Shellfish Contaminant Monitoring Programme Review

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Shellfish Contaminant Monitoring Programme Review

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NIWA Client Report HAM2012-116

NIWA Project: ARC13210

Executive Summary

Background

The Shellfish Contaminant Monitoring Programme (SCMP) has been run by Auckland Council (AC) (and formerly The Auckland Regional Council (ARC)) since 1987. AC has monitored bioaccumulative contaminant levels using Pacific oysters (*Crassostrea gigas*) in the Manukau Harbour every year since 1987 (excluding 2004). Annual mussel (*Perna canaliculus*) monitoring (with the exception of 2004) was introduced in the Waitemata Harbour and Tamaki Estuary in 1999 and in the Manukau Harbour in 2000.

As an assessment of all aspects of the SCMP, AC conducts regular audits. The previous audit in 2007 (Mills, 2007), recommended a follow-up in 5 years. AC has requested a status and trends analysis (preceding report; (Stewart et al., 2013)) and a separate in-depth review of the SCMP (this report). The scope of the review is detailed in the introduction. A summary of findings from this review is provided below.

The SCMP is mostly fulfilling its objectives. It is providing contaminant information that cannot (at present) be directly obtained by other monitoring programmes. Data from the SCMP complements that obtained from the sediment contaminant, benthic health and saline water quality monitoring programmes in the area, providing a holistic assessment of the state of the environment in the region. Concentrations of contaminants are able to be compared between sites allowing a relative assessment of contamination between each site (although differential uptake of some metals does exist between oysters and mussels). Furthermore, contaminant concentrations can also be compared with international shellfish monitoring programmes and against food standards guidelines, allowing a perspective of contamination against external benchmarks. Analysis of temporal trends is possible, due to continuity of sites and many contaminants over the lifetime of the SCMP, and provides the capacity to link changes in contaminant concentrations to regulatory measures taken to reduce, or prevent, contaminants entering the environment. The SCMP is also capable of providing a broad-scale link between contaminant concentrations, land use type and change in land use.

Findings from the quality assurance assessment

Heavy metal and organic contaminant analyses are currently undertaken by Watercare Laboratory Services Ltd and AsureQuality, respectively. Both are IANZ accredited laboratories and have comprehensive quality assurance (QA) procedures that provide sufficient information to measure analytical performance and provide confidence in data supplied for the SCMP. A change to the digestion procedure used by Watercare in 2011 does not appear to have significantly affected the results for samples from the SCMP, however an increase in variability was observed, which was more pronounced for cadmium, copper and zinc analyses on wet tissue samples.

The current analytical laboratories provide robust data at extremely low detection limits. This is especially true for the heavy metals lead, arsenic and cadmium, which - due to lower detection limits since 2005 – are now being detected consistently. Analytical instrumentation used by AsureQuality allows significantly lower detection limits for polychlorinated biphenyls (PCBs) than were achieved by NIWA, but no significant improvement has been observed for lindane, for which detection is still problematic.

Lower detection limits and reduced analytical variability have led to the provision of more robust datasets. This is important for continued trend analysis, particularly where concentrations have reduced to very low levels for some contaminants.

The major recommendations arising from the QA assessment are:

- We strongly recommend long-term storage of tissue samples (dried or frozen) for future investigations and retrospective analysis of e.g., emerging chemicals of concern;
- Consideration of a pilot study to measure any significant differences between levels of contaminants (metals and organics) when extracting either wet tissue or freeze-dried tissue.

Recommendations implemented from previous review

Several of the recommendations from the 2007 SCMP review and audit (Mills, 2007) have been implemented by Auckland Council. These include:

- Shellfish shucking is no longer undertaken by Auckland Council personnel;
- More shellfish material is being provided to the analytical laboratories to enable re-analysis;
- An assessment of whether a reduction in the number of replicates is possible (covered in section 4.5 of this report);
- Investigating measures of catchment land use to assist with interpretation of the monitoring data (examined in the preceding status and trends report (Stewart et al., 2013);
- The implications of reducing sampling frequency (covered in section 4.4 of this report;
- The implementation of formalised sample archiving. Surplus shellfish are now archived and tracked by a Chain of Custody system;
- Provision of annual summaries of QA data. These are now supplied by Watercare and AsureQuality laboratories;
- Analysis of ‘bulk reference’ QA samples. These are now analysed by both Watercare and AsureQuality laboratories to check inter-annual analytical variability;
- Improving detection limits for most metals. This has been in place since 2005;
- Improving detection limits for organics. This has been in place (especially for PCBs) since changing laboratories in 2009;
- Development of a user manual for data management;
- Carrying out comparisons between shellfish and sediment monitoring sites (covered in section 3.1 of this report);

However, some of recommendations from the 2007 review have not been implemented. These include dropping, combining, adding and relocating some sites and increasing the range of species monitored; these aspects are also discussed in this review.

Recommendations from this review

Temporal trend assessments would be affected by dropping components of the SCMP (such as removing some sites or removing specific analyte suites) or by significant changes to the programme (such as completely removing a species of shellfish). However, a review of the trend data suggests that not all changes would have a significant impact. A viable alternative to *removing* components of the SCMP would be to *reduce* certain aspects of the programme, controlling costs but still providing relevant information for the future. Substantial changes could be undertaken within the SCMP while having minimal impact on the ability of the programme to fulfil its objectives and allowing the programme to evolve and provide more valid environmental assessments for the future.

It is recommended to reduce the sampling frequency in the SCMP from annual to biennial (every two years) to realise significant cost savings. This will extend the time taken to fully establish long term trends for mussels. However, in terms of environmental relevance, most contaminant concentrations measured are considered low in an international context (with the exception of metals at some sites), have reduced accordingly over time (with the exception of PAHs and some metals at some sites) and are either still declining or have stabilised at very low concentrations.

Consolidation of some sites in the SCMP is recommended: specifically Pahurehure Inlet and Hingaia Bridge oyster sites and Upper Harbour Bridge and Chelsea mussel sites. Consolidating these sites would result in a loss of fine detail in organic contaminant concentrations in the respective catchments. However, this is a minor loss of information relative to the benefits that could be achieved by adding further components to the SCMP and still remaining cost neutral.

A statistical power analysis has shown that a reduction in the number of replicates analysed from five replicates (currently) to four would be suitable for continuing trend analysis in the future. However, this assessment did not include data from the recent change in digestion procedure undertaken at Watercare - with associated increase in variability – as there is only one year of data since this change. As such, it is recommended that reduction of replicates should only be undertaken for organic analyses until the increased variability of the digestion procedure for metals is better understood. Furthermore, for any new contaminants that are introduced to the SCMP - for example PBDEs or mercury - the variability should be assessed prior to any reduction of replicates.

Other than consolidating the Upper Harbour Bridge and Chelsea mussel sites it is not feasible to remove mussel sites from the SCMP as they are the only species with a record for both Manukau Harbour and east coast sites. However, there is potential for replacing oyster sites with mussel sites. This would provide contaminant data for one species, removing the complexities associated with comparing data from two different shellfish. The offset to this would be discontinuation of the longer term trends established for oysters (around 25 years), a potential loss of information on sediment dwelling species and a reduced ability to compare with international shellfish monitoring programmes and food safety guidelines.

The metals analytical suite should not be reduced or removed from routine contaminant monitoring. Temporal trend analyses have shown that metal concentrations are highly variable, however current concentrations at some sites are considered medium or high by international standards so continued assessment is justified. However, analysis of metals in shellfish could be reduced to every two years. Furthermore, we strongly recommend the inclusion of mercury in future monitoring which - along with arsenic - is a dominant contributor to human health toxicity associated with consumption of aquatic species (although note that the programme is not specifically designed to assess human health risk from shellfish consumption). It may also be worthwhile carrying out a single sampling analysis of nickel in the future, to assess whether there has been any significant change in shellfish concentrations since 2003. We do not recommend removal (partial or full) of the analytical suites of organochlorine contaminants. We recommend a reduction of the frequency of analysis of organochlorine contaminants in shellfish to every four years. We do not recommend the expansion of the PAH suite in the near future. Although this would provide useful information, the benefits are questionable with internationally low concentrations of PAHs around Auckland. However, this should be re-visited at a future date, if PAH concentrations continue to increase. Shellfish should be analysed for PAHs every two years.

Consideration should be given to the future inclusion of selected emerging chemicals of concern (ECCs) in the analytical suite to provide a more relevant suite of organic contaminants. It is recommended that a pilot study is initiated to analyse perfluorooctanesulfonic acid (PFOS) and brominated diphenyl ether congeners-47/99 (BDE-47/99) in mussels and oysters from the Auckland region. Furthermore - although outside the objectives of the SCMP, but within the general State of the Environment monitoring requirements - measurement of ECCs should also occur in sediment and water. Consideration should also be given to changing analytical suites of other environmental monitoring programmes in the region to achieve this.

Complete disestablishment of the SCMP would significantly limit the ability to fully understand the state of the environment in the region (particularly from a contaminant bioavailability perspective), unless a viable alternative was implemented. There are two potential avenues to explore to provide an assessment of bioavailable contaminants in the environment; an expanded sediment contaminant monitoring programme *in conjunction* with benthic health monitoring and passive sampling devices (PSDs). A feasibility study would be necessary to assess the suitability of each approach.

A combined sediment contaminant /benthic health programme would extend existing monitoring programmes which have significantly greater spatial coverage than the SCMP, while PSDs would require incorporation of emerging technologies. PSDs are being researched world-wide as cost-effective alternatives to shellfish monitoring. Research into organic PSDs is far more advanced than for metal PSDs, and assessments are being made into their suitability in regulatory monitoring. Therefore, PSDs are probably more suited to being a future development, as they become more widely implemented into monitoring programmes internationally. However, with the potential of PSDs to provide cost-effective and robust contaminant bioavailability data it is recommended that a feasibility study is performed within the next 3-5 years if this is the preferred option. Such a study could assess:

- The most appropriate PSDs for estuarine water samples;
- A cost-benefit analysis of replacing the SCMP with PSDs;
- The reliability of the data and ability to continue trend analyses using the existing data set.

Table of Contents

1.0 Introduction 8

2.0 Review of analytical procedures and data quality 13

3.0 Relationship to other marine monitoring programmes 15

  3.1 Sediment Contaminant Monitoring Programme 15

  3.2 Benthic Health Programme 19

  3.3 Saline Water Quality Monitoring Programme 19

4.0 Re-evaluation of the programme objectives 21

  4.1 Programme objectives 21

  4.2 Is the SCMP providing key information? 22

  4.3 Can the SCMP link contaminant changes to land use? 23

  4.4 Sampling frequency 23

  4.5 Replicates 24

5.0 Implementation of recommendations from 2007 review 32

  5.1 Sites 32

  5.2 Species monitored 34

  5.3 Shellfish processing 34

  5.4 Shellfish numbers 35

  5.5 Replicates analysed 35

  5.6 Relating trend data to changes in land use 35

  5.7 Sample management 35

  5.8 Analytical procedures and data management 36

  5.9 Reporting 37

  5.10 Summary 37

6.0 Implications of changing the programme 38

  6.1 Implications of dropping the whole programme 38

  6.2 Implications of dropping or changing parts of the programme 41

7.0 Future Monitoring 54

  7.1 Sampling frequency 54

  7.2 Sites 54

7.3 Species 55
7.4 Analytical Suites 56
7.5 Condition 61
7.6 Replicates 61
7.7 Alternatives to SCMP 62
8.0 Summary and Recommendations 63
8.1 Review of procedures and data quality..63
8.2 Relationship to other marine monitoring programmes 63
8.3 Re-evaluation of the programme objectives 64
8.4 Implementation of recommendations from the 2007 review 64
8.5 Implications of changing or dropping the SCMP..65
8.6 Implications of dropping or changing parts of the programme 66
8.7 Recommendations for future monitoring..67
9.0 Acknowledgements 69
10.0 References 70
Appendix A Descriptions of contaminants, their sources and impacts 73
Key metals 73
Organic Contaminants..76
Appendix B List of analyses on mussels performed over the period of the programme with associated laboratory providers 80
Appendix C List of analyses on oysters performed over the period of the programme with associated laboratory providers 86

List of Figures

Figure 1-1 Location of oyster and mussel monitoring sites in the Auckland Council Shellfish Contaminant Monitoring Programme....10
Figure 3-1 Map of sediment monitoring sites and SCMP sites 17
Figure 4-1 Comparison of mean concentration and variance for metals using five replicates and three replicates. 28
Figure 4-2 Comparison of mean concentration and variance for organics using five replicates and three replicates. 31
Figure 6-1 Condition index for oysters and mussels at each site in the Shellfish Contaminant Monitoring Programme. 43
Figure 6-2 Comparison of concentrations (2009-2011) of selected organic contaminants for Pahurehure vs Hingaia Bridge and Chelsea vs Upper Harbour....47

List of Tables

Table 1-1 Site names and coordinates (New Zealand Transverse Mercator) of oyster and mussel monitoring sites in the Auckland Council Shellfish Contaminant Monitoring Programme 9
Table 3-1 Coordinates of shellfish contaminant monitoring programme sites and proximal sediment contaminant programme sites 16
Table 6-1 Summary of median metal concentrations at selected oyster and mussel sites in the Shellfish Contaminant Monitoring Programme from 2009 to 2011 (mg/kg dry weight).44
Table 6-2 Summary of median concentrations of organic contaminants in oysters and mussels in the Shellfish Contaminant Monitoring Programme, from 2009 to 2011 (lipid normalised, mg/kg). 45
Table 6-3 Comparison of selected shellfish contaminants with data from US National Status and Trends Mussel Watch Program. 50
Table 7-1 Sediment concentration data for selected ECCs in the marine receiving environment around Auckland 58
Table 7-2 CECs recommended for initial monitoring by scenario and environmental matrix (i.e. aqueous, sediment, tissue) (Anderson et al., 2012)....59

1.0 Introduction

The Shellfish Contaminant Monitoring Programme (SCMP) has been run by Auckland Council (AC) (and formerly The Auckland Regional Council (ARC)) since 1987. AC has monitored contaminant levels in Manukau Harbour using Pacific oysters (*Crassostrea gigas*) for most years since 1987. Annual mussel (*Perna canaliculus*) monitoring was introduced in the Waitemata Harbour and Tamaki Estuary in 1999, and in the Manukau Harbour in 2000. Oysters are collected from wild populations while mussels are sourced from the Coromandel, seeded onto ropes and deployed for 3 months prior to harvesting. Both species are harvested for analysis in early summer. No sites contain both mussels and oysters.

As shellfish are filter feeders, they process large volumes of water and suspended material in the water and have the capacity to bioaccumulate certain contaminants, such as heavy metals, organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), which may be present in the environment. Bivalves are particularly valuable for monitoring bioaccumulation of certain pollutants, such as PAHs, that are metabolized by species at higher trophic levels. As such the SCMP uses contaminant levels in oysters and mussels to provide an indirect measure of ambient seawater quality.

Wild populations of oysters from four monitoring sites within the Manukau Harbour are analysed annually (Figure 1-1 and Table 1-1). An additional monitoring site at Mill Bay was sampled in 2008 and 2009 as a potential replacement for Cornwallis due to falling oyster numbers at the latter site, but sampling has since reverted back to Cornwallis due to similar issues with decreasing numbers at Mill Bay.

Mussels are deployed at seven monitoring sites; three in the Manukau Harbour, two in the Waitemata Harbour, one in the Tamaki Estuary and one (Illiomama) at the southern end of Rangitoto Island (Figure 1-1 and Table 1-1). Pre-deployment mussels are also analysed to provide a baseline measurement of contaminant loads prior to exposure at each monitoring site.

Table 1-1 Site names and coordinates (New Zealand Transverse Mercator) of oyster and mussel monitoring sites in the Auckland Council Shellfish Contaminant Monitoring Programme

Site Number	Site Name	Sentinel Shellfish	Easting	Northing
43914	Pahurehure	Oysters	1770911	5896630
44161	Cornwallis	Oysters	1742800	5903176
44164	Mill Bay	Oysters	1743159	5904578
1043823	Hingaia	Oysters	1769516	5893827
43911	Grannys Bay	Oysters	1756183	5911301
43900	Papakura Channel	Mussels	1753405	5900096
43912	Mangere Bridge	Mussels	1757583	5911004
43913	Weymouth	Mussels	1764909	5897819
7718	Illiomama	Mussels	1768255	5924625
7898	Upper Harbour Bridge	Mussels	1748951	5927685
8237	Upper Tamaki	Mussels	1765577	5913819
7717	Chelsea	Mussels	1754059	5923396
16	Pre-deployment Mussels	Mussels	n/a	n/a

Mill Bay was sampled in 2008 and 2009 only.

Figure 1-1 Location of oyster and mussel monitoring sites in the Auckland Council Shellfish Contaminant Monitoring Programme

Descriptions of contaminants currently measured in the SCMP are provided in Appendix A. A full history of contaminants measured and analytical providers over the life-time of the programme is provided in Appendix B for mussels and Appendix C for oysters.

The SCMP is used to provide information for state of the environment (SoE) monitoring, as required under section 35 of the Resource Management Act 1991 (RMA). The SCMP, in combination with the Saline Water Quality Monitoring Programme, the Sediment Contaminant Monitoring Programme and the Benthic Health Monitoring Programme, is used to monitor the SoE in Auckland's marine environment.

A previous review and audit of the SCMP was undertaken in 2007 (Mills, 2007). This review strongly recommended continuing with the SCMP for at least another 5 years. Auckland Council has since revisited these recommendations and called for a second review.

The National Institute of Water and Atmospheric Research Ltd (NIWA) has been contracted by Auckland Council to provide status and trends analyses on data provided by AC for both mussels and oysters. This is covered in a preceding report (Stewart et al., 2013).

AC also requested an independent review of the SCMP, which forms the basis of this report. Pertinent issues and the sections in this report that address these are outlined below:

1. Comprehensive history and background information on the programme including methods (**section 1.0**).
2. Reviewing analytical procedures and data quality (**section 2.0**) (including assessment of laboratories and interviews with Auckland Councils staff) to determine whether:
    a) The laboratories involved in the programme have systems which ensure a consistently high standard of analysis;
    b) The QA/QC procedures used are appropriate and adhered to;
    c) Reported detection limits are adequate for the intended purpose.
3. Investigate how the programme complements and overlaps with other marine monitoring programmes including The Saline Water Quality Programme, the Sediment Contaminant Programme and the Benthic Ecology Programme (**section 3.0**).
4. Re-evaluation of the programme objectives (**section 4.0**) and whether the programme is meeting these objectives and delivering value for money in the context of how the data is and can be used for the objectives (and beyond), for example:
    a) Is the programme continuing to provide key information on the quality of the marine environment which supports Auckland Council's resource management functions and other marine monitoring programmes?
    b) Is the programme, as a whole, capable of detecting changes in contaminant concentrations and broadly linking them to land use activity?

   c) Are sampling frequency and timing appropriate? Could the frequency be reduced?
   d) Could the number of replicates be reduced without losing statistical robustness?
   e) Should any individual components be added, modified or dropped (e.g., sites, analyses, species)?
   f) What components of the 2007 review and audit have been implemented, what were the benefits of these changes, and what changes are still required or recommended (**section 5.0**)?

5. What are the implications of dropping *the whole* programme (**section 6.1**). In particular:
   a) How it would affect Auckland Council's understanding of environmental quality?
   b) How would it affect Auckland Council's ability to identify emerging issues?
   c) How would it affect decision making in relation to Auckland Council's resource management functions?
   d) Is there any other feasible way of assessing bioavailability of contaminants in the water column?
6. What are the implications for the overall programme of dropping or changing *parts* of the programme (**section 6.2**), for example:
   a) What are the implications of dropping the oyster programme and retaining the mussel programme or vice versa? What are the implications of replacing the shellfish programme with more comprehensive organics monitoring in the sediment chemistry programme? What other options could be considered?
   b) Are each of the different elements of the programme useful and is the associated data capable of providing reliable trend detection?
7. Provide recommendations for future monitoring on each of the aspects listed above (**section 7.0**).

2.0 Review of analytical procedures and data quality

Methods have been reported previously for shellfish sampling (Kelly, 2007) and analysis (Stewart et al., 2013, Kelly, 2007) and are not repeated here.

Analytical procedures and QA data were assessed in a preceding status and trends report (Stewart et al., 2013). This included an assessment of whether changing analytical laboratories in 2005 (metals) and 2009 (organics) had any significant effect on the data. These sections will not be repeated in this report, however, a summary of the findings is provided below.

Metals have been analysed by Watercare Laboratory Services Ltd since 2005. Watercare Services Ltd are an IANZ accredited Laboratory. QA procedures are comprehensive and provide sufficient information to measure analytical performance of metals for the SCMP. As no QA data is available prior to 2005, the consequences in change of analytical provider could not be assessed. However, there was a change to the digestion procedure used in 2011 in order to provide better recoveries for selected metals (e.g., mercury and tin) in shellfish tissue. The change in digestion procedure does not appear to have significantly affected the results for samples from the SCMP, hence it is not expected to have any significant influence on the quantitative determination of metals in the shellfish tissue, however the variability was higher for selected metals and this would not favour a reduction in the number of replicates if on-going monitoring was to continue. Therefore, the 2011 data set can be used with confidence for comparison with earlier data for trends analysis.

The Environmental Section of AsureQuality Limited is an analytical laboratory with IANZ accreditation. QA procedures are comprehensive and provide sufficient information to measure analytical performance of organics for the SCMP. An assessment of QA data has revealed that there is substantially good agreement or better between organic contaminant data sets generated by NIWA and AsureQuality for the selected samples analysed.

As demonstrated by the QA procedures in place and analysis of the QA data, the current analytical laboratories provide robust data at extremely low detection limits. This is especially true for the heavy metals lead, arsenic and cadmium, which prior to 2005 were reported below, or close to, detection limits in a high proportion of samples. Since 2005, these three metals have been detected consistently. Some minor organic contaminants (e.g., lindane and minor PCB congeners) were not previously detected by NIWA due to detection limits around 0.1 to 0.2 ng/g (dw). Since 2009 organic contaminants have been analysed by AsureQuality laboratories. As such significantly lower detection limits can now be achieved with improved instrumentation, affording detection limits of between 0.001 and 0.01 ng/g for PCBs. Detection limits for lindane however, have not improved significantly and detection is still problematic.

The implications of more robust datasets - due to lower detection limits and reduced analytical variability - are significant for trend analysis, where concentrations have reduced to very low levels for some contaminants. However, the usefulness of continued annual monitoring of all these contaminants is questionable if principally being used for SoE reporting. Many legacy organic contaminant concentrations have reduced substantially since being banned, currently plateaued and are now extremely low.

3.0 Relationship to other marine monitoring programmes

The SCMP provides information for state of the environment (SoE) monitoring, as required under section 35 of the Resource Management Act 1991 (RMA). The four marine monitoring programmes used to monitor the state of the environment are the SCMP, the Sediment Contaminant Monitoring Programme, the Benthic Health Monitoring Programme, and the Saline Water Quality Monitoring Programme. The four programmes have varying degrees of overlap, but together provide a holistic overview of the state of the environment in the region.

3.1 Sediment Contaminant Monitoring Programme

There is partial overlap between SCMP sites and sediment contaminant monitoring sites (Table 3-1 and Figure 3-1). Most SCMP sites have a sediment contaminant monitoring site in close proximity, with the exception of Papakura Channel, Illiomama and Hingaia Bridge.

Contaminants routinely analysed by the sediment contaminant monitoring programme (hereafter called the sediment programme) are:

- Extractable metals – copper (Cu), lead (Pb), and zinc (Zn) – measured on the <63 µm sediment fraction, often described as the bioavailable metal fraction. The variability in metals data for the <63 µm fraction is typically lower than the associated larger particle size fractions, and has been selected as the preferred metals indicator for temporal trend assessment;
- Total recoverable metals – Cu, Pb, and Zn –are analysed on the <500 µm (<0.5 mm) fraction, which approximates the total sediment. The total metals data are used for comparison with sediment quality guidelines;
- A selection of PAHs have been measured in some years but at only a few sites;
- Total organic carbon (TOC), is determined for calculating TOC-normalised concentrations of PAHs for comparisons with sediment quality guidelines;
- Particle size distribution.

