Contaminants in estuarine and riverine sediments and biota in Southland

Landcare Research
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Summary

Project and Client

- Estuarine and riverine sediments and biota in Southland were sampled for a range of contaminants by Environment Southland in May 2013. This report assesses the potential environmental and human health effects arising from the contaminants observed in sediments and biota from the Jacobs River and New River estuaries and surrounding rivers and provides recommendations for ongoing monitoring.

Methods

- Estuarine sediment samples were collected during low tide, with samples taken from eight 5-m quadrats within a 10×20 m grid to form a composite sample for analysis. In selected locations, replicate samples were collected. Cockles were collected from the sediment sampling sites when found.

- Riverine sediment samples were collected from the river margin, with several 'grab' samples used to form a single composite sample for analysis. Eels and fish were collected by fyke net from selected locations within the riverine systems.

- Sediment and biota samples were sent to Hill Laboratories for chemical analysis.

Results and conclusions

- Similar to previous studies, we found that several sites within New River Estuary and surrounding rivers were highly enriched with phosphorus and also contained elevated organic carbon. Levels of contamination from metals (including arsenic) in both estuaries were generally low and concentrations rarely exceeded the Australian and New Zealand Environment Conservation Council (ANZECC) ISQG-low guidelines. An exception was nickel in the upper arms of the New River Estuary, which exceeded the IQGS guideline at two locations that had a high proportion of fine sediment.

- Sediments collected from New River Estuary appeared to be well-mixed with contaminant loads (and organic carbon and phosphorus) and the contaminants were highly correlated with the amount of fine sediment present at the sites. In contrast, sediments collected from the Jacobs River Estuary appeared to be more influenced by source contributions at different locations and there was poor correlation of contaminant load with fine sediment contribution.

- Elevated contaminant concentrations were found in sediments collected from rivers and streams draining into the New River Estuary, and unsurprisingly those passing through Invercargill (Otepuni, Waihopai and Kingswell catchments) had higher metal concentrations than those rivers and streams draining more agricultural catchments (Oreti and Waikiwi). Nickel and zinc showed the greatest exceedance of sediment quality standards. $\sum$DDT concentration was also greater in sediments from the urban catchment compared with agricultural catchments. In contrast, cadmium was found at higher concentrations in some sediment samples from agricultural catchments (Waikiwi River). The presence of cadmium in the sediment, and its high correlation with phosphorus, likely suggests an input of agricultural soils to the drainage systems.

- Monitoring of eels and fish collected in the riverine systems highlighted the accumulation of mercury and ∑DDTs that were non-detectable or present at low concentrations in the sediments. Contaminant concentrations were typically higher in internal organs than in the flesh – an exception being mercury, which had higher concentrations in the flesh. There appear to be some species-specific differences in contaminant accumulation, with arsenic typically not detected in eel flesh (except for those collected from urban streams), and lead typically not detected in fish flesh. Cadmium and zinc were typically present at lower concentrations in fish flesh compared with eel flesh.

- Regardless of the concentrations determined in biota, there appears to be a negligible health risk generally associated with the consumption of eels and fish from these systems. Under a high consumption scenario or high-end contamination there may be some increase in risk from arsenic and mercury although this is still minor.

- Contaminant concentrations in cockles were typically low – zinc and arsenic were present in the highest concentrations – potentially suggesting that current bioaccumulation of contaminants in New River Estuary is minor. (Cockles from Jacobs River Estuary were not analysed). The results provide a baseline from which further monitoring can be undertaken to assess changes over time. However, the seemingly patchy distribution of cockles in the estuaries may limit their usefulness as a biomonitor.

Recommendations

- In order to assess contaminant accumulation over time it is recommended that ongoing monitoring of contaminants, particular mercury and DDTs – that were low and variably detected in sediment monitoring, is conducted in riverine biota in selected locations. A frequency of 2–5 years would be adequate, with additional parameters, such as length and weight, also collected to help assess variations (e.g. due to age, condition) in contaminant concentrations and aid interpretation of changes over time. Muscle tissue would be most useful to target, as it also enables assessment of potential human health risk arising from consumption of locally caught fish.

- Closer inspection of the basis of the sediment quality guideline for nickel should be undertaken to understand the implications of exceeding this guideline value, and whether further investigation of nickel-related effects is warranted.

- Given the presence of mercury in edible flesh of fish, and the increasing international focus on the global cycling of mercury, mercury should be included in ongoing monitoring programmes.

- Establishing sediment sampling locations in the rivers and streams discharging into New River Estuary is recommended to enable assessment of changes in contaminant load over time. This should be combined with estimates of sediment discharge (e.g. from suspended sediment and flow data) from the different systems to the estuary to identify key contributors.

- As urbanised catchments continue to show an input of contaminants, stormwater inputs and other significant discharge points to rivers should be identified, and options for contaminant removal prior to river discharge investigated.

1   Introduction

Sediment and biota (eels, trout, mullet, cockles) sampled from the New River and Jacobs River estuaries, the Oreti and Waihopai rivers, Waikiwi Stream and Otepuni and Kingswell creeks by Environment Southland in May 2013 were analysed for a suite of heavy metals and organochlorine pesticides with a view to assessing human health risk. Although primarily focused on the assessment of metal and organochlorine pesticide contaminants, this report also touches briefly on the nutrient loading of collected sediments, building on previous studies investigating sediment quality in the Waihopai River (Hodson 2011) and New River Estuary (Robertson & Stevens 2007, 2008, 2010, 2012a).

2   Background

A range of potential contaminants may be found in the sediments of rivers and estuaries. Of these, metals or metalloids such as arsenic (As), copper (Cu), chromium (Cr), lead (Pb) and zinc (Zn) are commonly investigated. Cadmium (Cd), nickel (Ni) and mercury (Hg) are less commonly examined but may also be of interest in understanding potential effects on riverine and estuarine biota. Organic contaminants such as organochlorine pesticides and polycyclic aromatic hydrocarbons (PAH) may also be elevated in sediments.

Some contaminants, such as mercury and organochlorine pesticides, accumulate in shellfish, eels and fish present in riverine and estuarine systems and assessment of these biota provides an alternative measure of contaminant accumulation. Further, assessment of biota provides the ability to assess human health risks arising from the consumption of locally caught fish. Eels in particular are typically considered to be quite tolerant of contaminant loadings and may bioaccumulate contaminants in the flesh, which in turn may be consumed by people.

The primary sources of sediment contamination in the study area – in the absence of significant commercial boating activity – arise from off-site movement of soil particles from land uses in the surrounding catchments. For the current study this land use includes urban areas (e.g. Invercargill and Riverton) and agriculture. Urban sources of metal contamination arise from current and historical industrial activities such as electroplating (Cd, Ni, Cr, Zn) and timber treatment (Cu, Cr, As), diffuse sources such as residues from leaded petrol (Pb), and brake and tyre wear from vehicles (Cu, Cd, Zn). In non-urban areas, contamination may arise from specific activities such as timber treatment activities (Cr, Cu, As), or from the use of specific chemicals in agriculture such as zinc in facial eczema remedies and pesticides such as copper-fungicides, or historical use of lead arsenate.

The metals and metalloids listed above are also naturally occurring, and thus will be present at some concentration regardless of any anthropogenic input. The concentrations at which they naturally occur are variable and will depend on the geology of a given area. Further, in addition to potential toxic effects, some metals are required for biological functioning and insufficient levels will also give rise to detrimental effects, i.e. those associated with deficiency. Of these copper and zinc are most important, although chromium and nickel are also required for biological functioning. In contrast, arsenic, cadmium, lead and mercury, which have recognised toxic effects, have no known beneficial biological function.

In terms of human health effects, arsenic is considered to have no threshold concentration below which effects are not observed, and internal cancers, such as bladder and liver cancers, are suggested to be the most sensitive endpoints (MfE 2011). Similarly, lead is also considered to cause effects at all concentrations, with the most significant critical effect of low concentrations of lead considered to be reduced cognitive development and intellectual performance in children (MfE 2011). Kidney damage arising from accumulation over a lifetime is considered to be the critical effect for cadmium (MfE 2011). Finally, the critical target for methylmercury toxicity is the nervous system and the developing fetus is considered to be at particular risk from methylmercury exposure (Li et al. 2010).

Organochlorine pesticides have been widely used in New Zealand agriculture, particularly during the 1950s and 1960s (Buckland et al. 1998). DDT had the most extensive use, due to its use to control grass grub (*Costelytra zealandia*) and porina (*Wiseana* sp.) caterpillars in agricultural pastures, as well as in lawns, market gardens and parks. Lindane (gamma-hexachlorocyclohexane) was used for grass and also for sheep ectoparasites. Aldrin and dieldrin typically had less spatially extensive uses as stock remedies in sheep sprays or dips for controlling sheep or cattle ectoparasites, and horticultural pests. Usage of organochlorine pesticides in agriculture and horticulture largely ceased by the mid-1970s due to international concerns about their environmental persistence and effects, in particular bird eggshell thinning. Registration of DDT was withdrawn in 1989 (Buckland et al. 1998), although residues still persist in agricultural soils (Boul et al. 1994; Buckland et al. 1998; Gaw et al. 2006). These soils may be sources of organochlorine pesticides in riverine and estuarine systems, although urban usage of these pesticides may also contribute to loadings.

3   Objective

- To assess the potential environmental and human health effects arising from contaminants observed in sediments and biota from Jacobs River Estuary, New River Estuary and surrounding rivers.

4 Methods

4.1 Sample locations

Sediment and biota (trout, eel, mullet, cockles) samples were collected from the lower reaches of rivers draining into the Jacobs River and New River estuaries in Southland in May 2013 (Figures 1–3). Details of the individual sampling sites are shown in Table 1.
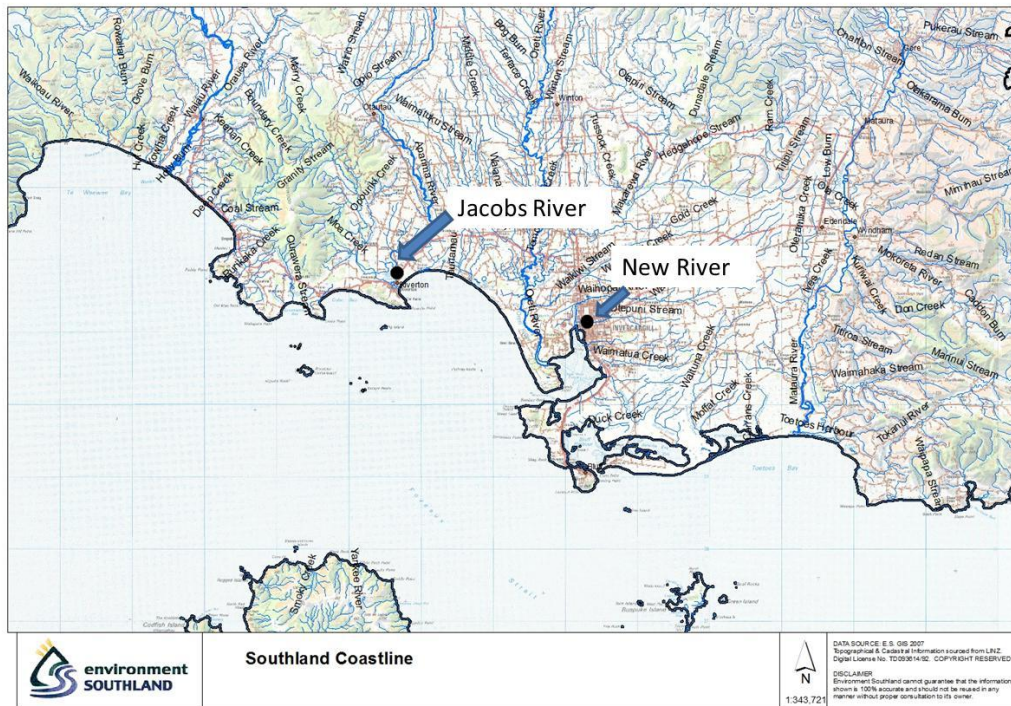
Figure 1 Map showing general location of sampling sites.

New River Estuary is a large (4100 ha) tidal lagoon estuary near Invercargill. Eutrophication and sedimentation have been identified as a major issue in the estuary since at least 2007 (Robertson & Stevens 2007). Some sampling sites for the current study have previously been included in studies on the long-term monitoring of the eutrophic state of the estuary. These sites can be considered high depositional areas where small sediment fractions will predominantly accumulate.

The Oreti and Waihopai rivers are the largest rivers draining into the New River Estuary. The Oreti River drains the third largest catchment in Southland – it is approximately 170 km long and runs from the headwaters near Mavora Lakes to New River Estuary adjacent to Invercargill City. En route, it runs near the townships of Lumsden and Winton before feeding into the north-west of the estuary. The middle and lower reaches of the Oreti catchment have been substantially modified by drainage, flood control and channel clearance work undertaken in order to develop productive farmland. Major tributaries of the Oreti mainstem include Winton Stream, Waikiwi Stream and the Makarewa River, which are each subject to point-source discharges of effluent from industry and municipal sewage treatment. The Waihopai is the second largest river feeding into the estuary. The Waihopai feeds into the

estuary directly from the north after draining the well-modified agricultural land further up the catchment and the industrialised/urbanised areas of Invercargill City.

Otepuni and Kingswell creeks, which run through industrial and urban areas of Invercargill, also discharge into the New River Estuary. Otepuni Creek runs through the southern part of Invercargill city. The Otepuni Creek catchment extends from Rimu in the east to the New River Estuary in the west and drains an area of 35 km^2. The Otepuni catchment has intensive agriculture in the upper catchment, lifestyle farms in the mid-catchment, and industrial, commercial and residential land uses in the lower part of the catchment. Kingswell Creek drains a much smaller area than the other streams, with land uses in its catchment ranging from a low level of agriculture, lifestyle blocks and low density residential.
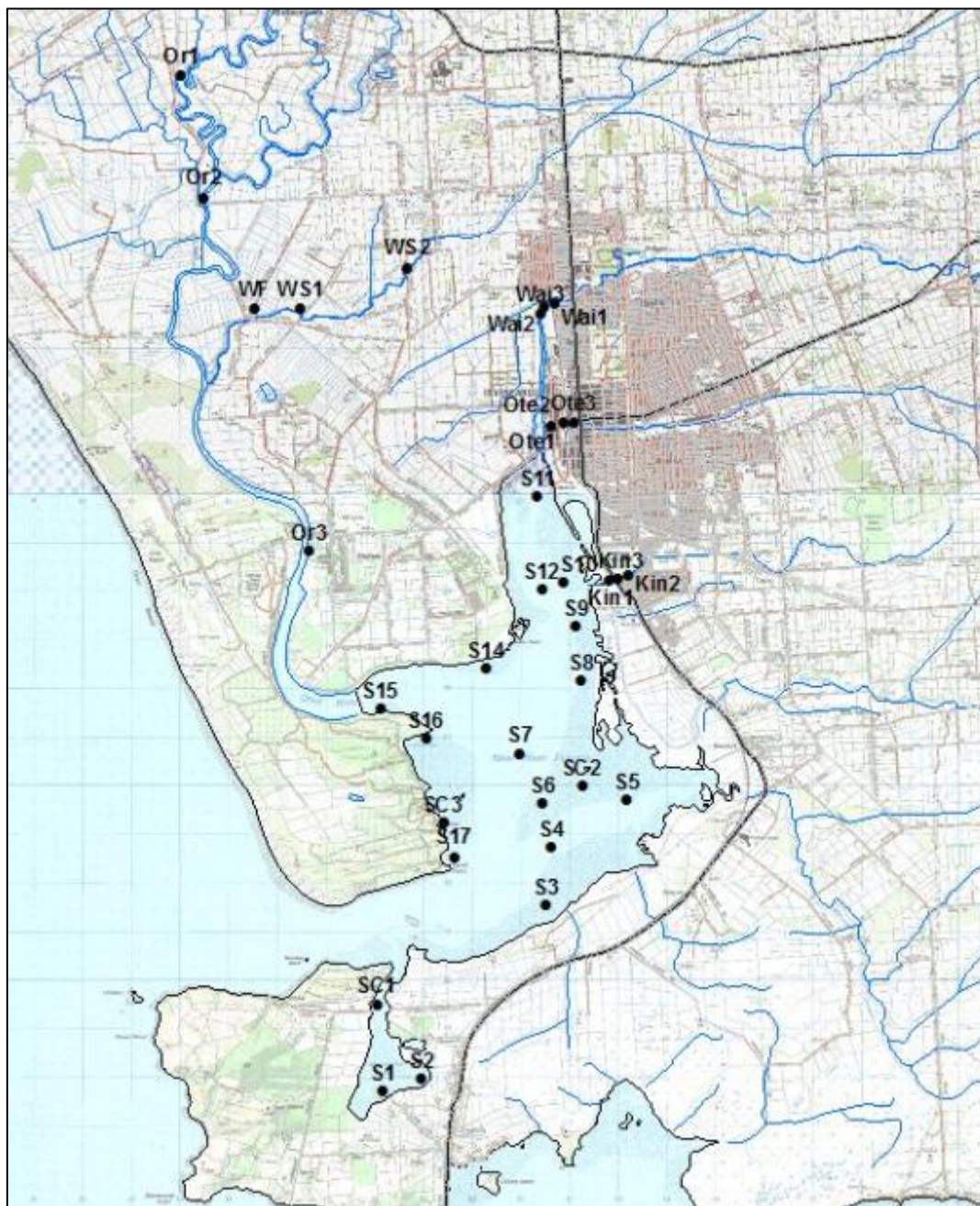
Figure 2 Sampling locations in the New River Estuary and surrounding rivers, near Invercargill. North is to the top of the map, which is altered from original scale.

