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**Sources and effects of
catchment-derived bioavailable contaminants
in Hamilton urban streams**

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THE UNIVERSITY OF
WAIKATO
Te Whare Wānanga o Waikato

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Abstract

Awareness of the consistently degraded state of urban streams, with lower biodiversity, has heightened worldwide, increasing restoration initiatives to ameliorate the adverse effects. The present study examined anthropogenically-derived contaminants in water and sediments and bioaccumulation in tissues and bile of shortfin eels (*Anguilla australis*) in Hamilton City urban streams. Bioassays were also conducted with two native Crustacea; the amphipod *Paracorophium lucasi* and freshwater crayfish (kōura) (*Paranephrops planifrons*) to test endpoints of survival, reburial behaviour and growth. Results of dissolved Cu, Pb and Zn showed the industrial Waitawhiriwhiri catchment, with higher impervious surfaces, to have the greatest potential for generating contaminants in stream waters. Relationships between sediment contaminant concentrations and upstream % impervious area suggest an association with stormwater runoff and metal accumulation. Shortfin eels from Gibbon's Creek and Lake Rotoroa bioaccumulated high concentrations of Pb and As respectively in livers, and the PAH metabolite pyrene-1-glucuronide in bile was found in many eels, highlighting the bioavailability of these contaminants. Muscle tissues concentrations of Pb and Hg in some sites triggered food safety guidelines presenting a low risk for human consumption. Amphipods exposed to sediments from Lake Rotoroa had significantly reduced survival compared with those exposed to other site sediments in a 10-day sediment toxicity test. Photo-induced toxicity is not of concern for biota exposed to Hamilton urban stream sediments and no sub-lethal toxicity effect on reburial behaviour was seen. Growth rates of kōura fed *Salix fragilis* leaf material incubated in Hamilton streams were not significantly different, and the short duration of the study meant conclusions could not be made on the significance of observed accumulated metals and metalloids on differences in growth rates. Results of this study highlight a number of locations in the Hamilton stream network, where contaminants are of concern, especially in streams with fully urbanised catchments with high effective imperviousness and legacies of past land use or pollution. Bioavailability of some metals, metalloids and PAHs is constraining the diversity of some species present in these streams, although this effect is not apparent for *A. australis*.

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Chapter 1:

General Introduction

1.1 Effects of urbanisation on streams

Concern over the adverse effects that urbanisation can have on aquatic ecosystems is only increasing as society becomes more urbanised. Built environments are designed for effective and efficient delivery of rainwater falling onto impervious surfaces to streams thereby altering hydrological regimes, degrading habitat quality and increasing levels of contaminants (Blakely and Harding 2005, Doyle 2005, Bernhardt and Palmer 2007). These effects have been widely documented in the literature as causes of the consistently degraded state of urban streams worldwide (Walsh 2000, Paul and Meyer 2001, Davis et al. 2003, Doyle 2005, Meyer et al. 2005, Brown et al. 2009), coined as the "Urban Stream Syndrome" by Walsh et al. (2005).

Hydrological changes in urban streams include reduced lag times, higher peak discharges and reduced groundwater recharge and base flows (Paul and Meyer 2001, Davis et al. 2003). These in turn can lead to channel incision and bank erosion, increasing turbidity and streambed resulting from elevated levels of sediment (Williamson 1985, Mangani et al. 2005, Collier et al. 2008, Thompson and Parkinson 2011), which is a contaminant in its own right. Urbanisation exposes organisms directly or indirectly to high concentrations of anthropogenically derived contaminants that include inorganic metals and metalloids, organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and nutrients (Blakely and Harding 2005, Doyle 2005, Bernhardt and Palmer 2007). The direct and indirect effects on streams and ultimately aquatic biota have been conceptualised in Figure 1-1, modified from Coleman et al. (2011).

The cumulative effect of a variety of different human activities in catchments, or the spatial heterogeneity in land use in urban areas, influences urban streams dramatically (Booth et al. 2004, Carter et al. 2009). Human-induced influences include the decrease of vegetation in riparian zones, the engineered nature of the stream (channelisation, culverts and pipes) and increased impervious surfaces (Meyer et al. 2005), as well as the effects of upstream agriculture and past land

use (Brown et al. 2009). Meyer et al. (2005) also suggested natural effects such as drainage gradient, rainfall intensities and duration, antecedent dry period, and natural sources of contaminants as significant factors influencing urban streams. Ward (1989) described a four-dimensional dynamic concept of river ecosystems, which can be applied to show the effects of aquatic contaminants: 1) longitudinal dimension (headwater land use impacting downstream); 2) transverse dimension (adjacent catchment land use, intactness of riparian vegetation); 3) vertical dimension (influences of groundwater and sediment composition); and temporal dimension (short-term, and long-term patterns, and seasonal changes). The complexity of these influences on urban waterways was apparent in an investigation of sub-catchments draining into Sydney Harbour (Beck and Birch 2012), where differences in storm water chemistry were found at different flow conditions despite similarities in land use, topography, location and geology.

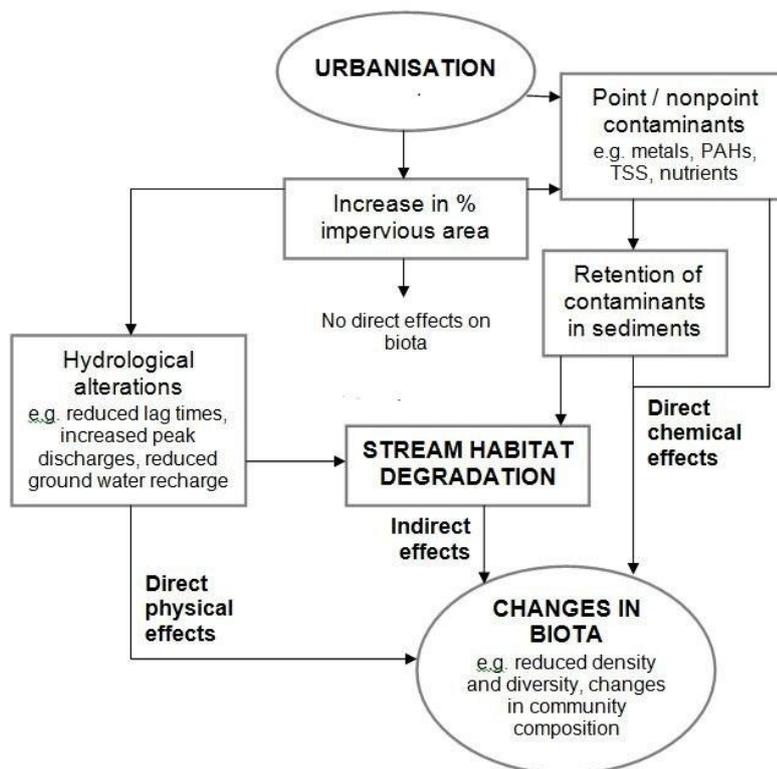


Figure 1-1. Conceptual model of the direct and indirect effects of urbanisation on streams and aquatic biota. Modified from Coleman et al. (2011).

1.2 Integrating studies of effects of contaminants

In terms of ecological health, contaminants such as metals and PAHs in any aquatic system are the most concerning because of their non-biodegradable nature and accumulative properties, leading to risk of lethal and sub-lethal effects on individuals and populations of organisms and possible biomagnification through food chains (Santoro et al. 2009; Wu et al. 2011). Aquatic biota such as invertebrates and fish can readily take up contaminants directly through permeable surfaces such as gills and skin, and indirectly through ingestion of contaminated food and sediment particles (Power and Chapman 1992, Spacie et al. 1995, van der Oost et al. 2003). Although some elements are essential for biota for physiological function, at higher concentrations they can be toxic. Toxicity can cause sub-lethal effects on aquatic life such as lower growth levels and reproduction rates and can also cause mortality in sensitive biota (Simas et al. 2001, Webster-Brown 2005, Brown and Peake 2006). However, the level of toxicity is highly dependent on the organism, its habitat and the contaminant in question (Helsel et al. 1979)

Analysing levels of contaminants in water and/or sediment is insufficient to assess ecological impacts. Levels must also be measured in biota to evaluate bioavailability and uptake, for example, through food web interactions (Chapman and Power 1992, Bervoets et al. 1994, Santoro et al. 2009). Chapman and Power (1992) term this an "Integrative Assessment" involving a combination of (preferably) three of the following: (i) sediment chemical analyses, (ii) sediment toxicity tests, (iii) tissue chemical analyses, (iv) pathological (disease) studies, and (v) community structure studies. This thesis has conducted the first three levels, as well as measuring contaminants in stream water, to assess contaminant effects in Hamilton urban streams.

There is very little information about contaminants within Hamilton urban streams and even less about their effects on biota. Lake Rotoroa has been the most widely studied water body due to the arsenic (As) contamination history outlined in Chapter 2 (see Tanner and Clayton 1990, Rajendram 1992, Rumsby 2011). Williamson (1985) reported the water quality parameters (including metals) in base flow and storm flow conditions from a residential catchment that was not a part of this study, and found that runoff was enriched with sediment particles as well as the metals copper (Cu), lead (Pb) and zinc (Zn). Hickey et al. (2001)

conducted a comparative study of commercial, industrial and new and old residential stormwater and its effects on Hamilton streams and ultimately the Waikato River. Conclusions were that stormwater contaminant concentrations and loads established were greatest in the industrial and commercial areas with the mature residential areas having the lowest of all concentrations. Copper and Zn were highlighted as the contaminants of concern because dissolved concentrations exceeded water quality guidelines. Wilding (1998) presented results on water quality parameters in Hamilton streams and suggested that metals and severe iron (Fe) flocculant may be issues for aquatic animals.

1.3 Restoration of urban streams

Although most urban waterways experience some form of degradation, they are also where local communities have easy access to the environment and encounter biodiversity (Paul and Meyer 2001, Collier et al. 2009). An increasing awareness of the effects of urbanisation on streams has resulted in an enhanced effort to maintain and restore their ecological integrity (Purcell et al. 2002, Davis et al. 2003, Collier et al. 2008). However, ameliorating constraints to ecological recovery, such as the effects of sediment contaminants, is difficult in urban landscapes (e.g. Blakely and Harding 2005, Suren and McMurtrie 2005, Nelson 2011).

Lake et al. (2007) discussed an important concept to assist with understanding the constraints that may limit restoration potential, that of hierarchical filters. Hierarchical filters are environmental constraints that limit the diversity of species present in a habitat by successively filtering them out from communities (Poff 1997, Johnson et al. 2004, King et al. 2005, Lake et al. 2007). Large-scale filters can include regional climate (e.g. causing droughts and floods, climate change), catchment geology and topography, and varying intensities of land use (e.g. exotic forestry, pasture, urban). Smaller scale environmental filters can consist of the presence and composition of riparian vegetation and refugia for habitat improvement, while interspecific interactions can also filter out possible species from an area. Although the scope of restoration will vary widely between organisms and processes, restoration that incorporates the maximum extent of environmental variability will be the most successful (Lake et al. 2007). Ebersole et al. (1997) also outlines the concept of anthropogenic influences constraining the "expression of potential capacity" of a habitat by limiting habitat

diversification. Restoration aims to increase the expression of potential capacity in space and time by reducing these constraints, although the ecosystem may never return to its former full capacity (Ebersole et al. 1997).

1.4 Objective of thesis

The main objective of this thesis was to determine to what extent urbanisation is affecting concentrations of contaminants in water, sediment and biota and whether this is constraining biotic potential of future restoration work within the Hamilton gully stream network. Specific aims were to:

1. Determine whether concentrations of contaminants in streams at base flow are impacted significantly by rain events in catchments with contrasting levels of upstream catchment imperviousness.
2. Quantify spatial and temporal trends in sediment metals and metalloids, as well as determine where PAH accumulation is occurring, and determine relationships with catchment imperviousness.
3. Investigate the bioavailability of sediment contaminants by (i) measuring the bioaccumulation of metals and metalloids in livers and muscles of shortfin eels (*Anguilla australis*), and (ii) determining exposure to PAHs by measuring a common PAH metabolite in bile.
4. Conduct bioassays to test the endpoints of mortality, reburial behaviour and growth in two New Zealand Crustacea, the amphipod *Paracorophium lucasi* and freshwater crayfish (kōura) *Paranephrops planifrons*.

1.5 Guidelines for contaminants in water, sediments and fish for consumption purposes

1.5.1 Water and sediment

The Australian and New Zealand Guidelines for Fresh and Marine Water Quality are generally based on the philosophy of ecologically sustainable development (ESD). In New Zealand, the equivalent is the promotion of sustainable management, which is the purpose behind the Resource Management Act (1991) (RMA) (ANZECC 2000). The Australian and New Zealand Environment and Conservation Council (ANZECC) has set guideline trigger values for toxicants in water and sediment in aquatic environments for use in both Australia and New

Zealand. In New Zealand, the guidelines are designed to assist managers (Councils) to implement the RMA (ANZECC 2000).

Water quality guidelines aim to protect ambient waters from chronic toxicity and are set at different protection levels which signify the percentage of species expected to be protected (99%, 95%, 90% and 80%) with 50% certainty. The data from this research were compared to the 95% protection level trigger values for dissolved contaminants representing slightly-to-moderately disturbed aquatic ecosystems.

One of the ANZECC (2000) sediment guideline aims is to identify sediments where contaminant concentrations are likely to result in adverse effects on sediment ecological health. Once the sediment trigger value is exceeded (for the <500 μm sediment fraction), compared with background levels within the local environment, then this should trigger further investigation to consider the bioavailability of the toxicant. The recommended guideline values are interim sediment quality guideline (ISQG) values (low and high) that correspond to the effects range of low and median used by the United States (U.S.) National Oceanic and Atmospheric Association (NOAA) in sediment toxicity tests (Long et al. 1995). In the absence of such trigger values, a value was derived on the basis of doubling natural background concentrations, as suggested in the ANZECC (2000) guidelines.

1.5.2 Metals and metalloids in fish muscle tissue for consumption

Contaminant concentrations in muscles of shortfin eels was measured not only to determine any bioaccumulation within these tissues, but also to quantify the risk posed to humans of consuming the flesh from these wild urban populations. There is a number of guidelines that set specific maximum limit concentrations as well as those that determine how many meals of that food can be consumed before the risk posed to human health become possible. Food Standards Australia New Zealand (FSANZ) provides Standard 1.4.1 that sets out the maximum levels of specified metals and non-metal contaminants and natural toxicants in nominated foods (FSANZ 2012).

The U.S. Environmental Protection Agency (USEPA) provides screening values representing concentrations in fish tissues of a given contaminant that are of

potential public health concern (based on non-carcinogenic and carcinogenic effects of the contaminants) to which tissue residue levels in fish can be compared (USEPA 2000). Based on these data, for an adult body weight of 70 kg and a meal size of 227 mg, monthly consumption limits for carcinogenic (1 in 100,000 risk level) and non-carcinogenic (above which chronic, systemic effects could occur) Risk-Based Consumption Limits (RBCL) are provided. Also, the 2009 New Zealand Total Diet Survey (NZTDS) analysed typical foods available at the point of sale to the New Zealand consumers for concentrations of various metals and metalloids (amongst other compounds) (Vannort and Thomson 2011). The NZTDS as well as both the FSANZ standards and USEPA RBCLs, were applied to the concentrations of metal and metalloids in muscle tissue of shortfin eels collected from Hamilton urban streams.

1.6 Outline of thesis

This thesis addresses the lack of information on contaminants within Hamilton urban streams and also links the effects of these to aquatic biota. Chapter 2 outlines the study area, main urban catchments and sampling sites and describes local contaminant influences in these streams. Chapters 3 and 4 have been written in the format of scientific papers and there is therefore some repetition, especially in relation to explanation of factors affecting bioavailability, descriptions of sampling sites and summarising of contaminant concentration data. Chapter 3 incorporates studies of dissolved metals in water during rain events, accumulation of organic and inorganic contaminants in sediment and bioaccumulation within shortfin eels. The fourth chapter summarises in vitro experiments on sensitive New Zealand Crustacea by examining lethal (mortality) and sub-lethal (reburial behaviour and growth rates) responses to contaminants found in Hamilton urban streams. The thesis concludes with a general discussion on the implications of these findings for biota communities in these urban streams.

Chapter 2:

Hamilton City streams and study sites

2.1 Hamilton gully stream network

Hamilton is New Zealand's largest inland city with a June 2012 population estimate of 148,200 (HCC 2012). It has a temperate climate with a mean annual temperature of 13.7°C and rainfall of 1190 mm (1971-2000 period) (NIWA 2012a). The Waikato River, flowing from Lake Taupo in the south to Port Waikato on the coast of the Franklin District, bisects the city. New Zealand's longest river has a mean flow of $370 \text{ m}^3 \text{ s}^{-1}$ (Hicks et al. 2004). Hamilton City is a highly modified environment with approximately 1.6% of the original vegetation remaining (Clarkson and McQueen 2004). About 750 hectares or 8% of land within the city boundary is dominated by a system of gullies (Downs et al. 2000). This gully network was created 15,000 years ago when the Waikato River began cutting down through the Hinuera formation to create its current channel and exposed springs along the riverbank which in turn cut down through the substrate creating the present-day streams (Clarkson and McQueen 2004).

There are four main catchments draining into the Waikato River within the city boundary of Hamilton, three of which are the subject of this study: Mangakotukutuku to the south west, Waitawhiriwhiri draining mainly Dinsdale, Frankton and Maeroa suburbs to the west and Kirikiriroa in the north-east (Fig. 2-1) (Collier et al. 2009). There are also a number of smaller catchments draining into the Waikato River within the city. These include two true left tributary streams near Waikato Hospital (Normandy Avenue and Graham Park streams), Gibbon's Creek (Hamilton East) and two true right tributaries draining through Fairfield and Chartwell (Ranfurlly Park and Bankwood streams) (Fig. 2-1). Streams that establish outside the city boundary have headwaters in low-gradient pasture farmland that were formerly peat wetlands (Collier and Clements 2011). Several larger urban streams have headwaters outside the city, and rural land use can be a significant influence in those streams draining considerable amounts of farmland. Taylor and Kim (2009), documented background metal and metalloid concentrations in Waikato soils and compared them with concentrations in

farmed soils, showing a significant increase in accumulation of metals and metalloids in the latter (see also Taylor et al. 2010).

High naturally-occurring iron (Fe) levels in groundwater in the Hamilton Basin are characteristic of deeper groundwater aquifers located in peat sediments around the Waikato Region (WRC 2012). With groundwater making 85% of base flows in streams draining the basin, creating high natural Fe concentrations occur in water and sediments of the streams. Iron flocculation is a common phenomenon on Hamilton streams, caused by the oxidation and subsequent precipitation of groundwater-borne dissolved ferrous Fe and other compounds and can form thick orange/brown mats on the stream sediment (Charette and Sholkovitz 2002, Clearwater and Valler 2012).

2.2 Catchments and sampling sites

The sediment and amphipod component of this study has been a collaboration between the National Institute for Water and Atmosphere Research (NIWA, Hamilton) and this current graduate research through the University of Waikato. Initial sediment sampling sites (also used for amphipod ecotoxicity testing) were selected in 2011 using GIS data for stream, road and stormwater infrastructure locations and knowledge of historic and current land use by S. Clearwater (Clearwater and Valler 2012). Water sampling sites were selected in 2012, over and above the collaborative study for addition to this research based specifically on comparisons between the three main catchments. Eel collection and the kōura growth experiment sites are aligned with sediment sampling sites.

Table 2-1. Site information and catchment characteristics for water and sediment sampling, eel collection, amphipod toxicity testing of sediments and leaf incubation sites. W, water sampling; S, sediment sampling; E, eel collection; A, sediments used for toxicity tests with amphipod (*Paracorophium lucasi*); I, leaf incubation and C, crayfish collection site. Alternate shading represents separate catchments.

Stream/Catchment	Site Label	NZTM2000		% Impervious	Site Description	Sampling
		Northing	Easting			
Rangitukia	CC	6357738	6357738	0	100% native forest catchment above collection site. Fast flowing cool mountain stream, Mt Pirongia.	C
Horsham Downs	EC	5824812	1796079	5	Pastoral stream, 100% rural inputs. True right tributary of Waikato R. Positive control for urban eel collection.	E
Mangakotukutuku	M1	5812777	1802320	18	Main channel near confluence with Waikato. River, Sandford Park.	W
	M2	5812414	1802018	17	Main channel, mid Sandford Park.	W
	M3	5811042	1802040	23	Small Te Anau trib., below Ohaupo Rd, stormwater culvert.	W
	PB	5811469	1803357	5	Main channel of Peacocks branch, rural.	S, A
	PC	5812376	1802560	7	Main channel of Peacocks branch, Peacocks Road, residential.	S, A
	PD	5811516	1803378	5	Small tributary to main Peacocks channel, rural.	S, A, I
	RK_B	5811920	1801016	13	Main Rukuhia channel. Receiving inputs from Ohaupo Rd.	S, E
	RK_D	5812430	1802271	20	Main Rukuhia channel. Upstream from confluence with Peacocks branch.	S, E
Normandy Ave	NA	5813293	1801341	71	Downstream of old hospital landfill, stormwater pipe, discharge upstream. Fe flocculant.	S, E, A, I
Graham Park	GA	5813684	1801191	58	Small stream located in grassed urban park adjacent to Cobham Drive.	S, E, A
Waitawhiriwhiri	W1	5816907	1799925	41	Main channel outlet to Waikato River.	W
	W2	5816178	1799467	40	Mainstem, downstream from Seddon Rd overpass. Stormwater culvert	W
	W3	5814004	1798112	26	From Greenwood/Duke St industrial area, upstream highly culverted, downstream from WA. Fe flocculant.	W
	WA	5814304	1799865	47	Lake Rotoroa outlet, Innes Common.	S, E, A, I
	WB	5813547	1797749	7	Karen Cres./Kahikatea Park. Rural inputs. Fe flocculant	S, E
	WF	5816041	1799457	40	Upstream of Seddon Rd (true right tributary to main channel). Probable stormwater inputs. Edge of catchment.	S, E
Gibbons	PR_A	5815315	1801468	70	Located in urban park (Parana). Fe flocculant.	W, S, A
	SA	5815683	1801849	68	Restored bush site (Seeley's Gully). Eels collected here because of restoration site at PR_A. Fe flocculant	E, S
Ranfurly Park	RN_A	5817176	1800468	53	Grassed urban park (Ranfurly), fully urbanised catchment.	S, E, A, I
Bankwood	BA	5818728	1800027	65	Located in urban park (Donny), fully urbanised catchment.	S, E, A
Kirikiriroa	K1	5820265	1798831	49	Main channel outlet to Waikato River under River Rd.	W
	K2	5820051	1800001	68	Directly under Wairere Dr. Straight channel.	W
	K3	5821604	1800830	56	Upstream of Thomas Road, rural inputs possible.	W
	K4	5818367	1801923	68	Downstream of Snell Drive - Chedworth tributary. Fe flocculant.	W
	KA	5819375	1802147	5	Rural location, deep layer of sludge. High Fe flocculant	S, E, A, I
	KB	5820340	1799944	44	Tauhara Park. Old landfill inputs.	S, E, A
	KC	5820093	1799243	48	Mainstem location, Tauhara Park. Outlet to Waikato River.	S, E, A, I

% impervious data provided by Waikato Regional Council.

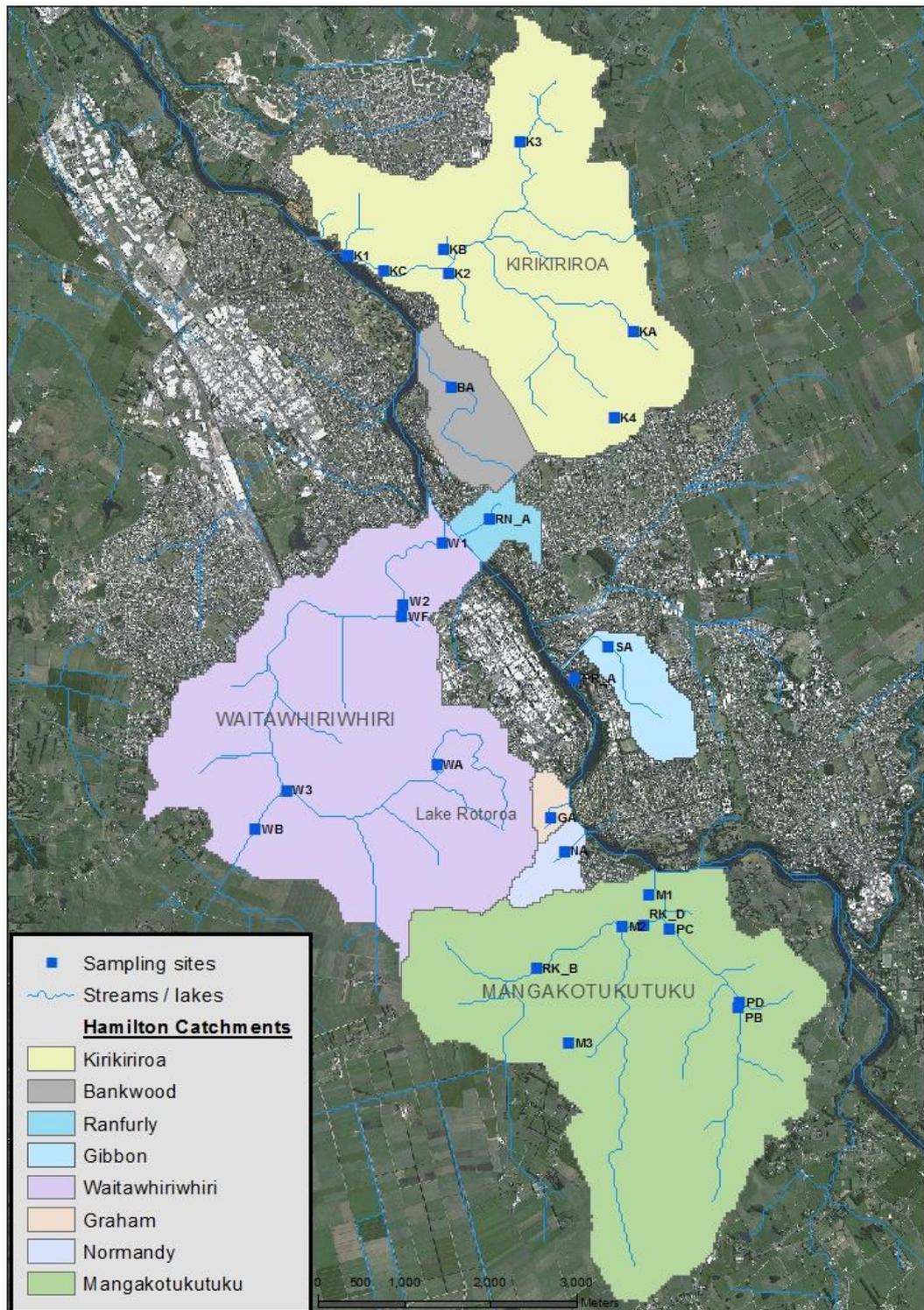


Figure 2-1. Map of Hamilton, Waikato, indicating the urban catchments studied and water (M1-3; W1-3; K1-4; PR_A) and sediment and eel (PB-D; RK_B-D; NA; GA; WA, B and F; SA and PR_A; RN_A; BA; KA-C) sampling sites. Key to site labels is provided in Table 2-1.

2.2.1 Eel collection control and crayfish collection sites

The control eel collection site (EC) was a true right tributary stream discharging directly into the Waikato River south of Hereford Drive, Horsham Downs (Plate 2-1a). The stream drains dairy pasture with no riparian vegetation or fencing or urban influence. Freshwater crayfish (*P. planifrons*) were collected from the headwaters of the Rangitukia Stream located on the slopes of Mount Pirongia (CC) (Plate 2-1b). The stream has high channel gradient and is therefore fast flowing. The headwaters are entirely in native forest with riparian understorey of parataniwha (*Elotostema rugosum*).



Plate 2-1. a) EC, rural control eel collection site, south of Hereford Drive, Horsham Downs; and b) CC, crayfish collection site, Rangitukia Stream, Mount Pirongia.

2.2.2 Mangakotukutuku

The Mangakotukutuku is located in the south of the city on the true left side of the Waikato River and is the largest catchment with the least urbanisation and imperviousness in this study. Suburbs within this catchment include parts of Melville, Fitzroy, Glenview and Deanwell. The Rukuhia, Te Anau and Peacockes channels are the three main arms, with the majority of the main Rukuhia channel and Te Anau land use being urban and Peacockes, mainly lifestyle blocks and farmland. Riparian vegetation comprises of a mixture of exotic trees including grey willow (*Salix cinerea*), *Pinus radiata* and *Ulmus* spp., and native species (mainly understorey ferns). The lower half of the Rukuhia channel flows through Sandford Park with grey willow and grass with some recent plantings of native flax and grass species (Mangakotukutuku Stream Care Group; www.streamcare.org.nz). Headwaters of the Peacockes tributary are in farmland but parts of which flow through *P. radiata*, thick scrub and regenerating native

bush (Plate 2-2e). This tributary is scheduled for urban development over the next 5 to 10 years (Clearwater and Valler 2012). The water sampling site of M1 is the main channel approximately 100 metres from the confluence with the Waikato River (Plate 2-2a). M2, is upstream on the main Rukuhia channel near the corner of Bruce Avenue and Lewis Street, Glenview (Plate 2-2b), and M3 is on the corner of Dixon and Ohaupo Roads on the Te Anau branch of the Mangakotukutuku (Plate 2-2c). This water sampling site has very low base flows but high storm water inputs from Ohaupo Road. Sediment sampling sites PB-D are all on the Peacockes tributary with PB sampled in thick scrub upstream and PC downstream above the culvert under Peacockes Road (Plate 2-2d & e). PD is a small tributary of the Peacockes branch flowing through a mixture of exotic and native trees and understorey plants including native ferns and blackberry. Two sediment and eel collection sites are located on the main Rukuhia channel; RK_B having stormwater inputs from State Highway 3 and being upstream of RK_D which is situated in mid-Sandford Park



Plate 2-2. Mangakotukutuku catchment sampling sites, a) M1, main channel outlet Sandford Park; b) M2, main Rukuhia channel, mid Sandford Park; c) M3, Te Anau tributary, Ohaupo Road; d) PC, Peacockes tributary upstream of Peacockes Road; e) PB and PD, confluence of small bush covered tributary with main Peacockes arm; f) RK_D, main Rukuhia channel, Sandford Park; and g) RK_B, Rukuhia channel downstream from Ohaupo Road.

