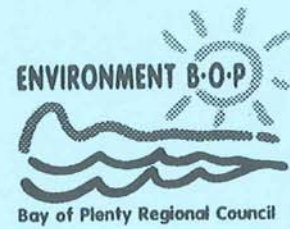
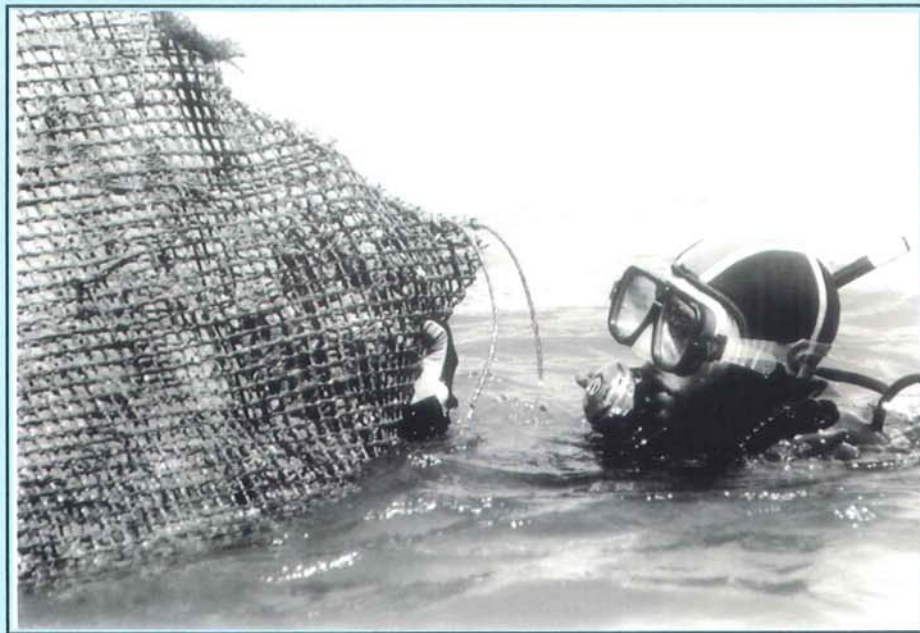


Environment B.O.P
Environmental Report 94/9
05 July 1994



ENVIRONMENT B.O.P
TAURANGA HARBOUR REGIONAL PLAN
ENVIRONMENTAL INVESTIGATIONS

SENTINEL SHELLFISH



Diver collecting Pacific Oyster sentinel shellfish from Tauranga Harbour.

Prepared by:

Fergus M Power
Manager Environmental Investigations

Environment B.O.P
Quay Street
PO Box 364
WHAKATANE

ISSN 1172-5850

ACKNOWLEDGEMENTS

Thanks goes to Environment B·O·P Director of Environmental Monitoring, Paul Dell, and Environmental Scientist Stephen Park for supervising and assisting with the deployment and recovery of oysters. Thanks also go to Sean Hodges, Environmental Scientist, who assisted with data management and report editing.

CONTENTS

ACKNOWLEDGEMENTS	ii
CONTENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	v
EXECUTIVE SUMMARY	viii

CHAPTER ONE: INTRODUCTION

1.1 <u>BACKGROUND</u>	1
---------------------------------	---

CHAPTER TWO: METHODS

2.1 <u>SELECTION OF CONTAMINANTS</u>	5
2.1.1 <u>Metals</u>	5
2.1.2 <u>Tributyltin (TBT)</u>	6
2.1.3 <u>PCB's</u>	6
2.1.4 <u>Chlordanes</u>	7
2.1.5 <u>Polynuclear Aromatic Hydrocarbons</u>	7
2.1.6 <u>Organochlorine Insecticides</u>	8
2.1.7 <u>Chlorophenols</u>	8
2.1.8 <u>General</u>	8
2.1.9 <u>Microbiological contaminants</u>	9
2.2 <u>DEPLOYMENT OF SENTINEL SHELLFISH</u>	9

CHAPTER THREE: RESULTS

3.1 <u>SHELLFISH TISSUE LIPID LEVELS</u>	13
3.2 <u>COMPARISON WITH 'HIGH' CONTAMINANT LEVELS</u>	13
3.3 <u>METALS</u>	16
3.3.1 <u>Silver</u>	16
3.3.2 <u>Arsenic</u>	16
3.3.3 <u>Cadmium</u>	16
3.3.4 <u>Chromium</u>	16
3.3.5 <u>Copper</u>	21
3.3.6 <u>Iron</u>	21
3.3.7 <u>Mercury</u>	21
3.3.8 <u>Lead</u>	21
3.3.9 <u>Zinc</u>	26

3.4	<u>TRIBUTYL TIN (TBT)</u>	26
3.5	<u>POLYNUCLEAR AROMATIC HYDROCARBONS (PAH's)</u>	26
3.6	<u>PCB's</u>	30
3.7	<u>CHLORDANES</u>	33
3.8	<u>ORGANOCHLORINE INSECTICIDES</u>	33
3.9	<u>CHLORINATED PHENOLICS</u>	33

CHAPTER FOUR: DISCUSSION

4.1	<u>GENERAL</u>	39
4.2	<u>METALS</u>	39
4.3	<u>PCB's</u>	39
4.4	<u>CHLORDANES</u>	39
4.5	<u>PAH's</u>	41
4.6	<u>TBT</u>	41
4.7	<u>MICROBIOLOGY</u>	51
4.8	<u>SUMMARY</u>	52

BIBLIOGRAPHY. Environmental Report 94/11

APPENDICES

- Appendix 1 (a) Sentinel shellfish metal and organic concentrations for each site replicate in Tauranga Harbour
- Appendix 1 (b) Polychlorinated biphenyl congener concentrations for each site replicate in Tauranga Harbour

LIST OF TABLES

3.1	Geometric mean and 'high' concentrations from analyses on oysters collected in 1990 at 107 sites in the United States (214 sites for As, Cd, Hg, Ni and Se) (O'Connor 1992)	15
3.2	Geometric mean organic and metal contaminants in Tauranga Harbour sentinel shellfish (1990). All samples n=5, except Waikareao (replicate 1 = ferral, replicates 2, 3 and 5 = sentinel shellfish)	32
4.1	Geometric mean and 'high' concentrations (on a dry weight basis) from analyses of oysters collected in the US Mussel Watch Project and the Tauranga Harbour Project	40
4.2	Lethal and sublethal toxicity threshold values for various life stages of a number of marine organisms in relation to the UK EQS for seawater of 2 ng TBT / L (equivalent to 0.8 ng Sn / L) (After Cleary 1991)	44
4.3	Approximate degree of TBT contamination as reflected by TBT tissue concentrations in field populations of mussels (Page and Widdows 1991)	48
4.4	Relative Penis Size (ratio (mean female penis length)/(mean male penis length) x 100%) of dogwhelks from various New Zealand locations in 1988 (P J Smith, MAF NZ, <i>pers. comm.</i>)	50

LIST OF FIGURES

2.1	Location of sentinel shellfish deployment sites	11
3.1	Lipid levels in sentinel shellfish deployed in Tauranga Harbour	14
3.2	Silver levels in sentinel shellfish deployed in Tauranga Harbour	17
3.3	Arsenic levels in sentinel shellfish deployed in Tauranga Harbour.	18
3.4	Cadmium levels in sentinel shellfish deployed in Tauranga Harbour	19
3.5	Chromium levels in sentinel shellfish deployed in Tauranga Harbour.	20
3.6	Copper levels in sentinel shellfish deployed in Tauranga Harbour.	22
3.7	Iron levels in sentinel shellfish deployed in Tauranga Harbour.	23
3.8	Mercury levels in sentinel shellfish deployed in Tauranga Harbour	24
3.9	Lead levels in sentinel shellfish deployed in Tauranga Harbour	25

3.10	Zinc levels in sentinel shellfish deployed in Tauranga Harbour	27
3.11	Tributyltin levels in sentinel shellfish deployed in Tauranga Harbour	28
3.12	Polynuclear aromatic hydrocarbon levels in sentinel shellfish deployed in Tauranga Harbour	29
3.13	PCB levels in sentinel shellfish deployed in Tauranga Harbour	31
3.14	Total chlordane levels in sentinel shellfish deployed in Tauranga Harbour	34
3.15	DDT levels in sentinel shellfish deployed in Tauranga Harbour	35
3.16	Dieldrin levels in sentinel shellfish deployed in Tauranga Harbour	36
3.17	Chlorinated phenolic levels in sentinel shellfish deployed in Tauranga Harbour	37

EXECUTIVE SUMMARY

1 INTRODUCTION

This report presents the results a study which used oysters, deployed in various areas of Tauranga Harbour, to investigate the presence of organic and inorganic pollutants. This study is one aspect of an integrated environmental investigation of Tauranga Harbour and catchment undertaken as part of the Tauranga Harbour Regional Plan Project (THRPP). Other modules of the THRPP Environmental Investigations studies include catchment geology and hydrology, inputs of nutrients, harbour sediments, harbour chemistry, harbour ecology, and investigations into the occurrence of toxic dinoflagellates.

Over recent years, increasing concern has been expressed about the ecological state of the harbour. These concerns have largely been based on experiences with nuisance algal blooms over recent years, and a general perception that industrial and municipal wastewater inputs to harbour waters have been steadily increasing.

The harbour receives effluent from New Zealand's highest-producing superphosphate manufacturer (Bay of Plenty Fertiliser Limited), a number of other industries, the treated waste from Tauranga City (population approx. 67,000), coastal subdivision septic tank seepage, wastes carried via the numerous rivers and streams entering the harbour, and effluent from point-source agricultural discharges such as piggeries.

Industrial discharges, diffuse source pollution (eg application of herbicides and pesticides), urban development, atmospheric deposition and entry into New Zealand coastal waters of foreign-generated oceanic contaminants means that seafood resources in Tauranga Harbour contain various contaminants.

Because of their hydrophobicity (reluctance to dissolve in water), some chemical substances tend to occur in higher concentrations in aquatic biota than in the water column, a process known as bioaccumulation. The degree of bioaccumulation depends on the nature of the chemical and the species of organism.

Some highly-hydrophobic substances, such as PCB's, dioxin, DDT and chlordane, are often found in aquatic biota in concentrations 10,000 times higher than in the surrounding water.

2 METHODS

The Tauranga Harbour Regional Plan Project sentinel shellfish programme monitored concentrations of various trace metals and organic compounds in Pacific oysters (*Crassostrea gigas*).

With the exception of chlorinated organic compounds such as DDT and PCB, which exist entirely as a result of human activities, a certain natural concentration of chemicals exists in molluscs even in the absence of human activity. Chemical concentrations exceeding natural levels should be considered 'contamination', and the exact line demarcating natural concentrations from contamination is not easily drawn. It depends upon the species of mollusc itself as well as on many local and regional conditions (O'Connor 1992).

Several groups of organic compounds have been analyzed in sentinel shellfish from Tauranga Harbour. Two of the groups, total DDT and total chlordane, are chlorinated pesticides. Approval for agricultural use of DDT was withdrawn in New Zealand in 1970, while the approval for horticultural use of DDT was withdrawn in August 1989. Chlordane has never been registered for agricultural or horticultural use in New Zealand, and its use in the timber industry was stopped in October 1992.

On 24 October 1990, Pacific oysters collected from Ohiwa Harbour were deployed as sets of five replicates throughout Tauranga Harbour at four locations (Waikareao Estuary, Port Area, Southern Harbour and Northern Harbour). Oysters were enclosed in plastic mesh bags and suspended just above the sea floor by marine grade stainless steel spikes driven into the sediment.

Oysters were recovered on 17 December 1990, and forwarded to various laboratories for bacterial, trace metal, tributyltin (TBT), hydrocarbon and organic contaminant analysis. Two of the five Waikareao Estuary replicates were lost, and so one set was replaced with a feral oyster sample. This sample also provides insight into the likely differences between persistent contaminant loads of feral and introduced sentinel oysters.

3 RESULTS

Contaminant concentrations for sentinel shellfish in Tauranga Harbour were compared with the United States Mussel Watch Programme. This programme derived "high values" for particular contaminants.

Metal levels in the sentinel shellfish did not show any significant location differences. Cd, Cu, Hg and Zn levels were considerably higher in the single feral oyster sample analyzed (Waikareao Estuary Replicate No. 1) than in the sentinel shellfish sets. All organic groups showed significant location differences, with the Waikareao Estuary and Port Area displaying markedly higher levels of organic contamination than the Northern or Southern Harbour locations (Table 3.2).

Polynuclear aromatic hydrocarbon levels in sentinel shellfish from the Waikareao Estuary and the Port Area were considerably higher than those in sentinel shellfish from the Southern and Northern Basin groups. The sentinel

shellfish from the Northern Basin showed the lowest PAH levels, and were significantly cleaner than those sentinel shellfish from the Southern Basin site.

Waikareao Estuary sentinel shellfish displayed the highest levels of chlordane, and DDT and dieldrin levels in sentinels from this site were significantly higher than for sentinel shellfish from either the Northern or Southern Basin sites.

PCB contamination of the Waikareao Estuary was particularly elevated (relative to the remainder of the harbour), while tributyl-tin levels in sentinel shellfish from the Port Area were predictably much higher than from other locations.

Organic contamination levels in the sentinel shellfish were well below levels of concern to human consumers. The recommended action levels for chlorinated hydrocarbon residues in marine shellfish are as follows: aldrin/dieldrin, chlordane, 0.3 ug/g wet weight; DDT, DDE, TDE 5.0 ug/g wet weight; PCB's, 2.0 ug/g wet weight (US FDA 1989). The above recommendations can be re-expressed as approx. 2,250 ng/g for aldrin/dieldrin, chlordane and DDT etc, and 15,000 ng/g dry weight for PCB's. These levels considerably exceed those recorded in the present study.

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

The Tauranga Harbour Regional Plan Project (THRPP) commenced in July 1990. Tauranga Harbour is a coastal lagoon formed behind two tombolos and a sandy barrier island (Matakana). Tauranga Harbour receives inputs of industrial and secondary treated sewage effluent, urban runoff from the Tauranga metropolitan area, and point and non-point pollutant agricultural and horticultural additions from the surrounding catchments.

Over recent years, increasing concern has been expressed about the ecological state of the harbour. These concerns have largely been based on experiences with nuisance algal blooms over recent years, and a general perception that industrial and municipal wastewater inputs to harbour waters have been steadily increasing.

In order to prepare an effective Regional Plan, Environment B.O.P initiated an extensive investigation of the Tauranga Harbour environment and contributing catchments. Environment B.O.P's Environmental Reports produced as part of the THRPP covered:

- Rep. 94/8 The ecology of Tauranga Harbour including studies into the algal and macrofaunal communities of the sand flats and the freshwater ecology of the northern harbour catchment streams;
- Rep. 94/9 Sentinel shellfish studies using oysters deployed into areas of Tauranga Harbour to investigate the presence of organic and inorganic pollutants;
- Rep. 94/10 Water quality of Tauranga Harbour including catchment geology, harbour sediments, nutrient inputs and contaminants.
- Rep. 94/11 Complete Bibliography for all THRPP documents.
- Rep. 94/13 Cargo Vessel ballast water as a vector for the spread of toxic phytoplankton species to the port of Tauranga, investigations of risk assessment and baseline field monitoring to ascertain the presence of toxic species.

The harbour receives effluent from New Zealand's highest-producing superphosphate manufacturer (Bay of Plenty Fertiliser Limited), a number of other industries, the treated waste from Tauranga City (population approx. 67,000), coastal subdivision septic tank seepage, wastes carried via the numerous

rivers and streams entering the harbour, and effluent from point-source agricultural discharges such as piggeries.

Industrial discharges, diffuse source pollution (eg application of herbicides and pesticides), urban development, atmospheric deposition and entry into New Zealand coastal waters of foreign-generated oceanic contaminants means that seafood resources in Tauranga Harbour contain various contaminants.

Because of their hydrophobicity (reluctance to dissolve in water), some chemical substances tend to occur in higher concentrations in aquatic biota than in the water column, a process known as bioaccumulation. The degree of bioaccumulation depends on the nature of the chemical and the species of organism.

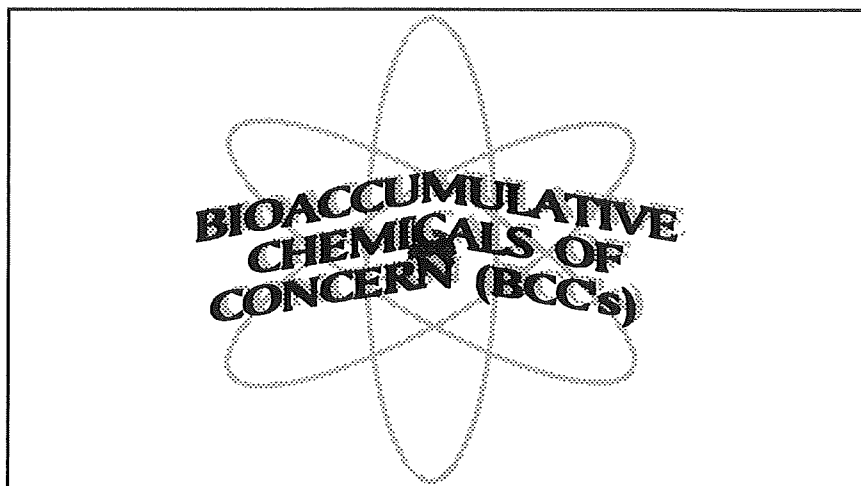
Some highly-hydrophobic substances, such as PCB's, dioxin, DDT and chlordane, are often found in aquatic biota in concentrations 10,000 times higher than in the surrounding water.

Using field data and 'food chain multipliers' (see Smith and Carr 1993), the US EPA has established a list of *Bioaccumulative Chemicals of Concern* for the Great Lakes.

These compounds accumulate in fish at concentrations 1,000 times greater than concentrations found in water. The list of BCC's consists primarily of discontinued pesticides (for example, DDT, chlordane, dieldrin) and industrial chemicals such as PCB's, hexachlorobenzene and mercury. The US EPA also provides a list of "potential" BCC's that includes some widely used compounds such as phthalates.

