Auckland Marine Sediment Contaminant Monitoring:
Drury Creek June 2015

August 2016

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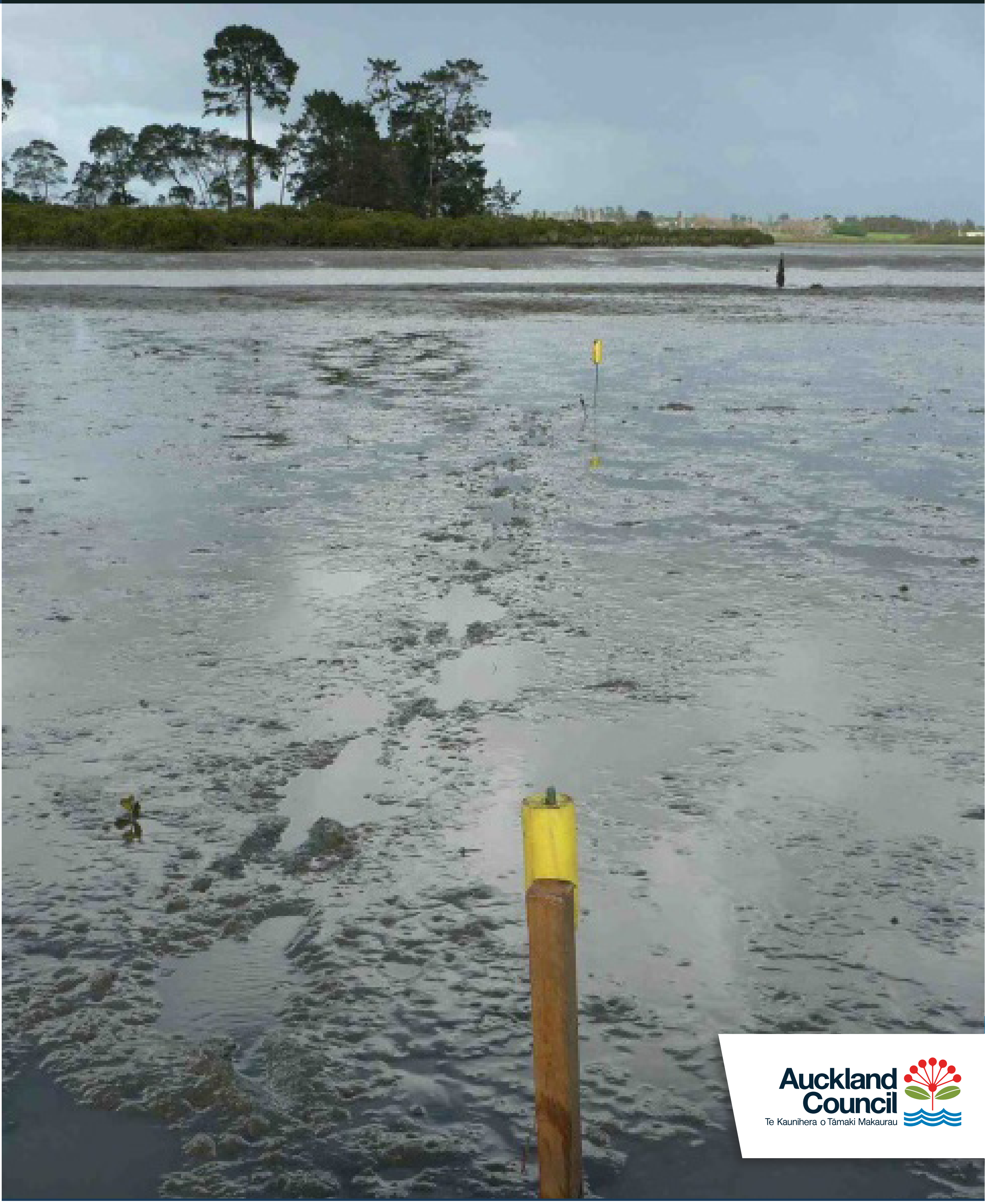

Auckland Council
Te Kaunihera o Tāmaki Makaurau

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Auckland Marine Sediment Contaminant Monitoring: Drury Creek, June 2015

Dr Geoff Mills

Diffuse Sources Ltd

Executive summary

Significant areas of land on the eastern boundary of Drury Creek estuary (South East Manukau Harbour) are currently undergoing urban development. In addition, large areas to the east and south of the estuary have been identified for future urban growth under the Proposed Auckland Unitary Plan. Auckland Council have therefore signalled a need to initiate sediment contaminant monitoring in Drury Creek estuary, to track the effects of current and future urban development on sediment quality in the estuarine receiving environment.

This document describes the marine sediment contaminant monitoring undertaken in Drury Creek in June 2015, for Auckland Council's Regional Sediment Contaminant Monitoring Programme (RSCMP).

Five new monitoring sites in Drury Creek estuary were established and sampled in June 2015. Sediment samples were analysed for the heavy metals copper (Cu), lead (Pb), zinc (Zn), arsenic (As), and mercury (Hg), and for particle size distribution (PSD).

This report provides:

- sediment metals data (analysis by R J Hill Laboratories);
- sediment PSD data (analysis conducted by NIWA); and
- quality assurance (QA) data for sediment metals and PSD.

The contamination status of these sites was assessed by comparing metal concentrations with Environment Response Criteria (ERC; ARC 2004). All sites had metal concentrations in the ERC Green range (Cu<19mg/kg, Pb<50mg/kg, and Zn<124mg/kg). This is consistent with the current catchment land use, which is predominantly rural. The Drury Inner site had generally highest metal concentrations, reflecting the location of the site in the main stem of Drury Creek estuary, whose catchment contains a greater amount of urbanised land than the other estuary arms (Whangapouri and Oira Creeks).

Overall, the quality of the sediment contaminant data set obtained in June 2015 was similar to that obtained in previous years. As found in previous years' monitoring, the key issue identified by QA data was the year-to-year consistency of extractable metals (in the <63µm fraction).

The continued use of extractable metals for trend monitoring is therefore not recommended unless further development and testing of this analytical method are undertaken to provide more reproducible results. Until this is done, on-going monitoring should be conducted using total recoverable metals (in the <500µm fraction), which QA data indicate are more consistent over time.

As recommended in previous reports, continued focus on quality assurance, is required to provide confidence in the comparability of monitoring data over time and hence the reliability of temporal trend information obtained by the monitoring.

The ERC-Green status of the sites would normally lead to resampling in five years' time. However, there is considerable urban development underway in the Drury catchment, and plans for extensive urban expansion in adjacent areas of the South East Manukau Harbour have been proposed. It is therefore recommended that more frequent monitoring (e.g. 2- or 4-yearly) be considered to ensure that the "pre-development" contamination baseline is well defined and future trends are well characterised.

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1.0 Introduction

Significant areas of land on the eastern boundary of Drury Creek estuary (South East Manukau Harbour) are currently undergoing urban development. In addition, large areas to the east and south of the estuary have been identified for future urban growth under the Proposed Auckland Unitary Plan. Auckland Council have therefore signalled a need to initiate sediment contaminant monitoring in Drury Creek estuary, to track the effects of current and future urban development on sediment quality in the estuarine receiving environment.

The monitoring sites in Drury Creek will build on the existing Auckland Council Regional Sediment Contaminant Monitoring Programme (RSCMP) network by providing data from an area not currently covered by the RSCMP.

This document provides a summary of marine sediment contaminant monitoring undertaken by Diffuse Sources Ltd (DSL) in June 2015.

This report provides a summary of:

- Sampling undertaken, including new site descriptions;
- Sediment chemistry and particle size distribution (PSD) results; and
- Quality assurance (QA) data.

Single Site Reports (SSRs), which summarise sediment contaminant status and trends at each site, have been reported separately to Auckland Council. Copies of the SSRs can be obtained from the Research and Evaluation Unit (RIMU).

2.0 Sampling and analysis

2.1 Sampling

Sampling was focused on new sites in the South East Manukau Harbour. After scoping visits to a range of potential site locations in the estuaries of Drury, Whangapouri, Whangamaire, Clarks', and Taihiki creeks, four sites in the Drury Creek estuary and one site in the Whangapouri Estuary were selected for sampling.

Sites were selected based on their locations (to reflect inputs from upstream sub-catchments, preferably in sediment/contaminant depositional zones), uniformity of texture, lack of encroachment from mangroves, lack of obvious signs of human or animal (stock) disturbance, and accessibility.

The locations of the sites are shown in Figure 2-1 and they are described in more detail in section 4.0 (and in the SSRs).

Sampling was conducted by DSL on 10 and 11 June 2015, following the procedures detailed in the Auckland Regional Council (ARC) "monitoring blueprint" document, ARC Technical Publication 168 (ARC 2004).

A list of sites, sampling dates, and analyses conducted at each site are given in Table 2-1.

Table 2-1 Sites sampled and analyses conducted in June 2015.

			<63 µm fraction	<500 µm fraction		
Site	Sampling Date	Sampled by	Cu Pb Zn	Cu Pb Zn As Hg	Benthic Ecology	Particle Size
Whangapouri	10/06/2015	DSL	✓	✓	x	✓
Doc Island Mud	10/06/2015	DSL	✓	✓	x	✓
Doc Island Sand	10/06/2015	DSL	✓	✓	x	✓
Bottle Top Bay	11/06/2015	DSL	✓	✓	x	✓
Drury Inner (Park Estate Rd)	11/06/2015	DSL	✓	✓	x	✓

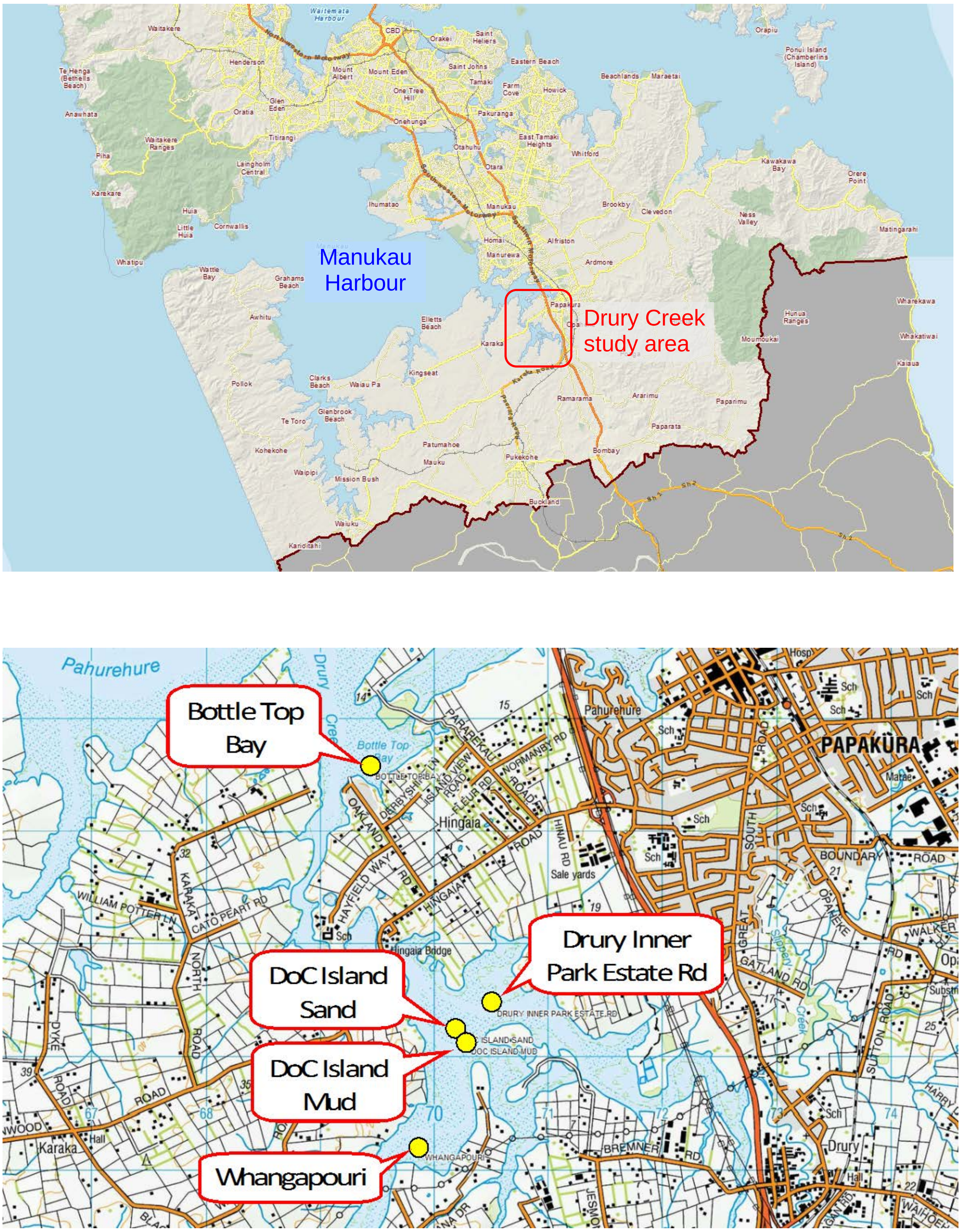


Figure 2-1 Locations of the Drury Creek estuary and sites sampled in Drury Creek and Whangapouri estuaries in June 2015

2.2 Sample preparation

2.2.1 Sediment chemistry samples

Five replicate samples for sediment chemistry were taken at each site, using the protocol described in ARC (2004). Samples were frozen on the day of sampling and delivered to NIWA Hamilton on 3 July 2015 for processing. All five replicates from each site were processed by homogenisation, sieving (<63µm and <500µm), and freeze drying.

Three replicates of the sieved and freeze-dried samples (<63µm and <500µm) from each site were provided to R J Hill Laboratories (Hamilton) for metal analysis on 31 July 2015. The remaining two replicates per site were retained for analysis checks if required – no analysis of replicates 4 and 5 were required.

Remaining freeze-dried <500µm sieved sediments were archived in glass jars. The <63µm and <500µm sediment samples remaining after metals analysis were also retained for archiving. The archived samples were returned to Auckland Council for storage with the RSCMP sample archive.

2.2.2 Particle size distribution samples

A composite sample for particle size distribution (PSD) analysis was made up from each site from 10 sub-samples, each sub-sample being taken from the top 2cm immediately adjacent to sediment chemistry sample replicate 5 (i.e. the PSD composite was equivalent to a sediment chemistry replicate sample). Each PSD sample was homogenised and a portion transferred into a 250 mL plastic bottle and frozen. The PSD samples were delivered to NIWA for analysis on 31 July 2015.

2.3 Analysis

Sediment samples were analysed for:

- Total recoverable metals – copper (Cu), lead (Pb), zinc (Zn), arsenic (As), and mercury (Hg) – on the <500µm fraction, by R J Hill Laboratories (3 replicates per site);
- 2 M HCl extractable metals – Cu, Pb, and Zn – on the <63µm fraction, by R J Hill Laboratories (3 replicates per site); and
- particle size distribution (PSD) – one composite sample per site. PSD analysis was undertaken by NIWA (Hamilton) using wet sieving/pipette separation into 6 size fractions, followed by oven drying each fraction to constant weight.

Sediment contaminant data are summarised in Appendix A, and PSD data are tabulated in Appendix B. The analytical lab report from R J Hill Laboratories is provided in Appendix C.

2.4 Concentration units for metals

As in 2013, the sediment samples provided to R J Hill Laboratories for metal analysis were freeze-dried. No correction for residual moisture in the freeze-dried samples has been made. NIWA staff (Greg Olsen, pers. comm. May 2014) have indicated that their freeze-dried sediments (including fine, organic-rich sediment) typically have moisture contents of less than 2 per cent, and for sandy marine sediments usually <1 per cent. NIWA's analyses have found that the weighing errors for moisture correction are often higher than the mass difference measured between wet weight and oven dry weight (overnight at 103°C). Therefore, moisture correction of the freeze-dried sediment results is not warranted, and has not been undertaken for the 2015 samples.

3.0 Quality assurance

For **metals analysis**, quality assurance (QA) was conducted by:

- Laboratory quality control samples – analysis of procedural blanks, duplicate samples reanalysed by the laboratory, analyses of Certified Reference Material (CRM; AGAL-10) and analysis of “in-house” reference sediment[1]. Spike recoveries were also reported. These data are reported in the Hill Laboratories QC Report, which is included in the lab report (Appendix C).
- Blind within-batch (WB) duplicate samples from the 2015 sampling – two samples, one sandy and one muddy textured, were submitted to the lab as additional samples.
- Three CRM samples dispersed through the analytical run as extra samples (in addition to the routine laboratory QC CRM samples).
- Analysis of Auckland Council “Bulk Reference Sediments” (BRS). BRS are sediments from two sites (a sandy sediment from Meola Outer Zone, and a muddy sediment from Middlemore), which have been archived in frozen and freeze-dried forms for repeated analysis with each year’s monitoring samples. Analysis of the BRS each year provides an on-going record of within-year and between-year analytical variability and changes over time (drift or trend). Three replicates of each of the Meola Outer and Middlemore BRS (in both frozen and freeze-dried forms) were analysed with the 2015 sample batch.

For **particle size distribution** (PSD), QA was conducted by:

- Analysis of three replicates of each of the sandy and muddy BRS sediments (frozen form only, as freeze-drying is likely to affect PSD); and
- Blind within-batch (WB) duplicate samples from the 2015 sampling – one sandy and one muddy textured (the same samples as analysed for metals) were submitted to the lab as additional samples.

Key features of the QA data are described in sections 3.1 to 3.5. An overall summary of the 2015 QA results is presented section 3.6.

[1] The R J Hill Laboratories “in-house” reference sediment – “QC A3” – is a sample made from a mixture of sediment, soil, and sludge. The material was dried and <63 µm sieved. Analysis is conducted directly on the <63 µm material. Compared with typical Auckland marine sediments, the QC A3 reference sediment has elevated concentrations of metals. Results are included in the RJ Hill Labs QA/QC report (Appendix C).

3.1 Procedural blanks

Metal concentrations in procedural blanks were below detection limits (D.L.):

- <1mg/kg for extractable Cu, <0.2mg/kg for extractable Pb, and <2mg/kg for extractable Zn.
- Total recoverable metals blanks were <0.2, <0.2, <0.04, <0.4, and <0.01mg/kg for As, Cu, Pb, Zn, and Hg respectively.

There was therefore no background contamination introduced in the laboratory that would contribute significantly to the reported metal concentrations.

3.2 Spike recoveries

Measuring the recovery of analytes added ("spiked") to sediment samples provides information on the accuracy and variability of the analytical data.

Spike recovery data were reported by R J Hill Laboratories for extractable metals (2M HCl) for two blanks and two spiked sediment samples. The data summarised in Table 3-1 show that, on average, extractable metals were reasonably well recovered (92–105 per cent) with relatively low variability (relative percentage differences (RPDs) of 1.9–6.3 per cent). Recoveries were lower for spiked sediments than for blanks (where no sediment is present). The lowest recovery recorded was 91 per cent (for Zn in a spiked sediment).

These results are similar to those obtained in 2013, and indicate that up to approximately 10 per cent of these metals could be unrecovered during sediment analysis.

Table 3-1 Spike recoveries (%) for extractable (2 M HCl, <63 µm) metals analysis (from R J Hill Laboratories QA report). RPD (%) are "relative percentage differences" between the results.

