

Trace Elements in the Sediment of Waikato West Coast Estuaries

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Limitations:

This report has been prepared using sediment and water sample data supplied by Environment Waikato. PDP takes no responsibility for the quality and accuracy of the sampling or analytical processes.

The information contained within this report applies to the locations and date of the sampling (2008). With time, the site conditions could change so that the reported conclusions are no longer valid. Thus, in the future, the report should not be used without confirming the validity of the report's information at that time.

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Executive Summary

This report provides a description of the sediment quality of four west coast estuaries (Aotea Harbour, Kawhia Harbour, Raglan Harbour and the river mouth of Port Waikato) as well as the water quality of the Waikato River at Port Waikato. Environment Waikato (EW) engaged Pattle Delamore Partners Limited (PDP) to prepare the report based on the results of water and sediment sampling of the estuaries undertaken by EW in 2008.

In 2008, as part of the regional estuary monitoring programme, EW undertook testing of the levels of trace elements and organic compounds in sediments of the inter-tidal sand and mudflats from five sites in Whaingaroa (Raglan) Harbour, 19 sites in Port Waikato, nine sites in Aotea Harbour and seven sites in Kawhia Harbour.

EW commissioned PDP to carry out this project with the following objectives:

1. To compare the concentrations of the various water and sediment sampling parameters with expected background concentrations, and to identify and discuss any levels of enrichment.
2. To compare the results against water and sediment quality guidelines (ANZECC, 2000) where they exist.
3. To comment on the significance of any trace organic compounds detected, their possible sources and future trends in their levels in the environment.
4. To comment on whether there are any discernible spatial trends observed within the concentration data.
5. For the six water samples at Port Waikato, comment on the possible significance of the estrogenic compound results and microbiological load in respect of potential impacts upon marine mammals, in particular upon Maui's dolphins using the river mouth.

Findings:

Aotea Harbour

- ▮ The concentration of trace elements tended to be more elevated in sediments near river mouths than in sediments found in the centre of the harbour or near the harbour mouth.
- ▮ The concentrations of most trace elements were at the lower end of the estimated natural range (as represented by regional soil concentrations) and no trace elements within the sediments were present in concentrations which exceed the ANZECC (2000) ISQG-low guideline values.

- ii Trace quantities of hexachlorobenzene were detected in two composite sediment samples, and trace quantities of one polycyclic aromatic hydrocarbon (phenanthrene) was detected in one composite sediment sample. All polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds were below the ANZECC (2000) ISQG-low guideline values.
- ii Overall, the sample results show little evidence of anthropogenic effects on the sediment quality of Aotea Harbour.

Kawhia Harbour

- ii The concentration of trace elements appeared to be more elevated in sediments near river mouths compared to sediments found in the centre of the harbour or near the harbour mouth.
- ii With the exception of arsenic near Kawhia Township, the concentrations of most trace elements were at the lower end of the estimated natural range and no trace elements within the sediments were present in concentrations which exceed the ANZECC (2000) ISQG-low guideline values.
- ii The geometric mean concentration of most trace elements was either similar or only slightly higher in Kawhia Harbour than in Aotea Harbour, but the differences for the most part were not statistically significant.
- ii The highest concentrations of PAHs were detected near Kawhia township. PAHs were detected in all other composite samples except for samples collected near the harbour mouth. However, the concentrations of PAHs that were detected were below the ANZECC (2000) ISQG-low guideline value. The ratio of anthracene to phenanthrene suggests that these PAHs were formed by petroleum combustion process (e.g. emissions from motor vehicles exhaust).
- ii Overall, anthropogenic effects may have resulted in the sediments in Kawhia Harbour being slightly enriched with some trace elements and organic compounds. However the concentrations that have been measured are all below ANZECC sediment quality guidelines (ANZECC,2000).

Raglan Harbour

- ii The concentrations of most trace elements were at the lower end of their estimated natural ranges, and no trace elements within the sediments were present in concentrations which exceed the ANZECC (2000) ISQG-low guideline values.
- ii The concentrations of trace elements tended to be higher in the samples collected in the southern part of the harbour than in samples from elsewhere in the harbour.

- ▮ Trace quantities of some PAHs (fluoranthrene, phenanthrene and pyrene) were detected in the composite sample collected from around Pongauui Creek. This sample is the closest to Raglan township of all samples collected. The PAH results may indicate a minor effect from the township.
- ▮ No organochlorine pesticide residues were detected in Raglan Harbour.

Port Waikato

Sediment quality at Port Waikato

- ▮ In general, the particle size of sediment at Port Waikato was either medium or coarse grain sands. Port Waikato had the coarsest grain sediments of the four estuaries.
- ▮ The concentration of arsenic exceeds the ANZECC (2000) ISQG-low guideline value at most sampling locations but does not exceed the ANZECC (2000) ISQG-high guideline values. Therefore the detected concentrations may pose a low-to-moderate risk to aquatic organism such as benthic macro-invertebrate communities.
- ▮ The concentration of most trace elements (except for arsenic, antimony and caesium) were within their expected natural background ranges in most samples. It is likely that arsenic, antimony and caesium are elevated at Port Waikato due to the geothermal inputs into the Waikato River.
- ▮ The concentrations of some trace elements (As, B, Ca, Li, Sb and Zn) were elevated in the samples which had the highest percentage of fine particles (less than 63 µm) and may exceed the estimated background concentrations.
- ▮ The distribution of trace elements and nutrients at Port Waikato appears to be strongly correlated to the grain size of the sediments.
- ▮ Trace quantities of dieldrin and hexachlorobenzene were detected at one sampling location. The concentration of dieldrin exceeded ANZECC (2000) ISQG-low guideline value. However the detection limit of the analytical method used to measure organochlorine pesticide residues was higher than the ANZECC (2000) ISQG-low guideline value for dieldrin, and therefore it cannot be concluded that dieldrin did not exceed the guideline for the samples in which dieldrin was not detected.
- ▮ Several PAH compounds were detected at a number of different locations. The ratio of PAHs in the samples suggest combustion processes as the source of these PAHs, however it is unclear from the PAH ratios whether coal/biomass combustion or petroleum combustion (e.g. car exhausts) is the primary source of the PAHs.

- π The concentrations of PAHs in all samples collected at Port Waikato are below the ANZECC (2000) ISQG-low guideline value.
- π Port Waikato sediments appear to be the most enriched by anthropogenic (as well as natural geothermal) activity of all the estuaries examined in this survey.

Water Quality at Port Waikato

- π Due to problems with sample analysis and/or sample handling, the interpretation of the water quality data collected for this study is limited.
- π The concentrations of *Escherichia coli* are elevated in the Waikato River samples at Port Waikato.
- π The results of the E-screen test show no endocrine-disrupting compounds (EDC) present in the Waikato River at Port Waikato. This is at odds with the results of previous EDC sampling undertaken on the Waikato River. In addition, there are several potential sources of EDC (wastewater treatment plants) which discharge into the river near Port Waikato.
- π Arsenic concentrations exceeded ANZECC (2000) water guidelines for both freshwater and marine ecosystems. Arsenic concentrations are likely to be between 1.2 to 6 times higher than the ANZECC (2000) water quality guidelines for arsenic (V). The arsenic concentration in the estuarine waters at Port Waikato may pose a risk to some sensitive marine species (e.g. phytoplankton).
- π The concentrations of most of the other trace elements were below the analytical method detection limit

Potential risks to Marine Mammals at Port Waikato

Marine mammals, including Maui's dolphins, are potentially vulnerable to a wide range of human and livestock pathogens. Additional stressors such as boat traffic, oil and wastewater pollution, human disturbance, or competition for food from human fishing pressure and immuno-suppression effects due to endocrine disruption compounds (EDCs) and (potentially) arsenic(III) may make marine mammals more susceptible to disease. The high levels of pesticide residues reported previously in Hector's dolphins, known inputs of EDCs into Port Waikato river waters, and the likely vulnerability of Maui's dolphins to EDCs (particularly in respect of endocrine and reproductive disruption), indicate that EDCs represent a possible, but inadequately described toxicological risk to Maui's dolphins in the Port Waikato area.

Note on terms

Heavy metals / trace elements

The focus of this report is on concentrations of thirty-two chemical elements: aluminium (Al), antimony (Sb), arsenic (As), barium (Ba), bismuth (Bi), boron (B), cadmium (Cd), caesium (Cs), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lanthanum (La), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), phosphorus (P), potassium (K), rubidium (Rb), selenium (Se), silver (Ag), sodium (Na), strontium (Sr), thallium (Tl), uranium (U), vanadium (V) and zinc (Zn). Some of 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, antimony, arsenic, boron and bismuth are not regarded as a true metal, but a metalloids or semi-metals and phosphorous is considered to be a non-metal. The terms 'trace element' and 'major element' are used in this report because as they are not ambiguous, and accurately describes the group of 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.

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 3.1). These conventions are followed in this report.

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1.0 Introduction

Environment Waikato (EW) carried out sampling of sediment of three west coast estuarine harbours (Aotea Harbour, Kawhia Harbour and Raglan Harbour) and sediment and water at Port Waikato in 2008. EW has engaged Pattle Delamore Partners Limited (PDP) to prepare an interpretive report of the sampling results. This report presents the results of the study. Detailed statistical and spatial analyses have not been conducted on the data.

1.1 Project Scope

Environment Waikato commissioned this project with the following objectives:

1. To compare the concentration of the various parameters with expected background concentrations, and identify and discuss any levels of enrichment.
2. To compare the results against ANZECC water and sediment quality guidelines where they exist.
3. To comment on the significance of any trace organic compounds detected, their possible sources and future trends in their levels in the environment.
4. To comment on whether there are any discernible spatial trends observed within the concentration data.
5. For the six water samples at Port Waikato, comment on the possible significance of the estrogenicity results and microbiological load in respect of potential impacts upon marine mammals, in particular upon Maui's dolphins using the river mouth.

2.0 Sample collection and analysis

In 2008, as part of the regional estuary monitoring programme, Environment Waikato monitored the levels of trace elements and organic compounds in sediments of the inter-tidal sand and mudflats from five sites in Whaingaroa (Raglan) Harbour, 19 sites in Port Waikato, nine sites in Aotea Harbour and seven sites in Kawhia Harbour.

Sampling locations were selected to broadly cover the intertidal areas. In Port Waikato, subtidal sediment samples were taken as well. The sample sites in Raglan Harbour were those of Environment Waikato's Regional Estuary Monitoring Programme (see e.g. Felsing & Singleton, 2008).

2.1 Method for sediment collection:

Intertidal samples were collected using a trowel, to a depth of around 2 cm. One sample was collected per sampling site.

All of the Port Waikato subtidal channel sediment samples were collected using a Petite Ponar sediment grab sampler deployed from a motorboat. Typically, the Petite Ponar sampler collected surface sediment samples from the upper 2 to 5 cm of the sediment column. The Petite Ponar sediment sampler uses a spring-loaded pinch-pin to trigger the sampling jaws to close when the line slackens. When the sampler strikes the bottom, the tapered cutting edges penetrate the bottom sediment. The sampler closes once the pinch-pin has been released and the sampler is being retrieved. The sampler is equipped with mesh screens which allow water to flow through the sampler as it descends and this lessens the frontal shock wave thereby reducing surface disturbance. Both screens are covered with neoprene rubber flaps that close during retrieval to prevent any sediments being lost.

Once an acceptable sample was obtained, the contents of the sampler were deposited into a plastic tray and then sub-sampled into 2 x 250g plastic soil jars and 250g glass soil jar supplied by Hill Laboratories. Each sample container was labelled with a unique sample identifier.

2.2 Water samples

Water samples at Port Waikato were collected 10 cm below water surface every 1/2 hour for 3 hours. Measurements of dissolved oxygen, salinity and water temperature were also collected at each monitoring site. Sampling commenced 3 hours after high tide to coincide with peak flows in the initial stages of sampling.

2.3 Sample analysis

Samples were sent to Hill Laboratories in Hamilton for immediate analysis. Chain of custody forms accompanied all samples submitted to the analytical laboratory and all samples were found to be acceptable when received by the laboratory

2.3.1 Chemical Analysis of Sediment Samples

Grab samples from Port Waikato and Raglan Harbour and three of the samples collected from Aotea Harbour (samples 1, 2 and 3) were analysed as individual samples. However, samples were analysed as composites for most of the Aotea Harbour samples and all of the samples from Kawhia Harbour. The composites were prepared in the laboratory to represent different areas of the estuary.

Analysis of composite samples allowed a wider range of analytical parameters to be determined than would otherwise have been possible.

The individual and composite samples were all analysed for total recoverable arsenic, cadmium, chromium, copper, iron, mercury, nickel, lead, phosphorus and zinc, polycyclic aromatic hydrocarbons (PAHs) and organochloride pesticide residues.

Samples collected from Port Waikato and Raglan and selected samples from Aotea Harbour were also analysed for total organic carbon. Total nitrogen was analysed on

all samples collected from Raglan Harbour as well as three samples collected from Aotea Harbour.

All analysis on the sediment samples was undertaken on the sub-2mm fraction of the sediments.

2.3.2 Chemical and microbiological analysis of water samples from Port Waikato

Water samples collected from Port Waikato were analysed for:

- ▯ dissolved trace elements (arsenic, boron, chromium, chloride, copper, lead, lithium, mercury, nickel and zinc) and total arsenic,
- ▯ nutrients (ammonia, nitrate, nitrite, total kjeldahl nitrogen, total nitrogen, dissolved reactive phosphorus and total phosphorus),
- ▯ Organic compounds and parameters including non-purgeable organic compounds and dissolved non-purgeable organic compounds, organo-nitrogen and organo-phosphorus pesticides and herbicide residues and;
- ▯ physicochemical parameters (pH, conductivity, temperature, total dissolved salts, absorbance (at 340, 440 and 780 nm) and total biological oxygen demand.

The water samples were analysed for various microbiological parameters, including Faecal Coliforms, *Escherichia coli*, *Enterococci* and Chlorophyll a. However, the results of the analyses should be treated with some caution as microbial results may be unreliable due to problems with the labelling of samples and the apparent loss of one sample..

2.3.3 Endocrine disrupting compounds (EDC) analysis

An "E-Screen" bioassay of six Waikato River water samples was performed by HortResearch's Food and Biological Chemistry Laboratory (HortResearch). The E-Screen bioassay is based on the ability of MCF7 human breast cancer cells to proliferate in the presence of estrogens. The degree of proliferation is used as a measure of the endocrine-disruption potential of substances in the sample. Certain organochlorines (DDT, DDT-derivatives), human estrogens, and estrogens derived from birth control pills are known to have estrogenic effects on the reproductive systems of marine mammals (Fair & Becker, 2000). The endocrine-disruption potential of the water sample is expressed as an EC₅₀¹ in nanograms per litre (ng/L), with cell

¹ The EC-50 is a measure of a dose response. It is the dose of a substance sufficient to produce a response halfway (50%) between baseline (0%) and a maximum response (100%).

proliferation compared to a known control estrogen. In this case, the MCF7 BOS strain of cancer cells was used for analysis, with estradiol 17 β -E2 used as the positive control estrogen.

It is noted that the E-Screen bioassay is not one of the methods recommended by the USEPA or European Commission for EDC analysis. It is also noted that the methodology reported in this case (HortResearch, 2008), was not the same as that referenced (Korner *et al.*, 1999), and that no explanation for the differences was provided. One of the known issues with the E-Screen bioassay is the variability of protocols used, and resultant significant differences in results reported, with false negatives and false positives observed (Leusch *et al.*, 2006). For this reason it would have been desirable for the differences in methodology to have been explained, possible impacts upon the EDC results described, and a separate validation assay performed and reported (USEPA, 1998).

2.3.4 Grain size analysis

Samples were analysed for grain size at the University of Waikato, using the Malvern LaserSizer. All organics and calcium carbonate were removed prior to grain size analysis by treating the sample with hydrogen peroxide to remove the organics and hydrochloric acid to remove the calcium carbonate. Particle size analysis was undertaken for all samples, however at the time of reporting grain size results were not available for Raglan Harbour.

The Malvern LaserSizer provides a near continuous distribution of data which is used to classify the sediments into different groups based upon particle (or grain) size. The sediments have then been classified into size ranges using the particle size descriptions developed by the New Zealand Geotechnical Society (2005)(See Table 1).

Sediments which contain more than 35% by mass of particles smaller than 0.06 mm (<63 μ m - the threshold between fine sand and silt) are classified as 'fine sediments'.

Sediment grain size is an important factor controlling the distribution of contaminants for both organic compounds and trace elements. Contaminants are frequently associated with the fine fraction of aquatic sediments due to the exponential increase in the surface area with decreasing grain size, and an increase in surface charge (Birch & Taylor, 2000).

The confounding effects that grain size distribution has on contaminant distribution are such that NOAA (1988) specifies post-analysis correction of sediment datasets by dividing total sediment concentrations by the proportion of the fine (<63 μ m) fraction, for samples with > 20% fine fraction. This assumes that the coarser sand fractions do not contain a significant fraction of the total recoverable contaminants.

Table 1: Particle Size Criteria (in mm)

Coarse								Fine	
Boulder	Cobble	Gravel			Sand			Silt	Clay
		Coarse	medium	Fine	Coarse	medium	Fine		
>200	200-60	60-20	20-6	6-2	2-0.6	0.6-0.2	0.2-0.06	0.06-0.002	<0.002

3.0 Guidelines

3.1 ANZECC sediment quality guidelines

To establish the degree of risk to sediment-dwelling organisms, the results from this survey have been 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 lower value 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 value 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 (e.g. arsenic(III) or arsenic(V)), natural background concentration, the amount of organic matter, iron oxides or reduced sulphide compounds can modify the toxicity of a particular compound. A detailed site-specific assessment has not been conducted as part of this report.

Values below the ISQG-low do not guarantee that the concentrations are safe, 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 some mercury compounds) have specific chemical forms (methyl-mercury, ethyl-mercury) which bio-

accumulate in organisms and bio-magnify up the food-chain. As bioaccumulation potential is site-specific, more detailed studies would be required to assess such risks. Therefore, the guidelines are designed to be trigger values to indicate which sites may warrant closer investigation.

For organic compounds, the sampling results should be normalised to 1% total organic carbon before they are compared to ANZECC (2000) ISQG trigger values. Carbon normalisation was only carried out for samples containing greater than 0.2% organic carbon (dry weight). This cut-off has been used because other effects such as particle size and sorption onto non-organic mineral surfaces become more important in sediments with lower organic carbon content (ANZECC, 2000).

It should be noted that the ANZECC (2000) guidelines are designed to protect aquatic ecosystems rather than to protect human health. Although ISQG-low values are generally lower than equivalent soil quality guidelines designed to protect human health, no assessment has been made on the potential human health risk from contaminants in marine sediments.

3.2 Water Quality Guidelines

3.2.1 New Zealand Microbiological Water Quality Guidelines

The New Zealand Microbiological Water Quality Guidelines (MfE, 2003) provide a procedure for monitoring recreational waters for public health purposes; they take precedence over the ANZECC Water Quality Guidelines for microbiological water quality. Guidelines are provided for marine contact recreation activities, freshwater contact recreation activities, and recreational shellfish gathering in marine waters.

The guidelines use a qualitative risk grading of the catchment in conjunction with the direct measurement of appropriate microbiological indicators, to assess the suitability of a site for recreation and to determine whether ongoing monitoring is required at the site. Where ongoing monitoring is required, routine sampling is carried out and sample results are compared against guideline values.

For the contact recreation guidelines a three-tiered framework is used to determine what action (if any) is necessary. The guidelines are set out in Table 2, below.

Table 2: Ministry for the Environment Assessment Framework for Contact Recreational Guidelines

	Marine contact recreation guidelines	Freshwater contact recreation guidelines
Green mode: Surveillance. Action required: Continue routine monitoring.	No single sample greater than 140 <i>enterococci</i> /100mL	No single sample greater than 260 <i>E. coli</i> /100 mL
Amber mode: Alert. Action required: increase sampling frequency and investigate possible sources.	A single sample greater than 140 <i>enterococci</i> /100mL.	Single sample greater than 260 <i>E. coli</i> /100 mL
Red mode: Action. Action required: increase sampling frequency, investigate possible sources, erect warning signs and inform public.	Two consecutive single samples greater than 280 <i>enterococci</i> /100mL (resample within 24 hours of receiving the first sample results or as soon as is practicable).	Single sample greater than 550 <i>E. coli</i> /100 mL
Level of risk	Risk of illness associated with recreational water use less than 2%.	5% of <i>Campylobacter</i> infections could be attributable to freshwater contact recreation.

The guidelines for recreational shellfish gathering are:

- ii The median faecal coliform content of samples taken over a shellfish-gathering season shall not exceed a Most Probable Number (MPN) of 14/100 mL; and
- ii Not more than 10% of samples should exceed an MPN of 43/100 mL (using a five-tube decimal dilution test).

3.2.2 ANZECC recreational water guidelines

The ANZECC (2000) recreational water quality guidelines aim to protect the health and safety of contact recreational users (as well as the aesthetic values) of water bodies. They are designed to protect water users from either the effects of toxic compounds or from the effects of chemicals which may irritate the skin or mucous membranes. They specify guideline values for physical, chemical and microbiological parameters. The relevant guideline values have been presented in Table E-4 in Appendix E, together with the Port Waikato water quality results.

3.2.3 ANZECC Water Quality Guidelines for protection of aquatic ecosystems

The ANZECC (2000) guidelines provide water quality guideline trigger values for the protection of aquatic ecosystems (either fresh or marine) against toxicants. These guidelines have been derived using data from single species toxicity tests on a range of test species. High reliability trigger values were calculated from 'chronic no observable effect concentrations' (NOEC) data. A statistical distribution method has been used to calculate four different protection levels (99%, 95%, 90% and 80% ecosystem protection) for high reliability trigger values. In this assessment generally the 95% protection trigger values have been used as the default values, however, for chemicals identified as having the potential for bioaccumulation (such as mercury), the 99% ecosystem protection trigger values have been used instead.

Moderate-reliability trigger values and low reliability trigger values have also been derived by ANZECC when there has been insufficient information to derive a high reliability trigger value. Moderate-reliability trigger values have been derived from short term acute toxicity data by applying acute-to-chronic ratio conversion factors. Where no high- or moderate-reliability trigger values are available for a particular compound, and no other international guideline derived using similar methodology is available, the low-reliability trigger values have been used in this assessment. Low-reliability trigger values have been calculated by applying an assessment factor to the lowest toxicity figure. Low reliability guideline values are only used as indicative interim working levels.

For chemicals such as mercury and organochlorine pesticides, the main issue of concern is not their direct short-term toxic effect but the indirect risks associated with their longer-term concentration in organisms and the potential for secondary poisoning. The ANZECC (2000) water quality guidelines are not designed to protect against the effects of dietary exposures and bioaccumulation. As bioaccumulation potential and dietary exposures are site-specific, more detailed studies would be required to assess such risks.

As salinity in the water samples collected from Port Waikato is greater than 2.5 parts per thousand, the ANZECC (2000) guidelines (section 8.3.4.4) recommend that marine ecosystem trigger values be used in preference to freshwater guideline values.

3.2.4 Environment Waikato adopted guidelines

Environment Waikato undertakes regular monitoring of water quality of the region's rivers, and has adopted guidelines that relate to either the protection of ecological health of rivers and streams, or to their suitability for contact recreation activities. The adopted values are included in Table E-4 in Appendix E, together with the Port Waikato water quality results. The sources of the guidelines are summarised in Table 3.

