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Contaminant monitoring in shellfish: results of the 2002 shellfish contaminant monitoring programme

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Contaminant monitoring in shellfish: Results of the 2002 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. Occasional sampling of shellfish from other locations has also been carried out since 1987.

The Shellfish Contaminant Monitoring Programme indicates that levels of organic contaminants are relatively high in the Mangere Inlet and Tamaki Estuary compared with other Auckland, and possibly New Zealand sites. Mussels and oysters in Mangere Inlet had elevated concentrations of DDT, chlordane, dieldrin and PCBs relative to the other monitoring sites. Dieldrin and PCBs were also relatively high in Tamaki Estuary. Marked declines in the levels of lindane, chlordane and dieldrin have been observed since these pesticides were deregistered in 1989-1990. PCBs declined between 1995-96, coincident with their banning, but recent increases have occurred which probably reflect the ubiquity of PCBs in the industrial catchments, on-going use of existing products, and significant stores in old material and contaminated soils.

Copper levels were elevated in the Manukau Harbour and are approaching concentrations considered to be indicative of contamination. Oyster data collected during a one-off survey of Waitemata Harbour and Hobson Bay in 1998 were also compared with those from the Manukau Harbour and international shellfish monitoring programmes. Contaminant levels were substantially higher in Waitemata and Hobson Bay oysters relative to the Manukau Harbour, although Manukau did experienced high levels during the same period. Copper levels in east coast oysters were approximately 2 to 4 times higher than international thresholds considered to be indicative of contamination. Zinc levels were also substantially above international thresholds of contamination and exceeded concentrations reported for the highly contaminated Russian port of Vladivostok. This is anaomolous with sediment quality data, which is relatively low by international standards. Further investigations are therefore recommended to determine the reason for the high copper and zinc concentrations in oysters.

Unfortunately, inconsistent and high analytical detection limits meant that inadequate information was available to assess the status of some key metal contaminants, such as lead. Procedures for increasing the sensitivity, reducing variability, and verifying the accuracy of metal analyses should therefore be investigated.

The condition of both oysters and mussels was consistently better at the cleanest sites, and poorer at sites impacted by urban or industrial development. However, the relationship between contaminant levels and condition was not simple. Other factors such as habitat type and primary production are also likely to affect the morphological characteristics currently used to determine condition. Shellfish condition provides a useful tool for assessing the general biological effects of environmental pressures, but its relationship with specific chemical contaminants requires further work to fully understand.

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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 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 time 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.

The use of oysters as a region wide monitoring tool is 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 are derived from sources such as vehicle emissions, tyre and brake lining wear, pesticides, industrial activity and roof runoff, entering the sea primarily through stormwater discharges. 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 –2002 Manukau Oyster and 1999 – 2002 Mussel Monitoring Programmes. Data from the 2002 Manukau Oyster Programme are also compared those from a 1998 Waitemata Harbour survey and overseas shellfish monitoring programmes to provide broader context for the concentrations of contaminants measured.

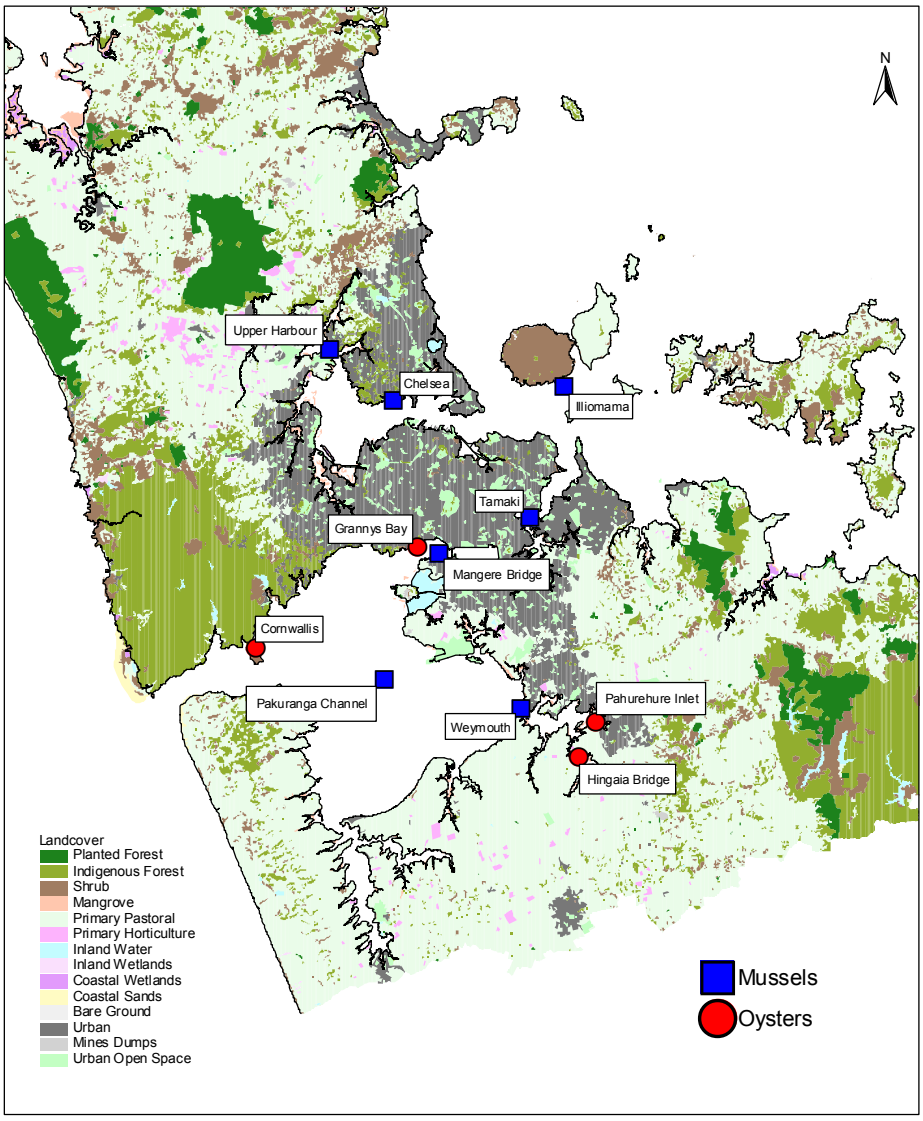
[1] http://www.foodstandards.gov.au/foodstandardscode/index.cfm#_FSCchapter1

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 Inlet (Fig. 1). 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 a levels due to a recent discharge event, samples are not collected until there has been five continuous days of little (< 5 mm) to no rain. 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

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 at 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. 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 included.

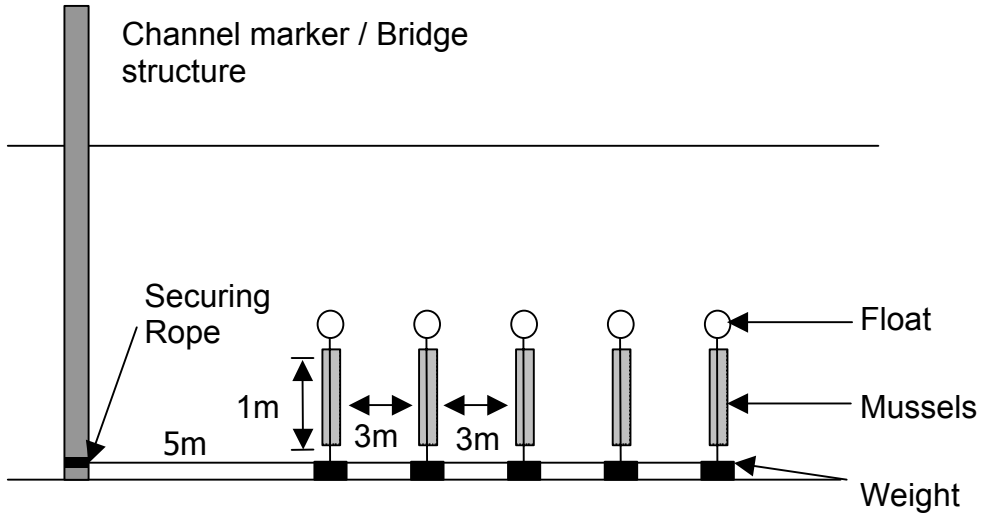
Mussel ropes approximately 1 metre long were seeded with approximately 55 mussels each, by feeding the rope and shellfish into a biodegradable mussel stocking. The stocking holds the mussels against the rope long enough for them to become attached. Six ropes were set onto a rig at each site by commercial 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 replicate (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 replicate 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.

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. Mangere Inlet 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

Oyster condition was compared among sites using analysis of covariance (ANCOVA) of the condition index proposed by Roper et al. (1990) (equation 1) with oyster total weight as a covariate. Regression techniques were also use to examine morphological differences among oysters from various sites.

Mussel condition was compared among sites using ANCOVA and regression techniques, rather than a specific index. The mussel condition index used in previous reports (equation 2, Hickman and Illingworth 1980) was not considered appropriate because:

- The condition index was developed to examine seasonal trends in mussel condition that are primarily related to reproduction – not site specific stressors such as contaminant load.
- The condition index provides a measure of the dry flesh weight / [wet flesh weight + cavity fluids] (equation 2). It was considered that contaminants were unlikely to affect this ratio.

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

2) $$\text{Mussel\_Condition} = 100 \times \frac{DFW}{(WTW - WSW)}$$

Where: DFW = Dry Flesh Weight
WTW = Wet Total Weight
WSW = Wet Shell Weight

The morphological parameters used in the condition analyses were measured by Watercare Services Ltd, Auckland.

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 appear (approximately 3 hours). The funnel was then removed, and the temperature increased to 120°C until the solution has 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.

Quantitative analysis of PAH's and PCB's was 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 and 1998 Waitemata Data

Contaminant levels in Manukau oysters and in oysters collected from the Waitemata Harbour and Hobson Bay in 1998 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 Systat statistical 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 are plotted close togeather, while samples that are dissimilar are widely seperated. Further details on MDS can be obtained in Clarke (1993).

5 Results

5.1 Oyster Condition

Pooled data from 2001 and 2002 indicate that there was a negative relationship between oyster size (weight) and the oyster condition index (Fig. 3). Analysis of covariance (ANCOVA) of pooled 2001 and 2002 oyster condition data was therefore used to compare the condition of oysters from each site using size as a covariate. No significant interaction was detected between site and total weight ($P = 0.462$), indicating that the slope of the relationship between total weight and oyster condition did not vary significantly between sites. Highly significant differences in condition were detected among sites ($P < 0.001$), with oysters from Cornwallis having the best condition, followed by oysters from Pahurehure, Hingaia, and Granny's respectively (Fig. 4).

However, linking differences in oyster condition to contaminant levels per se was somewhat problematic, because the morphology of oysters varied markedly between sites (Figs.5 & 6). 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 other sites (Fig. 5), and a strong linear relationship was found between shell weight and tissue weight (Fig. 6). 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. 5). 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. 6). 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. 6).