	Extractable metals (<63 µm)		
A. Sediment	Cu	Pb	Zn
Sediment	94	93	91
Sediment	96	99	93
mean sample spike recovery (%)	95.0	96.0	92.0
RPD (%)	2.1	6.3	2.2

	Extractable metals (<63 µm)		
B. Blank spikes	Cu	Pb	Zn
1	104	104	100
2	100	106	96
mean blank spike recovery (%)	102	105	98
RPD (%)	3.9	1.9	4.1

3.3 Reference materials

Two types of reference materials were used by Hill Laboratories as a quality control check for metals analysis:

- the certified reference material (CRM) “AGAL-10”, Hawkesbury River Sediment, prepared by the Australian Government Analytical Laboratories. This reference material has been used in the RSCMP and preceding monitoring programmes since 2002 to check data accuracy and consistency over time; and
- a new “in-house” laboratory reference material, “QC A3”, a sample prepared by Hill Laboratories from a mixture of contaminated sediment, soil, and sludge. The material was dried and <63µm sieved prior to analysis. Compared with typical Auckland marine sediments, the QC A3 reference sediment has elevated concentrations of metals.

The reference material analyses involved extraction/digestion and ICP-MS analysis only, and did not include the homogenising/sub-sampling/sieving/drying steps undertaken for analysis of field samples. Results are included in the Hill Laboratories QA/QC report (Appendix C), and are detailed in the following sections.

3.3.1 Certified Reference Material analyses

Three CRM samples (AGAL 10) were included through the analytical run as “unknowns”. In addition, R J Hill Laboratories’ in-house QC checks included separate CRM analysis – another one CRM sample was analysed for total recoverable metals in the analytical batch containing the RSCMP samples.

CRM data are summarised in Table 3-2 (for the three CRM samples added as “unknowns”) and Table 3-3 (for the single sample from the R J Hill Laboratories’ in-house QC programme).

All CRM results were within the laboratory in-house limits. This means that the data met the laboratory’s normal operating QC standards. Variability (coefficient of variation, CV %) for CRM analysis ranged between 0.8 per cent and 8 per cent for the various metals analyses, which is similar to previous years’ results.

Comparisons between measured CRM concentrations and certified concentrations for the three CRMs analysed as unknowns with the RSCMP samples showed that the total recoverable metals were, on average, within the certified ranges. [Note that Cr and Ni were much lower than the certified concentrations. This is because the USEPA 200.2 total recoverable metals digestion method recovers less of these metals than the stronger aqua regia digest used in the CRM certification – see footnote to the R J Hill Laboratories QC report, Appendix C].

Apart from Cr and Ni (see previous comment), average CRM concentrations were within approximately 20 per cent of the certified concentrations – for the three CRMs added to the 2015 sample batch, average total As was 20 per cent high, while the other metals ranged from 8 per cent low (Zn) to 8 per cent high (Pb). Individual CRM sample analyses were all within 10 per cent of the certified concentrations, except for As, which were up to 22 per cent high. Apart from the higher As results, these results are similar to previous years.

Overall, the CRM results indicate reasonable accuracy and good precision for metals in the 2015 sample analytical batch. However, these results apply only to the digestion and ICP-MS steps of the overall analysis method. Variability may be higher if sample sieving/drying steps were included (as for total analysis of field samples). The effects of these additional analysis steps are included in the BRS sample QA data (see section 3.5).

Note that there are no certified concentrations for extractable metals, and hence their accuracy cannot be assessed. However, the extractable metals results for the CRM samples were within the "in house" limits, and are therefore consistent with previous data generated by R J Hill Laboratories. The variability was low, with CVs of 4–5 per cent.

Comparisons of all the 2015 CRM results for total recoverable metals with those obtained in previous RDP and RSCMP monitoring conducted between 2002 and 2013 are shown in Figure 3-1, and for extractable metals in Figure 3-2. Trend plots for the 2002–2015 data are shown in Figure 3-3.

These data indicate that extractable Cu and Pb, and total Pb appeared somewhat elevated in 2015 compared with most previous years.

There were no significant trends over time for Pb or Zn (Mann Kendall test, all data used[2], $p<0.05$), but Cu showed an increase of 0.14 mg/kg/yr (0.59 per cent per year) for total recoverable Cu and 0.16 mg/kg/yr (0.87 per cent per year) for extractable Cu (Table 3-4). These values are comparable with these obtained in the last monitoring round in 2013.

The CRM results indicate that the metals data have been reasonably consistent over time (at <1 per cent of the median concentration per year), with significant trends found only for Cu. Variability for Cu, Pb, and Zn in 2015 was similar for extractable metals, and lower for total metals, to that observed in previous years.

Overall, the CRM QC data provide a useful tool for monitoring the accuracy and variability of the metals data over time in the sediment monitoring programme. Continued analysis and reporting of CRM data is recommended.

[2] The Mann Kendall trend test was conducted using TimeTrends software, using the "all data" option, which includes all the data within each time period (year). If the "median within each time period" option is used, none of the trends were significant (at $p<0.05$).

Table 3-2 Metal concentrations (mg/kg) in three Certified Reference Material (CRM; AGAL10) samples, included in the 2015 sediment analytical batch.

The Certified Upper and Lower Limits listed in the table are the reference value ±1 standard deviation. Yellow shaded values are outside this range (i.e. > ±1 s.d.). Means, as % of certified values, are colour coded: Green within 10%, Amber within 10–20%, Red greater than 20% of the certified concentrations. Note that Cr and Ni values are low because the USEPA 200.2 digestion method recovers less of these metals than the CRM certification method (which uses a stronger aqua regia digest).

	Extractable metals (<63 µm)			Total Recoverable Metals (<500 µm)							
Sample	Cu	Pb	Zn	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
CRM - Agal 10 - 1	20.0	39.8	43.0	20.7	9.4	43.1	24.4	42.4	11.3	11.7	51.9
CRM - Agal 10 - 2	18.6	37.4	41.0	21.0	9.5	47.9	23.3	43.0	11.4	12.1	52.1
CRM - Agal 10 - 3	19.5	40.2	45.6	20.0	9.3	50.7	24.3	45.1	11.5	12.4	53.2
mean	19.4	39.1	43.2	20.6	9.4	47.2	24.0	43.5	11.4	12.1	52.4
cv (%)	3.6	3.9	5.4	2.7	1.4	8.1	2.5	3.2	0.8	2.9	1.3
Mean % of certified value	n/a	n/a	n/a	119.6	100.6	57.6	103.5	107.7	98.0	67.9	91.9
In-house lower limit (mg/kg; mean - 99% C.L.)	14.1	27.9	32.2	16.18	7.82	27.17	19.58	32.48	10.023	9.52	46.1
In-house upper limit (mg/kg; mean + 99% C.L.)	22.9	46.5	52.2	23.09	11.03	71.86	26.39	48.42	13.61	14.02	62.74
In-house 99% C.I. (mg/kg)	8.8	18.6	20	6.91	3.206	44.69	6.8	15.9	3.587	4.49	16.6
In-house 99% C.I. (+/- % mean)	23.8	25.0	23.7	17.6	17.0	45.1	14.8	19.7	15.2	19.1	15.3
Certified Reference Value (mg/kg)	.... no reference values			17.2	9.33	82	23.2	40.4	11.6	17.8	57
Certified Lower Limit (mg/kg; reference value - 1 s.d.)	.... no reference values			14.2	8.69	71	21.3	37.7	10.5	15.1	52.8
Certified Upper Limit (mg/kg; reference value + 1 s.d.)	.... no reference values			20.2	9.97	93	25.1	43.1	12.7	20.5	61.2

Table 3-3 Metal concentrations (mg/kg) in Certified Reference Material (CRM; AGAL10) samples, analysed with the 2015 sediment analytical batch as part of the R J Hill Laboratories' in-house QC process.

The Certified Upper and Lower Limits are the reference value ±1 standard deviation. Yellow shaded values are outside this range (i.e. > ±1 s.d.). Means, as % of certified values, are colour coded: Green within 10%, Amber within 10–20%, Red greater than 20% of the certified concentrations. Note that Cr and Ni values are low because the USEPA 200.2 digestion method recovers less of these metals than the CRM certification method (which uses a stronger aqua regia digest).

	Extractable metals (<63 µm)			Total Recoverable Metals (<500 µm)									
Sample	Cu	Pb	Zn	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	Fe	Mn
CRM - 1				20.0	9.4	43.0	24.0	43.0	11.2	11.8	53.0		
mean				20.0	9.4	43.0	24.0	43.0	11.2	11.8	53.0		
cv (%)													
Mean % of certified value				116.3	100.8	52.4	103.4	106.4	96.6	66.3	93.0		
In-house lower limit (mg/kg; mean - 99% C.L.)	14.1	27.9	32.2	16.18	7.824	27.17	19.6	32.5	10.023	9.53	46.1	15423	215
In-house upper limit (mg/kg; mean + 99% C.L.)	22.9	46.5	52.2	23.09	11.03	71.86	26.4	48.4	13.61	14.02	62.7	21623	277
In-house 99% C.I. (mg/kg)	8.8	18.6	20	6.91	3.206	44.69	6.8	15.9	3.587	4.49	16.6	6200	62
In-house 99% C.I. (+/- % mean)	23.8	25.0	23.7	17.6	17.0	45.1	14.8	19.7	15.2	19.1	15.3	16.7	12.6
Certified Reference Value (mg/kg)	.... no reference values			17.2	9.33	82	23.2	40.4	11.6	17.8	57	18700	250
Certified Lower Limit (mg/kg; reference value - 1 s.d.)	.... no reference values			14.2	8.69	71	21.3	37.7	10.5	15.1	52.8	18830	230.5
Certified Upper Limit (mg/kg; reference value + 1 s.d.)	.... no reference values			20.2	9.97	93	25.1	43.1	12.7	20.5	61.2	21170	251.5

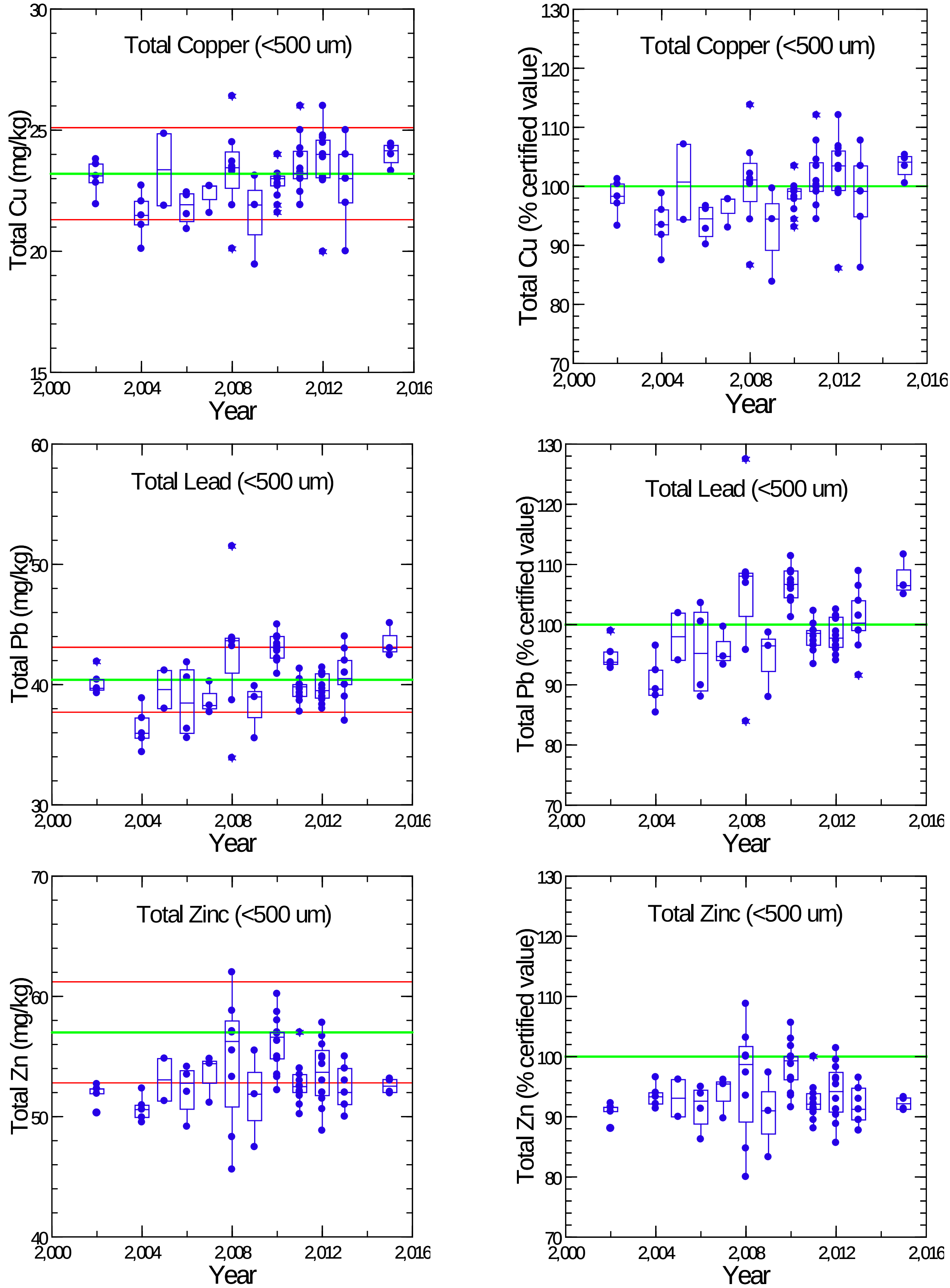


Figure 3-1 Certified Reference Material (CRM) quality control data for Total Recoverable Metals in CRM AGAL-10 for RDP and RSCMP samples analysed in 2002 to 2015. Plots show concentrations, with certified values (green central line) and upper and lower limits (±1 s.d., dashed red lines), and as percentages of the certified values.

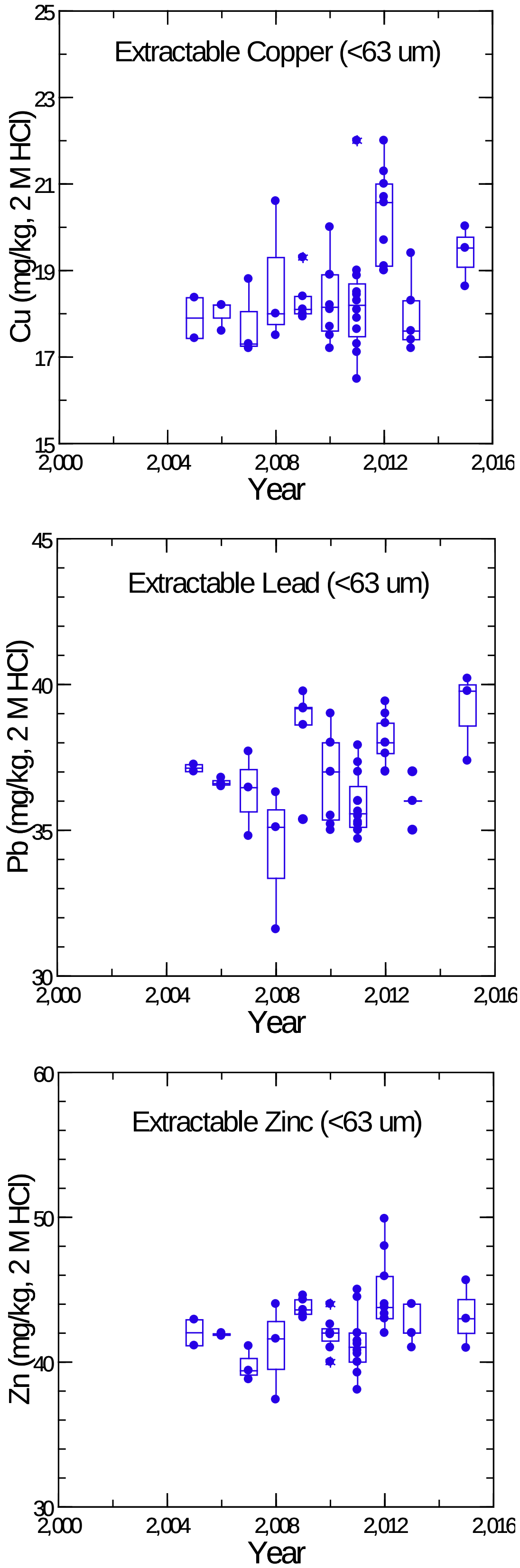


Figure 3-2 Certified Reference Material (CRM) quality control data for extractable metals (2 M HCl) in CRM AGAL-10 for samples analysed in 2005 to 2015. Note there are no certified values for extractable metals in AGAL-10.

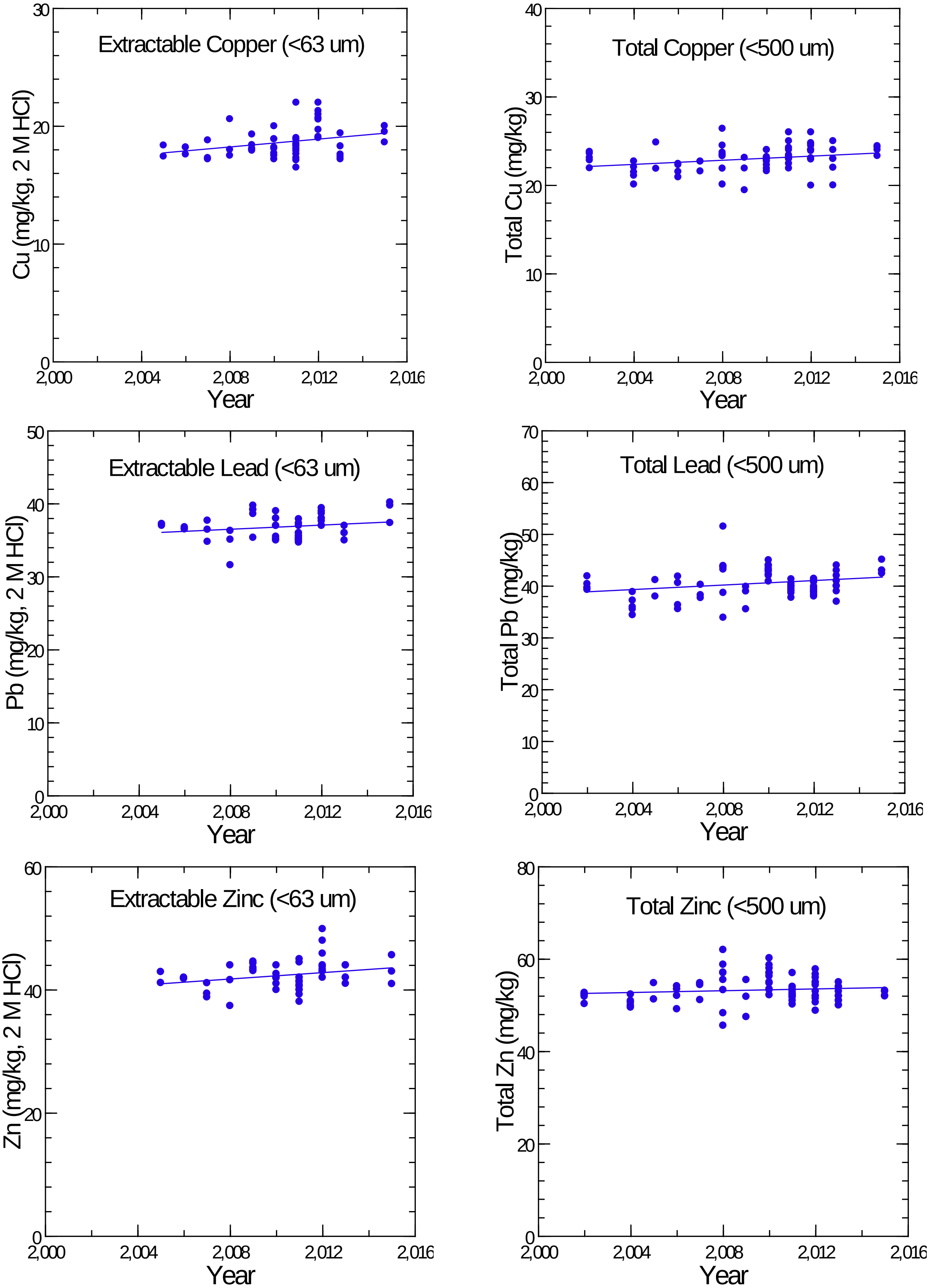


Figure 3-3 Trends in extractable and total recoverable metals in Certified Reference Material (CRM AGAL-10) for samples analysed from 2002–2015. Lines are linear regressions.