Table 3: Source of Adopted Guidelines

Parameter	Guideline source
Dissolved Oxygen	RMA Third Schedule, Classes AE, F, and FS.
pH	ANZECC (1992) and Canadian guidelines for freshwater aquatic life (1987).
Turbidity	Studies of adverse effects on underwater light—and thus on plant and invertebrate production—in certain South Island streams.
Ammoniacal-nitrogen	USEPA (1998) value for 1-hour exposure at pH 9.
Temperature	Environment Waikato Draft Regional Plan standards for trout fisheries and trout spawning (1997).
Total phosphorus, total nitrogen	From upper quartile values for 77 New Zealand rivers in NIWA's National Water Quality Network (after Smith & Maasdam, 1994).
<i>Escherichia coli</i>	Ministry for the Environment (2003) guidelines for the management of recreational and marine shellfish-gathering waters. Median guideline value taken from Ministry for the Environment (1999) guidelines for the management of recreational and marine shellfish-gathering waters.

4.0 Sources of Contaminants in West Coast Estuaries

4.1 Organic Carbon

4.1.1 Organic Carbon

Organic carbon in marine near-shore sediments is derived from two sources. Firstly, adjacent land runoff transports organic matter to the coastal environment and, secondly, near-shore processes generate organic carbon (such as algae biomass and aquatic plant growth) that is deposited in sediments. The organic carbon in coastal sediments plays an important role in determining the fate and toxicity of metals and organic compounds in the marine environment. Organic content can play an important role in determining redox (reduction-oxidation) potential of sediments. Metals are generally more mobile under oxidising conditions and therefore can be released into porewater and the water column overlaying the sediments, where they will be more bio-available to organisms. Organic compounds can also adsorb metals and other organic matter, thereby concentrating them into sediments and making them less bioavailable.

Total organic carbon concentrations typically range between 1 and 10% in most marine sediments, but sandy sediments can have significantly lower total organic compound concentrations (less than 0.2%).

4.2 Trace Elements

Detectable levels of trace elements in sediments can either be due to natural processes or the result of anthropogenic activities. Various trace elements will be found naturally within the minerals which comprise the sediments. Natural weathering and erosion of rock and soils release trace elements into the waterways where they can be deposited onto the sediments in estuarine and coastal areas. Human activities such as land clearance can result in increased weathering and erosion. Also, geothermal discharges contain elevated levels of trace metals and are an important source of trace elements such as arsenic, antimony and mercury into the environment.

Human activity can lead to release of trace metals. Urban stormwater runoff can transport many trace elements into waterways, including lead, copper and zinc. 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. Copper and zinc are also applied to horticultural areas in fungicide formulations.

Transportation of trace elements 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 onto 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 accumulation of sediment that may have elevated trace element concentrations.

It is difficult to determine the 'natural' background concentration of trace elements in sediments, and hence the degree of enrichment caused by anthropogenic effects, as the background concentration will depend on the concentration of trace elements in the soil and rocks within the catchment. In addition, trace element concentrations depend partly on the grain size (some trace elements preferentially attach to fine particles) and organic content of the sediments.

As there is insufficient data on the 'natural' background concentration of many trace elements within New Zealand sediments, the background concentration of trace elements in Waikato soils has been used as a proxy for the 'natural' background concentration (see Appendix B, Table B-1). As soils and rock are the primary ultimate

source of major and trace elements in sediments, natural chemical and physical weathering processes can alter the distribution of trace elements found in the sediments. Therefore differences observed between the abundance of trace elements in the sediments may not be a result of human activity; rather they could potentially be caused by natural processes.

4.3 Organic Compounds

4.3.1 Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) can occur within the environment as the result of natural processes such as forest fires and volcanic emissions, and PAHs are formed naturally in coal and oil. Generally natural processes release either negligible or minor amounts of PAHs into coastal and estuarine sediments. The most important sources of PAHs in coastal and estuarine environments are human activities such as emissions from motor vehicles, household fires and discharges of petroleum products (such as diesel and lubricants).

4.3.2 Organochlorine Pesticides

Persistent organochlorine pesticides (including DDT, dieldrin and lindane) were commonly used in New Zealand from the 1940s until the 1970s (MfE, 1999). Use declined in the 1980s as public awareness regarding the potential environmental harm of using them increased, and in 1989 all persistent organochlorine pesticides were formally deregistered by the Pesticides Board (except PCP, which was deregistered in 1991) (MfE, 1998). Persistent organochlorine pesticides are of concern in the environment as they are toxic to animals, including humans, do not degrade readily in the environment, and can bioaccumulate within the food chain. Evidence suggests they may be endocrine disrupting chemicals (EDCs) in marine mammals and other aquatic wildlife and they could potentially make marine mammals more susceptible to various diseases.

No persistent organochlorine pesticides occur naturally and they enter the environment only due to human activities. Therefore the natural background concentration of these types of compounds is zero.

In 1996, the Ministry for the Environment (MfE) collected 26 composite samples from 12 estuaries throughout New Zealand. This study found that the concentration of organochlorine pesticides in New Zealand estuaries is low, and in most cases markedly lower than the concentrations reported for estuaries in other countries (MfE, 1998).

5.0 Results

The results of the laboratory analysis for samples from Aotea Harbour are presented in Appendix C, results for Kawhia Harbour are presented in Appendix D, Port Waikato results are presented in Appendix E, and results for samples from Raglan Harbour are in Appendix F.

Details regarding data manipulation techniques used are provided in Appendix G.

5.1 Sediment Samples

5.1.1 Aotea Harbour

Particle Size

Sediments within the Aotea Harbour were generally sandy and on average contained less than 10% fines (<63 µm) (see Table C-1 in Appendix C). The geometric mean of particle size of all samples from within the Aotea Harbour was 198 µm, with most samples classifying as silty fine to medium sands. Grain size decreased closer to the shore, with samples A1, A3, A7, A15 and A19 containing between 25 to 50% fines. The sediment collected from around the mouths of the Te Maari and Makomako streams (sample A12) was very muddy, comprising over 86% fines.

Nutrients in sediment

Only three samples from around Te Kowiwi Creek and between Kakawa and Te Tuhiatewehi Points at the southern end of Aotea Harbour (samples A1, A2 and A3) were analysed for total nitrogen. Total nitrogen concentration measured in these samples ranged between 0.06 to 0.1% (see Table C-2 in Appendix C).

Total phosphorus concentrations in Aotea Harbour ranged between 340 to 680 mg/kg, with a geometric mean concentration of 530 mg/kg.

Trace elements

The concentrations of most trace elements in Aotea Harbour were at the lower end of the estimated natural ranges and were lower than the ANZECC (2000) ISQG-low guideline values, which is probably in part due to the high sand content of the sediments and the lack of any significant anthropogenic inputs (see Table C-2 in Appendix C). The concentration of boron, calcium, caesium, lithium and strontium were enriched in Aotea Harbour sediments compared to Waikato background soil (see Tables B-1 and C-2). These elements are naturally high in marine waters and this may be the source of enrichment within the harbour sediments. Alternatively, local geology differences within the catchment of the Aotea Harbour (such as the presence of limestone) may explain the enrichment of calcium and strontium.

Most metals (barium, bismuth, cadmium, caesium, chromium, copper, nickel and lead) were slightly elevated in composite sample '10, 12 & 13' collected from around the mouths of the Te Maari and Makomako Streams. This is probably because of the silty nature of the sediment in this location (86% fines, with a mean particle size of 39 µm). The highest concentrations of arsenic, boron, manganese and zinc were found at the southern end of the Aotea Harbour. This may be partly due to the elevated concentration of iron found in the southern part of the harbour, which may adsorb these elements, thereby enriching the concentration of these elements in this part of the harbour.

However, for most trace elements, the variations in concentration observed across Aotea Harbour do not appear to be significant.

Organic Compounds

A trace quantity of phenanthrene was detected in one composite sample (sample '10, 12 & 13'), made up of samples collected near the mouths of the Te Maari and Makomako streams (see Table C-2 in Appendix C). Several trace elements were also elevated at these locations due to the finer particle size of sediments found at the river mouths. In addition, trace quantities of hexachlorobenzene were detected in this composite sample and composite sample '14, 15 & 16' (collected from the northern end of Aotea Harbour).

Phenanthrene (a high molecular weight PAH) was the only PAH compound detected in any of the samples collected from Aotea Harbour and this compound was detected only in composite sample '10, 12 & 13'. The concentrations of polycyclic aromatic hydrocarbons in all other samples were below the method detection limit (approximately 2 ppb).

5.1.2 Kawhia Harbour

Particle Size

Sediments within Kawhia Harbour were generally sandy, on average containing less than 10% fines (<63 µm) (see Table D-1 in Appendix D). The geometric mean of particle size within the Kawhia Harbour samples was 112 µm, typical of fine sand. Particle size decreased closer to shore, with samples 1 to 8 and 16 to 19 containing between 25 and 80% fines.

The sediment samples collected from near major stream mouths (e.g. Mangawhero, Wainumia, Te Kauri, Owhiro streams), and within the upper reaches of Te Wharu Bay, were very muddy, containing over 70% fines. This is similar to the trend observed at Aotea Harbour; with sediments near major stream inputs being muddier (containing significantly higher percentage of fines).

Nutrients in sediment

No analysis of total nitrogen or total organic carbon was undertaken on any of the samples collected from Kawhia Harbour. Total phosphorus concentrations in Kawhia Harbour ranged from 570 to 780 mg/kg, with a geometric mean concentration of 642 mg/kg (see Table D-2 in Appendix D).

Trace elements

The concentration of many trace elements and the variability in the concentrations of most trace elements (measured as %RSD²) was higher in Kawhia Harbour than in

² %RSD =percent relative standard derivation

Aotea Harbour, but the concentration of most elements (except for arsenic, boron, calcium, lithium and strontium) were within their estimated natural ranges (see Table B-1 in Appendix B for data on the estimated background concentrations and Table D-2 in Appendix D for the analytical results for trace elements in Kawhia Harbour). This may indicate that there has been a very slight enrichment of trace elements within Kawhia harbour. This may be caused by different geochemical and natural factors such as grain size (Kawhia Harbour has slightly finer grain sizes which has a proportionally larger surface area to sorb trace elements), catchment geology and/or the influence of human activities within harbour catchments which discharge into the harbour. The levels of boron, calcium, lithium and strontium are naturally high in marine waters and this may be the source of enrichment of these elements within the Kawhia Harbour sediments. The level of enrichment of these elements does not appear to be significant as most of these compounds (except for arsenic) are not highly toxic. The concentration of arsenic was only elevated in one composite sample and further sampling would be required determine if arsenic is elevated in this area or if the elevated concentration in this sample was due to a geochemical anomaly.

The highest concentration of most elements was found near the mouth of the Manawhero stream, except for arsenic, iron and zinc which were elevated around Te Wharu Bay (where Kawhia township is located). The elevated concentration of iron in this area may be responsible for the higher concentrations of arsenic and zinc as these metals can be strongly sorbed onto iron. Although the concentration of arsenic was marginally above the ANZECC ISQG-low guideline value, if it is strongly sorbed onto the iron it may not be readily available to aquatic organisms, and it is therefore unlikely to have significant effects on the aquatic ecosystem.

Organic Compounds

The results for the sediment analysis of organic compounds in Kawhia Harbour are presented in Table D-3. The highest concentration of PAHs was detected in composite sample '1, 2 & 3' (Total PAHs of approximately 1 mg/kg), which encompasses sediment collected from around Kawhia township, and in composite sample '10, 11 & 12' (Total PAHs of approximately 0.3 mg/kg), which was from near the centre of the harbour south of Kawhia township. The presence of both low and high molecular weight PAHs in detectable concentrations may indicate that the PAHs have been relatively recently released or that conditions are less favourable for the degradation of PAHs at this location.

A limited number of high molecular weight PAHs were detected in all the other samples except for two composite samples (samples '13, 14 & 15' and '20, 21, 22 & 23') which were collected near the harbour mouth. The concentrations of the PAHs detected were near the analytical detection limit and the fact that more persistent high molecular PAHs were detected suggests that the lighter PAHs have been degraded or the sampled sediment has been transported some distance from the original source of the PAHs. However the degree of degradation cannot be

determined without knowing the original ratio of low to high molecular weight PAHs as the source may have been naturally low in low molecular weight PAHs.

Trace quantities of 4,4' DDT and hexachlorobenzene were detected in one composite sample (sample '10, 11 & 12') which was collected from near the centre of Kawhia Harbour. Organochlorine pesticide residues were not detected at any other site within Kawhia Harbour (detection limit typically 0.001 mg/kg).

5.1.3 Port Waikato

Particle size

Mean particle size at Port Waikato was greater than at any of the other estuarine harbours. The geometric mean particle size was 640 µm, and sediments at most locations contained less than 5% fines (see Table E-1 in Appendix E). Samples 9 and 10 had significantly higher percentages of fines (approximately 18% and 22% respectively), while sample 11 was comprised mainly (>90%) of particles larger than 2 mm in diameter. As expected, the sediment grain size distribution of Port Waikato estuary was more typical of a sandy river environment than a lower energy estuarine environment.

Nutrients in sediment

No analysis of total nitrogen was undertaken on any of the samples collected from Port Waikato (see Table E-2 in Appendix E). Total phosphorus concentrations at Port Waikato ranged between 190 to 940 mg/kg, with a geometric mean concentration of 290 mg/kg. The geometric mean concentration at Port Waikato was lower than the other harbours. This is probably because of the coarser grain sediment of sediments generally encountered at this site.

Total organic carbon concentrations ranged between <0.05 and 0.76%.

Trace elements

For most sediment samples, the concentrations of most trace elements at Port Waikato appear to be at the lower end of the expected natural range (see Table B-1 and Table E-2). However, the concentrations of arsenic and antimony appear to be elevated compared to other estuaries studied as part of this investigation. Arsenic, antimony and caesium are elevated within the Waikato River due to geothermal inputs into the Waikato River (both natural and man-made) (Aggett & Aspell, 1980; Pope *et al.*, 2005; Timperley & Hasser, 1996). Unlike the other estuaries in this study, boron, calcium, lithium and strontium were generally not enriched in the Port Waikato sediments compared to expected background levels (see Tables B-1 and E-2).

The highest concentrations of most trace elements were found in samples 9, 10 and 11. This is probably due to the higher percentage of fine particles in these samples providing a greater surface area to adsorb trace elements. In these samples the concentrations of some trace elements (arsenic, boron, cadmium, lithium, tin and zinc)

were elevated relative to expected background concentrations and may exceed the expected background concentrations. There are no known point source discharges at or near any of these sampling locations which could be a potential source of these trace elements.

Organic Compounds

Trace quantities of dieldrin and hexachlorobenzene were detected at sampling location 8 (See Table E-2 in Appendix E). No other organochlorine pesticide residues were detected at any of the other sampling locations at the detection limit of 0.001 mg/kg.

The highest concentrations of total PAHs were detected at sampling locations 9, 13 and 14 (approximately 0.046, 0.071 and 0.041 mg/kg respectively). At sampling locations 3, 5 and 10 trace quantities of some high molecular weight PAHs were detected. Phenanthrene was detected at sampling sites 3 and 10, and phenanthrene, benzofluoranthrene and benzo(g,h,i)perylene were detected at sampling location 5.

5.1.4 Raglan Harbour

Particle Size

No particle size results were available for Raglan Harbour at the time of reporting.

Nutrients in sediment

Total nitrogen concentration measured in the sediment samples from Raglan Harbour ranged between 0.074 and 0.12% (see Table F-1 in Appendix F). Nitrogen concentrations were highest in the southern arm of Raglan Harbour and lowest in the northern arm of the harbour.

Total phosphorus concentrations in Raglan Harbour ranged between 440 to 650 mg/kg, the geometric mean concentration was 590 mg/kg. Phosphorus concentrations were slightly higher in the southern arm than in the northern arm, but the concentration of total phosphorus was higher in the upper parts of the harbour than in the sample collected from Ponganui Creek near the harbour entrance.

The concentration of total organic carbon in samples collected from the southern arm of Raglan Harbour was higher than those collected from the northern arm of the harbour (0.92 and 0.82% compared to 0.4%).

Trace elements

The concentrations of most trace elements in Raglan Harbour were at the lower end of their expected natural ranges, which is possibly due to the lack of any significant anthropogenic inputs (see Tables B-1 and F-1). The concentration of boron, calcium, caesium, lithium and strontium were enriched in Raglan Harbour sediments compared to Waikato background soil. These elements are naturally high in marine waters and this may be the source of enrichment of these elements within the harbour sediments.

Alternatively, local geology differences within the catchment of the harbour (such as the presence of limestone) may explain the enrichment of calcium and strontium.

The concentrations of most elements were slightly elevated in the samples collected from Haroto Bay and Okete Bay but the concentrations of trace elements from these two sampling locations are within expected natural ranges and lower than ANZECC (2000) ISQG-low guideline values.

Trace element concentrations were slightly higher in the southern part of the Raglan Harbour than in the northern part, but there was an insufficient number of samples to determine if the difference was significant or not. Generally, the lowest concentrations of most elements were found in samples collected from around Ponganui Creek and Whatitirinui Island.

Organic Compounds

Trace quantities of fluoranthene, phenanthrene and pyrene were detected in the sample collected near Ponganui Creek (see Table F-2 in Appendix F). This sampling location is the closest to Raglan township which suggests the possibility that the township is the source of the PAHs, but further sampling would need to be undertaken to confirm this. No PAHs were detected in any other samples collected from Raglan Harbour. No organochlorine pesticide residues were detected either.

5.2 Comparison with ANZECC Sediment Quality Guidelines

Comparison of sampling results with ANZECC sediment quality guidelines is shown in tables in Appendixes C to F. Arsenic was the only trace element which exceeded ANZECC ISQG-low guideline values at any of the West Coast estuaries investigated as part of this study. At Port Waikato, arsenic concentrations were at or above the ANZECC ISQG-low guideline in all but one sample. Arsenic also marginally exceeded the ANZECC-ISQG-low guideline in one composite sample (sample '1, 2 & 3') from Kawhia. All samples complied with the ANZECC ISQC-high guideline for arsenic.

Polycyclic aromatic hydrocarbon concentrations were below the ANZECC ISQG-low concentration guideline level in all samples. Most organic pesticides were below ANZECC ISQG-low concentrations; however the detection limit for dieldrin in the samples was above the ANZECC ISQG-low guideline value, so although no dieldrin was detected in the samples, no conclusion can be drawn regarding the compliance with ANZECC ISQG-low with respect to this compound.

5.3 Port Waikato Water Quality

Six surface water samples were collected from various locations within the Waikato River, the analytical results together with field measurements are presented in Appendix E Table E-4. The high electrical conductivity and chloride concentration (between 5,500 to 20,000 g/m³) indicate the water samples were heavily marine-influenced (the average chlorine concentration of sea water is approximately 35,000 g/m³). The chloride concentration of the Waikato River at Tuakau Bridge

(approximately 24 km upstream of the site) is between 15 and 21 g/m³ (Environment Waikato, 2006). The pH of all the water samples was also elevated compared to typical values measured by Environment Waikato at Tuakau Bridge of between 7.1 to 7.7 pH units.

5.3.1 Trace Elements

The concentrations of many of the trace elements were below the method detection limits with the exception of arsenic which had a concentration range between <0.2 g/m³ and 0.030 g/m³ (see Table E-4 in Appendix E). Although trace analysis was undertaken on the water samples, the detection limit of the metals analyses was higher than the ANZECC trigger values and therefore direct comparison with the ANZECC trigger values is not possible. This high analytical detection limit is believed to be caused by the high salinity of the water samples and it is suggested that future samples be analysed using an analytical technique appropriate for saline water (e.g. dynamic reaction cell ICP-MS) to achieve lower analytical detection limits.

Previous analyses of Waikato River samples collected at Tuakau Bridge found concentrations of metals were typically below the ANZECC trigger values (see Table 4) (Environment Waikato, 2005).

Table 4: Summary of Environment Waikato monitoring of Waikato River at Tuakau Bridge 2005 (Environment Waikato, 2005) (all units are in g/m³).

	Minimum	Maximum	ANZECC (2000) 95% ecosystem protection for Marine Water
Arsenic	0.0083	0.022	No high reliability guideline recommended
Cadmium	<0.00001	<0.00001	0.0007 ^b
Chromium	<0.0005	0.0006	0.0044
Copper	0.0007	0.0011	0.0013
Lead	0.00018	0.00034	0.0044
Mercury	<0.00008	<0.00008	0.0001 ^b
Nickel	<0.0003	0.0003	No high reliability guideline recommended
Zinc	<0.0005	0.0009	0.015

Even though the values reported in the current study cannot be directly compared to the ANZECC (2000) trigger values because of the high detection limits, it is not expected that any of the metals (with the possible exception of arsenic) would exceed the ANZECC (2000) trigger values, on the basis of the previous monitoring results conducted by Environment Waikato (Environment Waikato, 2005).

Although there is no ANZECC (2000) high reliability guideline for arsenic (III) or arsenic (V) in marine waters, low reliability marine trigger values have been derived for arsenic(III) and arsenic(V) (0.0023 and 0.0045 g/m³ respectively). Previous studies conducted indicate that the ratio of arsenic(III) to arsenic(V) in the Waikato River varies from 10:90 to 50:50 (Freeman, 1983), however none of these studies have been conducted near the river mouth at Port Waikato. It is possible that biogeochemical process could alter the ratio of arsenic(III) to arsenic(V) and additional sampling would be required to confirm if these ratios are also observed at the river mouth. The reason for the seasonal changes in the speciation of arsenic within the Waikato River are unknown, however it has been speculated (Freeman, 1983) that they are biologically facilitated, by *Anabaena*-bacteria assemblages found naturally within the Waikato River.

However, assuming that the same trends in the speciation of arsenic are observed at Port Waikato as have been found in other parts of the Waikato River, and on the basis of the results from the current investigation and previous work conducted by Environment Waikato, the concentration of arsenic within the Waikato River is likely to

exceed the arsenic(V) trigger values almost all the time and may also exceed the arsenic(III) guideline values for a short period during summer months.

Although both of these guideline values are only indicative interim trigger values, the concentration of arsenic also exceeds ANZECC (2000) high reliability guideline values for arsenic(V) for freshwater species (0.013 g/m^3) and therefore on balance it seems likely that the arsenic concentrations in the estuarine waters at Port Waikato pose a credible risk to some sensitive marine species (such as phytoplankton and the early life stages of some marine organisms).

5.3.2 Organic Compounds

Trace quantities of MCPB (an acid herbicide) were detected in three water samples at concentrations ranging between 0.00007 and 0.0012 g/m^3 (see Table E-4 in Appendix E). No ANZECC water quality guidelines exist for MCPB, but a low reliability aquatic guideline of 0.0014 g/m^3 does exist for MCPA, a similar compound to MCPB. Limited aquatic testing undertaken on both MCPA and MCPB indicates that MCPB is approximately five times less acutely toxic to fish and over 100 times less toxic to invertebrates than MCPA (US EPA 2004, 2005). Therefore, adverse effects are unlikely to occur at the concentrations of MCPB detected by Environment Waikato.

No other organic pesticides were detected in the water samples at detection limits ranging from 0.00005 to 0.0002 g/m^3 .

Environment Waikato has routinely detected trace quantities of a number of organo-nitrogen or organo-phosphorus pesticide residues (in the low ppb concentration range) at Tuakau Bridge upstream of the estuary. However, the concentrations of agrichemicals detected in the Waikato River have consistently been lower than the relevant ANZECC (2000) water quality guidelines.

5.3.3 Endocrine disrupting compounds

The E-Screen bioassay results reported for the six water samples were all below the limit of detection for the assay of 0.5 ng/L .

