Auckland
Regional Council
TE RAUHITANGA TAIAO

Contaminant Monitoring in Shellfish

Results of the 2005 Shellfish Contaminant Monitoring Programme

June 2007 TP332

Auckland Regional Council
Technical Publication No. 332, 2007
ISSN 1175-205X
ISBN -13 : 978-1-877416-70-5
ISBN -10 : 1-877416-70-3

Contaminant monitoring in shellfish: Results of the 2005 Shellfish Contaminant Monitoring Programme.

Prepared by: S. Kelly

Peer reviewed by:
Geoff Mills  Date: June 2007

Approved for release by:
Grant Barnes  Date: June 2007

Acknowledgements

Samples were collected and processed by ARC technicians. Kelly Tarlton's Antarctic Encounter & Underwater World kindly provided tank facilities which allowed mussels to be stored prior to deployment. DiveCo Ltd. assisted in the deployment and retrieval of mussel rigs. Sample analysis was carried out by NIWA and Watercare Services Ltd.

Recommended Citation:

Kelly, S. (2007) Contaminant monitoring in shellfish: Results of the 2005 Shellfish Contaminant Monitoring Programme. Auckland Regional Council Technical Publication Number 332.

Table of Contents

1 Executive Summary

The Shellfish Contaminant Monitoring Programme has conducted annual sampling of metal and organic contaminants in Manukau Harbour oysters continuously since 1987. Mussel monitoring in the Waitemata Harbour and Tamaki Estuary was introduced into the programme in 1999, and in the Manukau Harbour in 2000.

In general, the levels of organic contaminants present in shellfish tissues were low by international standards, but clear differences were apparent between monitoring sites. Highest levels were detected in Mangere Inlet and Tamaki Estuary. DDT, chlordane, dieldrin and PCB levels were elevated in mussels and oysters from Mangere Inlet, and dieldrin and PCBs levels were elevated in mussels recovered from the Tamaki Estuary.

Marked changes in the concentrations of organic contaminants have been observed through time. Significant declines have been recorded in the levels of lindane, chlordane and dieldrin in Manukau oyster tissues since these pesticides were deregistered in 1989-1990. However, recent pulses in DDT, chlordane, and PCB concentrations were observed in oysters and mussels from sites in Mangere Inlet. These pulses coincide with the decommissioning, and return to the sea, of treatment ponds at the Mangere Sewage Treatment Plant.

2005 copper levels in Manukau Harbour oyster tissues were relatively high by international standards, and are at levels considered to be indicative of contamination by human activity. Zinc levels in oyster tissues were within the "typical" range reported from international databases. Cyclical fluctuations in the concentrations of these two contaminants appear to be partly driven by natural variation in weather patterns, and in particular, those associated with the Southern Oscillation Index. However, further investigation is required to confirm this link and determine the causative factors.

Overall, site quality can be ranked according to contaminant levels in oyster and mussel tissues as follows:

Oysters:		
Granny's Bay	Pahurehure Hingaia	Cornwallis

Mussels:					
Mangere Inlet	Tamaki Estuary	Upper Waitemata Chelsea	Illiomama	Weymouth Papakura Channel	Pre-deployment

2 Introduction

2.1 Programme Rationale and Objectives

The Shellfish Contaminant Monitoring Programme was established to allow the detection of long term trends in bioavailable suspended and dissolved seawater contaminants. Monitoring is carried out in the Waitemata Harbour, Manukau Harbour and Tamaki Estuary. The programme specifically targets urban harbour areas likely to be affected by stormwater and wastewater runoff. Relatively remote reference sites are also included to provide comparative data from less contaminated areas.

Obtaining a reliable measure of contaminant levels in coastal seawater through direct measurement of water samples is problematic because concentrations are generally very low in the water column, reliable analysis is difficult, concentrations vary rapidly due to water movement, and contaminant inputs are patchy in nature. Furthermore, while the concentration of contaminants in the water column may be very low, this may not reflect their potential toxicity because, even at low concentrations, plants and animals can accumulate many contaminants to toxic levels.

Sedentary, filter-feeding shellfish are therefore used as biomonitors. Filter-feeders process large amounts of water from a fixed location, and have the propensity to accumulate a wide range of contaminants in their tissues. Shellfish therefore provide an integrated history of contaminant exposure at a particular site, although the period integrated varies with contaminant (Mills 1998). Consequently, contaminant levels in mussels and oysters provide a good proxy for overall levels in the surrounding water body. Features that make oysters and mussels particularly appealing as biomonitors are:

- they are inexpensive and easily obtained;
- they are easy to handle and process;
- they are culturally, commercially and ecologically important;
- their biology is well understood;
- they are the most frequently used taxa in overseas shellfish monitoring programmes. This enables contaminants in Auckland shellfish to be put into the broader context of international programmes.

The objectives of the Shellfish Contaminant Monitoring Programme are to:

- determine the temporal and spatial variability of selected water contaminants at sites influenced by urban landuse;
- detect trends in contaminant body burdens of oysters and mussels through time;

- evaluate the effectiveness of pollution abatement activities;
- determine the effectiveness of policy and land use management practices to protect the health of marine receiving environments.

2.2 Programme Components

The Shellfish Contaminant Monitoring Programme has two components: the Manukau Oyster (*Crassostrea gigas*) Monitoring Programme and the Mussel (*Perna canaliculus*) Monitoring Programme.

The Manukau Oyster Monitoring Programme was initiated as part of the Manukau Harbour Action Plan (1987), following concerns over the environmental condition of the harbour. Initially 11 sites were monitored, however, following an assessment of 5 years data, the number of sites was reduced to 4 in 1992. The catchments adjoining the remaining sites were selected to represent different landuses ranging from highly urbanised to those dominated by rural activity and/or bush.

Historically, the use of oysters as a region wide monitoring tool has been constrained by the lack of "natural" populations, particularly at east coast locations, and need for persistent oyster populations at the monitoring sites. The intertidal habit of oysters also limited monitoring to these habitats. Consequently, the Shellfish Contaminant Monitoring Programme was expanded in 1999 by adding a mussel monitoring component. The advantages of using mussels are that they can be sourced from relatively uncontaminated areas, attached to ropes, and set at any subtidal or low intertidal location for a given period of time. The Mussel Monitoring Programme provides wider coverage of the Auckland metropolitan area and includes sites in the Manukau and Waitemata Harbours, and Tamaki Estuary. Annual samples are set at monitoring sites for approximately 3 months starting in September. Mussels sampled prior to deployment, and those set at the relatively clean Illiomama (Rangitoto Island) and Papakura Channel (Manukau Harbour) sites, provide "reference" material which is used for comparison with data from sites subject to greater levels of contaminant input.

2.3 Contaminants Measured

Two groups of contaminants are assessed: key metals and organic contaminants. These contaminants primarily enter the sea through stormwater discharges and are derived from sources such as vehicle emissions, wear from tyres and brake linings, pesticide use (including soils historically contaminated by chemicals such as organochlorines that are no longer legally used), industrial activity and roof runoff. Previously, the potential effects of these contaminants on oysters and mussels have been assessed using simple, non-specific, morphological indices of condition (Kelly 2004). However, this analysis was not carried out in the 2005.

The methods used in the Shellfish Contaminant Monitoring Programme are primarily designed to permit trend detection. The programme is not designed to assess shellfish quality for human health risk (note that the greatest health risk is from microbiological contamination, which is not monitored in this programme). Maximum permissible levels of (some) contaminants in commercially grown shellfish are provided by the New Zealand Food Safety Authority (NZFSA)[1]. Those standards are based on wet weights, which cannot be directly applied to the dry weight measurements obtained in this programme prior to 2005. Furthermore, the standards provided by the NZFSA may not be from the same chemical species measured in this programme. For instance, the standard given for arsenic applies to inorganic forms, whereas total arsenic is measured in the Shellfish Contaminant Monitoring Programme.

Details of the contaminants measured in the shellfish monitoring programme, potential sources, and toxic effects are provided in Appendix A.

2.4 Report Structure

This report describes the methods used in the Shellfish Contaminant Monitoring Programme and presents results from the 1987 –2005 Manukau Oyster and 1999 – 2005 Mussel Monitoring Programmes. Data from the most recent sampling event are also compared with overseas shellfish monitoring programmes to provide a broader context.

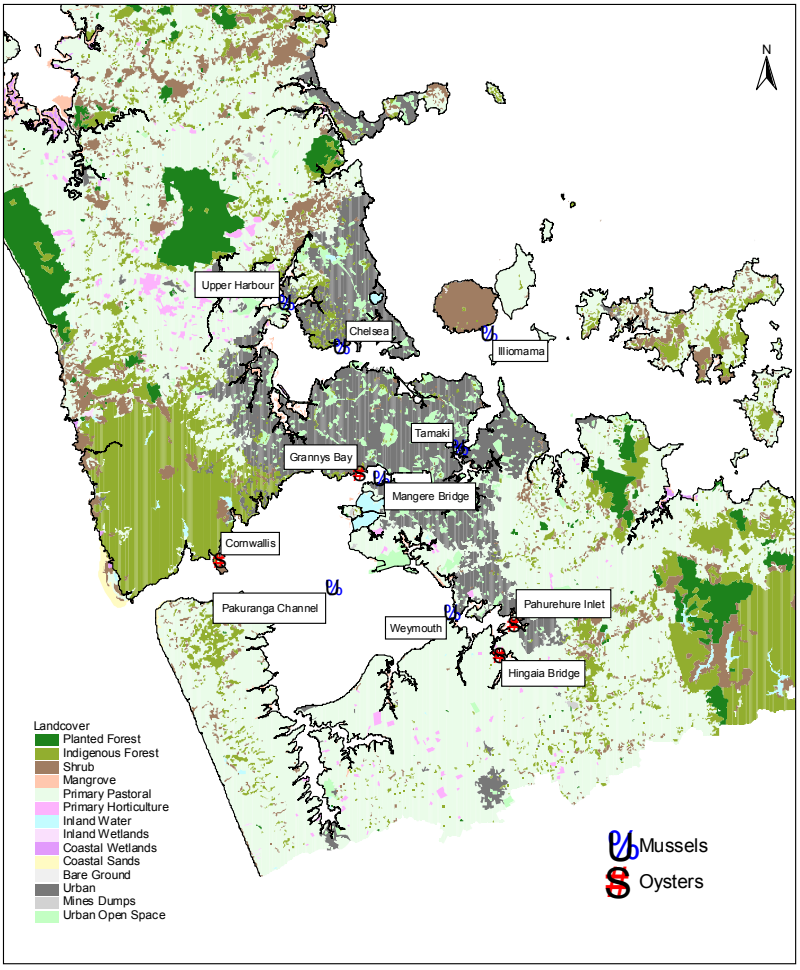
[1] http://www.foodstandards.gov.au/foodstandardscode/index.cfm#_FSCchapter1

3 Methods

3.1 Oyster Monitoring Programme

Oyster monitoring is currently carried out once a year at 4 sites within the Manukau Harbour: Granny's Bay, Cornwallis, Pahurehure, and Hingaia Inlets (Figure 3-1). Each year, all samples are collected on the same day, ideally during late November, to avoid seasonal differences between years. To ensure that contaminant levels reflect general water quality rather than recent pulses from distinct discharge events, samples are not collected until there has been at least five continuous days of little (< 5 mm) or no rain. Consequently, in some years samples were not collected until December (2000) or January (1996, 1997 & 1980).

Figure 3-1: Location of oyster and mussel monitoring sites in the Shellfish Contaminant Monitoring Programme.



3.1.1 Oyster Site Descriptions

A range of catchment types are included in the Manukau Oyster Programme. Oyster samples are collected from a site close to a major source of urban contaminants (Granny's Bay), a site adjacent to the southern motorway with a largely urban/industrial catchment (Pahurehure), a site representing a rural/light industry/residential catchment (Hingaia Inlet) and a reference site in the outer harbour (Cornwallis) (Figure 3-1). Brief descriptions of each site are provided below.

3.1.1.1 Granny's Bay

Granny's Bay is flushed by water from Mangere Inlet and is subject to both point and non-point source contamination from the extensively urbanised catchments adjoining the bay. Of the four Manukau oyster monitoring sites, Granny's Bay is likely to receive the greatest load of urban stormwater contaminants.

3.1.1.2 Pahurehure

Pahurehure receives stormwater runoff from the urban/industrial areas of Papakura and the surrounding rural catchment.

3.1.1.3 Hingaia Inlet

A predominantly rural catchment, with some urban runoff from the Drury residential/light-industrial area.

3.1.1.4 Cornwallis

An outer harbour reference site which is situated next to an ARC regional park. The catchment is dominated by regenerating bush and reserve land with very limited residential/urban development. The 1998, 1999 and 2000 samples were taken at the opposite end of Cornwallis Beach from that used previously. This was due to low oyster numbers at the original site. Catchment influences are similar at both ends of Cornwallis Beach.

3.1.2 Oyster Sample Collection

Five replicates were randomly collected from similar tidal zones at each site except Cornwallis, where random sampling was not possible because of low oyster numbers. Samples from five patches (which included most of the population) were therefore collected from this site. Each replicate consisted of:

- A composite of 12 oysters for the analysis of trace metals;
- A composite of 20 oysters for the analysis of organic contaminants.

3.2 Mussel Monitoring Programme

3.2.1 Mussel Monitoring Site Descriptions

Mussels are monitored at 2 sites within the Waitemata Harbour, 1 site in the Tamaki Estuary, 1 site at Illiomama (Rangitoto Island), and 3 sites in the Manukau Harbour. Monitoring of the east coast sites began in 1999, while the Manukau sites were introduced into the programme in 2000. Site descriptions are provided below.

3.2.1.1 Upper Tamaki (Tamaki Estuary)

The Tamaki estuary is a very sheltered water body with a highly urbanised/industrial catchment. The estuary has received industrial discharges over a long period and is generally considered to have relatively poor water quality.

3.2.1.2 Upper Waitemata Harbour (Greenhithe Bridge)

The Greenhithe Bridge marks a confluence of the extensive Upper Waitemata Harbour area with the downstream Middle Waitemata Harbour. The upper harbour extends to Kumeu and Riverhead (where it becomes Rangitopuni Stream) on one arm, and to Albany on the other. Historically, catchments of the Upper Waitemata Harbour have had relatively high proportions of horticultural landuse. Persistent pesticides, especially organochlorine pesticides such as DDT, which were previously applied to pasture and crops, may therefore have a continuing impact on marine water quality. Today much of the catchment is rural, with a growing 'lifestyle block' contingent, and an increasing level of urbanisation. On the incoming tide the upper harbour receives water that is largely influenced by urban catchments draining into the wider Waitemata Harbour.

3.2.1.3 Chelsea Bay (Waitemata Harbour)

Chelsea Bay, has an urban/industrial influence. Due to the proximity of the site to the harbour entrance, water flushing is high. Consequently, the site is likely to be influenced by contaminants originating from mixed sources.

3.2.1.4 Illiomama (Rangitoto Island)

The reference site for Waitemata Harbour and Tamaki Estuary. Illiomama, is located on the southern side of Rangitoto Island. Water quality is relatively good because of strong tidal flows and exposure to coastal waters.

3.2.1.5 Mangere Bridge (Manukau Harbour)

Mangere Bridge consists of mixed urban/industrial landuse, much of which is heavy industry. The discharge from the Mangere Sewage Treatment Plant is also likely to affect the water quality of this site. This area has historically been one of the most polluted coastal waterways in Auckland.

3.2.1.6 Papakura Channel (Manukau Harbour)

This site is the reference site for the Manukau Harbour component of the mussel monitoring programme and is situated in the centre of the harbour at the entrance to Papakura Channel.

3.2.1.7 Weymouth (Manukau Harbour)

The site is situated at the mouth of Pahurehure Inlet. The catchment for the site has a mixed landuse of rural, urban and light industry (Manurewa and Papakura).

3.2.2 Mussel Sampling

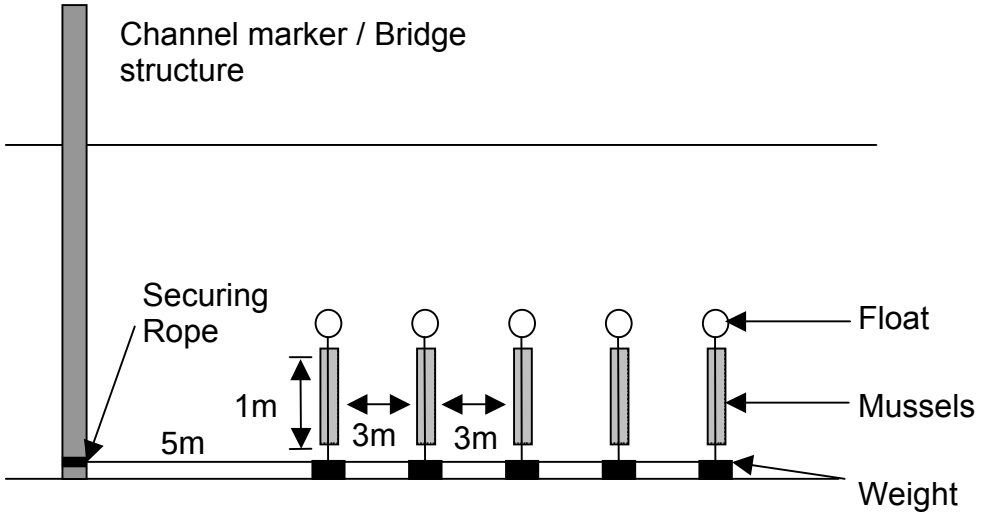
In the mussel monitoring programme, commercially grown mussels are transferred from a Coromandel mussel farm and re-seeded onto lines set at ARC monitoring sites. Mussels are transported as soon as possible after harvesting and stored in a flowing saltwater tank until they are seeded onto the lines. Only mussels which exhibit a disturbance response (i.e. closing their valves when disturbed) at the time of seeding are used. The size of mussels used is limited to shellfish between 50 and 90 mm in length.

Mussel ropes approximately 1 metre long were seeded with approximately 55 mussels each using biodegradable mussel stockings. Six ropes were set onto a rig at each site by divers who ensured that individual ropes were well spaced and oriented perpendicular to the tidal flow (see Figure 3-2). The rigs were secured to permanent structures such as channel markers or bridge pillars. Deployment occurred in early September, and rigs were collected in early December.

Upon collection, each mussel rope (replicate) was immediately bagged. Once the mussels were returned to shore they are removed from the ropes, cleaned in seawater, and separated into bags for analysis. From each mussel rope:

- A composite of 10 mussels was kept for the analysis of trace metals;
- A composite of 20 mussels was kept for the analysis of organic contaminants.

Figure 3-2. Five mussel ropes, with the separating ropes, floats and weights, making a complete "array"



3.3 Analytical Procedures

3.3.1 Key Metals

The history of laboratories carrying out the metal analyses is provided in Appendix D: History of laboratories conducting sample analyses. Prior to 1991, metal analyses were carried out by ARA Water Laboratory and DSIR Grassland Division. Metals were analysed using atomic absorption spectrometry (AAS), but no details are available on the methods they used to extract the metals. Since 1991, two laboratories have conducted the metal analyses: AgResearch and Watercare Services. Details of the methods they used to extract and analyse metals are provided below.

3.3.1.1 AgResearch

Key metals were extracted by placing approximately 300 mg of freeze-dried flesh into an acid-washed erlenmeyer flask. 10 ml of concentrated nitric acid was added, after which the erlenmeyer flask was placed in a heating block, covered with a funnel, and left overnight. The following morning, the heating block was set to 90°C. The solution was then allowed to reflux until the brown fumes no longer appeared (approximately 3 hours). The funnel was then removed, and the temperature increased to 120°C until the solution evaporated to near dryness. Five ml of 2M HCl was added to the flask and the contents transferred to a 15 ml polypropylene test tube. The flask was washed with 2 M HCl to collect any residual material, and the washings added to the test tube. Additional 2 M HCl was added, as required, to bring the total volume to in the test tube to 15 ml. The solution was then analysed by ICPMS (inductively coupled plasma mass spectroscopy) and arsenic, cadmium, chromium, copper, lead and zinc concentrations quantified.

3.3.1.2 Watercare Services

After weighing and thawing, the shellfish are homogenised, and a weighed sub-sample of the homogenate was digested for analysis using concentrated nitric acid. Samples were initially digested without heating for 1-2 days, and then in a water bath or on a heating block at approximately 60°C until the solution was a clear yellow. After digestion the solution was made up to the desired volume (usually 30 ml) with deionised distilled water, mixed thoroughly, and any lipid material present was allowed to settle. The settled digest was then filtered through a disposable nylon 66, 0.45µm filter. Digested samples were analysed by ICPMS.

The remainder of the homogenate was weighed, dried, and reweighed so the moisture content of the shellfish could be calculated. Tests indicate that the uncertainty of this calculation is ±10%. Once the metals analyses were completed, the dry weight percentage was used to calculate the metals content of the shellfish as mg/kg (dry wt).

3.3.2 Organic Contaminants

The analysis of organic contaminants was carried out by NIWA, Hamilton. Frozen shellfish were thawed, shucked, homogenised and freeze dried. Sub-samples were spiked with analytical surrogates representative of each class of compounds and extracted with dichloromethane (DCM) using Accelerated Solvent Extraction (ASE). A combination of silica/alumina, gel permeation, and silica gel chromatography was used to clean up and fractionate the extracts. Internal standards were added to all extracts before gas chromatography (GC) analysis.

