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Significance of Arsenic in Sediments of Lake Rotoroa (Hamilton Lake)

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Limitations:

This report has been prepared on the basis of visual observations of the lake, and limited sampling of the lake bed sediments and the lake water. This information has been used to describe the lake conditions in the vicinity of sample locations but the interpreted conditions cannot be guaranteed. Part of the assessment relies on information supplied by others. This information is believed to be correct but has not been independently verified by Pattle Delamore Partners Limited.

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time, the site conditions and environmental guidelines could change so that the reported assessment and conclusions are no longer valid.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

The report has been prepared for Environment Waikato, according to their instructions, for the particular objectives described in the report. The information contained in this report should not be used by anyone else or for any other purposes.

Executive Summary

Background

Environment Waikato has commissioned Pattle Delamore Partners Limited (PDP) to assist with the evaluation of the significance of arsenic in the sediment of Lake Rotoroa (Hamilton Lake), in Hamilton. Although this report focuses mainly on the significance of arsenic within the sediments of the lake, the concentrations of a number of other elements (Cd, Cr, Cu, Fe, Hg, Ni, P, Pb and Zn) were also measured in the sediment and overlaying waters. The results of all of these elements are presented in this report together with an assessment of the environmental significance of the elements, the method of deposition of the elements and the relationship of the lake chemistry to the chemistry of other lakes in the Waikato region.

Using a motor boat for access to the sampling locations, 34 grab samples of the top 10cm of the lake bed were obtained by PDP on a distorted grid of 130m spacing, together with 5 core samples with a maximum depth of 0.45m, and 4 water samples. These samples, together with 4 composite samples prepared from some of the lake bed samples were analysed by Hill Laboratory in Hamilton for a suite of metal and organic parameters.

Findings: Comparison to Environmental Guidelines

- Five elements (arsenic, copper, lead, mercury and zinc) exceeded the ANZECC (2000) guideline value at some of the surficial sediment sampling sites. The multi-element analysis of 33 metals on four composite samples revealed that antimony and polycyclic aromatic hydrocarbons (PAHs) exceed the ANZECC (2000) ISQG-low guideline value at some locations. The concentration of some PAHs exceeded the ANZECC (2000) ISQG-high guideline value at one location after organic carbon normalisation procedures where used.

- The average concentration of arsenic within Hamilton Lake surficial sediments was 170mg/kg. Arsenic concentrations exceeded the ANZECC (2000) ISQG-low guideline value in all 34 surficial sediment sampling sites and the ANZECC (2000) ISQG-high concentrations in 73% of the surficial sediment sampling sites.

- The average concentration of copper within Hamilton Lake surficial sediments was 32mg/kg. Copper concentrations exceeded the ANZECC (2000) ISQG-low guideline value at one sampling site and there were no exceedances of the ANZECC (2000) ISQG-high guideline value.

- The average concentration of lead within surficial sediments was 77.5mg/kg. Lead concentrations in the surficial sediments exceeded the ANZECC (2000) ISQG-low guideline at 19 sampling sites and the ANZECC (2000) ISQG-high guideline value at one sampling site.

- The average concentration of mercury within the surficial sediments was 0.13mg/kg. Mercury concentrations in surficial sediments exceeded the ANZECC (2000) ISQG-low guideline at five sampling locations but did not exceed the ANZECC (2000) ISQG-high guideline value at any of the sampling sites.

- The average concentration of zinc within surficial sediment samples was 182mg/kg. Zinc concentrations exceeded the ANZECC (2000) ISQG-low guideline value at 12 sampling sites and exceeded the ANZECC (2000) ISQG-high guideline value at 2 sampling sites.

- The concentration of all elements is generally greater in sediments collected near the top of the sediments cores and decreases in sediments collected at greater depth. The exception to this trend is arsenic in sediment core CS3, the highest concentrations of arsenic in this core occurs at 9-10cm below the water-sediment interface. It is believed that this sampling site may be impacted by high sediments rates caused by stormwater discharges.

- The concentration of both dissolved and total metals within the lake water are below the relevant ANZECC (2000) fresh water trigger values for 95% ecosystem protection and NZ Drinking Water Standards (2006). A majority of the metals present in the lake are associated with the dissolved phase.

Findings: Relative Enrichment

To determine if the elements in the sediments of Hamilton Lake have been significantly enriched above typical background concentrations, the concentration of elements in this survey were compared with the concentrations of elements measured in 9 rural lakes in the Waikato region. The enrichment ratios calculated for the elements examined in the surficial sediments of Hamilton Lake reveal that:

- The concentration of arsenic within Hamilton Lake is significantly enriched, with enrichment factors ranging from 4.5 to 105 times higher than those typically found in Waikato rural lakes.

- The concentration of antimony is significantly enriched within Hamilton Lake surficial sediments, with enrichment ratios ranging from 5.2 to 7.3 times higher than those typically found in Waikato rural lakes.

- The concentration of tin is significantly enriched within Hamilton Lake surficial sediments, with enrichment ratios ranging from 3 to 4.8 times higher than those typically found in Waikato rural lakes.

- The concentration of lead in surficial sediments of Hamilton Lake is significantly enriched in most sampling locations. Lead appears to be mostly enriched in sediment sampling locations in the southern portion of the lake, where a number of stormwater discharges occur into the lake.

- The concentration of silver in surficial sediments of Hamilton Lake is significantly enriched in some sampling locations.

- The concentration of aluminium in surficial sediments of Hamilton Lake is significantly enriched above background concentrations found in Waikato rural lakes, but is lower than the typical concentration within Waikato soils.

- The concentrations of chromium, copper and zinc are significantly enriched in some surficial sediment sampling locations (mainly around the southern portion of the lake).

- The average concentrations of mercury in the surficial sediments of the lake do not appear to be significantly enriched when compared to the average concentration of Waikato rural lakes. However, there is one sampling location which does appear to be enriched in mercury with respect to Waikato rural lakes. The source of the mercury is unknown, and the elevated mercury concentrations measured at this location may be due to sample inhomogeneity.

- The concentrations of cadmium and nickel do not appear to be significantly enriched in any of the sediments collected from Hamilton Lake.

- The concentration of phosphorus within the sediments of Hamilton Lake appears to be depleted when compared to other rural lakes within the Waikato region. This may be due to agricultural inputs of phosphorus into rural lakes due to surface water and groundwater discharges from superphosphate application to pastoral land.

Findings: Likely Sources of Enrichment

There appears to be two major sources of enrichment of elements found in the sediments of Hamilton Lake. These are the discharges of urban stormwater into the lake, and the application of herbicides.

- The historical application of sodium arsenite into the lake (as a herbicide) has significantly enriched the concentration of arsenic within the lake's surficial sediments. It may also be responsible for some of the enrichment of antimony, copper and tin observed in the lake's sediments; however stormwater discharges may also be responsible for some of the enrichment observed in these elements.

- Stormwater discharges into the lake appear to be the major source for the enrichment of copper, lead and zinc in the surficial sediments within the lake. The southern portion of the lake appears to be the area most impacted by stormwater discharges, with the highest concentrations of all of these elements.

Findings: Are the Sediments "Contaminated Land" and what are the Human Health Risks associated with the elevated arsenic concentrations?

Under the Resource Management Amendment Act (2005) the elevated concentrations of arsenic found within the surficial sediments of Hamilton would meet the criteria of being “contaminated land” on the basis that they are reasonably likely to have a significant adverse effect on the environment. Therefore, the lake bed of Hamilton Lake can be classified as “contaminated land”.

A human health risk assessment on the concentration of arsenic within the lake sediments concluded that:

- Although recreational users and workers may be potentially exposed to sediment and water within Hamilton Lake there are unlikely to be any significant health risks of these exposures due to the infrequent nature and short durations of typical exposures.
- Children playing in the lake bed mud could theoretical be exposed to an unacceptable level of arsenic. However, this is based on very conservative estimates of exposure frequencies and durations to the lake’s sediment. These assumptions may need to be verified.
- Recreational fishermen who are catching fish to supplement a significant part of their diet could exceed the index dose recommended by the US EPA and there is an increase risk to fisherman targeting catfish as a food species. However, further work is required to verify the consumption rates of fish from the lake, and what species are actually been eaten from the lake. In addition, investigation of the form of the arsenic within the fish form the lake would be useful as organic forms of arsenic (which are thought to be the prevalent form of arsenic within fish) are significantly less toxic than inorganic forms of arsenic.

Findings: Changes in Sediment Quality over time: Past and Future

A comparison between the results obtained by Gordon Rajendram in 1991 and the results of this survey is difficult because of the limited data available. However, from the limited data available it was found that there is no significant change in the concentration of arsenic in surficial sediments over the last 16 years, and there are significant concentrations of arsenic still within the upper 2cm of the sediments 48 years after the application of sodium arsenite herbicide to the lake in 1959. As there is little loss of arsenic from the lake over time, the upper 10cm of the sediment column could contain concentrations of arsenic which could be potentially harmful to aquatic life for between 500 and 8,000 years.

Recommendations

As the concentration of arsenic is likely to be significantly enriched in the surficial sediments for a long period of time and it appears that there may be an undesirable exposure of humans to arsenic if fish caught from the lake are consumed regularly by individuals, an environmental management plan (EMP) should be prepared for the site.

Further work should also be conducted to determine the potential long-term impacts of stormwater discharges into the lake and the rate of accumulation of metals within the sediments of the southern portion of the lake.

Note on terms

Heavy metals / trace elements

The focus of this report is on concentrations and sources of ten chemical elements (some of which are major elements, and some are trace): arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), nickel (Ni), lead (Pb), phosphorus (P) and zinc (Zn). Sometimes arsenic, cadmium, chromium, copper, nickel, mercury, lead and zinc are 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 and the group of elements covered by that term changes depending on the definition used. In addition, arsenic is not regarded as a true metal, but a metalloid. The term 'elements' is used in this report because it is not ambiguous, and accurately describes the group of ten elements that are the focus of this work.

The term trace element' is something which is not one of the ten major elements that occur in the earth's crust. Ninety-nine percent of the earth's crust is composed of these 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 100mg/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' is usually reserved for cases where a trace element's concentrations have become sufficiently high to cause significant adverse effects on the environment. For convenience, this is usually assessed by reference to sediment quality guidelines. Sites would normally be regarded as contaminated when trace elements are present at concentrations that significantly exceed the ANZECC ISQG-High (see Section 2.5). These conventions are followed in this report.

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Glossary

Analyte: A substance which is determined in an analytical procedure, such as a titration or analysis using an analytical instrument.

Anthropogenic: Made by people or resulting from human activities. Usually used in the context of emissions that is produced as a result of human activities.

Bioaccumulation: Bioaccumulation is a general term for the accumulation of substances, such as pesticides (DDT is an example), methyl mercury, or other organic chemicals in an organism or part of an organism.

Carcinogen: A substance that may cause cancer in animals or humans.

Correlation coefficients: A positive or negative number within the range of 0.00 to 1.00. A correlation coefficient of 0.00 indicates no relationship and a coefficient of 1.00 indicates the highest possible relationship, which is sometimes called a perfect relationship. Correlations are usually somewhere between no relationship and a perfect relationship.

Enrichment Factor: Enrichment Factor is the degree of enrichment or depletion of a substance above the background concentration of that substance.

Enrichment: Enrichment is when a substance is found in higher concentration than the background concentration. This can be cause be either chemical or physical processes or by the addition of that substances into the system by anthropogenic activities.

Epi-benthic species: Referring to organisms living on the bottom surface of the lake.

Flocculated: To cluster together or gather together into a large group of particles which results in the particulate settling out of the water column.

Herbicide: A chemical substance used to destroy or inhibit the growth of plants, especially weeds.

Hotspot: A hotspot is an area of elevated concentration of a substance, usually much higher than the surrounding concentration of that substance.

Hyperaccumulate: Accumulate appreciable quantities of metal in their tissue regardless of the concentration of metal in the water or sediment.

Index dose: The maximum concentration of a substance which a person can be exposed to without resulting in an increase in the risk factor of developing cancer as a result of the exposure to that substance. In New Zealand, a risk factor of 1 in 100,000 is normally used.

ISQG-low. The Australian and New Zealand Environmental Conservation Council (ANZECC) interim guideline values for sediment quality (ISQGs) low trigger value for the protection of aquatic ecosystems. The ISQG-low trigger value 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.

ISQG-high. The Australian and New Zealand Environmental Conservation Council (ANZECC) interim guideline values for sediment quality (ISQGs) high trigger value for the protection of aquatic ecosystems. The ISQG-high trigger value 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

LADD: Long term average daily dose. The amount of a substance that a person would receive, on average, over a long period of time (usually between 15-70 years).

Macrophyte: A large aquatic plant which is easily visible to naked eye.

Macro-invertebrate: An animal without a backbone large enough to be seen without a microscope.

Molecular Weight: The molecular weight of a compound in grams is the sum of the atomic weights of the elements in the compound.

PAH: Polycyclic aromatic hydrocarbons. Also synonymously known as 'Polycyclic Aromatics (PCA)' or 'Polynuclear Aromatics (PNA)'. Aromatic (ring structures) hydrocarbons with two or more (up to five or six) benzene rings joined in various, more or less clustered forms.

Pathogens: Micro-organisms that can cause disease in other organisms or in humans, animals, and plants. They may be bacteria, viruses, or parasites.

Physiochemical: The physical and chemical parameters. Includes parameters such as conductivity, temperature, pH, redox potential and chemical concentrations.

Receptor: The exposed individual relative to the exposure pathway considered.

Risk: The probability that a contaminant will cause an adverse effect in exposed humans or to the environment.

Seston: Suspended particulate matter in water including inorganic and organic matter.

Slope factor: An upper bound, approximating a 95% confidence limit, on the increased cancer risk from a lifetime exposure to an agent.

Suspended Particulate Matter: Finely divided solids (greater than 0.45μm) that may be dispersed through the water.

Total Recoverable: The concentration of analyte determined on an unfiltered sample following treatment with hot dilute mineral acid.

Toxicity: The degree to which a chemical substance elicits a deleterious or adverse effect upon the biological system of an organism exposed to the substance over a designated time period.

Tradewaste: Any waste discharged from an industrial site other than domestic waste.

1.0 Introduction

Pattle Delamore Partners Limited (PDP) was commissioned by Environment Waikato to undertake sediment sampling of Lake Rotoroa in Hamilton. Previous work undertaken on behalf of Hamilton City Council (HCC) by the Aquatic Plant Section of the Ministry of Agriculture and Fisheries (MAF) in 1983 indicated that the surficial lake bed sediments had concentrations of arsenic ranging between 540-780mg/kg. The elevated concentrations of arsenic in the sediment are the result of the application of sodium arsenite herbicides applied to the lake in 1959 to control the growth of aquatic weeds, in particular.

Environment Waikato commissioned this work to obtain more detailed and up-to–date information about the present state of this lake's sediment, so that Environment Waikato can determine whether surface sediment of the lake would still be regarded as meeting the Regional Plan definition of "contaminated land."

Although this report is primarily focused on the significance of arsenic within Hamilton Lake, a number of other chemical parameters were also measured in the sediment and water column and are discussed within this report. In particular, elements such as cadmium, chromium, copper, iron, lead, mercury, nickel, phosphorus and zinc are measured in the sediments, and the relative enrichment/depletion and sources of these elements are discussed and compared against the relative ANZECC (2000) sediment quality guidelines

PDP undertook the sampling between 24 and 25 May 2007.

This report presents the methodology and results of the sampling and analysis of sediments and water samples collected as part of this survey. Where appropriate, all concentrations are reported in terms of dry weight.

1.1 Aims of this Report

The aim of this project is to:

1. Determine if with the present concentration of arsenic, the sediments of Hamilton lake would still be regarded as contaminated land;

2. Assess if the concentration of arsenic within the sediments of the lake represent a health hazard to users of the lake.

In addition to these primary aims, Environment Waikato also requested PDP to:

a) To discuss any patterns in distribution of the contaminants.

b) Compare the results of this study with other studies.

c) Outline possible or likely sources for the obvious contaminants, and

d) Outline what might be happening with contaminants in the sediments over time.

1.2 History of Lake Rotoroa

Lake Rotoroa (37°48’ S, 175°E) is located approximately 650m west of the Waikato River and is located within Hamilton City urban area. The lake is roughly oval in shape and covers approximately 54ha, with a maximum length and width of 1.5km and 0.5km respectively. It is very shallow, with most of the lake (54%) having a depth of less than two metres; however, there are two basins, one in the north and the other in the south, where water depth can exceed more than 5m. The maximum depth of the lake is 6.5m. The lake is drained by a culverted drain located on the western side of the lake. There are 45 stormwater drains which discharge into the lake all from urban and parkland areas around the lake. Most of these drains are located either on the southern or on the eastern side of the lake (see Figure 1).

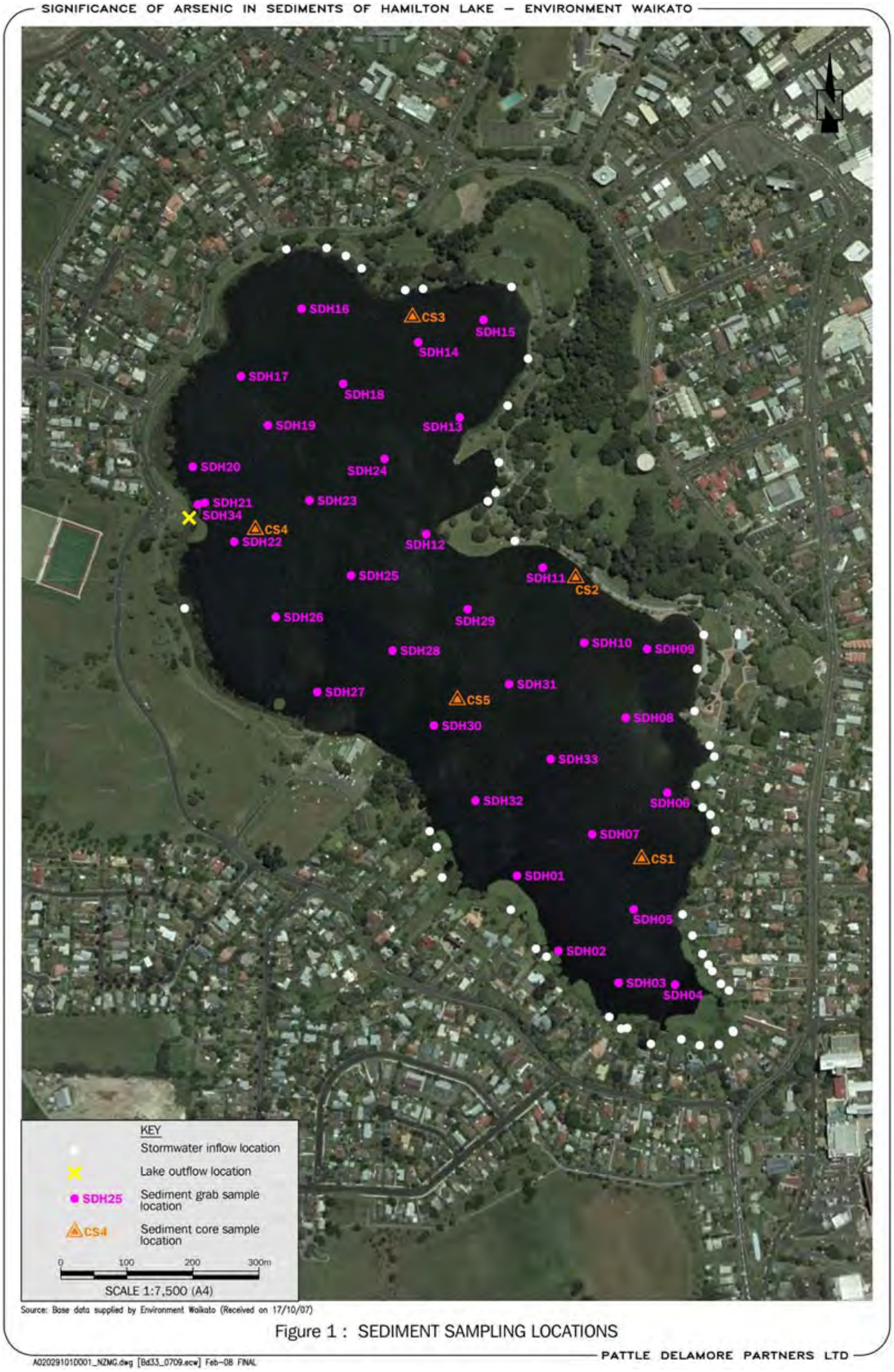
Water enters the lake from a number of sources including the 45 stormwater drains, direct rainfall, groundwater and surface runoff. The catchment area of the lake is approximately 138 ha, which includes the lake surface itself (40% total area), recreational reserves located on the edge of the lake (35%) and nearby residential housing (approximately 25%). The main outflow from the lake is located on the western side of the lake, and water is discharged via a weir though an underground culvert to the Waitewhiriwhiri stream, which in turn discharges into the Waikato River. The residence time of water in the lake is approximately 2.4 years (Kane, 1992).

Radiocarbon dating of lake sediments undertaken by Green and Lowe (1994) indicate that the Hamilton Lake was formed approximately 19,000 -20,000 yrs BP. In 1981, the University of Waikato extracted sediment cores (2.5 and 2.1m long) from the deepest point of the lake in the southern basin to determine the stratigraphy of the cores and sedimentation rate within the lake (Green and Lowe, 1994). On the basis of this data Green and Lowe determined that the average sedimentation rate in the lake varied between 0.145 and 0.184mm/yr, which is consistent with the sediment rates of other lakes in this area.

In 1959, after a trial application over 0.5 ha, sodium arsenite ($NaAs(III)O_2$) was applied to 39ha (approximately 72% of the total area of the lake) to control problem weed growths of *lagarosiphon major*. Approximately 11,000 L of a sodium arsenite formulation (71.5% active ingredient) at a concentration of approximately 10g/m^3 resulted in approximately 5,500kg of arsenic being supplied to the lake (Tanner and Clayton, 1990). This resulted in a spectacular reduction in aquatic weeds over a period of circa 5 years. In 1983, Hamilton City Council commissioned the Aquatic Plant Section of the Ministry of Agriculture and Fisheries (MAF) to undertake sampling of Lake Rotoroa to determine the levels of residual arsenic present in the lake. This investigation found that elevated concentrations of arsenic were present in the macrophytes contained within the lake (192-1200mg/kg) and in the surficial sediments (540-780mg/kg), but arsenic levels in fish tissues sampled and within the lake waters were below the detection limits of the analytical methods employed (1mg/kg and 0.01g/m^3 respectively) (Tanner and Clayton, 1990).

Subsequent studies by Gordon Randerjam (1992) and Daryl Kane (1995) have found elevated concentration of arsenic in fish from the lake.

Figure 1: Sediment Sampling Locations



1.3 Water Quality of Lake Rotoroa

Water quality monitoring of Lake Rotoroa began in 1976 (de Winton, 1994) and regular sampling and analysis of water for nutrients and general physiochemical parameter is now conducted by NIWA on behalf of Hamilton City Council (Putney, pers. Comms.). Data from a number of monitoring programmes indicate a change in the water quality of Lake Rotoroa (De Winton, 1994), with a decrease in water clarity and increases in phytoplankton abundance, particularly after the collapse of *Egeria densa* beds in 1989-90 (LERNZ, 2007). The mean value of pH of the lake water was found to be 7.0 with a range of 6.6-7.2 (Rajendram, 1992).

Metals such as copper, lead and zinc enter the lake via stormwater inflows from around the lake edge. Analysis of the total metal concentration in stormwater flowing into the lake and water within the main body of the lake by Gordon Rajendram in 1992 is summarized in Table 4-3 in Section 4.1.1. Metal concentrations in the stormwater do fluctuate greatly over time as result of such factors as traffic levels and metrological conditions (i.e. rainfall periodicity, duration and intensity).

The concentration of cadmium in the stormwater generally exceeds the ANZECC guidelines trigger values for freshwater protection, and concentrations of total copper, lead and zinc periodically exceed the ANZECC trigger values. The analytical results from the Gordon Rajendram study may overestimate the bio-availability (and therefore the toxicity) as the total metal fraction (dissolved plus metals sorbed onto suspended particulate matter) rather than the more bio-available dissolved fraction were measured in the study.

All concentrations of arsenic were below ANZECC guideline trigger values for freshwater ecosystems protection in both the lake water and in the stormwater entering the lake. This suggests that there is minimal input of dissolved arsenic entering the lake via the stormwater discharges.

High bacteria levels have been detected by Hamilton City Council within the lake since 1984 and have been noted at some locations and times since this time (Hamilton City Council, 2006). Due to these elevated concentration of bacteria, swimming in the lake has been discouraged.

1.4 Flora and Fauna of Hamilton Lake.

1.4.1 Flora

Since the collapse of oxygen weed (*Egeria densa)* beds in 1989-90 (which is suspected to be due to overgrazing of aquatic macrophytes by Rudd), there is little submerged aquatic vegetation in Hamilton Lake. In recent years some recovery of submerged aquatic vegetation has been observed (De Winton et al, 2006). The lake is phytoplankton dominant since the collapse of the submerged aquatic vegetation (LERNZ, 2007); although in a survey of the lake vegetation in 2005, charophytes (algae) covered approximately 30% of the lake’s area.

However, emergent macrophytes are still present, and dominate the marginal vegetation, which occupies approximately 50% of the lake (Kane, 1994). The most common aquatic vegetation species found in the lake are Iris pseudacorus (35%), Baumea articulate (22%), Eleocharis sphacelata (15%), Typha orientalis (14%), and Nympahea cultivars (11%) (Kane, 1994).

1.4.2 Fish.

A detailed survey of the fish population in the lake was conducted by Daryl Kane between 9 December 1993 and 2 March 1994. During this survey a total of 1073 fish were captured, comprising of nine different species:

- Catfish (Ictalurus nebulosus).
- Common Bully (Gobiomorphus cotianus).
- Goldfish (Carassuis auratus).
- Longfinned eel (Anguilla dieffenbachia).
- Shortfinned Eel (Anguilla australias).
- Perch (Perca fluviatilis).
- Mosquitofish (Gambusia affinis).
- Tench (Tinca tinca).
- Rudd (scardininius erythrop).

1.4.3 Macro-invertebrates

No published information was found on the status of macro-invertebrates within the Hamilton Lake. Tanner and Clayton (1990) state that the concentration of sodium arsenite applied to the lake (10g/m^3) would have been toxic to many of the lake's benthic invertebrates. Henriques (1979) found that the benthic macro-invertebrate species abundance and diversity are low in Hamilton Lake and suggests that continuing presence of arsenic could be one of the factors for this. Tanner and Clayton (1990) state that both the common freshwater mussel *Hydridella menziesi* and the snail *Potamopyrgus antipodarum* are missing from Hamilton Lake but are found in the near by Lake Rotokauri.

In 1994, Daryl Kane collected some macro-invertebrate samples from two locations within the lake. These samples found a number of different species; however, the most sensitive taxa were not present. The abundance of the macro-invertebrates found in the two samples varied greatly and an insufficient number of samples were collected to make a definitive statement on the status of the macro-invertebrate community within the lake. A copy of Daryl Kanes' macro-invertebrate results is presented in Table F-4 of Appendix F.

1.5 Previous Sediment Quality Investigations of Hamilton Lake

The first published sediment quality investigation of Hamilton Lake was conducted in 1983 by Tanner and Clayton (1990) 24 years after the application of sodium arsenite to control the growth of aquatic weeds. This study found elevated concentrations of arsenic in the aquatic macrophytes (193 to 1200mg/kg dry weight) and in the surficial sediments (540 to 780mg/kg dry wt). Tanner and Clayton (1990) found that the levels of arsenic recorded in the macrophytes and sediments were between one and two orders of magnitude greater than those reported from uncontaminated lakes. Arsenic in fish tissues collected by Tanner and Clayton were below 1 mg/kg wet weight which suggests that bio-accumulation of arsenic by fish is minimal. Arsenic concentrations in surface water samples (which were collected in winter) were below the analytical method detection limit (0.01mg/kg), but they did report that a previous study conducted by Henriques (1979) indicated that the concentration of arsenic in bottom waters in shallow areas of the lake ranged between 0.01 to 0.55mg/kg over summer months in 1978/1979.

In 1990/1991 Gordon Rajendram (1992) undertook an investigation of selected chemical constituents in water, sediments, plants and fish tissues in Hamilton Lake as part of an MSc Thesis at Waikato University. Gordon Rajendram found that the nature and location of stormwater inflows were critical in determining the distribution patterns of metals (except arsenic) with Hamilton Lake sediments. Gordon Rajendram found that the concentration of copper and lead decreased almost logarithmically with distance from the discharges, which he inferred was due to the association of these metals with heavier particular matter. Gordon Rajendram found that the distribution of zinc was almost uniform with increasing distance from inflows into the lake, which he believed was due to the greater mobility of zinc within the environment. Gordon Rajendram suggested that this might be due to a significant amount of zinc entering into the lake as dissolved zinc rather than particulate bound zinc, which then bound to suspended particulate matter within the lake before settling out.

Gordon Rajendram (1994) concluded that although the heavy metals do not currently appear to present a risk to biota in Hamilton Lake, lead, zinc and copper are accumulating in the lake sediments and they may become a long term ecological problem. He recommended that stormwater should be treated before it enters Hamilton Lake especially the stormwater inflows located in the southern basin where he found the greatest concentration of metals. It should be noted that Gordon Rajendram's thesis did not include a detailed ecological risk assessment and his conclusion on the impact of stormwater on the aquatic biota appears to be largely based on US EPA freshwater quality guidelines. These guidelines can be an order of magnitude higher than the current ANZECC (2000) freshwater guidelines for ecosystem protection and do not consider the impact of sediment quality on aquatic biota.

1.6 Chemistry of Arsenic in Sediments and Natural Waters

The chemistry of arsenic in freshwater systems has been reviewed by a number of authors (Aspell, 1979; Hamasaki *et al*, 1995; Meng *et al,* 2002; and Smedley and Kinniburgh, 2002) and has been there has been a number of investigations into the chemistry and fate of arsenic in the Waikato River (Aggett and Aspell, 1980; Aggett and O'Brien, 1985). These studies have shown that arsenate (As (V)) is thermodynamically favoured over As (III), in well oxygenated fresh waters and occurs mainly as $H_2AsO_4^-$ and $HAsO_4^{2-}$. Work conducted by Aggett and Aspell has shown that the common oxidation state of arsenic in the Waikato River (and hence most freshwater systems) is As (V); however, biological activity during summer months may be responsible for transforming up to *50%* of the total arsenic present in the system into As (III).

Under mildly reducing conditions, arsenious acid (H_3AsO_3 and the arsenites $H_2AsO_3^-$ and $HAsO_3^{2-}$) are formed. These species of arsenic are more toxic than As (V) species to humans and ecological receptors.

The concentration of arsenic in natural waters will be controlled by co-precipitation or adsorption onto particles, especially ferric oxide but to a lesser extent manganese oxides and clay particles. Sorption onto iron oxides is thought to be the major mechanism of removal of arsenic from the water column in well oxygenated environments, however, arsenite can also be scavenged by co-precipitation or adsorption onto metal sulphides (such as FeS) or directly precipitated as arsenic sulphide under reducing conditions. Chemical surveys conducted within Waikato Region of soils, stream sediments and marine sediments (unpublished Environment Waikato data) has shown a high correlation between arsenic and iron throughout the region and it is assumed that sorption onto iron oxides is the major immobilisation mechanism in controlling arsenic within the region.

There are two main triggers for the release of arsenic from sediments (Smedley and Kinniburgh, 2002). These are high pH conditions (>8.5), and strongly reducing conditions at near-neutral pH. Alkaline conditions (pH >8.5) lead either to the desorption of arsenic (especially As (V) species) from mineral oxides (i.e. hydrous iron oxides) and strongly reducing conditions can lead to the desorption of arsenic from iron oxide surfaces or reduced dissolution of iron and manganese oxides.

Studies conducted by Aggett and O'Brien (1985) of Lake Pohokura have shown that the arsenic cycle is dominated by inorganic processes. These studies also concluded that any As (III) that is released into the porewaters of the sediments would be immobilised by adsorption onto hydrous iron oxides near the sediment surface, provided that these sediments remained oxic.

Figure A-1 in Appendix A shows the geochemical cycling of arsenic in a stratified lake, including the cycling of arsenic between water and sediments.

1.7 Arsenic in New Zealand

Although arsenic is not thought to be a major health issue in New Zealand (Centeno, et al, 2005), elevated concentrations of arsenic have been detected in sediments, soils and water within New Zealand. Arsenic has entered the New Zealand environment via a number of different sources which are a result of either anthropogenic activity or natural processes.

The major natural sources of arsenic in the environment are geothermal discharges (especially in the central North Island) and weathering of rocks and soils which contain arsenic bearing sulphide minerals (such as arsenopyrite (FeAsS), realgar (AsS) and orpiment (As_2S_3) (i.e. Central Otago and Coromandel). The release of arsenic from these sources can be enhanced by anthropogenic activity such as land clearance (which enhances the rate of erosion), mining or geothermal energy production.

In the Waikato River, the single most important source of arsenic is the Wairakei geothermal power station which contributes up to 75% of the total arsenic in the river, with the rest of the arsenic mainly coming from naturally occurring geothermal sources (Aspell, 1979). A number of studies have been conducted on the concentration of arsenic in the Waikato River sediments (see Table B-1 in Appendix B) and water. These studies have shown that the concentration of arsenic in the sediments is typically around 30mg/kg, though there are large variations with concentrations of arsenic in some hydropower lakes exceeding 6,000mg/kg (see Table B-1 in Appendix B). Aggett and Apsell (1980) reported arsenic concentrations in the Waikato River waters varying between 0.005 to 0.079mg/L, with the highest concentrations occurring at Lake Aratiatia (caused by the Wairakei discharges) and the concentrations generally fall as the river proceeds northwards beyond the geothermal fields of Wairakai, Broadlands, and Orakei Korako.

The concentration of arsenic in Waikato River water at Hamilton ranges between 0.019 to 0.032mg/L (Aggett and Aspell, 1980). McLaren and Kim (1995) undertook a year long study of the arsenic concentration in the Waikato River at Hamilton, which found the mean concentration of arsenic of 0.0321 ± 0.0037mg/L. Both studies found that arsenic tended to be higher during summer months and Freeman (1985) reported that in spring and summer As (III) (which is the more toxic form of arsenic) often predominates. Freeman (1980) attributed the higher concentrations of arsenic to the action of *Anabaena oscillaroides*-bacteria, which are able to reduce arsenate (As (V) into the more toxic arsenite (As (III)). A review of the ranges of arsenic concentrations in natural water conducted by Smedley and Kinniburgh (2002) found that typical freshwater contained less than 0.010mg/L and frequently less than 0.001mg/L.

Groundwater in Central Otago can contain up to 0.1mg/L of arsenic due to high concentration of arsenopyrite in the Central Otago Schists (Caw et al, 2005) and land clearance activities in the Coromandel Peninsula are thought to be responsible for slightly elevated arsenic concentrations in the Firth of Thames (Environment Waikato, 2007a).

Anthropogenic activities such as timber treatment using CCA (copper, chromium and arsenic) preservatives, sheep dipping, tanneries, the use of arsenical pesticides and herbicides (such as lead arsenate, ortho and meta arsenite and methylarsinic acid) have also resulted in the release of arsenic into the environment. Other industries such as glass manufacturing, manufacturing of lead acid batteries, semi-conductor and pharmaceutical manufacturing are also a minor anthropogenic source of arsenic (USGS, 2007). Domestic and industrial waste landfills which contain treated wood and electronic wastes can result in leachate containing between 0.004 to 0.19mg/L in New Zealand (CAE, 2000). The combustion and disposal of coal ash is a significant anthropogenic source of arsenic in the environment in some countries (notably China), but New Zealand coals contain relativity low concentrations of arsenic (usually less than 20mg/kg) so are not thought to be such a significant environmental source (Moore, et al, 2005). The application of biosolids from waste water treatment plants can also result in elevated concentration of arsenic occurring in soils especially if the wastewater treatment plant receives wastewater from tanneries or timber treatment plants.

A survey of horticultural soils in 3 regions of New Zealand (Auckland, Tasman and Waikato) revealed elevated arsenic concentration ranging between <2 to 58mg/kg. The elevated concentrations of arsenic and other chemicals found in these soils were believed to be a result of the use of agrichemicals (Gaw et al, 2006).

1.8 Trace Elements in Urban Stormwater

Urban stormwater can contain a number of contaminants including copper, lead, zinc and organic compounds such as polycyclic aromatic hydrocarbons (PAHs), herbicides, pesticides and other hydrocarbon mixtures such as oil and grease. Fergusson et al (1980) found elevated concentrations of cadmium, copper, lead and zinc in roadside dust around Christchurch. Studies conducted by Harrison (1979) found elevated concentrations of cadmium, chromium, cobalt, copper, lead, nickel and zinc in roadside dust in the UK (see Table 1-1). Many of these contaminants are associated with motor vehicles.

Arsenic is not normally found in appreciable concentrations in stormwater unless the stormwater has come into contact with arsenic contaminated soils or arsenic has been used as an industrial chemical on the site (i.e. timber treatment yards or tanneries).

TABLE 1 - 1: CONCENTRATION OF SELECTED METALS IN ROADSIDE DUST IN THE UK.

Element	Concentration (mg/kg)
Pb	6630
Cd	7.0
Cr	37
Co	10
Ni	59
Cu	206
Zn	1600

In automobiles there are five main potential sources of contaminants to the urban stormwater system. These are summarised in Table 1.2 and below:

- Brake components – which contain various organic compounds and inorganic elements. Wear of brake components can give rise to deposition onto the road surface of a number of potential contaminants, typically in the form of fine particulate matter. The contaminants of potentially greatest significance are PAH, antimony, zinc, copper, lead, aluminium, manganese and iron. The concentration of antimony in some brake lining can reach concentrations in excess of 40,000mg/kg (Uexkull et al, 2005).

- Tyres – rubber contains various organic compounds and metals. During tyre wear, particles and pieces of rubber of various sizes are deposited on the road surface. Zinc, copper, lead, iron and PAHs are the most significant contaminants. (N. Haus, et al, 2007).

- Fuel, Oil, Grease and Lubricants – which are used in various components of a vehicle. During driving, these substances can be deposited on the road as a result of minor leaks and drips. Lubricating oils can contain vanadium, cadmium, copper, molybdenum and zinc. Fuel additives can include vanadium, cadmium, lead and zinc (N. Haus et al, 2007).

- Coolants and Radiator Fluid – which typically contain glycols, corrosion inhibitors and foam suppressors. Spillage to the road can occur through leaks and overflows, particularly in older and poorly maintained vehicles.
- Exhaust System Emissions – containing particulate matter, PAHs and metals. Rare earth elements such as platinum, palladium and iridium are used as catalytic converters to reduce the concentration of carbon monoxide in the exhaust, and these metals may be released into the environment via the exhaust system. Petroleum fuels also naturally contain some heavy metals (such as vanadium, etc) and these are released to the environment. Until 1996, tetra-ethyl lead was added to petrol as an anti-knocking agent, which was released into the environment as a result of vehicle exhaust emissions.

Stormwater from roads around Hamilton Lake may be a source of some trace elements to the lake, although impacts on sediments may be quite localised to the area immediately downstream of the stormwater discharge.

Table 1- 2: Contaminants in New Zealand stormwater (from Taylor et al. 2005).

