

**Ambient concentrations of
selected organochlorines in
rivers**

**Organochlorines Programme
Ministry for the Environment**

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

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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.

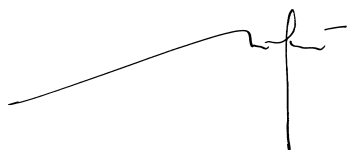
In view of the international concern, the Government decided that we needed better information on the New Zealand situation. The Ministry for the Environment was asked to establish an Organochlorines Programme to carry out research, assess the data, and to consider management issues such as clean up 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 report presents the findings of one component of the Organochlorines Programme of the Ministry for the Environment. A nation-wide environmental survey has been carried out to determine the background levels of organochlorine substances in terrestrial and aquatic media, and in ambient air. Here data are reported on the concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), organochlorine pesticides and chlorophenols measured in New Zealand rivers.

River water and fish were collected from 16 sites on eight North Island and five South Island rivers. Samples were taken from three reference sites and 13 sites impacted by agricultural and urban use. Reference sites were located in remote areas, usually in the upper reaches of the rivers, or above any human inputs to the river systems. Impacted sites were downstream of diffuse sources from agricultural runoff, and point source discharges from industrial and domestic activity. From these sites, a total of 16 composite river water samples, 16 composite eel samples and 12 composite trout samples were analysed for organochlorine contaminants.

The results from this environmental survey show that environmental levels of PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols in New Zealand rivers are low, and markedly lower than concentrations reported for rivers in other developed countries.

No PCDDs or PCDFs were detected in any of the 16 river water samples collected. Analytical limits of detection (LODs) were between 0.3 - 2 pg L⁻¹ for 2,3,7,8-TCDD and 10 - 60 pg L⁻¹ for OCDD.

Analysis of samples was undertaken for 25 PCB congeners, including the toxicologically significant non *ortho*- and mono *ortho*-PCBs. No PCBs were measured in any river water samples. Analytical LODs were between 0.01 - 0.03 ng L⁻¹ for the non *ortho*-PCB congeners, and 0.1 - 0.6 ng L⁻¹ for the mono and di *ortho*-PCB congeners. Taking half the LOD values for non-detected congeners, an upper boundary for the sum of PCB congeners can be estimated in the range 1.1 - 1.6 ng L⁻¹.

No organochlorine pesticides or chlorophenols were measured in any river water samples. The analytical detection limits obtained for the pesticides (including degradation products) were in the range 0.1 - 0.3 ng L⁻¹, with the exception of dieldrin and pp'-DDE which had maximum detection limits of 2 ng L⁻¹ and 0.9 ng L⁻¹ respectively. Detection limits for the chlorophenols were 2 - 3 ng L⁻¹.

A range of organochlorine contaminants were measured in the eel and trout samples. PCDDs and PCDFs were detected in a limited number of the fish, with at least one congener being detected in 10 of the 28 samples analysed. Total I-TEQ concentrations, calculated using half the LOD for non-detected congeners, ranged from 0.16 - 0.39 ng I-TEQ kg⁻¹ wet fillet weight basis for eel and 0.016 - 0.20 ng I-TEQ kg⁻¹ wet fillet weight basis for trout. For most samples incorporation of half the LOD was either the major or the only contributor to the total I-TEQ determined. The most commonly detected congener was 2,3,7,8-TCDF which was measured in four of the 12 trout samples, but was not measured in any of the eel samples.

All but one of the fish samples contained some PCBs, with PCB congeners #138 and #153 being the most commonly detected and present at the highest concentrations. The sum of PCBs ranged

from 0.39 - 18.5 $\mu\text{g kg}^{-1}$ wet fillet weight basis for eel and 0.11 - 8.80 $\mu\text{g kg}^{-1}$ wet fillet weight basis for trout. These concentrations correspond to PCB TEQ concentrations in the range 0.069 - 1.39 ng TEQ kg^{-1} wet fillet weight basis for eel and 0.065 - 0.32 ng TEQ kg^{-1} wet fillet weight basis for trout. For most samples, the contribution from the inclusion of half LOD values for non-detected PCB congeners to the PCB TEQ levels determined was generally less than the contributions made by inclusion of half LOD values for non-detected PCDD and PCDF congeners to the I-TEQ levels determined.

Dieldrin, pp'-DDE, pp'-TDE and pp'-DDT were detected in all of the 28 fish samples and HCB was detected in 27 of the 28 samples. Of the remaining pesticides analysed, only α -chlordane (15 of 28 samples) and op'-DDT (26 of 28 samples) were detected in more than half of the samples. Aldrin and heptachlor were not detected in any of the samples to a maximum analytical detection limit of 0.02 $\mu\text{g kg}^{-1}$ wet fillet weight basis.

No trichlorophenols or tetrachlorophenols were detected in any fish samples, to a maximum analytical detection limit of 0.6 $\mu\text{g kg}^{-1}$ wet fillet weight basis. Pentachlorophenol was detected in only two of the 16 eel samples at concentrations of 0.32 and 0.45 $\mu\text{g kg}^{-1}$ wet fillet weight basis and in one of the 12 trout samples at 0.8 $\mu\text{g kg}^{-1}$ wet fillet weight basis.

The contaminant concentration data sets for PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols in all river water and fish 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. Appendices B and C contain detailed information on the riverine sampling and analytical programmes, including the results from the analysis of field and laboratory quality control samples. Appendix A summarises the historical use of organochlorines in New Zealand.

The survey has demonstrated that New Zealand's riverine environments are relatively free of contamination with persistent organochlorines. The accumulation of only trace levels of these contaminants by fish is indicative of the generally low level of contamination in the New Zealand environment.

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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 this 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, river biota 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 rivers. Separate reports have been published on organochlorine concentrations in New Zealand soils (Buckland *et al.*, 1998), estuaries (Scobie *et al.*, 1998) and in ambient air (Buckland *et al.*, 1999). These data will be used in an environment risk assessment, which will be published as a separate report.

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

- 1) to obtain information on the background concentrations of organochlorine contaminants in New Zealand rivers;
- 2) to enable the level of contamination of New Zealand riverine environments 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.

The environmental survey was undertaken to determine the background concentrations of the target organochlorine substances in the New Zealand environment. This study was not intended to identify or characterise known environmental hot spots, 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 riverine 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 levels 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.

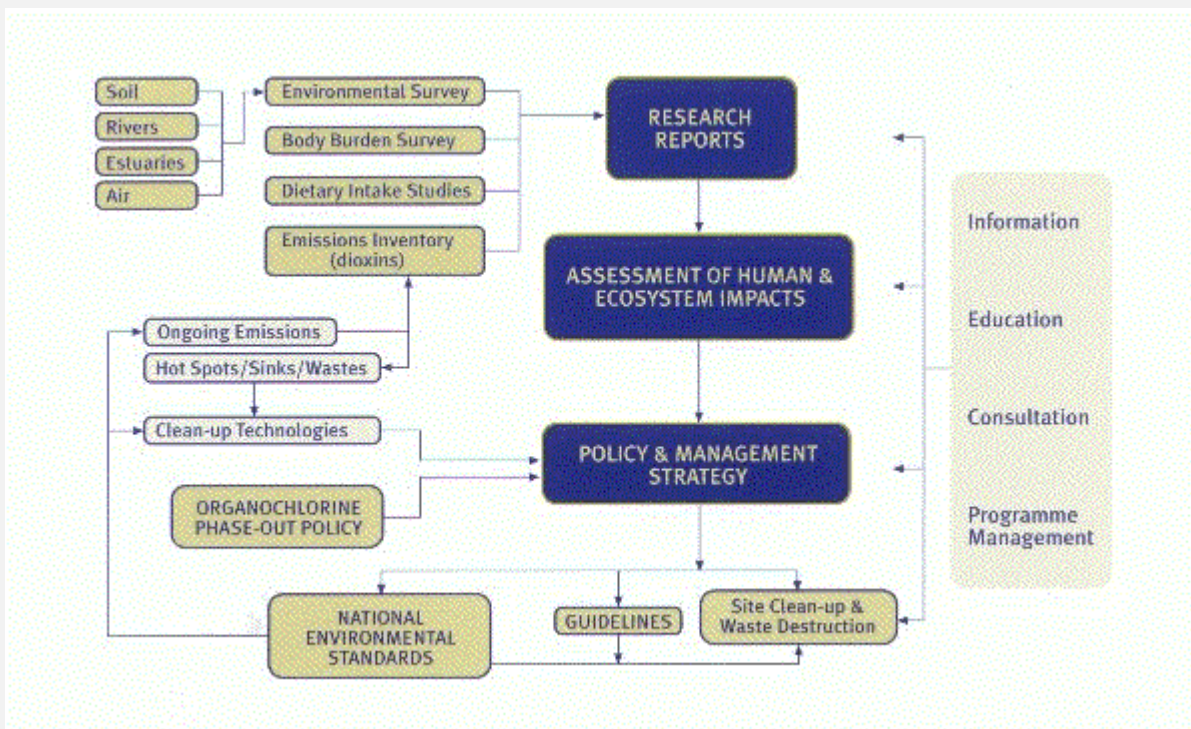


Figure 1.1 Overview of the New Zealand Organochlorines Programme

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.

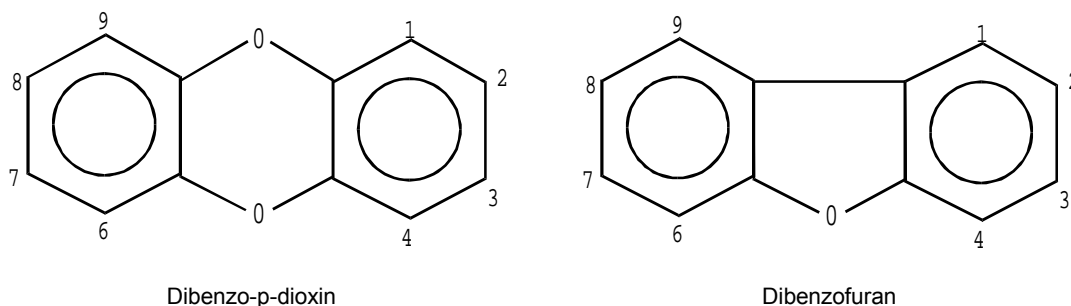


Figure 2.1 Structures of dibenzo-p-dioxin and dibenzofuran

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 birds¹.

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 <i>et al.</i> , 1990)	WHO-TEF (humans/mammals) (Van den Berg <i>et al.</i> , 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.

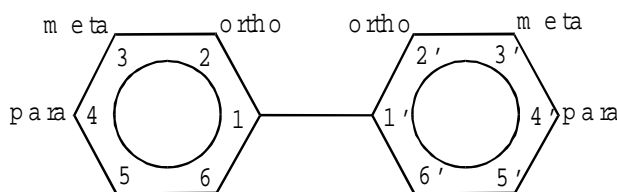


Figure 2.2 Structure of biphenyl

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 birds².

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 IUPAC No.	Structure	WHO/IPCS TEF (Ahlborg <i>et al.</i> , 1994)	WHO-TEF (humans/mammals) (Van den Berg <i>et al.</i> , 1998)
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	
<ul style="list-style-type: none"> • 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 (<i>Costelytra zealandia</i>) and porina (<i>Wiseana</i> 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 <u>officially</u> 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 <i>Pinus radiata</i>). 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 deregistered³ 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 concentrations of selected organochlorine contaminants in New Zealand riverine environments. A sampling programme was implemented for the collection of surface river water and freshwater biota from eight North Island and five South Island rivers (Figure 4.1). The full list of samples collected from the 16 sampling sites on these rivers is detailed in Table 4.1.

These rivers were selected for study because they:

- provided a broad spatial coverage of New Zealand;
- covered a broad range of catchments with respect to physiographical types and land uses;
- in the most part, incorporated a large catchment area;
- included both reference and impacted sites;
- were considered to be representative of the range of uses of New Zealand waterways.

At the point of sampling (downstream sites only for rivers with more than one sampling site), these rivers collectively represent 12.7% of the total New Zealand catchment area: 16.1% of the North Island catchment, and 10.1% of the South Island catchment.