Figure 3: Relationship between oyster size (weight in grams) and oyster condition in samples collected from Cornwallis (red), Granny's Bay (green), Pahurehure (yellow), and Hingaia (blue) in 2001 (circles) and 2002 (squares).

$$\text{Oyster\_Condition} = 100 \times \frac{\text{Dry Flesh Weight}}{\text{Wet Shell Weight}}$$

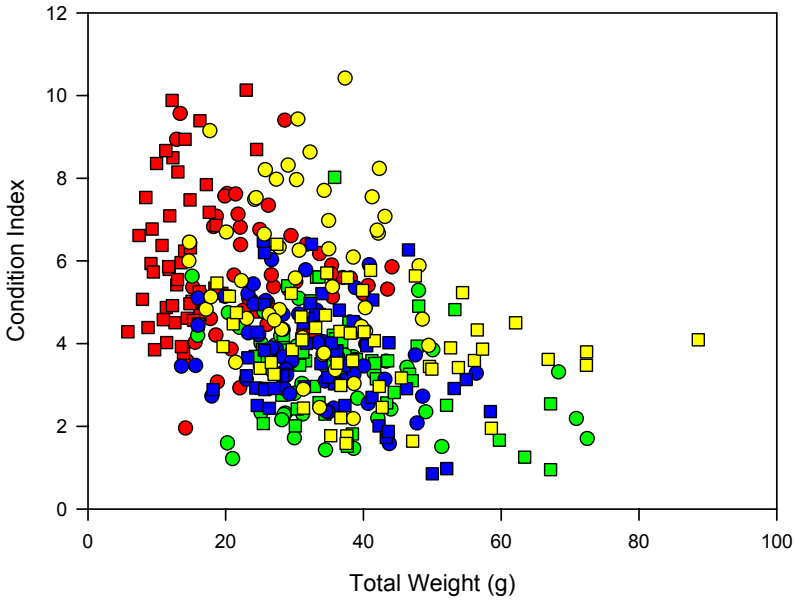


Figure 4: Adjusted least square means (+ s.e.) of oyster condition obtained from analysis of covariance using total weight as a covariate. .

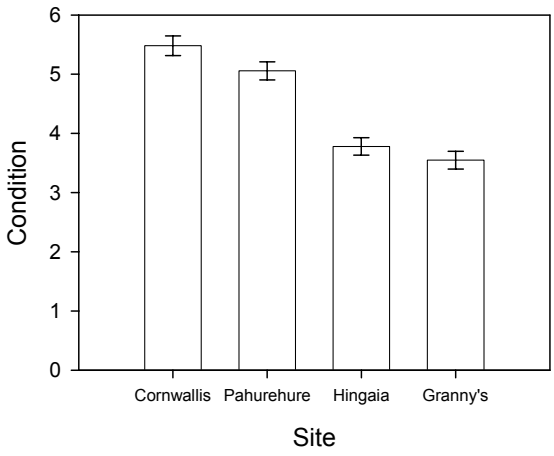


Figure 5: Length-width relationship for oysters collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 2000 and 2002. A linear regression has been fitted to data from Cornwallis, while an exponential growth function ($y = \exp^{(ax)}$) has been fitted to data from the other three sites.

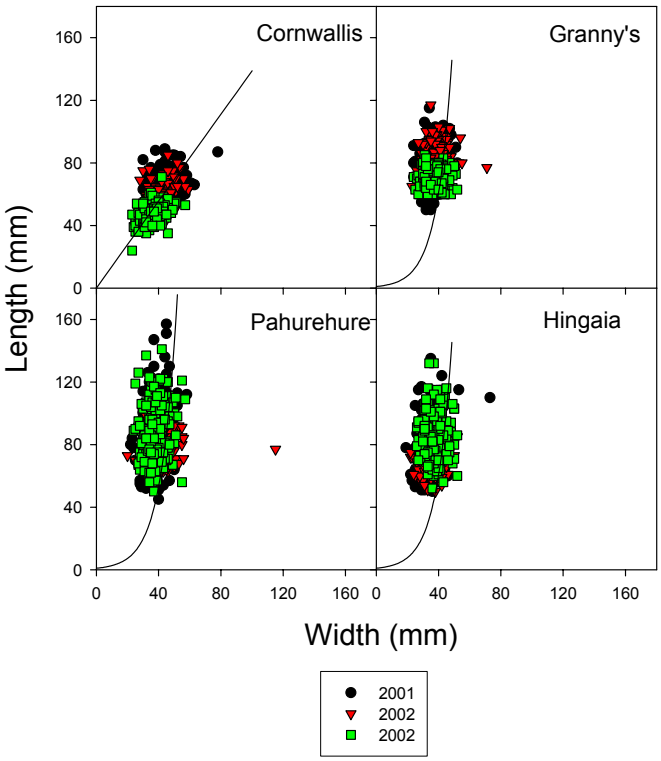
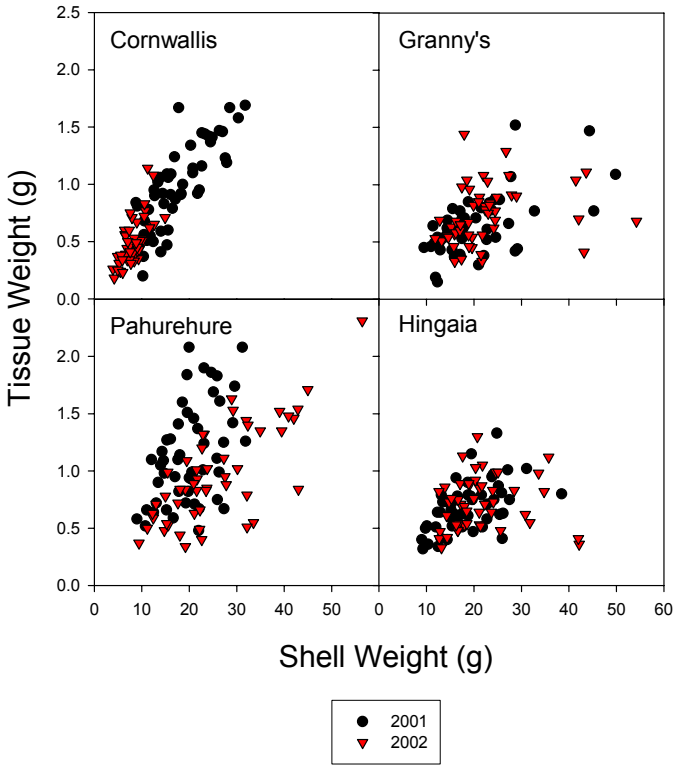


Figure 6: Relationship between oyster shell weight and dry tissue weight in samples collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia in 2000 and 2001.



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 2002 (Table 3). In contrast, arsenic, cadmium, and chromium levels were above detection limits in 76 - 82% of samples, while lead levels were above detection limits in only 15% of samples (Table 3). Checks were carried out to examine the effects of using 0.5 x D.L. for samples below detection limits, compared with replacing values below detection limits with zero (Fig. 7). The use of zero for data below detection limits resulted in a slight increase in the within-year variability of cadmium, chromium, and arsenic but did not change overall patterns for these elements, except for the 2002 values of arsenic, which were below, very high detection limits (36-44 ug/g). Copper and zinc determinations were all above detection limits, so these elements were unaffected by the method of data treatment. However, temporal patterns for lead were strongly affected by the way samples below detection levels were treated due to the low proportion of lead samples above detection limits and the relatively high detection

limits reported for lead. Extreme, care should therefore be taken in interpreting lead data.

Table 3: Number of samples collected between1987 and 2002 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	0.5	N/A
Mean Detection Limit	16.50	1.23	1.06	N/A	4.95	N/A
< Detection Limit	117	97	87	0	404	0
> Detection Limit	377	398	385	495	72	495
Total N°. Collected	494	495	472	495	476	495
% < Detection Limit	24%	20%	18%	0%	85%	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. 7). Within-year and within-site variation was relatively low (mean coefficients of variation of < 20% for all metals except chromium which was < 50%), but interannual variation in some metals was fairly 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 at individual sites, tracked each other closely through time, 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 examine the overall contaminant status of each site. Data from 1987 and 1999 were dropped from the MDS analysis due to samples not being available from all sites. Samples with missing values for one

or more metals were also removed prior to analysis. Multidimensional scaling revealed 2 patterns (Fig. 8).

1. A spatial trend running from the bottom left hand corner to top right of 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 right to top left 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 consistant 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 7: 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 (left-hand plots) or replacing values below detection limits with zero (right-hand plots).

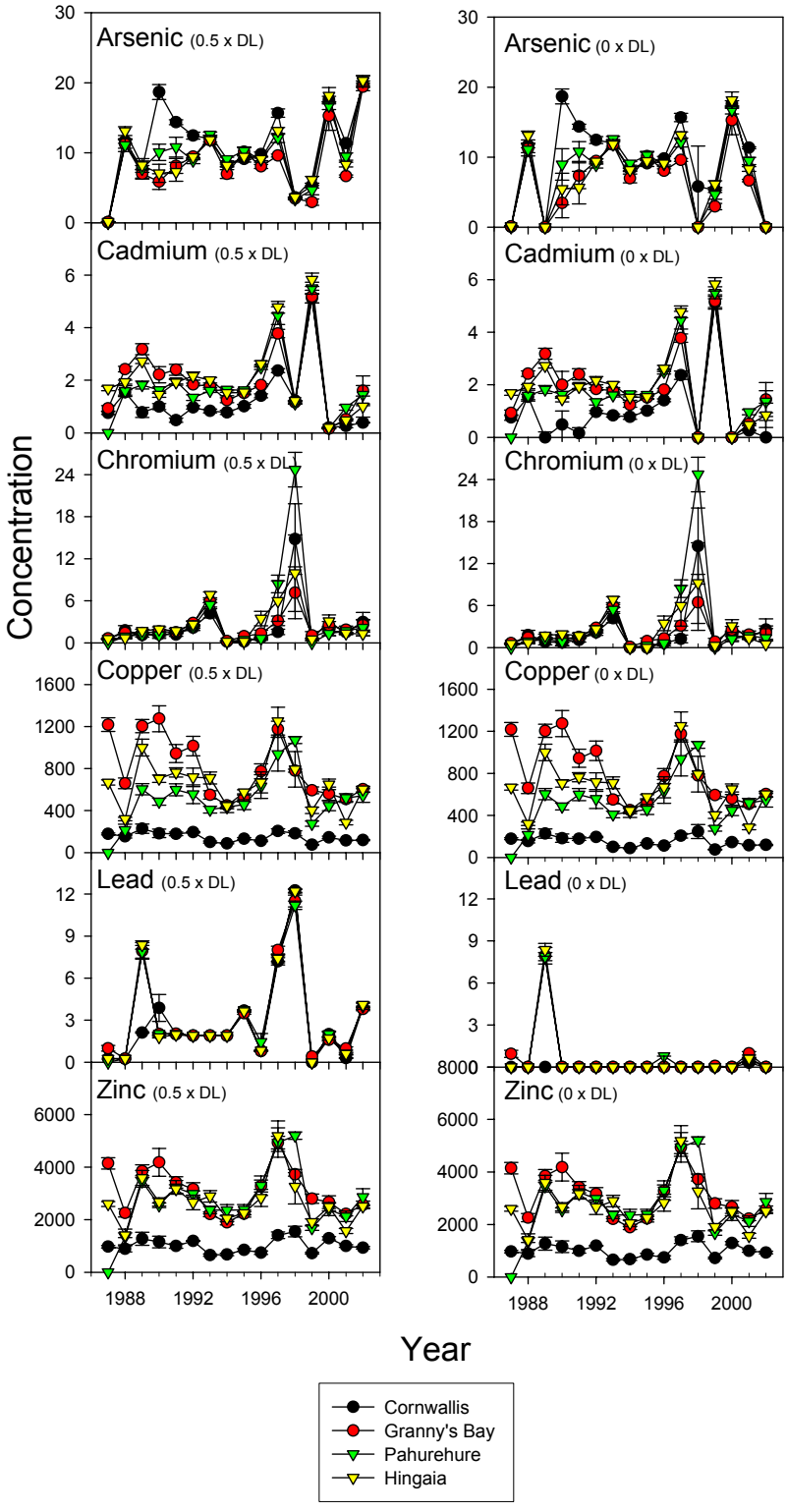
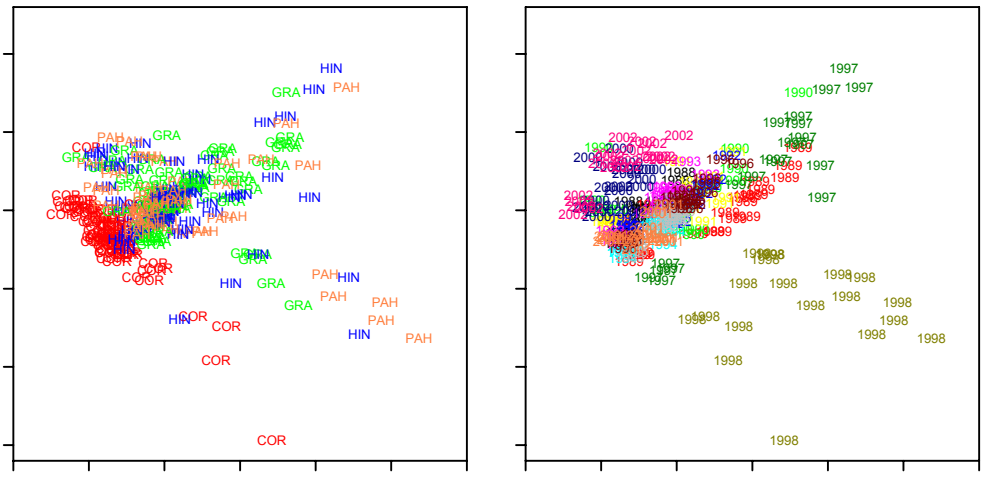


Figure 8: Multi-dimensional scaling (MDS) plots of metal concentrations in oysters. Plots are of the same data with site name (left hand plot) and year (right hand plot) labels for data points.