The lipid content of each sample was determined gravimetrically from the portion of the original ASE extract. Lipids are measured because organic contaminants bind to them. Consequently, organic contaminant concentrations are typically expressed as the weight of contaminant per unit weight of lipid.

Quantitative analyses of PAHs and PCB's were carried out by capillary gas chromatography using mass selective detection in selection ion mode (GC-MS-SIM). Organochlorine pesticides were analysed by GC with electron capture detection (GC-ECD) using dual-column confirmation.

Concentrations were corrected for surrogate recovery. Detection limits were approximately 0.1-0.5 ng/g dry weight. Quality assurance assessment was carried out by triplicate analysis of composite tissue samples and monitoring surrogate recoveries.

3.3.2.1 Oysters

The range of organic contaminants analysed within contaminant groups has varied considerably since the inception of the Manukau Oyster Monitoring Programme (Appendix B, Table B1). Prior to 1995 there was little consistency in the PAH (polycyclic aromatic hydrocarbons) and PCB (polychlorinated biphenyls) congeners measured from one year to the next. Only limited comparisons can therefore be made with earlier PCB

and PAH data sets. Since 1995, a reasonably regular suite of PAH and PCB congeners has been examined. Estimates of **total** PCBs and **total** PAHs presented in this report are therefore limited to the post-1995 period and those compounds consistently measured during this time (see Appendix B: Contaminants Measured). In 1995, trans-nonachlor and cis-nonachlor were also added to the list of chlordanes analysed. This enabled direct comparisons to be made with the National Status and Trends Mussel Watch Programme in the USA, which present **total** chlordane as the sum of cis-chlordane, trans–nonachlor, heptachlor, and heptachlor epoxide. Consequently, data for **total** chlordanes presented in this report are also limited to post-1995. DDT, lindane and dieldrin have been consistently analysed throughout the term of the monitoring programme. Accordingly, data for these contaminants are presented for the full period from 1987-2002.

To overcome the issues outlined above, Mills (1998) recommended a limited suite of compounds should be analysed for trends over the full duration of the programme. These included:

- **PAHs**: the sum of fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]-fluorathene, benzo[k]fluoranthene, and benzo[a]pyrene;
- **PCBs**: the sum of congeners 118, 138, 153 and 180;
- **DDTs**: the sum of p,p'-DDE, p,p'-DDD and p,p'-DDT;
- **Chlordane**: the sum of cis-chlordane and trans-chlordane.

These are also presented as **limited** PAH, **limited** PCB, **limited** DDT and **limited** chlordane.

Organic compounds are presented as total dry weight concentrations and/or lipid normalised concentrations where:

$$C_L = \frac{100 \times C_{DW}}{\%lipid}$$

C_L = contaminant concentration in ng/g lipid, C_{DW} = contaminant concentration in ng/g dry weight tissue, and % lipid is the shellfish lipid content expressed as a percentage of the tissue dry weight.

3.3.2.2 Mussels

The same group of organic compounds have been consistently measured since the inception of the Mussel Monitoring Programme. A list of the organic compounds measured in mussels is given in Appendix B (Table B2). Totals for each group are taken as the sum of the individual isomers and congeners within the group.

3.3.3 Comparisons with International Studies

Contaminant levels in Manukau oysters were compared with concentrations from international mussel and oyster watch programmes that have been published in the scientific literature. International programmes are generally based on the collection of "wild" bivalves of a certain size. The methods used in the ARC Mussel Monitoring Programme, which exposes transplanted mussels to contaminated water for a fixed period of approximately 3 months, are not consistent with these studies. Therefore the results from the ARC Mussel Monitoring Programme were not compared.

3.4 Data Analysis

Data were analysed graphically, and by using univariate and multivariate statistical techniques. Univariate analyses (ANOVA, least squares linear regression and correlations) were used to examine differences in the concentrations of individual contaminants among monitoring sites and trends through time. Because of the large number of variables and sites monitored, trend analysis (i.e. least squares linear regression) was only carried out when plotted data indicated that persistent and environmentally-significant temporal changes had occurred. In other cases, patterns in the plotted data were simply described.

Multivariate analyses were used to examine spatial and temporal differences based on the combined influence of organic contaminants. Multivariate analyses were initially carried out on the totalled concentrations on each class of organic contaminants (i.e. total DDT, total PAH, total PCB, total chlordane, lindane and dieldrin). PAH and PCB signatures were then examined by analysing the concentrations of individual congeners within these contaminant classes. Hierarchical agglomerative cluster analysis, including similarity profile permutation testing, and multidimensional scaling (MDS) were carried out to group sites and times with similar contaminant profiles. Similarity profile analysis links samples into clusters that are genuinely, statistically significant (Clarke and Gorley 2006). Principle component analysis was then carried out to examine the relative influence of each variable in the analysis.

Analyses were carried out on untransformed data. Draftsman plots were used to check for the even distribution of data and for curvilinear relationships between variables, as recommended in Clarke and Gorley (2006). Statistical normalisation was not carried out prior to analysis, because all of the organic contaminants were measured in the same way and are expressed in the same units. A consequence of not normalising the data is that contaminants with higher concentrations had a more dominant influence on the results. An advantage of this is that contaminants with higher concentrations are likely to be more accurately measured than minor ones close to detection limits (e.g. lindane). The analysis is therefore weighted towards more reliable data. The trade-off is that the total PAH concentrations are, typically, quite a bit higher than the concentrations of

organochlorines (especially for the mussels). The results of the analysis generally reflect this pattern.

Univariate analyses were carried out using the Statistica software package. The multivariate analyses were carried out using the PRIMER software package.

4 Results

4.1 Oyster Contaminants

4.1.1 Metals

4.1.1.1 Detection limits

Copper and zinc levels were consistently greater than detection limits between 1987 and 2003 (Table 1). In contrast, arsenic, cadmium, and chromium levels were below detection limits in 18 - 23% of samples, while lead levels were below detection limits in 77% of samples. Accordingly, extreme care should be taken when interpreting temporal trends in lead data.

Note, however, that analytical sensitivity has improved in recent years, and detectable concentrations of all six metals were obtained from all of the oyster samples analysed in 2003 and 2005.

Table 1: Number of samples collected between1987 and 2005 which were less than, or greater than, detection limits for each of the key metals at the four sites that have been continuously monitored over that period (Cornwallis, Granny's Bay, Pahurehure, and Hingaia). The maximum, minimum, and mean detection limits vary between samples. Values for these parameters were taken from only samples with concentrations less than the detection limits, hence the lack of detection limits for copper and zinc.

	Arsenic	Cadmium	Chromium	Copper	Lead	Zinc
Maximum Detection Limit	44	3.1	2.51	N/A	25	N/A
Minimum Detection Limit	6.3	0.3	0.31	N/A	0.2	N/A
Mean Detection Limit	16.5	1.2	1.1	N/A	4.9	N/A
N°. < Detection Limit	68	62	81	0	273	0
Total N°. Collected	354	354	354	354	354	354
% < Detection Limit	19%	18%	23%	0%	77%	0%

4.1.1.2 Temporal and spatial trends

Copper and zinc concentrations in oysters clearly distinguished Cornwallis from the other three monitoring sites. Oysters from the Cornwallis site have consistently had the lowest concentrations of copper and zinc since 1989. Concentrations of these two metals are generally similar at the other sites. Cadmium concentrations also tend to be lowest at Cornwallis, but no clear differences were apparent in the concentrations of arsenic, chromium, and lead between sites (note however, that values given for lead are relatively uninformative because of the large proportion of samples below detection limits).

Within-year variation in the concentration of key metals was low, but inter-annual variation was relatively high for some metals (Figure 4-1). In particular, relatively large, periodic fluctuations were apparent in the long-term plots of copper and zinc concentrations. Analysis also indicated that metal concentrations of all four sites were correlated through time, even though the sites are widely distributed in space and have quite different catchment characteristics (Appendix C: Correlations between metals in oysters and mussels). Together, these patterns suggested that broad-scale factors simultaneously affect the presence or uptake of contaminants at sites throughout the Manukau Harbour. The periodic fluctuations in copper and zinc did not mirror known changes in landuse or landuse activities, which could influence contaminant runoff. Rather, the pattern of periodicity appeared to be more consistent with longer-term, cyclical variability in weather patterns. Copper and zinc concentrations from Pahurehure and Hingaia (which were strongly correlated with those from Cornwallis and Granny's Bay) were therefore compared with the southern oscillation index (SOI) (Figure 4-2). A relatively good fit was obtained between the concentrations of these metals and the SOI. The concentrations of both contaminants matched fluctuations in the SOI associated with La Nina and El Nino weather patterns between 1987 and 1998, suggesting that these large scale climate patterns may be an important factor affecting the availability and/or uptake of metals. The fit was not as good between 1999 and 2000.

Figure 4-1: Key metal (mean µg / g (oyster dry weight) ± s.e.) concentrations in oysters collected from four sites in the Manukau Harbour between 1987 and 2005. Samples below detection limits (DL) were transformed by multiplying the detection limit by 0.5. The proportion (%) of samples with concentrations above detection limits is also indicated.

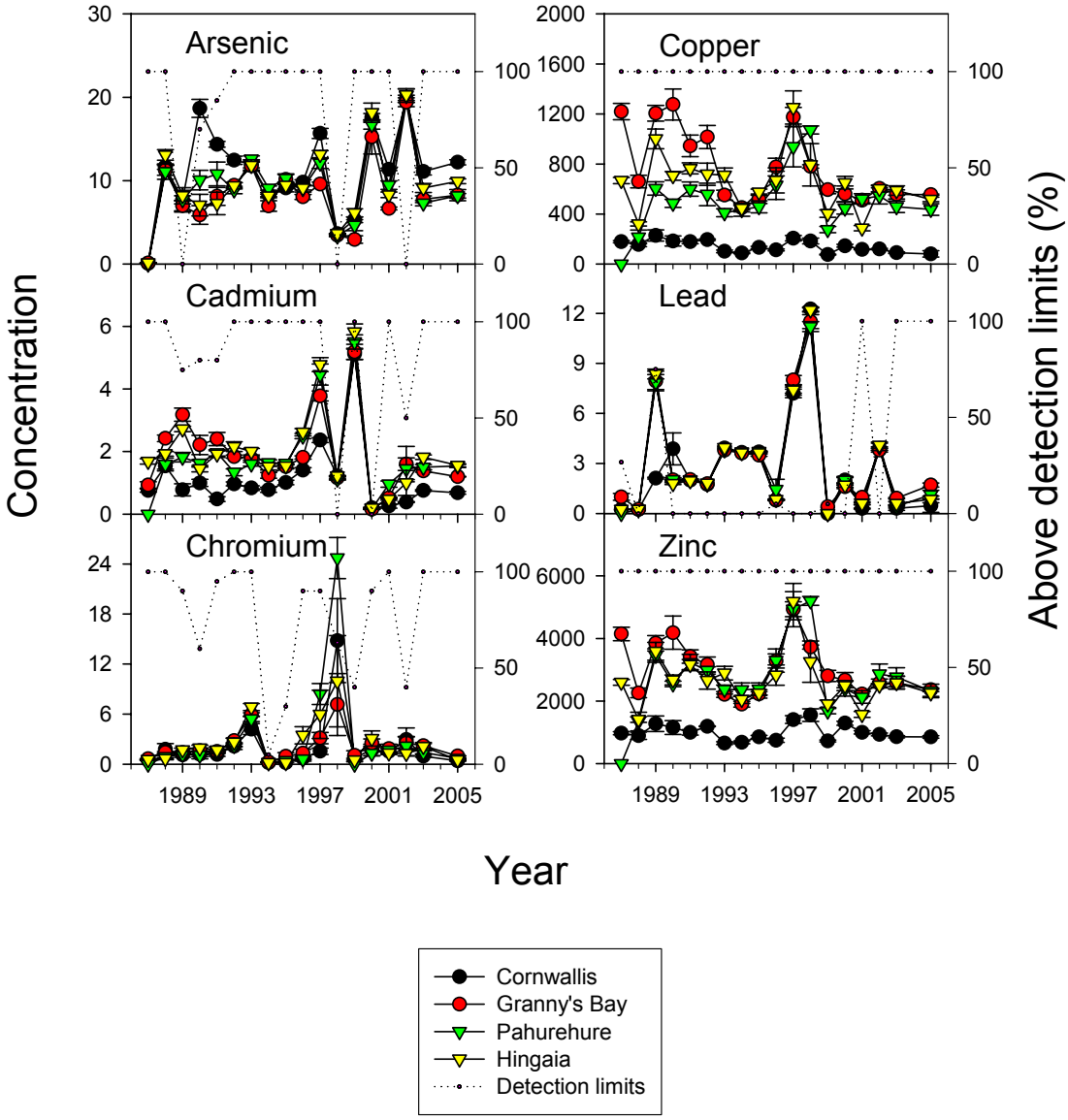
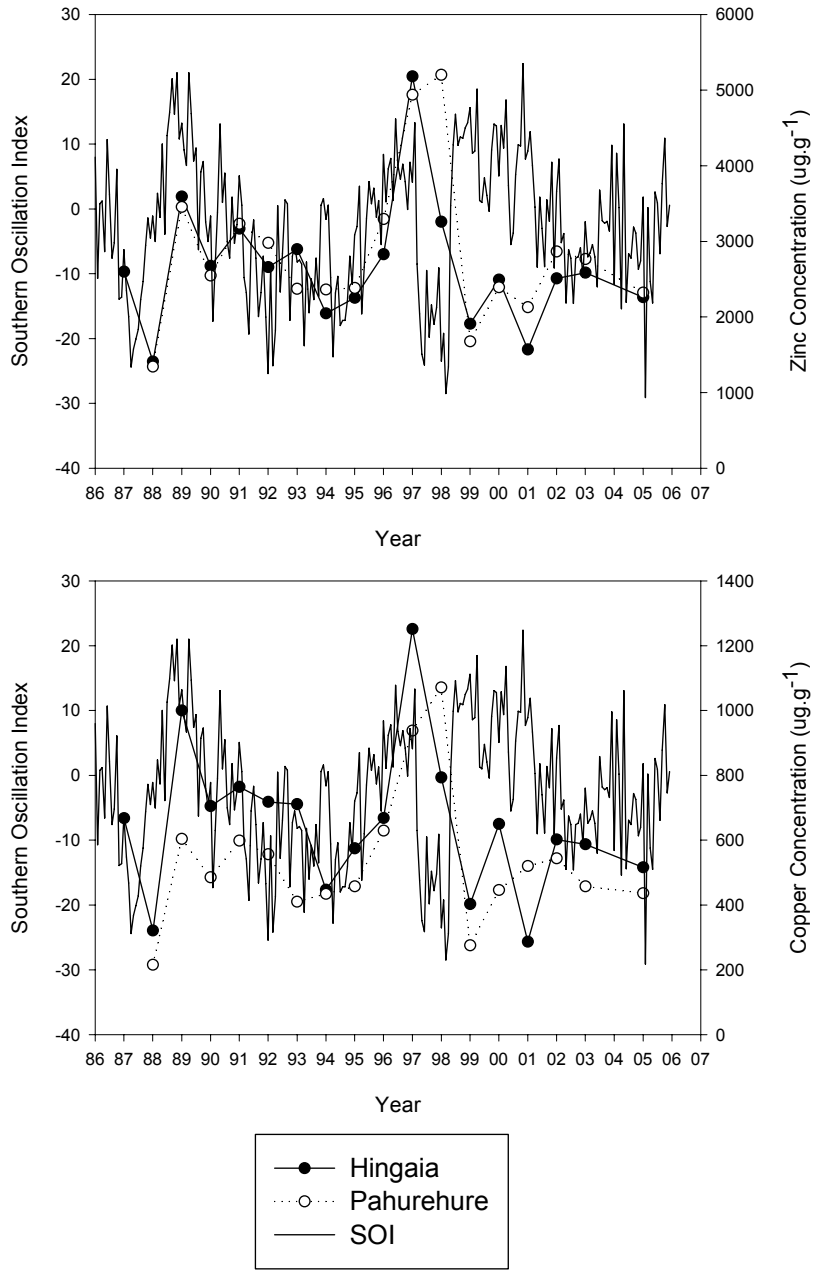


Figure 4-2: Concentrations of (a) zinc and (b) copper concentrations in oysters from Pahurehure and Hingaia, superimposed on the southern oscillation index between 1987 and 2005.



4.1.2 Comparison with International Studies

Mean metal concentrations in Manukau Harbour oysters were compared with those published in the international literature (Table 2). Data published from the USA National Status and Trends (NS&T), French Réseau National d'Observation de la Qualité du Mulieu Marin (RNO) and National Oceanic and Atmospheric Administration world-wide

bivalve databases (WMW) (Cantillo 1998) were compared to mean values from 2005. The NS&T and RNO datasets have an emphasis on shellfish collected from representative, rather than contaminated sites. The 85th percentiles of these datasets therefore reflect the upper bounds of the usual, or expected, range of contaminant concentrations in shellfish. Exceedances of the NS&T and RNO 85th percentiles are considered to be "indicative" of contamination from human activity (Cantillo 1998). The 85th percentiles of the WMW database are slightly higher because it specifically includes shellfish samples from contaminant "hotspots". Exceedances of the WMW 85th percentiles are therefore considered to provide a stronger signal for contamination.

Note that the values presented for World median & 85th percentile data vary between references. Those given in Cantillo (1998) tend to be greater than the values reported by other authors (Scanes and Roach 1999), the exceptions being values for arsenic and the 85th percentiles for zinc. Values from Cantillo (1998) were used for comparisons with ARC oyster data.

Arsenic: Arsenic concentrations were above the medians from the NS&T and WMW datasets, but below the 85th percentiles. Arsenic levels were negatively correlated with those of other metal contaminants, so the highest arsenic levels were obtained from the cleanest site, Cornwallis. However, differences among sites were very small compared with variation through time.

Cadmium: Cadmium levels in the Manukau Harbour were below the medians reported from the three international databases.

Chromium: Chromium levels in Granny's Bay and Pahurehure oysters, were equal to or greater than the median levels provided from the NS&T dataset, but were below those of the WMW dataset.

Copper: Copper levels at Granny's Bay, Pahurehure, and Hingaia were relatively high by international standards, and exceeded the 85th percentiles of the NS&T, and RNO datasets. However, levels were below the 85th percentile of the WMW database. In contrast, copper levels recorded at Cornwallis were below the median levels provided for the NS&T, RNO and the WMW databases.

Lead: Lead concentrations at all four sites were equal to or above the NS&T median values. Granny's Bay concentrations also exceeded the NS&T 85th percentiles. However, all sites were below the RNO and WMW median and 85th percentile values.

Zinc: Zinc levels at Granny's Bay, Pahurehure, and Hingaia were slightly greater than the medians given for the NS&T, RNO and the WMW databases. However, all Manukau Harbour sites were well below the 85th percentiles of the international datasets. Zinc levels at Cornwallis were approximately 2-3 times lower than the other Manukau sites.

Table 2: Comparison of 2005 mean metal concentrations (μg/g dry weight) in Manukau Harbour oysters with published medians from international databases.

Site/Programme	Taxa	Arsenic	Cadmium	Chromium	Copper	Lead	Zinc
Cornwallis	Oysters	12.2	0.68	0.41	80	0.47	852
Granny's		8.3	1.20	0.99	554	1.71	2360
Hingaia		9.9	1.56	0.52	516	0.85	2260
Pahurehure		8.2	1.54	0.70	436	1.12	2320
US NS & T	Oysters	7.9	3.2	0.55	120	0.47	2100
US NS & T 85th %		18	6.0	1.2	280	0.85	4300
RNO (France)	Oysters	-	2.3	-	130	1.4	2100
RNO (France) 85th %		-	6.0	-	320	2.4	3500
WMW (World) median	Oysters	5.7	4.1	2.5	160	2.5	1600
WMW (World) 85th %		14	21	10	680	8.6	4500

Notes: Values presented for World median & 85th% data vary between references. The values given are from Cantillo (1998), which tend to be the greater of the values reported by Scanes and Roach (1999) (exceptions are arsenic and 85th % for zinc).

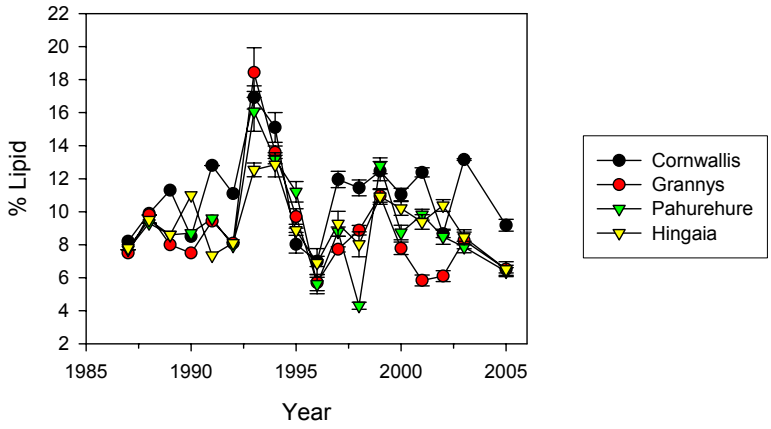
4.1.3 Oyster Organic Contaminants

4.1.3.1 Lipids

Considerable inter-annual variation was detected in the lipid content of oysters, but all sites tended to display similar temporal trends (Figure 4-3). Lipid levels have fluctuated around an overall annual average of 9.7%, with a range of 4.3% – 18.4%.

