



Project Twin Streams Catchment Monitoring

SEDIMENT QUALITY MONITORING REPORT

2005 - 2006



Project Twin Streams Sediment Quality Monitoring Summer 2005–2006

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Executive Summary

This report documents the stream and estuarine sediment quality monitoring conducted for the Project Twin Streams (PTS) Pressure-State-Response (PSR) monitoring programme in March 2006.

The report:

- documents the sediment quality data from the streams and estuary;
- provides a statistical summary of the data as a basis for comparison with past and future monitoring data;
- gives an overview of sediment quality, including comparison with guidelines for aquatic ecosystem health, and
- compares the concentrations of heavy metals measured in the March 2006 monitoring with those obtained approximately 2 years earlier, in December 2003.

Based on the results, recommendations for future monitoring are made.

Monitoring

Monitoring was conducted in March 2006 using the same protocols and sites as those used in December 2003 – i.e. two areas (banks and channel bed) from Henderson Creek estuary, and 15 stream sediment sites in the Opanuku, Oratia, and Waikumete Stream systems. In addition, four new stream sites in the Swanson Stream, and two sites in the downstream Huruhuru Creek estuary, were also sampled in March 2006.

Samples were analysed for texture (estuaries only), weak acid extractable Cu, Pb, and Zn in the <63 μ m (mud) fraction, and total recoverable Cu, Pb, and Zn in the <0.5 mm fraction.

Estuarine sediment results

Key findings of the March 2006 monitoring of the estuaries were:

- sediment textures in the bed and bank samples from Henderson Creek estuary were similar to those sampled in December 2003.
- concentrations of weak acid extractable Cu, Pb, and Zn in the mud fraction of Henderson Creek estuary were similar to those found in December 2003, within the variability of the laboratory analysis (as determined from quality assurance tests).
- Based on comparison of metals' concentrations with sediment quality guidelines
 (ARC Environmental Response Criteria and ANZECC guidelines), adverse
 effects on aquatic biota would be expected to be just beginning to occur, but
 concentrations are not currently high enough to cause marked or frequent
 impacts.
- The two sites in Huruhuru Creek estuary had similar Cu, Pb, and Zn levels, and these were also similar to the bank sediment samples from Henderson Creek estuary.

Stream sediment results

Key findings of the March 2006 monitoring of the stream sediments were:

- Spatial patterns of contamination in the Oratia, Opanuku, and Waikumete Stream systems in March 2006 were similar to those found in December 2003. Concentrations of Pb and Zn were markedly higher at urban sites than upstream rural or reference sites. Copper showed relatively smaller differences between urban and non-urban sites.
- Higher concentrations of Zn were recorded at the urban and urban/rural fringe sites in 2006 than in 2003. This was the most consistent difference between the samplings and is in line with the current view of generally increasing Zn loads to urban waterways over time. Whether this will continue is unknown at this stage, and will depend on the balance between changing catchment pressures and remedial responses.
- Sediments from the Swanson Stream had relatively low concentrations of Cu, Pb, and Zn, comparable with those in the non-urban sites in the other streams. It appears that urban effects are currently much less marked in the Swanson Stream, which is consistent with the lower degree of urbanisation in this catchment.
- Total recoverable metal concentrations exceeded only the most sensitive sediment quality guidelines (Canadian ISQG or ANZECC ISQG-low), and only for Pb (at 2 sites in the Waikumete Stream system) and Zn (for all urban sites in the Oratia, Opanuku and Waikumete system). This suggests that Zn is more likely to adversely affect aquatic life in urban stream reaches than Cu or Pb. No sediment quality guidelines were exceeded in the Swanson Stream.

Overall

The monitoring protocols are delivering consistent data that should be suitable for reliable on-going trend assessment. Variability is generally low at each site, enabling sensitive comparisons between samplings to be made.

Based on the findings of the data collected to date, it is recommended that the next round of sampling be conducted in summer 2008/9. Analysis should include sediment texture, Cu, Pb, and Zn (as determined in the 2003 and 2006 monitoring), and also PAH and organochlorine pesticides (mainly DDTs), for comparison with 2003 data.

The programme is highly dependent on consistent analytical results for sediment contaminants. On-going QA testing of analytical results, both within- and between-batch, is therefore essential to ensure reliable interpretation of trends can be made.

It is strongly recommended that the monitoring programme continue unchanged, for at least the next sampling round, to ensure consistent data is collected over time. This will provide a strong platform for trend analysis and for assessing the effects of changing land use in the PTS catchment(s).

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1 Introduction

As part of Project Twin Streams (PTS), Waitakere City Council has established a Pressure-State-Response (PSR) environmental monitoring programme that aims to improve the Council's understanding of the links between catchment activities and the quality of the streams and downstream estuary receiving environments.

The monitoring programme, described in EVA et al. (2003a-c), comprises:

- *pressure* monitoring, including land use, potential sources of contamination, and treatment;
- aquatic ecology and habitat quality assessment;
- *stream water quality* monitoring;
- stream sediment quality monitoring; and
- estuarine sediment quality monitoring.

The combined results of this monitoring will, over time, enable changes in the quality of the aquatic environment in the Twin Streams catchment resulting from changes in catchment land use to be measured, and the effectiveness of Council's management of land use pressures to be assessed.

This report documents the stream and estuarine sediment quality monitoring component of this programme, conducted in the Twin Streams catchment in March 2006 ("summer 2005–2006").

It represents the second set of monitoring – the first was undertaken in December 2003 ("summer 2003–2004", as reported by EVA et al. 2004).

This report:

- documents the sediment quality data from the streams and estuary as a basis for comparison with previous and future monitoring data; and
- compares the March 2006 data with those collected from the same sites in December 2003.

Based on these analyses, some recommendations for future monitoring are made.

2 Sampling and analysis

The stream and estuarine sediment sampling programmes are detailed in EVA et al. (2003a–c & 2004). Sampling was undertaken by Diffuse Sources Ltd on 1st and 2nd March 2006, as detailed below.

2.1 Estuarine sediment sampling

2.1.1 Henderson Creek estuary

Sampling in Henderson Creek estuary was undertaken on 1st March 2006 at five sites along the estuary (Figure 2.1; GPS references in Table 2.1), using the procedures described in EVA et al. (2003) and summarised below.

At each of five sites along the estuary (Figure 2.1), samples from the top 2 cm sediment are taken from two locations:

- beside the low tide channel on exposed mud banks ("bank" samples), and
- from the bed of the low tide channel ("bed" samples).

Within each location, a sample is taken every 2 meters along an approximately 16 m reach. Sample 1 is placed in replicate 1, sample 2 to replicate 2, sample 3 to replicate 3, sample 4 in replicate 1, sample 5 in replicate 2 etc. On reaching about 16 m, three replicates, each containing three sub-samples, have been collected. This process is repeated at the next site. On completing sampling the 5 sites, there are 3 bed sample replicates and 3 bank sample replicates, each replicate containing 15 sub-samples.

Each replicate is thoroughly mixed before submitting for chemical analysis.

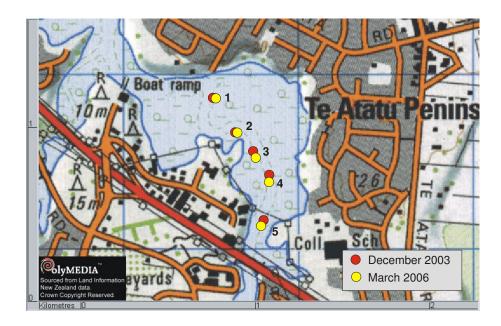


Figure 2.1 Henderson Creek estuary, showing sites sampled in December 2003 and March 2006.

The 2006 sediment samples were taken from the same general locations as those in 2003–4, but targeted visually uniform areas and avoided areas of obvious erosion or disturbance. The site GPS positions for sites 3–5 were therefore slightly different from those sampled in 2003-4 (Table 2.1).

Table 2.1 GPS references for the five estuarine sites in Henderson Creek estuary sampled on 1st March 2006

Site	Easting	Northing	Position compared with 2003-4
1	2656501 6482829		same
2	2656603	6482675	same
3	2656789	6482492	~70 m upstream
4	2656832	6482383	~60 m upstream
5	2656754	6482093	~50 m upstream

As observed during the 2003-4 sampling, some bank scouring and slumping along the channel reach upstream of site 3 were observed in March 2006, presumably reflecting the effects of flood events. Flow data from the Opanuku and Oratia Streams indicates there was a minor event some 3 weeks before sampling (9th February 2006) and a larger event on 25th January 2006. As described in previous monitoring reports (EVA et al. 2003c & 2004), it appears that the upper estuary is fairly unstable, and hence the need for sampling along an extended reach.

2.1.2 Huruhuru Creek estuary

Huruhuru Creek estuary connects the Swanson and Paremuka Streams to the main branch of the Henderson Creek estuary (Figure 2.2).

Two sites were sampled on 2nd March 2006 using a sampling protocol similar to that used by the ARC for Long Term Baseline (LTB) monitoring (ARC 2004a). This procedure produces a set of sediment samples that provide robust measures of sediment contamination and textural characteristics at each site, by replicated sampling and compositing. This approach wasn't used in the upper Henderson Creek estuary because of the lack of suitable stable bank sites (and hence the use of the modified sampling approach described in section 2.1.1).

Briefly, the sampling procedure involves taking a sample every ca. 2 m from two longitudinal pathways within each sample plot. Sample 1 is placed in replicate 1, sample 2 to replicate 2, sample 3 to replicate 3, sample 4 in replicate 1, sample 5 in replicate 2 etc. On completion, three replicates, each containing 10 sub-samples, have been collected.

The Upper Huruhuru Creek site is located on the true left bank mudflat opposite the boat ramp on Riverside Reserve, accessed via Bittern Place (GPS reference of upstream, channel side corner: 2654740 E, 6481727 N). The sampling plot was approximately 30 m long x 15 m wide. Sediment was ankle deep mud, slightly deeper towards the mangroves and shallower closer to the low tide channel.

The Lower Huruhuru Creek site is located on the true left bank mudflat, accessed via Taitapu Park, off Taitapu St (GPS reference of downstream, shore side corner: 2655703 E, 6483020 N). This site is a small area of sloping, calf-to-knee deep mud immediately upstream of the sewage pumping station structure. The sampling plot was approximately 30 m long x 5 m wide.

Two sites were sampled to check whether contaminant concentrations were similar at the head and mouth of the estuary, or whether there was likely to be a contaminant gradient along the estuary. If concentrations were similar at each site, one site may be adequately representative for future monitoring, thereby reducing future sampling costs.

Site locations and photos are shown in Figures 2.2 and 2.3.

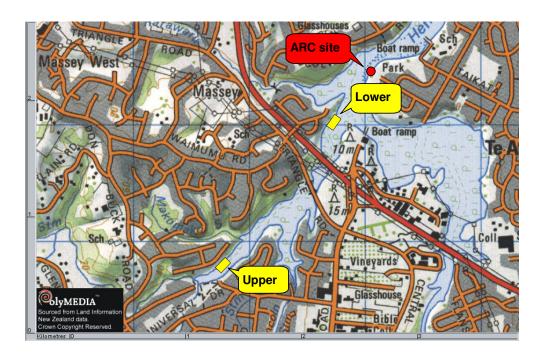


Figure 2.2 Huruhuru Creek estuary, showing the locations of the two sites sampled in March 2006.



Lower Huruhuru Creek estuary site viewed from the down stream true left bank (sewage pump station) looking upstream. Area sampled is marked in yellow.