5.2.2 Comparison with International Studies and 1998 Waitemata Data

Mean metal concentrations in Manukau Harbour and 1998 Waitemata Harbour oysters were compared with those published in the international literature (Table 4). Recent studies from the USA (NS&T data), France (RNO data), Australia (New South Wales (NSW)), Vladivostok (Russia - Sea Of Japan), and Taiwan were selected to provide comparisons from a range of sites with varying pollution levels. In addition, data obtained from the National Oceanic and Atmospheric Administration (NOAA) world-wide bivalve database (WMW) (Cantillo 1998) was compared to local data. The 85th percentiles of world-wide data are considered to be indicative of contamination (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 other values reported in Scanes and Roach (1999) (exceptions are arsenic and the 85th percentiles for zinc). Values from Cantillo (1998) were used for comparisons with ARC oyster data.

Manukau concentrations of arsenic were similar to values obtained from Taiwan. Arsenic concentrations were above the medians from the NS&T and WMW datasets, but below the 85th percentiles provided. They were considerably less than those obtained from NSW. 1998 Waitemata oysters had low arsenic concentrations by international standards. 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 similar to concentrations obtained from Taiwan, but were below the medians provided in all of the other international studies. In contrast, 1998 cadmium levels in oysters at some of the Waitemata sites (Beachhaven and Hobson Bay) were above the 85th percentiles for the NS&T, RNO datasets but well below the 85th percentile for the WMW dataset.

Manukau harbour chromium levels, were greater than the medians provided for the NS&T and WMW databases and NSW dataset. 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. Chromium levels are not available for 1998 Waitemata oysters.

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, NSW background concentrations and values reported from Taiwan. Copper concentrations recorded in 1998 Waitemata oysters were 2 - 4 times higher than the 85th percentiles of all datasets, suggesting that oysters from east coast sites were substantually contaminated with copper. 1998 Island Bay copper concentrations were approaching median levels recorded at highly contaminated Vladivostok sites.

Lead levels in Manukau oysters were below detection limits in a high proportion of samples (85%, see Table 3). 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 similar to NSW background levels, which are slightly greater than the medians given for the NS&T, RNO and the WMW databases. All Manukau Harbour sites were well below the 85th percentiles given for zinc. Zinc levels at Cornwallis were 2 to 3 times lower than the other Manukau sites, and were above those reported for Taiwan and the "pristine" Vladivostok site. Waitemata oysters had very high levels of zinc in 1998. Oysters at all Waitemata sites exceeded the 85th percentiles of the NS&T, WMW, and RNO datasets. Furthermore, 1998 Waitemata zinc levels were similar to those from highly contaminated Vladivostok sites. The Waitemata results suggest moderately high levels of contamination, but note that the 1997/1998 results from Manukau were also abnormally high compared with other years. Unfortunately, ongoing monitoring of oysters in the Waitemata was not maintained, so it is not known if high zinc levels have persisted or if Waitemata and Manukau metals follow similar trends.

Table 4: Comparison of mean metal concentrations (g / g) for data pooled for the years 1988 – 2002 from Manakau Harbour oyster monitoring sites with published medians from international studies. Notes: 1) local values for lead should be treated with caution (see text for further details). 2) Ranges are provided in brackets for Vladivostok contaminated site data. 3) 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 (exceptions are arsenic and 85th % for zinc - see Scanes and Roach (1999)).

Site/Programme	Taxa	Arsenic	Cadmium	Chromium	Copper	Lead	Zinc
Cornwallis	Oysters	11.9	1.4	4.6	126	<5	1080
Granny's		9.5	1.7	3.1	610	<5	2795
Hingaia		11.3	1.7	3.5	547	<5	2347
Pahurehure		10.9	1.8	7.5	571	<5	2852
Beachhaven	Oysters	1.28	8.28	1.568	1981	-	5863
Henderson Creek		3.16	1.52	0.429	1323	-	5315
Hobson Bay		1.24	8.42	0.414	2162	-	5031
Island Bay		1.22	5.427	0.408	2647	-	6597
Point Chevalier		1.27	5.962	0.418	2303	-	7116
Stanley Point		5.62	2.219	0.418	2070	-	5550
US NS & T[1]	Oysters	7.9	3.2	0.55	120	0.47	2100
US NS & T 85th %[1]		18	6.0	1.2	280	0.85	4300
RNO (France)[1]	Oysters	-	2.3	-	130	1.4	2100
RNO (France) 85th %[1]		-	6.0	-	320	2.4	3500
WMW (World) median[1]	Oysters	5.7	4.1	2.5	160	2.5	1600
WMW (World) 85th %[1]		14	21	10	680	8.6	4500
NSW All[2]	Oysters	15.8	3.2	2.7	390	1.3	4060
NSW Background levels[2]		15	5	2.4	170	0.6	2610
Vladivostok ("pristine")[3]	Oysters (same species as ARC)		6.3		54	4	839
Vladivostok (contaminated)[3]			11.6 (1.4-26)		3210 (250-6576)	18.4 (4.7-36)	4629 (1683-7262)
Taiwan[4]	Oysters (same species as ARC)	10.8	1.76	-	229	0.446	783

[1] Cantillo (1998)
[2] Scanes and Roach (1999)
[3] Shulkin et al. (2003)
[4] Jeng et al (2000)

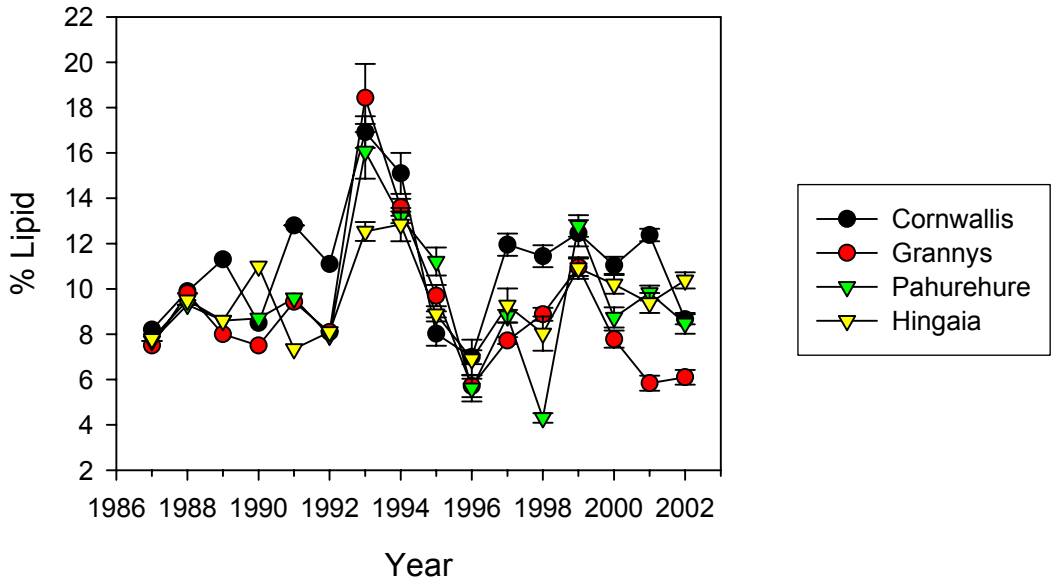
5.2.3 Oyster Organic Contaminants

5.2.3.1 Lipids

Considerable interannual variation was detected in the lipid content of oysters (Fig 9). Site differences were also apparent, however, these were not consistent among years and all sites tended to display similar temporal trends. Peak lipid levels were measured in 1993 (~ 12 - 20%). Levels subsequently declined over the next 3 years to reach a minima in 1996. Low lipid levels (<8%) were also recorded in oysters collected from Pahurehure in 1996 and Granny's Bay in 2001 and 2002. In other years lipid levels have fluctuated between, approximately, 8 – 12%.

Contaminant data are presented as concentrations based on total dry weight and as lipid normalised concentrations (Fig. 10). 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 9: 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

Clear patterns are evident in the levels of organic contaminants in oysters (Fig. 10). PAH levels were variable through time with no consistent directional trends. 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.

DDT levels appear to have been higher and more variable prior to 1995. Highest levels of DDT have been recorded at Granny's Bay in 11 of the 16 years of monitoring, with similar or slightly lower concentrations being recorded at Pahurehure and Hingaia. Lowest levels are generally found at Cornwallis. Three discrete peaks in DDT concentration were recorded at Pahurehure and Hingaia in 1988, 1990 and 1995, with levels rapidly returning to "background" concentrations. A recent increase DDT concentration at Granny's Bay is apparent, particularly in the lipid normalised data.

Chlordane levels have dropped exponentially since monitoring was initiated in 1987. 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. 11 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 levels of oysters collected from Granny's Bay between 1995 and 1996 (Fig. 10) is consistant with the longer term pattern of decline in levels at this site (Fig. 11).

Levels of lindane dropped significantly at all sites between 1987 and 1989. There remained relatively low, but detectable, concentrations of lindane from 1989 to 2002. Little spatial differentiation was apparent in lindane concentrations.

A regular decline in dieldrin concentrations was recorded at all sites between 1987 and 2002. Highest concentrations have tended to be recorded from Granny's Bay, with intermediate concentrations being recorded at Pahurehure and Hingaia, and lowest concentrations at Cornwallis.

PCB concentrations at Granny's Bay were consistently and substantially higher than the other sites. There was little, if any, difference in PCB concentrations at Cornwallis, Pahurehure, and Hingaia. PCB levels declined at all sites after the were banned in 1995, but concentrations in Granny's Bay oysters have been increasing again since 1999.

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

occurred between 1988-1989 (Fig. 12). Concentrations rose markely at Grannys Bay, Pahurehure and Hingaia in the subsequent year and remained consistently high until 1995-1996. Levels at Pahurehure and Hingaia declined between 1995 and 1998, and have been relatively stable since. In contrast, levels at Grannys Bay declined between 1995 and 1998, but increased again between 2001-2002.

Longer term patterns for **limited** chlordanes and **limited** DDT are consistant with the patterns shown in figures 10 and 11, and described above. However, the longer term record for **limited** PCBs in Grannys Bay oysters show that although levels declined between 1995-1996, they have been increasing again at a relatively steady rate since 1999. This is parallels recent increases in **limited** PAH and **limited** DDT, but must be considered in the context of overall concentrations, which are relatively low.

Patterns in the overall level of organic contaminants in oysters were also examined using MDS (Fig. 13). All of the organic contaminants that had been continuously recorded since 1996 were included in the analysis. Organic contaminants displayed similar spatial and temporal trends to the key metals in oysters, although there tended to be a greater degree of temporal overlap. The temporal gradient extended diagonally across the MDS plot from the top right to bottom left corners. A spatial gradient running from the bottom left to the top right of the plot was also apparent, with Cornwallis again separating out from the other three sites. Granny's Bay, Pahurehure and Hingaia, were also separable despite a degree of overlap among these sites.

