Sediment Quality Survey

South-West Christchurch Integrated Catchment Management Plan Technical Series

Report No. 2
July 2005

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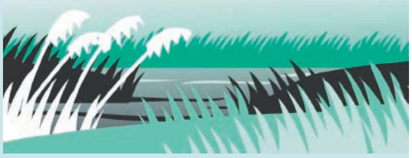

Sediment Quality Survey

South-West Christchurch Integrated Catchment Management Plan Technical Series

Report No. 2
July 2005

On behalf of

Christchurch City Council

Prepared by

Kingett Mitchell Ltd

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Executive Summary

An integrated catchment management plan is being developed by Christchurch City Council for an area of the south-western part of Christchurch. As part of this process Christchurch City Council will assess the potential effects of urban development on the catchments. The area has been partially urbanised and large green field areas are coming under pressure to be released for urban development.

Changes in catchment activities can result in detrimental effects on the sediment quality in catchment streams, which in turn can have a negative impact on freshwater biota inhabiting those waterways. Trace metals and polycyclic aromatic hydrocarbons (PAHs) are of primary toxicological concern because of their association with some forms of urbanisation.

Catchments of the Heathcote and Halswell rivers drain the south-western part of Christchurch. In 2003 a selective survey of sediments was carried out in the South-West Christchurch project area, including sediments in the downstream sections of the Heathcote and Halswell rivers. This survey was compared to a previous sediment survey to assess the change in sediment quality over time. A further comparison with similar studies in other regions provides an indication of how Christchurch sediments compare with those in waterways in other New Zealand cities.

Concentrations of the key metals copper, lead and zinc were generally lower in the Halswell River and tributary sediments compared to those in the Heathcote River catchment. In the Halswell catchment, the sediment texture appeared to have some influence on metal concentrations. In the Heathcote catchment, the natural occurrence of metals in the sediment samples were overprinted by other factors, including land use in the catchment.

In the Heathcote River catchment, the concentrations of metals generally increased from rural to residential, to mixed urban and industrial urban land-use. In the Halswell catchment, the metal concentrations generally increased from mixed land use (predominantly rural) to rural to mixed urban. This pattern has been observed in stream catchments in other cities in New Zealand.

A large proportion of sediment samples collected from the Heathcote River catchment exceeded ANZECC (2000) guidelines for lead and zinc and a small number also exceeded the guideline for copper. These samples were typically collected from industrial and urban sites in the catchment. In contrast, only five samples from the Halswell catchment exceeded ANZECC (2000) guidelines for copper, lead or zinc. None of these samples were collected from the Halswell River.

The exceedence of the ANZECC (2000) sediment guidelines provides an indication that sediment quality may be degraded to levels sufficient enough to influence the quality of the aquatic biological community inhabiting the sediments.

When data from the 2003 survey was compared to the earlier survey conducted in 1981, there was a general increase in zinc concentrations throughout the Heathcote catchment of South-West Christchurch and a general decrease in lead concentration. Copper concentrations were more variable. While there were more exceedances of the zinc ANZECC (2000) guidelines in the current survey than in the previous survey, the number of lead exceedances was slightly lower in the Heathcote River. The decrease in the lead concentration is thought to be related to the removal of lead from petrol some eight years ago. The change in the zinc concentration may reflect continual build-up of zinc from uses that have not changed.

The concentrations of PAHs in the Halswell catchment, in all three land uses, are typically lower than those in the Heathcote catchment. Within the Heathcote catchment, the background sites contained generally lower total PAH concentrations. The mixed and residential sites appeared to have the highest concentrations of total PAHs.

Overall, PAH concentrations are elevated and similar to those measured in sediments from streams in other large urban areas in New Zealand. Concentrations are sufficiently high in some parts of the Heathcote River catchment that PAHs may be contributing to potential adverse environmental effects.

Document Quality Assurance

This report has been prepared in accordance with Kingett Mitchell quality assurance procedures. All relevant quality control information in relation to biological and/or environmental data is identified within the document. The report has been reviewed and is approved for release as set out below.

	Name	**Signature**
Project Manager	**Paul May**	Paul May
Project Reviewer	**Nick Corlis**	
Director approval for release	**Paul Kennedy**	Paul Kennedy

Project Job Number	**500673**	

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Abbreviations and acronyms

ANZECC	Australian and New Zealand Environment and Conservation Council
As	Arsenic
BP	Before present
CCC	Christchurch City Council
Cd	Cadmium
Cr	Chromium
Cu	Copper
ISQG	Interim sediment quality guideline
mg/kg	concentration unit – milligrams per kilogram (equivalent to parts per million)
Ni	Nickel
NOAA	National Oceanic and Atmospheric Administration
Pb	Lead
µg/kg	concentration unit – micrograms per kilogram (equivalent to parts per billion)
USEPA	United States Environment Protection Agency
Zn	Zinc

1. Introduction

1.1 Background

Christchurch City Council (CCC) is currently in the process of developing an integrated catchment management plan and an area plan for the south-western area of Christchurch known as “South-West Christchurch” (Fig. 1.1). The area has been partially urbanised and large green field areas are coming under pressure to be released for urban development. The process for these plans involves the review of existing information, gathering of information to fill identified gaps, and assessment of information in terms of integrated catchment management and effects of urban development.

The initial review of existing information, identification gaps and preliminary assessment was completed in October 2003 (Kingett Mitchell, 2003a). This report identified that a large number of sediment samples were collected over the area in 1980 to 1981 by Robb (1988), and recommended that a repeat survey be carried out. This repeat sediment survey supplemented with water quality modelling, ecological assessment, groundwater assessment and water quantity modelling will assist the assessment of existing catchment conditions and help predict the effects and the mitigation required for the proposed development of the area.

1.2 Scope

Christchurch City Council engaged Kingett Mitchell to undertake a selective survey of sediments in the South-West Christchurch project area, including sediments in the downstream sections of the Heathcote and Halswell rivers. The location of the samples was based on:

- Sites within the upper Halswell catchment within South-West Christchurch.
- Sites from the Halswell River downstream of the South-West Christchurch project area.
- Sites within the upper Heathcote catchment within South-West Christchurch project area.
- Sites near the Heathcote River mouth at the estuary.

This report identifies the location of the study sites, the methods of sampling and analysis and includes all raw results. It provides interpretation of the results including comparisons with Robb (1988). A further comparison with similar studies in other regions provides an indication of how Christchurch sediments compare with those in waterways in other New Zealand cities.

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TITLE:
LOCATION MAP

DATE: JUNE 2005

PROJECT NO: 500673

CLIENT: Christchurch City Council

FIGURE NO: 1.1

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1.3 Report Structure

This report is presented in six sections as outlined below.

- Section 1: provides background information of urban sediment quality, sediment quality guidelines and previous studies in the project area.
- Section 2: describes the sampling of sediments from the Heathcote and Halswell River catchments.
- Section 3: presents information on the physical characteristics of the sediment samples.
- Section 4: presents the metal concentrations, factors influencing metal concentrations in sediment, compares the results to previous investigations in Christchurch and elsewhere in New Zealand, and discusses the significance of the concentrations in relation to potential sediment toxicity.
- Section 5: presents and discusses results obtained for polycyclic aromatic hydrocarbons (PAHs) in sediments, provides a comparison with other New Zealand cities, and discusses the significance of the concentrations identified in relation to potential sediment toxicity.
- Section 6: provides an overview and summary of the results of the investigation.

1.4 Background on Urban Sediment Quality

1.4.1 Introduction

The physical and chemical characteristics of sediment in any section of a stream reflects three key factors. These are:

1. The geological origin and nature of the soils and rocks in the catchment (this determines the propensity for weathering and erosion and the texture and composition of the particles).
2. The flow in the stream (i.e., whether it is a depositional (low-energy) or active section (high-energy) of the stream, fine sediments will accumulate in the depositional sections of streams)
3. The contributions from man-made sources (this depends on the land use in the catchment and discharges into stormwater).

1.4.2 Catchment Geology and Landscape Changes

The Heathcote River is nestled adjacent to the Port Hills, following the hills around from Ferrymead to Cashmere where it heads northwest and inland. The headwaters of the Heathcote and Halswell rivers are relatively close, sourcing their waters from springs in Holocene (post-glacial) outwash gravels that form the Canterbury Plains in the area around Riccarton and inland.

Basement rocks of the Port Hills are greywacke sandstones and mudstones that make up the main basement of much of New Zealand and form the bulk of the Southern Alps. The Port Hills are derived from recent (predominantly Miocene) volcanic activity that occurred about 5.8 to 15 million years ago. Lyttelton and Akaroa Harbours are the remnants of the craters of these volcanoes (refer Gage 1969, Suggate 1978 for more detail). The volcanic rocks are predominantly a series of hawaiites and mugearites which form part of the main volcanic dome at Lyttelton. The only other geochemically different group of rocks on the peninsula are a series of olivine basalt and hawaiite flows called the Diamond Harbour Group (Liggett & Gregg 1965). This group of Pliocene basalts is more common around Lyttelton Harbour but are also seen at Halswell quarry to the south of Christchurch City. The geology of the Banks Peninsula volcanics is described by Price & Taylor (1980).

The Heathcote River as we know it today is a relatively young feature of the landscape. From the end of the last significant glaciation about 14,000 years BP, the sea moved inland beyond where the Heathcote River is today. Following this transgression, sea level retreat resulted in shore being located somewhere around Riccarton about 6,500 years BP and at about 2,000 years BP the shore was located at Ferrymead. As noted by Deely (1992), the landscape changed rapidly following the arrival of settlers in the early 1840s. The landscape of the lower Heathcote was converted to pasture and orchards in the 1850s and industrial development occurred rapidly in the lower catchment between 1880 and 1925. Urbanisation in the Heathcote and greater Christchurch area is described in Macpherson (1979), Deely (1992) and others.

Soils of the Port Hills are developed from loess and andesitic basalt of the Lyttelton Group. The extensive loess deposits are quartzo-feldspathic and derived from greywacke and argillite. Likewise the Holocene coastal sands and alluvial silts and clays are also quartzo-feldspathic and derived from Torlesse terraine greywacke and argillite of the Southern Alps.

1.4.3 Stream Processes

Physical factors such as stream hydraulics have a direct influence on the movement of coarse and fine sediment particles through the stream system. It is important that these processes are considered when interpreting data on sediment quality.

Sediments are discharged into the streams and rivers throughout South-West Christchurch following their transportation in urban stormwater or erosion from stream banks. The particulates will either settle to the bed of the streams or be transported downstream into the Avon-Heathcote Estuary or Lake Ellesmere.

Sediment transport depends upon the size of the particles and their shape and density, and on stream flow. The flow in each section of the stream, whether it is an active section (high-energy) or depositional section (low-energy) determines whether fine sediments will accumulate. These physical sorting processes typically result in the accumulation of gravel and other coarser sediments adjacent to stormwater outfalls and the transport of fine material such as silts and clays downstream of the discharge point.

Transport of fine sediments downstream can result in the build-up of these sediments in estuarine areas due to two processes. A widening of the stream channel results in a slowing of the stream flow allowing fine sediments to settle. In addition, the change from freshwater to salt water results in electrostatic attraction between the particles and causes flocculation and the subsequent deposition of the fine sediments. This deposition can result in the associated accumulation of contaminants in estuarine areas such as the lower reaches and mouth of the Heathcote River and in the Avon-Heathcote estuary.

1.4.4 Catchment Activities and Stormwater Quality

The quality of freshwater sediments in drains and streams generally reflects catchment activities. In particular, stormwater runoff typically results in increases in the concentration of common metals such as copper, lead and zinc and PAHs in stream sediments.

Different activities throughout the city result in different materials and contaminants being present on the surface and available for transport to the stormwater system or directly to streams. Stormwater quality therefore (i.e., the types of contaminants present and their load) differs between parks, residential areas, commercial and industrial areas of land and relates to a complex interplay of anthropogenic variables including the types of industry in the adjacent catchment; the density of vehicles on roads in the catchment; the nature and aerial extent of roof surfaces (e.g., whether they are galvanised iron, Zincalume, concrete, tile or other materials); and the deposition of contaminants to land from activities discharging to air (house fires, vehicle emissions and industrial air discharges).

1.4.5 Sediment Quality Assessments

As the common contaminants in stormwater (copper, lead, zinc, PAHs) tend to be associated with particulate matter, the quality of urban stream sediments provides an indicator of the changes in the extent or degree of urbanisation and/or inputs of contaminants within a catchment.

The way in which the sediments provide an indication of the effects of urbanisation is dependent upon the sedimentary environment and the overall flux of sediments and contaminants.

Suspended sediments and bed sediments move through the catchment over different time scales. Suspended sediments may be transported through the stream system within the Halswell or Heathcote system within a matter of days. Some suspended particles may have a longer history within the stream if they have become suspended from the bed after previously settling. On the other hand, bed sediments may move very slowly (relatively) with some particles ‘saltating’ though the system. The overall dynamics of sediment particles through these two streams is not known. In waterways with relatively mobile beds where the sediments are continuously moving downstream, the sediments in the bed of the stream may not be that old (in terms of age since being discharged into the waterway) and hence the contaminants may only be of relatively recent origin.

In true depositional environments where the sediment is continually building up over time (as often occurs in large lakes, large estuaries and harbours), the sediments can provide a record of the contaminants buried over time and therefore the nature and changes in the catchment producing the contaminants.

The concentration of a given contaminant within a sediment sample is influenced by a number of factors including mineralogy, texture and total organic carbon content. Unless these factors are accounted for, the concentration of the contaminant at a given location can be highly variable and the results difficult to interpret.

Physical characteristics of sediments influence the level of natural (background) or anthropogenic contaminants detected. Variations in texture have two primary influences. The first is that very fine particles with high surface areas can adsorb and concentrate contaminants, and the second is that coarse sands can dilute contaminant concentrations through their poor sorption characteristics and also the low concentration of many elements in minerals such as quartz. The influence of texture on contaminant concentrations can be dealt with in one of two ways these are:

- Remove the coarse particulate fraction from the sediment leaving the fine sediment for analysis. This requires sufficient sediment sample to isolate the <0.063 mm fraction or a finer fraction (e.g., <0.004 mm).
- Measure the texture to allow the variation to be considered when examining the data.

In this investigation, whole samples were collected with minimal processing prior to analysis (<2 mm fraction examined). The approach was adopted to be consistent with the earlier 1980-1981 study (Robb 1988). The texture of each sample was however analysed for comparative purposes.

1.5 Sediment Quality Guidelines

The Australian and New Zealand guidelines for fresh and marine water quality (ANZECC 2000) provide sediment quality guidelines for metals and PAHs (and other contaminants) in both marine and freshwater environments (Table 1.1). These are provided as two values, the ISQG-low (interim sediment quality guideline) and ISQG-high. The guidelines are trigger values that if exceeded, prompt further action such as evaluation of bioavailability and background concentrations. Where the sediment concentration is below the ISQG-low, it is considered that there is low risk of adverse effects to aquatic species inhabiting the stream sediments.

Table 1.1: ANZECC (2000) sediment quality guidelines for metals and PAHs.

Contaminant	ISQG-Low	ISQG-High
Metals (mg/kg)		
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Nickel	21	52
Zinc	200	410
PAHs [a] (µg/kg)		
Acenapthene	16	500
Acenapthalene	44	640
Anthracene	85	1,100
Fluorene	19	540
Naphthalene	160	2,100
Phenanthrene	240	1,500
Low Molecular Weight PAHs [b]	552	3,160
Benzo(a)anthracene	261	1,600
Benzo(a)pyrene	430	1,600
Dibenzo(a,h)anthracene	63	260
Chrysene	384	2,800
Fluoranthene	600	5,100
Pyrene	665	2,600
High Molecular Weight PAHs [c]	1,700	9,600
Total PAHs	4,000	45,000

Notes: [a] Normalised to 1% organic carbon; [b] Sum of concentrations of acenapthene, acenapthalene, anthracene, fluorene, 2-methylnaphthalene, naphthalene and phenanthrene; [c] Sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, dibenzo(a,h)anthracene, chrysene, fluoranthene and pyrene.

The ANZECC trigger values are based on sediment guidelines developed by Long et al. (1995). Their guidelines were based on data collected from several hundred sites across the United States as part of the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends Program. The upper and lower guidelines were calculated from the chemical concentrations observed and predicted to be associated with adverse biological effects. The Effects Range Low (ER-L) is the 10-percentile concentration and the Effects Range Median (ER-M) is the median contaminant concentration. The ANZECC ISQG-Low is based on the ER-L and the ISQG-High is based on the ER-M. Guidelines for some parameters were amended based on other sediment quality guidelines used around the world.

The ANZECC (2000) trigger values, although based on coastal benthic species sensitivity to contaminants are considered to be suitable as a generic indicator of the effects of sediment quality in freshwater streams to freshwater biota inhabiting those waterways.

1.6 Previous Studies in the Catchment

A comprehensive survey of sediment quality was undertaken during 1980 and 1981 (Robb 1988). The objective of that investigation was to evaluate the concentration of heavy metal contamination in the Avon and Heathcote River catchments, the tidal flats and associated ecology. The survey included 47 sites in the Heathcote River catchment of the South-West Christchurch project area in both the river and in tributary drains. A further 33 samples were collected within the Heathcote River between South-West Christchurch and the estuary. The 1980-1981 study did not collect samples from the Halswell River catchment.

More recent sampling of sediment was conducted by NIWA in 1996 near the mouth of the Heathcote River, however no samples were collected from within the South-West Christchurch project area.

2. Sampling Sites and Methods

2.1 Sampling Sites and Methods used by Robb (1988)

The location of the 80 sites in the Heathcote Catchment studied by Robb (1988) are listed in Table 2.1 and Table 2.2 and are shown in Fig. 2.1. Sediments from these sites were analysed for six heavy metals (cadmium, copper, chromium, lead, nickel and zinc) and total organic carbon. Sediment texture was also determined. The analytical method used for the metals involved removal of the >2 mm fraction (material larger than sand), digestion with perchloric and nitric acid, followed by analysis by AAS (atomic absorption spectroscopy).

Table 2.1: Sediment samples collected from the Heathcote River catchment in the 1980-1981 survey by Robb (1988).

Waterway	Sample ID	Description of Location
Milnes Drain	1	10m below Sparks Road.
	2	10m upstream from confluence with Cashmere Stream.
Dunbars Drain	3	5m below Sparks Road.
	4	5m upstream from confluence with Cashmere Stream.
Hendersons Rd Drain	6	3m below bridge to dairy farm.
	9	50m below Sparks Road.
	12	100m upstream of confluence with Cashmere Stream at small bridge.
	15	From a point 20m below site 12 down to confluence.
Ballantines Drain and Associated Drains.	16	2m below Sparks Road.
	18	Upstream of confluence with Ballantines Drain on Sherrings Drain.
	19	Upstream of confluence with Ballantines Drain on Stillwells Drain.
	20	5m above Newland Street on Ballantines Drain.
	22	End of section at 156 Sparks Road on Ballantines Drain.
	23	Ballantines Drain, 20m below junction of side drains.
	24	5m above Cashmere Road, Ballantines Drain.
Cashmere Stream	26	25m upstream of confluence of Sutherlands Road tributary and stream from spring at site 27.
	27	Large open spring.
	28	Spring head.
	29	Between bridge and junction of two tributaries.
	31	10m below sharp bend.
	34	Just below confluence with Milnes Drain.
	36	Opposite the end of a large macrocarpa hedge.
	39	Below bridge, corner Hendersons Road and Cashmere Road.
	42	Bridge on Penruddock Rise.
	44	50m upstream of first house on Cashmere Road after Cashmere Downs Nursery (travelling east).
	46	Opposite 41 Waiau Street.
	49	20m below Worsleys Road bridge.
Haytons Drain	52	Downstream end of bend in drain.
	53	30m below Wigram Road.
Curletts Drain	55	2m below culvert on Watts Road where Curletts Road Drain emerges.
	59	1m below bridge into paddock along Wigram Road.
	65	500m below new motorway.

Table 2.2: Sediment samples collected from the Heathcote River in the 1980-1981 survey by Robb (1988).

Sample ID	Description of Location
77	Half-way between Nash Road and small side drain.
80	Half-way between sites 79 and 81.
83	End of Templetons Road, 6 m above bridge.
86	300 m downstream of site 85.
90	200 m upstream of site 91, under willow tree.
93	Just above new motorway bridge.
96	100 m above Lincoln Road, where river meets Annex Road.
99	15 m above footbridge to bowling club.
102	Opposite Christchurch United Associated Football Club.
106	Upstream end of West Spreydon School.
109	Opposite house between 1 and 3 Waimokihi Place on north bank.
112	130 m below Sparks Road bridge, off board fence.
115	Opposite 277 Hoon Hay Road.
118	In section at 134 Cashmere Road.
121	3m above footbridge opposite supermarket.
124	Opposite 243 Ashgrove Terrace.
127	400 m above Colombo Street bridge.
130	Malcolm Avenue bridge.
133	Opposite 199 Waimea Terrace.
136	Opposite 69 Eastern Terrace.
138	Half-way between Sandwhich Road and Fisher Avenue.
140	30 m below Wilsons Road bridge.
143	Opposite the end of Cholmondeley Avenue.
145	10 m above Beckford Road bridge.
147	Just upstream of Scout Den.
152	30 m above footbridge at end of Garlands Road.
154	Opawa road bridge.
156	Marshall Street.
157	Mackenzie Avenue footbridge.
158	Wildberry Street.
160	25 m upstream of confluence with Bells Creek.
161	10 m upstream of Radley Street bridge.
163	Opposite de Spa Wool Scourers.
164	Catherine Street footbridge.
165	Opposite Dunlop Industries.
167	Opposite Skellerup Industries.
169	Opposite Henry York Limited.
171	Opposite end of Bamford Street.
173	Opposite end of Staunton Street.
175	140 m downstream site 174. Opposite piles of shell at back of Independent Fisheries.
177	Opposite G. L. Bowron and Company, half-way along straight.
179	Tunnel Road bridge.
180	Opposite Charlesworth Street.
182	20 m downstream from pylon.
184	Sharp bend in river adjacent to row of pine trees.
186	360 m downstream form site 184 opposite slag heap.
188	Ferrymead Railway Station.
190	Ferrymead Bridge.

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TITLE:

LOCATION OF SAMPLING SITES IN THE HEATHCOTE RIVER CATCHMENT BY ROBB (1988)

CLIENT:

Christchurch City Council

DATE:
JUNE 2005

PROJECT NO:
500673

FIGURE NO:
2.1

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2.2 Sample Locations in the 2003 survey

2.2.1 Heathcote River Catchment

Sampling sites in the Heathcote catchment were selected with the following objectives:

1. To allow comparison with data from Robb (1988), particularly where land use has changed, or where data previously exceeded the ANZECC (2000) sediment guidelines.
2. To allow comparison between different land uses.
3. To geographically cover the catchment.

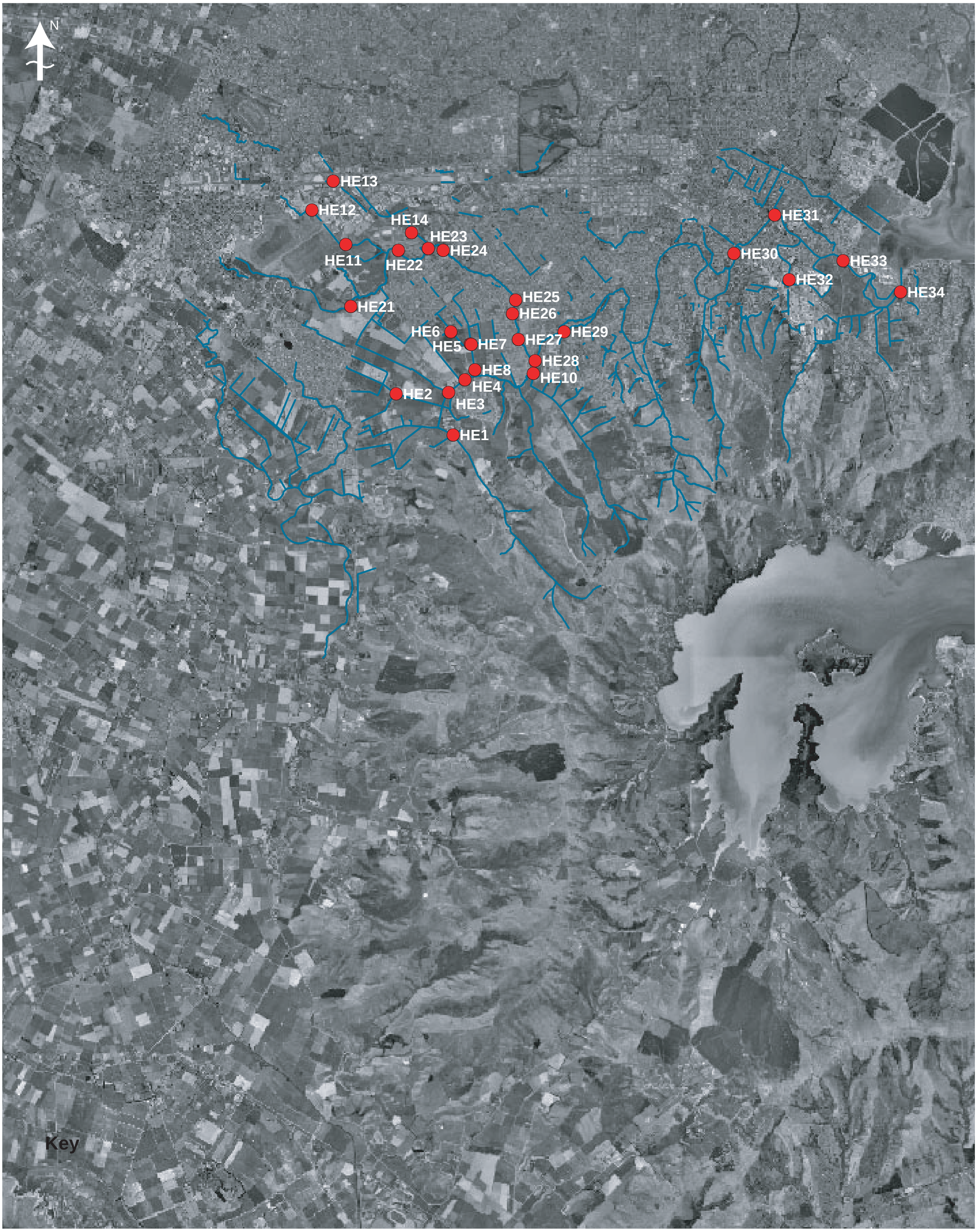
Nine sampling locations were selected in the main Heathcote River and 13 in the tributaries. A further five sites were located outside of the South-West Christchurch project area, near the mouth of the Heathcote River at estuarine sites surveyed by Robb (1988). Sampling sites were labelled sequentially and were preceded with ‘HE’ for ‘Heathcote’, refer to Fig. 2.2 and Table 2.3.

2.2.2 Halswell River Catchment

The selection of sampling sites from the Halswell River catchment reflected a lack of previous sediment studies for the area, and considered the following objectives:

- To sample downstream of a range of land use types where possible.
- To geographically cover the catchment within the South-West Christchurch project area.

Where possible, sites were located at the same location as water quality monitoring sites used by CCC Waste Management Unit Laboratory. Five sites were selected in the Halswell River, and nine sites were located in the tributaries of the river. A further five sites were located downstream of the South-West Christchurch project area. Samples were labelled sequentially and were preceded with ‘HA’ for ‘Halswell’. These sites are shown in Fig. 2.3 and listed in Table 2.4.