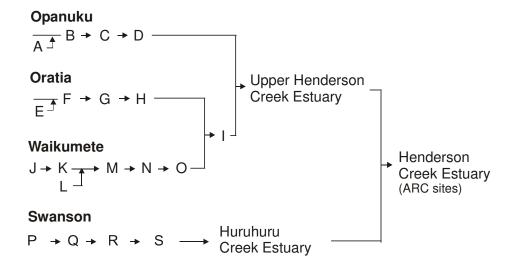
Upper Huruhuru Creek estuary site viewed from the boat ramp on the true right bank across the low tide channel. Area sampled is marked in yellow.

Figure 2.3 Huruhuru Creek estuary sites sampled in March 2006.

2.2 Stream sediment sampling

The 15 sites sampled in December 2003 were sampled again on 1st (site D only) and and 2nd (rest of sites) March 2006. In addition, four sites on the Swanson Stream were also sampled, at the sites shown in Figure 2.5 and Table 2.2.

Site locations and descriptions of the sites on the Oratia, Opanuku, and Waikumete Streams are given in Table 2.3 and Figure 2.4. The relationship between the stream sites, and the downstream estuaries, is shown below:



Three replicates of 10 sub-samples per replicate from the top 2 cm of streambed sediment were taken at each site. The length of stream channel sampled at each site varied from about 10–60 m, depending on the availability of suitable sediment (Appendix 1). Each replicate was thoroughly mixed before sending to R.J. Hill Laboratories (Hamilton) for analysis.

Descriptive notes on each site are appended (Appendix 1). As noted in 2003–4, some of the sites were not ideal, in that fine bed sediments were difficult to find, while others had bed sediments that were potentially influenced by bank collapse or erosion. Sampling avoided areas of obvious bank collapse and local disturbance.

Sites L, N, and (especially) O had very little collectible sediment, while sites J and H showed substantial amounts of bank collapse and channel erosion. These factors are probably an unavoidable "natural" feature of these streams, and contribute to the variability observed in the sediment chemistry results.

The Swanson Stream sites also contained little deposited fine sediment. The upstream bush reference site (P) consisted of coarse sands, gravel and cobbles. No sediment was found at the lower catchment water quality sampling site at Woodside Reserve (S, where the channel consists of rock ledges and pools) and therefore sediments were sampled upstream of Don Buck Rd bridge. Sediment was very sparse at Q – small amounts were found trapped in the willow root masses that formed much of the stream channel.

Table 2.2 Stream sediment sampling sites on the Swanson Stream	m
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Site Code	Access Point	Upstream land use	GPS Reference
Р	Tram Valley Rd	Native bush	E 2649676 N 6479356
Q	Parklands Ave	rural	E 2650475 N 6480931
R	u/s Birdwood Rd bridge	urban/rural	E 2652554 N 6481171
S	u/s Don Buck Rd bridge	urban	E 2653835 N 6481385

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 Table 2.3
 Stream sediment sampling sites in the Oratia, Opanuku, and Waikumete Streams.

Site Code	Stream Access Point	Catchment	SMU	Land use	Purpose	Grid Reference (NZMS 260 R11)
Α	Stoney Creek Sharp Track	Opanuku	16	Native bush	Headwaters reference site	265032 647623
В	Opanuku Stream Candia Road	Opanuku	16	Mixed rural	Mixed rural	265256 647729
С	Opanuku Stream Border Road	Opanuku	15	Peri-urban to urban boundary	Land use change	265434 647771
D	Opanuku Stream Sel Peacocke Drive	Opanuku	15	Intensive urban	Lower catchment cumulative effects	265595 647936
E	Potters Stream Bendalls Lane	Oratia	13	Native bush	Headwaters reference site	265214 647408
F	Oratia Stream West Coast Road	Oratia	13	Rural	Intensive peri-urban	265367 647462
G	Oratia Stream Parrs Cross Road	Oratia	13/10 boundary (SMU 10 d/s)	Peri-urban to urban boundary	Land use change	265518 647615
Н	Oratia Stream Aetna Place	Oratia	10	Industrial & mixed pastoral	Land use change (to urban)	265564 647695
I	Oratia Stream Westfield carpark	Oratia	10	Intensive urban	Lower catchment cumulative effects	265607 647874
J	Hibernia Stream Waerenga Place	Waikumete	12	Bush residential	Bush living reference	265763 647284
K	Hibernia Stream Ceramco Park	Waikumete	12	Bush residential	Bush residential	265761 647425
L	Whakarino Stream Withers Reserve	Waikumete	12	(Bush) residential	Bush residential + WWOFs	265696 647415
М	Waikumete Stream Glendale Road	Waikumete	11	Residential	Residential + WWOFs Confluence of tributaries	265739 647454
N	Waikumete Stream West Coast Road	Waikumete	11	Residential & reserve	Urban living	265685 647571
0	Waikumete Stream Benita Place	Waikumete	10	Light industrial & residential	Lower catchment cumulative effect	265595 647663

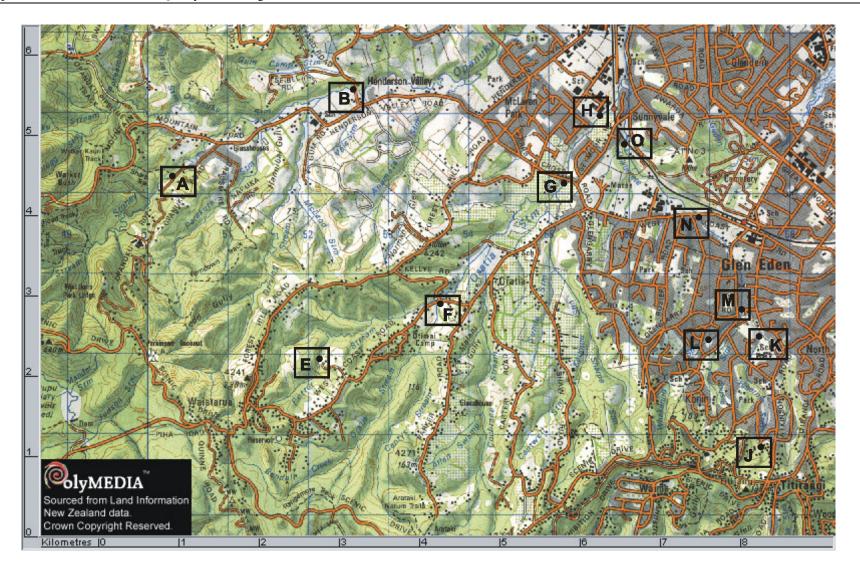


Figure 2.4 Stream sediment sampling sites on the Oratia, Opanuku, and Waikumete Streams

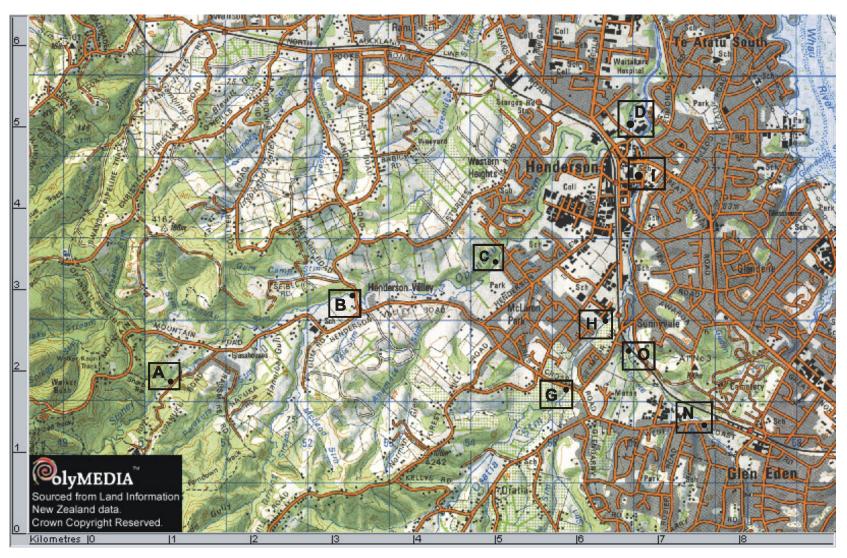


Figure 2.4 (cont.) Stream sediment sampling sites on the Oratia, Opanuku, and Waikumete Streams

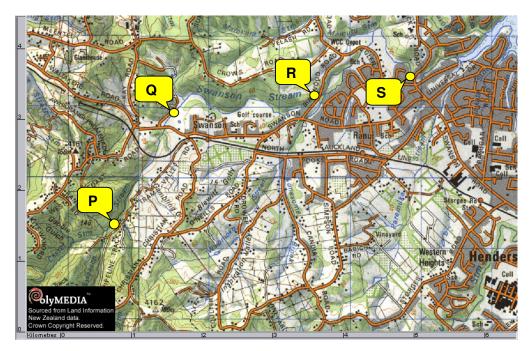


Figure 2.5 Stream sediment sampling sites on the Swanson Stream

2.3 Sediment analysis

2.3.1 Estuarine sediments

All estuarine sediments were analysed for copper (Cu), lead (Pb), zinc (Zn), by 2 M HCl extraction of the mud ($<63\mu m$) fraction. These data are used for temporal trend analysis and for comparisons between sites.

One replicate from each site was also analysed for total recoverable metals (in the <0.5 mm fraction), for comparison with sediment quality guidelines.

This methodology is the same as that used in the ARC State of the Environment (SoE) monitoring programme (ARC 2004a).

Particle size distribution (texture) was also analysed on one composite sample for each site.

Polycyclic aromatic hydrocarbons (PAH), organochlorine pesticides (OCP), and total organic carbon (TOC) were measured in 2003–4, but not in 2006. This is because the analytical variability of the PAH and OCP analyses are currently too high to provide useful data, especially when samplings are relatively close together (in this case only 2 years) and little change in concentrations would be expected. Costs of these analyses are also high. For similar reasons, .ARC no longer routinely conduct PAH or OCP analysis for every SoE monitoring round.

It is recommended that PAH and OCP be repeated in 2008–9 (5 years from the initial analyses conducted in 2003–4).

2.3.2 Stream sediments

All three replicate samples from each site were analysed for Cu, Pb, and Zn by 2 M HCl extraction of the mud (<63µm) fraction.

One replicate from each site was also analysed for total recoverable metals (in the <0.5 mm fraction), for comparison with sediment quality guidelines. This was not done in 2003–4, so this data fills an information gap identified in the 2003 monitoring.

TOC, PAH and OCP were not analysed, for the same reasons as given for the estuarine sediments.

All samples were analysed by RJ Hill Laboratories (Hamilton).

2.3.3 Quality assurance

The analysis of triplicate samples (i.e. 3 replicates per site) from each site provides a measure of variability in sampling and analysis. To further check the integrity of the sample analysis, blind replicates were included in the batch of samples submitted to the lab. These were:

- Four "within-batch" blind replicate stream sediment samples from the 2006 sampling, and
- Two "between-batch" replicates of archived estuarine sediments from the 2003–4 sampling. The results from these samples can be compared with the original data obtained in 2003 to assess differences attributable to changes in analytical performance over time. This provides a "reality check" for the changes in concentrations between December 2003 and March 2006 are any observed differences really attributable to environmental changes, or are they due to differences in the analysis?

The results of the QA analyses are summarised in Appendix 4, and have also been shown in Figure 3.3 (estuarine sediment results).

The laboratory analytical and quality control reports have been attached as Appendix 5.

2.4 Comparison with sediment quality guidelines

For estuary samples, concentrations were compared with the Auckland Regional Council's Environmental Response Criteria (ARC 2004a). There are no ARC Environmental Response Criteria (ERC) for freshwater sediments, so stream sediment concentrations were compared against ANZECC (2000) and Canadian (Environment Canada 2003) guidelines. In order to be consistent, concentrations in estuary samples were also compared against ANZECC (2000) guidelines.