Table 1 Summary of sample sites in New River Estuary and surrounding rivers

					Main streams in the New River Estuary catchment	
Code	Site name	Date sampled	Easting	Northing	Description	Samples collected
Or1	Oreti River 1	1-May-13	2144013	5418582	Upstream of the Makarewa River confluence	Sediment, eels, trout
Or2	Oreti River 2	1-May-13	2144468	5416085	Downstream of the Makawera River confluence, and upstream from the Waikiwi River confluence	Sediment, eels, trout, mullet
Or3	S19 Oreti lower reaches	16-May-13	2146630	5408806	Downstream of the Waikiwi River confluence	Sediment
WF	Waikiwi @ Ferry Rd	1-May-13	2145516	5413797		Sediment, eels
WS1	Waikiwi @ Staunton Rd 1 (lower crossing)	1-May-13	2146462	5413800	Lower reaches of Waikiwi River, after it passes by Wallacetown. Surrounding land use is predominantly agriculture	Sediment, eels, trout
WS2	Waikiwi @ Staunton Rd 2 (upper crossing)	1-May-13	2148662	5414642		Sediment, eels
Wai	Waihopai site	6-May-13	2151397	5413694	Lower reaches of Waihopai River, within Invercargill City	Sediment, eels, trout
Ote	Otepuni site	6-May-13	2151861	5411443	Lower reaches of Otepuni Creek, within Invercargill City	Sediment, eels, trout
Kin	Kingswell site	6-May-13	2152805	5408196	Lower reaches of Kingswell Creek, within Invercargill City	Sediment, eels, trout
S11	S11 Niwa Upper Waihopai	16-May-13	2151353	5409949	Part of the extensive mud flats of New River Estuary	Sediment
S12	S12 Niwa Lower Waihopai	16-May-13	2151421	5408036	Included in long-term monitoring of the eutrophic state of the estuary ≈ Site S16 ≈ Site E/C (Robertson & Stevens 2012a)	Sediment
S10	S10 N ICC WWP outlet	16-May-13	2151844	5408170	North of the municipal sewage treatment plant discharge	Sediment
S9	S9 S ICC WWP outlet	16-May-13	2152108	5407261	South of the municipal sewage treatment plant discharge	Sediment
S14	S14 NIWA Bushy Point	17-May-13	2150284	5406393	Included in long-term monitoring of the eutrophic state of the estuary ≈site D (Robertson & Stevens 2012a)	Sediment

S8	S8 E Shore opp Oreti Mouth	16-May-13	2152222	5406161	Included in long-term monitoring of the eutrophic state of the estuary ≈site A (Robertson & Stevens 2012a)	Sediment
S15	S15 Oreti Mouth	16-May-13	2148177	5405609	Likely high flocculation area as fresh water hits more saline conditions	Sediment
S6	S6 NIWA Shellybank	16-May-13	2152026	5403897	Site of intertidal bank between main estuary channel (Waihopai and Oreti contributiuons) and estuary channel from Mokotua	Sediment
SC2	SC2 Shellybank	16-May-13	2152026	5403897	Included in long-term monitoring of the eutrophic state of the estuary ≈site B (Robertson & Stevens 2012a)	Sediment
S5	S5 Mokotua Mouth N	16-May-13	2153142	5403687	Development within this small catchment may be contributing disproportionate sediment loads	Sediment
SC3	SC3 Whalers Bay	16-May-13	2149422	5403206	Area just south of Whalers Bay where some sediment changes have been anecdotally observed	Sediment
S4	S4 Btw Jamieson/Waipaka	16-May-13	2151596	5402738	Sample point within main channel from Mokotua	Sediment
S3	S3 W of Jamieson Drain	16-May-13	2151523	5401580	Sample point within extensive shellfish beds that stretch along eastern edge of estuary	Sediment
S7	S7 S Bushy Point near channel	16-May-13	2150949	5404631	Area of increasingly high deposition. (Robertson & Stevens 2012a)	Sediment, cockles
S16	S16 NIWA Daffodil Bay	16-May-13	2140937	5404953	Area of increasingly high deposition. (Robertson & Stevens 2012a)	Sediment
S17	S17 South Whalers Bay	16-May-13	2149612	5402519	Southern point of peninsula that has high local use	Sediment, cockles
S1	S1 Mokomoko West	16-May-13	2148080	5397686	Sub-inlet of New River Estuary with important historical value and high local use. The land surrounding it has undergone substantial development in the last 30 years	Sediment
S2	S2 Mokomoko East	16-May-13	2148926	5397970		Sediment
SC1	SC1 Mokomoko Mouth	16-May-13	2148029	5399486		Sediment, cockles

Figure 3 Sampling locations in the Jacobs' River Estuary (map not to scale).

The Jacobs River Estuary is a medium-sized (720 ha) tidal-lagoon-type estuary, discharging to the sea at Riverton township. Some of the sampling sites for this study are from previous long-term monitoring studies of the eutrophic state of the estuary. With the exception of Riverton, most of the land surrounding the rivers draining into the estuary is used for agriculture and forestry. Additionally there are some historical timber treatment plants and an active coal mine. The Aparima catchment is the smallest of the four main catchments in the region and extends from west of Mossburn to the coast at Riverton. The other river discharging into Jacobs River Estuary is the Pourakino, which drains an area predominantly in exotic and native forestry with some agriculture. Much of the lower area of both catchments has been extensively modified over the last century, with the drainage of wetlands and the straightening of streams to assist in flood management activities.

Table 2 Description of sampling sites in the Jacob's River Estuary

Code	Site name	Date sampled	Easting	Northing	Description	Samples collected[1]
JRE1	Jacobs River Estuary 1 Fish co-op	13-Jun-13	2126299	5416576	Sites JRE1 and JRE2 are located within the Riverton township, which has some small commercial activities, residential buildings and local fishing	Sediment, cockles
JRE2	Jacobs River Estuary 2 near estuary mouth	13-Jun-13	2126568	5416320		Sediment, cockles
JRE4	Jacobs River Estuary 4 South Bank of Aparima Mouth	13-Jun-13	2126205	5418419	Area selected to give greater spatial distribution of sites. Likely to be lower deposition of fines due to proximity to Aparima river mouth	Sediment
JRE6	Jacobs River Estuary 6 Northern flats	13-Jun-13	2125153	5419222	Included in long-term monitoring of the eutrophic state of the estuary ≈site E (Robertson & Stevens 2012b)	Sediment
JRE7	Jacobs River Estuary 7 Central Basin north	13-Jun-13	2124354	5418097	Area selected to give greater spatial distribution of sites. Likely to be higher deposition area due to proximity to estuary edge and restriction caused by 'the neck' – a rocky outcrop separating minor part of estuary from Pourakino arm	Sediment
JRE8	Jacobs River Estuary 8 Central Basin south	13-Jun-13	2124342	5417416	Included in long-term monitoring of the eutrophic state of the estuary ≈site B (Robertson & Stevens 2012b)	Sediment
JRE9	Jacobs River Estuary 9C Pourakino Arm	13-Jun-13	2122856	5418603	Included in long-term monitoring of the eutrophic state of the estuary ≈site D/C (Robertson & Stevens 2012b)	Sediment
JRE10	Jacobs River Estuary 10A Mid- Basin	13-Jun-13	2125972	5417282	Included in long-term monitoring of the eutrophic state of the estuary ≈site A (Robertson & Stevens 2012b)	Sediment, cockles

[1]Due to financial constraints, no biota collected from the Jacobs River Estuary underwent chemical analyses.

4.2   Sediment sampling

4.2.1   Estuarine sampling

New River Estuary sites were selected for their spatial representation of the estuary, accessibility and inclusion in the Environment Southland estuary monitoring programme, which includes several years of historical data. Site selection was determined prior to undertaking fieldwork. A total of 21 sites were selected and divided between four groups of samplers. Three groups accessed sites from the shore and one group accessed sampling sites via boat. The boat team accessed the areas from a shallow-hull jetboat launched from near the Water Ski Club on the Oreti River. This allowed access to areas as little as 300 mm deep.

The eight sites for Jacobs River Estuary were selected and sampled in much the same way. All sites where accessed via the jetboat, which was launched from Riverton boat ramp.

Sampling was undertaken within the 4-h window around low tide (2 h either side). Upon arrival at a site, markers were used to delineate a 10×20 m (5-m interval) grid (Figure 4). Characteristics of sites, such as GPS location, photos and any other comments, were noted and recorded. An equal volume of sediment from the top 20 mm was collected from each grid quadrat, using a plastic trowel, and composited into a 5-L mixing container. Upon vigorous mixing the sample was then split in the field into sampling containers for analysis. Samples were immediately placed into a chilly bin and sent to Hill Laboratories for analysis upon returning from the field. Each site was replicated by repeating the sample collection method at one or two nearby sites approximately 20 m away. Not all sites have replicates due to logistical constraints.
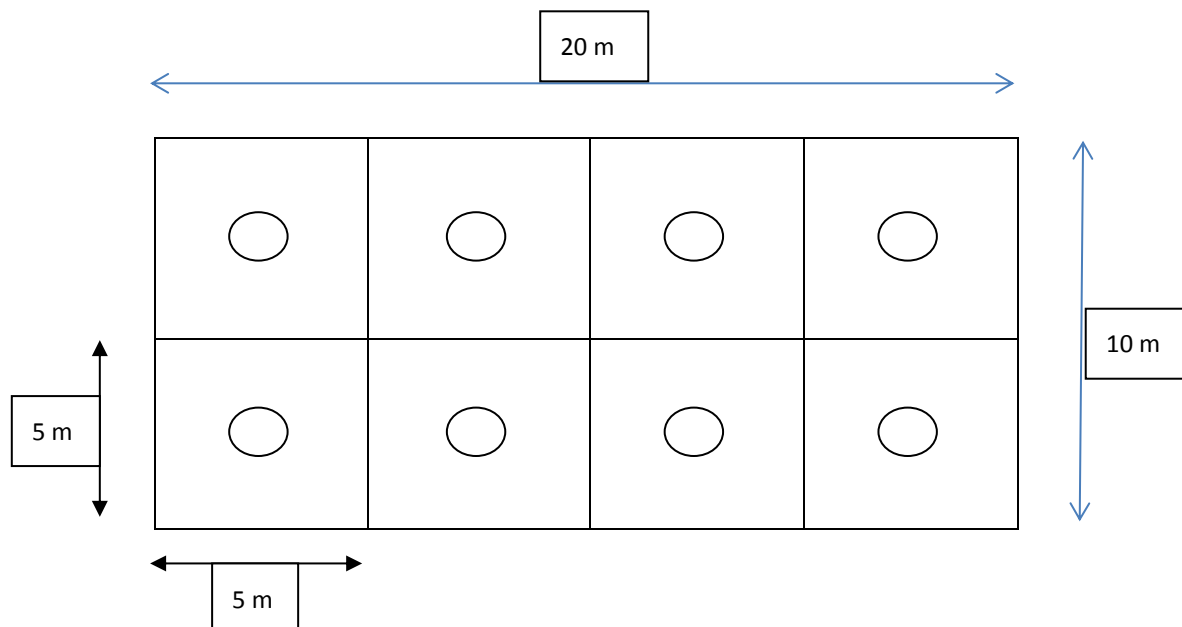
Figure 4 Diagrammatic layout of sample collection at estuarine sediment locations.

4.2.2   Lower river sediment sampling

Accessing sediment in the lower rivers was more difficult due to fast flows and deep water, and so at these sites areas of fine sediment deposition along the shallow river margins were targeted on foot. Areas of fine sediment deposition were identified in the field through visual observation. At each site, small scoops of sediment from multiple locations within a site were mixed together in a plastic bucket to produce a homogeneous mix that was representative of the site. This composite sample was then split and stored in a chilly bin on ice until received at Hill Laboratories for analysis.

At site S19 the sediment sample was taken just south of Dunns Road bridge on the Oreti by using a 'van deem' sediment sampler from a boat. Muslin cloth was placed over a bucket to drain the sample. Multiple grab samples were taken to form a composite. For this site areas of fine sediment deposition were identified in the field through visual observation and preliminary sampling, which delineated areas of coarser material with an overlying thin layer of fine material and areas of thicker fine material accumulation.

Sediment from the Oreti and Waikiwi Rivers was collected on the 1 May 2013, and from the Kingswell and Otepuni creeks and Waihopai River on the 7 May 2013.

4.3   Biota sampling

4.3.1   Cockle sampling

Where cockles (*Chione* (*Austrovenus*) *stuchburyi*) were present during estuarine sediment sampling, the grid was then further searched to collect 50 cockles. Cockles were placed in labelled bags and stored on ice in a chilly bin immediately after collection. In the laboratory these cockles were frozen for 24 h and then shucked from frozen to form a cockle homogenate that was then analysed for contaminants.

4.3.2   Lower river fish sampling

At each site of the lower riverine sites, three 3-funnel fyke nets were set. These had a 3.2-m body with a single 6-m-long wing fixed to the centre of the D-shaped hoop, with the dimensions of the first hoop being a height of 70 cm and width of 90 cm. Stretched mesh size was 32 mm for the main body and wings, and 20 mm for the innermost chamber. Fyke nets were set facing downstream, and baited with squid. They were set between 1400 and 1700 hours and retrieved the following morning between 0800 and 1200 hours. Eels (*Anguilla* spp.) and fish were chilled on ice in chilly bins and immediately couriered to Hill Laboratories.

Eels and fish were retrieved from the Oreti River and Waikiwi Stream on the 1 May 2013, and from Kingswell and Otepuni creeks and Waihopai River on the 7 May 2013.

4.4   Analysis

Sediment samples were sent for analysis as soon as possible to Hill Laboratories and Waikato University (sediment size only). Sediment size analysis did not include particles > 2 mm. The parameters measured are listed in Table 3.

Table 3 Parameters measured in sediment and biota samples

Sample type	Analytes
Sediment	Sediment size Metals Organochlorine pesticide suite Phosphorus (P) Total nitrogen (N) Total organic carbon (TOC) PAH (selected samples) Anticoagulants
Biota (cockles, eels, trout, mullet)	Metals Organochlorine pesticide suite Ivermectin (veterinary medicine) Anticoagulants (in flesh and livers)

Two sediment samples from the Jacobs River Estuary (S6 and S9; sites considered the most eutrophic and with higher fines content (Robertson & Stevens 2012b)) were analysed for polycyclic aromatic hydrocarbons, but no detectable concentrations (method detection limit 0.003 mg/kg dry wt ± 0.0014) were found. Analysis for the veterinary chemical ivermectin was also carried out by Hill Laboratories for all the biota samples but no detectable concentrations (detection limit 0.005 mg/kg) were found. Due to financial constraints no biota collected from the Jacobs River Estuary underwent chemical analyses.

Contaminant concentrations in the internal organs and muscle of eels and fish are tabulated in Appendix 1. A summary of the anticoagulant results from this study is provided in Appendix 2 and the implications of these results are discussed in Appendix 3.

4.5   Human health risk assessment

The potential human health risk arising from the consumption of eels, fish and cockles from the estuaries and rivers of our study area was assessed using a modification of the methods in Stewart et al. (2011). Specifically, we primarily used the toxicological intake values for our contaminants of interest that were recommended in MfE (2011) as the basis for assessing potential risk to human health from consumption of biota . MfE (2011) reviewed the toxicity of priority contaminants and reference health standards (RHS) developed by various international agencies. 'Reference health standards' refers to any value (set by a regulatory or advisory body on the basis of available scientific information) that provides an estimated daily (sometimes weekly or monthly) amount of a substance that can be taken into the body either without any, or with minimal additional, risk of detrimental health effects occurring.

