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Contaminant monitoring in shellfish: results of the 2003 shellfish contaminant monitoring programme

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Contaminant monitoring in shellfish: Results of the 2003 Shellfish Contaminant Monitoring Programme.

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1 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 also 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. In contrast, DDT levels in oyster and mussel tissues from the Mangere Inlet have increased substantially since 2000, possibly due to the release of contaminated sediments from decommissioned ponds at the Mangere Sewage Treatment Plant.

Copper levels in Manukau Harbour oyster tissues were relatively high by international standards, and approaching concentrations considered to be indicative of contamination. Mussels recovered from Tamaki Estuary and Mangere Inlet also had relatively high copper concentrations. Zinc levels in Manukau Harbour oyster tissues were within the "typical" range reported from international databases. However, inconsistent and high analytical detection limits meant that inadequate information was available to assess the status of some of the other key metal contaminants, particularly lead.

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	Weymouth Papakura Channel Illiomama	Pre-deployment

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3 Introduction

3.1 Programme Rationale and Objectives

The Shellfish Contaminant Monitoring Programme was established to allow the detection of long term trends in 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 in 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, the concentration of contaminants in the water column may not reflect their toxicity because, even at low concentrations, plants and animals 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 (ARC 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 bulk 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.

3.2 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 sites, provide "reference" material which is used for comparison with data from sites subject to greater levels of contaminant input.

3.3 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, tyre and brake lining wear, pesticides, industrial activity and roof runoff. The potential effects of these contaminants on oysters and mussels are also assessed using simple, non-specific, morphological indices of condition. Note that condition is also affected by factors other than contaminant levels, so correlations between condition and contaminants must be interpreted with care.

Details of the contaminants measured, potential sources, and toxic effects are provided in Appendix A. 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. Maximum permissible levels of (some) contaminants in commercially grown shellfish are provided by the New Zealand Food Safety Authority (NZFSA)[1]. However, those standards are based on wet weights, which cannot be directly applied to the dry weight measurements obtained in this programme. 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 Sentinel Shellfish Monitoring Programme.

3.4 Report Structure

This report describes the methods used in the Shellfish Contaminant Monitoring Programme and presents results from the 1987 –2003 Manukau Oyster and 1999 – 2003 Mussel Monitoring Programmes. Data from the most recent 5-year period are also compared with overseas shellfish monitoring programmes to provide a broader context.

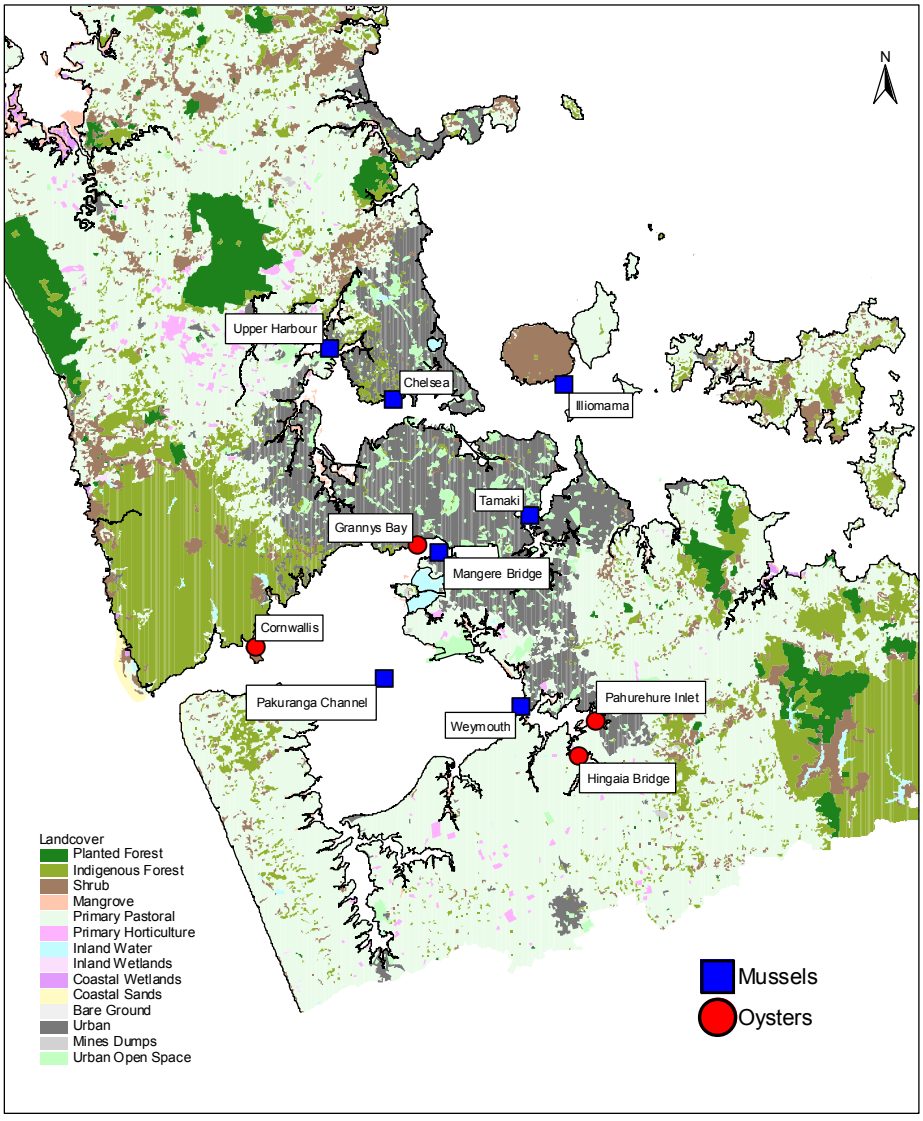
[1] http://www.foodstandards.gov.au/foodstandardscode/index.cfm#_FSCchapter1

4 Methods

4.1 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 (Fig. 1). Each year, all samples are collected on the same day, ideally during late November, to avoid seasonal differences between years. Samples are not collected until there has been five continuous days of little (< 5 mm) to no rain to ensure that contaminant levels reflect general water quality rather than recent pulses from distinct discharge events. Consequently, in some years samples were not collected until December (2000) or January (1996, 1997 & 1980).

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



4.1.1 Oyster Site Descriptions

A range of catchment types are included in the Manukau Oyster Programme. Oyster sample 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) (Fig. 1). Brief descriptions of each site are provided below.

4.1.1.1 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.

4.1.1.2 Pahurehure

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

4.1.1.3 Hingaia Inlet

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

4.1.1.4 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 Cornwallis sites.

4.1.2 Oyster Sample Collection

Each year, 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 82 oysters of similar size:

- 50 individual oysters were used for the analysis of condition;
- A composite of 12 oysters was used for the analysis of trace metals;
- A composite of 20 oysters was used for the analysis of organic contaminants.

4.2 Mussel Monitoring Programme

The Mussel Monitoring Programme involves transferring commercially grown mussels from Coromandel to ARC monitoring sites. To reduce the influence of mussel size, only mussels between 50 and 90 mm were used. Each year, mussels were transported as soon as possible after harvesting and stored in a flowing saltwater tank prior to seeding onto mussel ropes. Only mussels which exhibited a disturbance response (i.e. closing their valves when disturbed) at the time of seeding were used.

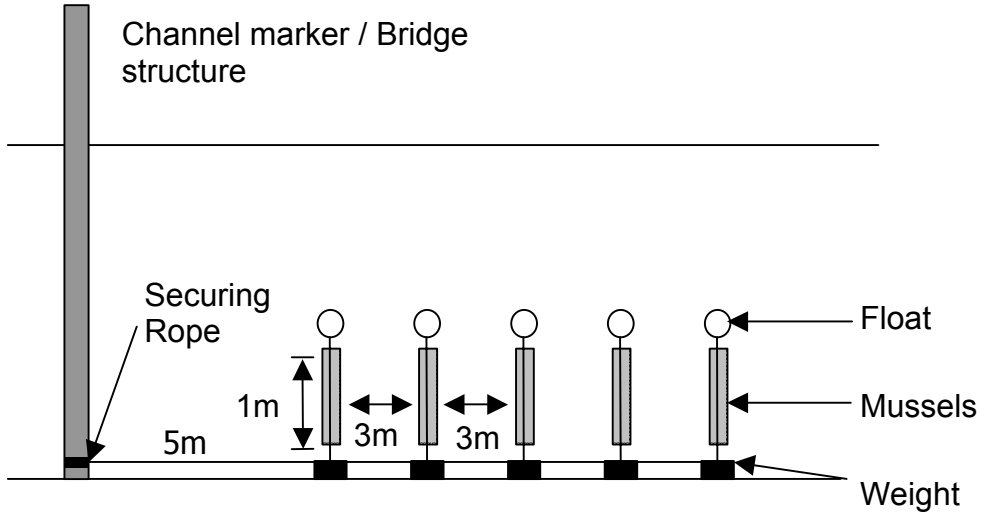
Mussel ropes approximately 1 metre long were seeded with approximately 55 mussels each using biodegradable mussel stockings. Six ropes were set onto a rig at each site by divers who ensured that individual ropes were well spaced and oriented perpendicular to the tidal flow (see Fig 2). The rigs were 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:

- 5 individual mussels were kept for the analysis of condition;
- 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.

Note: mussel samples from each rope within a site were pooled for condition analysis.

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



4.2.1 Mussel 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.

4.2.1.1 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.

4.2.1.2 Upper Waitemata Harbour (Greenhithe Bridge)

The Greenhithe Bridge marks a confluence of the extensive upper Waitemata Harbour area. The 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, that 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.

4.2.1.3 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.

4.2.1.4 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.

4.2.1.5 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 in Mangere Inlet. This area has historically been one of the most polluted coastal waterways in Auckland.

4.2.1.6 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.

4.2.1.7 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).

4.3 Analytical Procedures

4.3.1 Condition

Total weights were not measured for oysters in 2003, so the adjusted oyster condition index used in 2002 (ARC 2004) could not be determined (see Equation 1). However, the relationship between shell length and shell width, and dry tissue weight and shell weight were plotted against each other to check for changes in morphological characteristics.

Equation 1:

$$\text{Oyster\_Condition} = 100 \times \frac{\text{DFW}}{\text{WSW}}$$

Where: DFW = Dry Flesh Weight

WSW = Wet Shell Weight

Mussel condition was compared among sites and times using a condition index derived from the linear relationship between mussel shell weight and dry tissue weight. This condition measure was based on the assumption that mussels in poor condition contain less tissue for a given shell size. Linear regressions were fitted to annual data on shell and tissue weight, and the gradients of the regression slopes were used as an index of condition. Sites were then ranked, according to their index values, for every year sampled. Pre-deployment mussels were not included in the ranking, because they were collected at a different time and mussel condition varies widely throughout the year.

4.3.2 Key Metals

Metal analyses were carried out by AgResearch, Grasslands Research Centre, Palmerston North. 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. 5 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 ICP

("inductively coupled plasma" spectroscopy) and arsenic, cadmium, chromium, copper, lead and zinc concentrations quantified.

4.3.3 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 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 PAH's 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.

4.3.3.1 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 and PCB cogeners 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 cogeners 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). 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, ARC (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.

4.3.3.2 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.

4.3.4 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.

4.4 Data Analysis

Data were analysed graphically and by using univariate and multivariate statistical techniques. Univariate analyses were carried out using the Statistica software package. The multivariate technique, multi-dimensional scaling (MDS), was carried out using the Primer software package. Multi-dimensional scaling was used to visualise differences

between samples and sites by simultaneously comparing the levels of all metal contaminants or all organic contaminants. In MDS plots, samples with similar characteristics (contaminant signatures) are plotted close together, while samples that are dissimilar are widely separated. Further details on MDS can be obtained in Clarke (1993).