The following contaminants have been measured periodically:

- Mercury (Hg), arsenic (As), tin (Sn), cadmium (Cd), and antimony (Sb) were analysed in samples taken in 2005;
- OCPs - including DDTs, dieldrin, chlordanes, lindane, and endosulfans – were analysed in samples collected in 2003 and 2007;
- PCBs were analysed in samples taken in 2003.

Table 3-1 Coordinates of shellfish contaminant monitoring programme sites and proximal sediment contaminant programme sites

SCMP Site	Sentinel Shellfish	Easting	Northing	Closest sediment site	Sediment programme	Easting	Northing	Distance between sites (km)
Chelsea	Mussel	1754059	5923396	Chelsea	RDP	1754161	5923677	0.21
Upper Harbour	Mussel	1748951	5927685	Outer Main Channel	UWH	1748592	5928382	0.75
				Central Waitemata East (Ohbv)	UWH	1749807	5927056	1.1
Mangere Bridge	Mussel	1757583	5911004	Mangere Cemetery	SOE	1759928	5911221	1.9
Papakura Channel	Mussel	1753405	5900096	-				
Tamaki	Mussel	1765577	5913819	Bowden	RDP	1765251	5912952	1.0
Weymouth	Mussel	1764909	5897819	Pahurehure Middle	RDP	1767570	5896927	3.2
Illiomama	Mussel	1768255	5924625	Te Matuku	SoE	2700223	6483115	21.8
Grannys Bay	Oyster	1756183	5911301	Hillsborough	RDP	1756786	5911590	0.61
Hingaia	Oyster	1769516	5893827	-				
Pahurehure	Oyster	1770911	5896630	Pahurehure Papakura	SoE	1771260	5896689	0.31
Cornwallis	Oyster	1742800	5903176	Mill Bay	RDP	1743018	5904528	1.7
Mill Bay	Oyster	1743159	5904578	Mill Bay	RDP	1743018	5904528	0.15

- designates no sediment sites nearby; RDP = Regional Discharges Project; UWH = Upper Waitemata Harbour Ecological Programme; SoE = State of the Environment Programme.

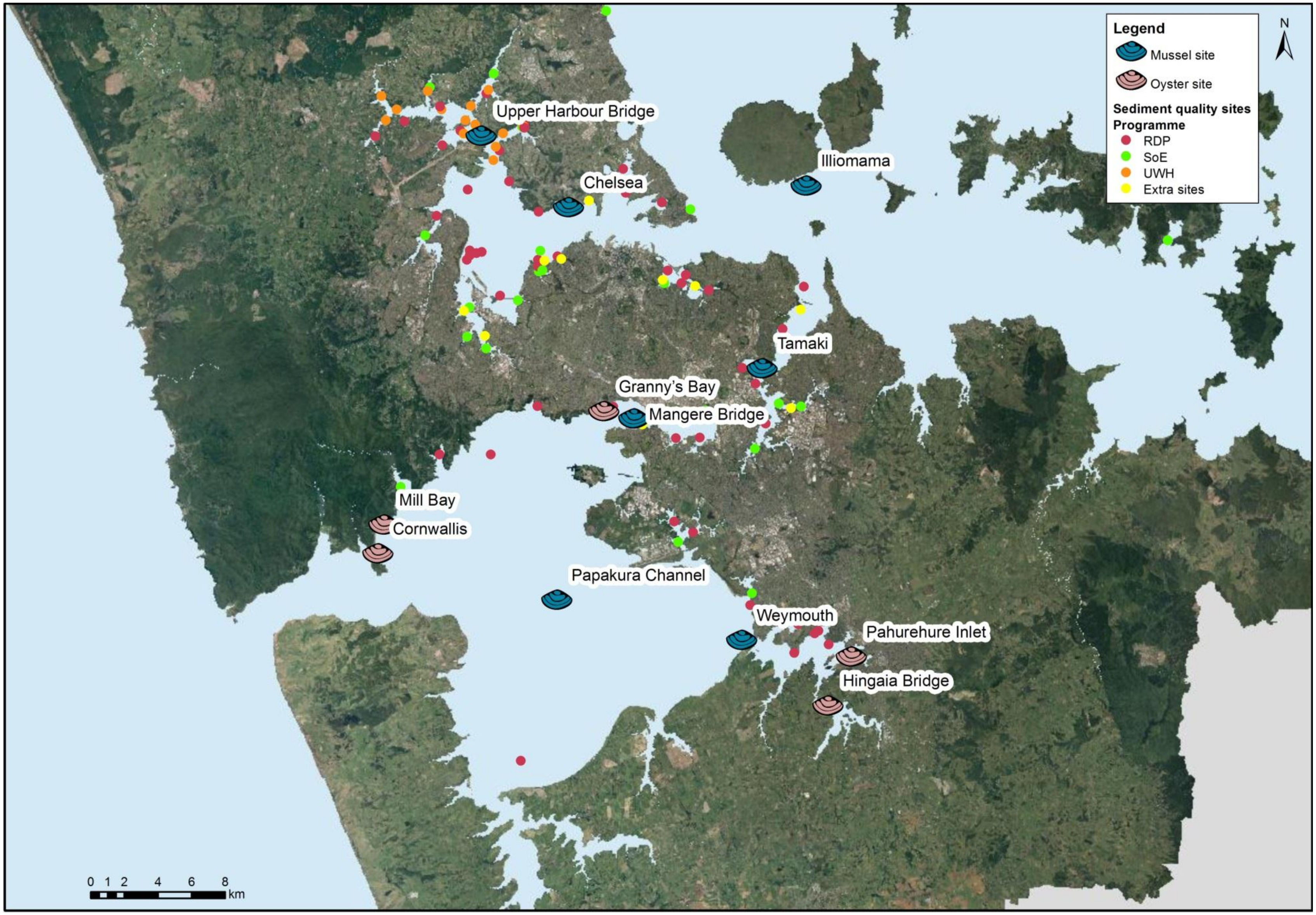


Figure 3-1 Map of sediment monitoring sites and SCMP sites

RDP = Regional Discharges Project; UWH = Upper Waitemata Harbour Ecological Programme; SoE = State of the Environment Programme.

Copper, lead, zinc and PAHs are routinely monitored contaminants in the sediment programme that are also routinely monitored by the SCMP. PAHs have only been monitored sporadically across the lifetime of the programme and the selection of PAHs measured may differ depending upon analytical provider carrying out the analyses.

As stated in the preceding Status and Trends report (Stewart et al., 2013), strong correlations were observed (2009-2011 median data) between copper, lead and zinc concentrations in shellfish and concentrations in sediment (both <500 µm, termed “total metal” and <63 µm, termed “extractable metal”) at nearby sites (see Table 3-1). Papakura Channel (mussels) and Hingaia Bridge (oysters) were excluded from analysis due to no relevant proximal sediment sites. Correlations were stronger between shellfish concentrations and “extractable” metal concentrations. Linear regression analysis provided R^2 values of 0.78, 0.98 and 0.92 for copper, lead and zinc in oysters and values of 0.86, 0.98 and 0.87 in mussels respectively (see section 6.5.1 in Stewart et al., 2013). However, these data are limited in both the number of correlations (four for oysters and six for mussels) and the concentration ranges being compared.

These data suggest – albeit with limited correlations to assess accurately – that sediment monitoring of these three urban metal contaminants *could potentially* be used as a surrogate for shellfish monitoring, i.e., high sediment concentrations translates to high shellfish concentrations. However, oysters and mussels concentrate these metals in different ways. Data from Auckland show copper, zinc and cadmium concentrations 50x, 30x, and 2x higher in oysters than mussels, respectively, while lead is 3x higher in mussels than oysters (Stewart et al., 2013). This same trend was noted internationally for copper, zinc and lead, although magnitudes for copper and zinc were much lower (10 times for both, see: Kimbrough et al., 2008). The physical parameters of the environment for each site should also be considered, e.g., currents, tidal movements, freshwater inflows, etc. These factors will also impact upon correlations, so each site should be assessed independently.

Another limitation of using sediment contaminant concentrations as a surrogate for shellfish contaminant concentrations is that the bulk sediment toxicant concentration does not always represent the bioavailable concentration, particularly for hydrophobic organic compounds in highly contaminated sediments (Maruya et al., 2009).

Contaminants that are not analysed routinely in the sediment programme – but are analysed in the SCMP – include arsenic, cadmium, chromium, PCBs and OCPs, so no accurate assessment can be made as to whether there are strong correlations between the two programmes for these contaminants. Furthermore, these contaminants have been measured in shellfish since 1987 (oysters) and 1999 (mussels), providing data suitable for trend assessments, which are not capable with the limited sediment data.

Although the sediment contaminant monitoring programme has many sampling sites that are in close proximity to the SCMP, the data generated in its current form is insufficient to replace the SCMP. It may be possible to replace the SCMP in the future with a combination of data from sediment chemistry (via an expanded Sediment Contaminant Monitoring Programme) and assessment of ecological effects (via the Benthic Health Monitoring Programme). However, a pilot study would be necessary to assess whether:

- Strong relationships exist between contaminants in shellfish and sediments *at the same sites*. This should include a comprehensive analysis of all contaminants measured in the SCMP and not just copper, lead and zinc.
- Strong relationships exist between sediment contaminant concentrations stated above and benthic health index *at the same sites*.

Another aspect to consider if the SCMP is replaced with sediment and benthic health monitoring is that historical data for organic legacy contaminants (which spans back up to 25 years) will be lost and trends will be terminated at this point. However, as concentrations of most of these contaminants have effectively plateaued off over the last decade this may be a minor loss of information. If strong correlations are observed (in a pilot study) between sediment and shellfish organic contaminants then future monitoring could feasibly be continued with sediment monitoring.

3.2 Benthic Health Programme

The Auckland Council Benthic Health Programme (BHP) assesses the health status of macrobenthic communities based on Benthic Health Model (BHM) and Traits-Based functional Index (TBI) scores. Separate models have been created for two of the key environmental contaminants in Auckland area estuaries: sediment mud content (percent silt+clay) and sediment heavy metal concentrations (copper, lead and zinc). The TBI is a functional traits based index developed for use in AC's SoE reporting. Health scores are: <0.2 (extremely good); 0.2 – 0.4 (good); 0.4 – 0.6 (moderate); 0.6 – 0.8 (poor); >0.8 (unhealthy with low resilience) (Hewitt et al., 2012).

The major overlap between the SCMP and BHP are the assessment of bioavailable contaminants, although this is restricted to copper, lead and zinc. The SCMP measures time-integrated concentrations of these contaminants while the BHP assesses how these contaminants affect macrobenthic communities. Even though major stressors have been defined as mud content and heavy metal concentrations it is likely that other contaminants contribute to degradation of macrobenthic health.

Sites monitored as part of this programme do not generally coincide with the shellfish monitoring sites, however there were general correlations between benthic health and shellfish site ranking (see section 4.4.1 in Stewart et al., 2013).

3.3 Saline Water Quality Monitoring Programme

There are only five SCMP sites and saline water quality monitoring (SWQM) sites in close proximity and another within ca. 2km (Grannys Bay SCMP site and Mangere Bridge water site, although on the opposite side of the channel). SCMP sites that are in close proximity with SWQM sites are all mussel sites, while oyster sites are generally not in close proximity to SWQM sites.

The SWQM complements, but does not overlap, with the SCMP. It is difficult to establish a link between saline water quality and shellfish contaminant concentrations as the SWQM programme provides transient short term indications of water quality at a site, whereas the SCMP measures bioaccumulative contaminants over a longer time period. Parameters measured by the SWQM are designed to establish water quality and include pH, temperature, salinity, turbidity, total suspended solids, chlorine, nitrate/nitrite and phosphorous (total and soluble).

For water quality parameters to be useful in long term monitoring programmes, frequent sampling events are necessary. If water quality monitoring was expanded to include the contaminants from the SCMP, then the cost would likely be prohibitive with such frequent analyses. Furthermore, the data would not be time integrated (as is provided by shellfish and sediment to some extent) and the potential would exist for information overload with too much data.

For more information on comparisons between shellfish site and water quality sites see Stewart et al. (2013).

4.0 Re-evaluation of the programme objectives

4.1 Programme objectives

The objectives of the Shellfish Contaminant Monitoring Programme (Cameron, 2012) are to:

1. *Identify contaminants with abnormally high concentrations in shellfish;*
2. *Detect changes in contaminant levels over time;*
3. *Detect differences in contaminant levels between locations, and;*
4. *Evaluate the effectiveness of measures aimed at reducing contaminant loads.*

Objective 1 is effectively being fulfilled. Concentrations of contaminants in the shellfish are able to be compared between sites, compared with international shellfish monitoring programmes and compared against food standards guidelines. However, with the number of sites limited it is not possible to give complete coverage of the region providing a potential for some hotspots of contamination to be missed. Furthermore, comparisons of contaminant concentrations between sites are limited by the low numbers. International comparisons provide perspective and a measure of the level of contamination at a site (or in the whole catchment). The proviso to this is that the same contaminants (or suites of contaminants) are measured across all sites and are consistent with international contaminants measured. This is especially true for organic suites which should measure the same congeners. This is the case for most organics suites, with the exception of PAHs. The NS&T mussel watch programme analyses 65 PAH congeners of which 24 (sum of 12 low molecular weight PAHs, plus 12 high molecular weight PAHs) are included in their ‘total’ suite used for trend analysis (O’Connor and Lauenstein, 2006). The Auckland SCMP ‘extended’ suite includes 15 high molecular weight PAHs - including all 12 NS&T high molecular weight PAHs. This may not be a significant difference if high molecular weight PAHs are the most prevalent in the shellfish, however this has not been established. While the programme covers a large suite of contaminants there is potential to introduce other relevant contaminants into the programme. This is discussed further in section 7.4.

Objective 2 is effectively being fulfilled. Temporal trend analyses have highlighted changes in contaminants over the life-time of the programme. Metals data have been problematic, especially in the early years, where high limits of detection for some metals and lack of QA data (prior to 2005) has made it difficult to make robust trend assessments. However, since 2005 these issues have been resolved so trend analysis since that time is much more robust. However, trends since 2005 are still on a short time scale and will require more time to be fully assessed; suggesting as frequent analysis of metals as is practical should be maintained. Organics (with the exception of PAHs) have generally decreased over time. The change in analytical laboratory from NIWA to AsureQuality in 2009 has led to markedly reduced detection limits for most organic contaminants and no significant change in reported concentrations (as shown by an assessment of QA data in Stewart et al., 2013). This makes it feasible to perform future trend analysis on even very low concentrations of organic contaminants. However, the environmental relevance of future trend analysis on such low concentrations of some organic contaminants is questionable. The SCMP would benefit from reducing focus on some legacy organic compounds and including appropriate emerging contaminants as discussed in section 7.4.

Objective 3 is mostly being fulfilled, but improvements could be made to more accurately assess contaminant concentration differences between sites. Differences in most contaminant concentrations can be highlighted between sites as shown in the current status section of the preceding status and trends report (Stewart et al., 2013). A proviso to this is that care must be taken comparing mussel and oyster metal concentrations as some metals are taken up preferentially by either species. The NS&T mussel watch programme observed that zinc and copper are generally 10-times higher in oysters and lead is generally 3 times higher in mussels (Kimbrough et al., 2008). Analyses of oyster and mussel metal concentrations around Auckland suggest that copper concentrations are 50 times higher and zinc 30-times higher in oysters than mussels, while lead was 3-times higher in mussels than oysters, which is broadly consistent with the NS&T mussel watch observations (Stewart et al., 2013). Furthermore, as there is no overlap between mussel and oyster monitoring sites - and in only one area are they in close proximity (Mangere Bridge mussel site and Grannys Bay oyster site) - it is difficult to correlate between oyster and mussel concentrations. Objective 3 would be better fulfilled if oysters were replaced with mussels to give a single species (as discussed in section 6.2.2), or shellfish were replaced with passive sampling devices (as discussed in section 6.1.4). However, removal of oysters would have some negative consequences, which are discussed further in section 6.2.2.

Objective 4 is being fulfilled in relation to the fact that robust methods are now in place to effectively monitor concentrations of a multitude of contaminants in shellfish. Temporal trend analyses provide the capability to link changes in contaminant concentrations to regulatory measures taken to reduce or remove them from entering the environment (e.g. deregistering of legacy pesticides and upgrades to the Mangere WWTP). Therefore, the programme is effective at picking up regional or large scale changes in contaminant inputs; however, it is less effective at picking up changes in diffuse inputs of contaminants on the scale of individual catchments due to the low number of sites across the region. That said, the SCMP overlaps and complements the sediment contaminant programme (which has a much greater coverage of sites) and, to a lesser extent, the saline and benthic monitoring programmes, to give a more wide-scale measure of contamination in the region. However, this is reliant on maintaining a high quality data set.

4.2 Is the SCMP providing key information?

The SCMP is providing contaminant information that cannot (at present) be obtained by the other state of the environment monitoring programmes. The SCMP provides information on bioavailable contaminants in the coastal environment as well as providing the ability to compare contaminant concentrations of selected contaminants in shellfish species consumed by humans with relevant food safety guidelines.

Replacing the SCMP with an expanded sediment monitoring programme – extended to routinely monitor contaminants currently covered in the SCMP – will not provide information on bioavailable contaminants, so is not currently a viable alternative. However, if this information is used in conjunction with the benthic health programme (as a proxy for bioavailable contaminants) this is potentially feasible (see section 3.1 for discussion). Replacing the SCMP with passive sampling devices (see section 6.1.4) has potential for future monitoring of bioavailable contaminants. Food safety assessment would be lost and although this is not an objective of the SCMP, this information is useful.

However, there is debate over whether the current analytical suite provides relevant information. Many legacy organic contaminants are decreasing steadily over time, as input into the environment has ceased or markedly reduced. As such, the usefulness of sustaining the current level of monitoring of these contaminants is questionable and is discussed further in section 6.2.3. Other (emerging) contaminants of relevance may be worth investigating in order to assess their potential impact and changes in their levels over time (see section 7.4.4).

4.3 Can the SCMP link contaminant changes to land use?

The SCMP is capable of detecting broad scale links between contaminant concentrations and land use. Multivariate analyses suggest that sites of the same category generally group together, i.e., reference sites group together, semi-urban sites group together and urban sites also group together. However, not all sites have clearly defined catchments. Only Tamaki, Pahurehure, Hingaia, Weymouth, Upper Harbour Bridge and Mangere Bridge have defined catchments. Of these, only Tamaki and Mangere Bridge have fully urban catchments. A more quantitative assessment would require incorporating known percentage land use types for each catchment.

However, changes in land use have been detected by the SCMP. The upgrade of the Mangere WWTP in 2001 was mirrored by spikes in concentrations of some contaminants (DDT, dieldrin and chlordanes) at Grannys Bay. Furthermore more recent (1999-2011) upward trending of DDT and dieldrin concentrations at Hingaia coincide with extensive development of rural land in the catchment to the south.

4.4 Sampling frequency

A reduction in the frequency of sampling will save money but will limit the usefulness of the data that is provided. A reduction from annual sampling to biennial (every two years) sampling would significantly reduce costs in deployment (of mussels), sampling and analysis but provide less power to detect trends.

However, temporal trend assessment shows that most organic contaminants are showing a general decrease in concentration, except PAHs which are generally more variable and increasing at some sites. Metals are also more variable and increasing in concentration at some sites. Reducing sampling frequency would lessen the ability to accurately monitor these changes in metals and PAHs.

The US NS&T mussel watch programme moved from annual to biennial sampling in 1994. This is in contrast to the San Francisco Regional Monitoring Programme who perform annual monitoring and argue that annual sampling provides substantially more power for trend detection than having more sites sampled less frequently (Melwani et al., 2008).

Another aspect to consider is that a reduction of sampling frequency will reduce the ability to detect short term spikes in contaminants due to point source contamination, such as a spillage. If these spillage events are known (e.g., a shipwreck leaking crude oil) then measures can be taken to assess the impact of these by introducing extra monitoring events. The danger exists when spillage events go undetected. The less frequent sampling would delay mitigation responses to such events and would make it more difficult to identify potential sources of contamination.

4.5 Replicates

An analysis was undertaken to ascertain if a reduction from five (currently) to three replicates (consistent with US NS&T mussel watch programme) significantly influences the results and variability of the data. Six key metals and selected organics suites (dieldrin, extended suite DDT and PCB, limited suite chlordanes and PAHs) – chosen to provide a range of concentrations from low (dieldrin and chlordanes) up to high (PCBs, PAHs and DDT) – along with percentage lipid were chosen for analysis. Means and standard deviations were calculated for dry weight mussel and oyster contaminant data from 2010. This year was chosen as it is a recent year that contains five replicates for all contaminants analysed. A further analysis was undertaken on three replicates by removing the first two replicates from each dataset.

Results for the six key metals are presented in Figure 4-1, while organic suites are presented in Figure 4-2. There was very little effect on the mean value or variability when reducing from five to three replicates.

Further statistical analysis was undertaken to determine whether this reduction would affect the ability to statistically compare between sites or over the years of monitoring (trend analysis). The effect on trend detection is through any increased variability of the individual mean estimates used in the regression. This cannot be analysed for directly but can be suggested using power analysis for detection of differences between two means from the same population.

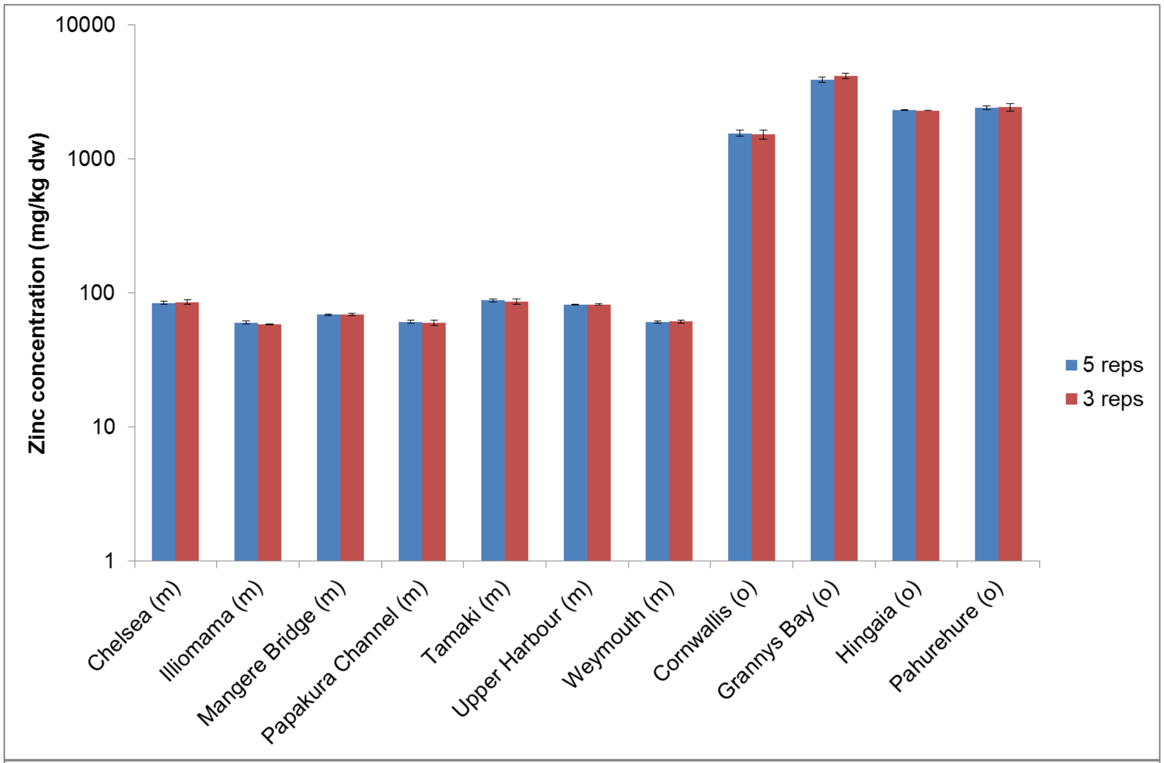
Comparisons of the minimum detectable difference (MDD) at different degrees of replication (from 5 to 1) will give an indication of the degree of information lost by dropping replicates. This approach is suitable for both trend analysis and comparisons between sites. Using the 2010 data as described above, the MDD was calculated for each site for key metals and organics using combinations of replicate results from n = 2 to 5. The MDD was then compared to the median concentration to indicate the degree of difference that the data could show. For example, in the Status and Trends report (Stewart et al., 2013) a difference of 1% change per year was defined as a meaningful trend. However a regression analysis has greater power to detect such differences, compared to a test between two means, as used to compare between sites. Therefore a degree of difference of 5% may be more appropriate.