A toxicological intake value for methylmercury was not considered in MfE (2011), but this is the primary form of mercury in fish, and is more toxic than inorganic mercury. Regulatory toxicological intake values for methylmercury range from 0.1 to 0.23 µg/kg.bw/day (Hansen & Gilman 2005). The more conservative value of 0.1 µg/kg.bw/day, derived by the US EPA (2001), is used here, for consistency with Stewart et al. (2011). Similarly, a toxicological intake value for zinc was not considered in MfE (2011) and the value of 300 µg/kg.bw/day, derived by the US EPA (2001), is used here, for consistency with Stewart et al. (2011).

When their effects on human health are being considered, contaminants are often referred to as either threshold or non-threshold contaminants. Threshold contaminants are those considered to manifest toxic effects only if exposure exceeds a threshold dose level, and include (by convention) non-genotoxic carcinogens and non-carcinogens. Non-threshold contaminants conventionally include genotoxic carcinogens, and are considered to have effects at all levels of exposure.

A summary of the recommended toxicological intake values for the contaminants of interest in the Southland estuaries and rivers examined here is given in Table 4; the values used in Stewart et al. (2011) are shown for comparative purposes. The majority of contaminants are generally considered to be threshold contaminants, except arsenic, which is considered to be carcinogenic and a non-threshold contaminant. The risk-specific dose provided for arsenic is the 'allowable' daily intake of arsenic that ensures the increased risk of cancer of 1 in 100 000 is not exceeded. In addition, it should be noted there are two values for chromium (Cr); Chromium exists in two oxidation states, CrIII and CrVI. CrIII is more widely present in the environment while CrVI is the more toxic, but is not widely distributed in the environment. As a conservative estimate of the risk associated with consumption of biota containing chromium, the toxicological intake value for Cr VI is used here.

Table 4 Summary of toxicological intake values for threshold priority contaminants used in this study

Contaminant	Oral (µg/kg bw/day) unless stated otherwise	Stewart et al. (2011)
Cadmium – daily	0.8 (25 ug/kg bw/month)	1
Copper	150	NC
Chromium III	1500	NC
Chromium VI	3	3
Lead	1.9	NC
Inorganic mercury	2	NC
Methylmercury[1]	0.1	0.1
Zinc	300	300
Dieldrin	0.1	NC
∑DDT (complex)	0.5	0.5 (DDT only)

	Non-threshold contaminant		
Contaminant	Oral risk-specific dose (µg/kg bw/day)	Oral risk-specific dose (µg/kg bw/day)[2]	Non-cancer risk (µg/kg bw/day)
Arsenic	0.0086	0.0067	0.3

[1]Not considered in MfE (2011).

[2]Calculated from a cancer slope factor of 1.5 (per mg/kg bw/day) for an acceptable risk level of 1 in 100 000 provided in Stewart et al. 2011).

NC – not considered.

As per Stewart et al. (2011), the risk associated with consumption of the contaminants in the flesh of the biota is assessed on the basis of 'margin of exposure' (MOE) with MOE > 1 indicating a potential risk from consumption.

For the purpose of risk assessment, all analyte concentrations below detectable concentrations were substituted with a value half the detection limit. The median and 95th percentile values for each contaminant across all sites sampled were calculated to provide a measure of the range of potential risks, with the 95th percentile representing a 'worst case' estimate for this assessment.

For average consumption rates we used those from Stewart et al. (2011), comprising indicative local average consumption rates of wild kai by Māori in South Canterbury (6.1 g/day for eels, 4.0 g/day for trout and 4.7 g/day for flounder; Tipa et al. 2010a in Stewart et al. 2011) and a New Zealand high energy diet (fish, 66 g/day). These consumption rates were based on a body weight of 80 kg. In addition, we used the average fresh fish consumption (13 g/day) for an adult female (70 kg) from the New Zealand Total Diet Survey, which was based on simulated diets (Vannoort & Thomson 2011). No data on consumption rates of cockles were available, instead a consumption rate for oysters (2 g/day for female and local consumption and 4 g/day for high energy diet) from the New Zealand Total Diet Survey (Vannoort & Thomson 2011) were used. Data were analysed individually for eels (longfin *Anguilla dieffenbachia* and shortfin *A. australis*) and fish (combined yellow-eye mullet (*Aldrichetta forsteri*) and brown trout (*Salmo trutta*)) and cockles (*Chione* (*Austrovenus*) *stuchburyi*) for each contaminant (organochlorines and heavy metals).

Table 5 Sediment contaminant concentrations protective of ecological receptors produced in different countries for the contaminants of concern

Country	Value name	Metals (mg/kg)								Organic contaminants (μg/kg)				Source
		Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Mercury	Zinc	DDT	DDE	DDD	Dieldrin	
Australia/ New Zealand	ISQG-low[2]	20	1.5		65	50	21		200	1.6	2.2	2	0.02	ANZECC/ ARMCANZ (2000)
	ISQG-high[2]	70	10		270	220	52		410	46	27	20	8	
The Netherlands	SRC$_{eco}$	5900	820		660	63000	2600		6600	10000	1300	34000	1900	Verbruggen et al. (2001)
	MPA	160	29		36	4500	10		530	10	6	4	10	
Canada	ISQG[1]	5.9	0.6	37.3	35.7	35	-	0.17	123	1.2	1.4	3.5	2.9	CCME (2003)
	PEL[1]	17	3.5	90	197	91	-	0.49	315	4.8	6.7	8.5	6.7	
	ISQG[2]	7.24	0.7	52.3	18.7	30.2	-	0.13	124	1.2	2.07	1.22	0.71	
	PEL[2]	41.6	4.2	160	108	112	-	0.7	271	4.8	384	7.81	4.3	
	TEC[1]	9.8	0.99		32	36	22.7		121	4.2	3.2	4.9	1.9	MacDonald et al. (2000)
	PEC[1]	33	4.98		149	128	48.6		459	63	31	28	62	

ISQG – interim sediment quality criteria; MPA – maximum permissible addition; PEC – probable effect concentration; PEL – probable effect level; SRC$_{eco}$ – serious risk concentration ecotoxicology; TEC – threshold effect concentration; - – data not available. [1]Freshwater sediments,[2] Marine estuarine

5   Results and discussion

5.1   Estuarine sediments and biota

5.1.1   New River Estuary – sediment

Sediment collected from the New River Estuary was typically between 63 μm and 2 mm in size. Sediment size analyses did not include particles larger than 2 mm, although Robertson and Stevens (2012a) found that larger particles may be present in some locations. The exceptions were sites S11, S12 and S15, which had a notable proportion of finer sediment (<63 μm) (Figure 5). As can be seen from Figures 5 and 6, these sites with finer sediment were also typically elevated in total organic carbon, phosphorus and various metals or metalloids. Analyses revealed a high correlation between proportion of finer sediment and all other parameters measured, as well as high correlation between all these other parameters except proportion of coarse sediment (Table 6). Arsenic tended to show slightly lower but still significant correlation with sediment size than other parameters. Mercury was detected in samples S11, S12, and S15 only, while no organochlorine pesticide residues were detected in any estuarine sediment sample.

While sites S11, S12 and S15 typically had elevated metal concentrations, these were below all sediment quality guidelines, with the exception of that for nickel (Figure 6). Robertson and Stevens (2012a) also found that nickel in some sediment samples collected from New River Estuary exceeded ANZECC ISQG-low guidelines. These sites were all located close to river mouths – the Oreti River (S15), Waikiwi Stream and Otepuni Creek (S11), and Kingswell Creek (S12) – and had relatively high proportions of fine sediment (Figure 5). Otepuni and Kingswell creeks both showed elevated metal loadings in sediment samples (see Section 5.2.1). Site S10, which was also located close to the mouth of Kingswell Creek, did not have elevated metal concentrations although this is likely due to the absence of any significant proportion of fine sediment in the sample.
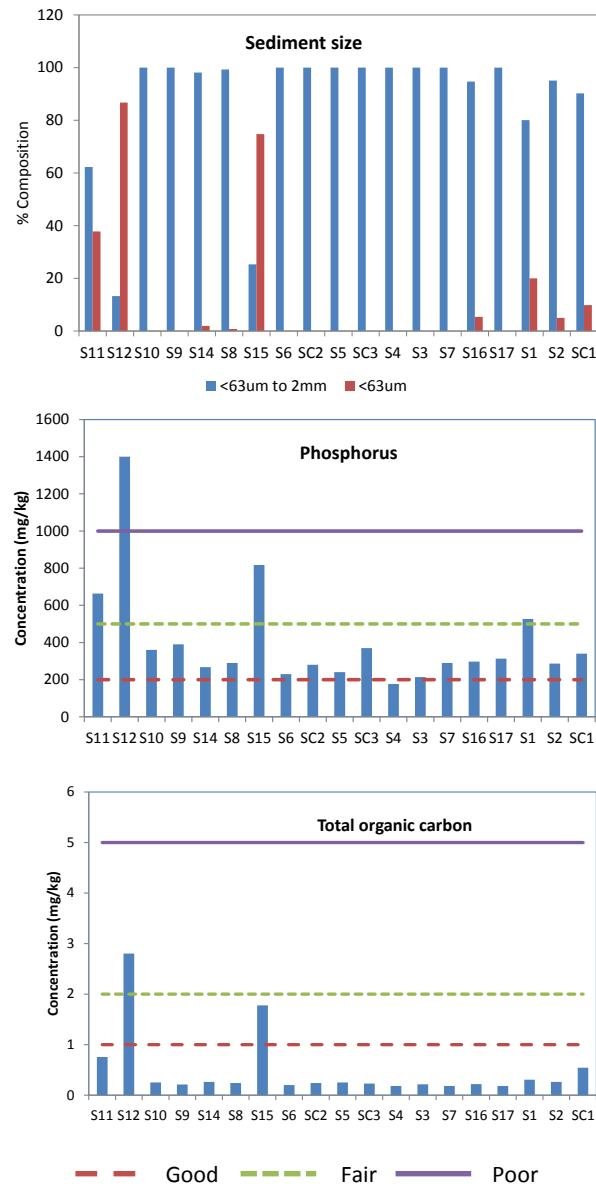
Figure 5 Sediment size, phosphorus and, total organic carbon distribution in sediment samples collected from New River Estuary.
Quality guidelines (see key) for total organic carbon and phosphorus are from Robertson & Stevens (2012a).

Figure 6 Metal concentrations and corresponding sediment quality guidelines for New River Estuary sediment samples.
Error bars are shown for samples that had replicates taken.

Table 6 Correlation coefficients for sediment samples collected within New River Estuary[1]

	Phosphorus	Total organic carbon (TOC)	Sediment size 63 um – 2 mm	<63 um	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Phosphorus	1										
TOC	**0.955753**	1									
63 um –2 mm	**−0.94628**	**−0.95889**	1								
<63 um	**0.946282**	**0.958893**	−1	1							
Arsenic	**0.869427**	**0.882893**	**−0.82518**	**0.82518**	1						
Cadmium	**0.963374**	**0.978225**	**−0.96424**	**0.964239**	**0.895169**	1					
Chromium	**0.970573**	**0.955712**	**−0.97292**	**0.972923**	**0.888158**	**0.979766**	1				
Copper	**0.971535**	**0.978996**	**−0.97658**	**0.976578**	**0.879654**	**0.98879**	**0.98828**	1			
Lead	**0.973425**	**0.978614**	**−0.96979**	**0.969793**	**0.887471**	**0.9911**	**0.986762**	**0.997772**	1		
Nickel	**0.974446**	**0.968389**	**−0.97072**	**0.970716**	**0.884578**	**0.986313**	**0.992727**	**0.997508**	**0.997093**	1	
Zinc	**0.969052**	**0.935662**	**−0.93749**	**0.93749**	**0.859711**	**0.965945**	**0.968004**	**0.975504**	**0.981048**	**0.983466**	1

[1]Bolded correlation coefficients indicate significant ($P < 0.05$) correlations.

5.1.2 New River Estuary – biota

Cockles were collected from three sites in the New River Estuary. Low concentrations of various trace elements, predominantly arsenic, nickel and zinc, were found in the cockles' flesh (Figure 7). Mercury and organochlorine pesticides were not detected.
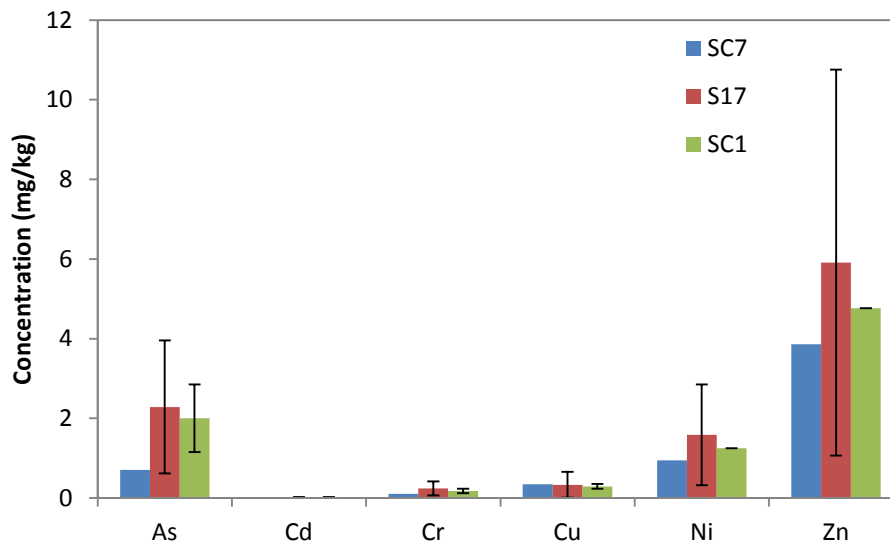
Figure 7 Metal concentrations (mg/kg wet wt) in cockles collected from New River Estuary.