5 Results

5.1 Oyster Morphology

The morphology of oysters varied markedly between sites (Figs. 3 & 4). These differences are likely to be related to a combination of physical, chemical, and biological factors. At Cornwallis the oysters grew on sandstone reef, and occurred in relatively low densities. Oysters at this site were substantially smaller and more rounded in shape than those from the other sites (Fig. 3), and a strong linear relationship was found between shell weight and tissue weight (Fig. 4). At Granny's Bay, Pahurehure, and Hingaia, oysters occur in much higher densities and grow in soft, muddy sediments. At these sites the shape of oysters appeared to be strongly influenced by competition for space. Oysters grew with their hinges buried in the sediment or pointing down if attached to hard substrate. In order to avoid being smothered by sediments and conspecifics, oysters at these sites are much more elongated than those from Cornwallis (Fig. 3). In Granny's Bay and Hingaia shell growth appears to occur at the expense of tissue growth, with tissue weight peaking at around 1.5 g (Fig. 4). In contrast, Pahurehure was similar to Cornwallis in that a linear relationship, albeit more variable, was found between shell weight and tissue weight over the size range sampled (Fig. 4).

Figure 3: Length-width relationship for oysters collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 2000 and 2003. A linear regression has been fitted to data from Cornwallis, while an exponential growth function ($y = \exp^{(ax)}$) has been fitted to data from the other three sites.

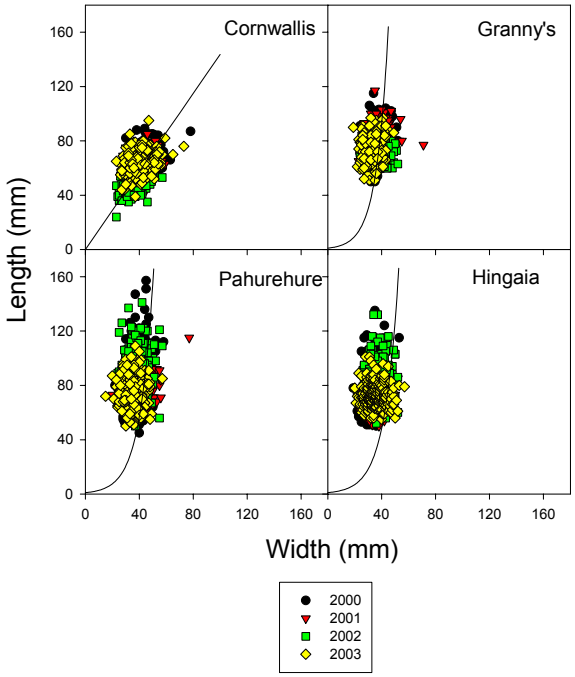
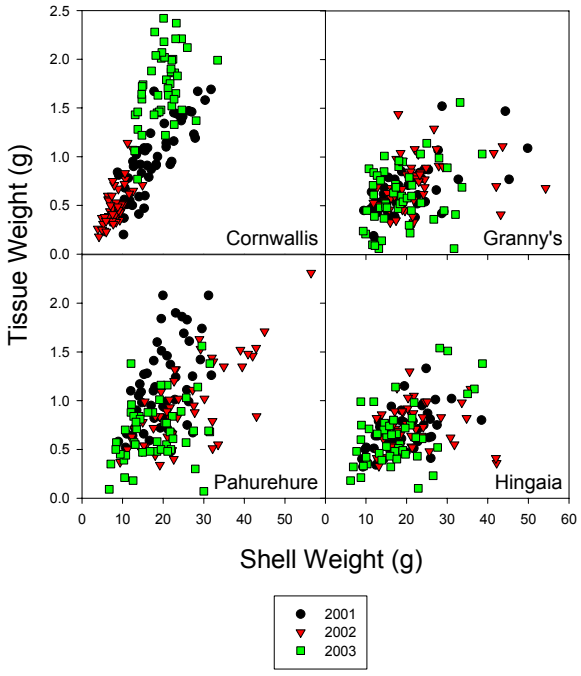


Figure 4: Relationship between oyster shell weight and dry tissue weight in samples collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 2001 and 2003.



5.2 Oyster Contaminants

5.2.1 Metals

5.2.1.1 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 above detection limits in 77 - 83% of samples, while lead levels were above detection limits in only 17% of samples. Extreme, care should therefore be taken in interpreting lead data.

Table 1: Number of samples collected between1987 and 2003 which were less than, or greater than, detection limits for each of the key metals. 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
< Detection Limit	117	97	87	0	408	0
Total N°. Collected	515	515	515	515	515	515
% < Detection Limit	23%	19%	17%	0%	83%	0%

5.2.1.2 Temporal and spatial trends

No consistent long-term trends were apparent in the levels of key metals in oysters between 1987 and 2002 (Fig. 5). Within-year and within-site variation was relatively low (mean coefficients of variation of < 20% for all metals except chromium which was < 47%), but interannual variation in some metals was relatively high.

No clear differences were apparent in the concentrations of arsenic, chromium, and lead between sites (although values given for lead are generally uninformative because of the large proportion of samples below high detection limits). Cadmium concentrations were generally lowest at Cornwallis, while large differences in the concentrations of copper and zinc were apparent between Cornwallis and the other three sites. In contrast there was no significant difference in the concentrations of these contaminants at Granny's Bay, Pahurehure and Hingaia.

Metal concentrations in oyster tissues where highly correlated between sites (Appendix C) indicating that:

- Metal contaminants entering Manukau Harbour are dispersed widely throughout the harbour and/or;
- Catchments at all sites have similar runoff patterns for metal contaminants and/or;
- The observed patterns reflect year-to-year analytical variability rather than real world variability and/or;

- Other, as yet unknown, environmental factors simultaneously affects the presence or uptake of contaminants at all sites.

Multidimensional scaling (MDS) was carried out to compare the metal contaminant signatures of the sites. Samples with missing values for one or more metals were also removed prior to analysis. Multidimensional scaling revealed 2 patterns (Fig. 6):

1. A spatial trend running from left to right in the MDS plot. Cornwallis can be separated out, but the other sites overlap indicating that they have similar key metal characteristics. Although further analysis was not carried out, it is likely that this trend is driven by low copper and zinc concentrations at Cornwallis.
2. A temporal trend running from the bottom left to top right with individual years spread along this axis.

It was apparent from MDS that temporal trends (i.e. year-to-year variability rather than monotonic trends indicative of real long-term changes) generally outweigh spatial trends for key metals, except where very large differences occur among sites. These results are consistent with the patterns observed for individual metals and indicate that the metals vary together from year to year, but there is little difference in levels among inner the harbour sites. Cornwallis was distinct, which reflects the cleaner outer harbour waters of the site.

Figure 5: Key metal (mean μg / g (oyster dry weight) ± s.e.) concentrations in oysters collected from four sites in the Manukau Harbour between 1987 and 2002. Samples below detection limits (DL) were transformed by multiplying the detection limit by 0.5.

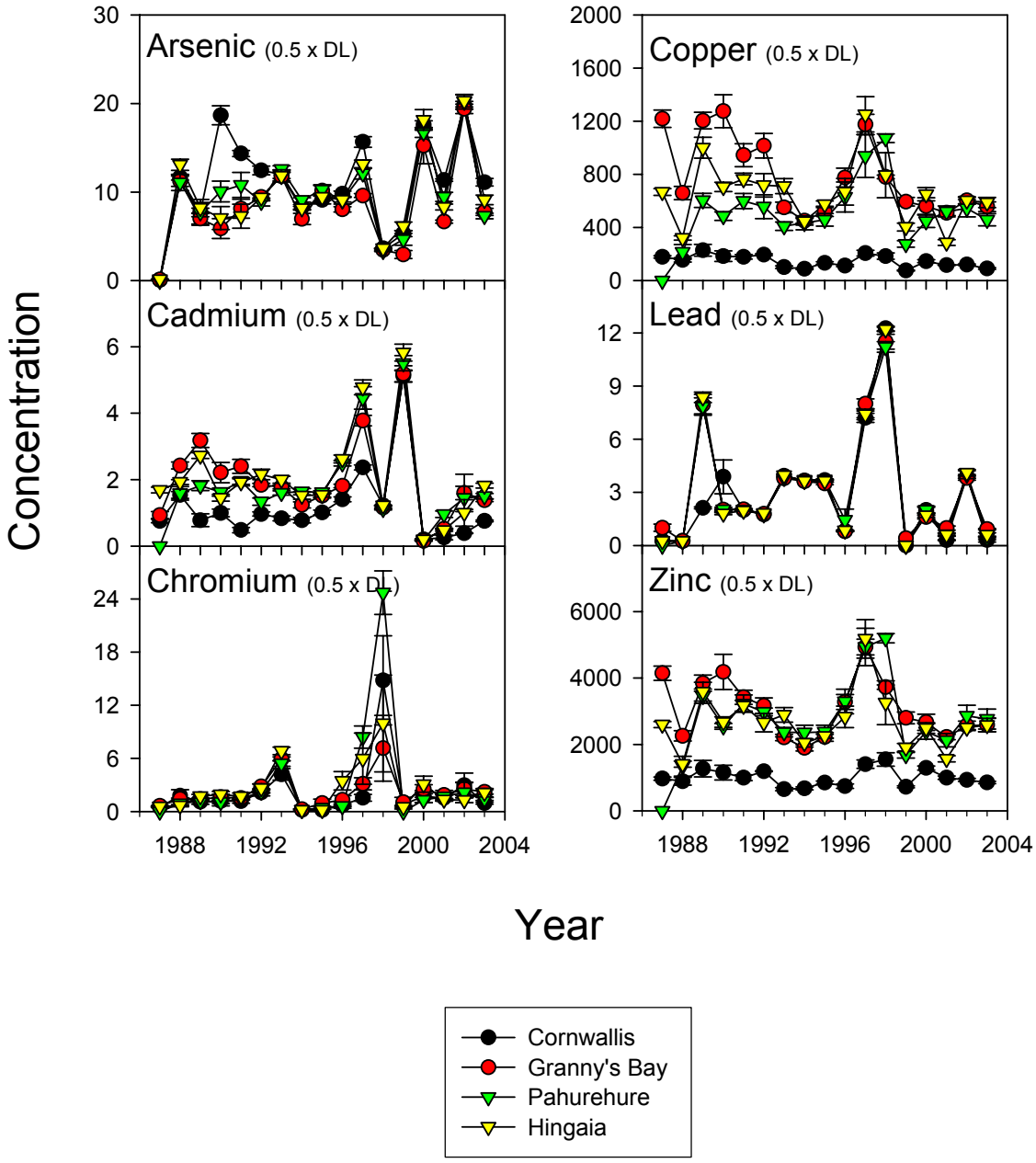
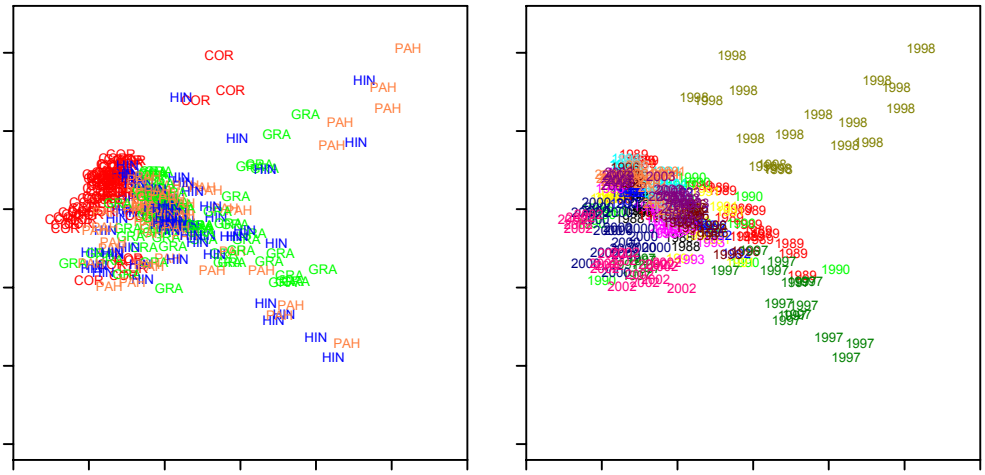


Figure 6: Multi-dimensional scaling (MDS) plots of metal concentrations in oysters. Plots are of the same data with site name (left hand plot) and year (right hand plot) labels for data points. Stress = 0.13.



5.2.2 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 local data (Cantillo 1998). The 85th percentiles of world-wide data are considered to be indicative of contamination, whereas those of the NS&T and RNO databases are the upper bounds of the usual, or expected, range of contaminant concentrations in shellfish (Cantillo 1998). Note that the values presented for World median & 85th percentile data vary between references. Those given in Cantillo (1998) tend to be the greater than 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 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 contaminants, so the highest arsenic levels were obtained from the cleanest site, Cornwallis. However, differences between sites were very small compared to differences between times.