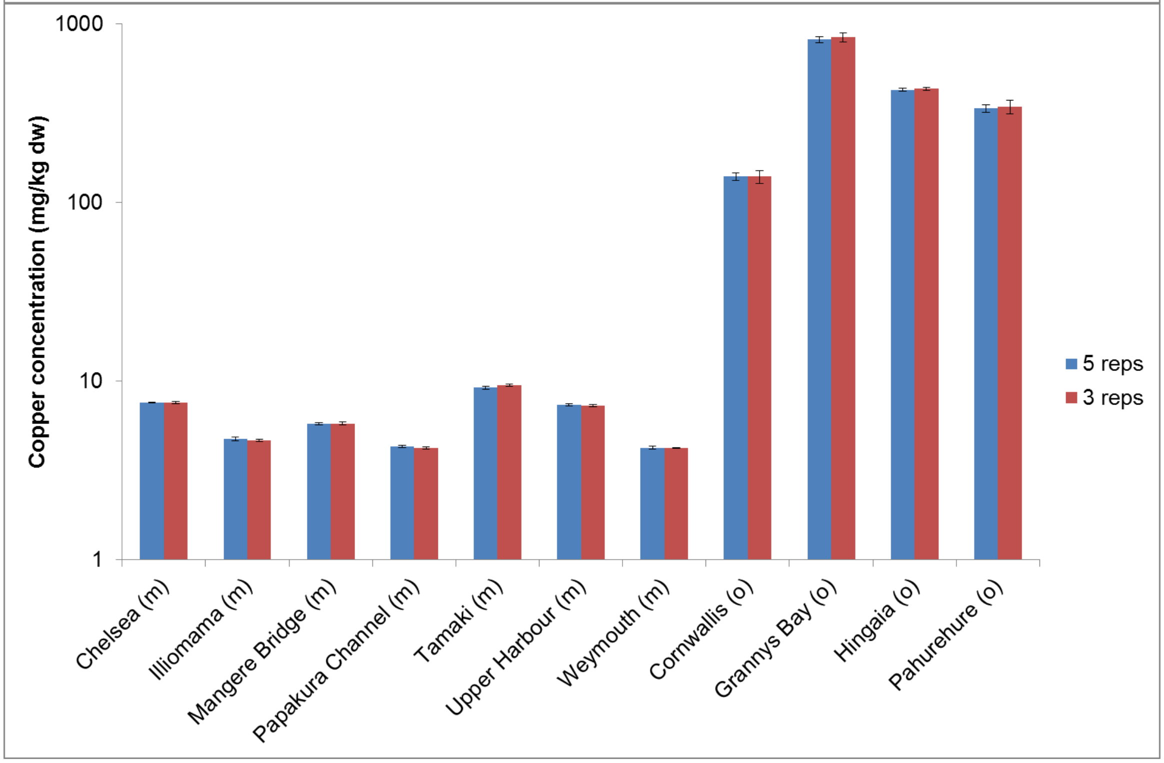
The MDD was < 1% of the median only for chlordane and only at two sites (Hingaia and Upper Harbour). This occurred whether the number of replicates was two or five. A MDD of <5% could be detected using three replicates at two sites for arsenic. A MDD <5% could be detected using four replicates at four sites for arsenic, one site for copper and two sites for zinc. A MDD <5% could be detected using five replicates at seven sites for arsenic, one site for copper, two sites for zinc and one site for lipids.

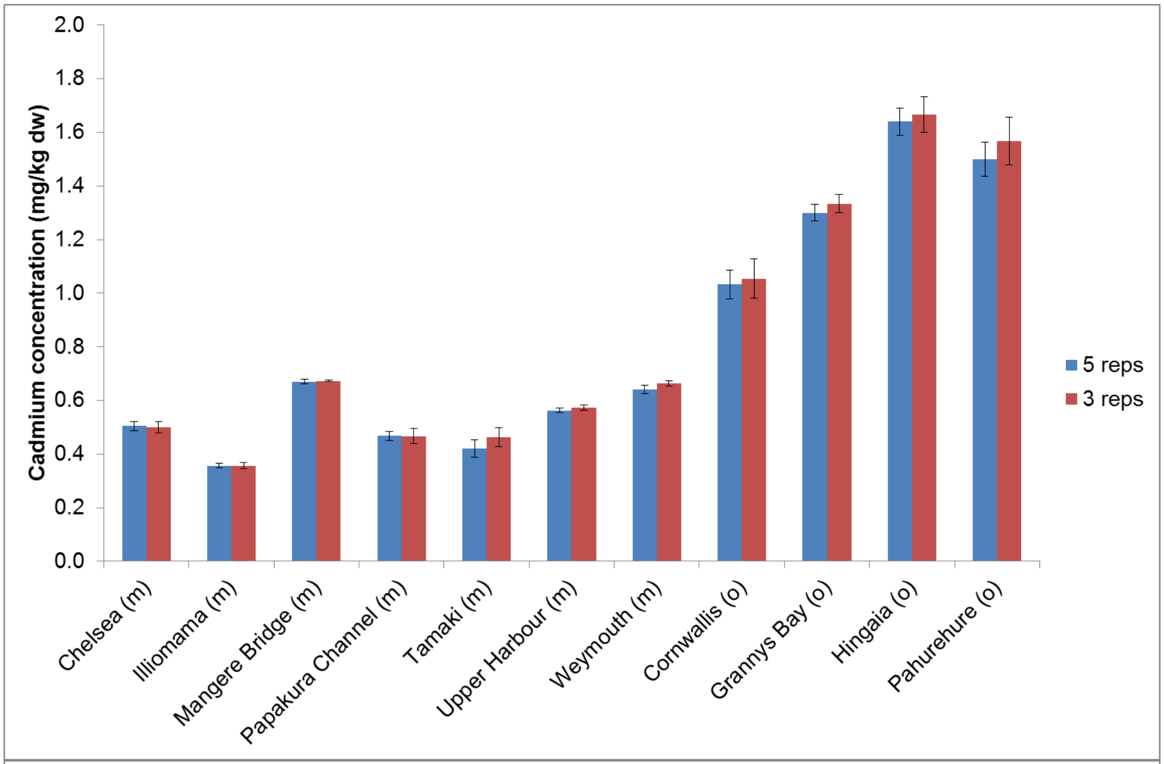
The increase in the MDD from three replicates to five varied from 4% (arsenic) to 17% (chlordane). However, much of this was driven by the increase from three to four replicates as the increase in the MDD from four replicates to five varied from 1% (arsenic) to 6% (Chromium). This suggests that reducing the number of replicates to four would have little effect on the result and would be suitable for continuing trend analysis in the future. If this reduction makes a difference in terms of the costs of the programme and its continuation in the future then it would be worthwhile.

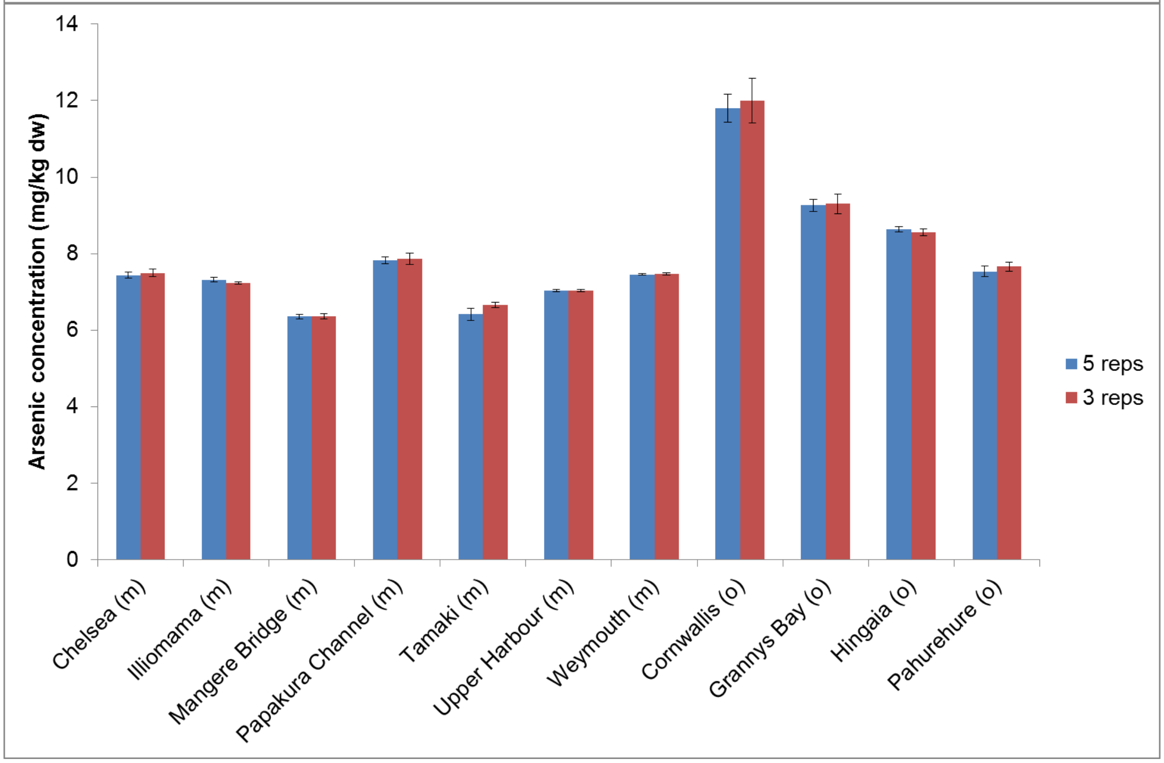
However, as stated in the status and trends report (section 4.1.3, (Stewart et al., 2013) the change in digestion procedure employed by Watercare Laboratory Services Ltd in 2011 provided an increase in variability for metals. Therefore, further caution should be taken in reducing metal replicate analyses from five to four until the cause and magnitude of the variability is better understood.

Reducing the number of replicates from five per site to four is more conservative than the US NS&T mussel watch program, which uses six composite samples, three for replicate organic contaminant analyses and three for trace metals (O’Connor and Lauenstein, 2006).


Zinc concentration (mg/kg dw)
10000
1000
100
10
1
Chelsea (m)
Illiomama (m)
Mangere Bridge (m)
Papakura Channel (m)
Tamaki (m)
Upper Harbour (m)
Weymouth (m)
Cornwallis (o)
Grannys Bay (o)
Hingaia (o)
Pahurehure (o)
5 reps
3 reps


Copper concentration (mg/kg dw)
1000
100
10
1
Chelsea (m)
Illiomama (m)
Mangere Bridge (m)
Papakura Channel (m)
Tamaki (m)
Upper Harbour (m)
Weymouth (m)
Cornwallis (o)
Grannys Bay (o)
Hingaia (o)
Pahurehure (o)
5 reps
3 reps


Cadmium concentration (mg/kg dw)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Chelsea (m)
Illiomama (m)
Mangere Bridge (m)
Papakura Channel (m)
Tamaki (m)
Upper Harbour (m)
Weymouth (m)
Cornwallis (o)
Grannys Bay (o)
Hingaia (o)
Pahurehure (o)
5 reps
3 reps


Arsenic concentration (mg/kg dw)
14
12
10
8
6
4
2
0
Chelsea (m)
Illiomama (m)
Mangere Bridge (m)
Papakura Channel (m)
Tamaki (m)
Upper Harbour (m)
Weymouth (m)
Cornwallis (o)
Grannys Bay (o)
Hingaia (o)
Pahurehure (o)
5 reps
3 reps

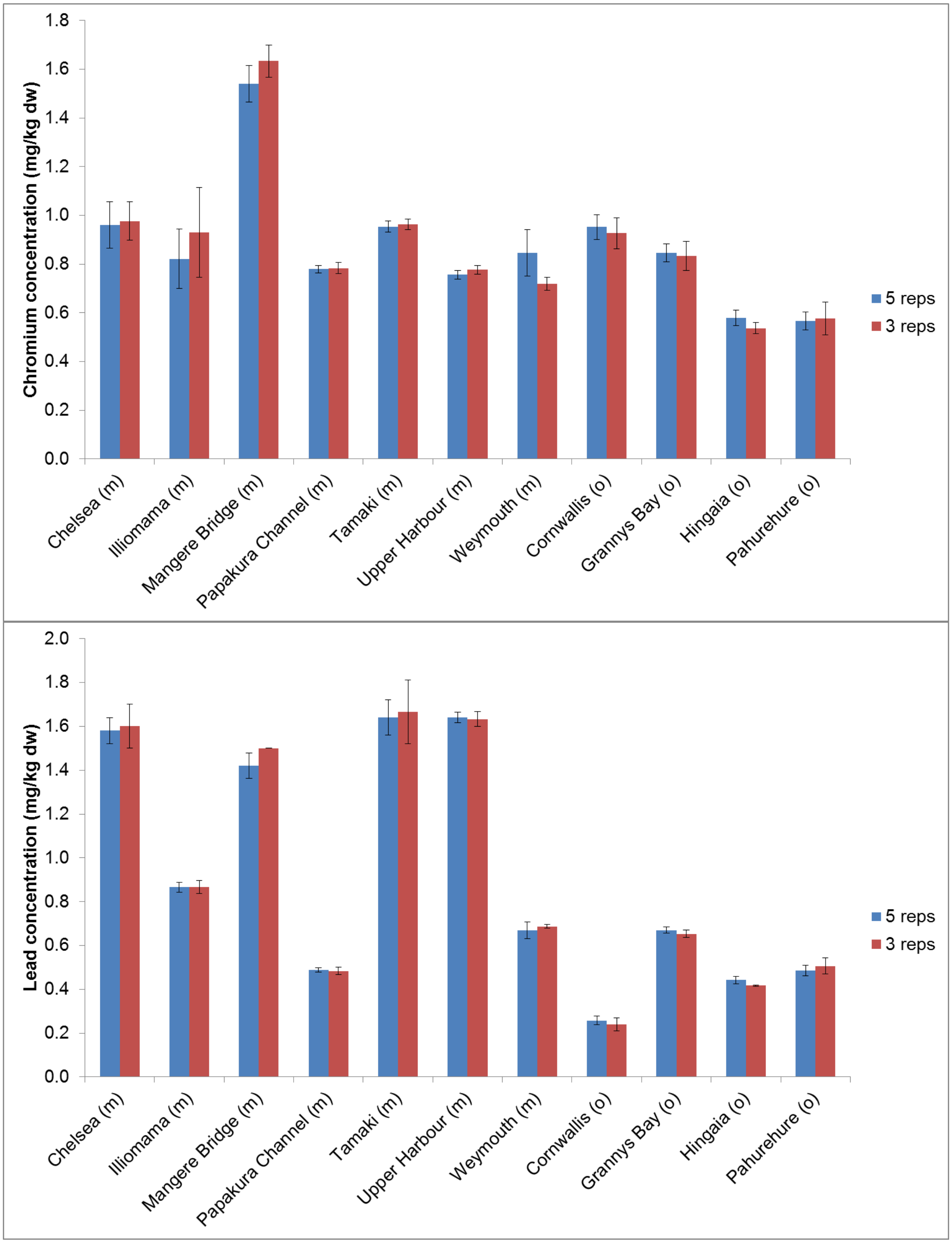
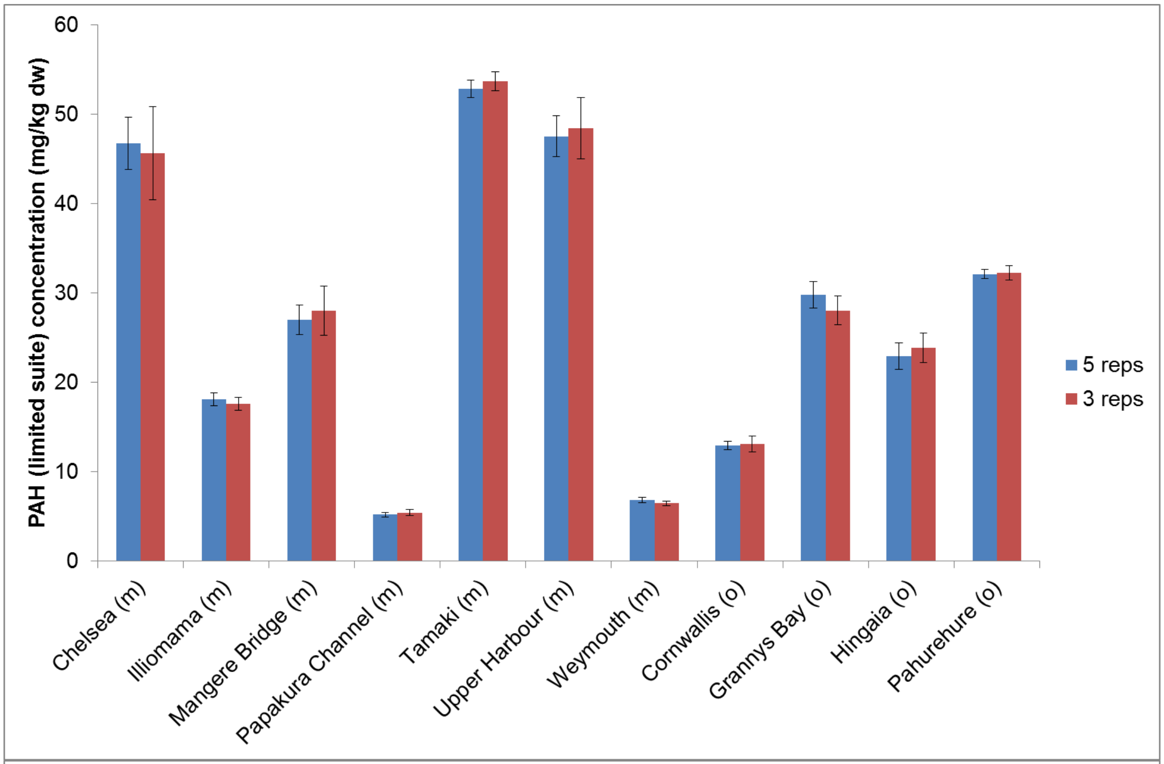
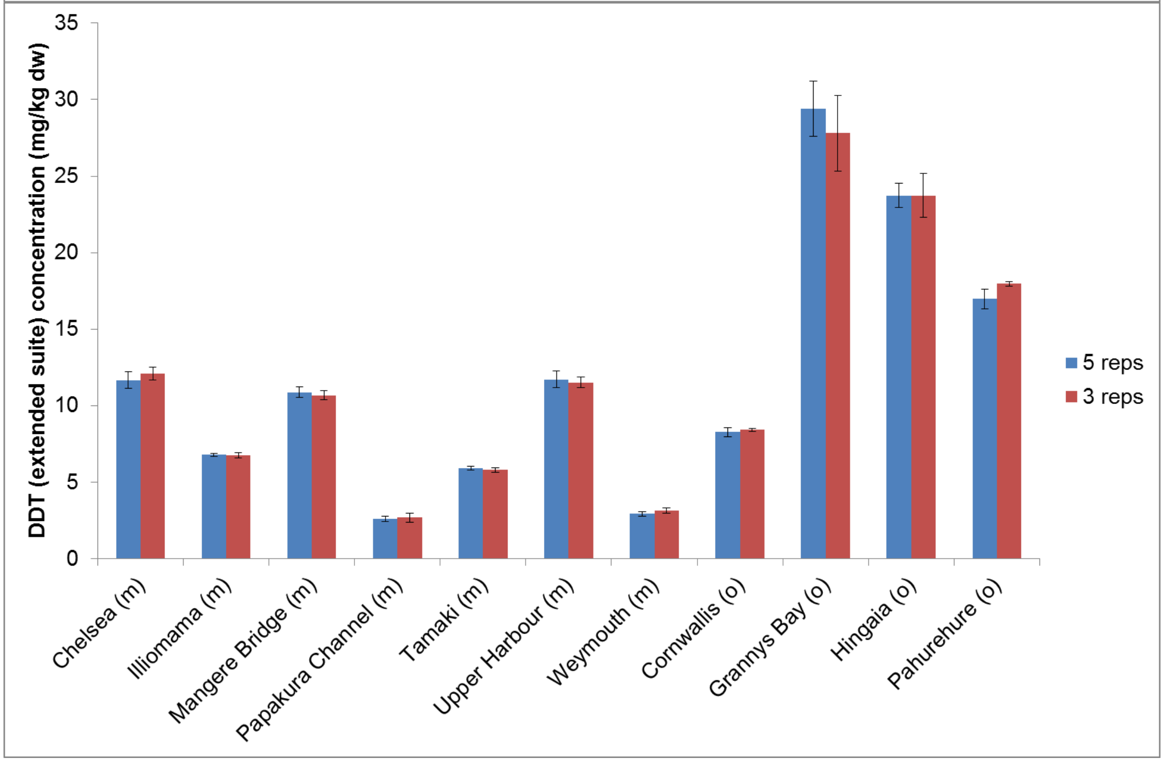


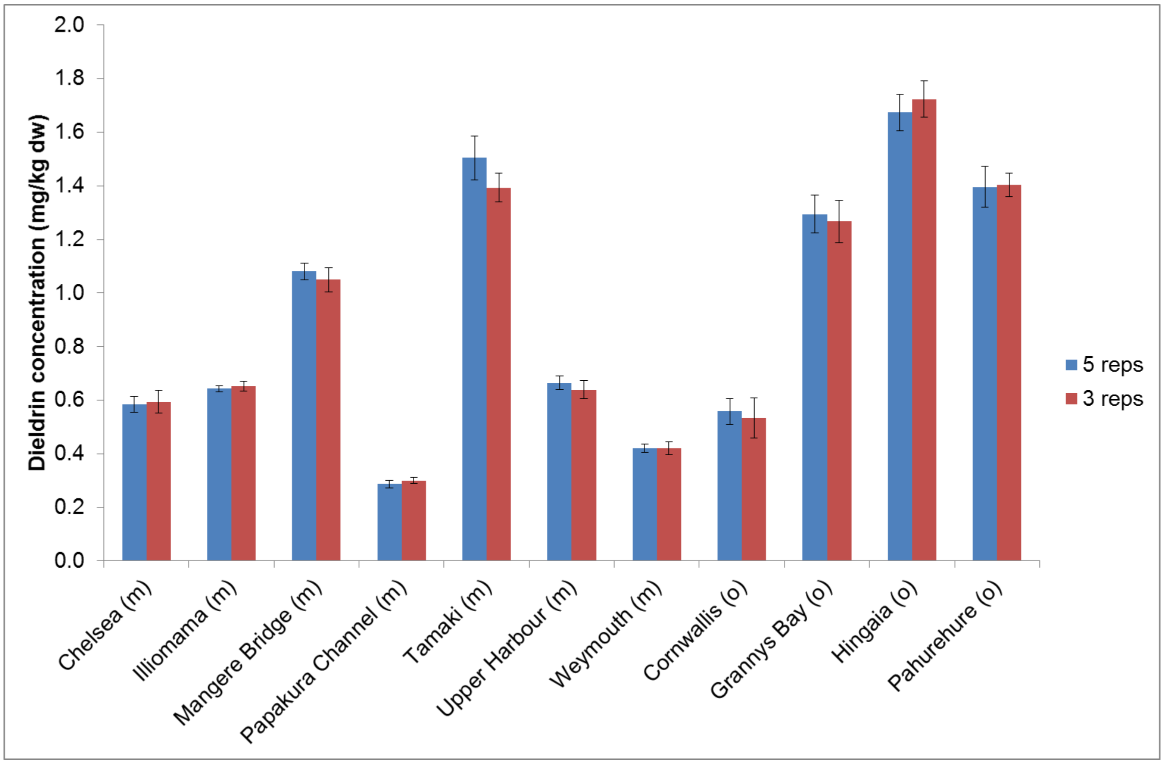
Figure 4-1 Comparison of mean concentration and variance for metals using five replicates and three replicates. 2010 data used; (m) denotes mussel sites and (o) denotes oyster sites; Error bars represent one standard error about the mean. Note log scale for copper and zinc.