Figure 10: Concentrations of organic contaminants in oysters collected from Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 1987 and 2002. 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.

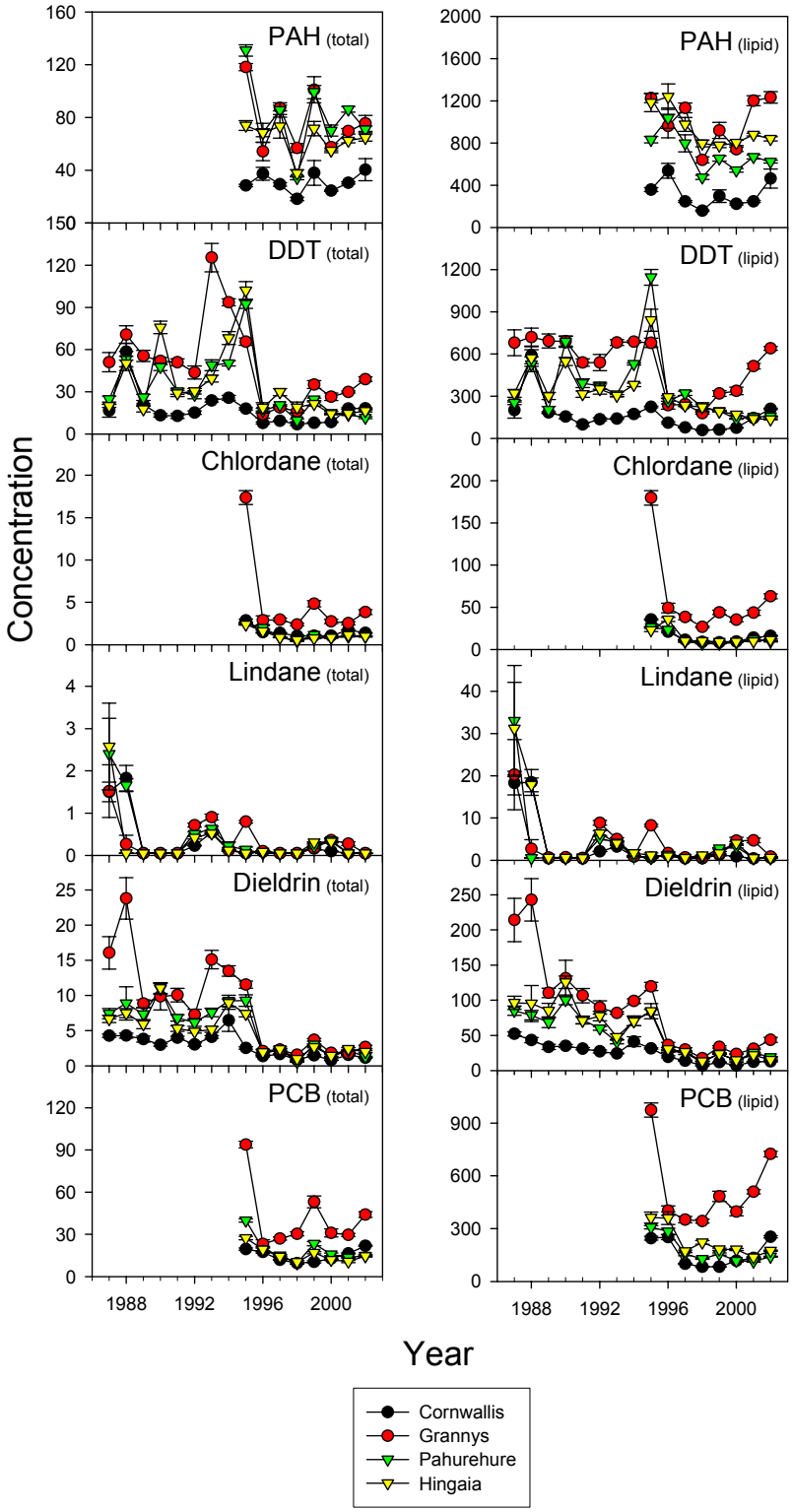


Figure 11: Concentrations (ng/g oyster dry weight ± s.e.) of lipid normalised chlordanes: cis-chlordane, trans-chlordane, trans-nonachlor, and cis-nonachlor in oysters collected from Granny's Bay between 1987 and 2002.

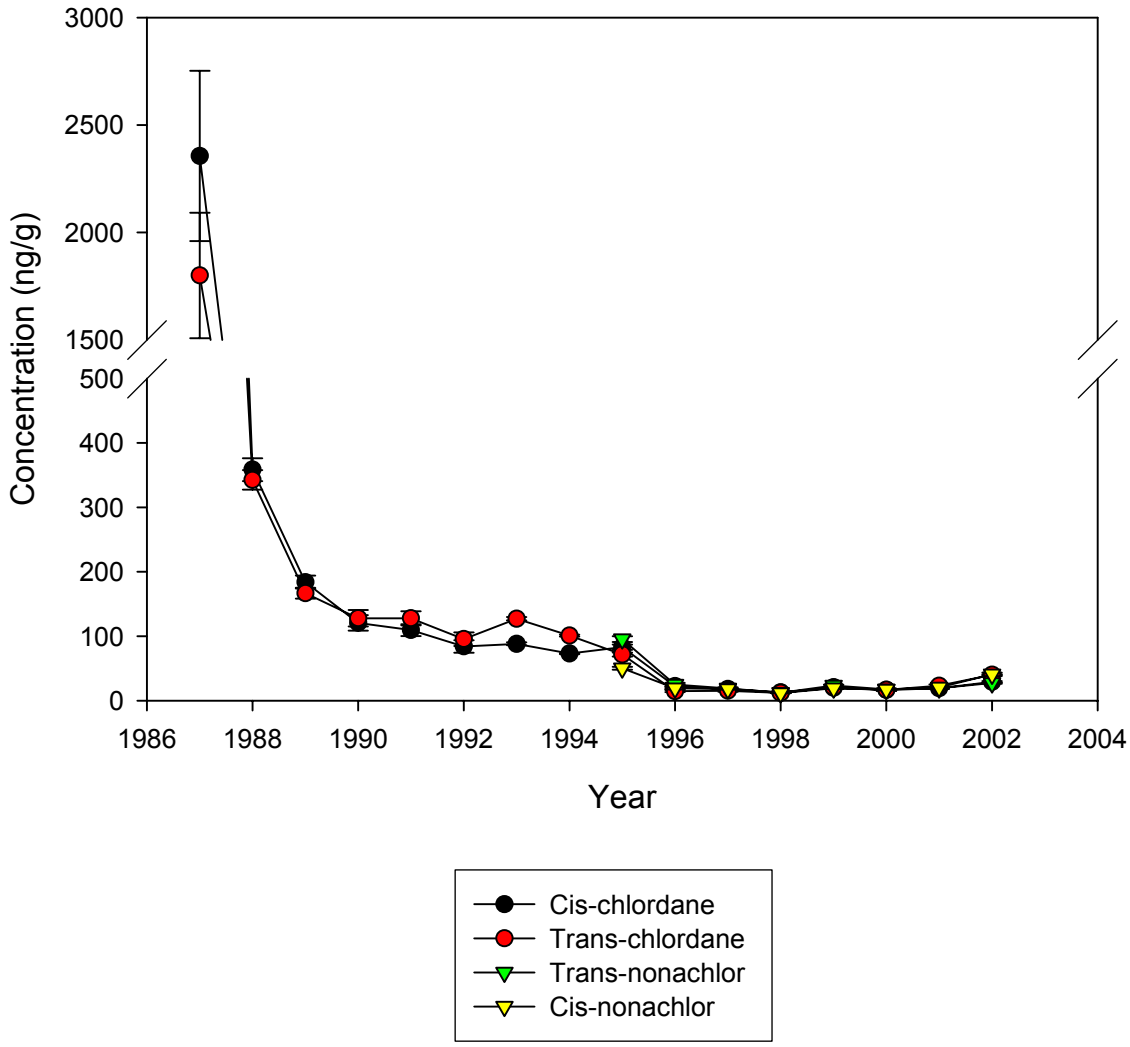


Figure 12: Concentrations (ng/g oyster dry weight ± s.e.) of lipid normalised **limited** PAHs (sum of fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]-fluorathene, benzo[k]fluoranthene, and benzo[a]pyrene) **limited** PCBs (sum of congeners 118, 138, 153 and 180), **limited** DTTs (sum of 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 (1987-2002). All data presented were above detection limits.

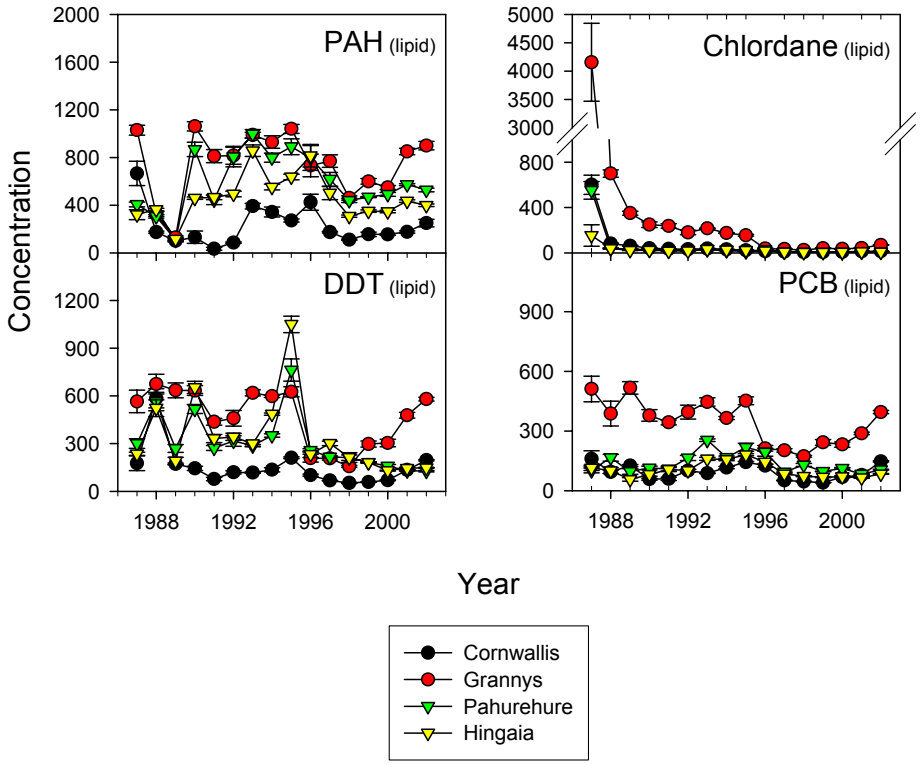
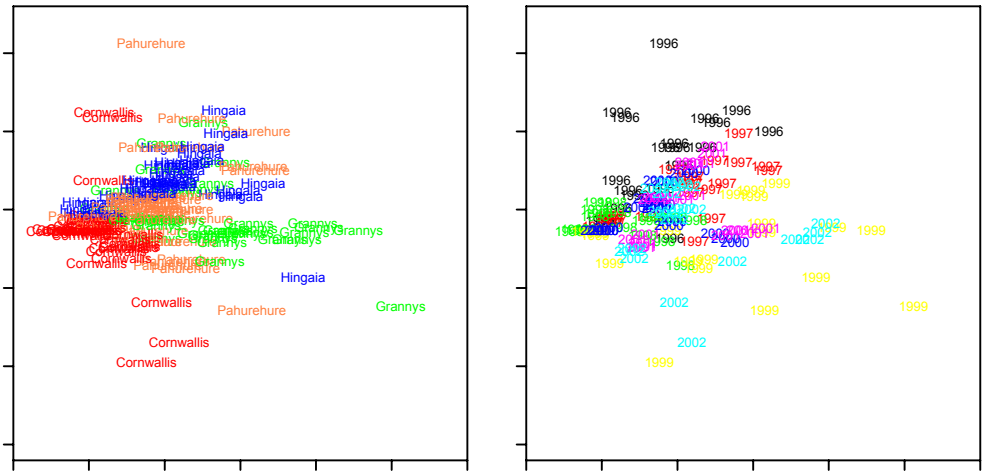


Figure 13: Multidimensional scale plots of organic contaminants present in oysters at Cornwallis, Granny's Bay, Pahurehure, and Hingaia between 1996 and 2002. The plot on the left has data points labelled with the name of the sampling site, while data in the plot on the right is labelled with sampling year. Stress = 0.13.