2.2.3 Waitawhiriwhiri

In contrast to the Mangakotukutuku, the Waitawhiriwhiri catchment is the most urbanised and industrialised catchment with large areas of imperviousness, especially around the Frankton industrial area which is highly culverted for efficient stormwater drainage. Riparian vegetation consists only of mown grass alongside many reaches (e.g. site W3, Plate 2-3b). Other suburbs within this catchment include Dinsdale, Maeroa and parts of Melville near Waikato Hospital. The catchment incorporates Lake Rotoroa (Hamilton Lake) and the surrounding residential areas as well as rural drains in the south of the catchment (Fig. 2-1; also see e.g. WB, Plate 2-3e). Lake Rotoroa has 45 stormwater drains discharging into it, the mostly at the southern and eastern sides (Rumsby 2011). In 1959, sodium arsenite (NaAsO_2) was applied to approximately 72% of the lake to control problem growth of aquatic weed (Rumsby 2011). Since then, there has been a persistent legacy of residual arsenic (As) in the surficial sediments of the lake (Tanner and Clayton 1990, Rajendram 1992, Rumsby 2011).

Water sampling sites incorporated one near the confluence with the Waikato River (W1) (Plate 2-3a), a site upstream on the main channel (W2), immediately downstream of Seddon Road (Plate 2-3c), and W3, the small drain-like stream that is the main arm downstream from Lake Rotoroa. This site is downstream of a long culverted, underground section of the Lake Rotoroa outlet extending under Innes Common and the Greenwood Street industrial area (Plate 2-3b), and was approximately 100 metres upstream from the confluence with the WB sediment sampling site (Figure 2-1). The May 2012 sediment sampling in conjunction with NIWA only focused on the lake in the Waitawhiriwhiri catchment. In August and November sediment samples were taken from WB and WF to obtain sediment metal concentrations to compare with eel tissue metals data and to obtain a wider view of this catchment. WA was the sediment and eel sampling site immediately upstream of the outlet of Lake Rotoroa (Plate 2-3d). WB is the confluence of two drains in the south-western boundary of the catchment (Plate 2-3e), and WF, a small true right tributary immediately upstream of Seddon Road draining the Mill Street area on the eastern boundary of the catchment (Plate 2-3f). This small stream has some native and exotic riparian vegetation but is also culverted at the upper reaches near Avon Street and has possible stormwater inputs.



Plate 2-3. Waitawhiriwhiri catchment sampling sites. a) W1, main channel outlet; b) W3, drain from Greenwood St industrial area; c) W2, main channel, downstream of Seddon Road; d) WA, Lake Rotoroa outlet; e) WB, confluence of two drains, Karen Crescent/Kahikatea Park, upstream from W3; and f) WF, true right tributary upstream of Seddon Road and W2.

2.2.4 Kirikiriroa

The north-eastern Kirikiriroa catchment incorporates the older residential Hamilton suburbs of Chartwell and Queenwood as well as new residential suburbs of Rototuna and Flagstaff. There are a number of tributaries which have headwaters in surrounding pasture farmland, for example site K3 and KA (Plate 2-4b & e). Much of the riparian vegetation includes exotic willow species, sometimes thick in areas, some native trees such as cabbage tree (*Cordyline australis*) and shrubs, and exotic understorey plants. Some areas have been the subject of recent restoration initiatives such as planting of native trees and shrubs (Mangaiti Park, Mangaiti Gully Restoration Group; gullyrestoration.blogspot.co.nz) and grasses and flaxes for stabilising banks (Tauhara Park, site KC, Plate 2-4c). However, riparian vegetation is less intact than the Mangakotukutuku. The water sampling site of K1 is approximately 100 metres from the confluence with the Waikato River (Plate 2-4a), K2 is upstream of this on the main channel under the Wairere Drive overpass in Tauhara Park (Plate 2-4d), K3 is in the upper catchment immediately upstream of Thomas Road and has rural inputs (Plate 2-

4b), and K4, which includes the Chedworth arm of Kirikiriroa, is immediately upstream of Snell Drive (Plate 2-4g). Sediment and eel sampling sites include one that is on the main channel upstream in Tauhara Park (KC) (Plate 2-4c) as well KA and KB which are tributary sites (Plate 2-4e & f).

The peri-urban site of KA is located adjacent to the Wairere Drive and Gordonton Road intersection with only rural inputs upstream. Site KB, a tributary to the main Kirikiriroa channel is near an old closed landfill in Tauhara Park (Clearwater and Valler 2012). Kirikiriroa C (KC) is the main channel at the western edge of Tauhara Park, near Tauhara Drive.



Plate 2-4. Kirikiriroa catchment sampling sites. a) K1, main channel outlet to the Waikato River; b) K3, upstream from Thomas Road; c) KC, main channel, upstream from K1, Tauhara Park; d) K2, under Wairere Drive overpass; e) KA, periurban drain Wairere Drive/Gordonton Road; f) KB, true right tributary upstream from K2; and g) K4, Chedworth tributary, Snell Drive.

2.2.5 Normandy Avenue and Graham Park

The two streams east and north-east of Waikato Hospital are small true left tributaries discharging directly into the Waikato River. The riparian vegetation of stream adjacent to Normandy Avenue (site NA) is dominated by mature eucalyptus trees with native understorey plants such as ferns (Plate 2-5a) and the confluence with the Waikato River is characterised by a very high perched concrete structure that would provide a barrier for many species.

The stream running through Graham Park (GA), adjacent to Cobham Drive, has mainly grasses and weeds as riparian vegetation although mature eucalypts are present at the headwaters. The northern banks of the lower reaches have larger exotic and native shrubs (Plate 2-5b). The stream runs through a culvert under Cobham Drive into the Waikato River.

2.2.6 Gibbon's Creek

Gibbon's Creek is a small catchment in the Hamilton East area discharging into the Waikato River. The water and sediment sampling sites were within Parana Park (PR_A), very near the confluence with the Waikato River just north of Bridge Street Bridge. Seeley's Gully site (SA) was solely chosen as an eel collection site because Parana Park is currently a fish monitoring site (B. Bartels, pers. comms) and restoration site (K. Collier, pers. comms.). Sediment was also taken from Seeley's Gully for comparison with eel tissue metals. Gibbons Creek at Parana Park has a narrow riparian margin whereas Seeley's Gully is mature native trees with little understorey vegetation (Plate 2-5c and f). There were high concentrations of Fe flocculant observed at both sampling sites.

2.2.7 Ranfurly Park

This sediment and eel collection site is located within an urban park in Fairfield with very little riparian vegetation other than grasses and exotic weeds (RN_A) (Plate 3-5e). The stream then flows through a large culvert under Ranfurly Street and eventually under River Road and into the Waikato River near the Fairfield Bridge (Aldridge and Hicks 2006).

2.2.8 Bankwood

This stream flows around the southern and western perimeter of Fairfield College and through the suburb of Chartwell where it discharges into the River at Swarbrick's Landing. The sediment and eel collection site was within an urban park with mature willow (*Salix* spp.) and elm (*Ulmus* spp.) trees as riparian vegetation and sparse understorey cover (Plate 2-5d).



Plate 2-5. Gibbon's Creek and other stream sampling sites. a) NA, Normandy Avenue; b) GA, Graham (archery) Park, Cobham Drive; c) PR_A, Gibbons Creek at Parana Park; d) BA, Donny Park; e) RA, Ranfurly Park; and f) SA, Gibbon's Creek at Seeley's Gully.

Chapter 3:

Contaminants in water and sediment, and bioaccumulation in shortfin eels (*Anguilla australis*).

3.1 Introduction

3.1.1 Sources of stream contaminants

Runoff from areas of human activity and impervious surfaces mobilises various suspended or dissolved contaminants that enter streams with stormwater (Helsel et al. 1979, Williamson 1986). Borchardt and Sperling (1997) suggested that 5% total impervious surfaces, as a percentage of catchment area, was a critical threshold above which biodiversity and density of biota become reduced because of increased hydrologic disturbance and contaminants from urban stormwater discharges. However, the term "effective imperviousness" gives a better gauge of stream degradation than just total impervious area, as it takes into account the connections (stormwater culverts or pipes) by which these impervious surfaces are linked directly with the stream system (Hatt et al. 2004, Walsh et al. 2005).

Stormwater contaminants include inorganic toxic metals and metalloids, and also organic substances such as (PAHs), suspended sediment and nutrients (Williamson 1986, Mangani et al. 2005). Sources of metals and metalloids and PAHs include motor vehicle emissions, drips of crankcase oil, vehicle tyre and brake wear, asphalt road surfaces, domestic fire emissions, spillage of waste oil and corrosion of roofing materials (Beasley and Kneale 2002, Moncrieff and Kennedy 2002, Chang et al. 2004, Brown and Peake 2006, Ermens 2007, Moores et al. 2009). Legacies from past land-use such as landfill leachate and industrial practices can affect stream ecosystems as well (Brown et al. 2009, Clearwater and Valler 2012). Aquatic sediments can accumulate these legacies, not only of past and present urban runoff, but also from upstream rural runoff (Arakel 1995, Santoro et al. 2009, Bonotto 2010). Ecological decline of macroinvertebrate communities has been linked to urbanisation, consistent with the impact of contaminated sediment (Beasley and Kneale 2002, Marshall et al. 2010).

3.1.2 Bioavailability

Partitioning of contaminants within aquatic environments is determined by a large range of environmental variables including grain size, organic carbon (OC) content, the chemical species present, sorptive behaviour of the contaminant, pH, and the redox potential of the sediments (Francis et al. 1984, Power and Chapman 1992, Chapman et al. 1998). The only definitive approach to determine bioavailability of compounds to biota is to measure accumulation within tissues or establish some form of biological response (Burton 1991, Power and Chapman 1992, Bervoets et al. 1994, ANZECC 2000, van der Oost et al. 2003, Santoro et al. 2009). It is important to acknowledge, however, that the accumulation of a contaminant within plant and animal tissues is not an adverse biological effect for the species concerned unless biological responses are induced by the presence of the chemical(s) (Spacie et al. 1995), although suitability for human consumption may be affected.

3.1.3 Bioaccumulation and toxicity in eels

Although some trace metals are essential for health, to maintain homeostasis a fish must coordinate acquisition and excretion, much of which occurs within the liver (Hinton et al. 2001, Bury et al. 2003). As the liver is the major site of metabolism, biotransformation and lipid storage (in many fish species), it is one of the main sites for the study of bioaccumulation of metals, metalloids and PAHs in fish (Jobling 1995, Spacie et al. 1995, Haluzova et al. 2011). Direct effects of metal toxicity can be seen at the cellular level, in organs and tissues and at the population level (Long et al. 1995, Campbell et al. 2003). Exposure to a variety of metals induces the production of, liver metallothioneins which are cysteine-rich proteins that enable the sequestration of both physiological and xenobiotic metals and which thereby mitigate metal toxicity (Hinton et al. 2001). The liver is also the main site of biotransformation for many potentially toxic organic substances, such as PAHs, by the cytochrome P450 enzyme superfamily which transform these lipophilic chemicals into more water-soluble compounds that are more easily excreted (Hinton et al. 2001).

Organic compounds such as PAHs are metabolised very efficiently in fish livers (Ariese 1993, van der Oost et al. 2003), and have been shown to cause deleterious effects (Aas et al. 1998, Collier et al. 1998, Myers et al. 2003). Metabolites produced in the liver are secreted into the bile and stored in the gall

bladder before being secreted into the intestine (Au et al. 1999). Krahn et al. (1984) determined that conjugated 1-hydroxypyrene (pyrene-1-glucuronide) was the major PAH metabolite in the bile of English sole from polluted sites in Puget Sound, and two subsequent studies of European eel (*Anguilla anguilla*) from polluted rivers confirmed that this metabolite also dominates in the bile of PAH-exposed eels (Ruddock et al. 2003, Nagel et al. 2012).

Eels are particularly suitable as bioindicator species for some environmental contaminants (Ruddock et al. 2003, Has-Schön et al. 2006, Belpaire and Goemans 2007, Nagel et al. 2012) because of their benthic and carnivorous habits and because they have high lipid content (Arleny et al. 2007, Belpaire and Goemans 2007, Stewart et al. 2011). Eel is not only an important traditional food resource in New Zealand, but also a moderate yield commercial fishery (Martin et al. 2009, Stewart et al. 2011). For the present study, concentrations of metals and metalloids in white muscle flesh was also of interest because of the potential risk for human health from consumption of eels caught in urban streams.

3.1.4 Study objective and aims

The overall objective of this study was to assess contaminant concentrations in water, sediment and shortfin eels in Hamilton urban streams.

In relation to water sampling, the aims were to: 1) determine base flow concentrations of dissolved metals and other relevant water quality parameters (pH, conductivity and total suspended solids) within the streams; 2) compare these concentrations with seasonal storm flow events; and 3) determine whether there were any differences in contaminant levels within catchments characterised by different urbanisation patterns: Mangakotukutuku - older residential with less development, Waitawhiriwhiri - high industrial with older residential, Kirikiriroa - new residential, and Gibbon's Creek - residential intensive.

The aims of the stream sediment study were to measure temporal and spatial variability in concentrations of metals, metalloids (above background levels) and PAHs in sediments and to determine the relationship between metal and metalloid concentrations and upstream catchment imperviousness.

Finally, the aims of the eel investigation study were to: 1) investigate if the common shortfin eel *Anguilla australis* from Hamilton urban streams were bioaccumulating metals or metalloids within liver or white muscle tissue and to assess exposure of these eels to pyrene through determining concentrations of its metabolite in bile; 2) determine any relationship between eel liver tissue concentrations and sediment contaminant concentrations; and 3) to establish any risk posed to humans of consumption of muscle tissue from shortfin eels caught in these streams.

3.2 METHODS

3.2.1 Site selection

Sites for the analysis of dissolved contaminants were selected to enable comparisons at upstream and downstream locations within the three main catchments (Table 3-1). Impervious cover estimates were supplied by Waikato Regional Council using the approach described in Collier and Clements (2011).

The sediment sampling sites were selected by the NIWA in 2011 using GIS data for stream, road and stormwater infrastructure locations and knowledge of historic and current land use as part of a broadscale survey of contaminant levels in urban streams (Clearwater and Valler 2012). These sites included streams where sediment metal concentrations were the highest reported, current restoration projects were underway (e.g. Gibbon's Creek at Parana Park and Bankwood Stream at Donny Park), or prospective urban development is planned (Peacockes branch of the Mangakotukutuku). Both the 2012 quarterly sediment sampling and eel collection sites were a subset of these sites.

Table 3-1. Site information for water sampling sites (W), sediment sampling sites, (S) and eel collection sites (E). Alternate shading represents separate catchments

Stream/Catchment	Site Label	NZTM2000		% Impervious	Site Description	Sampling
		Northing	Easting			
Horsham Downs	EC	5824812	1796079	5	Pastoral stream, 100% rural inputs. True right tributary of Waikato R. Positive control for urban eel collection.	E
	M1	5812777	1802320	18	Main channel near confluence with Waikato. River, Sandford Park.	W
	M2	5812414	1802018	17	Main channel, mid Sandford Park.	W
	M3	5811042	1802040	23	Small Te Anau trib., below Ohaupo Rd, stormwater culvert.	W
Mangakotukutuku	PB	5811469	1803357	5	Main channel of Peacockes branch, rural.	S
	PC	5812376	1802560	7	Main channel of Peacockes branch, Peacockes Road, residential.	S
	PD	5811516	1803378	5	Small tributary to main Peacockes channel, rural.	S
	RK_B	5811920	1801016	13	Main Rukuhia channel. Receiving inputs from Ohaupo Rd.	S, E
	RK_D	5812430	1802271	20	Main Rukuhia channel. Upstream from confluence with Peacockes branch.	S, E
Normandy Ave	NA	5813293	1801341	71	Downstream of old hospital landfill, stormwater pipe, discharge upstream. Fe flocculant.	S, E
Graham Park	GA	5813684	1801191	58	Small stream located in grassed urban park adjacent to Cobham Drive.	S, E
	W1	5816907	1799925	41	Main channel outlet to Waikato River.	W
	W2	5816178	1799467	40	Mainstem, downstream from Seddon Rd overpass. Stormwater culvert	W
Waitawhiriwhiri	W3	5814004	1798112	26	From Greenwood/Duke St industrial area, upstream highly culverted, downstream from WA. Fe flocculant.	W
	WA	5814304	1799865	47	Lake Rotoroa outlet, Innes Common.	S, E
	WB	5813547	1797749	7	Karen Cres./Kahikatea Park. Rural inputs. Fe flocculant	S, E
	WF	5816041	1799457	40	Upstream of Seddon Rd (true right tributary to main channel). Probable stormwater inputs. Edge of catchment.	S, E
Gibbons	PR_A	5815315	1801468	70	Located in urban park (Parana). Fe flocculant.	W, S
	SA	5815683	1801849	68	Restored bush site (Seeley's Gully). Eels collected here because of restoration site at PR_A. Fe flocculant	S, E
Ranfurly Park	RN_A	5817176	1800468	53	Grassed urban park (Ranfurly), fully urbanised catchment.	S, E,
Bankwood	BA	5818728	1800027	65	Located in urban park (Donny), fully urbanised catchment.	S, E
	K1	5820265	1798831	49	Main channel outlet to Waikato River under River Rd.	W
	K2	5820051	1800001	68	Directly under Wairere Dr. Straight channel.	W
	K3	5821604	1800830	56	Upstream of Thomas Road, rural inputs possible.	W
Kirikiroa	K4	5818367	1801923	68	Downstream of Snell Drive - Chedworth tributary. Fe flocculant.	W
	KA	5819375	1802147	5	Rural location, deep layer of sludge. High Fe flocculant	S, E
	KB	5820340	1799944	44	Tauhara Park. Old landfill inputs.	S, E
	KC	5820093	1799243	48	Mainstem location, Tauhara Park. Outlet to Waikato River.	S, E

% impervious data supplied by Waikato Regional Council

3.2.2 Water sampling

Base flow sampling was carried out during an antecedent dry period on 4/4/12, followed by sampling of two rain events on 27/4/12 and 3/9/12. Water samples were collected using a new 500 mL food grade plastic container from flowing water, excluding eddies, backwaters and reverse flows. Both the container and lid were rinsed in the stream water three times prior to obtaining the sample. Samples were returned to the laboratory as soon as possible after collection and refrigerated at 4-5°C prior to analysis.

Discharge

Wetted width, water depth and water velocity were measured to estimate discharge at the outlets of the three main catchments (M1, W1 and K1) on 4/4/12. Water depth and velocity were measured at up to 10 offsets along the transect line as in Protocols 2 and 3 of Harding et al. (2009). Water velocity was measured using a Marsh McBirney Model 2000 flow meter but was not measured during the rain events because of high flows. Discharge (L s^{-1}) was estimated from the cross-sectional area of water (m^2) and water velocity (m s^{-1}).

Water quality parameters

United States Environmental Protection Agency Method 160.2 was used to determine total suspended solids (TSS) on a 50 mL aliquot of well-shaken stream water. Glass fibre filters (47 mm) were prepared by placing them on the membrane filter apparatus with wrinkled surface up and vacuum applied. Three successive 20 mL volumes of milliQ water were passed through until all traces of water were removed by the vacuum. Filters were removed from the apparatus and dried in an oven at 105°C to constant weight (weight loss less than 0.5 mg). Filters were weighed using an analytical balance just prior to water samples being filtered. Each 50 mL sample was shaken vigorously before being filtered through the apparatus. All traces of water were removed by continuing to apply the vacuum. With suction on, the sample tube and lid, filter, non-filterable residue and filter tunnel were washed using three portions of 10 mL milliQ water allowing complete drainage between washing. Each filter was carefully removed from the filter support and dried for 1.5 hours at 105°C, cooled in a desiccator and weighed. The drying cycle was repeated until a constant weight was obtained.

Both pH and electrical conductivity were measured in the laboratory. The pH of water samples at 20°C was measured using a calibrated PHM210 pH meter and specific conductivity was measured using a YSI Model 30 conductivity meter. Specific conductivity, standardised to 25°C, was recorded in $\mu\text{S cm}^{-1}$. Water hardness was calculated from calcium (Ca) and magnesium (Mg) concentrations measured by Inductively Coupled Plasma-Pass Spectrometry (ICP-MS) as outlined below and expressed as equivalent of CaCO_3 .

Dissolved metals

From the original sample, 15 mL was filtered through a 0.45 μm sterile disposable filter for total dissolved metal and metalloid analysis. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) analysis was conducted on a 10 mL sample acidified to 2% with 1% of nitric acid (HNO_3) and 1% hydrochloric acid (HCl) as well as SLRS-5 (National Research Council 2009) by the University of Waikato Chemistry Department for a suite of 26 elements using a Perkin Elmer Sciex ELAN DRCII ICP Mass Spectrometer. All ICP-MS analyses by the University of Waikato for this thesis were for the same number of elements and carried out on this machine.

3.2.3 Sediment sampling

Sediment collection

Sediment samples were collected from multiple settling zones at each site in a downstream to upstream direction on 7-8/5/12, 28-29/8/12 and 29-30/11/12. Plastic trowels were used to remove approximately the top 20 mm of fine sediment with a total of approximately 1.5-3 kg collected (wet weight). Sediment was placed with some water in one or two clean plastic zip-lock bags and thoroughly mixed within and between bags to ensure collected sediment was homogeneous. Samples were double-bagged and placed on ice for transport back to the laboratory. At the laboratory, samples were either used immediately for contaminant analysis or frozen (-20°C).

Sediment analysis

A subset of the sediment samples from each sediment collection was wet-sieved to obtain the <500 μm fraction and digested using hot concentrated HNO_3 and

HCl to obtain total recoverable metals. Copper, Pb and Zn concentrations were measured using ICP-MS (Hill Laboratories, Hamilton) (Method Detection Limit (MDL) 2.0, 0.4 and 4 mg kg⁻¹, respectively). Subsequently these digests were analysed using ICP-MS by the University of Waikato Chemistry Department.

Samples collected in May 2012 were also analysed for OC and PAH content by Hills Laboratories, Hamilton. The samples were subjected to acid pre-treatment to remove carbonates if present. Organic carbon content was measured using an Elementar Combustion Analyser (MDL 0.05g 100g⁻¹ dry weight). For the PAH analysis, samples were sonicated, diluted and subjected to solid phase extraction (SPE) clean-up (if required) to extract PAHs. They were then analysed using Gas Chromatograph-Mass Spectrometry Selected Ion Monitoring analysis (modified USEPA protocol 8270).

3.2.4 Shortfin eel collection and analysis

Collection and dissection

Shortfin eels were specifically selected for collection because of their high relative abundance in Hamilton urban streams (Aldridge and Hicks 2006), B. Bartels pers. comm.), and also because they are not considered a threatened species (Allibone et al. 2010).

Eels were collected on 23/5/12, 11/6/12, 26/6/12 and 28/6/12 using a back-pack electric fishing machine (EFM300) according to the University of Waikato Animal Ethics Committee Standard Operating Procedure (SOP) 7 (Ling 2006a). Multiple pass removal methods were used to collect eels within the range of 450 to 800 mm total length, where possible. Three eels were collected from each urban site along with six from the Horsham Downs control site in an entirely rural catchment. Caught eels were temporarily held in a net bag in a fish bin with stream water. Sediments were simultaneously collected at sites WB, WF and SA (see Table 3-1) during eel collection for comparison with eel tissue concentrations.

Only threatened longfin eels (*A. dieffenbachi*) were found in the Peacockes branch of the Mangakotukutuku (sites PB and PC electrofished) and therefore no eels were kept from this less developed arm of the Mangakotukutuku. The water

depth of the main Kirikiriroa channel at site KC was too deep for backpack electrofishing methods and was abandoned in terms of eel collection.

Eels were euthanised on return to the laboratory by an overdose of benzocaine (ethyl-p-aminobenzoate) solution as outlined in the University of Waikato Animal Ethics Committee SOP 6 (Ling 2006b). Length was measured to the nearest mm on a measuring board followed by immediate dissection. Eel bile was sampled from gall bladders using 0.5 ml insulin syringes (Becton Dickinson, 30 G fixed needle) and stored at -20°C until analysis according to the method of Ariese et al. (1993). The whole liver was then dissected and placed into a sterile WhirlPak plastic bag (ethylene sterilised). Approximately 50 cm³ of muscle tissue was dissected from the left side posterior to the anus, the skin was removed and muscle tissue was then placed into a Whirlpak bag. Knives and dissection equipment were washed with tap water prior to each dissection to minimise contamination. All samples were immediately frozen at -20°C until digestion and analysis.

Tissue digestion and analysis

A suite of 25 elements was measured in eel liver and muscle tissue based on established methods (USEPA 1987). Approximately 2.0 g of tissue was placed in a new 50 mL falcon tube and 2.0 mL of tetramethylammonium hydroxide (TMAH) added prior to being placed into a 60°C water bath for one hour. The samples were mixed using a vortex mixer and placed back into the 60°C water bath for a further 60 min. The samples were then immediately placed into an ice bath to cool rapidly before the addition of 0.5 mL of ice cold hydrogen peroxide (H₂O₂) and stored overnight at 3-5°C. The following day, 2.0 mL of HNO₃ was added and samples were placed in a 90°C water bath for one hour, vortex mixed, and returned to the water bath for a further hour. Digests were then refrigerated at 3-5°C.

Each digest was made up to 50 mL with milliQ water and then shaken vigorously prior to an aliquot of this solution being filtered through a 0.45 µm sterile disposable filter into a 15 mL new sample tube. One mL of filtered tissue digest was then mixed with 8.8 mL of milliQ water and 0.1 mL of both HCl and HNO₃ in a new 15 mL sample tube for ICP-MS analysis. A certified reference material, DOLT-4 dogfish liver powder was also digested using the above method

(National Research Council Canada 2008). This certified reference material digest, reference standard SLRS-5 (National Research Council Canada 2009), two method blanks, and the digests were sent for analysis by ICP-MS. Dilution factors and tissue weights were then used to calculate final metal concentrations.

Bile analysis

Frozen bile was thawed and diluted 1:500 in ethanol:water (50:50) and analysed for pyrene-1-glucuronide by synchronous fluorescence spectrometry (SFS) using a Shimadzu RF-5301 scanning spectrofluorometer and a 1 cm path-length quartz cuvette. SFS spectra were scanned from 263 to 413 nm (excitation wavelength), scanning both monochromators simultaneously at a fixed wavelength difference ($\Delta\lambda$) of 37 nm and bandwidth of 5 nm. Quantification of pyrene-1-glucuronide concentration was determined by measuring the net peak area of the SFS spectrum from 375 to 390 nm (emission wavelength). Because pyrene-1-glucuronide standards are not available, peak areas were calibrated against a series of unconjugated 1-hydroxypyrene (Toronto Research Chemicals Inc.) standards and corrected for the greater fluorescence intensity and blue shifted emission spectrum (by 5 nm) of pyrene-1-glucuronide using a calibration factor of 2.2 (Ariese et al. 1993). Figure 3.1 shows representative SFS spectra of control and PAH exposed (site WF) eel bile and a 1-hydroxypyrene standard.

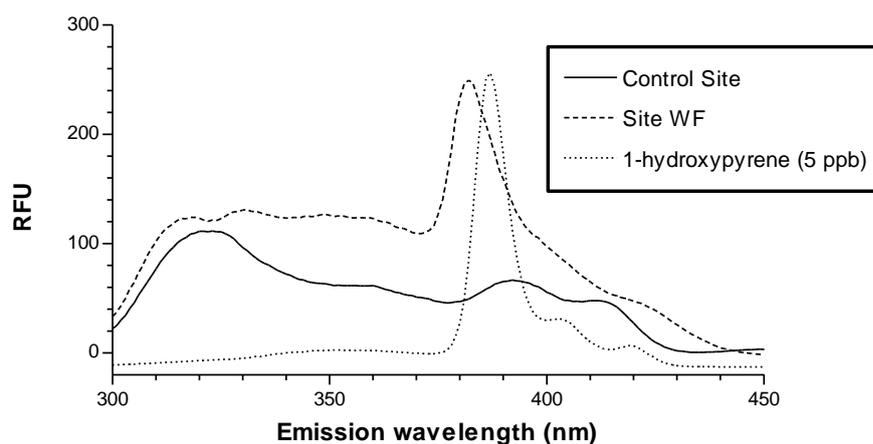


Figure 3-1. Representative synchronous fluorescence spectra (SFS) ($\Delta\lambda = 37$ nm) of control and PAH exposed (WF; see Table 3-1) eel bile and a 1-hydroxypyrene standard. RFU - relative fluorescence units.

3.2.5 Method detection limits and reporting

The MDL is the minimum concentration of a substance that can be measured and reported with a 99% confidence that the material concentration is greater than zero, which depends on the material, sample matrix and the sample volume to weight ratio (Ling 2012). Having concentrations that lie below the MDL is a common problem that occurs in tissue contaminant analysis (Ling 2012). Succop et al. (2004) suggested that these values be reported but that those below the MDL must be indicated as such. This approach has been taken here.

Dissolved metals reported were those associated with urban stormwater, Cu, Pb and Zn (anthropogenic) as well as Fe for estimates of dilution between base flows and rain events. Sediment metals and metalloid reported were those associated with urban stormwater as well those relevant to the Hamilton Basin with respect to current and previous land use and past pollution events, and for comparison with shortfin eel tissue concentrations. In addition, OC, Fe and manganese (Mn) were reported because of the affinity of metals to bind to OC and Fe and Mn oxides.

Statistical reporting is based on mean \pm standard error of the mean unless stated otherwise. Sediment concentrations are expressed as mg kg⁻¹ dry weight and tissue concentrations, mg kg⁻¹ wet weight.

3.2.6 Statistical analyses

Data analyses were performed using the statistical package Graphpad Prism, Version 4.0. Sediment and eel tissue concentrations were log transformed following tests for normality. Sediment concentrations between sites and between sampling periods were compared separately by comparing overall means from sites and overall means from sampling periods, respectively, using one-way Analysis of Variance (ANOVA). Mean eel tissue concentrations and bile PAH metabolite were log transformed because of non-conformity in normality testing and compared using ANOVA. Tukey's post hoc test was subsequently carried out when a significant difference was seen ($p < 0.05$).

Linear regressions were carried out between sediment with eel tissue concentrations and upstream imperviousness at sampling sites to determine if there were any relationships. Mean sediment metal and metalloid concentrations

were used in correlations with imperviousness. August samples were used for the regression with eel liver concentrations as there were no sediment data for sites RK_B and RK_D for the May sediment collection period (digests did not return from analysis at Hill Laboratories).

Separate correlations were carried out between sediment PAH concentrations and sediment concentrations of Cu, Pb and Zn as well as PAH bile metabolite concentrations and sediment PAH concentrations (May sediment sampling period).

