Auckland Marine Sediment Contaminant Monitoring: Data report for November 2015 sampling

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Auckland Marine Sediment Contaminant Monitoring: Data report for November 2015 sampling

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Executive summary

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

Sediments from a total of 21 sites were sampled for chemical contaminants: 20 RSCMP sites (of which, 17 were from the former Regional Discharges Project (RDP), and two from the former State of the Environment (SoE), monitoring programmes) and one site from the Central Waitemata Harbour benthic ecology programme (CWH).

The RSCMP sites were sampled by NIWA between 5 and 26 November 2015, and the one CWH site (Hobsonville) by Auckland Council (AC) on 12 October 2015.

This report summarises the sediment contaminant and particle size distribution (PSD) data obtained from the sampling.

Samples used for sediment chemistry analysis were processed (homogenised, freeze-dried and sieved) by the NIWA Hamilton laboratory. Five replicates from each site were analysed by R J Hill Laboratories (Hamilton) for the following heavy metals: copper (Cu), lead (Pb), zinc (Zn), arsenic (As), and mercury (Hg).

Only total recoverable metals, on the <500µm fraction, were analysed. This is a departure from previous sediment chemistry monitoring, in that the weak acid extractable metals in the <63µm fraction were not analysed. This is because quality assurance (QA) data accumulated since 2011, and field results from earlier SoE programme monitoring, indicate that year-to-year analytical variability for extractable metals has been too high for reliable use in trend monitoring. The QA data indicate that the total recoverable metals results have been more consistent, and therefore better suited for on-going monitoring. A summary of the QA data can be found in each annual monitoring report, the latest previous report including extractable metals data being Mills (2015).

Three replicate samples from each site were also analysed for particle size distribution (PSD) by NIWA (Hamilton).

Benthic ecology sampling was also conducted for 16 of the RSCMP sites (and from the Hobsonville CWH Eco site) and the preserved samples were analysed by NIWA. These data have been reported separately to the Auckland Council by NIWA.

This report provides:

- sediment metals data;
- sediment PSD data; and
- quality assurance data for sediment metals and PSD.

Single site reports (SSRs), which summarise the status and trends in sediment contaminants and PSD, have been updated to include the 2015 results, and have been provided separately to the Auckland Council.

The quality assurance data collected with the November 2015 samples indicated that the total recoverable metals data were of an acceptable quality, which was generally consistent with the previous RDP/RSCMP results.

The QA data for PSD showed low variability and good comparability with the results from the previous monitoring batches (November 2011 to June 2015). Based on the QA data collected to date, the PSD data are deemed to be reliable.

Overall, the November 2015 monitoring data for total recoverable metals and PSD were similar in quality to those obtained in previous years and are considered acceptable for use in the RSCMP status and trend assessment programme.

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1.0 Introduction

This document provides a summary of the marine sediment contaminant monitoring undertaken by NIWA in October-November 2015 for the Auckland Council Regional Sediment Contaminant Monitoring Programme (RSCMP). The RSCMP monitoring was formerly conducted as the Regional Discharges Project (RDP) and State of the Environment (SoE) programmes.

This report provides a summary of:

- Sampling undertaken;
- 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 the Auckland Council. Copies of the SSRs can be obtained from the Research and Evaluation Unit (RIMU).

2.0 Sampling and analysis

2.1 Sampling

Sediments from a total of 21 sites were sampled for chemical contaminant analysis: 20 RSCMP sites (of which, 17 were from the former Regional Discharges Project (RDP), and two from the former State of the Environment (SoE), monitoring programmes) and one site from the Central Waitemata Harbour benthic ecology programme (CWH).

The RSCMP sites were sampled by NIWA between 5 and 26 November 2015, and the one CWH site (Hobsonville) by the Auckland Council (AC) on 12 October 2015.

Sampling followed the procedures detailed in the ARC "monitoring blueprint" document, ARC Technical Publication 168 (ARC 2004).

Benthic ecology sampling was also done for 16 of the RSCMP sites (and for the Hobsonville CWH Eco site) and the preserved samples were analysed by NIWA. These data have been reported separately to the Auckland Council by NIWA.

A list of sites, sampling dates, and analyses conducted at each site are given in Table 2 1. More detailed information on the sites selected for monitoring, including their locations, key physical characteristics, and sediment contaminant status and trends, is provided in the SSRs. The rationale for the chemical contaminants measured and sampling strategy are given in TP 168 (ARC 2004).

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

Site	Marine Reporting Area	Programme	Sampling Date	Sampled by	<500 μm fraction Cu Pb Zn As Hg	Benthic Ecology	Particle Size
Benghazi	Tamaki	RSCMP	25/11/2015	NIWA	✓	✓	✓
Bowden	Tamaki	RSCMP	25/11/2015	NIWA	✓	✓	✓
Chelsea	Central Waitemata	RSCMP	24/11/2015	NIWA	✓	✓	✓
Coxs	Central Waitemata	RSCMP	6/11/2015	NIWA	✓	✓	✓
Harania	Manukau	RSCMP	26/11/2015	NIWA	✓	✓	✓
Henderson Lower	Central Waitemata	RSCMP	24/11/2015	NIWA	✓	✓	✓
Hillsborough	Manukau	RSCMP	5/11/2015	NIWA	✓	x	✓
Hobsonville CWH Eco	Upper Waitemata	CWH Eco	12/10/2015	AC	✓	✓	✓
Mill Bay	Manukau	RSCMP	5/11/2015	NIWA	✓	x	✓
Pahurehure Middle	Manukau	RSCMP	6/11/2015	NIWA	✓	✓	✓
Pahurehure Upper	Manukau	RSCMP	6/11/2015	NIWA	✓	✓	✓
Papakura Lower	Manukau	RSCMP	6/11/2015	NIWA	✓	✓	✓
Princes	Tamaki	RSCMP	25/11/2015	NIWA	✓	✓	✓
Puhinui Upper	Manukau	RSCMP	7/11/2015	NIWA	✓	✓	✓
Pukaki Airport	Manukau	RSCMP	7/11/2015	NIWA	✓	✓	✓
Rarawaru	Upper Waitemata	RSCMP	24/11/2015	NIWA	✓	x	✓
Roberta Reserve	Tamaki	RSCMP	26/11/2015	NIWA	✓	x	✓
Shoal Hillcrest	Central Waitemata	RSCMP	9/11/2015	NIWA	✓	✓	✓
Tararata	Manukau	RSCMP	24/11/2015	NIWA	✓	✓	✓
Waimahia Central	Manukau	RSCMP	5/11/2015	NIWA	✓	✓	✓
Whau Entrance	Central Waitemata	RSCMP	24/11/2015	NIWA	✓	✓	✓

2.2 Sample preparation

2.2.1 Sediment chemistry samples

Five replicate samples for sediment chemistry analysis were taken at each site, using the protocol described in ARC (2004). All five replicates from each site were processed by homogenisation, freeze-drying, and sieving (<500µm) at NIWA Hamilton.

A sub-sample of each of the five replicates of the sieved and freeze-dried samples (<500µm) from each site were provided to R J Hill Laboratories (Hamilton) by NIWA for metal analysis on 18 January 2016.

Remaining freeze-dried <500µm sieved sediment from each replicate was archived in glass jars in the Auckland Council store.

2.2.2 Particle size distribution samples

A composite sample from each site was used for particle size distribution (PSD) analysis. Each composite sample consisted of 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 therefore equivalent to a sediment chemistry replicate sample). The PSD samples were analysed by NIWA.

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 (five 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 six size fractions, followed by oven drying each fraction to constant weight. This methodology is the same as that employed in the RSCMP/RDP/SoE programmes since 2009.

Only total recoverable metals, on the <500µm fraction, were analysed. This is a departure from previous sediment chemistry monitoring, in that the weak acid extractable metals in the <63µm fraction were not analysed. This is because the quality assurance (QA) data accumulated since 2011, and field results from earlier SoE programme monitoring, indicate that year-to-year analytical variability for extractable metals has been too high for reliable use in trend monitoring. The QA data indicate that total recoverable metals results have been more consistent, and therefore better suited for on-going monitoring. A

summary of the QA data can be found in each annual monitoring report, the latest previous report including extractable metals data being Mills (2015).

Sediment contaminant data are summarised in Appendix A, and PSD data are tabulated in Appendix B.

A summary of QA checks performed by NIWA on the analytical data provided by R J Hill Laboratories is given in Appendix C.

The analytical lab report from R J Hill Laboratories is provided in Appendix D.

