

Report No. 1805 July 2010

Ecological Relevance of Copper (Cu) and Zinc (Zn) in Sediments Beneath Fish Farms in New Zealand





Ecological Relevance of Copper (Cu) and Zinc (Zn) in Sediments Beneath Fish Farms in New Zealand

Deanna Clement Nigel Keeley Ross Sneddon

Prepared for Marlborough District Council

Cawthron Institute 98 Halifax Street East, Private Bag 2 Nelson, New Zealand Ph. +64 3 548 2319 Fax. + 64 3 546 9464 www.cawthron.org.nz

Reviewed by:

Approved for release by:

Paul Gillespie

Rowan Strickland

Recommended citation:

Clement D, Keeley N, Sneddon R 2010. Ecological Relevance of Copper (Cu) and Zinc (Zn) in Sediments Beneath Fish Farms in New Zealand. Prepared for Marlborough District Council. Report No. 1805. 48 p. plus appendices

© Copyright: Apart from any fair dealing for the purpose of study, research, criticism, or review, as permitted under the Copyright Act, this publication must not be reproduced in whole or in part without the written permission of the Copyright Holder, who, unless other authorship is cited in the text or acknowledgements, is the commissioner of the report.



EXECUTIVE SUMMARY

This report reviews the potential risk of metal contaminants, particularly copper and zinc, associated with finfish farms and assesses whether the existing guidelines and analytical methods are adequate. The Marlborough District Council's (MDC) coastal management includes the salmon aquaculture industry, which is currently expanding and diversifying into other finfish species. The main environmental concerns with these metal contaminants for finfish culture include bioaccumulation, persistence and ecotoxicological effects on local ecology and biodiversity.

Based on the literature and a recent comprehensive review by Macleod & Eriksen (2009), copper from anti-foulant paints and zinc from fish feed products are the major environmentally significant metal contaminants within New Zealand finfish sites. Copper and zinc can enter the marine environment in several ways including:

- Uneaten food
- Leached from paint surfaces or chips, and/or
- Eaten by farmed fish and subsequently released in their faecal waste

The toxicity of a metal in the marine environment is largely determined by its chemical form and whether it is bioavailable (*i.e.* in a form that an organism can directly absorb or ingest). The more toxic, and thus bioavailable, state is the free ionic or dissolved form. However, most metals form insoluble sulphide complexes in the sediment. The toxicity and bioavailability of metals is complex and closely related to:

- Environmental conditions (e.g. temperature, salinity, pH)
- Chemical processes such as redox status
- Physical processes such as bioturbation and resuspension

Experimental studies have demonstrated that different marine organisms vary in their relative accumulation and tolerance of metals due to differences in:

- Uptake pathways
- Bioavailability and speciation of metals
- Biotic factors of the organisms
- Abiotic factors of the environment

As a result, marine organisms' responses to increasing concentrations of any one trace metal can vary considerably, even within a species. When metal concentrations in sediments reach extremely high levels, benthic assemblages can be adversely affected to the point that regular functions of benthic communities begin to fail.

The current monitoring practices in the Marlborough Sounds for salmon aquaculture assess bulk metal levels in the sediments from beneath the farm to ANZECC 2000 Interim Sediment Quality Guidelines

(ISQGs). Monitoring results irregularly exceed ANZECC (2000) ISQG-High and -Low trigger values. Several international studies demonstrated similar values in sediment concentrations of zinc that were attributed to corresponding trends in harvest cycles (*i.e.* feeding schedules). Other studies have suggested spatial variability in metals implied the involvement of different dispersions mechanisms, and spatial trends in sediment copper were likely due to heterogeneous distribution of paint flakes.

Based on New Zealand and overseas examples, it appears that the recovery of severely impacted/enriched sites through fallowing can take much longer than high flow and/or less enriched sites. Influenced by natural fluctuations between reduced and oxidised conditions, the fallowing process can be described as "progress and regression". Short-term temporal processes can vary considerably in coastal environments, and therefore monitoring needs to consider temporal and spatial variability to account for deviations in recovery. No study has yet empirically tested metal bioavailability from sediments over a fallowing period. Although it is assumed that bioavailability will increase as sediments re-oxidise this may not be the case, and this question requires further investigation.

This review has noted several additional questions where more information or research is needed before any definitive decisions can be made regarding the acceptability of current metal levels in sediments under finfish farms. Possible synergistic and/or antagonistic effects associated with metal contaminants have not yet been resolved, due in part, to similar benthic responses (*e.g.* decreased abundance or diversity) to different impacts (*i.e.* pollutant or metal). From existing data, it appears that further research around such effects will initially need to focus on the bioavailability of metals.

Several aquaculture monitoring studies have suggested that enriched sediments conditions resulted in binding of the free ionic forms of copper and zinc, making them less toxic than would otherwise be expected. However, few studies have tested these assumptions. Initial investigations have demonstrated the importance of testing the bioavailability of chemically bound sediment metals in assessing monitoring data for finfish farms. Most researchers advocate that future testing should concentrate on chemical estimates of bioavailability and ecotoxicology together, given the complexity associated with metal speciation and bioavailability.

An important information gap concerns the fate of metals once introduced to the marine environment and later during chemical remediation (*e.g.* during a fallowing period), as their concentrations in sediments have been documented to decrease with time, especially zinc. As conservative contaminants, metals do not degrade. Instead they are either mixed deeper into sediments and/or dispersed from the local environment. As locally relevant conditions can greatly affect metal speciation, the possible fate(s) of metals cannot be generalised across regions, instead it needs to be calculated on a site-by-site basis.

Finally, industry currently employs several measures aimed at minimising or reducing chemical source inputs from marine farms into the local environment. Given more research and/or information, there may be additional operational approaches that enable further reduction of the amount of metals released into the marine environment.



Suggested priorities

This review suggests that MDC continues to apply ANZECC (2000) thresholds to consent conditions of Marlborough Sounds' salmon farms. However, when compliance is not achieved in terms of bulk metal levels, we recommend these further investigations:

- More detailed sampling to investigate spatial and temporal variability
- Evaluate sediment toxicity with respect to speciation/bioavailability
- Examine and refine aquaculture operational issues and/or current monitoring protocols and guidelines for finfish farms

As a whole, locally relevant results will help MDC ensure they are detecting and minimising the impacts metals may be having on the benthic environment near salmon farms. Taking such actions now will also help inform future decisions relating to new finfish farm applications with regard to the environmental implications of metal inputs. Further national and international research is also necessary and vital towards fully understanding the long-term implications that metal usage in aquaculture farms may have on local marine environments.





A flowchart representing suggested priorities for MDC in working towards the sustainable use of copper and zinc associated with finfish aquaculture in the Marlborough Sounds. The flowchart demonstrates how steps by MDC can help refine future sediment guidelines and monitoring programmes. Based on information gained from this review, additional national and international research issues are also highlighted on the right side of the flowchart.

TABLE OF CONTENTS

EXE	CUTIVE SUMMARY	III
1.	INTRODUCTION	1
1.1.	Review objectives	2
2.	CURRENT KNOWLEDGE	3
2.1.	Focus on copper and zinc	3
2.2.	Copper sourced from anti-foulant paints	5
2.2.1.	Current anti-foulant usage in aquaculture	6
2.2.2	Possible pathways to the environment	6
2.3.	Zinc sourced from fish feeds products	11
2.3.1.	Current zinc usage in aquaculture feed products	11
2.3.2.	Possible pathways to the environment	12
2.4.	Possible biological effects of copper and zinc	15
2.4.1.		15
2.4.2	Possible effects on blota	16
2.4.3.		17
3.	CURRENT MONITORING GUIDELINES AND THE NEW ZEALAND SITUATION	19
3.1.	Sediment Quality Guidelines (SQGs)	19
3.1.1.	Aquaculture-specific guidelines	20
3.2.	New Zealand situation in a global context	21
3.2.1.	New Zeelend meniation date	21
3.2.2.	New Zealand monitoring data	21
3.3. 221	Fallowing of finish farms	25
332	Eallowing process	25
3.3.3	New Zealand fallowing data	27
4.	KNOWLEDGE GAPS	
4.1.	Overview	
4.2.	Svnergistic/antagonistic effects	30
4.2.1.	Adverse effects confounded with enrichment effects	30
4.2.2.	Interactions between metals	34
4.3.	Bioavailability	35
4.4.	Fate and metal conservation	36
4.5.	Operational	37
5.	SUGGESTED PRIORITIES	39
6.	ACKNOWLEDGEMENTS	42
7.	REFERENCES	42
8.	APPENDICES	47
8.1.	Additional information on possible biological effects of copper and zinc	47



LIST OF FIGURES

Figure 1.	Concentration of copper in sediments from reference stations (1); salmon farms not using copper treated nets (copper levels attributed to feed supplements) (2); and salmon farms where copper treated nets were in use (3)
Figure 2.	Average copper and zinc concentrations beneath the cages at five salmon farms in the Marlborough Sounds
Figure 3.	A comparison between the maximum, average and corresponding reference concentrations of copper and zinc reported beneath salmon farms in Tasmania, Canada and Scotland with New Zealand 23
Figure 4.	The average copper and zinc concentrations collected at various distances beneath cages at two salmon farms in Australia, two salmon farms in Canada, and from one salmon farm in New Zealand.
Figure 5.	Average AFDW, total infauna abundance, total number of taxa and copper and zinc concentrations found beneath the cages at a fallowed salmon farm in the Marlborough Sounds.
Figure 6.	Changes in sediment organic content or infaunal communities along typical salmon farm enrichment gradients
Figure 7.	Draftsman plot of sediment characteristics beneath salmon farms in the Marlborough Sounds
Figure 8.	 (A) MDS plot of fourth-root transformed infauna data based on Bray-Curtis similarity matrix from samples collected beneath and around Marlborough Sounds salmon farms. (B) MDS with relative copper concentration. (C) MDS with relative AFDW values and (D) MDS with relative zinc concentrations.
Figure 9.	A flowchart representing suggested priorities for MDC in working towards the sustainable use of copper and zinc associated with finfish aquaculture in the Marlborough Sounds . 41

LIST OF TABLES

Table 1.	Examples of dissolved copper concentrations within marine waters	8
Table 2	Examples of copper levels reported within marine sediments from a range of	
	environments	0
Table 3	Summary of sediment zinc concentrations observed at control stations, farms using the zinc methionine analog supplement and farms using feed supplemented with zinc	_
	sulphate1	2
Table 4.	Examples of dissolved zinc concentrations within marine waters	3
Table 5	Examples of zinc levels reported within marine sediments from a range of environments	
		4
Table 6	The sediment quality guideline values from New Zealand/Australia, United States and	
	Canada for copper and zinc levels in marine sediments	0
Table 7	Pearson correlation coefficients between pairs of environmental variables for samples	
	from the seabed beneath salmon farms in the Marlborough Sounds	2

1. INTRODUCTION

Finfish farming in New Zealand is currently undergoing an expansion due to a steadily growing demand for farmed salmon products and widespread interest in the aquaculture sector to diversify into other finfish species. One of the key factors contributing to this rapid growth is the continuous improvements of better fish husbandry techniques; in particular, enhanced water flow through sea cages and more conversion efficient feed products.

Naturally occurring marine species, such as sponges, sea squirts and algae, tend to colonise or 'foul' the predator exclusion nets surrounding most finfish sea cages. This fouling can be so dense that it reduces water flow through the cages themselves, causing a build-up of waste products and a reduction in oxygen levels. Such conditions can lead to unhealthy stock through significant stress, higher disease rates and even result in mortality (Braithwaite *et al.* 2007). To address this problem, the industry coats the exclusion nets in anti-foulant paints that discourage settlement of fouling species.

In order to ensure farmed finfish, particularly salmon, receive the essential micronutrients and oils necessary for healthy growth, the industry has focused on diet suitability. Feed products are mainly derived from fishmeal and fish oil, but are increasingly dependent on terrestrial sources of protein and oil (Wilding *et al.* 2006). Several micronutrients, including trace metals and vitamins, are essential for healthy fish production (*e.g.* Hall & Anderson 1999; WHO 2001). Natural sources of these nutrients within fishmeal are often inadequate as they cannot be sufficiently absorbed by the fish. Therefore different forms of these micronutrients are supplemented to feed products (Burridge *et al.* 2008).

Anti-fouling paints, feed and therapeutants (pharmaceutical products, or 'medicines') associated with the operation of finfish farms are all potential chemical sources to the marine environment. The New Zealand salmon industry has not needed to use therapeutants (Forrest *et al.* 2007). However, recent research has indicated that the use of improved anti-fouling and feed products within finfish farms may have a potential toxicant-related risk due to associated trace metals (*e.g.* Morrisey *et al.* 2000; Brooks & Mahnken 2003; Dean *et al.* 2007; Burridge *et al.* 2008; Obee 2009). While trace metals are naturally utilised by marine organisms, it is their increasing toxicity at levels above an organism's normal requirements that makes these chemicals effectively toxic agents (Hall & Anderson 1999). As trace metals are conserved (*i.e.* cannot be degraded or removed), they have the potential to accumulate in the marine environment and result in deleterious effects to biota (Morrisey *et al.* 1996). Potential adverse effects range from physiological and behavioural effects at the individual species level to changes in species composition and community structure.

Annual monitoring surveys around existing salmon farms in the Marlborough Sounds frequently identify elevated levels of copper and zinc beneath the cages (Forrest *et al.* 2007). Although sometimes above the Australian and New Zealand Environment and Conservation Council's (ANZECC 2000) guideline limits (ISQG-Low and -High), uncertainties remain as to the elevated metals' ecological relevance.



To date, there is little information available on the possible synergistic and/or cumulative effects of trace metals as they accumulate in sediments that become enriched under finfish farms (Macleod & Eriksen 2009). A clear understanding of the ecological effects that metal contaminants might have on farm sediments is essential for minimising and managing aquaculture impacts. To enable environmentally sustainable growth of the salmon farming industry in the Marlborough Sounds, the Council will need information on whether the current guideline levels for copper and zinc are adequate given their bioavailability, final fate, mechanisms for accumulation and possible compounding effects due to enriched environments.

1.1. Review objectives

In the time since this Envirolink project was proposed, the Australia's Fisheries Research and Development Corporation (FRDC)and the University of Tasmania released a two-year investigation entitled, "A review of the ecological impacts of selected antibiotics and anti-foulants currently used in the Tasmanian salmonid farming industry (Marine Farming Phase)" (Macleod & Eriksen 2009). The present assessment draws heavily on the Macleod & Eriksen (2009) review and, as a result of some of their findings, we have modified the original objectives of this report accordingly.

