# Porirua Harbour subtidal sediment quality monitoring

Results from the November 2008 survey

**Quality for Life** 







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J R Milne and P G Sorensen

Environmental Monitoring and Investigations Department Greater Wellington Regional Council

S Kelly Coast and Catchment Limited

FOR MORE INFORMATION, CONTACT GREATER WELLINGTON:

Wellington PO Box 11646

T 04 384 5708 F 04 385 6960

www.gw.govt.nz

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www.gw.govt.nz info@gw.govt.nz

### **Executive summary**

Contaminants in urban stormwater discharges have been identified as a potential medium to long-term risk to the health of the marine organisms living in our harbours, largely through the accumulation of these contaminants in the sediments. This report presents the results of the third survey of sediment quality and benthic community health at five subtidal sites in the Porirua Harbour. These sites were sampled in November 2008.

Consistent with the results of the 2004 and 2005 surveys, concentrations of total copper, lead and zinc are above 'early warning' sediment quality guidelines in the subtidal sediments of the Onepoto Arm of Porirua Harbour. Concentrations of the other metals analysed are currently below guideline levels in the Onepoto Arm, as are the concentrations of all metals in the subtidal sediments of the Pauatahanui Arm.

Sixty-four species of benthic fauna were identified in the November 2008 survey, with all but two found in the samples taken from sites in the Pauatahanui Arm. In contrast, only 32 of the 64 species were found in the samples taken from two sites in the Onepoto Arm. Overall, the fauna were composed predominantly of polychaetes (25 species), crustaceans (17 species), and bivalve and gastropod molluscs (6 and 4 species respectively). The biomass at each site was dominated either by the bivalve *Cyclomactra ovatra*, Sipunculida #2, the echinoderm *Paracaudina chilensis*, or a combination of these. A second bivalve, *Nucula hartvigiana*, was also a significant contributor to the biomass at some sites.

The benthic fauna monitoring data indicate that some of the environmental variables measured are influencing lower-order benthic community structure. However, at this stage any effects of metal contamination cannot be separated from the effects of differences in sediment texture and organic carbon content. Both monitoring sites in the Onepoto Arm clearly have higher sediment metal contaminant concentrations and support a lower diversity of benthic species than sites in the Pautahanaui Arm, but the mud and organic carbon contents are also higher in the sediments of these sites.

Variability in sediment particle size distributions between 2004 and 2008 is of some concern. However, the sediments at all sites presently contain a relatively high proportion of muds for contaminant trend monitoring and the methods used for the collection and analysis of information on chemical contamination of subtidal sediments in Porirua Harbour are providing good quality data, with low variability for most analytes. This allows very small changes in contaminant concentrations to be detected over time. Although, statistically significant trends in the concentrations of copper, lead and zinc have been detected since 2004, it is still too early to tell whether these trends are ecologically significant and whether they will continue into the future. The reliability of trend detection, and the ability to form meaningful conclusions from any detected trends, should continue to improve as more monitoring data are added and the length of the time-series increases.

#### Recommendations

1. The next subtidal sediment chemistry survey is undertaken in Porirua Harbour in late 2010 to continue the monitoring of trends in contaminant concentrations over time. This survey should include analysis of sediment samples for polycyclic

aromatic hydrocarbons (PAHs) and organochlorine pesticides (OCPs). Further surveys of metal contaminants should be conducted every two years thereafter, unless the results and/or major changes in the catchment indicate a greater or lesser survey frequency is desirable. The need for, and frequency of, ongoing analyses of PAHs and OCPs should be assessed once the results of the 2010 survey are available.

2. The next benthic fauna survey is undertaken in Porirua Harbour in 2010 in order to continue monitoring for changes in community structure with possible links to changes in sediment quality. The survey should be carried out in late October or November to minimise seasonal influences, and coincide with the sediment chemistry survey if possible.

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#### 1. Introduction

Porirua Harbour is regionally significant, offering a multitude of landscape, ecological, cultural, geological and recreational values. However, like other coastal environments surrounded by densely populated areas, the harbour receives significant urban stormwater inputs with the potential to adversely impact on the health of its ecosystems.

The Porirua Harbour subtidal sediment quality monitoring programme was initiated by the Greater Wellington Regional Council (Greater Wellington) as part of a broader investigation into the possible impacts of urban stormwater discharges on aquatic receiving environments<sup>1</sup>. Five subtidal sites are being used in the programme, two in the Onepoto Arm and three in the Pauatahanui Arm, with each site having adjoining sediment chemistry and benthic fauna collection areas.

This report presents the results of the third survey of Porirua Harbour subtidal sediment quality, including the results of the biological component of the survey reported by Stephenson (2009). Previous surveys were undertaken in May 2004 and October 2005 (Williamson et al. 2005; Stephenson & Mills 2006). This third survey differs from the first two in that the sediment chemistry component was restricted to assessments of sediment particle size, total organic carbon and heavy metals. In the earlier surveys, sediments were also tested for polycyclic aromatic hydrocarbons, organochlorine pesticides and organotin compounds.

#### 1.1 Monitoring objectives

The Porirua Harbour subtidal sediment quality monitoring programme has the following objectives:

- 1. To make regular assessments of the Porirua Harbour receiving environment in terms of sediment quality and benthic community health to provide a sound scientific basis for any management response in relation to urban stormwater discharges.
- 2. To detect changes in sediment quality and benthic community health over time, thereby allowing the ongoing evaluation of urban stormwater management actions directed at maintaining or enhancing the Porirua Harbour receiving environment.

<sup>&</sup>lt;sup>1</sup> The reader is referred to Williamson et al. (2001) for further background on the effects of urban stormwater discharges on aquatic receiving environments in the Wellington region and the need for marine receiving environment monitoring.

#### 2. Sites and methods

#### 2.1 Sampling sites

A description of the sampling sites, including the rationale for the selection of subtidal (as opposed to intertidal) sites, can be found in Williamson et al. (2005). To be suitable for long-term monitoring, the sites must be:

- 1. representative of the area of concern;
- 2. likely to accumulate contaminants in a manner which reflects accumulation over the area; and
- 3. not likely to change markedly, particularly in their sediment texture, over time periods of decades.

In addition, the sediment at the sites should preferably have a relatively high proportion of mud because many contaminants tend to bind to fine sediment particles, and their low settling velocities mean that they are likely to be widely dispersed (i.e., represent far-field sources) (Ray et al. 2003).

Taking into account the above critiera, Williamson et al. (2005) identified four locations in Porirua Harbour at which long-term sediment quality monitoring could be conducted (in parallel with assessments of benthic community health). An additional site, PAH3, was subsequently added by Greater Wellington to monitor any impacts arising from urbanisation of land to the northwest of the Pauatahanui Arm, giving a total of five long-term monitoring sites (Table 2.1, Figure 2.1). These sites represent a selection of the subtidal habitats present in the harbour (Stephenson<sup>2</sup>, pers. comm.).

Site	Location	Date	Position (NZM	G coordinates)	Depth <sup>1</sup>
			Easting	Northing	(m)
PAH1 PAH1B	Pauatahanui Arm off Browns Bay	10/11/2008 10/11/2008	2668177 2668156	6009767 6009789	2.0
PAH2 PAH2B	Pauatahanui Arm off Duck Creek	10/11/2008 10/11/2008	2669747 2669779	6009854 6009831	1.8
PAH3 PAH3B	Pauatahanui Arm off Camborne	10/11/2008 10/11/2008	2668171 2668174	6010921 6010937	1.7
POR1 POR1B	Onepoto Arm South	20/11/2008 20/11/2008	2664884 2664854	6007585 6007604	2.0
POR2 POR2B	Porirua Harbour North	20/11/2008 20/11/2008	2665199 2665178	6008220 6008252	2.9

 Table 2.1: Site position and collection details for the Porirua Harbour subtidal

 sediment quality monitoring undertaken in November 2008

<sup>1</sup> Approximate water depth at mean low water neap tide

B = Benthic fauna collection area

<sup>&</sup>lt;sup>2</sup> Gary Stephenson, Coastal Marine Ecology Consultants (and former Greater Wellington coastal scientist).

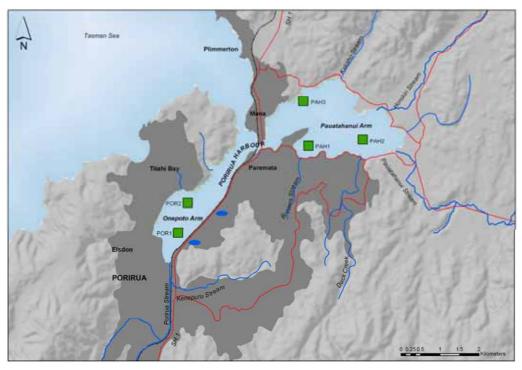


Figure 2.1: Map of Porirua Harbour showing the five subtidal locations sampled in November 2008

#### 2.2 Sediment particle size distribution and chemistry

#### 2.2.1 Sample collection

Sampling was conducted using a boat and divers equipped with SCUBA. At each site, the centre of the sediment chemistry collection area (a circle 20 m in diameter) was located by a Global Positioning System (GPS) and the boat anchored at this point. On the seabed, the collection area was divided into quadrants on the cardinal points of the compass and six 50 mm diameter x 120 mm deep sediment cores were collected at random from each quadrant by the divers. A separate screw-top polyethylene bottle, with the bottom cut off and replaced with a plastic insert, was used for each core (Figure 2.2). Bearings and distances from the boat to the dive points were determined from random number tables and measured by compass (nearest 10°) and tape (nearest m) respetively. A further sediment core was taken from near the centre of the collection area to give a total of 25 samples. The samples were kept upright whilst being brought to the surface and placed in an insulated bin containing ice-packs for transport to the laboratory.



Figure 2.2: Example of a sediment core from Porirua Harbour. Only the top 30 mm of the sediment is used to analyse sediment particle size distribution and chemistry. (Photo: G. Stephenson)

The sediment samples were stored upright in a refrigerator at 4°C for a minimum of 12 hours to allow the water content of the surface sediment to reduce. The 25 samples from a site were randomly assigned to five groups. These groups became the five replicate composite samples for that site. With each sample, the bottle was placed on a tray, the top cap removed, and any overlying water carefully siphoned off. The bottom plug was loosened and the core extruded until the top 30 mm remained unexposed. The core was cut at this level with a plastic ruler and the sediment beyond 30 mm depth was discarded. The top 30 mm of the sediment was transferred into a polyethylene bag along with that from the four other samples in the group<sup>3</sup>. The composite sample was then frozen.

#### 2.2.2 Sample preparation

Sample preparation was consistent with previous surveys and followed the steps shown in Figure 2.3. Each thawed replicate composite sample was homogenised by mixing it in a shallow plastic tray. A sub-sample was wet-sieved through a nylon mesh to obtain a representative <63  $\mu$ m fraction that was then freeze-dried for later analysis of weak acid-extractable metals and for long-term storage. The remainder of each whole replicate sample was freeze-dried in preparation for analysis of sediment particle size, total organic carbon and total metals (Olsen et al. 2009). Prior to these analyses, the freeze-dried replicate samples were dry-sieved through a 500  $\mu$ m screen to remove coarse debris (e.g., shell fragments).

<sup>&</sup>lt;sup>3</sup> Only the top 30 mm of the sediment column from each core sample was retained as this depth is equivalent to the average depth of the surface mixed layer observed in X-radiographs of dated sediment cores collected in an historical sedimentation survey of the Pauatahanui Arm by Swales et al. (2005).

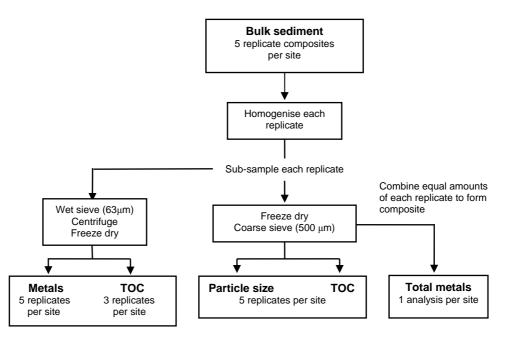


Figure 2.3: Sample preparation scheme (adapted from Williamson et al. 2005)

- 2.2.3 Sample analysis, quality assurance and storage
  - (a) Sediment particle size distribution

Particle size data (0-300  $\mu$ m range) were obtained for each <500  $\mu$ m fraction replicate sample using an Eyetech Particle Size Analyser<sup>4</sup>, with the material ultrasonically dispersed for four minutes before analysis. Traceable standards were used to ensure the reliability of particle size results. Particle volumes were calculated from the measured particle diameters, and used to produce a particle-size volume distribution for each sample (Olsen et al. 2009).

#### (b) Total organic carbon

A portion of the freeze-dried <500  $\mu$ m fraction of each replicate sample was analysed for total organic carbon (TOC) using an Elementar Combustion Analyser, after acid pre-treatment to remove carbonates. Organic carbon is usually included in sediment quality monitoring programmes because it can influence the bio-availability of toxic organic compounds and comparison of toxic organic compound concentrations with the sediment quality guidelines used in New Zealand requires concentrations to be normalised to 1% organic carbon. Although the 2008 Porirua Harbour sediment sample analyses focused on metals rather than organic contaminants, TOC was still analysed because it plays a central role as a binding phase for many trace metals, such as copper and zinc, and correlation of metal concentrations with organic carbon can allow detection of unusual contaminant depletion or enrichment patterns. For this reason, a portion of the <63  $\mu$ m fraction of three of the five replicate samples from each site was also analysed for TOC.

<sup>&</sup>lt;sup>4</sup> This differed from the 2004 and 2005 particle size assessments which were undertaken using a Galai CIS-100 'time-of-transition' stream-scanning laser particle sizer. However, comparable data sets are expected from both analysers (Olsen et al. 2009) with two archived 2005 sediment samples analysed on the Eyetech analyser for direct comparison (*see* subsection 2.2.3(e)).

#### (c) Total metals

A single composite was prepared from portions of the freeze-dried  $<500 \mu m$  sub-samples of the five replicates from each sampling site, digested using strong, hot hydrochloric and nitric acids, and the digest analysed by inductively coupled plasma-mass spectrometry (ICP-MS) for total recoverable antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver and zinc. Use of a single composite (rather than all replicates) is adequate for comparison with the sediment quality guidelines used in New Zealand because the precision of this comparison is of little interest.

#### (d) Weak acid-extractable metals

A portion of the  $<63 \mu m$  fraction of each replicate sample was extracted using weak (2M) cold hydrochloric acid and the extract analysed by ICP-MS for copper, lead and zinc. This technique minimises analytical variability, and therefore is better for trend analysis. In addition, the fine sediment fraction is the most ecologically relevant component of sediments in terms of contaminants, since it is more likely that benthic animals will ingest, or be in intimate contact with, fine rather than coarse materials. Hence the weak acid-extractable fraction is a better measure of bio-available metals (ARC 2004).

#### (e) Quality assurance

A subset of sediment samples was chosen for duplicate analysis, to assess "within-sample batch" variability. In addition, archived Porirua Harbour sediment samples collected in 2004 and 2005 were analysed to assess "between-sample batch" variability and method performance. Quality assurance analysis is summarised below:

- Particle size (500 µm fraction): 2 archived samples
- Total organic carbon (500 μm fraction): 2 duplicate samples, 1 archived sample
- Total organic carbon (63 µm fraction): 2 duplicate samples
- Total metals: 1 duplicate sample, 2 archived samples<sup>5</sup>
- Weak acid-extractable metals: 2 duplicate samples, 1 archived sample

#### (f) Long-term sediment sample storage

The remaining portions of all replicate samples have been stored in stable conditions to permit future analysis and quality control.

#### 2.3 Benthic fauna

#### 2.3.1 Sample collection

At each site the centre of the benthic fauna collection area (a circle 20 m in diameter) was relocated using a Global Positioning System and the boat anchored at this point. The collection area was divided into quadrants on the cardinal points of the compass and two 200 mm diameter x 250 mm deep

<sup>&</sup>lt;sup>5</sup> Initially one archived sample – a second was taken following poor agreement of results with the first sample. See Appendix 3.

sediment cores were collected from each quadrant by divers to give a total of eight samples. Bearings and distances from the boat to the dive points were determined from random number tables and measured by compass (nearest  $10^{\circ}$ ) and tape (nearest m) respectively. Two 50 mm diameter x 120 mm deep sediment cores were taken from near the centre of the collection area for particle size analysis.

#### 2.3.2 Sample preparation and analysis

Benthic fauna samples were transferred from the corers into labelled plastic bags for transport to the laboratory, where they were washed on a 500  $\mu$ m screen. The material retained by the screen was placed in 400 mL polyethylene jars and fixed in a solution of 5% formalin in seawater. Animals were picked out under a binocular microscope, identified as far as practicable<sup>6</sup>, counted, and preserved in 70% isopropyl alcohol. Shell lengths of selected species of bivalves were measured to the nearest 0.1 mm using an ocular micrometer ( $\leq 10$  mm) or digital callipers (>10 mm).

Sediment samples were prepared and analysed for particle size in the same manner as the sediment chemistry samples. For each site, the sediment in the top 30 mm of the two cores was removed and combined to form a composite, which was then homogenised, freeze-dried, and sieved at 500  $\mu$ m. Particle size analysis of the <500  $\mu$ m fraction was conducted using an Eyetech Particle Size Analyser, as described in Section 2.2.3.

At the conclusion of the analysis of the fauna, representative specimens of species not found in the 2004 or 2005 surveys were labelled and added to the existing Porirua Harbour benthic fauna reference collection.

#### 2.4 Data analysis

- 2.4.1 Sediment chemistry
  - (a) Sediment quality guidelines

Both the Australian and New Zealand Environment and Conservation Council (ANZECC 2000) and the Auckland Regional Council's (2004) "Environmental Response Criteria" (ERC)<sup>7</sup> sediment quality guidelines were used to assess the potential ecological effects of contaminants in the Porirua Harbour subtidal sediments (Table 2.2). These guidelines are generally considered to be reasonably robust, and conservative (i.e., they err on the side of environmental protection). They are not "pass or fail" numbers, and the developers of the guidelines emphasise that they are best used as one part of a "weight of evidence" approach to evaluating potential effects of contaminants on benthic biota.