2.4 Concentration units for metals

As per the previous two rounds of RSCMP monitoring conducted in 2013 and June 2015, 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 sample data reported here.

3.0 Quality assurance

For **metal analysis**, quality assurance (QA) was similar to previous years, and comprised the following:

- 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]. These data are reported in the Hill Laboratories QC Report, which is included in the lab report attached as Appendix D.
- Three CRM samples dispersed through the analytical run as extra samples (in addition to the routine laboratory CRM quality control samples).
- Analysis of the 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 freeze-dried form were analysed along with the 2015 sample batch for metals. No frozen BRS samples were analysed for metals in 2015, as previous BRS analysis has shown that total recoverable metals concentrations have been essentially equivalent in both forms (Mills 2015).

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).

A summary of QA checks performed by NIWA on the analytical data provided by R J Hill Laboratories is given in Appendix C. Key features of the QA data are summarised in sections 3.1 to 3.4, and an overall summary presented in section 3.5.

[1] The R J Hill Laboratories "in-house" reference sediment – "QC A5". Compared with typical Auckland marine sediments, the QC A5 reference sediment has elevated concentrations of metals. Results are included in the R J Hill Laboratories QA/QC report (Appendix D) and in the NIWA QA assessment report (Appendix C).

3.1 Procedural blanks

Metal concentrations in procedural blanks were below detection limits (D.L.). Total recoverable metal blanks were <0.2, <0.2, <0.04, <0.4, and <0.01mg/kg for As, Cu, Pb, Zn, and Hg respectively.

Therefore there was no background contamination introduced by the laboratory procedures that would contribute significantly to the reported metal concentrations.

3.2 Reference materials

Two types of reference materials were used by Hill Laboratories as a quality control check for metal 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
- an “in-house” laboratory reference material, “QC A5”, a sediment sample prepared by Hill Laboratories for use in their QA/QC programme. Compared with typical Auckland marine sediments, the QC A5 reference sediment has very high concentrations of metals (and the results are therefore probably of less relevance to the RSCMP).

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 D).

3.2.1 Certified Reference Material analyses

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

CRM data are summarised in Table 3-1 (for the three CRM samples added as “unknowns”) and Table 3-2 (for the four samples 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 1.7 and 3.5 per cent for the three CRM samples added as “unknowns” and between 1.5 and 6.7 per cent for the four CRM samples from Hill

Laboratories' in-house QC programme, for various metal analyses, which is similar to data collected in previous years.

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 ±1 s.d. of the certified concentration except for Zn, which was low.

All CRM concentrations were within 20 per cent of the certified concentrations:

- for the three CRM samples added to the 2015 sample batch, average total recoverable Zn concentrations were 12 per cent lower than the certified concentration, while the other metals ranged from 8 per cent low (Hg) to 1 per cent low (As). All individual CRM sample results for Zn were low, ranging from 10–14 per cent below the certified level, and a single Hg result was 11 per cent lower than the certified concentration.
- for the four CRM samples from Hill Laboratories' in-house QC programme which were analysed in the 2015 sample batch, the average total of Hg was 11 per cent low, while the other metals ranged from 10 per cent low (Zn) to 1 per cent high (As). All individual CRM sample results for Zn and two for Hg were low ranging from 8–14 per cent of the certified concentrations.

Overall, the CRM results indicate a reasonable level of accuracy and good precision for total recoverable metals in the November 2015 sample batch. However, these results apply only to the digestion and ICP-MS steps of the overall analysis method. Variability may be higher when sediment processing steps such as sieving and drying (which occur in the analysis of field samples) are included. The effects of these additional steps are included in the data obtained for the BRS QA samples (see section 3.4).

Comparisons of all the CRM results for the November 2015 sample batch, along with those obtained in previous RDP and RSCMP monitoring conducted between 2002 and November 2015, are shown in Figure 3-1 and Figure 3-2. These data indicate that the total metal results were comparable with those recorded in previous years.

There were no significant trends over time for total recoverable Cu, Pb or Zn (Mann Kendall test, annual medians[2], $p<0.05$). The CRM results therefore indicate that the total recoverable metals data have been reasonably consistent over time, showing overall trends of <1 per cent of the median concentration per year.

[2] The Mann Kendall trend test was conducted using TimeTrends software, using the "median within each time period" option.

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

Table 3-1: Total recoverable metals concentrations (mg/kg) in three Certified Reference Material (CRM; AGAL10) samples, included in the November 2015 sediment sample 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 (reference value ±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.

	Total Recoverable Metals (<500 μm)				
Sample	As	Cu	Pb	Hg	Zn
CRM - Agal 10 - 1	17.0	21.1	38.6	11.0	49.4
CRM - Agal 10 - 2	16.4	22.6	40.2	10.8	51.2
CRM - Agal 10 - 3	17.4	21.9	39.1	10.3	50.2
mean	17.0	21.9	39.3	10.7	50.2
cv (%)	2.9	3.3	2.2	3.5	1.7
Mean % of certified value	98.6	94.2	97.3	92.4	88.1
In-house lower limit (mg/kg; mean - 99% C.L.)	16.18	19.58	32.48	10.023	46.1
In-house upper limit (mg/kg; mean + 99% C.L.)	23.09	26.39	48.42	13.61	62.74
In-house 99% C.I. (mg/kg)	6.91	6.8	15.9	3.587	16.6
In-house 99% C.I. (+/- % mean)	17.6	14.8	19.7	15.2	15.3
Certified Reference Value (mg/kg)	17.2	23.2	40.4	11.6	57
Certified Lower Limit (mg/kg; reference value - 1 s.d.)	14.2	21.3	37.7	10.5	52.8
Certified Upper Limit (mg/kg; reference value + 1 s.d.)	20.2	25.1	43.1	12.7	61.2

Table 3-2: Total recoverable metal concentrations (mg/kg) in Certified Reference Material (CRM; AGAL10) samples, analysed with the November 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 (reference value ±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.

	Total Recoverable Metals (<500 μm)				
Sample	As	Cu	Pb	Hg	Zn
CRM - Agal 10 - 1	17.2	21.0	40.0		51.0
CRM - Agal 10 - 2	18.1	24.0	40.0	10.7	51.0
CRM - Agal 10 - 3	16.9	23.0	39.0	10.2	52.0
CRM - Agal 10 - 4				10.0	
mean	17.4	22.7	39.7	10.3	51.3
cv (%)	3.6	6.7	1.5	3.5	1.1
Mean % of certified value	101.2	97.7	98.2	88.8	90.1
In-house lower limit (mg/kg; mean - 99% C.L.)	16.18	19.6	32.5	10.023	46.1
In-house upper limit (mg/kg; mean + 99% C.L.)	23.09	26.4	48.4	13.61	62.7
In-house 99% C.I. (mg/kg)	6.91	6.8	15.9	3.587	16.6
In-house 99% C.I. (+/- % mean)	17.6	14.8	19.7	15.2	15.3
Certified Reference Value (mg/kg)	17.2	23.2	40.4	11.6	57
Certified Lower Limit (mg/kg; reference value - 1 s.d.)	14.2	21.3	37.7	10.5	52.8
Certified Upper Limit (mg/kg; reference value + 1 s.d.)	20.2	25.1	43.1	12.7	61.2