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 5) (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 6) 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 relatively high 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 exceeded levels indicative of significant copper contamination.
- Copper and zinc levels in oysters collected from the Waitemata Harbour and Hobson Bay in 1998 were very high and exceeded levels indicative of contamination. However, repeat sampling has not been carried out to confirm whether the high copper and zinc levels reflected the usual state of contaminants in these receiving environments or if the levels recorded in 1998 were atypical.
- 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 and have been increasing since 1999. PAH and DDT levels have also increased at this site over same period. Despite these recent increases, concentrations remain relatively low by international standards.
- Chlordane, lindane, and dieldrin have declined since monitoring began, consistent with them being de-registered as pesticides.

Table 5: 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 6: Comparison of mean organic contaminant concentrations in the Manukau Harbour oyster monitoring sites pooled from the last 5 years (1998-2002) 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 using ANCOVA to compare dry tissue weight among sites, using shell weight as a covariate. Linear regression was also used to examine the relationship between shell weight and dry tissue weight among sites (Fig. 14). An assumption of this method is that tissue weight decreases relative to shell size as condition declines, i.e. the slope of the relationship between shell weight and tissue weight declines with loss of condition. Both tissue weight and shell weight were log

[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.).

transformed prior to ANCOVA to meet the assumption of equal variance. Pooling among years was considered appropriate because there was little difference in the relationship between shell and tissue weight within a site (except pre-deployment mussel in 2002), but mussel sizes varied substantially between years (Fig . 13). Analysis of covariance indicated that the relationship between shell and tissue weight varied significantly among sites ($P<0.0001$).

Slopes functions were therefore obtained for each site by fitting linear regressions to the data. Both constrained (i.e. forcing the fit through the origin) and unconstrained regression analyses were carried out. Sites were then ranked according to the magnitude of their slope functions.

On the east coast the Upper Waitemata produced mussels with the poorest condition, i.e. had less tissue mass for a given shell length, regardless of whether the analysis was constrained or unconstrained (Table 7). Similarly, Illiomama and pre-deployment mussels were ranked 1st (= best) and 2nd for condition respectively regardless of constraining. However, the ranking of the condition of mussels from Upper Tamaki and Chelsea was dependent on whether the regressions were constrained or not.

Within Manukau Harbour, the condition of pre-deployed mussels was better than mussels from any site irrespective of the analysis used. Conversely, the mussels from Mangere Bridge were in poorest condition. However, the condition of mussels from Weymouth was ranked better than those from Papakura using the constrained analysis but worse using the unconstrained analysis.

When data from all sites were combined, Illiomama and pre-deployment mussels had the best condition, but comparisons of the ranks of other sites varied widely depending on whether the analyses were constrained or unconstrained.

Table 7: Condition ranks for each site based on the slope of the relationship between mussel shell weight and dry tissue weight. In constrained regressions dry tissue weight was forced through zero at zero shell weight.

East Coast

Condition rank	Constrained regression	Unconstrained regression
1	Illiomama	Illiomama
2	Pre-deployment	Pre-deployment
3	Upper Tamaki	Chelsea
4	Chelsea	Upper Tamaki
5	Upper Waitemata	Upper Waitemata

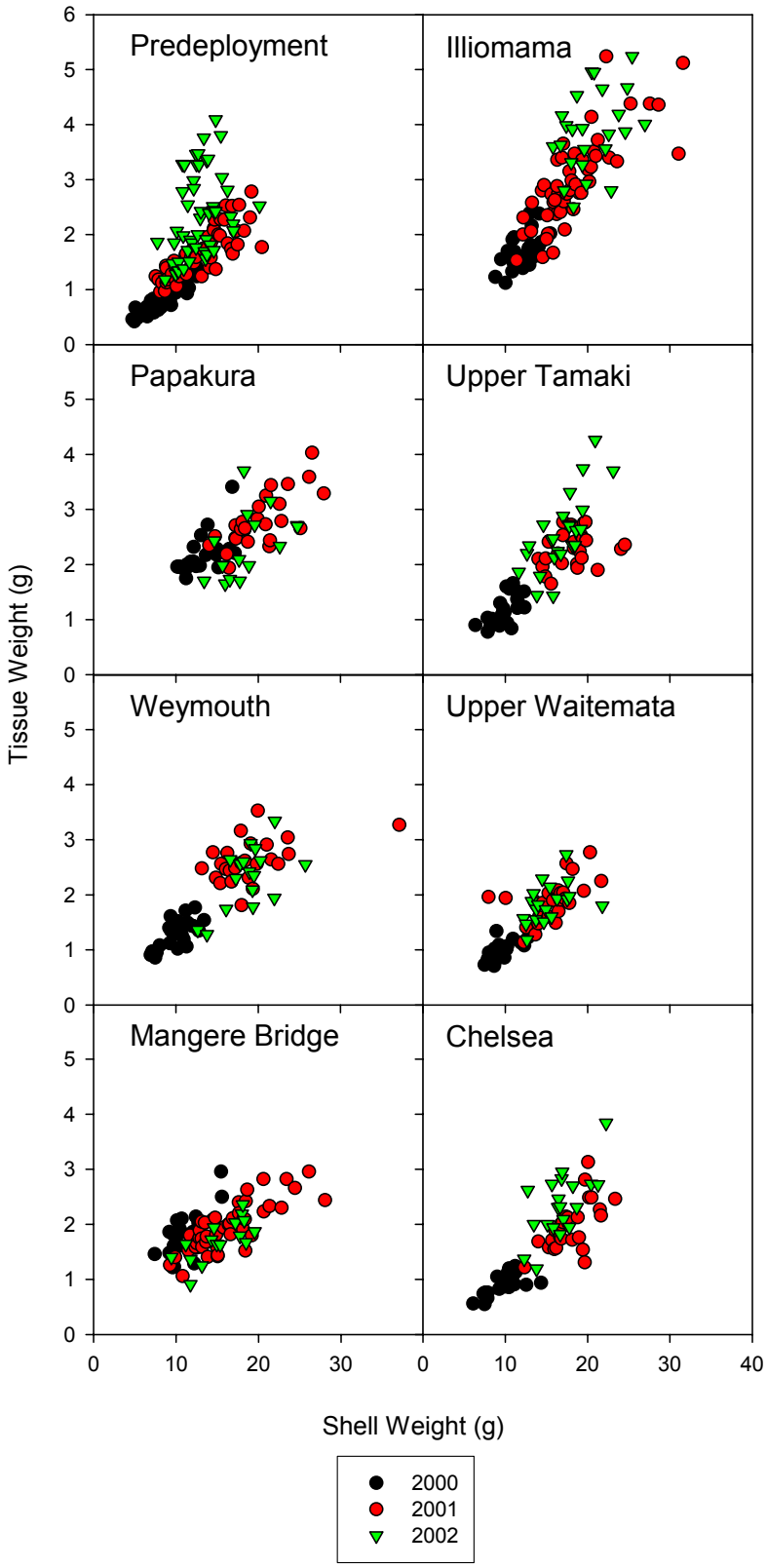
Manukau Harbour

Condition rank	Constrained regression	Unconstrained regression
1	Pre-deployment	Pre-deployment
2	Weymouth	Papakura
3	Papakura	Weymouth
4	Mangere Bridge	Mangere Bridge

Combined

Condition rank	Constrained regression	Unconstrained regression
1	Illiomama	Illiomama
2	Pre-deployment	Pre-deployment
3	Papakura	Chelsea
4	Upper Tamaki	Upper Tamaki
5	Weymouth	Upper Waitemata
6	Mangere Bridge	Weymouth
7	Chelsea	Papakura
8	Upper Waitemata	Mangere Bridge

Figure 14: Relationship between shell weight and dry tissue weight for each of the mussel monitoring sites between 2000 and 2002.



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 8, Fig. 15). 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 8).

Table 8: 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%

5.4.1.2 Contaminants

Between 1999 and 2001 mean arsenic levels in mussel samples fluctuated between 0.5-16.8 µg / g (Fig. 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, suggesting that interannual variation may be due to the degree of analytical accuracy (i.e. variation) rather than true temporal variation. Nevertheless, spatial variation was evident, with pre-deployment and Illiomama mussels consistently having the highest concentrations of arsenic between 1999 and 2001.

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) were 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.

Since 1999/2000 chromium concentrations have remained relatively stable at all sites except the Upper Waitemata Harbour and Weymouth. Average chromium levels at the

Upper Waitemata Harbour site jumped in 2001 and were still relatively high in 2002. Inter-sample variability was relatively high in both of these years. Chromium concentrations at Weymouth have steadily increased since the Manukau sites were introduced to the programme in 2000. There were also consistent differences in chromium concentrations among the remaining Manukau Harbour sites, with levels in mussels from Mangere Inlet greater than those from Papakura and in pre-deployment samples.

Spatial and temporal 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 contrast, in the Manukau Harbour highest sites copper levels have been consistently recorded in Mangere Inlet and levels at all sites increased in a uni-directional fashion between 2000 and 2002. However, monitoring has not been occurring in the Manukau for long enough to determine whether this is a persistent long-term trend. Also note that a similar temporal trend is also apparent in pre-deployment 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, except in pre-deployment mussels, since 1999/2000. On the east coast highest levels have always been recorded in the Tamaki Estuary. In the Manukau Harbour highest levels have consistently been recorded in Mangere Inlet. However, in both cases these differences were slight. Interestingly, mean zinc concentrations in pre-deployment mussels continually increased between 2000 and 2002. Moreover, pre-deployment mussels had the highest concentrations recorded in 2001 (although differences were not siginficant).

Multi-dimensional scaling of combined key metals data was not able to distinguish consistent spatial differences among sites, although samples from some sites were tightly clustered in some years e.g. Upper Tamaki in 2002 (Fig. 16). However, temporal trends in the data were clearly evident, with individual years able to be discriminated. 2002 was notable for it's greater degree of separation.

Figure 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 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.