The relevant guideline values have been included in Tables 3.4 and 4.2 for estuarine and stream sediments respectively.

3 Estuarine Sediment Results

This section describes the results for the estuarine sediments. Raw data are appended in Appendix 2, and are summarised in the following sections.

3.1 Sediment texture

As found in 2003–4, the channel bed sediments from Henderson Creek were much coarser than the bank samples (Figure 3.1). The bed sediments were mostly fine sands (85.4%), with smaller amounts of mud (9.9%) and coarse sand/gravel (4.7%). The bank samples were mostly mud (approximately 65%), but with considerable amounts of sand (35%) and very little coarse material (<0.01%).

These results were very similar to those obtained in December 2003, although the bed sediments had slightly less coarse material (>2 mm) and more sand (0.063–2 mm) in March 2006 than in December 2003 (Figure 3.1). These small differences are of little practical significance for the monitoring because metals' concentrations used to track trends over time or compare sites are measured on the <63 μ m fraction.

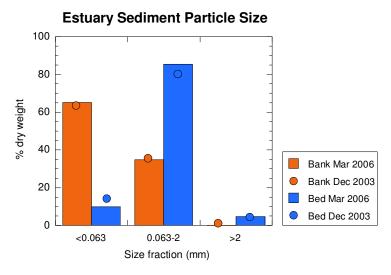


Figure 3.1 Sediment texture in Henderson Creek estuary sediments in March 2006. The circles indicate the data obtained in December 2003.

The texture of Huruhuru Creek estuary sediments were similar at the upper and lower sites, with the upper site having slightly higher proportions of sandy, coarse material (and less mud) than the lower site (Figure 3.2).

Huruhuru Creek sediments had a higher proportion of mud (88% and 92% <63 μ m) than the bank sediments from Henderson Creek (65% <63 μ m).

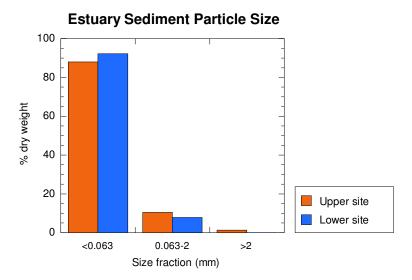


Figure 3.2 Sediment texture in Huruhuru Creek estuary sediments in March 2006.

3.2 Metals

3.2.1 Concentrations

The concentrations of Cu, Pb, and Zn in the bed and bank samples from Henderson Creek estuary, and the upper and lower sites in Huruhuru Creek estuary, are shown in Figure 3.3. A summary of the data is given in Tables 3.1 and 3.2.

As found in December 2003, the concentrations of Cu and Pb were very similar in bed and bank sediments in Henderson Creek, but Zn was considerably higher in the bed sediments than in the bank samples. Variability was very low in the bank samples, but generally higher in the bed samples. This reflects the coarser nature, and more variable particle size distribution, of the bed sediments¹.

The higher Zn concentration in the bed sediments presumably reflects a higher level of contamination in recent sediments leaving the catchment via stream flow than is present in older sediments on the banks, which have been deposited and mixed over time. The bed sediments provide an indicator of more recent concentrations, but they are likely to be subject to greater variability than the bank sediments (for example from recent storm events).

Metals' concentrations in Huruhuru Creek estuary sediments were similar to those in Henderson Creek (bearing in mind that Huruhuru Creek sediments were sampled from the bank only), and showed little difference between upper and lower estuary sites². Concentrations were more variable at the lower site (Table 3.2). Based on these initial results, the upper estuary site is probably more appropriate for long-term monitoring.

¹ The variability is greatly reduced by analysing the <63 mm fraction rather than the total sample, but a small amount of additional variability is still evident in the bed samples.

² Only the Pb concentrations were significantly different, being slightly lower at the lower site (41.5 cf 37.7 mg/kg; 2-sided t-test p<0.05).

Table 3.1 A summary of concentrations (mg/kg) and variability (coefficient of variation (cv, %), n=3) of weak acid extractable metals (2 M HCl, <63 μm fraction) and total recoverable metals (<0.5 mm fraction, n=1) in Henderson Creek estuary sediments (March 2006).

Analyte	Fraction	Bed		Bank	
	analysed	mean	cv (%)	mean	cv (%)
2 M HCl extractable metals (mg/kg, n=3)					
Cu	<63 μm	34.7	4.4	31.0	3.2
Pb	<63 μm	40.6	2.0	39.0	2.7
Zn	<63 μm	280	14.6	176	2.6
Total recoverable metals (mg/kg, n=1)					
Cu	<0.5 mm	14.7	_	26.7	-
Pb	<0.5 mm	18.2	_	28.0	-
Zn	<0.5 mm	112	_	149	_

Table 3.2 A summary of concentrations (mg/kg) and variability (coefficient of variation (cv, %), n=3) of weak acid extractable metals (2 M HCl, <63 μm fraction) and total recoverable metals (<0.5 mm fraction, n=1) in Huruhuru Creek estuary sediments (March 2006).

Analyte	Fraction	Upper Site		Lower Site	
	analysed	mean	cv (%)	mean	cv (%)
2 M HCl extractable metals (mg/kg, n=3)					
Cu	<63 μm	29.0	0.0	29.7	5.1
Pb	<63 μm	41.5	1.8	37.7	4.9
Zn	<63 μm	170	0.9	163	5.3
Total recoverable metals (mg/kg, n=1)					
Cu	<0.5 mm	28.3	_	29.4	-
Pb	<0.5 mm	30.8	_	31.7	-
Zn	<0.5 mm	133	-	148	-

3.2.2 Comparisons between December 2003 and March 2006 concentrations

Comparison of the December 2003 and March 2006 samples from Henderson Creek estuary indicates that metals' concentrations have not changed much in the 28 months between samplings.

The data plotted in Figure 3.3 (and summarised in Table 3.3) suggest that concentrations may have dropped between December 2003 and March 2006 by approximately:

- 5% for Cu, 10% for Pb, and 0.1% for Zn in the bed sediments, and
- 14% for Cu, 11% for Pb, and 15% for Zn in the bank sediments.

Statistical analysis of the data indicates that the concentrations of Cu, Pb, and Zn in the bank samples were all significantly (2-sided t-test, p<0.05) lower in March 2006 than in December 2003. In the bed sediments, none were lower (at p<0.05).

However, the concentrations found in the 2003 sediments archived and reanalysed in 2006 as QA samples were also lower than those found in the original 2003 analysis – by approximately 6% (bank sediments) and 9% (bed) for Cu, 13% for Pb, and 7% for Zn.

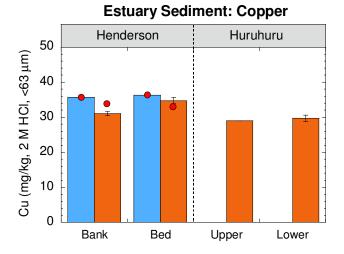
This indicates that differences in analytical method performance between 2003 and 2006 are likely to have made a significant contribution to the observed drop in most metals' concentrations. These results highlight the need for on-going QA assessment to facilitate reliable interpretation of the data.

The Zn concentration recorded in the bed sediment was the same in 2006 as it was in 2003, despite generally lower concentrations in 2006 associated with sample analysis. It may be, therefore, that the Zn concentrations in the bed sediments are somewhat higher (possibly about 7 %) in March 2006 than in December 2003.

At present, it appears that the concentrations of metals have not changed enough for the laboratory analysis to reliably detect differences. Differences (and trends over time) will be revealed after additional monitoring is conducted over the next 2–5 years.

Table 3.3 Comparison of metals' concentrations (mg/kg, 2 M HCl extraction, <63 μm fraction) in Henderson Creek estuary sediments sampled in December 2003 and March 2006.

Samples	Mean concent	ration (mg/kg)	Difference	Significance
	2003	2006	%	p (2-sided t-test))
Bank:				
Cu	35.7	31.0	-14.1	<0.01
Pb	43.6	39	-11.1	<0.01
Zn	205	176	-15.2	<0.01
Bed:				
Cu	36.3	34.7	-4.5	0.18
Pb	44.7	40.6	-9.6	0.14
Zn	280	280	0.1	0.98
QA Bank:				
Cu	36.0	34.0	-5.7	-
Pb	44.3	38.8	-13.2	-
Zn	204	191	-6.6	-
QA Bed:				
Cu	36.0	33.0	-8.7	_
Pb	43.4	37.9	-13.5	_
Zn	272	254	-6.8	-



Estuary Sediment: Lead Henderson Huruhuru 50 40 30 Bank Bed Upper Lower

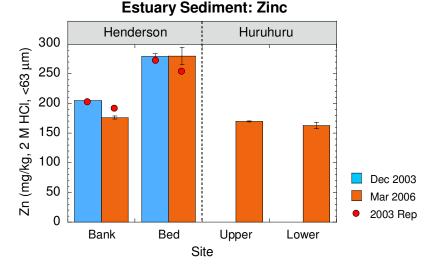


Figure 3.3 Concentrations of Cu, Pb, and Zn (2 M HCl extraction of <63 μ m) in Henderson and Huruhuru Creek estuary sediments. Error bars are \pm S.E. in mean (n=3). The "2003 rep" data are values for bed and bank QA samples taken in 2003, analysed in 2003 and again in 2006. Ideally, the concentrations should be the same each year, but a small decrease was recorded (see text for details of QA assessments).

3.2.3 Comparisons with sediment quality guidelines

Concentrations of total recoverable Cu, Pb and Zn in the <0.5 mm fraction of the estuary bank sediments are generally close to the ARC green/amber ERCs (Table 3.4), but are below (although only just for Zn) the ARC ERC amber/red threshold. Levels are well below the ANZECC Interim Sediment Quality Guideline-Low (ISQG-Low) thresholds.

This indicates that metal concentrations are in the range where adverse biological effects might be expected to be beginning to occur, but are not yet high enough for a high frequency of impacts.

Note that the concentrations of total recoverable metals in the Henderson Creek bed sediments are considerably lower than in sediments from the other estuary sites. This is because the bed sediment has a much higher proportion of coarse sandy material (with low metal content) than the predominantly muddy-textured bank sediments.

Table 3.4 Concentrations of total recoverable metals (mg/kg, <0.5 mm fraction) in Henderson and Huruhuru Creek estuaries compared with sediment quality guidelines: ARC Environmental Response Criteria (ERC; ARC 2004a) and ANZECC (2000). Bolded values exceed ARC ERC.

Site	Cu	Pb	Zn
Henderson Creek – Bank	26.7	28.0	149
Henderson Creek – Bed	14.7	18.2	112
Huruhuru Creek – Upper	28.3	30.8	133
Huruhuru Creek – Lower	29.4	31.7	148
Guidelines:			
ARC ERC green/amber	19	30	124
ARC ERC amber/red	35	50	150
ANZECC ISQG-low	65	50	200
ANZECC ISQG-high	270	220	410

3.2.4 Comparisons with ARC Henderson Creek monitoring site

The ARC has a State of the Environment (SoE) monitoring site in Henderson Estuary, situated at Taipari Rd, immediately below the confluence of Huruhuru Creek and the upper reaches of Henderson Creek (as monitored in the Project Twin Streams programme). The location is shown in Figure 2.2.

The concentrations of metals found at the ARC SoE site in 2003 (ARC 2004b) are summarised in Table 3.5.

Table 3.5 Concentrations (mg/kg) of metals in sediments from the ARC SoE monitoring site at Taipari Rd, Henderson Creek estuary in 2003 (ARC 2004b).