The Waikato and Tarawera Rivers were purposefully excluded from this study. This was because both these rivers are recipients for bleached kraft pulp mill effluents, and contaminant concentration data already exists for organochlorines in biota from these waterways (see for example: Hickey *et al.*, 1997; Jones *et al.*, 1995; Jones, 1996; Power, 1994). The high cost of the current study necessitated avoiding the duplication of any existing research.

The entry of chemical contaminants into aquatic environments can occur via:

- point source discharges directly into a watercourse;
- diffuse discharges, commonly from land runoff;
- ground water discharges;
- wet or dry atmospheric deposition.

For this study, sites that were upstream of any point source discharges or agricultural runoff were considered to be reference sites. Of the 16 sampling sites, three were identified as being reference sites. There were the Mohaka River at Raupunga, the Haast River at Roaring Billy and the Maitai River at Parawa. Sites downstream of any point source discharge, or where the river ran through a highly agricultural area, were considered to be impacted. These included sites that were impacted by agricultural activity, urban development or industrial activity. The most commonly encountered discharges (point and diffuse sources) included:

- urban stormwater;
- sewage effluent;
- agricultural run-off;
- landfill leachate;
- dairy effluent;
- freezing works effluent;
- timber processing effluent.

The organochlorine contaminants, particularly the PCDDs, PCDFs, PCBs and organochlorine pesticides, are highly lipophilic substances, and have a very low solubility in water. In riverine environments, these contaminants are strongly associated with particulate matter in the water column and in bottom sediments. The lipophilic nature of these chemicals also means that they readily bioconcentrate and biomagnify in biota. Emphasis was therefore placed on the collection of freshwater biota samples in which these organochlorines would have bioaccumulated.

The use of river biota as a biomonitor provides a time-integrated measure of contaminant concentrations, and therefore provides useful long-term monitoring data on the state of riverine environments.

In the current study, longfinned eels (*Anguilla dieffenbachii*) and brown trout (*Salmo trutta*) were the preferred species collected. Both these fish are widely distributed in New Zealand rivers. In addition, eel and trout are commonly consumed by New Zealanders, and dietary intake represents a key pathway for human exposure to organochlorines. At sites where these species could not be caught shortfinned eel (*Anguilla australis*) or rainbow trout (*Oncorhynchus mykiss*) were collected. There are life history differences, particularly with respect to growth rates and migration patterns, between longfinned and shortfinned eel, and between brown and rainbow trout. These differences were considered at the time of sample collection and are discussed in the evaluation of the study results.

A total of 16 river water, 16 eel and 12 trout samples were collected, along with 6 associated quality control samples. Full details of the project design, together with a description of the river catchments and the sample collection programme, are provided in Appendix B.

4.1 Collection of river water and river biota samples

Monthly river water samples were collected in consecutive months during the period January through to March 1996. Each monthly sample was obtained as a series of four individual grab samples taken from across the width of the river in the flowing reaches. This sample consisted of a total of 10 litres of river water, sampled into four amber glass 2.5 litre bottles. Typically, sampling points were accessed by personnel wading into the river. Samples were taken facing upstream to the river flow, and with the bottles fully submerged. The river flow was recorded at the time of sampling.

Eel and trout were collected at, or as near as possible to, the sampling point where river water samples were collected. Each sample consisted of a number of individual fish which were later composited for analysis. Whenever possible, a minimum of 6 individual fish within a defined size range were collected. In a few instances, for sites with low capture rates, a smaller number of individual fish were taken.

Table 4.1 Riverine sampling sites and samples collected

River	Sampling site	Samples collected	Discharges ^{1,2}
Waipa River	Whatawhata	Water, longfinned eel, brown trout	Stormwater/sewage: Te Awamutu (Pop. 13,710). Dairy industry, freezing works, timber processing, mining/quarrying, agricultural runoff (light).
Rangitaiki River	Te Teko	Water, all four fish species	Stormwater/sewage: Murupara (Pop. 2,206). Agricultural runoff (light).
Waingongoro River	State Highway 45	Water, longfinned eel	Stormwater/sewage: Eltham (Pop. 2,004). Freezing works, timber processing, mining/quarrying, agricultural runoff (significant).
Wanganui River	Te Maire	Water, longfinned eel, rainbow trout	Stormwater/sewage: Taumarunui (Pop. 5,833).
Manawatu River	Opiki Bridge	Water, shortfinned eel	Stormwater/sewage: Palmerston North (Pop. 73,095). Dairy industry, freezing works, agricultural runoff (significant), biochemical processing plant.
Mohaka River	Raupunga	Water, longfinned eel	No point source discharges. Reference site.
Tukituki River	Tamumu Bridge	Water, shortfinned eel, rainbow trout	Stormwater/sewage: Waipukurau (Pop. 4,001), Waipawa (Pop. 1,915), Takapau (Pop. 580). Landfill leachate, timber processing, agricultural runoff (moderate).
Ruamahanga River	State Highway 2	Water, longfinned eel	Agricultural runoff (light).
Ruamahanga River	Waihenga	Water, longfinned eel, brown trout	Stormwater/sewage: Masterton (Pop. 19,688), Carterton (Pop. 6,812) and Greytown (Pop. 1,943). Timber processing, mining/quarrying, agricultural runoff (significant).
Haast River	Roaring Billy	Water, longfinned eel	No point source discharges. Reference site.
Waimakariri River	Old H/W Bridge	Water, longfinned eel, brown trout	Freezing works.
Halswell River	McCartney's Bridge	Water, longfinned eel, brown trout	Agricultural runoff (significant).
Taieri River	Sutton Stream	Water, longfinned eel, brown trout	Stormwater/sewage: Middlemarch (Pop. 202). Agricultural runoff (light).
Taieri River	Allanton	Water, longfinned eel, brown trout	Stormwater/sewage: Mosgiel (Pop. 11,133). Agricultural runoff (significant).
Mataura River	Parawa	Water, longfinned eel, brown trout	No point source discharges. Reference site.
Mataura River	Seaward Downs	Water, longfinned eel, brown trout	Stormwater/sewage: Gore (Pop. 13,279). Dairy industry, freezing works, paper mill, agricultural runoff (significant).

¹ Population data from the 1996 Census of Population and Dwellings (Statistics New Zealand).

² The potential for agricultural runoff was assessed as being 'light', 'moderate' or 'significant' on the basis of information provided by Regional Councils.

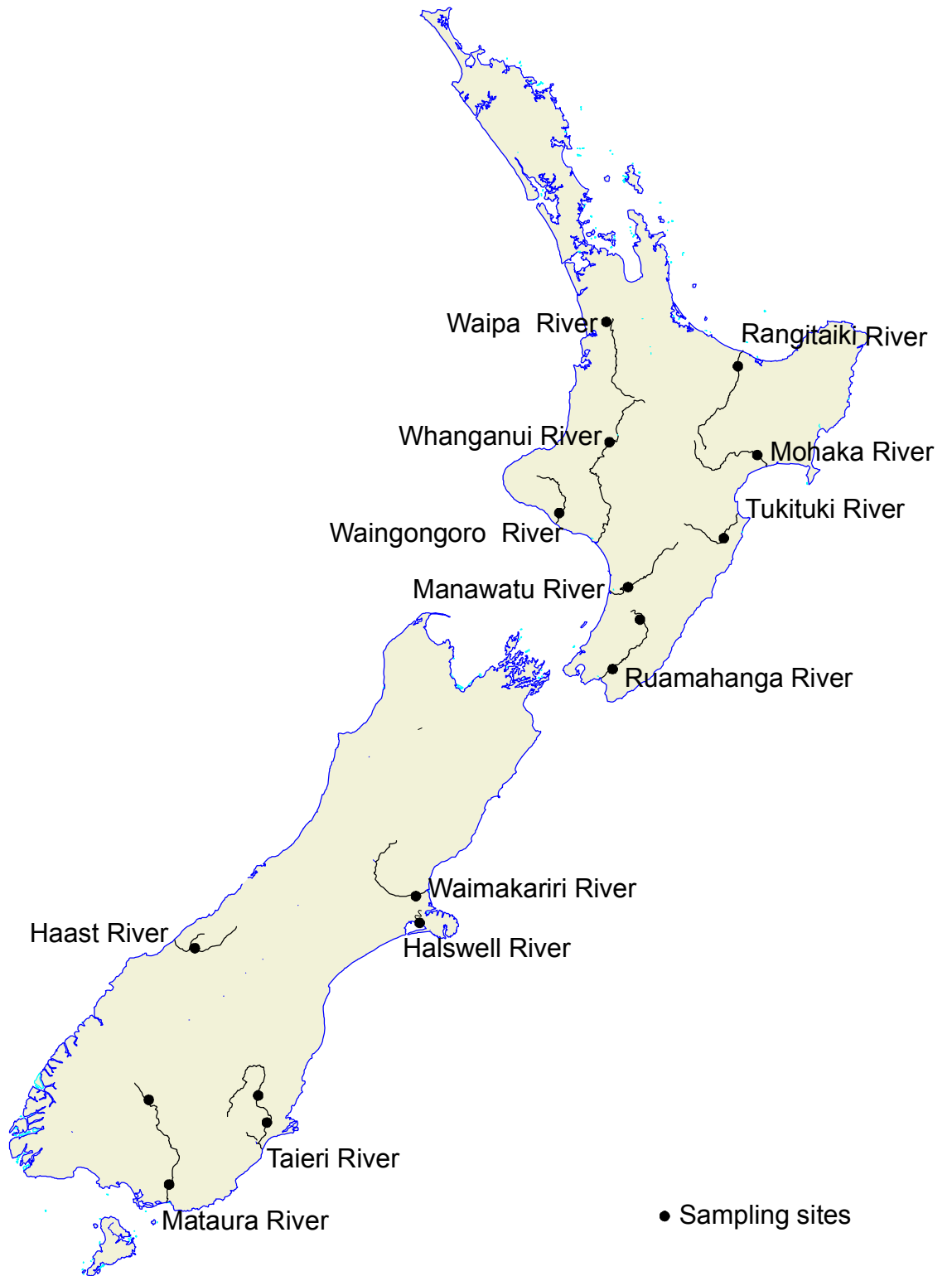


Figure 4.1 Rivers studied and sampling sites

All samples were collected in accordance with the study quality assurance project plan. River water quality control samples consisting of blind duplicates (two samples) and field blanks (two samples) were collected. Two blind duplicate eel samples were collected. Sampling procedures were fully documented in field logs, unique identification numbers were attached and a full chain of custody record was established. Details of the sampling programme and field log information are given in Appendix B.

4.2 Chemical analysis

A composite river water sample was prepared by combining equal volumes of water from the three individual monthly samples collected from each sampling site. For eel and trout, skinned, freeze-dried fillets were prepared from each individual fish collected from each sampling site, and these fillets were then composited for analysis.

All river water, eel and trout 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 also 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 congeners⁴ 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, #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.

The analysis for PCDDs, PCDFs, PCBs and organochlorine pesticides in river water was carried out on each 3-monthly composite river water sample. Each composite sample were filtered prior to analysis, the particulate and aqueous phases extracted separately then combined for clean-up and quantification. Contaminant concentration data reported is for the total sample. Chlorophenol analysis was undertaken on each individual monthly river water sample. These samples were not filtered for analysis. Analysis of eel and trout samples for organochlorines was undertaken on the freeze-dried composite material.

Quantification for PCDDs, PCDFs, PCBs and organochlorine pesticides was by ¹³C isotope dilution using capillary gas chromatography-high resolution mass spectrometry. All data reported are corrected for recovery of the ¹³C surrogate standards. Chlorophenols were 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)

4.2 Statistical analysis

Because environmental residue data of the type collected in this study are typically non-Gaussian, all statistical analyses were conducted using non-parametric methods. All statistical and graphical procedures were performed using the SYSTAT package (Wilkinson, 1996).

5 Organochlorine concentrations in New Zealand rivers

No PCDDs or PCDFs were detected in any of the river water samples collected. Analytical LODs were between 0.3 - 2 pg L⁻¹ for 2,3,7,8-TCDD and 10 - 60 pg L⁻¹ for OCDD.

Similarly, no PCBs were detected in any of the river water samples. Analytical LODs were between 0.01 - 0.03 ng L⁻¹ for the non *ortho*-PCB congeners and 0.1 - 0.6 ng L⁻¹ for the mono and di *ortho*-PCB congeners analysed.

