1	9.8	17.1	457	32.1
CV	12%	2%	6%	3%	109%

Table 4-3 Quality control data for total metals (all µg/L unless specified).

	Total	Total	Total	Total iron	Total zinc
	arsenic	chromium	copper		
Sample spike recovery (%)				•	•
WHN-OUT	113	104	97	136 ^b	102
Sample from batch run with	111	107	87	120	101
WPK samples					
GHB-OUT	104	102	91	135 ^b	96
MFD-UPPER	83	106	97	117	101
Т6	N/A	N/A	95	N/A	98

Notes: ^a Blank value $\leq 10\%$ sample concentrations, blank values subtracted from sample results. ^b Spike recovery outside desirable range for iron of 80 - 100%; this is typical of a sample at this level when the dilution factor of 20x is taken into account regarding the iron spike level.

Recovery was generally within the acceptable range of 80-120% except for total iron in two samples where recovery was 135-136%. According to the analytical laboratory this is due to the dilution factor required when analyzing saline water samples.

For many of the samples one or more of the samples analysed in duplicate by the laboratory was below the detection limit and as such the RPD could not be reliability calculated (Table 4-4). Where both duplicates measured above the detection limit, the RPD ranged from 4-24% for total copper, 2-31% for total iron and 16-37% for total zinc. The wider variation in the duplicate analyses for total zinc is consistent with the variation noted for the seawater QC sample, and as stated previously, suggests that results for total zinc concentrations in saline water samples are of fairly low reliability even at these moderate concentrations.

All procedural blanks for diuron were below the detection limits of 40 ng/L (Table 4-5). The surrogate recovery was close to 100% for all samples. However, in spikes, the recovery of diuron was low, at 36-55%. The laboratory suggests that the diuron data is suitable only for screening of possible diuron presence, rather than quantitative comparisons between samples.
Table 4-4 Results of	duplicate analys	es from the sam	e bottle for total	metals (all ug/l	unless specified)
	uupiicate analys			metais (an µy/L	uniess specifieu).

Duplicate samples	Total	Total Total		Total iron	Total zinc
	arsenic	chromium	copper		
WHN-OUT - 1	< 4	< 1.1	6.3	54.4	7.5
WHN-OUT - 2	< 4	< 1.1	6.9	74.1	6.4
Mean	< 4	< 1.1	6.6	64.3	7.0
Relative Percent	NC ^b	NC	9%	31%	16%
Difference					
Sample from batch run	4.4	< 1.1	< 1.1	560	< 4.2
with WPK samples - 1					
Sample from batch run	4.1	< 1.1	< 1.1	524	< 4.2
with WPK samples - 2					
Mean	4.3	< 1.1	< 1.1	542	< 4.2
Relative Percent	7%	NC	NC	7%	NC
Difference					
GHB-OUT - 1	5.29	< 1.1	2.7	105.8	5.6
GHB-OUT - 2	< 5	< 1.1	2.8	103.5	< 4
Mean	3.9 ^a	< 1.1	2.8	104.7	3.8 ^a
Relative Percent	NC	NC	4%	2%	NC
Difference					
MFD-UPPER - 1	< 4.2	< 1.1	2.4	466.1	22
MFD-UPPER - 2	< 4.2	< 1.1	2.9	480.5	32
Mean	< 4.2	< 1.1	2.7	473.3	27
Relative Percent	NC	NC	19%	3%	37%
Difference					
T6 - 1	N/A	N/A	2.9	N/A	4.8
T6 - 2	N/A	N/A	3.7	N/A	6.3
Mean	N/A	N/A	3.3	N/A	5.6
Relative Percent	N/A	N/A	24%	N/A	27%
Difference					
T11 - 1	N/A	N/A	N/A	N/A	< 4
T11 - 2	N/A	N/A	N/A	N/A	5.6
Mean	N/A	N/A	N/A	N/A	4.4 ^a
Relative Percent	N/A	N/A	N/A	N/A	NC ^b
Difference					

Notes: ^a Based on substituting half the limit of detection where concentration reported as below detection limit. ^b NC Not calculated as sample below detection limit. Table 4-5 Quality control data for diuron.

	Diuron	Diuron	Surrogate
	concentration	recovery	(triphenylphosphate)
	(ng/L)	(%)	recovery (%)
Procedural blank conc.		-	-
Batch 1 (WHN, OKA)	< 40	-	-
Batch 2 (HMB, PHB)	< 40	-	-
Batch 3 (WPK)	< 40	-	-
Batch 4 (GHB)	< 40	-	-
Batch 5 (BSW, MFD)	< 40	-	-
Batch 6 (WHB)	< 40	-	-
Surrogate Recovery			
OKA-MID	-	-	106
WHN-MID	-	-	106
HMB-MID	-	-	105
PHB-MID	-	-	105
WPK-MID	-	-	102
GHB-MID	-	-	103
BSW-MID	-	-	103
MFD-MID	-	-	100
WHB-Central	-	-	96
Recovery of spikes			
Batch 1 - 4 Spike recovery (%)	-	46	-
Batch 1 - 4 Duplicate spike recovery (%)	-	50	-
Batch 1 - 4 Lab control spike recovery (%)	-	36 ^a	-
Batch 5 - 6 Spike recovery (%)	-	55	-
Batch 5 - 6 Duplicate spike recovery (%)	-	39 ^a	-
Batch 5 - 6 Lab control spike recovery (%)	-	42	-

Notes: ^a Result outside normal control limit for spike recovery (40-140%). Results only useable for screening for possible presence.

4.1.2 NIWA Laboratory QA/QC results

Results of duplicate analyses for TSS (from the same sample bottle) are presented in Table 4-6 below. These analyses gave RPDs ranging from 0 to 14%, with a mean of 4.4%, which are within an acceptable range for laboratory variation.

	Analysis 1	Analysis 2	Average	Difference	Relative Percent
					Difference
OKA-OUT	2.8	3.0	2.9	0.1	3.4
PHB-OUT	10.6	10.6	10.6	0	0
MFD-OUT	6.4	7.4	6.9	1	14
WHB-CENTRAL	9.2	9.2	9.2	0	0

Table 4-6 Results of duplicate analyses from the same bottle for TSS (all mg/L).

The low carbon CRM (LCW) results for the TOC analyser (Table 4-7) were all outside the acceptable range, however these values were also below the detection limit used by NIWA for this analysis (0.2 mg/L), which serves as a 'zero' point. There was considerable variation in the concentrations measured at this level (CV of 370%). The higher carbon CRM (DCW) was within the acceptable range for most batches but one value was slightly lower in batch 3. The variation in the results for this higher concentration CRM was much lower than for the LCW and was within the acceptable range.

Table 4-7 CRM results for DOC (all mg/L).

	LCW	DCW
Acceptable range	0.012 – 0.024	0.492 – 0.528
Batch 1 (WHN, OKA, HMB, PHB, field blank,	-0.016, -0.004	0.503, 0.496
laboratory filtration blank)		
Batch 2 (GHB, WPK, BSW, MFD)	0.033, 0.042, -0.016	0.525, 0.513
Batch 3 (WHB)	-0.015, 0.009, -0.016	0.503, 0.488, 0.494
Mean	0.006	0.503
CV	370%	2%

4.1.3 Marina survey data quality results

A field blank prepared at one of the marinas showed that concentrations of all parameters except total iron were below the detection limits. The concentration of total iron in this blank was well below that in the marina samples (see later) and therefore highly unlikely to affect the results. A laboratory blank was prepared to assess the filtration of water samples for DOC and returned a concentration of < 0.2 mg/L.

Marina survey field blank
< 0.2
< 4
< 4.2
< 1
< 1.1
< 1
< 1.1
< 4
5.3
< 4
< 4.2

Table 4-8 Results for blanks (all data µg/L unless stated)

A field duplicate was collected at Westpark Marina, at the inner site. As described in Section 3.4.2, the duplicate consists of two separate batches of sampling bottles collected in the same manner at the same site. The results of the field duplicate are compared to the 'primary sample' in Table 4-9. For many parameters there was only a minor difference (< 20%) in the concentration between the two samples. However, for dissolved and total copper and zinc, the relative percent difference was 24-38%. This variation is likely to be partly due to differences in sampling, however, given that other parameters measured from the same sample bottles (such as iron) had lower RPD (Table 4-9), it is likely that much of the variation is due to the analytical variation of the methods, as reported in section 4.1.1.

	WPK-IN (primary sample)	WPK-IN (field duplicate)	Average	Difference	Relative percent difference
TSS (mg/L)	5.5	5.6	5.6	0.1	1.8
DOC (mg/L)	1.5	1.6	1.6	0.1	6.5
Dissolved Arsenic	< 4	< 4	< 4	0	0
Total Arsenic	< 4.2	< 4.2	< 4.2	0	0
Dissolved Chromium	< 1	< 1	< 1	0	0
Total Chromium	< 1.1	< 1.1	< 1.1	0	0
Dissolved Copper	6.7 ^a	9.6 ^a	8.2	2.9	36
Total Copper	5.7 ^a	8.4 ^a	7.1	2.7	38
Dissolved Iron	7	6	7	1	15
Total Iron	62	67	65	5	7.8

Table 4-9 Results for duplicates (µg/L unless stated).

	WPK-IN (primary sample)	WPK-IN (field duplicate)	Average	Difference	Relative percent difference
Dissolved Zinc	5	7	6	2	33
Total Zinc	12.1	9.5	11	2.6	24

Note: ^a The dissolved copper concentration is slightly higher than the total copper concentration for this sample. This is considered to be within the analytical variation of the methods (Hill Laboratories).

4.1.4 Export analysis data quality results

A field blank was also prepared during the export analysis sampling, as the sampling method used differed from that used in the marina survey. The field blank had no detectable concentrations of dissolved or total copper or zinc (Table 4-10). A sample of Milli-Q water used to prepare the blank was also analysed for dissolved copper and zinc and also had no detectable concentrations (Table 4-10).

Table 4-10 Results for field blank (all μ g/L).

	Export survey field	Export survey MQ
	blank	blank
Dissolved Copper	< 0.5	< 0.5
Total Copper	< 0.53	N/A
Dissolved Zinc	< 1.0	< 1.0
Total Zinc	< 1.1	N/A

Additional samples were collected during the export survey for analysis of metals, however these were not 'duplicates' as the bottles used were prepared in a different laboratory. However, three of these samples were also analysed to validate the results of the primary samples. The results for these three samples are shown in Table 4-11.

The data show considerable variation between the samples collected in two different bottles, particularly for total copper and zinc. For the three samples, the results for total metals were lower in the 'spare' samples compared to the initial samples analysed. Of concern is that the results for total copper were lower than the results for dissolved copper in two of the three samples. This provides low confidence in the results for these 'spare' samples. Only data from the original set of samples was used in the export assessment.