Metal	2 M HCl extractable mg/kg, <63 μm fraction	Total recoverable mg/kg, <0.5 mm fraction
Cu	32.6	37.0
Pb	40.1	40.8
Zn	179	187

Comparison of the data in Tables 3.1, 3.2 and 3.4 indicates that similar concentrations of weak acid extractable metals (2 M HCl, <63 µm fraction) were present at the SoE site as found in the bank samples from the PTS sites further upstream in Henderson Creek and Huruhuru Creek estuaries. However, total recoverable metal concentrations were lower in the upstream PTS sites than at the ARC SoE site. The reason for the lower concentrations of total metals is unknown.

4 Stream Sediment Results

Stream sediment data are listed in Appendix 3. A summary is presented in the following sections.

4.1 Texture

As found in December 2003, stream sediment texture varied considerably between sites (see descriptions in Appendix 1). Headwater sites in the Opanuku (site A) and Oratia (site E) had bouldery beds with pockets of sandy sediment. The headwater site in the Hibernia Stream (site J) had a hard clay subsoil streambed, with only sparse amounts of fine loose sediments.

The lower sites in the Oratia Stream (sites F, G, H and, to a lesser degree, I) were sandy, with evidence that bank erosion was contributing sediments to the stream. The Opanuku Stream was also dominated by sands at the lower sites, but with varying amounts of gravel and boulders at some sites. Local influences, for example road gravel, debris (including metallic objects such as wire, trolleys, car parts etc), and localised bank erosion, were evident at urban sites.

There was generally little loose sediment in the Waikumete Stream system. It appears that this system is relatively sediment-starved compared with the Oratia or Opanuku Streams. The stream banks and bed were mostly clay sub-soils with reaches of rock chutes and pools, gravel, and debris at various locations.

Site O was particularly difficult to sample, with virtually no loose sediment. Obtaining a sample unaffected by clay basement material was probably not achieved, as evidenced by the low metals' concentrations in the sediments collected (section 4.2).

Site K (Hibernia at Ceramco Park) was unique in that it contained organic-rich, anaerobic, vegetative debris that had accumulated in rocky pools.

The Swanson Stream sediments were of variable texture. The headwater site (P) was similar to the headwater sites in the Oratia and Opanuku Streams, being comprised of coarse sand, gravel, and cobbles. Pockets of finer sand and silty material were found behind boulders and in small backwater areas of the stream channel. The sites downstream had very different character:

- Q (Parklands Ave) had little sediment to sample, with very small amounts of fine material trapped in the willow root masses.
- R (u/s of Birdwood Rd bridge) was affected by local bank collapse, and the sediment sampled was a fairly heterogeneous mixture of sand, muddy sand, clay, and organic debris.
- S (u/s of Don Buck Rd bridge) had variable bed and bank composition, mostly compact clay with abundant woody debris and urban litter. Sediments sampled were a mixture of muddy sand and fine organic matter found in pockets behind in-stream debris.

4.2 Metals

4.2.1 Metals' concentrations and spatial patterns

Concentrations of metals in the stream sediments are shown in Figures 4.1–4.3 (2 M HCl extractable metals in the mud fraction) and Figure 4.4 (total recoverable metals), and summarised in Tables 4.1 and 4.2 (appended to the end of this section).

The spatial patterns of metal concentrations between the streams and along each stream channel were similar to those observed in December 2003. The variability in metals concentrations at each site was generally low (Table 4.1) and comparable with 2003 results.

Metals' concentrations were lowest in the headwaters and rural stream reaches and increased markedly in the urban reaches (e.g. sites D, I, and K–N). Exceptions were:

- Copper in the Opanuku Stream, which showed concentrations at the rural site B (Candia Rd) that were comparable with those in the urban, "bottom of the catchment", site D;
- Copper at site G (Parrs Cross Rd, Oratia Stream), which was significantly higher than at the rural site F upstream, and comparable with the more urban site H further downstream, and
- All metals at site O (Waikumete Stream at Benita Place), which were substantially lower than those further upstream.

These results were consistent with those obtained in December 2003, although the concentrations at site O were markedly lower in March 2006 than found in December 2003. The elevated Cu levels in the rural stream sites B and G may be related to the effects of horticultural land uses (use of Cu as a fungicide). The low concentrations of metals at site O are probably due to the lack of "urban" sediments at the site – much of the sample may have been made up of less contaminated clay stream bank and bed material.

Copper – Figure 4.1

Copper levels did not change as markedly between sites as Pb and Zn, with smaller increases occurring between the rural and urban sites. This may reflect some inputs from Cu from rural land uses (e.g. horticulture) and also the relatively smaller inputs in urban areas – Cu loads are approximately 1/8th of the Zn loads in Auckland urban stormwater.

Concentrations of Cu in the headwater sites ("background" levels) were higher in the Opanuku and Oratia Streams than in the Waikumete Stream. This presumably reflects differences in sediment mineralogy between the stream systems.

In the Opanuku Stream, there were no clear trends in Cu concentrations with distance below the headwaters. As mentioned previously, concentrations in the Opanuku Stream system were somewhat higher at sites B (rural) and D (urban) than at sites A (reference) and C (rural/urban).

In the Oratia Stream system, Cu increased with distance below the headwaters, with marked increases occurring between sites F and G (rural to rural/urban fringe), and between H and I (increasingly urbanised between these sites). The increase between sites F and G may reflect the effects of horticultural land use.

Copper concentrations in the Waikumete Stream system were higher in the urban sites (sites K–N) than in the headwater site (J). However, Cu levels in the urban Waikumete sites were not as markedly elevated above background as Pb or Zn, and were slightly lower than those found in the urban and urban fringe sites in the Oratia and Opanuku Streams. As mentioned previously, this is probably the result of higher Cu levels in the base rocks of the Oratia and Opanuku Streams, and possible inputs from horticulture in these streams.

Concentrations of Cu changed little with distance below the headwaters of the Swanson Stream, and were comparable with those present in the headwaters and upper rural sites of the Opanuku and Oratia streams.

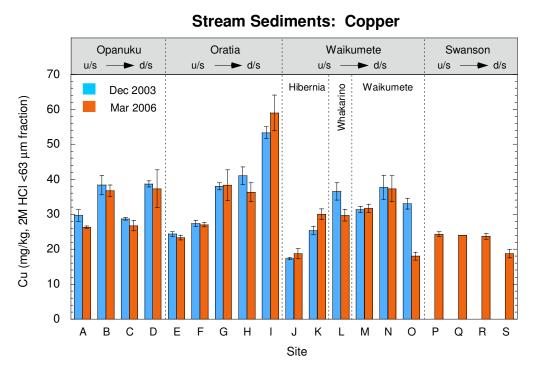


Figure 4.1 Copper concentrations (mg/kg, 2 M HCl extractable, in <63 μ m fraction) in stream sediments sampled in December 2003 and March 2006. Error bars are \pm S.E. in mean (n=3). Swanson Stream sites were not sampled in 2003.

Zinc – Figure 4.2

Zinc levels in the Opanuku and Oratia Stream sediments increased markedly between the urban fringe sites (C, G, H) and the urban sites (D and I), indicating that urban activities are having a dramatic effect on Zn concentrations in these streams.

All the Waikumete Stream sites below the headwaters (site J) had elevated Zn levels. The marked increase in Zn occurring between sites H and I in the Oratia Stream presumably reflects the effects of contaminated inflows from the Waikumete Stream.

Zinc concentrations in the sediments of the upper three sites in the Swanson Stream (P-3) were relatively low, comparable with those in the headwaters and rural reaches of the Oratia and Opanuku Streams. Only the lower Swanson site (S), had significantly elevated Zn concentrations, but these were considerably lower than those in the urban reaches of the other streams. This is consistent with the relatively lower proportion of urban land use in the Swanson Stream catchment.

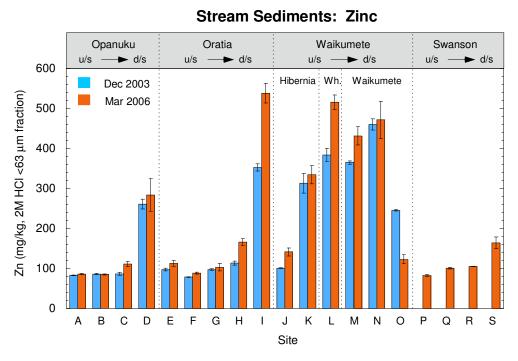


Figure 4.2 Zinc concentrations (mg/kg, 2 M HCl extractable, in <63 μm fraction) in stream sediments sampled in December 2003 and March 2006. Error bars are ± S.E. in mean (n=3). Swanson Stream sites were not sampled in 2003

Lead – Figure 4.3

Spatial patterns in Pb concentrations were similar to those described for Zn. However, the change between sites J and K in the Hibernia Stream were not as marked as those observed for Zn.

This is probably because Pb loads are smaller than for Zn, especially since the removal of Pb from petrol (in 1996). While Pb concentrations in urban stream sediments should eventually drop, increases may still occur due to continued additions from Pb stored in catchment soils.

Stream Sediments: Lead Opanuku Oratia Waikumete Swanson u/s น/ร **→** d/s u/s — **→** d/s → d/s u/s → d/s Hibernia Wh. Waikumete Dec 2003 100 Pb (mg/kg, 2M HCl <63 µm fraction) Mar 2006 80 60 40 20 С D Ε F 0 G Н -1 J Κ L M Ν Site

Figure 4.3 Lead concentrations (mg/kg, 2 M HCl extractable, in <63 μ m fraction) in stream sediments sampled in December 2003 and March 2006. Error bars are \pm S.E. in mean (n=3). Swanson Stream sites were not sampled in 2003.

4.2.2 Comparison of December 2003 and March 2006 concentrations

Concentrations of metals (2 M HCl extractable in $<63 \mu m$ fraction) found in December 2003 and March 2006 are shown in Figures 4.1–4.3. These figures show that the spatial trends in metals' levels throughout the catchment were similar in 2003 and 2006.

Comparisons of concentrations between the two samplings show some differences - a summary is provided in Table 4.3, appended to this section). At this early stage of monitoring, these are just differences, not trends - more sampling is required to assess the overall direction or magnitude of any trends.

Key features of the data are:

- Concentrations of Cu, Pb, and Zn were much lower at site O (Waikumete Stream at Benita Place) in 2006 than in 2003. This was most probably associated with sampling difficulties at this sediment-starved site, as described previously.
- For Cu, most of the differences were either small or negative i.e. concentrations were either the same (not significantly different) or slightly lower in 2006 than in 2003. Only at site K (Hibernia Stream, Ceramco Park) was a significant (although relatively small) increase recorded.
- For Pb, differences were generally too small (compared with data variability) to be significant. Only at one site (L, Whakarino at Withers Reserve) was a significantly higher concentration in 2006 observed, while lower concentrations were found at sites I and N.
- For Zn, concentrations in the headwater sites of the Oratia (site E) and Opanuku (site A) were similar in 2003 and 2006, but were slightly higher in 2006 in the headwaters of the Waikumete Stream system (site J, Hibernia Stream at Waerenga Place). At most urban sites, Zn concentrations were higher in 2006. Very large increases were measured at sites I (Oratia at Westfield carpark) and L (Whakarino at Withers Reserve). No sites had significantly lower Zn concentrations in 2006 than in 2003.

These results generally indicate that the monitoring protocols are delivering acceptably consistent data because there are few unexplained changes. Metals' concentrations at the reference sites (e.g. A and E) and upper rural sites (e.g. B and F) were similar in 2003 and 2006, while a number of changes were recorded at downstream urban sites. We expected Cu and Pb concentrations in each year to be similar, while greater changes in Zn in the urban reaches were anticipated. This is generally what has been observed.