Table 3-4 Trends in metals in CRM (AGAL-10) analysed from 2002–2015. Results from Mann Kendal trend test (all data used). Significant trends ($p<0.05$) highlighted in red.
Note that none of the trends are statistically significant ($p \geq 0.099$) for Mann Kendal trend test on annual median concentrations.

Metal	Period	Median (mg/kg)	P	Median annual Sen slope (mg/kg/yr)	Sen Slope 5% confidence limit	Sen Slope 95% confidence limit	RSSE (% median value per year)
Extractable Cu	2005 to 2015	18.3	0.013	0.16	0.05	0.28	0.87
Extractable Pb	2005 to 2015	37.0	0.283	0.10	-0.06	0.28	0.27
Extractable Zn	2005 to 2015	42.0	0.071	0.20	0.00	0.45	0.48
Total Cu	2002 to 2015	23.0	0.001	0.14	0.07	0.21	0.59
Total Pb	2002 to 2015	40.1	0.124	0.14	0.00	0.31	0.35
Total Zn	2002 to 2015	53.0	0.905	0.00	-0.16	0.14	0.00

3.3.2 Hill Laboratories' in-house reference sediment

Results from analysis of R J Hill Laboratories' in-house reference sediment QCA3 are presented in Table 3-5. The data show reasonably consistent extractable metals results (CVs <10%, n=4) that were within the lab control limits. Only two total recoverable metals analyses were undertaken, which limits the assessment of data variability. However, Cu and As both showed one value outside the lab control limits – the lab QA report (included in Appendix C) commented on these results, and based on the other set of QCA3 sample results it was concluded that the batch were acceptable.

Table 3-5 Results from analysis of R J Hill Laboratories' in-house reference sediment QCA3.
The upper and lower control limits are the reference value ±3 standard deviations (ca. 99% CLs). Yellow shaded values are outside this range (i.e. >±3 s.d. from reference value).

	Extractable metals (<63 µm)			Total Recoverable Metals (<500 µm)							
Sample	Cu	Pb	Zn	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
QC A3 Sample 1	50.0	149.0	380.0	64.0	1.3	58.0	59.0	137.0	0.16	16.4	470.0
QC A3 Sample 2	49.0	128.0	400.0	114.0	1.5	89.0	75.0	158.0	0.17	19.0	490.0
QC A3 Sample 3	54.0	153.0	410.0								
QC A3 Sample 4	52.0	149.0	460.0								
mean	51.3	144.8	412.5	89.0	1.4	73.5	67.0	147.5	0.16	17.7	480.0
cv (%)	4.3	7.8	8.3	39.7	7.6	29.8	16.9	10.1	3.4	10.4	2.9
In house reference value (mg/kg)	51	146.5	415	71.5	1.4	69	60	139	0.16	18	480
In-house lower control limit (mg/kg; mean - 99% C.L.)	37	93	350	45	1.00	48	49	78	0.12	15	400
In-house upper control limit (mg/kg; mean + 99% C.L.)	65	200	480	98	1.80	90	71	200	0.20	21	560
In-house 99% C.L. (+/- mg/kg)	14	53.5	65	26.5	0.40	21	11	61	0.040	3.00	80
In-house 99% C.L. (+/- % mean)	27.5	36.5	15.7	37.1	28.6	30.4	18.3	43.9	25.0	16.7	16.7

3.4 Within-batch data variability

Two RSCMP site samples were analysed as blind within-batch duplicates for metals and PSD (mud content, % <63 µm). Results are tabulated in Table 3-6.

The relative percentage differences (RPDs) between duplicates were mostly <15 per cent. Mercury (Hg) had poorer agreement between duplicates (RPD 33 per cent) for one sample (Whangapouri), but not for the other sample (DoC Island Mud, RPD 3.4 per cent). All duplicate results, apart from the Whangapouri Hg result, were within the USEPA (2010) Measurement Quality Objective (MQO) limit for acceptable agreement between within-batch replicates (a 30 per cent difference).

Differences between blind within-batch duplicates for 2 M HCl extractable metals (<63 µm fraction) ranged from 0.1–11 per cent.

Apart from Hg, differences between blind within-batch duplicates for total recoverable metals (<500 µm fraction) ranged from 0.1–21 per cent.

Agreement between blind duplicates for mud content (% <63 µm) was good; 1.5 per cent and 5.8 per cent for the two samples analysed.

Table 3-6 Within-batch variation for metals and mud content in RSCMP samples submitted to the laboratory as blind duplicates.
Differences between duplicates (expressed as relative percentage difference; RPD) are colour coded: Green <15%, Amber 15–30%, Red >30%.

		Extractable metals (<63 µm)			Total Recoverable Metals (<500 µm)					
Site	Rep	Cu	Pb	Zn	As	Cu	Pb	Hg	Zn	% mud
Whangapouri	2	6.94	13.9	67.3	10.4	5.17	9.66	0.040	47.7	44.8
	WB	7.72	15.0	72.4	11.8	6.36	11.0	0.056	57.2	45.4
difference (mg/kg)		0.78	1.1	5.0	1.4	1.20	1.31	0.016	9.6	0.7
RPD (%)		10.6	7.9	7.2	12.5	20.7	12.7	33.4	18.3	1.5
Doc Island Mud	2	6.12	12.3	62.9	9.19	4.10	7.63	0.033	47.4	31.3
	WB	5.96	12.3	61.1	9.53	4.10	7.52	0.032	48.7	33.1
difference (mg/kg)		-0.16	0.0	-1.8	0.34	0.01	-0.11	-0.001	1.3	1.9
RPD (%)		2.6	0.1	2.9	3.7	0.1	1.5	3.4	2.7	5.8

3.5 Bulk Reference Sediment results

Bulk Reference Sediment (BRS) sample analysis consisted of:

- Three samples from each of the sandy Meola Outer and muddy Middlemore sites, both frozen and freeze-dried forms, were analysed for metals. The results for metals are summarised in section 3.5.1; and
- Three samples (frozen form only) from each of the Middlemore and Meola Outer sites were analysed for particle size distribution (PSD). The results for PSD are summarised in section 3.5.2.

Single Site Reports (SSRs) for the BRS samples have been updated with the 2015 results and provided separately to Auckland Council. Copies of the SSRs can be obtained from the Research and Evaluation Unit (RIMU), Auckland Council.

3.5.1 Metals

BRS metals analysis results from the June 2015 sample batch are summarised in Table 3-7. A comparison of the June 2015 BRS results with those obtained in earlier RSCMP monitoring rounds in November 2011, 2012, and 2013 is summarised in Table 3-8 and Table 3-9, and shown graphically in Figure 3-4 to Figure 3-6.

The BRS metals data for June 2015 had within-batch variability (CVs, N = 3) of 1–6.8 per cent for extractable metals (<63µm), and 0.9–24 per cent for total recoverable metals (<500µm). The variability for total recoverable Hg in the sandy Meola Outer BRS (CV of 24 per cent) was markedly higher than for other analytes.

For the primary monitoring metal contaminants (Cu, Pb, and Zn), CVs for total recoverable metals ranged from 0.9–5.1 per cent. These results were similar to previous BRS data.

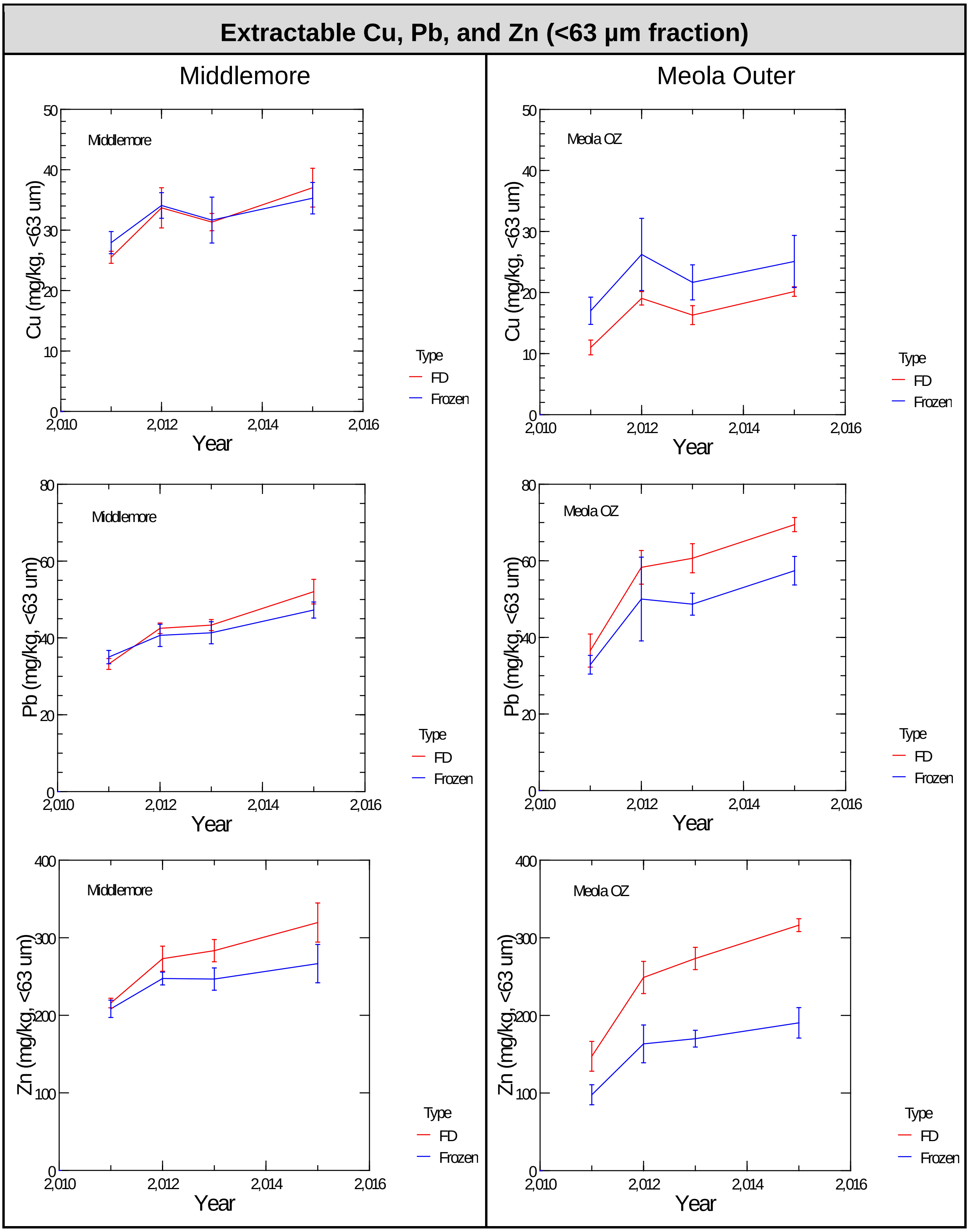


Figure 3-4 Extractable Cu, Pb, and Zn results for frozen and freeze-dried (FD) bulk reference sediments (BRS) analysed with RSCMP samples in 2011, 2012, 2013 and 2015. Bars are means ±95% confidence intervals in the means (N=6 in 2011 and 2012, N=3 in 2013 and 2015).

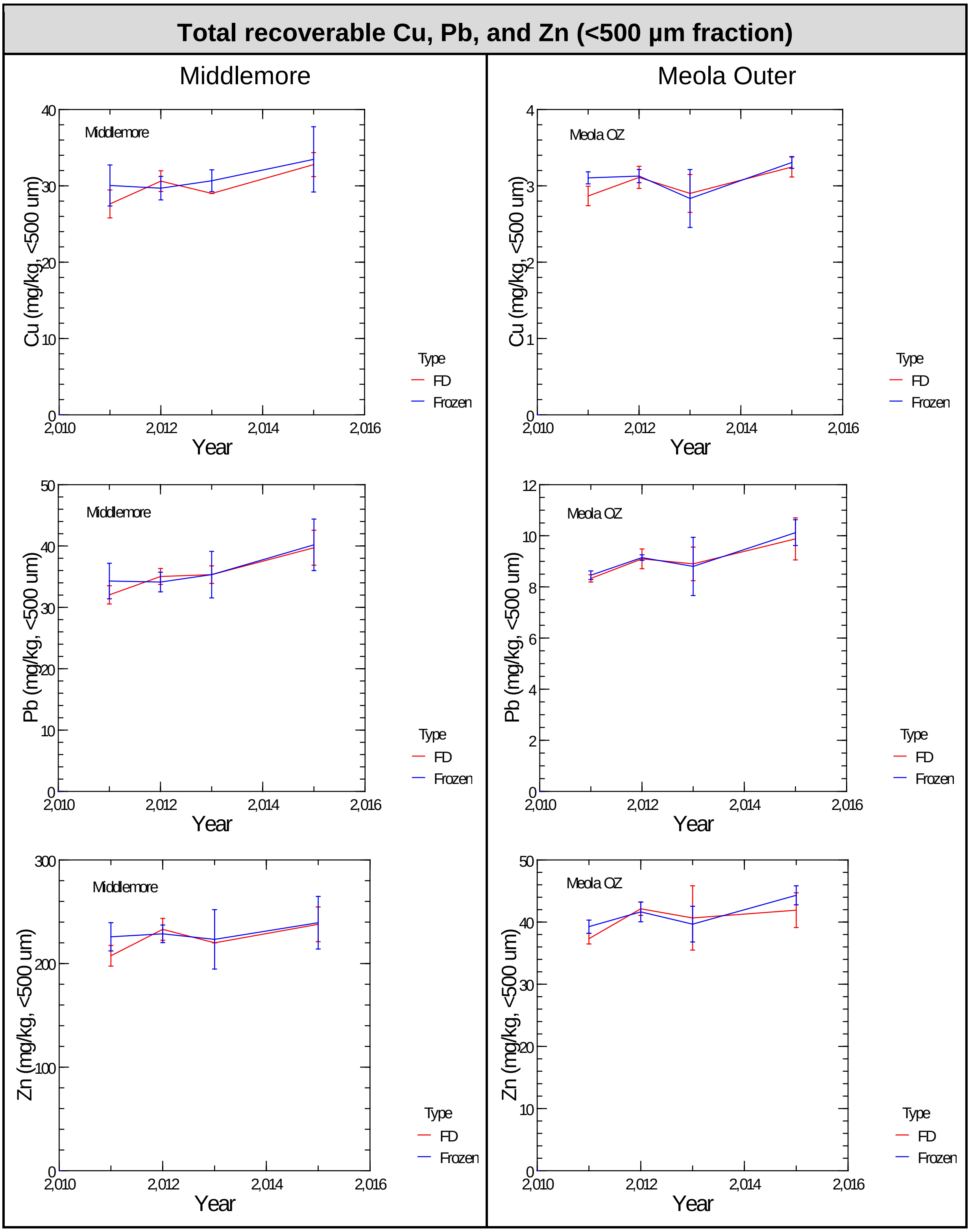


Figure 3-5 Total recoverable Cu, Pb, and Zn results for frozen and freeze-dried (FD) bulk reference sediments (BRS) analysed with RSCMP samples in 2011, 2012, 2013 and 2015. Bars are means ±95% confidence intervals in the means (N=6 in 2011 and 2012, N=3 in 2013 and 2015).

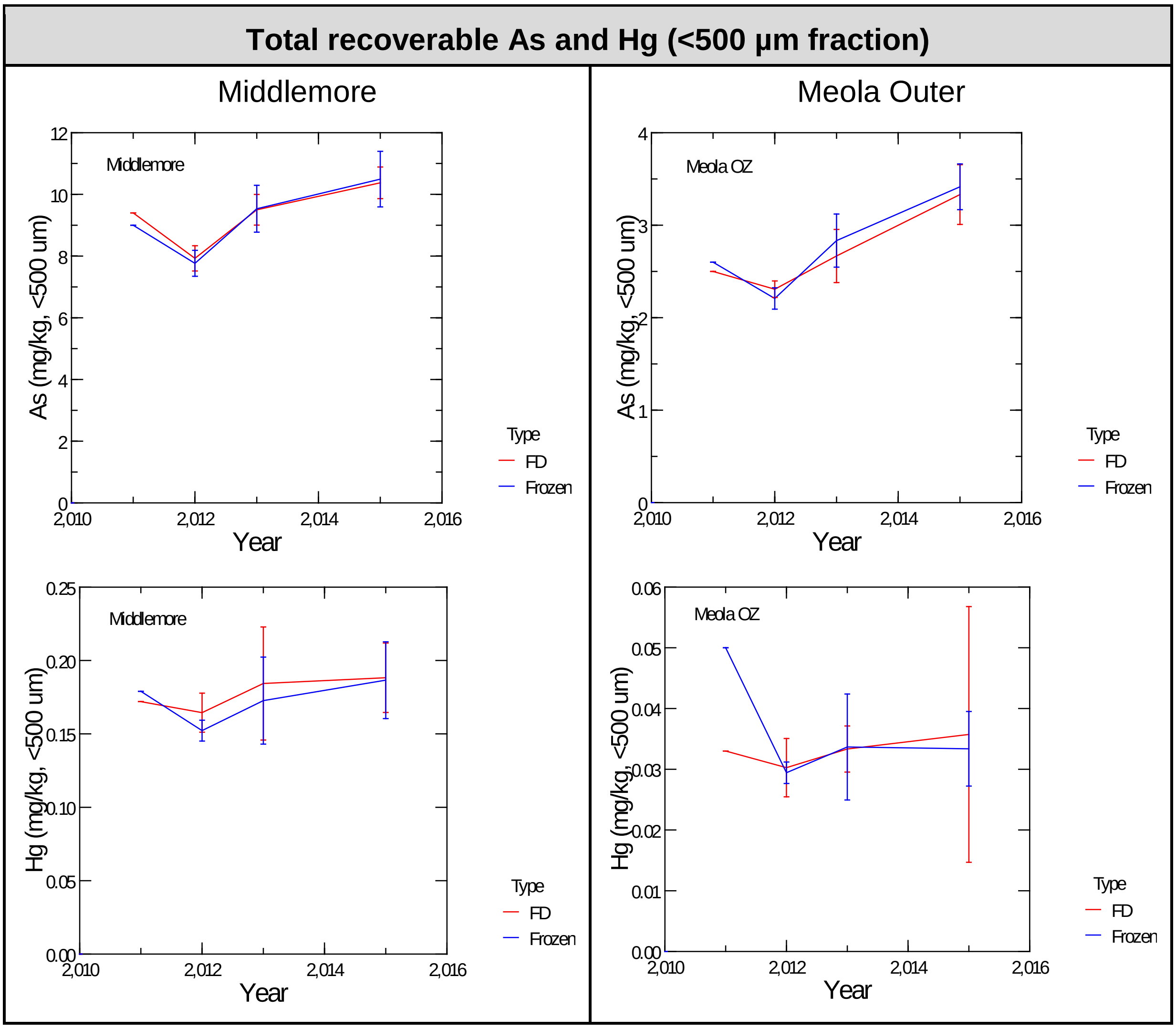


Figure 3-6 Total recoverable As and Hg results for frozen and freeze-dried (FD) bulk reference sediments (BRS) analysed with RSCMP samples in 2011, 2012, 2013 and 2015. Bars are means ±95% confidence intervals in the means (N=1 in 2011, N=6 in 2012, N=3 in 2013 and 2015).

Table 3-7 Summary of Bulk Reference Sediment (BRS) results from June 2015 for metals (mg/kg freeze-dry weight).
Comparison of frozen and freeze-dried (FD) samples – t-test significance Red $p<0.05$, Green $p \geq 0.05$. N = 3 replicates for each sample type.