Section 2 reviews national and international literature to determine what is currently known about metal contaminants associated with marine finfish aquaculture, specifically:

- The range of potential metal contaminants originating from salmon farms (other than copper and zinc).
- Mechanisms that dictate copper and zinc accumulation and biological impact in sediments beneath finfish farms.

Section 3 considers the current New Zealand situation in relation to metal contaminants associated with overseas finfish farms:

- Current standards and/or guidelines used to predict the potential impact of copper and zinc levels.
- Long-term implications of elevated metal concentrations with respect to the expected rate of reduction after removal of cages.

Section 4 examines unresolved issues pertaining to potential contaminants in sediments associated with finfish aquaculture, in particular:

- Possible synergistic and/or antagonistic effects of elevated levels of copper or zinc with enrichment effects, and other metals.
- Bioavailability, final fate and conservation of copper and zinc.
- Potential remediation measures.



The final section suggests several management and research recommendations towards resolving the sustainability issue around current and future levels of copper and zinc associated with finfish farms in the Marlborough Sounds.

2. CURRENT KNOWLEDGE

This review focuses on the metals copper and zinc, with copper derived from anti-fouling paints and zinc contained in fish feed. Based on our literature search and the recent comprehensive review by Macleod & Eriksen (2009), we consider it unlikely that contaminants other than copper and zinc would be present at environmentally significant levels within New Zealand finfish sites. The following sections intend to:

- Highlight the specific chemical form of the metals that are added, current usage rates in finfish aquaculture and the pathways in which copper and zinc enter and/or exist once in the marine environment
- Provide a general review of how copper and zinc may adversely affect local biota and benthic communities

2.1. Focus on copper and zinc

In New Zealand, issues surrounding the use of trace metal compounds at finfish sites have received little scientific attention (Forrest *et al.* 2007). This is largely due to the relatively small scale of finfish farming and the minimal use of other chemicals (*i.e.* therapeutants) to maintain healthy stock. However, as finfish farming in New Zealand expands into new species and growing regions, the use of trace metals and other chemicals may increase.

The main sources of trace metal inputs associated with finfish farms are anti-fouling paints and fish feed products. Burridge *et al.*'s (2008) review of chemical use in aquaculture found that the main active agent used in most commercial anti-fouling products (~95%) worldwide (including New Zealand) was copper, the proportion of which varied from 15-50% depending on the product. A few anti-fouling products use zinc oxide and zinc pyrithione as active agents and/or as a way to control the rate of coating erosion. While anti-fouling products generally utilise only one or two metals, manufactured feed products contain an assortment of trace metals in various concentrations and chemical forms including: zinc, copper, cadmium, iron, manganese, cobalt, nickel, lead, magnesium, selenium and mercury (Dean *et al.* 2007). These metals may be naturally occurring within the fishmeal or added for nutritional reasons (Burridge *et al.* 2008).

Despite the range of possible trace metals contaminants associated with finfish production, only copper and zinc are consistently found in environmentally significant levels within sediments beneath finfish farms worldwide (*e.g.* Morrisey *et al.* 2000 – New Zealand; Brooks *et al.* 2003 – Canada; Dean *et al.* 2007 – Scotland). A study by Dean *et al.* (2007) calculated



that the input of zinc and copper from uneaten feed, as well as faecal waste products, accounted for 87% and 4.3% respectively, of the resulting metals found in sediments under the farms. As such, finfish feed products have been identified as the main anthropogenic source of zinc in sediments. Macleod & Eriksen (2009) consider anti-fouling paint as the major contributor of copper contamination in sediment where anti-fouled nets are used. Their conclusion was based on the findings of Dean *et al.* (2007), experimental evidence from Brooks & Mahnken (2003 – Figure 1) and further anti-fouling residue trials in Tasmanian salmon farms. Preliminary tests on biofouled nets by the Tasmanian Salmonid Growers Association Ltd (TSGA) determined that 21% of the copper agent from the original coating of a net enters the marine environment.



Figure 1. Concentration of copper in sediments from reference stations (1); salmon farms not using copper treated nets (copper levels attributed to feed supplements) (2); and salmon farms where copper treated nets were in use (3). Modified from Brooks & Mahnken (2003).

The extent to which cadmium, mercury or other elemental compounds are elevated in the New Zealand environment due to fish farm activities is still unknown (Forrest *et al.* 2007). Dean *et al.* (2007) assessed the level of cadmium in sediments under Scottish finfish cages, and found that 14% could be attributed to feed products. Cadmium is highly associated with zinc (S. Gaw – University of Canterbury, pers. comm.) and may occur as a minor component in feed products, but it is not considered essential or beneficial to living organisms (Thurberg *et al.* 1973). A British Columbian study indicated that mercury can also be locally elevated in the vicinity of fish farms, due in part to trace levels in uneaten feed and/or residual (*i.e.* naturally occurring) amounts in sediments (Debruyn *et al.* 2006).

Benthic conditions associated with finfish farms may promote the conversion and/or mobilisation of existing metals to a more biologically available form within the sediments beneath fish cages than would be normally available, and in the case of mercury, lead to



biomagnification through the food chain (Debruyn *et al.* 2006). However, both studies showed that elevated levels of these metals were more likely the result of altered cycling of metals from the anoxic sediment conditions associated with finfish farming than additional inputs associated with farm operations (Debruyn *et al.* 2006; Dean *et al.* 2007).

2.2. Copper sourced from anti-foulant paints

Due to their significant and historical use in the boating industry, the environmental impacts of anti-foulants have been extensively researched (Braithwaite *et al.* 2007). Anti-foulant usage within the aquaculture industry, however, presents several new and unique environmental risk factors that are presently not well understood, particularly any antagonistic or synergistic effects associated with other farm impacts (*e.g.* organic enrichment of sediments). The main environmental concerns with anti-foulant contamination include bioaccumulation and any subsequent changes to local ecology and biodiversity, and any effects on ecosystem functions such as microbial processes in the sediments (Macleod & Eriksen 2009).

Anti-fouling of nets and farm structures is an essential part of most sea-based finfish operations. Excessive growth of biofouling organisms (ascidians, kelp, mussels, bryozoans *etc.*) can significantly reduce water flow through the nets, which adversely affects fish health and dispersion of waste products, while substantially adding to the water drag, which places additional strains on the farm structure and mooring network (Braithwaite *et al.* 2007, M. Gillard – New Zealand King Salmon, pers. comm.). Farm structures that are less prone to fouling and require less, or no, anti-fouling coatings have been developed (*e.g.* the polyethylene PolarcirkelTM), but this is a relatively new innovation and it is unlikely to replace the many existing structures quickly due to the capital costs involved and the different farming methods that the polyethylene structures dictate. Therefore, anti-foulants are expected to be a commercial necessity for most existing farms and many new farms for some time to come.

Currently, the most effective anti-foulant products consist of biocides (chemical substances that selectively kill living organisms), which are mixed into an adhesive substance such as polymer paints or epoxies for direct application to vessel hulls, harbour structures and/or aquaculture nets (Braithwaite *et al.* 2007). As this matrix slowly dissolves in the seawater, the biocides or active agents continually leach into the water immediately around the farm structure at toxic concentrations that will inhibit most organisms from settling on any nearby surfaces. Finfish farms most commonly use copper-based anti-foulant paints in combination with mechanical de-fouling methods (Burridge *et al.* 2008). In the Marlborough Sounds, New Zealand King Salmon (NZKS) uses copper-based paints on external predator nets only, as manual de-fouling alone is not feasible.

Non-toxic anti-foulant products are currently being tested, however, these products are usually silicon-based and reliant on strong water movements across the coated surfaces to be effective (Macleod & Eriksen 2009). Currently these newer products are not considered acceptable alternatives to active agent-based paints in aquaculture.



2.2.1. Current anti-foulant usage in aquaculture

Little is known about the actual volume of anti-foulant paints used in finfish aquaculture worldwide as there are currently few reporting requirements in most countries, with the exception of Scotland and Tasmania (Burridge *et al.* 2008; Macleod & Eriksen 2009). These limited data suggest a considerable volume of anti-foulant is coated on to finfish nets each year. Tasmania's annual usage of anti-foulant (in terms of cuprous oxide - Cu₂O) in 2006 was 1.51 kg of Cu₂O /tonne of fish produced compared to 0.27-0.66 kg of Cu₂O /tonne of fish produced as Eriksen 2009).

In comparison, individual salmon farms in the Marlborough Sounds use approximately 500 to 1500 litres of anti-foulant paint per year (M. Gillard - New Zealand King Salmon, pers. comm.). This equates to approximately 0.34-0.89 kg of Cu₂O /tonne fish produced¹. Variation in overall usage is expected due to different farming methods as well as varying environment conditions, such as water temperatures and flow rates.

As predator nets become significantly bio-fouled, they are removed and replaced with a clean, newly coated net. The cleaning protocol for salmon farms within the Marlborough Sounds is to partially water-blast nets while still in the water and/or remove any larger fouling organisms (such as mussels) as the net is pulled from the water and fed through a type of wringer. Removed nets are fully cleaned once on shore, where they are re-coated and allowed to dry (M. Gillard - New Zealand King Salmon, pers. comm.).

2.2.2. Possible pathways to the environment

Anti-foulant toxicants from aquaculture usage potentially enter the marine environment in three ways;

- Leaching of active paint surface to the surrounding water column (water exposure)
- Release from accumulated paint in the sediments (sediment exposure), and subsequently settling out as particulates to the seabed
- Ablated or physical damage to paint surface from natural causes or from *in situ* net cleaning (paint particles)

The toxicity of a metal in a particular environment is largely determined by its chemical form (speciation). For the metal to be toxic to an organism, it has to be biologically available or bioavailable (*i.e.* in a form that an organism can directly absorb or ingest). For copper, the more toxic form (species), and thus bioavailable, is the free cupric ion - Cu²⁺ - rather than total copper in the water (Kim *et al.* 1999; Eriksen *et al.* 2001). It is important to note that the speciation and bioavailability of metals is complex, and closely related to environmental conditions (*e.g.* temperature, salinity, pH) as well as dependent on the degree of organic

¹ Anti-foulant usage for the Marlborough Sounds were calculated from a total paint application of an estimated 9,000 L per year, of which 2,232 to 5,823 kg is cuprous oxide (Cu₂O), depending on the strength of antifoulant used (HempaNet medium strength and Interclene 175 respectively). This range was divided by an estimated 6,500 tonnes fish produced each year from this region to calculate annual usage. Estimates supplied by M. Gillard, New Zealand King Salmon.



enrichment, the redox status of surficial sediments and the extent of physical processes such as bioturbation and resuspension (*e.g.* Eriksen *et al.* 2001; Chapman & Wang 2001).

Water exposure

Anti-foulant paints are designed to slowly and continuously leach small concentrations of active agents (*i.e.* copper) into the water at levels that are toxic to biofouling organisms. Mean concentrations of dissolved copper inside and outside of copper-treated salmon nets in British Columbia were recorded between 0.54 and 0.55 μ g Cu/L (respectively), and were elevated from background concentrations of 0.37 and 0.38 μ g Cu/L within the same bay (Lewis & Metaxas 1991). The authors note that dissolved concentrations of copper were partially dependent on current flow rates, which in turn may affect residence time and potential accumulation.

Macleod & Eriksen (2009) summarised typical dissolved copper concentrations from a variety of marine and estuarine water bodies, including measurements around finfish cages using copper-based anti-foulant paint (Table 1). As expected, dissolved copper levels are generally highest within harbours/marinas and lowest in open ocean areas, while aquaculture net levels are most similar to the ranges observed within estuaries.

It is generally thought that dissolved copper is more bioavailable than particulate copper; however, metals such as copper have low solubility in water. Low solubility means that any dissolved copper ions not taken up by nearby organisms or larvae, will quickly adhere to the surface of particulate material in the water column that eventually contribute to bottom sediments (Eriksen *et al.* 2001).

However, it has been suggested that most dissolved copper may associate with colloidal material, and thus may not be available as 'dissolved copper' (Eriksen *et al.* 2001). Approximately 98-99% of copper in seawater is bound to naturally occurring organic material, with less than 0.08% actually present as a cupric ion (Hall & Anderson 1999). Any remaining copper is likely to be in complexes with ligands, such as humic compounds, chloride or sulphide (Eriksen *et al.* 2001). As a result, the concentration of free copper ion biologically available within the water column may be many orders of magnitude lower than the total copper concentration leached from the paint.



Study Region	Study Region Dissolved copper concentration µg/L	
Bodies of Water		
Pacific Ocean - surface	0.027 - 0.092	WA Environment Dept 2005 [†]
NE Pacific Ocean – 20 - 1400 m	0.04 - 0.14	Coale & Bruland 1988 ¥
Tasman Sea - marine waters	0.06	Batley 1995 †
NSW - marine waters	0.10	WA Environment Dept 2005†
NSW - coastal waters	0.031	WA Environment Dept 2005 ⁺
Marinas/Harbours		
Ireland – harbour	2.2 - 18.4	Clancy et al. 1987 *
Sweden - marina	0.69 - 3.83	Ohrn 1995 *
Greece - harbour/urban area	0.45 - 20.7	Dassenakis et al. 1996 *
France - harbour	1.0 - 10.0	Alliot & Frenet-Piron 1990 *
NZ - Lyttelton Harbour ‡	19.0 - 35.0	Bennett & Barter 2006
NZ - Lyttelton Harbour control site	1.0 - 5.0	Bennett & Barter 2006
Estuaries		
England - estuary	0.2 - 3.2	Harper 1991 *
Bathurst Harbour – Australia pristine estuary	0.012 - 0.38	Mackey et al. 1996 †
Maquarie Harbour – Australia contaminated estuary	2.9 - 19	Eriksen et al. 2001
Aquaculture		
British Columbia - inside finfish cages	0.1 - 0.87	Lewis & Metaxis 1991
British Columbia - outside finfish cages	0.06 - 0.93	Lewis & Metaxis 1991

Table 1. Examples of dissolved copper concentrations within marine waters (modified from Macleod & Eriksen 2009).

As reported in Hall & Anderson 199

† As reported in Macleod & Eriksen 2009

¥ As reported in Lewis & Metaxis 1991

Highly contaminated site adjacent (~5-40 m) to dry-dock discharge effluent

Sediment exposure

Most anthropogenic inputs of trace metals into the marine environment become incorporated into nearby sediments (Table 2). Copper and zinc are both ubiquitous trace contaminants found in sediments from urban areas, ports and marinas (e.g. Forrest et al. 1997; Fichet et al. 1998). As such, sediments are often used as a proxy for seabed health. Contaminant loads within sediments can also be used to monitor the magnitude and scale of various anthropogenic impacts (Macleod & Eriksen 2009).