Of the differences observed between samplings, the higher concentrations of Zn at the urban and urban/rural fringe sites in 2006 is the most consistent "trend" and is in line with the current view of generally increasing Zn loads to urban waterways over time, and the higher urban loads of Zn than Cu or Pb. Whether the observed changes will continue in future is unknown at this stage, and will depend on the balance between changing catchment pressures and remedial responses.

4.2.3 Comparison with sediment quality guidelines

Concentrations of total recoverable Cu, Pb, and Zn (in <0.5 mm fraction) are tabulated in Table 4.2 (appended to the end of section 4) and shown in Figure 4.4 (including comparison with sediment quality guidelines; SQGs).

When interpreting these data, it must be remembered that sediment texture varies considerably between the sites, and therefore spatial patterns are better assessed from the mud fraction metals' data (section 4.2.1).

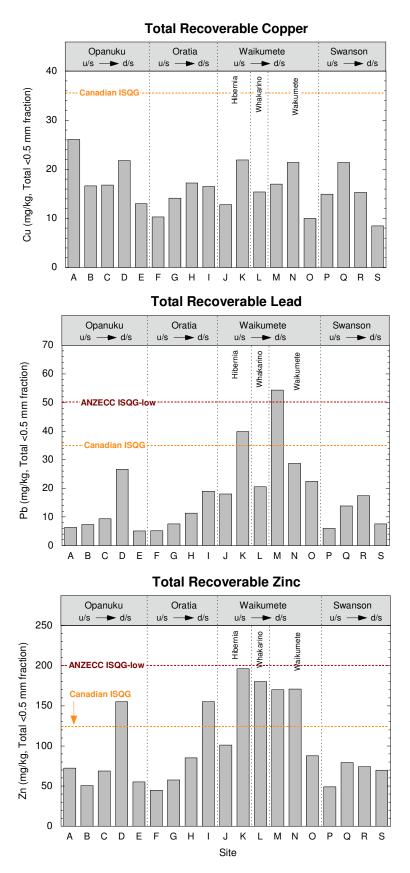


Figure 4.4 Total recoverable metals' concentrations in Twin Streams stream sediments. ANZECC and Canadian sediment quality guidelines are shown by dotted lines.

Concentrations of total recoverable metals were below SQGs at all headwater and rural sites, and at all Swanson Stream sites. Concentrations only exceeded SQGs at urban sites on the Opanuku (site D), Oratia (site I), and sites K–N in the Waikumete Stream system.

Only the lowest SQG thresholds were approached or exceeded, indicating that adverse biological effects may be expected to be beginning to occur due to metal contamination at some urban sites. However, marked effects associated with Cu, Pb, or Zn should not yet be occurring.

However, as mentioned above, the total recoverable metals' concentrations are influenced by sediment texture – for coarse sediments, total concentrations may be relatively low because of the dilution effect from relatively uncontaminated sand and gravel in the sample. This can be seen by comparing the concentrations of Zn in the mud fraction ($<63~\mu m$ – Figure 4.1) with the total recoverable Zn concentrations (measured in the <0.5~mm fraction – Figure 4.4). Despite a weaker acid extraction, concentrations in the mud fraction at contaminated urban sites are double (or more) those in the <0.5~mm fraction.

If benthic aquatic animals are exposed to the fine sediment fraction (e.g. via ingestion of fine sediments during grazing), it may be that concentrations of metals (particularly Zn) are high enough to cause significant adverse effects at the urban sites.

Copper concentrations were fairly consistent throughout the catchment, and were below sediment quality guidelines at all sites. There appears to be little or no increase at the urban sites, which is consistent with the $<63 \mu m$ fraction metals' results (section 4.2.1).

Lead concentrations were above the Canadian ISQG at sites K (Hibernia Stream at Ceramco Park) and M (Waikumete at Glendale Rd). Even though major sources of Pb have been removed from use, Pb residues of potential concern remain in the aquatic receiving environment.

Zinc concentrations exceeded the Canadian ISQG at all urban sites (except site O, which has sampling difficulties, as described previously). Highest concentrations were found in the Waikumete Stream system.

Table 4.1 Concentrations (mg/kg, 2 M HCl <63 μ m) and variability (coefficient of variation, %; n = 3) of metals in Twin Stream catchment stream sediments

	Cu		Pb		Zn	
Site	mean	cv (%)	mean	cv (%)	mean	cv (%)
Α	26.3	2.2	8.8	5.2	86.3	3.3
В	36.7	7.9	17.7	11.3	85.3	2.9
С	26.7	9.4	16.9	12.4	111.0	9.1
D	37.3	24.9	46.7	26.2	283.7	24.9
E	23.3	4.9	15.2	5.3	112.7	10.4
F	27.0	3.7	15.4	4.1	88.7	4.6
G	38.3	19.9	19.8	15.5	103.3	15.7
Н	36.3	13.0	25.6	12.1	166.0	8.9
1	59.0	15.1	65.7	8.7	538.0	7.9
J	18.7	13.5	27.5	13.1	141.3	12.4
K	30.0	8.8	34.7	6.4	334.3	11.6
L	29.7	9.7	68.0	12.0	515.3	6.0
М	31.7	6.6	66.1	7.0	431.3	9.2
N	37.3	17.2	74.8	7.2	471.3	17.2
0	18.0	11.1	41.8	15.0	123.0	15.5
Р	24.3	4.7	13.3	7.4	82.3	4.6
Q	24.0	0.0	20.7	2.4	101.0	3.6
R	23.7	6.5	28.2	10.5	105.0	1.0
S	18.7	11.2	16.4	11.8	164.3	15.5

Table 4.2 Concentrations (mg/kg, total recoverable metal in <0.5 mm fraction) of metals in Twin Stream catchment stream sediments. Bolded values are above ANZECC ISQG-low or Canadian ISQG thresholds.

Site	Cu	Pb	Zn
Α	26.1	6.33	72.3
В	16.6	7.38	50.7
С	16.8	9.36	69
D	21.8	26.6	155
E	13	5.11	55.1
F	10.3	5.21	44.6
G	14.1	7.56	57.5
Н	17.2	11.4	85.2
1	16.5	19	155
J	12.8	18	101
K	21.9	39.8	196
L	15.4	20.6	180
M	17.0	54.4	170
N	21.4	28.7	171
0	10	22.5	87.8
P	14.9	6.06	49
Q	21.4	13.9	79.3
R	15.3	17.4	74.1
S	8.5	7.6	69.8
<u>Guidelines:</u>			
Canadian ISQG ¹	35.7	35	123
Canadian PEL ¹	197	91.3	315
ANZECC ISQG-low	65	50	200
ANZECC ISQG-high	270	220	410

 $^{1. \} Interim\ Sediment\ Quality\ Guideline\ and\ Probable\ Effects\ Level\ (similar\ to\ the\ ANZECC\ ISQG-low\ and\ ISQG-high\ respectively),\ Environment\ Canada\ (2003).$

Table 4.3 Comparison of metals' concentrations (mg/kg, 2 M HCl extractable, <63 μ m fraction) in Twin Stream catchment stream sediments between samples taken in December 2003 and March 2006¹. Significance of differences in mean concentrations (p) assessed by 2-sided t-test. Bolded values p \leq 0.1.

			Copper					Lead					Zinc		
	me	ean		difference		me	ean		difference		me	an		difference	
Site	2003	2006	mg/kg	%	р	2003	2006	mg/kg	%	р	2003	2006	mg/kg	%	р
Α	29.7	26.3	-3.3	-11.9	0.19	10.9	8.8	-2.0	-20.6	0.02	83.0	86.3	3.3	3.9	0.18
В	38.3	36.7	-1.7	-4.4	0.64	18.4	17.7	-0.7	-3.7	0.63	86.3	85.3	-1.0	-1.2	0.68
С	28.7	26.7	-2.0	-7.2	0.31	14.9	16.9	2.0	12.6	0.22	86.7	111.0	24.3	24.6	0.04
D	38.7	37.3	-1.3	-3.5	0.83	44.6	46.7	2.1	4.7	0.79	261.0	283.7	22.7	8.3	0.65
E	24.3	23.3	-1.0	-4.2	0.35	14.9	15.2	0.4	2.4	0.61	97.3	112.7	15.3	14.6	0.14
F	27.3	27.0	-0.3	-1.2	0.77	16.3	15.4	-0.9	-5.9	0.18	78.7	88.7	10.0	12.0	0.03
G	38.0	38.3	0.3	0.9	0.95	22.5	19.8	-2.7	-12.9	0.25	97.3	103.3	6.0	6.0	0.60
н	41.0	36.3	-4.7	-12.1	0.28	27.6	25.6	-2.0	-7.5	0.55	113.7	166.0	52.3	37.4	0.01
1	53.3	59.0	5.7	10.1	0.40	79.1	65.7	-13.4	-18.5	0.04	352.3	538.0	185.7	41.7	<0.01
J	17.3	18.7	1.3	7.4	0.47	24.2	27.5	3.2	12.5	0.27	101.0	141.3	40.3	33.3	0.06
K	25.3	30.0	4.7	16.9	0.07	33.8	34.7	0.9	2.6	0.74	313.0	334.3	21.3	6.6	0.56
L	36.5	29.7	-6.8	-20.7	0.15	44.0	68.0	24.0	42.9	0.04	383.7	515.3	131.7	29.3	<0.01
М	31.3	31.7	0.3	1.1	0.83	68.1	66.1	-2.0	-3.0	0.56	365.0	431.3	66.3	16.7	0.10
N	37.7	37.3	-0.3	-0.9	0.95	89.3	74.8	-14.5	-17.6	0.12	459.7	471.3	11.7	2.5	0.83
0	33.0	18.0	-15.0	-58.8	<0.01	74.8	41.8	-33.0	-56.5	<0.01	245.3	123.0	-122.3	-66.4	<0.01

^{1. %} difference calculated as 100 x (2006 result – 2003 result)/average of 2003 & 2006 results.

5 Summary and recommendations

5.1 Estuarine sediment monitoring

Monitoring of estuarine sediments in Upper Henderson Creek and Huruhuru Creek estuaries was conducted in March 2006. Henderson Creek monitoring followed the protocols used in December 2003 (EVA et al. 2004), allowing direct comparison of data with monitoring conducted in December 2003.

Huruhuru Creek estuary was sampled at two sites (upper and lower estuary) using methodology similar to that used in ARC SoE monitoring (ARC 2004a). This estuary had not been sampled before in the PTS programme.

Samples were analysed for texture, weak acid extractable Cu, Pb, and Zn in the <63 μ m (mud) fraction, and total recoverable Cu, Pb, and Zn in the <0.5 mm fraction.

Key findings were:

- sediment textures in the bed and bank samples from Henderson Creek estuary were similar to those sampled in December 2003.
- concentrations of mud-fraction extractable Cu, Pb, and Zn in Henderson Creek estuary were mostly slightly lower than those recorded in 2003, although QA data indicate that much of the reduction may be attributable to laboratory analysis rather than real world changes. Further sampling will be required to determine the direction and magnitude of any trends over time.
- Total recoverable metals in the estuary sediments were similar to ARC green/amber ERC, but were well below ANZECC ISQG-low levels. On this basis, adverse effects on aquatic biota might be expected to be just beginning to occur, but effects would not be expected to be marked or frequent.
- Total recoverable metals levels were lower than those measured in 2003 from the ARC SoE site at Taipari Rd, Henderson estuary. The reasons for this are unknown.
- The two sites in Huruhuru Creek estuary had similar Cu, Pb, and Zn levels, and these were also very similar to the bank samples from Henderson Creek.
 Based on these results the Upper Huruhuru Creek site is recommended for future monitoring.