No organochlorine pesticides were detected in the river water samples. Limits of detection for α -, β - and γ -HCH, HCB, aldrin, heptachlor, heptachlor-epoxide, α - and γ -chlordane, pp'-TDE, op'-DDT and pp'-DDT were between 0.1 - 0.3 ng L⁻¹. Detection limits for pp'-DDE and dieldrin were < 0.9 ng L⁻¹ and < 2 ng L⁻¹ respectively.

No chlorophenol compounds were detected in river waters above detection limits of 2-3 ng L⁻¹.

Whilst none of the organochlorine contaminants were detected above the method detection limit in any of the river water samples analysed, low concentrations of some organochlorines were detected in the flesh of eel and trout collected from the same sampling site. Median and mean⁵ concentrations for PCDDs, PCDFs, PCBs, organochlorine pesticides (or degradation products) and PCP determined in fish are given in Table 5.1. Throughout this report, all contaminant concentration data for fish are reported on a wet fillet weight basis unless otherwise stated.

PCDD and PCDF congeners were detected in a limited number of fish samples, with at least one congener being detected in 10 of the 28 samples analysed. The most commonly detected congener was 2,3,7,8-TCDF, which was measured in four of the 12 trout samples. However, this congener was not quantified in any of the 16 eel samples. I-TEQ concentrations, calculated using half LOD values for non-detected congeners, ranged from 0.016 - 0.39 ng I-TEQ kg⁻¹ for eels and 0.016 - 0.20 ng I-TEQ kg⁻¹ for trout.

All but one of the fish samples collected contained a detectable level of some PCB congeners. PCB #138 and #153 were present at the highest concentrations, and this is consistent with overseas data. The sum of PCBs ranged from 0.39 - 18.5 $\mu\text{g kg}^{-1}$ in eels and from 0.11 - 8.80 $\mu\text{g kg}^{-1}$ in trout. These concentrations corresponded to PCB TEQ levels of 0.069 - 1.39 ng TEQ kg⁻¹ for eels and 0.065 - 0.32 ng TEQ kg⁻¹ for trout when half LOD values were used for non-detected congeners.

Dieldrin, pp'-DDE, pp'-TDE and pp'-DDT were detected in all of the 28 fish samples and HCB was detected in 27 of the 28 samples. Of the remaining pesticides analysed, only α -chlordane (15 of 28 samples) and op'-DDT (26 of 28 samples) were detected in more than 50% of samples. Aldrin and heptachlor were not detected in any of the samples analysed to a maximum detection limit of 0.02 $\mu\text{g kg}^{-1}$.

⁵ A mean concentration has been calculated only if the organochlorine contaminant was determined in more than two-thirds of the samples analysed (i.e. on 66% or more of occasions). The rationale for this was that, if the contaminant was not frequently quantified in the samples, the mean value determined might not be truly representative of the entire data set, yet could be taken and misinterpreted as being a 'national average' for New Zealand.

Contaminant concentration data

Comprehensive contaminant concentration data for PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols in river waters and fish are reported in:

Appendix D	PCDDs and PCDFs
Appendix E	PCBs
Appendix F	Organochlorine pesticides
Appendix G	Chlorophenols

Supporting quality assurance (QA) data consisting of blind duplicate samples, and split quality control (QC) samples for each of the analytes in each of the matrices are also provided in the relevant appendices.

A Microsoft Access database holding all analytical results and relevant associated sampling information on this environmental survey and a user's manual (Microsoft Word) detailing the structure and operational (data search and processing) aspects of this database are available from the Ministry for the Environment's website (<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 determined on each 3-month composite sample and chlorophenols determined in each individual monthly sample;
- concentration data for PCDDs, PCDFs, organochlorine pesticides in QC splits of the 3-monthly 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;
- river flows and total suspended solids data for individual monthly samples;
- surrogate standard recoveries for all samples and laboratory quality control samples analysed;
- results of analyses for moisture and lipid contents of fish tissue samples;
- biometric data for individual fish including; length, weight and age;
- field sampling parameters, including grid references of sampling positions.

Table 5.1 Summary of PCDD, PCDF, PCB, organochlorine pesticide and PCP concentrations in New Zealand fish^{1,2}

Organochlorine	Eel (n=16)		Trout (n=12)	
	Median	Mean	Median	Mean
PCDDs and PCDFs				
Sum of PCDD/Fs ³	0.87	1.01	1.73	3.43
Sum of PCDD/Fs ⁴	0	0.17	0.11	2.30
Total I-TEQ ³	0.033	0.060	0.042	0.056
Total I-TEQ ⁴	0	0.026	0.0055	0.018
PCBs				
Sum of PCBs ³	5.04	6.37	1.38	2.35
Sum of PCBs ⁴	4.98	6.30	1.34	2.29
Total PCB TEQ ³	0.23	0.33	0.13	0.15
Total PCB TEQ ⁴	0.14	0.23	0.039	0.061
Pesticides				
α-HCH	< 0.02	nc	< 0.01	nc
β-HCH	< 0.01	nc	< 0.01	nc
γ-HCH	0.017	nc	< 0.01	nc
HCB	0.25	0.23	0.032	0.044
Aldrin	< 0.01	nc	< 0.01	nc
Dieldrin	1.73	2.80	0.27	0.34
Heptachlor	< 0.01	nc	< 0.01	nc
Heptachlor epoxide	< 0.01	nc	< 0.01	nc
α-Chlordane	0.036	0.16	< 0.02	nc
γ-Chlordane	< 0.01	nc	< 0.01	nc
pp'-DDE	33.9	50.0	8.08	16.1
pp'-TDE	2.73	6.57	0.63	0.76
op'-DDT	0.21	0.23	0.038	0.062
pp'-DDT	4.30	5.60	0.46	0.50
Chlorophenols				
PCP	< 0.3	nc	< 0.2	nc

1. For the sum of PCDD/Fs, I-TEQ and PCB TEQ, units are ng kg⁻¹ wet weight.
 2. For the sum of PCBs, pesticide and PCP concentrations, units are µg kg⁻¹ wet weight.
 3. Includes half LOD values for non-detected congeners.
 4. Excludes LOD values for non-detected congeners.
- nc = Not calculated (detected on fewer than 66% of occasions).

No trichlorophenols or tetrachlorophenols were detected in any of the fish fillet samples analysed to a maximum detection limit of 0.6 µg kg⁻¹. Pentachlorophenol was detected, but in only two of the 16 eel samples at concentrations of 0.32 and 0.45 µg kg⁻¹ and in one of the 12 trout samples at a concentration of 0.8 µg kg⁻¹.

For the purposes of comparison of contaminant levels within New Zealand, three sites were defined as 'reference' sites. This designation was based principally on lack of any identifiable discharges at or upstream of the sampling location. Other sites in the study were impacted to various degrees by agricultural, urban or industrial use (see Chapter 4 of this report).

The survey has demonstrated that New Zealand's riverine environments are relatively free of contamination with organochlorine pollutants. The accumulation of only trace levels of these pollutants by fish is indicative of the generally low level of contamination in the New Zealand environment.

Comparative overseas data

To assist in the interpretation of the organochlorine contaminant concentration data found in the current study, a comparison has been made with overseas water and fish concentration 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.

A summary of relevant comparative data is reported in:

Appendix H	PCDDs and PCDFs
Appendix I	PCBs
Appendix J	Organochlorine pesticides
Appendix K	Pentachlorophenol

Since environmental residue data are typically 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.

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

Some of the studies reporting PCDD and PCDF concentrations are from work done in the late 1980s and early 1990s. As no more recent studies appear to be available, there are few alternatives other than to use this data. However, it must be kept in mind that levels in industrialised environments have fallen during the last decade due to many government restrictions that have been enforced since the eighties.

In reviewing overseas data, it is not always possible to clearly distinguish between background samples remote from areas of known contamination and rivers known to have received inputs of organochlorines. Particular care therefore needs to be taken, and the uncertainties recognised, when comparing the data from the current study with data compiled and summarised from the published literature.

A further 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 level of detection, and still others assume a non-detection equated to a concentration level of zero. Where possible this information, and the specific TEF scheme used, are tabulated with the comparative data in Appendix H.

In spite of the constraints imposed by these issues, a comparison with international data remains useful to provide a benchmark for placing the concentrations of organochlorines observed in freshwater environments in the current study into perspective.

5.1 Organochlorines in river water

5.1.1 PCDDs and PCDFs

5.1.1.1 New Zealand data

No PCDDs or PCDFs were determined in any of the river water samples collected. The limits of detection for 2,3,7,8-TCDD were generally at or below 1 pg L⁻¹ and for OCDD at or below 30 pg L⁻¹. Maximum LODs achieved for the 2,3,7,8-chlorinated PCDD and PCDF congeners are reported in Table 5.2.

Table 5.2 Maximum LODs for 2,3,7,8-chlorinated PCDDs and PCDFs in river water

Congener	Maximum LOD (ng L ⁻¹)
2,3,7,8-TCDD	2
1,2,3,7,8-PeCDD	3
1,2,3,4,7,8-HxCDD	2
1,2,3,6,7,8-HxCDD	2
1,2,3,7,8,9-HxCDD	2
1,2,3,4,6,7,8-HpCDD	5
OCDD	60
2,3,7,8-TCDF	0.9
1,2,3,7,8-PeCDF	0.6
2,3,4,7,8-PeCDF	0.6
1,2,3,4,7,8-HxCDF	0.8
1,2,3,6,7,8-HxCDF	0.8
2,3,4,6,7,8-HxCDF	0.7
1,2,3,7,8,9-HxCDF	1
1,2,3,4,6,7,8-HpCDF	4
1,2,3,4,7,8,9-HpCDF	2
OCDF	6

The only available comparative data for PCDD and PCDF concentrations in New Zealand waters are for the Lake Rotorua catchment, comparing water samples from streams impacted by timber treatment leachates and unimpacted streams in the same area (Gifford *et al.*, 1996). PCDDs and PCDFs were not detected in the unimpacted streams while levels of 1.2 pg I-TEQ L⁻¹ and 5.4 pg I-TEQ L⁻¹ were determined for two samples collected at locations downstream of sawmill sites. The principle congeners found in these samples were the hepta- and octa-chlorinated PCDDs, consistent with PCP formulations being the main source of this contamination.

5.1.1.2 Comparative overseas data

Only limited comparative data are available for PCDD and PCDF concentrations in water. A range of the available data from overseas studies is provided in Table H1 (Appendix H). A comparison of the I-TEQ levels found in these studies with the data from the current study is illustrated in Figure 5.1.

The scarcity of comparative data reflects the limited number of studies that have investigated this particular medium. It can be reasonably assumed that this is primarily due to the low water solubility of PCDDs and PCDFs and therefore the extremely low concentrations of these

contaminants found in waters. These low concentrations make the determination of PCDDs and PCDFs in water technically challenging.

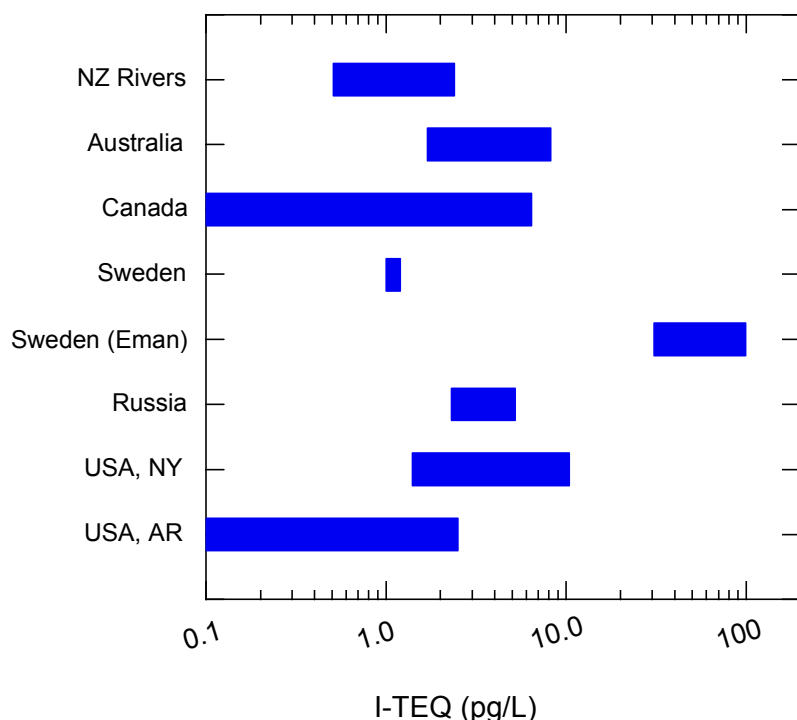


Figure 5.1 Water concentrations of I-TEQ in New Zealand and overseas

New Zealand data includes half LOD values for non-detected congeners. Overseas data is for treated water and raw water as given in Table H1 (Appendix H). All results are in I-TEQ. Data for Australia, Sweden (Eman), Russia and USA (NY) include half LOD values for non-detected congeners in calculation of I-TEQ level. Data for Canada, Sweden and USA (AR) exclude LOD values for non-detected congeners.