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

1.9 Pollution incidents and Discharges into Hamilton Lake.

There are 45 known stormwater discharges (Environment Waikato, 2007) although most of these discharges are small and probably have had no significant effect on the lake sediment quality. Also there has been at least 4 occasions where pesticides have been applied directly into the lake or where accidental discharges could have resulted in the contamination of sediment within the lake. These are:

- Application of sodium arsenite to Lake Rotoroa in 1959 to control aquatic weed growth (Tanner and Clayton, 1990).
- A single aerial application of insecticide dieldrin in December 1960 (HCC, 2006).
- The application of diquat to the lake in 1970s to present day to control aquatic weed growth (Tanner and Clayton (1990), Clayton and De Winter (1994) and Nick Kim, pers. comms).
- The accidental discharge of aluminium to the lake in the 1990s as the result of cleaning cooling towers at Waikato Hospital (Nick Kim, pers. Comms.).

2.0 Study Methodology

Thirty-four surficial lake bed sediment samples were collected on 24 May 2007 from the main body of the lake. A distorted 130m x 130m grid was used to locate the sediment sampling sites to give a 95% confidence that a hotspot of greater than 150m diameter would be identified (see Figure 1). Grid sampling was undertaken to provide a detailed understanding of where contamination was present and to provide information on any spatial patterns occurring within the lake.

Distortion in the grid was allowed so that:

- no samples were located on the land,
- sampling would occur at least 10m from any stormwater outlet,
- good coverage was obtained of the near shore environment (10-20m from the bank) compared with the wider lake.

2.1 Sample Collection Methodology

2.1.1 Manual grab samples collection

Grab samples were taken from the upper 100mm of the lake bed as this zone (a) provides the greatest exposure to lake-dwelling organisms. A petite ponar sediment grab sampler was used to collect the sediment samples. This 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.

To ensure that grab samples were consistent and suitable for benthic sampling, the following criteria were utilised before the sample was accepted;

i. Sediment has not extruded from the sampler;

ii. Water was still present in the sampler (i.e. the grab remained closed during retrieval);

iii. Sediment surface is relatively flat; and,

iv. Appropriate sediment penetration has occurred (>100mm in silty sediments).

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[a] The upper 100mm of lake bed sediments have the most ecological importance because some epibenthic species (e.g. shrimps, certain amphipods) might only be exposed to surficial sediments (0-10mm)) while others (e.g. bivalves and polychaetes) can be exposed to sediments that are tens of millimetres deep.

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

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.

Field records were taken at each sampling location which included site identifier, site location (recorded by GPS with a precision of ± 15m RMS), depth of water column, time and date of sample collection, sample identifier and number.

All sampling equipment was rinsed and scrubbed clean with lake water between each sampling site.

2.1.2 Core Samples Collection

Core samples were obtained from five locations using a light weight open-barrel gravity corer obtained from Waikato University. A gravity corer was used to collect the samples to preserve any fine lamination in the core and to minimise the disturbance to the sediment-water interface. The gravity corer used was able to recover a maximum core length of 0.45m. The core was extruded using a piston extruder once the corer had been recovered on the boat and it was sub-sampled into 20mm sections (except at 40-50, 90-100, 140-150, 190-200, 240-250mm intervals where the core was sectioned into 10mm sections).

The core samples were collected from the following locations (see Figure 2):

- CS1 was collected in the southern area of the lake between sample location SDH007, SDH006 and SDH005 (NZMG 2710792 6375422). This core sample was collected in relatively deep water (approximately 4.8m). This location was chosen to represent a deep water area which had potentially been influenced by stormwater inputs from the adjacent urban area.

- CS2 was collected near the shore between SDH11 and SDH10. This area was selected as it did not have any known stormwater inputs within the immediate vicinity. The sample was collected at NZMG 27101792 6375422 with a water depth of 1.6m.

- CS3 was collected at the northern end of the lake near sampling location SDH 016. This sample was collected to characterise sediments near the shore which may be influenced by stormwater inputs (there are 4 stormwater drains within 30m of the sampling location). This sample was collected at NZMG 2710455 6376243, with a water depth of 1.6m.

- CS4 was collected at the north-western side of the lake between samples SDH019, SDH020, SDH021 and SDH023. This core sampling location was selected to represent the sediment quality in the northern shallow areas.

These areas are least influenced by stormwater inputs. This sample was collected at NZMS 2710204 6375925 in 1.5m of water.

- CS5 was collected from the centre of the lake near the location of grab samples SDH030, SDH031, SDH028 and SDH 029. This sample was collected at NZMS 2710513 6375663 in 1.7m of water. This core sampling location was selected to represent sediment quality within the central part of the lake.

2.1.3 Surface Water Samples Collection.

Surface water samples were collected from 4 locations on the lake on 24 May 2007. All water samples were collected 300mm beneath the lake surface. Water samples were collected from each of the following locations to represent surface water conditions throughout the lake:

- One water sample was collected from the southern portion of the lake (near SDH007),
- one water sample was collected from the central part of the lake (near SDH010),
- one water sample was collected from the northern part of the lake (near SDH019)
- one water sample was collected from near the outflow of the lake.

Once the water sample was collected, the depth of water, dissolved oxygen concentration, temperature, conductivity, pH and redox potential were measured at each water sample collection site. All physiochemical parameters were measured using a TPS 90-FLMV multi-parameter meter. Before use, the pH and conductivity probes were calibrated using NTIS (US National Technical Information Service-formerly known as the National Bureau of Standards) traceable calibration solutions supplied by Eutech instruments. The pH meter was calibrated against a pH 4.01 and pH 7.00 calibration solution and the conductivity probe was calibrated against a 1413 μS calibration solution.

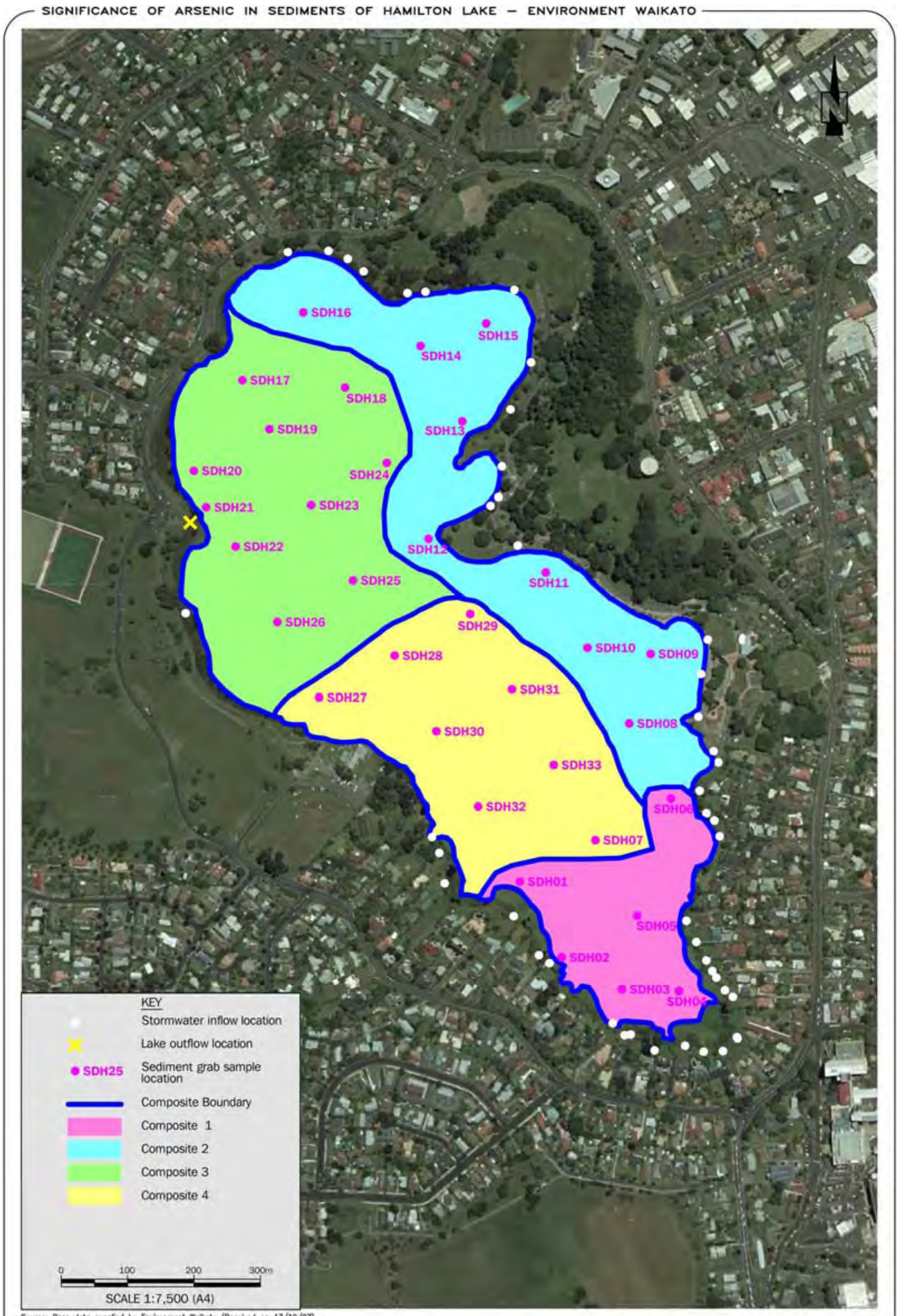
An additional water sample was collected from in front of the yachting/rowing club on 13 September 2007 using a mighty gripper. No physiochemical parameters were measured in the field with this sample; however, the sample was transported to the Hill Laboratory immediately after collection for analysis.

2.1.4 Sample Analysis

Once the sediment and water samples had been collected, they 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. An analysis was undertaken on the sub 2mm fraction of the sediments. Total recoverable arsenic, cadmium, chromium, copper, iron, mercury, nickel, lead, phosphorus and zinc were analysed on all samples.

Environment Waikato requested that four composite samples were prepared by the laboratory from the grab samples submitted. The composite samples were created to represent the different zones of the lake based upon PDP's understanding of the physical environment and the vicinity to stormwater inputs. The purpose of preparing the composite samples was to screen the samples for a wider range of analytical parameters to identify if there were any other contaminants which might be of environmental concern within the sediment, and which might warrant future study at a later date.

Figure 2: Sediment Composite Samples Locations



Source: Base data supplied by Environment Waikato (Received on 17/10/07)

Figure 2 : SEDIMENT COMPOSITE SAMPLES LOCATIONS

PATTLE DELAMORE PARTNERS LTD

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The rationale and the sub-samples that were used to prepare each composite sample, as shown in Figure 2, are listed below:

- Southern portion of the lake, which is heavily influenced by stormwater inputs. Grab samples SDH1-6 were composited together to prepare this sample (composite 1).
- Near shore environment influenced by stormwater. Grab samples SHD8-14 plus SDH 16 were composited together to prepare this sample (composite 2).
- Northern section of the lake. Grab samples SDH15 plus SDH17-25 were composited together to prepare this sample (composite 3).
- Central section of the lake. Grab samples SDH27- SDH33 plus SDH 7 were composited together to prepare this sample (composite 4).

These samples were analysed for an extended elements suite (33 elements to trace level (0.2mg/kg) using a total recoverable digestion as well as organo-chlorine pesticides and poly-aromatic hydrocarbons (PAHs) to screen level, and total organic carbon (TOC).

For each core sample, the sub-samples created from the sediment core were composited together into 50mm intervals by the laboratory. The subsamples were then analysed for total recoverable arsenic, cadmium, chromium, copper, iron, mercury, nickel, lead, phosphorus and zinc. Each individual sub-sample was placed into cold storage for further analyses if required.

The water samples (SWH001 to SWH004) were analysed in the laboratory for pH, conductivity, dissolved arsenic and dissolved lead. Water sample LRW001 was analysed in the laboratory for pH, conductivity and total and dissolved metals (arsenic, antimony, cadmium, chromium, copper, lead, mercury, and zinc).

2.1.5 Quality Assurance/Quality Control

A laboratory QA/QC report was requested from Hill laboratories to evaluate the procedural blanks, certified reference material values and duplicate sample analysis. To confirm the accuracy and reproducibility of the analysis a certified reference material prepared from river sediments (Agal-10) was analysed ten times. The QA/QC results are described in the Appendix D.

2.2 Use of ANZECC sediment quality guidelines

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

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

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

Concentrations between the ISQG-low and ISQG-high are thought to pose a moderate level of risk to aquatic organisms. Concentrations of trace elements or other chemicals either below or above the ANZECC (2000) trigger values should not be thought of as safe or unsafe, but rather posing a lower or higher level of risk. This is because site-specific factors such as the chemical form of compound or element (i.e. As (III) or As (V)), natural background concentration, the concentration of organic matter, iron oxides or reduced sulphide compounds can all modify the toxicity of a particular compound. A detailed site specific assessment has not been conducted as part of the assessment.

Values below the ISQG-low do not guarantee that the concentrations are safe either because complex chemical mixtures of certain compounds are more toxic than their individual chemical components and the ANZECC (2000) guidelines are not designed to protect against those mixtures. Also certain compounds such as mercury have specific chemical forms (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 are required to assess such risks. Therefore, the guidelines are designed to be trigger values to indicate which sites may warrant closer investigation.

It should also be noted that the ANZECC (2000) guidelines are designed to protect aquatic ecosystem rather than to protect human health. Although ISQG-low values are lower than equivalent soil quality guidelines designed to protect human health, no conclusion should be made on the potential human health risk. A detailed human health risk assessment is provided in Appendix G and discussed in Section 6. This should be referred to when determining human health risks.

3.0 Results

3.1 Raw results and summary statistics

Thirty-four grab samples were collected across Hamilton Lake on the 24 and 25 May 2007. The results of the analysis of these samples together with the sampling location and water depth are shown in Appendix C Table C-1 and Figure 1 shows the location of the sampling sites. A summary of results obtained at each sampling site is presented in Table 3-1.

The results of the analysis of the composite samples (created from the grab samples from different zones) for inorganic analytes and TOC are presented in Appendix C Table
C-2. Composited sample results for PAHs are presented in Appendix C Table C-3 and results for organo-chlorine pesticides (OCPs) are presented in Appendix C Table C-4.

Table 3 - 1: Summary of trace element concentrations at sampling sites and comparison to ANZECC (2000) sediment quality guidelines (all values in mg/kg dry weight).

	Mean	Min	Max	Std. Error	5% LCL	95% UCL	ISQG-low	ISQG-high
Arsenic	***170***	**25**	***592***	26.3	**38**	***548***	20	70
Cadmium	0.31	0.12	0.68	0.02	0.13	0.48	1.5	10
Chromium	11.3	5.2	23.1	0.6	6.0	16.5	80	370
Copper	32	11.6	**114**	3.1	14.3	45.5	65	270
Mercury	0.13	0.06	**0.32**	0.008	0.06	**0.21**	0.15	1
Nickel	6.3	3.3	8.4	0.2	3.5	8.2	21	52
Lead	**77.5**	10.4	***303***	10.2	14.2	**171.5**	50	220
Zinc	184	68.6	***613***	19.8	69.8	***440.8***	200	410
Iron	17535	9000	24300	697	9314	23695	-	-
Phosphorus	503	55	775	29	192	758	-	-

Note: Bold entries exceed ANZECC (2000) ISQG-Low values; the bold italic entry exceeds an ISQG-High value.

3.2 Core Samples

Five core samples were collected from various locations (See Section 2.1.2) and divided into various sub-samples depending on depth. Each sub sample was analysed for total recoverable metals as outlined in Section 2.1.4 and the results of the analysis as well as the location of the sample and water depth, are presented in Appendix C Table C-5.

The core samples were inspected upon recovery and found to consist of a uniform grey-black silty material with very low cohesion. There was no visual evidence of oxic/anoxic boundary within the sediment, nor was there any evidence of an iron pan layer. Most of the sediment cores appeared to have an indistinct water/sediment interface, with the overlaying water very murky with significant concentration of seston (suspended particulate matter). The exception to this was core sample 3 which had a very distinct water/sediment interface, with algae observed on the sediment surface.

At a depth of 10-15cm in core sample 4, a white pumice layer was observed. This pumice layer was tentatively identified as most likely being from the 186 AD Taupo eruption, which would indicate a very slow rate of sedimentation (approximately 0.05mm per year). This sedimentation rate is within the range reported by Green and Lowe (1994).

3.3 Surface Water Samples

Five surface water samples were collected from various locations of the lake (see Section 2.1.3) and the analytical results together with field measurements are presented in Appendix C Table C-6. The results of the analysis of the water quality suggests that the lake water is well mixed as there is little or no change in the concentration of arsenic and lead at the five sampling locations. The analytical results indicate that most of the metals are associated with the dissolved fraction (<0.45μm) rather than the particulate fraction (i.e. sorbed onto suspended solids).

3.4 Comparison with sediment quality guidelines

3.4.1 Grab Samples

To ascertain the potential ecological significance of the data collected from all the sites, the average concentrations for each trace element were divided by sediment quality guidelines, the ANZECC (2000) ISQG-low and ISQG-high (for more about which refer to Section 2.2). This gives a figure which demonstrates how many times greater (or lesser) than the average concentration of each element is compared to the guideline values. Results of the comparison of average concentrations with the ISQG-low and ISQG-high are provided in Table 3-2, together with the number of samples where concentrations were higher than the ANZECC (2000) ISQG-low and ISQG-high guideline values.

TABLE 3 - 2: SUMMARY OF RESULTS EXPRESSED AS THE NUMBER OF SAMPLES ABOVE ISQG-LOW AND ISQG-HIGH AS WELL AS A FRACTION OF ISQG-LOW AND ISQG-HIGH.

	Average (mg/kg)	Number of Samples Above $ISQG_{low}$ (n=34)	Number of samples Above $ISQG_{High}$ (N=34)	Fraction of $ISQG_{low}$	Fraction of $ISQG_{high}$
Arsenic	167.5	34	25	8.4	2.4
Cadmium	0.3	0	0	0.20	0.03
Chromium	11.2	0	0	0.14	0.03
Copper	31.7	1	0	0.49	0.12
Mercury	0.13	5	0	0.86	0.13
Nickel	6.3	0	0	0.30	0.12
Lead	76.5	19	1	1.5	0.35
Zinc	181.8	12	2	0.91	0.44

Five elements (arsenic, copper, mercury, lead and zinc) exceeded the lowest sediment quality guideline value (the ANZECC (2000) ISQG-low) at some locations (Tables 3-1 and 3-2). However, only arsenic, lead and zinc exceeded the highest sediment quality guideline value (the ANZECC (2000) ISQG-high) at some locations.

- Arsenic concentrations exceeded the ANZECC (2000) ISQG-low at all 34 sampling sites and exceeded the ANZECC (2000) ISQG-high concentration at 73% of the sampling locations. Arsenic averaged 8.4 times the ANZECC (2000) ISQG-low (20mg/kg) and 2.4 times the ISQG-high (70mg/kg) guidelines.

- Copper concentrations exceeded the ANZECC (2000) ISQG-low only at one sampling site and there were no exceedances of the ANZECC (2000) ISQG-high at any of the sampling sites. Copper averaged approximately 50% of the ANZECC (2000) ISQG-low (65mg/kg) and only 10% of the ISQG-high guideline value.

- Mercury concentrations exceeded the ANZECC (2000) ISQG-low at five sampling locations but do not exceed ANZECC (2000) ISQG-high at any sampling sites. The average mercury concentration was 86% of the ANZECC (2000) ISQG-low (0.15mg/kg) and only 13% of the ANZECC (2000) ISQG-high (1mg/kg) guideline value.

- Lead concentrations exceeded the ANZECC (2000) ISQG-low at 19 sampling sites and exceeded the ANZECC (2000) ISQG-high value at one sampling site (southern end of the lake). The average lead concentration is 1.5 times the ANZECC (2000) ISQG-low (50mg/kg) and 35% of the ANZECC (2000) ISQG-high (220mg/kg) value. The highest lead concentrations were found in the southern part of the lake.

- Zinc concentrations exceeded the ANZECC (2000) ISQG-low at 12 sampling sites and exceeded the ANZECC (2000) ISQG-high value at two sampling site (southern end of the lake). The average zinc concentration is 91% of the ANZECC (2000) ISQG-low (200mg/kg) and 44% of the ANZECC (2000) ISQG-high (410mg/kg) value. The highest zinc concentrations tend to occur in the southern part of the lake.

3.4.2 Composite Samples

The multi-element scan of the composite samples revealed that the concentration of lead exceeds the ANZECC (2000) ISQG-low guideline value in all of the composite samples and the concentration of antimony exceeded the ANZECC (2000) ISQG-low guideline value in composite sample 1, 2 and 3. Concentration of zinc also exceeded the ANZECC (2000) ISQG-low guideline value in composite sample 1 and the concentration of copper was elevated in this sample. The concentration of PAHs in composite sample 2 was elevated. No organochlorine pesticides were detected in any of the composite samples. Arsenic exceeded the ISQG-high guideline value in all composite samples.

To compare polycyclic aromatic hydrocarbons (PAHs) results with the ANZECC (2000) ISQG-low and ISQG-high values, the results need to be normalised to 1% total organic carbon to remove the influence that variation in organic carbon content has on the concentration of organic compounds such as PAHs. The ANZECC sediment quality guidelines recommend that all hydrophobic organic compounds are normalised to 1% total organic content to facilitate comparison to sediment quality guidelines.

Organic carbon normalisation was conducted according to the procedure recommended by the Washington Department of Ecology (2002) and the organic normalised data together with the ANZECC ISQG guideline values are presented in Table 3-3.

Many of the individual PAHs compounds measured in the composite samples were present in concentrations less than the detection limit of the analytical method. Therefore to calculate low and high molecular weight PAHs as well as total PAHs, half the value of the analytical detection was used in the calculation when the concentration of a particular compound was below the analytical detection limit.

Although the detection limit of the individual compounds is below the ANZECC (2000) sediment guidelines values, the aggregate sum of the detection limits using the method described above was above the ANZECC (2000) ISQG-low guideline value for low molecular weight PAHs as shown in Table 3-3. Therefore, no conclusion can be made as whether the sum of the low molecular weight PAHs complies or does not comply with the ANZECC (2000) guideline value.

TABLE 3 - 3: CONCENTRATION OF POLY-NUCLEAR AROMATIC HYDROCARBONS (PAHS) MEASURED IN COMPOSITE SAMPLES.

Sample Name:	**Composite 1**	**Composite 2**	**Composite 3**	**Composite 4**	**ANZECC ISQG-low**	**ANZECC ISQG-high**
Units:	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Dry Matter	16.5	19.2	13.4	15.9		
TOC	11.6	9.27	11.5	10.7		
Organic Carbon	1.42	2.07	1.17	1.49		
Acenaphthene	<1.72	<1.08	<1.72	<1.72	0.016	0.500
Acenaphthylene	<1.72	<1.08	<1.72	<1.72	0.044	0.640
Anthracene	<1.72	<1.08	<1.72	<1.72	0.085	1.100
Benzo[a]anthracene	<1.72	***3.24***	<1.72	<1.72	0.261	0.540
Benzo[a]pyrene (BAP)	<1.72	***7.55***	<1.72	<1.72	0.430	2.100
Benzo[b]fluoranthene	<1.72	10.79	<1.72	<1.72		
Benzo[g,h,i]perylene	<1.72	6.47	<1.72	<1.72		
Benzo[k]fluoranthene	<1.72	8.63	<1.72	<1.72		
Chrysene	<1.72	***5.39***	<1.72	<1.72	0.384	2.800
Dibenzo[a,h]anthracene	<1.72	<1.08	<1.72	<1.72	0.063	0.260
Fluoranthene	<1.72	***11.87***	<1.72	<1.72	0.600	5.100
Fluorene	<1.72	<1.08	<1.72	<1.72	0.019	0.540
Indeno[1,2,3-c,d]pyrene	<1.72	0.03	<1.72	<1.72		
Naphthalene	<6.90	<2.16	<7.83	<7.48	0.160	2.100
Phenanthrene	<1.72	0.02	<1.72	<1.72	0.240	1.500
Pyrene	1.72	***15.10***	0.02	<0.019	0.665	2.600
low MW PAH	<7.76	***7.55***	<8.26	<8.41	0.552	3.160
High MW PAH	<6.03	***54.48***	<6.09	<6.54	1.700	9.600
Total PAH	<13.79	***62.03***	<14.35	<14.95	4.400	45.000

Note: The concentrations have been normalised to 1% organic carbon for comparison to ANZECC (2000) sediment quality guidelines. Bold entries exceed ANZECC (2000) ISQG-Low values; the bold italic entry exceeds an ISQG-High value.

The organic carbon normalisation procedure has made it difficult to compare the PAH results with the ANZECC (2000) sediment guidelines values because after normalisation the analytical detection limit has become higher than the ISQG-low guideline value. However, in examining the data from composite sample 2 (which comprises sediments from near the eastern shore of the lake), the sum of high molecular weight and total PAHs exceed both the ANZECC (2000) ISQG-low and ISQG-high guidelines values. An examination of the raw laboratory results (see Appendix C Table C-3) shows that the non-normalised PAH results for composite sample 2 exceed ISQG-low for the same compounds as identified using the organic carbon normalised data, as well the ISQG-low guidelines values for the sum of high molecular weight and total PAHs. From this data it can be inferred that the concentration of PAHs is elevated around the eastern shore of the lake.

3.4.3 Sediment Cores

The most ecological significant fraction of the sediment cores is the samples collected from 0-2cm, 2-10cm (Simpson et al, 2005). This is because the sediments within the 0-2cm depth interval are the sediments which most surface dwelling (epi-benthic) organisms come in contact with. The sediments within the 0-10cm depth intervals are the typical depth interval that most burrowing organisms and shallow rooted plants come in contact with. Roots in deeper rooting plants can penetrate down to 0.5m, but a majority of aquatic plants roots do not penetrate this far into the sediments.

Therefore to ascertain the potential ecological significance of the data collected from sediment cores, the data from all of the sediment cores has been grouped into 3 depth intervals 0-2cm, 2-10cm, greater than 10cm. The average concentration for each trace element in each depth grouping was then divided by the sediment quality guidelines, the ANZECC (2000) ISQG-Low and ISQG-High. Results of the comparison of average concentrations with the ANZECC (2000) ISQG-Low and ISQG-High are provided in
Table 3-4, together with the number of samples with concentration higher than the ANZECC (2000) ISQG-Low and ISQG-High guideline values.

TABLE 3 - 4: SUMMARY STATISTICS OF CONCENTRATION OF TRACE ELEMENTS IN SEDIMENT CORE SAMPLES.

Element	Depth (cm)	Average	Number above ISQG-low	Number above ISQG-high	Fraction of ISQG-low	Fraction of ISQG-high
As	0-2	378.6	5 (5)	5 (5)	18.93	5.41
	2-10	111.5	24 (32)	16(32)	5.57	1.59
	10+	208.2	4(6)	3(6)	10.41	2.97
Cd	0-2	0.3	0(5)	0(5)	0.22	0.03
	2-10	0.3	0(32)	0(32)	0.20	0.03
	10+	0.3	0(6)	0(6)	0.19	0.03
Cr	0-2	13.5	0(5)	0(5)	0.17	0.04
	2-10	11.7	0(32)	0(32)	0.15	0.03
	10+	10.6	0(6)	0(6)	0.13	0.03

Cu	0-2	44.2	0(5)	0(5)	0.68	0.16
	2-10	35.4	0(32)	0(32)	0.55	0.13
	10+	27.4	0(6)	0(6)	0.42	0.10
Hg	0-2	0.14	1(5)	0(5)	0.92	0.14

Note: The value in brackets refers to the total number of samples collected in this depth grouping.

Table 3 - 4: Summary statistics of concentration of trace elements in sediment core samples (continued).

Element	**Depth (cm)**	**Average**	**Number above ISQG-low**	**Number above ISQG-high**	**Fraction of ISQG-low**	**Fraction of ISQG-high**
	2-10	0.11	2(32)	0(32)	0.75	0.11
	10+	0.1	0(6)	0(6)	0.71	0.11
Ni	0-2	7.4	0(5)	0(5)	0.35	0.14
	2-10	6.6	0(32)	0(32)	0.31	0.13
	10+	6.7	0(6)	0(6)	0.32	0.13
Pb	0-2	89.1	5(5)	0(5)	1.78	0.41
	2-10	65.9	13(32)	0(32)	1.32	0.30
	10+	50.0	3(6)	0(6)	1.00	0.23
Zn	0-2	231.2	4(5)	0(5)	1.16	0.58
	2-10	187.6	10(32)	0(32)	0.94	0.46
	10+	132.0	1(6)	0(6)	0.66	0.32

Note: The value in brackets refers to the total number of samples collected in this depth grouping.

Based on the data shown in Table 3-4, the following comments can be made.

- Arsenic concentrations exceeded the ISQG-low in most of the samples (except two samples collected at 15 cm depths in core samples CS4 and CS5) and exceeded the ANZECC (2000) ISQG-high concentration in all of the 0-2 cm cores.

- Arsenic averaged 18.9 times the ISQG-low (20mg/kg) and 5.4 times the ANZECC (2000) ISQG-high (70mg/kg) in the 0-2cm samples.

- The average concentration of arsenic decreases in most of the samples between 2-10cm except in CS3 where there was a significant increase in arsenic concentrations in samples collected from greater than 5cm.

- There was a significant variability in concentration of arsenic between the different cores. Concentration of arsenic in core samples CS4 and CS5 was generally lower than the concentration of the arsenic found in the other cores at a specific depth. The concentration of arsenic in cores (CS4 and CS5) ranged between 17.7 to 0.7 times the ANZECC (2000) ISQG-low guideline values.

- At all specific depths the concentration of arsenic was the greatest in sediment core CS3. The arsenic concentrations found in CS3 ranged between 7.8 to 60 times the ANZECC (2000) ISQG-low guidelines, with the highest concentration (1190mg/kg) occurring in a sample collected from a depth of 7-9cm below the surface.

- Copper concentrations exceeded the ANZECC (2000) ISQG-low only at one sampling site (at 2-10cm) and there were no exceedances of the ANZECC (2000) ISQG-high at any of the sampling sites at any depth. Concentration of copper decreased with depth in all of the core samples. Average copper concentrations decreased with depth from approximately 68% of the ANZECC (2000) ISQG-low and only 16% of the ISQG-high value in samples collected within 0-2m of the surface to 42% of the ANZECC (2000) ISQG-low (65mg/kg) and only 10% of the ISQG-high value in samples collected at depths greater than 0.1m.

- Mercury concentrations exceeded the ISQG-low in three samples (1 collected at 0-2cm and two collected between 2-10cm), but did not exceed ANZECC (2000) ISQG-high in any of the samples. The average mercury concentration was 86% of the ANZECC (2000) ISQG-low (0.15mg/kg) and only 13% of the ANZECC (2000) ISQG-high (1mg/kg) value at all the depth ranges examined. The concentration of mercury generally decreased with depth but there was little variation in concentration of mercury in any of the samples.

- Lead concentrations exceeded the ANZECC (2000) ISQG-low guidelines values in all of the surface samples and over half of the samples collected from between 2-10cm below the surface. The average lead concentration in the samples from 0-2cm is 1.78 times the ANZECC (2000) ISQG-low (50mg/kg) and 58% of the ANZECC (2000) ISQG-high (220mg/kg). This decreases to 1.00 times the ISQG-low guideline value in samples collected below 10cm.

- Zinc concentrations exceeded the ANZECC (2000) ISQG-low in most of the samples collected in the surface sediment samples and slightly less than half of the samples collected 2-10cm below the lake bed. The average zinc concentration in the samples collected from 0-2cm is 1.16 times the ANZECC (2000) ISQG-low (200mg/kg) and 44% of the ANZECC (2000) ISQG-high (410mg/kg) value. The concentration of zinc decreases with depth below the lake bed in all of the cores and samples collected from below 10cm from the lake bed are 66% of the ANZECC (2000) ISQG-low and 32% of the ISQG-high guideline value.

- Cadmium, chromium and nickel concentrations were less than 25% of the ANZECC (2000) ISQG-low concentrations in all of the samples and the concentrations of these elements decreased with depth.

3.4.4 Water Samples

The concentration of total and dissolved metal found in the surface water samples are all below the ANZECC (2000) fresh water trigger values for 95% ecosystem protection and below drinking water guidelines. The concentration of total and dissolved arsenic in the water samples is lower than the average concentration in the Waikato River of 32 µg/L reported by Kim and McLaren (1990). In the water sample collected on 13 September 2007, almost all of the metals present in the surface water of the lake are associated with the dissolved phase (<0.45 µm). The concentrations of metals analysed in the surface water samples are very similar at all the sampling locations, which indicates that the surface waters are generally well mixed.

3.5 Key findings

- Arsenic concentrations within the sediments of the lake are highly elevated and exceed ANZECC (2000) ISQG-high guideline value in most sampling locations to a depth of at least 10cm. The concentration of arsenic exceeded the ANZECC (2000) ISQG-high guideline values in all of the composite samples.

- The concentration of copper, lead and zinc, which are commonly associated with stormwater discharges, exceeded the ANZECC (2000) ISQG-low guideline values in some locations. The highest concentrations of these elements tended to be in the southern portion of the lake where numerous stormwater discharges into the lake are located. In the case of lead and zinc several samples exceeded the ANZECC (2000) ISQG-high guideline values.

- Antimony exceeded the ANZECC (2000) ISQG-low guideline value in composite samples 1, 2 and 3.

- The concentrations of several PAHs (mainly high molecular weight PAHs) exceed several ANZECC (2000) ISQG-low guideline values including those for high molecular weight PAHs and total PAHs in composite sample 2. When the influence of organic carbon in the sediment is taken into account then these values also exceed ANZECC (2000) ISQG-high guideline values.

- The concentration of both dissolved and total metals within the lake water are below relevant ANZECC (2000) fresh water trigger values for 95% ecosystem protection and NZ Drinking Water Standards (2005). The majority of the metals present within the lake surface waters are associated with the dissolved phase, with the exception of lead; of which more than 60% is associated with suspended particulate material.

- The concentration of all elements is generally greater in sediments collected at the surface of the lake bed and decreases in sediments collected at greater depths.

4.0 Comparison with other Data

4.1 Comparison with Historical Data for Hamilton Lake

Two other surveys of the sediment quality of Hamilton Lake were identified in the literature review as part of this project. The first was a sediments survey undertaken by Ministry of Agriculture and Fisheries in 1983, approximately 24 years after the application of sodium arsenite herbicide (Tanner and Clayton, 1990). As part of this study, 4 sediment cores were collected by SCUBA divers to a maximum depth of 0.3m below the surface of the lake bed at the sampling locations shown on Figure 3. These sediment samples were then subdivided into 0.15m sections for digestion using a dilute acid digests (5:2 $HNO_3/HClO_4$). Tanner and Clayton (1990) found concentrations of arsenic in the sediments of Lake Rotoroa between 540-780mg/kg in the top 15cm of the sediments (see Table 4.1). The concentration of arsenic found during this survey was approximately 20 times higher than those found in the nearby Lake Rotokauri in the sediments in the upper 0.15m in both lakes, and Hamilton Lake sediments collected from 0.15-0.3m approximately 5 times higher than those collected from Lake Rotokauri over the same sampling interval. No other metals were measured as part of this survey.

Direct comparison of the results obtained by Tanner and Clayton and the findings of concentrations of arsenic measured in the sediments in this investigation is difficult as different digestion techniques were used to liberate the arsenic from the sediments in each investigation and different sampling intervals were used. However, over the upper 0.15m in the 5 core samples collected in this survey the concentration of arsenic ranged from 100 to 583mg/kg dry weight, which is between 1.4 to 7.8 times less than the concentrations reported by Tanner and Clayton. The use of $HClO_4$ in the acid digestion by Tanner and Clayton would be more effective at liberating arsenic bound to organic matter (and the sediments in Hamilton lake have a high organic carbon content), the differences in digestions techniques are unlikely to account for more than a 50% variation in the concentration of arsenic in the two studies.

It should not be concluded that since 1983 the concentration of arsenic has decreased by a factor of 2 to 8 times as there is significant spatial variability in the concentration of arsenic in the surficial sediments and differences in the analytical techniques employed.

It is even more difficult to compare the concentration of arsenic in the deeper sediments from the two studies as this current study only analysed sediment to a depth of 0.2m below the lake bed as opposed to Tanner and Clayton study in which sediments up to 0.3m below the lake bed were examined.

TABLE 4 - 1: CONCENTRATION OF ARSENIC OF SEDIMENTS IN LAKE ROTOROA (HAMILTON LAKE) AND LAKE ROTOKAURI (APRIL-JUNE 1983) (FROM TANNER AND CLAYTON, 1990)

Sediments	**0-0.15 M**	**0.15-0.30 M**
Lake Rotoroa (water depth**)**		
Site 1 (2m)	640	160
Site 2 (4.5m)	560	120
Site 3 (2m)	540	700
Site 4 (5.5m)	780	100
Lake Rotokauri (water depth)		
Site 5 (2 m)	40	26

Note: Concentration of arsenic reported in mg/kg dry wt.

Figure 3: Sediment Sampling Locations of Other Studies

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE – ENVIRONMENT WAIKATO

Source: Base data supplied by Environment Waikato (Received on 17/10/07)

Figure 3 : SEDIMENT SAMPLING LOCATIONS OF OTHER STUDIES

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The second survey of sediment quality of Hamilton Lake was undertaken by Gordon Rajendram in 1991 (G. Rajendram, 1992). The objective of Gordon Rajendram's study was to determine the major sources and areas of contamination within the lake and to investigate the role of metals in the decline of submerged vegetation in the lake. In this study, 94 surficial (0-0.05m) sediments samples were collected along seven transects which extend up to 200m from a stormwater input. The study found that Cu and Pb concentrations reached maxima close to the stormwater drains and then dissipated logarithmically with distance from the source (Rajendram, 1994). A similar trend was seen with zinc, except that zinc showed a uniform decrease with distance from the source. Arsenic concentrations appeared to be elevated across the lake, but appeared to increase with increasing water depth. This study also found that extensive areas of the southern sector of the lake had highly elevated metals concentrations presumably due to the high number of major stormwater inflows in this part of the lake.

Comparing the average concentration of elements in surficial sediments between Gordon Rajendram's and the current study reveals that there is a significant difference in the concentration of elements typically associated with stormwater discharges (i.e. Cr, Cu, Ni, Pb and Zn) (see Table 4-1 and Table 4-2). The average concentrations of these metals are between 2 and 4 times higher in Gordon Rajendram's survey than the concentrations found during this study. These differences are probably due to the differences in sampling methodology. In Gordon Rajendram's study, sediment samples were collected within 2, 5, 10 and 20m of major stormwater inflows, whereas in this study no sediment samples were collected within 20m of any stormwater inflow and a majority of sediment samples were collected from distances greater than 200m from the stormwater inflows.

TABLE 4 - 2: CONCENTRATION OF TOTAL RECOVERABLE METALS AND METALLOIDS IN SEDIMENTS OF 3 WAIKATO LAKES.

Element	Lake Rotoroa (n=96)	Lake Rotokauri (n=10)	Lake Waahi (n=1)	Current Study (Average)
As	192 (12-900)	10 (6-13)	9	167.5
Cd	0.27 (<0.06-0.87)	1.19 (0.19-2.77)	<0.06	0.3
Cr	36.4 (10-120)	15 (9.6-17)	36	11.2
Cu	78 (16-640)	21 (13-26)	17	31.7
Hg	0.19 (0.02-0.78)	0.24 (0.21-0.27)	0.5	0.13
Ni	11.4 (2.8-78)	7.0 (3.5-2.77)	15	6.3
Pb	292 (12 -2800)	19 (8.8-40)	19	76.5
Zn	310 (68-1120)	216 (80-308)	122	181.8
Fe	2.6 (1.0-6.8)	2.9 (1.3-5.1)	3.7	1.8
Mn	415 (126-2504)	574 (306-880)	913	-

N = number of samples collected.

