# REPORT

Characterisation of Sediment Quality within the Lower Hawkesbury Estuary



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Hornsby Shire Council Estuary Management, Natural Resources Branch 296 Pacific Highway, Hornsby, NSW, 2077

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### **Executive Summary**

The objective of the Characterisation of Sediment Quality within the Lower Hawkesbury Estuary was to assess the distribution and major sources of persistent contaminants in sediment and the quality of sediment referencing ANZECC/ARMCANZ (2000) interim sediment quality guidelines. In addition, temporal trends in contaminant concentrations were assessed by comparing sediment data collected in 2013 to those collected in 2006.

A stainless steel grab sampler was deployed from a 5 m sampling vessel over four days of fieldwork, commencing on 6 May 2013. Sampled were collected at 52 locations (H1 to H39 and H43 to H55) that had been previously sampled in December 2006. At each location, three grab samples were collected to assess small-scale spatial variability of selected contaminants.

A second stage of grab sampling was undertaken over four days commencing on 29 June 2013 in which 17 locations were resampled. A single grab sample was collected from 17 selected locations previously sampled in May, and at five additional locations in Berowra Creek to assess potential sources of contamination. All samples were photographed and logged, and the physical/biological characteristics of sediments recorded.

The analytical suite for all samples included trace metals and selected elements polycyclic aromatic hydrocarbons (PAHs), total petroleum hydrocarbons (TPHs), polychlorinated biphenols (PCBs), organochlorine pesticides (OCs), organophosphorus pesticides (OPs), nutrients (TKN, TOC, NOX, reactive inorganic phosphorus), ammonia and TOC. Sixteen samples were analysed for organotin compounds from locations near boating facilities where this analyte had been tested in 2006. Samples from 11 locations were analysed for Diruon, Chlorothalonil, Irgarol 1051and Diclorofluanid. Sediments were collected at three locations in Sandbrook Inlet, five locations in Berowra Creek, two locations in Marramarra Creek, and five locations in the upper estuary were analysed for an extensive suite of contaminants including synthetic pyrethroids carbamates, triazines/triazoles, phenoxy acid herbicides, urea herbicides, fungicides, insecticides, OP's and miscellaneous biocides. The particle size distribution of sediment samples were analysed in triplicate for selected trace metals aluminium and arsenic to assess laboratory variability and analytical 'robustness'. Duplicate sample analyses (10% of primary samples), method blank samples (i.e. 'field blanks') and dried, in house laboratory standards were used to assess the accuracy of selected inorganic analyses.

The majority of samples collected throughout the Lower Hawkesbury Estuary were muddy (predominantly <63  $\mu$ m) sediments, but sediment textures were markedly coarser, i.e. sandy near Dangar Island, in Marramarra Creek and in the upper reaches of the study area towards Wisemans Ferry. The small-scale spatial variability of trace metal and PAH concentrations as assessed by whole sediment analyses of triplicate grab samples was close to that of analytical variability, except for two locations at which the sediment texture in triplicate grabs varied markedly, concentrations were close to LOR, and at one location where metallic debris was collected in one out of three grab samples.

Contaminant concentrations in the Lower Hawkesbury Estuary were generally low in comparison to urbanised and industrialised areas in other parts of Australia. Concentrations of arsenic, barium, beryllium, cobalt, manganese, nickel and vanadium in the Lower Hawkesbury Estuary are (with several possible exceptions) not measurably influenced by anthropogenic sources. In contrast, concentrations of boron, cadmium, chromium, copper, lead, manganese, mercury, silver and zinc varied markedly throughout study area and are significantly higher in the upper reaches of Berowra Creek and Cowan Creek (i.e. Bobbin Head, and Akuna and Apple Tree Bays).

The highest concentrations of copper, lead, zinc and mercury in the Lower Hawkesbury Estuary were located in close proximity to marinas suggesting a significant contribution of these trace metals from marina and boating related activities. TBT was not analysed at all locations, but was detected at sampling locations adjacent to marinas where this contaminant would have been previously used on vessels as an antifoulant. Low concentrations of TPH in sediments at Berowra Waters, Bobbin Head and Akuna Bay suggest refuelling of vessels is a minor source of these contaminants. Urban runoff and discharge from sewage treatment plants (notably for silver) have likely contributed to contaminant concentrations in sediment accumulating at Berowra Waters. Concentrations of PAHs in Sandbrook Inlet are typical of that found in sediment near many urbanised areas. The distribution of PAHs elsewhere is consistent with the use of tar products to preserve oyster racks. Low concentrations of pesticide residues in sediment, predominantly in Berowra Creek, probably represent historic domestic usage of pesticides in urbanised catchments. Concentrations of the extensive suite of other organic contaminant analysed in this study were uniformly below their respective limits of reporting.

Concentrations of copper, lead, silver and zinc in sediment exceeded ANZECC/ARMCANZ (2000) ISQG-L values only in the upper reaches of Berowra and Cowan Creeks. Concentrations of arsenic exceeded the ANZECC/ARMCANZ (2000) ISQG-L value in the lower reaches of Berowra and Cowan Creeks, Mullet and Mooney Mooney Creeks and Sandbrook Inlet. The concentrations of nickel exceeded the ANZECC/ARMCANZ (2000) ISQG-L value only in a single sample collected at Brooklyn. One sediment sample at both Bobbin Head and Akuna Bay exceeded ANZECC/ARMCANZ (2000) ISQG-H values for copper and zinc. Concentrations of all other inorganic contaminants did not exceed ANZECC/ARMCANZ (2000) ISQG-H values. Concentrations of total, normalised Chlordane and normalised TBT exceeded ANZECC/ARMCANZ (2000) ISQG-L values in Berowra Creek and Cowan Creek. Concentrations of normalised, total DDT exceeded the ANZECC/ARMCANZ (2000) ISQG-L value in the upper reaches of Berowra Creek, Bobbin Head, Akuna Bay, Mooney Mooney and Brooklyn. Normalised concentrations of all other organic contaminants (individual PAHs, low and high molecular weight PAHs, total PAHs, PCB, OCCs and OCPs) did not exceed available ANZECC/ARMCANZ (2000) ISQG-L values. Concentrations of organic contaminants in the Lower Hawkesbury Estuary did not exceed ANZECC/ARMCANZ (2000) ISQG-High values.

Sediment textures varied markedly at some locations in the Lower Hawkesbury Estuary between late 2006 and mid-2013. Sediment textures in 2013 were finer at more locations compared to 2006, possibly reflecting a decrease in rainfall related high flow events during prolonged dry periods between the sampling events. The overall trends in contaminant concentrations in samples collected in the Lower Hawkesbury Estuary during 2013 were similar to those identified in samples collected in later 2006. The highest concentrations of anthropogenic contaminants were found in sediment in Berowra and Cowan Creeks and Sandbrook Inlet. Apparent temporal changes in contaminant concentrations (not considering grainsize variations) were around one order of magnitude higher than the small-scale spatial and analytical variability. Due to the relationship between sediment texture and adsorptive capacity, changes in contaminant concentrations between late 2006 and mid 2013 were most pronounced at those locations

in which sediment texture varied markedly. Changes in concentrations of iron and aluminium in sediment generally reflected changes in the fine sediment fraction. Marked apparent temporal changes in concentrations of most contaminants are therefore likely the result of significant changes in sediment texture. In contrast, concentrations of lead were generally lower throughout the Lower Hawkesbury Estuary, except for a few locations at which sediment grainsize was markedly coarser in 2013. After consideration of changes in sediment grainsize, concentrations of TKN in sediment increased throughout most of the Lower Hawkesbury Estuary, with the exception of sediment in Cowan Creek where concentrations of TKN almost uniformly decreased.

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# 1 Project Background

The NSW Government's Estuary Management Program was initiated in 1992 to produce and implement Estuary Management Plans for all estuaries in NSW. The program focuses on improving or maintaining the overall health and functionality of estuaries by holistically maintaining the integrity of each system; the chemical, physical and biological properties, as well as the economic, recreational and aesthetic values.

The Lower Hawkesbury Estuary Management Plan (2009) provides strategic management for the area from Wisemans Ferry to Broken Bay excluding Pittwater and Brisbane Water. This plan was adopted by Hornsby Shire and Gosford City Councils in 2009 and fulfills the requirements of the NSW Estuary Management Policy 1992 and the NSW Coastal Policy 1997.

Hornsby Shire Council routinely investigates sediment quality in the Lower Hawkesbury Estuary as part of the Estuary Management Program to determine sources and the regional extent of sediment contamination and prioritise remedial actions. The outcomes and recommendations of these investigations will be incorporated in the Lower Hawkesbury Estuary Management Plan implemented progressively over a 7-10 year time frame.

This project assessed the contaminant status of the Lower Hawkesbury Estuary within Hornsby Shire, identified the distribution and temporal changes in contaminants and assessed the risks posed to the ecological values of the Lower Hawkesbury Estuary.

In natural waters contaminants typically adsorb onto suspended particulate material and tend to accumulate and ultimately become immobilised in sediment. Sediments are therefore useful in assessing the distribution and sources of contaminants and can provide a historical record of contamination not available in other sampling media. In addition, sediments are widely used to assess contamination in urban environments because of the comparatively low temporal and small-scale spatial variability in concentrations compared to other sampling media e.g. water or biota.

Sediments have been recognised as a contaminant sink, but contaminants may also be released to the overlying water column (in dissolved or particulate forms) as a secondary source which may adversely influence water quality. The concentrations of trace metals associated with particulate material are typically 3 to 5 orders of magnitude higher than in the dissolved phase. Sediments can also be analysed with high precision and accuracy and with a low risk of sample contamination and are therefore suitable for cost-effective assessment of spatial trends of contaminants.

Contaminants are usually associated with fine particulate material in sediment due to the proportionally greater surface area and composition of the fine particles, predominantly clays and organic matter. Fine particles generally have a high adsorption capacity, therefore particle size and contaminant concentrations in sediments are commonly positively correlated. As variation in sediment grainsize may alter contaminant concentrations in sediment, consideration of sediment grainsize in sampling programs assessing contaminant sources is important.

# 1.1 Previous Contaminant Investigations of Sediments and Biota in the Hawkesbury Estuary

The Hawkesbury River has been studied for the presence of anthropogenic trace metal contaminants for over 20 years. Early work included the determination of the speciation of iron, copper and zinc in waters of the Hawkesbury River by Pik et al. (1982) and the assessment of heavy metal enrichment in the surface microlayer of the Hawkesbury-Nepean River system (Barnes et al., 1982). Markich and Brown (1998) surveyed trace metal concentrations in the freshwater reaches of the Hawkesbury River, the first such survey of a permanent coastal river in Australia using 'clean' sampling and handling techniques. That study established that concentrations of nutrients, organic carbon and trace metals in the Hawkesbury River increased as a consequence of anthropogenic inputs, particularly point discharges from sewage treatment plants (STPs) as well as diffuse urban and agricultural runoff during storm events.

Anthropogenic heavy metal contaminants in sediments in the Hawkesbury River have only been systematically studied since the mid-1990s and many of contaminant investigations of sediments in the Hawkesbury Estuary have been conducted by the Environmental Geology Group (EGG) at the University of Sydney, led by Professor Gavin Birch (i.e. Hardiman and Pearson, 1995; Hayes and Buckney, 1998; Birch et al., 1998; Simonovski et al., 2003). In addition there has been monitoring by the Water Resources Laboratory, EPA and CSIRO.

Birch et al. (1998) established that the concentrations of trace metals in bed sediments of the Hawkesbury River were generally low and close to background, but were substantially elevated in the headwaters of Berowra Creek, Cowan Creek and in southeast Pittwater. In addition, high levels of contamination of sediments were found in the upper and lower sections of the river adjacent to the West Hornsby STP and the Calna Creek STP. Simonowski et al. (2003) reported that sediments in the upper Hawkesbury-Nepean River were not heavily polluted by heavy metals, although elevated concentrations of heavy metals were found in sediments near industrialized areas and sewage treatment plants.

In late 2006, Sediments from 52 locations in the lower Hawkesbury-Nepean River and tributaries were analysed for trace metals, major elements, nutrients, TOC, organic contaminants and grainsize, and 16 of these locations were selected to determine concentrations of tributyltin (TBT) in the sediments (URS, 2007; Matthai et al., 2009). Organic booster biocides (diuron, chlorothalonil, irgarol and dichlofluanid), which augment Cu-based antifoulants since TBT was banned in 1989, were analysed in sediments from four locations near marinas. Analysis for these compounds in sediments is rarely undertaken in Australia and the study was the first of its kind in the Lower Hawkesbury Estuary. Concentrations of diuron of up to 40  $\mu$ g/kg were detected in sediments near a marina compared with 51  $\mu$ g/kg at the reference location, suggesting an impact from booster biocides used in antifoulants on sediments in areas of high boating activity. Regionally, only few heavy metals and no organic contaminants exceeded ANZECC/ARMCANZ sediment quality guideline values in sediments of the Lower Hawkesbury Estuary.

However, sediments near marinas and riverside settlements in upper Berowra and Cowan Creeks contain elevated concentrations of TBT and trace metals that may pose adverse effects to aquatic biota.

### 1.2 Sediment Quality Guidelines

The ANZECC/ARMCANZ (2000) guidelines provide sediment quality guideline (SQG) values (a Trigger/Screening value and a High value) for a range of common contaminants. These SQG values are intended for use in the screening level assessment and to assist decisions when accompanied by additional lines of evidence (LOEs), e.g. bioavailability and ecotoxicology data.

The ANZECC/ARMCANZ (2000) SQG values are based on the effects of sediment contaminants on benthic organisms. The interim SQG trigger value (TV or ISQG-low) is based on the lower 10<sup>th</sup> percentile of an effects database (ANZECC/ARMCANZ, 2000). This is used as a screening value that if exceeded, additional investigations are made to determine whether there is indeed a risk posed by the guideline exceedance. A second upper guideline value, the ISQG-high, is also derived from the median of the effects data. It has no particular significance except as being indicative of a value above which there is a high probability of toxicity to benthic organisms.

Concerns continue to be expressed for the reliability of SQG values, however, it is important to recognise that as multiple stressors will be present in most sediments and organisms will have varying responses to different stressors, that the guidelines will never provide an ability to predict when ecotoxicological effects will occur. The purpose of the TVs is to act as a guide to when effects will not occur in any sediments and the upper values as a guide to when effects may become more likely to occur. Because the empirical guidelines were derived from a ranking of toxicity and other effects data, and because contaminants typically co-occur (e.g. metals and organics) then any toxicity was equally attributed to all components of the mixture. The toxicity 'ranking' used to derive the guidelines considered each of the contaminants individually and did not consider co-contributions to effects. As a consequence, toxicity in any one sediment sample may be due to high concentrations of a different contaminant in that sediment, but this is equally ascribed to the contaminant being considered even though its concentration was not sufficient to be causing effects. For many contaminants, the guidelines may then become overly conservative (Batley and Simpson, 2008).

An additional factor influencing the use for SQG values for screening relates to the fact that values exist for only the most common and well-studied contaminants. However, in many urban or industrialised environments, typically a much greater range of contaminants exists within sediments. As a consequence, it is not uncommon to observe toxic effects that cannot alone be attributed to contaminants for which SQG values exist. For most urban/industrialised locations, sediment may be expected to contain a range of unassessed chemical contaminants (including emerging contaminants), but typically these are at low concentrations.

The application of sediment guidelines involves a tiered, decision-tree approach (see Figure below).



Figure: The tiered framework (decision tree) for the assessment of contaminated sediments for metals

Following this risk-based framework, the total concentrations of contaminants are compared to SQG values. The initial comparison is usually made with the lower interim SQG values (ISQG-Low), termed 'trigger values' (TVs). If the contaminant concentrations exceed the TVs, further investigations should be initiated to determine whether there is indeed an environmental risk associated with the exceedance. It is important to recognise that the TVs were not intended for use as a pass/fail basis, but as a means of identifying contaminants of potential concern (COPCs).

The first-level screening compares the TV with the measured value for the total contaminant concentration in the sediment. If the TV is exceeded, the next step is to consider the background concentrations and potentially bioavailable of the contaminants. Exceedance of the TV is usually acceptable if it is below the background concentration. The contaminants whose concentrations exceed TVs following consideration of contaminant bioavailability are a refined list COPCs. Where concentrations of bioavailable contaminants exceed the TV, the SQG framework decision-tree then proceeds to the evaluation of additional lines of evidence (LOEs) to determine whether the contaminants are likely to affect ecosystem health (e.g. ecotoxicology, bioaccumulation, ecology).

### 1.3 TBT and Antifouling Paint Booster Biocides

Effective antifoulants are required to prevent the settlement and growth of marine organisms on submerged structures, such as buoys, fish cages and ship hulls. For many years, tributyltin (TBT) compounds were the most widely used active ingredients in paint formulations, but the use of TBT has been regulated internationally since 1990 due to its severe impact on the aquatic ecosystem and the demonstrated effects of TBT on the disruption of endocrine systems.

Restrictions on the use of TBT-based antifouling paints were implemented in New South Wales (NSW) in 1989. However, despite the partial ban on the use of TBT in Australia, a survey along the NSW coast found imposex in gastropods was still widespread 10 years after the introduction of the ban, in particular within harbour/bay areas, where contamination "hotspots" are still present and where physical remobilization and dispersion processes may be less pronounced compared to high-energy coastal areas (Gibson and Wilson, 2003).

Copper-based antifouling paints, particularly those that continually erode (ablating antifoulings) have been widely used since the banning of tributyltin and represent a major source of copper. Marinas are a possible source of trace metal contaminants to the estuaries as antifouling is applied and removed from vessels on slipways.

An additional aspect of the potential environmental impact of antifouling products for use in boating and marine infrastructure is the use of organic booster biocides in antifouling paints, which have replaced TBT-based coatings. This may represent an alternative that could represent toxic effects as a result of the synergistic interactions between various biocides used in these alternative products (Evans et al., 2000). The most commonly used biocides in antifouling paints following the introduction of the ban on TBT include Irgarol 1051, diuron, Sea-nine 211, dichlofluanid, chlorothalonil, zinc pyrithione, TCMS (2,3,3,6-tetrachloro-4-methylsulfonyl) pyridine, TCMTB [2-(thiocyanomethylthio) bezothiazole], and zineb. These compounds were shown to be present in increasing concentrations in waters and sediments in coastal environments in countries worldwide, including Australia (Konstantinou and Albanis, 2004).

There are currently limited data available on the potential ecotoxicological effects of the increasingly widespread use of organic booster biocides in the aquatic environment, although the review by Konstantinou and Albanis (2004) suggests that alternative antifouling products, which are based on copper metal oxides and organic biocides, may require continued research regarding potential environmental effects in water and sediments and ecotoxicity in biota. The monitoring, behaviour and toxicity of degradation products of these compounds should be emphasized in establishing criteria for the occurrence, fate and effects of organic antifouling paint booster biocides.

# 2 Objectives

The objectives for the Characterisation of Sediment Quality within the Lower Hawkesbury Estuary were as follows:

- 1. Assess the distribution of contaminants in sediment within the Lower Hawkesbury Estuary including "sinks", i.e. locations at which contaminants may accumulate;
- 2. Assess the quality of sediment referencing ANZECC/ARMCANZ (2000) interim sediment quality guidelines (ISQG);
- 3. Assess the small-scale spatial variability of selected contaminants;
- 4. Determine temporal trends in contaminant concentrations by comparing data collected in 2013 to those collected in 2006 (URS, 2007);
- 5. Identify major sources of contaminants to the receiving environment of the Lower Hawkesbury Estuary; and
- 6. Provide recommendations and remedial management actions based on outcomes of the study, as appropriate.

## 3 Scope of Work

Geochemical Assessments Pty Ltd was awarded Hornsby Shire Council's Invitation to RFQ3/2013 entitled "Characterisation of Sediment Quality within the Lower Hawkesbury Estuary". Sediment quality within the Lower Hawkesbury Estuary was characterised in two stages (Stage 1 and Stage 2) with a hold point following Stage 1 and review of Stage 1 outcomes by Hornsby Shire Council:

• Stage 1 addressed the Project Brief prepared by Hornsby Shire Council, including collection and analysis of sediment grab samples throughout the Lower Hawkesbury Estuary; and

• Stage 2 involved follow up of results in Stage 1, contaminant source assessment and a greatly expanded suite of contaminants analysed at selected locations.

This project was funded by the NSW Office of Environment and Heritage.

Sediment quality within the Lower Hawkesbury Estuary (Figure 1) was characterised in two stages (Stage 1 and Stage 2).

### 3.1 Stage 1

Sediment grab samples were collected at the 52 locations in the Lower Hawkesbury Estuary previous characterised for sediment quality by URS (2007). All samples were photographed and logged, and the physical/biological characteristics of sediments recorded.

Sediments from all locations were submitted to Advanced Analytical Australia Pty Ltd for the whole sediment chemical analyses of a suite of trace metals and elements, organic compounds, total organic carbon and nutrients (Section 4.3). Sediment samples from 16 locations were analysed for organotin compounds and samples from four locations were analysed for common antifouling biocides.

At each sampling location three grab samples were collected to assess small-scale spatial variability of selected contaminants (Section 4.5).

The particle size distribution of 52 primary sediment samples were assessed by wet and dry sieving into seven fractions. The particle size distributions results were used to assist in the assessment of grainsize/contaminant associations.

## 3.2 Stage 2

The scope of work comprising Stage 2 investigation was developed in response to a request by Hornsby Shire Council following review of the outcomes of Stage 1.

Three samples from Sandbrook Inlet and four samples from Berowra Creek were analysed common antifouling biocides to further assess the distribution of these contaminants in areas subject to high levels of boating activity.

Berowra Creek was identified in Stage 1 as having higher concentrations of many contaminants compared to other sections of the Lower Hawkesbury Estuary. Five additional samples were collected in Berowra Creek and analysed for the same suite of contaminants assessed in Stage 1 to further assess the source(s) of various contaminants in Berowra Creek.

Dithiocarbamates (i.e. Ferbam, Mancozeb, Maneb, Metham, Metiram, Propineb, Thiram, Zineb, Ziram) (as  $CS_2$ ) are the latest generation of antifouling biocides. Samples were collected from four locations in Sandbrook Inlet and five locations in Berowra Creek, as these locations are subject to high levels of boating activity. The laboratory attempted analyses of these compounds, but found that naturally occurring levels of  $CS_2$  confounded the analyses and concentrations of Dithiocarbamates could not be reported.

Concentrations of synthetic pyrethroids and 200 individual organic contaminants (including carbamates, triazines/triazoles, phenoxy acid herbicides, urea herbicides, fungicides, insecticides, OP's and miscellaneous biocides) that may accumulate in sediment were assessed at three locations in Sandbrook Inlet, five locations in Berowra Creek, two locations in Marramarra Creek, and five locations in the upper reaches of the study area.

In addition to analyses to meet the above objectives, the grain size and total organic content of all Stage 2 samples were determined to characterise the texture of sediments and normalise concentrations of organic compounds.

The Stage 2 field and analytical program also included a QAQC program designed to allow the precision and accuracy of the analyses to be assessed. Laboratory analytical variability and 'robustness' was also assessed by undertaking triplicate analyses of selected trace metals.

# 4 Methodology

## 4.1 Sediment Grab Sampling

Geochemical Assessments used its purpose-designed, 5 m sampling vessel to collect samples in the Lower Hawkesbury Estuary.

A stainless steel Tall Eckman<sup>TM</sup> grab sampler was previously used to collect sediment in the Lower Hawkesbury Estuary. The same grab was used for previous characterisation of sediment quality in the Lower Hawkesbury Estuary in 2006 (URS, 2007) (Plate 1).