3.3 RESULTS

3.3.1 Water sampling

Very little precipitation fell in Hamilton in the month following late March except for one significant rain event on the evening of 11/4/12 (Fig. 3-2), which was not sampled. Base flow sampling was conducted on 4/4/12 after 10 days of no precipitation and rain events were sampled on 27/4/12 and 3/9/12 (Figs. 3-2 & 3-3).

Discharges and water quality parameters

The April rain event was consistent light rain for several hours prior to sampling of the streams. Observations when sampling indicated that the light rain increased flow and turbidity considerably, especially at site W1. Samples were collected within 2-3 hours. Hourly rainfall for April and September are shown in Figures 3-2 and 3-3.

Water samples were slightly acidic, even at base flows prior to rainfall (Table 3-2). Conductivity and hardness decreased with rainfall while TSS increased. The Kirikiriroa catchment sites had the four highest conductivity levels of all sampling sites during base flow with the highest being at K4 ($261.7 \mu\text{S cm}^{-1}$). Overall catchment conductivity was in the order Gibbons Creek < Mangakotukutuku < Waitawhiriwhiri < Kirikiriroa. The highest TSS concentration was seen on 3/9/12 at site W2 (298 mg L^{-1}). Other high concentrations were seen at M2 (246 mg L^{-1}) and W1 (234 mg L^{-1}) on 27/4/12. The Gibbons Creek site PR_A, W3 and K4 decreased TSS concentrations in both rain events compared with base flows. Overall catchment TSS was in the order Gibbons Creek < Kirikiriroa < Mangakotukutuku < Waitawhiriwhiri. Raw water sampling data are presented in Appendix A.

Base flow discharges for the streams on 4/4/12, estimated from measurements taken near confluences with the Waikato River, were 92, 176, and 119 L s^{-1} for the Mangakotukutuku, Waitawhiriwhiri and Kirikiriroa streams, respectively.

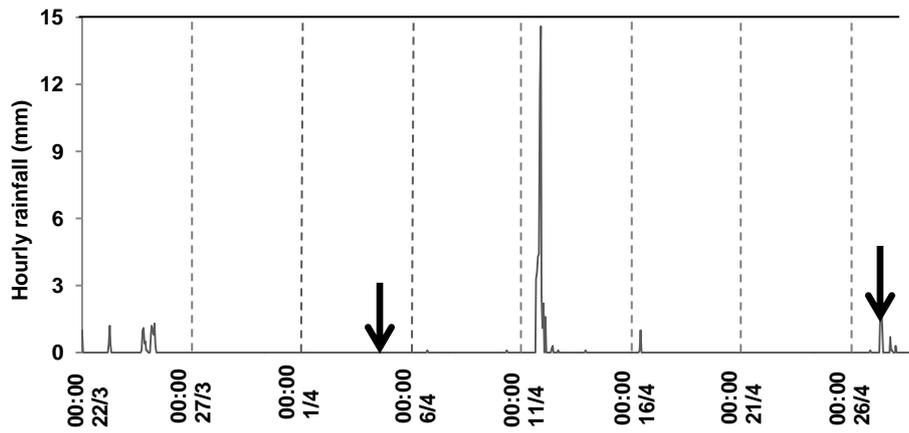


Figure 3-2. Hamilton hourly rainfall (AgResearch, Ruakura Road, Hamilton 5816572N, 1803010E) from 00:00 22 March 2012 to 00:00 29 April 2012 (NIWA 2012a). Arrows represent sampling on 4 and 27 April 2012.

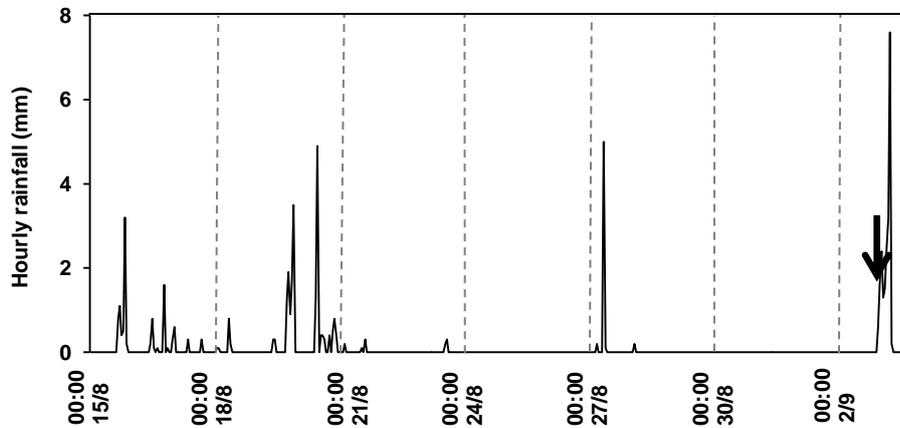


Figure 3-3. Hamilton hourly rainfall (AgResearch, Ruakura Road, Hamilton 5816572.052 N, 1803010.359 E) from 00:00 15 August 2012 to 00:00 4 September 2012 (NIWA 2012a). Arrow represents sampling on 3 September 2012.

Table 3-2. Mean water quality measurements of pH, conductivity, total suspended solids (TSS) and hardness of water samples from the Mangakotukutuku, Waitawhiriwhiri, Kirikiriroa, and Gibbon's Creek catchments collected during an antecedent dry period (4/4/12), autumn and spring rain events (27/4/12 and 3/9/12). Data for sites is the mean (range) of all dates and for sampling dates is the mean (range) of all sampling sites.

Catchment/ Date	pH	Conductivity ($\mu\text{S cm}^{-1}$)	TSS (mg L^{-1})	Hardness* ($\text{mg CaCO}_3 \text{ L}^{-1}$)
Mangakotukutuku	5.8 (5.3-6.2)	139.3 (63-192.8)	105.8 (79-245.6)	32.6 (18.1-43.4)
Waitawhiriwhiri	5.5 (5.0-6.0)	142.4 (72.3-209.1)	137.5 (66.4-298.0)	32.2 (16.2-48.1)
Kirikiriroa	5.6 (5.3-6.0)	188.3 (69.4-261.7)	76.1 (24.4-182.2)	41.3 (15.1-58.5)
Gibbons	5.7 (5.2-6.1)	126.0 (69.5-201.2)	43.1 (23-74.2)	26.4 (15.4-41.3)
4/4/12	5.8 (5.0-6.0)	202.7 (93.6-261.7)	66.8 (24.6-120.8)	45.9 (58.5-39.2)
27/4/12	5.7 (5.1-6.1)	127.5 (72.3-204.3)	120.9 (26.2-245.6)	26.7 (16.2-49.1)
3/9/12	5.5 (5.2-5.7)	140.1 (63-228.8)	106.2 (23-124.4)	32.7 (15.1-57.7)

* calculated from Ca and Mg concentrations.

Dissolved metal concentrations and loads

All base flow concentrations of dissolved Cu, except those of W1, were below the MDL of $0.5 \mu\text{g L}^{-1}$. However, dissolved Cu exceeded the ANZECC (2000) 95% trigger value of $1.4 \mu\text{g L}^{-1}$ during all rain events at all sites except for K1-3 (Fig. 3-4A).

Dissolved Pb concentrations for all of the base flow samples and many of the rain event samples, did not meet the MDL of $0.20 \mu\text{g L}^{-1}$ (Fig. 3-4B). Concentrations at all sites during every sampling occasion did not surpass the 95% trigger value of $3.4 \mu\text{g L}^{-1}$.

Base flow Zn concentrations at all sites except M3 and K3 surpassed the ANZECC 95% trigger value of $8 \mu\text{g L}^{-1}$ as did all rain events sampled, except at site K3 (Fig. 3-4C).

Dissolved Fe concentrations are presented here as a basis for an estimation of dilution of base flows within the streams by the first rain event (Fig 3-4D). There was a 47%, 72% and a 60% reduction in dissolved Fe concentrations in water from the Mangakotukutuku, Waitawhiriwhiri and Kirikiriroa outlets, respectively, to the Waikato River. Using these dilutions and the concentrations from each outlet site, Cu load increased approximately 14-fold at M1, 16-fold at W1 and 9-fold at K1 between the antecedent dry spell and the first rain event on 27/4/12. Estimated increases in Zn concentrations from 4/4/12 and 27/4/12 were 2-fold at M1, 12-fold at W1 and 3-fold at K1. The greatest dilution in Fe concentration of 97% was seen at W3, indicating that concentrations of Cu and Zn had increased from 4/4/12 to 27/4/12 approximately 165-fold and 150-fold, respectively, during the April rain event. Dissolved Fe concentrations reduced at all water sampling sites from 4/4/12 to 27/4/12, except for sites K3 and 4 and PR_A.

Estimated loads of metals delivered to the Waikato River from the Mangakotukutuku, Waitawhiriwhiri and Kirikiriroa catchments during baseflow discharges were, respectively: 1) Cu, 9.1 mg hr^{-1} , 53.2 mg hr^{-1} , and 12.9 mg hr^{-1} ; 2) Pb, 2.0 mg hr^{-1} , 5.2 mg hr^{-1} and 0.6 mg hr^{-1} ; and 3) Zn, 290 mg hr^{-1} , 1581 mg hr^{-1} and 486.4 mg hr^{-1} .

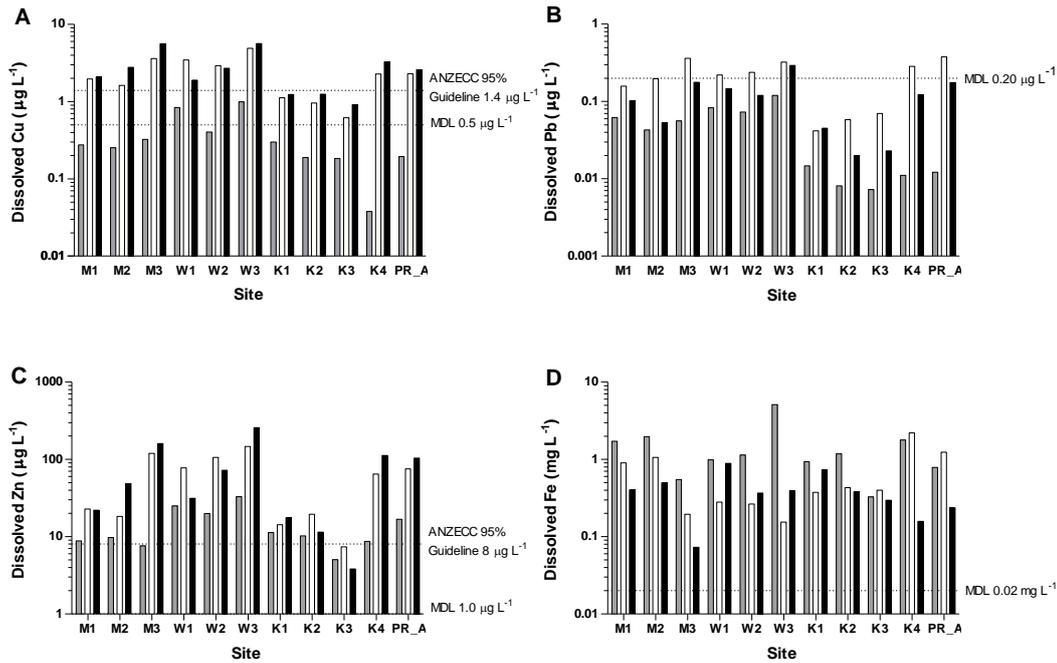


Figure 3-4. Dissolved concentrations of A) copper (Cu) ($\mu\text{g L}^{-1}$), B) lead (Pb) ($\mu\text{g L}^{-1}$), C) zinc (Zn) ($\mu\text{g L}^{-1}$) and D) iron (Fe) (mg L^{-1}) measured in water from the Mangakotukutuku (M1-3), Waitawhiriwhiri (W1-3), Kirikiriroa (K1-4) and Gibbons Creek (PR_A) stream water sampling sites during base flow (4/4/12) (grey), and rain events on 27/4/12 (white) and 3/9/12 (black). ANZECC Guidelines are appropriate for a water hardness of 30 g m^{-3} of CaCO_3 .

3.3.2 Sediment

Metals and metalloids

Sediment concentrations of Cu, Pb and Zn measured by the University of Waikato correlated well with those measured by Hill Laboratories for all sampling periods in 2012 (Mean R^2 : May, 0.992; August, 0.993; November, 0.995). MDLs were well below concentrations measured (Cu, 0.1; Pb, 0.04; Zn, 0.2; Fe, 4.0; Mn, 0.1; As, 0.2; barium (Ba), 0.1; cadmium (Cd), 0.01; nickel (Ni), 0.2; and mercury (Hg), 0.4 mg kg^{-1} dry weight).

There were highly significant statistical differences between sites with reference to mean metal or metalloid concentrations ($F_{15,28}$, p -value) (Cu, 4.20, $p < 0.001$; Pb, 8.39, $p < 0.001$; Zn, 6.08, $p < 0.001$; Fe, 5.44, $p < 0.001$; Mn, 3.83, $p < 0.01$; As, 8.36, $p < 0.001$; Cd, 5.94, $p < 0.001$; and Ni, 10.64, $p < 0.001$). There was a moderately significant statistical difference between sites with respect to Ba concentrations (2.30, $p < 0.05$) and no differences between sites with respect to Hg concentrations (0.46, $p > 0.05$).

No sites in the Hamilton gully streams sampled exceeded the ANZECC ISQG Low value for Cu. The PR_A site had the overall highest concentrations of Pb and Zn (Fig. 3-5A-C), with mean sediment concentrations for Pb and Zn exceeding ANZECC (2000) ISQG Lows of 50 mg kg⁻¹ and 200 mg kg⁻¹, respectively. Lead measured in sediments collected in May at RN_A also exceeded the ISQG Low and the Zn ISQG Low was also exceeded in sediments collected from RN_A and KA, and in May sediments from site BA. The ISQG-High value of 410 mg kg⁻¹ was exceeded by PR_A (588.5 mg kg⁻¹) and RN_A (418.1 mg kg⁻¹) in May sediment samples.

Comparisons between sampling dates only revealed a significant difference between May, August and November samples for Cu concentrations at all sites ($F_{2,41} = 5.39$, $p < 0.01$), with no difference for Pb and Zn. May concentrations of Cu (18.9 ± 4.0 mg kg⁻¹) were significantly higher than August (6.6 ± 1.1 mg kg⁻¹) but not November concentrations. There was no difference between August and November concentrations. There were however, large decreases at individual sites where initial concentrations (of Cu, Pb and Zn) in May were high in comparison to August (e.g. PR_A, RN_A and BA). Concentrations at the peri-urban site of KA were quite similar throughout the sampling periods (210.2 ± 27.9 mg kg⁻¹).

Sediment Fe concentrations were highest at the peri-urban site KA compared with the other stream sites (Fig. 3-5D). However, KA was not statistically different from the other Kirikiriroa and PR_A sites. There were no temporal differences in sediment Fe concentrations.

Manganese concentrations did not exceed the range found in Waikato soils and were only significantly higher in sediments at site PB of the Peacockes branch of the Mangakotukutuku compared with most other sites (Fig. 3-5E). There was a significant difference between sampling periods with reference to Mn concentrations ($F_{2,41} = 8.12$, $p < 0.01$). Comparisons between May and August and May and November were significant, but August and November sampling period concentrations of Mn were not significantly different in the post-hoc test.

The most consistently high site in terms of As concentrations throughout the three sampling periods was WA (Lake Rotoroa) sediments with a mean of 47.1 ± 3.9 mg kg⁻¹, although the highest concentration was at KB, in November, with

94.2 mg kg⁻¹, exceeding the ISQG-High of 70 mg kg⁻¹ (Fig. 3-5F). Mean sediment As for both these sites exceeded the ISQG Low value of 20 mg kg⁻¹. This value was exceeded also by sites RN_A, BA, KB, KC and PR_A from the May samples although this value is at the top end of the background Waikato soil range. Comparison of differences between sampling periods revealed a significant difference again between May (20.3 ± 3.8 mg kg⁻¹) and August (8.4 ± 2.4 mg kg⁻¹) mean concentrations of As over all sites ($F_{2,41} = 4.83$, $p < 0.05$) but not with November concentrations. There was no difference between August and November mean concentrations.

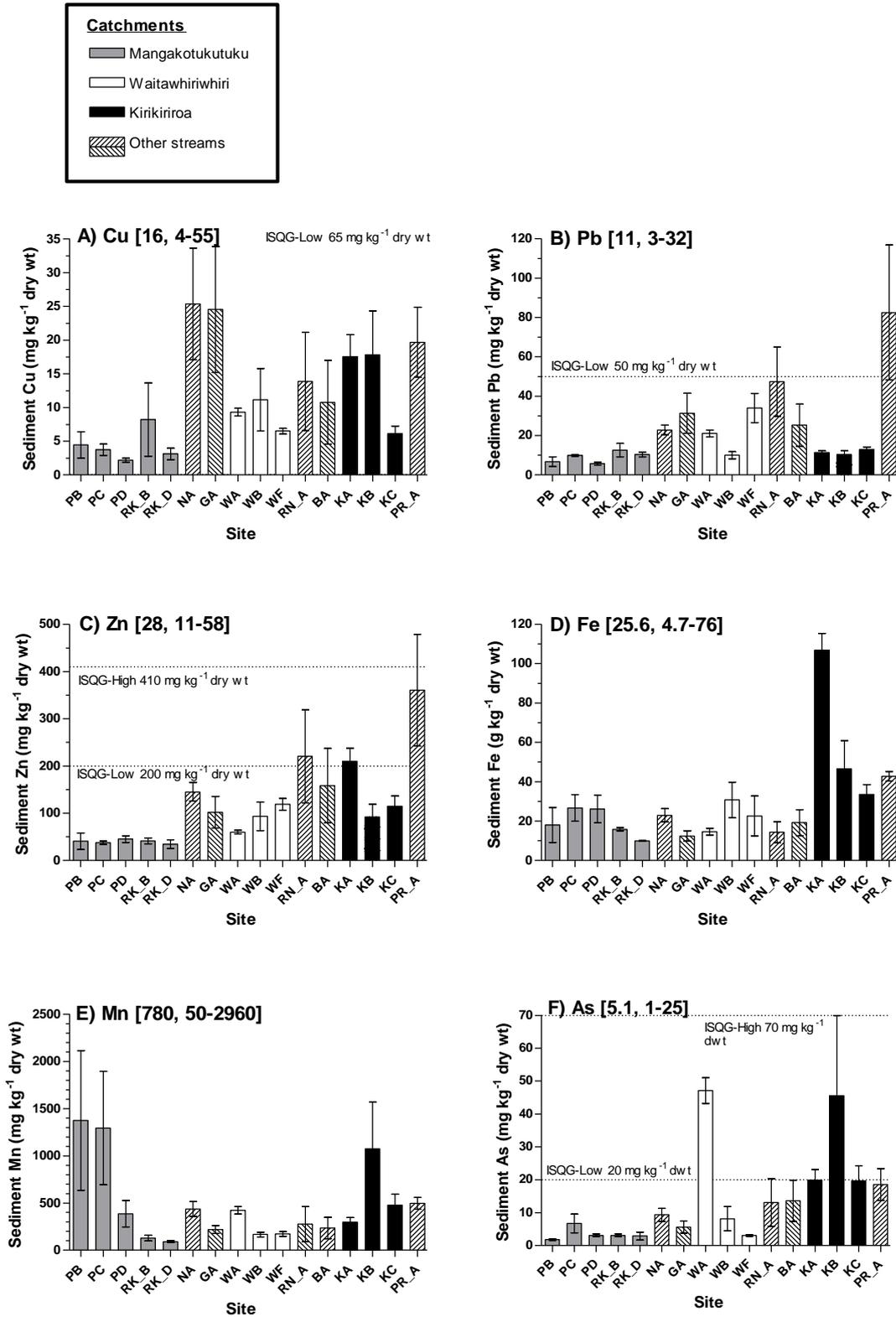
Site KB had the highest concentration of Ba although it was only moderately significantly higher than site WF ($p < 0.05$) (Fig. 3-5G). In the absence of ISQG values and with background concentrations in Waikato soils averaging 97 mg kg⁻¹ (range 15-310 mg kg⁻¹), KB had over 7 times the average concentration reported in Taylor and Kim (2009). Site KA also had over double the average Waikato soil concentration of Ba. Comparison between sampling periods across all sites showed that May concentrations of 208.3 ± 24.1 mg kg⁻¹ were significantly higher than those in August (78.8 ± 13.5 mg kg⁻¹) and November (137.4 ± 40.9 mg kg⁻¹) ($F_{2,41} = 12.5$, $p < 0.001$), but there was no difference between August and November.

Cadmium concentrations in Hamilton stream sediments did not exceed the ISQG-Low value of 1.5 mg kg⁻¹ at any sites (Fig. 3-5H). Kirikiriroa A (KA) had significantly higher Cd concentrations compared with all other sites. There were no significant differences in concentrations of Cd between sampling periods across all sites.

The ISQG-Low value for Ni of 20 mg kg⁻¹ was only approached by NA in May with a concentration of 18 mg kg⁻¹, but was not exceeded by any site during 2012 (Fig. 3-5I). There were no significant differences in Ni concentrations between sampling periods across all sites.

Most of the exceedances of the ISQG-Low value for Hg of 0.15 mg kg⁻¹ were all within the range of background soil concentrations (0.019 - 0.50 mg kg⁻¹) (Fig. 3-5J). There were significant differences in temporal variability ($F_{2,41} = 5.394$, $p < 0.01$), with May sediment samples significantly higher than August. There were no differences between May and November and August and November

concentrations. All elements measured in sediments from each sampling period are presented in A Appendix B.



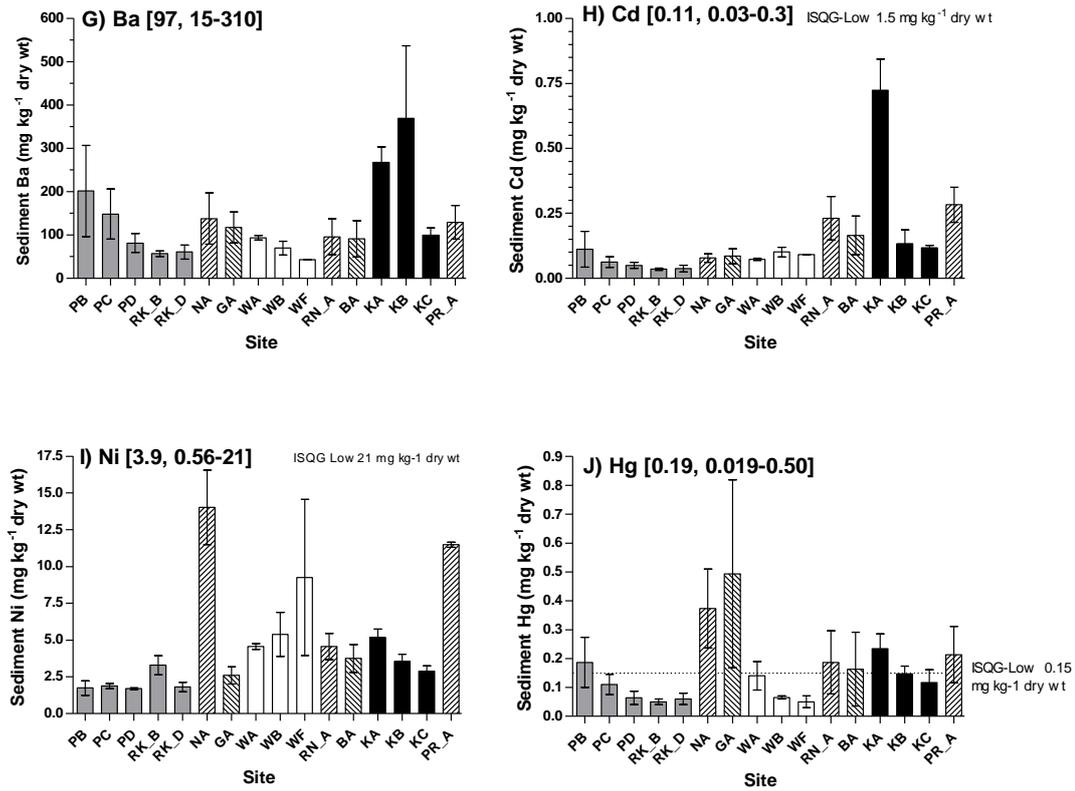


Figure 3-5. (current and previous page). Sediment metal and metalloid concentrations (<500µm fraction) (mg kg⁻¹ dry weight) (mean ± SE) of A) copper (Cu), B) lead (Pb), C) zinc (Zn), D) iron (Fe), E) manganese (Mn), F) arsenic (As), G) barium (Ba), H) cadmium (Cd), I) nickel (Ni), and J) mercury (Hg), measured in Hamilton urban streams. Background soil concentrations from Taylor and Kim (2009) are shown at the top of each figure [mean, range]. Key to site labels is found in Table 3-1. Note: Fe concentrations are g kg⁻¹ dry weight.

Sediment metal and metalloid and imperviousness relationships

Comparison between % impervious area of the catchment above the sampling site showed a significant relationship with mean sediment concentration of: (F_{1,14}, p-value) Cu, 9.52, p <0.01; Pb, 9.70, p <0.01; Zn, 5.98, p <0.05; Hg, 5.22, p <0.05, and Ni, 7.11, p <0.05 (Fig. 3-6A-C,G,H). Correlations between % impervious area and concentrations of As, Ba and Cd showed no significant relationship (As, 2.0, p >0.05; Ba, 0.01, p >0.05; Cd, 0.01, p >0.05) (Fig. 3-6D-F).

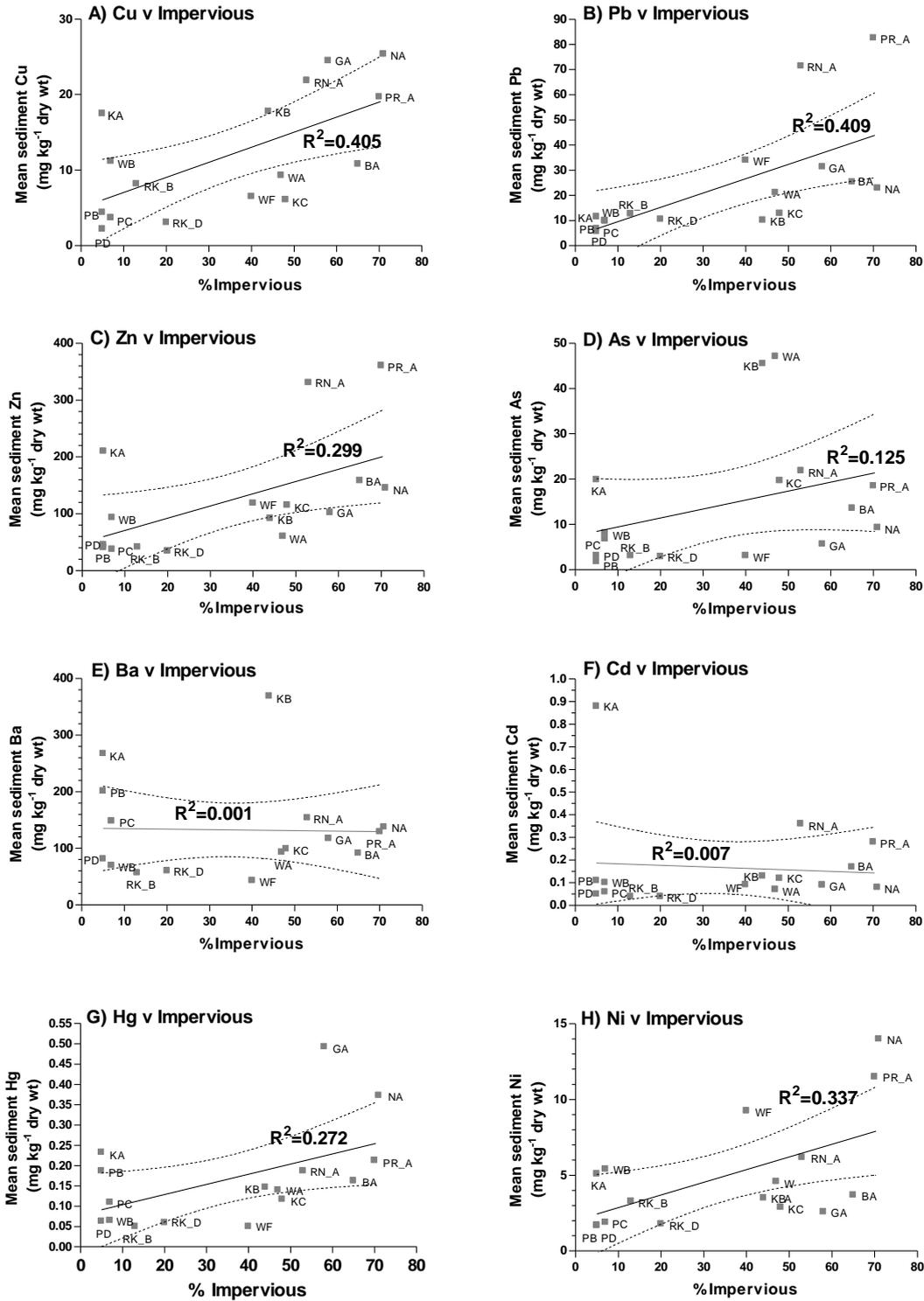


Figure 3-6. Relationships between 2012 mean A) copper (Cu), B) lead (Pb), C) zinc (Zn), D) arsenic (As), E) barium (Ba), F) cadmium (Cd), G) mercury (Hg), and H) nickel (Ni) sediment concentrations and % catchment impervious above sampling site. Coefficient of determination (R^2) for solid best-fit line. Dotted lines represent 95% confidence bands. Key to site labels is provided in Table 3-1.

Polycyclic aromatic hydrocarbons and organic carbon

Ten of the 16 PAHs measured by Hill Laboratories were greater than the MDL (Clearwater and Valler 2012). Polycyclic aromatic hydrocarbons were only detected at 6 of the 14 sites sampled in the May 2012 sediments (Table 3-3). None of the concentrations exceeded ANZECC (2000) ISQG Low trigger values for individual PAHs or for total low and high molecular weight PAHs normalised to 1% OC (Table 3-3). There were no relationships between sediment PAH concentrations and sediment metals concentrations of Cu, Pb and Zn.

Table 3-3. Organic carbon (OC) and polycyclic aromatic hydrocarbons (PAHs) in Hamilton stream sediments collected 7-8/5/12. Interim Sediment Quality Guidelines Low (ISQG-Low) refers to the ANZECC (2000) sediment quality guideline for that PAH. Molecular weight - Mwt. Alternate shading represents separate catchments and ISQG-Low. See footer for PAH abbreviations.