The deployment of sentinel shellfish in Tauranga Harbour at seasonally-consistent five-yearly intervals would provide a very useful measure of trends in contaminant availability to harbour seafood resources.

This survey represents the baseline for such a long-term pollution monitoring tool.



Aldrin
 4-Bromophenyl phenyl ether
 Chlordane
 4,4'-DDD; p,p'-DDD; 4,4'-TDE
 4,4'-DDE; p,p'-DDE
 4,4'-DDT; p,p'-DDT
 Dieldrin
 Endrin
 Heptachlor
 Heptachlor epoxide
 Hexachlorobenzene
 Hexachlorobutadiene; hexachloro-1,3-butadiene
 Hexachlorocyclohexane; BHC
 alpha-Hexachlorocyclohexane; alpha-BHC
 beta-Hexachlorocyclohexane; beta-BHC
 delta-Hexachlorocyclohexane; delta-BHC
 Lindane; gamma-BHC; gamma-hexachlorocyclohexane
 Mercury
 Methoxychlor
 Mirex, dechlorane
 Octachlorostyrene
 PCB's; polychlorinated biphenyls
 Pentachlorobenzene
 Photomirex
 2,3,7,8-TCDD; dioxin
 1,2,3,4-Tetrachlorobenzene
 1,2,4,5-Tetrachlorobenzene
 Toxaphene

POLLUTANTS THAT ARE POTENTIAL BIOACCUMULATIVE CHEMICALS OF CONCERN:

Benzo[a]pyrene; 3,4-benzopyrene
 3,4-Benzofluoranthene; benzo[b]fluoranthene
 1,12-Benzoperylene; benzo[ghi]perylene
 4-Chlorophenyl phenyl ether
 1,2:5,6-Dibenzanthracene; dibenz[a,h]anthracene
 Dibutyl phthalate; di-n-butyl phthalate
 Indeno[1,2,3-cd]pyrene; 2,3-o-phenylene pyrene
 Phenol
 Toluene; methylbenzene

For the current study, a selection of contaminants considered to be of relevance for the Tauranga Harbour catchment was selected for analysis.

These included:

- metals
- tributyltin
- chlorophenols
- polychlorinated biphenyls (PCB's)
- chlordanes
- polynuclear aromatic hydrocarbons
- organochlorine insecticides.

CHAPTER TWO

METHODS

2.1 SELECTION OF CONTAMINANTS

The Tauranga Harbour Regional Plan Project sentinel shellfish programme monitored concentrations of various trace metals and organic compounds in Pacific oysters (*Crassostrea gigas*).

With the exception of chlorinated organic compounds such as DDT and PCB, which exist entirely as a result of human activities, a certain natural concentration of chemicals exists in molluscs even in the absence of human activity. Chemical concentrations exceeding natural levels should be considered 'contamination', and the exact line demarcating natural concentrations from contamination is not easily drawn. It depends upon the species of mollusc itself as well as on many local and regional conditions (O'Connor 1992).

Several groups of organic compounds have been analyzed in sentinel shellfish from Tauranga Harbour. Two of the groups, total DDT and total chlordane, are chlorinated pesticides. Approval for agricultural use of DDT was withdrawn in New Zealand in 1970, while the approval for horticultural use of DDT was withdrawn in August 1989. Chlordane has never been registered for agricultural or horticultural use in New Zealand, and its use in the timber industry was stopped in October 1992.

2.1.1 Metals

A number of metals were selected for analysis, including those of direct toxic significance to humans, and those indicative of certain industrial process discharges.

The metals selected included:

- silver
- arsenic
- cadmium
- chromium
- copper
- iron
- mercury
- lead; and
- zinc.

2.1.2 Tributyltin (TBT)

TBT is an antifoulant compound. It is highly toxic to marine life. Regulatory controls have been enacted (both in New Zealand and overseas) to control the extent of its use as an antifoulant (refer discussion later in this document).

TBT can induce a condition known as imposex. This is the masculinization of females of a species. In severe cases, this can lead to reproductive sterility for the population, and extinction of affected populations.

As Tauranga Harbour has previously been demonstrated to have severely imposex-impacted neogastropod (eg the oyster borer *Lepsiella scobina*) populations (see later discussion), TBT levels in sentinel shellfish were examined to provide a measure of the current status of TBT in Tauranga Harbour waters.

2.1.3 PCB's

Polychlorinated biphenyls (PCB's) are a mixture of chlorinated compounds first used in the 1920's for a number of industrial purposes. Their high heat capacities and low dielectric constants were exploited for use in electrical transformers and capacitors. The use or storage of PCB in New Zealand is illegal after 31 December 1993.

Commercial PCB formulations (Arochlors) have been shown to contain over 100 of the 209 possible PCB congeners, the identity and proportion of each being dependant on the overall chlorination level achieved in manufacture. Where recent and relatively high pollution by PCB's has occurred the pattern of congeners can be determined by calibration against standards of the appropriate Arochlor formulation. Pattern recognition can be difficult at low levels such as those found in the current Tauranga Harbour study, or where a number of different formulations have contributed. Moreover, PCB's are gradually metabolised and transferred in the environment with accumulation of a subset of more resistant congeners. Thus PCB quantitation is a difficult problem and there is no international consensus as to the 'correct' approach (Patrick Holland, MAF, *pers comm.*).

Of the 209 possible PCB congeners that can be produced by the extensive chlorination of biphenyl, only 20 have non-*ortho* chlorine substitutions in the biphenyl rings. These congeners can attain planarity which makes their structure similar to the highly toxic dibenzo-p-dioxins and dibenzofurans.

Particularly important in this group are the PCB's having four, five or six chlorines in non-*ortho* positions, for example, congeners 3,3',4,4'-tetrachlorobiphenyl (IUPAC No. 77), 3,3',4,4',5-pentachlorobiphenyl (IUPAC No. 126), and 3,3',4,4',5,5'-hexachlorobiphenyl (IUPAC No. 169) which are very potent mimics of the 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF) both in P-450 induction and toxic effects, eg body weight loss, dermal disorders, liver damage, thymic atrophy, reproductive toxicity and immunotoxicity (Sericano et al 1992).

In the current study, the following PCB's (IUPAC numbers) were analysed for: 15, 18, 31, 28, 52, 49, 44, 40, 121, 101, 86, 77, 151, 118, 153, 141, 138, 156, 180, 170, 194, 206, 209.

2.1.4 Chlordanes

Chlordane was quite widely used in New Zealand as a broadcast insecticide and also for timber treatment, and is very persistent in the environment. It is composed of a complex mixture of components. Agricultural/horticultural use ceased many years ago and were always minor, relative to DDT or dieldrin.

In this study chlordane has been quantified by analysis of the two major components of technical chlordane, trans and cis chlordane. The concentrations of cis and trans chlordane were determined from calibrations against pure standards of the isomers. These two compounds comprise 43% of pure technical chlordane. Thus the equivalent technical chlordane concentrations were obtained by multiplying the sum of the cis and trans chlordane concentrations by 2.33.

2.1.5 Polynuclear Aromatic Hydrocarbons

In this study eight PAH's were quantified, with benzo[g,h,i]perylene used as an internal standard, since it is generally found in negligible amounts. This group of PAH's provides a good measure of the extent of 'oil' pollution in the harbour:

- anthracene
- fluoranthene
- pyrene
- chrysene
- benz[a]anthracene
- benzo[b]fluoranthene
- benzo[k]fluoranthene
- benzo[a]pyrene.

2.1.6 Organochlorine Insecticides

The pesticide DDT is metabolised to DDE and DDD in the environment, but those compounds degrade very slowly under environmental conditions. DDT is a combination of both the 'op' and 'pp' isomers in varying proportions depending upon the manufacturer.

The following organochlorines were analysed for:

- heptachlor epoxide
- heptachlor
- endrin
- dieldrin
- p,p DDT
- p,p DDD
- p,p DDE
- o,p DDT
- o,p DDD
- o,p DDE
- gamma - BHC (lindane)

Endrin and dieldrin are closely-related organochlorine compounds. Dieldrin is formed by the epoxidation of aldrin which occurs as an industrial process and naturally in the environment. Endrin is a stereoisomer of aldrin, and of higher toxicity. However, it tends to be removed rapidly from biological systems on termination of exposure. This group of organochlorine compounds has been used in New Zealand as insecticides. Due to their toxicity and persistence, their purchase requires a permit from MAF for application to land or plant material.

Lindane has been widely used in horticultural/agricultural areas as an insecticide following the decline of acceptance of DDT use in New Zealand. Lindane was not detected at any site in this study.

2.1.7 Chlorophenols

Chlorophenols have been used in New Zealand for a variety of industrial and agricultural purposes. Pentachlorophenol (PCP) has been used as a timber treatment chemical.

2.1.8 General

All of these trace metals and groups of organic compounds can be acutely or chronically toxic to marine life and to humans under some conditions. On the other hand, while the elements arsenic, chromium, copper, nickel and zinc can be toxic at high concentrations, they are also essential to the maintenance of life (Nielsen 1988).

2.1.9 Microbiological contaminants

Sentinel shellfish were examined for enterococci, faecal coliforms, *Salmonella*, *Vibrio parahaemolyticus*, and *Clostridium perfringens*.

These results should be contrasted against the results of the biennial Shellfish Quality Assessment (SQA) undertaken by Environment B.O.P (see, for example, BOPRC 1992). An explanation of the significance of the above microbiological parameters can also be found in the SQA series.

2.2 DEPLOYMENT OF SENTINEL SHELLFISH

On 24 October 1990, Pacific oysters collected from Ohiwa Harbour were deployed as sets of five replicates throughout Tauranga Harbour at four locations (Waikareao Estuary, Port Area, Southern Harbour and Northern Harbour). Oysters were enclosed in plastic mesh bags and suspended just above the sea floor by marine grade stainless steel spikes driven into the sediment.

Oysters were recovered on 17 December 1990, and forwarded to various laboratories for bacterial, trace metal, tributyltin (TBT), hydrocarbon and organic contaminant analysis. Two of the five Waikareao Estuary replicates were lost, and so one set was replaced with a feral oyster sample. This sample also provides insight into the likely differences between persistent contaminant loads of feral and introduced sentinel oysters.

The four deployment locations were as follows (refer also Figure 2.1):

ZONE	DESCRIPTION
Waikareao Estuary	Three replicates plus one 100g sample of naturally-occurring oysters gathered between 8:30 - 9:30am.
Port	Five replicates retrieved between 10:15 - 11:30am.
Upper Southern Basin	Five replicates retrieved between 11:30am - 1:30pm.
Northern Harbour	Six replicates retrieved between 2:30 - 3:15pm between Ongare Point and Kauri Point.

All replicates were at a depth of 1.5 - 2.5 metres below chart datum except the following:

Waikareao Estuary - Site 1: oysters were collected from the mid-tide level.

Port - Site 2: oysters were deployed at a depth of 10m.

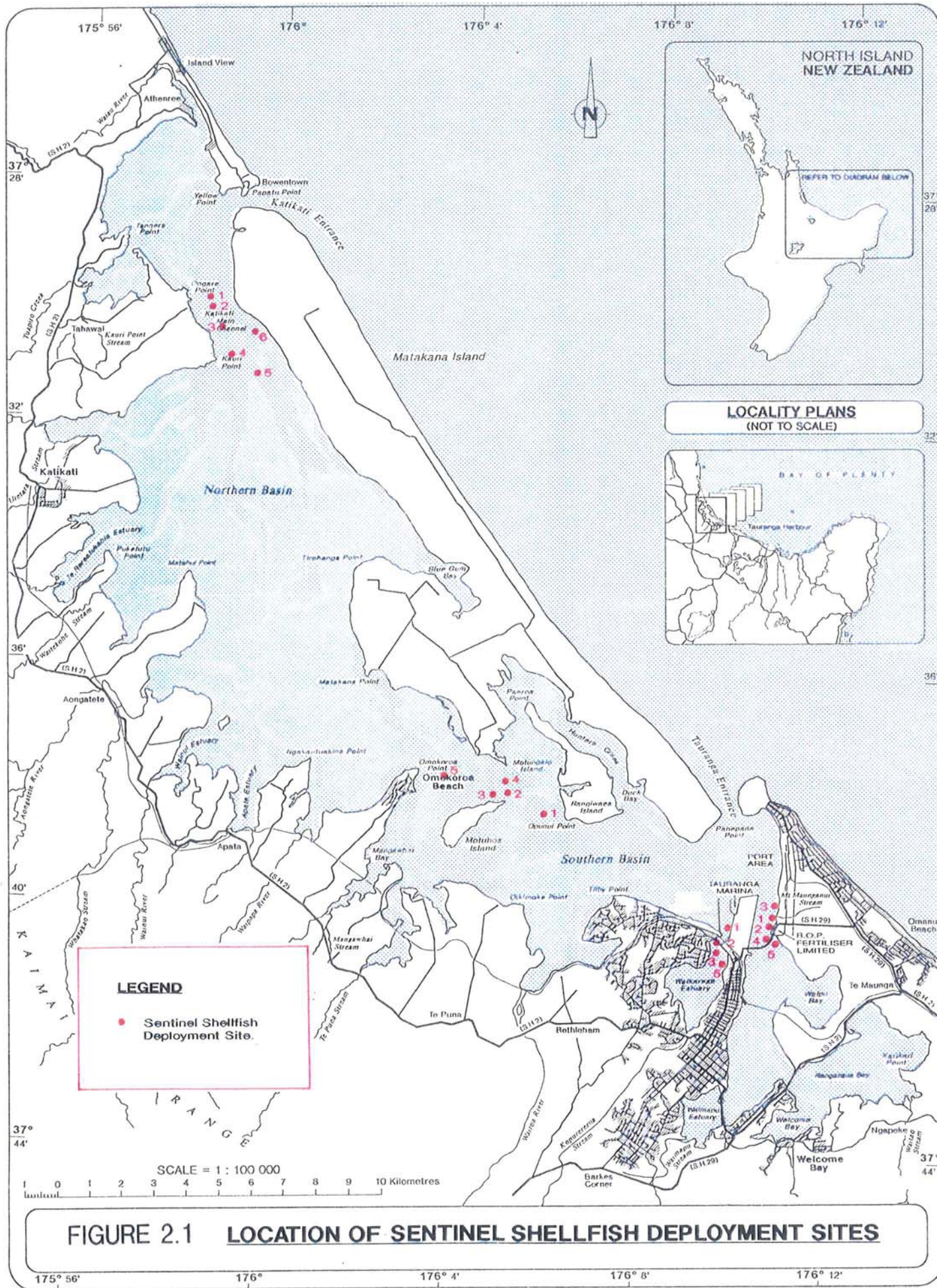
Upper Southern Basin - Sites 1-3: oysters were deployed at a depth of 3-4 m.

Only two replicates from the relatively shallow Waikareao Estuary were lost during the period of deployment. Mortality of oysters was checked one week after initial deployment. Initial mortality for some replicates was large. Sufficient numbers of oysters had been deployed to accommodate this. Following these early mortalities, however, subsequent mortalities were low, being of the order of 10-15% maximum for the remainder of the deployment.

Fouling of all shallow replicate baskets by small filamentous algae was high, leading to a build-up of silt and a restriction of water flow. Replicate baskets under the Port wharves or at greater depth had less fouling overall.

Graphics

Note that for Figures 3.1- 3.17, the top graphic (mean \pm 95% confidence interval) relates to the Geometric Mean.



CHAPTER THREE

RESULTS

3.1 SHELLFISH TISSUE LIPID LEVELS

Generally, highly-bioaccumulative compounds are lipophilic. Consequently, they have a tendency to accumulate in lipids. Two species which exhibit differing lipid levels in their tissues, but which are exposed to the same level of a lipophilic contaminant, will display differing tissue burdens of that contaminant after exposure. The species or population with the higher tissue lipid concentrations will tend to accumulate more of the contaminant.

Consequently, as a first step in considering site differences in pollutant levels, it is important to assess whether any significant differences exist in tissue lipid levels between the sampling sites.

Figure 3.1 provides this information. There were no significant differences in tissue lipid levels between the four sets of sentinel shellfish .

3.2 COMPARISON WITH 'HIGH' CONTAMINANT LEVELS

The following results provide information on spatial differences in sentinel shellfish contaminant concentrations. However, it is also important to gain some appreciation for how 'polluted' with persistent contaminants Tauranga Harbour is in comparison to other coastal waters.

To permit such a comparison, data from the world's most extensive sentinel shellfish pollutant monitoring programme (the United States "*Mussel Watch*") has been accessed.

This US monitoring programme not only uses mussels, but oysters also. Data related to oysters has been used for comparative purposes in this report. An indication of contaminant levels regarded as 'high' in oyster populations from the US Mussel Watch Programme is included with many of the graphics recording the contaminant levels in oyster tissues from Tauranga Harbour.

