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Trace Elements in Sediments of the Lower Eastern Coast of the Firth of Thames

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Executive summary

Background

In 2004, Environment Waikato tested for trace elements in shallow sediments from five sites spread across the lower Firth of Thames. Results indicated the presence of moderately elevated mercury in sediments at three of the sampling locations and suggested a need for further investigation. Environment Waikato then commissioned URS New Zealand Ltd (URS) to undertake more extensive sediment sampling of the eastern coast of the lower Firth of Thames and to produce a report on this. During June 2005, URS collected 78 sediment samples from the following 11 locations: Kuranui Bay, Piako River mouth, Tararu, Tapu, Te Mata, Te Puru, Thames mudflats, Thames urban area, Thornton Bay, Waihou River mouth, and Waiomu. All sediment samples were analysed for arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc. Samples collected from selected sites also underwent analysis for grain size, lithium, iron and aluminium, to aid in interpreting the results. Statistical tests were applied to ascertain if there were significant differences between sites. URS submitted their final report and assessment to Environment Waikato in 2006. This review has been adapted from the URS report and incorporates additional data and information which has come to light since sampling was carried out.

Findings: relative enrichments

Arsenic, cadmium, copper, mercury, lead and zinc are enriched in sediments of the lower eastern coast of Firth of Thames, relative to concentrations present before Polynesian and European colonisation, and reference concentrations in sediments from Raglan Harbour. Concentrations of the other five elements measured in some or all samples (chromium, nickel, aluminium, iron and lithium) are more typical of those observed in harbour sediments in other areas. Relative to its expected background concentration, the most highly enriched element is mercury. Mercury concentrations are on average about seven times higher in Firth of Thames sediments than those of reference sites. In mass terms, the most highly enriched element is zinc. Firth of Thames sediments contain about 10 mg/kg more zinc than reference sites.

Findings: local and general sources

Only one area (at two adjacent sampling locations) stands out as a hotspot of localised metal contamination, which looks likely to have been from an urban industrial source. This is the sediment in Kuranui Bay and south of this in the area of the Thames pipeline. Results from depth profile samples suggest that the worst contamination in this area may have been historic. Subsequent information suggests an association with industrial fill or landfill as a part of historic land reclamation in the area - the Moanataiari reclamation. Risks associated with this contamination are to organisms living in nearby marine sediments. There is currently little evidence of risk to people living on the reclamation.

Apart from this area, the influence of local sources appears minor. The results provide little evidence that former mining sites along the lower eastern coast of the Firth of Thames had, or continue to have, a significant impact on the quality of their nearest coastal sediments, relative to the more general impact from other sources.

Although there is some evidence for the presence of the occasional grain of a metal-rich mineral in sediments, more generally the data suggests that elevated arsenic, copper, lead, cadmium and zinc concentrations along the lower eastern coast of the Firth of Thames are likely to be dominated by larger-scale sources, which have been capable of causing an impact over the area as a whole. The three most likely large-scale sources are enhanced weathering and erosion following land clearance (arsenic and copper), the impact of distant historic mining operations which involved disposal of large volumes of tailings directly to the Ohinemuri River (zinc, cadmium, and lead) and agricultural inputs (zinc and cadmium). A fourth possible source identified in this work (for mercury) is dissolved organic matter entering the Firth of Thames from wetlands and peatlands of the Hauraki Plains. Further work is needed to confirm this hypothesis.

Findings: comparison to guidelines

Although concentrations of copper, cadmium, lead and zinc were higher than typical values for uncontaminated sediments, they are still well below the lowest sediment quality guideline values, and are believed to pose a low level of risk to health of aquatic ecosystems. The two elements that are nearest to or occasionally exceed guideline values for sediments are arsenic and mercury. Arsenic concentrations in coastal sediments at some locations in the Firth of Thames are at a point where they may adversely affect some sediment-dwelling organisms. Sediments in the area of the Moanataiari reclamation are substantially enriched in mercury, and consistently exceed relevant sediment quality guideline values. In URS NZ Ltd's sampling round, arsenic exceeded its ISQG-Low guideline (20 mg/kg) at eight out of nine (89% of) sites. Mercury exceeded its ANZECC (2000) ISQG-Low guideline (0.15 mg/kg) at four out of nine (44% of) sites.

Findings: most likely sources where enriched

Lead

Results for lead are consistent with the existence of one significant diffuse source of additional lead to the Firth of Thames, which is most likely to have been the influence of past mining in the Ohinemuri catchment. The Waihou River is known to have received between 500-800 tonnes per annum of mine tailings from the Ohinemuri River for over 50 years. This source is also likely to have contributed substantial zinc and cadmium (see below).

Zinc and cadmium

Results for zinc and cadmium are most consistent with the existence of two significant diffuse sources to the Firth of Thames: past mining, and current agricultural treatments. The Ohinemuri mining source (see lead above) may have been a significant source of three metals: lead, zinc and cadmium. Agriculture may be associated with two metals: zinc and cadmium. The most likely agricultural source of zinc is zinc sulphate, which is used in large volumes as a remedy for facial eczema in stock. The most likely agricultural source of cadmium is phosphate fertilisers (primarily superphosphate), in which cadmium is present as an impurity.

Arsenic and copper

Results for arsenic and copper are consistent with one primary diffuse source to the Firth of Thames: weathering of minerals such as pyrite in coastal areas of the Coromandel Peninsula. It is likely that the rate and extent of weathering and erosion, and influx of arsenic and copper, was enhanced by historic land clearance activities around the coastal areas of the Coromandel Peninsula, following Polynesian and European settlement of the area.

Mercury

There is no positive evidence that past mining, erosion of natural minerals, or agricultural treatments have been significant sources of mercury to the Firth of Thames sediments. Rather, the results suggest a source of mercury which is delivered to the Firth of Thames *via* the Piako River. Based on recent literature, it is thought that significant inputs of mercury may originate from drainage of the wetlands and peatlands of the Hauraki Plains. This form of mercury is most likely to be associated with dissolved organic carbon in the drainage waters. In addition, the base of the Moanataiari reclamation in Thames appears to be a localised hotspot of mercury contamination to marine sediments.

Recommendations

The following recommendations are made. (For further details of each recommendation, and its rationale, see Section 4.2.)

1. Sediments of the Firth of Thames be sampled once every five years, to allow early warning in the event that concentrations of one or more trace elements are gradually increasing.

2. Further work on mercury is commissioned, with a focus on:

    - Quantifying the relative significance of wetlands and peat deposits in the Hauraki Plains as sources of mercury to the Firth of Thames, relative to other sources.

    - Identifying land management factors that would increase or decrease mercury inputs to the Firth of Thames.

    - Identifying the most significant risks associated with mercury which has entered the Firth of Thames sediment reservoir, focusing on the significance of mercury to wildlife and human food sources, and the impact of mangrove colonisation on mercury chemistry.

3. The feasibility of simple erosion control measures that might work to reduce the flux of arsenic entering the Firth of Thames be investigated.

4. Contaminated site investigations be carried out on sediments in the area of the Moanataiari reclamation to determine hazards to the ecosystem, pathways, risks to the marine ecosystem, and management options.

Note on terms

Heavy metals / trace elements

The focus of this report is on concentrations and sources of eight chemical elements: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). These elements are often referred to as 'heavy metals.' However, this term is falling out of favour because it is an ambiguous one. A range of different definitions for 'heavy metal' exist in the scientific literature. In addition, arsenic is not regarded as a true metal, but a metalloid. The term 'trace element' is used in this report because it is not ambiguous, and accurately describes the group of eight elements that are the focus of this work. A 'trace element' is something which is not one of the ten major elements. Ninety-nine percent of the earth's crust is composed of the ten major elements: silicon, oxygen, aluminium, iron, calcium, potassium, sodium, magnesium, titanium and phosphorus. All other elements are 'trace elements', and most are present at natural concentrations of well under 100 mg/kg (parts per million) in the earth's crust. The term 'metal' is sometimes used in this report in discussing an element other than arsenic.

Enrichment / contamination

Trace elements occur naturally. When their concentrations are higher than expected, they are usually referred to as being 'enriched,' or 'elevated' above their natural concentrations. The terms 'contaminated' or 'contamination' are usually reserved for cases where a trace element's concentrations have become sufficiently high to cause significant adverse effects on the environment. For convenience, this is usually assessed by reference to sediment quality guidelines. Sites would normally be regarded as contaminated when trace elements are present at concentrations that significantly exceed the ANZECC ISQG-High (see Section 2.5). These conventions are followed in this report.

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1 Introduction

In 2004, Environment Waikato tested for trace elements in shallow sediments from five sites spread across the lower Firth of Thames. Results indicated the presence of moderately elevated mercury in sediments at three of the sampling locations, and suggested a need for further investigation. URS New Zealand Ltd (URS) was commissioned by Environment Waikato to undertake more extensive sediment sampling of the eastern coast of the lower Firth of Thames. In the expanded programme, samples were collected from sites stretching from the Piako River mouth eastward and then north, as far as Te Mata. The programme aimed partly to investigate whether elevated metal concentrations in surface sediments could be attributed to run-off from natural sulphide mineralisation, run-off from former mining operations/tailings dams, longer range transport of contaminants from the Waihou River (primarily from agricultural run-off or past mining) or from urban sources (*e.g.* stormwater or sewer pipelines from Thames). URS undertook the sampling between 22 and 24 June 2005.

Concentrations of eight elements were measured in samples collected by URS as part of this study: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn).

This report presents the methodology and results of the sampling and analysis programme undertaken by URS, and combines this with previous data and new information to give an overall assessment of (a) trace element enrichments in sediments of the lower Firth of Thames, and (b) the most likely sources in cases where element concentrations are elevated.

1.1 Potential sources of the elements

At the outset of this work, it was recognised that trace element enrichment in Firth of Thames sediment may come about through four main sources: the influence of natural mineralisation, tailings from former mining operations, agricultural activities, and urban inputs. These possible sources are discussed below. As an outcome of this work, a fifth possible source has been identified. This is discussed in Section 3.6.5.

1.1.1 Weathering and erosion

- *Natural weathering and erosion*. Trace elements occur naturally in rocks and minerals in the earth's crust and soils and sediments derived from these. Key primary minerals for 16 trace elements are shown in Table 1-1. The Coromandel range contains a significant natural abundance of volcanic hydrothermal minerals, including a number of notable ore deposits that have been mined commercially. Release of trace elements into surface run-off and streams which enter the Firth of Thames can come about through natural weathering and erosion processes.

- *Enhanced weathering and erosion.* Enhanced loadings of trace elements are likely to have come about as a result of historic land clearance activities around the coastal areas of the Coromandel Peninsula, following Polynesian and European settlement in the area. Grazed hill country yields two to five times more sediment than similar terrain under native bush (Ritchie, 2000), while production forestry practices at planting and harvest remove groundcover and expose topsoil to erosion by overland flow (Basher, 2003).

Table 1-1 Environmentally significant metals which occur at elevated concentrations in some New Zealand rocks (adapted from Metals in New Zealand Environment, University of Otago).

Metal	Principal primary minerals	Geological setting	Environmental mobility
Aluminium, Al	Most rock-forming minerals	All settings	High at low pH (AMD)
Antimony, Sb	Stibnite, Sb_2S_3	Schist-hydrothermal	High
Arsenic, As	Arsenopyrite, FeAsS; pyrite, FeS_2 (trace As); tetrahydrite other sulphide minerals	Schist–hydrothermal; volcanic-hydrothermal; sulphurous coals; trace in most rocks	High
Cadmium, Cd	Sphalerite ZnS (trace Cd)	Volcanic–hydrothermal	High at low pH (AMD)
Chromium, Cr	Chromite, $FeCr_2O_4$; Fe-Mg minerals	Gabbro; ultramafic rocks; trace in most rocks	Moderate at low pH (AMD)
Copper, Cu	Chalcopyrite, $CuFeS_2$	Other sulphide minerals. Volcanic–hydrothermal; schist (rare)	High at low pH (AMD)
Iron, Fe	Many rock-forming minerals	All settings	High at low pH (AMD)
Lead, Pb	Galena, PbS	Volcanic-hydrothermal	High at low pH (AMD)
Manganese, Mn	Many rock-forming minerals (with Fe)	All settings	High at low pH (AMD)
Mercury, Hg	Cinnabar, HgS; some pyrite (trace Hg); some silver	Volcanic-hydrothermal	Moderate-low, volatile
Molybdenum, Mo	Molybdenite, MoS_2	Volcanic-hydrothermal	Low
Nickel, Ni	Many rock-forming minerals (with Fe, Mg)	All settings	Moderate at low pH, especially coal AMD
Tin, Sn	Cassiterite, SnO_2	Volcanic-hydrothermal	Low
Tungsten, W	Scheelite, $CaWO_4$	Schist-hydrothermal	Low
Uranium, U	Uraninite, UO_2	Rare, coaly sediments, Paparoa Range, Westland	High at high pH
Zinc, Zn	Sphalerite, ZnS	Volcanic-hydrothermal; trace in most rocks	High at low pH (AMD)

Once released, trace elements can be transported in surface or ground waters for considerable distances from the mine. Transportation is dependent on speciation, pH, redox conditions, precipitation of iron oxides, and the concentrations of suspended solids and dissolved organic matter within the water column. Trace elements may precipitate out and accumulate into sediments in areas where there is a sudden change of redox conditions, salinity or pH. Such changes are encountered where fresh water mixes with seawater. In addition, trace elements associated with colloidal material and suspended particulate matter may settle out as sediment as water velocities slow. Lakes and estuaries provide suitable conditions for sediment accumulation that may have elevated trace element concentrations.

1.1.2 Past mining

The Coromandel Peninsula was the site of the first discovery of gold in New Zealand, at Driving Creek in 1852. From 1894 to 1910, low-grade quartz-vein deposits were actively worked using the cyanide extraction process. These mines generated significant volumes of waste rock and mine tailings (a term for finely-crushed mine waste rock). The type of historical mining practised in the Coromandel Peninsula can cause trace element enrichment of waterways through two mechanisms: direct entry of mine tailings to surface water, and acid mine drainage:

- In the past, large volumes of mine tailings were disposed of directly to the Ohinemuri River, which enters the Waihou River, which enters the Firth of Thames. Specifically, the Waihou River is known to have received between 500-800 tonnes per annum of tailings from the Ohinemuri River for over 50 years.

- In acid mine drainage (or AMD), minerals are released through the oxidation of the sulphide minerals, liberating trace elements, which are then flushed out of the mine workings or tailings dam by rain or groundwater into the local environment. AMD leachate is normally characterised by low pH, high concentrations of sulphate, ferrous iron (Fe^{2+}_{aq}) and trace elements (*e.g.* lead, copper, nickel, zinc, cadmium, mercury, arsenic, antimony, thallium).

Table 1-2 lists the various streams within the Coromandel Peninsula where historical mining has been undertaken within the stream catchments.

Historical mining has had some severe localised environmental impacts, most notably the Tui Mine tailings dam (Tay, 1981). Acid mine drainage and the subsequent release of metals from base metal sulphides into the aquatic environment is a significant long-term legacy from historical mining at this site (Rumsby, 1996).

Mines situated in ore bodies with base metal sulphide mineralisation (such as Buffalo, Monowai and Cromstock within the Waiomu Catchment) could potentially have an impact on the water and sediment quality of the local receiving environment and ultimately the Firth of Thames. Many of the mines with vein deposits containing significant base-metal sulphides (>3%) which are listed in Table 1-2 (e.g. Komata, Jubilee, Tui and Waiorongomai) are located on streams which form part of the Waihou River Catchment.

There is a high correlation of arsenic with iron (R^2=0.77 with n=34; p=0.001) in several former mines in the Coromandel area (Hollinger, 2002). Electron microprobe data suggest the two main arsenic containing sulphide minerals are pyrite/marcasite which generally have an arsenic concentration of 0.1 to 1.6% and tetrahedrite (copper antimony sulphide, general formula $Cu_{12}Sb_4S_{13}$) which can have an arsenic concentration of up to 20% (Hollinger, 2002). Pyrite (iron sulphide, FeS_2) is listed as being ubiquitous in the Hauraki Goldfield and, therefore, pyrite would be the most important source of arsenic as it occurs in both the host rock and ore bearing rock (whereas tetrahedrite is only in the ore-bearing rock). Therefore, historic mining may be a source of several trace metals but especially arsenic.

Table 1-2 Alteration, mineralisation and old mine workings in the Coromandel area (modified from Livingston 1987, including data from Jenkins 1991 and Moore et al. 1996).

Stream	Country Rock Alteration	Mineralisation	Mine Workings	Mullock Tips, Tailings
Waitawheta	Mainly unaltered or weakly propylitised	Some veins with minor base materials	None known	None known
Waipupu	Mainly unaltered or weakly propylitised	None known	None known	None known
Waitekauri	Mainly Strongly clay-altered and silicified	Several large veins, with trace base metals	Extensive (Golden Cross)	Present
Komata	Both propylitised and silicified rocks	Several large veins, minor base metals	Extensive (Komata, Te-ao-marama)	Extensive, contain minor base metals
Mangakara	Mainly strongly clay-altered and silicified	Numerous small, commonly pyritic veins	Extensive (Scotia, Maoriland)	Present
Buffalo	Mainly propylitised or clay-altered	Minor veins with minor base metals		Present
Mangatoetoe	Mainly unaltered; strong local clay alteration	None known	Extensive on Martha Hill	Present
Waiorongomai	Mainly propylitised, minor silication	Several large base-metal bearing veins	Extensive mine Workings	Present, probably contain minor base metals
Jubilee	Mainly clay-altered, minor propylitisation	Large, locally base-metal bearing vein	Extensive mine workings	Extensive, contain significant base metals
Cromstock	Propylitised	Several veins with minor base metals	Some minor workings	Not known
Waiomu	Propylitised	Several veins with minor base metals	Some mine workings (Cromstock)	Present
Paroquet	Mainly clay altered	Base-metal bearing vein	Extensive mine workings (Monowai)	Present contain base metals
Waitatia	Propylitised, clay-altered and silicified	Many small veins, several larger veins	Extensive mine workings (Waitatia)	Present
Tui	Propylitised, clay-altered and minor silicified	Several large base-metal bearing veins	Extensive mine workings (Tui)	Extensive, contain significant base metals

1.1.3 Agricultural and horticultural inputs

Some agricultural activities involve the application to land of some materials that contain significant concentrations of one or more trace elements. There can be some loss of these elements from farms to the wider environment, including freshwater and marine sediments. In pastoral areas, zinc sulphate is used extensively to protect against the liver damage that causes facial eczema in both cattle and sheep. In addition, most superphosphate fertiliser contains significant amounts of several trace elements as impurities, most notably cadmium and fluorine (Table 1-3). Copper and zinc are also applied to horticultural areas in fungicide formulations.

Table 1-3 Concentrations of selected elements in phosphate fertiliser, soils and rocks.

Element	Average upper continental crust[1]	Waikato soils (average)[2]	Phosphate rock (PR) (mg/kg P)	Single superhosphate fertiliser (mg/kg P)
Cadmium, Cd	0.15	0.70	1-90	<280
Uranium, U	2.7	2.2	6-420	8-37[3]
Zinc, Zn	70	67.8	0.2-21	46-370
Cobalt, Co	25	6.5	0.2-21	
Antimony, Sb	0.2	0.7	0.1-3	
Mercury, Hg	0.085	0.2	0.4-2.1	5
Arsenic, As	1.8	7.6	2-300	
Lead, Pb	14	19.3	3-35	200
Fluorine, F	585	411	340,000	170,000

[1] CRC Handbook of Chemistry and Physics.

[2] Waikato Regional Council data. (For some elements such as cadmium and fluorine, current concentrations are above their natural levels in Waikato soil due to farming history.)

[3] Taylor 1997a

Superphosphate application in New Zealand has lead to a gradual increase in cadmium concentrations in soil (Taylor, 1997b). High cadmium concentrations are found in rock phosphate, the fertiliser source material (Moore et al, 2005). Cadmium may be leached from soil and/or fertiliser into waterways (Moore et al., 2005, Gray et al., 2003, Bennet-Chambers et al., 1999; Martin & McCulloch, 1999). Butler and Timperley (1996) found that elevated cadmium concentrations in the Mahurangi Harbour were associated with fertiliser application. Therefore, superphosphate may be a source of cadmium. At the outset of this study it was thought that fertiliser application may, therefore, be a source of cadmium in the Firth of Thames due to the intensive agricultural activities within the catchments of the Waihou and Piako Rivers. Similarly, facial eczema treatments may be a source of zinc.

1.1.4 Urban inputs

Urban stormwater can contain a number of contaminants including copper, lead, zinc and organic compounds such as polyaromatic hydrocarbons (PAHs), herbicides, pesticides and other hydrocarbon mixtures such as oil and grease (Table 1-4). Many of these contaminants are associated with motor vehicles. Contaminants in road run-off from vehicles can originate from tailpipe emissions, tyres, brake components, and leaks of fuel, oil or coolants. Stormwater from small towns such as Waihi, Paeroa and Te Ahora may be a source of some trace elements to the Waihou River, although impacts on sediments may be quite localised to the area immediately downstream of the urban source. A survey conducted by Webster (1995) indicates that concentrations of some metals (lead and zinc) are elevated in some sections of the Waihou River.

Table 1-4 Contaminants in New Zealand stormwater (from Taylor et al. 2005).

Urban area	Suspended Sediment (mg/L)	Total Cu (µg/L)	Total Pb (µg/L)	Total Zn (µg/L)	Total P (mg/L)	Dissolved fluoranthene (µg/L)	Dissolved pyrene (µg/L)
Tauranga	611	67	61	588	43	0.20	0.13
Cambridge	528		55	416	29	0.13	0.05
Hamilton	238	22	19	328	-	0.19	0.12

1.2 Previous data

URS New Zealand Ltd undertook a literature survey to identify additional data from other sediment quality surveys conducted on the Firth of Thames. Few sediment quality surveys of the Firth of Thames have been reported in the literature.

- Livingston (1987), focusing mainly on the Coromandel Peninsula itself, studied impacts of mining on stream sediment, water quality and macro-invertebrate communities, as well as metal concentrations in shellfish and fin-fish.

- The Department of Conversation (1992) commissioned an investigation of the effects of Polynesian and European land use on sedimentation on Coromandel estuaries in 1992. As part of that work, metal concentrations were measured in a number of cores.

- Research has also been conducted by Webster (1995) on chemical processes affecting trace metal transportation in the Waihou River and estuary.

- More recently both the Auckland Regional Council and Environment Waikato have undertaken monitoring at selected sites within the Firth of Thames. One of the ARC sites is at Waiheke Island (Te Matuku).[1] The previous Environment Waikato monitoring sites around the Firth of Thames have involved shallow (0-2 cm) sediment samples, because the primary survey purpose was ecological monitoring, but have been included in the data analysis of this study (Section 3.3.1).

- The National Water and Soil Conservation Authority (NWSCA) conducted a survey of stream sediment and water quality within various streams on the Coromandel Peninsula. The NWSCA also conducted biological monitoring within the streams and measured metal concentrations in shellfish and fin-fish. Unfortunately, the results of the NWSCA study are not usable in this study as no marine sediment samples were collected in that work.

A summary of trace element concentrations reported at specific sites by Livingston (1987), the Department of Conversation (1992), Webster (1995) and the Auckland Regional Council is presented in Table 1-5. Results of previous (2003) sampling carried out by Environment Waikato are presented as part of this report (see Section 3.3.1 and Appendix 6).

In addition to these studies, Hume and Dahm (1991) of the Department of Scientific and Industrial Research (DSIR) used marine sediment cores to investigate the impact of Polynesian and European land use on sedimentation in Coromandel estuaries. Results revealed that trace element concentrations deposited in European times are elevated over pre-settlement background levels. Specific observations were as follows:

- Concentrations of lead in pre-settlement sediments ranged from 8-18 mg/kg. In younger sediments lead ranged from 16-66 mg/kg, with typical values around 30 mg/kg. Lead was typically enriched to between 1.5 to 2 times background levels, although lead enrichment of up 4-5 times was noted near the Waihou River Mouth.

- Zinc concentrations were reported to range from 36-78 mg/kg in pre-settlement sediments to 174 mg/kg (typically 80-90 mg/kg) in younger sediments. Overall, zinc levels were elevated at approximately 1.5-2 times background levels (Hume and Dahm, 1991).

- Background concentrations of copper ranged between 6-21 mg/kg, with post-European settlement concentrations ranging between 13-26 mg/kg. Copper was elevated only in sediments post-dating European settlement, with enrichment factors of between 1.5-2 noted in the core samples.

- Arsenic was slightly elevated in post-settlement sediments to approximately 1.2-2 times background levels.

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[1] Unfortunately the ARC analytical protocol (analysis of only the sub-63 µm fraction) makes it difficult to compare results. The other ARC monitoring locations represent estuary environments which have been impacted by urbanisation.

Table 1-5 **Sediment quality data (mg/kg) obtained by other authors prior to this study.** (Refer to Table 1-1 for the element name associated with each chemical symbol.)