Note: Concentration of all elements reported in mg/kg dry weight except Fe which is *reported in % dry weight. The range of the analytical results is denoted in brackets.*

The average concentration of arsenic in surficial sediments found by Gordon Rajendram's study and in this current study is statistically identical, which indicates that there has been no significant change in the concentration of arsenic in the surface sediments over the last 16 years. This is in contrast with the results obtained by Tanner and Clayton (which were collected 8 years before Gordon Rajendram's study and 24 years before this study), which are significantly different from the two more recent studies. If the differences between the three studies had been caused by actual changes in the concentration of arsenic in the surficial sediments then a consistent change in arsenic concentration over time would be expected. However this was not observed. It is likely that the small number of samples collected by Tanner and Clayton do not accurately reflect the average concentration in arsenic in the surficial sediments in 1983.

4.1.1 Comparison of Water Quality Data with Previous Studies

Gordon Rajendram collected monthly water samples from 8 sampling sites around Hamilton Lake between 29 September 1990 and 30 September 1991. A summary of his data is provided below in Table 4-3 and a full set of the data is presented in Table F-1 in Appendix F. The results of his study showed that the concentration of most parameters examined were similar between the three sampling sites in the main body of the lake (northern basin, southern basin and outflow). Generally, the arsenic concentrations are lower than the NZ Drinking Water Standards (2005), however, exceedance of the drinking water standards maximum acceptable value for arsenic does periodically occur during the spring and summer periods.

This is consistent with the results that were obtained in this study. The concentration of arsenic measured in the lake water in this study was within the range of arsenic concentrations measured by Gordon Rajendram. However, Gordon Rajendram measured total arsenic where this study measured mainly dissolved arsenic. In the one sample collected in this study where both dissolved and total arsenic was measured it was found that almost all of the arsenic was associated with the dissolved phase.

The concentration of arsenic in Gordon Rajendram's study appears to be higher during spring and summer months, which is similar to the trend observed in the arsenic concentration observed in the Waikato River.

The concentrations of all other metals measured in this study were either less than or at the lower end of the concentration range found by Gordon Rajendram.

TABLE 4 - 3: CONCENTRATION OF TOTAL RECOVERABLE METALS IN SURFACE WATERS AND STORM WATER INFLOWS TO HAMILTON LAKE AND LAKE ROTOKAURI AS MEASURED BY GORDON RAJENDRAM BETWEEN SEPTEMBER 1990 - SEPTEMBER 1991

	Hamilton Lake	**Hamilton Lake Inflows**	**Lake Rotokauri**	**ANZECC(2000)**	**NZ Drinking Water Standards (2005)**
pH	7.0 (6.6-7.3)	6.9 (3.9-8.0)	6.7		

As	7 (3-15)	0.5 (<1-35)	<1	24/13[a]	10
Pb	3 (1-9)	(1-275)	2	3.4	10
Zn	(<10-30)	(<10-2300)	<10	8	1500[b]

Note: The concentration of all elements is μg/L and pH is in pH units.

Table 4 - 3: Concentration of Total Recoverable Metals in Surface Waters and Storm water inflows to Hamilton Lake and Lake Rotokauri as Measured by Gordon Rajendram between September 1990 - September 1991 (continued)

	Hamilton Lake	**Hamilton Lake Inflows**	**Lake Rotokauri**	**ANZECC(2000)**	**NZ Drinking Water Standards (2005)**
Cu	<1	(<10-2060)	<10	1.4	2000
Fe	(60-0.760)	(60-5400)	1010	ID	200[c]
Cd	0.5 (<0.1-1.9)	(<0.1-2.5)	0.5	0.2	4
Mn	(<100-180)	(<10-600)	380	1900	40[c]

Note: The concentration of all elements is μg/L and pH is in pH units.

[a] The ANZECC (2000) freshwater guidelines for 95% ecosystem protection have two guideline values for arsenic, which depends on the chemical speciation of the arsenic compounds being measured. The first guideline value is for arsenic (III) which is the less toxic arsenic species and the second guideline is for arsenic (V) which is more toxic to aquatic species.

[b] No Health based NZ Drinking Water Standard exists for these elements. Instead the New Zealand Ministry for Health has set guideline values to prevent aesthetic (i.e. taste, odour or staining of laundry) impacts.

An equilibrium partitioning co-efficient (K_d) can be derived for arsenic in the sediments by dividing the average concentration of arsenic in the sediments (in mg/kg) by the average concentration of arsenic in the overlaying water (in mg/L). This gives a K_d of 24,000 (or a log K_d of 4.38), which implies that only about 0.004% of the arsenic is released from the sediments into the overlaying waters. Care needs to be taken with this figure as equilibrium partitioning theory was derived principally to determine the toxicity of sediments by the influence they have on the porewaters that they are in contact with. The theory is based on the assumption that the concentration is in equilibrium (which is unlikely because of the influence that biological activity (i.e. Anabaena-bacteria) has on the distribution of arsenic). Also, no studies have been done to date on the effectiveness of mixing of bottom and surface water in the lake. It is possible that the concentration of arsenic could be much higher in water immediately in contact with sediments in the bottom of the two basins within the lake and it is considered likely that the concentration of arsenic in the porewaters of the sediments are several orders of magnitude higher than those in the surface water. Further work needs to be conducted to determine the vertical gradient of arsenic down the water column and within the porewaters, and to determine the seasonal fluctuation in arsenic in both the surface and bottom waters of the lake.

The US EPA (Allison and Allison, 2005) recommends using an equilibrium partitioning co-efficient of approximately 250 (log Kd of 2.4 L/kg) for arsenic, which indicates that the theoretical concentration of arsenic within the porewaters could be as high as 2mg/L (or 2,000mg/m^3).

4.2 Comparison with Sediment Quality in Other Waikato Lakes.

To determine if elements in sediments within Hamilton Lake have been significantly enriched above the background concentration, enrichment ratios for each element have been calculated using sediment quality data of rural lakes collected by Environment Waikato as de facto background concentrations. This assumes that the sediment quality in rural lakes has not been significantly impacted by anthropogenic activities. This assumption may not be valid for metals such as cadmium, fluoride and uranium where there may be significant agricultural impacts on the lake sediment quality due to use of fertilisers. Many of the rural lakes sediments sampled by Environment Waikato appear to be significantly elevated in zinc due to agricultural inputs. Based on soil and sediment data collected in the Environment Waikato State of the Environment Monitoring programmes, Environment Waikato estimates that the background concentration of zinc in soils and sediments is approximately 35mg/kg rather than 118mg/kg, which is the average rural lake concentration.

As part of the Environment Waikato sediment sampling programme (Environment Waikato, unpublished data), sediment grab samples were collected from 11 lakes within the Waikato region. The results of the Environment Waikato sampling programme are shown in Table F-5 in Appendix F. The results of the sampling programme show that the concentration of most elements (except for mercury in several of the lakes and arsenic, lead and zinc in Lake Te Koutu) are generally below the ANZECC (2000) ISQG-low guideline values.

The elevated mercury concentrations found in Lake Waikare are due to geothermal inputs. Although elevated arsenic concentrations can be due to geothermal inputs, the elevated arsenic concentrations in Lake Waikare may be due to stormwater inputs from timber treatment sites (Environment Waikato, Unpublished data). Elevated lead and zinc concentrations found in Lake Te Koutu are mainly due to urban stormwater inputs as this lake is located in urban Cambridge. As the sediment quality in both of these lakes is unlikely to represent the sediment “background” concentration of Hamilton Lake, the data from these lakes was not included in calculating the average background concentration used to calculate the enrichment factor.

Table F-6 in Appendix F shows the minimum, average and maximum concentration of elements in the sediments of rural lakes within the Waikato region and Hamilton Lake as well as the average concentration of elements found in Waikato soils. A low, average and high enrichment factor has been calculated using the minimum, average and maximum concentrations of the specific elements in the rural lakes and Hamilton Lake.

Elements with an enrichment factor of less than 1 indicate that the concentration of the element is depleted with respect to the typical concentration of that element in other Waikato rural lakes. Elements with an enrichment factor of greater than 1 indicates that the concentration of that element is enriched with respect to the typical concentration of that element in other Waikato rural lakes. Elements which have an enrichment factor of greater than 2 are considered to be significantly enriched in that element. Those elements which have an enrichment factor of less than 0.5 are considered to be significantly depleted in that element. A summary of the enrichment factors are presented in Table 4-4.

TABLE 4 - 4: COMPARISON OF SELECTED ELEMENTAL DATA WAIKATO LAKE SEDIMENT DATA WITH SEDIMENT QUALITY DATA FROM HAMILTON LAKE (LAKE ROTOROA)

Element	Minimum Rural Lake Range	Average Rural Lake Concentration	Maximum Rural Lake Range	Minimum Hamilton Lake	Average Hamilton Lake	Maximum Hamilton Lake	Enrichment Factor-low	Enrichment Factor-Typical	Enrichment Factor-High
P	414	838	1280	55	503	775	0.07	0.60	0.93
Fe	8020	24428	38900	9000	17535	24300	0.37	0.72	0.99
Mn	100	717	1710	358	379	411	0.50	0.53	0.57
Ag	0.07	0.1	0.17	0.2	0.2	0.22	1.95	**2.07**	**2.15**
Al	14900	22325	34600	43300	47575	51300	1.94	**2.13**	**2.30**
As	2.3	5.6	12.3	25	167	592	**4.45**	**29.84**	**105.48**
Cd	0.19	0.4	0.69	0.12	0.31	0.68	0.28	0.72	1.59
Co	3.8	10	16.9	11.6	12.83	13.4	1.12	1.24	1.29
Cr	4.8	7.6	11.3	5.2	11.21	23.1	0.68	1.47	**3.03**
Cs	0.39	1.9	5.26	2.61	3.06	3.86	1.35	1.58	1.99
Cu	13	17	19.2	11.6	31.7	114	0.69	1.89	**6.79**
Hg	0.10	0.14	0.19	0.06	0.13	0.32	0.44	0.94	**2.35**
La	8.85	17	27.1	22.2	26.23	29.1	1.30	1.54	1.71
Mo	0.32	0.6	0.9	0.87	0.94	1.03	1.42	1.53	1.69
Ni	2.5	7.0	14.8	3.3	6.26	8.4	0.47	0.90	1.21
Pb	13.5	28	82.6	10.4	76.5	303	0.37	**2.72**	**10.77**
Sb	0.14	0.3	0.65	1.74	2.15	2.46	**5.19**	**6.41**	**7.34**
Se	2	2.0	2	2	2.75	3	1.00	1.38	1.50
Sn	0.6	1.1	2	3.2	3.93	5.2	**2.98**	**3.65**	**4.84**
Tl	0.13	0.4	0.76	0.48	0.5	0.52	1.28	1.34	1.39
V	26	38	57	55	63	67	1.45	1.82	1.76
Zn	40.2	118	180	68.6	182	613	0.58	1.54	**5.19**

Note: All concentrations are in mg/kg dry weight.

The enrichment ratio calculated for the elements examined in sediment of Hamilton Lake reveals that:

- The arsenic concentration in the sediment is significantly enriched, with enrichment factors ranging between 4.5 to 105 times the typical concentrations found in rural lakes around the Waikato region. Generally the arsenic concentration exceeds ANZECC (2000) ISQG-high guideline values.

- The concentration of antimony is significantly enriched within the Hamilton Lake sediments, with enrichment factors between 5.2 to 7.3 times those found in rural lakes around the Waikato region. The concentration of antimony exceeds ANZECC (2000) ISQG-low values within the southern portion of the lake. Antimony is a known contaminant found in stormwater run-off from roads.

- The concentration of tin is significantly enriched within Hamilton Lake sediments, with enrichment factors between 3 to 4.8 times those found in rural lakes around the Waikato region. There are no ANZECC sediment quality guidelines for tin; however, the ANZECC guidelines do recommend that the concentration of an element without a guideline value should not exceed the background concentration by more than a factor of two. The sources of tin in the lake sediments are unknown.

- The average concentration of lead in the sediments is significantly enriched. However, in the low range concentrations, lead appears to be depleted. The concentration of lead exceeds the ANZECC (2000) ISQG-low sediment guideline values at a number of locations across the lake and appears to be elevated in the southern portion of the lake.

- The average concentration of silver in the sediments is enriched to significantly enrich in the sediments in some locations within Hamilton Lake but does not exceed the ANZECC (2000) ISQG-low sediment quality guidelines. The source of silver in the sediments is not known.

- The average aluminium concentration in Hamilton Lake sediments appear to be significantly enriched above background, but is lower than the typical concentration of aluminium normally found in Waikato soils (approximately 71,000mg/kg) (Environment Waikato, Unpublished data)(see Table F-5 in Appendix F). There are no sediment quality guidelines for aluminium because aluminium has a very low solubility and aluminium in sediments is generally not believed to be eco-toxic. The concentration of aluminium found in the sediments of Hamilton Lake is unlikely to have any significant ecological impacts as long as the concentration of dissolved aluminium in the water column is below ANZECC (2000) water quality guidelines trigger values.

- The high range concentrations of chromium, copper and zinc are significantly enriched in Hamilton Lake. The average concentration of these metals only appears to be slightly enriched in the sediments in the lake, but the low range concentrations may in fact be slightly depleted. All these metals are known urban stormwater contaminants. With respect to zinc the appearance of only slight enrichment may be misleading as rural lakes appear to be elevated in zinc due to agricultural inputs. If the Environment Waikato estimates of the concentration of zinc in non-impacted sediment (35mg/kg), then the majority of the sediments within Hamilton Lake are significantly elevated in zinc.

- The average concentration of mercury in the sediments of the lake does not appear to be enriched when compared with the average concentration of rural lakes. However, the high range concentrations of mercury do appear to be significantly enriched. The source of the mercury is unknown.

- The concentration of cadmium and nickel do not appear to be significantly enriched in any of the sediments collected from Hamilton Lake, even though they are known urban stormwater contaminants. The concentration of cadmium in the sediments of Hamilton Lake appears to be depleted with respect to the sediments in rural lakes. This may be due to agricultural inputs of cadmium from superphosphate application enriching the concentration of cadmium in rural lakes.

- The concentration of phosphorus within the sediments of Hamilton Lake appears to be depleted when compared to other rural lakes within the Waikato Region.

4.3 Key Findings

Arsenic, aluminium, antimony, lead, silver and tin are significantly enriched in the surficial sediments of Hamilton Lake relative to the concentration of those elements found in rural lakes around the Waikato region. Copper and zinc also appear to be significantly enriched in some sampling locations, but average concentration of these metals do not typically exceed more than two times the concentration found in Waikato rural lakes. However, in the case of zinc this may be misleading as it appears that rural lakes are significantly impacted by agricultural inputs of zinc. If this is the case then most of the sediments within Hamilton Lake are significantly impacted by zinc.

A similar situation occurs with cadmium where agricultural inputs of cadmium into rural lakes have resulted in rural lakes being significantly elevated in cadmium compared to Hamilton Lake. When the concentration of cadmium in surficial sediments of Hamilton Lake is compared against the concentration of cadmium in rural lake, the concentration of cadmium in Hamilton Lake appears to be depleted with respect to Waikato rural lakes.

In the case of mercury, comparison to Waikato rural lakes sediment quality data indicates that with the exception of one sampling location the concentration of mercury does not appear to be significantly enriched in Hamilton lake, rather the concentration appears to be near the typical concentration that one would expect within the Waikato region. Therefore, although the concentration of mercury is near and may exceed the ANZECC (2000) ISQG-low guideline value, the concentration found in the sediment of Hamilton Lake represents typical background concentration for mercury within the Waikato region.

Comparing the sediment quality results with previous studies undertaken on Hamilton Lake there does not appear to be a significant change in concentration of arsenic in surficial sediments between the results obtained during this study and those obtained 16 years earlier by Gordon Rajendram. A comparison of sediment quality data for cadmium, copper, lead and zinc between the two studies does show significant differences, but this may be due to differences in the sampling methodology rather than actual changes in sediment quality over time.

Direct comparison between this work and the work conducted by Tanner and Clayton in 1983 (24 years earlier) is not possible as the Tanner and Clayton study only includes a limited number (four) of samples. Therefore, the Tanner study cannot be seen as representative of the concentration of arsenic in the sediment of Hamilton Lake at the time.

The concentration of arsenic in the water of Hamilton Lake measured during this study is within the arsenic concentration range of Hamilton lake surface water determined by Gordon Rajendram. However, Gordon Rajendram's data indicates that the arsenic concentration varies seasonally and is typically higher during spring and summer months rather than in winter when the samples in study were collected. Gordon Rajendram's data indicated that during spring and summer months the water quality within Hamilton Lake could sometimes exceed the maximum acceptable value for arsenic specified in the NZ Drinking Water Standards (2005).

5.0 Correlations and Spatial Trends

5.1 Approach and Correlation Matrix

Data collected at each site underwent statistical analysis to determine means, medians, standard deviations; confidence intervals and normality (see Tables D-1 to D-5 in Appendix D). A full summary of the results of the tests is presented in Appendix D.

Pearson's correlation coefficients were determined for element concentrations in sediments collected as part of this study. Interpretation of the correlations is provided in the subsequent sections. Data sets for arsenic, copper, nickel, mercury, lead and phosphorus were log-normalised prior to derivation of the correlation matrix; data sets for cadmium, chromium and zinc did not require log-normalisation (see Appendix F for the results of the statically tests to determine if the data is normally distributed). The inter-element correlation matrix is provided in Table 5-1. When pairs of variables have a positive correlation and a correlation co-efficient below 0.05, this indicates that these two variables tend to increase together (i.e. if the concentration of one increases then the concentration of the other also increases). For pairs of variables which have a negative correlation co-efficient and the correlation co-efficient is below 0.05 then this indicates that as one variable decreases the other variables tends to increase (i.e. an inverse relationship between variables).

Table 5 - 1: Pearson correlation co-efficients between elements

	Cd	Cr	Zn	Fe	P	Log As	Log Cu	Log Hg	Log Ni	Log Pb
Depth	🟥 -0.46	🟪 -0.544	🟨 -0.377	🟨 -0.456	🟥 -0.428	🟨 -0.337	🟨 -0.479	🟨 -0.506	🟥 -0.553	🟪 -0.583
Cadmium		🟪 0.899	🟪 0.852	🟥 0.517	🟨 0.337	🟥 0.572	🟪 0.805	🟪 0.713	🟪 0.791	🟪 0.87
Chromium			🟪 0.893	🟪 0.613	🟥 0.52	🟥 0.513	🟪 0.934	🟪 0.68	🟪 0.841	🟪 0.899
Zinc				🟥 0.516	🟥 0.585	🟨 0.429	🟪 0.866	🟥 0.515	🟪 0.656	🟪 0.795
Iron					🟥 0.523	🟪 0.622	🟪 0.59	🟨 0.481	🟪 0.715	🟪 0.656
Phosphorous						0.292	🟪 0.609	0.162	🟨 0.359	🟥 0.473
Log Arsenic							🟥 0.505	🟨 0.388	🟪 0.675	🟪 0.727
Log Copper								🟪 0.611	🟪 0.835	🟪 0.816
Log Mercury									🟪 0.723	🟪 0.621
Log Nickel										🟪 0.82
Log Lead										🟪 1

🟪 P=<0.0001 Highly Significant

🟥 P=<0.001 - >0.0001 Highly Significant

🟨 P=<0.05 - >0.001 Significant

The Pearson's correlation matrix indicates that the correlation between most metals are highly significant. The Pearson correlation co-efficient indicate that water depth may be important for controlling the distribution of some elements such as cadmium, chromium, phosphorus, nickel and lead but water depth is not as important for controlling the distribution of arsenic, copper, iron, mercury and zinc. The negative correlation co-efficient indicates that as water depth increases the concentration of most elements decreases. This may be due to:

1. Stormwater discharges occurring in mainly shallow areas.

2. That arsenic may have been applied in greater volumes, or may not have dispersed as much in the shallower areas of the lake. This could have resulted in slighter higher concentrations in shallower sediments than in deeper sediments.

An examination of the surfer plot (Figure A2 in Appendix A) shows that the arsenic concentrations appear to be highest between the 2.5 to 3m water depth contour intervals. This may explain part of the correlation between water depth and the distribution of arsenic. Examination of the distribution of the chemical elements in the surficial sediments of the lake (see Figure A2-A12 in Appendix B) suggests that the elements are distributed mainly within the two basins of the lake and tend to be lower within the central ridge (where depths are typically between 1 to 1.5m below water level) which divides the two basins. The reason for the lower concentration of metals found in sediments along this ridge is uncertain, as the surface water chemistry in the lake is reasonably uniform and the water in the lake has a reasonably short resident time (approximately 2.6 years). It is possible that the recent sediments along this ridge have been removed by some physical process (such as turbulence caused by the action of wind driven waves).

Although there appears to be an overall inverse correlation with water depth and the distribution of elements over most of the lake, this trend does not occur for the samples collected along the central ridge (SDH012, SDH025 and SDH026) and in front of the rowing/yacht club.

The low concentration of metals in front of the rowing/yacht club may be due to:

1. Its distance from major input sources in the northern and southern edge of the lake.
2. The sheltered nature of the bay which might limit the volume of metal enriched suspended particulate matter or sediment reaching this location.
3. Other physical process which is removing sediment from this location.

Further studies would be required to identify what physical processes are controlling the distribution of elements in the surficial sediments and why the concentration of many elements is low along the central ridge and in front of the rowing/yacht club.

Another reason for a high correlation between the elements is that they have a common source or the chemistry controlling the distribution of the metals is the same. Metals such as cadmium, copper, lead and zinc which are associated with stormwater are normally correlated together due to their common source; however it is unlikely to be the case for arsenic as it was introduced to the lake as a result of herbicide application. Also the concentrations of iron, mercury, nickel and phosphorus do not appear to be significantly enriched by anthropogenic activity as can be seen by their comparison in the Waikato rural lakes. The concentrations of iron, mercury, nickel and phosphorus elements may represent the natural background concentration of the lake. Therefore, a common source cannot explain the correlation observed for all the elements but may explain at least some of the correlations observed.

The high correlation of all the elements with iron may suggest that iron chemistry could be controlling the distribution of elements within the surficial sediments. Further investigations are required to confirm this as the high correlation exhibited between most parameters makes interpretation difficult.

The Pearson's correlation matrix indicates that there is a very low correlation in the distribution of phosphorus and arsenic and mercury. This indicates that the distribution of phosphorus is not related to either the concentration of arsenic or mercury and that there is no common source for these elements.

5.1.1 Correlation with Distance from Shore

A correlation of the inter-relationships of the elements with distance from the eastern shore (which has a high number of stormwater inputs) and the southern end of the lake (where the highest concentration of many elements are observed) was undertaken. The Pearson's correlation matrix for the interrelationship with distance is presented in
Table 5-2.

Table 5 - 2: Pearson's Correlation of Distribution of Elements with Distance from Southern and Eastern Shores of Hamilton Lake.

	log Southern	log Eastern
Cd	-0.451	-0.259
Cr	-0.472	-0.299
Zn	-0.674	-0.177
Fe	-0.295	-0.406
P	-0.341	-0.0701
Log As	-0.00932	-0.0217
Log Cu	-0.423	-0.202
Log Hg	-0.297	-0.199
Log Ni	-0.237	-0.213
Log Pb	-0.317	-0.219
	log Southern	log Eastern
🟪	P=<0.0001	Highly significant
🟥	P=<0.001 - >0.0001	Highly significant
🟧	P=<0.05 - >0.001	Significant
🟨	P=<0.1 ->0.05	

For the eastern shore the correlation matrix indicates that there is a significant (p=<0.05 ->0.001) correlation between iron only, with distance from the shore. Iron concentrations were found to decrease with increasing distance for the eastern shore. This suggests that there may be an iron input from the eastern side of the lake.

Looking at the southern shore, significant correlation was observed with cadmium, chromium, copper, lead and zinc with distance from the southern shore. The correlation analysis suggests that there is an inverse relationship between the concentrations of these elements and distance for southern end of the lake. These elements are normally associated with stormwater discharges, which suggest that stormwater inputs from the southern end of the lake are having a significant impact on sediment quality. This data supports the findings of the enrichment ratios which indicate that the higher concentrations of copper, lead and zinc occur in the same parts of the lake.

The concentration of phosphorus is also significantly correlated, with concentrations decreasing with distance from the southern shore. This might indicate that some phosphorus is entering the lake as a result of stormwater discharges. If this is occurring then the most likely source of the phosphorus would be fertiliser run-off from domestic gardens, lawns and parks. Even though the correlation analysis suggests that there may be a stormwater input of phosphorus into the lake, the overall concentration of phosphorus within the lake is low when compared to other rural lakes in the Waikato region. However, it may be assumed that phosphorous concentration are elevated in rural lakes as they are receiving a much greater input of phosphorus due to agricultural sources.

Concentrations of arsenic and nickel are not correlated with distance from the southern shore. Since the elements commonly associated with stormwater discharges are negatively correlated with distance from the southern shore, the fact that the concentrations of neither arsenic nor nickel show this trend suggests that the concentration of these two elements in the surficial sediments is not affected by stormwater discharges. In the case of nickel this data supports the finding of the enrichment analysis which indicates that the concentration of nickel has not been significantly enriched within the lake's surficial sediments. The concentration of nickel appears to be similar to the "background" concentration as seen in the rural lakes. This analysis also suggests that that the concentration of arsenic within the surface sediments is not affected by stormwater inflows and the source of arsenic in Hamilton Lake is the application of sodium arsenite in 1959. There is no evidence that stormwater discharges into the lake are having a significant impact on arsenic concentration in the lake's surficial sediments (either by diluting the sediments with sediments which contain low concentrations of arsenic or as an addition source of arsenic).

The concentration of mercury shows a significant inverse relationship with distance from the southern end of the lake. This seems to suggest that there might be a source of mercury near the southern end of the lake. Environment Waikato has indicated that Waikato hospital has a coal fired boiler which is a likely candidate to be the source of any mercury entering the lake. NZ coal has a relatively low level of mercury (the typical concentration of Waikato coal is 0.07 to 0.12mg/kg (Moore, *et al* 2005)) when compared to coal sourced internationally (especially china). During the combustion of coal a significant portion (greater than 90%) of it is released into the air because mercury is so volatile.

Therefore, aerial deposition of mercury into the lake from the discharge of the hospital boiler may explain the correlation observed in this study. However, the evidence at this stage is highly circumstantial. Further investigations such as accurate monitoring of the mercury discharge from the hospital, together with air dispersion monitoring and monitoring of the stormwater entering the lake would need to be conducted before it could be concluded if either (or both) stormwater discharges or aerial disposition of mercury into the lake are responsible for the presence of mercury.

Regardless of the source of the mercury, the comparison of the concentration of mercury in Hamilton Lake with the concentration of mercury in rural lakes (Section 4.2) suggests that there has been no significant enrichment in the concentration of mercury in Hamilton Lake surficial sediments.

5.1.2 Correlation with Water Depth

Pearson's correlation coefficients were determined for element concentrations with water depth. They show that while there are no highly significant correlations between element concentration and water depth, there is a significant relationship with the concentration of arsenic, copper, zinc, phosphorus and iron with water depth (see summary Table 5-3 and full data in Table D-6 in Appendix D). The relationship may be evidence that redox chemistry is partly controlling the deposition of these elements but further work would be needed to confirm this.

Changes in redox conditions could result in iron oxide precipitating which could result in the sorption or co-precipitation of other elements such as arsenic, copper, lead and zinc.

Table 5 - 3: Pearson's Correlation of Distribution of Elements with Water Depth

	Depth
Cd	-0.282
Cr	-0.356
Hg	-0.39
Ni	-0.216
Zn	-0.482
log As	-0.483
Log Cu	-0.422
log Pb	-0.438

5.2 Spatial Data

To aid in the spatial interpretation of the element distribution in the surficial sediments, the computer program Surfer (Version 8) was used to draw contour maps of the elemental distribution. To create the grid files to generate the contours a Kriging geo-statistical interpolation method was used. The contour maps for each element are presented in Appendix A as Figures A2-A12.

5.2.1 Arsenic

The distribution of arsenic in the surficial sediments is presented in Figure A2 in Appendix A. The concentration of arsenic is highest in the two basins and is typically lower along the central ridge in the lake. Concentrations of arsenic in the sediment are typically lower around the location of the boat and rowing club. According to Hamilton City Council records only 80% of the total lake area was treated with arsenic herbicide (Tanner and Clayton, 1990). This may account for the lower concentrations in certain areas such as adjacent to the boat club. The highest concentrations of arsenic in the lake do not occur at the deepest part of the lake; instead they seem to be clustered around the 2.5 to 3.5m depth contour in certain locations. Perhaps at this depth there is a change in redox chemistry in the lake which results in more arsenic being accumulated at these locations. Further studies would need to be conducted to confirm if this was the case.

As shown by the correlation calculation, the concentration of arsenic does not appear to be lower in areas where stormwater associated elements (such as copper, lead and zinc) are elevated. This suggests that sediment entering the lake from stormwater discharges are not having a significant diluting effect on the arsenic concentrations within the surficial sediments. However, it should be noted that the sediment sampling programme was designed so that sediment samples within 10 metres of any stormwater discharges were not collected and therefore if the area of significant deposition of sediments from the stormwater discharges is limited to less than 10 metres from the discharge point then this monitoring programme would not detect any diluting affect.

5.2.2 Copper and Zinc

The concentrations of both copper and zinc are the highest in the southern end of the southern basin, where a large number of stormwater inputs are located (see Figures A4 and A10 in Appendix A). The zone in which sediment quality appears to be impacted by zinc is larger than that of copper, which probably reflects the higher concentration of zinc in the stormwater entering the lake and the greater mobility of zinc in the environment.

The concentration of both of the elements also appears to be slightly elevated in the northern basin as well as in a limited area in front of the kiosks on the eastern shore of the lake. This is probably due to the presence of major stormwater inputs in these locations as both of these metals are commonly associated with stormwater.

As with arsenic the concentration of both of these metals in the surficial sediments appears to be lower along the central ridge within the lake and in front of the boat/rowing club.

5.2.3 Lead

With respect to exceedances of the ANZECC (2000) ISQG guideline values, lead is the most elevated element after arsenic. The spatial distribution pattern of lead is very similar to that of copper and zinc but the spatial extent of the impacted zone is far larger that either of those two metals (see Figure A6 in Appendix A). This may be a result of the concentration of lead in material entering the lake via stormwater discharge being higher than either copper or zinc.

The concentration of lead tends to be lowest in sediments along the central ridge of the lake and in front of the boat/rowing club. This follows the pattern of arsenic, copper and zinc.

5.2.4 Cadmium, Chromium and Nickel

The distribution of cadmium, chromium and nickel appears to be very similar to the other metals associated with stormwater discharges, and follows the same general spatial distribution trends (see Figure A3, A4 and A9 in Appendix A respectively). All of these metals tend to be elevated in the southern end of the southern basin of the lake. The lowest surficial sediment concentrations appear to be along the central ridge of the lake and in front of the boat/rowing club.

Although there is some limited evidence of anthropogenitic inputs of cadmium, chromium and nickel into the lake, the concentrations of these elements do not exceed the ANZECC (2000) ISQG-low guideline values in any of the surficial sediments samples collected as part of this study.

5.2.5 Mercury

Although the spatial distribution of mercury does appear to generally mirror the distribution of stormwater contaminants such as copper, lead and zinc; mercury is not an element commonly associated with stormwater discharges. There appears to be a hotspot of mercury in sediments along the central ridge within the lake. This hotspot is caused by a single sample (SDH025) which was found to contain 0.32mg/kg of mercury. The other two samples located on this ridge (SDH012 and SDH026) contain 0.10 and 0.14mg/kg respectively.

With the exception of the hotspot located on the central ridge, the exceedances of the ANZECC (2000) ISQG-low guideline values are mainly concentrated around the southern portion of the southern basin. Some concentrations of mercury at the ANZECC (2000) ISQG-low guideline level (0.15mg/kg) also occur in the surface samples (SDH09 and SDH16-SDH19) taken from areas where stormwater discharge are believed to be having an impact on surficial sediments. The concentration of mercury found in these samples is only 0.02mg/kg above the average concentration of mercury found in surficial sediments in Hamilton Lake and only 0.01mg/kg above the “background” concentration found in rural lakes.

Comparison of the mercury concentrations found in the surficial sediments of Hamilton Lake with those in rural lakes suggests that the mercury concentrations in the surficial sediments are not enrichment. This suggests that this high sample result in SDH025 (which has the elevated concentration of mercury) is a result of inhomogeneity in the sample matrix. Additional sampling around SDH025 would be needed to confirm that the sample result is a statistical outlier and is of no significant with respect to the sediment quality of the lake.

The only identified source of mercury which may be causing the elevated concentration of mercury in the surficial sediments is the possible aerial deposition of mercury emitted from burning of coal in the hospital boiler located on the southern end of the lake.

Therefore, although the concentration of mercury does exceed the ANZECC (2000) ISQG-low guideline value in some of the surficial sediment samples, it is similar to the background concentration of mercury found in rural lakes and no significant enrichment of mercury is believed to occurring. This may indicate that the concentration of mercury found in the sediments of Hamilton Lake is unlikely to be having a significant ecological impact.

5.2.6 Iron and Phosphorus

Iron and phosphorus concentrations appear to represent the natural background distribution as they were not found to be enriched when compared with rural lakes. The concentration of phosphorus and iron do tend to be lower along the central ridge and outside the front of the boat/rowing club. This trend is exhibited in the other elements investigated in this survey.

5.3 Spatial Distribution of Elements within the Sediment Cores

The concentration of elements between the cores is highly variable between sediment cores. Core samples CS1 and CS3 generally have higher concentration of all elements than sediment cores CS4 and CS5 (see Figures A16 to A17 in Appendix A). Core samples CS4 and CS5 were taken near the central ridge within the lake where the surficial sediment sampling found that the lowest concentrations of most metals tended to occur. Sediment cores CS1 and CS3 where taken in areas where significant stormwater inputs are known to occur. This is the likely explanation for the higher concentration of elements in these cores. Sediment core CS2 was taken near the eastern shore between two storm water discharges. Although this area was not significantly enriched, the concentration of most elements at this location tend to be similar to the average concentration of the elements in the lake.

The ranges of concentration of chromium, mercury and nickel are very similar between all sediment core samples and with depth, which suggests that these elements are not significantly enriched above background concentrations at these sampling locations.

A Pearson correlation analysis on the distribution of elements with depth down the sediment cores from the results reveals that there is highly significant correlation between depth and arsenic, chromium, lead, mercury, and zinc and a significant correlation with copper in the upper 10cm of the sediments of most cores. However, neither cadmium nor nickel displays much variation with depth, so the reasons for the highly significant correlation between these two elements and the other elements are unclear.

The concentration of all these elements decreases depth. When this correlation is performed on the composited sediment taken over the top 0-20cm; only arsenic, iron, phosphorus and zinc are significantly correlated with depth. Neither cadmium nor nickel is significantly correlated with depth and in the case of nickel there is no correlation with depth. The lack of correlation with depth with these two elements probably reflects the fact that the concentration of these elements is close to or at background concentration levels in the core samples and that the variation in the concentration of these metals between the top and bottom core samples is very small.

In the upper 10cm of the sediment cores there is a highly significant correlation with all elements (except chromium and arsenic), which is probably due to most elements being concentrated in the upper sediment layers and their concentrations generally reducing down the core.

The high correlation between arsenic and iron is to be expected as iron oxides are an important binding phase for arsenic in sediments. Work conducted by Aggett and O’Brien (1985) on Lake Ohakuri found that arsenic is accumulated in the sediments through the formation of arsenious sulphide and ferric arsenate and that iron was involved in the main mechanism for the adsorption of arsenic in surficial sediments. This is important because Aggett and O’Brien found that arsenic could diffuse though the sediment profile and that biological activity in the summer months could increase the flux of arsenic to the surface waters by up to 20%.

Further work would need to be conducted to determine if the same arsenic and iron chemistry is observed in Hamilton Lake as is observed in Lake Okakuri. However, the correlation of arsenic with depth, the seasonal variability in arsenic concentrations in surficial waters recorded by Gordon Randerjam (1992) and the apparent increase in the concentration of arsenic in sediments with a depth of between 2.5m and 3.5m suggests that redox chemistry of iron is having a significant effect on the behaviour of arsenic within the sediments.

The vertical distribution of arsenic in sediment core CS3 is different to that observed from the other sediments cores. There is a significant increase in the concentration of arsenic from between 5 to 10cm below the sediment-water interface, with the maximum concentration of arsenic being found at 9-10cm below the sediment-water interface. This increase does not appear to be related to a change in iron concentration at this depth, or any other element except perhaps copper. Sediment core CS3 was the only sediment core taken from immediately in front of a stormwater discharge (approximately 20 to 40m away) and this sediment core displayed the most laminar layering of the sediments of all the cores collected from the lake during this study.

Although the distribution of arsenic with depth in CS3 did not follow the pattern observed in all the other sediment cores samples collected in this study (i.e. the highest concentration of arsenic occurring at the surface), it was similar to the vertical distribution of arsenic observed by Gordon Rajendram in 1991 in his sediment cores samples. All of Gordon Rajendram sediment cores were collected in front of stormwater discharges, up to 150m from the discharge point. In Gordon Rajendram's study the maximum concentration of arsenic was typically found in samples collected from either the 25 to 75mm or 75 to 150mm depths (20 of the 26 sediments cores in front of stormwater discharges). Although in a few samples the depth of the arsenic maxima was much greater (in samples collected from the 225 to 400mm depth range). The greater depth of burial of the arsenic in some of the sediment cores collected in front of the stormwater discharges may reflect a higher sedimentation rate in these locations.

It should be noted that although the maximum concentration of arsenic occurs several centimetres in depth in the Gordon Rajendram's study; the concentration of arsenic is still highly elevated in the surficial sediments (up to 100mg/kg). This suggests that there is an upward migration of arsenic to the surficial sediments occurring.

5.4 Key Findings

The key findings of the statistical and spatial analysis are:

- That the elements are mainly distributed within the two basins of the lake and their concentrations tend to be lower within the central ridge which divides that lake. The concentration of most elements also appears to be lower in front of the rowing club/boat ramp.

- The concentration of cadmium, copper, lead and zinc decreases with distance from the southern end of the lake. This suggests that stormwater discharges in the southern portion of south basin are having an impact on sediment quality. An examination of the enrichment ratios of these elements in Section 4.2 suggests that the elements have been enriched in the surficial sediments in some parts of the Hamilton Lake compared with background concentrations in rural lakes. The greatest degree of enrichment occurs at the southern end of the lake.

- The spatial distribution of high concentrations of lead is far greater than that of either copper or zinc. This suggests that the mass of lead entering the lake has been greater than that of copper or zinc. The spatial extent of the sediments impacted by zinc is in turn greater than that of copper. This suggests that the mass of zinc entering the lake is greater than copper.

- Only the concentration of iron is significantly correlated with distance from the eastern shore of the lake. Although there are numerous stormwater discharges along the eastern side of the lake, concentrations of elements along this eastern shore do not appear to be significantly elevated.

- The concentration of arsenic in surficial sediments does not correlate with distance from the shore and stormwater outlets. This indicates that stormwater inflows are not a significant source of arsenic in the sediments of Hamilton Lake.

- The concentration of nickel also does not correlate with either distance from the eastern shore or distance from the southern end of the lake. This indicates that stormwater inflows are not a significant source of nickel in the sediments of Hamilton Lake. This is supported by the evidence found in Section 4.2 that shows that the concentration of nickel within the lake is not enriched and is similar to background levels found in other rural Waikato lakes.

- The concentration of mercury shows a significant inverse relationship with distance from the southern end of the lake. The reason for this enrichment is unknown. Examination of the enrichment ratio for mercury (Section 4.2) shows that the concentration of mercury is not significantly enriched within the sediments of the lake when compared to other rural Waikato Lakes.