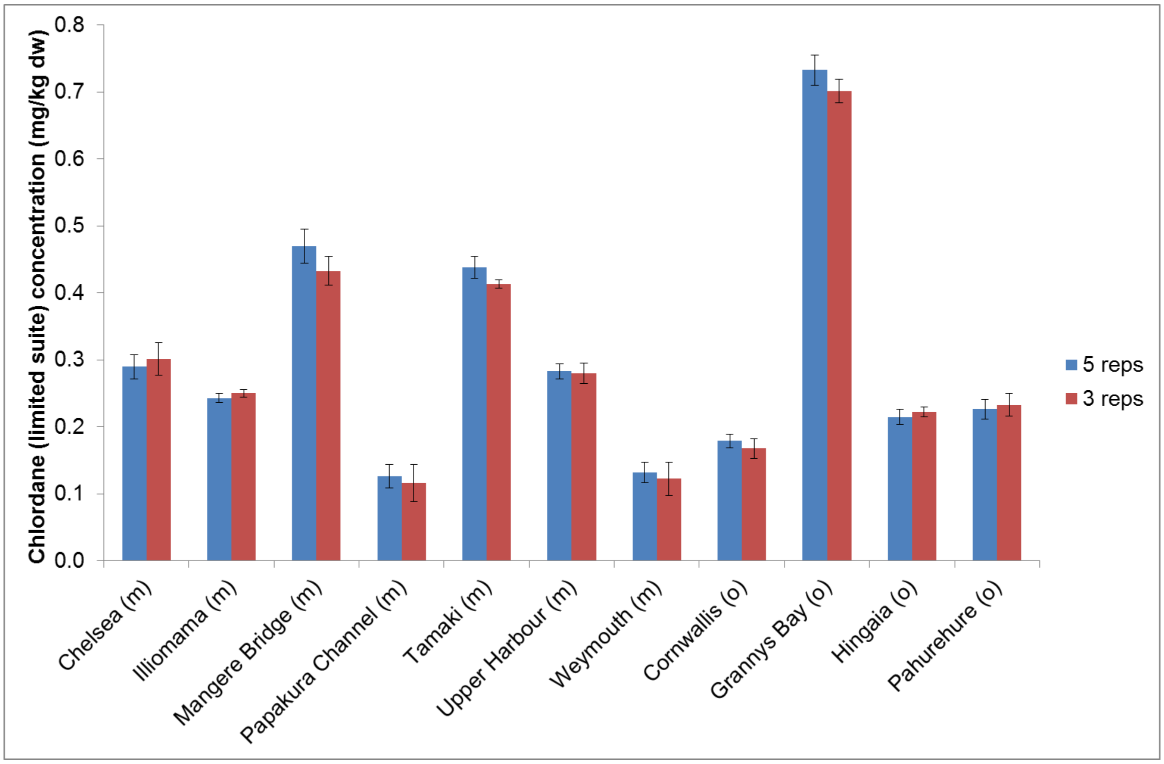


PAH (limited suite) concentration (mg/kg dw)
0
10
20
30
40
50
60
Chelsea (m)
Illiomama (m)
Mangere Bridge (m)
Papakura Channel (m)
Tamaki (m)
Upper Harbour (m)
Weymouth (m)
Cornwallis (o)
Grannys Bay (o)
Hingaia (o)
Pahurehure (o)
5 reps
3 reps



DDT (extended suite) concentration (mg/kg dw)
0
5
10
15
20
25
30
35
Chelsea (m)
Illiomama (m)
Mangere Bridge (m)
Papakura Channel (m)
Tamaki (m)
Upper Harbour (m)
Weymouth (m)
Cornwallis (o)
Grannys Bay (o)
Hingaia (o)
Pahurehure (o)
5 reps
3 reps


Dieldrin concentration (mg/kg dw)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Chelsea (m)
Illiomama (m)
Mangere Bridge (m)
Papakura Channel (m)
Tamaki (m)
Upper Harbour (m)
Weymouth (m)
Cornwallis (o)
Grannys Bay (o)
Hingaia (o)
Pahurehure (o)
5 reps
3 reps


Chlordane (limited suite) concentration (mg/kg dw)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Chelsea (m)
Illiomama (m)
Mangere Bridge (m)
Papakura Channel (m)
Tamaki (m)
Upper Harbour (m)
Weymouth (m)
Cornwallis (o)
Grannys Bay (o)
Hingaia (o)
Pahurehure (o)
5 reps
3 reps

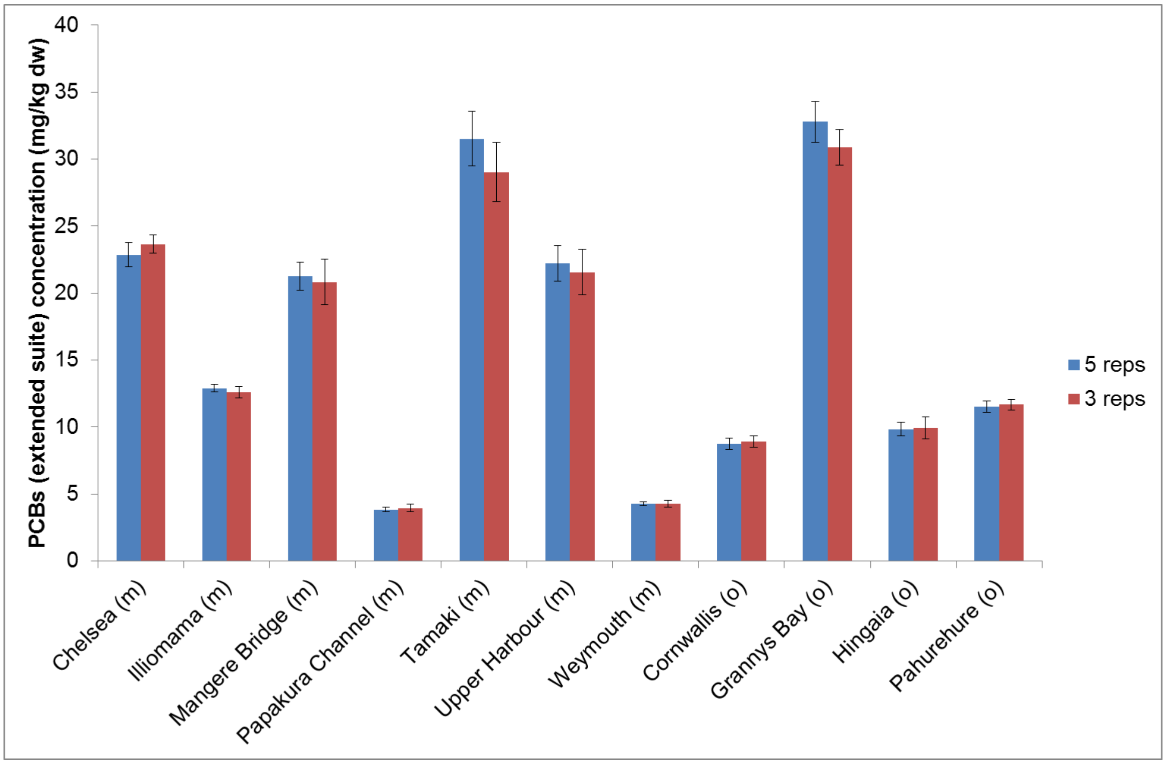


Figure 4-2 Comparison of mean concentration and variance for organics using five replicates and three replicates.

2010 data used; (m) denotes mussel sites and (o) denotes oyster sites; Error bars represent one standard error about the mean.

5.0 Implementation of recommendations from 2007 review

Auckland Council were interested in documenting in this report what components of the 2007 review and audit had been implemented, what were the benefits of these changes and what changes are still required or recommended.

Each recommendation from the 2007 review and audit (Mills, 2007) is included in italics, followed by a statement describing whether this has been implemented and if so what benefits (if any) have occurred as a result of this change.

5.1 Sites

Many recommendations were made in 2007 regarding site selection in the SCMP, most of which have not been implemented. These have been broken down by catchment. A more in-depth discussion on site selection is provided in section 6.2.1.

5.1.1 Manukau Harbour Oysters

Recommendation: It would be worth reviewing the reasons for including both Pahurehure and Hingaia sites, and considering whether a site further downstream (near the Weymouth mussel site or Kauri Point) might provide a better "integrated" measure of the effects of the Pahurehure Inlet catchment on the wider harbour. The Pahurehure Middle SoE sediment monitoring site may serve as a useful sediment comparison site here.

There has been no change in sites in the SCMP since 2007, with the exception of Mill Bay replacing Cornwallis (2008/2009 only) due to low oyster populations at the latter site. If oysters were to be removed from the SCMP, this provides an option to deploy mussels at a new site near Pahurehure Middle SoE sediment monitoring site to compare with Weymouth mussel data. However, with potential for significant future development of rural land to the south of the Manukau Harbour there is a case for maintaining these sites so potential spikes in contaminant concentrations can be assessed.

Recommendation: Cornwallis has lower contaminant levels than the other Manukau sites, and probably reflects the influences of a broad range of harbour influences, especially the northern shore catchments (including Mangere Inlet) via the Wairopa Channel. A better reference site, which would be more removed from the wider harbour influences, would be sites further up an undeveloped sub-estuary Big Muddy Creek seems a suitable candidate, and has an additional advantage of being an SoE sediment quality monitoring site.

A site at Mill Bay (in close proximity to Cornwallis) was assessed in 2008 and 2009 as an alternative to Cornwallis but suffered the same issues of falling oyster numbers as Cornwallis. Extensive surveys of the surrounding area have not as yet produced a suitable site to replace Cornwallis. As such Cornwallis has been retained as a reference oyster site in the Manukau Harbour (Cameron, 2012).

5.1.2 Manukau Harbour Mussels

Recommendation: ARC staff advise that the Weymouth site has been operationally problematic in the past, with interference with the mussel strings leading to incomplete recovery of deployed shellfish. This site is a useful location, providing an integrated measure of the effects of the south-eastern harbour catchments, and it is recommended that it remain in the programme. Installation of a permanent secure mooring or possibly moving to a nearby location that may not suffer from the same level of interference is recommended.

The Weymouth site is still part of the SCMP and it remains an important monitoring site, especially with issues surrounding oysters in Pahurehure inlet. AC has resolved the issues of incomplete recovery of deployed mussels by installing a wagon wheel mooring in 2007. No subsequent significant losses of mussels has occurred since this time (Cameron, 2012).

Recommendation: An area of the Manukau Harbour that seems lacking in coverage in both the oyster and mussel programmes is the southern shoreline (e.g., Waiuku River and Clarks Creek catchments). Historically there were monitoring site(s) in this area it would be worth reviewing the reasons for removing them from the programme to check they are still valid.

Oyster monitoring occurs at Glenbrook for New Zealand Steel. Monitoring includes benthic health; metals in sediment; and copper zinc and condition in oysters. Although not a complete dataset for comparison with the SCMP, it is a valuable resource and it is recommended that these data be acquired for comparison with other sites in the Manukau Harbour.

5.1.3 Waitemata Harbour Mussels

Recommendation: If contaminant concentrations at Upper Harbour Bridge and Chelsea are similar there is little point maintaining both sites. More spatially detailed information could be obtained by use of extra sites (e.g. inside the estuary arms rather than in the main body of the harbour). A review of previous biota contaminant monitoring data should be undertaken to help assess suitable sites.

Current contaminant concentrations and condition index between Upper Harbour Bridge and Chelsea are still very similar which is consistent with that observed in 2007. Implications and recommendations around dropping one of these sites are discussed in sections 6.2.1 and 7.2.

5.1.4 Tamaki Estuary

A comment was made that the one site in Tamaki Estuary was probably sufficient.

Recommendation: It would be useful to consider reinstating the “mixed species” resident shellfish monitoring programme conducted in the 1980s and early 1990s (last done in 1999). This approach would provide higher resolution (e.g., sub-catchment) information than monitoring from the main central channel. The use of natural populations of sediment-dwelling biota may also provide a more *direct measure of the availability of sediment contaminants (and hence also provide a link between the sediment and benthic ecology programmes).*

No “mixed species” resident shellfish monitoring has been implemented in the Tamaki estuary. Although this may provide further information it is not recommended at present as – given current budgetary constraints – the present focus is on consolidation rather than expansion.

5.1.5 Background locations

The suitability of two reference sites was questioned.

Recommendation: Replace Cornwallis oyster site with another site near Big Muddy Creek. Find a cleaner mussel reference site than Illiomama for the Hauraki Gulf.

Investigations have been made into replacing Cornwallis however no suitable sites have been found at this time (Cameron, 2012). Illiomama is a suitable clean mussel reference site and is discussed further in section 7.2.

5.1.6 Developing areas

Recommendation: An assessment of areas of future growth is required to identify sites that will monitor the future effects of developing catchments. A key area currently undergoing development is the Weiti River catchment. A site near Stillwater may therefore be worth investigating to track the effects of this.

As stated above, under the current budgetary constraints, addition of new sites can only be accommodated by removal of current sites. If recommendations in this report to consolidate sites are followed by AC then the option arises to include new sites to assess the environmental effects of developing areas. .

5.2 Species monitored

Recommendation: Review previous ARC monitoring surveys (e.g. Tamaki, Waitemata) that have used resident species such as amphibola, oysters, mussels, pipi, and cockles to monitor the spatial patterns and temporal trends in contaminants in locations not currently monitored.

These surveys are now dated with the last survey carried out in 1999. With a key aim now being to consolidate and simplify monitoring in the SCMP there is little use in re-visiting adding extra species at this time.

5.3 Shellfish processing

Recommendation: Shellfish shucking should no longer be undertaken at ARC.

This recommendation was enacted in 2007 and analytical laboratories have carried out the shucking of shellfish since this time (Cameron, 2012). The benefits of this change are to reduce the chance of contamination of the shellfish prior to analysis. This is good practise and should be continued.

5.4 Shellfish numbers

Recommendation: Increase the sample size provided to the laboratories, to enable repeat analyses and sample archiving.

After consultation with the analytical laboratories, from 2008 more shellfish are being provided per replicate for the metals and organics analyses so that enough material was available for the labs to carry out re-analysis, if required. Oysters per replicate increased from approximately 12 to 16 individuals for metals and approximately 20 to 30 individuals for organics. Mussels per replicate increased from approximately 10 to 15 individuals for metals and approximately 20 to 30 individuals for organics (Cameron, 2012).

5.5 Replicates analysed

Recommendation: The effect of reducing the number of replicates from five to three should be investigated.

The effect on mean and variance of reducing from five to three replicates was covered in section 4.5 of this report.

5.6 Relating trend data to changes in land use

Recommendation: For the SCMP (and the SoE and RDP sediment monitoring programmes), measures of catchment land use (and changes in land use over time) should be considered to assist the interpretation of the monitoring data (particularly temporal trends).

Auckland Council requested an “exploration of spatial variation in contaminant and condition levels and links to current land use and changes in land use activity over time” for the preceding status and trends report (Stewart et al., 2013).

5.7 Sample management

Recommendation: Production of a formalised sample archive

Since 2009, any remaining shellfish material has been stored indefinitely at the AsureQuality Wellington laboratory for archiving purposes. Left over freeze-dried material from 2007 and 2008 organics analyses by NIWA is also being stored indefinitely at an AC monitored storage facility. Surplus whole shellfish, sampled since 2008 are also being stored at the AC monitored storage facility.

The benefits of this change are that archived material is available for future analyses, if required. AC has stated that limitations on space will mean that some of this material will need to be relocated or disposed of in the next few years. We recommend relocation and advise AC not to dispose of any archived samples, at least until outcomes of this review are implemented.

In 2006, a Chain of Custody system was also initiated to track the location of samples from the various storage facilities to the laboratories in accordance with good lab practices (Cameron, 2012).

5.8 Analytical procedures and data management

Recommendation: Reducing the number of "outlying" results. This may not be a laboratory-sourced problem, but efforts to find the source(s) of these outliers must include examining potential contamination sources in the labs.

Shellfish processing for metals is now carried out by the analytical laboratories to reduce potential cross contamination, see section 5.3.

Recommendation: Increasing analytical sensitivity for As, Cd, Cr, and Pb, and for organochlorines (many of which are present near current detection limits at the cleaner sites).

Detection limits for most metals (including As, Cd, Cr, and Pb) have been improved since 2005, when Watercare took over analysis of metals in shellfish from AgResearch.

Detection limits for organics (especially PCBs) have been improved since changing organic laboratories from NIWA to AsureQuality in 2009. Analytical instrumentation used by AsureQuality allows significantly lower detection limits for PCBs than were achieved by NIWA, but no significant improvement has been observed for lindane, for which detection is still problematic

Recommendation: More complete reporting of quality assurance data, for both metals and organics. Information to be reported should include blank concentrations, within-batch replicate analyses, between-batch replicate analyses, certified reference material results, and spike/surrogate recovery data.

All QA data are now requested on an annual basis from the laboratory providers. A bulk reference QA sample collected by AC in 2007 has also been analysed on an annual basis for organics since 2007. Watercare analyse an in-house bulk shellfish reference sample and provide this information to AC as part of the annual QA data request (Watercare in-house QA data, dating back to 2006 has been made available for review).

This information along with shellfish standard reference material (SRM) data provides significant benefits for the robust assessment of QA for long-term trend detection.

Sampling information and results data can be exported from Hydstra (AC internal database) in excel format. Auckland Council's own QA sample data (derived from the analyses of bulk reference samples for organics analysis and between-batch and within-batch blind duplicates for both metals and organics analysis) have been imported to Hydstra since 2009. Laboratory in-house QA information has not been imported to Hydstra and is only available in separate spread-sheets or in the original laboratory data reports. It is recommended that a database of the QA/QC data from the laboratories be maintained and updated for future use in QA/QC reviews for long-term trend assessments.

5.9 Reporting

Recommendation: Reporting should also continue in line with the previous 2004 and 2007 reports. An assessment of trends, including evaluation of relationships with land use change, climatic factors, and other potential influencing variables, should be made every 5 years.

This recommendation has been implemented with a separate status and trends analysis (Stewart et al., 2013) and review of the SCMP (this report).

5.10 Summary

Other recommendations from the 2007 review that have been implemented include:

- Comparisons have been made between shellfish and sediment monitoring sites (this report).

Therefore several of the recommendations from the 2007 SCMP review and audit (Mills, 2007) have been implemented by Auckland Council. However, some recommendations from the 2007 review have not been implemented, some of these as a result of budget restrictions. These include dropping, combining, adding and relocating some sites and increasing the range of species monitored. If budget restrictions continue to prevent expansion of the programme there are several options for expanding what the programme can deliver within the existing budget as discussed in section 7.0.

6.0 Implications of changing the programme

6.1 Implications of dropping the whole programme

6.1.1 Understanding of environmental quality

Dropping the SCMP would limit the ability to accurately characterise contaminant concentrations and distributions throughout the region, unless a viable alternative was implemented. The SCMP contains over 20 years of data that has evolved throughout time as methods have evolved and information has been incorporated from reviews and audits. The SCMP overlaps to varying degrees with the other three SoE monitoring programmes in the region (see section 3.0) and complements them. In combination, they provide a holistic data set which can be used to assess the state of the environment in the region. Information from the other three programmes cannot *currently* be used instead of the SCMP, however there is potential to replace the SCMP by a combination of sediment and benthic monitoring once correlations have been established (see sections 3.1 and 3.2).

6.1.2 Ability to identify emerging issues

The SCMP (as it is currently run) can identify spatial and temporal trends in contaminants across the region, so to that effect it can identify (in association with other SoE monitoring programmes) those sites which are becoming more or less contaminated over time. By monitoring multiple contaminants (based upon a selection recommended for investigation), it may be possible to identify which are contributing to the decline in environmental condition and could be used to track possible sources of that contamination.

This is especially true for heavy metals, where increases may be associated with changes in land-use, or PAHs which can be linked to urban run-off or specific events such as oil spillages.

However, the SCMP (as it is currently run) does not account for the impact of emerging contaminants (also called emerging chemicals of concern *or* ECCs) or identify emerging contaminant issues. The organic contaminant groups currently assessed represent the legacy contaminants, or Persistent Organic Pollutants (POPs), all of which - with the exception of PAHs - are in decline or stabilised at very low levels. A modified analyte list (which may include a number of ECCs) would need to be assessed in order for AC to be able to identify whether ECCs are impacting on the environment. This is covered in more detail in section 7.4.4.

6.1.3 Resource management decision making

Dropping the SCMP would have minimal effects in relation to AC’s resource management functions. Most of the sites are influenced by large catchments, which contain multiple land use classes. This makes it difficult to relate a small change in land-use, or a resource management decision within a catchment, to changes in shellfish contaminant load or condition. This task is much simpler for sediments, which can be used for monitoring at more specific locations higher up in the catchments and within tidal creeks. A larger number of sediment sites also provide higher resolution of contaminants within a catchment than the limited sites within the SCMP. However, the SCMP does have the ability to pick up large scale changes in land use (such as the WWTP upgrade and development of ex horticultural soils in the Hingaia catchment) as well as removal of contaminant sources (such as the deregistering of many POPs in the 1980s and 1990s)

6.1.4 Alternatives to SCMP for assessing bioavailability of contaminants in the water column

An alternative to using shellfish to ascertain the bioavailable portion of contaminants in the environment is being sought internationally, due to the cost and inherent difficulties involved in running a shellfish monitoring programme.

Passive sampling is an approach that is gaining momentum worldwide in the determination of concentrations of dissolved contaminants. Passive sampling devices (PSDs) have been around for decades although much recent research has been undertaken to assess their suitability in regulatory monitoring. Recent reviews (Lohmann et al., 2012, Greenwood et al., 2009, Kot-Wasik et al., 2007, Seethapathy et al., 2008, Vrana et al., 2005) describe the advantages of using PSDs in environmental monitoring. Key points from these reviews are described below and discussed in further detail.

6.1.4.1 Organics

Almost all persistent organic pollutants (POPs) targeted by the Stockholm Convention are nonpolar or only weakly polar, hydrophobic substances, making them ideal targets for sampling in water using PSDs;

- This includes virtually all the organic contaminants measured in the SCMP and others that are not, e.g., the flame retardants hexabromobiphenyl, and tetra- to hepta-brominated congeners of polybrominated diphenyl ethers (PBDEs);
- In contrast to the established use of nonpolar PSDs, polar passive samplers (e.g., Polar Organic Chemical Integrative Samplers; POCIS) used for monitoring more water soluble contaminants (e.g., pharmaceuticals and pesticides) are insufficiently understood for regulatory purposes at present.