	Dissolved Copper	Total Copper	Dissolved Zinc	Total Zinc
T1	1.3	5.9	< 4	5.4
T1 - spare	2.3 ^a	< 1.1 ^a	< 4	< 4.2
Average	1.8	3.2 ^b	< 4	3.8 ^b
Difference	1.0	5.4 ^b	0	3.3 ^b
Relative percent difference (%)	56	166 ^b	0	88 ^b
Т5	1.7	2.9	< 4	6.4
T5 - spare	1.6 ^a	< 1.1 ^a	< 4	< 4.2
Average	1.7	1.7 ^b	< 4	4.3 ^b
Difference	0.1	2.4 ^b	0	4.3 ^b
Relative percent difference (%)	6	136 ^b	0	101 ^b
T11	< 1	2.1	< 4	5.5
T11 - spare	1.3	2.7	< 4	4.8
Average	0.9 ^b	2.4	< 4	5.2
Difference	0.8 ^b	0.6	0	0.8
Relative percent difference (%)	89 ^b	25	0	16

Table 4-11	Results for	analyses	of spare	samples (all data	ua/L	unless	specified)	
		analyooo	or opuro	oumpioo ,	un aata	M9' - '	41110000	opcomoa,	

Note: ^a The dissolved copper concentration is slightly higher than the total copper concentration for these samples. This is considered to be within the analytical variation of the methods (Hill Laboratories). ^b Based on substituting half the limit of detection where concentration reported as below detection limit.

4.1.5 Summary of QA/QC data and implications for the study

The laboratory QA/QC results indicate considerable variability in the concentrations of dissolved zinc in the seawater QC samples, and in the concentrations of total zinc in the seawater QC samples and duplicate measurements. The results for dissolved arsenic are also quite variable. These results suggest the analyses of dissolved and total zinc, and dissolved arsenic concentrations in saline water samples may not be accurately or precisely measured by the analytical laboratory. The implications of this must be considered if any decisions are made based on this data.

The QC results for dissolved and total copper are considerably more precise with less variation in the analysis of the seawater QC sample and between duplicates (RPD up to 24%). These QC results suggest that analyses of dissolved and total copper concentrations in saline water samples are generally reliable.

The recovery of diuron was low in spiked samples (36-50%), suggesting that the concentrations in measured field samples may be an underestimate of the true concentration. As this recovery varied from sample to sample, the sample results cannot easily be adjusted for recovery.

The TSS QA/QC results indicate acceptable precision. DOC QA/QC data suggests that the concentrations may not be accurate at very low concentrations (less than 0.02 mg/L).

The results of field blanks do not indicate any contamination of the water samples during their collection and handling with the exception of total iron, which was found in the blank at a low concentration. Any results for total iron at concentrations less than 10 μ g/L should be viewed with caution as sample contamination may be the cause of the measured concentrations.

The results of field duplicates for dissolved and total copper suggest that while the concentrations measured reflect the general concentration, there is likely to be considerable variation in the actual water from which samples are collected.

Overall the QA/QC data from the laboratory analyses and field blanks and duplicates suggest that the field measurements of copper and chromium are of reasonable reliability. Zinc concentrations measured in the water are likely to be of lower reliability and should be considered as estimates. Iron and arsenic concentrations are of moderate reliability, particularly if at concentrations close to the detection limit. Diuron concentrations may be underestimated.

4.2 Marina survey

4.2.1 Survey results

Copper and zinc results are tabulated in Table 4-12 and presented graphically in Figure 4-1 and Figure 4-2. Dissolved copper was detectable in most samples with values ranging from 1.2 to 20 μ g/L. Highest concentrations were measured in Westpark and Milford marinas, and lowest concentrations in Bayswater marina and in the Waitemata Harbour ambient samples. Total copper was detectable in all samples, with values ranging from 1.4 to 23 μ g/L, and was typically only slightly higher than dissolved copper. Particulate copper concentrations were calculated from the total and dissolved concentrations. On average around 70% of total copper was found in the dissolved phase for these samples (minimum 43%, maximum 100%).

For several marinas, that is Bayswater, Gulf Harbour, Orakei and Pine Harbour, the dissolved zinc concentrations were also below detection in all or most samples. Total zinc was detectable in slightly more samples at concentrations similar to, or up to 2x higher than dissolved zinc. Particulate zinc concentrations were calculated from the total and dissolved concentrations and were generally less than half the dissolved concentrations.

	Dissolved	Particulate	Total	Dissolved	Particulate	Total
Site code	copper	copper	copper	zinc	zinc	zinc
BSW-IN	< 1	0.9 ^a	1.4	< 4	NC ^b	< 4.2
BSW-MID	< 1	2.8	3.2	< 4	NC	< 4.2
BSW-OUT	1.8	0.4	2.2	< 4	6.3	8.3
GHB-IN	1.6	1.2	2.8	< 4	3.0	5.0
GHB-MID	2.0	2.7	4.7	< 4	2.7	4.7
GHB-OUT	1.8	0.9	2.7	5	0.6	5.6
HMB-IN	6.6	1.9	8.5	7	0	6.8
HMB-MID	5.0	0.9	5.9	5	3.4	8.4
HMB-OUT	1.2	0.1	1.3	< 4	NC	< 4.2
MFD-IN	9.5	5.2	14.7	21	8	29
MFD-MID	8.7	7.9	16.6	22	12	34
MFD-OUT	5.4	2.8	8.2	21	8	29
MFD-UPPER	1.5	0.9	2.4	10	12	22
OKA-IN	1.7	0.7	2.4	< 4	NC	< 4.2
OKA-MID	1.8	1.4	3.2	< 4	4.3	6.3
OKA-OUT	1.8	1.1	2.9	< 4	NC	< 4.2
PHB-IN	3.1	1.4	4.5	< 4	2.4	4.4
PHB-MID	4.0	2.1	6.1	< 4	4.5	6.5
PHB-OUT	2.8	2.3	5.1	< 4	4.0	6.0
WHN-IN	5.0	2.2	7.2	7	0	6.1
WHN-MID	3.8	1.0	4.8	5	0.1	5.1
WHN-OUT	5.1	1.2	6.3	6	1.5	7.5
WPK-IN	8.2	0	7.1	6	4.8	10.8
WPK-MID	20	3	23	13	4.6	17.6
WPK-OUT	2.8	0	2.8	11	0	6.5
Marina minimum	< 1	0	1.3	< 4	0	< 4.2
Marina median	3.0	1.3	4.8	< 4	3.4	6.2
Marina maximum	20	7.9	20	22	12	34
WHB-Upper	1.3	0.2	1.5	< 4	NC	< 4.2
WHB-Central	< 1	1.3	1.8	< 4	NC	< 4.2
WHB-Outer	< 1	1.1	1.6	< 4	NC	< 4.2

Table 4-12 Copper and zinc results for marina survey (all μ g/L).

Notes: ^a Italics font indicates particulate concentration calculated from data where dissolved form was below detection. Half the limit of detection substituted for this calculation. Low reliability. ^b NC Particulate concentration cannot be calculated as both total and dissolved forms below limit of detection.



Figure 4-1 Total and dissolved copper concentrations in the marinas.

Top of the box represents the maximum concentration measured, middle of the box represents the median and bottom of the box represents the minimum concentration measured. Values below detection limit are plotted at $\frac{1}{2}$ detection limit.





Top of the box represents the maximum concentration measured, middle of the box represents the median and bottom of the box represents the minimum concentration measured. Values below detection limit are plotted at $\frac{1}{2}$ detection limit.

Results for iron, arsenic and chromium are tabulated in Table 4-13 below. Dissolved iron was detectable in half of the samples with values ranging from 5 to 21 μ g/L, whereas total iron was detectable in all samples at 18 to 460 μ g/L, 5-50x higher than the dissolved phase. Total iron was weakly related to the TSS of the samples, as shown in Figure 4.3. There were no other correlations

between parameters such as total or dissolved copper and zinc. Particulate iron concentrations were calculated from the total and dissolved concentrations and show that the majority of the iron was in particulate form.

	Dissolved	Total	Particulate	Dissolved	Total	Dissolved	Total
Site code	iron	iron	iron	arsenic	arsenic	chromium	chromium
BSW-IN	< 4	138	136 ª	< 4	< 4.2	< 1	< 1.1
BSW-MID	< 4	140	138	< 4	< 4.2	< 1	< 1.1
BSW-OUT	< 4	210	208	< 4	< 4.2	< 1	< 1.1
GHB-IN	8	63	55	< 4	4.2	< 1	< 1.1
GHB-MID	< 4	80	78	< 4	< 4.2	< 1	< 1.1
GHB-OUT	< 4	106	104	< 4	5.3	< 1	< 1.1
HMB-IN	14	18	4	< 4	< 4.2	< 1	< 1.1
HMB-MID	7	29	22	< 4	< 4.2	< 1	< 1.1
HMB-OUT	8	90	82	< 4	< 4.2	< 1	< 1.1
MFD-IN	< 4	260	258	4	< 4.2	< 1	< 1.1
MFD-MID	21	230	209	< 4	< 4.2	< 1	< 1.1
MFD-OUT	6	290	284	< 4	< 4.2	< 1	< 1.1
MFD-UPPER	5	460	455	< 4	< 4.2	< 1	1.1
OKA-IN	< 4	48	46	< 4	< 4.2	< 1	< 1.1
OKA-MID	5	270	265	< 4	< 4.2	< 1	3.2
OKA-OUT	5	85	80	< 4	< 4.2	< 1	< 1.1
PHB-IN	8	197	189	< 4	< 4.2	< 1	< 1.1
PHB-MID	< 4	57	55	< 4	< 4.2	< 1	< 1.1
PHB-OUT	8	220	212	< 4	< 4.2	< 1	< 1.1
WHN-IN	5	30	25	< 4	< 4.2	< 1	< 1.1
WHN-MID	< 4	38	36	< 4	< 4.2	< 1	< 1.1
WHN-OUT	< 4	54	52	< 4	< 4.2	< 1	< 1.1
WPK-IN	7	65	58	< 4	< 4.2	< 1	< 1.1
WPK-MID	7	44	37	< 4	< 4.2	< 1	< 1.1
WPK-OUT	< 4	92	90	< 4	< 4.2	< 1	< 1.1
Marina minimum	2	18	4	< 4	< 4.2	< 1	< 1.1
Marina median	5	90	81	< 4	< 4.2	< 1	< 1.1
Marina maximum	21	460	455	4	5.3	0	3.2

Table 4-13 Iron, arsenic and chromium results for marina survey (all µg/L)

Site code	Dissolved iron	Total iron	Particulate iron	Dissolved arsenic	Total arsenic	Dissolved chromium	Total chromium
WHB-Upper	< 4	270	268	< 4	< 4.2	< 1	< 1.1
WHB-Central	< 4	200	198	< 4	< 4.2	< 1	< 1.1
WHB-Outer	< 4	140	138	5	< 4.2	< 1	< 1.1

Notes: ^a Italics font indicates particulate concentration calculated from data where dissolved form was below detection. Half the limit of detection substituted for this calculation. Low reliability.