- There are no highly significant correlations between the concentrations of elements with water depth. However, there does appear to be a significant correlation between arsenic, copper, lead, zinc and water depth. The surfer plots in Appendix A indicate that the highest concentrations of arsenic tend to occur in between the 2.5 to 3.5m depth contour in the lake. It is possible the redox conditions in this part of the lake cause these metals to precipitate. It is more likely that the redox conditions cause iron to precipitate, and these elements are then sorbed onto the iron oxides. However, there is no significant correlation between the distribution of iron and these elements to suggest that this is occurring.

- The concentration of arsenic, chromium, mercury, lead and zinc decreases with depth in the upper 10cm of the sediment cores. The exception to this trend is CS3 were there is an increase in the concentration of arsenic in core samples collected from a depth of between 5cm to 15cm below the surface of the sediments.
- There is evidence that the redox chemistry of iron may be playing an important role in controlling the distribution of arsenic within the sediments and surface water quality.

6.0 Human Health Risk Assessment

6.1 Introduction

A human health risk assessment was undertaken as part of this investigation to determine if there was an unacceptable health risk for users of Hamilton Lake. Human health risk associated with contaminated sites is thought of in terms of three components. These are: the source of contamination, the people who are likely to come into contact with the contamination, and the pathway which people may be exposured to the contamination. This is called the source-pathway-receptor model of risk, and underpins all contaminated site risk assessments.

As part of any risk assessment using a source-pathway-receptor model the toxicity of the contaminant is first assessed and a maximum “safe” exposure is determined (usually by an international body or government agency), which is referred to as an index dose. Then the potential sensitive receptors are identified and the likely exposure scenarios (i.e. how they are exposured to the contaminant, what frequency and duration of exposure) is may be calculated (which is also referred to as the pathway of exposure). For this assessment long term average daily doses (LADD) were calculated using algorithms and exposure factors recommended by the US EPA (1992, 1997 and 2004), and have been supplemented with exposure information obtained from anecdotal evidence on the use of the lake to determine exposure frequencies and durations. A detailed account of the Human health risk assessment including the methodology used to calculate the likely risk, is presented in Appendix G of this report.

For a risk to occur there must be a hazard, a receptor and an exposure mechanism. The contaminated sediment, contaminated fish and perhaps contaminated water, present a potential hazard. The lake is used for a variety of recreational activities, including fishing; model boating, yachting (Hamilton Yacht Club), dragon boating, canoeing and rowing. These uses fulfil the requirement for the presence of receptors. Finally, there are opportunities for exposure, through contact with sediments and water during these activities and through eating of fish.

It is apparent from examination of available sediment, fish and water sampling results that the contaminant of concern is arsenic. Other inorganic and inorganic pollutants, while present, will not be considered as they will not be critical.

6.2 Exposure Scenarios

As stated earlier the lake is used for a number of recreational water based activities including boating and fishing (catfish, eel, rudd, etc). The lake is not used for swimming anymore and this activity is discouraged by Hamilton City Council due to the periodical high concentrations of bacteria which have been detected at some locations since 1984 (Hamilton City Council, 2006). In addition to recreational users, Hamilton City Council staff and contractors can periodically come in contact with the water and sediments of the lake during maintenance work.

Based on information supplied by Hamilton City Council, Fish & Game (Auckland-Waikato) and Environment Waikato the following exposure scenarios have been assessed as being potential pathways which might be important routes for people to come into contact with contaminated sediments, water or fish within the lake. The exposure scenarios are summarised in Table 6-1 below.

Table 6 - 1: Exposure Scenarios

Activity	**Exposure Route**			
	Dermal with sediment	**Sediment Ingestion**	**Water Ingestion**	**Fish ingestion**
Fishing	Rarely. Generally fishing from shore. May enter water if problem with gear?	Rarely, insignificant	Small amounts, rarely	Yes
Child playing	Yes, wading, playing in mud	Yes	Small amounts	No
Yachting	Yes, while launching and recovering yachts	Possibly, from dirty hands when launching and recovering boats.	Yes, if fell out of yacht, but infrequent and small amounts	No
Rowing	Yes, while launching and recovering boats	Possibly, from dirty hands when launching and recovering boats.	Yes, if fell out of boat, but infrequent and small amounts	No
Dragon boating	Yes, while launching and recovering boats	Possibly, from dirty hands when launching and recovering boats. Less than for yachting?	Yes, if fall out of boat. Less frequent than yachting. Insignificant	No
Model boating	Possibly while launching and recovering boats	Insignificant	Very small amounts from getting hands wet.	No
Canoe and water bike hire operators	Yes, while launching and recovering boats	Possibly, from dirty hands when launching and recovering boats.	Small amounts, rarely	No
Maintenance Workers	Possibly while carrying out lake-edge maintenance clearing weed.	Possibly from dirty hands from carrying out maintenance work.	Small amounts, rarely	No

In all of the scenarios a likely “worst case” exposures frequency and duration has been calculated. This approach would significantly overestimate the exposure estimates to most members of the public who would only occasionally come in contact with the sediment and water of Hamilton Lake. Therefore, these exposure estimates are designed to calculate the maximum likely potential exposure that a person could receive for individuals who are likely to be engaged in regular (i.e. several times per week) activities in and around the lake.

6.3 Risk Assessment

For this risk assessment the US EPA equivalent index dose for arsenic of 0.0067 μg/kg-bw/day has been used. This is lower than the index dose used in the MoH/MfE Health and Environmental Guidelines for Selected Timber Treatment Chemicals (1997), but the toxicology of arsenic is currently under review as part of the process for revising soil guidelines for contaminated land (James Court, Ministry for the Environment, pers. Comm.). Consequently, the draft recommended toxicological value being considered by an expert panel is similar to the US EPA slope factor and the equivalent index dose (Jo Cavanagh, Landcare Research, pers. Comms.). A summary of the calculated LADDs is provided in Table 6-2.

Table 6 - 2: Summary of the Long term Average Daily Dose (LADD) of arsenic (in μg/kg-bw/day)

Activity	**Total Ingestion and Dermal**	**Fish LADD**
Fish ingestion	-	0.015
Yachting	0.0027	-
Canoe and Boat Hire	0.0017	-
Rowing	0.0048	-
Child playing	0.007	-

Note: Index dose range 0.3 – 0.0067 from Table G-1.(Appendix G)

The risk assessment found that there was little risk to council workers conducting work in and around the lake margins as it is assumed that the frequency of such exposures for particular individuals is likely to be low. However, those workers should use good hygiene practices (such as washing hands and face thoroughly before eating) to minimise any exposure that could occur. Due to the low risk, no long term average daily dose of arsenic was calculated for this particular route of exposure.

The exposure to arsenic from the lake's sediment or water of people using model boats on the lake is also considered to be very low and likewise considered to be negligible and therefore no long term average daily dose of arsenic was calculated for this particular route of exposure. Again, good hygiene practice should be undertaken to minimise any exposure that the individuals could possibly receive.

Yachting and rowing could potentially expose people engaged in those activities to arsenic in the lake sediment. The LADD for these activities has been calculated as being up to 0.0027-0.0048 ug/kg-bw/day for people who are engaged in regular long term training on the lake for up to 35 years. This equates to 40 to 70% of the index dose recommended by the US EPA.

Exposure durations (and therefore LADDs) for canoeing and dragon boating are likely to be less due to either lower frequency of contact with the lake or exposure duration being much lower. For most recreational yachters and canoeists the frequency of exposure is assumed to be much lower. Rowers' frequency of exposure (depending on how often they use the lake) and consequently their LADD would also be lower.

Operators and staff of the canoe and boat hire facilities which do operate in the Hamilton Lake domain can also potentially come into contact with the sediments and the water of the lake. The calculated LADDs for this type of activity are 0.0017, which is only 25% of the index dose recommended by the US EPA.

The calculated LADD for child playing in the sediments at the lake edge is 0.007 µg/kg-bw/day (as shown in Table 6-2). Therefore child playing within the sediments at the edge of the lake could potentially exceed the US EPA index for exposure to arsenic of 0.0067 µg/kg-bw/day. The child playing within the lake sediments at the waters edge is sensitive to the parameters assumed, particularly the arsenic concentration in the sediments at the waters edge and the sediment adherence factors (note that no sediment samples were collected in this area and therefore the results have been extrapolated from data collected within the lake basins).

The US EPA sourced (US EPA, 1997) adherence factors for “kids-in-mud” are very much higher than soil adherence factors for most other activities and may be more conservative than necessary. Also this assessment assumes that a child plays within the water’s edge eight times a year for seven years. This assumption needs to be validated to determine if there is any actual risk to children playing around the waters’ edge. It should also be noted that although there may be a theoretical risk associated with arsenic exposure to children playing in the sediments of the lake, periodic high bacteria counts (Hamilton City Council, 2006) found in the lake from time to time pose a much greater risk to children’s health and therefore children should be discouraged from playing within either the sediments of the lake or the lake water on the basis of the high bacteria counts.

The fish ingestion scenario has a LADD approximately twice the index dose derived from the US EPA slope factor (0.015 µg/kg-bw/day as shown in Table 6-2). The calculation assumes all the arsenic in the fish is in the most toxic inorganic form whereas it is probable that a considerable amount (>50%) (Slejkovec et al, 2004 and Ackley et al, 1999) is in the less toxic organic form. On that basis ingestion of fish may not exceed the index dose, but never-the-less, the indication is that a greater than desirable dose may be being obtained from eating fish from the lake for some high-consumption individuals. If fisherman are targeting catfish then they may be at twice the risk (LADD = 0.03) than fisherman collecting a variety of fish from the lake. Further work is recommended to get a better idea of actual consumption rates, which may have been over-estimated. In addition, investigation of the form of arsenic in fish from the lake would be helpful.

Although, the fish ingestion scenario does indicate there is a potential risk in consuming fish caught at the lake; the concentration of arsenic within the fish tissue is lower than the maximum acceptable concentration guideline value for arsenic in fish tissue set by the Food Safety Authority of Australia and New Zealand (2.0mg/kg of As)(FSA). The FSA guideline value only applies to commercially sold fish and not to wild fish caught by recreational fisherman. The reason for the differences between the two risk assessment methodologies may be due to differences in toxicological reference data and frequency of exposure in the two different methodologies.

It should be noted that the LADDs calculated for each exposure pathway are only for that particular exposure pathway and do not include any other incidental exposure to arsenic from other sources. This means that individuals who may be exposured to arsenic from other sources may be at greater risk than those whose only exposure is from contact with the lake alone.

6.4 Key Findings

The key findings of the Human health risk assessment are:

- Recreational users and Hamilton City Council staff and contractors may be potentially exposed to sediment and water within Hamilton Lake; however, due to the infrequent nature of the exposure it is unlikely to pose an unacceptable human health risk. Exposure to pathogens within the lake water is the most likely health risks that these users could potentially be exposed to.

- Children playing in the mud could theoretically be exposure to an unacceptable level of arsenic. However, this is based on very conservative estimates of exposure frequencies and durations of exposure to the lakes' sediment (see Table G-2 in Appendix G) and sediment adherence factor (Table G-3 in Appendix G). These assumptions need to be checked before any definitive statement can be made regarding the risk posed to children playing in the mud around the edge of the lake.

- Recreational fishermen who are catching fish to supplement a significant part of their diet could exceed the index dose recommended by the US EPA and there is an increased risk to fisherman targeting catfish as a food species. However, further work is required to verify the consumption rates of fish from the lake, and what species are actually been eaten from the lake. In addition, investigation of the form of the arsenic within the fish from the lake would be useful as organic forms of arsenic (which are thought to be the prevalent from of arsenic within fish) are significantly less toxic than inorganic forms of arsenic.

- The potential risk of exposure to both maintenance workers and children playing in the sediment around the lake edge could be greatly reduced by good hygiene practices (such as washing hands and face thoroughly before eating) as incidental sediment ingestion is the primary pathway for exposure.

7.0 Discussion

7.1 Are the sediments “Contaminated land”?

To determine if lake and river sediments containing elevated concentrations of chemical residues could be regarded as “contaminated land” it had to be first decided if lake and river sediments could be regarded as “land” under the definition of land specified in the Resource Management Amendment Act (2005). The Resource Management Act (1991) defines land in the Interpretation and Application section in Part 1 s(2) as including land covered by water and the air space above it. On this basis of lake and river sediments can be classified as “land”.

Section 4(1) of the Resource Management Amendment Act (2005) provided the first statutory definition of ‘contaminated land’ in New Zealand by inserting the following in section 2(1) of the RMA:

> ***Contaminated land*** *means land of 1 of the following kinds:*
>
> *(a) if there is an applicable national environmental standard on contaminants in soil, the land is more contaminated than the standard allows; or*
>
> *(b) if there is no applicable national environmental standard on contaminants in soil, the land has a hazardous substance in or on it that—*
>
> *(i) has significant adverse effects on the environment; or*
>
> *(ii) is reasonably likely to have significant adverse effects on the environment.*

Paragraph (a) of this definition cannot yet be applied, because there are no national environmental standards on contaminants in soil. Currently, only paragraph (b) can be applied.

In the Waikato Regional Plan ***contaminated land*** is defined as being any land where any hazardous substance has been added at above background levels as a result of human activity. Land in the Waikato Regional Plan has the same meaning as in the Resource Management Act (1990).

To determine if the concentration of arsenic (and other metals) in the sediments has had or is reasonably likely to had have a significant adverse effect on the environment, sediment quality guidelines for specific hazardous substances are normally used (in the absence of site-specific data). As stated in section 2.2, the ANZECC (2000) guidelines provide two numerical thresholds for sediments. The lowest of these, called the Interim Sediment Quality Guideline-Low (or ISQG-Low), denotes a concentration below which adverse effects are unlikely to occur. This corresponds to a statistical probability of effects of 10%. The higher value, called the ISQG-High, denotes a concentration at which significant effects are reasonably likely to occur. This corresponds to a statistical probability of effects of 50%. At concentrations above the ISQG-High, adverse effects *are reasonably likely to be occurring* in a significant proportion of organisms.

The analysis of surficial sediments of Hamilton Lake revealed that over 73% of samples collected from the lake had arsenic concentrations of over 70 mg/kg (ISQG-High) and that the average concentration of arsenic within the lake is 2.4 times (167 mg/kg) higher than the ISQG-high. An ecology survey of Hamilton Lake has revealed a decrease in species diversity in the benthic macro-invertebrate communities compared to most typical lakes (Lissa McKinnery, 1995). The Lissa McKinnery (1995) thesis also found that macro-invertebrates taken from Hamilton Lake are more susceptible to metal induced toxicity than other macro-invertebrates of the same species collected nearby Lake Rotokauri. This was attributed to the fact that the organisms had been subject to levels of toxic elements which had compromised their ability to detoxicify metals and has made the population more susceptible to metal induced toxicity.

On the basis of this evidence it is *reasonably likely* that the high concentrations of arsenic within the sediments of Hamilton Lake have had and are having a *significant adverse effect on the environment*. Therefore, the lake bed of Hamilton Lake can be classified as “contaminated land”.

7.2 Sources of Enrichment of Elements in Hamilton Lake Sediments

There are two major sources of enrichment of elements found in the sediments of Hamilton Lake. These are urban stormwater discharges and the application of herbicides to the lake.

7.2.1 Urban Stormwater

Urban stormwater appears to be the major source of contaminants within the southern end of Hamilton Lake. Correlation analysis (see Section 5.1.1) and the spatial distribution of contaminants (see Section 5.2) has identified that elevated concentrations of cadmium, chromium, copper, lead and zinc occur within the southern end of the lake where a large number of stormwater discharges occur. In addition, all of these elements (except cadmium) are significantly enriched in the southern part of the lake when compared to other Waikato rural lakes. In some locations copper, lead and zinc exceed ANZECC(2000) ISQG-low guideline values. All of these compounds are commonly found at elevated concentrations within urban stormwater (see Section 1.7) and it is likely that stormwater discharges are the major source of these metals.

In addition, comparison of the concentration of elements measured in the four composites with the concentration of elements found within the rural Waikato lakes have identified that antimony, aluminium and tin are also enriched in the surficial sediments of Hamilton Lake. Antimony exceeds ANZECC(2000) ISQG-low concentrations in all of the composite samples. High concentrations of antimony are found within automobile brakes where antimony is used as a hardening agent, or antimony may be present as a trace element in the formulation of the herbicide (sodium arsenite) used to control the aquatic weeds in the lake (see Section 7.2.2). The latter scenario would be more consistent with the data collected in this study, which shows antimony similarly enriched in all four composite samples rather than being more highly enriched in composite sample 1, where most other metals associated with stormwater are more highly enriched.

The enrichment of aluminium could be due to the lake having naturally high concentrations of aluminium, or it may be related to a discharge of aluminium into the lake from the hospital in the 1990s. According to information supplied by Hamilton City Council and Environment Waikato, aluminium was discharge into the lake as a result of Waikato Hospital cleaning their cooling towers with a caustic solution. This discharge resulted in the death of a number of aquatic plants within 25 metres of the stormwater discharge pipe. However, it is not certain if sufficient mass of aluminium would have been discharged during this event to explain the enrichment observed in this study.

A large mass of aluminium would have been required to be discharged to cause a significant enrichment in the concentration of aluminium in the sediment as the concentration of aluminium is normally very high (20,000mg/kg). To elevate the concentration of aluminium to between 40,000 to 50,000mg/kg would have required several tonnes of aluminium to be discharged into the lake.

Further, examination of the data from the central part of the southern basin (composite 4) of the lake shows that the aluminium is mostly enriched, compared with aluminium in the southern end of the southern basin (composite 1). However, the distribution of aluminium within the sediment may reflect where the aluminium flocculated out of the water column, rather than where it entered the lake. It should be noted that these conclusions are based on a small data set and further work is required to properly identify if aluminium has been enriched by anthropogenic activity and if so, what was the source.

It is possible that some phosphorus is entering the lake as a result of urban stormwater discharges but the phosphorus concentrations of sediments within the Hamilton Lake are depleted when compared against the typical concentrations of phosphorus found within the rural lakes. However, the concentration of phosphorus within rural lakes may be enriched due to agricultural inputs.

7.2.2 Herbicides Application

Arsenic is the only compound which is elevated in the surficial sediments of Hamilton Lake which is like to be introduced into the lake as a result of pesticide applications. An analysis of organo-chloro pesticides in the four composite samples collected as part of this investigation did not detect the presence of any of these compounds.

However, as the formulation of the herbicide is unlikely to be entirely pure (industrial grade chemicals are rarely more than 95% pure, (N. Kim, pers. Comms, 2007)) it is possible that other trace metals may also be present in the pesticide formulation. This is because most of the arsenic is obtained from the waste streams of other ores (particular copper) (USGS, 2006), therefore, arsenic is likely to be cross contaminated with other metals. Arsenic is normally associated with sulphide minerals (such as arsenopyrite, orpiment, realgar, lollingite and tennantite). Therefore, metals which are commonly associated with sulphide minerals (such as antimony, copper, lead, mercury and zinc) may also be present in trace quantities in the pesticide formulation. Arsenic and antimony have very similar chemistry, commonly co-occur, and they substitute for one another in minerals structures. This makes antimony very difficult to separate from arsenic ores and it is likely that antimony would be present as an important trace contaminant in arsenic tri-oxide formulations (such as sodium arsenite pesticides). It is possible that copper, nickel and tin may also have been mildly enriched in the sediments due to the application of sodium arsenite pesticides.

7.2.3 Natural background

The concentration of iron, nickel and perhaps mercury within surficial sediments do not appear to be enriched and may in fact represent the natural background concentration of these elements.

7.2.4 Other Sources

Silver and tin also appear to be enriched in the surficial sediments in Hamilton Lake when compared against the sediment quality of Waikato rural lakes. Elevated silver concentrations are normally associated with discharges from wastewater treatment plants or sewage overflows. This may be from sources such as tradewaste from industries using silver such as photographic shops and medical facilities which are equipped with x-ray machine (silver nitrate is used in developing photographic and x-ray films). Silver is not normally associated with urban stormwater flows unless sewage overflows contaminate the stormwater system.

PAHs are normally a by-product of combustion, but they are also found naturally in fossil fuels such as coal or petroleum products. As noted in Section 1.8, elevated PAHs are often found in stormwater and in sediments adjacent to stormwater discharges. However, the elevated PAHs detected in composite sample 2 are unlikely to be due to urban stormwater discharges. This is because the other elements normally associated with stormwater discharges are not highly elevated in this area and composite sample 1 (where there appears a significant impact) did not detect the presence of elevated PAHs compounds. Instead, the most likely source of the elevated PAHs in the near shore sediments from the eastern side of the lake may be coal used as fuel (either as coal dust or combustion residues entering the lake) from a small train which was operated (until recently) in a domain reserve adjacent to the lake. Aerial disposition of PAHs could be a possible source of the PAHs, but this is considered unlikely as it is expected that this would result in widespread elevation of PAHs across the lake, which was not observed. Composite sample 2 shows that there are elevated concentrations along the eastern side of the lake but obscures the source of contamination and to a certain extent the size of the affected area. As compositing samples together can result in the concentration of few highly impacted samples to be diluted by a large number of cleaner samples it is possible the PAHs concentration found in composite sample 2 are the result of only a few highly elevated samples, which are limited only to a small area of the lake.

Correlation analysis suggests that mercury is elevated in the southern part of the lake; although the sediments do not appear to be significantly enriched when compared to the sediment quality of rural lakes. Mercury is not normally associated with stormwater discharges and it is possible that the correlation observed with mercury and distance to the southern end of the lake may be due to the aerial deposition of mercury discharged from the hospital boiler. However, further investigations are needed to confirm whether this is occurring.

7.3 Changes in sediment quality over time

Comparison between the surficial sediment quality survey conducted by Gordon Rajendram and the current survey has shown that there has been no significant change in the concentration of arsenic in the sediments in the last 16 years. Differences in sampling methodology, analytical testing procedures and the low number of samples collected by Tanner and Clayton in 1983 makes it impossible to make any meaningful comparison between the Tanner study and the current investigation.

Examination of the distribution of arsenic concentrations in the sediment cores reveals that for most sediment cores (expect CS3) the highest concentration of arsenic occur in the upper 2cm layer. However, there has been re-distribution of the arsenic, so it is no longer confined to a single discrete layer. In all of the cores collected, the upper 15cm (CS4 and CS5) to 20+cm (CS1, CS2 and CS3) still contains elevated concentrations of arsenic (core samples CS1 and CS3 contain 153mg/kg to 238mg/kg of arsenic at 15-20cm respectively).

On the basis of the upper sedimentation rate reported by Lowe et al (1994), a maximum sedimentation rate has been calculated for the lake of 0.2mm/yr. Based on this calculation, 9.6mm of sediment is likely to have accumulated since 1959 when the arsenic was introduced. Assuming there was no bio-turbation, or physical and geochemical processes which would result in the re-distribution of arsenic based on this sedimentation rate in would take:

- Over 100 years for the sediments to be buried to below 20mm (below this depth most surficial organisms are unlikely to be exposured to arsenic), and
- Over 500 years for contaminated sediments to accumulate a sufficiently deep layer of clean material above them to prevent most burrowing organisms from coming into contact with the contaminants.
- It may take over 2,500 years before sufficient clean sediment has accumulated over the contaminated material to ensure that the arsenic is no longer available to deep burrowing organisms and deep rooted aquatic plants.

However, this is not the case as the sediment cores already show the redistribution of arsenic is already occurring.

Therefore assuming that the average rate of sediment entering the lake is 0.2mm/yr and it has an average of concentration approximately 6mg/kg and a density of 1.6kg/m^3 and assuming the redistribution of arsenic is limited to only the top 20cm of the sediment it would take between 7,500 to 8,000 years for the sediment in the upper 20cm of the lake bed to be diluted below the ISQG-low guideline value and this sediment accumulation would result in approximately a 1.5 to 1.6m reduction in the lake depth. This calculation is likely to prove to be the worst case scenario. However, considering there is likely to be little arsenic loss out of the lake, the sediments within the lake are likely to contain concentrations of arsenic which could be potentially harmful to aquatic organisms within the upper 10cm of the sediment column for between 500 to 8,000 years.

The concentration of most stormwater source contaminants (except lead) is likely either to increase or remain elevated in the sediments of the lake as they continue to enter the lake via the stormwater discharges. The concentration of lead is likely to slowly decrease as the concentrations of lead within roadside dust decrease following the removal of tetra-ethyl lead from automotive fuels in 1996. Further work should be conducted to determine the rate of accumulation of metals in sediments to determine if stormwater discharges are accumulating within the sediments at a fast enough rates to potentially contaminant the lake bed (i.e. exceed ISQG-high sediment quality guidelines) some time in the future.

Re-sampling of the lake should be undertaken in 10 to 15 years time (2017-2023) to determine the change in the surficial concentration of arsenic. This sampling should be undertaken using the same methodology as used in this study, and Gordon Rajendram's study, to allow the results of each survey to be directly comparable.

7.4 Long term Management of the Sediments

Since the sediments are likely to be regarded as being contaminated for a long period of time (500 to 8,000 years) an environmental management plan (which could be incorporated into the Lake Domain Management Plan) is recommended. This environmental management plan (EMP) should cover such items as:

- How to dispose of any contaminated sediment that is removed from the lake.
- The safe disposal of aquatic vegetation removed from the lake (which may contain concentrations of arsenic up to 1,000mg/kg and therefore must be disposed of into an approved landfill).
- The EMP should also note that because of the potential for aquatic plants to hypo-accumulate arsenic, aquatic plants which can be used as food species (such as watercress) should not be introduced to the Lake. If they do become established they should be removed.
- The EMP should also recommend that people coming into contact with either the lake water or sediments should use good hygiene practices to minimise their exposure to both arsenic and any potential pathogens which may be present in either of these two media.

8.0 Conclusions and Recommendations

The application of 11,000 L of sodium arsenite to Hamilton Lake in 1959 to control *lagarosiphon major* has resulted in elevated concentrations of arsenic being present in the lake sediment at concentrations which would meet the RMA definition of being contaminated land. As the lake bed may be considered land under the RMA, the lake sediments must be considered to be contaminated land

The concentration of arsenic in the sediments is highly elevated in the sediments and exceeds ANZECC (2000) ISQG-high guideline values in most locations. It is expected that the concentration of arsenic found in the sediments of Hamilton Lake would have a significant adverse effect on the environment.

The concentration of copper, lead and zinc exceeded the ANZECC (2000) ISQG-low guideline value in some locations around the lake, most notably in the southern end of the lake where stormwater discharges for the hospital enter the lake.

In the composite samples at some locations, antimony and PAHs also exceed the ANZECC (2000) ISQG-low guideline values.

Arsenic, aluminium, antimony, lead, silver and tin are significantly enriched in the surficial sediments of Hamilton Lake relative to the concentration of those elements found in rural lakes around the Waikato region. Copper and zinc also appear to be significantly enriched in some sampling locations. The sources for the enrichment may be due to the application of the sodium arsenite herbicide in 1959 (in the case of antimony and perhaps tin) or stormwater discharges into the lake (copper, lead and zinc). There appears to be a significant input of metals into the lake from stormwater discharges located in the southern portion of the lake. On-going discharges of these metals may lead to a continued increase in the concentration of these metals (particularly copper and zinc) in the sediments of the lake.

The source of silver within the lake is unknown; it could be associated with stormwater discharges from the hospital or other sources. Aluminium enrichment in the sediment of the lake may be due to the release of aluminium during a pollution incident in the 1990s or it may be natural.

As arsenic is a known human carcinogen and present in the sediments of the lake in highly elevated concentrations a preliminary human health risk assessment was conducted to determine if the concentration of arsenic within the sediments could potentially be a health risk to users of the lake. The preliminary human health risk assessment found that most recreational users of the lake would not be exposed to an unacceptable (greater than 1x 10^{-5}) health risk. However, it did identify that there could be an increased risk if children were frequently playing within the sediments along the lake edge or people were routinely (more than twice a week over summer) catching fish (particularly catfish) to supplement their diets. It should be noted that human health risk assessment conducted as part of this study was very conservative and may overestimate the risk to individuals. A more detailed assessment of the frequency and duration of contact that the lake users have with the lakes' sediment and an assessment of the chemical form the arsenic is in within the fish is required before it can be determined if there is an actual health risk to some frequent users of the lake as a result of the elevated arsenic within the sediments.

An assessment of the changes in the arsenic concentration within the sediments between Gordon Rajendram and this current study found no significant change in the surficial sediments in the past 16 years. A meaningful comparison between the results obtained by Clayton and Tanner in 1983 and this study could not be undertaken due to the differences in sampling methodology, analytical techniques and the low number of samples collected by Clayton and Tanner. Estimates of the burial rate of the sediments based upon sedimentation rates obtained by Lowe et al (1994) indicate that arsenic concentration could remain elevated in the surficial sediments (the upper 10cm of the sediment column) for between 500 and 8,000 years. Therefore, long term management of the sediments is required to minimise the risk to users of the lake and to the wider environment.

To manage the sediments of the lake an environmental management plan for the lake should be developed. This management plan should consider how any sediment or vegetation removed from the lake should be managed, and the health and safety of workers who may potentially come into contact with lake sediment and water. Consideration also should be given the management and/or treatment of stormwater discharges which enter the southern portion of the lake.

Further work could be conducted to:

- Determine the rate of accumulation of metals in sediments to determine if the rate of accumulation of metals within the sediments entering the lake via stormwater discharges could become a potential cause for concern some time in the future.

- Determine the concentration of arsenic in the porewaters and the bottom waters within the northern and southern basins. If this work is undertaken then the influence that iron species (Fe(II)/Fe(III) and iron oxides have on the distribution deposition of arsenic within the basins and porewaters of the sediments should be considered.

- Determine what physical or chemical processes are causing the low concentrations of most metals along the central ridge in the lake and in front of the rowing/yacht club.

- Assess human health risk in more detail by surveying lake users to establish how often, and how long, they come into contact with the sediment and the waters of the lake. As part of this assessment it would be useful to determine the speciation of arsenic within tissue of the fish (especially catfish) which are caught within the lake.

- Sample the eastern site of the lake for PAHs to help to identify the source of the PAHs and the area that has been impacted and help identify the source.

- Establish if there are any ongoing discharges of aluminium, antimony, mercury, silver and tin into the lake.

9.0 References

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Appendix A: Figures

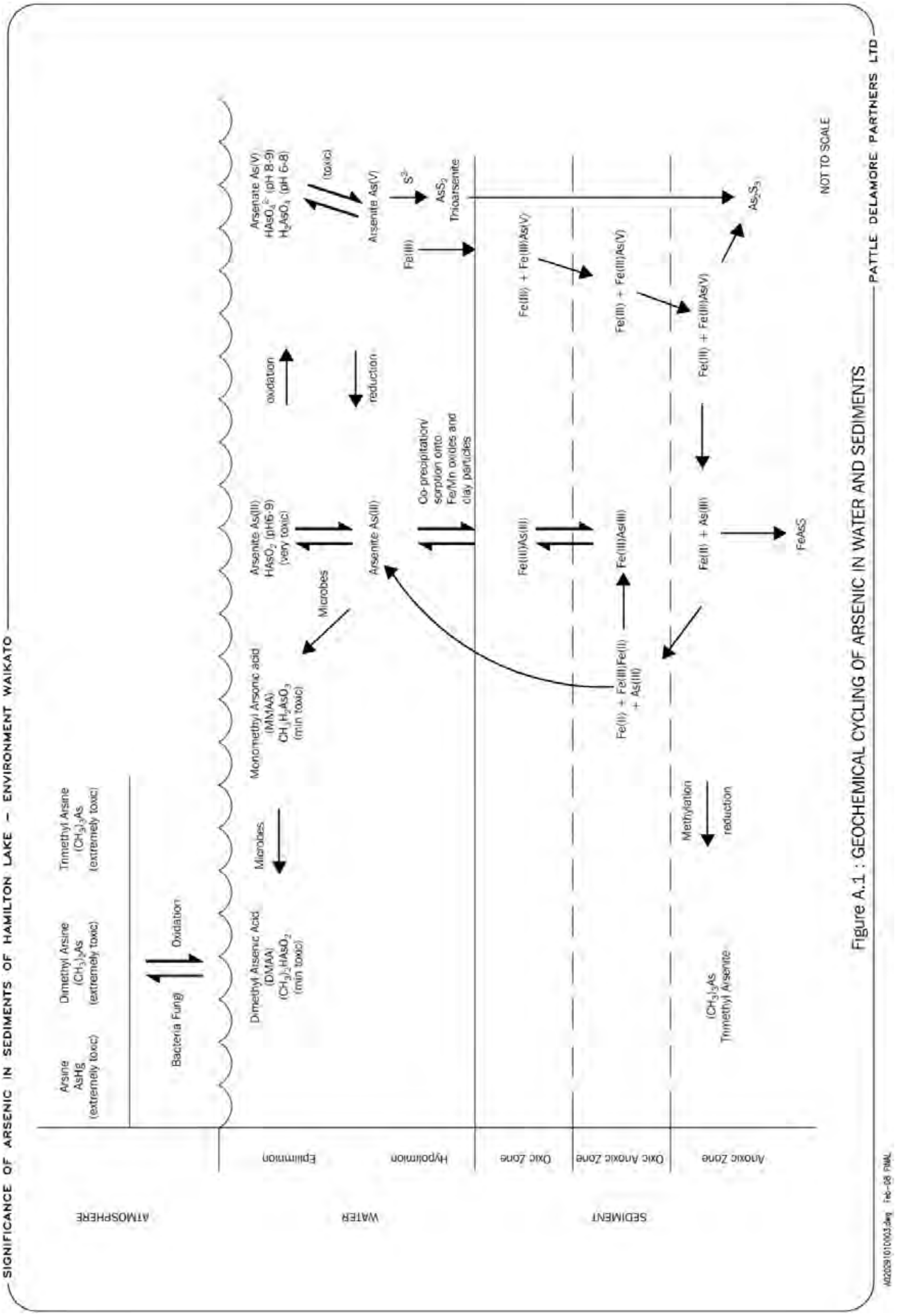


Figure A.1 : GEOCHEMICAL CYCLING OF ARSENIC IN WATER AND SEDIMENTS

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE – ENVIRONMENT WAIKATO

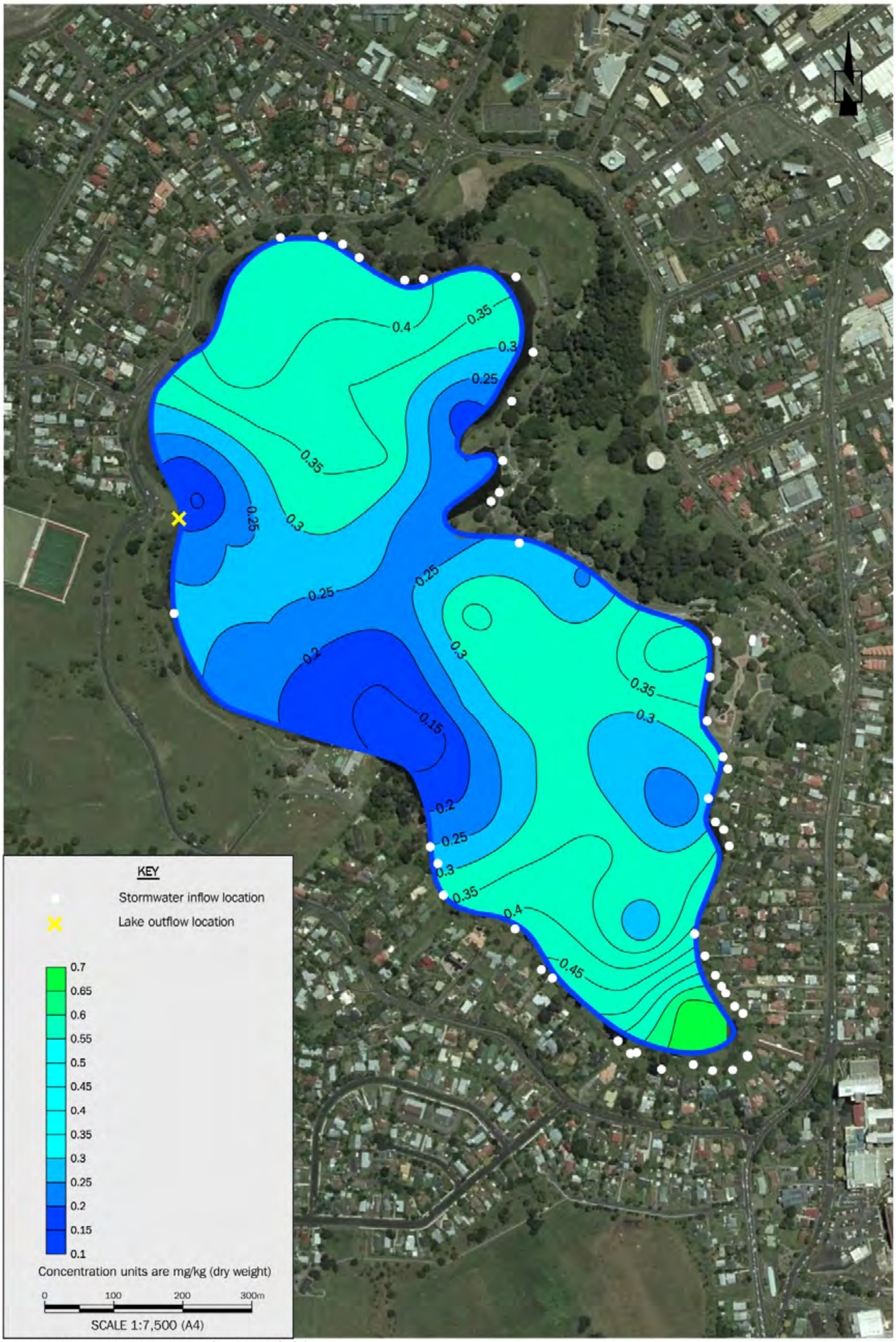
Source: Base data supplied by Environment Waikato (Received on 17/10/07)

Figure A.2 : DISTRIBUTION OF ARSENIC IN SURFICIAL SEDIMENTS

A02029101D001_NZMG.dwg [Bd33_0709.ecw] Feb–08 FINAL

PATTLE DELAMORE PARTNERS LTD

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE — ENVIRONMENT WAIKATO

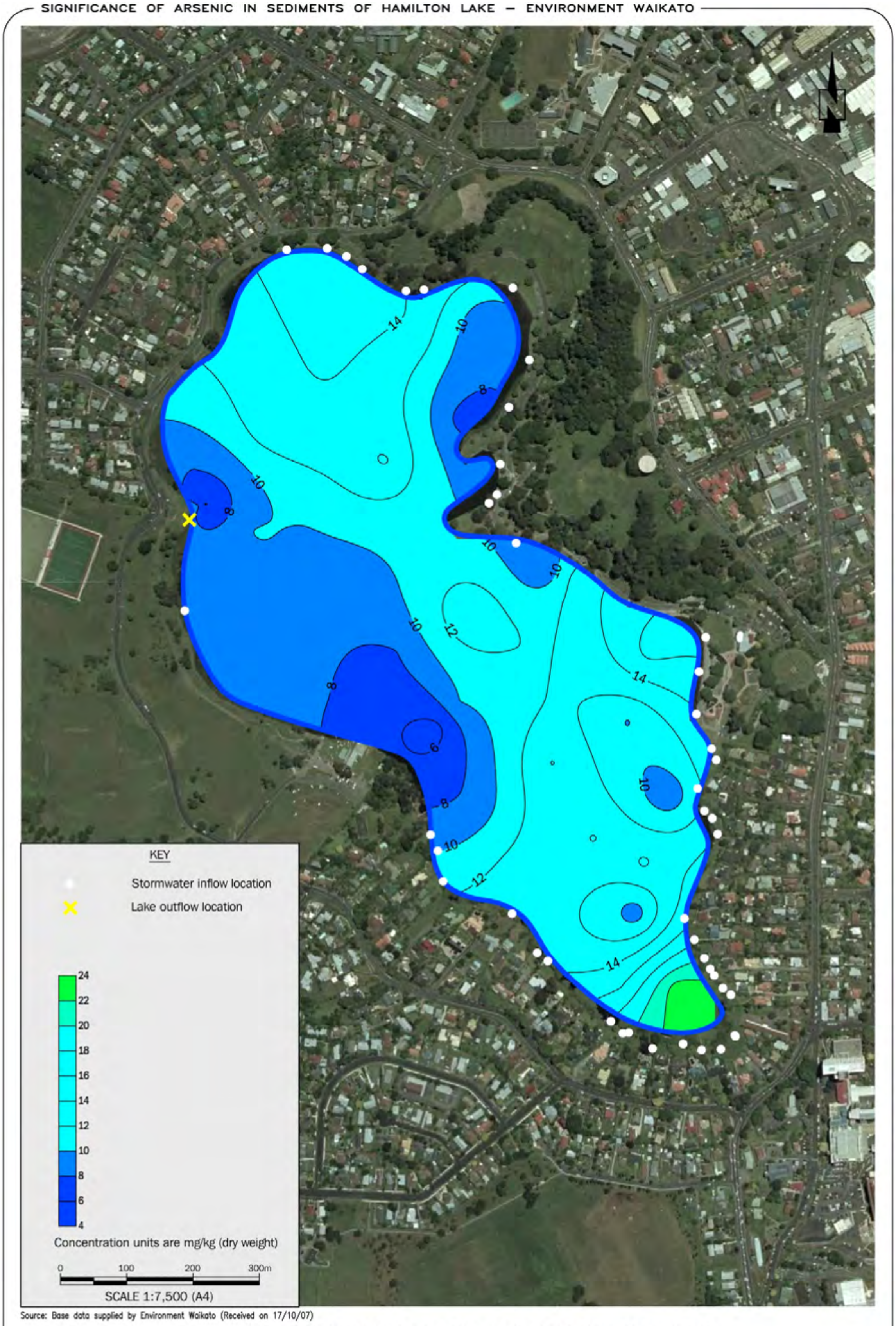


Source: Base data supplied by Environment Waikato (Received on 17/10/07)