However, the varying capacities of sediments to bind metals make it difficult to compare trace metal loads across sediment types. Copper, like other metals, tends to adsorb to fine-grained

particles (*e.g.* <63 μ m, silt and clay) due to their high surface to volume ratio, particularly in sediments with high amounts of sulphide present (Morrisey *et al.* 2000; Brooks & Mahnken 2003). This affinity results in high levels of contamination within sheltered, low-energy depositional areas in which finer particles accumulate. Sandy sediments that are low in organic carbon or fine silt generally have lower levels of metal contamination (Morrisey *et al.* 1996).

Finfish aquaculture is known to lead to significant organic deposition beneath farm structures (Karakassis *et al.* 1999; Forrest *et al.* 2009). As this organic matter is broken down, oxygen from the surrounding sediments and water is consumed. Significant build-up of organic matter (*e.g.* enrichment) can lead to anoxic or hypoxic conditions in which sulphides are generated by sulphate reduction (Macleod & Eriksen 2009). Under these low oxygen conditions, most metals form insoluble sulphides and are thought to be biologically unavailable (Morrisey *et al.* 2000).

Copper is highly conservative once introduced into a system, and particularly within exposed sediments (Petersen *et al.* 1997; Ranke 2002; Burridge *et al.* 2008). The only way to reduce metal levels in a local area is by dispersal or removal in the form of either biological bioturbation or hydrological resuspension (Smith & Williamson 1986). Several studies found evidence that resuspension (*e.g.* dredging, strong storms) of contaminated sediments into oxygenated seawater could cause a portion of bound trace metals to be re-mobilised from sediments (Petersen *et al.* 1997; Simpson *et al.* 1998). Decreasing pH and salinity is known to cause metal desorption from colloidal and particulate matter (Chapman & Wang 2001; Eriksen *et al.* 2001). Metal release can also take place when enriched sediments are allowed to recover and return to normal oxygenated levels, such as fallowing former finfish farms (Brooks & Mahnken 2003). Once released, metals are likely to re-adsorb to particulate matter or disperse with the currents to other regions if in highly flushed areas.

Despite being bound to sediments, metals are still available through both a porewater and solid phase exposure route, and therefore can still be toxic to benthic organisms (Chapman *et al.* 2002; Macleod & Eriksen 2009). Porewater is the water that fills the spaces between sediment particles, and may make up 50% of sediment volume. While generally observed to be low relative to sediment loads, metal concentrations within porewater may be more biologically available to benthic organisms, particularly those that burrow or filter through sediments (Chapman *et al.* 2002). Solid phase exposure occurs when metals become available to benthic fauna through ingestion and filtering of contaminated organic matter and any associated sediments, and is considered the dominant uptake pathway for burrowing deposit-feeding infauna (Chapman *et al.* 2002; Macleod & Eriksen 2009).

Table 2 lists typical copper concentrations from a variety of marine and estuarine sediments, including measurements around finfish cages using copper-based anti-foulant paint. Reported sediment copper levels are highly variable, depending on the location (open water, coastal or estuarine) and the level of possible contamination. Recent assessments of sediments under salmon farm sites in the Marlborough Sounds have recorded locally elevated copper levels



(Forrest *et al.* 2010a,b). In general, sediment copper levels associated with active finfish farms, particularly ones with high organic enrichment, were within the range of those reported for moderately to heavily impacted estuaries.

Table 2.Examples of copper levels reported within marine sediments from a range of environments
(modified from Macleod & Eriksen 2009). Values represent ranges or averages unless otherwise
indicated.

Study Region	Total copper concentration mg/kg (dry weight)	Reference
Bodies of Water		
Sydney continental shelf offshore	0.6 - 19.83	Matthai & Birch 2001†
Estuaries		
Huon Estuary - Australia baseline data	35 - 47	Macleod & Helidoniot 2005 †
Derwent Estuary - Australia contamination hotspots	2350	DEP 2007 †
Havelock Estuary –NZ slight to moderately impacted	9.1 - 12	Robertson et al. 2002
Waimea Estuary –NZ moderately impacted	5.7 - 15	Robertson et al. 2002
Delaware Estuary –NZ 'pristine' estuary	8.8 - 15	Gillespie et al. 2009
Aquaculture		
Scotland - Loch Craignish finfish site	805 (max)	Dean et al. 2007
Canada – New Brunswick High organic, finfish site	54.5	Chou <i>et al.</i> 2002
Australia - Huon High organic, finfish site	5 - 1372	AMD (2004 – 2007) †
Australia - Huon Low organic, finfish site	19 - 153	AMD (2004 – 2007) †
NZ - Te Pangu Bay Low organic, finfish site	12 - 180	Forrest et al. 2010a
NZ - Ruakaka Bay High organic, finfish site	51 - 200	Forrest et al. 2010b

†As reported in Macleod & Eriksen 2009

Paint particles

Due to regular use and/or *in situ* cleaning, paint flakes can break away from the painted nets and deposit under the farm in the sediments. These chips will continue to leach active agents similar to the remaining paint, the differences being that they now have direct exposure to sediment porewater and can affect non-target organisms (Singh & Turner 2009). It is noted that water movement within porewater will be considerably lower than flow around fish cages in the water column; hence the rates at which metals leach (and diffuse) from the paint is likely lower in sediments versus the water column.

Similar to previous exposure pathways, the rate and fate of metal leached from the paint chip is dependent on environment factors such as salinity and pH. Research focused on the boat industry also found that paint flakes and chips had significantly higher release rates than the painted hulls due to surface area effects (Turner *et al.* 2008; Turner *et al.* 2009). However, Singh & Turner (2009) found that the type of paint matrix used had more of an effect on leaching rates than the actual particle size. How long the leached copper may remain dissolved in porewater and/or how quickly it adsorbs to particulate material is unknown. Macleod & Eriksen (2009) note that paint chips constitute a significant localised source of contamination, and the greatest impact(s) could occur from direct ingestion of new chips by sensitive benthic organisms (*e.g.* filter feeders) and/or early life stages (*e.g.* larvae).

2.3. Zinc sourced from fish feed products

With a currently unsustainable reliance on fishmeal and fish oil products, the aquaculture industry is moving more towards alternative sources for finfish feed (Wilding *et al.* 2006). Certain trace metals are essential for fish development and growth, and must be present in feed products to ensure a healthy diet. New Zealand salmon and kingfish farms use a standard feed that does not contain antibiotics, vaccines, steroids or other growth enhancers. The feed contains zinc, an essential micronutrient for the prevention of cataract formation and other health problems (M. Gillard, New Zealand King Salmon, pers. comm.). The main environmental concerns with fish feeds are similar to those with anti-foulant paint usage and include bioaccumulation, persistence and ecotoxicological effects on the local ecosystem. Unknown are the cumulative and/or interactive effects of elevated levels of zinc coupled with high levels of copper in the sediments.

Dean *et al.* (2007) measured zinc levels in Scottish salmon feed, waste products and associated sediments. Based on the concentrating effect of zinc occurring within salmon (196.4 mg/kg in feed to 364.52 mg/kg in faeces) and feed loss to the environment, the authors calculated that 87% of the resulting zinc found in sediments could be directly attributed to the feed products. The authors noted that the amount of feed input increases and decreases in relation to the growing and harvest cycle. A correlated trend in sediment zinc concentrations with these cycles reiterates the fact that feed products are the main source of zinc contamination in farms.

The general background and details around metal speciation, bioavailability, organisms' exposure and uptake routes covered in Section 2.2.2 also apply for zinc. In the following sections, we discuss the usage of zinc in feed products and any differences in pathways to the environment versus those for copper associated with anti-foulant paints.

2.3.1. Current zinc usage in aquaculture feed products

The salmon feed products used within Marlborough Sound sites contain approximately 100 mg zinc/kg of feed (M. Gillard, New Zealand King Salmon, pers. comm.). For comparison, the concentration of zinc in Atlantic salmon feeds ranges from 6 to 240 mg of zinc/kg of feed

(Burridge *et al.* 2008). Skretting's (producer of 90% of finfish feed products used in New Zealand) Pacific salmon feed products had a total zinc content of 210 mg/kg prior to 2007. Recent reductions in zinc supplements equates to around 160 mg/kg (100 mg/kg supplemented zinc with approximately 60 mg/kg naturally occurring zinc in the fishmeal) being presently used in their products (Skretting 2010).

Most supplemented zinc is currently added to feed products in an inorganic form as zinc sulphate (Brooks & Mahnken 2003). Skretting is currently researching the use of an organic form where the zinc is bound with protein or amino acid, and therefore can be more efficiently absorbed by fish (Skretting 2010). Using this organic form can decrease the overall zinc content in feed to 90 mg/kg, based on Skretting's Canadian production. Other feed groups are starting to change to a zinc supplement that is in a more bioavailable form known as zinc methionine (Burridge *et al.* 2008). By decreasing the amount of zinc in finfish feed to the minimum levels necessary for fish health and ensuring more efficient uptake by the fish, the amount of zinc released into the marine environment is predicted to decrease by about 50% (Table 3 - Brooks & Mahnken 2003; Burridge *et al.* 2008).

Table 3.Summary of sediment zinc concentrations observed at control stations, farms using the zinc
methionine analog supplement and farms using feed supplemented with zinc sulphate (modified
from Brooks & Mahnken 2003).

Sample Locations	# Farms	# Samples	Zinc Levels (μg/g DW)	Mean ± 95% CI
Farms using zinc methionine	4	10	4.6-82.0	30.6 ± 14.7
Farm using zinc sulfate	1	4	51.6-255.0	178.2 ± 87.3
Reference stations	5	5	11.7-73.0	30.7 ± 21.3

2.3.2. Possible pathways to the environment

As with anti-foulant paints, trace metals within finfish feed productions can enter the environment through several pathways;

- Eaten by farmed fish and subsequently released in their faecal waste products (water and sediment exposure)
- Released from uneaten feed particles (0.5% wastage) that break down in the water column (water exposure)
- Uneaten feed (1-4% wastage) accumulated underneath the farm on sediments (sediment exposure)

Similar to copper, the zinc released into the marine environment can occur in various forms. Its speciation dictates its bioavailability and thus potential toxicity to target and non-target organisms.



Water exposure

The zinc in feed is designed to be absorbed and utilised by the fish for nutritional reasons. However, naturally occurring zinc found in association with fishmeal is not absorbed by fish as high levels of calcium and other factors inhibit intestinal uptake (Burridge *et al.* 2008). Therefore, this form of zinc is released, along with any excess 'organic zinc', as waste products into the water column and sediments below.

Zinc is considered to be most toxic to marine organisms in its ionic form, Zn^{2+} , although less so than copper (Burridge *et al.* 2008). Zinc, like copper, is fairly insoluble in water however it has its greatest effect on aquatic organisms under low pH, low salinity, low dissolved oxygen and elevated temperatures (Eisler 1993). Most dissolved zinc will quickly bind to sulphides and/or fine particles such as silt and clay, and eventually accumulate on the seafloor. The World Health Organisation (2001) reported low baseline levels of dissolved zinc in surface ocean waters, between 0.002–0.1 µg/L, in comparison to other sources such as harbours and estuaries (Table 4).

Study Region	Dissolved zinc concentration µg/L	Reference
Bodies of Water		
North Atlantic Ocean – 20 - 3715 m	0.065 - 0.124	Yeats 1988 †
NE Pacific Ocean – 100 - 3500 m	0.23 - 0.4	Yeats 1988 †
SW Pacific Ocean - surface (Australia)	<0.04	Batley 1995 †
Marinas/Harbours		
San Diego USA – harbour	2.6	Sprague 1986 *
NZ - Lyttelton Harbour ‡	10 - 2467	Bennett & Barter 2006
NZ - Lyttelton Harbour control site	5	Bennett & Barter 2006
Estuaries		
W. Mediterranean estuary	10	Sprague 1986 *
UK – estuary contaminated estuary	26	Sprague 1986 *

Table 4. Examples of dissolved zinc concentrations within marine waters.

* As reported in Eisler 1993

†As reported in WHO 2001

‡ Highly contaminated site adjacent (~5-40 m) to dry-dock discharge effluent

Sediment exposure

Zinc is considered mostly unavailable once bound to particles. Given the high sulphide load and negative redox potential due to enrichment of sediments under finfish farms, it is expected that the zinc bound to sediments is biologically unavailable (Burridge *et al.* 2008; Macleod & Eriksen 2009). However, zinc will continue to concentrate in sediments under farms unless it is dispersed to other areas. Several overseas studies and monitoring programmes have

measured zinc levels under salmon farms at concentrations exceeding local sediment quality guidelines, and that are similar or often higher than levels measured in contaminated estuary sediments (Table 5). An assessment beneath salmon farms in the Marlborough Sounds in 2009 found that zinc levels ranged between 56-620 mg/kg, exceeding the ANZECC (2000) sediment quality guideline for 'probable' ecological effects (410 mg/kg) at several sites with low flushing (Forrest *et al.* 2010a,b).

Zinc-bound sediments can still exert adverse and toxic effects on benthic organisms through direct ingestion and there is also a potential for exposure to zinc in porewaters. Dean *et al.* (2007) observed high levels of zinc present in porewater (250 μ g/L) and sediments (450 μ g/L) under fish cages in Scotland. As zinc associated with porewater can be in a more toxic form, lower concentrations are expected to have more adverse effects than higher concentrations of zinc bound to the sediments.

Table 5.Examples of zinc levels reported within marine sediments from a range of environments (modified
from Macleod & Eriksen 2009). Values represent ranges or averages unless otherwise indicated.