The choice of grab sampler is a very important consideration in achieving comparable samples to be used for temporal assessments, as the type and size of grab determines the area and depth of sampling. This is particularly important in circumstances where the load of sediment contaminants have changed, as different depths of sampling would represent different periods of sediment accumulation.

Sampling positions were located using Geochemical Assessments' differentially corrected global positioning system (GPS) with an accuracy of about 2 m.

Sediment sampling for Stage 1 was undertaken over four days of fieldwork, commencing on 6 May 2013. At each Stage 1 sampling location three grab samples were collected to assess small-scale spatial variability of selected contaminants. About 500 mL of sediment was collected for primary (i.e. not including QA/QC) subsamples and 250 mL subsampled for triplicate samples.

Sediment sampling for Stage 2 was undertaken over four days of fieldwork, commencing on 29 June 2013. At each sampling location a single grab sample was collected and a subsample was submitted to the laboratories. The majority of samples were collected from previously sampled locations, however five samples in Berowra Creek were collected at new locations to assess potential sources of contamination. About 500 mL of sediment was collected for primary subsamples

All samples were photographed and logged, and the physical/biological characteristics of sediments were recorded.

All sample handling and processing was performed to minimise contamination and sample mix-ups. The workspace on the vessel was washed down regularly with ambient seawater to clean working surfaces and minimize dust contamination of samples. Nitrile gloves were worn by all field personnel handling the sediment, and gloves were disposed after processing each sample.

The penetration of the grab sampler was measured. Each subsample was collected in a clean, stainless steel bowl for homogenization, prior to the filling of analytical laboratory-supplied clean sampling jars.

Sample containers were labelled and filled with zero headspace. Samples were placed in eskies on ice on board the vessel, and then stored in a refrigerator for up to two and a half days prior to the submission of the samples to the analytical laboratory for processing. Sediments were submitted to the laboratories in a single batch at the conclusion of each sampling stage.

All samples were delivered to appropriate laboratories under Geochemical Assessments' Chain of Custody (CoC) protocol.



Plate 1 Sediment Grab in Operation at Berowra Creek (Location H7)

## 4.2 Sampling Locations

Fifty-two locations (H1 to H39 and H43 to H55) sampled by URS (2007) in December 2006 were sampled in Stage 1 (Table 1, Figure 2). Three grab samples were collected at each sampling location in Stage 1 as replicates. Samples prefixed with "2", e.g." 2H13" indicated that the locations were resampled as part of Stage 2 sampling program, but analysed for different chemicals.

Five additional samples (H56 to H60) were collected in Berowra Creek and analysed for the same suite of contaminants assessed in Stage 1 to further assess the source(s) of various contaminants in Berowra Creek. Despite extensive searches to locate fine grained sediment in Berowra Creek upstream of location H11 at Berowra Waters and in the lower reaches of Crossland Creek, potentially contaminated sediment representing input catchment sources could not be located. In addition, point sources such as major stormwater drains were not identified. Two of the five samples (H57 and H59 were collected near boat maintenance facilities at Berowra Waters. Three samples (H56, H58 and H60) were located between previous sample locations to further assess contaminant gradients in sediment at Berowra Waters.

In Stage 2, sample locations H11, H53 and H54 were moved (<100 m) closer to the shoreline to locate finer grained sediment that was more likely to accumulate contaminants.

### 4.3 Whole Sediment Chemical Analyses

The analytical suite for all 52 primary Stage 1 samples included:

• Trace metals and elements (Ag, Al, As, Ba, Be, Bo, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, Sr, V and Zn);

- Polycyclic aromatic hydrocarbons (PAHs);
- Total petroleum hydrocarbons (TPHs);
- Polychlorinated biphenols (PCBs);
- Organochlorine pesticides (OCs);
- Organophosphorus pesticides (OPs);
- Nutrients (TKN, TOC, NOX, reactive inorganic phosphorus);
- Ammonia; and
- TOC.

Samples from 16 sediment sampling locations (H7-H10, H17, H18, H21-26, H28, H31, H37 and H38) and two field duplicates (total 18 samples) were analysed for MBT, DBT and TBT.

Sediment samples from four locations (H9, H31, H37 and H38) and one field duplicate (total 5 samples) were analysed for the following common antifouling biocides:

- Diruon;
- Chlorothalonil;
- Irgarol 1051; and
- Diclorofluanid.

The particle size distribution of 73 sediment samples were assessed by wet and dry sieving into seven fractions ( <62.5  $\mu$ m; 62.5-125  $\mu$ m; 125-250  $\mu$ m; 250-500  $\mu$ m; 500-1000  $\mu$ m; 1-2 mm; >2 mm) by Geochemical Assessments.

Eleven samples were analysed in triplicate (total 33 analyses) for trace metals (Co, Cu, Cr, Ni, Pb and Zn), As and Al to assess laboratory variability and analytical 'robustness'.

Seven samples in Sandbrook Inlet (locations H17, H18 and H39) and Berowra Creek (locations H7, H8, H10 and H11) were collected and analysed for Diuron, Chlorothalonil, Irgarol 1051, Dichlhlofluanid.

Five samples in Berowra Creek were analysed for:

• Trace metals and elements (Ag, Al, As, Ba, Be, Bo, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Ni, P, Pb, Sr, V and Zn);

- Polycyclic aromatic hydrocarbons (PAHs);
- Total petroleum hydrocarbons (TPHs);
- Polychlorinated biphenols (PCBs);

- Organochlorine pesticides (OCs);
- Organophosphorus pesticides (OPs);
- Nutrients (TKN, TOC, NOX, reactive inorganic phosphorus);
- Ammonia; and
- TOC.

Sediments were collected at three locations in Sandbrook Inlet (H17, H18 and H38), five locations in Berowra Creek (H7, H8, H9, H10 and H11), two locations in Marramarra Creek (H12 and H13), and the upper estuary (H51, H52, H53, H54 and H55) and analysed for synthetic pyrethroids: Bioresmethrin, Bifenthrin, Phenothrin, Cyhalothrin, Permethrin, Cyfluthrin, Cypermethrin, Fenvalerate, Fluvalinate, and Deltamethrin.

The concentrations of a suite of carbamates, triazines/triazoles, phenoxy acid herbicides, urea herbicides, fungicides, insecticides, OP's and miscellaneous biocides were assessed in sediment collected from three locations in Sandbrook Inlet (H17, H18 and H38), five locations in Berowra Creek (H7, H8, H9, H10 and H11), two locations in Marramarra Creek (H12 and H13), and five locations in the upper estuary (H51, H52, H53, H54 and H55).

Sampling locations and analytes are summarised in Table 2.

### 4.4 Analytical Methodologies

#### **Moisture Content**

An aliquot of well-mixed sediment was placed in a pre-weighted clean aluminium dish and vegetation and foreign material (including rocks, gravel, concrete, and seashell) were removed before weighing accurately. After drying in a preheated 105°C oven for a minimum of 12 h, the aliquot was allowed to cool to ambient temperature. The dried sample in the dish was again accurately weighed and the difference used to determine the moisture content.

#### **Trace Elements by ICP-OES**

A sample aliquot was oven-dried at 40°C until sufficient, homogenized and then sieved through 2 mm grid. A portion of dried sample was then heat-digested in acids and cooled to ambient temperature. The digest was then diluted in water with an appropriate internal standard followed by analysis by ICP/OES.

#### **TPH C6-C9**

Sediments were first spiked with a surrogate solution then extracted with methanol and an aliquot of this solution was mixed with organic free water. The volatile compounds were introduced into a gas chromatograph by the purge and trap technique and after separation were detected by an ion trap mass spectrometer operating in Electron Impact Ionization and full scan modes.

#### **TPH C10-C36**

Sediment samples were extracted with organic solvent after addition of an appropriate surrogate using ultrasonic extraction. The sediment sample extracts were then concentrated and analysed by GC-FID.

#### PAHs

Sediment samples were extracted with DCM / acetone / hexane after addition of an appropriate surrogate using ultrasonic extraction. The sediment sample extracts were then concentrated. Sample extracts were analysed by GCMS in Positive Electron Impact Ionization SIM Mode.

#### OCs/OPs

Sediment samples were extracted with organic solvent after addition of an appropriate surrogate using ultrasonic extraction. The sediment sample extracts were then concentrated. Sample extracts were analysed by GCMS in Positive Electron Impact Ionization SIM Mode.

#### PCBs

Sediment samples were extracted with organic solvent after addition of an appropriate surrogate using ultrasonic extraction. The sediment sample extracts were then concentrated and analysed by GCMS in Positive Electron Impact Ionization SIM Mode.

#### Organotins

Samples were spiked with an appropriate surrogate then extracted with acidified solvent containing a chelating agent. Organotins extracted this way were ethylated using a derivatising agent, extracted into hexane and analysed by GCMS.

#### **Synthetic Pyrethroids**

Sediment samples were extracted with organic solvent after addition of an appropriate surrogate using ultrasonic extraction. The sediment sample extracts were then concentrated. Sample extracts were analysed by GCMS in Positive Electron Impact Ionization SIM Mode.

#### **Organic Booster Biocides**

Sediment samples were extracted with organic solvent after addition of an appropriate surrogate using ultrasonic extraction. The sediment sample extracts were then concentrated and an analyte protectant was added to prevent breakdown of chlorothanolil on the GCMS. Sample extracts were analysed by GCMS in Positive Electron Impact Ionization SIM Mode.

### LCMS Screening

Pesticide residues were extracted from soils and sediments using modified QUECHERS extraction. This involves solvent extraction, use of buffering salts, shaking and centrifuging. Further, extracts were concentrated and filtered and analysed using LCMSMS. Quantification was performed using Matrix based calibration standards and an internal standard, which was added to the samples before extraction.

#### Ammonia

A wet, unprepared sample was dissolved in cold, deionised water at a ratio of 1:5, stirred well and allowed to settle overnight in the fridge. The supernatant was then analysed by Flow Injection Analyser using the standard colorimetric reaction (Phenate method).

#### TKN

A dry and crushed (<1 mm) sample was digested with sulphuric acid and Kjeldahl reagent to 400°C. The digest was then distilled with caustic soda in a distillation unit and titrated to determine the ammonia released and hence the TKN.

#### NOx

A wet, unprepared sample was dissolved in cold, deionised water at a ratio of 1:5, stirred well and allowed to settle overnight in the fridge. The supernatant was then analysed by Flow Injection Analyser using the standard colorimetric reaction (Cadmium Reduction Method).

#### **Reactive Inorganic Phosphorus**

A wet, unprepared sample was dissolved in cold, deionised water at a ratio of 1:5, stirred well and allowed to settle overnight in the fridge. The supernatant was then analysed by Flow Injection Analyser using the standard colorimetric reaction (Molybdenum Blue Method).

#### тос

A dry and crushed (<150  $\mu$ m) sample was heated with hydrochloric acid on a hotplate to remove any carbonate present. The dried sample was then analysed by a combustion analyser at 900°C with an infrared detector to measure the amount of carbon dioxide released on heating, and hence the amount of organic carbon in the sediment.

### 4.5 Assessment of Small-Scale Spatial Variability

Samples from three separately collected grab samples were analysed for selected contaminants (Al, As, Co, Cu, Cr, Ni, Pb and Zn) to assess their small-scale spatial variability. Aluminium was also analysed in each sample (as a proxy for sediment grainsize) to assess whether apparent variability in reported contaminant concentrations of triplicate samples was controlled by sediment texture.

The small-scale variability of trace metals such as Cu, Pb and Zn in deeper water, depositional areas in the Lower Hawkesbury Estuary was expected to be only slightly higher than the analytical variability (Birch et al., 2001). Elements expected to be present at concentrations close (or below) to detection limits at many locations (e.g. cadmium and mercury) would also display higher apparent spatial variability as a result of higher analytical variability and were therefore not tested. In addition, concentrations of analytes controlled by other factors (e.g. manganese by redox conditions) were also expected to display higher small-scale spatial variability were not analysed in triplicate. Sr, Ba, Be and V were not considered primary contaminants of concern and were therefore also not analysed in triplicate.

The small-scale spatial variability of PAHs was assessed at 15 selected locations thought to contain concentrations greater than the limit of reporting (LOR). The variability of TOC was not assessed in triplicate samples and the small-scale variability of PAH concentration was based on unnormalised data. From the URS (2007) investigation, concentrations of other organic contaminants were expected to be low (commonly below LOR) and the small-scale spatial variability of OCs, OPs, PCBs and TPH was not assessed.

### 4.6 Quality Assurance/Quality Control Samples

In addition to the 57 primary subsamples analyses in Stages 1 and 2 the following QA/QC samples were analysed:

- QA/QC duplicate sample analyses (10% of primary sample);
- Three method blank samples ('field blank') comprising acid washed sand, were analysed for trace metals;
- Two "medium" and "low" dried, in house laboratory standards (total 4 samples) submitted for trace metal analyses were compared to mean concentrations from historical analyses. These standards were used to assess the accuracy of selected inorganic analyses.
- Eleven samples (previously analysed in duplicate) were reanalysed in triplicate (total 33 analyses) to assess laboratory variability (including small-scale, spatial variability) and the laboratory' ability to replicate results over time, i.e. the robustness of the temporal assessment of contaminant concentrations.

# 4.7 Data Quality Objectives

Laboratory Limits of Reporting (LoRs) for the analysis of sediments are stipulated in the following Table:

### Laboratory Limits of Reporting

Analyte	Limits of Reporting	
Trace Metals		
As, Cr, Cu, Ni, Pb, Zn	1 mg/kg	
Cd	0.1 mg/kg	
Hg	0.01 mg/kg	
Organotin compounds (TBT, DBT, MBT)	0.5 μgSn/kg	
PAHs	5 μg/kg (Sum: 100 μg/kg)	
TPHs	10-50 μg/kg	
OCPs	1 μg/kg (individual species)	
Total Nitrogen, Including TKN, Nox	20 mg/kg	
Reactive Phosphorus	0.1 mg/kg	
Ammonia	0.1 mg/kg	
Total Organic Carbon	0.01%	
Moisture Content	0.1%	
Biocide additives	0.0101 mg/kg	
Dithiocarbamates (as CS <sub>2</sub> )	0.1 mg/kg	
Phenoxy Acid Herbicides	0.01-0.05 mg/kg	
Carbamates	0.005 mg/kg	
Triazines	0.01 mg/kg	
Synthetic Pyrethroids	0.05 mg/kg	
Sulphonyl Urea	0.01- 0.05 mg/kg	
Bisphenol A	0.05 mg/kg	
Antibiotics and Antimicrobials	0.005-0.05 mg/kg	
Miscellaneous multi-residues	0.01-0.1 mg/kg	

Proposed Data Quality Objectives (DQOs) for the field and analytical programs are outlined in the Table below.

### Analytical Data Quality Objectives

Parameter	Data Quality Objective
Blank Samples	At or near the Limit of Reporting (LOR)
Sample Condition	Samples received intact and cold
Analytical Holding Time	Organic compounds 2 weeks, trace metals 6 months
Field Duplicate Samples (1 in 10 samples)	RPD <50%
Lab Duplicate Samples (1 in 10 Samples)	RPD <35% or as per laboratory requirement
Surrogate (Every Sample)	Recovery as per laboratory requirement

Note: At low concentrations (i.e. within 5 times LOR) the level of precision, as characterised by Relative Percent Differences (RPDs) specified in the above Table may not be achievable. For concentrations within 5 times LOR the acceptable range was 0-100% RPD.

## 5 Results

### 5.1 Field Observations

The sediment grab collected around 10 cm of soft, muddy sediment, but penetration in coarser sediment was lower, typically 6 cm (Table 3). Photographs of sediment samples are provided in Appendix A.

The majority (85%) of samples collected throughout the Lower Hawkesbury Estuary were muds (silt and clay). A surficial layer of brown, hydrous (oxic) material typically overlay more cohesive grey/brown mud (Plate 2). Deeper water areas in Berowra and Cowan Creeks typically contained fine grained (>90%, <63 µm) sediment (Table 3).



Plate 2 Typical Muddy Sample from Berowra Creek (Location H4)

Sediment textures were markedly coarser in the upper reaches of the study area towards Wisemans Ferry (H53 and H54). Samples H12 (Marramarra Creek) (Plate 3) and H36 (Dangar Island), and H53 and H54 (upstream near Wisemans Ferry) consisted of sand.



Plate 3 Sandy Sample Collected in Marramarra Creek (Location H12)

The field observed texture of the majority of triplicate sediment samples were similar, with the exception of triplicate grab samples at locations H26 and H27 in Cowan Creek and location H55 in the main channel that were notably different in grain size.

A moderate 'organic' odour was noted from sediments collected at locations H10 and H11 in Berowra Creek.

Biological activity observed in/on sediment included bioturbation, worm burrows, faecal pellets, gastropods, bivalves, prawns and fish (Table 3).

Few live flora were observed, but abundant leaves and sticks were present in sediment at some locations. Abundant filamentous algae were present lying on sediment at location H47.

### 5.2 Sediment Textures

The fine (<63 mm, silt and clay) fraction content of samples H1 to H60 varied from 1.1 to 99.2% (mean 70.5%) (Table 4, Figure 3).

The fine fractions of sediment were highest (>95%) at locations in Berowra Creek (H5, H6 and H7), Cowan Creek (H23, H24, H29, H30 and H31), Mullet and Mooney Mooney Creeks and Sandbrook Inlet (H18 and H38). The fine fraction of sediment was lower in the main Hawkesbury Channel. Coarser gained (sandy) sediment was present near Milson Island (H44 and H45), southeast of Dangar Island (H36), upstream near Wisemans Ferry (H53 and H54), at Cottage Point (H27) and at Apple Tree Bay (H22).

The sand (63 - 2000  $\mu$ m) content of all samples varied from 0.8 to 98.7% (mean 29%). The sand fractions were predominantly fine to medium (63 to 500  $\mu$ m), rather than coarse (500- 2000  $\mu$ m).

The gravel fraction of all samples was less than 5% in all samples (mean 0.50%) except at north of both Gunyah Point (H34, 15.4%) and Milson Island (H45, 5.9%).

## 5.3 Concentrations of Inorganic Contaminants in Sediment

Chemical and grainsize laboratory reports and Chain of Custody documents are provided in Appendix B (Laboratory Results).

Concentrations of trace metals in the Lower Hawkesbury Estuary were generally highest in the upper reaches of Berowra and Cowan Creeks and in Sandbrook Inlet (Table 5).

Concentrations of aluminium (range, 527 to 20,333 mg/kg) (Figure 4) and iron (range, 1,300 to 41,000 mg/kg) in sediment displayed the same spatial distribution as the fine (<63  $\mu$ m) faction component of sediment. Concentrations of both aluminium and iron were notably low at locations H12, H22 H27, H36, H53 and H54. Sediment in deeper water areas in Cowan and Berowra Creeks contained higher concentrations of aluminium and iron.

Concentrations of copper in sediment (range, 0.4 to 343 mg/kg) exceeded 65 mg/kg in the upper reaches of Berowra Creek, Akuna Bay and Bobbin Head, and were between 30 and 65 mg/kg in Sandbrook Inlet (Figure 5).

Concentrations of lead in sediment (maximum 110 mg/kg) were higher (>50 mg/kg) in the upper reaches of Berowra and Cowan Creeks and generally low (<20 mg/kg) in the main Hawkesbury River channel (Figure 6).

Concentrations of zinc in sediment (range, 3.5 to 413 mg/kg) were higher (>150 mg/kg) in upper reaches of Berowra Creek, Akuna Bay and Bobbin Head, and were lower in the main Hawkesbury channel (Figure 7).

Concentrations of cadmium (maximum 0.4 mg/kg) in sediment were generally low (<0.1 mg/kg) throughout the Lower Hawkesbury Estuary, but exceeded 0.3 mg/kg in the upper reaches of Berowra Creek and exceeded 0.2 mg/kg in Akuna Bay.

Concentrations of chromium in sediment (range, 21.6 to 32 mg/kg) were higher (28 mg/kg) in the upper reaches of Berowra Creek and in Cowan Creek compared to elsewhere in the Lower Hawkesbury Estuary.

Concentrations of mercury in sediment (maximum 0.74 mg/kg) exceeded 0.25 mg/kg in the upper reaches of Berowra Creek, and in Akuna Bay, Cottage Point and Bobbin Head in Cowan Creek (Figure 8).

Sediment containing 0.15 to 0.25 mg/kg of mercury were widely distributed at Brooklyn (H16 and H38), Cowan Creek (H23), Mooney Mooney (H43), downstream of Spencer (H48), Wisemans Ferry (H54) and Berowra Creek (H59). Concentrations of mercury in the main Hawkesbury River channel were low.

Concentrations of silver in sediment (maximum 0.7 mg/kg) exceeded 0.15 mg/kg only in the upper reaches of Berowra Creek (not including location H11); elsewhere the concentrations of silver in sediment were low (Figure 9).

Concentrations of strontium in sediment (range, 59.9 to 210 mg/kg) were markedly higher (>80 mg/kg) at locations H23 to H32 in the middle and lower reaches of Cowan Creek, location H34 in the main channel and location H11 in Berowra Creek compared to elsewhere in the Lower Hawkesbury Estuary (Figure 10).

Concentrations of arsenic in sediment (range, 14.8 to 28 mg/kg) exceeding 18 mg/kg were located in lower reaches of Berowra and Cowan Creeks, Mullet and Mooney Mooney Creeks and Sandbrook Inlet (Figure 11).

Concentrations of nickel and vanadium in sediment (maximum 34.0 and 170 mg/kg, respectively) were higher in the middle reaches of Berowra and Cowan Creeks, Mullet and Mooney Mooney Creeks, Sandbrook Inlet and in the main Hawkesbury River channel upstream of Spencer.

The distributions of barium and beryllium (maximum 47.0 and 1.5 mg/kg, respectively) were similar to that of arsenic and higher concentrations were present in lower reaches of Berowra and Cowan Creeks, Mullet and Mooney Mooney Creeks, Sandbrook Inlet and the main Hawkesbury River channel upstream of Spencer.

Concentrations of boron in sediment (range, 23.6 to 58.0 mg/kg) were higher in upper reaches of Berowra and Cowan Creeks and lower in the main Hawkesbury River channel, with the exception of location H45 at the northern end of Milson Island (39 mg/kg).

Concentrations of cobalt in sediment (range, 0.7 to 13.0 mg/kg) were highest (>10 mg/kg) in the lower reaches of Berowra Creek and up and downstream of Spencer. Concentrations of cobalt in sediment were generally lower (<10 mg/kg) in the upper reaches of Berowra and Cowan Creeks.

Concentrations of manganese in sediment (range, 14.0 to 1,300 mg/kg) were highest (>600 mg/kg) in the mid reaches of Berowra and Cowan Creeks, Mullet and Mooney Mooney Creeks, Sandbrook Inlet and locations H50 to H53 in the main Hawkesbury River channel (Figure 12). Concentrations of manganese in sediment were relatively low (<200 mg/kg) in the upstream reaches of Berowra and Cowan Creeks.

The distribution of calcium in sediment (range, 9.2 to 41,000 mg/kg) was similar to that of strontium, but also high (>9,000 mg/kg) at location H45 north of Milson island and location H14 in the main channel at Mooney Mooney.

## 5.4 Concentrations of Organic Contaminants in Sediment

Concentrations of organic contaminants reported above the limit of resolution (LOR) in the Lower Hawkesbury Estuary are presented in Table 6. Concentrations of organic contaminants were normalised to 1% total organic carbon (TOC) (in the range 0.2 to 10% TOC) to allow comparison with ANZECC/ARMCANZ (2000) guideline values.