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TITLE:

LOCATION OF SAMPLING SITES IN THE 2003 SURVEY FROM THE HEATHCOTE RIVER CATCHMENT

CLIENT:
Christchurch City Council

DATE:
JUNE 2005

PROJECT NO:
500673

FIGURE NO:
2.2

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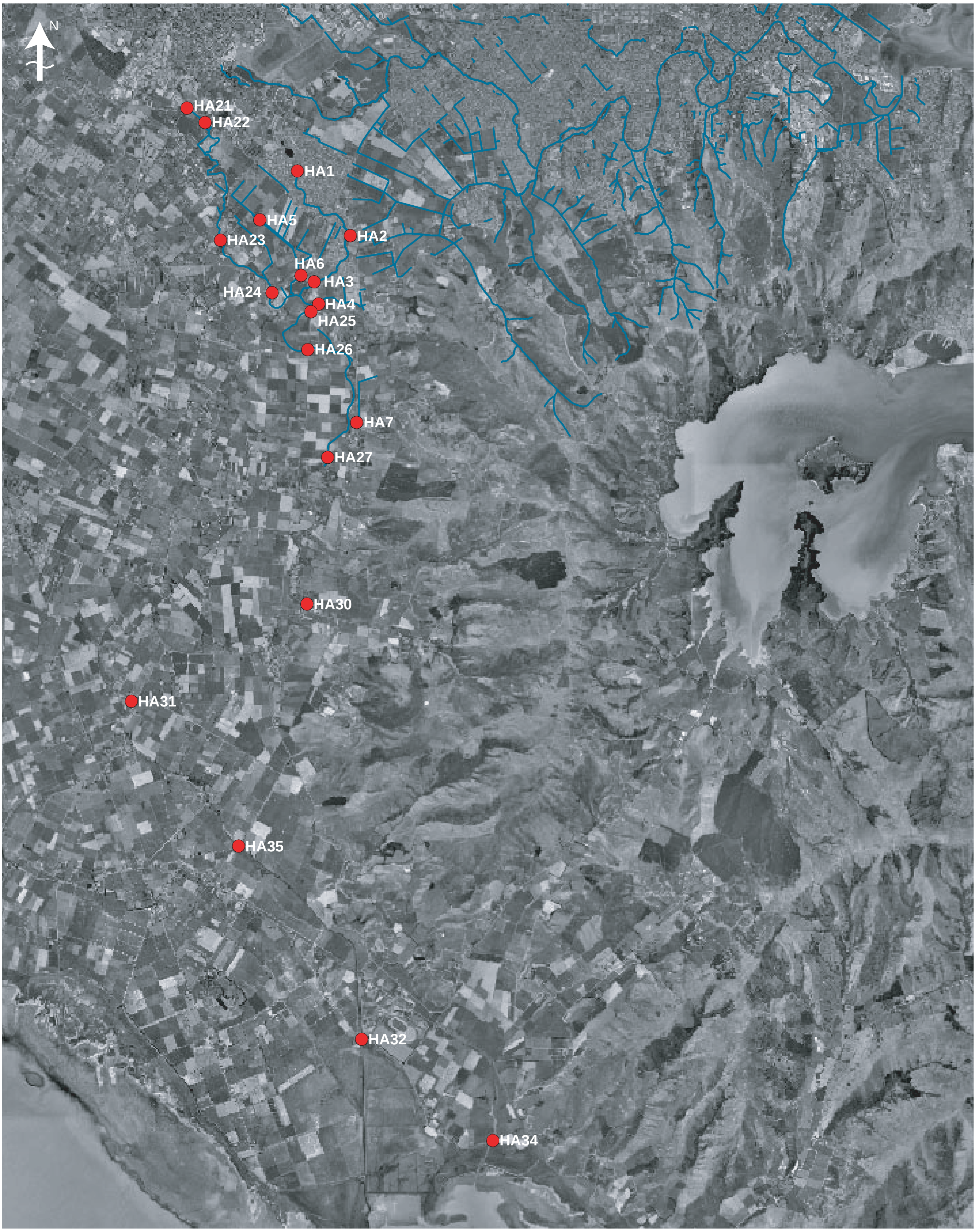
Table 2.3: Location of sampling sites in the 2003 survey in the Heathcote River catchment.

Site ID	Waterway	Description	Easting[a]	Northing[a]	Robb Site ID
HE1	Milnes Drain	Milnes Drain	2477404	5735505	2
HE2	Dunbars Drain	Upstream Sparks Rd	2476251	5736337	3
HE3	Dunbars Drain	Upstream from confluence (428 Cashmere Road)	2477313	5736373	4
HE4	Hendersons Rd drain	Hendersons Rd drain	2477644	5736630	15
HE5	Ballantines drain	2 m below Sparks Rd	2477358	5737601	16
HE6	Sherrings drain	Sherrings drain	2477758	5737347	18
HE7	Stillwells drain	Stillwells drain	2477771	5737344	19
HE8	Ballantines drain	5 m above Cashmere Rd	2477847	5736824	24
HE10	Cashmere Stream	Opposite Cracroft	2479030	5736757	49
HE11	Haytons Drain	30 m below Wigram Rd	2475230	5739373	53
HE12	Haytons Drain	200 m downstream of where 2 parts of the drain join	2474543	5740071	52
HE13	Curletts Drain	On Cable Road	2474979	5740655	55
HE14	Curletts Drain	Opposite Canterbury Agricultural Park	2476567	5739611	65
HE21	Heathcote River	At St John of God School	2475333	5738114	80
HE22	Heathcote River	Behind 10 Bidwell Place	2476297	5739254	90
HE23	Heathcote River	In reserve upstream of Curletts Road	2476903	5739290	93
HE24	Heathcote River	At Annex Road, opposite Spreydon School	2477208	5739248	96
HE25	Heathcote River	Waimokihi Rd	2478675	5738244	109
HE26	Heathcote River	130 m below Sparks Rd bridge	2478607	5737969	112
HE27	Heathcote River	At the back of 277 Hoon Hay Rd	2478726	5737443	115
HE28	Heathcote River	D/s road bridge, below Cashmere Stream confluence	2479071	5737010	118
HE29	Heathcote River	3 m upstream of footbridge, opposite the corner of Valley Road and Cashmere Road.	2479655	5737595	121
HE30	Heathcote River	50 m upstream Opawa Road Bridge	2483103	5739185	154
HE31	Heathcote River	50 m upstream Radley Street Bridge	2483432	5739968	160
HE32	Heathcote River	King Edward Terrace	2484222	5738660	169
HE33	Heathcote River	Opp. Charlesworth St	2485310	5739041	180
HE34	Heathcote River	200 m upstream Ferrymead Bridge	2486481	5738404	190

Notes: [a] New Zealand Map Grid projection / NZGD1949



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TITLE:

LOCATION OF SAMPLING SITES IN THE 2003 SURVEY FROM THE HALSWELL RIVER CATCHMENT

DATE:	JUNE 2005
PROJECT NO:	500673
FIGURE NO:	2.3

CLIENT:

Christchurch City Council

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Table 2.4: Location of sampling sites in the 2003 survey in the Halswell River catchment.

Site ID	Waterway	Description	Easting[a]	Northing[a]
HA1	Nottingham Stream	Nottingham Ave	2474220	5736966
HA2	Nottingham Stream	Halswell Junction Rd	2475296	5735653
HA3	Nottingham Stream	Upstream Candys Rd	2474562	5734713
HA4	Greens Drain	Near Wroots Road	2474649	5734264
HA5	Quaiffes Drain No. 1	Along Quaiffes Rd, near Murphys Rd	2473464	5735971
HA6	Creamery Drain	Upstream Sabys Rd	2474295	5734848
HA7	Jones Creek	At first house on Early Valley Rd	2475425	5731864
HA21	Knights Stream	D/S of Halswell Junction	2471979	5738243
HA22	Knights Stream	Along Halswell Junction Road	2472350	5737952
HA23	Knights Stream	Upstream Whincops Rd	2472659	5735565
HA24	Halswell River	Upstream Sabys Rd	2473709	5734496
HA25	Halswell River	Downstream Wroots Rd	2474500	5734113
HA26	Halswell River	Upstream of corner Leadleys & Halswell Rd	2474432	5733341
HA27	Halswell River	Upstream of Osterholt Rd	2474834	5731158
HA30	Halswell River	At Taitapu Domain	2474411	5728178
HA31	Halswell River	On River Rd	2470848	5726202
HA32	Halswell River	Upstream of Duck Pond Rd	2475522	5719342
HA34	Halswell River	Seabridge Rd	2478190	5717290
HA35	Halswell River	End of McCartneys Rd	2473024	5723262

Notes: [a] New Zealand Map Grid projection / NZGD1949

2.3 Sampling Methods

At each site, samples were collected within a slow flowing area and upstream of any obvious point sources such as stormwater pipes. Core samples were collected to a depth of 2 to 3 cm using plastic box corers with an area of 60 cm^2. Five sub-samples were collected from each site and combined to form a composite sample.

The sampling aimed to collect sediment that was texturally similar between sites. Fine sediments (<2 mm) were preferentially collected to ensure there was sufficient material for laboratory analysis.

Samples were stored in a chilli bin on ice until delivery to the laboratory at the end of the day.

At each sampling location a field sheet was completed describing the site characteristics and the presence of upstream discharges. GPS co-ordinates were recorded at each site and photographs were taken of the general stream environment and of the stream-bed (where visible through the water).

2.4 Laboratory Methods

All samples were sent to R J Hill Laboratories Limited (Hamilton) packed with ice, under chain of custody conditions for determination of texture, and analysis of heavy metals and total organic carbon (TOC). A sample of each composite was also sent to NIWA (Hamilton) for PAH analysis.

Sediments were classified based on their grain size, by determining the percentage by weight of particles within the different size ranges. The classification used in this study is based on the Wentworth scale (Table 2.5). Sediment texture was assessed by wet sieving over 2 mm, 0.5 mm, 0.25 mm and 0.063 mm, then gravimetric measurement after drying at 103 °C.

Table 2.5: Grain size classification of sediments.

Grain size	Wentworth Classification
<0.063 mm	Silt and clay (mud)
0.063 – 0.25 mm	Fine sand and very fine sand
0.25 – 0.50 mm	Medium sand
0.50 – 2mm	Coarse sand and very coarse sand
>2 mm	Gravel and cobbles

Analysis of sediments for metals can be conducted using a variety of methods, which vary depending on the fraction of sediment analysed, the digestion method used and the instrumental method used. Different analytical procedures often result in the large differences seen in the final results reported in different studies.

The previous studies in the catchment (Robb 1988) analysed the whole sediment sample (after removal of >2 mm particles) (Robb 1988). It is noted that the whole sediment sample may be more appropriate for assessing the effects on aquatic biota, and sediment quality guidelines such as ANZECC (2000) assume the whole sample has been analysed.

For the samples collected in the 2003 survey, metal analysis was undertaken on the <2 mm fraction. Total recoverable metals (copper, lead and zinc) were analysed by ICP-MS after digestion with nitric acid and hydrochloric acid for 30 minutes at 85 ºC. For comparative purposes a subset of samples was also analysed for metals following the digestion method used by Robb (1988); i.e., by perchloric acid/nitric acid extraction (2.5 mL/4.0 mL) for 2 hours.

Selected samples were also analysed for PAHs and total organic carbon. Total organic carbon analysis was by combustion following acid pretreatment to remove carbonates.

For PAH analysis, samples were sieved to 0.5 mm, then freeze-dried and extracted by accelerated solvent. All samples were spiked with seven deuterated PAH surrogates before extraction. The extracts were cleaned by silica/alumina column chromatography and sulphur was removed from samples using activated copper chips. Internal standards were added to all extracts before analysis to monitor surrogate recoveries. Quantitative analysis of PAHs was carried out by capillary gas chromatography using mass selective detection in selected ion mode (GC-MS-SIM).

2.5 Statistical Methods/Data Analysis

Differences between land use in the catchment and contaminant concentrations were initially investigated using JMP Version 5.0.1 (SAS Institute). However, lead, copper, and zinc data was not compared in its entirety for the Heathcote and Halswell sites due to differences in land use categories between areas. Land use for each site was therefore independently compared using an analysis of variance (ANOVA). Where significant differences were recorded, a Tukeys HSD means comparison test was used to extract the land use types that were most influential. Any differences between land use types were determined to be significant at the 95% confidence level.

The analyses were repeated with texture information (% mud) partialled out of the ANOVA. Tukeys HSD mean comparisons were then repeated when relevant.

Differences between the perchloric/nitric digestion and total recoverable digestion were investigated using paired t-tests to determine whether the two analytical methods resulted in different concentrations of metals.

3. Physical Characteristics of Sediment

3.1 Introduction

This section of the report examines the physical characteristics of the sediments collected from the Halswell and Heathcote river catchments. The sediment texture data from samples collected by Robb (1988) and in this survey are presented. It should be noted when reading this section that the texture data provided is for samples as collected. Although the sediments sampled were selected in the field to emphasise fine sediments required for analysis, the results are still considered to reflect general stream physical characteristics. Information on man-made items found in the sediments collected in this study is also summarised and discussed.

3.2 Previous survey

The texture of sediments reported by Robb (1988) for the Heathcote River catchment is summarised in Table 3.1. The texture was extremely variable in the total sample set, with the mud content ranging from 1 to 100% of the total sample. The gravel content ranged from 0 to 85%.

Table 3.1: Summary of sediment texture reported by Robb (1988) (all data %, n = 80).

Grain size	Median	Minimum	Maximum
Mud	45	1.0	100
Fine sand	15	0.36	76
Medium sand	4.6	0	52
Coarse sand	0.85	0	34
Gravel	0.31	0	85

The range in textures through the whole Heathcote catchment is not unexpected. Many of the samples, particularly those in the tidal reaches of the Heathcote River (sites 140 to 190) were dominated by mud and fine sand. Samples upstream of the tidal zone (sites 77 to 140) generally contained lower proportions of mud and higher proportions of sand. Several sites (115, 118, 121, 124) also contained high proportions of gravels (approximately 70%) indicating a high-energy section of the river.

Fig. 3.1 summarises the proportion of mud in the 80 samples collected from the Heathcote catchment. This bimodal plot indicates two groups of sediment samples, one with average mud content of 70 to 90% (which includes those in the tidal reaches of the Heathcote River) and one within the range of 0 - 10% mud (which were generally in the upper river and in tributaries).

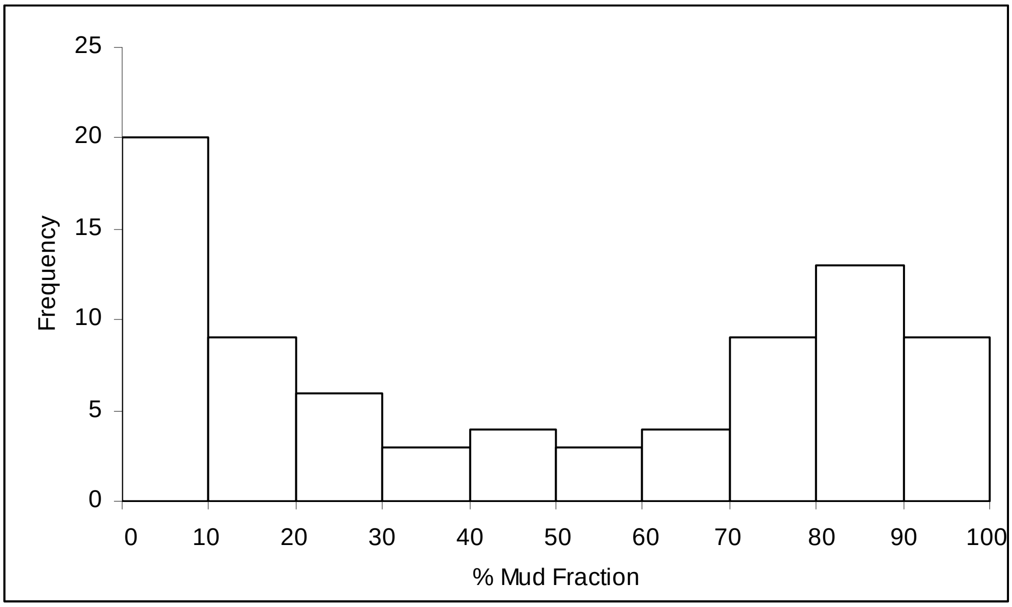


Fig. 3.1: **Histogram showing the proportion of mud in the 80 samples collected from the Heathcote catchment (Robb 1988).**

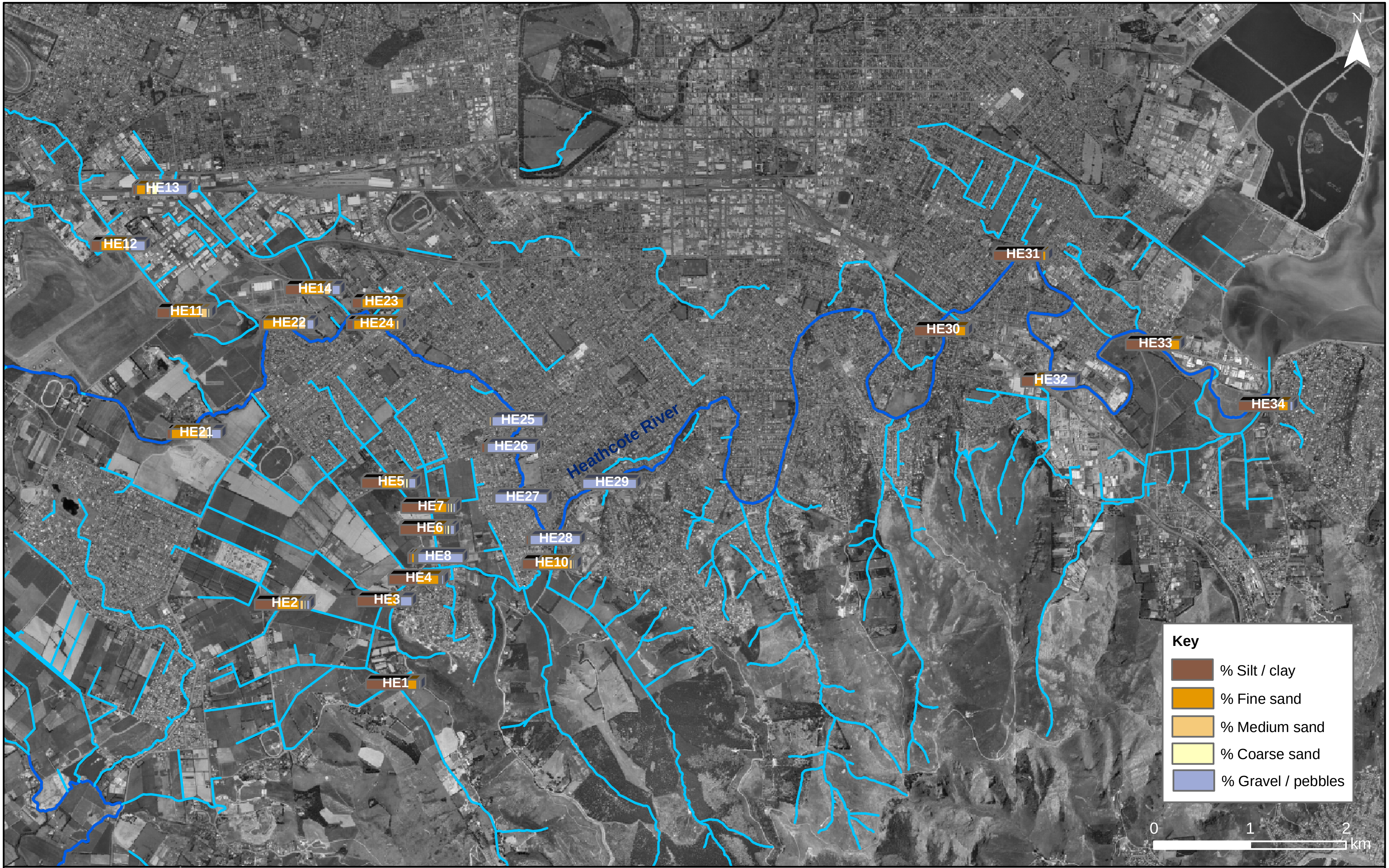
3.3 2003 Survey Results

3.3.1 Heathcote River Catchment

All sediment samples were examined for basic physical textures (gravel, coarse sand, medium sand, fine sand, mud). The texture of sediments collected from the Heathcote River and tributaries is shown in Fig. 3.2.

The sediments ranged from coarse (predominantly gravel and coarse sand) to fine (muddy sand) in the tributaries of the Heathcote River. Tributaries in the southern part of the Heathcote River catchment, including the tributaries of Cashmere Stream generally contained fine sediments (over 70% fine sand and mud). Sediments from tributaries in the northern part of the catchment, including Curletts Drain and Haytons Drain, were more variable and samples contained gravel at up to 54%.

Sediments in the main stem of the Heathcote River were dominated by fine sand in the upper reaches, gravel in the middle reaches and mud in the estuarine reaches downstream of the South-West Christchurch catchment. The raw data is provided in Appendix A and is summarised in Table 3.2. The gravel content of the samples ranged from 0.1 to 99.4%, with a median of 13.9%. Fig. 3.3 shows at least two groups of samples, those containing a low gravel content and those with high gravel. The majority of sites contained between 0.1 and 30% gravel. Six samples contained a much higher proportion of gravel than other samples. Samples collected at sites HE25 to HE29 contained at least 90% gravel and sample HE8 contained 84% gravel.



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TITLE:
PHYSICAL CHARACTERISTICS OF SAMPLES COLLECTED FROM THE HEATHCOTE RIVER CATCHMENT IN 2003

CLIENT:
Christchurch City Council

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 3.2

Table 3.2: Summary of sediment textures from Heathcote catchment collected in 2003.

Grain size	Median %	Minimum %	Maximum %
Gravel	13.9	0.1	99.4
Coarse sand	1.7	0.1	12.4
Medium sand	2.6	0.1	18.3
Fine sand	20.3	0.1	77.7
Mud	25.8	< 0.1	90.1

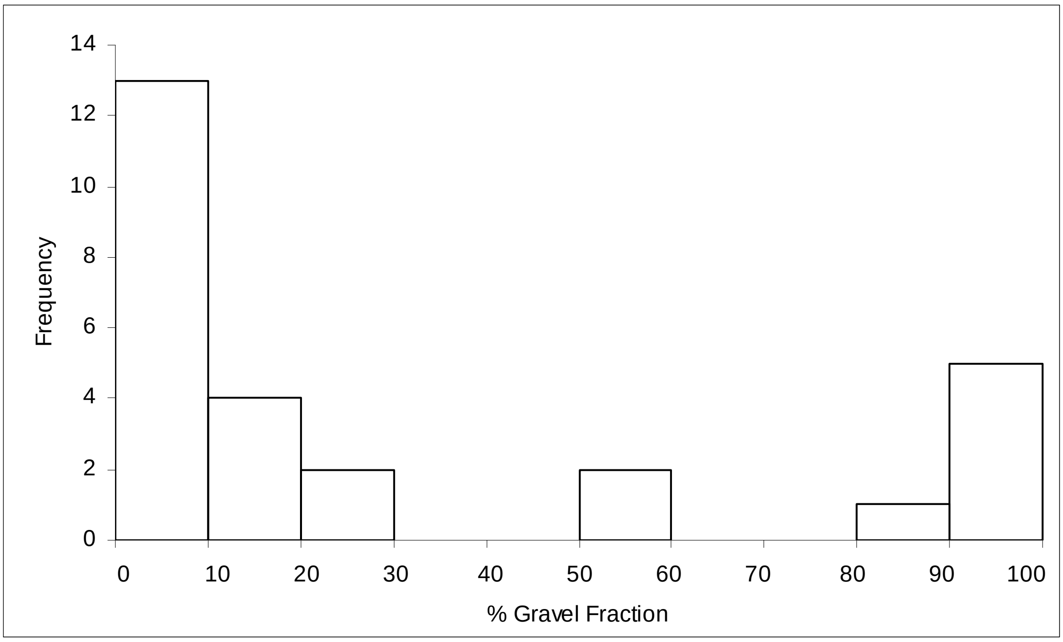
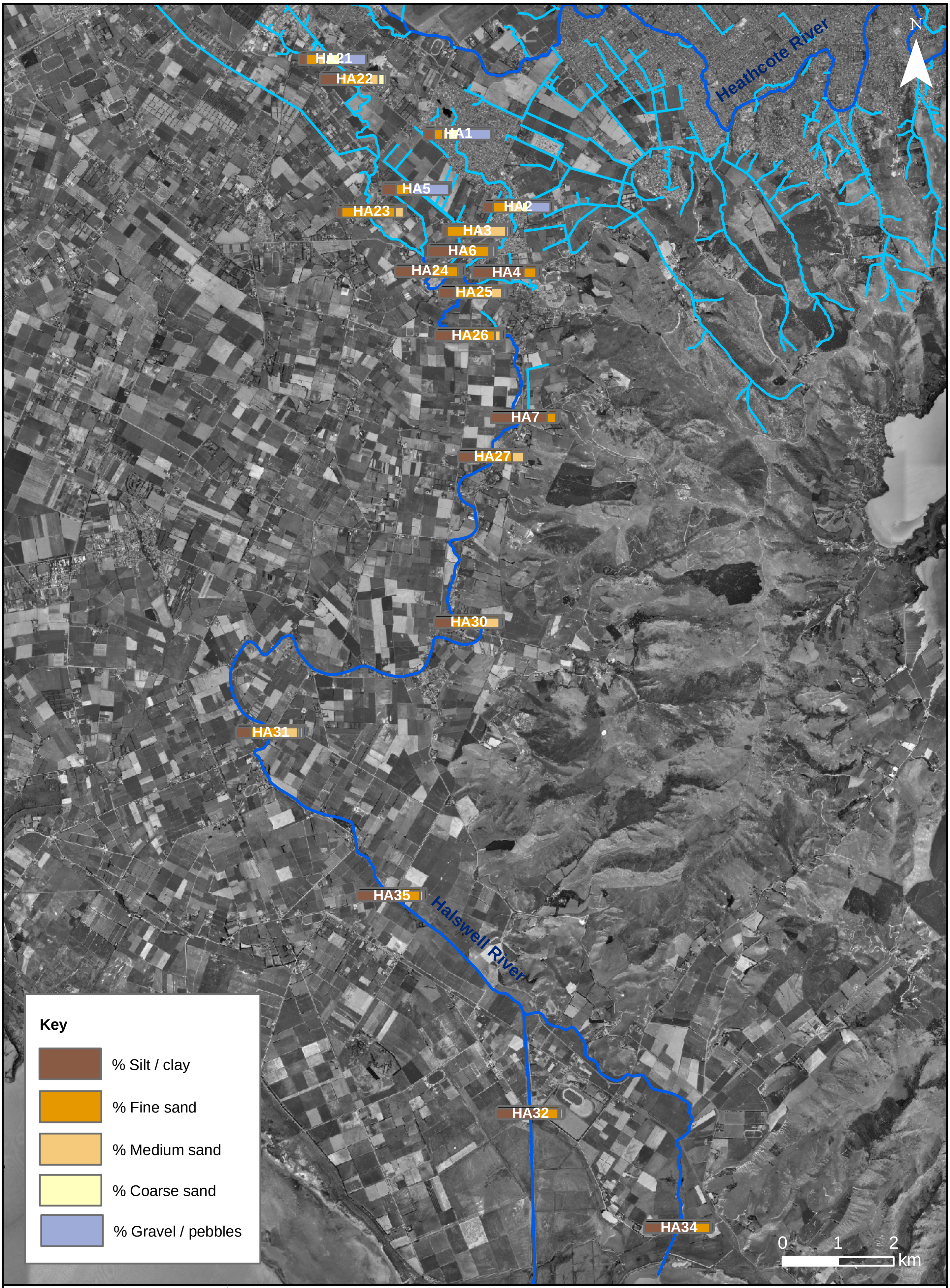


Fig. 3.3: Histogram showing the proportion of gravel in the 27 samples collected from the Heathcote catchment during 2003.

3.3.2 Halswell River Catchment

The texture of sediments collected from the Halswell River and tributaries is shown in Fig. 3.4. The sediments in the upper tributaries of Halswell catchment were typically coarse (predominantly gravels and coarse sand, e.g., in the upper Nottingham and Knights Streams). In contrast, the main stem of the Halswell River contained mainly fine sediments (muddy sands, sites HA23 to HA35). The raw data is provided in Appendix A and is summarised in Table 3.3.



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PHYSICAL CHARACTERISTICS OF SAMPLES COLLECTED FROM THE HALSWELL RIVER CATCHMENT IN 2003

CLIENT: Christchurch City Council

DATE: JUNE 2005

PROJECT NO: 500673

FIGURE NO: 3.4

Table 3.3: Summary of sediment textures from Halswell catchment.

Grain size	Median %	Minimum %	Maximum %
Gravel	2.2	0.1	52.9
Coarse sand	1.9	0.2	20.4
Medium sand	8	0.5	42.5
Fine sand	38.7	12.6	80.1
Mud	26.5	6.8	83.5

The texture data for the Halswell catchment was generally less variable than the Heathcote catchment. The gravel content of the samples collected from the Halswell catchment ranged from 0.1 to 52.9%, with a median of 2.2%. As shown in Fig. 3.5, there were 15 samples containing less than 10% gravel and four samples contained between 34.4 % and 52.9%. These were all collected from tributaries of the Halswell River at sites HA1, HA2, HA5 and HA21.

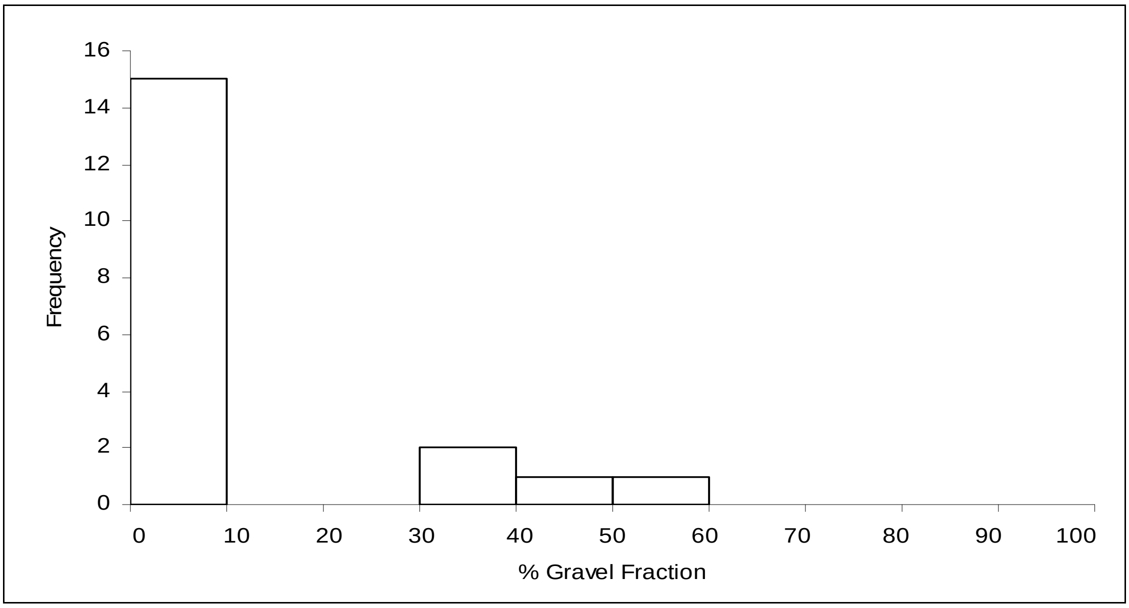


Fig. 3.5: Histogram showing the proportion of gravel in the 17 samples collected from the Halswell catchment in 2003.