		Extractable Metals (<63 µm)			Total Metals (<500 µm)							
Site	Type	Cu	Pb	Zn	Cu	Pb	Zn	As	Hg	Cd	Cr	Ni
Middlemore	FD mean (mg/kg)	37.0	52.0	319.5	32.8	39.7	237.9	10.4	0.188	0.165	30.3	12.3
	FD stdev (mg/kg)	1.29	1.29	10.14	0.63	1.15	6.74	0.21	0.010	0.009	1.08	0.47
	FD c.v. (%)	3.5	2.5	3.2	1.9	2.9	2.8	2.0	5.1	5.3	3.6	3.8
	Frozen mean (mg/kg)	35.3	47.3	266.6	33.5	40.2	239.4	10.5	0.187	0.166	30.3	12.4
	Frozen stdev (mg/kg)	1.05	0.84	9.94	1.72	1.69	10.21	0.36	0.011	0.008	0.78	0.38
	Frozen c.v. (%)	3.0	1.8	3.7	5.1	4.2	4.3	3.5	5.6	4.8	2.6	3.1
	difference in means (mg/kg)	-1.7	-4.8	-53.0	0.7	0.5	1.5	0.1	-0.002	0.002	-0.1	0.111
	difference in means (%)	-4.8	-9.6	-18.1	2.1	1.2	0.6	1.1	-0.9	1.1	-0.2	0.9
	p (2-sample t-test)	0.147	0.009	0.003	0.571	0.708	0.841	0.654	0.848	0.797	0.948	0.766
Meola Outer	FD mean (mg/kg)	20.2	69.5	316.2	3.2	9.9	41.9	3.3	0.036	0.068	4.492	2.0
	FD stdev (mg/kg)	0.31	0.74	3.31	0.05	0.33	1.13	0.13	0.008	0.009	0.17	0.13
	FD c.v. (%)	1.6	1.1	1.0	1.6	3.4	2.7	3.9	23.7	13.5	3.8	6.8
	Frozen mean (mg/kg)	25.1	57.4	190.4	3.3	10.1	44.3	3.4	0.033	0.075	4.845	2.0
	Frozen stdev (mg/kg)	1.72	1.50	7.89	0.03	0.20	0.61	0.10	0.002	0.004	0.14	0.16
	Frozen c.v. (%)	6.8	2.6	4.1	0.9	2.0	1.4	2.9	7.4	5.6	2.9	7.9
	difference in means (mg/kg)	4.9	-12.0	-125.9	0.1	0.2	2.4	0.1	-0.002	0.007	0.353	0.079
	difference in means (%)	21.8	-19.0	-49.7	1.8	2.4	5.5	2.5	-6.8	9.5	7.6	3.9
	p (2-sample t-test)	0.034	0.001	0.000	0.182	0.351	0.046	0.428	0.683	0.333	0.052	0.551

Table 3-8 Comparison of median metal concentrations (mg/kg dry weight) and mud content (% <63 µm) in Bulk Reference Sediment (BRS) analysed in June 2015 with results obtained between 2011, 2012, and 2013: Concentration data.

Data are medians, with sample numbers varying between years and analytes. For Cu, Pb, and Zn, N=6 for 2011 and 2012, and N=3 for 2013 and 2015. For As and Hg, N=1 for 2011, N=6 for 2012, and N=3 for 2013 and 2015. For Cd, Cr and Ni, N=1 for 2011, and N=3 for 2013 and 2015 – Cd and Ni were not measured in 2012.

The shading colour reflects the difference between the 2015 and earlier years' results (medians) – Green indicates no significant difference, blue indicates values lower than in 2015, and red shaded values are higher than the 2015 results. Significance determined by Kruskal Wallis test (p<0.05). No shading is given for Total As, Hg, Cd, Cr, and Ni for 2011 because only a single analysis was undertaken for these metals in 2011, and therefore the significance of difference between 2011 and 2015 for these analytes could not be determined.

			Chemistry Processing			Extractable Metals (<63 um)			Total Metals (<500 um)							
BRS Sample	Type	Year	Lab	Method	% Mud	Cu	Pb	Zn	Cu	Pb	Zn	As	Hg	Cd	Cr	Ni
Meola Outer	Freeze dried	2011	Hills	Air dried	-	10.7	35.4	140.2	2.85	8.35	37.5	2.50	0.033	0.061	3.90	1.70
		2012	Hills	Air dried	-	19.0	58.6	243.6	3.12	9.14	42.2	2.31	0.031	-	-	-
		2013	NIWA	Freeze dried	-	16.5	61.0	270.0	2.90	8.80	40.0	2.60	0.033	0.073	4.70	1.70
		2015	NIWA	Freeze dried	-	20.2	69.5	315.7	3.26	10.06	42.2	3.41	0.040	0.073	4.40	1.92
	Frozen	2011	Hills	Air dried	3.03	16.7	33.3	95.7	3.10	8.44	39.2	2.60	0.050	0.067	3.70	1.70
		2012	Hills	Air dried	3.07	27.9	53.4	170.7	3.12	9.15	42.0	2.21	0.030	-	-	-
		2013	NIWA	Freeze dried	2.95	21.0	48.0	172.0	2.80	8.70	39.0	2.90	0.034	0.062	4.40	1.50
		2015	NIWA	Freeze dried	2.79	25.3	58.3	194.2	3.30	10.24	44.4	3.40	0.033	0.075	4.91	2.08
Middlemore	Freeze dried	2011	Hills	Air dried	-	25.8	32.8	216.5	27.4	31.6	204.1	9.40	0.172	0.147	26.0	11.0
		2012	Hills	Air dried	-	33.7	42.5	274.6	31.1	35.2	234.7	8.06	0.164	-	-	-
		2013	NIWA	Freeze dried	-	31.0	43.0	280.0	29.0	35.0	220.0	9.50	0.184	0.160	30.0	11.9
		2015	NIWA	Freeze dried	-	36.4	51.7	319.7	32.6	39.2	234.8	10.27	0.190	0.161	29.7	12.1
	Frozen	2011	Hills	Air dried	66.91	28.4	34.7	211.3	29.6	34.2	225.6	9.00	0.179	0.161	24.0	11.3
		2012	Hills	Air dried	69.16	34.5	40.9	247.4	29.6	33.7	229.6	7.81	0.151	-	-	-
		2013	NIWA	Freeze dried	68.29	32.0	42.0	250.0	31.0	35.0	230.0	9.60	0.169	0.153	26.0	12.1
		2015	NIWA	Freeze dried	66.77	35.0	47.7	263.9	34.2	41.2	242.3	10.62	0.188	0.169	30.6	12.6

Table 3-9 Comparison of metal concentrations and mud content in Bulk Reference Sediment (BRS) analysed in June 2015 with results obtained in 2011, 2012, and 2013: Relative Percentage Differences (RPDs) between annual medians.

Data are Relative Percentage Differences (RPDs) between the 2015 median concentrations and the 2011, 2012, and 2013 medians. Sample numbers vary between years and analytes. For Cu, Pb, and Zn, N=6 for 2011 and 2012, and N=3 for 2013 and 2015. For As and Hg, N=1 for 2011, N=6 for 2012, and N=3 for 2013 and 2015. For Cd, Cr and Ni, N=1 for 2011, and N=3 for 2013 and 2015 – Cd and Ni were not measured in 2012.

As for Table 3-8, the shading colour reflects the difference between the 2015 and earlier years' results – Green indicates no significant difference, blue indicates values lower than in 2015, and red shaded are higher than the 2015 results (Kruskal Wallis test, $p<0.05$). Unshaded values where no significance test could be undertaken (see Table 3-8). The **bolded red values indicate RPDs >±30%**, which exceed the maximum allowable RPD between duplicates recommended by USEPA (2010).

BRS Sample	Type	Year	Chemistry Processing		% Mud	Extractable Metals (<63 um)			Total Metals (<500 um)							
			Lab	Method		Cu	Pb	Zn	Cu	Pb	Zn	As	Hg	Cd	Cr	Ni
Meola Outer	Freeze dried	2011	Hills	Air dried	-	**-61.3**	**-64.8**	**-77.0**	-13.3	-18.5	-11.8	**-30.7**	-20.4	-17.8	-12.1	-12.1
		2012	Hills	Air dried	-	-6.2	-17.0	-25.8	-4.4	-9.5	0.0	**-38.3**	-28.1			
		2013	NIWA	Freeze dried	-	-20.3	-13.0	-15.6	-11.6	-13.3	-5.4	-26.8	-20.4	0.1	6.5	-12.1
		2015	NIWA	Freeze dried	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Frozen	2011	Hills	Air dried	8.01	**-41.0**	**-54.4**	**-67.9**	-6.2	-19.2	-12.5	-26.7	**41.9**	-10.9	-28.1	-20.1
		2012	Hills	Air dried	9.38	9.7	-8.6	-12.9	-5.7	-11.2	-5.6	**-42.4**	-8.6			
		2013	NIWA	Freeze dried	5.40	-18.7	-19.3	-12.1	-16.4	-16.2	-13.0	-15.9	3.9	-18.7	-10.9	**-32.4**
		2015	NIWA	Freeze dried	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Middlemore	Freeze dried	2011	Hills	Air dried	-	**-34.2**	**-44.7**	**-38.5**	-17.4	-21.3	-14.0	-8.9	-9.9	-9.1	-13.4	-9.8
		2012	Hills	Air dried	-	-7.8	-19.6	-15.2	-4.7	-10.7	-0.1	-24.1	-14.8			
		2013	NIWA	Freeze dried	-	-16.1	-18.4	-13.2	-11.8	-11.3	-6.5	-7.8	-3.2	-0.7	0.9	-2.0
		2015	NIWA	Freeze dried	-	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Frozen	2011	Hills	Air dried	0.21	-21.0	**-31.4**	-22.1	-14.3	-18.5	-7.1	-16.5	-4.8	-5.0	-24.2	-10.9
		2012	Hills	Air dried	3.52	-1.3	-15.2	-6.5	-14.4	-20.0	-5.4	**-30.6**	-21.9			
		2013	NIWA	Freeze dried	2.26	-8.9	-12.7	-5.4	-9.7	-16.2	-5.2	-10.1	-10.6	-10.1	-16.3	-4.0
		2015	NIWA	Freeze dried	0.00	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Significant differences (as determined by Kruskal Wallis test, $p<0.05$) between the median concentrations obtained in 2015 and the previous years were recorded for many analyses, with almost all the 2011–2013 results being lower than those obtained in 2015 (Table 3-8). The magnitude of the differences in median concentrations between the years was generally <30 per cent (a recommended maximum RPD for duplicate results; USEPA 2010), as summarised in Table 3-9.

Extractable metals (<63µm fraction) in 2011 were the analytes most often >30 per cent different (lower) than the 2015 results. Extractable metals in 2012 and 2013 were mostly within 20 per cent of the 2015 values, the exception being Zn in the freeze-dried BRS from Meola Outer in 2012 (-26 per cent).

The data showed generally increasing “trends” (variation over time) for metals (Table 3-10). Mann Kendall trend tests gave trends (Sen Slopes) ranging from 1 per cent of the median concentration per year (Total Cu in Meola Outer frozen BRS) to 21 per cent per year (for extractable Zn in Meola Outer freeze-dried BRS), the trend values depending somewhat on whether the “all data” or “annual median” trend analysis approach was used (see footnote to Table 3-10).

The “trends” were larger for extractable Cu, Pb, and Zn (5–21 per cent per year) than for total recoverable Cu, Pb, and Zn (1–6 per cent per year), particularly in the sandy Meola Outer BRS, which has a low mud content (% <63µm of ca. 3 per cent).

Differences between the freeze-dried and frozen BRS sample results were observed for extractable metals in the <63µm fraction (Figure 3-4). Extractable Pb and Zn were higher in the freeze-dried samples for both the sandy Meola Outer and muddy Middlemore sediments, and Cu was higher in the frozen sample for Meola Outer (but not for the muddy Middlemore sediment). The effect was most marked for the sandy (i.e. low proportion of <63µm material) Meola Outer BRS.

Total recoverable metals results were essentially the same in both freeze-dried and frozen BRS samples (Figure 3-5 and Figure 3-6).

Table 3-10 Trends (Sen Slopes, given as % of median concentrations per year) in metals and mud content from BRS analyses conducted in 2011, 2012, 2013, and June 2015.
A. Results from Mann Kendall trend test using "all data" option, where N varied between analyte and year: for Cu, Pb, and Zn, N=6 in 2011 and 2012, and N=3 in 2013 and 2015. For As and Hg, N=1 in 2011, 6 in 2012, and 3 in 2013 and 2015. For mud content N=3 in each year. Red values are significant (Mann Kendall test, $p<0.05$).

			Extractable Metals (<63 µm)			Total Metals (<500 µm)				
BRS Sample	Type	% Mud	Cu	Pb	Zn	Cu	Pb	Zn	As	Hg
Meola Outer	Freeze dried	-	16.0	17.3	21.2	3.3	4.6	3.5	16.0	6.1
	Frozen	-3.1	11.1	14.9	17.3	1.0	5.2	3.1	18.7	3.2
Middlemore	Freeze dried	-	10.1	13.0	11.6	4.3	6.2	4.0	9.9	4.8
	Frozen	-0.9	6.4	8.9	6.9	2.8	3.8	1.0	11.8	7.2

B. Results from Mann Kendall trend test using "annual median" option, where N =1 (the median) for each year, total N=4 (2011, 2012, 2013, and 2015). Red values are significant (Mann Kendall test, $p<0.05$).

			Extractable Metals (<63 µm)			Total Metals (<500 µm)				
BRS Sample	Type	% Mud	Cu	Pb	Zn	Cu	Pb	Zn	As	Hg
Meola Outer	Freeze dried	-	15.2	13.3	16.3	2.9	4.9	3.2	10.9	7.1
	Frozen	-3.0	10.1	14.3	13.0	1.2	5.5	3.1	10.7	-9.0
Middlemore	Freeze dried	-	8.9	12.4	10.5	3.9	5.5	3.7	4.2	3.2
	Frozen	-0.7	5.7	9.0	5.1	4.5	4.9	1.9	6.4	4.6

Notes: The trends summarised in Table 3-10 have been assessed in two ways because of the variable numbers of samples analysed each year. The data given in table A) are from the Mann Kendall trend test using all the data from each year. The values in table B) are from annual median data only, to remove potential bias caused by unequal sample numbers across the years.
The results show that nearly all trends are significant when using "all data", but relatively few when using the "annual median" data (for which N is much smaller, N=4 years). However, the "all data" approach is likely to be biased by variable sample numbers in each year (see above).
The two approaches give trends of generally similar magnitude (and direction) except for total Hg in the Meola Outer frozen BRS (3.2% per year using all data, but -9.0% per year using annual medians). This is because of an unusually high N=1 result in 2011 – this had little weight in the "all data" approach, but equal weight to other years in the "annual median" approach.

Overall, the BRS data results obtained to date indicate that:

- A realistic target for agreement between annual median concentrations using current sample processing and analysis protocols is approximately 20–30 per cent. Further rounds of BRS analyses are required to refine this target.
- Results for extractable metals (Cu, Pb, and Zn in the <63µm fraction) have not been consistent between years over the 2011–2015 period, with the data showing generally increasing "trends" in concentrations of between 5 per cent and 21 per cent per year (depending on analyte, form of BRS sample, and trend analysis approach). These changes over time are too large for reliable trend analysis, and suggest that extractable metals analysis is not sufficiently consistent between analytical batches for monitoring of temporal trends. The differences in the results for extractable metals between the frozen and freeze-dried forms of the BRS,

particularly for the sandy Meola Outer BRS, also suggests the method is sensitive to sample type, preparation (e.g. possibly freeze drying), and/or storage, which reduces the suitability of extractable metals for routine monitoring.

- Results for total recoverable metals have been more consistent. There was no difference of any practical importance between the frozen and freeze-dried BRS samples. “Trends” of 1–6 per cent per year for Cu, Pb, and Zn, and 3–7 per cent per year for Hg (excluding the -9 per cent per year result for Meola Outer frozen – see footnote to Table 3-10) have been measured. Total As showed somewhat greater “trends” (4–19 per cent per year). While the trends for total recoverable Cu, Pb, and Zn were smaller than for extractable Cu, Pb, and Zn, the trend values for 2011 to June 2015 were greater than the 1–2 per cent per year trend detection target currently used for the RSCMP. Continued assessment of the BRS results is required to check that the 1–2 per cent per year target is realistically achievable.

If extractable metals analysis is to be continued, the BRS data obtained to date suggest that the frozen BRS may give more consistent results, especially for Pb and Zn. If total recoverable metals are to be used for on-going monitoring, either the freeze-dried or frozen BRS could be used.

The freeze-dried material is more easily stored (no freezer required) and emulates the room temperature storage and physical form used for archived sediments. However, analysis of the freeze-dried BRS involves rewetting with lab deionised water before sample processing (homogenising, sieving, freeze drying), which is not done for field samples.

Frozen BRS samples are analysed exactly as for field samples (no rewetting step is required). However, long-term freezer storage is required.

3.5.2 Particle size distribution

A summary of the June 2015 PSD results is given in Table 3-11, and a comparison of 2011, 2012, 2013, and June 2015 data in Table 3-12 and Figure 3-7.

The BRS results indicate that the sieve/pipette method is giving reproducible “mud content” (% <63µm) results. Variability is low, with CVs of 2.3 per cent for the muddy sediment (Middlemore) and 2.5 per cent for the sandy sediment (Meola Outer). The variability in mud content for the Middlemore BRS was slightly higher in June 2015 than in previous years (Figure 3-7).

Comparison of 2015 results with those from 2011–2013 showed:

- For Middlemore: Mud content (silt + clay fractions) was relatively consistent – means were 66.7 per cent in 2011, 69.1 per cent in 2012, 68.1 per cent in 2013, and 66.1 per cent in 2015. While these differences in mud content were relatively small, the 2012 and 2013 values were significantly higher than the results for 2011 and 2015 (Kruskall Wallis test between medians, $p<0.05$). This reflects the high precision (low within-batch variability) of the PSD analysis method. Substantial differences in the proportions of silt and clay fractions were measured between 2011 and 2012, but much smaller differences between 2012, 2013, and 2015.
- For Meola Outer: Consistent results for all fractions were obtained between years, even for the minor fractions with <2 per cent abundance (Table 3-12). Again, because of the low within-year variability of the analyses, small but significant differences in mud content between the years were recorded, with 2011 and 2012 being slightly higher than 2015 (Kruskall Wallis test between medians, $p<0.05$).

The 2011–2015 data showed trends in mud content (% <63µm) of -3.1 per cent of the median per year for the sandy Meola Outer BRS (significant, Mann Kendall test, $p<0.05$) and -0.9 per cent per year for the higher mud content Middlemore BRS (trend not statistically significant).

Overall, the results obtained to date indicate the sieve/pipette PSD method is providing mud content data with low variability and good year-to-year reproducibility. Continued use of this method is therefore recommended.

Table 3-11 Summary of particle size distribution (PSD) results for Bulk Reference Sediment (BRS) obtained with the June 2015 monitoring sample batch. BRS for PSD are archived in frozen form.