Study Region	Total Zinc Concentration mg/kg (dry weight)	Reference	
Bodies of Water			
Sydney continental shelf offshore	4.7 - 82.4	Matthai & Birch 2001†	
Estuaries			
Huon Estuary - Australia baseline data	20 - 30	Macleod & Helidoniot 2005 †	
Derwent Estuary - Australia contamination hotspots *	58700	DEP 2007 †	
Havelock Estuary –NZ slight to moderately impacted	31 - 53	Robertson et al. 2002	
Waimea Estuary –NZ moderately impacted	29 - 54	Robertson et al. 2002	
Delaware Estuary –NZ 'pristine' estuary	35 - 78	Gillespie et al. 2009	
Aquaculture			
Scotland - Loch Craignish finfish site	921 (max)	Dean <i>et al.</i> 2007	
Canada – New Brunswick High organic, finfish site	253	Chou et al. 2002	
Australia - Huon High organic, finfish site	13 - 254	AMD (2004 – 2007) †	
Australia - Huon Low organic, finfish site	19 - 305	AMD (2004 – 2007) †	
NZ - Te Pangu Low organic, finfish site	68 - 130	Forrest et al. 2010a	
NZ - Ruakaka High organic, finfish site	180 - 620	Forrest et al. 2010b	
* As reported in Macleod & Eriksen 2009			

* Contaminated site adjacent to zinc refinery



2.4. Possible biological effects of copper and zinc

2.4.1. Overview

It is assumed that sediment copper and zinc concentrations above guideline trigger values will adversely affect local biota, and potentially ecosystem functions, as they concentrate and persist near farm sites (Macleod & Eriksen 2009). After several decades of single-species toxicity studies, researchers have demonstrated that marine organisms vary in their relative accumulation and tolerance of trace metals, due in part to differences in uptake pathways and metals changing bioavailability and speciation. Metal toxicity is also influenced by biotic factors, such as the age, sex and size of an organism (WHO 2001). Numerous studies have shown that most embryo and larval stages are much more vulnerable to contaminants compared to adults (*e.g.* Macleod & Eriksen 2009). As a result, marine organisms' responses to increasing concentrations of any one trace metal vary considerably, even within a species.

Benthic community dynamics (*e.g.* species composition, abundance and diversity) and functions (*e.g.* microbial mineralisation processes) are known to be highly dependent on the physical, geological, chemical and biological conditions of the local environment. When metal concentrations in sediments reach extremely high levels, benthic assemblages can be adversely affected to the point that the regular functioning of such communities is comprised (*e.g.* Rygg 1985, 1986; Magalhaes *et al.* 2007 as cited in Macleod & Eriksen 2009).

The organism to community level effects of copper and zinc contamination on individual biota, benthic communities and ecosystem functions can include:

- Increased metal concentrations above a threshold cause a breakdown in an organism's internal metal regulation or accumulation, leading to sub-lethal or acute (mortality) toxicity effects
- Common sub-lethal effects in marine organisms include inhibited growth and settlement of larvae, interference with respiration, metabolism, reproduction and/or abnormal behaviours
- High variability in chronic and/or acute toxicity effects in both pelagic and benthic organisms ranging from phytoplankton, zooplankton, crustacea, molluscs, echinoderms, annelids and fish
- Generalised community effects including absence (due to avoidance or mortality) of intolerant species and/or temporary increases in abundance of tolerant species
- Extreme metal concentrations generally leading to reduced diversity and composition of benthic fauna
- Changes to microbiota affecting benthic functions through altered geochemical processes that regulate the cycling, bioavailability, and fate of micro and macronutrients

It is important to note that most of the metal toxicity results discussed were obtained experimentally and often involved adding soluble copper or zinc to clean seawater (*e.g.* no complexing agents), implying much higher concentrations of free metal ions were biologically



available to test organisms than would naturally occur around a farm site. Additional and more detailed information on the possible biological impacts of copper and zinc on individual marine taxa can be found in the Appendix.

2.4.2. Possible effects on biota

In order to understand and mitigate how metal contaminants concentrated underneath a farm might generally affect the local system, we first need to determine how individual metals can affect particular benthic taxa. Essential trace metals are needed by marine organisms for normal physiological development and metabolic functions, and as such are either regulated or bioaccumulated. Regulation means that an organism will take up metals at levels present in the surrounding environment, yet control internal concentrations of particular metals within their body by actively removing excess amounts (WHO 2001). Bioaccumulation means that organisms will take up contaminants from the surrounding environment, and store any unused amounts within their bodies (Smith & Williamson 1986; Culshaw *et al.* 2002).

Copper is a component of some enzymes and proteins that are important for iron utilisation as well as osmoregulation (Thurberg *et al.* 1973). Zinc is present in over 300 enzymes, and used for membrane stability and the metabolism of proteins and nucleic acids (WHO 2001). If levels greatly exceed an organism's normal requirements, these particular trace metals begin to interfere and/or compete for enzymes or membrane protein sites. If regulation processes start to breakdown, this can lead to a greater influx of metals that can no longer be removed and are bioaccumulated instead. As metals internally accumulate past an organism's threshold, they become increasingly toxic to the animal itself (Thurberg *et al.* 1973).

Marine species are exposed to metal contaminants through the water column (*e.g.* across the body wall and/or gills) and/or from accumulation in their prey sources. Depending on their lifestyle (*e.g.* pelagic versus benthic), some species may also come in contact with and/or ingest contaminated sediments and porewater (Chapman *et al.* 2002; King *et al.* 2006). Most marine invertebrates are sedentary in their lifestyle, moving only small distances over their lifetimes. Hence they are most vulnerable to localised contaminants as they can accumulate metals through all three of the pathways described above.

Single-species toxicity tests attempt to quantify the biological response of an organism to different metal contaminants. Chronic tests focus on how sub-lethal concentrations affect the physiology or behaviour of a species, while acute tests determine what concentration and/or exposure rates are lethal. Toxicity from copper can quickly interrupt the normal metabolic process of the cells causing reductions in growth rates, loss of osmoregulatory functions, weight and biomass loss, dysfunctional sensory responses, shortened lifespan and/or reduced resistance to infectious diseases (*e.g.* Atchison *et al.* 1987; Rainbow 1995; Brooks & Mahnken 2003; Dauvin 2008). Potential adverse effects of zinc range from interference with growth, reproduction, ATP production and mitochondrial electron-transport activity, osmoregulatory failure, pancreatic, gill or immunity damage, and/or behaviour abnormalities (*e.g.* Stauber & Florence 1990; Eisler 1993; Burridge *et al.* 2008). Toxicity effects are often intensified



through additional environmental stressors, such as low salinity or warmer water temperature (Thurberg *et al.* 1973; Chapman & Wang 2001).

McLusky *et al.* (1986) was one of the first to conclude that experimental toxicity values needed to be determined over a range of environmental conditions and species life stage to be meaningful. Based on species living in estuaries in various degrees of metal contamination, the authors proposed a general trend of decreasing sensitivity of different taxonomic groups to metal pollutants. They suggested that annelids were the most sensitive, followed by crustaceans and molluscs as the least sensitive. Similar approaches have compared the sensitivity of a particular species to different metals. For instance, toxicity tests on sea urchin larvae with different metals found mercury to be the most toxic, followed by copper and lead, with cadmium as the least toxic (Fernandez & Beiras 2001). Due to their range of sensitivities to environmental contaminants and the variety of habitats they occupy, several marine invertebrate species are used as proxies for potential contamination.

We found little information on the toxicity effects from ingesting metal-contaminated food (biomagnification) and/or the long-term persistence of metals within marine organisms. Macleod & Eriksen (2009) note that trophic transfer and biomagnification of metals is an environmental concern associated with finfish farms, however, according to Smith & Williamson (1986) biomagnification of metals is not common. The authors noted only a few instances in which metals have been found to transfer between two successive trophic levels, mercury being the exception. According to the World Health Organisation (WHO 2001), zinc is not biomagnified up the food chain. There also appears to be no evidence that metal biomagnification (copper, zinc or cadmium) occurs within estuarine food chains (Dauvin 2008).

2.4.3. Possible effects on benthic ecology

If the individual toxicity effects of copper or zinc are chronic enough to hinder the reproductive capabilities of a large portion of a particular species, then the local population of the species as a whole begins to decrease (Morrisey *et al.* 1996). As the metal loading continues, the more sensitive species will leave and/or be replaced until only the most robust or tolerant species remain.

Studies in Australia and Norway, in which the concentrations of copper in marine sediments were experimentally or naturally enhanced, found that increased copper loads impacted benthic diversity and abundance. Morrisey *et al.* (1996) experimentally increased copper concentrations in sediments above ambient levels. They found that either taxa abundance decreased or remained constant with increasing copper levels, while the abundance at control sites increased or were also constant through time. In general, the authors found that benthic diversity tended to decrease when sediment copper concentrations were greater than 100 to 150 mg/kg dry weight. Rygg (1985) observed similar responses between species diversity and copper concentrations, as well as a much weaker correlation with zinc concentrations, in Norwegian fjords. That study described intolerant species (*e.g.* some annelids, crustaceans,

and bivalves) as absent from sediments with copper concentrations greater than 200 mg/kg. Only a few annelid species, considered to be highly tolerant, were present at the most polluted sites, >500 mg/kg copper.

While the nature of the response varied among taxa in both studies, Morrisey *et al.* (1996) and Rygg (1985) concluded that increased sediment copper (and to a lesser extent zinc) reduced the diversity and composition of benthic fauna. Based on similar observations, McLusky *et al.* (1986) derived a general ranking system for benthic community responses to metal toxicity in estuary sediments: the most toxic was mercury > cadmium > copper > zinc > chromium > nickel > lead > arsenic as the least toxic.

Morrisey *et al.* (1996) noted that changes in the abundance or diversity of benthic macrofauna in turn can affect microbiota, either directly through predation or indirectly through alteration of sediment conditions (*e.g.* bioturbation). Benthic microbiota are the microorganisms (*e.g.* bacteria, protozoa, microalgae) that naturally occur within marine sediments, and are linked to such primary processes as nutrient cycling (decomposition) and redox (Cooper *et al.* 2005).

As with previous taxa, different microorganisms exhibit varying levels of sensitivity to metal contaminants. Earlier studies have found that microbial communities are extremely sensitive to even very low levels of free copper ion (Jonas 1989). Flemming & Trevors (1989) found that some microbial populations could develop a tolerance to sustained copper levels in a relatively short time scale, given their short generation time. These more tolerant species tended to out-compete other species, and dominate decomposition and redox processes, potentially affecting the many other biogeochemical processes within benthic habitats (Cooper *et al.* 2005).

In general, Flemming & Trevors (1989) found that increased copper levels in sediments caused a decrease in microbial abundance and diversity, which led to an associated decrease in mineralisation and production processes. For example, a study by Magalhaes *et al.* (2007), as described in Macleod & Eriksen (2009), found that copper and zinc inhibited certain stages of the denitrification process in both high organic (silty sediments) and low organic (sandy sediments) sites to varying degrees. As the authors pointed out, this interference from trace metals can negatively affect the overall effectiveness of the estuary at removing nitrogen while allowing its release in the form of greenhouse gases, N_2O .



3. CURRENT MONITORING GUIDELINES AND THE NEW ZEALAND SITUATION

The available ecotoxicological and biological assessments discussed in the previous section, while highly variable between taxa, can be used to establish guidelines that predict the general concentrations at which metals in marine sediments will have biological effects on the local ecology. To place current copper and zinc concentrations reported under New Zealand salmon farms in context, this section will:

- Examine current monitoring data on copper and zinc levels under salmon farms in the Marlborough Sounds, and compares these results to overseas data as well as the current New Zealand and international guidelines used to predict the general concentrations at which metals in marine sediments will have biological effects on the local ecology
- Investigate what lessons may have been gained from monitoring metal levels under inactive finfish sites (fallowed) that are allowed to recover

3.1. Sediment Quality Guidelines (SQGs)

In general, current guideline values for metal contaminants in New Zealand aquatic sediments (including finfish farms) are fairly similar and only slightly less conservative than overseas guidelines (Table 6). New Zealand's guideline values are determined by the Australian and New Zealand Environment and Conservation Council's (ANZECC) 2000 Interim Sediment Quality Guidelines (ISQGs). ANZECC guidelines represent risk-based criteria developed using the best available overseas data, and mainly formed around the US National Oceanic and Atmospheric Administration (NOAA) research that applies the known effects of a contaminant into concentration ranges known as trigger values. The values are further refined with any new or existing New Zealand or Australian data on metal levels in sediments.

The values of the ISQG indicate the threshold concentrations of metals at which 'possible' (*i.e.* low) and 'probable' (*i.e.* high) biological effects have been found to occur (Table 6). The ANZECC ISQG trigger low value is equivalent to the effects range low (ERL) in the NOAA system. Contaminant concentrations below this value are expected to cause rare to minimal biological effects. The ISQG-High value is equal to effects range median (ERM) meaning the contaminant levels exceeding this value are expected to have adverse biological effects.

Some countries, such as Canada, use sediment criteria based on marine sediment quality standards developed originally by the Florida Department of Environmental Protection (FDEP). Canadian Environmental Quality Guidelines (CEQG) for marine sediments include a lower ISQG trigger value and a higher probable effects level (PEL) value (Table 6).

Guideline	Trigger Value	Copper (Cu) (mg/kg)	Zinc (Zn) (mg/kg)
ANZECC	ISQG-Low 10% Possible biological effects	65	200
(AU & NZ)	ISQG-High 50% Probable biological effects	270	410
NOAA	Effects range low (ERL)	34	150
(USA)	Effects range medium (ERM)	270	410
CEQG	ISQG-Low	18.7	124
(CAN)	Probable effects level (PEL)	108	271

Table 6.The sediment quality guideline values from New Zealand/Australia, United States of America and
Canada for copper and zinc levels in marine sediments.

3.1.1. Aquaculture-specific guidelines

Tasmanian finfish farm permits to operate in Australia are dependent on farms not exceeding the ANZECC (2000) IQSG-High trigger values within the lease area. Currently in New Zealand, there are no definitive courses of action if the ANZECC limits under a finfish farm are exceeded due to the recognised uncertainties over whether the levels are biologically relevant, or if they are in fact contributing to the observed impacts. Alternatively, the impacts may be dictated solely by organic enrichment so that metal impacts are not manifested.

Worldwide there are only a few aquaculture-specific guidelines and sediment monitoring protocols associated with finfish farms. The Scottish Environment Protection Agency (SEPA) has developed a regulatory tool, called the Allowable Zone of Effect (AZE), which is placed at 100 m beyond the farm perimeter (SEPA 2000). SEPA has derived sediment quality criteria (SQC) that correspond to standards inside the AZE, a SQC-Low value of 108 mg/kg for copper and 270 mg/kg for zinc indicating "potentially problematic" benthic impacts, that are higher than criteria outside the farm (34 mg/kg copper and 150 mg/kg zinc). SQC-High trigger values are the same inside and outside the AZE; 270 mg/kg for copper and 410 mg/kg for zinc representing "probably adverse" impacts.

The AZE approach acknowledges that concentrations will be higher under a farm (hence the different trigger values inside and outside the AZE), and is designed to control the degree and spatial extent of impacts from farms on marine sediments. In addition, SEPA has developed *Seabed Monitoring and Assessment* (2008) protocols that recommend survey strategies for assessing benthic health within existing and new farm sites. Such databases are used when issuing new licensees or upgrades to existing farms. Canada also has developed *Protocols for Marine Environment Monitoring* (2002) to support new regulations around finfish aquaculture



waste controls. The protocols were developed with regard to aquaculture, ensuring benthic monitoring standards were assessed based on high quality, relevant data.