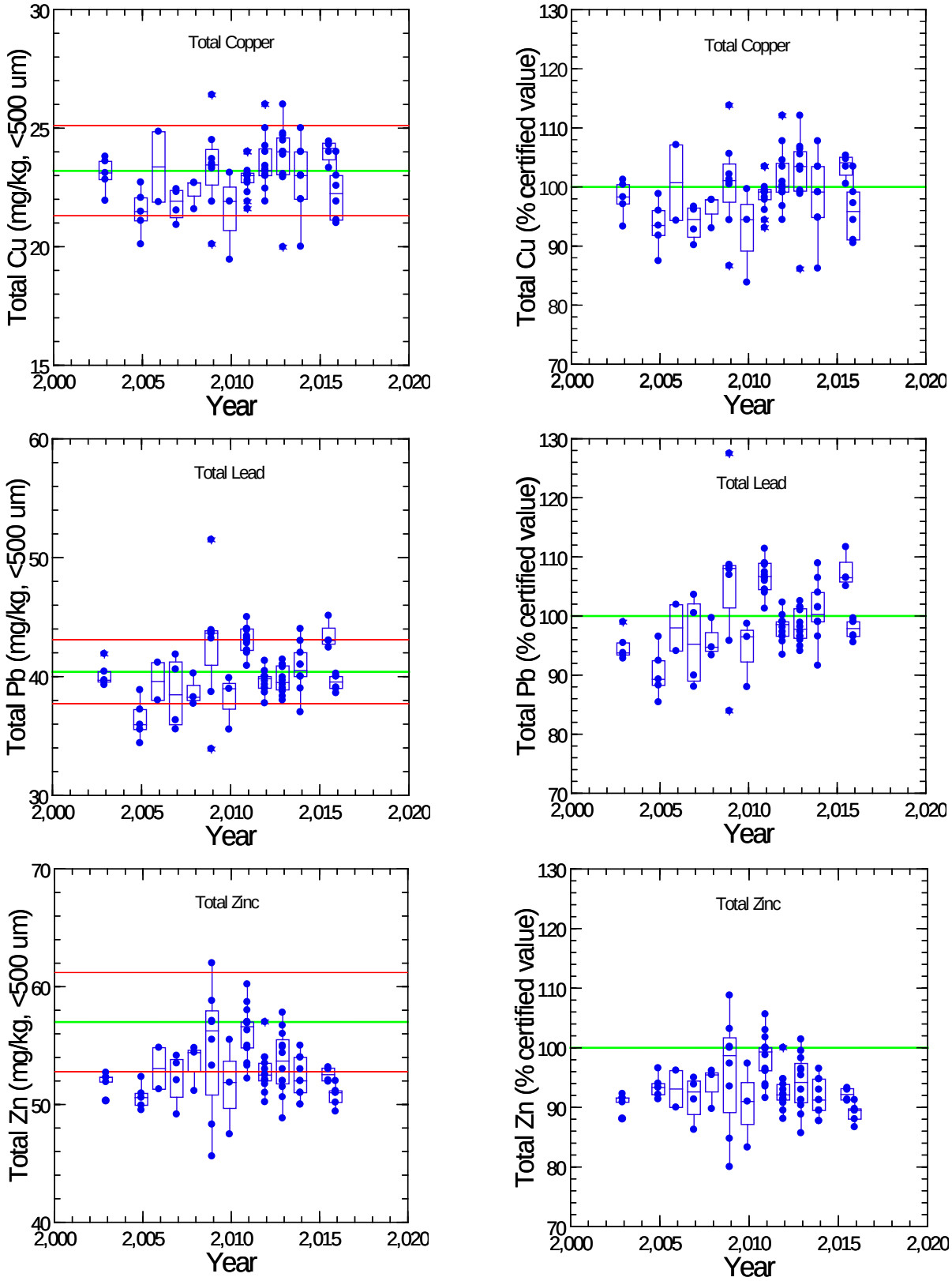

Figure 3-1: Certified Reference Material (CRM) quality control data for Total Recoverable Metals in CRM AGAL-10 for RDP and RSCMP samples analysed from 2002 to November 2015.
Plots show concentrations, with certified values (green central line) and upper and lower limits (±1 s.d., dashed red lines), and as percentages of the certified values. Note there are two sets of data for 2015, from sampling undertaken in June (Drury Creek survey, Mills 2015) and November (routine RSCMP survey reported here). No RSCMP sampling was carried out in 2014.

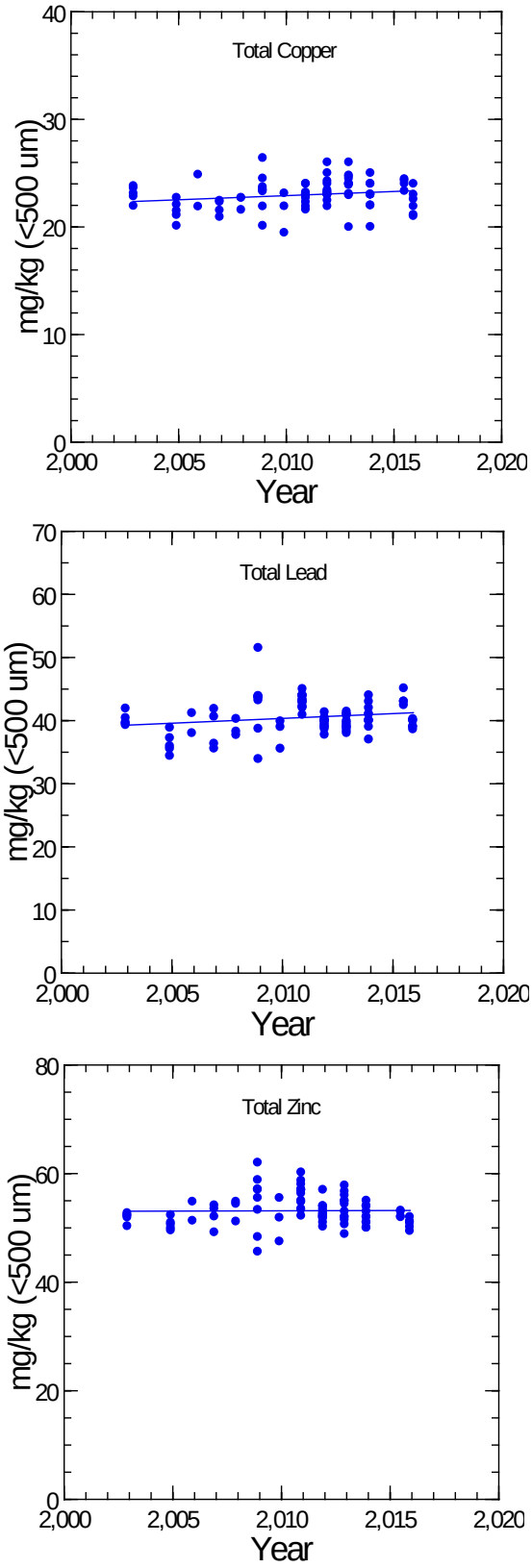

Figure 3-2: Trends in total recoverable metals in Certified Reference Material (CRM AGAL-10) for sampling undertaken from 2002 to November 2015. Lines are linear regressions.
Note there are two sets of data for 2015, from sampling undertaken in June (Drury Creek survey, Mills 2015) and November (routine RSCMP survey reported here). No RSCMP sampling was carried out in 2014.

Table 3-3: Trends in metals in CRM (AGAL-10) analysed with RSCMP samples from 2002–2015. Results from Mann Kendal trend test (annual median data used). Note that the trend test uses only the annual RSCMP monitoring data, and does not include the June 2015 sampling data (which was from a survey undertaken in Drury Creek, Mills 2015).

Metal	Period	N	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)
Total Cu	2002 to 2015	12	23.0	0.582	0.053	-0.08	0.21	0.23
Total Pb	2002 to 2015	12	39.6	0.373	0.140	-0.10	0.39	0.35
Total Zn	2002 to 2015	12	52.6	1.000	-0.003	-0.30	0.32	-0.01

3.2.2 R J Hill Laboratories' in-house reference sediment

Results from the analysis of R J Hill Laboratories' in-house reference sediment QC A5 are presented in Table 3-4. The data show reasonably consistent metal analysis results (CVs 5–13 per cent, n=12), with mean concentrations that were within the laboratory control limits and within 11 per cent of the reference concentrations. Arsenic concentrations were, on average, approximately 11 per cent below reference concentrations, while other metals were within 7 per cent of the reference concentrations. Cu and Zn both showed one individual value outside the lab control limits (99 per cent CLs) – the lab QC report (included in Appendix D) commented on these results, and based on the other sets of QC results, it was concluded that the batch was acceptable.

Table 3-4: Results from analysis of Hill Laboratories' in-house reference sediment QC A5.
Red values are outside the upper and lower control limits (reference value ±3 standard deviations; ca. 99% CLs). Means, as % of reference values, are colour shaded: Green within 10%, Amber within 10–20%, Red greater than 20% of the reference concentrations.

	Total Recoverable Metals (<500 μm)				
Sample	As	Cu	Pb	Hg	Zn
QC A5 Sample 1	103	122	125		820
QC A5 Sample 2	87	106	127		770
QC A5 Sample 3	101	114	115	0.39	790
QC A5 Sample 4	104	105	109	0.37	760
QC A5 Sample 5	93	107	119	0.34	810
QC A5 Sample 6	95	118	110	0.35	780
QC A5 Sample 7	115			0.35	
QC A5 Sample 8	109				
QC A5 Sample 9				0.34	
QC A5 Sample 10				0.35	
QC A5 Sample 11		153			960
QC A5 Sample 12		125			920
Mean	101	119	118	0.36	826
cv (%)	8.9	13.3	6.4	5.1	8.9
Mean (% of reference value)	88.9	99.0	95.5	93.6	97.8
In-house lower limit (mg/kg; mean - 99% C.L.)	77	100	86	0.29	750
In-house upper limit (mg/kg; mean + 99% C.L.)	150	140	160	0.47	940
In-house reference value (mg/kg)	113.5	120	123	0.38	845

3.3 Within-batch data variability

No blind duplicate samples were submitted along with the November 2015 sample batch to the lab. However, seven samples were analysed as blind within-batch duplicates for some or all of the total recoverable metals by R J Hill Laboratories as part of their in-house QA/QC regime. Results are given in the lab QC report (Appendix D) and are tabulated in Table 3-5.