Contaminant data are presented as concentrations based on total dry weight and as lipid normalised concentrations (Figure 4-4). Data are generally comparable, however, some differences are apparent. For instance, the 1993-1994 peak in DDT concentration for total dry weight data is not reflected in the lipid normalised data. This is due to the dilution effects of relatively high lipid levels in those years.

Figure 4-3: Lipid levels as a percentage of total dry weight in oysters collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 1987 and 2002.



4.1.3.2 Detection limits

Total PAH, total DDT, total chlordane, and total PCB levels were above detection limits in all samples analysed, while dieldrin was detected in >99% of samples. However, lindane concentrations were above detection limits (0.1 – 0.2 ng/g dry weight) in only 41% of samples. Lindane levels below detection limits are presented as 0.5 x D.L.

4.1.3.3 Contaminants

PAH: PAH concentrations in oysters have been reasonably variable since 1995 (i.e. since a consistent set of congeners has been monitored). However, no consistent temporal trends are apparent in oysters from Cornwallis, Granny's Bay, or Pahurehure. In contrast, a significant decline in PAH concentrations has occurred in Hingaia oysters (least squares linear regression, P = 0.032). Clear differences are also apparent among sites. Highest concentrations were recorded at Granny's Bay, Pahurehure and Hingaia. Over the same period (i.e. since 1995) PAH levels in oysters collected from Cornwallis have been consistently low.

Examination of longer term trends in the limited suite of PAHs recommended in the 1998 programme review (Mills 1998) indicates that concentrations have fluctuated around mean values of 218 to 731 ng/g depending on the site, but there have been no persistent, long-term temporal trends (Figure 4-5). However, marked declines in Limited PAH concentrations did occur at all sites between 1995/96 and 1998. Since then concentrations have remained at relatively low and stable at Cornwallis, Hingaia and Pahurehure, but have fluctuated at Grannys Bay. Limited PAH concentrations tend to be highest in Granny's Bay oysters, with a trend for lower concentrations in Pahurehure, Hingaia, and Cornwallis oysters respectively.

DDT: Highest levels of DDT have been recorded at Granny's Bay in 13 of the 18 years that monitoring has occurred (Figure 4-4). A relatively large increase in DDT concentrations in Granny's Bay oysters occurred between 2000 and 2003, coincident

with the decommissioning of the oxidation ponds at the Mangere Sewage Treatment Plant. However, concentrations have since dropped, and 2005 concentrations were the lowest recorded since 2001.

In recent years, DDT concentrations have been similar in oysters from Cornwallis, Hingaia, and Pahurehure. This was repeated in 2005, with no significant differences being detected among these sites. However, DDT concentrations in oysters from all three sites remain significantly lower than those from Granny's Bay (Tukey HSD: P = 0.0002 (all contrasts)).

Longer term patterns for the limited suite of DDT's recommended in Mills (1998) (Figure 4-5) are consistent with the patterns shown in Figure 4-4.

Chlordane: Concentrations of chlordane have dropped exponentially since monitoring began in 1987, due to the phasing out, and eventual deregistration, of this group of compounds (Kelly 2004). The relatively large drop in the chlordane concentrations in oyster tissues at Granny's Bay between 1995 and 1996 (Figure 4-4) is consistent with the longer term pattern of decline (Kelly 2004). However, concentrations increased slightly between 2000 and 2003, matching a rise in DDT concentrations at this site. Since 2003, chlordane concentrations in Granny's Bay oysters have returned to pre-2000 levels.

Oysters from Cornwallis, Hingaia and Pahurehure have had similar, low, concentrations of chlordane since 1997.

Longer term patterns for the limited suite of chlordanes recommended in Mills (1998) (Figure 4-5) are consistent with the patterns for total chlordanes shown in Figure 4-4,

Lindane: Levels of lindane dropped significantly at all sites between 1987 and 1989. Low concentrations of lindane have remained in oysters since then, with little differentiation between sites.

Dieldrin: Dieldrin concentrations in oysters have declined at all sites since monitoring began in 1987. Concentrations have remained at very low levels since 1996, and no significant differences were detectable among sites in 2005 (ANOVA, P = 0.2357).

PCB: PCB concentrations declined at all sites between 1995 and 1997, but rose again in Granny's Bay oysters between 1998 and 2002. Granny's Bay concentrations have subsequently declined, and in 2005, where the lowest recorded at this site. However, they are still significantly greater than the concentrations in oysters from other sites (ANOVA of 2005 data, P = 0.0002). PCB concentrations in oysters from Cornwallis, Pahurehure and Hingaia are consistently low, and in 2005 no significant differences were detected among these sites (Tukeys HSD, P>0.9 (all contrasts)). Longer term patterns for the limited suite of PCB's recommended in Mills (1998), indicate that there was little change in mean PCB concentrations in oysters from Cornwallis, Hingaia and Pahurehure between 1987 and 2005 (Figure 4-5). However, PCB concentrations in oysters from Mangere Inlet have been more variable. At this site, concentrations were relatively high between 1987 and 1995, then dropped suddenly in 1996. They gradually

increased again over the next 6 years before falling again between 2002 and 2005. Overall, PCB concentrations have declined, reflecting their removal from use (officially banned in New Zealand in 1995).

Figure 4-4: Concentrations of organic contaminants in oysters collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 1987 and 2005. Data in plots on the left are expressed as ng/g oyster dry weight (± s.e.) and those on the left are expressed as ng/g lipid. Data below detection limits (DL) are presented as 0.5 x DL.

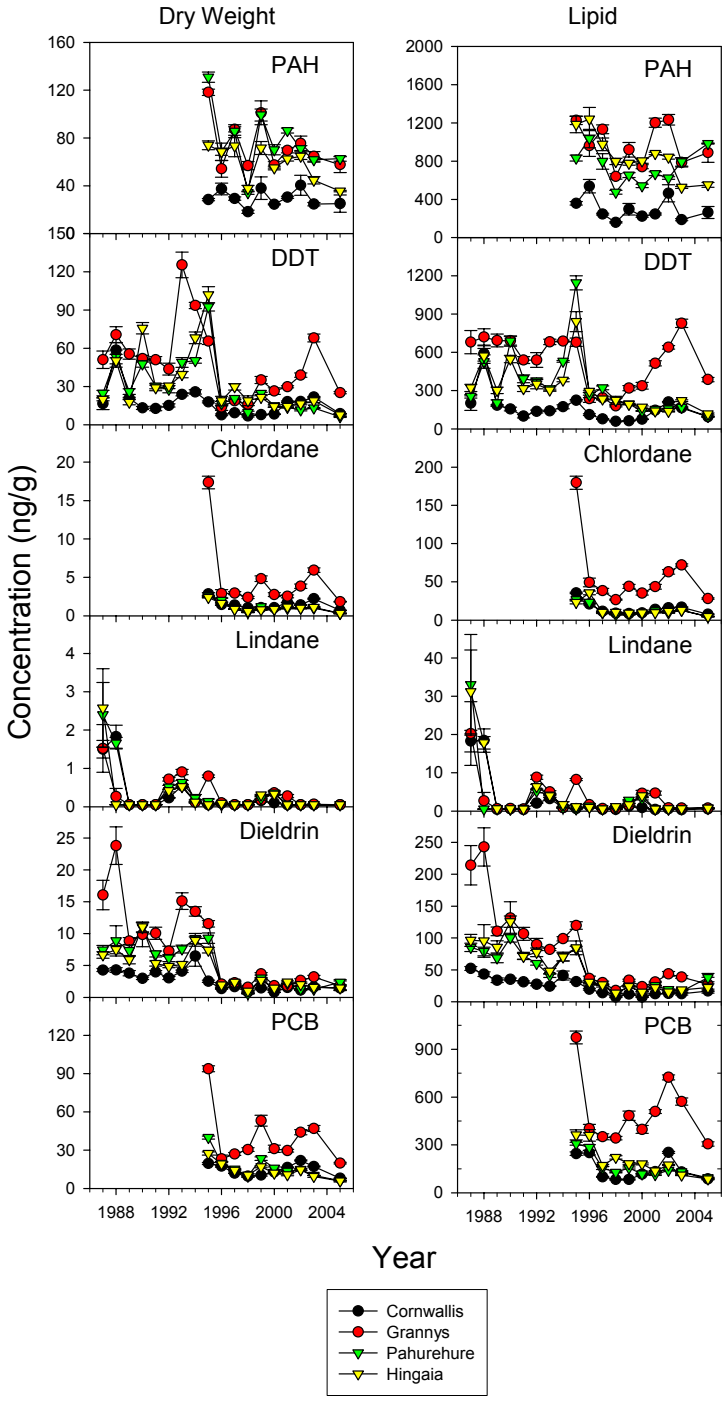
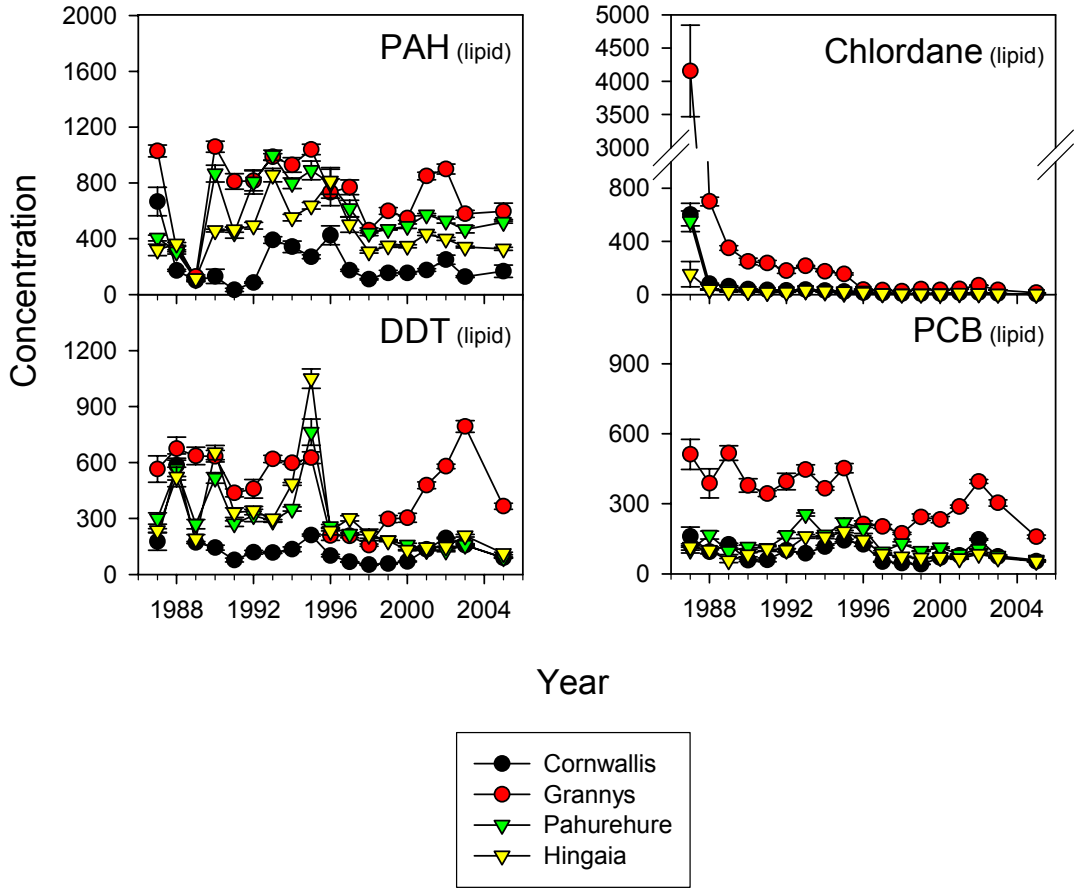


Figure 4-5: Concentrations (ng/g lipid ± s.e.) of lipid normalised **limited** PAHs (sum of fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]-fluorathene, benzo[k]fluoranthene, and benzo[a]pyrene) **limited** PCBs (sum of congeners 118, 138, 153 and 180), **limited** DDTs (sum of p,p′-DDE, p,p′-DDD and p,p′-DDT) and **limited** chlordanes (sum of cis-chlordane and trans-chlordane) recommended by Mills (1998) over the full period of monitoring (1987-2005). All data presented were above detection limits.



Multivariate analyses were used to examine differences among sites in more detail. Cluster and similarity profile analysis indicated statistically significant clusters could be differentiated at Euclidian distances of less than 300 based on oyster concentrations of total PAH, total DDT, total chlordane, lindane, dieldrin and total PCB (Figure 4-6 and Figure 4-7). Clusters could be differentiated into the following general groups:

1. Cornwallis samples (with the exception of two 2002 and one 2005 samples);
2. Hingaia and Pahurehure samples plus the Cornwallis samples listed above;
3. 2000 Granny's Bay samples plus three 2005 Granny's Bay samples;
4. 2001 Granny's Bay samples;
5. 2002 Granny's Bay samples plus two 2005 Granny's Bay samples;
6. 2003 Granny's Bay samples.

Principal Component Analysis (PCA) indicated that samples could be separated along two gradients that were primarily explained by: PAH concentrations; and combined lindane, dieldrin, PCB, chlordane and DDT concentrations (Figure 4-8). Cornwallis, Pahurehure and Hingaia separated in a direction strongly influenced by PAH concentrations, whereas samples from Granny's Bay were much more variable, and reflected the combined influences of PAH and the other organic contaminants.

The general conclusions drawn from the above analyses were that Hingaia and Pahurehure oysters show similar organic contaminant "profiles", differing mainly in their PAH content. Cornwallis oysters were generally different from other sites (although less so in 2002), while Granny's Bay were markedly different from the other sites and showed the greatest variability (both between and within years).

Figure 4-6: Cluster analysis of lipid normalised total PAH, total DDT, total chlordane, lindane, dieldrin and total PCB concentrations in Manukau oysters from 2000 to 2005. Samples grouped by similarity profile analysis are linked in red. The horizontal reference line indicates a Euclidian distance of 300.

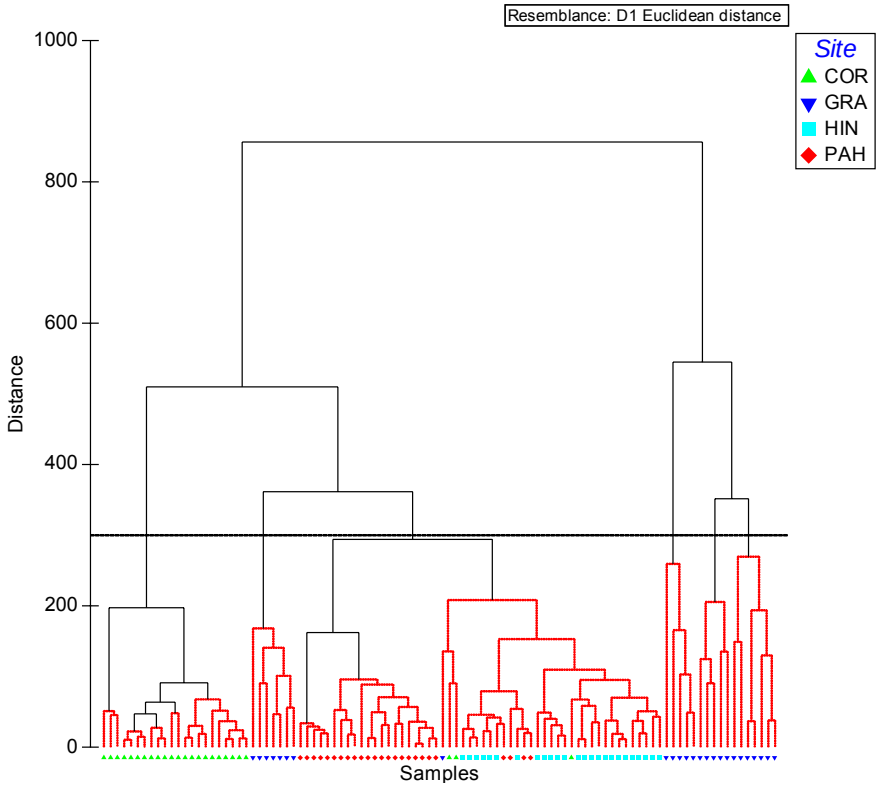


Figure 4-7: Multiple dimensional scaling (MDS) plot of lipid normalised total PAH, total DDT, total chlordane, lindane, dieldrin and total PCB concentrations in Manukau oysters from 2000 to 2005.

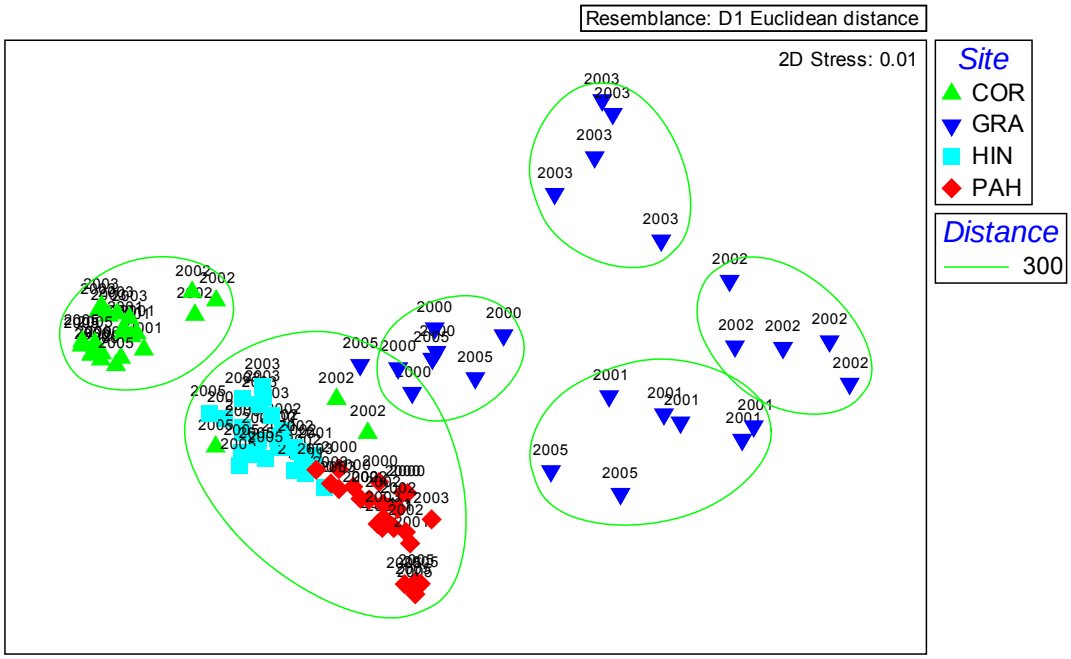
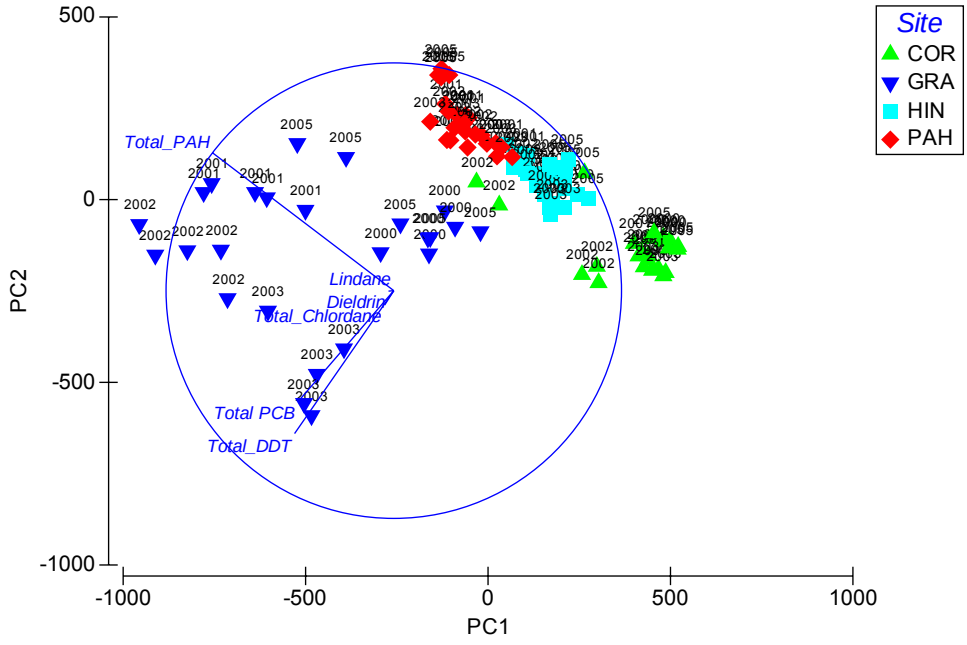


Figure 4-8: Principal components analysis (PCA) of lipid normalised total PAH, total DDT, total chlordane, lindane, dieldrin and total PCB concentrations in Manukau oysters from 2000 to 2005.



PAH and PCB signatures were then examined to determine if the characteristics of these contaminant classes varied among sites and/or times. Individual congeners were only included if they were above detection limits in greater than 50% of samples. Where concentrations were below detection limits, a value of half the detection limit was used.