5.3.4 Comparison with Microbiological Water Quality Guidelines

The microbial analysis results for the Port Waikato waters showed low levels of microbial contamination. However, there are difficulties with the reported sampling procedures (see section 2.3.1); showers and rain were observed on the sampling day, and a one-off spot sample on one day only is not adequate to provide an accurate picture of microbial levels and trends in the water column (MfE Guidelines for Microbiological Analysis 2003). Because of these factors it is not possible to accurately assess the water quality of Port Waikato against MfE microbiological water quality guidelines. However, it should be noted that the geometric mean concentration of faecal coliforms is higher than the MfE amber alert level.

6.0 Discussion

6.1 Comparison of sediment quality between harbours and background concentrations

A comparison of the results between harbours was undertaken to determine if there was a difference in sediment between harbours using significance tests (t-tests and Mann-Whitney U tests). The results of the statistical analysis are presented in Table H-5.

It should be noted that significance tests such as t-tests and Mann-Whitney U tests are designed to determine if the difference in the two sample populations is probably true (i.e. not due to chance), however they do not assess if the differences are practically significant (i.e. important). Therefore, there may be statistically significant differences in the concentration of some major and minor trace elements between the harbours which are of no practical importance (i.e. the concentration of element may be slightly enriched in one harbour but the concentration of the element in both harbours is still very low).

The result have also been compared against the expected background concentration range to determine if there is evidence for enrichment in any trace elements in the estuary and to aid in assessing whether any statistical differences detected using the statistical analysis are of practical importance.

6.1.1 Trace and Major elements

The concentration of most elements appears to be at the lower end of the estimated natural ranges. However the following trends were noted:

- ▮ Changes in the proportion of finer grain size fractions within the sediment appear to explain the majority of the differences in trace element concentrations within and between estuaries. Sediments closer to river mouths have a much greater proportion of particle sizes less than 63 μm and higher concentrations of most trace elements.
- ▮ The mean concentration of aluminium was lower at Aotea Harbour compared to Kawhia and Port Waikato, possibly a result of the lower fraction of clay particles (less than 2 μm) in Aotea Harbour than in Kawhia Harbour. Differences in the surrounding geology may explain the differences in the mean concentration of aluminium between Aotea Harbour and Port Waikato.
- ▮ Generally, Port Waikato sediments contained the lowest concentrations of aluminium. This is probably due to lower concentration of alumino-silicate minerals such as clays, which is indicated by the particle size analysis undertaken at Port Waikato.
- ▮ The concentration of copper is slightly lower in Aotea than in Kawhia and Raglan harbours.

- ▮ The mean concentrations of most trace elements were generally similar for Aotea and Kawhia harbours; however the mean concentrations of most trace elements were statistically lower at Port Waikato.
- ▮ Concentrations of antimony, arsenic and caesium in sediments at Port Waikato were elevated compared to the other West Coast estuaries in this study.
- ▮ Boron and lithium were enriched in all the West Coast estuaries included in this investigation compared to Waikato soils, however, this is probably due to the fact that seawater contains elevated concentrations of these elements compared to freshwater.
- ▮ Calcium and strontium were enriched in all the West Coast estuaries included in this investigation compared to Waikato soils. This may be due to the weathering of limestone rock found adjacent to these estuaries and/or because seawater contains elevated concentration of these elements.

Due to the low level of urbanisation and because significant urban development is not expected within the Aotea and Kawhia catchments, a significant change in the concentration of trace elements in these two harbours is not expected in the short-to-medium term. Development within the Raglan Harbour catchment is likely to be more significant than that in either of Aotea or Kawhia harbours. This could have a measurable impact on the sediment quality in the medium-term but at this point it is not possible to estimate the magnitude of the change.

Changes and development within the Waikato River catchment, such as increasing intensification of dairy farms, and population growth and increasing urbanisation within Franklin District, may have potential future impacts on the quality of sediments at Port Waikato, depending on what controls are imposed on land use and development.

In the future, the concentrations of some trace elements in the sediments at Port Waikato could increase as a result of increasing nitrification of the eight hydrolakes along the Waikato River. Increased nitrification could result in low oxygen conditions (due to eutrophication), thereby releasing arsenic (and other trace elements such as antimony) back to the overlying water as a result of reductive dissolution of iron oxides to which the arsenic (and other trace elements) is bound. This could result in an increased loading of arsenic in the Waikato River and result in more arsenic (and other trace elements) being sorbed onto sediments at Port Waikato.

6.1.2 Organic Compounds

Polycyclic Aromatic Hydrocarbons

Concentrations of total PAHs in all samples were below ANZECC ISQG-low trigger values and in most samples the concentrations of PAHs were below analytical

detection limits. The highest concentration of PAHs was detected in Kawhia Harbour and Port Waikato, whereas Aotea Harbour had the lowest concentrations of PAHs, with trace quantities of phenanthrene being detected in only one sample.

PAH ratios may be used to infer the source of the PAHs. PAHs of molecular mass 178 and 202 are commonly used to distinguish between combustion and petroleum sources (Yunker, 2002). There are several different PAHs ratio commonly used to infer the source of the PAHs, however only four of these ratios can be used for the 16 PAHs analysed for during this investigation (see Table 5). While the technique is imprecise, a coarse differentiation between petroleum product spills, combustion of petroleum products (i.e. vehicle sources) or combustion of biomass or coal (home fires, forest fires or industrial use) can be inferred by determining whether the various PAH ratios fall within particular ranges (Yunker, 2002).

Table 5: Critical ratios of PAH used for Source Identification

Source	Anthracene/anthracene + phenanthrene (An/178)	Fluorantene/fluoranthene + pyrene (Fl/Fl+Py)	Benzo[a]anthracene/benzo[a]anthracene+chrysene (BaA/228)	Indeno[1,2,3-c,d]pyrene/indeno[1,2,3-c,d]pyrene + benzo[g,h,i]-pyrene (IP/IP+BghiP)
Petroleum products	>0.10	<0.40	<0.20	<0.2
Combustion of petroleum products	<0.10	0.4-0.5	0.20-0.35	0.2-0.5
Combustion of biomass or coal	<0.10	>0.5	>0.35	>0.5

Table 6: Ratios of various PAHs in Kawhia and Port Waikato sediments

Sample	Anthracene/ anthracene +phenanthrene (An/178)	Fluorantene/ fluoranthene + pyrene (Fl/Fl+Py)	Benzo[a]anthracene/ benzo[a]anthracene+ chrysene (BaA/228)	Indeno[1,2,3-c,d] pyrene/ indeno[1,2,3-c,d] pyrene + benzo[g,h,i]-pyrene (IP/IP+BghiP)
Kawhia 1, 2 & 3	0.182	0.500	0.39	0.423
Kawhia 10, 11 & 12	0.354	0.445	0.42	0.455
Port Waikato 9	NC	0.569	0.491	0.433
Port Waikato 13	NC	0.567	0.506	0.442
Port Waikato 14	NC	0.606	0.442	NC

NC = Not calculated. Insufficient data to calculate PAH ratio.

Only Kawhia Harbour and Port Waikato sediments had sufficient concentrations of PAHs to allow PAH ratios to infer the source of the PAHs (see Table 6).

Two of the composite sediment samples collected from Kawhia had sufficient concentrations to be able to use this technique. Both of these samples had an anthracene to anthracene plus phenanthrene (An/178) ratio greater than 0.1 which indicates that combustion processes rather than petroleum are the more probable source of the PAHs found in the Kawhia Harbour sediments. Calculation of Fl/Fl+Py and IP/IP+B(ghi)P ratios suggests the source was combustion of petroleum (e.g. vehicle sources), as both fell within the range 0.4 to 0.5.

Three of the Port Waikato samples had sufficient concentrations of some of the required PAHs to calculate some of the ratios. All three samples had BaA/228 ratios greater than 0.35 suggestive of combustion sources. Calculation of the Fl/Fl+Py and IP/IP+BghiP ratios provided ambiguous results, with the former suggesting a biomass and coal combustion source while the latter suggesting a petroleum combustion source for the two samples for which these ratios could be calculated.

Environmental fractionation and degradation processes can potentially obscure sources of PAHs, therefore the results of this ratio analysis should be treated with caution.

Concentrations of PAHs are expected to remain low in the short term (barring any major oil spills in the catchment) due to the low level of urban development in the catchment areas relative to estuary size.

Organochlorine Compounds

Both the current sediment survey and an earlier one undertaken by MfE in 1996 (MfE, 1998) show only trace quantities of OCPs in the West Coast Harbours. The MfE (1998) study found ultra-trace (less than 1 ppb) quantities of Dieldrin and DDT in both composite samples collected from Kawhia Harbour and the current survey found hexachlorobenzene (HCB) and DDT at Kawhia, HCB at Aotea and Port Waikato and dieldrin in one sample at Port Waikato. No organochlorine pesticide residues were detected in Raglan Harbour.

Low levels of hexachlorobenzene were found in several sediments from Aotea, Kawhia and Port Waikato (approximately 0.0011 to 0.0037 mg/kg). This result is unusual, because this compound was only used as an experimental fungicide on cereal from 1970 to 1972, although it is a contaminant of some other chlorinated pesticides (including pentachlorophenol). Although hexachlorobenzene is very persistent it is unusual that it would be detected in any of estuaries after such a long period of time considering its very limited and low volume use in the early 1970s. The fact that hexachlorobenzene was not detected in Kawhia Harbour, or any of the other estuaries sampled, during the 1996 MfE survey (MfE, 1998) means the current results should be treated with some caution.

No ANZECC sediment quality guidelines exist for hexachlorobenzene.

Traces (approximately 0.001 mg/kg) of 4,4' DDT were detected at one location in Kawhia Harbour, but no degradation daughter products were detected. The concentration of 4,4' DDT was slightly higher than that detected by the MfE survey in 1996 (0.00003 mg/kg), which also detected the presence of a number of daughter products, particularly 4,4' DDE (0.0002 mg/kg). The concentration range of the DDT isomers and congeners detected in the MfE 1996 study was below the detection limit of the current study. The concentrations of DDT isomers and congeners in the West Coast harbours were below ANZECC ISQG-low guideline values and lower than the concentration of DDT in Waikato pastoral soils. Although this indicates it is unlikely to have direct toxicity effects on sediment dwelling organisms, the ANZECC sediment quality guidelines are not designed to protect aquatic ecosystems from indirect exposure (such as bio-magnification and bioaccumulation within the food chain).

Analysis of acidic and organo-nitrogen and organo-phosphorus pesticide residues, but not organochlorine pesticide residues, was undertaken as part of the water quality analysis of six samples collected from the Waikato River. Trace quantities of the acid herbicide MCPB were detected in three water samples at concentrations ranging between 0.000007 and 0.00012 g/m³.

Previous water quality sampling undertaken by Environment Waikato between September 2003 and June 2004 has detected a variety of organo-nitrogen and organo-phosphorus compounds, which were not detected during the current monitoring round.

The detection or non-detection of any pesticide residue in water will be controlled by the recent usage of the compound within the catchment area, which may be very sporadic and partly seasonal, and the analytical detection limits employed. Due to the limited and infrequent sampling conducted to date no inference can be made about either maximum exposure concentrations or exposure frequency. Some pesticide residues are detected more often than others (such as hexazinone and terbutylazine, which are mainly used in forestry). The concentrations of agrichemicals appear to be low (low ppb levels) within the Waikato River, therefore significant accumulation of these compounds in the estuary is not expected within the short to medium term.

The previous and current concentrations of the various detected pesticide residues were lower than ANZECC water quality guidelines for 95% ecosystem protection. However these guidelines may not be sufficiently protective to guarantee no adverse effects on higher trophic level organisms for persistent organic pollutants which are known to bio-accumulate.

Persistent organic pollutants (POPs)(such as DDT) are no longer used in NZ, however, residues of these compounds are still found in agricultural soils within the Waikato region. These residues may continue to be an on-going low-level diffuse contaminant source to the West Coast Harbours for many years. The very low concentrations detected and the large number of sediment samples for which organochlorine pesticides were below the analytical detection limit suggests that the transportation of contaminated soil/sediment from rural pastures into the West Coast harbours has not had a significantly impact on sediment quality to date.

The concentration of both hexachlorobenzene and DDT (as well as DDE and DDD) are likely to decrease slowly over time, but detectable concentrations of these compounds may continue to be found for a number of years, even though these compounds are no longer used in NZ.

6.2 Impacts on Marine Mammals

Marine mammals are known to frequent Port Waikato and both the Department of Conservation and Environment Waikato have expressed concerns that reduced Waikato River water quality could potentially impact the health of marine mammals (in particular Maui's Dolphin, which is classified as critically endangered).

6.2.1 Arsenic

Arsenic is a highly toxic metalloid which is present in the Waikato River at elevated concentrations, due to both natural geothermal inputs and anthropogenic activity such as the discharge of geothermal fluids from the Wairakei geothermal power station. The typical concentration of arsenic in seawater is 1.5 mg/m³ with typically 0.1 to 2.0 mg/m³ in freshwater.

Arsenic concentrations in the Waikato River at Port Waikato were typically between 10 and 30 mg/m³, 5 to 15 times higher than typical concentrations found in other

freshwater systems and up to 20 times higher than levels typically found in marine water. Arsenic(III) and arsenic(V) are the two main arsenic species present in natural waters. Arsenic(V) is the thermodynamically favoured chemical form of arsenic in oxygenated circum-neutral pH waters (Freeman, 1985) and is the predominate arsenic species in marine waters (ANZECC, 2000). Generally arsenic (III) is only stable under reducing conditions (Freeman, 1985).

In general, inorganic arsenic is more toxic than organic arsenic and arsenic(III) is more toxic than arsenic(V). The ratio of the arsenic measured in the Waikato River is about 5-10% arsenic (III) to 90-95% arsenic(V) most of the time, however during the summer months the concentration of arsenic(III) to arsenic(V) in the Waikato River can reach as high as 50:50 (Aggett & Aspell, 1980; Freeman, 1985). Freeman linked that to the cyanobacteria *Anaebena* metabolising arsenic(V) to (III) in the summer.

Although arsenic concentrations at Port Waikato exceeded ANZECC water quality guidelines (see section 5.3.1), and during summer months up to 50% of the inorganic arsenic species within the Water River can be in the form of the more toxic arsenic(III) species, the risk to marine mammals is thought to be low for standard eco-toxicity end points (such as mortality, reproductive effects and growth). This is due to two main reasons:

1. The concentration range associated with which adverse effects have been seen in fish species is between 232 and 16,030 mg/m³. This range is higher than the concentration of arsenic found in the Waikato River. Due to the greater body weight of marine mammals compared to the fish species used in these tests, it is considered that the onset of direct toxicity in marine mammals is likely to occur at or above the higher end concentrations found in fish.
2. Marine mammals, in particular dolphins, are transitory and are unlikely to spend a significant amount of time feeding within the Waikato River mouth at Port Waikato. Marine mammal exposure to the elevated concentrations of arsenic at Port Waikato will tend to be as a result of multiple short exposures rather than continuous long-term exposures assumed by the ANZECC (2000) water quality guidelines.

Dietary exposure to arsenic for marine mammals may be a low risk even if they are eating fish species which have high concentrations of arsenic within their tissues. This is because the dominant form of arsenic within most marine species is arsenobetaine, which is relatively non-toxic to humans and thought to have a very low toxicity to marine mammals (Kunito *et al.*, 2008).

Recent research on the effects of arsenic on marine mammals and seabirds (Kunito *et al.*, 2008) indicates that repeated exposures may increase the risk of immunosuppression or oxidative stress which could promote tumour formation (especially due to low level exposure to arsenic (III)). Recent studies have also suggested that inorganic arsenic may also act as an endocrine disruptor. These types of toxicological

effects are not considered in the ANZECC water quality guidelines and therefore these guidelines are not designed to protect aquatic organisms for these types of toxicological endpoints. As inorganic arsenic species can exert these types of toxicological effects at low concentrations, further work is required before the risk to marine mammals of carcinogenicity effects, endocrine disruption or immunosuppression as a result of intermittent exposure to low-levels of inorganic arsenic can be quantified.

If further research does indicate that there is a credible risk to marine mammals from the elevated arsenic concentrations at Port Waikato, Environment Waikato options for reducing this risk are limited because over 50% of the arsenic within the Waikato River comes from natural sources. The current approach taken by Environment Waikato of working with Contact Energy to reduce the input of arsenic-containing geothermal fluids from the Wairakei geothermal power station remains the best option for reducing the arsenic load within the Waikato River. However, arsenic concentrations within the Waikato River could potentially increase if arsenic contained within the sediments of the six hydro-electric lakes on the Waikato River is released. Eutrophication of the hydro-lakes caused by nutrient runoff can cause oxygen depletion within the hydrolakes giving rise to anaerobic conditions. Under anaerobic conditions iron oxides containing high concentrations of arsenic may undergo reductive dissolution which would result in the release of arsenic into the Waikato River. A significant increase in the levels of arsenic within the Waikato River would increase the risk of ecotoxic effects adversely impacting both freshwater and marine aquatic organisms within and around the river mouth.

6.2.2 Organic Compounds

Persistent organic pollutants (POP) such as organochlorine pesticides are known to biomagnify up the food chain; dolphins can bio-concentrate organochlorines and hormones up to 1,000,000 times the concentrations in water (Fair & Becker, 2000). In addition, dietary exposure is thought to be more important than direct contact with either sediment or water. The organochlorine compounds in organisms dwelling in sediments can be up to 20 times higher than the sediment itself (Hickey *et al.*, 1997).

Bioaccumulation of POPs in marine mammals, and in particular Hector's dolphins (Maui's dolphin is a subspecies of Hector's dolphins), has been reported in New Zealand (Table 7).

Table 7: Mean organochlorine TEQ³ levels of southern ocean cetaceans

Cetacean	TEQ (pg/g)
Baleen Whales	1.7
Beaked Whales	11.0
Pilot Whales	12.2
Oceanic Dolphins	12.5
Hector's Dolphins	83.3
Source: MFish & DoC (2007)	

Evidence that common dolphins (*Delphinus* sp.) accumulate POPs to high levels has also been reported from a mass stranding at Lucas Creek, Auckland (Stockin *et al.*, 2007). Total DDT (Σ DDT) levels in blubber ranged from 17 to 337 and 654 to 4430 μ g/kg wet weight in females and males, respectively. Transfer of Σ DDT species from mothers to dolphin calves was reported at 46% (Stockin *et al.*, 2007).

These levels are close to those suspected to cause adverse effects in other animal species (Stockin *et al.*, 2007). In the case of Hector's dolphins, the reported levels are probably a result of the dolphins' close inshore habitat, and therefore higher exposure to POPs in water, sediment, and prey species. It is very likely that Maui's dolphins can bioaccumulate POPs present in water or their diets at levels of about 10^{-14} to 10^{-15} grams (1 to 10 femtograms), well below most analytical detection limits.

POPs have been detected in sediment and soil within the Waikato River catchment and it is possible that some POPs are still entering river and coastal waterways at levels which are below current analytical detection limits. Therefore, given the possible presence of POPs in river and coastal waters, on-going exposure of Maui's dolphins and other marine mammals to toxicological risk from these residues cannot be ruled out.

6.2.3 Endocrine Disrupting Compounds

No estrogenic activity was found in any of the water samples analysed and HortResearch advised Environment Waikato that this is the first time that no estrogenic activity has been found in any sample that the laboratory has analysed (Environment Waikato, pers. comm.). However, because of limitations of the E-Screen bioassay, and problems with the methodology as discussed in section 2.3.2, the E-Screen results cannot be regarded as reliable.

Both dairy farm effluent and sewage effluent from a number of waste water treatment plant which discharge into the Waikato River are known to contain high levels of EDC (Saramah *et al.*, 2006). However, the potential of these wastes to cause endocrine

³ TEQ stands for toxic equivalents, which is a method to summarise the toxic effects of various organochlorine compounds.

disruption in the Waikato River is unknown at present (Saramah *et al.*, 2006). EDC from industrial wastewater discharges (such as the bleached kraft pulp mill at Kinleith) may also result in some risk to aquatic organisms within the Waikato River. However, research undertaken by Judd *et al.* (1995) on the mill discharge found that the concentration of potentially EDC declined to background levels 38 kilometres downstream of the mill.

Due to the ability of marine mammals to bio-accumulate POPs in the low femtograms level it is possible that POPs such as DDT may be present at levels which may present toxicological risk, and in particular reproductive risk, and immunosuppression to Maui's dolphins and other marine mammals. However, the information reviewed is insufficient to properly assess the level of toxicological risk presented by EDC to Maui's dolphins, or other marine mammals, in the Port Waikato area.

6.2.4 Microbiological Impacts

Marine mammals, including Maui's dolphins, are potentially vulnerable to a wide range of human and livestock pathogens. One case of the presence of the brucellosis pathogen has been reported for a deceased Maui's dolphin calf, but it is not known whether the brucellosis was the primary cause of death (Department of Conservation, 2007). Marine mammals may be more susceptible to bacterial disease if already suffering from stress and immuno-suppression due to EDCs, boat traffic, oil and wastewater pollution, human disturbance, or competition for food from human fishing pressure (Fair & Becker, 2000; Beck & Rice, 2002).

Currently there are no guidelines developed to protect marine mammals, but the European Council is working on possible standards and approaches. Using human contact recreation standards as proxy standards is being considered (pers. comm. Professor Paul Thompson, University of Aberdeen). Human recreation standards may or may not be sufficient for dolphin protection, because of the dolphin's ability to bioconcentrate pollutants from very low levels in water and food (Thompson, 2007).

Results of the microbial analysis for the Port Waikato water samples showed that microbial contamination was present. However, there are difficulties with the reported sampling procedures (see section 2.3.2). Showers and rain were observed on the sampling day, and a one-off spot sample on one day only is not adequate to provide an accurate picture of microbial levels and trends in the water column (MFE Guidelines for Microbiological Analysis, 2003).

A more comprehensive seasonal and weather-adjusted microbial sampling programme over a minimum 12 month period would be required to enable a more reliable analysis of the risk (if any) to Maui's dolphins presented by microbial contamination of waters.

7.0 Conclusions

7.1 Aotea, Kawhia and Raglan Sediment Quality

Overall, the sediment quality in Aotea, Kawhia and Raglan Harbours was good. The concentrations of most major and trace elements in the sediment are at the lower end of their estimated natural ranges and below ANZECC Interim Sediment Quality Guidelines - Low (ISQG-Low); the exception was one sediment sample collected in Kawhia Harbour which marginally exceeded the ISQG-low guideline for arsenic but was lower than the ANZECC ISQG-high trigger value. Boron, calcium, lithium and strontium were enriched in the sediments of Aotea, Kawhia and Raglan harbours compared to Waikato background soil. Seawater contains relatively high concentrations of boron, calcium, lithium and strontium and this may be the source of the enrichment of these elements in the sediments of these harbours. The spatial variation of trace elements within and between the harbours correlated with sediment particle size variation, although it is also possible that sediments near river mouths and towns may be slightly enriched due to anthropogenic activities and/or due natural variations in concentration in the geology near the river mouths.

The range of total phosphorus was between 340 and 780 mg/kg. Much of the variation of total phosphorus concentration in sediments appeared to be related to changes in the grain size distribution within the harbours. Generally the highest concentration of phosphorus was found near river mouths, where the finer grain sediments were also located. This is probably due to two factors; one is the finer grain sediments found at the river mouths are more effective at sorbing phosphorus than the sandier sediments in the main part of the harbours. The other is that the rivers are transporting phosphorus and phosphorus-laden sediments into the harbour. Grain size normalisation would be required to determine the relative importance of each mechanism.

An insufficient number of samples were analysed for total nitrogen or total organic carbon to undertake any interpretation of the data.