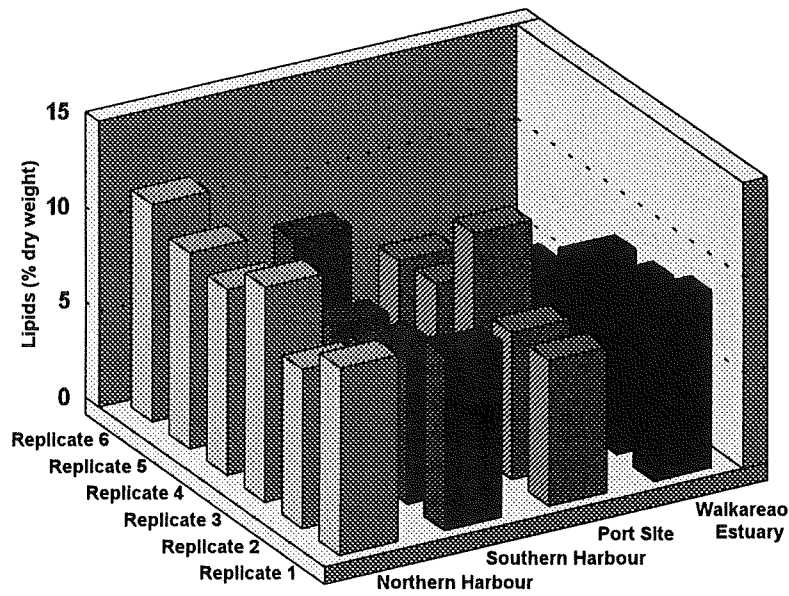
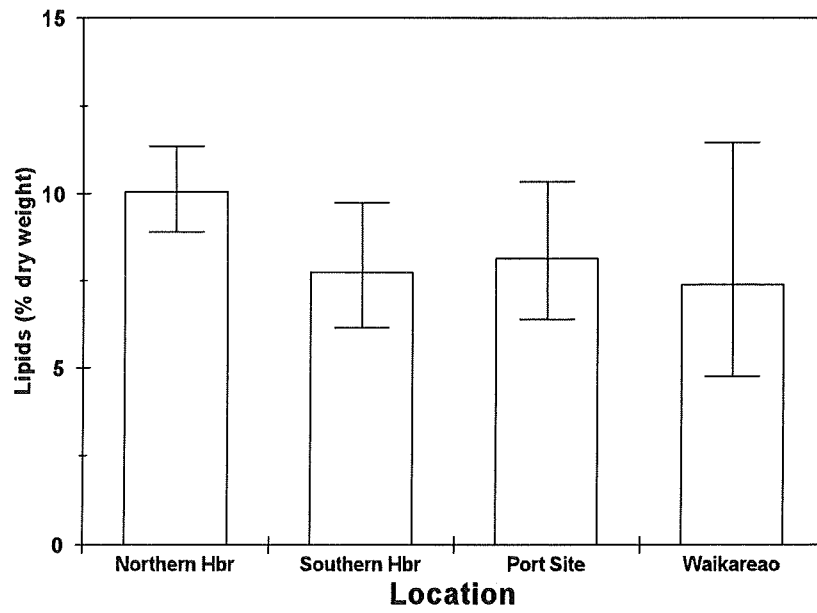


Figure 3.1 Lipid levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean dry weight and 95% confidence intervals about the mean; Bottom = levels for each replicate.

Table 3.1 Geometric mean and 'high' concentrations^a from analyses on oysters collected in 1990 at 107 sites in the United States (214 sites for As, Cd, Hg, Ni and Se) (O'Connor 1992).

CHEMICAL	UNITS	GEOMETRIC MEAN	HIGH VALUES EXCEED
Arsenic	ug/g dry weight	10	17
Cadmium	ug/g dry weight	2.7	5.7
Chromium	ug/g dry weight	0.48	0.93
Copper	ug/g dry weight	150	360
Lead	ug/g dry weight	0.52	0.94
Mercury	ug/g dry weight	0.094	0.24
Silver	ug/g dry weight	1.9	3.7
Zinc	ug/g dry weight	2400	5200
tPCB	ng/g dry weight	0.11	0.47
tDDT	ng/g dry weight	37	120
tCdane	ng/g dry weight	14	31
tPAH	ng/g dry weight	260	890
tBT	ng/g dry weight	81	350

^a All concentrations on a dry-weight basis of whole soft parts of molluscs. The 'high' concentrations correspond to the mean plus one standard deviation of the logarithms of the individual site means (O'Connor 1992).

tDDT = the sum of concentrations of DDT (dichlorodiphenyltrichloroethane) and its metabolites DDE (dichlorodiphenyltrichloroethylene) and DDD (dichlorodiphenyl dichloroethylene).

Total chlordane (*tCdane*) = the sum of concentrations of two major constituents of chlordane mixtures, *cis*-chlordane and *trans*-nonachlor and two minor components, heptachlor and heptachlorepoide.

Total polychlorinated biphenyls (*tPCB*) = the sum of the concentrations of di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, and nonachlorobiphenyls.

Total polycyclic aromatic hydrocarbons (*tPAH*) = the sum of concentrations of 18 PAH compounds: six 2-ring compounds (biphenyl, naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene and acenaphthene); four 3-ring compounds (fluorene, phenanthrene, 1-methylphenanthrene, and anthracene); three 4-ring compounds (fluoranthene, pyrene, and benz[*a*]anthracene); and five 5-ring compounds (chrysene, benzo[*a*]pyrene, benzo[*e*]pyrene, perylene, and dibenz[*a,h*]anthracene).

Total butyltin (*tBT*) = the sum of the concentrations of tributyl tin and its breakdown products dibutyltin and monobutyltin (concentrations in units of ng of Sn (as *tBT*)/g dry tissue).

3.3 METALS

3.3.1 Silver

Table 3.2 provides geometric means for each of the contaminants measured in sentinel shellfish. Silver levels were similar at all four locations, and were well below levels considered to be 'high' by the United States Mussel Watch Programme (Figure 3.2).

3.3.2 Arsenic

Arsenic levels were around 1/100th of average United States Mussel Watch Programme levels (Tables 3.1 and 3.2), with no significant differences in levels between the four Tauranga Harbour sampling locations (Figure 3.3).

This arsenic would be expected to be dominantly organic arsenic. The New Zealand Department of Health has an inorganic arsenic limit for shellfish of 2 µg/g. Even if all of the arsenic detected in the current study were in the inorganic form (which is highly unlikely, refer BOPRC 1992d), arsenic levels would remain at around 1/20th of those which might breach New Zealand guidelines for consumption.

3.3.3 Cadmium

Cadmium levels were around 1/10th of average United States Mussel Watch Programme levels (Tables 3.1 and 3.2), with no significant differences in levels between the four Tauranga Harbour sampling locations (Figure 3.4).

3.3.4 Chromium

Chromium levels were around 1/4 of average United States Mussel Watch Programme levels (Tables 3.1 and 3.2) There was a clear indication of elevated chromium contamination of sentinel shellfish from the Waikareao Estuary (Tables 3.1 and 3.2, Figure 3.5). Chromium levels in shellfish from the other three Tauranga Harbour sampling locations were similarly low (Figure 3.5).

Two of the Waikareao Estuary replicates breached the United States Mussel Watch Programme 'high' limit for chromium.

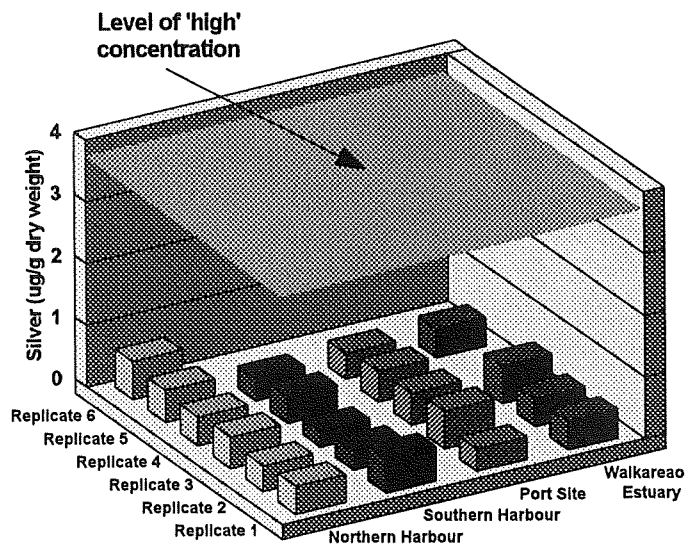
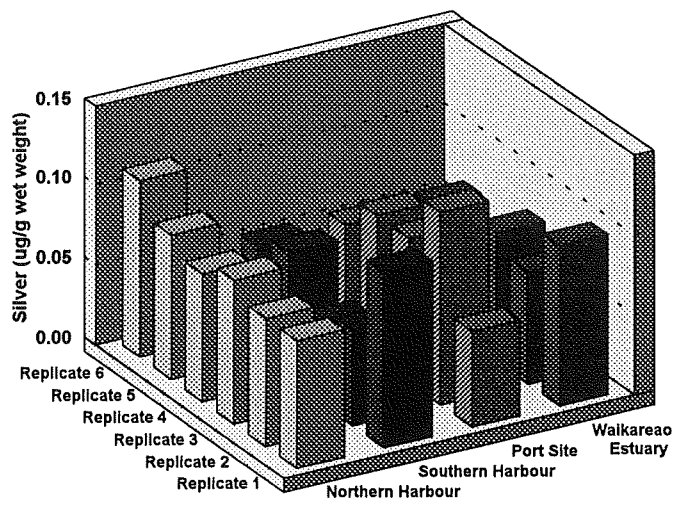
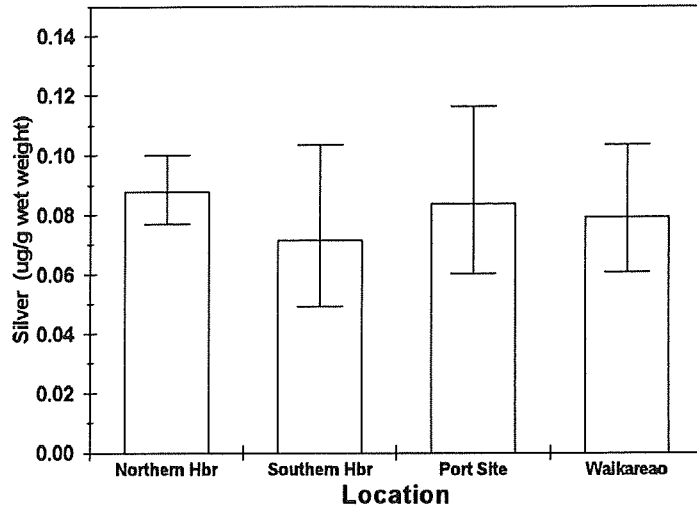


Figure 3.2

Silver levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

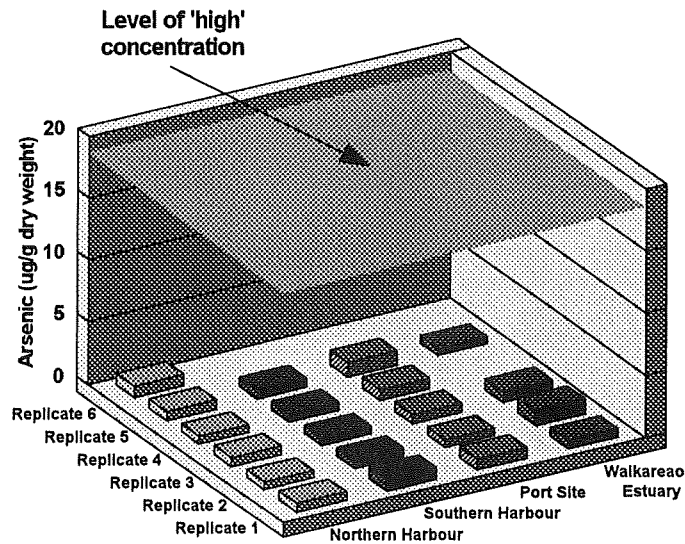
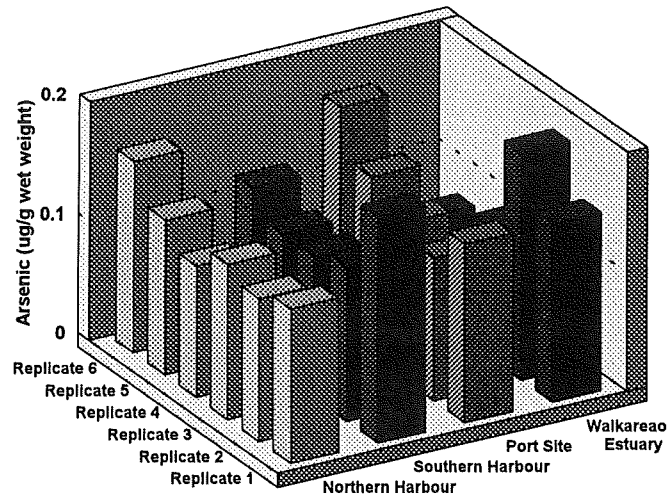
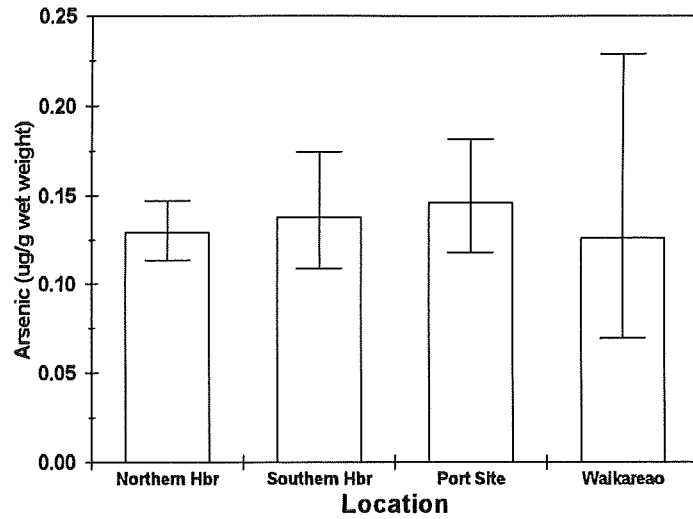


Figure 3.3 Arsenic levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

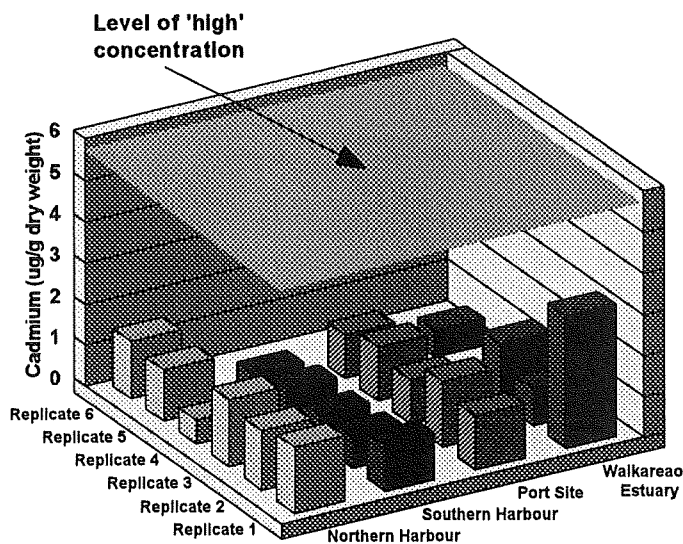
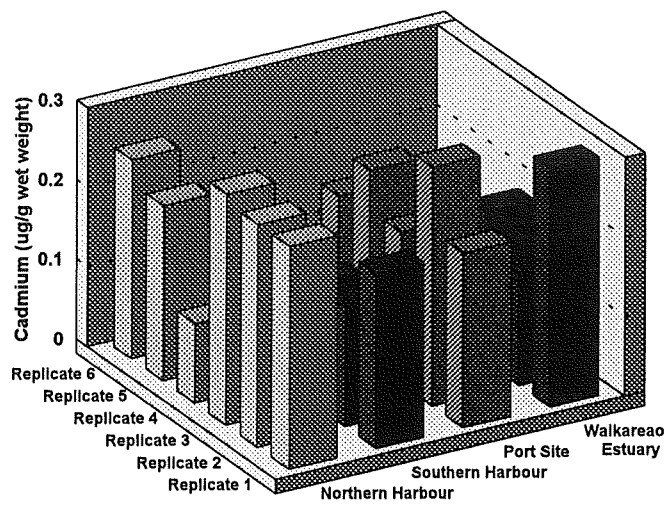
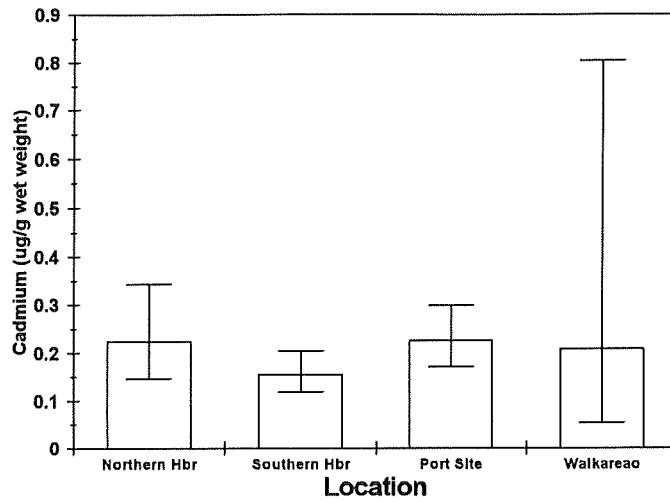


Figure 3.4

Cadmium levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

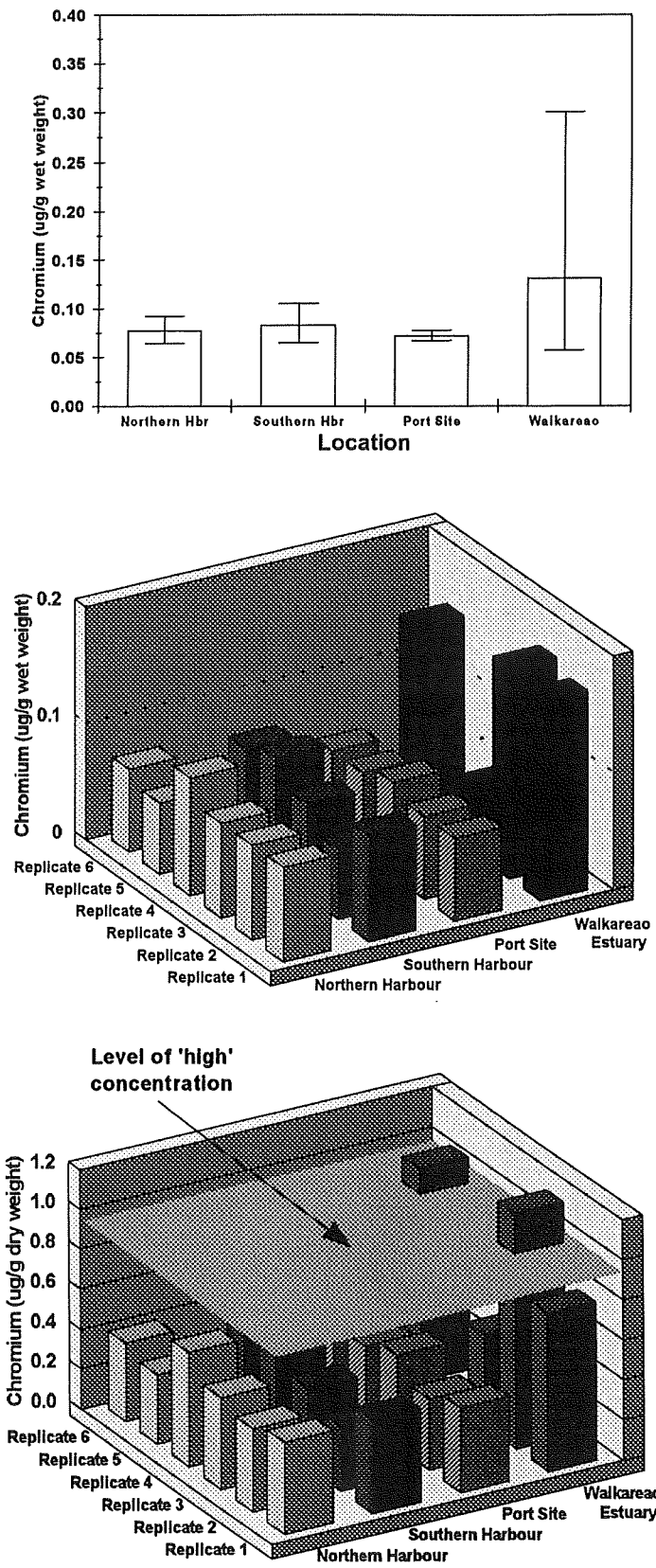


Figure 3.5 Chromium levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

3.3.5 Copper

Copper levels were around 1/10th of average United States Mussel Watch Programme levels (Tables 3.1 and 3.2), with no significant differences in levels between the four Tauranga Harbour sampling locations (Figure 3.6). Replicate 1 at Waikareao Estuary displayed a markedly higher copper level than the other replicates. This is due to this replicate being a feral oyster sample (see Methods Section) rather than an introduced sentinel shellfish replicate, and probably represents elevated seawater copper levels from antifoulants. An absence of any concomitant elevation in arsenic for this replicate indicates that this copper was unlikely to be due to copper/chrome/arsenic (CCA) contamination from timber treatment plant operations.