Concentrations of TPH C6-9 and TPH C10-14 were below LOR (10-20 mg/kg) in all samples. Concentrations of total TPH varied from less than LOR to 850 mg/kg. Concentrations of total, normalised TPH in sediment varied from less than LOR to 125 mg/kg (Berowra Waters, H9) (Figure 13). Concentrations of total, normalised TPH exceeding 45 mg/kg were restricted to sediments at Berowra Waters, Bobbin Head and Akuna Bay.

The maximum concentration of low molecular weight, high molecular weight and total PAHs in sediment were 305, 1,900 and 3,713  $\mu$ g/kg, respectively. Maximum concentration of individual PAHS varied from 19  $\mu$ g/kg (Acenaphthene) to 553  $\mu$ g/kg (Benzo(b)&(k)fluoranthene). The maximum concentrations of normalised, low molecular weight, high molecular weight, and total PAHs in sediment were 110, 655 and 1,280  $\mu$ g/kg (Sandbrook Inlet, H18), respectively. The distribution of total, normalised PAHs in sediment is shown in Figure 14. Concentrations of total, normalised PAHs exceeded 500 mg/kg in Sandbrook Inlet, near the confluence of Marramarra Creek (Locations H12 and H2) and in Mooney Mooney and Mullet Creeks.

The concentrations of total, normalised PCBs exceeded detection limits only at Bobbin Head (location H21, 4.5  $\mu$ g/kg) and Berowra Waters (location H57, 1.5  $\mu$ g/kg).

The concentration of TBT in sediment exceeded the detection limit  $(0.5 \ \mu gSn/kg)$  in 18 out of 21 samples (Figure 15). Concentrations of normalised TBT exceeded (5  $\mu gSn/kg$ ) at Bobbin Head (7.7  $\mu gSn/kg$ ), in two samples collected at Akuna Bay (maximum, 9.5  $\mu gSn/kg$ ) and in two samples from Berowra Creek (maximum, 43.7  $\mu gSn/kg$ ).

Concentrations of total, chlordane (maximum 14  $\mu$ g/kg) exceeded detection limits at 9 out of 57 samples (Table 6). Concentrations of total, normalised chlordane (maximum 1.4  $\mu$ g/kg) exceeded detection limits at eight locations in upper Berowra Creek and at Bobbin Head (location H21).

Concentrations of total, DDT in sediment in the Lower Hawkesbury Estuary varied from less than LOR to 34.0 µg/kg. Concentrations of total, DDT exceeding 10 µg/kg were present in sediment in the upper reaches of Berowra Creek, Bobbin Head and at location H14 at Mooney Mooney. The maximum concentration of total, normalised DDT in sediment in the Lower Hawkesbury Estuary was 10.3 µg/kg (Figure 16). Concentrations of total, normalised DDT exceeded 1.6 µg/kg in sediment in the upper reaches of Berowra Creek, Bobbin Head (H21), Brooklyn (locations H16 and H35) and at Mooney Mooney (location H14).

The concentration of all other organochlorine and organophosphate pesticide residues, with the exception of a single analysis of Heptachlor Epoxide at the furthest upstream sampling location in Berowra Creek (location H11,  $4 \mu g/kg$ ), were below their respective detection limits (Table 6).

Concentrations of Chlorothalonil, Dichlofluanid and Irgarol 1051 were below the detection limit  $(50 \ \mu g/kg)$  in all samples analysed.

Concentrations of Diruon exceeded the detection limit (50  $\mu$ g/kg) only in two samples collected from Sandbrook Inlet (maximum 95  $\mu$ g/kg) (Appendix B).

The concentrations of all other organic analytes were reported as below their respective detection limits (Appendix B). This unexpected outcome was the subject of repeated and extensive reanalyses, and evaluation to confirm the reported results.

# 5.5 Concentrations of Nutrients in Sediment

Concentrations of nutrients in the Lower Hawkesbury Estuary are presented in Table 7.

Concentrations of ammonia in sediment varied from 0.5 to 8.7 mg/kg. Ammonia concentrations exceeding 5 mg/kg were present in sediment at four locations in Berowra Creek, Cottage Point (H27), Akuna Bay (H25) and at locations H50 and H51 upstream of Spencer (Figure 17). Concentrations of ammonia in the central section of the Lower Hawkesbury Estuary including Sandbrook Inlet were generally low (<1.5 mg/kg).

Concentrations of NOx (as N) in sediment throughout the Lower Hawkesbury Estuary were low. Only two samples (H18 and H53) contained concentrations of NOx (as N) greater than LOR (0.1 mg/kg) and the maximum concentration was 0.4 mg/kg.

Concentrations of Total Kjeldahl Nitrogen in sediment (range, 150 to 5,560 mg/kg) exceeded 3,500 mg/kg in the upper reaches of Berowra Creek and Cowan Creek (except in Apple Tree Bay, H22) (Figure 18).

Concentrations of phosphorus in sediment varied from 38 to 1,800 mg/kg. Phosphorus was higher (>800 mg/kg) in Berowra and Cowan Creeks and lower (<500 mg/kg) in the main Hawkesbury River channel (Figure 19). Concentrations of reactive phosphorus in sediment were less than LOR in sediment apart from Berowra Waters (7 samples, maximum 4.0 mg/kg).

The total organic carbon (TOC) content of sediment varied from 0.5 to 13.0%. Higher contents of TOC (>5%) was present in Berowra Creek and upstream sections of the Lower Hawkesbury Estuary (except location H54) (Figure 20). Sediment contained a low (<5%) content of TOC downstream of Mooney Mooney, in Cowan Creek, except at Bobbin Head (location H21), and Akuna Bay (location H26).

# 5.6 Small-Scale Spatial Variability of Contaminant Concentrations

The small-scale spatial variability (including laboratory variability) of aluminium, arsenic, cobalt, chromium, copper, nickel, lead and zinc in sediment, was assessed by analysis of triplicate samples collected at 52 locations. A relative standard deviation (RSD) of three or more values is the standard deviation of the data divided by the mean value and expressed as a percentage. The small-scale spatial

variability of aluminium, arsenic, cobalt, chromium, copper, nickel, lead and zinc, expressed as a mean RSD of triplicate grab samples of all locations (5.8, 5.0, 4.5, 4.7, 8.0, 4.9, 5.2 and 6.2% RSD, respectively) were low (Table 8).

The small-scale spatial variability (including laboratory variability) of PAHs in sediment (expressed as RSD) was assessed in triplicate samples collected at 15 locations. The maximum RSD of individual PAHs was 80.5%. The mean RSD of individual PAHs varied from 3.6 to 20.7%. The variability of low molecular weight PAHs (e.g. 2-Methylnaphthalene, Acenaphthylene, Acenaphthene and Fluorene) was generally lower than that of high molecular weight PAHs (Fluoranthene, Pyrene, Benz(a)anthracene, Benzo(a)pyrene and Indeno(1,2,3-cd)pyrene). The RSD of 15 total (i.e. un-normalised) PAHs varied from 0.6 to 79.1% (mean 16.0%).

### 5.7 Analytical Robustness

Eleven dried and ground samples (also analysed as laboratory duplicates) were analysed in triplicate to assess variability expressed as RSD and robustness of analyses in different batches several months apart (Table 9).

The mean analytical variability of Al, As, Co, Cu, Cr, Ni, Pb and Zn was very low and varied from 1.1% to 1.9 % RSD. The precision of individual triplicate analyses varied from 5.4% RSD for zinc to 10.8% RSD for arsenic.

Mean concentrations reported in Stage 2 triplicate analyses were compared to mean concentrations reported in laboratory duplicate analyses of Stage 1 analyses of the same samples. The mean concentrations derived by duplicate and triplicate analyses varied from 1.4% relative percent difference (RPD) for arsenic to 4.4% RPD for lead. These results are similar to the precision of laboratory duplicates reported in Stage 1 analyses and indicated that the analytical methodology was robust over time and for different sample batches.

### 5.8 Data Validation

The primary objective of the data validation process was to ensure that the data reported can be used to achieve the project objectives. The validity of all analytical data reported was assessed by critical review of the QA/QC sample results.

Accuracy and precision measurements from the appropriate QA/QC samples were compared with the analytical Data Quality Objectives (DQOs) to assess the quality of the analytical data. QA/QC validation results are summarised below and QA/QC data tables are compiled in Appendix C (QA/QC Data Validation).

### 5.8.1 CoCs

CoCs were checked, signed and provided by the analytical laboratories.

The CoCs and sample receipt notices indicated that samples were received in chilled conditions.

All holding times complied with laboratory protocols.

### 5.8.2 Blank Samples

All analyses of beryllium, boron, cadmium and cobalt in the three method blank analyses were below LOR.

The laboratory supplied sand contained aluminium, calcium and iron but low concentrations of chromium, copper, nickel, lead, vanadium and zinc.

Anomalous concentrations of silver (0.34 mg/kg) and mercury (0.89 mg/kg) were reported in one of the three blank samples.

As the majority of analyses of organic contaminants were reported as less than LOR, the potential for contamination from organic compounds derived from sampling equipment was also negligible.

# 5.8.3 Laboratory Duplicate Samples

The relative percent difference (RPD) of two numbers is the absolute difference in the numbers, divided by the mean of the two numbers and expressed as a percentage (i.e. multiplied by 100). The RPD of all laboratory duplicate pairs (in which concentrations were greater than 5 times LOR) was considerably less than the Data Quality Objective (DQO) of 35%.

Twenty two laboratory duplicate pairs of samples were analysed by Advanced Analytical Australia Pty Ltd and the mean relative per cent difference (RPD) of all individual trace metal analyses (excluding boron 17%) were less than 6%. Commonly accepted DQO state that the RPD of laboratory duplicates should be less than 35%.

The precision of laboratory duplicates for PAHs was somewhat higher than for trace metals, but was also good for these hydrophobic compounds analysed at ultra-trace levels. A single duplicate pair of Acenaphthene, Fluorene, Pyrene and Benz(a)anthracene marginally exceeded the DQO of 35 % (maximum 41.9%). The mean RPD of nine laboratory duplicate pairs of samples analysed for various individual PAHs varied from 3.3 to 10.1%.

The precision of TPH analyses as indicated by laboratory duplicates was high (maximum 12.8 % RPD).

The precision of TPH analyses as indicated by field duplicates was high (<17 % RPD) except for a single pair of duplicates for TPH C15-28 (66.7% RPD).

The precision of laboratory duplicates for nutrients, biocide additives were well within DQOs.

Laboratory duplicates for two pairs of TBT analyses met the DQOs, but the maximum variability of the third pair was 128.4% RPD and did not meet the DQO.

The precision of TOC and ammonia analyses as indicated by analyses of laboratory duplicates pairs was high.

### 5.8.4 Field Duplicate Samples

Seven field duplicate pairs of samples were analysed and the mean RPD of all inorganic duplicates (apart from boron 15.2 % and calcium 17.0%) were less than 10%. Commonly accepted Data Quality Objectives state that the RPD of field duplicates should be less than 50% (where concentrations of the analyte exceed five times the detection limit).

The mean RPD of seven field duplicate pairs of samples analysed for various individual PAHs varied from 8.2 to 18%. The precision of individual PAH analyses as indicated by field duplicates was high and met the DQO except for a single pair of duplicates for Benz(a)anthracene (36.3% RPD).

The precision of TPH analyses as indicated by field duplicates was high (<17 % RPD) except for a single pair of duplicates for TPH C15-28 (66.7% RPD).

Field duplicate pairs for nutrients, biocide additives were within DQOs except for a single duplicate pair of reactive phosphorus analyses at close to LOR (RPD 66.7%).

Field duplicates for two pairs of TBT analyses met the DQOs, but marginally exceeded the DQO in the third pair (40% RPD).

### 5.8.5 Surrogate Analyses

The recovery of surrogate analytes was assessed for TPHs (one surrogate) PAHs (three surrogates), OC pesticide residues (one surrogate) and PCBs (two surrogates), Synthetic Pyrethrods (one surrogate), and TBT (one surrogate).

Three surrogate analyses out of 498 were outside the acceptable range (75 to 125% recovery) in Stage 1 analyses. One surrogate analyses out of 63 were outside the acceptable DQO (75 to 125% recovery) in Stage 2 analyses.

### 5.8.6 Internal Laboratory Standard Analyses

Four dried in house laboratory standard was submitted and analysed for Cd, Cr, Cu, Ni, Pb and Zn and compared to mean concentrations from a database of historical analyses.

The accuracy of trace metal analyses as indicated by analyses of the internal laboratory standards, was high. The RPD of all internal laboratory standards analysed with the primary samples was less than 25%.

### 5.8.7 Grainsize Analyses

Laboratory duplicates of six samples were analysed for grainsize. The RPD of duplicate pairs of <63  $\mu m$  fraction analyses varied from 0.3 to 1.7%, indicating high precision.

The RPDs of six out of thirty-six duplicate pairs of >63  $\mu$ m analyses exceeded the DQO of 35%, due to the very low percentages of the reported fractions.

### 5.8.8 Data Validation Summary

The potential for contamination of subsamples by the sampling equipment, as indicated by blank samples, was negligible, except perhaps for silver and mercury.

The precision of trace metal and nutrient analyses as indicated by field and laboratory duplicates was high. The accuracy of trace metal analyses, indicated by analyses of internal laboratory standards, was also high.

The majority of analyses of organic compounds were reported at concentrations below their respective LORs, but precision of analyses at concentrations greater than LOR was acceptable, particularly in respect of low concentrations of contaminant present in sediment. The precision of TBT analyses was acceptable given the low absolute concentrations and the common occurrence of this analyte as 'flakes' in sediment.

In summary, the QA/QC analyses and data validation indicated that the quality of the data was acceptable for environmental interpretative purposes.

# 6 Discussion

## 6.1 Analytical Variability

Eleven dried and ground samples (previously analysed as laboratory duplicates) were reanalysed as laboratory triplicate to assess variability (expressed as RSD) and robustness of analyses in different batches analysed several months apart. The analytical variability for selected chemicals analysed in 2013 is summarised in Table 10.

The mean analytical variability of Al, As, Co, Cu, Cr, Ni, Pb and Zn was very low (1.1% to 1.9% RSD). The precision of individual triplicate analyses varied from 5.4% RSD for zinc to 10.8% RSD for arsenic. This represents the precision of (only) the digestion and analysis components of the trace metal analytical method, i.e. not including variability within the sample jar itself.

The laboratory and field duplicate data for trace metals summarised in Table 10 indicates a variability of 0.6 to 7.1% RPD. These results are well within the DQO of 35% RPD for these data, but are somewhat higher than for laboratory triplicate samples, because these duplicate analyses include variability as a result of inhomogeneity within the sample jar. The laboratory and field duplicates for other inorganic chemicals were also higher (e.g. up to 17% RPD for boron) and the lower precision of the analyses reflects reported concentrations that approach the limit of resolution of the techniques (e.g. mercury and silver), or analytical difficulties with interferences or other issues (e.g. calcium and boron).

The precision of individual PAH analyses as indicated by field duplicates was lower, but still very good for these hydrophobic compounds (analysed at ultra-trace levels), compared to that of inorganic analyses. The mean RPD of field duplicate pairs of samples analysed for various individual PAHs varied from 8.2 to 18%.

In summary, analytical precision, assessed using field duplicate samples, was high for all groups of analytes and indicates the total analytical variability for primary samples. Analytical variability was well within the DQO of 35% RPD. Total analytical variability is compared to small-scale spatial variability of sediment in the following Section.

# 6.2 Small-Scale Spatial Variability

The small-scale spatial variability of Al, As, Co, Cr, Cu, Ni, Pb and Zn expressed as a relative standard deviation (RSD) of triplicate grab samples were low (mean 5.8, 5.0, 4.5, 4.7, 8.0, 4.9, 5.2 and 6.2%, respectively) (Table 10). Small-scale spatial variability is defined as intra-locational variability at the scale of several meters and includes analytical variability. This small-scale spatial variability is of similar magnitude to analytical variability (0.6 to 7.1% RPD) discussed in Section 7.1.

Triplicate sandy samples collected at location H12 in Marramarra Creek contained concentrations of trace metals at levels close to detection limits and therefore variability in reported concentrations at this location was relatively high compared to that at other locations.
Triplicate samples collected at locations H26 and H27 in Cowan Creek were noted in the field as having significantly different sediment textures (Table 3) and the higher variability (i.e. larger RSD) of reported trace metal concentrations at these sites is attributed to the variable content of fine fraction material collected in each grab. Low trace metal concentrations (notably copper) in triplicate sample H27 correlated with low concentration of aluminium in that grab sample and also reflects the variable sediment texture collected at that location. Note this variability would have been markedly reduced by only subsampling grabs that collected sediment of similar grain size at each location.

Anomalous concentrations of zinc in triplicate samples from location H25 (Akuna Bay) were further investigated by the laboratory. 'Smeared' fragments of elemental zinc were identified in triplicate sample H25B. The metallic fragments were possibly derived from zinc anodes on boats moored directly above this location and could account for the anomalous results.

Triplicate analyses of trace metals at 52 locations indicated that the small-scale spatial variability was generally low, but influenced by anomalous results at several locations. Removing these anomalous results caused by higher analytical variability at concentrations near LOR (location H12), samples in which sediment texture markedly influenced results and gross contamination by metallic debris (Zn in sample H25B), the mean small-scale spatial variability for all analysed trace metals varied from 2.7 to 4.5% RSD. This small-scale spatial variability is very low and partially accounted for by analytical variability.

The small-scale spatial variability of PAHs was higher than for trace metals. The maximum RSD of individual PAHs was 80.5% and the RSD of 15 total (i.e. un-normalised) PAHs varied from 0.6 to 79.1% (mean 16.0%). The mean RSD of individual PAH analyses varied from 3.6 to 20.7% (mean 13.0% RSD). These results indicate that the small-scale spatial variability of PAHs is similar to the analytical variability for these compounds (Table 10).

The data discussed above indicate that the apparent small-scale spatial variability of trace metals in sediment is almost entirely accounted for by analytical variability, except in the rare (2 out of 52) instances where sediment texture varied markedly in the scale of 1 to 2 m. In this assessment, variable sediment textures were accepted at locations H26 and H27 in an unbiased assessment of small-scale spatial variability, however the rare intra-locational variability could be overcome by compositing grab samples prior to subsampling, rather than triplicate analyses.

The analytical variability of reported PAH data was higher than that of trace metals due to analyses at concentrations that are several orders of magnitudes lower, and because these organic contaminants are hydrophobic and not evenly distributed through aqueous sediment samples. However, similar to trace metals, the apparent small-scale spatial variability of PAHs is of similar magnitude to the analytical variability.

In summary, the small-scale spatial variance of contaminants in sediment assessed by subsamples from multiple grabs (even before consideration of analytical variability) was low. These results give confidence that a single subsample would adequately represent concentrations of inorganic and organic chemicals at nearly all locations.

#### 6.3 Chemical Distributions in the Lower Hawkesbury Estuary

Concentrations of all inorganic analytes correlated positively with the fine (<63  $\mu$ m) fraction of sediment but the correlation of both aluminium and sediment fine fraction with copper, mercury and silver was not significant (i.e. P>0.05) (Table 11). Conversely, concentrations of all inorganic analytes correlated negatively with the sand (63-2000  $\mu$ m) fraction of sediment. Concentrations of all inorganic analytes except strontium and calcium correlated negatively with the gravel (>2000  $\mu$ m) fraction of sediment. This is likely to be accounted for by the higher proportion of shells and shell fragments composed of calcium carbonate in gravel-sized materials. Strontium is also incorporated into shells of some marine organisms as strontium sulphate.

Concentrations of iron and aluminium correlated strongly and positively with most inorganic analytes, but relatively weakly with copper, calcium and mercury. Concentrations of copper, lead, mercury and zinc correlated strongly (r>0.6). Concentrations of arsenic correlated strongly with barium, beryllium, chromium and nickel (n=60, r>0.6), but less strongly with other elements.

Concentrations of nutrients including ammonia correlated strongly (r > 0.5), but only weakly with trace metals. The TOC content of sediment also correlated relatively weakly with inorganic contaminants.

The strong correlation between the proportion of fine sediment fraction and contaminant concentrations has been noted in many sediment assessments and evaluations of contaminant sources are commonly confounded by variable grainsize within study areas that control contaminant distributions.

The distributions of chemicals reported in Sections 5.3 to 5.5 are further discussed in the following Sections and the relationship between contaminants and suspected sources is examined in Section 6.4.

### 6.3.1 Distribution of Inorganic Contaminants

Quiet depositional environments, i.e. "sinks" in mid sections of Berowra and Cowan Creeks and the upper sections of Mullet and Mooney Mooney Creeks contained both finer grain sized sediment (Figure 3) and higher concentrations of iron and aluminium (Figure 4). The same areas also contained relatively high concentrations of trace metals (e.g. cadmium, chromium, vanadium and magnesium).

Sediments collected at Berowra Waters, Bobbin Head and Akuna Bay were enriched in copper, lead, zinc and mercury relative to other parts of the study area. Boron displayed a similar distribution to other trace metals, but was anomalously high at location H45 at the northern tip north of Milson Island. Concentrations of silver were notably higher in Berowra Creek in comparison to other areas in the Lower Hawkesbury Estuary.

The distribution of manganese was similar to that of the fine sediment fraction, except that manganese concentrations were notably low in sediment at Berowra Waters, Bobbin Head and Apple Tree Bay. In contrast, concentrations of manganese were relatively high at locations H50 and H51 upstream of Spencer and the distribution of manganese suggests influence of this non-anthropogenically enriched element by factors other than grainsize (e.g. local redox conditions).

Concentrations of cobalt and nickel in sediment varied little throughout the Lower Hawkesbury Estuary, but were somewhat higher in the lower reaches of Berowra Creek and in the main river channel near Spencer and lower in sediment at Berowra Waters, Bobbin Head and Apple Tree Bay.

The distributions of strontium and metalloid arsenic were markedly different to that of other inorganic analytes. The range of arsenic concentrations was small compared to that of trace metals, but arsenic was relatively high in Sandbrook Inlet, the lower sections of Cowan Creek and in Mullet and Mooney Mooney Creeks. The highest concentrations of arsenic were present in sediment near Refuge Bay and the distribution of this element is likely to be related sediment adsorptive capacity rather than anthropogenic input. The distributions of barium and beryllium were also similar to arsenic.

Concentrations of strontium in sediment were low throughout much of the Lower Hawkesbury Estuary, but relatively high in Berowra Waters with even higher concentrations present throughout Cowan Creek. The distribution of strontium in Berowra and Cowan Creeks suggests a non-anthropogenic input of this element, possibly from the mafic dykes that intrude the Hawkesbury Sandstone.

#### 6.3.2 Distribution of Organic Contaminants

In contrast to inorganic analyses, nearly all organic contaminants were reported at concentrations less than the limit of reporting. The typically low concentrations of organic contaminant mean that distribution patterns are hard to interpret. However, locations containing sediment with concentrations of organic compounds exceeding detection limits are expected to be close to the source of that contaminant.

Higher concentrations (>45 mg/kg) of total, normalised (1% TOC) TPH were restricted to sediments at Berowra Waters, Bobbin Head and Akuna Bay. Concentrations of total, normalised PAHs exceeded 500 mg/kg in Sandbrook Inlet, near the confluence of Marramarra Creek (Locations H12 and H2) and in Mooney Mooney and Mullet Creeks. The concentrations of total, normalised PCBs exceeded detection limits only at Bobbin Head and Berowra Waters (location H57, 1.5 µg/kg).