<sup>&</sup>lt;sup>6</sup> Where genus and species names could not be assigned with certainty due to damage to the specimens, small size, immaturity, or taxonomic difficulties, the species were designated "#1", "#2", "#3", etc., following the class, family or generic name as appropriate.

<sup>&</sup>lt;sup>7</sup> Note that these guidelines are currently under appeal.

The ANZECC guidelines, and other international sediment quality guidelines on which they are based (i.e., Long & Morgan 1990), provide 'low' and 'high' values:

- 1. ANZECC ISQG-Low trigger values nominally indicative of the contaminant concentrations where the onset of biological effects could possibly occur. These values provide an early warning, enabling management intervention to prevent or minimise adverse environmental effects.
- 2. ANZECC ISQG-High trigger values nominally indicative of the contaminant concentrations where significant biological effects are expected. Exceedance of these values therefore indicates that adverse environmental effects are probably already occurring, and management intervention may be required to remediate the problem.

The Auckland Regional Council's amber and red ERC were derived from the Threshold Effect Levels (TEL) and Effects Range Low (ERL) values (with rounding) of MacDonald et al. 1994 and Long & Morgan (1990) respectively (Kelly 2007). These guidelines provide a conservative, yet practical<sup>8</sup> early warning of environmental degradation which allows time for investigations into the causes of contamination to be carried out and the options for limiting the extent of degradation to be developed (Kelly 2007, ARC 2004).

Analyte	ANZECC tr	igger values	ARC ERC t	hresholds
	ISQG-Low	ISQG-High	amber	red
Metals (mg/kg dry wt):				
Antimony	2	25		
Arsenic	20	70		
Cadmium	1.5	10		
Chromium	80	370		
Copper	65	270	19	34
Lead	50	220	30	50
Mercury	0.15	1		
Nickel	21	52		
Silver	1	3.7		
Zinc	200	410	124	150

Table 2.2: Sediment quality guidelines used in assessing the results of theNovember 2008 Porirua Harbour subtidal sediment quality survey. Guidelinevalues are taken from ANZECC (2000) and ARC (2004).

<sup>1</sup> Arsenic is, strictly speaking, a metalloid (ANZECC 2000)

#### (b) Statistical analyses

Differences in the concentrations of copper, lead and zinc (obtained using weak acid digestion), and the proportion of TOC and mud (<63  $\mu$ m), were plotted using means and 95% confidence intervals<sup>9</sup> so that differences among sites and

<sup>&</sup>lt;sup>8</sup> Some of the ANZECC guideline values are not practical. For example, the organochlorine pesticide dieldrin has an ANZECC ISQG-Low value of 0.02 µg/kg (parts per billion), which is below the analytical detection limits of almost all laboratories, and probably represents a level that would be present at most rural and urban estuaries in New Zealand. Some other examples of differences between the ANZECC and ARC ERC guidelines are discussed in ARC (2004).

<sup>&</sup>lt;sup>9</sup> Points with confidence intervals that don't overlap are significantly different from each other.

changes through time (i.e., between 2004 and 2008) could be visualised. Least-squares linear regression was then used to identify statistically significant temporal trends. Note that the results of the regression analyses should be treated very cautiously because only three data points were available for each site.

#### 2.4.2 Benthic fauna

The number of species, wet weight of each species (biomass), mean number of species per sample and mean number of individuals per sample were determined for each site. The size frequency distributions of selected species of bivalves were determined and summarised in diagrammatic form as dot plots.

Spatial and temporal variation in the composition of benthic communities was examined using diversity indices and multivariate analyses. Multivariate analysis was also used to examine the relationship between community structure and environmental variables (i.e., sediment texture, metal concentrations and TOC). All analyses were carried out using Primer-E, and readers are referred to Clarke & Gorley (2006) and Clarke & Warwick (2001) for further details on most of the analyses used.

Species were also assigned to one or more of five feeding modes (herbivores, predators + carrion feeders + scavengers, surface deposit feeders, subsurface deposit feeders, and suspension feeders) based on the literature (*see* Stephenson & Mills 2006). However, as the feeding biology of many of the species encountered has yet to be studied, it was often necessary to utilise data on their nearest taxonomic relatives and/or apparent ecological equivalents elsewhere to predict the most likely feeding mode for the species. Species whose feeding mode was uncertain or could not be predicted from the available data were placed in a separate class, giving six categories in all. For species which were assigned to more than one feeding mode, equal proportions of the individuals of that species were arbitrarily assigned to each mode; if the numbers would not divide equally the last individual was placed in what was known or considered to be the dominant feeding mode for the species in this environment. The percentage of individuals in each feeding mode at each site was calculated.

#### (a) Diversity

The Shannon diversity index is a commonly used measure of diversity that takes into account the number of species present (species richness) and how evenly the number (or biomass) of individuals is spread amongst these species (equitability). The latter consideration is an important feature of the index, as one community may have more species, but lower diversity than another, if one (or a few) species are numerically dominant. Interpretation of Shannon's diversity index is therefore aided by specific information on species richness and equitability. Three measures of diversity were therefore examined:

- the number of species per sample;
- the Shannon diversity index (using base *e*); and

• Pielou's evenness index.

Pielou's evenness index is a measure of how even (i.e., similar) the abundances of individual species are at a site. Low index values indicate that the site is dominated by a single, or a few, species which occur in high abundance(s). The remaining species occur in relatively low abundances. In contrast, high index values indicate that the abundances of all species are fairly similar. Temporal variation in the number of species, the Shannon diversity index and Pielou's evenness index were examined by plotting mean ( $\pm$  95% CI) values for each of the sites sampled in 2004, 2005 and 2008.

#### (b) Community structure

Non-metric multi-dimensional scaling (MDS) and cluster analysis were used to identify patterns in ecological data, based on the similarity (or dissimilarity) of species assemblages. Untransformed (i.e., raw) and  $\log x+1$  transformed count data, using Bray Curtis similarity, were used to examine spatial differences and temporal changes in the composition of the benthic communities. These techniques were used to identify patterns in ecological data, based on the similarity (or dissimilarity) of species assemblages. Note that the use of raw data emphasised the influence of the most abundant species, while log transformation reduced the influence of these species. The results of these analyses were presented as MDS plots with clusters overlaid. These provide an easily interpretable representation of the data (i.e., samples that are close together on an MDS plot are more similar than samples that are further apart). Identification of the key species involved in producing the observed patterns was obtained by looking at similarity percentages (using Primer's SIMPER routine) and overlaying bubbleplots of species abundance on the MDS plots. Similarly, the relationship between community structure and various environmental variables (both physical and chemical) was examined by overlaying bubbleplots of the variables on MDS plots.

For the above analyses, the mean values for environmental variables from a site and year were applied to all eight replicate benthic fauna samples obtained from that site and year. Although the locations of sediment chemistry and benthic fauna collection areas differ slightly at each site, Stephenson & Mills (2006) could find no evidence of significant faunal or environmental differences between each set in the 2004 and 2005 surveys, and the same appeared to be the case in the 2008 survey (Stephenson pers. comm.). It is therefore assumed that the data obtained from each sediment chemistry collection area is representative of its adjoining benthic fauna collection area.

The above methods provide a relatively good representation of the dominant patterns in benthic community structure, and allow the visualisation of relationships between a representation of community structure (which emphasised the influence of the most abundant species) and a range of environmental variables. However, the most abundant species are not necessarily the most sensitive species to environmental change. Canonical analysis of principal coordinates (CAP) was therefore used to examine more subtle relationships between the environmental variables and benthic community structure. Readers are referred to Anderson et al. (2002) and Anderson et al. (2006) for a description of CAP and the methods used.

Two variations of CAP were used for the analysis of lower order community effects. These included constraining species counts by:

- A quantitative index of 'environmental quality' obtained by a principal component analysis (PCA) of environmental variables. PCA reduced the 11 environmental variables (copper, lead, zinc, silver, arsenic, cadmium, chromium, mercury, nickel, TOC and sediment texture (% mud)) into a single measure (PCA axis 1). Linear regression was then used to examine the relationship between the primary PCA axis and CAP scores of community structure.
- Categorical site groupings based on cluster analysis of environmental variables. This analysis was carried out to validate the CAP using "leave-one-out" allocation success (see Anderson et al. (2002) and Anderson et al. (2006) for a description of this test). Clusters were selected based on significant groupings using similarity profile analysis (SIMPROF routine) and through arbitrary selection of major breaks on the cluster dendrogram. Species differences between site groupings were then examined using SIMPER analysis. This provided more detail on how species assemblages changed in response to changes in environmental quality.

Canonical analysis of principal coordinates was carried out using Bray Curtis similarities of square root transformed species counts (using total counts for each site-year), and PCA1 values derived from Principal Component Analysis (PCA) of the normalised environmental variables: copper, lead, zinc, silver, arsenic, cadmium, chromium, mercury, nickel, TOC and sediment texture (% mud (<63  $\mu$ m)). Normalisation allowed a combination of variables with different measurement scales to be included in the analysis (i.e., metal concentrations, and TOC and sediment texture percentages). An important consequence of normalisation is that it "equalises" the contributions of each variable to the multivariate analysis. This was considered to be desirable for metals, because the ecological effects of small changes in the concentration of another metal (e.g., zinc).

#### 3. Results

The sediment particle size and chemistry results from the November 2008 Porirua Harbour subtidal sediment quality survey are summarised in this section, along with the benthic fauna results. Comparisons are also made with the results of the 2004 and 2005 subtidal surveys. The complete list of sediment particle size and chemistry results are presented in Appendices 1 and 2 respectively, and their associated quality assurance results in Appendix 3. The benthic fauna results are presented in Appendix 4.

#### 3.1 Sediment particle size and chemistry – 2008

#### 3.1.1 Sediment particle size distribution

Mean particle size and the mean percentage of particles  $<63 \mu m$  in the sediments of the five monitoring sites are shown in Table 3.1. Consistent with previous surveys, the mean percentages of particles  $<63 \mu m$  in the sediments of sites in the Pauatahanui Arm (20–43%) were lower than those of sites in the Onepoto Arm (74–90%). Variability in the mean percentage was reasonably low (coefficient of variation [c.v.] 3.5–8.0%), with a tendency to be higher at the Pauatahanui sites with the sandier sediments.

#### 3.1.2 Total organic carbon

The mean total organic carbon (TOC) contents in the <63  $\mu$ m and <500  $\mu$ m fractions of the sediments of the five monitoring sites are shown in Table 3.1. Consistent with previous surveys, the mean TOC contents in the sediments of sites in the Pauatahanui Arm (0.97–1.66%) were lower than those of sites in the Onepoto Arm (1.95–2.22%), reflecting the greater proportions of sand in the Pauatahanui Arm sediments. Variability in the mean TOC content of the <500  $\mu$ m fraction was reasonably low for all sites (c.v. 1.3–5.1%).

#### 3.1.3 Total metals

The total concentrations of each of the nine metals tested were generally higher in the sediments of sites in the Onepoto Arm than in those of sites in the Pauatahanui Arm (Table 3.1). This is consistent with the results of the 2004 and 2005 surveys.

Total copper and lead concentrations in the sediments of both sites in the Onepoto Arm exceeded the ARC (2004) ERC amber thresholds for these metals, but were below their respective ANZECC ISQG-Low trigger values. Total zinc concentrations at these sites exceeded the ERC red threshold, with the concentration at site POR1 (Onepoto Arm south) equal to the ANZECC ISQG-Low trigger value of 200 mg/kg.

Total arsenic, cadmium, chromium, mercury, nickel and silver concentrations in the sediments of sites in both arms of Porirua Harbour were all below their respective ANZECC ISQG-Low trigger values (Table 3.1). However, mercury approached the ISQG-Low trigger value in the sediments of both sites in the Onepoto Arm.

Table 3.1: Mean particle size, percentage of particles <63 µm, and summary of concentrations and variability (coefficient of variation [c.v., %], n = 5)
of TOC and metals in sediments of five sites sampled in Porirua Harbour in November 2008. Sediment quality guidelines for comparison are
ANZECC (2000) and Auckland Regional Council Environmental Response Criteria (ARC ERC; ARC 2004). Values in amber exceed the ARC ERC
amber threshold and values in red exceed the ARC ERC red and/or ANZECC ISQG-Low thresholds.

Analyte	Fraction	ANZ	ECC	ARC	ERC	PA	H1	PA	H2	PA	H3	PO	R1	PO	R2
	analysed	ISQG-Low	ISQG-High	amber	red	mean	c.v.								
Mean particle size (µm)	<500 µm	-	-	-	-	77.17	4.9	66.09	4.7	99.88	2.7	47.49	6.9	33.07	14.2
% particles <63 µm	<500 µm	-	-	-	-	39.19	5.8	43.27	8.0	20.41	6.0	73.83	3.5	89.89	4.8
Total Organic Carbon (%)	<63 µm	-	-	-	-	1.44	2.4	1.54	1.7	1.09	4.6	1.47	4.5	1.70	1.2
Total Organic Carbon (%)	<500 µm	-	-	-	-	1.66	3.2	1.59	5.1	0.97	3.4	2.22	2.5	1.95	1.3
Metals (mg/kg, 2 M HCI):															
Copper	<63 µm	-	-	-	-	8.7	3.4	7.9	2.3	7.2	3.3	14.0	0	13.2	3.4
Lead	<63 µm	-	-	-	-	21.0	0	17.6	3.1	16.8	2.7	32.2	1.4	34.4	1.6
Zinc	<63 µm	-	-	-	-	67.4	2.5	57.0	1.2	54.2	2.7	145.8	1.7	127.4	1.6
Total Metals (mg/kg):															
Silver	<500 µm	1	3.7	-	-	0.09	-	0.07	-	0.06	-	0.18	-	0.13	-
Arsenic	<500 µm	20	70	-	-	11	-	7.5	-	9.0	-	12	-	13	-
Cadmium	<500 µm	1.5	10	-	-	0.04	-	0.06	-	0.04	-	0.17	-	0.04	-
Chromium	<500 µm	80	370	-	-	21.9	-	15.7	-	17.1	-	21.6	-	23.9	-
Copper	<500 µm	65	270	19	34	14.6	-	10.5	-	9.5	-	23.4	-	20.6	-
Mercury	<500 µm	0.15	1	-	-	0.09	-	0.08	-	0.07	-	0.12	-	0.14	-
Nickel	<500 µm	21	52	-	-	15	-	11	-	12	-	14	-	16	-
Lead	<500 µm	50	220	30	50	22.7	-	17.3	-	16.2	-	40.2	-	37.2	-
Zinc	<500 µm	200	410	124	150	88.6	-	70.1	-	69.7	-	200	-	150	-

The sediment concentrations of most metals were strongly correlated, in particular total copper, lead and zinc concentrations (Pearson r = 0.973-0.993).

#### 3.1.4 Weak acid-extractable metals

The mean concentrations of weak acid-extractable copper, lead and zinc in the <63  $\mu$ m fraction of the sediments followed similar spatial patterns to their total metal concentrations, being higher in the sediments of sites in the Onepoto Arm than in those of sites in the Pauatahanui Arm (Table 3.1). The data showed low variability (c.v. 0–3.4%) which, as with previous surveys, confirms that it should be possible to detect relatively small changes in metal concentrations over time.

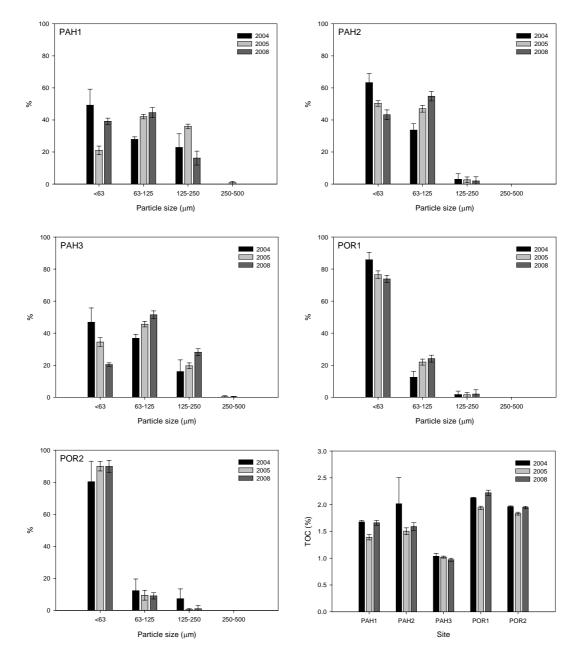
## 3.2 Comparison with 2004 and 2005 sediment particle size and chemistry

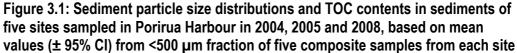
#### 3.2.1 Sediment particle size distribution

Substantial changes in particle size distribution are evident at all but one of the monitoring sites between the 2004, 2005 and 2008 surveys (Figure 3.1). The percentage of mud (<63  $\mu$ m) particles in the sediments at sites PAH2, PAH3 and POR1 has decreased progressively, with corresponding increases in the very fine sand (63–125  $\mu$ m) and, in the case of site PAH3, fine sand (125–250  $\mu$ m) fractions. The very fine sand fraction in the sediments at site PAH1 has also increased progressively, but here the mud fraction decreased in 2005 and increased again in 2008 while the fine sand fraction showed the opposite pattern (i.e., an increase in 2005 and a decrease in 2008). Sediment particle size distribution has changed the least at site POR2; following a slight increase in 2005, the 2008 results show almost no change.

#### 3.2.2 Total organic carbon

Differences in mean TOC contents between the the 2004 and 2005 surveys reflected changes in the percentage of mud particles present in the sediments (Figure 3.1), except at site POR2. However, this pattern only continued at sites PAH1 and (to a lesser extent) PAH3 in 2008. At the remaining sites mean TOC content increased in 2008 even though the mud fraction decreased (sites PAH2 and POR1) or remained the same (site POR2). Quality assurance results indicate that the differences observed are probably not due to analytical variation as good agreement (within 8%) was obtained in the "between-sample batch" comparison (Appendix 3).