5.1.3 Jacobs River Estuary – sediment

Sediment collected from sites towards the mouth of the Jacob River Estuary (JRE1, JRE2) had a greater proportion of coarse sediment (63 µm – 2 mm), while the remaining sites had a reasonably high proportion of fine sediment (63 µm) (Figure 8). In contrast to the New River Estuary samples, there was a less clear relationship between the fine sediment and other parameters such as total organic carbon, phosphorus and metals (Figures 8 and 9) and there was poor correlation of fine sediment with all other parameters (Table 7). With the exception of arsenic, metals were highly correlated with each other across the sites and with phosphorus (Table 7) suggesting a similar source of contaminants. Site JRE8 typically had lower concentrations of metals ,while sites JRE4 and JRE6 typically had elevated metal concentrations and were also elevated in total organic carbon and phosphorus. Mercury was present at concentrations just above the detection limit (0.01 mg/kg) in six out of eight samples collected, while no organochlorine pesticide residues were detected in any of the estuarine sediment samples from Jacobs River Estuary.
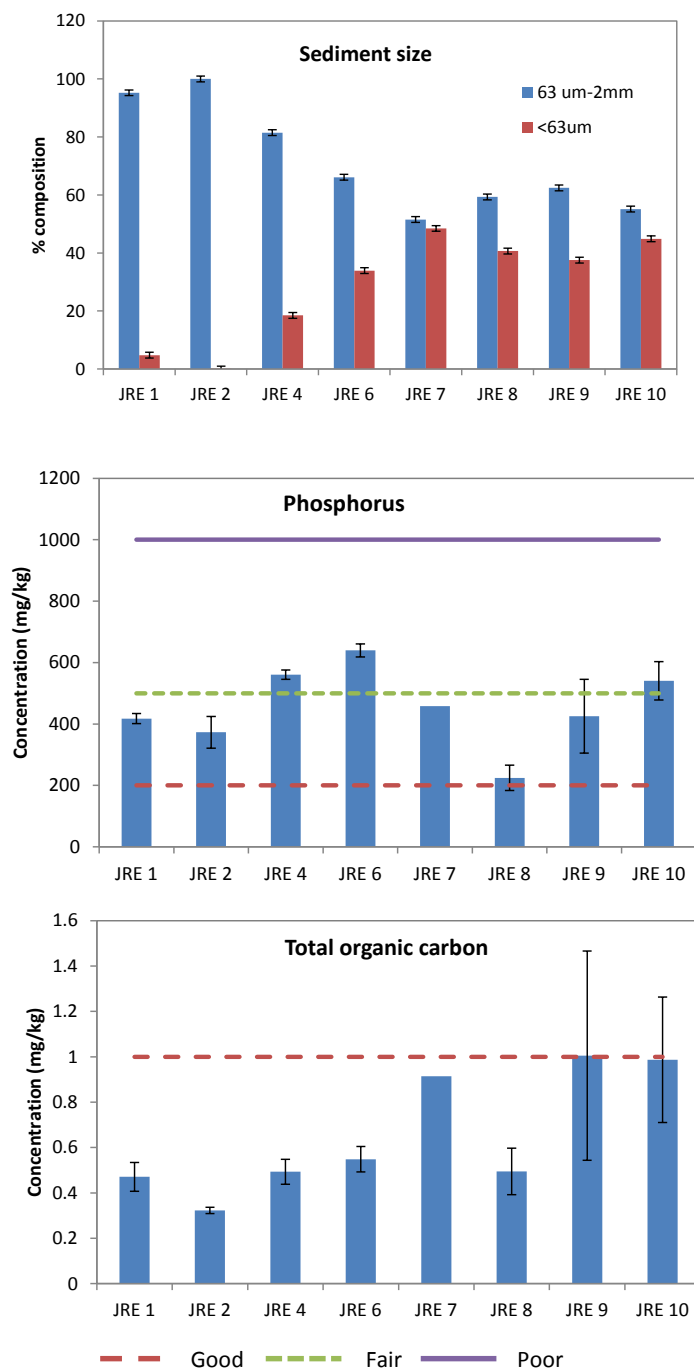
Figure 8 Sediment size, total organic carbon and phosphorus distribution in sediment samples collected from Jacobs River Estuary.
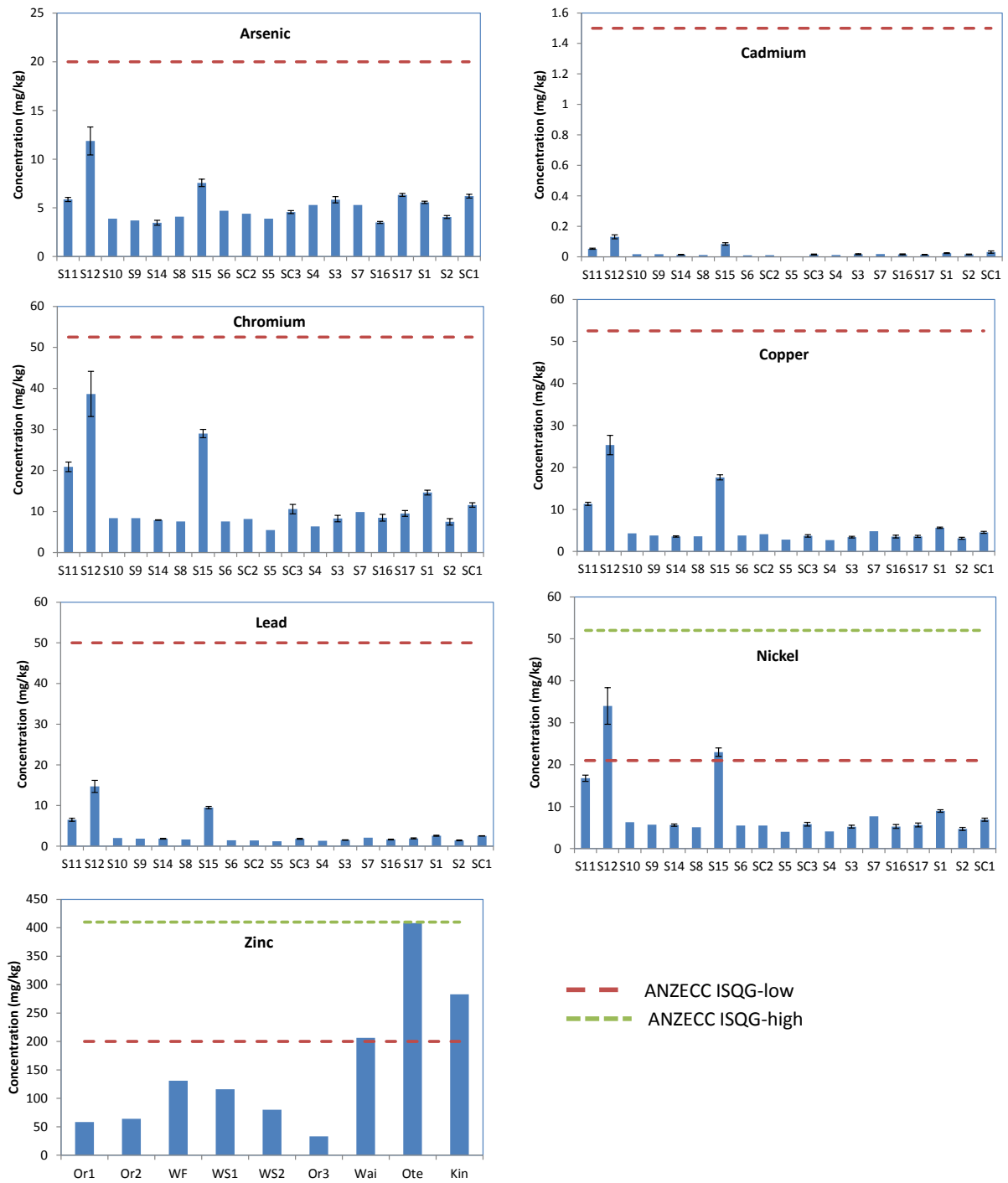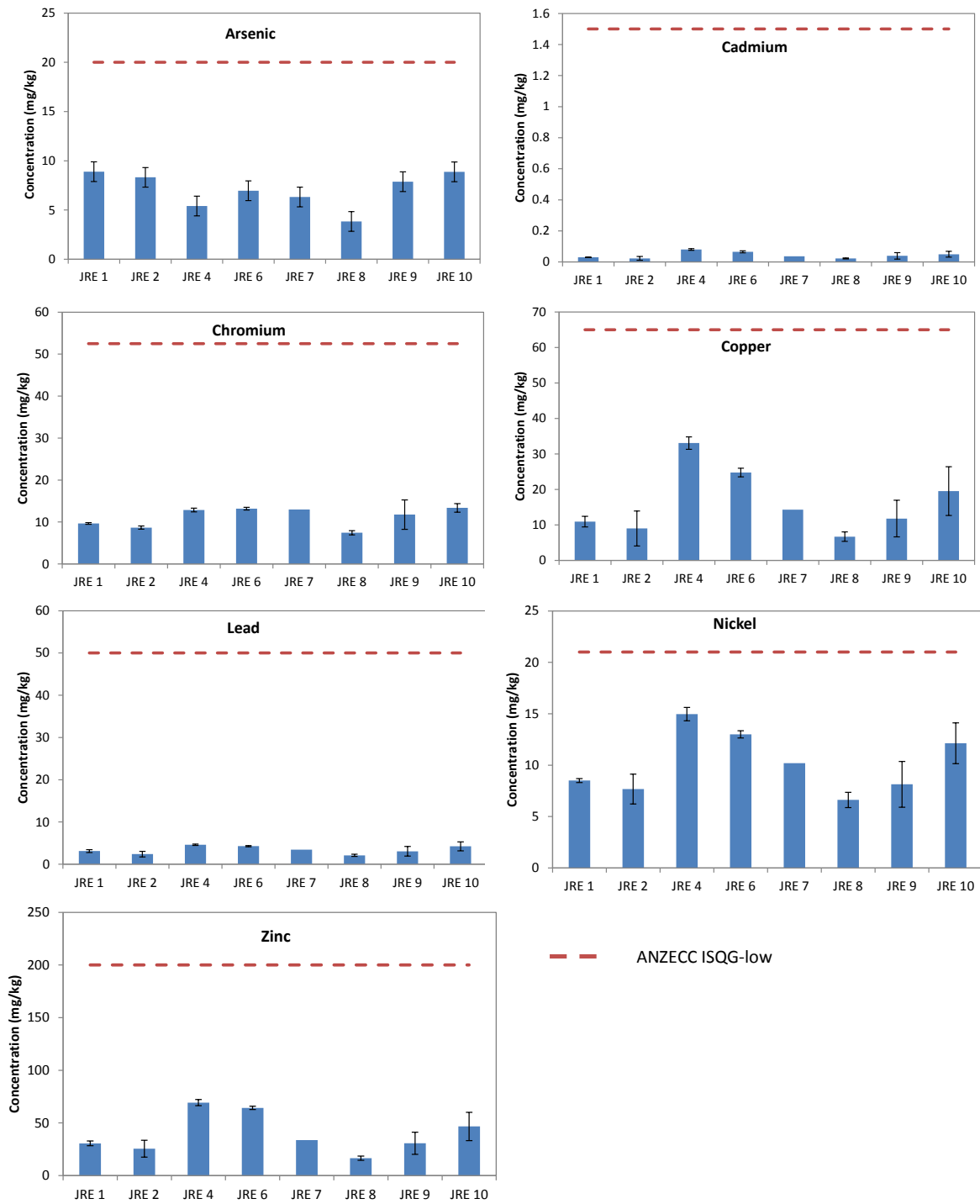
Figure 9 Metal concentrations and corresponding sediment quality guidelines for Jacobs River Estuary sediment samples.

Error bars are shown for samples that had replicates taken . SQG for chromium is taken from CCME (2003) for estuarine waters (Table 5).

Table 7 Correlation coefficients for sediment samples collected from Jacobs River Estuary[1]

	Phosphorus	Total organic carbon (TOC)	Sediment size 63 um – 2 mm	<63 um	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Phosphorus	1										
TOC	0.346154	1									
63 um –2 mm	−0.15026	−0.67301	1								
<63 um	0.150263	0.673006	−1	1							
Arsenic	0.331195	0.245566	0.282072	−0.28207	1						
Cadmium	**0.84522**	0.292525	−0.21356	0.213558	−0.072	1					
Chromium	**0.898643**	0.648893	−0.40755	0.40755	0.237638	**0.803614**	1				
Copper	**0.837911**	0.176163	−0.12779	0.127792	−0.05705	**0.978436**	0.755867	1			
Lead	**0.914856**	0.446484	−0.26459	0.264588	0.180701	**0.933555**	0.884993	0.921073	1		
Nickel	**0.889279**	0.237264	−0.1706	0.170604	0.029226	**0.959538**	0.822364	0.981001	0.953776	1	
Zinc	**0.908185**	0.163183	−0.11525	0.115249	0.032549	**0.963958**	0.790966	0.980054	0.929344	0.977109	1

[1]Bolded correlation coefficients indicate significant ($P < 0.05$) correlations.

5.2 Riverine sediments and biota

5.2.1 Sediments

Sediment samples collected from rivers typically had a high proportion of fine sediment, an exception being Or2 and Or3, collected from the lower reaches of the Oreti River (Figure 10). There were no clear relationships between fine sediment and other parameters, with the correlation between all parameters generally poor when all sites were included (Figure 10, Table 8), potentially indicating there are different sources of the contaminants in the different systems. The correlation between parameters improved if only samples collected from the Oreti River and Waikiwi Stream were considered, suggesting a more consistent source of contamination (Table 9).
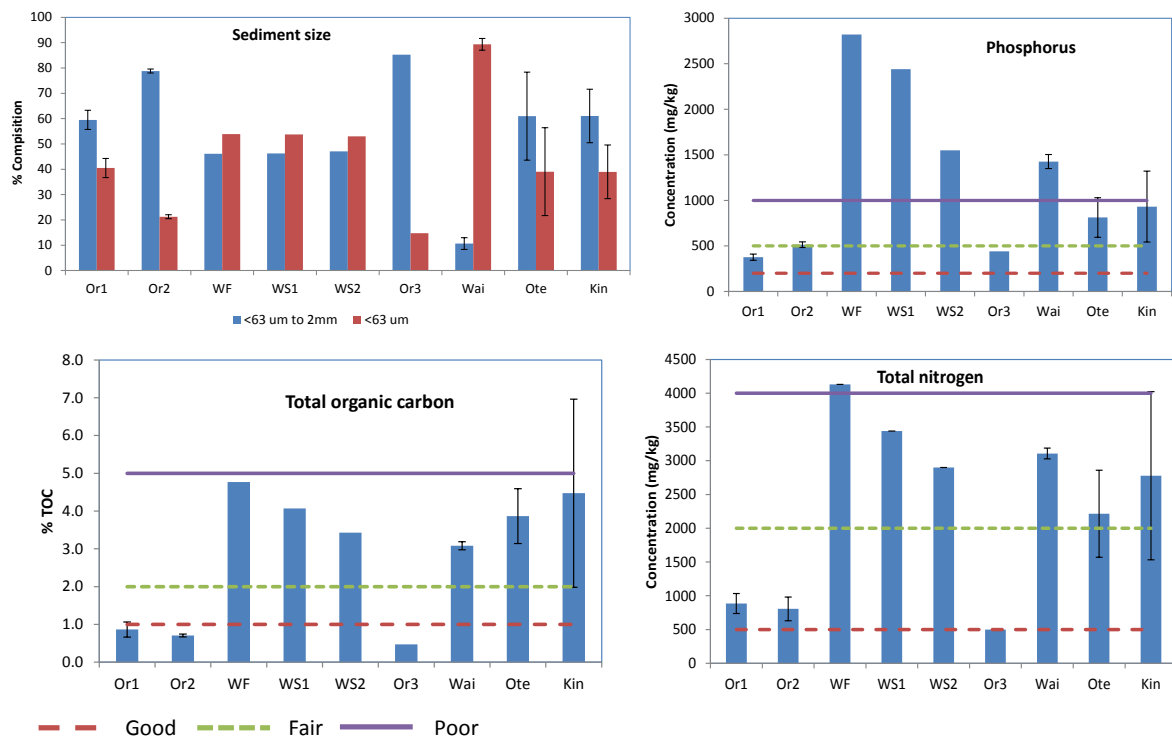
Figure 10 Sediment size (<63 µm is considered mud), total organic carbon, phosphorus and total nitrogen content in sediments collected from the Oreti, Waikiwi and Waihopai Rivers and Otepuni and Kingswell creeks. Error bars are shown for site where replicate samples were collected. Quality guidelines for phosphorus, total organic carbon and total nitrogen in estuarine waters from Robertson & Stevens (2012a).

In general, sediment collected from the urbanised catchments (Otepuni, Waihopai and Kingswell) had higher contaminant loadings for all metals except cadmium compared with sediment from the more agricultural catchments (Oreti, Waikiwi) (Figure 11). This pattern was particularly notable for arsenic, copper, lead, nickel and zinc, but less so for chromium and mercury, potentially suggesting more diffuse sources of the latter two metals. Interestingly, the mercury profile is similar to the cadmium profile, with the exception that urban sites have higher concentrations of mercury than the agricultural sites. This difference

may be attributed to the input of cadmium from soils to which phosphate fertilisers have been applied. A strong correlation between cadmium and phosphorus was observed in the Oreti/Waikiwi samples that were analysed (Table 9).

Figure 11 Metal concentrations and corresponding sediment quality guidelines for sediments collected from the Oreti,Waikiwi and Waihopai Rivers and Otepuni and Kingswell creeks.
Error bars are shown for samples that had replicates taken.

Table 8 Correlation between parameters in all riverine sediment samples[1]

	Phosphorus	Total organic carbon (TOC)	Sediment size 63 um – 2 mm	<63 um	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Phosphorus	1										
TOC	0.576555	1									
63 um –2 mm	−0.51466	−0.25356	1								
<63 um	0.514664	0.253563	−1	1							
Arsenic	0.189912	0.475845	−0.60863	0.60863	1						
Cadmium	0.697455	**0.810935**	−0.09614	0.096135	0.210084	1					
Chromium	0.086632	−0.04524	−0.68487	0.684875	0.69394	−0.16616	1				
Copper	−0.04438	0.426988	-0.19297	0.19297	0.828015	0.338429	0.515958	1			
Lead	−0.15428	0.527371	0.095544	-0.09554	0.577512	0.449509	0.097434	**0.866049**	1		
Nickel	−0.15462	0.239425	0.0471	-0.0471	0.608598	0.273746	0.425001	**0.835422**	0.676128	1	
Zinc	−0.02467	0.697846	0.017021	-0.01702	0.640633	0.531055	0.12692	**0.809484**	0.905835	0.74512	1

[1]Bolded correlation coefficients indicate significant ($P < 0.05$) correlations.

Table 9 Correlation between parameters in sediments collected from the Oreti/Waikiwi system[1]

	Phosphorus	Total organic carbon (TOC)	Sediment size 63 um – 2 mm	<63 um	Arsenic	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Phosphorus	1										
TOC	**0.981469**	1									
63 um –2 mm	−0.75604	−0.84104	1								
<63 um	**0.756036**	**0.841041**	−1	1							
Arsenic	**0.799402**	**0.700563**	−0.47269	0.472689	1						
Cadmium	**0.973459**	**0.995046**	**−0.83198**	**0.831982**	0.654608	1					
Chromium	−0.29648	−0.32254	0.0072	−0.0072	0.181564	−0.39257	1				
Copper	0.351416	0.308007	−0.4801	0.480097	0.697686	0.237533	0.782179	1			
Lead	**0.956865**	0.937027	−0.8057	0.805701	**0.873844**	**0.908836**	−0.01331	0.592715	1		
Nickel	−0.39805	−0.44043	0.149745	−0.14974	0.114031	−0.50863	0.981833	0.711376	−0.13431	1	
Zinc	**0.983494**	**0.937445**	−0.68303	0.683029	**0.885509**	**0.921203**	−0.19447	0.43753	**0.968045**	−0.29323	1

[1]Bolded correlation coefficients indicate significant ($P < 0.05$) correlations.