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

Manukau harbour chromium levels, were greater than the medians provided for the NS&T and WMW databases. They were also above the 85th percentile level provided from the NS&T dataset but were considerably less than the 85th percentile level of the WMW dataset.

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

Lead levels in Manukau oysters were below detection limits in a high proportion of samples (85%, see Table 2). Furthermore, detection limits varied from year to year and were generally above the 85th % values provided for the NS&T, RNO and the WMW databases. Local mean values for lead are therefore considered to be unsuitable for comparisons.

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 2 to 3 times lower than the other Manukau sites.

Table 2: Comparison of mean metal concentrations (μg/g) in Manukau Harbour oysters with published medians from international databases. Data from the Manukau Harbour sites: Cornwallis; Granny's Bay, Hingaia; and Pahurehure; were pooled from the preceding 5 years (1999-2003). Notes: 1) local values for lead are unreliable because of high detection limits (see text for further details). 2) 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).

Site/Programme	Taxa	Arsenic	Cadmium	Chromium	Copper	Lead	Zinc
Cornwallis	Oysters	13.0	1.3	1.7	110	<5	960
Granny's		10.4	1.8	2.1	565	<5	2568
Hingaia		12.4	1.9	1.8	506	<5	2213
Pahurehure		11.7	1.9	1.6	449	<5	2365
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

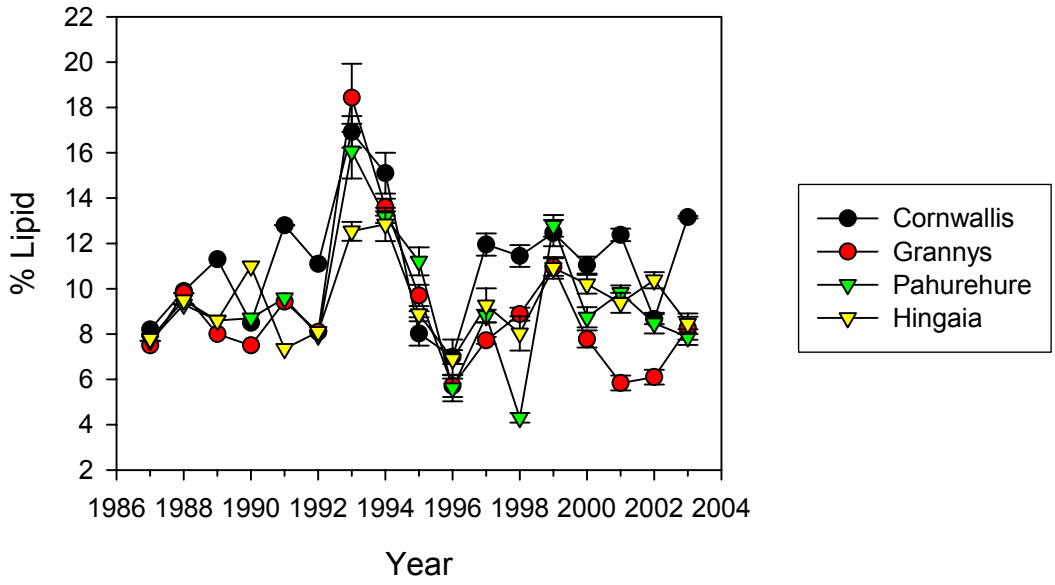
5.2.3 Oyster Organic Contaminants

5.2.3.1 Lipids

Considerable interannual variation was detected in the lipid content of oysters, but all sites tended to display similar temporal trends (Fig 7). 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 (Fig. 8). 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 7: Lipid levels as a percentage of total dry weight in oysters collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 1987 and 2002.



5.2.3.2 Detection limits

PAH, DDT, chlordane, and 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.

5.2.3.3 Contaminants

PAH levels were variable through time with no consistent directional trends (Fig. 8). However, there were clear differences among sites. Highest concentrations were recorded at Granny's Bay, Pahurehure and Hingaia. Over the same period PAH levels in

oysters collected from Cornwallis have been consistently low. Although uni-directional trends were not observed through time, similar interannual fluctuations were recorded among sites.

Highest levels of DDT have been recorded at Granny's Bay in 12 of the 17 years of monitoring. Lowest levels are generally found at Cornwallis. DDT levels were higher and more variable in oysters from Hingaia and Pahurehure prior to 1995. Discrete peaks in DDT concentration were recorded at these sites in 1988, 1990 and 1995, with levels rapidly returning to "background" concentrations. A recent, relatively large, increase in DDT concentrations in Granny's Bay oysters has occurred, coincident with the decommissioning of the ponds at the Mangere Sewage Treatment Plant.

Chlordane levels have dropped exponentially since monitoring began in 1987, due to the phasing out and eventual deregistration of this group of compounds. Concentrations recorded in oysters are largely due to the presence of cis-chlordane, trans-nonachlor, trans-chlordane, and cis-nonachlor, all of which tend to be highly correlated (see Fig 9 for trends in these chlordanes at Granny's Bay). Heptachlor and heptachlor epoxide have consistently remained below or near detection limits throughout the monitoring programme. Total chlordane concentrations (cis-chlordane + trans-nonachlor + heptachlor + heptachlor epoxide) were highest at Granny's Bay, with the remaining sites maintaining similar levels through time. The relatively large drop in the chlordane concentrations in oyster tissues at Granny's Bay between 1995 and 1996 (Fig. 8) is consistent with the longer term pattern of decline (Fig. 9). A recent increase in chlordane levels in Granny's Bay oysters matches the rise in DDT levels at this site. Despite this, current levels of chlordane remain well below those recorded pre-1996.

Levels of lindane dropped significantly at all sites between 1987 and 1989. Low, but detectable concentrations of lindane have remained since then. Little spatial differentiation was apparent in lindane concentrations. Dieldrin concentrations also declined between 1987 and 1997 and concentrations have since remained continuously low.

PCB levels declined at all sites after they were banned in 1995. However, PCB concentrations rose again at Granny's Bay between 1998 and 2002. PCB levels in Granny's Bay oysters have remained consistently and substantially higher than in oysters from other sites. There was little, if any, difference in PCB concentrations at Cornwallis, Pahurehure, and Hingaia, and levels have remained low and stable at these sites.

Patterns in the levels of combined organic contaminants in oysters were also examined using MDS (Fig. 10). All of the organic contaminants that had been continuously recorded since 1996 were included in the analysis. There tended to be a high degree of temporal overlap, but 1997 stood out as having a distinct combination of contaminant concentrations. Granny's Bay and Cornwallis also stood out as having relatively distinct contaminant signatures, while Pahurehure and Hingaia were fairly similar.

Examination of longer term trends in the limited suite of PAHs, DDTs, chlordanes, and PCBs recommended by ARC (1998) indicates that limited PAH levels have fluctuated

around mean values of 221 to 739 ng/g depending on the site, but there has been no consistent trend in limited PAH concentrations (Fig. 11). 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.

Longer term patterns for limited chlordanes, limited DDT, and limited PCBs are consistent with the patterns shown in figures 8 and 9, and described for total chlordanes and DDT, and PCB's.

Figure 8: Concentrations of organic contaminants in oysters collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 1987 and 2003. 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 (D.L.) and presented as 0.5 x D.L.

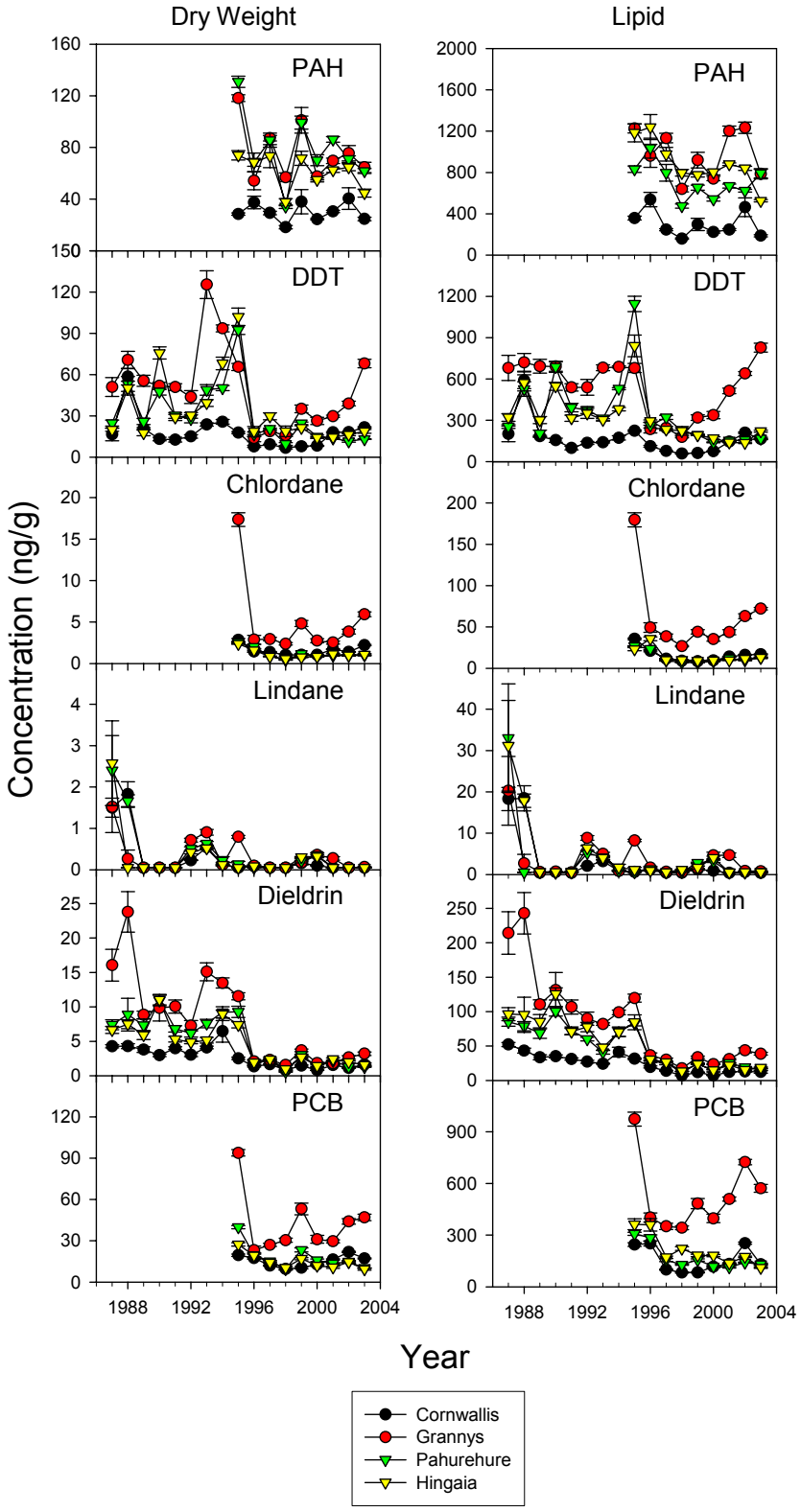


Figure 9: Concentrations (ng/g lipid ± s.e.) of lipid normalised chlordanes: cis-chlordane, trans-chlordane, trans-nonachlor, and cis-nonachlor in oysters collected from Granny's Bay between 1987 and 2003.

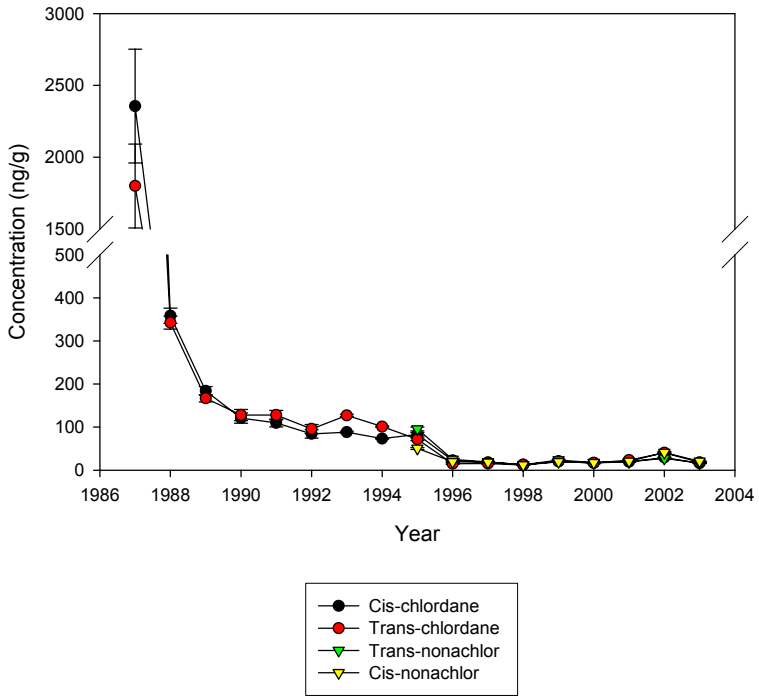


Figure 10: Multidimensional scale plots of organic contaminants present in oysters at Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 1996 and 2002. The plot on the left has data points labelled with the name of the sampling site, while data in the plot on the right is labelled with sampling year. Stress = 0.13.