Widely used nonpolar PSDs include semi-permeable membrane devices (SPMDs), low-density polyethylene (LDPE) and silicone rubber;

- Solid-phase microextraction (SPME) techniques have been trialled on sediment pore-water, including poly-(dimethylsiloxane) (PDMS) coated fibres (Maruya et al., 2009, Mayer et al., 2000) and Low-Density Polyethylene Strips (Fernandez et al., 2009);
- Sampling rates and variability have been determined by inter-laboratory research;

- Performance reference compounds still provide the most accurate means of determining sampling rates. These are analogous to surrogate chemicals in contaminant analysis and assess the effectiveness of PSDs in sampling contaminants.

Variability can be controlled much better for PSDs over alternative matrices applicable in trend monitoring (e.g., sediments or biota) leading to a *potential* reduction of the number of analysed samples required to obtain results with comparable statistical power;

- PSDs are significantly cheaper than shellfish to deploy and do not require specialised training;
- PSDs do not suffer from environmental variability that shellfish do, such as species, seasonal and condition variability, and mortality. They do not suffer the same issues as deployed shellfish having a potential existing body burden of contaminants;
- Booij et al. (2006) argue that SPMDs will generally yield more reliable estimates of exposure concentrations than mussels, because in situ bioaccumulation values are difficult to estimate, whereas the in situ exchange kinetics of SPMDs can be quantified by measuring the dissipation rates of performance reference compounds.

Assessments have been made of the relationship between PSDs and sediment dwelling organisms. A Dutch study revealed a strong correlation between concentrations of PCBs and PAHs in mussels and PSD-derived aqueous concentrations (Smedes, 2007). Similarly, a laboratory study in which polychaetes and LDPE were exposed to contaminated sediments also showed a strong relationship between both sets of results (Friedman et al., 2009). Therefore, in theory at least for organics, PSDs have the *potential* to replace biomonitoring.

6.1.4.2 Metals

Like organic contaminants, PSDs are being developed for metal contaminants, however understanding is not as advanced for metal PSDs as it is for organic PSDs. Perhaps the most widely studied technique for metals is diffusive gradients in thin films (DGT). In a DGT device, metals diffuse across an outer hydrogel layer and are trapped in a gel impregnated with an ion exchange resin. Like shellfish, DGT devices pre-concentrate dissolved trace metals to provide a time-integrated measure of their concentration in water. Only ionic and easily dissociable metal complexes are taken up by DGT, which are more likely to represent a bioavailable fraction rather than the total metal.

Two reports comparing DGT devices and mussels (Webb and Keough, 2002, Schintu et al., 2008) claimed that DGT devices were more sensitive than mussels in determining differences between sites.

From a regulatory perspective, there is a push towards more cost effective monitoring techniques that don’t suffer from the same variability as biota or water sampling. DGT devices are being investigated as alternatives to water sampling in the EU (Montero et al., 2012), with the conclusion that DGT devices are likely to be a suitable monitoring tool for water chemical evaluation within the Water Framework Directive.

6.1.4.3 Discussion

Shellfish bio-monitoring has some advantages over PSDs, such as obtaining contaminant levels directly in species consumed by humans, and providing information on bioaccumulation and bioavailability of POPs and metals under field conditions.

For passive sampling devices to be considered instead of shellfish for monitoring, a full review would be necessary to investigate the following:

- Which passive sampling techniques are most applicable to estuarine water samples? This would include assessing which sampler configurations have reliable known uptake values for contaminants, what are the levels of resistance to biofouling and what deployment time period is required for units to reach equilibrium. In the first instance this can be a desktop review, but significant progress on design and application would be gained from input from world experts;
- A cost-benefit analysis, which should include (but is not limited to);
  - A financial breakdown, comparing costs of the SCMP with PSDs, in order to measure whether significant cost savings can be made;
  - Practicalities of installation and comparisons with the SCMP on costs required per site to maintain current monitoring purposes;
  - Determining the flexibility of such an approach to enable monitoring to be undertaken more frequently and in different time periods, as required;
  - An assessment of whether less replicates per site can also be analysed;
- The reliability of the information obtained from deployed PSDs. This would include a measurement of the variability and how it compares with existing data, possible effects of seasonal variation and an assessment of whether it is still possible to continue trend analyses from the existing data set.

As stated previously, if a move towards PSDs was to occur in the future, both the SCMP and implementation of PSDs would need to occur simultaneously before removing shellfish in order to measure the level of correlation between data sets and assess whether the samplers are providing comparable information to shellfish. This could be a pilot study on a few selected sites of different (low, medium and high) concentration levels. As PSDs are likely to replace shellfish monitoring in the medium term, we recommend that AC stay up-to-date with international developments and implement a review of PSDs that is relevant to local conditions within 3-5 years.

6.2 Implications of dropping or changing parts of the programme

On-going trend assessment for the SCMP would be affected by dropping components (such as decreasing the number of sites or removing specific analyte suites) or by significant changes to the programme (such as completely removing a species of shellfish). However, a review of the trend data suggests that not all changes would have a significant impact. For example, reducing the frequency of analysis of PCBs and organochlorine pesticides is not expected to significantly affect trends analysis as these groups of compounds have continued to reduce over time, or stabilised at very low levels.

6.2.1 Sites

At present there are sufficient sites around the two harbours, the Tamaki estuary and inner Hauraki Gulf to provide adequate spatial coverage of contamination in the region, although gaps do exist in some areas. Reducing the number of sites would reduce the coverage and hence increase the uncertainty surrounding predictions about possible contaminant sources and impacts on water quality. However, there is the opportunity to consolidate some sites and provide the potential to improve coverage through the addition of extra sites. Site changes were recommended in the 2007 review (Mills, 2007) and included:

- Consolidation of Pahurehure Inlet and Hingaia Bridge oyster sites;
- Consolidation of Upper Harbour Bridge and Chelsea mussel sites;
- An alternative control mussel reference site in place of Illiomama in the Hauraki Gulf;
- Replacement of the oyster reference site (Cornwallis) with another site near Big Muddy Creek;
- Addition of a site in the southern Manukau Harbour.

In order to assess the implications of dropping or changing sites it is necessary to compare contaminant concentrations and condition index for shellfish at each site. Present status (2009-2011) condition scores across sites are shown in Figure 6-1, while contaminant concentrations are provided in Table 6-1 (metals; dry weight data) and Table 6-2 (organics; lipid normalised data).

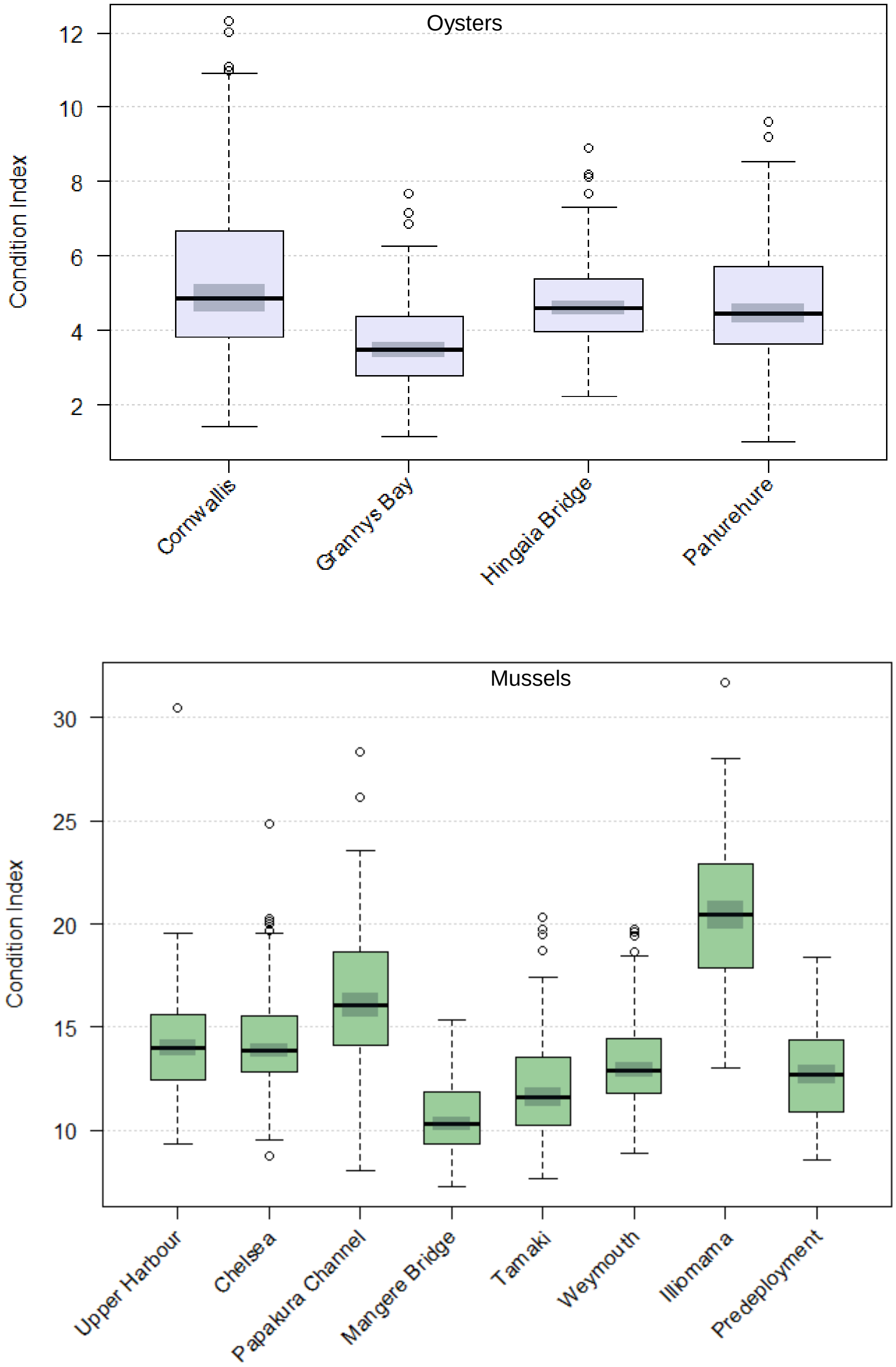


Figure 6-1 Condition index for oysters and mussels at each site in the Shellfish Contaminant Monitoring Programme.

Shaded boxes overlaid on box plots indicate the confidence interval about the median. Whiskers represent 1.5 x interquartile range with circles representing data outliers outside this range.

Table 6-1 Summary of median metal concentrations at selected oyster and mussel sites in the Shellfish Contaminant Monitoring Programme from 2009 to 2011 (mg/kg dry weight).

Site	Arsenic	Cadmium	Chromium	Copper	Lead	Zinc
Oysters						
Cornwallis	13	0.95	0.82	110	0.24	1500
Grannys Bay	9.7	1.2	0.91	870	0.68	4000
Hingaia Bridge	9.2	1.6	0.66	420	0.42	2300
Pahurehure Inlet	8.6	1.4	0.58	310	0.46	2400
Mussels						
Chelsea	8.8	0.50	1.0	7.6	1.6	81
Upper Harbour Bridge	7.8	0.54	0.89	7.6	1.6	82
Mangere Bridge	6.8	0.62	1.5	5.9	1.2	71
Tamaki	7.7	0.37	1.1	12	1.7	93
Weymouth	8.3	0.56	0.95	4.3	0.67	68
Illiomama	8.6	0.35	0.64	5.0	0.88	60
Papakura Channel	8.7	0.41	0.82	4.5	0.44	66
Pre-deployment	6.9	0.85	0.17	3.6	0.51	72

Table 6-2 Summary of median concentrations of organic contaminants in oysters and mussels in the Shellfish Contaminant Monitoring Programme, from 2009 to 2011 (lipid normalised, mg/kg).

Site	DDTs	Dieldrin	Chlordanes	Lindane	Endosulfans	PCBs	PAHs
Oysters							
Cornwallis	101	6.3	5.5	0.2	0.019	90	154
Grannys Bay	550	27.2	33.5	0.8	0.023	570	976
Hingaia Bridge	344	24.8	7.9	0.2	0.138	133	542
Pahurehure Inlet	253	24.0	8.8	0.2	0.091	161	769
Mussels							
Chelsea	138	8.3	10.7	0	0.013	291	1137
Upper Harbour Bridge	167	10.9	12.3	0	0.032	359	1498
Mangere Bridge	211	22.1	23.9	1.8	0.026	400	931
Tamaki	103	32.5	23.6	0	0.038	505	1777
Weymouth	54	9.2	1.7	0.4	0.028	87	304
Illiomama	73	6.3	6.5	0	0.000	136	354
Papakura Channel	40	5.1	1.9	0.6	0.0	64	171
Pre-deployment	1	0.3	0	0.6	0.018	1	9

Data for DDTs, chlordanes, PCBs and PAHs are based upon the extended AC suites.

Consolidating Pahurehure Inlet and Hingaia Bridge oyster sites and Upper Harbour Bridge and Chelsea mussel sites would reduce the number of sites monitored in the SCMP by two. Pahurehure Inlet and Hingaia Bridge oysters have essentially the same condition index (Figure 6-1) and metal concentrations (Table 6-1), however, the concentrations of some organic contaminants are different; namely DDTs, PCBs and PAHs (Table 6-2, Figure 6-2). Statistical tests (Wilcoxon rank sum test) of the contaminant concentrations at these two sites, based on the 2009-2011 data, show significant differences ($p<0.05$) for arsenic, cadmium, copper and lead, but not chromium and zinc. For the organic contaminants, there were significant differences between the two sites for DDTs, PCBs and PAHs but not dieldrin, chlordanes, lindane or endosulfans. While the testing shows these *statistically* significant differences, the *magnitude* of these differences is small compared to the other two oyster sites, with organic contaminant and most metal concentrations at Cornwallis consistently lower, and concentrations at Grannys Bay consistently higher.

For the mussels, there are only minor differences in the condition indexes (Figure 6-1) and metal concentrations (Table 6-1) for Upper Harbour Bridge and Chelsea sites, but varying organics concentrations, which are generally slightly higher at Upper Harbour Bridge (Table 6-2, Figure 6-2). Again, statistical tests (Wilcoxon rank sum test), based on the 2009-2011 data, show some significant differences ($p<0.05$) in the contaminant concentrations for arsenic, chromium, DDT, PCBs, chlordanes, dieldrin and endosulfans at these two sites but not for the other four metals, PAHs or lindane. For the organic contaminants, the concentrations at these two sites are intermediate with Mangere Bridge and Tamaki having higher concentrations while Weymouth and the reference sites at Papakura and Illiomama have lower concentrations.

Consolidating these sites would result in a loss of fine detail in organic contaminant concentrations in the respective catchments. However, this is a minor loss of information relative to the benefits that could be achieved. Future monitoring could benefit from consolidation and is discussed further in section 7.2.

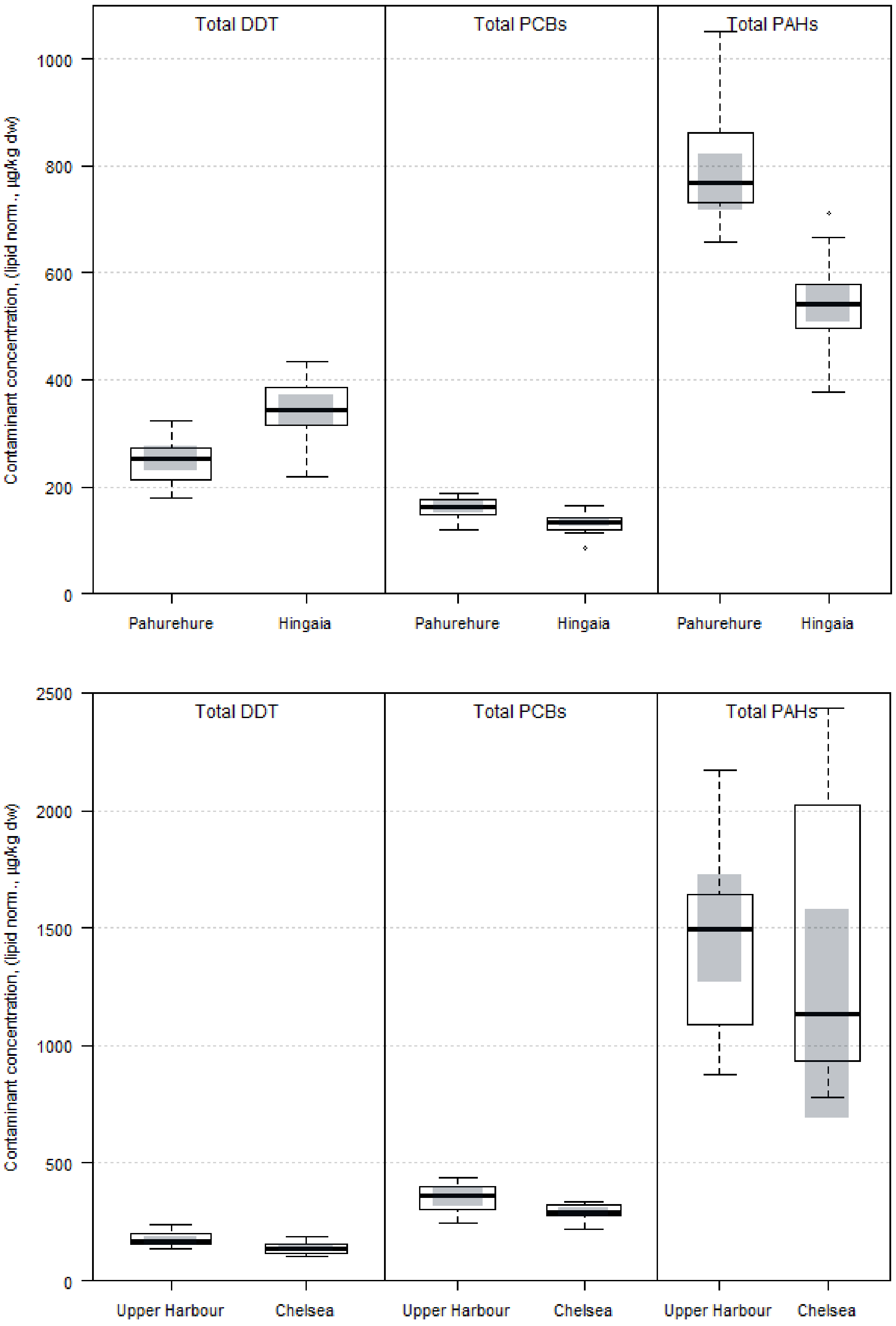


Figure 6-2 Comparison of concentrations (2009-2011) of selected organic contaminants for Pahurehure vs Hingaia Bridge and Chelsea vs Upper Harbour

Shaded boxes overlaid on box plots indicate the confidence interval about the median. Whiskers represent 1.5 x interquartile range with circles representing data outliers outside this range.

6.2.2 Mussels versus Oysters

The major benefit from using a single species for monitoring is that between-site comparisons of condition and contaminant concentrations are more robust, due to equivalent morphology and contaminant uptakes. However, this consistent approach has disadvantages. The use of different species, with different populations (deployed versus wild) and different habitats (sub-tidal versus intertidal) may provide a better overall measure of contaminant exposure. With different contaminant uptake mechanisms and different morphology it is difficult to compare between oyster and mussel sites. Mussel watch programmes like the US NS&T (Kimbrough et al., 2008) and the French RNO (RNO, 2006) use oysters and mussels because it is not possible to use a single species to cover the wide geographical area under investigation.

It is not feasible to remove mussels from the SCMP as monitoring would then be reliant on wild populations of oysters, which are only present in viable numbers in the Manukau Harbour. Furthermore, the wild populations of oysters have declined over the years and if this trend continues, stocks may not be plentiful enough for future monitoring.

Removing oysters from the SCMP is a possibility, especially if mussels could be deployed at, or near, these sites. Of the four oyster sites currently monitored, Grannys Bay already has a mussel site (Mangere Bridge) in close proximity. Pahurehure Inlet and Hingaia Bridge have a mussel site at the entrance to the Manukau Harbour (Weymouth) that would cover the same catchment, but it would be preferable to situate a second mussel site further up the inlet, near the current oyster sites. As stated in section 6.2.1, there is some value in consolidating Pahurehure Inlet and Hingaia Bridge oyster sites. Alternatively, a suitable mussel site could be situated in this area in place of the current oyster sites. However, there are potential practicality issues with water depth that need to be addressed if considering deployment of mussels in these tidal creeks. Cornwallis is the oyster reference site at the mouth of Manukau Harbour; however a reference mussel site already exists in the central Manukau Harbour (Papakura Channel). Organic contaminant concentrations at Cornwallis and Papakura Channel are similar and both have lowest site rankings (metals are difficult to compare between the two species due to differential uptake) (Stewart et al., 2013), suggesting Papakura Channel could be used as the single reference site for the Manukau Harbour. This would allow further consolidation of sites due to the removal of one of the two reference sites in the Manukau Harbour.

Removing oysters from the SCMP would limit comparisons that can be made to other shellfish monitoring programmes and to food safety standards for oysters. As stated above, international mussel watch programmes such as US NS&T (Kimbrough et al., 2008) and the French RNO (RNO, 2006) use both mussels and oysters in their monitoring programmes. Differences in contaminant uptake are evident by comparisons of Auckland data with that of US NS&T mussel watch (Table 6-3). The NS&T mussel watch programme sets low, medium and high categories for contamination, which are species specific. Note: the NS&T categories are ranges and the values quoted in Table 6-3 are the maximum value for each category. All Auckland mussel contaminant data fits within the NS&T low category. Most oyster contaminant data are in the NS&T low category range, with the exception of the heavy metals As, Cu, Pb and Zn. Arsenic in oysters falls within the NS&T medium category range at Cornwallis and Mill Bay. Oyster copper concentrations are within the NS&T high category range at Grannys Bay and in the medium category range at Hingaia, Pahurehure and for all oysters (median data) in the Manukau Harbour. Lead and zinc concentrations in oysters are within the NS&T medium category range at Grannys Bay.

Therefore, replacing oysters with mussels in the SCMP would potentially give a biased assessment of bioavailable contaminant concentrations in the region. Replacing oysters with mussels would also discontinue the trend data for oysters in existence since 1987. Removing oysters from the programme would also reduce temporal coverage of contaminant bioavailability as oysters are collected from in situ populations while mussels are only deployed for three months per year. If this termination of trend data for oysters could be mitigated by assessment of correlations of contaminants at current oyster sites to new mussel replacement sites (for metals especially), then the case for discontinuing oysters is strengthened.

Table 6-3 Comparison of selected shellfish contaminants with data from US National Status and Trends Mussel Watch Program.

Mussels	As	Cd	Cu	Pb	Zn	DDT	Chlordanes	Dieldrin	PAHs	PCBs
Chelsea	9	0.5	8	1.6	81	8	0.4	0.5	65	18
Illiomama	9	0.4	5	0.9	60	6	0.4	0.5	25	11
Mangere Bridge	7	0.6	6	1.2	71	11	0.7	1.3	38	20
Papakura Channel	9	0.4	5	0.4	66	2	0.2	0.3	9	3
Tamaki	8	0.4	12	1.7	93	5	0.8	1.6	73	23
Upper Harbour	8	0.5	8	1.6	82	10	0.5	0.7	68	19
Weymouth	8	0.6	4	0.7	68	2	0.1	0.5	11	4
Pre-Deployment	7	0.9	4	0.5	72	1	0.1	0.4	7	1
Mussels (Median)	8	0.5	6	1.2	71	6	0.4	0.6	37	14
NS&T low	11	3	16	3	139	112	8	8	1187	153
NS&T medium	22	9	39	6	320	286	20	34	4434	478
NS&T high	41	20	857	13	11500	520	49	95	7561	1413
Oysters	As	Cd	Cu	Pb	Zn	DDT	Chlordanes	Dieldrin	PAHs	PCBs
Cornwallis	13	1	110	0.2	1500	10	0.4	0.7	17	8
Mill Bay	12	0.6	83	0.2	890	14	0.4	0.8	17	8
Grannys Bay	10	1.2	870	0.7	4000	32	0.9	1.5	42	25
Hingaia	9	1.6	420	0.4	2300	27	0.4	1.9	34	7
Pahurehure	9	1.4	310	0.5	2400	18	0.5	1.9	51	10
Oysters (Median)	10	1.2	310	0.4	2300	21	0.4	1.6	38	9
NS&T low	11	3	211	0.5	3260	34	7	5	828	38
NS&T medium	22	6	636	0.9	9165	105	21	30	2511	87
NS&T high	57	15	1660	2.2	18950	202	55	65	10717	157

Site values are median data from 2009-2011; Mill Bay 2009 data only; metals data are mg/kg dry weight; organics data are µg/kg dry weight; chromium and lindane were not covered by NS&T Mussel Watch report.