For almost all samples, the concentrations of dissolved arsenic, total arsenic, dissolved chromium and total chromium were below the detection limits. Particulate concentrations were not calculated for these parameters due to the large number of samples below the limit of detection.





Results for general water quality parameters are tabulated in Table 4-14 below. The water temperature ranged between 19.3 and 22.6°C for all marinas and was slightly cooler in the Waitemata Harbour (though this was sampled later in the year). Salinity was close to seawater for most marinas, with the exception of Milford Marina. The salinity at Orakei Marina was lower than expected given its location near the mouth of the Waitemata Harbour. The pH was also similar to seawater at most sites but slightly lower in the more estuarine marinas (Milford, Westpark). Dissolved oxygen ranged from 6.9 to 9.9 mg/L, with DO saturation typically 90-100%, with the exceptions of Milford and Westpark marinas. TSS ranged from 1.0 mg/L in Westhaven marina to 12.4 mg/L in the upper Waitemata Harbour. DOC had a narrow range in values, from a minimum of 1.1 mg/L in the outer Waitemata Harbour to a maximum of 2.1 mg/L in Milford marina.

Site code	Temp-	Salinity	рН	DO ^a	DO ^b	TSS °	DOC d
	°C	taa	No unit	ma/L	%	ma/L	ma/L
BSW-IN	19.7	33.1	8.07	8.37	92.1	7.7	1.5
BSW-MID	19.3	32.9	8.08	8.62	93.8	10.3	1.6
BSW-OUT	18.9	32.8	8.06	8.22	89.1	10.5	1.9
GHB-IN	20.0	34.7	8.14	9.31	101.4	2.5	1.2
GHB-MID	19.8	34.7	8.16	9.12	100.2	2.5	1.2
GHB-OUT	19.7	34.7	8.17	9.10	99.1	3.7	1.2
HMB-IN	22.3	33.8	8.11	8.37	95.7	1.9	1.6
HMB-MID	22.0	33.8	8.02	8.30	95.2	2.3	1.5
HMB-OUT	22.0	33.8	8.10	8.89	101.5	6.5	1.4
MFD-IN	20.0	26.5	8.11	7.93	88.3	8.3	1.9
MFD-MID	20.8	28.0	7.91	7.53	84.0	6.2	1.7
MFD-OUT	20.2	26.8	7.92	6.91	77.2	6.4	2.1
MFD-UPPER	21.0	NM	7.86	7.06	79.3	NM	NM
OKA-IN	22.6	30.5	8.03	8.56	98.2	2.0	1.9
OKA-MID	22.3	31.0	7.99	9.92	111.1	3.0	1.3
OKA-OUT	22.5	26.9	7.98	8.22	94.6	2.9	1.3
PHB-IN	21.1	34.7	8.10	8.35	93.2	8.9	1.6
PHB-MID	21.3	34.6	8.11	8.44	94.7	3.7	1.7
PHB-OUT	20.9	34.8	8.08	8.13	90.8	10.6	1.7
WHN-IN	22.4	30.8	8.04	7.56	87.1	1.0	1.5
WHN-MID	22.5	30.7	8.00	8.28	95.6	2.1	1.4
WHN-OUT	22.4	30.8	8.00	8.20	94.5	1.0	1.5
WPK-IN	20.3	33.3	7.82	7.70	84.2	5.6	1.6
WPK-MID	20.3	33.3	7.82	7.70	84.2	4.7	1.3
WPK-OUT	20.3	33.3	7.80	8.11	87.5	8.0	1.2
WHB-Upper	20.1	33.1	7.84	8.45	92.2	12.4	1.5
WHB-Central	18.0	33.0	8.27	9.55	98.8	9.2	1.4
WHB-Outer	18.3	35.3	8.22	9.24	95.8	7.2	1.1

Table 4-14 General water quality parameter results for marina survey

Notes: ^a DO = Dissolved oxygen concentration; ^b DO = Dissolved oxygen saturation; ^c TSS = total suspended solids; ^d DOC = Dissolved organic carbon.

Diuron was detectable in all samples except those from Bayswater Marina and the central Waitemata Harbour (Table 4-15). For most marinas the concentrations were around 100-200 ng/L⁻ The maximum concentration was 280 ng/L in Milford Marina. The measured concentrations are within the range

previously measured in marinas by Stewart (2003, 2006). However, as the laboratory QA/QC data indicates low recovery rates for the spiked samples, these concentrations are likely to be underestimates of the actual environmental concentrations and can be considered only estimates.

	Diuron
Site code	ng/L
BSW-MID	< 40
GHB-MID	150
HMB-MID	200
MFD-MID	280
OKA-MID	40
PHB-MID	120
WHN-MID	170
WPK-MID	170
WHB-Central	< 40

Table 4-15 Summary of diuron results

The copper concentrations at inner, mid and outer sites for all marinas are compared in Figure 4-4. This suggests that dissolved copper concentrations were similar at inner and mid sites, but typically somewhat lower at outer sites. A similar pattern is shown for total copper, which was also lower at the outer sites. There were no statistical differences between the sites based on a t-test (p-value >0.05).



Figure 4-4 Differences between dissolved and total copper concentrations between marina sites. Bold bar indicates median of data with range shown by upper and lower whiskers. Horizontal lines indicate detection limits for dissolved and total copper.

4.2.2 Comparison to guidelines

An assessment of copper concentrations in relation to toxicity based on the ANZECC (2000) trigger values for 95% level of protection of 1.3 μ g/L indicates exceedance of the trigger value at every marina (Figure 4-1) and also in the upper area of the Waitemata Harbour. Using the trigger values for 90% level of protection of 3 μ g/L, there is exceedance of the trigger value in five out of eight marinas (Table 4-16).

Site-specific chronic and acute guidelines were derived based on the concentration of DOC for each sample (Table 4-16). Comparison of measured copper concentrations to these guidelines indicates that at four of the eight marinas, and in the Waitemata Harbour, there appears to be low risk of adverse effects on aquatic organisms due to copper as measured concentrations were all below the chronic guideline. However, at the remaining four marinas, the site-specific chronic guidelines were exceeded in two out of three samples. This suggests there is a potential risk to aquatic organisms living in Half Moon Bay, Milford, Westhaven and Westpark marinas.

Furthermore, the site-specific acute guidelines were also exceeded for two samples at Milford and Westpark, indicating a greater risk of adverse effects in these marinas.

	Measured dissolved	ANZECC 90% TV	Site-specific chronic guidelines		Site-spec guide	ific acute elines
Site code	copper (µg/L)	exceeded? (3 µg/L)	Value (μg/L)	Exceeded?	Value (μg/L)	Exceeded?
BSW-IN	< 1	No	4.6	No	7.2	No
BSW-MID	< 1	No	4.8	No	7.4	No
BSW-OUT	1.8	No	5.3	No	8.2	No
GHB-IN	1.6	No	4.0	No	6.3	No
GHB-MID	2.0	No	4.0	No	6.3	No
GHB-OUT	1.8	No	4.0	No	6.3	No
HMB-IN	6.6	Yes	4.8	Yes	7.4	No
HMB-MID	5.0	Yes	4.6	Yes	7.2	No
HMB-OUT	1.2	No	4.4	No	6.9	No
MFD-IN	9.5	Yes	5.3	Yes	8.2	Yes
MFD-MID	8.7	Yes	4.9	Yes	7.7	Yes
MFD-OUT	5.4	Yes	5.6	No	8.8	No
OKA-IN	1.7	No	5.3	No	8.2	No
OKA-MID	1.8	No	4.2	No	6.6	No
OKA-OUT	1.8	No	4.2	No	6.6	No

Table 4-16 Comparison of copper concentrations from marina survey with water quality guidelines.

	Measured dissolved	ANZECC 90% TV	Site-specific chronic guidelines		Site-spec guide	tific acute
Site code	copper (µg/L)	exceeded? (3 µg/L)	Value (µg/L)	Exceeded?	Value (µg/L)	Exceeded?
PHB-IN	3.1	Yes	4.8	No	7.4	No
PHB-MID	4.0	Yes	4.9	No	7.7	No
PHB-OUT	2.8	No	4.9	No	7.7	No
WHN-IN	5.0	Yes	4.6	Yes	7.2	No
WHN-MID	3.8	Yes	4.4	No	6.9	No
WHN-OUT	5.1	Yes	4.6	Yes	7.2	No
WPK-IN	8.2	Yes	4.8	Yes	7.4	Yes
WPK-MID	20	Yes	4.2	Yes	6.6	Yes
WPK-OUT	2.8	No	4.0	No	6.3	No
WHB-Upper	1.3	No	4.6	No	7.2	No
WHB-Central	< 1	No	4.4	No	6.9	No
WHB-Outer	< 1	No	3.8	No	5.9	No

Dissolved zinc concentrations in all marinas except Milford Marina were below the ANZECC trigger value for 95% level of protection of 15 μ g/L. At Milford Marina, all three samples collected within the marina exceeded this trigger value. However when compared to the ANZECC trigger value for 90% level of protection of 23 μ g/L, all samples were below the guidelines. This indicates that at all marina sites sampled, there is low risk of adverse effects on aquatic organisms due to zinc.

All concentrations of chromium were below the ANZECC trigger values for 90% level of protection for both chromium (III) and chromium (VI), of 48.6 and 20 μ g/L respectively. There are currently no ANZECC guidelines for marine waters for arsenic or iron.

For diuron, all samples measured below the ANZECC (2000) low reliability trigger value and ERMA EEL of 1800 ng/L and also below the Netherlands MPC of 430 ng/L. However, in all marinas where diuron was detected (all except Bayswater Marina), it was measured above the proposed NZEPA and ECHA PNEC's of 5.48 and 32 ng/L respectively (see Section 3.6.3). However, as the laboratory QA/QC data indicates that these diuron concentrations are estimates only, it is difficult to assess the true risk of adverse effects due to diuron on aquatic organisms in these environments. The implications of these guideline exceedances are discussed further in Section 5.1.

4.3 Export analysis

4.3.1 Results

Dissolved copper, total copper and total zinc were above the detection limits in almost all samples collected from the marina entrance (Table 4-17). Dissolved zinc concentrations were below detection for all but two samples. Particulate copper concentrations were calculated from the total and dissolved concentrations and indicate that generally around half of total copper was found in the dissolved phase for these samples. Particulate zinc concentrations were also calculated from the total and dissolved concentrations, however as dissolved zinc concentrations were below the limit of detection in most samples, these are of low reliability.