Cluster and similarity profile analysis identified ten statistically significant PAH clusters at a Euclidian distance of 90 (Figure 4-9). Cluster and MDS analyses (Figure 4-9 and Figure 4-10) indicated that samples with disguisable PAH signatures could be broadly grouped into the following:

1. Samples from Cornwallis;
2. Hingaia samples, most of Pahurehure 2001 to 2003 samples, and most of Granny's Bay 2000, 2003 and 2005 samples;
3. Pahurehure 2005 samples plus one 2002 and one 2003 Pahurehure sample;
4. Remaining Granny's Bay samples.

PCA suggested that the separation of samples along the primary PCA axis, which explained 75.5% of the variation among samples, was due to relatively similar changes in the concentration of most PAH compounds (Figure 4-11) (i.e. the concentrations PAH compounds changed but the ratios between them stayed the same). The secondary axis explained 18.3% of the variation and was mainly influenced by variation in perylene concentrations in Pahurehure samples. Perylene is unusual in that it is a "naturally sourced" PAH formed from plant pigments during sediment diagenesis. It is also present in fuels, oils and other road-related petrogenic materials (e.g. tires and bitumen), which are likely sources for this site, given that it is situated next to the southern motorway.

Figure 4-9: Cluster analysis of lipid normalised oyster PAHs from 2000 to 2005. Samples grouped by similarity profile analysis are linked in red. The horizontal reference line indicates a Euclidian distance of 3.5.

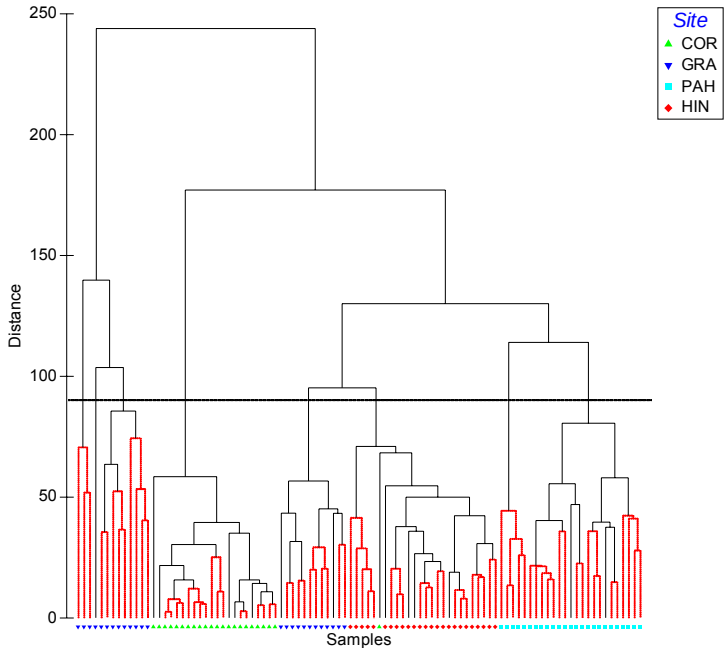


Figure 4-10: Multiple dimensional scaling (MDS) plot of lipid normalised oyster PAHs between 2000 and 2005. Samples are grouped at a Euclidian distance of 90.

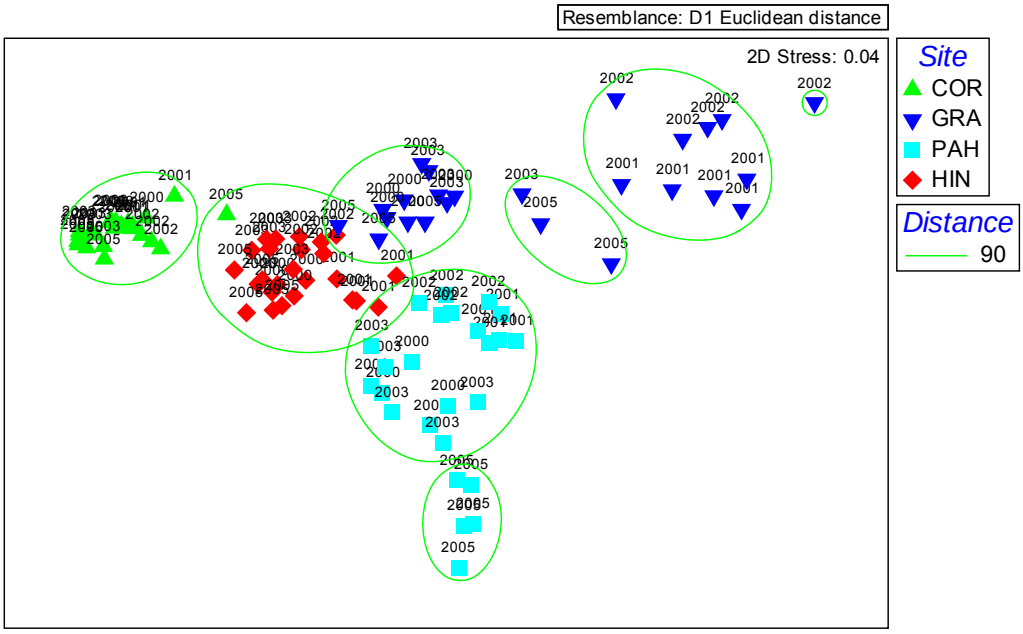
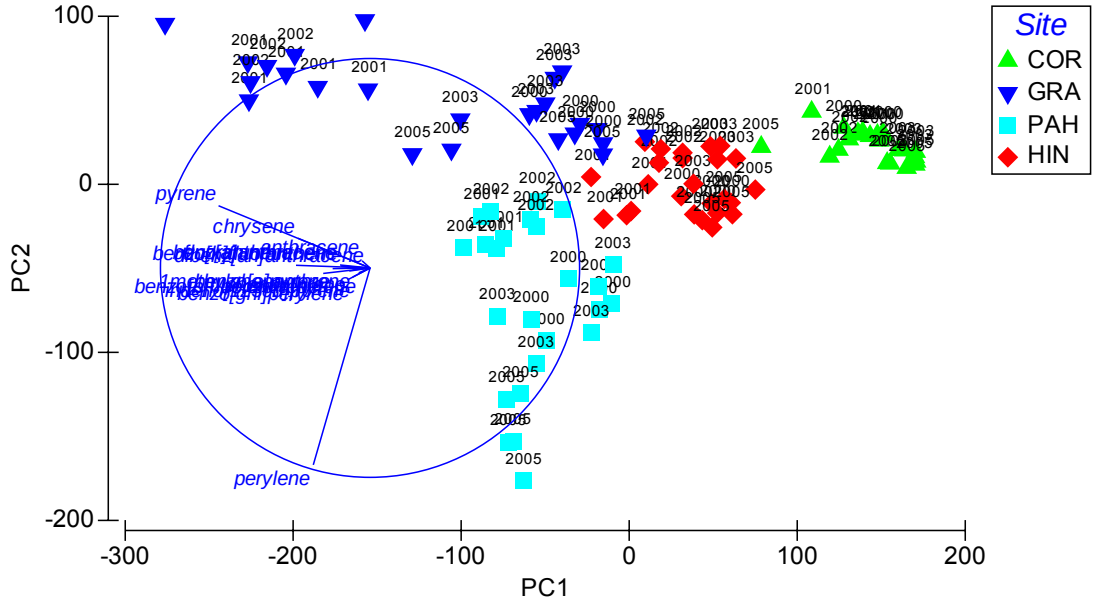


Figure 4-11: Principal components analysis (PCA) of lipid normalised oyster PAHs between 2000 and 2005.



Cluster analysis and MDS broadly split samples into the following groups based on their PCB signatures:

1. Hingaia, Pahurehure and Cornwallis (excluding 2002 samples from this site);
2. 2002 Cornwallis and 2005 Granny's Bay samples;
3. Remaining Granny's Bay samples separated by year.

A PCA of individual PCB congeners in oyster tissues was relatively non-informative, with the primary axis explaining 99% of the variability. The primary axis was not strongly influenced by any particular congener or subset of congeners (Figure 4-11). Rather, it reflected changes in the concentrations of all PCB congeners, but the ratios between individual congeners were maintained. Sites and years were spread along the primary axis in accordance with the patterns obtained from the cluster and MDS analysis.

Figure 4-12: Cluster analysis of lipid normalised oyster PCB's from 2000 to 2005. Samples grouped by similarity profile analysis are linked in red. The horizontal reference line indicates a Euclidian distance of 40.

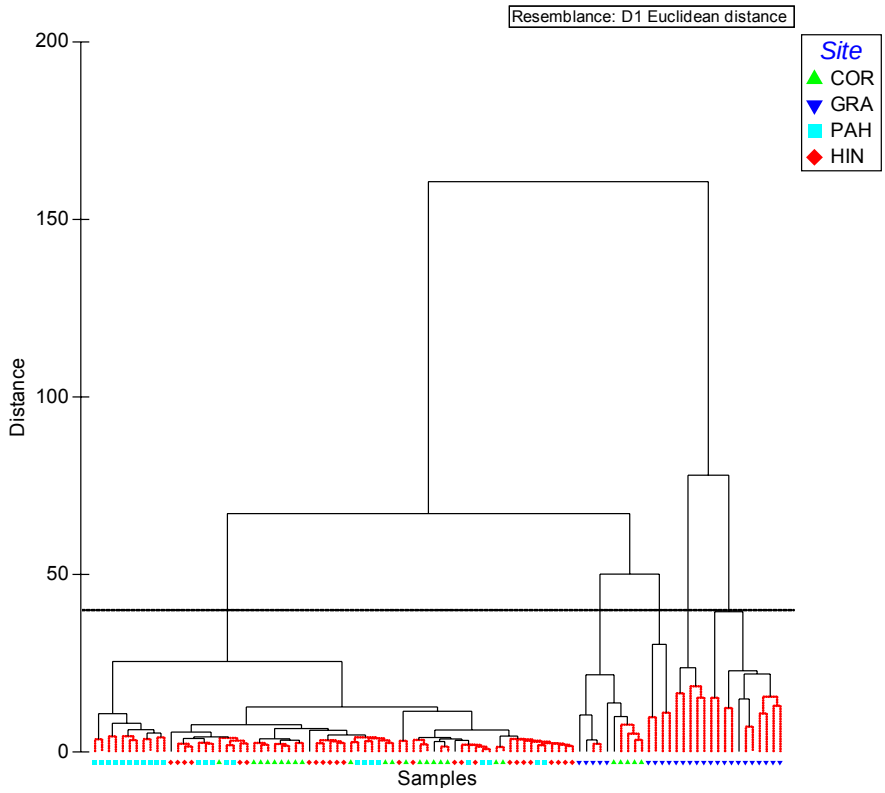


Figure 4-13: Multiple dimensional scaling (MDS) plot of lipid normalised oyster PCB's between 2000 and 2005. Samples are grouped at a Euclidian distance of 40 (refer to Figure 4-12).

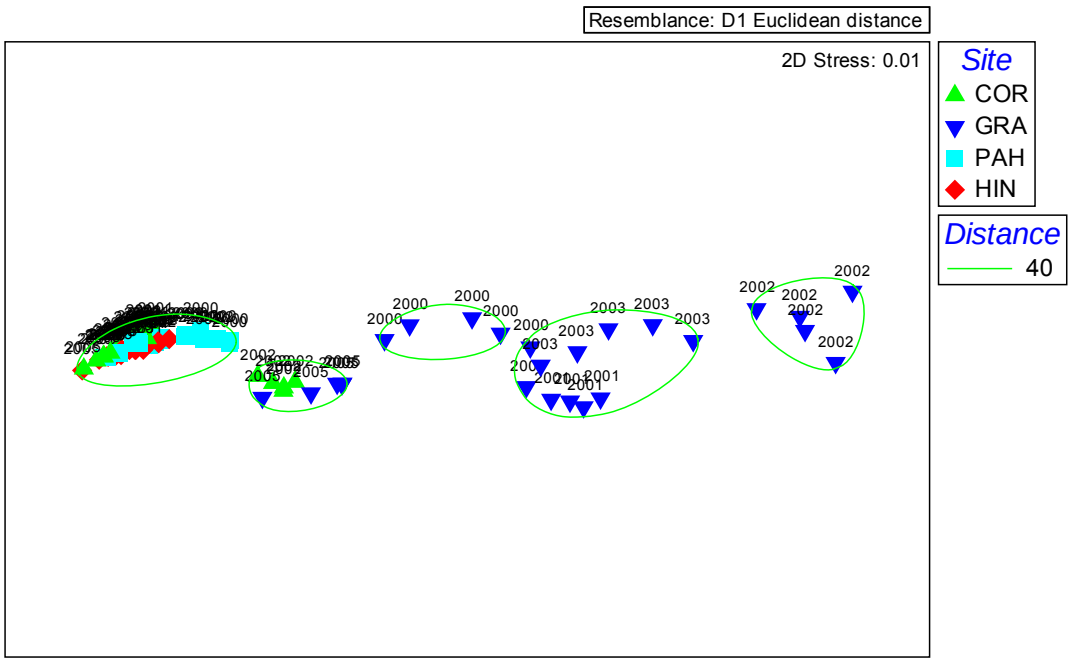
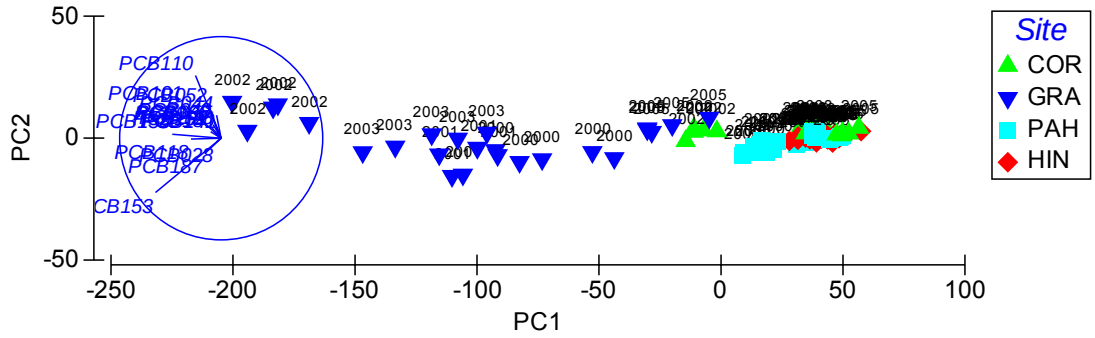


Figure 4-14: Principal components analysis (PCA) of lipid normalised oyster PAHs between 2000 and 2005.



4.1.4 Comparisons with International Studies

Comparisons of organic contaminants were made with two published studies from the USA and South America: Sericano et al. (1995) and Lauenstein et al. (2002). Total PAH levels derived from the ARC monitoring programme were not directly comparable with the published values because of differences in the suite of PAH compounds analysed (Table B3 in Appendix B: Contaminants Measured) (note that fewer PAH compounds are included in Sericano et al. (1995) and Lauenstein et al. (2002) than are actually measured in the NS&T programme (see Lauenstein and Cantillo 1998)). Dieldrin levels reported in Sericano et al. (1995) and Lauenstein et al. (2002) were derived from the sum of dieldrin and aldrin, and therefore are not directly comparable with ARC data. However, aldrin is generally a very minor component of this set because it is transformed to dieldrin in the environment (Geoff Mills pers. comm.). Consequently, comparisons of dieldrin levels in Manukau oysters with published levels of dieldrin+aldrin are still informative. Overseas data on lindane levels were not obtained. However, chlordane, PCB, and DDT levels could be directly compared with the summary data reported (Lauenstein et al. (2002) and Sericano et al. (1995)).

The overall conclusion from the comparison of organic contaminants in Manukau oysters with international datasets, was that local concentrations were relatively low (Table 4). The degree of variability observed in Manukau oysters should therefore be interpreted within this context, i.e. observed levels are highly variable from year to year (within a fairly limited range of concentrations), but overall concentrations are low by international standards.

4.1.5 Summary of Contaminants in Oysters

- Zinc concentrations were highest at Granny's Bay, Pahurehure, and Hingaia, where they were comparable to moderate levels of zinc reported in international studies.
- Copper levels were relatively high at Granny's Bay, Pahurehure, and Hingaia. Concentrations at these sites were approaching levels that are indicative of copper contamination.

- Concentrations of arsenic, cadmium, chromium and lead were relatively low.
- Granny's Bay has a distinguishable organic contaminant signature that reflects the combined influence of PAH and other organic contaminants in oyster tissues. The contaminant signatures of the other Manukau sites is mainly driven by PAH concentrations.
- PAH levels are highest at the most urbanised site (Granny's Bay) and the site adjacent to the southern motorway (Pahurehure).
- Pahurehure has a clearly distinguishable PAH signature related to elevated concentrations of perylene (which has natural origins, as well as being found in road-related "petrogenic" sources (e.g. tires, bitumen), non-combusted fuels and oils and their combustion by-products).
- PCB concentrations at Granny's Bay are relatively high compared with other Manukau sites, but they have fallen over time, including over the last two monitoring periods.
- PCB concentrations vary among monitoring sites, but the ratios of individual cogeners are relatively similar.
- A pulse in DDT levels was observed in Granny's Bay oysters between 2000 and 2003, coincident with the decommissioning of oxidation ponds at the Mangere Sewage Treatment Plant. Concentrations of DDT have subsequently returned to levels recorded in 2000.
- Chlordane, lindane, and dieldrin have declined to low levels since monitoring began, consistent with them being de-registered as pesticides.

Table 3: Comparison of mean, 2005 organic contaminant concentrations in Manukau Harbour oysters with published values from international studies. Data for Central and South Americas are based on values for 76 monitoring sites and includes data pooled for oysters, mussels and other bivalves. Data for the Gulf of Mexico and US are derived from oysters and mussels collected at 51 sites. All data are presented as ng/g total dry weight. Concentrations among different bivalves collected from the same site may vary by up to a factor of four, while differences between oysters and mussels generally agree within a factor of two (see Sericano et al. 1995).

Site/Programme	Taxa					Dieldrin	
Cornwallis	Oysters	25.02	8.58	0.70	0.1	1.48	7.98
Granny's		57.64	25.13	1.83	0.1	1.82	19.89
Hingaia		35.51	7.73	0.31	0.1	1.47	5.72
Pahurehure		62.61	6.20	0.28	0.1	2.38	6.03
Central and South America.[6]	24% Oysters, 45% mussels, 31% other bivalves	n/a	45% < 10 41% 10-100 14% >100 (n=76)	95% <10 4% 10-100 1% >100 (n=76)			42% <10 46% 10-100 9% 100-1000 3% > 1000 (n=76)
Gulf of Mexico[6]	Oysters	n/a	8% < 10 86% 10-100 6% >100 (n=51)	63% < 100 37% 10-100 0% > 100 (n=51)			0% <10 86% 10-100 14% 100-1000 0% > 1000 (n=51)
US NS & (median)	Oysters	n/a	33 (n=280)	10 (n=280)		5. (n=280)	(n=280)
US NS & T 85th %[7]		n/a	140	32		15[8]	450[9]

[1] ARC data not comparable with international data due to differences in the types of PAHs analysed. PAHs included in estimates are provided in Table 3.
[2] Sum of DDTs, DDEs, and DDD's.
[3] Sum of *cis*- chlordane, *trans* – nonachlor, heptachlor, and heptachlor epoxide.
[4] Data not provided in the international studies examined.
[5] ARC values derived from only those congeners listed in Lauenstein et al. (2002) as analysed by the NS&T programme (given in Table 3). A specific list of congeners was not provided for Central and South America and Gulf of Mexico, but the latter data were a subset of data from the NS&T programme and both sets are assumed to be consistent with data presented in Lauenstein et al. (2002).
[6] Sericano et al. (1995).
[7] Lauenstein et al. (2002).
[8] Sum of dieldrin and aldrin.
[9] Sum of the concentrations of homologs which is approximately 2 x the sum of the 18 congeners given for the NS&T programme in Table 5 (Lauenstein et al. 2002). Note that the 18 congeners listed in Table 5 are major ones and probably constitute approximately 50% of the total PCBs present. However, estimating total PCBs by doubling the measured concentrations of a limited number of congeners is somewhat unusual (Geoff Mills pers. com.).

4.2 Mussel Contaminants

4.2.1 Key Metals

4.2.1.1 Detection limits

Trends in the concentration of some key metals in mussels were strongly influenced by analytical detection limits. Most or all mussel samples had concentrations below the detection limits for arsenic in 2002, cadmium in 2000 & 2002, and lead in 2000 & 2002 (Table 5). In some cases the detection limits were higher than values that are indicative of elevated contaminant levels. For instance, the mean detection limit for arsenic in 2002 was 38 µg / g, which was substantially higher than the levels measured in mussels in previous years, and is greater than the 85th percentiles reported from US mussel watch programme and world database (Cantillo 1998). The variability in analytical sensitivity therefore made comparisons between years problematic. The laboratory used to analyse metal concentrations was changed in 2005, and issues related to detection limits should now be resolved.

Table 5: Proportion of mussel samples with key metal concentrations above detection limits between 1999 and 2005. Average detection limits are provided in brackets where concentrations were below detection in some, or all, samples.