Location	Date	Ref.	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Waiomu Stream										
WC	1982	1	0.41	<0.4		<0.35			0.23	<0.66
WP2	1982	1	<0.08	<0.6		0.72			0.86	10.4
P2	1982	1	<0.06	0.015		0.74			0.31	1.6
B4	1982	1	1.9	0.023		<0.28			0.24	3.7
Waiomu										
T4 (3-5 cm)		2	16			17.9		12.9	32	93.3
T4 (24-26 cm)		2	6.7			9.5		12.1	14.8	64.6
T4 (63-68cm)		2	11.2			11.9		12.4	13.5	65.2
T4 (96-90 cm)		2	11			10.3		12	11.3	63
T4 (150-152 cm)		2	6.2			8.9		14.4	12.1	71.1
Tararu										
T1A (3-5cm)		2	24.1			25.9		11.5	66.4	174
T1A (9-11 cm)		2	8.7			10.8		11.1	11.3	65.9
T1A (23-25 cm)		2	9.7			14		13	15.7	77.6
T1A (56-59 cm)		2	11.1			14.8		11.9	14.8	74.4
Mid-Firth of Thames										
T2A (0.2 cm)		2	7.3			6.1		6.2	13.3	33.9
T2A (2-5 cm)		2	7.7			5.9		11.3	10	45.6
T2A (7-8 cm)		2	8.4			11.1		12.6	12.4	58.3
T2A (29-33 cm)		2	6.2			5.6		9.1	7.7	35.9
T2A (82-83 cm)		2	9.6			8.2		14.1	10.8	62.8
Coromandel Harbour										
C1(3-5cm)		2	18.6			15.9		7.5	30.2	91.9
C1(11-15 cm)		2	24.2			14.7		6.1	23.1	82.6
C1 (20-25 cm)		2	12			9.8		6.6	11.3	41.8
C1 (32-34 cm)		2	13.9			11.6		9.5	14.8	53.3
C1 (37-39 cm)		2	13.6			20.9		8.4	14.9	54.2
C2 (0-3 cm)		2	15.3			17		8.8	28.4	76.6
C2 (6-8 cm)		2	14.7			11.5		8.6	16.3	57
C2 (18-20 cm)		2	9			11.8		8.2	12.4	52.1
C2(37-39 cm)		2	9			8.4		7.3	12.5	48.4
C2 (101-103 cm)		2	15.5			14		13.5	17.8	69.3
C4 (6-8 cm)		2	9.3			13.4		9.2	15.7	47.4
C4 (35-36 cm)		2	8.5			8.5		7.6	10.4	44.8
C4 (74-76 cm)		2	13.2			11.7		9.9	8.9	55.4
C4 (95-97 cm)		2	13.4			10.5		9.7	10.9	54.4

Location	Date	Ref.	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
C4 (138-140 cm)		2	9.5			6.4		8.4	10.4	45.4
Waihou River										
W11b (0-5 cm)1985		3				16.5			67.2	259
W11b (5-10 cm)		3				25.6			100.6	200
W11b (10-15 cm)		3				20			73	146
W11b (15-20 cm)		3				8.2			24.6	64.3
W13 (0-5 cm)		3				29.8			60.5	276
W13 (5-10cm)		3				23.5			78	185
W13 (10-15 cm)		3				17.8			75.4	179
W13 (15-20 cm)		3				18.1			79.4	201
W26		3	3.7		35.1	17.6			19.5	137
Tararu Beach										
W27	1985	3	9.63		37.5	237			91.1	1478
Te Matuku		4								
	2001					3.0			1.9	38.5

Sources: 1. Livingston (1987); 2. Department of Conservation (1992); 3. Webster (1995); 4. Auckland Regional Council (2001).

The authors concluded that the elevated metal concentrations are probably due to anthropogenic effects related to European land use. This may be due to greater contributions from weathering of natural minerals caused by increased surface water run-off following land clearance, and more direct contributions from mining operations. Arsenic, copper, lead and zinc are commonly associated with mine waste run-off, and large volumes of mine tailings that were dumped into the Ohinemuri River in early European times.

Hume and Dahm’s (1991) estimates of relative enrichments of lead, zinc, copper and arsenic are in good agreement with those determined by comparing sediments’ quality in Raglan Harbour with that in the Firth of Thames, as part of this work. These estimates are presented in Section 3.3.1 of this report.

2 Study methodology

2.1 Sampling objectives

As part of this work, URS was commissioned to undertake new sediment sampling of the eastern coast of the lower Firth of Thames for the purposes of assessing sediment quality and identifying the potential sources of trace elements in these sediments. Concentrations of eight elements were measured in all samples collected: arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). A sampling programme was designed that would maximise the possibility of being able to discriminate between a number of possible sources of an element in sediments of the intertidal zone. These sources include:

- Run-off from natural and enhanced weathering and erosion of sulphide minerals;
- Run-off or legacy of tailings inputs from former mining sites;
- Longer-range transport from agricultural, urban and mining areas (for example, large river mouths);
- Urban sources.

Sampling also included control sites that were not likely to have been significantly impacted by the above sources. Key features and catchments in the study area are shown in Figure 2-1.

2.2 Sampling locations

2.2.1 General

Samples were collected from 11 locations on the eastern side of the Firth of Thames: the Waihou River mouth, the Piako River mouth, various areas around Thames, Opani mudflat, Tararu, Tapu, Te Puru, Thornton Bay, Waiomu, Te Mata, and Kuranui Bay (Table 2-1; Figure 2-2).

Sampling by URS New Zealand Ltd was undertaken between 22 and 24 June 2005, with sample locations selected to characterise each of the potential sources identified. Targeted sampling of selected areas was undertaken, utilising a mix of composite sampling techniques in order to obtain representative samples and targeted depth sampling (Table 2-1). Sampling locations were recorded using a handheld Global Positioning System (GPS) unit.

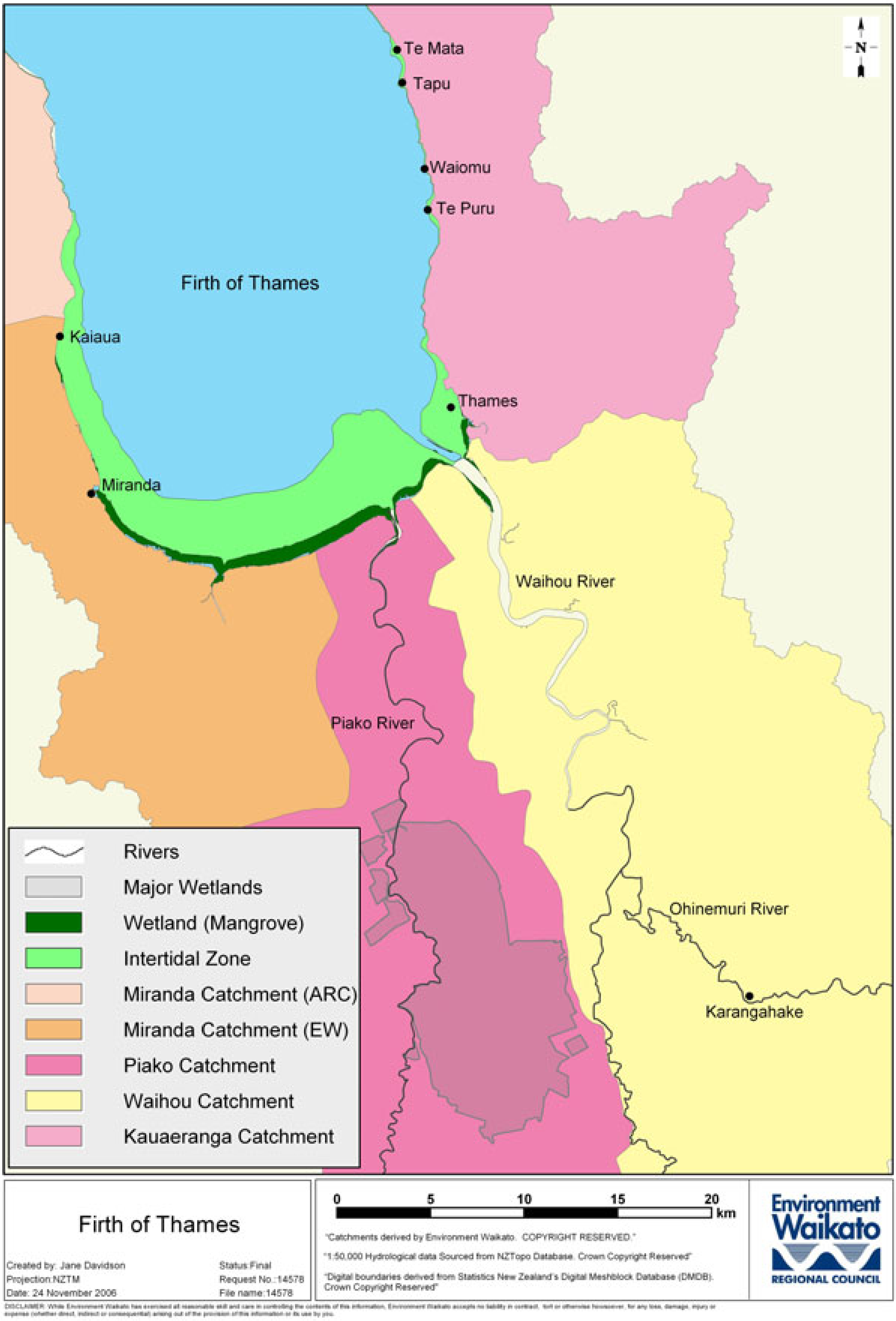

Figure 2-1: Context of the study area, showing catchment boundaries and other key features.
Samples collected by URS NZ Ltd (Table 2-1) were collected from the Piako River mouth to Te Mata. In previous work also reviewed in this report, shallow surface (0-2 cm) samples were collected from Miranda to Te Puru.

Table 2-1 Details of sediment samples collected by URS New Zealand Ltd in 2005.

Location	Sample ID	Approximate GPS location (NZMS)	Sample type	Sampling method and depths	Number of samples analysed
Waihou River mouth	SDB574	NZMS T12 361446	Composite made of five subsamples	Mix of Eckman grab sampling and hand sampling (plastic trowel). Nominal depth 10 cm.	2 composites
	SDB575	NZMS T12 362455	Composite made of five subsamples		
Piako River mouth	SDB571	NZMS T12 321430	Composite made of five subsamples	Eckman grab sampling. Nominal depth 10 cm.	3 composites
	SDB578	NZMS T12 379441	Composite made of five subsamples		
	SDB579	NZMS T12 321437	Composite made of five subsamples		
Thames pipeline area	SDB564	NZMS T12 351489	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	3 composites, plus:
	SDB565	NZMS T12 351489	Composite made of five subsamples		
	SDB566	NZMS T12 351489	Composite made of five subsamples		
	SDB810, 811	NZMS T12 351489	Vertical profile	Push corer: 0-2 cm and 2-10 cm	2 individual depth samples.
Thames mudflats	SDB580	See Figure 2-2	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	8 composites: 2 of these (SDB573 and SDB576) analysed twice for QA/QC.
	SDB581		Composite made of five subsamples		
	SDB582		Composite made of five subsamples		
	SDB583		Composite made of five subsamples		
	SDB584		Composite made of five subsamples		
	SDB585		Composite made of five subsamples		
	SDB573		Composite made of five subsamples		
	SDB576		Composite made of five subsamples		
Thames wharf & stormwater	SDB567	NZMS T12 362477	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	2 composites
	SDB602		Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	
Thames deeper harbour	SDB569	NZMS T12 330449	Composite made of five subsamples	Eckman grab sampling. Nominal depth 10 cm.	1 composite

Table 2-1 continued...

Location	Sample ID	Approximate GPS Location (NZMS)	Sample type	Sampling method and depths	Number of samples analysed
Opani mudflat	SDB568	NZMS T12 334449	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	1 composite
Tararu Stream	SDB595	NZMS T11 341515	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	6 composites. One analysed (SDB595) twice for QA/QC.
	SDB597		Composite made of five subsamples		
	SDB598		Composite made of five subsamples		
	SDB599		Composite made of five subsamples		
	SDB600		Composite made of five subsamples		
	SDB601		Composite made of five subsamples		
Tapu Stream	SDB796	NZMS T11 328656	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	6 composites
	SDB797		Composite made of five subsamples		
	SDB798		Composite made of five subsamples		
	SDB799		Composite made of five subsamples		
	SDB800		Composite made of five subsamples		
	SDB801		Composite made of five subsamples		
Te Puru	SDB603	NZMS T12 344590	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	6 composites, plus:
	SDB604		Composite made of five subsamples		
	SDB606		Composite made of five subsamples		
	SDB607		Composite made of five subsamples		
	SDB608		Composite made of five subsamples		
	SDB609		Composite made of five subsamples		
	SDB816, 817, 818 and 819		Vertical profile	Push corer: 0-2 cm, 2-10 cm, 15-20 cm and 25-30 cm	4 individual depth samples.
Thornton Bay	SDB802	NZMS T12 345563	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	6 composites
	SDB803		Composite made of five subsamples		
	SDB804		Composite made of five subsamples		
	SDB615		Composite made of five subsamples		
	SDB616		Composite made of five subsamples		
	SDB621		Composite made of five subsamples		

Table 2-1 continued...

Location	Sample ID	Approximate GPS Location (NZMS)	Sample Type	Sampling method and depths	Number of samples analysed
Waiomu Stream	SDB611	NZMS T11 342607	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	6 composites. One analysed (SDB594) twice for QA/QC, plus:
	SDB612		Composite made of five subsamples		
	SDB613		Composite made of five subsamples		
	SDB614		Composite made of five subsamples		
	SDB615		Composite made of five subsamples		
	SDB594		Composite made of five subsamples		
	SDB619A, 619B, 619C, and 619D		Vertical profile	Push corer: 0-2 cm, 2-10 cm, 15-20 cm and 25-30 cm	4 individual depth samples.
Te Mata	SDB790	NZMS T11 333672	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	6 composites
	SDB791		Composite made of five subsamples		
	SDB792		Composite made of five subsamples		
	SDB793		Composite made of five subsamples		
	SDB794		Composite made of five subsamples		
	SDB795		Composite made of five subsamples		
Kuranui Bay	SDB558	NZMS T12 345505	Composite made of five subsamples	Hand sampling (plastic trowel): 0-10 cm	6 composites. One (SDB591) sampled and analysed twice for QA/QC, plus:
	SDB559		Composite made of five subsamples		
	SDB560		Composite made of five subsamples		
	SDB561		Composite made of five subsamples		
	SDB562		Composite made of five subsamples		
	SDB563		Composite made of five subsamples		
	SDB591		Composite made of five subsamples		
	SDB812, 813, 814 and 815		Vertical profile	Push corer: 0-2 cm, 2-10 cm, 15-20 cm and 25-30 cm	4 individual depth samples.
Various			Composites made of five subsamples, and individual samples		12 composite or individual samples analysed as part of QA/QC

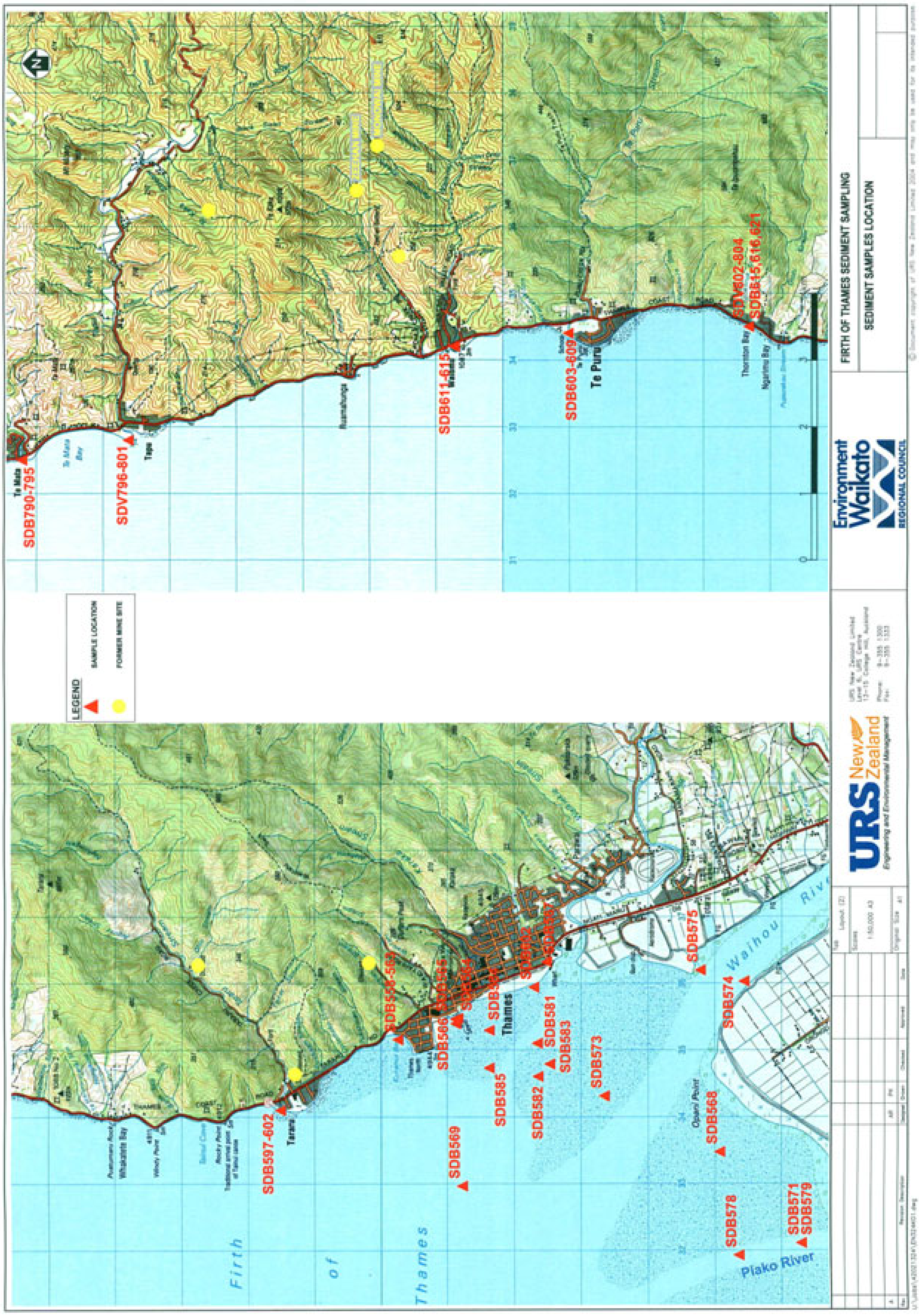

Figure 2-2 Locations of sites where sediment was sampled in 2005 and old mining sites. Exact coordinates of the sediment sampling sites, and details about the numbers of samples collected, are provided in Table 2-1.

2.2.2 History of the sample locations

There are at least four possible sources of historic trace element contamination in the Firth of Thames: natural erosion, tailings and run-off from mining, agricultural sources, and urban inputs (Section 1.1).

Thames Harbour receives input from stormwater discharged from Thames and the Piako, Waihou and Kauaeranga Rivers. The Waihou River is the largest river within the study area, and all four sources of contamination may have contributed to the contaminant load carried by this watercourse. Water and sediment sampling conducted in the catchment has previously indicated significant trace element contamination (Livingston, 1987). Mining in the area has involved significant workings at the following locations:

- Karangahake Gorge – sections of which were mined between 1882-1933.
- Mt Te Aroha (Tui Mine) – a base metal mine which operated between 1967 and 1973 and is regarded as one of New Zealand's most contaminated sites.
- Martha Hill mine in Waihi – which is currently operational.

Of these, inputs from the first source were substantial (500-800 tonnes of mine tailings per annum from the Ohinemuri River for over 50 years), impacts of Tui Mine were/are likely to be more localised, and present day mining operations at Martha Hill are carried out under resource consent conditions designed to eliminate any significant adverse effects. The Kauaeranga Valley was mined for cinnabar (mercuric sulphide, HgS) between 1899 to approximately 1906 (Watson, 1989) and the Kauaeranga River discharges into Thames Harbour. In addition to historic and present day mining in the Waihou River catchment, there are agricultural activities and urban inputs from Waihi, Paeroa and Te Ahora townships.

In contrast, there is no known mining influence in the Piako River catchment area, but agricultural inputs are a potential source of trace elements in this area. A feature of this catchment is that it includes a substantial wetland, the Kapouatai peat bog.

Historical mining activities were undertaken at several locations within the Tararu, Tapu and Waiomu stream catchments. The Waiomu stream catchment has received the most study. A number of mines operated within this valley between 1890 and 1936 (including Paroquet, Broken Hill, Monowai and Comstock Mines). Exploration in this area between 1971 and 1984 revealed the presence of unmined ore bodies within this region (Moore et al. 1996). The ore deposit has been described as being an epithermal vein deposit with significant base metal sulphides (>3%). These would have the potential to elevate concentrations of elements in sediments if the ore body undergoes oxidation. In 1981, a preliminary survey of the Waiomu stream conducted by the Department of Scientific and Industrial Research (DSIR), National Water and Soil Conservation Authority (NWASCA), the Ministry of Agriculture and Fisheries (MAF) and the Hauraki Regional Water Board (Livingston, 1987) detected elevated concentrations of various trace elements (in particular, arsenic, cadmium and zinc) in the water and sediment of the Comstock Stream (a tributary of the Waiomu Stream). Slightly elevated concentrations of copper, lead and zinc have been detected in several locations within the Waiomu Stream water, and elevated concentrations of lead and zinc have been detected in Waiomu Stream sediments (Livingston, 1987).

Kuranui Bay, the northern boundary of Thames township has been sampled in the past by Environment Waikato and elevated mercury and zinc concentrations were detected.

Three control sites without any significant past mining or agricultural activities within their catchments were also sampled. They were Te Puru, Thornton Bay and Te Mata.

More specific details of each location from which sediment samples were collected in 2005 as part of this study are provided in Appendix 1.

2.3 Sample types

2.3.1 Manual grab samples

Usually, six composite samples were tested from each of the locations sampled in 2005 (Table 2-1). Each composite sample was made up of five sub-samples.

In several cases, samples were collected in the intertidal area in the vicinity of a stream mouth. Sampling around small stream mouths was undertaken by dividing the area around the stream mouth into six sections (refer to Figure 2-3).

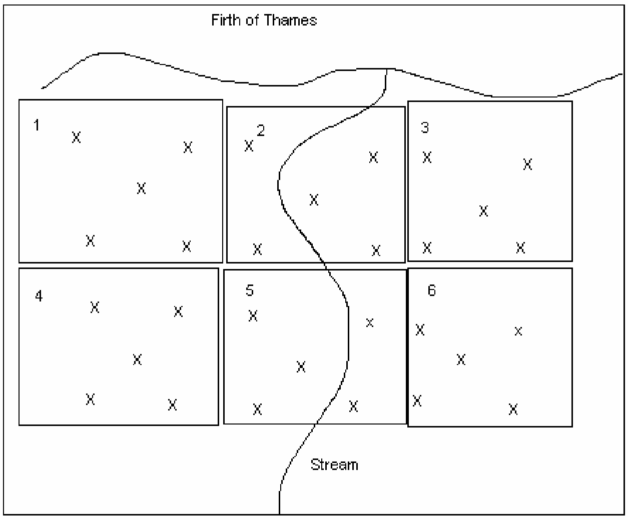

Figure 2-3 **Diagram indicating approach to collection of composite samples obtained from stream mouths.**

All of these samples collected for use in sediment composites were collected from the top 10 cm of sediments. Most epifaunal and infaunal organisms are found in the top 10 cm of sediment. Some epibenthic species (e.g. shrimps, certain amphipods) might be exposed only to surficial sediments (0-1 cm) while others (e.g. bivalves and polychaetes) can be exposed to sediments that are several centimetres deep.

A similar grid-type method was used at other sites (for example large river mouths and control sites with no stream outflows), as depicted in Figure 2-4.

Samples were collected using a plastic hand trowel (trowel length 10 cm) and placed within individual plastic sample containers. Other data recorded at each site included site and sample identifier, site location (recorded by GPS wherever possible), and time and date of sample collection.

The six composite samples for each location were prepared from the individual sub-samples by the analytical laboratory (Hill Laboratories, Hamilton). Equipment was rinsed with site water between each sub-sample.

2.3.2 Vertical profiles

At four sites, vertical profile samples were also collected using push-corers (see Table 2-1). Samples from three of these sites (Te Puru, Waiomu and Kuranui Bay) were divided into four sub-samples for analysis, to the following sediment depths: 0-2 cm, 2-10 cm, 15-20 cm and 25-30 cm. Samples from the fourth site (Thames stormwater pipeline area) were divided into two depths for analysis: 0-2 cm and 2-10 cm.

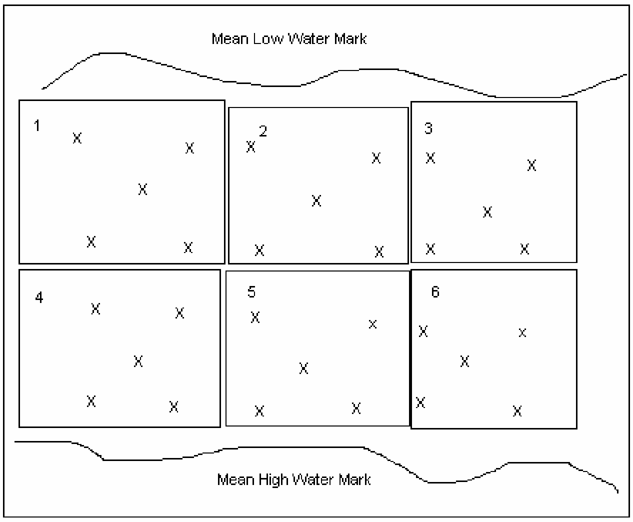

Figure 2-4 **Diagram indicating approach to collection of composite samples obtained from intertidal zone with no significant inputs.**

2.3.3 Grab sampling

Grab samples were collected from areas covered by water by use of an Eckman grab sampler. Where water flow was too fast for the Eckman grab sampler to operate, at some locations near the Waihou River mouth, subsamples were hand-collected by URS staff. To ensure that grab samples were consistent and suitable for benthic sampling, the following criteria were utilised before the sample was accepted:

- Sediment had not extruded from the sampler.
- Water was still present in the sampler (*i.e.* the grab remained closed during retrieval).
- The sediment surface was relatively flat.
- Appropriate sediment penetration had occurred (>10 cm in silty sediments).

If a collected sample failed to meet any of these conditions, the sample was discarded and another sample collected at the site. The location of consecutive attempts was made as close to the original attempt as possible and located in the upstream direction of any existing current. The rejected sample was discarded in a manner that would not have affected subsequent samples.

2.4 Analysis and analytical quality assurance

Seventy-seven sediment samples were analysed by Hill Laboratories, Hamilton. Chain of custody forms accompanied all samples submitted to the analytical laboratory. All analysis was undertaken on the sub-2 mm fraction of sediments. Total recoverable arsenic, cadmium, chromium, copper, mercury, nickel, lead, and zinc were analysed on all samples, with several samples being analysed in duplicate (Table 2-1).

Grain size, aluminium, iron and lithium were measured in selected samples.