3.2. New Zealand situation in a global context

3.2.1. Overview

Current monitoring practices of salmon farming operations in the Marlborough Sounds assess bulk metal levels in the sediments from beneath the farm only. Monitoring results have shown a general rise in average metal levels within most operative farm sites since 2002, with values of zinc generally greater than copper. Frequent, but irregular exceedance of ANZECC metal trigger values (high and low) is commonly reported from year to year with little to no consistency. Most farms demonstrate a general decrease in both metal levels with distance from the farm, yet, samples are highly variable.

The New Zealand situation is not unusual, with similar levels of variability noted in most overseas farms as well. Several studies demonstrated short-term temporal trends in sediment concentrations of zinc that were attributed to corresponding trends in harvest cycles (*i.e.* feeding schedules). Other studies have suggested spatial variability implied the involvement of different dispersion mechanisms, or that spatial trends in copper were likely due to heterogeneous distribution of paint flakes/chips in sediments.

3.2.2. New Zealand monitoring data

As part of their resource consent conditions, NZKS are required to undertake annual seabed monitoring of their salmon farm sites in the Marlborough Sounds. The average copper and zinc levels of sediments underneath these farms have been documented for at least the last five years, along with a fallowed site (Forsyth Bay) and reference sites in Pelorus and Queen Charlotte Sounds. As demonstrated in Figure 2, average levels of both metals are highly variable showing few temporal trends over the sampling years or between farm sites. The only exceptions are the fairly steady results within reference sites, and a general annual increase in both metals within the newer Clay Point farm site.



Figure 2. Average copper and zinc concentrations beneath the cages at five salmon farms in the Marlborough Sounds, one of which (Forsyth) has been fallowed since 2001, and from two control sites in the Pelorus (P.S.) and Queen Charlotte (Q.C.) Sounds (modified from Forrest *et al.* 2010a).

Monitoring results have shown a general rise in average copper levels within most operative farm sites since 2002. Over the past five monitoring years, all sites operating since 2006 have exceeded ANZECC (2000) ISQG-Low trigger values for at least two years or more, and ISQG-High values one of the five years (Figure 2). However, annual copper levels vary considerably from one year to the next (Forrest *et al.* 2010a,b,c). This irregular variance may be due to outside factors, such as the timing of predator net defouling in relation to monitoring surveys (Hopkins *et al.* 2006), or more likely the fact that anti-fouling paint tends to ablate in flakes or chips that continue to leach copper (Singh & Turner 2009). Turner *et al.* (2008) found that copper levels within sediment samples near boating maintenance facilities had considerable variation among different sample and within replicate subsamples. They attributed these 'hotspots' to heterogeneous distribution of paint chips in sediments.

The average zinc levels under the same farm and reference sites have been generally greater than copper, and exceeded ISQG-Low and -High trigger values more frequently (Figure 2).

The exceptions are the newer Clay Point and Te Pangu site, both areas associated with higherenergy environmental conditions that potentially lead to greater dispersion of any farm wastes (Hopkins *et al.* 2006). Similar to the copper results, no temporal trends in zinc concentrations were apparent (Figure 2).

Inconsistent variability and frequent, but irregular exceedance of metal trigger values is commonly reported in other New Zealand and overseas farms (Figure 3). Morrisey *et al.* (2000) measured the concentration of copper and zinc within sediments beneath a poorly flushed farm site in Big Glory Bay (Stewart Island) that had been fallowed for 12 months prior to sampling. Zinc concentrations were consistently high and exceeded ISQG-High trigger values, while copper levels were similar to control sites, but with a few high subsamples recorded. Dean *et al.* (2007) found a large proportion, but not all of the sediment samples within the AZE of Scottish farms exceeded ISQG-High and -Low levels for both copper and zinc. Brooks & Mahnken (2003) found that eight out of 27 British Columbian farms exceeded zinc levels, while five out of 14 farms using anti-foulant nets exceeded sediment levels for copper. Schendel *et al.* (2004) also recorded several of their British Columbian sediment samples had zinc levels greater than CEQG ISQG-Low levels within the farm site, but copper was highly variable.



Figure 3. A comparison between the maximum, average and corresponding reference concentrations of copper and zinc reported beneath salmon farms in Tasmania, Canada and Scotland with New Zealand (Te Pangu and Ruakaka 2009 monitoring data).

A few recent studies have noted short-term temporal trends in sediment concentrations of zinc, but not copper. Brooks & Mahnken (2003) and Dean *et al.* (2007) measured sediment levels over an 18-24 month and seven month harvest cycle, respectively. Temporal trends in zinc levels were attributed to corresponding trends in harvest cycles; as fish are growing, feed is increased but closer to the harvest time, feed levels dramatically decreased as did zinc levels. Copper concentrations were not observed to increase over a growing season.

Spatial variations in metal concentrations inside and around farms is another aspect commonly reported with benthic monitoring results, but still not well understood. Dean *et al.* (2007) noted that copper and zinc concentrations within sediments under Scottish salmon farms decreased with increasing distance away from the farm. The authors found that background levels of these metals (based on constant metal concentrations found between 8-17 cm deep) were reached within surface sediments approximately 300 m from the centre of the farm in line with the direction of the residual current. Brooks & Mahnken (2003) spatial analyses of metal levels in surface sediments around British Columbian farms found elevated levels declines to background levels between 30-75 m down-current of the farm. Two additional Canadian studies at New Brunswick (Chou *et al.* 2002) and British Columbia (Schendel *et al.* 2004) both found a major reduction of zinc concentrations in sediment from over 50 m and 100 m away, respectively.

In Stewart Island, Morrisey *et al.* (2000) noted that earlier monitoring work prior to fallowing had shown that metal effects did not extend past 50 m. After 12 months in fallowing, the authors collected metal levels in surface sediment under and out to 100 m from the farm. Zinc levels, while high, declined with distance while copper levels tended to vary more spatially. Chou *et al.* (2002) also noted some elevated copper levels at 50 m samples however they appeared to be related to the organic carbon levels and/or particle size. Schendel *et al.* (2004) found no spatial trends in copper levels within surface sediments as farm samples were lower than all others. Schendel *et al* (2004) suggested that these spatial results implied that different mechanisms are involved in copper and zinc dispersion under the farm, while Morrisey *et al.* (2000) thought that a locally high, yet spatially variable trend in copper was likely due to still existing particles of paint within the sediments.

Figure 4 shows a comparison of the spatial distribution of copper and zinc concentrations in sediments under farms, at compliance sites (usually between 30-50 m) and at reference sites as reported in the literature for Australia (Tasmania – Macleod & Eriksen 2009), Canada (New Brunswick – Chou *et al.* 2002, British Columbia – Obee 2009) and in the Marlborough Sounds, New Zealand (Forrest *et al.* 2010a,b,c). While the above reports all discuss some level of variability in individual samples, these examples show a general decrease in both metal levels to control concentration within 50 to a few hundred metres of the farm. However, it is important to note that this distance appears to be variable, depending on site conditions and production levels.





Figure 4. The average copper and zinc concentrations collected at various distances beneath cages at two salmon farms in Australia, two salmon farms in Canada, and from one salmon farm in New Zealand. Compliance site distances ranged from 30-50 m and reference sites were located between 200-500 m from the farm centre. * indicates that the only Marlborough Sounds farm with spatial sampling is the Forsyth Bay site, in fallow.

3.3. Fallowing of finfish farms

3.3.1. Overview

A recovering salmon farm in Forsyth Bay (Marlborough Sounds) has demonstrated slow but steady chemical and biological remediation since the site was fallowed in 2001. However after eight years, copper and especially zinc concentrations in sediments have remained elevated (Forrest *et al.* 2010c). While it appears the farm is recovering, we cannot rule out the possibility that elevated zinc, and to a lesser extent copper, levels have slowed benthic recovery.

Based on overseas examples, it appears fallowing of severely impacted/enriched farm sites (*e.g.* Forsyth Bay) or within low current/high depositional locations will take much longer than the six months to two years originally predicted by Brooks *et al.* (2003). It seems that fallowing, in general, is influenced by several different factors that result in "progress and

regression" of the recovery process (Karakassis *et al.* 1999). For example, fluctuations between reduced and oxidised conditions in recovering surface sediment released phosphorous, causing a benthic algal bloom that slowed the benthic fallowing process under a Greece finfish farm. Section 2.4.3 also indicated that metal-related reductions in microbial abundance and diversity may also negatively affect long-term benthic mineralisation and production processes (*e.g.* Flemming & Trevors 1989).

Karakassis *et al.* (1999) concluded that short-term temporal processes can vary considerably in coastal environments, and therefore monitoring needs to be based on several variables and adequate time scales to account for short-term deviations in recovery. Fallowing work on a Stewart Island salmon farm also suggested that adequate spatial and temporal replication in studies of impact and recovery are needed to overcome the inherit variability in sediment metal concentrations (Morrisey *et al.* 2000).

3.3.2. Fallowing process

Fallowing entails a rotational use of available finfish farm sites (Karakassis *et al.* 1999). The idea is that by leaving a few sites empty for a period of time, the surrounding environment will have a chance to completely recover from any farm-associated impacts. By continuing to monitor a fallowing farm site as it 'recovers', scientists are able to study how and at what rate sediment chemistry and benthic fauna can be expected to improve. Determining the fate of metal contaminants is essential for understanding their continued interactions with ecosystem processes and how they might affect the recovery process.

Brooks *et al.* (2003, 2004) observed that the complete remediation of an impacted farm site occurs on a variable time scale from several months to several years depending on the level of impact and recovery conditions such as water currents, dissolved oxygen in the water column and the availability of opportunistic, tolerant species for recruitment into the affected area. The authors described two types of remediation during fallowing periods: chemical and biological remediation.

Chemical remediation generally occurs first and is signified by a decrease in organic carbon to reference levels with an associated reduction in free sediment sulphides, and a return in sediment redox potential to levels in which more than half the reference area taxa can recruit and survive. The authors considered biological remediation had occurred when infauna taxa whose individual abundance equals or exceeds 1% of the total invertebrate abundance return to the site. The authors point out that biological remediation does not consider the return of rare infauna species necessary as they are often much slower to recruit back to a site.

Brooks *et al.* (2003) study of several British Columbian salmon farms found that chemical remediation generally began as soon as harvest was initiated (as feed input decreased), and was often completed by the time the harvest finished six to nine months later. Biological remediation was slower, but usually completed within six months after chemical remediation.

However, Brooks *et al.* (2003) definition of chemical remediation does not take into account trace metal levels in sediments. During fallowing, the first stage of recovery is the mineralisation of accumulated wastes. By re-oxidising sediments, the amount of metal-binding phases decreases and the remobilisation of any previously bound metals occurs (Morrisey *et al.* 2000). Several studies have proposed that high levels of bound zinc and copper in fallowing sediments would become toxic (*i.e.* bioavailable) during chemical remediation, and adversely affect further biological remediation and/or accumulate from one production cycle to the next (*e.g.* Morrisey *et al.* 2000; Brooks & Mahnken 2003; Dean *et al.* 2007; Obee 2009).

3.3.3. New Zealand fallowing data

NZKS' salmon farm in Forsyth Bay (Marlborough Sounds) has been in fallow (including all structures) since 2001. Some chemical remediation appears to have begun within the site as the percentage of organic content (ADFW) in sediments has slowly, yet steadily declined since 2003 (Figure 5a). This improvement in benthic conditions is also evident by a general increase in species richness (number of taxa) and abundance in sediments beneath and adjacent to the site (Figure 5b,c). In addition, these changes have been associated with a large reduction in the number of opportunistic polychaetes (*Capitella capitata*). Community composition analyses suggest that there is still evidence of some existing enrichment gradient (Forrest *et al.* 2010c).

However, copper and zinc concentration in sediments remain elevated (Figure 5d,e). Unfortunately we do not know the initial concentrations of these metals within the farm site prior to fallowing, as they have only been sampled since 2005. No temporal trends in metal levels are evident, although copper concentrations are generally low compared to even Canadian sediment guidelines (CEQG). Yet, zinc concentrations have remained high (near ANZECC 2000 ISQG-Low) and variable after eight years in fallow.

The Forsyth Bay farm presents an interesting situation in which chemical and biological remediation are evident, however have taken significantly longer than other sites in the Marlborough Sounds. Prior to being fallowed, the sediments beneath the site were highly enriched, with extensive coverage of the seabed by bacterial mats, highly elevated organic contents and out-gassing at the water surface. Infaunal abundance and richness were both markedly suppressed, indicative of near-azoic conditions (Forrrest *et al.* 2007). Since it has been fallowed, there has been a reduction in the magnitude of effects, including reduced sediment organic content, increased species diversity and abundance, and a corresponding decrease in the number of opportunistic species. While it appears elevated zinc levels have not prevented infauna communities from recovering, we cannot rule out the possibility that they have slowed/inhibited the recovery rate as suggested above.



Figure 5. Average AFDW, total infauna abundance, total number of taxa and copper and zinc concentrations found beneath the cages at a fallowed salmon farm in the Marlborough Sounds. Note the farm was fallowed in 2001 and no zinc or copper data was collected prior to 2005. Error bars represent standard deviation (s.d.).



Fish farm studies in New Zealand and overseas indicate timescales of recovery ranging from months to years. The rate largely depends on the spatial extent and magnitude of effects, and the flushing characteristics of the environment (Karakassis *et al.* 1999; McLeod & Eriksen 2009); essentially larger and more heavily impacted sites, or sites in areas of relatively weak currents, take longer to recover. A number of overseas studies describe partial recovery within the first 3-6 months after the cessation of farming (Mazzola *et al.* 2000; Brooks *et al.* 2003; Macleod *et al.* 2006), but complete recovery (*i.e.* comparable to background conditions) can take many years and is often not fully realised in the timeframe of monitoring programmes (*e.g.* Karakassis *et al.* 1999).

A similar fallowing situation to Forsyth Bay has recently been reported by Obee (2009) in Canada. An atypical British Columbia farm site, known for being significantly high in free sediment sulphides and sediment copper and zinc concentrations (*i.e.* a maximum of 220.9 mg/kg and 1062.0 mg/kg respectively), was monitored two years prior to fallowing and continued for another six years after. Monitoring has demonstrated a slow and significant remediation in sediment enrichment with time and distance from the farm, but not in metal concentrations. Both copper and zinc levels remained high, although zinc more so than copper, and generally variable from year to year. Obee (2009) noted the presence of some benthic macrofauna, mainly carbon-tolerant species, and considered this an indication of remaining enrichment in the site. Despite elevated metal concentrations at the same sites, the author did not mention metals as a possible reason.