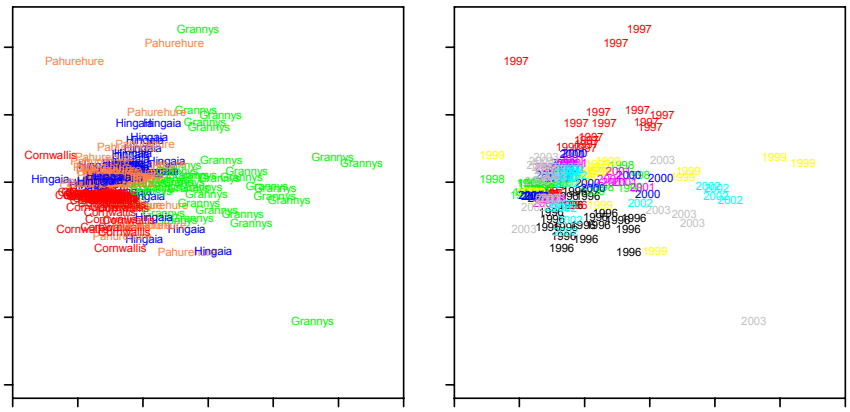
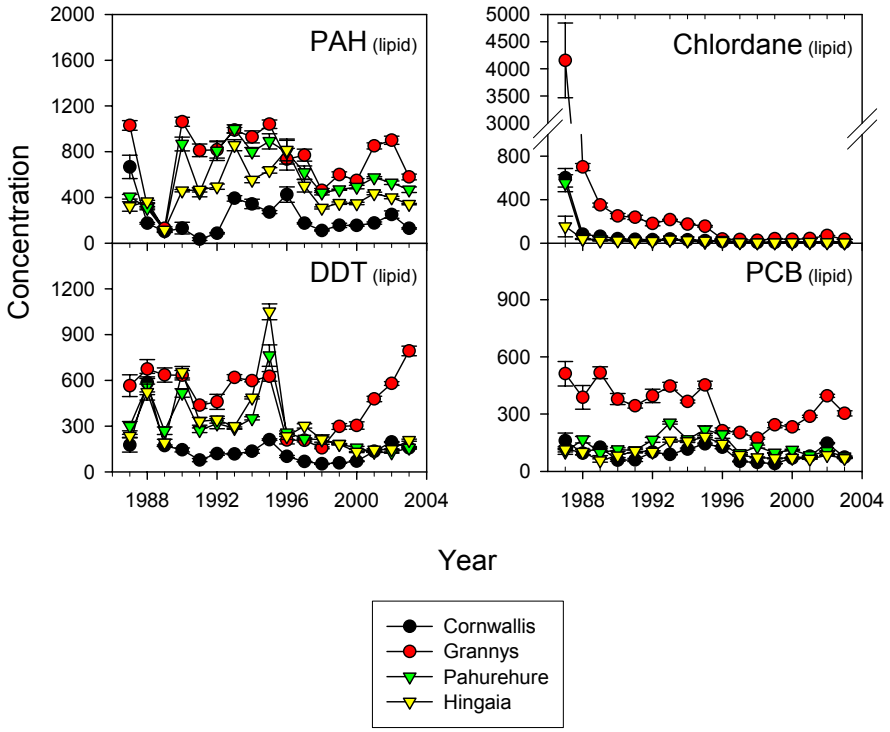


Figure 11: Concentrations (ng/g lipid ± s.e.) of lipid normalised **limited** PAHs (sum of fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]-fluorathene, benzo[k]fluoranthene, and benzo[a]pyrene) **limited** PCBs (sum of congeners 118, 138, 153 and 180), **limited** DTTs (sum of p,p'-DDE, p,p'-DDD and p,p'-DDT) and **limited** chlordanes (sum of cis-chlordane and trans-chlordane) recommended by ARC (1998) over the full period of monitoring (1987-2003). All data presented were above detection limits.



5.2.4 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 3) (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 deildrin+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)).

Concentrations of organic contaminants in Manukau oysters were relatively low in relation to the data reported from the USA and South America (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, but overall concentrations are relatively low by international standards.

5.2.5 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 high at Granny's Bay, Pahurehure, and Hingaia. Concentrations at these sites are approaching international levels used to indicate copper contamination.
- Concentrations of arsenic, cadmium, and chromium were relatively low.
- Interpretation of lead concentrations is not possible due to the high detection limits reported and the large proportion of samples below detection limits.
- PAH levels are highest at the most urbanised site (Granny's Bay) and the site adjacent to the southern motorway (Pahurehure).
- PCB concentrations at Granny's Bay are relatively high compared with other Manukau sites.
- DDT levels have increased markedly in Granny's Bay oysters since 2000, coincident with the decommissioning of ponds at the Mangere Sewage Treatment Plant.
- Chlordane, lindane, and dieldrin have declined since monitoring began, consistent with them being de-registered as pesticides.

Table 3: Comparison of PCB's and PAH's 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	✓	✓			

Table 4: Comparison of mean organic contaminant concentrations in the Manukau Harbour oyster monitoring sites pooled from the last 5 years (1999-2003) with published levels 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	PAH[1]	DDT[2]	Chlordane[3]	Lindane[4]	Dieldrin	PCB[5]
Cornwallis	Oysters	30.0	11.8	1.3	0.1	1.2	15.2
Granny's		72.0	29.2	3.3	0.2	2.3	40.9
Hingaia		58.1	17.0	0.9	0.2	1.9	13.7
Pahurehure		72.0	14.9	0.9	0.1	1.7	16.4
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 & T[7] (median)	Oysters	n/a	33 (n=280)	10 (n=280)		5.1[8] (n=280)	100[9] (n=280)
US NS & T 85th %[7]		n/a	140	32		15[8]	450[9]

5.3 Mussel Condition

Mussel condition was assessed by examining the relationship between shell weight and dry tissue weight (Fig. 12). Clear patterns were apparent when mussel condition was compared among sites (Fig. 13). The 2 Waitemata Harbour sites, Chelsea and Waitemata, were generally ranked worst for mussel condition, while Illiomama generally ranked best. The condition of mussels from Mangere was highly variable, while mussel condition at Papakura and Weymouth was generally ranked relatively highly. Tamaki mussels tended to have intermediate condition values.

[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 5.
[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 5). 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 cogeners 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.).

Figure 12: Relationship between shell weight and dry tissue weight for each of the mussel monitoring sites between 2000 and 2003.

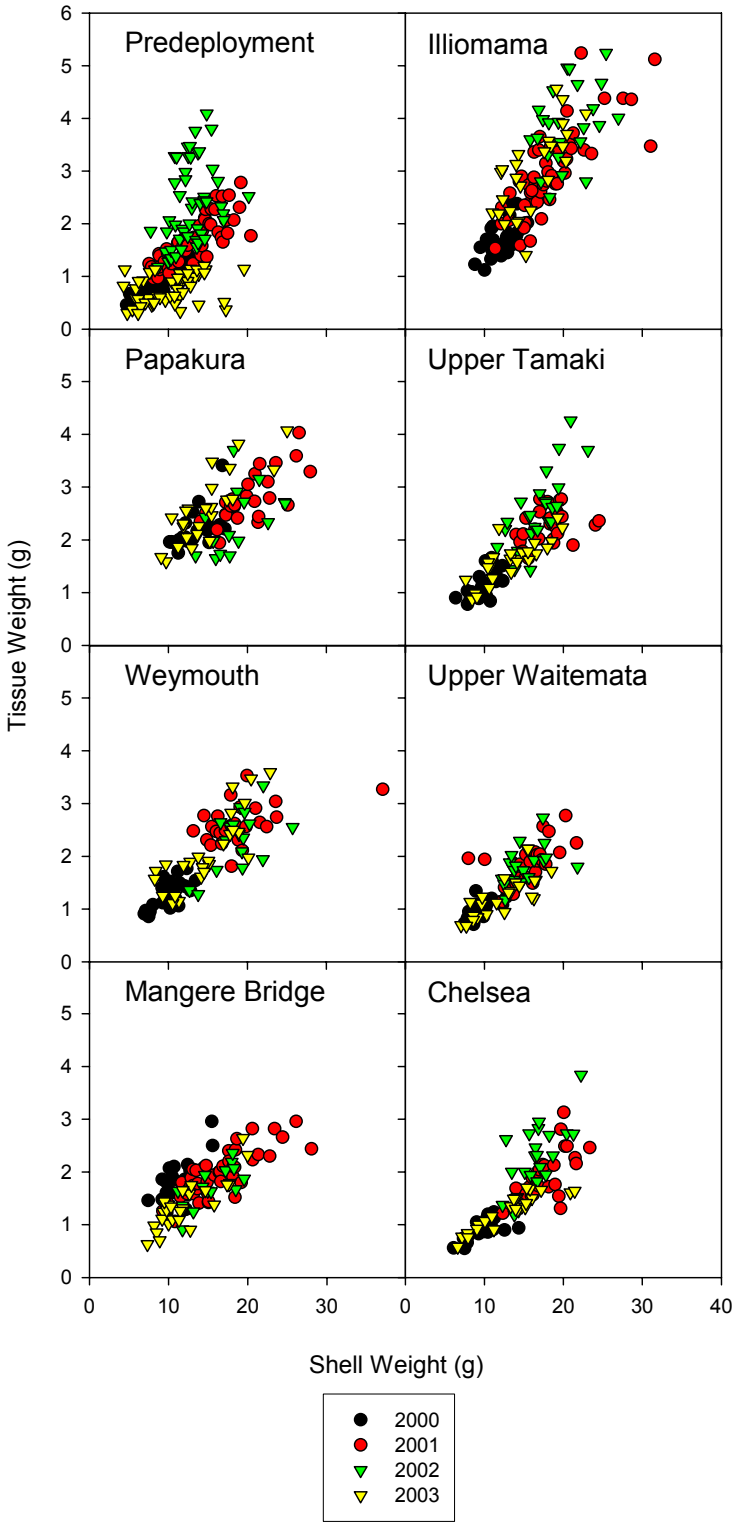
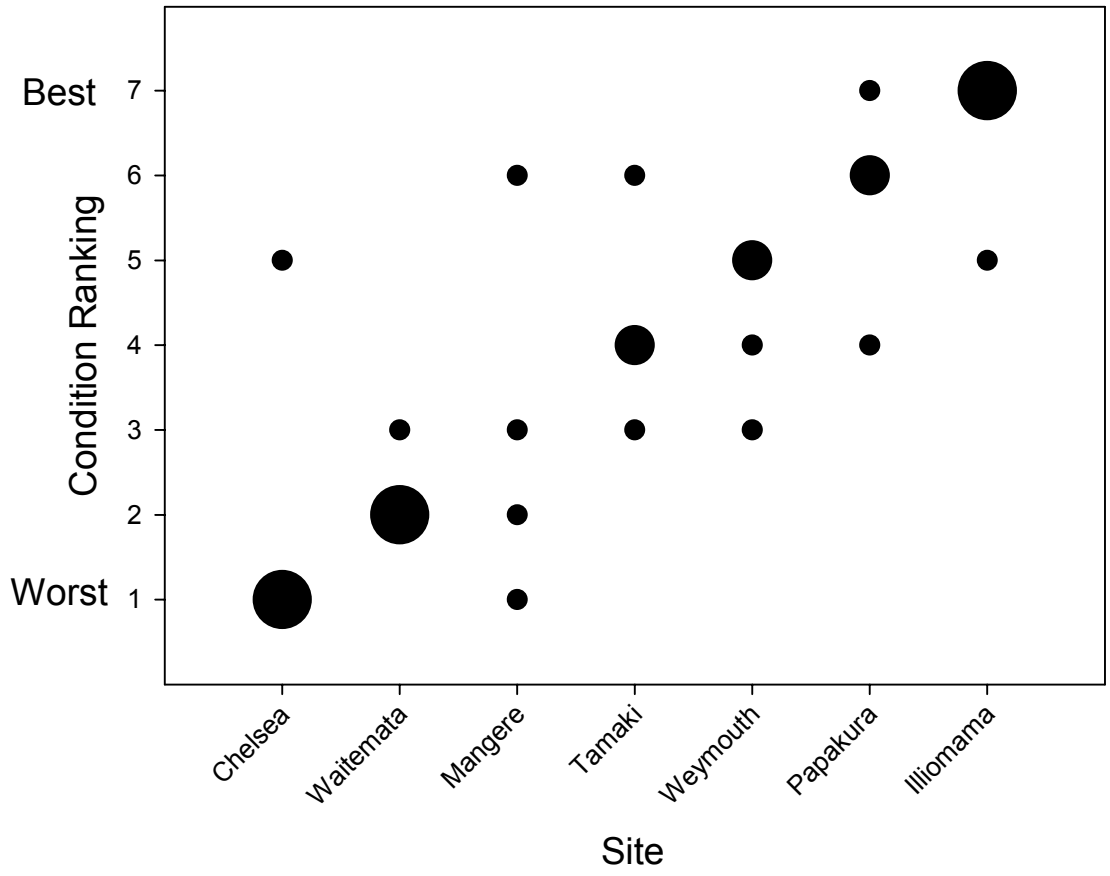