Five quality assurance/quality control (QA/QC) samples were collected adjacent to grab samples to evaluate small-scale variations (nugget effects) and variability of both field and laboratory operations.

In addition, five composited samples were re-composited by the laboratory to evaluate the variability in compositing. A laboratory QA/QC check was also provided.

2.5 Use of ANZECC sediment quality guidelines

To establish the degree of risk to sediment-dwelling organisms, the results from this survey can be compared with Australian and New Zealand Environmental Conservation Council (ANZECC) interim guideline values for sediment quality (ISQGs) for the protection of aquatic ecosystems. For each trace element, there are two ANZECC (2000) guidelines for sediment quality.

- The lowest is the Interim Sediment Quality Guideline-Low (**ISQG-Low**) which represents a concentration below which adverse effects are unlikely. Concentrations of contaminants below the ISQG-Low pose a low level of risk to aquatic organisms.

- The higher is the **ISQG-High**, which is a median level at which adverse effects are expected in half of the exposed organisms. Contaminant concentrations above the ISQG-High are interpreted as being reasonably likely to cause significant adverse effects on aquatic organisms.

Concentrations between the ISQG-Low and ISQG-High are thought to pose a moderate level of risk to aquatic organisms. Concentrations of trace elements or other chemicals either below or above the ANZECC (2000) trigger values should not be thought of as safe or unsafe, but rather posing a lower or higher level of risk. This is because site-specific factors such as the chemical form of compound or element, natural background concentration, the concentration of organic matter or reduced sulphide compounds can all modify the toxicity of a particular compound.

Values below the ISQG-Low do not guarantee that the concentrations are safe either because complex chemical mixtures of certain compounds are more toxic than their individual chemical components and the ANZECC (2000) guidelines are not designed to protect against those mixtures. Also certain compounds such as mercury have specific chemical forms (methylmercury, ethylmercury) which bioaccumulate in organisms and biomagnify up the food-chain. As bioaccumulation potential is site-specific, more detailed studies are required to assess such risks. Therefore, the guidelines are designed to be trigger values to indicate which sites may warrant closer investigation.

It should also be noted that the ANZECC (2000) guidelines are designed to protect aquatic ecosystem rather than to protect human health. Although ISQG-Low values are lower than equivalent soil quality guidelines designed to protect human health, the aim of this study and the guidelines used in this study is related to the protection of aquatic ecosystems. Therefore, no conclusion should be made on the potential human health risk.

3 Results and discussion

3.1 Raw results and summary statistics

A complete list of the results for eight trace elements in all sediment samples is provided in Appendix 2. A summary of results obtained at each sampling site is presented in Table 3-1. A discussion of results from quality assurance and quality control samples is provided in Appendix 3. Normalised data is provided in Appendix 4, and a statistical summary of results for each sampled area in Appendix 5.

Table 3-1 Summary of trace element concentrations at sampling sites and comparison to ANZECC (2000) sediment quality guidelines (all values in mg/kg dry weight). Site locations are listed from south (Waihou and Piako River mouths) to north (Te Mata). **Bold** entries exceed ANZECC (2000) ISQG-Low values; the ***bold italic*** entry exceeds an ISQG-High value. Refer to Table 1-1 for the element name associated with each chemical symbol.

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
ANZECC (2000)	ISQG-Low	20	1.5	80	65	0.15	21	50	200
	ISQG-High	70	10	370	270	1.0	52	220	410
Location									
Waihou River mouth (N=2)		7.3	0.11	30.8	9.9	**0.22**	9.2	26.5	91.7
Piako River mouth (N=3)		9.2	0.23	24.3	10.4	**0.32**	8.5	29.5	104
Opani mudflat (N=1)		7.5	0.17	25.1	9.7	**0.27**	8.4	28.9	98.5
Thames wharf & stormwater (N=2)		14.6	0.11	24.8	12.0	**0.28**	8.2	27.8	90
Thames mudflats & harbour (N=9)		14.2	0.09	24.8	13.8	**0.35**	8.5	20.5	73.8
Thames pipeline (N=5)		***106***	0.40	24	16.9	**0.47**	8.7	35.6	149
Kuranui Bay (N=9)		**36.1**	0.41	22.7	16.4	**0.76**	8.1	29.9	146
Tararu Stream (N=7)		**24.5**	0.17	16.3	23.0	**0.18**	6.0	25.6	99.1
Thornton Bay (N=6)		**23.0**	0.03	21.5	17.8	0.08	8.1	22.2	72.7
Te Puru (N=8)		**24.3**	0.05	21.7	21.5	0.09	7.8	20.4	72.2
Waiomu Bay (N=8)		**27.3**	0.10	26	31.8	0.09	8.8	35.3	82.3
Tapu (N=6)		**21.2**	0.02	19.6	14.0	0.12	8.3	8.15	54.4
Te Mata (N=6)		**26.7**	0.03	20.7	11.3	**0.15**	8.6	29.9	63.4
Minimum		7.3	0.02	16.3	9.7	0.08	6.0	8.15	54.4
Maximum		106	0.41	30.8	31.8	0.76	9.2	35.6	149
Average		26.3	0.15	23.2	16.0	0.26	8.3	26.2	92.0
Standard deviation		25.5	0.13	3.5	6.4	0.19	0.8	7.2	28.6
95% confidence error		16.0	0.08	2.2	4.0	0.12	0.5	4.6	18.0

3.2 Comparison with sediment quality guidelines

3.2.1 Comparison to the ISQG-Low

To ascertain the potential ecological significance of the data collected from all the sites, the *average* concentrations for each trace element at each site were divided by sediment quality guidelines, the ANZECC (2000) ISQG-Low and ISQG-High (for more about which refer to Section 2.5). Results of the comparison of average concentrations with the ISQG-Low are provided in Table 3-2.

Table 3-2 Summary results expressed as a fraction of the lowest ANZECC (2000) sediment quality guideline (the ISQG-Low). Refer to Table 1-1 for the element name associated with each chemical symbol.

	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Waihou River mouth	0.37	0.07	0.39	0.15	**1.47**	0.44	0.53	0.46
Piako River mouth	0.46	0.15	0.30	0.16	**2.13**	0.40	0.59	0.52
Opani mudflat	0.38	0.11	0.31	0.15	**1.80**	0.40	0.58	0.49
Thames wharf & stormwater	0.73	0.07	0.31	0.18	**1.87**	0.39	0.56	0.45
Thames mudflats & harbour	0.71	0.06	0.31	0.21	**2.33**	0.40	0.41	0.37
Thames pipeline	**5.30**	0.27	0.30	0.26	**3.13**	0.41	0.71	0.75
Kuranui Bay	**1.81**	0.27	0.28	0.25	**5.07**	0.39	0.60	0.73
Tararu Stream	**1.23**	0.11	0.20	0.35	**1.20**	0.29	0.51	0.50
Thornton Bay	**1.15**	0.02	0.27	0.27	0.53	0.39	0.44	0.36
Te Puru	**1.22**	0.03	0.27	0.33	0.60	0.37	0.41	0.36
Waiomu Bay	**1.37**	0.07	0.33	0.49	0.60	0.42	0.71	0.41
Tapu	**1.06**	0.01	0.25	0.22	0.80	0.40	0.16	0.27
Te Mata	**1.34**	0.02	0.26	0.17	1.00	0.41	0.60	0.32
Average	1.32	0.10	0.29	0.25	1.73	0.39	0.52	0.46

Two elements exceeded the lowest sediment quality guideline value (the ANZECC (2000) ISQG-Low) in surface sediments at some locations (Tables 3-1 and 3-2):

- Average arsenic concentrations in sediments exceeded the ISQG-Low at eight (62%) of the thirteen sites. Arsenic averaged 1.32 times the ISQG-Low (20 mg/kg) and 38% of the ISQG-High (70 mg/kg).

- Average mercury concentrations in sediments also exceeded the ISQG-Low at eight (62%) of the thirteen sites. Mercury averaged about 1.7 times the ISQG-Low (0.15 mg/kg) in surface samples (range 0.53 to 5.1 times). Mercury averaged about 26% of the ISQG-High.

These results put arsenic and mercury in the Firth of Thames sediments at a point where they may be starting to have adverse effects on some sediment-dwelling organisms, at some locations (Section 2.5).

Mercury exceeded guidelines at the southern sites and the four sites immediately north from Thames, but remained below guidelines at the five most northern sites. The highest concentrations were found at Kuranui Bay, and the nearby pipeline sampling site in northern Thames. The Kuranui Bay site is also atypical of the other sites sampled to depth, in that concentrations at depth were significantly greater than those at the surface. After this localised hotspot is excluded, the highest mercury concentrations are associated with the Thames mudflats and the Piako River mouth (Tables 3-1 and 3-2). Bioaccumulation of the mercury up the food chain is the main risk associated with elevated concentrations of mercury. The ANZECC (2000) guideline levels are not designed to protect against this type of risk, therefore compliance or non-compliance with the ANZECC (2000) trigger levels does not provide any information about potential risks to wildlife, or people consuming seafood. A discussion about potential sources of mercury appears in Section 3.6.5.

3.2.2 Comparison to the ISQG-High

Results of the comparison of average concentrations with the ISQG-High are provided in Table 3-3.

Table 3-3 Summary results expressed as a fraction of the upper ANZECC (2000) sediment quality guideline (the ISQG-High).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Waihou River mouth	0.10	0.01	0.08	0.04	0.22	0.18	0.12	0.22
Piako River mouth	0.13	0.02	0.07	0.04	0.32	0.16	0.13	0.25
Opani mudflat	0.11	0.02	0.07	0.04	0.27	0.16	0.13	0.24
Thames wharf & stormwater	0.21	0.01	0.07	0.04	0.28	0.16	0.13	0.22
Thames mudflats & harbour	0.20	0.01	0.07	0.05	0.35	0.16	0.09	0.18
Thames pipeline	**1.51**	0.04	0.06	0.06	0.47	0.17	0.16	0.36
Kuranui Bay	0.52	0.04	0.06	0.06	0.76	0.16	0.14	0.36
Tararu Stream	0.35	0.02	0.04	0.09	0.18	0.12	0.12	0.24
Thornton Bay	0.33	0.00	0.06	0.07	0.08	0.16	0.10	0.18
Te Puru	0.35	0.01	0.06	0.08	0.09	0.15	0.09	0.18
Waiomu Bay	0.39	0.01	0.07	0.12	0.09	0.17	0.16	0.20
Tapu	0.30	0.00	0.05	0.05	0.12	0.16	0.04	0.13
Te Mata	0.38	0.00	0.06	0.04	0.15	0.17	0.14	0.15
Average	0.38	0.01	0.06	0.06	0.26	0.16	0.12	0.22

Only one site was found to exceed the ISQG-High, on average, and this was for only one element (Table 3-3). This was for arsenic in the sample collected from the vicinity of the Thames pipeline.

- On closer examination it is evident that the high result for arsenic in this sample (125 mg/kg) is the result of a single result containing 433 mg/kg arsenic in one of the sub-samples (Appendix 2). This result is considered to be a sampling outlier because the sample was collected within an area of sediment containing an iron-pan layer which is known to accumulate arsenic. Therefore, although the 433 mg/kg is likely to be close to the true concentration of arsenic in this sample (it is not likely to be an *analytical* outlier), the result does not adequately represent the composition of the sediment in this location, but the arsenic concentration of an iron-pan sample, making it a *sampling* outlier.

When the Thames pipeline outlier is removed, no site is found to exceed the ISQG-High, on average, for any element (Tables 3-1 and 3-3).

3.2.3 Key findings

- Arsenic and mercury concentrations in the Firth of Thames coastal sediments are not extremely high, but are at a point where they may have adverse effects on some sediment-dwelling organisms at some locations.

- There is an apparent hotspot at Kuranui Bay and an adjacent site in northern Thames. A further assessment of this is provided in Section 3.5.4.

- Mercury and arsenic do not behave like one another. Excluding the Kuranui/northern Thames hotspot, the highest mercury concentrations are at the southern sites, where arsenic concentrations are lowest. By contrast, the highest arsenic concentrations are along the eastern coast.

3.3 Comparison between the Firth of Thames and other areas

3.3.1 Comparison to coastal sediments in Raglan Harbour

Trace element concentrations in the Firth of Thames sediments can be compared with what would be expected in clean Waikato soils, crustal abundances, and data for Raglan Harbour. The most relevant comparison is between samples from a previous Environment Waikato study of sediments from the Firth of Thames and Raglan harbour. In that survey, sediment samples (0-2 cm) had been collected in October 2003 as part of an ecological survey from five locations in Raglan Harbour (Ponganui Creek, Whatitirinui Island, Te Puna Point, Okete Bay and Haroto Bay), and five locations in the southern Firth of Thames (Kaiaua, Miranda, Thames, Kuranui Bay and Te Puru).

At each of the ten locations, five 2 m x 2 m squares had been sampled, and each of these consisted of 12 sub-samples. Composites from each of the ten locations were analysed for 33 chemical elements, organic contaminants, and a range of major variables. Full results are archived and summarised separately.[2] Results for the 33 trace elements, total organic carbon (TOC) and percent dry matter at the ten locations are provided in Appendix 6 of this report. Average concentrations of selected elements are presented in Table 3-4. In this table, five elements are identified as crustal indicators. This term is used to describe elements whose only significant source is likely to be the geological parent matrix of the sample.[3]

Comparison of the results for Raglan Harbour with those for the Firth of Thames and those for clean Waikato soils shows that:

- Concentrations of all elements in the Raglan sediments with the possible exception of lithium[4] are (analytically) equivalent to or below those expected for clean Waikato soils.[5]

- Comparison of means and medians between the two harbours shows very similar concentrations of elements that could be taken as crustal markers: aluminium, iron, lithium, chromium, and nickel.

These two factors suggest that Raglan sediments (0-2 cm) can be used as a control site to represent clean Firth of Thames sediments. Average concentrations found in 0-2 cm sediments from around each harbour, and relative enrichment ratios for the Firth of Thames (0-2 cm) sediments are shown in Table 3-4.

Relative to Raglan, the Firth's sediments appear to be enriched in mercury, lead, cadmium, copper, zinc and arsenic (in this order).[6]

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[2] Data set: Environment Waikato document 922343; summary of results as an Environmental Indicator: http://www.ew.govt.nz/enviroinfo/indicators/coasts/waterquality/co12a/report.htm

[3] The term 'crustal' reflects the fact that soils and sediments are produced through weathering of the earth's crust.

[4] Higher concentrations of lithium might be expected in coastal sediments than terrestrial soils due to the presence of elevated lithium in seawater.

[5] Average background concentrations of these elements in Waikato surface (0-10 cm) soils by pseudo-total strong acid extraction are currently estimated to be aluminium: 36,000 mg/kg; arsenic: 8 mg/kg; cadmium: 0.2 mg/kg; chromium: 15 mg/kg; copper: 25 mg/kg; iron: 24,000 mg/kg; lithium: 8 mg/kg; mercury: 0.16 mg/kg; nickel: 7 mg/kg, lead: 15 mg/kg, zinc: 67 mg/kg (based on up to 50 soils sampled from a range of soil types; some sites omitted for arsenic, copper and lead to account for contamination from horticultural sprays; cadmium estimate based on reserves and forest areas with limited phosphate fertiliser use).

[6] This finding that the Firth of Thames sediments are likely to be enriched in mercury, lead, cadmium, copper, zinc and arsenic should not be taken to imply that concentrations of these elements in Firth of Thames sediments are at unacceptably high levels for ecosystem health. Comparisons to ANZECC (2000) guideline values for the elements in sediments are provided in Section 3.2.

Table 3-4 Average concentrations of eleven elements in shallow surface (0-2 cm) sediments collected from Raglan Harbour and the Firth of Thames in earlier work, and comparison of averages between the two areas.

Element	Average concentration in 0-2 cm sediment samples		Ratio of means (Firth of Thames / Raglan)	Interpretation for Firth of Thames
	Firth of Thames	Raglan		
Aluminium	9300	10300	0.9	crustal indicator
Iron	24700	23100	1.1	crustal indicator
Chromium	14.9	14.4	1.0	crustal indicator
Nickel	6.23	8.06	0.8	crustal indicator
Lithium	14.3	13.5	1.1	crustal indicator
Arsenic	12.7	8.34	1.5	potential contaminant
Cadmium	0.087	0.024	3.6	potential contaminant
Copper	12.5	6.76	1.9	potential contaminant
Mercury	0.289	0.026	11.1	potential contaminant
Lead	24.3	6.09	4.0	potential contaminant
Zinc	80.5	47.7	1.7	potential contaminant

Results from the earlier shallow (0-2 cm) sampling are in general keeping with the results from this survey (surface grab or 0-10 cm sampling), which indicate varying degrees of enrichment in Firth of Thames sediments for the same six elements. As noted earlier (Section 3.2), in this work mercury and arsenic are the two elements most likely to exceed sediment quality guidelines at some sites. Based on 0-2 cm sediments, average Firth sediments contain about 4.4 mg/kg more arsenic and 0.26 mg/kg more mercury than the Raglan Harbour sediments that were sampled to the same depth (Table 3-4).

In Section 3.5.4, evidence is presented that the Kuranui Bay site in the Firth of Thames is an area of specific localised contamination by some elements, above that occurring at other sites. A case might be made that this site should be excluded from the comparison between the Firth of Thames and Raglan sediments, on the basis that it is a more localised hotspot. Removal of this site from the 0-2 cm sediment data set has no effect on which elements are identified as crustal indicators, but does have an impact on the relative enrichments of mercury, cadmium and zinc in Firth of Thames sediments relative to those of Raglan. Mercury drops from an average enrichment factor of 11 to 7; cadmium drops from 4 to 1.5, and zinc drops from 1.7 to 1.2. Enrichment ratios for the other elements are not substantially altered.

In absolute mass terms, the most enriched element is zinc. Including the Kuranui Bay sample, the shallow Firth of Thames samples also contain (on average) 33 mg/kg more zinc than Raglan sediments. Excluding it, the Firth sediments still contain 9.2 mg/kg more zinc than those of Raglan Harbour.

The relative enrichment results determined in this work are in good agreement with previous estimates of the effect of Polynesian and European land use on lead, zinc, copper and arsenic concentrations in Firth of Thames sediments, which are reviewed in Section 1.2. For example, based on sediment cores the DSIR estimated that arsenic was elevated 1.2–2 times in more recent sediments compared to old sediments in the Firth of Thames samples (Hume and Dahm, 1991). This compares well with an average enrichment of 1.5 times compared with the uncontaminated sediments of Raglan Harbour (Table 3-4).

Overall, comparison between harbours provides evidence that arsenic, cadmium, copper, mercury, lead and zinc are enriched in coastal sediments of the Firth of

Thames. This result is in agreement with earlier work carried out on four of these elements by the DSIR (Section 1.2). The results for mercury and cadmium are new.

- Relative to its expected background concentration, the most highly enriched of the eight elements measured in this study is mercury. On average, mercury appears to be present in Firth of Thames shallow (0-2 cm) surface sediments at approximately 7-11 times its usual concentration, with the difference depending on whether or not the hotspot associated with Kuranui Bay is excluded.

- In absolute mass terms, the most highly enriched element is zinc. Firth of Thames sediments contain between 9-33 mg/kg more zinc than would otherwise be expected, with the difference depending on whether or not the sample from Kuranui Bay is excluded.

3.3.2 Comparison of this survey’s data with historical data

In samples collected in the URS survey (Table 3-1), lead concentrations ranged from 8.1 mg/kg (Tapu) to 65.3 mg/kg (Waiomu Bay), with typical values being around 25 mg/kg, and an overall average of 26 mg/kg. These values are higher than pre-European concentrations reported in the DSIR study, again indicating some lead enrichment. The low concentrations of lead found in Tapu were in a similar concentration range as those found in pre-settlement times. Tapu had the lowest sediment concentrations of all metals except for arsenic and mercury (Table 3-1 and Appendix 2).

Arsenic concentrations ranged from 8.7 mg/kg around the Thames wharf to 433 mg/kg near the stormwater pipe outfall, with the latter result assumed to be a non-representative sampling outlier (Section 3.2.2). The typical arsenic concentration was around 23 mg/kg (overall average 26 mg/kg), which is elevated above natural concentrations (typically 6-8 mg/kg). Higher concentrations still were found at Kuranui Bay and near the Thames pipeline.

Cadmium concentrations were elevated around Kuranui Bay and the Thames pipeline, but they also appeared slightly enriched around the Piako River Mouth.

Copper concentrations ranged between 7.6 mg/kg (Waihou River Mouth) to 41.6 mg/kg Waiomu Bay, with typical levels of around 16 mg/kg being found at most sites. For copper, many sites fell within the background concentration range reported in the DSIR study. However both Waiomu Bay and Tararu Stream showed signs of enrichment of copper compared with pre-settlement samples and other samples collected during this study.

Mercury concentrations varied over the study area from 0.05 mg/kg at Te Puru up to 1.58 mg/kg within Thames Harbour. Typically, mercury concentrations tended to be approximately 0.1 mg/kg at the northern sites, but elevated concentrations were observed around the Thames Harbour, Waihou and Piako River mouths, Thames sewer outfall and Kuranui Bay. Mercury concentrations previously reported for sediments from Miranda and Kaiaua were approximately 0.05 mg/kg, which probably represents the pre-European background concentration.

Zinc concentrations ranged from 51.5 mg/kg (at Tapu) to 206 mg/kg (Kuranui Bay), although typically the concentration of zinc within the Firth of Thames is between 70-80 mg/kg. These concentrations are similar to those found in the DSIR report, where the additional zinc was attributed to widespread anthropogenic enrichment (Hume and Dahm, 1991). The zinc concentration at Miranda and Kaiaua was between 37-43 mg/kg, which indicate about 1.5-2 times enrichment of zinc in sediments at most sites.

Nickel and chromium concentrations were very similar between sites. These elements are not significant contaminants in acid mine drainage discharges from the Tui Mine

Tailings (Rumsby, 1996) and are unlikely to be a significant component of discharges from historic mining operations in this section of the Coromandel Peninsula.

3.3.3 Key findings

Arsenic, cadmium, copper, mercury, lead and zinc are enriched in coastal sediments of the Firth of Thames, relative to concentrations present before Polynesian and European colonisation, and relative to reference concentrations in sediments from Raglan Harbour.

Relative to its expected background concentration, the most highly enriched element is mercury, which may be present at approximately seven times its usual concentration (excluding the anomaly at Kuranui Bay). In absolute mass terms, the most highly enriched element is zinc, with Firth of Thames sediments containing about 10 mg/kg more zinc than would otherwise be expected.

3.4 Small scale variability

3.4.1 Assessment

Five samples were collected within a one metre radius of each other on the Thames Harbour mudflats, to evaluate small-scale variations present in the sediments. Results are provided in Table 3-5.

Table 3-5 Small scale variability in chemical composition (mg/kg). (%RSD stands for per cent relative standard deviation, also known as the Coefficient of Variation).

Sample No	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SDB576A	14.7	0.05	28	16.6	0.2	9	16	70.2
SDB576B	16.3	0.04	21.7	14.6	0.17	7.2	12.5	52.5
SDB576C	17.8	0.04	30.7	17	1.58	8.8	15.3	64.3
SDB576D	15.8	0.04	24.4	16.1	0.2	8.5	13.2	55.8
SDB576E	12.7	0.07	30.3	16	0.22	9.4	17.5	72.9
Average	**15.5**	**0.05**	**27.0**	**16.1**	**0.5**	**8.6**	**14.9**	**63.1**
Standard deviation	1.9	0.01	3.9	0.9	0.6	0.8	2.0	8.9
Mean	15.5	0.05	27.0	16.1	0.5	8.6	14.9	63.1
95% confidence error	2.4	0.02	4.8	1.1	0.77	1.0	2.5	11.0
%RSD	12.3	20.8	14.4	5.6	127	9.3	13.4	14.1

These results show reasonable variation in the per cent relative standard deviations (%RSDs) for both mercury (127%) and cadmium (20%).

- In the case of cadmium, this is due to the fact that the measured concentrations are reasonably close to instrumental detection limits (0.01 mg/kg). Under these conditions the signal-to-noise ratio is naturally higher and results in a high %RSD as a result of measurement uncertainty.

- In the case of mercury, some variability may also be due to this cause, but in addition, sample SDB576C has an abnormally high concentration relative to the other samples. This is probably due to a grain of cinnabar (HgS) or another mineral being present in the sub-sample that was tested (typically less than 0.5 grams of the total), a well-known phenomenon known as a ‘nugget effect.’ If sample SDB576C was removed from the dataset the %RSD for mercury would be 10.4%.

The variability in the chemical composition observed for the other metals was between 5.6% for copper to 14.4% for chromium, which would be considered normal.

Overall, the results indicate that samples are reasonably likely to be representative of each sampling location, but finding an occasional high value caused by presence of a mineral grain (a nugget effect) would not be unusual. The results give tentative evidence for presence of grains of mercury-rich minerals in sediments of some areas of the Firth of Thames.

3.4.2 Key finding

Samples appear to be representative of sampled areas. There is some tentative evidence for the presence of grains of mercury-rich minerals (*e.g.* cinnabar, HgS) in sediments of some areas of in the Firth of Thames.

3.5 Comparisons between sites in the Firth of Thames

3.5.1 Statistical analysis and data normalisation

Data collected at each site underwent statistical analysis to determine means, medians, standard deviations, confidence intervals and normality. Student's t-tests were used to compare sites with each other. A range of comparisons were made both with and without grain size normalisation, and elemental normalisation.

Grain size-normalisation requires separation of the sediment into two or more size fractions prior to analysis (de Groot et al., 1982; Salomons and Förstner, 1980). Separation techniques have long been used in geochemical exploration to enhance the signal from ore deposits and are becoming more widespread in environmental investigations. These techniques generally involve the separation of fractions less than 62.5 μm by sieving and settling methods. Ackermann et al. (1980) and Louma (1990) reviewed several methods for separation of fine sediment and recommended a 62.5 μm cutoff size. Many studies have been carried out using this sediment fraction, and data are comparable if the extraction techniques and analytical methods are similar (e.g. Birch and Taylor 1999). Separation at 62.5 μm and 2 mm is common (Klamer, 1990) and represents the grain size and hydrodynamic divisions of mud, sand and gravel, respectively, but other mesh sizes are also used. NOAA (1988) simply divided total sediment concentrations by the proportion of the fine (<64 μm) fraction in sediment for samples with >20% mud. In this study, post-analysis correction was conducted on the <63 μm in selected sediment samples. Normalised data is presented in Appendix 4.