6.2.3 Analytical suites

The analytical suites of chemicals measured over the lifetime of the SCMP have not been static and have been modified on the basis of current knowledge and analytical capability. There were 22 inorganic parameters measured prior to 2005, but this has now been reduced to the six key metals; arsenic, cadmium, chromium, copper, lead and zinc. Minor OCPs (those other than DDTs, chlordanes, dieldrin and lindane) were not reported prior to 2009. These are aldrin, 3 isomers of hexachlorocyclohexane (HCH) (excluding lindane), endrin (and breakdown products endrin aldehyde and endrin ketone), pentachlorobenzene, and three endosulfans.

As outlined in section 6.2.2, the current status data indicates that some metal concentrations lie within the medium to high range of the US NS&T mussel watch programme (Table 6-3). Furthermore, temporal trend analyses indicate that - high variability notwithstanding - some metals have not reduced in concentration over the life-time of the SCMP and are either static or increasing. Continued monitoring of these metals in the SCMP is recommended in order to measure on-going changes to bioavailable contaminants in the water column in the region. In addition, future monitoring should also include mercury (see section 7.4.1).

Changing aspects of the organic contaminant analyses may be realised with minimal impact on long-term trend assessments, if managed carefully. Temporal trend analyses show that most organic contaminants have been reducing over the life-time of the SCMP. PAHs are the one exception, where concentrations are considerably more variable. Variability of PAHs notwithstanding, all organic contaminant concentration data falls within the low category range of the US NS&T programme (Kimbrough et al., 2008) and at most sites and for most organic suites (Table 6-3) are markedly lower than the maximum value of the low category range, suggesting environmental risk of these contaminants may be considered to be low.

It is recognised that the analytical costs of contaminant analyses are high, especially for organic contaminants. As such, one component of the SCMP that could be reduced to realise cost savings is the modification of aspects of the organic contaminants suites. There are two logical options:

- Reduction or removal of the organic suites;
- Reduction of frequency of analysis.

Complete removal of organic contaminants from the SCMP immediately impacts on the ability to monitor current status and respond to potential changes which may arise as a result of some unrecorded spillage events or mobilisation of sediment (due to land-use changes). However, removal of some organic suites may not have a significant impact on the ability to accurately assess the state of the environment in the region. This is especially true for DDTs, PCBs, chlordanes and dieldrin.

We do not recommend complete removal or reduction of the organic contaminants suite. However, this could be re-assessed in the future if concentrations remain at their current low levels.

A more prudent approach would be to reduce the frequency of analysis of suites of organic contaminants. With the exception of PAHs, all other organic contaminants currently measured have been consistently reducing over time (other OCPs cannot be assessed as they have only been analysed since 2009: see Appendix B and Appendix C) and there are no expected new inputs (except by mobilisation of sediment due to land-use changes) that would increase the risk of these contaminants increasing in the environment in the future.

We recommend reducing the frequency of analysis of all organic contaminant suites (except PAHs) to every four years. This would equate to analysis every second sampling if the recommendation to reduce sampling frequency in the SCMP to biennial is adopted by AC (see section 7.1).

As discussed in section 4.4, this would reduce the ability to perform temporal trend analyses and would be a trade-off for either reducing cost or adding other components to the SCMP (and remaining cost neutral).

6.2.4 Condition

Condition data (shell length and width; shell and tissue wet and dry weights; condition index) have been measured in the SCMP since 2006 (see Table Appendix 3 for mussels and Table Appendix 8 for oysters). An assessment of the condition data was made in the preceding Status and Trends report (Stewart et al., 2013) and is summarised as follows:

- The condition index for oysters was similar across sites, although it was highest (and most variable) at Cornwallis. The lowest median was at Grannys Bay. For mussels, the condition index was substantially higher at Illiomama compared to the other sites and was lowest at Mangere Bridge. Condition index for the pre-deployment mussels was lower than for four of the monitoring sites (Illiomama, Upper Harbour, Chelsea and Papakura Channel), higher than Mangere Bridge and similar for Weymouth and Tamaki Estuary;
- For site rankings, the condition score appears to follow an inverse relationship with average contaminant score;
- There were no significant trends in either the mussel or oyster condition data over the 2006-2011 time period;
- There is no significant correlation between the trends in contaminant concentrations and the trends in condition.

There appears to be an inverse relationship between higher shellfish contaminant concentrations and lower shellfish condition index. There are no significant trend relationships, probably due to the short time frame (2006-2011). So, discontinuing condition analysis would prevent longer term trends being established and potentially create a knowledge gap in the SCMP, this is discussed further in section 7.5.

6.2.5 Reliable trend detection

Historically, the quality of metals data has been questionable. There are no metals QA data prior to 2005 and variability of concentrations is more pronounced. The lack of QA data for metals prior to 2005 makes assessment of reliability very difficult for data prior to this time, potentially affecting long-term trend detection. More recent metal QA data show that the latest data sets (2006-2011) have acceptable coefficient of variation (%CV) of generally less than 10% (for freeze dried material). The exception to this is chromium, which still has high variability of around 20% (Stewart et al., 2013). Of course, outliers do still exist and these should be removed from trend analyses.

The approach of performing pre-deployment subtraction of contaminant concentrations in mussels prior to trend analyses was requested by Auckland Council. However, the data generated by this approach suggested the technique was not effective or conducive for the evaluation of temporal trends, especially for metals (Stewart et al., 2013). Over the period of time (3 months) in which the mussels are deployed the mussel contaminant levels will reach an equilibrium, which reflects the concentrations found in the water and suspended material being exchanged. The levels of contaminants in the mussel tissue will almost certainly change (depending upon the nature of the contaminant) and may be higher or lower than pre-deployment contaminant levels. This issue was apparent for some metals data, where pre-deployment subtraction afforded negative concentrations for some metals at some sites. This result was less apparent for organics data where contaminants tend to accumulate in shellfish over time rather than reaching equilibrium.

Lower detection limits realised for some organic contaminants since 2009 have proven to be useful and enable better trend detection for the future. In addition, our review of QA data [see Status and Trends report (Stewart et al., 2013) for full explanation or section 2.0 of this report for a summary] has shown that there was no obvious change to data from switching to an alternative analytical supplier. Similarly for metals, detection limits are adequate for reliable trend detection. A review of AC metals data (2011) for both oysters and mussels have shown that minimum concentrations reported are typically more than ten times greater than the minimum detection limits (MDLs) for most metals except copper. The MDL for copper is 2 mg/kg and this is relatively close to levels observed in mussels from most sites except Tamaki (12 mg/kg). Mussels typically have markedly lower levels of copper in their tissue than oysters. As such, improvement of the MDL for copper in mussels may be a useful approach for future trend analysis, especially as copper is trending downwards (although not significantly: see section 6.3.1.3 of Status and Trends report (Stewart et al., 2013)) at all mussel sites except Upper Harbour. This would be especially important if oysters were removed from the SCMP and replaced with mussels, as discussed in section 6.2.2.

7.0 Future Monitoring

7.1 Sampling frequency

There is scope to make significant cost savings to the SCMP by reducing the sampling frequency from annual to biennial (every two years). Long term trends (25 years) have already been established for oyster contaminant concentrations whereas mussel contaminant trends have been in place for only half this time (13 years). However, in terms of environmental relevance, most contaminant concentrations measured are considered low by international standards and (with the exception of some metals and PAHs) have reduced accordingly over time and are either still declining or have stabilised at very low concentrations.

As such, even though a reduction of sampling frequency will extend the time taken to fully establish long term trends (for mussels), the cost saving benefits likely outweigh this.

7.2 Sites

There is scope for consolidation of some sites in the SCMP; specifically Pahurehure Inlet and Hingaia Bridge oyster sites and Upper Harbour Bridge and Chelsea mussel sites (section 6.2.1). Although these sites show statistically significant differences in the concentrations of some contaminants these differences are relatively minor compared with concentrations from other sites in the region. The most practical way to achieve this is simply to remove one of each of the sites and temporal trends for the retained sites can continue uninterrupted.

Kelly (2007) states “Chelsea is subject to urban and industrial influences. Due to its proximity at the harbour entrance, water flushing is high so the site is likely to be influenced by contaminants originating from mixed sources. Upper harbour marks a confluence of the extensive upper Waitemata harbour with downstream middle Waitemata harbour. Historically, the upper Waitemata harbour catchments have had a high proportion of agricultural use. Today much of the catchment is rural with growing lifestyle blocks and increasing urbanisation. On the incoming tide the upper harbour receives water that is largely influenced by urban catchments draining into the wider Waitemata harbour.” Therefore, of the two sites, Upper Harbour would be more useful to keep due to more land use changes occurring in the catchment, it is less mixed than Chelsea and integrates a wider area.

Pahurehure is adjacent to the southern motorway with a largely urban/industrial catchment (stormwater runoff from Papakura and surrounding rural catchment), while Hingaia represents rural/light industry/residential catchment (predominantly rural with urban runoff from Drury). Hingaia is probably better to keep due to a lot of current and future development occurring around Pukekohe.

This is dependent upon keeping both oysters and mussels in the SCMP. If oysters were removed and replaced with mussel sites (as discussed in section 6.2.2 and section 7.3), then there is no requirement to maintain the same sites, and other sites in the vicinity could be considered.

Consolidating these sites would result in a loss of fine detail in organic contaminant concentrations in the respective catchments. However, this is a minor loss of information relative to the benefits that could be achieved. Benefits realised would depend on the necessity of AC to reduce costs or remain cost neutral. If a reduction in costs is required, then consolidation of these sites would realise this, with minimal other changes required to the programme. If there is the capacity to remain cost neutral then consolidation of these sites would allow the introduction of two new monitoring sites at other locations, adding value to the programme in the future.

This could include new sites such as: an alternative control mussel reference site in place of Illiomama in the Hauraki Gulf; site(s) to monitor changes in land use development across the region; or the addition of a site in the southern Manukau Harbour. By consolidating the sites above and adding two extra sites, there would be no added analytical costs but likely added cost in deployment and sampling due to the wider geographical area of the sampling. Illiomama has generally lower contaminant concentrations compared with the other mussel sites, with the exception of Papakura Channel (selected as a mussel reference/control site for the Manukau Harbour). As such, Illiomama can still function as a reference site for the Hauraki Gulf and incorporates flows from the Waitemata Harbour and Tamaki estuary. Because of this, the addition of a second reference/control site in the Hauraki Gulf may not be the best use of resources. With the ability to monitor on-going land-use changes a priority for the future, the addition of a sampling site in areas of new development, such as the Weiti River catchment, south of the Whangaparaoa Peninsula, an area recommended previously (Mills, 2007), is likely to be more valuable. The Mahurangi Harbour is another possibility as growth is predicted in the Warkworth area. Adding a site to the southern Manukau Harbour is a possible option to give a broader scale of monitoring and obtain information from the largely rural catchment.

7.3 Species

It is not feasible to remove mussel sites from the SCMP and this should not be considered.

There are only four oyster sites, all of which are in the Manukau Harbour. Consideration should be given to replacing oyster sites with mussel sites, assuming that this is logistically possible. This would provide contaminant data for one species, removing the complexities associated with comparing metal data from two different shellfish with different preferential uptake, wild versus deployed populations and with different growth rates. For organic contaminants it is possible to compare across all sites because both species have a similar capacity to bioaccumulate these contaminants.

If oysters are removed from the SCMP, the ability to compare metals data with international programmes is reduced, however this is a relatively minor issue. The US NS&T mussel watch programme monitors 108 mussel sites and 105 oyster sites (Kimbrough et al., 2008) in geographical distinct regions. Mussels are monitored in the more temperate regions of Alaska, Northeast, Southwest and Northwest USA, while oysters are monitored in the more tropical Southeast and Gulf of Mexico. As such, mussel sites in the NS&T mussel watch programme are more relevant to Auckland conditions. The French RNO mussel watch programme also uses predominantly mussels (50 sites) over oysters (10 sites) for monitoring (RNO, 2006).

As stated in section 5.2, with a key aim now being to consolidate and simplify monitoring in the SCMP there is little use in re-visiting adding extra species at this time.

The potential for using passive sampling devices (PSDs) instead of shellfish is covered in section 7.7.

7.4 Analytical Suites

7.4.1 Metals

As discussed in section 6.2.3, there should be no consideration given to reducing or removing the metals analytical suite from routine contaminant monitoring. We strongly recommend the inclusion of mercury in future monitoring. Mercury is one of the most toxic heavy metals found in the environment, derived from both natural and anthropogenic sources. Along with arsenic, mercury is elevated in areas of geothermal activity and both bioaccumulate in biota. Both metals are dominant contributors to human health toxicity associated with consumption of aquatic species as was evident in recent studies in geothermally influenced (Phillips et al., 2011) and non-geothermally influenced (Stewart et al., 2011) areas. Other contaminants which contributed to the risk profile in these studies were DDTs, PCBs, lindane, dieldrin, chlordanes, HCB, cadmium, zinc, nickel and chromium - all of which (with the exception of nickel) are currently measured in the SCMP. Analysis of nickel was discontinued in the SCMP in 2003. Median concentrations of nickel in that year were 0.9 mg/kg and 0.7 mg/kg for mussels and oysters, respectively. Although nickel is a very low human health risk in the consumption of shellfish (Phillips et al., 2011), it may be worthwhile carrying out a single sampling analysis of nickel in future sampling regimes to assess whether there has been any significant change in shellfish concentrations since 2003.

7.4.2 Organochlorines

We do not recommend reducing or removing the analytical suites of organochlorine contaminants, which include organochlorine pesticides and PCBs. If cost saving measures are a priority for AC it would be more prudent to reduce the frequency of analysis of organochlorines. We recommend analysis once every four years. However, this recommendation is predicated on the continual decrease or maintenance of low stable concentrations of these contaminants.

If new sites are introduced into the SCMP to monitor the environmental consequences around land-use changes, i.e., greenfield developments, then it is recommended that organochlorine pesticides (DDT, chlordane, dieldrin, etc.) be analysed on a more frequent biennial frequency at these sites.

7.4.3 PAHs

Pressures due to an increasing urban population dictate that environmental concentrations of PAHs are not likely to decline in the future and will most likely increase in some areas. As such, it would be logical to carry out more frequent analysis of PAHs than other organic contaminants. We recommend biennial analysis of PAHs.

Ideally, future monitoring of PAHs would include compounds that have been identified as key PAH source markers, to more accurately identify the source origins of PAHs (Larsen and Baker, 2003), although benefits need to be weighed up against costs. There are three components to consider; low molecular weight PAHs, alkylated PAHs and general marker compounds.

The inclusion of a larger suite of PAHs and alkylated PAHs into future monitoring of the SCMP would allow closer comparisons of PAH data with the US NS&T mussel watch programme. However, concentrations of PAHs around Auckland are all within the low category range of the US NS&T programme (Kimbrough et al., 2008). Therefore, even though it would be desirable to have a closer suite of PAHs for comparison, it is unlikely to make a significant difference to the overall result.

Marker compounds, such as dibenzothiophenes and hopanes are useful indicators of fuel and oil contamination in sediment monitoring and provide a measure of the impacts of events such as oil spills. Although not a PAH, C_{30}-hopane is considered to be a useful petroleum marker that does not degrade over time.

Although useful information, the benefits are questionable with internationally low concentrations of PAHs around Auckland. Therefore, on balance, we do not recommend the expansion of the PAH suite in the near future. However, this should be re-visited at a future date, if PAH concentrations continue to increase.

7.4.4 Emerging chemicals of concern

In order for the SCMP to critically assess current concentrations of relevant environmental contaminants, the organic analytical suite should be appended. Historically, the analytical suite has been tailored around heavy metal contaminants and legacy POPs. Major sources of many POPs (i.e., PCBs and organochlorine pesticides) have effectively been mitigated over time, with their corresponding environmental concentrations reducing.

The analytical suite should include priority emerging chemicals of concern (ECCs) or at least a pilot study should be undertaken to better understand their distribution in biota. ECCs are not under current regulatory scrutiny in New Zealand, but this is likely to change in the near future and they represent a myriad of chemical contaminants which have been identified internationally as having environmental impacts. Unlike legacy contaminants, sources of some ECCs are increasing, so environmental concentrations are likely to follow suit.

Auckland Regional Council (now AC) took initial steps to identify ECCs in the region, with a literature review of ECCs in use in Auckland (Ahrens, 2008) and a follow-up field survey of ECCs in sediments in the Auckland marine receiving environment (Stewart et al., 2009). The field survey revealed that several ECCs were detectable in Auckland estuarine sediments, including: polybrominated diphenyl ether (PBDE) flame retardants; fungicides (dithiocarbamates); herbicides (especially glyphosate); plasticisers (phthalates); surfactants (alkylphenols); and steroid estrogens. Sediment concentrations ranged from low part per billion (ppb) levels for steroid estrogens to part per million (ppm) levels for 4-nonylphenol and bis (2-ethylhexyl) phthalate (BEP) (Table 7-1). Pharmaceutical residues were also detected in a secondary study using archived sediments from the initial survey, which revealed concentrations up to 7.7 ppb for acetaminophen (Stewart, 2013). The list of ECCs surveyed was far from comprehensive, however it provided background information to assist in identifying emerging contaminant issues in the Auckland area. Sediment concentrations of ECCs in the initial study (pharmaceuticals were not comparable due to few relevant reported data) were generally comparable to aquatic concentrations internationally (Stewart, *et al.* unpublished data).

Any attempt to interpret the risk profile of ECCs in the Auckland region requires concentration data for ECCs in water, sediment and biota, due to the vast array of chemicals, physico-chemical properties and toxicological profiles of these contaminants. The suite of ECCs measured in sediment (Table 7-1) were selected on information from the literature review (Ahrens, 2008) and the ability of analytical laboratories to measure them. This list is not comprehensive, however it is not logistically possible to analyse for all ECCs.

Table 7-1 Sediment concentration data for selected ECCs in the marine receiving environment around Auckland

	Concentration (ng/g)			
Compound	Minimum	Median	Maximum	Number of sites detected
4-nonylphenol	145	153	32000	12
BEP	3200	4000	11500	3
glyphosate	58	120	950	8
PBDEs	0.55	10.3	573	13
dithiocarbamates	20	58	110	9
estrone	0.71	1.35	2.2	6

BEP = Bis(2-ethylhexyl)phthalate; PBDE = polybrominated diphenyl ether; dithiocarbamates were detected as released carbon disulphide; the minimum concentration provided was the lowest reported value above the detection limit.

Internationally, the US based National Oceanic and Atmospheric Administration (NOAA) – who oversee the NS&T mussel watch programme – have reported concentrations of PBDEs in sediment and biota (Kimbrough et al., 2009). The urgency in analysing PBDEs over other ECCs may be in part due to the inclusion of some PBDE congeners as POPs in the Stockholm Convention (see section 7.4.4.1).

An example of a risk-based assessment of ECCs was recently carried out in California (Anderson et al., 2012). Thousands of ECCs were considered before being condensed to sixteen priority compounds for initial screening (Table 7-2). All sixteen were recommended for screening from WWTP effluent, while to assess environmental impacts, three receiving water scenarios were considered:

- Scenario 1: a WWTP effluent-dominated inland (freshwater) waterway;

- Scenario 2: a coastal embayment that receives both WWTP effluent and stormwater discharge, and;
- Scenario 3: offshore ocean discharge of WWTP effluent.

For effluent dominated freshwater systems (Scenario 1), 10 compounds [17-β estradiol, and estrone (hormones); bifenthrin, permethrin, and chlorpyrifos (insecticides); bisphenol A (plastic additive); ibuprofen, galaxolide, diclofenac, and triclosan (pharmaceuticals and personal care products)] were identified for aqueous phase monitoring. For coastal embayments (Scenario 2), 8 of the 10 compounds identified in Scenario 1 were identified for monitoring. Diclofenac and ibuprofen were the exceptions. No aqueous phase CECs were identified for monitoring near WWTP ocean outfalls (Scenario 3). For sediments in coastal embayments (Scenario 2), bifenthrin, permethrin, perfluorooctane sulfonate (PFOS) and two polybrominated diphenyl ether (PBDE) flame-retardants (BDE 47 and 99) were identified for monitoring. For ocean sediments (Scenario 3), the high volume production chemicals, bis (2-ethylhexyl) phthalate, butylbenzyl phthalate, p-nonylphenol and BDE 47 and 99 were identified for monitoring. For tissue monitoring - and of most relevance to the SCMP - BDE-47/BDE-99 and PFOS were prioritized for monitoring (see section 7.4.4.1 and section 7.4.4.2 for explanation).

Table 7-2 CECs recommended for initial monitoring by scenario and environmental matrix (i.e. aqueous, sediment, tissue) (Anderson et al., 2012)

Compound	WWTP Effluent	Scenario 1 Inland Waters Aqueous	FW Stream - Storm-water (Aqueous and Sediment)	Scenario 2 Embayment Aqueous	Scenario 2 Embayment Sediment	Scenario 3 Marine Sediment	All Scenarios Tissue
Bis(2-ethylhexyl) phthalate	M-O	NA	NA	NA	NA	M	NA
Bisphenol A	M–E/F	M	M	M	NA	NA	NA
Bifenthrin	M-E/F	M	M	M	M	NA	NA
Butylbenzyl phthalate	M-O	NA	NA	NA	NA	M	NA
Permethrin	M-E/F	M	M	M	M	NA	NA
Chlorpyrifos	M-E/F	M	M	M	NA	NA	NA
Estrone	M-E/F	M	M	M	NA	NA	NA
Ibuprofen	M-F	M	M	NA	NA	NA	NA
17-β estradiol	M-E/F	M	M	M	NA	NA	NA
Galaxolide (HHCB)	M-E/F	M	M	M	NA	NA	NA
Diclofenac	M-F	M	M	NA	NA	NA	NA
p-Nonylphenol	M-O	NA	NA	NA	NA	M	NA
BDE-47 and 99	M-E/F/O	NA	M	NA	M	M	M
PFOS	M-E/F/O	NA	M	NA	M	M	M
Triclosan	M-F	M	M	NA	NA	NA	NA

M = include in monitoring program (discharges to: E = embayments, F = freshwater, O = ocean waters); NA = not applicable.

This approach shows the validity of performing a risk-based assessment prior to committing to expensive and time-consuming analyses. However, the risk-based approach does carry certain assumptions and is a continuously evolving process as more information becomes available. The ECCs listed in Table 7-2 are common to all industrialised countries and so provide a good cross reference to validate the 2008 Auckland field study of ECCs. This local study of ECCs measured thirteen ECCs prioritised in the Californian study. Those that were not measured were bifenthrin, galaxolide and PFOS. Interestingly, these three contaminants are recommended for coastal embayments that receive both WWTP effluent and stormwater discharge, i.e., Manukau Harbour.

These data suggest that the 2008 study was valid but could be updated with the inclusion of measurement of bifenthrin, galaxolide and PFOS in sediments. In relation to the SCMP, it is recommended that a pilot study is initiated to analyse PFOS and BDE-47/-99 in mussels and oysters (if retained in the SCMP) from the Auckland region. This could initially involve analysis of pooled replicate samples to provide an indicative assessment of contaminant concentrations.