3.3.3 Man-Made Materials in Sediment

The >2 mm fraction of all sediment samples collected in 2003 was examined by eye and the presence of man-made materials recorded. A summary of the man-made materials identified is provided in Appendix A.

Visible man-made items larger than 2 mm in size were found in 11 of the 46 samples, nine from the Heathcote (41% of samples) and two from the Halswell River catchments (10.5% of samples). The majority of samples in which man-made objects (primarily glass and plastic) were found were from urban catchments.

Fig. 3.6 shows the >2 mm fraction collected from sites HE5, HE21, HE26, HA5 and HA25. Sites HE21 and26 were located in mixed-urban catchments, while sites HE5 and HA5 and HA25 were from residential and rural catchments respectively.

Fig. 3.6: Examples of the nature of the greater than 2 mm fraction in sediments.

3.4 Summary

The physical characteristics of the sediments collected in the Heathcote catchment showed variable texture within the tributaries and typically fine sediment within the upper and lower sections of the Heathcote River. The middle section of the Heathcote River contained coarse sediments. These characteristics were identified in both the 1980 to1981 and 2003 survey.

The tributaries of the Halswell typically contained coarser sediments than the Halswell River. The sediments of the Halswell River were dominated by fine sand and mud.

There were very few man-made materials found in the sediment samples collected from the Heathcote and Halswell catchments in this survey. The predominant items found were plastic and glass fragments.

4. Metals in Sediments

4.1 Introduction

Examination of the environmentally significant metals used in our society shows that copper, lead and zinc are the dominant metals (both past and present use) (Sorme et al. 2001).

These elements typically have soil concentrations within urban areas that are on average several times natural concentrations (Linde et al. 2001). Although other elements such as mercury may be present in concentrations that are higher in terms of the elevation above the natural concentration, the greatest mass of contaminants usually lies with these three elements.

The use of the three elements in urban areas has changed over time. Lead usage in New Zealand is now much lower than it was 20 years ago. Lead was a common constituent in the paint used on house exterior walls. Lead use is now very uncommon (see summary of lead in paints in exterior house paints in Kennedy et al. 1988). Lead (tetraethyl lead) was also used in petrol in New Zealand until 1996. Although lead use has reduced significantly (probably by more than 95% in 20 years), there are still large reservoirs of lead in the soils of urban areas in New Zealand that allow the contaminant to be transported to waterways. Lead is still contributed by vehicles to road surfaces (lead in tyres).

Copper is emitted to road surfaces from the wear of vehicle brake pads that contain copper and brass metal.

Zinc is a common metal or metal coating (through its use in galvanising) and has been a relatively common metal in paints. Zinc is also emitted from vehicles through the wear of tyres and brake pads. Exposed surfaces containing zinc (e.g., galvanised iron roofs and surfaces such as road crash barriers etc, and roof and building paint) all result in the contribution of this contaminant to waterways via stormwater.

All three metals may also be released through their use by specific industries. For example between 1880 and 1925, the Heathcote river (especially around Woolston) received waste from woollen mills, tanneries, metal works, a glue factory and a gas works (Deely 1992).

This section of the report examines the concentration of copper, lead and zinc in sediments from the Halswell and Heathcote River catchments in South-West Christchurch. The methods and results of the 1980 to 1981 and 2003 surveys are compared and discussed.

4.2 1980-1981 Survey

Tables 4.1 and 4.2 provide a summary of the metal concentrations (cadmium, copper, chromium, lead, nickel and zinc) in the samples collected from the 80 sites in the Heathcote catchment by Robb (1988).

The results showed generally low metal concentrations in the sediment of tributaries and drains, particularly the Cashmere Stream. The low concentrations of metals in Cashmere Stream was attributed to fresh sediment deposited in the stream from housing developments over the six years previous to sample collection (Robb 1988).

Table 4.1: Summary of sediment data collected in 1981 from the Heathcote River catchment in South-West Christchurch (all results mg/kg dry wt).

Waterway	Sample ID	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
Milnes Drain	1	<0.05	10.3	6.3	13.7	7.4	57.8
	2	0.1	12.5	12.0	31.0	10.0	162.0
Dunbars Drain	3	0.1	17.0	18.0	**71.0**	13.0	**234.0**
	4	0.1	16.0	11.0	**72.0**	15.2	167.0
Hendersons Road Drain	6	<0.05	10.3	6.0	9.0	7.8	46.0
	9	<0.05	13.9	14.0	25.0	11.1	106.0
	12	<0.05	17.0	17.0	33.0	13.8	126.0
	15	0.1	14.7	18.0	41.0	13.0	155.0
Ballantines and Associated Drains	16	0.3	17.9	26.0	**194.0**	12.1	**435.0**
	18	0.2	12.9	15.0	**77.0**	9.8	**215.0**
	19	<0.05	17.5	17.0	**54.0**	13.4	120.0
	20	<0.05	16.1	15.0	33.0	11.0	95.0
	22	0.05	8.4	17.5	**140.0**	7.0	95.0
	23	0.2	14.6	20.0	**101.0**	11.6	**220.0**
	24	0.05	16.2	19.0	**95.0**	9.3	**212.5**
Cashmere Stream	26	<0.05	10.2	5.0	1.0	7.2	35.0
	27	<0.05	16.6	13.0	17.0	11.9	68.0
	28	<0.05	18.8	12.0	15.0	11.1	67.0
	29	<0.05	16.8	12.0	14.0	11.8	66.0
	31	<0.05	15.5	10.0	12.0	10.1	66.0
	34	<0.05	10.3	5.0	5.0	7.2	52.0
	36	<0.05	10.3	7.0	6.0	7.1	55.0
	39	<0.05	8.0	8.0	20.5	7.9	55.0
	42	<0.05	12.7	10.0	26.0	8.9	95.0
	44	<0.05	12.4	9.0	17.0	9.7	90.0
	46	<0.05	11.4	10.0	18.0	7.6	94.0
	49	0.1	12.2	10.0	27.0	8.2	122.0
Haytons Drain	52	0.2	13.0	10.5	**78.0**	2.2	98.5
	53	0.2	13.3	8.0	18.0	6.0	176.0
Curletts Drain	55	**2.3**	25.9	**159.0**	**560.0**	13.2	**885.0**
	59	0.3	18.0	19.0	32.0	6.2	**341.0**
	65	**8.0**	41.9	**220.0**	81.0	8.9	**768.0**

Note: colour coding identifies samples where the concentration exceeds the ANZECC (2000) ISQG-low (amber) and ISQG-high (red) criteria.

Ballantines Drain and the associated drains were identified as containing elevated concentrations of lead and zinc, however copper concentrations remained low.

Curletts Drain contained high concentrations of cadmium, chromium, copper, lead and zinc compared to the other tributaries. Copper concentrations were particularly high, at 159 and 220 mg/kg, with some of the highest measurements in the Heathcote River and catchment. Robb (1988) attributed this to historical discharges of copper salt from the cable manufacturing factory in the upper part of the Curletts Drain catchment.

Table 4.2: Summary of sediment data collected in 1981 from the Heathcote River (all results mg/kg dry wt).

Site ID	Cadmium	Chromium	Copper	Lead	Nickel	Zinc
77	0.2	12.6	13.0	41.0	8.1	180.0
80	0.4	11.6	20.0	**64.0**	6.8	153.0
83	<0.05	5.2	3.5	14.0	4.0	48.5
86	0.4	14.8	23.0	**78.0**	9.7	149.0
90	0.2	12.8	7.0	22.0	7.3	95.0
93	0.4	11.7	11.0	33.0	6.9	188.0
96	**5.0**	16.6	**159.0**	43.0	8.1	**379.0**
99	0.6	12.1	63.0	**62.0**	9.5	164.0
102	0.4	9.9	**94.5**	**145.5**	5.9	91.5
106	0.8	11.4	**111.0**	**93.0**	6.7	143.0
109	**3.0**	14.1	**191.0**	**115.0**	7.0	**303.0**
112	**1.7**	11.8	**93.0**	48.0	6.6	198.0
115	**1.5**	13.7	**330.0**	**195.0**	10.7	**269.0**
118	0.2	6.6	20.5	23.5	3.9	56.0
121	0.35	8.1	16.5	**245.0**	6.9	131.5
124	0.3	6.3	10.5	21.0	4.4	87.0
127	0.5	11.3	18.0	**88.0**	8.1	172.0
130	1.1	13.1	34.0	**70.0**	8.0	**259.0**
133	0.45	9.1	21.5	36.5	7.8	149.5
136	0.25	8.0	15.5	**50.0**	6.6	137.5
138	0.35	10.3	25.5	47.5	5.9	152.0
140	0.7	13.2	39.0	**100.0**	7.6	**256.0**
143	0.7	11.3	24.0	**63.0**	6.8	**208.0**
145	0.2	11.6	43.0	42.0	13	167.0
147	0.3	12.4	19.0	**72.0**	7.7	**320.0**
152	0.2	14.4	53.0	**67.0**	8.4	**202.0**
154	0.25	9.3	19.5	**555.0**	9.1	156.5
156	0.4	14.2	33.0	**69.0**	7.0	**215.0**
157	0.3	17.5	26.0	**150.0**	11.6	**215.0**
158	0.4	14.6	22.0	**212.0**	8.0	**259.0**
160	0.8	49.0	**72.0**	**420.0**	**21.3**	**536.0**
161A	0.2	35.7	29.0	**83.0**	12.9	199.0
161B	0.6	62.7	**65.0**	**240.0**	13.4	**374.0**
163	0.7	**113.0**	**79.0**	**250.0**	17.4	**465.0**
164	0.4	59.2	50.0	**1250.0**	14.9	**367.0**
165	0.7	**103.0**	**72.0**	**270.0**	13.9	**433.0**
167	0.6	**82.0**	50.0	**270.0**	12.1	**393.0**
169	0.8	**315.0**	**115.0**	**450.0**	20.1	**528.0**
171	0.5	**93.0**	45.0	**220.0**	12.0	**333.0**
173	0.9	**420.0**	**113.0**	**330.0**	13.0	**381.0**
175	0.50	**290.0**	**76.0**	**223.0**	15.2	**358.0**
177	0.3	20.1	21.0	**114.0**	11.7	**215.0**
179	0.60	**140.0**	37.0	**119.0**	13.2	**244.0**
180	<0.05	32.0	14.0	34.0	11.2	98.0
182	0.10	57.1	23.0	**74.0**	12.7	170.0
184	<0.05	26.2	14.0	25.0	9.0	76.0
186	<0.05	31.6	12.0	35.0	9.7	93.0
188	0.10	56.9	18.0	**52.0**	10.6	157.0
190	<0.05	46.6	16.0	45.0	11.3	122.0

Note: colour coding identifies samples where the concentration exceeds the ANZECC (2000) ISQG-low (amber) and ISQG-high (red) criteria

Sites in the upper Heathcote River (77 to 93 of Table 4.2) had generally lower concentrations of metals than sites downstream of Curletts Drain (site 96 onwards). However, there were two elevated lead measurements in the upper Heathcote River at sites 80 and 86.

The section of the Heathcote River immediately downstream of Curletts Drain (sites 96 to 115) was found to be elevated in copper, lead and, to a lesser extent, zinc. This was likely to be due to the elevated concentrations in Curletts Drain at the time.

Downstream of the confluence with Cashmere Stream, concentrations of metals in the Heathcote River were lower, but increased with distance downstream. The highest concentrations of lead and zinc and elevated levels of chromium were found in the tidal reaches of the Heathcote River, which is also an industrial area (around Woolston). Robb (1988) reported that this was mainly due to historical industrial discharges from tanneries, gas works and a battery factory. While discharges from these industries had reportedly ceased at the time of sampling, the contaminated sediment remained in place.

Tables 4.1 and 4.2 also compare the data reported by Robb (1988) with the ANZECC (2000) sediment quality guidelines. Any location where concentrations exceed the ANZECC (2000) ISQG-high is shaded red. Any location where any sediment sample exceeds the ISQG-low but does not exceed the ISQG-high is shaded amber. Those where concentrations are lower than the ISQG-low are unshaded (this corresponds to green in this traffic light approach).

Sediment samples collected from Milnes Drain, Hendersons Road Drain, and Cashmere Stream contain metals at concentrations below the ANZECC (2000) sediment quality guidelines.

As shown in Table 4.1 and 4.2, Dunbars Drain, Ballantines Drain, Haytons Drain, Curletts Drain and Heathcote River have locations where copper, zinc, cadmium and lead are at concentrations above the ANZECC ISQG-low trigger level. Sediment contamination within Curletts Road Drain and Heathcote River are attributed to past industrial pollution. Although the above exceedences suggest that further studies of possible effects of the elevated concentrations is warranted, Robb (1988) states that the ‘benthic community does not appear to be adversely affected by these (fairly high) conditions’ (pp 72 of Robb 1988).

Overall, for cadmium 7.5% of the sites sampled fell into the amber category; for chromium 9.8% of sites sampled fell into the amber and red categories (8.6% amber, 1.2% red); for copper 18.5% of sites fell into the amber and red categories (17.3% red, 1.2% red); for lead 47.9% of sites fell into the amber and red categories (35.8% amber, 12.1% red), and for zinc 38.24% fell into either the amber or the red categories (29.6% amber, 8.6% red).

4.3 Comparison of Extraction Methods in the 2003 Survey

As mentioned previously, all samples were analysed for metals using nitric/hydrochloric acid (or total recoverable digestion). A sub-set of samples from the Heathcote catchment was also digested using the perchloric/nitric digestion method previously used by Robb (1988). Raw results are presented in Appendix B. The concentrations of copper, lead and zinc measured after both digestions are summarised in Table 4.3. The samples analysed cover the range of concentrations found in the majority of samples from the 1980 to1981 investigation. The results indicate that the concentrations measured in the two separate digestions are generally very close. A paired Student's t-test confirmed that there was no significant difference between the copper, lead and zinc concentrations from the two digestions.

Table 4.3: Comparison of metal concentrations from perchloric/nitric digestion and total recoverable digestion (all data mg/kg).

	Perchloric/nitric digestion			Nitric/hydrochloric acid (Total Recoverable) digestion		
Site ID	**Copper**	**Lead**	**Zinc**	**Copper**	**Lead**	**Zinc**
HE1	8.1	10.1	68.8	8.5	10.9	66.1
HE3	12	30	101	12.3	33.8	96.9
HE4	10.4	21.5	98.9	10.7	22.9	95.6
HE5	17.1	46.6	289	17.9	50.6	300
HE6	20	60.2	344	22	59.7	344
HE8	38	118	351	40.2	198	364
HE10	7.8	16.6	114	7.6	14.3	106
HE11	21.8	66.9	592	24.2	66.1	603
HE12	32.5	96.8	695	36.7	101	796
HE13	206	202	613	194	378	714
HE30	38.8	71.4	545	43.9	74.2	592
HE31	55.9	93.7	700	60.9	89.2	706
HE32	27.1	54.2	251	28.6	53.3	258
HE33	21.2	37.7	198	23	35.7	209
HE34	16.1	29.2	139	16.5	26.1	135

Fig. 4.1 further compares the concentrations of copper, lead and zinc measured after digestion of sediments by the two different methods. The equations presented on each graph provides an indication of the relative difference of the two data sets; an equation of y=1x would represent a perfect correlation. As illustrated on Fig. 4.1 the lead data shows a very close correlation. The copper and zinc data showed that perchloric/nitric acid digestion extracted slightly less of each element than the total recoverable extraction (by about 10% relative).

Copper concentrations were found to be slightly lower when using the perchloric/nitric digestion. The average difference in copper concentration was 1.9 mg/kg and the average relative difference between the two digests was 6.1%.

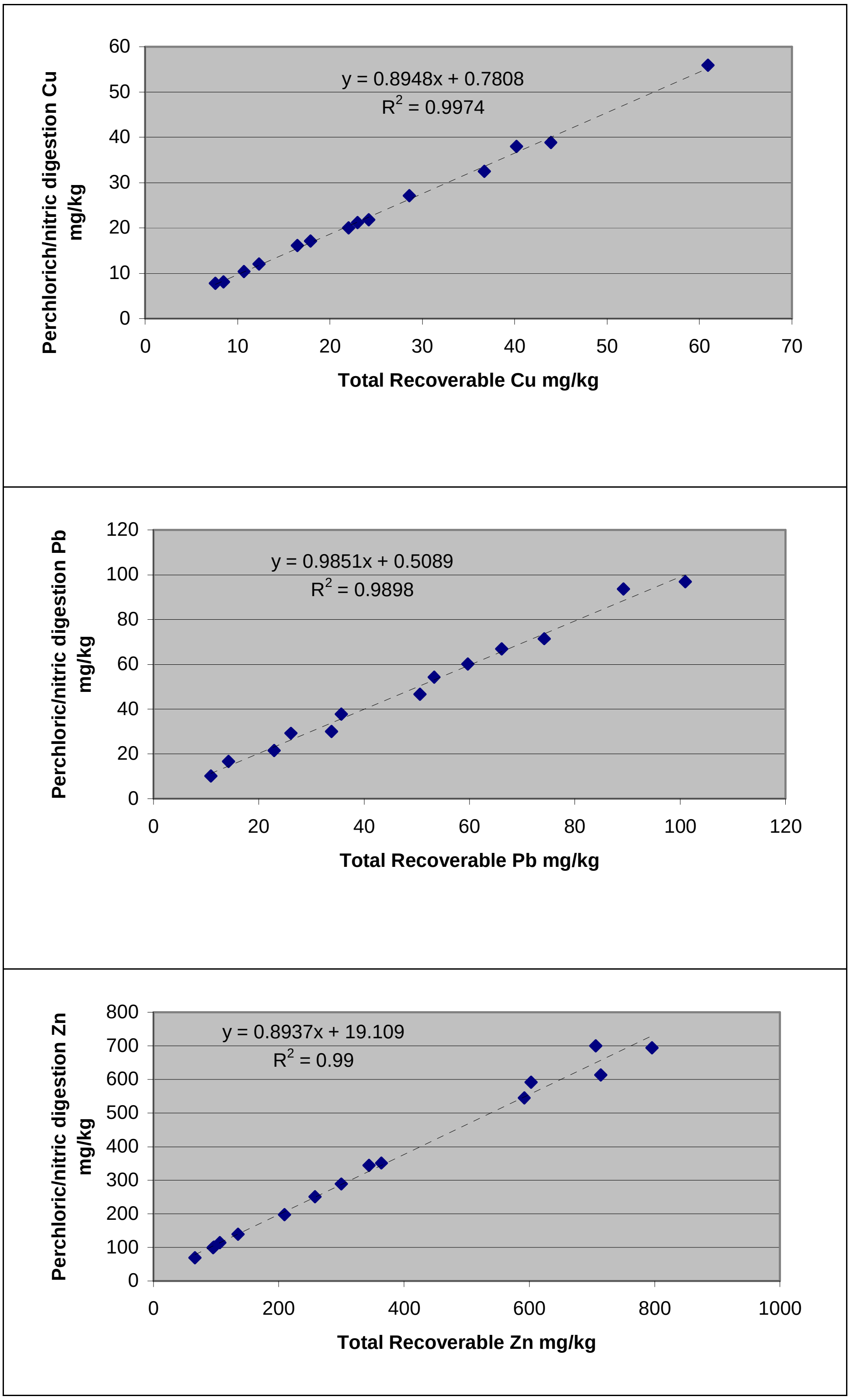


Fig. 4.1: **Relationship between copper, lead and zinc concentrations after digestion used by Robb (1988) and this study.**

As the concentrations of lead and zinc increase in the sample, it appears that less metal is extracted when using the perchloric/nitric digestion than the total recoverable digestion. Fig. 4.1 does not show the two samples that had higher concentrations of lead. The two samples which were found to contain 198 and 378 mg/kg lead were found to contain 50 to 60% of that concentration when extracted using the nitric/perchloric extraction. Overall, at concentrations below 100 mg/kg, results obtained by perchloric/nitric digestion are essentially the same as those obtained by total recoverable digestion. The average difference between the pairs of lead results was 2.5 mg/kg and the relative difference averaged 6.1%.

The zinc extracted using the perchloric/nitric digestion at concentrations over 600 mg/kg appears to be more variable and can be lower than that obtained using the total recoverable extract. As for lead, when these values are excluded from the statistical analysis, the results are essentially equivalent by both digestions. For zinc, the average difference in concentration was 5 mg/kg and the average relative difference between the two digests was 3.4%. Therefore, the lead and zinc results from the Robb (1988) survey, undertaken by perchloric/nitric digestion can be quantitatively compared to the results from this study for concentrations below 100 and 600 mg/kg respectively. Above these concentrations, the results can be more variable and differences between the studies may be related to analytical differences rather than changes in the environment.

In summary, similar concentrations of lead and zinc are obtained using perchloric/nitric digestion and total recoverable digestion when concentrations are below 100 mg/kg and 600 mg/kg, respectively. Copper concentrations were similar between the two digestions at concentrations below 200 mg/kg. The analytical methods were not compared for copper concentrations greater than 200 mg/kg.

4.4 2003 Survey Results

4.4.1 Heathcote Catchment

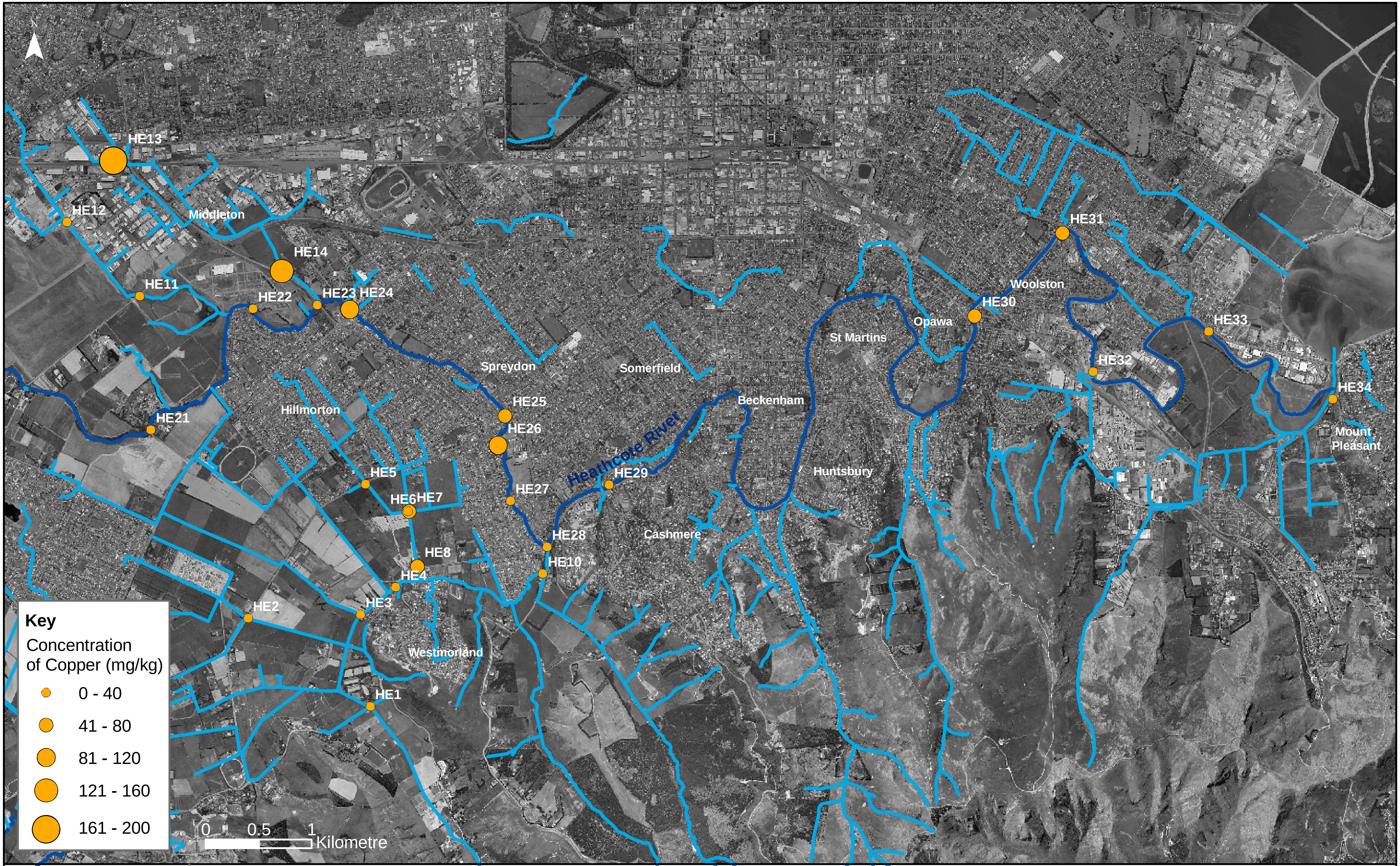
The total recoverable copper, lead and zinc concentrations in the sediment from the Heathcote catchment are presented in Table 4.4 (see Appendix B for raw results). Figs. 4.2 to 4.4 show the data geographically. The overall median copper concentration was 24 mg/kg (range 7.6 to 194 mg/kg). Concentrations of copper were highest at sites HE13 and HE14 (Curletts Drain), measuring 194 and 132 mg/kg respectively. Curletts Drain has been previously identified as being contaminated with copper (Section 1.5.2). Copper concentrations in the Heathcote River show an increase downstream of Curletts Drain, from 16.3 mg/kg upstream at site HE23 to 98.9 mg/kg downstream at site HE24. From here, the copper concentrations showed a general decrease towards the bottom of the South-West Christchurch catchment (Fig. 4.2), measuring 21.4 mg/kg at site HE29.

Table 4.4: Total recoverable copper, lead and zinc concentrations in sediment from the Heathcote river catchment (all data mg/kg).

Site ID	Copper	Lead	Zinc
Tributaries			
HE1	8.5	10.9	66.1
HE2	11.6	54.3	171
HE3	12.3	33.8	96.9
HE4	10.7	22.9	95.6
HE5	17.9	50.6	300
HE6	22.0	59.7	344
HE7	54.7	128	524
HE8	40.2	198	364
HE10	7.6	14.3	106
HE11	24.2	66.1	603
HE12	36.7	101	796
HE13	194	378	714
HE14	132	64.6	830
Heathcote River			
HE21	12.4	35.3	441
HE22	8.8	24.5	529
HE23	16.3	46.2	1240
HE24	98.9	47.4	631
HE25	76.4	36.7	381
HE26	96.0	75.3	666
HE27	39.6	50.8	427
HE28	38.7	26.3	287
HE29	21.4	67.8	264
Outside SWCPA			
HE30	43.9	74.2	592
HE31	60.9	89.2	706
HE32	28.6	53.3	258
HE33	23.0	35.7	209
HE34	16.5	26.1	135

The median lead concentration of all samples collected from the catchment was 51 mg/kg (range 11 to 378 mg/kg). Lead concentrations were highest in Heathcote River tributaries at sites HE7, HE8, HE12 and HE13, where 100 mg/kg was exceeded. Lead concentrations in the Heathcote River varied between 24.5 and 75.3 mg/kg, and appeared to increase slightly with distance downstream.

Zinc ranged from 66 to 1240 mg/kg (median 381 mg/kg). Highest concentrations were found in the tributaries at sites HE11 to HE14, and at site HE23 in the Heathcote River downstream of Haytons Drain. Overall, zinc concentrations were slightly higher in the main stem of the Heathcote River than in the tributaries.