In 1983 a survey of 49 drinking water supplies in Ontario, Canada, was conducted (Jobb *et al.*, 1990). The surface waters were taken from a range of facilities including some in the vicinity of chemical plants and pulp and paper mills. This study reported detection of dioxins in 37 of 399 water samples, with OCDD accounting for 36 of the positive results. The remaining positive result was for a non 2,3,7,8-TCDD congener. OCDD concentrations ranged from 9 - 175 pg L^{-1} . Concentrations of OCDD were lower in treated water (9 - 46 pg L^{-1}), presumably due to the removal of the particulate matter to which the dioxins would absorb. As only TCDD and OCDD were analysed in these samples, derivation of TEQ levels was not possible.

During 1986 a survey of 20 community water supply systems taking surface waters was conducted in New York State (Meyer *et al.*, 1989). Sites included those receiving industrial discharges and those known to contain PCDD and PCDF contaminated fish. A range of PCDD and PCDF congeners (tetra- to octa-) were detected in one of the 20 water supplies. In the affected supply TCDDs were measured at 1.7 pg L^{-1} while TCDFs were measured at 2.1 and 2.6 pg L^{-1} in duplicate samples. The only other possibly affected supply showed a trace of OCDF. No PCDDs or PCDFs were detected at the other 18 locations.

European data for PCDDs and PCDFs in surface waters are also limited. Rappe *et al.* (1989b) detected 2,3,7,8-TCDF at 0.022 - 0.026 pg L⁻¹ in river water and drinking water supplies before treatment. There was a general increase in the concentrations of PCDD congeners with increasing chlorine content with HpCDD and OCDD being present at 120 and 170 pg L⁻¹ respectively. This study also noted a higher abundance of PCDF than PCDD congeners. Amirova *et al.* (1997) reported low PCDD and PCDF concentrations in river waters from 8 sites in the central Eurasian Republic of Bashkortostan (Russia). PCDD congener sums ranged from 7.1 - 24.4 pg L⁻¹ while PCDF congener sums ranged from 14.6 - 40 pg L⁻¹, resulting in TEQ concentrations ranging from 2.3 - 5.2 pg TEQ L⁻¹. Rose *et al.* (1994) reported water PCDD and PCDF concentrations of < 6000 pg L⁻¹ for 40 sites in England and Wales. These concentrations resulted in TEQ values of < 80 pg TEQ L⁻¹. The relatively high detection limits in this study make interpretation of the data difficult.

In general these studies demonstrate that the more highly chlorinated congeners are the most abundant in fresh waters. It should be noted that even in locations presumed or known to be receiving PCDD and PCDF inputs, such as the two North American studies, water concentrations of these compounds are generally low. This reflects the physicochemical properties of these compounds which are very insoluble in water. Therefore, in waters, PCDD and PCDF congeners will be strongly associated with particulate matter where it is present. The effect of suspended matter on the concentrations of organochlorines in water samples is discussed further in Section 5.3.1.

5.1.1.3 Regulatory approaches

The toxicity and highly bioaccumulative nature of PCDDs and PCDFs has led to the implementation of various regulatory schemes for the protection of human health and the environment. As has been discussed, concentrations of PCDDs and PCDFs in water are relatively low due to the association of these compounds with particulate matter. Removal of this particulate matter, as occurs during the treatment of drinking water, generally also removes the associated PCDD and PCDF congeners. For this reason many regulatory authorities utilise sediment quality criteria in preference to water quality for these highly lipophilic compounds. However, limits for PCDDs and PCDFs in water have been set in the US and the Netherlands.

For the protection of human and wildlife health, the US EPA have specified a water quality criteria (WQC) of 0.013 pg L⁻¹ for 2,3,7,8-TCDD (US EPA, 1993). The WQC for 2,3,7,8-TCDD generally falls in the range of 0.003 - 0.07 pg L⁻¹ for the protection of wildlife (US EPA, 1995).

The Health Council of the Netherlands has derived an ecotoxicological recommended exposure limit for aquatic ecosystems of 0.1 pg L⁻¹ for 2,3,7,8-TCDD in water (Health Council of the Netherlands, 1996). This exposure limit is considered to be protective of aquatic organisms, birds and mammals.

The technological requirements to measure such low concentrations of 2,3,7,8-TCDD and other PCDDs and PCDFs are considerable, as high-volume water sampling is usually required. As a consequence, the detection limits for PCDD and PCDF concentrations in the river water samples from the current study are well above the exposure criteria discussed above. It is therefore unwise to draw any conclusions about the relevance of these criteria to the New Zealand situation.

5.1.2 Polychlorinated biphenyls

5.1.2.1 New Zealand data

No PCBs were detected in any river water samples analysed. The maximum analytical LODs achieved for individual PCB congeners are listed in Table 5.3. More than 80% of the samples had LODs less than these maximum values (Table E1, Appendix E). The analytical procedures followed provided very low LODs in the range $< 0.01 - < 0.03 \text{ ng L}^{-1}$ for the most biologically potent non *ortho*-PCB congeners. LODs for the majority of the other congeners were marginally higher, typically at or below 0.2 ng L^{-1} .

Table 5.3 Maximum LODs for PCB congeners in river water

Chlorination group	Congener	Maximum LOD (ng L^{-1})
Non- <i>ortho</i>	PCB #77	0.03
	PCB #126	0.01
	PCB #169	0.01
Trichloro-	PCB #28 + PCB #31	0.6
Tetrachloro-	PCB #52	0.2
Pentachloro-	PCB #101, #123, #118	0.2
	PCB #99, #114, #105	0.1
Hexachloro-	PCB #153, #167, #156, #157	0.1
	PCB #138	0.2
Heptachloro-	PCB #187, #183, #180, #170, #189	0.1
Octachloro-	PCB #202, #194	0.1
Nonachloro-	PCB #206	0.2

Although no PCBs were detected in any water samples, by taking half the LOD for non-detected congeners, an upper boundary for the sum of PCB congeners can be estimated in the range $1.1 - 1.6 \text{ ng L}^{-1}$.

5.1.2.2 Comparative overseas data

Comparative data from overseas studies are summarised in Table I1 (Appendix I). PCB concentrations are rarely reported below 0.1 ng L^{-1} and the lowest detection limit reported in water was 0.05 ng L^{-1} (Iwata *et al.*, 1994). In overseas studies, concentrations for total PCBs typically range between $1 - 100 \text{ ng L}^{-1}$, with concentrations of $100 - 1000 \text{ ng L}^{-1}$ reported for more impacted locations. This is illustrated in Figure 5.2.

In the current study, the upper boundary for the sum of PCB congeners ($1.1 - 1.6 \text{ ng L}^{-1}$; see Section 5.1.2.1) is generally as low as the lower concentrations reported for the northern hemisphere (Figure 5.2). This is particularly the case for the comparison with the more densely populated areas of northern Europe and North America.

The lowest PCB water concentrations for various Asian countries (i.e. Malaysia, Thailand, Vietnam, Indonesia and Taiwan) reported by Iwata *et al.* (1994) are lower than the upper boundary data for the sum of PCB congeners obtained from the current study, suggesting higher PCB concentrations in New Zealand waters. However, the study by Iwata *et al.* (1994) analysed larger sample volumes and to lower detection limits than the current study. Since the estimated upper boundary concentrations for the sum of PCB congeners is derived solely from inclusion of half

LOD values for non-detected congeners, the apparently higher concentrations found in New Zealand is primarily an artifact of the reporting technique used. Significantly, in all these Asian countries, the maximum PCB concentrations reported by Iwata *et al.*(1994) were greater than the New Zealand upper boundary concentrations.

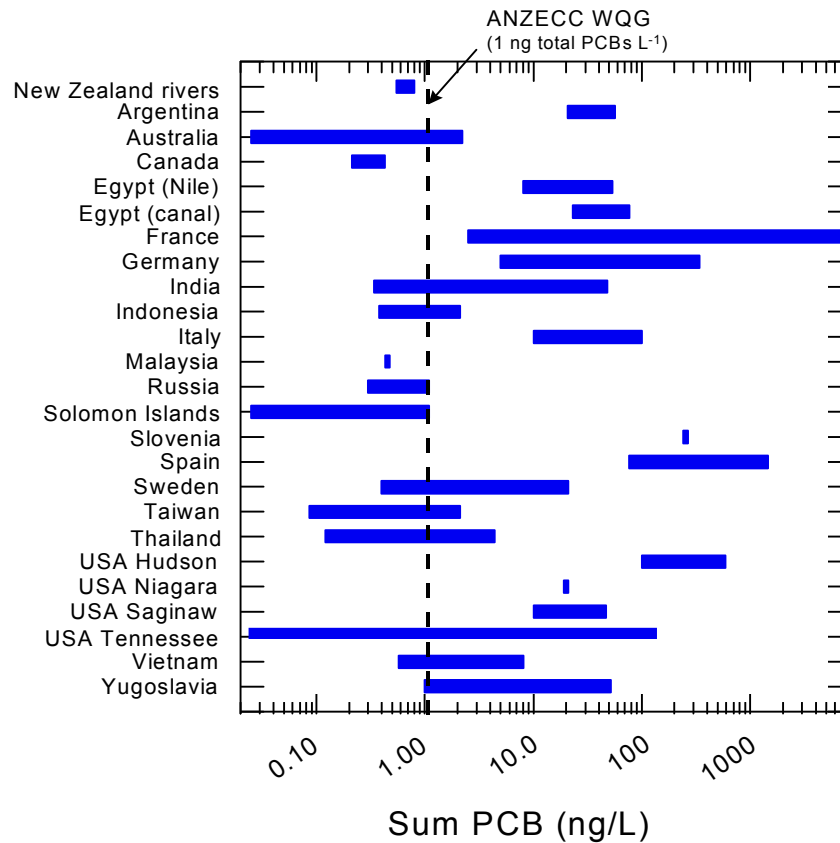


Figure 5.2 Water concentrations of total PCBs in New Zealand and overseas

New Zealand data includes half LOD values for non-detected congeners. The dashed line represents the current Australian and New Zealand Environment and Conservation Council (ANZECC) water quality guideline (WQG) for the protection of aquatic ecosystems (see Section 5.1.2.3). Overseas data taken from Table I1 (Appendix I).

The limited amount of high quality data published in the literature for individual PCB congeners in waters is summarised in Appendix I. Only four papers provided adequate data (Bush *et al.*, 1985; Colombo *et al.*, 1990; Fernandez *et al.*, 1992; Friege *et al.*, 1989), and even this was for a limited number of comparable congeners (maximum 10), while other papers identified congeners either using non-standard nomenclatures for groups of congeners (Bremle *et al.*, 1995) or only presented congener data graphically (Kucklick *et al.*, 1994). Other papers only reported results as congener sums (Verbrugge *et al.*, 1995). It can be concluded from these studies that, in general, less highly chlorinated congeners predominate in water samples (Bush *et al.*, 1985; Fernandez *et al.*, 1992; Bremle *et al.*, 1995) with di-, tri- and tetra-chlorinated congeners being the most abundant. This generalisation is, however, not valid during flood events when large amounts of particulate-associated PCBs can be resuspended. In these instances the more highly chlorinated congeners, which have a greater propensity to bind to organic matter, can predominate in 'raw' water samples.