5.2 Stream sediment monitoring

Stream sediments from 15 sites in the Twin Streams catchment were sampled on 1st & 2nd March 2006 using the same protocols as those used in December 2003. In addition, four new sites on the Swanson Stream were also sampled using the same approach.

Samples were analysed for texture, weak acid extractable Cu, Pb, and Zn in the <63 μ m (mud) fraction, and total recoverable Cu, Pb, and Zn in the <0.5 mm fraction.

Key findings of the stream sediment monitoring were:

- Spatial patterns of contamination in the Oratia, Opanuku, and Waikumete Stream were similar to those found in December 2003. Concentrations of Pb and Zn were markedly higher at urban sites than upstream rural or reference sites. Copper showed relatively smaller differences between urban and nonurban sites.
- Comparison of December 2003 concentrations with March 2006 results indicates that the monitoring protocols are delivering consistent data that should be suitable for on-going trend assessment. Only site O (Waikumete Stream at Benita Place) gave anomalous results (greatly lower concentrations in 2006) and this is likely to be attributable to a lack of suitable urban-derived sediment at this site.
- Higher concentrations of Zn were recorded at the urban and urban/rural fringe sites in 2006. This was the most consistent "trend" (difference) and is in line with the current view of generally increasing Zn loads to urban waterways over time. Whether this will continue is unknown at this stage, and will depend on the balance between changing catchment pressures and remedial responses.
- Sediments from the Swanson Stream had relatively low concentrations of Cu, Pb, and Zn, comparable with those in the non-urban sites in the other streams. Concentrations of Pb were slightly higher at site R (Birdwood Rd) and Zn was higher at the most downstream site (S; Don Buck Rd). It appears that urban effects are currently much less marked in the Swanson Stream, which is consistent with the lower degree of urbanisation in this catchment.
- Total recoverable metal concentrations exceeded only the most sensitive sediment quality guidelines (Canadian ISQG or ANZECC ISQG-low), and only for Pb (at 2 sites in the Waikumete Stream) and Zn (for all urban sites in the Oratia, Opanuku and Waikumete streams). This suggests that Zn is more likely to adversely affect aquatic life in urban stream reaches than Cu or Pb. No SQGs were exceeded in the Swanson Stream.

5.3 Overall conclusions

Overall, the March 2006 sediment monitoring has confirmed the concentrations and spatial patterns of metals' contamination found in December 2003.

The monitoring protocols appear to be sufficiently robust for reliable on-going trend monitoring. Variability is generally low at each site, enabling reasonably sensitive comparisons between samplings to be made.

The changes in metals' concentrations in Henderson Creek estuary over the 28 months between samplings were generally relatively small, and could not be distinguished from analytical variation. On-going QA testing, both within- and between-batch, is therefore essential to ensure reliable interpretation of trends is made.

The results from the two Huruhuru Creek estuary sites were very similar. However, it is recommended that both these sites continue to be used for future monitoring, at

least for the next sampling round, to verify that the sites are indeed giving equivalent data.

The monitoring approach used in Henderson Creek estuary is unique for Auckland, employing analysis of both bank and channel bed sediments from an extended reach. It is worthwhile continuing this sampling, as it serves as an important reference for studies that may be done in similar estuaries around Auckland. It also permits more robust trend monitoring to be made in this more infilled, "riverine", estuarine environment.

All stream monitoring sites are providing useful information, so it is recommended that the programme continue as is. Only site O (Waikumete Stream at Benita Place) has provided anomalous data, and this is probably associated with the lack of urbanderived sediment at this site. It is recommended that this site continued to be monitored, until a more suitable site in this reach can be found³.

While some sites are problematic with regard to having enough fine sediment, or being compromised by localised bank collapse, it is important to keep all sites operational. Problems may shift from site to site over time in response to local activities and in-stream variations. Dropping sites at this stage may end up seriously compromising the program and result in trends being unable to be assessed.

Based on the findings of the data collected to date, it is recommended that the next round of sampling be conducted in summer 2008/9. Analysis should include texture, Cu, Pb, and Zn (as determined in the 2003and 2006 monitoring), and also PAH and organochlorine pesticides (mainly DDTs), for comparison with 2003 data.

The programme is highly dependent on consistent analytical results for sediment contaminants. On-going QA testing of analytical results, both within- and between-batch, is therefore essential to ensure reliable interpretation of trends can be made.

³ No better site was found during the establishment of the programme, so it may be that the lack of suitable sampling areas in the lower reaches of the Waikumete Stream is something that has to be accepted, and the results from site O assessed with caution.

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Appendix 1. Stream sediment sampling notes

Sampled approximately 2 cm depth using small plastic scoop to obtain 10 sub-samples over 10–60 m reaches into each of 3 reps per site. Each rep well mixed then transferred into Hills lab plastic soil jars. Sampling reaches depended on stream site characteristics – some required a long distance to find suitable sediments, others were limited by access into & along streambed. Sites sampled (in order first to last) on 1st March (D only) & 2nd March 2006 (rest of sites):

- 1. **Site D. Sel Peacock Dr (library).** Tidal (sampled at low tide 1st March). Sampled 2nd pool below bridge on west side of island, same as 2003 Sand & silty sand among boulders and logs.
- Site A. Sharp Track. As for 2003. Started u/s of track & pipe entering on true right bank. Sampled over ca. 60 m targeting sparse patches of sandy sediment behind boulders. Mostly rocky bottom.
- 3. **Site B. Candia Rd.** Same as 2003. Patch ca. 10 x 5 m, starting approx 5-10 m u/s of bridge. Sands from between cobbles and boulders.
- 4. **Site C. Border Rd.** Same as 2003. Sand in deepish run. Sampled patches of sand under boulders and right bank over ca. 30 m reach.
- 5. **Site E. Bendall's Lane.** Sampled ca. 50 m above & below the "waterpipe". Same location as wq site. Appears high flow event has eroded banks? Sand deposited in pools and behind rocks.
- 6. Site F. Kelly's Rd. Same as 2003. Sampled 25 m reach u/s bridge. Sand. Bank erosion a significant source?
- 7. Site G. Parrs Cross Rd. Same as 2003. Sand. Bank erosion evident.
- 8. **Site H. Aetna Place.** Same area as 2003. Lots of bank erosion. Banks have been cleared more than in 2003. Lots of fine sandy sediment. Plentiful debris in stream channel.
- 9. **Site O. Benita Place.** Deep incised channel. Cohesive sediment, hard clay bottom, little sediment accumulation. Lots of rubbish. Sediment sampled may be local bank clays. Not good site.
- **10. Site N. West Coast Rd.** As for 2003. Sampled 30 m reach from above to below bridge mostly riffle. Very hard to find fine sediment. Small pockets in backwaters below boulders. Lots of rubbish battery, radiator, blocks etc.
- **11. Site M. Glendale Rd**. As for 2003. Sampled pool and lower reach below confluence (where water quality sampled). Total length ca. 40 m. Gravelly & silty sands. Some in-stream debris evident.
- **12. Site K. Ceramco Park.** As for 2003. Anaerobic, vegetative debris in rocky pools. Hard to sample. Unpleasant!
- 13. **Site L. Withers Park.** As for 2003. Sampled d/s bridge over ca. 100 m reach. Small patches sandy gravel collected from pockets in stream channel. Abundant debris (metallic, rubber etc). Probably variable site?
- 14. **Site J. Waerenga Place.** As for 2003. Stream flow barely a trickle. Lots of bank collapse. Sandy, silty & organic material sampled up to waterfall pool.
- 15. **Site P.** Sampled ca. 50 m reach below obvious large kauri (where T sensor sited). Coarse sands & gravels.
- 16. **Site Q.** Sampled ca. 50–100 m u/s of where path drops to stream (WQ). Most sediment trapped in willow root mats. Found small pockets in the right channel (beside golf course). Combination of sand, mud, fibrous root mass.
- 17. **Site R.** Sampled reach ca. 20 m u/s of bridge. Local bank collapse (avoided). Difficult to find sediment. Mix of sand, muddy sand, clay, organic debris. Not good sediment site.
- 18. **Site S.** No sediment at WQ site in Woodside Reserve. Sampled u/s of Don Buck Rd bridge, starting about 70 m upstream of the bottom steps on walkway (behind first group of poplars). Bed variable mostly compact clay, abundant woody debris and litter. Sampled mix of muddy sand, organic & sandy pockets over ca. 50 m reach to below large pool below log lying across stream.
- 19. **Site I. Westfield carpark.** As for 2003. Abundant sandy sediment lenses and accumulation in backwaters. Sampled d/s bridge ca. 30 m downstream. Some rubbish trolleys, car parts etc. Large amount of orange sludge running down true right bank under bridge.

Appendix 2. Estuarine Sediment Data

	l	Jpper Huruhui	ru	l	Lower Huruhu	ru	Hend	erson Creek:	Bank	Henc	derson Creek:	Bed
Analyte	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Metals (mg/kg, 2 M HCl, <63 μm):												
Cu	29	29	29	31	30	28	32	30	31	36	35	33
Pb	42.3	41.2	40.9	38.9	38.7	35.6	39.1	37.9	40.0	41.5	43.4	36.8
Zn	170	168	171	169	167	153	179	171	179	297	292	251
Metals (mg/kg, Total, <0.5 mm):												
Cu		28.3			29.4			26.7			14.7	
Pb		30.8			31.7			28.0			18.2	
Zn		133			148			149			112	
Texture (%):												
>2 mm		1.47			0.06			<0.01			4.67	
0.063 – 2 mm		10.5			7.75			34.8			85.4	
<0.063 mm		88.0			92.2			65.2			9.92	

Appendix 3. Stream Sediment Metals' Data

Concentrations (mg/kg) of Cu, Pb, and Zn in stream sediments sampled March 2006.

			Copper				Lead				Zinc	
	2 M HCl e	extractable, <	63 μm fraction	Total, <0.5 mm	2 M HCl e	xtractable, <60	3 μm fraction	Total, <0.5 mm	2 M HCl e	xtractable, <6	3 μm fraction	Total, <0.5 mm
Site	Rep 1	Rep 2	Rep 3	Rep 2	Rep 1	Rep 2	Rep 3	Rep 2	Rep 1	Rep 2	Rep 3	Rep 2
Α	27	26	26	26.1	9.1	9.1	8.3	6.33	88	83	88	72.3
В	40	35	35	16.6	19.9	16	17.2	7.38	83	85	88	50.7
С	27	29	24	16.8	16.8	19.1	14.9	9.36	109	122	102	69
D	40	45	27	21.8	56.2	51	32.9	26.6	288	352	211	155
Е	24	22	24	13	14.5	16.1	15.1	5.11	104	126	108	55.1
F	28	26	27	10.3	15	16.1	15	5.21	88	93	85	44.6
G	30	40	45	14.1	17.1	19.1	23.1	7.56	89	100	121	57.5
Н	40	31	38	17.2	27.1	22	27.6	11.4	173	149	176	85.2
1	62	49	66	16.5	68.2	59.2	69.8	19	583	498	533	155
J	19	21	16	12.8	27.6	31	23.8	18	143	158	123	101
K	33	29	28	21.9	37.3	33.4	33.5	39.8	379	309	315	196
L	28	33	28	15.4	66.4	60.8	76.9	20.6	486	548	512	180
М	34	30	31	17.0	71.4	63.7	63.1	54.4	463	387	444	170
N	30	40	42	21.4	74.9	80.1	69.4	28.7	378	514	522	171
0	20	18	16	10	48.6	40.7	36.2	22.5	145	113	111	87.8
Р	25	23	25	14.9	14	12.2	13.8	6.06	85	78	84	49
Q	24	24	24	21.4	21.3	20.5	20.4	13.9	104	97	102	79.3
R	22	24	25	15.3	25.4	28	31.3	17.4	105	106	104	74.1
S	17	18	21	8.5	15.3	15.2	18.6	7.6	156	144	193	69.8