#### 3.2.3 Total metals

The total concentrations of each of the nine metals analysed were generally higher in the 2008 survey than in 2005 and similar to those recorded in the first survey in 2004 (Figures 3.2–3.4). While some of the differences between the surveys may be attributable to changes in sediment texture, quality assurance results suggest they may also reflect changes in analytical performance. The archived Porirua Harbour sediment sample from 2004 used in the "between-sample batch" comparison returned markedly higher results for silver and zinc, and moderately higher results for cadmium, chromium and nickel, when reanalysed with the 2008 samples. A second archived sediment sample from 2005 was analysed to provide a further check and returned a markedly higher

result for arsenic and a moderately higher result for lead (Appendix 3). While such analytical performance issues are not ideal they are not critical as the concentrations of total metals are being used solely for comparison with sediment quality guidelines<sup>10</sup>.

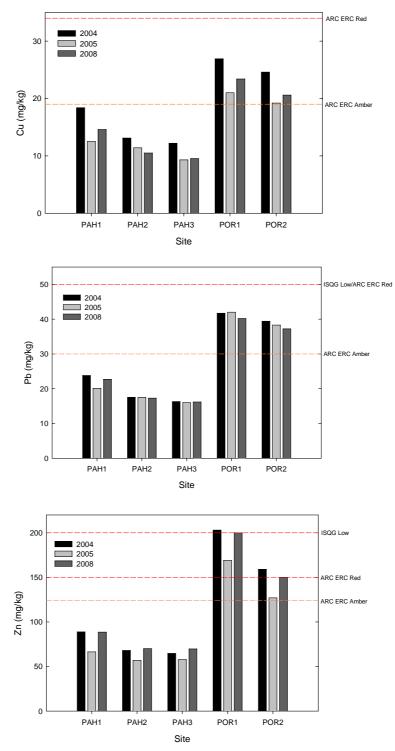
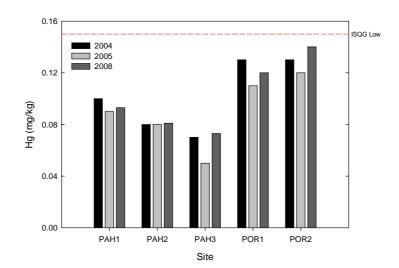
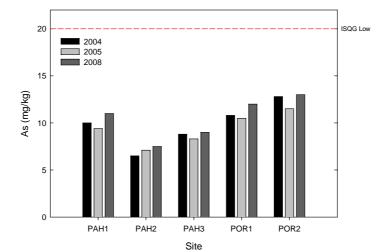


Figure 3.2: Concentrations of total copper (Cu), lead (Pb) and zinc (Zn) in sediments of five sites sampled in Porirua Harbour in 2004, 2005 and 2008, based on the <500  $\mu$ m fraction of a single composite sample from each site

<sup>&</sup>lt;sup>10</sup> Only the 'ranking' of zinc (in terms of the actual guideline exceeded) at sites in the Onepoto Arm may have been affected across the period of the surveys. Rankings for all other metals have remained unchanged.





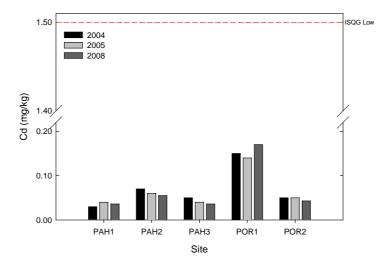


Figure 3.3: Concentrations of total mercury (Hg), arsenic (As) and cadmium (Cd) in sediments of five sites sampled in Porirua Harbour in 2004, 2005 and 2008, based on the <500  $\mu$ m fraction of a single composite sample from each site

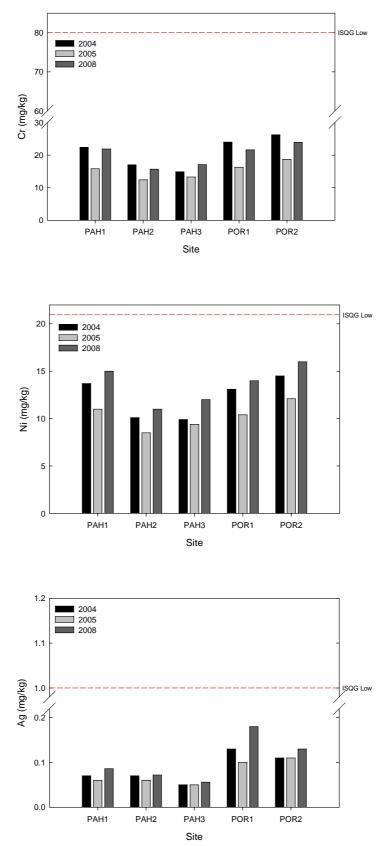


Figure 3.4: Concentrations of total chromium (Cr), nickel (Ni) and silver (Ag) in sediments of five sites sampled in Porirua Harbour in 2004, 2005 and 2008, based on the <500  $\mu$ m fraction of a single composite sample from each site

#### 3.2.4 Weak acid-extractable metals

At most sites the mean concentrations of weak acid-extractable copper, lead or zinc in the <63  $\mu$ m fraction of the sediments varied significantly between the 2004, 2005 and 2008 surveys (Figure 3.5). The differences in mean concentrations between years were relatively small, but quality assurance results (Appendix 3) indicate that they are outside of the range that is potentially explained by analytical variation.

Regression analysis detected significant (p < 0.05) temporal trends in copper, lead and zinc concentrations at a number of sites (Table 3.2). However, data plots (Figure 3.5) indicated that consistent downward or upward changes only occurred for copper and lead at site POR1 (declining trends), lead at site PAH1 (declining trend) and zinc at site PAH2 (increasing trend). Note that these results must be treated very cautiously because they are based on only three data points. The reliability of trend analyses to detect environmentally meaningful changes should improve as more monitoring data are added and the length of the time-series increases.

Table 3.2: R<sup>2</sup> and probability values from least squares linear regression models of the change in weak acid-extractable copper, lead and zinc concentrations (<63  $\mu$ m sediment fraction), mud content (% <63  $\mu$ m), and TOC (%<500  $\mu$ m)<sup>1</sup> in sediments of five sites sampled in Porirua Harbour in 2004, 2005 and 2008. Concentrations that have changed significantly over time are highlighted in red and the direction of change is indicated as + (increase) or – (decrease).

Site	Copper		Lead		Zinc		М	ud	TOC	
	R <sup>2</sup>	p	R <sup>2</sup>	p	R <sup>2</sup>	p	R <sup>2</sup>	p	R <sup>2</sup>	p
PAH1	0.6832	0.0001 (-)	0.8394	<0.0001 (-)	0.1036	0.2420	0.0047	0.8085	0.0448	0.4490
PAH2	0.0199	0.6163	0.2940	0.0368 (+)	0.8170	<0.0001 (+)	0.6625	0.0002 (-)	0.1213	0.2033
PAH3	0.2602	0.0521	0.0069	0.7763	0.1204	0.1204	0.1249	0.1963	0.3330	0.0243 (-)
POR1	0.5132	0.0027 (-)	0.9131	<0.0001 (-)	0.1106	0.2258	0.4864	0.0038 (-)	0.3204	0.0278 (+)
POR2	0.4835	0.0040 (-)	0.7861	<0.0001 (-)	0.0018	0.8793	0.1146	0.2171	0.0245	0.5776

1 <63 µm TOC fraction data could not be used as TOC was only tested on the <500 µm fraction in 2004 and 2005

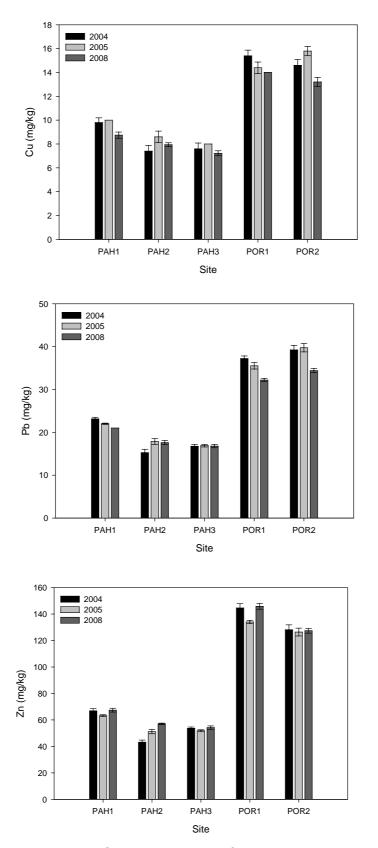


Figure 3.5: Mean (± 95% CI) concentrations of weak acid extractable copper (Cu), lead (Pb) and zinc (Zn) in sediments of five sites sampled in Porirua Harbour in 2004, 2005 and 2008, based on the <63  $\mu$ m fraction of five composite samples from each site

#### 3.3 Benthic fauna – 2008

#### 3.3.1 Sediment particle size distribution

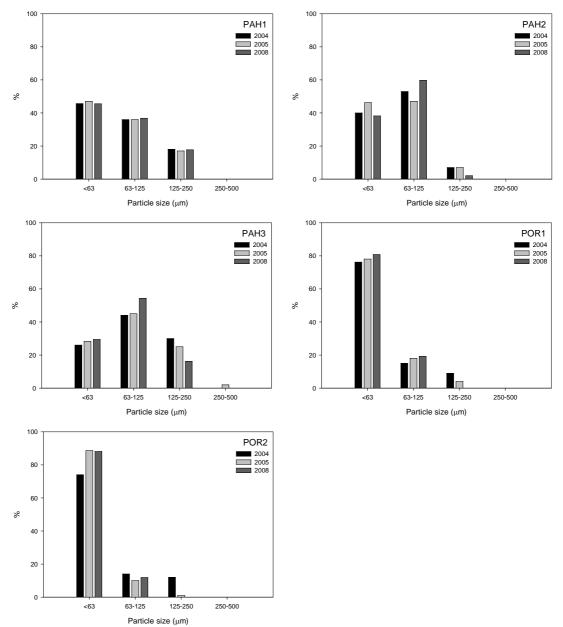
A summary of the particle size results from the five benthic fauna collection areas sampled in Porirua Harbour during November 2008 is presented in Table 3.3. The <300  $\mu$ m fraction of the near-surface sediments at sites in the Pauatahanui Arm was very muddy sand or muddy sand (<63  $\mu$ m fraction 29–45%), while at sites in the Onepoto Arm it was sandy mud (<63  $\mu$ m fraction 81–88%). At all sites the near-surface sediments also contained a minor gravel component made up primarily of shell fragments.

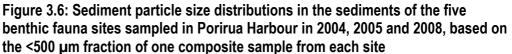
Table 3.3: Particle size results from each of the five benthic fauna collection areas sampled in Porirua Harbour in 2008, based on a single composite sample from each site

Site	Mean (µm)	<63 µm (%)	63–125 μm (%)	125–250 μm (%)	250–300 <sup>1</sup> μm (%)	Description of <300 <sup>1</sup> µm fraction
PAH1	70.92	45.51	36.82	17.67	0	Very muddy sand
PAH2	69.83	38.20	59.75	2.05	0	Muddy sand
PAH3	87.03	29.45	54.29	16.26	0	Muddy sand
POR1	41.85	80.83	19.17	0	0	Sandy mud
POR2	36.22	88.09	11.91	0	0	Sandy mud

<sup>1</sup> Although particle size data were restricted to a range of 0-300 µm, the data effectively represent the 0-500 µm fraction

On average across all three surveys, the mud content (<63  $\mu$ m fraction) in sediments from the benthic fauna collection areas was within 8.3% (± 4.2%, 95% CI) of the mud content in sediments from the corresponding chemistry collection areas, but three groups of samples had differences of 20% to 26% (PAH2 and PAH3 in 2004, and PAH1 in 2005). Samples from the benthic fauna collection areas displayed less temporal variability than those from the adjoining sediment chemistry collection areas, varying by only 2 to 14% among years (Figure 3.6).





#### 3.3.2 Number of species

A total of 64 species were identified in the samples collected from the November 2008 survey, the fauna being composed predominantly of polychaetes (25 species), crustaceans (17 species), and bivalve and gastropod molluscs (6 and 4 species respectively). Sixty-two of the 64 species were found in the samples taken from sites PAH1, PAH2 and PAH3 in the Pauatahanui Arm (Stephenson 2009), with the total number of species at each site ranging from 37–45 (Table 3.4). Only 32 of the 64 species were found in the samples taken from sites POR1 and POR2 in the Onepoto Arm (Stephenson 2009), with a total number of 26 species found at each site.

Feature			Site		
-	PAH1	PAH2	PAH3	POR1	POR2
Number of species	40	37	45	26	26
Estimated total individuals per m <sup>2</sup> 1	10,656	4,224	3,520	3,360	9,120
Dominant species by numbers <sup>2</sup>	Tanaidacea 1	Heteromastus filiformis	Nucula hartvigiana	Cossura consimilis	Tanaidacea 1
	Arthritica 1	Nucula hartvigiana	Asychis 1	Asychis 1	Arthritica 1
		Arthritica 1	Phoxocephalidae 1	Nucula hartvigiana	Asychis 1
		Cossura consimilis	Arthritica 1	Phoxocephalidae 1	
		Asychis 1	Phoxocephalidae 2	Arthritica 1	
			Heteromastus filiformis		
			Glycinde 1		
			Cossura consimilis		
			Theora lubrica		
Dominant species by biomass <sup>3</sup>	Sipunculida 2	Cyclomactra ovata	Cyclomactra ovata	Cyclomactra ovata	Paracaudina chilensi
	Paracaudina chilensis	Cominella adspersa	Nucula hartvigiana	Nucula hartvigiana	Sipunculida 2
	Cyclomactra ovata	Nucula hartvigiana	Macomona liliana	Asychis 1	Asychis 1
Shannon diversity index (mean $\pm$ 95% CIs)	1.38 ± 0.4	2.28 ± 0.1	2.58 ± 0.1	2.16 ± 0.1	1.59 ± 0.1
Trophic structure:4					
Predators/scavengers (%)	76.52	17.75	23.06	22.41	50.31
Surface deposit feeders (%)	4.84	21.62	30.37	22.53	3.82
Subsurface deposit feeders (%)	7.61	44.57	28.08	42.19	14.89
Suspension feeders (%)	9.60	15.86	12.56	12.63	30.76
Unknown (%)	1.43	0.19	5.93	0.24	0.22

#### Table 3.4: Summary of features of the subtidal benthos at 5 sites in Porirua Harbour in 2008

<sup>1</sup> Estimate based on a sample area of 0.03 m<sup>2</sup> and a conversion factor of "mean number of individuals per sample multiplied by 32" (n = 8).

<sup>2</sup> Species are listed in descending order of mean number of individuals per sample, with the sum of the individuals of these species comprising 75–80% of the individuals recorded at the site.

<sup>3</sup> Species are listed in descending order of mean biomass per sample, based on wet weight measurements made prior to the specimens being preserved in alcohol.

<sup>4</sup> For allocation of each species to a feeding mode (or modes) see Appendix 4.

#### 3.3.3 Number of individuals

A total of 7,716 individuals were counted in the Porirua Harbour samples. Crustaceans were the most abundant group (46.9% of all individuals), followed by polychaetes (25.1%) and bivalve molluscs (24.9%). The most abundant crustaceans were Tanaidacea sp.#1 (78.1%) of all crustaceans), Phoxocephalidae sp.#1 (9.8%) and Phoxocephalidae sp.#2 (7.0%). The most abundant polychaetes were Asychis sp.#1 (42.1% of all polychaetes), then Cossura consimilis (18.2%), Heteromastus filiformis (14.3%) and Glycinde sp.#1 (7.0%). Arthritica sp.#1 and Nucula hartvigiana were the most abundant bivalves (62.7% and 30.8% of all bivalves respectively). In contrast, the biomass of the five monitoring sites was dominated either by the bivalve Cyclomactra ovatra, Sipunculida sp.#2, the echinoderm Paracaudina chilensis, or a combination of these (Table 3.4). A second bivalve, Nucula hartvigiana, was also a significant contributor to the biomass of some sites.

The mean number of individuals per sample varied widely between some sites, ranging from 105 at site POR1 to 333 at site PAH1. This equates to an estimated total number of individuals of 3,360 to 10,656 per  $m^2$  (Table 3.4).

#### 3.3.4 Shannon diversity index

Mean Shannon diversity index values ranged from  $1.38 (\pm 0.4, 95\% \text{ CI})$  at site PAH1 to  $2.58 (\pm 0.1, 95\% \text{ CI})$  at site PAH3, which equated to 48% to 83% of their theoretical maximum based on the number of individuals being evenly spread across each species present at the site (Table 3.4).

#### 3.3.5 Trophic structure

All feeding modes except herbivores were represented in the benthic fauna of the sites. Deposit feeders dominated the benthic community at sites PAH2, PAH3 and POR1, but at sites PAH1 and POR2 the community was dominated by predators and scavengers (Figure 3.7, Table 3.4). Subsurface deposit feeders were generally more numerous than surface deposit feeders, although at site

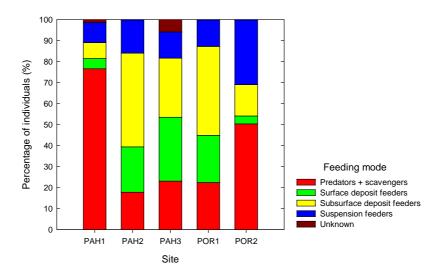


Figure 3.7: Percentage of individuals in each feeding mode at each of five sites sampled in Porirua Harbour in November 2008

PAH3 surface deposit feeders slightly outnumbered subsurface deposit feeders. Suspension feeders accounted for 10–16% of individuals at all sites, except at site POR2 (31%).

#### 3.3.6 Bivalve populations

The shell lengths of three species of bivalves were measured to try and establish their population structure at each of the sites. Measurements for each species from individual samples are detailed in Stephenson (2009).

#### Cyclomactra ovata (Oval trough shell)

*Cyclomactra ovata* was recorded at all monitoring sites except POR2 at the northern end of the Onepoto Arm, with estimated densities ranging from 8–28 per m<sup>2</sup>. All but one of the 19 individuals measured had a shell length >20 mm (Figure 3.8).