Low concentrations of PAHs were detected in at least one sample from each of Aotea, Kawhia and Raglan Harbours. The highest concentrations of PAHs in sediment collected from Kawhia and Raglan Harbours were found in sediment samples collected nearest to the two townships, which suggests the towns may be the source. Preliminary data analysis of the PAH ratios from Kawhia Harbour tentatively suggests that a petroleum combustion source (i.e. car exhaust) rather than petroleum spills or coal/biomass combustion (such as forest fires and home heating) was the probable source of the PAHs, but more work would be needed to confirm this. Overall, the concentration of PAHs was low or below trace analytical detection limits in the estuaries and was below ANZECC (2000) ISQG-low guideline values. Therefore the PAHs detected in the sediments are unlikely to be having an adverse effect on the aquatic ecosystem.

With the exception of the trace detection of DDT and hexachlorobenzene in one sample collected from Kawhia Harbour and trace levels of hexachlorobenzene in one sample from Aotea Harbour, the concentration of organochlorine pesticide residues was generally below the analytical detection limit (1 ppb). The concentration of DDT detected in the sample from Kawhia Harbour was below the ANZECC ISQG-low guideline value. There is no ANZECC guideline for hexachlorobenzene.

7.2 Port Waikato

7.2.1 Sediment Quality

The concentrations of most trace elements in the sediments at Port Waikato were at the lower end of the range detected across the estuaries in this study. The exceptions to this were antimony, arsenic and caesium, which were elevated in Port Waikato sediments compared to the sediments from other estuaries. It is likely that these elements are elevated at Port Waikato due to the geothermal inputs into the Waikato River. The concentrations of arsenic exceeded ANZECC (2000) ISQG-low guideline values but did not exceed the ANZECC (2000) ISQG-high guideline values. Therefore the detected concentrations are thought to pose a low-to-moderate risk to aquatic organisms such as benthic macro-invertebrate communities. However, at their current levels they are not present at concentrations known to pose a risk to higher tropic levels.

The concentrations of all other elements were lower than the ANZECC (2000) ISQG-low guideline values, and within their estimated natural ranges. However, there was extensive spatial variation of concentrations of elements, most probably related to variations in the grain size of the sediments within the river channel. For the most part, sediments at Port Waikato were comprised of medium-to-coarse grain sands which have low sorption capability.

Concentration of phosphorus in the sediments ranged from some of the lowest observed in any of the West Coast estuaries to some of the highest. Sediment grain size distribution appears to be the most important factor in controlling the concentration of phosphorus within the sediment. Consequently, the changes in concentrations between various sampling sites are thought to reflect the differences in the grain size at the sampling location rather than differences in nutrient inputs between sampling locations.

Trace quantities of organochlorine pesticides and polycyclic aromatic hydrocarbons were detected at a limited number of sampling sites in Port Waikato. PAH ratio analysis suggests that a combustion source is most likely for these samples, however the data analysis was inconclusive whether petroleum combustion or coal/biomass combustion was the potential source of the PAHs. It is possible that environmental fractionation and degradation processes have potentially obscured sources of PAHs or that there is a mixed source for the PAHs in Port Waikato sediments. The results of this ratio analysis should be treated with caution.

The concentrations of all organic compounds detected were below ANZECC-ISQG-low guideline values and therefore are thought to pose a low risk to aquatic organisms.

7.2.2 Water Quality

The concentration of arsenic in the estuarine water at Port Waikato was elevated. It is likely that most of the measured arsenic (90%) was in the form of arsenic (V) and therefore would exceed the ANZECC (2000) low reliability marine trigger value for arsenic(V). Studies (Freeman, 1985) have found that during the summer months up to 50% of the total concentration of arsenic may be present as As(III) and therefore the arsenic concentration would exceed both the ANZECC (2000) low reliability marine trigger values for arsenic(III) and arsenic(V).

Although both of these guideline values are only indicative interim trigger values, the concentration of arsenic is also likely to exceed ANZECC (2000) high reliability guideline values for arsenic(III) freshwater species and may exceed ANZECC (2000) high reliability freshwater trigger value for arsenic(V), during summer months. Therefore it is likely that the arsenic concentrations in the estuarine waters at Port Waikato pose a credible risk to some sensitive marine species (e.g. phytoplankton) and potentially early life stage of some marine organisms.

The concentrations of most of the other trace elements were below the analytical method detection limit but previous work undertaken by Environment Waikato indicates that their concentrations are unlikely to exceed ANZECC (2000) guideline values.

No endocrine disrupting compounds were detected in any of the water samples submitted for EDC analysis by E-screen. The EDC analysis by E-Screen bioassay is not regarded as reliable due to known methodological issues and weaknesses associated with this test method. The presence of several EDC inputs to the river, including on-going low-level pesticide residue inputs, and domestic and industrial waste water discharges, would suggest that EDC should have been detected in river waters.

One-off microbial samples on a single day are not adequate to give a reliable picture of the microbial health of a water body and therefore it is not possible to comment of the microbial health of the Waikato River. A more representative sample regime would be required to adequately determine the status of the water quality at Port Waikato with respect to microbiological water quality criteria.

7.2.3 Potential Risk to Marine Mammals

Marine mammals, including Maui's dolphins, are potentially vulnerable to a wide range of human and livestock pathogens. Additional stressors such as boat traffic, oil and wastewater pollution, human disturbance, competition for food from human fishing pressure, and immuno-suppression effects due to EDC and (potentially) arsenic(III) may make marine mammals more susceptible to bacterial disease. The high levels of pesticide residues reported previously in Hector's dolphins, known inputs of EDC into

Port Waikato river waters, and the likely vulnerability of Maui's dolphins to EDC (particularly in respect of endocrine and reproductive disruption), indicate that EDC represent a possible, but inadequately described toxicological risk to Maui's dolphins in the Port Waikato area.

8.0 Recommendations

Future routine sediment quality monitoring could be limited to sampling Port Waikato and Raglan Harbour. The concentration of trace elements does not significantly vary between Aotea, Kawhia and Raglan Harbours.

Routine analysis for organochlorine pesticide residues in the sediments from the West Coast Harbours appears to be unnecessary as concentrations of these compounds are barely detectable and it is likely that the concentrations will decrease over time.

Should Environment Waikato wish to better understand the risk presented to Maui's dolphins by EDC in Port Waikato waters, it is recommended that EDC assays be undertaken in accordance with USEPA protocols for Tier 1 and Tier 2 EDC assessments (USEPA 1998).

Should Environment Waikato wish to better understand the microbiological health of Port Waikato, it is recommended that microbial sampling of Port Waikato waters be undertaken over a minimum 12 month timeframe, in accordance with the MfE Guidelines for Microbiological Water Quality investigations (MfE 2003).

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Appendix A: Sampling Locations

Sample	NZMG	NZMG	NZTM	NZTM
Aotea 1	2670525	6352484	1760311	5790793
Aotea 2	2671602	6352470	1761388	5790780
Aotea 3	2671876	6351793	1761663	5790104
Aotea 4	2672615	6353344	1762399	5791656
Aotea 5	2672607	6354352	1762390	5792664
Aotea 6	2672975	6355780	1762756	5794092
Aotea 7	2674116	6355255	1763898	5793569
Aotea 8	2673799	6356469	1763579	5794783
Aotea 9	2674702	6357501	1764481	5795816
Aotea 10	2673898	6357878	1763676	5796192
Aotea 11	2675962	6358708	1765739	5797025
Aotea 12	2674520	6359348	1764296	5797663
Aotea 13	2672751	6359442	1762527	5797754
Aotea 14	2672630	6360303	1762405	5798615
Aotea 15	2671189	6358993	1760965	5797303
Aotea 16	2671403	6357920	1761181	5796230
Aotea 17	2672027	6356767	1761807	5795078
Aotea 18	2669804	6358000	1759582	5796308
Aotea 19	2670287	6356459	1760067	5794768
Aotea 20	2671701	6355850	1761482	5794161
Aotea 21	2671095	6354608	1760878	5792918

Sample	NZMG E	NZMG N	NZTM	NZTM
Kawhia 1	2671125	6348772	1760916	5787081
Kawhia 2	2673128	6348327	1762919	5786639
Kawhia 3	2675064	6348643	1764855	5786958
Kawhia 4	2674805	6347295	1764598	5785609
Kawhia 5	2676165	6346658	1765959	5784974
Kawhia 6	2677677	6345265	1767473	5783583
Kawhia 7	2677014	6344723	1766810	5783040
Kawhia 8	2675678	6344921	1765474	5783236
Kawhia 9	2672270	6346407	1762064	5784718
Kawhia 10	2670457	6346464	1760251	5784772
Kawhia 11	2671920	6344861	1761716	5783171
Kawhia 12	2670919	6343471	1760717	5781780
Kawhia 13	2668542	6344571	1758338	5782877
Kawhia 14	2668649	6343040	1758447	5781346
Kawhia 15	2669798	6341301	1759598	5779608
Kawhia 16	2671458	6340452	1761260	5778761
Kawhia 17	2672846	6338625	1762650	5776936
Kawhia 18	2670608	6337629	1760413	5775937
Kawhia 19	2670132	6339085	1759935	5777392
Kawhia 20	2667149	6342054	1756948	5780358
Kawhia 21	2666408	6340480	1756209	5778783
Kawhia 22	2665389	6341926	1755188	5780227
Kawhia 23	2666673	6343705	1756470	5782008

Sample	NZTM_X	NZTM_Y	NZMG_X	NZMG_Y
Port Waikato 1	1751424	5862203	2661750	6423908
Port Waikato 2	1752400	5861181	2662724	6422884
Port Waikato 3	1753553	5861397	2663877	6423098
Port Waikato 4	1754377	5862065	2664703	6423764
Port Waikato 5	1754774	5862683	2665101	6424382
Port Waikato 6	1755028	5863280	2665356	6424979
Port Waikato 7	1755287	5863944	2665616	6425642
Port Waikato 8	1755285	5864757	2665616	6426455
Port Waikato 9	1752785	5860735	2663108	6422437
Port Waikato 10	1754070	5861030	2664394	6422731
Port Waikato 11	1755003	5862355	2665329	6424053
Port Waikato 12	1755421	5862946	2665748	6424644
Port Waikato 13	1755854	5863528	2666182	6425225
Port Waikato 14	1756226	5864119	2666555	6425816
Port Waikato 15	1755881	5864306	2666210	6426004
Port Waikato 16	1756150	5864844	2666480	6426541
Port Waikato 17	1756673	5865211	2667004	6426907
Port Waikato 18	1755194	5865344	2665525	6427043
Port Waikato 19	1754908	5865733	2665240	6427432

Sample	NZMG E	NZMG N
Raglan WI	2679307	6380510
Raglan TU	2678891	6378988
Raglan OB	2679095	6377346
Raglan HB	2681515	6377897
Raglan X	2675315	6378062

Raglan samples: WI = Whatititirinui Island, TU = Te Puna Point, OB = Okete Bay, HB = Haroto Bay, X = Ponganui Creek.

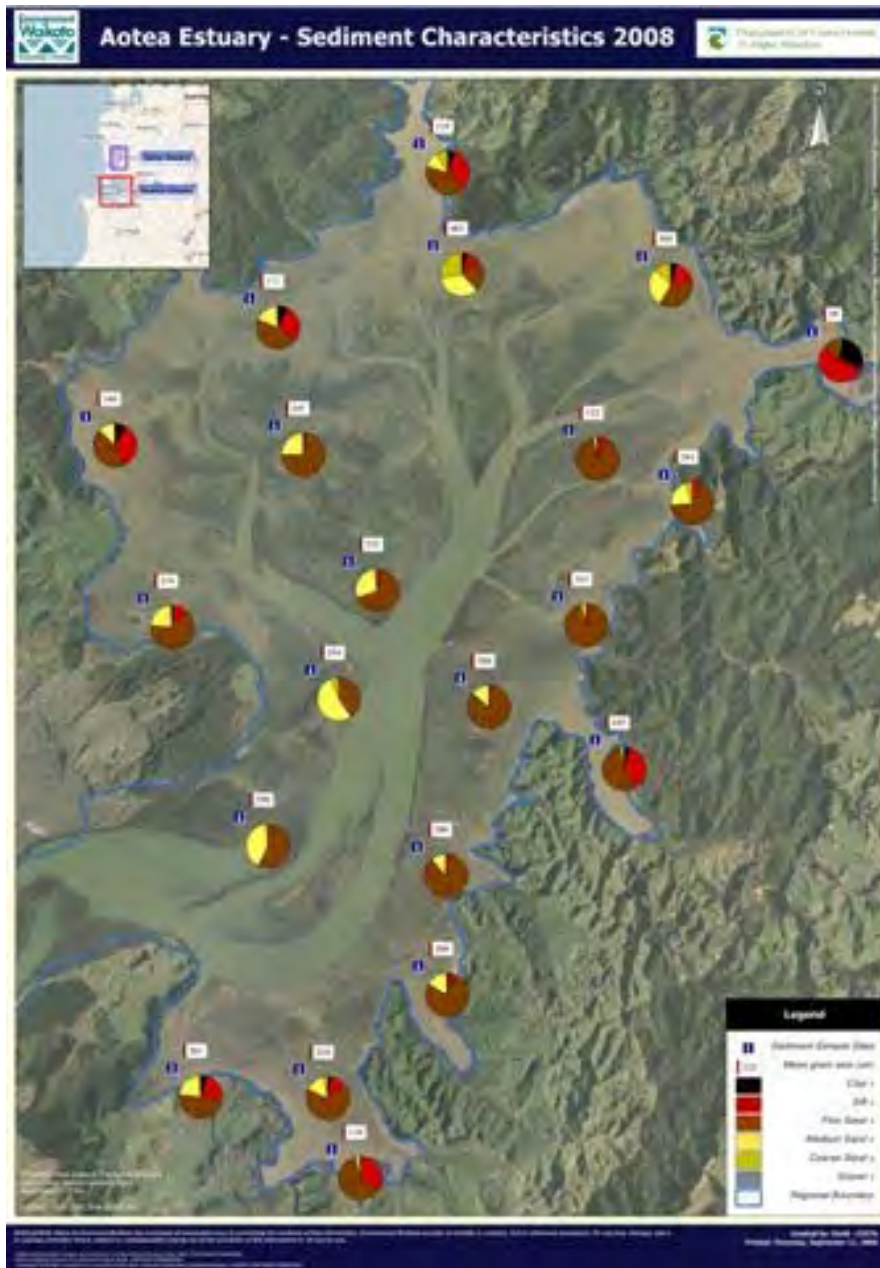


Figure A-1 Sampling location and sediment characteristics Aotea Harbour

WEST COAST ESTUARINE SEDIMENT CONTAMINANT ANALYSIS

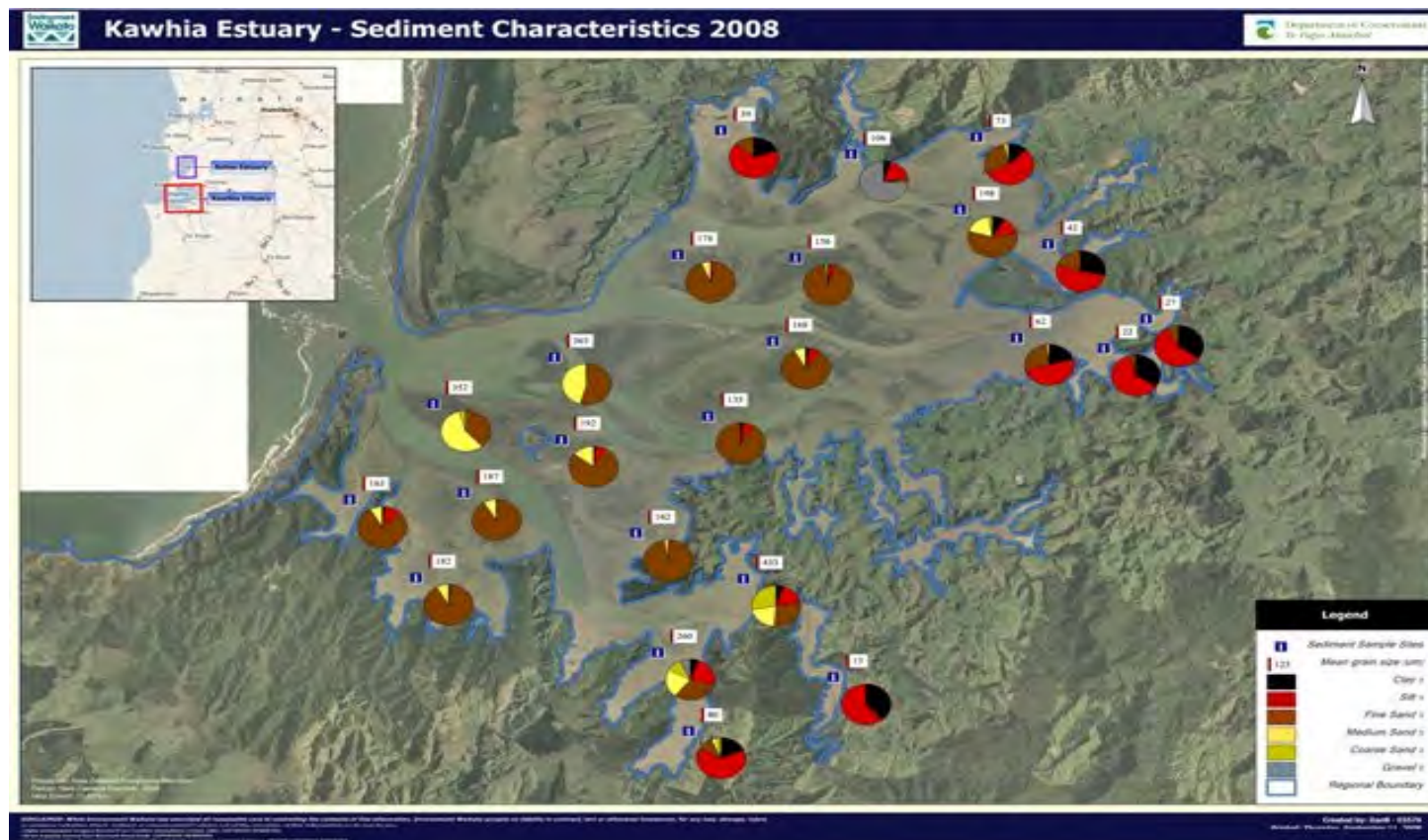


Figure A-2 Sample locations and sediment characteristics of Kawhia Harbour

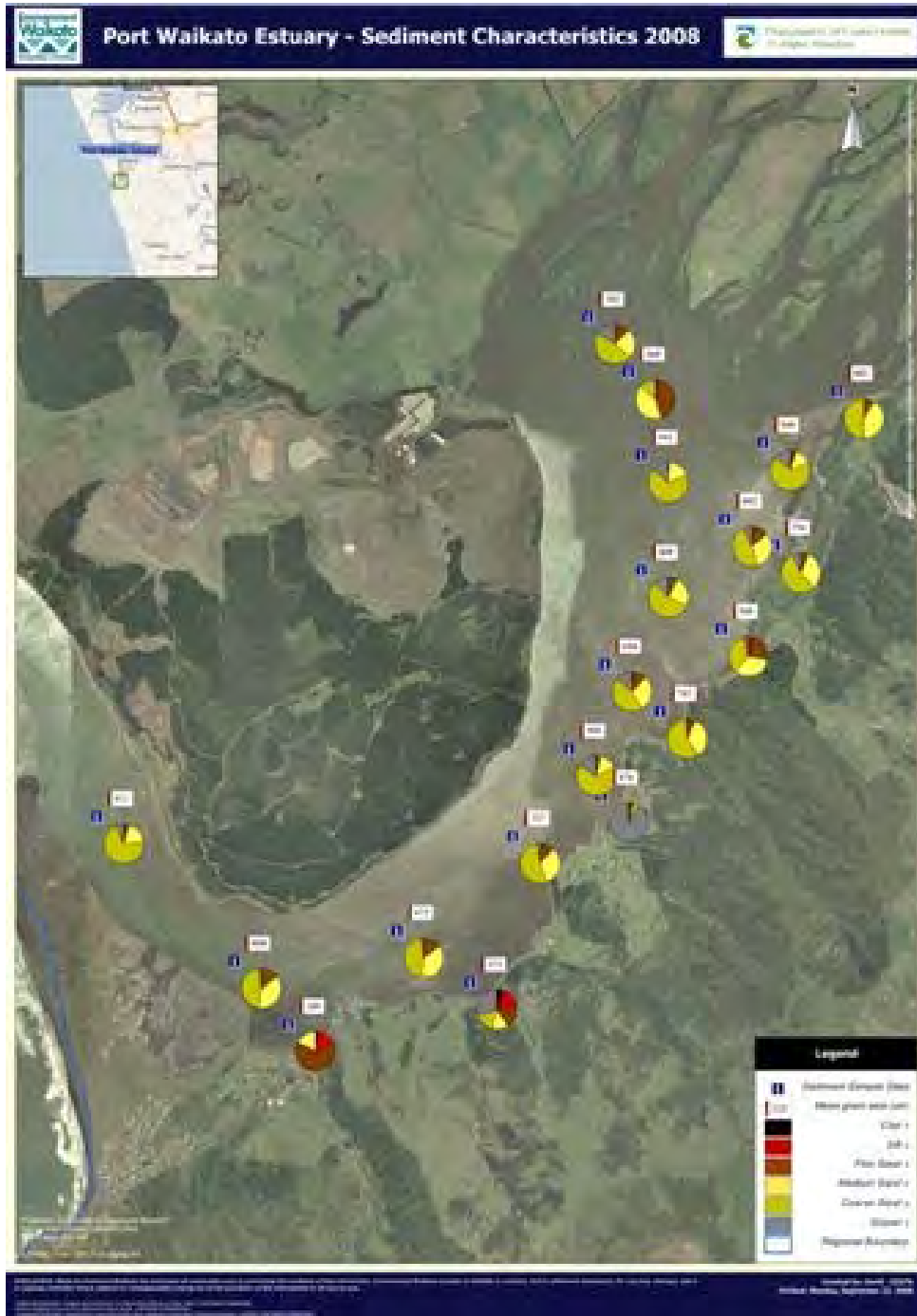


Figure A-3 Sample locations and sediment characteristics of Raglan Harbour

Appendix B: Background Soil Concentrations

Table B-1 The natural background concentration of major and trace elements in Waikato soils (Environment Waikato, 2008).

