Ambient concentrations of selected organochlorines in estuaries

Organochlorines Programme
Ministry for the Environment

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Organochlorines in New Zealand:
Ambient concentrations of selected organochlorines in estuaries

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Foreword

People around the world are concerned about organochlorine contaminants in the environment. Research has established that even the most remote regions of the world are affected by these persistent chemicals.

Organochlorines, as gases or attached to dust, are transported vast distances by air and ocean currents – they have been found even in polar regions. Organochlorines are stored in body fat and accumulate through the food chain. Even a low concentration of emission to the environment can contribute in the long term to significant risks to the health of animals, including birds, marine mammals and humans.

The contaminants of concern include dioxins (by-products of combustion and of some industrial processes), PCBs, and a number of chlorinated pesticides (for example, DDT and dieldrin). These chemicals have not been used in New Zealand for many years. But a number of industrial sites are contaminated, and dioxins continue to be released in small but significant quantities.

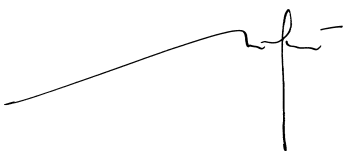
In view of the international concern, the Government decided that we needed better information on the New Zealand situation. The Ministry for the Environment was asked to establish an Organochlorines Programme to carry out research, assess the data, and to consider management issues such as clean up targets and emission control standards. As the contaminants are of high public concern, the Programme established networks for consultation and is keeping the public informed.

The fundamental research carried out under this programme has established for the first time the actual concentrations of these contaminants in the New Zealand environment – country-wide – in air, soil, rivers and estuaries. In addition, the dietary intakes of New Zealanders has been estimated through a study of organochlorine concentrations in food. The existing "body burdens" of the New Zealand population – the concentrations of organochlorines stored in fatty tissue – are also being assessed.

The publication of these New Zealand research reports marks an important contribution to international knowledge about these toxic chemicals. The comprehensive data contained in these reports is made all the more significant because of the scarcity of other data from the southern hemisphere.

The work has been peer reviewed internationally by experts and we are assured it is of the highest quality. We acknowledge the important contribution made by all those involved in the project within government and the private sector, from within New Zealand and abroad.

Finally, these reports lay a solid foundation in science for the development of policy. What message can we take from these results about the state our environment? Internationally, it appears that New Zealand could be categorised as being "moderately clean". While providing some comfort, this leaves no room for complacency. This research will assist the Government in preparing national environmental standards and guidelines for these contaminants to safeguard the health of New Zealanders and the quality of our environment.



Simon Upton
MINISTER FOR THE ENVIRONMENT

Executive summary

This study is one component of the Ministry for the Environment's Organochlorines Programme, which also includes a nation-wide survey to determine the background concentrations of organochlorines in soils, rivers, and in ambient air. This report presents data on the concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), organochlorine pesticides and chlorophenols measured in New Zealand estuarine sediments and shellfish.

A total of 26 composite sediment samples and 26 composite shellfish samples were collected from 12 estuaries throughout New Zealand. The land uses within the catchments of these estuaries range from highly urbanised to relatively remote from anthropogenic influences.

The results from this survey demonstrate that concentrations of PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols in New Zealand estuaries are low, and in most cases markedly lower than concentrations reported for estuaries in other countries.

Concentrations of PCDDs and PCDFs (including half LOD values for non-detectable congeners) were in the range 0.081 - 2.71 ng I-TEQ kg^{-1} DW for sediments, and 0.015 - 0.26 ng I-TEQ kg^{-1} WW for shellfish. Exclusion of LOD values resulted in lower TEQ concentrations, in the range 0 - 1.38 ng I-TEQ kg^{-1} DW for sediments and 0 - 0.23 ng I-TEQ kg^{-1} WW for shellfish. The higher chlorinated congeners were most abundant and most frequently detected in sediments and shellfish.

PCBs were detected more frequently in shellfish (18 samples) than in sediments (9 samples). The sum of 25 congeners was in the range 0.12 - 8.80 μg kg^{-1} DW for sediments and 0.11 - 12.9 μg kg^{-1} WW for shellfish (including half LOD values). The most frequently detected congeners in both sediments and shellfish were PCB #153 and 138. Of the non *ortho*- congeners, PCB #77 was quantified in two sediments samples and four shellfish samples. PCB #126 was only quantified in one shellfish sample.

Aldrin, α- and β-HCH were not detected in either the shellfish or sediments. The most frequently detected pesticides were: dieldrin, <0.05 - 0.38 μg kg^{-1} DW for sediment, <0.02 - 0.56 μg kg^{-1} WW for shellfish; and DDT and its degradation products, with pp'-DDE the most abundant, <0.01 - 3.29 μg kg^{-1} DW in sediments and <0.01 - 2.77 μg kg^{-1} WW in shellfish. The only location where dieldrin and DDT (and its degradation products) were not detected was Parengarenga Harbour, a site chosen for its distance from large urban areas and agricultural activity. However, lindane (γ-HCH) was quantified in both shellfish samples taken from this site. Heptachlor and heptachlor epoxide were not detected in any shellfish samples and were measured in only one sediment sample.

No tri- or tetrachlorophenol were detected in any samples. Pentachlorophenol was quantified in two sediment and two shellfish samples at concentrations close to the limits of detection. Concentrations ranged from <0.03 - 0.4 μg kg^{-1} DW in sediments and from <0.1 - 0.25 μg kg^{-1} WW in shellfish.

The contaminant concentration data sets for PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols in all samples analysed are detailed in full in Appendices D to G and in the Organochlorines Programme Environmental Survey database available from the Ministry's website (http://www.mfe.govt.nz/issues/waste/organo.htm). A summary of comparative international data

is provided in Appendices H to K. Appendix A provides information on the status of organochlorine pesticides in New Zealand. Appendices B and C contain detailed information on the sampling and analytical programmes, including the results from the analysis of field and laboratory quality control samples.

The survey has demonstrated that New Zealand's estuarine environments are relatively free of organochlorine contaminants, although concentrations in some estuaries are approaching those reported for urbanised estuaries overseas.

Acknowledgments

The success of this study has been dependent upon the involvement of many people who have contributed in various ways and at various stages of the project, from the initial study design, through the sample collection and analysis phase, to the final report writing and peer review.

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1 Introduction

In 1995, the Ministry for the Environment commenced a national Organochlorines Programme to characterise the extent of contamination of the New Zealand environment by selected organochlorine contaminants, and establish risk-based environmental acceptance criteria for these substances. The organochlorines that are the focus of the programme are:

- The polychlorinated dibenzo-p-dioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs). These are often referred to generically as 'dioxins', but throughout this report the PCDD and PCDF nomenclature is used;
- Polychlorinated biphenyls (PCBs);
- Organochlorine pesticides including DDT, aldrin, dieldrin and chlordane;
- Chlorophenols, in particular pentachlorophenol (PCP).

The development of risk-based acceptance criteria for organochlorines requires information on the background concentrations of these contaminants in the environment, in humans, and on exposure pathways. To support this process, the Organochlorines Programme has undertaken a series of detailed scientific investigations, including a major survey to determine the concentrations of PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols in environmental media. This environmental survey has involved the collection and analysis of approximately 250 samples of air, soil, river water and finfish, and estuarine sediment and shellfish.

This report presents the findings of the environmental survey to determine the background concentrations of PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols in New Zealand estuaries. Separate reports have been published on organochlorine concentrations in New Zealand soils (Buckland *et al*., 1998a), rivers (Buckland *et al*., 1998b) and in ambient air (Buckland *et al*., 1999). These data will be used in an environment risk assessment, which will also be published in a separate report.

The objectives of the estuarine study described in this report were:

1) to obtain information on the background concentrations of organochlorine contaminants in New Zealand estuarine sediments and shellfish;
2) to enable the concentration of contamination of New Zealand estuaries to be seen in an international context;
3) to provide scientific data for use in a risk-based approach to support the development and application of national environmental standards and guidelines for organochlorine contaminants.

This study was not intended to identify or characterise known environmental hot spots (such as contaminated sites), or to directly assess emissions from known point sources. The sampling strategy for this survey was therefore designed to avoid areas of known contamination considered not to be representative of New Zealand estuarine environments.

The Organochlorines Programme

The Organochlorines Programme was initiated in response to a recognition of the need to minimise industrial emissions of PCDDs and PCDFs to air and water, clean-up sites contaminated with organochlorine residues and manage the safe disposal of waste stocks of organochlorine chemicals such as the PCBs and persistent pesticides. The Organochlorines Programme is consistent with current international concerns on persistent organic pollutants (UNEP, 1997).

The Organochlorines Programme as a whole comprises the study of environmental and human concentrations of organochlorine substances; the development of an inventory of ongoing PCDD and PCDF emissions; and the estimation of the risk posed by these substances. The integration of these and other components of the Organochlorines Programme is shown in Figure 1.1. The outcomes from the overall programme will be:

- National environmental standards for PCDDs and PCDFs and where necessary environmental guidelines or standards for PCBs, organochlorine pesticides and chlorophenols;
- Identified clean-up technologies that can safely and effectively destroy organochlorine wastes;
- An integrated management strategy for PCDDs, PCDFs and other organochlorine contaminants and wastes in New Zealand;
- Identification of issues for the phase-out of organochlorines;
- Informed public input to Government decisions on the management of organochlorines in the New Zealand environment.

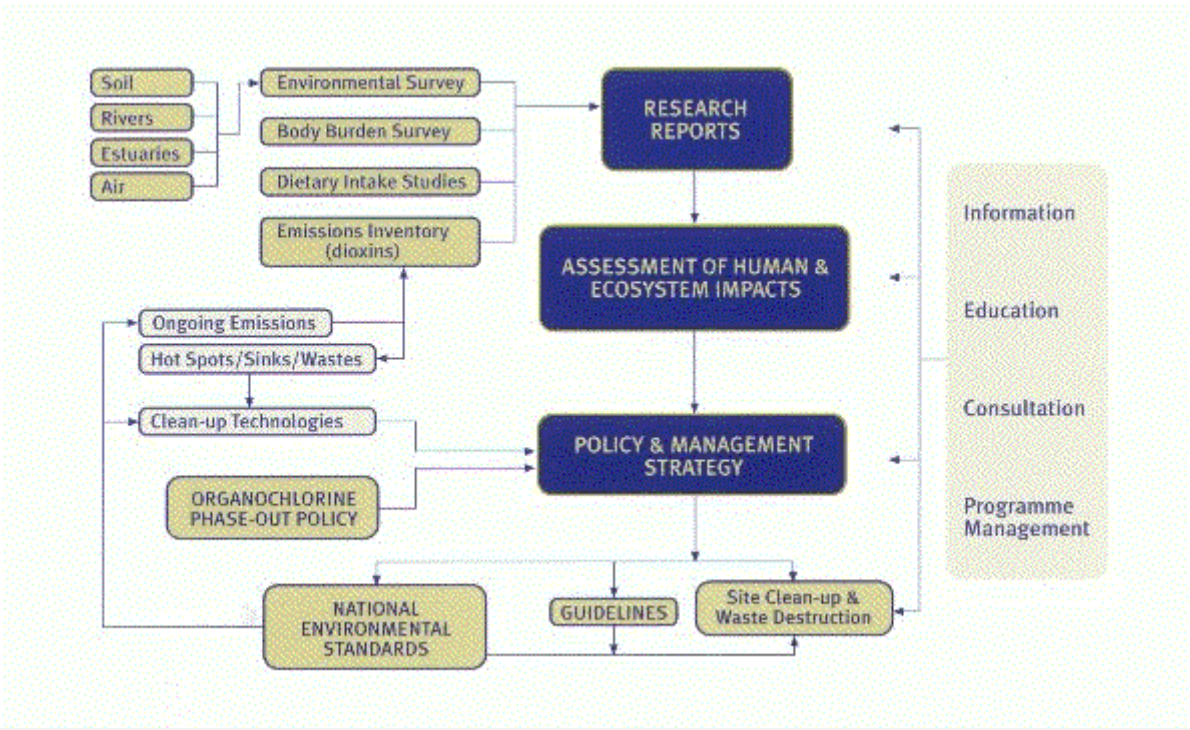
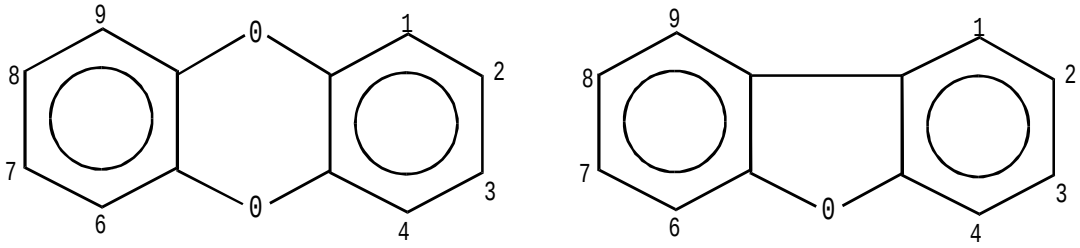


Figure 1.1 Overview of the New Zealand Organochlorines Programme

2 Background information on PCDDs, PCDFs and PCBs

2.1 PCDDs and PCDFs

The PCDDs and PCDFs are two groups of aromatic compounds having the basic structures shown in Figure 2.1.



Dibenzo-p-dioxin Dibenzofuran

Figure 2.1 Structures of dibenzo-p-dioxin and dibenzofuran

Both groups of chemicals may have up to eight chlorine atoms attached at carbon atoms 1 to 4 and 6 to 9. Each individual compound resulting from this is referred to as a congener. Each specific congener is distinguished by the number and position of chlorine atoms around the aromatic nucleus. In total, there are 75 possible PCDD congeners and 135 possible PCDF congeners. Groups of congeners with the same number of chlorine atoms are known as homologues. The number of congeners in each homologue group is shown in Table 2.1.

Toxicity

Congeners containing 1, 2 or 3 chlorine atoms are thought to be of no toxicological significance. However, the 17 congeners with chlorine atoms substituted in the 2,3,7,8-positions are thought to pose a risk to human and environmental health. Toxic responses include dermal toxicity, immunotoxicity, carcinogenicity, and adverse effects on reproduction, development and endocrine functions. Of the 17 congeners, the most toxic, and widely studied, congener is 2,3,7,8-TCDD. Increasing substitution from 4 to 8 chlorine atoms generally results in a marked decrease in potency.

Toxic equivalents

In environmental media, the PCDDs and PCDFs occur as complex mixtures of congeners. To enable a complex, multivariate dataset to be reduced to a single number, a system of toxic equivalents (TEQs) has been developed. The toxic equivalents method is based on the available toxicological and *in vitro* biological data, and knowledge of structural similarities among the PCDDs and PCDFs, to generate a set of weighting factors, each of which expresses the toxicity of a particular PCDD or PCDF congener in terms of an equivalent amount of 2,3,7,8-TCDD. Multiplication of the concentration of a PCDD or PCDF congener by this toxic equivalents factor (TEF) gives a corresponding 2,3,7,8-TCDD TEQ concentration. The toxicity of any mixture of PCDDs and PCDFs, expressed as 2,3,7,8-TCDD, is derived by summation of the individual TEQ concentrations. This is reported as the 'Total TEQ' for a mixture.

Table 2.1 Homologues and congeners of PCDDs and PCDFs

Abbreviation	Homologue name	No. of possible congeners	No. of possible 2,3,7,8-chlorinated congeners
MCDD	Monochlorodibenzo-p-dioxin	2	0
DiCDD	Dichlorodibenzo-p-dioxin	10	0
TrCDD	Trichlorodibenzo-p-dioxin	14	0
TCDD	Tetrachlorodibenzo-p-dioxin	22	1
PeCDD	Pentachlorodibenzo-p-dioxin	14	1
HxCDD	Hexachlorodibenzo-p-dioxin	10	3
HpCDD	Heptachlorodibenzo-p-dioxin	2	1
OCDD	Octachlorodibenzo-p-dioxin	1	1
MCDF	Monochlorodibenzofuran	4	0
DiCDF	Dichlorodibenzofuran	16	0
TrCDF	Trichlorodibenzofuran	28	0
TCDF	Tetrachlorodibenzofuran	38	1
PeCDF	Pentachlorodibenzofuran	28	2
HxCDF	Hexachlorodibenzofuran	16	4
HpCDF	Heptachlorodibenzofuran	4	2
OCDF	Octachlorodibenzofuran	1	1

Although a number of toxic equivalents schemes have been developed, the most widely adopted system to date is that proposed by the North Atlantic Treaty Organisation, Committee on Challenges to Modern Society (NATO/CCMS), known as the International Toxic Equivalents Factor (I-TEF) scheme (Kutz *et al*., 1990). This approach assigns a TEF to each of the 17 toxic 2,3,7,8-chlorinated PCDDs and PCDFs (Table 2.2). The remaining non 2,3,7,8-chlorinated congeners are considered biologically inactive and are assigned a TEF of zero.

The I-TEF scheme has recently been revised and expanded through the auspices of the World Health Organisation (WHO) to provide TEF values for humans and wildlife (Van den Berg *et al*., 1998). Thus WHO-TEFs are now available for humans/mammals (Table 2.2), fish and birds[1].

Sources

PCDDs and PCDFs are not produced intentionally, but are released to the environment from a variety of industrial discharges, combustion processes and as a result of their occurrence as unwanted by-products in various chlorinated chemical formulations.

Historically the manufacture and use of chlorinated aromatic chemicals have been major sources of PCDDs and PCDFs in the environment. Most notable examples include the wood preservative and biocide PCP, 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and the PCBs.

Other processes, such as the manufacture of chlorine-bleached pulp, have led to environmental contamination by PCDDs and PCDFs, as well as the trace contamination of pulp and paper products.

[1] The PCDD and PCDF TEQ data given in this report have been calculated using the I-TEFs, since most comparative literature data also use this scheme to report TEQ results. However, all PCDD and PCDF concentrations are tabulated, allowing the reader to recalculate the total TEQ concentration for any sample using the new WHO-TEF values (Van den Berg *et al*., 1998).

Table 2.2 Toxic equivalents factors for PCDDs and PCDFs

PCDD and PCDF congener	I-TEF (Kutz *et al*., 1990)	WHO-TEF (humans/mammals) (Van den Berg *et al*., 1998)
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0.5	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.001	0.0001
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.001	0.0001

Combustion processes are recognised as being another important source of PCDDs and PCDFs. Most thermal reactions which involve the burning of chlorinated organic or inorganic compounds appear to result in the formation of these substances. PCDDs and PCDFs have been detected in emissions from the incineration of various types of wastes, particularly municipal, medical and hazardous wastes, from the production of iron and steel and other metals, including scrap metal reclamation, from fossil fuel plants, domestic coal and wood fires, and automobile engines (especially when using leaded fuels) as well as accidental fires. An extensive review of PCDD and PCDF sources has been published by Fiedler *et al*., (1990), and more recently by the United States Environmental Protection Agency (US EPA, 1998).

Although natural, non-anthropogenic, combustion sources (like forest fires) have probably always been a source of PCDDs and PCDFs, the background levels associated with the pre-industrial processes (before the 1930s/1940s) are found to be negligible when compared to those resulting from more recent industrial activities (Kjeller *et al*., 1991; Beurskens *et al*., 1993; Jones and Alcock, 1996).

Tighter Government regulations, improved industrial processes and the use of modern pollution control equipment have resulted in a lowering of PCDD and PCDF emissions from known industrial sources in many countries. However, it is unlikely that a complete elimination of these contaminants will be possible due to uncontrolled releases, such as forest fires and other accidental fires.

2.2 Polychlorinated biphenyls

The PCBs were commercial products prepared industrially by the chlorination of biphenyl. The commercial preparations were graded and marketed according to their chlorine content, for example Aroclor 1232 contains 32% by weight of chlorine and Aroclor 1260 contains 60% by weight of chlorine.

PCBs comprise 209 congeners. The basic aromatic biphenyl nucleus is shown in Figure 2.2, and the distribution of PCB congeners arising from the attachment of chlorine atoms to this nucleus is given in Table 2.3.

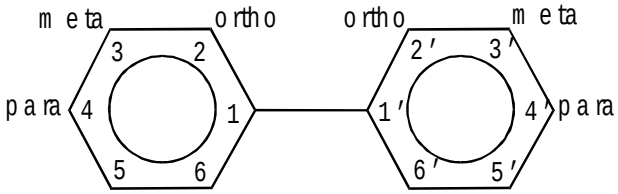


Figure 2.2 Structure of biphenyl

Table 2.3 Distribution of PCB congeners

No. of Cl substituents	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}
No. of congeners	3	12	24	42	46	42	24	12	3	1

Toxicity and toxic equivalents

As with the PCDDs and PCDFs, the biologic and toxic effects of PCBs are highly dependent both on the degree of chlorination and on the position of the chlorine atoms (i.e. whether they are *ortho*, *meta* or *para* to the phenyl-phenyl bridge at carbon-1). To account for the varying toxicity of the PCB congeners, the WHO-European Centre for Environmental Health (WHO-ECEH) and the International Programme on Chemical Safety (IPCS) have developed a suite of TEFs for 'dioxin-like' PCBs (Table 2.4) (Ahlborg *et al*., 1994). These TEFs, which are applied in a manner identical to the I-TEFs developed for the PCDDs and PCDFs, embrace those PCBs that bind to the Ah-receptor and elicit dioxin-specific biochemical and toxic responses. The WHO has recently revised and expanded these TEFs (Van den Berg *et al*., 1998) to include TEFs for humans/mammals (Table 2.4) as well as fish and birds[2].

PCBs also exhibit 'non-dioxin-like' toxicity in which the toxic effects are not mediated through the Ah-receptor (Safe and Hutzinger, 1987; Safe, 1994). These effects include cancer promotion, endocrine disruption and neuro-behavioural toxicity. Importantly, the TEF concept developed for the PCDDs and PCDFs and the 'dioxin-like' PCBs cannot be applied to 'non-dioxin-like' effects that are not Ah-receptor mediated.

[2] The PCB TEQ data given in this report have been calculated using the 1994 WHO-TEFs. However, all PCB concentrations are tabulated, allowing the reader to recalculate the total TEQ concentration for any sample using the revised WHO-TEF values (Van den Berg *et al*., 1998).

Table 2.4 Toxic equivalents factors for PCBs

Type	Congener		WHO/IPCS TEF (Ahlborg *et al.*, 1994)	WHO-TEF (humans/mammals) (Van den Berg *et al.*, 1998)
	IUPAC No.	Structure		
Non-*ortho*	PCB #81	3,4,4',5-TCB		0.0001
	PCB #77	3,3',4,4'-TCB	0.0005	0.0001
	PCB #126	3,3',4,4',5-PeCB	0.1	0.1
	PCB #169	3,3',4,4',5,5'-HxCB	0.01	0.01
Mono-*ortho*	PCB #105	2,3,3',4,4'-PeCB	0.0001	0.0001
	PCB #114	2,3,4,4',5-PeCB	0.0005	0.0005
	PCB #118	2,3',4,4',5-PeCB	0.0001	0.0001
	PCB #123	2',3,4,4',5-PeCB	0.0001	0.0001
	PCB #156	2,3,3',4,4',5-HxCB	0.0005	0.0005
	PCB #157	2,3,3',4,4',5'-HxCB	0.0005	0.0005
	PCB #167	2,3',4,4',5,5'-HxCB	0.00001	0.00001
	PCB #189	2,3,3',4,4',5,5',-HpCB	0.0001	0.0001
Di-*ortho*	PCB #170	2,2',3,3',4,4',5-HpCB	0.0001	
	PCB #180	2,2',3,4,4',5,5'-HpCB	0.00001	

Historical uses of PCBs

PCBs have been widely used in industry as heat transfer fluids, hydraulic fluids, solvent extenders, flame retardants and dielectric fluids (Waid, 1986). The unusual industrial versatility of PCBs is directly related to their chemical and physical properties which include resistance to acids and bases, compatibility with organic materials, resistance to oxidation and reduction, excellent electrical insulating properties, thermal stability and nonflammability.

The widespread use of PCBs, coupled with industrial accidents and improper disposal practices, has resulted in significant environmental contamination by these substances in many northern hemisphere countries.

3 Organochlorines in New Zealand

3.1 PCDDs and PCDFs

No rigorous estimate has ever been made of the total emissions of PCDDs and PCDFs to the New Zealand environment. However, an inventory of emissions to air, land and water is currently being undertaken as a component of the Organochlorines Programme.

Historic releases of PCDDs and PCDFs to the environment are thought to have resulted from the manufacture and use of the herbicide 2,4,5-T, the use of PCP in the timber industry and from spillages and other accidental releases of PCBs. 2,4,5-T was used in New Zealand for the control of gorse, blackberry and other woody weeds. In the 1980s there were a number of investigations into the effects of the manufacture and use of 2,4,5-T in this country, in part due to concerns relating to the presence of 2,3,7,8-TCDD as a microcontaminant of this herbicide (Coster *et al*., 1986; Brinkman *et al*., 1986; Ministry for the Environment, 1989). The manufacture of 2,4,5-T in New Zealand ceased in 1987, although some stocks remained which were likely to have been used after this date.

PCP was used in New Zealand primarily in the timber industry, but also to a relatively minor extent by the pulp and paper industry and the tanning industry, in mushroom culture and in home gardens. Its use (as sodium pentachlorophenate) in the timber industry was for the control of sapstain fungi in freshly cut timber. PCP in oil was also used in lesser amounts as a timber preservative. These historical activities, involving the use in the order of 5,000 tonnes of PCP, have resulted in the contamination of a number of sites throughout the country (Ellis, 1997, and references therein).

Two large bleach kraft pulp mills operate in the central North Island. These mills have historically used elemental chlorine in the bleach plant, although the concentrations of PCDDs and PCDFs in effluent discharges to receiving waters, and in pulp sludges, were low compared to contamination concentrations that have been reported in North America (NCASI, 1990). The use of elemental chlorine at both these mills has now been superseded by bleaching sequences based on chlorine dioxide following oxygen delignification.

There are no municipal waste incinerators in New Zealand. In the last decade, a number of smaller hospital waste incinerators have closed. However, there are still currently operating approximately 30 incinerators around the country that burn a variety of medical, pathological, quarantine and animal wastes. With the exception of a limited number of these plants that burn in excess of 500 kg of waste per hour, these are primarily small units with an average throughput of approximately 100 - 200 kg per hour.

Other incineration facilities include a small sewage sludge incinerator, wood and coal boilers, and units burning wood processing and wood manufacturing wastes. The domestic burning of wood and coal is also expected to emit PCDDs and PCDFs to the environment, along with uncontrolled and accidental fires.

PCDD and PCDF emissions will arise from a number of metallurgical plants, from cement kilns (predominantly from two major plants, including one kiln that burns waste oil as an auxiliary fuel) and from a single (small) hazardous waste incinerator that operates in New Zealand.

Leaded petrol, which has been associated with PCDD and PCDF emissions due to the use of ethylene dichloride and ethylene dibromide as scavengers for the lead in exhaust, has largely been phased out in New Zealand. Unleaded (91 octane) regular petrol was introduced in 1986, and in early 1996, premium (96 octane) petrol was changed to an unleaded formulation. A small amount of leaded fuel is still used for piston-engined aeroplanes and for specialist motor racing.

The major historical and current inputs of PCDDs and PCDFs to the New Zealand environment is given in Table 3.1.

Table 3.1 New Zealand sources of PCDDs and PCDFs

Historical inputs

Source	*PCDD/PCDF contaminant*
Agrichemicals from the use of 2,4,5-T	2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)
Timber treatment from the use of PCP	Primarily the more highly chlorinated PCDDs and PCDFs
Electricity industry from the use of PCBs	Primarily PCDFs, but also PCDDs if chlorobenzenes present
Pulp and paper (chlorine bleach process)	Primarily TCDFs
Combustion of fuels and incineration of wastes	Broad range of PCDDs and PCDFs
Motor vehicles (particularly from leaded fuels)	Broad range of PCDDs and PCDFs

Current inputs include

- Waste incineration, including medical and hazardous waste;
- Metallurgical industries, including metal smelting, refining and recycling;
- Industrial and domestic coal and wood combustion;
- Exhaust emissions from vehicles running on diesel and unleaded petrol;
- Controlled burn-offs;
- Uncontrolled and accidental fires;
- Sewage wastes;
- Ongoing releases from reservoirs, including sludge ponds and contaminated sites.

3.2 Polychlorinated biphenyls

Internationally, large-scale production of PCBs commenced in the 1930s for use in a variety of industrial applications. PCBs were never manufactured in New Zealand, but have been imported and used extensively in the electricity industry as insulating fluids or resins in transformers and capacitors. PCBs were also used in smaller quantities as heat transfer fluids, plasticisers, printing inks, flame retardants, paint additives, sealing liquids and immersion oils.

In March 1986, the New Zealand Customs Department placed a prohibition on importing PCBs, and later that year regulations to control the importation of PCBs were promulgated as an amendment to the Toxic Substances Regulations 1983. In 1988, a further amendment to the Toxic Substances Regulations 1983 prohibited the use and storage of PCBs with effect from 1 January 1994. Following two extensions, this regulation came into effect on 1 August 1995. A summary of the legislative status of PCBs in New Zealand is given in Table A1 (Appendix A).

Information relating to the quantity of PCBs imported into New Zealand is extremely limited, although some estimates have been made (OECD, 1987; Ministry for the Environment, 1988). Whilst the current holdings of PCBs are uncertain, more accurate assessments have been made of the quantity of PCBs that has been shipped overseas for destruction. These estimates put the

quantity of PCBs (including PCB contaminated material) exported from New Zealand since 1987 at approximately 1300 - 1600 tonnes (Ministry of Health, 1998).

3.3 Organochlorine pesticides

From the mid 1940s until the 1970s persistent organochlorine pesticides, including DDT, dieldrin and lindane, were used heavily in New Zealand. Although few records were kept of the volumes imported into the country, the most substantial quantities are likely to have been imported during the 1950s and 1960s. The main areas of use were agriculture, horticulture, timber treatment and public health (Table 3.2). Smaller amounts were also used for amenity purposes and in households.

Table 3.2 Summary of the historic usage of persistent organochlorine pesticides in New Zealand

Pesticide	Application
DDT	Used as a pasture insecticide to control grass grub (*Costelytra zealandia*) and porina (*Wiseana* sp.) caterpillars. Frequently mixed with fertiliser or lime and applied particularly to agriculture pastures, as well as lawns, market gardens and parks.
Lindane (γ-HCH)	Used as an insecticide in agriculture for the control of lice on cattle, ectoparasites (lice, keds and blowflies) in sheep and grass grub in pasture. Also used for insect control on vegetables and in orchards. Household use: flyspray, flea control, and carpet moth. Commercial hexachlorocyclohexane (HCH) was not officially used in New Zealand, although many dip sites show evidence of the use of crude HCH.
Aldrin and Dieldrin	Introduced in 1954 for use as stock remedies in sheep sprays or dips for controlling sheep ectoparasites. Aldrin was used to control horticultural pests such as wireworm, soldier fly and blackvine weevil, and in limited quantities to control household spiders. Dieldrin was used for controlling carrot rust fly, crickets and armyworm and was also used for timber preservation (mostly in plywood glues) and to mothproof carpets.
Chlordane	Broad spectrum agricultural insecticide, also used in the timber industry as a treatment against termites and borer, and as an insecticide in glues used for the manufacture of plywood, finger jointed and laminated timber.
Hexachlorobenzene (HCB)	Used experimentally between 1970 and 1972 as a seed dressing fungicide for cereal grain.
Heptachlor, Endrin and Toxaphene	Only small amounts of these pesticides were ever used in New Zealand. [Endrin and toxaphene were not included in the New Zealand survey].
PCP	In the order of 5,000 tonnes of PCP is estimated to have been used in the New Zealand timber industry over a 35 to 40 year period as an antisapstain (fungicidal) treatment for freshly cut timber (mainly *Pinus radiata*). Its use in the timber industry ceased in 1988. PCP was also used to a relatively minor extent by the pulp and paper industry and the tanning industry, in mushroom culture in home gardens and on roofs to control moss and algae.

The use of pesticides in New Zealand was not subject to compulsory regulatory control until the Agricultural Chemicals Act 1959 established the Agricultural Chemicals Board. The use of persistent organochlorine pesticides was then progressively restricted by a succession of legislation, so that, by the mid 1970s their use had effectively ceased in agriculture and horticulture. All persistent organochlorine pesticides except PCP were formally deregistered[3] by the Pesticides Board in 1989, and PCP was deregistered in 1991.

[3] Importation, manufacture or sale prohibited, though existing stocks can be used.

A chronology of persistent organochlorine pesticides in New Zealand and a summary of relevant legislation are given in Table A2 (Appendix A).

3.4 Global transportation of organochlorines

Organochlorine emissions or use in other countries, and their global transportation, represent an additional and ongoing source of these contaminants to the New Zealand environment. Considerable research has taken place in the northern hemisphere on the transboundary transport and global redistribution of contaminants. Studies have also investigated the transport in air and water of contaminants from the northern to the southern hemisphere. These phenomena are particularly relevant to the transportation of organochlorines and their deposition in New Zealand. However, the significance of these inputs relative to 'local' sources of organochlorines is difficult to assess and quantify.

4 Project design

This study was designed to determine the concentration of selected organochlorine contaminants in New Zealand estuarine sediments and biota.

4.1 Sampling locations

Twelve estuaries were chosen for this study (Figure 4.1a and b, and Table 4.1). Further details of the locations are provided in Table B1 (Appendix B). They include estuaries with no known point source discharge within the catchment area and estuaries which receive a variety of inputs including: industrial discharges; sewage; and surface run-off from industrial, urban and agricultural areas. Major regional estuaries and small sub-estuaries were included.

Sampling sites were chosen, wherever possible, in areas of deposition where sediments accumulate from upstream catchment sources and as a result of transport processes within the estuary.

Deposition zones are usually sheltered, muddy estuaries where the wind fetches are small and the currents are low. For an assessment of contaminants in estuarine ecosystems, they have the following advantages:

- Sediments are fine-textured, and therefore more likely to bind organochlorine contaminants than coarser sediments.
- Sediments are likely to be recently deposited.
- There are very steep concentration gradients. Away from point source outlets (often only approximately 10 metres), surface sediments are well mixed because of wavelet action and because the depositional environment changes with tidal movements.

4.2 Sample collection

4.2.1 Sediments

For all estuaries, up to three composite sediment samples were collected, depending upon the size and nature of each particular estuary. Each composite consisted of samples taken from five 'sampling stations' randomly selected within a defined (1 - 2 km^2) region of the estuary. Each sampling station encompassed an area of approximately 25 m^2 based on a 5 m x 5 m grid.

From within each station, five sediment cores were randomly collected and composited together. Each sample for chemical analysis therefore consisted of 25 individual sediment cores taken to a depth of 5 cm. Cores were placed in precleaned, wide-mouth glass sample jars. Excess water was decanted off from the top of the jar as the sediment settled.

4.2.2 Shellfish

Shellfish were collected to provide some indication of the extent of bioaccumulation of organochlorine contaminants within the estuarine ecosystem. The species chosen was the bottom-dwelling filter feeder, New Zealand cockle (*Austrovenus stutchburyi*). Where no cockles were found at or near a sampling station, Pacific oysters (*Crassostrea gigas*) were collected. The latter

species is also a filter feeder but attaches to hard substrates. It therefore occupies a different position in the water column and is subject to a different exposure regime than the cockle.

Table 4.1 Location and description of estuaries, and number of samples collected

Region	Estuary	Area (km^2)	Composite samples collected		Discharges and industries within catchment
			Shellfish[a]	Sediment	
Northland	Parengarenga Harbour	62.5	2 x cockles	2	No point source discharges
	Whangarei Harbour	65	2 x oysters	2	Stormwater and sewage from Whangarei (pop. 45,892)[b] and Portland industrial area; cement and fertiliser manufacture; oil refineries; general port activities
Auckland	Manukau Harbour	344	3 x cockles	3	Sewage and stormwater from Auckland (pop. 991,796)[b]; industrial wastes; agricultural runoff
	Hellyers Creek, Waitemata Harbour	1	1 x cockles 1 x oysters	2	Urban stormwater
Waikato	Kawhia Harbour	67	2 x oysters	2	No point source discharges; agricultural runoff
Bay of Plenty	Tauranga Harbour	200	3 x cockles	3	Stormwater (and in the past, sewage) from Tauranga (pop. 82,287)[b] and stormwater from Mt Maunganui (pop. 13,707)[b]; timber processing; fertiliser manufacture; agricultural runoff
Marlborough	Wairau Estuary		2 x cockles	2	Agricultural runoff
Tasman	Whanganui Inlet	25	2 x cockles	2	Kahurangi National Park
	Moutere Inlet	7.1	2 x cockles	2	Stormwater from Motueka (pop. 7,158)[b]; fish processing factory; sawdust dumps; agricultural runoff
Canterbury	Avon-Heathcote Estuary	8	2 x cockles	2	Stormwater and sewage from Christchurch (pop. 325,250)[b]
Otago	Otago Harbour	46	2 x cockles	2	Stormwater and sewage from Dunedin (pop. 110,801)[b]; fertiliser manufacturer; agricultural runoff
Southland	New River Estuary	35	2 x cockles	2	Stormwater and sewage from Invercargill (pop. 49,403)[b]; agricultural runoff

[a] Cockle = *Austrovenus stutchburyi*; Oyster = *Crassostrea gigas*.
[b] Population data taken from the 1996 Census of Population and Dwellings (Statistics New Zealand).

After taking the sediment samples, each sampling station was excavated to obtain sufficient shellfish for chemical analysis. The shellfish taken from each of the five sampling stations were composited prior to analysis.

4.3 Sample analysis

All sediment and shellfish samples were analysed for the following organochlorine contaminants:

PCDDs and PCDFs All 2,3,7,8-chlorinated congeners were determined congener specifically. Total concentrations for non 2,3,7,8-PCDDs and PCDFs for each homologue group were determined. Total TEQs were calculated, both excluding limit of detection (LOD) values and including half LOD values, using the I-TEFs (Table 2.2).

PCBs. 25 PCB congeners[4] were determined, (PCB #77, #126, #169, #28 + #31, #52, #101, #99, #123, #118, #114, #105, #153, #138, #167, #156, #157, #187, #183, #180, #170, #189, #202, #194, and #206). PCB TEQs were calculated, both excluding LOD values and including half LOD values, using the 1994 WHO-TEFs (Table 2.4).

Pesticides. Hexachlorocyclohexanes (α-, β- and γ-HCH), hexachlorobenzene (HCB), aldrin, dieldrin, heptachlor, chlordanes (α- and γ-isomers), op'-DDT and pp'-DDT were determined, along with the pesticide degradation products, heptachlor epoxide, pp'-DDE and pp'-TDE (also known as pp'-DDD).

Chlorophenols. 2,4,6-trichlorophenol (TCP), 2,3,5-TCP, 2,4,5-TCP, 2,3,6-TCP, 2,3,4-TCP, 2,3,5,6-tetrachlorophenol (TeCP), 2,3,4,6-TeCP, 2,3,4,5-TeCP and PCP were determined.

Analysis was undertaken on freeze-dried shellfish and air dried sediment. Quantitation for PCDDs, PCDFs, PCBs and organochlorine pesticides was by ^{13}C isotope dilution using capillary gas chromatography-high resolution mass spectrometry. Data reported are corrected for recovery of ^{13}C surrogate standards. Chlorophenols were analysed on field moist sediment, and quantified using capillary gas chromatography with electron capture detection.

Full details of the sample preparation and analytical procedures are given in Appendix C.

[4] PCB numbering by Ballschmiter and Zell (1980).