TBT was analysed in sediment near suspected sources in Berowra and Cowan Creeks and in Sandbrook Inlet, but was not analysed in other areas of the Lower Hawkesbury Estuary. Concentrations of TBT away from marinas and areas of recreational boating are assumed to be low. Concentrations of normalised TBT exceeded 5  $\mu$ gSn/kg at Bobbin Head and Akuna Bay and in two samples from Berowra Creek, but concentrations in Sandbrook Inlet were lower.

Concentrations of pesticide residues in sediment were low in the Lower Hawkesbury Estuary. Concentrations of total, normalised chlordane (maximum 1.4  $\mu$ g/kg) exceeded the detection limit only at eight locations in upper Berowra Creek and at Bobbin Head (location H21).

Concentrations of total, normalised DDT exceeded 1.6 µg/kg in sediment in the upper reaches of Berowra Creek, Bobbin Head (H21), Brooklyn (locations H16 and H35) and at Mooney Mooney (location H14).

Concentrations of Diuron exceeded the detection limit only in two samples collected from Sandbrook Inlet (maximum 95  $\mu$ g/kg).

Concentrations of synthetic pyrethroids, Diuron, Chlorothalonil, Irgarol 1051, Dichlhlofluanid, 200 individual organic contaminants (including carbamates, triazines/triazoles, phenoxy acid herbicides, urea herbicides, fungicides, insecticides, organophosphate pesticides and miscellaneous biocides) in five samples in the Lower Hawkesbury Estuary, three samples from Sandbrook Inlet and four samples from Berowra Creek were reported at less than the limit of reporting. The distributions of this extensive suite of chemicals in sediment could therefore not be determined.

#### 6.3.3 Distribution of Nutrients

Concentrations of ammonia in the central section of the Lower Hawkesbury Estuary including Sandbrook Inlet were generally low, but exceeded 5 mg/kg at four locations in Berowra Creek, Cottage Point, Akuna Bay and upstream of Spencer (locations H50 and H51).

Concentrations of NOx (reported as nitrogen) in sediment were low throughout the Lower Hawkesbury Estuary. Concentrations of Total Kjeldahl Nitrogen in sediment exceeded 3,500 mg/kg in the upper reaches of Berowra Creek and Cowan Creek (except in Apple Tree Bay, location H22).

Concentrations of phosphorus were higher (>800 mg/kg) in Berowra and Cowan Creeks and lower in the main Hawkesbury River channel. Concentrations of reactive phosphorus in sediment were less than LOR in sediment in the Lower Hawkesbury Estuary, apart from in Berowra Waters.

The contents of TOC and concentrations of ammonia in sediment correlated only weakly with concentrations of inorganic contaminants.

#### 6.4 Contaminant Sources in the Lower Hawkesbury Estuary

Sediments in close proximity to point sources of contaminants generally receive higher loading of contaminants, resulting in elevated concentrations of contaminants relative to areas that are distant from sources. However, the sediment dynamics and chemistry that controls the accumulation and dispersal of contaminants in the aquatic environment is complex. All persistent contaminants (e.g. trace metals, nutrients, pesticide residues and non-volatile organic compounds) preferentially adsorb to fine-grained particulate materials. A variable sand content in sediment act as a variable diluent, which may confound the interpretation of contaminants reported in whole sediment analyses typically only indicate where the sediment texture (i.e. grain size) is finest.

Concentrations of contaminants in whole sediment analyses of sandy sediments within the Lower Hawkesbury Estuary are low (Sections 5.3 and 5.4). In contrast, due to their greater adsorptive capacity, concentrations of contaminants in fine-grained materials (silts and clays) are substantially higher.

#### 6.4.1 Sources of Inorganic Contaminants

Normalising contaminant concentrations to aluminium in sediment containing a low (<20%) fine fraction component (i.e. H12, H22, H27, H36, H45, H53 and H54) yielded anomalously high contaminant concentrations without nearby potential sources. This outcome would likely be markedly improved by normalising sediment by analysing only the fine fraction of sediment, rather than normalising using a fine fraction proxy such as aluminium.

When the confounding effects of variable grainsize are removed by normalisation, resultant concentrations of arsenic, barium, beryllium, cobalt, manganese, nickel and vanadium are relatively invariant. Unlike other trace metals, these elements are not enriched in Berowra and Cowan Creeks and Sandbrook Inlet, but have slightly higher grainsized normalised concentrations in the main Hawkesbury River channel and middle sections of the study area. The exception is in Akuna Bay where normalised concentrations indicate that sediment is enriched in arsenic, barium, beryllium, cobalt, manganese and vanadium (but not nickel). These results indicate that arsenic, barium, beryllium, cobalt, manganese, nickel and vanadium in the Lower Hawkesbury Estuary are (generally) not measurably influenced by localised anthropogenic sources.

In contrast to the elements described above, normalised concentrations of boron, cadmium, chromium, copper, lead, manganese, mercury, silver and zinc varied markedly throughout study area and are significantly higher in the upper reaches of Berowra Creek and Cowan Creek (Bobbin Head, and Akuna and Apple Tree Bays).

The highest concentrations of copper, lead, zinc and mercury were located in close proximity to marinas (e.g. locations H21, H25, H57 and H59) suggesting a significant contribution of these elements from marina and boating related activities. Size normalised data also highlights a likely contribution from boating activities to copper, chromium and nickel concentrations in sediment east of Sandbrook Inlet at Brooklyn (locations H16, H33, H35 and H37).

In addition to contributions from marinas, it is highly likely that urban runoff and discharge from sewage treatment plants have contributed to contaminant concentrations in sediment accumulating at Berowra Waters. To test this hypothesis, Geochemical Assessments attempted to collect sediment upstream of location H11 at Berowra Waters, but fine grained sediment could not be located. It is likely that persistent contaminants released in the catchment upstream of Berowra Waters would accumulate in quiet depositional areas downstream of location H11. Sediment grainsize is fine (>95%, <63  $\mu$ m) at locations H5 to H7 downstream of Berowra Waters, but (normalised and unnormalised) contaminant concentrations are higher in sandier sediment closer to the apparent source(s) of contaminants (locations H8 to H10 and H56 to 60) further upstream suggesting a strong relationship with proximity to source.

Concentrations of silver were notably higher in sediment in Berowra Creek (Figure 9) and suggests a strong anthropogenic input of this element. Silver was a common anthropogenic contaminant in sewage associated with disposal of photographic materials and has been effectively used as a sewage tracer in other studies. The enrichment of silver in sediments in Berowra Creek may be related to sewage discharge.

#### 6.4.2 Sources of Organic Contaminants

Overall, concentrations of organic contaminants in sediment were low, but contaminants at concentrations exceeding their limits of reporting in several areas suggest localised sources. Comparatively high concentrations of TPH identified in sediments at Berowra Waters, Bobbin Head and Akuna Bay may indicate that a minor source of these contaminants is refuelling of vessels. PCBs exceeded detection limits only at Berowra Waters and Bobbin Head. PCBs are persistent compounds that were previously used extensively in electrical switching equipment, but the usage of these compounds at Berowra Waters and Bobbin Head is not apparent.

Concentrations of PAHs were slightly higher in Sandbrook Inlet, near the confluence of Marramarra Creek and in Mooney Mooney and Mullet Creeks compared to other locations in the Lower Hawkesbury Estuary. Concentrations of PAHs in Sandbrook Inlet are typical of that found in sediment in many urbanised areas. The distribution of PAHs elsewhere may reflect the past practice of oyster farmers who coated oyster racks with tar to prevent decay and attack from marine borers.

TBT was analysed in sediment near suspected sources, i.e. marinas in Berowra and Cowan Creeks and in Sandbrook Inlet, but was not analysed in other areas of the Lower Hawkesbury Estuary. Concentrations of TBT away from marinas and areas of recreational boating are assumed to be low. Concentrations of normalised TBT exceeded  $5 \mu g Sn/kg$  in close proximity to marinas at Bobbin Head and Akuna Bay and in two samples from Berowra Creek, but concentrations throughout Sandbrook Inlet were lower. Concentrations of Diuron, an antifouling additive, exceeded the detection limit only in two samples collected from Sandbrook Inlet.

Concentrations of total, normalised DDT were highest in sediment in the upper reaches of Berowra Creek, Bobbin Head, Brooklyn and at Mooney Mooney. Concentrations of other pesticide residues were uniformly low with only total chlordane at eight locations in upper Berowra Creek and at Bobbin Head and Heptachlor Epoxide at one location in Berowra Creek exceeding detection limits. These low concentrations of pesticide residues in sediment are consistent with that found in estuarine sediment around Australia and probably represent historic domestic usage of pesticides in urbanised catchments. Illegal dumping of unwanted or banned chemicals has also been identified as the source of pesticide residues in sediment in similar catchments.

#### 6.5 Sediment Quality in the Lower Hawkesbury Estuary

Sediment Quality in the Lower Hawkesbury Estuary is assessed referencing ANZECC/ARMCANZ (2000) Interim Sediment Quality Guideline (ISQG) High (H) and Low (L) values for organic and inorganic contaminants in the following sections.

#### 6.5.1 Inorganic Contaminants

Concentrations of cadmium, chromium and mercury in sediment did not exceed their respective ANZECC/ARMCANZ (2000) ISQG-L values in sediment in the Lower Hawkesbury Estuary.

Apart from arsenic and nickel, concentrations of inorganic contaminants in sediment exceeded ANZECC/ARMCANZ (2000) ISQG-L values only in the upper reaches of Berowra and Cowan Creeks.

Concentrations of arsenic in sediment exceeded the ANZECC/ARMCANZ (2000) ISQG-L value (20 mg/kg) in the lower reaches of Berowra and Cowan Creeks, Mullet and Mooney Mooney Creeks, location H34 in the main channel and in Sandbrook Inlet.

Concentrations of nickel in sediment exceeded the ANZECC/ARMCANZ (2000) ISQG-L value (21 mg/kg) in a single sample collected at Brooklyn (location H37, 34 mg/kg).

Concentrations of copper and lead in sediment exceeded their respective ANZECC/ARMCANZ (2000) ISQG-L values (65 and 50 mg/kg, respectively) in the upper reaches of Berowra and Cowan Creeks.

Concentrations of silver were notably higher in Berowra Creek than elsewhere in the Lower Hawkesbury Estuary, but exceeded the ANZECC/ARMCANZ (2000) ISQG-L value (1 mg/kg) only at location H7.

Only copper in sediment at Bobbin Head (location H21, 343.3 mg/kg) and zinc at Akuna Bay (location H25, 413.3 mg/kg) exceeded their respective ANZECC/ARMCANZ (2000) ISQG-High values (270 and 400 mg/kg, respectively). All other inorganic contaminants in the Lower Hawkesbury Estuary did not exceed ANZECC/ARMCANZ (2000) ISQG-High values.

#### 6.5.2 Organic Contaminants

Concentrations of total, normalised chlordane exceeded the ANZECC/ARMCANZ (2000) ISQG-L value at five locations in Berowra Creek and one location in Cowan Creek.

Concentrations of normalised TBT exceeded the ANZECC/ARMCANZ (2000) ISQG-L value (5 µgSn/kg) near marinas in Berowra Creek (locations H57 and H59), Bobbin Head (location H21) and Akuna Bay (locations H25 and H26).

Concentrations of normalised, total DDT exceeded the ANZECC/ARMCANZ (2000) ISQG-L value (1.6 µg/kg) at eight locations in the upper reaches of Berowra Creek, Bobbin Head (location H21), Akuna Bay (locations H25 and H26), Mooney Mooney (location H14) and at Brooklyn (locations H16 and H35).

Normalised concentrations of all other organic contaminants (individual PAHs, low and high molecular weight PAHs, total PAHs, PCB, OCCs and OCPs) did not exceed available ANZECC/ARMCANZ (2000) ISQG-L values.

Normalised concentrations of organic contaminants in the Lower Hawkesbury Estuary did not exceed ANZECC/ARMCANZ (2000) ISQG-High values.

#### 6.5.3 Sediment Quality Summary

Sediment quality in the Lower Hawkesbury Estuary is good compared to many estuaries in urbanised and industrialised areas around Australia (Birch and Taylor, 1999a). Trace metal concentrations are generally

low and concentrations of organic contaminants were generally below ultra-trace limits of detection. Comparable mean concentrations of trace metals in (fine grained sediment in) Port Jackson and other estuaries on the east Australian coast (Birch and Taylor, 1999a) commonly exceed the maximum concentrations found within the Lower Hawkesbury Estuary.

#### 6.5.4 Mean Contaminant Quotients

Mean contaminant quotients have been used to rank the contaminant status of sediment containing multiple contaminants. Adopting the Sediment Quality Guideline Quotient (SQGQ) methodology (Long et al., 2006), each contaminant concentration at each location were normalised to (i.e. divided by) their respective ANZECC/ARMCANZ (2000) ISQG-L values. The resultant quotients were then summed and divided by the number of analytes in each contaminant group to yield a mean quotient (i.e. organic, n=16; inorganic, n=9; organic and inorganic n=25). The resultant mean contaminant quotients provide an overall assessment of sediment quality against ANZECC/ARMCANZ (2000) ISQG-L values. The outcomes of the SQGQ may be used to rank (i.e. prioritise) areas of sediment warranting further investigation, but do not necessarily indicate that environmental receptors are adversely effected. Mean quotient values exceeding 1 indicate that ANZECC/ARMCANZ (2000) ISQG-L values are exceeded, but do not account for antagonistic and synergistic effects.

The mean contaminant quotients for organic, inorganic, and organic and inorganic contaminants are presented in Figures 21 to 23 using the same scale for the quotients to allow direct comparison.

The mean contaminant quotients for inorganic contaminants varied from 0.03 to 1.76 (mean 0.51). Inorganic contaminant quotients exceeded 0.5 in the upper reaches of Berowra Creek, mid sections of Cowan Creek (notably Cottage Point) and in Sandbrook Inlet, and exceeded 1.0 at Berowra Waters, Bobbin Head and Akuna Bay.

The mean contaminant quotients for organic contaminants varied from 0.03 to 0.65 (mean 0.10). Mean organic contaminant quotients exceeded 0.14 in the upper reaches of Berowra Creek, Akuna Bay and in Sandbrook Inlet and exceeded 0.25 at Berowra Waters and Bobbin Head. Note, mean contaminant quotients for organic contaminants appear anomalously high in at locations in which many analytes were reported at less than LOR, (e.g. Marramarra and Mooney Mooney Creek) and is due to values less than LOR being allocated a value of half LOR.

The mean contaminant quotients for organic contaminants are substantially less than those of inorganic contaminants, which may suggest the risks posed to environmental receptors in the Lower Hawkesbury Estuary are greater from inorganic contaminants. However, sediment toxicity is likely to be conservatively estimated for inorganic (compared to organic) contaminants due to the derivation of sediment quality guidelines from sediment containing mixtures of both inorganic and organic contaminants in which laboratory bioassays attribute sediment toxicity from organic compounds to inorganic contaminants.

The mean contaminant quotients for combined organic and inorganic contaminants varied from 0.10 to 0.83 (mean 0.25). Organic and inorganic mean contaminant quotients exceeded 0.25 in the upper reaches of Berowra Creek, Cowan Creek and in Sandbrook Inlet, and exceeded 0.4 at Berowra Waters, Bobbin Head and Akuna Bay.

The mean contaminant quotients indicate that sediments in the upper reaches of Berowra Creek (i.e. Berowra Waters), Bobbin Head, Akuna Bay and to a lesser extent Sandbrook Inlet, contained higher concentrations of multiple contaminants compared to sediment in the remainder of the Lower Hawkesbury Estuary. However, contaminant concentrations are generally below ANZECC/ARMCANZ (2000) ISQG-L values and adverse effects to environmental receptors are therefore unlikely.

# 6.6 Temporal Changes in Sediment texture and Contaminant Concentrations

#### 6.6.1 Temporal Changes in Sediment Textures

Considerable time and care was taken at every location to collect sediment samples that matched sediment textures reported in the 2006 sampling program. However, the texture of sediment at many locations, within a reasonable distance (<30 m) of the exact 2006 sampling location, did not match the grain size reported by URS (2007).

To compare the mud (<63  $\mu$ m), sand and gravel component of samples collected in 2006 and 2013, the recent data were recalculated into the same three size fractions as reported in 2006. At 31 of the 52 sampling locations, the fine sediment fraction varied by more than 5% (Table 12). At fourteen locations, sediment grain size varied between 10 and 30%, and at a further six locations differences in grainsize exceeded 30%.

Locations south of Fishermans Point (H2), upstream of Cottage Point (H27), north of Milson Island (H45), and in the main channel between Spencer and Wisemans Ferry (H51 and H53) contained a fine fraction component that was at least 30% lower in 2013 compared to that in December 2006 (Figure 24). In contrast, the sediment textures at Cottage Point (H28 8%), Akuna Bay (H25, 23.6%) and up and downstream of Spencer (H50, 10.2% and H48, 6%) was finer grained (>5%,  $<63 \mu$ m) in 2013 compared to that in 2006. Sediment at location H11 (furthest upstream in Berowra Creek) and the surrounding (>100 m) area comprised black, anoxic sandy mud, in marked contrast to the previously reported sandy sample. The fine fraction component of sediment collected at this location in 2013 was 68% higher than in 2006.

These changes in sediment texture are significant when assessing temporal changes in contaminant concentrations as most contaminants are associated with a fine fraction component that has a greater adsorptive capacity compared to sands and coarser materials. If contaminants associated with the coarse (>63  $\mu$ m) fraction were negligible, contaminant concentrations at 31 of the 52 sampling locations, could be expected to vary between 2006 and 2013 by more than 5% due to changes in sediment texture alone.

#### 6.6.2 Temporal Changes in Concentrations of Inorganic Contaminants

Changes in concentrations of selected contaminants at each of 52 locations between 2006 and 2013 are provided as relative percent differences (RPD) in Table 12. Contaminants for which the majority of samples reported concentrations below LOR are not included in the table.

Mean RPDs for (absolute) temporal change in contaminant concentrations varied from 13.3 to 40.7% and maximum RPDs for (absolute) temporal change in contamination concentrations varied from 96 to 198%. These changes are around one order of magnitude greater than the combined analytical and spatial variability for the 2013 sampling program, but also include analytical and spatial variability inherent in the 2006 dataset. This finding gives confidence that this study is able to detect apparent changes in concentrations regardless of analytical and spatial variability in both data sets Note that these apparent changes in concentrations are strongly influenced by grainsize variations and in most cases probably do not reflect a change in contaminant load to the sediment.

Due to the small-scale spatial variability of contaminants (including analytical variability), temporal variability of inorganic contaminants of less than 5% are not considered significant. Importantly, changes in sediment texture (Section 7.5) at many locations between 2006 and 2013 were significantly greater than the small-scale spatial variability of contaminant concentrations (Section 7.2). This section assesses the reasons for significant temporal changes in contaminant concentrations in which possible changes to contaminants sources and loadings have been confounded by large and widespread changes in sediment textures in the Lower Hawkesbury Estuary.

The detection limits for cadmium and mercury in the current study were significantly lower compared to those in the 2006 study. The detection limits for cadmium and mercury in the 2006 study were too high to allow meaningful comparison of temporal changes in these elements.

Concentrations of trace metals in sediment were higher at the eight locations in which the fine fraction component of sediment had increased (or varied insignificantly). Concentrations of trace metals were typically higher in sediment collected at locations H1, H11, H19, H25, (marginal in H28), H48 and H50 in the 2013 sampling program compared to 2006.

Reported concentrations of aluminium, iron and manganese were higher in many of the sediment samples collected in 2013. Concentrations of aluminium (Figure 25), and iron displayed very similar trends and concentrations of these elements were higher in 44 out of 52 samples collected in the Lower Hawkesbury Estuary, except those collected at locations H2, H12, H21, H22, H26, H27 and H51 to H54.

Concentrations of elements were markedly lower in sediment samples collected in 2013 at locations H2 and H12 (except Mn), H20 (except Al, Ba and Fe), H21 and H26 (except Be), H22, H27and H32 (except Ba, Fe and Sr), H38 (except Al, Ba and Fe), H45 (except Al, Fe and Sr), H46 (except Al and Fe), H49 (except Ba and Fe), H51 and H52 (except Ba), H53 and H54.

Concentrations of lead in sediment collected in 2013 were lower at most locations, except at locations H11 (103.1% higher), H25 (62.4% higher), H36, H48 and H50 (Figure 26).

Concentrations of chromium, cobalt, copper, manganese, vanadium and zinc (Figure 27) were generally lower in samples collected at locations H28 to H49 in samples collected in 2013.

Sediments with lower fine fraction content in 2013 generally correlated with lower organic and inorganic contaminant concentrations. Samples with lower concentrations of aluminium and iron in 2013 generally contained lower concentrations of trace metals (except anomalous samples such as H55). These findings suggests that temporal changes in contaminant concentrations are largely explained by differences in sediment texture, rather than changes in concentrations of contaminants associated with fine fraction material.

Temporal changes in concentrations of inorganic chemicals in several samples were anomalous (inconsistent with sediment grainsize changes) and these may reflect a change in the contaminant status of sediment, or possibly confounding by unknown factors. Sediment at location H34, north of Gunyah Point, contained a lower fine fraction content in 2013 and similar concentrations of aluminium, but concentrations of non-anthropogenic influenced elements (i.e. As, Ba, Be, Fe, Mg, Mn and Sr) were higher in 2013 than in 2006. Similarly, sediment at location H55, in the main channel upstream of Haycock Reach, contained a lower fine fraction content and concentration of aluminium in 2013, but higher concentrations of barium, beryllium, copper, chromium, nickel, vanadium and zinc. In contrast, sediment collected at location H38 in Sandbrook Inlet contained a higher fine fraction content and concentration of aluminium in 2013, but lower concentrations of trace metals than in 2006, suggesting an actual decrease in contaminant concentrations. There was negligible change in the fine fraction content of sediment at location H20 in Mullet Creek, but concentrations of aluminium were higher and the concentrations of trace metals were markedly lower.

Changes in the fine fraction of component of sediment correlated strongly (r>0.7) for most trace metals, but less strongly (r<0.5) for magnesium, manganese, strontium, and calcium. Concentrations of manganese in sediment are commonly controlled by redox conditions, and strontium and calcium correlate positively to the gravel component containing higher concentrations of shell material.

Changes in the concentrations of aluminium, arsenic, chromium, cobalt, copper, iron, lead, nickel, vanadium and zinc correlated very strongly and positively (n=52, r > 0.90, P <0.001). Changes in the concentrations of manganese, magnesium and strontium also correlated positively, but far less strongly (n=52, r = 0.3 to 0.6). The strong correlation of changes in anthropogenically enriched trace metal concentrations (chromium, copper, lead, nickel, and zinc) with sediment fine fraction, aluminium and iron indicates that changes in these elements measured in 2006 and 2013 are related to variations in sediment texture, rather than changes in contaminant concentration due to different contaminant loads. In addition, the strong correlation between analytes in samples separated by up to 37 km in a straight line (and much further following the river channel) suggests that measured changes in concentrations could not result from changes in (localised) point sources of contaminants. The possibility of regional changes in contaminant loads yielding the measured changes in trace metals concentrations is remote, with the exception of lead. Concentrations of lead in throughout the Lower Hawkesbury Estuary were almost universally lower in sediment collected in 2013, except at the eight locations at which changes in sediment texture could readily explain higher concentrations of lead. A trend of decreasing lead

concentrations in sediment has been well-documented in other studies including in Port Jackson (Taylor, 2000).