3.3.6 Iron

Iron can play an important role in altering the rate of other toxic metal uptakes by shellfish. Iron levels were similar for all four sampling locations (Table 3.2 and Figure 3.7).

3.3.7 Mercury

When converted to dry weights, mercury levels in Waikareao Estuary oysters were almost double those from the other three sites (0.09 µg/g dry weight for Waikareao versus 0.05 µg/g dry weight for all other sites).

Overall, however, these mercury levels were around 1/10th of average United States Mussel Watch Programme levels (Tables 3.1 and 3.2, Figure 3.8).

Mercury levels were well within the New Zealand Department of Health limit of 0.5 µg/g wet weight.

3.3.8 Lead

Lead levels were around 1/4 of average United States Mussel Watch Programme levels (Tables 3.1 and 3.2), with the exception of Waikareao Estuary, where geometric mean lead levels exceeded the United States Mussel Watch Programme 'high' limit.

The New Zealand Department of Health consumption limit for lead is 2 µg/g wet weight. Waikareao Estuary oysters displayed levels around 1/8th of this limit.

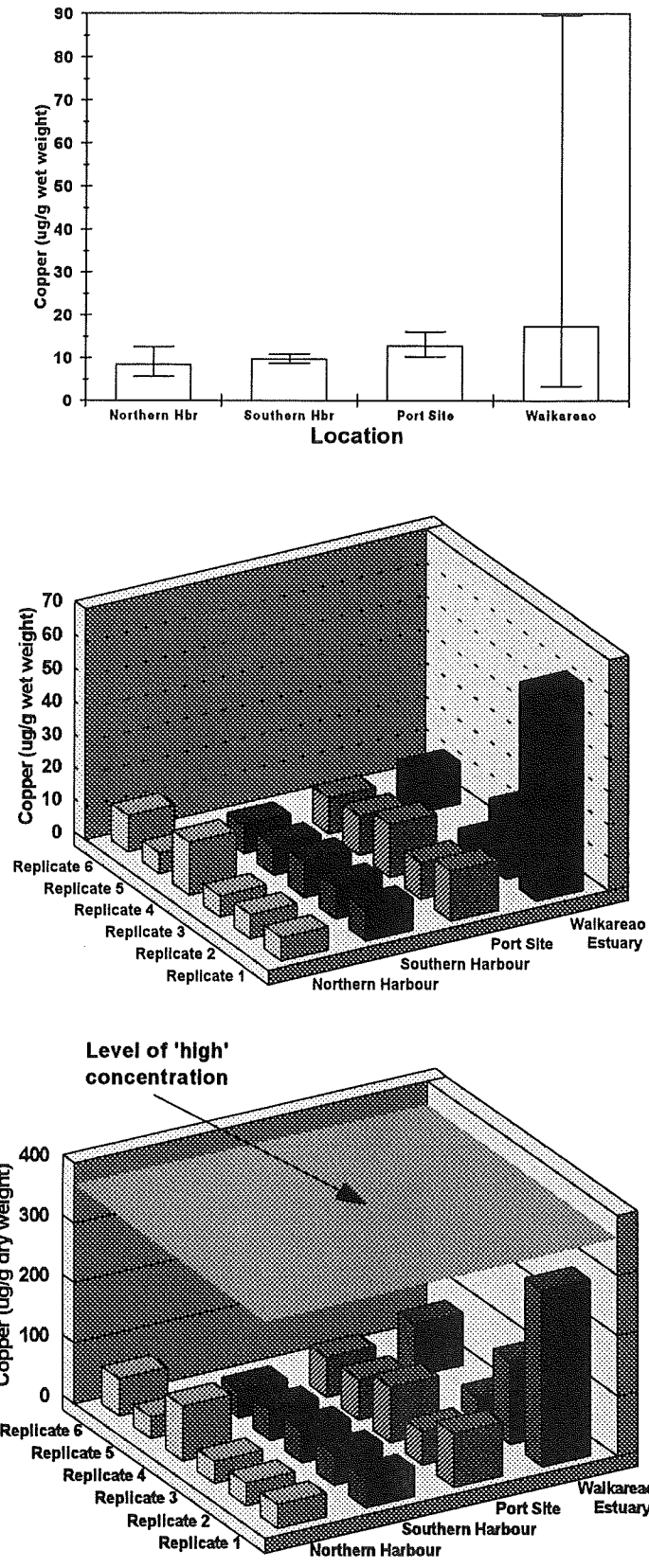


Figure 3.6 Copper levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

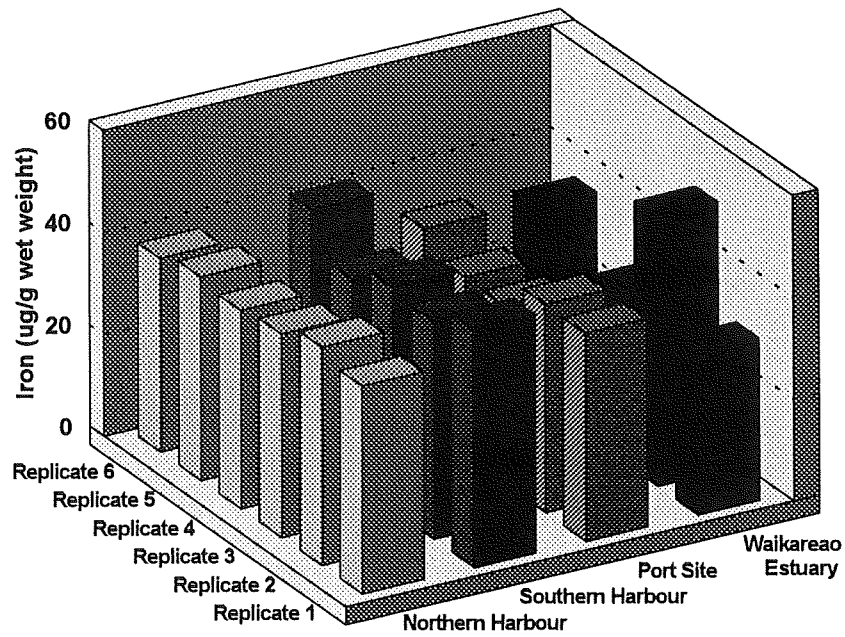
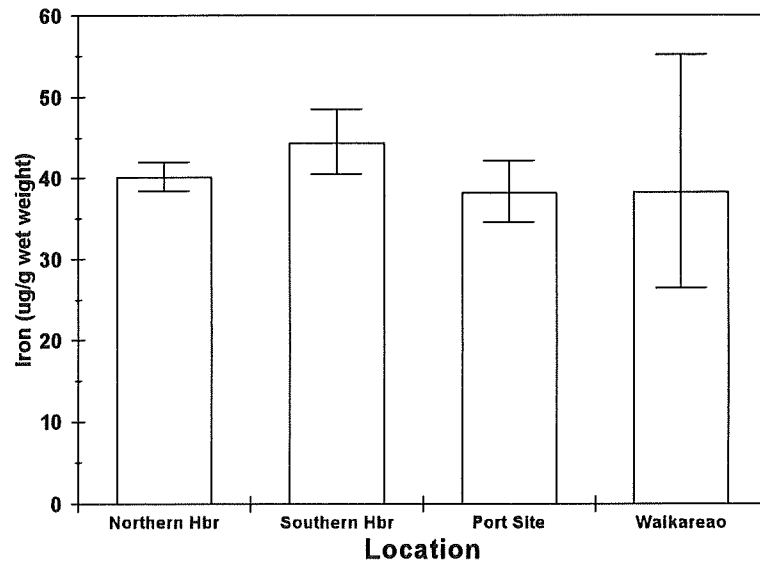


Figure 3.7 Iron levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Bottom = levels for each replicate.

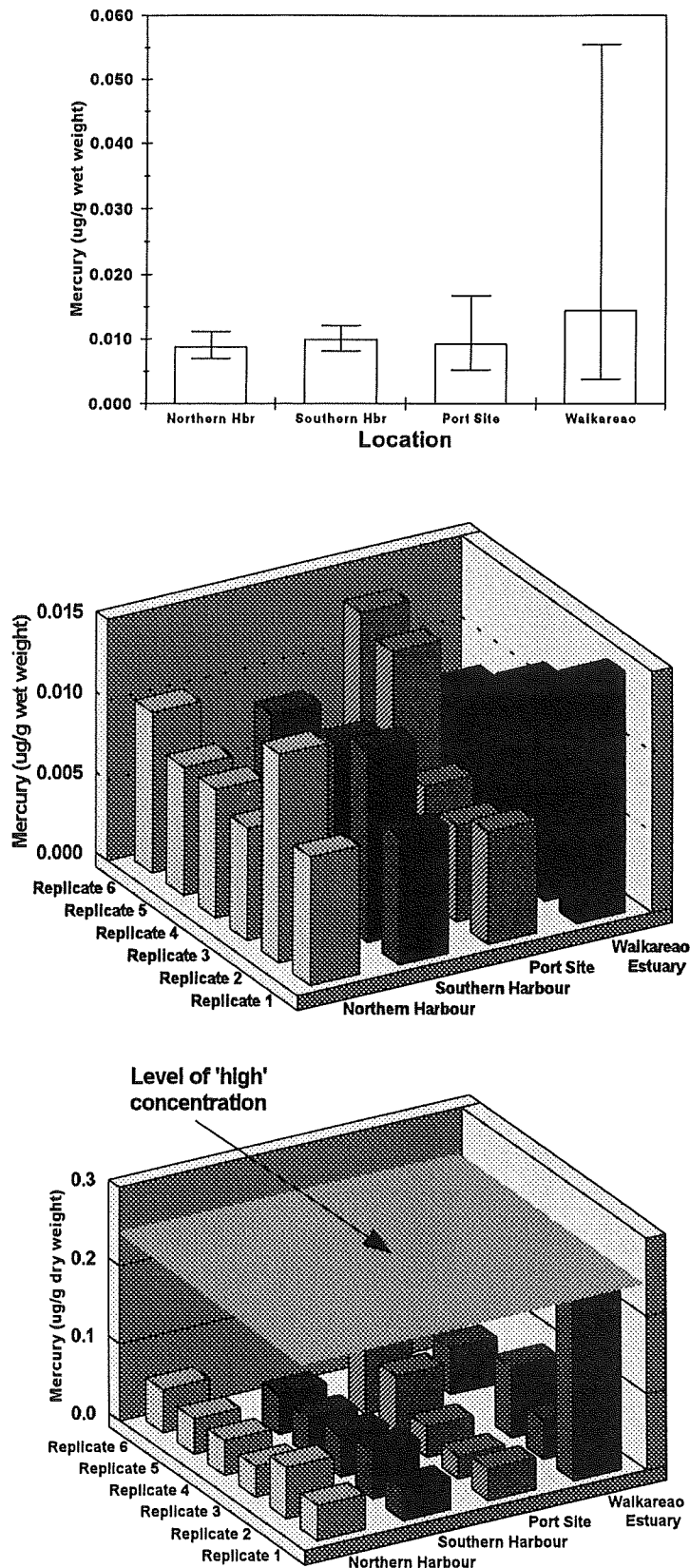


Figure 3.8 Mercury levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

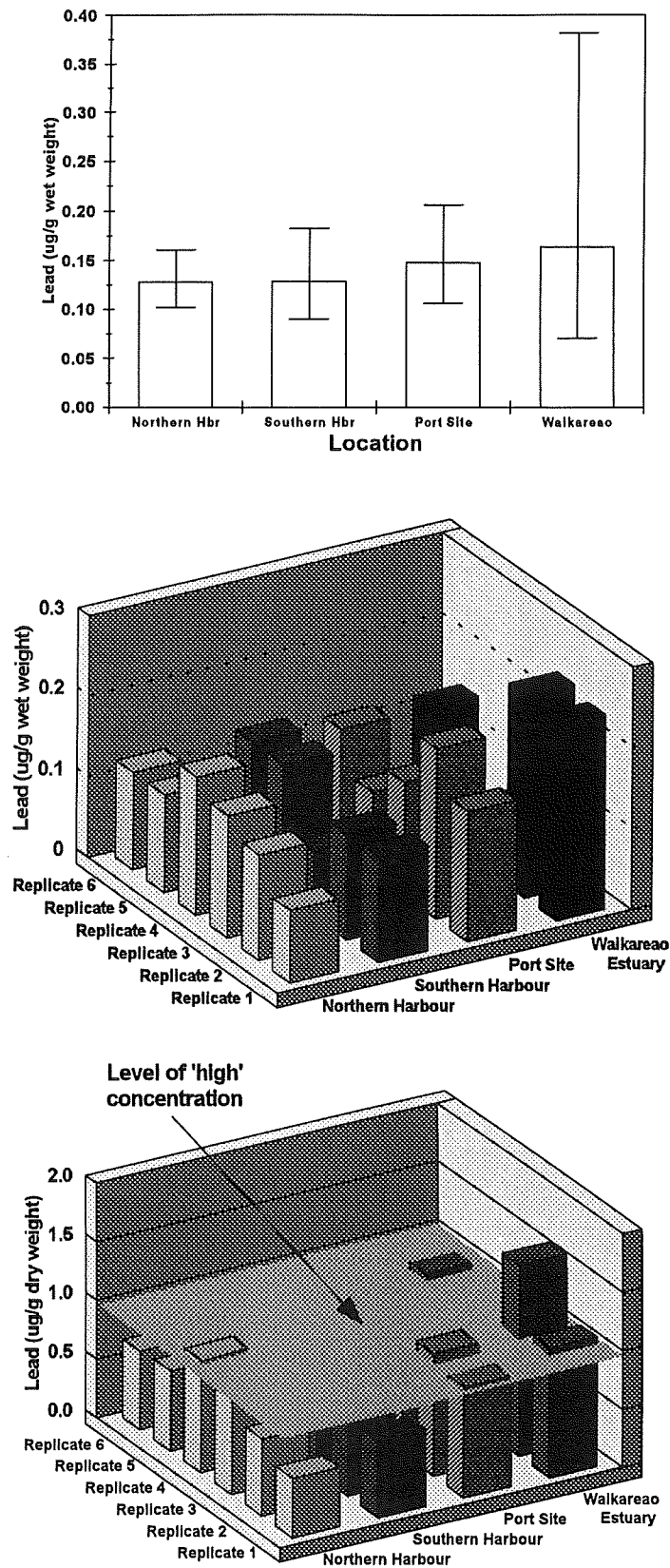


Figure 3.9

Lead levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

3.3.9 Zinc

Zinc levels were around 1/10 - 1/20th of average United States Mussel Watch Programme levels (Tables 3.1 and 3.2), with the exception of Replicate 1 for Waikareao Estuary (the feral oyster replicate), where geometric mean zinc levels were considerably higher than for other sentinel shellfish replicates, including those from the Waikareao Estuary. However, the Replicate 1 zinc levels still did not breach the United States Mussel Watch Programme 'high' limit (Figure 3.10).

3.4 TRIBUTYL TIN (TBT)

The effect of port operations on TBT levels in Tauranga Harbour waters (as evidenced by TBT levels in sentinel shellfish) can be clearly seen in Table 3.2 and Figure 3.11 (note: TBT-Sn levels have been converted to TBT).

Unfortunately, the Waikareao Estuary Replicate 1 (feral oyster) sample was destroyed during analysis, so no comparison can be made with Waikareao feral oysters.

However, Northern Harbour TBT levels in sentinel shellfish were negligible in comparison with the Southern Harbour, which was impacted by port operations. Geometric mean TBT levels in sentinel shellfish from the port area were 2800% higher than those from the Northern Harbour.

3.5 POLYNUCLEAR AROMATIC HYDROCARBONS (PAH's)

In this study eight PAH's were quantified, with benz[*g,h,i*]perylene used as an internal standard, since it is generally found in negligible amounts.

The Port and Waikareao areas displayed considerably elevated PAH levels relative to the Northern and Southern Harbour zones (Table 3.2, Figure 3.12).

The most toxic PAH is benzo[*a*]pyrene, a known carcinogen. It is a minor component of the PAH's determined in sentinel shellfish from Tauranga Harbour, with levels below 3 ng/g for all sites.

Port and marine operations markedly affect levels of oil contamination in sentinel shellfish in the Port and Waikareao Estuary areas.