Element	Minimum	Maximum
Al	2260	70000
Fe	3540	76000
Mn	50	2960
Ag	0.03	0.32
As	0.7	25.3
B	2	8.5
Ba	14.8	310
Bi	0.03	0.4
Ca	390	3300
Cd	0.03	0.3
Co	0.54	27.8
Cr	1.5	150
Cs	0.3	5.3
Cu	3.3	55
F	68	300
Hg	0	0.26
La	1.53	65
Li	0.5	11.5
Mo	0.16	1.8
Ni	0.56	21
P	160	906
Pb	2.57	32.1
Rb	1.1	22
Sb	0.04	0.17
Se	2.2	4
Sn	0.38	2.6
Sr	5.3	57
Tl	0.03	0.6
U	0.114	2.5
V	10	300
Zn	11	83.7

Appendix C: Aotea Harbour Result Summary Tables

	% clay	% silt	% non-sand	% fine sand	% med sand	% coarse sand	Sand	mean grain size (µm)
Aotea 1	4.87	20.74	25.61	50.96	21.38	2.05	74.39	200.80
Aotea 2	2.40	11.18	13.58	68.35	14.98	3.10	86.42	209.50
Aotea 3	1.37	31.73	33.09	63.52	3.38	0.00	66.91	116.20
Aotea 4	1.59	4.76	6.35	77.34	16.30	0.01	93.65	205.70
Aotea 5	0.00	3.00	3.00	85.62	11.38	0.00	97.00	200.10
Aotea 6	0.00	2.27	2.27	83.78	13.94	0.01	97.73	208.02
Aotea 7	4.66	36.13	40.79	56.69	2.51	0.00	59.21	106.70
Aotea 8	0.00	2.94	2.94	93.36	3.70	0.00	97.06	162.50
Aotea 9	0.11	5.88	5.99	67.84	20.67	5.50	94.01	242.86
Aotea 10	1.57	6.48	8.05	89.19	2.76	0.00	91.95	152.25
Aotea 11	31.11	54.90	86.02	12.08	1.56	0.00	13.64	39.47
Aotea 12	4.73	17.89	22.62	36.00	28.40	12.98	77.38	302.78
Aotea 13	3.46	10.07	13.53	24.49	33.74	28.24	86.47	463.12
Aotea 14	5.33	30.84	36.17	43.67	11.03	9.12	63.83	219.06
Aotea 15	7.68	26.14	33.81	47.41	17.61	1.17	66.19	171.10
Aotea 16	0.00	2.19	2.19	72.49	24.76	0.57	97.81	240.68
Aotea 17	0.59	3.78	4.37	65.09	28.49	2.05	95.63	252.04
Aotea 18	8.42	34.87	43.30	43.83	12.46	0.42	56.70	140.33
Aotea 19	1.34	11.39	12.73	63.63	21.95	1.70	87.27	217.70
Aotea 20	0.00	0.00	0.00	40.58	53.13	6.29	100.00	354.00
Aotea 21	0.00	0.00	0.00	57.00	41.88	1.12	100.00	298.37

Table A-2: Aotea harbour sediment samples - Trace and major elements (all results expect for TOC and TN in mg/kg dry weight. TOC and TN are in g/100g dry weight)																	
Analyte	Laboratory results									Descriptive statistics						Guidelines	
	Aotea 1	Aotea 2	Aotea 3	Aotea 4, 5 & 6	Aotea 7, 8 & 9	Aotea 10, 12 & 13	Aotea 14, 15 & 16	Aotea 17, 18 & 19	Aotea 20, 21 & 22	Minimum	Maximum	Arithmetic mean	Geometric mean	Stdev	%RSD	ANZECC interim sediment quality guidelines	
Total Organic Carbon	0.27	0.33	0.16														
Total Nitrogen	0.071	0.1	0.06														
Aluminium	9900	14000	12000	11000	8600	15000	9200	12000	8100	8100	15000	11089	10865	2386.1	22.0%		
Antimony	< 0.040	0.062	0.052	0.076	0.042	0.046	0.042	0.048	0.053	< 0.040	0.076	0.049	0.046	0.015	32.9%	Antimony	2 25
Arsenic	12	8.3	6.3	6.5	6.3	6.8	7.8	8.4	6.2	6.2	12	7.6	7.5	1.9	25.0%	Arsenic	20 70
Barium	10	14	15	12	9.1	16	17	14	11	9.1	17	13.1	12.9	2.7	21.3%		
Bismuth	0.024	0.032	< 0.020	0.077	0.024	0.1	0.066	0.022	< 0.020	< 0.020	0.1	n/c ¹	n/c ¹	n/c ¹	n/c ¹		
Boron	18	13	11	10	16	17	15	12	7.7	7.7	18	13.3	12.9	3.5	26.8%		
Cadmium	0.014	0.017	0.013	0.022	0.016	0.029	0.018	0.02	0.018	0.013	0.029	0.019	0.018	0.005	26.6%	Cadmium	1.5 10
Caesium	0.52	0.54	0.45	0.3	0.39	0.8	0.86	0.38	0.19	0.19	0.86	0.5	0.4	0.2	49.0%		
Calcium	7400	16000	9500	14000	13000	5500	3100	7800	6100	3100	16000	9156	8192	4322.9	52.8%		
Chromium	15	12	14	12	11	15	12	11	10	10	15	12.4	12.3	1.8	14.7%	Chromium	80 370
Cobalt	9.8	5.8	7.6	5.6	3.9	5.4	4.9	4.5	6.5	3.9	9.8	6.0	5.8	1.8	30.9%		
Copper	6.2	6.4	6.2	6.4	4.3	7.9	4.6	6	7.2	4.3	7.9	6.1	6.0	1.1	18.7%	Copper	65 270
Iron	47000	24000	27000	20000	14000	17000	22000	18000	23000	14000	47000	23556	22220	9632.1	43.3%		
Lanthanum	5.4	6.5	6.7	6.8	5.3	8.9	6.7	6.5	4.7	4.7	8.9	6.4	6.3	1.2	19.2%		
Lead	3.6	3.8	3	3	3	7.2	5.3	3.2	2.4	2.4	7.2	3.8	3.6	1.5	41.5%	Lead	50 220
Lithium	9.6	12	9.7	8.9	7.6	20	11	7.4	4.5	4.5	20	10.1	9.4	4.3	46.1%		
Magnesium	3600	3300	3200	2500	2500	3600	2600	2600	2300	2300	3600	2911	2872	511.0	17.8%		
Manganese	360	230	260	220	150	170	190	190	230	150	360	222.2	215	61.8	28.7%		
Mercury	0.011	< 0.010	< 0.010	< 0.010	0.013	0.037	0.019	0.014	< 0.010	< 0.010	0.037	n/c ¹	n/c ¹	n/c ¹	n/c ¹	Mercury	0.1 5 1
Molybdenum	0.24	0.2	0.18	0.36	0.27	0.37	0.27	0.5	0.17	0.17	0.5	0.3	0.3	0.11	40.2%		
Nickel	6	5.2	5.5	4.8	4.2	9	5.4	4.4	4.6	4.2	9	5.5	5.3	1.4	27.2%	Nickel	21 52
Phosphorus	590	560	510	680	340	460	340	610	670	340	680	529	513.7	127.7	24.9%		
Potassium	1400	1100	960	670	1000	1400	1000	870	510	510	1400	990	948	295.1	31.1%		
Rubidium	6.5	6.2	4.8	3.4	5.9	7.7	6.6	3.9	2.1	2.1	7.7	5.2	4.9	1.8	36.9%		
Selenium	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	n/c ¹	n/c ¹	n/c ¹	n/c ¹		
Silver	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	< 0.020	n/c ¹	n/c ¹	n/c ¹	n/c ¹	Silver	1 3.7
Sodium	4400	5500	4500	4700	4900	7000	4500	4600	3000	3000	7000	4789	4686	1058.8	22.6%		
Strontium	53	100	78	120	120	64	28	99	74	28	120	81.8	75.3	30.9	41.1%		
Thallium	0.038	0.061	0.046	0.041	0.036	0.059	0.062	0.047	< 0.020	< 0.020	0.062	0.044	0.040	0.016	40.5%		
Tin	0.36	0.36	0.43	0.34	0.35	0.56	0.65	0.38	0.32	0.32	0.65	0.42	0.41	0.11	28.0%		
Uranium	0.25	0.46	0.3	0.62	0.39	0.57	0.39	0.63	0.2	0.2	0.63	0.42	0.39	0.16	40.2%		
Vanadium	120	78	100	110	41	36	69	80	130	36	130	84.9	78.2	33.1	42.3%		
Zinc	54	40	48	35	27	36	38	28	34	27	54	37.8	36.9	8.7	23.6%	Zinc	200 410

Notes:

n/c = not calculated

1. Descriptive statistics not calculated for analytes where more than 20% of samples were below the detection limit.

Exceeds ANZECC ISQG-Low guideline

Table C-3: Aotea Harbour sediment samples - Organic compounds

		Laboratory results						Descriptive statistics			Guidelines			
		Aotea 4, 5 & 6 Composite	Aotea 7, 8 & 9 Composite	Aotea 10, 12 & 13 Composite	Aotea 14, 15 & 16 Composite	Aotea 17, 18 & 19 Composite	Aotea 20, 21 & 22 Composite	Minimum	Maximum	Percentage of samples above detection limit	ANZECC interim sediment quality guidelines			
	Analyte name	Analyte units												
Organochlorine pesticides	Dieldrin ^{9,10}	mg/kg dry wt	< 0.0010	< 0.00099	< 0.0010	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	0.0%	Dieldrin	0.00002	0.008
	Hexachlorobenzene	mg/kg dry wt	< 0.0010	< 0.00099	0.0015	0.0014	< 0.00099	< 0.00099	< 0.00099	0.0015	33.3%			
	2,4'-DDD	mg/kg dry wt	< 0.0010	< 0.00099	< 0.0010	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	0.0%			
	4,4'-DDD	mg/kg dry wt	< 0.0010	< 0.00099	< 0.0010	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	0.0%	4,4'-DDE	0.0022	0.027
	2,4'-DDE	mg/kg dry wt	< 0.0010	< 0.00099	< 0.0010	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	0.0%			
	4,4'-DDE	mg/kg dry wt	< 0.0010	< 0.00099	< 0.0010	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	0.0%			
	2,4'-DDT	mg/kg dry wt	< 0.0010	< 0.00099	< 0.0010	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	0.0%			
	4,4'-DDT	mg/kg dry wt	< 0.0010	< 0.00099	< 0.0010	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	0.0%			
	Total DDD^{1,6,9}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d	n/d	0.0%	Total DDD	0.002	0.02
Total DDT^{2,6,9}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d	n/d	0.0%	Total DDT	0.0016	0.046	
Polycyclic Aromatic Hydrocarbons	Acenaphthene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Acenaphthene	0.016	0.5
	Acenaphthylene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Acenaphthylene	0.044	0.64
	Anthracene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Anthracene	0.085	1.1
	Benzo[a]anthracene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Benzo[a]anthracene	0.261	1.6
	Benzo[a]pyrene (BAP)	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Benzo[a]pyrene (BAP)	0.43	1.6
	Benzo[b]fluoranthene + Benzo[j]fluoranthene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%			
	Benzo[g,h,i]perylene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%			
	Benzo[k]fluoranthene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%			
	Chrysene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Chrysene	0.384	2.8
	Dibenzo[a,h]anthracene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Dibenzo[a,h]anthracene	0.063	0.26
	Fluoranthene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Fluoranthene	0.6	5.1
	Fluorene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Fluorene	0.019	0.54
	Indeno(1,2,3-c,d)pyrene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%			
	Naphthalene	mg/kg dry wt	< 0.010	< 0.010	< 0.011	< 0.010	< 0.010	< 0.010	< 0.010	< 0.011	0.0%	Naphthalene	0.16	2.1
	Phenanthrene	mg/kg dry wt	< 0.0020	< 0.0020	0.0034	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.0034	16.7%	Phenanthrene	0.24	1.5
Pyrene	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0021	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0021	0.0%	Pyrene	0.665	2.6	
Total PAHs^{3,6}	mg/kg dry wt	n/d ⁶	n/d ⁶	0.0236	n/d ⁶	n/d ⁶	n/d ⁶	n/d	0.0236	1.04% ⁷	Total PAHs	4	45	
Low Molecular Weight PAHs^{4,6}	mg/kg dry wt	n/d ⁶	n/d ⁶	0.0121	n/d ⁶	n/d ⁶	n/d ⁶	n/d	0.0121	2.8% ⁷	Low Molecular Weight PAHs	0.552	3.16	
High Molecular Weight PAHs^{5,6}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d	n/d	0.0%	High Molecular Weight PAHs	1.7	9.6	

Notes:

- Total DDD calculated from sum of the DDD isomers, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Total DDT calculated from the sum of the DDT, DDD and DDE isomers, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Total PAHs calculated by summing the data, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Low molecular weight PAHs are the sum of concentrations of acenaphthene, acenaphthalene, anthracene, fluorene, naphthalene and phenanthrene.
- High molecular weight PAHs are the sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene.
- Total values could not be calculated where none of the individual compounds were above the detection limit.
- Percentage of individual compounds above the detection limit in all samples.

Calculated value

Exceeds ISQG-Low value

n/c= not calculated

ND = none of the individual PAH compounds were recorded above the laboratory limit of detection.

Appendix D: Kawhia Harbour Result Summary Tables

	% clay	% silt	% non-sand	% fine sand	% med sand	% coarse sand	% sand	% gravel	mean grain size (µm)
Kawhia 1	19.36	67.81	87.17	12.77	0.06	0.00	12.83	0.00	39.00
Kawhia 2	4.68	17.38	22.07	2.52	0.34	1.59	4.46	73.5	106.00
Kawhia 3	12.13	56.33	68.46	28.19	2.57	0.78	31.54	0.00	72.506
Kawhia 4	8.16	13.76	21.92	57.61	17.69	2.78	78.08	0.00	197.699
Kawhia 5	28.01	51.50	79.51	20.09	0.07	0.00	20.16	0.00	42.474
Kawhia 6	35.16	55.72	90.88	8.77	0.00	0.00	8.77	0.00	26.80
Kawhia 7	34.02	61.72	95.73	3.95	0.00	0.00	3.95	0.00	21.90
Kawhia 8	20.29	51.36	71.65	26.23	1.90	0.00	28.14	0.00	62.20
Kawhia 9	1.01	4.12	5.12	93.13	1.75	0.00	94.88	0.00	156.00
Kawhia 10	0.00	3.29	3.29	90.58	6.13	0.00	96.71	0.00	177.70
Kawhia 11	2.70	7.34	10.04	82.14	7.83	0.00	89.96	0.00	168.30
Kawhia 12	1.13	7.12	8.26	91.43	0.31	0.00	91.74	0.00	135.00
Kawhia 13	0.00	0.00	0.00	54.24	45.21	0.55	100.00	0.00	303.00
Kawhia 14	1.04	6.69	7.73	77.93	14.33	0.01	92.27	0.00	192.00
Kawhia 15	0.00	1.72	1.72	95.61	2.67	0.00	98.28	0.00	162.40
Kawhia 16	4.79	17.53	22.32	28.95	20.87	27.86	77.68	0.00	433.49
Kawhia 17	38.86	60.67	99.53	0.47	0.00	0.00	0.47	0.00	15.49
Kawhia 18	18.37	64.45	82.82	10.55	3.29	3.34	17.18	0.00	80.00
Kawhia 19	5.16	23.85	29.01	31.64	22.47	9.87	63.99	7.00	259.50
Kawhia 20	0.00	0.79	0.79	90.45	8.76	0.00	99.21	0.00	187.00
Kawhia 21	0.00	1.37	1.37	90.56	8.07	0.00	98.63	0.00	182.28
Kawhia 22	1.89	10.84	12.73	79.01	8.25	0.00	87.27	0.00	163.37
Kawhia 23	0.00	0.00	0.00	38.39	57.33	4.28	100.00	0.00	352.00

Table D-2: Kawhia sediment samples - Trace and major elements																
	Laboratory results							Descriptive statistics						Guidelines		
	Kawhia 1, 2 & 3	Kawhia 4, 5 & 6	Kawhia 7, 8 & 9	Kawhia 10, 11 & 12	Kawhia 13, 14 & 15	Kawhia 16, 17, 18 & 19	Kawhia 20, 21, 22 & 23	Minimum	Maximum	Arithmetic mean	Geometric mean	Stdev	%RSD	ANZECC interim sediment quality guidelines		
Laboratory Sample No.	643810.51	643810.52	643810.53	643810.54	643810.55	643810.56	643810.57							ISQG-Low	ISQG-High	
Analyte																
Total Organic Carbon																
Total Nitrogen																
Aluminium	17000	26000	17000	13000	14000	17000	13000	13000	26000	16714.3	16273.3	4498.7	27.6%			
Antimony	< 0.040	0.047	0.044	< 0.040	0.054	< 0.040	< 0.040	< 0.040	0.054	n/c ¹	n/c ¹	n/c ¹	n/c ¹	Antimony	2	25
Arsenic	21	14	7.6	7	8.2	13	7.6	7	21	11.2	10.3	5.2	49.9%	Arsenic	20	70
Barium	17	27	18	16	17	19	18	16	27	18.9	18.6	3.7	20.0%			
Bismuth	0.16	0.17	0.13	0.03	< 0.020	0.12	< 0.020	< 0.020	0.17	n/c ¹	n/c ¹	n/c ¹	n/c ¹			
Boron	20	25	16	12	8.7	18	10	8.7	25	15.7	14.7	5.9	39.7%			
Cadmium	0.023	0.039	0.031	0.02	0.013	0.025	0.019	0.013	0.039	0.024	0.023	0.009	37.1%	Cadmium	1.5	10
Caesium	1.1	1.1	0.94	0.45	0.24	1.1	0.29	0.24	1.1	0.75	0.63	0.40	63.7%			
Calcium	6400	13000	5200	11000	11000	6300	12000	5200	13000	9271.4	8759.7	3187.8	36.4%			
Chromium	15	22	13	9.2	5.9	12	7.5	5.9	22	12.1	11.1	5.4	48.6%	Chromium	80	370
Cobalt	7.6	8.7	6.6	5.9	4.2	7.9	5.2	4.2	8.7	6.6	6.4	1.6	24.9%			
Copper	9	13	9.9	7.7	8.1	9.8	8.6	7.7	13	9.4	9.3	1.8	19.0%	Copper	65	270
Iron	34000	28000	22000	21000	16000	31000	18000	16000	34000	24285.7	23473.4	6799.9	29.0%			
Lanthanum	14	15	12	7	6.2	10	6.2	6.2	15	10.1	9.5	3.7	39.3%			
Lead	10	12	8.3	3.8	3.3	9	2.9	2.9	12	7.0	6.1	3.7	59.7%	Lead	50	220
Lithium	33	33	26	12	7.3	24	8.9	7.3	33	20.6	17.6	11.1	62.8%			
Magnesium	5600	5300	4500	3500	2400	5000	2700	2400	5600	4142.9	3955.3	1281.7	32.4%			
Manganese	330	410	230	250	190	250	220	190	410	268.6	260.5	75.8	29.1%			
Mercury	0.047	0.064	0.034	0.012	< 0.010	0.035	0.011	< 0.010	0.064	0.030	0.022	0.022	98.9%	Mercury	0.15	1
Molybdenum	0.29	0.4	0.24	0.25	0.42	0.33	0.27	0.24	0.42	0.31	0.31	0.07	23.4%			
Nickel	11	13	9.1	5.7	3.4	9.2	4.4	3.4	13	8.0	7.2	3.6	49.3%	Nickel	21	52
Phosphorus	780	600	570	610	650	650	660	570	780	645.7	642.9	67.5	10.5%			
Potassium	1900	2000	1600	930	660	1800	720	660	2000	1372.9	1252.5	582.5	46.5%			
Rubidium	10	11	9	4.6	2.5	11	3.1	2.5	11	7.3	6.3	3.8	60.1%			
Selenium	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	n/c ¹	n/c ¹	n/c ¹	n/c ¹			
Silver	0.025	0.034	0.023	< 0.020	< 0.020	0.025	< 0.020	< 0.020	0.034	n/c ¹	n/c ¹	n/c ¹	n/c ¹	Silver	1	3.7
Sodium	6300	9100	6800	5200	5400	6400	4900	4900	9100	6300.0	6177.4	1418.9	23.0%			
Strontium	66	110	72	130	150	71	150	66	150	107.0	101.2	37.5	37.1%			
Thallium	0.044	0.087	0.054	0.042	< 0.020	0.059	0.039	< 0.020	0.087	0.05	0.04	0.02	56.6%			
Tin	0.76	0.87	0.63	0.78	0.27	0.68	0.32	0.27	0.87	0.62	0.57	0.23	40.9%			
Uranium	0.5	0.76	0.54	0.41	0.25	0.73	0.34	0.25	0.76	0.50	0.47	0.19	40.4%			
Vanadium	62	48	44	85	68	48	92	44	92	63.9	61.5	19.0	30.8%			
Zinc	55	50	46	35	27	49	31	27	55	41.9	40.6	10.7	26.5%	Zinc	200	410

Notes:

n/c = not calculated

1. Descriptive statistics not calculated for analytes where more than 20% of samples were below the detection limit.

Exceeds ANZECC ISQG-Low guideline

Table D-3: Kawhia Harbour sediment samples - Organic compounds															
			Laboratory results						Descriptive statistics			Guidelines			
			Kawhia 1, 2 & 3	Kawhia 4, 5 & 6	Kawhia 7, 8 & 9	Kawhia 10, 11 & 12	Kawhia 13, 14 & 15	Kawhia 16, 17, 18 & 19	Kawhia 20, 21, 22 & 23	Minimum	Maximum	Percentage of samples above detection limit	ANZECC interim sediment quality guidelines		
Lab sample No.			643810.51	643810.52	643810.53	643810.54	643810.55	643810.56	643810.57					ISQG-Low	ISQG-High
Analyte name	Analyte units														
Organochlorine pesticides	Dieldrin ^{9,10}	mg/kg dry wt	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.0010	0.0%	Dieldrin	0.00002	0.008
	Hexachlorobenzene	mg/kg dry wt	< 0.00099	< 0.0010	< 0.00099	0.0037	< 0.00099	< 0.0010	< 0.00099	< 0.00099	0.0037	14.3%			
	2,4'-DDD	mg/kg dry wt	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.0010	0.0%			
	4,4'-DDD	mg/kg dry wt	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.0010	0.0%			
	2,4'-DDE	mg/kg dry wt	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.0010	0.0%			
	4,4'-DDE	mg/kg dry wt	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.0010	0.0%	4,4'-DDE	0.0022	0.027
	2,4'-DDT	mg/kg dry wt	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.00099	< 0.0010	< 0.00099	< 0.00099	< 0.0010	0.0%			
	4,4'-DDT	mg/kg dry wt	< 0.00099	< 0.0010	< 0.00099	0.0013	< 0.00099	< 0.0010	< 0.00099	< 0.0010	0.0013	14.3%			
	Total DDD^{1,6,9}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d	n/d	0.0%	Total DDD	0.002	0.02
Total DDT^{2,6,9}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	0.0038	n/d ⁶	n/d ⁶	n/d ⁶	n/d	0.0038	2.38% ⁷	Total DDT	0.0016	0.046	
Polycyclic Aromatic Hydrocarbons	Acenaphthene	mg/kg dry wt	< 0.0020	< 0.0021	< 0.0022	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0022	0.0%	Acenaphthene	0.016	0.5
	Acenaphthylene	mg/kg dry wt	< 0.0020	< 0.0021	< 0.0022	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0022	0.0%	Acenaphthylene	0.044	0.64
	Anthracene	mg/kg dry wt	0.0058	< 0.0021	< 0.0022	0.0093	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.0093	28.6%	Anthracene	0.085	1.1
	Benzo[a]anthracene	mg/kg dry wt	0.046	< 0.0021	< 0.0022	0.025	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.046	28.6%	Benzo[a]anthracene	0.261	1.6
	Benzo[a]pyrene (BAP)	mg/kg dry wt	0.11	< 0.0021	< 0.0022	0.031	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.11	28.6%	Benzo[a]pyrene (BAP)	0.43	1.6
	Benzo[b]fluoranthene + Benzo[j]fluoranthene	mg/kg dry wt	0.21	< 0.0021	< 0.0022	0.033	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.21	28.6%			
	Benzo[g,h,i]perylene	mg/kg dry wt	0.082	0.0033	0.0031	0.024	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.082	57.1%			
	Benzo[k]fluoranthene	mg/kg dry wt	0.1	< 0.0021	< 0.0022	0.02	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.1	28.6%			
	Chrysene	mg/kg dry wt	0.071	< 0.0021	< 0.0022	0.035	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.071	28.6%	Chrysene	0.384	2.8
	Dibenzo[a,h]anthracene	mg/kg dry wt	0.028	< 0.0021	< 0.0022	0.0048	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.028	28.6%	Dibenzo[a,h]anthracene	0.063	0.26
	Fluoranthene	mg/kg dry wt	0.12	0.0026	< 0.0022	0.057	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.12	42.9%	Fluoranthene	0.6	5.1
	Fluorene	mg/kg dry wt	< 0.0020	< 0.0021	< 0.0022	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0022	0.0%	Fluorene	0.019	0.54
	Indeno(1,2,3-c,d)pyrene	mg/kg dry wt	0.06	< 0.0021	< 0.0022	0.02	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.06	28.6%			
	Naphthalene	mg/kg dry wt	< 0.010	< 0.011	< 0.011	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.011	0.0%	Naphthalene	0.16	2.1
	Phenanthrene	mg/kg dry wt	0.026	0.0078	0.013	0.017	< 0.0020	0.003	< 0.0020	< 0.0020	0.026	71.4%	Phenanthrene	0.24	1.5
Pyrene	mg/kg dry wt	0.12	0.0036	0.0037	0.071	< 0.0020	0.0022	< 0.0020	< 0.0020	0.12	71.4%	Pyrene	0.665	2.6	
Total PAHs^{3,6}	mg/kg dry wt	0.9868	0.0349	0.0385	0.3588	n/d ⁶	0.0232	n/d ⁶	n/d	0.9868	29.5% ⁷	Total PAHs	4	45	
Low Molecular Weight PAHs^{4,6}	mg/kg dry wt	0.0398	0.0175	0.0656	0.0343	n/d ⁶	0.0120	n/d ⁶	n/d	0.0656	16.7% ⁷	Low Molecular Weight PAHs	0.552	3.16	
High Molecular Weight PAHs^{5,6}	mg/kg dry wt	0.4950	0.0104	0.0092	0.2238	n/d ⁶	0.0072	n/d ⁶	n/d	0.4950	38.1% ⁷	High Molecular Weight PAHs	1.7	9.6	

Notes:

- Total DDD calculated from sum of the DDD isomers, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Total DDT calculated from the sum of the DDT, DDD and DDE isomers, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Total PAHs calculated by summing the data, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Low molecular weight PAHs are the sum of concentrations of acenaphthene, acenaphthalene, anthracene, fluorene, naphthalene and phenanthrene.
- High molecular weight PAHs are the sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene.
- Total values could not be calculated where none of the individual compounds were above the detection limit.
- Percentage of individual compounds above the detection limit in all samples.