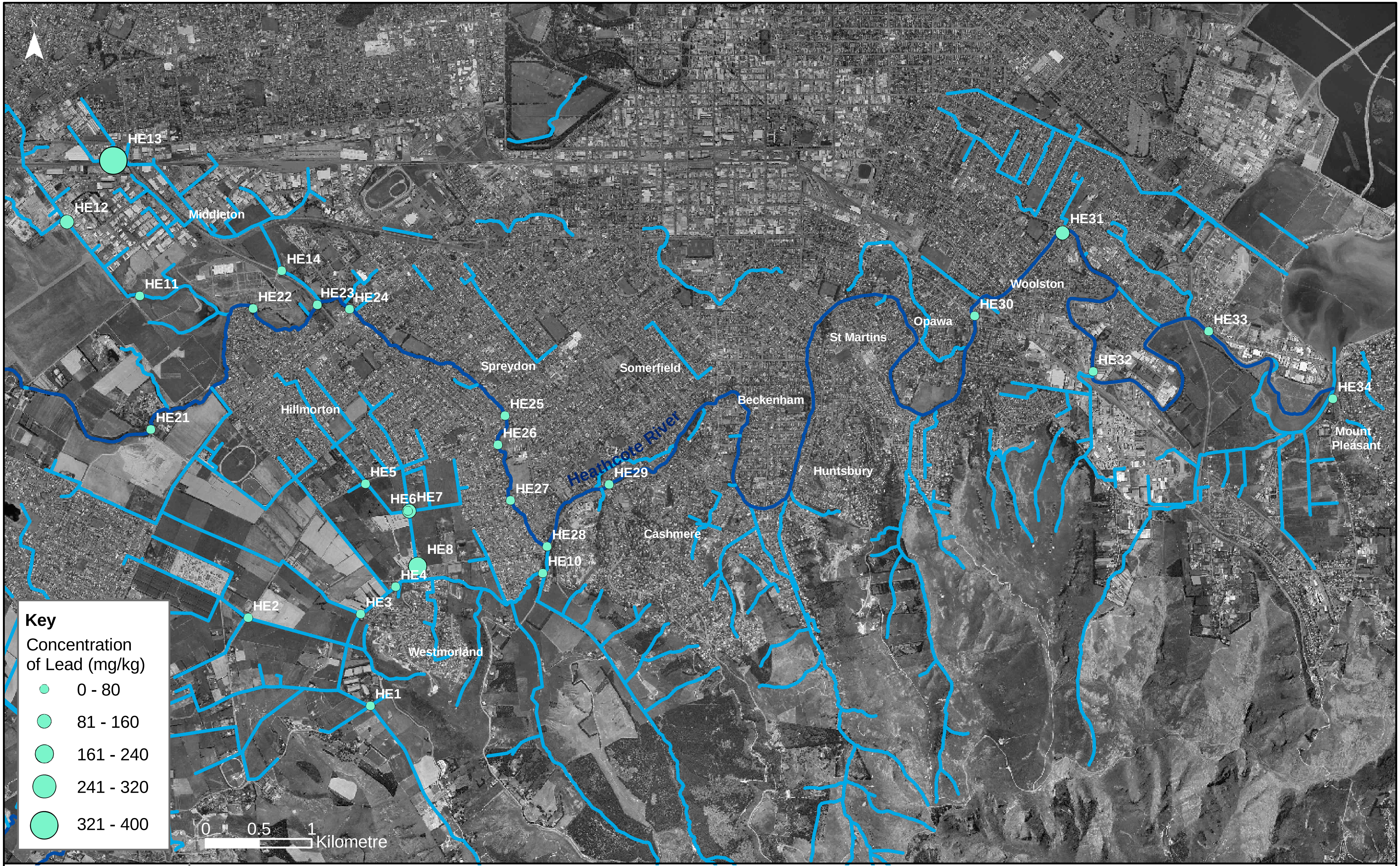


Kingett Mitchell Ltd
RESOURCE & ENVIRONMENTAL CONSULTANTS

TITLE:
COPPER CONCENTRATION IN HEATHCOTE CATCHMENT SEDIMENTS

CLIENT:
CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 4.2



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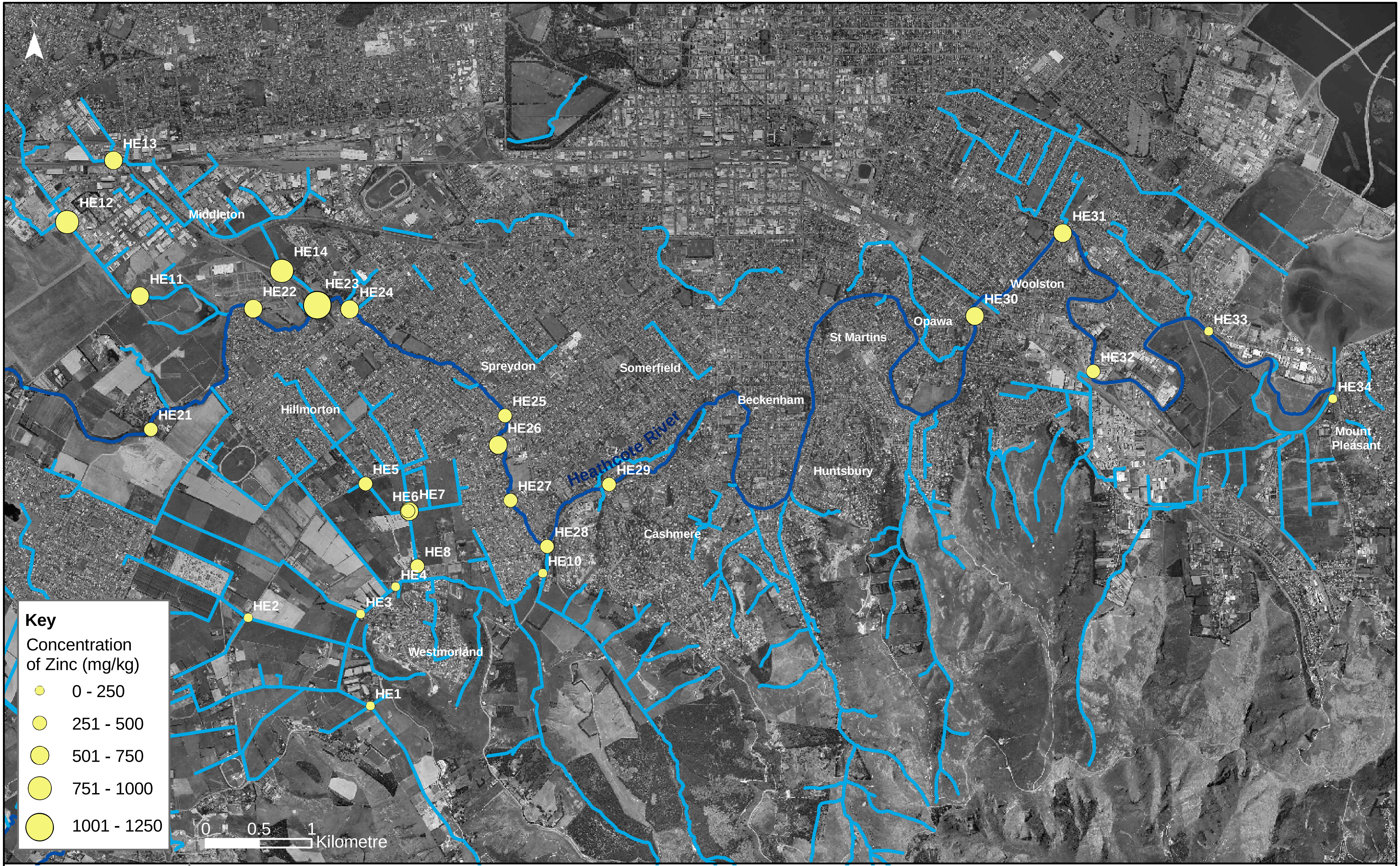
TITLE:	LEAD CONCENTRATION IN HEATHCOTE CATCHMENT SEDIMENTS	DATE:	JUNE 2005
		PROJECT NO:	500673
CLIENT:	CHRISTCHURCH CITY COUNCIL	FIGURE NO:	4.3



Kingett Mitchell Ltd
RESOURCE & ENVIRONMENTAL CONSULTANTS

TITLE:
ZINC CONCENTRATION IN HEATHCOTE CATCHMENT SEDIMENTS

CLIENT:
CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 4.4

Figs. 4.2 to 4.4 indicate that in general, higher concentrations of metals were found in the tributaries and drains in the north east of the catchment (Haytons Drain and Curletts Drain). With lower concentrations of metals generally detected in Cashmere Stream and its upper tributaries. Outside the South-West Christchurch catchment, metal concentrations decreased with proximity to the estuary, with the exception of site HE31. This may be due to the texture of this sample, which was 92% mud, compared to 54 to 80% for HE30 to HE34.

4.4.2 Halswell River Catchment

The total recoverable copper, lead and zinc concentrations in the stream sediment samples from the Halswell catchment are presented in Table 4.5. (see Appendix B for raw results). The overall median copper concentration was 9.3 mg/kg (range 2.9 to 66.5 mg/kg). Concentrations of copper were highest at tributary sites HA1, HA2, HA4 and HA21.

Table 4.5: Total recoverable copper, lead and zinc concentrations in sediment from the Halswell river catchment (all data mg/kg).

Site ID	Copper	Lead	Zinc
Tributaries			
HA1	35.9	56.5	587
HA2	14.5	38.8	219
HA3	5.1	23.2	150
HA4	17.5	25.7	243
HA5	9.6	17.6	58.3
HA6	6.4	14.4	58.1
HA7	9.3	16.2	67.2
HA21	66.5	77.2	693
HA22	29.6	45.1	420
Halswell River			
HA23	2.9	6.04	37.0
HA24	8.6	18.0	64.4
HA25	8.7	20.6	77.8
HA26	6.4	12.8	79.2
HA27	4.2	9.69	52.0
Outside SWCPA			
HA30	5.6	12.9	59.5
HA31	7.7	17.4	77.2
HA32	12.2	22.8	99.1
HA34	10.3	17.3	61.3
HA35	10.5	19.6	88.7

The median lead concentration was 18 mg/kg (range 6 to 77 mg/kg). Lead concentrations were also highest in samples collected from the tributaries at sites HA1, HA2, HA21 and HA22. The median zinc was 78 mg/kg and concentrations ranged from 37 to 693 mg/kg. Highest concentrations were also measured at sites HA1, HA21 and HA22.

The metal concentrations are presented graphically in Figs. 4.5 to 4.7. and confrim that concentrations of metals were considerably higher in the tributaries than in the main stem of the river.

The median copper concentration in the tributaries was 14.5 mg/kg compared to 6.4 mg/kg in the river, median lead concentrations were 25.7 and 12.8 mg/kg respectively and zinc concentrations were 219 and 64.4 mg/kg respectively. The highest concentrations for all three metals were measured at site HA21. This site was adjacent to the Halswell Junction and receives stormwater from the Halswell Junction stormwater treatment pond.

4.4.3 Summary

The survey of metal concentrations in sediments from the Heathcote and Halswell River catchments has shown that the concentrations were generally lower in the Halswell River and stream sediments compared to those in the Heathcote catchment. The range of metal concentrations in the 2003 survey was moderate with the range being smallest for copper and at least ten fold for lead and zinc.

Concentrations in some of the Halswell River tributaries however, were similar to those measured in the tributaries of the Heathcote River. The similarity of these sites and those relatively unaffected by urban development is discussed in following sections.

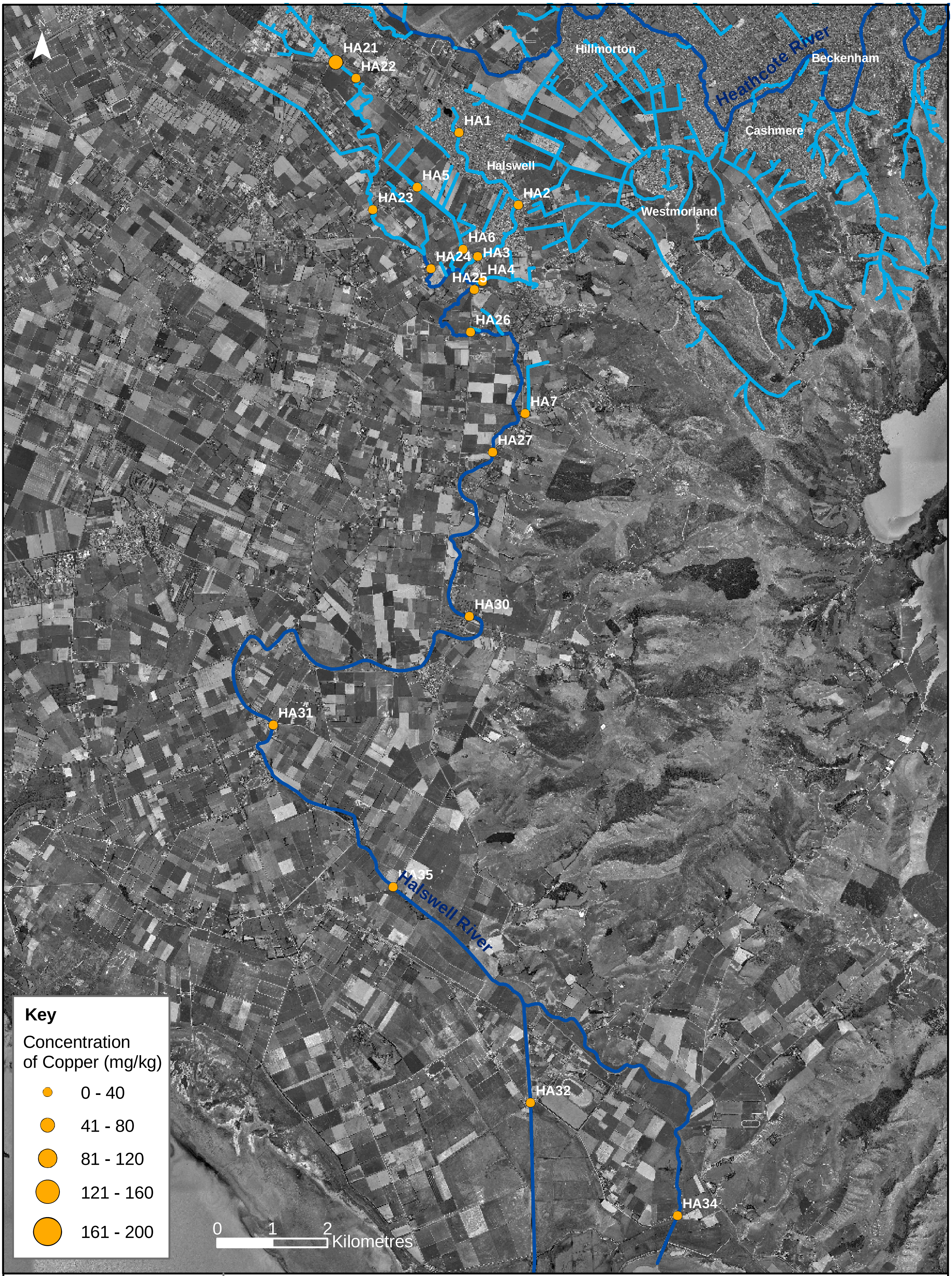
4.5 Influence of Sediment Texture on Metal Concentrations

4.5.1 Introduction

As discussed in Section 2, the physical characteristics of sediments influence the concentrations of metals (of both natural and anthropogenic origins). The texture of the sediment samples were discussed in Sections 3.3.1 and 3.3.2. The following sections re-examine the concentrations of contaminants with respect to texture.

4.5.2 Heathcote Catchment

Fig. 4.8 provides a summary of the physical characteristics of sediments in the less than 2 mm fraction for samples collected from the Heathcote River catchment. The median percentage of mud in the samples collected was 43%. Although Fig. 4.8 indicates variability in the proportions of mud in the samples analysed, this does not appear to be the predominant influence on the metal concentrations measured in the <2 mm fraction of the sediments as high concentrations are encountered in samples with little fine sediment (e.g., <20 % mud). Fig. 4.9 presents the relationship between mud content and metal concentrations in the Heathcote and Halswell catchments.



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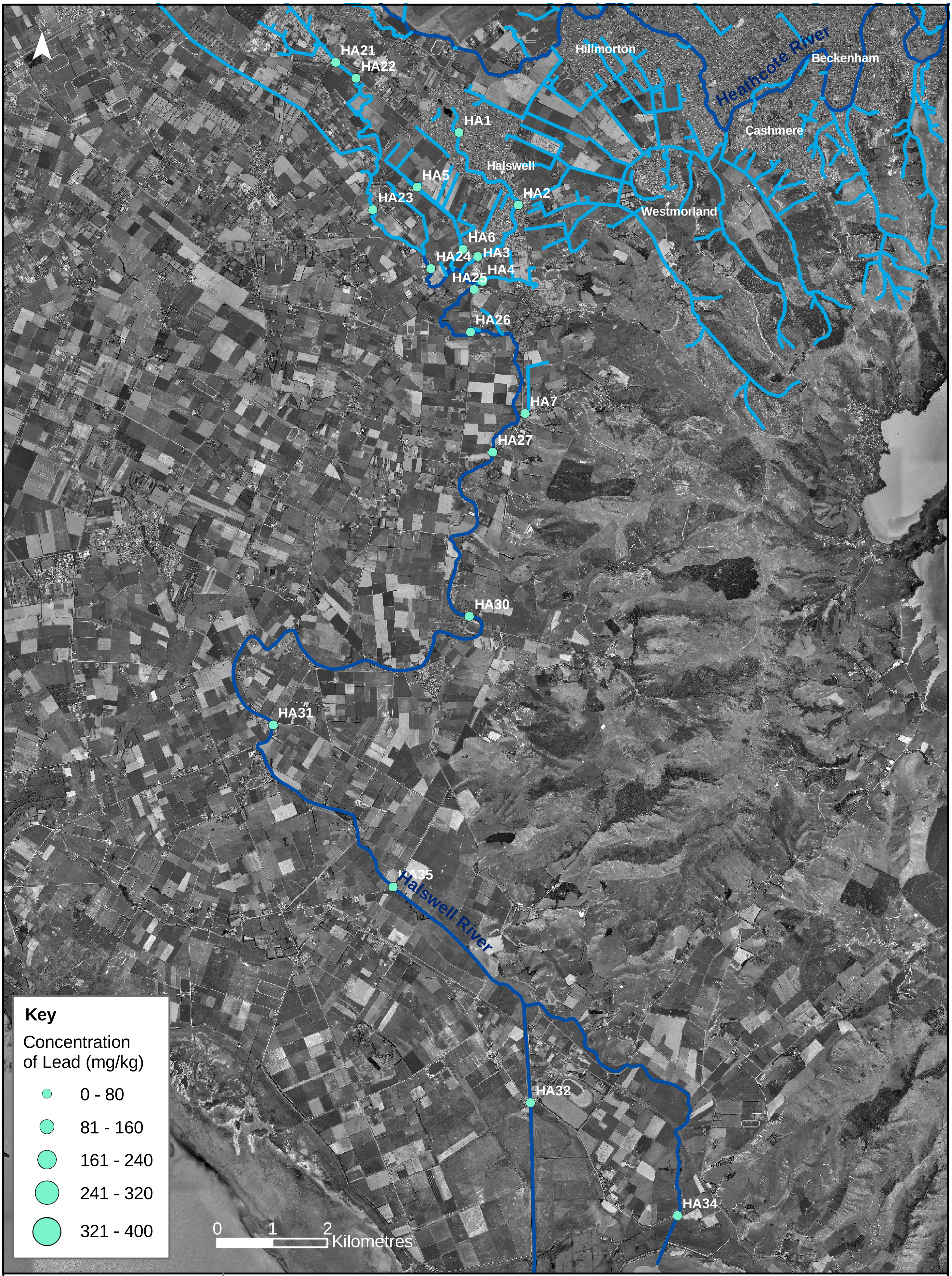
TITLE:
COPPER CONCENTRATION IN
HALSWELL CATCHMENT SEDIMENTS

CLIENT:
CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 4.5



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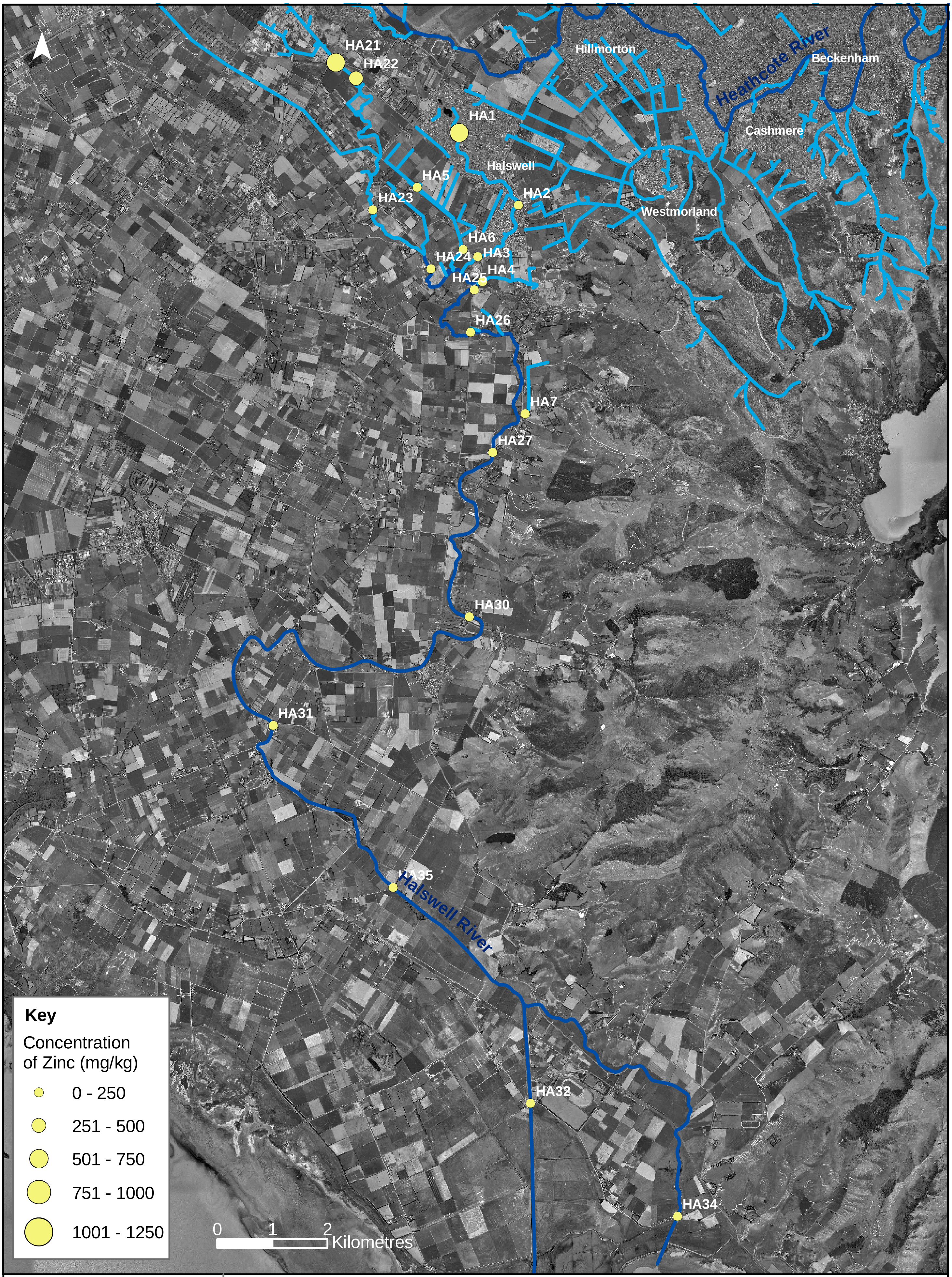
TITLE:
LEAD CONCENTRATION IN
HALSWELL CATCHMENT SEDIMENTS

CLIENT:
CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 4.6



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TITLE:
ZINC CONCENTRATION IN
HALSWELL CATCHMENT SEDIMENTS

CLIENT:
CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005

PROJECT NO: 500673

FIGURE NO: 4.7

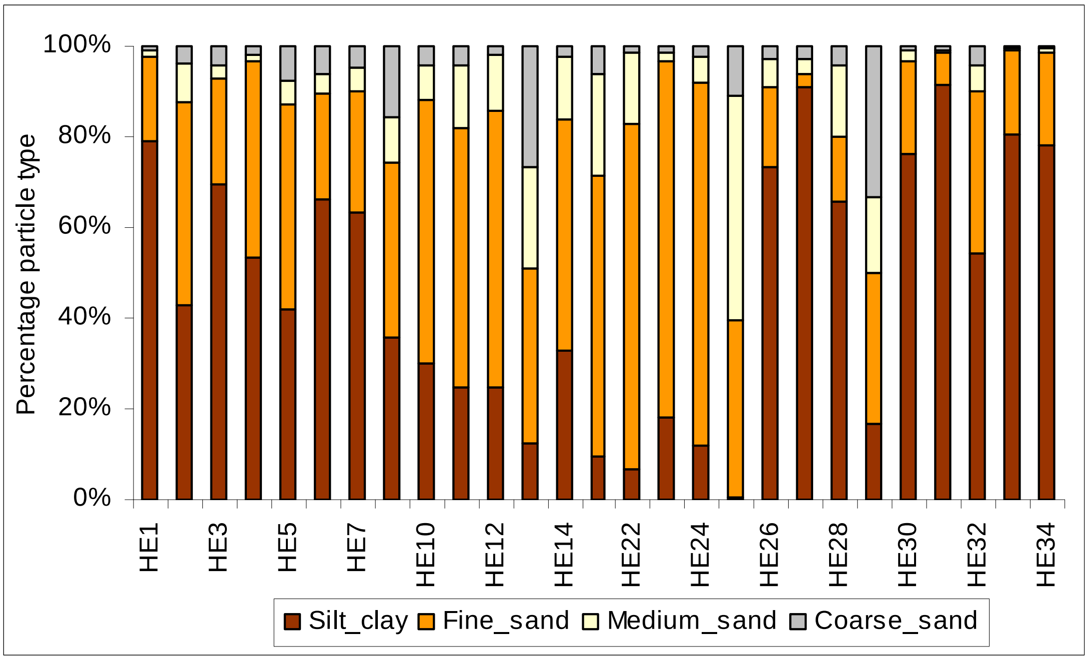


Fig. 4.8: **Physical characteristics of <2 mm fraction of samples collected from the Heathcote catchment.**

Samples collected at sites HE1 to HE4 generally contained lower concentrations of metals than most of the other sites in the catchment. Fig. 4.8 demonstrates that this is unlikely to be due to a textural influence as the proportion of mud in these samples was between 40 and 80% and was higher than samples from sites HE11 to HE14 (<40% mud). Similarly, samples collected near the Heathcote River mouth (HE30 to HE35) contained a high proportion of mud, however only two of these exceeded the zinc ISQG-high.

Fig. 4.9 indicates that sample HE25 contained very little mud. Unlike the samples upstream and downstream of this site this sample contained zinc at concentrations below the ISQG-high criteria. If a sample containing more fine sediment was able to be collected at this site, it is likely that it would have also exceeded the ISQG-high for zinc.

4.5.3 Halswell Catchment

Fig. 4.10 presents the physical characteristics of sediments in the <2 mm fraction for samples collected from the Halswell catchment. This indicates generally less variability than for samples from the Heathcote catchment. In the samples collected the mud content ranged from 6.8 to 83.6% with a median percentage of 32%. The majority of samples contained between 24 and 59% mud.