Figure 13: Rankings of mussel condition among monitoring sites from 2000 to 2003. Condition was defined by the slope of a linear regression between shell weight and dry tissue weight. Sites were ranked according to the gradient of the slope in each year, with rank 1 indicating worst, and rank 7 best, condition. Bubble size indicates the number of times (years) each site obtained a particular rank (total number of years = 4 for each site). For example, Chelsea mussels had the worst condition (rank 1) during 3 of the 4 years sampled, and were ranked 5 for condition in the remaining year.



5.4 Mussel Contaminants

5.4.1 Key Metals

5.4.1.1 Detection limits

Trends in the concentration of some of the key metals in mussels were strongly influenced by detection limits. Most, or all, 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 levels that may be indicative of elevated contaminant levels. For instance, the mean detection limit provided 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 85 percentiles reported from US mussel watch programme and world database (Cantillo 1998).

Table 5: Proportion of mussel samples with key metal concentrations above detection limits between 1999 and 2002. 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%

5.4.1.2 Contaminants

Between 1999 and 2001 mean arsenic levels in mussel samples fluctuated between 0.5-16.8 µg / g (Fig. 14). 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 > 0.87, Appendix D), suggesting that interannual variation may be due to the degree of analytical accuracy (i.e. variation) rather than true temporal variation.

Cadmium levels declined markedly at all east coast sites between 1999 and 2000. 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 were therefore considered to be unreliable. In 2000 no samples exceeded relatively low detection limits (mean D.L. = 0.37 µg / g). Average concentrations at individual sites have remained less than 1.4 µg / g since 2000. No spatial patterns are apparent in cadmium concentrations, but cadmium levels were highly correlated (correlation coefficients > 0.75) among sites in 50% of site-site comparisons.

Since 1999/2000 chromium concentrations have remained relatively stable at all sites except the Upper Waitemata Harbour and Weymouth, where considerable intra- and interannual variability is evident. In the Manukau Harbour chromium levels in mussels from Mangere Inlet have tended to be slightly greater than those from Papakura and in pre-deployment samples.

Clear spatial trends were discernable in copper concentrations. On the east coast highest copper concentrations were consistently recorded in mussels from the Tamaki Estuary. Upper Waitemata Harbour and Chelsea sites yielded concentrations intermediate between Tamaki Estuary and Illiomama. Pre-deployment concentrations were below or similar to Illiomama. No consistent temporal trends were apparent in east coast copper data. In the Manukau Harbour highest copper levels have been consistently recorded in Mangere Inlet, while copper levels in Weymouth and Papakura mussels tend to be similar to those recorded in pre-deployments mussels.

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.

Zinc levels have remained relatively stable at all sites since 1999/2000, with no clear differences between sites.

Multi-dimensional scaling of combined key metals data was not able to distinguish consistent spatial differences in the signatures of metal contaminants among sites (Fig. 15). However, temporal trends in the data were clearly evident, with individual years able to be discriminated.

Figure 14: 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 2002. Data below detection limits (D.L.) are presented as 0.5 x D.L. The pooled proportion (%) of samples exceeding detection limits is also given adjacent to annual data points.

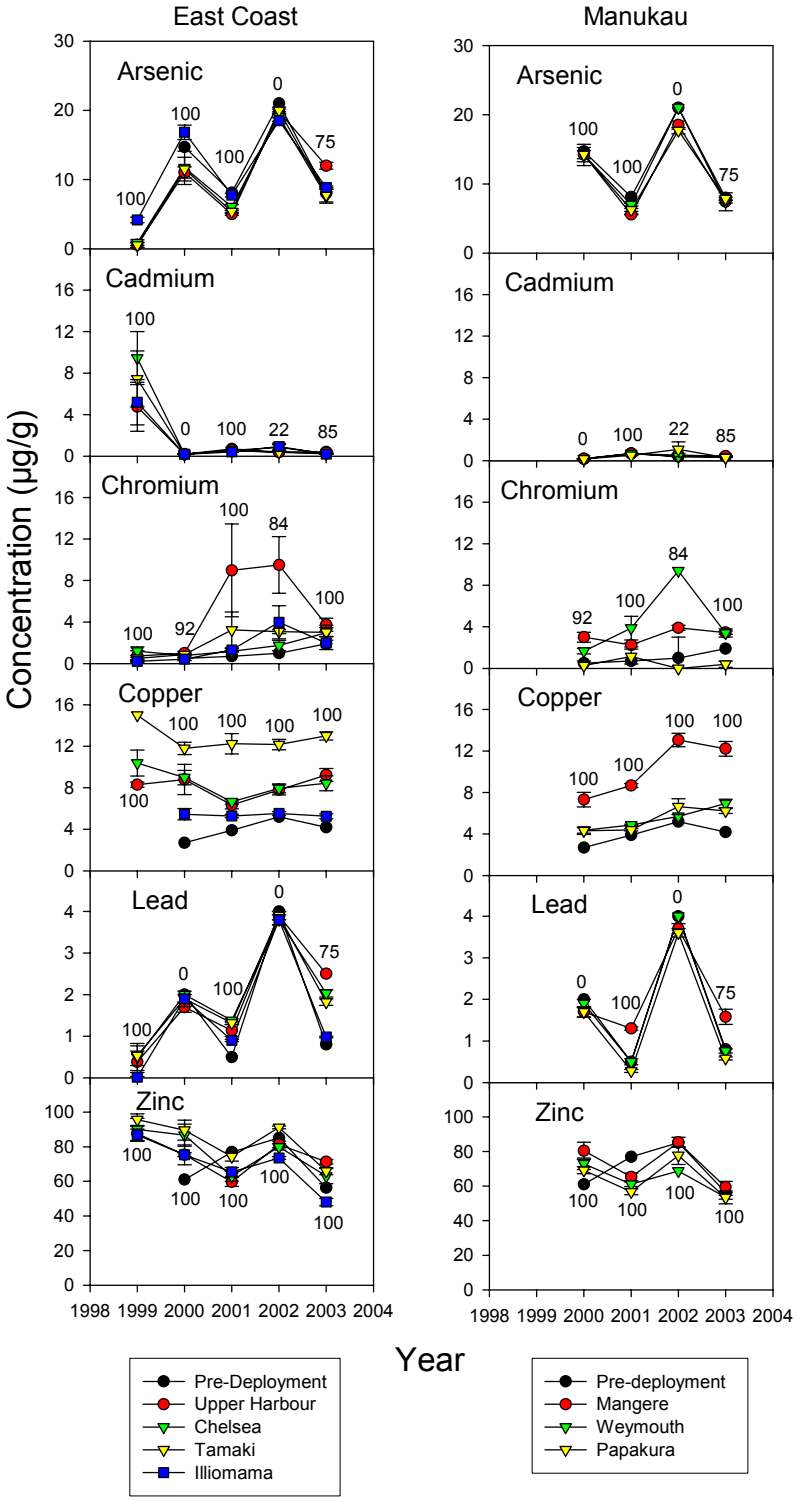
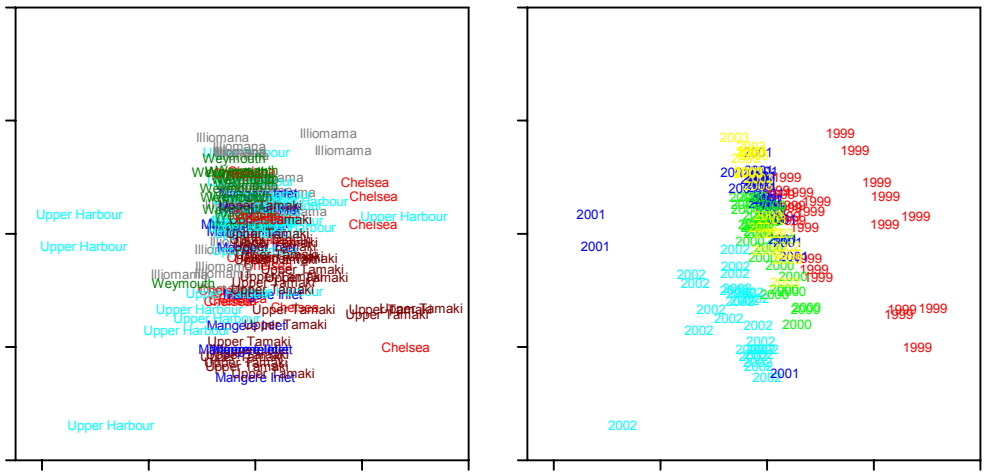


Figure 15: Multidimensional scaling plots of key metals present in mussels between 1999 and 2002. The plot on the left has data points labelled with the name of the sampling site, while data in the plot on the right is labelled with sampling year. Stress = 0.11.

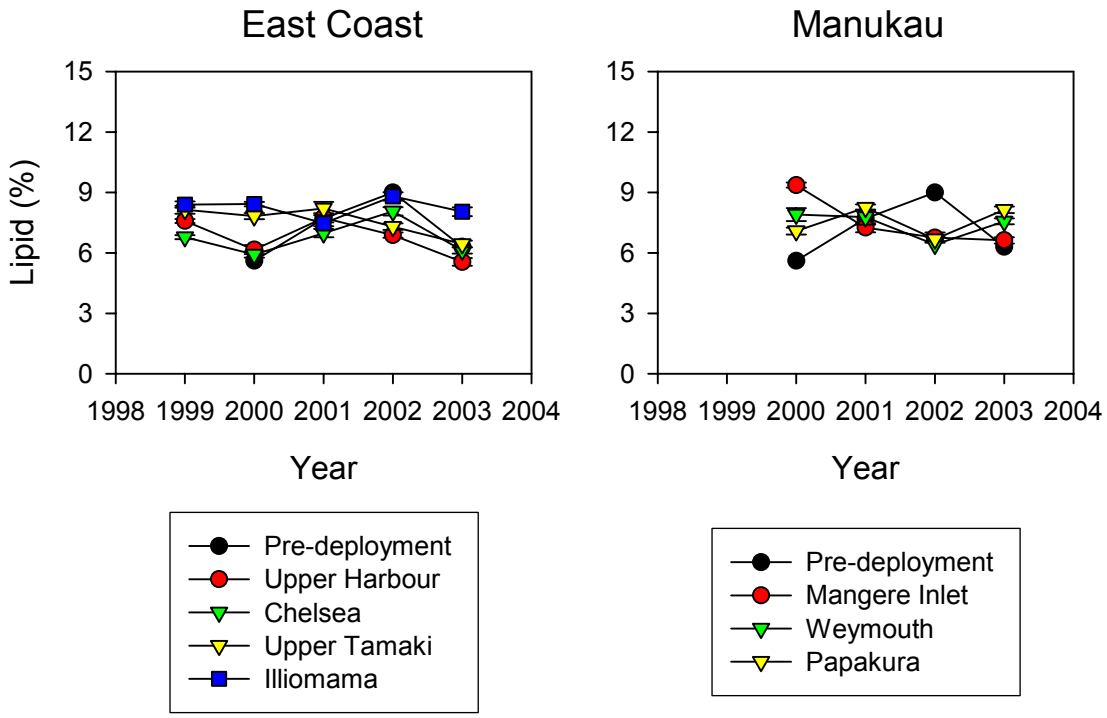


5.4.2 Mussel Organic Contaminants

5.4.2.1 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 (Fig. 16). Consequently, the trends in lipid normalised data were very similar to the trends in non-normalised data (Figs. 17 and 18).