Calculated value

Exceeds ISQG-Low value

n/c= not calculated

ND = none of the individual PAH compounds were recorded above the laboratory limit of detection.

Appendix E: Port Waikato Result Summary Tables

	%clay	% silt	% non-sand	% fine sand	% medium sand	% coarse sand	% sand	% gravel	mean grain size (µm)
Port Waikato 1	0.00	0.00	0.00	4.57	18.74	70.69	94.00	5.75	911
Port Waikato 2	0.00	0.00	0.00	14.74	37.72	45.54	98.00	2.12	660
Port Waikato 3	0.00	0.00	0.00	14.65	36.50	46.85	98.00	1.77	672
Port Waikato 4	0.00	0.61	0.61	11.13	32.36	52.60	96.09	3.32	727
Port Waikato 5	0.00	0.66	0.66	3.19	13.17	66.98	83.34	16.06	960
Port Waikato 6	0.09	1.71	1.80	10.81	29.35	43.65	83.80	14.44	694
Port Waikato 7	0.00	0.55	0.55	6.68	24.24	55.83	86.75	12.67	808
Port Waikato 8	0.00	0.00	0.00	1.12	17.37	67.52	86.00	14.26	941
Port Waikato 9	2.00	15.54	17.54	65.31	16.94	0.21	82.46	0.00	189
Port Waikato 10	5.33	17.03	22.37	18.27	12.91	17.05	48.23	29.44	373
Port Waikato 11	0.16	1.03	1.19	2.66	2.58	2.87	8.11	90.74	476
Port Waikato 12	0.00	0.50	0.50	6.34	32.83	58.83	98.00	1.54	767
Port Waikato 13	0.40	4.24	4.64	23.32	33.23	34.51	91.06	4.31	548
Port Waikato 14	0.00	0.00	0.00	6.03	32.64	54.53	93.20	6.80	754
Port Waikato 15	0.00	0.78	0.78	12.81	32.37	46.14	91.32	7.91	692
Port Waikato 16	0.20	1.63	1.83	3.45	13.23	67.60	84.27	13.95	948
Port Waikato 17	0.00	0.00	0.00	8.92	41.11	49.97	100.00	0.00	682
Port Waikato 18	0.43	2.08	2.51	43.04	40.80	13.65	97.49	0.00	369
Port Waikato 19	0.07	1.16	1.23	11.50	22.39	48.38	82.27	16.50	763

Table E-2: Port Waikato sediment samples - Trace and major elements

Analyte	Laboratory results																			Descriptive statistics					Guidelines		
	PW 1	PW 2	PW 3	PW 4	PW 5	PW 6	PW 7	PW 8	PW 9	PW 10	PW 11	PW 12	PW13	PW 14	PW 15	PW 16	PW 17	PW 18	PW19	Min.	Max.	Arithmeti c mean	Geometr ic mean	St. dev	%RSD	ANZECC ISQG	
Aluminium	4200	6000	6800	4200	4000	4700	3900	3200	11000	24000	16000	4400	6400	4500	4500	3500	3900	5300	3700	3200	24000	6536	5480	5229	95%		
Antimony	0.13	0.084	0.092	0.13	0.17	0.15	0.18	0.14	0.19	0.13	0.29	0.18	0.24	0.13	0.15	0.17	0.17	0.28	0.17	0.084	0.29	0.2	0.2	0.1	34%	2	25
Arsenic	41	22	20	28	41	24	24	32	28	33	61	26	32	20	24	25	19	22	29	19	61	29.0	27.7	10.0	36%	20	70
Barium	39	19	22	46	31	33	23	26	17	37	28	34	37	28	28	34	31	31	52	17	52	31.4	30.2	8.7	29%		
Bismuth	0.061	0.022	0.029	0.026	0.03	0.024	0.028	0.033	0.14	0.37	0.11	0.044	0.053	0.041	0.035	0.036	0.025	0.032	0.043	0.022	0.37	0.1	0.0	0.1	183%		
Boron	6.6	4.6	3.3	3.9	3.7	3.4	2.1	< 2.0	12	7.9	6.6	2.3	3.5	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	12	n/c ¹	n/c ¹	n/c ¹	n/c ¹		
Cadmium	0.012	0.01	< 0.010	0.010	0.011	0.010	0.012	0.014	0.042	0.05	0.043	0.012	0.024	0.010	0.013	0.024	0.015	0.019	0.027	< 0.010	0.05	n/c ¹	n/c ¹	n/c ¹	n/c ¹	1.5	10
Caesium	4.7	3.8	3.9	4.8	5.8	8.1	5.8	8.3	1.9	9.8	8.9	6.8	8.1	9.2	8.4	11	9	9.1	14	1.9	14	7.4	6.8	2.9	43%		
Calcium	1100	3100	3300	1300	910	1000	1000	820	5300	2200	4500	900	1500	970	1000	840	1100	1500	1200	820	5300	1765	1455	1323	91%		
Chromium	2.6	4.4	6	3	3.3	3	3.2	2.7	16	14	7.7	2.9	4.3	3	3.2	2.8	2.9	5.1	3.5	2.6	16	4.9	4.1	3.8	92%	80	370
Cobalt	3.6	4	4.4	2.8	2.9	2.7	2.4	2.7	9.6	13	11	3.1	3.6	2.5	2.5	2.6	2.5	3.5	3	2.4	13	4.3	3.7	3.2	86%		
Copper	1.9	2.9	3.8	1.5	1.4	1.4	1.5	1.5	9	28	16	1.7	2.6	1.6	1.7	1.6	1.4	2.2	1.9	1.4	28	4.4	2.6	6.7	262%	65	270
Iron	15000	14000	16000	12000	13000	11000	11000	11000	33000	44000	60000	11000	13000	9400	10000	10000	8800	13000	13000	8800	60000	17274	14533	1354	93%		
Lanthanum	5.3	4.6	4.5	4.7	4.9	3.4	4.2	4.5	7.6	14	8.9	4.4	4.5	3.6	5	3.8	3.5	4.4	5.2	3.4	14	5.3	5.0	2.5	50%		
Lead	2	1.9	2.2	1.6	1.8	1.8	1.8	1.5	5.7	17	10	2.2	3	1.7	2	1.8	1.7	2.7	1.9	1.5	17	3.4	2.5	3.9	154%	50	220
Lithium	9.2	7.3	7.5	6.3	7.5	8.5	7	7.4	12	32	17	8.5	10	8.2	7.6	7.9	8.2	9.6	7.5	6.3	32	10.0	9.1	5.8	64%		
Magnesium	1500	1900	1800	1200	1000	1100	790	870	3600	7100	4600	920	1200	820	850	670	710	1000	890	670	7100	1712	1314	1657	126%		
Manganese	500	260	230	330	350	160	390	240	530	710	1000	400	340	280	220	400	440	310	650	160	1000	407	369	203	55%		
Mercury	0.014	< 0.010	0.034	0.013	0.010	0.013	< 0.010	0.010	0.024	0.051	0.029	0.014	0.02	0.01	0.011	< 0.010	0.011	0.015	0.013	< 0.010	0.051	n/c ¹	n/c ¹	n/c ¹	n/c ¹	0.15	1
Molybdenum	0.22	0.11	0.12	0.16	0.17	0.074	0.19	0.1	0.23	0.31	0.44	0.17	0.11	0.079	0.1	0.1	0.093	0.11	0.14	0.074	0.44	0.2	0.1	0.1	64%		
Nickel	2.9	3.9	4.3	2.4	2.2	2.4	2.1	2.3	8.3	13	5.4	2.4	2.8	2.4	2.6	2	2.1	2.9	2.5	2	13	3.6	3.1	2.7	88%	21	52
Phosphorus	230	310	360	220	260	210	240	220	690	780	940	190	270	200	220	210	230	270	260	190	940	332	291	218	75%		
Potassium	890	730	570	700	610	590	480	380	1100	3100	2000	600	720	460	470	440	380	510	410	380	3100	797	661	670	101%		
Rubidium	4.5	3.5	3.8	3.5	4.4	4	3.8	4.2	5.8	16	11	6.1	5.4	4.9	4.1	5.8	5.2	5.7	5.3	3.5	16	5.6	5.2	3.0	58%		
Selenium	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 0.20	< 0.20	n/c ¹	n/c ¹	n/c ¹	n/c ¹		
Silver	0.020	< 0.020	< 0.020	0.020	< 0.020	0.020	< 0.020	0.020	0.032	< 0.020	< 0.020	< 0.020	0.020	0.020	< 0.020	< 0.020	< 0.020	< 0.020	0.020	< 0.020	0.032	n/c ¹	n/c ¹	n/c ¹	n/c ¹	1	3.7
Sodium	4400	3400	2200	3900	2000	1700	1300	580	5400	3300	1900	820	1400	620	660	530	410	550	460	410	5400	1870	1347	1519	112%		
Strontium	16	31	32	17	14	11	10	8.3	47	31	51	13	17	9.6	10	8.7	9.3	12	10	8.3	51	18.8	15.7	13.1	834%		
Thallium	0.036	0.051	0.027	0.051	0.046	0.044	0.04	0.045	0.041	0.1	0.1	0.064	0.055	0.056	0.045	0.089	0.053	0.066	0.11	0.027	0.11	0.1	0.1	0.0	43%		
Tin	0.28	0.22	0.22	0.2	0.28	0.2	0.23	0.28	0.57	1.2	0.66	0.25	0.32	0.2	0.25	0.29	0.2	0.31	0.34	0.2	1.2	0.3	0.3	0.2	81%		
Uranium	0.17	0.11	0.13	0.14	0.16	0.13	0.14	0.11	0.36	0.55	0.67	0.17	0.2	0.12	0.17	0.12	0.11	0.19	0.14	0.11	0.67	0.2	0.2	0.2	89%		
Vanadium	11	26	40	13	11	12	14	10	120	54	62	11	15	< 10	12	11	11	26	17	< 10	120	25.3	17.8	27.7	156%		
Zinc	29	25	29	23	27	23	25	24	60	92	75	28	33	23	26	26	24	37	32	23	92	34.8	31.6	19.3	61%	200	410

Notes:

n/c = not calculated

1. Descriptive statistics not calculated for analytes where more than 20% of samples were below the detection limit.

Exceeds ANZECC ISQG-Low guideline

		Laboratory results																			Descriptive statistics			Guidelines	
		PW 1	PW 2	PW 3	PW 4	PW 5	PW 6	PW 7	PW 8	PW 9	PW 10	PW 11	PW 12	PW 13	PW 14	PW15	PW 16	PW 17	PW 18	PW 19	Min	Max	% of samples above DL	ANZECC ISQG	
Analyte name																									
Organochlorine pesticides	Total Organic Carbon	0.059	< DL	0.052	0.063	0.059	0.053	0.067	0.1	0.76	0.45	0.33	0.055	0.61	0.077	0.091	0.11	0.086	0.12	0.056					
	Dieldrin ^{7,10}	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0011	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.00098	0.0011	5.3%	0.0002 0.008	
	Hexachlorobenzene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0019	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.00098	0.0019	5.3%		
	2,4'-DDD	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.00098	< 0.0010	0.0%		
	4,4'-DDD	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.00098	< 0.0010	0.0%		
	2,4'-DDE	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.00098	< 0.0010	0.0%		
	4,4'-DDE	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.00098	< 0.0010	0.0%	0.0022 0.027	
	2,4'-DDT	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.00098	< 0.0010	0.0%		
	4,4'-DDT	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.00098	< 0.0010	0.0%		
	Total DDD^{1,6,9}	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d	n/d	0.0%	0.002 0.02	
Total DDT^{2,6,9}	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d	n/d	0.0%	0.0016 0.046		
Polycyclic Aromatic Hydrocarbons	Acenaphthene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.0020	< 0.0024	0.0%	0.016 0.5	
	Acenaphthylene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.0020	< 0.0024	0.0%	0.044 0.64	
	Anthracene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.0020	< 0.0024	0.0%	0.085 1.1	
	Benzo[a]anthracene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0027	< DL	< DL	< DL	0.0045	0.0024	< DL	< DL	< DL	< DL	< DL	< 0.0020	0.0045	10.5%	0.261 1.6	
	Benzo[a]pyrene (BAP)	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0046	< DL	< DL	< DL	0.0061	0.0028	< DL	< DL	< DL	< DL	< DL	< 0.0020	0.0061	15.8%	0.43 1.6	
	Benzo[b]fluoranthene + Benzo[j]fluoranthene	< DL	< DL	< DL	< DL	0.0032	< DL	< DL	< DL	0.0057	0.002	< DL	< DL	0.0077	0.0035	< DL	< DL	< DL	0.002	< DL	< 0.0020	0.0077	31.6%		
	Benzo[g,h,i]perylene	< DL	< DL	< DL	< DL	0.0021	< DL	< DL	< DL	0.0044	< DL	< DL	< DL	0.0053	0.0024	< DL	< DL	< DL	< DL	< DL	< 0.0020	0.0053	21.1%		
	Benzo[k]fluoranthene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0021	< DL	< DL	< DL	0.0032	< DL	< DL	< DL	< DL	< DL	< DL	< 0.0020	0.0032	10.5%		
	Chrysene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0028	< DL	< DL	< DL	0.0044	0.0022	< DL	< DL	< DL	< DL	< DL	< DL	0.0044	15.8%	0.384 2.8	
	Dibenzo[a,h]anthracene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.0024	< 0.0024	0.0%	0.063 0.26	
	Fluoranthene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0066	< DL	< DL	< DL	0.011	0.0066	< DL	< DL	< DL	< DL	< DL	< DL	0.011	26.3%	0.6 5.1	
	Fluorene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.0024	< 0.0024	0.0%	0.019 0.54	
	Indeno[1,2,3-c,d]pyrene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0035	< DL	< DL	< DL	0.0042	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.0042	10.5%		
	Naphthalene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.010	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< 0.012	< 0.012	0.0%	0.16 2.1	
	Phenanthrene	< DL	< DL	0.0028	< DL	0.003	< DL	< DL	< DL	0.0033	0.0022	< DL	< DL	0.0038	0.0044	< DL	0.002	< DL	< DL	< DL	< DL	0.0044	42.1%	0.24 1.5	
	Pyrene	< DL	< DL	< DL	< DL	< DL	< DL	< DL	< DL	0.005	< DL	< DL	< DL	0.0084	0.0043	< DL	< DL	< DL	< DL	< DL	< DL	0.0084	15.8%	0.665 2.6	
	Total PAHs^{3,6}	n/d ⁶	n/d ⁶	< DL	n/d ⁶	0.0272	n/d ⁶	n/d ⁶	n/d ⁶	0.0507	0.0150	n/d ⁶	n/d ⁶	0.0706	0.0406	n/d ⁶	0.0210	n/d ⁶	0.0232	n/d ⁶	n/d	0.0706	12.8% ⁷	4 45	
Total PAHs TOC normalised^{8,9}	-	-	< DL	-	n/c ¹⁰	-	-	-	0.0667	0.0332	-	-	0.1157	n/c ¹⁰	-	n/c ¹⁰	-	n/c ¹⁰	-						
Low Molecular Weight PAHs^{4,6}	n/d ⁶	n/d ⁶	< DL	n/d ⁶	0.0120	n/d ⁶	n/d ⁶	n/d ⁶	0.0123	0.0112	n/d ⁶	n/d ⁶	0.0128	0.0134	n/d ⁶	0.0110	n/d ⁶	0.0112	n/d ⁶	n/d	0.0134	7.0% ⁷	0.552 3.16		
Low Molecular Weight PAHs TOC normalised^{8,9}	-	-	< DL	-	n/c ¹⁰	-	-	-	0.0162	0.0249	-	-	0.0210	n/c ¹⁰	-	n/c ¹⁰	-	n/c ¹⁰	-						
High Molecular Weight PAHs^{5,6}	n/d ⁶	n/d ⁶	< DL	n/d ⁶	0.0079	n/d ⁶	n/d ⁶	n/d ⁶	0.0227	n/d ⁶	n/d ⁶	n/d ⁶	0.0356	0.0193	n/d ⁶	n/d ⁶	n/d ⁶	0.0070	n/d ⁶	n/d	0.0356	14.9% ⁷	1.7 9.6		
High Molecular Weight PAHs TOC normalised^{8,9}	-	-	< DL	-	n/c ¹⁰	-	-	-	0.0299	n/c ¹⁰	-	-	0.0584	n/c ¹⁰	-	n/c ¹⁰	-	n/c ¹⁰	-						

- Notes:
- Total DDD calculated from sum of the DDD isomers, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
 - Total DDT calculated from the sum of the DDT, DDD and DDE isomers, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
 - Total PAHs calculated by summing the data, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
 - Low molecular weight PAHs are the sum of concentrations of acenaphthene, acenaphthalene, anthracene, fluorene, naphthalene and phenanthrene.
 - High molecular weight PAHs are the sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene.
 - Total values could not be calculated where none of the individual compounds were above the detection limit.
 - Percentage of individual compounds above the detection limit in all samples.
 - Values normalised to 1% TOC for comparison with ANZECC ISQGS
 - Carbon normalisation not carried out for samples below detection limit.
 - Carbon normalisation not carried out for samples with Total Organic Carbon of less than 0.2%.

Calculated value

Exceeds ISQG-Low value

n/c = not calculated

n/d = no detection

<DL= less than detection limit.

Table E-4: Water quality samples at Port Waikato																	
		Laboratory results						Descriptive statistics				Guidelines					
		Port Waikato 1	Port Waikato 2	Port Waikato 3	Port Waikato 4	Port Waikato 5	Port Waikato 6	Minimum	Maximum	Median	Geometric mean	ANZECC 95% protection of aquatic ecosystems ³	Low reliability trigger values (marine ecosystems)	ANZECC recreational water guidelines	EW adopted guidelines	NZ Microbiological Water Quality guidelines ⁴	
Physiochemical	Dissolved oxygen	%	97.2	99.1	99.4	99.1	99.9	100.2							80%	> 80%	
	Temperature	°C	19.9	19.2	19	19.1	19.2	19.1								< 12°C (May-Sept) < 20°C (Oct-Apr)	
	Turbidity	NTU	3.2	3.3	6.6	7.6	9.6	13	3.2	13.0	7.1	6.4				5	
	pH	pH Units	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0			6.5-8.5	6.5-9	
	Electrical Conductivity (EC)	mS/m	3000	1900	1900	1600	880	480	480	3000	1750	1393					
	Total Dissolved Solids (TDS)	g/m ³	20000	12000	13000	10000	5500	2800	2800	20000	11000	8850			1,000		
	Total Biochemical Oxygen Demand (TBOD5)	g.O2/m ³	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	< 0.40	n/c ¹	n/c ¹					
	Absorbance at 340 nm	AU, 1 cm cell	0.0061	0.0077	0.0078	0.0082	0.0095	0.012	0.006	0.012	0.008	0.008					
	Absorbance at 440 nm	AU, 1 cm cell	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020	0.0024	0.002	0.002	n/c ¹	n/c ¹					
Absorbance at 780 nm	AU, 1 cm cell	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020	n/c ¹	n/c ¹						
Metals	Total Arsenic	g/m ³	< 0.021	0.014	0.021	0.025	0.025	0.024	0.014	0.025	0.024	0.021	ID	0.0023/0.0045	0.05	0.01	
	Acid Soluble Arsenic	g/m ³	< 0.020	0.030	0.026	0.026	0.027	0.025	0.025	0.030	0.026	0.027	ID	0.0023/0.0045	0.05	0.01	
	Acid Soluble Chromium	g/m ³	< 0.010	< 0.0050	< 0.0050	< 0.0050	< 0.0025	< 0.0025	< 0.0025	< 0.010	n/c ¹	n/c ¹	0.0274/0.0044		0.05		
	Acid Soluble Copper	g/m ³	< 0.010	< 0.0050	< 0.0050	< 0.0050	< 0.0025	< 0.0025	< 0.0025	< 0.010	n/c ¹	n/c ¹	0.0013		1		
	Acid Soluble Lead	g/m ³	< 0.0020	< 0.0010	< 0.0010	< 0.0010	< 0.00050	< 0.00050	< 0.00050	< 0.0020	n/c ¹	n/c ¹	0.0044		0.05		
	Acid Soluble Nickel	g/m ³	< 0.010	< 0.0050	< 0.0050	< 0.0050	< 0.0025	< 0.0025	< 0.0025	< 0.010	n/c ¹	n/c ¹	0.07		0.1		
	Acid Soluble Zinc	g/m ³	< 0.020	< 0.010	< 0.010	< 0.010	< 0.0050	< 0.0050	< 0.0050	< 0.020	n/c ¹	n/c ¹	0.015 ^c		5		
	Acid Soluble Mercury	g/m ³	< 0.000080	< 0.000080	< 0.000080	< 0.000080	< 0.000080	< 0.000080	< 0.000080	< 0.000080	n/c ¹	n/c ¹	ID	0.0004	0.001		
	Boron	g/m ³	1.7	1.8	1.5	1.2	0.76	0.52	0.520	1.800	1.350	1.138	ID	5.1		1.4	
Lithium	g/m ³	0.13	0.13	0.12	0.12	0.10	0.096	0.096	0.130	0.120	0.115						
Nutrients	Total Phosphorus	g/m ³	0.042	0.05	0.06	0.062	0.078	0.09	0.042	0.090	0.061	0.062				0.04	
	Dissolved Reactive Phosphorus	g/m ³	0.0072	0.018	0.018	0.026	0.034	0.036	0.007	0.036	0.022	0.021					
	Chloride	g/m ³	10000	6600	6500	5600	2800	1500	1500	10000	6050	4649			400		
	Total Kjeldahl Nitrogen (TKN)	g/m ³	0.13	0.16	0.22	0.21	0.25	0.3	0.130	0.300	0.215	0.204					
	Total Ammoniacal-N	g/m ³	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	n/c ¹	n/c ¹	0.91			0.88	
	Nitrite-N	g/m ³	< 0.010	< 0.010	< 0.010	< 0.010	0.0034	0.0034	< 0.010	0.003	n/c ¹	n/c ¹			1		
	Nitrate-N	g/m ³	0.013	< 0.010	< 0.010	< 0.010	0.18	0.2	< 0.010	0.200	n/c ¹	n/c ¹	ID	0.7	10		
	Nitrate-N + Nitrite-N	g/m ³	0.013	< 0.010	< 0.010	< 0.010	0.18	0.21	< 0.010	0.210	n/c ¹	n/c ¹					
Total Nitrogen (calculated)	g/m ³	0.143	0.165	0.225	0.215	0.43	0.51								0.5		
Biological	Faecal Coliforms	cfu / 100mL	150	120	130	150	170	130	120	170	140	141			150 (median)		14 (median) 43 (10% of samples) (MPN)
	Escherichia coli	cfu / 100mL	150	110	120	150	170	130	110	170	140	137				550 / 126 (median)	260
	Enterococci	cfu / 100mL	24	27	31	29	56	30	24	56	30	32			35 (median)		140
	Chlorophyll a	g/m ³	0.0042	0.0043	0.0054	0.0072	0.009	0.011	0.004	0.011	0.006	0.006				0.02	
Organics	MCPB	g/m ³	0.000045	< 0.000040	0.0001	0.00007	0.00012	0.000081	< 0.000040	0.000120	0.000081	0.000079					
	Dissolved Non-Purgeable Organic Carbon (DNPOC)	g/m ³	1.4	1.3	1.1	1.2	1.4	1.3	1.100	1.400	1.300	1.279					
	Non-Purgeable Organic Carbon (NPOC)	g/m ³	1.9	2.1	2.1	2.3	2.9	2.7	1.9	2.9	2.2	2.3					

Notes:

n/c = not calculated

1. Descriptive statistics not calculated for analytes where more than 20% of samples were below the detection limit.

2. Total nitrogen was calculated by summing the values for Total Kjeldahl Nitrogen and Nitrate-N + Nitrite-N. Where values were below detect, a value of half the detection limit was used.