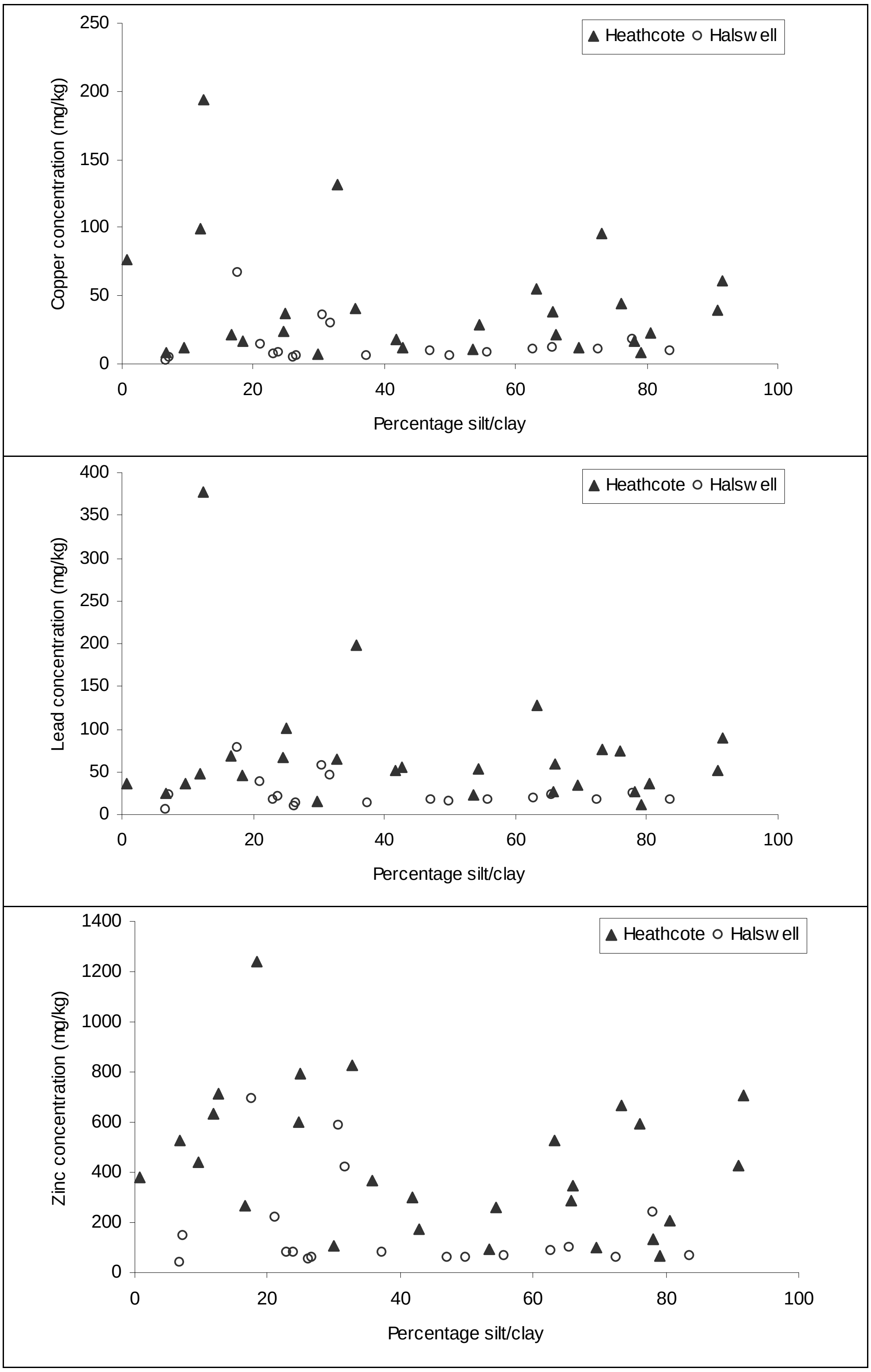


Fig. 4.9: **Relationship between percentage mud and metal concentrations in sediments from the Heathcote and Halswell River catchments.**

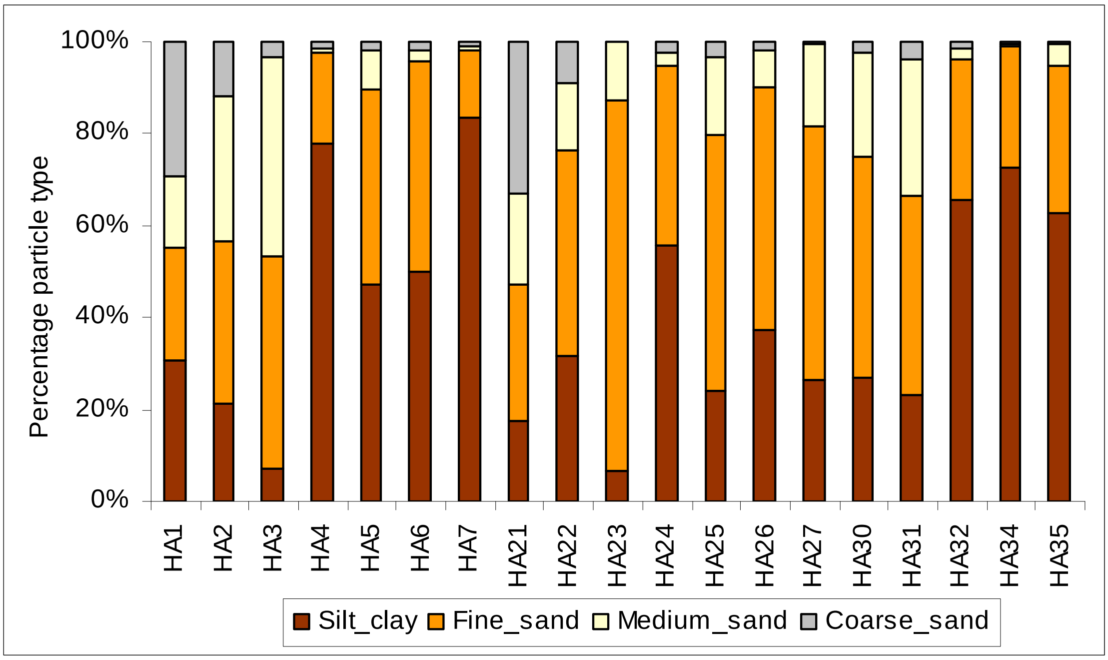


Fig. 4.10: **Physical characteristics of <2 mm fraction of samples collected from the Halswell catchment.**

Fig. 4.10 does not indicate an obvious relationship between the mud content and metals concentration, when the samples collected from urban catchments are removed from the data set, there does appear to be a relationship between the percentage of fines and metal concentrations. Fig. 4.11 shows a gradual increase in copper concentrations as the percentage of mud increases in samples within the catchment. Sample HA2 is marked separately on this chart as it receives stormwater from an urban area.

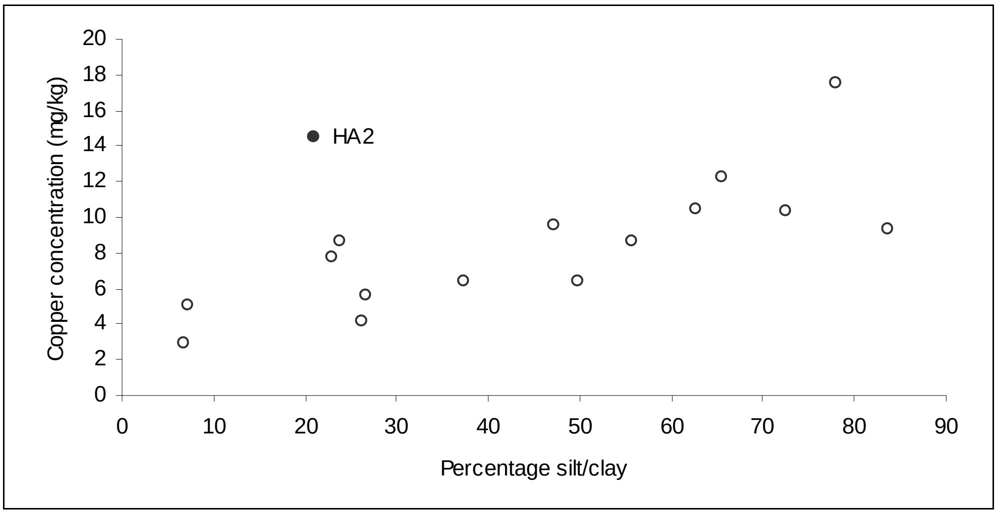


Fig. 4.11: **Relationship between percentage mud and copper concentrations in sediment samples from the Halswell River catchment.**

Linear relationships between metal concentrations and physical parameters such as % mud (silt plus clay) or % clay are typically observed in sediments where the metal concentration represents a natural origin i.e., from local soil or rocks. Such relationships are common in sediments derived from greywackes and argillites eroded from the Southern Alps. While the data for copper in Fig. 4.11 suggests that the copper present may be ‘natural’ in origin the fine particles may have also adsorbed a portion of this contaminant from anthropogenic discharges.

The variation in the data at any one point on the x-axis in Fig. 4.11 is about 4 mg/kg. Fig. 4.12 shows a range of copper data for sediments collected in Pegasus Bay from the Avon-Heathcote estuary north to the Ashley River. The concentrations in the dataset increase steadily from 2 to 4 mg/kg of copper in sands to 6 to 11 mg/kg in muds (i.e., 100% silt+clay); with a typical variation of about 2 mg/kg. At the sandy end of the data, the Halswell stream sediments have similar concentrations to sandy sediments in Pegasus Bay. As the sediments become muddier, the concentrations may be slightly higher than those found in Pegasus Bay sediments. Given that there were no specific independent controls between the various studies to ensure comparability of data, much of the Halswell stream copper concentration data is close to the concentrations that would be expected without anthropogenic contributions of copper.

For lead, examination of sediments in Pegasus Bay indicates that concentrations in sandy sediments would be expected to lie between 5 to 10 mg/kg and in muds would be about 20 mg/kg. A comparison with the data in Fig. 4.9 shows that much of the measured lead data is higher than that measured in sediments from Pegasus Bay.

For zinc, examination of sediments in Pegasus Bay indicates that concentrations in sandy sediments would be expected to lie between 30 to 40 mg/kg and in muds would be about 60 mg/kg. A comparison with the data in Fig. 4.9 shows that much of the measured zinc data is higher than that measured in sediments from Pegasus Bay (of similar physical characteristics).

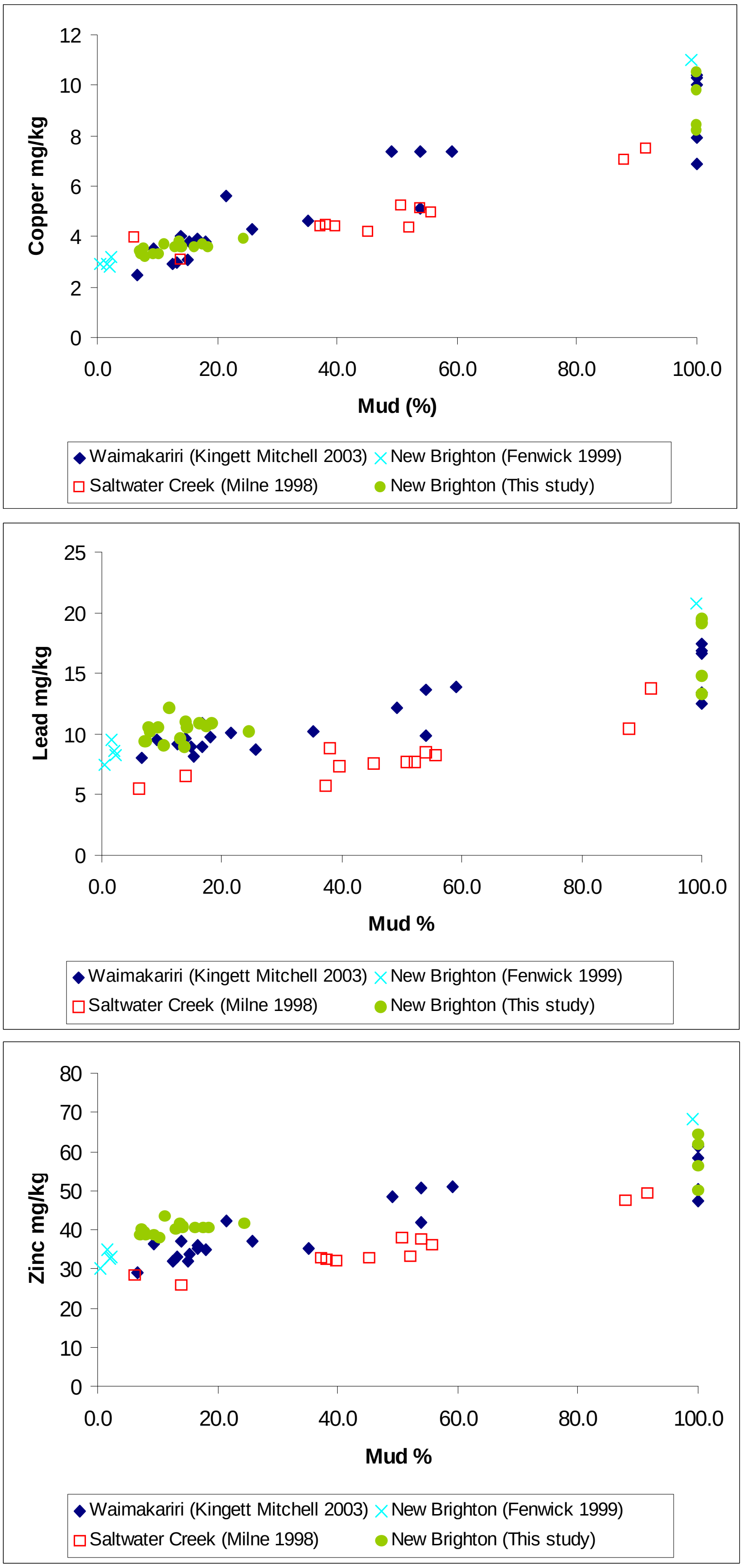


Fig. 4.12: **Copper, lead and zinc in sediments from Pegasus Bay (This study in the key refers to Kingett Mitchell 2003b).**

4.5.4 Summary

Sediment texture (particle size distribution) is an important factor in determining the levels of a contaminant in a sediment at a given site. The natural variation may be relatively large compared to the base-line concentration (i.e., the concentration in the absence of any contamination) but the overall concentration change from coarse to fine sediments is not large and for all elements this difference is typically about three times.

The presence of fine sediment in stream beds can also result in greater concentrations of metal contaminants. This arises for two reasons. Firstly because the contaminants may be associated with fine particles at the source (e.g., soils and road surface dusts) and secondly because the fine particles provide sites for the sorption of metals through the increased presence of organic matter, clays and iron / manganese oxides and oxyhydroxides on particle surfaces.

4.6 Influence of Landuse

4.6.1 Introduction

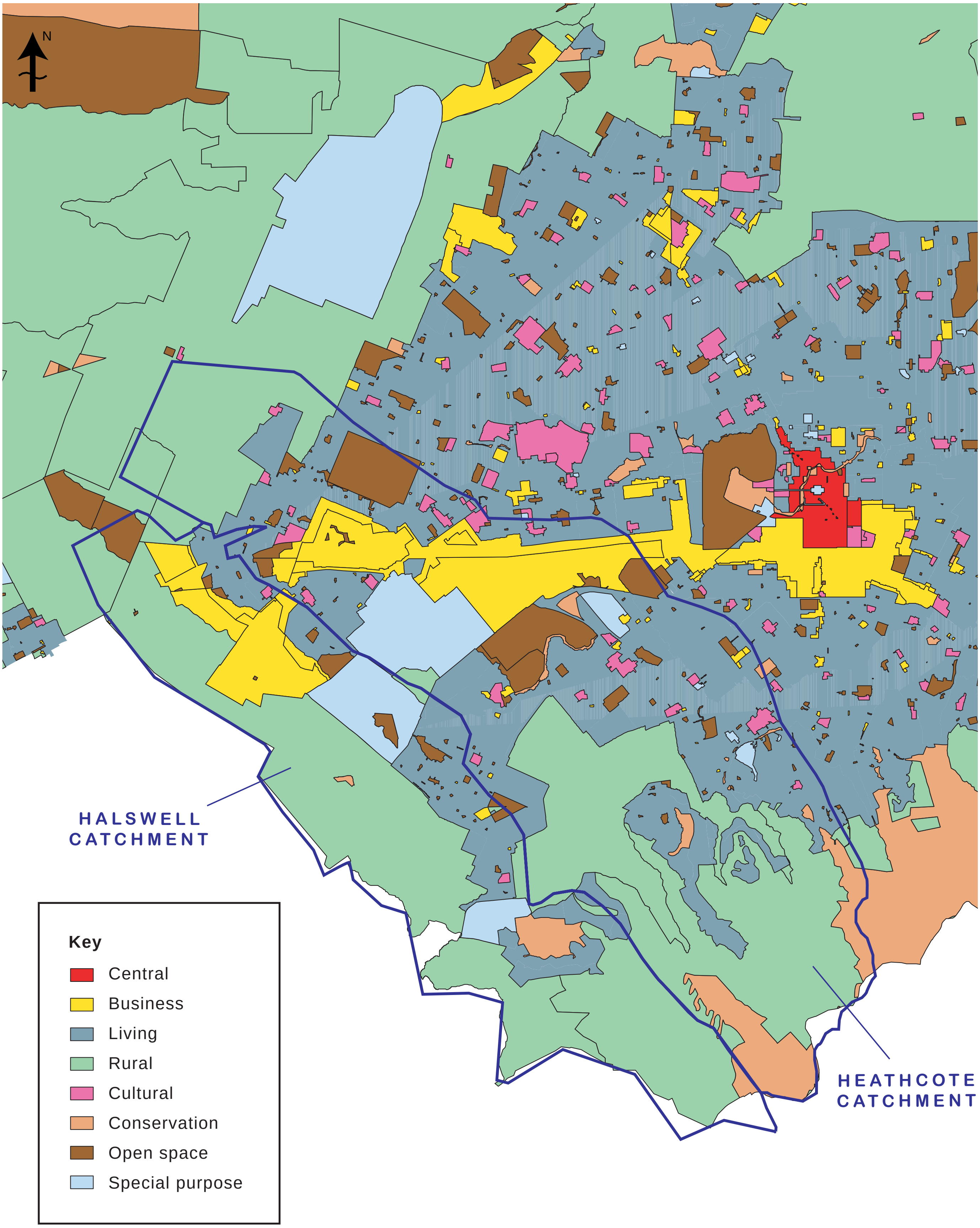
Land-use in the South-West Christchurch project area is shown in Fig. 4.13 by District Plan Zones and ranges from industrial to rural.

In the Heathcote catchment, the landuse includes:

- Industrial land use in Hornby and around Blenheim Road.
- Residential land use around the Cashmere Stream and the main Heathcote River.
- Rural land use in the upper Cashmere Stream and its tributaries.

The Halswell catchment is predominantly rural, however there are several urban areas including:

- Industrial land use near Halswell junction.
- Commercial land use near Nottingham Stream.
- Residential land use in the catchment of Nottingham Stream.



Source: Geodata Services Christchurch City Council

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TITLE:

CITY ZONING WITHIN THE HEATHCOTE CATCHMENT AND THE HALSWELL CATCHMENT

DATE:
JUNE 2005

PROJECT NO:
500673

CLIENT:
Christchurch City Council

FIGURE NO:
4.13

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4.6.2 Differences between land uses

Different land uses within the catchment can be expected to generate different contaminant loads that may enter the stream systems. The influence of land use on sediment quality was examined by categorising sampling sites by their land use (Table 4.6). The placement of each site into a particular land-use category was based upon catchment knowledge and examination of aerial photographs. CCC is currently obtaining quantitative data on catchment land-use.

Table 4.6: Land use categories.

Land use category	Sites Included
Heathcote catchment	
Rural	HE1, HE2, HE3
Residential	HE5, HE6, HE7
Industrial	HE12, HE13, HE14
Mixed	HE24, HE25, HE29
Halswell catchment	
Rural	HA5, HA6, HA7
Mixed Urban	HA1, HA2, HA21
Mixed	HA25, HA26, HA27

There were no pristine bush sites located within the project area that would have been suitable as background/control sites. Pristine sites outside the study area may have different geology resulting in different sediment characteristics so this approach was not used. Each of the two catchments includes areas of rural land use and these were considered to be ‘background’ for the purposes of this study.

Due to the smaller area of residential, commercial and industrial land use in the Halswell catchment, these land uses were grouped together as ‘mixed urban’ for the purposes of statistical analyses. The sites included in this category were HA1, HA2 and HA21.

It should be noted that the sites are not statistically independent. Several of the sites are in the same tributary (e.g., HE13 and HE14; HA1 and HA2; HA5 and HA6). Sites in the main stem of the river are also not independent.

4.6.3 Differences in metals by land use

The different land uses in the two catchments are compared in Fig.4.14. This indicates that copper concentrations in the sediments from industrial land use in the Heathcote catchment were much higher than those from rural/background sites. However, a one-way analysis by ANOVA showed no significant difference between land uses in the Heathcote catchment or the Halswell catchment.

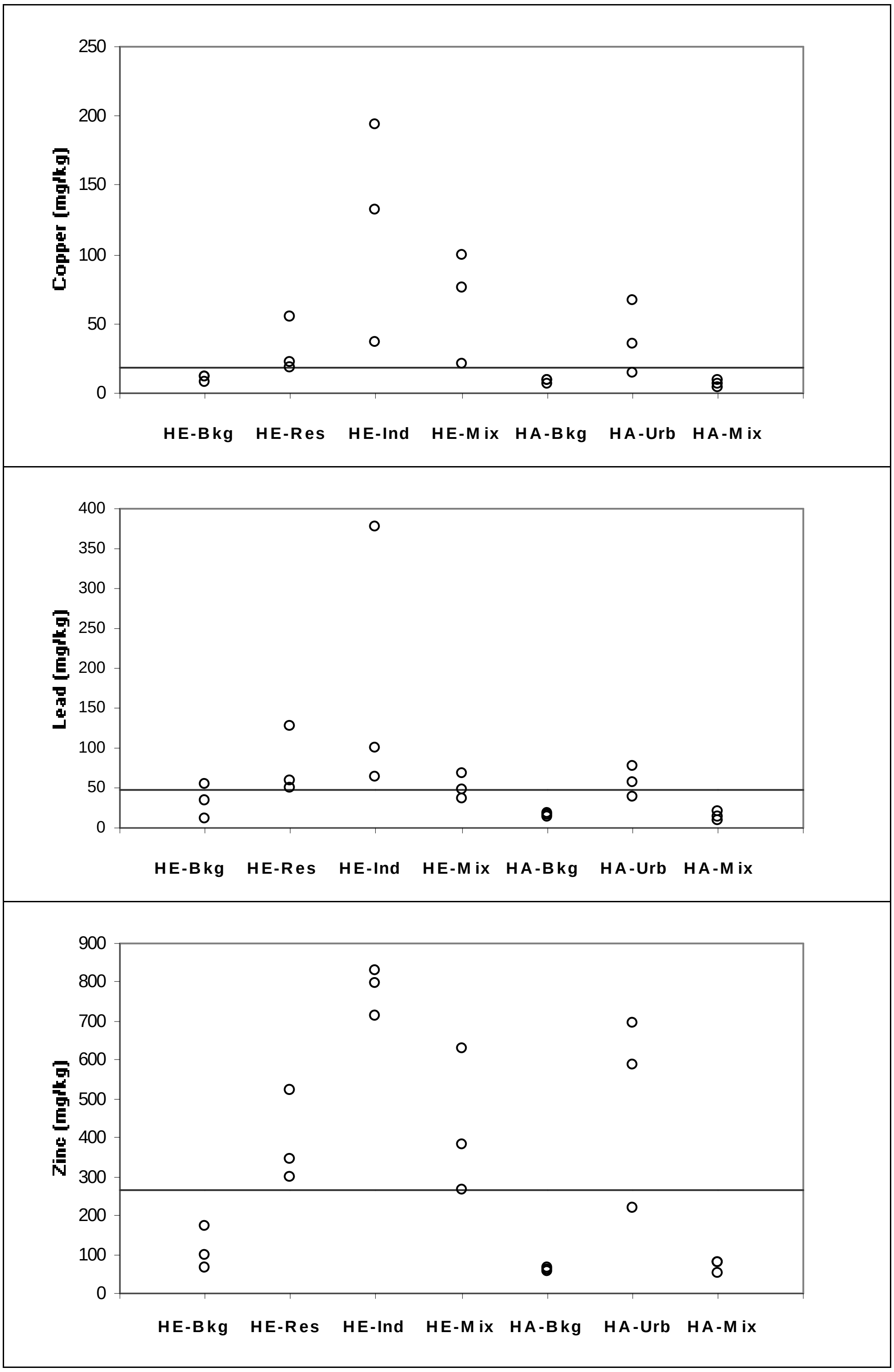


Fig. 4.14: **Comparison of copper, lead and zinc concentrations in sediments from different land uses. Note: solid line is overall median.**

Lead concentrations show a similar trend in the Heathcote catchment, being highest at the industrial sites (although variable), lower at the residential and mixed sites and lower again in the ‘background’ sites. The difference between land uses was not statistically significant for the Heathcote catchment. The percentage of mud in the sample was included in the analysis, and the interaction term was statistically significant. The mud content may vary with land use, therefore any change in lead concentrations may actually be due to the change in mud content.

The Halswell catchment showed higher concentrations of lead in sediment from urban sites compared to ‘background’ and mixed sites. This was statistically significant, when mud content was included in the analysis. There was no difference between the data for ‘background’ and other land use types.

Fig. 4.14 shows the difference in zinc concentrations between land use types in the Heathcote catchment. There was a statistically significant difference between land uses. The Tukey HSD indicated that industrial land use was significantly different from ‘background’ land use. In the Halswell catchment, there was also a significant difference in zinc concentrations with land use, where urban land was statistically different from mixed land.

In summary, in the Heathcote catchment, the lead and zinc concentrations in sediments were highest from industrial catchments, followed by mixed urban and residential catchments, which were higher than the background (rural) catchments. For the Halswell catchment, sediments from urban catchments had higher metals than the mixed and background (rural) catchments. The mixed land use sites were all in the main stem of the Halswell River, and the catchment was predominantly rural, with some upstream urban influences.

4.7 Comparison to Other Urban Areas

There have been a number of other studies that have examined the quality of sediments in streams elsewhere in New Zealand. The most significant published studies are two undertaken in Auckland (Kingett Mitchell 1998 and Mills et al. 1998). A number of studies have also been undertaken in Auckland where estuarine sediments have been sampled at the mouth of streams; some data from one of these (Meritec 2000) is presented.

When comparing the Auckland data to that obtained in the current study, of the following factors need to be considered: the geology, the grain size of the analysed sediment, and the adopted extraction method.

Mills et al. (1998) examined stream sediments collected from streams within Auckland City. Samples for total metals were freeze dried then sieved to <0.5 mm to remove coarse material. Samples were digested using hot aqua-regia (3:1 $HCl:HNO_3$).

The Kingett Mitchell (1998) study examined stream sediment quality in Waitakere City (west of Auckland City). Analysis were conducted using the <2 mm fraction and total recoverable metals digest using nitric acid.

The Meritec (2000) study examined stream sediments within North Shore City. Total recoverable metals (USEPA 3051 digestion using nitric acid) were examined on <0.5 mm fraction of sediments.

Overall, the methods used in the two stream studies are likely to be generally comparable. Studies of the comparability of extraction techniques and inter-laboratory errors have shown that for sediment quality assessments, agreement is often reasonable (e.g., Cook et al. 1997).

Fig. 4.15 presents information from these studies and compares it with sediment data from the Heathcote and Halswell catchments. Examination of the data from the South-West Christchurch study and the earlier study shows that within any group of samples that were placed into a particular land-use category, the variation between results is very large. As such, the median data for each collection of sites placed into a particular land-use is generally representative of that location. In most cases the number of samples in each land-use is 3 to 7. Data used from the North Shore City study (Meritec, 2000) includes one data point from Wairau Creek and a number of samples collected from the lower esturarine reaches of the creek.

Examination of the data presented in Fig. 4.15 shows that the metal concentrations from sediment samples collected from Auckland and Christchurch follow a general trend from undeveloped to rural to urbanised.

For copper, concentrations increased from rural to residential, to mixed urban and industrial urban. This pattern was seen in the other cities shown.

For lead and zinc the pattern is similar to copper with the concentrations increasing from rural to residential, to mixed urban and industrial urban. This pattern was also seen in the other cities shown.

The differences seen in stream sediment quality are a function of several factors. These include the input of contaminants to the stream from sources such as urban stormwater and inputs from soils within the catchment. These inputs can be seen as current inputs from active industries and the number of motor vehicles within the catchment, and from historic effects. Consequently, the age of the urbanisation within the catchment is an important factor. When the quality of stream sediments in newer residential areas are compared with older more ‘historic’ residential areas contaminant concentrations appear higher in the latter. This is not surprising given the greater presence of leaded paints in older residential catchments (e.g., compare Waitakere residential with the higher Waitakere mixed in Fig. 4.15).

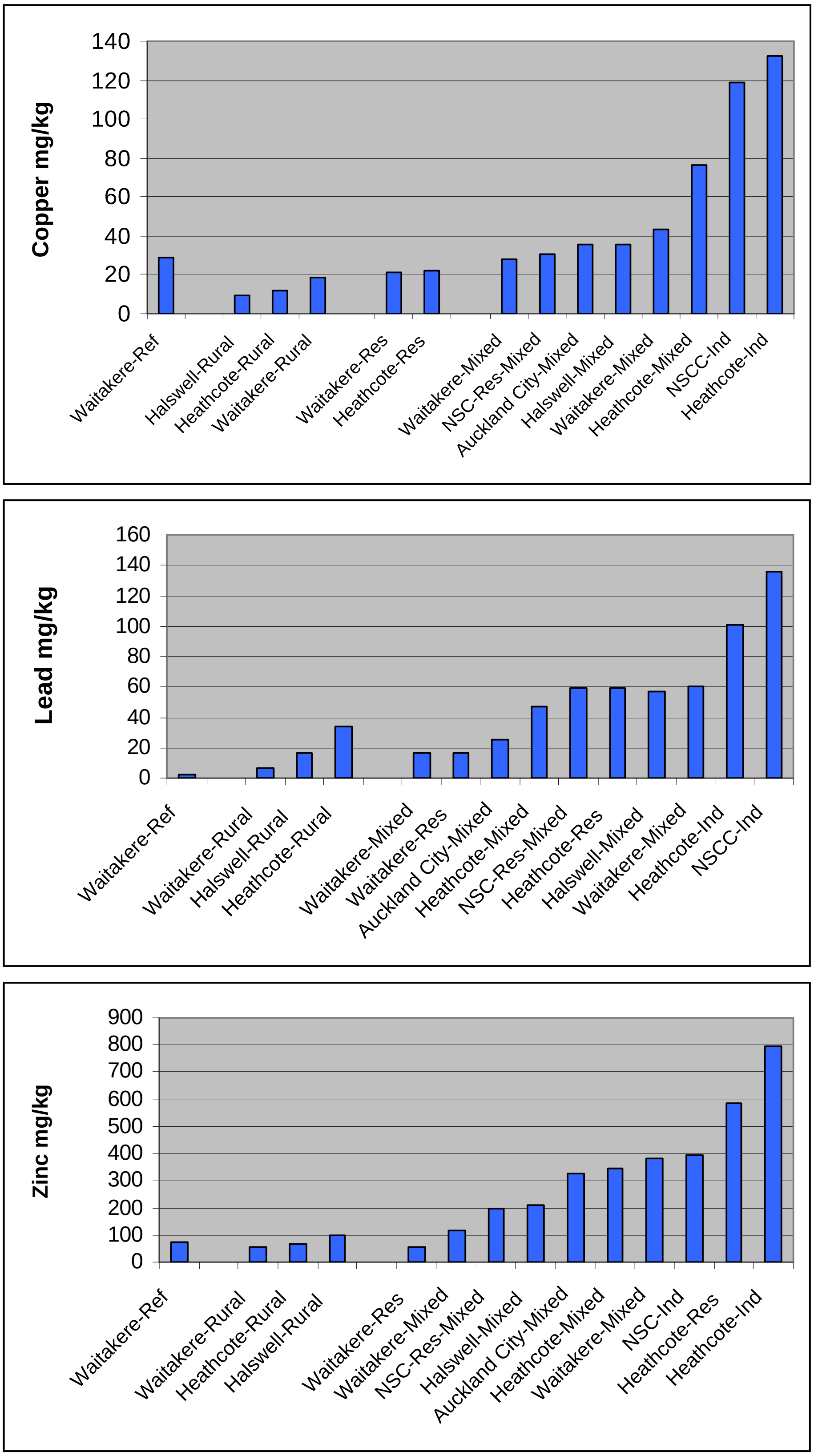


Fig. 4.15: **Geographical comparison of copper, lead and zinc concentrations measured in sediments from Auckland and Christchurch.**

4.8 Comparison to the 1980-1981 Survey

The concentrations of copper, lead and zinc for the 1980 to 1981 (Robb, 1988) and current study are compared in Fig. 4.16. This comparison is of the raw data only and does not take into account any differences due to sample texture. The data indicates a general increase in zinc concentrations throughout the Heathcote catchment of South-West Christchurch and a general decrease in lead. Copper concentrations were more variable, increasing at 5 sites, decreasing at 8 sites and remaining the same at 14 sites (Table 4.7).