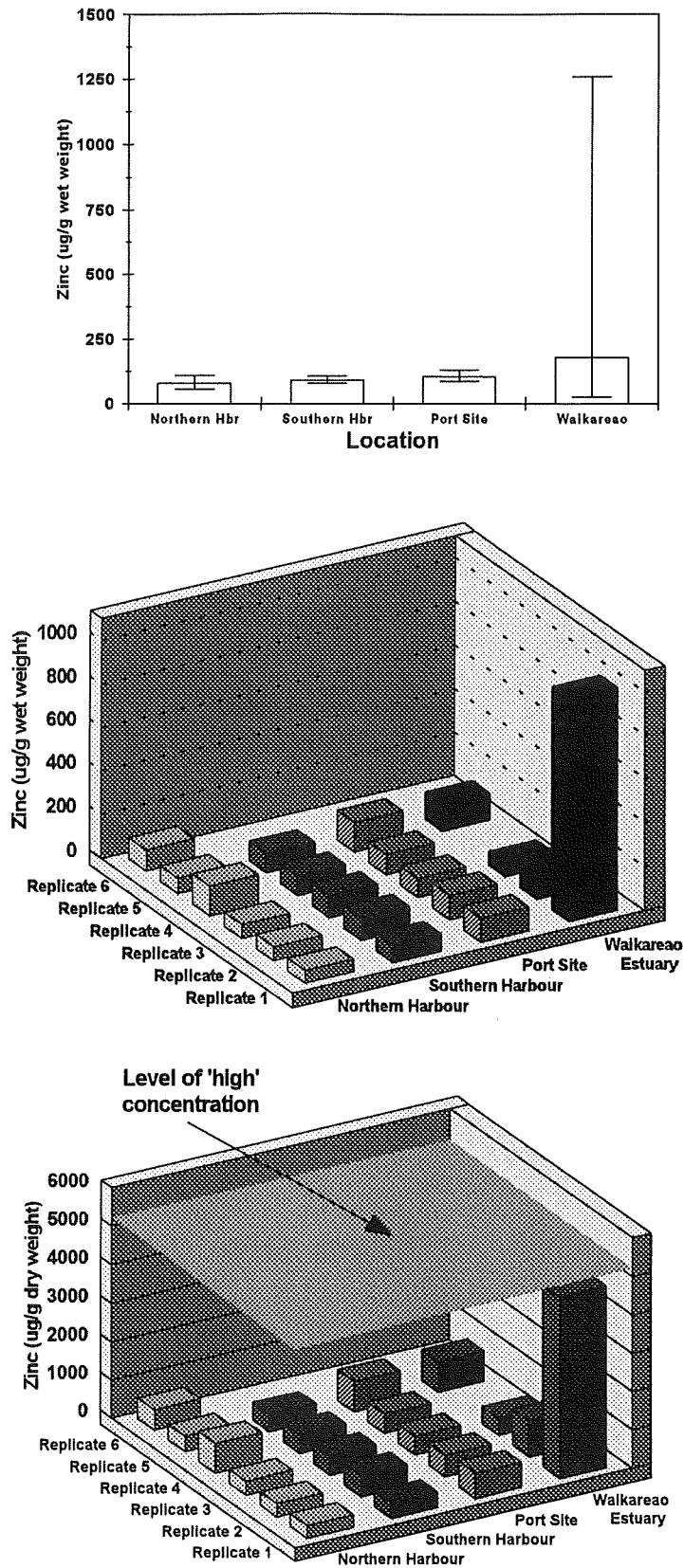


Figure 3.10

Zinc levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean wet weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

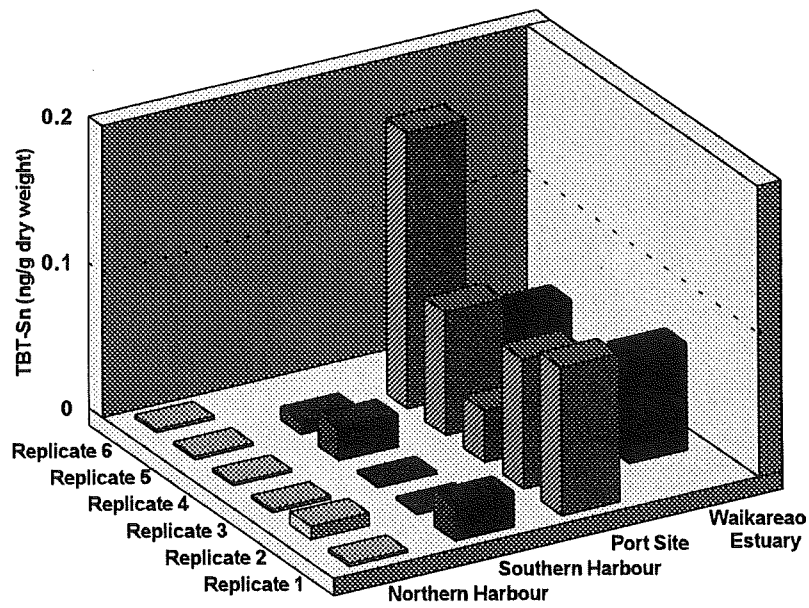
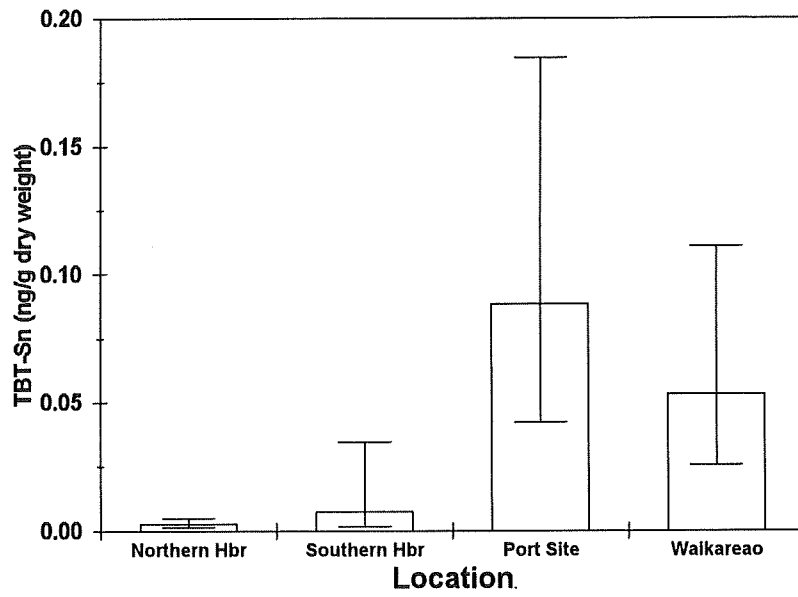


Figure 3.11 Tributyltin levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean dry weight and 95% confidence intervals about the mean; Bottom = levels for each replicate.

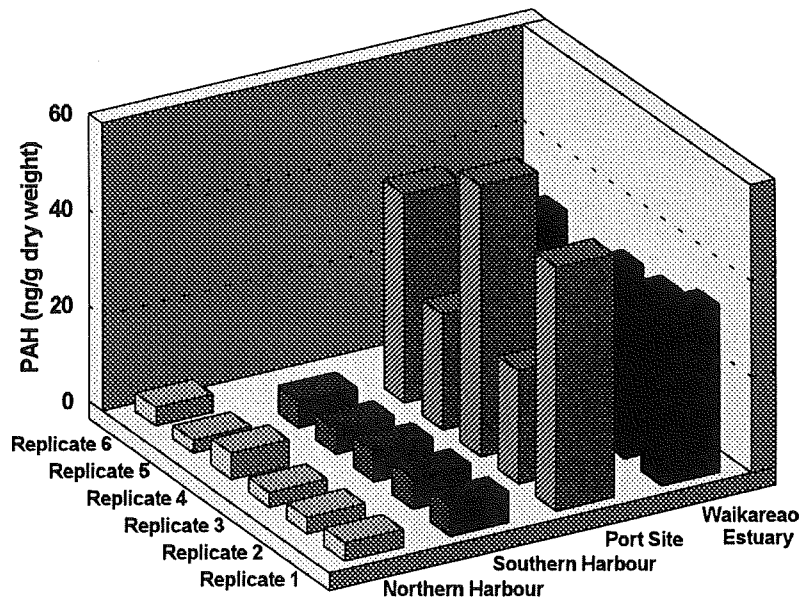
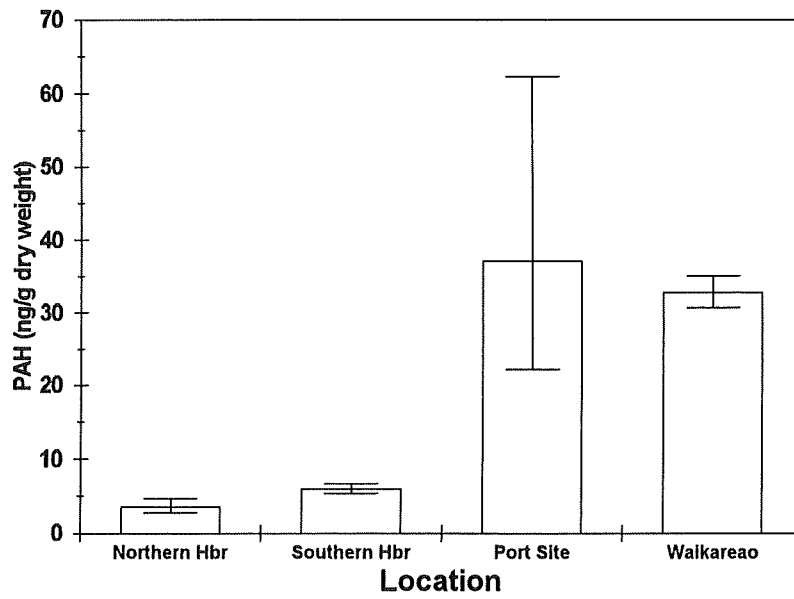


Figure 3.12 Polynuclear aromatic hydrocarbon levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean dry weight and 95% confidence intervals about the mean; Bottom = levels for each replicate.

3.6 PCB's

A subset of 22 individual congeners were quantified. This subset included all of the predominant persistent congeners, and accounted for the majority of PCB in weathered residues of the most common Arochlor formulations. The sum of the levels of these congeners was then taken as the 'total PCB'. As all congeners were not analysed (due to lack of standards) this total is an underestimate but does give a sound basis for comparison. This method has been used in a number of overseas studies including those of the National Research Council of Canada.

Geometric mean total PCB levels at each site are given in Table 3.2 and the individual congener data is provided in Appendix 1. The Waikareao Estuary oysters contained the highest concentration of PCB (Figure 3.13). The persistent congeners 101, 138 and 153 predominated indicating substantial weathering. The pattern of residues was similar to that found in the Manukau Harbour and appears to represent weathering of relatively non-specific pollution by Arochlors from a variety of sources including global contributions.

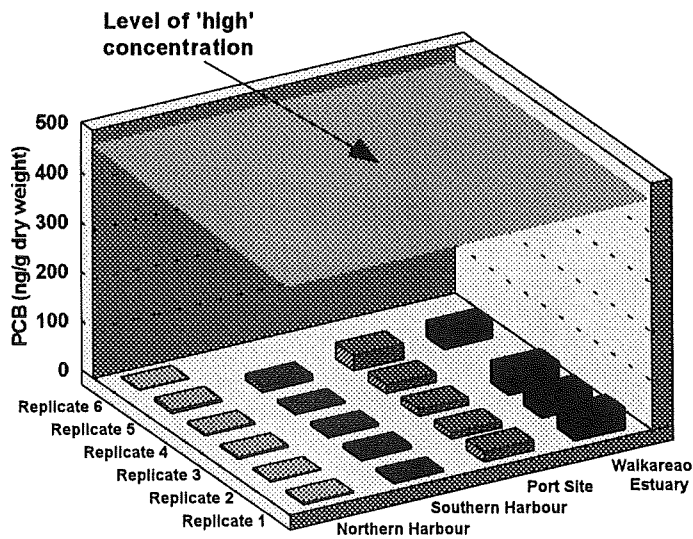
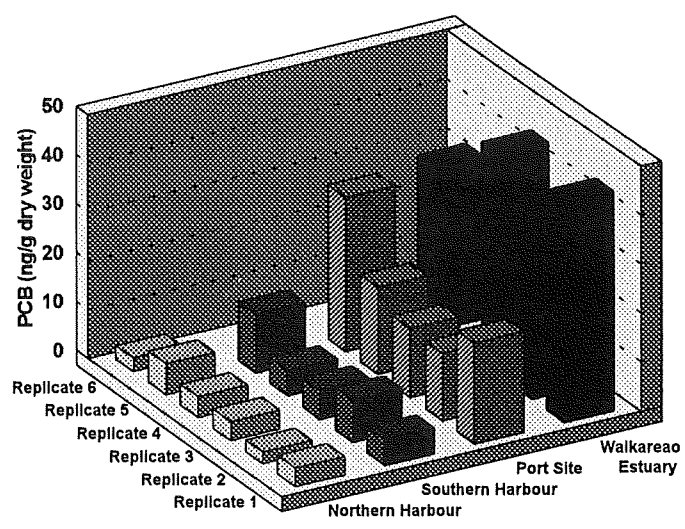
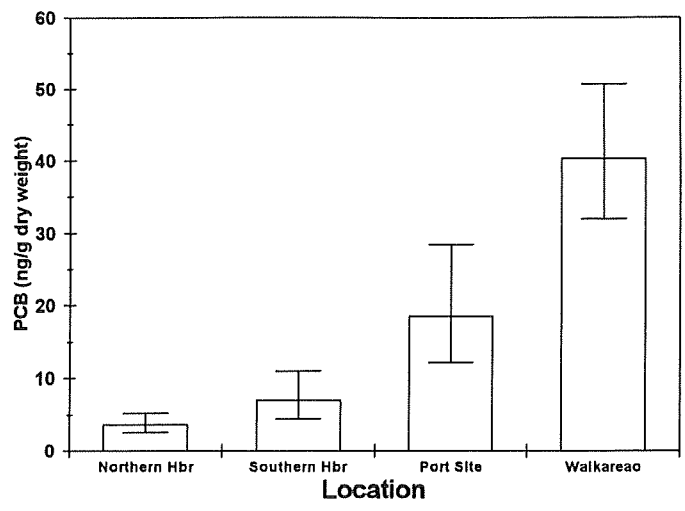


Figure 3.13 PCB levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean dry weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

Table 3.2 Geometric mean organic and metal contaminants in Tauranga Harbour sentinel shellfish (1990). All samples n=5, except Waikareao (replicate 1 = feral, replicates 2, 3 and 5 = sentinel shellfish).

Parameter	Units	Waikareao Estuary	Port Area	Southern Harbour	Northern Harbour
Total PAH	ng/g dry weight	32.9	37.1	6	3.6
Total PCB	ng/g dry weight	40.2	18.6	7	3.7
Technical chlordane	ng/g dry weight	2.9	1.6	0.3	0.29
Total DDT	ng/g dry weight	31.6	25.3	12.9	13.8
Dieldrin	ng/g dry weight	2.2	1.6	1	1.2
Chlorophenols	ng/g dry weight	7	6.2	2.9	2.7
Silver	ug/g wet weight	0.08	0.08	0.07	0.09
Arsenic	ug/g wet weight	0.13	0.15	0.14	0.13
Cadmium	ug/g wet weight	0.21	0.23	0.16	0.22
Chromium	ug/g wet weight	0.13	0.07	0.08	0.08
Copper	ug/g wet weight	17.4	12.8	9.7	8.4
Iron	ug/g wet weight	38.2	38.1	44.3	40.1
Mercury	ug/g wet weight	0.014	0.009	0.01	0.009
Lead	ug/g wet weight	0.16	0.15	0.13	0.13
Zinc	ug/g wet weight	179.2	105.1	92.1	78
Tributyltin-Sn	ug/g dry weight	0.053	0.088	0.007	0.003

It is of interest to note the obviously-elevated PCB levels in the Waikareao Estuary. The nature and source of these PCB's have been investigated by the University of Waikato in the form of an MSc thesis prepared by Shane Burgraaf.

Geometric mean PCB levels in Waikareao Estuary sentinel shellfish were ten times higher than those from the Northern Harbour.

Nevertheless, PCB levels, even in shellfish from the Waikareao Estuary, were well below levels considered to be 'high' by the United States Mussel Watch Programme (Figure 3.13).

3.7 CHLORDANES

Chlordane levels were generally low at all sites (Table 3.2, Figure 3.14). The Northern Harbour and Southern Harbour areas had negligible levels. The Waikareao Estuary and Port areas had chlordane as a mixture recognisable as being similar to technical chlordane and probably had local sources.

Geometric mean chlordane levels in Waikareao Estuary sentinel shellfish were ten times higher than those from the Northern and Southern Harbours.

3.8 ORGANOCHLORINE INSECTICIDES

DDT and its metabolites DDD and DDE were detected at all sites. The ratio of DDT/DDE varied between sites. However the ratio was always less than 1, which indicates no major fresh inputs of DDT into Tauranga Harbour.

DDT levels were relatively low in comparison to the 'high' guideline provided by the United States Mussel Watch Programme (Table 3.2, Figure 3.15).

Dieldrin was detected at low levels at all sites, and there were no marked geographical differences in sentinel shellfish dieldrin levels between sampling locations (Table 3.2, Figure 3.16).

3.9 CHLORINATED PHENOLICS

Chlorinated phenolics are displayed in Figure 3.17. Elevated levels were observed in the Port and Waikareao Estuary areas.