Texture Class	Gravel	Coarse Sand	Medium Sand	Fine Sand	Silt	Clay	% of total sediment		% of <500um fraction
Particle size range	>2000 µm	500-2000 µm	250-500 µm	62.5-250 µm	3.9-62.5 µm	0-3.9 µm	<63 um	<500 um	<63 um
Middlemore:									
MID PS 2	0.00	0.00	0.52	32.30	46.62	20.57	67.18	100.00	67.18
MID PS 24	0.00	0.06	0.50	32.67	46.02	20.75	66.77	99.94	66.81
MID PS 85	0.00	0.13	0.57	34.97	45.03	19.30	64.33	99.87	64.41
mean	0.00	0.06	0.53	33.32	45.89	20.21	66.10	99.94	66.14
s.d.	-	0.06	0.03	1.45	0.80	0.79	1.54	0.06	1.50
c.v. (%)	-	102.84	6.36	4.35	1.74	3.91	2.33	0.06	2.27
Meola Outer:									
MO PS 13	0.96	0.30	0.92	94.97	0.00	2.85	2.85	98.74	2.88
MO PS 36	0.76	0.28	0.96	95.21	1.12	1.68	2.79	98.96	2.82
MO PS 68	0.76	0.23	0.98	95.32	1.36	1.36	2.71	99.01	2.74
mean	0.82	0.27	0.95	95.17	0.82	1.96	2.78	98.90	2.82
s.d.	0.11	0.04	0.03	0.18	0.72	0.79	0.07	0.14	0.07
c.v. (%)	13.79	13.37	2.85	0.19	87.81	40.06	2.42	0.14	2.55

Table 3-12 Summary of particle size distribution (PSD) results for Bulk Reference Sediment (BRS) obtained with the 2011, 2012, 2013, and June 2015 monitoring sample batches. BRS for PSD are archived in frozen form.

		Middlemore: Mud				Meola Outer: Sand			
Class	Particle size range	2011	2012	2013	2015	2011	2012	2013	2015
Gravel	>2000 µm	0.00	0.00	0.03	0.00	0.70	0.72	1.01	0.82
Coarse Sand	500-2000 µm	0.15	0.11	0.17	0.06	0.33	0.31	0.26	0.27
Medium Sand	250-500 µm	0.74	0.52	0.59	0.53	1.13	0.94	0.94	0.95
Fine Sand	62.5-250 µm	32.45	30.29	31.12	33.32	94.83	94.94	94.91	95.17
Silt	3.9-62.5 µm	57.31	50.50	46.08	45.89	1.08	0.91	1.39	0.82
Clay	<3.9 µm	9.35	18.58	22.00	20.21	1.93	2.18	1.48	1.96
"Mud" - % of total sediment <63 um		66.66	69.09	68.09	66.10	3.01	3.09	2.87	2.78
"Mud" - % of <500um fraction <63 um		66.76	69.16	68.23	66.14	3.04	3.12	2.91	2.82

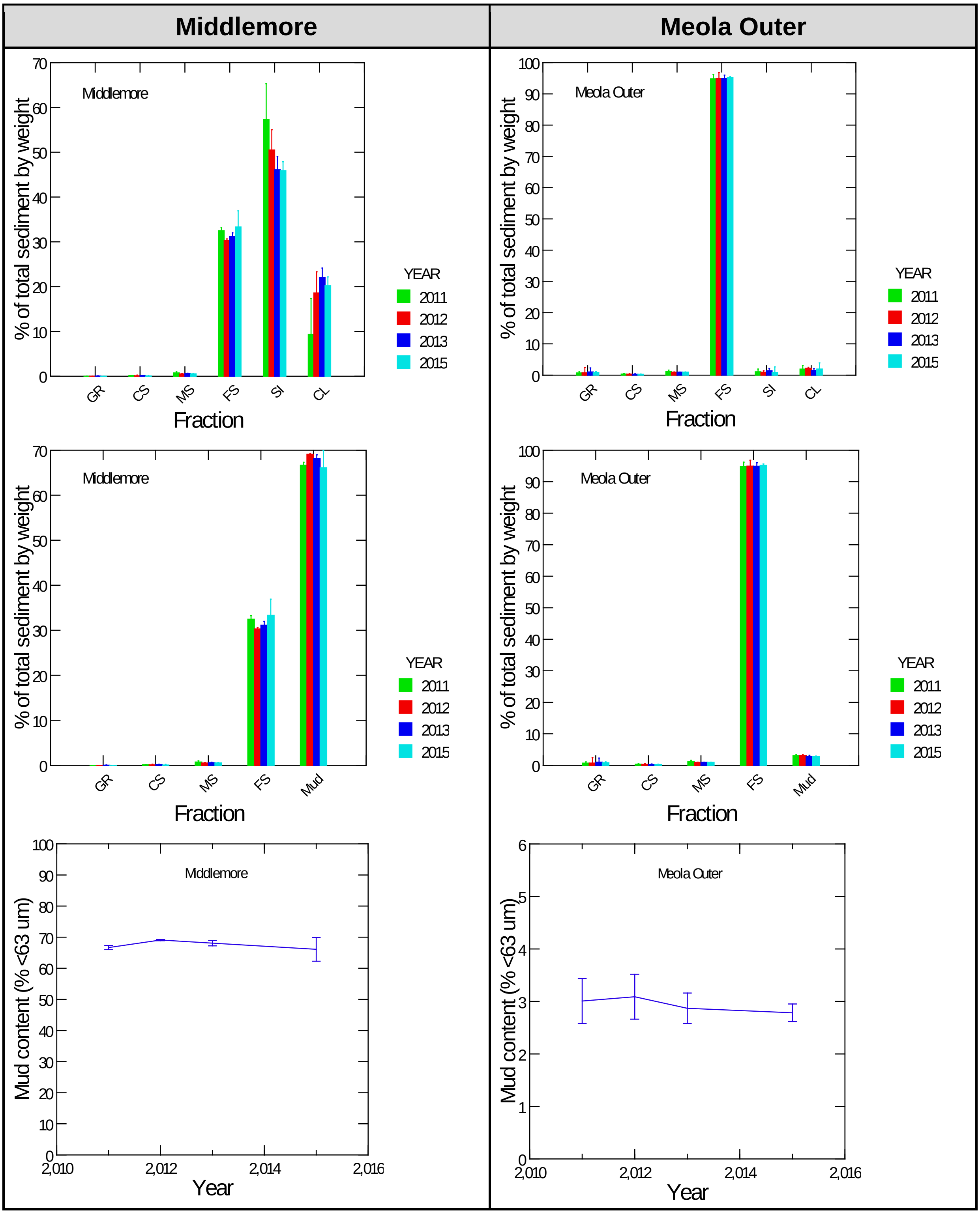


Figure 3-7 Particle size distribution (PSD) results for frozen bulk reference sediments (BRS) analysed with RSCMP samples taken in 2011, 2012, 2013, and June 2015.

Bars are means ±95% confidence intervals in the means (N=3 in each year). The top plots show data for each particle size range (abbreviations given below), while the middle plots combine the silt and clay fractions in to a single “mud” fraction (<63 µm). The bottom plots show changes in mud content (% <63 µm) over time.

GR – gravel (>2 mm), CS – coarse sand (0.5–2 mm), MS – medium sand (0.25–0.5 mm), FS – fine sand (0.063–0.25 mm), SI – silt (3.9–63 µm), CL – clay (<3.9 µm).

3.6 Data quality summary

Table 3-13 summarises the QA information obtained for the June 2015 sample analyses.

The quality assurance data described above indicate that the June 2015 metals data were of variable quality, which was generally consistent with previous RDP/RSCMP results.

Within-batch variation was relatively low, and the data were, on average, reasonably accurate, as shown by the results of the CRM analyses (although, as noted above, the CRM data reflect the accuracy and reproducibility of the digestion and ICP-MS analysis steps rather than the entire analytical method including sample processing (sieving, drying, sub-sampling).

However, the BRS results have confirmed problems with year-to-year consistency for extractable metals (<63µm fraction) data, especially for sandy sediment with low mud fraction content.

The BRS results suggest that extractable metals analysis is not sufficiently robust for reliable trend analysis, where consistent year-to-year (or batch-to-batch) results must be obtained. Extractable metals results were different for frozen and freeze-dried BRS samples, suggesting that the test method may be sensitive to sample processing and/or storage.

Total recoverable metals data have been more consistent over time than extractable metals. However, changes over time for total recoverable metals exceed the QA data stability (trend) target of <±2 per cent per year. Further analyses are needed to assess whether this continues over time after a greater number of years' data have been collected (only N=4 years have been obtained to date).

The PSD data from the BRS analyses conducted in June 2015 showed generally low variability and good comparability with 2011–2013 results. Despite the consistency of the PSD data, a "trend" of -3 per cent per year for mud content (% <63µm) was recorded for the sandy Meola Outer BRS. Additional data is required to assess whether the "<2 per cent per year" trend QA target is realistically achievable for sandy sediments with low mud content. Overall, based on the BRS data collected to date, the PSD data are judged to be reliable.

Overall, the 2015 monitoring data were similar in quality to those obtained in previous years (see annual RDP and RSCMP monitoring reports from 2002 to 2013, available from RIMU, Auckland Council). Given the potential for large batch-to-batch changes in extractable metals results to occur, it seems unlikely that they are suitable for trend assessment in the RSCMP, where changes over time at most sites are small. PSD and total recoverable metals QA results indicate these analyses are more robust, and should provide reliable data for trend assessments. However, on-going QA, in particular for total metals, is still required to validate each year's data.

Table 3-13 Summary of analytical quality assurance results for the June 2015 sample batch

QA Measure	Target	Pass Note Fail	Comments
Blanks	All values less than detection limits	Pass	All < detection limits.
Spike Recoveries	All values within lab QC limits (preferably in 90-110% range)	Pass	Metals: 2 sediments and 2 blanks, extractable Cu, Pb, Zn only. Mean recoveries 92-105%. Lowest recovery 91% (Zn, spiked sediment). Overall slightly low for sediments (by up to ca.10%).
Within Batch blind duplicates	95% of RPDs <30%	Pass	Metals: Two samples analysed in duplicate. All RPDs <20% (mostly <15%), except for 1 Total Hg result (RPD 33%) and 1 Total Cu (RPD 22%). Overall, good WB agreement.
		Pass	Particle size: Two samples analysed in duplicate. RPDs for mud content (% <63 um) were 1.5% and 5.8%. Overall, good WB agreement.
Between Batch blind duplicates	95% of RPDs <30%	N/A	No between batch duplicate samples analysed.
Certified Reference Material	Accuracy: 95% of results within certified range	Pass	Three CRM samples analysed as unknowns for metals. Means within 8% of certified values for total Cu, Pb, Zn, & Hg. Total As ca. 20% high. Individual samples within 10% of reference values, except As (up to 22% high). Variability low - CVs 0.8-8%. Trends over time 2002 to 2015 not significant, except for extractable Cu (0.16 mg/kg/yr, 0.87% per year) and Total Cu (0.14 mg/kg/yr, 0.59% per year).
Lab In-House Reference Material	Temporal stability: Trends over time <1% of median concentration per year.	Pass	Four samples of "QC A3" analysed as unknowns for extractable metals, and two samples for total metals. Variability for extractable metals (CVs) <10%. Total Cu and As both showed one value outside the lab control limits – the lab QA report commented on these results, and based on the other set of QCA3 sample results concluded that the batch were acceptable.
Bulk Reference Sediments:	All results within lab control		
Extractable metals	Within-year variability: 95% of WB CVs <30%.	Pass	Within-year variability meets targets (CVs 1-7%).
	Between-year variability: 95% of between-year RPDs <30%.	Note	2015 results generally higher than in previous years - mostly by <20% compared with 2012 & 2013, but mostly by >30% cf 2011. Between year variation remains a problem.
	Temporal stability: Trends over time <2% of median concentration per year.	Fail	Trends over time 5-21% per year (depending on analyte, sample & assessment method). May be due to "low" 2011 results? N=4 years of data only, so trends very sensitive to low/high results.
Total Recoverable Metals	Within-year variability: 95% of WB CVs <30%.	Pass	Within-year variability meets targets (CVs 1-8% for all metals except one Cd result, CV=14%, and one Hg, CV=24%).
	Between-year variability: 95% of between-year RPDs <30%.	Pass (Cu Pb Zn) Note (As, Hg)	2015 results generally higher than in previous years, but mostly by <20%. All Cu, Pb, and Zn results within 20% of 2015 medians, except one Pb in 2011 (-21%). As & Hg more variable between years (up to 42% difference cf 2015).
	Temporal stability: Trends over time <2% of median concentration per year.	Fail	Trends over time 1-6% per year (depending on analyte, sample & assessment method). Only one result (Zn in Middlemore frozen BRS) was <2% per year. These are smaller than for extractable metals but still exceed the QA data stability target. N=4 years of data only, so trends very sensitive to low/high results. Continued monitoring required.
Particle Size Distribution	Within-year variability: 95% of WB CVs <30%.	Pass	% mud results had low variability (CV, n=3, of 2.3% for Middlemore and 2.5% for Meola Outer).
	Between-year variability: 95% of between-year RPDs <30%.	Pass	2015 results within 9.4% (Meola Outer) and 3.5% (Middlemore) of any of the previous median results for 2011-2013.
	Temporal stability: Trends over time <2% of median concentration per year.	Pass/Note	Trends for % mud for 2011-2015 in Meola Outer were -3.1% per year, and for Middlemore -0.9% per year. Meola Outer mud content is low (ca. 3%) so <2% per year QA target may not be realistic. Data quality for PSD looks very good (consistent, low variability).
OVERALL ASSESSMENT		**Extractable metals not OK**	Extractable metals batch-to-batch variability remains an issue. Need to consider suitability for future trend assessment.
		Total metals Trends, As/Hg require on-going scrutiny	Total recoverable metals generally OK. Watch for year-to-year changes from CRM and BRS results. Trends in BRS results & As/ Hg variability require on-going assessment.
		PSD OK	PSD data look good. Low variability, trends small (although 2%/yr target for sandy samples may be unrealistic).

4.0 New site descriptions

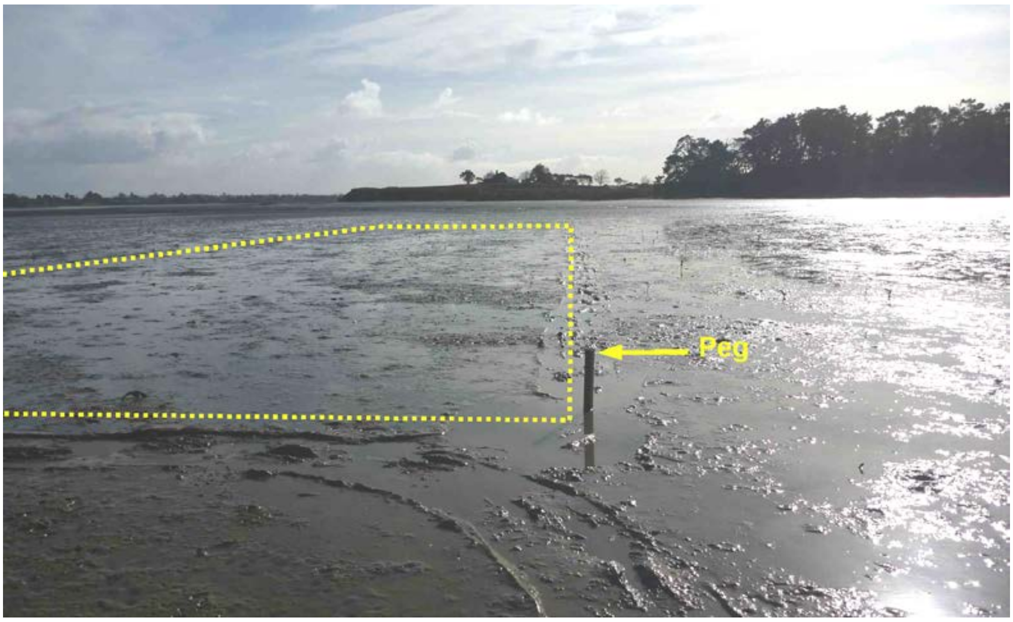
4.1 Bottle Top Bay

Grid Reference: NZTM 1769435 East 5895583 North

Access: From boat ramp car park at the end of Oakland Road. Walk across the rock platform bearing to the right and across the first drainage channel (deep mud).

Notes: Site is located on large smooth mud flat, with long (50 m) side aligned to house on the northern side of the bay (335 deg). 50 x 20m plot. Mud is smooth & knee deep. Bearings from peg are 335 deg along 50 m axis looking north towards the house, and 245 deg across the estuary towards the tallest gum tree on the opposite side of Drury Creek (20m axis). Peg is located at south-eastern corner of plot, driven to ca. 20cm.

Site photos:



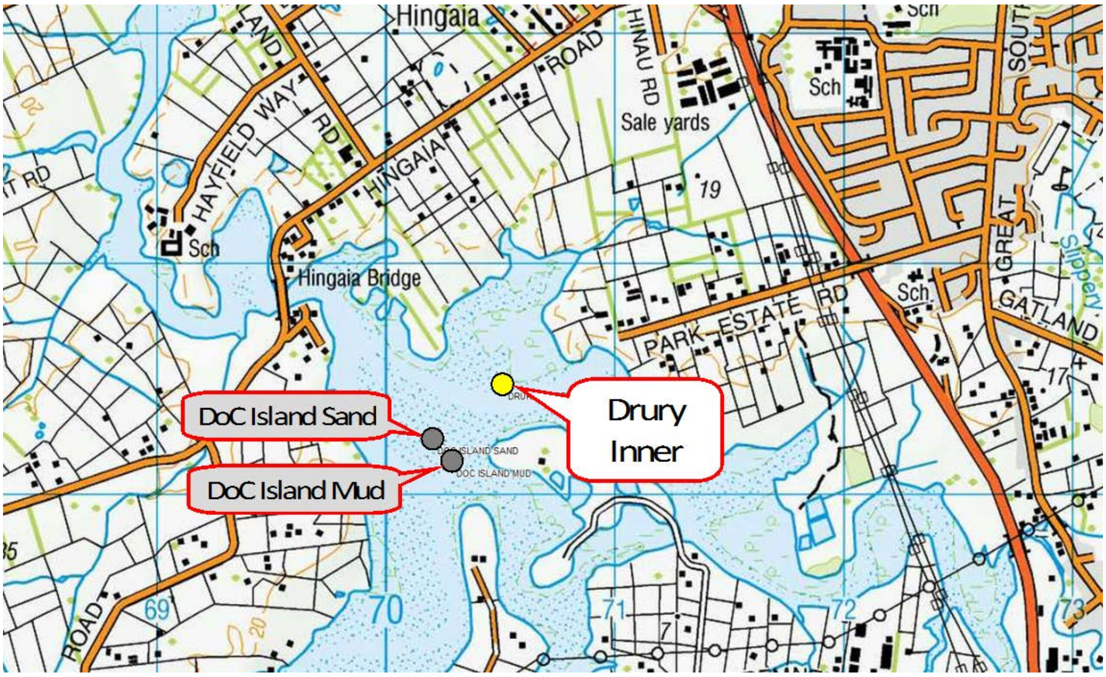
Bottle Top Bay: View from peg northwards along the 50m axis.

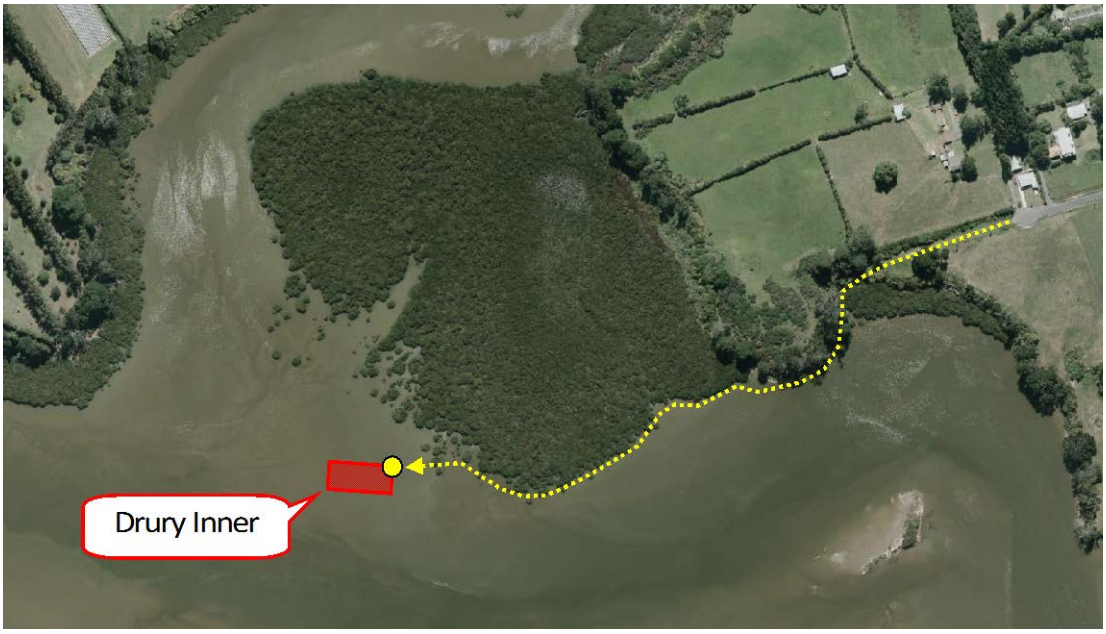
Bottle Top Bay: View from peg looking across Drury Creek estuary (20m axis) towards prominent gum tree on horizon.