Overall, the study predicted at least 13-15 years in fallow was needed for free sediment sulphide levels to return to background conditions with metal remediation expected to take even longer. Obee (2009) makes an important point that metal contaminants will continue to accumulate over production cycles if fallowing management only requires farms to recover from organic enrichment, and not the potentially longer periods needed for metal remediation. However, the author noted that further chemical remediation may result in metals becoming more bioavailable, therefore recommended that further evaluations of metal speciation and bioavailability were needed to explain metal trends and any potential for continued or future impacts. Interestingly, despite numerous studies highlighting the assumption that metal bioavailability/toxicity increases within recovering sediments and that this might hinder biological remediation, our literature review did not find any studies that empirically tested metal bioavailability from sediments over a fallowing period.

4. KNOWLEDGE GAPS

4.1. Overview

This review has noted several issues in which more information or research is needed before any definitive decisions around current metal levels in sediments under finfish farms in the Marlborough Sounds can be considered. From the current literature, we are unable to fully resolve how elevated metal levels underneath finfish farms may add to or compound the known effects of organic enrichment. This issue is complicated due to similar benthic responses (*e.g.* decreased abundance or diversity) to these different impacts (*i.e.* enrichment or metal). Further research focused on the bioavailability of metals is required in order to better understand any synergistic/antagonistic factors that may affect recovery rates.

Several aquaculture monitoring studies have suggested that enriched sediments appear to be binding most trace metals to a high degree, making them less toxic than would otherwise be expected. However, few studies have tested these assumptions. Initial investigations by Macleod & Eriksen (2009) demonstrated the importance of testing the bioavailability of sediment-bound metals in assessing monitoring data of finfish farms. Most researchers advocate that future testing should concentrate on chemical estimates of bioavailability and ecotoxicology together, given the complexity associated with metal speciation and bioavailability.

An important information gap concerns the fate of metals once introduced to the marine environment and later during chemical remediation (*e.g.* during a fallowing period), as their concentrations in sediments have been documented to decrease with time, especially zinc (Brooks *et al.* 2003). As conservative contaminants, metals do not degrade. Instead they are either mixed deeper into sediments and/or dispersed from the local environment. As locally relevant conditions can greatly affect metal speciation, the possible fate(s) of metals cannot be generalised across regions. Instead, final fate needs to be calculated on a site-by-site basis.

Finally, industry currently employs several measures aimed at minimising or reducing chemical source inputs from marine farms into the local environment. Given more research and/or information, there may be additional operational issues that may help further reduce the amount of metal released into the marine environment.

4.2. Synergistic/antagonistic effects

4.2.1. Adverse effects confounded with enrichment effects

One of the most common environmental effects of finfish aquaculture worldwide is the production of large amounts of concentrated organic wastes (uneaten feed, faeces and biofouling biomass detached from cage structures) that are deposited within a fairly localised area of the benthos under and around the farm structure (*e.g.* Karakassis *et al.* 1999; Pearson & Black 2001; Forrest *et al.* 2007). Particulate organic material is typically degraded by

microbes in the benthos. However, the large amount of organic wastes generated under farms quickly depletes oxygen from sediment porewaters. When oxygen demand exceeds supply, the sediments can become anoxic and generate sulphides through sulphate reduction, the dominant anaerobic process in coastal sediments (Pearson & Black 2001; Dean *et al.* 2007).

Organic enrichment disrupts sediment biogeochemical processes and functions, which in turn negatively affects benthic macrofauna and microbial communities. Macrobenthic communities affected by finfish farm enrichment generally are lower in both abundance and diversity, but the impacts tend to diminish with increasing distance from the cages (Karakassis *et al.* 1999; Brooks *et al.* 2003). Enriched sediments are generally dominated by a few small, opportunistic and carbon-tolerant species that can occur in very high abundances (Figure 6; *e.g.* Karakassis *et al.* 1999; Pearson & Black 2001). Typically, species richness declines with increasing enrichment, although an area of increased richness can sometimes be evident in mildly enriched regions just beyond the highest impact zone. Particular taxa are considered indicative of enrichment. These include subsurface deposit feeders or particular polychaetes, such as *Capitella capitata* and *Ophryotrocha* spp. (Karakassis *et al.* 1999; Brooks *et al.* 2003).



Figure 6. Changes in sediment organic content or infaunal communities along typical salmon farm enrichment gradients – a stylised depiction of changes in infaunal abundance and species richness (number of taxa – modified from Forrest *et al.* 2007).

Depending on the loading rate of wastes, length of impact and oceanographic conditions, enrichment usually results in a decreasing gradient of organic enrichment outward from the farm structures. Benthic communities and functional processes can be similar to background conditions within a few hundred metres of a farm (*e.g.* Brooks *et al.* 2003).

Studies of metal enrichment in sediments exposed to extensive mining or smelting operations, and/or industrial sewage discharge have shown similar effects on the benthos. As metal concentrations increase, benthic community structure is generally impacted with a loss of diversity and abundance. Metal burdens of sampled species are highest near the most impacted sites; generally affecting reproduction and/or growth, and survival of individual species (*e.g.* Hornberger *et al.* 2000; Borgmann *et al.* 2004).

A manipulative field study of copper toxicity (Morrisey *et al.* 1996) was conducted with fairly coarse and oxic sediments (ensuring that enrichment factors were not significant in the strength with which copper was bound to sediments). Their study demonstrated that copper in marine sediments significantly affects benthic assemblages. Taxa responses in terms of abundance were varied, but diversity was generally reduced when sediment copper was greater than 100-150 mg/kg. The bioavailability of copper in their study, although not tested, would likely have been relatively large and observed effects greater than in finer sediments with some organic enrichment.

Such responses of benthic fauna to both organic enrichment and metal impacts complicates attempts to identify any separate or cumulative effects that elevated metals might have on a benthos already enriched organically by finfish farming. Analysis of the environmental data collected as part of the annual monitoring of salmon farms in the Marlborough Sounds illustrates this problem.

There is a high correlation between the organic content in the sediments (AFDW) and copper and zinc concentrations (Table 7, Figures 7-8). There is also a strong negative relationship between AFDW (and therefore copper and zinc concentrations) and species richness (*i.e.* number of different infauna taxa present). These patterns are evident in the MDS plot (Figure 8), which graphically represents differences between sites due to the relative abundances of taxa in the sample. AFDW, copper and zinc concentrations have been overlaid on the MDS distribution to illustrate their relationships with the infauna community. Most notable is the similarity in the patterns of the zinc and AFDW (Figure 8).

Table 7.Pearson correlation coefficients between pairs of environmental variables for samples from the
seabed beneath salmon farms in the Marlborough Sounds. The variables Cu (copper), abundance
and the number of capitellids were log transformed with 'missing' values interpolated using
missing function in Primer v6.

	Zn	logCu	%Mud	AFDW	logAbund.	Richness
logCopper	0.726					
%Mud	-0.318	-0.414				
AFDW	0.875	0.620	-0.131			
logAbundance	-0.096	0.195	-0.518	-0.272		
Richness	-0.757	-0.657	0.056	-0.828	0.319	
logCapitellids	0.143	0.524	-0.591	0.053	0.789	-0.103





Figure 7. Draftsman plot of sediment characteristics beneath salmon farms in the Marlborough Sounds. Copper concentrations, infauna abundance and the number of capitellids were log transformed.



Figure 8. (A) MDS plot of fourth-root transformed infauna data based on Bray-Curtis similarity matrix from samples collected beneath and around Marlborough Sounds salmon farms. (B) MDS with relative copper concentration. (C) MDS with relative AFDW values and (D) MDS with relative zinc concentrations.

Chou *et al.* (2002) also recorded similar correlations between organic carbon and metal concentrations. They found that copper, zinc, organic carbon and smaller sized particles all increased as environmental conditions became more degraded. However, this study did not test associated trends in benthic fauna. Instead, they measured accumulated metal levels in lobsters, an epibenthic species known to be a bioindicator of metals.

Rygg's (1985) Norwegian fjord study found differences in benthic community responses to the effects of organic pollution versus the effects of metal pollution. Rygg noted that increased levels of copper (and to a lesser extent, zinc) resulted in decreased species diversity, with similar declines present for both rare and common species. Alternatively, high levels of organic matter also resulted in a decrease in diversity, but with an associated increase in total abundance of tolerant species. He noted that these subtle differences were only evident when loads were moderate. Extremely high levels of either pollutant resulted in both a drop in diversity and elimination of non-tolerant species.

Macleod & Eriksen (2009) discussed a recent study by Simpson & Spadara (2008) that determined copper bioavailability within finfish sediments from Australian sites with varying organic content levels. Standard chemical tests established that 50% of all high organic content samples exceeded ANZECC ISQG-High values for total copper. Additional bioavailability analyses on the same samples reported much lower copper concentrations, suggesting that most of the copper found from standard tests was essentially unavailable. Further toxicity testing showed that sediment samples were non-toxic to juvenile amphipods after 10 days of exposure. As the amphipod species tested (*Melita plumulosa*) is known to be sensitive to dissolved copper, Simpson & Spadara (2008) concluded that very little copper was available to the organisms and, with the results of the acid-solubility tests, confirmed that most of the copper must be bound to sediment.

It is still unclear how elevated metal levels underneath finfish farms affect benthic communities in addition to organic enrichment. The toxicity of metals appears dependent more on the conditions under the farms and varying levels of enrichment. Morrisey *et al.* (1996) summarised the situation best when they stated that "...the toxicity of copper is dependent on its activity rather than on its total concentration."

4.2.2. Interactions between metals

Since elevated levels of copper and zinc occur together in sediments below salmon cages, it is possible that they may interact with each other in a synergistic way to cause even more deleterious effects (Burridge *et al.* 2008). Eisler (1993) listed several previous studies that found mixtures of zinc and copper were generally "more-than-additive" in toxicity to a variety of freshwater and marine organisms (mainly larvae, plankton and fish), but "less-than-additive" in toxicity to some marine amphipods. It appears that if one metal is present in much greater concentrations than the other, the greater of the two may depress or interfere with the normal nutritional or physiological functions of the lesser. However, simultaneous exposure of copper and zinc generally resulted in enhanced uptake of both metals by marine organisms.



4.3. Bioavailability

As discussed previously (Section 2.2.2), the issue of metal bioavailability is highly complex. Bioavailability is determined by metal speciation, which is strongly influenced by environmental conditions as well as physical processes. The literature suggests that metal bioavailability associated with finfish farms is largely diminished due to chemical binding within organically enriched and highly reducing sediments underneath farms (*e.g.* Morrisey *et al.* 2000; Brooks *et al.* 2003; Burridge *et al.* 2008). For example, Dean *et al.* (2007) found that the benthic community under Scottish salmon farms was considered "typical" for an enriched environment, despite sediment zinc and copper levels exceeding the SEPA sediment quality guidelines. The authors suggest that this result indicates one of two possible scenarios; either the few remaining species are very robust and can withstand a range of habitat impacts, or metal contaminants are not biologically available therefore not as toxic to fauna as predicted by guidelines.

We cannot assume that chemically bound metals will not have any biological effects or not adversely affect local fauna at some point in the future (see next section). It is important to reiterate that bound metals may still be biologically available through porewater exposure and/or ingestion (Chapman *et al.* 2002; Macleod & Eriksen 2009). There are also assumptions that re-oxidising sediments re-mobilise metals into various chemical forms, which may affect or at least slow down recolonisation by local fauna during recovery periods (see Section 3.3).

Simpson & Spadara's (2008) study, as described in Macleod & Eriksen (2009) and discussed above in relation to enrichment effects, provide an example of how testing metal bioavailability and toxicity together can help establish whether or not elevated sediment metal concentrations adversely affect local fauna. As one of their main review conclusions, Macleod & Eriksen (2009) emphasised that being able to assess the bioavailability of sediment-bound metals is vital to understanding any monitoring data around finfish impacts and progressing environmentally sustainable development of the industry.

There are a wide range of existing chemical tests presently used to estimate bioavailability including anodic stripping voltammetry (ASV-labile), ion selective electrodes (ISE) or ligand competition to name only a few. Hansen *et al.* (1996) used the ratio between simultaneously extracted metal (SEM) and acid-volatile sulphides (AVSs) from sediments as a proxy for the bioavailability (*i.e.* toxicity) of metals.

Simpson & Spadara's (2008) study used an acute, single-species toxicity test with sediments collected from underneath farms. Such tests, known as whole-sediment toxicity tests, are widely used for assessing contaminated sediments (King *et al.* 2006). Chapman & Wang (2001) recommend that whole sediment assessments should also be conducted on either locally relevant species or species more typically associated with finfish sites. In addition, any sediment standards implemented need to at least consider ambient sediment conditions and/or environmental conditions relevant to finfish aquaculture (Dean *et al.* 2007; Macleod & Eriksen 2009).

However, all of the discussed tests and methods have their limitations, as there is still uncertainty around solubility equilibria for trace metals. Macleod & Eriksen (2009) point out that the measurement of dilute acid-soluble metals (ASM) can be problematic, with significant variation in test results occurring within and between testing laboratories. Simpson *et al.* (1998) argued that using SEM/AVS to predict copper bioavailability is also flawed due to differences in solubility between copper sulphide phases and the hydrochloric acid used for extraction methods. Additional, acute testing for short-term toxicity ignores chronic (sublethal) toxicity and/or long-term effects that high metal concentration within sediments could have through ingestion pathways, bioturbation and/or chemical remediation. Therefore, it is important not to rely on any one test to estimate bioavailability (Chapman *et al.* 2002; Burridge *et al.* 2008).

Macleod & Eriksen (2009) suggested future developments around long-term monitoring guidelines should establish the relationship between toxicity tests and bioavailability estimates in order to develop monitoring protocols based either on chemical estimates of bioavailability or some surrogate for bioavailability. The authors advocate the testing of these factors over a range of operational and environmental conditions relevant to local industry and species. This combination of data would also increase the effectiveness of new modelling tools (such as the MAMPEC described below) aimed at modelling distribution and fate of metal contaminants.

4.4. Fate and metal conservation

Several authors have emphasised that a crucial step in working towards the sustainable development of finfish aquaculture is determining the final fate of persistent anthropogenic inputs of chemicals, such as copper and zinc (Dean *et al.* 2007; Burridge *et al.* 2008; Macleod & Eriksen 2009). As a conservative contaminant, any decrease in concentration simply means that metals are being 'moved' somewhere else. It is not yet known to what extent metals may be mixed deeper in sediments due to bioturbation, re-mobilised into porewater and the water column, or finally dispersed from the local environment. Burridge *et al.* (2008) summarised the two major unanswered questions concerning conservative metals: where are they transported to once re-mobilised under farms and what effects are they having on other environments?