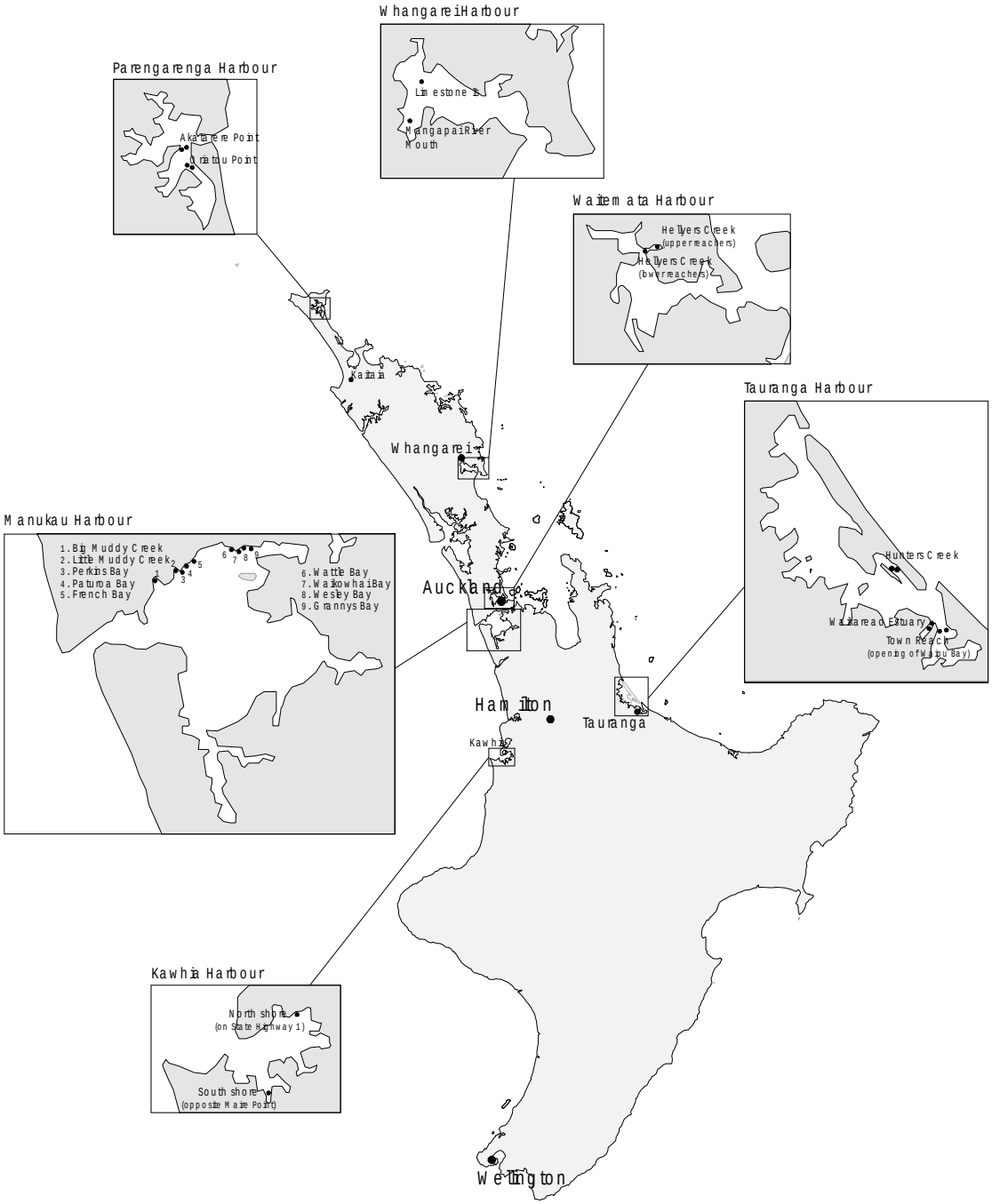


Figure 4.1a North Island sampling sites

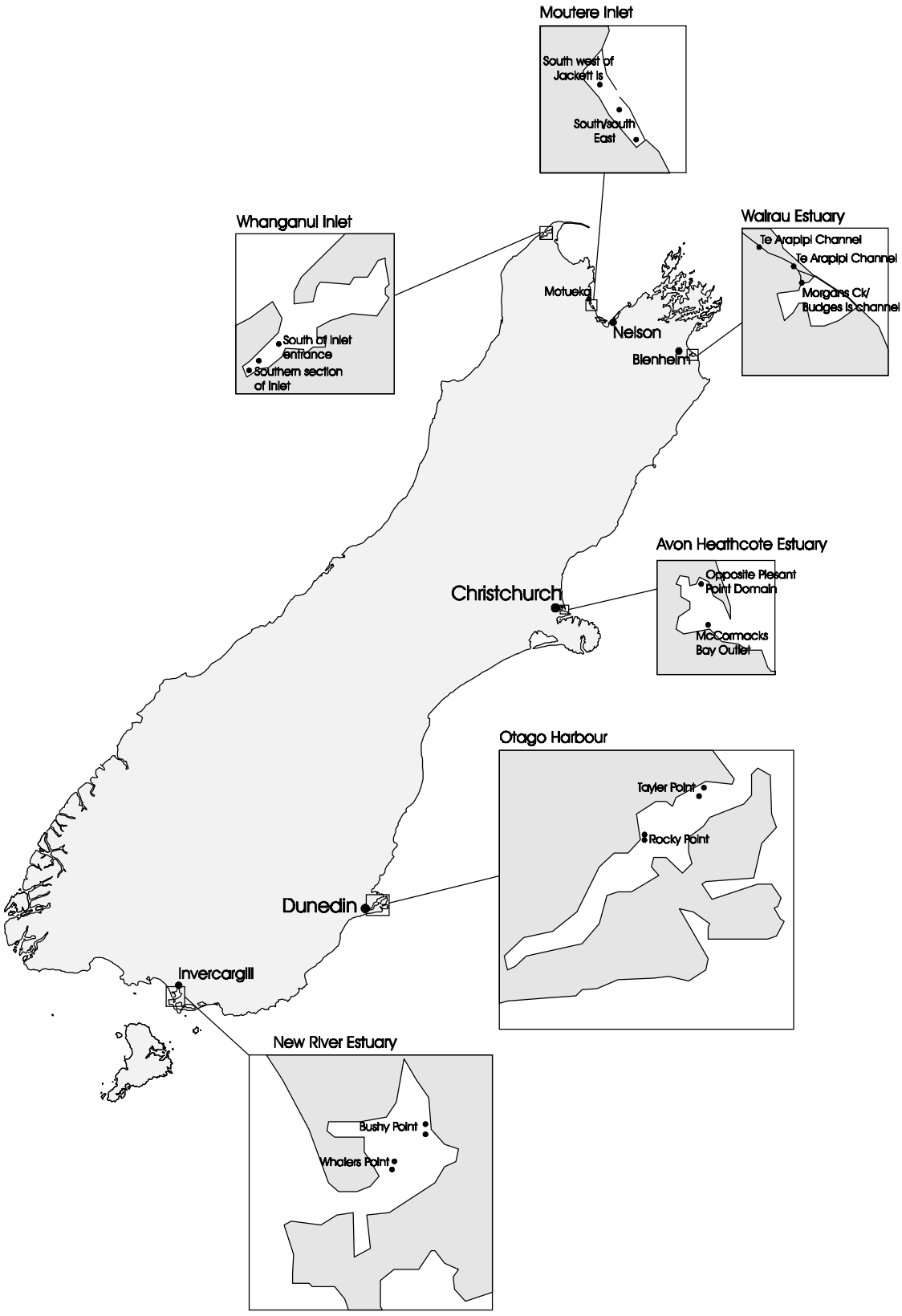


Figure 4.1b South Island sampling sites

5 Organochlorine concentrations in New Zealand estuaries

A summary of concentration data for PCDDs, PCDFs, PCBs and organochlorine pesticides (or their degradation products) determined in estuarine sediments and shellfish is provided in Table 5.1. Sites where contaminants were measured in at least one sample are indicated in Table 5.2.

Table 5.1 Concentrations of PCDDs, PCDFs, organochlorine pesticides and PCP in New Zealand estuarine sediments and shellfish

	Sediment (DW, n=26)			Shellfish (WW, n=26)		
	Min.	**Max.**	**Median**	**Min.**	**Max.**	**Median**
PCDDs and PCDFs						
Sum of PCDD/Fs (ng kg^{-1})						
Including half LOD values	2.50	722	30.8	0.21	71.5	3.20
Excluding LOD values	0	714	28.0	0	70.8	2.90
Total I-TEQ (ng kg^{-1})						
Including half LOD values	0.081	2.71	0.28	0.015	0.26	0.032
Excluding LOD values	0	1.38	0.044	0	0.23	0.0031
PCBs						
Sum of PCB congeners (μg kg^{-1})						
Including half LOD values	0.12	8.80	0.16	0.11	12.9	0.18
Excluding LOD values	0	8.79	0	0	12.8	0.082
Total TEQ (ng kg^{-1})						
Including half LOD values	0.065	0.62	0.16	0.065	0.60	0.065
Excluding LOD values	0	0.31	0	0	0.36	0
Pesticides (μg kg^{-1})						
α-HCH	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01
β-HCH	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
γ-HCH (Lindane)	<0.01	0.046	<0.02	<0.01	0.046	0.012
HCB	<0.01	0.83	<0.02	<0.01	0.016	<0.01
Aldrin	<0.01	<0.03	<0.01	<0.01	<0.01	<0.01
Dieldrin	<0.05	0.38	0.15	<0.02	0.56	0.078
Heptachlor	<0.01	0.018	<0.01	<0.01	<0.01	<0.01
Heptachlor epoxide	<0.01	<0.06	<0.02	<0.01	<0.01	<0.01
α-Chlordane	<0.02	0.098	<0.02	<0.01	0.18	<0.01
γ-Chlordane	<0.02	0.089	<0.03	<0.01	0.14	<0.01
pp'-DDE	<0.01	3.29	0.11	<0.01	2.77	0.21
pp'-TDE	<0.01	1.59	0.075	<0.01	1.46	0.073
op'-DDT	<0.01	0.062	<0.01	<0.01	0.032	<0.01
pp'-DDT	<0.01	0.43	0.031	<0.01	0.11	<0.02
Chlorophenols (μg kg^{-1})						
Pentachlorophenol[a]	<0.03	0.4	<0.03	<0.1	0.25	<0.2

[a] PCP was the only chlorophenol measured in any sample.

Concentrations of PCDDs and PCDFs (including half LOD values for non-detectable congeners) were in the range 0.081 - 2.71 ng I-TEQ kg^{-1} DW for sediments, and 0.015 - 0.26 ng I-TEQ kg^{-1} WW for shellfish. Exclusion of LOD values resulted in lower TEQ concentrations, in the range 0 - 1.38 ng I-TEQ kg^{-1} DW for sediments and 0 - 0.23 ng I-TEQ kg^{-1} WW for shellfish.

The sum of PCDD and PCDF concentrations were in the range 2.50 - 722 ng kg^{-1} DW for sediments and 0.21 - 71.5 ng kg^{-1} for shellfish (including half LOD values). The more highly chlorinated congeners were most abundant and most frequently detected in both sediments and shellfish.

Table 5.2 Sites where organochlorine contaminants were quantified in at least one sample

Estuary	PCDD/F	PCB	γ-HCH	HCB	Dieldrin	Heptachlor	α-CHL	γ-CHL	pp DDE	op TDE	op DDT	pp DDT	PCP
Parengarenga Harbour	●		☆										
Whangarei Harbour	✪	✪	●	●	✪				✪	✪	●	✪	
Manukau Harbour	✪	✪	✪	✪	✪		☆	☆	✪	✪		●	☆
Hellyers Creek	✪	✪	✪	✪	✪	●	✪	✪	✪	✪	✪	✪	●
Kawhia Harbour	✪	☆			☆				✪	✪		✪	
Tauranga Harbour	✪	✪	☆	●	✪				✪	✪	●	●	
Wairau Estuary	☆		☆		☆				✪	☆			●
Whanganui Inlet	☆		☆		☆				✪	●		●	
Moutere Inlet	✪				✪				✪	✪	●	✪	
Avon-Heathcote Estuary	✪	✪		☆	✪		☆	☆	✪	✪	●	✪	☆
Otago Harbour	●	☆		☆	☆		☆	☆	☆	☆			
New River Estuary	✪	☆	☆	☆	✪		☆	☆	✪	✪	☆	✪	

☆ Shellfish only; ● Sediment only; ✪ Both shellfish and sediment.

PCBs were detected more frequently in shellfish (18 samples) than in sediments (9 samples). The sum of 25 congeners was in the range 0.12 - 8.80 μg kg^{-1} DW for sediments and 0.11 - 12.9 μg kg^{-1} WW for shellfish (including half LOD values). The most frequently detected congeners in both sediments and shellfish were PCB #153 and #138. Of the non *ortho*- congeners, PCB #77 was detected in two sediment samples and four shellfish samples. PCB #126 was only detected in one shellfish sample.

The most frequently detected pesticides were: dieldrin and DDT and its degradation products with pp'-DDE the most abundant. Dieldrin concentrations were, <0.05 - 0.38 μg kg^{-1} DW for sediment, <0.02 - 0.56 μg kg^{-1} WW for shellfish; and pp'-DDE concentrations were <0.01 - 3.29 μg kg^{-1} DW in sediments and <0.01 - 2.77 μg kg^{-1} WW in shellfish. The only location where dieldrin and DDT (and its degradation products) were not detected was Parengarenga Harbour, a site chosen for its distance from large urban areas and agricultural activity. However, lindane (γ-HCH) was measured in both shellfish samples taken from this site. Heptachlor and heptachlor epoxide were not measured in any shellfish samples and were measured in only one sediment sample. Aldrin, α- and β-HCH were not detected in either shellfish or sediments.

No tri- or tetrachlorophenols were detected in any samples. Pentachlorophenol was detected in two sediment and two shellfish samples. Concentrations ranged from <0.03 - 0.4 μg kg^{-1} DW in sediments and from <0.1 - 0.25 μg kg^{-1} WW in shellfish.

The survey has demonstrated that New Zealand's estuarine environments are relatively free of organochlorine contaminants, although some concentrations in estuaries are approaching those reported for highly urbanised estuaries overseas.

Contaminant concentration data

A Microsoft Access database holding all analytical results and relevant associated sampling information on this environmental survey and a user's manual (Microsoft Word 6) detailing the structure and operational (data search and processing) aspects of this database are available from the Ministry for the Environment's web site (http://www.mfe.govt.nz/issues/waste/organo.htm).

The Organochlorines Programme Environmental Survey database contains the following information:

- Concentration data for PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols determined on each composite sample;
- Concentration data for PCDDs, PCDFs, and organochlorine pesticides in QC splits of the composite samples analysed by a second independent cross-check laboratory;
- Results of all laboratory quality control samples, including replicate analyses, matrix spikes and laboratory blanks;
- Surrogate standard recoveries for all samples and laboratory quality control samples analysed;
- Results of analyses for moisture and lipid contents of shellfish tissue samples;
- Biometric data for shellfish (length, width);
- Grain size and total organic carbon data for sediments;
- Field sampling parameters, including grid references of sampling sites.

5.1 Shellfish

Species with different feeding modes and habitats may show different patterns of contaminant accumulation (Hickey *et al*., 1995; Hunter *et al*., 1995). Season, reproductive status, age and condition also affect residue concentrations (Granby and Spliit, 1995). For this reason sampling should be performed at the same time of year and should collect similar-sized animals from similar habitats. However, due to difficulties encountered during the current programme, sampling was undertaken in May (autumn) at ten estuaries and in November (spring) at the Otago Harbour and New River Estuary.

Variability among individuals and species (including within-species, between-seasons variability) can present problems when interpreting data, but this can be overcome by expressing concentrations on a lipid basis (Randall *et al.*, 1991; NAS, 1980). Because two different species were collected in different seasons in this study contaminant data have been lipid-normalised for the purpose of comparing samples. Shellfish biometric data and lipid content are given in Table B2 (Appendix B).

5.2 Sediment

The organic content of sediments is a strong determinant of lipophilic contaminant concentrations. Therefore, sediment contaminant data were normalised to total organic carbon to reduce the variability between samples due to this parameter, which ranged from 0.11 - 1.87%. Clay content

also varied widely (0 - 38%) but normalisation to total organic carbon was considered a suitable surrogate for this parameter also. Sediment texture and total organic carbon data are reported in Table B3 (Appendix B).

Fine particulate matter and particle-bound contaminants are preferentially transported within estuaries to areas of deposition. The absence of fine-grained particles in some of the locations sampled may therefore have affected the concentrations of contaminants measured at these sites. For example, in the Avon-Heathcote estuary, PCBs were measured at the site with 79% sand (Pleasant Point), but were not quantified at the other site with 97% sand (McCormack's Bay outlet).

In their study of Liverpool Bay, England, Camacho-Ibar and McEvoy (1996) found that concentrations of PCBs were significantly correlated with both the amount of fine particles and with the organic content of the sediments. Piérard *et al.* (1996) also found that PCBs were preferentially associated with fine-grained sediment and organic material. They found a specific association of less highly chlorinated congeners with the sand-silt fraction and of more highly chlorinated congeners with the clay fraction.

In the current study the geographic variability between sites, together with the high frequency of non-detected compounds, means that it is not possible to draw any conclusions as to the association of organochlorines with particular sediment fractions.

5.3 Data quality

The organochlorine concentration data determined in the current study are supported by comprehensive field and laboratory quality control (QC) data. These QC data are included in the relevant appendices to this report and the Organochlorines Programme Environmental Survey database.

Blind duplicate samples were field collected as a check on the laboratory performance. Laboratory QC also involved ongoing monitoring for laboratory contamination, together with sample replicates, matrix spikes and split cross-check analyses. Strict QC criteria were established for the identification and quantification of analytes (Appendix C). These included criteria with respect to analyte signal to noise ratios, chlorine cluster ratios and laboratory blank contamination.

Recoveries of the ^{13}C surrogate standards from the PCDD and PCDF, PCB and organochlorine pesticide analyses were monitored for all samples. Generally excellent ^{13}C recoveries were obtained that were well within the 25-150% criteria established for analyte quantification. Mean ^{13}C recoveries for each sample type are reported in Appendices D to F. ^{13}C recoveries for individual samples are reported in the Organochlorines Programme Environmental Survey database.

Analysis of blind duplicates was undertaken on three sediment samples and three shellfish samples. Split primary samples were also prepared and analysed by an independent cross-check laboratory. The results of the blind duplicate and split cross-check analyses (Appendices D to G) were generally in excellent agreement, particularly given the low concentrations of organochlorine contaminants found in the New Zealand samples.

Comparative international data

To assist in the interpretation of the organochlorine concentration data found in the current study, a comparison has been made with international shellfish and sediment data published in the literature. In undertaking this comparison, care has been taken to select studies that:

- Are as comparable as possible to the current study;
- Provided sufficient experimental information to demonstrate data quality.

The current study focused on the determination of organochlorine concentrations in New Zealand's environment, which is relatively unimpacted compared to the northern hemisphere. Therefore, overseas studies aimed at determining contaminant concentrations in similar situations are the main focus of the comparative data and overseas data from heavily impacted environments are not considered. Some studies were included which presented data for 'reference' sites. However, some of these 'reference' sites would be considered as impacted in New Zealand and so a range of studies was chosen to reflect global background concentrations of contamination.

A compounding factor in reporting data for PCDDs, PCDFs and PCBs is the inconsistency in the treatment of non-detectable congeners for the calculation of TEQ concentrations. Some studies derive TEQ data on the assumption that non detected congeners were present at half the LOD, while others assume they were present at the concentration of detection, and still others assumed a non-detection equated to a concentration of zero. Where possible this information, and the specific TEF scheme used are tabulated with the comparative data in Appendix H and I.

Recognising these issues, a comparison with international data remains useful in order to provide a benchmark for placing the concentrations of organochlorines observed in estuarine environments in the current study into perspective.

Compared to air, freshwater and soil, there is a large volume of available PCB and organochlorine pesticide residue data for shellfish, collected primarily for environmental monitoring reasons. In addition there is also data collected for food safety purposes.

Picer and Picer (1994) highlighted the fact that, as residue data are non-Gaussian, standard parametric methods of data analysis are inappropriate. This has been recognised in compiling the tables of comparative data where ranges have been quoted. While median values would be desirable they can seldom be extracted from the information available.

6 PCDDs and PCDFs

6.1 New Zealand data

Detectable concentrations of PCDDs and PCDFs were observed in all estuaries, either in the sediment and/or shellfish, but not necessarily at all sites within an estuary (Table 6.1). Analytical limits of detection for non-quantified congeners (excluding OCDD) were typically in the range 0.1 - 0.6 ng kg^{-1} DW for sediments and 0.01 - 0.04 ng kg^{-1} WW for shellfish. The LODs for one sediment sample, Tayler Point (Otago Harbour), were high in comparison, ranging from 0.5 - 4 ng kg^{-1} DW.

Table 6.1 Concentrations of PCDDs and PCDFs (ng I-TEQ kg^{-1}) in sediments and shellfish (calculated including half LOD values)[a]

Location	Sediment		Shellfish	
	DW	TOC	DW	Lipid weight
Parengarenga, AP	0.15	79.0	0.26	3.48
Parengarenga, OP	0.15[b]	93.8[b]	0.30	4.12
Whangarei, MR	0.24	24.5	0.52	3.57
Whangarei, LI	0.32	27.1	0.71	6.63
Manukau, GB	0.94	130	1.24	13.0
Manukau, BM	0.21	52.5	0.59	7.01
Manukau, FB	0.54	80.6	0.32	4.25
Hellyers, upper	2.71	145	3.17	28.9
Hellyers, lower	1.47	155	1.98	20.7
Kawhia, NS	0.23	30.3	0.61	6.38
Kawhia, SS	0.32	47.1	0.51	4.91
Tauranga, HC	1.38	511	0.51	6.54
Tauranga, TR	0.32	160	0.39	4.78
Tauranga, WE	1.24	200	1.64	19.4
Wairau, AC	0.15	79.0	0.16	2.21
Wairau, MC	0.16	34.8	0.34	3.92
Whanganui, SS	0.16	13.3	0.41	8.13
Whanganui, SI	0.19	13.2	0.37	5.65
Moutere, SE	0.37	50.7	0.53	9.09
Moutere, SW	0.42	54.6	0.28	4.63
Avon-Heathcote, MC	0.16	88.9	0.18	2.05
Avon-Heathcote, PP	0.73	197	0.60	6.06
Otago, RP	0.081	54	0.17	1.77
Otago, TP	0.77[c]	700[C]	0.22	3.04
New River, BP	0.13	56.5	0.37	2.98
New River, WB	0.096	60	0.29	2.62

[a] Shaded areas indicate TEQ concentrations derived wholly from half LOD values.
[b] Non-2,3,7,8-TCDF and non 2,3,7,8-PeCDF were measured in this sample.
[c] Sample with high LOD relative to other samples.

The Hunters Creek site, Tauranga Harbour, had the greatest sediment concentration of PCDDs and PCDFs (on an organic carbon basis), measured as either the sum or total I-TEQ.

Surprisingly, at one of the two most remote sites, Parengarenga Harbour, non 2,3,7,8-TCDF and non 2,3,7,8-PeCDF were detected in sediments at concentrations of 2.05 and 1.59 ng kg^{-1} DW. This could possibly be a result of global transport or forest fires. However, there were several other sites, closer to human activities, where no PCDDs or PCDFs were measured in the sediments: Wairau Estuary (both sites), Avon-Heathcote (one site). In general, PCDDs were detected more frequently and were more abundant in sediments than PCDFs.

In shellfish, the sum of PCDDs and PCDFs ranged from 46.0 - 8220 ng kg^{-1} lipid, including half LOD values for non-quantified congeners. Highest concentrations were measured in cockles from the lower reaches of Hellyers Creek. This sample had an unusually high concentration of OCDD, comprising 86% of the congener sum, in contrast to 50 - 60% of the congener sum for other samples. The sediment OCDD concentrations were similar to those from the upper reaches of Hellyers Creek. It is possible that the differences in tissue concentrations between these two sites are a result of metabolic and exposure differences between the two species.

Total I-TEQs ranged from 1.77 - 28.9 ng I-TEQ kg^{-1} lipid, including half LODs, with the greatest concentration measured in the oysters from the upper reaches of Hellyers Creek, 0.26 ng I-TEQ kg^{-1} WW, including half LOD values. At sites where PCDDs and PCDFs were actually measured, exclusion of LOD values from total I-TEQ calculations made little difference to the outcome. For example, quantified congeners accounted for >90% of the total TEQ from the upper Hellyers Creek sample, with 60% of the total derived from 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF, and 20% from 2,3,7,8-TCDF.

The most frequently detected PCDDs and PCDFs in sediments were non 2,3,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, non 2,3,7,8-HpCDD, and OCDD in particular. In the shellfish, non 2,3,7,8-TCDD and TCDF, and non 2,3,7,8-PeCDD and PeCDF were frequently detected, together with the hepta- and octa-chlorinated congeners.

6.1.1 Biota sediment accumulation factors for PCDDs and PCDFs

Because the concentrations measured were equal to or less than the method detection limits at many sites, it was difficult to draw conclusions about the bioaccumulation of PCDDs and PCDFs in shellfish, relative to sediment concentrations. Biota sediment accumulation factors (BSAF) for shellfish were calculated for four sites (Table 6.2) by dividing the concentration in shellfish (lipid basis) by the concentration in sediment (TOC basis).

The samples selected were those with a wide range of congeners actually measured in both shellfish and sediments. It is possible that there may be differences in bioaccumulation between oysters and cockles due to differences in metabolism and exposure, but more data would be needed to adequately assess this.

6.1.2 Other New Zealand studies

There is little other published data on concentrations of PCDDs and PCDFs in New Zealand estuaries or coastal environments.

Table 6.2 Biota sediment accumulation factors for PCDDs and PCDFs in selected shellfish samples

Homologue group	Oysters, Hellyers Ck, UR	Cockles, Hellyers Ck, LR	Cockles, Manukau GB	Cockles, Tauranga WE
TCDD	0.48	0.25	0.16	0.20
PeCDD	0.31	0.21	0.09	0.65
HxCDD	0.13	0.10	0.03	0.11
HpCDD	0.02	0.04	0.02	0.03
OCDD	0.02	0.24[a]	0.02	0.02
TCDF	0.72	0.18	0.06	0.10
PeCDF	0.35	0.08	0.07	0.10
HxCDF	0.06	0.05	0.02	0.05
HpCDF	0.02	0.04	0.00	0.03
OCDF	0.02	0.00	0.00	0.02

[a] Unusually high OCDD in shellfish sample.

As part of the technical investigations in support of the Tarawera River Regional Plan, Environment Bay of Plenty (Power, 1994) examined concentrations of organic contaminants in two species of shellfish, tuatua (*Paphies subtriangulata)* and Venus shell *(Dosinia anus)*. The Tarawera River receives domestic sewage and bleached kraft pulp mill effluent.

PCDD and PCDF concentrations of 0.074 - 0.13 ng I-TEQ kg^{-1} WW were reported for tuatua collected within an area 2.5 km west and 3.7 km east of the river mouth during 1993. The greatest concentration in Venus shell from the same area was 0.076 ng I-TEQ kg^{-1} WW reported from a site 100 m west of the river mouth. The concentrations measured at the river mouth in 1993 were approximately 50% of those measured in 1991 (0.29 ng I-TEQ kg^{-1} WW). Concentrations at a reference site 40 km east of the river mouth were 0.042 ng I-TEQ kg^{-1} WW for tuatua, and 0.009 ng I-TEQ kg^{-1} for Venus shell. These concentrations include half LOD values for non-quantified congeners.

Though not directly comparable, due to differences in species, habitat and physical environment, the concentrations of PCDDs and PCDFs in shellfish from the current study are generally higher than those from the Tarawera river mouth study (1993 data).

Jones *et al.* (1996) determined a mean PCDD and PCDF concentration of 1.31 ng I-TEQ kg^{-1} DW in estuarine and coastal sediments in and around Banks Peninsula as part of an assessment of biomagnification of these contaminants in Hector's dolphin. Samples from the Avon-Heathcote estuary were included in the sampling, but the data for individual sites are not available.

6.2 Comparative international data

Many studies have investigated the concentrations of PCDDs and PCDFs in marine sediments (for example, Rappe *et al*., 1989; Luksemburg *et al.,* 1997; Hashimoto *et al.,* 1995); however, only a few report concentrations in estuarine sediments. Comparable data for shellfish from estuarine and coastal areas are summarised in Table 6.3 and sediment data in Table 6.4. Further information relating to these studies is reported in Appendix H. A selection of data is also represented in Figures 6.1 and 6.2, in order to compare the data from New Zealand with those from other countries.

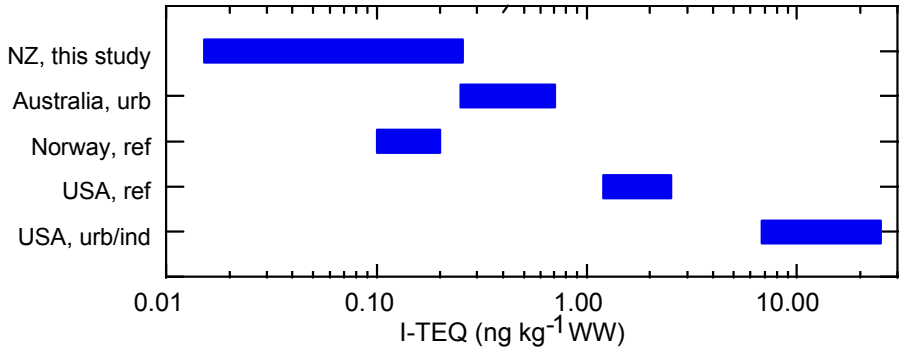


Figure 6.1 PCDD and PCDF concentrations (I-TEQ) in estuarine shellfish in New Zealand and other countries (data sources indicated in Table 6.3)

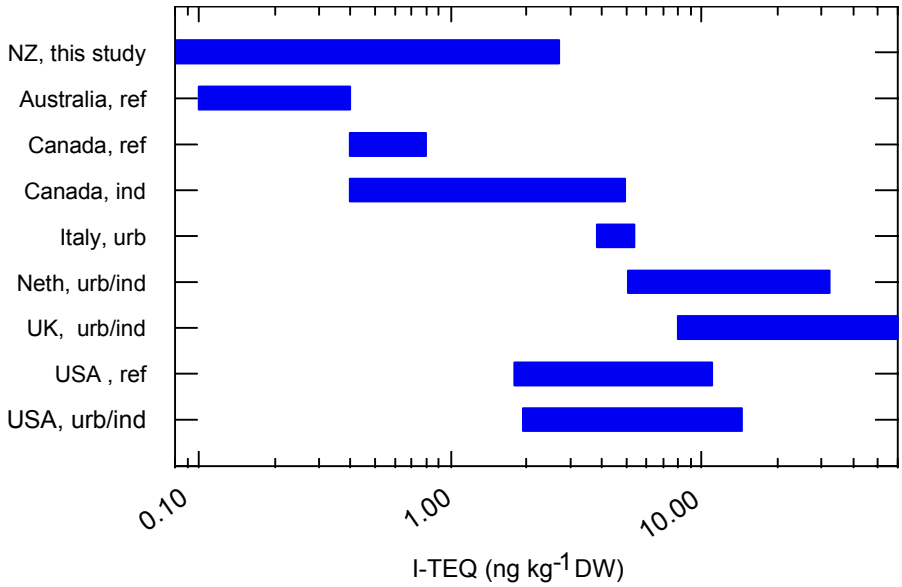


Figure 6.2 PCDD and PCDF concentrations (I-TEQ) in estuarine sediments in New Zealand and other countries (data sources indicated in Table 6.4)

The largest data set for contaminants in bivalves is that of the International Mussel Watch (IMW) and National Oceanographic and Atmospheric Administration (NOAA) Status and Trends programmes, both of which collect data on concentrations of contaminants from sites unimpacted by point source discharges (Goldberg, 1975). Wade *et al.* (1996) report concentrations ranging from none detected - 3 ng TEQ kg^{-1} WW (none detected - 40 ng TEQ kg^{-1} DW) for 55 bivalve samples collected from Gulf, East and West Coast sites in the USA. They also analysed sediments from the Gulf sites, reporting concentrations of 182 - 3302 ng kg^{-1} DW, but no assessment was made of the toxic equivalents for these data.

Oysters from Galveston Bay, Texas, preferentially accumulated the lesser chlorinated congeners (Wade *et al.,*1996). A similar finding was reported for mussels in coastal areas of Japan (Hideaki *et al*., 1987).

Table 6.3 Concentrations of PCDDs and PCDFs in shellfish from other countries

Country	Species	Sample type	Concentration TEQ (ng kg^{-1}) Min.	Max.	Conc. basis	Reference
Australia, Victoria	Mussels, Port Phillip Bay	Industrial	0.23	0.41	WW	Haynes and Toohey, 1995*
	Mussel tissue, Port Phillip Bay	Industrial	0.25	0.71	WW	Haynes and Toohey, 1995*
Canada, St Lawrence Estuary	Whelks, *Buccinum undatum*	Background	0.23	2.19	DW	Brochu *et al*., 1995
	Whelks, *Buccinum undatum*	Industrial	0.85	2.54	DW	Brochu *et al*., 1995
Japan, Tokyo Bay	Japanese cockle, *Fulvia mutica*	Urban	3.6		WW	Masunaga *et al*., 1997
Netherlands, Scheldt Estuary	Mussels	Urban/ind	1.3			de Boer *et al.*, 1993
Norway, Frierfjord	Mussels, *Mytilus edulis*	Background	9.2	9.6	WW	Knutzen and Oehme, 1989
	Mussels, *Mytilus edulis*	Industrial	60		WW	Knutzen and Oehme, 1989
Norway	Mussels, *Mytilus edulis*	Background	0.1	0.2	WW	Knutzen and Schlabach, 1996*
Poland	Mussels, *Mytilus trossulus*	Background	310		Lipid	Falandysz *et al*., 1997
USA, New York	Clams, *Mya arenaria*, Newark Bay	General	15	25	WW	Brown *et al*., 1994*
	Clams, *Mya arenaria,* Elizabeth, New Jersey	General	6.8	11	WW	Brown *et al*., 1994*
	Clams, *Mya arenaria,* Wards Point	General	1.2	2.1	WW	Brown *et al*., 1994*
	Clams, *Mya arenaria,* Tuckerton	General	1.5	2.1	WW	Brown *et al*., 1994*
	Clams, *Mya arenaria*, Chesapeake Bay	General	0.3		WW	Brown *et al*., 1994
East, Gulf and West Coasts	Bivalves	Background	nd	3	WW	Wade *et al.*, 1996
Texas, Galveston Bay	Oysters	Background	3.1	4.7	?DW	Gardinali and Wade, 1996
	Oysters	Urban	12.2	24.1	?DW	Gardinali and Wade, 1996

* Data used to generate Figure 6.1.
?DW assumed to be dry weight.
nd = Not detected.

No PCDD and PCDF data have been reported for Australian estuaries. The closest comparable data are from Ninety Mile Beach in Victoria (Mosse and Haynes, 1993; Haynes *et al.,* 1996), and Port Phillip Bay (Haynes and Toohey, 1995), the heavily industrialised harbour for Melbourne.

At Ninety Mile Beach, nearshore sediment and shellfish samples were taken prior to the commissioning of an outfall to discharge domestic sewage and secondary treated pulp and paper effluents. Mosse and Haynes (1993) found concentrations ranging from 0.10 - 0.40 ng I-TEQ kg^{-1} DW for sediments taken from three sites. For the sub-tidal bivalve, *Scaeoleda crassa*, they reported concentrations of 0.24 - 1.3 ng kg^{-1} WW (no TEQ given). These concentrations are lower than those reported for mussels from Port Phillip Bay in 1993: 33.6 - 133 ng kg^{-1} WW (0.25 - 0.71 ng I-TEQ kg^{-1} WW) (Haynes and Toohey, 1995).

Table 6.4 Concentrations of PCDDs and PCDFs in estuarine and coastal sediments from other countries

Country	Locality	Type	TEQ (ng kg^{-1} DW) Min.	Max.	Reference
Australia, Victoria	Woodside Beach	Background	0.20	0.30	Mosse and Haynes, 1993*
	Seaspray Beach	Background	0.10	0.10	Mosse and Haynes, 1993*
	Delray Beach	Background	0.20	0.40	Mosse and Haynes, 1993*
Canada	Saguenay Fjord	Industrial	0.4	2.3	Brochu *et al.*, 1995*
	Baie des Mille Vaches	Reference	0.4	0.8	Brochu *et al.*, 1995*
	Baie des Anglais	Industrial	4.9		Brochu *et al.*, 1995*
Italy	Venice Lagoon	Urban	3.8	5.3	Jimenez *et al*., 1997*
		Reference	2.4		Jimenez *et al*., 1997
		Industrial	34.8		Jimenez *et al*., 1997
Japan	Tokyo Bay, Harbour	Urban	50.6		Masunaga *et al*., 1997
Netherlands	Wadden Sea Estuary	Urban/ind	5[a]	32[a]	Evers *et al*., 1993*
Sweden	Landsorts	Urban	6.8	28	de Wit *et al*., 1990
United Kingdom	Clyde Estuary	Urban/ind	8	60	Tyler *et al*., 1994*
	Dee Estuary	Urban/ind	10	23	Tyler *et al*., 1994
	Humber Estuary	Urban/ind	9	39	Tyler *et al*., 1994
		Urban/ind	16[a]	267[a]	Evers, *et al*., 1993
USA, Casco Bay	Eastern Bays	Reference	1.8	18	Wade *et al*., 1997*
	West Bay	Reference	2.6	11	Wade *et al*., 1997*
	Inner Bays	Urban/ind	4.6	27	Wade *et al*., 1997*
	Outer Bays	Urban/ind	6.3	18	Wade *et al*., 1997*
USA, Texas	Galveston Bay	Urban/ind	0.9	7.7	Gardinali and Wade, 1996*

[a] Fraction <1000 μm.

[b] Fraction <63 μm

* Data used to generate Figure 6.2.

In the Netherlands, as part of a broad study of PCDDs and PCDFs in freshwater and marine environments, de Boer *et al.* (1993) measured concentrations in mussels, *Mytilus edulis,* of 1.3 ng I-TEQ kg^{-1} WW from the Eastern Scheldt estuary. Evers *et al.* (1993) sampled a number of estuarine and North Sea sediments and reported concentrations of 15 -16 ng I-TEQ kg^{-1} DW for the Western Scheldt estuary, 9.8 ng I-TEQ kg^{-1} DW for the Ems-Dollard estuary, and 43 - 48 ng I-TEQ kg^{-1} DW for the Rhine-Meuse estuary. However, it should be noted that these data are for the PCDD and PCDF concentrations in the silt/clay fraction (<63 μm) only. Sediment samples were also taken from intertidal areas in the Wadden Sea (one of the largest wetlands in Europe), where concentrations in the silt/clay fractions (<63 μm) ranged from 13 - 35 ng I-TEQ kg^{-1} and in the whole bulk sediment samples (<1000 μm) from 5 - 32 ng I-TEQ kg^{-1}. Across all sampling sites, PCDFs were more abundant than PCDDs.

A number of estuarine and harbour sediments in the United Kingdom have been analysed for PCDDs and PCDFs. A concentration of 209 ng kg^{-1} (no TEQ given) has been reported for the Tweed Estuary which only receives urban inputs, and from 31 - 5990 ng kg^{-1} for industrialised estuaries, with the lowest concentration measured in the Tees and the greatest in the Clyde Estuary (Tyler *et al.*, 1994).

6.3 Regulatory approaches

There are a number of guidelines or standards regulating concentrations of PCDDs and PCDFs in sediments and biota, for the purposes of protecting both aquatic life and human health (Table 6.5). Canada (CCME, 1995) has developed the most comprehensive set of values which are intended to protect aquatic life from direct effects of PCDDs and PCDFs, and also to protect piscivorous wildlife from bioaccumulative effects. A limit value in fish tissue has also been set for the protection of human health (Gilman *et al.,* 1995).

Table 6.5 Summary of available guidelines for PCDDs and PCDFs in estuarine and marine sediments and biota

Water type	Guideline	Application	Country
Marine	0.25 ng I-TEQ kg^{-1} (@1% carbon)	Sediment quality objective to protect aquatic life	Canada[a]
	0.30 ng I-TEQ kg^{-1} (@1%carbon)	Sediment quality objective to protect piscivorous wildlife	Canada[a]
	50 ng I-TEQ kg^{-1} lipid	Tissue quality objective to protect aquatic life	Canada[a]
	0.66 ng I-TEQ kg^{-1} lipid	Tissue quality objective to protect piscivorous wildlife	Canada[a]
Unspecified	20 ng I-TEQ kg^{-1} WW	Limit concentration for consumption of fish by humans	Canada[b]

[a] CCME (1995).
[b] Gilman *et al.* (1995).

For 2,3,7,8-TCDD, the Health Council of the Netherlands has recommended an ecotoxicological exposure limit for aquatic ecosystems of 13 ng 2,3,7,8-TCDD kg^{-1} dry matter (Health Council of the Netherlands, 1996). This exposure limit is considered to be protective of aquatic organisms, birds and mammals.

Sediment samples from 12 of the 18 sites where PCDDs and PCDFs were measured in the current study were above the Canadian sediment quality objectives for the protection of aquatic life and protection of piscivorous wildlife, if half LOD values were included in the total TEQ calculation. This number decreased to 6 if LOD values were excluded. The sites where sediments exceeded the Canadian guidelines were: Manukau Harbour (Grannys/Wesley/Waikowhai/Wattle Bays); Hellyers Creek (both sites) in Waitemata Harbour; Tauranga Harbour (Hunters Creek and Waikareao Estuary); and the Avon-Heathcote Estuary (opposite Pleasant Point domain).

All shellfish samples fall below the Canadian limit concentration for fish (Gilman *et al.* 1995) and the tissue quality objective for the protection of aquatic life (CCME, 1995). However, shellfish samples from 10 sites exceed the Canadian tissue quality objective for the protection of piscivorous wildlife if total TEQs excluding half LOD values are used. These samples were collected from the same sites as those which exceeded the Canadian sediment quality objectives (discussed above), with the addition of the following: Whangarei Harbour (both sites); Tauranga Harbour (Hunters Creek); and Moutere Inlet (south side). All 20 sites where PCDDs and PCDFs were measured were in exceedance if total TEQ concentrations derived using half LOD values were assessed against the same tissue quality objective.

Combining I-TEQs (Table 6.1) and PCB TEQs (Table 7.1) results in slightly higher total TEQ in sediments at seven sites (calculated excluding half LOD), with the I-TEQs contributing the greatest proportion (75-80%). In shellfish, summing the TEQ gives a markedly higher total, with the proportion contributed by PCBs being higher (60-70%) than PCDDs and PCDFs.

Further research is needed to investigate concentrations in other biota, such as wading birds which feed on shellfish, to ascertain what effects the PCDD and PCDF concentrations may be having on food webs at sites which exceed the guideline concentrations.

6.4 Summary

PCDD and PCDF concentrations in New Zealand estuarine sediments and shellfish are generally lower than those reported from comparable studies in other countries. However, because of differences in species, habitat and physical environments, comparison can only be approximate.

The total I-TEQ concentrations measured in shellfish at several sites (Hellyers Creek in particular) approach those determined from sites with known industrial inputs, such as Port Phillip Bay in Australia (Haynes and Toohey, 1995). Sediment total I-TEQ concentrations were generally at the lower end of the range found in other studies. As for the shellfish, concentrations in Hellyers Creek sediments were within the range of other urbanised estuaries elsewhere, for example, Galveston Bay, Texas (Gardinali and Wade, 1996).

7 Polychlorinated biphenyls

7.1 New Zealand data

PCBs were measured in sediment from nine of the 26 sites samples (Table 7.1). All PCB concentrations in the sediment samples were below 10 μg kg^{-1} DW, ranging from 0.12 - 8.80 μg kg^{-1} DW. The greatest concentration was measured in the upper reaches of Hellyers Creek, Waitemata Harbour. However, if concentrations were normalised to organic carbon, Waikareao Estuary, Tauranga Harbour, had the greatest PCB concentration. On a dry weight basis, these two sites had similar PCB TEQs.

In the New Zealand sediments, as in other locations (see Table I3, Appendix I) congeners #101, #118, #153, #138, #180 and #170 made up a large proportion of the sum of PCBs. This is consistent with PCB congeners reported for metropolitan and provincial centre soils in another strand of the Organochlorines Programme (Buckland *et al*., 1998a). The congener profile in all New Zealand sediments is relatively uniform, suggesting a common source(s) of contamination and similar environmental mixing and sorting processes.

Table 7.1 Concentrations of PCBs as sum of 25 congeners and TEQ in sediments and shellfish (calculated including half LOD values)[a]

Location	Sediment		Shellfish	
	Sum PCB (μg kg^{-1} TOC)	PCB TEQ (ng kg^{-1} TOC)	Sum PCB (μg kg^{-1} lipid)	PCB TEQ (ng kg^{-1} lipid)
Parengarenga, AP	68.4	34.2	15.9	9.42
Parengarenga, OP	75.0	40.6	16.2	9.56
Whangarei, MR	32.7	23.5	83.9	5.24
Whangarei, LI	46.6	11.0	192	14.6
Manukau, GB	215	33.3	88.0	7.50
Manukau, BM	40.0	30.0	24.7	8.44
Manukau, FB	133	29.9	26.0	9.04
Hellyers, upper	471	33.2	1433	66.7
Hellyers, lower	218	17.9	103	43.7
Kawhia, NS	21.1	8.68	27.6	11.2
Kawhia, SS	23.5	9.56	24.5	12.3
Tauranga, HC	459	30.7	36.5	12.5
Tauranga, TR	60.0	32.5	17.4	9.42
Tauranga, WE	926	98.4	46.8	10.5
Wairau, AC	68.4	63.2	16.2	9.56
Wairau, MC	32.6	30.4	13.9	8.23
Whanganui, SS	10.8	25.8	34.4	20.3
Whanganui, SI	9.72	15.3	23.9	14.1
Moutere, SE	23.3	16.4	33.3	19.7
Moutere, SW	42.9	8.44	26.8	15.9
Avon-Heathcote, MC	77.8	36.1	26.5	8.07
Avon-Heathcote, PP	257	35.1	66.7	10.6
Otago, RP	80.0	43.3	13.3	5.75
Otago, TP	109	59.1	14.7	6.37
New River, BP	65.2	28.3	17.6	5.11
New River, WB	81.3	40.6	14.5	4.55

[a] Shaded areas indicate concentrations derived wholly from half LOD values.