The relative percentage differences (RPDs) between duplicates ranged from 0–10 per cent, indicating good agreement. All duplicate results were within the USEPA (2010) Measurement Quality Objective (MQO) limit for acceptable agreement between within-batch replicates (a 30 per cent difference).

Table 3-5: Within-batch variation for total recoverable metals analysed by R J Hill Laboratories as blind duplicates.
Differences between duplicates (expressed as relative percentage difference; RPD) are colour coded: Green <15%, Amber 15–30%, Red >30%.

		Total Recoverable Metals (<500 μm)				
Site	Rep	As	Cu	Pb	Hg	Zn
2562.72 - Rep -1	1			22.30		
2562.72 - Rep -2	2			20.6		
difference (mg/kg)				-1.70		
RPD (%)				7.9		
2562.68 - Rep -1	1		21.40	28.70		192.0
2562.68 - Rep -2	2		20.50	27.40		181.0
difference (mg/kg)			-0.90	-1.30		-11.0
RPD (%)			4.3	4.6		5.9
2562.47 - Rep -1	1	10.00				
2562.47 - Rep -2	2	9.56				
difference (mg/kg)		-0.44				
RPD (%)		4.5				
2562.61 - Rep -1	1				0.147	
2562.61 - Rep -2	2				0.133	
difference (mg/kg)					-0.014	
RPD (%)					10.0	
2562.33 - Rep -1	1	11.70	26.10	29.30	0.134	132.0
2562.33 - Rep -2	2	12.00	26.50	29.20	0.133	132.0
difference (mg/kg)		0.30	0.40	-0.10	-0.001	0.0
RPD (%)		2.5	1.5	0.3	0.7	0.0
2562.73 - Rep -1	1		17.50	23.10	0.134	153.0
2562.73 - Rep -2	2		17.40	23.20	0.131	149.0
difference (mg/kg)			-0.10	0.10	-0.003	-4.0
RPD (%)			0.6	0.4	2.3	2.6
2562.21 - Rep -1	1	10.10	13.20	17.30	0.058	101.0
2562.21 - Rep -2	2	10.10	13.20	17.30	0.053	101.0
difference (mg/kg)		0.00	0.00	0.00	-0.005	0.0
RPD (%)		0.0	0.0	0.0	8.3	0.0

3.4 Bulk reference sediment results

Bulk Reference Sediment (BRS) sample analysis consisted of:

- Five samples from each of the sandy Meola Outer and muddy Middlemore sites, in freeze-dried forms, were analysed for metals. The results for the metal analyses are summarised in section 3.4.1; and
- Three samples (frozen form) from each of the Middlemore and Meola Outer sites were analysed for particle size distribution (PSD). The results for PSD are summarised in section 3.4.23.4.2.

Single Site Reports (SSRs) for the BRS samples have been updated with the 2015 results and provided separately to the Auckland Council.

3.4.1 Metals

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

The within-batch variability (CVs, N = 5) was 1.8–13.8 per cent. The variability for total recoverable Hg in sediments in both BRS sediments was markedly higher than for other analytes. For the primary monitoring metal contaminants (Cu, Pb and Zn), CVs for total recoverable metals ranged from 1.9 to 3.5 per cent. These results were similar to previous years.

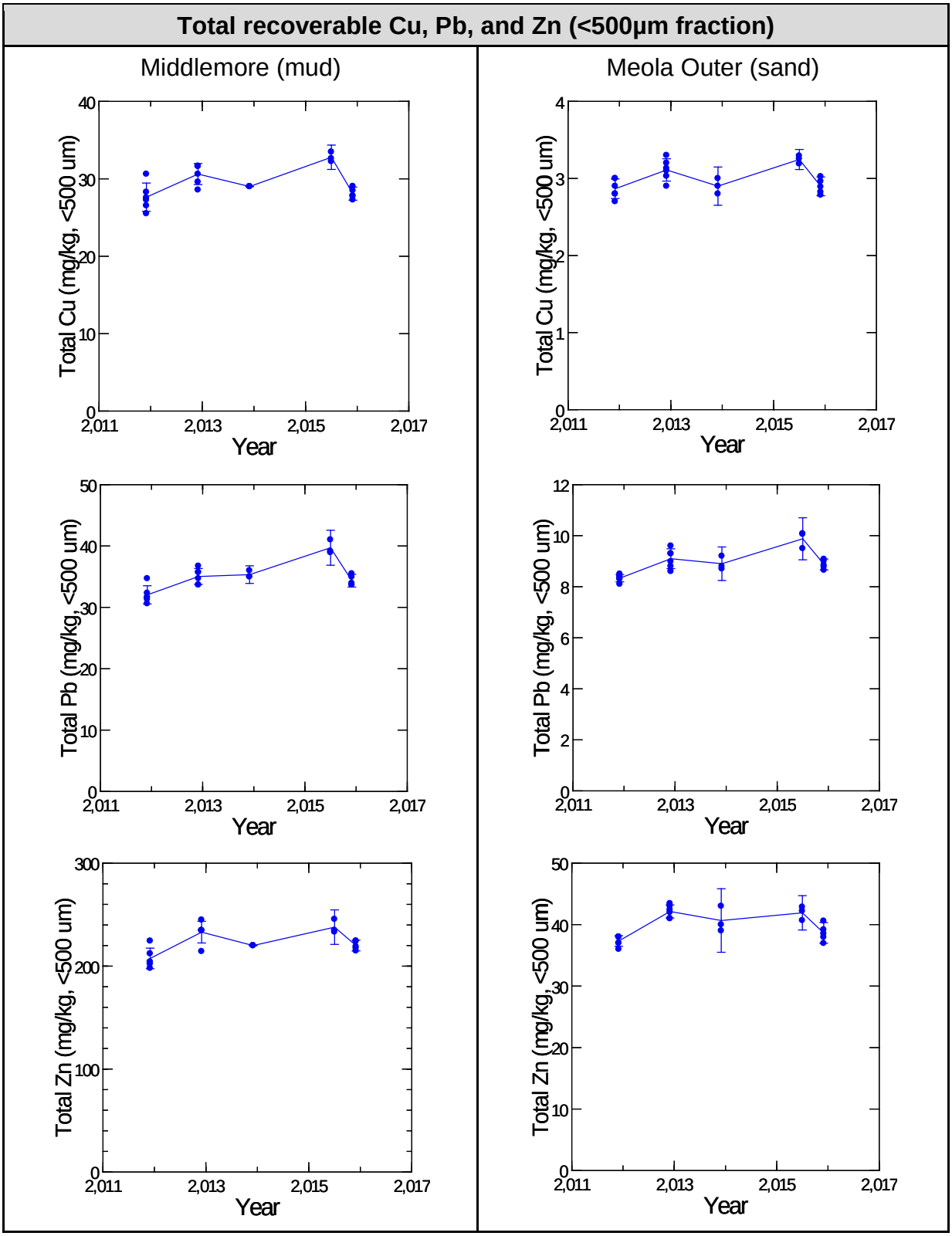

Figure 3-3: Total recoverable Cu, Pb, and Zn results for freeze-dried (FD) bulk reference sediments (BRS) analysed with RSCMP samples taken in November 2011, 2012, 2013, June 2015, and November 2015. Bars are means ±95% confidence intervals in the means (N=6 in 2011 and 2012, N=3 in 2013 and June 2015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