Site	OC	B[a]A	B[a]P	B[b]F	B[g,h,i]P	B[k]F	Chry	FA	IPyr	Phe	Pyr	Low Mwt PAHs*	High Mwt PAHs†
	%	$\mu\text{g kg}^{-1}$ dry weight (normalised to 1% OC)											
PB	9.8	-	-	-	-	-	-	-	-	-	-	-	-
PC	3.0	-	-	-	-	-	-	-	-	-	-	-	-
PD	2.1	-	-	-	-	-	-	-	-	-	-	-	-
RK_B	3.5	-	-	-	-	-	-	-	-	-	-	-	-
RK_D	1.4	-	-	-	-	-	-	-	-	-	-	-	-
NA	1.6	-	-	-	-	-	-	-	-	-	-	-	-
GA	1.9	27	32	37	32	21	27	43	21	27	53	27	182
WA	2.8	136	182	218	150	89	125	186	89	71	225	71	854
PR_A	4.8	13	13	19	13	8	13	25	-	13	29	13	93
RN_A	6.4	22	25	38	31	19	22	33	20	-	28	-	130
BA	4.6	-	-	-	-	-	-	-	-	-	9	-	-
KA	6.3	-	-	-	-	-	-	-	-	-	-	-	-
KB	2.2	-	-	-	-	-	-	-	-	-	14	-	-
KC	1.8	-	-	-	-	-	-	-	-	-	-	-	-
ISQG-Low	-	261	430	-	-	-	384	600	-	240	665	552	1700

*Low molecular weight PAHs: Phe, phenanthrene

†High molecular weight PAHs: B[a]A, benzo[a]anthracene; B[a]P, benzo[a]pyrene; Chry, chrysene; FA, fluoranthene; Pyr, pyrene.

Other: B[b]F, benzo[b]fluoranthene and benzo[j]fluoranthene; B[g,h,i]P, benzo[g,h,i]perylene; B[k]F, benzo[k]fluoranthene; IPyr, indeno(1,2,3-c,d)pyrene.

3.3.3 Bioaccumulation within *Anguilla australis*

Forty-two shortfin eels were collected from Hamilton urban stream sites (n=3 from all urban sites, n=6 from rural control). Mean length of all eels collected was 623 ± 13.9 mm.

Metals and metalloids in liver tissue

Analysis of Variance conducted on metal and metalloid concentrations in shortfin eel livers all showed a significant difference between sites ($F_{12,29}$, = Cu 2.7, $p < 0.05$; Pb 9.8, $p < 0.001$; Zn 2.2, $p < 0.05$; As 5.3, $p < 0.001$; Cd 45.4, $p < 0.001$; Hg 26.1, $p < 0.001$).

Shortfin eels from BA had the highest concentrations of Cu and Zn, and those from SA, the highest Pb, in their livers compared with many other sites (Fig. 3-7A, B & C). Mercury concentrations in livers from eels at sites RK_B and the two sites near Waikato Hospital (NA and GA) were significantly higher than those measured from most other sites (Fig. 3-7D). One of the most notable differences compared with all other sites occurred in eel livers from WA where high concentrations of As were found accumulated.

Eel liver and sediment metal and metalloid relationships

Eel liver and sediment metal and metalloid concentrations generally did not correlate well, with only two significant relationships (As, $R^2 = 0.795$, $p < 0.001$; Zn, $R^2 = 0.433$, $p < 0.05$). However, the As relationship was driven by the high As concentrations in sediments and eel livers from Lake Rotoroa (WA). In terms of the Zn relationship, there was a moderate negative relationship between liver and sediment concentrations in that Zn eel liver concentrations decreased with an increase in sediment Zn concentrations.

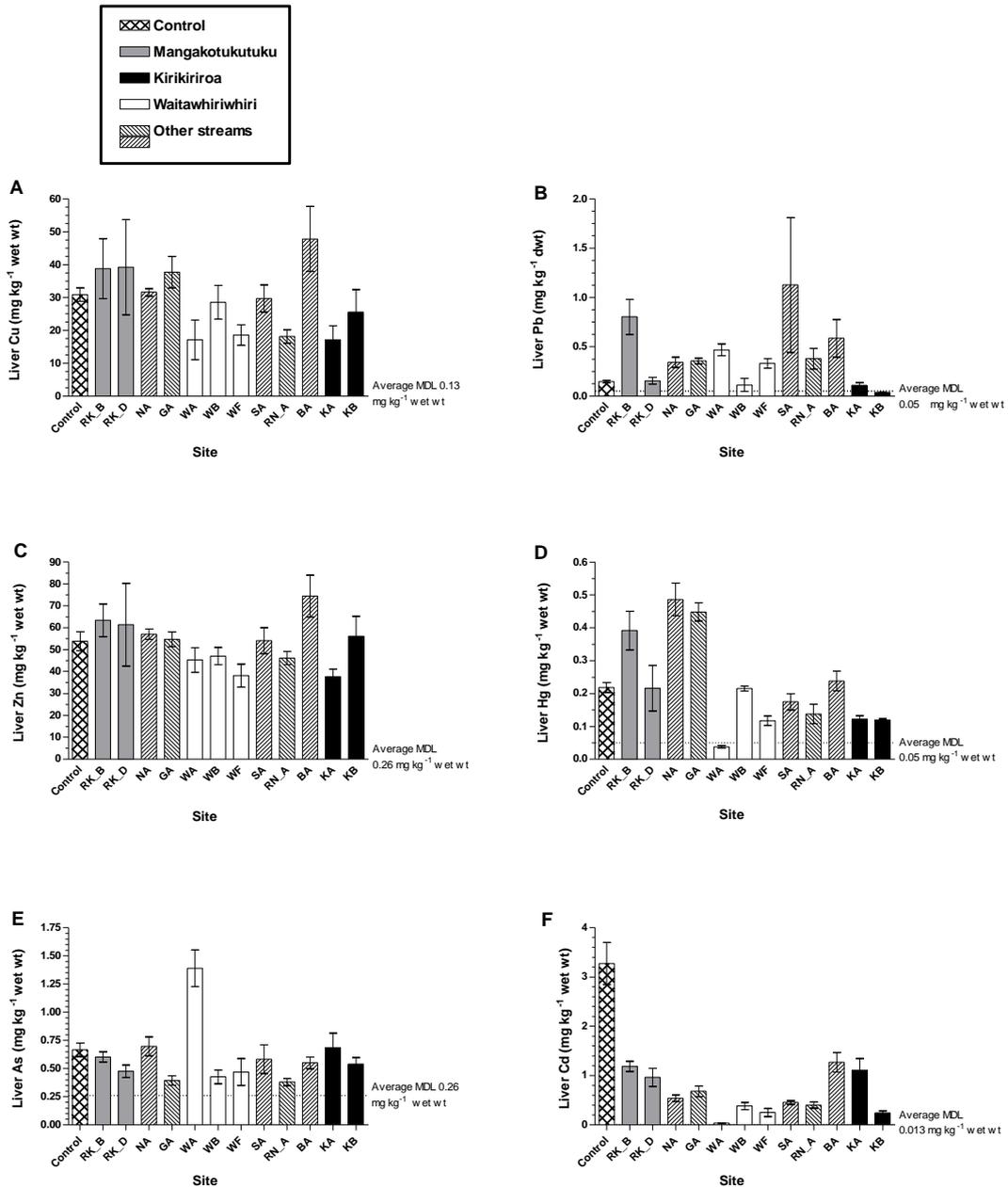


Figure 3-7. Concentrations (mg kg⁻¹ wet weight) (mean ± SE) of A) copper (Cu), B) lead (Pb), C) zinc (Zn), D) mercury (Hg), E) arsenic (As), and F) cadmium (Cd) in livers of shortfin eels (*Anguilla australis*) from a rural control and Hamilton urban stream sites. Key to site labels is provided in Table 3-1. Dotted lines are average Method Detection Limit (MDL) for each metal.

Metals and metalloids in muscle tissue

Muscle tissue metal concentrations were generally an order of magnitude lower than those in the liver in Hamilton urban stream eels, the exception being Hg, for which liver and muscle concentrations were comparable at each site (Fig. 3-8). The only significant differences between sites was in muscle Cu and Hg tissue

concentrations: ($F_{12,29}$, p -value) (Cu, 6.6, $p < 0.001$; Pb 1.4, $p > 0.05$; Zn 1.3, $p > 0.05$; As 1.6, $p > 0.05$; Hg 25.3, $p < 0.001$).

Lead ($0.017 \pm 0.002 \text{ mg kg}^{-1}$) and As ($0.267 \pm 0.015 \text{ mg kg}^{-1}$) concentrations in muscle from eels from all sites were well below the FSANZ maximum standards in fish of 0.5 and 2.0 mg kg^{-1} , respectively. Lead appears to be accumulating in muscles tissue of eels from sites SA, consistent with highest liver tissue concentrations in eels from this site, although all mean concentrations were below average MDL of 0.5 mg kg^{-1} (Fig. 3-9B,D). Arsenic is not accumulating in the muscle tissues of Hamilton eels to an extent where consumption would pose a risk to humans. In comparison with concentrations in a range of store-bought seafood items in the 2009 NZTDS (fish fingers, 1.02 mg kg^{-1} ; battered fish, 2.66 mg kg^{-1} ; canned fish, 0.66 mg kg^{-1} ; fresh fish, 3.99 mg kg^{-1}), concentrations were low (Vannort and Thomson 2011) (Fig. 3-9D). Although still below the FSANZ maximum standard allowed in eel of 0.5 mg kg^{-1} , three of the six muscle samples from sites NA and GA had concentrations of Hg approaching that concentration (Fig 3-9E). Redmayne et al. (2000) assessed the Hg content in longfin eel (*A. dieffenbachii*) muscle tissue to be 84% methylmercury and the 2009 New Zealand Total Diet Survey applied the ratio of methylmercury to total mercury of 70% (Vannort and Thomson 2011). Using the lower percentage as a base for calculating the amount of methylmercury in muscle tissues of shortfin eels in this study, eels collected in this study were determined should only be eaten 3-7.9 times per month on the basis of the USEPA RBCL for noncarcinogenic health endpoints for methylmercury (Redmayne et al. 2000, USEPA 2000, Vannort and Thomson 2011). The exception is eels from Lake Rotoroa (WA) which have sufficiently low levels of Hg in their muscle tissues to have no such restriction. There are no RBCLs for Pb in food.

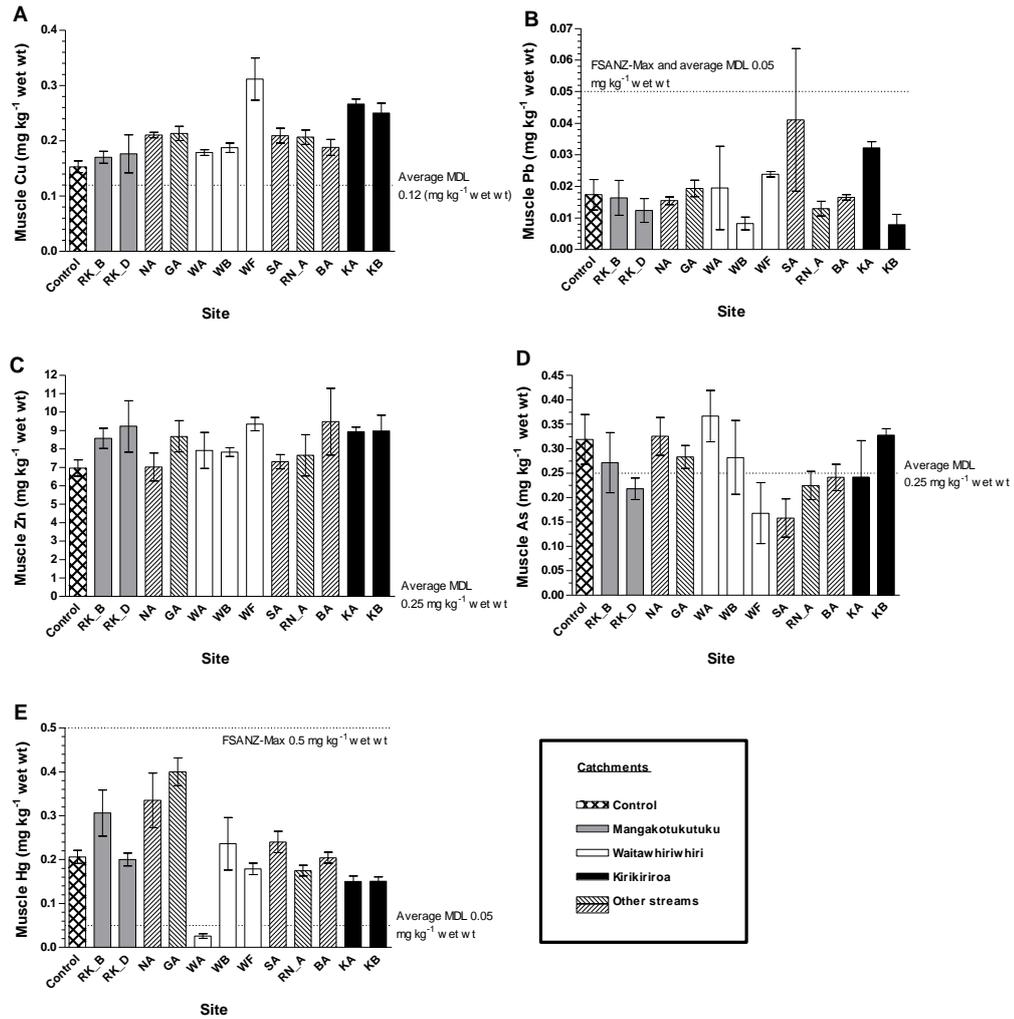


Figure 3-8. Concentrations (mg kg⁻¹ wet weight) (mean ± SE) of A) copper (Cu), B) lead (Pb), C) zinc (Zn), D) arsenic (As), and E) mercury (Hg) in muscle tissue of shortfin eels (*Anguilla australis*) from a rural control and Hamilton urban stream sites. Key to site labels is provided in Table 3-1. Dotted lines are either average Method Detection Limit (MDL) for each metal or metalloid or Food Standards Australia New Zealand (FSANZ) maximum standards in fish for consumption purposes.

Polycyclic aromatic hydrocarbon metabolite in bile

Varying concentrations of the fish PAH metabolite pyrene-1-glucuronide were found in eel bile from Hamilton urban stream collection sites (Fig. 3-9). Lowest concentrations were seen in eels from the rural control site and the peri-urban site of KA and the Lake Rotoroa outlet (WA). Comparisons between mean concentrations revealed there were significant differences between sites ($F_{11,24} = 5.75$, $p < 0.001$). Multiple comparisons showed statistically significant differences ($p < 0.05$) between most sites and KA (except WA and WB), and RK_B, RK_D, NA, and RN_A compared with WA. Correlations with sediment PAH concentrations in May were not significant ($R^2 = 0.44$, $p > 0.05$).

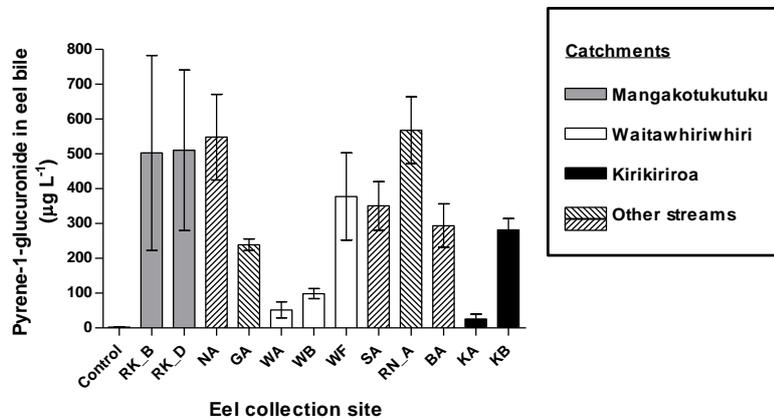


Figure 3-9. Concentrations of the polycyclic aromatic hydrocarbon metabolite pyrene-1-glucuronide ($\mu\text{g L}^{-1}$) measured in bile from shortfin eels (*Anguilla australis*) from the rural control site and Hamilton urban streams. Key to site labels is provided in Table 3-1.

3.4 DISCUSSION

3.4.1 Water quality and contaminants

The water sampling carried out was limited spatially and temporally and therefore caution should be taken with making general inferences regarding stormflow chemistry from the data. This was not a study of a "first flush" event, the major reason being that samples could not be taken simultaneously. The first flush phenomenon has many definitions based around a central concept that there are higher concentrations of stream contaminants in the first runoff of a critical volume into streams in rain events after a prolonged dry spell (Deletic 1998, Mangani et al. 2005, Grogan 2008, Hathaway and Hunt 2011). Grogan (2008) suggests that in many situations the compounding effects of small discharges through stormwater from urban areas, in particular industrial areas, leads to the build-up of contaminants to the point where adverse effects occur to the aquatic communities in the receiving environments. Nevertheless, both water quality parameters and the contaminants measured have highlighted areas within the Hamilton urban stream network where further investigation is required to determine whether any restoration initiatives may be constrained due to water-borne contaminants carried during stormflows.

pH, conductivity and water hardness

Hamilton urban stream water in 2012 tended to be low in pH, even at base flows prior to rainfall. Although ANZECC default trigger values for slightly modified ecosystems in New Zealand were exceeded, Hamilton urban streams are generally more highly impacted ecosystems. Also, the use of pH as a trigger value may not be useful because of high variability in diurnal and seasonal ranges (ANZECC 2000). Low pH of streams at base flow levels may be a result of high humic substances from groundwater that have a high affinity for hydrogen ions (Gao et al. 1999). Hamilton streams were observed to have some tannin staining during base flow sampling. Wilding (1998) commented, in a study comparing Hamilton streams with reference forested sites in Te Miro, that the peat soils are partially responsible for lower pH of lowland streams.

Bioavailability of metals in sediments is a complex function of many factors controlling chemical speciation, including pH (Elder 1989, John and Leventhal 1996, Hund-Rinke and Kördel 2003). Once pH falls below neutral, there can be a

tendency towards desorption of metals (Elder 1989). Although ideal surfaces for sorption for contaminants are created with high Fe in sediment, with low pH of water seen in these streams in 2012, there may be some risk of desorption of metals influencing the bioavailability of some of these contaminants.

There are no trigger values set for conductivity in New Zealand, however, lowland rivers can have higher values during low flows, as also noted in the present study catchments sampled over 2012 (ANZECC 2000). Mean conductivities for catchments in the present study were Mangakotukutuku $139.3 \mu\text{S cm}^{-1}$, Waitawhiriwhiri $142.4 \mu\text{S cm}^{-1}$, and $188.3 \mu\text{S cm}^{-1}$ for the Kirikiriroa catchment. Mean conductivity was slightly higher for these catchments (different sites) in the Regional Rivers Water Quality Monitoring Programme Wilding (Wilding 1998), but were still ranked the same from lowest to highest conductivity. In the study conducted by Aldridge and Hicks (2006), mean conductivity for the catchments of Mangakotukutuku, Waitawhiriwhiri, Kirikiriroa and Gibbons Creek were all higher than the present study with values of 195, 203, 270 and $205 \mu\text{S cm}^{-1}$, respectively.

There is a complex interplay between surface water, topography and groundwater that affects conductivity. In short, conductivity levels can be based around weathering and erosion increasing ion concentration in surface waters (Luo and Pederson 2012). However, conductivity is also related to land use (Goddard et al. 2008). Conductivity, is a significant problem in some countries, especially in cities where de-icing salts run off impervious areas into aquatic waterways (Morgan et al. 2012). Development and construction sites also can have an effect on conductivity. Conductivity was negatively correlated to % urban area in a study of land use change from forested to urban in South Carolina (Goddard et al. 2008). With respect to Hamilton urban streams, however, it is not believed conductivity per se has a significant effect on the biota present.

Total suspended solids

Total suspended solids, or the mass of organic and inorganic particulate matter in water, are considered a contaminant because they lead to physical, chemical and biological changes to the water body. This can occur by acting directly on organisms, or indirectly by causing a reduction in light and carrying sorbed contaminants (USEPA 1986, Hickey et al. 2001, Bilotta and Brazier 2008).

Sources of TSS can include forestry and agriculture (Quinn and Cooper 1997), mining (Davies-Colley et al. 1992), and urbanisation, especially during periods of initial development of catchments (Hogg and Norris 1991, Paul and Meyer 2001), with concentrations increasing greatly in storm events (Mallin et al. 2009, Hathaway and Hunt 2011). A study of stream contaminants from a highly urbanised catchment discharging during different flow conditions into Sydney Harbour found that high flow conditions contributed greater than 90% of metal and TSS concentrations (Beck and Birch 2012). Mallin et al. (2009) compared water quality parameters in urban, suburban and rural streams during wet and dry periods in North Carolina and found, over all sampling periods combined, that urban streams yielded the highest TSS and concentrations were significantly higher during rain events when compared to dry periods.

The historical and ongoing problem of sedimentation from continuing urban development was highlighted as potentially constraining the response of invertebrate communities to habitat restoration in part of an urban Christchurch stream (Suren and McMurtrie 2005). In another Australian example, high concentrations of suspended solids (maximum 560 mg L^{-1}) in runoff from urban land clearing and development was attributed to low diversity and density of macroinvertebrates downstream from the outflow into the Murrumbidgee River (Hogg and Norris 1991).

Maximum concentrations of TSS in the present study were found at sites W2 on 3/9/12 and M2 and W1 on 27/4/12, both above 230 mg L^{-1} . The Waitawhiriwhiri catchment had the highest mean and maximum concentration (137.5 and 298 mg L^{-1}) which may be attributable in part to the more highly urbanised catchment with greater atmospheric dust and other material (Hickey et al. 2001). The origins of this "dust" are wide ranging and include non-point sources like wet and dry deposition, vehicle exhausts, vehicle and road wear and soil erosion (Mangani et al. 2005). Previously measured concentrations of TSS in stormwater from a number of Hamilton urban catchments range from 1 to 3104 mg L^{-1} (Williamson 1985), 5 to 151 mg L^{-1} in a mature residential and 69 to 460 mg L^{-1} in an industrial catchment (Hickey et al. 2001). Stream water will dilute stormwater, as seen at most sites in this study where concentrations were less than reported in Hickey et al. (2001).

High sediment loads in the lower reaches of the Mangakotukutuku were apparent during the surveying of fish in the summer of 2005-2006, although concentrations were not measured (Aldridge and Hicks 2006). Erosion of exposed banks may be the major reason for higher TSS concentrations in the catchment from the hydrological impacts of stormwater inputs, especially along the lower reaches of the main Rukuhia channel. However, it was observed during field work that there are high exposed banks in parts of all the lower reaches of the three catchments.

Bilotta and Brazier (2008) provided a comprehensive summary of data on effects of various concentrations of, and duration of exposure to, TSS on invertebrates, stressing the importance of exposure time to biological populations as well as concentrations. Shaw and Richardson (2001) examined the effects on naturally colonising invertebrate assemblages and rainbow trout (*Oncorhynchus mykiss*) of pulses of increasing duration (0-6 hours) of TSS concentration of 700 mg L⁻¹ in streamside flow channels. Total abundance of benthic invertebrates and family richness declined and invertebrate drift increased as sediment pulse duration increased. Trout length and mass gain over the experimental period was negatively correlated with pulse duration. Although concentrations of TSS in Hamilton streams are lower than previously documented, based on results of concentrations measured in stormwater from the same catchments, and from other urban catchments overseas in previous studies, maximum levels, seen in the lower reaches of the Mangakotukutuku and Waitawhiriwhiri, are of concern to the health of these streams, especially if there is a constant build-up through successive pulses of TSS from rain events.

Dissolved metals and water hardness

The presence of dissolved metals in urban runoff is of concern as they are the most toxic due to enhanced bioavailability. Although there is a strong affinity with TSS, the investigation of the concentration of metals in solution is an important bioavailability indicator (ANZECC 2000, Hengren et al. 2005). New Zealand waters tend to be 'soft' with a mean hardness for 77 rivers and streams in New Zealand's National River Water Quality Network of 32.7 mg L⁻¹ (CaCO₃) (Hickey 2000; see also Hickey and Pyle 2001). Water hardness in this study was slightly higher than this national average during base flows of all streams, although still soft, and generally decreased with dilution of Ca²⁺ and Mg²⁺ ions to around this average value during the rain events. The Kirikiriroa catchment had the highest

water hardness of all streams measured, although still in the soft range (0-60 mg L⁻¹). Increasing hardness reduces the toxicity of several metals, including Cu and Zn, to freshwater organisms (Hickey 2000, Hickey and Pyle 2001). In addition, New Zealand's generally low ionic water in rivers can be expected to result in high sensitivity of organisms to metals, and soft water should be used in most cases in evaluating the toxicity of metals in New Zealand (Hickey 2000).

However, there are also other features of receiving waters that influence concentrations of metals within them, ultimately affecting aquatic organisms. These include settlement of particulate matter and dilution (which is a function of stormwater flow, size and flow of the receiving water) within the receiving water (Moncrieff and Kennedy 2002, Gardiner and Armstrong 2007). Evidence of how the size and flow of the receiving water can dilute dissolved metal concentrations can be seen in the present study. Water sampling sites M3, W3, K4 and PR_A are small receiving waters which, in times of high stormwater runoff, had higher concentrations of Cu and Zn than the other larger receiving waters.

Exceedance of the ANZECC 95% trigger value for dissolved Cu was generally widespread across the Mangakotukutuku and Waitawhiriwhiri catchment sampling sites during rain events, as well as in Gibbons Creek. Moreover, the ANZECC 95% trigger value for Zn was exceeded at most sites, even at base flow levels. Hickey et al. (2001) found that the highest Cu and Zn concentrations in stormwater flowing into the Waikato River was from commercial (Grantham Street) and industrial (Northway Street, Te Rapa) stormwater samples. This was also true for concentrations of Zn in streams in the present study where Waitawhiriwhiri (industrial catchment) sites had in general, higher concentrations than the residential catchments of Mangakotukutuku and Kirikiriroa. In the year from August 2009, maximum dissolved Zn measured at the outlet of the Waitawhiriwhiri in another study was in May 2010 (151 µg L⁻¹) and the maximum measured at the same location where site KC is in the present study on the Kirikiriroa main channel, was 59 µg L⁻¹ in June 2010 (Kim 2011), showing higher concentrations in water from the Waitawhiriwhiri catchment generally. However, no such conclusion can be made in regards to dissolved Cu for the present study, as the concentrations in samples from the less-developed Mangakotukutuku sites were not dissimilar to concentrations at sampling sites in the industrialised Waitawhiriwhiri catchment, both being higher than for the Kirikiriroa. As Cu is one of the more common metal contaminants originating from vehicles (Moncrieff and

Kennedy 2002), dissolved Cu in the Mangakotukutuku and Waitawhiriwhiri could be a reflection of higher vehicle use, specifically along Ohaupo Road in the Mangakotukutuku catchment and Greenwood, Mill and Ulster Streets in the Waitawhiriwhiri catchment compared with smaller inputs from less busy roads in the Kirikiriroa catchment. Hickey et al. (2001) linked higher usage of impervious surfaces to higher concentrations of dissolved Cu and Zn in stormwater in the Waitawhiriwhiri catchment. Ohaupo Road (the main road south to Te Awamutu and the Waitomo Caves) has stormwater drains into the Rukuhia channel upstream of M1 and M2 and directly into M3.

In general, when Zn concentrations are high, a significant proportion (70-80%) of the Zn is present in dissolved form (Moncrieff and Kennedy 2002, Mangani et al. 2005, Kim 2011). This indicates that Zn flushing is not merely a function of sediment transport, but represents actual solubilisation of Zn in rainwater (Kim 2011). Although most Zn in urban streams has been flushed off roads into urban stormwater and ultimately to streams, rural land use also has some effect on Zn concentrations in streams. About 10% of the Waikato Regional Council regional water monitoring sites (excluding the Waikato River) had concentrations that exceed guidelines with no apparent source other than farming, where Zn is used as a remedy for facial eczema (Kim 2011).

Sites that exceed ANZECC water quality 95% trigger values for Cu and/or Zn may warrant further investigations to consider metal speciation and biological effects assessment (e.g. toxicity assessment) to ascertain the risk to aquatic species (ANZECC 2000). Hickey et al. (2001) found that Hamilton industrial and commercial catchment stormwater (sampled at Northway Road and Grantham Street) had the potential to cause adverse effects on biota and that a 28-50 fold dilution within the receiving water would be required to safeguard against possible effects to sensitive organisms. Observed toxic responses of the sensitive cladoceran *Ceriodaphnia dubia* and amphipod *Paracollope fluviatilis* were attributed to the concentrations of dissolved Cu and Zn in that study. However, toxicity was less than predicted from measured soluble Cu and Zn which indicated that they were not completely bioavailable.

Dissolved Pb concentrations in the present study were similar in magnitude to those measured by Hickey et al. (2001) in stormwater from Hamilton catchments with different landuse. Although there are still inputs of Pb from road surfaces to

waterways, dissolved Pb levels are now generally much lower than when the use of leaded petrol was commonplace prior to the mid 1990's (Wilson and Horrocks 2008).

Loads of dissolved Cu, Pb and Zn were concluded to be low in terms of the total load carried to the Waikato River by Hickey et al. (2001). This is also the case for estimated loads in this study over a decade later from the Mangakotukutuku, Waitawhiriwhiri and Kirikiriroa catchments during base flows. However, the Waitawhiriwhiri, with increased flow and highest overall metal concentrations had by far the greatest loads to the Waikato River out of the three main catchments studied, not only because of increase flows, but also due to higher dissolved contaminant concentrations. This confirms that industrial catchments have the highest potential to generate contaminants.

3.4.2 Sediment metal and metalloid concentrations and organic carbon

Sediments serve as a reservoir and source of stream contaminants and represent the greatest potential source of water pollution (Power and Chapman 1992, Arakel 1995, Williamson and Morrisey 2000). The processes of sorption and desorption of stream contaminants to and from sediments is extremely complicated. The most significant sink for metals in aerobic freshwaters are OCs and $\text{Fe}(\text{OH})_3$ and MnO_2 (Harrison and Laxen 1984, Rand et al. 1995, Chapman et al. 1998, USEPA 2007). The organic acids typically present in organic matter have a high affinity for metals (USEPA 2007). Particle size, pH and redox potential are also driving factors for the sorption of contaminants (Ermens 2007).