Table 4.7: Relative change in metal concentrations.

		Number of sites	
	Increase by > 50%	**Decrease by > 50%**	**Change within 50%**
Copper	5	8	14
Lead	3	13	11
Zinc	11	4	12

As previously mentioned, the proportion of the silt + clay (mud) in the sediment samples has a major influence on the concentration of metals in the samples. The proportion of sediment <63 µm in the samples analysed (i.e. after removal of the greater than 2 mm fraction) for the 1980-1981 and current study is shown in Fig. 4.17. This figure shows that the proportion of fine sediment was generally slightly higher for samples collected by Robb (1988) at sites HE2 to HE5, and this is considered likely to account for the slightly higher metal concentrations found at these sites (Fig. 4.16). Sites HE26, HE27 and HE28 contained substantially more mud in the samples collected in the current survey than in the previous survey (Robb 1988), and zinc showed the anticipated trend with concentrations being higher in this study than the 1980 to 1981 investigation. Concentrations of lead and copper in these samples were variable and did not show the typical trend.

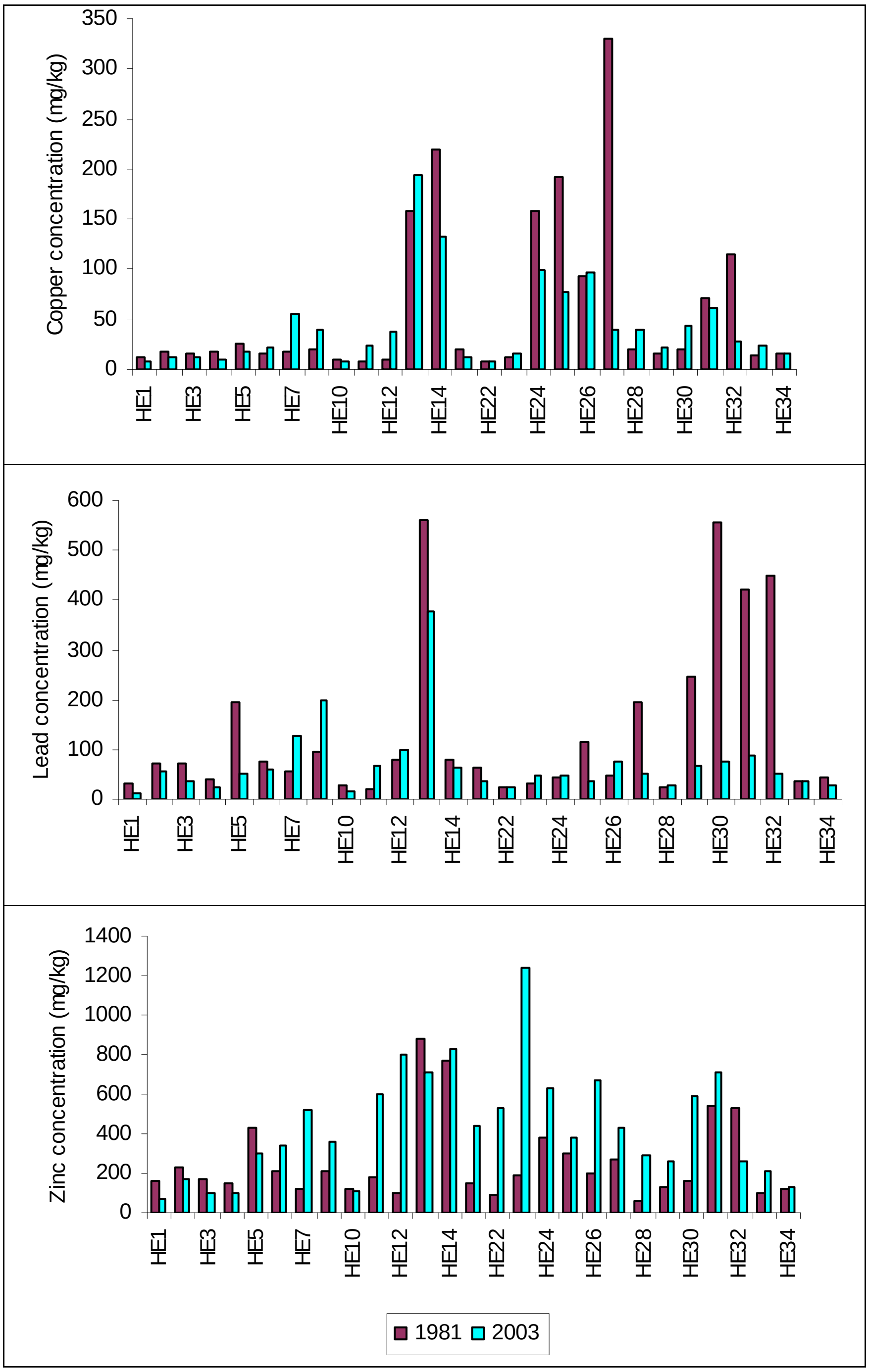


Fig. 4.16: **Comparison of copper, lead and zinc concentrations measured by Robb (1988) and this study (2003).**

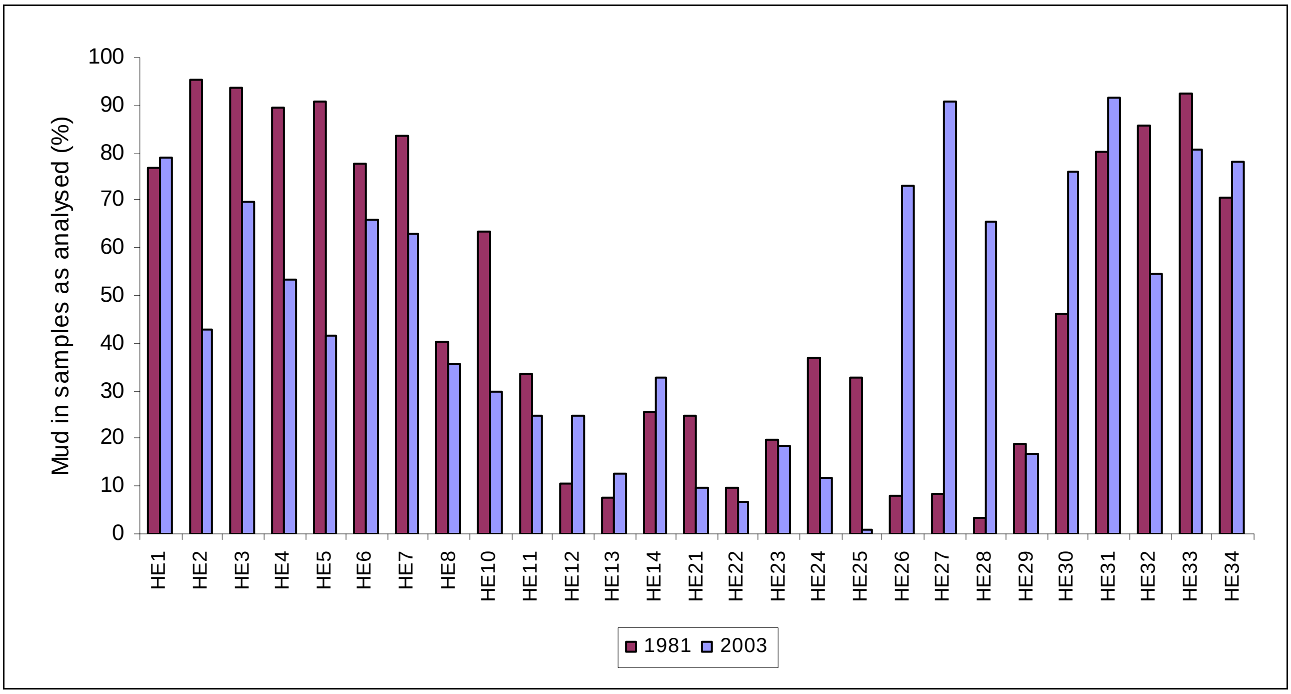


Fig. 4.17: **Comparison of mud fraction of sediment analysed in 1981 samples and this survey (2003).**

4.9 Implications of Changes in Metal Concentrations in Sediment

4.9.1 Introduction

As described in Section 1.5, sediment quality guidelines are a tool commonly used to provide a preliminary assessment of the implications of changes in sediment quality in sediments (both freshwater and marine). The ANZECC (2000) sediment quality trigger values (refer Section 1.5 and Table 1.1) are used in this section to assess the likely effects that sediment quality may have on biological communities inhabiting the stream.

Increased concentrations of metals in stream sediments have the potential to adversely affect stream biota that inhabit these sediments. Toxicity arises through the exposure of organisms to pore water within the sediments. Metals associated with the sediment are in equilibrium with the metals in the pore water. The concentration in the pore water is a function of many factors including the redox state of the sediment (how much oxygen is present) and the rate of diffusion between the pore water and the overlying stream waters. Concentrations can in some situations become high enough to exert toxic effects on biota. It should be noted however, that toxicity may arise from constituents other than metals. Ammoniacal nitrogen is common in stream-bed sediments especially if organic matter builds up and the sediments become anaerobic. A number of studies have shown that ammoniacal nitrogen in sediments is often implicated as the prime causal agent of toxicity.

Elevated concentrations of contaminants in stream water and in stream sediment is also likely to result in increased elemental concentrations in biofilms within stream systems. These biofilms, which include coatings of bacteria and fungi and other organisms (periphyton) on hard substrates and plants within streams, can contain significantly elevated concentrations of metals (many times higher than stream sediments). These high concentrations occur because the combination of organic matter and chemical precipitates in the coatings tend to have an affinity for trace metals. Because these biofilms are utilised as a food source by grazing organisms within stream systems, associated contaminants can be transferred to other organisms within the stream food web.

4.9.2 Heathcote Catchment

The total recoverable copper, lead and zinc concentrations in the sediment from the Heathcote catchment are presented in Table 4.8. The shading in the table represents exceedance of the ANZECC (2000) sediment guidelines. Amber shading represents exceedance of the ISQG-Low (but below the ISQG-High) and red shading represents exceedance of the ISQG-High. This information is summarised in Fig. 4.18.

It is apparent from this comparison, that zinc is the parameter of most biological concern. Out of the 27 samples examined, 21 samples exceeded the ISQG-low for zinc (200 mg/kg) and 13 of these also exceeded the ISQG-high (410 mg/kg). Six of the 13 samples that exceeded the ISQG-high criteria were collected from the main Heathcote River, five were collected from tributaries and two were collected outside the South-West Project Area.

Only one sample exceeded the ISQG-high for lead, of 220 mg/kg. This was the sample collected from Curletts Drain, downstream of Blenheim Road (378 mg/kg). However, 15 samples exceeded the ISQG-low of 50 mg/kg. The majority of these were collected from the tributaries to the Heathcote River.

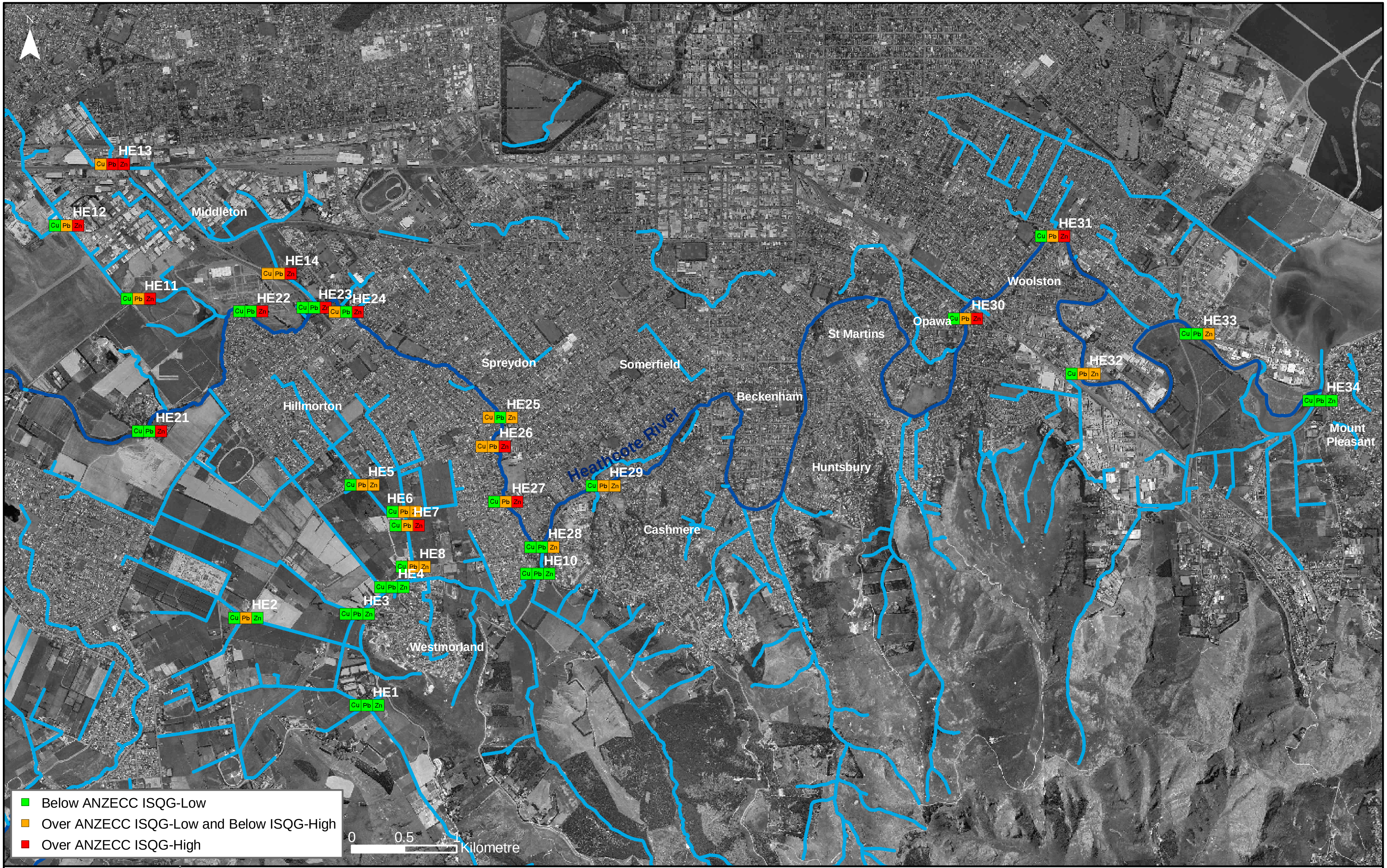
Five samples exceeded the ISQG-low for copper (65 mg/kg). Two of these were from Curletts Drain (HE13 and 14) and the other three from the Heathcote River, downstream of Curletts Drain. No samples exceeded the ISQG-high for copper of 270 mg/kg, however the sample from HE13 did approach this trigger level.

There were only four samples collected that did not exceed any of the ANZECC (2000) guidelines. These were from Milnes Drain (HE1), Dunbars Drain (HE3), Hendersons Drain (HE4) and Cashmere Stream (HE10) and from the estuarine part of the Heathcote River near Ferrymead Bridge (HE 34).

Table 4.8: Comparison of metal concentrations with ANZECC guidelines (all data mg/kg).

Site ID	Copper	Lead	Zinc
ANZECC ISQG-Low	**65**	**50**	**200**
ANZECC ISQG-High	**270**	**220**	**410**
Tributaries			
HE1	8.5	10.9	66.1
HE2	11.6	54.3	171
HE3	12.3	33.8	96.9
HE4	10.7	22.9	95.6
HE5	17.9	50.6	300
HE6	22.0	59.7	344
HE7	54.7	128	524
HE8	40.2	198	364
HE10	7.6	14.3	106
HE11	24.2	66.1	603
HE12	36.7	101	796
HE13	194	378	714
HE14	132	64.6	830
Heathcote River			
HE21	12.4	35.3	441
HE22	8.8	24.5	529
HE23	16.3	46.2	1240
HE24	98.9	47.4	631
HE25	76.4	36.7	381
HE26	96.0	75.3	666
HE27	39.6	50.8	427
HE28	38.7	26.3	287
HE29	21.4	67.8	264
Outside SWPA			
HE30	43.9	74.2	592
HE31	60.9	89.2	706
HE32	28.6	53.3	258
HE33	23.0	35.7	209
HE34	16.5	26.1	135

Overall, the metal concentrations indicate the potential for adverse effects to aquatic organisms. The ANZECC guidelines provide a decision tree for assessment of contaminated sediments. This indicates that for results above the ISQG-low criteria, the background concentrations should be checked. As sites in rural parts of the catchment contained copper, lead and zinc at concentrations below the ISQG-low, it is evident that the high concentrations are not due to naturally elevated concentrations in the sediment. The guidelines then suggest that factors controlling bioavailability be examined or the sediments be tested for acute and chronic toxicity before initiating remedial actions.



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TITLE:
COMPARISON OF COPPER, LEAD AND ZINC IN THE HEATHCOTE CATCHMENT TO ANZECC (2000) SEDIMENT QUALITY GUIDELINES

CLIENT:
CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 4.18

4.9.3 Comparison to previous survey

The concentrations of metals reported by Robb (1988) were compared to the ANZECC (2000) guidelines in Section 4.2. Previously, no sediment samples from sites in Cashmere Stream or Hendersons Road Drain exceeded the ANZECC (2000) guidelines for copper, lead or zinc. In the current survey, sites in these tributaries (HE1, HE4 and HE10) remained below the guidelines.

Curletts Drain exceeded the ANZECC ISQG-low for copper and lead and the ISQG-high for zinc at two sites in the 1980-1981 survey (sites 55 and 65). Both these sites were retested in the current survey (HE13 and HE14) and again exceeded the ISQG-low for copper and lead and the ISQG-high for zinc. In addition, one of the samples (HE13) also exceeded the ISQG-high for lead, measuring 378 mg/kg compared to the previous 159 mg/kg.

Dunbars Drain had previously exceeded the ISQG-low for lead (site 3 and 4) and zinc (site 3 only). The current survey indicated only an exceedance for lead (HE2).

Ballantines Drain and associated drains had also exceeded the ISQG-low for lead and zinc, with one sample also exceeding the ISQG-high for zinc. The sites retested (16, 18, 19, 24 now HE5 to HE8) also exceeded these guidelines and site HE7 now also exceeded the zinc ISQG-high.

In the main Heathcote River, the concentrations of copper, lead and zinc had previously exceeded guidelines at many sites. Of the nine sites that were retested in the current survey, five had previously exceeded the ISQG-low for copper, four sites had exceeded the ISQG-low for lead and three sites had exceeded in ISQG-low for zinc. In the current survey, there was a slight reduction in copper and lead exceedances, with three sites each exceeding the copper and lead guidelines. However, zinc concentrations in the main river now exceed the ISQG-high at six out of nine sites.

Downstream of the South-West Christchurch project area, the results were similar to the previous study for the sites closest to the river mouth (HE33 and HE34). Previously there had been no guideline exceedances, whereas there was an exceedance of the zinc ISQG-low in the current survey. At sites HE30 to HE32, lead concentrations had previously exceeded the ISQG-high, whereas in the current survey, the levels were below this, while exceeding the ISQG-low. Zinc levels remained above the ISQG-high at two out of three sites.

4.9.4 Halswell Catchment

In comparison to the Heathcote catchment, the Halswell catchment had far fewer samples exceeding ANZECC (2000) guidelines (Table 4.9), with only five of the 19 samples collected exceeding guidelines. The samples with exceedences were collected from tributaries of the Halswell River, Nottingham Stream, an unnamed drain and Knights Stream. Samples collected from the main stem of the Halswell River (both inside and outside the South-West catchment area) did not exceed ANZECC sediment quality guidelines. This indicates that there is low risk of adverse effects to aquatic organisms in the Halswell River from the presence of copper, lead or zinc. Fig. 4.19 provides a summary of the data.

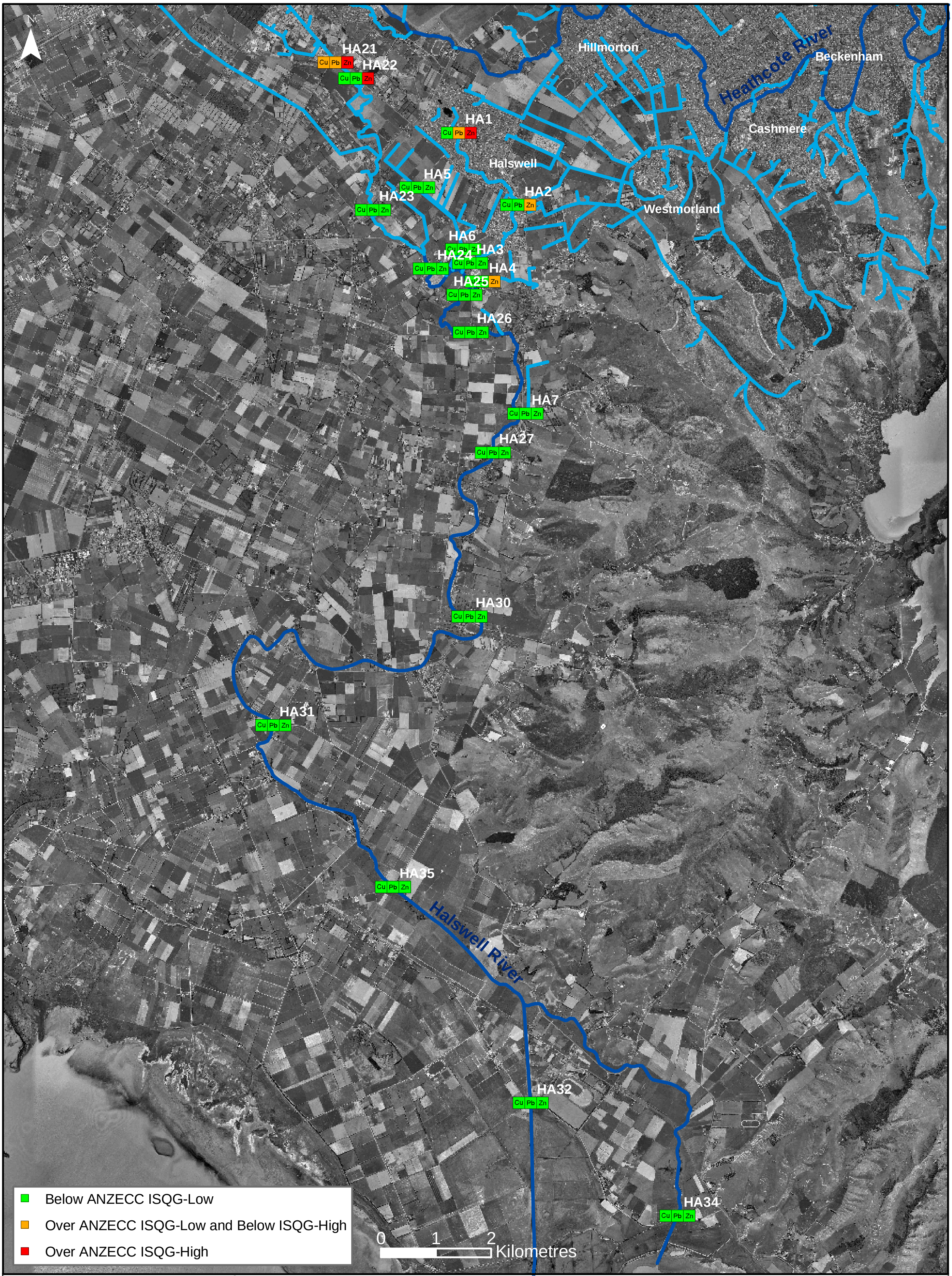
Table 4.9: Total recoverable copper, lead and zinc concentrations in sediment from the Halswell catchment (all data mg/kg).

Site ID	Copper	Lead	Zinc
ANZECC ISQG-low	**65**	**50**	**200**
ANZECC ISQG-high	**270**	**220**	**410**
Tributaries			
HA1	35.9	56.5	587
HA2	14.5	38.8	219
HA3	5.1	23.2	150
HA4	17.5	25.7	243
HA5	9.6	17.6	58.3
HA6	6.4	14.4	58.1
HA7	9.3	16.2	67.2
HA21	66.5	77.2	693
HA22	29.6	45.1	420
Halswell River			
HA23	2.9	6.04	37.0
HA24	8.6	18.0	64.4
HA25	8.7	20.6	77.8
HA26	6.4	12.8	79.2
HA27	4.2	9.69	52.0
Outside SWCPA			
HA30	5.6	12.9	59.5
HA31	7.7	17.4	77.2
HA32	12.2	22.8	99.1
HA34	10.3	17.3	61.3
HA35	10.5	19.6	88.7

Note: SWCPA – South-West Christchurch Project Area.

Five samples exceeded the ISQG-low for zinc and three of these also exceeded the ISQG-high. Two samples also exceeded the ISQG-low for lead and one of these also exceeded the ISQG-low for copper (Table 4.9). This particular sample (HA21) was collected from Knights Stream, adjacent to Halswell Junction.

The samples collected at sites HA1, HA21 and HA22 which exceeded the ISQG-high for zinc, indicate the potential for sediment quality to have an advers effect on instream biota. However, because these sites contained little (HA1) or no water (HA21, HA22) during sampling at baseflow conditions, the presence of elevated zinc in the sediments at these sites is considered unlikely to pose an immediate threat to aquatic organisms.



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TITLE:	COMPARISON OF COPPER, LEAD AND ZINC IN THE HALSWELL CATCHMENT TO ANZECC (2000) SEDIMENT QUALITY GUIDELINES	DATE:	JUNE 2005
		PROJECT NO:	500673
CLIENT:	CHRISTCHURCH CITY COUNCIL	FIGURE NO:	4.19

While there is potential for contaminated sediments to be transported downstream to locations which do have baseflow water, this is considered unlikely to occur at sites HA21 and HA22, where observations suggest that the sediments are not likely to be readily moved. Water is discharged into these sites from the Halswell detention pond and therefore flash floods are unlikely here.

4.9.5 Summary

Sediment samples from the Heathcote catchment of South-West Christchurch displayed elevated concentrations of copper, lead and zinc. A large proportion of samples exceeded ANZECC (2000) guidelines for lead and zinc and a small number also exceeded the guideline for copper.

There were more exceedances of the zinc ISQG-high criteria in the current survey than in the previous survey (Robb 1988). However, the number of lead exceedances was slightly lower in the Heathcote River.

In contrast, only five samples from the Halswell catchment exceeded the ANZECC (2000) guidelines for copper, lead or zinc. None of these samples were collected in the Halswell River.

4.10 Overview and Summary

The survey of metal concentrations in sediments from the Heathcote and Halswell River catchments has shown that the concentrations were generally lower in the Halswell River and stream sediments compared to those in the Heathcote catchment. Concentrations in some tributaries in the Halswell catchment were similar to those measured in the tributaries of the Heathcote River.

Sediment texture is an important factor in determining the level of a contaminant in a sediment at a given site. In the Halswell catchment, the sediment texture appeared to have some influence on metal concentrations. In the Heathcote catchment, the metal concentrations appeared to be influenced by other factors, including the surrounding land use.

In the Heathcote catchment, the concentrations of metals generally increased from rural to residential, to mixed urban and industrial urban. This pattern has been observed for other cities in New Zealand. In the Halswell catchment, the metal concentrations generally increased from mixed land use (predominantly rural) to rural to mixed urban.