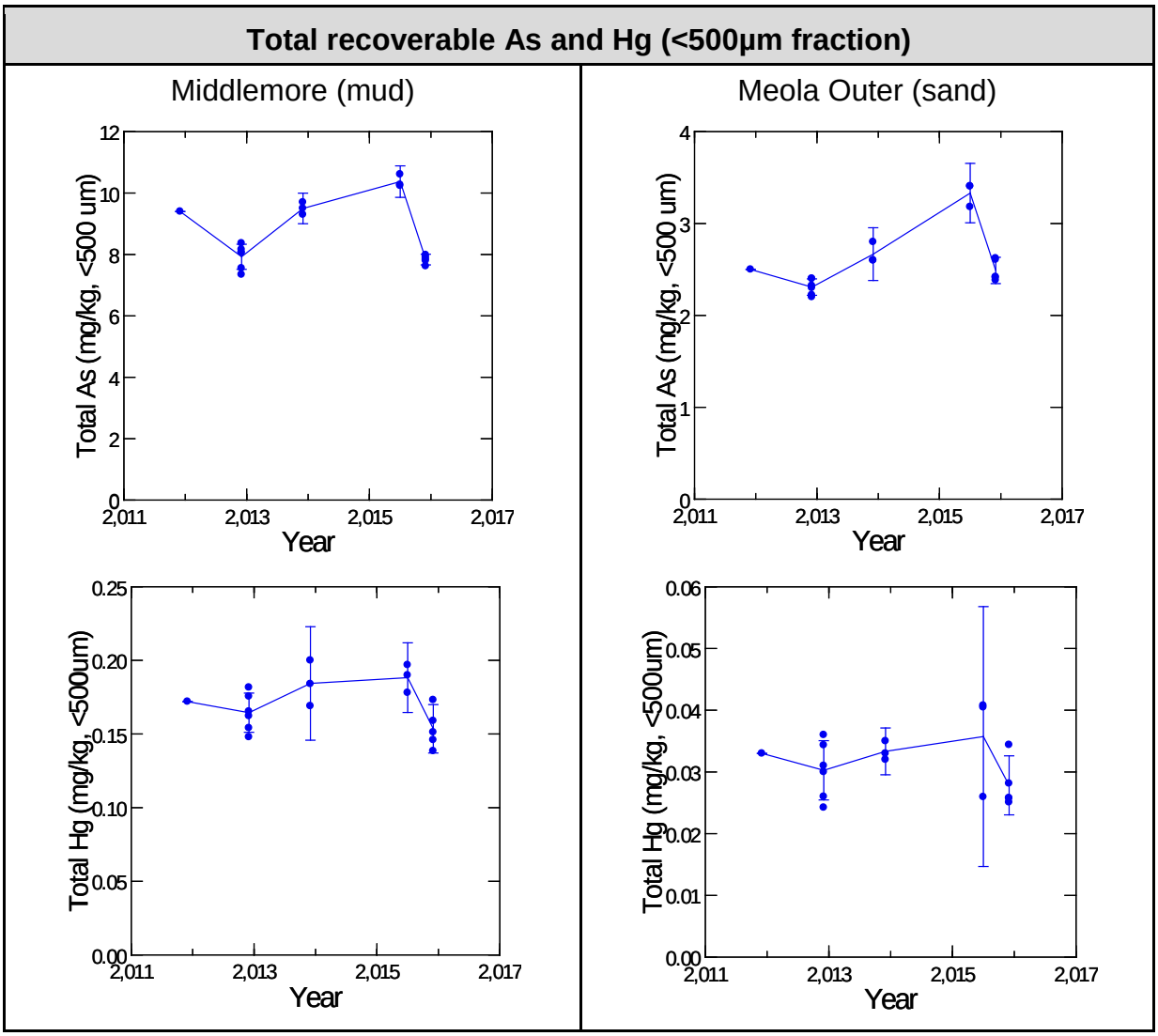

Figure 3-4: Total recoverable As and Hg results for freeze-dried (FD) bulk reference sediments (BRS) analysed with RSCMP samples taken in in November 2011, 2012, 2013, June 2015, and November 2015. Bars are means ±95% confidence intervals in the means (N=6 in 2011 and 2012, N=3 in 2013 and June 2015 and N=5 in November 2015).

Table 3-6: Bulk Reference Sediment (BRS) results from the November 2015 sampling batch.
Metal analysis results are from freeze-dried BRS samples (mg/kg freeze dry weight, <500µm fraction), N=5.
Mud content data are from frozen BRS samples (% <63µm, oven dry weight, N=3).

			Total Recoverable Metals (mg/kg, <500 µm)				
BRS Sample	Replicate	Mud %	Cu	Pb	Zn	As	Hg
Middlemore	1	69.4	29.0	35.5	224.6	7.98	0.173
	2	65.8	27.8	33.7	217.5	7.62	0.138
	3	65.2	27.3	33.6	214.8	7.85	0.151
	4		28.5	35.0	224.1	7.92	0.159
	5		27.8	33.9	219.0	7.80	0.146
	Mean	66.8	28.1	34.3	220.0	7.83	0.154
	stdev	2.31	0.69	0.83	4.23	0.14	0.013
	CV %	3.5	2.4	2.4	1.9	1.8	8.6
Meola Outer	1	2.82	2.96	8.78	38.5	2.41	0.0344
	2	2.87	2.89	9.08	40.6	2.62	0.0281
	3	3.01	2.78	8.85	37.0	2.38	0.0251
	4		2.82	8.65	38.0	2.42	0.0258
	5		3.02	9.00	39.2	2.61	0.0258
	Mean	2.90	2.90	8.9	38.6	2.49	0.0278
	stdev	0.10	0.10	0.17	1.36	0.12	0.0038
	CV %	3.5	3.4	1.9	3.5	4.6	13.8

Table 3-7: Comparison of median metal concentrations (mg/kg dry weight) and mud content (% <63µm) in Bulk Reference Sediment (BRS) analysed with the November 2015 sample batch with results obtained between November 2011 and June 2015: Concentration data.

Data points are medians, with sample numbers varying between years and analytes. For Cu, Pb, and Zn, N=6 for 2011 and 2012, N=3 for 2013 and June 2015, and N=5 for November 2015. For As and Hg, N=1 for 2011, N=6 for 2012, N=3 for 2013 and June 2015, and N=5 for November 2015. For mud content, N=3 in each year.

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

		Chemistry Processing			Total Metals (mg/kg, <500 um)				
BRS Sample	Sampling Date	Lab	Method	% Mud	Cu	Pb	Zn	As	Hg
Meola Outer	Nov-2011	Hills	Air dried	3.03	2.85	8.35	37.5	2.50	0.033
	Nov-2012	Hills	Air dried	3.07	3.12	9.14	42.2	2.31	0.031
	Nov-2013	NIWA	Freeze dried	2.95	2.90	8.80	40.0	2.60	0.033
	Jun-2015	NIWA	Freeze dried	2.79	3.26	10.06	42.2	3.41	0.040
	Nov-2015	NIWA	Freeze dried	2.87	2.89	8.85	38.5	2.42	0.026
Middlemore	Nov-2011	Hills	Air dried	66.9	27.4	31.6	204.1	9.40	0.172
	Nov-2012	Hills	Air dried	69.2	31.1	35.2	234.7	8.06	0.164
	Nov-2013	NIWA	Freeze dried	68.3	29.0	35.0	220.0	9.50	0.184
	Jun-2015	NIWA	Freeze dried	66.8	32.6	39.2	234.8	10.3	0.190
	Nov-2015	NIWA	Freeze dried	65.8	27.8	33.9	219.0	7.85	0.151

Table 3-8: Comparison of metal concentrations and mud content in Bulk Reference Sediment (BRS) analysed with the November 2015 sampling batch with results obtained between November 2011 and June 2015: Relative Percentage Differences (RPDs) between annual medians.

Data points are Relative Percentage Differences (RPDs) between the November 2015 median concentrations and the medians for each of the 2011 to June 2015 data. Sample numbers vary between years and analytes. For Cu, Pb, and Zn, N=6 for 2011 and 2012, N=3 for 2013 and June 2015, and N=5 for November 2015. For As and Hg, N=1 for 2011, N=6 for 2012, N=3 for 2013 and June 2015, and N=5 for November 2015. For mud content, N=3 in each year.

The shading colour reflects the difference between the November 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 3-7). The bolded red values indicate RPDs >±30%, which is the maximum allowable RPD between duplicates recommended by USEPA (2010).