To estimate the proportion of metal contamination in sediments attributed to finfish feed products, Dean *et al.* (2007) traced the fate of metals originating from these products through their use in Scottish salmon farms. Each month, the number and mean weight of fish were measured in order to calculate the total biomass for fish present in each cage. The total concentration of zinc (and other metals) within the feed products along with total feed input to the cages determined the overall mass of metals added to the farm.

Sample fish were dissected and their whole organs along with muscle, bone and adipose tissues were tested for metal content. Metal concentrations within each tissue were scaled up (see Dean *et al.* 2007 for more specific details) and, along with the monthly biomass of fish, used to estimate the total metal mass taken up by the farmed fish themselves. Any remaining

metal mass was assumed to be released to the environment, including metals lost from the farm in the form of faecal wastes. This calculated metal mass lost from feed was then compared to the total mass of metals found in farm sediments and porewaters to predict the percent available for impacts from feed products.

Macleod & Eriksen (2009) cite two studies by Dalgliesh (2008a,b) that used a similar mass balance approach to calculate the loss of copper to the environment in relation to the different deployment stages of nets coated with anti-foulant paints and *in situ* cleaning methods. Similar to the example above, the initial mass of copper loadings of the nets was estimated from the cuprous oxide concentration in the paint and the volume of paint actually used on the farm site. The net was removed after approximately nine months and washed. The remaining paint on the net and from washing was quantified to estimate the overall loss to the marine environment. Unfortunately, neither study tested any resulting concentrations of copper in sediments and/or water the column and therefore, the final fate of copper lost to the environment could not be determined.

Dean *et al.* (2007) points to several weaknesses with this type of mass balance approach to contaminant fate. Most involve uncertainty and/or errors around the calculations of uptake and retention of metals in farmed fish, or accounting for both background values of contaminant levels in sediments and the previous use(s) of the farm sites. However, Dean *et al.* (2007) notes that these sources of error are usually minor in their influence on budget interpretations.

Instead of a mass balance approach to questions of metal fate, Macleod & Eriksen (2009) suggest the use of computer modelling. A marine anti-foulant model to predict environmental concentrations (MAMPEC) was commissioned by the Anti-foulant Working Group of the European Paint Makers Association. While still highly dependent on appropriate and detailed data, this model simulates scenarios to predict the concentration and fate of anti-foulant products based on a range of marine environmental and physical parameters.

4.5. Operational

In New Zealand, salmon farming companies make efforts to minimise contaminant inputs in a variety of ways:

- The use of copper anti-foulant paints is minimised to structures where it is essential, and manual defouling is used on other structures.
- Together with feed supply companies, the New Zealand industry is progressively reducing levels of nutritional therapeutants in feed (*e.g.* zinc).
- The industry and feed supply companies are aiming to reduce trace contaminants in feed by replacing fish products with alternatives, and sourcing raw fish products from regions where contaminants are relatively low.

It is important that similar measures are encouraged as part of 'best management practice' with the further development of the finfish farming industry, especially where new companies and new species are involved (Forrest *et al.* 2007). Yet, there are still several unknown operational issues around the use of trace metals within finfish aquaculture which, given more information, may help resolve questions around sustainability.

For instance, further information around the levels of soluble and particulate copper that *in situ* net washing (*i.e.* water blasting and/or barge based stripping) contributes to the environment compared to net changes are vital for regional councils assessing the efficacy of current best practice standards and guidelines. Macleod & Eriksen (2009) found that *in situ* cleaning contributed a significant amount of copper in particulate form. Brooks & Mahnken (2003) noted that *in situ* cleaning is labour intensive and stressful on the fish themselves. However, the removal of nets (on barges or to land) to be cleaned and recoated can be more costly and involves the movement of fish between nets. Yet, British Columbian and Australian salmon farmers are moving towards washing nets at inland facilities and disposing of biofouling wastes at approved landfills instead of near the farm (Brooks & Mahnken 2003; Macleod & Eriksen 2009).

Currently, feed products are thought to be generally over-formulated in supplemented minerals, mainly due to lack of knowledge around nutritional requirements (Dean *et al.* 2007). As discussed earlier (Section 2.3.1), continuing research around organic versus inorganic forms of zinc and their relative level of absorption within fish is extremely important in potentially limiting the amounts of zinc and other feed-related minerals released into the marine environment. Brooks & Mahnken (2003) noted that British Columbian salmon farms that supplemented feed with the methionine analog form of zinc had significantly lower sediment zinc concentrations than zinc sulphate feed products, and these levels were similar to reference site levels.

5. SUGGESTED PRIORITIES

Annual monitoring programmes in the Marlborough Sounds currently assess bulk copper and zinc levels in sediments collected from under local salmon farms. This review found that compared to published levels from overseas, New Zealand sediment concentrations of both copper and zinc are within similar ranges to other salmon farm values, with zinc values tending more towards the higher end (Section 3.2 and Tables 2, 5). Such geographic differences in bulk metal concentrations can be attributed to natural variation in background metal levels (*i.e.* geology), the amount of initial metal input (*e.g.* variation in feed products and amounts), hydrodynamic characteristics or even methodological differences in metal testing. Resulting impacts, in turn, depend upon environmental factors that control speciation and bioavailability (*i.e.* sediment physical and chemical properties).

Metal toxicity is highly complex, and separating out individual effects is extremely difficult as evident by the paucity of crucial knowledge identified in this review. As such, several of the Envirolink's original objectives were unattainable. From the information that is available, we have outlined several actions that MDC can undertake towards achieving environmentally sustainable growth of the local finfish aquaculture industry. These suggested priorities, as discussed in detail below, are also listed in the following flowchart (Figure 9).

We recommend that MDC continues to apply ANZECC (2000) ISQG thresholds to consent conditions for salmon farm in the Marlborough Sounds (Figure 9 - #1). Any sites not achieving compliance in terms of bulk metal levels, we suggest further spatial and temporal investigation is required as a first step (Figure 9 - #2). Based on the monitoring data to date, it is unclear whether bulk accumulation of metals under farms is occurring, mainly due to variability. A better understanding of the extent of metal distribution spatially will help Marlborough Sounds' farms determine possible dispersion mechanisms; for example, whether copper is uniformly distributed across sediments or only in small, random hotspots of paint flakes in sediments. More detailed temporal sampling is also recommended to establish any corresponding short-term trends with seasonal or operational cycles.

If additional spatial and temporal sampling clearly identifies that bulk accumulation of metals under farms is a potential problem, then the second recommended step is to assess bioavailability of sediment metal concentrations through chemical estimates and ecotoxicity testing (Figure 9 - #3). Macleod & Eriksen (2009) describe in detail the approach they used to estimate bioavailability and toxicity of sediment copper concentrations associated with Tasmanian salmon farms. Following their example, three environmental scenarios could be tested within the Marlborough Sounds using annual monitoring results to help in site selections: active farms with high organic levels (>5% TOC), active farms with low organic levels (<5% TOC), and fallowed or recovering farms with high organic levels. Decisions around the appropriate tests should be determined in consultation with experts in speciation, bioavailability and toxicology. In addition, Macleod & Eriksen (2009) provide a thorough evaluation of the different analytical approaches and tests used to measure metals (p.43-48),

and suggest how to incorporate ecotoxicology data from local species into guidelines (p.41-43).

Based on the obtained bioavailability and toxicity results, the next recommended step would involve examining the appropriateness of ANZECC (2000) ISQG trigger values for assessing sediment copper and zinc toxicities in salmon farm sediments. For instance, if test results suggest that metal concentrations (even those in excess of ISQG-High) are not bioavailable and/or acutely toxic to test organisms (Figure 9 - #4), MDC may choose to refine current guidelines for finfish farms in a manner similar to Scotland's Allowable Zone of Effect (AZE-SEPA 2000). As discussed in Section 3.1.1, SEPA developed an AZE up to 100 m from farms in which low trigger values were set higher than outside the AZE. By raising this standard, the Council would be acknowledging that metal concentrations are expected to be greater under farms, but that the biological effects are not, as metals will be mainly chemically bound and thus effectively non-toxic.

Alternatively, bioavailability results may demonstrate a toxic effect on test organisms that is in agreement with current ISQG-Low and/or High trigger values. If this is the case, then current metal inputs associated with finfish aquaculture may be adversely affecting the local biota and/or ecology. Councils' options would include re-examining aquaculture operational issues that could help reduce metal inputs and/or impacts (Figure 9 - #5), in particular the issues discussed in Section 4.5. With additional research (Figure 9 - #6), the Council and/or industry may also be able to identify other remediation ideas, such as a more efficient fallowing schedule that helps reduce the long-term accumulation or conservation of metals in sediments at farm sites (*i.e.* metal remediation).

In addition to the three suggested scenarios, Macleod & Eriksen (2009) suggest testing metal bioavailability and toxicity across a range of operational and environmental conditions relevant to the local salmon industry (Figure 9 - #7). As a whole, locally relevant results will help further refine current monitoring protocols, ensuring they are detecting and minimising the impacts metals may be having on the surrounding environment. Taking steps now towards evaluating sediment metal bioavailability will also inform future decisions relating to new finfish farm applications with regard to the environmental implications of metal inputs.

It is important to emphasise that fully understanding the long-term implications that metal usage in aquaculture farms may have on local marine environments will take the involvement of further national and international research. This review discusses several research recommendations throughout the document, most of which have been placed in context with the suggested priorities for MDC in Figure 9 - #8. Several of these research themes, and many additional suggestions, are explained in further detail by Macleod & Eriksen (2009) and Burridge *et al.* (2008).





Figure 9. A flowchart representing suggested priorities for MDC in working towards the sustainable use of copper and zinc associated with finfish aquaculture in the Marlborough Sounds. The flowchart demonstrates how steps by MDC can help refine future sediment guidelines and monitoring programmes.



6. ACKNOWLEDGEMENTS

Cawthron Institute would like to acknowledge the help New Zealand King Salmon Company Ltd (Mark Gillard) in making available their long-term annual monitoring database for the salmon farm sites within the Marlborough Sounds, in addition to various information on feed products, anti-fouling paints and protocols.

7. REFERENCES

- ANZECC 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000 Volume 1. National Water Quality Management Strategy Paper No.4. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra.
- Atchison GJ, Henry MG, Sandheinrich MB 1987. Effects of metals on fish behaviour: a review. Environmental Biology of Fishes 18(1): 11-25.
- Ayling GM 1974. Uptake of cadmium, zinc, copper, lead and chromium in the Pacific oyster, *Crassostrea gigas*, grown in the Tamar River Tasmania. Water Research 8: 729-738.
- Bennett C, Barter P 2006. Assessment of ecological resource at the LPC dry-dock. Prepared for Lyttelton Port of Christchurch. Cawthron Report. 7 p.
- Borgmann U, Nowierski M, Grapentine LC, Dixon DG 2004. Assessing the cause of impacts on benthic organisms near Rouyn-Noranda, Quebec. Environmental Pollution 129: 39-48.
- Braithwaite RA, Cadavid-Carrascosa MC, McEvoy LA 2007. Biofouling of salmon cage netting and the efficacy of a typical copper-based anti-foulant. Aquaculture 262: 219-226.
- Brooks KM, Mahnken CV 2003. Interactions of Atlantic salmon in the Pacific Northwest environment III. Accumulation of zinc and copper. Fisheries Research 62: 295-305.
- Brooks KM, Stierns AR, Mahnken CV, Blackburn DB 2003. Chemical and biological remediation of the benthos near Atlantic salmon farms. Aquaculture 219: 355-377.
- Brooks KM, Stierns AR, Backman C 2004. Seven year remediation study at the Carrie Bay Atlantic salmon (*Salmo salar*) farm in the Broughton Archipelago, British Columbia, Canada. Aquaculture 239: 81-123.
- Burridge L, Weis J, Cabello F, Pizarro J 2008. Chemical use in salmon aquaculture: a review of current practices and possible environmental effects. Report to Salmon Aquaculture Dialogue, World Wildlife Fund. (http://www.worldwildlife.org/aquadialogues).
- Chapman PM, Wang F, Germano J, Batley G 2002. Pore water testing and analysis, the good, the bad and the ugly. Marine Pollution Bulletin 44: 359-366.
- Chapman PM, Wang F 2001. Assessing sediment contamination in estuaries. Environmental Toxicology and Chemistry 20(1): 3–22.
- Chou CL, Haya K, Paon LA, Burridge L, Moffatt JD 2002. Aquaculture-related trace metals in sediments and lobsters and relevance to environmental monitoring program ratings for near-field effects. Marine Pollution Bulletin 44: 1259-1268.

- Cooper DC, Neal AL, Kukkadapu RK, Brewe D, Coby A, Picardal FW 2005. Effects of sediment iron mineral composition on microbially mediated changes in divalent metal speciation: Importance of ferrihydrite. Geochimica Et Cosmochimica Acta 69: 1739-1754.
- Culshow C, Newton L, Weis I, Bird DJ 2002. Concentrations of Cd, Zn, and Cu in sediments and brown shrimp (*Cragnon cragnon* L.) from the Severn Estuary and Bristol Channel, UK. Marine Environmental Research 54: 331-334.
- Dalgleish C 2008a. Copper mass balance. Fate of copper through the deployment cycle of fish nets. Tassal Operations Pty Ltd.
- Dalgleish C 2008b. Mass balance. Fate of copper and zinc through the in-situ cleaning of fish nets. Tassal Operations Pty Ltd.
- Dauvin JC 2008. Effects of heavy metals contamination on the macrobenthic fauna in estuaries: The case of the Seine estuary. Marine Pollution Bulletin 57: 160-169.
- DeBruyn AMH, Trudel M, Eyding N, Harding J, McNally H, Mountain R, Orr C, Urban D, Verenitch S, Mazumder A 2006. Ecosystemic effects of salmon farming increase mercury contamination in wild fish. Environmental Science and Technology 40(11): 3489-3493
- Dean RJ, Shimmield TM, Black KD 2007. Copper, zinc, and cadmium in marine cage fish farm sediments: An extensive survey. Environmental Pollution 145: 84-95.
- Eisler R 1993. Zinc hazards to fish, wildlife, and invertebrates: A synoptic review. US Department of the Interior Fish and Wildlife Service. Biological Report No. 10. Contaminant Hazard Reviews 26. 126 p.
- Eriksen R, Mackey DJ, van Dam R, Nowak B 2001. Copper speciation and toxicity in Macquarie Harbour, Tasmania: an investigation using a copper ion selective electrode. Marine Chemistry 74: 99-113.
- Fernandez N, Beiras R 2001. Combined toxicity of dissolved mercury with copper, lead, and cadmium on embryogenesis and early larval growth of the *Paracentrotus lividus* sea urchin. Ecotoxicology 10: 263-271.
- Fichet G, Radenac G, Miramand P 1998. Experimental Studies of Impacts of Harbour Sediments Resuspension to Marine Invertebrates Larvae: Bioavailability of Cd, Cu, Pb and Zn and Toxicity. Marine Pollution Bulletin 36: 509-518.
- Flemming CA, Trevors JT 1989. Copper toxicity and chemistry in the environment; A review. Water, Air and Soil Pollution 44: 143-158.
- Forrest B, Barter P, Stevens L 1997. Assessment of sediment quality and aquatic ecology in Port Nelson and the lower Maitai River. Prepared for Port Nelson Ltd and Nelson City Council. Cawthron Report No. 403. 53 p.
- Forrest B, Keeley N, Gillespie P, Hopkins G, Knight B, Govier D 2007. Review of the ecological effects of marine finfish aquaculture: final report. Prepared for Ministry of Fisheries. Cawthron Report No. 1285. 71 p.
- Forrest R, Dunmore R, Keeley N 2010a. Seabed impacts of the Te Pangu Bay salmon farm: Annual monitoring 2009. Prepared for New Zealand King Salmon Company Limited. Cawthron Report No. 1733. 32 p.
- Forrest R, Dunmore R, Keeley N 2010b. Seabed impacts of the Ruakaka Bay salmon farm: Annual monitoring 2009. Prepared for New Zealand King Salmon Company Limited. Cawthron Report No. 1736. 33 p.