Figure A.3 : DISTRIBUTION OF CADMIUM IN SURFICIAL SEDIMENTS

PATTLE DELAMORE PARTNERS LTD

A02029101D001_NZMG.dwg [Bd33_0709.ecw] Feb–08 FINAL



Source: Base data supplied by Environment Waikato (Received on 17/10/07)

Figure A.4 : DISTRIBUTION OF CHROMIUM IN SURFICIAL SEDIMENTS

PATTLE DELAMORE PARTNERS LTD

A020291010001_NZMG.dwg [Bd33_0709.ecw] Feb-08 FINAL

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE — ENVIRONMENT WAIKATO

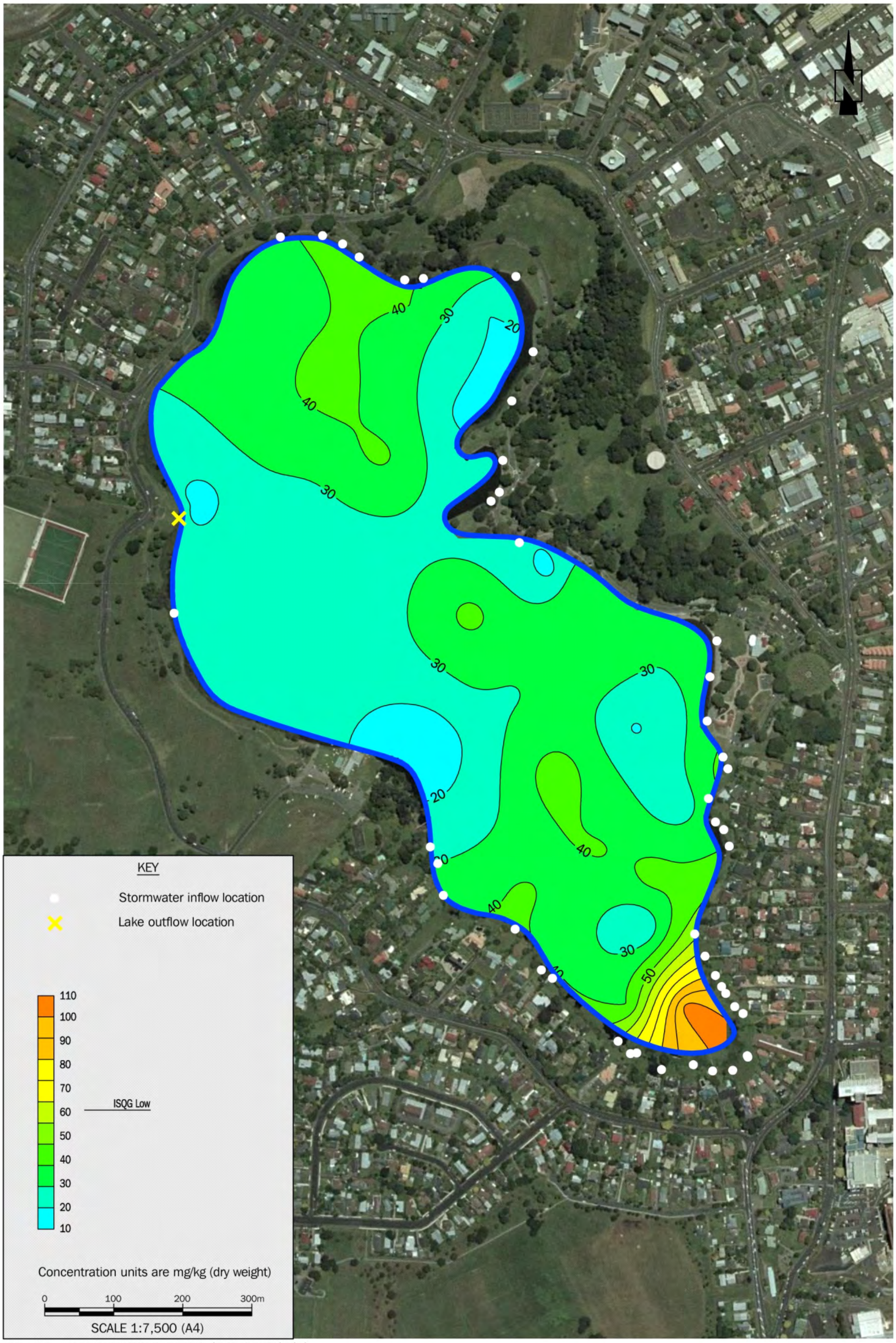


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Figure A.5: DISTRIBUTION OF COPPER IN SURFICIAL SEDIMENTS

A02029101D001_NZMG.dwg [Bd33_0709.ecw] Feb-08 FINAL

PATTLE DELAMORE PARTNERS LTD

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE – ENVIRONMENT WAIKATO

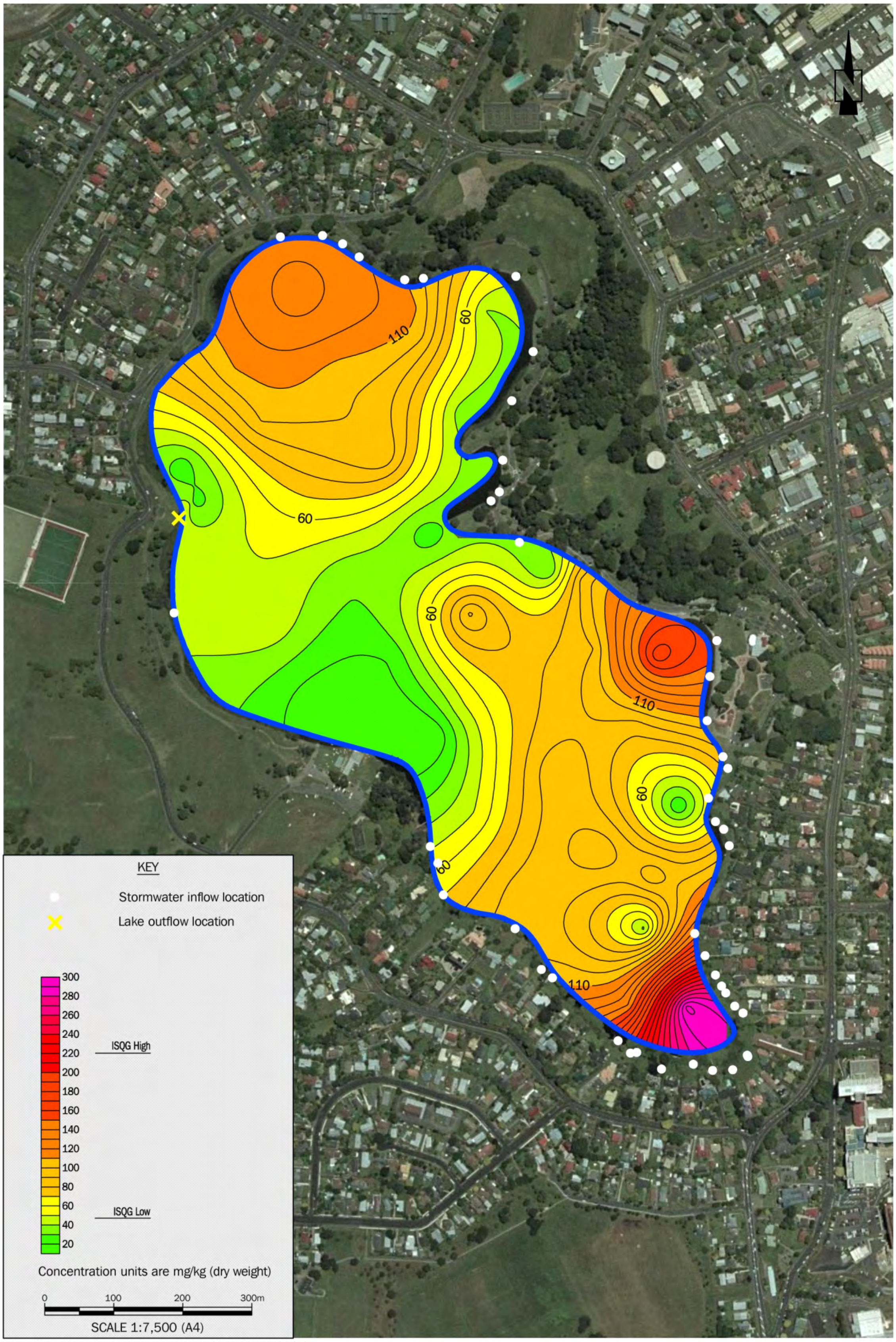

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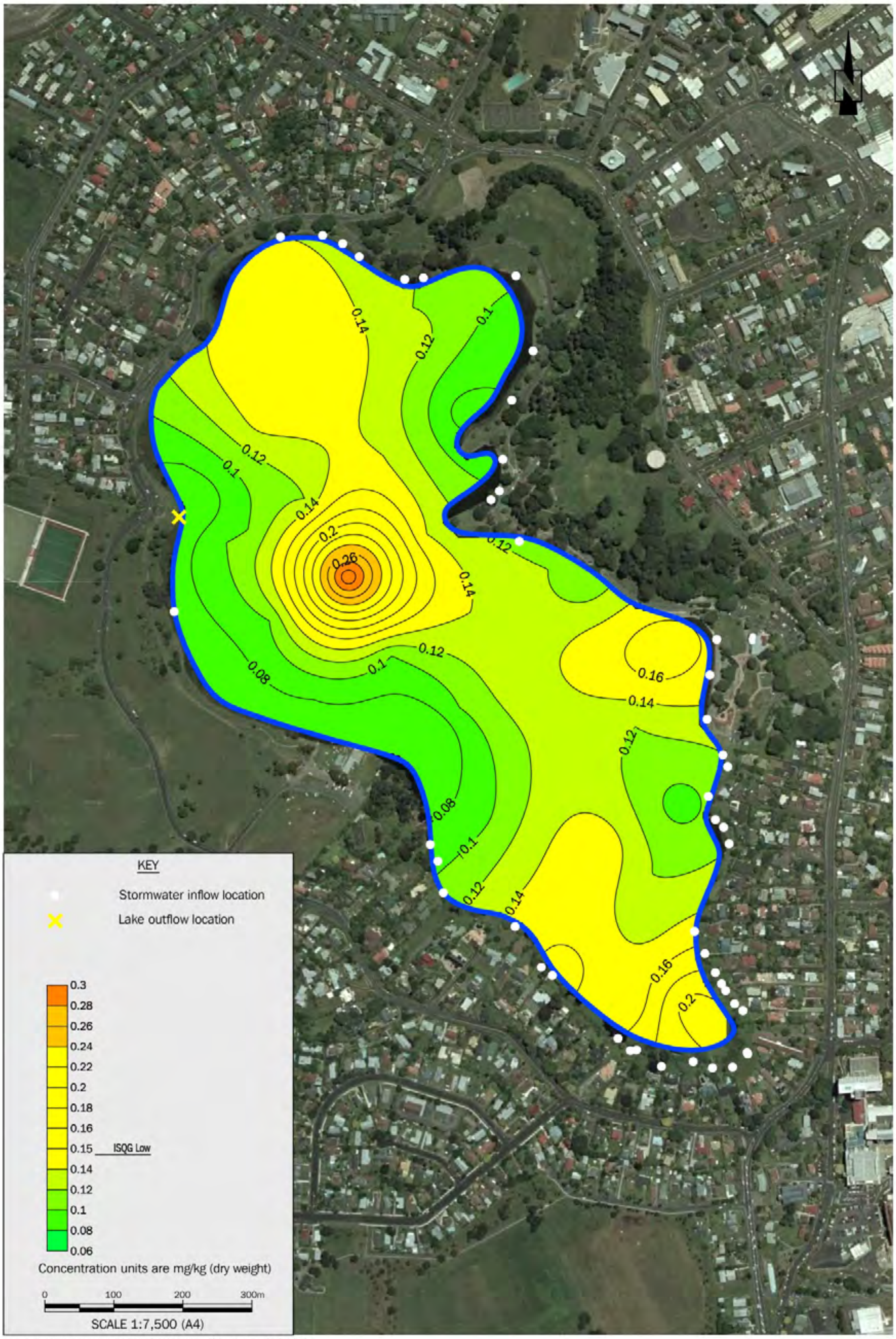
Figure A.6 : DISTRIBUTION OF LEAD IN SURFICIAL SEDIMENTS

A02029101D001_NZMG.dwg [Bd33_0709.ecw] Feb-08 FINAL

PATTLE DELAMORE PARTNERS LTD

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE — ENVIRONMENT WAIKATO



Source: Base data supplied by Environment Waikato (Received on 17/10/07)

A.7: DISTRIBUTION OF MERCURY IN SURFICIAL SEDIMENTS INCLUDING HOT SPOT

PATTLE DELAMORE PARTNERS LTD

A02029101D001_NZMG.dwg [Bd33_0709.ecw] Feb-08 FINAL

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE — ENVIRONMENT WAIKATO

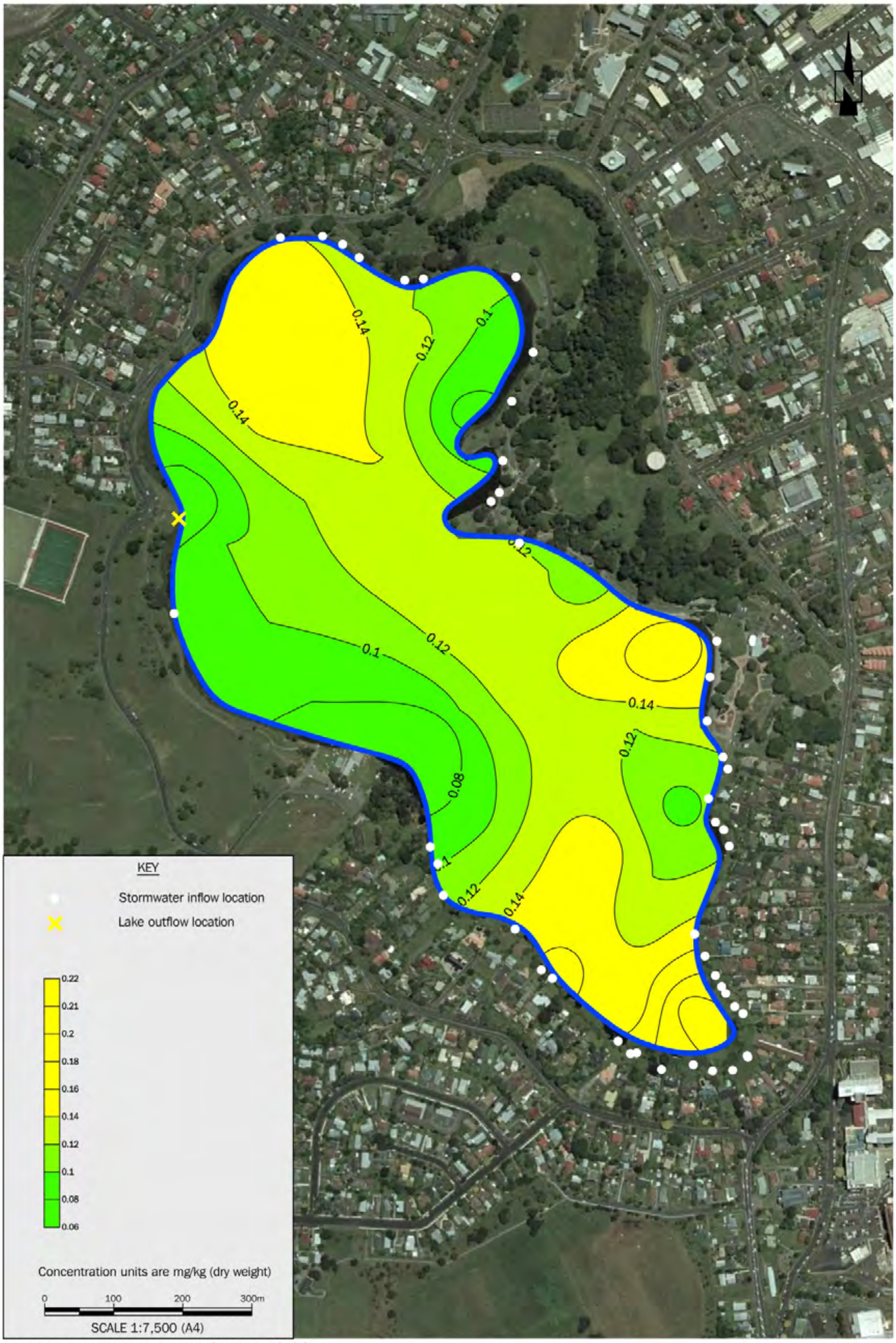


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Figure A.8 : DISTRIBUTION OF MERCURY IN SURFICIAL SEDIMENTS EXCLUDING HOT SPOT

PATTLE DELAMORE PARTNERS LTD

A02029101D001_NZMG.dwg [Bd33_0709.ecw] Feb–08 FINAL

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE – ENVIRONMENT WAIKATO

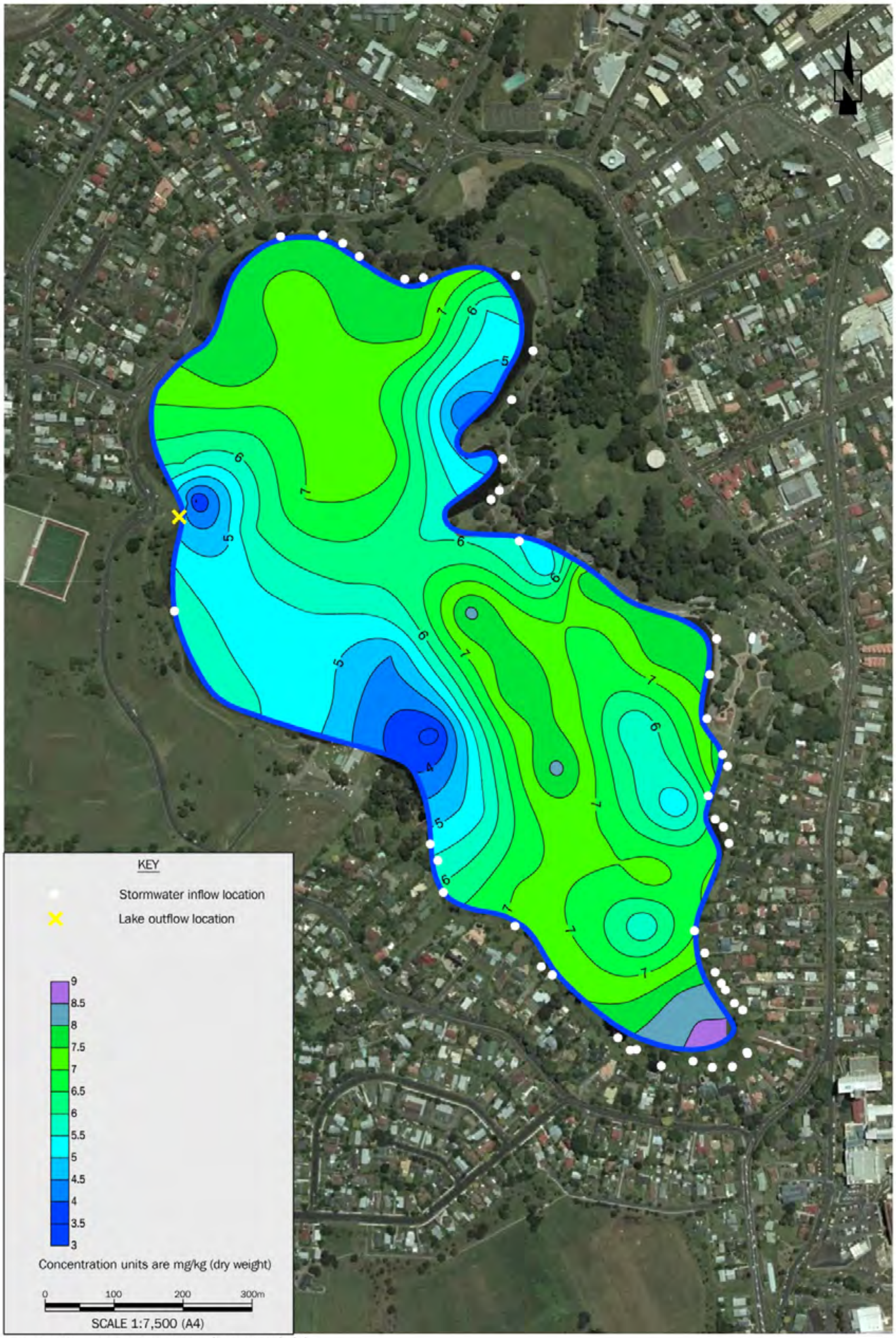

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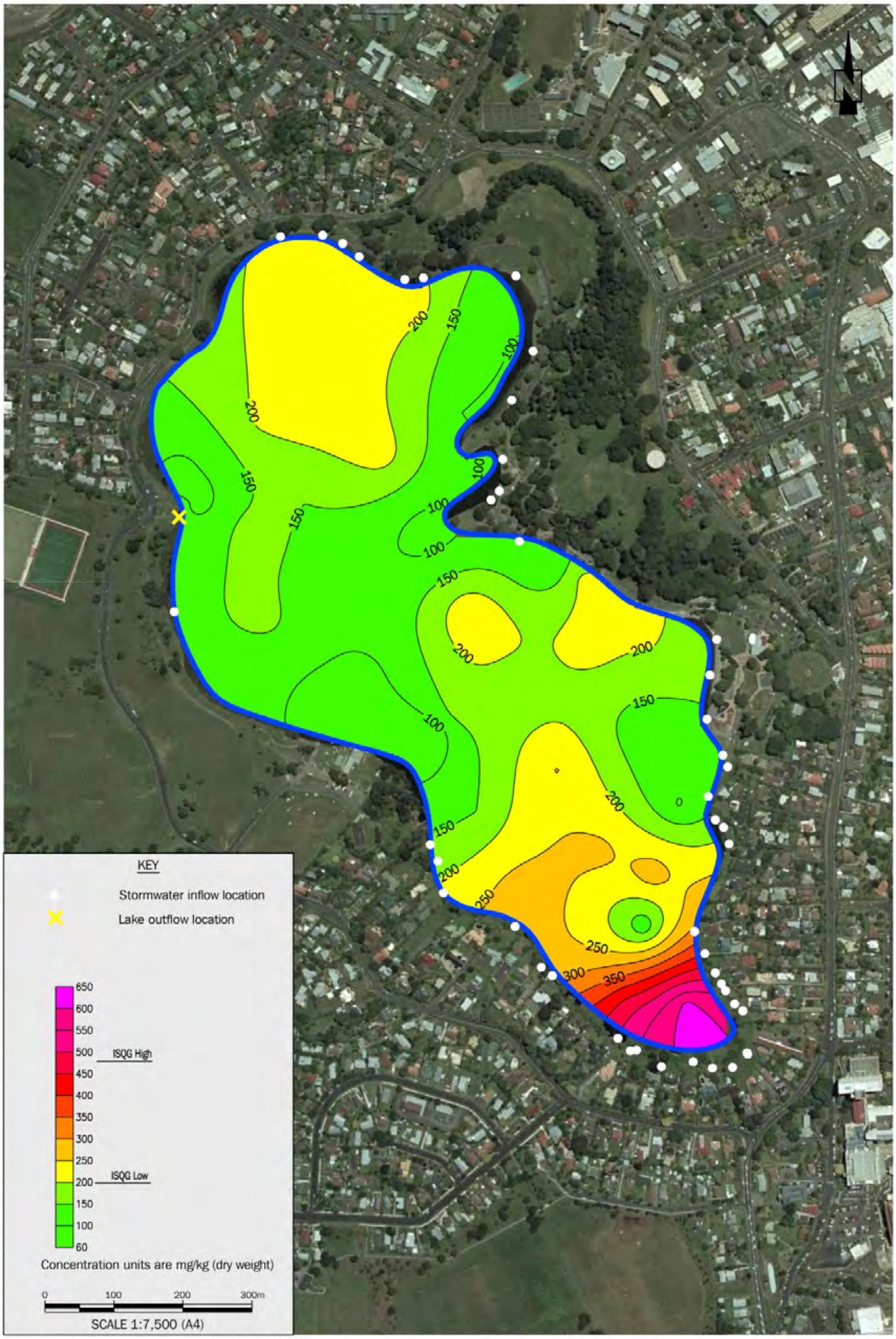
Figure A.9: DISTRIBUTION OF NICKEL IN SURFICIAL SEDIMENTS

PATTLE DELAMORE PARTNERS LTD

A02029101D001_NZMG.dwg [Bd33_0709.ecw] Feb–08 FINAL

SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE — ENVIRONMENT WAIKATO



Source: Base data supplied by Environment Waikato (Received on 17/10/07)

Figure A.10: DISTRIBUTION OF ZINC IN SURFICIAL SEDIMENTS

PATTLE DELAMORE PARTNERS LTD

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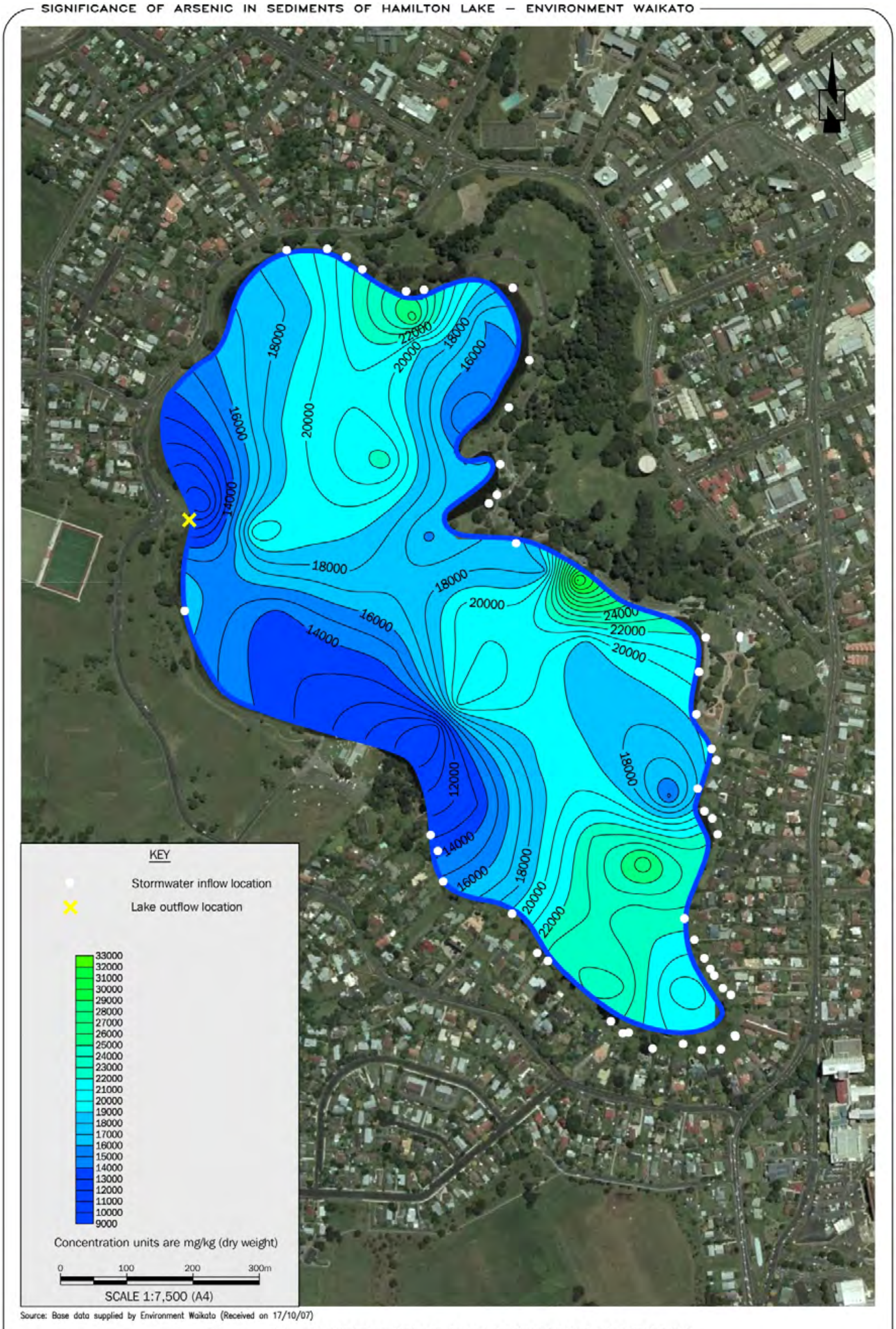

Source: Base data supplied by Environment Waikato (Received on 17/10/07)

Figure A.11: DISTRIBUTION OF IRON IN SURFICIAL SEDIMENTS

PATTLE DELAMORE PARTNERS LTD

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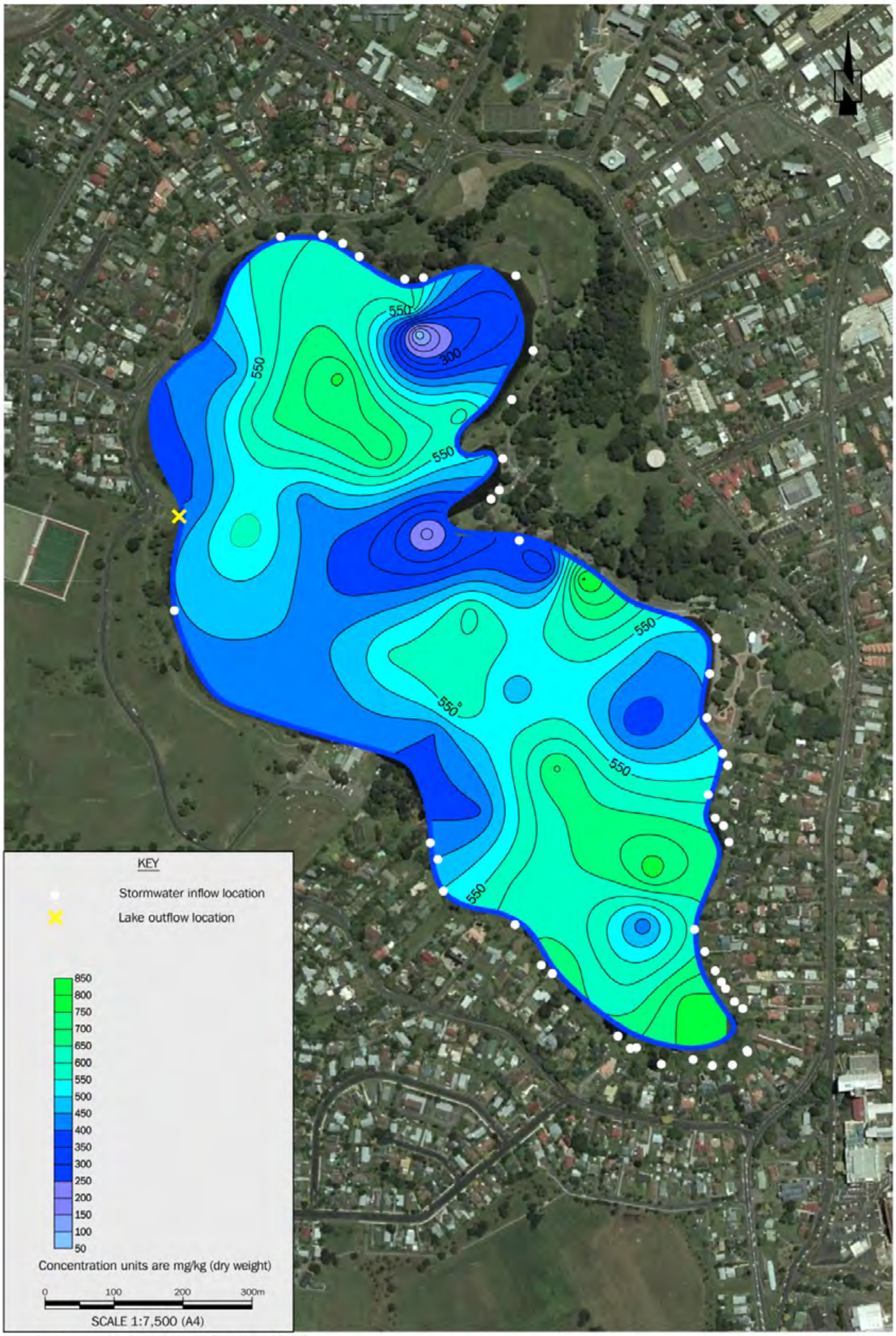
SIGNIFICANCE OF ARSENIC IN SEDIMENTS OF HAMILTON LAKE – ENVIRONMENT WAIKATO



Source: Base data supplied by Environment Waikato (Received on 17/10/07)

Figure A.12 : DISTRIBUTION OF PHOSPHORUS IN SURFICIAL SEDIMENTS

PATTLE DELAMORE PARTNERS LTD

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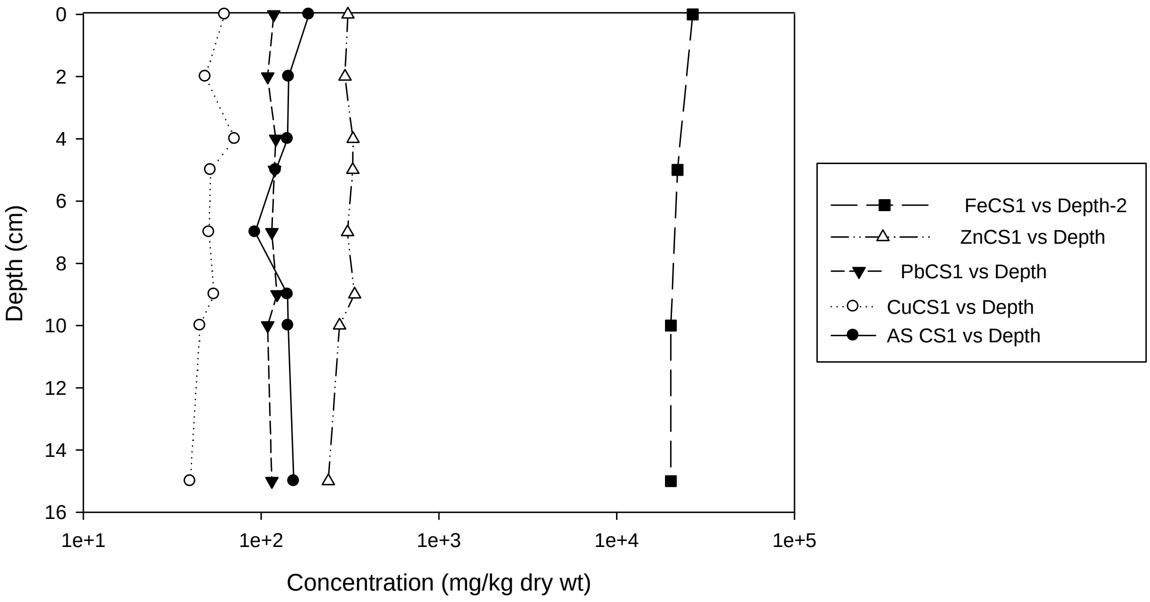