Higher concentrations of ∑DDTs were found in the sediments of streams draining urban catchments (Otepuni, Waihopai and Kingswell) as compared with rivers draining more agricultural catchments (Oreti and Waikiwi) (Figure 12). This may reflect a greater historical usage in urban areas in Southland, compared with agricultural areas – where DDT was often widely used.

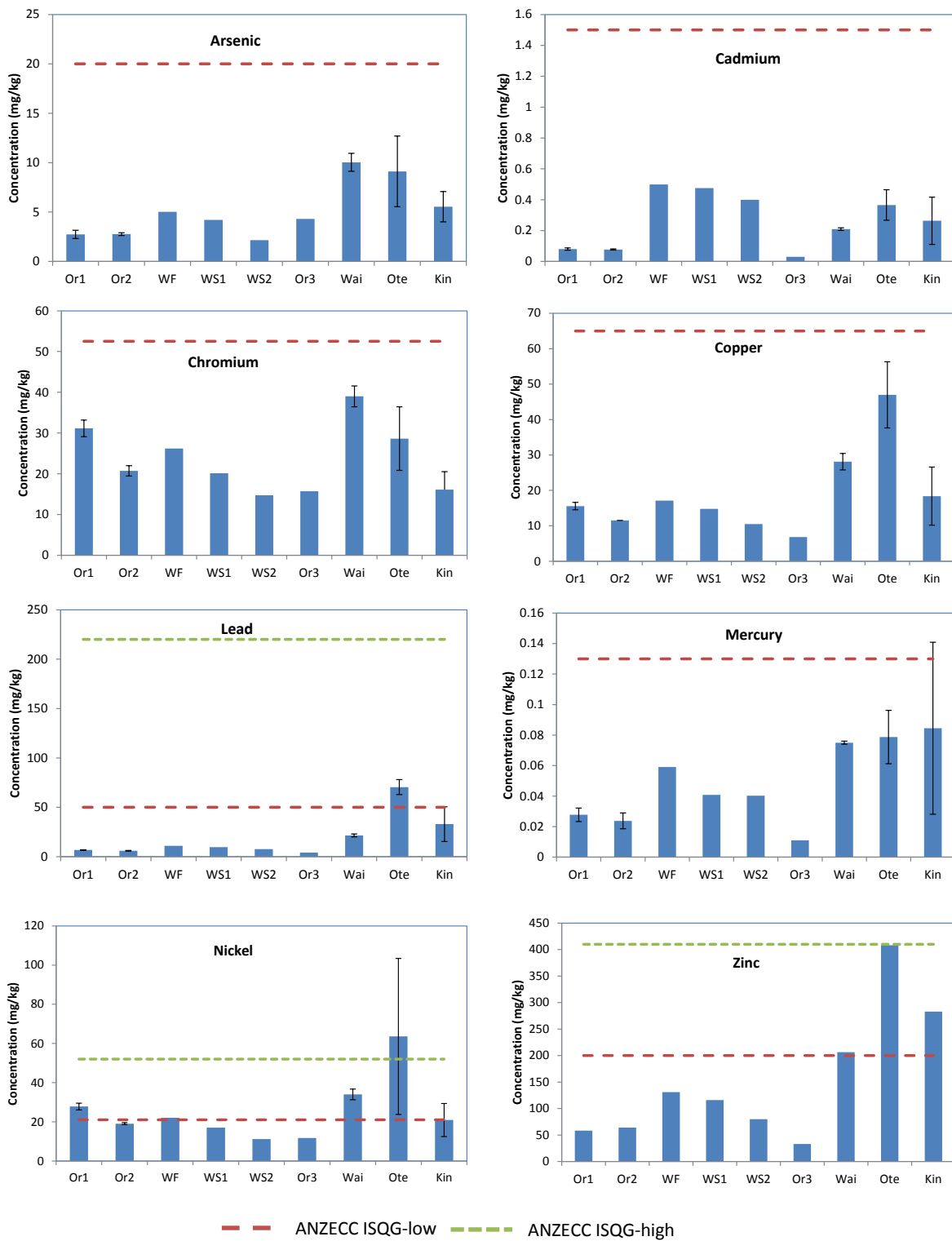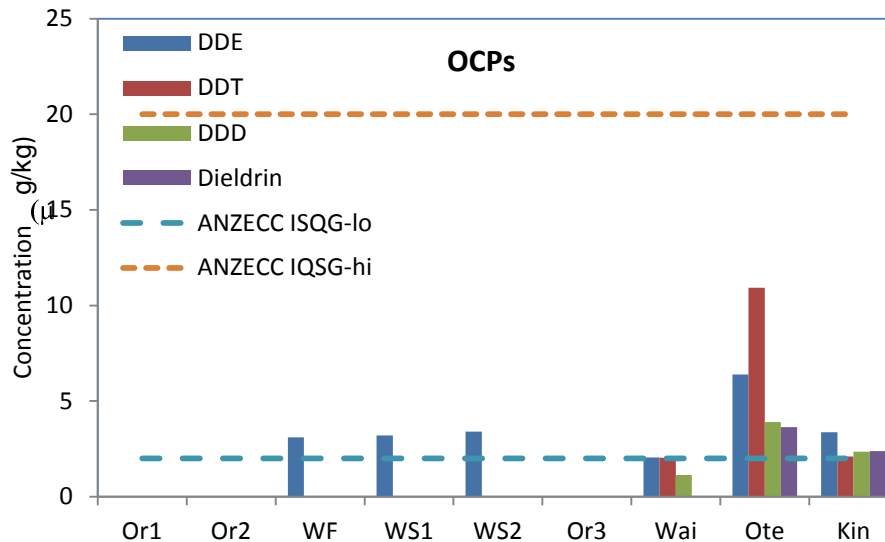**Figure 12** Organochlorine pesticide concentrations (OCPs) and corresponding sediment quality guidelines for sediments collected from the Oreti,Waikiwi and Waihopai Rivers and Otepuni and Kingswell creeks. Error bars are shown for samples that had replicates taken.

5.2.2   Biota

Some species-specific differences in the accumulation of metals were observed in tissues of the biota sampled (Figures 13 and 14). For example, no arsenic was found in eel tissue, while limited amounts of cadmium and lead were found in trout tissue – these were similar observations to those made by Stewart et al. (2011). Copper and zinc are both essential elements, and their uptake is able to be regulated by organisms, thus the similarity in concentrations across different samples is not surprising. Trout appear to have less zinc in their flesh than eels. Chromium (not shown) was not detected in eels and fish collected in the Oreti River above the Waikiwi confluence, but was detected at all other locations. Nickel (not shown) was found in the flesh of one eel collected from Or2, at concentration just above the detection limit (0.01 mg/kg). Eels from the upper Oreti River appear to have higher concentrations of mercury in their flesh.

Concentrations of the majority of trace elements are typically greater in the internal organs than in the tissue – a notable exception is mercury, which was present in higher concentrations in tissue (Table 10).

No ivermectin was detected in any biota samples.
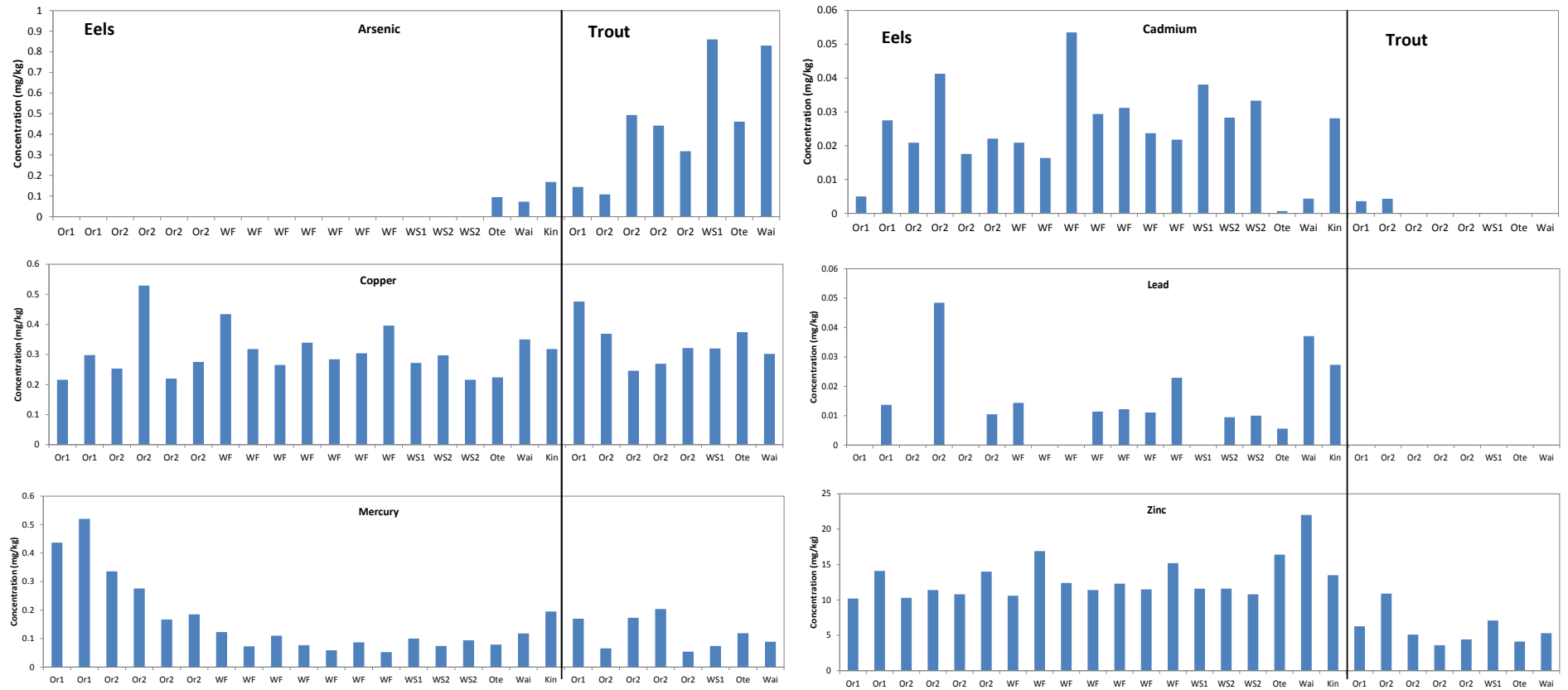
Figure 13 Concentrations (mg/kg wet wt) of metals in the flesh of eels, trout and mullet.
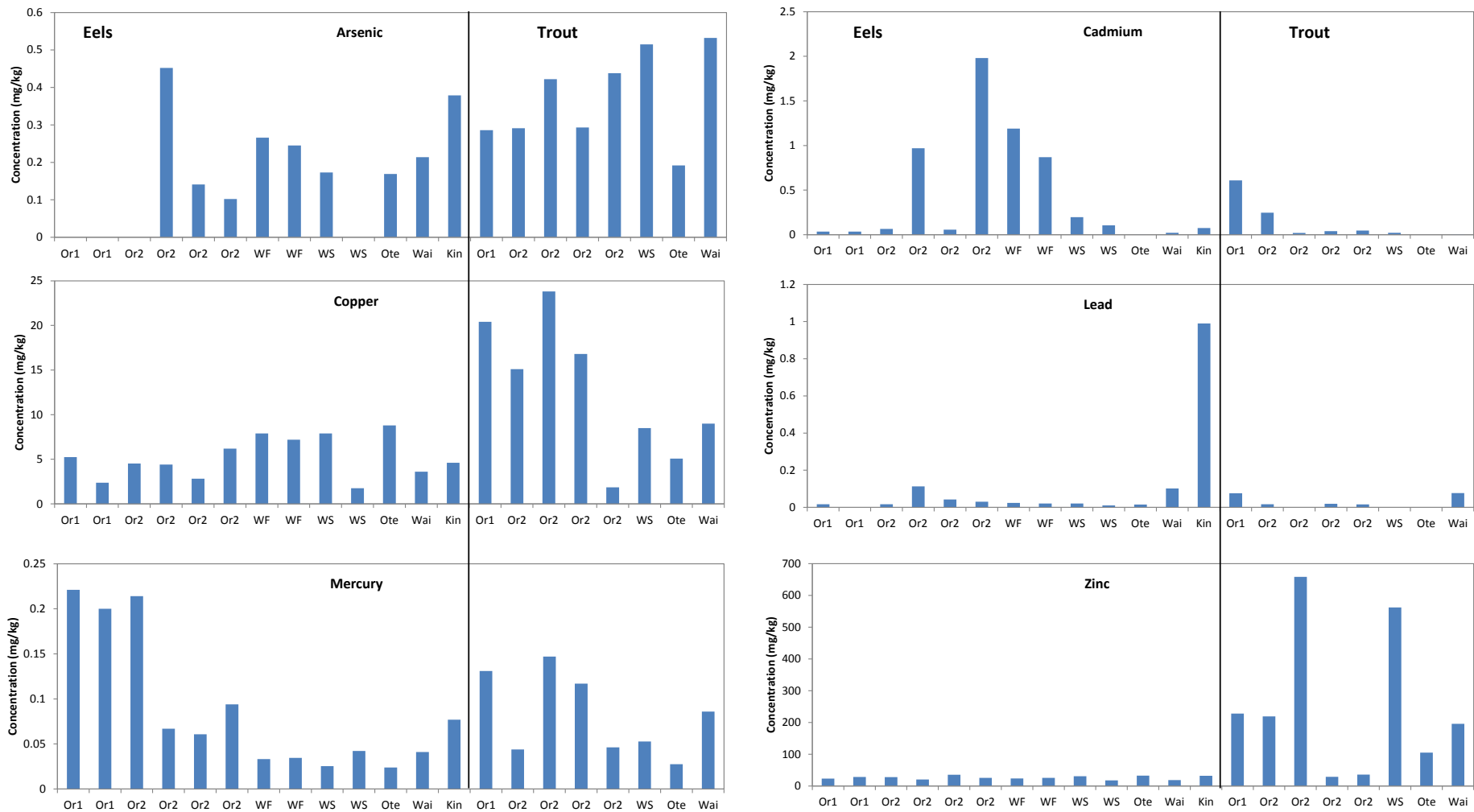
Figure 14 Concentrations(mg/kg wet wt) of contaminants in the internal organs of eels and trout.