Appendix 4. Quality Assurance Data

Between-batch replicates. 2 M HCl extraction, $< 63 \mu m$ fraction, mg/kg

Sample	Year	Cu	Pb	Zn
Henderson Creek estuary Bed R1	2003	36	43.4	272
Henderson Creek estuary Bed R1	2006	33	37.9	254
% difference		-8.7	-13.5	-6.8
Henderson Creek estuary Bank R1	2003	36	44.3	204
Henderson Creek estuary Bank R1	2006	34	38.8	191
% difference		-5.7	-13.2	-6.6

Within-batch replicates. 2 M HCl extraction, < 63 µm fraction, mg/kg

Sample	Year	Cu	Pb	Zn
Swanson Stream Site Q Rep 2	2006	24	20.5	97
Swanson Stream Site Q Rep 2	2006	22	19.8	91
% difference		-8.7	-3.5	-6.4
Opnauku Stream Site C Rep 2	2006	29	19.1	122
Opnauku Stream Site C Rep 2	2006	30	16	111
% difference		3.4	-17.7	-9.4
Oratia Stream Site I Rep 2	2006	49	59.2	498
Oratia Stream Site I Rep 2	2006	58	73.1	533
% difference		16.8	21.0	6.8
Waikumete Stream Site M Rep 2	2006	30	63.7	387
Waikumete Stream Site M Rep 2	2006	29	65.5	382
% difference		-3.4	2.8	-1.3

Appendix 5. Laboratory Reports

Hill Laboratories

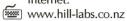
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Client: Diffuse Sources Limited Address: P O Box 13002, Hillcrest

HAMILTON

Contact: Geoff Mills

Laboratory No: 409749
Date Registered: 8/03/2006
Date Completed: 9/05/2006
Page Number: 1 of 6

Amended Report: This is an amended report which replaces a report issued on the 12/4/06. The metals results for sample 409749/167 have been checked at the client's request, and altered results are now reported – see Analyst's Comments [QOWQ 14017]

Client's Reference: DS TS 2005

The results for the analyses you requested are as follows:

Sample Type: Environmental Solids, Sediment

Sample Name	Lab No	Fraction passing through 500 um sieve*	
		(g/100g)	
EST Bank R2 1/3/06	409749/2	99.4	
EST Bed R2 1/3/06	409749/5	58.3	
U. Huru R2 2/3/06	409749/8	98.5	
L. Huru R2 2/3/06	409749/11	99.9	
A R2 2/3/06	409749/14	4.5	
B R2 2/3/06	409749/17	30.1	
C R2 2/3/06	409749/20	15.2	
D R2 1/3/06	409749/23	50.2	
E R2 2/3/06	409749/26	25.9	
F R2 2/3/06	409749/29	32.3	
G R2 2/3/06	409749/32	29.2	
H R2 2/3/06	409749/35	24.9	
I R2 2/3/06	409749/38	10.6	
J R2 2/3/06	409749/41	14.6	
K R2 2/3/06	409749/44	48.6	
L R2 2/3/06	409749/47	19.7	
M R2 2/3/06	409749/50	25.1	
N R2 2/3/06	409749/53	11.1	
O R2 2/3/06	409749/56	50.9	
S1 R2 2/3/06	409749/59	16.0	
S2 R2 2/3/06	409749/62	32.9	
S3 R2 2/3/06	409749/65	28.2	
S4 R2 2/3/06	409749/68	29.5	

^{*} This test is not accredited.





This Laboratory is accredited by International Accreditation New Zealand (IANZ), which represents New Zealand in the International Laboratory Accreditation Cooperation (ILAC). Through the ILAC Mutual Recognition Arrangement (ILAC-MRA) this accreditation is internationally recognised. The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Sample Name	Lab No	Extractable Copper*	Extractable Lead*	Extractable Zinc*
		(mg/kg dry wt)	(mg/kg dry wt)	(mg/kg dry wt)
EST Bank R1 1/3/06 (<63um Fraction)	409749/76	32	39.1	179
EST Bank R2 1/3/06 (<63um Fraction)	409749/77	30	37.9	171
EST Bank R3 1/3/06 (<63um Fraction)	409749/78	31	40.0	179
EST Bed R1 1/3/06 (<63um Fraction)	409749/79	36	41.5	297
EST Bed R2 1/3/06 (<63um Fraction)	409749/80	35	43.4	292
EST Bed R3 2/3/06 (<63um Fraction)	409749/81	33	36.8	251
U.Huru R1 2/3/06 (<63um Fraction)	409749/82	29	42.3	170
U. Huru R2 2/3/06 (<63um Fraction)	409749/83	29	41.2	168
U. Huru R3 2/3/06 (<63um Fraction)	409749/84	29	40.9	171
L. Huru R1 2/3/06 (<63um Fraction)	409749/85	31	38.9	169
L. Huru R2 2/3/06 (<63um Fraction)	409749/86	30	38.7	167
L. Huru R3 2/3/06 (<63um Fraction)	409749/87	28	35.6	153
A R1 2/3/06 (<63um Fraction)	409749/88	27	9.1	88
A R2 2/3/06 (<63um Fraction)	409749/89	26	9.1	83
A R3 2/3/06 (<63um Fraction)	409749/90	26	8.3	88
B R1 2/3/06 (<63um Fraction)	409749/91	40	19.9	83
B R2 2/3/06 (<63um Fraction)	409749/92	35	16.0	85
B R3 2/3/06 (<63um Fraction)	409749/93	35	17.2	88
C R1 2/3/06 (<63um Fraction)	409749/94	27	16.8	109
C R2 2/3/06 (<63um Fraction)	409749/95	29	19.1	122
C R3 2/3/06 (<63um Fraction)	409749/96	24	14.9	102
D R1 2/3/06 (<63um Fraction)	409749/97	40	56.2	288
D R2 2/3/06 (<63um Fraction)	409749/98	45	51.0	352
D R3 2/3/06 (<63um Fraction)	409749/99	27	32.9	211
E R 2/3/06 (<63um Fraction)	409749/100	24	14.5	104
E R2 2/3/06 (<63um Fraction)	409749/101	22	16.1	126
E R3 2/3/06 (<63um Fraction)	409749/102	24	15.1	108

Sample Name	Lab No	Extractable Copper* (mg/kg dry wt)	Extractable Lead* (mg/kg dry wt)	Extractable Zinc* (mg/kg dry wt)
F R1 2/3/06 (<63um Fraction)	409749/103	28	15.0	88
F R2 2/3/06 (<63um Fraction)	409749/104	26	16.1	93
F R3 2/3/06 (<63um Fraction)	409749/105	27	15.0	85
G R1 2/3/06 (<63um Fraction)	409749/106	30	17.1	89
G R2 2/3/06 (<63um Fraction0	409749/107	40	19.1	100
G R13 2/3/06 (<63um Fraction)	409749/108	45	23.1	121
H R1 2/3/06 (<63um Fraction)	409749/109	40	27.1	173
H R2 2/3/06 (<63um Fraction)	409749/110	31	22.0	. 149
H R3 2/3/06 (<63um Fraction)	409749/111	38	27.6	176
I R1 2/3/06 (<63um Fraction)	409749/112	62	68.2	583
I R2 2/3/06 (<63um Fraction)	409749/113	49	59.2	498
I R3 2/3/06 (<63um Fraction)	409749/114	66	69.8	533
J R1 2/3/06 (<63um Fraction)	409749/115	19	27.6	143
J R2 2/3/06 (<63um Fraction)	409749/116	21	31.0	158
J R3 2/3/06 (<63um Fraction)	409749/117	16	23.8	123
K R1 2/3/06 (<63um Fraction)	409749/118	33	37.3	379
K R2 2/3/06 (<63um Fraction)	409749/119	29	33.4	309
K R3 2/3/06 (<63um Fraction)	409749/120	28	33.5	315
L R1 2/3/06 (<63um Fraction)	409749/121	28	66.4	486
L R2 2/3/06 (<63um Fraction)	409749/122	33	60.8	548
L R3 2/3/06 (<63um Fraction)	409749/123	28	76.9	512
M R1 2/3/06 (<63um Fraction)	409749/124	34	71.4	463
M R2 2/3/06 (<63um Fraction)	409749/125	30	63.7	387
M R3 2/3/06 (<63um Fraction)	409749/126	31	63.1	444
N R1 2/3/06 (<63um Fraction)	409749/127	30	74.9	378
N R2 2/3/06 (<63um Fraction)	409749/128	40	80.1	514
N R3 2/3/06 (<63um Fraction)	409749/129	42	69.4	522
O R1 2/3/06 (<63um Fraction)	409749/130	20	48.6	145

- R J Hill Laboratories Ltd -

Sample Name	Lab No	Extractable Copper*	Extractable Lead*	Extractable Zinc*	
;		(mg/kg dry wt)	(mg/kg dry wt)	(mg/kg dry wt)	
O R2 2/3/06 (<63um Fraction)	409749/131	18	40.7	113	
O R3 2/3/06 (<63um Fraction)	409749/132	16	36.2	111	
S1 R1 2/3/06 (<63um Fraction)	409749/133	25	14.0	85	
S1 R2 2/3/06 (<63um Fraction)	409749/134	23	12.2	78	
S1 R3 2/3/06 (<63um Fraction)	409749/135	25	13.8	84	
S2 R1 2/3/06 (<63um Fraction)	409749/136	24	21.3	104	
S2 R2 2/3/06 (<63um Fraction)	409749/137	24	20.5	97	
S2 R3 2/3/06 (<63um Fraction)	409749/138	24	20.4	. 102	
S3 R1 2/3/06 (<63um Fraction)	409749/139	22	25.4	105	
S3 R2 2/3/06 (<63um Fraction)	409749/140	24	28.0	106	
S3 R3 2/3/06 (<63um Fraction)	409749/141	25	31.3	104	
S4 R1 2/3/06 (<63um Fraction)	409749/142	17	15.3	156	
S4 R2 2/3/06 (<63um Fraction)	409749/143	18	15.2	144	
S4 R3 2/3/06 (<63um Fraction)	409749/144	21	18.6	193	
S2 R4 2/3/06 (<63um Fraction)	409749/145	22	19.8	91	
C R4 2/3/06 (<63um Fraction)	409749/146	30	16.0	111	
I R4 2/3/06 (<63um Fraction)	409749/147	58	73.1	533	
M R4 2/3/06 (<63um Fraction)	409749/148	29	65.5	382	
EST Bed 1 2003 2/12/03 (<63um Fraction)	409749/149	33	37.9	254	
EST Bank 1 2003 2/12/03 (<63um Fraction)	409749/150	34	38.8	191	

^{*} This test is not accredited.