As in other environmental matrices and in fish samples (see Section 5.2), PCB congeners #138 and #153 are frequently detected in water samples. Bush *et al.* (1985) analysed water samples from the Hudson River and reported concentrations for congener #153 ranging from not detected to 1.2 ng L⁻¹, while congener #138 was detected at concentrations between 0.4 - 2.8 ng L⁻¹. In the same samples, congener #52 was detected at concentrations ranging from 2.3 - 10 ng L⁻¹, again showing the predominance of the less highly chlorinated congeners. Fernandez *et al.* (1992) also reported #138 (up to 95 ng L⁻¹) as being more abundant than #153 (up to 20 ng L⁻¹); however, they did not analyse for any congeners with less than 5 chlorines. In contrast to the above studies, Friege *et al.* (1989) reported #153 as being more abundant than #138. This study also showed that congener #28 was more frequently detected and was present at the highest concentrations.

Some of the above studies reported concentrations for individual PCB congeners at levels considerably higher than the concentrations for the sum of PCB congeners found in the current study. This again emphasises the relatively low levels of organochlorine contamination present in the New Zealand riverine environment.

5.1.2.3 Regulatory approaches

A valuable summary of water quality criteria and guidelines is available from MacDonald (1994). While focusing on criteria for North America, this summary offers global coverage. Water criteria are provided for a range of chemicals and a range of resource uses (e.g. drinking water, industrial water) as well as the protection of wildlife.

Based on total PCB concentrations, drinking water quality criteria in the US States are generally around 1 ng L⁻¹ but are as low as 0.079 ng L⁻¹ in some states (MacDonald 1994). Criteria for the protection of aquatic life are generally as low or lower (e.g. 0.0079 ng L⁻¹ in Missouri) than those for the protection of human health.

The current Australian and New Zealand Environment and Conservation Council (ANZECC) water quality guideline (WQG) for the protection of aquatic life is 1 ng total PCBs L⁻¹ (ANZECC, 1992).

In contrast to the above criteria that are based on total PCB concentrations, British Columbia and the Netherlands provide criteria based on specific congener concentrations (MacDonald 1994; Stortelder *et al.* 1989). In the Netherlands these range from 0.45 ng L⁻¹ for PCB #153 to lower values for the more toxic non *ortho*-congeners (e.g. 0.00025 ng L⁻¹ for PCB #126). The Netherlands criteria also distinguish between total and dissolved concentrations of individual congeners (e.g. 0.43 ng L⁻¹ for total #153 but 0.05 ng L⁻¹ for dissolved #153).

The detection limits for PCBs in river water from the current study are similar to or above the criteria discussed above. Therefore any comparison of PCB concentrations in New Zealand waters relative to these criteria would require analysis of water samples to considerably lower detection limits.

5.1.3 Organochlorine pesticides

5.1.3.1 New Zealand data

Data for organochlorine pesticides in river water from the current study are provided in Appendix E. No organochlorine pesticides were detected in any of the water samples. Typical LOD values were at or below the maximum LODs given in Table 5.4. These LODs are somewhat higher than those attained in a number of overseas studies, notably where solid-phase extraction was used. However, it should be remembered that the samples in this current study were used for the determination of an extensive range of analytes, and therefore some compromise in detection limits for some compounds was required.

Table 5.4 Maximum LODs for organochlorine pesticides in river water

Pesticide	Maximum LOD (ng L ⁻¹)
α-HCH	0.2
β-HCH	0.2
γ-HCH	0.3
HCB	0.1
Aldrin	0.1
Dieldrin	2
Heptachlor	0.2
Heptachlor epoxide	0.3
α-chlordane	0.3
γ-chlordane	0.3
pp'-DDE	0.9
pp'-TDE	0.1
op'-DDT	0.1
pp'-DDT	0.2

Other New Zealand work has involved a survey of organochlorine pesticides in the Avon and Heathcote River and Estuary. In this 1991-92 study, dieldrin was measured in water at 10 out of the 24 sampling sites on at least one of the three sampling occasions (Thomson and Davies, 1993). Concentrations were measured between < 1 - 6.8 ng L⁻¹, with an average concentration of 1.4 ng L⁻¹. γ-HCH was also measured at nine of the sampling sites with concentrations between < 0.8 - 3.0 ng L⁻¹. DDT and its degradation products, heptachlor, heptachlor epoxide, and α- and γ-chlordane were not detected in any water samples.

5.1.3.2 Comparative overseas data

A summary of comparative overseas data is provided in Appendix J for concentrations of DDT and its degradation products (Table J1), aldrin and dieldrin (Table J3) and HCH (Table J5, Appendix J) in water. Detection limits for DDE, dieldrin and HCB are compared with overseas data and with current ANZECC WQGs in Figure 5.3. Data are provided for these three organochlorines because they were the most frequently detected pesticides (including degradation products) and were present at the highest concentrations in the fish samples analysed in the current study (see Section 5.2.3).

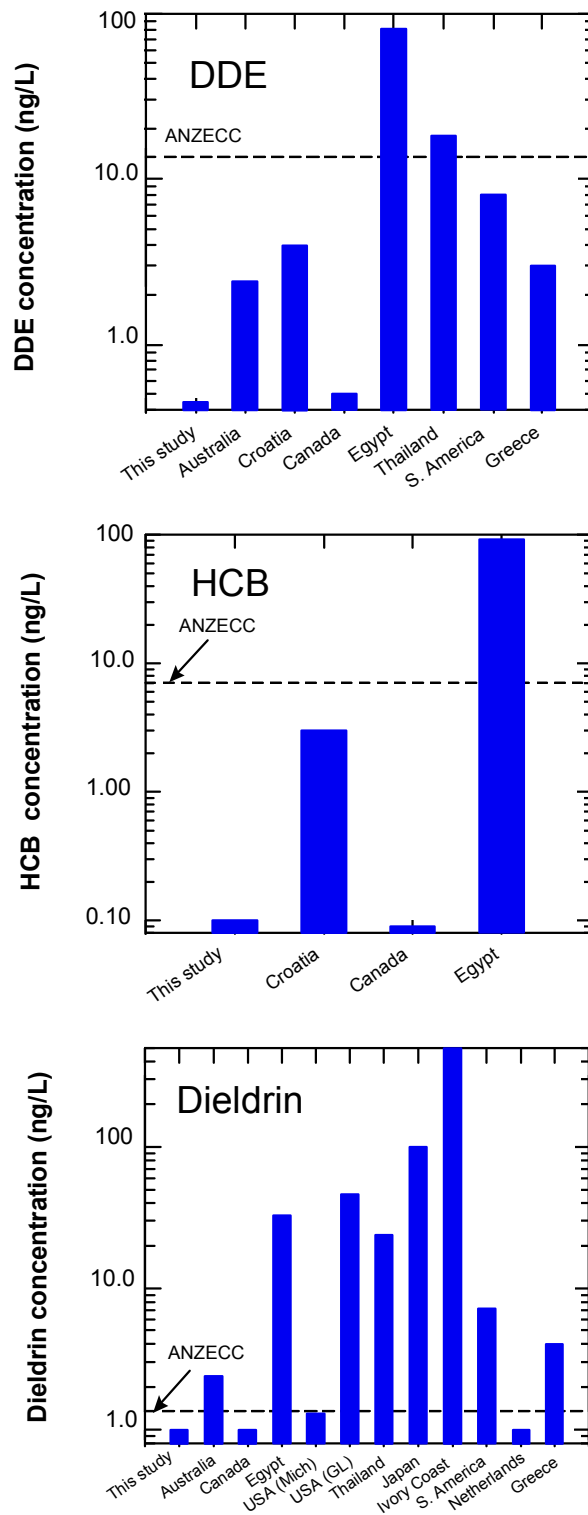


Figure 5.3 Maximum pesticide detection limits in New Zealand river water compared to maximum pesticide concentrations in overseas water
 The dashed lines represent the current ANZECC WQG for the protection of aquatic ecosystems (see Section 5.1.3.3). Overseas data taken from Tables J1 (DDE), J3 (Dieldrin) and J5 (HCB) (Appendix J).

For all the organochlorine pesticides except dieldrin, the New Zealand river water data (as represented by the analytical detection limits) from the current study were well below the ANZECC WQGs (see Section 5.1.3.3), and were low compared to most overseas data. For dieldrin, the maximum detection limit for two samples in the current study was the same as the current ANZECC guideline of 2 ng L⁻¹, but the LODs for the remaining 14 samples were at or below 1 ng L⁻¹. These detection limits for dieldrin in water samples were considerably lower than comparative overseas data (Table J3, Appendix J). It is apparent that dieldrin concentrations detected in water samples from many overseas countries exceed the current ANZECC WQG (ANZECC, 1992) and also the Canadian guideline (CCREM, 1991).

5.1.3.3 Regulatory approaches

There are a large number of water quality criteria for pesticides both in water and fish. These criteria differ in their bases: protection of aquatic life, increased cancer risk etc.; and in their goals: protection of drinking water, protection of industrial water, protection of water for stock watering. Canadian (CCREM, 1991) and ANZECC (ANZECC, 1992) guidelines for the protection of aquatic life are given in Table 5.5. The data from the current study compares favourably with these guidelines. A comprehensive list of criteria for many environmental compartments is given by MacDonald (1994).

Table 5.5 Canadian and Australia and New Zealand Environment and Conservation Council water quality guidelines for the protection of aquatic life

Compound	CCREM (1991) (ng L ⁻¹)	ANZECC (1992) (ng L ⁻¹)
Aldrin		10
Dieldrin	4	2
Chlordane	6	4
DDT	1 (ΣDDTs)	1
DDE		14
Heptachlor and heptachlor epoxide	10	10 (Heptachlor)
ΣHCH	10	3 (Lindane)
HCB	6.5	7

5.1.4 Chlorophenols

5.1.4.1 New Zealand data

No chlorophenols were detected in any of the water samples above the analytical detection limits of 2-3 ng L⁻¹. In general, where comparative data are available (Table K1, Appendix K), concentrations of chlorinated phenols (as represented by the analytical detection limits) in the background river water samples from the current study are lower than the levels which have been observed in samples collected from both unimpacted and impacted overseas rivers and lakes.

Other data for PCP in New Zealand freshwaters were provided by a study of streams impacted or unimpacted by discharges from timber treatment facilities in the Lake Rotorua catchment (Gifford *et al.*, 1995; Gifford *et al.*, 1996). In the Lake Rotorua study, unimpacted streams had PCP concentrations generally < 10 ng L⁻¹ while a highly impacted stream had a PCP concentration of 3620 ng L⁻¹. It should be stressed that the catchment in which this study was conducted has one

very large timber treatment facility from which discharges of PCP to the environment are known to have occurred (Ministry for the Environment, 1992). In addition, other smaller timber treatment facilities in the catchment may also have discharged PCP to the environment.

Pentachlorophenol has also been measured at a number of sites in the Avon and Heathcote River and Estuary system, with concentrations between $< 2.5 - 68 \text{ ng L}^{-1}$ (Thomson and Davies, 1993). 2,3,4,5-Tetrachlorophenol was also measured to a maximum concentration of 13 ng L^{-1} . No 2,4,5- or 2,4,6-trichlorophenol was detected.

5.1.4.2 Comparative overseas data

As PCP was the only chlorophenolic compound detected in the eel and trout samples collected in the current study, the following discussion and the compilation of overseas data (Table K1, Appendix K) are limited to this compound.

The detection limit for PCP in New Zealand water samples is compared to overseas data in Figure 5.4. The New Zealand PCP data are clearly well below these overseas concentrations. It should be noted, however, that the overseas data used for this comparison were mostly collected in the 1970s and 1980s (Table K1, Appendix K). More recent data could not be found with which to make a more valid comparison with the PCP data from the current study.

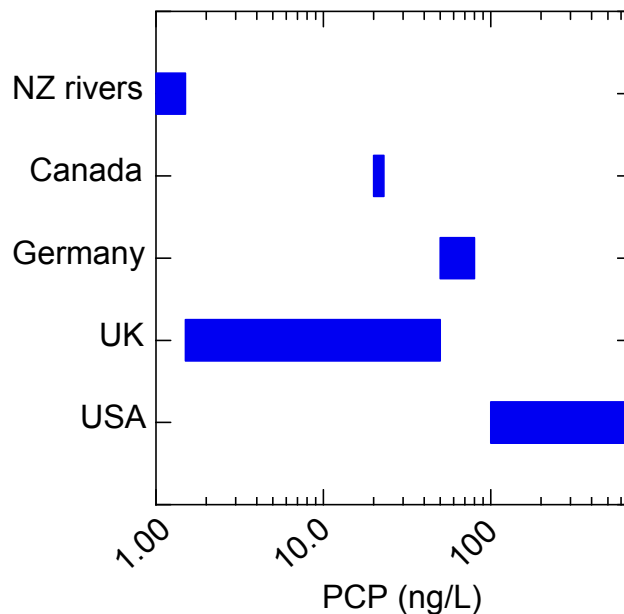


Figure 5.4 Detection limits for PCP in New Zealand river water compared to data for overseas river water
Overseas data from Table K1 (Appendix K).