Congener profiles for sediment and oysters from the upper reaches of Hellyers Creek are shown in Figures 7.1 and 7.2. The greatest concentrations found in both sample types in this survey were measured at this site.

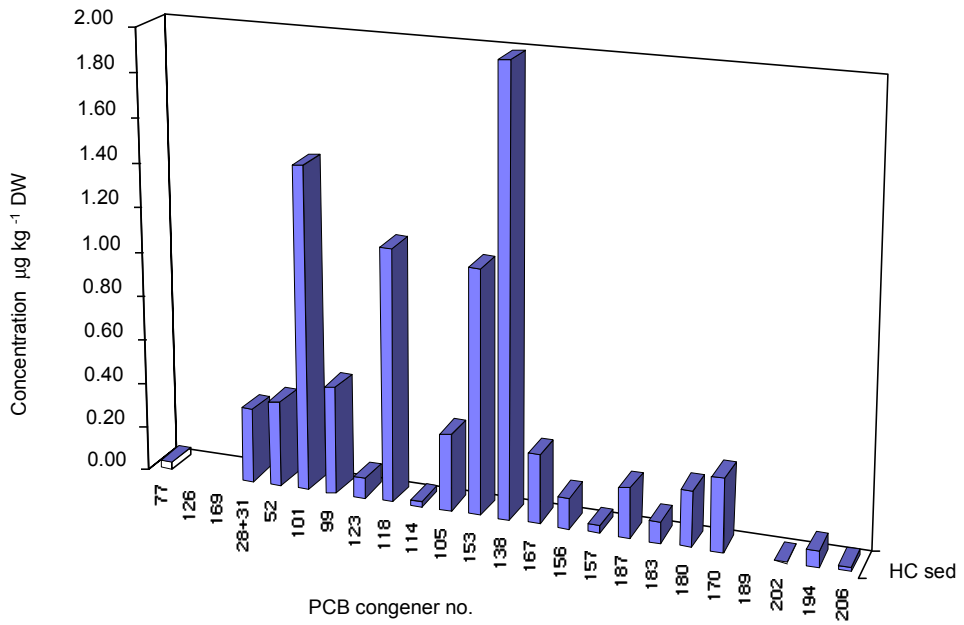


Figure 7.1 PCB congener profile for Hellyers Creek sediment (upper reaches)

PCBs were detected more frequently in shellfish than in sediments, as may be expected due to the lipophilic and bioaccumulative nature of these contaminants. There were four estuaries where no PCBs were measured in shellfish: Parengarenga Harbour, Wairau Estuary, Whanganui Inlet and Moutere Inlet. These are locations which have little or no industry within their catchments. Even at the site with the greatest concentrations (12.9 µg kg^{-1} WW oysters, Hellyers Creek, upper reaches), six congeners were below the analytical LODs in the range 0.001 - 0.06 µg kg^{-1} WW. For the next greatest sample (1.71 µg kg^{-1} WW, oysters from Whangarei Harbour near Limestone Island), 11 of the 24 congeners were 'less than' values.

7.1.1 Biota sediment accumulation factors for PCBs

As for the PCDD and PCDF data, it is not possible to draw any firm conclusions as to the bioaccumulation of PCBs in shellfish as many congeners were at or below the limits of detection at the majority of sites. However, it is of interest that the BSAF for individual PCB congeners in oysters in the upper reaches of Hellyers Creek was consistently >1, while the BSAF for cockles from the lower reaches of Hellyers Creek and Waikareao Estuary (Tauranga Harbour) was consistently <1 for each congener measured. Overall, the BSAFs for sum of PCBs were also >1 for oysters and <1 for cockles.

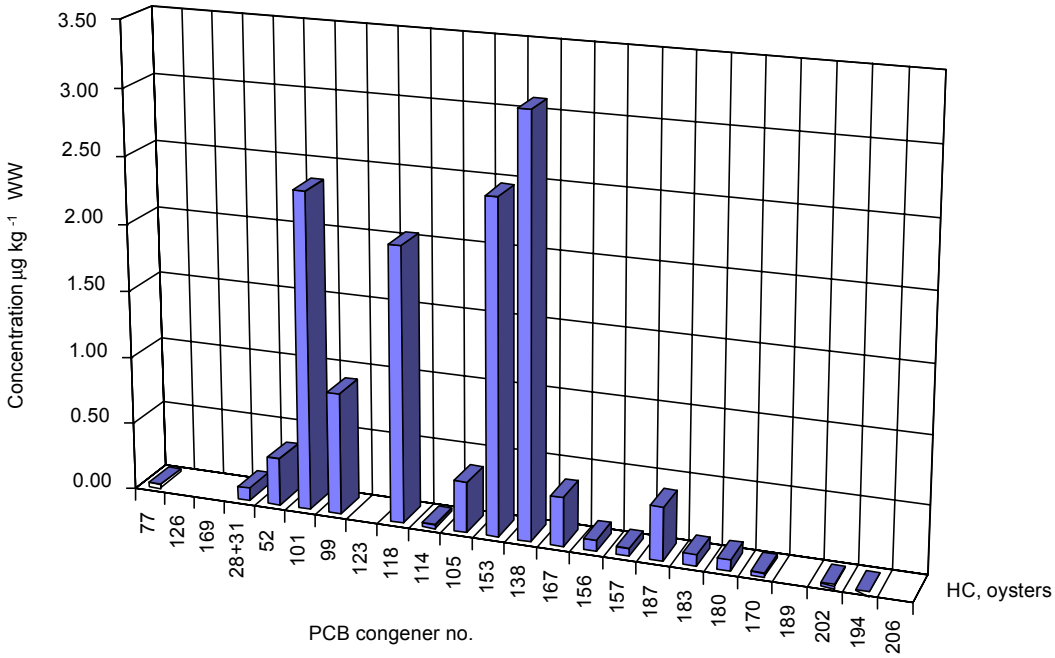


Figure 7.2 PCB congener profile for Hellyers Creek oysters (upper reaches)

Concentrations of organic contaminants (PCBs and organochlorine pesticides) in cockles (*A. stutchburyi*) have been reported up to ten times lower than in oysters (*C. gigas*) sampled in the Manukau Harbour, with the differences attributed to metabolic and exposure differences between species (Hickey *et al*. 1995). However, Hickey *et al*. (1995) reported a mean BSAF of 3.90 for PCBs in cockles, which is much higher than the BSAF for cockles collected from 5 sites in a similar area in the current study (BSAF 0.41).

7.1.2 Other New Zealand studies

Results from several other studies of PCB concentrations in New Zealand estuaries are reported in Table 7.2.

The concentrations of PCBs in Manukau Harbour in the current study fall approximately within the range previously measured in Pacific oysters (ARWB, 1990), cockles (Hickey *et al*., 1995) and sediments (Holland *et al*., 1993). Direct comparison is difficult because not all the same congeners were determined in the separate studies. Holland *et al.* (1993) found the greatest PCB concentrations in sediments from Wesley and Grannys Bays, both of which were included in the composite sample with the greatest PCB concentrations of the three Manukau Harbour sites in the current study.

Table 7.2 PCB concentrations reported in other New Zealand estuarine studies

Location	Sample	Date sampled	No. of sites	Concentration (μg kg^{-1}) Min.	Max.	Conc. basis	Reference
Manukau Harbour	NZ cockle, *A. stutchburyi*	Dec 1989	15	2.15[a]	8.97[a]	DW	Hickey *et al*., 1995
	Wedge shell, *Macomona liliana*	Dec 1989	15	3.43[a]	13.9[a]	DW	Hickey *et al*., 1995
	Sediment	Dec 1989	15	0.20[b]	2.08[b]	DW	Holland *et al*., 1993
	Pacific oyster, *C. gigas*	1988-89	2	1.6	3.4	Lipid	ARWB, 1990
	Sediment		5	0.5[d]	14.2[d]	DW	Fox *et al*., 1988
Tamaki Estuary	Pacific oyster, *C. gigas*	1989-90	6	<0.6	130.4	DW	ARC, 1992
	Sediment	1990	6	0.57	16.7	DW	ARC, 1992
Waikareao Estuary, Tauranga Harbour	NZ rock oyster, *Saccostrea glomerata*	Feb 1992	5	119[c]	272[c]	DW	Burggraaf *et al*., 1996
	Wedge shell, *M. liliana*	Feb 1992	4	11[c]	54[c]	DW	Burggraaf *et al*., 1996
	Sediment	1991-92	15	<0.1	73.8	DW	Burggraaf *et al*., 1994
Avon-Heathcote Estuary	Sediment	1991-92	13	0.03	3.0	DW	Thomson and Davies, 1993
	NZ cockle (3 samples)	1991-92	13	nd	21.4	DW	Thomson and Davies, 1993
Banks Peninsula	Sediment			1.33		DW	Jones *et al*., 1996
Wellington Harbour	Sediment	1995	17	2.70[e]	92.5[e]	DW*	Day, 1996

[a] Sum of 14 congeners.
[b] Sum of 7 congeners.
[c] Sum of 9 congeners.
[d] Sum of 51 congeners.
[e] Sum of 19 congeners.
* Converted from WW using %moisture data provided in original reference.

The Waikareao Estuary had higher PCB concentrations than other sites sampled within the Tauranga Harbour (Burggraaf *et al.*, 1994). The source of the PCBs was attributed to two stormwater drains servicing an adjacent industrial area. Concentrations of 68.6 and 73.8 μg kg^{-1} DW were measured in sediments at the drain outfalls, compared to <0.1 μg kg^{-1} DW measured on the opposite side of the estuary to the drains. PCB concentrations (sum of 9 congeners) in two bivalve species, wedge shell and New Zealand rock oyster, collected from the same sites as the sediment samples ranged from 271 - 2326 μg kg^{-1} lipid (Burggraaf *et al.,* 1996). These concentrations were far higher than those measured in cockles collected during the current study (46.8 μg kg^{-1} lipid, sum of 25 congeners). The Waikareao Estuary had the greatest sediment PCB concentration of the three sites sampled in the Tauranga Harbour in the current study.

PCB concentrations in the Manukau and Tauranga harbours have been reported as somewhat higher than those of the current study at 14.2 and 24.1 μg kg^{-1} DW, respectively (Fox *et al.* 1988; Burggraaf *et al.* 1994).

Total PCB concentrations recorded from sediments and shellfish in the Avon-Heathcote Estuary during this study were lower than reported for the same sites in 1991-92 by Thomson and Davies (1993).

7.2 Comparative international data

Data for sum of PCB concentrations in estuarine shellfish and sediments from international studies are provided in Tables 7.3 and 7.4 respectively. Few, if any, studies from other countries include TEQ concentrations or report full congener data.

Iwata *et al.* (1994b) undertook a major investigation of concentrations of PCBs (and organochlorine pesticides) in sediments from Asia and western Pacific areas, sampling both urban and rural sites.

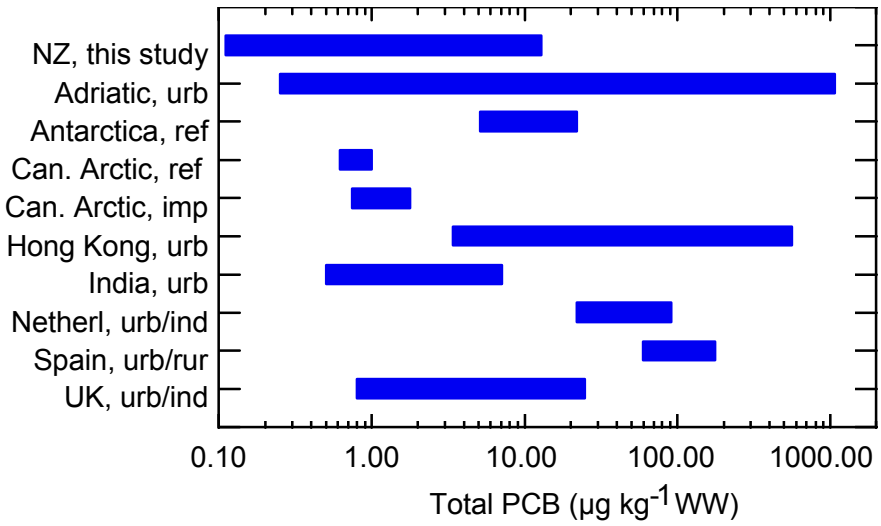


Figure 7.3 PCB concentrations in estuarine shellfish in New Zealand and other countries (data sources indicated in Table 7.3)

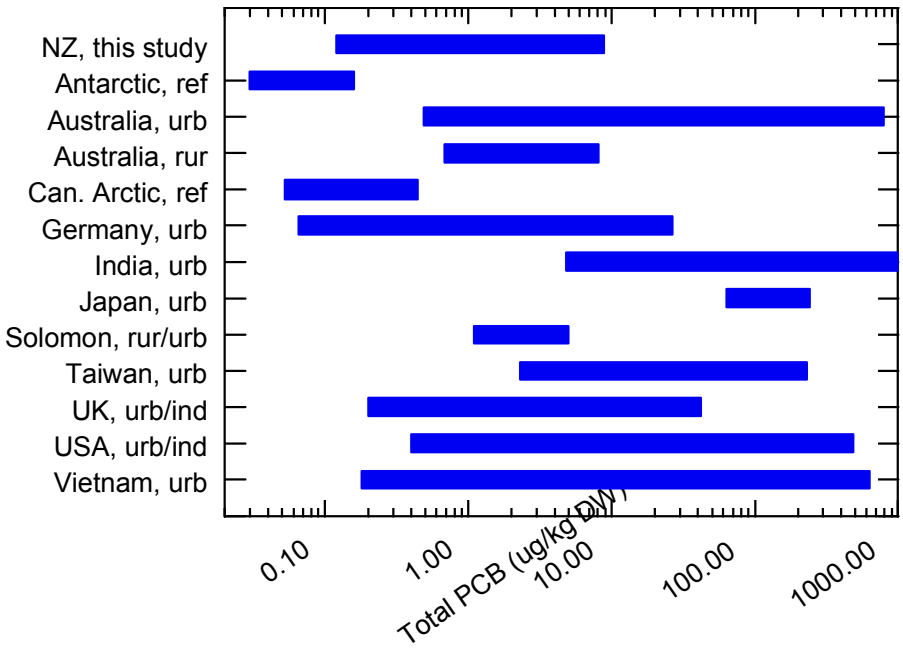


Figure 7.4 PCB concentrations in estuarine sediments in New Zealand and other countries (data sources indicated in Table 7.4)

This study reported PCB concentrations in Australian sediments in the range 0.49 - 790 μg kg^{-1} DW for urban sites, and 0.68 - 8.1 μg kg^{-1} DW for rural sites. As part of a broad survey of coastal sediments and shellfish near Perth, Western Australia, Burt and Ebell (1995) found PCBs to be below the limits of detection in both sediments and mussels.

Table 7.3 Concentrations of PCBs in estuarine shellfish (μg kg^{-1} WW) in other countries

Country	Species	Location type	Concentration		Data type	Reference
			Min.	Max.		
Adriatic	North Adriatic, "mussels"	Urban/ind	<0.3	771	Total PCB	Picer and Picer, 1991
	Eastern Adriatic "mussels"	Urban/ind	<0.5	1072	Total PCB	Picer and Picer, 1995*
Antarctica	McMurdo Sound, bivalve, *Laternula elliptica*	Impacted	380	430	Total PCB	Kennicutt *et al*., 1995
	McMurdo Sound	Reference	5.1	22	Total PCB	Kennicutt *et al*., 1995*
Argentina	Rio de la Plata, *Corbicula fluminea*	Urban/ind	223[a]	236[a]	Total PCB	Colombo *et al*., 1990
	Arroyo Parejas	Background	110[b]		Total PCB	Sericano *et al*., 1995
Australia	Port Phillip Bay, *Mytilus edulis*	Urban/ind	<10[b]	879[b]	Total PCB	Phillips *et al*., 1992
	Curio Bay, *M. edulis*	Urban/ind	20[b]	930[b]	Total PCB	Phillips *et al*., 1992
	Curio Bay, *M. edulis*	Urban/ind	13.8	14.8	Sum 47 con.	Prest *et al*., 1995
	Perth, *M edulis*	Background	<10		Total PCB	Burt and Ebell, 1995
Brazil	Guanabara Bay	Background	170[b]		Total PCB	Sericano *et al*., 1995
Canada	Arctic, Cambridge Bay, 3 spp.	Impacted	0.89	3.2	Sum 47 con.	Bright *et al*., 1995*
	Arctic, 2 spp.	Reference	0.62	0.99	Sum 47 con.	Bright *et al*., 1995*
Chile	Punta Arenas	Background	130[b]		Total PCB	Sericano *et al*., 1995
Greece	Mussels, *M. galloprovincialis*	Urban/ind	7.6	83	Total PCB	Satsmadjis and Gabrielides, 1983
Hong Kong	Mussels, *P. viridis*	Urban/ind	3.4	560	Total PCB	Tanabe *et al*., 1987*
India	Mussels, *Perna viridis*	Urban/ind	<1	7.1	Total PCB	Ramesh *et al*., 1990*
Mexico	Laguna Madre	Background	110[b]		Total PCB	Sericano *et al*., 1995
Netherlands	Mussels, *M. edulis*	Urban/ind	22	92	Sum 7 con.	Stronkhorst, 1992*
North Greenland	Scallops, *Chlamys islandicus*		6[b]	36[b]	Total PCB	Kjolholt and Munk Hansen, 1986
NW Spain	Feral and cultivated mussels	Urban/ind	59.4	177	Total PCB	Alvarez Pineiro *et al*., 1995*
Oman	Oysters and mussels	Urban/ind	0.87	9.1	Total PCB	Burns *et al*., 1982
Peru	Callao	Background	120[b]		Total PCB	Sericano *et al*., 1995
United Kingdom	Mussels, *M. edulis*	Urban/ind	0.9	39	Sum 21 con.	Thompson *et al*., 1996
	Mussels, *M. edulis*	Urban/ind	0.8	25	Sum 21 con.	Thompson *et al*., 1996*
USA	"Mussel watch",	Background	4.1[b]	790[b]	Σ18 con. (x2)	Lauenstein, 1995
	"Mussel watch"	Background	0[b]	720[b]	Σ18 con. (x2)	Lauenstein, 1995
	Gulf of Mexico, oysters	Background	10[b]	630[b]	Total PCB	Sericano *et al*., 1995
Vietnam	Food shellfish		15		Total PCB	Kannan *et al*., 1992

* Data used to generate Figure 7.3.
[a] Reported on lipid weight basis. Converted to wet weight using lipid content of 3.1%.
[b] Dry weight basis

Three studies have reported PCB concentrations in sediments from Pacific Island countries, with the lowest concentrations determined in Vanuatu <0.07 - 0.20 μg kg^{-1} DW (Harrison *et al*., 1996) and the greatest in Fiji 0.97 - 68.5 μg kg^{-1} DW (Morrison *et al*., 1996). Concentrations in Papua New Guinea were in the range 3.3 - 54 μg kg^{-1} DW and in the Solomon Islands 1.1 - 5.0 μg kg^{-1}

DW (Iwata *et al*., 1994b). No data are available for PCB concentrations in shellfish from these countries.

Table 7.4 Concentrations of PCBs in estuarine sediments (μg kg^{-1} DW) in other countries

Country	Location	Location type	Concentration (μg kg^{-1} DW) Min.	Max.	Data type	Reference
Adriatic Sea	Coastal sites	Urban/ind	4.14	129	Total PCB	Galassi *et al.*, 1993
Australia	Perth, WA coastal	Urban	< 10		Total PCB	Burt and Ebell, 1995
	Sydney, NSW	Urban	52	790	Con. sum	Iwata *et al*., 1994b*
	Perth, WA	Rural	0.68	0.85	Con. sum	Iwata *et al*., 1994b*
	Perth, WA	Urban	0.49	18	Con. sum	Iwata *et al*., 1994b*
	Hobart, TAS	Rural	0.85	8.1	Con. sum	Iwata *et al*., 1994b*
	Hobart, TAS	Urban	2.4	470	Con. sum	Iwata *et al*., 1994b*
Antarctica		Background	< 0.01	0.8	Total PCB	Risebrough *et al*., 1990
	McMurdo Sound	Background	2.8	4.2	Total PCB	Kennicutt *et al*., 1995
	McMurdo Sound	Impacted	2.1	1400	Total PCB	Risebrough *et al*., 1990
	McMurdo Sound, Winter Quarters Bay	Impacted	250	4200	Total PCB	Kennicutt *et al*., 1995
	Ross Sea/Terra Nova Bay	Background	0.03	0.16	Total PCB	Fuoco *et al*., 1995*
Argentina	Rio de la Plata	Urban/ind	3	998	Total PCB	Colombo *et al.*, 1990
Canada	St Lawrence Estuary	Urban/ind	82.7	770		Coakley *et al.*, 1993
	Arctic, Cambridge Bay	Impacted	0.14	45	Sum 47 con.	Bright *et al.*, 1995
	Arctic	Reference	0.052	0.44	Sum 47 con.	Bright *et al.*, 1995*
Egypt	Nile sediments	Urban/ind	6.91	3155	Total PCB	El-Gendy *et al.*, 1991
Germany	Oder River Estuary	Urban/ind	<0.1	26.3	Sum 13 con.	Dannenberger *et al*., 1997*
India		Urban	4.8	1000	Con. sum	Iwata *et al*., 1994b*
Indonesia		Urban	5.9	220	Con. sum	Iwata *et al*., 1994b
Japan	Osaka Bay	Urban/ind	63	240	Con. sum	Iwata *et al*., 1994b*
Malaysia		Rural	< 5		Con. sum	Iwata *et al*., 1994b
Mexico	San Quintin Bay	Rural	<10		Total PCB	Gallindo *et al*., 1996
Netherlands	Scheldt Estuary	Urban/ind	86.8	Mean	Sum 13 con.	Stronkhorst *et al.*, 1994
Papua New Guinea		Urban	3.3	54	Con. sum	Iwata *et al*., 1994b*
Solomon Islands		Rural/urban	1.1	5.0	Con. sum	Iwata *et al*., 1994b*
South France	Mediterranean	Urban/ind	29	181	Sum 20 con.	Pierard *et al.*, 1996
Spain	Alicante	Urban/ind	0.2	2.9	Sum 10 con.	Prats *et al*., 1992
Sweden	Gulf of Bothnia	Urban/ind	23.4	262	Sum 86 con.	van Bavel *et al.*, 1995
Taiwan		Urban	2.3	230	Con. sum	Iwata *et al.*, 1994b*
Tanzania	Dar es Salaam Harbour	Urban/ind	nd	7000	Total PCB	Machiwa, 1992
Thailand		Urban/ind	11	520	Con. sum	Iwata *et al.*, 1994b
United Kingdom	Thames Estuary	Urban/ind	1	40	Total PCB	Scrimshaw and Lester, 1995
	Essex salt marshes	Urban/ind	<1	243	Total PCB	Scrimshaw *et al*., 1996
	Coastal sites	Urban/ind	0.2	42	Sum 21 con.	Thompson *et al*., 1996*
United States	Casco Bay, Maine	Urban/ind	0.4	485	Total PCB	Kennicutt *et al.*, 1994*
Vietnam		Rural/urban	0.18	630	Con. sum	Iwata *et al.*, 1994b*

* Data used to generate Figure 7.4.

nd = Not detected.

Kennicutt *et al.* (1995) investigated PCB contamination of Antarctic sediments and bivalves in proximity to McMurdo Station and remote from this base. They reported concentrations of 2.8 -4.2 μg kg^{-1} DW and 5.1 - 22 μg kg^{-1} WW for unimpacted sediments and shellfish respectively. Concentrations in the impacted areas were 250 - 4200 μg kg^{-1} DW for sediments and 380 - 430 μg kg^{-1} WW for shellfish. PCB concentrations in sediments for the Ross Sea have been reported at a lower concentration, 0.03 - 0.16 μg kg^{-1} DW (Fuoco *et al.,* 1995).

Thompson *et al.* (1996) investigated PCB concentrations in mussels (7 - 168 μg kg^{-1} DW) and sediments (0.2 - 42 μg kg^{-1} DW) from estuaries and harbours around the Irish Sea, and in mussels from the North Sea and Scotland (3 - 162 μg kg^{-1} DW). Higher concentrations were measured on the east coast of Scotland in comparison to the west coast, reflecting higher concentrations of urbanisation and industrialisation on the east coast.

In the Canadian Arctic, PCB concentrations have been reported for both reference sites (0.052 - 0.44 μg kg^{-1} DW sediment and 0.62 - 0.99 μg kg^{-1} WW shellfish), and an impacted site in Cambridge Bay (0.14 - 45 μg kg^{-1} DW sediment and 0.89 - 3.2 μg kg^{-1} WW shellfish (Bright *et al.,* 1995)).

A significant amount of data has been collected for PCB concentrations in shellfish from the USA (Lauenstein 1995) and South and Central America (Sericano *et al.,* 1995) as part of the International Mussel Watch programme. The sites used are chosen for their distance from known point source discharges. Concentrations in mussels and oysters from USA sites ranged from 0 - 720 μg kg^{-1} DW in 1991-92, and in South and Central America from 110 - 170 μg kg^{-1} DW.

Unfortunately only two papers provided congener-specific data for shellfish (Bright *et al.*, 1995; Colombo *et al*., 1990) and one of these provided data for non *ortho*- substituted congeners only (Bright *et al*., 1995).

7.3 Regulatory approaches

Several countries have promulgated guidelines for PCB concentrations in sediments (Table 7.5).

United States

The approach developed by Long *et al.* (1995) used a wide range of studies of various contaminants and their effects on sediment biota *in vivo* and in laboratory exposures (Long *et al.* 1995). A statistical method was then used to calculate the "Effects Range Low" ER-L as the 10^{th} percentile of concentrations at which adverse effects were observed. The "Effects Range Median" ER-M was calculated as the median of concentrations where adverse effects were observed. The strength of this method is that it used numerous species and exposure conditions and has proved very useful for predicting the effects of some contaminants. The method is not, however, completely satisfactory for predicting PCB toxicity as a poor correlation was observed between PCB concentrations and adverse effects. This poor correlation can be attributed to our relatively poor understanding of the effects of complex PCB mixtures interacting with sediments and living organisms and our limited understanding of the effects of chronic exposure to low concentrations of PCBs.

Table 7.5 Summary of available sediment quality criteria and guidelines for PCBs

Data type	Water type	Concentration (μg kg^{-1} DW)	Application	Country	Reference
Total PCB	Estuarine/ marine	22.7	Effects range-low	USA	Long *et al*., 1995
		180	Effects range-median		
	Marine	21.5	Threshold effects concentration	Canada	Smith *et al*., 1996
		189	Probable effects concentration		
PCB 28, 52, 101, 138, 153, 180 (individually)		4	Limit value	Netherlands	MoHSPE[1], 1994
Σ6 PCBs (28, 52 101, 138, 153, 180)		20	Target value	Netherlands	MoHSPE, 1994
Σ7 PCBs (28, 52 101, 118, 138, 153, 180)		100	Intervention value	Netherlands	MoHSPE, 1994

[1] Ministry of Housing, Spatial Planning and the Environment.

Canada

Environment Canada has developed interim national guidelines for marine sediment quality (Smith *et al*., 1996). The guideline concentrations have been developed using a modified version of the "weight of evidence" approach based on available toxicological data derived from field studies (Long *et al*., 1995) discussed above. The Canadian approach also includes spiked sediment toxicity data, and assesses the influence of sediment characteristics on the bioavailability of chemicals.

The threshold effects concentration (TEL) is the concentration at which adverse effects are rarely expected to occur. The probable effects concentration (PEL) is the concentration at which adverse effects are frequently expected to occur. The TEL and PEL values are very similar to the ER-L and ER-M of Long *et al.* (1995). However, Smith *et al.* (1996) unlike Long *et al.* (1995) considered that there was good concordance between the TEL/PEL values and the incidence of adverse biological effects. Therefore the TEL and PEL values for these chemicals are considered to adequately represent the concentrations at which adverse effects are either not expected to occur or are likely to occur.

Netherlands

In the Netherlands, a series of sediment quality objectives (Table 7.5) have also been developed (Ministry of Housing, Spatial Planning and the Environment, 1994).

The target values represent a concentration which will be protective of ecological functions, and will not result in contamination of the overlying water. Sediments which meet these concentrations can be dredged and spread on land without restrictions.

The limit values apply to newly deposited sediments (the top 5-10 cm) and were derived from the limit values for surface waters based on the equilibrium partitioning approach. Limit values may not be exceeded and are considered by regulatory authorities to be requirements which must be met. The intervention values are indicative of "serious pollution" and may require clean-up action to be taken, depending on the nature and scale of risk at a site.

PCB concentrations in sediments are well below the guideline concentrations set by other countries, even at the most impacted site, the upper reaches of Hellyers Creek, Waitemata Harbour (8.8 μg kg^{-1} DW).

7.4 Summary

PCB concentrations determined in New Zealand shellfish in the current study (median 0.18 μg kg^{-1} WW) were considerably lower than those reported for shellfish from other countries, on a wet weight basis, with the exception of the oysters from Hellyers Creek.

On a dry weight basis, the PCB concentrations in oysters from Hellyers Creek (155 μg kg^{-1} DW) and Whangarei Harbour (20.6 and 12.2 μg kg^{-1} DW) are within the ranges reported for a number of urban sites in other countries.

Concentrations in sediments in the current study are generally lower (median 0.16 μg kg^{-1} DW) than those reported from other countries. However, concentrations at two locations (Hellyers Creek and Waikareao Estuary, Tauranga Harbour) are within the ranges reported for urban sites in other countries.

8 Organochlorine pesticides

8.1 New Zealand data

The concentrations of pesticides most frequently detected in shellfish and sediments are shown in Figure 8.1. Full pesticide concentration data are reported in Appendix J.

DDT residues

DDT residues were detected in 18 of the 26 sediment samples. Parent DDT was present in only 15 of the samples and concentrations were low compared to DDE and TDE. The presence of significant concentrations of TDE suggests that conversion from DDT within anoxic sediment has occurred.

No DDT residues were measured in the Parengarenga Harbour sediments, but were measured at low concentrations in Whanganui Inlet samples. These two sites were the most remote from anthropogenic influences,

Residues of DDT were detected in 24 of the 26 shellfish samples, with the Parengarenga Harbour shellfish samples being the only two where concentrations were below the analytical LODs, which were in the range 0.01 - 0.02 µg kg^{-1} WW. Concentrations of parent DDT were low and were determined in less than half the samples. TDE was prevalent, suggesting that DDT had been converted under anaerobic and reducing conditions. This process is likely to have occurred in sediments prior to uptake by shellfish. The presence of similar amounts of TDE in the sediment samples supports this contention.

Total residues were low by international standards. Concentrations detected in both the French (Claisse, 1989) and US (Lauenstein, 1995; Stephenson *et al.,* 1995) Mussel Watch programmes were far higher than those detected in this study.

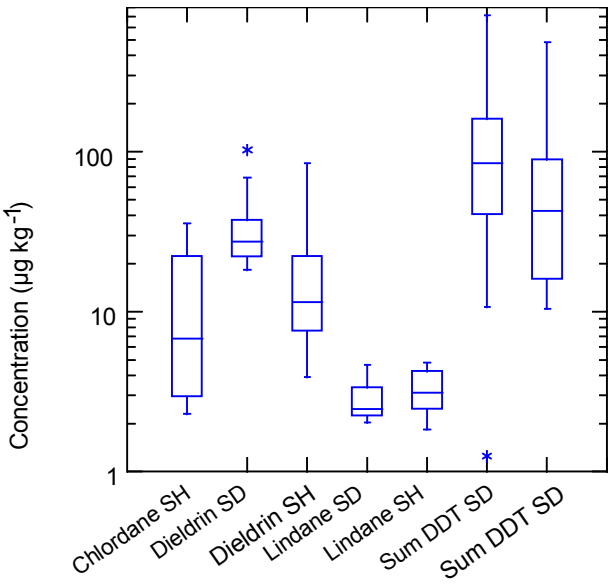


Figure 8.1 Organochlorine pesticides most frequently detected in sediments and shellfish (SH shellfish lipid weight basis: SD sediment TOC basis)

HCH residues

Of the three isomers of HCH, only γ-HCH (lindane) was detected in either sediments or shellfish. Lindane was measured in three sediment samples at concentrations close to the detection limit of 0.01 μg kg^{-1} DW, and in 14 of the 26 shellfish samples. The maximum concentration in sediment was 0.046 μg kg^{-1} DW in the upper reaches of Hellyers Creek, and in shellfish was 0.046 μg kg^{-1} WW in cockles from Manukau Harbour.

This is comparable with other available New Zealand data (Hickey *et al*., 1995) if allowance is made for the weight basis. Concentrations compare very favourably with those recorded overseas (Tables J3 and J4, Appendix J).

HCB

HCB residues were detected in sediments at less than a quarter of the sites sampled. At only two sites did it exceed 0.1 μg kg^{-1} DW. These concentrations are comparable to those reported elsewhere (Table J5, Appendix J) but in absolute terms they are low.

HCB was measured in only five of 26 shellfish samples at concentrations close to the detection limit of 0.01 μg kg^{-1} WW. These concentrations are consistent with, but generally lower than, those reported elsewhere (Tables J6, Appendix J).

Chlordane and heptachlor

Chlordane and heptachlor were only detected in one sediment sample each. Concentrations measured were similar to those reported in New Zealand previously (Table 8.2). New Zealand concentrations of chlordane are comparable with the very lowest that have been reported for other countries. The positive heptachlor measurement (0.018 μg kg^{-1} DW) is also lower than reports from elsewhere (Table J5, Appendix J), but there is a lack of extensive survey data on these compounds.

Heptachlor and its epoxide were not detected in any shellfish samples. Hickey *et al.* (1995) did detect heptachlors at low concentrations in Manukau Harbour. New Zealand concentrations of heptachlors are amongst the lowest in the world, and very much lower than those frequently reported from the USA.

Chlordanes were detected in 10 of the shellfish samples, but at concentrations that are very low relative to those elsewhere in the world (Table J6, Appendix J).

Aldrin and dieldrin

Aldrin was below the limit of detection in all samples, but dieldrin was measured in nine sediments (to a maximum of 0.38 μg kg^{-1} DW) and 23 shellfish samples (to a maximum of 0.56 μg kg^{-1} WW). These data are consistent with other reports from New Zealand (Table 8.2). Dieldrin concentrations are low compared to those reported for other countries.

8.1.1 Other New Zealand studies

There are a number of other studies reporting organochlorine pesticide concentrations in New Zealand estuaries (Tables 8.1 and 8.2). The Manukau Harbour has been most frequently studied, partly due to concerns over contaminants conveyed by stormwater discharges from Auckland and its environs.

Table 8.1 Concentration ranges (μg kg^{-1} DW) of DDT residues in sediment and shellfish from other New Zealand studies

Location	Sample type	Date sampled	No. of sites	pp'-DDT		pp'-DDE		pp'-TDE		Sum DDT		Reference
				Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Manukau Harbour	Sediment	1989	5	<0.02	1	0.02	0.45	<0.02	14	0.07	22	Holland *et al*., 1993
	NZ cockle	1989	5	<0.02	0.79	0.4	18	0.6	18	1.2	4.96	Hickey *et al*., 1995
	Sediment	1980s	5	0.1	0.1	0.3	0.8	0.1	0.6	1.2	4.3	Fox *et al*., 1988
	Sediment	1987	5	0.08	0.13	0.34	0.78	0.14	0.63	0.9	1.5	Hume *et al*., 1989
Waikareao Estuary	Sediment	1991-92	19	tr	0.5	0.2	1.2	0.1	0.5			Burggraaf *et al*., 1994
Tauranga Harbour	NZ cockle[a]	1992	11							3	180	Burggraaf *et al*., 1996
Avon-Heathcote Estuary	Sediment	1991	13	nd	0.30	nd	2	nd	1.1	0.06	3.84	Thomson and Davies, 1993
	NZ cockle	1991-92	13							0.5	13.5	Thomson and Davies, 1993

[a] Lipid basis.
tr = Trace.
nd = Not detected.

Table 8.2 Concentration ranges of lindane, chlordane, heptachlor epoxide and dieldrin residues (μg kg^{-1} DW) in sediment and shellfish from other New Zealand studies

Location	Sample type	Date sampled	No. of sites	γ-HCH		α-CHL		γ-CHL		Heptachlor epoxide		Dieldrin		Reference
				Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Manukau Harbour	Sediment	1989	5	0.03	0.5	<0.02	0.19	<0.02	0.22	<0.02	0.06	0.07	0.4	Holland *et al*., 1993
	NZ cockle	1989	5	0.4	5.5	0.5	12	0.6	9.2	<0.02	7.2	1.9	8.7	Hickey *et al*., 1995
	Sediment	1991	1			0.04	0.07	0.06	0.07					Simpson *et al*., 1996
	NZ cockle[a]	1991	1			35		26						Simpson *et al*., 1996
	Sediment	1980s	5	<0.1	1.4	0.2	1.3	0.3	1.6	nd	0.3	0.3	0.5	Fox *et al*., 1988
Waikareao Estuary	Sediment	1991-92	19			nd	tr					tr	7	Burggraaf *et al*., 1994
Tauranga Harbour	NZ cockle[a]	1992	11			nd	5							Burggraaf *et al*., 1996
Avon-Heathcote Estuary	NZ cockle	1991-92	13	nd	3.2	nd[b]	12.2[b]			nd	2.5	12.7		Thomson and Davies, 1993
	Sediment	1991	13	nd	0.30	nd	2	nd	1.1	0.06	3.84			Thomson and Davies, 1993

[a] Lipid basis.
[b] Sum α and γ chlordane
tr = Trace.
nd = Not detected.

Experiments involving the dosing of *in situ* sediments with technical chlordane have been undertaken to determine the effects on resident shellfish abundance and population structure (Pridmore *et al.,* 1992). It was concluded that technical chlordane affects macrofaunal abundance at low concentrations (7.5 ng CHL g^{-1} dry fines), and that bivalves were more affected than either polychaetes or crustacea. Pridmore *et al*., suggested that, for bivalves, the result may be due to behavioural-escape responses of juveniles (0.5 - 2.5 mm in size). However, they also suggested that the observed effects could not have been predicted from existing literature on chlordane toxicity.

8.2 Comparative international data

The results of numerous studies investigating concentrations of organochlorine pesticides in other countries are summarised in Tables J1 to J6, Appendix J, and compared with data from the current study in Figures 8.2 and 8.3.

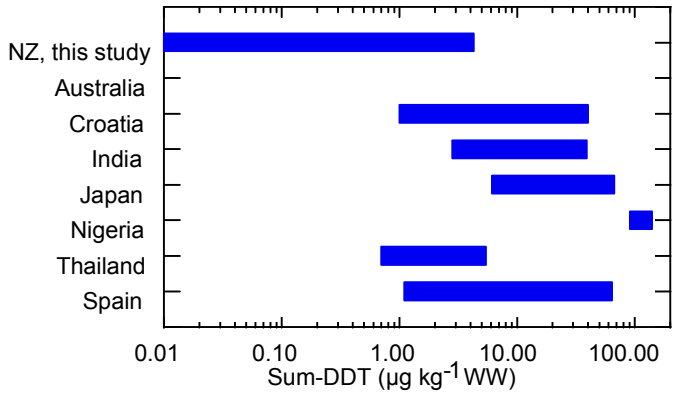


Figure 8.2 DDT concentrations in estuarine shellfish in New Zealand and other countries (data sources indicated in Table J2, Appendix J)

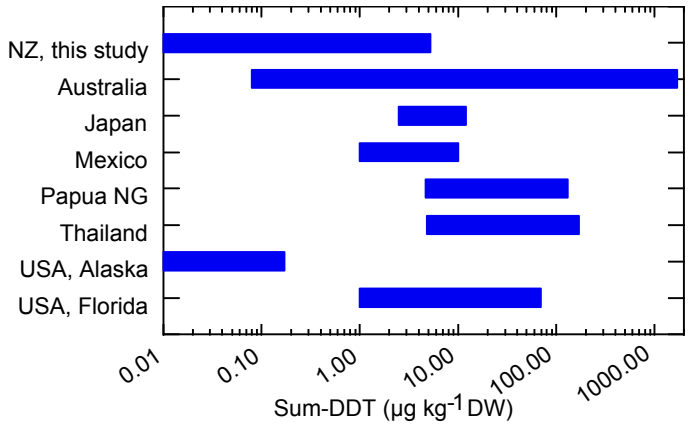


Figure 8.3 DDT concentrations in estuarine sediments in New Zealand and other countries (data sources indicated in Table J1, Appendix J)

Sediment DDT residues elsewhere in the Asia/Pacific region (Iwata *et al.,* 1994b) are appreciably higher than those in New Zealand. The very high DDT residues reported for Australia by Iwata *et al.* (1994b) only occurred at 2 sites (suburban NSW) of 19, the remainder having a similar range to those found in the current study.

DDT concentrations reported for shellfish in the French (Claisse, 1989) and United States of America (Stephenson *et al.,* 1995) Mussel Watch programmes were far higher than those reported in the current study.

8.3 Regulatory approaches

The regulation of pesticide residues in shellfish tissues is usually aimed at the protection of human health (Table 8.3). There are currently no New Zealand guidelines or standards specifically for the concentrations of organochlorine pesticides in shellfish other than a maximum residue limit for dieldrin and aldrin of 0.1 mg kg^{-1} WW.

Table 8.3 Regulatory limits for organochlorine pesticides in fish and fisheries products for the protection of human health (from MacDonald 1994)

Pesticide	Limit (mg kg^{-1} WW)	Country
ΣDDT	2-5	Denmark
	5	Canada
	5	Thailand
	5	United States
DDE	5	Canada
	5	United States
DDD	5	Canada
	5	United States
γ HCH (Lindane)	0.1	Canada
	0.2	Sweden
	2	Germany
	0.5	Iceland
	0.5	Thailand
Aldrin + dieldrin	0.1	Canada
	0.1	Sweden
	0.1 - 0.3	Thailand
	0.3	United States
	0.5 - 1	Germany
Chlordane	0.01	Germany
	0.1	Canada
	0.3	United States
Heptachlor + heptachlor epoxide	0.01	Germany
	0.1	Canada
	0.3	Thailand
	0.3	United States
HCB	0.2	Sweden
	0.5	Germany

Netherlands

In the Netherlands, a series of sediment quality objectives have been developed for environmental contaminants (Ministry of Housing, Spatial Planning and the Environment, 1994). Concentrations for organochlorine pesticides are shown in Table 8.4 (see also section 7.3).