Spatial differences

Natural processes and human activities such as point sources of waste water, animal waste applications on soils and other agricultural practices have resulted in increased OC content in waterways (Mueller et al. 1982, Moore and Jackson 1989). Highest OC was found in site PB in the Peacockes branch of the Mangakotukutuku (9.8%). This site had regenerating native bush and exotic trees which would provide organic matter, as well as receiving possible inputs from the surrounding agricultural land use. Site KA, immediately downstream of fully pastoral farmland had the second highest concentration (6.3%). Of the stream sites measured within the boundary of Hamilton City for OC in May, sites RN_A

(6.4%), PR_A (4.8%) and BA (4.6%), which have completely urbanised catchments, had the highest.

High Fe concentrations in Hamilton streams may also be a significant factor in absorption of metals to sediments. The highest mean Fe concentration was in the peri-urban site of KA ($106.9 \pm 8.5 \text{ g kg}^{-1}$) which is in the rural headwaters of the Kirikiriroa catchment. Completely urban sites with highest Fe concentrations in sediments were KB and PR_A. Highest mean Mn concentrations were seen again in the Peacockes branch of the Mangakotukutuku at site PB ($1374 \pm 739 \text{ mg kg}^{-1}$), while the highest of the completely urban stream sites was KB.

Suburban streams and some of the smallest tributaries (e.g. stormwater drains) receive a high proportion of surface runoff (Webster et al. 2000) and it appears that Hamilton stream sediments conform to this model, at least in relation to anthropogenically derived Pb and Zn concentrations. Sediment from some sites in the Hamilton stream network exceeded guidelines for Pb and Zn, and these sites all appear to be those that have entire catchments within the Hamilton City boundary (PR_A, RN_A, BA, NA, GA and WF) and therefore are smaller streams with lower flow. Lower flows and smaller catchments not only reduce the dilution of the source of contaminants but also particulate matter has less ability to become entrained in the water column and settles out faster (Moncrieff and Kennedy 2002, Gardiner and Armstrong 2007).

Concentrations of Cu within Hamilton urban stream sediments are not of concern as concentrations did not exceed the ISQG guidelines. The reason for the low Cu concentrations in sediment at sites sampled, even though dissolved Cu was measured to be high in many water samples, may be because 75 to 80% of Cu in stormwater is in the suspended phase, which is more influenced by water flow and therefore settles out faster (Moncrieff and Kennedy 2002, Nagano et al. 2003).

Mean sediment Pb concentrations exceeded the ANZECC ISQG Low value of 50 mg kg^{-1} at Gibbons Creek at PR_A whereas other sites were relatively low (except RN_A where mean concentrations were just below the ISQG Low value). Despite being phased out in petroleum products, Pb is still widely distributed in the environment and is generally a historical record of past leaded petroleum use in New Zealand (Pearson et al. 2010). There have been high inputs of lead from

the use of vehicles in the past to Gibbons Creek and this may be an ongoing problem to aquatic organisms. There are still inputs to waterways from this historic use, but also from current use (Pb is present in tyres) and localised industrial point sources (Moncrieff and Kennedy 2002), although the latter would not be applicable to PR_A which is situated in high density residential catchment.

Zinc is accumulating in the farmed soils of the Waikato Region from use as a facial eczema remedy and some of this has leached into streams and accumulated in the sediment of regional lakes (Kim 2011). Evidence of this in the present study can be seen from high Zn concentrations in sediments at site KA. It is difficult to determine exactly the anthropogenic sources of Zn in sediments, but downstream of KA, site KC, has mean Zn sediment concentrations higher than the range found in Waikato soils by Taylor and Kim (2009), an unknown proportion of which may be from agricultural Zn use. The most significant non-point sources of Zn to urban stormwater are, however, wear of vehicle tyres which contain approximately 1-2% Zn by weight (Rhodes et al. 2012), and the corrosion and leaching of roofing materials (Van Metre and Mahler 2003, Chang et al. 2004, Faller and Reiss 2005). Gibbon's Creek (at site PR_A) and RN_A are obvious sites of most concern with mean sediment concentrations exceeding ANZECC (2000) ISQG Low values even though agricultural inputs of Zn in these catchments are nil as they are completely urban catchments.

Kirikiroa A was also very high in Cd in comparison with other sites, and this is probably the result of the application of superphosphate fertilisers which comprise the dominant potential anthropogenic source of Cd to Waikato farmland soils (Kim 2005), which occur in the upper catchment. However, strong attenuation with distance from source means that Cd may be less of an influence on urban streams than Zn (Kim 2005). This is apparent in this present study where Cd concentration measured in sediments from streams within the city boundary was very low and did not exceed ISQG values.

Mean As concentrations were high at WA and KB in comparison to ISQG values and should be of concern for the ecological health of these two sites. Arsenic was raised in many of the streams sampled on the true right of the Waikato River. The historical herbicidal application of NaAsO₂ has provided a long-term legacy of elevated arsenic concentrations in sediments of Lake Rotoroa (Tanner and Clayton 1990, Rajendram 1992, Rumsby 2011). Rumsby (2011) concluded that

there had not been a significant change in concentrations of As in Lake Rotoroa in comparison to those measured by Rajendram (1992). The present study is very limited with only one site tested for sediment As. Results from the comprehensive study by Rumsby (2011) documented an average and range of As of 167 and 25-592 mg kg⁻¹, respectively. This average is far higher than the present study and strongly indicates that results presented here are not representative of the whole lake system. The investigation by Rumsby (2011) found As concentrations that were comparable to the present study near the outflow of the lake (50-100 mg kg⁻¹). There are a number of other sites where May As concentrations in sediment exceeded the ISQG Low value of 20 mg kg⁻¹, RN_A, BA, KA and KC. The concentrations observed in these sites during this sampling period, although at the upper limit of observed background soil concentrations, may be mostly naturally-derived.

High concentrations of As and Ba at KB may be caused by leachate from an old landfill site as these two metals are potential components of landfill leachate (Christensen et al. 2001, Kjeldsen et al. 2002). However, more investigation is required at this site to reach a definite conclusion about the source of these contaminants. Concentrations of Ba among the upper concentrations seen in background soils at sites PB and KA could be a result of additions of Ba from fertilisers used in farming practices. Fertilisers manufactured from phosphate and carbonate rocks have the highest content of Ba (Senesi et al. 1983). Correlations carried out between total phosphorous and metals found in rural surface waters in Sweden, found that Ba had the strongest relationship possibly indicating a common source and showing the greatest potential as a tracer for an individual anthropogenic source of nutrient inputs to surface waters (Ahlgren et al. 2012). However, natural variation in sediment Ba concentrations across sampling sites in the present study cannot be ruled out.

Nickel at sites NA, PR_A and WF appeared to be accumulating in sediments above average levels found in local soils more than other sites in Hamilton streams. Nickel has a high affinity for clay minerals (Beasley and Kneale 2002), and suspended clay particles, along with Fe and Mn hydroxides, and OC can remove Ni from the water column by absorption and adsorption (Beasley and Kneale 2002).

Mercury concentrations were elevated at sites NA and GA in comparison with the range of terrestrial concentrations, but these sites were not significantly higher than others in the Hamilton stream network. There are a number of reasons that could explain this observation. Generally, all of these sites are affected by stormwater runoff from impervious surfaces that contain Ni (present in tyres and brake pads) and Hg (from asphalt and bitumous binders) (Moncrieff and Kennedy 2002, Mangani et al. 2005). In addition to these inputs to NA, however, other sources for Ni and Hg may include groundwater leachate from a historic landfill and coal-fired boiler use in the area and a chemical courier accident that spilled chemicals directly into the stream in 2002 (Clearwater and Valler 2012).

Temporal differences

Compared with prior collection periods, sediment accumulation on all stream beds was reduced noticeably in November, possibly attributable to a prolonged wet period during the Spring of 2012 that flushed sediment out. Generally, due to annual variation in flows, river sediments may reflect deposition of materials over a relatively short time in comparison to lentic systems (Kamman et al. 2005). This is generally typical of low relief, soft-bottomed watercourses in New Zealand, where there is a gradual build up of bed sediments that, over time, may be balanced by irregular flood flows that transport accumulated sediments downstream (Gardiner and Armstrong 2007). It is possible that the surficial layer of sediments (upper few cm), which is the more ecosystem-active portion, had been flushed from some of the stream beds leaving deeper sediments that are more permanent (Burton 1991). In some streams, settling zones with sediment were very difficult to locate in November and less sediment was sampled and homogenised as a result. This was particularly the case at sites PB, RK_B, PR_A and RN_A. Temporal differences in sediment metal and metalloid concentrations in Hamilton streams generally were attributable to May concentrations being higher than those in August, but these were quite often not significantly different than those measured in November.

When comparing sampling dates at individual sites in relation to Cu, Pb and Zn concentrations, there were only decreases in Cu concentrations between the May to August period. There were no temporal changes in Pb and Zn. This may have been caused by the flushing of finer sediments from the system carrying these

metals which are sorbed to them. It is unknown why Cu followed the general trend of other metals when Pb and Zn did not.

The rise in Zn concentrations at site KA during the sampling periods would be a result of the increased leaching of Zn built up in the surrounding soils from use as a facial eczema remedy over the winter months. Also, this site is a very small stream where stream bed erosion would be minimal even in high rainfall. Mercury concentrations decreased significantly between all sampling periods and may be a reflection of higher Hg concentration in smaller grain sizes that are more easily flushed away. Kamman et al. (2005) suggested that any distributional studies of Hg in sediments should account for sediment grain size as well as OC content.

Rajendram (1992) suggested that As concentrations in Lake Rotoroa have seasonal fluctuations such that the summer months see a change in As speciation. Higher concentrations in early May, this may be a legacy of the summer months especially after a warm, dry autumn, and this may explain the differences in As concentrations between May and August sampling periods. Speciation of As occurs under different redox states in sediments. In aerobic systems, reduced forms of As tend to be oxidised to arsenate, which co-precipitates with ferric hydroxide (Ferguson and Gavis 1972). In oxygen-depleted sediments, reduction of ferric Fe, arsenate and arsenite can lead to solubilisation and diffusion through the sediment or mixing by benthic organisms or currents, causing As to re-enter the water column (Ferguson and Gavis 1972). Rumsby (2011) suggested the redox chemistry of Fe may be playing a role in controlling the distribution of As within the sediments and surface water quality of Lake Rotoroa.

Kirikiroa B (KB) had notable increases in concentrations of some metals in the final sediment sampling period when, in comparison with August concentrations, there was a greater than 3-fold increase in Cu, more than 2-fold increase in Zn, almost 5-fold increase in Ba, and 5-fold increase in As, respectively. These metals and metalloids are potential components of landfill leachate (Christensen et al. 2001, Kjeldsen et al. 2002). The increase seen in November compared with August concentrations may be the result of the reduction in surficial sediments by flushing over the previous months exposing deeper sediments characterised by past influence from groundwater leachate emanating from the local historic landfill site.

The moderate correlations between metal concentrations in sediment and % impervious surfaces in this study are typical of similar relationships elsewhere (Hatt et al. 2004). Hatt et al. (2004) stated that hydraulic efficiency can explain a large proportion of the variation in this relationship. Sites PR_A, RN_A, NA, GA, and to a lesser extent BA, and WF, which all had Pb and Zn sediment concentrations above background levels, have high to moderate effective imperviousness, in other words, efficient delivery of contaminants to streams. Also, as discussed previously, with a large % of Cu being in the suspended phase, it would settle out sooner and not flow as far downstream. Another explanation for the variation, specifically at site KA with respect to Cu and Zn is increased metal contamination from pasture farming practices leading to higher concentrations in sediments even though it has low imperviousness. Nevertheless, the statistically significant relationships with impervious area for some metals do suggest an association between stormwater runoff and sediment metal accumulation.

3.4.3 Polycyclic aromatic hydrocarbons

Augusto et al. (2011) evaluated sources of PAHs in urban streams in Portugal based on land use and results indicated that the main anthropogenic sources were most likely to be traffic and urban-industrial pollution. They also found that the PAHs were correlated with sources that also release Cu and Zn, which suggests a traffic-related origin, a conclusion supported by many other studies (Hickey et al. 2001, Beasley and Kneale 2002, Moores et al. 2009, Rumsby 2011). The highest site by far for total PAHs in the present study was WA, however, all Hamilton urban stream concentrations were low and did not exceed any of the ISQG-Low values. There was no significant correlation between PAH concentrations in sediment and concentrations of Cu, Pb and Zn, respectively across sampling sites. Rumsby (2011) carried out a comprehensive study on sediments of Lake Rotoroa and found Cu, Pb, Zn, and PAHs exceeded ISQG-Low guideline values, mostly at the southern end of the lake where the majority of stormwater inflows discharge. The one sampling site in the present study in Lake Rotoroa was situated at the north-western edge of the lake where stormwater may not have as much of an influence on sediments since Cu, Pb and Zn were also not highly elevated. This suggests that PAH concentrations may have been affected by other factors such as non-point sources (Rumsby 2011).

3.4.4 Bioaccumulation within *Anguilla australis*

Eels were first thought to be tolerant to aquatic toxicants until the 1990's, when it was acknowledged that they may be more susceptible than previously assumed (Brusle 1991), although it is difficult to pinpoint actual effects of contaminants in anguillid species. A study in Belgium concluded that there was a significant negative relationship between metal concentration in muscle tissue and condition of European eels (*A. anguilla*) in that condition decreased with increasing muscle metal concentrations (Maes et al. 2005). Quantification of PAH metabolites, which can be toxic in themselves, is rarely available for assessment and even more difficult to translate into levels of effects (Menzie and Coleman 2007). Although studies by Stein et al. (1990) and Myers et al. (2003) have linked PAH exposure to toxicopathic liver lesions in English sole (*Pleuronectes vetulus*), and Jia et al. (2011) found Cd caused DNA damage from lipid peroxidation and oxidative stress in livers of common carp (*Cyprinus carpio* var. *color*), contaminant effects are not easily generalised and should be assessed on a species-specific basis (Menzie and Coleman 2007). There is also a risk to human health through consumption of contaminated muscle flesh of wild eels (Brusle 1991, Has-Schön et al. 2006, Stewart et al. 2011). However, a study comparing metal and metalloid concentration in muscle tissues of five fish species included in human diets, from a catchment with heavy horticultural land use and high tourism traffic in Croatia, recommended eel as a constituent human food because of the lowest total concentrations of metals analysed (Has-Schön et al. 2006).

During the growth and maturation phase of their life cycle eels are relatively sedentary and much of their time is spent in close contact with sediments (Mason and Barak 1990). There are two significant studies focusing on the more spatially and temporally limited movements of eels within freshwater environments in New Zealand (Chisnall and Kalish 1993, Jellyman and Sykes 2003). The earlier study conducted in a minor tributary to the Waipa River in the Waikato yielded a 40% shortfin and 60% longfin recapture rate after three years (n=25 for both species). The shortfins that were recaptured had very small home ranges with most large individuals having remained within the same pools or runs of each 20 metre site for 1-3 years. A more comprehensive study using radio tags to ascertain diel, weekly and seasonal movements was conducted in streams in North Canterbury (Jellyman and Sykes 2003). Both species typically moved over restricted distances, occupying the same position for long periods and returning frequently

to the same daytime resting area. No indication of any seasonal differences in distances moved was found. The movements of anguillid eels shown by these two studies suggest an association can be made between eel tissue metal concentrations and site specific sediment contaminant concentrations (i.e. contaminant bioavailability).

Monitoring programmes and general surveys to determine the occurrence and distribution of contaminants in fish typically target the liver as it contains generally higher metal concentrations (Crawford and Luoma 1993, Al-Yousuf et al. 2000, Neto et al. 2011). Muscle metal concentrations, although not the best indicator of whole fish body contamination, can be higher for As and Hg (Has-Schön et al. 2006, Neto et al. 2011).

A number of studies have correlated various fish and eel tissue metal concentrations as a function of eel size and/or length (Batty et al. 1996, Allen-Gil et al. 1997, Redmayne et al. 2000, Arleny et al. 2007, Pierron et al. 2008, Neto et al. 2011). These relationships were not assessed in the present study due to the small sample size (n=3) which may restrict the assumptions that can be made. Nevertheless, an attempt was made to account for this possibility by selecting eels of similar size at all sites where possible.

There is relatively little information about metal and metalloid concentrations in eel livers in New Zealand, especially for urban environments. In general, it is difficult to eliminate the normal spatial and temporal variability of eel liver metal concentrations as the main explanation for the differences seen. No conclusions can be drawn regarding the connection between sediment and eel liver Cu and Zn concentrations because both metals are under physiological control (Brusle 1990), and may be related to increased metallothionein synthesis (Batty et al. 1996, Chapman et al. 1998, Neto et al. 2011).

Because site PR_A is currently a fish monitoring and restoration site, bioavailability of Pb was assessed at the upstream site of SA, which had similarly high levels of overall metals and metalloids. Eels collected from SA had significantly higher Pb concentrations in their livers than those from other sites suggesting that Pb is bioavailable to biota at this site as well. Another site of bioavailability concern is RK_B but it is not understood why Pb at this site is more available to eels, especially given that sediment concentrations were not high, but

may involve heterogeneity in environmental conditions, including relationships of metal sorption and grain size as described in Neto et al. (2011) and/or an unknown additional source of Pb. One of the eels collected from Gibbon's Creek (SA) has muscle tissue concentrations of 0.08 mg kg^{-1} exceeding the FSANZ maximum allowable concentration of Pb in fish of 0.05 mg kg^{-1} highlighting a low risk to consumers, although mean concentrations ($n=3$) were lower than the FSANZ maximum.

Mean As concentrations in Lake Rotoroa (WA) eel livers ($1.39 \pm 0.16 \text{ mg kg}^{-1}$) were well above those found in muscle tissues ($0.37 \pm 0.05 \text{ mg kg}^{-1}$) and livers from other sites. Arsenic is omitted from being a metalloid measured in eel liver and muscle tissues in many studies. In contrast to my results, Has-Schon (1996) found concentrations in *A. anguilla* from a Croatian catchment with high horticultural land use to be higher in muscles ($0.10 \pm 0.01 \text{ mg kg}^{-1}$) than livers ($0.068 \pm 0.02 \text{ mg kg}^{-1}$). The observed concentrations of As in the livers of eels from WA show that the As is bioaccumulating in these tissues. No conclusions can be made on whether this bioaccumulation would be causing adverse effects, specifically on the growth of these eels, but it is apparent that these levels are not being transferred to muscle tissues. Based on estimates of levels of inorganic As being 10% of total arsenic in residential freshwater fish, Hamilton eels, including those from site WA, are unrestricted in terms of meals/month in terms of USEPA RBCL (USEPA 2000, 2003, Vannort and Thomson 2011). The RBCL is based on an adult body weight of 70 kg and a meal size As content of 227 mg. No RBCLs have been set by the USEPA for the consumption of fish meals containing Cu, Zn and Pb.

In a study assessing bioaccumulation of Cd in *A. anguilla* collected from a southwestern French estuary, organ concentrations classified in ascending order as muscle < gills < liver, and average concentrations in muscle and livers were 0.07 ± 0.01 and $1.81 \pm 0.16 \text{ mg kg}^{-1}$, respectively (Pierron et al. 2008). The maximum mean concentration within eels in Hamilton urban stream sites was $1.27 \pm 0.2 \text{ mg kg}^{-1}$ at site BA and $3.28 \pm 0.43 \text{ mg kg}^{-1}$ present in livers from the rural control site. There was no relationship between liver Cd concentrations and sediment concentration in the present study. However, it is obvious that shortfin eel are at risk of bioaccumulation of Cd in rural catchments where superphosphate fertilisers are used. The risk posed to humans in terms of Cd exposure through eating eel flesh from Hamilton urban streams is extremely low. Cadmium

concentrations within muscle flesh were extremely low in these eels and also in those collected at control site illustrating that this metal does not readily accumulate in this tissue.

Mason and Barak (1990) suggest that eel liver concentration of Hg may be a good indicator of current Hg pollution of a site. However, the relationship between eel liver tissue and sediment Hg concentrations was poor in Hamilton urban streams indicating another other variables such as environmental heterogeneity. Again we see RK_B eels with disproportionately high metal (Hg) concentrations in their livers showing that Hg at this site is highly bioavailable and/or there are unknown sources of Pb contamination. Livers contain the inorganic form of Hg, and muscle, the organic form (methylmercury, MeHg) (Burrows and Krenkel 1973). The toxicological problem of Hg bioaccumulation in fish is connected to the methylation of inorganic Hg to form the more toxic MeHg (Arleny et al. 2007). However, there is some accumulation of Hg within muscle tissues of eels from most sites sufficient to warrant a low restriction in terms of USEPA RBCLs for non-carcinogenic endpoints for MeHg.

The fish metabolite pyrene-1-glucuronide or conjugated 1-hydroxy pyrene was screened for exposure of Hamilton urban stream shortfin eels for PAH exposure. This metabolite is the by-product of metabolising pyrene, a widespread and common PAH (Ariese et al. 1993; Ruddock et al. 2003). The maximum concentrations of the metabolite were seen at sites RN_A and NA, with concentrations of 567.9 ± 95.6 and $548.2 \pm 122.9 \mu\text{g L}^{-1}$, respectively. Ruddock et al. (2003) analysed PAH metabolites in *A. anguilla* bile from a number of industrialised U.K. estuaries where mean pyrene-1-glucuronide concentrations ranged from $325.6 \mu\text{g L}^{-1}$ in the Severn to $6965.8 \mu\text{g L}^{-1}$ in the Tyne. Concentrations within Hamilton urban stream eels are therefore equivalent to eels in less-affected industrialised catchments. Although Ruddock et al. (2003) suggested eels are a good monitor of PAH contamination in sediments in habitats where this species is found, they do not comment on what effects that these levels may have on *A. anguilla*.

As PAHs are metabolised very efficiently by eels (Ariese 1993, van der Oost et al. 2003), comparing sediment concentrations from May to concentrations of a PAH metabolite in bile in eels collected from a range of dates at least a month later is possibly a crude analysis. The cost of PAH analyses precluded a more

comprehensive sampling regime examining temporal variation in sediment PAHs so no assumptions can be made about the consistency of sediment PAH contamination or exposure by eels. Concentrations of pyrene-1-glucuronide in Hamilton shortfin eel bile shows that they are being exposed to bioavailable PAHs at most sites except KA, WA and WB and this species appears to be a good biomonitor of current exposure to PAHs in these streams.

3.4.5 Summary

The most affected areas for TSS include the lower reaches of the Mangakotukutuku and Waitawhiriwhiri catchments, with the latter, more industrialised catchment having a higher proportion sourced from impervious surfaces and therefore higher metal contamination. Measurements of dissolved stormwater-related metals of Cu and Zn exceeded ANZECC 95% water quality guidelines at many sites, especially during a rain event after an antecedent dry period, and particularly in small streams such as M3 and W3 where water flow is generally low. Sediment concentrations of Zn and Pb exceeded ANZECC ISQG values at many sites in different catchments. The sites most affected with dissolved and sediment contamination of these stormwater metals were those that had catchments within the city boundary and therefore were smaller catchments with lower flows representing smaller dilution capacity of stormwater in streams.

Results in general illustrate that the industrialised Waitawhiriwhiri catchment had the greatest potential to generate contaminants in stream waters, and sediment relationships with impervious area suggest an association with this stormwater runoff and metal accumulation. It appears that highest sediment concentrations generally occur prior to winter rains when sediment can be flushed from stream beds due to high flows, although past legacies (e.g. historic landfills) and present upstream land use (e.g. agricultural inputs) can increase concentrations of certain metals that deviate from this temporal trend. Low pH measured in Hamilton streams may result in desorption of metals from sediments and increase effects on biota with already higher sensitivity because of soft water.

Bioaccumulation of metals and metalloids in shortfin eels from sediments appears to be occurring at a number of sites, especially Pb in livers from eels collected from Gibbon's Creek and RK_B, As in livers from those collected from

Lake Rotoroa and minor concern over Hg concentrations in muscle flesh from most sites. Site RK_B has been highlighted for having an unknown source of Pb contamination causing high concentrations of Hg in eel livers relative to sediment. There is also concern over exposure of eels to PAHs at most sites except WA and the peri-urban sites. This species appears to be a good indicator species of bioavailability of these contaminants irrespective of the lack of relationships between sediment and tissues concentrations. The effects of high concentrations of contaminants, especially As on eels are unknown, however, it is apparent that this species is very common in the study streams and can be found in relatively large sizes.

Chapter 4:

Bioassays assessing endpoints of mortality, reburial and growth in two native Crustacea.

4.1 INTRODUCTION

4.1.1 Toxicity and macroinvertebrates

The bioavailability of contaminants in receiving waters is governed by a host of factors including pH, water hardness, redox potential of the sediments, dissolved organic matter concentration, and sorptive behaviour of the contaminant (Power and Chapman 1992, Chapman et al. 1998, Hickey and Golding 2002). Avenues for exposure of toxicants to aquatic organisms depend on feeding behaviour, direct uptake via the gills or skin, uptake of suspended particles or consumption of contaminated food items (Power and Chapman 1992, Spacie et al. 1995, van der Oost et al. 2003). Species sensitivity is affected by metal assimilation and toxic effects as well as the life stage of the organism (juveniles or adults) (King et al. 2006).

As noted by Metcalfe (1989), macroinvertebrates are particularly good indicators of contaminant impacts compared to fish because:

- they are abundant and easy to collect;
- they have sufficiently long life spans to integrate environmental conditions;
- they are relatively sedentary and therefore representative of local conditions; and
- they have a wide variation in sensitivity to different contaminants.

Individual toxic responses of aquatic macroinvertebrates to contaminants include increased mortality of the most sensitive species as well as alterations to growth and reproduction in the more resistant species (Amisah and Cowx 2000). Macroinvertebrate assemblages can be altered as a result of these individual effects, particularly through decline in abundance of sensitive species (e.g., taxa in the orders Ephemeroptera, Plecoptera and Trichoptera) and increases in

pollution-tolerant taxa (oligochaetes, chironomids and snails) (Hickey and Clements 1998, Walsh et al. 2001, Suren and McMurtrie 2005).

Organ contaminants such as PAHs can absorb energy from ultraviolet (UV) light, leading to possible oxidative stress and toxicity to organisms that have accumulated these contaminants in their tissues from their aquatic environment (Ankley et al. 1995, McDonald and Chapman 2002, Wernersson 2003). However, the only approach to determine bioavailability of toxic compounds such as inorganic metals and PAHs to biota is to measure accumulation within tissues or establish some form of biological response (Burton 1991, Power and Chapman 1992, Bervoets et al. 1994, van der Oost et al. 2003, Santoro et al. 2009). It is important to acknowledge, however, that the accumulation of a contaminant within tissues is not necessarily an adverse biological effect, unless the biological response(s) induced by the presence of the chemical(s) are adverse (Spacie et al. 1995).

4.1.2 Laboratory toxicity tests

Toxicity testing is regularly utilised to analyse the biological responses of aquatic organisms to a single chemical, complex effluents, whole-sediment and pore-water (Hickey and Clements 1998, Nipper et al. 1998, Long et al. 2001). Laboratory tests can include acute and chronic (sub-lethal) bioassays which are simple tests assessing a response, usually from a single test organism under controlled conditions (Prato et al. 2010). Because the most commonly tested endpoint is mortality, acute tests provide rapid results, but may fail to detect the effects of moderately toxic, sediment-bound contaminants (Scarlett et al. 2007). Laboratory bioassays have been used to test lethal and sub-lethal endpoints of toxicity with metal and oil-spiked sediments (Bat and Raffaelli 1998, De Witt et al. 1999, King et al. 2006, Scarlett et al. 2007) and whole sediments and their elutriates (Swartz et al. 1982, Davenport and Spacie 1991, Höss et al. 2010, Prato et al. 2010).

Sediment reburial tests are occasionally carried out following a standard 10-day acute sediment toxicity test to provide data on sub-lethal effects of contaminants (Bat and Raffaelli 1998). Amphipods are regularly used in both acute and chronic sediment bioassays as they are sensitive to contaminants, many species inhabit sediment where they can be abundant and they are ecologically important as the

prey of many other species (De Witt et al. 1999, McCready et al. 2004, Scarlett et al. 2007, Prato et al. 2010). Therefore, reburial tests conducted on amphipods are ecologically relevant, as animals that are not able to rebury themselves are not likely to survive in nature (NIWA 1995). The New Zealand amphipod *P. lucasi* has been widely used in laboratory assessments of acute and chronic effects of contaminated sediments (Mischewski 1994, Nipper and Roper 1995, Nipper et al. 1998).

4.1.3 Effect of urbanisation on leaf litter and macroinvertebrate communities

The extreme landscape alteration indicative of urbanisation, not only alters hydrological regimes, reduces habitat quality and increases contaminants in sediments and aquatic organisms, but can also affect aquatic ecosystem processes. Ecosystem processes such as leaf decomposition, primary productivity and nutrient cycling have predominantly been overlooked in urban streams in the past (Paul and Meyer 2001), although the former has been measured in a small number of urbanised watercourses (Collier and Winterbourn 1986, Chadwick et al. 2006, Paul et al. 2006). The rate at which leaves break down in lotic systems is influenced by several factors, including the size and topography of the stream, water chemistry and temperature, microbial activity, animal feeding and physical abrasion (Davis and Winterbourn 1977, Mutch and Davies 1984). Microorganisms on the surfaces of leaves and other organic material, referred to as "biofilms", can not only affect breakdown rates but also play a key role in sequestering metals from urban runoff and transferring them to invertebrates and fish that graze them (Ancion et al. 2010). Metal contamination affecting stream processes can ultimately affect organic matter availability, possibly influencing survival and secondary production of consumers through the uptake of these metals by microorganisms (Carlisle and Clements 2005, Paul et al. 2006). Differential microorganism colonisation and decomposition of leaves may also affect the palatability of organic matter to invertebrates (Collier and Winterbourn 1986, Lester et al. 1994). As allochthonous leaf material is an important source of organic matter for stream invertebrates (Yeates and Barmuta 1999), understanding the influences urban streams can have on species growth and secondary production of species feeding on leaves is important for understanding ecosystem impacts

4.1.4 Freshwater crayfish

Freshwater crayfish occupy a broad trophic niche and display burrowing and/or bioturbation behaviour, and therefore are an important species ecologically (Momot et al. 1978, Whitmore et al. 2000, Parkyn et al. 2001, Reynolds and Souty-Grosset 2011). Although generally thought of as omnivorous, studies have shown crayfish to be particularly important in freshwater ecosystems as consumers of leaf material and detritus (Huryn and Wallace 1987, Usio 2000, Zhang et al. 2004, Bondar et al. 2005, Olsson et al. 2008), and they may act as "ecosystem engineers" by altering the supply of resources to other species by changing biotic or abiotic factors in their physical environment (Jones et al. 1994, Parkyn 2000). In terms of urban contaminants, crayfish in general readily accumulate metals within their tissues and are thought to be potential suitable bioindicators of metal contamination of freshwater ecosystems (Alikhan et al. 1990, Kouba et al. 2010). This is important, not only for the health of individual crayfish and populations but also for risks posed to humans through consumption of crayfish harvested from wild populations. The New Zealand freshwater crayfish, also known as kōura (*Paranephrops* spp.; Parastacidae), are a significant traditional food source for Māori (Kusabs and Quinn 2009), and are currently classified as being in gradual decline by the Department of Conservation (Hitchmough et al. 2007).