Figure A1: Concentration of Selected Metals versus Depth in CS1

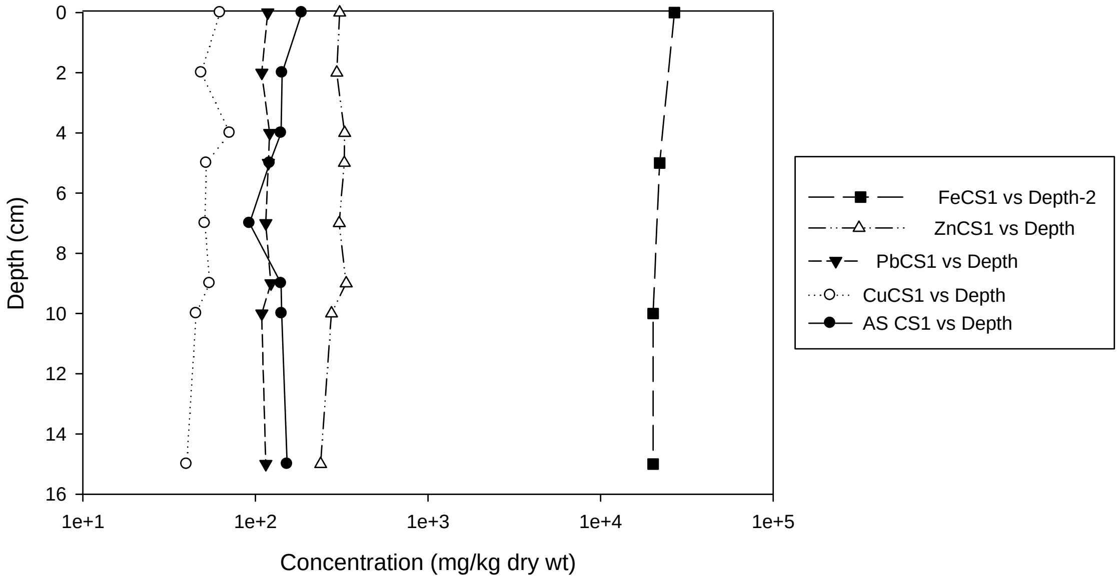

Figure A2: Concentration of Selected Metals versus Depth in CS2

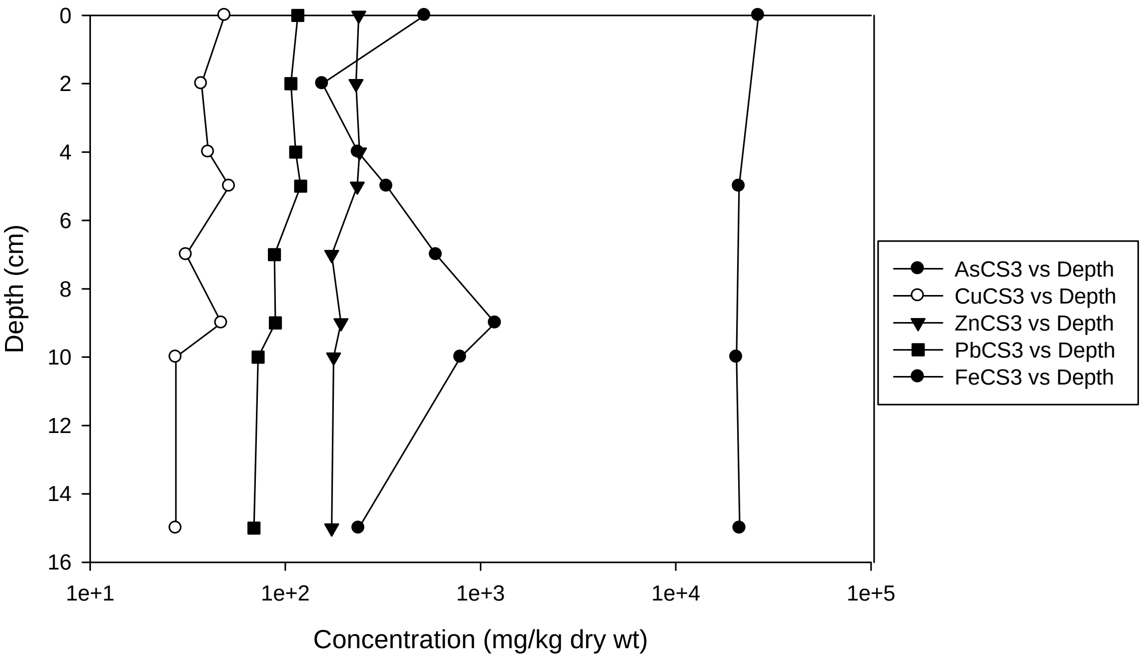

Figure A3: Concentration of Selected Metals versus Depth in CS3

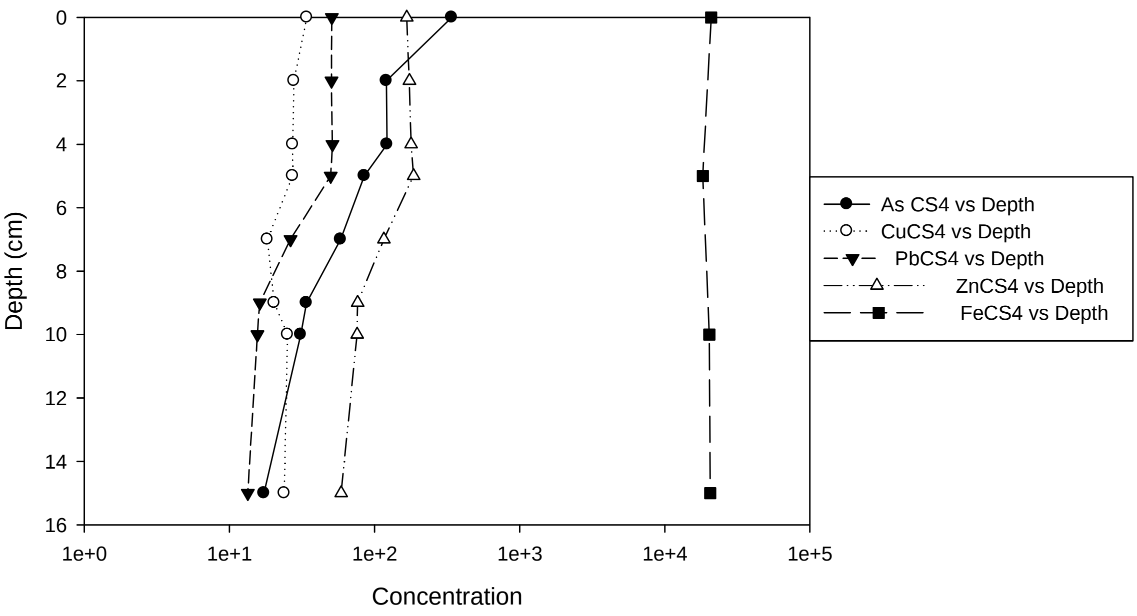

Figure A4: Concentration of Selected Metals versus Depth in CS4

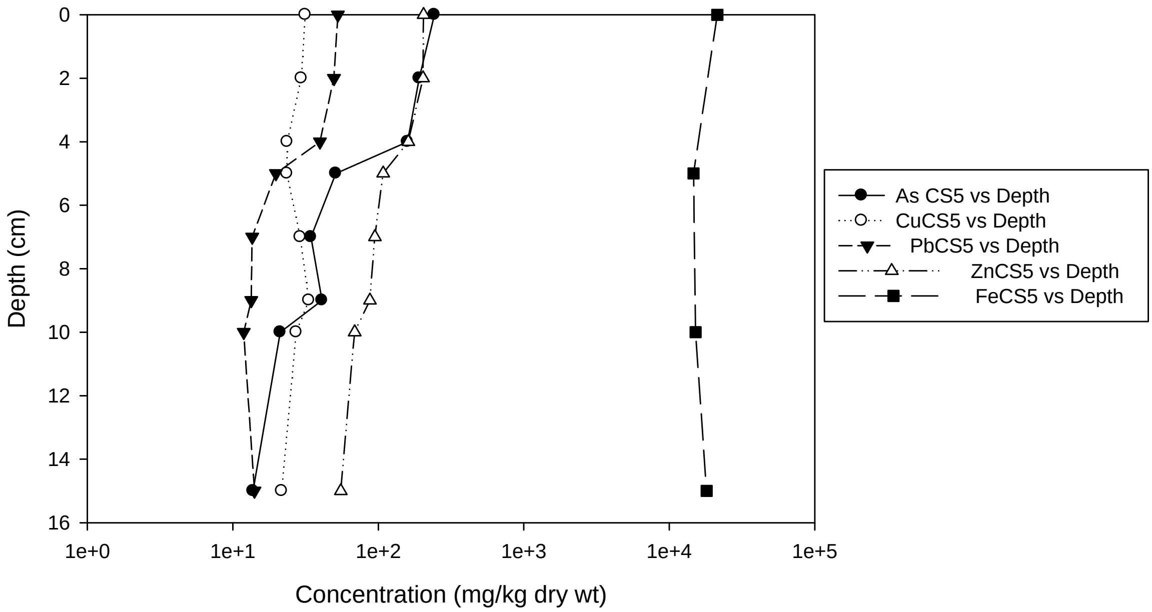

Figure A5: Concentration of Selected Metals versus Depth in CS5

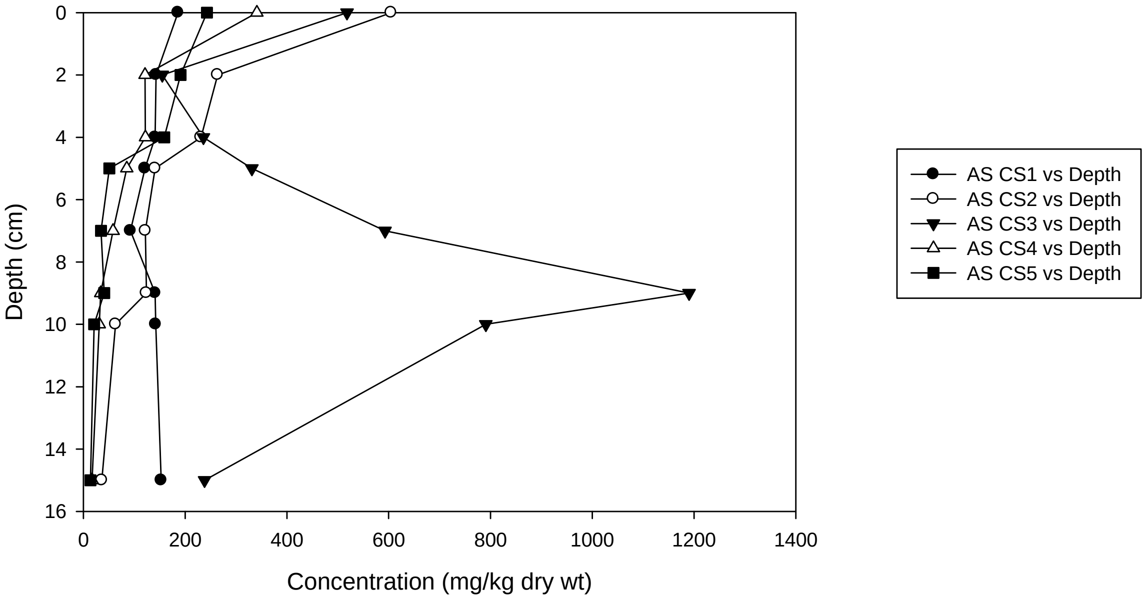

Figure A6: Concentration of Arsenic versus Depth all Cores

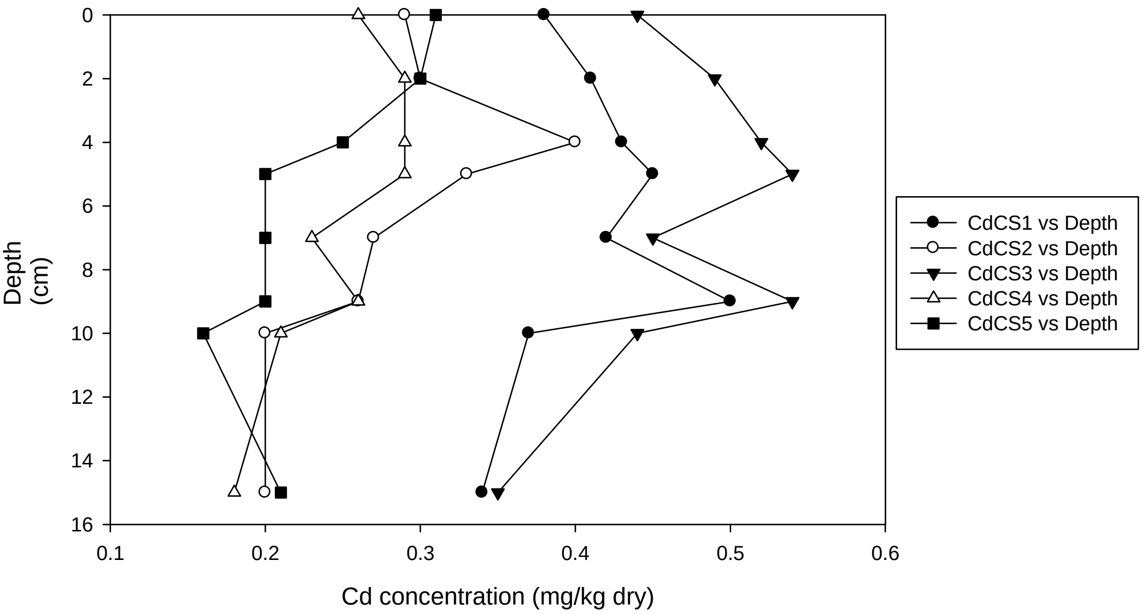

Figure A7: Concentration of Cadmium versus Depth all Cores

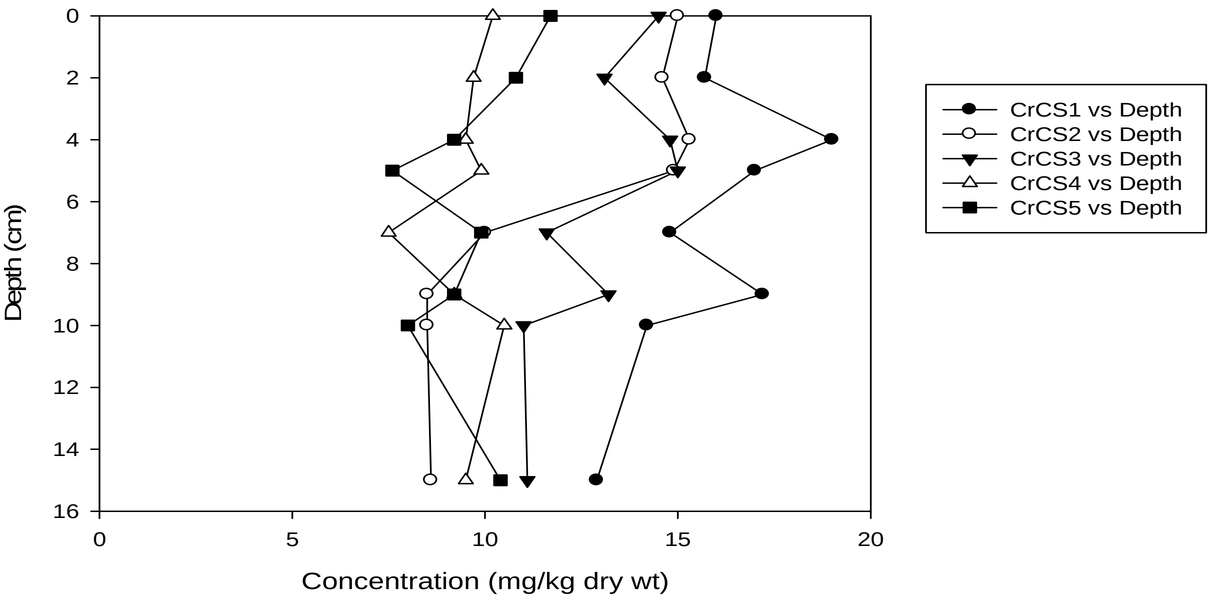

Figure A8: Concentration of Chromium versus Depth all Cores

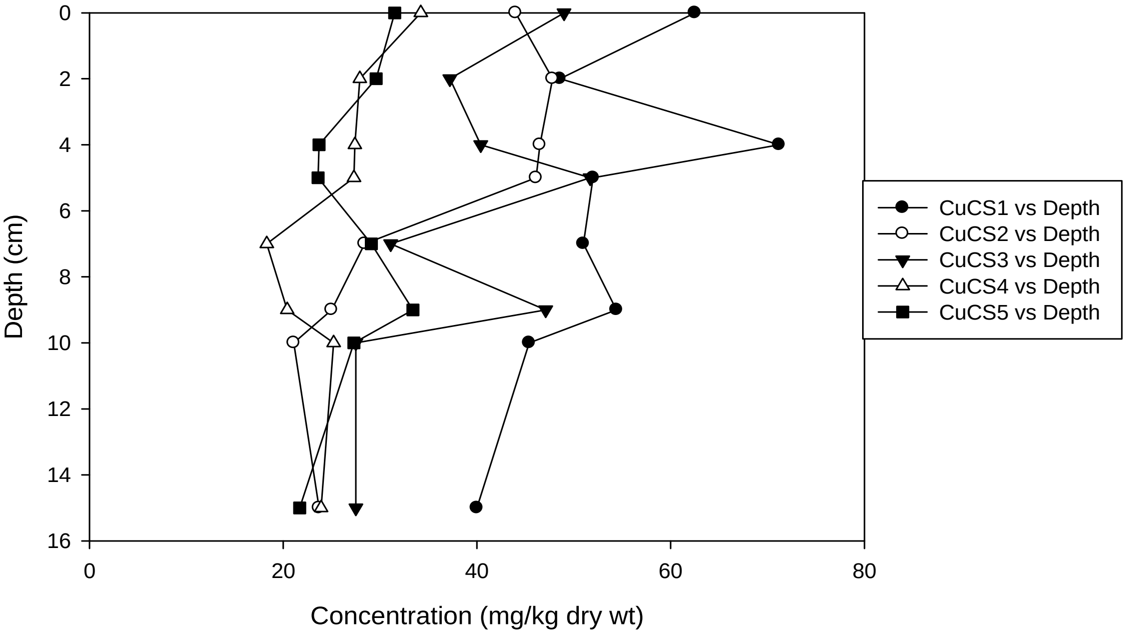

Figure A9: Concentration of Copper versus Depth all Cores

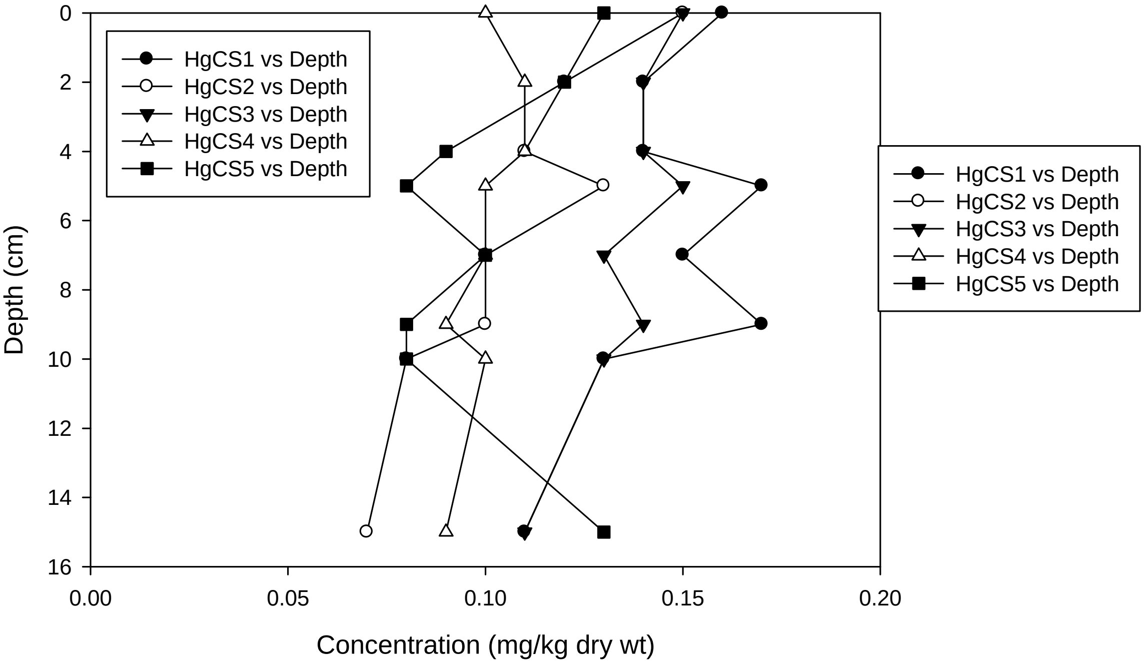

Figure A10: Concentration of Mercury versus Depth all Cores

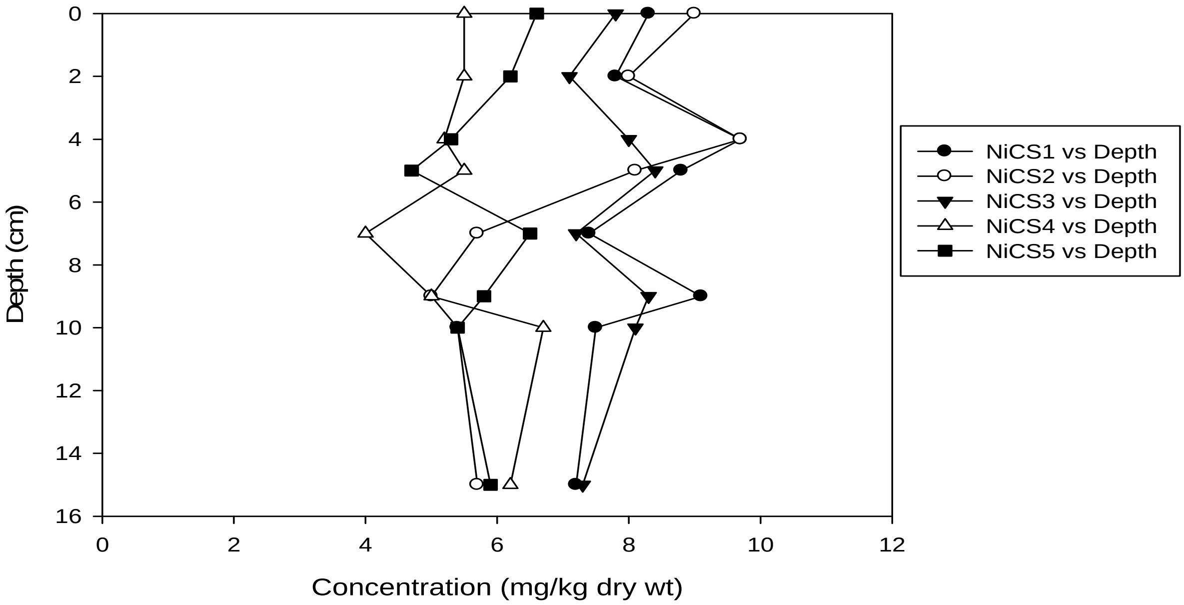

Figure A11: Concentration of Nickel versus Depth all Cores

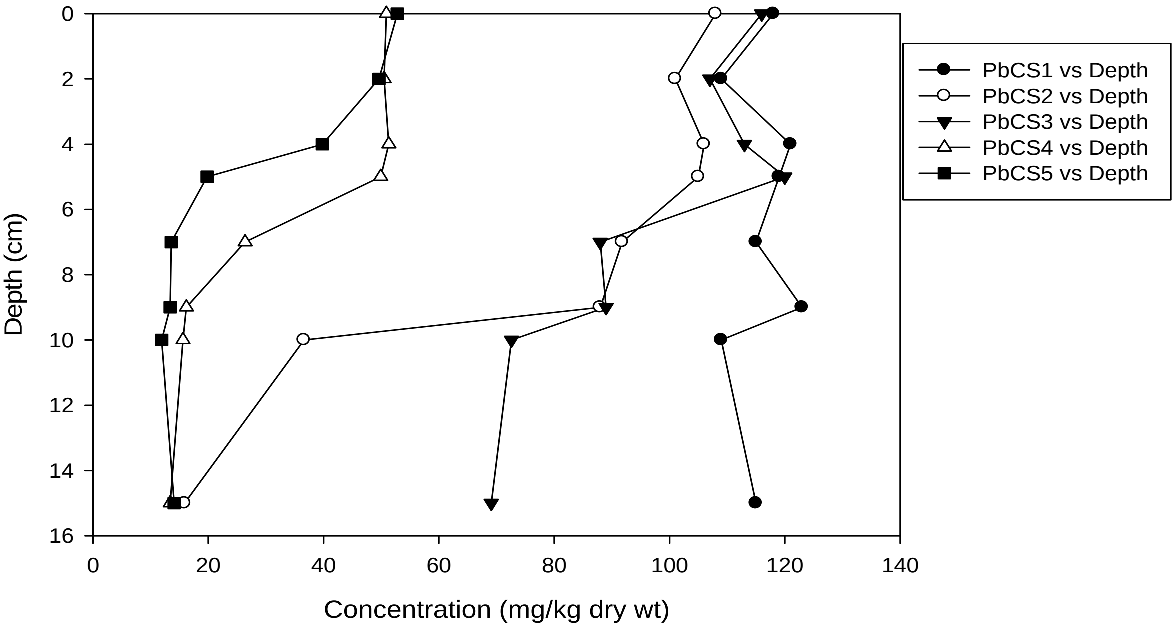

Figure A12: Concentration of Lead versus Depth all Cores

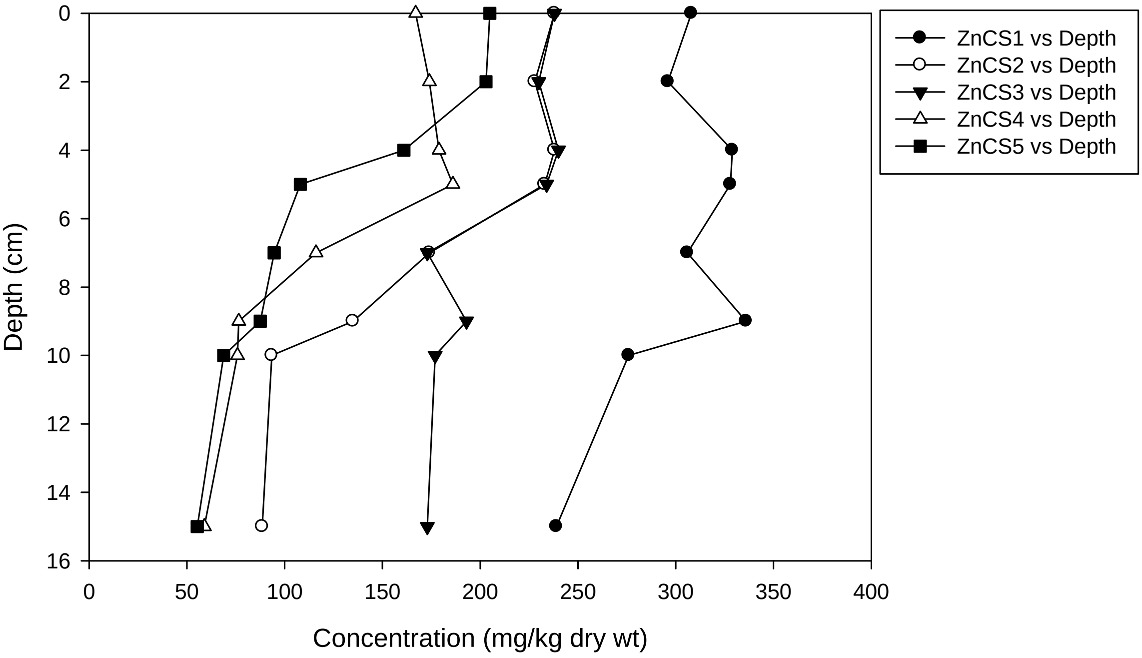

Figure A13: Concentration of Zinc versus Depth all Cores

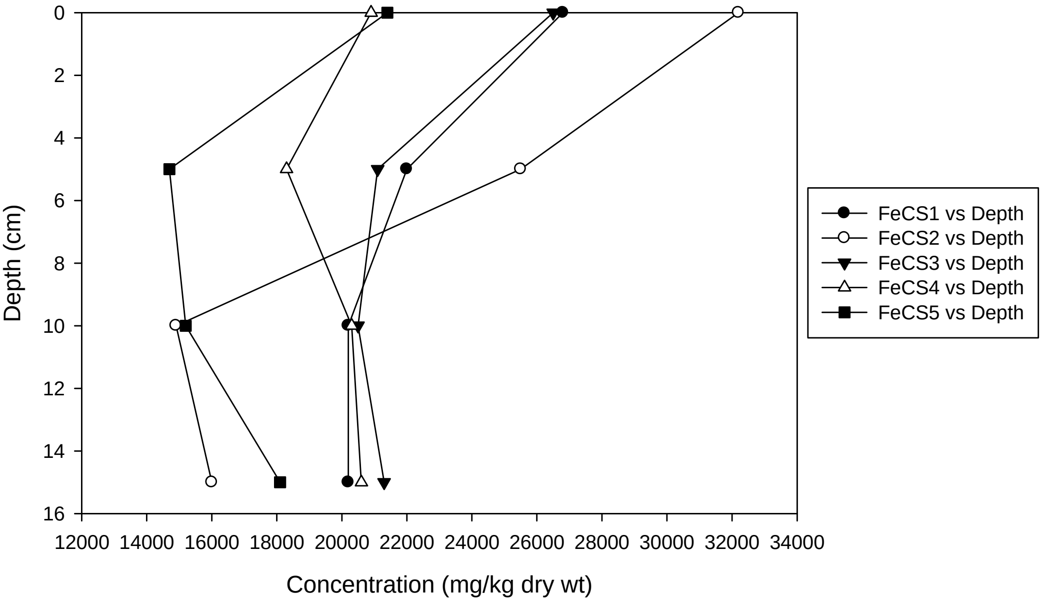

Figure A14: Concentration of Iron versus Depth all Cores

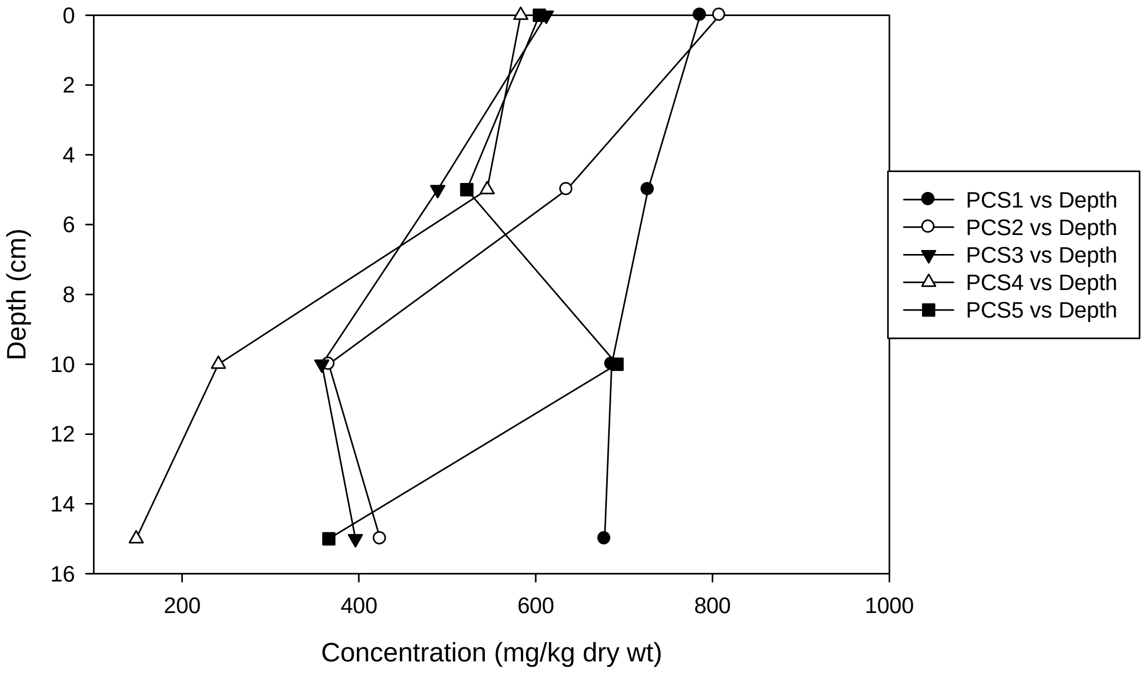

Figure A15: Concentration of Iron versus Depth all Cores

Appendix B: Background Data of Waikato River Arsenic Concentrations

TABLE B - 1: CONCENTRATIONS OF ARSENIC IN SEDIMENTS REPORTED FOR LAKE TAUPO, FIVE LAKES IN THE WAIKATO RIVER HYDROELECTRIC LAKE SYSTEM, AND THE WAIKATO RIVER SEDIMENTS

LAKE	LAKE AREA (KM^2)	REPORTED ARSENIC CONCENTRATIONS IN SEDIMENTS (MG/KG DRY WEIGHT)	SOURCE DOCUMENT
Taupo		7.9	Hickey et al. (1995)
Huka Falls	-	8.7	Robinson et al (1995)
Aratiatia	0.6	*69.4*	Hickey et al. (1995)
		37.1	Robinson et al (1995)
Ohakuri	12.9	**111**	Hickey et al. (1995)
		27.3	Robinson et al (1995)
		103, 1340	Timperley (2006)
		[1] Mean of **335 mg/kg** over 48 core samples; [2] Mean of **484 mg/kg** in cores about 1 km from southern end of lake; [3] Mean of **420 mg/kg** in vicinity of Ohakuri dam; [4] Mean of **116 mg/kg** in Whirinaki arm about 6 km from the dam; [5] Maximum observed in surface sediments of the Waikato River section of the lake: over **6000 mg/kg**.	Aggett and Aspell (1980) and Aggett and O'Brien (1985)
Atiamuri	2.2	*37.1*	Robinson et al (1995)
Whakamaru	7.1	*31.4*	Robinson et al (1995)
Maraetai	5.1	**101, 233**	Hickey et al. (1995)
		28.4	Robinson et al (1995)
Waipapa	1.6	**859, 1520**	Hickey et al. (1995)
		156.1	Robinson et al (1995)
Arapuni	*9.5*	*27.6*	*Robinson et al (1995)*
Karapiro	7.7	**222**	Hickey et al. (1995)
		41.7	Robinson et al (1995)
Hamilton (Cobham Bridge)	-	*60.1*	Hickey et al. (1995)
Ngaruawahia	-	19.6	Robinson et al, (1995)
Rangariri	-	*57.1*	Robinson et al, (1995)
Port Waikato	-	*27.3*	Robinson et al, (1995)
Raglan	-	12.1	Robinson et al, (1995)

TABLE B - 1: CONCENTRATIONS OF ARSENIC IN SEDIMENTS REPORTED FOR LAKE TAUPO, FIVE LAKES IN THE WAIKATO RIVER HYDROELECTRIC LAKE SYSTEM, AND THE WAIKATO RIVER SEDIMENTS

LAKE	LAKE AREA (KM^2)	REPORTED ARSENIC CONCENTRATIONS IN SEDIMENTS (MG/KG DRY WEIGHT)	SOURCE DOCUMENT

Note: Numbers in italics exceed the ANZECC (2000) guidelines low effects threshold for arsenic in sediments (ISQG-Low, 20 mg/kg). Numbers in bold exceed the ANZECC (2000) guidelines high effects threshold for arsenic in sediments (ISQG-High, 70 mg/kg). Estimated lake areas are taken from Aggett and O'Brien (1985).

Appendix C: Results

Table C- 1: Sampling Location, Water Depth and Chemical Analysis for Sediment Grab Samples from Lake Rotoroa, Hamilton

Sample Location	Depth m	Northing	Easting	Arsenic mg/kg	Cadmium mg/kg	Chromium mg/kg	Copper mg/kg	Mercury mg/kg	Nickel mg/kg	Lead mg/kg	Zinc mg/kg	Iron mg/kg	Phosphorus mg/kg
IQSG-low				20	1.5	80	65	0.15	21	50	200		
ISQG-high				70	10	370	270	1	52	220	410		
SDH01	3.0	6375396	2710603	171	0.39	13.2	41.4	0.14	7.1	97.1	278	17600	627
SDH02	2.3	6375283	2710666	592	0.47	13.2	39	0.17	7.4	104	281	23800	684
SDH03	2.2	6375234	2710757	143	0.48	15.9	40.5	0.14	7.5	140	469	24300	620
SDH04	2.5	6375232	2710843	145	0.68	23.1	114	0.21	8.4	303	613	19400	775
SDH05	2.9	6375346	2710780	57.5	0.25	8.9	20.1	0.13	5.5	37.6	114	22200	411
SDH06	1.4	6375522	2710831	47.2	0.2	8.5	24.3	0.09	5	20.6	96.6	14800	604
SDH07	5.6	6375459	2710717	168	0.37	14.1	40.7	0.16	7.1	109	260	23100	675
SDH08	4.6	6375636	2710768	248	0.27	9.9	18.8	0.12	5.5	83.5	121	18100	357
SDH09	3.3	6375740	2710800	154	0.43	16.6	30.9	0.18	7.8	177	197	20400	446
SDH10	4.1	6375750	2710705	149	0.32	13	39.7	0.15	6.6	88.8	214	18200	587
SDH11	1.9	6375863	2710642	59.6	0.28	8.3	17.2	0.12	5.1	29.9	99.9	17800	317
SDH12	1.1	6375914	2710466	36.6	0.2	10.6	27.5	0.14	5.9	23.4	71.8	15800	172
SDH13	2.0	6376091	2710517	85.4	0.17	7.3	17.3	0.07	4	34.1	100	14100	616
SDH14	2.7	6376205	2710454	409	0.39	12.8	33.1	0.13	7.6	105	183	19400	55
SDH15	2.0	6376239	2710552	53.2	0.35	8.3	20.2	0.1	5.5	39.7	106	16000	302
SDH16	2.9	6376256	2710277	185	0.41	14.3	37.9	0.15	7.2	135	216	18300	625
SDH17	2.5	6376153	2710185	559	0.43	12.6	35.4	0.15	7.9	109	191	16800	437
SDH18	5.5	6376142	2710340	138	0.35	13.9	41.8	0.15	7.3	102	224	20900	762

Table C- 1: Sampling Location, Water Depth and Chemical Analysis for Sediment Grab Samples from Lake Rotoroa, Hamilton (continued)

Sample Location	Depth m	Northing	Easting	Arsenic mg/kg	Cadmium mg/kg	Chromium mg/kg	Copper mg/kg	Mercury mg/kg	Nickel mg/kg	Lead mg/kg	Zinc mg/kg	Iron mg/kg	Phosphorus mg/kg
IQSG-low				20	1.5	80	65	0.15	21	50	200		
ISQG-high				70	10	370	270	1	52	220	410		
SDH19	4.0	6376079	2710226	149	0.36	13.4	37.9	0.15	6.7	100	211	18400	642
SDH20	0.8	6376016	2710112	60.7	0.18	8	22.4	0.08	6	24.8	91.5	10700	379
SDH21	0.5	6375962	2710131	74.8	0.13	5.8	13.8	0.06	3.4	25.2	69.5	9070	405
SDH22	1.4	6375902	2710175	129	0.25	9.2	23.5	0.1	4.9	46.9	147	15700	544
SDH23	2.6	6375965	2710289	483	0.34	10.3	25.6	0.12	7	68.4	151	19600	431
SDH24	5.2	6376028	2710403	155	0.36	14.2	42	0.14	7.5	100	222	22500	732
SDH25	1.8	6375852	2710352	75.7	0.26	8.8	21.5	0.32	6.1	31.3	102	17800	367
SDH26	1.1	6375789	2710238	120	0.25	9.4	26.1	0.1	5.3	50	159	13200	457
SDH27	1.2	6375675	2710301	43.3	0.17	8.3	23.9	0.08	5.4	13.1	83.8	12700	414
SDH28	1.3	6375738	2710415	67.5	0.16	7.8	25.8	0.1	4.5	21.8	108	14700	559
SDH29	3.1	6375801	2710528	184	0.37	13.9	43.5	0.14	8.2	102	248	20800	617
SDH30	1.7	6375624	2710478	25	0.12	5.2	11.6	0.06	3.3	10.4	68.6	9000	400
SDH31	2.7	6375687	2710591	425	0.33	11.3	29	0.13	8	72.9	173	20800	471
SDH32	1.6	6375510	2710540	72.4	0.22	8.6	24.8	0.09	5.3	52.3	152	12900	390
SDH33	5.0	6375573	2710657	145	0.32	14.1	45.9	0.13	8.2	100	252	19800	709
SDH34	0.3	2710120	6375959	84.6	0.17	8.2	22.2	0.07	4.5	44.2	108		

Table C- 2: Extended element suite of inorganic analytes in composite samples.

		Composite 1	**Composite 2**	**Composite 3**	**Composite 4**	**ISQG-low**	**ISQG-high**
Dry Matter	g/100g as rcvd	15.7	19.2	13.4	15.9		
TOC	g/100g	11.6	9.27	11.5	10.7		
Aluminum	mg/kg	47300	48400	43300	51300		
Arsenic	mg/kg	170	199	197	149	20	70
Antimony	mg/kg	2.46	2.22	2.17	1.74	2	25
Bismuth	mg/kg	0.3	0.32	0.27	0.25		
Boron	mg/kg	6	5	6	5		
Cadmium	mg/kg	0.47	0.43	0.39	0.34	1.5	10
Cesium	mg/kg	553	457	471	569		
Chromium	mg/kg	14.3	13.3	11.7	11.7	80	370
Cobalt	mg/kg	13.1	13.2	13.4	11.6		
Copper	mg/kg	56.1	31.7	30.6	31.2	65	270
Iron	mg/kg	18900	19900	15200	17400		
Lanthanum	mg/kg	22.2	27.5	29.1	26.1		
Lead	mg/kg	124	100	62.4	59.2	50	220
Lithium	mg/kg	0.3	0.32	0.27	0.25		
Magnesium	mg/kg	13.1	13.2	13.4	11.6		
Manganese	mg/kg	3.04	3.86	2.72	2.61		
Mercury	mg/kg	0.14	0.14	0.13	0.13	0.15	1
Molybdenum	mg/kg	0.91	0.87	1.03	0.93		
Nickel	mg/kg	8.1	7.2	7.1	6.4	21	52
Phosphorus	mg/kg	553	457	471	569		
Potassium	mg/kg	605	608	494	583		
Rubidium	mg/kg	10.1	15.1	9.48	9.5		
Selenium	mg/kg	2	3	3	3		
Sliver	mg/kg	0.2	0.22	0.22	0.21	1	3.7
Sodium	mg/kg	326	298	300	388		
Strontium	mg/kg	44.3	41.2	44.1	46.1		
Tin	mg/kg	4	5.2	3.3	3.2		
Titanium	mg/kg	0.5	0.48	0.5	0.52		
Uranium	mg/kg	1.4	1.56	1.42	1.29		
Vanadium	mg/kg	55	67	66	64		
Zinc	mg/kg	349	184	167	180	200	410

Table C- 3: Analysis of Concentration of Poly-aromatic Hydrocarbons (PAHs) in Composite samples of Hamilton Lake Sediments.