3. Trigger values for marine water.

4. Values for "Alert mode: amber".

Bold = exceeds ANZECC 95% protection of aquatic ecosystems guideline

Red = exceeds ANZECC recreational water guideline

Blue = exceeds EW adopted guideline

Shaded = NZ Microbiological Water Quality guideline

ID = Insufficient data to derive a reliable trigger value. Where this is the case the ANZECC marine "low-reliability trigger value" has been included.

Appendix F: Raglan Harbour Result Summary Tables

Table F-1: Raglan Harbour sediment samples - Trace and major elements															
		Laboratory results					Descriptive statistics						Guidelines		
		Raglan HB	Raglan OB	Raglan TU	Raglan WI	Raglan X	Minimum	Maximum	Arithmetic mean	Geometric mean	Stdev	%RSD	ANZECC interim sediment quality guidelines		
Laboratory Sample No.		663933.6	663933.7	663933.8	663933.9	663933.10								ISQG-Low	ISQG-High
Analyte	Analyte units														
Dry Matter	g/100g as rcvd	51	59	72	67	69	51	72	63.6	63	8.5	13.52%			
Total Organic Carbon	g/100g dry wt	0.92	0.82	0.4	0.39	0.54	0.39	0.92	0.61	0.576	0.24	42.29%			
Total Nitrogen	g/100g dry wt	0.12	0.11	0.076	0.074	0.1	0.074	0.12	0.096	0.094	0.02	21.70%			
Aluminium	mg/kg dry wt	22000	20000	13000	16000	11000	11000	22000	16400	15870	4615	29.08%			
Antimony	mg/kg dry wt	0.059	0.063	0.06	0.049	0.057	0.049	0.063	0.058	0.057	0.005	9.19%	Antimony	2	25
Arsenic	mg/kg dry wt	12	13	8.3	9.7	10	8.3	13	10.6	10.5	1.9	17.99%	Arsenic	20	70
Barium	mg/kg dry wt	23	21	16	16	12	12	23	17.6	17.2	4.4	25.62%			
Bismuth	mg/kg dry wt	0.082	0.058	< 0.020	< 0.020	< 0.020	< 0.020	0.082	n/c ¹	n/c ¹	n/c ¹	n/c ¹			
Boron	mg/kg dry wt	23	22	12	17	21	12	23	19	18.5	4.5	24.47%			
Cadmium	mg/kg dry wt	0.034	0.031	0.019	0.023	0.024	0.019	0.034	0.026	0.026	0.006	23.96%	Cadmium	1.5	10
Caesium	mg/kg dry wt	1.2	1	0.51	0.7	0.71	0.51	1.2	0.82	0.79	0.27	34.71%			
Calcium	mg/kg dry wt	9700	16000	50000	41000	20000	9700	50000	27340	22947	17275	75.28%			
Chromium	mg/kg dry wt	17	18	14	16	13	13	18	15.6	15	2.07	13.39%	Chromium	80	370
Cobalt	mg/kg dry wt	8.7	8.6	8.8	9.3	4.4	4.4	9.3	8.0	7.7	2.01	26.11%			
Copper	mg/kg dry wt	9.5	9.5	6.5	7.3	3.9	3.9	9.5	7.3	7.0	2.34	33.45%	Copper	65	270
Iron	mg/kg dry wt	32000	29000	29000	32000	18000	18000	32000	28000	27420	5787	21.11%			
Lanthanum	mg/kg dry wt	12	9.6	9.9	9.3	6.6	6.6	12	9.5	9.3	1.93	20.70%			
Lead	mg/kg dry wt	9.1	7.5	4	5.2	4.7	4	9.1	6.1	5.8	2.13	36.60%	Lead	50	220
Lithium	mg/kg dry wt	23	19	9.9	14	11	9.9	23	15.4	14.6	5.52	37.84%			
Magnesium	mg/kg dry wt	5700	5200	3700	5000	3800	3700	5700	4680	4610	887	19.24%			
Manganese	mg/kg dry wt	410	450	430	410	200	200	450	380	365	101	27.92%			
Mercury	mg/kg dry wt	0.063	0.061	0.027	0.028	0.028	0.027	0.063	0.041	0.038	0.018	49.27%	Mercury	0.15	1
Molybdenum	mg/kg dry wt	0.33	0.35	0.34	0.19	0.28	0.19	0.35	0.30	0.29	0.06	22.71%			
Nickel	mg/kg dry wt	10	11	7.6	9.1	6.3	6.3	11	8.8	8.6	1.87	21.72%	Nickel	21	52
Phosphorus	mg/kg dry wt	610	630	650	640	440	440	650	594	588	87	14.85%			
Potassium	mg/kg dry wt	2500	2000	1300	1700	1900	1300	2500	1880	1838	438	23.84%			
Rubidium	mg/kg dry wt	12	11	6.2	8.1	9	6.2	12	9.26	9.0	2.30	25.59%			
Selenium	mg/kg dry wt	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0	n/c ¹	n/c ¹	n/c ¹	n/c ¹			
Silver	mg/kg dry wt	0.031	0.026	< 0.020	< 0.020	< 0.020	< 0.020	0.031	n/c ¹	n/c ¹	n/c ¹	n/c ¹	Silver	1	3.7
Sodium	mg/kg dry wt	6800	7800	5900	5900	6500	5900	7800	6580	6544	785	12.00%			
Strontium	mg/kg dry wt	73	110	250	230	100	73	250	152.6	135	81	59.82%			
Thallium	mg/kg dry wt	0.073	0.074	0.055	0.061	0.065	0.055	0.074	0.0656	0.0651977	0.0080498	12.35%			
Tin	mg/kg dry wt	0.82	0.75	0.43	0.54	0.43	0.43	0.82	0.594	0.5723229	0.1817416	31.76%			
Uranium	mg/kg dry wt	0.6	0.56	0.52	0.45	0.49	0.45	0.6	0.524	0.521375	0.0585662	11.23%			
Vanadium	mg/kg dry wt	50	77	100	92	36	36	100	71	66.238458	27.313001	41.23%			
Zinc	mg/kg dry wt	56	50	43	48	33	33	56	46	45.297719	8.6313383	19.05%	Zinc	200	410

Notes:

n/c = not calculated

1. Descriptive statistics not calculated for analytes where more than 20% of samples were below the detection limit.

Exceeds ANZECC ISQG-Low guideline

Raglan samples: WI = Whatititirinui Island, TU = Te Puna Point, OB = Okete Bay, HB = Haroto Bay, X = Ponganui Creek

Table F-2: Raglan Harbour sediment samples - Organic compounds													
			Laboratory results					Descriptive statistics			Guidelines		
			Raglan HB	Raglan OB	Raglan TU	Raglan WI	Raglan X	Minimum	Maximum	% of samples above detection limit	ANZECC interim sediment quality guidelines		
Analyte	Analyte units												
Total Organic Carbon	g/100g dry wt		0.92	0.82	0.4	0.39	0.54						
Organochlorine pesticides	Dieldrin ⁹	mg/kg dry wt	< 0.00099	< 0.00098	< 0.00099	< 0.0010	< 0.00099	< 0.00098	< 0.0010	0.0%	Dieldrin	0.00002	0.008
	Hexachlorobenzene	mg/kg dry wt	< 0.00099	< 0.00098	< 0.00099	< 0.0010	< 0.00099	< 0.00098	< 0.0010	0.0%			
	2,4'-DDD	mg/kg dry wt	< 0.00099	< 0.00098	< 0.00099	< 0.0010	< 0.00099	< 0.00098	< 0.0010	0.0%			
	4,4'-DDD	mg/kg dry wt	< 0.00099	< 0.00098	< 0.00099	< 0.0010	< 0.00099	< 0.00098	< 0.0010	0.0%			
	2,4'-DDE	mg/kg dry wt	< 0.00099	< 0.00098	< 0.00099	< 0.0010	< 0.00099	< 0.00098	< 0.0010	0.0%			
	4,4'-DDE ⁹	mg/kg dry wt	< 0.00099	< 0.00098	< 0.00099	< 0.0010	< 0.00099	< 0.00098	< 0.0010	0.0%	4,4'-DDE	0.0022	0.027
	2,4'-DDT	mg/kg dry wt	< 0.00099	< 0.00098	< 0.00099	< 0.0010	< 0.00099	< 0.00098	< 0.0010	0.0%			
	4,4'-DDT	mg/kg dry wt	< 0.00099	< 0.00098	< 0.00099	< 0.0010	< 0.00099	< 0.00098	< 0.0010	0.0%			
	Total DDD^{1,6,9}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d	n/d	0.0%	Total DDD	0.002	0.02
	Total DDT^{2,6,9}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	n/d	n/d	0.0%	Total DDT	0.0016	0.046
Polycyclic Aromatic Hydrocarbons	Acenaphthene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%	Acenaphthene	0.016	0.5
	Acenaphthylene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%	Acenaphthylene	0.044	0.64
	Anthracene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%	Anthracene	0.085	1.1
	Benzo[a]anthracene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%	Benzo[a]anthracene	0.261	1.6
	Benzo[a]pyrene (BAP)	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%	Benzo[a]pyrene (BAP)	0.43	1.6
	Benzo[b]fluoranthene + Benzo[j]fluoranthene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%			
	Benzo[g,h,i]perylene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%			
	Benzo[k]fluoranthene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%			
	Chrysene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%	Chrysene	0.384	2.8
	Dibenzo[a,h]anthracene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%	Dibenzo[a,h]anthracene	0.063	0.26
	Fluoranthene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	0.0037	< 0.0020	0.0037	20.0%	Fluoranthene	0.6	5.1
	Fluorene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%	Fluorene	0.019	0.54
	Indeno(1,2,3-c,d)pyrene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0026	0.0%			
	Naphthalene	mg/kg dry wt	< 0.013	< 0.012	< 0.010	< 0.010	< 0.010	< 0.010	< 0.013	0.0%	Naphthalene	0.16	2.1
	Phenanthrene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	0.0031	< 0.0020	0.0031	20.0%	Phenanthrene	0.24	1.5
	Pyrene	mg/kg dry wt	< 0.0026	< 0.0023	< 0.0020	< 0.0020	0.0031	< 0.0020	0.0031	20.0%	Pyrene	0.665	2.6
	Total PAHs^{3,6}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	0.0269	n/d	0.0269	1.25% ⁷	Total PAHs	4	45
Total PAHs TOC normalised^{8,9}	mg/kg dry wt	-	-	-	-	0.0498				Total PAHs	4	45	
Low Molecular Weight PAHs^{4,6}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	0.0121	n/d	0.0121	3.33% ⁷	Low Molecular Weight PAHs	0.552	3.16	
Low Molecular Weight PAHs TOC normalised^{8,9}	mg/kg dry wt	-	-	-	-	0.0224				Low Molecular Weight PAHs	0.552	3.16	
High Molecular Weight PAHs^{5,6}	mg/kg dry wt	n/d ⁶	n/d ⁶	n/d ⁶	n/d ⁶	0.0108	n/d	0.0108	6.67% ⁷	High Molecular Weight PAHs	1.7	9.6	
High Molecular Weight PAHs TOC normalised^{8,9}	mg/kg dry wt	-	-	-	-	0.0200				High Molecular Weight PAHs	1.7	9.6	

Notes:

- Total DDD calculated from sum of the DDD isomers, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Total DDT calculated from the sum of the DDT, DDD and DDE isomers, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Total PAHs calculated by summing the data, where a concentration was below the detection limit half the detection limit was used as a value. Where all values were below the detection limit a total value could not be calculated.
- Low molecular weight PAHs are the sum of concentrations of acenaphthene, acenaphthalene, anthracene, fluorene, naphthalene and phenanthrene.
- High molecular weight PAHs are the sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene.

- Total values could not be calculated where none of the individual compounds were above the detection limit.
- Percentage of individual compounds above the detection limit in all samples.
- Values normalised to 1% TOC for comparison with ANZECC ISQGs
- Carbon normalisation not carried out for samples below detection limit.
- Carbon normalisation not carried out for samples with Total Organic Carbon of less than 0.2%.

Calculated value

Exceeds ISQG-Low value

n/c= not calculated

n/d = no detection

Raglan samples: WI = Whatititirini Island, TU = Te Puna Point, OB = Okete Bay, HB = Haroto Bay, X = Ponganui Creek

Appendix G: Data Handling

- **PAHs**

Total PAHs were calculated by summing the concentrations of the individual PAHs. The sum of the low molecular weight PAHs was calculated from the sum of concentrations of acenaphthene, acenaphthalene, anthracene, fluorene, naphthalene and phenanthrene. The sum of the high molecular weight PAHs was calculated from the sum of concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene and pyrene.

When a component compound was below the level of detection, a value of half the detection limit was used. Where all components were below the level of detection then a total value could not be calculated.

- **DDT and DDD**

Total DDD was calculated by summing the values of the two isomers of DDD. Total DDT was calculated by summing the values for all DDT, DDD and DDE isomers. Environment Waikato requested that this approach be used, because this is the approach that has been previously used and is consistent with the approach used in handling soil quality data in New Zealand. Using this approach makes it easier for Environment Waikato to compare concentration of DDT in the soil with concentrations found in the sediment.

The ANZECC (2000) guidelines do not specify whether total DDT includes the sum of all isomers and congeners, however, PDP understands that the authors of the ANZECC(2000) sediment quality guidelines only intended that the DDT isomers should be summed (G. Bately, pers. comm). Using the approach recommended by Environment Waikato had no effect on the interpretation of the results and did not alter the result of the summation of DDT results significantly. Note that the summing of all the isomers over-estimates the risk and therefore is conservative.

When a component compound was below the level of detection, a value of half the detection limit was used. If all components were below the level of detection then a new detection limit was calculated, from the sum of the detection limits.

- **Values below the detection limit**

In calculating total values or descriptive statistics, where the concentration of an analyte was below the detection limit, a value of half the detection limit was used for that sample in the calculation. If more than 20% of the samples were below the detection limit then descriptive statistics were not calculated. This is because it was considered that substituting half the detection limit for the value below the detection limit would change the population distribution and therefore result in an incorrect estimate of the mean.

Total values could not be calculated where none of the individual compounds were above the detection limit.

- **Carbon normalisation**

Concentrations of organic contaminants and their toxicity in sediment have been found to correlate to the organic carbon content of the sediment (Michelsen, 1992). The ANZECC sediment quality guidelines for organic contaminants have been normalised to 1% organic carbon, and so for comparison with the guidelines, the analysis results for the organic contaminants have been normalised to 1% organic carbon (for samples where total organic carbon (TOC) had been analysed). The procedure used was that outlined in Michelsen (1992). Carbon normalisation was not carried out for samples with Total Organic Carbon of less than 0.2% as per the recommendations in ANZECC (2000), Chapter 8.3.4.2.

Carbon normalisation was not carried out for samples below detection limit or on samples where Total organic carbon was not analysed.

- **Statistical Analysis of the data.**

Statistical summaries of the data for Aotea, Kawhia, Raglan Harbours and Port Waikato are presented in tables H-1, H-2, H-3 and H-4 respectively. To determine if there is a significant statistical difference the concentration of major and minor trace

elements and nutrients between the harbours the differences in the mean concentration between harbours either using a student t-test or a Mann-Whitney U test. A student t-test requires the data to be normally distributed and variance in the data sets are due to random sampling differences. Therefore, before undertaking the student t test, a test of whether the data was normally distributed using a Kolmogorov-Smirnov normality test and an analysis of variance using Levene Median test (to assess the equality of variance within the dataset being analysed) was undertaken. If the p value for the Levene Median test was less than 0.05 then the differences in the sample variances are unlikely to be due to random sampling and the assumption of equal variance was rejected. If the data was shown to be normally distributed and the variance in the dataset was shown to be equal the a student t-test was undertaken, if however the data set being analysed to meet either one or all of these two conditions then a Mann-Whitney U test was undertaken. A Mann-Whitney U test is a non-parametric test for assessing whether the two groups of observations come from the same distribution (i.e. To determine whether the concentration of major and minor elements between the harbours are statistically similar or not). In both tests a 95% confidence level was used to assess if there is a statistically significant difference between the two harbours, therefore if the p-value in Table H-5 is greater than 0.05 then there is no significant difference between the two harbours.

Due to the relatively small number of samples collected at each harbour there is a greater likelihood of rejection of the hypothesis tested when the hypothesis is true (type 1 error). To determine this, the power of the performed test was elevated with the alpha value set at 0.05. If the power of the performed test was less than desired power (0.8), this indicates that the test is less likely to detect a difference when one actually exists. Therefore negative results from either the student t-tests or Mann-Whitney U should be interpreted cautiously as there are an insufficient number of samples to assess if there is a difference or not (it still maybe true but there is a greater likelihood of the statistical tests of detecting a difference). No results of significant tests (student t-tests or Mann-Whitney U tests) have been presented for Raglan Harbour because too few samples were collected at this location to be confident in the results of the statistical tests. For the other harbours, when the

No statistically tests were undertaken on any dataset were more than 50% of the data was below the detection limit or there were fewer than 6 observations.

Table H-1 Summary Statistics for Aotea Harbour

Column	Size	Below Detection Limit	Mean	Std Dev	Std. Error	C.I. of Mean	Range	Max	Min	Median	25%	75%	Skewness	Kurtosis	K-S Dist.	K-S Prob.
Total Organic Carbon	3	0	0.253	0.0862	0.0498	0.214	0.17	0.33	0.16	0.27	0.188	0.315	-0.837	--	0.243	0.52
Total Nitrogen	3	0	0.077	0.0207	0.0119	0.0513	0.04	0.1	0.06	0.071	0.0628	0.0927	1.196	--	0.281	0.386
Total Recoverable Aluminum	9	0	11088.89	2386.129	795.376	1834.141	6900	15000	8100	11000	9050	12500	0.42	-0.935	0.135	0.762
Total Recoverable Antimony	9	1	0.0526	0.0115	0.00407	0.00961	0.034	0.076	0.042	0.05	0.044	0.0575	1.353	1.648	0.237	0.203
Total Recoverable Arsenic	9	0	7.622	1.861	0.62	1.431	5.8	12	6.2	6.8	6.3	8.325	1.875	3.912	0.227	0.197
Total Recoverable Barium	9	0	13.122	2.74	0.913	2.106	7.9	17	9.1	14	10.75	15.25	-0.128	-1.308	0.181	0.482
Total Recoverable Bismuth	9	2	0.0493	0.0315	0.0119	0.0291	0.078	0.1	0.022	0.032	0.024	0.0742	0.738	-1.239	0.28	0.099
Total Recoverable Boron	9	0	13.3	3.451	1.15	2.653	10.3	18	7.7	13	10.75	16.25	-0.183	-1.041	0.133	0.77
Total Recoverable Cadmium	9	0	0.0186	0.0048	0.0016	0.00369	0.016	0.029	0.013	0.018	0.0155	0.0205	1.304	2.236	0.213	0.273
Total Recoverable Cesium	9	0	0.492	0.22	0.0732	0.169	0.67	0.86	0.19	0.45	0.36	0.605	0.633	-0.289	0.192	0.408
Total Recoverable Calcium	9	0	9155.556	4322.936	1440.979	3322.903	12900	16000	3100	7800	5950	13250	0.366	-1.053	0.179	0.5
Total Recoverable Chromium	9	0	12.444	1.81	0.603	1.392	5	15	10	12	11	14.25	0.44	-1.189	0.264	0.071
Total Recoverable Cobalt	9	0	6	1.792	0.597	1.377	5.9	9.8	3.9	5.6	4.8	6.775	1.253	1.7	0.211	0.282
Total Recoverable Copper	9	0	6.133	1.126	0.375	0.865	3.6	7.9	4.3	6.2	5.65	6.6	-0.338	0.0755	0.231	0.18
Total Recoverable Iron	9	0	23555.56	9632.122	3210.707	7403.905	33000	47000	14000	22000	17750	24750	2.078	5.186	0.259	0.082
Total Recoverable Lanthanum	9	0	6.389	1.21	0.403	0.93	4.2	8.9	4.7	6.5	5.375	6.725	0.807	1.719	0.256	0.092
Total Recoverable Lead	9	0	3.833	1.503	0.501	1.156	4.8	7.2	2.4	3.2	3	4.175	1.72	2.714	0.287	0.032
Total Recoverable Lithium	9	0	10.078	4.318	1.439	3.319	15.5	20	4.5	9.6	7.55	11.25	1.547	3.722	0.217	0.249
Total Recoverable Magnesium	9	0	2911.111	510.99	170.33	392.782	1300	3600	2300	2600	2500	3375	0.373	-1.839	0.284	0.035
Total Recoverable Manganese	9	0	222.222	61.802	20.601	47.505	210	360	150	220	185	237.5	1.419	2.758	0.228	0.194
Total Recoverable Mercury	9	4	0.0188	0.0106	0.00474	0.0132	0.026	0.037	0.011	0.014	0.0125	0.0235	1.84	3.427	0.292	0.173
Total Recoverable Molybdenum	9	0	0.284	0.108	0.0359	0.0829	0.33	0.5	0.17	0.27	0.195	0.362	0.992	0.561	0.22	0.233
Total Recoverable Nickel	9	0	5.456	1.448	0.483	1.113	4.8	9	4.2	5.2	4.55	5.625	2.148	5.312	0.266	0.067
Total Recoverable Phosphorus	9	0	528.889	127.715	42.572	98.17	340	680	340	560	430	625	-0.522	-1.003	0.153	0.675
Total Recoverable Potassium	9	0	990	295.085	98.362	226.822	890	1400	510	1000	820	1175	-0.0372	-0.317	0.153	0.672
Total Recoverable Rubidium	9	0	5.233	1.806	0.602	1.388	5.6	7.7	2.1	5.9	3.775	6.525	-0.507	-0.664	0.2	0.354
Total Recoverable Selenium	9	9	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Total Recoverable Silver	9	9	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Total Recoverable Sodium	9	0	4788.889	1058.825	352.942	813.885	4000	7000	3000	4600	4475	5050	0.722	2.768	0.246	0.121
Total Recoverable Strontium	9	0	81.778	30.947	10.316	23.788	92	120	28	78	61.25	105	-0.34	-0.594	0.156	0.657
Total Recoverable Thallium	9	1	0.0488	0.0106	0.00373	0.00882	0.026	0.062	0.036	0.0465	0.0395	0.06	0.233	-1.919	0.209	0.354
Total Recoverable Tin	9	0	0.417	0.113	0.0377	0.087	0.33	0.65	0.32	0.36	0.347	0.463	1.503	1.21	0.294	0.024
Total Recoverable Uranium	9	0	0.423	0.159	0.0529	0.122	0.43	0.63	0.2	0.39	0.287	0.583	0.0539	-1.446	0.156	0.657
Total Recoverable Vanadium	9	0	84.889	33.104	11.035	25.446	94	130	36	80	62	112.5	-0.228	-1.092	0.13	0.782
Total Recoverable Zinc	9	0	37.778	8.729	2.91	6.71	27	54	27	36	32.5	42	0.744	0.186	0.177	0.509

Note: All results are expressed in mg/kg dry weight except for Total Organic Carbon and Total Nitrogen which are expressed as %. Skewness, Kurtosis, Kolmogorov-Smirnov distance (K-S Dist.) and Kolmogorov-Smirnov probability values (K-S Prob.) are all unitless.