Table 8.4 Sediment quality objectives and guidelines for organochlorine pesticides

Pesticide	Concentration (µg kg^{-1} DW)	Application	Country	Reference
pp'-TDE	1.22	Threshold effects concentration	Canada	Smith *et al.*, 1996
	7.81	Probable effects concentration		
pp'-DDE	2.07	Threshold effects concentration	Canada	Smith *et al.*, 1996
	374	Probable effects concentration		
pp'-DDT	1.19	Threshold effects concentration	Canada	Smith *et al.*, 1996
	4.77	Probable effects concentration		
ΣDDT	3.89	Threshold effects concentration	Canada	Smith *et al.*, 1996
	51.7	Probable effects concentration		
	2.5	Target value	Netherlands	MoHSPE[1], 1994
	10	Limit value		
	400	Intervention values		
Dieldrin	0.715	Threshold effects concentration	Canada	Smith *et al.*, 1996
	4.30	Probable effects concentration		
	0.5	Target value	Netherlands	MoHSPE, 1994
	20	Limit value		
	400	Intervention value (aldrin + dieldrin)		
Chlordane	2.26	Threshold effects concentration	Canada	Smith *et al.*, 1996
	4.79	Probable effects concentration		
	10	Target value	Netherlands	MoHSPE, 1994
	20	Limit value		
	500	Intervention value		
Heptachlor + heptachlor epoxide	2.5	Target value	Netherlands	MoHSPE, 1994
	20	Limit value		
	500	Intervention values		
γ- HCH (lindane)	0.32	Threshold effects concentration	Canada	Smith *et al.*, 1996
	0.99	Probable effects concentration		
	0.05	Target value	Netherlands	MoHSPE, 1994
	1	Limit value		
	200	Intervention values (all isomers)		

[1] Ministry of Housing, Spatial Planning and the Environment.

All sediment samples were well below the Dutch sediment quality target values for all pesticides determined in this study, except sum DDT. The sum of DDT concentrations in the sample from Moutere Inlet (south/south east) at 5.22 µg kg^{-1} DW exceeded the target value of 2.5 µg kg^{-1} DW but was lower than the limit value of 10 µg kg^{-1} DW.

Canada

Environment Canada has developed interim national guidelines for marine sediment quality (Smith *et al.* 1996). The guideline concentrations, shown in Table 8.4, were developed using a modified version of the "weight of evidence" approach based on available toxicological data derived from

field studies (Long *et al.* 1995). The Canadian approach also includes spiked sediment toxicity data, and assesses the influence of sediment characteristics on the bioavailability of chemicals. The threshold effects concentration (TEL) is the concentration at which adverse effects are rarely expected to occur. The probable effects concentration (PEL) is the concentration at which adverse effects are frequently expected to occur.

For total DDT, Smith *et al.* (1996) found the incidence of adverse effects occurring below the TEL was high (48%), indicating that this value may not adequately represent a minimal effects range. The incidence of adverse effects did not increase markedly between the TEL and PEL for total DDT. For the other pesticides listed in Table 8.4, the incidence of adverse effects increased significantly with increased concentration. Therefore the TEL and PEL values for these chemicals are considered to adequately represent the concentrations at which adverse effects are either not expected to occur or are likely to occur.

In the current study, concentrations of all pesticides in sediments, except pp'-TDE and pp'-DDE, were below their respective TEL values. The sediment sample from the south/south east side of Moutere Inlet exceeded the TEL for pp'-TDE, pp'-DDE and total DDT.

8.4 Summary

Based on the diverse sites sampled in this study, organochlorine pesticide concentrations are low in New Zealand sediments and shellfish. Nearly a third of the sediments contained none of the pesticides tested for in detectable amounts. More shellfish samples contained residues, but this is consistent with their ability to bioaccumulate lipophilic contaminants. The major organochlorine pesticide residues in New Zealand sediments are those originating from DDT. These are an order of magnitude higher than other pesticide residues, but are nevertheless low by international standards.

9 Chlorophenols

9.1 New Zealand data

In almost all cases, the chlorinated phenolic compounds investigated in the current New Zealand estuarine study were below the analytical limits of detection of 0.3 - 0.4 μg kg^{-1} DW for sediment and 0.1 - 0.3 μg kg^{-1} WW for shellfish. Pentachlorophenol was measured in sediment from Hellyers Creek and Wairau Estuary, and in shellfish from Manukau Harbour and Avon-Heathcote Estuary. In all cases, the levels were close to the analytical limit of detection.

9.1.1 Other New Zealand data

Few estuarine studies have included analyses for chlorophenols. As part of its review of water quality in the Tamaki Estuary in 1989-90, the Auckland Regional Council (ARC, 1992) reported total chlorophenol concentrations of 0.8 - 12.0 μg kg^{-1} DW in sediments, and 4.3 - 19.1 μg kg^{-1} DW in oysters. These are mean values obtained from sampling six sites within the estuary. One of the findings of the review was the presence of a contaminant gradient from the inner to outer reaches of the estuary.

Judd *et al.* (1996) reported a concentration of 1.6 μg kg^{-1} DW for sediments in the Matata Lagoon. This equates to 10 μg kg^{-1} normalised to organic carbon from data in the original report (16% loss on ignition). This lagoon is at the mouth of the Tarawera River (which is a recipient for pulp and paper mill effluent discharges), but has been cut off from the river since the 1960s (Judd *et al*., 1996).

Data for the Avon-Heathcote Estuary were reported by Thomson and Davies (1993).

9.2 Comparative international data

Direct comparisons with overseas literature results are complicated by the fact that the New Zealand samples were almost all below the specified limits of detection, and it is difficult to determine which of the overseas studies were performed on non-impacted sites. For the shellfish samples there is the additional problem that there is only one other report investigating chlorophenol concentrations in oysters - all other studies were of different species.

In spite of these restrictions, it can be generally concluded that background New Zealand chlorophenol concentrations in estuarine sediment (as represented by the current study's limits of detection) are at the lower end of results reported from overseas studies (Table I1 and I2, Appendix I). Similarly, background concentrations of chlorophenols in New Zealand samples of oysters and cockles are at the lower end of results reported for similar shellfish species.

9.3 Regulatory approaches

As discussed in Section 8.3, the Ministry of Housing, Spatial Planning and the Environment (1994) have developed sediment quality objectives for sediments in the Netherlands for a range of chemicals. The values for chlorophenols are shown in Table 9.1.

Table 9.1 Sediment quality objectives for chlorophenols in the Netherlands

Chlorophenol group	Concentration (µg kg^{-1} DW)	Application
Pentachlorophenol	2	Target value
	20	Limit value
	500	Intervention value
Tetrachlorophenols	1	Target value
	90	Limit value
Trichlorophenols	1	Target value
	100	Limit value

Chlorophenol concentrations in all sediments sampled in this study were below the Dutch values.

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Appendix A Status of organochlorines in New Zealand

This appendix provides a brief chronology and a summary of relevant New Zealand legislation for the polychlorinated biphenyls (PCBs) and organochlorine pesticides which are being studied as part of the Organochlorines Programme. Its purpose is solely to provide background information to the reader. It is not a comprehensive history of PCBs or persistent organochlorine pesticides in New Zealand.

Table A1 Summary of relevant New Zealand legislation for PCBs from 1979 to present

Year	Legislation/Publication	Regulatory status	Comments
1979	Toxic Substances Act	Establishes Toxic Substances Board: provides advice to Minister and Director-General of Health on wide range of matters associated with human health and the environment in relation to toxic substances within various schedules, and advises the Minister accordingly on matters relating to the scheduling, sale, labelling, storage, licensing and importation of toxic substances.	No immediate effect on PCBs, but see later regulations under the Act.
1984	The Electrical Supply Regulations	Labels required on equipment containing PCBs with cautions to handle with care; transformers that had previously been filled with PCB required to have details of time and name of substance replacing the PCB, the date of the treatment to reduce PCB residues, and the tested level of PCB residue remaining in ppb.	The Electrical Supply Regulations revoked April 1993 by s. 173(3) of the Electricity Act 1992.
1984	United Nations	UN recommendations on the Transport of Dangerous Goods identified PCBs under Class 9 No. 2315. Interdepartmental group agreed, in 1985, that Class 9 is inappropriate for PCBs and recommended PCBs be classified as Class 6: toxic substance packing group 2.	This specified the type of hazard warning label required in New Zealand when transporting PCBs, applied to the truck carrying PCBs as well as to each PCB container or drum during transport.
1986	The Toxic Substances Regulations 1983, Amendment No. 1	Controls placed on importation of PCBs.	Customs Department prohibits importation of PCBs in March 1986 and the import controls were incorporated into Amendment No. 1 in December 1986.
1987	OECD and UNEP Guidelines	NZ is obliged to meet OECD and UNEP guidelines on use and disposal of PCBs.	
1988	The Toxic Substances Regulations 1983, Amendment No. 3	Imposed controls on PCBs. Owners of PCBs were required to notify the Medical Health Officer up until 1 June 1989. Strict safety criteria on storage and disposal of PCBs (and continued prohibition on importation). Controls on PCBs were to ensure that all PCBs were phased out over the next five years, with prohibition on both use and storage effective from 1 January 1994 (but see below for extensions of this date). Code of practice "*Safe Management of PCBs*" was released by the Department of Health.	On application, the Director of the Toxic Substances Act 1979 may exempt companies from the use and storage prohibition on PCBs. However, storage and handling of PCBs must conform at all times with the code of practice "*Safe Management of PCBs*" in order to qualify for the exemption.
1988	The Toxic Substances Regulations 1983, Amendment No. 3, Sec. 54A.	The legislation (s.54) provides people who adhere to the code of practice "*Safe Management of PCBs*" a special defence against conviction under the PCB regulations relating to storage, use, transportation and disposal of PCBs. Transportation of all PCB material must comply with the requirements of NZS: *5433 "Code of Practice for the Transportation of Hazardous Substances on Land*".	

Year	Legislation/Publication	Regulatory status	Comments
1993	The Toxic Substances Regulations 1983, Amendment No. 4	Use of PCBs is prohibited from 1 January 1994. Storage of PCBs is prohibited effective from 1 August 1994. Disposal and storage of PCBs must comply with the Code of Practice.	The Code of Practice "*Safe management of PCBs*" was reprinted in 1993. A revision of the disposal policy resulted in the disposal of small amounts of PCB at suitable landfills being considered to be environmentally unacceptable.
1994	The Toxic Substances Regulations 1983, Amendment No. 5	PCB storage deadline extended by one year, to 1 August 1995, to give owners of PCB-containing equipment more time to safely dispose of their PCB holdings.	The Basel convention in 1992, covering the control of trans-boundary movement of hazardous wastes and their disposal, led to delay in export of PCBs from New Zealand to France for destruction. This effectively meant there was no disposal option for PCB owners in New Zealand between 1992 and 1994, hence the need to extend the storage deadline.

Table A2 Status of organochlorine pesticides in New Zealand

Included substances	Year	Legislation/Publication	Regulatory status	Comments
All potential stock remedies	1934	The Stock Remedies Act	Appoints a board of control, The Stock Remedies Registration Board. All remedies must be registered with details of properties attached to packages; inspectors given powers to sample and analyse.	A stock remedy is defined as any substance used to prevent or cure disease, or to destroy pests in stock, or to improve stock health (not including food).
All stock remedies and pesticides	1934	The Agricultural (Emergency Powers) Act	Regulates marketing and production of agricultural products and provides provision for financing the use of substances for the eradication of disease in dairy herds under special circumstances.	
Aldrin, Chlordane, DDT, Dieldrin, Endrin, HCB, PCP, Toxaphene	1934	The Poisons Act (Schedule 4)	General controls on registration and carriage of substances listed in the Act schedules. Only licensees can sell these substances at wholesale, and only professionals can sell them at retail.	Schedule 4 was reprinted (as S.R. 1952/45) specifying these pesticides and other chemicals.
All agricultural and horticultural pesticides and weed killers	1937	The Poisons (General) Regulations (Schedule 3)	Under the Poisons Act 1934. General controls on sales, importation, carriage and use: stringent labelling, packaging, invoicing requirements; Governor-General given powers to regulate aspects of sale, importation, carriage and use.	Removes the agricultural/horticultural chemicals under schedule 4 of the Act and places them under schedule 3. Stronger regulations thus apply.
DDT	1945		Early trials as a pesticide.	
DDT	1947		Residue results published.	
DDT	1951		Use as pesticide mixtures with fertiliser widespread for treatment of pasture.	
Aldrin, Dieldrin	1954	Under the Stock Remedies Act (1934)	Introduced to NZ and licensed as stock remedies.	
Agricultural chemicals	1959	Agricultural Chemicals Act	Establishes Agricultural Chemicals Board. All agricultural chemicals required to be registered including stringent requirements on labelling, packaging, sales, advertising, warranties; registrations able to be revoked for substances likely to prejudice health and safety of humans, stock or beneficial species.	This Act covers all agricultural chemicals defined as substances or mixtures sold for the purpose of controlling insect pests, plant diseases and weeds in agriculture and horticulture and for influencing plant growth or behaviour.

Included substances	Year	Legislation/Publication	Regulatory status	Comments
Aldrin, Dieldrin	1961	*Gazette*, March 1961	Department of Agriculture (under The Stock Remedies Act) advises that it intends to revoke licences for all preparations containing aldrin or dieldrin. The revocation, however, is unable to be implemented without changing the legislation.	The Agricultural (Emergency Powers) Act (1934) still allows limited finance for the rehabilitation of the dairy industry and some other emergencies.
DDT	1961	The Agricultural Chemicals (Insecticides) Regulations	Specifies strict terms for application of DDT on farm land: only pelleted formulations allowed; application required to be in accord with strict limits to acreage, pasture type, time and rate of application.	
Specified organochlorine insecticides	1961	The Agricultural Chemicals (Insecticides) Regulations	Permit required from Department of Agriculture to use organochlorine pesticides on farm land.	Still legal to use for non-agricultural (i.e. residential, horticultural) pest control without permits. Industrial pest control and timber treatment uses not within the scope of the Act.
DDT	1961	The Agricultural Chemicals (Insecticides) Notice	Placed more stringent permit requirements on use of DDT: specifies dry/dust application only, application forbidden on pasture where stock are grazing, specifies stand down periods for when pasture can subsequently be grazed, specifies strict acreage controls and packages containing DDT formulations required to have clear instructions attached.	
All pesticides	1961	The Stock (Insecticides and Oestrogens) Regulations	Under the Agricultural (Emergency Powers) Act, 1934, all uses of stock treatments subject to general regulations. Users must supply on general request, to the Director-General of Agriculture, information on intended use, and details of the substance.	
Aldrin, Dieldrin, DDT, Lindane (BHC)	1961	*Gazette*, September 1961	Prohibition of selected substances as active ingredients in stock treatments under the Stock (Insecticides and Oestrogens) Regulations 1961.	
BHC (mixed isomers)	1962	*Gazette*, June 1962	Last product withdrawn.	

Included substances	Year	Legislation/Publication	Regulatory status	Comments
DDT	1963	The Agricultural Chemicals (DDT Pellets) Notice	Further restrictions on types of formulations and terms of application allowed: no dust formulations; liquid and wettable powders subject to permits and restricted to commercial horticultural use.	
DDT	1964	The Agricultural Chemicals (Insecticides) Notice	Further restrictions on allowable pellet formulations and terms of application.	
Aldrin, Dieldrin	1963-1964			Disposed of by spraying on Government Land and Survey blocks in 6 areas around New Zealand.
Aldrin, Dieldrin	1964	*Gazette*, January 1964	Application in dust form no longer permitted.	Disposal by spraying of Land and Survey blocks ceased but some special dispensations were allowed.
Aldrin, Dieldrin	1966		Agricultural Chemicals Board recommends no further permits for use on agricultural land. By November 1966 no more permits were issued for agricultural use by the Department of Agriculture.	
Animal remedies	1967	Animal Remedies Act	Establishes Animal Remedies Board. Consolidates and amends the Stock Remedies Act (1934); prohibition on manufacturing, selling, importing, using an animal remedy without a licence; stringent labelling, container, advertising requirements; accuracy of information required.	An animal remedy is defined as any substance used to cure or treat disease, to destroy or prevent parasites, to maintain or improve health in animals.
All OC pesticides	1968	The Agricultural Chemicals Regulations	General controls on sales, permits, transport, storage; powers given to inspectors.	
Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Toxaphene	1968	The Agricultural Chemicals Regulations	14 week withholding period for livestock from pasture treated with these pesticides.	
DDT	1968	The Agricultural Chemicals Regulations	Restrictions on amount of DDT allowed in packages for home garden use; 12 week withholding period placed on livestock.	

Included substances	Year	Legislation/Publication	Regulatory status	Comments
Lindane	1968	The Agricultural Chemicals Regulations	6 week withholding period for livestock from pasture treated with these pesticides.	
DDT	1968	The Agricultural Chemicals Notice, June 1968	Further limits placed on DDT formulations including stricter control on permits, pasture types allowed, dry conditions, pellet sizes, abrasion criteria on pellets and acreage allowable. Use on dairy land is prohibited.	Permits were required for use on dairy land but none were issued (an effective prohibition). For other uses a permit was required but few permits were issued.
Aldrin, Chlordane, Dieldrin, DDT, Lindane	Up to 1970		Non-agricultural uses (timber and industrial pest control) not within the scope of the Agricultural Chemicals Act.	Heavy use of these substances for non-agricultural, industrial purposes during this period, also in timber treatment for borer control (dieldrin, DDT, chlordane). Lindane used as timber preservative.
Heptachlor, Endrin, Toxaphene	Up to 1970			Limited use only, from the time of introduction of products containing these substances, up to 1970.
DDT, Lindane	1970	The Agricultural Chemicals (Pelleted Insecticides Specification) Notice	Specifies sizes, densities, abrasion criteria to be met, and standard testing methods for these.	
DDT	1970	Revocation of Agricultural Chemical Notice 1968	All remaining DDT purchase and use subject to Department of Agriculture permit.	Permits then issued only for limited horticulture use where non-organochlorine pesticides were ineffective.
Heptachlor	1971	*Gazette*, September 1971	Last product withdrawn.	
HCB	1972	*Gazette*, October 1972	HCB deregistered for use as a horticultural pesticide, making it no longer legal to sell, manufacture or use HCB as a pesticide; thus effectively banned.	Between 1970 and 1972 HCB had only limited registration.
Aldrin, Dieldrin	1975		Agricultural Chemicals Board recommends the cessation of permit issuing for any use. The Department of Agriculture ceases issuing permits. This amounts to an effective ban for agricultural usage because usage required a permit in most cases.	It is not certain whether any more permits were in fact issued or not by the Department of Agriculture, unofficial sources suggest that indeed none were issued after this date.

Included substances	Year	Legislation/Publication	Regulatory status	Comments
Endrin	1976	*Gazette*, October 1976	Last product withdrawn.	
All pesticides	1979	Pesticides Act	Establishes Pesticides Board. No sales can be made unless the substance is registered with Pesticides Board; the Board can revoke registration; stringent requirements placed on labels, packaging, warranties, advertising, transport, and application methods.	The Agricultural Chemicals Board had had a confirmed policy to phase out all OC pesticides a policy which is endorsed by the now appointed Pesticides Board.
OC pesticides	From 1979	Pesticides Act		The phasing out of OC pesticides was managed gradually by the Pesticides Board. First by permit control and then by deregistering of specific products containing OC formulations.
Refer to schedules under the Regulations	1979	Toxic Substances Act	Establishes Toxic Substances Board. Empowers Department of Health to classify substances; sales restricted; Minister of Health can prohibit imports, sales, manufacture, possession and use; stringent requirements placed on labelling, packaging, advertisement, storage, invoices. Importers must notify Department of Health Officers and provide Customs with details of the substances.	Enforcement of importation restrictions has been largely up to the vigilance and discretion of Customs officers.
All OC pesticides	1983	The Pesticides Regulations	Permits are required to sell or use scheduled pesticides with exceptions for chlordane, DDT and lindane. No livestock are allowed near premises where pesticides are kept.	The Board polices the phase out of all OCs as suitable alternatives become available. Carry-over of earlier restrictions and extension of these to cover non-agricultural uses (e.g. timber treatment and industrial pest control).
Chlordane, DDT, Lindane	1983	The Pesticides Regulations	Allowed without permit for domestic use.	
Chlordane	1983	The Toxic Substances Regulations (Schedules 3-4)	Licensees must specify usage and nature of substances sold or purchased. Other stringent controls on handling, carriage, importation, labelling etc. apply. Information must be supplied to Officers (of the Act) under request. There are restrictions on who can act as an agent for the licensees.	Schedules 3 and 4 are classified as "standard poisons" and "harmful substances" respectively. Electrical equipment has exemptions.
Aldrin, DDT, Dieldrin, Lindane, PCP	1983	The Toxic Substances Regulations (Schedules 1-2)	Sales of these substances must be recorded in a "Sale of Poisons" book. Stricter criteria on advertising, storing, labelling also apply to substances in this schedule.	Schedule 1 are "deadly poisons" and Schedule 2 are "dangerous poisons".

Included substances	Year	Legislation/Publication	Regulatory status	Comments
Aldrin	1985	*Gazette*, September 1985	Last product withdrawn.	
PCP	1988			PCP use ceased voluntarily in the timber treatment industry.
DDT	1989	*Gazette*	The last remaining products containing DDT deregistered by the Pesticides Board, effective as from 31 December 1989.	This means it is illegal to use DDT as a pesticide. Other novel uses are legal, subject to existing legislation (e.g. Toxic Substances Regulations), (e.g. as an anti-cancer agent in the 1970s).
Dieldrin	1989	*Gazette*	The last remaining dieldrin products deregistered by the Pesticides Board.	This means it is illegal to use dieldrin as a pesticide.
Chlordane	1989		Application for registration of chlordane products declined by the Pesticides Board.	It is illegal to sell, manufacture or import chlordane for use as a pesticide.
Lindane	1990	*Gazette*, December 1990	Last remaining lindane products deregistered and the substance effectively banned.	
PCP	1991	*Gazette*	The last remaining PCP product deregistered by the Pesticides Board.	This makes it illegal to use PCP as a pesticide, but other uses are presumably allowable subject to Toxic Substances Regulations.
PCP	1992	*Gazette*, May 1992	Pesticides Board agrees in principle to the tightly controlled use of PCP in timber treatment plants subject to stringent environmental protections, particularly of waste materials. The agreement to use in principle required a "closed circuit" of PCP and PCP product to be maintained.	Conditions set by the Pesticides Board have not been taken up and currently no PCP-based products are registered. Thus PCP use as a pesticide is not permitted, and it is effectively banned.

Appendix B Sampling programme

This appendix provides further detail on sampling locations used in this study; biometric data for shellfish; and results of grain size and total organic carbon data for sediments.

Table B1 Summarised data from field logs

Harbour	Site name	Map ref.[1]	Sampling time (ddmmyy)	Samples	Weather	Comments
Parengarenga Harbour	Akatarere Point	N02/062,404-066,406	290596	1 x SEDIMENT 5 x SEDIMENT (blind duplicate) 1 x SHELL	Light air, 1-3 knots northerly, 7/8 cloud cover, fine, previously fine	The shellfish were cockles.
	Oriatou Point	N02/069,393-071,391	290596	1 x SEDIMENT 1 x SHELL	Light NW breeze 4-6 knots, 5/8 cloud cover, fine, previously fine	The shellfish were cockles.
Whangarei Harbour	Mangapai River mouth	Q07/308,960-314,965	160596	1 x SEDIMENT 1 x SHELL	Moderate SW breeze, 6/8 cloud cover, fine, previously showers	The shellfish were oysters.
	Limestone Island	Q07/336,013-339,010	160596	1 x SEDIMENT 1 x SHELL	Moderate SW breeze, 6/8 cloud cover, fine, previously showers	One of the sediment stations had a rock shelf below 40 mm depth. The shellfish were oysters.
Manukau Harbour	Grannys Bay Wesley Bay Waikowhai Bay Wattle Bay	R11/642,725-668,730	080596	1 x SEDIMENT 1 x SEDIMENT (field blank) 1 x SHELL 1 x SHELL (blind duplicate)	Fine, sunny, high broken cloud, westerly of 5 knots	The mud was reasonably gritty. The shellfish were cockles. Blind duplicate samples were collected from only one of five sampling stations. Cockles were collected for the 4 remaining BD sample sites on 170596.
	Big Muddy Creek	R11/545,678-548,681	090596	1 x SEDIMENT 1 x SHELL	Dense cloud, gusty wind, SW at about 15 knots	The tide rose quite rapidly and limited the sampling. Two bags of oysters were taken from beds 50 m west of sites, three bags of cockles were hand collected within 8 m^2 areas and were of average size.

Harbour	Site name	Map ref.[1]	Sampling time (ddmmyy)	Samples	Weather	Comments
Manukau Harbour	French Bay, Paturoa Bay, Perkins Bay, Little Muddy Creek	R11/570,697-588,710	100596	1 x SEDIMENT 1 x SHELL	Fine, sunny, no cloud, 2-3 knot SE wind	The tide rose quite rapidly and limited the sampling. The shellfish were cockles and were hand collected within 1-2 m^2 areas and were of average size. At some sites no cockles were found so cockles were collected from nearby sandier sites.
Waitemata Harbour	Hellyers Creek (upper reaches)	R11/615,898-623,906	020596	1 x SEDIMENT 1 x SHELL	Fine, blue sky, 5 knot SW wind	The mud was very soft and made it hard to keep things clean. The shellfish were oysters.
	Hellyers Creek (lower reaches)	R11/601,892-612,897	030596	1 x SEDIMENT 1 x SHELL	Fine, blue sky, 5 knot SW wind	A boat was used to reach sites, which made the sampling cleaner. The shellfish were cockles.
Kawhia Harbour	North shore on State Highway 31	R15/751,487	100696	1 x SEDIMENT 1 x SEDIMENT (field blank) 1 x SHELL	Cloudy and raining, no wind	The shellfish were oysters collected along the shoreline, 50-70 m from sediment sample sites.
	South shore opposite Maire Point	R16/708,385	100696	1 x SEDIMENT 1 x SHELL	Cloudy, slight rain, no wind	Similar procedure used as for Kawhia north shore sampling. The shellfish were oysters.
Tauranga Harbour	Hunters Creek	U14/904,860-912,864	020596	1 x SEDIMENT 1 x SHELL	Fine, sunny, 1/10 cloud cover, moderate to strong SE wind	The shellfish were cockles.
	Town Reach, opening of Waipu Bay	U14/845,934-857,935	020596	1 x SEDIMENT 1 x SHELL	Fine, 1/10 cloud cover, 20 knot SSW wind	The shellfish were cockles.
	Waikareao Estuary	U14/888,857-891,862	020596	1 x SEDIMENT 1 x SEDIMENT (blind duplicate)	Fine, 1/10 cloud cover, 20 knot SSW wind	Both sediment samples were collected for only 4 out of 5 sample sites. A follow up sampling for the remaining site was carried out on the date of 060596 at grid ref. U14:847,882.
		U14/887,861-892,873		1 x SHELL		The shellfish were cockles.

Harbour	Site name	Map ref.[1]	Sampling time (ddmmyy)	Samples	Weather	Comments
Wairau Estuary	Arapipi Channel	P28/956,658-986,659	140596	1 x SEDIMENT 1 x SEDIMENT (rinsate blank) 1 x SHELL	Overcast, breezy, NW wind	The shellfish were cockles.
	Morgans Creek/Budges Island channel	P28/993,633-996,639	140596	1 x SEDIMENT 1 x SHELL	Overcast, still	The cockles were collected outside the sediment site area. Hard to find the cockles but some were located in a narrow sand strip alongside the main channel into the lagoon.
Whanganui Inlet	Southern section of Inlet	M25/687,642-693,653	150596	1 x SEDIMENT 1 x SHELL	Fine, clear sky, 10 to 15 knot SW wind	Sediments were mud plus fine sand. 90% of cockles were collected from within 50 m of sediment sample locations. The shellfish were cockles.
	South of Inlet entrance	M25/697,651-706,657	150596	1 x SEDIMENT 1 x SHELL	Fine, clear sky, 5 to 10 knot SW wind	Sites were similar to south inlet; the second sample site was slightly sandier here though. The shellfish were cockles.
Moutere Inlet	South/south east	N27/136,027-143,044	140596	1 x SEDIMENT 1 x SHELL 1 x SHELL (blind duplicate)	Overcast with drizzle, calm	The sediment was of glutinous mud type and samples were taken from about 0.5 to 1.5 m below the MHWS. The shellfish were cockles.
	South west of Jackett Island	N27/121,057-128,066	140596	1 x SEDIMENT 1 x SHELL	Fine, overcast, variable wind below 5 knots	The sediment was of glutinous mud type and samples were taken from about 0.5 to 1.5 m below the MHWS. The shellfish were cockles.
Avon-Heathcote Estuary	McCormacks Bay outlet	M25/880,416	060596	1 x SEDIMENT 1 x SHELL 1 x SHELL (blind duplicate)	Fine, sunny, no cloud, light NE wind	Sampling was done in a 200 m radius. The shellfish samples were cockles.
	Opposite Pleasant Point Domain	M36/881,391	060596	1 x SEDIMENT 1 x SHELL	Fine, sunny, no cloud, very light NE wind	Sampling was done in a 200 m radius. The shellfish samples were cockles.

Harbour	Site name	Map ref.[1]	Sampling time (ddmmyy)	Samples	Weather	Comments
Otago Harbour Estuary	Rocky Point	I44/265,864-267,866	141196	1 x SEDIMENT 1 x SEDIMENT (blind duplicate) 1 x SHELL	Fine, sunny, little cloud, light SE wind	The harbour area consisted of a sandy deposit next to the main shipping channel, uninhabited and unused. A peg and rope were used to mark circular sample areas. The shellfish were cockles.
	Tayler Point	I44/292,876-297,884	141196	1 x SEDIMENT 1 x SHELL	Fine, sunny, gathering cloud, light SE wind	Similar conditions as at Rocky Point site. The shellfish were cockles.
New River Estuary	Bushy Point	E47/525,057-529,062	181196	1 x SEDIMENT 1 x SEDIMENT (field blank) 1 x SEDIMENT (rinsate blank) 1 x SHELL	Overcast, light SW wind	The sampling sites were uninhabited, unused mudflats. Cockles were not found at the sediment station; when some were located the tide was in and the field workers were in ankle deep water.
	Whalers Bay	E47/505,029-506,032	181196	1 x SEDIMENT 1 x SHELL	Overcast, moderate westerly wind	Samples were taken close to the water edge. Sample sites were near a recreation area with plenty of summer activity. The shellfish were cockles.

[1] NZMS 260 Series (1:50,000).

Table B2 Shellfish characteristics: lipid content, moisture content and size

Location	Site	Species[a]	Number collected	Lipid content (%)	Moisture content (%)	Mean length (mm)	Mean width (mm)
Parengarenga Harbour	Akatarere Point	cockle	255	0.69	90.6	31	28
	Oriatou Point	cockle	255	0.68	90.8	31	27
Whangarei Harbour	Mangapai River mouth	oyster	130	1.43	90.2	69	45
	Limestone Island	oyster	130	0.89	91.7	64	42
Manukau Harbour	Grannys, Wesley, Waikowhai, and Wattle Bays	cockle	216	1.08	88.7	24	21
	Big Muddy Creek	cockle	75	0.77	90.8	28	25
	French, Paturoa, and Perkins Bays: Little Muddy Creek	cockle	200	0.73	90.4	26	23
Hellyers Creek	Upper reaches	oyster	115	0.90	91.8	57	35
	Lower reaches	cockle	285	0.87	90.1	18	16
Kawhia Harbour	North shore SH31	oyster	180	0.58	93.9	55	35
	South shore opp. South Maire Pt	oyster	180	0.53	94.9	52	34
Tauranga Harbour	Hunters Creek	cockle	250	0.52	93.3	32	28
	Town reach, opening of Waipu Bay	cockle	250	0.69	91.6	33	29
	Waikareao Estuary	cockle	250	0.62	92.7	25	22
Wairau Estuary	Arapipi Channel	cockle	175	0.88	90.6	33	30
	Morgans Creek/Budges Island channel	cockle	118	0.79	89.9	26	25
Whanganui Inlet	Southern section of inlet	cockle	400	0.32	93.6	21	19
	South of inlet entrance	cockle	400	0.46	93.0	22	19
Moutere Inlet	South/Southeast	cockle	255	0.33	94.3	26	23
	SW of Jackett Island	cockle	255	0.41	93.3	26	24
Avon-Heathcote Estuary	McCormacks Bay outlet	cockle	200	0.83	90.8	41	37
	Opp. Pleasant Point	cockle	250	0.66	93.3	34	31
Otago Harbour Estuary	Rocky Point	cockle	189	1.13	88.4	43	38
	Tayler Point	cockle	165	1.02	86.2	51	45
New River Estuary	Bushy Point	cockle	220	1.31	89.4	29	27
	Whalers Bay	cockle	213	1.45	87.1	28	26

[a] Cockle = *Austrovenus stutchburyi;* oyster = C*rassostrea gigas*.

Table B3 Sediment characteristics: organic carbon, grain size

Location	Site	(%) TOC	(%) Sand	(%) Silt	(%) Clay
Parengarenga Harbour	Akatarere Point	0.19	99.60	0.41	0.00
	Oriatou Point	0.16	99.30	0.70	0.00
Whangarei Harbour	Mangapai River mouth	0.98	50.39	27.88	21.73
	Limestone Island	1.18	42.58	31.18	26.24
Manukau Harbour	Grannys, Wesley, Waikowhai, and Wattle Bays	0.72	59.40	29.19	11.41
	Big Muddy Creek	0.40	91.05	7.23	1.72
	French, Paturoa, and Perkins Bays: Little Muddy Creek	0.67	73.38	19.43	7.19
Hellyers Creek	Upper reaches	1.87	26.07	35.85	38.08
	Lower reaches	0.95	61.01	18.40	20.50
Kawhia Harbour	North shore SH31	0.76	55.47	32.06	12.47
	South shore opp. South Maire Pt	0.68	25.67	56.57	17.76
Tauranga Harbour	Hunters Creek	0.27	90.86	8.16	0.98
	Town Reach, opening of Waipu Bay	0.20	97.25	2.75	0.00
	Waikareao Estuary	0.62	83.25	13.06	3.70
Wairau Estuary	Arapipi Channel	0.19	89.62	7.47	2.91
	Morgans Creek/Budges Island channel	0.46	33.05	52.55	14.40
Whanganui Inlet	Southern section of inlet	1.20	32.33	63.75	3.92
	South of inlet entrance	1.44	38.03	54.04	7.93
Moutere Inlet	South/southeast	0.73	35.04	43.00	21.96
	SW of Jackett Island	0.77	30.49	53.38	16.13
Avon-Heathcote Estuary	McCormacks Bay outlet	0.18	97.11	2.89	0.00
	Opp. Pleasant Point	0.37	78.64	16.61	4.75
Otago Harbour Estuary	Rocky Point	0.15	97.66	1.80	0.55
	Tayler Point	0.11	98.65	1.35	0.00
New River Estuary	Bushy Point	0.23	95.58	1.88	2.54
	Whalers Bay	0.16	91.79	3.90	4.31

Appendix C Analytical methods

This appendix describes the methods of analysis of estuarine sediment and shellfish samples including determination of the following organochlorines:

- Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)
- Polychlorinated biphenyls (PCBs)
- Organochlorine pesticides
- Chlorophenols

C1 Organochlorine contaminants

C1.1 Sample preparation

C1.1.1 Sediment

Samples were stored at 4 ºC pending analysis. Each sediment sample was collected into a number of individual sample jars. For each jar, the sediment was sieved through a 2 mm sieve and the extraneous matter was discarded. The sediment was then thoroughly homogenised by mixing. An equal portion of sieved, homogenised, sediment from each jar was taken and mixed thoroughly (Figure C1). Moisture determinations were carried out on the composite sample by oven drying at 105 ºC to constant weight. Analysis for PCDDs, PCDFs, PCBs and organochlorine pesticides was undertaken on an air dried sample. Analysis for chlorophenols was undertaken on the field moist sample.

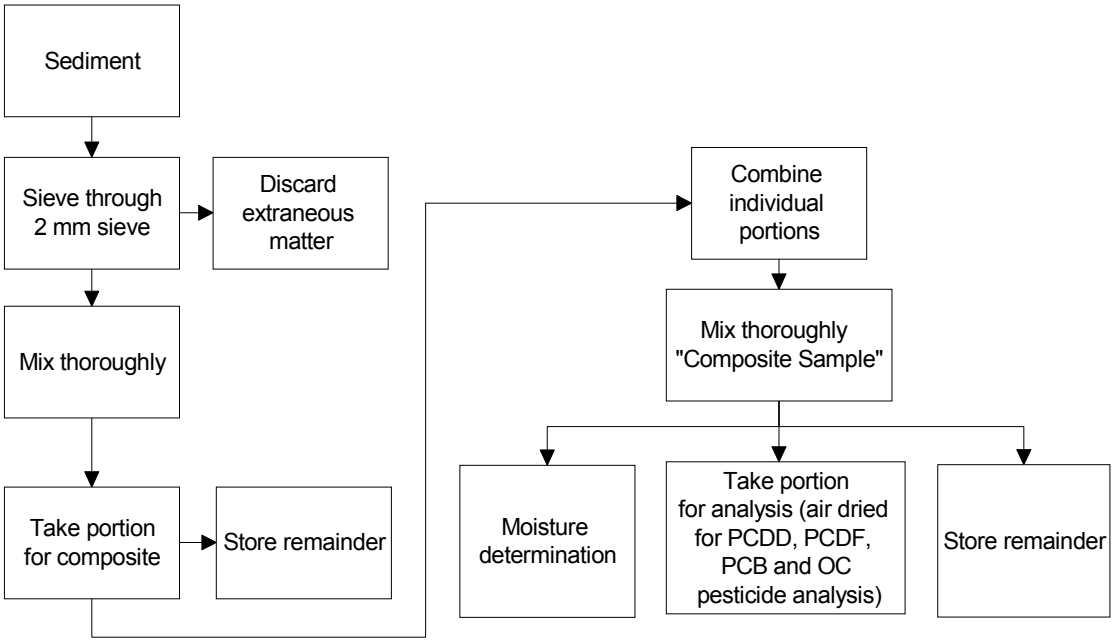

Figure C1 Preparation of composite sediment samples

C1.1.2 Shellfish

Each shellfish sample consisted of a minimum of 75 individuals. The length and width of each individual were recorded. Each shellfish was then shucked and the flesh was composited and freeze dried to form the analytical sample.

Moisture determination was carried out on the composite sample by oven drying to constant weight. Lipid content was determine using a portion of the sample following extraction for organochlorine analysis (Figure C3).

C1.2 Sample extraction

C1.2.1 Sediment

PCDDs, PCDFs, PCBs and organochlorine pesticides

A weight (20 g air dried) of prepared sediment was taken, loaded into an accelerated solvent extractor cell and spiked with a range of isotopically labelled PCDD, PCDF, PCB and organochlorine pesticide standards (Cambridge Isotope Laboratories, Massachusetts, USA). The nominal amounts of each surrogate standard added are given in Table C1. The sediment was extracted by accelerated solvent extraction (ASE) (Dionex 200) with acetone/hexane (1:1) followed by toluene. Both extracts were reduced using rotary evaporation, combined, solvent exchanged into dichloromethane, (DCM) washed with water, dried (anhydrous Na_2SO_4), and solvent exchanged into hexane. This extract was then split: 40% for PCDD and PCDF analysis, 40% for PCB and organochlorine pesticide analysis and 20% reserve (Figure C2).

Table C1 Nominal amounts of isotopically labelled surrogate standards added to samples

$^{13}C_{12}$ PCDD congener	ng added	$^{13}C_{12}$ PCDF congener	ng added
2,3,7,8-TCDD	0.5	2,3,7,8-TCDF	0.5
1,2,3,7,8-PeCDD	0.5	1,2,3,7,8-PeCDF	0.5
1,2,3,4,7,8-HxCDD	0.5	2,3,4,7,8-PeCDF	0.5
1,2,3,6,7,8-HxCDD	0.5	1,2,3,4,7,8-HxCDF	0.5
1,2,3,4,6,7,8-HpCDD	0.5	1,2,3,6,7,8-HxCDF	0.5
OCDD	1	2,3,4,6,7,8-HxCDF	0.5
		1,2,3,7,8,9-HxCDF	0.5
		1,2,3,4,6,7,8-HpCDF	0.5
		1,2,3,4,7,8,9-HpCDF	0.5
$^{13}C_{12}$ PCB congener	**ng added**	**^{13}C OC pesticide**	**ng added**
#28	20	γ-HCH	10
#52	10	HCB	5
#77	10	Dieldrin	10
#101	10	pp'-DDE	10
#126	10	pp'-DDT	20
#153	20		
#169	10		
#180	10		
#202	20		

Chlorophenols

A weight (10 g wet weight) of prepared sediment was taken and spiked with surrogate standard (2,6-dibromo-4-methyl phenol, 50 ng). The sample was acidified and extracted with acetone/hexane using sonication followed by shaking. Water was added and the upper layer was removed following centrifugation.

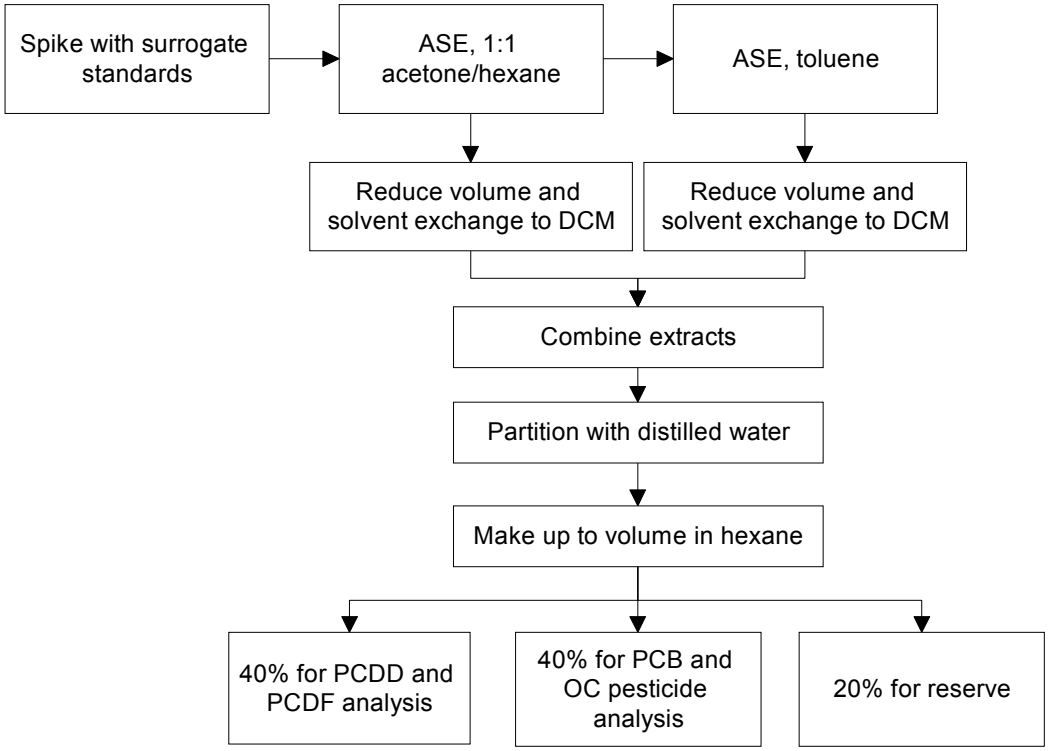

Figure C2 Extraction of sediment for PCDD, PCDF, PCB and organochlorine pesticide analysis

C1.2.2 Shellfish

PCDDs, PCDFs, PCBs and organochlorine pesticides

A weight (from 6-25 g) of freeze-dried shellfish was taken, loaded into a Soxhlet unit and spiked with a range of isotopically labelled PCDD, PCDF, PCB and organochlorine pesticide standards. The nominal amounts of each surrogate standard added are given in Table C1. The sample was subject to Soxhlet extraction with acetone/hexane (1:1) followed by toluene. Both extracts were reduced using rotary evaporation, combined, solvent exchanged into dichloromethane, washed with water, dried (anhydrous Na_2SO_4), and solvent exchanged into hexane. This extract was then split: 50% for PCDD and PCDF analysis, 40% for PCB and organochlorine pesticide analysis and 10% for lipid determination (Figure C3).