Elemental normalisation methods assume that contaminant concentrations vary in direct proportion to grain size (*i.e.* are a grain size proxy). Elemental normalisation of trace metals requires total extraction of the whole sample and correction to a 'conservative' element. Aluminium and iron are widely used as normalising elements (e.g. Din, 1992), but should not be used to normalise contaminant concentrations in laterites and where the abundance of alumina is high, e.g. in tropical areas (Loring, 1991; Loring and Rantala, 1992). Normalisation elements including caesium, lithium, silicon and scandium, and total organic carbon, have also been used to overcome textural variability in contaminant studies of sediments (Loring and Rantala, 1992). In this project iron, aluminium and lithium were chosen for normalising the data due to ease of analysis, and the fact that the relative abundance of these elements was sufficiently high to avoid problems caused by measuring near detection limits.

Comparisons that were made between sites and samples in the following sections were carried out using both the original data (Appendices 2 and 5) and normalised data (Appendix 4).

3.5.2 Local historical mining sites versus control sites

Three sites selected on the basis of local mining in their catchments were Tararu, Waiomu, and Tapu. The three control sites which are not known to have had local mining in their catchments were Thornton Bay, Te Puru and Te Mata (Section 2.2.2). Data from the three control sites was consistent enough to be pooled in a single control data set for use in student's t-tests. Results for Tararu, Waiomu, and Tapu were compared with this pooled data from the control sites. Results are shown in Table 3-6.

Table 3-6 Results of Student's t-tests between Tararu, Waiomu, and Tapu and pooled data from the three mining control sites. Mean values are in mg/kg (dry weight), and have not been normalised to any other variable. Ratios of means are unitless.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Mean of control sites (Te Puru, Thornton and Te Mata) (N=20)	24.7	0.040	21.3	17.3	0.105	8.16	23.8	69.7
Mean at Tapu (N=6)	21.2	0.022	19.55	13.98	0.123	8.333	8.147	54.38
Pooled t-test: concentration significantly higher than control site	No	No	No	No	No	No	No	No
Probability value (p)	0.9958	0.8942	0.9444	0.9525	0.1727	0.2937	1.0000	1.0000
Ratio of means where significant	-	-	-	-	-	-	-	-
Mean at Waiomu (N=8)	27.3	0.089	26.0	31.8	0.079	8.80	35.3	82.3
Pooled t-test: concentration significantly higher than control site	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
Probability value (p)	0.0334	0.0022	0.0004	0.0001	0.9451	0.0297	0.0014	0.0001
Ratio of means where significant	1.1	2.2	1.2	1.8	-	1.1	1.5	1.2
Mean at Tararu (N=7)	24.5	0.166	16.3	23.0	0.179	6.04	25.6	99.1
Pooled t-test: concentration significantly higher than control site	No	Yes	No	Yes	Yes	No	No	Yes
Probability value (p)	0.55	0.0001	0.99	0.0056	0.0012	1.0	0.16	0.0001
Ratio of means where significant		4.2	-	1.3	1.7	-	-	1.4

Interpretive note

It should be borne in mind that this comparison relates to effects that may have been caused by small mine operations in a specific sub-catchment, which are substantive enough to stand out above more general trace element enrichments in Firth of Thames sediments. At the more general level, the control sites themselves show evidence of trace element enrichment. For example, there is consistent arsenic enrichment at all three of the control sites, which have an average arsenic concentration in surface sediments of 24.7 mg/kg (dry weight).

Tapu

Tapu is the northernmost of the three sites selected on the basis of historical mining activity. No statistically significant difference was found in trace element concentrations between Tapu and the control sites. Results for Tapu were indistinguishable from those of the control sites, including the presence of generally elevated arsenic (Table 3-6). In the case of Tapu, there is no specific evidence for a localised effect from historic mining in the Tapu catchment which is over and above other enrichments in the Firth of Thames sediments.

Waiomu Bay

Moving down the coast, Waiomu Bay was the middle of the three mining areas selected. Anecdotal evidence has indicated that iron staining occurs periodically on the foreshore which indicates that metals may still be discharged from the old Monowai mine and precipitate on the foreshore. By contrast with Tapu, and by comparison with the control sites, sediments of Waiomu Bay are significantly enriched with seven of the eight trace elements tested – all but mercury.

However, although statistically significant, in most cases these enrichments are not substantial. Only one of the elements exceeds its expected concentration by a factor of more than two, and this is cadmium (Table 3-6). Adding to this picture, contaminant depth profiles taken at Waiomu Bay show no significant difference in trace element concentrations with depth down to 30 cm (Appendix 2). In this regard, sediments of Waiomu Bay are no different from those of the control site of Te Puru (Appendix 2). This lack of a change with depth, coupled with the fact that the local enrichments (relative to control sites) are only marginal or modest, suggests that the results from Waiomu Bay may reflect slight differences in sediment composition this area, rather than being caused by run-off from mining in the catchment.

Tararu

The southernmost of the three areas was Tararu. Relative to controls, this site shows statistically significant enrichment in half of the elements: cadmium, mercury, zinc and copper. However, once again, the magnitude of enrichment is modest with the exception of cadmium. The apparent enrichment of mercury is also caused by one moderately elevated result, which could be treated as a data outlier (Appendix 2). Depth samples were not collected at Tararu. The results for this area do not provide any convincing evidence for a more than minor localised effect from past mining.

Benefits of normalisation

It was found that normalisation of data for any of the sites did not assist in interpretations of potential sources, but tended only to confuse matters. In the case of Waiomu Bay, normalising the data against lithium suggested that arsenic, copper, lead and zinc may be moderately enriched. Normalising using iron concentrations suggested that only arsenic, copper and lead were enriched. Normalising using aluminium suggested that most of the elements were enriched at this site. Elemental normalisation did not indicate that any of the other sites have undergone any geochemical enrichment.

Effect of localised mining sites - overall picture

Overall, the results suggest that either local mining operations may not have contributed substantially to trace elements in the nearest Firth of Thames sediments, or that any local impact was lost against more significant contributions from other sources, which also impacted the mining control sites.

Data gathered in this work, and the former DSIR study, both indicate that trace element concentrations in coastal sediments of the lower Firth of Thames sediments are generally elevated above their natural levels (Section 3.3). Of the sources discussed in Section 1.1, those most likely to have caused this general elevation are enhanced weathering and erosion following land clearance, and the impact of historic mining operations which involved disposal of large volumes of tailings directly to the Ohinemuri River. An explanation of the lack of any evidence of metal enrichment from historical mining (except perhaps at Waiomu Bay) may be due to the relatively low volumes of metals being discharged from the mining point sources, relative to contributions from these other sources. This would lead to the mining discharges being diluted by much larger volumes of sediment from elsewhere within the catchments which are also elevated in arsenic and copper.

The results of this work, with little evidence for significant localised impacts from former mining sites in the Coromandel Peninsula itself, are in agreement with the work of Craw and Chappell (2000). These authors examined metal redistribution in historic Coromandel mine wastes and found that the decomposition of sulphides in such wastes is slow, resulting only in millimetre-scale alteration zones over one hundred years. The authors concluded that the combination of slow decomposition, localised incorporation of metals into iron oxyhydroxide cements, low permeability, and almost constant water saturation in a moist climate ensures that metal discharges into the environment from wastes in the Coromandel area are generally at low levels.

Cadmium and zinc

The only results which stand out in this comparison are apparent trends for both cadmium and zinc. Relative enrichment factors for these two elements (compared with the mining control sites) increase as the sampling location moves further south. The three control sites cover a reasonable geographical spread of the area north of Thames, and their pooled results can be taken to represent averages of this area. Cadmium and zinc appear to become more enriched the closer the samples are collected from the Waihou/Piako river mouths (Table 3-7 and Figure 3-1). In this comparison, data for Kuranui Bay and Thames is excluded because these sites show strong evidence of localised trace element enrichments, which may be associated with fill and reclamation (Section 3.5.4).[7]

Table 3-7 **Apparent enrichment of cadmium and zinc in sediments relative to the three mining control sites moving from south to north.** Numbers are enrichment ratios, representing the average concentration in sediments at a given site divided by the pooled average for the mining control sites.

Location	Enrichment ratios	
	Cd	Zn
Waihou and Piako river mouths and Opani mudflat	4.5	1.42
Tararu	4.2	1.4
Waiomu	2.2	1.2
Tapu	0.5	0.8

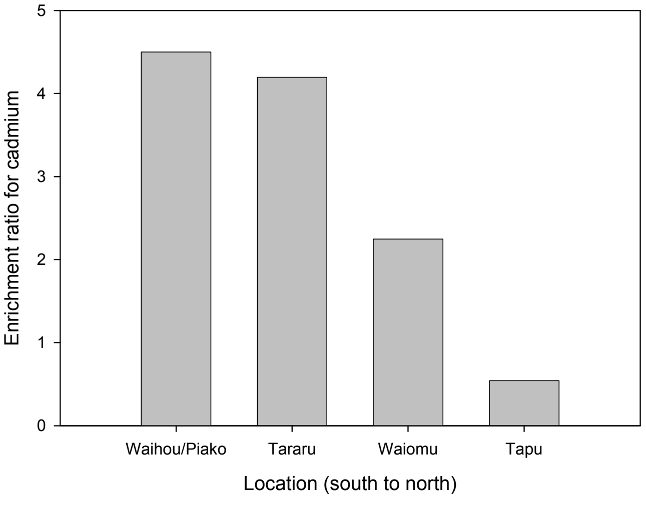

Figure 3-1 **Apparent enrichment of cadmium relative to the three mining control sites moving from south to north.**

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[7] The enrichment factors for cadmium at Kuranui Bay and the Thames stormwater pipeline are 10.3 and 10.0 respectively, whereas the Thames mudflats, deep harbour, wharf and near-shore stormwater sites (combined) show an enrichment factor of 2.2.

This trend is tentative evidence of long-range transport of these two elements dominating over local sources. Spatial trends in element concentrations in the Firth of Thames sediments are examined in further detail in Section 3.6.

3.5.3 Seaward versus landward

Trace element concentrations in samples collected from nearest the Firth of Thames water (seaward) were compared with those from samples collected closer to the land (landward) (see Figures 2-3 and 2-4 for an indication of each class of sample).

Data was compared on a site-by-site basis, and by grouping data into all seaward sites versus all landward sites. When grouping data, this type of comparison requires a paired t-test rather than data pooling, to ensure that real differences are not lost in the noise caused by changes in concentrations between sampling sites. There were twenty data pairs for each element in the paired t-test.

On a site-by-site basis, and with or without normalisation, no statistical difference (to $p=0.05$) was found between seaward and landward samples. Using grouped data, marginal differences emerged for copper ($p<0.048$) and arsenic ($p<0.062$). The result for arsenic is not significant at the conventional 95% cut-off, but is significant at a 93.8% level of confidence.

In the case of both elements, the grouped data suggests that concentrations are higher in landward samples than in seaward samples. Arsenic concentrations are on average 23% higher in the landward samples (at a 94% confidence level), and copper is about 8% higher (at a 95% confidence level). These results provide tentative evidence that some copper and arsenic in the Firth of Thames may be sourced from the land through weathering, erosion and surface run-off (Section 1.1).

3.5.4 Urban areas versus control sites

Several samples were collected from the vicinity of urban sources in the Thames area: adjacent to the Thames pipeline, stormwater discharge, wharf and Kuranui Bay. Samples were also collected from Thames mudflats and inner harbour.

Concentrations of trace elements measured in surface sediments in these areas were compared with those measured in all the other coastal sites: Te Mata, Tapu, Waiomu Bay, Te Puru, Thornton, and Tararu. Data from non-coastal sites were excluded from the comparison set. Excluded were the Waihou and Piako River mouth samples and the Opani mudflat samples. Data from deeper than 10 cm was also excluded.

Results of pooled Student's t-tests are shown in Table 3-8.

Results for sites in the Thames area were also compared with those from the mining control sites (Tararu, Waiomu, and Tapu (Section 3.5.2). Student's t-tests between the Thames and Kuranui samples and the mining control samples gave very similar results in terms of which elements were significantly enriched and are provided in Appendix 7.

Relative to other coastal sites, samples collected from the Thames area were significantly enriched in mercury (Table 3-8). Mercury concentrations are approximately three to six times higher than their expected values at Kuranui Bay (six times), samples collected from the vicinity of the stormwater discharge pipeline (four times), and other areas including the Thames mudflats (three times) (Table 3-8).

Mercury concentrations often exceed sediment quality guidelines for mercury (Sections 2.5 and 3.2). The Kuranui Bay and Thames stormwater pipeline samples are also substantially enriched in cadmium (by 5.7 – 5.9 times relative to reference sites), and significantly elevated in zinc (by about two times). In contrast, on average, sediment samples collected from the group of sites including the Thames mudflats, deep harbour, wharf and (near-shore) stormwater (N=11) do not show significant elevation of either cadmium or zinc (as a group).

Table 3-8 Results of Student's t-tests between Thames and Kuranui Bay sites and other coastal sites. Mean values are in mg/kg (dry weight), and have not been normalised to any other variable. Ratios of means are unitless.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Mean of reference sites (N=41)	24.6	0.069	21.1	20.6	0.119	7.95	24.0	74.9
Mean at Kuranui Bay (N=9)	36.1	0.407	22.7	16.4	0.763	8.10	29.9	146
Pooled t-test: concentration significantly higher than reference sites	Yes	Yes	No	No	Yes	No	No	Yes
Probability value (p)	0.02	0.0019	0.58	0.98	0.0001	0.82	0.18	0.0001
Ratio of means where significant	1.5	5.9			6.4			1.9
Mean at Thames stormwater pipeline (N=5, except N=4 for arsenic due to one outlier being removed)	24.4	0.396	24.0	16.9	0.470	8.74	35.6	149
Pooled t-test: concentration significantly higher than reference sites	No	Yes	No	No	Yes	No	Yes	Yes
Probability value (p)	0.55	0.0001	0.08	0.84	0.0001	0.08	0.01	0.0001
Ratio of means where significant		5.7			4.0		1.5	2.0
Mean at Thames mudflats, deep harbour, wharf and stormwater sites (N=11)	14.2	0.084	24.8	14.0	0.355	8.48	19.9	72.4
Pooled t-test: concentration significantly higher than reference sites	No	No	Yes	No	Yes	No	No	No
Probability value (p)	1.0	0.25	0.004	0.99	0.0003	0.08	0.89	0.68
Ratio of means where significant			1.2		3.0			

Trace element enrichments in the area of the Thames stormwater discharge pipeline and Kuranui Bay are very similar (Table 3.8), implying that a common source is responsible for the locally elevated mercury, cadmium, and zinc. Of these, mercury and cadmium are the most enriched.

A possible natural source of mercury is the cinnabar (mercuric sulphide) deposit situated in the Kauaeranga Valley; Thames Wharf is located on the Kauaeranga River. The Kauaeranga Valley was mined for cinnabar between 1899 and approximately 1906 (Section 2.2.2). However, based on subsequent review of historic information from this area, the most likely source is mine tailings and other municipal or industrial fill that has been deposited in the immediate vicinity as part of historic land reclamation. This is because the area between the two anomalous sampling points (Kuranui Bay and the Thames pipeline) is a large area of reclaimed land known as the Moanataiari reclamation. The Moanataiari subdivision of the town of Thames and the Thames landfill both sit on this reclaimed land, as shown in Figure 3-2.

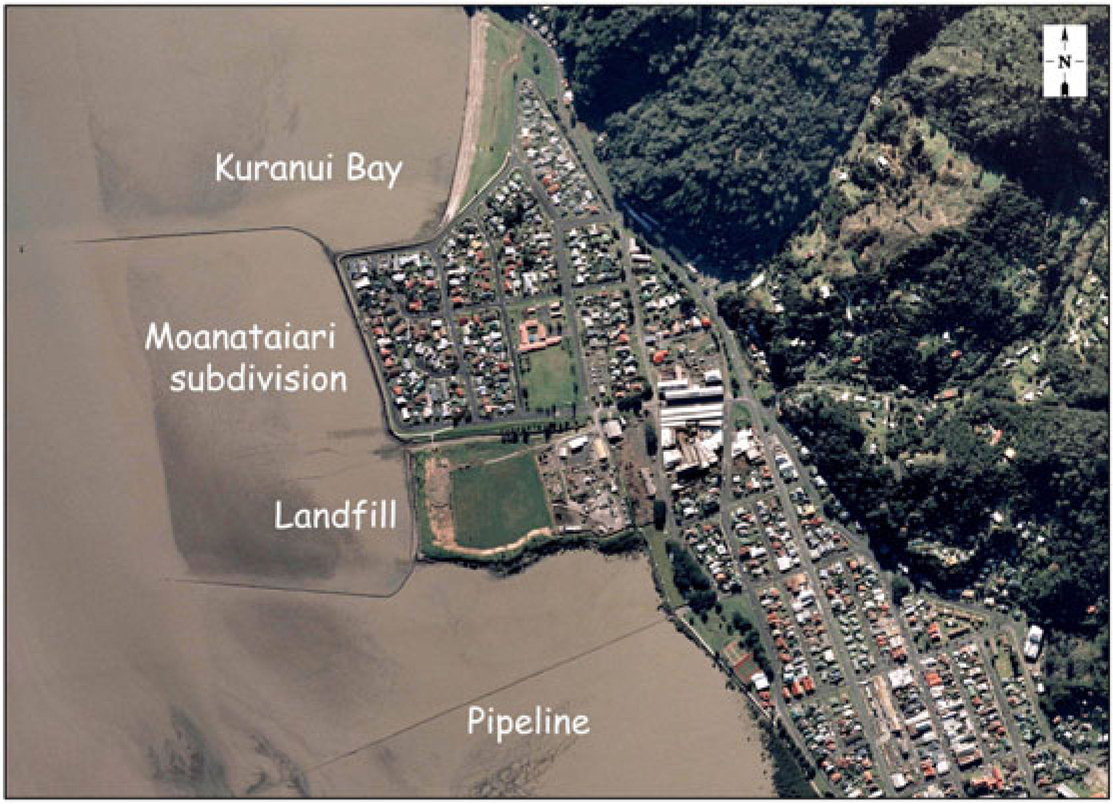

Figure 3-2 **Aerial photograph of the Moanataiari reclamation dated 24 June 2006.** Imagery sourced from Terralink International Ltd (TIL) 2006 and is the property of TIL and the Waikato Regional Aerial Photography Service (WRAPS) 2006. Copyright Reserved.

The following summary of the reclamation appears in a report prepared for the Ministry for the Environment (2001) in relation to the effect of climate change on coastal areas:

> *"The Moanataiari reclamation was formed progressively from the turn of the century, initially by dumping mine tailings and mullock[8] over intertidal flats. Dumping dredgings from the port further reclaimed the area, which was then capped with a raft of weathered rock and clay from the hills under more controlled conditions in the mid to late 1960s. Housing construction was generally underway in the 1970s. The end result was a 'little Holland' extending 500 m from the line of the coast into the sea."*

In addition to mine tailings, the area of the hot-spot is near a significant historic foundry, and a coastal landfill. It is therefore likely that this reclaimed area also received foundry slag or other forms of industrial fill during the long history of Thames.[9]

There are two possibilities about the source of local mercury contamination. Deeper sediment samples collected from this area may represent the physical tail of the reclamation's fill material (such as old mine tailings). This tail may extend some distance beyond the present-day seawall. Secondly, sediments in this immediate area of the Firth of Thames are likely to be receiving leachate from the base of the Moanataiari reclamation, as rainwater and groundwater enter and flow through it.

Three additional threads of evidence are available which either support the case that this general area is a localised hotspot, or suggest that the fill material is having an impact on concentrations of some trace elements in nearby sediments of the Firth.

1. *Vertical core sample from Kuranui Bay, collected as part of this work*. Results from analysis of sediments from different depths in this core reveals a strong increase in

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[8] Mullock is defined as rubbish, refuse or dirt.

[9] Under the umbrella of current legislation, foundry slag is deposited in an authorised landfill.

concentrations of arsenic, cadmium, mercury and zinc with depth (Appendix 2). The deepest sample (25 -30 cm) was found to contain 149 mg/kg arsenic, 2.07 mg/kg cadmium, 5.14 mg/kg mercury and 469 mg/kg zinc (Appendix 2). This contrasts with the results for vertical core samples from Waiomu Bay and Te Puru. Such a relationship, where the oldest sediments contain the highest trace element concentrations, suggests that the contamination at Kuranui Bay is primarily a result of historic filling and reclamation. It is not yet clear whether the highest result at depth may represent the depth where leachate in groundwater has the strongest impact on sediment quality, or represents the fill material itself. It might be expected that the fill will extend beyond the base of the seawall (Figure 3.2).

2. *Results from Environment Waikato's 2003 shallow sediment sampling*. As discussed in Section 3.3.1, shallow (0-2 cm) sediment samples have previously been collected from five locations in the Firth of Thames and analysed for 33 elements (results are provided in Appendix 6). One of these locations was Kuranui Bay. A statistical comparison can be made between the results from Kuranui Bay composite with those from the other four sampling sites in the same data set. Concentrations of 12 of the 33 elements are statistically higher in the Kuranui Bay sample (Table 3-9). Of the elements which are present at significantly greater concentrations in the Kuranui Bay sample, concentrations of cadmium, silver, mercury, zinc, manganese and antimony are substantially enriched, by factors of three or more. In addition to these, arsenic is probably enriched in the Kuranui Bay sample (at confidence level of just under 95%), by a factor of two. For the elements in common with those assayed in the URS sampling round (2005), relative enrichments are consistent (compare Table 3-8 with Table 3-9) despite the different sampling depths (0-2 cm in the 2003 samples and 0-10 cm in the 2005 samples). Cadmium and mercury are the most enriched elements of those in common between the two surveys.

Table 3-9 Trace element concentrations in shallow (0-2 cm) sediment samples from Kuranui Bay which are statistically higher than those at four other sites in the Firth of Thames at a 95% confidence level.

Element	Measured concentrations (mg/kg dry weight)				Enrichment ratio
	Four non-Kuranui Bay sites			Kuranui Bay	
	Mean	Confidence interval		(Composite result)	
		Lower	Upper		
Cadmium	0.035	0.010	0.060	0.34	9.7
Silver	0.067	0.030	0.100	0.30	4.5
Mercury	0.198	0	0.520	0.84	4.2
Zinc	53.1	28.9	77.3	199	3.7
Manganese	474	127	820	1480	3.1
Antimony	0.26	0	0.64	0.81	3.1
Molybdenum	0.47	0	1.02	1.22	2.6
Lead	19.7	7.3	32.2	42.9	2.2
Caesium	0.74	0.48	0.99	1.2	1.6
Lithium	12.4	7.5	17.3	18.7	1.5
Tin	0.40	0.27	0.53	0.6	1.5
Boron	10.4	8.1	12.7	13.0	1.3

3. *Sediment sampling carried out in the same area in 2004, as part of a resource consent for closure of the Thames Landfill* (Kingett Mitchell Ltd., 2004). In this work, sediment samples were collected from 16 locations around the coast of the Moanataiari reclamation (Figure 3-2) to a depth of 14 cm. Of these samples, three were in Kuranui Bay, four were seaward of the Thames landfill (Figure 3-2), six were south of the landfill, and three were southwest of the landfill. In this case there is no specific control group of samples also collected to a depth of 14 cm elsewhere in the Firth of Thames from which a statistical comparison might be made.

However, results for mercury show evidence of substantial local enrichment, and can be directly compared with sediment quality guidelines (Section 2.5). This comparison is made in Table 3-10.

Table 3-10 Concentrations of mercury in 0-14 cm sediment samples collected from the vicinity of the Moanataiari reclamation, and comparison to ANZECC (2000) guideline values for sediment quality. Data source: Kingett Mitchell Ltd, 2004.

	Location			
	Kuranui Bay	Seaward of landfill	South of landfill	Southwest of landfill
Mercury concentrations in sediment samples (mg/kg dry weight)	2.67; 2.55; 2.37	1.47; 1.29; 1.91; 1.73	0.59; 0.35; 0.86; 0.60; 1.31; 0.6	1.02; 0.82; 2.99
Average mercury concentration (mg/kg) & proportion of the ANZECC ISQG-High of 1 mg/kg (a ratio)	2.53	1.56	0.60	1.61
Factor by which average mercury concentration exceeds the ANZECC ISQG-Low of 0.15 mg/kg	16.9	10.4	4.0	10.7

This data shows that samples collected from the vicinity of the reclamation by Kingett Mitchell in 2004 were strongly enriched with mercury, to a point where sediment in this area would meet a reasonable test of the Resource Management Act and Waikato Regional Plan definitions of 'contaminated land,' on the basis of its mercury content.

Risks associated with this contamination would be primarily to organisms living in the marine sediment. Currently there is no evidence of presence of risks to residents of the Moanataiari subdivision, due to the likelihood of a deep capping layer of clean overburden having been placed over the older mine tailings or other fill layers. As part of a separate project on contaminants in urban soils, a single composite soil sample (consisting of 16 x 0-10 cm subsamples) was collected from Moanataiari school in January 2007, and was found to contain only normal background concentrations of arsenic, cadmium, copper, chromium, lead, mercury, nickel, and zinc.

Further work is needed to determine the contaminant loadings and environmental significance of fill that was used in the Moanataiari reclamation on sediment quality nearby in the Firth of Thames, and quantify its significance in relation to other sources of contaminants.

3.5.5 Agriculturally proximate versus control sites

Sediment samples were collected around the mouth of the Waihou and Piako Rivers to determine if agricultural discharges were having an adverse impact on sediment quality in the lower Firth of Thames. For this analysis, the data was divided into six composite samples representing areas that might be most influenced by agricultural sources – these were the Waihou and Piako River mouths and the Opani mudflat between them – and 52 other composites for comparison.