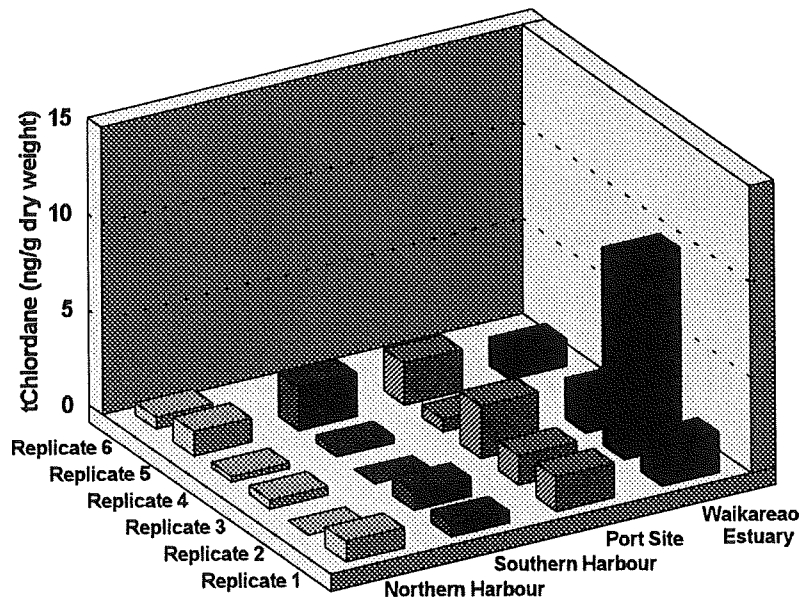
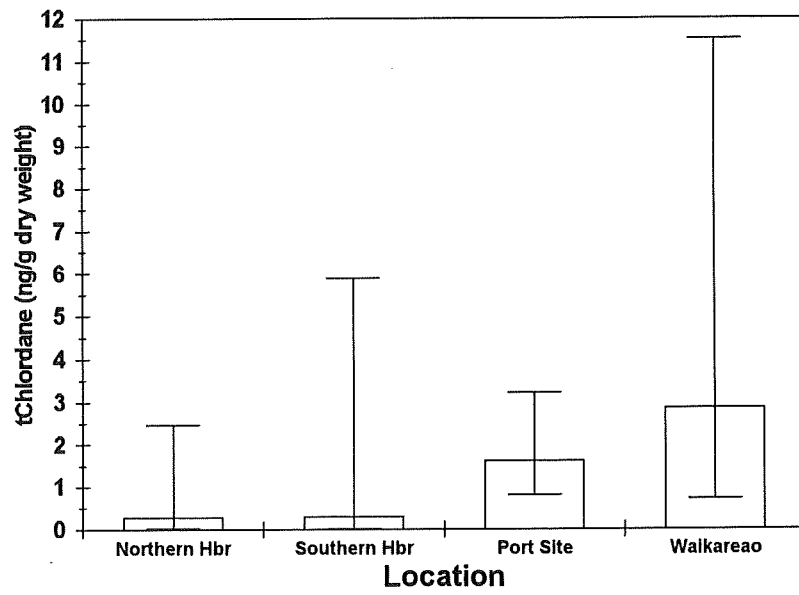


Figure 3.14 Total chlordane levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean dry weight and 95% confidence intervals about the mean; Bottom = levels for each replicate.

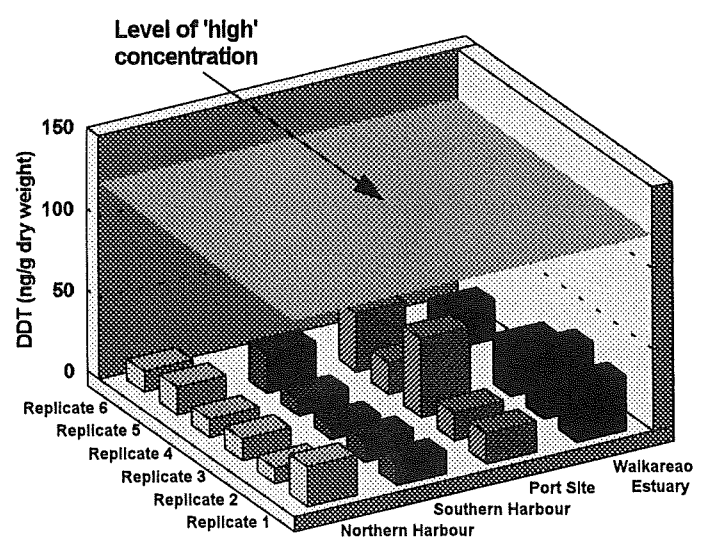
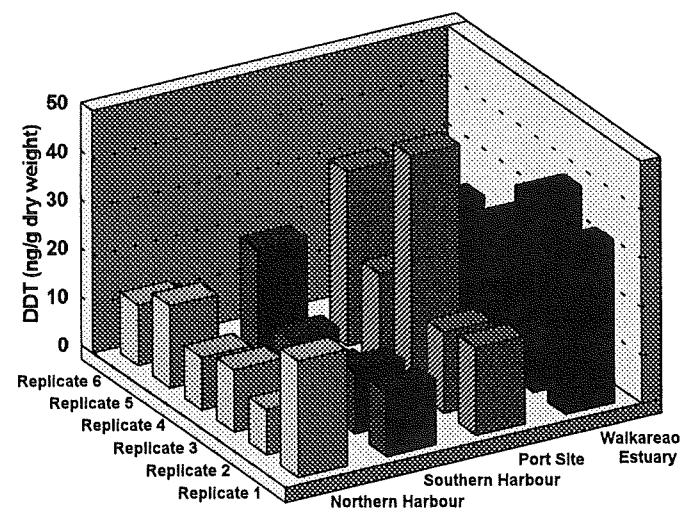
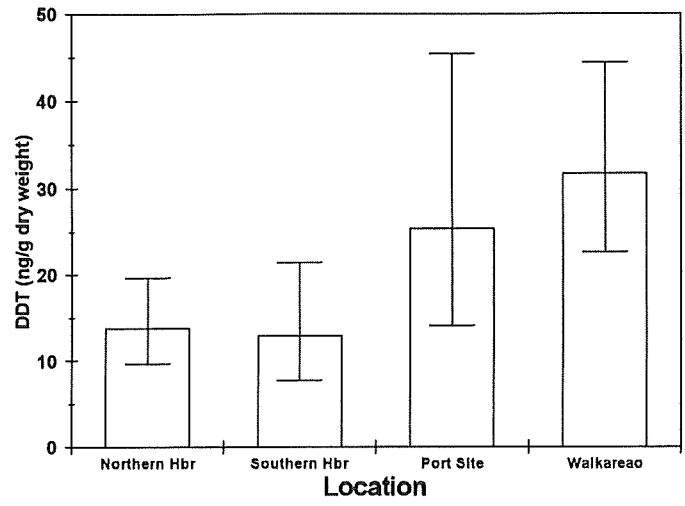


Figure 3.15 DDT levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean dry weight and 95% confidence intervals about the mean; Middle = levels for each replicate; Bottom = comparison with the level considered to be a 'high' concentration as assessed according to the method of the NOAA Mussel Watch Project (O'Connor 1992).

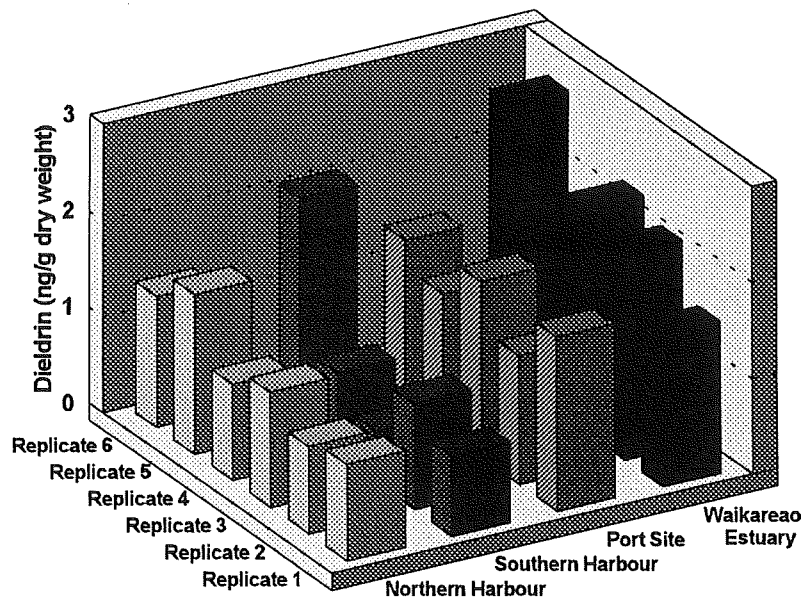
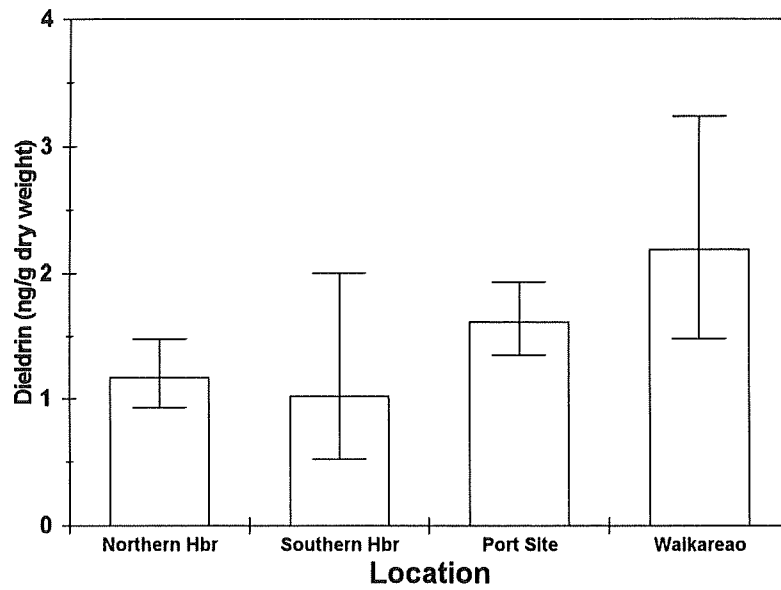


Figure 3.16 Dieldrin levels in sentinel shellfish deployed in Tauranga Harbour.
 Top graph = mean dry weight and 95% confidence intervals about the mean;
 Bottom = levels for each replicate.

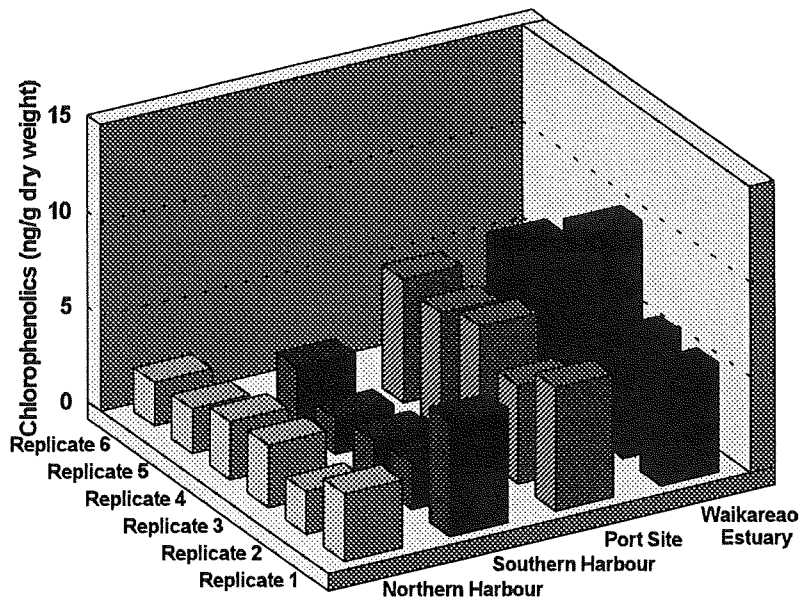
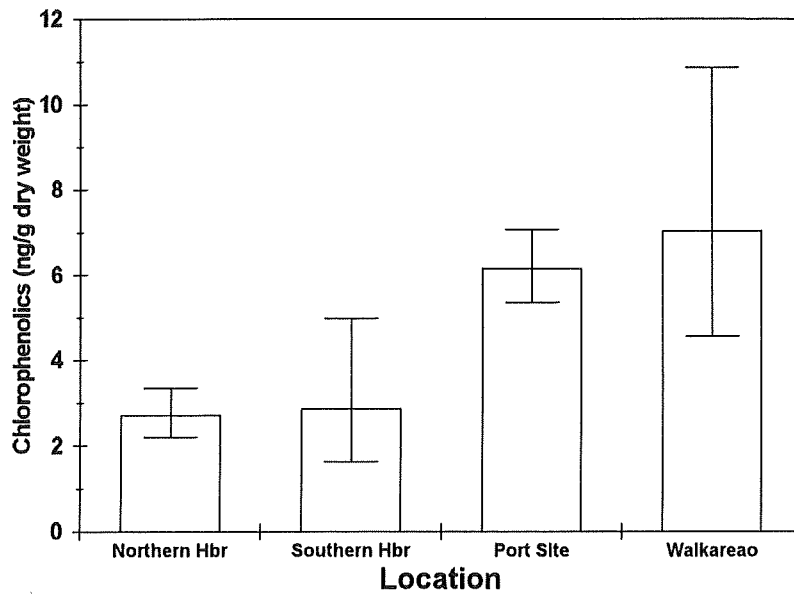


Figure 3.17 Chlorinated phenolic levels in sentinel shellfish deployed in Tauranga Harbour. Top graph = mean dry weight and 95% confidence intervals about the mean; Bottom = levels for each replicate.

CHAPTER FOUR

DISCUSSION

4.1 GENERAL

Table 4.1 provides an overview of geometric mean contaminant concentrations in Tauranga Harbour sentinel shellfish in comparison with oyster data collected for the United States Mussel Watch Programme (with the exception of TBT).

All contaminants (excepting TBT, see later discussion) occurred at generally considerably lower levels in the Tauranga Harbour sentinel shellfish than for the average United States Mussel watch Project oyster data.

4.2 METALS

Generally, metal levels in sentinel shellfish from Tauranga Harbour were low.

Weis and Weis (1992) have reported on the transfer of copper, chromium and arsenic from CCA-treated lumber to aquatic biota. Algae (*Ulva lactuca* and *Enteromorpha intestinalis*), which had accumulated CCA from treated woods, killed grazing molluscs which fed upon them. As well as oysters, sediment-dwelling crabs showed elevated metal levels (in the latter case, as a result of the elevated levels of metals in the sediments in which they resided).

4.3 PCB's

PCB's were found at generally low levels at all sites. There was some evidence of localised elevations in PCB levels in the Waikareao Estuary.

4.4 CHLORDANES

Chlordane levels in Tauranga Harbour sentinel shellfish were low.

Table 4.1 Geometric Mean and "High" concentrations (on a dry weight basis) from analyses of oysters collected in the US Mussel Watch Project and the Tauranga Harbour Project

Shading indicates value exceeding high concentration determined from US Mussel Watch Project

Parameter	Dry weight Units	United States Mussel Watch Project		Tauranga Harbour Project 1990			
		Geometric Mean	'High' Concentration	Northern Hbr Geometric Mean	Southern Hbr Geometric Mean	Port Area Geometric Mean	Waikareao Geometric Mean
Silver	ug/g	1.9	3.7	0.49	0.37	0.47	0.50
Arsenic	ug/g	10	17	0.72	0.72	0.82	0.79
Cadmium	ug/g	2.7	5.7	1.25	0.81	1.27	1.30
Chromium	ug/g	0.48	0.93	0.43	0.43	0.41	0.82
Copper	ug/g	150	360	46.82	50.56	72.37	108.92
Mercury	ug/g	0.094	0.24	0.05	0.05	0.05	0.09
Lead	ug/g	0.52	0.94	0.71	0.67	0.83	1.03
Zinc	ug/g	2400	5200	434.72	480.62	592.55	1123.18
tPCB	ng/g	110	470	3.66	6.97	18.56	40.21
tCdane	ng/g	14	31	0.29	0.30	1.61	2.87
tDDT	ng/g	37	120	13.79	12.92	25.34	31.65

4.5 PAH's

Polycyclic aromatic hydrocarbons (PAH's) are similar to metals in the sense that they occur naturally. They are found in fossil fuels such as coal and oil. Their existence, however, is also attributable to humans because they are produced when organic matter is burned. A multitude of human activities, from coal and wood burning to waste incineration, create PAH compounds in excess of those that would exist naturally. In addition, human production, transport, and use of oil releases more PAH's to the environment, on a globally-averaged basis, than does natural seepage.

Because they are relatively more concentrated in oil than in combustion products, 2- and 3-ring compounds, especially those with alkyl groups on a ring such as methyl- and dimethylnaphthalene and methylphenanthrene, are sometimes classified separately from the higher molecular weight 4- and 5-ring compounds. Since high concentrations of both types of compounds tend to be found in the same locations, all PAH compounds have been combined into a single group in this report.

4.6 TBT

The biocide tri(n-butyl)tin (TBT) has been described as the most toxic substance ever deliberately introduced into natural waters (Goldberg 1986).

Prior to the widespread use of TBT, cuprous oxide had been the primary biocide in marine antifouling paints since the mid-19th century. However, because copper-based paints generally became ineffective within a year, more effective biocides were sought. Tributyltin satisfied this need.

Early organotin antifoulants contained bis(tributyltin) oxide or tributyltin halides. The earliest formulations had the tributyltin compound(s) simply mixed into the paint. These were referred to as free association paints. More effective coatings were developed which incorporated tributyltin monomers, such as tributyltin methacrylate, with other monomers to form copolymers. Some of these formulations were effective for five years or more. The copolymer paints release TBT into the water at a slower and more controlled rate because the release is controlled by hydrolysis of the paint film rather than by diffusion as in the case of free association varieties.

Once the biocide is released from the paint film, a thin envelope of highly-concentrated TBT is formed around the vessel hull. The larvae of fouling or nuisance organisms, such as barnacles, are killed or repelled when they encounter this layer, thus protecting the vessel.

Although it is an excellent antifoulant, TBT-based products having many advantages over the more conventional copper ones, TBT has been shown to have deleterious effects upon non-target marine organisms.

TBT has been demonstrated to cause shell malformations in oysters at concentrations as low as 2 ng/L, and to cause larval mortality in fish, the Pacific oyster and dogwhelk.

A wide variety of marine organisms accumulate TBT.

Additionally, imposex (the superimposition of male sexual characteristics upon the female) was first noticed in the snail *Nucella lapillus* in the UK in 1970 (Blaber 1970), and later on between 1973 and 1978 in that species as well as in French populations of *Nassarius reticulatus* and *Ocenebra erinacea* (although at the time, nothing was known about its cause). Imposex is now known to be a sub-lethal effect caused by TBT contamination (Bryan et al 1986, 1987).