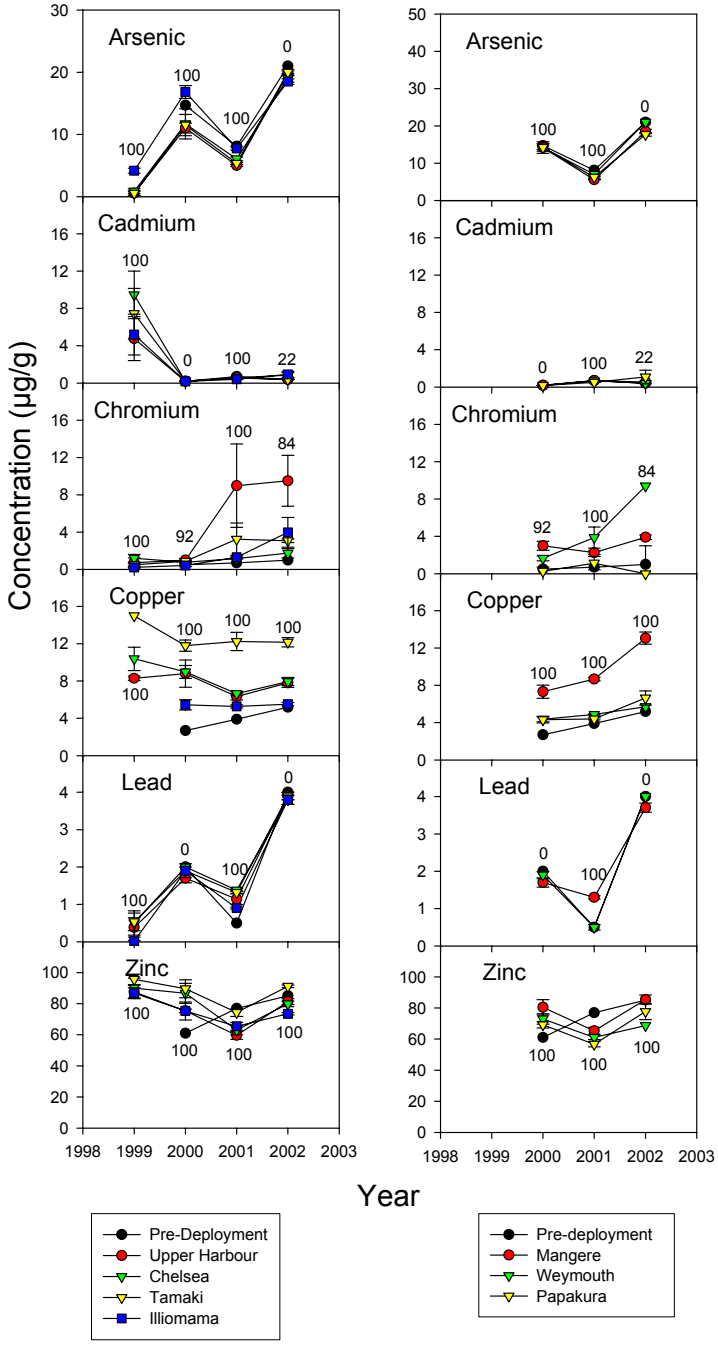
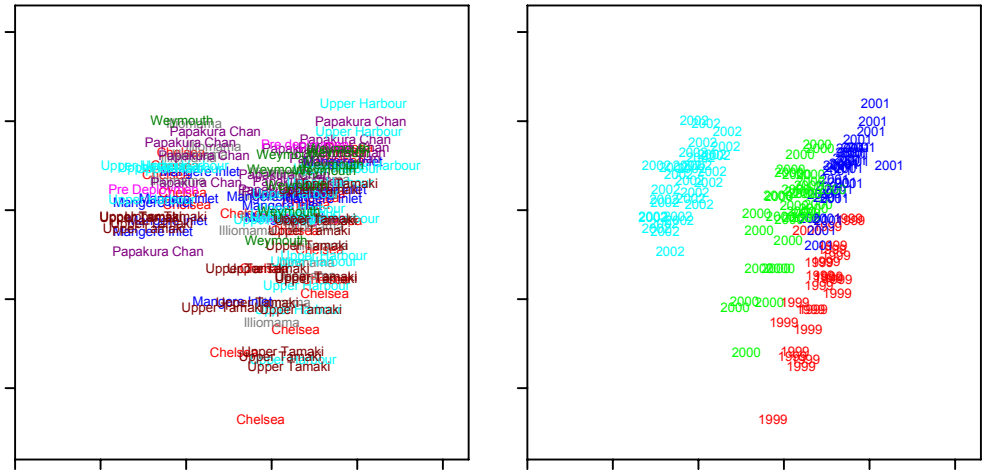


Figure 16: Multidimensional scaling plots of key metals present in mussels between 1999 and 2002. The plot on the left has data points labelled with the name of the sampling site, while data in the plot on the right is labelled with sampling year. Stress = 0.05.

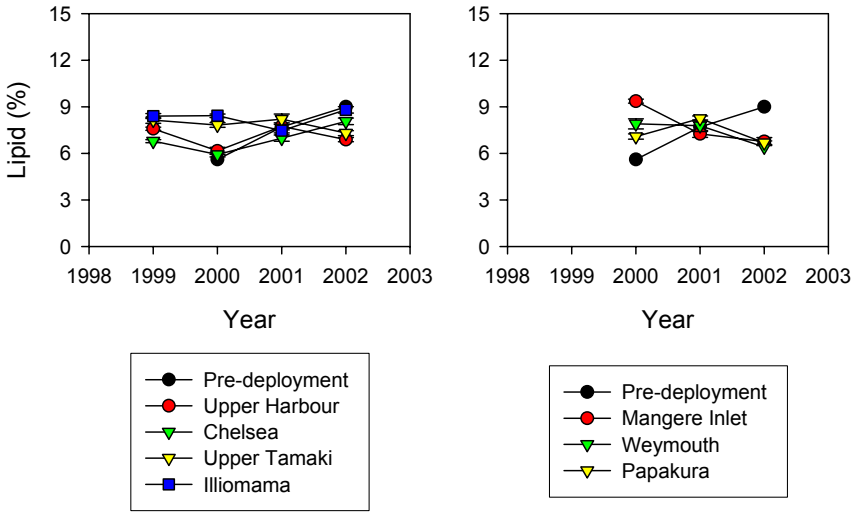


5.4.2 Mussel Organic Contaminants

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 (approximately 5-10% lipids) over the monitoring period, with no discernable differences among sites (Fig. 17). Consequently, the trends in lipid normalised data were very similar to the trends in non-normalised data (Figs. 17 and 18).

Figure 17: 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 9). Lindane levels below detection limits are therefore presented as 0.5 x D.L.

Table 9: Proportion of samples with lindane levels greater than detection limits.

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

5.4.2.3 Contaminants

PAH levels remained relatively stable, or declined slightly at all sites between 1999/2000 and 2002 (Figs. 17 & 18). Concentrations in mussels set on the east coast tended to be greater than those in mussels set in the Manukau Harbour, while those in pre-deployment mussels were, in all-but-one case, lowest. 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 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). 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. In the Manukau Harbour DDT levels were greatest in mussels from Mangere Inlet. Weymouth and Papakura Channel mussels had DDT concentrations only slightly above pre-deployment concentrations.

Chlordane concentrations were also relatively 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. 18 & 19 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. However, mussels from Weymouth had consistently higher dieldrin concentrations than those from Papakura. Lowest dieldrin concentrations were always recorded in pre-deployment mussels.

PCB levels steadily declined at all east coast sites between 1999 and 2002 (Figs. 18 & 19). 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 much higher PCB concentrations than those from the other Manukau Harbour sites. Furthermore, PCB levels increased substantially in Mangere mussels between 2000 and 2002.

The strong spatial differences apparent in the plot of individual organic contaminants are reflected in the MDS plots (Fig. 20). Mangere Inlet, Upper Tamaki, the Upper Waitemata Harbour, Chelsea and Illiomama can all be discriminated from each other and the two remaining sites. Mussels from Papakura and Weymouth are similar and are relatively close to 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;
- Interannual differences are apparent in key metals but there is no directional trend except for Manukau copper levels;
- Copper levels increased steadily at all Manukau Harbour sites between 2000 and 2002, but this trend must be considered cautionously because similar patterns were also observed in pre-deployment mussels;
- Substantial differences are apparent in the overall concentrations of organic contaminants between sites, but not between years, however;
- DDT and PCB levels have increased in Mangere Inlet since sampling began, but PCB levels have been trending down on the east coast;
- Overall it appears that mussel monitoring is providing useful data on spatial patterns and temporal trends for organic contaminants (and possibly copper), but the value of mussel monitoring for other metals is less certain.

Figure 18: Organic contaminant concentration (ng / g (mussel dry weight)) of mussels trans-located into the Waitemata Harbour (left column) 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.

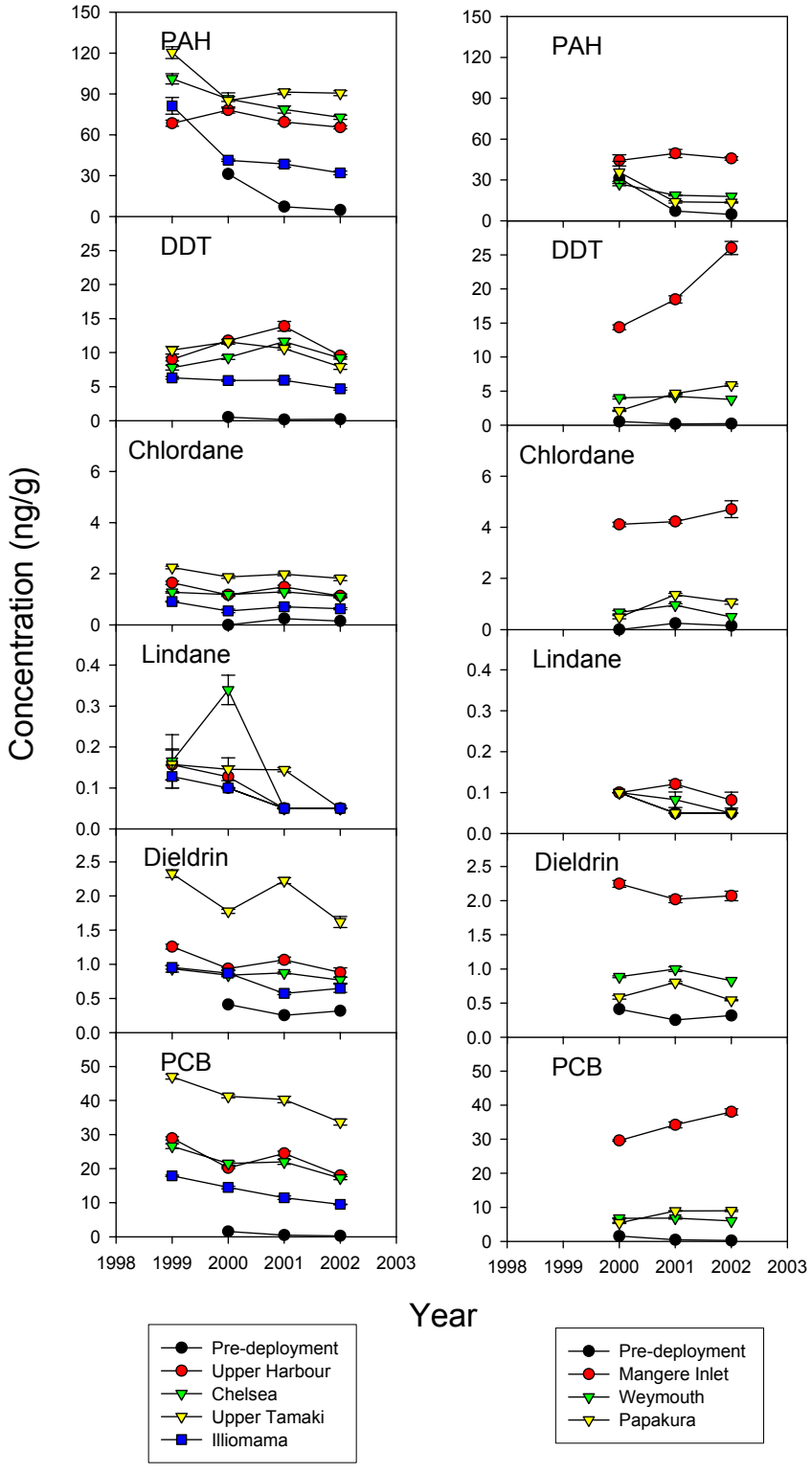


Figure 19: Lipid normalised organic contaminant concentrations (ng / g (lipid)) of mussels trans-located into the Waitemata Harbour (left column) and the Manukau Harbour (right), from 1999 to 2002. Values are also given for contaminant levels in samples prior to deployment. The lower Tamaki site was only sampled in 1999. Data below detection limits (D.L.) and presented as 0.5 x D.L.