Year	Arsenic	Cadmium	Chromium	Copper	Lead	Zinc
1999	100%	100%	100%	100%	100%	100%
2000	100%	0% (0.36)	92% (0.97)	100%	0% (3.7)	100%
2001	100%	100%	100%	100%	100%	100%
2002	0% (38)	22% (0.77)	84 %(2)	100%	0% (7.6)	100%
2003	75% (22)	84% (0.44)	100%	100%	75% (4.4)	100%
2005	100%	100%	100%	100%	100%	100%

4.2.1.2 Contaminants

Arsenic: Between 1999 and 2001 mean arsenic levels in mussel samples fluctuated between 0.5-16.8 µg / g (Figure 4-15). Arsenic levels reported for 2002 reflected means of 0.5 x detection limits rather than true values, and should therefore be regarded only as indicative. Arsenic concentrations were highly correlated among sites and coasts (correlation coefficients all > 0.83, see Appendix C: Correlations between metals in oysters and mussels), suggesting that inter-annual variation may be due to the degree of analytical sensitivity rather than true temporal variation.

Cadmium: Cadmium levels appeared to decline markedly at all east coast sites between 1999 and 2000. However, the exceptionally high 1999 values are anomalous in that they were: 1) recorded from all sites including "clean" reference sites; 2) found in mussels prior to deployment; 3) have not been repeated since. The 1999 cadmium levels are therefore considered to be unreliable. In 2000 no samples exceeded relatively low detection limits (mean D.L. = 0.37 µg / g) and average concentrations at individual sites have remained less than 1.4 µg / g ever since. No spatial patterns are

apparent in cadmium concentrations, but cadmium levels were highly correlated among sites in 50% of site-site comparisons (correlation coefficients > 0.75).

Chromium: Since 1999/2000 chromium concentrations have remained relatively stable at all sites except the Upper Waitemata Harbour and Weymouth, where considerable intra- and inter-annual variability is evident. A pulse of high chromium concentrations was recorded in Upper Waitemata mussels in 2001-02, and in Weymouth mussels in 2002.

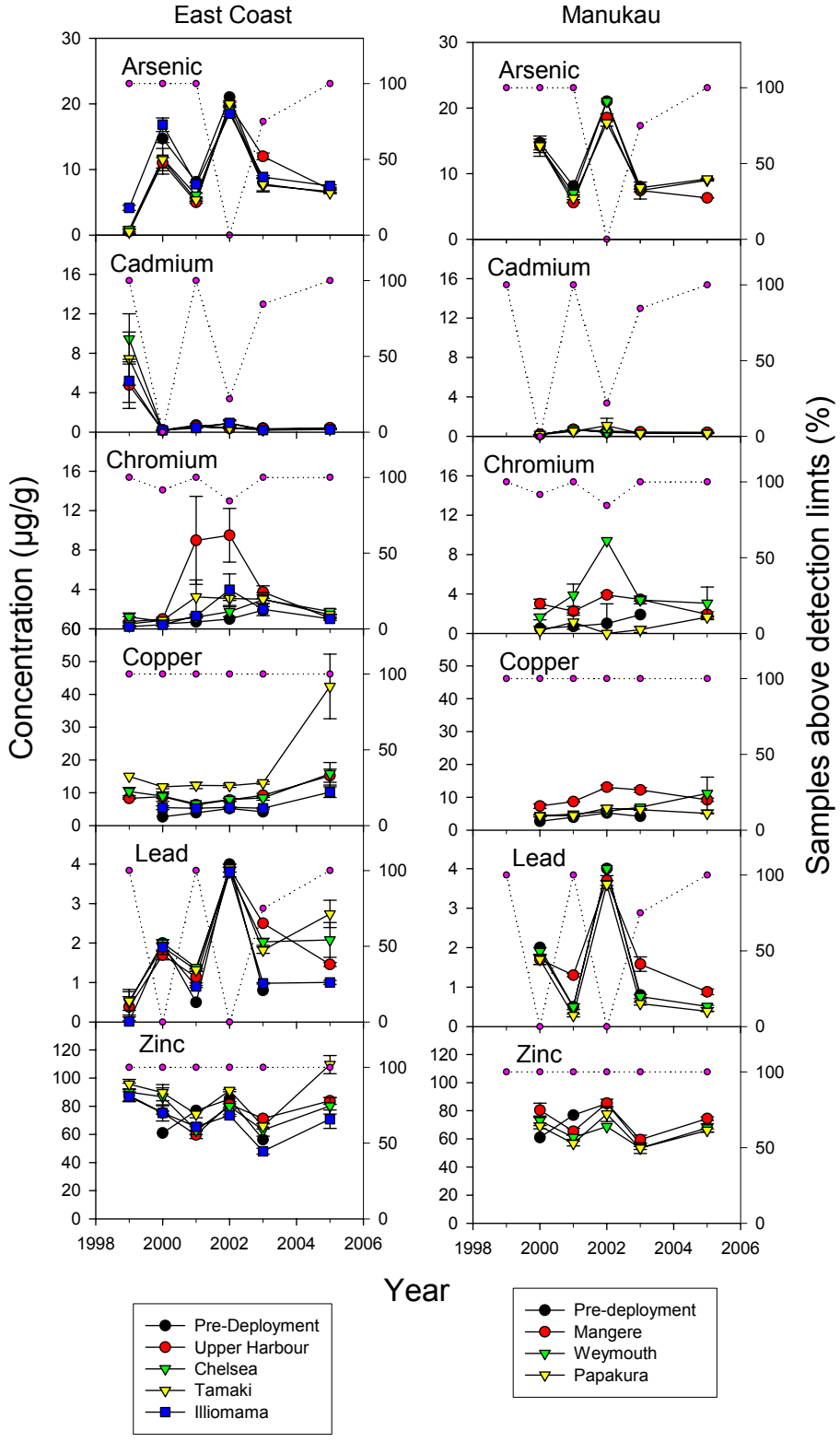
Copper: Clear spatial trends are discernable in copper concentrations. On the east coast highest copper concentrations are consistently recorded in mussels from the Tamaki Estuary and a distinct spike in Tamaki copper concentrations was recorded in 2005. The Upper Waitemata Harbour and Chelsea sites have yielded relatively low copper concentrations, which are marginally higher than those in mussels recovered from Illiomama. Pre-deployment concentrations are generally similar to those obtained from mussels set at Illiomama. In the Manukau Harbour between 2000 and 2003, highest copper levels were recorded in mussels from Mangere Inlet, while copper levels in Weymouth and Papakura mussels were similar to those recorded in pre-deployments mussels. Between 2003 and 2005, copper levels increased slightly in mussels recovered from Weymouth and reached concentrations similar to those from Mangere Inlet.

Lead: No trends are apparent in mussel lead concentrations. However, the analysis of lead is limited by high detection limits for lead in 1999 and 2001 and the fact that concentrations in all samples were below detection limits in these years

Zinc: Zinc levels have remained relatively stable at all sites except Tamaki, since 1999/2000, with no clear differences between sites. Tamaki differs from the other sites only in the comparatively large increase in zinc concentrations recorded between 2003 and 2005.

Overall, the metals results generally indicate little or no change over time, and relatively little difference between sites. The most consistent indication of metal contamination is the slightly higher concentrations of copper in mussels deployed at Tamaki and Mangere. It appears that metals' content of mussel tissue (for a 3 month deployment) is a relatively insensitive measure of differences in contamination between sites (e.g. compare mussel results with those for copper and zinc in Manukau oysters), or that the water quality at these sites is not greatly different over the deployment period.

Figure 4-15: Mean concentrations (µg/g (mussel dry weight) ± s.e.) of key metals in mussels at sites in the east coast (left) and Manukau Harbour (right) between 1999 and 2005. Data below detection limits (DL) are presented as 0.5 x DL. The pooled proportion (%) of samples exceeding detection limits is also given (pink symbol & dotted line).

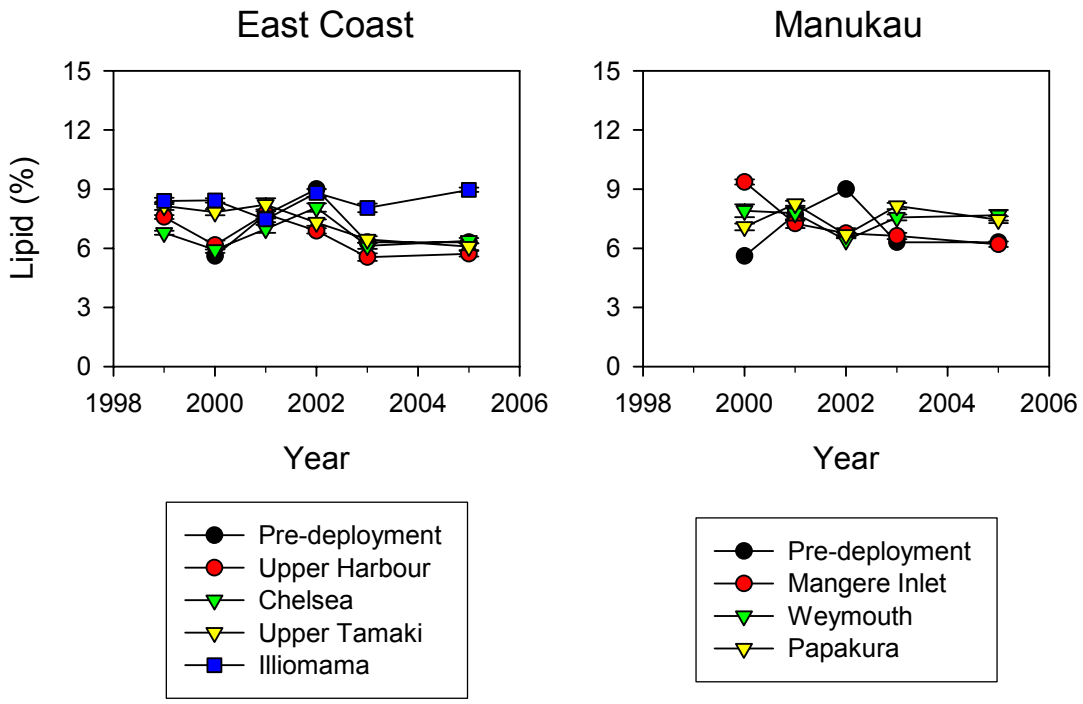


4.2.2 Mussel Organic Contaminants

4.2.2.1 Lipids

Organic contaminant data are presented as concentrations based on total dry weight and as lipid normalised concentrations. The lipid contents of mussels were relatively consistent over the monitoring period (approximately 5-10% lipids), with no discernable differences among sites (Figure 4-16). Consequently, the trends in lipid normalised data were very similar to the trends in non-normalised data. Lipid normalised data were therefore used for subsequent analyses.

Figure 4-16: Lipid content (% ± s.e.) as a proportion of total dry weight in mussels set on the east coast (left) and Manukau Harbour (right) between 1999 and 2002.



4.2.2.2 Detection limits

PAH, DDT, chlordane, and PCB levels were above detection limits in all samples analysed, while dieldrin was able to be quantified in 99% of samples. However, lindane concentrations were above detection limits (0.1 – 0.2 ng/g dry weight) in only 21% of samples. Lindane levels below detection limits are therefore presented as 0.5 x DL.

4.2.2.3 Contaminants

PAH: Mean PAH concentrations were consistently highest in mussels from the Upper Waitemata Harbour, Chelsea, and Upper Tamaki sites between 2000 and 2005. Over the same period, PAH concentrations were intermediate in samples from Illiomama and Mangere Inlet, and lowest in pre-deployment, Papakura, and Weymouth samples. PAH

concentrations have varied through time, but apart from a drop in mussels recovered from Illiomama between 1999 and 2000, no consistent temporal trends are apparent.

DDT: A temporally-consistent gradient in DDT concentrations was apparent among sites. On the east coast DDT concentrations in mussels from the Upper Waitemata Harbour and Chelsea were > Upper Tamaki > Illiomama > pre-deployment. In Manukau Harbour, DDT concentrations in mussels from Mangere Inlet were >> Papakura and Weymouth > pre-deployment[2].

Between 2000 and 2002, DDT concentrations increased markedly in Mangere Inlet and remained elevated through to 2005 (compare with Manukau oysters, where concentrations also increased to 2003, but decreased in 2005). Inter-annual variation at the other sites was relatively low and no consistent temporal trends are apparent.

Chlordane: Concentrations of chlordane have been consistently highest in Mangere Inlet. Furthermore, a marked pulse in chlordane concentration occurred in Mangere Inlet between 2000 and 2005. A gradient is apparent at the other sites whereby, on the east coast chlordane concentrations in mussels from Upper Tamaki are > Upper Harbour and Chelsea > Illiomama > pre-deployment. In Manukau Harbour, Mangere Inlet chlordane concentrations are >> Papakura and Weymouth > pre-deployment[2]. Inter-annual variation was relatively low with some indication of a slight downward trend in the concentration of chlordane in mussels recovered from east coast sites.

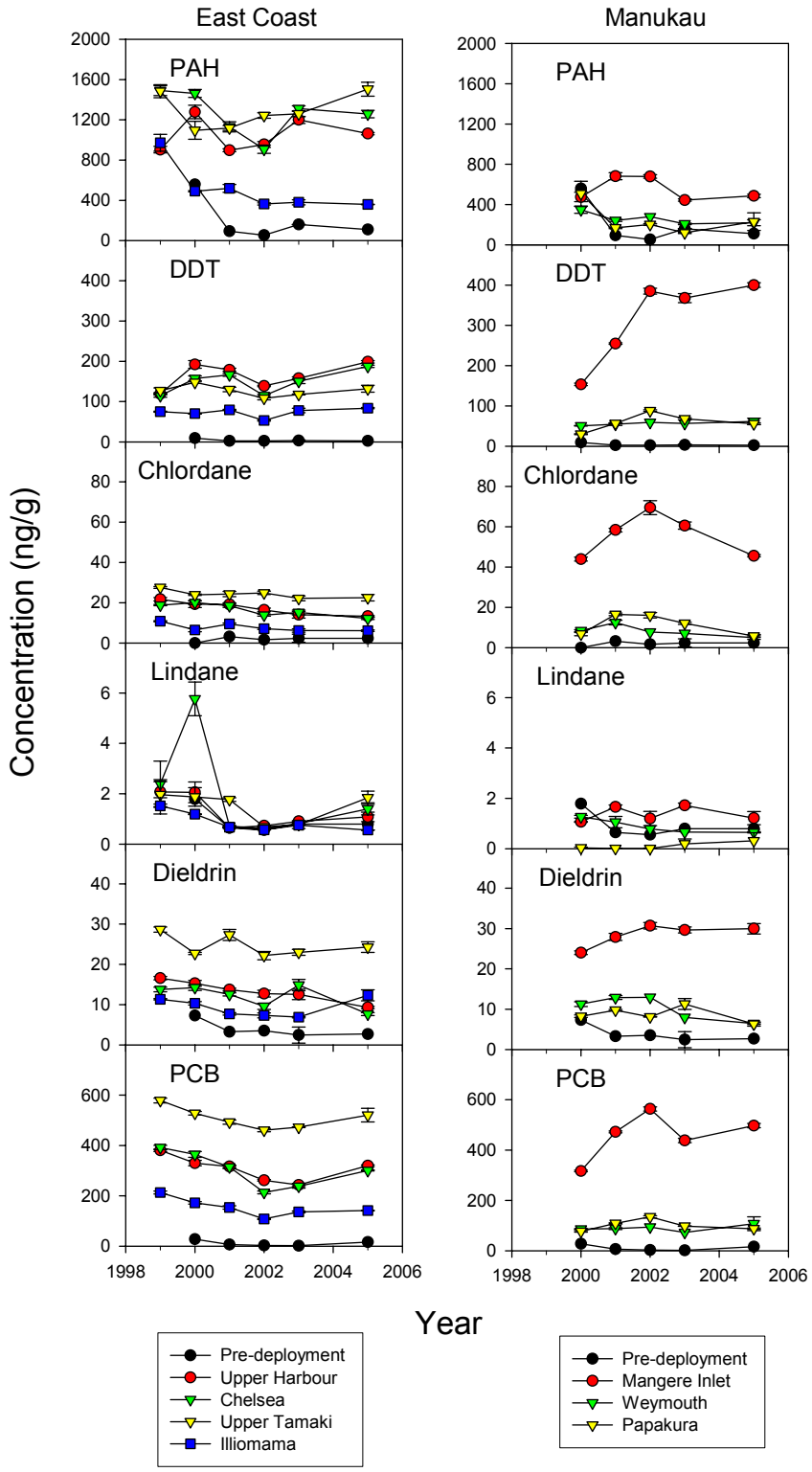
Lindane: Apart from Chelsea in 2000, concentrations of lindane have been consistently low at all sites since 1999-2000.

Dieldrin: A gradient in dieldrin concentration occurred with Upper Tamaki concentrations > Upper Harbour, Chelsea and Illiomama > pre-deployment on the east coast. And: Mangere Inlet concentrations >> Papakura and Weymouth > pre-deployment in Manukau Harbour. Inter-annual variation was relatively low, but there has been a slight downward trend in dieldrin concentrations at the Upper Waitemata Harbour site. Conversely, dieldrin concentrations increased slightly in mussels recovered from Mangere inlet between 2000 and 2002.

PCB: A consistent gradient on PCB concentrations was apparent, with: Upper Tamaki concentrations > Upper Harbour and Chelsea > Illiomama > pre-deployment on the east coast. And: Mangere Inlet >> Papakura and Weymouth > pre-deployment in Manukau Harbour. Consistent temporal trends were not apparent through time in the east coast, Papakura and Weymouth sites. PCB concentrations in mussels recovered from Mangere Inlet were more variable than in mussels from the other sites, but there was no consistent temporal trend.

[2] > = greater than, >> = much greater than.

Figure 4-17: Lipid normalised organic contaminant concentrations (ng / g (lipid)) of mussels trans-located into the east coast (left) and the Manukau Harbour (right), from 1999 to 2005. Values are also given for contaminant levels in samples prior to deployment. Data below detection limits (DL) are presented as 0.5 x DL.



Multivariate analyses were then used to examine differences among sites in more detail. Cluster and similarity profile analysis indicated statistically significant clusters could be differentiated at Euclidian distances of less than 275 (Figure 4-17). Clusters differentiated at this level and superimposed on an MDS plot (Figure 4-18) could be broadly placed into the following groups:

1. Mangere Inlet 2001-2005 samples;
2. Mangere Inlet 2000 samples;
3. Upper Tamaki, Upper Harbour and Chelsea samples;
4. Pre-deployment, Illiomama, Papakura, and Weymouth samples.

Figure 4-17: Cluster analysis of lipid normalised total PAH, total DDT, total chlordane, lindane, dieldrin and total PCB concentrations in mussels. Samples grouped by similarity profile analysis (SIMILARITY PROFILE) are linked in red. A reference line showing a Euclidian distance of 275 is provided.