4.2 Drury Creek Inner

Grid Reference: NZTM 1770502 East 5893480 North

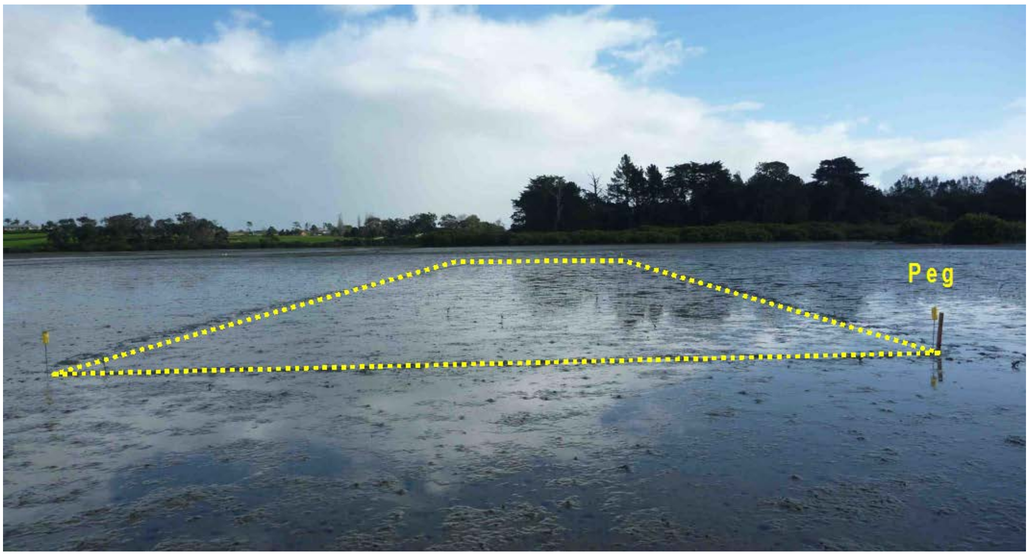
Access: From Park Estate Road. Park at the end. Through gate, follow grass track to estuary edge. Walk around edge of estuary, carefully past the point and onto main channel mud flats. Walk around to site following mangrove edge (mud is shallower). Peg is ca. 45m from mangrove edge on large mud flat.





Notes: Site is on large smooth mud flat. Calf deep, wet mud. 50 x 20m plot. Bearings from peg are 265 deg down the estuary (along 50m axis, parallel to the low tide channel, looking towards tallest of pines), and 165 deg across the estuary towards a prominent pine at end of peninsula (20m axis). Peg is located at north-western corner of plot (upstream landward corner), driven to ca. 20cm).

Site photos:



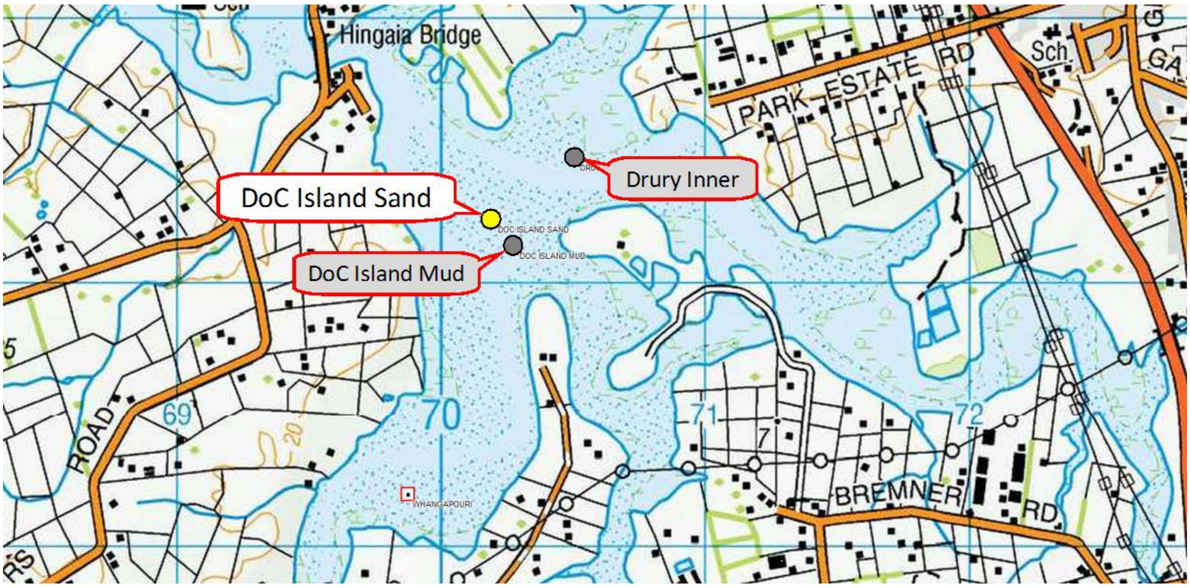
Drury Inner: View from upstream end of the plot, looking downstream along the plot.

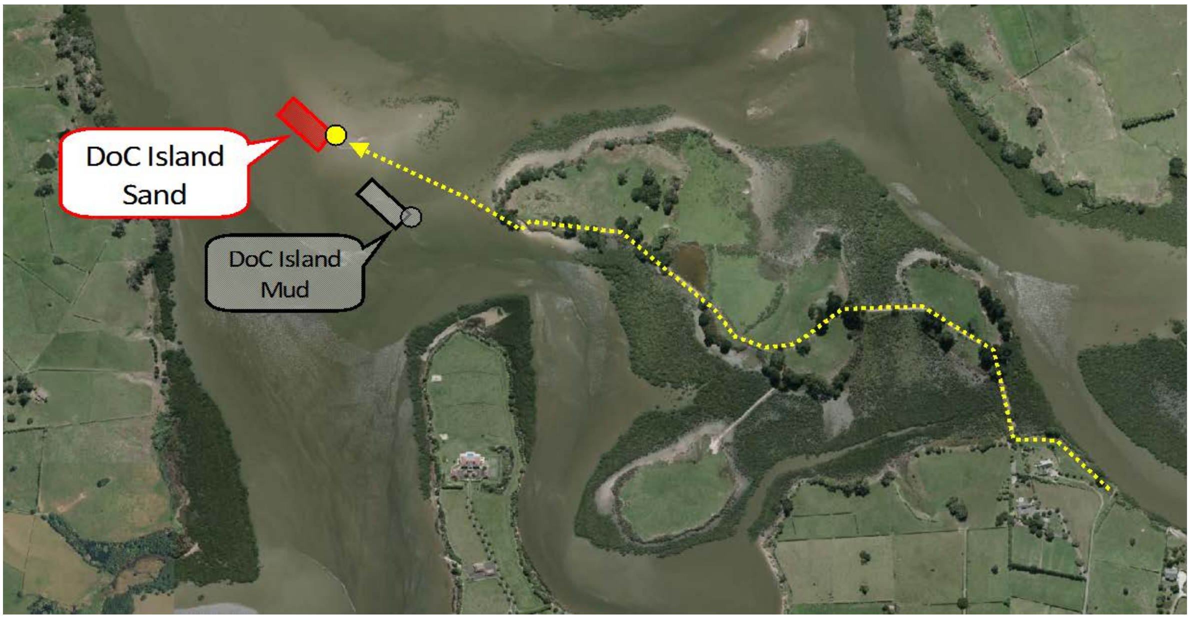
Drury Inner: View from peg across estuary to edge of prominent trees (20m axis)

4.3 DoC Island Sand

Grid Reference: NZTM 1770193 East 5893245 North

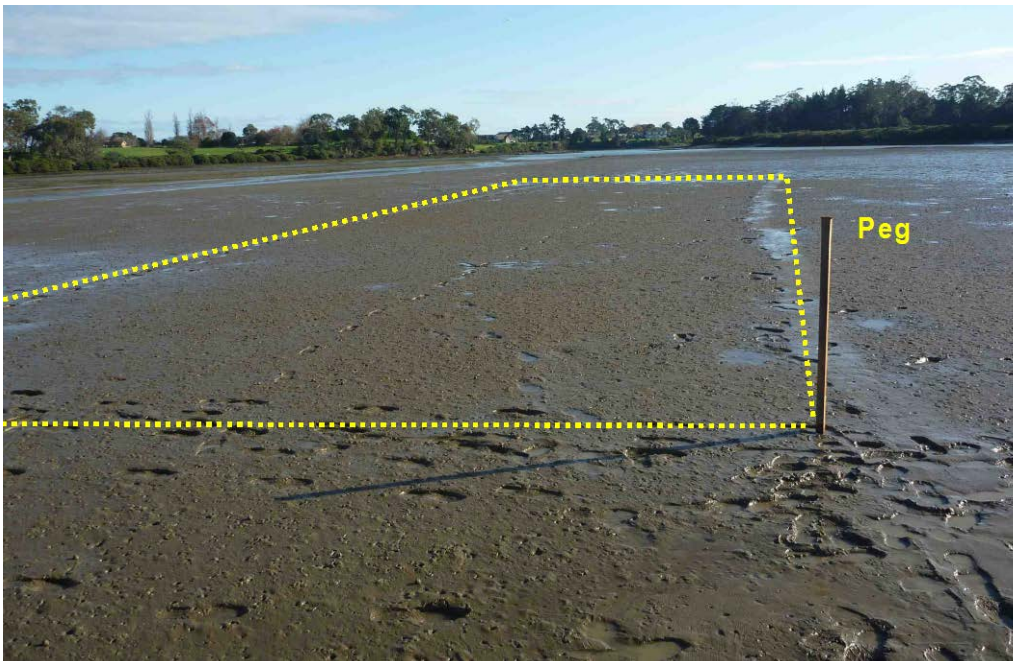
Access: From long shared driveway off Bremner Road. Park at the end where drive swings hard left. Leave note on vehicle to inform locals of purpose and contact details. Through gate, follow grass esplanade around estuary to gate/low fence at gravel access road to DoC Drury Creek Islands Recreation Reserve. Follow track all the way to the end of the reserve peninsula (approx.15min walk. Could drive if access arranged via DoC, probably 4WD best). Drop down to estuary on true left side of peninsula. Walk around edge of estuary/peninsula, then out across mud flats and finally to sandy zone.





Notes: Site is on gently sloping sand flat. Firm, slightly muddy on surface. 50 x 20m plot. Bearings from peg are 330 deg down the estuary (along 50 m axis, looking towards trees right of point), and 225 deg across the estuary (tallest gum tree, 3rd from left across estuary on 20m axis). Peg is located at south-eastern corner of plot (upstream landward corner).

Site photos:



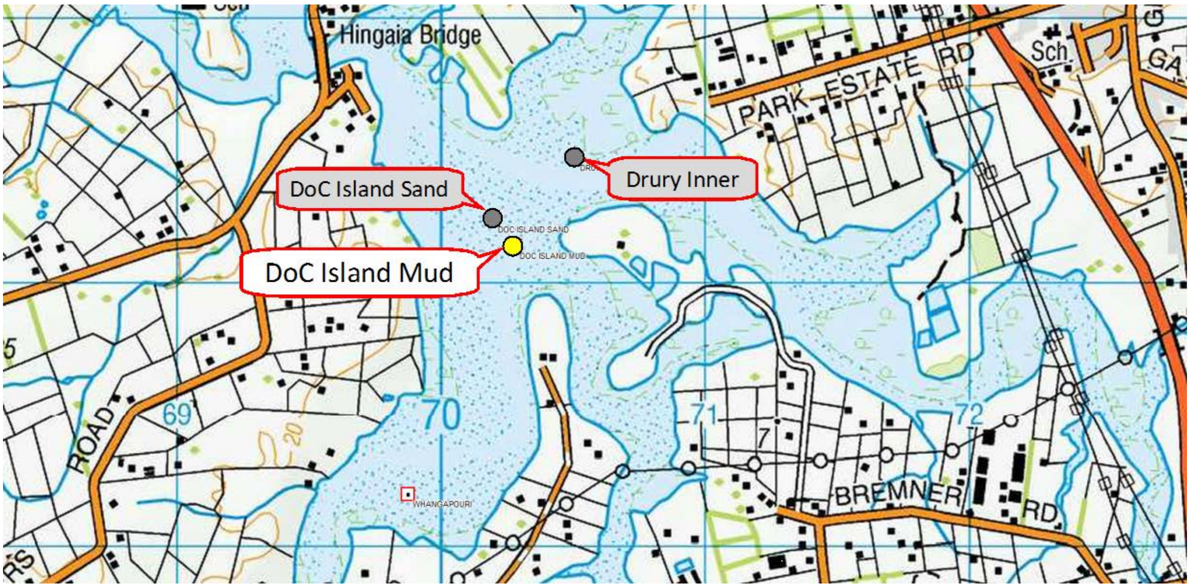
DoC Island Sand: View from upstream end of the plot, looking downstream along the plot.

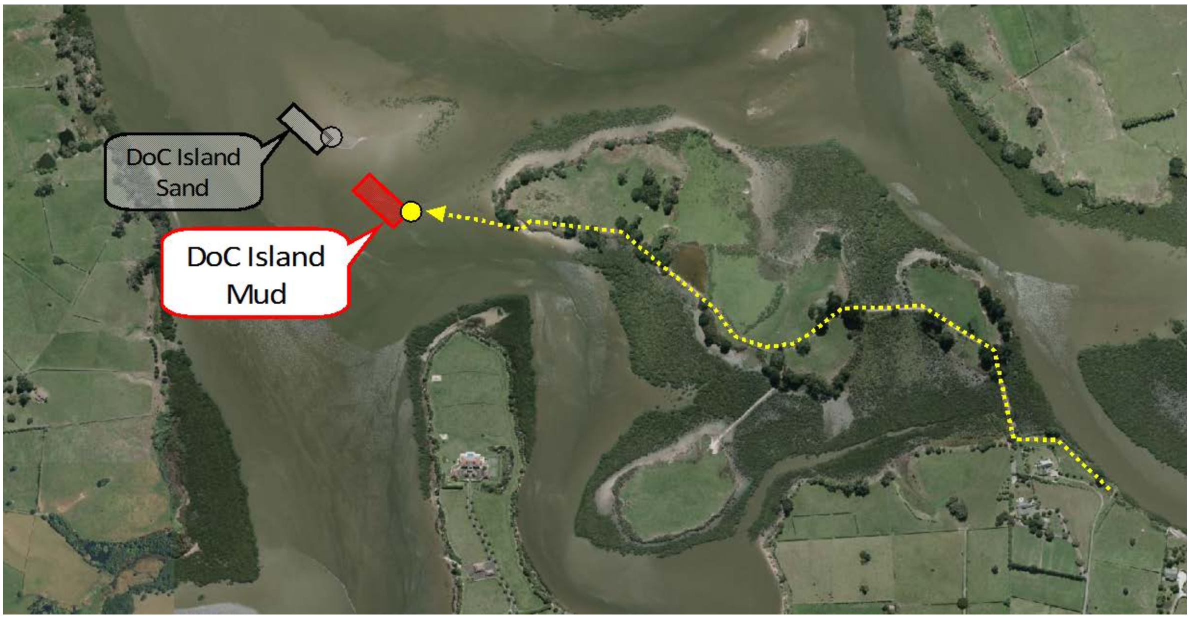
DoC Island Sand: View from peg across estuary to prominent trees (20m axis)

4.4 DoC Island Mud

Grid Reference: NZTM 1770275 East 5893145 North

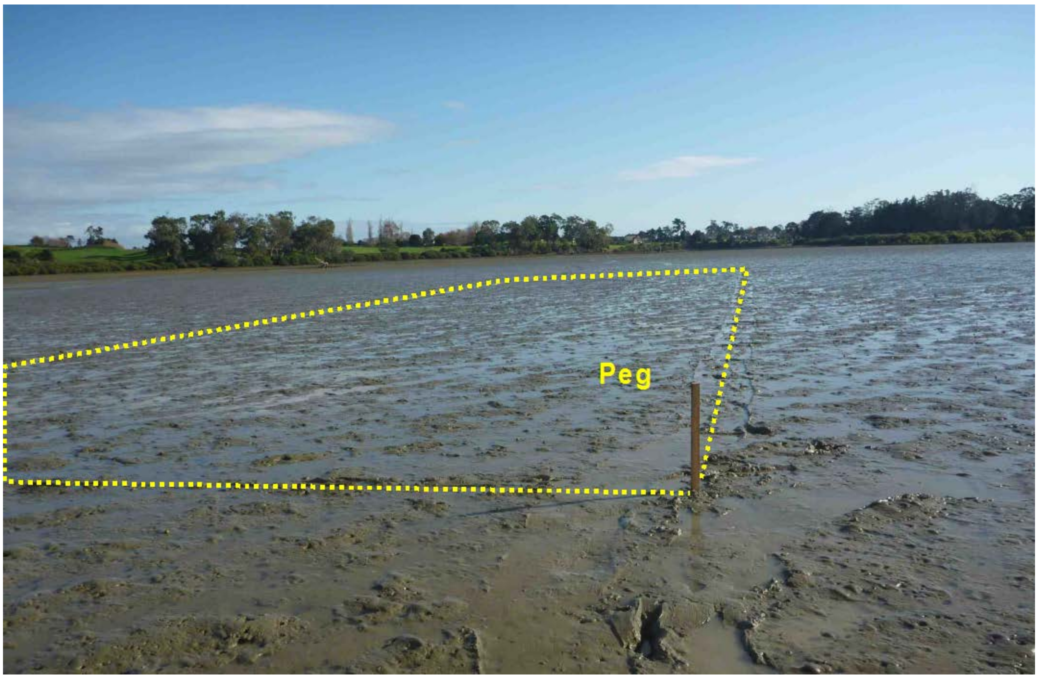
Access: As for DoC Island Sand, from long shared driveway off Bremner Road. Park at the end where drive swings hard left. Leave note on vehicle to inform locals of purpose and contact details. Through gate, follow grass esplanade around estuary to gate/low fence at gravel access road to DoC Drury Creek Islands Recreation Reserve. Follow track all the way to the end of the reserve peninsula (approx.15min walk. Could drive if access arranged via DoC, probably 4WD best). Drop down to estuary on true left side of peninsula. Walk around edge of estuary/peninsula, then out across mud flat.





Notes: Site is on gently sloping mud flat. 50 x 20m plot. Bearings from peg are 305 deg down the estuary (along 50m axis, looking towards trees right of point), and 210 deg across the estuary (spindly Norfolk pine, across estuary on 20m axis). Peg is located at south-eastern corner of plot (upstream landward corner).