Growth rates of freshwater crayfish are well documented in the international literature (Lowery 1988, Harpaz et al. 1998, Cortés-Jacinto et al. 2003, Olsson et al. 2008). In New Zealand growth studies have been conducted either in vitro or in situ (Hopkins 1967, Jones 1981, Parkyn 2000, Parkyn et al. 2002, Hammond et al. 2006). Parkyn (2000) not only found that the main sources of food for all sizes of crayfish from both native forest and pasture streams was leaf detritus and aquatic invertebrates, but also that large crayfish consumed more leaf matter (crack willow, *Salix fragilis*) but assimilated less than juvenile crayfish. Willows, especially *S. fragilis*, have been planted widely on the margins of New Zealand's freshwater ecosystems and is an appropriate species to exploit for study of feeding by macroinvertebrates as it represents an important allochthonous input to many streams (Collier and Winterbourn 1986, Lester 1994).

4.1.5 Study objective and aims

The overall objective of this study was to test three biological endpoints (mortality, reburial behaviour and growth) in two species of native freshwater Crustacea, the amphipod *P. lucasi* and the crayfish *P. planifrons*, exposed to stream sediments from, or fed leaf detritus incubated in, Hamilton urban streams.

The aims of the amphipod toxicity test were to 1) measure mortality (% survivorship) in a 10-day whole sediment contact test using stream sediments collected from 14 urban sites in Hamilton; 2) determine whether there was any sediment-associated phototoxicity in the same animals after exposure to UV light; and 3) establish whether sediment toxicity and/or exposure to UV light had any effects on the reburial behaviour of the amphipod.

The crayfish bioassay was conducted to measure growth rates and survivorship of *P. planifrons* fed an exclusively detritus diet of *S. fragilis* leaf material incubated at 6 Hamilton stream sites along a sediment metal gradient established in Chapter 3. Metal concentrations on leaves were measured to determine any relationship with survivorship and measured growth rate.

4.2 METHODS

4.2.1 Site selection

Sites chosen for sediment collection for the amphipod sediment toxicity tests and for leaf incubation for the crayfish growth bioassay were a subset of the 25 sites selected in 2011 by NIWA for a complementary study specifically on Hamilton urban stream contaminants in sediments (Clearwater and Valler 2012) (Table 4-1). These sites were selected for sampling using GIS data for stream, road and stormwater infrastructure locations and knowledge of historic and current land use in Hamilton (Clearwater and Valler 2012). The sites included streams where sediment metal concentrations were the highest reported, where current restoration projects (e.g. Gibbon's Creek at Parana Park and Bankwood stream at Donny Park) were underway, or where prospective development is planned (Peacockes branch of the Mangakotukutuku). Sites for the reburial and phototoxicity tests were chosen because of the presence of PAHs with varying concentrations (see Table 4-2).

Sites for incubation of *S. fragilis* leaves were selected based on May 2012 sediment metal concentrations. Six sites were chosen to represent (i) a gradient from highest total metal concentration to lowest, (ii) the main catchments, and (iii) particular sites with unusually high single metal concentrations. Sites chosen included NA (most elevated concentrations of a wide range of contaminants), RN_A (highest copper (Cu), lead (Pb) and zinc (Zn) concentrations), WA (highest arsenic (As) concentrations), KC (representative of this catchment and with lower total metal concentrations), PD (lowest total metal concentrations) and KA (highest Fe concentrations) (Table 4-1).

Table 4-1. Site information for sediment collection (S), leaf incubation (I) and crayfish collection (C) for use in an amphipod 10-day sediment toxicity test and a crayfish growth bioassay. Shading indicates separate catchments.

Stream/ Catchment	Site Name	Site Label	NZTM2000		% Impervious	Site Description	Sampling
			Northing	Easting			
Rangitukia	Crayfish collection	CC	6357738	6357738	0	Mt Pirongia. Fast flowing, high gradient mountain stream. 100% native forest vegetation.	C
	Peacockes B	PB	5811469	1803357	5	Main channel of Peacockes branch, rural.	S
	Peacockes C	PC	5812376	1802560	7	Main channel of Peacockes branch, Peacockes Road, residential.	S
Mangakotukutuku	Peacockes D	PD	5811516	1803378	5	Small tributary to main Peacockes channel, rural.	S, I
	Rukuhia B	RK_B	5811920	1801016	13	Main Rukuhia channel. Receiving inputs from Ohaupo Rd.	S
	Rukuhia D	RK_D	5812430	1802271	20	Main Rukuhia channel. Upstream from confluence with Peacockes branch.	S
Normandy Avenue	Normandy A	NA	5813293	1801341	71	Downstream of old hospital landfill, stormwater pipe, discharge upstream may drain new hospital carpark.	S, I
Graham Park	Graham A	GA	5813684	1801191	58	Small stream located in Grahams Park adjacent to Cobham Drive.	S
Waitawhiriwhiri	Waitawhiriwhiri A	WA	5814304	1799865	47	Lake Rotoroa outlet, Innes Common.	S, I
Gibbon's Creek	Parana A	PR_A	5815315	1801468	70	Located in urban park garden.	S
Ranfurlly Park	Ranfurlly A	RN_A	5817176	1800468	53	Grassed urban park, fully urbanised catchment.	S, I
Bankwood	Bankwood A	BA	5818728	1800027	65	Donny Park, fully urbanised catchment.	S
	Kirikiroa A	KA	5819375	1802147	5	Rural location, deep layer of sludge.	S, I
Kirikiroa	Kirikiroa B	KB	5820340	1799944	44	Tauhara Park. Old landfill inputs.	S
	Kirikiroa C	KC	5820093	1799243	48	Mainstem location, western Tauhara Park.	S, I

% impervious data supplied by Waikato Regional Council.

4.2.2 Amphipod sediment toxicity test

Collection and preparation of sediments

Sediment samples were collected from multiple settling zones at 14 sites (Table 4-1) in a downstream to upstream direction on 7/5/12 and 8/5/12. Plastic trowels were used to remove approximately the top 20 mm of fine sediment with a total of approximately 3 kg collected (wet weight). Sediment and some water was collected in two clean plastic zip-lock bags per site and thoroughly mixed within and between bags to ensure collected sediment was homogeneous. Samples were double-bagged and placed on ice for transport back to the laboratory.

At the laboratory, samples were either separated for use immediately in contaminant analysis (see Chapter 3), or refrigerated at 1°C for 3-4 days when they were sieved to retain the <500 µm fraction for use in the bioassay. This was done using small amounts of added dechlorinated Hamilton City tap water (DHTW) without disposing of any water to retain contaminants. The slurry from each sediment site was added to three 680 ml plastic containers to a depth of approximately 30 mm. Evaporation was reduced by covering the containers with Perspex plastic covers that were lined with plastic cling film while being left to settle at 12°C. After 5-6 days, aeration was introduced in the containers, and two days later, when the suspended particles had settled out, overlying water was siphoned from the containers. The remaining sediment was thoroughly mixed and adjusted to a depth of 25-30 mm. Approximately 580 mL of DHTW was carefully added to the containers after a circle of plastic was laid on top of the sediments to prevent mixing. The plastic was then removed and aeration recommenced. A piece of plastic mesh (20 x 100 mm) was added to each container to provide firm substrate for amphipods if needed, to reduce the possibility of mortality due to smothering by fine sediments.

Collection of control sediments and amphipods

Paracorophium lucasi specimens were collected from the top 20 mm of the littoral zone of Lake Rotorua near the outlet of Hamurana Stream (6346832N, 2796212E) on 14/5/12 and 28/5/12. Both amphipods and sediment were transported together with a shallow layer of overlying lake water. On both occasions, the sediments were sieved to remove the >2 mm fraction, whereas

on 14/5/12 the <500 μm fraction was also removed. Separating the >2 mm fraction assisted with the subsequent sieving of the >500 μm fraction to either remove any resident amphipods for control sediments (<500 μm fraction) or to extract amphipods for counting and use in the bioassay. For 14 days after the first sediment collection, all sediments (with amphipods) were stored in a constant temperature room with added DHTW and constant aeration. The <500 μm sediments were added to six 680 ml plastic containers as described above to act as control replicates (25 to 30 mm deep). After the second amphipod collection on 28 May 2012, the constant temperature room was set at 15°C as this was similar to the temperature of the littoral waters of Lake Rotorua (13°C).

Sediment toxicity test, reburial and phototoxicity

The day after collection, amphipods were sieved from the >500 μm fraction and counted into groups of 10. Twenty amphipods were added to each sediment replicate. Daily observations included monitoring aeration and checking for mortalities. Mortalities were removed from the container if found. Every second or third day, dissolved oxygen and conductivity were measured using a Hach HQ40d multimeter and pH was measured by a Radiometer analytical PHM220 pH meter. Water temperature was also measured. These water quality parameters were also measured in containers on the days when any mortalities were found. After ten days, amphipods were sieved from the sediments and counted to determine survivorship.

The response criterion of reburial was examined to discriminate moribund individuals from healthy, active ones. Sediments collected on 28/5/12 from Lake Rotorua, and stored as described above, were sieved on 7/6/12 to remove the <500 μm fraction for use in the test. Sediment sieved was only from the top approximately 30 mm to reduce any risk that storage of the sediments had caused bottom layers to become anoxic. The <500 μm fraction was added to 36 250 mL plastic containers in a layer approximately 20 mm deep and 170 mL of DHTW was gently added onto a layer of plastic covering the sediment. The plastic was removed and the containers were held overnight in a constant temperature room (15°C).

Nine of the 14 Hamilton stream sites used in the sediment toxicity test were chosen for the reburial and subsequent phototoxicity tests because they

contained varying PAH concentrations (Table 4-2), or in the case of sites PB, RK_D and KC sediments, these lacked any PAH concentrations but were chosen as additional controls. Aeration was added to the reburial containers containing Lake Rotorua sediments (<500 µm fraction). Surviving amphipods from the sediment toxicity test sites (as outlined above) were transferred to the corresponding replicate in the reburial test. Numbers of amphipods on the surface of the sediment were recorded after one hour. The amphipods were sieved from the sediment the following day and the sediments were placed back into the reburial cups.

Each replicate of amphipods was then placed into 40 mL of DHTW in small plastic cups (50 mL). The cups were floated in a large tub of iced water under six Osram Ultra-Vitalux lamps (each 240 V, 300 Watt) for one hour. During the exposure to UV light, water temperature was monitored closely to maintain temperatures at approximately 15°C. At the end of the exposure time, amphipods were checked and returned to their respective reburial replicate with freshly added DHTW. The containers were returned to the constant temperature room and aeration recommenced. Amphipods on the surface of the sediments were counted after an hour and the following day, were sieved from the sediments and counted to determine survival rates.

Test conditions for both the sediment toxicity and phototoxicity tests are summarised in Appendix C.

4.2.3 Crayfish growth experiment

Incubation of leaf material

Pre-abscission leaves from a single *S. fragilis* tree were dried and stored at air temperature prior to the experiment. Twenty-three 1 mm nylon mesh bags (150 x 150 mm) were filled with approximately 10 g each of the leaf material and these bags were placed in larger 200 x 200 mm nylon net bags (2 mm mesh). Some of the leaf material was retained for analysis of initial leaf metal concentrations.

On 28/8/12, four leaf bags were placed at each of sites PD, NA, WA, RA and KC and three at KA (Table 4-2). The bags were tied to brick weights and, where possible, placed in depositional zones of streams with similar substrate

size (typically pools with silty bottom sediment) and secured with rope to riparian vegetation. Each stream had a Hobo Tidbit temperature logger measuring temperature every hour for the duration of the incubation period. When the leaves were removed from the streams after 17 days incubation, they were placed into labelled zip-lock bags and returned to the laboratory for processing the same day.

On returning to the laboratory, leaves from each site were carefully rinsed through a 2 mm sieve with DHTW (without rubbing) to remove loosely adhering sediment. Invertebrates were removed from the leaves and leaf bags and preserved in isopropyl alcohol in individual labelled containers for identification. The leaves were then placed into labelled zip-lock plastic bags and frozen at -20°C for use in the feeding experiment and for analysis of leaf metal concentrations.

Food digestion and analysis

Metal and metalloid concentrations were measured on all food sources supplied to crayfish during the feeding experiment. Several original *S. fragilis* leaves, small subsamples of each frozen leaf material and one block from three separate frozen Aqua One chironomid larvae pellets (see Crayfish collection) were placed in separate new 50 mL falcon tubes. All samples were then freeze-dried for approximately 36 hours to obtain a dry weight measurement of leaves or chironomids. Approximately 0.2 g of dried leaf material or chironomid was used for the digestion. A suite of 25 elements was measured in food sources and two method blanks based on established methods (USEPA 1987), as outlined in Chapter 3 (3.2.4, p. 30) and also undiluted reference standard SLRS-5.

Crayfish collection

Sixty-three crayfish of 8.8-20.7 mm orbit-carapace length (OCL) were collected using spotlighting, and electrofishing methods from Rangitukia Stream, a first-order forested tributary on Mount Pirongia, Waikato (6357738N, 2696343E) on 23/9/12 and 25/9/12. Crayfish were transported back to the laboratory in aerated buckets of stream water with bracken for shelter. Crayfish were kept in a darkened room at 16°C in two large bins of aerated DHTW with PVC pipes

and bracken for shelter for 3-5 days prior to being transferred to the experimental aquaria described below. During this time and for six days for the experimental equilibration (see Experimental design), crayfish were fed "Aqua One" chironomid larvae.

Experimental set up

Within five days of collection, 60 crayfish were placed individually into separate 2-litre ice cream containers ("aquaria") to equilibrate to experimental conditions. These aquaria had lids with a 100 x 100 mm square of 2 mm nylon mesh glued with a general purpose contact adhesive (Ados) to allow a continuous flow of water to drain from the containers and provide a dappled light environment (Plate 4-1a). Lids were soaked in DHTW for approximately two weeks prior to the commencement of the experiment and containers were cleaned with DHWT. Continuous flushing of each aquarium to control ammonia build up was achieved by pumping DHTW at a slow rate. An air stone was used to diffuse oxygen into each aquarium and two 100 mm lengths of PVC piping (32 and 40 mm diameter) were provided for shelter (Plate 4-1a). The experimental room had a natural diurnal light cycle and water temperature increased from 15.5°C at the start to 17.0°C at the termination of the experiment due to the natural increase in diurnal temperatures affecting the DHTW supply. Mean temperature was $15.7 \pm 0.02^\circ\text{C}$. Each of 60 aquaria was randomly assigned a position to minimise any possible effects that container colour or location would have on crayfish behaviour (Plate 4-1b).



Plate 4-1. Set up of *Paranephrops planifrons* growth experiment; a) crayfish housed individually in single 2-litre icecream "aquaria" with PVC pipes for shelter, and b) aquaria set up with air and water lines.

Experimental design

After six days of equilibration (one crayfish died during this period), the last two of which crayfish were not fed, initial weights and OCLs were measured from the 59 experimental crayfish. Weighing crayfish involved each animal being wet weighed to the nearest 0.1 mg in a small amount of pre-weighed water, after having been placed on folded paper towels for a short time to soak up excess water. Occipital carapace length of each crayfish was measured with electronic callipers to the nearest 0.1 mm.

Crayfish were evenly distributed among feeding treatments within four size categories based on OCL lengths (≤ 10.5 mm, 10.6 - 14 mm, 14.1 - 17.5 mm and ≥ 17.6 mm) so that each treatment had a spread of evenly sized crayfish. The seven different feeding treatments comprised leaf material incubated at sites PD, NA, WA, RN_A, KA, KC and one treatment fed chironomid larvae thawed from frozen pellets of commercial chironomids. There were nine replicates for PD and WA; eight in NA, RN_A, KA and chironomid treatments and seven crayfish fed leaves incubated at site KC. There was no significant difference between treatments in mean initial crayfish weight ($F_{6,52} = 0.121$, p -value = 0.993).

Crayfish were fed ad libitum every second day. Each aquarium was completely emptied of water, and uneaten food and faeces, prior to being filled with water once more and the crayfish supplied with fresh leaf material. This was not completed every time for chironomid-fed crayfish as faecal build up and uneaten food were generally far less. Daily observations were made of crayfish to record any moults and to remove any crayfish exuviae from aquaria. Weekly measurements of weight and OCL length were conducted, as described above.

At the termination of the experiment, crayfish were humanely euthanised by hypothermia and archived for future tissue analysis (freezer storage at -20°C). Tissues (hepatopancreas and tail flesh) were not analysed for metals and metalloids as part of this study due to cost constraints.

4.2.4 Statistical Analyses

Data analyses were performed using the statistical package Graphpad Prism, Version 4.0. Percentage survival of amphipods from each site in the sediment

toxicity test were transformed using Arcsine square-root after tests for normality, then compared for significant differences using ANOVA. Tukey's Multiple Comparison post hoc test was then conducted for differences between treatments.

Correlations were conducted to determine relationships between August sediment metal concentrations and leaf metals. Mean initial weights of crayfish in each feeding treatment were analysed for differences using ANOVA. Growth rates (GR) (% weight gain day⁻¹) in all treatments were calculated using the difference of initial weight and final weight (either at the end of the experiment or last live weight). They were compared between treatments and the control (chironomids) using ANOVA. Growth rates and individual mean metal and metalloid concentrations of food were compared with linear regression. A correlation was also conducted to determine the relationships between mean temperature of the streams in which the willow leaves were incubated and GR.

Statistical reporting is based on mean \pm standard error of the mean unless stated otherwise.

4.3 RESULTS

4.3.1 Stream sediment contaminant summary

Metals, metalloids and PAHs in sediments of Hamilton streams relative to ANZECC (2000) ISQG Low values, as well as background concentrations in soils are provided in Table 4-2.

4.3.2 Amphipod sediment toxicity test

Water quality parameters

Throughout the duration of the toxicity test mean water quality parameters were: dissolved oxygen, $10.2 \pm 0.03 \text{ mg L}^{-1}$; temperature, $15.5 \pm 0.06^\circ\text{C}$; conductivity (except sites KB and NA), $222.5 \pm 3.9 \mu\text{S cm}^{-1}$ and pH (except sites KA, KB and NA), 7.46 ± 0.04 . Mean conductivity at sites KB and NA was $412.0 \pm 9.2 \mu\text{S cm}^{-1}$ and $450.7 \pm 13.8 \mu\text{S cm}^{-1}$, respectively, and pH at sites KA, KB and NA was 6.1 ± 0.24 , 8.2 ± 0.04 and 8.4 ± 0.04 , respectively.

Table 4-2. Summarised results for organic carbon (OC), sediment metal/metalloids and polycyclic aromatic hydrocarbon concentrations (PAH) in Hamilton stream sites used for bioassays in 2012. Key to site labels is provided in Table 4-1. Background Waikato soil concentrations (BWS) are, from Taylor and Kim (2009). Interim Sediment Quality Guidelines Low (ISQG-Low) refers to the ANZECC (2000) sediment quality guidelines for each contaminant. Highlighted concentrations exceed relevant ISQG-Low (shaded).

Site	OC %	Metals / metalloids [†] Average 2012 concentration (mg kg ⁻¹ dry weight)									PAHs* May 2012 concentrations (µg kg ⁻¹ dry weight) (normalised to 1% OC)									
		Cu	Pb	Zn	Fe	As	Ba	Cd	Hg	Ni	B[a]A	B[a]P	B[b]F	B[g,h,i]P	B[k]F	Chry	FA	IPyr	Phe	Pyr
PB	9.8	4.4	6.8	40.9	18036	1.8	201.5	0.11	0.19	1.7	-	-	-	-	-	-	-	-	-	-
PC	3.0	3.7	9.9	37.6	26679	6.8	148.4	0.06	0.11	1.9	-	-	-	-	-	-	-	-	-	-
PD	2.1	2.2	5.7	45.5	26174	3.1	81.4	0.05	0.06	1.7	-	-	-	-	-	-	-	-	-	-
RK_B	3.5	8.2	12.6	41.5	15880	3.1	56.7	0.04	0.05	3.3	-	-	-	-	-	-	-	-	-	-
RK_D	1.4	3.1	10.5	34.7	9964	2.9	60.6	0.04	0.06	1.8	-	-	-	-	-	-	-	-	-	-
NA	1.6	25.4	22.9	145.4	22935	9.3	137.8	0.08	0.37	14.0	-	-	-	-	-	-	-	-	-	-
GA	1.9	24.5	31.4	102.4	12427	5.7	117.4	0.09	0.49	2.6	27	32	37	32	21	27	43	21	27	53
WA	2.8	9.3	21.1	60.4	14630	47.1	93.5	0.07	0.14	4.6	136	182	218	150	89	125	186	89	71	225
PR_A	4.8	19.7	82.6	360.8	42799	18.5	129.4	0.28	0.21	11.5	13	13	19	13	8	13	25	-	13	29
RN_A	6.4	21.9	71.4	331.3	20467	21.9	154.1	0.36	0.19	6.2	22	25	38	31	19	22	33	20	-	28
BA	4.6	10.8	25.4	158.6	19277	13.6	91.4	0.17	0.16	3.7	-	-	-	-	-	-	-	-	-	9
KA	6.3	17.5	11.5	210.2	106890	19.9	267.6	0.72	0.23	5.1	-	-	-	-	-	-	-	-	-	-
KB	2.2	17.8	10.2	92.3	46576	45.5	369.2	0.13	0.15	3.5	-	-	-	-	-	-	-	-	-	14
KC	1.8	6.1	12.9	115.1	33530	19.7	99.3	0.12	0.12	2.9	-	-	-	-	-	-	-	-	-	-
BWS	-	16	11	28	25600	5.1	97	0.11	0.19	3.9	-	-	-	-	-	-	-	-	-	-
ISQG-Low	-	65	50	200	-	20	-	1.5	0.15	21	261	430	-	-	-	384	600	-	240	665

[†]Cu, copper; Pb, lead; Zn, zinc; Fe, iron; As, arsenic; Ba, barium; Cd, cadmium; Hg, mercury; Ni, nickel.

*B[a]A, benzo[a]anthracene; B[a]P, benzo[a]pyrene; B[b]F, benzo[b]fluoranthene and benzo[j]fluoranthene; B[g,h,i]P, benzo[g,h,i]perylene; B[k]F, benzo[k]fluoranthene; Chry, chrysene; FA, fluoranthene; IPyr, indeno(1,2,3-c,d)pyrene; Phe, phenanthrene; Pyr, pyrene.

- not detectable or not applicable

Survival and reburial

Overall mean survival in all the controls was $92.5 \pm 2.5\%$, demonstrating that the conditions for conducting the 10-day sediment toxicity test, met the NIWA protocol (where mean survival should be $\geq 90\%$) (NIWA 1995). There were significant differences in amphipod survival between sites ($F_{14,33} = 2.362$, $p < 0.05$) with site WA significantly lower than five other sites as well as the control sediments (Figure 4-1).

Of the surviving amphipods in the control sediment, $97.4 \pm 1.2\%$ were able to rebury within one hour. Mean percentage reburial of amphipods exposed to sediment at sites PB, RK_D, WA and RN_A was 100% for the same time period. Mean percentage reburial with amphipods exposed to sediments from other sites included GA, $98.3 \pm 1.8\%$; PR_A, $98.0 \pm 2.0\%$; BA, $96.3 \pm 1.9\%$; KB, $94.1 \pm 3.6\%$; and KC, $98.3 \pm 1.7\%$. There was no statistically significant difference between treatments in this reburial behaviour ($F_{9,23} = 1.234$, $p > 0.05$).

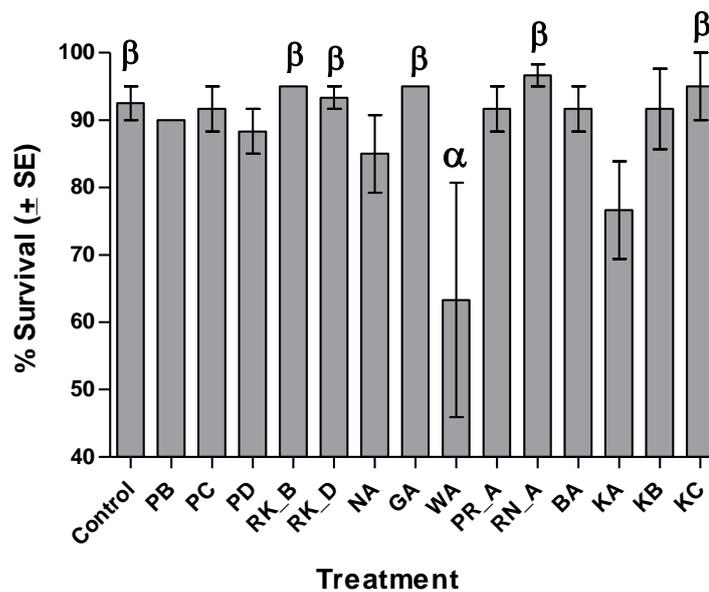


Figure 4-1. Percentage survival (\pm SE) of amphipod *Paracorophium lucasi* at the completion of a 10-day exposure to sediment from Lake Rotorua (control) and Hamilton urban stream sediments. Alpha symbol denotes survival significantly different ($p < 0.05$) than sites with beta symbol. Key to site labels is provided in Table 4-1.

Amphipod phototoxicity test - survival and reburial

Percentage of amphipods that were able to rebury after being exposed to UV light was $98.0 \pm 1.3\%$ for control sediments and 100% in most treatments except WA sediments ($96.3 \pm 3.7\%$). There was no difference between treatments in reburial behaviour ($F_{9,23} = 1.234, p > 0.05$).

Mean percentage survival of amphipods exposed to the control sediments, measured the following day after the phototoxicity test was $98 \pm 1.3\%$. Mean percentage survival of the treatment amphipods was: PB, $98.2 \pm 1.8\%$; RK_D, 100%; GA, $98.3 \pm 1.7\%$; WA, $95.5 \pm 2.4\%$; PR_A, 100%; RN_A, 100%; BA, 100%; KB, $98.3 \pm 1.7\%$; and KC, $97.9 \pm 2.1\%$, none of which were significantly different from each other ($F_{9,23} = 0.821, p > 0.05$).

4.3.2 Crayfish growth experiment***Leaf incubation***

Mean daily water temperatures over the 17 day incubation period were, PD, $10.9 \pm 0.07^\circ\text{C}$; NA, $14.6 \pm 0.04^\circ\text{C}$; WA, $13.6 \pm 0.04^\circ\text{C}$; RN_A, $12.6 \pm 0.05^\circ\text{C}$; KA, $12.7 \pm 0.07^\circ\text{C}$; and KC, $12.9 \pm 0.04^\circ\text{C}$. The high variation in temperature at PD and KA may be due to the fact that they were the smallest streams with the least flow and therefore more affected by diurnal temperature fluctuations. There was a noticeable variety in texture and colour of leaves retrieved from the various sites (Plate 4-2). NA, RN_A and KC leaves showed the most visible decomposition with the leaves being very fragile. Normandy A (NA) leaves were a very dark grey and almost black in colour while those from RN_A and KC sites were dark brown. KA leaves appeared to be less decomposed and were a lighter brown colour. Leaves that were incubated at sites PD and WA were by far the least decomposed and remained orange/brown like the original willow leaves.



Plate 4-2. *Salix fragilis* leaves after incubation and freezing, prior to being fed to *Paranephrops planifrons* showing lighter colouration of Waitawhiriwhiri A and Peacockes D leaves.

Macroinvertebrate colonisation of incubated leaves

A qualitative assessment of macroinvertebrate taxa colonising different leaf packs was conducted to determine whether any leaf-shredding invertebrates were present. Peacockes D (PD) was the most notable site in terms of sensitive macroinvertebrates colonising leaf bags incubated in the streams with the mayfly *Deleatidium* spp. (Ephemeroptera) most common. Also occurring on leaves from this site was a Hydrobiosidae (Trichoptera) larva. The most numerous macroinvertebrate located at WA was the amphipod *P. fluviatilis* and others included tolerant species such as Oligochaeta and Chironomidae, and a Platyhelminthes (flatworm) spp. Ranfurly Park (RA) leaf macroinvertebrate colonisation consisted of Oligochaeta, Chironomidae, Platyhelminthes and Hydrobiosidae spp. The peri-urban KA, as well as NA, were very depauperate in that only Oligochaete worms were observed. The site located on the main channel of the Kirikiriroa stream (KC) was marginally better in terms of diversity with Chironomidae and Oligochaeta collected on and within leaf bags incubated in this stream. No leaf-shredding invertebrates were collected from any of the leaf bags.

Leaf and chironomid metal and metalloid concentrations

All concentration of metals and metalloids in leaves and chironomids were above the average MDL for each key metal/metalloid analysed (Cu, 1.4; Pb, 0.6; Zn, 2.8; As, 2.8; Cd, 0.15; Hg, 0.55; Ni 2.8 mg kg⁻¹; Fe, 0.06; and Ba, 0.0014 g kg⁻¹). Original leaves and chironomids had low concentrations of metals and metalloids compared with the incubated leaf material except for concentrations of Cu in chironomids (high concentrations) and Cd (moderate concentrations) in the control leaves (Fig. 4-2).

Leaves incubated at RA had the highest Pb and Zn concentrations (Fig. 4-2B & C), whereas NA had the highest Cu, Ba and Ni concentrations of all incubation sites (Fig. 4-2A, F and I). The leaves incubated at the peri-urban site KA had the highest Fe and Hg concentrations (Fig. 4-2D and H). Hamilton Lake (WA) and KA incubated leaves had significantly higher levels of As and Cd, respectively, compared with the other sites (Fig. 4-2E and G).

Some relationships between August sediment sampling concentrations of individual metals correlated well with leaf metals (R^2 , p -value: As, 0.693, $p < 0.05$; Cd, 0.775, $p < 0.05$; Pb, 0.886, $p < 0.01$; Hg, 0.886, $p < 0.01$; Ni, 0.927, $p < 0.01$), while others did not (Cu, 0.412, $p > 0.05$; Zn, 0.089, $p > 0.05$; Ba, 0.518, $p > 0.05$).