Sample Name	Lab No	Total Recoverable Copper (mg/kg dry wt)	Total Recoverable Lead (mg/kg dry wt)	Total Recoverable Zinc (mg/kg dry wt)
EST Bank R2 1/3/06 (<500um Fraction)	409749/151	26.7	28.0	149
EST Bed R2 1/3/06 (<500um Fraction)	409749/152	14.7	18.2	112
U. Huru R2 2/3/06 (<500um Fraction)	409749/153	28.3	30.8	133
L. Huru R2 2/3/06 (<500um Fraction)	409749/154	29.4	31.7	148
A R2 2/3/06 (<500um Fraction)	409749/155	26.1	6.33	72.3

Sample Name	Lab No	Total Recoverable Copper	Total Recoverable Lead	Total Recoverable Zinc
		(mg/kg dry wt)	(mg/kg dry wt)	(mg/kg dry wt)
B R2 2/3/06 (<500um Fraction)	409749/156	16.6	7.38	50.7
C R2 2/3/06 (<500um Fraction)	409749/157	16.8	9.36	69.0
D R2 2/3/06 (<500um Fraction)	409749/158	21.8	26.6	155
E R2 2/3/06 (<500um Fraction)	409749/159	13.0	5.11	55.1
F R2 2/3/06 (<500um Fraction)	409749/160	10.3	5.21	44.6
G R2 2/3/06 (<500um Fraction)	409749/161	14.1	7.56	57.5
H R2 2/3/06 (<500um Fraction)	409749/162	17.2	11.4	85.2
I R2 2/3/06 (<500um Fraction)	409749/163	16.5	19.0	. 155
J R2 2/3/06 (<500um Fraction)	409749/164	12.8	18.0	101
K R2 2/3/06 (<500um Fraction)	409749/165	21.9	39.8	196
L R2 2/3/06 (<500um Fraction)	409749/166	15.4	20.6	180
M R2 2/3/06 (<500um Fraction)	409749/167	17.0#	54.4	170
N R2 2/3/06 (<500um Fraction)	409749/168	21.4	28.7	171
O R2 2/3/06 (<500um Fraction)	409749/169	10.0	22.5	87.8
S1 R2 2/3/06 (<500um Fraction)	409749/170	14.9	6.06	49.0
S2 R2 2/3/06 (<500um Fraction)	409749/171	21.4	13.9	79.3
S3 R2 2/3/06 (<500um Fraction)	409749/172	15.3	17.4	74.1
S4 R2 2/3/06 (<500um Fraction)	409749/173	8.5	7.60	69.8

[#] Amended result – see Analyst's Comments

Texture (2 mm, 63 um sieves)*

Sample Name	EST Bank R2 1/3/06	EST Bed R2 1/3/06	U. Huru R2 2/3/06	L. Huru R2 2/3/06
Lab No	409749/2	409749/5	409749/8	409749/11
Units	(g/100g)	(g/100g)	(g/100g)	(g/100g)
Dry matter (as rcvd)	42.3	62.9	39.2	40.3
>2mm fraction (dry wt)	< 0.01	4.67	1.47	0.06
63um - 2mm fraction (dry wt)	34.8	85.4	10.5	7.75
<63um fraction (dry wt)	65.2	9.92	88.0	92.2

^{*} The test producing the results in this table is not yet accredited.

Sample Containers

The following table shows the sample containers that were associated with this job.

Container Description	Container Size (mL)	Number of Containers
Plastic Jar (Soils)	400	75

Details of sample bottle preparation procedures are available upon request.

Summary of Methods Used and Detection Limits

The following table(s) gives a brief description of the methods used to conduct the analyses for this job.

The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Substance Type: Environmental Solids

Parameter	Method Used	Detection Limit
ARC 2M HCI Extraction*	Extraction with 2M HCI. Solid:Liquid 1:50 w/v. 24 hrs ARC Tech Publication No. 47, 1994.	N/A
Total Recoverable digest	Nitric / hydrochloric acid digestion. US EPA 200.2	N/A
Sieving through 63 um sieve, no weight fraction*	Wet sieving, centrifugation, no gravimetric determination of fraction passing sieve.	N/A
Fraction passing through 500 um sieve*	Wet Sieving, dried at 35 °C, gravimetric	0.1 g/100g
Extractable Copper*	2M HCl extraction (< 63µm fraction), ICP-MS. ARC Tech Publication No. 47, 1994.	1 mg/kg dry wt
Total Recoverable Copper	Nitric / hydrochloric acid digestion, ICP-MS (Low level). US EPA 200.2	0.2 mg/kg dry wt
Extractable Lead*	2M HCl extraction (< 63µm fraction), ICP-MS. ARC Tech Publication No. 47, 1994.	0.2 mg/kg dry wt
Total Recoverable Lead	Nitric / hydrochloric acid digestion, ICP-MS (Low level). US EPA 200.2	0.04 mg/kg dry w
Extractable Zinc*	2M HCl extraction (< 63µm fraction), ICP-MS. ARC Tech Publication No. 47, 1994.	2 mg/kg dry wt
Total Recoverable Zinc	Nitric / hydrochloric acid digestion, ICP-MS (Low level). US EPA 200.2	0.4 mg/kg dry wt
Texture (2 mm, 63 um sieves)*	Sieving, gravimetric. All drying 35 °C, overnight.	N/A

^{*} This test is not accredited.

Analyst's Comments:

These samples were collected by yourselves and analysed as received at the laboratory. Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the submitter. This report must not be reproduced, except in full, without the written consent of the signatory.

409749/167 was repeated in duplicate on eltr 836 and the results are as follows:

	CuTRLI	ZnTRLI	PbTRLI
409749/167 dup 1	16.8	160	54.7
409749/167 dup 2	17.2	164	78.6
409749/167 avg	17.0	162	66.7

The repeated result for Cu does not confirm with the original result of 145ppm and is now at the level the client was expecting for this sample. It was noted on the repeat worksheet that 409749/167 was brown in colour with brick red flecks throughout the sample. It is possible that when the original sample was weighed out there were a large number of red flecks included, which could account for the variable Cu results. All other metal results confirm within experimental variation so there has been no sample swap at the digestion or dilution stages. Please report a result of 17ppm Cu for 409749/167. RF 09.06.06

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Client: Diffuse Sources Limited Address: P O Box 13002, Hillcrest

HAMILTON

Contact: Geoff Mills

Laboratory No: 409749qc Date Registered: 8/03/2006 Date Completed: 9/05/2006 Page Number: 1 of 6

Client's Reference: DS TS 2005

Quality Control Report for 409749

This report includes quality control data for the following analytes:

Trace Elements

Extractable Metals (Copper, Lead and Zinc).

- Procedural Blanks
- Certified Reference Material (CRM)
- Duplicate Sample Analysis
- Spiked Samples
- Routine Repeats of samples

Total Recoverable Metals (Copper, Lead and Zinc).

- Procedural Blanks
- Certified Reference Material (CRM)
- Duplicate Sample Analysis
- Routine Repeats of samples





This Laboratory is accredited by International Accreditation New Zealand (IANZ), which represents New Zealand in the International Laboratory Accreditation Cooperation (ILAC). Through the ILAC Mutual Recognition Arrangement (ILAC-MRA) this accreditation is internationally recognised. The tests reported herein have been performed in accordance with the terms of accreditation, with the exception of tests marked *, which are not accredited.

Quality Control Data for Samples 409749/76 - 100, 102 - 109.

Sample Name	Lab No	Extractable Copper* (mg/kg dry wt)	Extractable Lead* (mg/kg dry wt)	Extractable Zinc* (mg/kg dry wt)
Procedural Blank	-	< 2	< 0.4	< 4
CRM (AGAL 10)	-	19.73	40.4	44.8
CRM In House Limits (AGAL 10)	-	14.0 – 23.0	28.4 – 46.0	29.8 – 54.6
Duplicate Sample 1	409749/108	45.6	23.59	122.4
Duplicate Sample 2	409749/108	44.5	22.67	118.8
Sample Spike[% Recovery]	409749/109	106	106	118

Quality Control Data for Samples 409749/101, 110 - 139.

Sample Name	Lab No	Extractable Copper* (mg/kg dry wt)	Extractable Lead* (mg/kg dry wt)	Extractable Zinc* (mg/kg dry wt)
Procedural Blank	-	< 2	< 0.4	< 4
CRM (AGAL 10)	-	18.4	36.3	45.5
CRM In House Limits (AGAL 10)	-	14.0 – 23.0	28.4 – 46.0	29.8 – 54.6
Duplicate Sample 1	409749/139	21.9	25.6	107.4
Duplicate Sample 2	409749/139	21.3	25.1	102.6
Sample Spike[% Recovery]	409749/139	100	97	108
Routine Repeat (es2M 72)	409749/76	31.8	39.1	178.7
Routine Repeat (es2M 73)	409749/76	29.6	36.5	174.2

Quality Control Data for Samples 409749/140 - 150.

Sample Name	Lab No	Extractable Copper* (mg/kg dry wt)	Extractable Lead* (mg/kg dry wt)	Extractable Zinc* (mg/kg dry wt)
Procedural Blank	-	< 2	< 0.4	< 4
CRM (AGAL 10)	-	18.3	37.29	42.6
CRM In House Limits (AGAL 10)	-	14.0 – 23.0	28.4 – 46.0	29.8 – 54.6
Duplicate Sample 1	409749/150	33.4	38.80	191.0
Duplicate Sample 2	409749/150	33.8	38.77	191.0
Sample Spike[% Recovery]	409749/150	98	98	106
Routine Repeat (es2M 73)	409749/101	21.8	16.1	126.2
Routine Repeat (es2M 74)	409749/101	20.4	14.1	102.5

Quality Control Data for Samples 409749/155 - 168, 170, 172, 173.

Sample Name	Lab No	Total Recoverable Copper (mg/kg dry wt)	Total Recoverable Lead (mg/kg dry wt)	Total Recoverable Zinc (mg/kg dry wt)
Procedural Blank	-	< 0.2	< 0.04	< 0.4
CRM (AGAL 10)	-	22.01	41.66	50.21
CRM Certified Range (AGAL 10)	-	23.2 <u>+</u> 1.9	40.4 <u>+</u> 2.7	57 <u>+</u> 4.2
CRM In House Limits (AGAL 10)	-	19.1 – 25.3	31.79 – 46.55	43.3 – 58.5
Duplicate Sample 1	409749/173	8.63	7.22	69.23
Duplicate Sample 2	409749/173	8.31	7.98	70.52

Quality Control Data for Samples 409749/151 - 154

Sample Name	Lab No	Total Recoverable Copper (mg/kg dry wt)	Total Recoverable Lead (mg/kg dry wt)	Total Recoverable Zind (mg/kg dry wt)
Procedural Blank	-	< 0.2	< 0.04	< 0.4
CRM (AGAL 10)	-	22.19	36.46	50.25
CRM Certified Range (AGAL 10)	-	23.2 <u>+</u> 1.9	40.4 <u>+</u> 2.7	57 <u>+</u> 4.2
CRM In House Limits (AGAL 10)	-	19.1 – 25.3	31.79 – 46.55	43.3 – 58.5
Routine Repeat (ELTR795)	409749/170	14.93	6.06	49.0
Routine Repeat (ELTR796)	409749/170	13.95	5.27	48.6

Quality Control Data for Samples 409749/169, 171

Sample Name	Lab No	Total Recoverable Copper (mg/kg dry wt)	Total Recoverable Lead (mg/kg dry wt)	Total Recoverable Zinc (mg/kg dry wt)
Procedural Blank	_	< 0.2	< 0.04	< 0.4
CRM (AGAL 10)	-	20.87	35.81	48.3
CRM Certified Range (AGAL 10)	-	23.2 <u>+</u> 1.9	40.4 <u>+</u> 2.7	57 <u>+</u> 4.2
CRM In House Limits (AGAL 10)	-	19.1 – 25.3	31.79 – 46.55	43.3 – 58.5
Routine Repeat (ELTR796)	409749/154	29.39	31.72	148.1
Routine Repeat (ELTR797)	409749/154	30.02	33.06	148.9
Duplicate Sample 1#	412856/9	255.2	2767	12460
Duplicate Sample 2#	412856/9	280.5	2711	10440

[#] A duplicate analysis of 409749 was not performed, however a duplicate sample was analysed in the same batch as 409749 and these results are included in this QC report.

Analyst's Comments:

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