Solvent extractable lipid content was determined gravimetrically by taking 10% of the hexane extract (Figure C3) and drying to constant weight.

Chlorophenols

A weight (2 g) of freeze-dried shellfish was taken and spiked with surrogate standard (2,6-dibromo-4-methyl phenol, 25 ng). The sample was acidified and extracted with acetone/hexane using sonication followed by shaking. Water was added and the upper layer was removed following centrifugation.

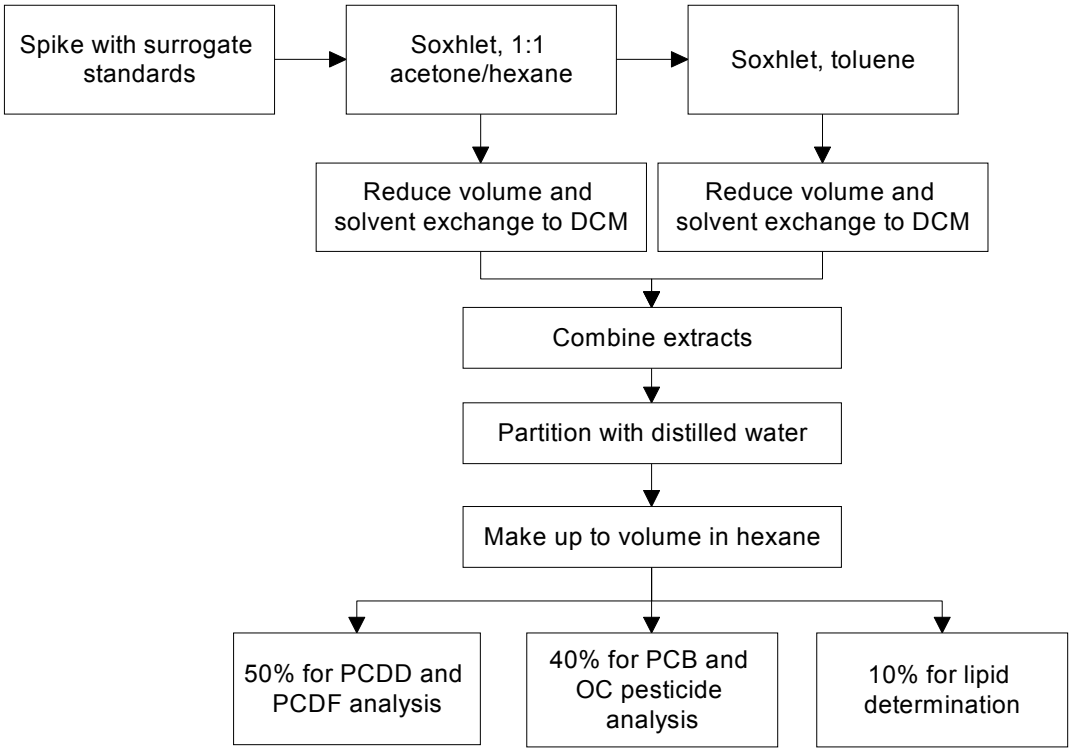

Figure C3 Extraction of shellfish for PCDD, PCDF, PCB and organochlorine pesticide analysis

C1.3 Sample purification

C1.3.1 Sediment

PCDDs and PCDFs

The PCDD and PCDF split was partitioned with concentrated sulphuric acid, washed with water, dried (anhydrous Na_2SO_4) and reduced by rotary evaporation. The extract was further purified by column chromatography as follows:

- acid and base modified silica gel (eluent: hexane)
- alumina (neutral) (eluent: hexane, 1:20 diethyl ether/hexane, diethyl ether)
- Carbopack C (18% dispersed on Celite 545) (eluent: 1:1 DCM/cyclohexane, 15:4:1 DCM/methanol/toluene, toluene)

A volume of $^{13}C_{12}$ labelled syringe spike (1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD) in tetradecane was added and the extract was reduced by rotary evaporation, blown down gently under a stream of nitrogen and transferred to a vial for analysis using capillary gas chromatography-high resolution mass spectrometry (GCMS).

PCB and organochlorine pesticides

The PCB and organochlorine pesticide split was reduced by rotary evaporation, filtered (0.45 µm pore size) and purified by gel permeation chromatography (GPC) (Bio-Beads SX-3, 1:1 ethyl acetate/hexane eluent). The sample extract was further purified by Florisil column chromatography (eluent: hexane, 1:15 diethyl ether/hexane), which also effected the fractionation of the non *ortho*-PCBs (#77, #126 and #169) from the *ortho*-substituted congeners. Each fraction was reduced by

rotary evaporation, then blown down gently under a stream of nitrogen. A volume of $^{13}C_{12}$ labelled syringe spike (PCB #80 and #141) was added and each fraction was transferred to a vial for analysis for *ortho*-PCB and non *ortho*-PCB congeners by GCMS. The *ortho*-and non *ortho*-PCB fractions were subsequently recombined for GCMS analysis for organochlorine pesticides.

Chlorophenols

Sample extracts were purified by treatment with concentrated sulphuric acid, extracted into aqueous base and derivatised using phase transfer acetylation in preparation for analysis by gas chromatography using electron capture detection (GC-ECD).

C1.3.2 Shellfish

PCDDs and PCDFs

The PCDD and PCDF split was partitioned with concentrated sulphuric acid, washed with water, dried (anhydrous Na_2SO_4) and reduced by rotary evaporation. The extract was further purified by column chromatography as follows:

- acid and base modified silica gel (eluent: hexane)
- alumina (neutral) (eluent: hexane, 1:20 diethyl ether/hexane, diethyl ether)
- Carbopack C (18% dispersed on Celite 545) (eluent: hexane, 1:1 DCM/cyclohexane, 15:4:1 DCM/methanol/toluene, toluene)

A volume of $^{13}C_{12}$ labelled syringe spike (1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD) in tetradecane was added and the extract was reduced by rotary evaporation, blown down gently under a stream of nitrogen, and transferred to a vial for analysis using GCMS.

PCB and organochlorine pesticides

The PCB and organochlorine pesticide split was partitioned with acetonitrile, and the combined acetonitrile extracts reduced by rotary evaporation. The extract was further purified by GPC (Bio-Beads SX-3, 1:1 ethyl acetate/hexane eluent) followed by Florisil column chromatography (eluent: hexane, 1:15 diethyl ether/hexane), which also effected the fractionation of the non *ortho*-PCBs (#77, #126 and #169) from the *ortho*-substituted congeners. Each fraction was reduced by rotary evaporation, then blown down gently under a stream of nitrogen. A volume of $^{13}C_{12}$ labelled syringe spike (PCB #80 and #141) was added and each fraction was transferred to a vial for analysis for *ortho*-PCB and non *ortho*-PCB congeners by GCMS. The *ortho*- and non *ortho*-PCB fractions were subsequently recombined for GCMS analysis for organochlorine pesticides.

Chlorophenols

Sample extracts were purified by treatment with concentrated sulphuric acid, extracted into aqueous base and derivatised using phase transfer acetylation in preparation for analysis by GC-ECD.

C1.4 Sample analysis

PCDDs and PCDFs

Extracts were analysed by GCMS on an HP5890 Series II Plus GC interfaced to a VG-70S high resolution mass spectrometer (resolution 10,000). All extracts were run on an Ultra2 capillary column. If a peak was detected at the correct retention times for 2,3,7,8-TCDF, 2,3,7,8-TCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF or 1,2,3,7,8,9-HxCDD, the extract was re-analysed on a SP2331 capillary column for full congener-specific quantification. Chromatographic conditions are given below, and the mass spectral ions monitored are detailed in Table C2.

Column	25 m Ultra2	60 m SP2331
Carrier gas head pressure	150 kPa	200 kPa
Injector temperature	260 ºC	260 ºC
Injection	2 µl splitless	2 µl splitless
Temperature programme	Initial temp 210 ºC (hold 4 min), 3 ºC min^{-1} to 275 ºC (11 min).	Initial temp 170 ºC (hold 1 min), 10 ºC min^{-1} to 210 ºC (1 min), 3 ºC min^{-1} to 250 ºC (30 min).

Table C2 Ions monitored for PCDDs and PCDFs

Congener group	^{12}C Quantification ion (m/z)	^{12}C Confirmation ion (m/z)	^{13}C Quantification ion (m/z)	^{13}C Confirmation ion (m/z)
TCDF	305.8987	303.9016	317.9389	315.9419
TCDD	321.8936	319.8965	333.9339	331.9368
PeCDF	339.8597	337.8626	351.9000	349.9029
PeCDD	355.8546	353.8575	367.8949	365.8978
HxCDF	373.8207	375.8178	385.8610	387.8580
HxCDD	389.8156	391.8127	401.8559	403.8530
HpCDF	407.7818	409.7788	419.8220	421.8191
HpCDD	423.7767	425.7737	435.8169	437.8140
OCDF	443.7398	441.7428		
OCDD	459.7347	457.7377	471.7750	469.7780

PCBs

Extracts were analysed by GCMS on an HP5890 Series II Plus GC interfaced to a VG-70S high resolution mass spectrometer (resolution typically 6,000). Chromatographic conditions are given below, and the mass spectral ions monitored are detailed in Table C3.

Column	25 m Ultra2
Carrier gas head pressure	100 kPa
Injector temperature	240 ºC
Injection	1 µl splitless
Temperature programme	Initial temp 60 ºC (hold 0.8 min), 40 ºC min^{-1} to 170 ºC (0.5 min), 5 ºC min^{-1} to 250 ºC (23 min).

Table C3 Ions monitored for PCBs

Congener group	^{12}C Quantification ion (m/z)	^{12}C Confirmation ion (m/z)	^{13}C Quantification ion (m/z)	^{13}C Confirmation ion (m/z)
Tri PCBs[1]	255.9613	257.9584	269.9986	271.9957
Tetra PCBs[2]	291.9194	289.9224	303.9597	301.9627
Penta PCBs[3]	325.8804	327.8775	337.9207	339.9178
Hexa PCBs[4]	359.8415	361.8385	371.8818	373.8788
Hepta PCBs[5]	393.8025	395.7995	405.8428	407.8398
Octa PCBs[6]	427.7635	429.7606	439.8038	441.8009
Nona PCBs[7]	463.7216	461.7245		

[1] PCB #28, #31
[2] PCB #52, #77
[3] PCB #101, #99, #123, #118, #114, #105, #126
[4] PCB #153, #138, #167, #156, #157, #169
[5] PCB #187, #183, #180, #170, #189
[6] PCB #202, #194
[7] PCB #206

Organochlorine pesticides

Extracts were analysed by GCMS on an HP5890 Series II Plus GC interfaced to a VG-70S high resolution mass spectrometer (resolution typically 6,000). Chromatographic conditions are given below, and mass spectral ions monitored detailed in Table C4.

Column	25 m Ultra2
Carrier gas head pressure	100 kPa
Injector temperature	180 ºC
Injection	1 µl splitless
Temperature programme	Initial temp 60 ºC (hold 0.8 min), 40 ºC min^{-1} to 170 ºC (0.5 min), 5 ºC min^{-1} to 250 ºC (13 min).

Table C4 Ions monitored for organochlorine pesticides

Analyte	^{12}C Quantification ion (m/z)	^{12}C Confirmation ion (m/z)	^{13}C Quantification ion (m/z)	^{13}C Confirmation ion (m/z)
α-HCH	216.9145	220.9086		
β-HCH	216.9145	220.9086		
γ-HCH	216.9145	220.9086	227.9660	231.9601
HCB	285.8072	283.8102	291.8273	289.8303
Aldrin	262.8570	260.8599		
Dieldrin	262.8570	260.8599	268.8674	266.9704
Heptachlor	271.8102	273.8072		
Heptachlor epoxide	262.8570	260.8599		
α-Chlordane	372.8260	374.8230		
γ-Chlordane	372.8260	374.8230		
pp'-DDE	317.9351	315.9380	329.9753	327.9783
pp'-TDE	235.0081	237.0052		
op'-DDT	235.0081	237.0052		
pp'-DDT	235.0081	237.0052	247.0483	249.0453

Chlorophenols

Extracts were analysed by GC-ECD on a Varian 3500. All extracts were run on a 30 m DB17 capillary column with confirmation analyses carried out on a 25 m Ultra2 capillary column. Conditions are detailed below.

Column	30 m DB17	25 m Ultra2
Carrier gas head pressure	245 kPa	320 kPa
Injector temperature	250 ºC	240 ºC
Injection	1 µl splitless	1 µl splitless
Temperature programme	Initial temp 90 ºC (hold 1 min), 20 ºC min^{-1} to 160 ºC (0 min), 5 ºC min^{-1} to 224 ºC (0 min), 50 ºC min^{-1} to 280 ºC (5 min).	Initial temp 85 ºC (hold 1 min), 40 ºC min^{-1} to 150 ºC (2 min), 2 ºC min^{-1} to 220 ºC (0 min), 50 ºC min^{-1} to 300 ºC (8.67 min).

C1.5 Analyte identification and quantification criteria

PCDDs and PCDFs

For positive identification and quantification, the following criteria must be met:

- The retention time of the analyte must be within 1 second of the retention time of the corresponding $^{13}C_{12}$ surrogate standard.
- The ion ratio obtained for the analyte must be ±10% of the theoretical ion ratio.
- The signal to noise ratio must be greater than 3:1.
- Levels of PCDD and PCDF congeners in a sample must be greater than 5 times any level found in the corresponding laboratory blank analysed (3 times the level in the blank for OCDD).
- Surrogate standard recoveries must be in the range 25-150%.

PCBs and organochlorine pesticides

For positive identification and quantification, the following criteria must be met:

- Where relevant, the retention time of the targeted analyte must be within 2 seconds of the corresponding ^{13}C surrogate standard. For congeners with no ^{13}C surrogate standard, the retention time must be within 2 seconds of the relative retention time for that congener as calculated from the calibration standards.
- The ion ratio obtained for the analyte must be ±20% of that obtained for the calibration standards.
- The signal to noise must be greater than 3:1.
- Levels of PCB congeners and organochlorine pesticides in a sample must be greater than 5 times any level found in the corresponding laboratory blank analysed.
- Surrogate standard recoveries must be in the range 25-150%.

Chlorophenols

For positive identification and quantification, the following criteria must be met:

- The retention time of the targeted analyte on both GC columns must be within 2 seconds of the corresponding external standard.
- The peak shape of the targeted analyte on both GC columns must be sharp and with minimal tailing.
- The signal to noise must be greater than 5:1.
- Surrogate standard recoveries must be in the range 25-150%.

C1.6 Quantification

PCDDs, PCDFs, PCBs and organochlorine pesticides

Quantification was by the isotope dilution technique using the surrogate standards listed in Table C1. Relative response factors (RRFs) were calculated for each targeted analyte from a series of calibration standards analysed under the same conditions as the samples. Non 2,3,7,8-substituted PCDD and PCDF congeners were quantified using the RRF of the first eluting surrogate standard in each mass spectral group. Targeting of all analytes was performed by the MS software (OPUS). Text files created by OPUS were electronically transferred to a customised spreadsheet for further data reduction and preparation of the final analytical report.

Chlorophenols

Quantification was by multi-point calibration using the Waters Millennium chromatography data system. Data was electronically transferred to a customised spreadsheet for further data reduction and preparation of the final analytical report.

C1.7 Limits of detection

PCDDs, PCDFs, PCBs and organochlorine pesticides

If no peak was distinguishable above the background noise at the retention time for a targeted analyte, the area was recorded as being less than the limit of detection. The limit of detection was calculated by multiplying by three the area of the section of baseline noise at the retention time of the analyte. If a peak was present at the correct retention time for the targeted analyte but failed to meet all analyte identification and quantification criteria, the area due to that analyte was recorded, and the calculated concentration was reported as a limit of detection.

Chlorophenols

Limits of detection were calculated according to the standard US EPA procedure based on standard deviation of low level spikes.

C1.8 Surrogate standard recoveries

PCDDs, PCDFs, PCBs and organochlorine pesticides

The recovery of each isotopically labelled surrogate standard was calculated from the ratio of the area of the surrogate standard in the sample normalised to its syringe spike to the area of the surrogate standard in the calibration standards normalised to its syringe spike.

C1.9 Quality control

PCDDs, PCDFs, PCBs and organochlorine pesticides

- The batch size was typically 8-10 samples.
- A laboratory blank was analysed with each batch of samples.
- A laboratory control sample (LCS) was analysed with each batch of samples as a replicate to assess method precision.
- The GCMS resolution, performance and sensitivity were established for each MS run.
- The recoveries of all isotopically labelled surrogate standards were calculated and reported.

- Ten percent of all samples were analysed by an independent cross-check QC laboratory.

Chlorophenols

- The batch size was typically 8-10 samples.
- A laboratory blank was analysed with each batch of samples.
- A matrix spike was analysed with each batch of samples.
- The recovery of the surrogate standard was calculated and reported.
- Ten percent of all samples were analysed by an independent cross-check QC laboratory.

C1.10 Method precision data

Method precision data for organochlorine analyses are summarised in Tables C5 and C6. Data were calculated from replicate analysis of a sediment or shellfish LCS.

Table C5 Method precision data for organochlorine analyses of sediment samples

Contaminant class	Measure	QC sample	n	Range Min.	Range Max.	Mean	Confidence interval[1]
PCDDs and PCDFs	Total I-TEQ[2] (ng kg^{-1})	LCS[3]	5	0.234	0.265	0.245	±0.011
	OCDD (ng kg^{-1})	LCS	5	83.6	96.7	88.0	±4.71
PCBs	PCB TEQ[2] (ng kg^{-1})	LCS	5	0.013	0.018	0.015	±0.0017
	PCB #153 (µg kg^{-1})	LCS	5	0.11	0.12	0.11	±0.0039
OC pesticides	Dieldrin (µg kg^{-1})	LCS	5	0.24	0.57	0.34	±0.12

[1] 95% confidence level.
[2] Calculated excluding LOD values.
[3] Laboratory control sample.

Table C6 Method precision data for organochlorine analyses of shellfish samples

Contaminant class	Measure	QC sample	n	Range Min.	Range Max.	Mean	Confidence interval[1]
PCDDs and PCDFs	Total I-TEQ[2](ng kg^{-1})	LCS[3]	3[4]	0.0085	0.010	0.0091	±0.00088
	TCDF (ng kg^{-1})	LCS	3[4]	0.085	0.100	0.091	±0.0088
PCBs	PCB TEQ[2] (ng kg^{-1})	LCS	5	0.0044	0.0071	0.0058	±0.0010
	PCB #153 (µg kg^{-1})	LCS	5	0.16	0.17	0.016	±0.0048
OC pesticides	Dieldrin (µg kg^{-1})	LCS	5	0.13	0.15	0.13	±0.0078

[1] 95% confidence level.
[2] Calculated excluding LOD values.
[3] Laboratory control sample.
[4] Precision data calculated for only three of the five LCS due to LOD values being obtained for 2,3,7,8-TCDF in the other two LCS (2,3,7,8-TCDF was the sole contributor to the total I-TEQ calculated for the three LCS).

C1.11 Data reporting

The bases of reporting for primary and quality control samples are given in Tables C7 and C8 for sediment, and Tables C9 and C10 for shellfish.

Concentration data are reported in Appendices D through to G. PCDD, PCDF, PCB and organochlorine pesticide data are corrected for recovery of ^{13}C surrogate standards. Chlorophenol data is uncorrected for recovery of surrogate standard. For all samples, data for quantified analytes are reported to 2 or 3 significant figures. Limit of detection data for non-quantified analytes are reported to 1 significant figure.

Table C7 Reporting basis for contaminant concentrations in sediment

Contaminant class	Reporting basis
PCDDs and PCDFs	ng kg^{-1} on a dry weight basis. Toxic equivalents (TEQs) were calculated using the International Toxic Equivalency Factors (I-TEFs).
PCBs	µg kg^{-1} on a dry weight basis. TEQs were calculated using the WHO/IPCS TEFs (Ahlborg *et al*., 1994) and reported in ng kg^{-1}.
OC pesticides	µg kg^{-1} on a dry weight basis.
Chlorophenols	µg kg^{-1} on a dry weight basis.

Table C8 Reporting basis for sediment quality control samples

QC sample	Reporting basis
Laboratory blanks	Calculated using the average dry weight of all samples analysed in the batch. Reported on a weight per weight basis.
Field blanks	Calculated using the dry weight of sediment collected in a single jar for the corresponding field sample. Reported on a weight per weight basis.
Rinsate blanks	Calculated using the volume of rinsate analysed. Reported on a weight per volume basis.

Table C9 Reporting basis for contaminant concentrations in shellfish

Contaminant class	Reporting basis
PCDDs and PCDFs	ng kg^{-1} on a wet (whole body) weight basis. TEQs were calculated using the I-TEFs.
PCBs	µg kg^{-1} on a wet (whole body) weight basis. TEQs were calculated using the WHO/IPCS TEFs (Ahlborg *et al*., 1994) and reported in ng kg^{-1}.
OC pesticides	µg kg^{-1} on a wet (whole body) weight basis.
Chlorophenols	µg kg^{-1} on a wet (whole body) weight basis.

Table C10 Reporting basis for shellfish quality control samples

QC sample	Reporting basis
Laboratory blanks	Calculated using the average wet weight of all samples analysed in the batch. Reported on a weight per weight basis.

C2 Miscellaneous analyses

C2.1 Total organic carbon

Total carbon was determined using a LECO CNS-2000 analyser. In this analyser, the sediment was combusted in the furnace at a temperature of 1050 ºC in pure oxygen. The evolved carbon dioxide was measured with an infra-red detector calibrated against a pure organic standard compound. Total organic carbon was calculated after correcting for the presence of any inorganic carbon (carbonate) in the sample.

C2.2 Grain size

All samples were friable and uncemented and did not need disaggregation or treatment for carbonate. A weight of each prepared sediment was taken and washed through a 63 μm sieve, the coarser fraction then being dried and dry sieved. The known weight of finer fraction was mixed with dispersant and run through a Serigraph grain size analyser. The two sets of grain size results were combined to give percentages of sand, silt and clay.

Appendix D Concentrations of PCDDs and PCDFs in New Zealand estuarine sediments and shellfish

This appendix reports the concentrations of PCDDs and PCDFs in estuarine sediments and shellfish collected as part of the Organochlorines Programme. Results from field quality control samples are also provided.

Congener specific concentrations for all 2,3,7,8- PCDDs and PCDFs are reported, along with total concentrations for non 2,3,7,8- PCDDs and PCDFs for each homologue group. Total TEQ levels were calculated, both excluding LOD values and including half LOD values, using the International TEF scheme (Kutz *et al*., 1990).

PCDD and PCDF data are reported in the following tables:

Table D1 Concentrations of PCDDs and PCDFs in New Zealand estuarine sediment (ng kg^{-1}, dry wt basis)

Congener	Parengarenga Harbour Akatarere Point (n=2)[3]	Parengarenga Harbour Oriatou Point	Whangarei Harbour Mangapai River mouth	Whangarei Harbour Limestone Island	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay	Manukau Harbour Big Muddy Creek	Manukau Harbour French Bay, Paturoa Bay Perkins Bay, Little Muddy Creek	Hellyers Creek (upper reaches) Waitemata Harbour	Hellyers Creek (lower reaches) Waitemata Harbour	Kawhia Harbour north shore on State Highway 31	Kawhia Harbour south shore, opposite Maire Point
2,3,7,8 TCDD	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.5	< 0.2	< 0.1	< 0.1
Non 2,3,7,8 TCDD	< 0.1	< 0.1	< 0.3	< 0.2	4.47	< 0.2	1.81	8.81	3.57	1.31	< 1
1,2,3,7,8 PeCDD	< 0.1	< 0.1	< 0.2	< 0.2	< 0.3	< 0.1	< 0.2	< 1	< 0.6	< 0.1	< 0.1
Non 2,3,7,8 PeCDD	< 0.2	< 0.2	< 0.5	< 0.3	8.28	< 0.3	3.35	15.1	7.27	< 0.4	< 0.4
1,2,3,4,7,8 HxCDD	< 0.1	< 0.1	< 0.2	< 0.2	< 0.4	< 0.1	< 0.3	< 1	< 1	< 0.2	< 0.2
1,2,3,6,7,8 HxCDD	< 0.1	< 0.1	< 0.2	< 0.2	< 1	< 0.1	< 0.4	< 2	< 1	< 0.2	< 0.2
1,2,3,7,8,9 HxCDD	< 0.1	< 0.1	< 0.3	< 0.3	< 0.8	< 0.2	< 0.5	< 4	< 2	< 0.4	< 0.4
Non 2,3,7,8 HxCDD	< 0.2	< 0.2	< 2	2.34	19.6	2.54	7.69	29.5	17.5	3.24	3.76
1,2,3,4,6,7,8 HpCDD	< 0.4	< 0.4	< 2	2.76	22.3	2.60	11.1	53.6	31.8	2.09	2.35
Non 2,3,7,8 HpCDD	< 0.3	< 0.4	< 3	4.78	33.8	5.01	20.1	70.9	44.5	2.75	2.89
OCDD	< 1	< 3	10.7	23.3	202	16.9	79.1	420	284	16.3	40.6
2,3,7,8 TCDF	< 0.1	< 0.3	< 0.2	< 0.4	< 0.7	< 0.1	< 0.7	1.58	< 0.8	< 0.3	< 0.5
Non 2,3,7,8 TCDF	< 0.1	2.05	< 0.2	< 2	3.52	< 0.7	2.51	13.3	5.97	2.10	3.60
1,2,3,7,8 PeCDF	< 0.1	< 0.1	< 0.2	< 0.2	< 0.2	< 0.1	< 0.2	< 1	< 0.3	< 0.1	< 0.2
2,3,4,7,8 PeCDF	< 0.1	< 0.2	< 0.1	< 0.2	< 0.4	< 0.1	< 0.2	< 1	< 0.5	< 0.1	< 0.2
Non 2,3,7,8 PeCDF	< 0.1	1.59	< 0.6	< 0.2	4.91	< 0.2	3.19	13.7	6.89	< 0.7	2.48
1,2,3,4,7,8 HxCDF	< 0.1	< 0.2	< 0.2	< 0.4	< 0.4	< 0.2	< 0.4	< 1	< 0.6	< 0.2	< 0.4
1,2,3,6,7,8 HxCDF	< 0.1	< 0.1	< 0.2	< 0.2	< 0.4	< 0.2	< 0.3	< 1	< 0.4	< 0.1	< 0.2
2,3,4,6,7,8 HxCDF	< 0.1	< 0.1	< 0.2	< 0.2	< 0.4	< 0.1	< 0.3	< 1	< 0.5	< 0.1	< 0.2
1,2,3,7,8,9 HxCDF	< 0.1	< 0.1	< 0.2	< 0.2	< 0.1	< 0.1	< 0.1	< 1	< 0.3	< 0.1	< 0.1
Non 2,3,7,8 HxCDF	< 0.1	< 0.2	< 0.3	< 0.5	6.30	< 0.2	1.88	17.0	10.8	< 0.6	1.49
1,2,3,4,6,7,8 HpCDF	< 0.2	< 0.4	< 0.8	< 2	6.92	1.10	3.88	24.2	14.0	< 1	1.18
1,2,3,4,7,8,9 HpCDF	< 0.3	< 0.1	< 0.3	< 0.3	< 0.3	< 0.2	< 0.3	< 1	< 1	< 0.2	< 0.2
Non 2,3,7,8 HpCDF	< 0.2	< 0.1	< 0.5	< 0.9	5.38	< 0.7	2.06	21.1	12.5	< 0.7	0.96
OCDF	< 0.5	< 0.4	< 0.6	< 1	8.72	< 0.6	< 3	25.6	14.7	< 1	1.33
Sum of PCDD/Fs (inc)[1]	2.50	7.19	17.4	38.3	329	30.5	140	722	458	31.1	62.8
Sum of PCDD/Fs (exc)[2]	0	3.64	10.7	33.2	326	28.2	137	714	454	27.8	60.6
Total I-TEQ (inc)[1]	0.15	0.19	0.24	0.32	0.94	0.21	0.54	2.71	1.47	0.23	0.32
Total I-TEQ (exc)[2]	0	0	0.011	0.051	0.50	0.054	0.23	1.38	0.76	0.037	0.077

Table D1 Concentrations of PCDDs and PCDFs in New Zealand estuarine sediment (ng kg^{-1}, dry wt basis) (Cont.)

Congener	Tauranga Harbour Hunters Creek	Tauranga Harbour Town Reach, opening of Waipu Bay	Tauranga Harbour Waikareao Estuary (n=2)[3]	Wairau Estuary Arapipi channel	Wairau Estuary Morgans Creek/Budges Island channel[3]	Whanganui Inlet southern section of Inlet	Whanganui Inlet south of Inlet entrance	Moutere Inlet south/south east	Moutere Inlet south west of Jackett Island	Avon Heathcote Estuary McCormacks Bay outlet	Avon Heathcote Estuary opposite Pleasant Point Domain
2,3,7,8 TCDD	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2
Non 2,3,7,8 TCDD	< 0.2	< 0.2	4.41	< 0.1	< 0.1	< 0.3	< 0.2	< 0.2	< 0.2	< 0.7	2.23
1,2,3,7,8 PeCDD	< 0.3	< 0.2	< 0.4	< 0.1	< 0.1	< 0.1	< 0.2	< 0.2	< 0.2	< 0.1	< 0.4
Non 2,3,7,8 PeCDD	2.41	< 0.4	4.02	< 0.2	< 0.1	< 0.2	< 0.2	< 0.3	< 0.4	< 0.3	3.82
1,2,3,4,7,8 HxCDD	< 0.4	< 0.2	< 0.5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.2	< 0.1	< 0.3
1,2,3,6,7,8 HxCDD	< 1	< 0.3	< 1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.3	< 0.3	< 0.1	< 0.5
1,2,3,7,8,9 HxCDD	< 0.8	< 0.3	< 0.9	< 0.1	< 0.2	< 0.2	< 0.1	< 0.3	< 0.3	< 0.2	< 0.6
Non 2,3,7,8 HxCDD	17.7	3.97	18.3	< 0.3	< 0.4	< 0.4	< 0.5	2.15	2.76	< 0.9	5.30
1,2,3,4,6,7,8 HpCDD	45.6	5.71	36.0	< 0.5	< 1	< 0.5	< 0.5	7.33	8.94	< 0.9	11.3
Non 2,3,7,8 HpCDD	52.8	9.14	45.2	< 0.5	< 1	< 0.6	< 1	8.95	11.2	< 1	13.6
OCDD	380	51.2	304	< 2	< 6	< 2	< 2	54.6	72.7	< 6	110
2,3,7,8 TCDF	< 0.2	< 0.1	< 0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.2	< 0.1	< 0.4
Non 2,3,7,8 TCDF	< 0.1	< 0.1	2.52	< 0.4	< 0.2	< 0.7	< 0.6	< 0.3	< 1	< 0.6	4.16
1,2,3,7,8 PeCDF	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.3
2,3,4,7,8 PeCDF	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.3
Non 2,3,7,8 PeCDF	1.46	< 0.1	3.75	< 0.2	< 0.1	< 0.1	< 0.2	< 0.2	< 0.3	< 0.2	2.96
1,2,3,4,7,8 HxCDF	< 0.3	< 0.1	< 0.6	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.2	< 0.1	< 0.4
1,2,3,6,7,8 HxCDF	< 0.3	< 0.1	< 0.5	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.3
2,3,4,6,7,8 HxCDF	< 0.4	< 0.1	< 0.6	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3
1,2,3,7,8,9 HxCDF	< 0.2	< 0.1	< 0.2	< 0.1	< 0.1	< 0.2	< 0.2	< 0.2	< 0.2	< 0.1	< 0.3
Non 2,3,7,8 HxCDF	9.21	< 1	8.33	< 0.1	< 0.1	< 0.1	< 0.1	< 0.5	1.39	< 0.1	2.11
1,2,3,4,6,7,8 HpCDF	18.1	1.75	13.4	< 0.3	< 0.6	< 0.3	< 0.5	3.10	4.01	< 0.4	5.37
1,2,3,4,7,8,9 HpCDF	< 0.6	< 0.2	< 0.5	< 0.3	< 0.2	< 0.3	< 0.3	< 0.3	< 0.1	< 0.1	< 0.5
Non 2,3,7,8 HpCDF	21.9	1.86	13.8	< 0.2	< 0.3	< 0.2	< 0.3	2.14	2.62	< 0.3	6.62
OCDF	27.5	2.14	16.1	< 0.7	< 0.5	< 0.7	< 0.7	3.11	5.58	< 0.4	15.3
Sum of PCDD/Fs (inc)[1]	579	77.7	473	3.50	5.95	3.90	4.30	83.3	111	6.60	185
Sum of PCDD/Fs (exc)[2]	577	75.8	470	0	0	0	0	81.4	109	0	183
Total I-TEQ (inc)[1]	1.38	0.32	1.24	0.15	0.16	0.16	0.19	0.37	0.42	0.16	0.73
Total I-TEQ (exc)[2]	1.04	0.13	0.81	0	0	0	0	0.16	0.21	0	0.29

Table D1 Concentrations of PCDDs and PCDFs in New Zealand estuarine sediment (ng kg^{-1}, dry wt basis) (Cont.)

Congener	Otago Harbour Rocky Point (n=2)[3]	Otago Harbour Tayler Point	New River Estuary Bushy Point	New River Estuary Whalers Bay	Number of positives	Minimum	Maximum	Median[4]	Mean[5,6]	Mean of ^{13}C surrogate standard recoveries, %, (n=29)
2,3,7,8 TCDD	< 0.05	< 0.5	< 0.08	< 0.06	0	< 0.05	< 0.5	< 0.1	-	101
Non 2,3,7,8 TCDD	< 0.2	< 0.6	< 0.3	< 0.3	7	< 0.1	8.81	< 0.3	-	
1,2,3,7,8 PeCDD	< 0.06	< 0.6	< 0.09	< 0.07	0	< 0.06	< 1	< 0.2	-	78
Non 2,3,7,8 PeCDD	< 0.09	< 0.6	< 0.1	< 0.09	7	< 0.09	15.1	< 0.4	-	
1,2,3,4,7,8 HxCDD	< 0.07	< 0.6	< 0.08	< 0.06	0	< 0.06	< 1	< 0.2	-	100
1,2,3,6,7,8 HxCDD	< 0.07	< 0.5	< 0.09	< 0.07	0	< 0.07	< 2	< 0.2	-	91
1,2,3,7,8,9 HxCDD	< 0.07	< 0.5	< 0.1	< 0.09	0	< 0.07	< 4	< 0.3	-	
Non 2,3,7,8 HxCDD	< 0.1	< 0.6	< 0.1	< 0.1	14	< 0.1	29.5	2.25	-	
1,2,3,4,6,7,8 HpCDD	< 0.07	< 1	< 0.7	< 0.6	14	< 0.07	53.6	2.22	-	78
Non 2,3,7,8 HpCDD	< 0.6	< 2	< 0.6	< 0.6	14	< 0.3	70.9	2.22	-	
OCDD	3.74	< 8	6.09	4.77	18	< 1	420	16.6	80.6	72
2,3,7,8 TCDF	< 0.06	< 0.4	< 0.07	< 0.05	1	< 0.05	1.58	< 0.2	-	90
Non 2,3,7,8 TCDF	< 0.07	< 0.4	< 0.07	< 0.09	9	< 0.07	13.3	< 0.7	-	
1,2,3,7,8 PeCDF	< 0.04	< 0.3	< 0.05	< 0.04	0	< 0.04	< 1	< 0.1	-	90
2,3,4,7,8 PeCDF	< 0.04	< 0.4	< 0.07	< 0.04	0	< 0.04	< 1	< 0.1	-	92
Non 2,3,7,8 PeCDF	< 0.07	< 0.4	< 0.08	< 0.1	9	< 0.07	13.7	< 0.3	-	
1,2,3,4,7,8 HxCDF	< 0.06	< 0.9	< 0.06	< 0.06	0	< 0.06	< 1	< 0.2	-	75
1,2,3,6,7,8 HxCDF	< 0.05	< 0.5	< 0.06	< 0.05	0	< 0.05	< 1	< 0.1	-	74
2,3,4,6,7,8 HxCDF	< 0.07	< 0.6	< 0.09	< 0.09	0	< 0.07	< 1	< 0.1	-	90
1,2,3,7,8,9 HxCDF	< 0.08	< 0.7	< 0.1	< 0.08	0	< 0.08	< 1	< 0.1	-	76
Non 2,3,7,8 HxCDF	< 0.09	< 1	< 0.1	< 0.08	9	< 0.08	17.0	< 0.5	-	
1,2,3,4,6,7,8 HpCDF	< 0.1	< 2	< 0.2	< 0.2	12	< 0.1	24.2	1.14	-	68
1,2,3,4,7,8,9 HpCDF	< 0.09	< 2	< 0.1	< 0.1	0	< 0.09	< 2	< 0.3	-	75
Non 2,3,7,8 HpCDF	< 0.3	< 1	< 0.3	< 0.2	11	< 0.1	21.9	< 0.8	-	
OCDF	< 0.6	< 4	< 0.8	< 0.8	10	< 0.4	27.5	< 1	-	
Sum of PCDD/Fs (inc)[1]	5.47	15.1	8.29	6.78		2.50	722	30.8	131	
Sum of PCDD/Fs (exc)[2]	3.74	0	6.09	4.77		0	714	28.0	127	
Total I-TEQ (inc)[1]	0.081	0.77	0.13	0.096		0.081	2.71	0.28	0.53	
Total I-TEQ (exc)[2]	0.0038	0	0.0061	0.0048		0	1.38	0.044	0.22	

1 = Including half LOD values.
2 = Excluding LOD values.
3 = Mean of primary and blind duplicate samples.
4 = For any individual congener, calculation of the median includes half LOD values.
5 = Mean value reported only if a PCDD/F congener detected on more than 66% of occasions (minimum of 17 positive determinations).
6 = For any individual congener, calculation of the mean includes half LOD values.

Table D2 Concentrations of PCDDs and PCDFs in New Zealand estuarine shellfish (ng kg^{-1}, wet wt basis)

Congener	Parengarenga Harbour Akatarere Point[3]	Parengarenga Harbour Oriatou Point[3]	Whangarei Harbour Mangapai River mouth[4]	Whangarei Harbour Limestone Island[4]	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay (n=2)[3,5]	Manukau Harbour Big Muddy Creek[3]	Manukau Harbour French Bay, Paturoa Bay Perkins Bay, Little Muddy Creek[3]	Hellyers Creek (upper reaches) Waitemata Harbour[4]	Hellyers Creek (lower reaches) Waitemata Harbour[3]	Kawhia Harbour north shore on State Highway 31[4]	Kawhia Harbour south shore, opposite Maire Point[4]
2,3,7,8 TCDD	< 0.02	< 0.02	< 0.02	< 0.01	< 0.08	< 0.03	< 0.01	< 0.03	< 0.05	< 0.02	< 0.02
Non 2,3,7,8 TCDD	< 0.02	< 0.03	0.43	0.39	1.09	0.39	< 0.06	2.04	0.80	< 0.07	0.35
1,2,3,7,8 PeCDD	< 0.02	< 0.03	< 0.02	< 0.03	< 0.09	< 0.09	< 0.04	0.14	< 0.1	< 0.04	< 0.02
Non 2,3,7,8 PeCDD	< 0.05	< 0.05	0.12	0.28	1.13	1.29	0.77	2.14	1.37	< 0.06	< 0.04
1,2,3,4,7,8 HxCDD	< 0.01	< 0.01	< 0.03	< 0.01	< 0.1	< 0.02	< 0.03	< 0.05	< 0.09	< 0.03	< 0.01
1,2,3,6,7,8 HxCDD	< 0.01	< 0.02	< 0.02	< 0.02	< 0.09	< 0.04	< 0.04	0.18	< 0.09	< 0.03	< 0.02
1,2,3,7,8,9 HxCDD	< 0.01	< 0.02	< 0.02	< 0.02	< 0.2	< 0.04	< 0.05	0.13	< 0.1	< 0.03	< 0.02
Non 2,3,7,8 HxCDD	< 0.03	< 0.04	0.20	0.16	0.75	0.80	0.82	1.50	1.55	< 0.04	< 0.03
1,2,3,4,6,7,8 HpCDD	< 0.04	< 0.06	< 0.04	0.69	0.82	0.18	0.25	0.60	1.29	< 0.08	< 0.05
Non 2,3,7,8 HpCDD	< 0.04	< 0.06	< 0.06	0.51	1.23	0.29	0.46	0.78	1.52	< 0.08	< 0.07
OCDD	< 0.2	< 0.2	< 0.2	5.41	5.56	1.03	1.23	3.24	61.7	< 0.3	< 0.3
2,3,7,8 TCDF	< 0.01	< 0.02	0.19	0.24	< 0.9	< 0.02	< 0.02	0.48	0.11	< 0.02	< 0.02
Non 2,3,7,8 TCDF	< 0.01	< 0.02	0.77	1.23	0.32	0.14	< 0.03	4.67	0.86	< 0.03	0.14
1,2,3,7,8 PeCDF	< 0.02	< 0.01	< 0.02	< 0.03	< 0.06	< 0.01	< 0.01	< 0.05	< 0.03	< 0.02	< 0.01
2,3,4,7,8 PeCDF	< 0.01	< 0.01	< 0.04	< 0.01	< 0.07	< 0.01	< 0.01	0.14	< 0.04	< 0.02	< 0.01
Non 2,3,7,8 PeCDF	< 0.02	< 0.03	0.36	0.41	0.53	0.12	0.10	2.16	0.48	< 0.04	< 0.04
1,2,3,4,7,8 HxCDF	< 0.01	< 0.01	< 0.01	< 0.02	< 0.1	< 0.02	< 0.01	< 0.01	< 0.07	< 0.02	< 0.01
1,2,3,6,7,8 HxCDF	< 0.01	< 0.01	< 0.01	< 0.02	< 0.07	< 0.02	< 0.01	< 0.02	< 0.05	< 0.02	< 0.01
2,3,4,6,7,8 HxCDF	< 0.02	< 0.02	< 0.01	< 0.02	< 0.1	< 0.02	< 0.01	< 0.04	< 0.05	< 0.02	< 0.02
1,2,3,7,8,9 HxCDF	< 0.03	< 0.03	< 0.02	< 0.02	< 0.1	< 0.03	< 0.02	< 0.01	< 0.06	< 0.03	< 0.04
Non 2,3,7,8 HxCDF	< 0.01	< 0.02	< 0.03	< 0.08	0.17	0.11	0.10	0.50	0.47	< 0.04	< 0.03
1,2,3,4,6,7,8 HpCDF	< 0.02	< 0.03	< 0.02	< 0.07	< 0.3	< 0.04	< 0.06	0.13	0.32	< 0.04	< 0.03
1,2,3,4,7,8,9 HpCDF	< 0.02	< 0.03	< 0.02	< 0.02	< 0.2	< 0.02	< 0.03	< 0.05	< 0.08	< 0.05	< 0.03
Non 2,3,7,8 HpCDF	< 0.01	< 0.02	< 0.02	< 0.03	< 0.2	< 0.06	< 0.05	0.11	0.28	< 0.04	< 0.02
OCDF	< 0.1	< 0.1	< 0.05	< 0.1	< 0.6	< 0.1	< 0.07	0.26	< 0.6	< 0.2	< 0.1
Sum of PCDD/Fs (inc)[1]	0.38	0.45	2.39	9.57	12.8	4.62	4.01	19.3	71.5	0.69	0.97
Sum of PCDD/Fs (exc)[2]	0	0	2.06	9.32	11.4	4.33	3.73	19.2	70.8	0	0.49
Total I-TEQ (inc)[1]	0.024	0.028	0.051	0.059	0.14	0.054	0.031	0.26	0.18	0.037	0.026
Total I-TEQ (exc)[2]	0	0	0.019	0.036	0.014	0.0028	0.0037	0.23	0.088	0	0

Table D2 Concentrations of PCDDs and PCDFs in New Zealand estuarine shellfish (ng kg^{-1}, wet wt basis) (Cont.)