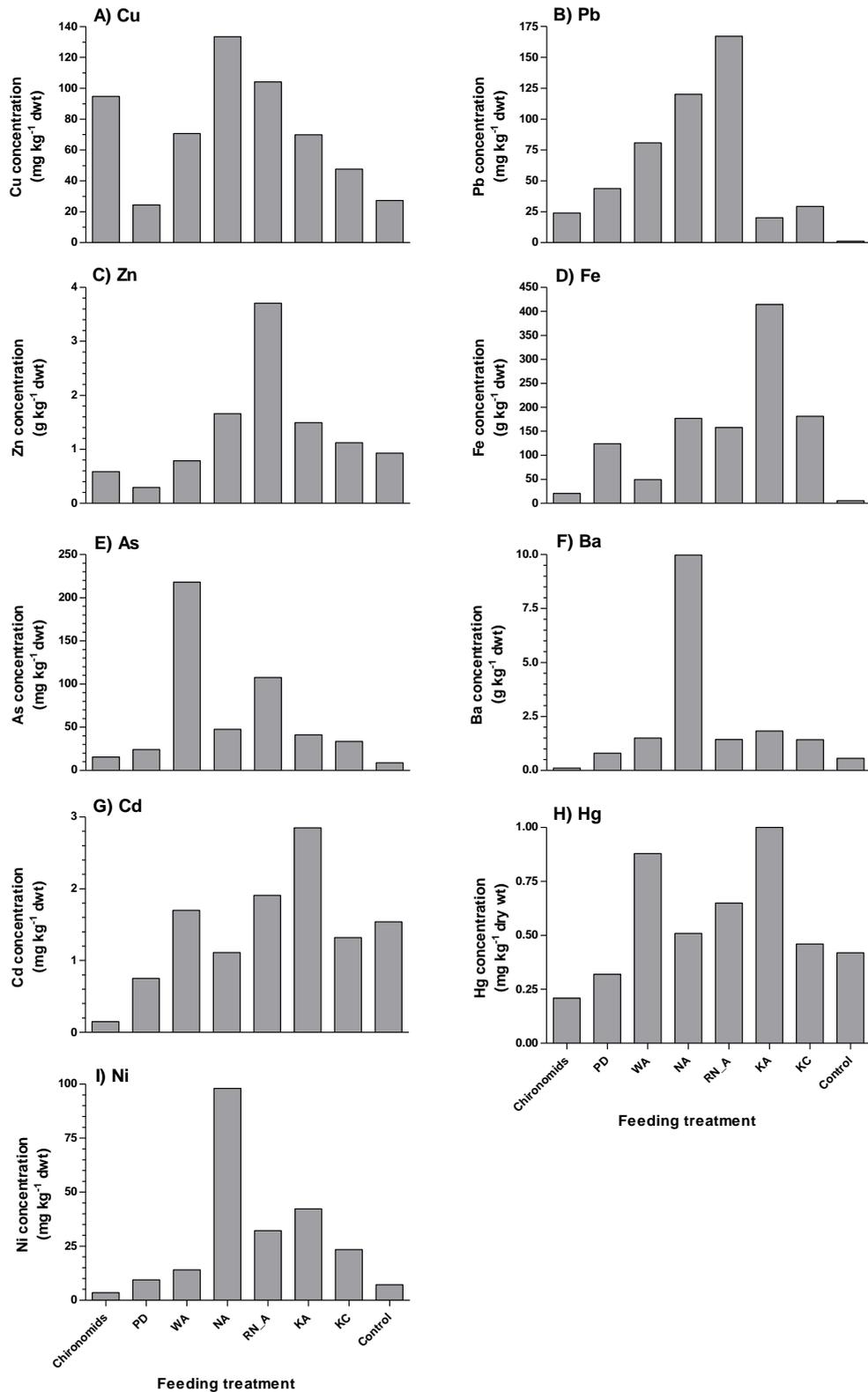


Figure 4-2. Metal and metalloid concentrations of A) copper (Cu); B) lead (Pb); C) zinc (Zn); D) iron (Fe); E) arsenic (As); F) barium (Ba); G) cadmium (Cd); H) mercury (Hg) and I) nickel (Ni) measured in chironomid larvae (mean, n=3) or crack willow (*Salix fragilis*) leaf material incubated in Hamilton urban stream or unincubated (Control). Key to site labels is provided in Table 4-1.

Crayfish survival

Survival of crayfish was high (75-100%) for the experiment in general (Table 4-3). The lowest survival rate was for those crayfish being fed leaf material from site NA where two crayfish died. There was one mortality each from site WA and the chironomid-fed treatment. Of the four crayfish that died, two died whilst moulting (NA and WA treatments) - these moults were not included in calculating % moulted for each feeding treatment which was highest for PD, followed by WA and KC (Table 4-3). No moults were recorded for KA, RN_A or NA.

Table 4-3. Survival and percentage moulted for crayfish fed for five weeks on chironomid larvae or leaf detritus incubated in Hamilton urban streams. Key to site labels is provided in Table 4-1.

Treatment	Survival (%)	Moulted once (%)
Chironomid larvae (n=8)	88	25
PD (n=9)	100	33
NA (n=8)	75	0
WA (n=9)	89	22
RN_A (n=8)	100	0
KA (n=8)	100	0
KC (n=7)	100	14

Growth

The growth experiment terminated at five weeks when the supply of incubated leaves from the single *S. fragilis* was exhausted (Figure 4-4). Leaf material incubated at KA ran out just after the fourth week, due to only three bags of leaf material being incubated whereas the other sites had four bags. Mean increase in OCL for those treatments where crayfish moulted were: chironomids, 0.67 ± 0.15 mm; PD, 1.03 ± 0.09 mm; WA, 0.7 ± 0.4 mm and KC, 0.7 mm. These increment increases were not statistically significantly different ($F_{2,5} = 1.193$, $p > 0.05$). Individual GRs varied greatly within treatments and were low overall with a range over all leaf-fed treatments of -0.122 to 1.702% (both extremes fed leaves from site KA), and -0.521 to 0.692% in chironomid-fed crayfish. Mean GRs were not significantly different between feeding treatments ($F_{6,45}=0.51$, $p > 0.05$) (Fig. 4-3).

Individual weights remained relatively constant and did not increase markedly (Fig. 4-4).

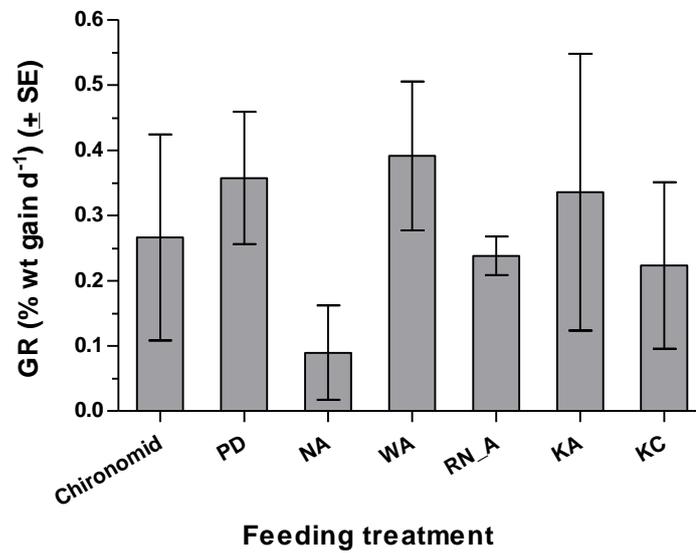


Figure 4-3. Mean growth rates (GR) (\pm SE) of freshwater crayfish (*Paranephrops planifrons*) that survived at least four weeks fed chironomid larvae or *Salix fragilis* leaf material incubated in Hamilton urban streams sites PD, WA, NA, RN_A, KA and KC. Key to site labels is provided in Table 4-1.

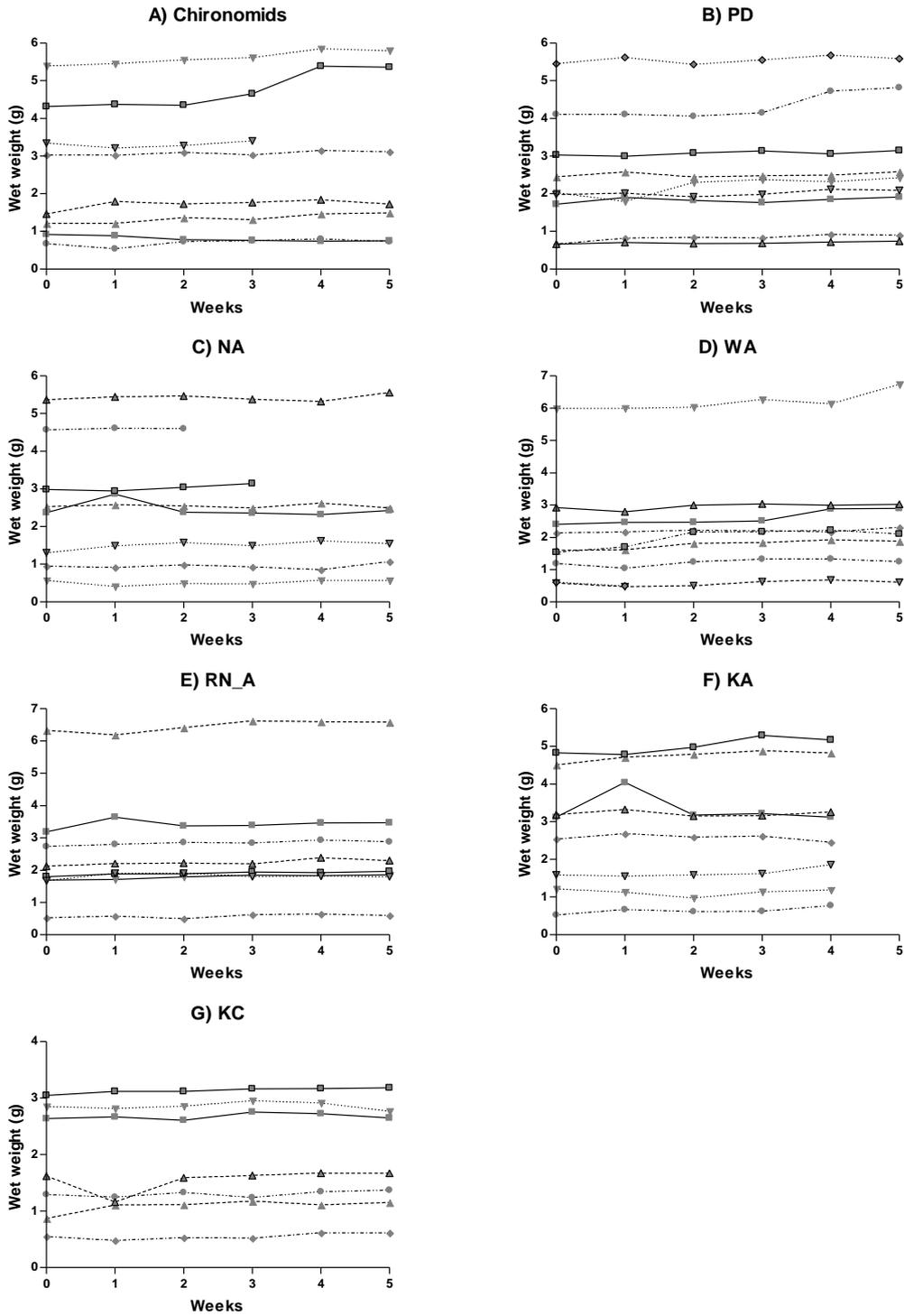


Figure 4-4. Wet weights (g) of individual crayfish (n=7-9) over five weeks fed (A) chironomid larvae or (B-G) leaf material (*Salix fragilis*) incubated in Hamilton urban stream sites (treatments). Key to site labels is provided in Table 4-1. Discontinuation of lines less than 5 weeks represents mortality (NA, WA and chironomids) or termination at week 4 because of lack of leaf material (KA).

Relationships between GR and individual metal and metalloid concentrations on food sources did not generally correlate well (R^2 , p -value) (Cu, 0.489, $p > 0.05$; Pb, 0.173, $p > 0.05$; Zn, 0.150, $p > 0.05$; Fe, 0.002, $p > 0.05$; As, 0.145, $p > 0.05$; Cd, 0.05, $p > 0.05$). However, the relationships between GR and Ba and Ni concentrations within feeding treatments were significant (Ba, 0.579, $p < 0.05$; Ni, 0.574, $p < 0.05$) (Fig. 4-5). Both of these relationships were driven by the high Ba and Ni content of site NA and (not significantly) lower GR. Leaf incubation temperature and GRs did not correlate well ($R^2 = 0.396$, $p > 0.05$).

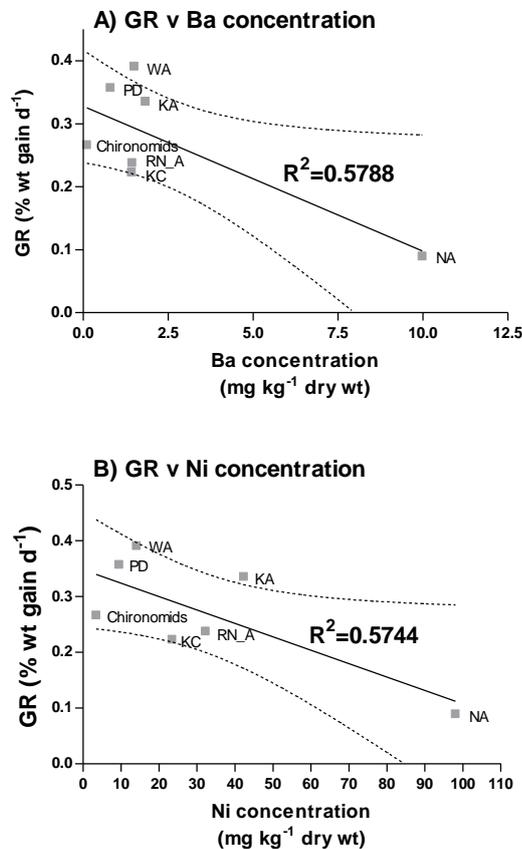


Figure 4-5. Relationship between growth rate (GR) (% weight gain day⁻¹) of freshwater crayfish (*Paranephrops planifrons*) fed chironomid larvae and crack willow (*Salix fragilis*) leaves incubated in Hamilton stream sites PD, NA, WA, RN_A, KA and KC and A) barium (Ba) and B) nickel (Ni) concentrations. Coefficient of determination (R^2) for solid best-fit line. Dotted lines represent 95% confidence bands. Key to site labels is provided in Table 4-1.

4.4 DISCUSSION

The studies outlined in this chapter were carried out to ascertain whether there were any toxic lethal or sub-lethal (reburial behaviour, growth rate) effects on Crustacea associated with benthic habitats in Hamilton urban streams. Crustaceans are widely used to reflect differential accumulation of contaminants among the wider aquatic invertebrate community (Rainbow 2002). Insights provided by sediment exposure for the amphipod *P. lucasi* and leaves fed to *P. planifrons* therefore ultimately may explain the presence or absence of species in the wider macroinvertebrate communities within these streams.

4.4.1 Ecological relevance of *Paracorophium lucasi* and *Paranephrops planifrons* to Hamilton urban streams

Paracorophium lucasi is found on both the west and east coasts of the North Island, mainly in brackish water, but also in freshwater habitats, including lakes in the Rotorua region (Stevens and Hogg 2004). Previously in the genus *Chaetocorophium*, it was reallocated to *Paracorophium* (Chapman 2002; see also Chapman et al. 2011). Like a number of other corophioid amphipods, it constructs loose, U-shaped burrows in soft sediments (De Witt et al. 1999). The use of corophioid amphipods for use in toxicity bioassays is widespread because of their sensitivity to toxicants (Hyne and Everett 1998, De Witt et al. 1999, Marsden and Wong 2001), although arguably they have lower sensitivity than other amphipod species (Picone et al. 2008). *Paracorophium lucasi* is considered more tolerant than the amphipod *P. fluviatilis*, cladoceran *Ceriodaphnia dubia* and the migratory shrimp *Paratya curvirostris* for sensitivity to Cd (Hickey 2000, but although not found in Hamilton urban streams, has been selected as a test species for the present study because of its suitability to be cultured under laboratory conditions, its known sensitivity to toxicants (contaminants such as metals and PAHs) and its burrowing behaviour (NIWA 1995).

Paranephrops planifrons White is one of two *Paranephrops* species recognised in New Zealand, and is found in a wide variety of freshwater habitats throughout the North Island and north-west of the South Island (Hopkins 1970, Chapman et al. 2011). Both species of crayfish are also associated with the benthos of aquatic environments through their method of feeding (Goddard 1988, Parkyn et al. 1997) and active burrowing behaviour (Hopkins 1970). Crayfish generally

bioaccumulate metals very well into their tissues, which is a good indicator of bioavailability (Alikhan et al. 1990, Antón et al. 2000, Kouba et al. 2010). However, concentrations of metals within the environment may not be sufficient to be a direct cause of death, although sub-lethal effects cannot be ruled out (Roldan and Shivers 1987, Kouba et al. 2010). Crayfish are found in some urban streams within Hamilton city, but are absent from most, raising the possibility that metal contamination may be a factor limiting their distribution (Collier et al. 2009).

4.4.2 Sediment toxicity testing

There have been many tests assessing toxicity of particular contaminants to amphipods, generally to assess the individual suitability of amphipod species as toxicity test organisms for single metals through dose-dependent effects (Bat and Raffaelli 1998, Hyne and Everett 1998, De Witt et al. 1999, Marsden and Wong 2001, King et al. 2006, Picone et al. 2008). De Witt et al. (1999) found the potential for laboratory-based tests to be applicable for investigating contaminated sediments from the field by conducting an experiment to evaluate the in vitro and in situ concentration-mortality response of *P. lucasi* exposed to sediment contaminated with different concentrations of Cd. They found that laboratory-based tests can be as sensitive (and possibly over-sensitive) as in situ tests of the same duration for a single metal. Studies that compare results of toxicity tests with field effects are important to compare the predictions made by in vitro testing (Hickey and Clements 1998). Field observations have found very low invertebrate diversity at stream sites corresponding to >10% impervious area in Hamilton urban streams (Collier et al. 2009).

It is well understood that in reality, metals interact together as well as with other compounds, to have additive, synergistic and antagonistic effects (Rand et al. 1995). Testing the toxicity of whole sediments has been used to assess effects on the presence or absence of populations of amphipods and macroinvertebrates in general (Swartz et al. 1982, Nipper et al. 1998, McCready et al. 2004). A review article analysing laboratory toxicity data of amphipod survival and infaunal populations revealed that the diversity and/or abundance of benthic invertebrates were markedly reduced in the majority of samples determined to be toxic compared to samples that had the highest diversity and/or abundance (Long et al. 2001), supporting the use of mortality and reburial end points for assessing sediment toxicity.

However, there are weaknesses to laboratory sediment toxicity tests that cannot be overlooked. Collection methods of sediments can alter physical, chemical and microbiological components, ultimately affecting bioavailability to organisms (Burton 1992, Burton et al. 1992, Chapman et al. 1998), with Cu, Fe and Zn appearing to be particularly sensitive to sample handling (Burton 1992). Furthermore, homogenisation of sediments, as carried out in the present study, has been shown to decrease toxicity of some metals (Anderson et al. 2001), and increase toxicity of other compounds in sediments (Burgess and McKinney 1997). However, complete elimination of the artefacts of in vitro sediment toxicity testing is difficult (Clearwater and Valler 2012). It may be that some releasing of metal species occurred in the present study by the removal of overlying waters following equilibration prior to the commencement of the test, causing alterations in sediment toxicity to *P. lucasi*. However, the net effects of any changes is likely to be minor given the muted response of *P. lucasi* to reburial in the present study.

4.4.3 Response of exposure of *Paracorophium lucasi* to Hamilton urban stream sediments

Although some sites sampled in the Hamilton stream network exceeded the ANZECC ISQG Low guidelines for concentrations of Pb, Zn, As and Hg (Table 4-2), toxicity in terms of the endpoint of survival in *P. lucasi* was only noticeable in organisms exposed to Lake Rotoroa sediments (WA) (Fig. 4-1). The stand-out contaminant in WA sediments is high As concentrations ($47.1 \pm 3.9 \text{ mg kg}^{-1}$) from the legacy of the application of NaAsO₂ in the lake as an herbicide. Copper concentrations are not considered a concern in Hamilton urban stream sediment due to no sites exceeding ANZECC ISQG Low guidelines (Table 4-2).

General processes of sorption and desorption of stream contaminants to and from sediments is outlined in Chapter 3 (3.4.2, p. 55) and further discussed in relation to As speciation (3.4.2, p. 60). The sediment toxicity tests carried out in this study were on sediments obtained in May with a concentration of As of 52.7 mg kg^{-1} , whereas sediment sampling in August and November 2012 contained lower concentrations (39.6 and 49.0 mg kg^{-1}), showing some site-specific seasonal variations. It is unclear what effect this magnitude of reduction would have had on the toxicity of site WA sediment to *P. lucasi*, if any.

Incubation of *S. fragilis* leaf material near the Lake Rotoroa outlet for 17 days from late August resulted in the leaves having an As concentration of 217.9 mg kg⁻¹ whereas original willow leaves As concentration was 8.9 mg kg⁻¹ (Fig. 4-2). Despite this, *P. fluviatilis* were observed to be abundant on leaves incubated at this site. This species of amphipod is amongst the most commonly occurring in New Zealand surface waters, including lakes (Winterbourn 2000, Hogg et al. 2006, Chapman et al. 2011). There may be a number of reasons why there were large numbers of *P. fluviatilis* on these leaves in August-September when May sediments were toxic for *P. lucasi*, assuming that both species are detritivores that feed mainly on decaying organic matter and their colonising microfauna (Chapman et al. 2011). One difference between these species is that *P. fluviatilis* is not a hypogean species and is commonly found among vegetation and algae (Hogg et al. 2006, Chapman et al. 2011), whereas *P. lucasi* burrows into sediments. Although the leaf bags were weighted to the bottom sediments at this site, the bags themselves were not in the sediments and therefore *P. fluviatilis* may not have been affected by the sediments in the same way the burrowing *P. lucasi* was in the sediment toxicity testing.

Santoro et al. (2009) assessed the occurrence in sediment and bioaccumulation of various metals including As in aquatic insects with a range of larval feeding behaviours in a river in Italy. They found mean sediment As concentrations of 9.4 to 17.3 mg kg⁻¹, far less than those in the present study, and concluded that all kinds of organisms, collector-gatherers, predators and filterers take up increasing amounts of As as contamination of the sediment increases. However, one crucial conclusion for this study was that ingestion of sediment or substratum was the most likely uptake route of these metals, instead of water or other organisms. It is unlikely that the *P. fluviatilis* is less sensitive to As than *P. lucasi* because *P. fluviatilis* is ranked above *P. lucasi* in sensitivity to Cd and *P. fluviatilis* is ranked second only in sensitivity of New Zealand freshwater invertebrates to both Cu and Zn behind *C. dubia* (Hickey 2000).

Although not measured in the present study as an endpoint, increased emergence of *P. lucasi* from WA sediment was observed on the first day of the test after the initial adding of amphipods to sediments and their burial, with some individuals floating on the water surface. This possibly indicates that WA sediments may have had a sub-lethal effect even though there was no difference in reburial behaviour following the sediment toxicity tests. Marsden and Wong

(2001) also measured the non-lethal endpoints of reburial and emergence in the New Zealand corophiid *P. excavatum* after exposure to Cu-spiked sediments. Individuals that survived the toxicity test were able to rebury themselves effectively as in the present study. However, the emergence response to sediment Cu was not immediate and increased over time, possibly because of their dependence on sediments for survival. They concluded that although this species is more sensitive to Cu than many other species, both sub-lethal endpoints were ineffective in distinguishing toxic and non-toxic sediments. Bat and Raffaelli (1998) found the same response in the estuarine amphipod *Corophium volutator* from Scotland, exposed to sediments spiked with solutions of Cu, Zn or Cd for 10 days, whereby emergence increased with increasing metal concentrations. Cadmium was found to be much more toxic than Cu or Zn to this species, possibly because the accumulation characteristics of amphipods may depend on whether the metals are essential (as Cu and Zn are) or not (Cd) (Marsden and Wong 2001). Sediment concentrations of over 30 and 21 mg kg⁻¹ for Cu and Zn respectively, showed marked decreases in amphipod survival and reburial in that study where concentrations of Zn were vastly lower than some of the Zn concentrations of sediments in Hamilton streams (e.g. sites PR_A, RN_A, KA, BA, NA, GA, see Table 4-2). It may be that Zn in particular is generally not bioavailable in Hamilton streams because of adsorption to other compounds such as abundant Fe and Mn hydroxides or OC.

Since PAHs are resistant to degradation, have carcinogenic properties and can bioaccumulate through the food chain, their risk to aquatic organisms is long term (Haritash and Kaushik 2009, Wu et al. 2011). Sediment toxicity tests are used for assessing toxicity of aquatic organisms, including amphipods, to organic contaminants such as PAHs as well as metals and metalloid contaminants (Reichert et al. 1985, Wirth et al. 1998, Brack et al. 1999, Scarlett et al. 2007, Morales-Caselles et al. 2008), with toxicity to organisms of some PAHs able to be influenced by UV light (Barron 2007). Studies that include exposure to UV light and evaluation of phototoxic effects have been conducted in sediment toxicity tests (Ankley et al. 1995, Boese et al. 1999, Bell et al. 2004).

Significant mortality and reduction in reburial behaviour were measured effects of exposure of the amphipod *Rhepoxynius abronius* to sediments in a 10-day sediment toxicity test containing mixtures of the PAHs anthracene, benz[a]anthracene, 2-methylanthracene, benzo[b]-fluoranthene and fluoranthene

followed by a one-hour UV exposure (Boese et al. 1999). Two photoproducts of benzo[a]pyrene and benzo[a]pyrenequinone were the most toxic PAH photoproducts tested with *Daphnia magna* (Lampi et al. 2006). Four of these PAHs were present in some sediments collected from the Hamilton urban stream sites (benz[a]anthracene, benzo[b]fluoranthene, fluoranthene and benzo[a]pyrene, see Table 4-2). Although concentrations of these PAHs were highest in Lake Rotoroa sediment (WA), they were all well below the ANZECC ISQG Low guidelines. Almost all *P. lucasi* individuals that survived the initial sediment toxicity test in the present study, survived and reburied following exposure to UV light. From these results, it can be concluded that there is no added photo-induced toxicity of Hamilton urban stream sediments (in particular site WA) to *P. lucasi*. In general, however, reduced survival of *P. lucasi* after the initial exposure to whole sediments from the Lake Rotoroa outlet site means the effects of PAHs in addition to As cannot be ruled out.

4.4.4 Growth and survival in *Paranephrops planifrons*

Growth and survival were endpoints measured in the experiment involving *P. planifrons* fed *S. fragilis* leaf material incubated in Hamilton stream sites. Detritus, or decomposing leaf fragments and associated micro-organisms is an important source of food for freshwater crayfish (Huryn and Wallace 1987, Usio 2000, Zhang et al. 2004, Bondar et al. 2005, Olsson et al. 2008). Plant food items were found in 94% of noble crayfish (*Astacus astacus*) guts (Olsson et al. 2008) and represented over 80% of all items found in guts of *P. planifrons* (Parkyn 2000).

The amount of leaf material used for this experiment was based on mean consumption rates of adult *P. planifrons* (n=7) fed *S. fragilis* measured by Parkyn (2000); 14.3 ± 2.0 mg dry weight h^{-1} . This was measured after starving crayfish for 72 hours to empty their guts and left to feed for four hours. Although the consumption rates measured in the study by Parkyn (2000) were quite high, and consumption rates were not measured in my study, partly due to limited incubated leaf material available, this amount proved to be an underestimate. This underestimate is illustrated by the termination of the experiment at 5 weeks when little growth had occurred. From the initial stages of the present experiment, it was evident that the larger crayfish (above 5 g especially) processed and consumed considerable amounts of the leaf material provided. In their study of protein requirements in juvenile *Cherax quadricarinatus*, Cortés-Jacinto et al.

(2003) found that food intake tended to decrease with an increase in dietary protein content (Olsson et al. 2008). It was observed that crayfish in the present study consumed far more food than those fed chironomids probably to meet energy requirements.

Survival of crayfish was high in all treatments, with lowest survival for those fed leaves incubated at site NA (75%, n=8). Survival was higher in the present study than for juvenile *P. planifrons* fed leaf detritus for 9 weeks by Parkyn (2000), however, tree fern was fed to crayfish in that study, and its low food quality probably contributed to the poor survival rates (13 - 63%). Wigginton and Birge (2007) found that moulting was a sensitive life stage in *Orconectes* and *Procambarus* crayfish during exposure to metals, with most individuals that died having moulted shortly before or during exposure to Cd. Only two deaths occurred whilst moulting in the present study, in NA and WA, which could be the result of increased sensitivity to the diet-fed metals or possibly stress from handling (Parkyn et al. 2000).

A number of studies concur with the conclusion of Parkyn (2000), that juvenile crayfish have higher protein requirements during the early stages of development (Olsson et al. 2008), and consequently young crayfish are more predatory in their natural environments (Goddard 1988, Whitledge and Rabeni 1997, Coreia 2003). This is unlikely to be the cause of death for the crayfish in this experiment since mean crayfish OCL measured prior to death was 14.8 ± 1.9 mm, which is larger than juveniles characterised in other studies where predation was the dominant feeding method. Riordan (2000) estimated *P. planifrons* would reach an estimated 10 mm OCL by the end of the first year and 16 mm in the second year of growth. The juvenile cohort tested by Parkyn (2000) had OCLs of 4.9 - 9.3 mm, much smaller than the crayfish used in the present study.

The sexes of crayfish in the present study were not distinguished and may not be relevant to growth rates since Hopkins (1967) and Whitmore and Huryn (1999) found no discernible difference between male and female growth increment at moult in *Paranephrops* spp. Because no crayfish moulted twice in the present study, comparisons could not be made of intermoult periods.

Parkyn (2000) found high variation between individual juvenile crayfish in GR (approximately less than 0.2 % weight gain per day⁻¹) when fed leaf detritus (tree

fern and subsequently *S. fragilis*). Hammond et al. (2006) also reported low GRs of 0.53 ± 0.05 % weight gain day⁻¹ in *P. zealandicus* and described them as a slow growing species. Similarly, GR was low across feeding treatments in the present study; Chironomid, 0.27 ± 0.16 ; PD, 0.38 ± 0.1 ; NA, 0.09 ± 0.07 ; WA, 0.39 ± 0.11 ; RN_A, 0.24 ± 0.03 ; KA, 0.34 ± 0.2 ; KC, 0.22 ± 0.12 % weight gain day⁻¹. All GR for *Paranephrops* reported above are much lower than the mean of 3.4% weight gain day⁻¹ seen in *C. quadricarinatus* fed an "optimal diet" of 31% crude protein in a study conducted by Cortés-Jacinto et al. (2003).