The metal concentrations in the export analysis were considerably lower than those measured in the marina survey at Westpark Marina for the inner and mid site, but similar to those measured at the outer site. This is as expected as the site sampled in the export analysis was in the marina entrance, whilst the outer site used for the survey was still within the marina basin. Moreover, for the export study samples were collected from the middle of the water column whereas samples were collected from the marina survey, where concentrations are expected to be somewhat higher.

Time	Approx.	Dissolved	Particulate	Total	Dissolved	Particulate	Total
Step	sampling time	copper	copper	copper	zinc	zinc	zinc
1	6:50	1.3	4.6	5.9	< 4	3.4 ^a	5.4
2	7:45	< 1	2.2 ^a	2.7	< 4	NC	< 4.2
3	8:45	1.1	1.4	2.5	< 4	2.5	4.5
4	9:45	1.6	0.3	1.9	< 4	NC	< 4.2
5	10:40	1.7	1.2	2.9	< 4	4.4	6.4
6	11:30	1.8	1.1	2.9	< 4	2.8	4.8
7	12:25	2.4	0	2.3	14	NC	< 4.2
8	13:25	2.1	1.6	3.7	< 4	3.5	5.5
9	14:20	1.6	3.6	5.2	< 4	7.6	9.6
10	15:15	1.7	0.2	1.9	< 4	5.7	7.7
11	16:10	< 1	1.6	2.1	< 4	3.5	5.5
12	17:05	< 1	0.8	1.3	< 4	3.4	5.4
13	18:05	< 1	1.5	2.0	4	2.7	4.7

Table 4-17 Metal concentrations during export analysis (all μ g/L).

Notes: ^a Italics font indicates particulate concentration calculated from data where dissolved form was below detection. Half the limit of detection substituted for this calculation. Low reliability.

When the copper concentrations are compared to the water depth in the marina basin, there appears to be a weak inverse relationship between dissolved copper and the tidal cycle (Figure 4-5). Dissolved copper concentrations were typically lower around high tide (07:05 and 19:00), and higher around low tide (12:50). Total copper concentrations were more variable, with the highest concentrations measured at high tide and at the start of the incoming tide, at 13:25 and 14:20. Lowest concentrations occurred later in the incoming tide.

For total zinc, the highest concentrations were also measured on the incoming tide, from 13:25 to 16:10, with lower concentrations at high tide (Figure 4-6). In most cases the dissolved zinc concentration was not detectable.



Figure 4-5 Concentrations of dissolved and total copper at the marina entrance over the tidal cycle, and relative water depth. (Note: Half-detection limit ($0.5 \mu g/L$) used for dissolved copper values at method detection limit).



Figure 4-6 Concentrations of dissolved and total zinc at the marina entrance over the tidal cycle, and relative water depth. (Note: Half-detection limit ($2 \mu g/L$) used for zinc values at method detection limit).

4.3.2 Water column measurements

Field measurements were made at each sampling time of temperature, salinity, pH and dissolved oxygen. These (Table 4-18) showed that salinity varied only slightly during the tidal cycle, from a minimum of 31.1 just after low tide, to a maximum of 32.6 at high tide. Water temperature also varied only slightly from 17.5°C in the morning to a maximum of 18.0°C; and pH was consistently around 8.0. Dissolved oxygen concentrations were between 6.8 and 7.6 mg/L, being slightly lower in the morning on the outgoing tide and slightly higher in the afternoon on the incoming tide.

In addition, measurements were made of the salinity profile just after mid tide (at 16.20). This showed slightly lower salinity just below the water surface and no stratification with depth below 1.0 m, indicating the water column was well mixed.

	Approx.					DO	
	sampling	Water				concen-	DO satu-
Time Step	time	depth	Temp.	Salinity	рН	tration	ration
		m	С	ppt	No units	mg/L	%
1	6:50	5.3	17.5	32.6	8.01	7.2	92
2	7:45	5	18.0	32.2	8.00	6.8	87
3	8:45	4.7	17.8	32.2	8.00	6.9	88
4	9:45	4.4	17.8	32.0	8.02	7.1	90
5	10:40	3.9	18.0	32.4	8.04	6.8	87
6	11:30	3.6	17.8	32.1	8.02	7.3	93
7	12:25	3.1	17.8	32.0	8.03	7.3	94
8	13:25	2.8	17.9	31.7	8.07	7.3	93
9	14:20	3.2	17.9	31.1	7.99	7.1	90
10	15:15	3.6	18.0	31.4	8.02	7.2	92
11	16:10	4.1	18.0	32.1	8.02	7.5	95
12	17:05	5	17.9	32.5	8.04	7.6	97
13	18:05	5.2	17.9	32.6	8.05	7.5	97

Table 4-18 Field measurements of water depth, temperature, salinity, pH and dissolved oxygen.

 Table 4-19 Water column salinity profile taken at 16:20

Depth (from surface, m)	Salinity (ppt)
0.5	31.9
1.0	32.0
1.5	32.2
2.0	32.2
2.5	32.2
3.0	32.2
3.5	32.2
4.0	32.2

4.3.3 Metal flux

As described in the methods (section 3.2.4), the metal flux was calculated on a five-minute basis using two approaches to estimate metal concentrations between measurements. These calculations were not undertaken for dissolved or particulate zinc as so few samples (2 out of 13) contained dissolved zinc above the limit of detection (LOD). Based on this, it is likely that most of the total zinc measured

was in particulate form. Metal flux was calculated using concentrations from the original samples analysed as the results for the 'spare' samples appeared unreliable for total metals.

For dissolved copper, four samples were below the detection limit of 1 μ g/L and for total zinc, three samples were below the detection limit of 4.2 μ g/L. For the initial calculations, a value of half the limit of detection (0.5 μ g/L for dissolved copper and 2.1 μ g/L for total zinc) was substituted for these data points. This is a fairly coarse method and could potentially affect the results for the total flux, so a range of values were tested as substitutes. During the laboratory QA analysis for the export batch, sample T11 was analysed twice, with one reading for dissolved copper at <1 μ g/L and one at 1 μ g/L. The calculations were repeated using a value of 1 μ g/L for this sample, whilst 0.5 μ g/L was used for the other calculations. The net flux was also re-calculated using the limit of detection value and also a value one-tenth the limit of detection. This provides a range for the estimated total flux of dissolved copper and total zinc from the marina. All samples contained total copper above the detection limit and so no substitutions were required.

A positive flux in Table 4-20 indicates export from the marina, whilst a negative flux indicates import. Whilst these different methods for the calculation and the different concentrations used to substitute for data below the limit of detection show some variation in the actual values for net flux (Table 4-20), the results are robust as to the direction and relative magnitude of the flux, with around a two- to three-fold variation.

Regardless of the methods used to calculate the flux, there appears to be a net export of dissolved copper, but a net import of particulate copper and a minor net export of total copper. There was also a net import of total zinc, which is likely to be predominantly in the form of particulate zinc. These findings are discussed further in Section 5.5 and in Section 5.6 in relation to their applicability to other marinas. It should be noted however that the laboratory QA/QC data for total zinc shows poor accuracy for these concentrations which in turn affects the accuracy of the calculated flux. The flux for total zinc is therefore considered less reliable than the fluxes for dissolved and total copper.

Method	Dissolved	Particulate	Total copper	Total zinc
	copper	copper ^a		
Projected concentrations using half	130	-130	5.4	-700
LOD (where applicable)				
Interpolated concentrations using	130	-110	18	-680
half LOD (where applicable)				
Interpolated concentrations using	100	-80	NA ^b	NC °
half LOD except for T11 (1 µg/L)				
Interpolated concentrations using	67	NC	NA ^b	-430
LOD				
Interpolated concentrations using	180	NC	NA ^b	-880
1/10 LOD				
Range in estimated loads	67-180	110-130	5-18 export	430-880
	export	import		import

Table 4-20 Metal flux from the marina (all data g/tide, negative value indicates import of metal).

Note: LOD = Limit of detection. ^a Estimates for particulate copper are based on data where dissolved copper was less than detection in some samples so the concentration of particulate copper is an estimate only for these samples. ^b Not applicable, no data below detection limit. ^c Not calculated.

4.4 Copper predictions from MAMPEC

4.4.1 Initial predictions

The concentrations of total and dissolved copper measured during the marina survey are compared to those predicted by Gadd et al. (2011) in Figure 4-7 as well as the new predictions for Orakei and Milford Marinas. The bars for the modelled data represent the minimum, mean and maximum concentrations predicted by the model. The bars for the measured data represent the minimum, mean and maximum concentrations of the three samples collected in each marina.

This comparison (Figure 4-7) shows that the PECs were generally in the same range as the measured concentrations, though Westpark and Milford marinas measured considerably higher concentrations than predicted. For the other marinas, the maximum predicted concentration was often somewhat higher, and the results generally more variable than the measured concentrations.



Figure 4-7 Concentrations of predicted and measured dissolved and total copper concentrations in each marina.

4.4.2 Revised predictions

Data gathered in the marina survey of suspended solids, salinity, pH and DOC were used to revise the model inputs and re-model the PECs for each marina, to see if the revised predictions were closer to the measured concentrations. In addition, in the initial modelling default values were used for the parameters that are important in predicting sediment quality. These were revised to enable an assessment of predicted sediment quality with sediment quality measured in the marinas (typically for dredging or as part of consent conditions). All the revised data used is shown in Table 4-21.

	Gulf Har- bour	West- park	West- haven	Bays- water	Half Moon Bay	Pine Har- bour	Ora- kei	Mil- ford
Revised parameters based	on new v	vater qua	lity data					
Silt / SS conc. (mg/L)	2.9	6.0	1.4	9.5	3.5	7.7	2.6	7.0
Salinity (ppt)	35	33	31	33	34	35	30	27
рН	8.2	7.8	8.0	8.1	8.1	8.1	8.0	8.0
DOC conc. (mg/L)	1.2	1.4	1.4	1.5	1.5	1.7	1.5	1.9
POC conc. (mg/L)	0.4	0.8	0.2	1.3	0.5	1.1	0.4	1.0
Revised parameters used t	o predict	sedimen	nt quality					
Sediment density (kg/m ³)	1500	670	1000	1000	1000	1000	1000	670
Nett sedimentation velocity (m/d)	1	3	1	1	3	2	1	3

Table 4-21 Revised input data for all marinas

The revised predictions for total and dissolved copper in the water column are shown in Figure 4-8. For total copper there is little difference in the PECs from the initial prediction to the revised prediction. For dissolved copper there is a slight difference for Half Moon Bay, Westpark and Westhaven. Overall, the revised inputs did not result in any major improvement in predictions when compared to the measured concentrations.



Figure 4-8 Concentrations of predicted and measured dissolved and total copper concentrations in each marina.

As stated, the PECs for Westpark and Milford Marinas were generally below those measured on site. This may be due to ambient concentrations in marina waters which were not included in the initial or revised modelling. The presence of ambient concentrations of copper in the water outside the marina (or upstream in the case of Milford) could add to the copper levels predicted solely from leaching.