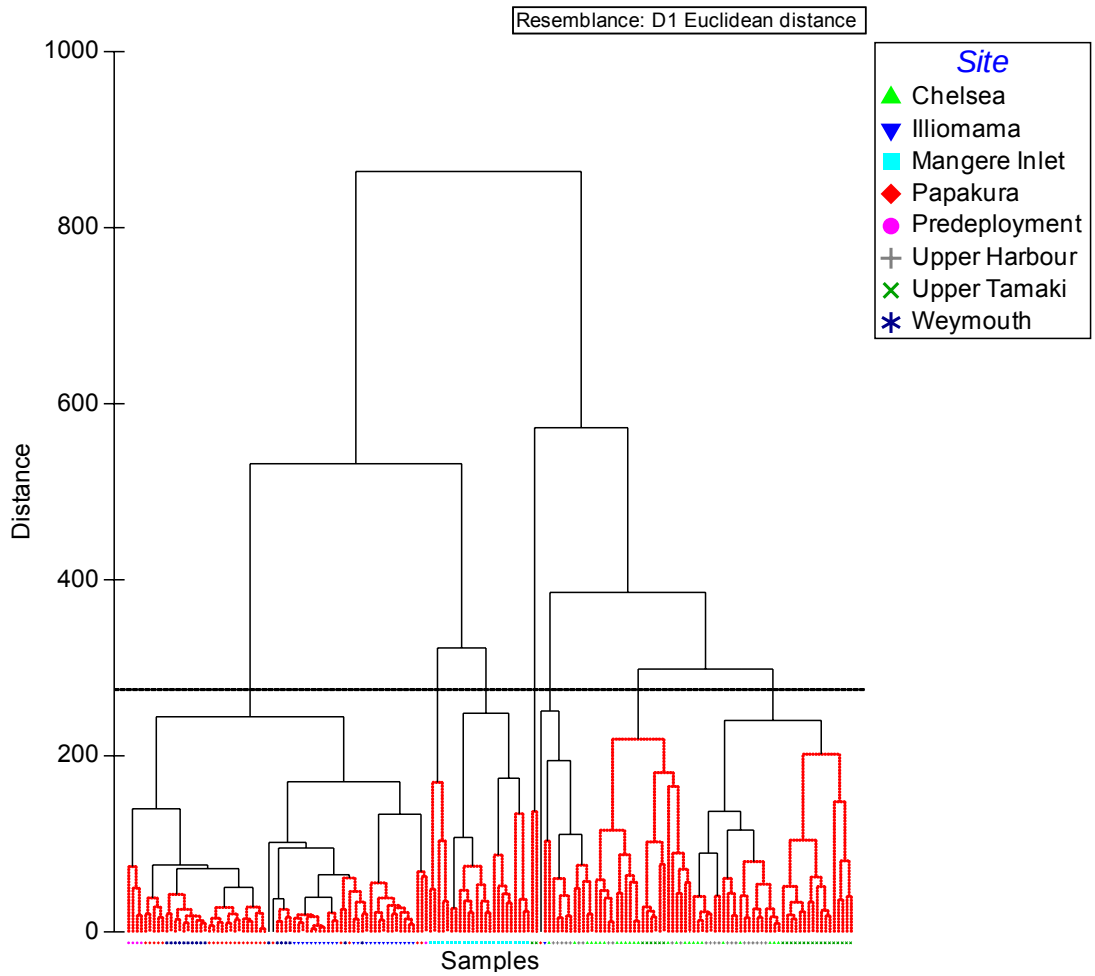
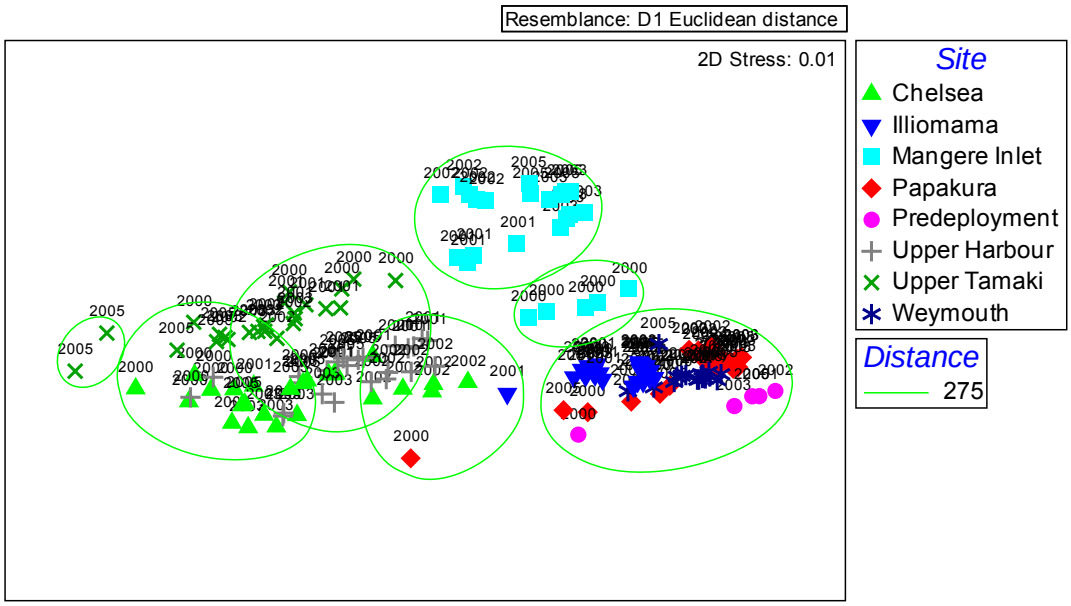
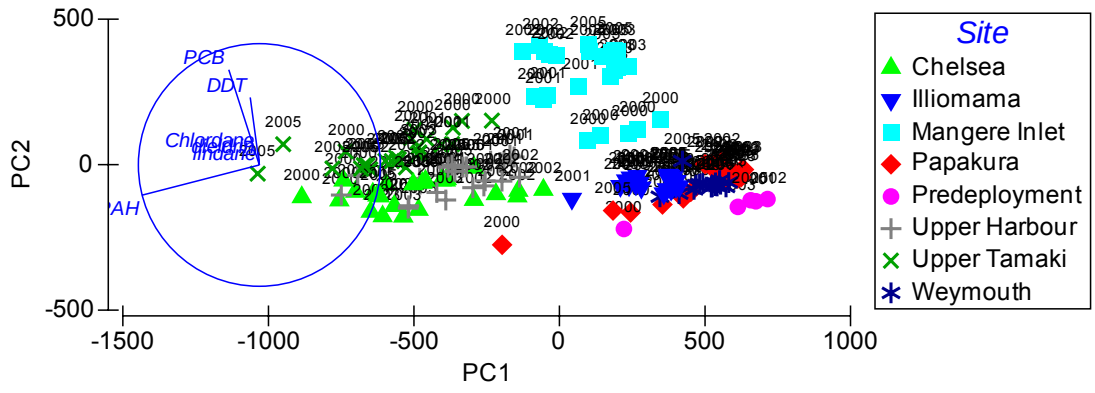


Figure 4-18: Multiple dimensional scaling (MDS) plot of lipid normalised total PAH, total DDT, total chlordane, lindane, dieldrin and total PCB concentrations in mussels. Samples are grouped at a Euclidian distance of 275 (refer to Figure 4-17).



Principal component analysis was then carried out on concentrations of total PAH, total DDT, total chlordane, lindane, dieldrin and total PCB to examine the relative influence of each variable. This indicated that samples could be separated along similar axes to those found in oysters, i.e. PAH concentrations and other organic contaminant concentrations (Figure 4-19). The primary axis explained 90% of the variation and was strongly influenced by PAH concentrations. The secondary axis reflected high concentrations of DDT and PCBs in Mangere Inlet. Chlordane and dieldrin also varied along the secondary axis, but concentrations of these two contaminants were substantially less than those of DDT and PCBs, so their influence on PCA trends was also less.

Figure 4-19: Principal components analysis (PCA) of lipid normalised total PAH, total DDT, total chlordane, lindane, dieldrin and total PCB concentrations in mussels.



The PAH and PCB congeners were then examined to determine if the characteristics of these contaminant classes varied among sites and/or times. Concentrations below analytical detection limits were replaced by a value of half the value of the detection limit.

Cluster and similarity profile analysis, together with multiple dimensional scaling (MDS) indicated that the PAH signatures of samples collected in 2000 were distinctly different from other years (Figure 4-20 and Figure 4-21). PCA indicated that this was due to unusually high concentrations of fluoranthene in the 2000 samples (Figure 4-22). The high fluoranthene concentrations obtained from 2000 masked patterns obtained from other years. Data from 2000 was therefore dropped and the analyses re-run.

Cluster analysis and MDS of the reduced data-set distinguished the following broad groups based on their PAH signatures:

1. Mangere Inlet 2003 and 2005 samples, Illiomama, Papakura, Weymouth and pre-deployment samples;
2. Mangere Inlet 2001 and 2002 samples;
3. Chelsea and Upper Harbour samples;
4. Upper Tamaki samples.

The primary PCA axis explained 90% of sample variation, but it was not strongly influenced by any particular PAH congeners (Figure 4-24 (a)). Perylene and pyrene tended to have higher concentrations than other PAH congeners and explained some of the additional variation among sites on the secondary axis. (Figure 4-24).

Figure 4-20: Cluster analysis of lipid normalised mussel PAHs. Samples grouped by similarity profile analysis (SIMILARITY PROFILE) are linked in red. A reference line showing a Euclidian distance of 160 is provided.

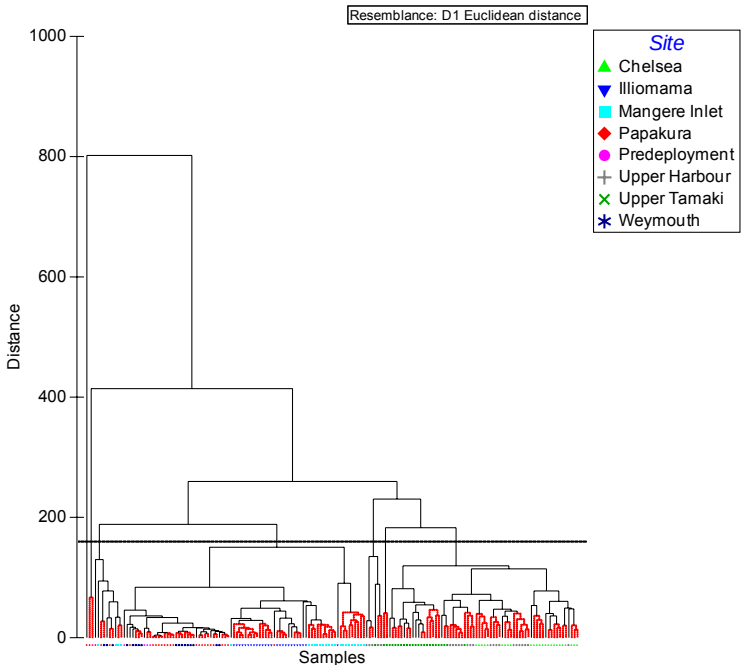


Figure 4-21: Multiple dimensional scaling (MDS) plot of lipid normalised mussel PAHs. Samples are grouped at a Euclidian distance of 4.5 (refer to Figure 4-20). Samples are grouped at a Euclidian distance of 160 (refer to Figure 4-20).

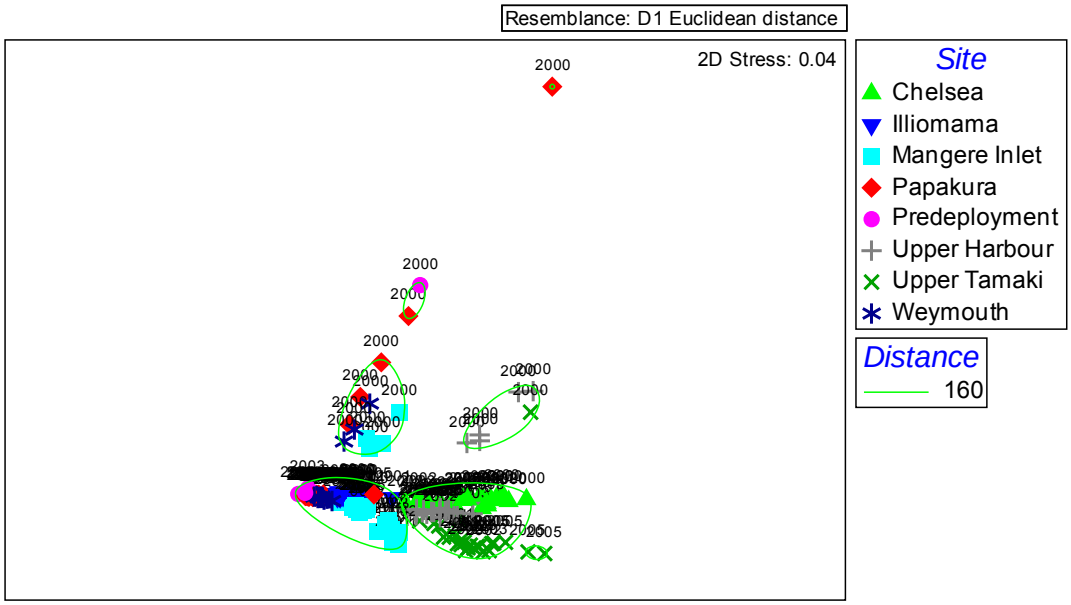


Figure 4-22: Principal components analysis (PCA) of lipid normalised mussel PAHs between 2000 and 2005.

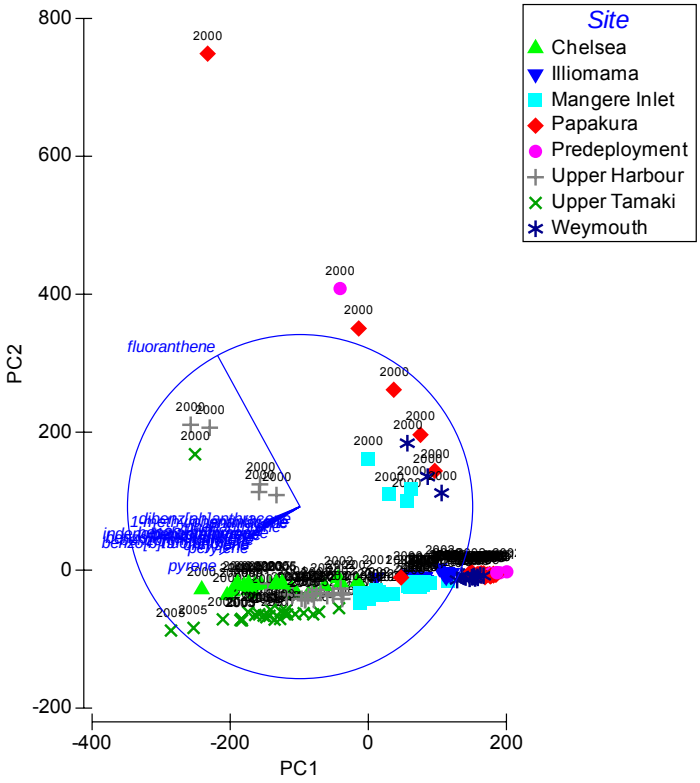


Figure 4-23: Multiple dimensional scaling (MDS) plot of lipid normalised mussel PAHs in samples collected from 2001 – 2005 (i.e. excluding 2001). Samples are grouped at a Euclidian distance of 90.

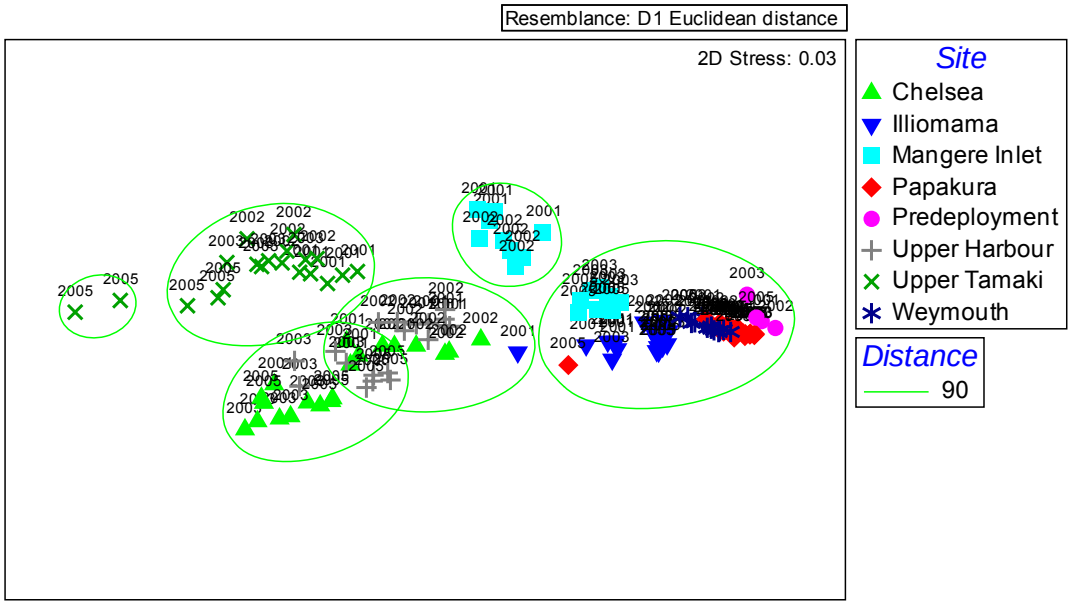
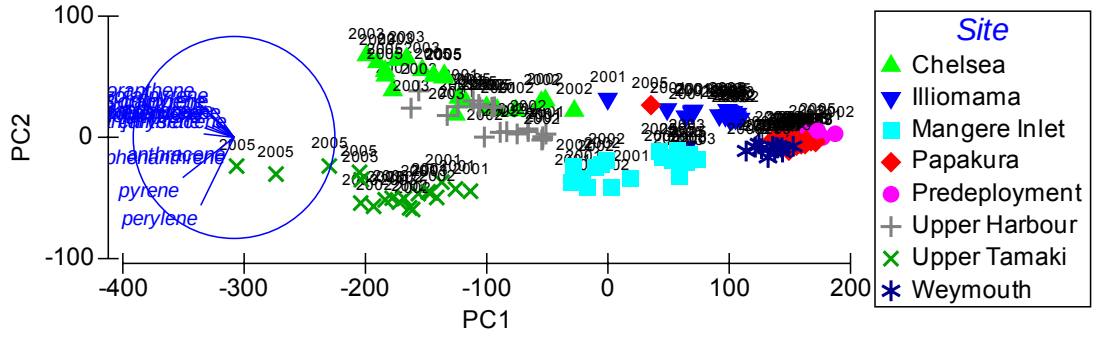


Figure 4-24: Principal components analysis (PCA) of lipid normalised mussel PAHs between 2001 and 2005 (i.e. excluding 2001).



Cluster analysis, similarity profile and MDS analysis of constituent PCB's broadly distinguished the following groups of samples (Figure 4-25 and Figure 4-26):

1. Weymouth, Papakura, and Illiomama samples;
2. Pre-deployment samples;
3. Chelsea and Upper Harbour samples;
4. Upper Tamaki samples;
5. Mangere Inlet samples distinguished by year.

Variation along the primary principal component axis, which explained 96% percent of the variation, was largely related to the concentrations of PCB's 153 and 138 (Figure 4-27). Concentrations of these two PCBs were: high relative to other PCBs; highly correlated to each other ($r = 0.99$); and varied significantly among sites ($P < 0.0001$). The mean ratios of PCBs 153 + 138 to the totals of other PCBs ranged from 0.17 to 1.13 among sites. A one way ANOVA and Tukey HSD post-hoc comparisons (with years pooled for each site and pre-deployment samples excluded due to the lack of sample replication), indicated that these ratios increased from Mangere < Papakura, Weymouth < Upper Tamaki, Chelsea and Illiomama & Upper Harbour ($P<0.05$)[3]. Note that the lowest ratio was obtained from pre-deployment samples. Concentrations of most other PCB's tended to vary along the secondary principal component axis. Mangere Inlet was clearly distinguishable on this axis.

[3] < = less than, << = much less than

Figure 4-25: Cluster analysis of lipid normalised PCB concentrations in mussels. Samples grouped by similarity profile analysis (SIMILARITY PROFILE) are linked in red.

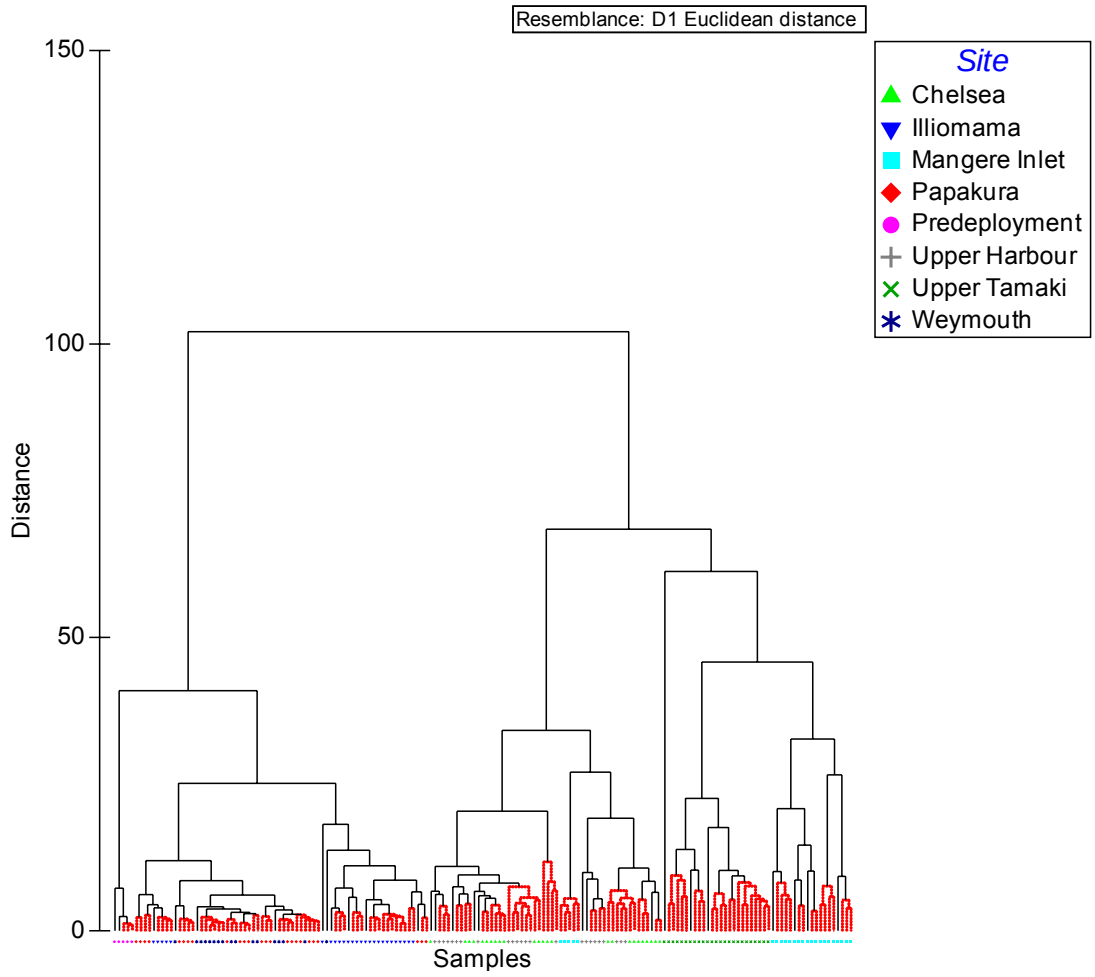


Figure 4-26: Multiple dimensional scaling (MDS) plot of lipid normalised mussel PAHs. Samples are grouped at a Euclidian distance of 25 (refer to Figure 4-25).