Figure 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.



5.4.2.2 **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 (Table 6). Lindane levels below detection limits are therefore presented as 0.5 x D.L.

Table 6: Proportion of samples with lindane levels greater than detection limits.

	1999	2000	2001	2002	2003
< Detection Limits	18	26	24	33	26
> Detection Limits	6	8	11	2	9
Total number of samples	24	34	35	35	35
% > Detection Limits	25%	24%	31%	6%	26%

5.4.2.3 **Contaminants**

PAH levels remained relatively stable, or declined slightly at all sites between 1999/2000 and 2003 (Figs. 17 & 18). Concentrations in mussels set on the east coast tended to be greater than those in pre-deployment mussels and those set in the Manukau Harbour. On the east coast, highest concentrations were consistently detected at the Upper Tamaki site. Chelsea mussels tended to have slightly higher PAH concentrations than those from the Upper Waitemata Harbour site, and Illiomama generally had the lowest PAH levels, 1999 being the only exception. Within Manukau Harbour, PAH concentrations were highest in Mangere Inlet. Similar levels occurred at

Papakura and Weymouth, which had PAH concentrations similar to, or slight above pre-deployment levels.

DDT levels remained stable at all sites except Mangere Inlet where concentrations nearly doubled between 2000 and 2002 (Figs. 17 & 18). DDT levels appear to have stabilised in mussels set at this site in 2003. In the Manukau Harbour DDT levels were highest in mussels from Mangere Inlet, while Weymouth and Papakura Channel mussels had DDT concentrations only slightly above pre-deployment concentrations. On the east coast, similar DDT concentrations were recorded in mussels set in the Upper Tamaki, Chelsea, and Upper Waitemata Harbour sites. Illiomama concentrations were somewhat lower, but well above pre-deployment levels.

Chlordane concentrations were relatively low and stable over the monitoring period (Figs. 17 & 18). A trend of highest to lowest chlordane concentrations was apparent in east coast mussels, with: Upper Tamaki > Chelsea and Upper Waitemata Harbour > Illiomama > pre-deployment. Overall, chlordane concentrations were greatest in Mangere Inlet mussels. Weymouth and Papakura mussels had chlordane levels similar to those obtained from the Waitemata Harbour.

Lindane levels were low and the trends shown in Figs. 17 & 18 reflect detection limits rather than real changes in lindane concentrations.

Highest dieldrin concentrations were recorded in mussels set in the Upper Tamaki and Mangere Inlet (Figs. 17 & 18). Concentrations at the other east coast sites tended to be similar and were comparable to those obtained from Weymouth and Papakura. Lowest dieldrin concentrations were always recorded in pre-deployment mussels.

PCB levels steadily declined at all east coast sites between 1999 and 2003 (Figs. 17 & 18). Spatial differences in PCB levels among east coast sites closely matched those recorded for chlordane with: Upper Tamaki > Chelsea and Upper Waitemata Harbour > Illiomama > pre-deployment. Mussels from Mangere Inlet had higher PCB concentrations than those from the other Manukau Harbour sites, which had concentrations slightly above pre-deployment levels.

The strong spatial differences apparent in the plot of individual organic contaminants were reflected in MDS plots (Fig. 19). The contaminant signatures of Mangere Inlet, Upper Tamaki, and pre-deployment mussels were distinct from the other sites. Chelsea and the Upper Waitemata Harbour grouped together, as did Papakura, Weymouth and Illiomama. Contaminant signatures from the latter three sites are most similar to those in pre-deployment mussels. The strong temporal trends evident in MDS plots of key metal contaminants were not apparent in the plots of organic contaminants.

5.4.3 Summary of Contaminants in Mussels

- Detection limits of some contaminants, particularly lead, are too high to provide useful data;

- Clear spatial differences are apparent in mussel copper concentrations, with Tamaki Estuary and Mangere Inlet having the highest levels;
- Spatial differences are also apparent in the concentrations of organic contaminants, with Tamaki Estuary and Mangere Inlet generally having the highest levels;
- DDT levels have increased in Mangere Inlet since sampling began;
- PCB levels appear to be showing a downward trend on the east coast;

Figure 17: Organic contaminant concentration (ng / g (mussel dry weight)) of mussels trans-located into the east coast (left) and the Manukau Harbour (right), from 1999 to 2002. Values are also given for contaminant levels in samples prior to deployment. Data below detection limits (D.L.) and presented as 0.5 x D.L.

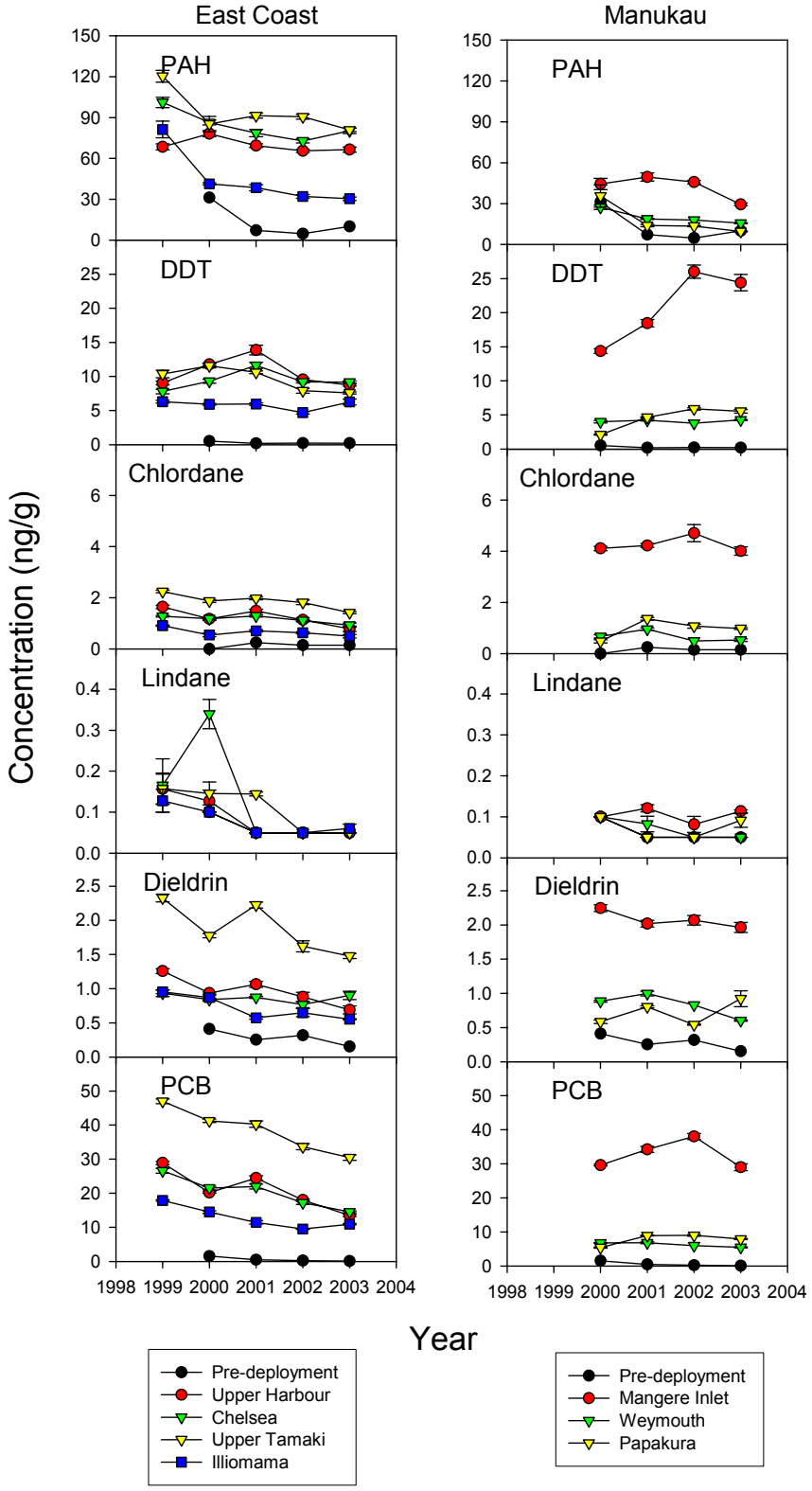


Figure 18: Lipid normalised organic contaminant concentrations (ng / g (lipid)) of mussels trans-located into the east coast (left) and the Manukau Harbour (right), from 1999 to 2002. Values are also given for contaminant levels in samples prior to deployment. The lower Tamaki site was only sampled in 1999. Data below detection limits (D.L.) and presented as 0.5 x D.L.

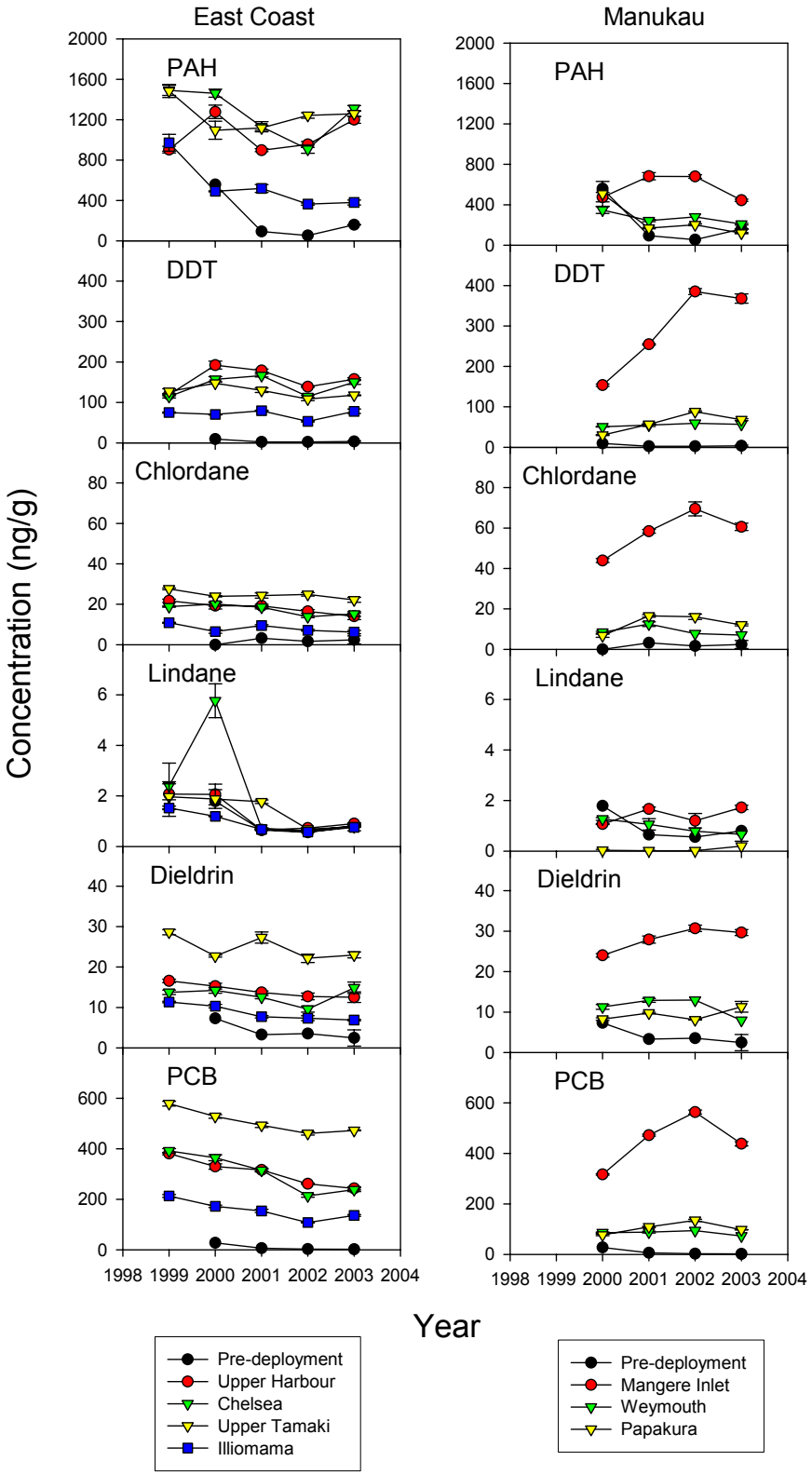
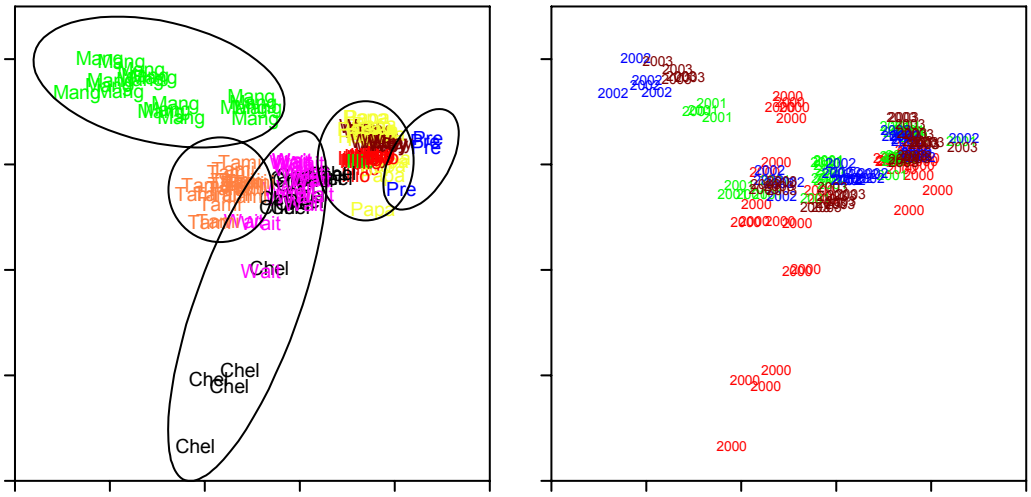