Table 10 Summary of lipid content (%) and contaminant concentrations (mg/kg wet wt) in the tissue and internal organs of eels and fish

Analyte	Eels						Fish[1]					
	Tissue			Internal organs			Tissue			Internal organs		
	Median[2]	Max	Min	Median[2]	Max	Min	Median[2]	Max	Min	Median[2]	Max	Min
Lipid (%)	4.4 (n=19)	10.4	2.1	2.1 (n=9)	6.3	1.4	1.05 (n=8)	1.6	0.3	5.1 (n=8)	7.6	1.3
Arsenic	0.095 (n=3)	0.168	0.073	0.214 (n=9)	0.452	0.102	0.452 (n=8)	0.86	0.108	0.356 (n=8)	0.532	0.192
Cadmium	0.0237 (n=19)	0.054	0.0007	0.076 (n=13)	1.98	0.0044	0.0040 (n=2)	0.0043	0.0036	0.031 (n=8)	0.609	0.003
Chromium	0.11 (n=8)	0.125	0.04	0.156 (n=8)	0.504	0.103	0.036 (n=3)	0.099	0.029	0.103 (n=7)	0.313	0.098
Copper	0.28 (n=19)	0.529	0.216	4.6 (n=13)	8.8	1.75	0.3205 (n=8)	0.476	0.246	12.05 (n=8)	23.8	1.86
Lead	0.012 (n=13)	0.0484	0.0056	0.023 (n=12)	0.99	0.0102	ND	ND	ND	0.0198 (n=5)	0.077	0.016
Mercury	0.11 (n=19)	0.52	0.0526	0.061 (n=13)	0.221	0.024	0.104 (n=8)	0.204	0.0543	0.069 (n=8)	0.147	0.028
Nickel	0.147 (n=1)	0.147	0.147	0.163 (n=6)	0.313	0.104	ND	ND	ND	0.290 (n=2)	0.436	0.29
Zinc	11.6 (n=19)	22	10.2	25.9 (n=13)	35.5	17.8	5.21 (n=8)	10.9	3.61	207.5 (n=8)	658	29.2
4,4'-DDD	0.0015 (n=18)	0.037	0.0007	0.0009 (n=7)	0.019	0.0005	0.0008 (n=6)	0.0032	0.0005	0.0016 (n=6)	0.0062	0.0005
4,4'-DDE	0.024 (n=19)	0.128	0.012	0.0046 (n=9)	0.033	0.0018	0.0091 (n=8)	0.016	0.004	0.034 (n=7)	0.043	0.0036
4,4'-DDT	0.0019 (n=16)	0.022	0.00052	0.00097 (n=4)	0.0116	0.0005	0.0010 (n=4)	0.0016	0.0005	0.0026 (n=6)	0.0042	0.0005
Dieldrin	0.0009 (n=5)	0.0034	0.00067	ND	ND	ND	ND	ND	ND	ND	ND	ND

[1]Primarily brown trout; yellow-eye mullet collected at two locations

[2]Median of concentrations above the detection limit

DDTs were found in the majority of flesh samples, and internal organ samples (Figure 15). While the eel concentrations appear higher, this is largely related to the greater lipid content. When expressed on a per-lipid basis, concentrations in the trout flesh are similar, and in some cases higher, than in the eel flesh. The concentrations found in the current study appear to be lower than that found in eels and fish in South Canterbury (Stewart et al. 2011), and during a nationwide study (Buckland et al. 1998) (Table 11).
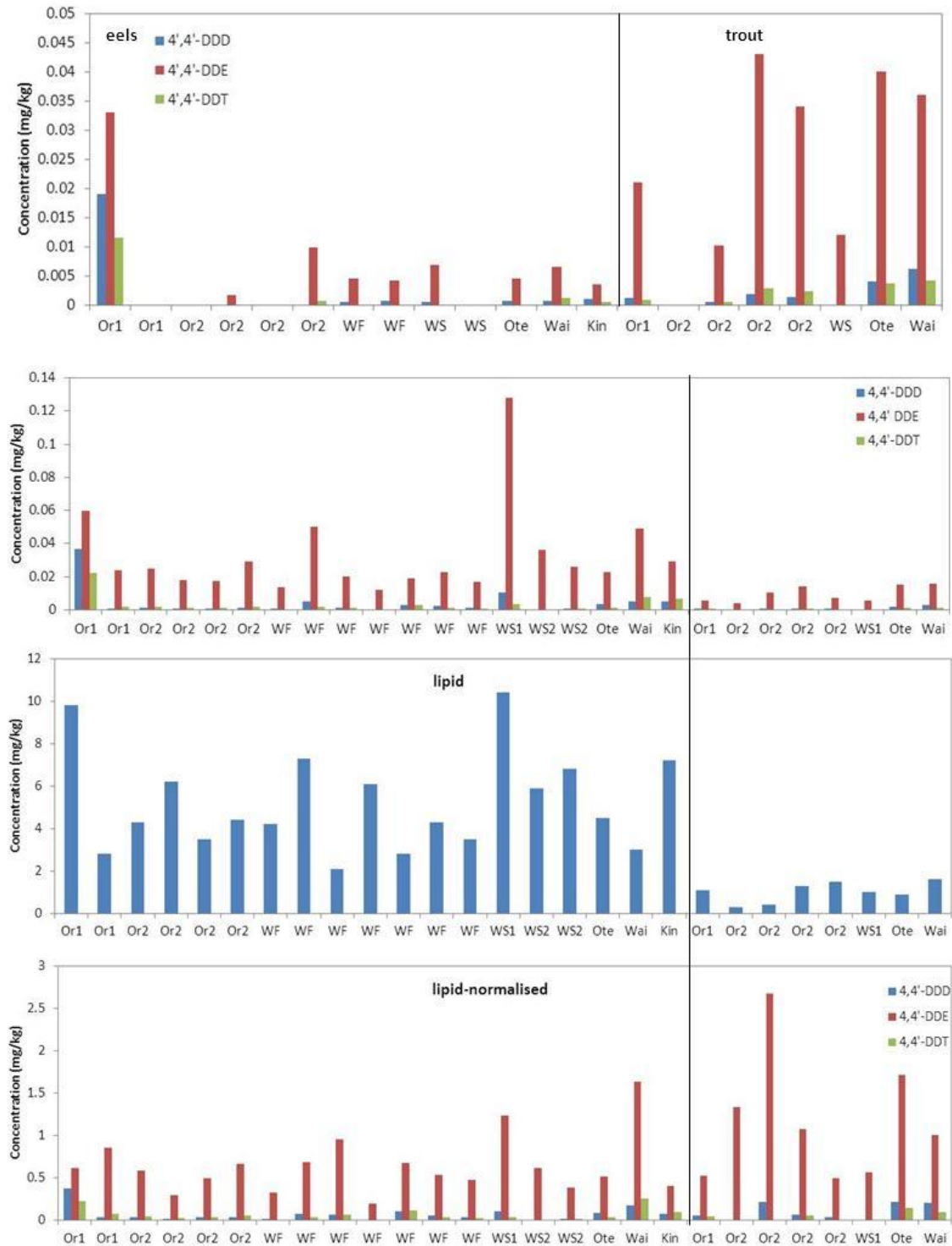
Figure 15 DDTs concentrations (mg/kg wet wt) in the internal organs and flesh of eels and fish, lipid content and lipid-normalised flesh concentrations.

Table 11 Comparison of organochlorine pesticide concentrations in the current study with those determined by Stewart et al. (2011) and Buckland et al. (1998)

Species	Contaminant	This study (µg/kg ww)		Stewart et al. (2011)		Buckland et al. (1998)	
		Max	Min	Max	Min	Max	Min
Eel	DDT	22	<0.5	27	0.22	25.5	0.1
	DDD	37	<0.5	60.2	0.12	33.1	0.032
	DDE	128	12	287	8.6	155	0.67
	Dieldrin	3.4	<0.5	16.3	<0.005	11.4	<0.01
Trout	DDT	1.6	<0.5	0.36	0.07	0.91	0.16
	DDD	3.2	<0.5	0.37	0.04	1.97	0.043
	DDE	16	4	18.5	2.2	73.9	1.82

5.3 Sediment quality

Comparison of contaminant concentrations in sediment with sediment quality guidelines is a useful and conventional way of assessing sediment quality. As shown in Figures 6, 9 and 11, some contaminants are present at concentrations that exceed the Australian and New Zealand Environment Conservation Council (ANZECC) interim sediment quality guidelines (ANZECC/ARMCANZ 2000). Of these, levels of zinc and particularly nickel in Otepuni Creek potentially trigger the most concern, as they exceed or almost exceed the ISQG-high guideline (Table 5), and nickel is the only metal sampled in the New River Estuary sediments that exceeds sediment quality guidelines.

In terms of understanding the significance of these exceedances, it is useful to consider the origin of these guidelines. The sediment quality guidelines presented in the ANZECC/ARMCANZ water quality guidelines (2000) are primarily sourced from Long et al. (1995), who derived criteria using a weight-of-evidence approach. These criteria are for marine and estuarine sediments, and use international (US) data. There are other sediment quality guidelines that have been developed internationally, generally using a similar approach to Long et al. (1995). Hubner et al. (2009) provides a good overview, and some additional guidelines are shown in Table 7. However, using different guidelines, e.g. for copper, would indicate an even greater level of exceedance of sediment quality guidelines.

Differences in the available criteria arise from differences in the methodology and data used. However, most sediment quality guidelines follow the 'weight-of-evidence' approach, and define some low-effect concentration and a high (median) effect concentration, based on assessment of the literature and the concentration at which effects have been observed. Some sediment quality guidelines may be normalised to an organic carbon content of 1% (e.g. ANZECC/ARMCANZ 2000), although various studies (e.g. Ingersoll et al. 2001; McCready et al. 2006) have shown that normalisation to organic carbon content has either a marginal effect or no effect on the predictive abilities (in terms of toxicological effect) of sediment quality guidelines.

Chapman et al. (1999) suggest that appropriate use of sediment quality guidelines (SQGs) requires that they are used solely in the region where they were developed. This is not always feasible, however, because the majority of the SQGs have been developed in and for North America – although there are some exceptions (e.g. Menchaca et al. 2012). However, to develop guidelines appropriately is a significant cost and, as noted by Hubner et al. (2009), is not always advisable since geography is not the only aspect that should be taken into account. Despite these reservations, to ascertain whether an effect is actually occurring, biological testing should be used, particularly if management actions are going to be implemented.

Aside from comparing sample concentrations against sediment quality guidelines, another useful way of considering inputs to sediment contamination is to look at trends over time, and the spatial distribution of elevated concentrations, and to consider whether these can be minimised. For example, Figure 11 highlights the elevated concentrations present in streams flowing through urban areas (Otepuni, Waihopai and Kingswell catchments). This is not unexpected; copper and zinc are known to have a range of diffuse sources in urban environments, and stormwater is a known significant contributor to sediment contaminant loads. However, the origin of the elevated nickel concentrations is less clear. Nickel is typically more associated with industrial activities such as electroplating and certain products such as stainless steel, certain batteries and special alloys and thus may be expected to be found in sewage treatment effluent (via trade waste discharges) – although a significant input via stormwater would be unusual. Nickel may also be naturally elevated in cetain rock types e.g. ultramafic rocks, (Kabiata-Pendias 2001), which may lead to elevated sediment concentrations. Regardless of sources, changes to stormwater management systems to allow for contaminant removal prior to discharge to rivers and streams would improve sediment quality.

Nickel was the only metal to exceed sediment quality guidelines in either estuary (Figures 5 and 9). In addition to riverine discharges (Oreti, Waihopai, Otepuni, Kingswell catchments), the Clifton Wastewater Treatment Plant also discharges into New River Estuary. Information on metal loadings from the Clifton plant indicate that nickel is about one-third the loading of either copper or zinc, yet in the sediments nickel concentrations are at similar levels to copper and zinc concentrations are two to three times higher than nickel concentrations. This may suggest differences in metal partitioning of these different metals upon reaching the estuarine environment, as well as other potential sources. Further, although nickel sediment quality guidelines are exceeded, whether this is causing a biological impact remains to be demonstrated.

5.4 Potential human health risks

To provide context for the contaminants found in the eel and fish tissue, we compared the concentrations with the New Zealand food standards (FSANZ 2005), where they exist, and to concentrations determined in fish collected as part of the most recent New Zealand Total Diet Survey (NZTDS; Vannoort & Thomson 2011). Concentrations in fish in the NZTDS are determined on an as-consumed basis, i.e. cooked, although an approximate comparison can be made on a wet weight basis. Food standards are set on a wet-weight basis. The median, maximum and minimum concentrations determined in eel and fish tissue are shown in Table 12, alongside relevant food standards and data from the NZTDS.

As can be seen (Table 12), concentrations of arsenic, lead and mercury determined in the current study are generally lower than the food standards, although one eel exceeded the standard for mercury. Stewart et al. (2011) also found that mercury in some eel samples collected from South Canterbury exceeded the Australia/New Zealand food standards. Arsenic and mercury concentrations in our study were lower than the results from the NZTDS, but concentrations of cadmium and lead were higher in the eels and fish we analysed from Southland than results in the NZTDS (Table 12).

In addition to comparing concentrations against food standard levels, we determined the potential risk to human health arising from consumption of locally caught eels and fish determined using margin of exposure (MOE) (as per Section 4.5). The results of the risk modelling are shown in Table 13; an elevated risk is shown by MOE > 1. As can be seen from Table 13, the MOE is typically <1, with the exceptions being some exposures for the New Zealand high energy consumer and upper estimates of contaminant concentrations for the NZTDS female adult. Consumption of trout by a high energy consumer gives rise to an MOE > 1 for both the median and 95th percentile concentrations for arsenic, indicating an increase in cancer risk over the accepted risk of 1 in 100 000 up to $8 \times 100\,000$. Estimates for arsenic have assumed that 10% of the total arsenic is inorganic arsenic – this percentage may be less (e.g. Storelli and Marcotrigiano (2000) indicated that inorganic arsenic in fish was more typically 0.5% to a maximum of 4%) – a lower percentage of inorganic arsenic would reduce the calculated MOE. The estimated consumption (66 g/day) for this consumer is between 5 to 8 times greater than fish consumption for the other consumers considered (New Zealand female (13 g/day) and local consumers (8.7 g/day trout and flounder)) and thus is a conservative assessment of risk. Consumption of both eel and trout by the high energy consumer also gives rise to an MOE > 1 for the 95th percentile concentration of mercury, indicating exposure at greater than the selected safe level. As noted earlier, the toxicological value used to calculate the MOE (0.1 µg/bw/wk) is the most conservative international estimate and a provisional tolerable weekly intake (PTWI) of 1.6 µg/kg body wt/wk (or 0.23 µg/ kg bw/day) is used in the New Zealand Total Diet Survey as the basis for comparison for mercury intakes. This is based on protection of developmental neurotoxicity and intakes up to two times higher are still considered protective of neurotoxicological effects in adults (WHO (2006). Comparing intakes to this tolerable intake will reduce the calculated MOE. Overall, the results of the risk modelling indicate minimal risk to human health arising from consumption of locally caught eels, fish and cockles.

Table 12 Concentrations of contaminants in eel and fish flesh (mg/kg wet weight) and comparison with concentrations measured in the New Zealand Total Diet Survey (NZTDS; Vannoort & Thomson 2011), and food standards (FSANZ 2005)

Analyte	Eel (mg/kg wet weight)			Trout/mullet (mg/kg wet weight)			Cockles (mg/kg wet weight)			NZTDS (mg/kg wet weight)			Maximum level FSANZ (mg/kg wet weight)
	Mean[1]	Max	Min	Mean[1]	Max	Min	Mean[1]	Max	Min	Mean[1]	Max	Min	
Arsenic[2]	0.060	0.168	<0.1	0.46	0.86	0.11	1.67	2.29	0.71	3.98	6.31	2.08	2 (inorganic)
Cadmium	0.024	0.054	0.001	0.002	0.004	<0.0004	0.01	0.01	0.01	0.002	0.005	0.001	-
Chromium	0.07	0.13	0.04	0.052	0.099	0.029	0.18	0.25	0.11	NT			-
Copper	0.31	0.53	0.22	0.36	0.48	0.25	0.33	0.35	0.29	NT			-
Lead	0.014	0.048	<0.1	ND			0.006	0.007	0.005	0.004	0.006	<LOD	0.5
Mercury	0.17	0.52	0.053	0.119	0.204	0.054	NT			0.12	0.3	0.05	0.5
Nickel	0.0553	0.147	<0.10	ND			1.26	1.59	0.95	NT			-
Zinc	13	22	10.2	5.7	10.9	3.6	4.9	5.9	3.9	NT			-
4,4'-DDD	0.004	0.037	<0.0005	0.001	0.003	<0.0005	NT			ND			-
4,4'-DDE	0.033	0.128	0.012	0.010	0.016	0.004	NT			ND			-
4,4'-DDT	0.003	0.022	<0.0005	0.001	0.002	<0.0005	NT			ND			-
Dieldrin	0.001	0.003	<0.0005	ND			NT			ND			0.1

ND – not detected, NT – Not tested.

[1]Calculated by inserting the value for 'not detected' with half the lowest observed detection concentration.

[2]Total arsenic is measured, whereas the food standard is based on inorganic arsenic. Inorganic arsenic is considered to comprise less than 10% of total arsenic in fish flesh.

[3]Nickel detected in one eel.

Table 13 Risk assessment margin of exposure (MOE) calculations of chronic health risk[1] for three consumption-rate scenarios for median and 95th percentile concentrations in eels, fish and cockles from Southland.

Species	Analyte	Consumption rate scenario					
		'Local' consumption rates		NZTDS adult female		NZ high energy consumer	
		Median	95th percentile	Median	95th percentile	Median	95th percentile
Eel	Arsenic[2]	0.044	0.646	0.108	**1.6**	0.480	**7.0**
	Cadmium	0.0019	0.0037	0.0047	0.0091	0.0210	0.0405
	Chromium	0.0013	0.0031	0.0031	0.0075	0.0138	0.0332
	Lead	0.0002	0.0014	0.0005	0.0033	0.0022	0.0148
	Mercury	0.084	0.310	0.204	0.755	0.908	**3.4**
	Zinc	0.003	0.004	0.007	0.010	0.031	0.046
	DDTs	0.004	0.019	0.010	0.045	0.045	0.200
Trout/mullet[3]	Arsenic[2]	0.26	0.50	0.98	**1.8**	**4.3**	**8.1**
	Cadmium	0.0001	0.0002	0.0002	0.0009	0.0010	0.0041
	Chromium	0.0008	0.0014	0.0031	0.0051	0.0138	0.0225
	Mercury	0.052	0.097	0.193	0.359	0.858	**1.6**
	Zinc	0.001	0.002	0.003	0.006	0.014	0.026
	DDTs	0.0010	0.0020	0.0037	0.0074	0.0165	0.0330
Cockles	Arsenic[2]	0.48	0.66	0.55	0.75	0.97	**1.3**
	Cadmium	0.0003	0.0004	0.0004	0.0005	0.0007	0.0008
	Chromium	0.0015	0.0020	0.0017	0.0023	0.0029	0.0040
	Zinc	0.0001	0.0001	0.0001	0.0001	0.0002	0.0003

[1] Cancer risk for arsenic, non-cancer risk for remaining contaminants.