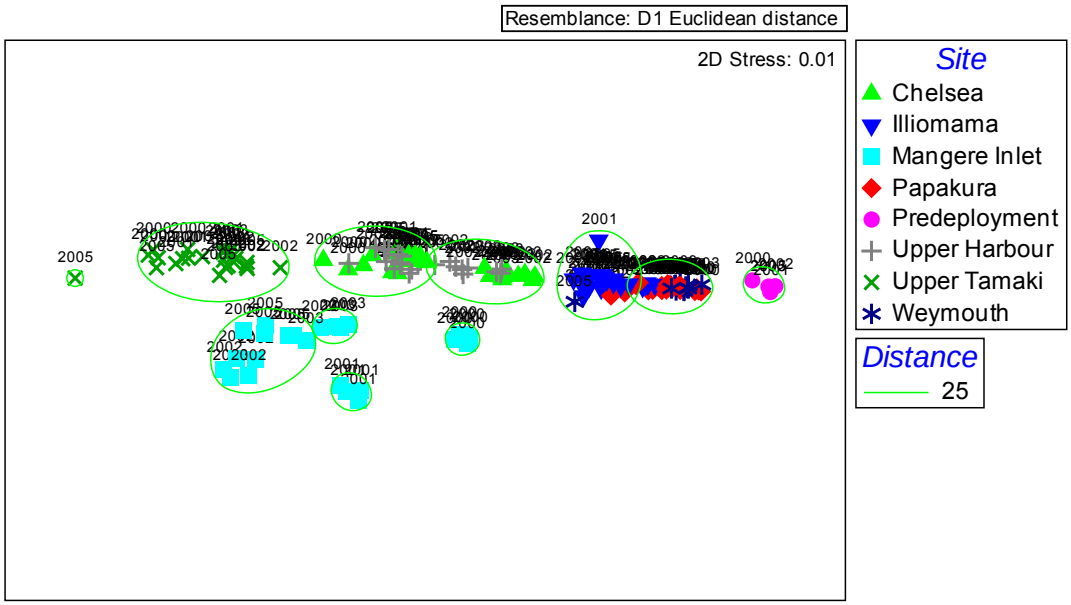
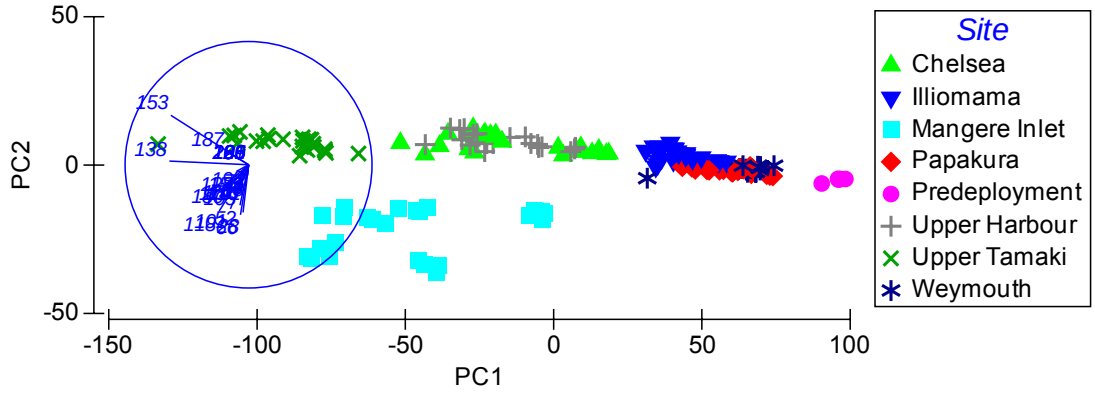


Figure 4-27: Principal components analysis (PCA) of lipid normalised mussel PCB's between 2000 and 2005.



4.2.3 Summary of Contaminants in Mussels

- High detection limits of some metal contaminants, particularly lead, have hampered the interpretation of mussel data. However, this issue appears to have been resolved, and detectable levels of all metals have been measured in most samples during the last two sampling periods;
- Sites could not be consistently differentiated based on the concentrations of arsenic, cadmium, chromium, lead or zinc in mussel tissues.

- Spatial differences are apparent in mussel copper concentrations, but these differences are not consistent over time. Between 2003 and 2005 a relatively large increase in copper concentration occurred in mussels recovered from the Upper Tamaki (the reason for which remains unknown);
- Spatial differences are clearly apparent in the concentrations of all organic contaminants. Multivariate analysis of organic contaminants broadly grouped the monitoring sites into: Mangere Inlet (2000 samples could also be differentiated from 2001-2005 samples); Upper Waitemata Harbour, Upper Tamaki and Chelsea; and, pre-deployment, Illiomama, Papakura and Weymouth.
- DDT and PCB levels increased in mussels recovered from Mangere Inlet between 2000 and 2002, coincident with the decommissioning of oxidation ponds at the Mangere Sewage Treatment Plant. They remained elevated in 2003 and 2005 (unlike oysters from a nearby site, which dropped after 2003);
- Slight downward trends have been recorded for some organic contaminants at some sites (e.g. dieldrin at the Upper Waitemata Harbour site), but these changes represent small changes in low concentrations, and they may not continue into the future.
- Analysis of PAH signatures showed a strong fluoranthene signal in 2000 samples that was not apparent in other years. Once the influence of this year was removed, PCA indicated that the remaining differences in PAH signatures were primarily due to the combined influence of most other PAHs acting in unison. However, perylene, and to a lesser degree pyrene, did provide some additional distinction among sites. Again, these are quite subtle variations occurring at low concentrations, so their cause or practical significance are, as yet, unknown.
- Analysis of PCB signatures indicated that sites were distinguishable, primarily by the concentrations of PCB 138 and PBC 153.

5 Discussion

In most cases, the results from the Manukau Harbour oyster and mussel programmes are reasonably consistent, even though the locations of the monitoring sites differed between the two species. For instance, similar results were obtained for: the absolute concentrations of organic contaminants in oysters and mussels; relative differences in the concentrations of organic contaminants among sites; and, trends in organic contaminants through time. The concentrations of arsenic, cadmium, chromium and lead also tend to be similar in mussels and oysters.

The key difference between the two species was in the body burdens of zinc and copper. The concentration of zinc was high in both mussels and oysters, relative to the other metals measured, but it was two orders of magnitude higher in oysters compared with mussels. Furthermore, there was no significant difference in zinc concentrations among mussel monitoring sites, but marked differences were apparent among oyster monitoring sites. Copper concentrations were also 1-2 orders of magnitude higher in oysters (c.f. mussels) and differences in copper concentrations were apparent among oyster monitoring sites. However, unlike zinc, copper concentrations in mussels did vary slightly from site to site.

Copper and zinc concentrations are often elevated in marine sediments contaminated by urban stormwater. Including the guts of mussels and oysters in the samples could potentially bias analytical results because the gut contents may contain contaminated sediment. However, the whole-body burdens of copper and zinc in oysters from Granny's Bay, Pahurehure and Hingaia were 1-2 orders of magnitude greater than the concentrations in nearby sediments (Williamson and Kelly 2003). Therefore, the inclusion of gut sediments would, if anything, lead to the whole body copper and zinc concentrations being slightly underestimated.

Large differences in the body burdens of other oysters, relative to sediment and water concentrations have also been recorded. Brook and Rumsby (1965) compared the concentrations of essential elements in seawater, sediments, and tissues of the New Zealand dredge oyster (*Ostrea sinuate* = *Tiostrea lutaria*, Dinamani and Bei 1981). The mean concentration of zinc in the visceral mass of dredge oysters (including the gut contents) was 1122 ppm, while zinc concentrations in sediments collected from the same site were below detection limits (<100 ppm). In comparison, whole body concentrations of zinc were 1103 ppm, with organ concentrations (excluding shell) ranging from 369-4760 ppm. Brook and Rumsby (1965) estimated that the whole body enrichment factor for zinc (relative to seawater) was 110,300. Kennedy (1986) subsequently estimated that <0.1 % of copper and zinc in the tissues of the dredge oysters *Tiostrea lutaria* could be attributed to gut sediments. The results from ARCs Shellfish Contaminant Monitoring Programme appear to be reasonably consistent with

these findings, which suggest that any bias due to the inclusion of sediments in the gut is likely to be minimal.

5.1 Temporal Variability in Shellfish Contamination

The concentrations of copper and zinc in oysters from Granny's Bay, Hingaia and Pahurehure have varied considerably over time, but sustained positive or negative trends have not occurred. Rather, temporal variability has involved cyclical and highly correlated fluctuations in copper and zinc concentrations. These fluctuations have simultaneously occurred at the three, widely separated, sites - even though their adjoining catchments have markedly different landuse characteristics. This suggests that the variability is due to large-scale, natural processes, such as temperature variations that moderate biological processes, or the remineralisation from bed sediments, rather than variation in contaminant loads from the catchments immediately adjacent to the monitoring sites.

This conclusion is supported by the relatively good fit between the SOI (an indicator of El Nino and La Nina weather patterns), and copper and zinc concentrations between 1987 and 1998. However, the fit was not as strong from 1999 to 2005, indicating that other factors are also influencing the uptake and accumulation of metals.

Possible mechanisms for linking climate patterns to contaminant concentrations in shellfish include:

- fluctuations in the discharge and delivery of stormwater contaminants due to variation in the frequency and intensity of rain events; and/or,
- remobilisation and redistribution of contaminants in marine sediments due to changes in wind direction and intensity;
- temperature changes which affect the uptake and bio-accumulation of metals in oysters.

Ongoing monitoring is required to verify the link between climate patterns and metal concentrations in oysters. However, the available data highlights the importance of long term datasets, which allow short-term fluctuations in contaminant concentrations to be considered within the context of longer term variation due to natural processes.

In contrast to metals, temporal trends in organic contaminants can be directly connected to human activity. For instance, during the 1990s the concentration of chlordane, lindane and dieldrin in oysters declined from relatively high concentrations to consistently low concentrations. This decline can be linked directly to the de-registration or reduced use of these pesticides in 1989-1990. The use of DDT on farmland was also banned in 1970, so it is reasonable to expect that the most significant declines occurred prior to the start of oyster monitoring, although the runoff of contaminated soils during the urbanisation of rural land represents an on-going source of contamination. However, DDT was available for use in a limited number of

applications until it was finally deregistered as a pesticide in 1989. The recent pulse of DDT, chlordane, and PCBs in the north-eastern section of the Manukau, which is evident in both mussel and oyster tissues, is likely to be due to the remobilisation of contaminated sediments within the decommissioned ponds of the Mangere Sewage Treatment Plant. Similar trends have also been recorded in oysters monitored by Watercare Services Limited in the vicinity of the plant (Bioresearches 2005a). Sediment concentrations of DDT, chlordane and dieldrin, were elevated in the area previously occupied by the treatment ponds, and concentrations dropped markedly after the ponds were re-opened to the sea (Bioresearches 2005b). Since 2003, the concentrations of DDT, chlordane, and PCBs in Granny's Bay oysters have declined to levels observed prior to the decommissioning of the ponds, but DDT and PCB concentrations remain elevated in mussel tissues. Mussel concentrations are expected to follow the pattern observed in oysters, and decline over the next few years.

5.2 Spatial Patterns in Shellfish Contamination

Clear differences are apparent in the concentrations of organic contaminants in oysters and mussels within Manukau Harbour and in mussels among east coast sites.

As discussed above, Mangere Inlet was notable for having relatively high levels of most of the organic contaminants analysed. The upper Tamaki site was also notable for having relatively high dieldrin and PCB concentrations in mussels. Dieldrin and PCB concentrations are also elevated in surface sediments within Tamaki Estuary, although they remain below the ANZECC ISQG-Low sediment quality guideline values (ANZECC 2000). PCBs were commonly used in a broad range of industrial, commercial, and even domestic applications and appliances, and were fairly ubiquitous within industry. The catchment adjoining the upper Tamaki has a relatively long history of industrial activity, and elevated PCB concentrations are likely to reflect the ongoing release from PCB contaminated land and older, PCB-containing, machinery and devices. The sources of dieldrin are more puzzling, but possibilities include: golf courses where it may have been used to control turf pests, sites where dieldrin was stored or packaged, timber processing facilities, and horticultural and agricultural uses.

The Manukau Harbour sites could also be separated into two groups based on the concentrations of zinc and copper in oyster tissues. Concentrations of copper and zinc in oysters from the Cornwallis reference site were significantly lower than at the other sites with urban or semi-urban catchments. This is likely to reflect differences in the ambient concentration of metals among sites, and fact that oysters are strong accumulators of zinc and copper (Rainbow 1995). In contrast, zinc concentrations in mussels, which are poor zinc accumulators (Rainbow 1995), where not significantly different among sites.

On the east coast, contaminant levels were greatest in the Upper Tamaki. Highest concentrations of copper, PAH, chlordane, dieldrin and PCBs were recorded at this site.

Illiomama had the best shellfish quality with lowest concentrations of PAH, DDT, chlordane and PCBs. The two Waitemata Harbour sites, Chelsea and Upper Harbour, had very similar contaminant profiles with contaminant levels intermediate between Tamaki and Illiomama.

Spatial differences were also apparent in the PAH and PCB signatures of the monitoring sites. For instance, the Pahurehure oyster monitoring site, which is situated beside the southern motorway, had a distinct PAH signature due to elevated perylene concentrations, possibly reflecting inputs of petroleum products, tire wear and/or bitumen. In most other cases, spatial differences reflected the combined influence of multiple PAH or PCB congeners rather than a small subset of congeners.

5.3 Auckland in an International Context

In 2005, concentrations of copper in oysters from Granny's Bay, Pahurehure and Hingaia were above the 85th percentile for copper in the NS&T and RNO datasets. Exceedances of the 85th percentiles in these datasets are considered to be "indicative" of contamination from human activity (Cantillo 1998). However, all of the monitoring sites had oyster copper concentrations that were less than the 85th percentile of the WMW database. This database includes samples from contaminant "hotspots" and is probably a better guide of environmentally-significant contamination.

The concentrations of other metals in Manukau oysters were below the 85th percentiles of all three datasets, indicating that they are within the ranges expected for relatively uncontaminated sites.

6 Conclusions

The ARC shellfish monitoring programme provides a relatively consistent, long-term dataset which is particularly sensitive to variations in the level of organic contaminants in the marine environment. While none of the sites were heavily contaminated, clear differences in the levels of organic contaminants are seen among monitoring sites. Mangere Inlet and Tamaki Estuary have the worst water quality with respect to these organic contaminants. Shellfish from the Waitemata Harbour had intermediate concentrations of organic contaminants, and shellfish from the southern Manukau, Tamaki Strait (Rangitoto) and outer Manukau had slightly elevated to low concentrations. In recent years, the quality of shellfish in Mangere Inlet has been significantly affected by contaminants released during the rehabilitation of sewage treatment ponds and the Mangere Wastewater Treatment Plant. However, contaminant levels in shellfish are expected to improve again over the next few years.

Metal concentrations in mussels were relatively low, and with the exception of copper did not discriminate between sites. This is likely to reflect the low levels of most metals in the environment and the fact that mussels are not strong accumulators of zinc (Rainbow 1995). In contrast, clear differences were apparent in the concentrations of both copper and zinc in oysters from the inner Manukau Harbour sites compared with the reference site at Cornwallis, near the harbour entrance.

Fluctuations in the concentrations of copper and zinc appear to track variations in the Southern Oscillation Index, suggesting that large-scale, periodic climate patterns may influence contaminant availability or uptake. This observation highlights the importance of long-term datasets, which allow changes in contaminants due to human activity to be discriminated from changes due to natural processes. It is important that any trends are assessed within the context of these long-term, large-scale "natural" cycles to ensure reliable conclusions are drawn on the effects of human influences on aquatic receiving environments.

7 References

ANZECC (2000) Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment & Conservation Council, and Agriculture and Resource Management Councils of Australia & New Zealand., Canberra, Australia., 316 pp.

Bioresearches. (2005a) Harbour Environment Monitoring Programme 2004-2005. Client report for Watercare Services Ltd., Bioresearches, Auckland, 231 pp.

Bioresearches. (2005b) Watercare Services Ltd project Manukau pond recovery monitoring programme 2004-2005. Client report for Watercare Services Ltd., Bioresearches, Auckland, 149 pp.

Brooks R.R. and Rumsby M.G. (1965) The biogeochemistry of trace element uptake by some New Zealand bivalves. Limnology and Oceanography 10: 521-527

Cantillo, A.Y. (1998) Comparison of results of mussel watch programmes of the United States and France with worldwide mussel watch studies. Marine Pollution Bulletin 36: 712-717.

Clarke K.R., Gorley R.N. (2006) PRIMER v6: User manual / tutorial. PRIMER-E Ltd. Plymouth, United Kingdom. 190 pp.

Dinamani, P., Bei, A. G. (1981) Description of a new species of incubatory oyster from northern New Zealand, with notes on its ecology and reproduction. New Zealand Journal of Marine and Freshwater Research 15:109-119.

Kelly, S. (2004) Contaminant monitoring in shellfish: results of the 2003 shellfish contaminant monitoring programme. ARC Technical Publication, TP273, Auckland Regional Council, Auckland.

Kennedy, P.C. (1986) The use of molluscs for monitoring trace elements in the marine environment in New Zealand 1. The contribution of ingested sediment to the trace element concentrations in New Zealand molluscs. New Zealand Journal of Marine and Freshwater Research 20: 627-640

Lauenstein, G.G., Cantillo A.Y. (1998) Sampling and analytical methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 update. NOAA Technical Memorandum NOS ORCA 130

Lauenstein, G.G., Cantillo, A.Y., O'Conner, T.P. (2002) The status and trends of trace element and organic contaminants in oysters, *Crassostrea virginica*, in the waters of the Carolinas, USA. The Science of the Total Environment 285: 79-87.

Mills, G. N. (1998) Sentinal shellfish monitoring programme review. NIWA Client Report ARC70220, NIWA, Hamilton.

Nicholson, B.C. (1984) Australian water quality criteria for organic compounds. Department of Resources and Energy, Australian Water Resources Council. Technical Paper 82, 224 pp.

Rainbow, P. S. (1995) Biomontoring of heavy metal availability in the marine environment. Marine Pollution Bulletin 31:183-192.

Scanes, P.R., Roach, A.C., (1999) Determining natural 'background' concentrations of trace metals in oysters from New South Wales, Australia. Environmental Pollution 105: 437-446.

Sericano, J.L., Wade, T.L., Jackson, T.J., Brooks, J.M., Tripp, B.W., Farrington, J.W., Mee, L.D., Readmann, J.W., Villeneuve, J.P., Goldberg, E.D., (1995) Trace organic contamination in the Americas: An overview of the US National Status & Trends and the International "Mussel Watch" Programmes. Marine Pollution Bulletin 31: 214-225.

Williamson, R.B., Kelly, S. (2003) Regional Discharges Project. Marine Receiving Environment Status Report 2003. ARC Technical Publication, TP203, Auckland Regional Council, Auckland 53 pp.

8 Appendix A: Descriptions of Contaminants

8.1 Key Metals

8.1.1 Total Arsenic (As)

Arsenic is a non-essential element and known carcinogen. It is toxic to both humans and aquatic organisms. Arsenic can exist in a number of inorganic and organic forms that have different toxicities and abilities to accumulate in aquatic organisms. Arsenic enters the environment through both man-made and natural sources. The predominant commercial use of arsenic in the Auckland region is by timber treatment companies for wood preservation. 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.

8.1.2 Cadmium (Cd)

Cadmium is a very toxic, non-essential element for humans that 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).

Cadmium occurs in natural deposits as ores that also include other elements such as zinc. Natural concentrations are extremely low in unpolluted seawater. Its primary uses are in batteries, plastic stabilisers, pigments, metal plating, and in the manufacture of alloys and solders.

8.1.3 Chromium (Cr)

Chromium is an essential element to humans, but is toxic at higher concentrations. In the Shellfish Contaminant Monitoring Programme it is measured as a total element, but is commonly found in two oxidation states in the environment, chromium III and

chromium VI. The hexavalent form (Cr VI) is more harmful, probably because it is more mobile and is a stronger oxidiser. Chromium is carcinogenic to humans, and is accumulated by marine and freshwater organisms. Bio-concentrations factors range from 100 – 1,000 (ANZECC 2000). There is little evidence that cadmium is accumulated through the food chain.

Chromium is used for:

- the production of alloys;
- electroplating;
- the production of refractory products, fungicides, oxidants and catalysts, and pigments;
- leather tanning.

8.1.4 Copper (Cu)

Copper is also an essential element in metabolic processes, and has a low toxicity for humans. Aquatic organisms have widely varying sensitivities to copper. Algae in particular are sensitive to relatively low copper concentrations, hence it's use in algaecides and antifoulants. It is readily accumulated by plants and animals with bio-concentrations factors ranging from 100 – 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. 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.

8.1.5 Lead (Pb)

Lead is a cumulative metabolic poison in humans. Infants, children and pregnant women are probably the most sensitive groups to environmental lead exposure. It is also 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.

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.

8.1.6 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.

8.2 Organic Compounds

8.2.1 PAH (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.

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). PAHs are carcinogenic and chronic exposure has been linked to the formation of cancerous tumours in humans and animals (Nicholson 1984).

8.2.2 Dieldrin and Lindane

Lindane was used in New Zealand as an insecticide for controlling lice and other ectoparasites on sheep and cattle, and insect pests in pastures, crops, orchards and households. Dieldrin was used in similar applications and was also used as a timber preservative.

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. Lindane was deregistered in 1990.