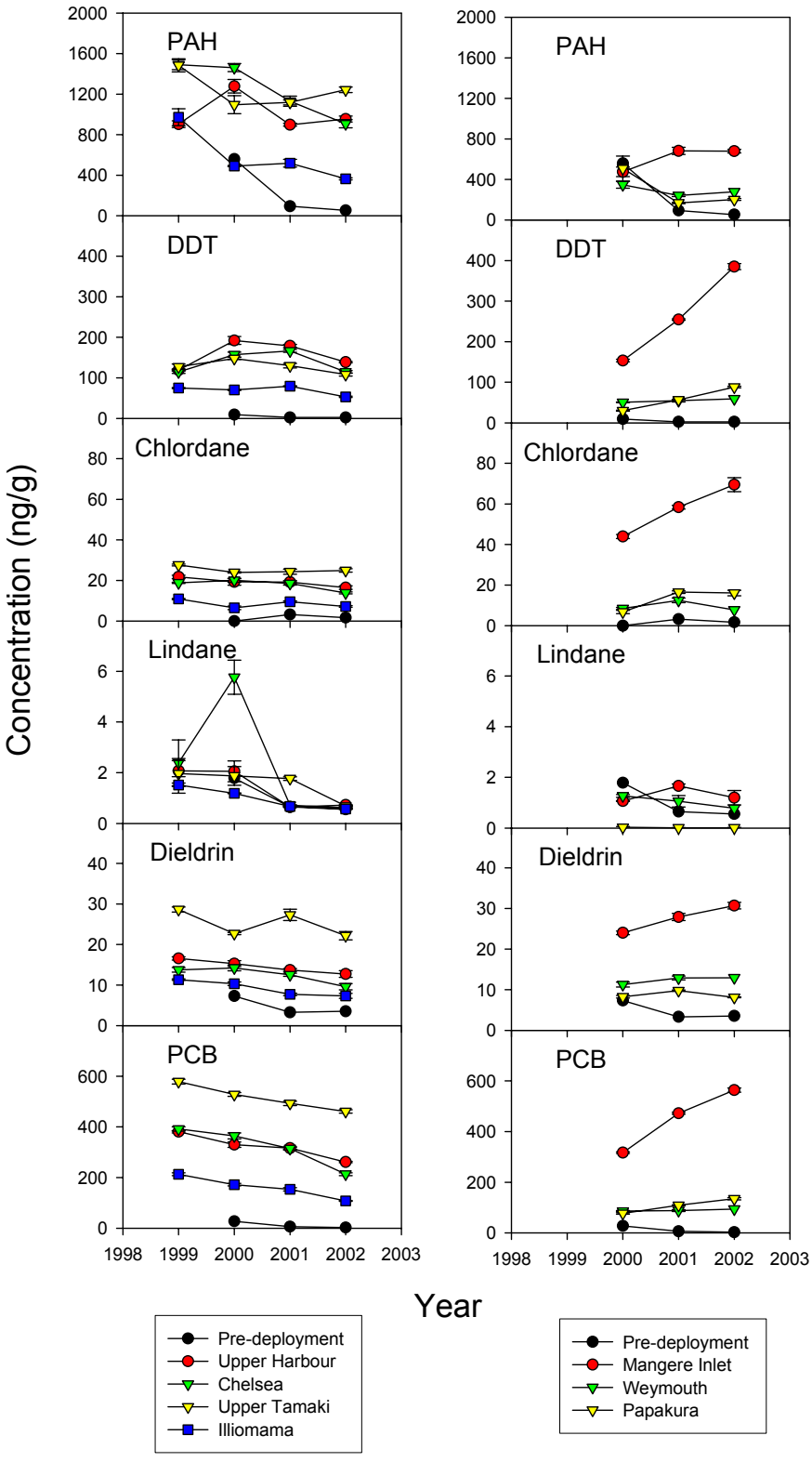
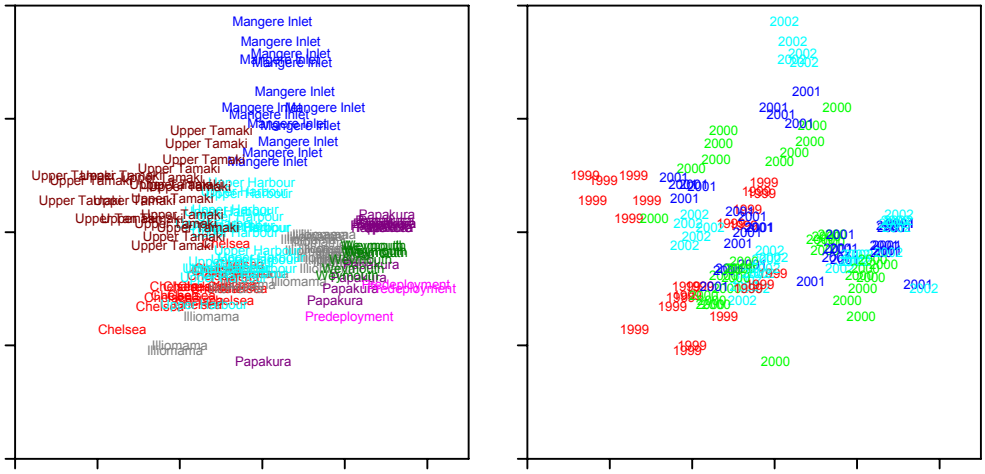


Figure 20: Multidimensional scale plots of organic contaminants present in mussels between 1999 and 2002. The plot on the left has data points labelled with the name of the sampling site, while data in the plot on the right is labelled with sampling year. Stress = 0.01.



6 Discussion

6.1 Shellfish Condition

Similar trends were exhibited in the condition of both oysters and mussels. Condition was consistently best at the clean reference sites, and in the case of mussels, in pre-deployment samples. The condition of oysters and mussels was poorer in sites with degraded water quality.

However, the relationship between shellfish condition and contaminant levels was not a simple, linear trend. The condition of mussels in the Upper Waitemata Harbour tended to be worse than those from Tamaki Estuary, whereas measured contaminant levels tended to be higher in the Tamaki. This suggests that other factors besides contaminants influence condition measures based on morphological characteristics and a causal relationship between contaminants and condition has not be clearly established.

This is particularly evident in the Manukau oysters, whose morphology 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. Consequently, while condition data is consistent with expected patterns, some caution should be exercised in its interpretation

6.2 Detection Limits

The full potential of the Shellfish Contaminant Monitoring Programme has not been realised because of high analytical detection limits for some metals. Excessively high analytical detection limits for lead mean that very little useful information is available for this contaminant. Of particular concern is the fact that lead detection limits often exceeded the 85th percentiles of levels reported in the international literature (Cantillo 1998, Scanes and Roach 1999, Shulkin et al. 2003), which are indicative of contamination (Cantillo 1998). Mean detection limits for lead (4.95 µg / g) are also well above those reported for the US mussel watch programme (0.1- 0.11 µg / g, see Lauenstein and Cantillo 1998). Other metals are not as badly affected, but arsenic, cadmium and chromium were still below, relatively high, detection limits in approximately 20% of samples.

In contrast, organic detection limits were consistently low (0.1 - 0.2 ng/g), and with the exception of lindane, contaminants generally occurred in measurable concentrations.

6.3 Temporal and Spatial Patterns in Contaminant Levels

6.3.1 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 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 mobilisation of a historic pool of contaminated sediments. Alternatively, it may simply be an artifact, whereby 1997-1999 levels were unusually low compared with the longer term record, and recent "increases" are a return to "normal" levels.

PCB levels also declined following their banning in 1995. However, levels in Granny's Bay oysters and Mangere mussels have been increasing since 1999/2000. This is likely to be due to the ubiquity of PCBs in the industrial catchments surrounding the Mangere Inlet. Significant stores of PCBs are likely to persist for some time, and it may be a number of years before an environmental response to the ban on PCBs is manifested as lower body burdens in Mangere shellfish.

6.3.1.1 Metal Correlations Among Sites

Metal levels in both oysters and mussels tended to be correlated between sites, so changes in contaminant levels at one site were generally mirrored by relatively similar changes at other sites. This is may be due to:

1. Widespread water mixing ensuring that contaminants are rapidly dispersed among sites;

2. The ratio of metal contaminants entering each site remaining similar, but contaminant loads varying from year to year;
3. Analytical accuracy varying from year to year;
4. Other natural or anthropogenic agents that affect the uptake of metals at a regional scale.

Widespread water mixing is unlikely to be responsible for the observed patterns because metal concentrations in mussels from east and west coast sites were correlated. Significant rainfall events generally influence both coasts so interannual variation in rainfall has the potential to explain correlations between east and west coast sites. However, patterns in rainfall data from Onehunga (1990-2002, Appendix B) are inconsistent with temporal patterns in the concentration of metal contaminants, so rainfall is unlikey to be responsible for the observed correlations. Other, natural or anthropogenic factors cannot be ruled out, however, two points suggest that the strong correlations in metal concentrations between sites may be linked to variations in analytical accuracy:

1. Organic contaminants are not well correlated among sites. This suggests that the causal agent is unique to metals.
2. Correlations are strongest in metals with concentrations close to detection limits, suggesting that the observed patterns may be related to the sensitivity of the analyses used.

Metal laboratory reports do not provide information on variablity among inter-batch replicates, or the results of analyses of reference material. Checks of the laboratory used for metal analyses should therefore be undertaken out to determine:

- Within-batch and between-batch reproducibility (precision);
- The accuracy of analyses using reference material (accuracy);
- The reasons for high detection limits (sensitivity).

6.3.2 Spatial Patterns

Despite the uncertainties about temporal fluctuations in metal concentrations, clear spatial patterns in contaminant levels were still 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 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, were also distinguishable due to Chelsea having slightly higher levels of PAHs than the Upper Harbour sites, and the Upper Harbour site having slightly higher levels of dieldrin than Chelsea.

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.

Nevertheless, clear differences were apparent in the levels of organic contaminants in mussels:

- PAH levels tended to be higher on the east coast, with levels in the east coast reference site similar to those from the worst Manukau site: Mangere Inlet;
- DDT was much higher in Mangere Inlet and is showing a short-term increasing trend;
- Chlordane levels were much higher in Mangere Inlet than in other sites, but concentrations were relatively stable through time;
- Dieldrin and PCB levels were high in Tamaki Estuary and Mangere Inlet compared with other sites.
- DDT and PCB levels were relatively low at the Weymouth and Papakura Channel sites.

Overall, the quality of the mussel organics data is very good. It shows: 1) good separation between sites; 2) good consistency; 3) low variability; 4) most pre-deployment samples have lower concentrations than deployed samples and; 5) reference sites usually have the lowest site concentrations. This indicates that mussel deployment is a useful monitoring tool for organics, but it's utility for tracking current levels of metal contamination is less certain.

6.4 Auckland in an International Context

Data from Vladivostok (Shulkin et al 2003) and Taiwan (Jeng et al 2000) are from the same species of oyster used in the ARC programme (Pacific oysters, *Crassostrea gigas*) and are therefore directly comparable with ARC data. However, data presented from other studies includes information from a range of species.

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 heavily contaminated sites, while Pacific oysters were more suitable as an indicator of initial or moderate 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 contaminant 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" limits of trace element concentrations (Cantillo 1998).

Mean levels of most contaminants in Manukau Harbour oysters were similar to, or slightly above, medians reported in international studies (Sericano et al 1995, Cantillo 1998, Scanes and Roach 1999, Jeng 2000, Shulkin et al 2003). The exception was copper levels, which were above the 85th percentiles of NS&T and RNO datasets

(Cantillo 1998) at Granny's Bay, Pahurehure and Hingaia. 1998 copper levels recorded from the Waitemata Harbour and Hobson Bay were substantially higher than those obtained from the Manukau Harbour, and exceeded the 85th percentiles of all datasets examined by 2-4 times. Copper levels at these sites were similar to the lower half of those obtained from contaminated Vladivostok sites. Sediment samples taken at the same Vladivostok sites had copper concentrations of 1 to 2281 µg/g (weak acid extraction (1M HCL) of the < 0.1 mm fraction), indicating very high levels of contamination. In contrast, the highest copper concentration obtained from an Auckland sediment contaminant monitoring site is 45 µg/g (Auckland Regional Council 2003). Copper levels in east coast oysters ranged from 1323-2647 µg/g. It is not known what, if any, effect these levels have on oysters. However, concentrations greater than 4000 µg/g have led to green discoloration and mollusc mortality in Taiwan (Han and Hung 1990). Whether high copper levels were maintained in east coast oysters, or if the levels recorded in 1998 were abnormally high, is also unclear because repeat sampling was not carried out. Note that relatively high concentrations of copper were also detected in Manukau oysters between 1996 and 1998 (although concentrations were substantually less than those recorded from the east coast sites (mean values of ~ 630-1250 ug/g excluding Cornwallis)), but levels dropped to relatively low concentrations in subsequent years.