Spooner et al (1991) have provided evidence that the induction of imposex by exposure of female *Nucella lapillus* to TBT in seawater is accompanied by an increase in testosterone concentration. When testosterone levels in females were artificially increased by injection of the steroid, imposex was induced in the absence of TBT.

Three butyltin compounds, aggregated as tBT, are found in molluscs because tributyltin (TBT) has been used as an antifouling agent in the paint commonly used on ships and some marine underwater facilities.

Concern about the effects of TBT-based anti-foulants on non-target marine species has led to restrictions on their use in many countries. In New Zealand the use of organotin-based anti-foulants was reviewed in 1987. The problems were thought to be primarily associated with recreational boating, and it was assumed that banning the use of TBT paints on small craft would alleviate adverse effects. Hence, in July 1989, a partial ban on the sale and use of organotin-based paints on craft less than 25 metres in length (except aluminium construction) was enforced. However, other possible sources of TBT include commercial shipping and dry dock operations.

Tributyltin degrades to dibutyltin and then to monobutyltin, which itself does not persist, so unlike the chlorinated compounds, tBT should degrade relatively quickly.

It has been recognised for several years that molluscs (bivalves and gastropods) are particularly sensitive to tributyltin (TBT). The metabolism of TBT by marine animals and possible linkages to effects has been discussed by Lee (1991), who observed that among various invertebrate groups, the molluscs appear to be the most affected by TBT.

Molluscs are characterised by very low cytochrome P-450 content and mixed-function oxygenase activity (important elimination mechanisms for polar hydrophobic compounds such as TBT) in the digestive gland. This low detoxifying activity may explain this group's sensitivity to TBT (Lee 1991).

Gibbs (1991) observed a TBT-induced virtual complete elimination of the American Oyster Drill (*Urosalpinx cinerea*) from an Essex estuary.

Bailey and Davies (1991) have reported the deleterious impact of TBT previously used in mariculture on dogwhelk populations in a Scottish Sea Loch. Gibbs et al (1991) have indicated that TBT-induced imposex in the dogwhelk (*Nucella lapillus*) was uniform in this species throughout its geographical range.

Harris et al (1991) simulated the release and dispersion of TBT in the Tamar Estuary, UK, and compared these simulations with field measurements. While a multitude of complicating factors meant that the absolute values of their results may be questioned, the results do provide a general indication of the order of magnitude of reductions in TBT which might be expected due to legislative actions to reduce TBT input to the marine environment. They considered that observed TBT concentrations in the estuary would be compatible with leach rates of about $1 \mu\text{g}/\text{cm}^2/\text{day}$.

A predominantly particulate component for TBT uptake in deposit feeding clams (*Scrobicularia plana*) has been demonstrated by Langston and Burt (1991). Their preliminary data indicated that clam populations could be affected at TBT concentrations in sediment of $0.3 \mu\text{g}/\text{g}$, and possibly lower. These authors also pointed out that TBT burdens in some organisms cannot be predicted from simple partitioning coefficients, and the mode of nutrition/route of uptake may result in TBT tissue concentrations significantly higher than those predicted from equilibrium studies based on dissolved TBT. A portion of the TBT accumulated by *Scrobicularia* was eliminated at extremely slow rates. Similarly persistent pools of TBT have also been described for oysters (*Crassostrea gigas*) and scallops (*Pecten maximus*). An organism's capacity for TBT bioaccumulation could therefore partly relate to the relative size of this slowly-exchanging pool. Thus, even among related groups, occupying similar habitats, there may be marked inter-specific differences in TBT bioaccumulation potential (Langston and Burt 1991).

Because of the high toxicity and the threat posed to many forms of marine life that are sensitive to TBT, in July 1987 (under the Food and Environmental Protection Act (1985), anti-fouling paints containing TBT were prohibited in the United Kingdom for use on vessels less than 25 metres, and in mariculture.

The environmental quality target (EQT) for seawater of $20\text{ng TBT}/\text{L}$ set by the UK Department of the Environment in 1985, was replaced by an environmental quality standard (EQS) of $2 \text{ng TBT}/\text{L}$ in March 1989 due to the low concentrations of TBT then known to be toxic to some organisms.

Cleary (1991) demonstrated that TBT levels could be considerably higher in the surface microlayer in comparison to the bulk of a water body. Levels of TBT up to 50 ng Sn/L were detected in UK waters in 1989. These levels compare with an EQS of 0.8 ng Sn/L (refer Table below).

Table 4.2: Lethal and sublethal toxicity threshold values for various life stages of a number of marine organisms in relation to the UK EQS for seawater of 2 ng TBT/L (equivalent to 0.8 ng Sn/L) (After Cleary 1991).

Organism	Toxicity threshold (ng Sn/L)	Biological effect
Mussel adult	94	Reduced growth
Mussel juvenile	82	Reduced growth
Mussel larvae	40	15 day LC50 value
Copepod	35	6 day 21% survival
Oyster spat	4	Compensation for hypoxia
Oyster adult	1	Gel-formation-shell-chambering
Dogwhelk	1	Induction of imposex
Mud snail	1	Induction of imposex
EQS	0.8	UK value for TBT in seawater

Bailey and Davies (1991) found that in 1988-89 that the rate of imposex development in juvenile Dogwhelks was decreasing. They concluded that the effects of the 1987 British legislation were beginning to be detectable, but that it was likely that it would be many years before populations free from imposex would be found within the loch.

Davies and Bailey (1991), in an assessment of the relative effects of large vessels, studied the impacts of oil terminal traffic on dogwhelk populations in Sullom Voe (Shetland) and Scappa Flow (Orkney). The oil terminal at Sullom Voe usually handles 700-900 oil and gas tankers each year. Scapa Flow has about a third the traffic. Unlike Sullom Voe, Scappa Flow also supports several fish farms. Dogwhelk populations at Sullom Voe were severely TBT-affected, whereas females in Scapa Flow were still able to reproduce.

Jones (1992) has undertaken research aimed at assessing the extent of TBT impact on New Zealand neogastropod species. Imposex was found in *Lepsiella scobina*, *Thais orbita*, *Haustorium haustorium*, *Taron dubius*, *Cominella adspersa*, *Cominella maculosa*, *Cominella (Josephia) glandiformis*, *Cominella (Josephia) virgata virgata*, and *Buccinulum linea linea*.

Jones (1992) found that the imposex gradient in Tauranga Harbour was much more pronounced than for the Waitemata Harbour. The first mesogastropod to be shown to exhibit imposex (*Cabestana spengleri*) was observed in Tauranga Harbour.

Jones (1992) also believed the oyster-borer (*Lepsiella scobina*), to be particularly-affected by TBT.

However, it should be noted that Nias et al (1993), in a study of imposex in *Lepsiella vinosa* from Southern Australia, found evidence to indicate that other factors, including copper, paint matrix and environmental stress, may also induce imposex.

In 1982 the Minister of the Environment in France passed an ordinance banning the use of TBT-based paints on boats less than 25 metres in length.

Alzieu (1991), in reporting on environmental problems caused by TBT in France, and associated assessment, regulations and prospects, has questioned whether the European ban on use of TBT on vessels under 25 metres in length is sufficient to protect coastal ecosystems.

In the late 1980's, Dutch coastal waters suffered massive TBT contamination, particularly in marinas with poor water circulation. TBT concentrations in Dutch marinas ranged from 120 to 4,000 ng/L (Ritsema et al 1991).

Alzieu et al (1991) reported substantial DBT (dibutyltin) and TBT (tributyltin) contamination of Spanish, French Midi, French Riviera, Monaco and Italian seas. The French ban on TBT use in 1982 very effectively reduced contamination within shellfish farming areas such as Arcachon Bay on the Atlantic Coast of France. However, Alzieu et al (1991) considered that the efficacy of the legislation did not extend to the Mediterranean coast. The most likely explanation of this was believed to be that the movement of vessels between countries in the Mediterranean is more extensive and many of the vessels berthed in French ports and marinas probably received their antifouling treatments in countries which did not then legislate against the use of TBT.

This observation endorsed the need for region-wide legislation, control measures and enforcement. The Contracting Parties to the Convention for the Protection of the Mediterranean Sea Against Pollution and its related protocols, at their 6th Ordinary meeting (Athens, 3-6 October 1989) (UNEP, 1989) agreed to adopt the following recommendations. They agreed:

- (1) *As from 01 July 1991, not to allow the use in the marine environment of preparations containing organotin compounds intended for the prevention of fouling by micro-organisms, plants and animals:*
 - (a) *On hulls of boats having an overall length (as defined by ISO Standard No. 8666) of less than 25 metres;*

- (b) *On all structures, equipment and apparatus used in mariculture. This measure should not apply to any ships owned or operated by a state party to the land-based sources (LBS) protocol and used only on government non-commercial service.*

Contracting Parties not having access to substitute products for organotin compounds by 01 July 1991 would be free to make an exception for a period not exceeding 2 years, after having so informed the Secretariat. After agreement, the Secretariat would inform the other Contracting Parties at the earliest opportunity.

- (2) *To report to the Secretariat on measures taken in accordance with this decision.*
- (3) *That a code of practice be developed in minimizing the contamination of the marine environment in the vicinity of boat-yards, dry-docks, etc., where ships are cleaned of old anti-fouling paint and subsequently repainted.*

Alzieu et al (1991) considered that once enacted, these measures should substantially reduce contamination of the Mediterranean coast with TBT.

In New Zealand the use of organotin-based antifoulants was reviewed in 1987. The problems were believed to be primarily associated with recreational boating, and it was assumed that banning the use of TBT-based paints on small craft would alleviate any adverse effects. In July, 1989, a partial ban on the sale and use of organotin-based antifoulants on craft <25 metres in length (Except of aluminium construction) was enforced.

Aluminium boats were exempted because application of the alternative antifouling agent, copper, would result in severe corrosion.

In California, TBT use was restricted to large vessels (>25 metres in length) in January 1988 (Stephenson 1991).

The Organotin Paint Control Act (OPACA) was enacted in the US in 1988. The Act contained interim and permanent TBT use restrictions as well as research and monitoring requirements. The application of TBT antifoulant was prohibited for vessels under 25 metres and the maximum average daily release rate was set at 4 ug/cm²/day. These requirements of OPACA were designed to reduce the total amount of TBT entering the marine environment, possibly by as much as 90% of the pre-OPACA levels (Wade et al 1991).

Oysters (*Crassostrea virginica*) were used by Wade et al (1991) to assess the effectiveness of this legislation in reducing TBT levels in the marine environment. *Crassostrea virginica* is considerably less sensitive to TBT than the Pacific oyster (*Crassostrea gigas*) (Hugget et al 1992).

Wade et al (1991) noted that the legislation did appear to be effective in reducing TBT levels. They also noted that while the water-column half-life of butyltins is from 4 to 16 days (and a half-life of almost two years in anaerobic sediments (Waldock et al 1990)), the environmental half-life of butyltins available to oysters at the sites which they studied appeared to be of the order of years.

de Mora et al (1989) have studied TBT in sediments from the Tamaki Estuary, New Zealand. The degradation rate for TBT in sediments exhibited first order kinetics, with a rate constant of 0.375/year. They estimated that TBT had a half-life of 1.85 years in the sediments.

Waldock et al (1990) believe that contaminated sediments may prove to be a source of TBT for several years to come. This belief is borne out by the publication of many research papers which indicate a reduction in water TBT levels, but inconclusive trend analysis results for sediment TBT levels (see, for example, Waite et al 1991).

The longevity of TBT in sediments in and around marinas was estimated by Evans and Hugget (1991) using data gathered from two tidal creeks of the Chesapeake Bay, USA. All of the nine stations sampled showed a significant annual variation superimposed upon a decreasing linear trend. These authors estimated the half-life of TBT in sediments to be around three years.

It is interesting to note the research of Suzuki et al (1992), who found that TBT-tolerant bacteria accounted for 90% of the flora in natural seawater to which TBT was added. These tolerant bacteria were all *Vibrio* species. Total counts of viable bacteria did not decrease upon storage of the TBT-treated seawater, indicating that enrichment of tolerant strains took place.

Land-based sources (LBS's) of TBT's may also be contributors to marine sediment TBT loads. Fent et al (1991) has reported that municipal wastewaters and sewage sludges contaminated with TBT provide only minimal degradation. Contrary to the situation in seawaters and freshwaters in which TBT is primarily dissolved, TBT in municipal wastewater and sewage sludge is primarily sorbed onto particulate matter.

Based on Fent et al's (1991) results, caution should therefore be exercised with respect to the assumption that antifouling washwaters may be adequately disposed of via collection and discharge to a municipal treatment works.

Sources of TBT

Commercial shipping is largely unaffected by the ban on use of TBT-based paints.

The use of TBT as an active ingredient in marine antifouling paints began in the mid-1960's and for the next decade its popularity rose as its cost-effectiveness became widely recognised by paint users. By 1980, antifouling paints accounted for 7-10% of total butyltin production (some 29,000 tons), other major uses being as PVC stabilizers (dibutyltin, about 70% of the total) and wood preservatives (TBT, 10-14%). Just how much of the organotin in these other applications eventually gets into the marine environment from industrial and domestic land-based sources is still a matter of speculation (Mee and Fowler 1991).

Human health implications of TBT in Tauranga Harbour shellfish

The Japanese Ministry of Health and Welfare has proposed an Acceptable Daily Intake (ADI) of 1,500 ng TBT/kg body weight (IMO 1989, cited in Jones 1992). A 60kg person would be permitted to ingest up to 90,000 ng TBT daily.

If the most-contaminated sentinel oysters are considered from the present Tauranga Harbour study, this would equate to the consumption (on a wet weight basis) of approximately 6.5 kg of oysters/day.

Consequently, it is considered that TBT does not presently represent a threat to human consumers of shellfish.

Its significance is in the realm of ecological effects due to the elimination of sensitive marine species from contaminated zones.

Summary

Page and Widdows (1991) have provided guidance on the approximate relationship between tissue TBT levels in mussels, and the degree of contamination/biological effects associated with this (Table 4.3).

Table 4.3: Approximate degree of TBT contamination as reflected by TBT tissue concentrations in field populations of mussels (Page and Widdows 1991).

Tissue TBT concentration (ug/g dry tissue weight)	Degree of contamination
0.05-0.5	Virtually none to low levels of TBT input: no significant effects observable in adult mussels.
0.5-2	Moderate TBT inputs.
>2	Heavy TBT inputs: significant biological effects in adult mussels that can be measured.

The reliability of analytical data for TBT in sea water and its implications for water quality criteria/standards has been discussed by Readman and Mee (1991). An interlaboratory comparison exercise indicated that there are inherent difficulties in obtaining good precision below approximately 20 ng TBT/L. As imposex and other effects seem to become manifested at levels of 1-2 ng/L, these authors believed that it would be difficult to validate the efficacy of any legislative and voluntary control methods to reduce TBT levels in coastal waters through analysis of sea waters. Readman and Mee (1991) indicated that the best avenue to pursue in the interim is the analysis of marine sediments and biota.

Transplanted shellfish have been used to monitor TBT contamination in US waters (Salazar and Salazar 1991). In the latter case, water and tissue TBT concentrations were related to growth effects in mussels.

Stephenson (1991) used transplanted Pacific Oysters (*Crassostrea gigas*) to assess TBT toxicity in 25 marinas in the US. TBT tissue concentrations ranged from 0.03 - 0.05 ug/g dry weight in uncontaminated sites to 4 ug/g TBT dry weight in oysters taken from San Diego. San Diego mussels (*Mytilus edulis*) showed lower rates of TBT bioaccumulation in comparison to these oyster results (Valkirs et al 1991).

King et al (1989) have reported on TBT levels in waters and shellfish from various parts of New Zealand. They pointed out that TBT-contaminated sediments could be remobilised by storms, currents, and dredging of marines, mooring areas and shipping channels.

Smith and McVeagh (1991) have reported on widespread organotin pollution in New Zealand waters as indicated by imposex in two species of dogwhelk. These authors measured Relative Penis Size (RPS) at various sites throughout New Zealand.

Interestingly, by far the greatest environmental impact was observed in Tauranga Harbour (Table 4.4).

It would be of interest to see comparative figures for the present day, so that the effectiveness of the 1989 partial ban on TBT-based antifoulants, introduced in New Zealand in late 1989, could be assessed.

Table 4.4: Relative Penis Size (ratio (mean female penis length)/(mean male penis length) × 100%) of dogwhelks from various New Zealand locations in 1988 (P J Smith, MAF NZ, *pers. comm.*).

LOCATION	RELATIVE PENIS SIZE
Tairua Wharf	2.6
Tairua Harbour	0.2
Ferry landing, Whitianga	10.1
Flaxmill Bay	14.7
Simpsons Beach	0.003
Buffalo Beach, Whitianga	0.7
Lonely Bay, Cooks Beach	0
Whangapoua	0
Manaroa Bay	0
Pilot Wharf, Mount Maunganui, Tauranga Harbour	72
Ferry jetty, Mount Maunganui, Tauranga Harbour	99
Rabbit Island, Mount Maunganui, Tauranga Harbour	0
Kai-iti foreshore	8.1

Stewart and de Mora (1990), in reviewing the degradation of TBT in the marine environment, noted that TBT is very stable in heavily contaminated sediments and may continue to exert toxic effects after primary anthropogenic inputs have stopped.

Stewart et al (1992) have reported on continuing TBT-contamination and imposex in various New Zealand neogastropod species.

Until TBT-based antifoulants are phased out internationally, the input of TBT into New Zealand coastal waters will continue.

Mee (1991) has sounded a warning about the possible replacement of one environmental dilemma (TBT) with another (triphenyltin, TPT), and questioned the adoption of new formulations using, for example, triazine compounds with a relatively poorly-characterised marine environmental behaviour.

4.7 MICROBIOLOGY

Viral assessment of the Tauranga District Council Wastewater Treatment Plant final effluent failed to detect human enterovirus (or *Salmonella*) in any of several effluent and adjacent shellfish sampling runs (BOPRC 1990a).