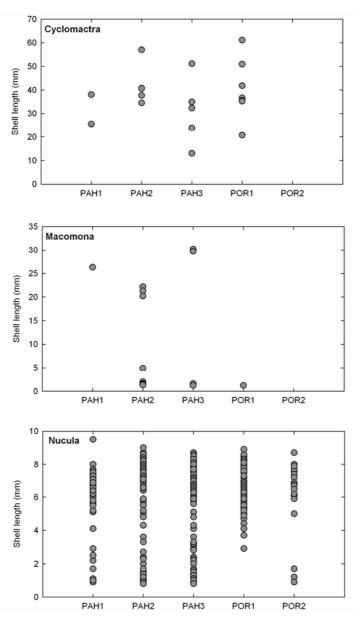


Figure 3.8: Size distribution of *Clyclomactra ovata, Macomona liliana* and *Nucula hartvigiana* at each of five sites sampled in Porirua Harbour in November 2008

#### Macomona liliana (Wedge shell)

*Macomona liliana* was recorded at all monitoring sites except POR2, with the greatest numbers present at sites PAH2 and PAH3. Estimated densities ranged from 4-52 per m<sup>2</sup>. The population structure was bimodal at sites PAH2 and PAH3, and all but one of the 22 individuals measured had a shell length <2 mm or >20 mm (Figure 3.8).

#### *Nucula hartvigiana* (Nut shell)

*Nucula hartvigiana* was recorded at all monitoring sites, with estimated densities ranging from 88 per  $m^2$  at site POR2 to 760 per  $m^2$  at site PAH3. The population structure was bimodal at all sites except POR1, with most individuals falling into the 1–2 mm or 5–9 mm size classes (Figure 3.8).

#### 3.4 Comparison with 2004 and 2005 benthic fauna

The assessment of changes in benthic ecology between 2004 and 2008 is limited to looking at changes in species diversity and benthic community structure. Further assessment of the data, particularly in terms of temporal changes, is not warranted this early in the monitoring programme.

#### 3.4.1 Species diversity

Plots of diversity indices (mean  $\pm$  95% CI) indicated that a significant decline in Shannon diversity occurred at site PAH1 between 2004-05 and 2008, and site POR2 between 2004 and 2005 (Figure 3.9). The decline in Shannon diversity at site PAH1 was due more to changes in the dominance of individual species (i.e., reduced evenness) rather than changes in the number of species as the number of species actually increased at site PAH1 between 2004 and 2008. A large influx of tanaid crustaceans (Tanaidacea sp.#1) in 2008 was particularly influential in reducing Shannon diversity and Pielou's evenness at site PAH1 (Figure 3.9). Shannon diversity also declined slightly at site POR2 between 2004 and 2005, again due to a decline in evenness caused by an influx of tanaids (Tanaidacea sp.#1).

In contrast, Shannon diversity at sites PAH2 and PAH3 increased significantly between 2004-05 and 2008 due to increasing trends in both the number of species and species evenness at these sites. Shannon diversity at site POR1 was relatively stable (Figure 3.9).

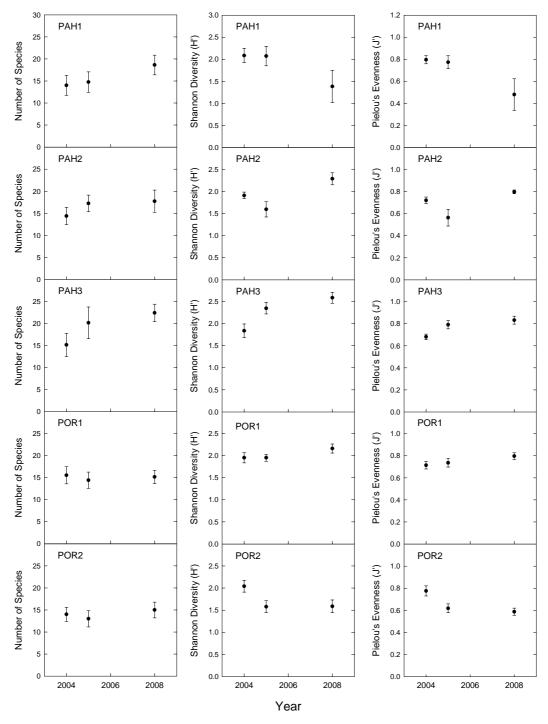


Figure 3.9: Mean number of species, Shannon diversity index values and Pielou's evenness index values ( $\pm$  95% CI) at each of five sites sampled in Porirua Harbour in 2004, 2005 and 2008

#### 3.4.2 Community structure

Multi-dimensional scaling of untransformed (i.e., raw) and (log x+1) transformed abundance data indicated that there was a trend in community composition which ran from site PAH2 to PAH3, POR1, PAH1 and POR2 (Figure 3.10). This trend did not reflect the proximity of the sites to each other or patterns in physical exposure. The raw data provided a better two-dimensional representation of the benthic fauna data (as indicated by the lower stress value of 0.18), greater discrimination between groups of samples, and was more reflective of the influence of dominant species. The two-dimensional representation of the transformed data was poor, as indicated by the stress value of 0.24. Clarke & Warwick (2001) warn that MDS results with stress values of between 0.2 and 0.3 should be treated should be treated with a great deal of scepticism, and that results should be discarded at the upper half of this range.

Cluster analysis of the untransformed data differentiated three major groups of samples which had <35% similarity<sup>11</sup> in species composition (Figures 3.10A and 3.11). These groups were:

- 1. Site PAH2 in 2004 and 2005;
- 2. Site POR2 in 2005 and 2008, and site PAH1 in 2008 (note that Simprof tests split these two sites); and
- 3. All other samples.

Greatest temporal variability was displayed in samples from group 1 and 2 sites (i.e., sites PAH1, PAH2 and POR2). However, clear spatial patterns were not apparent in either the sample groupings or the level of temporal variability (Figure 3.10 and Figure 3.11). For instance, site POR1 (which is the southernmost, and nominally, most impacted site), consistently grouped with site PAH3 (the northernmost, and nominally, least impacted site), and samples from both sites displayed similar amounts of temporal variability.

<sup>&</sup>lt;sup>11</sup> Major splits in the cluster analysis dendrogram occurred between 25% and 35% similarity. No clusters with <35% similarity could be discriminated using the transformed data, and clusters with greater similarity values were less informative than those obtained with the untransformed data.

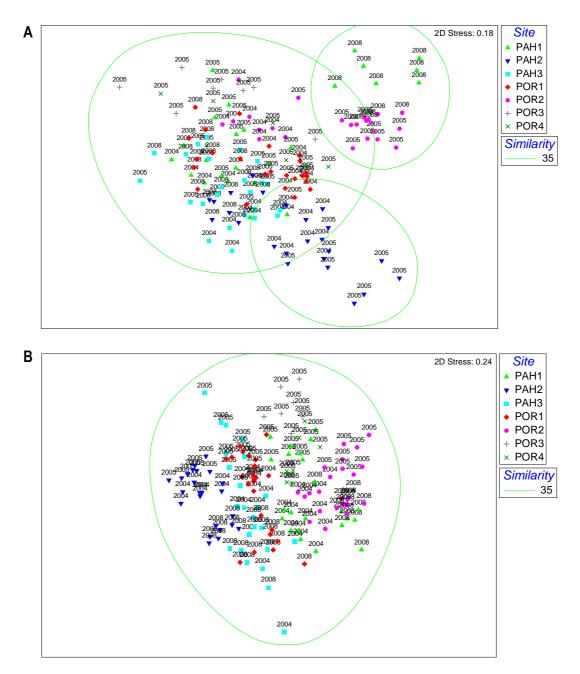


Figure 3.10: MDS plots of benthic fauna samples collected from five sites in the Porirua Harbour in 2004, 2005 and 2008, using A) untransformed data, and B) log x+1 transformed data. Samples are grouped using the results of cluster analysis, with separate clusters having <35% similarity.

Note: Sites POR3 and POR4 in the Onepoto Arm were sampled on one occasion in 2005 (see Stephenson & Mills 2006)

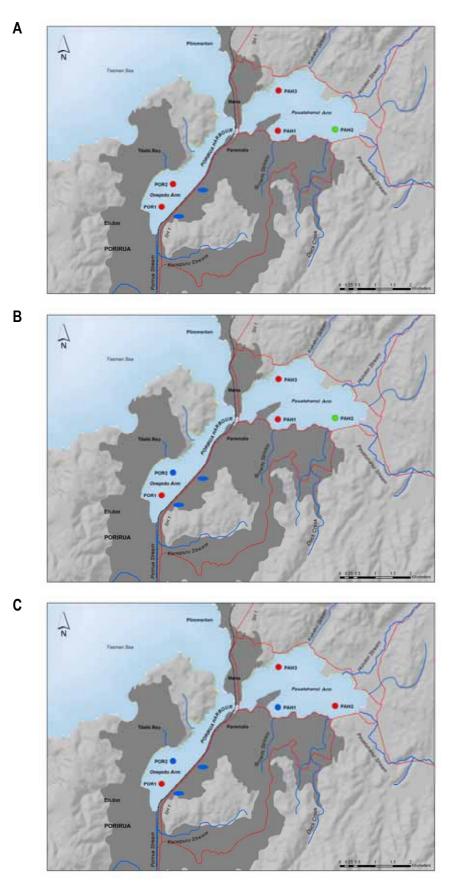


Figure 3.11: Map showing ecological groupings in A) 2004, B) 2005, and C) 2008. Colours group sites with similar benthic communities based on multidimensional scaling and cluster analysis.

Similarity percentages (SIMPER) using untransformed data indicated that over 90% of the dissimilarity between the groups identified by cluster analysis were driven by eight species for groups 1 and 2, 10 species for groups 2 and 3; and, 11 species for groups 1 and 3 (see Appendix 5). The most influential of these species were:

- *Heteromastus filiformis*, and to a lesser extent *Cossura consimilis*, in samples from site PAH2 in 2004 and 2005 (group 1 above), which together explained over 54% of the dissimilarity between these samples and samples within group 3 (all other sites see above).
- *Tanaidacea* sp.#1 and *Arthritica* sp., in samples from site POR2 in 2005 and 2008, and site PAH1 in 2008 (group 2 above), which together explained over 59% of the dissimilarity between these samples and samples within group 3 (all other sites see above).
- *Heteromastus filiformis* and *Cossura consimilis* in samples from site PAH2 in 2004 and 2005 (group 1 above), and *Tanaidacea sp.#1* in samples from site POR2 in 2005 and 2008, and site PAH1B in 2008 (group 2 above), which together explained over 65% of the dissimilarity in these two groups of sites.

The distributional patterns of the above species were clearly shown on MDS plots overlain with bubbles of species abundance (Figure 3.12).

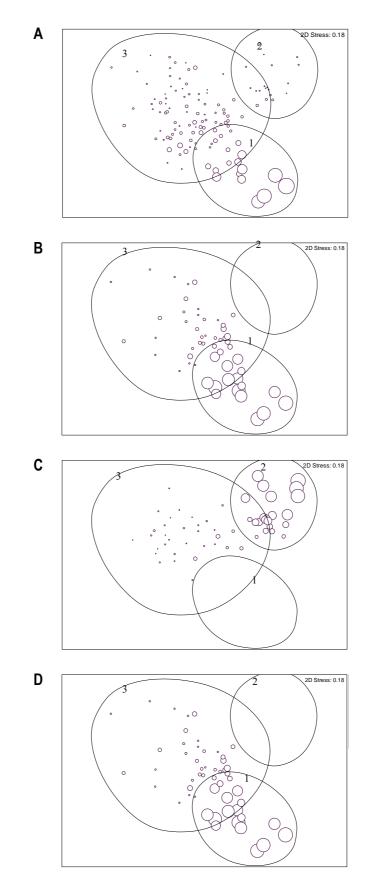


Figure 3.12: MDS plots with abundance bubbles of A) *Heteromastus filiformis*, B) *Cossura consimilis*, C) *Tanaidacea* sp.#1, and D) *Arthritica* sp. overlain. The three groups identified by cluster analysis are also shown.

## 3.5 Linking the benthic community to environmental variables

MDS plots were overlain with bubble plots of each environmental variable (metal concentrations, sediment texture (mud content) and TOC content) to examine any relationships between benthic communities and 'environmental quality' (Figure 3.13, note that only copper, lead and zinc are presented but similar plots were also prepared for the other metals). No clear relationships were apparent between benthic fauna and environmental data. Sediments from the sites associated with ecological groups 2 and 3 had overlapping, and highly variable, mud content (particles <63  $\mu$ m), TOC content and metal concentrations. Sediments from site PAH2 associated with group 1 samples tended to have lower values for all of these variables, reflecting the relatively high quality of this site, but the values overlapped with group 2 and/or group 3 sites. These results suggest that the environmental variables examined did not strongly influence the abundance of numerically dominant species and high-level community structure.

More subtle, lower order, community effects were then examined by carrying out a CAP of species counts, constrained by a quantitative index of 'environmental quality' obtained by a PCA of environmental variables, and categorical site groupings based on a cluster analysis of environmental variables. Species differences between site groupings were then examined using SIMPER analysis.

The first principal component obtained from the PCA explained 76% of the variation in environmental variables, and therefore, provided a good proxy for overall environmental quality (Figure 3.14). Canonical analysis of principal coordinates indicated that there was a strong relationship between community structure and the 1<sup>st</sup> principal components axis (Figure 3.15). This suggests that the benthic communities at all five monitoring sites were influenced by environmental quality. However, it was not possible to determine which aspects of environmental quality were responsible (i.e., the analysis could not discriminate between the effects of sediment texture, TOC and metal contaminants, because these variables tended to be highly correlated with each other).

Cluster analysis indicated that the monitoring sites/times could be split into two (using major splits on the cluster dendrogram) to three (using similarity profile analysis) groups based on measures of environmental quality (using metal concentrations, TOC and mud content). CAP carried out using the two group split (number of principal coordinate axes (m) = 9) indicated that benthic community structure differed between these groups of sites. These differences were clearly reflected in the results of the 'leave-one-out' analysis, which allocated 13 out of the 15 sites to their correct groups (i.e., 88.9% success) based on the characteristics of the benthic community. The three group split was not as reliable, with only 73.3% allocation success using the 'leave-one-out' test.

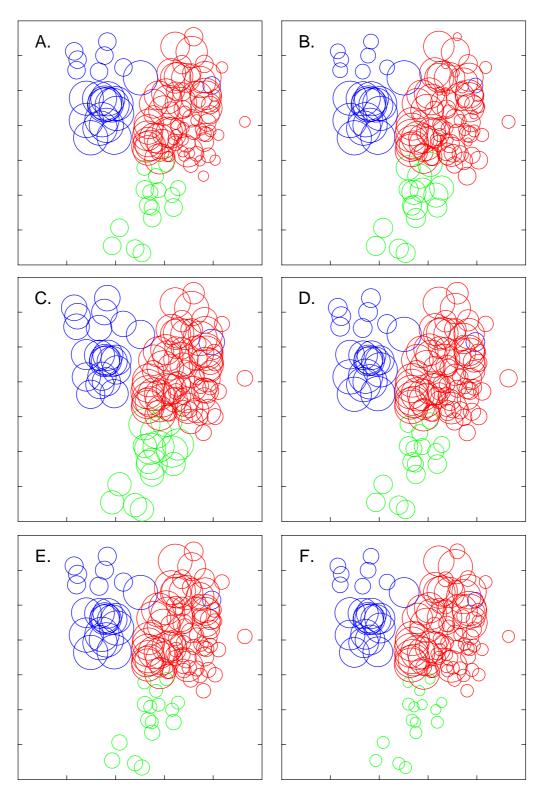


Figure 3.13: MDS plots of benthic fauna samples overlain with bubble plots showing the relative values of A) sediment texture ( $\% < 63 \mu m$ ) obtained from benthic fauna core samples, B) sediment texture ( $\% < 63 \mu m$ ) obtained from sediment chemistry samples, C) TOC, D) weak acid copper concentration, E) weak acid lead concentration, and F) weak acid zinc concentration. Samples contained in ecological groups 1 (green), 2 (blue) and 3 (red) are also indicated. Circle diameters proportional to the percentage or concentration at each site on a linear scale.

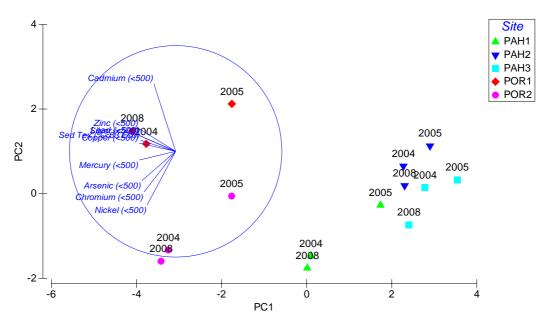


Figure 3.14: Principal Component Analysis (PCA) analysis of normalised sediment-metal concentrations (extracted using strong acid digestion of the <500 µm sediment fraction), total organic carbon and sediment mud (<63 µm) content

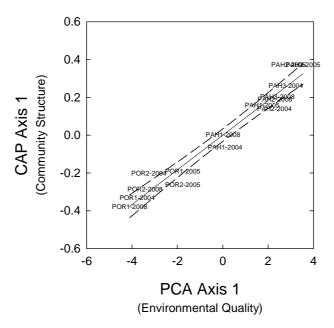


Figure 3.15: Canonical analysis of principal coordinates (CAP) based on Bray Curtis similarities of square root transformed species counts and the PCA1 values derived from Principal Component Analysis of environmental variables (see Figure 3.13). Note that the CAP axis can be viewed as an index of ecological community structure and the PCA axis viewed as an index of 'environmental quality'. Least squares regression and 95% confidence intervals are shown.

Similarity percentages (SIMPER) indicated that species differences between the two groups were not driven by large differences in the abundance of a few taxa. Rather, the differences were due to small differences in the abundance of many species. Thirty-nine taxa were involved in explaining 90% of the dissimilarity between the two groups, with no individual taxa explaining >10.5% dissimilarity. Eight of these taxa (*Heteromastus filiformis*, Tanaidacea sp.#1, *Arthritica* sp.#1, *Cossura* sp.#1, *Nucula hartvigiana*, Oligochaeta sp.#1, *Asychis* sp.#1, and Phoxocephalidae sp.#2) explained approximately 50% of the dissimilarity.