Figure 19: Multidimensional scale plots of organic contaminants present in mussels between 2000 and 2003. The plot on the left has data points labelled with the name of the sampling site and sites with similar contaminant signatures are grouped, while data in the plot on the right is labelled with sampling year. Stress = 0.06.



6 Discussion

6.1 Condition

Mussel condition does not appear to be a particularly good predictor of contaminant exposure. While the cleanest sites (Illiomama, Papakura and Weymouth) generally produce mussels with the best condition, sites with the worst contaminant levels (Tamaki Estuary and Mangere Inlet) have tended to produce mussels with moderate condition. Conversely, mussels from the two Waitemata Harbour sites (Upper Waitemata Harbour and Chelsea) accumulate only moderate concentrations of contaminants but generally have the worst condition. This suggests that other factors besides contaminants influence condition measures based on morphological characteristics. The influence of both biotic and abiotic factors on morphology is particularly evident in the Manukau oysters, whose growth form is strongly influenced by substrate type and intraspecific competition for space. Oysters growing at relatively low densities on rocky substrates tend to have a more squat, rounded shape than those growing in muddy sediments where competition for space is strong.

6.2 Temporal and Spatial Patterns in Contaminant Levels

6.2.1 Temporal Patterns

The detection of apparent trends is highly dependent on the period chosen. For instance the 1994-97 oyster metals data would indicate rapidly increasing levels of chromium, copper and zinc, but in the next five years (1997-2002) the opposite would be inferred. Such interannual variablity is likely to reflect natural variablity due to factors such as climate, hydrodynamic and biological processes, as well as changes in contaminant loads coming off the land. The value of the monitoring programme is that it allows such short-term fluctuations, which can be relatively large, to be considered within the context of longer term trends. In many cases better information on catchment "pressures" and natural factors is required to understand what causes the concentrations to fluctuate at various time scales. Metal levels in particular, have fluctuated substantually through time, and the programme would benefit greatly if these fluctuations could be independently linked to terrestrial contaminant loads.

In contrast, the patterns of some organic contaminants are more clear-cut. For instance, recent declines in the concentration of chlordane, lindane and dieldrin in oysters can be linked directly to their removal at the source. The deregistration of these pesticides in 1989-1990 resulted in a rapid decline in oyster tissue concentrations. The use of DDT on farmland was banned in 1970, so it is reasonable to expect that the most significant declines occurred prior to the start of oyster monitoring. However, DDT was available for use in a limited number of applications until it was finally deregistered as a pesticide in 1989. The recent trend of increasing

DDT in the north-eastern section of the Manukau, which is evident in both mussel and oyster tissues, may be due to the remobilisation of contaminated sediments within 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 2004). The increase in shellfish DDT levels in and around the Mangere Inlet coincides with the restoration of the foreshore area previously occupied by sewage treatment ponds.

6.2.2 Spatial Patterns

Clear spatial patterns in contaminant levels were apparent. In the Manukau Harbour pollution levels were greatest in the north-eastern corner, where there is the longest history of urbanisation and industrial landuse. Levels were lower in the south eastern parts of the harbour, and lowest toward the harbour mouth. This is reflected in MDS plots of Manukau oysters. The cleanest site, Cornwallis, was distinct for metal and organic contaminants due to substantially lower concentrations of copper, zinc, and cadmium, PAH, DDT, and to a lesser extent dieldrin and PCBs. The other oyster monitoring sites had similar levels of metal contaminants, but DDT, chlordane and PCBs tended to be highest at the most urbanised site, Granny's Bay. Similarly, in Manukau Harbour mussels, highest levels of copper, PAH, DDT, chlordane, dieldrin and PCBs were consistently recorded in Mangere Inlet. Levels of organic contaminants were similar at Weymouth and Papakura Channel, which had concentrations only slightly above pre-deployment values.

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, dieldrin and PCBs. The two Waitemata Harbour sites, Chelsea and Upper Harbour, had very similar contaminant profiles with contaminant levels intermediate between Tamaki and Illiomama.

For mussels the only clear metal signal was obtained from copper. Other metals tended to be similar in the pre-deployment, reference site and impacted sites, which suggests mussels are less sensitive than oysters at relatively low levels of metal contamination. This is consistent with patterns found elsewhere, which show that oysters are more useful in sites with low- moderate metal contamination, whereas mussels are better at monitoring heavily contaminated sites (Shulkin et al 2003). It is also possible that metals accumulate more slowly in mussels and the deployment time is not long enough for metals to build up in their tissues to levels where site differences become apparent.

6.3 Auckland in an International Context

Oysters and mussels differ in their ability to concentrate trace elements and are therefore not directly comparable (O'Conner 1992). Shulkin et al (2003) found that zinc,

copper and lead accumulation in Pacific oysters was logarithmically related to bioavailable contaminants in sediments. These contaminants rapidly accumulate in oyster tissues at sites with low-moderate sediment concentrations, but accumulation rates decline as sediment concentrations increase, presumably due to physiological control. In contrast, distinct increases in the concentration of zinc, copper, and cadmium in mussel tissues (*Crenomytilus grayanus*) were only observed above threshold sediment concentrations of 800 µg/g, 100 µg/g, and 2 µg/g respectively. Linear relationships between sediment concentrations and concentrations in mussel tissues were observed above these thresholds. Shulkin et al (2003) therefore recommended that the mussel *C. grayanus* is suitable for monitoring sites heavily contaminated with metals, while Pacific oysters were more suitable as an indicator of initial or moderate metal contamination.

The RNO, NS&T, and WMW databases include data from a number of different mussel and oyster species, and information from these two taxa groups are reported separately. Median values from the RNO and NS&T datasets are very similar, suggesting that although slight interspecific variations may occur, reasonable comparisons can still be made among oyster or mussel species (but not between oysters and mussels). Cantillo (1998) therefore suggests that the values presented in the RNO, NS&T, and WMW databases are useful for classifying metal concentrations in mussel and oyster monitoring programmes from around the world.

The WMW database is different from the RNO and NS&T databases because it includes data from studies specifically designed to sample "hot spots" of contamination (note: the WMW database does not include data contained in the RNO and NS&T databases). In contrast, the RNO and NS&T datasets emphasise the collection of samples from representative sites, rather than sites of extreme contamination. Consequently, the median values and 85th percentiles of the WMW database are generally higher than those of the other two datasets. Exceedance of the 85th percentiles of the WMW database in oysters or mussels is therefore considered to denote contamination, whereas the 85th percentiles of the NS&T and RNO datasets are more indicative of the "typical" range of trace element concentrations (Cantillo 1998).

Mean levels of most contaminants in Manukau Harbour oysters were similar to, or slightly above, medians reported from international databases (Cantillo 1998), indicating that arsenic, cadmium, chromium and zinc levels are within the "normal" range. The exception was copper levels, which were above the 85th percentiles of NS&T and RNO datasets in oysters collected from Granny's Bay, Pahurehure and Hingaia. Copper levels therefore appear to be somewhat elevated, but have not yet reached levels indicative of significant contamination (as indicated by the WMW database).

7 Conclusions

Clear spatial differences related to the level of urban development and industrial landuse are apparent in the contaminant burden of oysters and mussels. In particular, Mangere Inlet and Tamaki Estuary have relatively high shellfish contaminant levels compared with other monitoring sites. Tissue concentrations of persistent pesticides, PCB's and copper differentiated these two sites from other sites in the Manukau and Waitemata Harbours. Despite these differences, contaminant levels are generally low by international standards. The exception being copper in Manukau oyster tissues, which is approaching thresholds that are indicative of contamination.

8 References

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9 Appendix A: Descriptions of Contaminants

9.1 Key Metals

9.1.1 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 it's 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.

9.1.2 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 bioconcentration 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.

9.1.3 Chromium (Cr)

Chromium is an essential element to humans, but is toxic at higher concentrations. In the Sentinel 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. Bioconcentrations 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.

9.1.4 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 bioconcentrations 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.

9.1.5 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 bioconcentration 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.

9.1.6 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 an ubiquitous element in urban areas. Examples of its use include: galvanising, the production of alloy materials, in plasticisers for synthetic rubbers such as tyres and in paint manufacture.

9.2 Organic Compounds

9.2.1 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 PAH's are chronically and/or acute toxic to a range of aquatic organisms. Their toxicity can be magnified significantly by photoactivation with UV light (ANZECC 2000). PAH's are carcinogenic and chronic exposure has been linked to the formation of cancerous tumours in humans and animals (Nicholson 1984).

9.2.2 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.

9.2.3 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.

9.2.4 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).

9.2.5 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).

10 Appendix B: Contaminants Measured

Table B1: 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.