Zinc levels recorded from oysters at the east coast sites were also exceptionally high by international standards. 1998 zinc concentrations in oysters obtained from Waitemata Harbour and Hobson Bay exceeded the 85th percentiles of all datasets. Levels of zinc in east coast oysters were also above the median obtained from contaminated Vladivostok sites (Shulkin et al 2003). In contrast to the high zinc concentrations in east coast oysters, sediment concentrations of zinc in Auckland are relatively low by international standards. The maximum value obtained from an Auckland sediment contaminant monitoring site is 351 µg/g (Auckland Regional Council 2003). This compares with values of up to 3326 µg/g in contaminated Vladivostok sites (Shulkin et al 2003).

Several possibilities may explain the apparent discrepancies between the shellfish and ARC sediment contaminant monitoring programmes.

- Loads of both sediment and contaminants to the marine environment are high, so low zinc and copper concentrations in the sediment samples reflect dilution by sediments rather than small mass loads of contaminants.
- Zinc and copper remain in the water column for longer, and are dispersed more widely than previously considered. This would increase availablity for filter feeders such as oysters and spread the contaminants over a wider area, thereby increasing the level of dilution.
- Pacific oysters in New Zealand uptake zinc and copper more efficiently than overseas.

- Data obtained from Hobson Bay and the Waitemata Harbour in 1998 may not reflect typical contaminant levels as repeat sampling was never carried out to confirm the results.

Further testing is therefore recommended to determine if high zinc and copper levels in oysters were elevated because of: high contaminant loads that are not being picked up by other monitoring programmes; atypical conditions; or because of unusual features of the Auckland environment. Initial sampling should:

- Confirm the 1998 results from the Waitemata Harbour and Hobson Bay;
- Determine whether contaminant levels in oysters and mussels are correlated with those in sediments from the same site.

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 contaminant levels compared with other Auckland sites. Despite recent increases in PCBs and DDT being recorded in Mangere Inlet, the banning of several persistent pesticides and PCBs has markedly reduced the level of these contaminants in shellfish over the past 15 years or so. Comparisons with overseas studies indicate that oysters from the east coast sites surveyed in 1998 had relatively high levels of copper and zinc by international standards. Manukau oysters also had elevated copper levels, particularly between 1996 and 1998, but concentrations were significantly less than those recorded from the Waitemata Harbour and Hobson Bay. High zinc and copper levels in oysters are inconsistent with recorded concentrations of these contaminants in marine sediments. It is unclear why concentrations in oysters are not reflected in sediment quality and further investigations are recommended to clarify the reasons for the discrepancy.

Large differences in oyster zinc and copper levels between the Manukau Harbour and the east coast sites were not reflected in the mussel samples. This is consistent with patterns found in Vladivostok, which showed that oysters are good indicators of initial or moderate contamination while mussels are useful as biomonitors in heavily contaminated sites (Shulkin et al 2003). The short deployment period for mussles may also be a factor.

The status of some key metals, such as lead, remains unclear because of high and variable detection limits. Temporal trends in metal concentrations also appear to be influenced by as yet unexplained variations, that possibly include the accuracy of assays. This is particularly apparent for metals with concentrations close to analytical detection limits. It is therefore recommended that the precision, accurracy and sensitivity of metals analyses be checked, and where necessary, improved.

Indices used to estimate mussel and oyster condition in the ARC Shellfish Contaminant Monitoring Programme suggest that the contaminant levels observed in Auckland's harbours and estuaries may be a factor affecting the growth of shellfish. Mussels and oysters from polluted sites tend to be in poorer condition than those from "clean" sites, but the relationship is complicated by other factors that also affect morphology and growth. Levels of copper are still below those known to cause green discoloration and mortality in oysters, but chronic toxicity cannot be ruled out.

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, although there is evidence of 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.

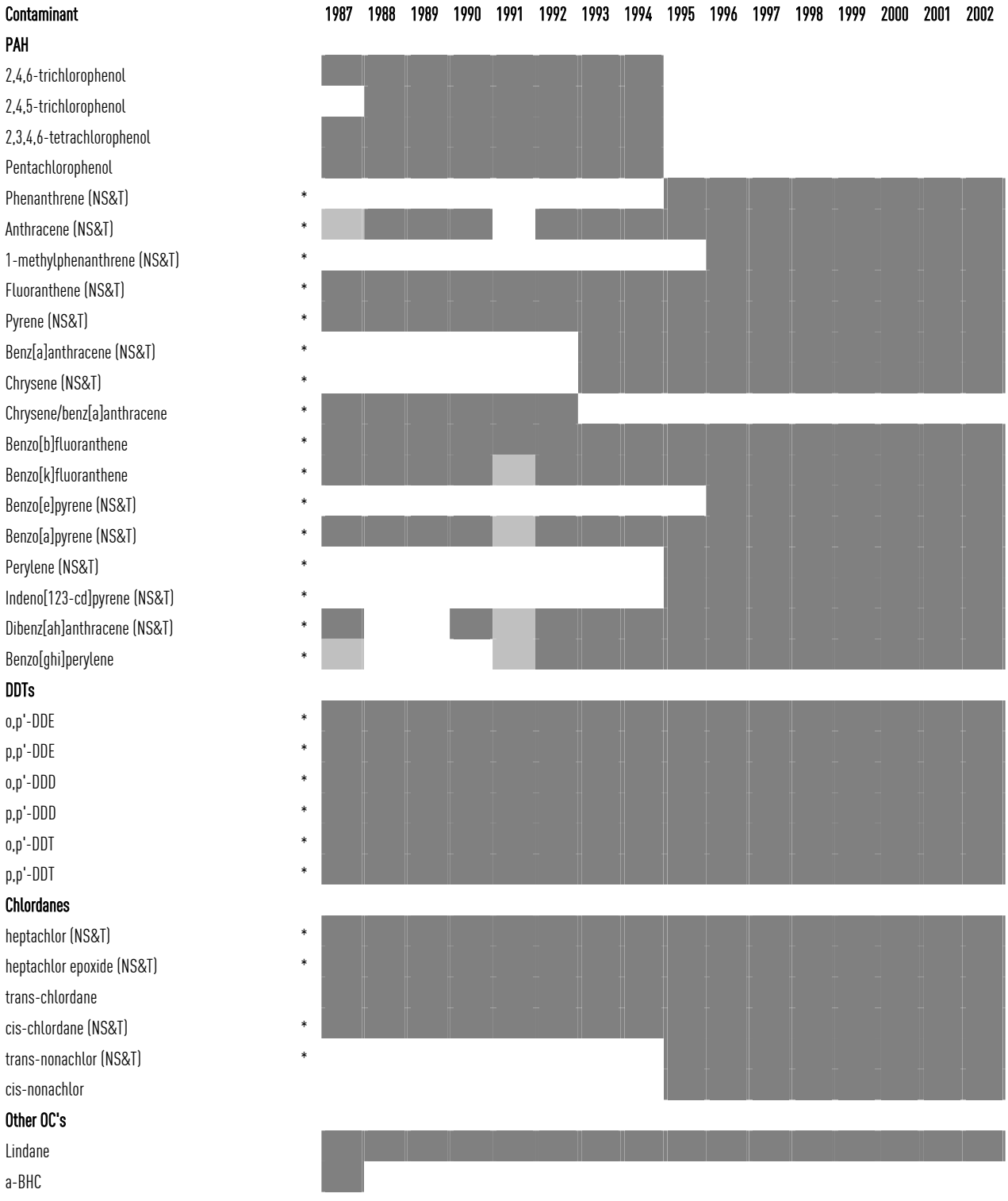

Table B1: Continued

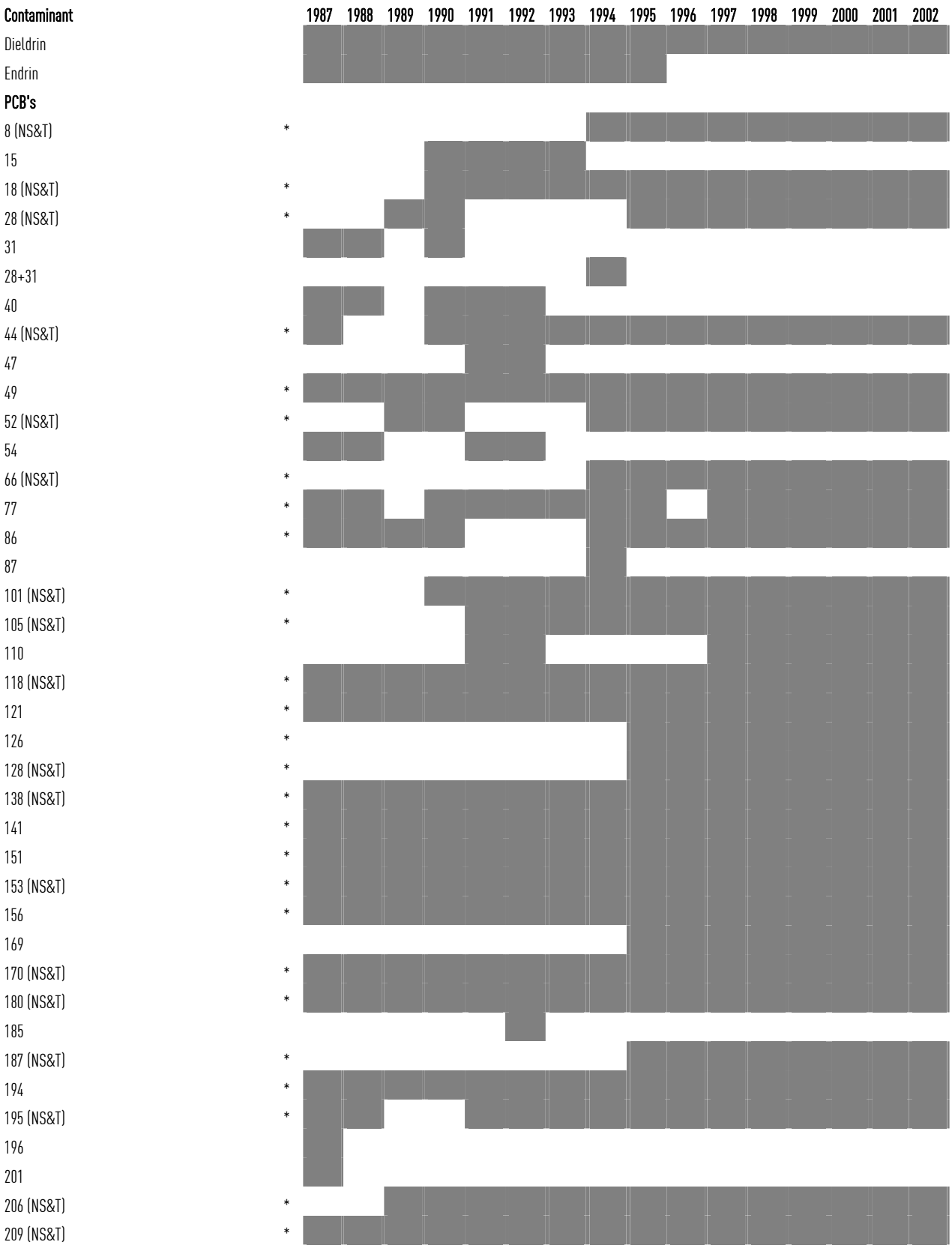

Table B2: List of organic contaminants measured in the ARC Mussel Monitoring Programme.

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: Onehunga Rainfall

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