7.4.4.1 PBDEs

In recent years, polybrominated diphenyl ethers (PBDEs - used as flame retardants) have generated international concern due to their global distribution and associated adverse environmental and human health effects.

In 2009, four brominated diphenyl ethers (BDE) [hexabromodiphenyl ether and pentabromodiphenyl ether, the main components of commercial octabromodiphenyl ether; tetrabromodiphenyl ether and pentabromodiphenyl ether, the main components of commercial pentabromodiphenyl ether] were listed as POPs in Annex A of the Stockholm Convention. Parties to the convention (New Zealand ratified the convention in 2004) must take measures to eliminate the production and use of the chemicals listed under Annex A (UNEP, 2010).

Tetra- to octa-BDE are highly persistent and have a high potential for bioaccumulation and food-web biomagnification, as well as for long-range transport. These chemicals have been detected in humans in all regions. There is evidence of potential for toxic effects in wildlife, including mammals (UNEP, 2010).

PBDEs have been called “the new PCBs,” and while there are some similarities, a major difference between them is the source of exposure. PCBs were primarily point source industrial contaminants, while PBDEs are primarily found in consumer goods and are more diffuse in their sources. A comparison of the NS&T Mussel Watch PCB data (Kimbrough et al., 2008) with NS&T Mussel Watch PBDE data (Kimbrough et al., 2009) suggests environmental concentrations of major PBDE and PCB congeners are in a similar concentration range. With the continued use of DecaBDE and the current pool of consumer goods that contain PBDEs, environmental concentrations of PBDEs could surpass that of PCBs in certain locations.

7.4.4.2 PFOS

Perfluorooctanesulfonic acid or perfluorooctane sulfonate (PFOS), is a man-made fluorosurfactant and global pollutant. PFOS is both intentionally produced and an unintended degradation product of related anthropogenic chemicals. The current intentional use of PFOS is widespread and includes: electric and electronic parts, firefighting foam, photo imaging, hydraulic fluids and on textiles as a protector and stain repellent (UNEP, 2010).

PFOS is extremely persistent and has substantial bioaccumulating and biomagnifying properties, although it does not follow the classic pattern of other POPs by partitioning into fatty tissues but instead binds to proteins in the blood and the liver. It has a capacity to undergo long-range transport and also fulfils the toxicity criteria of the Stockholm Convention. As such, PFOS (along with perfluorooctane sulfonyl fluoride (PFOSF) was added to Annex B of the Stockholm Convention on POPs in May 2009. Parties to the convention must take measures to restrict the production and use of the chemicals listed under Annex B in light of any applicable acceptable purposes and/or specific exemptions listed in the Annex. DDT is the only other POP in Annex B (UNEP, 2010).

7.5 Condition

The condition index is calculated on approximately 50 individual shellfish from each site for each year, which is a considerable resource requirement, especially for oysters where numbers are reducing. Whether the continuing measurement of condition is a good use of resources is questionable even though doubt exists as to whether loss of important trend information may occur.

The general health of an area is much better assessed by benthic species monitoring, via the BHM (see section 3.2). Therefore, the loss of information from discontinuing condition measurement is not likely to be large and it should be considered.

7.6 Replicates

The current analytical methods for organic contaminants and some heavy metals provide robust data with low variability between replicates. An analysis of 2010 data reducing replicates from five (current) to three was performed in section 4.5 and indicated that there was no significant effect on the mean value or variability of the data. However, there has been a change to the digestion methodology since 2011 for metals, which has led to increased variability for some metals. We would recommend continuing with five replicates for future heavy metals monitoring if continuing to use this digestion methodology, until the variability is able to be reduced.

With respect to the future monitoring of organic contaminants, it would be reasonable to reduce the number of replicates from five to three, hence providing a significant cost saving. This reduction in replicates should only be implemented on contaminants for which variability has been assessed. For any new contaminants that are introduced to the SCMP - for example PBDEs or mercury - the variability should be assessed prior to reduction of replicates. Five replicates could be analysed in the first year and, following the approach in section 4.5, the variability of replicate reduction assessed. If variability is not significant, then three replicates can continue for the future. If variability is significantly affected then five replicates could be analysed for those contaminants that are problematic.

7.7 Alternatives to SCMP

The SCMP is a unique monitoring programme that delivers high quality data of time averaged organic and inorganic contaminant concentrations across the region. It has some overlap, and complements the three other SoE monitoring programmes, but cannot be replaced by them. Accurate assessment of bioavailable contaminants cannot be made by sediment or water quality measurements. Benthic health monitoring gives an overview of total environmental stressors to sediment dwelling organisms but its link to contaminants is based on sediment concentrations of the heavy metals copper, lead and zinc.

Currently there are no established alternatives to the SCMP that have passed regulatory scrutiny. Passive sampling is a technique that will most likely gain world-wide acceptance in years to come for monitoring programmes, due to lower inherent variability and cost than biota. But before this can happen, more research must be undertaken to ensure that the data is reliable and that it can act as a proxy for determining bioavailable environmental contaminants. Organic passive sampling devices (PSDs) are much more advanced in this regard than metal PSDs.

One option to consider within the next 3-5 years is a more comprehensive feasibility study of PSDs than has been performed as part of this review. This would include an assessment of appropriate types, expected variability and cost-benefit analysis, followed by a small pilot scale study to assess any significant correlations of contaminants measured by these samplers with shellfish contaminant concentrations.

8.0 Summary and Recommendations

8.1 Review of procedures and data quality

QA procedures and data were assessed in the previous status and trends report (Stewart et al., 2013) and therefore only summarised here.

Watercare Laboratory Services Ltd is an IANZ accredited laboratory and have measured metals for the SCMP since 2005. QA procedures are comprehensive and provide sufficient information to measure analytical performance of metals for the SCMP. A change to the digestion procedure used in 2011 does not appear to significantly affect the results for samples from the SCMP, however an increase in the variability was observed which was more pronounced for cadmium, copper and zinc analyses on wet samples.

QA procedures undertaken by AsureQuality are comprehensive and provide sufficient information to measure analytical performance of organics for the SCMP. An assessment of QA data has revealed that there is good agreement between organic contaminant data sets generated by NIWA and AsureQuality for the selected samples analysed.

As demonstrated by the QA procedures and analysis of the QA data, the current analytical laboratories provide robust data at extremely low detection limits. This is especially true for the heavy metals lead, arsenic and cadmium, which - due to lower detection limits since 2005 - have been detected consistently. Analytical instrumentation used by AsureQuality allows significantly lower detection limits for PCBs than were achieved by NIWA, but no significant improvement has been observed for lindane, for which detection is still problematic.

Lower detection limits and reduced analytical variability have led to the provision of more robust datasets. This is important for continued trend analysis, particularly where concentrations have reduced to very low levels for some contaminants; in particular organochlorine pesticides and PCBs.

The major recommendations arising from the QA assessment are as follows:

- We strongly recommend long-term storage of tissue samples (dried or frozen) for future investigations and retrospective analysis of e.g., emerging chemicals of concern.
- Consideration of a pilot study to measure any significant differences between levels of contaminants (metals and organics) when extracting either wet tissue or freeze-dried tissue.

8.2 Relationship to other marine monitoring programmes

The SCMP is providing contaminant information that cannot (at present) be directly obtained by other marine monitoring programmes. Data obtained by the SCMP complements the environmental data obtained from sediment contaminant, benthic health and saline water quality programmes in the area, affording a holistic assessment of contaminant concentrations and distributions in the region.

8.3 Re-evaluation of the programme objectives

The objectives of the Shellfish Contaminant Monitoring Programme are to:

1. Identify contaminants with abnormally high concentrations in shellfish;
2. Detect changes in contaminant levels over time;
3. Detect differences in contaminant levels between locations, and;
4. Evaluate the effectiveness of measures aimed at reducing contaminant loads.

The SCMP is mostly fulfilling its objectives. Robust methods are now in place to effectively monitor concentrations of a multitude of contaminants in shellfish. Concentrations of contaminants are able to be compared between sites, with international shellfish monitoring programmes and against food standards guidelines, affording a perspective of contamination at a site (or in the whole catchment). Care must be taken in interpreting concentration differences between oyster and mussel sites, especially for metals, due to differential uptakes. Temporal trends are possible due to continuity of sites and many contaminants over the lifetime of the SCMP. Early metals data has proved problematic - due to lack of QA data and high variability - however this is currently of a high standard. Temporal trend analyses provide the capability to link changes in contaminant concentrations to regulatory measures taken to reduce or remove them from entering the environment, such as the legacy organochlorine contaminants DDTs, dieldrin and PCBs.

The SCMP is capable of establishing a broad-scale link between contaminant concentrations and land use, however a more quantitative assessment would require incorporating known percentage land use types for each catchment.

A reduction from annual sampling to biennial (every two years) sampling would significantly reduce costs in deployment (of mussels), sampling and analysis, but double the time required for ongoing trend assessment.

The results of a statistical analysis on contaminant data from 2010 indicated that reducing the number of replicates from five (currently) to four (proposed) had no significant effect on the average or the variability of contaminant concentrations. Accordingly, there is scope to reduce the number of replicates and reduce the sampling frequency.

8.4 Implementation of recommendations from the 2007 review

Several of the recommendations from the 2007 review (section 5.0) have been implemented by Auckland Council. These include:

- Shellfish shucking is no longer undertaken by Auckland Council personnel;
- More shellfish material is being provided to the analytical laboratories to enable re-analysis;

- An assessment of whether a reduction in the number of replicates is possible (covered in section 4.5 of this report);
- Investigating measures of catchment land use to assist with interpretation of the monitoring data (examined in the preceding status and trends report (Stewart et al., 2013);
- The implications of reducing sampling frequency (covered in section 4.4 of this report;
- The implementation of formalised sample archiving. Surplus shellfish are now archived and tracked by a Chain of Custody system;
- Provision of annual summaries of QA data. These are now supplied by Watercare and AsureQuality laboratories;
- Analysis of ‘bulk reference’ QA samples. These are now analysed by both Watercare and AsureQuality laboratories to check inter-annual analytical variability;
- Improving detection limits for most metals. This has been in place since 2005;
- Improving detection limits for organics. This has been in place (especially for PCBs) since changing laboratories in 2009;
- Development of a user manual for data management;
- Carrying out comparisons between shellfish and sediment monitoring sites (covered in section 3.1 of this report);

However, some of the recommendations from the 2007 review (section 5.0) have not been implemented by Auckland Council. These include:

- There has been no change in sites, including potential consolidation, replacing reference sites, or creating new sites to provide a broader coverage of the region, although the feasibility of site changes has been covered in this report (sections 6.2.1 and 7.2);
- No “mixed species” monitoring programme has been reinstated in the Tamaki estuary;
- No review of previous monitoring surveys of resident species has been carried out to monitor the spatial patterns and temporal trends in contaminants in locations not currently monitored.

8.5 Implications of changing or dropping the SCMP

Disestablishing the SCMP would significantly limit the ability to fully understand the state of the environment in the region, unless a viable alternative was implemented. The SCMP contains over 20 years of data that has evolved throughout time as methods have evolved and information has been incorporated from reviews and audits. The SCMP overlaps to varying degrees with the other three SoE monitoring programmes in the region and complements them. In combination, they provide a holistic data set which can be used to assess the state of the environment in the region.

In regards to viable alternatives to the SCMP there are two potential avenues to explore to provide an assessment of bioavailable contaminants in the environment; an expanded sediment contaminant monitoring programme *in conjunction* with benthic health monitoring and passive sampling devices (PSDs). A feasibility study would be necessary to assess the suitability of each approach. A combined sediment contaminant /benthic health programme would extend existing monitoring programmes which have significantly greater spatial coverage than the SCMP, while PSDs would require incorporation of emerging technologies. PSDs are being researched world-wide as cost-effective alternatives to shellfish monitoring to determine the bioavailable portion of contaminants in the environment. Research into organic PSDs is considerably more advanced than for metal PSDs, and assessments are being made into their suitability for regulatory monitoring. Therefore, PSDs are probably more suited to being a future development, as they become more widely implemented into monitoring programmes internationally.

For PSDs to be considered over shellfish monitoring around Auckland, a feasibility study is also necessary to assess the following:

- The most applicable PSDs to estuarine water samples;
- A cost-benefit analysis including;
    - potential savings,
    - logistics of implementation,
    - ability to sample more sites with less replicates;
- Quality of the information obtained and ability to continue trend analyses using the existing data set.

8.6 Implications of dropping or changing parts of the programme

On-going trend assessment for the SCMP would be affected by dropping components (such as decreasing the number of sites or removing specific analytes) or by significant changes to the programme (such as completely removing a species of shellfish). However, a review of the trend data suggests that not all changes would have a significant impact. For example, reducing the frequency of analysis of PCBs and organochlorine pesticides is not expected to significantly affect trends analyses as these groups of compounds have continued to reduce over time, or have stabilised at very low levels.

Consolidation of some sites in the SCMP could be achieved with minimal impact on the ability to carry out the necessary functions of the programme. Consolidation of Pahurehure Inlet and Hingaia Bridge oyster sites and Upper Harbour Bridge and Chelsea mussel sites would reduce the number of sites monitored in the SCMP by two. With the exception of PAHs at Pahurehure and Hingaia Bridge, current shellfish contaminant concentrations between these neighbouring sites are not significantly different.

Furthermore, the cost saving gained by consolidation of these sites will provide the ability to make other changes to the SCMP and remain cost neutral. This would allow the addition of new sites to the SCMP, such as:

- The addition of a sampling site in areas of new development, such as the Weiti River catchment (south of the Whangaparaoa Peninsula), or in the Mahurangi estuary.
- The addition of a site in the southern Manukau Harbour to give a broader scale of monitoring and obtain information from the largely rural catchment.

8.7 Recommendations for future monitoring

As discussed throughout this report, there is the potential to make modifications to the SCMP. Most changes proposed will be associated with loss of some information but would have minimal impact on the ability of the programme to fulfil its objectives and would allow the programme to evolve and provide more valid environmental assessments for the future.

Major recommendations are as follows:

1) *Sampling frequency:* It is recommended to reduce the sampling from annual to biennial (every two years) to introduce significant cost savings that will either allow the SCMP to continue as is or allow the introduction of changes that will provide more relevant outputs to the programme in the future.
2) *Site consolidation*: It is recommended to consolidate some sites in the SCMP; specifically Pahurehure Inlet and Hingaia Bridge oyster sites and Upper Harbour Bridge and Chelsea mussel sites.
3) *Number of replicates:* For future monitoring of organic contaminants, it would be reasonable to reduce the replicates from five to four, however we recommend continuing with five replicates for future heavy metals monitoring if continuing to use the new digestion methodology - introduced in 2011 - until variability is reduced. For any new contaminants that are introduced to the SCMP - for example PBDEs or mercury - the variability should be assessed prior to reduction of replicates.
4) *Species consolidation*: It is not feasible to remove mussel sites in the SCMP and this should not be considered. We recommend giving serious consideration to replacing oyster sites with mussel sites, assuming that this is logistically possible. This would provide contaminant data for one species, removing the complexities associated with comparing metal data from two different shellfish with different preferential uptake, wild versus deployed populations and with different growth rates. The offset to this would be discontinuation of the longer term trends established for oysters (around 25 years), a potential loss of information on sediment dwelling species and a reduced ability to compare with food safety guidelines and international shellfish monitoring programmes. However, mussel sites in the NS&T mussel watch programme are

more relevant to Auckland conditions and the French RNO mussel watch programme uses predominantly mussels for monitoring.

5) *Current contaminants analysed*: We do not recommend reducing or removing the metals analytical suite from routine contaminant monitoring. Shellfish should be analysed for metals every two years.

   We do not recommend removal (partial or full) of the analytical suites of organochlorine contaminants. We recommend a reduction of the frequency of analysis of organochlorine contaminants in shellfish to every four years.

   We do not recommend the expansion of the PAH suite in the near future. Although this would provide useful information, the benefits are questionable with internationally low concentrations of PAHs around Auckland. However, this should be re-visited at a future date, if PAH concentrations continue to increase. Shellfish should be analysed for PAHs every two years.

6) *New contaminants:* We strongly recommend the inclusion of mercury in future shellfish monitoring which - along with arsenic - is a dominant contributor to human health toxicity associated with consumption of aquatic species. It may be worthwhile carrying out a single sampling analysis of nickel in future sampling regimes to assess whether there has been any significant change in shellfish concentrations since it was last analysed in 2003.

   Consideration should be given to the future inclusion of emerging chemicals of concern (ECCs) in the analytical suite. The current analytical suite has been tailored around heavy metal contaminants and legacy POPs, many of which have effectively been mitigated over time, with their corresponding environmental concentrations reducing. ECCs of high priority for inclusion in the SCMP analytical suite are PFOS and BDE-47/-99. It is recommended that a pilot study is initiated to analyse PFOS and BDE-47/-99 in mussels and oysters from the Auckland region. However, measurement of a wider range of ECCs should also occur in sediment and water environmental compartments to obtain a holistic assessment of these contaminants and consideration should be given to changing analytical suites of other environmental monitoring programmes in the region to achieve this.

7) *Alternatives to SCMP:* Consideration should be given to an expanded sediment contaminant monitoring programme *in conjunction* with benthic health monitoring, or carrying out an assessment within 3-5 years of the suitability of passive sampling devices, as potential future replacements for the SCMP.

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Appendix A Descriptions of contaminants, their sources and impacts

Information for Appendix A was taken primarily from two sources.

Information on sources and potential human health effects was obtained from the US Agency for Toxic Substances and Disease Registry (ATSDR) online portal (ATSDR, 2012) and US EPA Integrated Risk Information System (IRIS) (US EPA, 2012), respectively.

Most region specific information was taken from Appendix A of Auckland Regional Council Technical Publication TP332 (Kelly, 2007), from which much information was referenced from reports of the Australian and New Zealand Environment and Conservation Council (ANZECC) Australian and New Zealand Guidelines for Fresh and Marine Water Quality (Vol 1-3) (ANZECC, 2000). These guidelines have not been updated at this time. Where this information was not available, it was obtained from the Ministry for the Environment (MfE) website (MfE, 2012), or the Ministry for Primary Industries (MPI) website (MPI, 2012).

Key metals

Total Arsenic (As)

Arsenic is a naturally occurring element widely distributed in the Earth's crust. In the environment, arsenic is combined with oxygen, chlorine, and sulphur to form inorganic arsenic compounds. Arsenic also forms organic arsenic compounds (ATSDR, 2012). Total arsenic consists of both organic and inorganic forms. Inorganic arsenic is classified by the US EPA as a carcinogen (US EPA, 2012).

The predominant commercial use of arsenic in the Auckland region is by timber treatment companies for wood preservation (Kelly, 2007). Other examples of its use include:

- herbicides and insecticides;
- lead-acid batteries;
- small amounts of pure arsenic metal are used in the manufacture of semiconductors for the computing and electronic industries.

Heavy industries such as mining, smelting, pulp and paper production, glass manufacturing, cement manufacturing may also release arsenic to the environment.

Natural sources include volcanoes, ground water, and hydrothermal vents.

Arsenic has acute and chronic toxicity to many aquatic organisms (ANZECC, 2000).

Cadmium (Cd)

Cadmium is a natural element in the Earth's crust. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulphur (cadmium sulphate, cadmium sulphide). All soils and rocks, including coal and mineral fertilizers, contain some cadmium. Cadmium does not corrode easily and has many uses, including batteries, pigments, metal coatings, and plastics (ATSDR, 2012).

The US EPA classifies cadmium as a probable human carcinogen (US EPA, 2012) Cadmium can also be toxic to aquatic organisms at very low concentrations. It may exist in a number of forms which influence its toxicity, bioavailability and mobility in the environment. Cadmium is accumulated by many aquatic organisms with bio-concentration factors in the order of 100 – 100,000 (ANZECC, 2000). There is also some evidence to suggest that cadmium is also accumulated through the food chain (ANZECC, 2000).

Chromium (Cr)

Chromium is a naturally occurring element found in rocks, animals, plants, and soil. It can exist in several different forms. Depending on the form it takes, it can be a liquid, solid, or gas. The most common forms are Cr(0), Cr(III), and Cr(VI). No taste or odour is associated with chromium compounds. The metal chromium, which is the Cr(0) form, is used for making steel. Cr(VI) and Cr(III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving (ATSDR, 2012).

Cr (VI) is the most toxic form to humans. It has been classified as a known or likely human carcinogen by the inhalation route but unclassified by the oral route. Cr(III) is not classified as a human carcinogenic risk (US EPA, 2012).

Chromium is accumulated by marine and freshwater organisms. Bio-concentrations factors range from 100 to 1000. There is little evidence that cadmium is accumulated through the food chain (ANZECC, 2000).

Copper (Cu)

Copper is a metal that occurs naturally throughout the environment, in rocks, soil, water, and air. Copper is an essential element in plants and animals (including humans). Copper is used to make many different kinds of products like wire, plumbing pipes, and sheet metal. Copper is also combined with other metals to make brass and bronze pipes and taps. (ATSDR, 2012). Copper is widely used in the electrical, construction, plumbing, and automotive industries, in antifouling paints, in horticultural sprays and as a trace element in some stock foods and supplements (Kelly, 2007).

Aquatic organisms have widely varying sensitivities to copper. Algae in particular are sensitive to relatively low copper concentrations, hence its use in algaecides and antifoulants. It is readily accumulated by plants and animals with bioconcentrations factors ranging from 100 to 26,000 being recorded (ANZECC, 2000).

Natural sources of copper in aquatic environments include the weathering of copper minerals and native copper. However, by far the greatest source of copper is from anthropogenic activities.

Lead (Pb)

Lead is a naturally occurring bluish-gray metal found in small amounts in the Earth’s crust. Lead can be found in all parts of our environment. Much of it comes from human activities including burning fossil fuels (particularly petrol containing tetraethyl lead additives), mining and manufacturing. Lead has many different uses. It is used in the production of batteries, ammunition, metal products (solder and pipes), and devices to shield X-rays. Because of health concerns, lead from paints and ceramic products, caulking, and pipe solder has been dramatically reduced in recent years (ATSDR, 2012).

Historically the major source of lead in New Zealand was from fuel additives. However, lead was withdrawn a petrol additive in 1996. Other sources include industrial processes, paints, pigments, batteries and shot pellets (Kelly, 2007).

Lead can damage the nervous system, kidneys, and reproductive system (ATSDR, 2012). The US EPA has classified lead as a probable human carcinogen (US EPA, 2012).

Lead is acutely and chronically toxic to aquatic life at very low concentrations. It is accumulated by molluscs and may be passed up the food chain. There is evidence of lead bio-concentration at higher trophic levels (Kelly, 2007).

Zinc (Zn)

Zinc is an essential element for plants and animals and is not particularly toxic to humans, although it can be harmful at high concentrations. Zinc toxicity to aquatic biota is highly variable with some organisms being very sensitive to zinc levels and others being particularly tolerant. Many organisms accumulate zinc to relatively high concentrations.

Zinc is a ubiquitous element in urban areas. Examples of its use include: galvanising, the production of alloy materials, in plasticizers for synthetic rubbers such as tyres and in paint manufacture (Kelly, 2007).

Mercury (Hg)

Mercury is not currently monitored in the SCMP, but has occasionally been measured in the sediment monitoring programme. Recommendations from this report are to include mercury in future analyses (see section 7.4.1), so it is included here for reference.

Mercury is a naturally occurring metal which has several forms. Mercury combines with other elements, such as chlorine, sulphur, or oxygen, to form inorganic mercury compounds or “salts”. Mercury also forms organic mercury compounds, of which methylmercury is the most common. Metallic mercury is used to produce chlorine gas and caustic soda, and is also used in thermometers, dental fillings and batteries. Mercury salts are sometimes used in skin lightening creams, antiseptic creams and ointments (ATSDR, 2012).