Sample Name:	**Composite 1**	**Composite 2**	**Composite 3**	**Composite 4**
Units:	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
Acenaphthene	< 0.2	< 0.1	< 0.2	< 0.2
Acenaphthylene	< 0.2	< 0.1	< 0.2	< 0.2
Anthracene	< 0.2	< 0.1	< 0.2	< 0.2
Benzo[a]anthracene	< 0.2	0.3	< 0.2	< 0.2
Benzo[a]pyrene (BAP)	< 0.2	0.7	< 0.2	< 0.2
Benzo[b]fluoranthene	< 0.2	1	< 0.2	< 0.2
Benzo[g,h,i]perylene	< 0.2	0.6	< 0.2	< 0.2
Benzo[k]fluoranthene	< 0.2	0.8	< 0.2	< 0.2
Chrysene	< 0.2	0.5	< 0.2	< 0.2
Dibenzo[a,h]anthracene	< 0.2	< 0.1	< 0.2	< 0.2
Fluoranthene	< 0.2	1.1	< 0.2	< 0.2
Fluorene	< 0.2	< 0.1	< 0.2	< 0.2
Indeno[1,2,3-c,d]pyrene	< 0.2	0.3	< 0.2	< 0.2
Naphthalene	< 0.8	< 0.6	< 0.9	< 0.8
Phenanthrene	< 0.2	0.2	< 0.2	< 0.2
Pyrene	0.2	1.4	0.2	< 0.2

Table C- 4: Analysis of Organo-chlorine Pesticides Residues in the Composite Samples of Lake Rotoroa Sediments.

Sample Name:	**Composite1**	**Composite 2**	**Composite 3**	**Composite 4**
Lab No:	**455032 / 34**	**455032 / 35**	**455032 / 36**	**455032 / 37**
Units:	mg/kg	mg/kg	mg/kg	mg/kg
2,4'-DDD	< 0.01	< 0.01	< 0.01	< 0.01
2,4'-DDE	< 0.01	< 0.01	< 0.01	< 0.01
2,4'-DDT	< 0.01	< 0.01	< 0.01	< 0.01
4,4'-DDD	< 0.01	< 0.01	< 0.01	< 0.01
4,4'-DDE	< 0.01	< 0.01	< 0.01	< 0.01
4,4'-DDT	< 0.01	< 0.01	< 0.01	< 0.01

Table C- 4: Analysis of Organo-chlorine Pesticides Residues in the Composite Samples of Lake Rotoroa Sediments (continued).

Sample Name:	**Composite1**	**Composite 2**	**Composite 3**	**Composite 4**
Lab No:	**455032 / 34**	**455032 / 35**	**455032 / 36**	**455032 / 37**
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01
Alpha-BHC	< 0.01	< 0.01	< 0.01	< 0.01
Beta-BHC	< 0.01	< 0.01	< 0.01	< 0.01
Delta-BHC	< 0.01	< 0.01	< 0.01	< 0.01
Gamma-BHC (Lindane)	< 0.01	< 0.01	< 0.01	< 0.01
Cis-Chlordane	< 0.01	< 0.01	< 0.01	< 0.01
Trans-Chlordane	< 0.01	< 0.01	< 0.01	< 0.01
Total Chlordane ((cis+trans)*100/42)	< 0.05	< 0.05	< 0.05	< 0.05
Dieldrin	< 0.01	< 0.01	< 0.01	< 0.01
Endosulphan I	< 0.01	< 0.01	< 0.01	< 0.01
Endosulphan II	< 0.01	< 0.01	< 0.01	< 0.01
Endosulphan sulphate	< 0.01	< 0.01	< 0.01	< 0.01
Endrin	< 0.01	< 0.01	< 0.01	< 0.01
Endrin aldehyde	< 0.01	< 0.01	< 0.01	< 0.01
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.01
Heptachlor epoxide	< 0.01	< 0.01	< 0.01	< 0.01
Hexachlorobenzene	< 0.01	< 0.01	< 0.01	< 0.01
Methoxychlor	< 0.01	< 0.01	< 0.01	< 0.01

Table C- 5: Analysis of Core Samples Taken at Selected Location in Lake Rotoroa.

Sample Location	Depth m	Northing	Easting	Arsenic mg/kg	Cadmium mg/kg	Chromium mg/kg	Copper mg/kg	Mercury mg/kg	Nickel mg/kg	Lead mg/kg	Zinc mg/kg	Iron mg/kg	Phosphorus mg/kg
ISQG-low				20	1.5	80	65	0.15	21	50	200		
ISQG-high				70	10	370	270	1	52	220	410		
CS1 0-5	4.8	6375424	2710790	156	0.33	14.3	44.3	0.12	7.4	108	278	26800	786
CS1 5-10	4.8	6375424	2710790	137	0.39	15.5	49.7	0.13	8.6	107	302	22000	727
CS1 10-15	4.8	6375424	2710790	142	0.37	14.2	45.4	0.13	7.5	109	276	20200	686
CS1 15-20	4.8	6375424	2710790	153	0.34	12.9	40	0.11	7.2	115	239	20200	678
CS2 0-5	1.6	6375850	2710690	382	0.24	13	39.2	0.1	7.8	94.8	212	32200	808
CS2 5-10	1.6	6375850	2710690	167	0.24	11.1	31.3	0.27	6.6	109	175	25500	635
CS2 10-15	1.6	6375850	2710690	63.5	0.2	8.5	21.1	0.08	5.4	36.6	93.5	14900	366
CS2 15-19	1.6	6375850	2710690	36.2	0.2	8.6	23.7	0.07	5.7	15.9	88.6	16000	424
CS3 0-5	2.0	6376245	2710442	309	0.42	13.8	39.7	0.12	7.8	113	233	26500	612
CS3 5-10	2.0	6376245	2710442	651	0.48	13.6	36.9	0.12	8.6	102	218	21100	489
CS3 10-15	2.0	6376245	2710442	791	0.44	11	27.5	0.13	8.1	72.6	177	20500	358
CS3 15-20	2.0	6376245	2710442	238	0.35	11.1	27.5	0.11	7.3	69.1	173	21300	396
CS4 0-5	1.5	6375924	2710205	207	0.24	10.1	29.2	0.1	5.9	50.7	168	20900	583
CS4 5-10	1.5	6375924	2710205	91.2	0.23	9	23	0.1	4.9	35.9	144	18300	545
CS4 10-15	1.5	6375924	2710205	31.1	0.21	10.5	25.2	0.1	6.7	15.6	75.9	20300	241

Table C- 5: Analysis of Core Samples Taken at Selected Location in Lake Rotoroa (continued)

Sample Location	Depth m	Northing	Easting	Arsenic mg/kg	Cadmium mg/kg	Chromium mg/kg	Copper mg/kg	Mercury mg/kg	Nickel mg/kg	Lead mg/kg	Zinc mg/kg	Iron mg/kg	Phosphorus mg/kg
CS4 15-20	1.5	6375924	2710205	17.3	0.18	9.5	23.9	0.09	6.2	13.4	58.9	20600	148
CS5 0-5	1.7	6375666	2710510	228	0.24	9.9	26.8	0.1	5.5	45.5	185	21400	604
CS5 5-10	1.7	6375666	2710510	47.3	0.19	8.3	24.2	0.1	5.5	17.6	99.6	14700	522
CS5 10-15	1.7	6375666	2710510	21.2	0.16	8	27.3	0.08	5.4	11.9	68.8	15200	692
CS5 15-20	1.7	6375666	2710510	13.8	0.21	10.4	21.7	0.13	5.9	14.1	55.3	18100	366

Table C- 6: Water Quality Analysis of Surface Water in Lake Rotoroa

	Units	SWH001	SWH002	SWH003	SWH004	LRW001	Water Quality Guidelines[1]	NZ DWS (2005)[2]
Sampling Date		25 May 2007	25 May 2007	25 May 2007	25 May 2007	13 Sept 2007		
Water Depth	m	5.3	1.5	5	0.3	0.35		
Sample Location		**Southern Section**	**Northern Section**	**Central Section**	**Discharge out of lake**	**In front of boat club**		
pH-Field	pH units	7.02	7.02	7.27	7.37		6-9	7.0-8.5

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[1] ANZECC (2000) Trigger values for 95% freshwater ecosystem protection.

[2] New Zealand Drinking Water Standards (2005)

ph-Lab	pH units	7	7.2	7.2	7.2	7.2	6-9	7.0-8.5

Table C- 6: Water Quality Analysis of Surface Water in Lake Rotoroa (continued)

	Units	SWH001	SWH002	SWH003	SWH004	LRW001	Water Quality Guidelines[1]	NZ DWS (2005)[2]
Dissolved Oxygen	mg/L	11.98	12.5	11.77	11.6		-	
Dissolved Oxygen	% sat. (calculated)	122	127	119	118		>80%	
Temp	°C	16.3	16	16	16.2	15.8	-	
Conductivity-field	mS/m	10.2	10.2	10.3	10.1		-	
Conductivity-lab	mS/m	12.3	12.3	12.2	12.1	11.9	-	
Redox Potential	mV	209	218	216	205		-	
Dissolved Arsenic	mg/L	0.009	0.009	0.009	0.009	0.007	0.024/0.013	
Total Arsenic	mg/L					0.008		0.010
Dissolved Antimony	mg/L					0.0002	ID (0.009)	
Total Antimony	mg/L					<0.0002		0.02
Dissolved Cadmium	mg/L					<0.00005	0.0002	
Total Cadmium	mg/L					<0.00005		0.004
Dissolved Chromium	mg/L					<0.0005	0.001	
Total Chromium	mg/L					<0.0005		0.05

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[1] ANZECC (2000) Trigger values for 95% freshwater ecosystem protection.

[2] New Zealand Drinking Water Standards (2005)

Dissolved Copper	mg/L					0.001	0.0014	

Table C- 6: Water Quality Analysis of Surface Water in Lake Rotoroa (continued)

	Units	SWH001	SWH002	SWH003	SWH004	LRW001	Water Quality Guidelines[1]	NZ DWS (2005)[2]
Total Copper	mg/L					0.0011		2
Dissolved Mercury	mg/L					<0.00008	0.0006	
Total Mercury	mg/L					<0.00008		0.002
Dissolved Lead	mg/L	0.0002	0.0002	0.0002	0.0002	0.0004	0.0034	
Total Lead	mg/L					0.001		0.01
Dissolved Zinc	mg/L					0.004	0.008	
Total Zinc	mg/L					0.004		1.5

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[1] ANZECC (2000) Trigger values for 95% freshwater ecosystem protection.

[2] New Zealand Drinking Water Standards (2005)

Appendix D: Statistical Reports

Table D- 1: Descriptive Statistical Summary of Grab Samples.

	Size	**Missing**	**Mean**	**Std Dev**	**Std. Error**	**C.I. of Mean**
Arsenic	34	1	170	151	26.3	53.6
Cadmium	34	1	0.31	0.119	0.021	0.042
Chromium	34	1	11.3	3.6	0.6	1.3
Copper	34	1	32	17.6	3.1	6.2
Mercury	34	1	0.13	0.05	0.008	0.017
Nickel	34	1	6.3	1.4	0.25	0.51
lead	34	1	77.5	58.6	10.2	20.8
Zinc	34	1	184	114	19.8	40.4
Iron	34	1	17535	4005	697	1420
Phosphorus	34	1	503	169	29	60
	Range	**Max**	**Min**	**Median**	**5%**	**95%**
Arsenic	567	592	25	143	38	548
Cadmium	0.56	0.68	0.12	0.32	0.13	0.48
Chromium	17.9	23.1	5.2	10.6	6.03	16.50
Copper	102.4	114	11.6	27.5	14.31	45.54
Mercury	0.26	0.32	0.06	0.13	0.06	0.21
Nickel	5.1	8.4	3.3	6.6	3.49	8.20
lead	292.6	303	10.4	72.9	14.23	171.45
Zinc	544.4	613	68.6	159	69.85	440.80
Iron	15300	24300	9000	18100	9314.50	23695.00
Phosphorus	720	775	55	471	191.50	757.50
	Skewness	**Kurtosis**	**K-S Dist.**	**K-S Prob.**	**Sum**	**Sum of Squares**
Arsenic	1.697	2.06	0.279	<0.001	5609.9	1683774
Cadmium	0.721	1.368	0.0758	0.81	10.26	3.645
Chromium	0.924	1.885	0.123	0.229	372.8	4637.28
Copper	3.228	14.688	0.197	0.002	1057.1	43768.57
Mercury	1.792	6.376	0.191	0.004	4.3	0.636
Nickel	-0.421	-0.735	0.141	0.096	208.2	1378.54

Table D- 1: Descriptive Statistical Summary of Grab Samples (continued)

	Size	Missing	Mean	Std Dev	Std. Error	C.I. of Mean
lead	1.855	5.706	0.174	0.012	2557.8	308091.3
Zinc	2.133	6.044	0.155	0.042	6073.7	1532858
Iron	-0.426	-0.308	0.112	0.343	578670	1.07E+10
Phosphorus	-0.49	0.136	0.119	0.264	16589	9254379

Table D- 2: Descriptive Statistical Summary of Sediment Core Samples

Analyte	Size	Missing	Mean	Std Dev	Std. Error	C.I. of Mean
As	40	0	208.075	235.768	37.278	75.402
Cd	40	0	0.329	0.11	0.0174	0.0352
Cr	40	0	11.983	3.048	0.482	0.975
Cu	40	0	36.093	12.868	2.035	4.116
Hg	40	0	0.118	0.0266	0.0042	0.0085
Ni	40	0	6.865	1.478	0.234	0.473
Pb	40	0	71.13	40.805	6.452	13.05
Zn	40	0	188.02	81.281	12.852	25.995
Analyte	**Range**	**Max**	**Min**	**Median**	**5%**	**95%**
As	1176.2	1190	13.8	141	19.25	698
Cd	0.38	0.54	0.16	0.3	0.19	0.53
Cr	11.5	19	7.5	11.05	7.8	17.1
Cu	52.9	71.2	18.3	31.3	20.75	58.45
Hg	0.1	0.17	0.07	0.115	0.08	0.165
Ni	5.7	9.7	4	6.9	4.85	9.4
Pb	111.1	123	11.9	80.3	13.4	120.5
Zn	280.7	336	55.3	182.5	63.85	328.5
Analyte	**Skewness**	**Kurtosis**	**K-S Dist.**	**K-S Prob.**	**Sum**	**Sum of Squares**
As	2.54	7.522	0.241	<0.001	8323	3899679.64
Cd	0.381	-0.99	0.129	0.093	13.16	4.803
Cr	0.41	-0.937	0.139	0.05	479.3	6105.57
Cu	0.739	-0.16	0.168	0.006	1443.7	58564.95
Hg	0.129	-0.89	0.129	0.093	4.73	0.587

Table D- 2: Descriptive Statistical Summary of Sediment Core Samples (continued)

Analyte	Size	Missing	Mean	Std Dev	Std. Error	C.I. of Mean
Ni	0.144	-0.954	0.118	0.169	274.6	1970.36
Pb	-0.222	-1.587	0.172	0.004	2845.2	267315.28
Zn	0.0686	-0.89	0.0995	0.387	7520.8	1671716.86

Table D- 3: Descriptive Statistical Summary of Shallow Sediment Core Samples (0-2 cm)

Analyte	Size	Missing	Mean	Std Dev	Std. Error	C.I. of Mean
As	5	0	378.6	178.595	79.87	221.755
Cd	5	0	0.336	0.073	0.0326	0.0906
Cr	5	0	13.48	2.43	1.087	3.018
Cu	5	0	44.24	12.442	5.564	15.449
Hg	5	0	0.138	0.0239	0.0107	0.0296
Ni	5	0	7.44	1.394	0.623	1.731
Pb	5	0	89.14	34.253	15.318	42.53
Zn	5	0	231.2	51.959	23.237	64.515
Analyte	**Range**	**Max**	**Min**	**Median**	**5%**	**95%**
As	419	605	186	341	186	605
Cd	0.18	0.44	0.26	0.31	0.26	0.44
Cr	5.8	16	10.2	14.5	10.2	16
Cu	31	62.5	31.5	44	31.5	62.5
Hg	0.06	0.16	0.1	0.15	0.1	0.16
Ni	3.5	9	5.5	7.8	5.5	9
Pb	67.1	118	50.9	108	50.9	118
Zn	141	308	167	238	167	308
Analyte	**Skewness**	**Kurtosis**	**K-S Dist.**	**K-S Prob.**	**Sum**	**Sum of Squares**
As	0.338	-2.2	0.183	0.665	1893	844275
Cd	0.703	-1.003	0.239	0.404	1.68	0.586
Cr	-0.591	-1.819	0.263	0.291	67.4	932.18
Cu	0.674	-0.271	0.19	0.639	221.2	10405.14
Hg	-1.264	1.099	0.292	0.174	0.69	0.0975
Ni	-0.525	-0.998	0.202	0.589	37.2	284.54

Table D- 3: Descriptive Statistical Summary of Shallow Sediment Core Samples (0-2 cm) (continued)

Analyte	Size	Missing	Mean	Std Dev	Std. Error	C.I. of Mean
Pb	-0.558	-3.257	0.309	0.124	445.7	44422.65
Zn	0.508	0.962	0.248	0.36	1156	278066

Table D- 4: Descriptive Statistical Summary of Mid-depth Sediment Core Samples (2-10 cm)

Analyte	Size	Missing	Mean	Std Dev	Std. Error	C.I. of Mean
As	32	0	133	117	21	42
Cd	32	0	0.29	0.09	0.02	0.03
Cr	32	0	11.7	3.3	0.6	1.2
Cu	32	0	35.4	13.6	2.4	4.9
Hg	32	0	0.11	0.03	0.00	0.01
Ni	32	0	6.64	1.56	0.28	0.56
Pb	32	0	64.7	42.3	7.5	15.3
Zn	32	0	183	89	16	32
Analyte	**Range**	**Max**	**Min**	**Median**	**5%**	**95%**
As	591.2	605	13.8	122	17.69	333.3
Cd	0.34	0.5	0.16	0.29	0.182	0.448
Cr	11.5	19	7.5	10.3	7.64	17.18
Cu	52.9	71.2	18.3	29.35	20.47	61.69
Hg	0.1	0.17	0.07	0.11	0.08	0.169
Ni	5.7	9.7	4	6.2	4.73	9.64
Pb	111.1	123	11.9	51.1	13.4	120.8
Zn	280.7	336	55.3	176.5	59.89	328.9
Analyte	**Skewness**	**Kurtosis**	**K-S Dist.**	**K-S Prob.**	**Sum**	**Sum of Squares**
As	2.333	7.878	0.195	0.003	4271	992000
Cd	0.585	-0.476	0.127	0.209	9.39	3.00
Cr	0.614	-0.928	0.208	0.001	375	4727
Cu	0.887	0.00234	0.196	0.003	1132.2	45777
Hg	0.519	-0.552	0.161	0.034	3.64	0.44
Ni	0.529	-0.775	0.151	0.062	212.4	1485
Pb	0.0834	-1.73	0.179	0.01	2070.5	189531
Zn	0.218	-1.179	0.12	0.271	5862.8	1321381

Table D- 5: Descriptive Statistical Summary of Deep depth Sediment Core Samples (10+cm)

Analyte	**Size**	**Missing**	**Mean**	**Std Dev**	**Std. Error**	**C.I. of Mean**
As	6	0	208	299	122	314
Cd	6	0	0.29	0.11	0.04	0.11
Cr	6	0	10.6	1.5	0.6	1.6
Cu	6	0	27.4	6.6	2.7	6.9
Hg	6	0	0.11	0.02	0.01	0.02
Ni	6	0	6.7	0.9	0.4	1.0
Pb	6	0	50.0	42.2	17.2	44.3
Zn	6	0	132	75	31	79
Analyte	**Range**	**Max**	**Min**	**Median**	**5%**	**95%**
As	777	791	14	95	14	791
Cd	0.26	0.44	0.18	0.275	0.18	0.44
Cr	4.3	12.9	8.6	10.7	8.6	12.9
Cu	18.3	40	21.7	25.7	21.7	40
Hg	0.06	0.13	0.07	0.11	0.07	0.13
Ni	2.4	8.1	5.7	6.7	5.7	8.1
Pb	102	115	13	43	13	115
Zn	184	239	55	131	55	239
Analyte	**Skewness**	**Kurtosis**	**K-S Dist.**	**K-S Prob.**	**Sum**	**Sum of Squares**
As	1.999	4.153	0.294	0.11	1249.3	707534
Cd	0.439	-1.659	0.267	0.196	1.72	1
Cr	0.33	0.43	0.197	0.559	63.5	683
Cu	1.815	3.658	0.326	0.045	164.3	4716
Hg	-0.668	-0.446	0.223	0.41	0.64	0.071
Ni	0.358	-1.536	0.214	0.463	40.4	276
Pb	0.631	-1.15	0.291	0.117	300.1	23902
Zn	0.328	-1.764	0.218	0.441	791.8	132756

Table D- 6: Pearson Correlation Matrix for Distribution of Elements of Surficial Grab Sediment Samples

	Cd	Cr	Zn	Fe	P	Log As	Log Cu	Log Hg	Log Ni	Log Pb
Depth Of Water	-0.46 0.00321 39	-0.544 0.000339 39	-0.377 0.0179 39	-0.456 0.004 38	-0.428 0.00731 38	-0.337 0.0361 39	-0.479 0.00205 39	-0.506 0.00103 39	-0.553 0.000264 39	-0.583 9.86E-05 39
Cadmium		0.899 8.43E-15 39	0.852 6.16E-12 39	0.517 0.000885 38	0.337 0.0388 38	0.572 0.000143 39	0.805 6.69E-10 39	0.713 3.56E-07 39	0.791 2.05E-09 39	0.87 6.66E-13 39
Chromium			0.893 2.11E-14 39	0.613 4.34E-05 38	0.52 0.000822 38	0.513 0.000849 39	0.934 3.66E-18 39	0.68 1.94E-06 39	0.841 2.14E-11 39	0.899 7.52E-15 39
Zinc				0.516 0.000904 38	0.585 0.000116 38	0.429 0.00643 39	0.866 1.15E-12 39	0.515 0.000801 39	0.656 5.88E-06 39	0.795 1.55E-09 39
Iron					0.523 0.000762 38	0.622 3.01E-05 38	0.59 9.79E-05 38	0.481 0.00223 38	0.715 4.49E-07 38	0.656 7.63E-06 38
Phosphorous						0.292 0.0756 38	0.609 4.89E-05 38	0.162 0.331 38	0.359 0.0271 38	0.473 0.00269 38
log Arsenic							0.505 0.00103 39	0.388 0.0147 39	0.675 2.43E-06 39	0.727 1.64E-07 39
log Copper								0.611 3.62E-05 39	0.835 4.03E-11 39	0.816 2.56E-10 39
log Mercury									0.723 2.07E-07 39	0.621 0.000025 39
log Nickel										0.82 1.76E-10 39

Legend:

0.703	Correlation Coefficient
0.000552	P Value
20	Number of Samples

Colour Coding:

🟪	P=<0.0001	Highly significant
🟥	P=<0.001 - >0.0001	Highly significant
🟧	P=<0.05 - >0.001	Significant
🟨	P=<0.1 ->0.05	

The pair(s) of variables with positive correlation coefficients and P values below 0.050 tend to increase together. For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to decrease while the other increases. For pairs with P values greater than 0.050, there is no significant relationship between the two variables.

Table D- 7: Pearson Correlation Matrix for Distribution of Elements with Depth in Sediment Cores (based on Composite Sample 0-5 cm, 5-10 cm, 10-15 cm, 15-20 cm depths).

	Cr	Ni	Pb	Zn	P	log10 As	log10 Cd	log10 Cu	log10 Hg	log10 Fe
depth	-0.311 0.183 20	-0.147 0.537 20	-0.38 0.0983 20	-0.479 0.0325 20	-0.597 0.00542 20	-0.517 0.0196 20	-0.196 0.406 20	-0.402 0.0785 20	-0.207 0.382 20	-0.524 0.0177 20
Cr		0.878 3.56E-07 20	0.878 3.7E-07 20	0.886 2E-07 20	0.51 0.0216 20	0.56 0.0103 20	0.807 1.7E-05 20	0.925 5.2E-09 20	0.472 0.0358 20	0.706 0.000506 20
Ni			0.778 5.4E-05 20	0.722 0.00032 20	0.257 0.275 20	0.647 0.00207 20	0.851 1.9E-06 20	0.78 5.02E-05 20	0.419 0.0659 20	0.63 0.0029 20
Pb				0.922 7.9E-09 20	0.627 0.00309 20	0.751 0.000136 20	0.81 1.5E-05 20	0.882 2.7E-07 20	0.599 0.00525 20	0.7 0.000595 20
Zn					0.703 0.00055 20	0.734 0.000233 20	0.806 1.8E-05 20	0.918 1.19E-08 20	0.425 0.0617 20	0.627 0.00312 20
P						0.403 0.0781 20	0.267 0.254 20	0.725 0.000298 20	0.249 0.289 20	0.425 0.0621 20
log10 As							0.792 3.1E-05 20	0.547 0.0126 20	0.368 0.11 20	0.584 0.00682 20
log10 Cd								0.694 0.000693 20	0.424 0.0625 20	0.479 0.0326 20
log10 Cu									0.386 0.0924 20	0.644 0.00219 20
log10 Hg										0.501 0.0245 20

Legend:

0.703	Correlation Coefficient
0.000552	P Value
20	Number of Samples

Colour Coding:

🟪	P=<0.0001	Highly significant
🟥	P=<0.001 - >0.0001	Highly significant
🟧	P=<0.05 - >0.001	Significant
🟨	P=<0.1 ->0.05	

The pair(s) of variables with positive correlation coefficients and P values below 0.050 tend to increase together. For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to decrease while the other increases. For pairs with P values greater than 0.050, there is no significant relationship between the two variables.

Table D- 8: Pearson Correlation Matrix for Distribution of Elements with Depth in Sediment Cores (based on Discrete Sample 0-2 cm, 2-4 cm, 4-5 cm, 5-7 cm, 7-9 cm, 9-10 cm depths)

	Cd	Cr	Hg	Ni	Zn	log10 As	log10 Cu	log10 Pb
Depth	-0.282 0.0781 40	-0.356 0.0243 40	-0.39 0.0128 40	-0.216 0.181 40	-0.482 0.00165 40	-0.483 0.00161 40	-0.422 0.0067 40	-0.438 0.00468 40
Cd		0.76 1.26E-08 40	0.815 1.57E-10 40	0.739 5.19E-08 40	0.768 7.27E-09 40	0.709 3.11E-07 40	0.717 1.89E-07 40	0.805 3.83E-10 40
Cr			0.857 1.79E-12 40	0.926 1.21E-17 40	0.892 1.04E-14 40	0.478 0.0018 40	0.939 3.54E-19 40	0.767 7.72E-09 40
Hg				0.769 6.92E-09 40	0.824 6.37E-11 40	0.551 0.000229 40	0.776 4.08E-09 40	0.749 2.74E-08 40
Ni					0.753 2.14E-08 40	0.544 0.000288 40	0.863 7.75E-13 40	0.685 1.1E-06 40
Zn						0.588 6.68E-05 40	0.878 1.07E-13 40	0.891 1.33E-14 40
log10 As							0.515 0.000669 40	0.779 3.3E-09 40
log10 Cu								0.752 2.21E-08 40

Legend:

0.703	Correlation Coefficient
0.000552	P Value
20	Number of Samples

Colour Coding:

🟪	P=<0.0001	Highly significant
🟥	P=<0.001 - >0.0001	Highly significant
🟧	P=<0.05 - >0.001	Significant
🟨	P=<0.1 ->0.05	

The pair(s) of variables with positive correlation coefficients and P values below 0.050 tend to increase together. For the pairs with negative correlation coefficients and P values below 0.050, one variable tends to decrease while the other increases. For pairs with P values greater than 0.050, there is no significant relationship between the two variables.

Normality Test (Kolmogorov-Smirnov)

Data source: Surficial Grab Samples

As: K-S Dist. = 0.227 P < 0.001 Failed

Cd: K-S Dist. = 0.095 P > 0.200 Passed

Cr: K-S Dist. = 0.119 P = 0.170 Passed

Cu: K-S Dist. = 0.181 P = 0.002 Failed

Hg: K-S Dist. = 0.173 P = 0.005 Failed

Ni: K-S Dist. = 0.144 P = 0.041 Failed

Pb: K-S Dist. = 0.156 P = 0.018 Failed

Zn: K-S Dist. = 0.136 P = 0.068 Passed

Fe: K-S Dist. = 0.081 P > 0.200 Passed

P: K-S Dist. = 0.130 P = 0.103 Passed

log10 As: K-S Dist. = 0.106 P > 0.200 Passed

log10 Cu: K-S Dist. = 0.116 P > 0.200 Passed

log10 hg: K-S Dist. = 0.126 P = 0.121 Passed

log10 Ni: K-S Dist. = 0.160 P = 0.013 Failed

log10 Pb: K-S Dist. = 0.162 P = 0.011 Failed

log10Fe: K-S Dist. = 0.131 P = 0.100 Passed

log10 P: K-S Dist. = 0.160 P = 0.015 Failed

A test that fails indicates that the data varies significantly from the pattern expected if the data was drawn from a population with a normal distribution.

A test that passes indicates that the data matches the pattern expected if the data was drawn from a population with a normal distribution.

Normality Test (Kolmogorov-Smirnov)

Data source: Sediment Cores

Depth: K-S Dist. = 0.129 P = 0.092 Passed

As: K-S Dist. = 0.241 P < 0.001 Failed

Cd: K-S Dist. = 0.129 P = 0.093 Passed

Cr: K-S Dist. = 0.139 P = 0.050 Passed

Cu: K-S Dist. = 0.168 P = 0.006 Failed

Hg: K-S Dist. = 0.129 P = 0.093 Passed

Ni: K-S Dist. = 0.118 P = 0.169 Passed

Pb: K-S Dist. = 0.172 P = 0.004 Failed

Zn: K-S Dist. = 0.100 P > 0.200 Passed

log As: K-S Dist. = 0.157 P = 0.015 Failed

log Cu: K-S Dist. = 0.131 P = 0.083 Passed

A test that fails indicates that the data varies significantly from the pattern expected if the data was drawn from a population with a normal distribution.

A test that passes indicates that the data matches the pattern expected if the data was drawn from a population with a normal distribution.

Appendix E: Quality Assurance / Quality Control

Analysis of a certified reference material (CRM) was requested by Environment Waikato to determine the accuracy and reproducibility of the analytical results. To determine the accuracy and reproducibility of the results a certified reference material (Agal-10) was analysed ten times. A median value and standard deviation of the replicate results were then calculated.

To determine accuracy of the analysis, the median value of the replicates plus/minus the standard deviation of the results was compared to the certified range in concentration of the reference material.

To determine the precision of analysis, the relative percentage differences (RPD) were calculated for the replicate samples via the procedure outlined in section 1020 of the APHA standard methods (20th Edition). If the RPD is within ± 25% then the analysis precision is considered to be acceptable.

The analysis of the certified reference material indicates that the results of the analysis conducted by Hill Laboratories are accurate for arsenic, cadmium, copper, lead, mercury and zinc. The precision of the results are excellent with the relative standard derivation (%RSD) being less than 10% for all analysis undertaken on the certified reference material. However, the reported concentration of chromium (50% of the certified value) and nickel (63% of the certified value) for the certified reference material are lower than the certified range specified in the report of analysis. It is likely that the differences between the laboratory results and the certified values for the reference material are due to different extraction methodology used to liberate the metals from the sediment matrix.

Reference values were assigned from results submitted by laboratories which used aqua regia, aqua regia/H_2O_2 or reserve aqua regia digestion followed by ICP-MS or ICP-AES. Aqua Regia digestion is a standard digestion for geological samples which uses a 3:1 mixture of concentrated hydrochloric and nitric acids. Peroxide (H_2O_2) is added to the mixture sometimes to destroy organic matter which can strongly bind metals such as copper and mercury. In reverse aqua regia digestion, nitric acid and hydrochloric acid are combined in a 3:1 proportion, exactly the reverse of the standard aqua regia digestion.

US EPA method 200.2 (Sample preparation for total extractable metals) uses more dilute nitric and hydrochloric acid (at a ratio of approximately 50:50) which is refluxed for 30 minutes to release the metal bound to the soil or sediment matrix. As a weaker concentration of acid is used, the digestion technique is not capable of liberating metals bound to resistant matrixes such as crystalline oxides. Both chromium and nickel can be incorporated into crystalline oxides (such as Cr_2O_3 and Ni_2O_3) which would be resistant to acid attack. However, metals associated with anthropogenic sources (except mining sources) tend to be associated with much weaker phases (i.e. adsorbed onto clay minerals, sorbed on to or into amorphous iron oxides, or bound to sulphide minerals (i.e. FeS) which are released by the total extractable metal digestion technique. Therefore, the total extractable metal digestion is a partial digestion and is not capable of liberating metals associated with all minerals phases (such as some oxide and silicate minerals phases) but it is effective at recovering most anthropogenic metals.

An examination of all the results obtained from the measurement of the certified reference material indicates that all the results may be slightly lower than the actual concentration as the total extractable metals digestion technique is not liberating all of the metals from the sediment matrix. However, the metals retained by the sediment matrix probably represent natural background metal phases which are not biologically available as they are bound to resistant mineral phases.

The aim of this study is to determine if the surface sediment could be regarded as contaminated or not with respect to Environment Waikato Regional Plan. As the total extractable metal digestion would recover metals introduced to the lake from anthropogenic activity (such as the spray application of sodium arsenite) and this methodology has been used to define natural “background” concentration of metals in soils in New Zealand, the inability of this extraction method to recover all the metals within the sediments does not affect the findings of this study.

The laboratory QA/QC report indicates that there is a positive interference in the analysis of chromium caused by the formation of ^{35}ClOH ions in the lower temperature region of the plasma. Hydrochloric acid is introduced to the sample matrix as part of the digestion process (US EPA 200.2) which results in the formation of ^{35}ClOH ions. This species has the same charge to mass ratio as the chromium-52 ion. The isobaric polyatomic ion interface can not be avoided by choosing an alternative analytical isotope for chromium as the abundance of the other isotopes of chromium is very low. A blank subtraction was used to remove the small positive influence caused by the presence of these ions. The use of such a correction method for dealing with polyatomic ion interferences is approved under US EPA method 200.8. This inference was not present in procedure blank in batch 455185; the laboratory has stated that the absence of the interference was due to a subtle change in the operating parameters of the instrument.

In quality assurance report for batch 455032 the Agal-10 CRM results for magnesium, lithium, iron, aluminium and phosphorus were outside the range for the certified limits, however a separate reference material (QC A2) complied within the quality control range. The fact that one reference material was inside the quality control range indicates that the instrument was running correctly and calibration of the instrument was also correct. The reported value for magnesium, iron, aluminium and phosphorus was within the normally accepted uncertainty of analytical results of 20%. The reported concentration for lithium was 36% higher than the reported certified value for Agal-10; this higher value might be partly due to inhomogeneity within the reference material itself. The laboratory also indicate that a small weighing error might have resulted in slightly higher values

The QA/QC report highlights some problems with the recoveries of the spikes and spike duplicates in the poly-aromatic hydrocarbon and organochlorine pesticides.

There appears to be a slight positive inference for some compounds and matrix protection of methoxychlor. Both of these problems seem to be matrix related and the samples that the QA/QC testing was conducted on were not from Lake Rotoroa, therefore the results are not applicable to the samples analysed in this investigation.

The laboratory QA/QC report also indicates that the relative percentage difference (RPD) for the duplicates samples is very low (less than 25%), which meets QA/QC for duplicate analysis as specified by section 1020 of the APHA standard methods (APHA 1999).

An independent duplicate analysis was carried out on composite 1 after a problem was discovered in the initial compositing of the samples. The purpose of the duplicate analysis was to confirm the results of the re-analysis of the composite samples and to identify if any elements are significant influenced by “nugget effects”. Nugget effects are caused by small scale variability in the concentration of a sample. The aim of the duplicate analysis is not to quantify the extent of the variability but just to quickly identify if small-scale variability could potentially complicate the interpretation of the sampling results. The duplicate analysis indicates that the RPD for the duplicate samples is very low (less than 25%) for most elements except silver and selenium. Although both of these elements have relatively high RPD, it is believed that this is due to the fact that the concentration of those two elements are close to the detection limit of the method. Analyses that are very close to the method detection limits (less than 10 times method detection limit), normally have very high RPDs. Due to the high RPD in these two elements care will be needed in interpreting any differences between sampling locations for these two elements.

Table E- 1: Quality Assurance/Quality Control results for Analysis of Certified Reference Material Agal-10.