In summary, inorganic contaminants analysed in sediment collected in 2006 and 2013 indicate that concentrations of commonly anthropogenically enriched elements were typically higher in sediment collected at locations H1, H11, H19, H25, (marginally in H28), H48 and H50 and markedly lower at locations H2, H12, H21, H26, H22, H27, H32, H38, H45, H46, H49, H51, H52, H53 and H54.

Concentrations of chromium, cobalt, copper, manganese, vanadium and zinc were generally lower in samples collected at locations H28 to H49 in samples collected in 2013. These changes in contaminant concentration correlated strongly with changes in sediment texture and proxies for sediment texture (i.e. concentrations of iron and aluminium). Concentrations of contaminants at the following locations changes markedly and contrary to sediment textures suggesting significant changes to contaminant status at those locations:

- Location H34, north of Gunyah Point, contained higher concentrations of non-anthropogenic elements in 2013;
- Location H55, upstream of Haycock Reach, contained generally higher concentrations of trace metals in 2013;
- Location H38 in Sandbrook Inlet contained lower concentrations of trace metals in 2013; and
- Location H20 in Mullet Creek contained markedly lower concentrations of trace metals in 2013.

The change in contaminant concentrations were also calculated after normalising both the 2006 and 2013 datasets to the percentage of sediment fine fraction. Sediment at locations H11, H20, H26 and H38 (and to a lesser extent H7) contained generally lower normalised concentrations of trace metals. Sediment at locations H1, H2, H4, H12, H13, H15, H16, H22, H27, H32 to H36, H39 to H43, H50, H51, H53 and H54 contained generally higher normalised concentrations of trace metals.

Normalised concentrations of lead were similar or somewhat lower in 2013, except at location H12, H27, H33, H34, H36, H43, H44, H45, H50, H51, H53 and H54. Normalised concentrations of manganese were markedly lower at locations H7 to H11 in Berowra Waters in 2013. Normalised concentrations of copper and zinc in Cowan Creek (locations H26 to H30, but not H27) were also markedly lower.

#### 6.6.3 Temporal Changes in Concentrations of Organic Contaminants

Of the 52 locations sampled in 2006, TBT, TPH and PAHs (to ultra-trace levels) were analysed at 16 locations (H7, H8, H9, H10, H17, H18, H21, H22, H23, H24, H25, H26, H28, H31, H37 and H38). The fine sediment fraction in Cowan Creek decreased between 2006 and 2013 at locations H21 and H22 (17.7% and 29.4% RPD, respectively), but increased at location H25 (23.6% RPD). The fine sediment fraction varied by less than 8% RPD at all other locations.

Concentrations of TPH reported in the 2006 study were predominantly (202 out of 208 individual analyses) less than LOR and it is therefore difficult to quantify temporal changes in these compounds. TPH was reported at concentrations greater than LOR at only two locations sampled in 2006 (Berowra Waters H10 and Bobbin Head H21) and TPH concentrations at both these locations were reported as being higher in 2013. Concentrations of TPH (C15-28 and C29-36) in the current study are apparently higher in sediment from locations H6 to H11 in Berowra Creek, H23 to H26 in Cowan Creek and at locations H30 (Jerusalem Bay) and H50 (upstream of Spencer). At all other locations, concentrations reported in 2013 were consistent with the detection limits of analyses in 2006.

Concentrations of total PAHs were (insignificantly, <7% RPD) higher at three locations (H10, H17 and H23) in 2013. At the other 13 sampling locations, concentrations of total, normalised PAHs were lower, notably at locations H18 and H37 in Sandbrook Inlet (73.9% and 57.2% lower, respectively), and locations H22 and H26 in Cowan Creek (109.5% and 180.7% lower, respectively).

Concentrations of TBT in all sediments analysed in 2013 were markedly (>30% RPD) lower than those collected at the same locations in 2006, except at location H18 in Sandbrook Inlet where the concentration was effectively unchanged (-1.9% RPD).

In summary, comparable analyses of sediment collected in 2006 and 2013 indicate that concentrations of TBT and PAHs in sediment have generally decreased, irrespective of changes in sediment texture at the 16 sampled locations. Due to high limits of reporting for 2006 data, a temporal trend for TPH concentrations cannot be determined.

#### 6.6.4 Temporal Changes in Concentrations of Nutrients

Concentrations of nitrate and nitrite in sediment at all locations in the Lower Hawkesbury Estuary were low and close to the LOR in 2006 and 2013. Four samples (locations H19, H20, H38 and H54) containing concentrations of nitrate and nitrite marginally above LOR in 2006 contained concentrations at less than LOR in 2013. Similarly, the two locations (Sandbrook H18 and upstream main channel H53) containing nitrate and nitrite above LOR in 2013 contained concentrations at less than LOR in 2006.

Concentrations of TKN in sediment were generally higher in Berowra Creek, Sandbrook Inlet, Mooney Mooney and Mullet Creeks and near Brooklyn in 2013 (Figure 28). Concentrations of TKN were markedly in higher Berowra Creek (location H11) and lower in Marramarra Creek (location H12) as a result of a higher sediment fine fraction component in 2013. A lower concentration of TKN at Berowra Waters location H7 was not explained by changes in grain size.

Concentrations of TKN in Cowan Creek and Parsley Bay (except location H25 where the fine fraction of sediment had markedly increased) were consistently lower in 2013. Concentrations of TKN in the main channel upstream to location H50 and at location H55 were higher in 2013. Lower concentrations of TKN correlated positively with markedly lower sediment fine fraction component at locations H51 to H54.

Concentrations of reactive phosphorus in sediment in the Lower Hawkesbury Estuary were generally low and close to LOR, therefore interpreting changes is difficult. However concentrations appear to be marginally lower in sediment in 2013. Of the 19 locations that reactive phosphorus was reported at greater than LOR in 2006, only location H10 reported a concentration greater than LOR in 2013.

## 7 Recommendations

Contaminant concentrations in the Lower Hawkesbury Estuary are relatively low compared to those in many industrialised and urbanised Australian estuaries. Although contaminant concentrations in Berowra and Cowan Creeks exceeded ANZEC (2000) ISQG-L values for several trace metals, DDT, total chlordane and TBT, only copper in sediment in one sample at Bobbin Head and zinc in one sample at Akuna Bay exceeded their respective ANZECC/ARMCANZ (2000) ISQG-High values. Exceedence of ANZEC (2000) ISQG-L values triggers additional studies to assess whether contaminant concentrations may adversely (or have potential to adversely) affect environmental receptors. The highest priority areas for further investigations are Berowra Waters, Bobbin Head, Akuna Bay and to a lesser extent Sandbrook Inlet. As the 2006 and 2013 studies have addressed the total concentration of contaminants in sediment, further investigations should firstly assess the proportion of contaminants of concern in sediment that are available to biota (bioavailable concentrations), e.g. using weak digestions that mimic uptake of contaminants in the guts of sediment dwelling organisms.

Comparison of chemical analyses of sediment collected in 2006 and 2013 in the Lower Hawkesbury Estuary indicated that the regional distributions and temporal assessment of contaminant concentrations were confounded by temporal variations in sediment adsorptive capacity which in turn is related to factors including sediment grainsize, mineralogy, cation exchange capacity, sorption, complexation, and redox reactions. Normalisation of sediment contaminant concentrations in future studies would reduce the confounding effects of variable sediment grain size and enhance identification of trace metal sources in the Lower Hawkesbury Estuary. This methodology would also enhance identification of temporal changes in concentrations of selected inorganic contaminants in future assessments. Geochemical Assessments recommends archiving a dried sample of fine fraction material for future comparison of concentrations of inorganic contaminants.

Changes in the annual mass of contaminant that arrives into the receiving environment indicate increases, or decreases of activities in the surrounding catchments that act as sources. This information at key locations in the Lower Hawkesbury Estuary would likely assist Hornsby Shire Council in making informed decisions regarding management of contaminant related issues in the Lower Hawkesbury Estuary. Geochemical Assessments recommends calculating sedimentation rates at a minimum of one location in Berowra Waters, Bobbin Head, Akuna Bay and Sandbrook Inlet using radioisotopic dating methods. Together with vertical contaminant profiles, sedimentation rates would allow historical loads of contaminants of concern to be assessed. Contaminant sources and potential source control measures should be assessed in areas where contaminant loads are high or are trending higher.

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# Table 1 Sample Locations

Stage 1 Sample ID	Easting	Northing	Stage 2 Sample ID	Easting	Northing	
H1	329005	6288761	H56	325596	6279755	
H2	328389	6287878	H57	325636	6280707	
H3	327506	6287314	H58	325274	6281488	
H4	328081	6286684	H59	326022	6280618	
H5	326962	6283927	H60	325711	6280367	
H6	326568	6282695	2H7	325530	6282107	
H7	325530	6282107	2117	325808	6281083	
H8	325808	6281083	2110	325771	6280706	
H9	325771	6280706	2113	325685	6280026	
H10	325685	6280026	2010	326003	6279668	
H11	326003	6279668	21111	323802	6289158	
H12	323833	6289190	2112	327106	6288797	
H13	323033	6288797	21113	323220	6286561	
H13	222105	6287690	21117	335098	6287024	
H15	337165	62881/0	2010	22/220	6286858	
H16	335501	6286753	2030	222001	6286823	
H10 H17	222220	6286561	2039	220250	6206200	
H17 L10	225020	6280301	2001	217620	6200272	
	222214	620/024	2052	216502	6202169	
H19	333314	6294009	2H53	212040	6204456	
H2U	337402	0292300	2H54	222249	6205422	
	329680	6273756	2H55	322248	0295431	
HZZ	328980	6274926				
HZ3	330452	6277834				
H24	332960	6277113				
H25	336465	6275815				
H26	336487	6276077				
H27	333057	62/8/69				
H28	333768	6278915				
H29	334691	6281184				
H30	333122	6281/2/				
H31	337481	6280993				
H32	337698	6282897				
H33	335/34	6286524				
H34	336820	6284267				
H35	335841	6286743				
H36	336703	6287441				
H37	335462	6286738				
H38	334339	6286858				
H39	332991	6286823				
H43	331655	6287910				
H44	330849	6290033				
H45	330826	6290941				
H46	328602	6289491				
H47	328741	6292472				
H48	329042	6295174				
H49	328042	6295972				
H50	324958	6295225				
H51	320359	6296200				
H52	317628	6299272				
H53	316542	6302275				
H54	313085	6304478				
H55	322248	6295431				

Area	Sample ID	Metals, Metaloid and Calcium	PAHS, TPHs PCBs	PAHs in Triplicate	Organo- chlorine and phosphate Pesticides	Nutrients, Ammonia and TOC	Diruon, Chlorothalonil Irgarol 1051, Diclorofluanid	MBT, DBT, TBT	Synthetic Pyrethroids, Carbamates, Triazines/triazoles, Herbicides, Fungicides, Insecticides,
Lower Berora Creek	H1	Х	Х		Х	Х			
Lower Berora Creek	H2	Х	Х		Х	Х			
Lower Berora Creek	H3	Х	Х		Х	Х			
Lower Berora Creek	H4	Х	Х		Х	Х			
Berowra Ck	H5	Х	Х		Х	Х			
Berowra Ck	H6	Х	Х		Х	Х			
Berowra Ck	H7	Х	Х	Х	Х	Х	Х	Х	Х
Berowra Ck	H8	Х	Х	Х	Х	Х	Х	Х	Х
Berowra Ck	H9	Х	Х	Х	Х	Х	Х	Х	Х
Berowra Ck	H10	Х	Х	Х	Х	Х	Х	Х	Х
Berowra Ck	H11	Х	Х		Х	Х	Х		Х
Marramarra CK	H12	Х	Х		Х	Х			Х
Marramarra CK	H13	Х	Х		Х	Х			Х
Main Channel	H14	Х	Х		Х	Х			
Main Channel	H15	Х	Х		Х	Х			
Brooklyn	H16	Х	Х		Х	Х			
Sandbrook Inlet	H17	Х	Х	Х	Х	Х	Х	Х	Х
Sandbrook Inlet	H18	Х	Х	Х	Х	Х	Х	Х	Х
Mooney Mooney Ck	H19	Х	Х		Х	Х			
Mullet Ck	H20	Х	Х		Х	Х			
Bobbin Head	H21	Х	Х	Х	Х	Х		Х	
Bobbin Head	H22	Х	Х	Х	Х	Х		Х	
Cowan Ck	H23	Х	Х	Х	Х	Х		Х	
Smith Ck	H24	Х	Х	Х	Х	Х		Х	
Akuna Bay	H25	Х	Х	Х	Х	Х		Х	
Akuna Bay	H26	Х	Х	Х	Х	Х		Х	
Cottage Pt	H27	Х	Х		Х	Х			
Cottage Pt	H28	Х	Х	Х	Х	Х		Х	
Jerusalem Bay	H29	Х	Х		Х	Х			
Jeruslaem Bay	H30	Х	Х		Х	Х			
Refuge Bay	H31	Х	Х		Х	Х	Х	Х	
Main Channel	H32	Х	Х		Х	Х			
Parsely Bay	H33	Х	Х		Х	Х			
Main Channel	H34	Х	Х		Х	Х			
Brooklyn	H35	Х	Х		Х	Х			
Dangar Is	H36	Х	Х		Х	Х			
Brooklyn	H37	Х	Х	Х	Х	Х	Х	Х	
Sandbrook Inlet	H38	Х	Х	Х	Х	Х	Х	Х	Х
Sandbrook Inlet	H39	Х	Х		Х	Х	Х		
Main Channel	H43	Х	Х		Х	Х			
Milson Passage	H44	Х	Х		Х	Х			
Milson Is	H45	Х	Х		Х	Х			
Main Channel	H46	Х	Х		Х	Х			
Main Channel	H47	Х	Х		Х	Х			
Marlow	H48	Х	Х		Х	Х			
Spencer	H49	Х	Х		Х	Х			
Main Channel	H50	Х	Х		Х	Х			
Main Channel	H51	Х	Х		Х	Х			Х
Main Channel	H52	Х	Х		Х	Х			Х
Main Channel	H53	Х	Х		Х	Х			Х
Main Channel	H54	Х	Х		Х	Х			Х
Main Channel	H55	Х	Х		Х	Х			Х
Berowra Ck	H56	Х	Х		Х	Х			
Berowra Ck	H57	Х	Х		Х	Х			
Berowra Ck	H58	Х	Х		Х	Х			
Berowra Ck	H59	Х	Х		Х	Х			
Berowra Ck	H60	Х	Х		Х	Х			

# Table 2 Sampling Locations and Analytes

#### Table 3 Sediment Descriptions

ID	Date	Water Depth (m)	Sample Depth (m)	Texture	Description
H1	08-May-13	2.8	0.08	Mud (0-0.01 m) over mud, tr. sand	Brown over grey/brown. Burrows and faecal pellets
H2	08-May-13	1.3	0.1	Mud	Brown over grey/brown. Fish and yabbie. Abundant faecal pellets
H3	08-May-13	1.0	0.09	Mud, nil sand (0-0.02 m) over mud, tr. Sand	Brown over grey/brown. Faecal pellets
H4	08-May-13	0.5	0.1	Mud	Brown over grey mud
H5	08-May-13	4.1	0.12	Mud	Brown over grey mud. Soft. Abundant faecal pellets
H6	08-May-13	8.9	0.12	Mud	Brown to grey/black. Oxic layer (0.008 m) over anoxic layer (0.002 m) over massive, grey mud
H7	08-May-13	14.9	0.11	Mud	Brown to grey/black. Oxic layer (0.002 m) over anoxic layer (0.002 m) over massive, grey mud
H8	08-May-13	7.7	0.1	Mud	Brown to grey. Some vegetation
H9	08-May-13	8.0	0.11	Mud, nil sand (0-0.02 m) over mud	Brown to grey
H10	08-May-13	4.6	0.13	Mud, tr. sand (0-0.02 m) over mud, some sand	Some vegetative material. Moderate sulphur odour
H11	08-May-13	2.4	0.12	(Gravelly) mud	Black, abundant vegetation - sticks and leaves. Very thin (0.002 mm) surface layer. Strong organic odour. Faint sheen
H12	08-May-13	0.8	0.04	Sand	Light brown. Quartz sand, gravel sized timber and charcoal
H13	08-May-13	1.4	0.09	Mud	Brown/grey over green/grey. Faecal pellets
H14	08-May-13	2.6	0.05	(Gravelly), sandy mud	Grey. Abundant bivalves
H15	09-May-13	11.9	0.05	Mud, tr. sand (0-0.005 m) over sandy mud	Brown to grey/brown. Soft. Very thin worms
H16	09-May-13	0.6	0.1	Mud	Brown to grey/brown. Soft
H17	09-May-13	1.5	0.07	Mud (0-0.01 m) over mud, some sand	Brown to grey/brown. Soft
H18	08-May-13	2.0	0.1	Mud, tr. sand (0-0.02 m) over mud	Brown to grey/brown
H19	06-May-13	3.5	0.08	Mud (0-0.01 m) over mud, tr. sand	Brown to grey/brown. Worm burrows and faecal pellets
H20	06-May-13	3.6	0.09	Mud (0-0.02 m) over mud, nil sand	Brown to grey/brown. Soft
H21	06-May-13	3.0	0.12	Mud, some sand	Dark grey. Abundant leaves
H22	06-May-13	3.7	0.06	Muddy sand	Quartz sand. Occasional shells and some leaves. A and B samples slightly muddier
H23	06-May-13	21.8	0.08	Mud, tr. sand	Grey. Thin, black surficial layer. Occ. Vegetation fragments. Bioturbation - worm holes
H24	06-May-13	21.2	0.1	Mud, tr. sand	Grey. Some vegetation. Highly bioturbated - 1 mm worm holes

# Table 3 Sediment Descriptions

ID	Date	Water Depth (m)	Sample Depth (m)	Texture	Description
H25	06-May-13	8.9	0.5	Sandy mud	Black, abundant vegetation. H2S odour
H26	06-May-13	14.1	0.08	Mud, some sand	Grey, some leaves and sticks. A and B samples contain more sand
H27	06-May-13	18.1	0.08	Sandy mud	Brown, Quartzose sand with anoxic patches. A and B less muddy
H28	06-May-13	15.5	0.07	Mud (0.005 m) over mud, tr. sand	Brown hydrous layer over grey mud
H29	06-May-13	10.0	0.12	Mud	Brown, very soft to soft. Faecal pellets
H30	06-May-13	14.4	0.1	Mud	Brown hydrous layer (0.03 m) over grey/green mud. Abundant mud burrows (1.5 cm dia. 6 cm) long
H31	06-May-13	5.2	0.1	Mud, tr. sand	Brown, soft hydrous layer over brown mud
H32	08-May-13	12.1	0.08	Mud	Brown, soft
H33	08-May-13	2.1	0.11	Mud	Brown to brown/grey
H34	08-May-13	19.0	0.04	Gravelly, sandy mud	Grey, bivalve shells
H35	09-May-13	1.8	0.1	Mud (0.02 m) over gravelly, sandy mud	Brown to brown/grey. Shells
H36	09-May-13	0.8	0.06	Muddy sand	Brown. Gastropod, polychaete, worm burrows
H37	09-May-13	2.2	0.1	Mud (0-0.02 m) over sandy mud	Brown to grey. Large burrow
H38	07-May-13	2.5	0.09	Mud (0-0.02 m) over mud, nil sand	Very soft to soft
H39	09-May-13	1.3	0.12	Mud	Brown to brown/grey
H43	09-May-13	2.0	0.07	Mud (0-0.015 m) over sandy mud	Brown over grey/brown. Fine quartzose sand. Some shells. Anoxic below 0.05 m
H44	08-May-13	0.4	0.09	Sandy mud	Brown to grey/brown
H45	07-May-13	4.3	0.5	Gravelly, sandy mud	Bivalve shells, abundant vegetation. Prawn
H46	08-May-13	2.2	0.08	Mud (0-0.01 m) over mud, tr. Sand	Brown to grey. Faecal pellets
H47	07-May-13	0.9	0.07	Sandy mud	Brown to grey. Abundant fibrous algae on surface. Anoxic patches- dark grey
H48	07-May-13	4.0	0.07	Mud, some sand (0-0.01 m) over mud	Worm burrows
H49	07-May-13	0.7	0.08	Sandy mud (0-0.025 m) over mud	Brown- dark grey. Worm burrows
H50	07-May-13	3.3	0.07	Sandy mud (0-0.002 m) over mud, tr. sand	Brown, cohesive mud. Worm burrows
H51	07-May-13	3.4	0.07	Sandy mud (0-0.005 m) over mud	Fine, sandy mud over grey/green cohesive mud. Some bioturbation- worm burrows
H52	07-May-13	15.8	0.12	Sandy mud (0-0.005 m) over mud	Thin, brown hydrous layer
H53	07-May-13	6.4	0.05	Sand	Red/brown (Fe staining?) Quartzose with charcoal fragments
H54	07-May-13	5.2	0.05	Sand, tr. mud	Quartzose, muddier below 3 cm
H55	07-May-13	6.8	0.06	Sandy mud (0-0.002 m) over mud, tr. Sand	Dark brown/dark grey. Different overall grainsize in triplicate samples

ID	Date	Water Depth (m)	Sample Depth (m)	Texture	Description
STAGE 2					
H56	29-Jul-13	3.3	0.08	Mud	Green/brown hydrous material over dark grey mud. Gastropod, worm and faecal pellets
H57	29-Jul-13	6.5	0.06	Sandy mud	Brown over dark grey
H58	29-Jul-13	10.2	0.1	Mud, tr. Sand	Brown over dark grey
H59	29-Jul-13	5.6	0.05	Sandy mud	Dark grey/black. Abundant vegetation - sticks and leaves
H60	29-Jul-13	5.8	0.09	Mud	Green/brown hydrous material (0.02 m) over dark grey mud
2H7	29-Jul-13	15.5	0.07	Mud	Brown hydrous material (0.015 m) over dark grey mud
2H8	29-Jul-13	7.6	0.08	Mud	Brown hydrous material (0.015 m) over grey consolidated mud
2H9	29-Jul-13	7.6	0.1	Mud	Brown hydrous material (0.01 m) over green/grey mud
2H10	29-Jul-13	4.6	0.1	Mud	Grey hydrous material over dark grey mud
2H11	29-Jul-13	1.5	0.06	Sandy mud (0-0.01 m) over gravelly mud	Abundant vegetation - sticks and leaves. Dark grey, moderate organic odour
2H12	28-Jul-13	1.5	0.05	Sandy mud	Abundant vegetation - sticks and leaves
2H13	28-Jul-13	1.2	0.09	Mud	Brown hydrous layer (0.03 mm) over grey/brown mud. Worm burrows (<1 mm). Green filamentous algae on surface
2H17	30-Jul-13	2.3	0.09	Mud	Brown hydrous layer (0.01 m) over grey/brown mud. Very thin algal mat on surface
2H18	30-Jul-13	1.6	0.09	Mud	Brown hydrous layer (0.02 m) over grey/brown mud
2H38	30-Jul-13	2.3	0.08	Mud	Brown hydrous layer (0.02 m) over grey/brown mud.
2H39	30-Jul-13	2.6	0.1	Mud	Brown hydrous layer (0.02 m) over grey/brown mud
2H51	29-Jul-13	2.7	0.09	Mud, trace sand	Brown hydrous material over dark grey mud
2H52	29-Jul-13	9.3	0.09	Sandy mud (0-0.005 m) over black mud, tr. sand	Highly bioturbated. Anoxic with slight sulphitic odour
2H53	29-Jul-13	4.8	0.05	Muddy sand (0.005 m) over sandy mud	Abundant vegetation - sticks and leaves
2H54	29-Jul-13	4.4	0.06	Mud with fine sand (0.005 m) over sandy mud	Brown hydrous material over black sandy mud. Some vegetation
2H55	29-Jul-13	5.8	0.07	Mud	Brown hydrous material over dark grey mud