# 4. Discussion

Concentrations of copper, lead, zinc (Figures 4.1–4.2), and to a lesser extent mercury, have been consistently elevated in the subtidal sediments of the Onepoto Arm of Porirua Harbour since sediment quality monitoring began in 2004. Total recoverable copper, lead and zinc concentrations currently exceed low or 'alert level' sediment quality guideline values at both monitoring sites in this arm, while total recoverable mercury concentrations are approaching low level guideline values. In contrast, the concentrations of these metals, although elevated relative to background levels (e.g., in Browns Bay), are well below guideline values in the subtidal sediments of the Pauatahanui Arm.

Arsenic concentrations also tend to be slightly elevated in subtidal sediments throughout the harbour, suggesting that the concentrations of this metal are naturally elevated, or that it also has a non-urban source. Elevated arsenic concentrations have been recorded in "unpolluted" estuaries and harbours of the Auckland region, which is consistent with the patterns observed in Porirua Harbour. This supports the notion that this may be a natural feature of marine sediments in New Zealand. Total recoverable cadmium, chromium, nickel and silver concentrations are all below low level sediment quality guideline values.

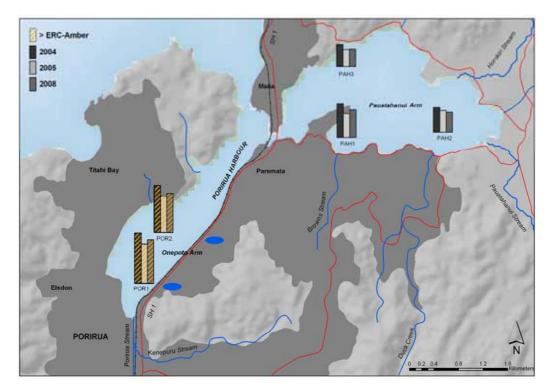


Figure 4.1: Relative concentrations of total copper in the sediments at each of the five sites sampled in Porirua Harbour in 2004, 2005 and 2008, based on the <500  $\mu$ m fraction of a single composite sample from each site. Note that the scale used for the bars is unique to this map.

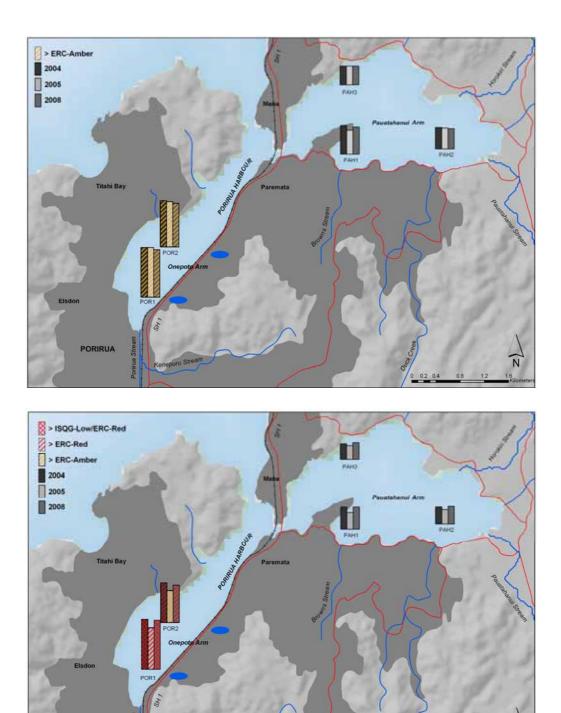


Figure 4.2: Relative concentrations of (top) total lead and (bottom) total zinc in the sediments at each of the five sites sampled in Porirua Harbour in 2004, 2005 and 2008, based on the <500  $\mu$ m fraction of a single composite sample from each site. Note that the scale used for the bars is unique to each map.

The elevated sediment concentrations of copper, lead, zinc and mercury in the highly urbanised Onepoto Arm are consistent with spatial patterns in contaminant concentrations observed close to urban contaminant sources in coastal environments elsewhere in New Zealand (e.g., McHugh & Reed 2006, Kelly 2007, Stephenson et al. 2008). Stormwater and stream investigations

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(e.g., Cameron 2001, KML 2005, Milne & Watts 2008), and other sediment quality investigations in Porirua Harbour (e.g., Glasby et al. 1990, Sorensen & Milne 2009) have demonstrated that urban stormwater is contributing to metal (and other) contamination of the Onepoto Arm sediments, either directly via outfalls adjacent to Porirua City or indirectly via the Porirua Stream.

The methods used for the collection and analysis of information on chemical contamination of subtidal sediments in Porirua Harbour are providing good quality data, with low variability for most analytes. This allows very small changes in contaminant concentrations to be detected over time. However, changes observed in sediment particle size distributions at several of the sites over the monitoring period are of some concern because, as noted in subsection 2.1, one of the prerequisites for long-term monitoring of trends in contaminant concentrations is that sediment texture remains stable over long time periods, preferably decades.

At this early stage of the monitoring programme it is unclear whether the observed variability in sediment particle size distributions is "real" (e.g., possibly in response to changing hydrodynamic conditions) or an artefact of the current method of analysis (Galai/Eyetech laser). The same method of analysis is employed in the Auckland region with similar temporal variability in sediment particle sizes recorded in sediment samples from some "stable" intertidal sites (e.g., Mathieson et al. 2001, Reed & Webster 2004, McHugh & Reed 2006). Because of concerns about data variability and interpretation, the Auckland Regional Council has commissioned a review of this method's use (Walker<sup>12</sup> pers. comm.). This review will involve verification of the sediment texture results using another method of analysis (e.g., wet sieving). It is recommended that a similar verification process is undertaken in the next survey of subtidal sediments in Porirua Harbour. Consideration should also be given to analysing sediment particle size in a greater number of sediment samples from each benthic fauna collection area in future surveys to better assess variability between the benthic fauna and sediment chemistry sample collection areas.

Although statistically significant trends in the concentrations of copper, lead and zinc have been detected since 2004, it is still too early to tell whether these trends are ecologically significant and whether they will continue into the future. Variability in trend detection can be expected during the early stages of a long-term monitoring programme when time-series data are limited, because individual data points have a major influence on statistical trends. The reliability of trend detection, and the ability to form meaningful conclusions, should continue to improve as more monitoring data are added and the length of the time-series increases. Continuation of the programme at sampling intervals of two years would reduce the time needed to detect meaningful trends. Due to the significant expense in analysing sediment samples for organic contaminants, organic analysis may need to be undertaken less frequently. However, periodic analysis of organic contaminants is likely to be important because the 2004 and 2005 monitoring results showed that elevated concentrations of the organochlorine pesticide DDT (and its derivatives) are present in the subtidal sediments (Stephenson & Mills 2006).

<sup>&</sup>lt;sup>12</sup> DrJarrod Walker, Project Leader – Marine Environmental Research, Auckland Regional Council

To date, sediment metal concentrations have been compared against the Auckland Regional Council's Environmental Response Criteria (ERC), as well as the ANZECC (2000) interim sediment quality guideline (ISQG) values. The ERC guidelines are based on a combination of the internationally recognised sediment quality guideline values developed by the US National Oceanic and Atmospheric Administration (NOAA) (Long & Morgan 1990) and the Florida Department of Environmental Protection (FDEP) (MacDonald 1994). With the Auckland Regional Council now considering changing the use of the relevant guideline values from 'response criteria' to 'indicators' (McCarthy<sup>13</sup>, pers. comm.), future reporting should therefore compare sediment contaminant concentrations against the original guidelines (i.e., the ERL's and ERM's<sup>14</sup> of Long & Morgan (1990)), and the TEL's and PEL's<sup>15</sup> of MacDonald (1994)), as well as the ANZECC (2000) guidelines. The ANZECC guidelines, which are currently under review, are essentially the Long & Morgan (1990) guidelines with some modifications.<sup>16</sup>

Measures of diversity and multivariate analyses indicate that the composition of benthic communities at some of the subtidal monitoring sites in Porirua Harbour has varied between 2004 and 2008. Greatest temporal variation has occurred at sites PAH1 and PAH2 in the Pauatahanui Arm, and at site POR2 in the Onepoto Arm. These changes have primarily been driven by fluctuations in the abundance of small, numerically dominant species. The most significant of these are the polychaetes *Heteromastus filiformis* and *Cossura consimilis*; tanaid crustaceans (Tanaidacea sp.#1) and the bivalve *Arthritica* sp. Spatial patterns and temporal changes in community structure driven by the numerically dominant species do not appear to be related to the environmental variables measured (i.e., metal concentrations, TOC and mud content). Such high-order changes may be associated with natural recruitment pulses, hydrodynamics, habitat features or other unknown factors.

While a relationship between the environmental variables examined and changes in high-order community structure could not be found, the results of the CAP analysis indicate that there is a strong relationship between environmental quality and lower-order community structure. However, it was not possible to determine which aspects of environmental quality were responsible because the analysis could not separate the influence of sediment texture and TOC from the influence of metal concentrations due to the high degree of correlation between these environmental variables. Concentrations of organic contaminants such as pesticides and polycyclic aromatic hydrocarbons were also not taken into account in this analysis. However, the results are consistent with other New Zealand studies, which have shown that similar lower-order changes in benthic communities are linked to the sediment concentrations of copper, lead and zinc (e.g., Thrush et al. 2008, Hewitt et al. 2009). Further investigations would be required to confirm such a link exists in Porirua Harbour. These would involve the analysis of benthic fauna and sediment samples from sites with similar sediment textures but varying contaminant concentrations.

<sup>&</sup>lt;sup>13</sup> Domincic McCarthy, Manager Environmental Policy, Auckland Regional Council

<sup>&</sup>lt;sup>14</sup> Environmental Response Low (ERL) and Environmental Response Medium (ERM)

<sup>&</sup>lt;sup>15</sup> Threshold Effect Levels (TEL) and Probable Effects Levels (PEL)

<sup>&</sup>lt;sup>16</sup> For example, changes introduced into the ANZECC guidelines include increases in the sediment quality guideline values for zinc and copper, and the use of organic carbon normalisation for organic contaminants.

# 5. Conclusions and recommendations

Consistent with the results of the 2004 and 2005 surveys, concentrations of total copper, lead and zinc are above 'early warning' sediment quality guidelines in the subtidal sediments of the Onepoto Arm of Porirua Harbour, especially at site POR1 in the southern end of the Onepoto Arm. Concentrations of the other metals analysed are currently below guideline levels in the Onepoto Arm, as are the concentrations of all metals in the subtidal sediments of the Pauatahanui Arm. The benthic fauna monitoring data indicate that some of the environmental variables measured are influencing lower-order benthic community structure. However, at this stage any effects of metal contamination cannot be separated from the effects of differences in sediment texture and organic carbon content.

Although statistically significant trends in the concentrations of copper, lead and zinc have been detected since 2004, it is still too early to tell whether these trends are ecologically significant and whether they will continue into the future. The reliability of trend detection, and the ability to form meaningful conclusions from any detected trends, should continue to improve as more monitoring data are added and the length of the time-series increases.

## 5.1 Recommendations

- 1. The next subtidal sediment chemistry survey is undertaken in Porirua Harbour in late 2010 to continue the monitoring of trends in contaminant concentrations over time. This survey should include analysis of sediment samples for PAHs and OCPs. Further surveys of metal contaminants should be conducted every two years thereafter, unless the results and/or major changes in the catchment indicate a greater or lesser survey frequency is desirable. The need for, and frequency of, ongoing analyses of PAHs and OCPs should be assessed once the results of the 2010 survey are available. Future surveys should:
  - Follow the same sampling methods, sample preparation and replication procedures used in the surveys to date but also consider analysing sediment particle size in samples from each site using both existing and traditional wet sieving methods to help gauge the true extent of changes in sediment texture at some sites.
  - Continue with a rigorous QA programme that includes analysis of an appropriate marine sediment standard reference material (SRM) and re-analysis of at least three archived 2004, 2005 or 2008 samples as blind replicates, to check consistency with previous results.
  - Prepare a "Porirua Reference Sediment" using a large bulk sample from one of the subtidal monitoring sites and analyse it in triplicate each time a survey is carried out.
  - Compare contaminant concentrations against the NOAA (Long & Morgan 1990), FDEP (MacDonald et al. 1994), and ANZECC (2000) sediment quality guidelines.

- 2. The next benthic fauna survey is undertaken in Porirua Harbour in 2010 in order to continue monitoring for changes in community structure with possible links to changes in sediment quality. The survey should be carried out in late October or November to minimise seasonal influences, and coincide with the sediment chemistry survey if possible. Future surveys should:
  - Follow the same sampling methods used in the previous surveys, with the fauna identified to at least the same taxonomic levels.
  - Give consideration to increasing the number of samples taken for sediment particle size analysis to allow more rigorous comparison with sediment particle size data from the adjoining sediment chemistry collection areas.
  - Use analytical methods capable of linking changes in the benthic community to measures of 'environmental quality', with greater focus given to assessing temporal trends on a site-by-site basis to account for the variation in habitat characteristics that exists between some sites.
  - Ensure that the reference collection established during the 2004 baseline survey continues to be maintained and representative specimen(s) of any additional species encountered, either at the existing sites or elsewhere, added to the collection.

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# 7. Acknowledgements

Gary Stephenson (Coastal Marine Ecology Consultants) co-ordinated and oversaw the collection of sediment chemistry and benthic fauna samples, identified the benthic fauna samples and provided valuable peer review comments on a draft version of this report.

Greg Olsen (NIWA) oversaw the sediment chemistry analytical work and assisted with interpretation of the quality assurance data.

Some paragraphs and tables in the report and its appendices have been copied or adapted from Stephenson & Mills (2006); their use has not been acknowledged individually in the text, so we do so here.

# Appendix 1: Sediment particle size results

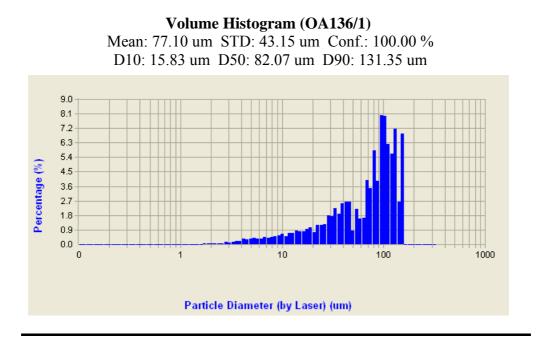
The National Institute of Water and Atmospheric Research Limited (NIWA), Hamilton, carried out both the sample preparation and particle size analyses. The outputs on the following pages are from the analytical report prepared by Olsen et al. (2009).

Sample	Mean (µm)	<63 µm (%)	63–125 μm (%)	125–250 μm (%)	250–300¹ μm (%)	Description of <300 <sup>1</sup> µm fraction
PAH1/1	77.10	37.06	46.32	16.61	0	Muddy sand
PAH1/2	83.27	37.00	38.46	24.53	0	Muddy sand
PAH1/3	77.28	39.54	47.89	12.57	0	Muddy sand
PAH1/4	74.54	42.42	45.21	12.37	0	Very muddy sand
PAH1/5	73.66	39.94	44.97	15.10	0	Muddy sand
PAH2/1	71.46	39.21	53.64	7.16	0	Muddy sand
PAH2/2	64.40	47.39	50.86	1.75	0	Very muddy sand
PAH2/3	64.43	43.60	56.40	0	0	Very muddy sand
PAH2/4	66.24	40.40	59.60	0	0	Very muddy sand
PAH2/5	63.91	45.76	53.49	0.75	0	Very muddy sand
PAH3/1	103.8	20.86	48.18	30.97	0	Muddy sand
PAH3/2	98.70	20.88	52.37	26.74	0	Muddy sand
PAH3/3	97.66	21.94	49.94	28.12	0	Muddy sand
PAH3/4	101.5	18.86	51.16	29.98	0	Muddy sand
PAH3/5	97.68	19.53	55.62	24.84	0	Muddy sand
POR1/1	47.59	72.85	27.15	0	0	Sandy mud
POR1/2	49.04	72.23	24.28	3.48	0	Sandy mud
POR1/3	46.95	74.10	25.90	0	0	Sandy mud
POR1/4	51.41	71.73	21.65	6.62	0	Sandy mud
POR1/5	42.48	78.24	21.76	0	0	Sandy mud
POR2/1	40.83	82.58	12.24	5.18	0	Sandy mud
POR2/2	29.39	92.74	7.26	0	0	Slightly sandy mud
POR2/3	32.42	90.56	9.44	0	0	Slightly sandy mud
POR2/4	29.34	93.31	6.69	0	0	Slightly sandy mud
POR2/5	33.36	90.26	9.74	0	0	Slightly sandy mud

 Table A1.1: Summary of particle size results from the sediment chemistry collection

 areas of sites sampled in the Porirua Harbour in November 2008

<sup>1</sup> Although particle size data were restricted to a range of 0-300 µm, the data effectively represent the 0-500 µm fraction

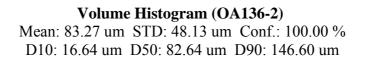


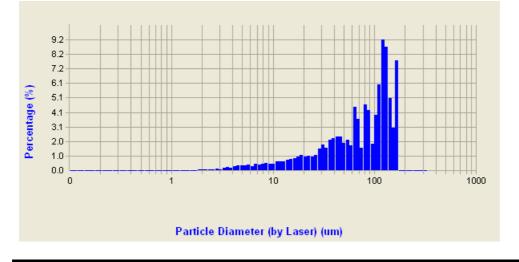
## Volume Ranges Table (OA136/1)

Range	Local(%)	Under(%)
0.0-3.9	1.12	1.12
3.9-7.8	3.22	4.34
7.8-15.6	5.46	9.81
15.6-31.2	10.12	19.92
31.2-62.5	17.14	37.06
62.5-125.0	46.32	83.39
125.0-250.0	16.61	100.00
250.0-300.0	0.00	100.00

### Surface Ranges Table (OA136/1)

Range	Local(%)	Under(%)
0.0-3.9	15.81	15.81
3.9-7.8	19.18	34.98
7.8-15.6	16.08	51.06
15.6-31.2	14.70	65.76
31.2-62.5	13.44	79.20
62.5-125.0	16.86	96.07
125.0-250.0	3.93	100.00
250.0-300.0	0.00	100.00