Sample Number	**Arsenic**	**Cadmium**	**Chromium**	**Copper**	**Mercury**	**Nickel**	**Lead**	**Zinc**
	mg/kg	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**	**mg/kg**
AGAL 10 Rep 1	17.9	8.86	46.6	24.7	11.3	12.4	41.3	55.1
AGAL 10 Rep 2	18.3	8.35	45.3	22.8	10.4	11.7	38.4	52.7
AGAL 10 Rep 3	18.3	8.98	45.3	22.3	10.7	11.2	40.7	53.5
AGAL 10 Rep 4	18.6	8.86	44.8	21.2	10.3	10.6	38.3	50.9
AGAL 10 Rep 5	17.6	8.69	43.5	21.1	10.4	10.8	39	50.9
AGAL 10 Rep 6	17.5	8.47	45.9	20.9	10.2	10.6	38.3	50.5
AGAL 10 Rep 7	18.6	8.25	48.6	21.2	10.2	11.1	36.7	51.3
AGAL 10 Rep 8	17.3	8.49	47.4	22.2	10.7	11.8	41	52.3
AGAL 10 Rep 9	18.5	8.99	47.6	22.9	11.1	12.2	40.2	54.7
AGAL 10 Rep 10	17.9	8.15	45.5	20.7	10.1	10.9	37.3	49.2
Summary Statistics								
Minimum	17.3	8.2	43.5	20.7	10.1	10.6	36.7	49.2
Maximum	18.6	9.0	48.6	24.7	11.3	12.4	41.3	55.1
Median	18.1	8.6	45.7	21.7	10.4	11.2	38.7	51.8
Standard Derivation	0.7	0.4	2.6	2.1	0.6	0.9	2.3	3.0
%RSD	3.6	4.9	5.6	9.6	6.0	8.3	6.0	5.7
Comparison with Certified Values								
CRM	17.2	9.33	82	23.2	11.6	17.8	40.4	57
CRM Range (1 Sd)	14.2-20.2	8.87-9.79	71-93	21.3-25.1	10.5-12.7	15.1-20.5	37.7-43.1	52.8-61.2
Replicate mean Range (1 Sd)	17.6-18.6	8.2-8.9	44.0-47.4	20.3-23.1	10.0-10.8	10.5-11.8	37.0-40.4	49.0-53.1

Table E- 2: Duplicate Analysis of Composite 1

Analytes	**Composite 1**	**Composite 1 (duplicate)**	**%RPD**	**Analytes**	**Composite 1**	**Composite 1 (duplicate)**	**%RSD**
	mg/kg	mg/kg			mg/kg	mg/kg	
Dry Matter (%)	16.5	15.7	5.1%	Acenaphthene	< 0.2	< 0.1	
Calcium	4190	4400	-4.8%	Acenaphthylene	< 0.2	< 0.1	
Magnesium	911	936	-2.7%	Anthracene	< 0.2	< 0.1	
Sodium	296	326	-9.2%	Benzo[a]anthracene	< 0.2	< 0.1	
Potassium	606	605	0.2%	Benzo[a]pyrene (BAP)	< 0.2	< 0.1	
Lithium	19.2	23.3	-17.6%	Benzo[b]fluoranthene	< 0.2	< 0.1	
Rubidium	11.3	10.1	11.9%	Benzo[g,h,i]perylene	< 0.2	< 0.1	
Phosphorus	543	553	-1.8%	Benzo[k]fluoranthene	< 0.2	< 0.1	
Boron	6	6	0.0%	Chrysene	< 0.2	< 0.1	
Iron	19400	18900	2.6%	Dibenzo[a,h]anthracene	< 0.2	< 0.1	
Manganese	385	362	6.4%	Fluoranthene	< 0.2	0.1	
Silver	0.26	0.2	30.0%	Fluorene	< 0.2	< 0.1	
Aluminum	40500	47300	-14.4%	Indeno[1,2,3-c,d]pyrene	< 0.2	< 0.1	
Arsenic	183	170	7.6%	Naphthalene	< 0.8	< 0.7	
Barium	264	267	-1.1%	Phenanthrene	< 0.2	< 0.1	
Bismuth	0.31	0.3	3.3%	Pyrene	0.2	0.2	0%
Cadmium	0.53	0.47	12.8%				
Cobalt	12.7	13.1	-3.1%				
Chromium	14.2	14.3	-0.7%				

Table E- 2: Duplicate Analysis of Composite 1 (continued)

Analytes	**Composite 1**	**Composite 1 (duplicate)**	**% RPD**	**Analytes**	**Composite 1**	**Composite 1 (duplicate)**	**% RSD**
	mg/kg	mg/kg			mg/kg	mg/kg	
Cesium	3.33	3.04	9.5%				
Copper	48.8	56.1	-13.0%				
Mercury	0.16	0.14	14.3%				
Lanthanum	24.4	22.2	9.9%				
Molybdenum	1.03	0.91	13.2%				
Nickel	7.5	8.1	-7.4%				
Lead	128	124	3.2%				
Antimony	2.51	2.46	2.0%				
Selenium	3	2	50.0%				
Strontium	50.7	44.3	14.4%				
Tin	4.5	4	12.5%				
Titanium	0.5	0.5	0.0%				
Uranium	1.38	1.4	-1.4%				
Vanadium	57	55	3.6%				
Zinc	335	349	-4.0%				

Appendix F: Data from Other Studies

Table F- 1: Water Quality Data obtained by Gordon Randerjam (September 1990 to September 1991). (Units as reported by Gordon Randerjam. Note the conductivity units are incorrect)

Date	P	S	Mg	Ca	Na	K	Cl^-	NO_3	NH_3	Mn	Zn	Cu	Fe	Cd	As	B	Pb	pH	Cond.
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	pH units	μS
25th Sept 1990	0.02	2.5	1.6	5.7	8.1	2	18	0.4	0.1	0.13	<0.01	<0.01	0.62	0.0003	0.006	0.05	0.002	7.2	100
30th Nov 1990	0.02	2.3	1.6	8.7	6.4	2.5	15	0.2	0.1	<0.01	0.03	<0.01	0.05	0.0002	0.005	0.05	0.004	7.2	95
12th Dec 1990	0.01	2.2	1.5	6.4	8.3	2.1	15	0.2	0.1	0.03	0.02	<0.01	0.32	<0.0001	0.006	0.05	0.002	7.2	96
31st Jan 1991	0.01	2.4	1.6	6.7	8.9	2.4	18	0.2	0.3	0.06	<0.01	<0.01	0.41	0.0019	0.007	0.07	0.001	7.3	90
28th Feb 1991	0.01	2.4	1.7	7.5	9.5	2.7	15	<0.1	0.4	<0.01	0.01	<0.01	0.21	0.0002	0.011	0.07	0.004	7	94
27th March 1991	0.01	2.4	1.8	6.8	9.3	2.6	17	0.1	0.2	<0.01	<0.01	<0.01	0.26	0.0001	0.008	0.07	0.001	7.5	95
30th April 1991	0.01	2.3	1	6.5	9	2.4	15	0.2	0.2	<0.01	<0.01	<0.01	0.2	0.0002	0.005	0.12	0.003	7.1	94
31st May 1991	0.01	2.4	1.9	6.2	9.5	2.5		0.1	<0.1	0.01	0.01	<0.01	0.1	<0.0001	0.003	0.15	0.001	7	95
20th June 1991	0.02	2.4	1.6	6.6	9.4	2.6	15.5	0.13	0.1	0.05	0.03	<0.01	0.32	0.0012	0.002	0.07	0.005	6.70	91
31st July 1991	0.02	2.2	1.7	6.6		2.5	15	0.1	0.3	0.14	0.01	<0.01	0.47	0.0001	0.004	0.06	0.004	7	2
30th August 1991	0.01	2.2	1.6	6.3	6.9	2.2	15	0.1	0.4	0.15	<0.01	<0.01	0.78	0.0012	0.01	0.06	0.006	6.6	90
30th Sept 1991	0.01	2	1.7	6.3	8.7	2.1	14	0.2	0.1	0.18	<0.01	<0.01	0.63	0.001	0.012	0.09	0.006	6.7	88
average	0.01	2.3	1.6	6.7	8.5	2.4	15.4	0.18	0.2	0.09	0.02	<0.01	0.36	0.0006	0.007	0.08	0.003	7.0	86
minimum	0.01	2	1	5.7	6.4	2	14	0.1	0.1	0.01	0.01	0	0.05	0.0001	0.002	0.05	0.001	6.6	2
maximum	0.02	2.5	1.9	8.7	9.5	2.7	18	0.4	0.4	0.18	0.03	0	0.78	0.0019	0.012	0.15	0.006	7.5	100

Table F- 2: Concentration of Selected Elements in Macrophytes (Analysis Conducted by Gordon Randerjam, 1991)(mg/kg dry weight)

Sample Site	**species**	**Mn**	**Fe**	**As**	**Zn**	**Cu**	**Pb**	**Cd**	**Ni**	**Cr**	**B**
Lake Rotoroa In1/30m	Egeria densa	3000	15000	376	1280	48	110	0.79	2	3.2	74
Lake Rotoroa In1/50m	Egeria densa	8600	40000	1220	396	16	16.6	0.52	2.2	3	85
Outlet n=3	Egeria densa	15121 (9,360-25,560)	26650 (6,370-58,590)	370 (40-700)	376 (251-490)	19 (14-27)	12.7 (2.3-23)	0.55 (0.50-0.60)	-	14.2 (1.2-40)	66 (57-116)
Lake Rotokauri)	Egeria densa	21759 (11,200-310,000)	7000 (1,160-36,424)	3.9 (1.4-12.5)	241 (160-320)	8 (4-16)	0.2 (<0.2-1.1)	2.84 (0.6-9.58)	2.1 (1.6-1.5)	1.2 (1.1-1.5)	60 (47-98)
L. Rotoroa	Water Lily	196	194	2.5	56	9	5.5	0.29	0.6	0.5	22
L. Rotoroa	Rush	443 (190-710)	144 (107-189)	1.9 (1.1-2.4)	31 (25-38)	5.0 (25-38)	2.4 (0.8-3.2)	0.07		0.2	

Table F- 3: Concentration of Selected Elements in Fish Species present in Hamilton Lake (Analysis Conducted by Daryl Kane, 1995) (mg/kg wet weight)

Fish species	Arsenic	Zinc	Copper	Lead
Catfish	1.03	4	0.6	<0.1
Catfish	0.33	3.8	<0.4	<0.1
Catfish	0.97	4.4	0.6	0.2
Catfish	0.52	7.3	0.5	<0.1
Catfish	1.26	4.4	0.7	<0.1
Catfish	0.74	3.7	0.7	<0.1
Catfish	0.89	5	0.9	<0.1
Catfish	1.01	4.5	1.1	<0.1
Catfish	0.17	8	<0.4	<0.1
Catfish	0.65	4.4	1.1	0.1
Catfish	0.77	3.7	<0.4	<0.1
Catfish	0.99	5.5	1	<0.1
average	**0.78**	**4.89**	**0.80**	**0.15**
Goldfish	0.2	7.2	0.5	0.2
Goldfish	0.13	10.6	0.9	0.2
Goldfish	0.19	10.5	1	<0.1
Goldfish	0.1	8.5	0.5	<0.1
Goldfish	0.11	9.1	1	<0.1
Goldfish	0.18	11	1.1	<0.1
Goldfish	0.18	18.4	0.6	1.1
Goldfish	0.22	8.4	0.8	0.2
Goldfish	0.3	16.9	0.5	0.4
Goldfish	0.16	19.3	<0.4	0.1
Goldfish	0.13	11.5	1.2	0.1
average	**0.17**	**11.95**	**0.81**	**0.33**
Perch	0.13	5.5	0.5	0.3
Perch	<0.03	3.2	<0.4	<0.1
Perch	0.06	4.5	0.5	0.1
Perch	0.08	3.5	<0.4	0.2

Table F- 3: Concentration of Selected Elements in Fish Species present in Hamilton Lake (Analysis Conducted by Daryl Kane, 1995) (mg/kg wet weight) (continued)

Fish species	Arsenic	Zinc	Copper	Lead
Perch	0.06	5.9	0.8	<0.1
Perch	0.09	4.1	0.9	<0.1
Perch	0.15	3.5	0.7	<0.1
Perch	0.11	3.9	0.7	<0.1
Perch	0.08	4.4	<0.4	0.1
Perch	0.03	3.7	0.8	<0.1
Perch	0.05	2.7	<0.4	0.5
Perch	0.24	4.5	0.9	0.1
Perch	0.06	6.1	1.1	0.1
average	**0.10**	**4.3**	**0.8**	**0.2**
Short fin eel	0.19	8.1	<0.4	1.3
Short fin eel	0.05	14.4	<0.4	0.2
Short fin eel	0.06	11.9	<0.4	<0.1
Short fin eel	0.13	13.8	0.9	<0.1
Short fin eel	0.34	13	0.9	0.3
Short fin eel	0.21	15.6	0.9	<0.1
Short fin eel	0.33	13.9	1	<0.1
Short fin eel	0.06	12.1	<0.4	<0.1
Short fin eel	<0.03	9.2	0.9	0.2
Short fin eel	0.14	7.1	<0.4	0.1
Short fin eel	0.15	6.9	0.8	0.4
Short fin eel	0.05	11.4	0.8	<0.1
average	0.16	11.45	0.89	0.42
Tench	0.41	4	<0.4	0.4
Tench	0.56	3.8	0.6	<0.1
Tench	0.2	3.2	<0.4	<0.1
Tench	0.37	2.8	<0.4	<0.1
Tench	0.54	3.3	1.1	<0.1
Tench	0.26	5.5	0.6	<0.1

Table F- 3: Concentration of Selected Elements in Fish Species present in Hamilton Lake (Analysis Conducted by Daryl Kane, 1995) (mg/kg wet weight) (continued)

Fish species	Arsenic	Zinc	Copper	Lead
Tench	0.47	3.6	0.8	<0.1
Tench	0.34	5	1.1	<0.1
Tench	0.4	3.6	<0.4	<0.1
Tench	0.17	4.4	0.9	<0.1
Tench	0.33	3.7	<0.4	0.2
Tench	0.43	5.8	0.8	0.3
average	**0.37**	**4.06**	**0.84**	**0.30**
average concentration in fish present in the lake	0.31	7.32	0.82	0.28

TABLE F- 4: RELATIVE ABUNDANCE OF INVERTEBRATES IN SURFICIAL SEDIMENTS OF HAMILTON LAKE. RESULTS OBTAINED BY DARYL KANE ON 29 SEPTEMBER 1993.

Species	Hamilton Lake Sample 1	Hamilton Lake Sample 2
Phylum Annelida		
Class Oligochaeta		
Oligochaeta	11	310
Phylum Nematoda		
Nematoda indet	35	9
Phylum Mollusca		
Class Gastropoda		
Physa sp		6
Potamopyrgus		3
Phylum Arthropoda		
Subphylum Crustacea		
Class Copepoda		
Copedod Indet	2	
Class Ostracod		
Ostracod indet	16	1
Subphylum Uniromia		
Class Insecta		

Table F- 4: Relative abundance of invertebrates in surficial sediments of Hamilton Lake. Results obtained by Daryl Kane on 29 September 1993 (continued)

Species	Hamilton Lake Sample 1	Hamilton Lake Sample 2
Ephemeroptera *Deleatidium Lillii*	2	
Trichoptera *indet* (case only)	1	2
Diptera *A. ungulatum*		
Chironomid indet. (L)	68	4
Chironomid indet. (P)	5	

TABLE F- 5: CONCENTRATION OF MAJOR ELEMENTS IN WAIKATO REGION LAKES (MG/KG DRY WEIGHT)

Element	Waahi	Hakanoa	Waikare	Whangapae	Maratoto	Rotomanuka	Serpentine North	Serpentine East	Ngaroto	Te Koutu	Parkinson
Ca	3120	3110	2280	5530	5740	4560	6280	6860	4250	4580	
Mg	1280	1060	1660	1840	1420	520	735	857	894	2240	
Na	259	266	195	211	308	238	166	263	241	283	
K	638	616	712	904	178	464	470	463	629	806	
Li	15	10.9	18.4	15.6	1	3.2	7.2	9	8.3	12.9	
Rb	12.3	14.8	17.5	13.3	1.43	4.35	6.69	7.31	8.35	9.45	
P	414	969	411	552	843	888	826	1280	929	1320	
B	11	9	4	8	4	8	4	3	3	5	
Fe	25100	29300	21400	38900	8020	19900	17400	22700	34100	16800	
Mn	878	982	1060	767	100	820	201	279	1710	296	
Ag	0.07	0.1	0.05	0.08	0.07	0.1	0.12	0.17	0.11	0.15	
Al	24100	19400	15000	18100	15100	14900	28000	34600	24400	20600	
As	7.8	12.3	19.9	8.5	2.3	4.1	2.6	3.1	4.2	25.3	10
Ba	143	220	169	141	122	129	52.6	28	410	156	
Bi	0.27	0.22	0.23	0.19	0.1	0.1	0.12	0.13	0.15	0.26	
Cd	0.19	0.58	0.16	0.23	0.25	0.5	0.42	0.69	0.56	0.77	0.5
Co	10.2	8.65	8.12	6.77	3.8	16.9	7.98	11.8	16.8	6.48	
Cr	9	7.2	7.3	11.3	4.8	9.5	5.9	6.6	6.7	17.6	28
Cs	2.17	5.26	8.42	1.82	0.39	0.93	1.63	1.62	1.7	3.8	
Cu	14	15.5	14.4	17	13	19.2	18.6	18.7	18.3	49.1	23

Table F- 5: Concentration of major elements in Waikato Region Lakes (mg/kg dry weight) (continued)

Element	Waahi	Hakanoa	Waikare	Whangapae	Maratoto	Rotomanuka	Serpentine North	Serpentine East	Ngaroto	Te Koutu	Parkinson
Hg	0.13	0.18	0.48	0.14	0.1	0.11	0.1	0.14	0.19	0.15	<0.1
La	12.8	12	15.7	11.2	8.85	18.4	20.2	27.1	25.8	13.7	
Mo	0.82	0.51	0.29	0.9	0.53	0.64	0.51	0.66	0.32	1.79	
Ni	12.7	5.8	4	14.8	2.5	5.6	4.3	5	4.9	8.9	19
Pb	17.6	27.9	18.3	16.6	24	82.6	25	17.8	13.5	316	13.1
Sb	0.33	0.62	0.51	0.26	0.26	0.65	0.25	0.17	0.14	1.32	
Se	< 2	< 2	< 2	< 2	2	< 3	< 2	2	< 2	< 2	
Sr	57.1	41.8	25.9	49.5	65.4	48.9	46.4	65.1	36.1	32.4	
Sn	1.3	2	1.1	1	0.6	0.7	1.1	1.1	0.8	4	
Tl	0.2	0.29	0.2	0.19	0.13	0.52	0.37	0.53	0.76	0.23	
U	0.973	0.933	1.3	1.11	0.388	0.54	0.623	0.68	0.969	0.899	
V	35	26	45	35	32	57	40	45	34	61	
Zn	89.1	136	49.9	80.3	40.2	180	133	141	146	390	260

Note: Lakes Waikare and Te Kouto have not been used in the dataset to evaluate the "typical" background concentration of rural lakes in the Waikato region because Lake Waikare is influence by geothermal discharges and Lake Te Kohou is an urban lake within Cambridge.

TABLE F- 6: COMPARISON OF WAIKATO LAKES SEDIMENT DATA WITH SEDIMENT QUALITY DATA FROM HAMILTON LAKE (LAKE ROTOROA)(MG/KG DRY WEIGHT)

Element	Minimum Rural Lake Range	Maximum Rural Lake Range	Typical Rural Lake Concentration	Minimum Hamilton Lake	Maximum Hamilton Lake	Average Hamilton Lake	Minimum Enrichment Factor	Enrichment Factor	max EF	Typical soil median
Ca	3110	6860	4931	3340	4400	3853	0.68	0.78	0.89	15000
Mg	520	1840	1076	672	936	821	0.62	0.76	0.87	5000
Na	166	308	244	298	388	328	1.22	1.34	1.59	5000
K	178	904	545	494	608	573	0.91	1.05	1.12	14000
Li	1	15.6	8.8	19.8	24.3	22.8	2.26	2.60	2.77	25
Rb	1.43	14.8	8.6	9.48	15.1	11.0	1.11	1.29	1.76	150
P	414	1280	838	55	775	503	0.07	0.60	0.93	800
B	3	11	6.3	5	6	5.5	0.80	0.88	0.96	20
Fe	8020	38900	24428	9000	24300	17535	0.37	0.72	0.99	40000
Mn	100	1710	717	358	411	379	0.50	0.53	0.57	1000
Ag	0.07	0.17	0.1	0.2	0.22	0.2	1.95	2.07	2.15	0.05
Al	14900	34600	22325	43300	51300	47575	1.94	2.13	2.30	71000
As	2.3	12.3	5.6	25	592	167	4.45	29.84	105.48	6
Ba	28	410	156	267	305	292	1.71	1.87	1.96	500
Bi	0.1	0.27	0.2	0.25	0.32	0.29	1.56	1.78	2.00	0.2
Cd	0.19	0.69	0.4	0.12	0.68	0.31	0.28	0.72	1.59	0.35
Co	3.8	16.9	10	11.6	13.4	12.83	1.12	1.24	1.29	8
Cr	4.8	11.3	7.6	5.2	23.1	11.21	0.68	1.47	3.03	70
Cs	0.39	5.26	1.9	2.61	3.86	3.06	1.35	1.58	1.99	4
Cu	13	19.2	17	11.6	114	31.7	0.69	1.89	6.79	30
Hg	0.10	0.19	0.14	0.06	0.32	0.13	0.44	0.94	2.35	0.06
La	8.85	27.1	17	22.2	29.1	26.23	1.30	1.54	1.71	40
Mo	0.32	0.9	0.6	0.87	1.03	0.94	1.42	1.53	1.69	1.2
Ni	2.5	14.8	7.0	3.3	8.4	6.26	0.47	0.90	1.21	50
Pb	13.5	82.6	28	10.4	303	76.5	0.37	2.72	10.77	12
Sb	0.14	0.65	0.3	1.74	2.46	2.15	5.19	6.41	7.34	1
Se	2	2	2.0	2	3	2.75	1.00	1.38	1.50	0.4

Table F- 6: Comparison of Waikato Lakes Sediment Data with Sediment Quality data from Hamilton Lake (Lake Rotoroa)(mg/kg dry weight) (continued)

Element	Minimum Rural Lake Range	Maximum Rural Lake Range	Typical Rural Lake Concentration	Minimum Hamilton Lake	Maximum Hamilton Lake	Average Hamilton Lake	Minimum Enrichment Factor	Enrichment Factor	max EF	Typical soil median
Si										
Sr	36.1	65.4	51	41.2	46.1	43.9	0.80	0.86	0.90	250
Sn	0.6	2	1.1	3.2	5.2	3.93	2.98	3.65	4.84	4
Tl	0.13	0.76	0.4	0.48	0.52	0.5	1.28	1.34	1.39	0.2
U	0.388	1.11	0.8	1.29	1.56	1.42	1.66	1.82	2.01	2
V	26	57	38	55	67	63	1.45	1.82	1.76	90
Zn	40.2	180	118	68.6	613	182	0.58	1.54	5.19	90

Appendix G: Human Health Risk Assessment

Introduction

To assess the risk, the long term average daily dose will be calculated for various pathways and compared with an allowable daily dose. The algorithms and exposure factors presented by the US EPA (1992, 1997, 2004) will form the basis of this assessment, with exposure information supplemented by largely anecdotal evidence on the use of the lake to determine exposure frequencies and durations. Given the lack of detailed information of lake use a large degree of professional judgement is required in assessing exposure.

Arsenic Toxicity

Arsenic is classified as a known human carcinogen (Group 1) by the International Agency for Research (IARC 1987, 2004) and a known human carcinogen (Group A) by the US EPA (1993). For the purposes of this assessment it will therefore be treated as a non-threshold substance.

A number of agencies have developed toxicological intake values or guideline values for arsenic. It is not the purpose to discuss the detail of the various values, or their basis, here. However, it is appropriate to present the range of non-threshold values, for comparison purposes (see Table G-1). In calculating the index doses for the particular cancer slope factors a risk level of 1 x 10^{-5} has been assumed. This value is typically used for drinking-water and soil guideline calculation in New Zealand (e.g. MoH/MfE, 1997).

Table G- 1: Selected Toxicological values of arsenic as a non-threshold substance

Jurisdiction	Cancer slope factor (1/(mg/kg-bw/day))	Index dose[1] (µg/kg-bw/day)	Reference
New Zealand	0.15	0.067	MfE & MoH (1997)
United Kingdom	-	0.3	DEFRA & EA (2002)
US EPA (oral)	1.5	0.0067	US EPA (1998)

[1] *For acceptable risk level of 10^{-5}*

The toxicology of arsenic is currently being reviewed as part of the process for revising soil guidelines for contaminated land (James Court, pers. comm.). It will be some time before a value is approved by a committee of officials, but the draft recommendation is similar to the US EPA slope factor and the equivalent index dose (Jo Cavanagh, pers. comm.).

The Food Safety Authority (FSA) has set a maximum permissible limit of arsenic in fish of 2mg/kg, which is higher than the index dose calculated by the US EPA. It is not certain how this value was calculated.

Exposure Scenarios

Receptors

Hamilton Lake is used for a variety of recreational water-based activities including boating of various sorts and fishing. The lake is not generally used for swimming (the dirtiness of the water apparently discouraging this). The lake is also popular for walking around (there is a boardwalk around the edge of the lake) and the surrounding domain popular for many other activities. While the lake is not used for swimming, children paddling cannot be precluded. In addition, maintenance or construction workers may, from time to time, be exposed to lake sediments or water. A commercial canoe hire and boat hire operations also occur on the lake.

The main water-based sports appear to be rowing and yachting. The Hamilton Yacht Club has regular midweek and weekend sailing throughout the summer. The season approximately coincides with the school terms 4 and 1 (HYC, 2005). This is the equivalent of about six months sailing. There may be some keen individuals who sail for a longer period than this.

The rowing club anecdotally has boats out on the water every day during the season, with on-the-water training typically starting in September and going through until March the following year. A few regattas are held on the lake, but exposure would principally be during training sessions, which could amount to four or five sessions a week for individuals.

Dragon boat and Waka Ama training commences on the lake in early October. As the season goes through until mid-March (with national and regional festivals) it can be assumed that training will continue until at least that time. The frequency of training for the keenest of individuals is not known, but it could amount to three or four times per week.

The frequency of canoeing and model boating activities on the lake is not known. However, it is assumed that such activity will be no greater than that of one of the other water sports and therefore not a critical activity.

A commercial canoe and boat hire business is operated on the lake weekends, school holidays and public holidays. This amounts to approximately 180 days per year.

A local representative of Fish and Game New Zealand has reported that typically four to five people would be fishing on the lake each day in summer. The lake supports a coarse fishery (catfish, rudd, perch) which apparently are taken for eating (Ben Wilson, pers. comm.). Seemingly the lake is regarded as a food source for members of some ethnic communities (Asian, East European, Maori). The lake is not regarded as a significant eel fishery by local iwi (Kemble Pudney, pers comm.) nor is it used for gathering edible plants.

The activity of maintenance workers is not known. While working in and around the lake margins could give rise to significant exposure to sediment, the frequency of such exposure for particular individuals is likely to be low. This exposure scenario will not be considered further.

Children playing at the water's edge are potential receptors. The frequency at which an individual child is likely to do this is unknown. As a matter of judgement, a child is unlikely to visit the lake unsupervised therefore events are likely to be organised visits with an adult or family as a summer activity. A visit every second weekend over four months including summer, for a total of eight events has been assumed. An age range of three to ten inclusive has been assumed, a child two and under being unlikely to be allowed to play in the water and the upper limit chosen as being when a child is less likely to get as dirty when playing.

The various exposure scenarios for these activities are summarized in Table G-2.

Table G - 2: Exposure Scenarios

Activity	Exposure to			
	Dermal with sediment	Sediment Ingestion	Water Ingestion	Fish ingestion
Fishing	Rarely. Generally fishing from shore. May enter water if problem with gear?	Rarely, insignificant	Small amounts, rarely	Yes
Child playing	Yes, wading, playing in mud	Yes	Small amounts	No
Yachting	Yes, while launching and recovering yachts	Possibly, from dirty hands when launching and recovering boats.	Yes, if fell out of yacht, but infrequent and small amounts	No
Rowing	Yes, while launching and recovering yachts	Possibly, from dirty hands when launching and recovering boats.	Yes, if fell out of yacht, but infrequent and small amounts	No
Dragon boating	Yes, while launching and recovering boats	Possibly, from dirty hands when launching and recovering boats. Less than for yachting?	Yes, if fall out of boat. Less frequent than yachting. Insignificant	No
Model boating	Possibly while launching and recovering boats	Insignificant	Very small amounts from getting hands wet.	No
Canoe and water bike hire operators	Yes, while launching and recovering boats	Possibly, from dirty hands when launching and recovering boats.		
Maintenance Workers	Possibly while carrying out lake-edge maintenance clearing weed.	Possibly from dirty hands from carrying out maintenance work.	Small amounts, rarely	No

Exposure Mechanisms and Rates

Boating

Boating activities involve launching and retrieving boats at the beginning and end of the activity. Where this launching involves going into the water, the feet and lower legs are exposed to lake-bed sediments and to the lake water. There is also the potential to be exposed to sediment from incidental ingestion from getting sediment on the hands. In addition, it can be expected that a small amount of water will be ingested during the activity, particularly if a participant falls into the water during the activity.

Children (under six) are assumed to have no significant exposure to sediment and water from boating activities on the lake, as a matter of judgement being unlikely to be involved in frequent boat launching or recovery activities and/or involved in boating as a sport).

With respect to dermal exposure to sediment, Weston (2005), in carrying out a risk assessment of recreational canoeist on the Housatonic River in New England, has assumed that the feet, lower legs, forearms, hands and face are variously exposed to sediment sticking to these body parts. Following US EPA (2004) a weighted average soil adherence factor is calculated depending on the soil adherence factor of the body part and the skin area involved. The hands and feet have the greatest soil (sediment) adherence while the forearms and face have least.

Few studies exist as to how much sediment might stick to body parts from boating activities. The closest studies are those looking at reed workers (reported in US EPA, 2004) and, more recently, by Shoaf, et al (2005a, 2005b), studying clam diggers and children at play on tidal flats. Weston (2005) used the sediment adherence values from US EPA (2004) in the absence of other values, but the Shoaf et al, values are used here as being slightly more relevant, although arguably the values will be conservative compared with the incidental contact with sediment from boat launching and retrieval.

Little arsenic is absorbed through the skin from attached soil. The US EPA applies a default dermal absorption factor of 3%, however, recent work by Lowney et al (2007) for soils indicates that absorption is more typically 0.5%. This value is used here.

With respect to incidental ingestion of sediment, Weston (2005) assumed as a basis the residential exposure to soil, factored up or down according to the perception of contact intensity relative to residential activity. For adult canoeist the rate was assumed to be 100 and 50mg/day for a 95th percentile and median value, respectively. These seem high relative to the adult residential ingestion rate assumed in New Zealand for soil guidelines of 25mg/day. As a “first look”, 25mg/day has been assumed for adults for this study.

With respect to dermal exposure to water, principally to the feet and lower legs during wading (e.g. during boat launching) this exposure pathway is considered insignificant compared with other potential pathways, and will not be considered further. This is on the basis that the lake water typically complies with the MAV for arsenic in the New Zealand Drinking-water Standard (MoH, 2005), being typically around 0.007 mg/l (Gordon, Rajendram, 1992) compared with the MAV of 0.01mg/l. The default dermal permeability factor for the absorption of arsenic in aqueous solution through the skin is 0.001cm/hr (US EPA, 2004). The dose per event for a 75kg adult, assuming an event duration of 30 minutes (considered to be the typical time that an individual might spend in the water to launch and retrieve a boat) would be only 1.7×10^{-4} µg/kg-bw/day compared with, say, an adult drinking 1 L of water per day at half the MAV of 6.7×10^{-2} µg/kg-bw/day, almost 400 times higher.

Similarly, incidental ingestion of water is not considered significant. Even if a person fell out of a boat and swallowed a mouthful of water, this would not occur on each occasion that person was boating and any one event would probably not involve more than, say, 50ml of water. For comparison, the dose per event would be 14 times lower than an adult drinking a litre of water at half the MAV. By the time the infrequency of the event is taken into account, the daily average dose is perhaps an order of magnitude lower still.

Food gathering

Fishing is considered to be the predominant exposure pathway with respect to gathering of food from the lake. The lake is not known for collection of edible plants and will not be considered further. This aspect may need further study, as arsenic is known to concentrate in some edible plants, for example water cress.

Exposure through fishing is by indirect exposure through eating of contaminated flesh and the possibility of also being exposed to contaminated water and sediment during fishing. However, it is assumed that the fishing is mostly carried out from the lake shore with no need to go into the water most of the time, certainly when compared to people more highly exposed to water and sediment such as those involved in boating activities. Therefore the principle exposure mechanism will be from eating fish and exposure to water or sediment will be ignored as small.

No data exists as to how often a particular individual might take fish at the lake and therefore might consume fish. This is a subject for further study. It is well known that members of the Asian community are frequent fish eaters. As a matter of judgement it is assumed that a small number of individuals might obtain fish meals from the lake on two occasions per week during the summer, say 50 occasions per year. Further, it is assumed that an adult could be fishing for the family, and therefore both children and adults would be exposed.

The exposure rate, that is, how much fish might be consumed at a sitting or on a daily average basis, is also difficult to ascertain. EW (2005) in considering discharges to the Waikato River from the Kinleith pulp and paper mill discussed various daily average consumption rates of around 30g/day (wet weight,) however, these were based on assumed diets, rather than real data. The US EPA (1997) reports a high (95th percentile) consumption rate of 54g/day. However, it is questionable whether these sorts of figures are applicable to possible members of high-rate fish consuming communities who supplement their fish consumption by fishing. It is perhaps a better approach to calculate a fish consumption rate using a typical serving size and using the judgement above that perhaps two meals a week are from fishing for a small number of individuals. Such a judgement needs verifying at a later date by questioning those who are fishing. If a serving is taken as 150g (with half that amount for a child) (Food Safety Australia New Zealand, 2004), then the adult consumption of potentially contaminated fish equates to 22g/day averaged over the year. The consumption rate for children (up to six years) is assumed to be half this.

A child playing

As noted previously, a child playing is a potential exposure route. Soil adherence factors for “kids-in-mud” playing on a lakeshore (US EPA, 1997) are considered relevant for this activity. Factors are given for hands, arms, legs and feet. Following US EPA (2004) a skin-area weighted adherence factor may be calculated.

Exposure Durations

There is no information as to the length of time an individual might carry out an activity. Durations have been decided as a matter of judgement in Table G- 2. For the keenest of rowers and yachtsmen it has been assumed the sport has been taken up in early teenage years and continued until age 50, say 35 years. This assumes being resident in Hamilton and a member of the same club for that period of time, probably an extreme assumption. This is also likely to be at the high end of dragon boating, which is too new a sport in New Zealand to be able to make informed judgements on.

Occupational exposure through operation of a canoe and boat hire business is expected to be less than the 20 years assumed for the standard occupational exposure in New Zealand guidelines. In the absence of any information, as a matter of judgement, the turnover in staff or ownership for a small business such as canoe hire is likely to be greater than is likely to be greater than for a more career orientated job. Ten years has been chosen.

Exposure to fish is assumed to be on the same basis as residential exposure for New Zealand guidelines, as a first look, 6 years as a child and 24 years as an adult.

The various exposure scenarios and assumed exposure rates and durations are summarised in Tables G-2 to G-4.

Table G- 3: Summary of Estimated Exposure Frequencies and Durations to Sediment

Activity	**Exposure Frequency (days/year)**	**Duration (Years)**
Fishing	Fishing twice per week during summer, 50 days. No sediment exposure.	6 as child, 24 as adult
Child Playing	One every two weeks through the summer, eight occasions per year	8 as younger and older child – ages 3 to 10 inclusive.
Yachting	Seasonal, Saturday afternoon, Wednesday evening, October to March, additional one and two day regattas[1]. Keen yachtsman perhaps a further day a week for rest of year, say 85 occasions total.	35 as adult
Canoe and water bike hire	Weekends, School holidays and Public Holidays - 180 days approx.	10 as adult
Rowing	Seasonal September to March, Keen rower five occasions/week, 150 days approx.	35 as adult
Canoeing	No data. Say 3 occasions a week through summer and one occasion a week otherwise, 100 days approx.	35 as adult
Dragon boating	October to March four occasions/week, 100 days approx.	Not assessed, less critical than rowing

Table G- 4: Summary of adherence, ingestion, body weight and skin areas for sediment risk assessment

		Sediment Adherence (mg/cm^2)	Sediment Ingestion (mg/day)	Body Weight (kg)	Skin area exposed (cm^2)
Boating Activities		4.7	25	75	6065
Child	(3 – 6)	21	100	19	2210
Playing	(7 – 10)		50	30	2900

<u>Sediment and Fish Concentrations</u>

Sediment concentrations over the bed of the lake are shown in summary form in Figure A.2. For the boat launching area (rowing club, yacht club, boat ramp area) concentrations range up to 50 mg/kg. It is assumed that those carrying out boating activities are exposed to 50 mg/kg, on average.

For children at play it is assumed that they could contact sediment anywhere around the lake's shoreline. Concentrations range up to in excess of 500 mg/kg with 300 mg/kg a typical value. It is assumed that children at play are exposed to 50 mg/kg on average.

Sampling and analysis of various fish by Daryl Kane (1995) (see Table in Appendix F) found average concentrations of 0.38 mg/kg (range 0.06 – 1.26). A value of 0.4 mg/kg is used here. It should be noted that the concentration of arsenic found in fish tissues is very species dependant with goldfish, perch and short-fin eels generally have very low concentrations of arsenic within their tissues (typically between 0.10 to 0.17 mg/kg) and catfish having a much higher concentration of arsenic in their tissues (typically 0.78 mg/kg). The variations in arsenic concentrations found in different fish species probably reflect the different feeding habits of the fish. Catfish tend to be bottom feeders and are likely to have a higher exposure to the sediments than other fish species present in the lake and because of their feeding behaviour they are likely to be directly exposed to more arsenic than other fish species. Rudd are also elevated in arsenic compared to other fish species present in the lake, again this is likely to be due to feeding behaviour as they tend to eat aquatic macrophytes which have been showed by Clayton and Tanner (1991) and Gordon Rajendram (1992) to contain elevated concentrations of arsenic.

Long Term Average Daily Dose Calculations

The calculation of a long term average daily dose (LADD) has used the basic equation:

$$\text{Intake} = \frac{\text{Concentration x Contact Rate x Exposure Frequency x Exposure Duration}}{\text{Body Weight x Averaging Time}}$$

Contact rate in mg/day has been calculated for dermal absorption from skin adherence, absorption factor and skin area, but is otherwise mg/day or g/day of sediment or fish ingestion. Averaging time is 70 years x 365 days, by convention for non-threshold substances. Also, for non-threshold substances age-adjusted rates have been calculated for fish consumption (other exposures are for a child or adult alone).

Results and Discussion

Calculations have not been performed for all scenarios listed in the exposure scenarios section, as by examination of Tables G-2, G-3 and G-4 it is immediately apparent that some boating activity scenarios are not critical, e.g. exposure durations for dragon boating and canoeing are less than that for rowing or yachting. The results of the remaining scenarios are set out in Table G-5.

Table G- 5: Long term Average Daily Dose (LADD) of arsenic

Activity	Dermal LADD	Ingestion LADD	Total Ingestion and Dermal	Fish LADD
Fish ingestion	-	-	-	0.015
Yachting	0.0008	0.0019	0.0027	-
Canoe and Boat Hire	0.0005	0.0015	0.0017	-
Rowing	0.0014	0.0034	0.0048	-
Child playing	0.005	0.002	0.007	-

Note: Index dose range 0.3 – 0.0067 from Table G-1.

None of the scenarios exceed the UK index dose and only one of the calculated values is close to the index dose calculated from the cancer slope factor used in the Timber Treatment Guidelines. On this basis there does not appear to be a substantial risk for boating activities or fish activities. A child playing, however, appears to be marginally at risk when compared with the US EPA toxicological value. The child playing scenario is sensitive to the parameters assumed, particularly the arsenic concentrations in the sediment and the sediment adherence factors. The US EPA-sourced sediment adherence factors for “Kids-in-mud” are very much higher than soil adherence factors for most other activities and may be more conservative than necessary. The sample size used to derive the factors is small (12 measurements).

To check the upper age range assumed, this value was recalculated for an age-range of 3 to 14, rather than 3 - 10. The result was very similar, showing a relative insensitivity to the larger skin area which is essentially balanced out by a greater body weight.

The LADDs for two of the scenarios exceed the index dose calculated from the US EPA cancer slope factor, children playing and fish ingestion. The rowing scenario is about 70% of this index dose. The comments above about the adherence factors and arsenic concentrations apply to the child playing scenario and while the LADD marginally exceeds (approximately 1.04 times the index dose) the index dose there is probably not a significant risk to children playing in the mud due to the arsenic concentrations. However, due to the low microbiological quality of the water and probably the sediment in the lake, children playing in the mud or paddling in the lake should be discouraged.

The fish ingestion scenario has a LADD approximately twice the index dose derived from the US EPA slope factor. The calculation assumes all the arsenic in the fish is the most toxic inorganic form whereas it is probable that a considerable amount (>50%) is in the less toxic organic form. On that basis ingestion of fish may not exceed the index dose, but never-the-less the indication is that a greater than desirable dose may be being obtained from eating fish from the lake for some high-consumption individuals. If fisherman are targeting catfish then they may be at twice the risk (LADD = 0.03) than some other fish species present in the lake. Further work is recommended to get a better idea of actual consumption rates, which may have been over-estimated. In addition, investigation of the form of arsenic in fish from the lake would be helpful.