# Table 3 Sediment Descriptions

Sample	<63 micron (%)	63 to 125 micron (%)	125 to 250 micron (%)	250 to 500 micron (%)	500 to 1000 micron (%)	1000 to 2000 micron (%)	>2000 micron (%)
Stage 1							
H1	67.2	26.9	4.4	1.1	0.3	0.0	0.0
H2	64.8	6.9	17.9	9.4	1.0	0.1	0.0
H3	93.0	6.3	0.3	0.3	0.1	0.0	0.0
H4	82.0	14.6	2.0	1.2	0.2	0.0	0.0
H5	99.0	0.4	0.2	0.3	0.1	0.0	0.0
H6	98.5	0.7	0.2	0.4	0.2	0.0	0.0
H7	97.0	1.9	0.6	0.2	0.3	0.0	0.0
H8	88.1	9.9	1.2	0.5	0.2	0.2	0.0
H9	96.0	2.5	0.6	0.5	0.3	0.0	0.1
H10	77.5	16.2	3.2	2.0	1.0	0.1	0.0
H11	76.1	14.0	3.5	2.6	2.6	1.0	0.3
H12	1.1	0.0	2.1	69.4	26.2	1.0	0.2
H13	86.0	13.0	0.6	0.3	0.0	0.0	0.0
H14	62.9	27.5	4.4	2.1	0.4	0.4	2.4
H15	47.5	40.1	10.0	0.7	0.4	0.3	1.0
H16	67.8	20.5	5.4	5.7	0.5	0.1	0.0
H17	89.5	7.7	1.8	0.9	0.2	0.0	0.0
H18	98.8	0.8	0.3	0.1	0.0	0.0	0.0
H19	98.0	0.7	0.6	0.5	0.1	0.0	0.0
H20	99.2	0.2	0.1	0.5	0.0	0.0	0.0
H21	76.3	14.1	3.3	3.0	2.3	0.7	0.3
H22	12.6	5.5	27.3	45.7	8.7	0.1	0.1
H23	96.7	1.4	0.3	0.6	1.0	0.0	0.0
H24	97.9	1.1	0.6	0.4	0.0	0.0	0.0
H25	54.6	17.5	16.1	9.2	2.0	0.5	0.1
H26	87.8	5.0	3.2	3.2	0.6	0.1	0.0
H27	18.0	3.5	51.9	23.0	3.3	0.2	0.0
H28	87.0	4.3	4.9	2.7	0.7	0.3	0.1
H29	98.2	1.3	0.2	0.3	0.0	0.0	0.0
H30	98.5	0.8	0.5	0.0	0.2	0.0	0.0
H31	96.2	2.3	0.9	0.5	0.1	0.0	0.0
H32	74.3	24.0	1.2	0.3	0.2	0.0	0.0
H33	70.9	25.2	2.4	1.2	0.2	0.0	0.1
H34	63.3	12.0	5.8	1.5	0.8	1.1	15.4
H35	50.3	14.2	18.7	13.5	3.0	0.2	0.1
H36	16.4	31.1	30.4	17.0	4.5	0.7	0.0
H37	82.9	6.2	5.5	3.4	1.0	0.5	0.4
H38	96.5	2.9	0.2	0.3	0.1	0.0	0.0
H39	84.0	14.3	1.1	0.3	0.2	0.0	0.0
H43	50.1	8.8	3.5	28.8	7.5	1.1	0.1
H44	34.7	23.1	37.7	4.2	0.3	0.0	0.0
H45	19.3	20.7	46.9	5.4	1.0	0.8	5.9
H46	88.4	9.1	0.9	1.0	0.5	0.1	0.0
H47	51.6	10.0	11.0	19.9	6.6	0.8	0.1
H48	66.0	18.2	13.2	2.1	0.3	0.1	0.1
H49	60.0	33.7	4.7	1.3	0.2	0.0	0.0
H50	87.2	11.2	1.3	0.3	0.1	0.0	0.0
H51	59.4	37.8	2.0	0.6	0.2	0.0	0.0
H52	73.1	16.4	9.0	1.1	0.3	0.0	0.0
H53	1.8	0.2	4.5	76.4	17.0	0.1	0.1
H54	4.7	1.2	49.5	38.9	5.0	0.7	0.0
H55	89.8	6.5	2.1	0.8	0.7	0.1	0.0

#### Table 4 Sediment Grainsize

Sample	<63 micron (%)	63 to 125 micron (%)	125 to 250 micron (%)	250 to 500 micron (%)	500 to 1000 micron (%)	1000 to 2000 micron (%)	>2000 micron (%)
Stage 2							
2H56	87.1	9.5	0.5	1.9	0.6	0.3	0.2
2H57	52.0	33.3	9.7	2.5	1.4	0.5	0.6
2H58	93.6	3.9	0.5	1.8	0.2	0.1	0.0
2H59	60.4	18.7	4.6	11.7	2.8	1.1	0.8
2H60	84.8	9.3	2.3	2.4	0.4	0.3	0.5
2H7	98.3	0.7	0.1	0.6	0.2	0.1	0.1
2H8	93.4	4.6	0.6	1.0	0.2	0.1	0.1
2H9	95.3	3.9	0.1	0.5	0.1	0.1	0.0
2H10	87.2	8.2	1.2	1.7	0.7	0.7	0.3
2H11	79.0	8.7	3.0	5.6	2.0	0.9	0.7
2H12	34.6	2.3	1.2	45.8	13.6	1.9	0.7
2H13	87.3	11.4	0.5	0.8	0.1	0.0	0.0
2H17	89.6	7.7	0.6	1.8	0.2	0.1	0.0
2H18	98.9	0.8	0.0	0.2	0.0	0.0	0.0
2H38	98.4	1.2	0.0	0.0	0.3	0.0	0.0
2H39	87.5	11.1	0.6	0.6	0.1	0.1	0.0
2H51	77.7	19.6	1.3	1.2	0.2	0.0	0.0
2H52	87.7	9.6	0.9	1.4	0.3	0.0	0.0
2H53	74.2	8.2	1.1	7.4	5.4	1.8	1.9
2H54	40.9	19.0	22.3	16.1	1.1	0.4	0.2
2H55	90.1	4.8	1.1	3.4	0.4	0.1	0.0

#### Table 4 Sediment Grainsize

Table 5Concentrations of Inorganic Contaminants in Sediment

	Alumin-		_	_	_					
Sample ID	ium	Arsenic	Barium	Beryllium	Boron	Cadmium	Chromium	Cobalt	Copper	Iron
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
ANZECC		20	-	-	-	1.5	80	-	65	-
ISQG-L								/ <b>-</b> -		0 / 0
H1	13,000	15.7	33	1.2	14	0.1	21.0	12.7	16.0	34,000
H2	12,333	16.7	30	1.1	14	0.11	20.3	11.3	15.7	32,000
H3	15,333	18.3	37	1.4	16	0.11	24.3	11.7	20.7	34,000
H4	14,667	19.0	36	1.3	16	0.13	23.7	12.0	20.3	35,000
H5	17,667	18.3	40	1.5	15	0.12	25.7	13.0	23.0	38,000
H6	19,000	21.3	42	1.5	19	0.13	27.3	13.0	27.7	40,000
H7	20,000	16.7	38	1.5	21	0.12	28.0	11.7	38.0	41,000
H8	19,000	12.7	38	1.2	30	0.24	29.0	9.3	67.7	35,000
H9	20,333	11.3	38	1.3	31	0.23	29.0	8.8	73.3	36,000
H10	14,667	9.0	29	1.1	51	0.4	27.3	7.4	75.0	28,000
H11	14,667	9.1	33	1.1	51	0.35	25.0	8.5	66.3	27,000
H12	527	0.5	3.5	0.05	2.5	0.05	0.7	0.7	0.4	1,300
H13	14,000	17.3	35	1.3	16	0.11	23.0	11.0	19.0	33,000
H14	10,200	13.3	30	1.2	23	0.13	18.3	9.9	16.3	28,000
H15	9,567	14.0	30	0.84	20	0.05	16.7	7.9	12.7	24,000
H16	9,967	17.3	32	0.91	19	0.1	18.7	8.1	25.7	27,000
H17	15,667	20.3	36	1.3	18	0.14	24.3	11.0	42.0	35,000
H18	17,333	22.7	40	1.3	21	0.12	26.7	11.7	55.7	36,000
H19	17,333	20.7	40	1.4	20	0.14	27.0	11.0	20.3	37,000
H20	17,667	24.0	41	1.4	23	0.15	27.0	11.0	21.3	37,000
H21	16,000	14.0	32	0.74	49	0.31	32.0	4.4	343	26,000
H22	3,133	4.1	7	0.2	17	0.05	7.0	1.0	26.0	5,700
H23	17,667	13.3	36	1	42	0.13	29.0	9.2	59.7	32,000
H24	18,667	14.3	42	1.2	40	0.12	29.0	10.0	58.0	31,000
H25	9,333	16.3	26	0.78	58	0.23	22.3	4.1	170	23,000
H26	8,833	10.0	36	1.1	47	0.26	16.6	4.5	65.0	30,000
H27	7,367	11.4	12	0.47	20	0.05	14.7	5.4	16.0	16,000
H28	18,000	19.7	40	1.2	33	0.13	28.3	10.0	56.3	35,000
H29	17,000	26.7	44	1.4	28	0.15	28.0	10.7	24.3	37,000
H30	19,000	18.7	42	1.4	31	0.11	30.0	10.0	31.3	37,000
H31	17,667	28.0	42	1.3	28	0.17	28.0	10.7	23.7	38,000
H32	11,667	18.0	34	1	19	0.12	20.3	8.5	15.7	28,000
H33	9,633	17.0	27	0.88	18	0.11	18.3	8.1	14.7	27,000
H34	12,000	20.3	31	1.1	31	0.15	19.7	9.2	16.0	27,000
H35	9,000	17.7	27	0.92	19	0.11	16.0	8.4	16.3	26,000
H36	4,033	9.0	12	0.39	8	0.05	8.4	4.9	4.0	13,000
H37	14,667	17.3	40	1.2	23	0.13	25.3	9.3	59.3	30,000
H38	16,000	21.3	42	1.3	23	0.13	25.7	11.0	51.0	35,000
H39	14,000	18.0	37	1.2	21	0.12	23.0	10.0	31.3	32,000
H43	10,367	13.7	25	0.82	15	0.05	17.0	7.8	14.0	21,000
H44	7,533	10.6	18	0.62	12	0.05	12.7	6.7	9.8	18,000
H45	7,100	10.7	24	0.84	39	0.05	13.7	9.9	13.7	21,000
H46	15,000	16.0	37	1.3	18	0.12	23.7	11.3	20.7	34,000
H47	8,700	10.0	26	0.77	11	0.05	15.0	8.6	11.0	22,000
H48	12,000	9.9	33	1.1	14	0.05	19.7	12.0	17.0	27,000
H49	10,167	11.7	35	1	12	0.05	17.3	9.3	14.0	26,000
H50	14,667	13.7	47	1.3	15	0.11	23.7	13.0	21.0	35,000
H51	9,800	9.5	41	0.97	7.9	0.05	16.7	10.0	14.7	26,000
H52	13,000	9.3	47	1.2	9.3	0.05	21.3	11.7	20.3	31,000
H53	1,003	1.6	11	0.13	2.5	0.05	1.8	2.2	1.6	4,100
H54	2,667	1.9	20	0.29	2.5	0.05	4.7	2.9	3.5	8,100
H55	15,667	13.0	44	1.5	8.8	0.13	25.3	13.0	30.3	33,000
H56	18,000	9.8	34	1.1	36	0.26	28.0	6.9	78.0	33,000
H57	12,000	12.0	33	0.93	37	0.39	23.0	6.8	100	27,000
H58	20,000	15.0	41	1.4	30	0.15	28.0	11.0	58.0	40,000
H59	14,000	11.0	32	0.97	40	0.41	26.0	7.0	250	31,000
H60	17,000	11.0	33	1.1	42	0.32	27.0	7.6	95.0	33,000
Excode A				10	Evened		2000) 1900	-High vol		

Table 5Concentrations of Inorganic Contaminants in Sediment

Comela ID	المعا	Magnes-	Mangan-	Maxer	Nichel	Cilver	Other stimute	Vanad-	7:	Calcium
Sample ID	Lead	ium ma/ka	ese ma/ka	ma/ka	NICKEI	Silver	Strontium	ium		
ANZECC	тід/кд	тту/кд	тіў/кд	шу/кд	шу/кд	тід/кд	шу/кд	тід/кд	шу/кд	шу/кд
ISQG-L	50	-	-	0.15	21	1	-	-	200	-
H1	21.0	4,000	430	0.05	15.3	0.05	41	43	83.0	1,900
H2	21.3	4,000	470	0.04	14.3	0.05	40	42	74.7	1,900
H3	25.0	4,800	520	0.06	17.0	0.05	50	52	81.3	2,500
H4	24.7	4,700	720	0.08	16.7	0.05	50	49	83.7	2,400
H5 LLC	26.3	5,200	1200	0.05	18.3	0.05	53	56	94.0	2,500
П0 Ц7	29.U	0,∠UU 6.000	1300	0.07	10.3	1.05	0U 67	00	103	2,900 2,200
	54.0	6,500	020 320	0.00	10.0	0.17	יס 72	50	120 170	3,300 4 400
H9	52.7	7,000	220	0.11	16.7	0.17	73	170	170	4 700
H10	58.3	6.500	120	0.10	15.0	0.16	75	41	227	4.600
H11	56.3	6,700	120	0.09	14.7	0.13	82	40	230	4,600
H12	1.1	280	210	0.01	0.5	0.05	4.5	1.5	3.5	210
H13	24.3	4,300	370	0.05	16.0	0.05	45	48	78.3	2,100
H14	22.0	4,000	220	0.07	13.7	0.05	65	39	64.0	8,300
H15	18.0	3,700	260	0.05	11.0	0.05	65	36	52.0	6,300
H16	26.0	4,000	260	0.15	12.0	0.05	38	39	75.0	2,500
H17	29.0	4,900	520	0.07	16.0	0.05	48	89	90.0	2,400
H18	34.7	5,400	650	0.14	16.7	0.05	50	57	110	2,300
H19	28.0	5,400	660	0.06	17.0	0.05	53	57	83.7	2,600
H20	27.7	5,800	770	0.06	17.0	0.05	53	59	80.7	2,500
H21	110.0	7,000	62	0.74	13.7	0.05	72	48	287	6,600
H22	28.0	1,800	14	0.13	2.8	0.05	22	11	53.0	2,000
H23	57.7	8,800	470	0.16	14.3	0.05	120	73	147	15,000
H24	44.3	8,700	620	0.10	16.0	0.05	140	69	130	18,000
П25 Цре	01.0	0,000	130	0.27	8.6 7.0	0.05	110	41	413	12,000
⊡20 H27	37.U 15 7	9,700 2 000	590 510	0.25	7.U 7 A	0.05	130	00	00.1 12 0	∠∠,000 16.000
H28	10.7	∠,900 7.200	510 650	0.07	7.4 16.2	0.05	92 85	20 59	40.U 117	8 300
H29	-+3.0 30.0	7 000	780	0.43	16.7	0.05	86	62	88.7	7 400
H30	35.3	7,700	400	0.14	17.0	0.05	81	64	107	7,500
H31	29.0	6.800	760	0.10	16.7	0.05	84	63	85.7	8,400
H32	23.3	4.800	310	0.06	13.0	0.05	92	46	63.3	9,500
H33	24.3	4,100	280	0.11	11.7	0.05	37	38	71.3	2,400
H34	22.0	4,900	350	0.06	13.0	0.05	210	42	57.7	41,000
H35	19.0	3,800	310	0.05	10.6	0.05	53	37	66.3	5,100
H36	8.2	1,700	120	0.02	4.8	0.05	14	17	32.0	780
H37	41.0	5,200	260	0.11	34.0	0.05	53	48	110	3,200
H38	31.7	5,300	580	0.20	16.7	0.05	50	57	100	2,300
H39	27.0	4,900	510	0.07	15.0	0.05	51	49	79.7	2,600
H43	18.0	3,000	290	0.19	11.7	0.05	38	31	54.7	2,600
H44	13.3	2,300	250	0.03	8.8	0.05	27	25	44.7	2,100
H45	14.0	3,400	320	0.06	11.0	0.05	66	30	42.7	9,100
H46	24.0	4,700	360	0.06	16.7	0.05	50	49	79.3	2,600
H47	14.3	2,900	280	0.06	11.0	0.05	31	31	53.7	1,600
H48	18.7	3,900	340	0.20	14.7	0.05	41	42	54.0	2,400
H49	17.0	18	360	0.08	13.0	0.05	0.5	39	60.7	9
UCH LLE1	23.3	23	670	0.10	18.7	0.05	U.5	50	87.3 64.0	13
нсл Цсл	0.01 0.02	3,100 3,600	890 640	0.08	14.0	0.05	41	34 15	04.U 70.0	∠,000 2,700
H52	20.3 2.1	3,000 340	040 ∕\QA	0.10	17.3 25	0.00	40 5.2	40 // //	12.3 10.0	∠,700 220
H54	۲. ۱ ۲	730	90 96	0.01	2.J 1 2	0.05	J.∠ 12	4.4 11	18.0	220 180
H55	7.7 24 0	4 300	370	0.17	18.3	0.05	45	55	72 7	2 000
H56	61.0	6.000	130	0.59	15.0	0.17	74	44	190	5.000
H57	66.0	4,600	180	0.62	12.0	0.15	63	35	160	5,000
H58	45.0	6.500	590	0.12	17.0	0.17	64	58	140	3,400
H59	70.0	5.200	190	0.18	13.0	0.17	65	39	230	4,300
H60	59.0	5,900	180	0.13	16.0	0.19	79	44	190	5,900
Exceeds A		(2000) 1800			Evoodo					

Sample	Normalised Naphthalene	1- Methylnaphthal ene	2-Methylnaphth- alene	Normalised Acenaphth- ylene	Normalised Acenaph-thene	Normalised Fluorene	Normalised Phenanthrene
ISQG -L	160			44	16	19	240
H01	3.9	10.0	13.0	1.8	0.9	2.1	12.9
H02	4.4	9.0	12.0	3.0	0.9	2.6	17.8
H03	4.1	11.0	15.0	1.4	1.4	1.4	16.5
H04	3.4	10.0	13.0	1.3	1.3	1.3	12.4
H05	3.9	11.0	14.0	1.5	1.5	1.5	13.6
H06	3.8	5.0	14.0	1.4	1.4	1.4	12.4
H07	2.9	5.0	13.3	1.1	1.1	1.1	8.6
H08	3.0	17.3	22.7	2.2	0.8	0.8	10.4
H09	2.4	19.0	19.3	2.3	0.8	0.8	9.5
H10	1.9	16.7	24.3	1.8	0.5	0.5	9.3
H11	1.4	12.0	17.0	1.4	0.5	1.0	9.2
H12	10.4	2.5	2.5	10.4	10.4	10.4	10.4
H13	2.8	6.0	12.0	3.1	1.8	2.3	21.0
H14	4.0	10.0	14.0	1.3	0.6	1.8	11.3
H15	4.6	7.0	9.0	2.5	1.0	1.0	13.3
H16	9.6	16.0	21.0	9.6	3.6	6.4	60.0
H17	5.7	12.0	14.7	4.3	5.8	5.8	36.7
H18	6.0	11.0	15.3	11.8	3.4	10.3	53.9
H19	6.1	13.0	18.0	6.9	1.4	3.3	24.2
H20	5.3	12.0	14.0	1.6	1.6	1.6	17.8
H21	1.8	19.3	19.7	5.0	1.2	1.9	19.9
H22	1.3	2.5	2.5	1.3	1.3	1.3	6.2
H23	2.5	5.0	11.0	3.9	1.1	1.1	13.3
H24	1.0	5.0	5.0	1.0	1.0	1.0	6.5
H25	1.6	7.0	13.0	0.6	2.3	2.9	11.6
H26	2.0	2.5	2.5	0.4	0.4	0.4	37
H27	2.0	2.5	2.5	29	2.9	2.9	9.4
H28	31	5.0	5.0	2.7	14	1 4	11 4
H29	6.1	5.0	14 0	1.8	1.8	1.1	15.0
H30	35	5.0	5.0	1.5	1.5	1.5	10.0
H31	3.6	5.0	5.0	1.8	1.8	1.0	11.4
H32	59	10.0	15.0	2.6	0.9	2.2	17.4
H33	6.2	8.0	12.0	3.8	1.2	1 2	20.5
H34	4 Q	10.0	18.0	17	0.7	2.6	15 A
H35	5.0	8.0	10.0	25	21	2.0	21.3
H36	J.U 1 2	2.5	2.5	2.J	2.1 1.2	2.7 1 2	15.3
H37	4.2 5 Q	2.5	2.5	4.2	4.2 2.4	4.2	15.5 25.3
H38	5.7 5.2	5.0	13.0	4.0 5.8	2.4	4.0	25.5
H30	5.2	12.0	16.0	3.0	0.7	1.7 2.4	20.3
H13	J.J 4 5	7.0	10.0	3.Z 2.2	1 1	2.4	20.5
H43	4.5	7.0 5.0	7.0	2.5	1.1	2.7	20.J
	4.1 1 A	5.0	7.0 11 O	1.J 0.6	1.5 0.6	0.6	12.4
П4Э ЦИА	1.0 <i>A A</i>	0.0	11.0	0.0	0.0	0.0	4.7 15.0
П40 ЦИЛ	4.4 วา	11.U 2 E	14.U 4 O	∠. I 1 0	U./ 1 0	∠.I 1 0	10.3 0 F
П4/ Ц40	J.∠	2.0 2 E	0.0	1.3	1.3	1.3	7.U 4 D
	2.4	2.0 E 0	9.U 11.0	0.7	U. /	0.7	0.2
	2.0	5.0	11.0	0.8	0.8	0.8	8.7
	1.1	5.U E 0	11.0	1.1	1.1	1.1	0.4
	2.4	5.0	10.0	U./	U. /	U./	9.7
H52	1.4	5.0	12.0	1.4	1.4	1.4	8.3
H53	9.3	2.5	2.5	9.3	9.3	9.3	9.3
H54	3.3	2.5	2.5	3.3	3.3	3.3	3.3
H55	2.4	6.0	11.0	0.7	0.7	1.6	1.6
H56	2.1	18.0	18.0	1.9	0.3	0.6	9.0
H57	3.0	14.0	20.0	2.4	1.1	1.4	15.5
H58	2.6	10.0	12.0	2.3	0.5	1.1	9.1
H59	2.3	18.0	19.0	1.9	1.0	1.4	9.3
H60	2.1	20.0	22.0	2.1	0.3	0.9	8.0