Site photos:



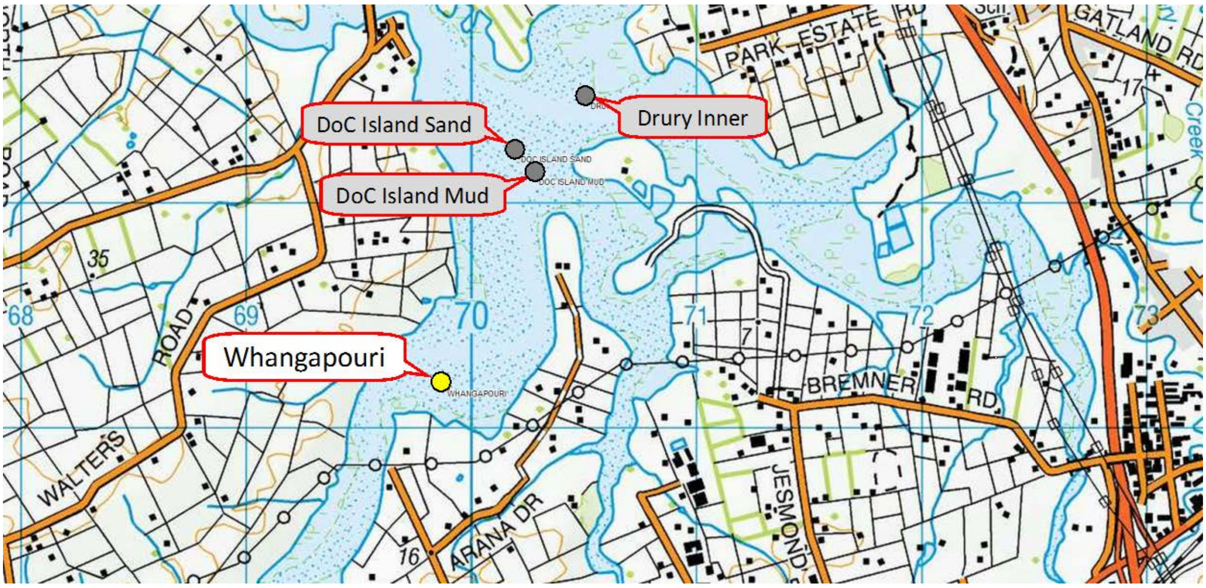
DoC Island Mud: View from upstream end of the plot, looking downstream along the plot.

DoC Island Mud: View from peg across estuary (20m axis)

4.5 Whangapouri

Grid Reference: NZTM 1769867 East 5892204 North

Access: From end of Whangapouri Rd. Leave note on vehicle to inform locals of purpose and contact details. Over fence, follow grass esplanade around estuary, then onto mud flats via cleared mangrove area. Site is downstream of the small island/maimai.



Notes: Site is on smooth mud flat bounded by rough raised areas towards LT channel. Shallow foot to ankle deep mud over hard base. 50 x 20m plot. Bearings from peg are 70 deg down the estuary (along 50m axis, looking towards large house), and 345 deg across the estuary (tallest pine tree across estuary on 20m axis). Peg is located at south-western corner of plot (upstream landward corner).

Site photos:

Whangapouri: View from upstream end of the plot, looking downstream along the plot.

Whangapouri: View from peg across estuary (20m axis)

5.0 Status assessment

A summary of the metal concentrations at the sites sampled in June 2015, and their status relative to Environmental Response Criteria (ERC, ARC 2004), is given in Table 5-1.

All sites had metal concentrations in the ERC Green range (Cu<19mg/kg, Pb<50mg/kg, and Zn<124mg/kg). This is consistent with the dominant current catchment land use, which is largely rural. Drury Inner had generally highest metal concentrations, which reflects the location of the site in the main stem of Drury Creek estuary, whose catchment contains a greater amount of urbanised land than the other estuary arms (Whangapouri and Oira Creeks).

The ERC-Green status of the sites would normally lead to resampling in five years' time. However, there is considerable urban development underway in the Drury catchment, and plans for extensive urban expansion in adjacent areas of the SE Manukau Harbour have been proposed. It is therefore recommended that more frequent monitoring (e.g. 2- or 4-yearly) be considered to ensure that the "pre-development" baseline is well defined and future trends are well characterised.

Note that the designation of the sampling sites' locations as being within "Settling Zones" (SZ) or "Outer Zones" (OZ) has not been undertaken, and therefore the status assessment in Table 5-1 is given for both extractable metals and total recoverable metals. Drury Creek was not included in the regional maps of SZs and OZs (ARC 2002), and it was noted that the estuary was complex, with multiple inputs, arms, and land uses. It is likely, given the large size of the contributing catchments and the muddy nature of the sediments at most sites (except DoC Island Sand), that the sites would be classed as SZs. If so, using current protocols for status assessment (ARC 2004), total metal concentrations would be used for determining the ERC status.

Table 5-1 Metals status of sites sampled in June 2015.
Shading colour indicates Environmental Response Criteria (ERC, ARC 2004) status (green, amber, red). All sites had metal concentrations in the ERC Green range (Cu<19 mg/kg, Pb<50 mg/kg, and Zn<124 mg/kg).

Sample	Replicate	Extractable metals, <63 um			Total Recoverable metals, <500 um		
		Cu	Pb	Zn	Cu	Pb	Zn
Bottle Top Bay	1	5.73	12.7	59.2	8.46	12.8	68.8
Bottle Top Bay	2	5.81	12.5	59.8	8.61	13.3	70.6
Bottle Top Bay	3	5.43	11.8	56.9	8.58	13.2	70.9
Bottle Top Bay	median	5.73	12.5	59.2	8.58	13.2	70.6
Whangapouri	1	6.82	13.4	64.7	5.65	10.5	52.1
Whangapouri	2	6.94	13.9	67.3	5.17	9.7	47.7
Whangapouri	3	6.55	13.0	63.5	5.50	10.2	50.8
Whangapouri	median	6.82	13.4	64.7	5.50	10.2	50.8
Drury Inner	1	7.54	14.4	81.1	8.37	12.4	71.1
Drury Inner	2	8.41	15.8	81.7	8.74	12.9	72.8
Drury Inner	3	7.69	14.7	75.8	7.66	11.7	68.4
Drury Inner	median	7.69	14.7	81.1	8.37	12.4	71.1
Doc Island Mud	1	5.53	11.7	57.7	4.48	8.17	49.6
Doc Island Mud	2	6.12	12.3	62.9	4.10	7.63	47.4
Doc Island Mud	3	6.02	11.9	61.2	4.34	7.88	49.6
Doc Island Mud	median	6.02	11.9	61.2	4.34	7.88	49.6
Doc Island Sand	1	5.24	10.8	58.3	2.43	10.3	28.3
Doc Island Sand	2	5.28	11.2	57.8	2.53	10.7	29.2
Doc Island Sand	3	5.01	11.1	54.7	2.50	10.3	29.3
Doc Island Sand	median	5.24	11.1	57.8	2.50	10.3	29.2

6.0 References

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Appendix A Sediment contaminant data

Metals data for June 2015 monitoring. Concentrations in mg/kg freeze dry weight.

QA sample data are included: Within-batch blind duplicates (WB dup), Certified Reference Material (CRM AGAL10), and Bulk Reference Sediments (BRS).

Note that the data have more significant figures than those given in the lab report (Appendix C). The raw data are provided on request from R J Hill Laboratories and are used for statistical data analysis.

		Extractable metals, <63 um			Total Recoverable metals, <500 um							
Sample	Replicate	Cu	Pb	Zn	Cu	Pb	Zn	As	Cd	Cr	Hg	Ni
Bottle Top Bay	1	5.73	12.7	59.2	8.46	12.8	68.8	12.9	-	-	0.050	-
Bottle Top Bay	2	5.81	12.5	59.8	8.61	13.3	70.6	12.6	-	-	0.035	-
Bottle Top Bay	3	5.43	11.8	56.9	8.58	13.2	70.9	12.6	-	-	0.041	-
Whangapouri	1	6.82	13.4	64.7	5.65	10.5	52.1	11.0	-	-	0.039	-
Whangapouri	2	6.94	13.9	67.3	5.17	9.66	47.7	10.4	-	-	0.040	-
Whangapouri	3	6.55	13.0	63.5	5.50	10.2	50.8	10.9	-	-	0.045	-
Whangapouri	2 WB dup	7.72	15.0	72.4	6.36	11.0	57.2	11.8	-	-	0.056	-
Drury Inner	1	7.54	14.4	81.1	8.37	12.4	71.1	12.7	-	-	0.049	-
Drury Inner	2	8.41	15.8	81.7	8.74	12.9	72.8	13.3	-	-	0.049	-
Drury Inner	3	7.69	14.7	75.8	7.66	11.7	68.4	11.9	-	-	0.045	-
Doc Island Mud	1	5.53	11.7	57.7	4.48	8.17	49.6	9.53	-	-	0.028	-
Doc Island Mud	2	6.12	12.3	62.9	4.10	7.63	47.4	9.19	-	-	0.033	-
Doc Island Mud	3	6.02	11.9	61.2	4.34	7.88	49.6	9.44	-	-	0.038	-
Doc Island Mud	2 WB dup	5.96	12.3	61.1	4.10	7.52	48.7	9.53	-	-	0.032	-
Doc Island Sand	1	5.24	10.8	58.3	2.43	10.3	28.3	15.9	-	-	0.022	-
Doc Island Sand	2	5.28	11.2	57.8	2.53	10.7	29.2	17.7	-	-	0.013	-
Doc Island Sand	3	5.01	11.1	54.7	2.50	10.3	29.3	16.5	-	-	0.023	-
CRM AGAL10	1	20.02	39.8	43.0	24.4	42.4	51.9	20.7	9.36	43.1	11.3	11.7
CRM AGAL10	2	18.63	37.4	41.0	23.3	43.0	52.1	21.0	9.53	47.9	11.4	12.1
CRM AGAL10	3	19.52	40.2	45.6	24.3	45.1	53.2	20.0	9.27	50.7	11.5	12.4
BRS Middlemore Frozen	12	34.42	46.3	258.2	31.5	38.2	228.0	10.1	0.157	29.4	0.175	12.0
BRS Middlemore Frozen	37	36.45	47.7	277.6	34.7	41.2	247.8	10.6	0.173	30.8	0.196	12.6
BRS Middlemore Frozen	42	35.00	47.8	263.9	34.2	41.2	242.3	10.8	0.169	30.6	0.188	12.6
BRS Meola Outer Frozen	4 & 7	23.27	55.7	181.3	3.34	10.2	44.9	3.52	0.070	4.94	0.036	2.18
BRS Meola Outer Frozen	25 & 37	26.68	58.3	195.7	3.30	9.89	43.6	3.32	0.079	4.68	0.031	1.87
BRS Meola Outer Frozen	49 & 60	25.32	58.3	194.2	3.28	10.2	44.4	3.40	0.075	4.91	0.033	2.08
BRS Middlemore Freeze Dried	1	36.16	50.9	309.3	33.5	41.0	245.6	10.6	0.175	31.6	0.197	12.8
BRS Middlemore Freeze Dried	2	36.42	51.7	319.7	32.2	38.9	233.2	10.2	0.161	29.7	0.178	11.9
BRS Middlemore Freeze Dried	3	38.51	53.5	329.6	32.6	39.2	234.8	10.3	0.158	29.7	0.190	12.1
BRS Meola Outer Freeze Dried	1 & 2	20.43	70.2	313.2	3.29	10.1	42.2	3.41	0.073	4.38	0.040	1.86
BRS Meola Outer Freeze Dried	3 & 4	20.23	69.5	315.7	3.26	10.1	42.9	3.41	0.073	4.69	0.026	2.11
BRS Meola Outer Freeze Dried	5 & 6	19.81	68.7	319.8	3.19	9.50	40.7	3.18	0.057	4.40	0.041	1.92

Appendix B Particle size distribution data

Sediment particle size distribution (PSD) data obtained for a composite surface (0–2 cm) sample per site. Samples were analysed by NIWA (Hamilton) by wet sieving/pipette analysis. The data are weight % for each fraction. Further details can be obtained from NIWA, Hamilton.

QA sample data are included: Within-batch blind duplicates (WB dup) and Bulk Reference Sediments (BRS).

Site	Gravel > 2 mm	Coarse Sand 0.5 - 2 mm	Medium Sand 0.25 - 0.5 mm	Fine Sand 0.063 - 0.25 mm	Silt 3.9 - 63 µm	Clay < 3.9 µm
Bottle Top Bay	0.00	0.06	0.06	20.08	67.41	12.40
DoC Island Mud	0.00	0.97	3.41	64.35	24.01	7.26
DoC Island Sand	0.59	7.86	11.90	62.64	12.00	5.00
Drury Inner	0.00	0.10	0.70	46.52	40.18	12.50
Whangapouri	0.00	0.28	2.35	52.59	34.97	9.82
DoC Island Mud WB Dup	0.13	0.71	2.91	63.12	24.21	8.92
Whangapouri WB Dup	0.00	0.43	2.39	51.74	36.92	8.52
BRS Middlemore Rep 1 (PS 2)	0.00	0.00	0.52	32.30	46.62	20.57
BRS Middlemore Rep 2 (PS 24)	0.00	0.06	0.50	32.67	46.02	20.75
BRS Middlemore Rep 3 (PS 85)	0.00	0.13	0.57	34.97	45.03	19.30
BRS Meola Outer Rep 1 (PS 13)	0.96	0.30	0.92	94.97	0.00	2.85
BRS Meola Outer Rep 2 (PS 36)	0.76	0.28	0.96	95.21	1.12	1.68
BRS Meola Outer Rep 3 (PS 68)	0.76	0.23	0.98	95.32	1.36	1.36

Appendix C R J Hill Laboratories report

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ANALYSIS REPORT

SPv1

Client:	Diffuse Sources Limited	**Lab No:**	1457377
Contact:	Dr G Mills	**Date Registered:**	31-Jul-2015
	C/- Diffuse Sources Limited	**Date Reported:**	21-Aug-2015
	PO Box 12476	**Quote No:**	70304
	Chartwell	**Order No:**	
	HAMILTON 3248	**Client Reference:**	DSL RSCMP 2014
		Submitted By:	Dr G Mills

Sample Type: Sediment

	Sample Name:	OA184/1 [<63um]	OA184/2 [<63um]	OA184/3 [<63um]	OA184/6 [<63um]	OA184/7 [<63um]
	Lab Number:	1457377.1	1457377.2	1457377.3	1457377.4	1457377.5
Extractable Copper*	mg/kg dry wt	5.7	5.8	5.4	6.8	6.9
Extractable Lead*	mg/kg dry wt	12.7	12.5	11.8	13.4	13.9
Extractable Zinc*	mg/kg dry wt	59	60	57	65	67

	Sample Name:	OA184/8 [<63um]	OA184/11 [<63um]	OA184/12 [<63um]	OA184/13 [<63um]	OA184/14 [<63um]
	Lab Number:	1457377.6	1457377.7	1457377.8	1457377.9	1457377.10
Extractable Copper*	mg/kg dry wt	6.6	7.7	7.5	8.4	7.7
Extractable Lead*	mg/kg dry wt	13.0	15.0	14.4	15.8	14.7
Extractable Zinc*	mg/kg dry wt	64	72	81	82	76

	Sample Name:	Agal10 - 1 [<63um]	OA184/17 [<63um]	OA184/18 [<63um]	OA184/19 [<63um]	OA184/22 [<63um]
	Lab Number:	1457377.11	1457377.12	1457377.13	1457377.14	1457377.15
Extractable Copper*	mg/kg dry wt	18.6	5.5	6.1	6.0	6.0
Extractable Lead*	mg/kg dry wt	37	11.7	12.3	11.9	12.3
Extractable Zinc*	mg/kg dry wt	41	58	63	61	61

	Sample Name:	OA184/23 [<63um]	OA184/24 [<63um]	OA184/25 [<63um]	OA184/QA1 [<63um]	OA184/QA2 [<63um]
	Lab Number:	1457377.16	1457377.17	1457377.18	1457377.19	1457377.20
Extractable Copper*	mg/kg dry wt	5.2	5.3	5.0	34	36
Extractable Lead*	mg/kg dry wt	10.8	11.2	11.1	46	48
Extractable Zinc*	mg/kg dry wt	58	58	55	260	280

	Sample Name:	OA184/QA3 [<63um]	Agal10 - 2 [<63um]	OA184/QA4 [<63um]	OA184/QA5 [<63um]	OA184/QA6 [<63um]
	Lab Number:	1457377.21	1457377.22	1457377.23	1457377.24	1457377.25
Extractable Copper*	mg/kg dry wt	35	20	23	27	25
Extractable Lead*	mg/kg dry wt	48	40	56	58	58
Extractable Zinc*	mg/kg dry wt	260	43	181	196	194

	Sample Name:	OA184/QA7 [<63um]	OA184/QA8 [<63um]	OA184/QA9 [<63um]	OA184/QA10 [<63um]	OA184/QA11 [<63um]
	Lab Number:	1457377.26	1457377.27	1457377.28	1457377.29	1457377.30
Extractable Copper*	mg/kg dry wt	36	36	39	20	20
Extractable Lead*	mg/kg dry wt	51	52	53	70	69
Extractable Zinc*	mg/kg dry wt	310	320	330	310	320

	Sample Name:	OA184/QA12 [<63um]	Agal10 - 3 [<63um]	OA184/1 [<500um]	OA184/2 [<500um]	OA184/3 [<500um]
	Lab Number:	1457377.31	1457377.32	1457377.33	1457377.34	1457377.35
Total Recoverable Arsenic	mg/kg dry wt	-	-	12.9	12.6	12.6
Extractable Copper*	mg/kg dry wt	19.8	19.5	-	-	-
Total Recoverable Copper	mg/kg dry wt	-	-	8.5	8.6	8.6
Extractable Lead*	mg/kg dry wt	69	40	-	-	-

Sample Type: Sediment						
Sample Name:		OA184/QA12 [<63um]	Agal10 - 3 [<63um]	OA184/1 [<500um]	OA184/2 [<500um]	OA184/3 [<500um]
Lab Number:		1457377.31	1457377.32	1457377.33	1457377.34	1457377.35
Total Recoverable Lead	mg/kg dry wt	-	-	12.8	13.3	13.2
Total Recoverable Mercury	mg/kg dry wt	-	-	0.050	0.035	0.041
Extractable Zinc*	mg/kg dry wt	320	46	-	-	-
Total Recoverable Zinc	mg/kg dry wt	-	-	69	71	71

Sample Name:		OA184/6 [<500um]	OA184/7 [<500um]	OA184/8 [<500um]	OA184/11 [<500um]	OA184/12 [<500um]
Lab Number:		1457377.36	1457377.37	1457377.38	1457377.39	1457377.40
Total Recoverable Arsenic	mg/kg dry wt	11.0	10.4	10.9	11.8	12.7
Total Recoverable Copper	mg/kg dry wt	5.7	5.2	5.5	6.4	8.4
Total Recoverable Lead	mg/kg dry wt	10.5	9.7	10.2	11.0	12.4
Total Recoverable Mercury	mg/kg dry wt	0.039	0.040	0.045	0.056	0.049
Total Recoverable Zinc	mg/kg dry wt	52	48	51	57	71

Sample Name:		OA184/13 [<500um]	OA184/14 [<500um]	Agal10 - 1 [<500um]	OA184/17 [<500um]	OA184/18 [<500um]
Lab Number:		1457377.41	1457377.42	1457377.43	1457377.44	1457377.45
Total Recoverable Arsenic	mg/kg dry wt	13.3	11.9	21	9.5	9.2
Total Recoverable Cadmium	mg/kg dry wt	-	-	9.4	-	-
Total Recoverable Chromium	mg/kg dry wt	-	-	43	-	-
Total Recoverable Copper	mg/kg dry wt	8.7	7.7	24	4.5	4.1
Total Recoverable Lead	mg/kg dry wt	12.9	11.7	42	8.2	7.6
Total Recoverable Mercury	mg/kg dry wt	0.049	0.045	11.3	0.028	0.033
Total Recoverable Nickel	mg/kg dry wt	-	-	11.7	-	-
Total Recoverable Zinc	mg/kg dry wt	73	68	52	50	47