Relationships between GR and treatment metal concentration were generally poor, except for relationships with Ba and Ni. Although these relationships were statistically significant, they must be treated with caution since they were driven solely by the high Ba and Ni concentrations and the low GR in crayfish fed leaves from this site. This aside, the high metal content of leaves from the outlying site NA cannot be ruled out as a reason for the lower survival and GR of crayfish fed leaves from this site. In contrast, high As concentrations on the incubated leaves from site WA (217.9 mg kg⁻¹ cf 8.9 mg kg⁻¹ in original *S. fragilis* material) did not appear to affect the GR of crayfish in this study with this site having the greatest increase of all treatments.

Aside from metal concentrations in food, it is possible that the varying breakdown rates of the leaves incubated in this study played an important role in the differential GRs seen between treatments. Contaminant-induced alterations of microbial communities can have some influence on the breakdown of leaf material but other factors may be far more important (Carlisle and Clements 2005), such as the species of plant from which the leaves came (Parkyn and Winterbourn 1997), quality and temperature of the water (Kaushik and Hynes 1968, Mutch and Davies 1984), high flows (Paul and Meyer 1996), and insect feeding (Mutch and Davies 1984, Collier and Winterbourn 1986). Although some authors have suggested an increased palatability of conditioned leaves to aquatic insects (Collier and Winterbourn 1986, Lester et al. 1994), it appeared that the visibly least processed leaves (those incubated in site PD and WA; see Plate 4-2), supported the greatest GR observed in crayfish in the present study. My observations of invertebrates colonising leaf packs suggest that invertebrate feeding was not a major influence of leaf breakdown, and most streams would have experience similar flood frequencies. Results showed there were no obvious effects of leaf incubation temperature on GRs, however.

4.4.5 Summary

In conclusion, *P. lucasi* and *P. planifrons* were chosen to test endpoints of mortality, and sub-lethal behaviour of reburial and growth with respect to contaminants in sediments from, or fed leaf material incubated in, Hamilton urban streams. Although *P. lucasi* is not found in the Hamilton stream network, and *P. planifrons* is only located in a few locations, they are relevant species to study in order to draw wider conclusions about whether stream contaminants are affecting macroinvertebrate diversity in these streams.

Whole sediments collected from streams in the Hamilton gully network were not toxic to *P. lucasi*, with one exception, those from the Lake Rotoroa outlet site, WA. The major contaminant that is thought to be causing this reduction in survival compared with many other sites is As from the legacy of the historic application of the herbicide NaAsO₂. However, this site also had, by far, the highest PAH concentration in sediment, and although these were well below the ANZECC ISQG Low values the interaction of these with As cannot be ruled out as a factor causing mortality. Burial behaviour and ingestion of contaminated sediment particles is the probable reason for the toxic response seen in *P. lucasi*. There were no phototoxic effects of the sediments or effects on reburial behaviour.

Without measurements of metals in crayfish tissues, it is difficult to draw conclusions on the bioaccumulation of the elevated metals and metalloids seen on incubated *S. fragilis* leaves on which they were fed. Although crayfish are generally good indicators of metal bioaccumulation, survival was high, and GR variable, indicating no lethal or sub-lethal effects of these metals on *P. planifrons* over a 5-week period. Longer term experiments may be required to determine whether metals that clearly accumulate on potential food sources have long-term effects on crayfish growth.

Chapter 5:

General Discussion

5.1 Objective of thesis

Chapters 3 and 4 of this thesis establish to what degree contaminants derived from the surrounding urban landscape of Hamilton City are carried in stream water and accumulate in sediments and ultimately whether these are having a constraining effect on freshwater biota. The contaminants that were the main focus of this study, metals, metalloids and PAHs, which are those derived by the human-induced influences of impervious surfaces (from vehicle use and building materials), upstream agricultural activities and past land use (e.g. historic landfills).

This main objective was achieved by: (i) measuring contaminants in stream water at base flow and during two rain events in catchments with contrasting levels of upstream imperviousness; (ii) quantifying spatial and temporal trends in sediment contamination and examining relationships upstream imperviousness; (iii) investigating the bioavailability of contaminants by measuring concentrations in shortfin eel tissues and bile; and (iv) assessing the effects of whole sediment exposure and diet-borne metals through measurement of lethal and sub-lethal endpoints in sensitive freshwater crustaceans.

5.2 Effects of rain events on contaminant concentrations

Storm flow concentrations of TSS and the main stormwater metals of Cu, Pb and Zn were compared with base flow data in the Mangakotukutuku (less developed residential), Waitawhiriwhiri (industrial) and Kirikiriroa (residential) catchments as well as the smaller completely urbanised catchment of Gibbon's Creek. Total suspended solids were highest in the lower reaches of the both the Mangakotukutuku and Waitawhiriwhiri catchments and TSS from the latter catchment contained higher metal content because of runoff from higher impervious area.

Dissolved Cu and Zn at many sites were impacted in rain events when concentrations exceeded ANZECC (2000) water quality guidelines, especially sites on smaller streams with entirely urban catchments and reduced flow influencing dilution capacity. These guidelines were set to protect 95% of species with 50% certainty. Because of a shift away from relying solely on chemical guideline values for managing water quality, the use of direct toxicity testing and/or biological monitoring is recommended (ANZECC 2000). Direct testing of stream water toxicity on biota was not conducted in this study as this had been conducted in 2001, using native and international standard aquatic organisms (Hickey et al. 2001). Results concluded that the old and new residential stormwater showed no acute toxicity on the invertebrates *Ceriodaphnia dubia*, *Paracollope fluviatilis* and *Potamopyrgus antipodarum*. The commercial and industrial stormwater samples showed toxicity to these invertebrates, although the effect on *P. antipodarum* was slight. Dissolved Cu (commercial 12.3 $\mu\text{g L}^{-1}$; industrial 5.7 $\mu\text{g L}^{-1}$) and Zn (commercial 503 $\mu\text{g L}^{-1}$; industrial 496 $\mu\text{g L}^{-1}$) were pinpointed as the cause of this toxicity (Hickey et al. 2001). Concentrations of Cu at sites M3 and W3 in rain events in the present study achieved levels similar to the industrial catchment measured by Hickey et al. (2001), however maximum Zn concentrations in these small streams were less than half that measured in stormwater from the commercial and industrial catchments in the 2001 study because of the effect of dilution by streamwater. Overall, especially in sites with low base flows, toxicity of stream water during rain events to sensitive macroinvertebrates such as crustaceans and EPT taxa could be occurring.

5.3 Sediment contaminants: bioaccumulation, bioavailability and toxicity

Because sediments serve as both a source and sink of stream contaminants and they represent the greatest potential for stream pollution (Power and Chapman 1992, Arakel 1995, Williamson and Morrissey 2000), the main focus of this study was sediment-bound contaminants. Analyses of metals and metalloids in sediment highlighted sites where there may be significant concerns for biota, especially where concentrations exceeded ANZECC ISQG Low and High values.

5.3.1 Copper, lead and zinc

Copper is not of concern in these stream sediments because no sites exceeded ISQG values, but Pb and Zn did reach levels of concern, especially, in the small, completely urbanised catchments of Gibbon's Creek, Ranfurly Park and to a lesser degree Bankwood Stream, all of which drain completely urban catchments on the true right side of the Waikato River. Although agricultural sources are affecting upstream peri-urban stream sediment Zn concentrations, as seen in lakes of the Waikato Region (Kim 2011), sources of contamination in the aforementioned streams with 100% urban catchments are solely related to runoff from impervious surfaces, a conclusion supported by the relationships between Cu, Pb and Zn sediment concentrations and upstream imperviousness. From results of the amphipod sediment toxicity test, it appears that Zn may not be completely bioavailable in these sediments with the muted response of *P. lucasi* with results from bioaccumulation of Zn in eel livers can neither support nor refute this because of this metal being under physiological control. Lead is accumulating in eels from Gibbon's Creek, where high Pb is found in sediments, and also in eels from the upper Rukuhia branch of the Mangakotukutuku (site RK_B) despite low levels in sediments suggesting an unknown source of lead contamination. The accumulation of Pb in muscle tissues was generally low except for one from Gibbon's Creek which exceeded the FSANZ maximum allowable level of Pb in fish posing a risk to consumers of eels caught in this stream. Moreover, toxicity testing revealed, however, that the sediments of these small, highly urbanised catchments are not toxic to the hypogean amphipod *P. lucasi*.

5.3.2 Arsenic

Other areas for concern within the boundary of Hamilton City, are those that are affected by past land use such as the historic application of NaAsO₂ in Lake Rotoroa (outlet site WA) and landfill leachate (site KB and possibly to a lesser degree the hospital site of NA). Lake Rotoroa sediment As concentrations have not significantly decreased over the past few decades between the MSc. research conducted by Rajendram (1992) and the more recent Waikato Regional Council investigation by Rumsby (2011). Arsenic in the sediments of Lake Rotoroa is bioavailable, not only to shortfin eels, which are bioaccumulating As in their livers, but is also to *P. lucasi* which showed significantly decreased survival compared with those amphipods exposed to sediments from other Hamilton urban stream sites, indicating direct toxic effects. The observation of abundant *P.*

fluviatilis amphipods, which have been shown to be a sensitive species (Hickey 2000) on willow leaves incubated above the sediments of this site (see Chapter 4) and suggests that direct ingestion of contaminants bound to sediments is the route for exposure. It is not known what effects, especially sub-lethal effects such as reduced growth, the bioaccumulation of this toxic metalloid is having on resident eels in the lake. Since this species is accumulating the metalloid in livers and not muscle tissue, measured concentrations did not trigger food safety guidelines.

5.3.3 Mercury

Mean Hg concentrations in sediments were quite high, exceeding ANZECC (2000) ISQG Low values at a number of sites, in particular the small catchment streams of Normandy Avenue (NA) and Graham Park (GA). This metal appears to bioaccumulate quite readily within both liver and muscle tissues of shortfin eels. The upper Rukuhia channel of the Mangakotukutuku is another site of interest, in that, similarly to the result of Pb in sediment and eels, there appears to be an unknown source of Hg contamination in eel livers from this site. According to Mason and Barak (1990), liver concentrations are indicative of the current contamination of a site, although this is not supported by the poor relationship between sediment and eel liver concentrations in the present study. Mercury concentrations in muscle tissue from most sites are sufficiently high to warrant a low recommended restriction on their consumption with respect to the USEPA non-carcinogenic Risk-Based Consumption Limits (RBCL). These non-carcinogenic RBCLs are for chronic, systemic effects that may occur to humans when consumed more often than is what is recommended.

5.3.4 Polycyclic aromatic hydrocarbons

The site with by far the highest sediment concentrations of PAHs was Lake Rotoroa outlet, although concentrations measured in May were still lower than the ANZECC (2000) ISQG Low values (for individual PAHs as well as combined high molecular and low molecular weight PAHs). However, these concentrations cannot be ruled out as a contributing factor to the decreased survival of *P. lucasi* to the whole sediments of this site. Exposure of amphipods to UV light did not produce either a lethal or sub-lethal phototoxic response. Analysis of the metabolite of pyrene, pyrene-1-glucuronide in bile showed that these eels are

being exposed to, and are metabolising, this PAH. Concentrations of pyrene-1-glucuronide in bile of these eels were comparable to those measured in European eels (*A. anguilla*) from some industrial estuaries in the U. K. (Ruddock et al. 2003).

5.3.5 *Anguilla australis* as an indicator species for Hamilton urban streams

In general, shortfin eels are a good indicator of the bioavailability of metals in these streams because of their resident nature (Chisnall and Kalis 1993, Jellyman and Sykes 2003), benthic and carnivorous habits, and they have high lipid content (Arleny et al. 2007, Belpaire and Goemans 2007, Stewart 2011). Although relationships between liver tissue concentrations and sediments were poor, most of the variability can be explained by the heterogeneity in environmental factors governing the bioavailability of these contaminants. An example this is seen in the low concentration of Pb and Hg in the sediments of RK_B compared to higher concentrations of these metals in livers of eels in comparison to other sites. These metals are obviously more bioavailable at this site because of these unknown environmental variables including relationships of metal sorption and grain size as described by Neto et al. (2011).

5.3.6 Is metal contamination constraining the macroinvertebrate biota in Hamilton urban gully streams?

Lotic invertebrate communities are comprised of various taxonomic groups that have different feeding mechanisms and requirements for food and habitat. Winterbourn (1999) described macroinvertebrates as the "integrators of information on stream ecosystem structure and function as well as water quality." Collier et al. (2009) reported that most urban streams were dominated by tolerant invertebrate species including *P. antipodarum* (31% of total number across all sites), Oligochaeta (26%) and Chironomidae (21%) indicative of degraded ecosystems. However, some Mangakotukutuku catchment sites had particularly diverse or abundant EPT faunas relative to the other sites in the Kirikiriroa and Waitawhiriwhiri catchments. The macroinvertebrates found on the incubating leaves in the present study, support the conclusion of Collier et al. (2009) that Hamilton urban streams generally have depauperate communities, raising the question whether this could partly be a result of metal exposure?

Hickey and Golding (2002) assessed the response of New Zealand macroinvertebrates to the presence of Cu and Zn mixtures in water in mesocosms. Specifically, caddisflies and chironomids were tolerant and mayflies and stoneflies were sensitive to metal exposure, a pattern also noted by Hickey and Clements (1998). Hickey and Golding (2002) recommended that the abundance of the mayfly *Deleatidium* spp. could be a good indicator of impacts of metals stress on communities. In support of this, *Deleatidium* spp. was found on willow leaves in the present study, only at PD, the site that is the least affected by all metals. *Paracorophium lucasi* is ranked fifth directly behind *Deleatidium* in terms of toxicity to Cd in laboratory bioassays (Hickey 2000), but there are no results for other metals or metalloids that can assist in directly comparing the sensitivity of species used in the present study.

Koura were absent from most of the urban sites surveyed by Collier et al. (2009). Although metal and metalloids clearly accumulated on leaves incubated in a range of urban streams for the kōura feeding experiment, correlations with sediment concentrations were generally good, survival was high in all crayfish and growth rates were not significantly different over 5 weeks, eliminating the possibility that diet-borne metals is a constraining factor influencing the presence of this species in these streams. However, dissolved metals, especially Zn, shown to be very high during rain events in these streams, could be directly affecting this species.

5.4 Recommendations for further study

This study leads to a number of recommendations for further research for the Hamilton gully stream network. The influence of high Fe concentrations is relatively unknown, especially the resulting Fe flocculation observed in the present study in many of these streams and the effect of redox potential and pH on the processes of adsorbing and releasing of metals. Also, investigating sub-lethal and lethal endpoints of metal bioaccumulation in eels, especially in response to As concentrations, would be beneficial to draw conclusions on actual effects of bioavailable contaminants seen in this study for this species. Also the data from eel bile analysis indicate progressive accumulation of PAH metabolites with increasing distance downstream in at least two catchments (Waitawhiriwhiri and Kirikiriroa) and are worthy of further investigation. Finally, during field work for this thesis, especially during the winter months, I observed flood disturbance

to vegetation dramatically higher than base flow stream levels, indicating, 1) massive increases in water discharge during storms; and, 2) very rapid changes in water levels and presumably velocities. Measuring these parameters in typical urban streams during storm flow events could assist in the understanding of the many constraints on biota within these streams.

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Appendices

Appendix A. Raw water quality measurements of pH, conductivity, total suspended solids (TSS) and hardness of water samples from the Mangakotukutuku, Waitawhiriwhiri, Kirikiriroa and Gibbon's Creek (PR_A) catchments collected during an antecedent dry period (4/4/12), and autumn and spring rain events (27/04/12 and 3/09/12).

Site	pH			Conductivity ($\mu\text{S cm}^{-1}$)			TSS (mg L^{-1})			Water hardness* (mg/L of CaCO_3)		
	4/04/2012	27/04/2012	3/09/2012	4/04/2012	27/04/2012	3/09/2012	4/04/2012	27/04/2012	3/09/2012	4/04/2012	27/04/2012	3/09/2012
M1	5.9	6.06	5.56	192.8	165	145.2	62.2	164	114.4	43.4	35.3	32.5
M2	6.01	5.9	5.51	188.1	140.5	130.2	79	245.6	118.6	40.8	30.6	29.2
M3	6.2	5.8	5.33	93.6	135.2	63	24.6	26.8	117	43.8	20	18.1
W1	5.95	5.68	5.73	209.1	94.6	173.2	66.4	234.2	124.4	48.1	20.3	41.3
W2	5.84	5.48	5.44	198	72.3	149.5	75.2	114.6	298	44.1	16.2	32.8
W3	5.01	5.14	5.44	193	85.8	106.4	120.8	98.4	105.8	44	19.6	24.7
K1	6.04	5.78	5.58	228.6	143.8	228.8	65.2	174.8	132.6	52.3	28	53.2
K2	5.6	5.6	5.46	227.4	147.3	187.1	63.8	182.2	62.6	49.5	30.2	40.1
K3	5.48	5.94	5.72	236	204.3	218.7	36	30.8	47.2	58.5	49.1	57.7
K4	5.58	5.48	5.34	261.7	106.8	69.4	67	26.2	24.4	39.2	22.2	15.1
PR_A	5.86	6.05	5.24	201.2	107.3	69.5	74.2	32.2	23	41.3	22.4	15.4

* calculated from Ca and Mg concentrations

Appendix B. Raw sediment element concentrations (mg kg⁻¹) for sampling conducted on 7-8/5/12 (May), 28-29/8/12, and 29-30/11/12 (Nov) in Hamilton urban stream sites. Key to site labels is provided in Table 2-1. Dashes indicate no data, HIGH indicates concentrations exceeding the measuring range of the mass spectrometer used for metals analysis using ICP-MS.

Site	Ag			Al			As			Ba			B			Ca			Cd			Co			Cr
	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May
PB	0.087	0.025	0.072	21382	HIGH	HIGH	10.7	1.53	2.38	412	85.0	108	2.86	0.411	0.723	2835	697	776	0.250	0.036	0.048	5.54	1.71	2.50	5.83
PC	0.043	0.030	0.046	12816	HIGH	HIGH	12.4	2.94	4.95	261	70.8	113	2.32	0.574	1.17	2177	1259	1418	0.103	0.035	0.054	3.65	2.44	2.57	4.99
PD	0.025	0.029	0.033	6001	HIGH	5439	3.91	2.59	2.93	123	50.2	71.1	0.83	0.198	0.473	1676	1005	1217	0.072	0.038	0.043	2.29	3.02	2.90	5.13
RK_B	-	0.026	0.028	-	HIGH	6260	-	2.77	3.51	-	50.4	63.0	-	0.491	0.705	-	1532	1965	-	0.031	0.041	-	1.56	2.59	-
RK_D	-	0.025	0.048	-	HIGH	HIGH	-	1.73	4.11	-	44.3	76.9	-	0.328	0.699	-	799	888	-	0.025	0.049	-	1.25	1.70	-
NA	BDL	0.106	0.178	7888	HIGH	HIGH	9.01	6.17	12.8	255	66.0	92.1	76.03	5.70	9.60	25438	2710	3051	0.062	0.061	0.112	10.0	4.08	3.80	12.2
GA	8.24	2.09	3.06	12951	HIGH	HIGH	9.33	3.49	4.14	189	80.7	82.6	2.04	1.01	1.13	1860	1008	1083	0.142	0.064	0.050	3.28	1.60	2.22	8.16
WA	0.062	0.046	0.058	12779	HIGH	HIGH	52.7	39.6	49.0	104	85.2	91.5	1.70	1.37	1.51	2278	2159	2355	0.082	0.068	0.066	3.29	2.91	3.69	7.44
WB	-	0.031	0.050	-	HIGH	HIGH	-	4.45	11.8	-	53.8	85.8	-	1.26	1.71	-	2221	2956	-	0.082	0.125	-	2.44	3.70	-
WF	-	0.121	0.096	-	HIGH	5354	-	3.34	2.81	-	42.5	43.9	-	1.15	1.15	-	1249	1250	-	0.092	0.088	-	3.00	2.68	-
PR_A	BDL	0.058	0.066	8057	HIGH	HIGH	24.9	9.09	21.6	202	70.7	115	5.39	1.56	3.19	3886	2640	3229	0.396	0.162	0.292	11.3	6.95	8.48	14.8
SA	-	0.033	-	-	HIGH	-	-	9.22	-	-	47.1	-	-	0.909	-	-	1554	-	-	0.077	-	-	3.32	-	-
RN_A	0.240	0.035	0.178	29913	HIGH	5272	53.8	5.43	6.30	353	56.3	52.7	7.01	0.872	1.48	6584	1496	1376	0.787	0.154	0.141	7.71	2.16	2.21	27.9
BA	BDL	0.021	0.035	9249	HIGH	5188	25.9	5.47	9.40	174	35.9	64.6	2.75	0.344	1.41	2583	808	1270	0.310	0.066	0.121	4.58	1.41	2.26	9.92
KA	BDL	0.077	0.084	12992	HIGH	HIGH	16.7	16.5	26.4	212	256	335	2.65	1.88	3.21	1887	3220	3929	0.486	0.805	0.884	3.66	4.52	5.80	9.59
KB	BDL	0.045	0.149	6481	HIGH	HIGH	24.3	17.9	94.2	263	145.7	699	4.66	3.05	12.0	2417	2071	6088	0.072	0.086	0.243	3.72	3.64	7.76	7.25
KC	BDL	0.048	0.116	5711	HIGH	HIGH	25.7	10.7	22.6	125	68.2	104	1.09	0.508	1.12	1903	1333	1886	0.123	0.099	0.125	5.48	2.91	5.27	4.79

Site	Cr		Cu			Fe			Hg			K			Mg			Mn			Na			Ni	
	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug
PB	2.53	3.67	8.34	2.17	2.82	35835	8709	9563	0.361	0.098	0.103	557	361	302	778	419	419	2843	495	748	264	128	177	2.68	1.06
PC	5.81	5.04	5.34	2.44	3.44	38655	26048	15333	0.182	0.084	0.067	444	249	318	606	404	493	2465	472	946	271	151	223	2.19	1.58
PD	8.36	6.60	2.76	1.72	2.10	20504	40100	17917	0.106	0.036	0.037	271	178	224	606	403	542	662	214	282	170	116	202	1.61	1.64
RK_B	4.30	5.96	-	2.80	13.6	-	16730	15030	-	0.060	0.038	-	296	259	-	682	943	-	98.7	159	-	179	213	-	2.63
RK_D	3.33	4.54	-	2.27	3.99	-	9776	10153	-	0.085	0.040	-	327	289	-	483	523	-	82.4	100	-	127	159	-	1.49
NA	9.67	14.89	41.1	13.1	21.9	21191	29468	18147	0.637	0.288	0.190	519	353	396	3227	2577	1944	583	308	418	1165	254	348	18.4	13.89
GA	3.88	4.81	42.9	12.7	18.0	17362	11422	8498	1.138	0.238	0.103	542	340	328	684	472	579	292	149	216	235	163	206	3.74	1.76
WA	6.07	8.06	10.5	8.84	8.67	12298	17985	13606	0.219	0.146	0.049	441	412	385	1090	993	1215	400	366	499	246	220	286	4.60	4.20
WB	6.27	16.56	-	6.51	15.2	-	21779	39703	-	0.072	0.064	-	370	376	-	952	1535	-	141	193	-	241	333	-	3.88
WF	8.54	7.31	-	6.09	6.93	-	32723	12590	-	0.070	0.026	-	226	280	-	756	912	-	200	146	-	133	241	-	3.96
PR_A	11.5	12.9	28.6	10.6	19.9	43020	46878	38500	0.400	0.165	0.070	618	429	471	1738	2508	2056	578	374	537	434	278	432	11.7	11.61
SA	7.44	-	-	5.27	-	-	43765	-	-	0.076	-	-	298	-	-	1089	-	-	292	-	-	195	-	-	4.75
RN_A	5.73	5.47	52.6	6.88	6.27	43098	11715	6589	0.753	0.116	0.037	1233	374	417	2463	975	1085	645	79.7	103	573	213	2069	11.2	3.81
BA	3.48	5.16	23.0	2.80	6.52	32416	13814	11603	0.424	0.042	0.027	495	205	247	1063	540	878	455	73.9	179	301	122	246	5.36	2.10
KA	7.84	9.56	13.9	14.5	24.1	107776	HIGH	HIGH	0.299	0.267	0.135	485	627	822	544	632	757	267	232	395	201	202	273	4.25	5.04
KB	5.62	11.1	14.4	8.57	30.4	27923	36975	74829	0.203	0.121	0.117	495	410	671	885	808	1195	695	468	2058	263	214	423	3.28	2.83
KC	3.42	5.09	7.53	3.80	6.95	43384	26816	30391	0.198	0.100	0.047	420	358	368	598	472	680	662	264	506	257	224	295	3.10	2.17

Site	Ni	P			Pb			Se			Sr			Tl			U			V			Zn		
		Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug	Nov	May	Aug
PB	1.48	1486	206	283	11.7	3.91	4.72	0.912	0.115	0.369	33.8	6.58	9.10	0.283	0.087	0.089	0.768	0.225	0.267	26.6	11.4	19.7	75.2	20.0	27.5
PC	1.86	680	371	373	10.7	9.30	9.77	0.521	0.227	0.341	24.1	8.41	14.7	0.141	0.045	0.060	0.509	0.254	0.319	21.8	53.1	26.5	42.5	39.3	31.0
PD	1.83	522	331	365	4.48	7.00	5.65	0.287	0.188	0.378	15.9	5.25	11.0	0.067	0.031	0.035	0.213	0.217	0.212	36.8	95.1	63.1	33.6	57.9	44.9
RK_B	3.95	-	928	1188	-	9.22	16.0	-	0.150	0.202	-	13.8	24.7	-	0.032	0.022	-	0.208	0.237	-	28.2	35.5	-	35.2	47.8
RK_D	2.14	-	335	1096	-	9.24	11.7	-	0.088	0.312	-	7.70	14.6	-	0.039	0.057	-	0.249	0.364	-	18.5	19.9	-	25.4	44.0
NA	9.71	414	423	450	21.8	19.4	27.5	1.09	0.343	0.471	294	48.7	63.9	0.088	0.056	0.042	0.453	0.226	0.267	41.2	49.0	29.1	172	107	157
GA	2.32	449	194	208	51.7	20.6	21.8	0.506	0.194	0.270	25.5	11.7	14.1	0.132	0.054	0.055	0.857	0.343	0.329	27.4	18.0	23.7	169	65.8	72.4
WA	4.88	212	301	273	24.4	18.3	20.7	0.553	0.344	0.426	29.0	28.8	29.7	0.083	0.047	0.046	0.467	0.407	0.408	34.5	34.7	49.9	65.5	52.8	62.7
WB	6.88	-	540	1082	-	8.15	11.9	-	0.209	0.484	-	33.9	51.5	-	0.066	0.091	-	0.227	0.337	-	41.1	78.8	-	63.0	124
WF	14.6	-	313	248	-	41.4	26.6	-	0.245	0.219	-	15.0	17.5	-	0.030	0.031	-	0.250	0.204	-	77.3	46.4	-	132	106
PR_A	11.1	974	572	1067	151	48.6	48.1	0.696	0.399	0.588	54.7	43.6	50.4	0.157	0.058	0.091	0.469	0.287	0.386	37.0	71.9	60.0	588	191	302
SA	-	-	645	-	-	44.2	-	-	0.213	-	-	17.7	-	-	0.038	-	-	0.204	-	-	65.3	-	-	106	-
RN_A	3.53	1675	300	296	154	33.4	26.5	2.01	0.191	0.289	88.6	19.7	18.8	0.310	0.064	0.045	1.421	0.229	0.195	74.8	19.7	15.9	750	128	116
BA	3.79	1182	330	609	46.5	11.9	17.8	0.702	0.139	0.288	31.4	7.50	13.5	0.157	0.042	0.047	0.513	0.112	0.186	37.0	23.4	25.1	315	62.8	97.8
KA	6.23	5112	6927	11962	10.7	10.5	13.2	1.01	1.050	1.68	22.1	29.6	47.0	0.226	0.346	0.360	0.764	0.745	1.019	45.7	45.3	57.8	166	203	262
KB	4.50	486	489	1905	10.5	6.43	13.8	0.277	0.223	1.05	35.5	26.5	106	0.043	0.053	0.089	0.262	0.230	0.358	19.8	29.6	27.4	70.6	60.8	145.
KC	3.38	477	283	509	14.6	10.2	13.7	0.321	0.233	0.400	22.5	12.2	21.4	0.090	0.081	0.092	0.336	0.246	0.297	18.2	18.5	18.1	147	73.5	125

Appendix C. Test conditions summary for amphipod 10-day sediment toxicity test and phototoxicity test.

Test Type	Toxicity test	Phototoxicity test
Test species	<i>Paracorophium lucasi</i>	<i>Paracorophium lucasi</i>
Test organism size and number	>500 µm, 20 per replicate	>500 µm, ≤20 per replicate (survivors from previous test)
Test organism source	Lake Rotorua littoral zone - Hamurana Springs confluence	Lake Rotorua littoral zone - Hamurana Springs confluence
Replicates	Six control, three per treatment	Six control, three per treatment
Control sediment	<500 µm sediment from Lake Rotorua collection site	-
Reburial sediment	<500 µm sediment from Lake Rotorua collection site	<500 µm sediment from Lake Rotorua collection site
Water volume	-	40 mL
Sediment volume	25-30 mm	20 mm
Test water	Dechlorinated Hamilton tap water	Dechlorinated Hamilton tap water
Test chambers	580 mL polypropylene containers, presoaked in freshwater	50 mL chamber under UV light 250 mL reburial chamber
Temperature	15°C	15°C
Salinity	0 ‰	0 ‰
Feeding	None	None
Aeration	Constant gentle with 1 whisker/container	Constant gentle with 1 whisker/container
Test duration	10 days	1 hour under UV (240 V, 330 W) 24 hours in reburial chambers
Observations	Daily, counting and removal of mortalities, checking aeration. Every 2-3 days measurements of pH, conductivity, temperature and dissolved oxygen. these conducted also if any mortalities occur	Constant measurement for temperature of water during exposure to UV.
Test endpoints	Survival and reburial	Survival and reburial
Test acceptability	≥ 90% survival in controls or >20% in any of the replicates	≥ 90% survival in controls or >20% in any of the replicates