- Forrest R, Dunmore R, Keeley N 2010c. Seabed impacts of the Forsyth Bay salmon farm: Annual monitoring 2009. Prepared for New Zealand King Salmon Company Limited. Cawthron Report No. 1758. 31 p.
- Gaw S pers comm. Environmental Chemist, University of Canterbury.
- Gillespie P, Clement D, Asher R 2009. Delaware Inlet fine-scale benthic baseline 2009. Prepared for Nelson City Council. Cawthron Report No. 1594. 28 p.
- Hall Jr LW, Anderson RD 1999. A deterministic ecological risk assessment for copper in European saltwater environments. Marine Pollution Bulletin 38: 207-218.
- Hansen DJ, Berry WJ, Mahoney JD, Boothman WS, Di Toro DM, Robson DL, Ankley GT, Ma D, Yan Q, Pasch CE 1996. Predicting the toxicity of metal-contaminated field sediments using interstitial concentration of metals and acid-volatile sulfide normalizations. Environmental Toxicology & Chemistry 15: 2080-2094.
- Hopkins G, Clarke M, Butcher R 2006. Seabed impacts of the Forsyth Bay salmon farm: Monitoring 2005. Prepared for The New Zealand King Salmon Company Ltd. Cawthron Report No. 1099. 36 p.
- Hornberger MI, Luoma SN, Cain DJ, Parchaso F, Brown CL, Bouse RM, Wellise C, Thompson JK 2000. Linkage of bioaccumulation and biological effects to changes in pollutant loads in south San Francisco Bay. Environmental Science & Technology 34: 2401-2409.
- Infante R, Pizarro R 2006. Feed conversion efficiency in the salmon industry in Chile. WWF Salmon Dialogue. November 2006 Steering Committee Meeting (http://www.worldwildlife.org/what/globalmarkets/aquaculture/WWFBinaryitem5354. pdf).
- Jonas RB 1989. Acute copper and cupric ion toxicity in an estuarine microbial community. Applied Environmental Microbiology 55: 43-49.
- Karakassis I, Hayziyanni E, Tsapakis M, Plaiti W 1999. Benthic recovery following cessation of fish arming: a series of successes and catastrophes. Marine Ecology Progress Series 184: 205-218.
- Kim SD, Ma H, Allen HE, Cha DK 1999. Influence of dissolved organic matter on the toxicity of copper to *Ceriodaphnia dubia*: effect of complexation kinetics. Environmental Toxciology & Chemistry 18(11):2433-2437.
- King CK 2001. Effects of metal contaminants on the development of the common Antarctic sea urchin *Sterechinus neumayeri* and comparisons of sensitivity with tropical and temperate echinoids. Marine Ecology Progress Series 215: 143-154.
- King CK, Gale SA, Stauber JL 2006. Acute toxicity and bioaccumulation of aqueous and sediment-bound metals in the estuarine amphipod *Melita plumulosa*. Environmental Toxicology 21: 489-504.
- Lewis AG, Metaxas A 1991. Concentrations of total dissolved copper in and near a coppertreated salmon net pen. Aquaculture 99: 267-276.
- Macleod C, Eriksen R 2009. A review of the ecological impacts of selected antibiotics and antifoulants currently used in the Tasmanian salmonid farming industry (Marine Farming Phase). Technical report prepared for FRDC Project 2007/246 by University of Tasmania. 155 p.
- Macleod CK, Moltschaniwskyj NA, Crawford CM 2006. Evaluation of short-term fallowing as a strategy for the management of recurring organic enrichment under salmon cages. Marine Pollution Bulletin 52: 1458-1466.



- Mazzola A, Mirto S, La Rosa T, Fabiano M, Danovaro R 2000. Fish-farming effects on benthic community structure in coastal sediments: analysis of meiofaunal recovery. ICES Journal of Marine Science 57: 1454-1461.
- McLusky DS, Bryant V, Campbell R 1986. The effects of temperature and salinity on the toxicity of heavy metals to marine and estuarine invertebrates. Oceanography and Biology, An annual review 24: 481-520.
- Ministry of Water, Land and Air Protection (MWLAP) 2002. Protocols for Marine Environmental Monitoring. Environmental Protection Division. British Columbia.
- Morrisey DJ, Underwood AJ, Howitt L 1996. Effects of copper on the faunas of marine softsediments: An experimental field study. Marine Biology 125: 199-213.
- Morrisey DJ, Gibbs MM, Pickmere SE, Cole RG. 2000. Predicting impacts and recovery of marine-farm sites in Stewart Island, New Zealand, from the Findlay-Watling model. Aquaculture 185: 257-271.
- Obee N 2009. Chemical and biological remediation of marine sediments at a fallowed salmon farm, Centre Cove, Kyuquot Sound, B.C. Technical report produced for the B.C. Ministry of Environment, Vancouver Island, British Columbia. 38 p.
- Pearson TH, Black KD 2001. The environmental impacts of marine fish cage culture. In: Black KD ed. Environmental impacts of aquaculture. Sheffield Academic Press, UK. Pp. 1-31.
- Petersen W, Willer E, Willamowski C 1997. Remobilization of trace elements from polluted, anoxic sediments after resuspension in oxic water. Water Air and Soil Pollution 99: 515-522.
- Rainbow PS 1995. Biomonitoring of heavy metal availability in the marine environment. Marine Pollution Bulletin 31: 183-192.
- Ranke J 2002. Persistence of antifouling agents in the marine biosphere. Environmental Science & Technology 36: 1539-1545.
- Robertson BM, Gillespie PA, Asher RA, Frisk S, Keeley NB, Hopkins GA, Thompson SJ, Tuckey BJ 2002. Estuarine Environmental Assessment and Monitoring: A National Protocol. Part A. Development, Part B. Appendices, and Part C. Application. Prepared for supporting Councils and the Ministry for the Environment, Sustainable Management Fund Contract No. 5096. Part A. 93 p. Part B. 159 p. Part C. 40 p plus field sheets.
- Rygg B 1985. Effect of sediment copper on benthic fauna. Marine Pollution Bulletin 25: 83-89.
- Rygg B 1986. Heavy-metal pollution and Log-normal distribution of individuals among species in benthic communities. Marine Pollution Bulletin 17: 31-36.
- Schendel EK, Nordström SE, Lavkulich LM 2004. Floc and sediment properties and their environmental distribution from a marine fish farm. Aquaculture Research 35: 483-493.
- SEPA 2000. Regulation and Monitoring of Marine Cage Fish Farming in Scotland: A Procedures Manual, Annex A & F. Scottish Environmental Protection Agency.
- Simpson SL, Apte SC, Batley GE 1998. Effects of short-term resupension events on trace metal speciation in polluted anoxic sediments. Environmental Science & Technology 32: 620-625.
- Simpson SL, Spadaro D 2008. Ecological effects due to contamination of sediments with copper-based antifoulants. CSIRO Land and Water Science, 53/08.



- Singh N, Turner A 2009. Leaching of copper and zinc from spent antifouling paint particles. Environmental Pollution 157: 371-376.
- Skretting 2010. Zinc in salmon diets: Advice to Pacifica Salmon March 2010. 6 p.
- Smith DG, Williamson RB 1986. Heavy metals in the New Zealand aquatic environment: A review. Ministry of Works and Development – Water & Soil Miscellaneous Publication No. 100. 108 p.
- Solberg CB, Saethre L, Julshamm K 2002. The effect of copper-treated net pens on farmed salmon (*Salmo salar*) and other marine organisms and sediments. Marine Pollution Bulletin 45: 126-132.
- Stauber JL, Florence TM 1990. Mechanism of toxicity of zinc to the marine diatom *Nitzschia closterium*. Marine Biology 105: 519-524.
- Sunda WG, Tester PA, Huntsman SA 1987. Effects of cupric and zinc ion activities on the survival and reproduction of marine copepods. Marine Biology 94: 203-210.
- Thurberg FP, Dawson MA, Collier RS 1973. Effects of copper and cadmium on osmoregulation and oxygen-consumption in two species of estuarine crabs. Marine Biology 23: 171-175.
- Turner A, Fitzer S, Glegg GA 2008. Impacts of boat paint chips on the distribution and availability of copper in an English ria. Environmental Pollution 151: 176-181.
- Turner A, Barret M, Brown M 2009. Processing of antifouling paint particles by *Mytilus edulis*. Environmental Pollution 157: 215-220.
- White SL, Rainbow PS 1985. On the metabolic requirements for copper and zinc in molluscs and crustaceans. Marine Environmental Research16(3): 215-229.
- WHO 2001. Zinc Environmental Health Criteria 221. Geneva. 383 p.
- Wilding TA, Kelly MS, Black KD 2006. Alternative marine sources of protein and oil for aquaculture feeds: State of the art and recommendations for further research. The Crown Estate. 63 p.



8. APPENDICES

8.1. Additional information on possible biological effects of copper and zinc

Phytoplankton and other single celled organisms are extremely vulnerable to the accumulation of trace metals from the water column, as ions are taken up by the cell. The metals can adsorb to the outside of algal cells, and later be transported into the cell passively via diffusion or through active transport (Stauber & Florence 1990). Marine zooplankton (*e.g.* copepods) are thought to be less sensitive to metal accumulation than phytoplankton, yet larval stages and eggs are generally more vulnerable to free ion activity than adults (Sunda *et al.* 1987; Burridge *et al.* 2008).

Some species of crustaceans known as decapods (*e.g.* crab, crayfish, shrimp) and most molluscs (*e.g.* oysters, mussels, snails) use copper as a respiratory pigment (haemocyanin), much like humans have iron-containing haemoglobin (White & Rainbow 1985). These species need to regulate copper and other essential metals to achieve homeostasis (Culshaw *et al.* 2002; Macleod & Eriksen 2009). However, if metal levels exceed the organism's ability to regulate them, osmoregulatory functions may be compromised, which can lead to further bioaccumulation, toxicity and even death (Thurberg *et al.* 1973; Dauvin 2008).

Several crustacean species cannot regulate their uptake of copper and/or zinc. Toxicity tests revealed that crustaceans can show sub-lethal behavioural effects, such as weight and biomass loss, disrupted oxygen consumption, inhibited feeding, and decreased survival depending on the metal concentrations (*e.g.* Culshow *et al.* 2002; Dauvin 2008; Burridge *et al.* 2008). Eisler's (1993) review noted that certain marine crustaceans were the most zinc-sensitive of the invertebrates tested.

Certain mollusc species have the unusual ability to preferentially accumulate specific trace metals to extremely high levels from both dissolved and particulate metal fractions before they are adversely affected (Ayling 1974). This factor makes these species particularly useful for detecting or 'bio-monitoring' metal levels within localised areas, as their accumulation often reflects the bioavailability of these metals in the surrounding environment (Rainbow 1995; Solberg *et al.* 2002). Studies in Australia are currently investigating the use of oysters as copper and zinc bio-monitors within finfish aquaculture as they preferentially accumulated extremely high concentrations of both metals in polluted areas over a relatively short time period (Macleod & Eriksen 2009). Other taxa, such as echinoderms (*e.g.* sea stars, sea urchins) larvae, are also used as toxicity indicators as they are extremely sensitive to metal concentrations at very low levels (King 2001; Macleod & Eriksen 2009).

The diversity of annelid (*e.g.* segmented worms) body types (*e.g.* swimming, sedentary) and feeding habits (*e.g.* filtering, deposit, generalist) means that this group of taxa is expected to exhibit a wide range of sensitivities to metal contaminants. Eisler (1993) reported the highest zinc uptake of an invertebrate was by a generalist-feeder, *Nereis diversicolor*, with no



significant effects. This species exhibited evidence of acquired zinc tolerance – the ability to function normally with increasing metal concentrations due to acclimatisation or genetic variation (Eisler 1993). However, sub-lethal toxicity and chronic effects have been observed in other annelid species exposed to only small amounts of copper and/or zinc in sediments (Eisler 1993; WHO 2001; Macleod & Eriksen 2009).

Fish are assumed to directly assimilate metals through their gills (and other mucous surfaces) and/or ingest them. As farmed fish have higher exposure rates to copper and/or zinc, several studies (as well as regular export standards monitoring) have examined metal residue levels in their tissues. Solberg *et al.* (2002) compared copper residues in samples from Atlantic salmon farmed in treated and untreated nets. Their study found no significant differences between tissue results, and concluded that the leaching rate was low enough for salmon to regulate copper levels.

A study of estuarine fish species exposed to highly contaminated sediments (*e.g.* cadmium, copper and zinc) found greater levels of accumulated metals than unexposed fish (Dauvin 2008). Exposed fish exhibited dysfunctional sensory responses, reproductive problems, reduced resistance to infectious diseases and a shortened lifespan (Atchison *et al.* 1987; Brooks & Mahnken 2003; Macleod & Eriksen 2009). It is likely that these differences are due to lifestyle, and bottom-feeding or demersal species will be more susceptible to contaminated sediments than pelagic fish species.