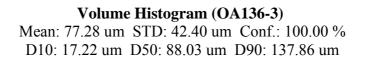


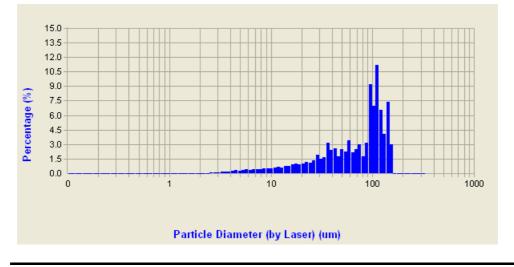


Range	Local(%)	Under(%)
0.0-3.9	1.08	1.08
3.9-7.8	2.98	4.06
7.8-15.6	5.21	9.27
15.6-31.2	9.52	18.78
31.2-62.5	18.22	37.00
62.5-125.0	38.46	75.47
125.0-250.0	24.53	100.00
250.0-300.0	0.00	100.00

## Volume Ranges Table (OA136-2)

Range	Local(%)	Under(%)
0.0-3.9	15.86	15.86
3.9-7.8	18.55	34.41
7.8-15.6	16.05	50.46
15.6-31.2	14.65	65.11
31.2-62.5	14.45	79.55
62.5-125.0	14.53	94.08
125.0-250.0	5.92	100.00
250.0-300.0	0.00	100.00

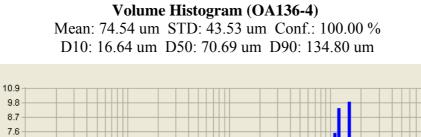


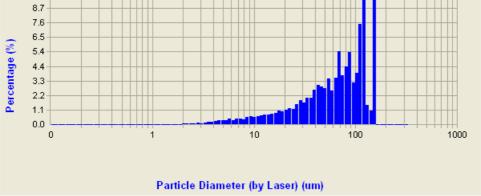


Range	Local(%)	Under(%)
0.0-3.9	0.97	0.97
3.9-7.8	2.88	3.85
7.8-15.6	5.07	8.92
15.6-31.2	10.19	19.11
31.2-62.5	20.42	39.54
62.5-125.0	47.89	87.43
125.0-250.0	12.57	100.00
250.0-300.0	0.00	100.00

## Volume Ranges Table (OA136-3)

Range	Local(%)	Under(%)
0.0-3.9	14.13	14.13
3.9-7.8	17.84	31.96
7.8-15.6	15.69	47.65
15.6-31.2	15.69	63.34
31.2-62.5	16.21	79.55
62.5-125.0	17.36	96.91
125.0-250.0	3.09	100.00
250.0-300.0	0.00	100.00



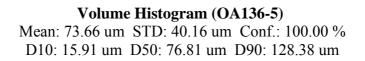


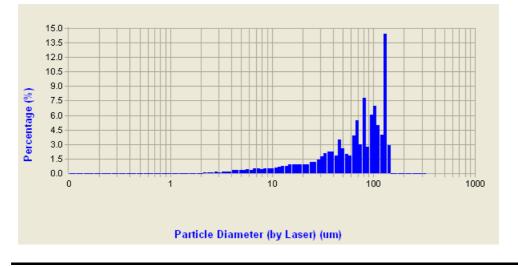
Range	Local(%)	Under(%)
0.0-3.9	0.91	0.91
3.9-7.8	2.85	3.75
7.8-15.6	5.47	9.23
15.6-31.2	10.50	19.73
31.2-62.5	22.69	42.42
62.5-125.0	45.21	87.63
125.0-250.0	12.37	100.00
250.0-300.0	0.00	100.00

#### Volume Ranges Table (OA136-4)

Range	Local(%)	Under(%)
0.0-3.9	12.90	12.90
3.9-7.8	17.33	30.22
7.8-15.6	16.67	46.89
15.6-31.2	15.84	62.74
31.2-62.5	17.39	80.13
62.5-125.0	17.03	97.15
125.0-250.0	2.85	100.00
250.0-300.0	0.00	100.00

#### Surface Ranges Table (OA136-4)



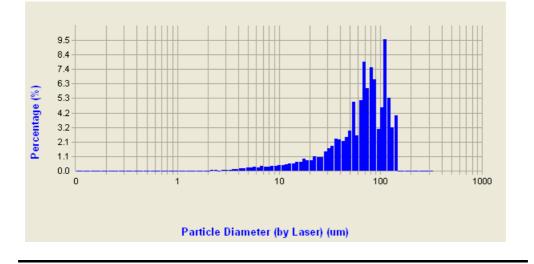


## Volume Ranges Table (OA136-5)

Range	Local(%)	Under(%)
0.0-3.9	1.07	1.07
3.9-7.8	3.12	4.19
7.8-15.6	5.55	9.74
15.6-31.2	9.46	19.20
31.2-62.5	20.74	39.94
62.5-125.0	44.97	84.90
125.0-250.0	15.10	100.00
250.0-300.0	0.00	100.00

Range	Local(%)	Under(%)
0.0-3.9	14.89	14.89
3.9-7.8	18.66	33.55
7.8-15.6	16.33	49.88
15.6-31.2	13.94	63.83
31.2-62.5	15.54	79.37
62.5-125.0	16.80	96.17
125.0-250.0	3.83	100.00
250.0-300.0	0.00	100.00

### **Volume Histogram (OA136-21)** Mean: 71.46 um STD: 35.44 um Conf.: 100.00 % D10: 22.03 um D50: 70.69 um D90: 118.77 um



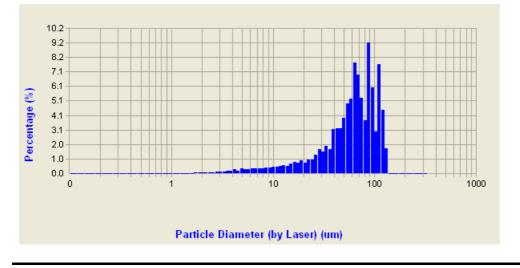
#### Volume Ranges Table (OA136-21)

Range	Local(%)	Under(%)
0.0-3.9	0.68	0.68
3.9-7.8	2.12	2.81
7.8-15.6	3.91	6.72
15.6-31.2	8.47	15.18
31.2-62.5	24.02	39.21
62.5-125.0	53.64	92.84
125.0-250.0	7.16	100.00
250.0-300.0	0.00	100.00

## Surface Ranges Table (OA136-21)

Range	Local(%)	Under(%)
0.0-3.9	11.32	11.32
3.9-7.8	14.62	25.94
7.8-15.6	13.46	39.40
15.6-31.2	14.33	53.74
31.2-62.5	20.22	73.96
62.5-125.0	24.01	97.97
125.0-250.0	2.03	100.00
250.0-300.0	0.00	100.00

### Volume Histogram (OA136-22) Mean: 64.40 um STD: 31.40 um Conf.: 100.00 % D10: 19.35 um D50: 63.91 um D90: 108.18 um

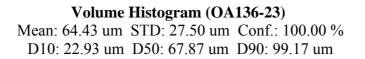


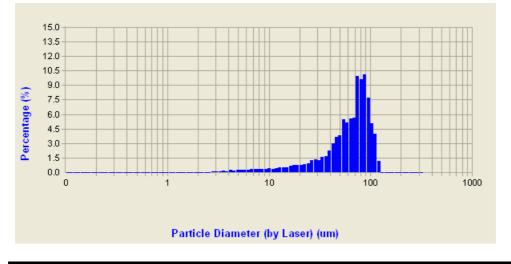
#### Volume Ranges Table (OA136-22)

Range	Local(%)	Under(%)
0.0-3.9	1.01	1.01
3.9-7.8	2.55	3.56
7.8-15.6	4.23	7.79
15.6-31.2	9.10	16.88
31.2-62.5	30.50	47.39
62.5-125.0	50.86	98.25
125.0-250.0	1.75	100.00
250.0-300.0	0.00	100.00

#### Surface Ranges Table (OA136-22)

Range	Local(%)	Under(%)
0.0-3.9	14.95	14.95
3.9-7.8	15.77	30.72
7.8-15.6	12.83	43.55
15.6-31.2	13.54	57.10
31.2-62.5	22.08	79.18
62.5-125.0	20.35	99.53
125.0-250.0	0.47	100.00
250.0-300.0	0.00	100.00



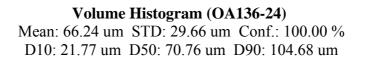


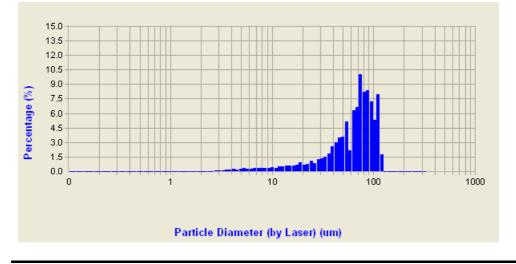
## Volume Ranges Table (OA136-23)

Range	Local(%)	Under(%)
0.0-3.9	0.69	0.69
3.9-7.8	2.13	2.82
7.8-15.6	3.55	6.37
15.6-31.2	8.03	14.40
31.2-62.5	29.20	43.60
62.5-125.0	56.40	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

#### Surface Ranges Table (OA136-23)

Range	Local(%)	Under(%)
0.0-3.9	11.29	11.29
3.9-7.8	14.43	25.72
7.8-15.6	11.97	37.69
15.6-31.2	13.38	51.07
31.2-62.5	23.21	74.28
62.5-125.0	25.72	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00





Range	Local(%)	Under(%)
0.0-3.9	0.86	0.86
3.9-7.8	2.40	3.26
7.8-15.6	3.82	7.08
15.6-31.2	7.68	14.76
31.2-62.5	25.64	40.40
62.5-125.0	59.60	100.00
125.0-250.0	0.00	100.00

## Volume Ranges Table (OA136-24)

Surface Ranges Table (OA136-2
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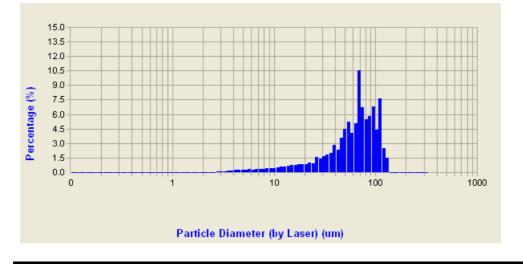
250.0-300.0

Range	Local(%)	Under(%)
0.0-3.9	13.46	13.46
3.9-7.8	15.83	29.29
7.8-15.6	12.41	41.71
15.6-31.2	12.31	54.02
31.2-62.5	20.23	74.25
62.5-125.0	25.75	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

0.00

100.00

#### **Volume Histogram (OA136-25)** Mean: 63.91 um STD: 30.55 um Conf.: 100.00 % D10: 19.55 um D50: 66.17 um D90: 106.97 um



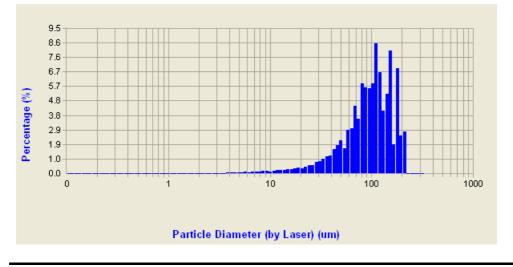
## Volume Ranges Table (OA136-25)

Range	Local(%)	Under(%)
0.0-3.9	0.75	0.75
3.9-7.8	2.37	3.12
7.8-15.6	4.59	7.72
15.6-31.2	9.17	16.88
31.2-62.5	28.88	45.76
62.5-125.0	53.49	99.25
125.0-250.0	0.75	100.00
250.0-300.0	0.00	100.00

## Surface Ranges Table (OA136-25)

Range	Local(%)	Under(%)
0.0-3.9	11.47	11.47
3.9-7.8	15.01	26.48
7.8-15.6	14.47	40.95
15.6-31.2	14.22	55.16
31.2-62.5	22.04	77.20
62.5-125.0	22.59	99.79
125.0-250.0	0.21	100.00
250.0-300.0	0.00	100.00

### Volume Histogram (OA136-6) Mean: 103.84 um STD: 48.39 um Conf.: 100.00 % D10: 41.11 um D50: 101.87 um D90: 175.30 um

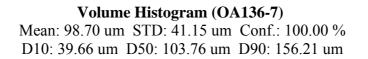


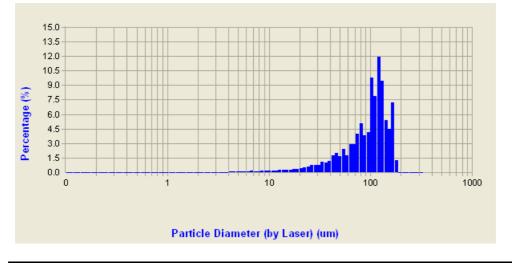
Range	Local(%)	Under(%)
0.0-3.9	0.16	0.16
3.9-7.8	0.68	0.83
7.8-15.6	1.49	2.33
15.6-31.2	3.89	6.22
31.2-62.5	14.63	20.86
62.5-125.0	48.18	69.03
125.0-250.0	30.97	100.00
250.0-300.0	0.00	100.00

#### Volume Ranges Table (OA136-6)

#### Surface Ranges Table (OA136-6)

Range	Local(%)	Under(%)
0.0-3.9	4.24	4.24
3.9-7.8	7.78	12.02
7.8-15.6	8.68	20.71
15.6-31.2	11.04	31.74
31.2-62.5	20.68	52.42
62.5-125.0	34.80	87.22
125.0-250.0	12.78	100.00
250.0-300.0	0.00	100.00



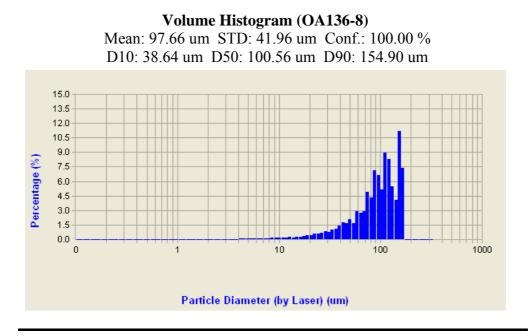


## Volume Ranges Table (OA136-7)

Range	Local(%)	Under(%)
0.0-3.9	0.22	0.22
3.9-7.8	0.77	0.99
7.8-15.6	1.63	2.62
15.6-31.2	4.40	7.02
31.2-62.5	13.86	20.88
62.5-125.0	52.37	73.26
125.0-250.0	26.74	100.00
250.0-300.0	0.00	100.00

#### Surface Ranges Table (OA136-7)

Range	Local(%)	Under(%)
0.0-3.9	5.83	5.83
3.9-7.8	8.50	14.33
7.8-15.6	9.04	23.37
15.6-31.2	11.83	35.20
31.2-62.5	18.87	54.08
62.5-125.0	34.48	88.56
125.0-250.0	11.44	100.00
250.0-300.0	0.00	100.00

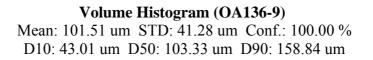


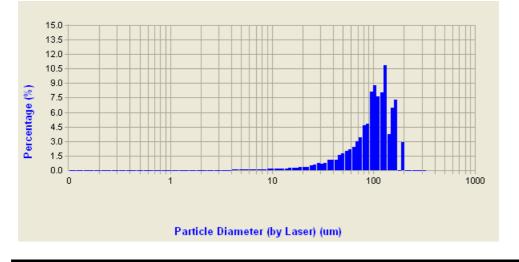
#### Volume Ranges Table (OA136-8)

Range	Local(%)	Under(%)
0.0-3.9	0.21	0.21
3.9-7.8	0.73	0.94
7.8-15.6	1.61	2.55
15.6-31.2	4.47	7.02
31.2-62.5	14.92	21.94
62.5-125.0	49.94	71.88
125.0-250.0	28.12	100.00
250.0-300.0	0.00	100.00

## Surface Ranges Table (OA136-8)

Range	Local(%)	Under(%)
0.0-3.9	5.54	5.54
3.9-7.8	8.01	13.55
7.8-15.6	8.86	22.41
15.6-31.2	12.02	34.43
31.2-62.5	20.12	54.54
62.5-125.0	33.68	88.22
125.0-250.0	11.78	100.00
250.0-300.0	0.00	100.00



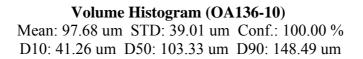


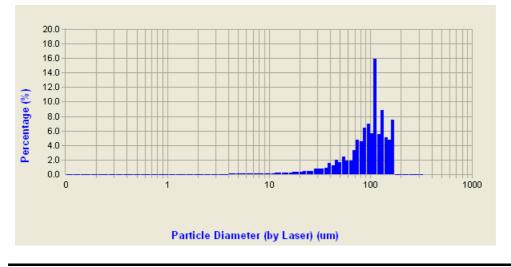
Range	Local(%)	Under(%)
0.0-3.9	0.18	0.18
3.9-7.8	0.61	0.79
7.8-15.6	1.43	2.22
15.6-31.2	3.91	6.13
31.2-62.5	12.73	18.86
62.5-125.0	51.16	70.02
125.0-250.0	29.98	100.00
250.0-300.0	0.00	100.00

#### Volume Ranges Table (OA136-9)

Surface Ranges Table (OA136-
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Range	Local(%)	Under(%)
0.0-3.9	5.01	5.01
3.9-7.8	7.26	12.26
7.8-15.6	8.46	20.72
15.6-31.2	11.14	31.86
31.2-62.5	18.21	50.07
62.5-125.0	36.28	86.35
125.0-250.0	13.65	100.00
250.0-300.0	0.00	100.00



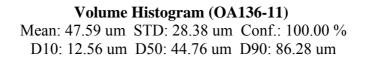


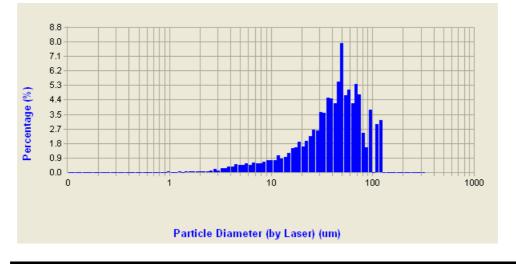
## Volume Ranges Table (OA136-10)