Congener	Tauranga Harbour Hunters Creek[3]	Tauranga Harbour Town Reach, opening of Waipu Bay[3]	Tauranga Harbour Waikareao Estuary[3]	Wairau Estuary Arapipi Channel[3]	Wairau Estuary Morgans Creek/Budges Island channel[3]	Whanganui Inlet southern section of Inlet[3]	Whanganui Inlet south of Inlet entrance[3]	Moutere Inlet south/south east (n=2)[3,5]	Moutere Inlet south west of Jackett Island[3]	Avon Heathcote Estuary McCormacks Bay outlet (n=2)[3,5]	Avon Heathcote Estuary opposite Pleasant Point Domain[3]
2,3,7,8 TCDD	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.02
Non 2,3,7,8 TCDD	< 0.01	< 0.06	0.90	< 0.01	< 0.03	0.21	0.18	< 0.03	< 0.02	< 0.05	0.29
1,2,3,7,8 PeCDD	< 0.02	< 0.03	0.13	< 0.01	< 0.05	< 0.04	< 0.03	< 0.02	< 0.02	< 0.02	< 0.02
Non 2,3,7,8 PeCDD	0.33	0.51	2.50	< 0.02	0.44	0.54	0.43	< 0.03	0.22	< 0.2	0.12
1,2,3,4,7,8 HxCDD	< 0.01	< 0.03	< 0.06	< 0.01	< 0.03	< 0.03	< 0.03	< 0.02	< 0.02	< 0.02	< 0.02
1,2,3,6,7,8 HxCDD	< 0.04	< 0.04	< 0.1	< 0.01	< 0.04	< 0.02	< 0.03	< 0.01	< 0.02	< 0.01	< 0.02
1,2,3,7,8,9 HxCDD	< 0.02	< 0.04	< 0.09	< 0.01	< 0.05	< 0.05	< 0.06	< 0.01	< 0.02	< 0.01	< 0.02
Non 2,3,7,8 HxCDD	0.76	0.66	1.97	< 0.02	0.43	0.39	0.56	< 0.04	0.18	< 0.03	0.29
1,2,3,4,6,7,8 HpCDD	0.70	0.48	0.90	< 0.02	0.11	< 0.06	0.13	0.19	< 0.07	< 0.07	0.29
Non 2,3,7,8 HpCDD	0.97	0.82	1.39	< 0.02	0.14	< 0.07	0.18	0.27	< 0.1	< 0.08	0.71
OCDD	5.97	2.48	5.39	< 0.1	< 0.3	< 0.2	< 0.3	5.35	< 0.6	< 0.6	8.27
2,3,7,8 TCDF	< 0.02	< 0.02	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.02	< 0.02
Non 2,3,7,8 TCDF	0.11	< 0.02	0.25	< 0.01	< 0.02	< 0.01	< 0.01	< 0.02	< 0.01	0.14	0.47
1,2,3,7,8 PeCDF	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01
2,3,4,7,8 PeCDF	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02
Non 2,3,7,8 PeCDF	0.20	< 0.03	0.38	< 0.01	< 0.02	< 0.03	< 0.02	< 0.03	< 0.03	< 0.07	0.23
1,2,3,4,7,8 HxCDF	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1,2,3,6,7,8 HxCDF	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
2,3,4,6,7,8 HxCDF	< 0.01	< 0.02	< 0.02	< 0.01	< 0.02	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.02
1,2,3,7,8,9 HxCDF	< 0.01	< 0.02	< 0.03	< 0.01	< 0.02	< 0.01	< 0.01	< 0.02	< 0.01	< 0.02	< 0.03
Non 2,3,7,8 HxCDF	0.28	0.13	0.40	< 0.01	< 0.03	< 0.03	< 0.02	< 0.03	< 0.04	< 0.04	0.12
1,2,3,4,6,7,8 HpCDF	0.19	< 0.09	0.23	< 0.01	< 0.03	< 0.03	< 0.03	< 0.04	< 0.03	< 0.03	0.088
1,2,3,4,7,8,9 HpCDF	< 0.01	< 0.03	< 0.02	< 0.01	< 0.03	< 0.03	< 0.02	< 0.02	< 0.02	< 0.02	< 0.03
Non 2,3,7,8 HpCDF	0.24	< 0.08	0.25	< 0.01	< 0.03	< 0.02	< 0.02	< 0.03	< 0.03	< 0.02	0.16
OCDF	0.34	< 0.1	0.30	< 0.05	< 0.08	< 0.07	< 0.09	< 0.03	< 0.09	< 0.06	< 0.2
Sum of PCDD/Fs (inc)[1]	10.2	5.41	15.2	0.21	1.55	1.52	1.85	6.01	1.00	0.83	11.3
Sum of PCDD/Fs (exc)[2]	10.1	5.08	15.0	0	1.13	1.14	1.48	5.50	0.40	0.14	11.0
Total I-TEQ (inc)[1]	0.034	0.033	0.12	0.015	0.031	0.026	0.026	0.031	0.019	0.017	0.040
Total I-TEQ (exc)[2]	0.015	0.0073	0.083	0	0.0011	0	0.0013	0.0070	0	0	0.012

Table D2 Concentrations of PCDDs and PCDFs in New Zealand estuarine shellfish (ng kg^{-1}, wet wt basis) (Cont.)

Congener	Otago Harbour Rocky Point[3]	Otago Harbour Tayler Point[3]	New River Estuary Bushy Point[3]	New River Estuary Whalers Bay[3]	Number of positives	Minimum	Maximum[6]	Median[7]	Mean[8,9]	Mean of ^{13}C surrogate standard recoveries, %, (n=29)
2,3,7,8 TCDD	< 0.01	< 0.02	< 0.02	< 0.03	0	< 0.01	< 0.08	< 0.02	-	95
Non 2,3,7,8 TCDD	< 0.03	< 0.04	0.84	0.85	13	< 0.01	2.04	0.11	-	
1,2,3,7,8 PeCDD	< 0.01	< 0.02	< 0.02	< 0.02	2	< 0.01	0.14	< 0.03	-	81
Non 2,3,7,8 PeCDD	< 0.02	< 0.04	0.24	0.21	17	< 0.02	2.50	0.23	0.50	
1,2,3,4,7,8 HxCDD	< 0.02	< 0.03	< 0.03	< 0.02	0	< 0.01	< 0.1	< 0.03	-	91
1,2,3,6,7,8 HxCDD	< 0.01	< 0.02	< 0.03	< 0.02	1	< 0.01	0.18	< 0.02	-	99
1,2,3,7,8,9 HxCDD	< 0.02	< 0.03	< 0.03	< 0.03	1	< 0.01	0.13	< 0.03	-	
Non 2,3,7,8 HxCDD	< 0.04	< 0.04	< 0.1	0.26	16	< 0.02	1.97	0.23	-	
1,2,3,4,6,7,8 HpCDD	< 0.06	< 0.08	0.26	0.16	15	< 0.02	1.29	0.15	-	80
Non 2,3,7,8 HpCDD	< 0.08	< 0.09	0.25	0.22	15	< 0.02	1.52	0.20	-	
OCDD	< 0.4	< 0.4	2.19	1.71	13	< 0.1	61.7	0.67	-	63
2,3,7,8 TCDF	< 0.04	< 0.02	< 0.05	< 0.05	4	< 0.01	0.48	< 0.02	-	95
Non 2,3,7,8 TCDF	< 0.04	< 0.03	0.20	0.23	13	< 0.01	4.67	0.063	-	
1,2,3,7,8 PeCDF	< 0.01	< 0.01	< 0.02	< 0.01	0	< 0.01	< 0.06	< 0.01	-	92
2,3,4,7,8 PeCDF	< 0.02	< 0.02	< 0.03	< 0.02	1	< 0.01	0.14	< 0.01	-	99
Non 2,3,7,8 PeCDF	< 0.03	< 0.04	0.13	0.22	12	< 0.01	2.16	< 0.06	-	
1,2,3,4,7,8 HxCDF	< 0.01	< 0.02	< 0.02	< 0.02	0	< 0.01	< 0.1	< 0.01	-	79
1,2,3,6,7,8 HxCDF	< 0.01	< 0.02	< 0.01	< 0.01	0	< 0.01	< 0.07	< 0.01	-	89
2,3,4,6,7,8 HxCDF	< 0.01	< 0.02	< 0.03	< 0.01	0	< 0.01	< 0.1	< 0.02	-	86
1,2,3,7,8,9 HxCDF	< 0.01	< 0.03	< 0.02	< 0.01	0	< 0.01	< 0.1	< 0.02	-	66
Non 2,3,7,8 HxCDF	< 0.02	< 0.03	< 0.05	< 0.08	9	< 0.01	0.50	< 0.04	-	
1,2,3,4,6,7,8 HpCDF	< 0.03	< 0.05	< 0.08	< 0.09	5	< 0.01	0.32	< 0.04	-	76
1,2,3,4,7,8,9 HpCDF	< 0.02	< 0.04	< 0.04	< 0.02	0	< 0.01	< 0.2	< 0.03	-	74
Non 2,3,7,8 HpCDF	< 0.03	< 0.03	< 0.08	< 0.06	5	< 0.01	0.28	< 0.03	-	
OCDF	< 0.06	< 0.1	< 0.1	< 0.1	3	< 0.03	0.34	< 0.1	-	
Sum of PCDD/Fs (inc)[1]	0.52	0.64	4.48	4.15		0.21	71.5	3.20	7.37	
Sum of PCDD/Fs (exc)[2]	0	0	4.10	3.85		0	70.8	2.90	6.93	
Total I-TEQ (inc)[1]	0.020	0.031	0.039	0.038		0.015	0.26	0.032	0.054	
Total I-TEQ (exc)[2]	0	0	0.0047	0.0033		0	0.23	0.0031	0.020	

1 = Including half LOD values.
2 = Excluding LOD values.
3 = New Zealand cockle (*Austrovenus stutchburyi*).
4 = Pacific oyster (*Crassostrea gigas*).
5 = Mean of primary and blind duplicate samples.
6 = Excludes any LOD value which is greater than a maximum measured value.
7 = For any individual congener, calculation of the median includes half LOD values.
8 = Mean value reported only if a PCDD/F congener detected on more than 66% of occasions (minimum of 17 positive determinations).
9 = For any individual congener, calculation of the mean includes half LOD values.

Table D3 Comparative PCDD and PCDF concentrations in primary and blind duplicate sediment sample analyses (ng kg^{-1}, dry wt basis)

Congener	Parengarenga Harbour Akatarere Point Primary	Parengarenga Harbour Akatarere Point Blind duplicate	Tauranga Harbour Waikareao Estuary Primary	Tauranga Harbour Waikareao Estuary Blind duplicate	Otago Harbour Rocky Point Primary	Otago Harbour Rocky Point Blind duplicate
2,3,7,8 TCDD	< 0.1	< 0.1	< 0.1	< 0.1	< 0.04	< 0.05
Non 2,3,7,8 TCDD	< 0.1	< 0.1	2.91	5.91	< 0.1	< 0.2
1,2,3,7,8 PeCDD	< 0.1	< 0.1	< 0.4	< 0.4	< 0.05	< 0.06
Non 2,3,7,8 PeCDD	< 0.1	< 0.2	4.31	3.72	< 0.09	< 0.09
1,2,3,4,7,8 HxCDD	< 0.1	< 0.1	< 0.4	< 0.5	< 0.07	< 0.07
1,2,3,6,7,8 HxCDD	< 0.1	< 0.1	< 1	< 1	< 0.06	< 0.08
1,2,3,7,8,9 HxCDD	< 0.1	< 0.1	< 0.8	< 0.9	< 0.07	< 0.07
Non 2,3,7,8 HxCDD	< 0.2	< 0.1	17.9	18.6	< 0.1	< 0.1
1,2,3,4,6,7,8 HpCDD	< 0.5	< 0.2	33.8	38.1	< 0.8	< 0.5
Non 2,3,7,8 HpCDD	< 0.4	< 0.2	43.2	47.1	< 0.6	< 0.5
OCDD	< 2	< 0.8	278	330	4.33	3.15
2,3,7,8 TCDF	< 0.1	< 0.1	< 0.3	< 0.3	< 0.05	< 0.06
Non 2,3,7,8 TCDF	< 0.1	< 0.1	2.11	2.92	< 0.06	< 0.07
1,2,3,7,8 PeCDF	< 0.1	< 0.1	< 0.2	< 0.2	< 0.03	< 0.04
2,3,4,7,8 PeCDF	< 0.1	< 0.1	< 0.2	< 0.2	< 0.04	< 0.04
Non 2,3,7,8 PeCDF	< 0.1	< 0.1	2.98	4.52	< 0.06	< 0.08
1,2,3,4,7,8 HxCDF	< 0.1	< 0.1	< 0.7	< 0.4	< 0.05	< 0.07
1,2,3,6,7,8 HxCDF	< 0.1	< 0.1	< 0.6	< 0.3	< 0.04	< 0.05
2,3,4,6,7,8 HxCDF	< 0.1	< 0.1	< 0.7	< 0.4	< 0.06	< 0.07
1,2,3,7,8,9 HxCDF	< 0.1	< 0.1	< 0.2	< 0.2	< 0.07	< 0.09
Non 2,3,7,8 HxCDF	< 0.1	< 0.1	8.00	8.66	< 0.1	< 0.07
1,2,3,4,6,7,8 HpCDF	< 0.3	< 0.1	12.9	13.8	< 0.03	< 0.2
1,2,3,4,7,8,9 HpCDF	< 0.2	< 0.3	< 0.5	< 0.5	< 0.08	< 0.1
Non 2,3,7,8 HpCDF	< 0.2	< 0.1	13.4	14.2	< 0.3	< 0.2
OCDF	< 0.4	< 0.5	14.6	17.6	< 0.6	< 0.5
Sum of PCDD/Fs (inc)[1]	2.95	2.05	437	508	6.10	4.83
Sum of PCDD/Fs (exc)[2]	0	0	434	505	4.33	3.15
Total I-TEQ (inc)[1]	0.15	0.15	1.20	1.27	0.076	0.086
Total I-TEQ (exc)[2]	0	0	0.76	0.87	0.0043	0.0032

1 = Including half LOD values.
2 = Excluding LOD values.

Table D4 Comparative PCDD and PCDF concentrations in primary and blind duplicate shellfish sample analyses (ng kg^{-1}, wet wt basis)

Congener	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Primary	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Blind duplicate	Moutere Inlet south/south east Primary	Moutere Inlet south/south east Blind duplicate	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Blind duplicate
2,3,7,8 TCDD	< 0.05	< 0.1	< 0.01	< 0.03	< 0.01	< 0.01
Non 2,3,7,8 TCDD	1.21	0.97	< 0.01	< 0.04	< 0.06	< 0.04
1,2,3,7,8 PeCDD	< 0.07	< 0.1	< 0.01	< 0.03	< 0.02	< 0.01
Non 2,3,7,8 PeCDD	1.57	0.68	< 0.02	< 0.03	< 0.4	< 0.02
1,2,3,4,7,8 HxCDD	< 0.09	< 0.2	< 0.01	< 0.02	< 0.02	< 0.01
1,2,3,6,7,8 HxCDD	< 0.07	< 0.1	< 0.01	< 0.01	< 0.01	< 0.01
1,2,3,7,8,9 HxCDD	< 0.1	< 0.2	< 0.01	< 0.01	< 0.01	< 0.01
Non 2,3,7,8 HxCDD	1.20	< 0.6	< 0.03	< 0.04	< 0.03	< 0.02
1,2,3,4,6,7,8 HpCDD	0.78	0.86	< 0.08	0.33	< 0.09	< 0.04
Non 2,3,7,8 HpCDD	1.12	1.34	< 0.08	0.49	< 0.1	< 0.06
OCDD	4.83	6.28	< 0.5	10.2	< 0.8	< 0.4
2,3,7,8 TCDF	< 0.08	< 0.1	< 0.01	< 0.02	< 0.02	< 0.01
Non 2,3,7,8 TCDF	0.54	< 0.2	< 0.01	< 0.02	0.16	0.12
1,2,3,7,8 PeCDF	< 0.03	< 0.08	< 0.01	< 0.02	< 0.01	< 0.01
2,3,4,7,8 PeCDF	< 0.03	< 0.1	< 0.01	< 0.01	< 0.01	< 0.01
Non 2,3,7,8 PeCDF	0.68	0.38	< 0.02	< 0.04	< 0.09	< 0.04
1,2,3,4,7,8 HxCDF	< 0.05	< 0.2	< 0.01	< 0.01	< 0.01	< 0.01
1,2,3,6,7,8 HxCDF	< 0.03	< 0.1	< 0.01	< 0.01	< 0.01	< 0.01
2,3,4,6,7,8 HxCDF	< 0.04	< 0.2	< 0.01	< 0.02	< 0.01	< 0.01
1,2,3,7,8,9 HxCDF	< 0.05	< 0.2	< 0.01	< 0.03	< 0.02	< 0.01
Non 2,3,7,8 HxCDF	0.25	< 0.2	< 0.02	< 0.03	< 0.04	< 0.03
1,2,3,4,6,7,8 HpCDF	< 0.2	< 0.3	< 0.03	< 0.04	< 0.04	< 0.02
1,2,3,4,7,8,9 HpCDF	< 0.05	< 0.3	< 0.01	< 0.03	< 0.02	< 0.01
Non 2,3,7,8 HpCDF	< 0.1	< 0.2	< 0.02	< 0.04	< 0.02	< 0.01
OCDF	< 0.3	< 0.9	< 0.1	< 0.4	< 0.05	< 0.07
Sum of PCDD/Fs (inc)[1]	12.9	12.7	0.53	11.5	1.11	0.56
Sum of PCDD/Fs (exc)[2]	12.2	10.5	0	11.0	0.16	0.12
Total I-TEQ (inc)[1]	0.090	0.19	0.015	0.046	0.019	0.015
Total I-TEQ (exc)[2]	0.013	0.015	0	0.014	0	0

1 = Including half LOD values.
2 = Excluding LOD values.

Table D5 Comparative PCDD and PCDF concentrations in primary and split QC sediment sample analyses (ng kg^{-1}, dry wt basis)

Congener	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Primary[3]	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Split QC[4,5]	Tauranga Harbour Waikareao Estuary Primary	Tauranga Harbour Waikareao Estuary Split QC	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Split QC
2,3,7,8 TCDD	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2
Non 2,3,7,8 TCDD	4.47	4.1	2.91	4.1	< 0.7	< 0.2
1,2,3,7,8 PeCDD	< 0.3	< 0.4	< 0.4	< 0.4	< 0.1	< 0.3
Non 2,3,7,8 PeCDD	8.28	6.2	4.31	1.6	< 0.3	< 0.3
1,2,3,4,7,8 HxCDD	< 0.4	< 0.6	< 0.4	< 0.6	< 0.1	< 0.3
1,2,3,6,7,8 HxCDD	< 1	1.1	< 1	1.1	< 0.1	< 0.1
1,2,3,7,8,9 HxCDD	< 0.8	< 1	< 0.8	1.3	< 0.2	< 0.1
Non 2,3,7,8 HxCDD	19.6	17	17.9	14	< 0.9	< 0.3
1,2,3,4,6,7,8 HpCDD	22.3	20	33.8	26	< 0.9	< 0.9
Non 2,3,7,8 HpCDD	33.8	28	43.2	38	< 1	< 0.9
OCDD	202	140	278	160	< 6	< 4
2,3,7,8 TCDF	< 0.7	0.97	< 0.3	< 0.4	< 0.1	< 0.1
Non 2,3,7,8 TCDF	3.52	4.8	2.11	2.2	< 0.6	< 0.2
1,2,3,7,8 PeCDF	< 0.2	< 0.3	< 0.2	< 0.2	< 0.1	< 0.09
2,3,4,7,8 PeCDF	< 0.4	0.58	< 0.2	< 0.3	< 0.1	< 0.09
Non 2,3,7,8 PeCDF	4.91	6.0	2.98	3.1	< 0.2	< 0.3
1,2,3,4,7,8 HxCDF	< 0.4	1.4	< 0.7	0.47	< 0.1	< 0.07
1,2,3,6,7,8 HxCDF	< 0.4	< 0.8	< 0.6	< 0.5	< 0.1	< 0.3
2,3,4,6,7,8 HxCDF	< 0.4	1.0	< 0.7	< 0.4	< 0.1	< 0.2
1,2,3,7,8,9 HxCDF	< 0.1	< 0.6	< 0.2	< 0.6	< 0.1	< 0.6
Non 2,3,7,8 HxCDF	6.30	5.6	8.00	6.2	< 0.1	< 0.2
1,2,3,4,6,7,8 HpCDF	6.92	5.5	12.9	5.2	< 0.4	< 0.4
1,2,3,4,7,8,9 HpCDF	< 0.3	< 0.4	< 0.5	< 0.6	< 0.1	< 0.2
Non 2,3,7,8 HpCDF	5.38	3.7	13.4	6.8	< 0.3	< 0.3
OCDF	8.72	5.7	14.6	12	< 0.4	< 0.5
Sum of PCDD/Fs (inc)[1]	329	254	437	284	6.60	5.58
Sum of PCDD/Fs (exc)[2]	326	252	434	282	0	0
Total I-TEQ (inc)[1]	0.94	1.45	1.20	1.13	0.16	0.30
Total I-TEQ (exc)[2]	0.50	1.14	0.76	0.77	0	0

1 = Including half LOD values.
2 = Excluding LOD values.
3 = Analysed by primary laboratory.
4 = Analysed by independent cross-check laboratory.
5 = Split QC analyses (all samples) not congener-specific for 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF or 1,2,3,7,8,9-HxCDD.

Table D6 Comparative PCDD and PCDF concentrations in primary and split QC shellfish sample analyses (ng kg^{-1}, wet wt basis)

Congener	Whangarei Harbour Mangapai River mouth Primary[3]	Whangarei Harbour Mangapai River mouth Split QC[4,5]	Kawhia Harbour north shore on State Highway 31 Primary	Kawhia Harbour north shore on State Highway 31 Split QC	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Split QC
2,3,7,8 TCDD	< 0.02	< 0.09	< 0.02	< 0.05	< 0.01	< 0.2
Non 2,3,7,8 TCDD	0.43	0.35	< 0.07	0.17	< 0.06	< 0.2
1,2,3,7,8 PeCDD	< 0.02	< 0.07	< 0.04	< 0.03	< 0.02	< 0.03
Non 2,3,7,8 PeCDD	0.12	< 0.2	< 0.06	< 0.05	< 0.4	< 0.08
1,2,3,4,7,8 HxCDD	< 0.03	< 0.05	< 0.03	< 0.03	< 0.02	< 0.08
1,2,3,6,7,8 HxCDD	< 0.02	< 0.03	< 0.03	< 0.02	< 0.01	< 0.07
1,2,3,7,8,9 HxCDD	< 0.02	< 0.03	< 0.03	< 0.02	< 0.01	< 0.07
Non 2,3,7,8 HxCDD	0.20	< 0.2	< 0.04	< 0.08	< 0.03	< 0.08
1,2,3,4,6,7,8 HpCDD	< 0.04	< 0.1	< 0.08	< 0.05	< 0.09	< 0.1
Non 2,3,7,8 HpCDD	< 0.06	< 0.1	< 0.08	< 0.04	< 0.1	< 0.2
OCDD	< 0.2	< 0.2	< 0.3	< 0.1	< 0.8	0.58
2,3,7,8 TCDF	0.19	0.20	< 0.02	< 0.04	< 0.02	< 0.2
Non 2,3,7,8 TCDF	0.77	0.51	< 0.03	< 0.1	0.157	< 0.2
1,2,3,7,8 PeCDF	< 0.02	< 0.04	< 0.02	< 0.02	< 0.01	< 0.1
2,3,4,7,8 PeCDF	< 0.04	< 0.05	< 0.02	< 0.01	< 0.01	< 0.1
Non 2,3,7,8 PeCDF	0.36	0.27	< 0.04	< 0.03	< 0.09	< 0.1
1,2,3,4,7,8 HxCDF	< 0.01	< 0.05	< 0.02	< 0.03	< 0.01	< 0.07
1,2,3,6,7,8 HxCDF	< 0.01	< 0.04	< 0.02	< 0.03	< 0.01	< 0.05
2,3,4,6,7,8 HxCDF	< 0.01	< 0.03	< 0.02	< 0.02	< 0.01	< 0.03
1,2,3,7,8,9 HxCDF	< 0.02	< 0.1	< 0.03	< 0.06	< 0.02	< 0.1
Non 2,3,7,8 HxCDF	< 0.03	< 0.1	< 0.04	< 0.03	< 0.04	< 0.1
1,2,3,4,6,7,8 HpCDF	< 0.02	< 0.06	< 0.04	< 0.04	< 0.04	< 0.09
1,2,3,4,7,8,9 HpCDF	< 0.02	< 0.05	< 0.05	< 0.03	< 0.02	< 0.07
Non 2,3,7,8 HpCDF	< 0.02	< 0.05	< 0.04	< 0.04	< 0.02	< 0.09
OCDF	< 0.05	< 0.2	< 0.2	< 0.1	< 0.05	< 0.2
Sum of PCDD/Fs (inc)[1]	2.39	2.25	0.69	0.70	1.11	1.89
Sum of PCDD/Fs (exc)[2]	2.06	1.33	0	0.17	0.16	0.58
Total I-TEQ (inc)[1]	0.051	0.11	0.037	0.049	0.019	0.011
Total I-TEQ (exc)[2]	0.019	0.020	0	0	0	0.00058

1 = Including half LOD values.
2 = Excluding LOD values.
3 = Analysed by primary laboratory.
4 = Analysed by independent cross-check laboratory.
5 = Split QC analyses (all samples) not congener-specific for 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF or 1,2,3,7,8,9-HxCDD.

Table D7 **Concentrations of PCDDs and PCDFs in sediment field blanks and equipment rinsate blanks (ng kg^{-1}, dry wt basis for field blanks; ng L^{-1} for equipment rinsate blanks)**

Congener		Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Field blank		Kawhia Harbour north shore on State Highway 31 Field blank		New River Estuary Bushy Point Field blank		Wairau Estuary Arapipi Channel Rinsate blank		New River Estuary Bushy Point Rinsate blank	Mean of ^{13}C surrogate standard recoveries, %, (n= 5)
2,3,7,8 TCDD	<	0.01	<	0.01	<	0.001	<	0.02	<	0.04	112
Non 2,3,7,8 TCDD	<	0.01	<	0.01	<	0.002	<	0.03	<	0.05	
1,2,3,7,8 PeCDD	<	0.01	<	0.01	<	0.001	<	0.03	<	0.04	90
Non 2,3,7,8 PeCDD	<	0.01	<	0.02	<	0.001	<	0.05	<	0.04	
1,2,3,4,7,8 HxCDD	<	0.01	<	0.01	<	0.001	<	0.04	<	0.04	104
1,2,3,6,7,8 HxCDD	<	0.01	<	0.01	<	0.001	<	0.04	<	0.04	97
1,2,3,7,8,9 HxCDD	<	0.01	<	0.01	<	0.001	<	0.05	<	0.04	
Non 2,3,7,8 HxCDD	<	0.01	<	0.05	<	0.002	<	0.06	<	0.04	
1,2,3,4,6,7,8 HpCDD	<	0.03	<	0.03	<	0.003	<	0.2	<	0.09	81
Non 2,3,7,8 HpCDD	<	0.02	<	0.03	<	0.003	<	0.2	<	0.09	
OCDD	<	0.1	<	0.09	<	0.01	<	2	<	0.3	67
2,3,7,8 TCDF	<	0.01	<	0.01	<	0.001	<	0.05	<	0.02	100
Non 2,3,7,8 TCDF	<	0.01	<	0.06	<	0.001	<	0.08	<	0.02	
1,2,3,7,8 PeCDF	<	0.01	<	0.01	<	0.001	<	0.04	<	0.02	104
2,3,4,7,8 PeCDF	<	0.01	<	0.01	<	0.001	<	0.04	<	0.02	104
Non 2,3,7,8 PeCDF	<	0.01	<	0.02	<	0.001	<	0.1	<	0.02	
1,2,3,4,7,8 HxCDF	<	0.01	<	0.02	<	0.001	<	0.2	<	0.03	71
1,2,3,6,7,8 HxCDF	<	0.01	<	0.01	<	0.001	<	0.09	<	0.03	76
2,3,4,6,7,8 HxCDF	<	0.01	<	0.01	<	0.001	<	0.03	<	0.04	95
1,2,3,7,8,9 HxCDF	<	0.01	<	0.01	<	0.002	<	0.04	<	0.05	78
Non 2,3,7,8 HxCDF	<	0.01	<	0.03	<	0.001	<	0.2	<	0.04	
1,2,3,4,6,7,8 HpCDF	<	0.01	<	0.06	<	0.002	<	0.3	<	0.05	60
1,2,3,4,7,8,9 HpCDF	<	0.01	<	0.01	<	0.002	<	0.08	<	0.06	73
Non 2,3,7,8 HpCDF	<	0.01	<	0.02	<	0.002	<	0.2	<	0.06	
OCDF	<	0.02	<	0.04	<	0.008	<	0.3	<	0.2	
Sum of PCDD/Fs (inc)[1]		0.19		0.30		0.026		2.24		0.74	
Sum of PCDD/Fs (exc)[2]		0		0		0		0		0	
Total I-TEQ (inc)[1]		0.012		0.015		0.0015		0.060		0.051	
Total I-TEQ (exc)[2]		0		0		0		0		0	

1 = Including half LOD values.
2 = Excluding LOD values.

Appendix E Concentrations of PCBs in New Zealand estuarine sediments and shellfish

This appendix reports the concentrations of PCBs in estuarine sediments and shellfish collected as part of the Organochlorines Programme. Results from field quality control samples are also provided.

Concentrations of 25 PCB congeners are reported. PCB TEQ levels were calculated, both excluding LOD values and including half LOD values, using the WHO TEFs (Ahlborg *et al*., 1994).

PCB data are reported in the following tables:

Table E1 Concentrations of PCBs in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis)[1]

Congener	Parengarenga Harbour Akatarere Point (n=2)[4]	Parengarenga Harbour Oriatou Point	Whangarei Harbour Mangapai River mouth	Whangarei Harbour Limestone Island	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay	Manukau Harbour Big Muddy Creek	Manukau Harbour French Bay, Paturoa Bay Perkins Bay, Little Muddy Creek	Hellyers Creek (upper reaches) Waitemata Harbour	Hellyers Creek (lower reaches) Waitemata Harbour	Kawhia Harbour north shore on State Highway 31	Kawhia Harbour south shore, opposite Maire Point
PCB #77	< 0.001	< 0.001	< 0.003	< 0.005	< 0.007	< 0.001	< 0.003	0.032	< 0.008	< 0.001	< 0.001
PCB #126	< 0.001	< 0.001	< 0.004	< 0.002	< 0.004	< 0.002	< 0.003	< 0.006	< 0.002	< 0.001	< 0.001
PCB #169	< 0.001	< 0.001	< 0.004	< 0.002	< 0.002	< 0.001	< 0.005	< 0.002	< 0.001	< 0.001	< 0.001
PCB #28 + PCB #31	< 0.04	< 0.04	< 0.09	< 0.08	< 0.2	< 0.06	< 0.3	0.33	< 0.06	< 0.07	< 0.08
PCB #52	< 0.01	< 0.01	< 0.02	< 0.03	< 0.05	< 0.02	< 0.04	0.38	0.043	< 0.02	< 0.02
PCB #101	< 0.02	< 0.01	< 0.04	0.080	0.13	< 0.02	0.080	1.45	0.21	< 0.02	< 0.02
PCB #99	< 0.01	< 0.01	< 0.02	0.026	0.056	< 0.01	0.025	0.48	0.075	< 0.01	< 0.01
PCB #123	< 0.01	< 0.01	< 0.04	< 0.01	< 0.01	< 0.01	< 0.01	0.090	< 0.02	< 0.01	< 0.01
PCB #118	< 0.01	< 0.01	< 0.04	0.062	0.11	< 0.02	< 0.06	1.13	0.19	< 0.02	< 0.01
PCB #114	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.021	< 0.01	< 0.01	< 0.01
PCB #105	< 0.01	< 0.01	< 0.01	0.014	< 0.03	< 0.01	< 0.02	0.34	0.046	< 0.01	< 0.01
PCB #153	< 0.02	< 0.01	0.041	0.079	0.17	< 0.02	0.10	1.09	0.35	< 0.02	< 0.01
PCB #138	< 0.02	< 0.01	0.078	0.13	0.30	< 0.03	0.19	1.98	0.54	< 0.02	< 0.02
PCB #167	< 0.01	< 0.01	< 0.01	0.015	0.025	< 0.01	< 0.02	0.31	0.067	< 0.01	< 0.01
PCB #156	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.02	0.14	0.030	< 0.01	< 0.01
PCB #157	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.039	< 0.01	< 0.01	< 0.01
PCB #187	< 0.01	< 0.01	< 0.01	0.022	0.17	< 0.01	0.056	0.22	0.12	< 0.01	< 0.01
PCB #183	< 0.01	< 0.01	< 0.01	< 0.01	0.055	< 0.01	0.025	0.092	0.041	< 0.01	< 0.01
PCB #180	< 0.01	< 0.01	< 0.01	0.014	0.14	< 0.01	0.068	0.25	0.11	< 0.01	< 0.01
PCB #170	< 0.01	< 0.01	< 0.02	0.015	< 0.04	< 0.01	0.091	0.32	0.12	< 0.01	< 0.01
PCB #189	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #202	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #194	< 0.01	< 0.01	< 0.01	< 0.01	0.11	< 0.01	< 0.02	0.071	0.030	< 0.01	< 0.01
PCB #206	< 0.01	< 0.01	< 0.01	< 0.01	0.081	< 0.01	< 0.03	0.022	< 0.02	< 0.01	< 0.01
Sum of PCBs (inc)[2]	0.13	0.12	0.32	0.55	1.55	0.16	0.89	8.80	2.05	0.16	0.16
Sum of PCBs (exc)[3]	0	0	0.12	0.45	1.34	0	0.64	8.79	1.98	0	0
Total PCB TEQ (inc)[1,2]	0.065	0.065	0.23	0.13	0.24	0.12	0.20	0.62	0.17	0.066	0.065
Total PCB TEQ (exc)[1,3]	0	0	0	0.0094	0.013	0	0.01	0.31	0.052	0	0

Table E1 Concentrations of PCBs in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis)[1] (Cont.)

Congener	Tauranga Harbour Hunters Creek	Tauranga Harbour Town Reach, opening of Waipu Bay	Tauranga Harbour Waikareao Estuary (n=2)[4]	Wairau Estuary Arapipi Channel	Wairau Estuary Morgans Creek/Budges Island channel	Whanganui Inlet southern section of Inlet	Whanganui Inlet south of Inlet entrance	Moutere Inlet south/south east	Moutere Inlet south west of Jackett Island	Avon Heathcote Estuary McCormacks Bay outlet	Avon Heathcote Estuary opposite Pleasant Point Domain
PCB #77	< 0.001	< 0.001	0.012	< 0.001	< 0.001	< 0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.007
PCB #126	< 0.001	< 0.001	< 0.009	< 0.002	< 0.002	< 0.005	< 0.004	< 0.002	< 0.001	< 0.001	< 0.002
PCB #169	< 0.001	< 0.001	< 0.003	< 0.001	< 0.005	< 0.01	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
PCB #28 + PCB #31	< 0.05	< 0.04	0.30	< 0.05	< 0.07	< 0.04	< 0.06	< 0.08	< 0.4	< 0.05	< 0.2
PCB #52	< 0.02	< 0.01	0.098	< 0.01	< 0.02	< 0.01	< 0.01	< 0.02	< 0.03	< 0.01	< 0.05
PCB #101	0.13	< 0.01	0.55	< 0.01	< 0.02	< 0.01	< 0.02	< 0.02	< 0.02	< 0.02	0.12
PCB #99	< 0.01	< 0.01	0.089	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.034
PCB #123	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #118	0.038	< 0.01	0.22	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	0.11
PCB #114	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #105	< 0.01	< 0.01	0.047	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03
PCB #153	0.24	< 0.01	0.99	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	0.11
PCB #138	0.36	< 0.01	1.57	< 0.01	< 0.02	< 0.01	< 0.01	< 0.02	< 0.02	< 0.02	0.27
PCB #167	0.028	< 0.01	0.15	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.021
PCB #156	< 0.02	< 0.01	0.081	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02
PCB #157	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #187	0.088	< 0.01	0.36	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.036
PCB #183	0.041	< 0.01	0.17	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02
PCB #180	0.10	< 0.01	0.43	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.029
PCB #170	0.12	< 0.01	0.53	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.042
PCB #189	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #202	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #194	0.019	< 0.01	0.11	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #206	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Sum of PCBs (inc)[2]	1.24	0.12	5.74	0.13	0.15	0.13	0.14	0.17	0.33	0.14	0.95
Sum of PCBs (exc)[3]	1.16	0	5.69	0	0	0	0	0	0	0	0.76
Total PCB TEQ (inc)[1,2]	0.083	0.065	0.61	0.12	0.14	0.31	0.22	0.12	0.065	0.065	0.13
Total PCB TEQ (exc)[1,3]	0.017	0	0.13	0	0	0	0	0	0	0	0.015

Table E1 Concentrations of PCBs in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis)[1] (Cont.)

Congener	Otago Harbour Rocky Point (n=2)[4]	Otago Harbour Tayler Point	New River Estuary Bushy Point	New River Estuary Whalers Bay	Number of positives	Minimum	Maximum[5]	Median	Mean[6]	Mean of ^{13}C surrogate standard recoveries, %, (n=29)
PCB #77	< 0.001	< 0.001	< 0.001	< 0.001	2	< 0.001	0.032	< 0.001	-	83
PCB #126	< 0.001	< 0.001	< 0.001	< 0.001	0	< 0.001	< 0.009	< 0.002	-	80
PCB #169	< 0.001	< 0.001	< 0.001	< 0.001	0	< 0.001	< 0.01	< 0.001	-	69
PCB #28 + PCB #31	< 0.04	< 0.04	< 0.05	< 0.04	2	< 0.04	0.33	< 0.06	-	82
PCB #52	< 0.01	< 0.01	< 0.02	< 0.01	3	< 0.01	0.38	< 0.02	-	84
PCB #101	< 0.01	< 0.01	< 0.02	< 0.02	8	< 0.01	1.45	< 0.02	-	88
PCB #99	< 0.01	< 0.01	< 0.01	< 0.01	7	< 0.01	0.48	< 0.01	-	
PCB #123	< 0.01	< 0.01	< 0.01	< 0.01	1	< 0.01	0.090	< 0.01	-	
PCB #118	< 0.01	< 0.01	< 0.02	< 0.01	7	< 0.01	1.13	< 0.02	-	
PCB #114	< 0.01	< 0.01	< 0.01	< 0.01	1	< 0.01	0.021	< 0.01	-	
PCB #105	< 0.01	< 0.01	< 0.01	< 0.01	4	< 0.01	0.34	< 0.01	-	
PCB #153	< 0.01	< 0.01	< 0.02	< 0.01	9	< 0.01	1.09	< 0.02	-	85
PCB #138	< 0.01	< 0.01	< 0.02	< 0.01	9	< 0.01	1.98	< 0.02	-	
PCB #167	< 0.01	< 0.01	< 0.01	< 0.01	7	< 0.01	0.31	< 0.01	-	
PCB #156	< 0.01	< 0.01	< 0.01	< 0.01	3	< 0.01	0.14	< 0.01	-	
PCB #157	< 0.01	< 0.01	< 0.01	< 0.01	1	< 0.01	0.039	< 0.01	-	
PCB #187	< 0.01	< 0.01	< 0.01	< 0.01	8	< 0.01	0.36	< 0.01	-	
PCB #183	< 0.01	< 0.01	< 0.01	< 0.01	6	< 0.01	0.17	< 0.01	-	
PCB #180	< 0.01	< 0.01	< 0.01	< 0.01	8	< 0.01	0.43	< 0.01	-	86
PCB #170	< 0.01	< 0.01	< 0.01	< 0.01	7	< 0.01	0.53	< 0.01	-	
PCB #189	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	
PCB #202	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	89
PCB #194	< 0.01	< 0.01	< 0.01	< 0.01	5	< 0.01	0.11	< 0.01	-	
PCB #206	< 0.01	< 0.01	< 0.01	< 0.01	2	< 0.01	0.081	< 0.01	-	
Sum of PCBs (inc)[2]	0.12	0.12	0.15	0.13		0.12	8.80	0.16	0.95	
Sum of PCBs (exc)[3]	0	0	0	0		0	8.79	0	0.81	
Total PCB TEQ (inc)[1,2]	0.065	0.065	0.066	0.065		0.065	0.62	0.12	0.16	
Total PCB TEQ (exc)[1,3]	0	0	0	0		0	0.31	0	0.021	

1 = Total PCB TEQ data in ng kg^{-1} dry wt. All other results in µg kg^{-1} dry wt.
2 = Including half LOD values.
3 = Excluding LOD values.
4 = Mean of primary and blind duplicate samples.
5 = Excludes any LOD value which is greater than a maximum measured value.
6 = Mean value reported only if a PCB congener detected on more than 66% of occasions (minimum of 17 positive determinations).