Ambient total copper concentrations were therefore added to the model for Westpark based on the concentration measured in this study in the upper area of Waitemata Harbour (1.5 μ g/L), and for Milford based on the concentration measured in this study upstream of the marina (2.4 μ g/L). The

revised PECs based on these inputs are shown in Figure 4-9, and are compared to the earlier model predictions and the measured data.

For both marinas, the incorporation of ambient concentrations resulted in an increase in the predicted concentrations, with a substantial increase for Milford Marina. However, the PECs generally remained below the measured concentrations for both marinas. Potential reasons for this are discussed further in Section 5.2.





4.4.3 Sediment predictions

Predicted sediment concentrations from MAMPEC are shown for each marina in Figure 4-10 after 2, 5 and 10 years of accumulation. These predictions are based solely on inputs due to vessel leaching, with the addition of ambient concentrations in the cases of Milford and Westpark. The predictions do not include any input from hard-stand areas associated with marinas. Much higher sediment concentrations are predicted for Half Moon Bay, Pine Harbour, Westpark and Milford marinas, when compared to Gulf Harbour, Westhaven, Orakei and Bayswater. This is most likely due to the greater sedimentation velocity used in the model inputs for the first four marinas mentioned. Copper concentrations in the latter four marinas are predicted to remain below the Auckland Council's amber (19 mg/kg) and red (34 mg/kg) environmental response criteria (ERC; Williamson and Kelly 2003) even after about 10 years.

Sediment copper concentrations at Half Moon Bay, Pine Harbour, Westpark and Milford marinas are predicted to exceed the amber ERC after 2-5 years, and exceed the red ERC after 5-10 years. The ANZECC (2000) interim sediment quality guideline (ISQG) - low of 65 mg/kg would also be exceeded after 10 years for these three marinas. No exceedance of the ANZECC (2000) ISQG-high of 270 mg/kg is predicted for any marina, even after 10 years.



Figure 4-10 Predicted copper concentrations in bottom sediment of each marina after 2, 5 and 10 years.

For six marinas measured concentrations of copper in sediment were available from monitoring data. Many of the marinas are regularly dredged, so the sediment in the marina at the time of monitoring generally reflects the accumulation since the last dredging, rather than the accumulation since the marina was developed. In Figure 4-11 the measured copper concentrations are compared to those predicted after the number of years since the previous dredging in each marina.



Figure 4-11 Predicted and measured copper concentrations in bottom sediment of selected marinas compared to ERC values.

For Half Moon Bay Marina, the marina basin was last dredged in 1999 and the monitoring data is from 2010 (Golder 2010), 11 years later. The predicted concentrations based on 10 years accumulation agree moderately well with the measured concentrations. For Pine Harbour Marina, the last date of dredging in the basin is uncertain, but may have been around 1999. The measured data was collected in 2009 (Bioresearches 2009), allowing 10 years of accumulation. The predicted sediment concentrations after 10 years also agree moderately well with the measured concentrations.

At Westpark Marina, the basin is dredged every year, although different parts are dredged each year, so in any one location the sediment is expected to have accumulated over a period of at least 2 years. The predicted copper concentrations after 2 years compares moderately well to the measured concentrations (Bioresearches 2010), with a very similar minimum and mean, though the maximum measured is over 2x higher than the maximum predicted. This measured maximum (90 mg/kg) is however closer to the maximum predicted after 5 years (70 mg/kg).

At Westhaven the marina is not regularly dredged and the sediment may have been accumulating since the last marina expansion in 1991, seven years prior to sediment monitoring by Bioresearches in 1998. However, the measured copper concentrations are much higher than predicted after 10 years.

At Milford the monitoring data is from 2006 (Kingett Mitchell 2006) and the previous dredging occurred in 2004/5, giving 1-2 years of sediment accumulation. The measured copper concentrations are however much higher than the predictions after 2 years and are in fact more similar to those expected after 10 years (see previous Figure 4-10).

Finally at Orakei Marina, there has been no dredging since the marina was developed in 2004/5. The monitoring data is from 2011 (Poynter 2011), giving 5-6 years of sediment accumulation. The measured copper concentrations are however much higher than the predictions after 5 years and even higher than those expected after 10 years (see earlier, Figure 4-10).

For Westhaven and Orakei marinas, no exceedance of the amber or red ERC was predicted by modelling even after 10 years; however the measured median copper concentration at Westhaven exceeded both the amber and red ERC. For Orakei Marina, the amber ERC was exceeded by all measured concentrations, but the ERC red was not exceeded.

4.4.4 Predicted fate and export

The MAMPEC predicted total copper loading to each marina due to leaching of antifouling paint from vessels is tabulated in Table 4-22. This is based on the number of vessels in the marina, the surface areas of those vessels and a standard leaching rate for copper of 8.2 μ g/cm²/day. The exchange volume of each marina is also tabulated. This indicates the amount of water from the marina replaced with every tidal cycle. A greater exchange volume indicates greater flushing. Bayswater Marina has an exchange volume of 87%, showing greater flushing than most of the other, more enclosed, marinas.

The fate and flux of copper at steady-state as provided by MAMPEC is also shown in Table 4-22. Copper is lost from the marina water column either by hydrodynamic exchange (i.e., leaving the marina along with the water each tide) or sedimentation (to benthic sediment within the marina).

The results suggest that for all marinas, hydrodynamic exchange is the major sink – that is, most of the copper leaching from a vessel in a marina is exported from the marina in the water column. The proportion of copper exported through hydrodynamic exchange does not appear to be related to the exchange volume for each marina.

For half of the marinas, sedimentation was a negligible sink, with less than 3% depositing in bottom sediments. However for Westpark, Half Moon Bay, Pine Harbour and Milford Marinas, sedimentation represented 8-14% of the total copper export. These are the four marinas identified in the previous section as having the highest predicted sediment concentrations.

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	Total copper loading (g/day)	Exchange volume (% per tide)	Copper loss due to:	
			Hydrodynamic Exchange (%)	Sedimentation (%)
Gulf Harbour	5200	50	97.1	2.9
Westpark	2800	57	87.6	12.4
Westhaven	6700	55	98.3	1.7
Bayswater	2100	87	98.4	1.6
Half Moon Bay	2000	51	91.6	8.4
Pine Harbour	2100	48	89.1	10.9
Orakei	515	53	98.8	1.2
Milford	1100	75	86.2	13.8

5.0 Discussion

5.1 Potential for adverse effects in marinas

The ANZECC trigger values for copper for a 90% level of protection (3 µg/L) were used for an initial screening of water quality in the marinas measured in this study. Dissolved copper exceeded this trigger value in five out of eight marinas. Dissolved zinc and chromium concentrations were below the 90% trigger values in all marinas. There are no guidelines for marine waters for arsenic or iron. Diuron was below the EEL and a Netherlands guideline in all marinas but above the PNECs used by the EPA (2012b) and ECHA (2012). However the accuracy of the diuron concentrations is low and it is difficult to assess the true risk of adverse effects due to diuron on aquatic organisms in these environments. Overall, the results suggest a potential risk to aquatic life in these marinas due to copper concentrations, but not in relation to the other contaminants measured, with the possible exception of diuron.

The ANZECC (2000) guidelines provide guidance on modification of trigger values to accommodate factors which modify bioavailability. An initial tier of this assessment is to consider dissolved metals, which are the primary cause of toxicity in marine and fresh waters. Copper is also affected by the organic matter present, binding to both particulate and dissolved organic matter, which may reduce toxicity compared to the free metal ions. While we have used the ANZECC guideline trigger values as the initial screening comparison with dissolved copper measurements, these guidelines do not provide guidance on adjustments for organic matter. However, more recent guidelines have been proposed by Arnold et al. (2006) and the European Copper Institute (2008) to derive site-specific guidelines by normalising to different DOC concentrations. We consider that DOC adjusted guidelines provide the most appropriate basis for copper effects assessment in the marine environment.

Site-specific chronic guidelines for dissolved copper were derived based on the concentration of DOC for each marina sample and for the harbour reference sites using equations provided by Arnold et al. (2006). The site-specific chronic guidelines for the marinas ranged from 4.0-5.3 μ g/L, compared with the ANZECC 90th percentile protection trigger values of 3 μ g/L. The site-specific chronic guidelines were exceeded in four out of the eight marinas, by <2-fold for Half Moon Bay, Milford and Westhaven but up to 4.8 fold for Westpark. This suggests there is a risk of adverse effects to sensitive aquatic organisms living in Half Moon Bay, Milford, Westhaven and Westpark marinas due to elevated copper concentrations. Only one of the three harbour reference sites had detectable dissolved copper concentrations and this was about 3-fold lower than the site-specific guideline derived for this site (see Table 4-16), indicating minimal risk of chronic effects in the Waitemata Harbour.

Site-specific acute guidelines derived based on the concentration of DOC ranged from 5.9 to 8.8 µg/L. These acute guidelines were exceeded in two out of the eight marinas, by up to 1.2-fold in Milford and up to 3-fold in Westpark. This suggests there is a high risk to aquatic organisms living in these marinas. Additionally, the harbour area immediately outside these marinas is potentially intermittently

adversely affected by copper exposure. However, it should be noted that the highest dissolved copper concentrations were at the middle or inner marina sites. In both these marinas, the dissolved copper concentration at the outer site was below the acute guideline and thus the exposure of organisms outside the marina would be tidally influenced and intermittent.

The area inside the marinas may be considered of relatively low ecological value and thus an environment where lower levels of protection might apply. This could relate to the site-specific chronic guidelines, while exceedance of the acute guideline indicates potential for adverse effects outside of the marina environment. However, the worst case data from this study indicates that chronic site-specific guidelines would be met with minimal dilution requirements (<5-fold), which are highly likely to be met within a short distance of the marina entrance. However it should be noted that elevated ambient concentrations may also exist outside some marinas (e.g. Westpark) thus requiring greater dilution for chronic site-specific guidelines to be met in these areas.

5.2 Comparison of measured and predicted copper

The MAMPEC model predicts copper at similar concentrations to those measured within each marina, with the exception of Westpark and Milford marinas, where measured concentrations were substantially higher. When ambient concentrations were taken into account at these sites, the model predictions were somewhat closer.

For Gulf Harbour, Pine Harbour, Westhaven and Orakei, the range of predicted concentrations was much broader than the range of measured concentrations. The model predicts the concentration in a large number of cells for each marina, and then reports the minimum and maximum. As only three samples were collected in each marina (compared to predictions in 100 cells in MAMPEC, van Hattum et al. 2011) it is likely that additional sampling in each of these marinas would result in concentrations that were both higher and lower than those measured in this project. In particular, sampling at high tide and at greater depths is likely to result in lower concentrations than measured in this survey.