Exposure to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys, and developing foetus. The detrimental effects on normal brain function include irritability, shyness, tremors, changes in vision or hearing, and memory problems (ATSDR, 2012). The US EPA does not classify metallic mercury as a human carcinogen, but classes methylmercury and mercuric chloride as possible human carcinogens (US EPA, 2012).

Organic Contaminants

PAHs (Polycyclic Aromatic Hydrocarbons)

PAHs are compounds formed by the incomplete combustion of organic material. Natural background levels of PAH are found in the environment from events such as forest fires and volcanic activities. However, the most significant sources are from anthropogenic activity such as motor vehicle emissions, roading materials such as coal tar, and wood and coal burning fires (Kelly, 2007).

There are more than 100 different PAHs. PAHs generally occur as complex mixtures (for example, as part of combustion products such as soot), not as single compounds (ATSDR, 2012).

The health effects of individual PAHs are not exactly alike, ranging from non-toxic to extremely toxic. The US EPA has determined that the following 7 PAHs are probable human carcinogens (ATSDR, 2012):

- benz[a]anthracene;
- benzo[a]pyrene;
- benzo[b]fluoranthene;
- benzo[k]fluoranthene;
- chrysene;
- dibenz[a,h]anthracene;
- indeno[1,2,3-c,d]pyrene

Many PAHs are chronically and/or acute toxic to a range of aquatic organisms. Their toxicity can be magnified significantly by photo activation with UV light (ANZECC, 2000).

Aldrin and Dieldrin

Aldrin and dieldrin are insecticides with similar chemical structures. Aldrin rapidly breaks down to dieldrin in the body and in the environment. Exposure to aldrin and dieldrin occurs mostly through eating contaminated foods, such as root crops, fish, or seafood. Aldrin and dieldrin accumulate in the body after years of exposure and can affect the nervous system (ATSDR, 2012). The US EPA has classified dieldrin as a probable human carcinogen (US EPA, 2012).

In New Zealand, aldrin and dieldrin were introduced in 1954 for use as stock remedies in sheep sprays or dips for controlling sheep ectoparasites. Aldrin was used to control horticultural pests such as wireworm, soldier fly and blackvine weevil, and in limited quantities, to control household spiders. Dieldrin was used for controlling carrot rust fly, crickets and armyworm and was also used for timber preservation (mostly in plywood glues) and to mothproof carpets (Buckland et al., 1998a). Dieldrin was deregistered as a pesticide in 1989 and permits for its use in horticulture and agriculture have been revoked. Use of dieldrin for commercial pest control in buildings did not require a permit and it is possible that old stocks are still used for this application (Kelly, 2007).

Dieldrin generally exhibits high to very high toxicity to aquatic species (ANZECC, 2000).

Lindane

Lindane (γ-HCH) is one of eight isomers formed during the manufacture of technical grade (crude) hexachlorocyclohexane (HCH), also known erroneously as benzene hexachloride (BHC). Technical grade HCH typically contained about 10–15% of γ-HCH as well as the alpha (α), beta (β), delta (δ), and epsilon (ε) forms. It is used as an insecticide on fruit, vegetables, and forest crops (ATSDR, 2012).

In New Zealand, lindane was used as an insecticide in agriculture for the control of lice on cattle, ectoparasites (lice, keds and blowflies) in sheep and grass grub in pasture. Lindane was also used for insect control on vegetable and fruit crops, and as an active component of fly sprays, flea control and carpet moth products for household use. Technical grade HCH was not officially used in New Zealand, although many dip sites show evidence of the use of crude HCH (Buckland et al., 1998a). Lindane was deregistered in 1990 (Kelly, 2007).

Exposure to lindane happens mostly from eating contaminated food or by breathing contaminated air in the workplace. Exposure to high levels of lindane can cause blood disorders, dizziness, headaches, seizures, and changes in the levels of sex hormones. The US EPA has determined there is not enough evidence to determine whether lindane is a human carcinogen (US EPA, 2012).

Lindane has moderate to high toxicity to aquatic organisms, although some molluscs are less sensitive (ANZECC, 2000).

DDT (dichlorodiphenyltrichloroethane)

Dichlorodiphenyltrichloroethane (DDT) is a pesticide that was used extensively throughout the world to control insects that affect agriculture and horticulture. It is still used in some countries as a control measure for insects, such as mosquitoes, that carry malaria. DDT was used largely as an insecticide to control grass grubs and porina caterpillars in New Zealand, with its use restricted in 1970 and finally banned in 1989 (Taylor et al., 1997). DDT breaks down in the environment to dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), all of which persist for years.

Exposure to DDT, DDE, and DDD occurs mostly from eating foods containing low concentrations of these compounds, particularly meat, fish and poultry. High levels of DDT can affect the nervous system causing excitability, tremors and seizures. In women, DDE can cause a reduction in the duration of lactation and an increased chance of having a premature baby (ATSDR, 2012). DDT is classified by US EPA as a probable human carcinogen (US EPA, 2012).

DDT is highly toxic to most aquatic species (ANZECC, 2000).

Chlordane

Technical chlordane is a mixture of chlordane and many related chemicals, of which the composition varies. Exposure to chlordane occurs mostly from eating contaminated foods, such as root crops, meats, fish, and shellfish, or from touching contaminated soil. High levels of chlordane can cause damage to the nervous system or liver (ATSDR, 2012). The US EPA classes technical chlordane as a probable human carcinogen (US EPA, 2012).

In New Zealand, chlordane was used as a broad spectrum agricultural insecticide, in the timber industry as a treatment against termites and borer, and as an insecticide in glues used for the manufacture of plywood, finger jointed and laminated timber (Buckland et al., 1998a).

Chlordane is highly toxic to aquatic organisms (ANZECC, 2000).

PCBs (Polychlorinated biphenyls)

Polychlorinated biphenyls (PCBs) are mixtures of up to 209 individual chlorinated compounds, referred to as congeners. PCBs have been used as coolants and lubricants in transformers, capacitors, and other electrical equipment because they have low flammability and are good electrical insulators (ATSDR, 2012).

Exposure to PCBs can be via multiple pathways. Skin exposure can occur via old electrical devices (>30 years old) that leak small amounts of PCBs and in the workplace where contact may be made with equipment or devices containing PCBs. Ingestion of PCBs is largely via contaminated food (fish, meat and dairy) and drinking contaminated well water, while inhalation exposure can occur by breathing air near hazardous waste sites (ATSDR, 2012).

Health effects that have been associated with exposure to PCBs include acne-like skin conditions in adults and neurobehavioral and immunological changes in children (ATSDR, 2012). The US EPA classifies PCBs as a probable human carcinogen (US EPA, 2012).

PCBs cause a variety of acute and chronic toxicity effects on aquatic biota (ANZECC, 2000).

In March 1986, the New Zealand Customs Department placed a prohibition on importing PCBs, and later that year regulations to control the importation of PCBs were promulgated as an amendment to the Toxic Substances Regulations 1983. In 1988, a further amendment to the Toxic Substances Regulations 1983 prohibited the use and storage of PCBs with effect from 1 January 1994. Following two extensions, this regulation came into effect on 1 August 1995 (Buckland et al., 1998b).

Hexaclorobenzene (HCB)

Hexaclorobenzene was widely used in the US as a pesticide to protect the seeds of onions and sorghum, wheat, and other grains against fungus until 1965 (ATSDR, 2012). In New Zealand HCB was used experimentally between 1970 and 1972 as a seed-dressing fungicide for cereal grain (MfE, 2012). HCB has been classified as a probable human carcinogen (US EPA, 2012).

Endosulfan

Endosulfan is an active ingredient present in some pesticide formulations used on crops to control insects. Endosulfan has been registered for use in New Zealand since the 1960s. In December 2008, ERMA New Zealand withdrew all approvals for products containing endosulfan under the HSNO Act. Endosulfan is an organochlorine pesticide but is not listed as a POP under the Stockholm Convention. Endosulfan has shown no potential to accumulate over time in animals. It is more water soluble than other organochlorines, such as DDT, and is less persistent in the body because it metabolises quickly (MPI, 2012).

Endosulfan has not been assessed by the US EPA for carcinogenicity, however rat studies note reduced body weight gain in males and females, increased incidence of marked progressive glomerulonephrosis and blood vessel aneurysms in males (US EPA, 2012).

Endrin

Endrin was used as a pesticide to control insects, rodents, and birds. Endrin has not been produced or sold for general use in the US since 1986. Little is known about the properties of endrin aldehyde (an impurity and breakdown product of endrin) or endrin ketone (a product of endrin when it is exposed to light) (ATSDR, 2012). Only small amounts of endrin was ever used in New Zealand (MfE, 2012).

The US EPA has determined that endrin is not classifiable as to human carcinogenicity, due to insufficient evidence (US EPA, 2012).

Mirex

Mirex was used to control fire ants, and as a flame retardant in plastics, rubber, paint, paper, and electrical goods from 1959 to 1972 (ATSDR, 2012). Mirex does not appear to have been used in any significant amounts in New Zealand due to its omission from the list of historical usage of persistent organochlorine pesticides in New Zealand (MfE, 2012). Mirex has not been assessed by the US EPA for carcinogenicity, however rat studies noted liver cytomegaly, fatty metamorphosis, angiectasis and thyroid cystic follicles.

Appendix B List of analyses on mussels performed over the period of the programme with associated laboratory providers

Table Appendix 1: Key of terms used in Appendix B and C.

General Key	
*	Limited suite totals (see TP332 for further details)
^	Extended suite totals (See TP332 for further details)
NS&T	Used in US National Status and Trends Totals (See TP332 for further details)
Key Metal	6 key metals for trends analysis
■	Analysis carried out in that year

Lab Provider Key	
Key	Laboratory
ARA Water Lab	ARA Water Laboratory
DSIR	DSIR Grassland Division
AgResearch	AgResearch, Grassland Research Centre
Watercare	Watercare Laboratory Services
Coastal Aquatic	Coastal Aquatic Systems Limited
Ruakura S&P	Ruakura Soil and Plant Research Laboratories
MAF	MAF Technology, Ruakura Agriculture Centre
HortRes	HortResearch, Ruakura Agricultural Centre
NIWA	NIWA, Hamilton
AsureQuality	AsureQuality, Wellington

Table Appendix 2: Inorganic Data for Mussels.

ANALYSIS	Key Metal	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
Inorganics		**AgResearch**					**N/A**	**Watercare**						
Calcium		▨	▨	▨	▨	▨								
Magnesium		▨	▨	▨	▨	▨								
Potassium		▨	▨	▨	▨	▨								
Sodium		▨	▨	▨	▨	▨								
Sulphur		▨	▨	▨	▨	▨								
Aluminium		▨	▨	▨	▨	▨								
Arsenic	✓	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Boron		▨	▨	▨	▨	▨								
Cadmium	✓	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Chromium	✓	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Cobalt		▨	▨	▨	▨	▨								
Copper	✓	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Iron		▨	▨	▨	▨	▨								
Lead	✓	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Manganese		▨	▨	▨	▨	▨								
Molybdenum		▨	▨	▨	▨	▨								
Nickel		▨	▨	▨	▨	▨								
Selenium		▨	▨	▨	▨	▨								
Silicon			▨											
Strontium		▨	▨	▨	▨	▨								
Tin		▨	▨	▨	▨	▨								
Zinc	✓	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Phosphorus		▨	▨	▨	▨	▨								

Table Appendix 3: Condition Data for Mussels.

ANALYSIS	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**
Condition	**Watercare**					**N/A**		**Coastal Aquatic**					
Shell length								■	■	■	■	■	■
Shell width								■	■	■	■	■	■
Total wet weight								■	■	■	■	■	■
Shell wet weight (blotted dry)								■	■	■	■	■	■
Shell wet weight (air dried 24hrs)		■	■	■	■								
Shell dry weight								■	■	■	■	■	■
Tissue wet weight								■	■	■	■	■	■
Tissue dry weight		■	■	■	■			■	■	■	■	■	■
Condition Index (Watercare)													
Condition Index (CASL)								■	■	■	■	■	■

Table Appendix 4: DDT and other OCP data for Mussels.

ANALYSIS	*****	**^**	**NS&T**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**
				NIWA					**N/A**	**NIWA**				**AsureQuality**		
Lipid																
Lipid Content (% DW)				■	■	■	■	■		■	■	■	■	■	■	■
DDTs																
o,p'-DDE (= 2,4'-DDE)		✓		■	■	■	■	■		■	■	■	■	■	■	■
p,p'-DDE (= 4,4'-DDE)	✓	✓		■	■	■	■	■		■	■	■	■	■	■	■
o,p'-DDD (= 2,4'-DDD)		✓		■	■	■	■	■		■	■	■	■	■	■	■
p,p'-DDD (= 4,4'-DDD)	✓	✓		■	■	■	■	■		■	■	■	■	■	■	■
o,p'-DDT (= 2,4'-DDT)		✓		■	■	■	■	■		■	■	■	■	■	■	■
p,p'-DDT (= 4,4'-DDT)	✓	✓		■	■	■	■	■		■	■	■	■	■	■	■
Chlordanes																
alpha Chlordane (cis)	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
gamma Chlordane (trans)	✓	✓		■	■	■	■	■		■	■	■	■	■	■	■
Heptachlor		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Heptachlor epoxide		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Cis-nonachlor		✓		■	■	■	■	■		■	■	■	■	■	■	■
Trans-nonachlor		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Other OCPs																
Aldrin														■	■	■
b-BHC (Beta-HCH)														■	■	■
d-BHC (Delta-HCH)														■	■	■
g-BHC (Gamma-HCH) - Lindane														■	■	■
a-BHC (= Alpha-HCH)														■	■	■
Dieldrin				■	■	■	■	■		■	■	■	■	■	■	■
Endrin														■	■	■
Endrin Aldehyde														■	■	■
Endrin Ketone														■	■	■
Lindane - g-BHC				■	■	■	■	■		■	■	■	■			
Hexachlorobenzene											■	■	■	■	■	■
Pentachlorobenzene (PeCB)														■	■	■
Endosulfan-A														■	■	■
Endosulfan-B														■	■	■
Endosulfan-Sufate														■	■	■

Table Appendix 5: PAH data for Mussels.

ANALYSIS	*	^	NS&T	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
PAHs				**NIWA**					**N/A**	**NIWA**				**AsureQuality**		
1-methylphenanthrene		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Anthracene		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
benz[a]anthracene	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Benzo(a)pyrene	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Benzo(b)fluoranthene	✓	✓		■	■	■	■	■		■	■	■	■	■	■	■
Benzo[e]pyrene		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Benzo(ghi)perylene		✓		■	■	■	■	■		■	■	■	■	■	■	■
Benzo(k)fluoranthene		✓		■	■	■	■	■		■	■	■	■	■	■	■
Chrysene	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Dibenz(a,h)anthracene		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Fluoranthene	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Indeno(1,2,3-cd)pyrene		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Perylene		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Phenanthrene		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Pyrene	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
Fluorene														■	■	■
Acenaphthylene														■	■	■
Acenaphthene														■	■	■
Mirex														■	■	■
2-methylphenanthrene														■	■	■

Table Appendix 6: PCB data for Mussels.

ANALYSIS	*	^	NS&T	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
PCB congener				**NIWA**					**N/A**	**NIWA**				**AsureQuality**		
4+10														■	■	■
8+5														■	■	■
8		✓	✓	■	■	■	■	■		■	■	■	■			
15														■	■	■
18		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
19														■	■	■
28		✓	✓	■	■	■	■	■		■	■	■	■			
28+31														■	■	■
37														■	■	■
44		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
49		✓		■	■	■	■	■		■	■	■	■	■	■	■
52		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
54														■	■	■
66		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
70														■	■	■
74														■	■	■
77		✓		■	■	■	■	■		■	■	■	■	■	■	■
81														■	■	■
86		✓		■	■	■	■	■		■	■	■	■	■	■	■
99														■	■	■
101+90														■	■	■
101		✓	✓	■	■	■	■	■		■	■	■	■			
104														■	■	■
105		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
110		✓		■	■	■	■	■		■	■	■	■	■	■	■
114														■	■	■
118	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
121		✓		■	■	■	■	■		■	■	■	■	■	■	■
123														■	■	■
126		✓		■	■	■	■	■		■	■	■	■	■	■	■
128		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
138	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
141		✓		■	■	■	■	■		■	■	■	■	■	■	■
151		✓		■	■	■	■	■		■	■	■	■	■	■	■
153	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
155														■	■	■
156		✓		■	■	■	■	■		■	■	■	■	■	■	■
157														■	■	■
167														■	■	■
169		✓		■	■	■	■	■		■	■	■	■	■	■	■
170		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
180	✓	✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
183														■	■	■
187		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
188														■	■	■
189														■	■	■
194		✓		■	■	■	■	■		■	■	■	■	■	■	■
195		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
196+203														■	■	■
202														■	■	■
205														■	■	■
206		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■
208														■	■	■
209		✓	✓	■	■	■	■	■		■	■	■	■	■	■	■

Appendix C List of analyses on oysters performed over the period of the programme with associated laboratory providers

Table Appendix 7: Inorganic data for Oysters.

ANALYSIS	**Key Metal**	**1987**	**1988**	**1989**	**1990**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**
Inorganics		**ARA Water Lab**			**DSIR**	**AgResearch**													**N/A**	**Watercare**						
Calcium							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			▨					
Magnesium							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Potassium							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Sodium							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Sulphur							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Aluminium							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			▨					
Arsenic	✓	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Boron							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Cadmium	✓	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Chromium	✓	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Cobalt							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			▨					
Copper	✓	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Iron							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Lead	✓	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Manganese							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Molybdenum							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Nickel							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Selenium							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Silicon							▨	▨	▨	▨	▨	▨	▨		▨											
Strontium							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨								
Tin							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			▨					
Zinc	✓	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
Phosphorus							▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨			▨					

Table Appendix 8: Condition data for Oysters.

ANALYSIS	**1987**	**1988**	**1989**	**1990**	**1991**	**1992**	**1993**	**1994**	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**
Condition														**Watercare**				**N/A**	**N/A**	**Coastal Aquatic**					
Shell length																				■	■	■	■	■	■
Shell width																				■	■	■	■	■	■
Total wet weight																				■	■	■	■	■	■
Shell wet weight (blotted dry)																				■	■	■	■	■	■
Shell wet weight (air dried 24hrs)														■	■	■	■								
Shell dry weight																				■	■	■	■	■	■
Tissue wet weight																				■	■	■	■	■	■
Tissue dry weight														■	■	■	■			■	■	■	■	■	■
Condition Index (Watercare)																									
Condition Index (CASL)																				■	■	■	■	■	■

Table Appendix 9: DDT and Other OCP data for Oysters.

ANALYSIS	*	^	NS&T	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
				Ruakura S&P			**MAF**	**N/A**	**HortRes**	**NIWA**											**N/A**	**NIWA**				**AsureQuality**		
Lipid																												
Lipid Content (% DW)				■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
DDTs																												
o,p'DDE (= 2,4'DDE)		✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
p,p'DDE (= 4,4'DDE)	✓	✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
o,p'DDD (= 2,4'DDD)		✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
p,p'DDD (= 4,4'DDD)	✓	✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
o,p'DDT (= 2,4'DDT)		✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
p,p'DDT (= 4,4'DDT)	✓	✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Chlordanes																												
alpha Chlordane (cis)	✓	✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
gamma Chlordane (trans)	✓			■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Heptachlor		✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Heptachlor epoxide		✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Cisnonachlor												■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Transnonachlor			✓									■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Other OCPs																												
Aldrin																										■	■	■
b-BHC (Beta-HCH)																										■	■	■
d-BHC (Delta-HCH)																										■	■	■
g-BHC (Gamma-HCH) - lindane																										■	■	■
a-BHC (= Alpha-HCH)				■																						■	■	■
Dieldrin				■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Endrin				■	■	■	■		■	■	■	■														■	■	■
Endrin Aldehyde																										■	■	■
Endrin Ketone																										■	■	■
Lindane (g-BHC)				■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■			
Hexachlorobenzene																								■	■	■	■	■
Pentachlorobenzene (PeCB)																										■	■	■
Endosulfan-A																										■	■	■
Endosulfan-B																										■	■	■
Endosulfan-Sufate																										■	■	■
Mirex																										■	■	■

Table Appendix 10: PAH data for Oysters.

ANALYSIS	*	^	NS&T	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
				Ruakura S&P			MAF	HortRes		NIWA											N/A	NIWA				AsureQuality		
PAHs																												
2,4,5-trichlorophenol					■	■	■		■	■	■																	
2,4,6-Trichlorophenol				■	■	■	■		■	■	■																	
Pentachlorophenol				■	■	■	■		■	■	■																	
chrysene/benz[a]anthracene				■	■	■	■		■																			
2,3,4,6-tetrachlorophenol				■	■	■	■		■	■	■																	
1-methylphenanthrene		✓	✓										■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Anthracene		✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
benz[a]anthracene	✓	✓	✓							■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Benzo(a)pyrene	✓	✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Benzo(b)fluoranthene	✓	✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Benzo[e]pyrene		✓	✓										■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Benzo(ghi)perylene		✓		■					■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Benzo(k)fluoranthene	✓	✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Chrysene	✓	✓	✓							■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Dibenz(a,h)anthracene		✓	✓	■			■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Fluoranthene	✓	✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Indeno(1,2,3-cd)pyrene		✓	✓									■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Perylene		✓	✓									■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Phenanthrene		✓	✓									■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Pyrene	✓	✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
Fluorene																										■	■	■
Acenaphthylene																										■	■	■
Acenaphthene																										■	■	■
Mirex																										■	■	■
2-methylphenanthrene																										■	■	■

Table Appendix 11: PCB data for Oysters.

ANALYSIS	*	^	NS&T	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
				Ruakura S&P			**MAF**	**HortRes**		**NIWA**											**N/A**	**NIWA**				**AsureQuality**		
PCB Congener																												
4+10																										■	■	■
8+5																										■	■	■
8		✓	✓								■	■	■	■	■	■	■	■	■	■		■	■	■	■			
15							■		■	■																■	■	■
18		✓	✓				■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
19																										■	■	■
28		✓	✓			■	■					■	■	■	■	■	■	■	■	■		■	■	■	■			
28+31											■															■	■	■
31				■	■		■																					
37																										■	■	■
40				■	■		■		■																			
44		✓	✓	■			■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
47									■																			
49		✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
52		✓	✓			■	■				■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
54				■	■				■																	■	■	■
66		✓	✓								■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
70																										■	■	■
74																										■	■	■
77		✓		■	■		■		■	■	■	■		■	■	■	■	■	■	■		■	■	■	■	■	■	■
81																										■	■	■
86		✓		■	■	■	■				■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
87											■																	
99																										■	■	■
101+90																										■	■	■
101		✓	✓				■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■			
104																										■	■	■
105		✓	✓						■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
110									■					■	■	■	■	■	■	■		■	■	■	■	■	■	■
114																										■	■	■
118	✓	✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■

ANALYSIS	*	^	NS&T	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011
				Ruakura S&P			MAF	HortRes		NIWA											N/A	NIWA				AsureQuality		
PCB Congener																												
121		✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
123																										■	■	■
126		✓										■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
128		✓	✓									■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
138	✓	✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
141		✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
151				■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
153	✓	✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
155																										■	■	■
156		✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
157																										■	■	■
167																										■	■	■
169												■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
170		✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
180	✓	✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
183																										■	■	■
185									■																			
187		✓	✓									■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
188																										■	■	■
189																										■	■	■
194		✓		■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
195		✓	✓	■	■				■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
196				■																								
196+203																										■	■	■
201				■																								
202																										■	■	■
205																										■	■	■
206		✓	✓			■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■
208																										■	■	■
209		✓	✓	■	■	■	■		■	■	■	■	■	■	■	■	■	■	■	■		■	■	■	■	■	■	■