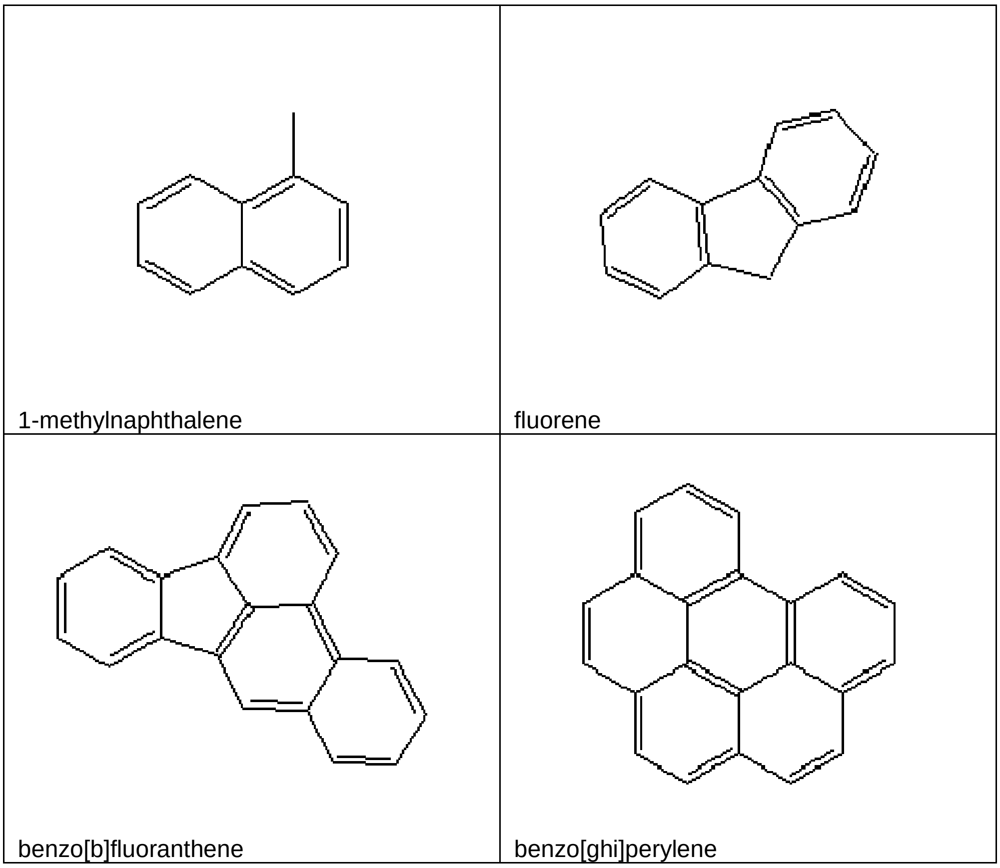
A large proportion of samples collected from the Heathcote catchment exceeded ANZECC (2000) guidelines for lead and zinc and a small number also exceeded the guideline for copper. These samples were typically collected from industrial and urban sites in the catchment. In contrast, only five samples from the Halswell catchment exceeded ANZECC guidelines for copper, lead or zinc. None of these samples were collected in the Halswell River.

When data was compared to the sediment quality data collected in the Robb (1988) survey, there was a general increase in zinc concentrations throughout the Heathcote catchment of South-West Christchurch, with more exceedances of the zinc ISQG-high criteria. The number of lead exceedances was slightly lower in the Heathcote River, and copper concentrations were more variable.

5. Polycyclic Aromatic Hydrocarbons

5.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are ubiquitous within urban environments. The literature on the distribution of PAHs in air, water, soils and sediments in and near urban environments is extensive. PAHs are a relatively complex group of aromatic compounds. Typically, environmental evaluations examine a limited number of key compounds based around the list of USEPA priority pollutants developed a number of years ago. Common examples such as those shown below range from two-ringed to multi-ringed compounds.



1-methylnaphthalene

fluorene

benzo[b]fluoranthene

benzo[ghi]perylene

Fig. 5.1: Common examples of PAHs.

PAHs are derived from many sources. These sources are often classified as petrogenic (derived from petroleum) or pyrogenic (derived from combustion processes including the use of fuels). The relative sources of PAH in any given urban area are site specific. As such, many studies show different source apportionment between vehicle emissions, combustion of coal and coke and other sources. For example, Simcik et al. (1999) estimated that around Chicago, coal combustion accounted for 48% of PAHs in the atmosphere, natural gas combustion 26%, coke ovens 14% and vehicle emissions 9%. Dickhut et al. (2000) examined contributions to Chesapeake Bay and found that motor vehicles were the most significant source of some PAHs (e.g., benzo[a]pyrene). 53% of the PAHs in the sea-surface microlayer near urban areas was identified as derived from motor vehicle emissions and 47% coal derived. When the sediments were examined 86% were coal derived and 14% vehicle derived. Another study near at Lake Calumet, Chicago, concluded that coke ovens contributed 47% of the PAHs in sediments; traffic 45% and residential fires 2.3%.

PAHs are present in urban runoff and in the runoff from motorways and roads. PAH concentrations in road surface dusts in New Zealand have been reported to be around 1,462 µg/kg (Waitakere City – Kennedy & Gadd 2003). A number of studies in New Zealand have reported PAH data for urban stormwater (e.g., Sherriff 1998, Brown et al. 2003, O'Reilly et al. 2002 and Timperley et al. 2003).

5.2 PAHs in Heathcote River Catchment Sediments

The PAH concentrations measured in selected samples from the Heathcote catchment are presented in Table 5.1 (see Appendix C for raw results). The concentration of total PAHs in the Heathcote catchment is shown in Fig. 5.2. The highest concentrations of PAHs were detected in samples from site HE5, HE6, HE7 and HE29.

Three PAH compounds (phenanthrene, pyrene and fluoranthene) were dominant in all samples, with each generally contributing 10 to 15% of the total PAHs measured. Other low molecular weight PAHs (molecular weight less than 200 g/mol) each contributed around 1 to 2% of the total PAHs. High molecular weight PAHs (molecular weight more than 200 g/mol) were generally measured at higher concentrations than the low molecular weight PAHs, and contributed around 3 to 7% of total PAHs.

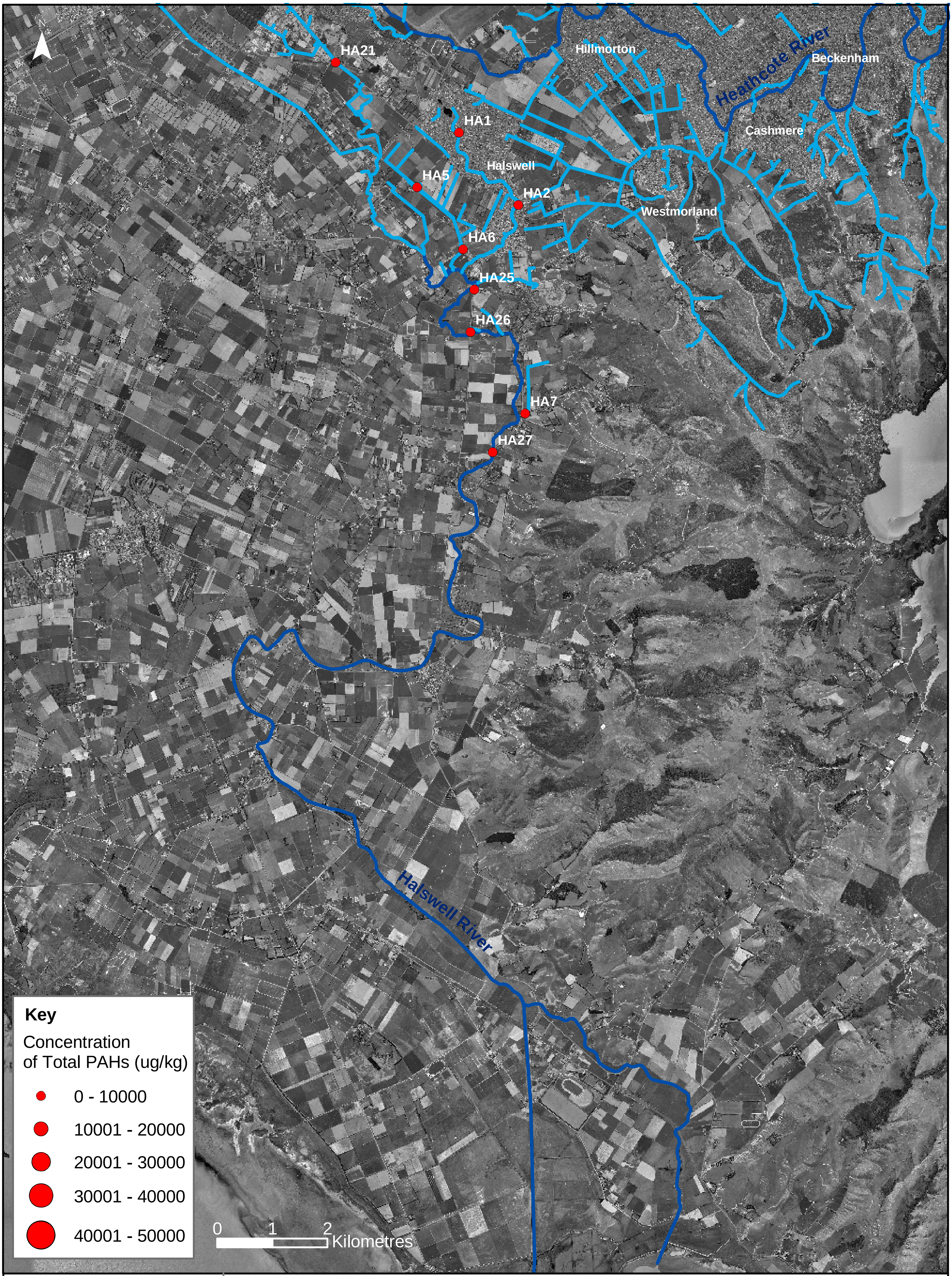
Examination of sandy sediments off New Brighton near the mouth of the Avon-Heathcote estuary showed that total PAH concentrations were less than 40 µg/kg (Kingett Mitchell, 2003b). The lowest concentration in the sediments from the Heathcote catchment was 117 µg/kg with the remainder ranging from 1,829 to 49,795 µg/kg.

5.3 PAHs in Halswell River Catchment Sediments

The PAH concentrations measured in selected samples from the Halswell River catchment are presented in Table 5.2 (see Appendix C for raw results). The concentration of total PAHs in the Halswell catchment is shown in Fig. 5.3. The concentrations in the Halswell catchment (total PAHs 183 to 2,448 µg/kg) were considerably lower than the concentrations measured in the Heathcote catchment (117 to 49,795 µg/kg). The highest concentrations of PAHs were detected in samples from sites HA1 and HA21 at 2,448 and 2,058 µg/kg, respectively.

Table 5.1: Concentrations of PAHs in Heathcote catchment and river sediment samples (all data μg/kg).

PAH	HE1	HE2	HE3	HE5	HE6	HE7	HE12	HE13	HE14	HE24	HE25	HE29
Low molecular weight PAHs												
naphthalene	3.3	16.6	34.4	256.1	98.8	195.0	82.3	39.1	32.4	51.6	30.7	292.9
2-methylnaphthalene	4.4	18.5	16.9	256.6	92.1	169.7	113.9	42.7	35.9	42.9	12.8	101.7
1-methylnaphthalene	2.9	19.8	11.0	276.0	102.5	190.1	81.2	26.9	24.4	23.7	7.8	90.9
biphenyl	1.6	7.4	8.6	96.1	36.4	67.5	24.8	12.4	10.0	13.1	5.3	49.2
2,6-dimethylnaphth (2 compounds)	5.1	17.1	13.8	184.3	68.1	136.9	96.9	32.9	29.0	26.9	9.5	70.2
acenaphthylene	1.2	45.7	13.1	289.9	139.4	310.6	55.1	23.8	33.0	26.8	55.2	632.4
acenaphthene	0.2	12.7	22.4	218.3	80.3	148.3	8.7	8.0	6.5	6.7	14.9	260.5
2,3,5-trimethylnaphthalene	0.7	5.6	4.5	65.2	29.1	52.4	72.6	7.1	7.3	8.6	5.1	51.1
fluorene	1.5	63.2	35.2	634.3	269.1	473.6	28.7	23.7	24.6	28.3	38.5	494.1
phenanthrene	8.3	374.7	306.9	3194.0	1496.1	2546.9	277.1	201.6	189.9	171.9	417.1	6057.2
anthracene	1.2	83.5	44.8	705.8	231.3	528.0	54.4	34.5	29.5	39.1	140.6	1033.4
1-methylphenanthrene	1.5	48.4	35.1	492.5	210.6	433.7	64.3	35.8	33.5	28.1	59.5	703.9
High molecular weight PAHs												
fluoranthene	10.7	330.1	391.4	1958.2	1079.2	1898.1	304.2	270.4	211.3	228.6	722.6	7149.6
pyrene	11.0	325.7	405.6	2352.5	1148.5	2087.9	409.3	310.6	238.7	242.7	745.8	7869.0
benz[a]anthracene	4.5	149.8	165.2	962.4	503.2	851.5	138.3	135.4	92.9	118.5	345.3	2960.5
chrysene+ triphenylene	6.6	156.4	204.8	1008.9	593.4	991.2	215.0	173.5	135.2	148.8	337.4	3391.2
benzo[b]fluoranthene	6.6	113.4	191.9	734.7	422.4	741.3	185.1	99.4	108.7	112.9	275.1	2925.6
benzo[k]fluoranthene	5.7	121.0	170.3	764.1	433.7	700.3	165.2	132.9	99.9	120.5	270.9	2576.2
benzo[e]pyrene	5.3	91.6	156.4	594.9	336.3	555.6	156.7	99.9	92.3	93.9	214.7	2229.4
benzo[a]pyrene	6.0	142.4	105.6	559.9	249.8	518.3	102.9	71.5	40.6	100.6	319.1	2076.9
perylene	8.2	61.4	171.3	603.3	264.7	390.0	55.2	43.6	57.8	61.0	131.0	1345.5
indeno[123-cd]pyrene	8.0	97.3	307.8	970.7	464.9	776.9	181.0	100.9	128.7	115.0	265.3	3503.5
dibenz[ah]anthracene	1.5	24.0	69.4	296.6	124.6	223.6	37.9	22.0	28.9	26.2	59.9	839.9
benzo[ghi]perylene	10.9	95.5	328.4	843.2	436.4	663.1	195.0	99.4	137.8	105.9	234.0	3090.1
Total PAHs	**117**	**2,422**	**3,215**	**18,319**	**8,911**	**15,651**	**3,106**	**2,048**	**1,829**	**1,943**	**4,718**	**49,795**



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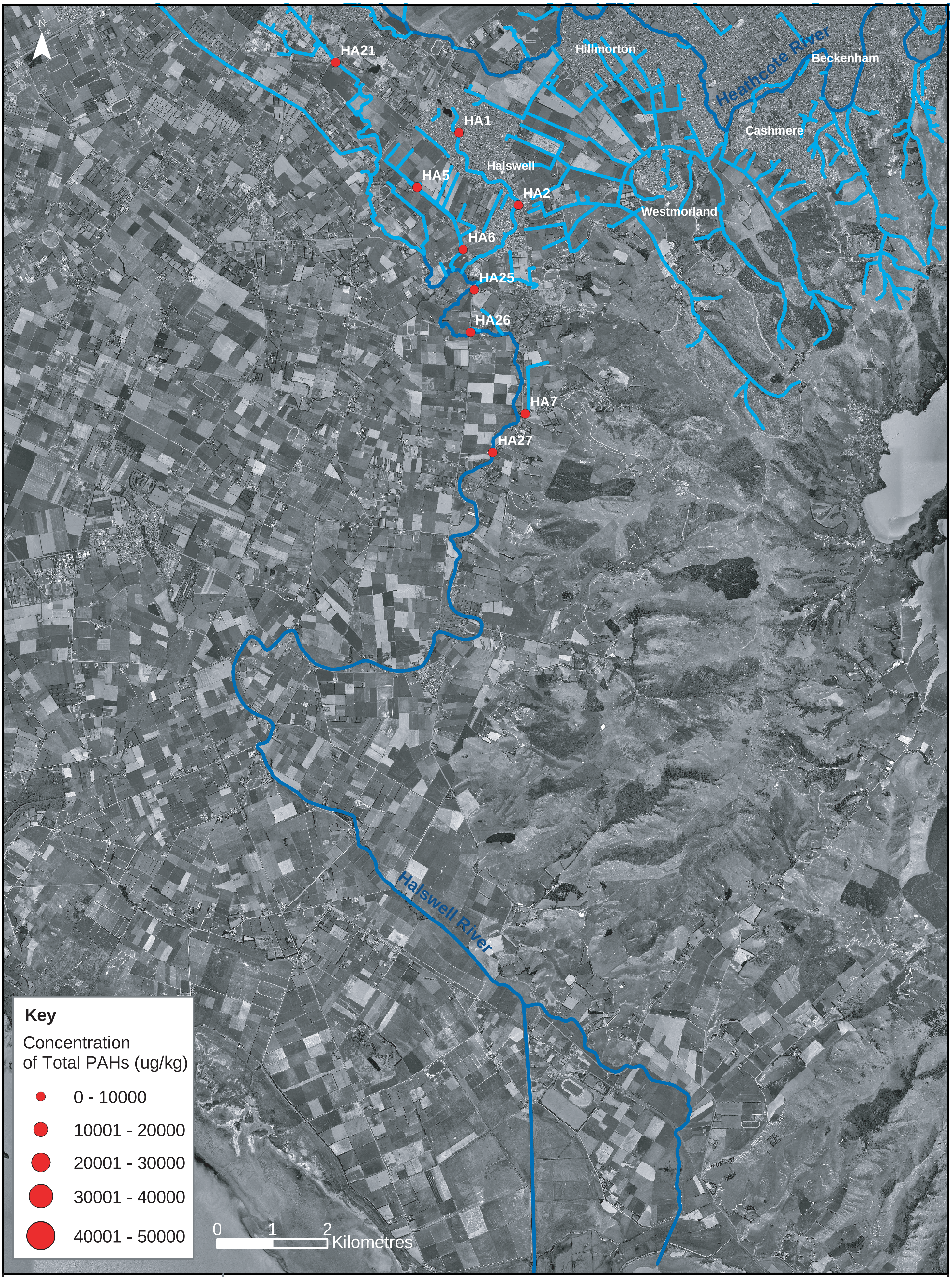
TITLE:
TOTAL PAH CONCENTRATION IN
HALSWELL CATCHMENT SEDIMENTS

CLIENT:
CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 5.3

Table 5.2: Concentrations of PAHs in Halswell catchment sediment samples (all data µg/kg).

PAH	HA1	HA2	HA5	HA6	HA7	HA21	HA25	HA26	HA27
Low molecular weight PAHs									
Naphthalene	47.0	11.5	4.9	11.2	7.6	71.0	8.6	7.8	5.9
2-methylnaphthalene	47.5	9.3	7.0	11.4	3.8	51.9	5.7	5.8	6.5
1-methylnaphthalene	29.8	6.2	3.6	8.4	2.1	29.4	3.7	2.8	2.7
Biphenyl	12.8	4.0	5.2	5.2	3.5	17.7	3.4	3.8	2.9
2,6-dimethylnaphth (2 compounds)	61.7	7.2	3.2	6.8	3.5	35.7	5.0	5.8	2.7
acenaphthylene	30.7	10.5	1.1	2.2	4.7	39.7	3.7	13.1	0.9
acenaphthene	8.1	3.0	0.6	2.5	0.2	5.1	1.8	1.8	0.4
2,3,5-trimethylnaphthalene	23.1	2.2	0.6	1.5	0.7	9.8	2.0	1.0	0.4
Fluorene	37.3	8.3	10.9	7.0	2.8	15.8	6.1	8.3	4.5
phenanthrene	296.6	75.2	25.4	148.4	16.2	167.7	33.2	58.6	12.6
Anthracene	50.5	15.5	1.6	4.0	3.0	35.9	8.0	20.1	1.9
1-methylphenanthrene	72.3	10.5	3.3	14.2	3.2	34.0	4.7	7.8	1.6
High molecular weight PAHs									
Fluoranthene	288.8	117.4	14.5	103.8	32.8	232.3	44.0	112.2	12.4
Pyrene	342.6	120.1	31.8	89.3	35.3	317.0	44.1	109.5	13.5
benz[a]anthracene	130.1	48.4	4.9	17.7	18.5	101.1	18.7	53.8	4.8
chrysene+ triphenylene	198.5	56.5	14.0	52.1	24.0	154.0	22.1	53.8	7.2
benzo[b]fluoranthene	137.2	44.6	28.7	35.8	22.5	124.9	20.0	41.2	6.8
benzo[k]fluoranthene	124.2	42.6	3.6	28.1	19.2	93.8	15.8	39.2	4.1
benzo[e]pyrene	112.1	35.1	13.5	24.5	15.9	116.8	14.1	30.4	4.8
benzo[a]pyrene	111.9	46.4	3.0	23.4	18.9	63.0	18.9	47.6	4.7
Perylene	32.7	16.8	660.6	69.9	30.7	34.8	41.0	54.7	67.2
indeno[123-cd]pyrene	100.4	30.5	16.0	26.6	31.7	115.6	16.3	40.0	5.3
dibenz[ah]anthracene	18.1	5.7	4.4	6.3	7.3	21.6	3.2	8.6	1.1
benzo[ghi]perylene	134.0	31.3	46.8	27.7	30.6	169.1	16.8	36.3	7.9
Total PAHs	**2,448**	**759**	**909**	**728**	**339**	**2,058**	**361**	**764**	**183**



Kincett Mitchell Ltd
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TITLE:
TOTAL PAH CONCENTRATION IN
HALSWELL CATCHMENT SEDIMENTS

CLIENT:
CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 5.3

As with the Heathcote catchment samples, three PAH compounds (phenanthrene, pyrene and fluoranthene) were dominant in all samples, with the exception of HA5. This contained a much higher concentration of perylene than other samples at 661 µg/kg, compared to 17 to 70 µg/kg for all other samples. In all other samples, the concentrations of low molecular weight PAHs were generally lower than high molecular weight PAHs.

As noted earlier in relation to the Heathcote catchment, examination of sediments off New Brighton near the mouth of the Avon-Heathcote estuary showed that total PAH concentrations were less than 40 µg/kg. The lowest concentration in the Halswell catchment was 183 µg/kg.

5.3.1 Summary

The examination of PAH concentrations in sediments from the Heathcote and Halswell River catchment showed that concentrations were highest at sites HE5, HE6, HE7, HE29, HA1 and HA21.

PAHs were dominated by phenanthrene, pyrene and fluoranthene. Low molecular weight PAHs were generally lower in concentration than high molecular weight PAHs.

Concentrations in sediments varied by 40 times in the Heathcote catchment and by less than 10 in the Halswell catchment.

5.4 Influence of Texture on PAH Concentrations

As with metals, the physical characteristics of sediments influence the concentrations of organic contaminants including PAHs. To reduce some of the variability in PAH concentrations due to texture, the analyses were undertaken on the less than 500 µm (<0.5 mm) fraction. All samples were dominated by mud and fine sand, with the exception of the sample from site HE25, which contained <1% mud. Fig. 5.4 presents total PAH concentrations by mud content. As illustrated in the figure there appears to be no relationship between the two parameters.

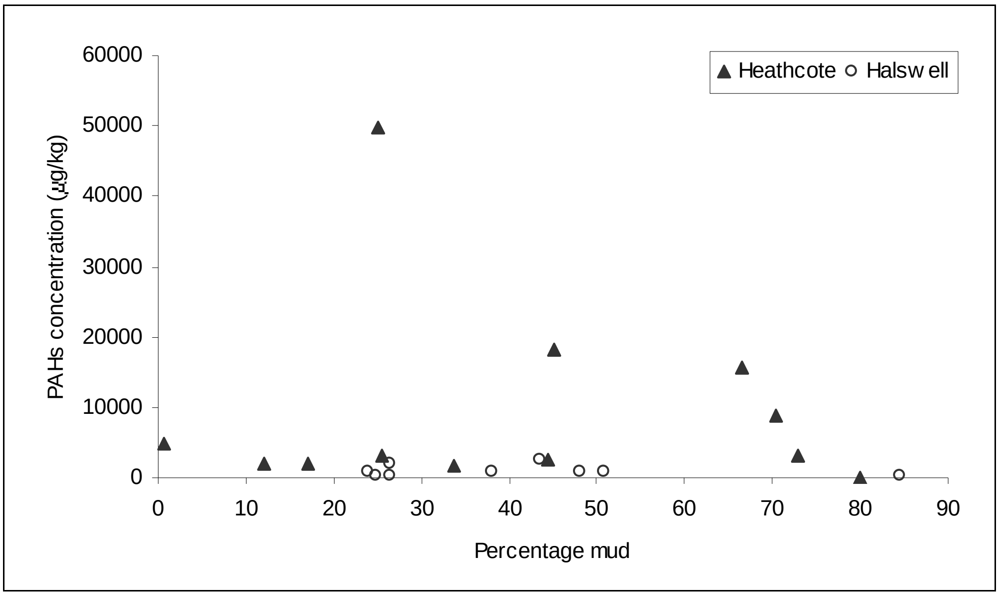

Fig. 5.4: **Relationship between percentage mud and total PAH concentrations.**

5.5 Influence of Organic Carbon on PAH Concentrations

The concentration of organic carbon in a sediment sample affects the concentrations of organic contaminants as these compounds readily adsorb to organic carbon. Sediments that contain high concentrations of organic carbon are therefore more likely to accumulate greater concentrations of organic contaminants (including PAHs) if available in the waterway.

The content of total organic carbon in the sediments examined ranged from 0.83 to 10.2% (median of 2.0%) (Fig. 5.5). Total organic carbon was highest in tributaries of the Heathcote River (median 3.9%), particularly at sites HE6 and HE7 (8.4 and 10.2% respectively). Concentrations in the river ranged from 1.0 to 1.6%. Total organic carbon was generally lower in the Halswell River catchment (median 1.7%), with elevated values for samples HA1, HA7 and HA21 (5.4, 2.9 and 5.3% respectively).

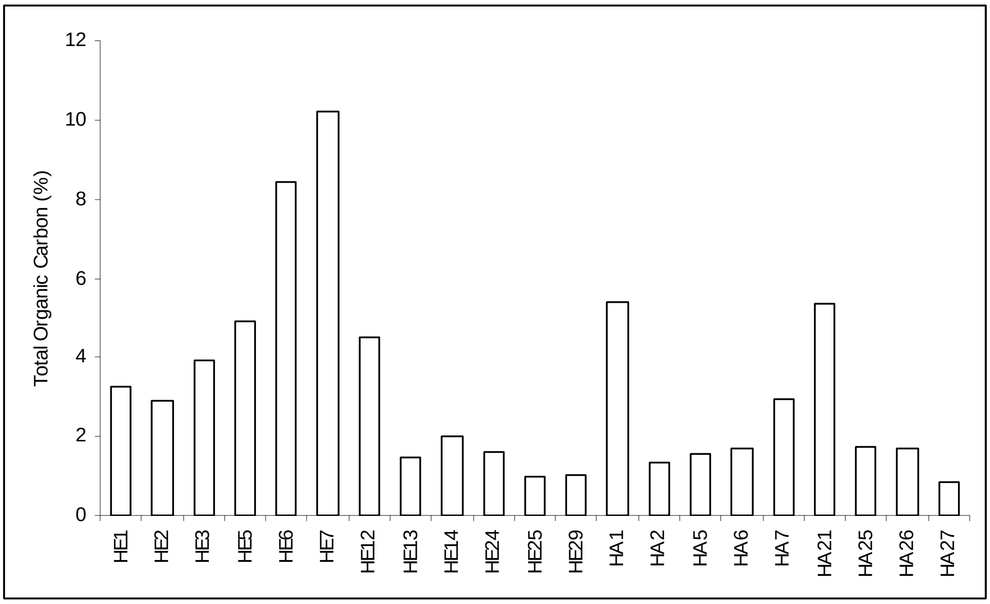

Fig. 5.5: **Total organic carbon concentration (%) in sediment samples.**

There is a general relationship between total PAHs and total organic carbon for samples containing less than 5,000 µg/kg PAHs (Fig. 5.6), where there is an increase in total PAHs with increasing total organic carbon content. There are however, several samples that do not follow this trend.

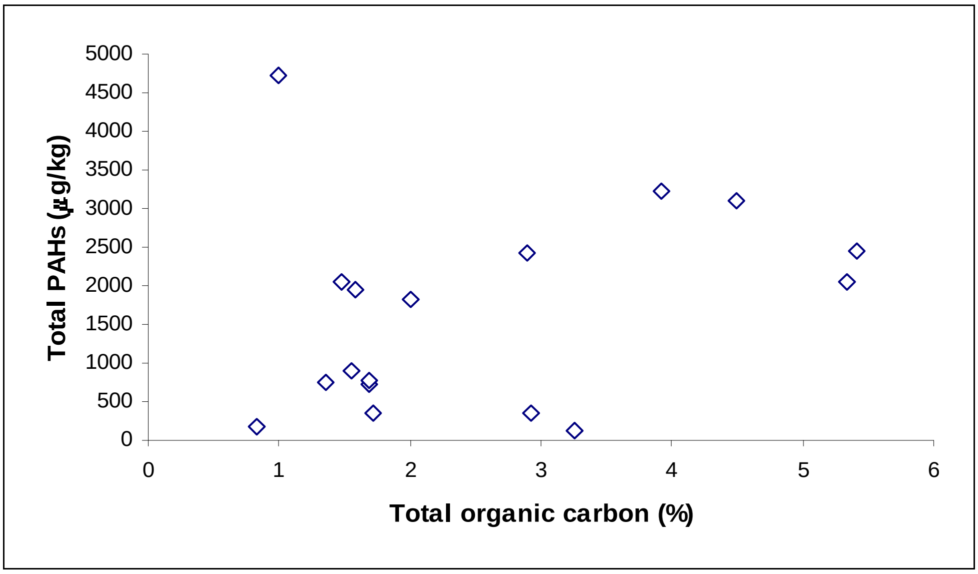

Fig. 5.6: **Relationship between total organic carbon concentration (%) and total PAHs.**

5.6 Effects of Landuse on PAH concentrations

The effects of land use on the PAH concentrations were investigated by categorising the sites according to land use as discussed in Section 4.6. The data shown in Fig. 5.7 has been normalised to total organic carbon content (i.e., the PAHs present based upon 1% TOC). Note that a value in the HE-mix category of 49,302 µg/kg at site HE29, is not shown on the plot for reasons of scale. Fig. 5.7 indicates that the concentrations of PAHs in the Halswell catchment, in all three land uses, are typically lower than those in the Heathcote catchment. Within the Heathcote catchment, the background sites contained generally lower total PAHs. The mixed and residential sites appeared to have the highest concentrations of total PAHs.