Samples for the Thames stormwater pipeline site and Kuranui Bay were removed from the comparison data set, because these sites show evidence of atypical localised enrichment (Section 3.5.4). Samples deeper than 10 cm were also excluded from the comparison set, and four non-detections were set equal to half their detection limits. Results of Student's t-tests are shown in Table 3-11.

Table 3-11 Results of Student's t-tests between sites closest to agricultural sources and other areas. Mean values are in mg/kg (dry weight), and have not been normalised to any other variable.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Average of sites closest to agricultural sources	8.27	0.178	26.6	10.1	0.275	8.70	28.4	98.8
Average of other sites	22.4	0.072	21.9	19.2	0.166	8.06	23.2	74.4
Pooled t-test for agricultural > other:								
Agricultural significantly greater	No	Yes	Yes	No	No	No	No	Yes
Probability value of pooled t-test; p=	1.0	0.0002	0.0059	1.00	0.11	0.09	0.11	0.0006
Ratio of averages (agricultural/other) where difference is significant		2.5	1.2					1.3

Pooled Student's t-tests indicate highly significant differences for cadmium, zinc and chromium, with sediments of sites closest to agricultural sources containing the highest concentrations of these three elements (Table 3-11). The fact that the same sites show no statistical elevation of arsenic, copper, mercury, nickel and lead (Table 3-6) suggests that the additional cadmium, zinc and chromium in sediments at these locations is less likely to be caused by the ongoing influence of historic mining discharges than the modern influence of agricultural sources. This idea is supported by the fact that many agricultural soils receive high annual loadings of both cadmium (from superphosphate fertiliser) and zinc (from facial eczema remedies), but overall, do not receive comparably high loadings of arsenic, copper, mercury, nickel or lead (Section 1.1.3).

- Relative to its background concentrations, the most enriched element of these three is cadmium, concentrations of which are 2.5 times higher at those sites closest to agricultural sources than other sites. In terms of total loadings, the most enriched is zinc, with the agriculturally influenced sediments containing 24.4 mg/kg more zinc than the other areas.

This statistical analysis suggests that agricultural activities may also contribute chromium to receiving environments. Additional loadings and concentrations of chromium are less substantial than those of cadmium or zinc (Table 3-11), and the source of additional chromium is not known. However, agricultural sources are not excluded, because the data of Franklin et al. (2005) indicates that phosphate fertiliser and certain N-P-K fertiliser blends can contain high concentrations of chromium.

3.5.6 Key findings

In Section 3.5, a range of statistical comparisons have been made between the various types of sites that were sampled in the Firth of Thames. Results suggest the following:

- Data gathered to date provides little evidence that former mining sites along the lower eastern coast of the Firth of Thames had, or continue to have, a substantive impact on the quality of their nearest coastal sediments, relative to the more general impact from other sources (Section 3.5.2).

- An apparent trend in cadmium and zinc enrichment is evident, with concentrations highest at sites closest to the mouths of the Waihou and Piako Rivers (Section 3.5.2). Student's t-tests indicate that sediments from the sites closest to agricultural sources contain more cadmium and zinc than other areas (Section 3.5.5).

- There is tentative evidence that a significant proportion of arsenic and copper in Firth of Thames sediments may be sourced from the land through weathering and erosion processes (Section 3.5.3).

- A site in the vicinity of Thames shows evidence of being a localised hotspot for mercury and cadmium (in particular), and zinc in the marine sediments (Section 3.5.4). This is from Kuranui Bay south to an area adjacent to the Thames stormwater discharge pipeline. Results of depth samples at Kuranui Bay suggest that the worst contamination was historic. Current evidence suggests that the most likely cause is mine tailings and industrial fill that were used as the base of the Moanataiari reclamation. The area may warrant closer investigation to evaluate contaminant loadings, potential to discharge and environmental significance of any industrially-sourced fill that was used in this area.

- Elevated arsenic, copper, lead, cadmium and zinc concentrations along the lower eastern coast of the Firth of Thames (Section 3.3) appear to be dominated by larger-scale sources, which are capable of causing an impact over the area as a whole. The three most likely larger-scale sources are enhanced weathering and erosion following land clearance, the impact of historic mining operations which involved disposal of large volumes of tailings directly to the Ohinemuri River (Section 1.1.2), and agricultural inputs (Section 1.1.3).

3.6 Correlations and spatial trends

3.6.1 Approach and correlation matrix

Pearson's correlation coefficients were determined for element concentrations in sediments collected as part of this work. Interpretation of the correlations is provided in the subsequent sections.

As previously, samples for the Thames pipeline site and Kuranui Bay were removed from the data set before deriving correlation coefficients, because of the evidence of strong localised enrichment from a common source in these two areas (Section 3.5.4). Data sets for cadmium, chromium, copper, mercury, lead and zinc were log-normalised prior to derivation of the correlation matrix. Data sets for arsenic and nickel did not require log-normalisation.

The inter-element correlation matrix is provided in Table 3-12.

Table 3-12 Pearson's correlation coefficients for relationships between element concentrations in sediments (N = 62 pairs). Yellow shaded boxes represent highly significant relationships with probability values of p<0.0001 (R>0.474) and p<0.001 (0.474>R>0.408). (See text for information about data set coverage.)

	[As]	Log[Cd]	Log[Cr]	Log[Cu]	Log[Hg]	[Ni]	Log[Pb]	Log[Zn]
[As]	1							
Log[Cd]	–0.255	1						
Log[Cr]	–0.232	0.063	1					
Log[Cu]	0.672	0.119	-0.073	1				
Log[Hg]	–0.479	0.412	0.157	– 0.485	1			
[Ni]	–0.098	–0.208	0.859	– 0.183	0.058	1		
Log[Pb]	0.202	0.546	0.260	0.241	–0.046	0.104	1	
Log[Zn]	–0.079	0.850	0.081	0.199	0.160	– 0.150	0.690	1

The relationship between element concentration and straight-line distance from the Waihou River mouth (in kilometres) was also examined, using the same data set but without any non-coastal sites (*i.e.* excluding the Thames mudflat, Thames harbour, and Piako River mouth samples). Results of this analysis are shown in Table 3-13.

Table 3-13 **Pearson's correlation coefficients between element concentrations at the coastal sites and distance from the Waihou River mouth (N = 49 pairs).** Yellow shaded boxes represent highly significant relationships with probability values of $p<0.0001$ ($R>0.527$) and $p<0.001$ ($0.527>R>0.456$). (See text for information about data set coverage.)

Element	Pearson's correlation coefficient (R)
Arsenic, As	0.454
Log cadmium, Cd	-0.646
Log chromium, Cr	0.001
Log copper, Cu	-0.080
Log mercury, Hg	-0.310
Nickel, Ni	0.348
Log lead, Pb	-0.245
Log zinc, Zn	-0.709

The proportion of fine particles in sediment can influence trace element concentrations. Fine particles have a larger surface area per unit weight than course particles and can therefore adsorb proportionately more of a given trace element. Measurement of the percentage fines was carried out on only 15 samples, across the range of sampling locations (Appendix 2). An assumption could be made that the percentage fines measured at each location is representative of that location, and this would allow this measured fines value to be assigned to all samples from that area. However, the validity of this assumption cannot be tested, so it is safer in this case to restrict the correlation analysis to the 15 sample pairs. Correlation coefficients between percentage fines and element concentrations in the same samples are provided in Table 3-14.

Table 3-14 **Pearson's correlation coefficients between element concentration and percentage of fines in the sediment (N = 15 pairs).** Yellow shaded boxes represent highly significant relationships with probability values of $p<0.001$ ($R>0.760$) and $p<0.01$ ($0.760>R>0.641$).

Variable	Pearson's correlation coefficient (R)
Distance	-0.747
Arsenic, As	-0.730
Log cadmium, Cd	0.705
Log chromium, Cr	0.323
Log copper, Cu	-0.636
Log mercury, Hg	0.383
Nickel, Ni	0.405
Log lead, Pb	0.327
Log zinc, Zn	0.709

3.6.2 Zinc, cadmium, and lead

Concentrations of zinc, cadmium and lead are very highly ($p<0.0001$) inter-correlated with each other, with zinc and cadmium being the mostly highly correlated of these elements (Table 3-12; Figure 3-3). Excluding the samples from the Thames mudflat, and retaining coastal samples only, zinc and cadmium also show a definite ($p<0.0001$) decrease in concentration with distance north from the Waihou River mouth (Table 3-13; Figure 3-4). Like zinc and cadmium, lead does appear to be generally elevated in Firth of Thames sediments compared with natural levels in other areas (Sections 3.3.1 and 3.3.2). However, concentrations of lead are fairly constant with distance from Thames except for an unexplained dip at the Tapu site (Appendix 2). Although concentrations of lead do correlate with those of zinc and cadmium (Table 3-12), lead does not show a significant decrease in concentrations with distance north.

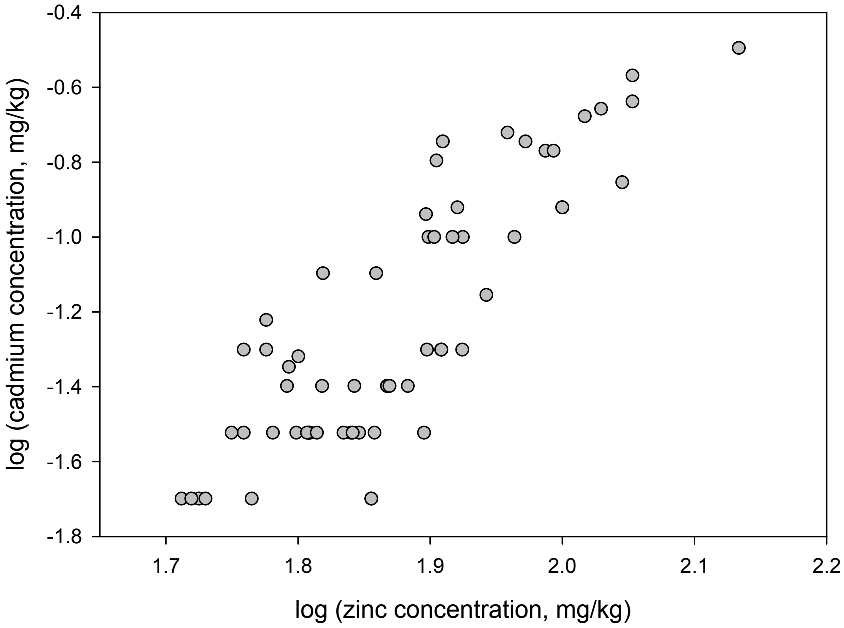

Figure 3-3 **Relationship between zinc and cadmium concentrations (mg/kg) in Firth of Thames sediment samples.** (See Section 3.6.1 for information about data set coverage.)

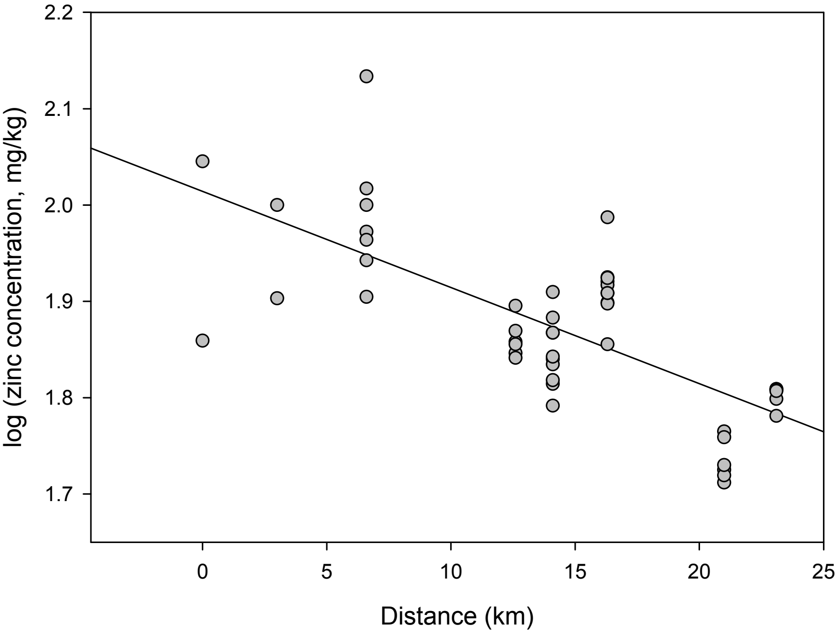

Figure 3-4 **Relationship between concentrations of zinc in sediments and distance from the Waihou River mouth in kilometres.** (See Section 3.6.1 for information about data set coverage.)

These differences in behaviour suggest the presence of two significant sources of zinc and cadmium, one of which is (or was) also a source of lead. In other words, the correlations suggest the presence of one significant source of all three metals (lead, cadmium and zinc) and another significant source of two metals only (cadmium and zinc). Possible sources in each category could include mining, and agriculture, respectively.

Both lead sulphide (galena) and zinc sulphide (sphalerite, which also contains a significant quality of cadmium) co-occur naturally in many epithermal mineral deposits in the Coromandel and Hauraki goldfields. This natural co-occurrence of these two metals could possibility explain the apparent correlation between lead and zinc/cadmium. A majority of the base metals sulphide deposits occur around or south of Thames (an exception being Monowai Mine on the Paroquet Stream at Waiomu).

In the fifteen samples where percentage fines in the sediment was measured, zinc and cadmium are also positively correlated with this variable (Table 3-14). The data also shows a decrease in the proportion of fines heading north. This suggests that an unknown proportion of the decrease in zinc and cadmium concentrations with distance from the Waihou River mouth *may* be caused by a decreasing content of fines. However, this result should be treated with caution, because not all elements show the same behaviour – for example, lead, nickel and chromium show no significant variation with percentage fines or distance (Table 3-14). In addition, mining itself is likely to have been a major source of fines, and it may be artificial to attempt to distinguish fines from element concentrations if both were caused by mining.

Geographical trends in zinc and cadmium concentrations that were detected using Pearson's correlation coefficients (Table 3-13 and Figure 3-3) are in keeping with those which became evident using a Student's t-test approach (Table 3-7 and Figure 3-1), where mining control sites were compared to other sites. The two statistical approaches are different ways of approaching the same question.

3.6.3 Arsenic and copper

Copper and arsenic are also highly ($p<0.0001$) correlated to each other in both the full data set, and the reduced data set (with Thames and Kuranui Bay samples excluded) (Table 3-12). This is despite the fact that where released, copper transport is limited compared to that of arsenic.

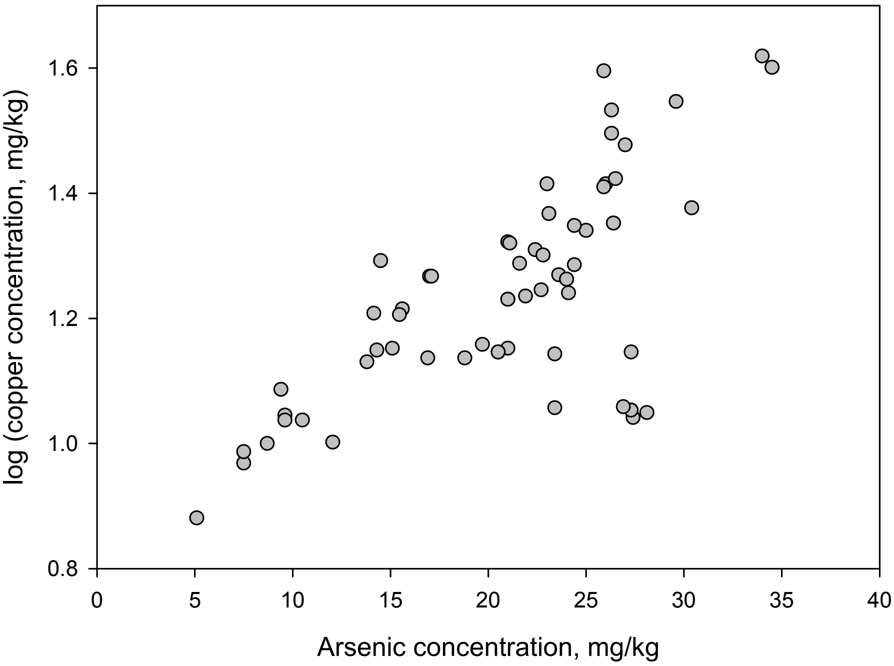

Figure 3-5 **Relationship between arsenic and copper concentrations (mg/kg) in Firth of Thames sediment samples.** (See Section 3.6.1 for information about data set coverage.)

Concentrations of arsenic and copper show no trend with distance up the coast (Table 3-13),[10] but for both elements do show an inverse relationship with the proportion of fines in the sediment (Table 3-14). This latter outcome is the opposite to the trend shown by zinc and cadmium. Though data pairs are limited for iron (N=20), the two elements most highly correlated to iron are also arsenic ($p<0.02$) and copper (not quite $p<0.05$).

Together these observations suggest that the moderately elevated arsenic and copper in the Firth of Thames surface sediments (Sections 3.3.1 and 3.3.2) may be due to the

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[10] Note: examination of the scatterplot between distance and arsenic concentration showed that the correlation coefficient (R=0.454, Table 3-11) does not represent a valid linear relationship in this case. This particular plot was skewed by the influence of three low results for the first sites (the Waihou River mouth and Thames stormwater), giving a pseudo two-point line. Arsenic concentrations show no convincing relationship with distance up the coast.

presence of natural minerals in the sediments that are enriched in arsenic and copper. Another possibility is that arsenic has more effectively spread throughout the Firth of Thames than other elements sourced from mining, but this idea is undercut by the correlative relationship between concentrations of arsenic and copper. Unlike arsenic, where released, copper is expected to be relatively immobile.

Three factors are consistent with an hypothesis that additional arsenic and copper in the Firth of Thames sediments is most likely to be mainly from weathering of minerals in coastal areas of the Coromandel Peninsula.

1. In Section 3.5.3 it was shown that arsenic and copper concentrations are likely to be slightly higher in samples collected from nearest the land (landward samples), compared with samples collected from nearest the Firth of Thames water (seaward samples).

2. The negative correlation with fines (Table 3-14) suggests that the larger particles contribute a greater mass of arsenic or copper to the concentration measurement. This behaviour is opposite to that observed for metal enrichment in sediments from most industrial sources, where the highest concentrations are commonly associated with the finest size fractions because these have the greatest surface areas available for metal re-adsorption from solution. However, it is not an unexpected behaviour in cases of natural mineralisation. Such a trend implies that movement of whole mineral particles may dominate the mass flow of arsenic and copper being washed into the Firth of Thames through weathering and erosion (rather than dissolution and leaching of arsenic and copper into the aqueous phase).

3. A mineral source would also explain an association between copper, arsenic and iron, given that the Coromandel range contains a significant natural abundance of volcanic–hydrothermal minerals such as arsenopyrite (FeAsS) and chalcopyrite $CuFeS_2$ (Section 1.1.1). Arsenic is a common trace component found in pyrite which occurs throughout the Hauraki Goldfield in both ore rock and the host rock. Copper is a major element found in chalcopyrite which co-occurs with pyrite, to a greater or lesser degree, with pyrite within the Coromandel and Hauraki goldfields.

However, the data does not rule out a past contribution to arsenic in sediments from mining. If the elevated arsenic were from an Ohinemuri mining source, some features of the observed pattern might be achieved through one of three mechanisms:

- The mining contribution did cause elevated arsenic as well as other elements in the Firth of Thames, but the arsenic spread more effectively than most of the other elements. This is possible and likely for dissolved arsenic, but would not explain the correlation with copper, which would be less mobile if it were in the dissolved phase. This explanation is therefore unlikely.

- Dissolved arsenic that entered the Firth during the mining era was flushed out to sea, and not much copper made it to the Firth in the first place. Zn-Cd-Pb and Hg were transported to the mouth of the Wiahou River, but salted out on entry into the Firth of Thames. Under this scenario the modern picture may be a mix of the residue of mining for Zn-Cd-Pb and Hg, and local sources for arsenic and copper.

- The Ohinemuri mining contribution did cause elevated arsenic in Firth sediments, but those most highly contaminated sediments are now usually buried deeper than 10 cm, and any remaining trends with distance (Zn-Cd-Pb-Hg) reflect a residual ongoing contribution from the Waihou River.

Overall, the correlation between arsenic and copper (and both to some extent with iron) in sediments, the inverse relationship of both elements with fines, the lack of a convincing trend in concentration of either element with distance north, and the apparent concentration gradient in moving from land to shore, suggest that most of the additional copper and arsenic in the Firth of Thames surface sediments (relative to Raglan Harbour – Section 3.3.1) may be caused by weathering and erosion of natural sulphide minerals in the Coromandel area. As discussed in Section 1.1.1, it is probable that such weathering and erosion has been accelerated by land clearance which accompanied progressive waves of human colonisation.

Although the idea that arsenic concentrations in modern surface sediments are dominated by local natural sources more readily accounts for observed correlations and trends, an influence of past mining operations cannot be ruled out.

3.6.4 Chromium and nickel

Chromium and nickel do not appear to be elevated in the Firth of Thames relative to Raglan, do not change with distance along the coast, and closely correlate with each other (Table 3-12). Concentrations of chromium and nickel in the Firth of Thames' surface sediments appear to be at their natural baseline levels.

3.6.5 Mercury

In concentration units (mg/kg), mercury is the most enriched of the elements measured in coastal sediments of the eastern coast of the lower Firth of Thames (Section 3.3.1). Despite this, correlation data for mercury provides little immediate indication of probable source for the additional mercury.

- Mercury concentrations are negatively correlated with concentrations of arsenic and copper (mercury concentrations tend to be higher in samples with less arsenic or copper), but are positively correlated with cadmium.[11] Mercury is uncorrelated with nickel, chromium, lead or zinc. There is no evidence that mercury concentrations are higher in seaward than landward samples (Section 3.5.3), or that mercury concentrations are highest in samples collected from nearest the mouth of the Waihou River (Table 3-13), or are influenced by fines (Table 3-14).

On the other hand, there is evidence of strong localised enrichment by mercury in the Kuranui Bay and Thames areas, including the Thames mudflats (Table 3-8). The correlation statistics discussed above are based on the data set with samples from Kuranui Bay and Thames stormwater pipeline area excluded, but the Thames mudflat samples retained.

Closer examination of the data for mercury (Appendix 2) reveals a feature that was missed in the statistical overview, and not included in the effect of distance assessment (Table 3-13). This is that samples collected from the Piako River mouth appear to be unexpectedly elevated in mercury, despite the fact that the catchment of this river is agricultural with no known mining influence. Average concentrations of mercury in surface samples are presented in Table 3-15 and Figure 3-6.

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[11] These statistics are based on the data set with samples from Kuranui Bay and Thames stormwater pipeline area excluded. See Section 3.6.1.

Table 3-15 **Average mercury concentrations in surface (0-10 cm or grab) sediment samples from all sites.** Sites in the vicinity of the Thames pipeline and Kuranui Bay are separated out due to evidence of a localised source of mercury, cadmium and zinc in this area (Section 3.5.4). One outlier of 1.52 mg/kg mercury for Thames mudflat sample SDB584 has been removed from the data set prior to calculating these averages.

Location	Mercury concentration (mg/kg dry weight)
Thames pipeline/Kuranui anomaly	
Thames stormwater pipeline	0.40
Kuranui Bay	0.41
Thames stormwater and wharf	0.28
Other sites (south to north)	
Piako River Mouth	0.32
Opani mudflat	0.27
Thames mudflats and harbour	0.23
Waihou River mouth	0.22
Tararu Stream	0.18
Thornton	0.08
Te Puru	0.09
Waiomu Bay	0.08
Tapu	0.12
Te Mata	0.15

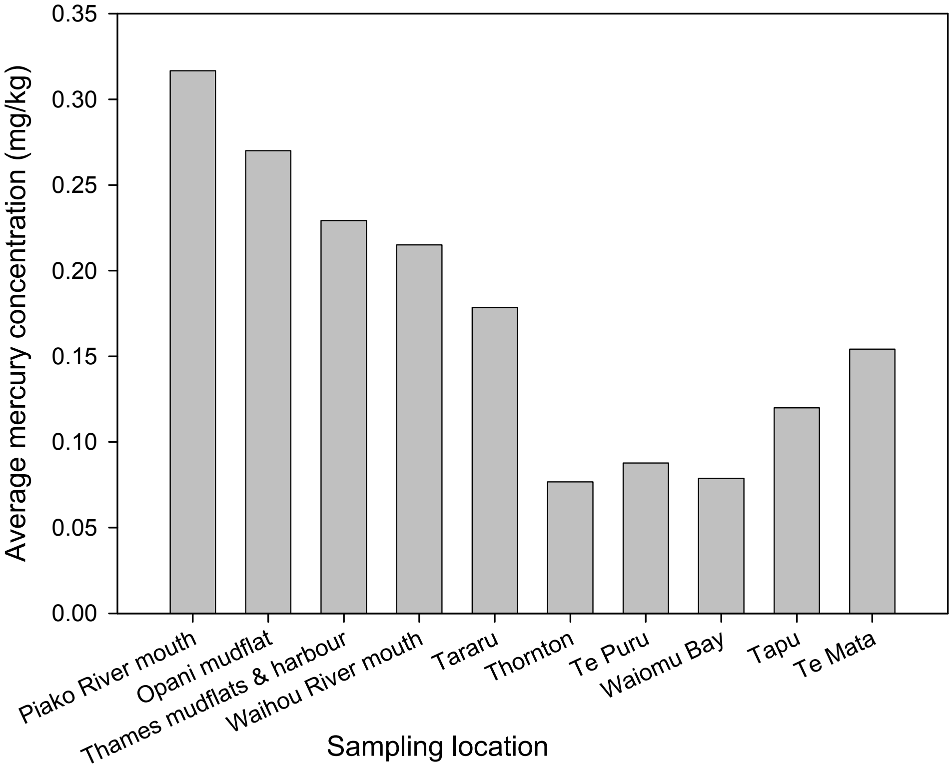

Figure 3-6 **Average concentrations of mercury moving from the Piako River mouth east and then north, excluding the Thames pipeline/Kuranui Bay anomaly.** (Other details are as for Table 3-15.)