		Chemistry Processing			Total Metals (<500 um)				
BRS Sample	Sampling Date	Lab	Method	% Mud	Cu	Pb	Zn	As	Hg
Meola Outer	Nov-2011	Hills	Air dried	5.2	-1.4	-5.8	-2.7	3.3	24.6
	Nov-2012	Hills	Air dried	6.6	7.5	3.3	9.1	-4.5	16.9
	Nov-2013	NIWA	Freeze dried	2.6	0.3	-0.5	3.7	7.2	24.6
	Jun-2015	NIWA	Freeze dried	-2.8	11.9	12.8	9.1	33.9	44.4
	Nov-2015	NIWA	Freeze dried	0.0	0.0	0.0	0.0	0.0	0.0
Middlemore	Nov-2011	Hills	Air dried	1.7	-1.4	-7.0	-7.1	18.0	12.9
	Nov-2012	Hills	Air dried	5.0	11.3	3.7	6.9	2.6	8.0
	Nov-2013	NIWA	Freeze dried	3.7	4.2	3.1	0.4	19.0	19.6
	Jun-2015	NIWA	Freeze dried	1.5	15.9	14.3	7.0	26.7	22.7
	Nov-2015	NIWA	Freeze dried	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 November 2015 and the previous years were recorded for many analyses (Table 3-7). Almost all the June 2015 results were higher than those obtained in November 2015.

The magnitude of the differences in median concentrations between November 2015 and previous years was generally <20 per cent, and was <30 per cent (a recommended maximum RPD for duplicate results; USEPA 2010) for all analytes except for As and Hg in the June 2015 sampling batch, which were 34 per cent and 44 per cent higher than the results obtained in November 2015 (Table 3-8).

No significant trends over time were measured from the BRS data from the November 2011, 2012, 2013, and 2015 samples batches (Table 3-9).

Table 3-9: Trends (Sen Slopes, given as % of median concentrations per year) in metal and mud content from BRS analyses conducted using samples taken in November 2011, 2012, 2013, and 2015.
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). No trends were significant (Mann Kendall test, p<0.05).

		Total Metals (<500 μm)				
BRS Sample	% Mud	Cu	Pb	Zn	As	Hg
Meola Outer	-1.30	0.10	0.84	-0.60	0.21	-6.1
Middlemore	-0.85	-0.88	0.54	0.74	-3.20	-3.2

3.4.2 Particle size distribution

A summary of the November 2015 particle size distribution (PSD) results is given in Table 3-10, and a comparison of 2011–2015 data is shown in Table 3-11 and Figure 3-5.

The BRS results indicate that the sieve/pipette method is giving reproducible "mud content" (% <63μm) results. Variability remains relatively low, with CVs of 3.5 per cent for both the muddy (Middlemore) and sandy (Meola Outer) BRS. The variability in mud content for the Middlemore BRS was slightly higher in November 2015 than in previous years (Figure 3-5).

Comparison of the November 2015 sample batch results with those from 2011 to June 2015 showed:

- For Middlemore: Mud content (silt + clay fractions) was relatively consistent. The means were 66.7 per cent in 2011, 69.1 per cent in 2012, 68.1 per cent in 2013, 66.1 per cent in June 2015, and 66.8 per cent in November 2015. Substantial differences in the proportions of silt and clay fractions were measured between 2011 and 2012, but these differences have decreased markedly between 2013 and November 2015 (see the top plot in Figure 3-5).
- For Meola Outer: Consistent results were obtained between years, for the dominant fine sand fraction and also for the minor size fractions (Table 3-11, Figure 3-5).

The 2011 to November 2015 data showed trends of -1.3 per cent of the median per year for the sandy Meola Outer BRS and -0.85 per cent per year for the higher mud content Middlemore BRS. Neither of these trends were statistically significant (Mann Kendall test, $p>0.05$).

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

Table 3-10: Summary of particle size distribution (PSD) results for Bulk Reference Sediments (BRS) obtained with the November 2015 sampling batch.

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 18	0.00	0.08	0.60	29.87	50.35	19.10	69.45	99.92	69.51
Mid PS 59	0.00	0.15	0.56	33.50	42.63	23.17	65.79	99.85	65.89
Mid PS 90	0.00	0.14	0.71	33.97	42.18	23.01	65.18	99.86	65.27
mean	0.00	0.12	0.62	32.45	45.05	21.76	66.81	99.88	66.89
s.d.	-	0.03	0.08	2.24	4.59	2.30	2.31	0.03	2.29
c.v. (%)	-	28.25	12.07	6.91	10.20	10.59	3.45	0.03	3.42
Meola Outer:									
MO PS 15	2.74	0.29	1.03	93.12	0.28	2.54	2.82	96.97	2.91
MO PS 30	0.16	0.27	0.98	95.72	0.96	1.91	2.87	99.57	2.88
MO PS 71	0.53	0.23	1.02	95.20	0.75	2.26	3.01	99.24	3.04
mean	1.14	0.27	1.01	94.68	0.66	2.24	2.90	98.59	2.94
s.d.	1.40	0.03	0.03	1.37	0.35	0.31	0.10	1.41	0.08
c.v. (%)	122.18	10.51	2.82	1.45	52.13	13.98	3.47	1.43	2.81

Table 3-11: Summary of particle size distribution (PSD) results for Bulk Reference Sediment (BRS) obtained with the November 2011, 2012, and 2013, June 2015, and November 2015 sampling batches.

		Middlemore: Mud					Meola Outer: Sand				
Class	Particle size range	Nov-11	Nov-12	Nov-13	Jun-15	Nov-15	Nov-11	Nov-12	Nov-13	Jun-15	Nov-15
Gravel	>2000 µm	0.00	0.00	0.03	0.00	0.00	0.70	0.72	1.01	0.82	1.14
Coarse Sand	500-2000 µm	0.15	0.11	0.17	0.06	0.12	0.33	0.31	0.26	0.27	0.27
Medium Sand	250-500 µm	0.74	0.52	0.59	0.53	0.62	1.13	0.94	0.94	0.95	1.01
Fine Sand	62.5-250 µm	32.45	30.29	31.12	33.32	32.45	94.83	94.94	94.91	95.17	94.68
Silt	3.9-62.5 µm	57.31	50.50	46.08	45.89	45.05	1.08	0.91	1.39	0.82	0.66
Clay	<3.9 µm	9.35	18.58	22.00	20.21	21.76	1.93	2.18	1.48	1.96	2.24
"Mud" - % of total sediment <63 um		66.66	69.09	68.09	66.10	66.81	3.01	3.09	2.87	2.78	2.90
"Mud" - % of <500um fraction <63 um		66.76	69.16	68.23	66.14	66.89	3.04	3.12	2.91	2.82	2.94