[2] Arsenic calculation reduced by a factor of 10 to reflect an approximate proportion of inorganic arsenic.

[3] No lead detected in fish flesh. Bolded results indicate MOE>1.

6 Conclusions

Sediment collected from rivers and streams draining into the New River Estuary had higher concentrations than the estuarine sediments. Sediment from Otepuni Creek, Waihopai River and Kingswell Creek, which pass through Invercargill, unsurprisingly had higher metal concentrations than those rivers and streams draining more agricultural catchments (Oreti River and Waikiwi Stream), with the exception of cadmium. Nickel and zinc showed the greatest exceedance of sediment quality, with nickel exceeding the ANZECC ISQG-high in Otepuni Creek. Stormwater discharge is the likely source of contamination. ∑DDT concentration was also greater in sediments from the urban catchment compared with agricultural catchments, which is a little surprising but may reflect a more intensive historical usage in urban areas in Southland compared with 'broad-acre' use in agricultural areas. In contrast, cadmium was found at higher concentrations in some sediments from agricultural catchments (e.g. Waikiwi River). The presence of cadmium in the sediment, and its high correlation with phosphorus, suggests likely input of agricultural soils to the drainage systems.

Monitoring of eels and fish collected in the riverine systems highlighted the accumulation of mercury and DDTs, which were not detected or present at low concentrations in the sediments. Contaminant concentrations were typically higher in internal organs as compared to flesh – an exception being mercury, which had higher concentrations in the flesh. There appear to be some species-specific differences in contaminant accumulation, with arsenic typically not detected in eel flesh (except for those collected from urban streams) and lead typically not detected in fish flesh. Cadmium and zinc were typically present at lower concentrations in fish flesh compared with eel flesh. Regardless of the concentrations determined, there appears to be a negligible health risk generally associated with the consumption of eels and fish from these water bodies. Under a high consumption scenario or high-end contamination there may be some increase in risk from arsenic and mercury although this is still minor.

Similar to previous studies (e.g. Hodson 2011; Robertson & Stevens 2012a), the current study showed that a number of sites within the New River Estuary and surrounding rivers are highly enriched with phosphorus and also contain elevated organic carbon. There were generally low levels of contamination from metals (including arsenic) in the estuaries themselves, with concentrations rarely exceeding the ANZECC ISQG-low. An exception was nickel in the New River Estuary, which exceeded the ISQG at two locations that had a high proportion of fine sediment. These locations were both in the upper arms of the estuary (near Invercargill).

Sediments collected from New River Estuary appeared to be well-mixed, with contaminant loads (and organic carbon and phosphorus) highly correlated with the amount of fine sediment present at the sites. In contrast, sediments collected from the Jacobs River Estuary appeared to be more influenced by source contributions at different locations and there was poor correlation of contaminant load with fine sediment contribution.

Contaminant concentrations in cockles were typically low – zinc and arsenic were present in the highest concentrations – potentially suggesting that current bioaccumulation of contaminants in the New River Estuary is minor. The results provide a baseline from which further monitoring can be undertaken to assess changes over time; however, the seemingly patchy distribution of cockles in the estuaries may limit their usefulness as a biomonitor.

7 Recommendations

- In order to assess contaminant accumulation over time it is recommended that ongoing monitoring of contaminants, particular mercury and DDTs – that were low and variably detected in sediment monitoring, is conducted in riverine biota in selected locations. A frequency of 2–5 years would be adequate, with additional parameters, such as length and weight, also collected to help assess variations (e.g. due to age, condition) in contaminant concentrations and aid interpretation of changes over time. Muscle tissue would be most useful to target, as it also enables assessment of potential human health risk arising from consumption of locally caught fish.

- Closer inspection of the basis of the sediment quality guideline for nickel should be undertaken to understand the implications of exceeding this guideline value, and whether further investigation of nickel-related effects is warranted.

- Given the presence of mercury in edible flesh of fish, and the increasing international focus on the global cycling of mercury, mercury should be included in ongoing monitoring programmes.

- Establishing sediment sampling locations in the rivers and streams discharging into New River Estuary is recommended to enable assessment of changes in contaminant load over time. This should be combined with estimates of sediment discharge (e.g. from suspended sediment and flow data) from the different systems to the estuary to identify key contributors.

- As urbanised catchments continue to show an input of contaminants, stormwater inputs and other significant discharge points to rivers should be identified, and options for contaminant removal prior to river discharge investigated.

8 Acknowledgements

9 References

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Appendix 1 – Contaminant concentrations in eels and fish

Table 14 Lipid content and contaminant concentrations (mg/kg dry wt) in the internal organs of eels and fish

Location	Sample name	Sample type	Lipid content (%)	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	4,4'-DDD	4,4'-DDE	4,4'-DDT	Dieldrin
Or1	Oreti #1 B Longfin Eel#1 Internal organs	Eel	6.3	0.10	0.0357	0.105	5.24	0.0167	0.221	0.107	23.5	0.019	0.033	0.0116	< 0.0005
Or1	Oreti #1 B Longfin Eel#2 Internal organs	Eel		0.10	0.0347	<0.10	2.38	<0.010	0.2	<0.10	28.4				
Or2	Oreti #2 B Longfin Eel#1 Internal organs	Eel		<0.10	0.0649	<0.10	4.53	0.0171	0.214	<0.10	28.1				
Or2	Oreti #2 B Longfin Eel#2 Internal organs	Eel	1.9	0.452	0.97	0.504	4.41	0.113	0.067	0.313	20.6	< 0.0005	0.00178	< 0.0005	
Or2	Oreti #2 B Longfin Eel#3 Internal organs	Eel		0.141	0.0564	0.161	2.82	0.0423	0.0607	0.122	35.5				
Or2	Oreti #2 B Longfin Eel#4 Internal organs	Eel	2.7	0.102	1.98	0.18	6.2	0.0307	0.094	0.203	25.9	<0.0005	0.0098	0.00073	
WF	Waikiwi @ Ferry Rd B Longfin Eel #1 Internal Organs	Eel	2	0.266	1.19	0.128	7.9	0.0243	0.0333	<0.10	23.8	0.00054	0.0045	< 0.0005	< 0.0005
WF	Waikiwi @ Ferry Rd B Longfin Eel #2 Internal Organs	Eel	2.1	0.245	0.87	0.103	7.2	0.0209	0.0345	<0.10	25.7	0.00071	0.0042	< 0.0005	< 0.0005
W1	Waikiwi @ Staunton Rd 1 B Longfin Eel Internal organs	Eel	3.8	0.173	0.198	<0.10	7.9	0.0213	0.0254	<0.10	31.1	0.0005	0.0068	< 0.0005	< 0.0005
W1	Waikiwi @ Staunton Rd 2 B Shortfin Eel Internal Organs	Sfeel		<0.10	0.105	< 0.10	1.75	0.0102	0.0423	< 0.10	17.8				

Location	Sample name	Sample type	Lipid content (%)	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	4,4'-DDD	4,4'-DDE	4,4'-DDT	Dieldrin
Ote	Otepuni 3 Shortfin Eel Internal Organs	Sfeel	2.1	0.169	0.00439	<0.02	8.8	0.0157	0.0239	<0.02	32.6	0.00079	0.0046	< 0.0005	
	Kingswell 2 Longfin Eel Internal Organs	Eel	1.4	0.379	0.076	0.214	4.6	0.99	0.077	0.29	32.5	0.00102	0.0036	0.00054	
Wai2	Waihopai 2 Longfin Eel Internal organs	Eel	1.8	0.214	0.0229	0.154	3.6	0.102	0.041	0.104	19	0.00075	0.0066	0.0012	
Or1	Oreti #1 B Trout Internal organs	Trout	5.1	0.286	0.609	0.313	20.4	0.076	0.131	0.436	228	0.00129	0.021	0.00091	<0.0005
Or2	Oreti #2 B Trout #1 Internal organs	Trout		0.291	0.248	0.098	15.1	0.0167	0.0439	<0.10	219				
Or2	Oreti #2 B Trout #2 Internal organs	Trout	1.3	0.422	0.0204	0.1	23.8	<0.010	0.147	<0.10	658	0.0005	0.0103	0.0005	<0.0005
Or2	Oreti #2 B Trout #3 Internal Organs	Trout	5.6	0.293	0.0401	0.117	16.8	0.0198	0.117	<0.10	29.2	0.00185	0.043	0.0028	
Or2	Oreti #2 B Mullet Internal Organs	Mullet	7.6	0.438	0.0472	<0.10	1.86	0.0164	0.0463	<0.10	35.9	0.00131	0.034	0.0024	
Ote	Otepuni 1 Trout Internal organs	Trout	5.1	0.192	0.00282	0.102	5.07	<0.002	0.0275	<0.02	105	0.0041	0.04	0.0037	
Wai2	Waihopai 2 Trout Internal Organs	Trout	4.5	0.532	0.0051	0.172	9	0.077	0.086	0.143	196	0.0062	0.036	0.0042	
WS	Waikiwi @ Staunton Rd 1 B Trout Internal Organs	Trout	4.2	0.515	0.0217	0.103	8.5	<0.010	0.0527	<0.10	562	<0.0005	0.0121	<0.0005	<0.0005

Table 15 Lipid content and contaminant concentrations (mg/kg dry wt) in the muscle tissue of eels and fish

Location	Sample name	Sample type	Lipid content (%)	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	4,4'-DDD	4,4'-DDE	4,4'-DDT	Dieldrin
Kin	Kingswell 2 Longfin Eel Tissue	Eel	7.2	0.168	0.0281	0.04	0.318	0.0273	0.195	<0.02	13.5	0.0051	0.029	0.0067	
Or1	Oreti #1 B Longfin Eel#1 Tissue	Eel	9.8	<0.10	0.00502	<0.10	0.216	<0.010	0.437	<0.10	10.2	0.037	0.06	0.022	<0.0005
Or1	Oreti #1 B Longfin Eel#2 Tissue	Eel	2.8	<0.10	0.0275	<0.10	0.298	0.0137	0.52	<0.10	14.1	0.00094	0.024	0.0021	<0.0005
Or2	Oreti #2 B Longfin Eel#1 Tissue	Eel	4.3	<0.10	0.0209	<0.10	0.253	<0.010	0.336	<0.10	10.3	0.00119	0.025	0.0017	
Or2	Oreti #2 B Longfin Eel#2 Tissue	Eel	6.2	<0.10	0.0413	<0.10	0.529	0.0484	0.276	<0.10	11.4	0.00097	0.0179	0.00115	
Or2	Oreti #2 B Longfin Eel#3 Tissue	Eel	3.5	<0.10	0.0176	<0.10	0.22	<0.010	0.167	<0.10	10.8	0.00104	0.0173	0.0011	
Or2	Oreti #2 B Longfin Eel#4 Tissue	Eel	4.4	<0.10	0.0221	<0.10	0.275	0.0105	0.185	0.147	14	0.00151	0.029	0.0021	
Wai	Waihopai 2 Longfin Eel Tissue	Eel	3	0.073	0.00436	0.123	0.35	0.0371	0.118	<0.02	22	0.0051	0.049	0.0076	
WF	Waikiwi @ Ferry Rd B Longfin Eel #1 Tissue	Eel	4.2	<0.10	0.0209	0.125	0.434	0.0144	0.123	<0.10	10.6	0.00073	0.0137	<0.0005	<0.0005
WF	Waikiwi @ Ferry Rd B Longfin Eel #2 Tissue	Eel	7.3	<0.10	0.0164	<0.10	0.318	<0.010	0.073	<0.10	16.9	0.0053	0.05	0.0021	0.0034
WF	Waikiwi @ Ferry Rd B Longfin Eel #3 Tissue	Eel	2.1	<0.10	0.0535	0.115	0.265	<0.010	0.11	<0.10	12.4	0.00139	0.02	0.00138	0.00067

Location	Sample name	Sample type	Lipid content (%)	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	4,4'-DDD	4,4'-DDE	4,4'-DDT	Dieldrin
WF	Waikiwi @ Ferry Rd B Longfin Eel #4 Tissue	Eel	6.1	<0.10	0.0294	<0.10	0.339	0.0114	0.077	<0.10	11.4	<0.0005	0.012	<0.0005	0.00207
WF	Waikiwi @ Ferry Rd B Longfin Eel #5 Tissue	Eel	2.8	<0.10	0.0312	<0.10	0.284	0.0122	0.0588	<0.10	12.3	0.0029	0.0189	0.0032	0.0009
WF	Waikiwi @ Ferry Rd B Longfin Eel #6 Tissue	Eel	4.3	<0.10	0.0237	0.115	0.304	0.0111	0.087	<0.10	11.5	0.0024	0.023	0.0014	<0.0005
WF	Waikiwi @ Ferry Rd B Longfin Eel #7 Tissue	Eel	3.5	<0.10	0.0218	<0.10	0.396	0.0229	0.0526	<0.10	15.2	0.00118	0.0167	0.00089	0.00072
WS1	Waikiwi @ Staunton Rd 1 B Longfin Eel Tissue	Eel	10.4	<0.10	0.0381	0.099	0.272	<0.010	0.1	<0.10	11.6	0.0106	0.128	0.0036	<0.0005
WS2	Waikiwi @ Staunton Rd 2 B Longfin Eel Tissue	Eel	5.9	<0.10	0.0283	0.095	0.297	0.0095	0.074	<0.10	11.6	<0.0005	0.036	<0.0005	
Ote	Otepuni 3 Shortfin Eel Tissue	Sfeel	4.5	0.095	0.00068	0.069	0.224	0.0056	0.079	<0.02	16.4	0.0036	0.023	0.00147	
WS2	Waikiwi @ Staunton Rd 2 B Shortfin Eel Tissue	Sfeel	6.8	<0.10	0.0333	<0.10	0.216	0.01	0.094	<0.10	10.8	0.00089	0.026	0.00052	
Or1	Oreti #1 B Trout Tissue	Trout	1.1	0.144	0.00361	<0.10	0.476	<0.010	0.17	<0.10	6.28	0.00062	0.0057	0.00051	<0.0005
Or2	Oreti #2 B Trout #1 Tissue	Trout	0.3	0.108	0.00432	<0.10	0.369	<0.010	0.0658	<0.10	10.9	<0.0005	0.004	<0.0005	<0.0005

Location	Sample name	Sample type	Lipid content (%)	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	4,4'-DDD	4,4'-DDE	4,4'-DDT	Dieldrin
Or2	Oreti #2 B Trout #2 Tissue	Trout	0.4	0.493	<0.0019	<0.10	0.246	<0.010	0.173	<0.10	5.11	0.00084	0.0107	<0.0005	<0.0005
Or2	Oreti #2 B Trout #3 Tissue	Trout	1.3	0.442	<0.0019	<0.10	0.269	<0.010	0.204	<0.10	3.61	0.00082	0.014	0.00073	
Or2	Oreti #2 B Mullet Tissue	Mullet	1.5	0.318	<0.002	<0.10	0.321	<0.010	0.0543	<0.10	4.43	0.00053	0.0074	<0.0005	
Ote	Otepuni 1 Trout Tissue	Trout	0.9	0.461	<0.0004	0.036	0.374	<0.002	0.119	<0.02	4.13	0.0019	0.0154	0.00128	
Wai	Waihopai 2 Trout Tissue	Trout	1.6	0.83	<0.0004	0.029	0.302	<0.002	0.089	<0.02	5.31	0.0032	0.016	0.00155	
WS1	Waikiwi @ Staunton Rd 1 B Trout Tissue	Trout	1	0.86	<0.002	0.099	0.32	<0.010	0.074	<0.10	7.1	<0.0005	0.0056	<0.0005	<0.0005

Appendix 2 – Results for anticoagulant concentrations in estuarine, riverine sediment and fish flesh and livers

Both coumatetralyl and bromadiolone were detected in fish livers, but warfarin, brodifacoum and flocoumafen were not (Table A2.1). Anticoagulants were detected in the livers of 5 out of 7 brown trout, compared with 2 out of 17 eels, and 1 out of 3 yellow-eye mullet. There was at least one fish with anticoagulants detected in each of the investigated subcatchments of the New River Estuary, i.e. Waikiwi River, Kingswell Creek, Otepuni Creek and the Waihopai River as well as the main stem of the Oreti River. The highest concentration detected was in a brown trout liver from Otepuni Creek, which had 0.034 µg/g of bromadiolone.