Lindane has moderate to high toxicity to aquatic organisms, although some molluscs are less sensitive (ANZECC 2000). The US EPA state that lindane causes neurotoxic effects in humans and also appears to cause kidney (renal) and liver (hepatic) toxicity. It is also a potential endocrine disruptor in birds, mammals, and possibly fish. Dieldrin generally exhibits high to very high toxicity to aquatic species (ANZECC 2000). In humans, dieldrin is known to affect the immune system, increase infant mortality, reduce reproductive success, damage kidneys, and cause cancer and birth defects.

8.2.3 DDT (dichlorodiphenyltrichloroethane)

DDT is a chlorinated hydrocarbon that was manufactured use as an insecticide to control grass grub and porina caterpillars. Large quantities were applied to New Zealand pasture throughout the 1950's and early 1960's. The use of DDT was regulated in 1968, when permits were required for pasture application. In 1970 the use of DDT on farm land was prohibited.

DDT is a combination of two isomers o,p' and p,p' and has several metabolites. DDT is broken down by chemical and biological action to form DDD and DDE, both of which are toxic and persist in the environment.

DDT is highly toxic to most aquatic species (ANZECC 2000). Known affects on humans include: liver damage, temporary damage to the nervous system, reduced reproductive success, and liver cancer. One of the best documented adverse effects of low levels of DDT in the environment is in reducing the reproductive success of predatory birds through bio-accumulation and bio-magnification (Nicholson 1984). Registration of all DDT products was withdrawn in 1989, but there may be some application of old stocks of DDT products by rural and domestic users. A significant historic pool of DDT remains in rural soils and can be released during land disturbance and development.

8.2.4 Chlordane

Chlordane is a persistent organochlorine which can remain in soils for over 20 years. In New Zealand chlordane was historically used for timber treatment and pest control. Applications for the registration of chlordane products were declined by the Pesticide Board from 1989, when it became illegal to sell, manufacture or import chlordane for use as a pesticide. Chlordane is accumulated and bio-magnifies up the food chain (Nicholson 1984). It affects the nervous and digestive systems, and the liver in humans (US EPA), and is highly toxic to aquatic organisms (ANZECC 2000).

8.2.5 PCBs (Polychlorinated biphenyls)

PCBs are complex mixtures isomers and congeners, manufactured by the reaction of biphenyl with chlorine. Due to their excellent thermal stability and inert chemical nature, they have been widely used as oil substitutes, mainly in electrical transformers, capacitors and hydraulic systems, but they are also used in solvents, fire retardants and as a component of adhesives. The use of PCBs in New Zealand has been illegal since 1995. However, PCBs persist in the environment and accumulate in the tissues of exposed organisms resulting in bioaccumulation through trophic levels of the food web. PCB's cause a variety of acute and chronic toxicity effects in both humans and aquatic biota (US EPA, Nicholson 1984, ANZECC 2000).

9 Appendix B: Contaminants Measured

Table B1(a): List of organic contaminants measured in oysters during the Manukau Oyster Monitoring Programme. Heavy shading = contaminant measured at all sites, Light shading = contaminant measured at some sites, No shading = contaminant not measured, * = concentration of that contaminant included in totals for that contaminant group.

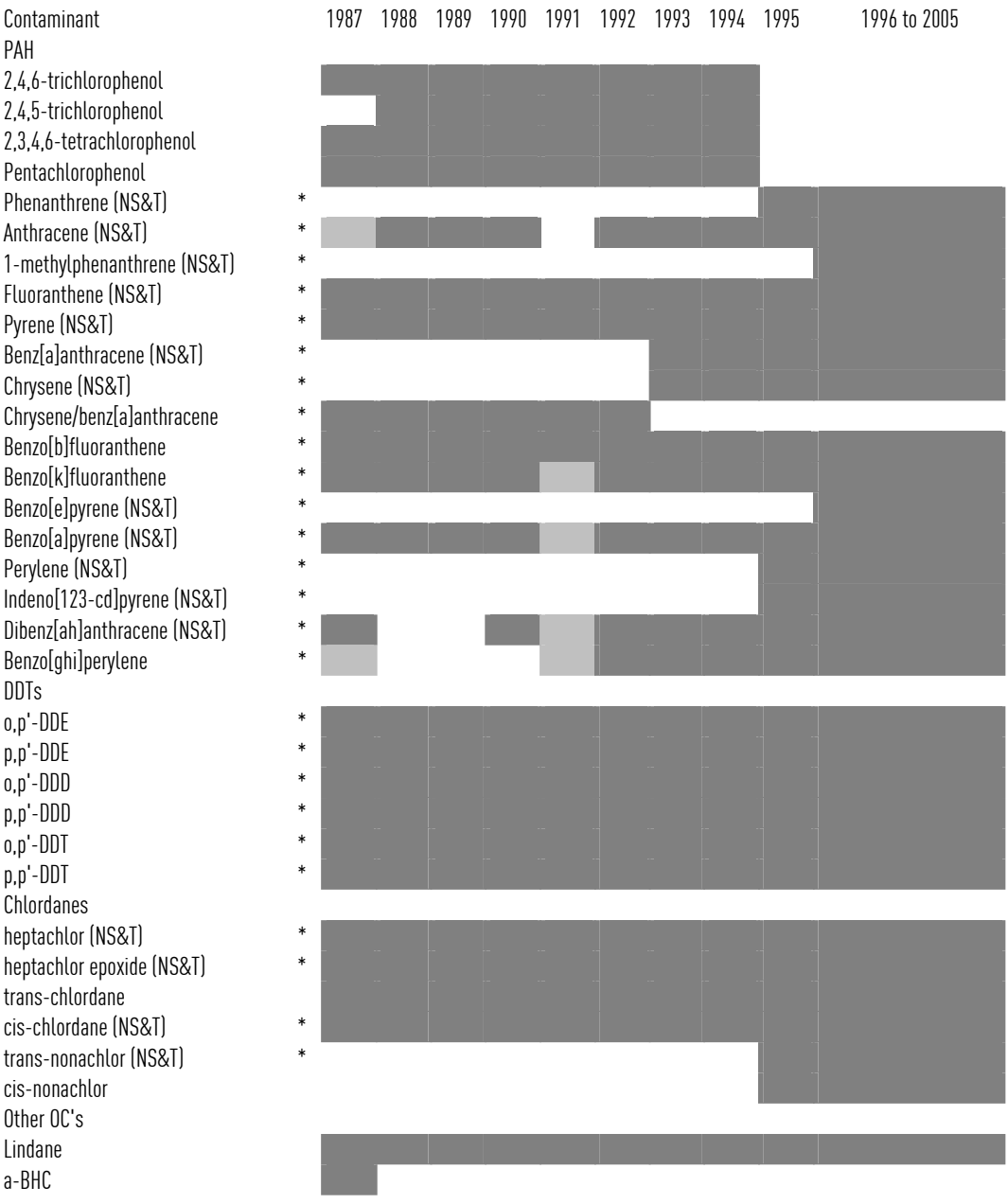


Table B1 (b): List of organic contaminants measured in oysters during the Manukau Oyster Monitoring Programme. Light shading = contaminant measured at some sites, No shading = contaminant not measured, * = concentration of that contaminant included in totals for that contaminant group.

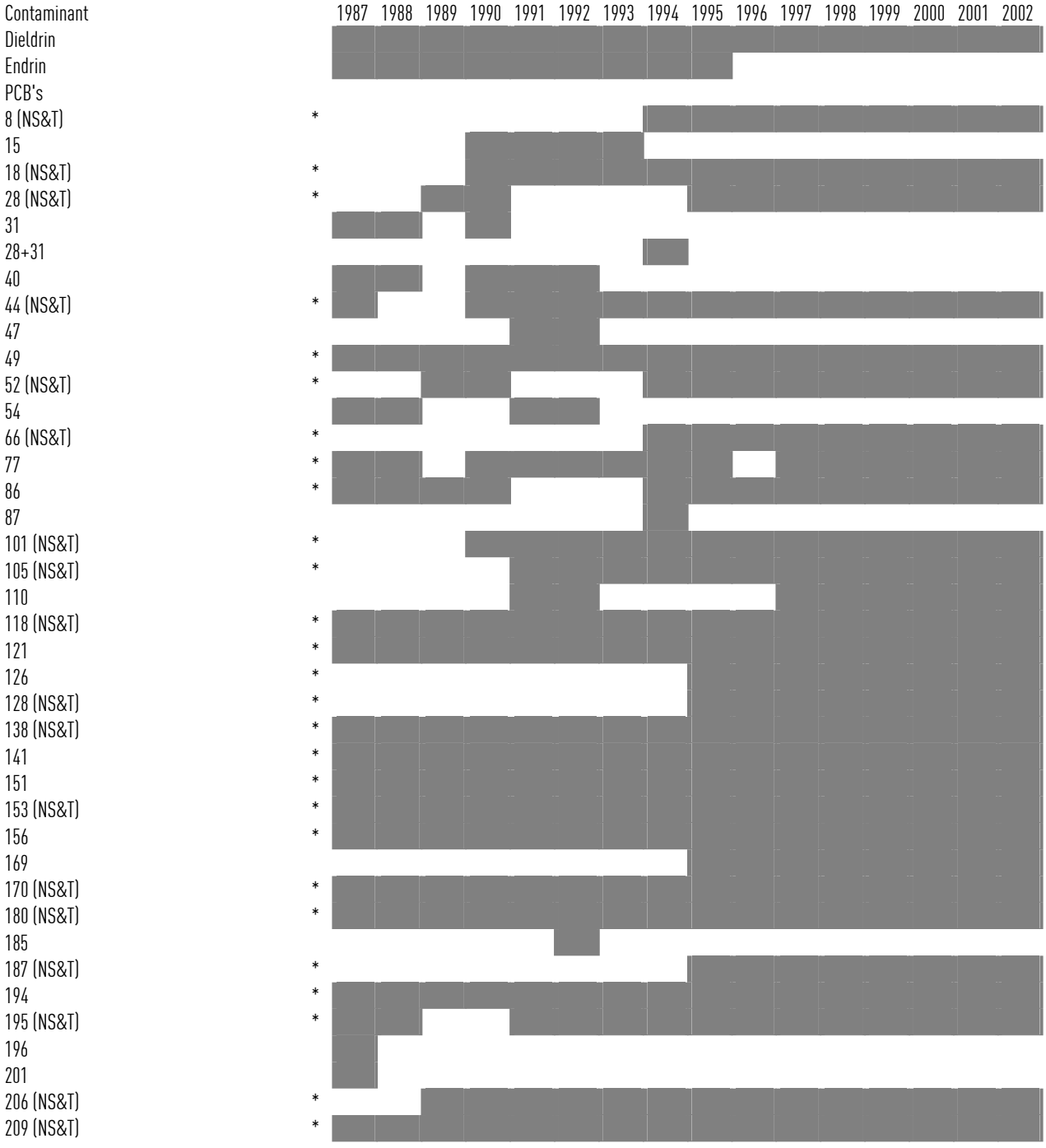


Table B2: List of organic contaminants measured in the ARC Mussel Monitoring Programme.

PCBs	PAHs	DDTs	Chlordanes	Other OCPs
8	phenanthrene	o,p-DDE	heptachlor	lindane
18	anthracene	p,p'-DDE	heptachlor epox	dieldrin
28	1-methylphenanthrene	o,p-DDD	trans-chlordane	
52	fluoranthene	p,p-DDD	cis-chlordane	
49	pyrene	o,p-DDT	trans-nonachlor	
44	benz[a]anthracene	p,p'-DDT	cis-nonachlor	
66	chrysene	Total DDT	Total Chlordane	
121	benzo[b]fluoranthene			
101	benzo[k]fluoranthene			
86	benzo[e]pyrene			
110	benzo[a]pyrene			
77	perylene			
151	indeno[123-cd]pyrene			
118	dibenz[ah]anthracene			
153	benzo[ghi]perylene			
105	Total PAH			
141				
138				
126				
187				
128				
156				
180				
169				
170				
195				
194				
206				
209				
Total PCB				

Table B3: Comparison of PCB's and PAHs analysed by the ARC and National Status and Trends Mussel Watch Project (NS&T) (from Lauenstien et al. 2002)

PCB's			PAH		
Congener	ARC	NS&T	Compound	ARC	NS&T
8	✓	✓	Phenanthrene	✓	✓
18	✓	✓	Anthracene	✓	✓
28	✓	✓	1-Methylphenanthrene	✓	✓
44	✓	✓	Fluoranthene	✓	✓
49	✓		Pyrene	✓	✓
52	✓	✓	Benz[a]anthracene	✓	✓
66	✓	✓	Chrysene	✓	✓
77	✓		Benzo[b]fluoranthene	✓	
86	✓		Benzo[k]fluoranthene	✓	
101	✓	✓	Benzo[e]pyrene	✓	✓
105	✓	✓	Benzo[a]pyrene	✓	✓
110	✓		Perylene	✓	✓
118	✓	✓	Indeno[123-cd]pyrene	✓	✓
121	✓		Dibenz[ah]anthracene	✓	✓
126	✓		Benzo[ghi]perylene	✓	
128	✓	✓	Naphthalene		✓
138	✓	✓	2-Methylnaphthalene		✓
141	✓		1-Methylnaphthalene		✓
151	✓		Biphenyl		✓
153	✓	✓	2,6-Dimethylnaphthalene		✓
156	✓				
169	✓				
170	✓	✓			
180	✓	✓			
187	✓	✓			
194	✓				
195	✓	✓			
206	✓	✓			
209	✓	✓			

10 Appendix C: Correlations between metals in oysters and mussels

Correlations between annual means for metals in oysters from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 1987 and 2005.

10.1 Oyster correlation coefficients and P values 1988-2005

	Correlation Coefficients				P values		
Arsenic							
	Cornwallis	Granny's	Pahurehure		Cornwallis	Granny's	Pahurehure
Granny's	0.666			Granny's	0.003		
Pahurehure	0.785	0.943		Pahurehure	<0.001	<0.001	
Hingaia	0.660	0.954	0.924	Hingaia	0.004	<0.001	<0.001
Cadmium							
	Cornwallis	Granny's	Pahurehure		Cornwallis	Granny's	Pahurehure
Granny's	0.577			Granny's	0.015		
Pahurehure	0.636	0.902		Pahurehure	0.006	<0.001	
Hingaia	0.631	0.934	0.965	Hingaia	0.007	<0.001	<0.001
Chromium							
	Cornwallis	Granny's	Pahurehure		Cornwallis	Granny's	Pahurehure
Granny's	0.889			Granny's	<0.001		
Pahurehure	0.944	0.843		Pahurehure	<0.001	<0.001	
Hingaia	0.827	0.927	0.872	Hingaia	<0.001	<0.001	<0.001
Copper							
	Cornwallis	Granny's	Pahurehure		Cornwallis	Granny's	Pahurehure
Granny's	0.766			Granny's	<0.001		
Pahurehure	0.676	0.452		Pahurehure	0.003	0.069	
Hingaia	0.670	0.733	0.709	Hingaia	0.003	0.001	0.001
Zinc							
	Cornwallis	Granny's	Pahurehure		Cornwallis	Granny's	Pahurehure
Granny's	0.365			Granny's	0.15		
Pahurehure	0.684	0.740		Pahurehure	0.002	0.001	
Hingaia	0.284	0.823	0.845	Hingaia	0.27	<0.001	<0.001

10.2 Mussel correlation coefficients 1999 to 2005

Arsenic

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.8386						
Chelsea	0.9861	0.9133					
Tamaki	0.9755	0.9344	0.9984				
Illiomama	0.9515	0.7613	0.9127	0.8978			
Mangere	0.983	0.8533	0.9691	0.9609	0.9845		
Weymouth	0.9994	0.8565	0.9904	0.9816	0.9513	0.9858	
Papakura	0.9793	0.8416	0.9618	0.9527	0.989	0.9996	0.9818

Cadmium

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.9873						
Chelsea	0.4474	0.5837					
Tamaki	0.9154	0.9533	0.6926				
Illiomama	0.2123	0.3647	0.9684	0.4948			
Mangere	0.9295	0.9681	0.6964	0.9018	0.5104		
Weymouth	0.9864	0.9921	0.546	0.9687	0.3197	0.9312	
Papakura	0.2784	0.4265	0.9767	0.5264	0.9938	0.5812	0.3722

Chromium

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	-0.0541						
Chelsea	0.9961	0.0249					
Tamaki	0.5056	0.807	0.5612				
Illiomama	0.3509	0.6824	0.429	0.6313			
Mangere	0.4654	0.0039	0.5002	0.0695	0.7316		
Weymouth	0.098	0.7727	0.1831	0.5677	0.9651	0.616	
Papakura	-0.0483	0.4121	0.0196	0.1226	0.8351	0.7952	0.8786

Copper

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	-0.2186						
Chelsea	-0.3676	0.9306					
Tamaki	0.4031	0.3041	-0.0653				
Illiomama	0.1928	0.0845	0.3584	-0.6698			
Mangere	0.9076	0.2001	-0.0094	0.6098	0.1336		

Weymouth	0.5962	0.4305	0.0994	0.9322	-0.3557	0.8303	
Papakura	0.846	0.3352	0.1567	0.5474	0.2416	0.9846	0.8054

Lead

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.8247						
Chelsea	0.9471	0.9596					
Tamaki	0.958	0.9387	0.9969				
Illiomama	0.9961	0.8286	0.9524	0.9677			
Mangere	0.955	0.9174	0.9877	0.9968	0.9706		
Weymouth	0.9996	0.8311	0.952	0.9638	0.9981	0.9624	
Papakura	1	0.8274	0.9485	0.9591	0.996	0.9558	0.9996

Zinc

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.0921						
Chelsea	0.0977	0.7325					
Tamaki	0.4805	0.6451	0.9182				
Illiomama	0.5398	0.3528	0.8077	0.9425			
Mangere	0.5088	0.7271	0.9023	0.9901	0.8938		
Weymouth	0.3314	0.5001	0.9308	0.9639	0.9638	0.9189	
Papakura	0.5611	0.7864	0.846	0.9536	0.8219	0.9861	0.8404

10.3 Mussel P-values

Arsenic

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.161						
Chelsea	0.014	0.087					
Tamaki	0.025	0.066	0.002				
Illiomama	0.049	0.239	0.087	0.102			
Mangere	0.017	0.147	0.031	0.039	0.015		
Weymouth	0.001	0.144	0.01	0.018	0.049	0.014	
Papakura	0.021	0.158	0.038	0.047	0.011	<0.001	0.018

Cadmium

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.013						
Chelsea	0.553	0.416					
Tamaki	0.085	0.047	0.307				
Illiomama	0.788	0.635	0.032	0.505			
Mangere	0.071	0.032	0.304	0.098	0.49		
Weymouth	0.014	0.008	0.454	0.031	0.68	0.069	
Papakura	0.722	0.573	0.023	0.474	0.006	0.419	0.628

Chromium

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.946						
Chelsea	0.004	0.975					
Tamaki	0.494	0.193	0.439				
Illiomama	0.649	0.318	0.571	0.369			
Mangere	0.535	0.996	0.5	0.93	0.268		
Weymouth	0.902	0.227	0.817	0.432	0.035	0.384	
Papakura	0.952	0.588	0.98	0.877	0.165	0.205	0.121

Copper

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.781						
Chelsea	0.632	0.069					
Tamaki	0.597	0.696	0.935				
Illiomama	0.807	0.916	0.642	0.33			
Mangere	0.092	0.8	0.991	0.39	0.866		
Weymouth	0.404	0.57	0.901	0.068	0.644	0.17	
Papakura	0.154	0.665	0.843	0.453	0.758	0.015	0.195

Lead

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.175						
Chelsea	0.053	0.04					
Tamaki	0.042	0.061	0.003				
Illiomama	0.004	0.171	0.048	0.032			
Mangere	0.045	0.083	0.012	0.003	0.029		
Weymouth	<0.001	0.169	0.048	0.036	0.002	0.038	
Papakura	<0.001	0.173	0.051	0.041	0.004	0.044	<0.001

Zinc

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.908						
Chelsea	0.902	0.268					
Tamaki	0.519	0.355	0.082				
Illiomama	0.46	0.647	0.192	0.057			
Mangere	0.491	0.273	0.098	0.01	0.106		
Weymouth	0.669	0.5	0.069	0.036	0.036	0.081	
Papakura	0.439	0.214	0.154	0.046	0.178	0.014	0.16

11 Appendix D: History of laboratories conducting sample analyses

Year	Metals	Organics
1987	ARA Water Laboratory: Titirangi	Ruakura Soil and Plant Research Laboratories: Hamilton
1988	ARA Water Laboratory: Titirangi	Ruakura Soil and Plant Research Laboratories: Hamilton
1989	ARA Water Laboratory: Titirangi	Ruakura Soil and Plant Research Laboratories: Hamilton
1990	DSIR Grassland Division: Palmerston North	MAF Technology, Ruakura Agriculture Centre: Hamilton
1991	AgResearch, Grassland Research Centre, Palmerston North	HortResearch, Ruakura Research Centre: Hamilton
1992	AgResearch, Grassland Research Centre, Palmerston North	HortResearch, Ruakura Research Centre: Hamilton
1993	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
1994	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
1995	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
1996	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
1997	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
1998	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
1999	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
2000	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
2001	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
2002	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
2003	AgResearch, Grassland Research Centre, Palmerston North	NIWA, Hamilton
2004	Not Sampled	Not Sampled
2005	Watercare Services	NIWA, Hamilton