Marine bacteria in the genus *Vibrio* have emerged as serious human pathogens via consumption of raw shellfish or puncture-type wounds involving seawater. Eleven species are now recognised as clinically significant. Several effluent discharge permit-related investigations into *Vibrio parahaemolyticus* contamination of shellfish and sediments in Tauranga Harbour have indicated low *Vibrio* levels in areas with nutrient or organic matter-enriched sediments, although to date, no sampling has been undertaken at the time when extreme densities of *Vibrio* are most likely to be observed (during warm spring/summer period). The organism generally resides in sediments during the winter months but, when water temperatures rise above 15°C during the spring and summer, it spreads throughout the marine environment. *Vibrio parahaemolyticus* may then be found in both fish and shellfish.

Tauranga Harbour waters appear to be generally free of *Campylobacter* and *Yersinia* (bacteria generally associated with animal wastes), while *Clostridium perfringens* (associated with both animal and human wastes) appears to be virtually ubiquitous throughout the Northern and Southern Basins, although levels detected in shellfish to date are well within the recommended guidelines for human consumption.

Table 4.5: Microbiological contaminants measured in sentinel shellfish deployed in Tauranga Harbour (1990).

LOCATION	Enterococci (n/100g)	Faecal coliforms (n/100g)	<i>Salmonella</i> per 25g	<i>Vibrio</i> <i>parahaemolyticus</i>	<i>Clostridium</i> <i>perfringens</i>
Port	<2	1700	0	Present	Present
Waikareao Estuary	<2	800	0	Present	Present
Southern Basin	1300	700	0	Present	Present
Northern Basin	<2	<2	0	Absent	Present

4.8 SUMMARY

Metal levels in the sentinel shellfish did not show any significant location differences. Cd, Cu, Hg and Zn levels were considerably higher in the single feral oyster sample analyzed (Waikareao Estuary Replicate No. 1) than in the sentinel shellfish sets. All organic groups showed significant location differences, with the Waikareao Estuary and Port Area displaying markedly higher levels of organic contamination than the Northern or Southern Harbour locations (Table 3.2).

Polynuclear aromatic hydrocarbon levels in sentinel shellfish from the Waikareao Estuary and the Port Area were considerably higher than those in sentinel shellfish from the Southern and Northern Basin groups. The sentinel shellfish from the Northern Basin showed the lowest PAH levels, and were significantly cleaner than those sentinel shellfish from the Southern Basin site.

Waikareao Estuary sentinel shellfish displayed the highest levels of chlordane, and DDT and dieldrin levels in sentinels from this site were significantly higher than for sentinel shellfish from either the Northern or Southern Basin sites.

PCB contamination of the Waikareao Estuary was particularly elevated (relative to the remainder of the harbour), while tributyl-tin levels in sentinel shellfish from the Port Area were predictably much higher than from other locations.

Organic contamination levels in the sentinel shellfish were well below levels of concern to human consumers. The recommended action levels for chlorinated hydrocarbon residues in marine shellfish are as follows: aldrin/dieldrin, chlordane, 0.3 ug/g wet weight; DDT, DDE, TDE 5.0 ug/g wet weight; PCB's, 2.0 ug/g wet weight (US FDA 1989). The above recommendations can be re-expressed as approx. 2,250 ng/g for aldrin/dieldrin, chlordane and DDT etc, and 15,000 ng/g dry weight for PCB's. These levels considerably exceed those recorded in the present study.

APPENDICES

APPENDIX 1 (a)

Sentinel Shellfish

**Metal and organic contaminant concentrations for
each site replicate in Tauranga Harbour**

Appendix I (a) Sentinel shellfish metal and organic concentrations (expressed as wet and dry weights where appropriate) for each site replicate within Tauranga Harbour

Sample Location	Replicate Number	Percent dry weight of Sample	Percent Lipid (dry weight basis)	Metal Results (wet weights)								
				Silver (ug/g wet weight)	Arsenic (ug/g wet weight)	Cadmium (ug/g wet weight)	Chromium (ug/g wet weight)	Copper (ug/g wet weight)	Iron (ug/g wet weight)	Mercury (ug/g wet weight)	Lead (ug/g wet weight)	Zinc (ug/g wet weight)
Waikareao Estuary	1	21.56%	9.25	0.1	0.15	0.7	0.17	63	32	0.050	0.24	1020
Waikareao Estuary	2	15.30%	8.66	0.07	0.19	0.14	0.18	21	53	0.008	0.25	144
Waikareao Estuary	3	13.09%	8.67	0.08	0.11	0.19	0.06	5.3	33	0.012	0.08	58
Waikareao Estuary	4											
Waikareao Estuary	5	15.00%	5.38	0.07	0.08	0.1	0.16	15	38	0.009	0.15	121
Port Site	1	16.73%	7.58	0.06	0.15	0.22	0.07	15	41	0.007	0.16	110
Port Site	2	20.00%	7.63	0.12	0.12	0.32	0.07	11	41	0.006	0.21	112
Port Site	3	17.47%	11.49	0.09	0.13	0.19	0.08	16	35	0.007	0.14	86
Port Site	4	17.96%	7.40	0.09	0.15	0.24	0.07	12	35	0.014	0.10	91
Port Site	5	16.72%	7.23	0.07	0.19	0.18	0.07	11	39	0.017	0.15	133
Southern Harbour	1	19.50%	9.18	0.11	0.19	0.22	0.09	9.7	47	0.008	0.13	80
Southern Harbour	2	18.89%	7.39	0.06	0.13	0.15	0.06	10	43	0.012	0.13	105
Southern Harbour	3	20.20%	6.65	0.05	0.12	0.15	0.08	11	44	0.011	0.08	102
Southern Harbour	4	18.11%	6.42	0.08	0.12	0.15	0.1	9.1	40	0.009	0.16	88
Southern Harbour	5	19.20%	9.64	0.07	0.14	0.12	0.09	8.8	48	0.010	0.16	88
Northern Harbour	1	17.61%	9.78	0.08	0.13	0.28	0.08	6.9	41	0.008	0.09	59
Northern Harbour	2	19.50%	8.30	0.08	0.12	0.28	0.08	7.3	43	0.013	0.13	66
Northern Harbour	3	17.65%	11.22	0.09	0.13	0.29	0.08	6.4	40	0.007	0.15	64
Northern Harbour	4	17.63%	9.69	0.08	0.11	0.1	0.1	16	39	0.008	0.17	136
Northern Harbour	5	17.45%	10.23	0.09	0.13	0.22	0.06	6.2	40	0.008	0.12	70
Northern Harbour	6	17.91%	11.40	0.11	0.16	0.25	0.07	11	38	0.010	0.12	95

Appendix I (a) Sentinel shellfish metal and organic concentrations (expressed as wet and dry weights where appropriate) for each site replicate within Tauranga Harbour

Sample Location	Replicate Number	Percent dry weight of Sample	Percent Lipid (dry weight basis)	Metal Results (dry weights)								
				Silver (ng/g dry weight)	Arsenic (ng/g dry weight)	Cadmium (ng/g dry weight)	Chromium (ng/g dry weight)	Copper (ng/g dry weight)	Iron (ng/g dry weight)	Mercury (ng/g dry weight)	Lead (ng/g dry weight)	Zinc (ng/g dry weight)
Waikareao Estuary	1	21.56%	9.25	0.46	0.70	3.25	0.79	292.21	148.42	0.23	1.11	4730.98
Waikareao Estuary	2	15.30%	8.66	0.46	1.24	0.92	1.18	137.25	346.41	0.05	1.63	941.18
Waikareao Estuary	3	13.09%	8.67	0.61	0.84	1.45	0.46	40.49	252.10	0.09	0.61	443.09
Waikareao Estuary	4											
Waikareao Estuary	5	15.00%	5.38	0.47	0.53	0.67	1.07	86.67	253.33	0.06	1.00	806.67
Port Site	1	16.73%	7.58	0.36	0.90	1.32	0.42	89.66	245.07	0.04	0.96	657.50
Port Site	2	20.00%	7.63	0.60	0.60	1.60	0.35	55.00	205.00	0.03	1.05	560.00
Port Site	3	17.47%	11.49	0.52	0.74	1.09	0.46	91.59	200.34	0.04	0.80	492.27
Port Site	4	17.96%	7.40	0.50	0.84	1.34	0.39	66.82	194.88	0.08	0.56	506.68
Port Site	5	16.72%	7.23	0.42	1.14	1.08	0.42	65.79	233.25	0.10	0.90	795.45
Southern Harbour	1	19.50%	9.18	0.56	0.97	1.13	0.46	49.74	241.03	0.04	0.67	410.26
Southern Harbour	2	18.89%	7.39	0.32	0.69	0.79	0.32	52.94	227.63	0.06	0.69	555.85
Southern Harbour	3	20.20%	6.65	0.25	0.59	0.74	0.40	54.46	217.82	0.05	0.40	504.95
Southern Harbour	4	18.11%	6.42	0.44	0.66	0.83	0.55	50.25	220.87	0.05	0.88	485.92
Southern Harbour	5	19.20%	9.64	0.36	0.73	0.63	0.47	45.83	250.00	0.05	0.83	458.33
Northern Harbour	1	17.61%	9.78	0.45	0.74	1.59	0.45	39.18	232.82	0.05	0.51	335.04
Northern Harbour	2	19.50%	8.30	0.41	0.62	1.44	0.41	37.44	220.51	0.07	0.67	338.46
Northern Harbour	3	17.65%	11.22	0.51	0.74	1.64	0.45	36.26	226.63	0.04	0.85	362.61
Northern Harbour	4	17.63%	9.69	0.45	0.62	0.57	0.57	90.75	221.21	0.05	0.96	771.41
Northern Harbour	5	17.45%	10.23	0.52	0.74	1.26	0.34	35.53	229.23	0.05	0.69	401.15
Northern Harbour	6	17.91%	11.40	0.61	0.89	1.40	0.39	61.42	212.17	0.06	0.67	530.43

Appendix I (a) Sentinel shellfish metal and organic concentrations (expressed as wet and dry weights where appropriate) for each site replicate within Tauranga Harbour

Sample Location	Replicate Number	Percent dry weight of Sample	Percent Lipid (dry weight basis)	Organic Results (dry weights)							
				TBT-Sn (ug/g dry weight)	TBT (ug/g dry weight)	PAH (ng/g dry weight)	PCB (ng/g dry weight)	Chlordane (ng/g dry weight)	DDT (ng/g dry weight)	Dieldrin (ng/g dry weight)	Chlorophenols (ng/g dry weight)
Waikareao Estuary	1	21.56%	9.25	.	.	35.00	44.80	2.11	33.8	1.59	5.7
Waikareao Estuary	2	15.30%	8.66	0.074	0.203	32.30	38.60	10.35	40.2	2.15	6
Waikareao Estuary	3	13.09%	8.67	0.042	0.115	32.10	45.40	2.12	30.5	2.34	10.4
Waikareao Estuary	4
Waikareao Estuary	5	15.00%	5.38	0.048	0.132	32.20	33.30	1.46	24.2	2.87	6.9
Port Site	1	16.73%	7.58	0.103	0.282	50.70	20.40	1.81	18.3	1.82	6.4
Port Site	2	20.00%	7.63	0.090	0.247	23.60	13.60	1.55	16.8	1.35	5.1
Port Site	3	17.47%	11.49	0.036	0.099	56.50	14.10	2.73	48.5	1.84	6.8
Port Site	4	17.96%	7.40	0.085	0.233	24.00	17.87	0.64	19.5	1.43	6.1
Port Site	5	16.72%	7.23	0.189	0.518	43.50	31.50	2.19	35.9	1.71	6.5
Southern Harbour	1	19.50%	9.18	0.025	0.069	6.34	5.24	0.61	13.5	0.85	5.9
Southern Harbour	2	18.89%	7.39	0.002	0.005	6.39	8.50	0.99	13.1	1.12	2.4
Southern Harbour	3	20.20%	6.65	0.002	0.005	6.33	5.92	0.005	8.08	0.55	2.2
Southern Harbour	4	18.11%	6.42	0.023	0.063	5.30	5.20	0.37	10.4	0.87	1.9
Southern Harbour	5	19.20%	9.64	0.009	0.025	5.65	12.00	2.28	24.2	2.41	3.2
Northern Harbour	1	17.61%	9.78	0.002	0.005	3.69	3.81	1.07	24.21	1.01	3.5
Northern Harbour	2	19.50%	8.30	0.009	0.025	3.48	2.36	0.005	9.41	0.92	2.2
Northern Harbour	3	17.65%	11.22	0.002	0.005	2.95	3.85	0.45	13.06	1.21	3.2
Northern Harbour	4	17.63%	9.69	0.002	0.005	5.46	4.18	0.29	10.96	1.01	3
Northern Harbour	5	17.45%	10.23	0.002	0.005	2.64	6.18	1.26	16.89	1.66	2.3
Northern Harbour	6	17.91%	11.40	0.002	0.005	3.75	2.96	0.61	12.48	1.36	2.3

APPENDIX 1 (b)

Sentinel Shellfish

**Polychlorinated biphenyl congener concentrations for
each site replicate in Tauranga Harbour**

Polychlorinated biphenyls

Wai (OC3011 - OC3014)

PCB #	Concentration (ng/g dry weight)			
	1	2	3	5
15	n.d.	n.d.	n.d.	n.d.
18	n.d.	n.d.	n.d.	n.d.
31	n.d.	n.d.	n.d.	n.d.
28	n.d.	n.d.	n.d.	n.d.
52	n.d.	n.d.	n.d.	n.d.
49	n.d.	n.d.	n.d.	n.d.
44	n.d.	n.d.	n.d.	n.d.
40	n.d.	n.d.	n.d.	n.d.
121	n.d.	n.d.	n.d.	n.d.
101	5.39	5.50	6.98	4.41
86	n.d.	n.d.	n.d.	n.d.
77	n.d.	n.d.	n.d.	n.d.
151	2.36	2.20	2.49	1.92
118	2.78	n.d.	n.d.	n.d.
153	17.88	16.03	18.14	14.28
141	1.20	1.02	1.10	0.80
138	9.06	9.06	10.79	8.18
156	0.78	0.58	0.74	0.57
180	2.69	2.03	2.58	1.48
170	2.71	2.23	2.50	1.68
194	n.d.	n.d.	n.d.	n.d.
206	n.d.	n.d.	n.d.	n.d.
209	n.d.	n.d.	n.d.	n.d.
Total PCB:	44.8	38.6	45.4	33.3

North (OC3015-OC3020)

PCB #	Concentration (ng/g dry weight)					
	1	2	3	4	5	6
15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
31	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
52	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
49	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
44	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
40	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
121	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
101	0.62	0.61	0.52	1.05	1.97	0.63
86	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
77	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
151	0.47	n.d.	0.55	0.48	0.48	n.d.
118	n.d.	n.d.	n.d.	n.d.	0.44	n.d.
153	1.69	1.00	1.78	1.70	2.29	1.39
141	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
138	0.90	0.75	1.00	0.95	1.02	0.94
156	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
180	0.13	n.d.	n.d.	n.d.	n.d.	n.d.
170	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
194	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
206	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
209	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total PCB:	3.81	2.36	3.85	4.18	6.18	2.96

South (OC3021-OC3025)

PCB #	Concentration (ng/g dry weight)				
	1	2	3	4	5
15	n.d.	n.d.	n.d.	n.d.	n.d.
18	n.d.	n.d.	n.d.	n.d.	n.d.
31	n.d.	n.d.	n.d.	n.d.	n.d.
28	n.d.	n.d.	n.d.	n.d.	n.d.
52	n.d.	n.d.	n.d.	n.d.	n.d.
49	n.d.	n.d.	n.d.	n.d.	n.d.
44	n.d.	n.d.	n.d.	n.d.	n.d.
40	n.d.	n.d.	n.d.	n.d.	n.d.
121	n.d.	n.d.	n.d.	n.d.	n.d.
101	0.97	1.25	1.27	0.63	2.85
86	n.d.	n.d.	n.d.	n.d.	n.d.
77	n.d.	n.d.	n.d.	n.d.	n.d.
151	0.34	0.66	0.60	0.55	0.54
118	n.d.	n.d.	n.d.	n.d.	0.93
153	2.45	2.90	2.50	2.51	4.21
141	n.d.	n.d.	n.d.	n.d.	0.20
138	1.29	1.27	1.20	1.16	2.29
156	n.d.	n.d.	n.d.	n.d.	0.12
180	0.19	0.41	0.36	0.35	0.48
170	n.d.	n.d.	n.d.	n.d.	0.40
194	n.d.	n.d.	n.d.	n.d.	n.d.
206	n.d.	n.d.	n.d.	n.d.	n.d.
209	n.d.	n.d.	n.d.	n.d.	n.d.
Total PCB:	5.24	6.50	5.92	5.20	12.0

Port (OC3026-OC3030)

PCB #	Concentration (ng/g dry weight)				
	1	2	3	4	5
15	n.d.	n.d.	n.d.	n.d.	n.d.
18	n.d.	n.d.	n.d.	n.d.	n.d.
31	n.d.	n.d.	n.d.	n.d.	n.d.
28	n.d.	n.d.	n.d.	n.d.	n.d.
52	n.d.	n.d.	n.d.	n.d.	n.d.
49	n.d.	n.d.	n.d.	n.d.	n.d.
44	n.d.	n.d.	n.d.	n.d.	n.d.
40	n.d.	n.d.	n.d.	n.d.	n.d.
121	n.d.	n.d.	n.d.	n.d.	n.d.
101	3.50	2.06	2.66	2.49	4.07
86	n.d.	n.d.	n.d.	n.d.	n.d.
77	n.d.	n.d.	n.d.	n.d.	n.d.
151	1.30	0.62	0.77	0.85	1.54
118	1.41	1.02	1.02	1.04	2.14
153	7.86	5.62	5.41	7.31	12.85
141	0.38	0.28	0.28	0.35	0.76
138	4.03	2.99	3.01	4.07	6.79
156	0.30	0.16	0.19	0.25	0.53
180	0.65	0.44	0.34	0.66	1.66
170	0.95	0.44	0.48	0.83	1.18
194	n.d.	n.d.	n.d.	n.d.	n.d.
206	n.d.	n.d.	n.d.	n.d.	n.d.
209	n.d.	n.d.	n.d.	n.d.	n.d.
Total PCB:	20.4	13.6	14.1	17.9	31.5