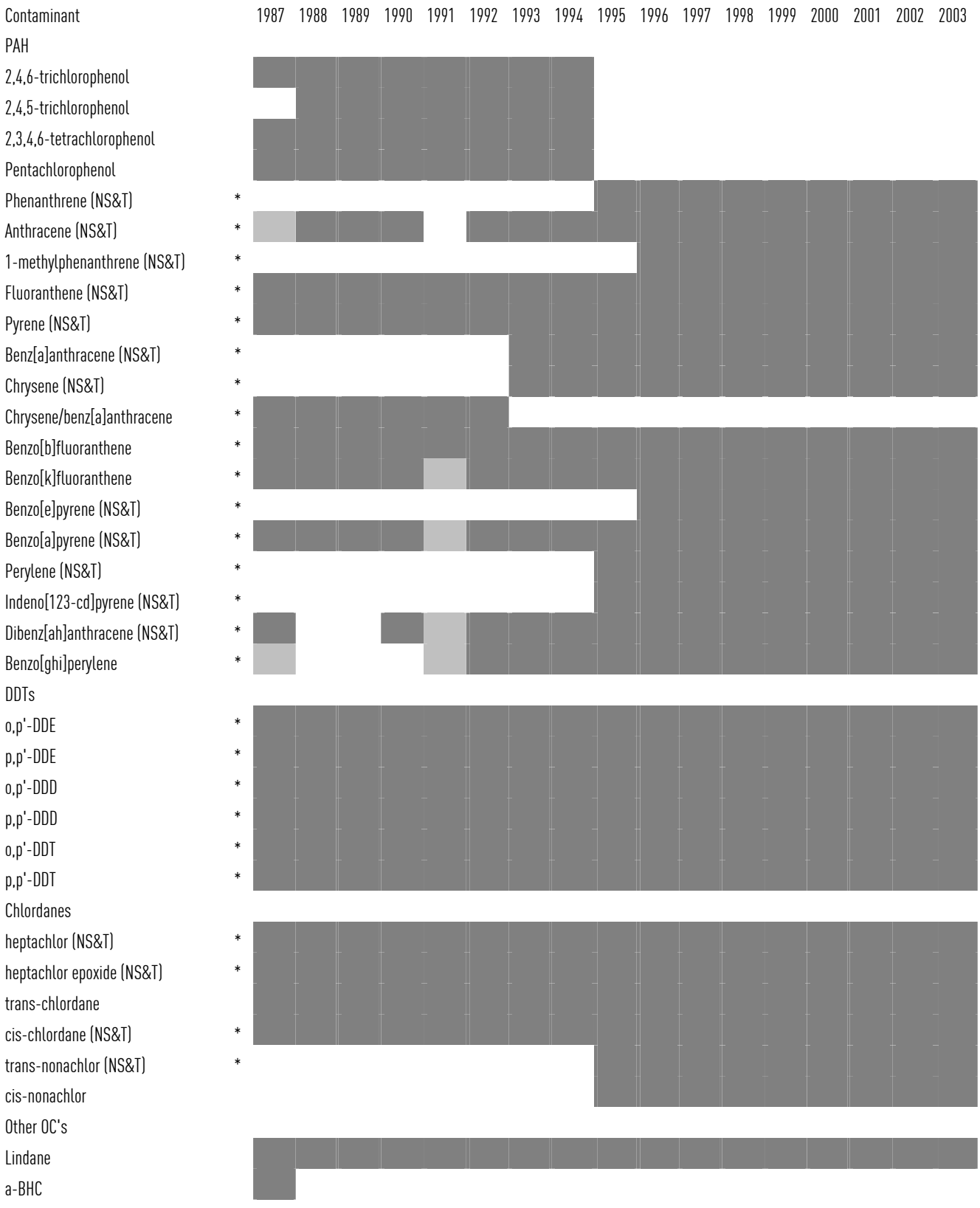

Table B1: Continued

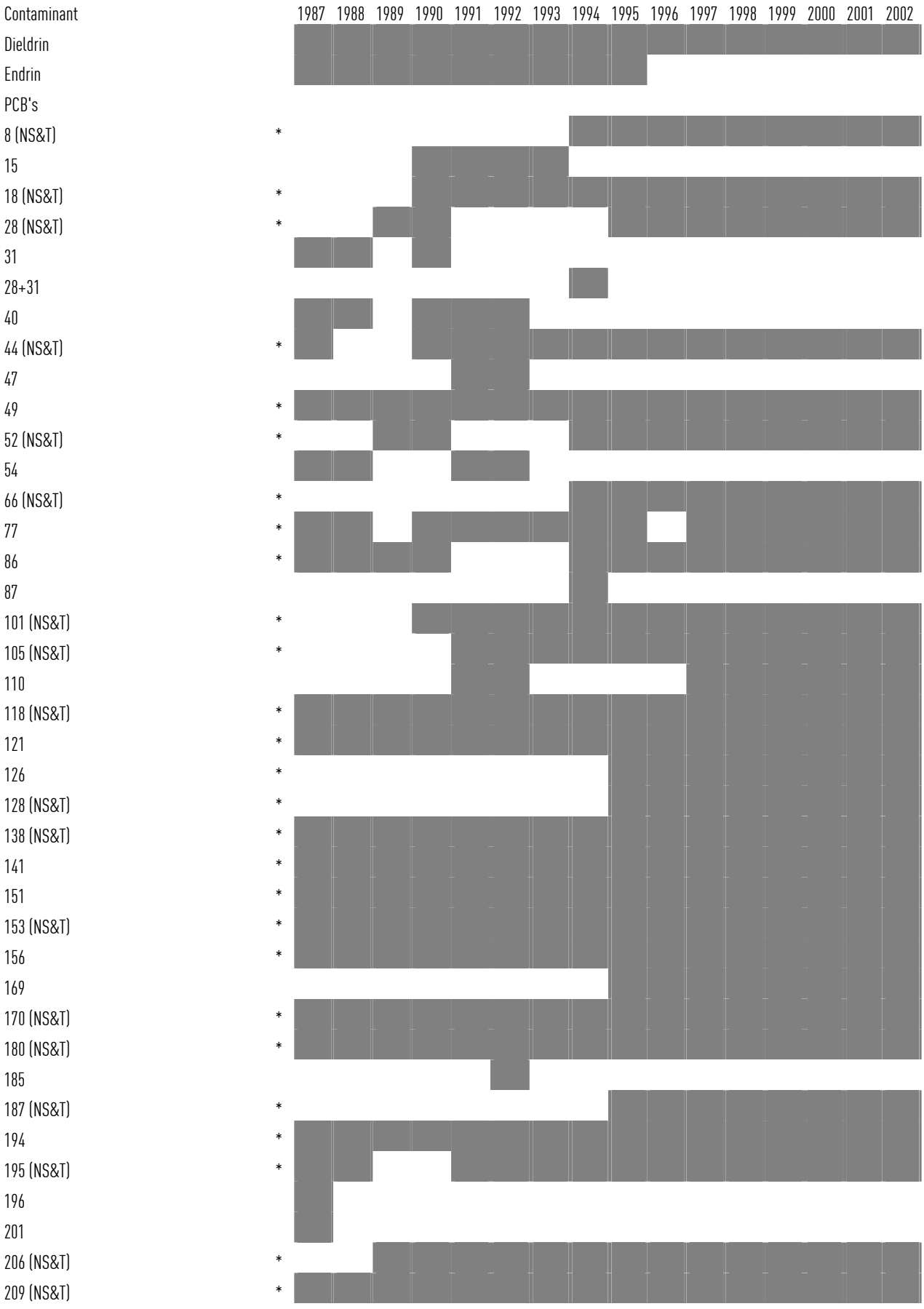

Table B2: List of organic contaminants measured in the ARC Mussel Monitoring Programme.

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				

11 Appendix C: Correlations between metals in oysters and mussels

Correlations between annual means for metals in oysters from Cornwallis, Grannys Bay, Pahurehure, and Hingaia between 1987 and 2003.

11.1 Oyster correlation coefficients and P values

	Correlation Coefficients				P values		
Arsenic							
	Cornwallis	Grannys	Pahurehure		Cornwallis	Grannys	Pahurehure
Grannys	0.78			Grannys	<0.001		
Pahurehure	0.88	0.96		Pahurehure	<0.001	<0.001	
Hingaia	0.79	0.96	0.95	Hingaia	<0.001	<0.001	<0.001
Cadmium							
	Cornwallis	Grannys	Pahurehure		Cornwallis	Grannys	Pahurehure
Grannys	0.83			Grannys	<0.001		
Pahurehure	0.87	0.90		Pahurehure	<0.001	<0.001	
Hingaia	0.89	0.93	0.93	Hingaia	<0.001	<0.001	<0.001
Chromium							
	Cornwallis	Grannys	Pahurehure		Cornwallis	Grannys	Pahurehure
Grannys	0.86			Grannys	<0.001		
Pahurehure	0.95	0.84		Pahurehure	<0.001	<0.001	
Hingaia	0.81	0.93	0.88	Hingaia	<0.001	<0.001	<0.001
Copper							
	Cornwallis	Grannys	Pahurehure		Cornwallis	Grannys	Pahurehure
Grannys	0.84			Grannys	<0.001		
Pahurehure	0.35	0.14		Pahurehure	0.166	0.598	
Hingaia	0.69	0.68	0.59	Hingaia	0.002	0.003	0.013
Zinc							
	Cornwallis	Grannys	Pahurehure		Cornwallis	Grannys	Pahurehure
Grannys	0.65			Grannys	0.004		
Pahurehure	0.59	0.39		Pahurehure	0.012	0.127	
Hingaia	0.57	0.77	0.70	Hingaia	0.017	<0.001	0.0016

11.2 Mussel correlation coefficients

Arsenic

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.84						
Chelsea	0.99	0.91					
Tamaki	0.98	0.93	1.00				
Illiomama	0.95	0.76	0.91	0.90			
Mangere	0.98	0.85	0.97	0.96	0.98		
Weymouth	1.00	0.86	0.99	0.98	0.95	0.99	
Papakura	0.98	0.84	0.96	0.95	0.99	1.00	0.98

Cadmium

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.99						
Chelsea	0.45	0.58					
Tamaki	0.92	0.95	0.69				
Illiomama	0.21	0.36	0.97	0.49			
Mangere	0.93	0.97	0.70	0.90	0.51		
Weymouth	0.99	0.99	0.55	0.97	0.32	0.93	
Papakura	0.28	0.43	0.98	0.53	0.99	0.58	0.37

Chromium

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	-0.05						
Chelsea	1.00	0.02					
Tamaki	0.51	0.81	0.56				
Illiomama	0.35	0.68	0.43	0.63			
Mangere	0.47	0.00	0.50	0.07	0.73		
Weymouth	0.10	0.77	0.18	0.57	0.97	0.62	
Papakura	-0.05	0.41	0.02	0.12	0.84	0.80	0.88

11.3 Mussel P-values

Arsenic

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.16						
Chelsea	0.01	0.09					
Tamaki	0.03	0.07	<0.01				
Illiomama	0.05	0.24	0.09	0.10			
Mangere	0.02	0.15	0.03	0.04	0.02		
Weymouth	<0.01	0.14	0.01	0.02	0.05	0.01	
Papakura	0.02	0.16	0.04	0.05	0.01	<0.01	0.02

Cadmium

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.01						
Chelsea	0.55	0.42					
Tamaki	0.09	0.05	0.31				
Illiomama	0.79	0.64	0.03	0.51			
Mangere	0.07	0.03	0.30	0.10	0.49		
Weymouth	0.01	0.01	0.45	0.03	0.68	0.07	
Papakura	0.72	0.57	0.02	0.47	0.01	0.42	0.63

Chromium

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.95						
Chelsea	<0.01	0.98					
Tamaki	0.49	0.19	0.44				
Illiomama	0.65	0.32	0.57	0.37			
Mangere	0.54	1.00	0.50	0.93	0.27		
Weymouth	0.90	0.23	0.82	0.43	0.04	0.38	
Papakura	0.95	0.59	0.98	0.88	0.17	0.21	0.12

Copper

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.78						
Chelsea	0.63	0.07					
Tamaki	0.60	0.70	0.94				
Illiomama	0.81	0.92	0.64	0.33			
Mangere	0.09	0.80	0.99	0.39	0.87		
Weymouth	0.40	0.57	0.90	0.07	0.64	0.17	
Papakura	0.15	0.67	0.84	0.45	0.76	0.02	0.20

Lead

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.18						
Chelsea	0.05	0.04					
Tamaki	0.04	0.06	<0.01				
Illiomama	<0.01	0.17	0.05	0.03			
Mangere	0.05	0.08	0.01	<0.01	0.03		
Weymouth	<0.01	0.17	0.05	0.04	<0.01	0.04	
Papakura	0.36	0.88	0.61	0.55	0.35	0.50	0.36

Zinc

	Pre-Deployment	Upper Harbour	Chelsea	Tamaki	Illiomama	Mangere	Weymouth
Upper Harbour	0.06						
Chelsea	0.10	0.01					
Tamaki	0.06	<0.01	0.01				
Illiomama	0.05	0.01	0.01	<0.01			
Mangere	0.06	<0.01	0.01	<0.01	0.01		
Weymouth	0.07	0.01	0.01	<0.01	<0.01	0.01	
Papakura	0.05	<0.01	0.02	0.01	0.01	<0.01	0.02

12 Appendix D: Onehunga Rainfall

Total rainfall at the ARC Onehunga weather station for the August-December periods from 1990 to 2002.