5.1.4.3 Regulatory approaches

The current ANZECC WQG for PCP for the protection of aquatic ecosystems is 50 ng L⁻¹ (ANZECC, 1992). This value is based on available acute and chronic toxicity data, but does not consider biomagnification as insufficient data are available. These values are comparable with other criteria, for example the Netherlands environmental quality objectives which specifies a target value of 20 ng L⁻¹ and a limit value of 50 ng L⁻¹ for surface water (Ministry of Housing, Spatial Planning and the Environment, 1994).

The detection limits for PCP in the current study were almost an order of magnitude lower than the above water quality criteria, indicating some margin of safety for PCP in New Zealand riverine environments.

5.2 Organochlorines in freshwater fish

5.2.1 PCDDs and PCDFs

5.2.1.1 New Zealand data

PCDD and PCDF concentrations ranged from 0.016 - 0.39 ng I-TEQ kg⁻¹ for eels and 0.016 - 0.20 ng I-TEQ kg⁻¹ for trout (including half LOD values for non-detected congeners). The maximum I-TEQ level in eel was observed in the sample collected from the Halswell River at McCartneys Bridge, and in trout in the sample collected from the Waipa River at Whatawhata (Figure 5.5). When zero was used instead of half LOD values for non-detected congeners, the maximum I-TEQ level for these particular samples decreased only marginally to 0.38 ng I-TEQ kg⁻¹ for eel and 0.14 ng I-TEQ kg⁻¹ for trout.

The sum of PCDD and PCDF congeners on a wet fillet weight basis ranged from 0.53 - 2.31 ng kg⁻¹ for eel and from 0.36 - 13.4 ng kg⁻¹ for trout when half the LOD values for non-detected congeners were used to calculate the congener sum. No 2,3,7,8-TCDD was determined in any of the 12 trout samples, and it was measured in only one of the 16 eel samples collected. In contrast, 2,3,7,8-TCDF was detected in four trout samples but no eel samples. OCDD was detected in only one eel sample at 1.81 ng kg⁻¹ but was detected in two trout samples at concentrations over 10 ng kg⁻¹. Similarly, OCDF was detected in two trout samples but no eel samples.

The detection of OCDD at 10.6 ng kg⁻¹ in two trout samples, one from the Rangitaiki River at Te Teko and the other from the Maitai River at Parawa (a reference site) seems abnormal. The fish in these samples were not particularly old and the flesh lipid contents were not particularly high. Both of these samples also showed a similar profile of three other congeners (1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF and OCDF) despite the fish being collected from opposite ends of the country. This congener profile was not detected in other species collected from the same two sites, nor at a second, downstream, site on the Maitai River. The OCDD values for these two samples are outside the 99.9% confidence interval for the mean OCDD concentration in all samples in trout and must therefore be considered as 'anomalous'. Although no PCDDs or PCDFs were measured in any of the field blanks collected, or in the laboratory blanks analysed with these samples, neither field or laboratory contamination cannot be excluded as the source of the OCDD measured. While the OCDD concentrations give comparatively elevated levels for the sum of

PCDD and PCDF congeners when compared to the other samples collected, they have little influence on the I-TEQ level determined. Using the revised WHO-TEFs (which have a TEF value for OCDD that is lower than the I-TEF value used, see Table 2.2), the impact on the TEQ level determined would be even less.

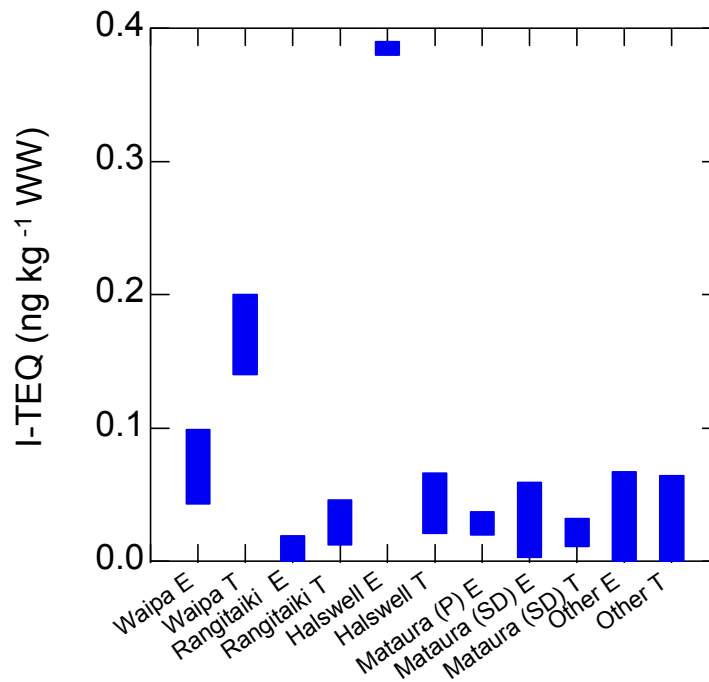


Figure 5.5 Minimum and maximum PCDD and PCDF I-TEQ concentrations in New Zealand fish

E = eel, T = trout at each site; Mataura (P) = Mataura River at Parawa; Mataura (SD) = Mataura River at Seaward Downs. Data are presented for these specific sites because both eel and trout were collected and PCDDs and PCDFs were quantified in at least one of the species. Other E and Other T = combined data for eel and trout from all other sites. The minimum value is taken as the I-TEQ concentration calculated excluding LOD values. The maximum value is taken as the I-TEQ concentration calculated including half LOD values.

Biometric data for the fish sampled at each location are summarised in Table 5.6. More comprehensive data is provided in Tables B7 and B8 (Appendix B). While efforts were made to collect similar samples, there are clearly differences in the average age of fish in some of the samples, particularly for eel. Not unexpectedly, the lipid content of eel tissue was also considerably higher than for trout from the same sampling site. Together these differences in age and lipid content along with species differences in contaminant accumulation make drawing direct comparisons between eel and trout difficult.

Table 5.6 Biometric data for eel and trout

River and sampling site	Species	Number of fish	Mean age ¹	Lipid (% WW)
Waipa River at Whatawhata	Longfinned eel	6	20	4.7
Rangitaiki River at Te Teko	Eel ²	6	23	2.2
Waingongoro River at State Highway 45	Longfinned eel	6	19	8.7
Wanganui River at Te Maire	Longfinned eel	6	22	6.5
Manawatu River at Opiki Bridge	Shortfinned eel	6	9	6.2
Mohaka River at Raupunga	Longfinned eel	4	23	4.3
Tukituki River at Tamumu Bridge	Shortfinned eel	6	23	8.8
Ruamahanga River at State Highway 2	Longfinned eel	6	20	4.6
Ruamahanga River at Waihenga	Longfinned eel	6	18	9.9
Haast River at Roaring Billy	Longfinned eel	6	33	11.7
Waimakariri River at Old H/W Bridge	Longfinned eel	8	20	3.3
Halswell River at McCartney's Bridge	Longfinned eel	6	23	10.5
Taieri River at Sutton Stream	Longfinned eel	6	18	10.3
Taieri River at Allanton	Longfinned eel	6 ³	19 ⁴	10.5 ⁴
Mataura River at Parawa	Longfinned eel	6	32	12.8
Mataura River at Seaward Downs	Longfinned eel	6 ³	17 ⁴	9.2 ⁴
Waipa River at Whatawhata	Brown trout	8	5,1	3.2
Rangitaiki River at Te Teko	Brown trout	3	3,10	1.8
Rangitaiki River at Te Teko	Rainbow trout	5	2,5	1.6
Wanganui River at Te Maire	Rainbow trout	5	1,9	4.6
Tukituki River at Tamumu	Rainbow trout	5	2,6	4.5
Ruamahanga River at Waihenga	Brown trout	3	3,6	5.4
Waimakariri River at Old H/W Bridge	Brown trout	4	nd	4.5
Halswell River at McCartney's Bridge	Brown trout	4	3,7	5.8
Taieri River at Sutton Stream	Brown trout	5	2,9	3.8
Taieri River at Allanton	Brown trout	5	2,7	4.5
Mataura River at Parawa	Brown trout	6	3,3	4.7
Mataura River at Seaward Downs	Brown trout	6	5,11	2.5

1. For eel the age is given to the nearest whole year and for trout age is given to the nearest whole year and months of a year (years,months). Further details on the fish ageing is provided in Section C2, Appendix C.
2. Sample mixture of one longfinned eel and five shortfinned eel.
3. There were 6 fish in both the primary and blind duplicate samples collected from these sites.
4. Mean data for the primary and blind duplicate samples.
nd = Not determined.

Only limited other PCDD and PCDF data are available for New Zealand freshwater fish. Jones *et al.* (1995) reported maximum 2,3,7,8-TCDD and OCDD concentrations of 5.76 and 8.42 ng kg⁻¹ wet weight respectively in eel collected from the Tarawera River which is impacted by sewage and pulp and paper mill effluents, as well as from geothermal inputs. These eels had a maximum I-TEQ concentration of approximately 10 ng I-TEQ kg⁻¹ wet weight. Jones (1996) did not measure any PCDD or PCDF congeners in eel or catfish from seven locations on the Waikato river. The same analytical facility and analytical methods were used as in the current study, with comparable detection limits being achieved for the PCDDs and PCDFs.

PCDDs and PCDFs have also been measured in rainbow trout from Lake Rotorua (Gifford *et al.*, 1996). Localised PCP contamination of the lake environment has occurred near an area where there was high use of this chemical for timber treatment. Concentrations of PCDDs and PCDFs measured in the eight trout analysed were between 0.59 - 0.88 ng I-TEQ kg⁻¹ wet weight, with a mean concentration of 0.74 ng I-TEQ kg⁻¹. These concentrations are higher than the concentrations measured for all samples in the current study.

The profiles of PCDD and PCDF congeners detected in eel flesh from the Halswell River and from the Mataura River at Seaward Downs are presented in Figure 5.6. These samples were chosen as they show the highest levels of I-TEQ (Halswell River) or show an OCDD-dominated profile.

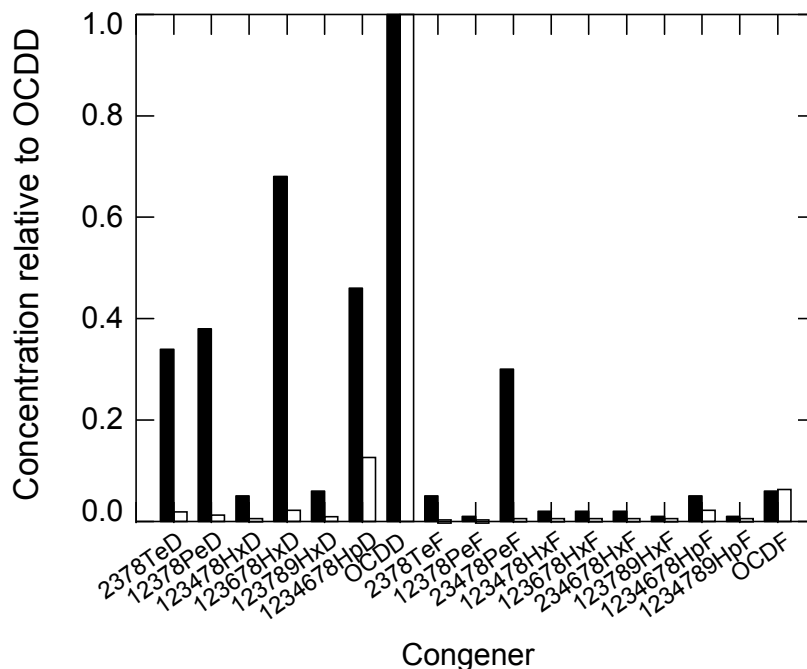


Figure 5.6 PCDD and PCDF congener profile for New Zealand fish flesh
 Profiles are for muscle tissue of eel collected from the Halswell River (solid bars) and Mataura River at Seaward Downs (open bars).