Range	Local(%)	Under(%)
0.0-3.9	0.26	0.26
3.9-7.8	0.76	1.02
7.8-15.6	1.40	2.42
15.6-31.2	3.76	6.18
31.2-62.5	13.35	19.53
62.5-125.0	55.62	75.16
125.0-250.0	24.84	100.00
250.0-300.0	0.00	100.00

## Surface Ranges Table (OA136-10)

Range	Local(%)	Under(%)
0.0-3.9	6.87	6.87
3.9-7.8	8.66	15.53
7.8-15.6	7.86	23.40
15.6-31.2	10.26	33.66
31.2-62.5	18.34	51.99
62.5-125.0	37.16	89.15
125.0-250.0	10.85	100.00
250.0-300.0	0.00	100.00



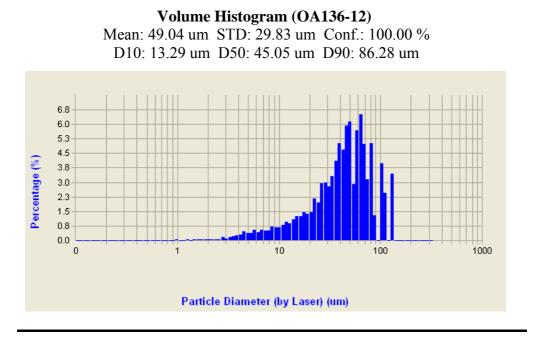


## Volume Ranges Table (OA136-11)

Range	Local(%)	Under(%)
0.0-3.9	1.60	1.60
3.9-7.8	4.05	5.64
7.8-15.6	7.18	12.82
15.6-31.2	17.65	30.48
31.2-62.5	42.37	72.85
62.5-125.0	27.15	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

## Surface Ranges Table (OA136-11)

Range	Local(%)	Under(%)
0.0-3.9	16.23	16.23
3.9-7.8	17.80	34.03
7.8-15.6	15.48	49.51
15.6-31.2	18.93	68.44
31.2-62.5	23.47	91.90
62.5-125.0	8.10	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

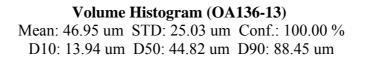


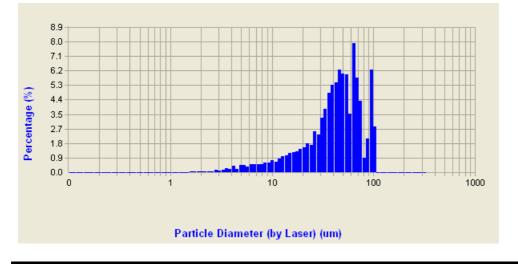
#### Volume Ranges Table (OA136-12)

Range	Local(%)	Under(%)
0.0-3.9	1.32	1.32
3.9-7.8	3.73	5.05
7.8-15.6	7.31	12.36
15.6-31.2	17.41	29.77
31.2-62.5	42.46	72.23
62.5-125.0	24.28	96.52
125.0-250.0	3.48	100.00
250.0-300.0	0.00	100.00

#### Surface Ranges Table (OA136-12)

Range	Local(%)	Under(%)
0.0-3.9	14.13	14.13
3.9-7.8	17.10	31.22
7.8-15.6	16.43	47.66
15.6-31.2	19.39	67.05
31.2-62.5	24.38	91.43
62.5-125.0	7.88	99.31
125.0-250.0	0.69	100.00
250.0-300.0	0.00	100.00



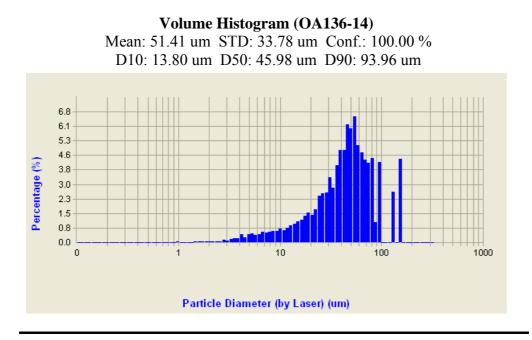


## Volume Ranges Table (OA136-13)

Range	Local(%)	Under(%)
0.0-3.9	1.16	1.16
3.9-7.8	3.57	4.73
7.8-15.6	6.92	11.65
15.6-31.2	16.02	27.68
31.2-62.5	46.43	74.10
62.5-125.0	25.90	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

#### Surface Ranges Table (OA136-13)

Range	Local(%)	Under(%)
0.0-3.9	13.04	13.04
3.9-7.8	16.79	29.83
7.8-15.6	15.91	45.75
15.6-31.2	18.27	64.01
31.2-62.5	27.35	91.37
62.5-125.0	8.63	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00



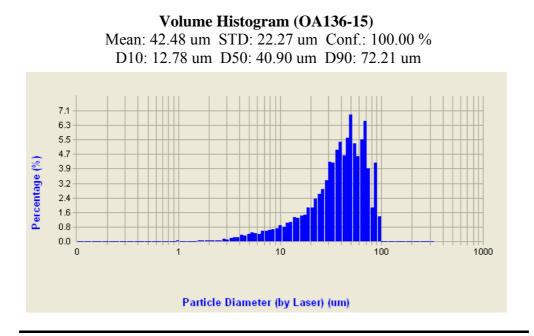
#### Volume Ranges Table (OA136-14)

Range	Local(%)	Under(%)
0.0-3.9	1.23	1.23
3.9-7.8	3.70	4.93
7.8-15.6	6.56	11.49
15.6-31.2	17.22	28.71
31.2-62.5	43.01	71.73
62.5-125.0	21.65	93.38
125.0-250.0	6.62	100.00
250.0-300.0	0.00	100.00

## Surface Ranges Table (OA136-14)

Range	Local(%)	Under(%)
0.0-3.9	13.94	13.94
3.9-7.8	17.46	31.39
7.8-15.6	15.24	46.63
15.6-31.2	19.61	66.25
31.2-62.5	25.14	91.38
62.5-125.0	7.40	98.78
125.0-250.0	1.22	100.00
250.0-300.0	0.00	100.00

### Site POR1/5

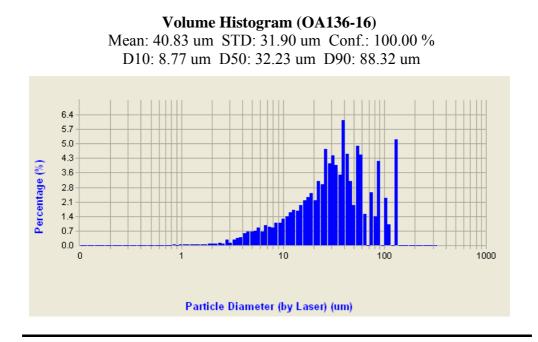


#### Volume Ranges Table (OA136-15)

Range	Local(%)	Under(%)
0.0-3.9	1.19	1.19
3.9-7.8	3.89	5.08
7.8-15.6	7.98	13.06
15.6-31.2	20.72	33.78
31.2-62.5	44.46	78.24
62.5-125.0	21.76	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

# Surface Ranges Table (OA136-15)

Range	Local(%)	Under(%)
0.0-3.9	12.53	12.53
3.9-7.8	16.81	29.34
7.8-15.6	17.07	46.42
15.6-31.2	21.73	68.15
31.2-62.5	24.66	92.81
62.5-125.0	7.19	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

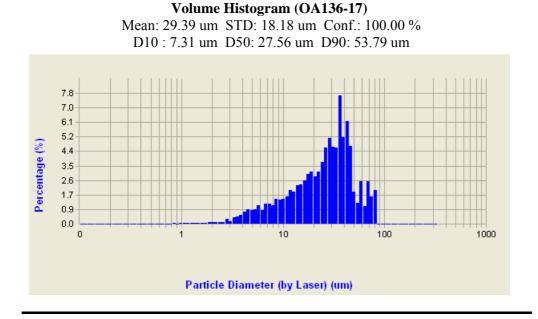


#### Volume Ranges Table (OA136-16)

Range	Local(%)	Under(%)
0.0-3.9	2.17	2.17
3.9-7.8	6.34	8.51
7.8-15.6	12.67	21.18
15.6-31.2	26.95	48.13
31.2-62.5	34.45	82.58
62.5-125.0	12.24	94.82
125.0-250.0	5.18	100.00
250.0-300.0	0.00	100.00

# Surface Ranges Table (OA136-16)

Range	Local(%)	Under(%)
0.0-3.9	17.22	17.22
3.9-7.8	21.24	38.46
7.8-15.6	20.95	59.41
15.6-31.2	22.09	81.50
31.2-62.5	15.08	96.58
62.5-125.0	2.67	99.25
125.0-250.0	0.75	100.00
250.0-300.0	0.00	100.00

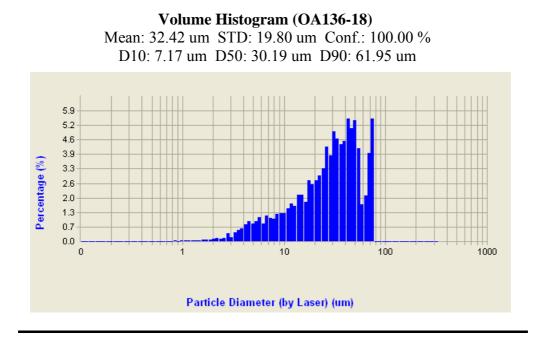


Range	Local(%)	Under(%)
0.0-3.9	2.73	2.73
3.9-7.8	8.03	10.75
7.8-15.6	15.58	26.34
15.6-31.2	31.32	57.66
31.2-62.5	35.09	92.74
62.5-125.0	7.26	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

#### Volume Ranges Table (OA136-17)

#### Surface Ranges Table (OA136-17)

Range	Local(%)	Under(%)
0.0-3.9	18.33	18.33
3.9-7.8	22.69	41.02
7.8-15.6	21.81	62.83
15.6-31.2	21.83	84.66
31.2-62.5	13.73	98.40
62.5-125.0	1.60	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

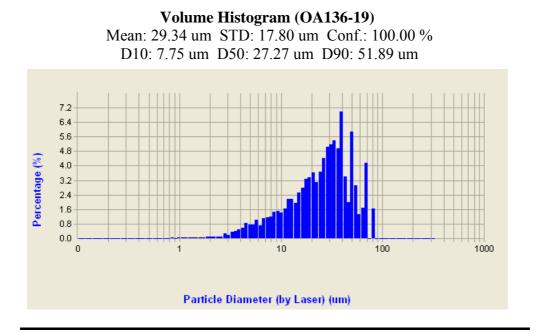


# Volume Ranges Table (OA136-18)

Range	Local(%)	Under(%)
0.0-3.9	3.01	3.01
3.9-7.8	7.82	10.83
7.8-15.6	13.44	24.27
15.6-31.2	27.39	51.65
31.2-62.5	38.91	90.56
62.5-125.0	9.44	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

# Surface Ranges Table (OA136-18)

Range	Local(%)	Under(%)
0.0-3.9	20.66	20.66
3.9-7.8	23.12	43.78
7.8-15.6	19.47	63.25
15.6-31.2	19.68	82.93
31.2-62.5	14.91	97.84
62.5-125.0	2.16	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

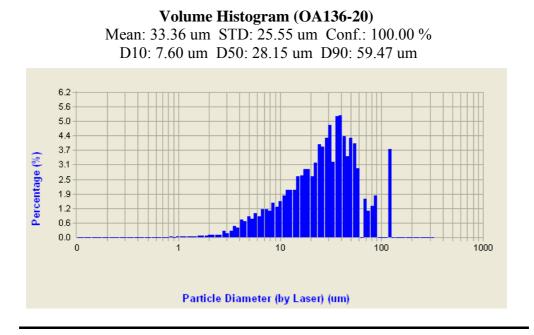


# Volume Ranges Table (OA136-19)

Range	Local(%)	Under(%)
0.0-3.9	2.48	2.48
3.9-7.8	7.41	9.90
7.8-15.6	15.69	25.59
15.6-31.2	32.53	58.12
31.2-62.5	35.19	93.31
62.5-125.0	6.69	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

# Surface Ranges Table (OA136-19)

Range	Local(%)	Under(%)
0.0-3.9	17.27	17.27
3.9-7.8	21.28	38.55
7.8-15.6	22.50	61.05
15.6-31.2	23.44	84.50
31.2-62.5	13.95	98.45
62.5-125.0	1.55	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00



# Volume Ranges Table (OA136-20)

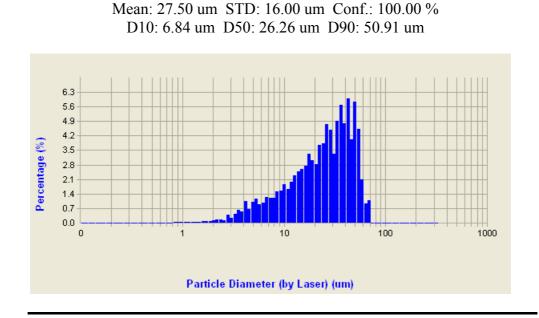
Range	Local(%)	Under(%)
0.0-3.9	2.45	2.45
3.9-7.8	7.84	10.29
7.8-15.6	15.97	26.25
15.6-31.2	29.85	56.10
31.2-62.5	34.16	90.26
62.5-125.0	9.74	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

#### Surface Ranges Table (OA136-20)

Range	Local(%)	Under(%)
0.0-3.9	17.21	17.21
3.9-7.8	22.89	40.11
7.8-15.6	23.17	63.28
15.6-31.2	21.70	84.98
31.2-62.5	13.24	98.22
62.5-125.0	1.78	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

# Quality Assurance sample 1: POR 2/8 (collected in 2005, re-analysed in 2008)

Volume Histogram (OA136/QA1) POR 2/8



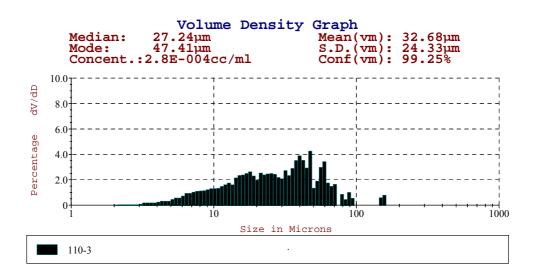
#### Surface Ranges Table (OA136/QA1)

Range	Local(%)	Under(%)
0.0-3.9	19.70	19.70
3.9-7.8	23.74	43.44
7.8-15.6	21.83	65.27
15.6-31.2	20.32	85.59
31.2-62.5	14.14	99.73
62.5-125.0	0.27	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

#### Volume Ranges Table (OA136/QA1)

Range	Local(%)	Under(%)
0.0-3.9	3.14	3.14
3.9-7.8	8.83	11.97
7.8-15.6	16.58	28.55
15.6-31.2	30.30	58.85
31.2-62.5	39.93	98.79
62.5-125.0	1.21	100.00
125.0-250.0	0.00	100.00
250.0-300.0	0.00	100.00

Quality Assurance sample 1 comparison: POR 2/8 (collected and analysed in 2005 on Galai CIS-100 laser particle sizer)



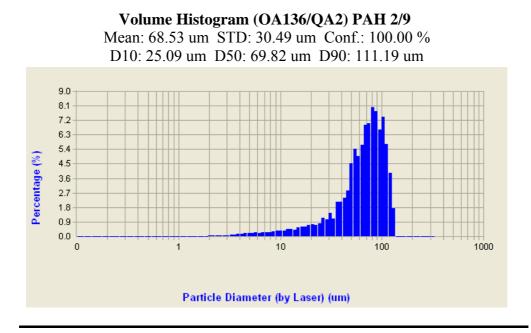
#### Area Ranges Table: POR 2/8

Size(microns)	Local(%)	Undersize(%)	Oversize(%)
2.0-3.9	5.76	5.76	94.24
3.9-7.8	22.42	28.18	71.82
7.8-15.6	29.84	58.02	41.98
15.6-31.0	24.34	82.36	17.64
31.0-62.5	15.88	98.24	1.76
62.5-125.0	1.59	99.83	0.17
125.0-250.0	0.17	100.00	0.00
250.0-500.0	0.00	100.00	0.00

#### Volume Ranges Table: POR 2/8

Size(microns)	Local(%)	Undersize(%)	Oversize(%)
2.0-3.9	1.00	1.00	99.00
3.9-7.8	7.28	8.28	91.72
7.8-15.6	18.35	26.63	73.37
15.6-31.0	28.35	54.99	45.01
31.0-62.5	37.14	92.13	7.87
62.5-125.0	6.48	98.60	1.40
125.0-250.0	1.40	100.00	0.00
250.0-500.0	0.00	100.00	0.00

# Quality Assurance sample 1: POR 2/8 (collected in 2005, reanalysed in 2008)



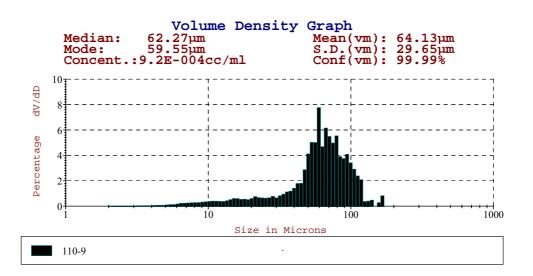
#### Surface Ranges Table (OA136/QA2)

Range	Local(%)	Under(%)
0.0-3.9	10.32	10.32
3.9-7.8	13.03	23.35
7.8-15.6	12.21	35.56
15.6-31.2	13.18	48.74
31.2-62.5	23.72	72.46
62.5-125.0	27.02	99.47
125.0-250.0	0.53	100.00
250.0-300.0	0.00	100.00

#### Volume Ranges Table (OA136/QA2)

Range	Local(%)	Under(%)
0.0-3.9	0.61	0.61
3.9-7.8	1.81	2.42
7.8-15.6	3.40	5.82
15.6-31.2	7.45	13.27
31.2-62.5	27.98	41.25
62.5-125.0	57.01	98.26
125.0-250.0	1.74	100.00
250.0-300.0	0.00	100.00

Quality Assurance sample 2 comparison: PAH 2/98 (collected and analysed in 2005 on Galai CIS-100 laser particle sizer)



#### Area Ranges Table: PAH 2/9

Size(microns)	Local(%)	Undersize(%)	Oversize(%)
2.0-3.9	2.96	2.96	97.04
3.9-7.8	11.85	14.80	85.20
7.8-15.6	16.99	31.80	68.20
15.6-31.0	14.12	45.92	54.08
31.0-62.5	29.68	75.59	24.41
62.5-125.0	23.86	99.46	0.54
125.0-250.0	0.55	100.00	0.00
250.0-500.0	0.00	100.00	0.00

#### Volume Ranges Table: PAH 2/9

Size(microns)	Local(%)	Undersize(%)	Oversize(%)
2.0-3.9	0.23	0.23	99.77
3.9-7.8	1.74	1.97	98.03
7.8-15.6	4.69	6.66	93.34
15.6-31.0	7.58	14.24	85.76
31.0-62.5	36.06	50.30	49.70
62.5-125.0	47.71	98.01	1.99
125.0-250.0	1.99	100.00	0.00
250.0-500.0	0.00	100.00	0.00

# **Appendix 2: Sediment chemistry results**

The National Institute of Water and Atmospheric Research Limited (NIWA), Hamilton, carried out the sample preparation. Hill Laboratories Limited, Hamilton, carried out the analyses of total organic carbon, weak acid-extractable metals and total recoverable metals.