Anticoagulants were not detected in the muscle tissue of the 8 individuals whose livers tested positive.

Table 16 List of fish samples whose livers were tested for various anticoagulant compounds.
 <MDL = less than method detection limit, which was 0.1 µg/g for warfarin, 0.01 µg/g for coumatetralyl and 0.005 µg/g for the rest. Sites with anticoagulant concentrations above detection limit, and the chemicals that were detected, are in bold

Sample	Brodifacoum (µg/g)	**Bromadiolone** (µg/g)	**Coumatetralyl** (µg/g)	Flocoumafen (µg/g)	Warfarin (µg/g)
Brown Trout, Oreti 1A, #1	<MDL	<MDL	**0.011**	<MDL	<MDL
Longfin eel, Oreti 1A, #2	<MDL	<MDL	<MDL	<MDL	<MDL
Shortfin eel, Oreti 1A, #3	<MDL	<MDL	<MDL	<MDL	<MDL
Yellow eye mullet, Oreti 2A#1	<MDL	<MDL	<MDL	<MDL	<MDL
Yellow eye mullet, Oreti 2A #2	<MDL	**0.0088**	<MDL	<MDL	<MDL
Brown Trout, Oreti 2A, #3	<MDL	<MDL	<MDL	<MDL	<MDL
Brown Trout, Oreti 2A, #4	<MDL	<MDL	<MDL	<MDL	<MDL
Shortfin eel, Oreti 2A #5	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Oreti 2A #6	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Oreti 2A #7	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Oreti 2A #8	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Waikiwi Ferry RdA#1	<MDL	<MDL	<MDL	<MDL	<MDL
Shortfin eel, Waikiwi Ferry RdA#2	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Waikiwi Ferry RdA #3	<MDL	<MDL	<MDL	<MDL	<MDL
Shortfin eel, Waikiwi Ferry RdA #4	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Waikiwi Ferry RdA #5	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Waikiwi Ferry RdA #6	<MDL	<MDL	<MDL	<MDL	<MDL
Yellow eye mullet, Waikiwi Ferry RdA #7	<MDL	<MDL	<MDL	<MDL	<MDL
Shortfin eel, Waikiwi Staunton 2A #1	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Waikiwi Staunton 2A #2	<MDL	<MDL	<MDL	<MDL	<MDL
Shortfin eel, Waikiwi Staunton RD1A #1	<MDL	<MDL	<MDL	<MDL	<MDL
Longfin eel, Waikiwi Staunton RD1A#2	<MDL	<MDL	**0.016**	<MDL	<MDL
Brown trout, Waikiwi Staunton RD1A #3	<MDL	<MDL	**0.024**	<MDL	<MDL
Brown trout, Otepuni 2	<MDL	**0.034**	<MDL	<MDL	<MDL
Brown trout, Waihopai 3 #1	<MDL	**0.012**	<MDL	<MDL	<MDL
Brown trout, Waihopai 3 #2	<MDL	**0.014**	<MDL	<MDL	<MDL
Longfin eel, Kingswell, #2	<MDL	**0.015**	**0.015**	<MDL	<MDL

Sediment

The anticoagulant compound flocoumafen was detected at two sites, S11 amd S12 in the Waihopai arm of the New River Estuary. No anticoagulants were detected in all other estuary and riverine sites.

Appendix 3 – Overview/summary: Environmental residues of anticoagulants used for pest animal control

Penny Fisher, Landcare Research[1]

Background

Anticoagulants are a group of compounds used as rodenticides worldwide. They inhibit Vitamin K metabolism in the liver, which in turns prevents the formation of chemical factors essential to processes of blood coagulation (clotting). Toxicity occurs when enough anticoagulant is absorbed for these clotting factors to become so depleted that blood can no longer clot. Death through anticoagulant poisoning generally occurs through massive internal haemorrhage after a number of days. Anticoagulant poisoning in humans and animals can be successfully treated through injections of Vitamin K1, until blood clotting time returns to normal range.

As shown below, anticoagulants can be classified by their chemical structure (as indandione or coumarin compounds) or by when they were first developed (as first- or second-generation anticoagulant rodenticides – FGAR or SGAR).
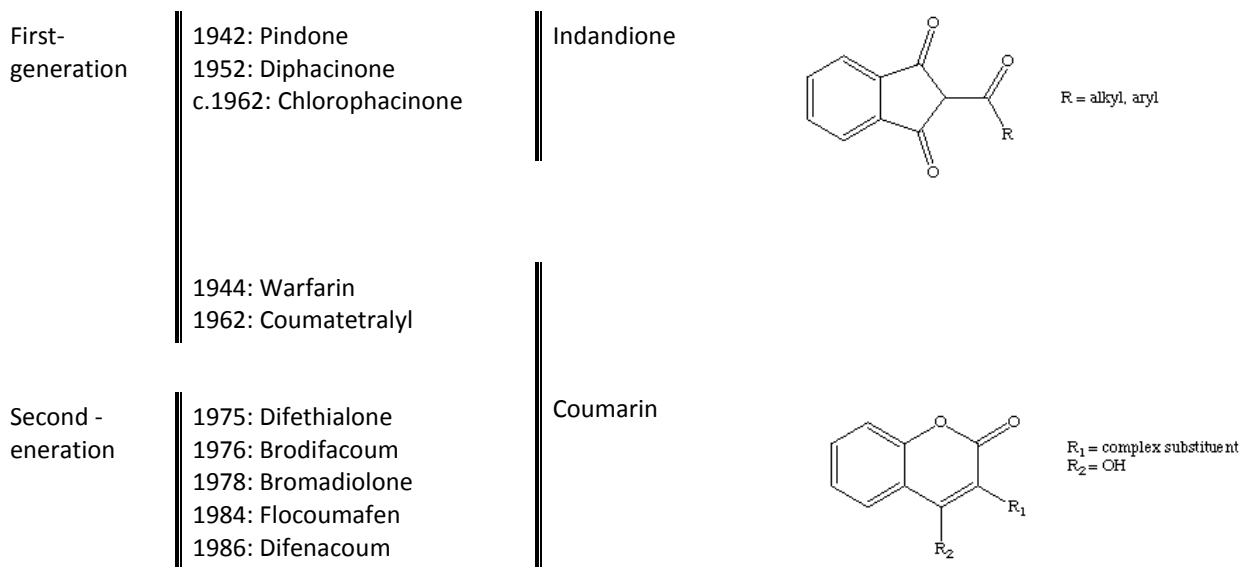

First-generation	1942: Pindone 1952: Diphacinone c.1962: Chlorophacinone	Indandione	R = alkyl, aryl
	1944: Warfarin 1962: Coumatetralyl		
Second-eneration	1975: Difethialone 1976: Brodifacoum 1978: Bromadiolone 1984: Flocoumafen 1986: Difenacoum	Coumarin	R_1 = complex substituent R_2 = OH

Figure 16 Structure and description of first- and second-generation anticoagulants.

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[1] The original of this appendix was presented to Environment Southland on 10 June 2013.

Toxicity and persistence

SGARs are the most toxic, so that targeted pests are likely to ingest a lethal amount in a single feed of bait. The lower toxicity of FGARs means that targeted pests need to consume small daily amounts of bait over a number of consecutive days for best efficacy. The carcasses of animals that have died of anticoagulant poisoning will contain residual concentrations and thus present potential secondary exposure to predators and scavengers.

SGARs are also more persistent than FGARs in animal tissues, and are eliminated very slowly from liver especially. Animals or birds that ingest sublethal amounts of an anticoagulant can carry residue burdens in tissue until they are eliminated, with the potential for SGAR residues to persist for months in liver. Repeated sublethal exposures within this time can result in accumulation of residues in liver, potentially to the point where harmful effects or mortality result.

Environmental transfer of anticoagulants

Environmental transfer of anticoagulant residues appears to be largely trophic (rather than through exposure to residues in water, air or soil). While primary exposure can be managed to some extent by preventing non-target animals from accessing bait applied for pest animal control, it is typical for rodents or possums to move bait from stations into the wider environment. This includes the potential for exposure of grazing livestock to bait in areas where anticoagulants are used in field applications for pest animal control.

Invertebrates appear less sensitive than mammals or birds to anticoagulant toxicity. However, invertebrates that feed on anticoagulant bait, or the carcasses of poisoned animals, can transfer residues in the wider environment.

Secondary exposure of predators, scavengers or insectivores through consumption of other animals or carcasses that contain anticoagulant residues is more problematic to manage. This includes the potential for some native wildlife and wild game animals, such as feral pigs (*Sus scrofa*), to incur anticoagulant residue burdens.

New Zealand uses of anticoagulants

Pindone: Field applications for rabbit control in broadcast or bait station applications using carrot or pellet bait. Controlled Substances Licence required for aerial broadcast applications. Pindone pellet bait also used in bait stations for rat (*Rattus* spp.) and possum (*Trichosurus vulpecula*) control.

Diphacinone & coumatetralyl: Bait station field applications (e.g. by the Department of Conservation (DOC)) for rodent control, and also available 'over the counter' to general public for rodent control around houses, farms, factories etc.

Brodifacoum: Available 'over the counter' to general public for rodent control around houses, farms, factories etc. Bait station field application by regional councils, conservation groups etc. for possum and rodent control, although DOC currently limits field uses of brodifacoum in mainland conservation areas.

DOC or other unitary authorities can undertake broadcast (aerial) application of pellet baits for the eradication of rodents on uninhabited offshore islands or fenced sanctuaries. Recent examples of such 'one off' broadcast applications include Rangitoto/Motutapu islands, Ulva Islands and Shakespear Park (Whangaparaoa Peninsula). Such applications usually have environmental monitoring for brodifacoum residues as a condition, as it is acknowledged this method of bait distribution creates high potential for exposure of non-target animals.

Broadcast applications that aim for eradication should be clearly distinguished from ongoing / sustained ground-based applications of brodifacoum that aim for control of rodent or possum populations, but are not associated with formal monitoring for residues.

Bromadiolone & flocoumafen: Available 'over the counter' to general public for rodent control around houses, farms, factories etc. Do not appear to currently have any field uses.

Note that warfarin is no longer registered as a rodenticide in New Zealand, but is a commonly used human therapeutic agent.

The use of anticoagulants, especially SGARs, in New Zealand is comparatively unrestricted compared with many other countries. In particular, over-the-counter availability, the absence of licensed-user requirements and allowed field applications in New Zealand differ from other parts of the world. For example, in the European Union and the United States, sale and use of SGARs is generally restricted to licensed professional pest controllers and limited to bait station use in and around buildings.

Recent research and monitoring in New Zealand

- Research in the late 1990s identified concerns about the transfer of brodifacoum residues in New Zealand environments, and secondary poisoning of wildlife, as the result of field applications for pest control (e.g. Eason et al. 1999).

- Subsequently, DOC implemented restrictions on its use of brodifacoum for conservation purposes on the mainland. However, field application of brodifacoum in bait stations for possum and rodent control by other agencies continues, with some programmes covering considerable areas (up to 300 000 ha) and may be sustained for a number of years.

- In 2004, the Ministry for Primary Industries notified a restricted procurement area for feral pigs in Marlborough, due to the detection of brodifacoum residues in liver samples, which applies only to pigs killed from the specified area that are sold to game processors. It is unclear whether surveillance of feral pigs for brodifacoum residues in other areas has since been carried out.

- Spurr et al. (2005) monitored brodifacoum residues in wildlife in and around the Rotoiti Nature Recovery Project area. The highest concentration of brodifacoum residues in mammalian livers was recorded during the period brodifacoum was used in the project area, but residues were still detected in some wildlife at least 24 months after brodifacoum use ceased. This study provided some of the first New Zealand evidence that anticoagulants used in household rodent control were also being transferred to the wider environment, as residues of flocoumafen, coumatetralyl, or warfarin, used only in a nearby village and on farms, were also detected in the livers of animals captured up to at least 8 km from the nearest source.

- Monitoring of hedgehogs (*Erinaceus europaeus*) and introduced birds as 'sentinel' wildlife species was undertaken in 2011, over sites in Hawke's Bay that had different histories of brodifacoum field use (Booth et al. 2012). Brodifacoum exposure of some vertebrate wildlife was apparently ubiquitous, with c. 50% incidence of brodifacoum-positive hedgehogs and birds across all sites, including one that had no history of brodifacoum use. Potential sources of brodifacoum were from both field bait station applications and its use for rodent control in and around farm and urban buildings.

- Other recent monitoring (Landcare Research, prepublication data) has included testing of liver tissue from road-killed harrier hawks (*Circus approximans*, *n* = 27) for brodifacoum, bromadiolone, flocoumafen , coumatetralyl and warfarin. Results indicate wideapread exposure of this species to anticoagulants, including those mostly used for household rodent control. Residues of at least one anticoagulant were detected in 22 out of the 27 harrier hawks. Three hawks had one anticoagulant only, and about half (13 of 27) had two anticoagulants present, most commonly brodifacoum and flocoumafen. Three anticoagulants were present in four of the 27 hawks, and four anticoagulants were present in another two hawks.

- Findings of residual brodifacoum in liver sampled from three of nine little blue penguins (*Eudyptula minor*) found dead on beaches following aerial application of brodifacoum bait on Rangitoto/Motutapu islands in 2009 (Fisher et al. 2011) prompted wider testing. In 2010, liver samples were obtained from 'beach wrecked' penguin carcasses (*n* = 26 from North Island, *n* = 12 South Island) and tested for brodifacoum, bromadiolone, flocoumafen , coumatetralyl and warfarin. No anticoagulants were detectable in 50% (*n* = 19) of the penguins, with 34.2% (*n* = 13) having one anticoagulant detected, 7.9% (*n* = 3) having two anticoagulants detected, 5.3% (*n* = 2) having three anticoagulants and 2.6% (*n* = 1) having four anticoagulants (Landcare Research, unpublished data). Of the total 38 penguins tested, 6 had brodifacoum concentrations, ranging from 0.001 to 0.003 mg/kg. These data further suggest that brodifacoum and other anticoagulant compounds used for domestic rodent control are reaching the wider environment through trophic transfer.

- Testing of liver and gut contents from two eels (*Anguilla* sp.) found dead in a Southland waterway (Tomoporakau Creek, Branxholme) in May 2012, measured 0.095 ppm brodifacoum in the gut contents of one eel (noting that other anticoagulants were not tested for). This suggests that the eel had recently ingested food containing brodifacoum, probably through scavenging the carcass of a poisoned possum. There was a bait station approximately 100 m from the location where a possum and eels (*n* = 13) were found dead in the water.

- Further samples of freshwater fish from Southland waterways were tested in May 2013, for the five coumarin anticoagulants brodifacoum, bromadiolone, flocoumafen, coumatetralyl and warfarin. Livers of yellow-eye mullet (*n* = 2), trout (*n* = 7), longfin eel (*A. dieffenbachia*, *n* = 7) and shortfin eel (*A. australis*, *n* = 6) were tested. No brodifacoum, flocoumafen or warfarin was detected in any liver sample. Bromadiolone was detected in one yellow-eye mullet (*Aldrichetta forsteri*), three brown trout (*Salmo trutta*) and one longfin eel. Coumatetralyl was detected in two trout and two longfin eel. No anticoagulant was detected in muscle samples from the five fish that had anticoagulant detected in liver.

Potential ecosystem and human health implications and anticoagulant residues

While the anticoagulants have an important role in pest animal management, there are currently few regulatory restrictions on their use in New Zealand. There is increasing evidence that uses of anticoagulants for both household rodent control and field pest management are resulting in widespread contamination of both terrestrial and aquatic wildlife. The latter is presumably through carcasses of poisoned animals entering waterways, rather than direct contamination of waterways by bait.

The occurrence of anticoagulant residues in meat-producing animals is of concern from a food safety perspective, as the Animal Products Act (Contaminant Specification) Notice 2008 sets maximum residue limit (MRL) for some of the anticoagulants, as the highest acceptable concentration of a residue in food. For the SGARs the MRL is 0.001 mg/kg, which is at or near the analytical limit of detection currently-available in New Zealand.

The implications of sublethal anticoagulant exposure for wildlife health are unclear. With the more persistent SGARs, there is potential for repeated sublethal exposure to accumulate residue burdens that eventually cause individual mortality – this is an important research question. Whether residues of multiple anticoagulant compounds in an individual animal have a cumulative effect is also not known.

The potential for sublethal exposure to affect reproductive success also requires investigation. Warfarin is widely recognised as a teratogen (i.e. can cause birth defects), but the status of other anticoagulants in this regard is not well known. Warfarin residues in wildlife (e.g. harrier hawks and penguins) may not originate from rodenticide uses but from human therapeutic use – excretion of warfarin in urine may be another environmental transfer pathway.

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