Exceeds ANZECC (2000) ISQG-Low value

Sample	Normalised Anthracene	Normalised Low Molecluar Weight PAHs	Normalised Fluoranthene	Normalised Pyrene	Normalised Benz(a)anthrac ene	Normalised Chrysene	Benzo(b)&(k)- fluoranthene
ISQG -L	85	552	660	665	261	384	
H01	3.2	29.5	35.7	39.3	18.6	22.1	110
H02	6.7	39.8	70.4	63.0	37.0	40.7	180
H03	4.3	33.0	70.3	67.6	32.4	37.8	240
H04	3.2	26.3	44.7	44.7	21.6	24.2	170
H05	3.9	30.3	48.5	48.5	23.6	27.6	160
H06	3.0	27.0	43.2	45.9	22.2	25.9	180
H07	2.3	20.1	31.9	33.3	15.0	19.6	170
H08	2.6	23.2	30.2	32.3	14.9	17.2	233
H09	2.3	21.4	28.3	30.6	13.4	17.2	213
H10	2.3	19.2	25.6	27.1	11.5	15.0	300
H11	2.3	17.5	20.0	22.0	11.0	12.0	290
H12	10.4	72.9	10.4	10.4	10.4	10.4	5
H13	5.9	40.0	87.2	82.1	46.2	48.7	330
H14	2.5	24.9	32.5	35.0	16.5	19.0	130
H15	2.9	29.2	36.7	37.5	22.9	22.9	94
H16	12.0	109.6	136.0	152.0	72.0	80.0	330
H17	10.4	73.4	119.4	110.8	57.0	59.1	313
H18	14.3	105.1	178.2	166.7	87.4	100.0	553
H19	6.7	53.6	91.7	102.8	52.8	61.1	330
H20	4.7	36.9	68.8	68.8	40.6	37.5	230
H21	5.3	37.6	48.1	53.7	24.7	26.8	457
H22	1.3	13.7	18.2	17.7	7.8	9.2	40
H23	3.8	28.3	36.4	40.2	18.2	21.9	210
H24	1.0	12.7	16.3	18.8	8.6	11.0	117
H25	2.3	22.8	17.9	19.8	7.7	8.2	125
H26	2.0	9.3	8.7	9.6	3.9	4.6	57
H27	2.9	27.1	32.9	34.1	20.0	20.0	35
H28	3.1	24.3	32.4	31.5	15.8	17.7	130
H29	1.8	33.2	42.9	42.9	23.2	26.1	120
H30	1.5	20.9	23.5	27.9	13.8	16.8	110
H31	1.8	23.9	34.3	35.7	17.9	20.7	100
H32	4.1	38.7	51.9	51.9	24.4	27.4	120
H33	4.8	43.3	71.4	76.2	35.2	39.0	150
H34	3.4	33.9	31.4	31.4	12.9	16.0	92
H35	4.6	42.5	50.0	50.0	25.0	26.7	100
H36	4.2	40.7	37.3	37.3	18.6	20.3	20
H37	6.7	54.5	85.8	86.7	43.3	54.2	333
H38	6.6	51.5	118.9	116.7	62.2	68.9	393
H39	4.1	40.1	52.9	55.9	28.8	32.4	190
H43	4.5	40.2	68.2	59.1	29.5	35.5	130
H44	1.5	26.5	39.4	37.6	19.4	22.9	65
H45	1.4	12.2	7.4	10.9	7.0	7.2	48
H46	3.8	32.5	44.1	41.2	24.7	24.4	140
H47	1.3	21.1	25.8	26.8	14./	16.8	57
H48	1.5	14.9	14.1	16.5	10.9	11.5	65
H49	1.9	19.2	22.9	23.9	13.5	15.5	82
H50	1.1	14.5	14.1	16.1	8.0	10.0	/6
H51	2.1	19.3	24.1	19.4	10.9	12.6	75
H52	1.4	18.9	18.0	20.0	9.4	13.1	/1
H53	9.3	64.8	9.3	9.3	9.3	9.3	5
H54	3.3	23.0	13.2	13.2	6.6	7.9	5
H55	1.8	17.6	16.1	17.9	10.3	12.9	/4
H56	2.2	18.4	24.4	25.6	12.2	15.4	250
H5/	4.6	30.8	33.8	36.6	18.3	18.3	260
H58	2.5	20.3	28.3	32.1	15./	18.5	200
H59	2.9	21.1	21.7	24.1	11./	13.3	230
HOU	۷.۵	10.4	22.0	Z3.Z	11.0	13.4	270

Exceeds ANZECC (2000) ISQG-Low value

Sample	Normalised Benzo(a)- pyrene	Indeno(1,2,3- cd)pyrene	Normalised Dibenz (a,h)- anthracene	Normalised High Molecluar Weight PAHs	Benzo(g,h,i) perylene
ISQG -L	430		63	1700	
H01	20.0	58.0	3.2	139	49.0
H02	34.1	90.0	5.9	251	70.0
H03	32.4	120.0	5.1	246	88.0
H04	23.9	87.0	3.7	163	69.0
H05	27.3	81.0	4.2	180	66.0
H06	25.9	95.0	4.3	168	74.0
H07	20.1	96.7	3.6	123	72.3
H08	19.8	143.3	3.6	118	126.7
H09	18.9	126.7	3.5	112	111.7
H10	16.5	170.0	3.2	99	160.0
H11	13.0	170.0	2.6	81	150.0
H12	10.4	2.5	10.4	63	2.5
H13	48.7	180.0	8.5	321	120.0
H14	17.8	63.0	3.0	124	54.0
H15	21.7	40.0	3.3	145	37.0
H16	84.0	150.0	12 0	536	140.0
H17	57.0	133 3	83	412	130.0
H18	103.4	296.7	19 5	655	220.0
H10	55 6	150.0	20.5 20	373	140.0
H20	37.5	95.0	5.9	250	90.0
H21	37.5	320.0	5.9	105	<sup>30.0</sup> 216.7
1121 LIDD	10.2	320.0	0.0	17J	210.7
	10.3	20.7	1.5	1/0	21.0
	27.3	143.3	4.8	149	100.0 E2 2
	12.3	12.1	2.3	09	53.3 E4 0
H25	8.7	83.3	1.5	64	56.0
H20	5.0	30.7	1.7	34	27.3
H27	22.4	19.0	2.9	132	14.0
H28	19.9	81.0	3.2	121	57.0
H29	25.0	67.0	3.9	164	55.0
H30	17.9	71.0	3.5	104	54.0
H31	21.4	59.0	3.6	134	50.0
H32	25.6	61.0	4.1	185	50.0
H33	41.4	/8.0	6.2	270	65.0
H34	14.0	46.0	2.0	108	37.0
H35	23.8	44.0	3.8	179	42.0
H36	18.6	8.0	4.2	136	8.0
H3/	44.2	156./	/.3	322	136.7
H38	/1.1	216.7	12.6	450	143.3
H39	29.4	/9.0	4./	204	//.0
H43	30.0	55.U	5.0	227	50.0
H44	19.4	32.0	2.9	142	27.0
H45	6./	25.0	0.6	40	23.0
H46	21.5	59.0	3.5	159	56.0
H47	15.8	31.0	3.2	103	26.0
H48	11.8	28.0	1.8	66	28.0
H49	14.2	37.0	2.9	93	38.0
H50	8.6	44.0	1.1	58	32.0
H51	11.8	32.0	2.1	81	30.0
H52	10.6	39.0	1.4	73	33.0
H53	9.3	2.5	9.3	56	2.5
H54	3.3	6.0	3.3	47	2.5
H55	10.3	40.0	1.8	69	34.0
H56	16.7	110.0	2.8	97	140.0
H57	21.1	100.0	2.7	131	120.0
H58	20.8	83.0	3.2	118	92.0
H59	15.7	120.0	2.9	89	120.0
H60	17.1	120.0	2.4	90	140.0
Exceeds ANZECC (2000)	ISOG-Low value				

Sample	Coronene	Benzo (e)pyrene	Perylene	Total PAHs	Total normalised PAHs
ISQG -L					4000
H01	5.0	49.0	130.0	880	314
H02	21.0	76.0	130.0	1370	507
H03	<20	100.0	150.0	1740	470
H04	<20	74.0	110.0	1240	326
H05	<20	71.0	120.0	1200	364
H06	<20	81.0	120.0	1280	346
H07	<20	77.3	106.3	1160	258
H08	30.7	110.0	110.0	1673	261
H09	29.3	98.3	97.3	1480	247
H10	45.7	130.0	146.7	2040	224
H11	61.0	120.0	220.0	2010	201
H12	5.0	2.5	2.5	<100	<100
H13	24.0	140.0	160.0	2370	608
H14	5.0	55.0	100.0	1010	253
H15	5.0	41.0	110.0	/40	308
H16	26.0	150.0	150.0	2570	1028
H1/	36.0	130.0	1/3.3	2400	//4
H18	39.0	236.7	1/3.3	3/13	1280
H19	24.0	150.0	150.0	2480	689
H20	<20	95.0	150.0	1620	506
	55.7	200.0	110./	3180	413
HZZ	5.0	18.0	9.7	257	128
	29.0	94.0 52 7	80.3 E4 7	1397	317
H24 U25	<20	53.7 54.7	00.7 16.2	1002	147
	20.0	04.7 25.7	40.3	1003	129
H20 H27	5.0	20.7	16.0	220	250
H27 H28	- 20	59.0	63.7	220	239
H20	<20	59.0	120.0	960	243
H30	<20	54.0	74 0	770	226
H31	< 20	52.0	90.0	770	275
H32	10.0	55.0	140.0	1060	393
H33	12.0	66.0	98.0	1130	538
H34	5.0	42.0	290.0	1020	291
H35	5.0	44.0	110.0	880	367
H36	5.0	9.0	22.0	150	254
H37	30.0	140.0	170.0	2497	624
H38	27.0	170.0	143.3	2560	853
H39	15.0	82.0	160.0	1450	426
H43	5.0	51.0	120.0	990	450
H44	5.0	28.0	73.0	510	300
H45	5.0	25.0	98.0	440	102
H46	5.0	60.0	160.0	1140	335
H47	5.0	27.0	79.0	450	237
H48	5.0	32.0	260.0	680	200
H49	5.0	38.0	120.0	660	213
H50	<20	36.0	160.0	630	143
H51	5.0	34.0	180.0	690	203
H5Z	<20	34.U 2 F	200.0	0/0	191
ПЭ <i>3</i> ЦБ <i>4</i>	5.U 5.0	2.0 5.0	2.5	< IUU ~100	< 100 ~100
1104 1155	5.0	3.U 25.O	27.U 210 0	< 100 Q20	< 100 016
Н56	25 O	110 O	58.0	1620	210
Н57	20.0 20.0	110.0	68 O	1860	200
H58	37.0 26 N	88.0	69.0	1310	202
H59	58.0	96.0	65.0	1630	196
H60	49.0	110.0	75.0	1670	204

Exceeds ANZECC (2000) ISQG-Low value

						Total Normalised
Sample	TPH C6-C9	TPH C10-14	TPH C15-28	TPH C29-36	Total TPH	TPH
Units	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
H01	<10	<10	<50	73	73	26
H02	<10	<10	<50	74	74	27
H03	<20	<20	<100	<100	0	0
H04	<20	<20	<100	<100	0	0
H05	<20	<20	<100	<100	0	0
H06	<20	<20	<100	130	130	35
H07	<20	<20	<100	200	200	44
H08	<20	<20	150	330	480	75
H09	<20	<20	270	480	750	125
H10	<20	<20	270	420	690	76
H11	<20	<20	370	480	850	85
H12	<10	<10	<50	<50	0	0
H13	<10	<10	<50	58	58	15
H14	<10	<10	<50	66	66	17
H15	<10	<10	<50	<50	0	0
H16	<10	<10	<50	60	60	24
H17	<10	<10	<50	55	55	18
H18	<20	<20	<100	<100	0	0
H19	<20	<20	<100	<100	0	0
H20	<20	<20	<100	<100	0	0
H21	<20	<20	250	380	630	82
H22	<10	<10	<50	70	70	35
H23	<20	<20	<100	190	190	43
H24	<20	<20	<100	130	130	27
H25	<20	<20	220	290	510	61
H26	<20	<20	140	230	370	62
H27	<20	<10	<50	<50	0	0
H28	<20	<20	<100	<100	0	0
H29	<20	<20	<100	<100	0	0
H30	<20	<20	<100	140	140	41
H31	<20	<20	<100	<100	0	0
H32	<10	<10	<50	57	57	21
H33	<10	<10	<50	<50	0	0
H34	<10	<10	<50	54	54	15
H35	<10	<10	<50	<50	0	0
H36	<10	<10	<50	<50	0	0
H37	<10	<10	61	89	150	38
H38	<20	<20	<100	<100	0	0
H39	<10	<10	<50	68	68	20
H43	<10	<10	<50	<50	0	0
H44	<10	<10	<50	<50	0	0
H45	<10	<10	<50	88	88	20
H46	<10	<10	<50	65	65	19
H47	<10	<10	<50	51	51	27
H48	<10	<10	<50	79	79	23
H49	<10	<10	<50	71	71	23
H50	<20	<20	<100	110	110	25
H51	<10	<10	51	85	136	40
H52	<20	<20	<100	<100	0	0
H53	<10	<10	<50	<50	0	0
H54	<10	<10	<50	<50	0	0
H55	<10	<10	<50	82	82	22
H56	<20	<20	220	360	580	74
H57	<20	<20	160	280	440	62
H58	<20	<20	<100	200	200	38
H59	<20	<20	210	450	660	80
H60	<20	<20	200	390	590	72

 Table 6 Concentrations of Selected Organic Contaminants in Sediment - Continued

Sample	Monobutyl tin	Dibutyl tin	Tributyl tin	Normalised TBT
ISQG -Low	-	-	-	5
Units	µgSn/kg	µgSn/kg	µgSn/kg	µgSn/kg
H07	<1	<1	0.5	0.1
H08	<1	3.2	2.4	0.4
H09	<1	3.7	2.7	0.5
H10	<1	2.1	2.5	0.3
H17	<1	1.7	2.1	0.7
H18	<1	1.7	1.8	0.6
H21	2.6	51	59	7.7
H22	<0.5	1.5	1.7	0.9
H23	<1	2.3	1.2	0.3
H24	<1	1.8	0.5	0.1
H25	2.3	44	67	8.0
H26	5.4	32	57	9.5
H28	1.2	7.2	4.7	1.3
H31	<1	<1	0.5	0.2
H37	<1	3.8	3.1	0.8
H38	1.1	2.7	1.9	0.6
H56	<1	5.1	4.8	0.6
H57	40	77	310	43.7
H58	<1	3.6	5.2	1.0
H59	13	24	120	14.5
H60	4.6	5	6.3	0.8

Exceeds ANZECC (2000) ISQG-Low value

	Total Organic			Total Kjeldahl	Reactive	
Sample	Carbon	Total Ammonia as N	NOx as N	Nitrogen	Phosphorus	Phosphorus
	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
H01	2.8	1.5	<0.1	1,540	0.0	590
H02	2.7	1.3	<0.1	1,460	0.0	550
H03	3.7	2.2	<0.1	2,040	0.0	660
H04	3.8	1.8	<0.1	2,050	0.0	640
H05	3.3	2	<0.1	2,090	0.0	730
H06	3.7	8.7	<0.1	2,540	0.0	970
H07	4.5	7.6	<0.1	3,090	0.0	1200
H08	6.4	4.5	<0.1	3,780	0.0	1100
H09	6	6.9	< 0.1	3,730	0.0	1000
H10	9.1	3.7	< 0.1	4,720	1.0	1100
H11	11.3	8.5	<0.1	5,560	1.0	1300
H12	0.24	3	<0.1	170	< 0.1	38
H13	3.9	2.4	< 0.1	2.000	< 0.1	630
H14	4	0.6	< 0.1	1 580	< 0.1	410
H15	24	21	< 0.1	1 280	< 0.1	410
H16	2.5	17	<0.1	1 250	0.0	490
H17	3.1	11	<0.1	1 720	0.0	640
H18	2.9	2.8	0.2	1.800	0.0	660
H19	3.6	1.8	<0.1	2 040	0.0	690
H20	3.0	2.8	< 0.1	1 970	0.0	690
H20	5.2 7 7	2.0	<0.1	3 680	0.0	770
H22	2	3.7	<0.1	890	<0.0	220
H23	2 1 1	1.2	<0.1	3 500	< 0.1	820
H23	4.4	4.2	<0.1	3,300	<0.1	840
H25	4.7	4.4 5 1	<0.1	3,700	0.0	580
H26	6	2 Q	<0.1	4 030	0.0 <0.1	1800
H20	0.85	ງ.ບ າ	<0.1	4,030	< 0.1	330
H28	37	5	<0.1	1 180	<0.1	830
H20	3.7 2.9	2.6	<0.1	2 000	0.0 <0.1	780
H20	2.0	2.0	<0.1	2,070	< 0.1	840
H31	3.4 2.8	J.7 2 7	<0.1	2,500	< 0.1	780
H32	2.0	2.7 1 <i>1</i>	<0.1	1,750	< 0.1	520
H33	2.7	1.4	<0.1	1,000	< 0.1	490
H34	2.1	3.8	<0.1	1,100	<0.1	520
H35	5.5 2 A	1 0	<0.1	1,000	0.0	500
H36	0.59	1.7	<0.1	300	0.0	230
H37	0.57	1 1	<0.1	1 980	0.0	630
H38	3	0.9	< 0.1	1,700	0.0	670
H30	3.4	0. <i>7</i> 1 <i>4</i>	<0.1	1,810	<0.0	590
НДЗ	5. <del>1</del> 2.2	1 5	<0.1	1 240	<0.1	390
H44	1 7	1.3	<0.1	920	<0.1	320
H45	4 3	2 3	<0.1	1 380	<0.1	290
H46	7.5 3.4	1 3	<0.1	1 940	<0.1	620
H47	1 0	1.5	<0.1	1 090	0.0	400
H48	3.4	0.8	<0.1	1 550	0.0	410
H49	3.1	19	<0.1	1 430	0.0	500
H50	4 4	6.2	<0.1	2 230	0.0	730
H51	3.4	6.6	<0.1	1 780	0.0	520
H52	3.5	2.6	<0.1	2 020	0.0	580
H53	0.27	0.5	0.4	150	0.0	88
H54	0.76	0.8	<0.1	380	0.0	150
H55	3.8	1 5	<0.1	1 930	0.0	520
H56	7 8	1.0	<0.1	4 250	4 0	1100
H57	7.0	1.7	<0.1	3 120	4.0	790
н57	52	2.2	~0.1	3,120	4.0	1000
Н50	ט.ט מיז	2.2 1 Q	~0.1	3, <del>4</del> 30 2 <i>4</i> 70		760
H60	8.2	2.9	<0.1	4,150	2.0	1000

#### Table 7 Concentrations of Nutrients in Sediment

Sample Units	Aluminium RSD (%)	Arsenic RSD (%)	Cobalt RSD (%)	Chromium RSD (%)	Copper RSD (%)	Nickel RSD (%)	Lead RSD (%)	Zinc RSD (%)
H01	0.0	3.0	37	0.0	51	31	0.0	10
	3.8	2.8	1.2	2.3	6.0	3.1	2.0	2.3
H03	3.0	5 1	4.2	1.9	23	0.0	0.0	0.6
H04	3.1	43	4.0 0.0	2.0	2.3	2.8	1.9	1.5
H05	3.Z 2.7	4.5 2.6	0.0	1.8	2.5	2.0	1.7	1.5
H06	2.7	5.8	0.0	1.0	17	2.0	0.0	1.7
	0.0	2.0	4.0	0.0	1.7 2 1	2.0	0.0	4.0
H08	0.0	2.0 7 A	2.0	0.0	0.7	0.0	1.5	0.0
	0.0	1.4	2.0	0.0	0.7	2.8	1.5	0.0
н107 Н10	2.5	4.2	0.5	0.0	3.8	2.0	0.8	0.0
H11	3.2	1.4	3.0	0.0	1 <i>1</i>	3.2	0.0	2.1
H12	18.7	1.7	18.2	20.6	30.2	20.0	24.5	22.9
H13	0.0	5.4	0.0	20:0	0.0	20.0	1 0	0.6
H1/	5.8	7 1	1 /	5.1	5.8	3.4	3.7	0.0
H15	0.5	0.0	1.4	2.8	3.0	0.0	0.0	1.4
H16	0.5	27	0.6	2.0	5.7	0.0	3.1	1.0
нто H17	3.0	2.7	0.0	2.5	1.0	0.0	5.1	1.7
H18	5.0	2.5	4.0	1.7	1.7	2.8	0.0 1 /	0.9
нто 1110	J.4 2 7	2.1	4.0	0.0	4.7	2.0	0.0	0.0
H20	2.7	2.5	0.0	0.0	2.5	0.0	0.0	0.6
H21	2.7	0.0	1 1	2.6	3.6	6.9	0.0	10.8
H22	0.0	3.1	1.1	2.0	3.0	4.5	5.8	10.0 1 1
H22	1.5	J. 1 1/ 1	3.0	4.7 2.8	0.8	4.5	5.0	4.1
H24	2.7	3 3	0.0	2.0	12.5	0.0	5.0	0.0
H25	2.5	2.5	0.0	10.6	12.5	0.0	J.7 27	0.0 71.3
H26	10.1 65 <i>1</i>	63.7	7.5 5/ 1	T0.0	70.7	7.4 60.6	2.7 8/1	64.0
H27	22.2	14.6	16 1	12.0	27.0	19.3	8.0	13 5
H28	0.0	2.4	0.5	1 7	1 7	2.9	5.7	10.0
H29	4.8	1.8	۵.5 ۲ ۸	2.9	1.7	2.7	27	4.0 1 <i>4</i>
H30	0.0	9.1	0.5	0.0	4.0	0.0	2.7	4 4
H31	27	0.0	4 4	2.9	2.0	2.8	2.7	1.1
H32	4.0	0.0	1 1	2.3	3.0	0.0	2.0	2.0
H33	3.0	0.0	1.2	2.6	3.2	4.0	1.9	1.3
H34	6.8	2.3	2.7	6.3	5.1	6.3	3.7	5.0
H35	5.1	2.7	2.5	5.1	5.8	9.4	4.3	7.5
H36	4.2	3.4	4.4	2.4	3.1	2.6	2.5	4.4
H37	3.2	5.4	0.5	1.9	1.0	0.6	3.4	0.0
H38	0.0	2.2	0.0	1.8	1.6	2.8	1.5	0.0
H39	0.0	0.0	0.0	0.0	1.5	0.0	0.0	0.6
H43	11.7	9.1	9.4	9.6	11.7	10.7	9.1	9.7
H44	12.0	9.1	11.8	13.4	10.0	10.8	9.4	12.2
H45	13.9	4.4	8.5	12.4	15.0	12.9	10.1	7.7
H46	0.0	0.0	4.2	2.0	2.3	2.8	0.0	2.1
H47	2.5	0.0	0.5	0.0	0.0	0.0	3.3	0.9
H48	6.8	1.3	11.8	2.4	4.8	6.4	6.7	7.9
H49	5.8	4.0	4.5	7.2	5.8	6.3	4.8	4.7
H50	3.2	3.4	0.0	2.0	3.9	2.5	4.0	2.4
H51	2.9	6.7	0.0	2.8	3.2	0.0	5.1	0.0
H52	6.3	4.6	4.0	4.4	16.7	5.4	4.6	3.3
H53	7.7	8.0	5.8	9.3	43.0	1.9	10.3	8.6
H54	10.8	9.1	7.2	10.5	11.7	9.6	8.7	9.1
H55	21.1	6.3	6.3	3.7	34.2	5.1	0.0	6.9
mean	5.8	5.0	4.5	4.7	8.0	4.9	5.2	6.2