Pooled Student's t-tests show significantly more mercury ($p<0.0001$) is present in samples from the Piako River mouth, and Opani and Thames mudflats and harbour ($N=16$) than reference sites comprising Tararu Stream, Thornton, Te Puru, Waiomu Bay, Tapu and Te Mata ($N=45$). The former areas contain about 2.3 times more mercury than the control sites.

To review, there is no correlation between mercury and two of the group of elements thought to have a significant mining source contribution (lead and zinc). Similarly, there is no positive correlation between mercury and elements that may be sourced from erosion of the Coromandel ranges (copper and arsenic). However, there is evidence that the Piako River may be a significant conduit by which mercury enters the Firth of Thames (Table 3-15 and Figure 3-6). Yet, unlike cadmium and zinc, there are no particularly substantive sources of mercury in agriculture (Section 1.1.3) and no evidence of mercury enrichment in sediments of Raglan Harbour, which is itself surrounded by agricultural land (Section 3.3.1).

Together these observations suggest the presence of a unique source of mercury to the Firth of Thames, which is not related to mining, erosion of Coromandel minerals, or treatments used in agriculture, but which is delivered to the Firth of Thames *via* the Piako River (potentially among other routes).

Recent work in mercury chemistry provides a likely reason for this. Wetlands can substantially increase the flux of mercury to nearby receiving environments systems (O'Driscoll et al, 2005). This is significant because the Piako River passes directly through the middle of New Zealand's largest area of wetlands and peatland (Figure 2.1 and Appendix 8) and is the main river draining the Hauraki Plains. Water of the Piako River can carry sufficient dissolved organic matter and iron to impart a distinct colour.

Mercury concentrations in the Piako river channel grab sample sediments are about four times greater than might otherwise be expected (Table 3-15). Excluding the Kuranui Bay anomaly, mercury concentrations in shallow surface sediments (0-2 cm) are about seven times higher than those in Raglan harbour (Section 3.3.1). The total area of the Piako catchment (Appendix 8) is approximately 1488 km^2. The area of major wetlands within this catchment (Figure 2.1) is approximately 108 km^2, or about 7% of the total Piako catchment area. A back-of-envelope calculation suggests that mercury enrichment in sediments of the Firth of Thames might be consistent with the Hauraki wetlands/peatlands causing a localised increase in mercury flux of about 70 times.[12] Although this is a very rough estimate and carries a number of untested assumptions, such a magnitude is consistent with O'Driscoll et al (2005), who note that in the Experimental Lakes Area reservoir project in Ontario, it has been found that wetland areas of catchment provide 26-79 times more methylmercury per unit area to downstream water than areas that contain no wetlands. In principle, contributions from the Piako catchment's wetlands (Figure 2.1) could, therefore, be capable (in theory) of causing most of the observed mercury enrichments in the Firth of Thames sediments.[13]

Mercury mobilised from wetlands to receiving environments is known to be mainly associated with dissolved organic matter. As concentrations of dissolved organic carbon in drainage waters increase, more mercury is transported. Peatlands would not necessarily contain more mercury than elsewhere, but dissolved organic carbon formed by oxidation and drainage of peat is likely to be a vehicle for enhanced mercury transport to downstream receiving environments. In conjunction with the results of this work (e.g. Figure 3.6), it is therefore thought probable that the peatlands of the Hauraki Plains contribute a substantial flux of mercury to the Piako River, and this becomes a significant source of mercury to the Firth of Thames.

Such a source would be consistent with the statistical observations about mercury in this study, including the fact that the Firth of Thames sediments appear 7-11 times more enriched in mercury than sediments of Raglan Harbour. The catchment of Raglan Harbour does not include significant areas of peatland.

The relationship between mercury and arsenic and copper concentrations is shown in Figure 3-7.

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[12] *i.e.* The wetland area is about 7% of the total Piako catchment. 7% of a 50 times enrichment in the wetland zone = an overall increase of 4 times (one end of the observed range), and 7% of a 96 times enrichment = 7 times (the other end of the observed range). The average of 50 and 96 is 73.

[13] Excluding the localised Kuranui Bay/Thames pipeline anomaly, which appears to be associated with the Moanataitiri reclamation (Section 3.5.4).

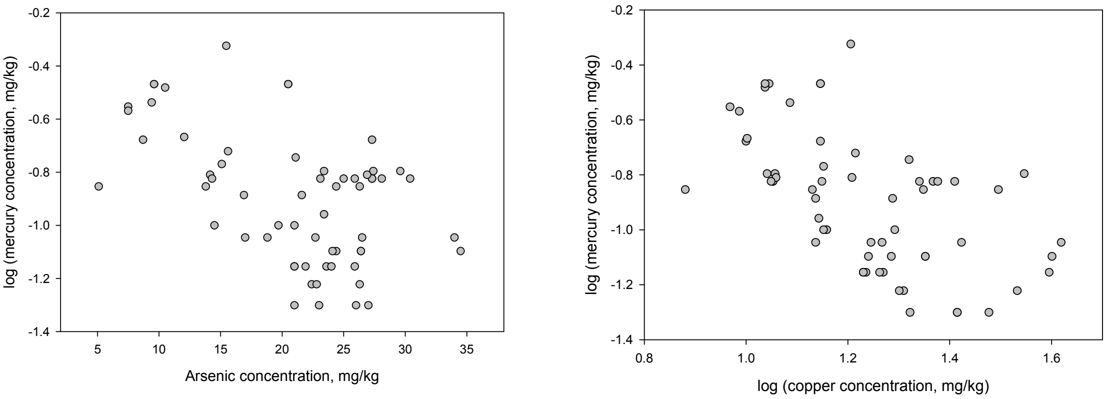

Figure 3-7 **Relationship between concentrations of mercury and arsenic, and mercury and copper, in Firth of Thames sediments.** Site coverage is as described in Table 3.15.

It is initially unclear why there is a negative correlation between concentrations of mercury and those of copper or arsenic (Table 3-12; Figure 3-7), given that concentrations of these two elements do not significantly change with distance north.

However, the observed relationships would be consistent with the idea that sites with proportionately more of the Coromandel range-sourced mineral grains (richer in copper and arsenic) have proportionately less of their sediment sourced from the Waihou and Piako Rivers (sediment which may be richer in mercury). The negative correlation between arsenic or copper and fines discussed previously (Table 3-14, Section 3.6.3) is also consistent with this interpretation.

Similarly, the positive correlation between mercury and cadmium (Table 3.12) may also reflect the influence of sediments sourced from the Piako River, which services an agricultural catchment. This correlation may represent two different sources sharing the common transport route. Whereas wetlands and peatlands may be a source of mobilised mercury, phosphate fertiliser is the most likely agricultural source of cadmium, but both elements would be carried to the Firth of Thames by the same river system.

Correlations between mercury and cadmium, arsenic or copper are all, therefore, consistent with an hypothesis that a significant amount of mercury entering the Firth of Thames may originate from the Hauraki Plains.

3.6.6 Principal Components Analysis

Principal Components Analysis (PCA) was also performed on the same data set as for the correlation matrix (Table 3.12, Section 3.6.1). Results are provided in Table 3-16.

As might be expected, PCA results are consistent with the inter-relationships shown in the correlation matrix and with interpretations made in the preceding sections. Ninety percent of the data variance in the eight elements was associated with the first four factors.

The meanings of factors generated in PCAs require a certain amount of interpretation, and for this reason the following descriptive interpretations should not be viewed as definitive. However, interpretations which might be placed on each factor are as follows:

Table 3-16 Results of Principal Components Analysis on the correlation matrix data set. Weightings less than -0.4 or greater than 0.4 are highlighted.

	F1	F2	F3	F4	F5	F6	F7	F8
As	0.26	-0.76	0.36	0.31	-0.32	0.14	-0.01	-0.09
Cd	-0.92	-0.11	-0.25	0.09	0.17	0.02	-0.20	-0.08
Cr	-0.31	0.51	0.76	0.06	0.17	-0.09	0.10	-0.13
Cu	-0.04	-0.81	0.33	0.29	0.36	-0.11	0.02	0.09
Hg	-0.42	0.60	-0.37	0.54	-0.18	-0.05	0.06	0.05
Ni	-0.04	0.54	0.81	0.04	-0.03	0.16	-0.12	0.11
Pb	-0.74	-0.33	0.35	-0.21	-0.37	-0.21	-0.01	0.05
Zn	-0.91	-0.27	-0.07	-0.12	0.06	0.24	0.15	0.03

- Factor 1 is a ‘zinc-cadmium-lead-mercury’ group, denoting the sum or positive inter-correlations between these elements, and accounts for 32% of the data set’s variation. This first factor probably represents the sum of mining and agricultural sources, with the mercury component reflecting this element’s mild correlation with cadmium (Table 3-12). It was speculated that the mild mercury-cadmium relationship may come about because the Piako River may act as a conduit for both agricultural cadmium, and wetland/peatland-sourced mercury (Section 3.6.5).

- Factor 2 is an ‘arsenic-copper and opposing elements’ group, and accounts for 29% of the data variation. This factor denotes that arsenic and copper follow each other, but are both inversely related to mercury, chromium and nickel. In terms of sources, this factor could be taken to represent direct contributions from erosion of the Coromandel (arsenic and copper), and the proportion of this material in relation to sediment sourced from elsewhere (mercury increases as arsenic and copper decrease). An inverse relationship between arsenic-copper and either chromium or nickel is not evident in the correlation matrix (Table 3-12), but the inverse relationship with mercury is. However, a PCA can occasionally detect underlying relationships that are masked when inter-element correlations pull in different directions. If there is a genuine inverse relationship between arsenic-copper and chromium-nickel, it might be for the same reasons as the inverse relationship between arsenic-copper and mercury (see Section 3.6.5 and Figure 3.7).

- Factor 3 groups the two metals nickel and chromium and accounts for 22% of the data set’s total variation. This ‘nickel-chromium’ factor could be taken to denote the natural state of sediments. These two elements are not enriched and in their natural state are correlated with each-other (Table 3-12).

- Factor 4 is a residual ‘mercury only’ factor, which accounts for 7% of the data variation. The existence of a ‘mercury only’ factor might be consistent with a source of mercury that is not bound up with the other sources (mining, agricultural treatments, or erosional contributions). In Section 3.6.5, it is suggested that the Hauraki peatlands and wetlands may be such a unique source.

3.6.7 Key findings

The focus in Section 3.6 was on inferences that might be made based on correlations between the elements. Results suggest the following:

- Concentrations of zinc, cadmium and lead are highly correlated with each other. However, zinc and cadmium concentrations decrease with distance north of the Waihou River mouth, whereas lead concentrations do not. For these three elements, correlations, trends and relative enrichments are consistent with the hypothesis that:

    - Past mining in the Ohinemuri catchment may have been a significant source of lead, zinc and cadmium to coastal sediments of the Firth of Thames.

  - Agricultural treatments (facial eczema remedies and phosphate fertilisers) may be a significant ongoing source of zinc and cadmium (respectively).

- Copper and arsenic concentrations are also highly correlated to each other and also show associations with iron. These elements are uncorrelated with the other elements. Several factors suggest that additional arsenic and copper in the Firth of Thames sediments may be primarily from weathering and erosion of minerals in coastal areas of the Coromandel Peninsula.

- Mercury is the most enriched element in coastal sediments of the eastern coast of the lower Firth of Thames, in concentration units (mg/kg). However, there is no evidence that this additional mercury may be sourced from past mining, erosion of natural minerals, or agricultural treatments. Instead, observations suggest the presence of a unique source of mercury to the Firth of Thames, which is delivered to the Firth of Thames *via* the Piako River (among other potential conduits). Based on recent literature, it is thought possible that a substantial flux of mercury may enter the Piako River from the wetlands and peatlands of the Hauraki Plains.

- Concentrations of chromium and nickel in the Firth of Thames' surface sediments correlate strongly with each other and appear to be at their natural baseline levels.

4 Summary and recommendations

4.1 Summary

4.1.1 Relative enrichments

Arsenic, cadmium, copper, mercury, lead and zinc are enriched in sediments of the lower eastern coast of Firth of Thames, relative to concentrations present before Polynesian and European colonisation, and reference concentrations in sediments from Raglan Harbour. Concentrations of the other five elements measured in some or all samples (chromium, nickel, aluminium, iron and lithium) are more typical of those observed in clean harbour sediments in other areas. Relative to its expected background concentration, the most highly enriched element is mercury. The average concentration of mercury in the lower Firth's sediments is approximately seven times higher than in otherwise comparable reference sediments. In absolute mass terms, the most highly enriched element is zinc. The Firth's sediments contain about 10 mg/kg more zinc than might otherwise be expected.

4.1.2 Comparison to guidelines

The two elements which are nearest to or occasionally exceed guideline values for sediments are arsenic and mercury. Arsenic and mercury concentrations in the Firth of Thames coastal sediments are not extremely high, but are at a point where they may have adverse effects on some sediment-dwelling organisms, at some locations. Both arsenic and mercury exceeded their respective ISQG-Low guidelines at eight of the thirteen (62% of) sites sampled by URS NZ Ltd. These were not the same sites. Sites with the highest mercury were not the sites with the highest arsenic. Although concentrations of copper, cadmium, lead and zinc were higher than typical values for uncontaminated sediments, they are still well below the lowest sediment quality guideline values. These elements are unlikely to pose a risk to the health of the Firth's aquatic ecosystems.

4.1.3 Local and general sources

Only one area (at two adjacent sampling locations) stands out as a hotspot of localised metal contamination, which looks likely to have been from mine tailings and urban/industrial fill deposited in the area as part of land reclamation. This is the sediment in Kuranui Bay and an adjacent area in northern Thames, which appears to have become contaminated as a result of the Moanataiari reclamation. Depth results suggest that the worst contamination in this area was historic, but an ongoing contribution from leachate from the base of the reclamation is also likely.

Apart from this area, the influence of local sources appears minor. The results provide little evidence that former mining sites along the lower eastern coast of the Firth of Thames had, or continue to have, a significant impact on the quality of their nearest coastal sediments, relative to the more general impact from other sources. The clearest evidence of a local effect from past mining is at Waiomu Bay, where sediment samples were statistically enriched with seven of the eight trace elements tested. However, although (statistically) *significant*, these enrichments were not particularly *substantial*.

Although there is some evidence for the presence of the occasional grain of a metal-rich mineral in sediments, more generally the data suggests that elevated arsenic, copper, lead, cadmium and zinc concentrations along the lower eastern coast of the Firth of Thames are likely to be dominated by larger-scale sources, which are capable of causing an impact over the area as a whole. The three most likely larger-scale sources are enhanced weathering and erosion following land clearance, the impact of historic mining operations which involved disposal of large volumes of tailings directly to the Ohinemuri River, and agricultural inputs. A fourth possible source identified in this work (for mercury) may be dissolved organic matter entering the Firth of Thames from wetlands and peatlands of the Piako River catchment.

4.1.4 Probable dominant sources by element

(*Note*: Sources of the trace elements discussed in this section are in addition to those responsible for the natural background.)

Zinc and cadmium

Results for zinc and cadmium are the most consistent with the existence of two significant diffuse sources of zinc and cadmium to the Firth of Thames: past mining in the Ohinemuri-Waihou catchment and current agricultural treatments.

- Ohinemuri catchment mining is thought to be the most likely mining-related source of zinc and cadmium, because of the large volumes of tailings involved. The Waihou River is known to have received between 500-800 tonnes per annum of tailings from the Ohinemuri River for over 50 years.

- Facial eczema remedies are the most substantial potential source of zinc from agriculture, and phosphate fertilisers are the most substantial source of cadmium

Lead

Results for lead are consistent with the existence of one significant diffuse source of additional lead, which is most likely to be the influence of past mining in the Ohinemuri catchment. This mining source appears to have been a source of significant lead, zinc and cadmium. Unlike zinc and cadmium, there is no evidence of an additional agricultural source of lead.

Copper and arsenic

Several factors suggest that additional arsenic and copper in the Firth of Thames sediments is primarily from weathering of minerals such as pyrite in coastal areas of the Coromandel Peninsula. It is likely that the rate and extent of weathering and erosion, and influx of arsenic and copper, was enhanced by historic land clearance activities around the coastal areas of the Coromandel Peninsula, following Polynesian and European settlement in the area.

Mercury

For mercury, the most enriched element, there is no positive evidence that past mining, erosion of natural minerals, or agricultural treatments have been significant sources to the Firth of Thames sediments. Rather, the results suggest a unique source of mercury which is delivered to the Firth of Thames *via* the Piako River among other potential conduits. Based on recent literature, it is thought likely that this mercury may originate from drainage of the wetlands and peatlands of the Hauraki Plains. In addition to this, the area around the Moanataiari reclamation is a localised hot-spot of mercury contamination.

4.2 Recommendations

In this section, specific recommendations are numbered and italicised. The rationale for each recommendation is provided in the non-italicised text immediately preceding the recommendation.

Although several elements are enriched in the Firth of Thames sediments, it is not yet clear whether their concentrations are at steady state, increasing or decreasing. In the face of a steady source of a given metal, concentrations can sometimes decrease as a result in a greater influx of clean sediment causing dilution. Conversely, better control of ‘clean’ sediment inputs can result in a relative increase in the concentrations of contaminants in deposited sediments.

1. *It is recommended that sediments of the Firth of Thames be sampled once every five years to allow for early warning, in the event that concentrations of one or more trace elements are gradually increasing. Future testing could also include related variables, such as concentrations of dissolved organic carbon in the Piako River.*

In terms of diffuse contamination, two elements stand out as a consequence of exceeding sediment quality guidelines at several locations. These are mercury and arsenic. There is reasonable evidence that the additional arsenic was caused by enhanced weathering and erosion of the Coromandel Peninsula, following colonisation and land clearance. There may be little that can be done about this source, but options may be worth investigating. Arsenic does not bioaccumulate. For mercury, there is tentative evidence that the element is mobilised in drainage water from the peatlands and wetlands of the Hauraki Plains. Mercury is of more inherent concern that arsenic, due to its ability to change its chemical form and accumulate both in organisms, and up food chains (bioaccumulation and biomagnification). This is particularly given that the Firth of Thames is an important site for waders and shorebirds, and the intertidal area from Kaiaua to the Waihou River mouth is listed as a wetland of international importance under the Ramsar Convention.

2. *For mercury, it is recommended that future work focus on:*

    a. *Quantifying the relative significance of wetlands and peat deposits in the Hauraki Plains as sources of mercury to the Firth of Thames, relative to other sources, including possible geothermal inputs. A reliable estimate of mercury fluxes from various sources would require ultra-trace measurements of mercury concentrations in waters and suspended sediments entering the Firth of Thames over one or more seasons, and flow volumes.*

    b. *Identifying land management factors that would increase or decrease mercury inputs to the Firth of Thames.*

    c. *Identifying the most significant risks associated with mercury which has entered the Firth of Thames sediment reservoir. This would need to include an assessment of likely trends in sediment mercury concentrations, and probable chemical transformations and their significance. A focus on the significance of mercury in the Firth of Thames to both wildlife, and human food sources, would be appropriate.*

    d. *Mangrove colonisation has the potential to substantially alter mercury chemistry in colonised areas. Ideally, the relationships between mangrove establishment and mercury cycling (including mobilisation and fixation) should also be investigated.*

3. *For arsenic, investigate the feasibility of any simple erosion control measures that could be brought to bear. Measures to limit erosion should also reduce the influx of*

arsenic (and copper), and should eventually result in a lower concentration of arsenic in surface sediments.

One area stands out as a localised hotspot of contamination by several elements, most notably mercury. This is Kuranui Bay and an adjacent part of northern Thames, in the area of the pipeline. Sediments in this area appear to have become contaminated as a result of fill material used in the base of the Moanataiari reclamation during the long history of Thames. Potential risks that the area may pose to the wider ecosystem have not been quantified. Potential ongoing discharges are unknown. Contaminated sites investigations are carried out in stages, called tiers. A tier I investigation would include a detailed review of history and limited specific sampling. Results of the tier I investigation are used to guide the tier II investigation, which typically includes more detailed sampling and a site-specific risk assessment.

4. *Specific tier I and II contaminated site investigations should be carried out in the area of the of the Moanataiari reclamation to determine hazards, pathways, risks to aquatic organisms, and management options.*

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Appendix 1. Further details of each location from which sediment samples were collected by URS as part of this study.

Waihou River mouth

The Waihou River is the largest river within the study area. The drainage catchment includes the following mining inputs:

- Mt Te Aroha (Tui Mine) – a base metal mine which operated between 1967 and 1973 and which is regarded as one of New Zealand's most contaminated sites.
- Karangahake Gorge, sections of which were mined between 1882 and1933.
- Martha Hill mine in Waihi, which is currently operational, but which operates under modern resource consent conditions which minimise potential impacts.

Historical evidence suggests that tailings from several different mines containing high concentrations of pyrite (FeS_2) and other metal sulphides, were deposited directly into the Waihou River and its tributaries during the early 1900s. Water and sediment sampling conducted in the catchment has previously indicated significant heavy metal contamination (Livingston, 1987).

In addition to possible metal contamination due to historical mining operations, agricultural activities may result in elevated cadmium concentrations in sediments. Urban inputs from Waihi, Paeroa and Te Ahora townships also drain to the Waihou River. Two composite samples were collected from this area, with each consisting of five sub-samples (Appendix 1). Sampling was conducted on the western and eastern banks of the river mouth using an Eckman grab sampling device deployed from a boat. Sub-samples collected and accepted using this method were surface samples, to a nominal depth of at least 10 cm (see Section 2.3.3 for further details). Several of the sub-samples were collected by URS staff on foot, as the fast-flowing current in the Waihou River prevented sampling using the Eckman bottom grabber.

Piako River mouth and Opani mudflats

There is no known mining influence in the Piako River catchment area, but agricultural inputs are a potential source of trace elements in this area. Three composite sediment samples were collected from this area, each consisting of five sub-samples (Appendix 1). Piako River mouth sampling was conducted on the western and eastern banks of the river mouth. Sites were accessed by boat on an incoming tide and the sub-samples collected with an Eckman bottom grab sampler (Section 2.3.3) to a nominal depth of 10 cm. Samples could not be collected from the edge of the channel beyond the location of SDB 578, as the sediment was too hard to penetrate. Sediment samples that were collected from the main channel contained mainly shell fragments and could not be analysed. A separate composite (made of five sub-samples of 0-10 cm depth) was collected from the Opani mudflat (see point SDB568 in Figure 2-2), which is situated between the mouths of the Waihou and Piako rivers (Appendix 1).

Thames urban samples

Discharges of stormwater from urban areas can result in elevated concentrations of copper, lead and zinc in sediments. Two general sampling locations near the Thames township were used as part of this sampling programme.

Stormwater pipeline vicinity

Three composite samples (each made of five sub-samples of 0-10 cm depth) and one vertical core consisting of two depths (0-2 cm and 2-10 cm) were collected from the area of the Thames stormwater pipeline (Appendix 1). Sub-samples were collected using a plastic hand trowel to a depth of 10 cm (*i.e.* 0-10 cm, Section 2.3.1), and vertical profile samples were collected with a sediment corer. One composite sample (consisting of five sub-samples) was taken along the walkable length of the pipeline. Two of the sub-samples for the other composite were collected along the channel of a small stream, which discharged from a small PVC pipe (approx. 50 mm OD) immediately adjacent to the pipeline outfall. Sediments were generally very fine-grained silty sediments, with the upper 2-3 cm centimetres appearing to be an oxic layer.

Thames stormwater outlet and wharf areas

One composite sediment sample (consisting of five 0-10 cm sub-samples) was collected from each of these two areas, using a plastic hand trowel (Appendix 1). Sub-samples for the stormwater composite sample were collected from the true right-hand side of the channel and adjacent to the Thames stormwater outlet. They were collected during a storm event. These samples were found to contain very fine-grained silty sediments, with the upper 2-3 cm appearing to be an oxic layer. The wharf area is also in the vicinity of the Kauaeranga River outflow (NZMS T13 360473). Samples from this area were found to contain mainly fine to medium grain silty sediments, with the upper 2-3 cm appearing to be an oxic layer.

Thames Harbour mudflats and deeper harbour

The Thames Harbour mudflats might receive trace element inputs from both distant and nearby sources. The Piako River mouth may contribute significant sediment carried from the Hauraki Plains. Inputs from the urban area could result in elevated concentrations of copper, lead and zinc as a result of road and roof run-off and industrial discharges. The Kauaeranga River also discharges into Thames Harbour. The Kauaeranga Valley was mined for cinnabar (mercuric sulphide, HgS) between 1899 to approximately 1906 (Watson, 1989). A total of eight composite sediment samples (each made of five sub-samples of 0-10 cm depth) were collected from the Thames mudflats (Appendix 1). The mudflats were observed to contain mainly fine to medium grain silty sediments, with the upper 2-3 cm appearing to be an oxic layer. Two of these samples were analysed in duplicate for quality assurance purposes. A separate composite sample (made of five sub-samples of 0-10 cm depth) was collected from further out into the Thames harbour (point SDB569 in Figure 2-2) to a nominal depth of about 10 cm, using the Eckman grab sampler.

Tararu Stream

Historical mining activities were undertaken at several locations within this catchment. Access to the site was gained from the shore. Six composite sediment samples (each comprising five sub-samples of 0-10 cm depth) were collected from the intertidal zone surrounding the stream mouth at this location using the plastic hand trowel (Appendix 1). These were mainly fine to medium grain gravels containing some medium grain sands. Two of these samples were analysed in duplicate for quality assurance purposes.

Tapu Stream

Historical mining activities have been undertaken at several locations (including Sheridan and Mahara) within this catchment between 1869 and 1906. Access to the site was gained from the shore. Six composite sediment samples (each comprising five sub-samples of 0-10 cm depth) were collected from the intertidal zone surrounding the stream mouth using the plastic hand trowel (Appendix 1). Sediments from this site were found to consist mainly of coarse grain gravels.

Te Puru

This was a control site, as there have not been any significant past mining or agricultural activities within the catchment. Access to the site was gained from the shore. As with Tararu and Tapu, six composite sediment samples (0-10 cm) were collected in the intertidal zone surrounding the stream mouth. In addition, a vertical profile sample was collected using a sediment corer, with sub-samples from depths 0-2 cm, 2-10 cm, 15-20 cm and 25-30 cm being analysed individually. Sediments from this site were found to consist mainly of medium to coarse grain sands.