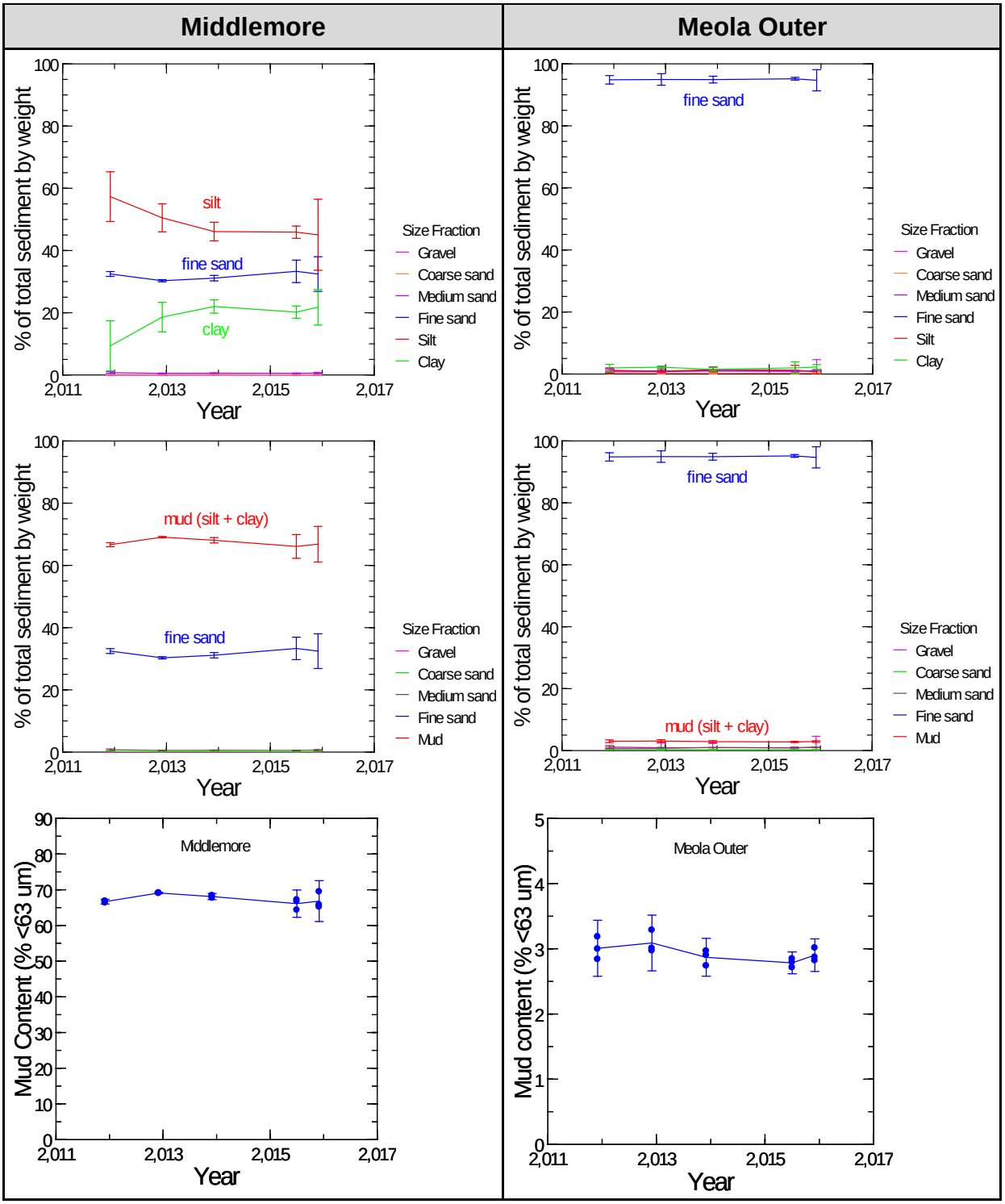

Figure 3-5: Particle size distribution (PSD) results for frozen bulk reference sediments (BRS) analysed with RSCMP samples taken in November 2011, 2012, and 2013, June 2015, and November 2015.
Bars are means ±95% confidence intervals in the means (N=3 in each year). The top plots show data for each particle size range, while the middle plots combine the silt and clay fractions in to a single “mud” fraction (% <63µm). The bottom plots show changes in mud content (% <63µm) over time.
Size fractions: gravel (>2 mm), coarse sand (0.5–2 mm), medium sand (0.25–0.5 mm), fine sand (0.063–0.25 mm), silt (3.9–63µm), clay (<3.9µm).

3.5 Data quality summary

Table 3-12 summarises the QA information obtained for the November 2015 sampling round analyses.

The quality assurance data described above indicate that the total recoverable metals data were of acceptable quality, which was generally consistent with previous RDP/RSCMP results. BRS results showed higher between-year variability at times for As and Hg than for Cu, Pb, and Zn, and therefore the CRM and BRS data for As and Hg should be checked to assess the reliability and meaningfulness of future trends for As and Hg. Note that extractable metals (in the <63µm fraction) were not analysed in the November 2015 samples.

The PSD data from the BRS analyses showed low variability and good comparability with the results from the previous BRS batches (November 2011 to June 2015). Overall, based on the BRS data collected to date, the PSD data are deemed to be reliable.

Overall, the November 2015 monitoring data for total recoverable metals and PSD were similar in quality to those obtained in previous years and are considered acceptable for use in the RSCMP status and trend assessment programme.

Table 3-12: Summary of analytical quality assurance results for the November 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)	N/A	No spike recoveries measured.
Within Batch blind duplicates	95% of RPDs <30%	**Pass**	Metals: 7 samples analysed in duplicate by Hill labs in-house QA. All RPDs <10%. Overall, good WB agreement.
		N/A	Particle size: No WB blind duplicates analysed
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 total recoverable metals. Means within 8% of certified values for total Cu, Pb, As & Hg. Total Zn 12% low. Individual samples within 10% of reference values, except one Hg result (11% low). Variability low - CVs 1.7-3.5%.
	Temporal stability: Trends over time <1% of median concentration per year.	**Pass**	Trends over time for 2002 to Nov 2015 small and not significant: Cu 0.23% per yr, Pb 0.35% per yr, Zn -0.01% per yr).
Lab In-House Reference Material	Accuracy: 95% of results within lab control limits	**Pass**	12 samples of "QC A5" analysed as unknowns for total metals. Variability for total metals (CVs) 5-13%. Mean concentrations within 11% of reference.Total Cu and Zn both showed one value outside the lab control limits – the lab QA report commented on these results, and based on the other set of QCA5 sample results concluded that the batch were acceptable.
Bulk Reference Sediments:			
Total Recoverable Metals	Within-year variability: 95% of WB CVs <30%.	**Pass**	Within-year variability meets targets (CVs 2-14% for all metals).
	Between-year variability: 95% of between-year RPDs <30%.	**Pass (Cu Pb Zn)** **Note (As, Hg)**	November 2015 results were within <30% of 2011 to June 2015 results, except for As & Hg (which were 34% and 44% higher in the June 2015 samples). All Cu, Pb, and Zn results within 16% of the Nov 2015 medians. As & Hg more variable between years (up to 44% difference cf Nov 2015).
	Temporal stability: Trends over time <2% of median concentration per year.	**Pass**	Trends over time for Nov 2011 to Nov 2015 were -0.9 to +0.8 % per year for total Cu, Pb, and Zn. None of these trends were statistically significant (MK test, p>0.05, N=4).
Particle Size Distribution	Within-year variability: 95% of WB CVs <30%.	**Pass**	% mud results had low variability: CV of 3.5% for Middlemore and Meola Outer BRS (N=3).
	Between-year variability: 95% of between-year RPDs <30%.	**Pass**	2015 results within 6.6% (Meola Outer) and 5.0% (Middlemore) of any of the previous median results for 2011 to June 2015.
	Temporal stability: Trends over time <2% of median concentration per year.	**Pass**	Trends for % mud for 2011 to Nov 2015 in Meola Outer were -1.3% per year, and for Middlemore -0.9% per year. Trends were not statistically significant (MK test, p>0.05, N=4).
OVERALL ASSESSMENT		Total metals **Cu, Pb, Zn: OK** **As & Hg: on-going checks required**	Total recoverable Cu, Pb, and Zn OK. As & Hg data more variable - use CRM and BRS results to check validilty of temporal trends.
		PSD: OK	PSD data look good. Low variability, temporal trends small.

4.0 References

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Appendix A Sediment contaminant data

Metal analyses data for November 2015 monitoring. Concentrations in mg/kg freeze-dry weight (<500µm fraction). QA sample data are included for Certified Reference Material (CRM AGAL10) and Bulk Reference Sediments (BRS).

		Total Recoverable metals, mg/kg freeze dried wt, <500 µm				
Sample	Replicate	Cu	Pb	Zn	As	Hg
Benghazi	1	10.2	14.8	83	6.3	0.067
Benghazi	2	9.8	14.5	77	5.9	0.067
Benghazi	3	10.3	15.4	88	6.1	0.076
Benghazi	4	10.5	15.5	95	6.3	0.060
Benghazi	5	10.3	15.3	81	6.1	0.060
Bowden	1	22	29	199	11.0	0.146
Bowden	2	21	29	192	10.0	0.147
Bowden	3	23	29	192	9.1	0.166
Bowden	4	22	29	190	8.6	0.144
Bowden	5	22	31	199	9.0	0.159
Chelsea	1	6.0	12.7	47	6.3	0.045
Chelsea	2	6.0	13.0	49	7.1	0.045
Chelsea	3	6.0	12.7	46	6.6	0.062
Chelsea	4	6.2	12.2	44	5.8	0.044
Chelsea	5	6.7	12.1	46	6.0	0.056
Coxs	1	6.2	14.8	80	2.9	0.054
Coxs	2	6.1	14.2	76	2.8	0.059
Coxs	3	5.9	14.0	75	3.0	0.050
Coxs	4	6.0	13.7	75	2.8	0.047
Coxs	5	6.2	14.0	78	2.9	0.054
Harania	1	16.1	22	120	12.0	0.062
Harania	2	18.0	22	138	12.0	0.058
Harania	3	18.1	22	138	12.0	0.060
Harania	4	18.5	22	143	12.4	0.052
Harania	5	19.0	22	144	12.3	0.058
Henderson Lower	1	26	29	133	11.0	0.127
Henderson Lower	2	32	28	157	12.0	0.121
Henderson Lower	3	27	29	135	10.7	0.137
Henderson Lower	4	28	30	137	10.6	0.150
Henderson Lower	5	26	29	132	11.7	0.134
Pahurehure Middle	1	2.2	6.0	33	10.3	< 0.01
Pahurehure Middle	2	2.0	5.8	30	8.1	< 0.01
Pahurehure Middle	3	2.1	5.7	31	8.5	< 0.01
Pahurehure Middle	4	1.9	5.8	32	10.2	0.019
Pahurehure Middle	5	2.3	5.9	34	9.5	0.016
Pahurehure Upper	1	7.0	10.7	70	11.3	0.028
Pahurehure Upper	2	7.0	10.8	70	10.8	0.044
Pahurehure Upper	3	7.0	10.6	68	11.0	0.029
Pahurehure Upper	4	7.2	10.7	70	11.3	0.037
Pahurehure Upper	5	7.3	11.6	72	11.4	0.031