The profile from the Halswell River is dominated by PCDD congeners, with OCDD being the most abundant followed by 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, 1,2,3,7,8-PeCDD and 2,3,7,8-TCDD. The most abundant PCDF was 2,3,4,7,8-PeCDF. In the sample from the Mataura River at Seaward Downs, only PCDD congeners were measured above the detection limit, with OCDD and 1,2,3,4,6,7,8-HpCDD being the most abundant.

In a national survey in the US, 1,2,3,6,7,8-HxCDD and 1,2,3,4,6,7,8-HpCDD were reported as being prevalent and abundant congeners (Kuehl *et al.*, 1994). 2,3,7,8-TCDF was also abundant and prevalent in this US survey, and it is also the dominant congener in many Great Lakes fish samples, although its abundance varies from lake to lake (Zacharewski *et al.*, 1989). These findings are in contrast to the current study, where 2,3,7,8-TCDF was not detected in any of the 16 eel samples collected. Although 2,3,7,8-TCDF was the most commonly detected congener in trout from the current study, being quantified in four of the 12 samples, its concentrations were very low (maximum of 0.82 ng kg⁻¹ in brown trout from the Waipa River). The absence of 2,3,7,8-TCDF in eel, and its presence in only a limited number of trout at low concentrations is reflective of the low levels of PCDDs and PCDFs present in fish living in New Zealand rivers.

5.2.1.2 Comparative overseas data

Concentrations of PCDDs and PCDFs have been studied in a great variety of fish species, and a selection of overseas studies are tabulated in Table 5.7 and Tables H2 and H3 (Appendix H). A comparison of the TEQ levels found in a number of these studies, particularly those that looked at eel and trout, with the data from the current study is illustrated in Figure 5.7.

Table 5.7 Representative concentrations of PCDDs and PCDFs in overseas freshwater fish tissue

Country	Species	TEQ (ng kg ⁻¹ WW)		Reference
		Min.	Max.	
Australia, Lake Coleman	Carp fillets	0.48	4.0	Ahokas <i>et al.</i> , 1994
Bavaria	Trout	0.16	0.74	Mayer, 1995
Bavaria	Carp	0.03	5.26	Mayer, 1995
Canada, British Columbia	Fish, background	nd	0.19	Van Oostdam and Ward, 1995
Canadian Great Lakes	All species	0.50	63	Reiner <i>et al.</i> , 1995
Finland	Rainbow trout	0.23	1.47	Vartiainen and Hallikainen, 1992
Finland, Ahvenkoskenlhti Bay	Burbot and bream	0.4	84.2	Korhonen <i>et al.</i> , 1997
Finland, Kymijoki River	Various	0.70	122	Korhonen <i>et al.</i> , 1997
Finland, Subarctic lakes	Trout muscle, NE Lapland		0.080 ¹	Vartiainen <i>et al.</i> , 1996
Germany, Elbe River	Bream, Muhlenberger	4.1	23.8	Luckas and Oehme, 1990
Germany, Hamburg	Bream and perch	1.4	94.4	Gotz and Schumacher, 1990
Germany, Neckar	Various	0.40	2.9	Frommberger, 1991
USA	Fish tissue, pristine sites	nd	3.02	US EPA, 1992
USA	Fish tissue, all data	nd	213	US EPA, 1992
USA, Mississippi River	Fillet, Mississippi	3.07	10.6	Reed <i>et al.</i> , 1990
World wide, various	Various, summary of data	nd	1430	Clarke <i>et al.</i> , 1996
Eel				
Canada, Lake Ontario	American eel	13.0	13.0	Reiner <i>et al.</i> , 1995
Canada, Quebec	Silver eel, Rivière aux Pins	0.80	0.80	Hodson <i>et al.</i> , 1994
Canada, Quebec	Silver eel, Kamouraska	0.16	2.30	Hodson <i>et al.</i> , 1994
Germany, Rhine and Neckar	Eel, fillet	0.94	5.4	Frommberger, 1991
Germany, Rhine	Eel, edible tissue	1.35	7.79	Rainer, 1996
Netherlands	Yellow eel, freshwater	0.32	4.2	de Boer <i>et al.</i> , 1993
Netherlands, Dutch waters	Eel, various locations	2.0	8.0	Turkstra and Pols, 1989
Norway	Eel, various locations	0.16	1.98	Knutzen and Schlabach, 1996
Norway, Frierfjord	Eel, fillet, saltwater	6.3	20	Knutzen and Oehme, 1989
Norway, Frierfjord	Eel, fillet, saltwater	6.38	42.6	Knutzen and Schlabach, 1996
Sweden	Eel, fillets	nd	9.6	Oehme <i>et al.</i> , 1989
World wide	Eel, summary of data	6.7	65.9	Clarke <i>et al.</i> , 1996

1. Mean concentration.

In the overseas studies, species analysed range from the small 'forage' fish such as herring and smelt to large carnivorous species such as pike (de Wit *et al.*, 1992). Many studies have focused on the analysis of bottom-feeding species such as carp or suckers (*Catostomus* spp.) which may be in close contact with and consume contaminated sediments. Carp (*Cyprinus carpio*, *Carasius auratus*) are also commonly analysed for organochlorines due to their omnivorous feeding habits and relatively high fat content. Trout (*Oncorhynchus* spp) and salmon (*Salmo* spp) have also been extensively studied due to their significance as sportfish and a human food source and due to their known sensitivity to PCDDs and PCDFs and related contaminants. Although eel (*Anguilla* spp.) are also a significant food source in some areas they do not appear to have been as widely studied as other species.

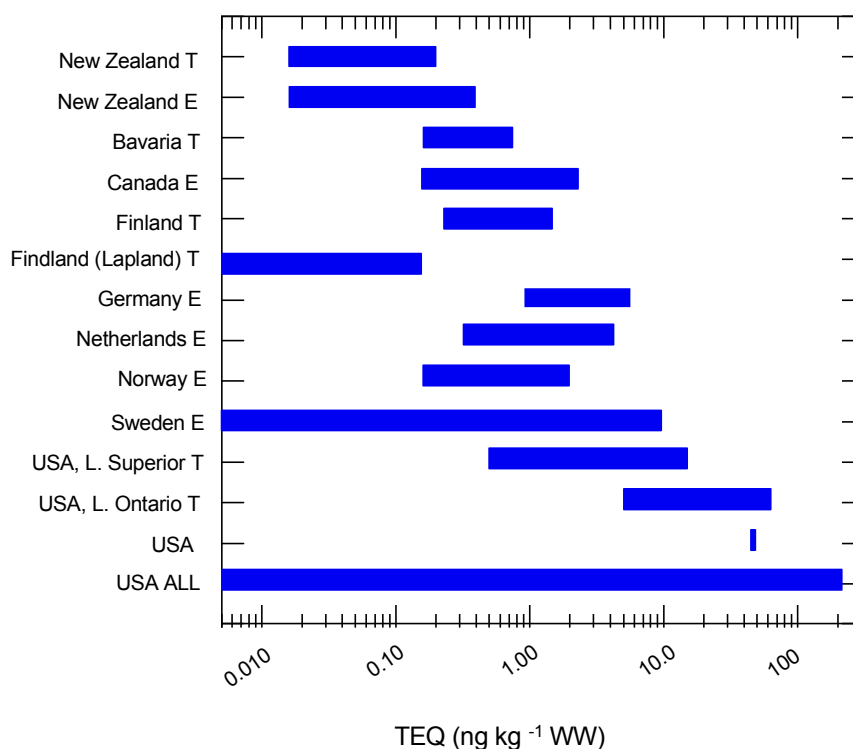


Figure 5.7 PCDD and PCDF TEQ concentrations in New Zealand and overseas fish
 E = eel; T = trout; ALL = all data from US EPA (1992). New Zealand data include half LOD values for non-detected congeners. Overseas data taken from Tables H2 and H3 (Appendix H).

Different fish species accumulate different amounts of PCDDs and PCDFs. For example, trout from Bavaria had I-TEQ ranges from 0.16 - 0.74 ng I-TEQ kg⁻¹ while carp from the same locations had concentrations of 0.03 - 5.26 ng I-TEQ kg⁻¹ (Mayer, 1995). PCDD and PCDF concentrations are also obviously affected by the fishes' migratory patterns: therefore while carp in the Columbia River showed 2,3,7,8-TCDD concentrations of 0.79 ng kg⁻¹, salmon and steelhead trout (migratory rainbow trout) from the same river had concentrations approximately 10 fold lower (Parsons *et al.*, 1991).

Areas not impacted by PCDDs and PCDFs are difficult to find in the northern hemisphere. Vartiainen *et al.* (1996) reported fillet I-TEQ concentrations of 0.056 - 0.101 ng I-TEQ⁻¹ for arctic char and 0.080 ng I-TEQ kg⁻¹ for trout from remote lakes in Finland. In the upper Rhine River in Germany, Rainer (1996) reported I-TEQ concentrations in eel of 1.35 - 7.79 ng I-TEQ kg⁻¹. PCDD and PCDF concentrations for eel, also in Germany, ranged from 0.94 - 5.4 ng I-TEQ kg⁻¹, and for various other species from 0.40 - 2.9 ng I-TEQ kg⁻¹ (Frommberger 1991). In comparison Luckas and Oehme (1990) reported Nordic-TEQ values of 4.1 - 23.8 ng TEQ kg⁻¹ for bream from the lower Elbe River in Germany.

PCDD and PCDF concentrations of 0.04 - 0.22 and 0.02 - 0.20 µg kg⁻¹ have been reported for fish (gray mullet) collected from a river in an urban area near Osaka, Japan (Watanabe *et al.*, 1995). TEQ data were not reported.

The only readily available overseas data from the southern hemisphere is an Australian study which reported an I-TEQ concentration of 0.48 ng I-TEQ kg⁻¹ for an unimpacted site (Ahokas *et al.*, 1994). The maximum PCDD and PCDF concentration found in this study was 4.0 ng I-TEQ kg⁻¹ at a site receiving industrial/municipal effluent.

Many studies on PCDDs and PCDFs in fish have focused on the effects of industrial effluents on aquatic ecosystems. Some of these studies report concentrations of PCDDs and PCDFs from 'control' sites above known discharges. In Canada, PCDD and PCDF concentrations between 0.78 - 23.8 ng TEQ kg⁻¹, with a mean of 3.80 ng TEQ kg⁻¹, were reported for fish above a paper mill discharge in Quebec (Hodson *et al.*, 1992b). Higher concentrations were measured downstream of the discharge.

Congener profiles for PCDDs and PCDFs in studies from the northern hemisphere are more complex than those detected in the samples from the current study due mainly to the higher concentrations of the various congeners and the diversity of PCDD and PCDF sources in these areas (Kuehl *et al.*, 1994; Zacharewski *et al.*, 1989). Species-specific accumulation and/or metabolism can further modify these profiles (Frommberger *et al.*, 1991).

Kuehl *et al.* (1994) demonstrated that the four most commonly detected PCDD and PCDF congeners in North American fish were 2,3,7,8-TCDF, 1,2,3,4,6,7,8-HpCDD, 2,3,7,8-TCDD, and 1,2,3,6,7,8-HxCDD (significantly, OCDD was not looked for). These four congeners were measured in fish samples from 89%, 89%, 70% and 69% respectively of nearly 400 sites throughout the USA, while a total of 15 2,3,7,8-chlorinated PCDD and PCDF congeners (not OCDD or OCDF) were detected at 1% or more of all these sites. This study used the slightly different EPA TEF values and noted that 75% of sites examined had fish TEQ concentrations less than 10 ng kg⁻¹.

Even when compared to the unimpacted sites in the northern hemisphere, the I-TEQ levels found in the current study (mean of 0.060 ng I-TEQ kg⁻¹ for eel and 0.056 ng I-TEQ kg⁻¹ for trout) are low.