The mean predicted total copper concentrations were very similar to those measured at Half Moon Bay, Pine Harbour, Orakei and Bayswater, whilst the mean concentration measured at Gulf Harbour was close to the minimum predicted, and the mean measured at Westhaven, Westpark and Milford was close to, or even above the maximum predicted. For dissolved copper, there were only three marinas where the mean predicted concentrations were very similar to those measured: Half Moon Bay, Pine Harbour, and Bayswater. At Gulf Harbour and Orakei the mean concentration measured was close to, or even below the minimum predicted. At Westhaven, Westpark and Milford the mean measured concentration was close to, or above the maximum predicted. This indicates that when using MAMPEC for risk assessments, it may be prudent to consider all summary statistics provided by the model, as the mean predicted concentration alone may not accurately reflect the range of concentrations in the marinas. The MAMPEC predictions were used in risk assessment by Gadd et al. (2011) which suggested that the ANZECC trigger value for 95% level of protection for copper would be exceeded at all of the Auckland marinas. This assessment was verified by the measured results. The predictions (Gadd et al. 2011) also indicated that the trigger value for 90% level of protection for copper would be exceeded at Westhaven, Westpark, Gulf Harbour, Pine Harbour and Half Moon Bay. New modelling undertaken in this project for Milford and Orakei Marinas indicated that this 90% trigger value would also be exceeded at both these marinas. This assessment was verified by the measured results for Half Moon Bay, Milford, Pine Harbour, Westhaven and Westpark, but was not verified for Gulf Harbour or Orakei. However, as only three samples were collected in each marina and at only one point in time, it is possible that additional sampling in Gulf Harbour or Orakei marinas could result in concentrations that exceed the 90% trigger value.

For three of the six marinas where sediment quality data was available (Half Moon Bay, Pine Harbour, Westpark), the sediment concentrations predicted by MAMPEC were similar to those measured. For Westhaven, Milford and Orakei marinas, the measured concentrations were substantially higher than predicted. Predictions regarding exceedance of ERC guidelines were correct for Half Moon Bay, Pine Harbour, Westpark and Milford, but at Westhaven and Orakei marinas, no exceedance of the amber or red ERC was predicted by modelling whilst measured data did indicate that at least the amber ERC was exceeded. The predictions could therefore have led to an assessment of no risk of adverse effects in these marinas, whilst there is some potential.

There are four possible reasons for the predicted and measured copper concentrations in sediment showing poor agreement:

- a longer accumulation period;
- greater sediment accumulation rates than used for the model;
- sampling site results not accurately reflecting concentrations across the marina; and
- additional sources of copper into the marina.

The sediment accumulation periods were calculated based on dredging and monitoring dates which is a fairly rough estimate. For many marinas, dredging is undertaken in selected areas of the marinas only. Monitoring is targeted to the areas of the marina to be dredged, rather than those previously dredged, so the accumulation periods are quite likely to be underestimated for most marinas.

For the marinas that do not regularly dredge (Orakei, Westhaven, Bayswater and Gulf Harbour) there was little information on which to base the sediment accumulation rates. A default value of 1 m/day was therefore used for the sedimentation velocity at these marinas. It is likely that site-specific information on the sediment accumulation rates in these marinas would result in improvements to the model predictions.

In addition, there are known to be additional sources of copper to many of the marinas, including stormwater discharging into the marinas from surrounding urban land use, direct stormwater discharges from marina car-park and roading areas, and runoff from boat hard-stand areas. These hard-stand areas have previously been identified as a significant source of copper in sediments (see

Williamson et al. 1995), though the effect of these discharges can be limited in their spatial extent. These additional potential sources are discussed further in the following section.

Overall the water column predictions of dissolved and total copper from MAMPEC, even based on the initial inputs from literature, are considered to be close enough to the measured concentrations to support the further use of this model in risk assessment, particularly for these Auckland marinas. The sediment predictions were in some cases close to measured but in other cases under-predicted the risk of adverse effects. At this stage the model does not appear to provide consistently useful information on sediment concentrations. Information on sediment density, depth of the mixed layer, degradation rates for organic carbon in sediment and sedimentation velocity for each marina is required for more accurate modelling as this assessment still used default values for some marinas. More accurate information on sediment dredging at each marina, and greater coverage of sampling sites, would also enable a better comparison of model predictions with measured sediment concentrations.

The EPA has recently used the MAMPEC model in their reassessment of antifouling biocides (EPA 2012b). For copper, an application rate of 100% and a higher leaching rate of 18 μ g/cm²/day were used. These inputs would result in approximately double the predicted copper concentrations in the marinas, which in most cases would be substantially higher than the concentrations measured in this study. However, use of these inputs and adjustment of the input parameters relating to sedimentation may provide a better match to the measured sediment concentrations in the marinas.

5.3 Sources of copper and zinc in marina water column

Sampling was conducted at three Waitemata Harbour reference sites (upper, central and outer harbour) to provide an estimate of the ambient concentrations outside marinas. Ambient concentrations of dissolved copper in the Waitemata Harbour were much lower than in most marinas (up to 6x lower), with the exception of Bayswater, where concentrations were relatively similar to ambient. Total copper concentrations were similarly low in Waitemata Harbour samples compared to marina samples (again typically up to 6x lower). Total zinc was not detected in Waitemata Harbour samples but was in most marina samples, typically at around 1.5-2x the limit of detection. Dissolved zinc was also not detected in Waitemata Harbour samples but was detected in about half the marina samples, again typically at 1.5-2x the limit of detection.

In addition, a single sample was collected in Wairau Creek upstream of Milford Marina, to provide an estimate of the possible ambient concentration for this marina. In this sample concentrations of dissolved and total copper were elevated but were about 6-7x lower than downstream within the marina. Dissolved and total zinc concentrations were also elevated but were about 1-2x lower than downstream within the marina.

No sampling was undertaken in the Tamaki Estuary outside Half Moon Bay Marina, or in the areas outside Gulf Harbour or Pine Harbour Marinas. As the latter two marinas are distant from urban land

use, the ambient concentrations of metals outside these marinas can be expected to be similar to or lower than those measured at the outer Waitemata Harbour site. The upper Tamaki Estuary is significantly affected by stormwater discharges (Kelly 2008) and so copper and zinc concentrations outside the Half Moon Bay Marina may be similar to those in the central Waitemata Harbour or somewhat higher.

Overall the comparisons of copper and zinc concentrations in marina and ambient waters suggest that there is significant environmental contamination of dissolved and total copper in the marina waters of up to 7x higher than ambient, and a minor contamination of dissolved and total zinc of up to 1.5-2x higher than ambient.

Leaching from antifouling paints is the most obvious and best studied source of copper into marinas. However there are potential additional sources such as:

- Stormwater inputs from urban sources;
- Discharges from hardstand areas;
- Leaching from Chromated Copper Arsenate (CCA) treated timber used in the marina pilings, piers and pontoons; and
- Indirect inputs via dissolution of copper contaminated sediments (due to previous discharges of stormwater or from hardstand areas).

All sampling was undertaken following dry periods to minimise the potential influence of urban stormwater which also contains copper at elevated concentrations compared to background. Urban stormwater is likely to be a source of copper into many of the marinas during wet weather. The time required for this stormwater to flush from each marina is not known. There is also the potential for copper sourced from urban stormwater to accumulate in the benthic sediment, thus providing an ongoing source of copper (discussed further below). Several of the marinas investigated are known to have considerable urban stormwater discharges into them, including Westhaven Marina and Milford Marina (into the upstream reaches of the Wairau Creek as well as directly into the marina). Many of the others have more minor inputs of stormwater, but do receive stormwater from roading, buildings and car-park areas of the marinas.

There were no observed discharges (such as boat wash-down water) from the hard-stand areas of the marinas while samples were being collected. However, this does not preclude the existence of these discharges just prior to sampling and if these did occur they could substantially influence the concentrations of copper in the marina waters. The potential input of copper from the hard-stand area is discussed further in Section 5.4.

Treated timber used in pilings and piers is a potential additional source of copper in the marinas. Timber treated with CCA contains copper, chromium and arsenic. The most common formulation of CCA, type C, is comprised of 47.5% CrO₃; 18.5% CuO and 34% As₂O₅. The ratio for chromium, arsenic and copper is 1.7:1.5:1, that is more chromium and arsenic than copper. No chromium or arsenic was detected in the marina water samples (excluding a couple of samples with concentrations around the detection limit) although the detection limit for arsenic is approximately four times higher than that for copper and chromium. However, this does not rule out CCA as a source of copper in the marina waters. Leaching tests indicate that the leaching rate from treated timber is much higher for copper than for arsenic, with chromium lowest of all (Breslin and Adler-Ivanbrook, 1998). Therefore CCA treated timber could be an additional source of copper in the marina waters. Leaching rates are initially high and decrease exponentially over time (Breslin and Adler-Ivanbrook, 1998), therefore the contribution of CCA treated timber to the total copper load in a marina would be expected to be highest shortly after marina development and be significantly lower after several years of immersion.

The final major source of dissolved and total copper into the marinas is from the benthic sediment. Copper concentrations in these sediments are typically elevated beyond background concentrations, not only from vessel leaching, but from discharges from the hard-stand areas and from stormwater external to the marina being transported to the marina and settling. Although generally considered a sink for metals, sediments can also act as a source through diffusion and/or resuspension of particulates and subsequent desorption. This resuspension and desorption from sediments was identified as a significant source of copper in the water column of San Francisco Bay (Gee and Bruland 2002). Later modelling showed that storm events are a major source of copper to settling particles and in the dry season these act as a source for desorption resulting in increased dissolved copper in the water column (Bessinger et al. 2006).

Zinc is not a major ingredient in most antifouling paints, but is found in stormwater at higher concentrations than copper (Griffiths and Timperley 2005). As with copper, stormwater, discharges from the hard-stand area and marina sediments may be a source. A further possible source of zinc in marina waters is sacrificial anodes that are attached to boat hulls and other metal surfaces in contact with the water in marinas. In the UK, sacrificial anodes were identified as a major source of increased zinc in marina waters and sediments (Bird et al. 1996; Matthiessen et al. 1999). Bird et al. (1996) reported that zinc concentrations in marina sediments were double that of background sediments and suggested that sacrificial anodes were primary cause.

5.4 Copper and zinc from hard-stand areas

Discharges of stormwater from hard-stand boat maintenance areas associated with marinas were not assessed within this project. There is however some information available on the concentrations of copper in stormwater from a hard-stand area adjacent to Half Moon Bay marina, where boat maintenance (including paint removal and application) is carried out (Vigar et al. 2012). The quality of stormwater (and the volumes associated with each storm event) is currently being monitored under a project by Auckland Council's Stormwater Technical Services team investigating stormwater treatment systems.