Sample	Replicate	Total Recoverable metals, mg/kg freeze dried wt, <500 μm				
		Cu	Pb	Zn	As	Hg
Papakura Lower	1	7.9	12.1	71	11.6	0.040
Papakura Lower	2	7.3	11.5	67	11.0	0.035
Papakura Lower	3	7.8	11.8	72	11.0	0.035
Papakura Lower	4	9.0	11.5	67	10.6	0.035
Papakura Lower	5	9.1	12.2	68	11.6	0.030
Princes	1	16.0	24	147	8.0	0.112
Princes	2	18.4	24	160	8.2	0.145
Princes	3	16.8	22	146	7.3	0.137
Princes	4	17.5	23	153	6.9	0.134
Princes	5	16.8	23	148	7.5	0.124
Shoal Hillcrest	1	15.7	27	97	8.0	0.174
Shoal Hillcrest	2	16.1	29	100	8.1	0.175
Shoal Hillcrest	3	15.5	27	94	8.5	0.161
Shoal Hillcrest	4	15.2	26	91	8.1	0.155
Shoal Hillcrest	5	15.6	27	92	8.5	0.175
Tararata	1	13.4	17.5	103	9.7	0.053
Tararata	2	13.4	17.6	102	9.8	0.050
Tararata	3	14.1	18.8	110	10.0	0.049
Tararata	4	13.2	17.3	101	10.1	0.058
Tararata	5	13.3	17.7	103	10.0	0.059
Whau Entrance	1	4.4	8.2	37	2.6	0.040
Whau Entrance	2	4.3	8.3	37	2.6	0.034
Whau Entrance	3	4.4	8.4	40	2.7	0.033
Whau Entrance	4	4.2	8.2	38	2.6	0.030
Whau Entrance	5	4.1	8.1	36	2.5	0.031
Hillsborough	1	7.7	12.1	68	7.0	0.031
Hillsborough	2	7.4	11.4	65	7.2	0.033
Hillsborough	3	7.4	10.8	63	7.1	0.025
Hillsborough	4	7.2	10.7	63	7.2	0.033
Hillsborough	5	7.1	10.8	63	7.2	0.034
Mill Bay	1	4.3	9.1	55	10.0	< 0.01
Mill Bay	2	4.2	8.3	51	10.8	< 0.01
Mill Bay	3	4.0	8.6	51	10.3	< 0.01
Mill Bay	4	4.0	8.6	51	13.6	< 0.01
Mill Bay	5	3.6	8.2	49	8.9	0.011
Rarawaru	1	15.5	19.5	73	7.5	0.128
Rarawaru	2	15.9	19.6	76	7.7	0.127
Rarawaru	3	15.7	19.4	75	7.5	0.108
Rarawaru	4	16.1	19.9	75	8.0	0.116
Rarawaru	5	16.1	21	76	7.4	0.123

Sample	Replicate	Total Recoverable metals, mg/kg freeze dried wt, <500 μm				
		Cu	Pb	Zn	As	Hg
Roberta Reserve	1	3.8	7.3	39	7.6	0.058
Roberta Reserve	2	3.6	7.4	37	6.6	0.031
Roberta Reserve	3	3.8	7.3	39	7.2	0.023
Roberta Reserve	4	3.5	7.3	38	7.3	0.026
Roberta Reserve	5	3.6	7.3	39	7.5	0.023
Hobsonsville	1	2.2	5.7	22	4.5	0.035
Hobsonsville	2	2.1	5.7	21	4.0	0.014
Hobsonsville	3	2.1	5.6	21	3.7	0.023
Hobsonsville	4	2.2	5.8	21	4.2	0.023
Hobsonsville	5	2.2	5.7	20	3.4	0.016
Puhinui Upper	1	8.7	12.0	99	12.0	0.026
Puhinui Upper	2	8.2	11.5	96	12.9	0.028
Puhinui Upper	3	7.8	11.0	92	12.2	0.039
Puhinui Upper	4	7.7	10.8	91	12.7	0.033
Puhinui Upper	5	7.7	10.8	90	13.3	0.038
Pukaki Airport	1	7.2	10.3	61	11.9	0.033
Pukaki Airport	2	6.9	9.8	59	11.4	0.027
Pukaki Airport	3	7.4	11.0	64	12.9	0.028
Pukaki Airport	4	7.2	10.6	63	13.0	0.030
Pukaki Airport	5	7.3	10.9	64	13.0	0.033
Waimahia Central	1	7.1	10.9	68	11.0	0.035
Waimahia Central	2	8.0	10.8	80	12.4	0.030
Waimahia Central	3	8.3	10.9	81	12.4	0.030
Waimahia Central	4	7.4	11.0	67	10.9	0.038
Waimahia Central	5	7.4	11.1	68	10.8	0.036
Middlemore BRS FD	1	29	35	220	8.0	0.173
Middlemore BRS FD	2	28	34	220	7.6	0.138
Middlemore BRS FD	3	27	34	210	7.9	0.151
Middlemore BRS FD	4	28	35	220	7.9	0.159
Middlemore BRS FD	5	28	34	220	7.8	0.146
Meola Outer BRS FD	1	3.0	8.8	39	2.4	0.034
Meola Outer BRS FD	2	2.9	9.1	41	2.6	0.028
Meola Outer BRS FD	3	2.8	8.8	37	2.4	0.025
Meola Outer BRS FD	4	2.8	8.6	38	2.4	0.026
Meola Outer BRS FD	5	3.0	9.0	39	2.6	0.026
CRM AGAL 10	1	21	39	49	17.0	11.0
CRM AGAL 10	2	23	40	51	16.4	10.8
CRM AGAL 10	3	22	39	50	17.4	10.3

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 % of the total sediment (by weight) in 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
Benghazi	3.63	5.24	10.13	53.71	16.83	10.47
Bowden	0.02	0.69	1.91	46.16	30.63	20.59
Chelsea	0.84	0.41	11.46	76.11	7.18	3.99
Coxs	0.63	0.68	8.76	80.83	3.58	5.53
Harania	0.00	0.08	0.31	12.72	64.44	22.45
Henderson Lower	0.00	0.07	0.14	10.03	66.23	23.53
Pahurehure Middle	2.61	4.04	14.07	65.47	9.59	4.22
Pahurehure Upper	0.04	0.35	0.70	24.52	60.11	14.28
Papakura Lower	0.00	0.05	0.24	18.20	68.41	13.11
Princes	0.00	1.12	4.05	59.69	19.53	15.62
Shoal Hillcrest	0.10	0.46	1.38	14.48	58.70	24.87
Tararata	0.00	0.08	0.18	8.26	77.22	14.25
Whau Entrance	1.00	0.19	1.06	84.10	9.23	4.42
Hillsborough	4.67	11.89	9.30	38.82	26.93	8.39
Mill Bay	0.98	15.55	28.68	48.93	3.23	2.64
Rarawaru	0.00	0.09	0.55	32.30	52.23	14.82
Roberta Reserve	3.65	1.34	10.19	78.41	2.92	3.50
Hobsonsville	1.22	4.08	32.71	58.08	1.04	2.86
Puhinui Upper	0.17	2.96	3.02	20.22	59.21	14.42
Pukaki Airport	0.00	0.07	0.20	28.31	57.35	14.07
Waimahia Central	0.00	0.12	0.35	22.93	62.95	13.66
Middlemore BRS Frozen	0.00	0.08	0.60	29.87	50.35	19.10
Middlemore BRS Frozen	0.00	0.15	0.56	33.50	42.63	23.17
Middlemore BRS Frozen	0.00	0.14	0.71	33.97	42.18	23.01
Meola Outer BRS Frozen	2.74	0.29	1.03	93.12	0.28	2.54
Meola Outer BRS Frozen	0.16	0.27	0.98	95.72	0.96	1.91
Meola Outer BRS Frozen	0.53	0.23	1.02	95.20	0.75	2.26

Appendix C NIWA metals data quality assurance check

Appendix D R J Hill Laboratories Report