Table E2 Concentrations of PCBs in New Zealand estuarine shellfish (μg kg^{-1}, wet wt basis)[1]

Congener	Parengarenga Harbour Akatarere Point[4]	Parengarenga Harbour Oriatou Point[4]	Whangarei Harbour Mangapai River mouth[5]	Whangarei Harbour Limestone Island[5]	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay (n=2)[4,6]	Manukau Harbour Big Muddy Creek[4]	Manukau Harbour French Bay, Paturoa Bay Perkins Bay, Little Muddy Creek[4]	Hellyers Creek (upper reaches) Waitemata Harbour[5]	Hellyers Creek (lower reaches) Waitemata Harbour[4]	Kawhia Harbour north shore on State Highway 31[5]	Kawhia Harbour south shore, opposite Maire Point[5]
PCB #77	< 0.001	< 0.001	< 0.002	0.0022	0.0034	< 0.001	< 0.001	0.025	0.0066	< 0.001	< 0.001
PCB #126	< 0.001	< 0.001	< 0.001	< 0.002	< 0.001	< 0.001	< 0.001	< 0.005	0.0034	< 0.001	< 0.001
PCB #169	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
PCB #28 + PCB #31	< 0.01	< 0.01	< 0.02	0.026	0.081	0.032	< 0.02	0.095	0.042	0.035	< 0.01
PCB #52	< 0.01	< 0.01	0.018	0.027	0.037	< 0.01	< 0.01	0.35	0.017	< 0.01	< 0.01
PCB #101	< 0.01	< 0.01	0.15	0.21	0.11	0.014	0.014	2.36	0.076	< 0.01	< 0.01
PCB #99	< 0.01	< 0.01	0.069	0.093	0.044	< 0.01	< 0.01	0.90	0.030	< 0.01	< 0.01
PCB #123	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.06	< 0.02	< 0.01	< 0.01
PCB #118	< 0.01	< 0.01	0.092	0.16	0.091	< 0.01	0.013	2.04	0.078	< 0.01	< 0.01
PCB #114	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.022	< 0.01	< 0.01	< 0.01
PCB #105	< 0.01	< 0.01	0.013	0.025	0.023	< 0.01	< 0.01	0.37	0.024	< 0.01	< 0.01
PCB #153	< 0.01	< 0.01	0.34	0.46	0.15	0.021	0.028	2.46	0.15	0.017	0.016
PCB #138	< 0.01	< 0.01	0.32	0.46	0.22	0.027	0.035	3.09	0.24	0.018	0.016
PCB #167	< 0.01	< 0.01	0.026	0.038	0.021	< 0.01	< 0.01	0.36	0.027	< 0.01	< 0.01
PCB #156	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.084	0.014	< 0.01	< 0.01
PCB #157	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.056	< 0.01	< 0.01	< 0.01
PCB #187	< 0.01	< 0.01	0.10	0.13	0.059	0.011	0.012	0.39	0.062	< 0.01	< 0.01
PCB #183	< 0.01	< 0.01	0.015	0.017	0.011	< 0.01	< 0.01	0.084	0.010	< 0.01	< 0.01
PCB #180	< 0.01	< 0.01	< 0.01	0.012	0.032	< 0.01	< 0.01	0.081	0.031	< 0.01	< 0.01
PCB #170	< 0.01	< 0.01	< 0.01	< 0.01	0.038	< 0.01	< 0.01	0.023	0.039	< 0.01	< 0.01
PCB #189	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #202	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.013	< 0.01	< 0.01	< 0.01
PCB #194	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01
PCB #206	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Sum of PCBs (inc)[2]	0.11	0.11	1.20	1.71	0.95	0.19	0.19	12.9	0.90	0.16	0.13
Sum of PCBs (exc)[3]	0	0	1.14	1.66	0.91	0.11	0.10	12.8	0.85	0.070	0.032
Total PCB TEQ (inc)[1,2]	0.065	0.065	0.075	0.13	0.081	0.065	0.066	0.60	0.38	0.065	0.065
Total PCB TEQ (exc)[1,3]	0	0	0.011	0.020	0.017	0	0.0013	0.34	0.36	0	0

Table E2 Concentrations of PCBs in New Zealand estuarine shellfish (µg kg^{-1}, wet wt basis)[1] (Cont.)

Congener	Tauranga Harbour Hunters Creek[4]	Tauranga Harbour Town Reach, opening of Waipu Bay[4]	Tauranga Harbour Waikareao Estuary[4]	Wairau Estuary Arapipi Channel[4]	Wairau Estuary Morgans Creek/Budges Island channel[4]	Whanganui Inlet southern section of Inlet[4]	Whanganui Inlet south of Inlet entrance[4]	Moutere Inlet south/south east (n=2)[4,6]	Moutere Inlet south west of Jackett Island[4]	Avon Heathcote Estuary McCormacks Bay outlet (n=2)[4,6]	Avon Heathcote Estuary opposite Pleasant Point Domain[4]
PCB #77	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.002
PCB #126	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
PCB #169	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
PCB #28 + PCB #31	< 0.03	< 0.01	0.026	< 0.01	< 0.02	< 0.02	< 0.02	< 0.01	< 0.01	< 0.03	< 0.04
PCB #52	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.020
PCB #101	0.013	< 0.01	0.019	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.023	0.057
PCB #99	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.017
PCB #123	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #118	< 0.01	< 0.01	0.015	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.018	0.037
PCB #114	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #105	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #153	0.028	0.011	0.047	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.029	0.066
PCB #138	0.042	0.015	0.069	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.051	0.11
PCB #167	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #156	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #157	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #187	0.011	< 0.01	0.020	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.010	0.026
PCB #183	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #180	< 0.01	< 0.01	0.012	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.017
PCB #170	< 0.01	< 0.01	0.016	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.015
PCB #189	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #202	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #194	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #206	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Sum of PCBs (inc)[2]	0.19	0.12	0.29	0.11	0.11	0.11	0.11	0.11	0.11	0.22	0.44
Sum of PCBs (exc)[3]	0.094	0.026	0.22	0	0	0	0	0	0	0.13	0.36
Total PCB TEQ (inc)[1,2]	0.065	0.065	0.068	0.065	0.065	0.065	0.065	0.065	0.065	0.067	0.070
Total PCB TEQ (exc)[1,3]	0	0	0.0032	0	0	0	0	0	0	0.0018	0.0054

Table E2 Concentrations of PCBs in New Zealand estuarine shellfish (µg kg^{-1}, wet wt basis)[1] (Cont.)

Congener	Otago Harbour Rocky Point[4]	Otago Harbour Tayler Point[4]	New River Estuary Bushy Point[4]	New River Estuary Whalers Bay[4]	Number of positives	Minimum	Maximum[7]	Median[8]	Mean[9,10]	Mean of ^{13}C surrogate standard recoveries, %, (n=29)
PCB #77	< 0.001	< 0.001	< 0.002	< 0.002	4	< 0.001	0.025	< 0.001	-	81
PCB #126	< 0.001	< 0.001	< 0.001	< 0.001	1	< 0.001	0.0034	< 0.001	-	71
PCB #169	< 0.001	< 0.001	< 0.001	< 0.001	0	< 0.001	< 0.001	< 0.001	-	71
PCB #28 + PCB #31	< 0.02	< 0.02	0.031	0.034	9	< 0.01	0.095	< 0.02	-	77
PCB #52	< 0.01	< 0.01	0.010	< 0.01	7	< 0.01	0.35	< 0.01	-	79
PCB #101	< 0.01	< 0.01	0.024	0.022	13	< 0.01	2.36	0.0090	-	77
PCB #99	< 0.01	< 0.01	< 0.01	< 0.01	6	< 0.01	0.90	< 0.01	-	
PCB #123	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.06	< 0.01	-	
PCB #118	< 0.01	< 0.01	0.015	0.013	11	< 0.01	2.04	< 0.01	-	
PCB #114	< 0.01	< 0.01	< 0.01	< 0.01	1	< 0.01	0.022	< 0.01	-	
PCB #105	< 0.01	< 0.01	< 0.01	< 0.01	5	< 0.01	0.37	< 0.01	-	
PCB #153	0.019	0.021	0.027	0.021	18	< 0.01	2.46	0.021	0.15	62
PCB #138	0.027	0.032	0.041	0.035	18	< 0.01	3.09	0.030	0.19	
PCB #167	< 0.01	< 0.01	< 0.01	< 0.01	5	< 0.01	0.36	< 0.01	-	
PCB #156	< 0.01	< 0.01	< 0.01	< 0.01	2	< 0.01	0.084	< 0.01	-	
PCB #157	< 0.01	< 0.01	< 0.01	< 0.01	1	< 0.01	0.056	< 0.01	-	
PCB #187	< 0.01	< 0.01	< 0.01	< 0.01	11	< 0.01	0.39	< 0.01	-	
PCB #183	< 0.01	< 0.01	< 0.01	< 0.01	5	< 0.01	0.084	< 0.01	-	
PCB #180	< 0.01	< 0.01	< 0.01	< 0.01	6	< 0.01	0.081	< 0.01	-	64
PCB #170	< 0.01	< 0.01	< 0.01	< 0.01	5	< 0.01	0.039	< 0.01	-	
PCB #189	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	
PCB #202	< 0.01	< 0.01	< 0.01	< 0.01	1	< 0.01	0.013	< 0.01	-	61
PCB #194	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	
PCB #206	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	
Sum of PCBs (inc)[2]	0.15	0.15	0.23	0.21		0.11	12.9	0.18	0.82	
Sum of PCBs (exc)[3]	0.046	0.053	0.15	0.13		0.0	12.8	0.082	0.73	
Total PCB TEQ (inc)[1,2]	0.065	0.065	0.067	0.066		0.065	0.60	0.065	0.10	
Total PCB TEQ (exc)[1,3]	0	0	0.0015	0.0013		0	0.36	0	0.029	

1 = Total PCB TEQ data reported in ng kg^{-1} wet wt. All other results in µg kg^{-1} wet wt.
2 = Including half LOD values.
3 = Excluding LOD values.
4 = New Zealand cockle (*Austrovenus stutchburyi*).
5 = Pacific oyster (*Crassostrea gigas*).
6 = Mean of primary and blind duplicate samples.
7 = Excludes any LOD value which is greater than a maximum measured value.
8 = For any individual congener, calculation of the median includes half LOD values.
9 = Mean value reported only if a PCB congener detected on more than 66% of occasions (minimum of 17 positive determinations).
10 = For any individual congener, calculation of the mean includes half LOD values.

Table E3 Comparative PCB concentrations in primary and blind duplicate sediment sample analyses (µg kg^{-1},dry wt basis)[1]

Congener	Parengarenga Harbour Akatarere Point Primary	Parengarenga Harbour Akatarere Point Blind duplicate	Tauranga Harbour Waikareao Estuary Primary	Tauranga Harbour Waikareao Estuary Blind duplicate	Otago Harbour Rocky Point Primary	Otago Harbour Rocky Point Blind duplicate
PCB #77	< 0.001	< 0.001	0.012	0.012	< 0.001	< 0.001
PCB #126	< 0.001	< 0.001	< 0.009	< 0.009	< 0.001	< 0.001
PCB #169	< 0.001	< 0.001	< 0.002	< 0.003	< 0.001	< 0.001
PCB #28 + PCB #31	< 0.04	< 0.04	0.30	0.29	< 0.04	< 0.03
PCB #52	< 0.01	< 0.01	0.10	0.095	< 0.01	< 0.01
PCB #101	< 0.02	< 0.01	0.57	0.53	< 0.01	< 0.01
PCB #99	< 0.01	< 0.01	0.091	0.086	< 0.01	< 0.01
PCB #123	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01
PCB #118	< 0.01	< 0.01	0.21	0.23	< 0.01	< 0.01
PCB #114	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #105	< 0.01	< 0.01	0.043	0.050	< 0.01	< 0.01
PCB #153	< 0.02	< 0.01	0.99	0.99	< 0.01	< 0.01
PCB #138	< 0.03	< 0.01	1.58	1.56	< 0.01	< 0.01
PCB #167	< 0.01	< 0.01	0.15	0.15	< 0.01	< 0.01
PCB #156	< 0.01	< 0.01	0.082	0.080	< 0.01	< 0.01
PCB #157	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01
PCB #187	< 0.01	< 0.01	0.34	0.37	< 0.01	< 0.01
PCB #183	< 0.01	< 0.01	0.16	0.17	< 0.01	< 0.01
PCB #180	< 0.01	< 0.01	0.41	0.45	< 0.01	< 0.01
PCB #170	< 0.01	< 0.01	0.51	0.54	< 0.01	< 0.01
PCB #189	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01
PCB #202	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #194	< 0.01	< 0.01	0.099	0.12	< 0.01	< 0.01
PCB #206	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01
Sum of PCBs (inc)[2]	0.14	0.12	5.70	5.78	0.12	0.12
Sum of PCBs (exc)[3]	0	0	5.65	5.73	0	0
Total PCB TEQ (inc)[1,2]	0.065	0.065	0.60	0.61	0.065	0.065
Total PCB TEQ (exc)[1,3]	0	0	0.13	0.13	0	0

1 = Total PCB TEQ data reported in ng kg^{-1} dry wt. All other results in µg kg^{-1} dry wt.
2 = Including half LOD values.
3 = Excluding LOD values.

Table E4 Comparative PCB concentrations in primary and blind duplicate shellfish sample analyses (µg kg^{-1}, wet wt basis)[1]

Congener	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Primary	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Blind duplicate	Moutere Inlet south/south east Primary	Moutere Inlet south/south east Blind duplicate	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Blind duplicate
PCB #77	0.0038	0.0030	< 0.001	< 0.001	< 0.001	< 0.001
PCB #126	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
PCB #169	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
PCB #28 + PCB #31	0.083	0.079	< 0.01	< 0.01	< 0.03	< 0.02
PCB #52	0.037	0.037	< 0.01	< 0.01	< 0.01	< 0.01
PCB #101	0.11	0.11	< 0.01	< 0.01	0.029	0.016
PCB #99	0.045	0.043	< 0.01	< 0.01	< 0.01	< 0.01
PCB #123	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #118	0.095	0.086	< 0.01	< 0.01	0.026	0.010
PCB #114	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #105	0.024	0.021	< 0.01	< 0.01	< 0.01	< 0.01
PCB #153	0.15	0.14	< 0.01	< 0.01	0.037	0.020
PCB #138	0.22	0.21	< 0.01	< 0.01	0.066	0.035
PCB #167	0.022	0.019	< 0.01	< 0.01	< 0.01	< 0.01
PCB #156	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #157	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #187	0.062	0.056	< 0.01	< 0.01	0.014	< 0.01
PCB #183	0.012	0.010	< 0.01	< 0.01	< 0.01	< 0.01
PCB #180	0.033	0.030	< 0.01	< 0.01	< 0.01	< 0.01
PCB #170	0.039	0.036	< 0.01	< 0.01	< 0.01	< 0.01
PCB #189	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #202	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #194	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #206	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Sum of PCBs (inc)[2]	0.98	0.92	0.11	0.11	0.26	0.17
Sum of PCBs (exc)[3]	0.94	0.88	0	0	0.17	0.081
Total PCB TEQ (inc)[1,2]	0.082	0.080	0.065	0.065	0.067	0.066
Total PCB TEQ (exc)[1,3]	0.018	0.016	0	0	0.0026	0.0010

1 = Total PCB TEQ data reported in ng kg^{-1} dry wt. All other results in µg kg^{-1} dry wt.
2 = Including half LOD values.
3 = Excluding LOD values.

Table E5 Comparative PCB concentrations in primary and split QC sediment sample analyses (µg kg^{-1}, dry wt basis)

Congener	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Primary[1]	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Split QC[2]	Tauranga Harbour Waikareao Estuary Primary	Tauranga Harbour Waikareao Estuary Split QC	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Split QC
PCB #77	< 0.007	0.013	< 0.012	0.019	< 0.001	< 0.002
PCB #126	< 0.004	< 0.002	< 0.009	0.0079	< 0.001	< 0.0004
PCB #169	< 0.002	< 0.0003	< 0.002	0.0011	< 0.001	< 0.0001
PCB #118	0.11	0.13	0.21	0.23	< 0.01	0.019
PCB #105	< 0.03	0.052	0.043	0.078	< 0.01	0.0071

1 = Analysed by primary laboratory.
2 = Analysed by independent cross-check laboratory.

Table E6 Comparative PCB concentrations in primary and split QC shellfish sample analyses (µg kg^{-1}, wet wt basis)[1]

Congener	Whangarei Harbour Mangapai River mouth Primary[1]	Whangarei Harbour Mangapai River mouth Split QC[2]	Kawhia Harbour north shore on State Highway 31 Primary	Kawhia Harbour north shore on State Highway 31 Split QC	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Split QC
PCB #77	< 0.002	0.0036	< 0.001	< 0.0003	< 0.001	0.0016
PCB #126	< 0.001	0.0015	< 0.001	< 0.0002	< 0.001	< 0.0003
PCB #169	< 0.001	< 0.0002	< 0.001	< 0.0002	< 0.001	< 0.0002
PCB #118	0.092	0.11	< 0.01	0.0063	0.026	0.021
PCB #105	0.013	0.027	< 0.01	0.0017	< 0.01	0.0086

1 = Analysed by primary laboratory.
2 = Analysed by independent cross-check laboratory.

Table E7 Concentrations of PCBs in sediment field blanks and equipment rinsate blanks (µg kg^{-1}, dry wt basis for field blanks; µg L^{-1} for equipment rinsate blanks)[1]

Congener		Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Field blank		Kawhia Harbour north shore on State Highway 31 Field blank		New River Estuary Bushy Point Field blank		Wairau Estuary Arapipi Channel Rinsate blank		New River Estuary Bushy Point Rinsate blank	Mean of ^{13}C surrogate standard recoveries, %, (n= 5)
PCB #77	<	0.001	<	0.001	<	0.001	<	0.002	<	0.001	89
PCB #126	<	0.001	<	0.001	<	0.001	<	0.001	<	0.001	77
PCB #169	<	0.001	<	0.001	<	0.001	<	0.001	<	0.001	85
PCB #28 + PCB #31	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	80
PCB #52	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	78
PCB #101	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	88
PCB #99	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #123	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #118	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #114	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #105	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #153	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	85
PCB #138	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #167	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #156	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #157	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #187	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #183	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #180	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	93
PCB #170	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #189	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #202	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	96
PCB #194	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
PCB #206	<	0.01	<	0.01	<	0.01	<	0.01	<	0.01	
Sum of PCBs (inc)[2]		0.11		0.11		0.11		0.11		0.11	
Sum of PCBs (exc)[3]		0		0		0		0		0	
Total PCB TEQ (inc)[1,2]		0.065		0.065		0.065		0.065		0.065	
Total PCB TEQ (exc)[1,3]		0		0		0		0		0	

1 = Total PCB TEQ data reported in ng kg^{-1} dry wt (field blanks) or ng L^{-1} (rinsate blanks). All other results in µg kg^{-1} dry wt (field blanks) or µg L^{-1} (rinsate blanks).
2 = Including half LOD values.
3 = Excluding LOD values.

Appendix F Concentrations of organochlorine pesticides in New Zealand estuarine sediments and shellfish

This appendix reports the concentrations of organochlorine pesticides and pesticide degradation products in estuarine sediments and shellfish collected as part of the Organochlorines Programme. Results from field quality control samples are also provided.

Organochlorine pesticide data are reported in the following tables:

Table F1 Concentrations of organochlorine pesticides in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis)

Pesticide	Parengarenga Harbour Akatarere Point (n=2)[1]	Parengarenga Harbour Oriatou Point	Whangarei Harbour Mangapai River mouth	Whangarei Harbour Limestone Island	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay	Manukau Harbour Big Muddy Creek	Manukau Harbour French Bay, Paturoa Bay Perkins Bay, Little Muddy Creek	Hellyers Creek (upper reaches) Waitemata Harbour	Hellyers Creek (lower reaches) Waitemata Harbour	Kawhia Harbour north shore on State Highway 31	Kawhia Harbour south shore, opposite Maire Point
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Gamma-HCH	< 0.02	< 0.01	< 0.02	0.024	< 0.02	< 0.02	0.031	0.046	< 0.03	< 0.02	< 0.02
HCB	< 0.01	< 0.01	< 0.02	0.83	0.29	< 0.01	0.029	0.075	0.036	< 0.01	< 0.01
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dieldrin	< 0.2	< 0.07	< 0.1	0.23	0.27	< 0.1	0.18	0.34	0.21	< 0.09	< 0.09
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.018	< 0.05	< 0.01	< 0.02
Heptachlor epoxide	< 0.01	< 0.02	< 0.03	< 0.01	< 0.06	< 0.03	< 0.01	< 0.04	< 0.03	< 0.01	< 0.02
Alpha-chlordane	< 0.02	< 0.02	< 0.04	< 0.02	< 0.09	< 0.04	< 0.05	0.098	< 0.06	< 0.02	< 0.02
Gamma-chlordane	< 0.02	< 0.02	< 0.04	< 0.02	< 0.1	< 0.04	< 0.06	0.089	< 0.04	< 0.03	< 0.02
pp-DDE	< 0.01	< 0.01	< 0.07	0.22	0.28	< 0.04	0.18	1.18	0.69	0.19	0.073
pp-TDE	< 0.01	< 0.01	< 0.06	0.16	0.47	< 0.02	0.088	0.33	0.18	0.083	< 0.02
op-DDT	< 0.01	< 0.01	< 0.01	0.054	< 0.01	< 0.01	< 0.03	0.032	0.046	< 0.01	< 0.01
pp-DDT	< 0.01	< 0.01	< 0.02	0.13	0.093	< 0.02	0.10	0.21	0.43	0.032	< 0.02

Table F1 Concentrations of organochlorine pesticides in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis) (Cont.)

Pesticide	Tauranga Harbour Hunters Creek	Tauranga Harbour Town Reach, opening of Waipu Bay	Tauranga Harbour Waikareao Estuary (n=2)[1]	Wairau Estuary Arapipi Channel	Wairau Estuary Morgans Creek/Budges Island channel	Whanganui Inlet southern section of Inlet	Whanganui Inlet south of Inlet entrance	Moutere Inlet south/south east	Moutere Inlet south west of Jackett Island	Avon Heathcote Estuary McCormacks Bay outlet	Avon Heathcote Estuary opposite Pleasant Point Domain
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Gamma-HCH	< 0.02	< 0.02	< 0.03	< 0.02	< 0.03	< 0.02	< 0.02	< 0.03	< 0.02	< 0.01	< 0.03
HCB	0.025	< 0.01	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01	< 0.03
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03
Dieldrin	< 0.08	< 0.06	0.20	< 0.05	< 0.2	< 0.2	< 0.2	< 0.2	0.24	< 0.08	0.38
Heptachlor	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01
Heptachlor epoxide	< 0.03	< 0.02	< 0.04	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.05
Alpha-chlordane	< 0.03	< 0.02	< 0.05	< 0.02	< 0.02	< 0.02	< 0.03	< 0.02	< 0.02	< 0.02	< 0.07
Gamma-chlordane	< 0.03	< 0.02	< 0.06	< 0.02	< 0.03	< 0.02	< 0.03	< 0.02	< 0.03	< 0.03	< 0.07
pp-DDE	0.10	< 0.02	0.52	< 0.07	0.18	0.085	0.11	3.29	1.22	0.062	0.57
pp-TDE	0.065	< 0.01	0.38	< 0.03	< 0.1	0.10	0.27	1.59	0.54	0.059	0.62
op-DDT	< 0.01	< 0.01	0.020	< 0.01	< 0.03	< 0.01	< 0.01	0.051	0.027	< 0.01	0.062
pp-DDT	0.063	< 0.01	0.11	< 0.03	< 0.03	0.030	0.054	0.29	0.13	< 0.01	0.072

Table F1 Concentrations of organochlorine pesticides in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis) (Cont.)

Pesticide	Otago Harbour Rocky Point (n=2)[1]	Otago Harbour Tayler Point	New River Estuary Bushy Point	New River Estuary Whalers Bay	Number of positives	Minimum	Maximum[2]	Median	Mean[3]	Mean of ^{13}C surrogate standard recoveries, %, (n=29)
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	
Gamma-HCH	< 0.01	< 0.01	< 0.01	< 0.01	3	< 0.01	0.046	< 0.02	-	49
HCB	< 0.01	< 0.01	< 0.01	< 0.01	6	< 0.01	0.83	< 0.02	-	57
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.03	< 0.01	-	
Dieldrin	< 0.04	< 0.04	0.11	< 0.09	9	< 0.05	0.38	0.15	-	49
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.01	1	< 0.01	0.018	< 0.01	-	
Heptachlor epoxide	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.06	< 0.02	-	
Alpha-chlordane	< 0.02	< 0.02	< 0.03	< 0.02	1	< 0.02	0.098	< 0.02	-	
Gamma-chlordane	< 0.02	< 0.02	< 0.03	< 0.02	1	< 0.02	0.089	< 0.03	-	
pp-DDE	< 0.02	< 0.01	0.12	0.099	18	< 0.01	3.29	0.11	0.35	71
pp-TDE	< 0.02	< 0.01	0.067	0.038	16	< 0.01	1.59	0.075	-	
op-DDT	< 0.01	< 0.01	< 0.02	< 0.01	7	< 0.01	0.062	< 0.01	-	
pp-DDT	< 0.01	< 0.01	0.074	0.024	15	< 0.01	0.43	0.031	-	56

1 = Mean of primary and blind duplicate samples.
2 = Excludes any LOD value which is greater than a maximum measured value.
3 = Mean value reported only if a pesticide detected on more than 66% of occasions (minimum of 17 positive determinations).

Table F2 Concentrations of organochlorine pesticides in New Zealand estuarine shellfish (µg kg^{-1}, wet wt basis)

Pesticide	Parengarenga Harbour Akatarere Point[1]	Parengarenga Harbour Oriatou Point[1]	Whangarei Harbour Mangapai River mouth[2]	Whangarei Harbour Limestone Island[2]	Manukau Harbour Grannys Bay, Wesley Bay	Manukau Harbour Waikowhai Bay, Wattle Bay (n=2)[1,3]	Manukau Harbour Big Muddy Creek[1]	Manukau Harbour French Bay, Paturoa Bay	Perkins Bay, Little Muddy Creek[1]	Hellyers Creek (upper reaches) Waitemata Harbour[2]	Hellyers Creek (lower reaches) Waitemata Harbour[1]	Kawhia Harbour north shore on State Highway 31[2]	Kawhia Harbour south shore, opposite Maire Point[2]
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Gamma-HCH	0.017	0.022	< 0.01	< 0.01	0.046	0.024	0.035	< 0.01	0.016	< 0.01	< 0.01	< 0.01	< 0.01
HCB	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	0.013	< 0.01	< 0.01	< 0.01	< 0.01
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dieldrin	< 0.02	< 0.02	0.11	0.12	0.43	0.11	0.15	0.39	0.29	0.041	0.047		
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Heptachlor epoxide	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Alpha-chlordane	< 0.01	< 0.01	< 0.01	< 0.02	0.16	0.022	0.028	0.18	0.067	< 0.01	< 0.01		
Gamma-chlordane	< 0.01	< 0.01	< 0.01	< 0.01	0.097	0.011	0.013	0.14	0.048	< 0.01	< 0.01		
pp-DDE	< 0.01	< 0.01	0.28	0.34	0.30	0.059	0.076	2.77	0.39	0.45	0.17		
pp-TDE	< 0.01	< 0.01	0.23	0.37	0.24	0.023	0.043	1.46	0.59	0.15	0.064		
op-DDT	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.032	< 0.02	< 0.01	< 0.01		
pp-DDT	< 0.01	< 0.01	< 0.02	0.041	< 0.03	< 0.02	< 0.02	0.093	0.039	0.020	< 0.02		

Table F2 Concentrations of organochlorine pesticides in New Zealand estuarine shellfish (µg kg^{-1}, wet wt basis) (Cont.)

Pesticide	Tauranga Harbour Hunters Creek[1]	Tauranga Harbour Town Reach, opening of Waipu Bay[1]	Tauranga Harbour Waikareao Estuary[1]	Wairau Estuary Arapipi Channel[1]	Wairau Estuary Morgans Creek/Budges Island channel[1]	Whanganui Inlet southern section of Inlet[1]	Whanganui Inlet south of Inlet entrance[1]	Moutere Inlet south/south east (n=2)[1,3]	Moutere Inlet south west of Jackett Island[1]	Avon Heathcote Estuary McCormacks Bay outlet (n=2)[1,3]	Avon Heathcote Estuary opposite Pleasant Point Domain[1]
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Gamma-HCH	0.015	0.029	0.029	< 0.01	0.016	0.014	0.014	< 0.01	< 0.01	< 0.01	0.015
HCB	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.016
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dieldrin	0.030	0.027	0.071	< 0.02	0.037	0.053	0.028	0.029	0.037	0.20	0.56
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Heptachlor epoxide	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Alpha-chlordane	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.033	0.090
Gamma-chlordane	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.035	0.065
pp-DDE	0.066	0.036	0.079	0.086	0.30	0.21	0.056	0.60	0.24	0.21	0.44
pp-TDE	0.082	0.036	0.050	0.017	0.029	< 0.01	< 0.01	0.27	0.12	0.14	0.24
op-DDT	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02
pp-DDT	< 0.02	< 0.01	< 0.02	< 0.01	< 0.02	< 0.01	< 0.01	0.049	0.026	< 0.02	0.047

Table F2 Concentrations of organochlorine pesticides in New Zealand estuarine shellfish (µg kg^{-1}, wet wt basis) (Cont.)

Pesticide	Otago Harbour Rocky Point[1]	Otago Harbour Tayler Point[1]	New River Estuary Bushy Point[1]	New River Estuary Whalers Bay[1]	Number of positives	Minimum	Maximum[4]	Median	Mean[5]	Mean of ^{13}C surrogate standard recoveries, %, (n=29)
Alpha-HCH	< 0.01	< 0.01	< 0.02	< 0.01	0	< 0.01	< 0.02	< 0.01	-	
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	
Gamma-HCH	< 0.01	< 0.01	< 0.01	0.010	14	< 0.01	0.046	0.012	-	64
HCB	0.010	< 0.01	0.013	0.013	5	< 0.01	0.016	< 0.01	-	56
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	
Dieldrin	0.085	0.090	0.32	0.27	23	< 0.02	0.56	0.078	0.14	58
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	
Heptachlor epoxide	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	
Alpha-chlordane	0.015	< 0.01	0.016	0.019	10	< 0.01	0.18	< 0.01	-	
Gamma-chlordane	0.011	< 0.01	0.019	0.024	10	< 0.01	0.14	< 0.01	-	
pp-DDE	0.090	0.10	0.64	0.49	24	< 0.01	2.77	0.21	0.33	83
pp-TDE	0.050	0.056	0.29	0.22	22	< 0.01	1.46	0.073	0.18	
op-DDT	< 0.01	< 0.01	0.022	0.015	3	< 0.01	0.032	< 0.01	-	
pp-DDT	< 0.02	< 0.03	0.11	0.079	9	< 0.01	0.11	< 0.02	-	53

1 = New Zealand cockle (Austrovenus stutchburyi).
2 = Pacific oyster (Crassostrea gigas).
3 = Mean of primary and blind duplicate samples.
4 = Excludes any LOD value which is greater than a maximum measured value.
5 = Mean value reported only if a pesticide detected on more than 66% of occasions (minimum of 17 positive determinations).

Table F3 Comparative organochlorine pesticide concentrations in primary and blind duplicate sediment sample analyses (µg kg^{-1}, dry wt basis)

Pesticide	Parengarenga Harbour Akatarere Point Primary	Parengarenga Harbour Akatarere Point Blind duplicate	Tauranga Harbour Waikareao Estuary Primary	Tauranga Harbour Waikareao Estuary Blind duplicate	Otago Harbour Rocky Point Primary	Otago Harbour Rocky Point Blind duplicate
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Gamma-HCH	< 0.01	< 0.02	< 0.02	< 0.03	< 0.01	< 0.01
HCB	< 0.01	< 0.01	< 0.02	< 0.02	< 0.01	< 0.01
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dieldrin	< 0.1	< 0.2	0.17	0.23	< 0.04	< 0.04
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01
Heptachlor epoxide	< 0.01	< 0.01	< 0.03	< 0.04	< 0.01	< 0.01
Alpha-chlordane	< 0.01	< 0.02	< 0.04	< 0.05	< 0.02	< 0.02
Gamma-chlordane	< 0.01	< 0.02	< 0.05	< 0.07	< 0.02	< 0.02
pp-DDE	< 0.01	< 0.01	0.49	0.54	< 0.02	< 0.02
pp-TDE	< 0.01	< 0.01	0.41	0.34	< 0.02	< 0.02
op-DDT	< 0.01	< 0.01	0.017	0.022	< 0.01	< 0.01
pp-DDT	< 0.01	< 0.01	0.085	0.14	< 0.01	< 0.01

Table F4 Comparative organochlorine pesticide concentrations in primary and blind duplicate shellfish sample analyses (µg kg^{-1}, wet wt basis)

Pesticide	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Primary	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Blind duplicate	Moutere Inlet south/south east Primary	Moutere Inlet south/south east Blind duplicate	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Blind duplicate
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Gamma-HCH	0.056	0.036	< 0.01	< 0.01	< 0.01	< 0.01
HCB	< 0.02	< 0.01	< 0.01	< 0.01	0.012	< 0.01
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Dieldrin	0.42	0.43	0.028	0.029	0.21	0.18
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Heptachlor epoxide	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Alpha-chlordane	0.17	0.15	< 0.01	< 0.01	0.036	0.029
Gamma-chlordane	0.10	0.093	< 0.01	< 0.01	0.045	0.025
pp-DDE	0.33	0.26	0.60	0.59	0.25	0.17
pp-TDE	0.27	0.20	0.27	0.27	0.22	0.064
op-DDT	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
pp-DDT	< 0.03	< 0.02	0.050	0.048	< 0.01	< 0.02

Table F5 Comparative organochlorine pesticide concentrations in primary and split QC sediment sample analyses (µg kg^{-1}, dry wt basis)

Pesticide		Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Primary[2]		Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay[1] Split QC[3]		Tauranga Harbour Waikareao Estuary Primary		Tauranga Harbour Waikareao Estuary Split QC		Avon Heathcote Estuary McCormacks Bay outlet Primary		Avon Heathcote Estuary McCormacks Bay outlet Split QC
Alpha-HCH	<	0.01	<	0.05	<	0.01	<	0.05	<	0.01	<	0.05
Beta-HCH	<	0.01	<	0.05	<	0.01	<	0.05	<	0.01	<	0.05
Gamma-HCH	<	0.02	<	0.05	<	0.02	<	0.05	<	0.01	<	0.05
HCB		0.29	<	0.05	<	0.02	<	0.05	<	0.01	<	0.05
Aldrin	<	0.01	<	0.05	<	0.01	<	0.05	<	0.01	<	0.05
Dieldrin		0.27		0.08		0.17	<	0.05	<	0.08	<	0.05
Heptachlor	<	0.01	<	0.05	<	0.01	<	0.05	<	0.01	<	0.05
Heptachlor epoxide	<	0.06	<	0.05	<	0.03	<	0.05	<	0.02	<	0.05
Alpha-chlordane	<	0.09		0.08	<	0.04	<	0.05	<	0.02	<	0.05
Gamma-chlordane	<	0.1	<	0.05	<	0.05	<	0.05	<	0.03	<	0.05
pp-DDE		0.28		0.17		0.49		0.27		0.062	<	0.05
pp-TDE		0.47		0.15		0.41		0.19		0.059	<	0.05
op-DDT	<	0.01	<	0.05		0.017	<	0.05	<	0.01	<	0.05
pp-DDT		0.093	<	0.05		0.085		0.12	<	0.01	<	0.05

1 = Mean of laboratory duplicate analyses.
2 = Analysed by primary laboratory.
3 = Analysed by independent cross-check laboratory.

Table F6 Comparative organochlorine pesticide concentrations in primary and split QC shellfish sample analyses (µg kg^{-1}, wet wt basis)

Pesticide	Whangarei Harbour Mangapai River mouth Primary[1]	Whangarei Harbour Mangapai River mouth Split QC[2]	Kawhia Harbour north shore on State Highway 31 Primary	Kawhia Harbour north shore on State Highway 31 Split QC	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Split QC
Alpha-HCH	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
Beta-HCH	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
Gamma-HCH	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
HCB	< 0.01	< 0.05	< 0.01	< 0.05	0.012	< 0.05
Aldrin	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
Dieldrin	0.11	0.19	0.041	< 0.05	0.21	0.21
Heptachlor	< 0.01	< 0.07	< 0.01	< 0.07	< 0.01	< 0.07
Heptachlor epoxide	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
Alpha-chlordane	< 0.01	< 0.05	< 0.01	< 0.05	0.036	< 0.05
Gamma-chlordane	< 0.01	< 0.05	< 0.01	< 0.05	0.045	< 0.05
pp-DDE	0.28	0.35	0.45	0.26	0.25	0.16
pp-TDE	0.23	< 0.05	0.15	< 0.05	0.22	< 0.05
op-DDT	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
pp-DDT	< 0.02	< 0.05	0.020	< 0.05	< 0.01	< 0.05

1 = Analysed by primary laboratory.
2 = Analysed by independent cross-check laboratory.

Table F7 Concentrations of organochlorine pesticides in sediment field blanks and equipment rinsate blanks (µg kg^{-1}, dry wt basis for field blanks; µg L^{-1} for equipment rinsate blanks)

Pesticide	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Field blank	Kawhia Harbour north shore on State Highway 31 Field blank	New River Estuary Bushy Point Field blank	Wairau Estuary Arapipi Channel Rinsate blank	New River Estuary Bushy Point Rinsate blank	Mean of 13C surrogate standard recoveries, %, (n= 5)
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Gamma-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	57
HCB	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	52
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Dieldrin	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	72
Heptachlor	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Heptachlor epoxide	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Alpha-chlordane	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Gamma-chlordane	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
pp-DDE	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	90
pp-TDE	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
op-DDT	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
pp-DDT	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	66

Appendix G Concentrations of chlorophenols in New Zealand estuarine sediments and shellfish

This appendix reports the concentrations of chlorophenols in estuarine sediments and shellfish collected as part of the Organochlorines Programme. Results from field quality control samples are also provided.

Chlorophenol data are reported in the following tables:

Table G1 Concentrations of chlorophenols in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis)

Chlorophenol	Parengarenga Harbour Akatarere Point (n=2)[1]	Parengarenga Harbour Oriatou Point	Whangarei Harbour Mangapai River mouth	Whangarei Harbour Limestone Island	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay	Manukau Harbour Big Muddy Creek	Manukau Harbour French Bay, Paturoa Bay Perkins Bay, Little Muddy Creek	Hellyers Creek (upper reaches) Waitemata Harbour (n=2)[2]	Hellyers Creek (lower reaches) Waitemata Harbour	Kawhia Harbour north shore on State Highway 31	Kawhia Harbour south shore, opposite Maire Point
2,4,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,4,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,5,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4,5 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Pentachlorophenol	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.4	< 0.3	< 0.3	< 0.3

Table G1 Concentrations of chlorophenols in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis) (Cont.)

Chlorophenol	Tauranga Harbour Hunters Creek	Tauranga Harbour Town Reach, opening of Waipu Bay	Tauranga Harbour Waikareao Estuary (n=2)[1]	Wairau Estuary Arapipi Channel	Wairau Estuary Morgans Creek/Budges Island channel	Whanganui Inlet southern section of Inlet	Whanganui Inlet south of Inlet entrance	Moutere Inlet south/south east	Moutere Inlet south west of Jackett Island	Avon Heathcote Estuary McCormacks Bay outlet	Avon Heathcote Estuary opposite Pleasant Point Domain
2,4,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,4,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,5,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4,5 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Pentachlorophenol	< 0.3	< 0.3	< 0.4	< 0.3	0.4	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3

Table G1 Concentrations of chlorophenols in New Zealand estuarine sediment (µg kg^{-1}, dry wt basis) (Cont.)

Chlorophenol	Otago Harbour Rocky Point (n=2)[1]	Otago Harbour Tayler Point	New River Estuary Bushy Point	New River Estuary Whalers Bay	Number of positives	Minimum	Maximum	Median	Mean[3]
2,4,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	0	< 0.4	< 0.4	< 0.4	-
2,3,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	0	< 0.4	< 0.4	< 0.4	-
2,4,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	0	< 0.4	< 0.4	< 0.4	-
2,3,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	0	< 0.4	< 0.4	< 0.4	-
2,3,4 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	0	< 0.4	< 0.4	< 0.4	-
2,3,5,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	0	< 0.4	< 0.4	< 0.4	-
2,3,4,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	0	< 0.4	< 0.4	< 0.4	-
2,3,4,5 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	0	< 0.4	< 0.4	< 0.4	-
Pentachlorophenol	< 0.3	< 0.3	< 0.3	< 0.3	2	< 0.3	0.4	< 0.3	-

1 = Mean of primary and blind duplicate samples.
2 = Mean of laboratory duplicate analyses.
3 = Mean value reported only if a chlorophenol detected on more than 66% of occasions (minimum of 17 positive determinations).

Table G2 Concentrations of chlorophenols in New Zealand estuarine shellfish (µg kg^{-1}, wet wt basis)

Chlorophenol	Parengarenga Harbour Akatarere Point[1]	Parengarenga Harbour Oriatou Point[1]	Whangarei Harbour Mangapai River mouth[2]	Whangarei Harbour Limestone Island[2]	Manukau Harbour Grannys Bay, Wesley Bay, Waikowhai Bay, Wattle Bay (n=2)[1,3]	Manukau Harbour French Bay, Paturoa Bay, Perkins Bay, Little Muddy Creek[1]	Hellyers Creek (Upper Reaches) Waitemata Harbour (n=2)[2,4]	Kawhia Harbour north shore on State Highway 31[2]	Kawhia Harbour south shore, opposite Maire Point[2]
2,4,6 Trichlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	< 0.2	< 0.2	< 0.1	< 0.1	< < 0.1
2,3,5 Trichlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	< 0.2	< 0.2	< 0.1	< 0.1	< < 0.1
2,4,5 Trichlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	< 0.2	< 0.2	< 0.1	< 0.1	< < 0.1
2,3,6 Trichlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	< 0.2	< 0.2	< 0.1	< 0.1	< < 0.1
2,3,4 Trichlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	< 0.2	< 0.2	< 0.1	< 0.1	< < 0.1
2,3,5,6 Tetrachlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	< 0.2	< 0.2	< 0.1	< 0.1	< < 0.1
2,3,4,6 Tetrachlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	< 0.2	< 0.2	< 0.1	< 0.1	< < 0.1
2,3,4,5 Tetrachlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	< 0.2	< 0.2	< 0.1	< 0.1	< < 0.1
Pentachlorophenol	< 0.1	< 0.1	< 0.3	< 0.3	0.25	< 0.2	< 0.1	< 0.1	< < 0.1

Table G2 Concentrations of chlorophenols in New Zealand estuarine shellfish (µg kg^{-1}, wet wt basis) (Cont.)

Chlorophenol	Tauranga Harbour Hunters Creek[1]	Tauranga Harbour Town Reach, opening of Waipu Bay[1]	Tauranga Harbour Waikareao Estuary[1]	Wairau Estuary Arapipi Channel[1]	Wairau Estuary Morgans Creek/Budges Island channel[1]	Whanganui Inlet southern section of Inlet[1]	Whanganui Inlet south of Inlet entrance[1]	Moutere Inlet south/south east (n=2)[1,3]	Moutere Inlet south west of Jackett Island[1]	Avon Heathcote Estuary McCormacks Bay outlet (n=2)[1,3]	Avon Heathcote Estuary opposite Pleasant Point Domain[1]
2,4,6 Trichlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1
2,3,5 Trichlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1
2,4,5 Trichlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1
2,3,6 Trichlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1
2,3,4 Trichlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1
2,3,5,6 Tetrachlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1
2,3,4,6 Tetrachlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1
2,3,4,5 Tetrachlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1
Pentachlorophenol	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.3	< 0.1	< 0.2	0.2

Table G2 Concentrations of chlorophenols in New Zealand estuarine shellfish (µg kg^{-1}, wet wt basis) (Cont.)