In this study, stormwater quality (TSS, dissolved and total copper and zinc) has been measured for 12 storms over a period of 14 months, with samples being collected after passing through a catchpit insert (Enviropod with 400 µm mesh). At this site, the stormwater is then passed through a filter device
before being discharged into the marine environment. Prior to filtration, the concentration of dissolved copper in the stormwater ranged from 300 to 1200 μ g/L, whilst total copper ranged from 1300 to 19,000 μ g/L. These concentrations are approximately 1000x higher than those measured in Half Moon Bay marina water. The concentration of dissolved zinc in the untreated stormwater ranged from 1400 to 6000 μ g/L, whilst total zinc ranged from 2800 to 16,000 μ g/L. Again, these concentrations are at least 1000x higher than those measured in the marina water.

The total load of copper and zinc from the hard-stand area (after the Enviropod) has been estimated based on the 12 storms monitored. This suggests annual loads of dissolved and total copper of 0.67 kg and 7.2 kg, and annual loads of dissolved and total zinc of 2.8 and 7.1 kg. These loads, particularly for copper, are far in excess of those that would be predicted for typical industrial land use of the same area (5000 m²), based on Auckland Council's Contaminant Load Model (CLM). This model (based on roof area of 1124 m², road (<1000 vpd) length of 100 m and other industrial paved area of 2176 m²) suggests that the total copper load would be ~0.23 kg and the total zinc load would be 1.3 kg. This comparison indicates that the activities undertaken on the hard-stand area are likely to contribute significantly to the total load measured and that antifouling paint application and removal is a highly likely source of the additional load.

The copper loads can also be compared to predictions by Gadd et al. (2011) based on the maintenance and repair of recreational boats. This suggested that for a marina hard stand area with 600 boats per year, the total copper release would be around 360 kg/year. However, fewer boats undergo maintenance and repair in the monitored area at Half Moon Bay marina.

Approximately 800-900 boats per year are hauled out on to the hard-stand at Half Moon Bay marina and approximately half of these will be temporarily located within the area draining to the stormwater treatment system being monitored. Of these boats, approximately half are undergoing maintenance on their antifouling system, such as paint removal and re-painting. This equates to approximately 225 boats per year. If the total copper release predicted by Gadd et al. (2011) is scaled to 225 boats per year, this suggests a total copper release of around 135 kg/year, still much higher than that measured in the stormwater. However, as mentioned, this stormwater does receive pre-treatment through a mesh screen, which has been observed to capture large particles of antifouling paints. It is feasible that in the absence of this mesh screen, copper loads could easily be an order of magnitude higher (~72 kg/year), and would therefore be much closer to those previously predicted.

At Half Moon Bay, the stormwater from this hard-stand area is not discharged into the marina itself, but is discharged to the Tamaki Estuary at a location adjacent to the marina. However, if this hardstand stormwater was discharged into the marina itself, it would add to the total copper load, but would not be the major source of copper in the marina. The loads from leaching are estimated at 730 kg/year (2000 g/day, Table 4-22), substantially higher than that measured from the hard-stand area of 7.2 kg/year (Vigar et al. 2012), or even that predicted for boat maintenance and repair (135 kg/year). Furthermore, the majority of the copper in the hard-stand stormwater is in particulate form. This suggests it will be less bioavailable than the copper released from leaching of antifouling paints on berthed vessels.

5.5 Copper export from Westpark Marina

The flux calculations for Westpark Marina suggest that there is export of dissolved copper, a minor net export of total copper, but a net import of particulate copper and total zinc (probably in the form of particulate zinc). This appears to be due to total copper and zinc being more elevated in the water on the incoming tide.

Although the export of dissolved copper (and a minor export of total copper) appears to be inconsistent with the import of particulate copper and zinc, there is an explanation for why this may be occurring. Westpark Marina is in the upper area of the Waitemata Harbour. Sedimentation within the marina has been at a much higher rate than expected prior to building the marina. This has been attributed by Beca Steven (1997) to two factors: elevated suspended solids in the water entering the marina, which is predominantly from Henderson Creek; and the low turbulence within the marina which allows settling.

Particulates from Henderson Creek contain metals from stormwater sources, particularly after storm events. These particulates are likely to be the source of the import of particulate copper and zinc into the marina. The benthic sediments of Henderson Creek also contain metals at concentrations well above background (Mills and Williamson 2012). As demonstrated by Gee and Bruland (2002) and Bessinger et al. (2006), elevated metal concentrations in benthic sediments can act as a source of particulate and dissolved metals in the absence of stormwater.

Despite a minor export of total copper, there was a significant export of dissolved copper (up to 180 g/tide), the form most bioavailable to aquatic organisms. This is likely to be dispersed throughout the Waitemata Harbour through tidal currents with some eventually being exported into the Hauraki Gulf. The dissolved copper concentrations exiting the marina were at times above the ANZECC 95% protection guideline of 1.3 μ g/L, but were at all times below a chronic site-specific guideline of 3.8 μ g/L, based on a DOC concentration of 1.1 mg/L, the lowest measured in Waitemata Harbour.

MAMPEC predicts that 2845 g copper per day are released into Westpark Marina from vessel leaching. Though the concentrations measured in the marina were slightly higher than predicted based on this load, this is considered a reasonable estimate of the load from leaching, as additional copper sources are likely to be the cause of the discrepancy between measured and predicted. This load from leaching equates to ~1470 g/tide of total copper.

The flux calculated from the export sampling suggests that only 5-18 g of total copper is exported per tide (0.3-1.2% of the total load). However, as discussed above, this is likely due to the influx of particulate copper from surrounding catchments. Around 67-180 g of dissolved copper is exported from the marina per tide, which is 5-12% of the total load from leaching. These calculated values are in contrast to the fate predicted by MAMPEC of ~88% exported through hydrodynamic exchange.

The flux calculated from the export sampling suggests that around 88-95% (1290-1403 g) dissolved copper per tide remains within the marina, presumably either within the benthic sediment or taken up

by biofouling organisms on the floating pontoons and piles. This compares with that predicted by MAMPEC of ~12% remaining in the benthic sediment.

Given that the predicted median copper concentration in the sediment was not far off the median measured value, it is somewhat surprising that the estimates of fate seem to be so different. The predictions for the water column were approximately half of that measured in the marina, suggesting that in reality there may be less hydrodynamic exchange than the model predicts. This may in part be due to water leaving the marina not being well-mixed outside the marina, with some returning into the marina before being fully diluted.

Additionally, the potential for uptake by other biofouling organisms is unknown. The measured concentrations are also potentially influenced by additional input sources, such as stormwater and hard-stand runoff. Stormwater from the housing area surrounding the marina is not discharged into the marina, however it does receive stormwater from areas directly associated with the marina, such as the car-park. Information from monitoring of the hard-stand area at Half Moon Bay Marina is not likely to be applicable to Westpark Marina as the stormwater treatment systems and management practices on the hard-stand area are likely to be different. Furthermore, the number of vessels undergoing antifouling paint maintenance and repair at Westpark Marina is not known. Moreover, the majority of the discharge from the hard-stand area at Westpark Marina is not directly into the marina, but into the inter-tidal mudflats to the north (Williamson et al. 1995).

Overall, although a complete budget for copper at Westpark Marina cannot be calculated, it appears likely that around 5-12% of the copper released within the marina from leaching of antifouling paint on berthed vessels is exported into the Waitemata Harbour, equating to around 47-127 kg/year.

5.6 Copper export from Auckland marinas

The results of the copper budget for Westpark Marina are unlikely to be widely applicable to other marinas around Auckland, as the copper dynamics for this marina are affected by the incoming water which can be elevated in particulate copper. However, the finding of dissolved copper export may be applicable more widely.

MAMPEC predicts that most of the copper emitted into a marina from vessel leaching leaves the marina through hydrodynamic exchange, with generally less than 10% remaining in the benthic sediment. Comparisons of the predicted concentrations in sediment with those measured in marina sediments suggest the model estimates may be valid for some of the marinas, but not for others. In general, sediment concentrations were greater than predicted, suggesting that more of the copper than predicted remains within the marina and less is exported through hydrodynamic exchange. Alternative explanations for the higher concentrations are that the marinas receive additional copper, either from vessel leaching, which may be at a higher rate than used in the modelling for this report; from urban stormwater which is deposited into the benthic sediment; or from discharges from the hard stand areas where vessel maintenance is undertaken. These are likely to be contributing factors at all

of the marinas, though the extent of each is not known or easily established with the available information.

It is likely that for most marinas, the proportion of copper exported is somewhere between that predicted by MAMPEC (~90%) and that measured at Westpark (5-12%). Marinas other than Westpark are likely to be less affected by stormwater contaminants in the water coming into the marina from outside, though this may also be an influence at Half Moon Bay Marina, located in the Tamaki Estuary, another location known to have high loads of stormwater associated contaminants. At Half Moon Bay Marina, there may also be lower net export of copper than predicted by MAMPEC, due to influx of stormwater derived copper.

Bayswater and Orakei marinas are located in the outer Waitemata Harbour and are less likely to be influenced by stormwater in the incoming water. Pine Harbour and Gulf Harbour marinas are located away from major urban sources and likewise are less likely to be influenced by stormwater in the incoming water. For these four marinas, the net export of copper is likely to be closer to that predicted by MAMPEC.

The proportion of copper exported from each of the marinas has been roughly estimated based on the characteristics of each marina, the measurements of export at Westpark Marina and the export modelled by MAMPEC. These estimates are shown in Table 5-1. For Westpark Marina, a value of 10% has been used, based on the approximate export of dissolved copper measured during this study. As discussed above, the situation at Westpark Marina is likely to be exceptional and greater export would be expected at other marinas. An estimate of 30% export has been used for Half Moon Bay, Pine Harbour, Westhaven and Milford marinas. This proportion is based on the assumption that these marinas receive some stormwater and are subject to regular dredging (which indicates higher sedimentation rates than may have been used in the modelling). An estimate of 50% export has been used for Gulf Harbour and Orakei marinas, which are in outer areas of the harbour or otherwise away from urban sources, and do not have regular dredging programmes. An estimate of 80% has been used for Bayswater Marina, closer to the 98% suggested by MAMPEC (see section 4.4.4), as this marina has floating walls, very little sedimentation and is in an outer area of the Waitemata Harbour.

The total load of copper exported from each of the marinas has therefore been estimated based on these estimated proportions of export and the total load from vessel leaching as modelled used MAMPEC (Table 5-1). These loads are rough estimates only, and are used purely to provide a general indication of the possible load of copper exported from marinas compared to urban stormwater.

	Total load (kg/yr)	Proportion exported	Total exported (kg/yr)
	(MAMPEC estimate)		
Westpark	1040	10%	100
Pine Harbour	750	30%	230
Westhaven	2440	30%	730
Half Moon Bay	730	30%	220
Milford	190	30%	60
Gulf Harbour	1890	50%	950
Orakei	410	50%	210
Bayswater	780	80%	620
Total	8230	-	3120

Table 5-1 Predicted total load of copper exported from marinas.