Site			PAH1		
Replicate (GWRC Code)	PAH1/1	PAH1/2	PAH1/3	PAH1/4	PAH1/5
<u>Total Organic Carbon (%, &lt;500 µm):</u>	1.69	1.58	1.68	1.71	1.63
<u>Total Organic Carbon (%, &lt;63 µm):</u>	1.44	1.4	1.47		
<u>Metals (mg/kg, weak acid, &lt;63 µm):</u>					
Copper	8.3	9.0	9.0	8.8	8.6
Lead	21	21	21	21	21
Zinc	66	67	68	70	66
		PAH1	/1–5 comp	oosite	
<u>Metals (mg/kg, strong acid, &lt;500 µm):</u>					
Arsenic			11		
Cadmium			0.036		
Chromium			21.9		
Copper			14.6		
Lead			22.7		
Mercury			0.093		
Nickel			15		
Silver			0.086		
Zinc			88.6		

Table A2.1: Total organic carbon and metals in replicate composite sediment samples collected at site PAH1 in November 2008

Site			PAH2		
Replicate (GWRC Code)	PAH2/1	PAH2/2	PAH2/3	PAH2/4	PAH2/5
<u>Total Organic Carbon (%, &lt;500 µm):</u>	1.54	1.68	1.5	1.67	1.56
<u>Total Organic Carbon (%, &lt;63 μm):</u>	1.52	1.57	1.53		
<u>Metals (mg/kg, weak acid, &lt;63 µm):</u>					
Copper	7.9	8.0	7.9	7.7	8.2
Lead	18	17	18	17	18
Zinc	57	56	58	57	57
	PAH2/1–5 composite				
<u>Metals (mg/kg, strong acid, &lt;500 µm):</u>					
Arsenic			7.5		
Cadmium			0.055		
Chromium			15.7		
Copper			10.5		
Lead			17.3		
Mercury			0.081		
Nickel			11		
Silver			0.072		
Zinc			70.1		

# Table A2.2: Total organic carbon and metals in replicate compositesediment samples collected at site PAH2 in November 2008

Site			PAH3		
Replicate (GWRC Code)	PAH3/1	PAH3/2	PAH3/3	PAH3/4	PAH3/5
<u>Total Organic Carbon (%, &lt;500 µm):</u>	0.925	1.00	0.949	0.989	0.996
<u>Total Organic Carbon (%, &lt;63 μm):</u>	1.08	1.14	1.04		
<u>Metals (mg/kg, weak acid, &lt;63 µm):</u>					
Copper	7.3	7.1	7.0	7.1	7.6
Lead	17	17	16	17	17
Zinc	54	55	52	54	56
	PAH3/1–5 composite				
<u>Metals (mg/kg, strong acid, &lt;500 µm):</u>					
Arsenic			9.0		
Cadmium			0.036		
Chromium			17.1		
Copper			9.54		
Lead			16.2		
Mercury			0.073		
Nickel			12		
Silver			0.056		
Zinc			69.7		

# Table A2.3: Total organic carbon and metals in replicate compositesediment samples collected at site PAH3 in November 2008

Site	POR1				
Replicate (GWRC Code)	POR1/1	POR1/2	POR1/3	POR1/4	POR1/5
<u>Total Organic Carbon (%, &lt;500 µm):</u>	2.27	2.27	2.15	2.24	2.17
<u>Total Organic Carbon (%, &lt;63 µm):</u>	1.46	1.55	1.39		
<u>Metals (mg/kg, weak acid, &lt;63 µm):</u>					
Copper	14	14	14	14	14
Lead	32	33	32	32	32
Zinc	144	150	145	144	146
		POR	/1–5 comp	osite	
<u>Metals (mg/kg, strong acid, &lt;500 µm):</u>					
Arsenic			12		
Cadmium			0.17		
Chromium			21.6		
Copper			23.4		
Lead			40.2		
Mercury			0.12		
Nickel			14		
Silver			0.18		
Zinc			200		

# Table A2.4: Total organic carbon and metals in replicate compositesediment samples collected at site POR1 in November 2008

Site			POR2		
Replicate (GWRC Code)	POR2/1	POR2/2	POR2/3	POR2/4	POR2/5
<u>Total Organic Carbon (%, &lt;500 µm):</u>	1.96	1.97	1.96	1.91	1.93
<u>Total Organic Carbon (%, &lt;63 µm):</u>	1.72	1.68	1.71		
Metals (mg/kg, weak acid, <63 µm):					
Copper	13	13	14	13	13
Lead	34	34	35	34	35
Zinc	130	126	129	125	127
		POR	2/1–5 comp	osite	
<u>Metals (mg/kg, strong acid, &lt;500 μm):</u>					
Arsenic			13		
Cadmium			0.043		
Chromium			23.9		
Copper			20.6		
Lead			37.2		
Mercury			0.14		
Nickel			16		
Silver			0.13		
Zinc			150		

# Table A2.5: Total organic carbon and metals in replicate compositesediment samples collected at site POR2 in November 2008

# **Appendix 3: Analytical quality assurance results**

The results of the within-batch (duplicate) and between-batch (archive) comparisons carried out as quality assurance (QA) for the November 2008 Porirua Harbour subtidal sediment quality survey are presented in Tables A3.1–A3.4. Archived Porirua Harbour subtidal sediment samples from the 2004 and 2005 surveys have been used for the between-batch comparisons. Results from these sample analyses are shown in the shaded sections of the tables. For all tables, any difference (%) between the new result (denoted with a "2") and the original result (denoted with a "1") is expressed as:

100 x (new result – original result)/mean of the two results

In summary, the analytical QA results (reported in Olsen et al. 2009) show:

- Good precision for all TOC analyses in both the  $<500 \mu$ m-fraction and the  $<63 \mu$ m-fraction (Tables A3.1, A3.2).
- Good precision for 500 µm-fraction total metals in the within-batch comparisons except for lead (15%), but variable precision for the between-batch comparison, in particular for silver and zinc in one sample and for arsenic the other (Table A3.3). Although total metals are not used for trend analysis (and therefore some variability is not a major concern), the larger differences in concentrations in the between-batch QA samples indicate that there is a need for on-going QA testing. Problems with between-batch variability in total metal concentrations have been encountered in previous harbour sediment quality surveys (e.g., Stephenson & Mills 2006, Stephenson et al. 2008).
- Good precision for weak acid-extractable metals, with differences in the results of both the within-batch and between-batch comparisons ranging from 0–7.4% (Table A3.4).

Site		POR1/14			PAH2/1	3
Result Number	1	2	Diff (%)	1	2	Diff (%)
Total Organic Carbon (%)	2.24	2.23	-0.5	1.50	1.50	0.0
Site	POR1/7 (2004 sample)					
Result Number	1	2	Diff (%)			
Total Organic Carbon (%)	1.94	2.09	7.4			

Table A3.1: Within-batch and between-batch comparisons for total organic carbon
in <500 μm fraction

#### Table A3.2: Within-batch comparisons for total organic carbon in <63 µm fraction

Site		PAH1/11			POR1/14	
Result Number	1	2	Diff (%)	1	2	Diff (%)
Total Organic Carbon (%)	1.44	1.43	-0.7	1.46	1.45	-0.7

Site		POR1/11-1	5	PAH2/	6-10 (2004	sample)
Result Number	1	2	Diff (%)	1	2	Diff (%)
Arsenic	12	12	0.0	7.1	7.4	3.8
Cadmium	0.17	0.17	0.0	0.06	0.07	16
Chromium	21.6	21.3	-1.4	12.4	14.3	14
Copper	23.4	22.9	-2.2	11.4	12.7	11
Lead	40.2	40.1	-0.2	17.5	19.3	10
Mercury	0.12	0.14	15	0.08	0.089	11
Nickel	14	14	0.0	8.5	10.0	16
Silver	0.18	0.19	5.4	0.06	0.08	28
Zinc	200	201	0.5	56.9	69.7	20
Site	POR	2/1-5 (2005	sample)	1		
Result Number	1	2	Diff (%)			

Table A3.3: Within-batch and between-batch comparisons for total metals in <500  $\mu$ m fraction. Concentrations in mg/kg dry weight.

Site	POR2/	POR2/1-5 (2005 sample)				
Result Number	1	1 2 Diff (9				
Arsenic	13.0	16.0	22			
Cadmium	0.05	0.05	0.0			
Chromium	26.2	22.0	-17			
Copper	24.6	27.7	12			
Lead	39.4	45.7	15			
Mercury	0.13	0.12	-11			
Nickel	14.5	15.0	3.4			
Silver	0.11	0.12	11			
Zinc	159	160	0.6			

Table A3.4: Within-batch and between-batch comparisons for weak acid-extractable metals in <63  $\mu$ m fraction. Concentrations in mg/kg dry weight.

Site		PAH1/11			POR1/14	
Result Number	1	2	Diff (%)	1	2	Diff (%)
Copper	8.3	8.5	2.4	14	14	0.0
Lead	21	20	-4.9	32	32	0.0
Zinc	66	69	4.4	144	144	0.0
Site		POR1/7				
Result Number	1	2	Diff (%)			
Copper	14	13	-7.4			
Lead	36	34	-5.7			

138

3.7

133

Particle size analyses were also the subject of QA checks. Two archived sediment samples from the 2005 subtidal survey were re-analysed on NIWA's Eyetech Particle Size Analyser and the results compared against the original results obtained using NIWA's Galai CIS-100 laser particle sizer. Olsen et al. (2009) conclude that comparable data sets were obtained with the Eyetech Particle Size Analyser; the differences in mean particle size for the two between-batch comparisons were -19% and 6.4%, and the particle volume and surface area distribution outputs were similar (see QA graphs in Appendix 2).

Zinc

# Appendix 4: List of species in the subtidal benthos

A list of the species identified in the subtidal samples collected during the November 2008 Porirua Harbour sediment quality survey is presented in Table A4.1. Where genus and species names could not be assigned with certainty due to damage to the specimens, small size, immaturity, or taxonomic difficulties, the species are designated "#1", "#2", "#3", etc., following the class, family, or generic name as appropriate.

Table A4.1: List of species identified during the November 2008 Porirua Harbour subtidal sediment quality survey. For feeding mode: P = predator, Sc = scavenger, SDF = surface deposit feeder, SSDF = subsurface deposit feeder, SF = suspension feeder, U = unknown.

Phylum COELENTERATA (1 species) Class ANTHOZOA	
Edwardsia sp.#1 <sup>1</sup> +	Р
Phylum NEMERTEA (4 species)	Р
	P P
	P
	P
Phylum ASCHELMINTHES	
Class PRIAPULIDA (1 species) Priapulopsis australis + +	Р
	r
Class NEMATODA (1 species)	
Nematoda sp.#1 +	U
Phylum ANNELIDA	
Class POLYCHAETA (26 species)	
	Р
	SDF
Asychis sp.#1 + + SS	SDF
	SDF
	DF
	SDF
	Р
	SDF
<b>5</b> 1	DF
	P
	P
	P
	SDF
	SDF
	F, Sc DF
	F, Sc
	F, SC SDF
5	SDF
	P
	DF
	F, SF
	SDF

Table A4.1 *cont*.: List of species identified during the November 2008 Porirua Harbour subtidal sediment quality survey. For feeding mode: P = predator, Sc = scavenger, SDF = surface deposit feeder, SSDF = subsurface deposit feeder, SF = suspension feeder, U = unknown.

Species	Onepoto Arm	Pauatahanui Arm	Feeding mode(s)
Class POLYCHAETA continued			
Sphaerosyllis hirsuta		+	Р
Terebellidae sp.#1		+	SDF
Terebellides sp.#1	+	+	SDF
Class OLIGOCHAETA (1 species)			
Oligochaeta sp.#1	+	+	SSDF
Phylum MOLLUSCA			
Class GASTROPODA (4 species)			
Cominella adspersa		+	P, Sc
Cominella glandiformis	+	+	P, Sc
Haminoea zelandiae	•	+	SDF
Xymene plebeius	+	+	P
			·
Class BIVALVIA (6 species) Arthritica sp.#1		4	SF
	+ +	+	SF
Cyclomactra ovata Macomona liliana	+ +	+	SDF
Mysella hounselli	+ +	+	SF
Nucula hartvigiana	+	+ +	SDF
Theora lubrica	+	+	SF
			01
Phylum ARTHROPODA			
Class CRUSTACEA (17 species)			
Amphipoda sp.#1		+	U
Amphipoda sp.#2	+	+	U
Amphipoda sp.#3		+	U
Eurylana cook <sup>a</sup>		+	P, Sc
Copepoda sp.#1		+	U
Copepoda sp.#3		+	U
Macrophthalmus hirtipes	+	+	SDF
Ostracoda sp.#2		+	U
Ostracoda sp.#3		+	U
Ostracoda sp.#4		+	U
Ostracoda sp.#5		+	U
Phoxocephalidae sp.#1	+	+	P, Sc
Phoxocephalidae sp.#2	+	+	P, Sc
Pontophilus australis		+	P, Sc
Tanaidacea sp.#1	+	+	Р
Tanaidacea sp.#2		+	
<i>Tenagomysis</i> <b>s</b> p.#1		+	SDF, SF
<u>Class INSECTA</u> (1 species)			
Chironomidae sp.#1		+	SDF
Phylum SIPUNCULIDA (1 species)			
Sipunculida sp.#2	+	+	SDF
Phylum ECHINODERMATA			
Class HOLOTHUROIDEA (1 species)			
Paracaudina chilensis	+	+	SSDF
Incorrectly identified as Sipunculida sp.#1 in the			0001

<sup>2</sup> Listed by Grange (1977) as a deposit feeder. The species is possibly ditrophic.

<sup>3</sup> Listed as Cirolana cooki in the 2004 and 2005 subtidal surveys (Stephenson 2005, Stephenson & Mills 2006).

# Appendix 5: Key species driving differences among sample groups

# Table A5.1: Groups 1 and 2

Species	Group 1 Mean Abundance	Group 2 Mean Abundance	Percent Dissimilarity Contribution	Cumulative Percent Dissimilarity Contribution
<i>Tanaidacea</i> sp.#1	0	130.63	27.83	27.83
Heteromastus filiformis	130.56	2.92	25.1	52.92
<i>Cossura</i> <b>s</b> p.#1	51.69	0	12.13	65.05
Arthritica sp.#1	54.38	73.96	9.74	74.79
Nucula hartvigiana	27.19	4.71	5.46	80.25
Asychis sp.#1	15.5	32.83	5.14	85.39
Oligochaeta sp.#1	2.19	18.04	4.19	89.58
Phoxocephalidae sp.#1	4.75	6.38	1.29	90.87

# Table A5.2: Groups 1 and 3

Species	Group 1 Mean Abundance	Group 3 Mean Abundance	Percent Dissimilarity Contribution	Cumulative Percent Dissimilarity Contribution
Heteromastus filiformis	7.07	130.56	35.83	35.83
<i>Cossura</i> sp.#1	1.75	51.69	18.47	54.3
Arthritica sp.#1	21.33	54.38	13.38	67.68
Nucula hartvigiana	22.26	27.19	5.88	73.56
Asychis sp.#1	21.83	15.5	5.22	78.78
Oligochaeta sp.#1	10	2.19	3.28	82.06
Phoxocephalidae sp.#1	6.04	4.75	2.37	84.43
Phoxocephalidae sp.#2	6.22	0.5	2.27	86.7
Nicon aestuariensis	1.3	4.88	1.43	88.13
<i>Glycinde</i> sp.#1	2.44	4.75	1.34	89.47
Cossura consimilis	3.56	0	1.34	90.8

# Table A5.2: Groups 2 and 3

Species	Group 2 Mean Abundance	Group 3 Mean Abundance	Percent Dissimilarity Contribution	Cumulative Percent Dissimilarity Contribution
<i>Tanaidacea</i> sp.#1	1.7	130.63	39.8	39.8
Arthritica sp.#1	21.33	73.96	19.92	59.72
Asychis <b>sp.</b> #1	21.83	32.83	7.34	67.05
Oligochaeta sp.#1	10	18.04	7.1	74.16
Nucula hartvigiana	22.26	4.71	6.41	80.57
Phoxocephalidae sp.#2	6.22	4.88	2.62	83.19
Phoxocephalidae sp.#1	6.04	6.38	2.36	85.55
Heteromastus filiformis	7.07	2.92	2.05	87.61
Paraonidae sp.#1	1.64	4.67	1.58	89.19
Cossura consimilis	3.56	0.42	1.36	90.55

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#### For more information, contact Greater Wellington:

Wellington officeMasterton officePO Box 11646PO Box 41Manners StreetMasterton 5840Wellington 6142T 06 378 2484T 04 384 5708F 06 378 2146 F 04 385 6960

Masterton office

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