# Table 8 Field Triplicate Sample Variability

Sample	Naphtha- lene	1- Methylnap hthalene	2- Methylnap hthalene	Acenaphth ylene	Acenaph- thene	Fluorene	Phenanthr ene	Anthra- cene	Fluoran- thene	Pyrene	Benz(a)an thracene	Chrysene	Benzo(b)&( k)fluoranth ene	Benzo(a)p yrene	Indeno- (1,2,3- cd)pyrene	Dibenz(a,h) anthracene	Benzo(g,h,i) perylene	Coronene	Benzo(e)p yrene	Perylene	Total PAHs
H07	6.3	0.0	3.5	0.0	0.0	0.0	4.4	4.8	8.7	5.4	7.9	4.8	4.8	1.9	4.2	10.2	12.7	0.0	4.3	4.9	4.3
H08	11.4	27.6	9.1	5.8	0.0	0.0	4.3	2.9	6.5	4.6	2.6	0.0	2.0	3.7	3.3	9.4	3.7	19.3	7.4	7.4	0.6
H09	26.3	26.3	19.5	11.7	0.0	0.0	5.2	13.8	19.2	9.3	6.7	9.6	8.0	8.3	7.4	6.7	10.6	13.7	10.4	3.9	9.9
H10	30.1	19.8	15.9	7.5	0.0	0.0	2.4	11.7	5.3	1.9	15.0	3.4	0.0	0.0	8.3	11.6	8.8	13.5	6.3	3.2	1.1
H17	2.7	0.0	3.2	9.4	0.0	0.0	59.9	75.9	53.5	44.6	45.4	33.4	30.9	37.4	30.2	25.7	27.4	0.0	27.4	15.1	38.3
H18	19.0	0.0	11.1	35.6	0.0	46.7	45.3	42.7	20.6	14.1	17.8	12.9	11.3	11.9	13.0	16.1	17.0	41.0	11.1	9.8	16.4
H21	10.1	6.5	6.3	8.1	9.1	8.7	8.1	8.1	3.8	4.6	4.3	6.0	3.7	5.2	2.6	1.9	7.8	20.9	0.0	4.0	3.8
H22	0.0	0.0	0.0	0.0	0.0	0.0	10.1	0.0	11.3	6.7	8.0	5.1	5.4	6.0	11.6	0.0	11.7	0.0	4.5	9.8	8.0
H23	7.4	0.0	0.0	2.7	0.0	0.0	2.1	2.8	8.8	2.7	3.5	2.0	0.0	0.0	3.3	4.4	0.0	0.0	0.0	3.8	0.9
H24	0.0	0.0	0.0	0.0	0.0	0.0	5.1	0.0	11.4	6.2	6.7	7.0	8.1	9.0	5.2	4.2	2.3	0.0	11.0	8.2	7.9
H25	17.2	0.0	0.0	0.0	10.5	30.6	16.7	25.5	21.8	20.4	25.4	23.8	22.9	28.2	28.3	31.3	24.5	0.0	21.8	18.8	19.3
H26	0.0	0.0	0.0	0.0	0.0	0.0	80.5	0.0	78.0	77.3	75.8	75.0	77.4	80.3	72.1	0.0	76.9	0.0	75.4	79.0	79.1
H28	16.6	0.0	0.0	0.0	0.0	0.0	16.6	4.3	18.0	14.6	16.7	15.5	10.9	13.2	8.6	18.0	11.7	0.0	12.3	4.1	14.0
H37	26.8	27.0	19.6	0.0	34.1	18.4	20.6	16.9	26.2	25.4	16.5	14.3	20.5	25.5	26.2	16.3	27.6	29.4	20.2	19.2	21.2
H38	3.2	0.0	0.0	14.4	0.0	0.0	19.3	20.9	16.9	16.8	13.4	12.1	13.5	13.4	15.2	11.9	8.7	0.0	14.4	14.3	14.5
Mean	11.8	7.1	5.9	6.3	3.6	7.0	20.0	15.3	20.7	17.0	17.7	15.0	14.6	16.3	16.0	11.2	16.8	9.2	15.1	13.7	16.0

Sample	Aluminium	Arsenic	Cobalt	Chromium	Copper	Nickel	Lead	Zinc
	RSD (%)	RSD (%)	RSD (%)	RSD (%)	RSD (%)	RSD (%)	RSD (%)	RSD (%)
H55B	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H47	1.3	0.0	0.6	3.3	0.0	0.0	0.0	0.8
H18A	2.6	0.0	0.0	0.0	0.9	0.0	0.0	0.0
H12	7.4	10.8	2.0	6.5	5.9	4.8	4.6	2.5
H04B	0.0	0.0	0.0	0.0	0.0	2.9	0.0	0.6
H44	1.2	2.1	1.6	0.0	0.6	1.1	4.0	1.2
H33A	0.0	0.0	0.6	0.0	0.0	4.2	3.8	0.6
QAQC12	1.9	1.1	0.0	2.7	3.0	4.0	2.7	5.4
H15B	2.2	0.0	1.6	0.0	3.8	0.0	0.0	0.0
H35	0.8	2.6	1.1	0.0	3.0	4.2	0.0	0.7
H17A	3.1	0.0	4.4	0.0	1.1	0.0	0.0	0.5
Mean	1.9	1.5	1.1	1.1	1.7	1.9	1.4	1.1

 Table 9 Laboratory Triplicate Sample Variability

Table 10	Summary	of Analytica	Small Scale	Spatial	Variability
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Trace Metals	Alumin- ium	Arsenic	Cobalt	Chrom- ium	Copper	Nickel	Lead	Zinc
Robustness (mean RSD %)	1.9	1.5	1.1	1.1	1.7	1.9	1.4	1.1
Laboratory Duplicates (mean RPD %)	3.1	1.3	1.1	0.2	1.6	1.0	1.1	1.6
Field Duplicates (mean RPD %)	3.2	3.3	2.6	0.6	7.1	1.0	1.6	2.0
Small scale spatial variabilty (mean RSD %)	5.8	5.0	4.5	4.7	8.0	4.9	5.2	6.2
SSSV not including anomalous samples at four locations (mean RSD %)	3.6	3.6	2.8	3.0	4.5	3.2	3.0	2.9

Inorganics and TPH	Silver	Barium	Beryllium	Boron	Calcium	Cadmium	Iron	Mercury	Magnes- ium	Mangan- ese	Phos- phorus	Strontium	Vanadium	TPH C15- 28	TPH C29- 36
Robustness (mean RSD %)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Laboratory Duplicates (mean RPD %)	0.0	0.0	0.2	17.0	3.9	1.7	2.9	5.9	2.6	0.7	0.5	3.5	1.2	4.3	2.7
Field Duplicates (mean RPD %)	0.0	6.1	2.7	15.2	16.7	3.1	2.1	9.0	2.4	7.6	3.8	4.8	1.6	1.3	7.1
Small scale spatial variabilty (mean RSD %)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Table 10	Summary	of Analytical	<b>Small Scale Spati</b>	al Variability											
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PAHs	Naphthale ne	1- Methylna phthalene	2- Methylnap hthalene	Acenapht hylene	Acenapht hene	Fluorene	Phenanth rene	Anthrace ne	Fluoranth ene	Pyrene	Benz(a)ant hracene	Chrysene	Benzo(b)&( k)fluoranth ene	Benzo(a)p yrene	Indeno(1,2 ,3- cd)pyrene
Robustness (mean RSD %)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Laboratory Duplicates (mean RPD %)	7.3	3.5	6.6	6.2	3.9	7.8	9.1	5.2	7.7	7.4	9.7	9.7	8.0	10.1	8.1
Field Duplicates (mean RPD %)	9.0	16.8	9.5	9.9	10.9	9.5	15.9	18.0	12.7	11.6	14.1	9.4	12.4	13.1	16.9
Small scale spatial variabilty (mean RSD %)	11.8	7.1	5.9	6.3	3.6	7.0	20.0	15.3	20.7	17.0	17.7	15.0	14.6	16.3	16.0

PAHs continued	Dibenz (a,h)anth- racene	Benzo (g,h,i) perylene	Coronene	Benzo(e) pyrene	Perylene	Total PAHs
Robustness (mean RSD %)	-	-	-	-	-	-
Laboratory Duplicates (mean RPD %)	7.3	10.0	3.3	6.6	5.3	7.7
Field Duplicates (mean RPD %)	12.5	17.5	17.2	14.5	8.2	12.8
Small scale spatial variabilty (mean RSD %)	11.2	16.8	9.2	15.1	13.7	16.0

 Table 11 Correlation Matrix

	Maria	0 and	0		<b>A</b> -	D	<b>D</b> -			0.	0.	0	Γ.					N.I.	A	0		7	0.				TOO
	Mud	Sand	Gravel	AL	As	ва	Ве	В	Cd	Cr	Co	Cu	⊦e	Чþ	Mg	Mn	Нg	NI	Ag	Sr	V	∠n	Ca	IKN	Ч	$NH_4$	TOC
Mud	1.00																										
Sand	-1.00	1.00																									
Gravel	-0.14	0.06	1.00																								
AL	0.93	-0.93	-0.10	1.00																							
As	0.70	-0.72	0.08	0.64	1.00																						
Ba	0.90	-0.90	-0.08	0.84	0.64	1.00																					
Be	0.93	-0.93	-0.02	0.88	0.72	0.91	1.00																				
В	0.34	-0.35	0.15	0.40	0.14	0.21	0.21	1.00																			
Cd	0.34	-0.34	0.00	0.41	0.04	0.23	0.24	0.77	1.00																		
Cr	0.91	-0.91	-0.09	0.97	0.64	0.82	0.84	0.55	0.53	1.00																	
Co	0.73	-0.74	0.01	0.70	0.66	0.80	0.88	-0.11	-0.10	0.63	1.00																
Cu	0.17	-0.17	-0.06	0.27	-0.02	0.11	0.01	0.66	0.71	0.43	-0.24	1.00															
Fe	0.94	-0.95	-0.08	0.93	0.75	0.91	0.97	0.29	0.31	0.90	0.83	0.13	1.00														
Pb	0.43	-0.43	-0.08	0.54	0.11	0.31	0.24	0.82	0.83	0.68	-0.07	0.88	0.36	1.00													
Mg	0.73	-0.73	-0.03	0.73	0.48	0.55	0.59	0.74	0.55	0.77	0.27	0.41	0.66	0.65	1.00												
Mn	0.49	-0.48	-0.10	0.43	0.56	0.55	0.54	-0.21	-0.25	0.31	0.61	-0.30	0.53	-0.23	0.22	1.00											
Hg	0.11	-0.10	-0.07	0.18	-0.04	0.11	-0.04	0.48	0.50	0.31	-0.24	0.67	0.07	0.70	0.30	-0.26	1.00										
Ni	0.79	-0.79	-0.05	0.80	0.60	0.82	0.83	0.16	0.20	0.79	0.77	0.09	0.81	0.30	0.45	0.37	0.02	1.00									
Ag	0.17	-0.16	-0.04	0.27	-0.01	0.09	0.20	0.10	0.17	0.21	0.09	0.09	0.23	0.17	0.21	0.02	0.01	0.14	1.00								
Sr	0.36	-0.41	0.54	0.38	0.33	0.27	0.29	0.68	0.39	0.44	0.07	0.27	0.32	0.42	0.73	0.07	0.19	0.17	0.07	1.00							
V	0.72	-0.72	-0.08	0.74	0.46	0.63	0.66	0.30	0.26	0.69	0.48	0.16	0.69	0.36	0.61	0.29	0.04	0.54	0.14	0.34	1.00						
Zn	0.35	-0.34	-0.11	0.43	0.09	0.24	0.21	0.81	0.77	0.58	-0.08	0.80	0.30	0.88	0.57	-0.24	0.52	0.23	0.18	0.39	0.29	1.00					
Ca	0.08	-0.13	0.72	0.06	0.16	0.03	0.04	0.49	0.17	0.12	-0.10	0.11	0.05	0.17	0.43	0.01	0.10	-0.07	-0.05	0.91	0.13	0.13	1.00				
TKN	0.56	-0.56	-0.07	0.62	0.06	0.45	0.44	0.82	0.82	0.69	0.12	0.58	0.50	0.81	0.72	-0.07	0.37	0.37	0.28	0.50	0.45	0.80	0.22	1.00			
Р	0.71	-0.70	-0.12	0.69	0.26	0.59	0.61	0.65	0.67	0.70	0.27	0.35	0.67	0.62	0.79	0.23	0.29	0.44	0.36	0.48	0.54	0.54	0.24	0.85	1.00		
$NH_4$	0.27	-0.28	0.05	0.35	0.02	0.26	0.22	0.40	0.26	0.33	0.10	0.19	0.24	0.33	0.37	0.28	0.05	0.15	0.37	0.31	0.35	0.40	0.18	0.52	0.52	1.00	
TOC	0.18	-0.17	-0.07	0.23	-0.02	0.19	0.28	-0.08	0.04	0.17	0.31	0.08	0.26	0.06	0.03	0.32	0.03	0.20	0.28	-0.11	0.09	0.03	-0.18	0.15	0.20	0.21	1.00

## <63 micron Sample ID Aluminium Arsenic Barium Beryllium Chromium Iron Lead Nickel Cobalt Copper Magnesium Manganese Strontium fraction RPD (%) 29.4 18.2 29.7 -3.8 11.2 9.5 15.4 14.1 6.5 0.0 -0.5 12.9 16.5 5.0 H1 -32.2 -14.1 -7.7 -28.6 -58.1 -24.5 -21.1 -37.9 -5.2 -33.8 -42.7 -22.7 -33.3 H2 4.3 -3.0 25.2 13.6 20.9 33.3 5.6 5.9 -6.2 17.3 -7.7 -9.7 9.3 6.1 H3 -2.0 -6.0 18.2 -3.2 25.8 -5.3 -1.9 81.3 H4 18.4 23.5 26.1 7.3 8.7 4.1 4.1 -5.4 28.6 -28.6 -13.0 28.2 26.8 6.7 -4.3 27.2 54.2 H5 1.0 8.0 1.8 1.9 H6 -1.5 22.9 16.9 4.9 -28.6 -2.4 0.0 -8.1 20.7 -9.8 -3.2 6.3 -3.6 -1.7 -5.1 -28.6 -14.6 22.5 -13.7 -9.8 -16.0 -5.4 -54.3 H7 -1.0 18.0 17.4 0.0 -2.8 -5.9 13.7 H8 30.3 14.1 -5.1 18.2 10.9 15.4 26.5 -5.4 3.3 -25.6 6.1 -31.6 -2.0 -12.1 -7.7 H9 21.4 3.0 -5.1 26.1 -3.4 -1.9 -11.2 17.5 -21.0 -42.3 -5.3 H10 -5.5 16.0 12.1 -31.9 9.5 5.0 5.1 2.7 15.0 -16.8 -1.8 -24.8 -6.5 14.3 H11 68.1 149.1 114.0 147.4 75.0 133.3 157.7 130.3 131.7 103.1 124.1 109.7 132.1 112.4 -20.9 -155.0 -96.3 -163.6 -163.5 -126.7 -174.6 -147.9 -157.0 -142.9 -156.6 -123.4 H12 -131.7 113.4 15.4 26.1 0.0 22.2 -2.7 H13 -9.0 19.6 14.4 4.4 9.5 -9.5 23.6 6.5 -6.5 -2.1 H14 21.5 10.5 40.0 18.2 1.8 -1.0 -9.7 31.9 -4.4 -5.4 35.3 5.0 20.3 -8.5 7.4 40.0 -16.9 22.7 -10.5 H15 22.9 50.7 -2.0 -1.7 -8.0 3.5 1.6 0.0 H16 -1.2 33.3 14.4 46.2 58.2 9.3 14.2 -5.1 32.3 -3.8 2.0 22.7 18.2 2.7 -10.5 -12.9 -8.2 -8.0 H17 -4.5 26.1 -2.7 0.0 -9.1 16.0 6.8 0.0 18.6 1.7 0.0 26.1 4.9 17.5 -6.5 -6.5 23.0 0.0 H18 -0.2 22.7 7.6 6.5 5.9 4.1 H19 3.0 28.6 8.4 28.6 33.3 11.8 0.0 1.7 23.2 -3.5 -4.3 34.9 6.1 5.8 H20 -0.8 19.7 2.5 -35.3 -3.6 -8.7 -11.8 11.4 -14.5 -17.3 -13.4 -11.1 -15.7 0.0 -17.7 -19.7 -6.9 -60.9 38.7 -17.1 -12.9 -7.7 H21 -13.5 -66.3 -47.8 -9.2 -21.7 -11.8 -29.4 -75.8 -84.4 -35.3 -85.7 -103.4 -70.3 -89.4 -98.2 -108.2 -82.4 -145.1 -86.7 -79.5 H22 -1.3 2.1 -29.8 -10.5 66.7 0.0 14.0 10.0 12.3 -37.2 8.0 10.1 2.4 31.9 H23 -11.0 -17.8 H24 -1.1 10.5 4.9 82.4 10.9 0.0 32.0 9.5 -1.5 18.9 6.5 28.6 23.6 57.9 43.8 60.2 69.6 67.7 67.4 62.4 59.8 H25 51.7 26.1 9.7 52.9 54.3 -2.2 -76.2 -66.7 -10.5 9.5 -71.1 -75.2 -83.9 -14.5 -67.9 -1.2 -11.7 -78.3 -12.3 H26 -65.0 -88.0 -72.1 -87.7 -93.2 -50.2 -73.9 -21.4 H27 -74.4 -27.6 -85.7 -59.2 -67.7 -61.2 8.0 18.2 -28.0 H28 27.1 8.8 28.6 16.6 10.2 -28.4 24.4 7.5 17.0 -4.0 13.8 H29 -1.8 -4.9 9.5 33.3 0.0 -3.1 -14.0 7.0 -15.4 -5.1 -11.5 -7.7 -1.2 3.6 9.3 -35.3 -9.9 -21.8 -8.2 -5.7 -6.0 H30 -0.5 0.5 4.9 -3.3 -16.6 3.6 -47.2 H31 15.4 4.9 26.1 0.0 11.7 -12.9 16.8 -3.8 7.4 -3.1 -5.5 1.2 37.1 -7.7 -19.2 -13.6 -7.4 H32 -13.7 -5.4 12.5 0.0 -7.9 -6.1 5.9 -14.6 -1.6 4.4 -1.1 55.1 7.5 -2.2 -3.4 22.7 5.9 14.5 H33 -16.1 18.8 6.1 29.8 1.7 16.4 -6.6 -6.6 -14.3 H34 -28.7 1.7 68.1 3.3 9.5 -26.1 -22.2 10.9 0.0 34.9 106.6 1.4 -8.3 -19.0 -15.5 H35 -15.7 11.3 3.8 29.8 -11.8 -7.3 -20.2 14.9 23.8 -3.7 1.9 -24.7 45.4 2.9 -6.9 H36 -10.6 25.2 -0.4 18.2 5.3 -2.0 18.5 -13.2 -0.8 17.5 -42.3 -7.1 12.0 -22.2 -16.9 -4.4 12.4 -10.2 25.6 -5.5 H37 1.9 18.2 -7.6 61.5 -12.8 -23.4 H38 1.5 -3.1 4.9 -42.4 -5.1 -8.7 7.1 -20.8 -10.2 -7.7 -11.3 9.2 H39 -10.0 17.9 0.0 20.9 18.2 0.0 0.0 -8.2 17.3 -10.5 -6.5 11.0 0.0 -5.7 -8.9 13.0 12.5 -20.4 15.4 -14.6 H43 23.1 22.2 48.5 11.2 0.0 17.6 0.0 -8.6 -10.5 46.3 H44 -7.3 21.5 6.1 21.4 -11.9 12.4 -25.1 9.1 -20.0 -2.6 -3.9 -4.9 -22.2 -17.4 -21.7 -30.3 -8.7 49.1 H45 -33.7 -8.8 -3.1 -1.3 -15.7 5.4 -12.9 57.0 -14.8 -11.8 -7.8 -42.4 -5.5 -5.7 -14.9 13.2 -19.4 -24.0 -7.7 H46 -6.6 10.5 -18.9 H47 -4.4 3.4 -18.2 -14.3 42.5 -6.5 -4.2 -24.0 8.5 -22.7 -23.4 7.8 -8.7 -12.1 14.5 12.5 5.5 20.0 6.0 31.9 -1.3 9.5 9.5 28.6 34.8 3.6 53.3 15.8 H48 -11.0 -10.8 -14.3 -21.1 -198.3 -7.4 -195.5 15.4 0.0 -6.9 -25.0 6.8 -9.5 H49 -4.2 10.2 5.0 27.2 26.1 27.0 25.8 53.3 35.8 -195.4 H50 46.9 44.2 26.1 45.6 -197.6 -38.3 -13.3 -36.6 2.5 -23.0 -18.2 -35.5 -31.6 -48.2 -30.5 -34.3 H51 -5.9 -3.0 -0.8 -16.9 -50.0 -12.3 -2.5 -57.7 -14.3 -14.4 H52 -0.8 -16.7 16.1 -11.8 -18.2 -24.5 -31.0 -179.8 -152.3 -172.1 -129.2 -155.0 H53 -96.2 -157.0 -127.9 -175.6 -169.2 -173.5 -158.8 -179.7 -166.0 -12.3 -35.3 -79.8 -157.4 -50.0 H54 -60.1 -29.0 0.0 -53.2 -25.0 -54.2 -38.0 -52.0 -33.8 H55 -4.2 -24.3 -7.4 37.8 40.0 14.1 0.0 41.1 0.0 -8.0 -39.6 -17.5 13.6 -12.5

## Table 12 Temporal Changes in Sediment Grain Size and Inorganic Contaminant Concentrations - Interpreted

KEY <-5% RPD >+5% RPD >-5% RPD to <+5% RPD

Vanadium	Zinc	Calcium
RPD (%)	RPD (%)	RPD (%)
9.8	14.2	-7.6
-32.0	-19.7	-36.2
0.0	1.7	-2.0
2.1	4.5	-0.8
1.8	0.0	-21.4
0.0	-2.5	-4.4
3.4	-3.3	-87.2
10.5	25.2	-111.1
109.1	-0.6	2.6
10.3	21.3	23.6
133.3	149.8	106.2
-165.7	-154.5	-128.2
4.3	5.7	-11.7
2.6	3.2	42.2
-2.7	-1.9	-8.2
13.7	1.3	-8.4
47.2	-4.3	-15.7
0.0	0.9	-5.1
7.3	5.7	2.3
-5.0	-8.7	-41.3
-20.6	-35.9	-1.4
-77.8	-84.2	-82.4
10.1	-2.9	50.2
-4.3	1.6	40.8
60.3	131.1	26.1
-20.9	-75.4	6.1
-76.2	-82.2	5.1
10.9	-2.0	10.5
-3.2	-10.0	-5.9
-0.1	-1.0	-4.0
-1.0	-4.9	30.0 10.1
- <del>4</del> .5	-63	13
-13 3	-0.6	1.5
-27	-16.2	-13.2
0.0	-3.1	-30.4
-8.0	-15.1	0.9
-8.4	-11.3	-18.9
-2.0	-1.7	-28.9
-6.3	13.0	-15.6
-7.7	6.2	-50.3
-23.5	-27.0	106.9
-9.7	-2.1	-16.3
-9.2	-4.3	-11.2
18.2	3.8	24.8
-7.4	-6.9	-198.3
29.9	42.0	-197.8
-23.4	-7.5	-35.7
-10.5	-17.3	6.9
-168.8	-159.7	-174.3
-24.0	-36.4	-66.7
1.8	6.6	-26.5























