Figure 5-1 compares the predicted annual copper load exported from marinas (from Table 5-1) to the annual load predicted for stormwater contaminants, from modelling of the Central Waitemata Harbour (Green 2008). This indicates that even if only a small proportion of the copper released into the marinas through vessel leaching is exported from the marina (i.e., the rest is deposited in sediment) the load exported remains significant, and is approximately equal to that from stormwater from the entire Waitemata Harbour catchment. Much of the copper load from stormwater, certainly from the Henderson and Whau catchments, is expected to be deposited within the tidal creeks, rather than reaching the wider harbour (Green 2008). In contrast, marinas are all located within areas of greater water depth, and often in areas of greater dispersion, so the copper exported from these marinas could potentially be expected to be more widely dispersed, particularly that in dissolved form.

The finding of antifouling paints as a significant source of copper to marine environments is not new. Matthiessen et al. (1999) reported over 10 years ago that boating traffic was the largest source of copper to estuaries in parts of the United Kingdom, and greatly exceeded the contribution from sewage treatment plant discharges and rivers. However, the contribution from stormwater does not appear to have been assessed in these estuaries, which were mainly rural.

Johnson et al. (1998) also identified leaching from antifouling paints on naval and civilian vessels as by far the greatest source of copper into Norfolk and Little Creek estuaries, Virginia; Pearl Harbour; and San Diego Bay. Stormwater inputs were estimated by Event Mean Concentrations and leaching was based on surface area and typical leaching rates. In all harbours, stormwater contributed less than 10% of the total copper input, whereas leaching from naval and civilian vessels contributed 44-74%.



Figure 5-1 Comparison of copper loads estimated to be exported from Auckland marinas with those from stormwater discharges in the Waitemata Harbour catchment.

6.0 Conclusions and recommendations

This study measured copper concentrations in the water column of marinas to compare to model predictions, assess the likelihood for adverse effects and calculate the export of copper to the wider coastal environment.

Dissolved and total copper were measured above the detection limit in samples from all marinas. The highest concentrations were measured at Westpark and Milford Marinas, which are both also influenced by stormwater. The lowest concentrations were measured at Bayswater Marina, which has floating walls rather than the rock revetment walls predominantly used at all other marinas. The results from the Waitemata Harbour indicated that dissolved and total copper concentrations are elevated in marina waters compared to ambient concentrations.

In five of the eight marinas, the concentrations exceeded ANZECC (2000) water quality guidelines for aquatic protection. In four of the eight marinas, the concentrations also exceeded site-specific chronic water quality guidelines for aquatic protection derived from the concentration of DOC at each site. In two of the eight marinas, the concentrations also exceeded site-specific acute water quality guidelines derived from the concentration of DOC at each site.

The measured concentrations of dissolved and total copper in the marinas were close to predictions from the MAMPEC model, even based on the initial inputs from literature. Revisions to model inputs based on data collected during this study, and with the incorporation of ambient concentrations, resulted in improvements to the predictions when compared to measured concentrations. MAMPEC predictions for sediment concentrations appeared valid for three out of six marinas where sediment quality data was available, but substantially under-predicted the copper concentrations for the remaining three where default values for sedimentation rates were used. This under-prediction is likely to be due to additional sources of copper and / or lack of site-specific inputs for the modelling.

Calculations of metal flux at Westpark Marina indicated that dissolved copper was exported at a rate of 67-180 g/tide, but total copper was exported only at 5-18 g/tide, due to import of particulate copper. Total zinc was imported into the marina. It is thought that the import of metals is predominantly associated with particulates being transported into the marina from stormwater in Henderson Creek on the incoming tide.

This study suggests that vessel leaching within marinas is a key source of copper to the marine environment, particularly for dissolved copper. In the Waitemata Harbour, copper inputs from vessel leaching are potentially equal to that from stormwater from the entire Waitemata Harbour catchment.

The key recommendations from this study in relation to the future use of the MAMPEC model are:

• Dissolved and total copper predictions in the water column from the MAMPEC model, even based on the initial inputs from literature, are considered to be close enough to the measured concentrations to support the further use of this model in risk assessment, particularly for these Auckland marinas.

• Predictions of copper sediment concentrations from MAMPEC may not be accurate without site-specific information on sedimentation rates and other sediment characteristics.

This study has also highlighted a number of areas for future work as follows:

- To work with existing analytical laboratories (or seek new analytical laboratories) to achieve more accurate measurement of metals (particularly zinc) and co-biocides in saline water samples.
- To work with existing analytical laboratories (or seek new analytical laboratories) to achieve lower detection limits for measurement of metals and co-biocides in saline water samples.
- Repeat the export analysis at marinas where the incoming tidal water is not affected by urban land use so that more robust validation and estimates of total copper exported from marinas can be made.
- Investigate potential for marina biofouling organisms as a significant sink for metals.

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Appendix A Metals in Marina Benthic Sediments

Marina	No. of	Date	Years	Reference	Total recoverable concentration(mg/kg)								
	sites sampled	sampled	since dredging		Statistic	Arsenic	Cadmium	Chromium	Copper	Lead	Mercury	Nickel	Zinc
Half Moon				Goldor	Median	8.7	0.058	33	62	33	0.178	14.1	136
	14/05/10	11	(2010)	Min.	8.1	0.048	31	47	27	0.163	12.5	121	
Day				(2010)	Max.	10.2	0.067	36	112	37	0.22	31	172
				Kingett	Median	17	0.52	36	107	124	0.18	26	515
Milford	9	15/02/06	1-2	Mitchell Ltd	Min.	14	0.28	30	71	66	0.13	21	351
				(2006)	Max.	19	0.86	39	161	178	0.25	55	611
		7/07/11	5-6	Poynter	Median				25	18.4			84
Orakei	3				Min.				17	17.8			80
			(2011)	Max.				32	19.3			95	
Pine 6 7/09/0 Harbour			Bioresearc hers (2009)	Median	9.9	0.042	34	78	19.5	0.11	12	109	
	7/09/09 Unknow	Unknown		Min.	8.6	0.036	26	41	16	0.11	9.8	82	
				Max.	11	0.052	35	150	22	0.14	13	130	
				Rioresearc	Median	6.1	<0.2	25	26	39			92
Westhaven	13	15/04/98	Unknown	hers (1998)	Min.	3.8	<0.2	9.3	8.2	12			32
				11013 (1990)	Max.	7.9	<0.2	35	131	69			152
				Bioresearc	Median	9.2	0.059	20	25	19.25	0.11	9.1	79
Westpark	8	12/07/10	07/10 1	hers (2010)	Min.	7.7	0.041	15	12	9.5	0.048	6.7	43
					Max.	11.2	0.064	24	90	31	0.152	12	129

Table A-1 Metals in benthic sediment measured by marina operators as part of consent conditions.

Appendix B Sampling Sites

Location of the three samples collected in each marina.



Pine Harbour

Half Moon Bay



Gulf Harbour

Milford





Bayswater



Westpark



Appendix C MAMPEC model inputs

Leaching rate for copper: 8.2 µg/cm²/day

Application rate: 95% of vessels

Table C-1 Input data for each marina environment	
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Condition	Gulf	West-	West-	Bays-	Half	Pine	Orakei	Milford
	Har-	park	haven	water	Moon	Har-	Marina	Marina
	bour				Bay	bour		
x2: Nominal length (m)	660	420	1050	400	310	340	300	270
x1: Distance from	990	640	1575	600	470	510	450	405
mouth (m)	000	010	1070	000	170	010	100	100
y1: Nominal width (m)	360	290	540	240	250	310	205	80
y2: Width of estuary	360	290	540	240	250	310	205	80
mouth (m)	500	230	540	240	200	510	200	00
Depth (m)	5	4.5	5.5	5	4	4.5	5.7	3.5
Mouth width (x3, m)	78	70	70	240	30	48	48	33
Flow velocity (m/s)	0.1	0.14	0.14	0.14	0.36	0.07	0.14	0.1
Tidal period (h)	12.41	12.41	12.41	12.41	12.41	12.41	12.41	12.41
Silt / SS conc. (mg/L)	3.7	14	6.6	6.6	9.7	9.7	6.6	8.5
POC conc. (mg/L)	0.5	2	0.9	0.9	1.4	1.4	0.9	1.2
DOC conc. (mg/L)	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Chlorophyll (µg/L)	2	2.3	2.3	2.3	2.3	2.3	2.3	2
Salinity (ppt)	34	30	33	33	32	32	33	28
Temp. (ºC)	17	17	17	17	17	17	17	17
рН	8.2	8.1	8.1	8.1	8.1	8.1	8.1	8.0
Tidal difference (m)	2.5	2.5	3	3	2	2.1	3	2.1
Density difference of	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
tide (kg/m ³)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Nontidal daily water	0	0	0	0	0	0	0	0
level change (m)	Ŭ	Ŭ	Ŭ	Ŭ	Ŭ	Ŭ	Ŭ	Ŭ
Discharges into	0	0	0	0	0	0	0	02
harbour (m ³ /s ¹)	Ŭ	U	Ŭ	Ŭ	Ŭ		Ŭ	0.2
Density diff. of	N/A	N/A	N/A	N/A	N/A	N/A	N/A	0.035
discharges (kg/m ³)		11/7			1 1/7 1	1.1// \		0.000
Depth in harbour	5	4.5	55	5	4	45	57	2.5
entrance (m)			0.0				0.7	2.0

Condition	Gulf Har- bour	West- park	West- haven	Bays- water	Half Moon Bay	Pine Har- bour	Orakei Marina	Milford Marina
Height of submerged dam (m)	0	0	0	1	0	0	0	1
Width of submerged dam (m)	0	0	0	240	0	0	0	33
Exchange volume	6.0	3.5	1.7	2.9	1.6	2.3	1.8 x	5.7 x
(m ³ tide⁻¹)	x10⁵	x10⁵	x10 ⁶	x10⁵	x10⁵	x10⁵	10 ⁵	10 ⁴
Volume exchanged per	50	64	55	61	51	19	52	75
tide (%)	50	04	55	01	51	40	55	75
Ambient concentration of copper (µg/L)	0	1.5	0	0	0	0	0	2.4

Table C-2 Input data for vessel numbers in each marina.

	5 – 11 m	11 - 20 m	21 – 30 m	31 – 40 m	Total
					vessels
Surface area	25	76	148	269	
Gulf harbour Marina	256	656	59	6	976
Westpark Marina	124	432	4	0	560
Westhaven Marina	596	862	31	3	1491
Bayswater Marina	31	298	20	4	353
Half Moon Bay Marina	248	247	5	0	500
Pine Harbour Marina	187	283	2	0	485
Orakei Marina	23	129	23	3	178
Milford Marina	170	31	0	0	201