Thornton Bay

Like Te Puru, this was also a control site, as there have not been any significant past mining or agricultural activities within the catchment. Access to the site was gained from the shore. Six composite sediment samples (each comprising five sub-samples of 0-10 cm depth) were collected from the intertidal zone surrounding the stream mouth using the plastic hand trowel (Appendix 1). Sediments from this site were found to consist of mainly medium to coarse grain sands.

Waiomu Stream

A number of mines operated within this valley between 1890 and 1936 (including Paroquet, Broken Hill, Monowai and Comstock Mines). Access to the site was gained from the shore. Exploration in this area from 1971 to 1973 and 1983 to 1984 has revealed the presence of ore bodies still within this region (Moore et al., 1996). The ore deposit has been described as being an epithermal vein deposit with significant base metal sulphides (>3%). These would have the potential to elevate concentrations of elements in sediments if the ore body undergoes oxidation. In 1981, a preliminary survey of the Waiomu stream conducted by the Department of Scientific and Industrial Research (DSIR), National Water and Soil Conservation Authority (NWASCA), the Ministry of Agriculture and Fisheries (MAF) and the Hauraki Regional Water Board (Livingston, 1987) detected elevated concentrations of various trace elements (in particular, arsenic, cadmium and zinc) in the water and sediment of the Comstock Stream (a tributary of the Waiomu Stream). Slightly elevated concentrations of copper, lead and zinc have been detected in several locations within the Waiomu Stream water, and elevated concentrations of lead and zinc have been detected in Waiomu Stream sediments (Livingston, 1987). Six composite sediment samples (each with five 0-10 cm sub-samples) were collected in the intertidal zone surrounding the stream mouth. One of these was analysed in duplicate for quality assurance purposes. In addition, a vertical profile sample was collected using a sediment corer, with sub-samples from depths 0-2 cm, 2-10 cm, 15-20 cm and 25-30 cm being analysed individually (Appendix 1). Sediments from this site were found to consist of mainly coarse grain gravels.

Te Mata

This was a third control site, as there have not been any significant past mining or agricultural activities within the catchment. Access to the site was gained from the shore. Six composite sediment samples (each comprising five sub-samples of 0-10 cm depth) were collected from the intertidal zone surrounding the stream mouth using the plastic hand trowel (Appendix 1). Sediments from this site were found to consist of mainly medium to fine grain sands.

Kuranui Bay

This location has been sampled in the past by Environment Waikato and elevated mercury and zinc concentrations were detected. No mining activities are known to have occurred in this catchment, but there are a number of old mines nearby surrounding the Thames township. Access to the site was gained from the shore. Seven composite sediment samples (each made of five 0-10 cm sub-samples) were collected in the intertidal zone surrounding the stream mouth, with a plastic hand trowel. One of these was analysed in duplicate for quality assurance purposes. In addition, a vertical profile sample was collected using a sediment corer, with sub-samples from depths 0-2 cm, 2-10 cm, 15-20 cm and 25-30 cm being analysed individually (Appendix 1). Sediments from this site were found to consist of mainly fine to medium grain silts. All sediment samples were collected from the south side of the Pukehinau Stream and SDB 562 was collected from around the area of a stormwater pipe.

Appendix 2. Measured concentrations of eight trace elements in 78 sediment samples collected as part of this study.

Unless otherwise indicated sampling depths are 0-10 cm or surface grab samples (see Appendix 1). All element concentrations are in mg/kg (ppm) dry weight.

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Li	Fe	Al	% Fines
Te Mata													
Near beach	SDV790	23.4	0.03	19.9	11.4	0.16	8.4	25.9	60.4				
	SDV795	27.3	0.03	21.5	11.3	0.15	9.1	30.6	64.4				
	SDV794	27.4	0.03	20.3	11	0.16	8.2	30	62.9				
Far beach	SDV791	27.3	0.03	21.5	11.3	0.15	9.1	30.6	64.4				
	SDV792	26.9	0.03	20.9	11.5	0.16	8.6	30.8	64.3	17	32300	18300	4.81
	SDV793	28.1	0.03	20	11.2	0.15	8.4	31.5	64.1				
Tapu													
Near beach	SDV796	23.4	0.02	22.7	13.9	0.11	8.7	9.32	58.2				
	SDV801	18.8	0.02	19.2	13.7	0.09	8.1	8.16	53.1				
	SDV800	16.9	0.03	19.5	13.7	0.13	8.4	11.1	57.4				
Far beach	SDV797	27.3	0.02	18.3	14	0.21	8.2	5.63	51.5				
	SDV798	19.7	0.02	17.8	14.4	0.1	8.4	6.74	52.4	16	25600	12900	1.36
	SDV799	21	0.02	19.8	14.2	0.1	8.2	7.93	53.7				
Waiomu Bay													
Near beach	SDB611	34.5	0.1	26.1	39.9	0.08	8.9	45	79.2				
	SDB613	26.3	0.12	30	34.1	0.06	9.8	37.5	83.3				
Far beach	SDB612	34	0.17	30.9	41.6	0.09	8.6	65.3	97.1	17	44900	8830	2.14
	QA/QC Duplicate (SDB 594)	25.9	0.1	29.2	39.4	0.07	9.8	29.7	84.1				
	SDB614	29.6	0.1	26.9	35.2	0.16	9.4	30.7	82.6	15	35900	8890	1.11
Stream	SDB 615	21	0.02	20.8	17	0.07	7.9	20.9	71.7				
Depth samples													
0-2 cm	SDB619A	21	<0.1	22	21	<0.1	8	26.5	79				
2-10 cm	SDB619B	26	<0.1	22	26	<0.1	8	26.9	81				
15-20 cm	SDB619C	23	<0.1	23	26	<0.1	9	28.9	81				
25-30 cm	SDB619D	27	<0.1	22	30	<0.1	8	31.6	84				
Te Puru													
Near beach	SDB604	22.4	0.03	22.4	20.4	0.06	8.2	19.2	69.2				
	SDB603	25	0.18	12.9	21.9	0.15	5.3	19.2	81.2				
	SDB606	26.4	0.04	24.3	22.5	0.08	8.3	20.9	73.7				
Far beach	SDB609	26.5	0.04	24.6	26.5	0.09	8.6	21.1	76.4				
	SDB608	26.4	0.04	24.3	22.5	0.08	8.3	20.9	73.7	23	38500	13100	2.1
	SDB607	22.8	0.03	22.5	20	0.06	8.3	18.6	68.3				
Depth samples													
0-2 cm	SDB816	21.6	0.03	20.9	19.4	0.13	8	20	65.2				
2-10 cm	SDB817	23.6	0.04	21.5	18.6	0.07	7.5	23.4	69.6				
15-20 cm	SDB818	14.5	0.04	16.4	19.6	0.1	6.1	16.2	61.9				
25-30 cm	SDB819	17	0.04	17	18.5	0.09	6.2	19.8	65.8				

Appendix 2 continued...

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Li	Fe	Al	% Fines
Thornton													
Near beach	SDV802	21.9	0.03	20.6	17.2	0.07	8.2	22.7	72.1				
	SDV803	24.4	0.03	22	19.3	0.08	7.8	20	70.2				
	SDV804	24	0.03	20.6	18.3	0.07	8	19.6	69.4				
Far beach	SDB615	21	0.02	20.8	17	0.07	7.9	20.9	71.7				
	SDB616	24.1	0.03	22.8	17.4	0.08	8.6	26.3	78.6	20	32400	11000	2.35
	SDB621	22.7	0.04	22.1	17.6	0.09	8.3	23.6	74				
Tararu Stream													
Near beach	SDB602	20.5	0.12	26.7	14	0.34	9	30.5	100	31	37500	23400	86.6
	SDB601	23.1	0.18	14.2	23.3	0.15	5	24.5	93.8				
	SDB600	30.4	0.07	13.9	23.8	0.15	5.5	25.4	87.6				
Far beach	SDB597	21.1	0.16	13.5	20.9	0.18	5.7	25.5	80.3				
	SDB598	25.9	0.1	15.3	25.7	0.15	5.8	24.4	92	18	40800	12500	2.99
	QA/QC Duplicate (SDB 595)	26.3	0.21	15.8	31.3	0.14	5.6	24.1	104				
	SDB599	24.4	0.32	14.8	22.3	0.14	5.7	24.8	136				
Kuranui Bay													
Near beach	SDB563	20.7	0.34	22.4	15.8	0.36	7.6	28.7	130				
	SDB560	20.7	0.34	22.4	15.8	0.36	7.6	28.7	130				
	SDB558	36.9	0.21	21.8	12.7	1.12	7.6	26.9	102				
	QA/QC Duplicate (SDB 591)	23.4	0.18	25	12.1	0.53	8.6	29.2	102				
Far beach	SDB561	73.7	0.69	16.1	22.3	1.43	6.8	30	206				
	SDB559	23.4	0.18	25	12.1	0.53	8.6	29.2	102	29	30000	23300	87.2
	SDB562	79.3	0.61	18.2	23.1	1.46	7.5	28.2	181	20	32900	13500	37.7
Depth samples													
0-2 cm	SDB812	16.8	0.19	29	12.9	0.35	9.5	33.9	116				
2-10 cm	SDB813	30	0.92	24.5	20.5	0.73	9.1	34.5	243				
15-20 cm	SDB814	50	0.71	24.6	22.7	0.89	9.5	48.8	222				
25-30 cm	SDB815	149	2.07	16.4	44.6	5.14	7.4	60.7	469	17	30300	12300	61.2
Thames Wharf and stormwater													
	SDB567	8.7	0.1	22.8	10	0.21	7.3	25	80				
	SDB602	20.5	0.12	26.7	14	0.34	9	30.5	100				
Thames mudflats													
	SDB580	14.2	0.05	26.9	16.2	0.16	8.7	14.3	62.1				
	SDB581	15.6	0.08	24.9	16.4	0.19	8.5	15.9	65.9	15	34700	20500	19.1
	SDB582	13.8	0.03	21.9	13.5	0.14	8.8	15.5	56.2				
	SDB583	15.1	0.05	23.6	14.2	0.17	8.6	17	59.7				
	SDB584	17.1	0.05	28.7	18.5	1.52	8.5	12.3	57.4	12	33200	16600	9.49
	SDB585	14.3	0.06	21.7	14.1	0.15	8.4	16.1	59.7				
	SDB576Av	15.5	0.05	27	16.1	0.47	8.6	14.9	63.1	14	34100	15300	4.76
	SDB573Av	12.1	0.12	22.3	10.1	0.22	8	24.9	78.9	21	29800	17000	58.8
Deeper Thames Harbour													
	SDB569	9.6	0.23	26.4	11.1	0.34	9	32.5	113				
Thames pipeline													
	SDB564	27.1	0.31	26.5	15.8	0.42	9.3	37.1	143				
	SDB565	25.7	0.53	26.3	18.5	0.54	9.5	39.5	183	27	31900	23300	94.6
	SDB566	433	0.32	22.9	16.5	0.53	8.5	40	145	23	53400	18900	77.7
0-2 cm	SDB810	16.3	0.32	25	14.3	0.37	8.7	30.7	124				
2-10 cm	SDB811	28.5	0.5	19.2	19.3	0.49	7.7	30.7	151				

Appendix 2 continued...

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Li	Fe	Al	% Fines
Waihou River mouth													
	SDB574	5.1	0.08	31.4	7.6	0.14	8.4	19	72.3				
	SDB575	9.4	0.14	30.1	12.2	0.29	10	34	111	31	33500	26500	95.8
Piako River mouth													
	SDB578	7.5	0.19	21.5	9.3	0.28	7.6	25.7	90.9				
	SDB579	10.5	0.27	25.3	10.9	0.33	8.9	30.8	113	22	24800	18800	93.7
	SDB571	9.6	0.22	26.1	10.9	0.34	8.9	31.9	107	26	27500	19600	94
Opani mudflat													
	SDB568	7.5	0.17	25.1	9.7	0.27	8.4	28.9	98.5				

Appendix 3. Quality assurance and quality control results

A. Sampling and measurement precision in relation to site heterogeneity

Six composited samples were re-composited by the laboratory to evaluate the variability in both the sample and the laboratory procedures. To determine the precision of the analysis, the relative percentage differences (RPD) is calculated for replicate samples via the procedure outlined in section 1020 of the American Public Health Association (APHA) standard method. If the RPD is within ± 25% the analysis is considered to be acceptable. RPD were calculated for various samples within each sample run and compared to one another. Results are provided in Table 1.

Table 1. Relative percentage difference (RPD) of replicate samples.

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	SDB612	34	0.17	30.9	41.6	0.09	8.6	65.3	97.1
QA/QC	SDB 594 (dup. SDB612)	25.9	0.1	29.2	39.4	0.07	9.8	29.7	84.1
	SDV792	27.4	0.03	20.3	11	0.16	8.2	30	62.9
QA/QC	SDB 593 (dup. SVB792)	26.5	0.03	21.4	11.9	0.15	9	31.5	65.6
	SDB558	36.9	0.21	21.8	12.7	1.12	7.6	26.9	102
QA/QC	SDB591 (dup. SDB558)	23.4	0.18	25	12.1	0.53	8.6	29.2	102
	SDB598	25.9	0.1	15.3	25.7	0.15	5.8	24.4	92
QA/QC	SDB 595 (dup. SDB598)	26.3	0.21	15.8	31.3	0.14	5.6	24.1	104
OZ	SDB573B	11.1	0.11	24.4	11.7	0.23	8.4	26.5	83.7
QA/QC	SDD573E	13	0.12	20.1	8.4	0.2	7.5	23.2	74
	SDB580	14.2	0.04	26.1	16	0.12	8.7	14	61.1
QA/QC	SDB590 (dup. SDB580)	14.1	0.05	27.7	16.3	0.19	8.6	14.5	63.1
Relative percentage difference									
	612/594	27.0	51.9	5.7	5.4	25.0	-13.0	74.9	14.3
	792/593	3.3	0.0	-5.3	-7.9	6.5	-9.3	-4.9	-4.2
	558/591	44.8	15.4	-13.7	4.8	71.5	-12.3	-8.2	0.0
	598/595	-1.5	-71.0	-3.2	-19.6	6.9	3.5	1.2	-12.2
	573B/573E	-15.8	-8.7	19.3	32.8	14.0	11.3	13.3	12.3
	580/590	0.7	-22.2	-5.9	-1.9	-45.2	1.2	-3.5	-3.2

The RPD for arsenic, cadmium, mercury and lead in sample SDB612/SDB594 are greater than the quality control criteria. The composites of this sample were re-analysed to determine if the variability was due to analytical variability, sample variability or sample heterogeneity. The lead concentration in sample SDB612 was significantly higher than in any other surficial sample collected in this study. To determine if result was caused by a single high sub-sample, each of the sub-samples was re-analysed. A comparison of the average values of the all of the sub samples with the reported values of the composite SDB612 shows that the RDP for cadmium, mercury and lead are outside the acceptable range. The high variability of cadmium and mercury may be due to low concentrations of those samples present in the sediment. Analytical values near the sample detection limit will have a larger signal-to-noise ratio and, therefore, a greater RDP between replicates. Several other QA/QC samples (SDB598/595 for cadmium and SDB580/590 and SDB558/591 mercury) also display high RDP for these compounds which may be due to relatively low concentrations of these compounds presents in the samples. The variability in the arsenic concentration in the sub-samples and the composite are similar, which suggest the variability between replicates SDB594 and SDB612 is not due to the compositing or sample heterogeneity. The large variability in lead between SDB594 and SDB612 was not reproduced in the subsequent re-analysis of the sub-samples (Table 2). It is likely, therefore, that this outlier was caused by a small grain of lead minerals or metallic lead being present in the sample, which skewed the analytical result. Therefore, the first result (the outlier) was not considered to adequately represent the composition of the sediment in this location.

Table 2. Analysis of individual sub-samples of Composite SDB612.

Sample number		**As**	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
SBD612A		31.7	0.08	22.1	35.5	0.06	8.6	33.8	79.9
SDB612B		34.1	0.1	32.7	39.6	0.05	9.2	31.5	85.8
SDB612C		41.4	0.12	25.5	35.4	0.07	7.9	32	90.3
SDB612D		29.8	0.11	24.2	39.8	0.06	8.7	35.3	84.4
SDB612E		34	0.1	24.5	39.7	0.06	8.2	28.2	81.5
	Average	34.2	0.10	25.8	38.0	0.06	8.5	32.2	84.4
	std dev	4.4	0.01	4.1	2.3	0.01	0.5	2.7	4.0
	95% conf error	5.5	0.02	5.0	2.9	0.01	0.6	3.3	5.0
	%conf error of mean	16.0	18.1	19.5	7.6	14.6	7.2	10.3	6.0
Value of Composite SDB612		34	0.17	30.9	41.6	0.09	8.6	65.3	97.1
	95% lower	28.7	0.08	20.8	35.1	0.05	7.9	28.8	79.4
	95% upper	39.7	0.12	30.8	40.9	0.07	9.1	35.5	89.4
	RDP	0.6	-50.0	-18.0	-9.0	-40.0	-0.9	-68.0	-14.0

Values highlighted in red exceed QA/QC criteria.

Quality control reports

Five quality control reports cover the analysis undertaken by Hills Laboratories for the various sample batches that were analysed. All quality control data contained with the reports were acceptable, except for sample batch 382278 (which includes samples collected from Te Mata Bay, Tapu, Thorton, Thames Harbour and Waihou River mouth). Duplicate samples for lead on sample 382504/4 had greater sample variation than would normally have been expected. Hills Laboratories believed that this variability was due to heterogeneity of the sample rather than analytical error or cross-contamination. This sample was not a sample submitted by URS and was not taken as part of this study.

Appendix 4. Metal concentrations in sediments normalised against various benchmark variables.

A. **Grain size normalisation: sediment metal concentration divided by percentage fines.** Normalised trace element concentrations are in mg/kg dry weight.

Location	Sample number	% Fines	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Waiomu Bay										
Far beach	SDB612	2.14%	1589	7.9	1444	1944	4.2	402	3051	4537
	SDB614	1.11%	2397	9.0	2424	3171	14.4	847	2766	7441
Te Mata										
Far beach	SDV792	4.81%	569.6	0.62	422.0	229	3.3	171	623.7	1308
Tapu										
Far beach	SDV798	1.36%	1449	1.5	1309	1059	7.4	618	495.6	3853
Thornton										
Far beach	SDB616	2.35%	1026	1.3	97	753	3.4	366	1119	3345
Kuranui Bay										
Far beach	SDB559	87.2%	27	0.21	28.7	13.9	0.61	9.9	33.5	117
	SDB562	37.7%	210	1.6	48.3	61.3	3.9	19.9	74.8	480
Depth samples	SDB815 (25-30cm)	61.2%	244	3.4	26.8	72.9	8.4	12.1	99.2	766
Te Puru										
Far beach	SDB608	2.1%	125	1.9	1157	1071	3.8	395	995	3510
Tararu Stream										
Near beach	SDB602	86.6%	23.7	0.14	30.8	16.2	0.39	10.4	35.2	116
Far beach	SDB598	2.99	866	3.3	512	860	5.0	194	816	3077
Thames Harbour										
	SDB581	19.1%	40.8	0.21	65.2	42.9	0.50	22.3	41.6	173
	SDB584	9.49%	180	0.53	302	195	16.0	90	130	605
	SDB576A	4.76%	309	1.1	588	349	4.2	186	336	1475
Thames stormwater pipeline										
	SDB565A	94.6%	27.2	0.56	27.8	19.6	0.57	10.0	41.8	193
	SDB566A	77.7%	557	0.41	29.5	21.2	0.68	10.9	51.5	187
Thames stormwater (near shore)										
	SDB602	86.6%	23.7	0.14	30.8	16.2	0.39	10.4	35.2	116
Waihao River										
	SDB573B	58.8%	18.9	0.19	41.5	19.9	0.39	14.3	45.1	142
Inland River mouth										
	SDB575	95.8%	9.8	0.15	31.4	12.7	0.30	10.4	35.5	116

Location	Sample number	% Fines	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	SDB579	93.7%	11.2	0.29	27.0	11.6	0.35	9.5	32.9	121
	SDB571	94.0%	10.2	0.23	27.8	11.6	0.36	9.5	33.9	114

B. Grain size normalisation. Metal concentration divided by lithium concentration (normalised figures are unitless).

			As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Location	**Sample number**	**Li (mg/kg)**	**Metal Conc/Li**							
Waiomu Bay										
Far beach	SDB612	16.5	2.1	0.01	1.9	2.5	0.01	0.52	4.0	5.9
	SDB614	15.2	1.9	0.01	1.8	2.3	0.01	0.62	2.0	5.4
Te Mata										
Far beach	SDV792	17.1	1.6	0.002	1.2	0.64	0.01	0.48	1.8	3.7
Tapu										
Far beach	SDV798	15.7	1.3	0.001	1.1	0.92	0.01	0.54	0.43	3.3
Thornton										
Far beach	SDB616	20.3	1.2	0.001	1.1	0.86	0.004	0.42	1.3	3.9
Kuranui Bay										
Far beach	SDB559	28.6	0.82	0.01	0.87	0.42	0.02	0.30	1.0	3.6
	SDB562	19.5	4.1	0.03	0.93	1.2	0.07	0.38	1.4	9.3
Depth samples	SDB815 (25-30cm)	17.0	8.8	0.12	0.96	2.6	0.30	0.44	3.6	27.6
Te Puru										
Far beach	SDB608	23.1	1.1	0.002	1.1	0.97	0.003	0.36	0.90	3.2
Tararu Stream										
Near beach	SDB602	31.4	0.65	0.004	0.85	0.45	0.01	0.29	0.97	3.2
Far beach	SDB598	17.7	1.5	0.01	0.86	1.5	0.01	0.33	1.38	5.2
Thames Harbour										
	SDB581	14.9	1.0	0.01	1.7	1.1	0.01	0.57	1.1	4.4
	SDB584	11.6	1.5	0.004	2.5	1.6	0.13	0.73	1.1	4.9
QA/QC	SDB576A	13.5	1.1	0.004	2.1	1.2	0.01	0.67	1.2	5.2
Thames stormwater pipeline										
	SDB565A	26.9	0.96	0.02	0.98	0.69	0.02	0.35	1.5	6.8
	SDB566A	22.6	19.2	0.01	1.0	0.73	0.02	0.38	1.8	6.4
Thames stormwater (near shore)										
	SDB602	31.4	0.65	0.004	0.85	0.45	0.01	0.29	0.97	3.2
Waihao River (outer zone)										
OZ	SDB573B	21.1	0.53	0.01	1.2	0.55	0.01	0.40	1.3	4.0
Inland river mouth										
	SDB575	30.8	0.31	0.005	0.98	0.34	0.01	0.32	1.1	3.6
	SDB579	22.2	0.47	0.01	1.1	0.49	0.01	0.40	1.4	5.1
	SDB571	25.8	0.37	0.01	1.0	0.42	0.01	0.34	1.2	4.1

C. Grain size normalisation Metal concentration divided by iron concentration

(normalised figures are unitless).

			As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Location	**Sample Number**	**Fe (mg/kg)**	**Metal Conc/Fe (x 10^{-4})**							
Waiomu Bay										
Far beach	SDB612	44900	7.6	0.04	6.9	9.3	0.02	1.9	14.5	21.6
	SDB614	35900	8.2	0.03	7.5	9.8	0.04	2.6	8.6	23.0
Te Mata										
Far beach	SDV792	32300	8.5	0.01	6.3	3.4	0.05	2.5	9.3	19.5
Tapu										
Far beach	SDV798	25600	7.7	0.01	7.0	5.6	0.04	3.3	2.6	20.5
Thornton										
Far beach	SDB616	32400	7.4	0.01	7.0	5.4	0.02	2.7	8.1	24.3
Kuranui Bay										
Far beach	SDB559	30000	7.8	0.06	8.3	4.0	0.18	2.9	9.7	34.0
	SDB562	32900	24.1	0.19	5.5	7.0	0.44	2.3	8.6	55.0
Depth samples	SDB815 (25-30cm)	30300	49.2	0.68	5.4	14.7	1.7	2.4	20.0	154.8
Te Puru										
Far beach	SDB608	38500	6.9	0.01	6.3	5.8	0.02	2.2	5.4	19.1
Tararu Stream										
Near beach	SDB602	37500	5.5	0.03	7.1	3.7	0.09	2.4	8.1	26.7
Far beach	SDB598	40800	6.3	0.02	3.8	6.3	0.04	1.4	6.0	22.5
Thames Harbour										
	SDB581	34700	4.5	0.02	7.2	4.7	0.05	2.4	4.6	19.0
	SDB584	33200	5.2	0.02	8.6	5.6	0.46	2.6	3.7	17.3
QA/QC	SDB576A	34100	4.3	0.01	8.2	4.9	0.06	2.6	4.7	20.6
Thames stormwater pipeline										
	SDB565A	31900	8.1	0.17	8.2	5.8	0.17	3.0	12.4	57.4
	SDB566A	53400	81.1	0.06	4.3	3.1	0.10	1.6	7.5	27.2
Thames stormwater (near shore)										
	SDB602	37500	5.5	0.03	7.1	3.7	0.09	2.4	8.1	26.7
Waihao River (outer zone)										
OZ	SDB573B	29800	3.7	0.04	8.2	3.9	0.08	2.8	8.9	28.1
Inland river mouth										
	SDB575	33500	2.8	0.04	9.0	3.6	0.09	3.0	10.1	33.1
	SDB579	24800	4.2	0.11	10.2	4.4	0.13	3.6	12.4	45.6
	SDB571	27500	3.5	0.08	9.5	4.0	0.12	3.2	11.6	38.9

D. Grain size normalisation. Metal concentration divided by aluminium concentration (normalised figures are unitless).

			As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
Location	**Sample Number**	**Al mg/kg**	**Metal Conc/Al (x 10^{-4})**							
Waiomu Bay										
Far beach	SDB612	8830	35.5	0.19	35.0	47.1	0.10	9.7	74.0	110.0
	SDB614	8890	33.3	0.11	30.3	40.0	0.18	10.6	34.5	92.9
Te Mata										
Far beach	SDV792	18300	15.0	0.02	11.1	6.0	0.09	4.5	16.4	34.4
Tapu										
Far beach	SDV798	12900	15.3	0.02	13.8	11.2	0.08	6.5	5.2	40.6
Thornton										
Far beach	SDB616	11000	21.9	0.03	20.7	15.8	0.07	7.8	23.9	71.5
Kuranui Bay										
Far beach	SDB559	23300	10.0	0.08	10.7	5.2	0.23	3.7	12.5	43.8
	SDB562	13500	58.7	0.45	13.5	17.1	1.1	5.6	20.9	134.1
Depth samples	SDB815 (25-30cm)	12300	121.1	1.7	13.3	36.3	4.2	6.0	49.3	381.3
Te Puru										
Far beach	SDB608	13100	20.2	0.03	18.5	17.2	0.06	6.3	16.0	56.3
Tararu Stream										
Near beach	SDB602	23400	8.8	0.05	11.4	6.0	0.15	3.8	13.0	42.7
Far beach	SDB598	12500	20.7	0.08	12.2	20.6	0.12	4.6	19.5	73.6
Thames Harbour										
	SDB581	20500	7.6	0.04	12.1	8.0	0.09	4.1	7.8	32.1
	SDB584	16600	10.3	0.03	17.3	11.1	0.92	5.1	7.4	34.6
QA/QC	SDB576A	15300	9.6	0.03	18.3	10.8	0.13	5.9	10.5	45.9
Thames stormwater pipeline										
	SDB565A	23300	11.0	0.23	11.3	7.9	0.23	4.1	17.0	78.5
	SDB566A	18900	229.1	0.17	12.1	8.7	0.28	4.5	21.2	76.7
Thames stormwater (near shore)										
	SDB602	23400	8.8	0.05	11.4	6.0	0.15	3.8	13.0	42.7
Waihao River (outer zone)										
OZ	SDB573B	17000	6.5	0.06	14.4	6.9	0.14	4.9	15.6	49.2
Inland river mouth										
	SDB575	26500	3.5	0.05	11.4	4.6	0.11	3.8	12.8	41.9
	SDB579	18800	5.6	0.14	13.5	5.8	0.18	4.7	16.4	60.1
	SDB571	19600	4.9	0.11	13.3	5.6	0.17	4.5	16.3	54.6

Appendix 5. Statistical summary of results for eight trace elements in each of the ten areas sampled.