Column	Size	Below Detection Limit	Mean	Std Dev	Std. Error	C.I. of Mean	Range	Max	Min	Median	25%	75%	Skewness	Kurtosis	K-S Dist.	K-S Prob.
Total Recoverable Aluminum	7	0	16714.29	4498.677	1700.34	4160.582	13000	26000	13000	17000	13250	17000	1.738	3.566	0.332	0.019
Total Recoverable Antimony	7	4	0.0483	0.00513	0.00296	0.0127	0.01	0.054	0.044	0.047	0.0448	0.0522	1.09	--	0.269	0.429
Total Recoverable Arsenic	7	0	11.2	5.159	1.95	4.771	14	21	7	8.2	7.6	13.75	1.316	1.204	0.291	0.075
Total Recoverable Barium	7	0	18.857	3.716	1.405	3.437	11	27	16	18	17	18.75	2.285	5.583	0.342	0.013
Total Recoverable Bismuth	7	2	0.122	0.0554	0.0248	0.0688	0.14	0.17	0.03	0.13	0.0975	0.163	-1.501	2.482	0.286	0.197
Total Recoverable Boron	7	0	15.671	5.853	2.212	5.413	16.3	25	8.7	16	10.5	19.5	0.39	-0.814	0.163	0.687
Total Recoverable Cadmium	7	0	0.0243	0.00854	0.00323	0.0079	0.026	0.039	0.013	0.023	0.0193	0.0295	0.683	0.417	0.181	0.594
Total Recoverable Cesium	7	0	0.746	0.401	0.152	0.371	0.86	1.1	0.24	0.94	0.33	1.1	-0.395	-2.427	0.257	0.173
Total Recoverable Calcium	7	0	9271.429	3187.849	1204.894	2948.268	7800	13000	5200	11000	6325	11750	-0.252	-2.294	0.278	0.106
Total Recoverable Chromium	7	0	12.086	5.404	2.043	4.998	16.1	22	5.9	12	7.925	14.5	0.95	1.006	0.152	0.734
Total Recoverable Cobalt	7	0	6.586	1.597	0.604	1.477	4.5	8.7	4.2	6.6	5.375	7.825	-0.217	-1.075	0.166	0.675
Total Recoverable Copper	7	0	9.443	1.767	0.668	1.634	5.3	13	7.7	9	8.225	9.875	1.554	2.887	0.255	0.182
Total Recoverable Iron	7	0	24285.71	6799.86	2570.105	6288.821	18000	34000	16000	22000	18750	30250	0.301	-1.57	0.203	0.46
Total Recoverable Lanthanum	7	0	10.057	3.716	1.405	3.437	8.8	15	6.2	10	6.4	13.5	0.209	-2.016	0.223	0.339
Total Recoverable Lead	7	0	7.043	3.661	1.384	3.386	9.1	12	2.9	8.3	3.425	9.75	-0.00231	-2.026	0.241	0.246
Total Recoverable Lithium	7	0	20.6	11.075	4.186	10.243	25.7	33	7.3	24	9.675	31.25	-0.0997	-2.182	0.21	0.418
Total Recoverable Magnesium	7	0	4142.857	1281.74	484.452	1185.412	3200	5600	2400	4500	2900	5225	-0.36	-1.84	0.181	0.593
Total Recoverable Manganese	7	0	268.571	75.813	28.655	70.115	220	410	190	250	222.5	310	1.28	1.104	0.311	0.039
Total Recoverable Mercury	7	1	0.0338	0.0204	0.00833	0.0214	0.053	0.064	0.011	0.0345	0.012	0.047	0.262	-0.775	0.191	0.591
Total Recoverable Molybdenum	7	0	0.314	0.0718	0.0272	0.0664	0.18	0.42	0.24	0.29	0.255	0.383	0.653	-1.36	0.204	0.455
Total Recoverable Nickel	7	0	7.971	3.56	1.346	3.293	9.6	13	3.4	9.1	4.725	10.55	0.028	-1.469	0.196	0.504
Total Recoverable Phosphorus	7	0	645.714	67.542	25.528	62.466	210	780	570	650	602.5	657.5	1.401	2.764	0.273	0.118
Total Recoverable Potassium	7	0	1372.857	582.486	220.159	538.71	1340	2000	660	1600	772.5	1875	-0.289	-2.375	0.223	0.339
Total Recoverable Rubidium	7	0	7.314	3.776	1.427	3.492	8.5	11	2.5	9	3.475	10.75	-0.356	-2.332	0.244	0.231
Total Recoverable Selenium	7	7	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Total Recoverable Silver	7	3	0.0268	0.00492	0.00246	0.00784	0.011	0.034	0.023	0.025	0.024	0.0295	1.773	3.388	0.389	0.034
Total Recoverable Sodium	7	0	6300	1418.92	536.301	1312.282	4200	9100	4900	6300	5250	6700	1.411	2.37	0.219	0.361
Total Recoverable Strontium	7	0	107	37.501	14.174	34.683	84	150	66	110	71.25	145	0.0564	-2.303	0.253	0.19
Total Recoverable Thallium	7	1	0.0542	0.0178	0.00726	0.0187	0.048	0.087	0.039	0.049	0.042	0.059	1.554	2.469	0.226	0.394
Total Recoverable Tin	7	0	0.616	0.232	0.0878	0.215	0.6	0.87	0.27	0.68	0.398	0.775	-0.801	-1.026	0.239	0.255
Total Recoverable Uranium	7	0	0.504	0.191	0.0721	0.176	0.51	0.76	0.25	0.5	0.358	0.683	0.22	-1.213	0.167	0.667
Total Recoverable Vanadium	7	0	63.857	18.96	7.166	17.535	48	92	44	62	48	80.75	0.548	-1.394	0.227	0.317
Total Recoverable Zinc	7	0	41.857	10.746	4.062	9.938	28	55	27	46	32	49.75	-0.308	-1.832	0.222	0.348

Note: All results are expressed in mg/kg dry weight. Skewness, Kurtosis, Kolmogorov-Smirnov distance (K-S Dist.) and Kolmogorov-Smirnov probability values (K-S Prob.) are all unitless.

Table H-3 Summary Statistics for Raglan Harbour Sediment Quality

Column	Size	Below detection limit	Mean	Std Dev	Std. Error	C.I. of Mean	Range	Max	Min	Median	25%	75%	Skewness	Kurtosis	K-S Dist.	K-S Prob.
Dry Matter	5	0	63.6	8.532	3.816	10.594	21	72	51	67	57	69.75	-0.878	-0.543	0.255	0.327
Total Organic Carbon	5	0	0.614	0.244	0.109	0.303	0.53	0.92	0.39	0.54	0.398	0.845	0.459	-2.607	0.219	0.504
Total Nitrogen	5	0	0.096	0.0204	0.00914	0.0254	0.046	0.12	0.074	0.1	0.0755	0.113	-0.0983	-2.529	0.236	0.42
Total Recoverable Aluminum	5	0	16400	4615.192	2063.977	5730.518	11000	22000	11000	16000	12500	20500	0.108	-2.117	0.182	0.669
Total Recoverable Antimony	5	0	0.0576	0.00527	0.00236	0.00655	0.014	0.063	0.049	0.059	0.055	0.0607	-1.314	2.283	0.255	0.327
Total Recoverable Arsenic	5	0	10.6	1.883	0.842	2.338	4.7	13	8.3	10	9.35	12.25	0.216	-1.456	0.225	0.476
Total Recoverable Barium	5	0	17.6	4.393	1.965	5.455	11	23	12	16	15	21.5	0.0637	-1.354	0.242	0.389
Total Recoverable Bismuth	5	3	0.07	0.017	0.012	0.152	0.024	0.082	0.058	0.07	0.058	0.082	--	--	0.26	0.481
Total Recoverable Boron	5	0	19	4.528	2.025	5.622	11	23	12	21	15.75	22.25	-1.131	0.239	0.271	0.256
Total Recoverable Cadmium	5	0	0.0262	0.00614	0.00275	0.00762	0.015	0.034	0.019	0.024	0.022	0.0318	0.303	-1.801	0.24	0.4
Total Recoverable Cesium	5	0	0.824	0.274	0.122	0.34	0.69	1.2	0.51	0.71	0.652	1.05	0.494	-1.063	0.262	0.296
Total Recoverable Calcium	5	0	27340	17275.07	7725.646	21449.83	40300	50000	9700	20000	14425	43250	0.553	-2.179	0.265	0.282
Total Recoverable Chromium	5	0	15.6	2.074	0.927	2.575	5	18	13	16	13.75	17.25	-0.236	-1.963	0.18	0.677
Total Recoverable Cobalt	5	0	7.96	2.008	0.898	2.494	4.9	9.3	4.4	8.7	7.55	8.925	-2.133	4.666	0.425	0.004
Total Recoverable Copper	5	0	7.34	2.338	1.046	2.903	5.6	9.5	3.9	7.3	5.85	9.5	-0.689	-0.305	0.222	0.49
Total Recoverable Iron	5	0	28000	5787.918	2588.436	7186.65	14000	32000	18000	29000	26250	32000	-1.87	3.711	0.369	0.025
Total Recoverable Lanthanum	5	0	9.48	1.928	0.862	2.394	5.4	12	6.6	9.6	8.625	10.425	-0.454	1.876	0.263	0.29
Total Recoverable Lead	5	0	6.1	2.13	0.952	2.644	5.1	9.1	4	5.2	4.525	7.9	0.734	-1.388	0.264	0.286
Total Recoverable Lithium	5	0	15.38	5.529	2.473	6.865	13.1	23	9.9	14	10.725	20	0.588	-1.558	0.199	0.604
Total Recoverable Magnesium	5	0	4680	887.13	396.737	1101.518	2000	5700	3700	5000	3775	5325	-0.232	-2.575	0.241	0.395
Total Recoverable Manganese	5	0	380	101.98	45.607	126.625	250	450	200	410	357.5	435	-2.086	4.5	0.416	0.005
Total Recoverable Mercury	5	0	0.0414	0.0188	0.00842	0.0234	0.036	0.063	0.027	0.028	0.0278	0.0615	0.613	-3.293	0.362	0.031
Total Recoverable Molybdenum	5	0	0.298	0.0661	0.0296	0.0821	0.16	0.35	0.19	0.33	0.258	0.343	-1.468	1.663	0.286	0.196
Total Recoverable Nickel	5	0	8.8	1.875	0.838	2.328	4.7	11	6.3	9.1	7.275	10.25	-0.313	-1.258	0.164	0.722
Total Recoverable Phosphorus	5	0	594	87.35	39.064	108.459	210	650	440	630	567.5	642.5	-2.081	4.421	0.373	0.022
Total Recoverable Potassium	5	0	1880	438.178	195.959	544.07	1200	2500	1300	1900	1600	2125	0.194	0.89	0.192	0.631
Total Recoverable Rubidium	5	0	9.26	2.308	1.032	2.866	5.8	12	6.2	9	7.625	11.25	-0.149	-1.174	0.175	0.694
Total Recoverable Selenium	5	5	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Total Recoverable Silver	5	3	0.0285	0.00354	0.0025	0.0318	0.005	0.031	0.026	0.0285	0.026	0.031	--	--	0.26	0.481
Total Recoverable Sodium	5	0	6580	785.493	351.283	975.319	1900	7800	5900	6500	5900	7050	1.029	0.686	0.207	0.566
Total Recoverable Strontium	5	0	152.6	81.233	36.329	100.864	177	250	73	110	93.25	235	0.513	-2.919	0.3	0.149
Total Recoverable Thallium	5	0	0.0656	0.00805	0.0036	0.01	0.019	0.074	0.055	0.065	0.0595	0.0732	-0.232	-1.734	0.221	0.496
Total Recoverable Tin	5	0	0.594	0.182	0.0813	0.226	0.39	0.82	0.43	0.54	0.43	0.767	0.441	-2.665	0.217	0.517
Total Recoverable Uranium	5	0	0.524	0.0586	0.0262	0.0727	0.15	0.6	0.45	0.52	0.48	0.57	0.0851	-0.949	0.131	0.742
Total Recoverable Vanadium	5	0	71	27.313	12.215	33.914	64	100	36	77	46.5	94	-0.374	-2.164	0.187	0.652
Total Recoverable Zinc	5	0	46	8.631	3.86	10.717	23	56	33	48	40.5	51.5	-0.746	0.764	0.192	0.633

Note: All results are expressed in mg/kg dry weight except for Dry Matter, Total Organic Carbon and Total Nitrogen which are expressed as %. Skewness, Kurtosis, Kolmogorov-Smirnov distance (K-S Dist.) and Kolmogorov-Smirnov probability values (K-S Prob.) are all unitless.

Table H-4 Summary Statistics for Port Waikato Sediment Quality Data																
Column	Size	<DL	Mean	Std Dev	Std. Error	C.I. of Mean	Range	Max	Min	Median	25%	75%	Skewness	Kurtosis	K-S Dist.	K-S Prob.
Dry Matter	19	1	0.178	0.214	0.0504	0.106	0.708	0.76	0.052	0.0815	0.059	0.12	1.925	2.706	0.384	<0.001
Total Recoverable Aluminum	19	0	6536.842	5229.426	1199.713	2520.503	20800	24000	3200	4500	3925	6300	2.631	7.008	0.322	<0.001
Total Recoverable Antimony	19	0	0.167	0.0545	0.0125	0.0263	0.206	0.29	0.084	0.17	0.13	0.18	0.944	0.888	0.196	0.052
Total Recoverable Arsenic	19	0	29	10.022	2.299	4.831	42	61	19	26	22.5	32	2.019	5.047	0.187	0.079
Total Recoverable Barium	19	0	31.368	8.687	1.993	4.187	35	52	17	31	26.5	36.25	0.589	0.683	0.118	0.627
Total Recoverable Bismuth	19	0	0.0622	0.0805	0.0185	0.0388	0.348	0.37	0.022	0.035	0.0283	0.0507	3.49	13.136	0.348	<0.001
Total Recoverable Boron	19	7	4.992	2.844	0.821	1.807	9.9	12	2.1	3.8	3.35	6.6	1.506	2.332	0.233	0.072
Total Recoverable Cadmium	19	4	0.0219	0.0132	0.0034	0.00729	0.04	0.05	0.01	0.015	0.012	0.0262	1.18	0.131	0.232	0.029
Total Recoverable Cesium	19	0	7.442	2.896	0.664	1.396	12.1	14	1.9	8.1	5.05	9.075	0.123	0.252	0.169	0.162
Total Recoverable Calcium	19	0	1765.263	1322.457	303.392	637.404	4480	5300	820	1100	977.5	2025	1.746	2.146	0.316	<0.001
Total Recoverable Chromium	19	0	4.926	3.796	0.871	1.83	13.4	16	2.6	3.2	2.925	4.925	2.314	4.67	0.292	<0.001
Total Recoverable Cobalt	19	0	4.337	3.154	0.724	1.52	10.6	13	2.4	3	2.625	3.9	2.058	3.062	0.334	<0.001
Total Recoverable Copper	19	0	4.4	6.743	1.547	3.25	26.6	28	1.4	1.7	1.5	2.825	2.94	8.801	0.378	<0.001
Total Recoverable Iron	19	0	17273.68	13545.35	3107.516	6528.649	51200	60000	8800	13000	11000	14750	2.439	5.481	0.38	<0.001
Total Recoverable Lanthanum	19	0	5.316	2.492	0.572	1.201	10.6	14	3.4	4.5	4.25	5.15	2.753	8.346	0.345	<0.001
Total Recoverable Lead	19	0	3.384	3.863	0.886	1.862	15.5	17	1.5	1.9	1.8	2.575	2.986	9.111	0.382	<0.001
Total Recoverable Lithium	19	0	9.958	5.842	1.34	2.816	25.7	32	6.3	8.2	7.5	9.5	3.385	12.352	0.339	<0.001
Total Recoverable Magnesium	19	0	1711.579	1657.087	380.162	798.69	6430	7100	670	1000	855	1725	2.458	6.016	0.305	<0.001
Total Recoverable Manganese	19	0	407.368	203.274	46.634	97.975	840	1000	160	350	265	485	1.58	2.934	0.199	0.047
Total Recoverable Mercury	19	5	0.0194	0.0116	0.00311	0.00671	0.041	0.051	0.01	0.014	0.013	0.024	1.847	3.358	0.291	0.002
Total Recoverable Molybdenum	19	0	0.159	0.0911	0.0209	0.0439	0.366	0.44	0.074	0.12	0.1	0.185	1.948	4.261	0.193	0.06
Total Recoverable Nickel	19	0	3.626	2.734	0.627	1.318	11	13	2	2.5	2.325	3.65	2.746	7.879	0.342	<0.001
Total Recoverable Phosphorus	19	0	332.105	217.577	49.916	104.869	750	940	190	240	220	300	2.069	3.187	0.349	<0.001
Total Recoverable Potassium	19	0	796.842	669.486	153.591	322.682	2720	3100	380	590	462.5	727.5	2.809	8.167	0.329	<0.001
Total Recoverable Rubidium	19	0	5.632	3.011	0.691	1.451	12.5	16	3.5	4.9	4.025	5.775	2.783	8.211	0.333	<0.001
Total Recoverable Selenium	19	19	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Total Recoverable Silver	19	18	0.032	--	--	--	0	0.032	0.032	0.032	0.032	0.032	--	--	--	--
Total Recoverable Sodium	19	0	1870	1518.786	348.433	732.031	4990	5400	410	1400	590	3025	1.013	0.0204	0.176	0.121
Total Recoverable Strontium	19	0	18.837	13.127	3.011	6.327	42.7	51	8.3	13	10	27.5	1.494	1.23	0.292	<0.001
Total Recoverable Thallium	19	0	0.0589	0.0237	0.00545	0.0114	0.083	0.11	0.027	0.051	0.0442	0.0655	1.072	0.102	0.233	0.008
Total Recoverable Tin	19	0	0.342	0.241	0.0553	0.116	1	1.2	0.2	0.28	0.22	0.318	2.914	9.255	0.346	<0.001
Total Recoverable Uranium	19	0	0.205	0.155	0.0355	0.0746	0.56	0.67	0.11	0.14	0.123	0.185	2.348	4.848	0.354	<0.001
Total Recoverable Vanadium	19	1	26.444	28.072	6.617	13.96	110	120	10	13.5	11	26	2.548	7.098	0.298	<0.001
Total Recoverable Zinc	19	0	34.789	19.309	4.43	9.307	69	92	23	27	24.25	32.75	2.212	4.162	0.326	<0.001

Note: All results are expressed in mg/kg dry weight except for Dry Matter which are expressed as %. Skewness, Kurtosis, Kolmogorov-Smirnov distance (K-S Dist.) and Kolmogorov-Smirnov probability values (K-S Prob.) are all unitless.

	Aotea Harbour		Kawhia Harbour
	Kawhia	Port Waikato	Port Waikato
Total Recoverable Aluminum	0.007	0.002	<0.001
Total Recoverable Antimony	ID	<0.001	ID
Total Recoverable Arsenic	<i>0.073</i>	<0.001	<0.001
Total Recoverable Barium	0.003	<0.001	<0.001
Total Recoverable Bismuth	<i>0.016</i>	0.867	0.013
Total Recoverable Boron	<i>0.327</i>	<0.001	0.001
Total Recoverable Cadmium	<i>0.11</i>	<i>0.165</i>	0.024
Total Recoverable Cesium	<i>0.128</i>	<0.001	<0.001
Total Recoverable Calcium	<i>0.954</i>	<0.001	<0.001
Total Recoverable Chromium	0.854	<0.001	0.003
Total Recoverable Cobalt	<i>0.508</i>	0.005	0.011
Total Recoverable Copper	<0.001	0.004	0.005
Total Recoverable Iron	<i>0.868</i>	0.005	0.008
Total Recoverable Lanthanum	0.056	0.007	0.002
Total Recoverable Lead	0.08	0.006	0.004
Total Recoverable Lithium	<i>0.992</i>	0.375	<i>0.977</i>
Total Recoverable Magnesium	0.071	0.004	0.003
Total Recoverable Manganese	<i>0.199</i>	0.003	0.06
Total Recoverable Mercury	ID	ID	<i>0.058</i>
Total Recoverable Molybdenum	<i>0.539</i>	0.002	0.008
Total Recoverable Nickel	0.185	0.002	0.002
Total Recoverable Phosphorus	<i>0.047</i>	0.006	0.007
Total Recoverable Potassium	ID	ID	0.013
Total Recoverable Rubidium	0.34	0.588	<i>0.524</i>
Total Recoverable Selenium	ID	ID	ID
Total Recoverable Silver	ID	ID	ID
Total Recoverable Sodium	0.023	<0.001	<0.001
Total Recoverable Strontium	<i>0.162</i>	<0.001	<0.001
Total Recoverable Thallium	0.488	0.457	<i>0.656</i>
Total Recoverable Tin	0.04	0.005	0.008
Total Recoverable Uranium	0.369	0.001	0.002
Total Recoverable Vanadium	0.157	<0.001	0.003
Total Recoverable Zinc	0.415	0.034	0.046

Notes

0.001	Significant difference at 95% Confidence Interval
0.34	No -significant difference at 95% Confidence Interval
ID	Insufficient data to undertake a student t-test
<i>0.073</i>	Value in italics indicates that the statistical tests are less likely to detect a difference (at 95% confidence interval) when one actually exists. Negative results should be treated cautiously.

- **References**

**Michelsen, T.C. 1992. *Organic Carbon Normalization of Sediment Data*. Washington Department of Ecology
Publication No. 05-09-050. PAHs**