Chlorophenol	Otago Harbour Rocky Point[1]	Otago Harbour Tayler Point[1]	New River Estuary Bushy Point[1]	New River Estuary Whalers Bay[1]	Number of positives	Minimum	Maximum[5]	Median	Mean[6]
2,4,6 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.1	-
2,3,5 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.1	-
2,4,5 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.1	-
2,3,6 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.1	-
2,3,4 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.1	-
2,3,5,6 Tetrachlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.1	-
2,3,4,6 Tetrachlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.1	-
2,3,4,5 Tetrachlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.1	-
Pentachlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	2	< 0.1	0.25	< 0.2	-

1 = New Zealand cockle (*Austrovenus stutchburyi*).
2 = Pacific oyster (*Crassostrea gigas*).
3 = Mean of primary and blind duplicate samples.
4 = Mean of laboratory duplicate analyses.
5 = Excludes any LOD value which is greater than a maximum measured value.
6 = Mean value reported only if a chlorophenol detected on more than 66% of occasions (minimum of 16 positive determinations).

Table G3 Comparative chlorophenol concentrations in primary and blind duplicate sediment sample analyses (µg kg^{-1}, dry wt basis)

Chlorophenol	Parengarenga Harbour Akatarere Point Primary	Parengarenga Harbour Akatarere Point Blind duplicate	Tauranga Harbour Waikareao Estuary Primary	Tauranga Harbour Waikareao Estuary Blind duplicate	Otago Harbour Rocky Point Primary	Otago Harbour Rocky Point Blind duplicate
2,4,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,4,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,5,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
2,3,4,5 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4	< 0.4
Pentachlorophenol	< 0.3	< 0.3	< 0.4	< 0.3	< 0.3	< 0.3

Table G4 Comparative chlorophenol concentrations in primary and blind duplicate shellfish sample analyses (µg kg^{-1}, wet wt basis)

Chlorophenol	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Primary	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Blind duplicate	Moutere Inlet south/south east Primary	Moutere Inlet south/south east Blind duplicate	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Blind duplicate
2,4,6 Trichlorophenol	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.1
2,3,5 Trichlorophenol	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.1
2,4,5 Trichlorophenol	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.1
2,3,6 Trichlorophenol	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.1
2,3,4 Trichlorophenol	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.1
2,3,5,6 Tetrachlorophenol	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.1
2,3,4,6 Tetrachlorophenol	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.1
2,3,4,5 Tetrachlorophenol	< 0.2	< 0.2	< 0.3	< 0.3	< 0.2	< 0.1
Pentachlorophenol	0.2	0.3	< 0.3	< 0.3	< 0.2	< 0.1

Table G5 Comparative chlorophenol concentrations in primary and split QC sediment sample analyses (µg kg^{-1}, dry wt basis)

Chlorophenol	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Primary[1]	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Split QC[2]	Tauranga Harbour Waikareao Estuary Primary	Tauranga Harbour Waikareao Estuary Split QC	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Split QC
2,4,6 Trichlorophenol	< 0.4	< 0.2	< 0.4	< 0.1	< 0.4	< 0.1
2,3,5 Trichlorophenol	< 0.4	< 0.1	< 0.4	< 0.1	< 0.4	< 0.1
2,4,5 Trichlorophenol	< 0.4	< 0.2	< 0.4	< 0.1	< 0.4	< 0.1
2,3,4 Trichlorophenol	< 0.4	< 0.1	< 0.4	< 0.1	< 0.4	< 0.1
2,3,5,6 Tetrachlorophenol	< 0.4	< 0.1	< 0.4	< 0.1	< 0.4	< 0.1
2,3,4,6 Tetrachlorophenol	< 0.4	< 0.1	< 0.4	< 0.1	< 0.4	< 0.1
2,3,4,5 Tetrachlorophenol	< 0.4	< 0.1	< 0.4	< 0.1	< 0.4	< 0.1
Pentachlorophenol	< 0.3	< 3	< 0.4	< 1	< 0.3	< 0.5

1 = Analysed by primary laboratory.
2 = Analysed by independent cross-check laboratory.

Table G6 Comparative chlorophenol concentrations in primary and split QC shellfish sample analyses (µg kg^{-1}, wet wt basis)

Chlorophenol	Whangarei Harbour Mangapai River mouth Primary[1]	Whangarei Harbour Mangapai River mouth Split QC[2]	Kawhia Harbour north shore on State Highway 31 Primary	Kawhia Harbour north shore on State Highway 31 Split QC	Avon Heathcote Estuary McCormacks Bay outlet Primary	Avon Heathcote Estuary McCormacks Bay outlet Split QC
2,4,6 Trichlorophenol	< 0.3	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1
2,3,5 Trichlorophenol	< 0.3	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1
2,4,5 Trichlorophenol	< 0.3	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1
2,3,4 Trichlorophenol	< 0.3	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1
2,3,5,6 Tetrachlorophenol	< 0.3	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1
2,3,4,6 Tetrachlorophenol	< 0.3	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1
2,3,4,5 Tetrachlorophenol	< 0.3	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1
Pentachlorophenol	< 0.3	< 0.1	< 0.1	< 0.1	< 0.2	< 0.2

1 = Analysed by primary laboratory.
2 = Analysed by independent cross-check laboratory.

Table G7 Concentrations of chlorophenols in sediment field blanks and equipment rinsate blanks (µg kg^{-1}, dry wt basis for field blanks; µg L^{-1} for equipment rinsate blanks)

Chlorophenol	Manukau Harbour Grannys Bay, Wesley Bay Waikowhai Bay, Wattle Bay Field blank	Kawhia Harbour north shore on State Highway 31 Field blank	New River Estuary Bushy Point Field blank	Wairau Estuary Arapipi Channel Rinsate blank	New River Estuary Bushy Point Rinsate blank
2,4,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.09	< 0.09
2,3,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.09	< 0.09
2,4,5 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.09	< 0.09
2,3,6 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.09	< 0.09
2,3,4 Trichlorophenol	< 0.4	< 0.4	< 0.4	< 0.09	< 0.09
2,3,5,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.09	< 0.09
2,3,4,6 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.09	< 0.09
2,3,4,5 Tetrachlorophenol	< 0.4	< 0.4	< 0.4	< 0.09	< 0.09
Pentachlorophenol	< 0.2	< 0.3	< 0.2	0.35	0.18

Appendix H Overseas data for PCDDs and PCDFs in sediment and shellfish

This appendix summarises comparative international PCDD and PCDF data for estuarine sediments and shellfish.

Table H1 Concentrations of PCDDs and PCDFs in estuarine sediments from other countries

Country	Location	Type	Date sampled	Number of sites	Concentration (ng kg^{-1} DW)				Analysis	Reference
					Sum PCDD/Fs		TEQ			
					Min.	Max.	Min.	Max.		
Australia	Nearshore, Woodside Beach	Background	1991-92	1	6.3	14.8	0.20	0.30	I-TEQ, half LOD	Mosse and Haynes, 1993
	Nearshore, Seaspray Beach	Background	1991-92	1	12.2	19.9	0.10	0.10	I-TEQ, half LOD	Mosse and Haynes, 1993
	Nearshore, Delray Beach	Background	1991-92	1	15.0	32.4	0.20	0.40	I-TEQ, half LOD	Mosse and Haynes, 1993
Canada	Saguenay Fjord	Industrial	1991	2	250	274	0.4	2.3	I-TEQ, LOD=0	Brochu *et al.*, 1995
	Baie des Mille Vaches	Reference	1991	2	106	204	0.4	0.8	I-TEQ, LOD=0	Brochu *et al.*, 1995
	Baie des Anglais	Industrial	1991	1	214		4.9		I-TEQ, LOD=0	Brochu *et al.*, 1995
Italy	Venice Lagoon	Urban	1995	2	146	190	3.8	5.3	I-TEQs, half LOD	Jimenez *et al.*, 1997
		Reference	1995	1	83.1		2.4		I-TEQ, half LOD	Jimenez *et al.*, 1997
		Industrial	1995	1	1330		34.8		I-TEQ, half LOD	Jimenez *et al.*, 1997
Japan	Tokyo Bay, harbour	Urban	1996	1	18200		50.6	50.6	I-TEQ, all above LOD	Masunaga *et al*., 1997
Netherlands	Wadden Sea Estuary	Urban/ind	1990	3	441[a]	1167[a]	5[a]	32[a]		Evers *et al*., 1993
	Wadden Sea Estuary	Urban/ind	1990	3	958[b]	1118[b]	13[b]	36[b]		Evers *et al*., 1993
	Rhine Estuary	Urban/ind	1990	2	2352[b]	4726[b]	43[b]	48[b]		Evers *et al*., 1993
	Ems-Dollard Estuary	Urban/ind	1990	1	1006[b]		9.8[b]			Evers *et al*., 1993
	Western Scheldt Estuary	Urban/ind	1990	1	1146[b]	1541[b]	15[b]	16[b]		Evers *et al*., 1993
Sweden	Landsorts, urban	Urban	1987-88	1	248	872	6.8	28	Nordic TEQ, LOD=0	de Wit *et al*., 1990
Texas	Galveston Bay	Urban/ind		1	592	2468	0.9	7.7	I-TEQ, LOD=0	Gardinali and Wade, 1996
United Kingdom	Tweed Estuary	Urban			209					Tyler *et al*., 1994
	Tees Estuary	Urban/ind			31					Tyler *et al*., 1994
	Tyne Estuary	Urban/ind			103					Tyler *et al*., 1994
	Mersey Estuary	Urban/ind			127					Tyler *et al*., 1994
	Clyde Estuary,	Urban/ind		5	387	5990	8	60		Tyler *et al*., 1994
	Dee Estuary	Urban/ind		9	870	2590	10	23		Tyler *et al*., 1994
	Humber Estuary	Urban/ind		5	559	3065	9	39		Tyler *et al*., 1994
		Urban/ind	1990	2	1846[b]	10560[b]	16[b]	267[b]		Evers *et al*., 1993
USA, Casco Bay	Eastern Bays	Reference	1994	5	340	2800	1.8	18		Wade *et al*., 1997
	Inner Bays	Urban/ind	1994	17	620	3400	4.6	27		Wade *et al*., 1997
	Outer Bays	Urban/ind	1994	4	790	2100	6.3	18		Wade *et al*., 1997
	West Bay	Reference	1994	4	390	1300	2.6	11		Wade *et al*., 1997
USA harbours	Long Island	Background		1	1714					Norwood *et al*., 1989
	New Bedford	Industrial		3	6997	14710				Norwood *et al*., 1989
	Eagle harbour	Industrial		4	4900	44000				Norwood *et al*., 1989

[a] Fraction <1000 μm.
[b] Fraction <63 μm.

Table H2 Concentrations of PCDDs and PCDFs in estuarine shellfish from other countries

Country	Location/Species	Type	Date sampled	Concentration(ng kg^{-1})				Conc. basis	Analysis	Reference
				Sum PCDD/F		TEQ				
				Min.	Max.	Min.	Max.			
Australia, Bass Strait	Bivalve, *Scaeoleda crassa*, off Woodside Beach	General	1992	1.3	1.3				I-TEQ, half LOD	Mosse and Haynes, 1993
	Bivalve, *Scaeoleda crassa*, off Seaspray Beach	General	1992	0.35	0.35				I-TEQ, half LOD	Mosse and Haynes, 1993
	Bivalve, Scaeoleda crassa, off Delray Beach	General	1992	0.24	0.24				I-TEQ, half LOD	Mosse and Haynes, 1993
Australia, Victoria	Mussels, Port Phillip Bay	Industrial	1992	51.6	145	0.23	0.41	WW		Haynes and Toohey, 1995
	Mussels tissue, Port Phillip Bay	Industrial	1993	33.6	133	0.25	0.71	WW		Haynes and Toohey, 1995
Canada, St Lawrence Estuary	Whelk, *Buccinum undatum*	Background	1991	3.5	68.1	0.23	2.19	DW		Brochu *et al*., 1995
	Whelk, *Buccinum undatum*	Industrial	1991	9.9	69.2	0.85	2.54	DW		Brochu *et al*., 1995
East, Gulf and West Coast	Bivalves (NOAA and IMW sites)	Background	1995	0.0	675	nd	40	DW		Wade *et al*., 1996
Japan, Tokyo Bay	Japanese cockle, *Fulvia mutica*	Urban	1996	1026	1026	3.6	3.6	WW	I-TEQ, all above LOD	Masunaga *et al*., 1997
Netherlands, Scheldt Estuary	Mussels		1991			1.3				de Boer *et al*., 1993
Norway	Mussels, *Mytilus edulis*	Background	1987-94			0.1	0.2	WW	Nordic TEQ	Knutzen and Schlabach, 1996
Norway, Frierfjord	Mussels, *Mytilus edulis*	Background	1987-88			9.2	9.6	WW	Nordic TEQ	Knutzen and Oehme, 1989
	Mussels, *Mytilus edulis*	Industrial	1987-88			60		WW	Nordic TEQ	Knutzen and Oehme, 1989
Poland	Mussels, *Mytilus trossulus*	Background	1991-93	23	590			Lipid		Falandysz *et al*., 1997
Texas, Taylor Bayou	Clams, *Rangia cuneata*	Background	1993	10.6	126			WW		Harrel and McConnell, 1995
Texas, Galveston Bay	Oysters	Background		66.0	138	3.1	4.7	?DW	I-TEQ, half LOD	Gardinali and Wade, 1996
	Oysters	Urban		214	257	12.2	24.1	?DW	I-TEQ, half LOD	Gardinali and Wade, 1996
USA, New York	Clams, *Mya arenaria*, Newark Bay	General	1986-87			15	25	WW		Brown *et al*., 1994
	Clams, *Mya arenaria,* Elizabeth, New Jersey	General	1987-89			6.8	11	WW		Brown *et al*., 1994
	Clams, *Mya arenaria,* Wards Point	General	1987			1.2	2.1	WW		Brown *et al*., 1994
	Clams, *Mya arenaria,* Tuckerton	General	1987			1.5	2.1	WW		Brown *et al*., 1994
	Clams, *Mya arenaria*, Chesapeake Bay	General	1989			0.3		WW		Brown *et al*., 1994

?DW assumed to be dry weight.
nd = Not detected.

Appendix I Overseas data for PCBs in sediment and shellfish

This appendix summarises comparative international PCB data for estuarine sediments and shellfish.

Table I1 Concentrations of PCBs in estuarine sediment in other countries

Country	Location	Type	Date sampled	Concentration (µg kg^{-1} DW) Min.	Max.	Data type	Reference
Adriatic Sea	Coastal sites	Urban/ind	1993	4.14	129	Total PCB	Galassi *et al*., 1993
Antarctica		Background	1988	< 0.01	0.8	Total PCB, congeners	Risebrough *et al*., 1990
	McMurdo Sound	Background	1989-93	2.8	4.2	Total PCB	Kennicutt *et al*., 1995
	McMurdo Sound	Impacted	1988	2.1	1400	Total PCB, congeners	Risebrough *et al*., 1990
	McMurdo Sound, Winter Quarters Bay	Impacted	1989-93	250	4200	Total PCB	Kennicutt *et al*., 1995
	Ross Sea/Terra Nova Bay	Background	1990-91	0.03	0.16	Total PCB	Fuoco *et al*., 1995
Argentina	Rio de La Plata	Urban/ind	1986	3	998	Total PCB	Colombo *et al*., 1990
Australia	Perth, WA coastal		1991	< 10		Total PCB	Burt and Ebell, 1995
	Brisbane River, Qld	Urban	1980s	nd	54	Total PCB	Shaw and Connell, 1980
	Sydney, NSW	Urban	1990	52	790	Congener sum	Iwata *et al*., 1994b
	Perth, WA	Rural	1990	0.68	0.85	Congener sum	Iwata *et al.,* 1994b
	Perth, WA	Urban	1990	0.49	18	Congener sum	Iwata *et al*., 1994b
	Hobart, TAS	Rural	1990	0.85	8.1	Congener sum	Iwata *et al*., 1994b
	Hobart, TAS	Urban	1990	2.4	470	Congener sum	Iwata *et al*., 1994b
Canada	St Lawrence upper estuary	Urban/ind	1989-90	82.7	770		Coakley *et al*., 1993
	Arctic, Cambridge Bay	Impacted	1991-92	0.14	45	Sum 47 congeners	Bright *et al*., 1995
	Arctic, reference	Reference	1991-92	0.052	0.44	Sum 47 congeners	Bright *et al*., 1995
Egypt	Nile sediments	Urban/ind		6.91	3155	Total PCB	El-Gendy *et al*., 1991
Fiji		Rural/urban	1991-92	0.97	68.5	Aroclor sum	Morrison *et al*., 1996
Germany	Oder River estuarine system	Urban/ind	1995	<0.1	26.3	Sum 13 congeners	Dannenberger *et al*., 1997
India		Urban	1989	4.8	1000	Congener sum	Iwata *et al*., 1994b
Indonesia		Urban	1991	5.9	220	Congener sum	Iwata *et al*., 1994b
Japan	Osaka Bay	Urban/ind	1990	63	240	Congener sum	Iwata *et al*., 1994b
Malaysia		Rural	1991	< 5		Congener sum	Iwata *et al*., 1994b
Mexico	San Quintin Bay	Rural	1992	<10		Total PCB	Galindo *et al*., 1996
Netherlands	Scheldt Estuary	Urban/ind	1989	86.8	Mean	Sum of 13 congeners	Stronkhorst *et al*., 1994
Papua New Guinea		Urban	1990	3.3	54	Congener sum	Iwata *et al*., 1994b
Solomon Islands		Rural/urban	1990	1.1	5.0	Congener sum	Iwata *et al*., 1994b
Sweden	Gulf of Bothnia	Urban/ind	1991-92	23.4	262	Sum 86 congeners	van Bavel *et al*., 1995
South France	Mediterranean	Urban/ind		29	181	Sum 20 congeners	Pierard *et al*., 1996
Spain	Alicante	Urban/ind	1989-90	0.2	2.9	Sum 10 congeners	Prats *et al*., 1992
Taiwan		Urban	1990	2.3	230	Congener sum	Iwata *et al*., 1994b
Tanzania	Dar es Salaam harbour	Urban/ind	1991	nd	7000	Total PCB	Machiwa, 1992
Thailand		Urban/ind	1990	11	520	Congener sum	Iwata *et al*., 1994b
Tonga		Rural/urban	1991	< 0.1	12.1	Three aroclors	Harrison *et al*., 1996
United Kingdom	Thames Estuary	Urban/ind	1993	1	40	Total PCB	Scrimshaw and Lester, 1995
	Essex salt marshes	Urban/ind	1993	<1	243	Total PCB	Scrimshaw *et al*., 1996
	Coastal sites	Urban/ind	1993	0.2	42	Sum 21 congeners	Thompson *et al*., 1996
United States	Casco Bay, Maine	Urban/ind	1991	0.4	485	Total PCB	Kennicutt *et al*., 1994
Vanuatu		Rural/urban	1991	< 0.07	0.20	Three aroclors	Harrison *et al*., 1996
Vietnam		Rural/urban	1990	0.18	630	Congener sum	Iwata *et al*., 1994b

nd = Not detected.

Table I2 Concentrations of PCBs in estuarine shellfish in other countries

Country	Location/Species	Date sampled	Concentration (μg kg^{-1} WW) Min.	Max.	Data type	Reference
Adriatic	North Adriatic, "mussels"	1972-90	<0.3	771	Total PCB	Picer and Picer, 1991
	Eastern Adriatic "mussels"	1972-92	<0.5	1072	Total PCB	Picer and Picer, 1995
Antarctica	McMurdo Sound, Winter Quarters Bay Bivalve, *Laternula elliptica*	1989-93	380	430	Total PCB	Kennicutt *et al*., 1995
	McMurdo Sound, remote site	1989-93	5.1	22	Total PCB	Kennicutt *et al*., 1995
Argentina	Rio de la Plata, *Corbicula fluminea*	1986	223[a]	236[a]	Total PCB	Colombo *et al*., 1990
	Arroyo Parejas	1991-92	110[b]			Sericano *et al*., 1995
Australia	Port Phillip Bay, *Mytilus edulis*		<10[b]	879[b]	Total PCB	Phillips *et al*., 1992
	Corio Bay, *Mytilus edulis*		20[b]	930[b]	Total PCB	Phillips *et al*., 1992
	Corio Bay, *Mytilus edulis*	1992	13.8	14.8	Sum 47 congeners	Prest *et al*., 1995
	Perth, *Mytilus edulis*	1991	<10		Total PCB	Burt and Ebell, 1995
	Brisbane R., *Mytilus corscus*	1980s	ND	52	Total PCB	Shaw and Connell, 1980
Brazil	Guanabara Bay	1991-92	170[b]	Single value given		Sericano *et al*., 1995
Canada	Arctic, Cambridge Bay, 3 species	1991-1992	0.89	3.2	Sum 47 congeners	Bright *et al*., 1995
	Arctic, reference, 2 species	1991-1992	0.62	0.99	Sum 47 congeners	Bright *et al*., 1995
Chile	Punta Arenas	1991-92	130[b]			Sericano *et al*., 1995
Greece	Mussel, *Mytilus galloprovincialis*		7.6	83	Total PCB	Satsmadjis and Gabrielides, 1983
Hong Kong	High and low impact, *Perna viridis*	1985	3.4	560	Total PCB	Tanabe *et al*., 1987
India	*Perna viridis*	1988-1989	<1	7.1	Total PCB	Ramesh *et al*., 1990
Irish Sea	Mussel, *Mytilus edulis* - 10 bays/ harbours	1992-93	0.8	25	Sum 21 congeners	Thompson *et al*., 1996
Mexico	Laguna Madre	1991-92	110[b]			Sericano *et al*., 1995
Netherlands	Mussel, *Mytilus edulis* in two estuaries	1985-1990	22	92	Sum 7 congeners	Stronkhorst, 1992
North Greenland	Scallops (*Chlamys islandicus*)	Mid 1980s	6[b]	36[b]	Total PCB	Kjolholt and Munk Hansen, 1986
North Sea and Scotland	Mussel, *Mytilus edulis* - 16 bays/ harbours	1992-93	0.9	39	Sum 21 congeners	Thompson *et al*., 1996
NW Spain	Feral and cultivated mussels	1990-91	59.4	177	Total PCB	Alvarez Pineiro *et al*., 1995
Oman	Oysters and mussels, 6 locations	1980	0.87	9.1	Total PCB	Burns *et al*., 1982
Peru	Callao	1991-92	120[b]			Sericano *et al*., 1995
Spain	Western Med. *G. Provincialis*	1989-92	15.7	54.7	Aroclor equivalents	Sole *et al*., 1994
Thailand	4 river mouths, *Mytilus viridis*	1979	2	110	Total PCB	Menasveta and Cheevaparanapiwat, 1981
United Kingdom	Mersey estuary, "mussels"	1990-92	20±1.1		Sum 6 congeners	Leah *et al*., 1997
USA	"Mussel watch", 51 sites nation wide	1977	4.1[b]	790[b]	Σ18 congeners (x2)	Lauenstein, 1995
		1991-1992	0[b]	720[b]	Σ18 congeners (x2)	Lauenstein, 1995
	Gulf of Mexico, oysters (NOAA sites)	1986-93	10[b]	630b[a]	Total PCB	Sericano *et al*., 1995
Vietnam	Food shellfish	1990-1991	15		Total PCB	Kannan *et al*., 1992

[a] Initially reported on a lipid weight basis. Converted to wet weight basis using lipid content of 3.1%.
[b] Dry weight basis.

Table I3 Congener specific data for PCBs in sediments from international studies (non *ortho*- and most frequently reported congeners only)

Country		Sample size	PCB congener (µg kg^{-1} DW)												Reference
			#77		#126		#169		#28 + #31		#52		#101		#118		
			Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Argentina	Rio de la Plata	17							nd	114	nd	24.4	0.09	12.5			Colombo *et al*., 1990
Baltic	Gulf of Bothnia	6							48	199	<15	160	90	463	131	757	van Bavel *et al*., 1995
Canada	Arctic, Cambridge Bay	Mean 65	0.05		0.01												Bright *et al*., 1995
Germany	Oder estuarine system	5					<0.01	<0.01	<0.01	0.79	<0.01	0.24	<0.01	1.37	<0.01	4.06	Dannenberger *et al*., 1997
Mediterranean	S. France	3							0.72	3.2	4.1	21	3.3	19	3.4	17	Pierard *et al*., 1996
Netherlands	Scheldt Estuary	4							2.9	2.9	4.4	4.4	9.6	9.6			Stronkhorst *et al*., 1994
United Kingdom	Thames Estuary	Mean 3	0.2		<0.1		<0.1		0.2		0.1				0.2		Scrimshaw and Lester, 1995

Country		Sample size	PCB congener (µg kg^{-1} DW)												Reference
			#105		#153		#138		#187		#180		#170		#206		
			Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Argentina	Rio de la Plata	17			0.08	18.6	0.05	14.5			0.06	18					Colombo *et al*., 1990
Baltic	Gulf of Bothnia	6	49	258	184[a]	854[a]	[a]	[a]	46[b]	268[b]	103	531	<15[c]	240[c]	<15	25	van Bavel *et al*., 1995
Canada	Arctic, Cambridge Bay	Mean 65															Bright *et al*., 1995
Germany	Oder estuarine system	5			<0.01	4.44	<0.01	9.02			<0.01	4.17					Dannenberger *et al*., 1997
Mediterranean	S. France	3	1.7	7.8	2.1	29	2.4	26	0.35	9.5	0.72	13	0.45	0.62	0.1	0.22	Pierard *et al*., 1996
Netherlands	Scheldt Estuary	4	5.3	5.3	15.4	25.4	13.2	13.2	5.5	5.5	10.1	10.1	5.2	5.2			Stronkhorst *et al*., 1994
United Kingdom	Thames Estuary	Mean 3	<0.1		0.1		0.2				0.2	0.2					Scrimshaw and Lester, 1995

[a] Reported as #138 + #160 + #153 + #164.
[b] Reported as #182 + #187.
[c] Reported as #170 + #190.
nd = Not detected.

Appendix J Overseas data for organochlorine pesticides in sediment and shellfish

This appendix summarises comparative international organochlorine pesticide data for estuarine sediments and shellfish.

Table J1 Concentrations of DDT residues in estuarine sediments (μg kg^{-1} DW) in other countries

Country	Date sampled	No. of sites	pp'-DDT		pp'-DDE		pp'-TDE		Sum DDT		Reference
			Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Australia	1990		low	90	low	55	1	13			McKenzie Smith *et al*., 1994
	1990	19	0.02	150	0.05	400	0.02	1300	0.08	1700	Iwata *et al*., 1994b
	1988-91						0.3				Mortimer and Connell, 1995
Greece	1992-93	4	nd		nd	60	nd				Albanis *et al*., 1994
India	1989	6	2.8	190	1.9	100	1.7	340	8	450	Iwata *et al*., 1994b
	1988-89	9							0.3	1.6	Ramesh *et al*., 1991
Indonesia	1991	4	0.86	4.4	0.95	21	0.94	15	3.4	42	Iwata *et al*., 1994b
Japan	1990	3	0.2	0.65	1.3	2.6	0.9	9.8	2.5	12	Iwata *et al*., 1994b
Malaysia	1991	1	0.63		0.22		0.89		1.8		Iwata *et al*., 1994b
Mexico	1992	9							nd	1.5	Gold Bouchot *et al*., 1995
	1992	39							<2	10	Galindo *et al*., 1996
		8			nd	18	nd	0.55			Gold Bouchot *et al*., 1993
Papua New Guinea	1990	3	0.44	89	1.9	11	1.6	25	4.7	130	Iwata *et al*., 1994b
Russia, Black Sea			nd		7.3		nd		7.3		Galiulin and Bashkin, 1996
Solomon Islands	1990	2	3.8	450	0.37	140	4.5	130	9.3	750	Iwata *et al*., 1994b
Taiwan	1990	3	0.12	1.2	0.16	5.2	0.07	3.9	0.39	11	Iwata *et al*., 1994b
Tanzania	1986		tr	7	tr	1	nd	3			Paasivirta *et al*., 1988
Thailand	1990	4	1.2	100	1.8	59	1.7	100	4.8	170	Iwata *et al*., 1994b
United Kingdom		5	0.1	2.8	0.1	3.6	0.1	3.6			Scrimshaw *et al*., 1994
USA, New Jersey	1990-93	81	5	480	5	110	20	420			Gillis *et al*., 1995
California	1985-87	3							6	960	Rice *et al*., 1993
Florida	1990s	18							1	69	Sherblom *et al*., 1995
Alaska	1990	3	0.0013	0.0095	0.0031	0.11	0.0016	0.054	0.0064	0.17	Iwata *et al*., 1994a
Vietnam	1990	18	0.05	63	0.21	540	0.08	210	0.37	790	Iwata *et al*., 1994b

nd = Not detected.
tr = Trace.

Table J2 Concentrations of DDT residues in estuarine shellfish (μg kg^{-1}) in other countries

Country	Date sampled	No. of sites	Conc. basis	pp'-DDT		pp'-DDE		pp'-TDE		Sum DDT		Reference
				Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Australia, NSW	1991	14	WW							nd	14	Hardiman and Pearson, 1995
Croatia	1974	4	WW							16	67	Picer and Picer, 1994
	1991	3	WW							1	40	Picer and Picer, 1994
	1981-88	8	WW							<10		Picer and Picer, 1990
Denmark	1985	26	WW							2.4		Granby and Kinze, 1991
France	1979-89	110	DW	<0.4	730	<0.1	250	<0.5	490			Claisse, 1989
Germany	1990-91	10	DW							7.4	88	Lee *et al*., 1996
India	1988-89	9	WW	nd	16	1.1	12	0.7	25	2.8	39	Ramesh *et al*., 1990
	1988-89		?WW	200*		80*		70*		60	2340	Nair and Pillai, 1992
Japan	1992	2	WW							6.1	67	Kannan *et al*., 1995
Mexico	1988	2	DW			18	22	<1.4	<2.5			Martin and Galindo, 1989
	1992	9	DW							0.39	1.5	Gold Bouchot *et al*., 1995
	1984	1	DW	10		275		21		323		DeLaune *et al*., 1990
	1984	3	WW							10	55	Galindo-Bect and Flores-Baez, 1991
		8	DW					1.2	4.1			Gold Bouchot *et al*., 1993
Nigeria	1987	2	WW	3	15	79	120	4	9	91	140	Osibanjo and Bamgbose, 1990
Papua New Guinea	1992		WW							0.34		Kannan *et al*., 1994
Portugal	1985-87	4	DW							4	97	Ferreira *et al*., 1990
Spain	1989-91	2 (51)	WW	nd	6.7	0.9	24	0.1	19			Galceran *et al*., 1993
Spain	1980-91	2	WW	0.1	48	1	20	0.9	33	1.1	64	Sole *et al*., 1994
Thailand	1989	9	WW	0.12	1.6	0.08	2.5	nd	3.6			Siriwong *et al*., 1991
Thailand	1991	9	WW	0.2	1.8	0.4	2	0.1	1.2	0.7	5.4	Ruangwises *et al*., 1994
USA	1976-78	51	DW							7	1500	Lauenstein, 1995
USA	1992	51	DW							0.5	1400	Lauenstein, 1995
California	1977	14-25	DW							10	7500	Stephenson *et al*., 1995
California	1992	14-25	DW							5	1200	Stephenson *et al*., 1995
Hawaii	1991	5	DW	<4		<3		<3				Hunter *et al*., 1995

* Average value.
nd = Not detected.
?WW assumed to be wet weight.

Table J3 Concentrations of HCH residues in estuarine sediments (μg kg^{-1} DW) in other countries

Country	Date sampled	No. of sites	γ-HCH		α-HCH		β-HCH		Sum HCH		Reference
			Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Australia	1990	19	0.01	0.57	0.01	9.9	0	5.8	0.02	17	Iwata *et al*., 1994b
	1988-91		1.4								Mortimer and Connell, 1995
Greece	1992-93	4	nd	315	nd	12	nd				Albanis *et al*., 1994
India	1989	6	0.5	3.8	0.32	13	0.08	23	0.58	38	Iwata *et al*., 1994b
	1988-89	9							0.9	9	Ramesh *et al*., 1991
Indonesia	1991	4	0.02	0.06	<0.002	0	0.01	0.04	0.04	0.1	Iwata *et al*., 1994b
Japan	1990	3	0.29	0.7	0.75	5.1	0.36	3.5	4.5	6.2	Iwata *et al*., 1994b
Malaysia	1991	1	0.11		<0.005		0.07		0.18		Iwata *et al*., 1994b
Mexico	1992	9	0.2	0.7							Gold Bouchot *et al*., 1995
		8	nd	0.57							Gold Bouchot *et al*., 1993
Papua New Guinea	1990	3	0.15	0.19	0.01	0.19	<0.04	0.04	0.17	0.34	Iwata *et al*., 1994b
Solomon Islands	1990	2	<0.14	0.79	<0.19	1.4	<0.04		<0.33	2.2	Iwata *et al*., 1994b
Taiwan	1990	3	0.05	0.07	0.12	0.38	0.12	0.34	0.29	0.79	Iwata *et al*., 1994b
Thailand	1990	4	0.2	1.7	0.28	1.2	<0.1	0.57	0.48	3.1	Iwata *et al*., 1994b
United Kingdom		28	5		25						Herrmann *et al*., 1984
		5	0.1	2.2	nd	0.1			nd	2.9	Scrimshaw *et al*., 1994
Tanzania	1986		nd	4							Paasivirta *et al*., 1988
USA, Florida	1990s	18	nd	2.0							Sherblom *et al*., 1995
Alaska	1990	3	0.0033	0.048	0.036	0.16	0.004	0.04	0.043	0.25	Iwata *et al*., 1994a
Vietnam	1990	18	0.11	9.3	0.21	3.5	0.06	2.3	0.43	12	Iwata *et al*., 1994b

nd = Not detected.

Table J4 Concentrations of HCH residues in estuarine shellfish (μg kg^{-1}) in other countries

Country	Date sampled	No. of sites	Conc. basis	γ-HCH Min.	γ-HCH Max.	α-HCH Min.	α-HCH Max.	β-HCH Min.	β-HCH Max.	Sum HCH Min.	Sum HCH Max.	Reference
Denmark	1985	26	WW	0.6	3.4	0.3	3.1					Granby and Kinze, 1991
Germany	1990-91	10	DW							1.5	22	Lee *et al*., 1996
India	1988-89	9	WW	0.5	2.5	1.4	6	0.5	8.4	4.3	16	Ramesh *et al*., 1990
	1988-89		?WW	60*		260*				20	710	Nair and Pillai, 1992
Japan	1992	2	WW							10	120	Kannan *et al*., 1995
Mexico		8	DW	0.45	1.3							Gold Bouchot *et al*., 1993
Nigeria	1987	2	WW	1.1	1.4			1.3	1.5			Osibanjo and Bamgbose, 1990
Spain	1989-91	2 (51)	WW	nd	11	nd	3.2	nd	4.4			Galceran *et al*., 1993
	1980-91	2	WW	0.1	0.6							Sole *et al*., 1994
Thailand	1989	9	WW	nd	0.19	nd	0.06	nd				Siriwong *et al*., 1991
	1991	9	WW	<0.02	0.04	<0.02	0.06					Ruangwises *et al*., 1994
USA, Hawaii	1991	5	DW	<0.8		<1		<3				Hunter *et al*., 1995
Louisiana	1995-86	7	WW					<10	560			Murray and Beck, 1990

* Average value.
nd = Not detected.
?WW assumed to be wet weight.

Table J5 Concentrations of HCB, chlordane and dieldrin residues in estuarine sediments (μg kg^{-1} DW) in other countries

Country	Date sampled	No. of sites	HCB Min.	HCB Max.	α-Chlordane Min.	α-Chlordane Max.	γ-Chlordane Min.	γ-Chlordane Max.	Heptachlor Min.	Heptachlor Max.	H. epoxide Min.	H. epoxide Max.	Dieldrin Min.	Dieldrin Max.	Aldrin Min.	Aldrin Max.	Reference
Australia	1988-91		0.9										0.3		0.6		Mortimer and Connell, 1995
Australia	1990	19			0.02	61	0.03	140									Iwata *et al*., 1994b
Greece	1992-93	4											nd		nd		Albanis *et al*., 1994
India	1989	6			0.13	33	0.02	60									Iwata *et al*., 1994b
Indonesia	1991	4			0.05	12	0.06	13									Iwata *et al*., 1994b
Japan	1990	3			0.14	0.56	0.08	0.42									Iwata *et al*., 1994b
Malaysia	1991	1			0.85		0.09	0.88									Iwata *et al*., 1994b
Mexico	1992	9											nd	2.3	nd	0.25	Gold Bouchot *et al*., 1995
	1992	39			<2												Galindo *et al*., 1996
		8	nd	0.32											nd	9	Gold Bouchot *et al*., 1993
Papua New Guinea	1990	3			0.19	1.4	0.33	1.8									Iwata *et al*., 1994b
Solomon Islands	1990	2			0.21	0.65	0.24	2.3									Iwata *et al*., 1994b
Taiwan	1990	3			0.06	2	0.04	1.6									Iwata *et al*., 1994b
Tanzania	1986												3	6			Paasivirta *et al*., 1988
Thailand	1990	4			0.43	56	0.36	94									Iwata *et al*., 1994b
United Kingdom		28	14														Herrmann *et al*., 1984
		5	nd	0.2													Scrimshaw *et al*., 1994
USA, Florida	1990s	18	0.1	2					0.1	1.0	0.1	123	0.1	17			Sherblom *et al*., 1995
Alaska	1990	3	0.035	0.079	0.005	0.019	0.0025	0.021									Iwata *et al*., 1994a
Vietnam	1990	18			<0.01	7.5	0.03	9									Iwata *et al*., 1994b

nd = Not detected.

Table J6 Concentrations of HCB, chlordane and dieldrin residues in estuarine shellfish (μg kg^{-1}) in other countries

Country	Date sampled	No. of sites	Conc. basis	HCB		α-Chlordane		γ-Chlordane		Heptachlor		Heptachlor epoxide		Dieldrin		Aldrin		Reference
				Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Denmark	1985	26	WW	0.05	0.74													Granby and Kinze, 1991
Germany	1990-91	10	DW	nd	5.2													Lee *et al*., 1996
India	1988-89		?WW											0.1	50	0.2	10	Nair *et al*., 1991
Japan	1992		WW	0.04	0.91	35	170											Kannan *et al*., 1995a
Nigeria	1987	2	WW	0.1	0.3					3	4.1					nd		Osibanjo and Bamgbose, 1990
Mexico		8	DW													nd	6.6	Gold Bouchot *et al*., 1993
Mexico	1992	9	DW			12	100			nd	0.63			nd	1.2	0.13	1	Gold Bouchot *et al*., 1995
Papua New Guinea	1992		WW	0.02		0.78	0.78			0.02		0.15		0.73		2.1		Kannan *et al*., 1994
Spain	1989-91	2 (51)	WW			nd	1.7	nd	1.9	nd	4.1	nd	1.4	nd	7.3	nd	2.9	Galceran *et al*., 1993
Spain	1980-91	2	WW	0.1	1.8													Sole *et al*., 1994
Thailand	1989	9	WW	nd	0.31					nd	0.18	nd		0.02	0.73	0.31	1.3	Siriwong *et al*., 1991
Thailand	1991	9	WW	<0.02	0.2					<0.02	2	<0.02	0.03	0.08	0.5	0.2	0.9	Ruangwises *et al*., 1994
USA	1976-78	51	DW			3	210											Lauenstein, 1995
	1992	51	DW			nd	34											Lauenstein, 1995
Gulf of Mexico	1986-90	80	WW			<0.25	120			<0.25	15	<0.25	30					Sericano *et al*., 1993
California	1977	14-25	DW			10	500											Stephenson *et al*., 1995
California	1992	14-25	DW			3	100											Stephenson *et al*., 1995
Hawaii	1991	5	DW			<1	88	<1	75	<1	7.4	<1	29	<1	200	<1		Hunter *et al*., 1995

nd = Not detected.
?WW assumed to be wet weight.

Appendix K Overseas data for chlorophenols in sediment and shellfish

This appendix summarises comparative international data for chlorophenols in estuarine sediments and shellfish.

Table K1 Chlorophenol concentrations in sediment from other countries

Country	Location	Type	Date sampled	PCP		2,3,4,6 TeCP		2,3,4,5 TeCP		2,3,5,6 TeCP		2,4,5 TCP		2,4,6 TCP		Reference
				Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Denmark	Holbaek Fjord		1982	<10	20											Folke *et al*., 1983
Finland	Baltic Sea	Impacted by pulp mills		0.7	1.1	1	3.1							0.1	0.4	Xie, 1983
	Gulf of Bothnia	Impacted by pulp mills	1982-83	<0.05	9	0.04	89							0.05	19	Xie *et al*., 1986
Germany	Weser Estuary	Industrial	1978	0.11	41.5	0.019	8.9	0.26	0.62	0.019	8.9	0.049	0.45	0.02	1.3	Eder and Weber, 1980
	Elbe Estuary	Urban/ind	1989													Goetz *et al*., 1993
	Jadebusen	Reference	1980	2.9				<1.2								Butte *et al*., 1985
	Jadebusen	Industrial	1981	4.9				28.3	30.9							Butte *et al*., 1985
Japan	Osaka	Impacted by sewage	1981-83	42	105							4.4	9	26	51	Watanabe *et al*., 1985
	Osaka	Reference	1981-83	0.3	18	0.6	5.2					<0.2	2	<0.2	6.5	Watanabe *et al*., 1985
United States	Galveston, Texas	Urban/ind	1980	0.18	0.26											Murray *et al*., 1981
	Nueces Estuary, Texas	Industrial	1980	0.1	0.25											Ray *et al*., 1983
	Nueces Estuary, Texas	Reference	1980	0.05	0.25											Ray *et al*., 1983
	Portland harbour, Maine	Industrial	1980	0.01	2.4											Ray *et al*., 1983

Table K2 Chlorophenol concentrations in shellfish from other countries

Country	Location	Species	Type	Date sampled	PCP		2,3,4,6 TeCP		2,3,4,5 TeCP		2,3,5,6 TeCP		Reference
					Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	
Denmark	Holbaek Fjord	Mussels, *Mytilus edulis*		1985	2	5	0.2	0.6	700	2550			Folke *et al*., 1986
	Kattegat Seat	Mussels, *M. edulis*		1985	12	32	0.4	2	700	46400			Folke *et al*., 1986
Germany	Jadebusen	Clams, *Mya arenaria*	Reference		270	530					<120	230	Butte *et al*., 1985
	Jadebusen	Clams, *M. arenaria*	Industrial		270	3200					<120	700	Butte *et al*., 1985
USA	Galveston Bay	Oysters, *C. virginica*	Urban/ind	1979	3.4	8.3							Murray *et al*., 1980
	Portland harbour	Clams	Industrial	1980	1.7	3.4							Ray *et al*., 1983