All results are mg/kg dry wt. Individual sample results highlighted in yellow exceed the ANZECC (2000) ISQG-Low; those in red exceed the ANZECC ISQG-High (refer to Section 2.5).

Waiomu Bay								
	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
SDB611	34.5	0.1	26.1	39.9	0.08	8.9	45	79.2
SDB613	26.3	0.12	30	34.1	0.06	9.8	37.5	83.3
SDB612	34	0.17	30.9	41.6	0.09	8.6	65.3	97.1
SDB614	29.6	0.1	26.9	35.2	0.16	9.4	30.7	82.6
SDB 615	21	0.02	20.8	17	0.07	7.9	20.9	71.7
SDB 594	25.9	0.1	29.2	39.4	0.07	9.8	29.7	84.1
SDB619A	21	0.05	22	21	0.05	8	26.5	79
Maximum	21	0.02	20.8	17	0.05	7.9	20.9	71.7
Minimum	34	0.17	30.9	41.6	0.16	9.8	65.3	97.1
Median	26.3	0.10	26.9	35.2	0.07	8.9	30.7	82.6
Average	27.5	0.09	26.6	32.6	0.1	8.9	36.5	82.4
Std dev	5.5	0.05	3.9	9.7	0.0	0.8	14.9	7.7
95% conf error	6.9	0.06	4.9	12.1	0.0	1.0	18.5	9.6
%conf error of mean	25.0	63.5	18.3	37.0	54.5	11.0	50.5	11.6
Guideline value	20	1.5	80	65	0.15	21	50	200
Definitely below TV	15.0	0.5	65.4	40.9	0.1	18.7	24.7	176.8
Definitely above GL	25.0	2.5	94.6	89.1	0.2	23.3	75.3	223.2
95% lower	20.6	0.0	21.7	20.5	0.0	7.9	18.1	72.9
95% upper	34.3	0.2	31.4	44.7	0.1	9.9	55.0	92.0

Te Mata								
	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
SDV790	23.4	0.03	19.9	11.4	0.16	8.4	25.9	60.4
SDV795	27.3	0.03	21.5	11.3	0.15	9.1	30.6	64.4
SDV794	27.4	0.03	20.3	11	0.16	8.2	30	62.9
SDV791	29.6	0.1	26.9	35.2	0.16	9.4	30.7	82.6
SDV792	27.4	0.03	20	11.2	0.15	8.4	31.5	64.1
SDV793	21	0.02	20.8	17	0.07	7.9	20.9	71.7
SDB 593	25.9	0.1	29.2	39.4	0.07	9.8	29.7	84.1
Minimum	21	0.02	19.9	11	0.07	7.9	20.9	60.4
Maximum	29.6	0.1	29.2	39.4	0.16	9.8	31.5	84.1
Median	27.3	0.03	20.8	11.4	0.15	8.4	30	64.4
Average	26.0	0.05	22.7	19.5	0.1	8.7	28.5	70.0
Std dev	2.9	0.04	3.8	12.4	0.0	0.7	3.8	9.7
95% conf error	3.6	0.04	4.7	15.4	0.1	0.9	4.7	12.1
%conf error of mean	13.8	90.3	20.7	79.0	39.9	9.9	16.6	17.3
Guideline value	20	1.5	80	65	0	21	50	200
Definitely below GL	17.2	0.1	63.4	13.7	0.1	18.9	41.7	165.5
Definitely above GL	22.8	2.9	96.6	116.3	0.2	23.1	58.3	234.5
95% lower	22.4	0.00	18.0	4.1	0.1	7.9	23.8	57.9
95% upper	29.6	0.09	27.4	34.9	0.2	9.6	33.2	82.1

Tapu								
	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
SDV796	23.4	0.02	22.7	13.9	0.11	8.7	9.32	58.2
SDV801	18.8	0.02	19.2	13.7	0.09	8.1	8.16	53.1
SDV800	16.9	0.03	19.5	13.7	0.13	8.4	11.1	57.4
SDV797	27.3	0.02	18.3	14	0.21	8.2	5.63	51.5
SDV798	19.7	0.02	17.8	14.4	0.1	8.4	6.74	52.4
SDV799	21	0.02	19.8	14.2	0.1	8.2	7.93	53.7
Minimum	27.3	0.03	22.7	14.4	0.21	8.7	11.1	58.2
Maximum	16.9	0.02	17.8	13.7	0.09	8.1	5.63	51.5
Median	20.35	0.02	19.4	14	0.11	8.3	8	53.4
Average	21.2	0.02	19.6	14.0	0.1	8.3	8.1	54.4
Std dev	3.7	0.004	1.7	0.3	0.04	0.2	1.9	2.8
95% conf error	4.6	0.01	2.1	0.3	0.1	0.3	2.4	3.4
%conf error of mean	21.7	23.4	10.9	2.5	44.9	3.2	29.3	6.3
Guideline value	20	1.5	80	65	0	21	50	200
Definitely below GL	15.7	1.1	71.3	63.4	0.1	20.3	35.4	187.4
Definitely above GL	24.3	1.9	88.7	66.6	0.2	21.7	64.6	212.6
95% lower	16.6	0.0	17.4	13.6	0.1	8.1	5.8	51.0
95% upper	25.8	0.0	21.7	14.3	0.2	8.6	10.5	57.8

Thornton								
	As	**Cd**	**Cr**	**Cu**	**Hg**	**Ni**	**Pb**	**Zn**
SDV802	21.9	0.03	20.6	17.2	0.07	8.2	22.7	72.1
SDV803	24.4	0.03	22	19.3	0.08	7.8	20	70.2
SDV804	24	0.03	20.6	18.3	0.07	8	19.6	69.4
SDB615	21	0.02	20.8	17	0.07	7.9	20.9	71.7
SDB616	24.1	0.03	22.8	17.4	0.08	8.6	26.3	78.6
SDB621	22.7	0.04	22.1	17.6	0.09	8.3	23.6	74
Minimum	21	0.02	20.6	17	0.07	7.8	19.6	69.4
Maximum	24.4	0.04	22.8	19.3	0.09	8.6	26.3	78.6
Median	23.35	0.03	21.4	17.5	0.075	8.1	21.8	71.9
Average	23.0	0.03	21.5	17.8	0.1	8.1	22.2	72.7
Std dev	1.6	0.01	0.7	1.1	0.0	0.2	1.4	1.3
95% conf error	2.0	0.01	0.8	1.3	0.0	0.2	1.7	1.6
%conf error of mean	8.8	20.7	3.9	7.4	8.1	2.6	7.7	2.2
Guideline value	20	1.5	80	65	0	21	50	200
Definitely below GL	18.2	1.2	76.9	60.2	0.1	20.5	46.1	195.7
Definitely above GL	21.8	1.8	83.1	69.8	0.2	21.5	53.9	204.3
95% lower	21.0	0.02	20.6	16.5	0.1	7.9	20.5	71.1
95% upper	25.0	0.04	22.3	19.1	0.1	8.3	23.9	74.2

Kuranui Bay								
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SDB563	20.7	0.34	22.4	15.8	0.36	7.6	28.7	130
SDB560	20.7	0.34	22.4	15.8	0.36	7.6	28.7	130
SDB561	73.7	0.69	16.1	22.3	1.43	6.8	30	206
SDB559	23.4	0.18	25	12.1	0.53	8.6	29.2	102
SDB562	79.3	0.61	18.2	23.1	1.46	7.5	28.2	181
SDB591	23.4	0.18	25	12.1	0.53	8.6	29.2	102
SDB812	16.8	0.19	29	12.9	0.35	22.4	33.9	116
EW KB	19.4	0.34	15.7	21.2	0.84	6.4	42.9	199
Minimum	16.8	0.18	15.7	12.1	0.35	6.4	28.2	102
Maximum	79.3	0.69	29	23.1	1.46	22.4	42.9	206
Median	22.05	0.34	15.8	22.4	0.53	7.6	29.2	130
Average	34.7	0.4	21.7	16.9	0.73	9.4	31.4	145.8
Std dev	25.9	0.2	4.7	4.6	0.5	5.3	5.0	43.0
95% conf error	32.2	0.24	5.9	5.8	0.6	6.6	6.2	53.3
%conf error of mean	92.9	67.5	26.9	34.0	79.3	69.6	19.8	36.6
Guideline value	20	1.5	80	65	0	21	50	200
Definitely below GL	1.4	0.5	58.4	42.9	0.0	6.4	40.1	126.8
Definitely above GL	38.6	2.5	101.6	87.1	0.3	35.6	59.9	273.2
95% lower	2.5	0.1	15.9	11.2	0.2	2.9	25.1	92.4
95% upper	66.9	0.6	27.6	22.7	1.3	16.0	37.6	199.1

Te Puru								
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SDB604	22.4	0.03	22.4	20.4	0.06	8.2	19.2	69.2
SDB603	25	0.18	12.9	21.9	0.15	5.3	19.2	81.2
SDB606	26.4	0.04	24.3	22.5	0.08	8.3	20.9	73.7
SDB609	26.5	0.04	24.6	26.5	0.09	8.6	21.1	76.4
SDB608	26.4	0.04	24.3	22.5	0.08	8.3	20.9	73.7
SDB607	22.8	0.03	22.5	20	0.06	8.3	18.6	68.3
SDB816	21.6	0.03	20.9	19.4	0.13	8	20	65.2
Minimum	21.6	0.03	12.9	19.4	0.06	5.3	18.6	65.2
Maximum	26.5	0.18	24.6	26.5	0.15	8.6	21.1	81.2
Median	25	0.04	22.5	21.9	0.08	8.3	20	73.7
Average	24.4	0.06	21.7	21.9	0.09	7.9	20.0	72.5
Std dev	2.1	0.06	4.1	2.4	0.03	1.1	1.0	5.4
95% conf error	2.6	0.07	5.1	3.0	0.04	1.4	1.2	6.7
%conf error of mean	10.8	122.6	23.5	13.5	46.1	18.0	6.2	9.3
Guideline value	20	1.5	80	65	0	21	50	200
Definitely below GL	17.8	-0.3	61.2	56.2	0.1	17.2	46.9	181.5
Definitely above GL	22.2	3.3	98.8	73.8	0.2	24.8	53.1	218.5
95% lower	21.8	-0.01	16.6	18.9	0.1	6.4	18.7	65.8
95% upper	27.1	0.12	26.8	24.8	0.1	9.3	21.2	79.2

Tararu Stream	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SDB602	20.5	0.12	26.7	14	0.34	9	30.5	100
SDB601	23.1	0.18	14.2	23.3	0.15	5	24.5	93.8
SDB600	30.4	0.07	13.9	23.8	0.15	5.5	25.4	87.6
SDB597	21.1	0.16	13.5	20.9	0.18	5.7	25.5	80.3
SDB598	25.9	0.1	15.3	25.7	0.15	5.8	24.4	92
SDB599	24.4	0.32	14.8	22.3	0.14	5.7	24.8	136
SDB 595	26.3	0.21	15.8	31.3	0.14	5.6	24.1	104
Minimum	20.5	0.07	13.5	14	0.14	5	24.1	80.3
Maximum	30.4	0.32	26.7	31.3	0.34	9	30.5	136
Median	24.4	0.16	14.8	23.3	0.15	5.7	24.8	93.8
Average	24.5	0.17	16.3	23.0	0.18	6.0	25.6	99.1
Std dev	3.4	0.08	4.6	5.2	0.07	1.3	2.2	18.0
95% conf error	4.2	0.10	5.8	6.5	0.09	1.7	2.8	22.4
%conf error of mean	17.2	62.4	35.4	28.1	50.4	27.3	10.8	22.6
Guideline value	20	1.5	80	65	0.15	21	50	200
Definitely below GL	16.6	0.6	51.7	46.8	0.07	15.3	44.6	154.8
Definitely above GL	23.4	2.4	108.3	83.2	0.23	26.7	55.4	245.2
95% lower	20.3	0.06	10.5	16.6	0.1	4.4	22.8	76.7
95% upper	28.8	0.27	22.1	29.5	0.3	7.7	28.4	121.5

Waihou River								
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SDB573B	11.1	0.11	24.4	11.7	0.23	8.4	26.5	83.7
SDD573E	13	0.12	20.1	8.4	0.2	7.5	23.2	74
SDB574	5.1	0.08	31.4	7.6	0.14	8.4	19	72.3
SDB575	9.4	0.14	30.1	12.2	0.29	10	34	111
SDB568	7.5	0.17	25.1	9.7	0.27	8.4	28.9	98.5
SDB569	9.6	0.23	26.4	11.1	0.34	9	32.5	113
SDB578	7.5	0.19	21.5	9.3	0.28	7.6	25.7	90.9
SDB579	10.5	0.27	25.3	10.9	0.33	8.9	30.8	113
SDB571	9.6	0.22	26.1	10.9	0.34	8.9	31.9	107
SDB580	14.2	0.04	26.1	16	0.12	8.7	14	61.1
SDB590	14.1	0.05	27.7	16.3	0.19	8.6	14.5	63.1
Minimum	5.1	0.04	20.1	7.6	0.12	7.5	14	61.1
Maximum	14.2	0.27	31.4	16.3	0.34	10	34	113
Median	9.6	0.14	26.1	10.9	0.27	8.6	26.5	90.9
Average	10.1	0.15	25.8	11.3	0.25	8.6	25.5	89.8
Std dev	2.9	0.08	3.3	2.8	0.08	0.7	7.1	20.1
95% conf error	3.6	0.09	4.1	3.4	0.10	0.8	8.8	24.9
%conf error of mean	35.0	63.8	15.8	30.6	39.06	9.9	34.5	27.8
Guideline value	20	1.5	80	65	0.15	21	50	200
Definitely below GL	13.0	0.54	67.4	45.1	0.09	18.9	32.8	144.5
Definitely above GL	27.0	2.46	92.6	84.9	0.21	23.1	67.2	255.5
95% lower	6.6	0.05	21.8	7.8	0.15	7.7	16.7	64.9
95% upper	13.7	0.24	29.9	14.7	0.35	9.4	34.4	114.7

Thames Harbour								
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SDB581	15.6	0.08	24.9	16.4	0.19	8.5	15.9	65.9
SDB582	13.8	0.03	21.9	13.5	0.14	8.8	15.5	56.2
SDB583	15.1	0.05	23.6	14.2	0.17	8.6	17	59.7
SDB584	17.1	0.05	28.7	18.5	1.52	8.5	12.3	57.4
SDB585	14.3	0.06	21.7	14.1	0.15	8.4	16.1	59.7
SDB576A	14.7	0.05	28	16.6	0.2	9	16	70.2
SDB576B	16.3	0.04	21.7	14.6	0.17	7.2	12.5	52.5
SDB576C	17.8	0.04	30.7	17	1.58	8.8	15.3	64.3
SDB576D	15.8	0.04	24.4	16.1	0.2	8.5	13.2	55.8
SDB576E	12.7	0.07	30.3	16	0.22	9.4	17.5	72.9
SDB567	8.7	0.1	22.8	10	0.21	7.3	25	80
SDB602	20.5	0.12	26.7	14	0.34	9	30.5	100
Thames GC	13.2	0.05	16.5	10	0.22	8.1	28.9	62.2
Minimum	8.7	0.03	16.5	10	0.14	7.2	12.3	52.5
Maximum	20.5	0.12	30.7	18.5	1.58	9.4	30.5	100
Median	15.1	0.05	24.4	14.6	0.2	8.5	16	62.2
Average	15.0	0.06	24.8	14.7	0.4	8.5	18.1	65.9
Std dev	2.8	0.03	4.0	2.5	0.5	0.6	6.0	12.8
95% conf error	3.5	0.03	5.0	3.1	0.63	0.8	7.5	15.9
%conf error of mean	23.3	54.1	20.3	21.3	154.7	9.3	41.3	24.1
Guideline value	20	1.5	80	65	0.15	21	50	200
Definitely below GL	15.3	0.69	63.8	51.1	-0.08	19.1	29.4	151.7
Definitely above GL	24.7	2.31	96.2	78.9	0.38	22.9	70.6	248.3

Thames stormwater pipeline								
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SDB564	27.1	0.31	26.5	15.8	0.42	9.3	37.1	143
SDB565	25.7	0.53	26.3	18.5	0.54	9.5	39.5	183
SDB566	433	0.32	22.9	16.5	0.53	8.5	40	145
SDB810	16.3	0.32	25	14.3	0.37	8.7	30.7	124
Minimum	16.3	0.31	22.9	14.3	0.37	8.5	30.7	124
Maximum	433	0.53	26.5	18.5	0.54	9.5	40	183
Median	26.4	0.32	25.65	16.15	0.48	9	38.3	144
Average	125.5	0.37	25.2	16.3	0.47	9.0	36.8	148.8
Std dev	205.0	0.11	1.7	1.7	0.08	0.5	4.3	24.7
95% conf error	254.5	0.13	2.1	2.2	0.10	0.6	5.3	30.7
%conf error of mean	202.8	35.8	8.2	13.3	22.3	6.6	14.4	20.6
Guideline value	20	1.5	80	65	0	21	50	200
Definitely below GL	-20.6	1.0	73.5	56.4	0.1	19.6	42.8	158.7
Definitely above GL	60.6	2.0	86.5	73.6	0.2	22.4	57.2	241.3
95% lower	-129.0	0.24	23.1	14.1	0.4	8.4	31.5	118.1
95% upper	380.1	0.50	27.2	18.4	0.6	9.6	42.1	179.4

Appendix 6. Concentrations of 33 elements, total organic carbon and dry matter in composite shallow (0-2 cm) sediment samples collected in October 2003 from five locations in the Firth of Thames and five locations in Raglan Harbour.

All trace element concentrations are in units of mg/kg (dry weight). In all cases but the first Te Puru entry, composites comprised five equal samples from each location, with each sample comprising twelve subsamples. In the case of first Te Puru entry, samples that made up the composite were analysed individually, and the reported result for each element is the average of the five results. Results for the Te Puru composite sample compare well with these averages. This is a means of validating the composite analysis approach.

	Firth of Thames sites						. Raglan Harbour sites				
Constituent	**Te Puru**	**Te Puru**	**Kaiaua**	**Miranda**	**Kuranui Bay**	**Thames**	**Ponganui Creek**	**Whatit-irinui Is**	**Te Puna Point**	**Okete Bay**	**Harot-o Bay**
Calcium	20960	22417	12100	27500	18600	10100	16300	26000	39200	13300	8980
Magnesium	5900	6147	3220	3390	5930	5560	2710	4040	3080	4130	4930
Sodium	4710	4938	3990	4210	5750	7920	5640	5930	5720	7070	8750
Potassium	908	934	1030	949	1110	1760	1150	1370	1090	1400	1970
Lithium	17.0	17.6	11.3	10.4	18.7	10.9	8.9	13.6	9.9	15.6	19.5
Rubidium	3.20	3.28	7.55	6.54	4.57	4.21	6.29	6.65	5.85	7.9	9.95
Phosphorus	376	385	212	215	364	343	347	552	554	649	543
Boron	8.60	8.83	11	10	13	12	15	16	14	18	22
Iron	32600	33033	15000	11200	29200	27200	13700	25300	23400	24900	28200
Manganese	549	567	327	272	1480	747	131	299	261	300	297
Silver	0.076	0.092	0.05	0.05	0.3	0.09	0.02	< 0.02	0.15	0.03	0.03
Aluminium	10140	10617	6470	4880	9300	14400	6020	10600	8180	12600	14300
Arsenic	16.84	17.3	5.3	4.3	19.4	13.2	6.9	7.7	7.2	9	10.9
Barium	4.82	4.91	6.76	5.16	4.94	9.12	7.66	12.8	11.6	14.2	18
Bismuth	0.294	0.285	0.07	0.04	0.3	0.13	0.04	0.05	0.04	0.07	0.1
Cadmium	0.04	0.04	0.02	0.03	0.34	0.05	0.03	0.02	0.02	0.02	0.03
Cobalt	11.3	11.7	9.11	5.85	12.2	11.2	3.85	8.23	7.74	8.27	8.98
Chromium	21.3	21.9	7.1	7.1	15.7	16.5	10.5	14.5	13.2	16.8	17.2
Caesium	0.752	0.763	0.92	0.74	1.2	0.53	0.59	0.73	0.61	0.9	1.17
Copper	17.5	17.6	5.4	3.7	21.2	10	3.3	7	6.1	8.4	9
Mercury	0.472	0.103	0.05	0.05	0.84	0.22	0.02	0.02	0.02	0.03	0.04
Lanthanum	4.86	5.12	10	9.26	5.98	7.85	5.74	8.4	9.39	9.16	12.9
Molybdenum	0.906	0.925	0.2	0.18	1.22	0.59	0.34	0.3	0.36	0.37	0.42
Nickel	7.30	7.48	4.2	3.9	6.4	8.1	4.9	8.4	6.9	9.8	10.3
Lead	23.3	23.9	15.3	11.5	42.9	28.9	4.34	5.6	4.6	6.73	9.19
Antimony	0.590	0.602	0.15	0.04	0.81	0.28	0.11	0.12	0.12	0.12	0.16
Selenium	<2	<2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Strontium	140	151	72.7	151	105	75.2	84.7	143	189	80.2	64.7
Tin	0.40	0.35	0.4	0.3	0.6	0.5	0.3	0.4	0.4	0.5	0.7
Thallium	0.025	0.030	0.06	0.15	0.09	0.11	0.06	0.06	0.05	0.07	0.07
Uranium	0.286	0.317	0.474	0.444	0.338	0.367	0.591	0.635	0.593	0.555	0.649
Vanadium	64.2	65.0	23	17	46	45	32	78	84	74	48
Zinc	69.4	71.8	43.8	37	199	62.2	31.6	48.4	45.6	51	61.8
Total Organic Carbon (%)	0.162	0.162	0.234	0.248	0.33	-	0.428	0.506	0.528	0.655	0.846
Dry Matter (%)	68.4	68.4	73.3	72.6	67.4	-	71.3	67.5	68.2	62.1	56.6

Appendix 7. Results of Student's t-tests between Thames and Kuranui Bay sites and three mining reference sites (Te Puru, Thornton and Te Mata).

Mean values are in mg/kg (dry weight) and have not been normalised to any other variable. Ratios of means are unitless.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Mean of control sites (Te Puru, Thornton and Te Mata) (N=20)	24.7	0.040	21.3	17.3	0.105	8.16	23.8	69.7
Mean at Kuranui Bay (N=9)	36.1	0.407	22.71	16.37	0.763	8.1	29.92	145.8
Pooled t-test: concentration significantly higher than control site	No	No	No	No	No	No	No	No
Probability value (p)	0.019	0.0001	0.122	0.69	0.0001	0.56	0.0004	0.0001
Ratio of means where significant	1.5	10.3	-	-	7.3	-	1.3	2.1
Mean at Thames stormwater pipeline (N=5, except N=4 for arsenic due to one outlier being removed)	24.4	0.396	23.9	16.9	0.47	8.74	35.6	149
Pooled t-test: concentration significantly higher than control site	No	Yes	Yes	No	Yes	No	Yes	Yes
Probability value (p)	0.56	0.0001	0.024	0.58	0.0001	0.07	0.0001	0.0001
Ratio of means where significant	-	10.0	1.1	-	4.5	-	1.5	2.1
Mean at Thames mudflats, deep harbour, wharf and stormwater sites (N=11)	14.2	0.084	24.81	14.01	0.355	8.48	19.89	72.36
Pooled t-test: concentration significantly higher than control site	No	Yes	Yes	No	Yes	No	No	No
Probability value (p)	1.0000	0.0048	0.0003	0.9805	0.0045	0.1096	0.9642	0.2778
Ratio of means where significant	-	2.1	1.2	-	3.4	-	-	-

Appendix 8. Map showing the full extent of catchments feeding the lower Firth of Thames.

For closer detail of the Firth of Thames area, refer to Figures 2-1 and 2-2.