Sample Name:		OA184/19 [<500um]	OA184/22 [<500um]	OA184/23 [<500um]	OA184/24 [<500um]	OA184/25 [<500um]
Lab Number:		1457377.46	1457377.47	1457377.48	1457377.49	1457377.50
Total Recoverable Arsenic	mg/kg dry wt	9.4	9.5	15.9	17.7	16.5
Total Recoverable Copper	mg/kg dry wt	4.3	4.1	2.4	2.5	2.5
Total Recoverable Lead	mg/kg dry wt	7.9	7.5	10.3	10.7	10.3
Total Recoverable Mercury	mg/kg dry wt	0.038	0.032	0.022	0.013	0.023
Total Recoverable Zinc	mg/kg dry wt	50	49	28	29	29

Sample Name:		OA184/QA1 [<500um]	OA184/QA2 [<500um]	OA184/QA3 [<500um]	Agal10 - 2 [<500um]	OA184/QA4 [<500um]
Lab Number:		1457377.51	1457377.52	1457377.53	1457377.54	1457377.55
Total Recoverable Arsenic	mg/kg dry wt	10.1	10.6	10.8	21	3.5
Total Recoverable Cadmium	mg/kg dry wt	0.157	0.173	0.169	9.5	0.070
Total Recoverable Chromium	mg/kg dry wt	29	31	31	48	4.9
Total Recoverable Copper	mg/kg dry wt	32	35	34	23	3.3
Total Recoverable Lead	mg/kg dry wt	38	41	41	43	10.2
Total Recoverable Mercury	mg/kg dry wt	0.175	0.196	0.188	11.4	0.036
Total Recoverable Nickel	mg/kg dry wt	12.0	12.6	12.6	12.1	2.2
Total Recoverable Zinc	mg/kg dry wt	230	250	240	52	45

Sample Name:		OA184/QA5 [<500um]	OA184/QA6 [<500um]	OA184/QA7 [<500um]	OA184/QA8 [<500um]	OA184/QA9 [<500um]
Lab Number:		1457377.56	1457377.57	1457377.58	1457377.59	1457377.60
Total Recoverable Arsenic	mg/kg dry wt	3.3	3.4	10.6	10.2	10.3
Total Recoverable Cadmium	mg/kg dry wt	0.079	0.075	0.175	0.161	0.158
Total Recoverable Chromium	mg/kg dry wt	4.7	4.9	32	30	30
Total Recoverable Copper	mg/kg dry wt	3.3	3.3	33	32	33
Total Recoverable Lead	mg/kg dry wt	9.9	10.2	41	39	39
Total Recoverable Mercury	mg/kg dry wt	0.031	0.033	0.197	0.178	0.190
Total Recoverable Nickel	mg/kg dry wt	1.9	2.1	12.8	11.9	12.1
Total Recoverable Zinc	mg/kg dry wt	44	44	250	230	230

Sample Name:		OA184/QA10 [<500um]	OA184/QA11 [<500um]	OA184/QA12 [<500um]	Waikawa Site A Rep 1	Agal10 - 3 [<500um]
Lab Number:		1457377.61	1457377.62	1457377.63	1457377.64	1457377.65
Total Recoverable Arsenic	mg/kg dry wt	3.4	3.4	3.2	6.5	20

Sample Type: Sediment

Sample Name:		OA184/QA10 [<500um]	OA184/QA11 [<500um]	OA184/QA12 [<500um]	Waikawa Site A Rep 1	Agal10 - 3 [<500um]
Lab Number:		1457377.61	1457377.62	1457377.63	1457377.64	1457377.65
Total Recoverable Cadmium	mg/kg dry wt	0.073	0.073	0.057	0.016	9.3
Total Recoverable Chromium	mg/kg dry wt	4.4	4.7	4.4	8.5	51
Total Recoverable Copper	mg/kg dry wt	3.3	3.3	3.2	3.2	24
Total Recoverable Lead	mg/kg dry wt	10.1	10.1	9.5	1.92	45
Total Recoverable Mercury	mg/kg dry wt	0.040	0.026	0.041	< 0.010	11.5
Total Recoverable Nickel	mg/kg dry wt	1.9	2.1	1.9	6.0	12.4
Total Recoverable Zinc	mg/kg dry wt	42	43	41	15.3	53

Sample Name:		Waikawa Site A Rep 2	Waikawa Site A Rep 3	Waikawa Moderate Rep 1	Waikawa Moderate Rep 2	Waikawa Moderate Rep 3
Lab Number:		1457377.66	1457377.67	1457377.68	1457377.69	1457377.70
Total Recoverable Arsenic	mg/kg dry wt	5.1	7.1	7.6	7.9	7.2
Total Recoverable Cadmium	mg/kg dry wt	0.016	0.014	0.050	0.043	0.043
Total Recoverable Chromium	mg/kg dry wt	7.9	7.1	15.1	15.7	15.3
Total Recoverable Copper	mg/kg dry wt	2.9	2.6	10.0	10.3	10.3
Total Recoverable Lead	mg/kg dry wt	1.88	1.73	6.4	6.6	6.6
Total Recoverable Mercury	mg/kg dry wt	0.013	< 0.010	0.028	0.030	0.032
Total Recoverable Nickel	mg/kg dry wt	6.2	5.8	10.3	10.9	10.8
Total Recoverable Zinc	mg/kg dry wt	13.9	12.9	44	46	45

Sample Name:		New River Daffodil Bay Rep 1	New River Daffodil Bay Rep 2	New River Daffodil Bay Rep 3		
Lab Number:		1457377.71	1457377.72	1457377.73		
Total Recoverable Arsenic	mg/kg dry wt	5.3	5.6	5.7	-	-
Total Recoverable Cadmium	mg/kg dry wt	0.022	0.029	0.028	-	-
Total Recoverable Chromium	mg/kg dry wt	11.9	12.1	12.9	-	-
Total Recoverable Copper	mg/kg dry wt	5.4	5.7	5.7	-	-
Total Recoverable Lead	mg/kg dry wt	2.7	2.9	2.8	-	-
Total Recoverable Mercury	mg/kg dry wt	0.013	< 0.010	< 0.010	-	-
Total Recoverable Nickel	mg/kg dry wt	8.1	8.4	8.7	-	-
Total Recoverable Zinc	mg/kg dry wt	23	24	24	-	-

SUMMARY OF METHODS

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.

Sample Type: Sediment

Test	Method Description	Default Detection Limit	Sample No
ARC 2M HCl Extraction*	<63µm Sieved Fraction, extracted with 2M HCl. Solid:Liquid 1:50 w/v. ARC Tech Publication No. 47, 1994.	-	1-32
Total Recoverable digestion	Nitric / hydrochloric acid digestion. US EPA 200.2.	-	33-73
Total Recoverable Arsenic	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.2 mg/kg dry wt	33-73
Total Recoverable Cadmium	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.010 mg/kg dry wt	43, 51-73
Total Recoverable Chromium	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.2 mg/kg dry wt	43, 51-73
Extractable Copper*	2M HCl extraction (<63µm fraction), ICP-MS. ARC Tech Publication No. 47, 1994.	1.0 mg/kg dry wt	1-32
Total Recoverable Copper	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.2 mg/kg dry wt	33-73
Extractable Lead*	2M HCl extraction (<63µm fraction), ICP-MS. ARC Tech Publication No. 47, 1994.	0.2 mg/kg dry wt	1-32
Total Recoverable Lead	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.04 mg/kg dry wt	33-73
Total Recoverable Mercury	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.010 mg/kg dry wt	33-73

Sample Type: Sediment			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Total Recoverable Nickel	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.2 mg/kg dry wt	43, 51-73
Extractable Zinc*	2M HCl extraction (<63µm fraction), ICP-MS. ARC Tech Publication No. 47, 1994.	2 mg/kg dry wt	1-32
Total Recoverable Zinc	Dried sample, sieved as specified (if required). Nitric/Hydrochloric acid digestion, ICP-MS, trace level. US EPA 200.2.	0.4 mg/kg dry wt	33-73

These samples were collected by yourselves (or your agent) 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 client.

Ara Heron BSc (Tech)
Client Services Manager - Environmental Division

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QUALITY ASSURANCE REPORT

Client:	Diffuse Sources Limited	**Lab No:**	1457377	QCPv1
Contact:	Dr G Mills	**Date Registered:**	31-Jul-2015	
	C/- Diffuse Sources Limited	**Date Reported:**	21-Aug-2015	
	PO Box 12476	**Quote No:**	70304	
	Chartwell	**Order No:**		
	HAMILTON 3248	**Client Reference:**	DSL RSCMP 2014	
		Submitted By:	Dr G Mills	

Blank QCs

20x Dilution 2M HCl extn Blank PrepWS ARCextn - Environmental Soils by ICP-MS: 9079.30

		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	mg/kg dry wt	< 1.0	-1.0 – 1.0	No
Extractable Lead	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Extractable Zinc	mg/kg dry wt	< 2	-2.0 – 2.0	No

2M HCl extn blank 2 PrepWS ARCextn - Environmental Soils by ICP-MS: 9079.31

		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	mg/kg dry wt	< 1.0	-0.050 – 0.050	No
Extractable Lead	mg/kg dry wt	< 0.2	-0.010 – 0.010	**Yes** #1
Extractable Zinc	mg/kg dry wt	< 2	-0.10 – 0.10	**Yes** #1

20x Dilution 2M HCl extn Blank PrepWS ARCextn - Environmental Soils by ICP-MS: 9086.13

		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	mg/kg dry wt	< 1.0	-1.0 – 1.0	No
Extractable Lead	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Extractable Zinc	mg/kg dry wt	< 2	-2.0 – 2.0	No

2M HCl extn blank 2 PrepWS ARCextn - Environmental Soils by ICP-MS: 9086.14

		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	mg/kg dry wt	< 1.0	-0.050 – 0.050	No
Extractable Lead	mg/kg dry wt	< 0.2	-0.010 – 0.010	**Yes** #1
Extractable Zinc	mg/kg dry wt	< 2	-0.10 – 0.10	**Yes** #1

10x Dilution Digest Blank PrepWS esDig - Env Soils by ICPMS (low level): 2504.10

		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Total Recoverable Cadmium	mg/kg dry wt	< 0.010	-0.010 – 0.010	No
Total Recoverable Chromium	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Total Recoverable Copper	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Total Recoverable Lead	mg/kg dry wt	< 0.04	-0.040 – 0.040	No
Total Recoverable Mercury	mg/kg dry wt	< 0.010	-0.010 – 0.010	No
Total Recoverable Nickel	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Total Recoverable Zinc	mg/kg dry wt	< 0.4	-0.40 – 0.40	No

10x Dilution Digest Blank PrepWS esDig - Env Soils by ICPMS (low level): 2504.11

		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Total Recoverable Cadmium	mg/kg dry wt	< 0.010	-0.010 – 0.010	No
Total Recoverable Chromium	mg/kg dry wt	< 0.2	-0.20 – 0.20	No

10x Dilution Digest Blank PrepWS esDig - Env Soils by ICPMS (low level): 2504.11				
		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Copper	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Total Recoverable Lead	mg/kg dry wt	< 0.04	-0.040 – 0.040	No
Total Recoverable Mercury	mg/kg dry wt	< 0.010	-0.010 – 0.010	No
Total Recoverable Nickel	mg/kg dry wt	< 0.2	-0.20 – 0.20	No
Total Recoverable Zinc	mg/kg dry wt	< 0.4	-0.40 – 0.40	No

10x Dilution Digest Blank PrepWS esDig - Env Soils by ICPMS (low level): 2508.11				
		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Mercury	mg/kg dry wt	< 0.010	-0.010 – 0.010	No

10x Dilution Digest Blank PrepWS esDig - Env Soils by ICPMS (low level): 2508.12				
		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Mercury	mg/kg dry wt	< 0.010	-0.010 – 0.010	No

100x Dilution Digest Blank PrepWS esDig - Env Soils by ICPMS (low level): 2509.11				
		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	< 2	-2.0 – 2.0	No

100x Dilution Digest Blank PrepWS esDig - Env Soils by ICPMS (low level): 2509.12				
		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	< 2	-2.0 – 2.0	No

Sample Spike QCs

2M HCl extn blank Spike PrepWS ARCextn - Environmental Soils by ICP-MS: 9079.32				
		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	%	104	80 – 120	No
Extractable Lead	%	104	80 – 120	No
Extractable Zinc	%	100	80 – 120	No

Spike PrepWS ARCextn - Environmental Soils by ICP-MS: 9079.60				
		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	%	94	80 – 120	No
Extractable Lead	%	93	80 – 120	No
Extractable Zinc	%	91	80 – 120	No

2M HCl extn blank Spike PrepWS ARCextn - Environmental Soils by ICP-MS: 9086.15				
		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	%	100	80 – 120	No
Extractable Lead	%	106	80 – 120	No
Extractable Zinc	%	96	80 – 120	No

Spike PrepWS ARCextn - Environmental Soils by ICP-MS: 9086.23				
		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	%	96	80 – 120	No
Extractable Lead	%	99	80 – 120	No
Extractable Zinc	%	93	80 – 120	No

Reference Material QCs

QC A3 2M HCl PrepWS ARCextn - Environmental Soils by ICP-MS: 9079.33				
		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	mg/kg dry wt	50	37 – 65	No
Extractable Lead	mg/kg dry wt	149	93 – 200	No
Extractable Zinc	mg/kg dry wt	380	350 – 480	No

QC A3 2M HCl PrepWS ARCextn - Environmental Soils by ICP-MS: 9079.63		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	mg/kg dry wt	49	37 – 65	No
Extractable Lead	mg/kg dry wt	128	93 – 200	No
Extractable Zinc	mg/kg dry wt	400	350 – 480	No

QC A3 2M HCl PrepWS ARCextn - Environmental Soils by ICP-MS: 9086.18		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	mg/kg dry wt	54	37 – 65	No
Extractable Lead	mg/kg dry wt	153	93 – 200	No
Extractable Zinc	mg/kg dry wt	410	350 – 480	No

QC A3 2M HCl PrepWS ARCextn - Environmental Soils by ICP-MS: 9086.48		Results	Control Limits	Outside Limit (Yes/No)
Extractable Copper	mg/kg dry wt	52	37 – 65	No
Extractable Lead	mg/kg dry wt	149	93 – 200	No
Extractable Zinc	mg/kg dry wt	460	350 – 480	No

QC A3 PrepWS esDig - Env Soils by ICPMS (low level): 2504.12		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	64	45 – 98	No
Total Recoverable Cadmium	mg/kg dry wt	1.32	1.0 – 1.8	No
Total Recoverable Chromium	mg/kg dry wt	58	48 – 90	No
Total Recoverable Copper	mg/kg dry wt	59	49 – 71	No
Total Recoverable Lead	mg/kg dry wt	137	78 – 200	No
Total Recoverable Mercury	mg/kg dry wt	0.160	0.12 – 0.20	No
Total Recoverable Nickel	mg/kg dry wt	16.4	15 – 21	No
Total Recoverable Zinc	mg/kg dry wt	470	400 – 560	No

QC A3 PrepWS esDig - Env Soils by ICPMS (low level): 2504.68		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	114	45 – 98	**Yes** #2
Total Recoverable Cadmium	mg/kg dry wt	1.47	1.0 – 1.8	No
Total Recoverable Chromium	mg/kg dry wt	89	48 – 90	No
Total Recoverable Copper	mg/kg dry wt	75	49 – 71	**Yes** #2
Total Recoverable Lead	mg/kg dry wt	158	78 – 200	No
Total Recoverable Mercury	mg/kg dry wt	0.168	0.12 – 0.20	No
Total Recoverable Nickel	mg/kg dry wt	19.0	15 – 21	No
Total Recoverable Zinc	mg/kg dry wt	490	400 – 560	No

AGAL-10 QC PrepWS esDig - Env Soils by ICPMS (low level): 2504.69		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	20	16 – 23	No
Total Recoverable Cadmium	mg/kg dry wt	9.4	7.8 – 11	No
Total Recoverable Chromium	mg/kg dry wt	43	27 – 72	No
Total Recoverable Copper	mg/kg dry wt	24	20 – 26	No
Total Recoverable Lead	mg/kg dry wt	43	32 – 48	No
Total Recoverable Mercury	mg/kg dry wt	11.2	10 – 14	No
Total Recoverable Nickel	mg/kg dry wt	11.8	9.5 – 14	No
Total Recoverable Zinc	mg/kg dry wt	53	46 – 63	No

QC A3 PrepWS esDig - Env Soils by ICPMS (low level): 2508.13		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Mercury	mg/kg dry wt	0.147	0.12 – 0.20	No

QC A3 PrepWS esDig - Env Soils by ICPMS (low level): 2508.19		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Mercury	mg/kg dry wt	0.147	0.12 – 0.20	No

AGAL-10 QC PrepWS esDig - Env Soils by ICPMS (low level): 2508.20		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Mercury	mg/kg dry wt	11.1	10 – 14	No

QC A3 PrepWS esDig - Env Soils by ICPMS (low level): 2509.13		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	64	45 – 98	No

QC A3 PrepWS esDig - Env Soils by ICPMS (low level): 2509.19		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	57	45 – 98	No

AGAL-10 QC PrepWS esDig - Env Soils by ICPMS (low level): 2509.20		Results	Control Limits	Outside Limit (Yes/No)
Total Recoverable Arsenic	mg/kg dry wt	18	16 – 23	No

Replicates

Environmental Soils by ICP-MS: 9079.59		Replicate 1	Replicate 2	Pass/Fail
Extractable Copper	mg/kg dry wt	5.2 ± 1.1	5.9 ± 1.2	Pass
Extractable Lead	mg/kg dry wt	10.8 ± 1.3	11.4 ± 1.4	Pass
Extractable Zinc	mg/kg dry wt	58.3 ± 8.3	63.1 ± 9.0	Pass

Environmental Soils by ICP-MS: 9086.22		Replicate 1	Replicate 2	Pass/Fail
Extractable Copper	mg/kg dry wt	5.3 ± 1.1	4.9 ± 1.1	Pass
Extractable Lead	mg/kg dry wt	11.2 ± 1.4	11.0 ± 1.4	Pass
Extractable Zinc	mg/kg dry wt	57.8 ± 8.3	55.7 ± 8.0	Pass

Env Soils by ICPMS (low level): 2504.57		Replicate 1	Replicate 2	Pass/Fail
Total Recoverable Cadmium	mg/kg dry wt	0.0163 ± 0.0064	0.0185 ± 0.0064	Pass
Total Recoverable Chromium	mg/kg dry wt	7.85 ± 0.96	8.6 ± 1.1	Pass
Total Recoverable Copper	mg/kg dry wt	2.85 ± 0.43	3.00 ± 0.45	Pass
Total Recoverable Lead	mg/kg dry wt	1.88 ± 0.23	1.99 ± 0.25	Pass
Total Recoverable Nickel	mg/kg dry wt	6.21 ± 0.64	7.23 ± 0.74	Pass
Total Recoverable Zinc	mg/kg dry wt	13.9 ± 2.3	15.0 ± 2.5	Pass

Analyst's Comments

[#1] It has been noted that the Extractable Lead and Zinc blanks showed as outliers, however the control limits have not taken into account the 20x dilution factor, the control limits for these should be disregarded.

[#2] It has been noted that the QCA3 for Arsenic and Copper is out of range for our In-House Confidence Limits, however a second QCA3 (our in-house QC) was also run, giving a Arsenic result of 64mg/kg which is well within our confidence limits of 45 98 mg/kg,and a Copper result of 59mg/kg which is well within our confidence limits of 49 71 mg/kg . The high Arsenic and Copper results for QCA3 was noted but the run was accepted based on the good results for the second QC sample and the CRM Agal 10.

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