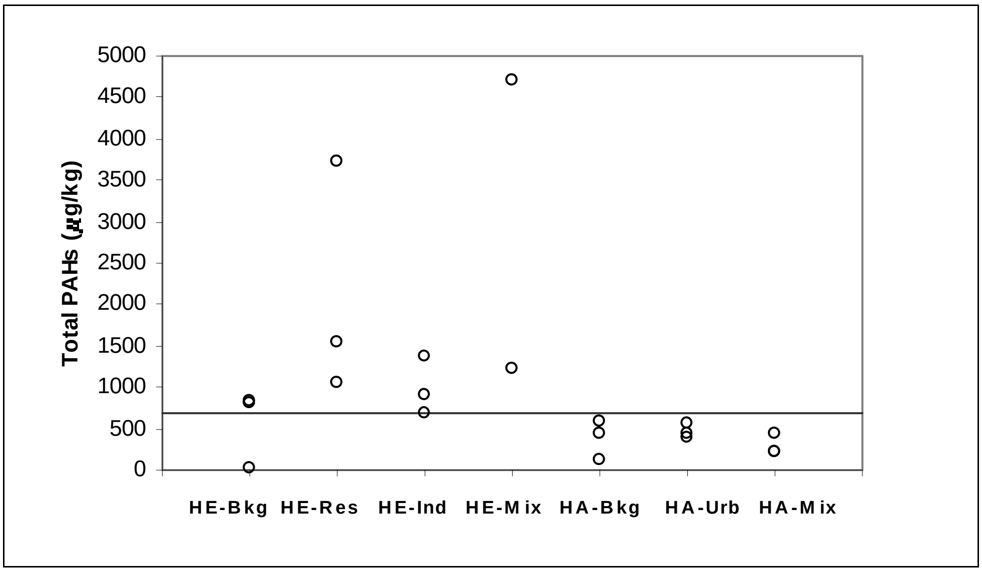

Fig. 5.7: **Comparison of total PAH concentrations in sediments from different land uses. Note: line is overall median.**

5.7 Comparison with other Areas

Table 5.3 summarises the concentrations of PAH present in the catchment sediments and compares the data obtained in this study with the results for Auckland sediments summarised by Mills et al. (1998). Total PAH concentrations determined for stream sediments are dependent upon the method of extraction and analysis, the particle size analysed, and the number of different PAHs included in the analytical programme. The two studies are relatively comparable as the same laboratory was used and the individual PAH compounds were the same.

Comparison of the two sets of data shows that there is a broad range of total PAH concentrations between the land-uses and study areas. The most notable observations that can be made from this small data set is that the Heathcote industrial, Halswell residential and Waitakere mixed urban catchments contained lower total PAH concentrations compared to the Heathcote Residential samples and the Auckland City mixed urban sites.

Table 5.3: Median PAH concentrations in land use categories in the South-West Christchurch catchments and elsewhere in New Zealand (all data µg/kg).

Location	Land-use	Sites Included	PAHs
Halswell River catchment	Rural	HA4, HA5, HA7	728
Halswell River catchment	Mixed	HA25, HA26, HA27	361
Heathcote River catchment	Rural	HE1, HE2, HE3	2,422
North Shore City*	Mixed Urban	-	247
Waitakere City*	Mixed Urban	-	1,418
Heathcote River catchment	Industrial	HE12, HE13, HE14	2,048
Halswell River catchment	Mixed Urban (res, ind, com)	HA1, HA2, HA21	2,058
Heathcote River catchment	Mixed	HE24, HE25, HE29	4,718
Heathcote River catchment	Residential	HE5, HE6, HE7	15,651
Auckland City*	Mixed urban	-	15,929

Note: * - source Mills et al. (1998).

5.8 Sediment Quality Guidelines

The ANZECC (2000) guidelines recommend that the PAH concentrations detected in sediments are normalised to the organic carbon content before comparison to the guidelines. The results for samples that exceeded the guidelines are presented in Table 5.4. These samples were all collected from the Heathcote catchment. Fig. 5.8 illustrates the exceedances geographically.

Table 5.4 shows that fluorene was the most common PAH in Heathcote catchment samples to exceed the ISQG-low ANZECC (2000) guidelines (no exceedences occurred in the Halswell catchment samples). A cluster of PAHs in samples HE5 and HE25 exceeded their corresponding ISQG-low triggers. Only in sample HE29 were ISQG-high triggers exceeded for a range of PAHs. When the overall PAH concentrations were considered, the ISQG-low for low and high molecular weight PAHs were exceeded in sample HE25 and the corresponding ISQG-high triggers in HE29 were exceeded.

The toxicity of PAHs in sediments has been shown in studies such as those of Geffard et al. (2003). The bioavailability (in terms of toxicity) of PAHs to organisms is determined by their solubility. The solubility of the various PAHs is approximately determined by their molecular weight (number of aromatic rings). There has also been considerable discussion about the possible role that phototoxicity (absorbtion of UV energy by some PAHs that then can adversely affect cell membranes) plays in enhancing the potential toxicity of PAHs present in aquatic ecosystems. McDonald & Chapman (2002) discuss the mechanisms and studies concluding that the ecological relevance is uncertain and more information is required.

Table 5.4: Normalised concentrations of PAHs in Heathcote catchment sediment samples (all data μg/kg).

PAH [a]	HE2	HE5	HE6	HE7	HE25	HE29
2-methylnaphthalene	6	52	11	17	13	101
naphthalene	6	52	12	19	31	290
acenaphthylene	16	59	17	30	55	626
acenaphthene	4.4	44	9.6	15	15	258
fluorene	22	129	32	46	38	489
phenanthrene	130	651	178	250	417	5,997
anthracene	29	144	28	52	141	1,023
Low Molecular Weight	206	1,079	275	412	697	8,684
fluoranthene	114	399	128	186	723	7,079
pyrene	113	479	137	205	746	7,791
benz[a]anthracene	52	196	60	83	345	2,931
chrysene+ triphenylene	54	205	71	97	337	3,358
benzo[a]pyrene	49	114	30	51	319	2,056
dibenz[ah]anthracene	8.3	60	15	22	60	832
High Molecular Weight	390	1,454	440	644	2,530	24,047
Total PAHs [b]	838	3,731	1,060	1,534	4,718	49,302

Notes: [a] Normalised to 1% organic carbon. [b] Only those PAHs with guideline values are included in the Total PAH. Total PAH is not the total PAH concentration based upon analysis.

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TITLE:

COMPARISON OF TOTAL PAHS IN THE HEATHCOTE AND HALSWELL CATCHMENTS TO ANZECC (2000) SEDIMENT QUALITY GUIDELINES

CLIENT:

CHRISTCHURCH CITY COUNCIL

DATE: JUNE 2005
PROJECT NO: 500673
FIGURE NO: 5.8

5.9 Overview and Summary

The examination of PAH concentrations in the Heathcote and Halswell River catchments has shown that the concentration varies geographically and varies significantly between urbanised catchments. PAHs in stream sediments are derived from atmospheric deposition of airborne PAHs (to soils etc., which are then transported to waterways) and localised point source emissions to soils and directly to streams. Geographic differences in atmospheric PAH concentration and deposition rates related to the proximity to urban areas are well recognised. PAH distribution in the air of Christchurch has been described by Cretney et al. (1985). Herrmann & Baumgartner (1987) provided some general information on PAH distribution in the South Island and Christchurch that showed gradients and patterns that reflected proximity to sources.

PAHs are a relatively complex group of compounds. The solubility varies considerably from PAHs such as naphthalene that are highly soluble compared to higher molecular weight PAHs such as indeno[123-cd]pyrene which are by comparison insoluble. As a consequence, the fate of the various PAHs differs when they enter the aquatic environment. While the total PAH concentration between samples may be similar the different properties and chemical structure of individual compounds can therefore result in different PAH profiles.

Fig. 5.9 illustrates the similarity of the relative concentrations of the different PAHs in the sediments. Preliminary examination of the data indicates that the concentrations measured at each site are in most cases a reflection of the load of PAHs contributed to sediment at that site and not to different sources. Two exceptions were noted for samples collected from the Halswell catchment. Sites HA5 had proportionally elevated concentrations of perylene compared to other sediment samples (refer Fig. 5.9).

Fig. 5.10 provides comparative data for sediments from the Auckland region examined by Mills et al. (1998). Comparison of the individual PAH data in Figs. 5.9 and 5.10 shows that the relative concentrations of the PAHs is similar between the two locations. Amongst the Auckland samples, there are few irregularities with similar relative concentrations seen in most samples.

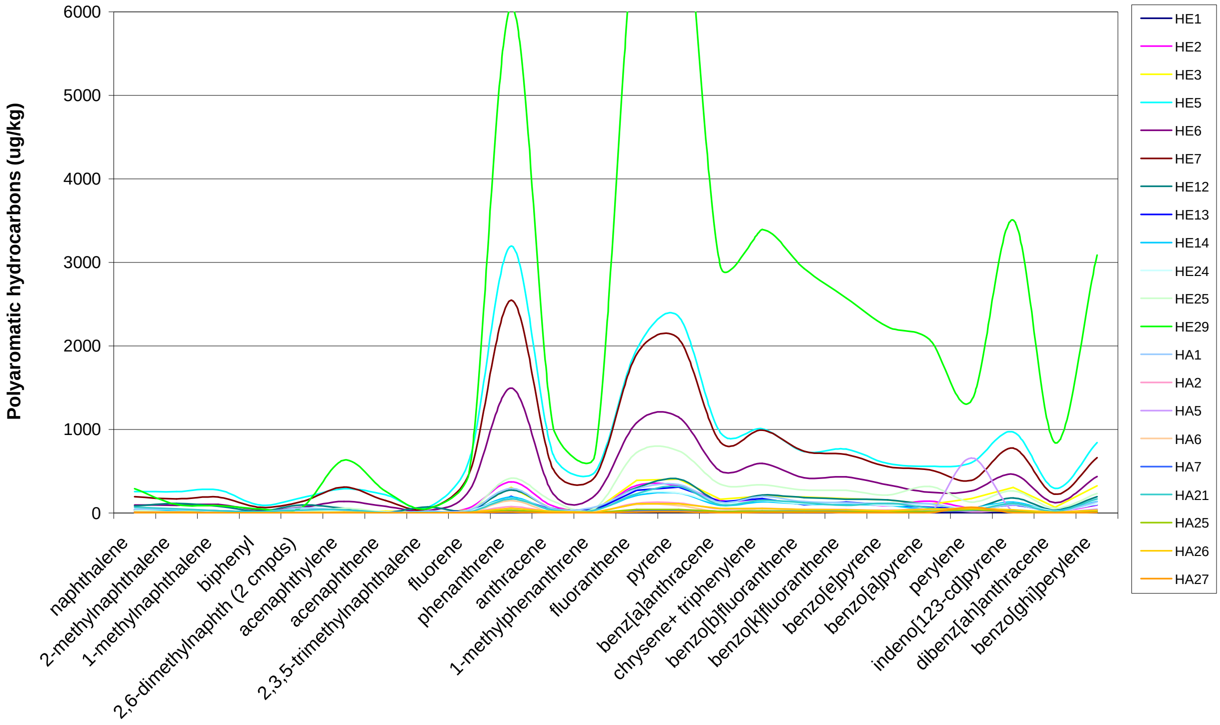

Fig. 5.9: PAH compound profiles for sediments from the Heathcote and Halswell River catchments.

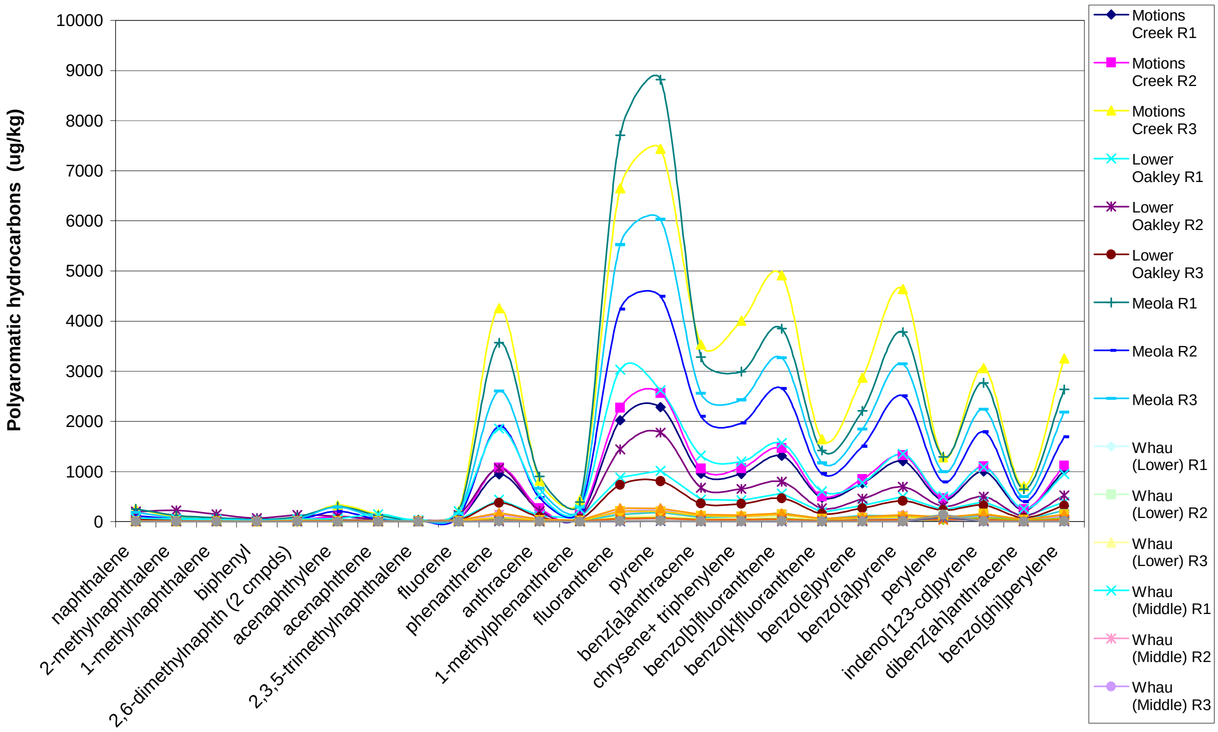

Fig. 5.10: PAH compound profiles for sediments from streams draining to the Waitemata Harbour (data from Mills et al. 1998).

The comparison of the Auckland and Christchurch data indicates that the concentration profiles in sediments are generally similar. The lower molecular weight PAHs are of less importance than the compounds typically heavier than fluorine. The lower concentrations of low molecular weight PAHs in the sediments reflect the higher solubility, the greater volatility and higher degradation rates. The Auckland samples appear to show some increased relative importance of benzo[a]pyrene and benzo[b]fluoranthene compared to South-West Christchurch. However, the similar PAH profiles for sediment samples collected from Christchurch and Auckland generally suggest that the weathering of these compounds will overprint signatures that may represent different PAH sources.

The preliminary examination of the PAH data collected has not specifically determined the reason for the much greater concentrations present in the samples collected from the Heathcote residential catchment compared to other samples. Further fingerprinting and comparison of the PAH profiles with other urban areas will be required to confirm that the differences in concentration are solely due to difference in load within sub-catchments.

Overall, PAH concentrations are elevated and similar to those measured in sediments from streams in other large urban areas in New Zealand. PAH concentrations are sufficiently high in some parts of the Heathcote River catchment that they may result in adverse environmental effects.

6. Summary and Conclusions

Concentrations of the key metals copper, lead and zinc were generally lower in the Halswell River and tributary sediments compared to those in the Heathcote River catchment. Concentrations in some tributaries in the Halswell catchment were similar to those measured in the tributaries of the Heathcote River.

In the Halswell catchment, the sediment texture appeared to have some influence on metal concentrations. In the Heathcote catchment, the natural occurrence of metals in the sediment samples were overprinted by by other factors, including land use in the catchment.

In the Heathcote River catchment, the concentrations of metals generally increased from rural to residential, to mixed urban and industrial urban land-use. In the Halswell catchment, the metal concentrations generally increased from mixed land use (predominantly rural) to rural to mixed urban. This pattern has been observed in stream catchments in other cities in New Zealand.

A large proportion of sediment samples collected from the Heathcote River catchment exceeded ANZECC (2000) guidelines for lead and zinc and a small number also exceeded the guideline for copper. These samples were typically collected from industrial and urban sites in the catchment. In contrast, only five samples from the Halswell catchment exceeded ANZECC (2000) guidelines for copper, lead or zinc. None of these samples were collected from the Halswell River.

The exceedence of the ANZECC (2000) ISQG-Low trigger values provides an indication that sediment quality may be degraded to levels sufficient enough to influence the quality of the aquatic biological community inhabiting the sediments.

When data from the 2003 survey was compared to the earlier survey conducted in 1981 (Robb 1988), there was a general increase in zinc concentrations throughout the Heathcote catchment of South-West Christchurch and a general decrease in lead concentration. Copper concentrations were more variable. While there were more exceedances of the zinc ISQG-high criteria in the current survey than in the previous survey (Robb 1988), the number of lead exceedances was slightly lower in the Heathcote River. The decrease in the lead concentration is thought to be related to the removal of lead from petrol some eight years ago. This eliminated the contribution of lead from active vehicle emissions which reached the stream via stormwater and atmospheric deposition. Lead from historical vehicle emissions is still likely to be present in soils of the Christchurch region, and the erosion of these soils may still be contributing to the load of this contaminant in stream sediments. It is also possible that natural processes (stream bed scouring etc., from floods) have removed some of the higher concentrations present in streams that arose from past industrial activities in the catchment. The change in the zinc concentration may reflect continual build-up of zinc from uses that have not changed (vehicle sources, building roofs etc.).

The concentrations of PAHs in the Halswell catchment, in all three land uses, are typically lower than those in the Heathcote catchment. Within the Heathcote catchment, the background sites contained generally lower total PAH concentrations. The mixed and residential sites appeared to have the highest concentrations of total PAHs.

Overall, PAH concentrations are elevated and similar to those measured in sediments from streams in other large urban areas in New Zealand. Concentrations are sufficiently high in some parts of the Heathcote River catchment that PAHs may be contributing to potential adverse environmental effects.

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Appendices

Appendix A

Physical Characteristics

Appendix A: Physical Characteristics

Table 1: Texture of sediments collected from the Heathcote and Halswell Rivers (all data g/100g).

Site ID	Gravel	Coarse Sand	Medium Sand	Fine Sand	Silt Clay
HE1	4.1	1	1.1	17.9	75.9
HE2	7.3	3.5	8	41.6	39.7
HE3	21.5	3.5	2	18.4	54.6
HE4	4.6	1.7	1.7	40.9	51
HE5	13.9	6.4	4.8	39	36
HE6	8.5	5.5	4.3	21.2	60.5
HE7	6.4	4.6	4.6	25.2	59.1
HE8	84.3	2.5	1.5	6.1	5.6
HE10	4	4.1	7.4	55.9	28.7
HE11	3.2	4	13.4	55.6	23.9
HE12	27.7	1.3	9.2	43.8	18.1
HE13	53.6	12.4	10.4	17.8	5.8
HE14	16	2.1	11.5	42.8	27.6
HE21	18.5	5	18.3	50.4	7.8
HE22	14	1.1	13.8	65.4	5.8
HE23	1.1	1.4	2.1	77.3	18.1
HE24	2.7	2.1	5.9	77.7	11.5
HE25	94.1	0.8	3.7	2.9	0.05
HE26	90.2	0.3	0.6	1.7	7.1
HE27	96.7	0.1	0.1	0.1	3
HE28	93	0.3	1.1	1	4.6
HE29	99.4	0.2	0.1	0.2	0.1
HE30	0.9	1.1	2.4	20.3	75.4
HE31	1.7	0.9	0.6	6.7	90.1
HE32	55.9	1.9	2.6	15.6	24
HE33	0.1	0.3	0.6	18.6	80.4
HE34	6.8	0.5	0.7	19.2	72.8
HA1	48.3	15.2	8	12.6	15.8
HA2	34.4	7.8	20.6	23.4	13.8
HA3	2.2	3	42.5	45.2	7.1
HA4	1.1	1.3	1.2	19.3	77.2
HA5	52.9	0.9	3.9	20.1	22.2
HA6	3.8	1.9	2.3	44	48
HA7	0.2	1.1	0.9	14.4	83.5
HA21	38.7	20.4	12.1	18.1	10.8
HA22	2.9	8.8	14.3	43.2	30.8
HA23	0.3	0.2	12.6	80.1	6.8
HA24	1.5	2.1	2.8	38.7	54.9
HA25	3	3.4	16.1	54.3	23.2
HA26	1	1.9	7.7	52.4	37
HA27	0.1	0.5	18.1	55.1	26.2
HA30	0.6	2.4	22.6	47.9	26.5
HA31	5	3.4	28.6	41.2	21.9
HA32	4.1	1.4	2	29.6	62.9
HA34	0.2	0.6	0.5	26.3	72.5
HA35	0.7	0.4	4.7	31.9	62.4

Table 2: **Man-made materials in the >2 mm fraction of sediments collected from the Heathcote and Halswell Rivers.**

Site ID	Glass	Plastic	Metal	Miscellaneous Rubbish
HE1	0	0	0	0
HE2	0	0	0	0
HE3	0	0	0	0
HE4	0	0	0	0
HE5	0	0	2	1 piece of paper
HE6	0	0	0	0
HE7	0	0	0	4 pieces of paper
HE8	0	0	0	0
HE10	0	4	0	0
HE11	0	0	0	0
HE12	0	0	0	0
HE13	0	0	0	0
HE14	0	1	0	0
HE21	0	2	0	1 piece of thread
HE22	0	0	0	0
HE23	0	0	0	0
HE24	0	0	0	1 paint chip
HE25	0	0	0	0
HE26	1 (5 cm)	0	0	0
HE27	0	0	0	0
HE28	0	0	0	0
HE29	0	0	0	0
HE30	0	0	0	0
HE31	0	1	0	0
HE32	0	0	0	0
HE33	0	0	0	0
HE34	0	0	0	0
HA1	0	0	0	0
HA2	4	1	0	0
HA3	0	0	0	0
HA4	0	0	0	0
HA5	0	0	0	0
HA6	0	0	0	0
HA7	0	0	0	0
HA21	1	1	0	0
HA22	0	0	0	0
HA23	0	0	0	0
HA24	0	0	0	0
HA25	0	0	1	0
HA26	0	0	0	0
HA27	0	0	0	0
HA30	0	0	0	0
HA31	0	0	0	0
HA32	0	0	0	0
HA34	0	0	0	0
HA35	0	0	0	0

Appendix B

Compilation of Metal Results

Appendix B: Compilation of metal results

Table 1: Total recoverable and perchloric/nitric extractable copper, lead and zinc in sediments collected from the Heathcote and Halswell Rivers.

Site ID	Total Recoverable Copper (mg/kg)	Total Recoverable Lead (mg/kg)	Total Recoverable Zinc (mg/kg)	Copper (Perchloric/nitric extractable) (mg/kg)	Lead (Perchloric/nitric extractable) (mg/kg)	Zinc (Perchloric/nitric extractable) (mg/kg)
HE1	8.5	10.9	66.1	8.1	10.1	69
HE2	11.6	54.3	171	-	-	-
HE3	12.3	33.8	96.9	12	30	101
HE4	10.7	22.9	95.6	10.4	21.5	99
HE5	17.9	50.6	300	17.1	46.6	289
HE6	22	59.7	344	20	60.2	344
HE7	54.7	128	524	-	-	-
HE8	40.2	198	364	38	118	351
HE10	7.6	14.3	106	7.8	16.6	114
HE11	24.2	66.1	603	21.8	66.9	592
HE12	36.7	101	796	32.5	96.8	695
HE13	194	378	714	206	202	613
HE14	132	64.6	830	-	-	-
HE21	12.4	35.3	441	-	-	-
HE22	8.8	24.5	529	-	-	-
HE23	16.3	46.2	1240	-	-	-
HE24	98.9	47.4	631	-	-	-
HE25	76.4	36.7	381	-	-	-
HE26	96	75.3	666	-	-	-
HE27	39.6	50.8	427	-	-	-
HE28	38.7	26.3	287	-	-	-
HE29	21.4	67.8	264	-	-	-
HE30	43.9	74.2	592	38.8	71.4	545
HE31	60.9	89.2	706	55.9	93.7	700
HE32	28.6	53.3	258	27.1	54.2	251
HE33	23	35.7	209	21.2	37.7	198
HE34	16.5	26.1	135	16.1	29.2	139
HA1	35.9	56.5	587	-	-	-
HA2	14.5	38.8	219	-	-	-
HA3	5.1	23.2	150	-	-	-
HA4	17.5	25.7	243	-	-	-
HA5	9.6	17.6	58.3	-	-	-
HA6	6.4	14.4	58.1	-	-	-
HA7	9.3	16.2	67.2	-	-	-
HA21	66.5	77.2	693	-	-	-
HA22	29.6	45.1	420	-	-	-
HA23	2.9	6.04	37	-	-	-
HA24	8.6	18	64.4	-	-	-
HA25	8.7	20.6	77.8	-	-	-
HA26	6.4	12.8	79.2	-	-	-
HA27	4.2	9.69	52	-	-	-
HA30	5.6	12.9	59.5	-	-	-
HA31	7.7	17.4	77.2	-	-	-
HA32	12.2	22.8	99.1	-	-	-
HA34	10.3	17.3	61.3	-	-	-
HA35	10.5	19.6	88.7	-	-	-

Appendix C

Compilation of PAH Results

Appendix C: Compilation of PAH results

Table 1: Polyaromatic hydrocarbons in sediments collected from the Heathcote and Halswell Rivers (all data ug/kg).

Site ID	naphthalene	2-methylnaphthalene	1-methylnaphthalene	biphenyl	2,6-dimethylnaphth (2 cmpds)	acenaphthylene	acenaphthene	2,3,5-trimethylnaphthalene	fluorene	phenanthrene	anthracene	1-methylphenanthrene	fluoranthene	pyrene	benz[a]anthracene	chrysene+ triphenylene	benzo[b]fluoranthene	benzo[k]fluoranthene	benzo[e]pyrene	benzo[a]pyrene	perylene	indeno[123-cd]pyrene	dibenz[ah]anthracene	benzo[ghi]perylene
HE1	3	4	3	2	5	1	0	1	2	8	1	1	11	11	4	7	7	6	5	6	8	8	2	11
HE2	17	18	20	7	17	46	13	6	63	375	84	48	330	326	150	156	113	121	92	142	61	97	24	96
HE3	34	17	11	9	14	13	22	5	35	307	45	35	391	406	165	205	192	170	156	106	171	308	69	328
HE5	256	257	276	96	184	290	218	65	634	3194	706	492	1958	2352	962	1009	735	764	595	560	603	971	297	843
HE6	99	92	103	36	68	139	80	29	269	1496	231	211	1079	1149	503	593	422	434	336	250	265	465	125	436
HE7	195	170	190	67	137	311	148	52	474	2547	528	434	1898	2088	852	991	741	700	556	518	390	777	224	663
HE12	82	114	81	25	97	55	9	73	29	277	54	64	304	409	138	215	185	165	157	103	55	181	38	195
HE13	39	43	27	12	33	24	8	7	24	202	34	36	270	311	135	173	99	133	100	72	44	101	22	99
HE14	32	36	24	10	29	33	7	7	25	190	30	33	211	239	93	135	109	100	92	41	58	129	29	138
HE24	52	43	24	13	27	27	7	9	28	172	39	28	229	243	119	149	113	120	94	101	61	115	26	106
HE25	31	13	8	5	9	55	15	5	38	417	141	60	723	746	345	337	275	271	215	319	131	265	60	234
HE29	293	102	91	49	70	632	260	51	494	6057	1033	704	7150	7869	2961	3391	2926	2576	2229	2077	1346	3504	840	3090
HA1	47	48	30	13	62	31	8	23	37	297	51	72	289	343	130	198	137	124	112	112	33	100	18	134
HA2	11	9	6	4	7	11	3	2	8	75	16	11	117	120	48	56	45	43	35	46	17	31	6	31
HA5	5	7	4	5	3	1	1	1	11	25	2	3	15	32	5	14	29	4	13	3	661	16	4	47
HA6	11	11	8	5	7	2	2	2	7	148	4	14	104	89	18	52	36	28	25	23	70	27	6	28
HA7	8	4	2	4	4	5	0	1	3	16	3	3	33	35	19	24	22	19	16	19	31	32	7	31
HA21	71	52	29	18	36	40	5	10	16	168	36	34	232	317	101	154	125	94	117	63	35	116	22	169
HA25	9	6	4	3	5	4	2	2	6	33	8	5	44	44	19	22	20	16	14	19	41	16	3	17
HA26	8	6	3	4	6	13	2	1	8	59	20	8	112	110	54	54	41	39	30	48	55	40	9	36
HA27	6	6	3	3	3	1	0	0	5	13	2	2	12	14	5	7	7	4	5	5	67	5	1	8