5.2.1.3 Regulatory approaches

Due to the bioaccumulative nature of PCDDs and PCDFs, their regulation for the protection of human health has focused on management of intake via food. The World Health Organisation Tolerable Daily Intake (TDI) for 2,3,7,8-TCDD was 10 pg kg⁻¹ bw day⁻¹ (WHO 1991). This TDI, which has been adopted by several countries including Canada, the Netherlands and the United Kingdom, has recently been revised downwards by WHO to a range of 1-4 pg TEQ kg bw/day (WHO, 1998). The Health Council of the Netherlands has specified a health based exposure limit of 1 pg TEQ/kg bw/day (Health Council of the Netherlands 1996).

In addition to these TDIs some countries have regulations for 2,3,7,8-TCDD concentrations or I-TEQ in specific food types (summarised in Buckland *et al.*, 1998c). In the United States, a limit value has been set for 2,3,7,8-TCDD in fish. This guideline states not to consume fish with 2,3,7,8-TCDD levels greater than 25 ng kg⁻¹ on a wet weight basis (Food and Drug Administration, cited in US EPA 1987). Similarly, in Canada, for fish from the Great Lakes, a limit concentration of 20 ng I-TEQ kg⁻¹ wet weight has been set (Ryan *et al.*, 1983a). In Ontario, there is a guideline value for sport fish of 15 ng TEQ kg⁻¹.

The regulation of PCDDs and PCDFs for the protection of wildlife is complicated by the bioaccumulative nature of these compounds. To address this issue the Canadian Council of Ministers of the Environment has proposed both a tissue residue guideline (50 ng I-TEQ kg⁻¹ fat) and a dietary intake guideline (1.1 ng I-TEQ kg⁻¹ fresh weight) for the protection of aquatic wildlife (CCME 1995).

5.2.2 Polychlorinated biphenyls

5.2.2.1 New Zealand data

PCB congeners were detected in all but one of the fish samples, with concentrations between 0.11 - 18.5 µg kg⁻¹. The sum of PCB congeners, were lower in trout, at 0.11 - 8.80 µg kg⁻¹, than in eel, at 1.29 - 18.5 µg kg⁻¹.

The profile of PCB congeners detected in the samples was generally similar in eel and trout (Figure 5.8), although the concentration of PCB #118 relative to the other congeners was slightly higher in eel than in trout. As the profiles presented in Figure 5.8 are the average profiles for all samples analysed, this variation indicates a difference in the accumulation and/or elimination of this congener between eel and trout.

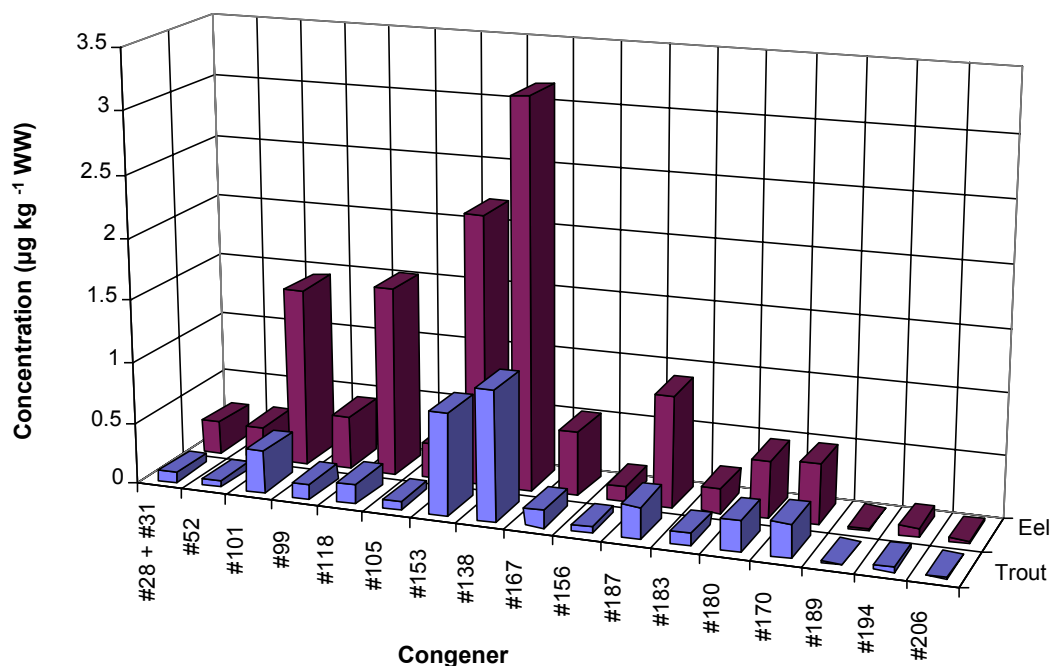


Figure 5.8 PCB congener profile in New Zealand eel and trout

Profiles are for the mean concentrations of all samples of the same fish type on a fillet tissue basis.

The most commonly measured PCB congeners were #52, #101, #118, #153, #138, #187, #180 and #170, which were detected in all eel samples and at least nine of the 12 trout samples. PCB #138

and #153 were present at the highest concentrations, and this is consistent with overseas data (see Tables I3 to I14, Appendix I). Of the three non *ortho*-congeners (i.e. PCB #77, #126 and #169) only #126 was detected, and that only in one sample at a concentration of 0.010 $\mu\text{g kg}^{-1}$. The most prevalent mono *ortho*-PCB congeners were #118 and #105 which occurred in 26 and 23 of the fish samples respectively. Concentrations for PCB #118 ranged from 0.026 - 2.75 $\mu\text{g kg}^{-1}$ in eel and < 0.01 - 0.96 $\mu\text{g kg}^{-1}$, while #105 ranged from < 0.01 - 0.54 $\mu\text{g kg}^{-1}$ in eel and < 0.01 - 0.17 $\mu\text{g kg}^{-1}$ in trout.

PCB TEQ ranged from 0.069 - 1.39 ng TEQ kg^{-1} in eel and from 0.065 - 0.32 ng TEQ kg^{-1} in trout. These TEQs were derived using the 1994 WHO TEF values (Ahlborg *et al.*, 1994, see Section 2.2). It should be noted that PCB congeners, especially the mono *ortho*-PCBs induce hardly any biological or toxic response in fish, which is in distinct contrast with mammals. This is reflected in the new TEFs recently established by WHO (Van den Berg *et al.*, 1998).

When the PCB TEQs are added to the PCDD and PCDF derived TEQs, this results in ranges of total TEQ of 0.089 - 1.78 ng TEQ kg^{-1} for eel and 0.085 - 0.52 ng TEQ kg^{-1} for trout. In eel, the PCBs contributed between 69 - 95% of the total TEQs, while in trout, the PCBs contributed between 61 - 83% of the total TEQs determined.

Concentration data for PCBs in freshwater fish from other New Zealand studies are relatively scarce. One study (Jones, 1996) reported PCB concentrations ranging from 1.04 to 21.1 $\mu\text{g kg}^{-1}$ in eel collected from three sites on the Waikato River. These results are consistent with the those reported in the current study.

5.2.2.2 Comparative overseas data

Data on PCB concentrations in freshwater fish, focusing on trout and eel are presented in Table 5.8 and Table I2 (Appendix I). These results are also summarised in Figure 5.9.

Reports of PCB concentrations in aquatic environments in the southern hemisphere are scarce. Subramanian *et al.* (1983) reported PCB concentrations of 0.08 - 0.77 $\mu\text{g kg}^{-1}$ in marine fish from the Antarctic, while concentrations in marine fish from the Falkland Islands ranged from 2.9 - 3.1 $\mu\text{g kg}^{-1}$ (de Boer and Wester, 1991). In the freshwater ecosystem of South Africa's Wilderness Lakes System PCBs could not be detected above 1 $\mu\text{g kg}^{-1}$ (De Kock and Boshoff, 1987).

Few areas in the northern hemisphere have fish with such low PCB concentrations. A study by Bengston (1974) reported a concentration of 0.13 $\mu\text{g kg}^{-1}$ in the livers of trout from Iceland. Typically however, PCB concentrations in Europe and North America regularly exceed 100 $\mu\text{g kg}^{-1}$, which is in stark contrast to the maximum PCB concentration found in the current study of 18.8 $\mu\text{g kg}^{-1}$ in eel.

One of the most studied contaminated freshwater ecosystems is the North American Great Lakes. Due to the large amount of data available for the Great Lakes ecosystem only a selection of the most relevant papers have been tabulated here (Table 5.8, and Table I2, Appendix I). The Great Lakes have received a wide variety of pollution discharges from the numerous industrial and population centres on their shores. High levels of PCB contamination in the Great Lakes are reflected by trout and salmon muscle PCB concentrations reaching 4300 $\mu\text{g kg}^{-1}$ and above (Oliver

and Niimi, 1988). While these concentrations have declined since the highs of the 1970s values now appear to have levelled off at approximately 2000 $\mu\text{g kg}^{-1}$ (Stow, 1995). In contrast to salmon and trout which have access to the Great Lakes, brown trout from Michigan whose access to the lakes is prevented by hydroelectric dams have PCB concentrations of only 20 - 60 $\mu\text{g kg}^{-1}$ (Giesy *et al.*, 1994). The relatively high concentrations of PCBs detected in trout and salmon are also reflected in eel. Eel leaving the Great Lakes via the St Lawrence river to breed have PCB concentrations ranging from 612 - 2130 $\mu\text{g kg}^{-1}$ (Hodson *et al.*, 1994).

Table 5.8 Representative concentrations of PCBs in overseas freshwater fish tissue

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		References
		Min.	Max.	
Antarctic	Marine fish	0.08	0.77	Subramanian <i>et al.</i> , 1983
Canada	Lake whitefish	2.8	9.61	Lockhart <i>et al.</i> , 1992
Falklands	Marine fish	2.9	3.1	de Boer and Wester, 1991
Finland	Salmon muscle	572	6850	Paasivirta <i>et al.</i> , 1990
Germany	Bream, River Elbe	365	2100	Luckas and Oehme, 1990
Iceland	Brown trout, liver	0.13	0.13	Bengston, 1974
Italy	RBT, River Po caged 30 days	10.2	62	Vigano <i>et al.</i> , 1994
Portugal	Tagus estuary	73	286	Benoiel and Shirley, 1988
South Africa	Wilderness Lakes System	< 1	< 1	De Kock and Boshoff, 1987
Spain	Carp, Ebro delta	210	210	Ruiz and Llorente, 1991
Sweden	Lake salmonids	0.6	41	Andersson <i>et al.</i> , 1988
Sweden	Arctic char and whitefish	3.8	191	Jansson <i>et al.</i> , 1993
Switzerland	Brown trout, Lake Geneva	140	575	Devaux and Monod, 1987
USA	Various, 3 Michigan rivers	20	6000	Giesy <i>et al.</i> , 1994
USA	Catfish, Mississippi	< 5	138	Leiker <i>et al.</i> , 1991
USA	All species, all sites ¹	< 15	124000	US EPA, 1992
		1898	(Mean)	US EPA, 1992
		209	(Median)	US EPA, 1992
Vietnam	Food fish, marine and fresh		10	Kannan <i>et al.</i> , 1992
Eel				
Canada	Eels, St Lawrence River	612	2130	Hodson <i>et al.</i> , 1994
Netherlands	Eel, Amsterdam	393	877	van der Oost <i>et al.</i> , 1996
Netherlands	Eel, various rivers	39.1	1930	de Boer <i>et al.</i> , 1993
Spain	Eel, Ebro delta	235	235	Ruiz and Llorente, 1991
Sweden	Eel	101	347	Atuma <i>et al.</i> , 1996
United Kingdom	Eel, reedbeds	< 10	910	Mason, 1993

1. 314 locations, most samples of 14 species of fish although a total of 119 species were collected.

Levels of PCB contamination of freshwater fish from Europe are in the same range as those reported from North America (Figure 5.9), with a maximum concentration of 6850 $\mu\text{g kg}^{-1}$ reported for salmon in Finland (Paasivirta *et al.*, 1990). Fish with such levels of contaminants clearly cannot be called unimpacted; however, they are not influenced by single point sources and the particular salmon have a feeding range in the Baltic sea.

Congeners #77 and #169 were not detected above the detection limit in any fish samples collected in the current study, and PCB #126 was detected in only one sample at a concentration of 0.010 $\mu\text{g kg}^{-1}$. In contrast to these results, non *ortho*-PCB congeners are frequently detected in fish from overseas locations, with congener #77 being the most abundant (Tables I3-I5, Appendix I).

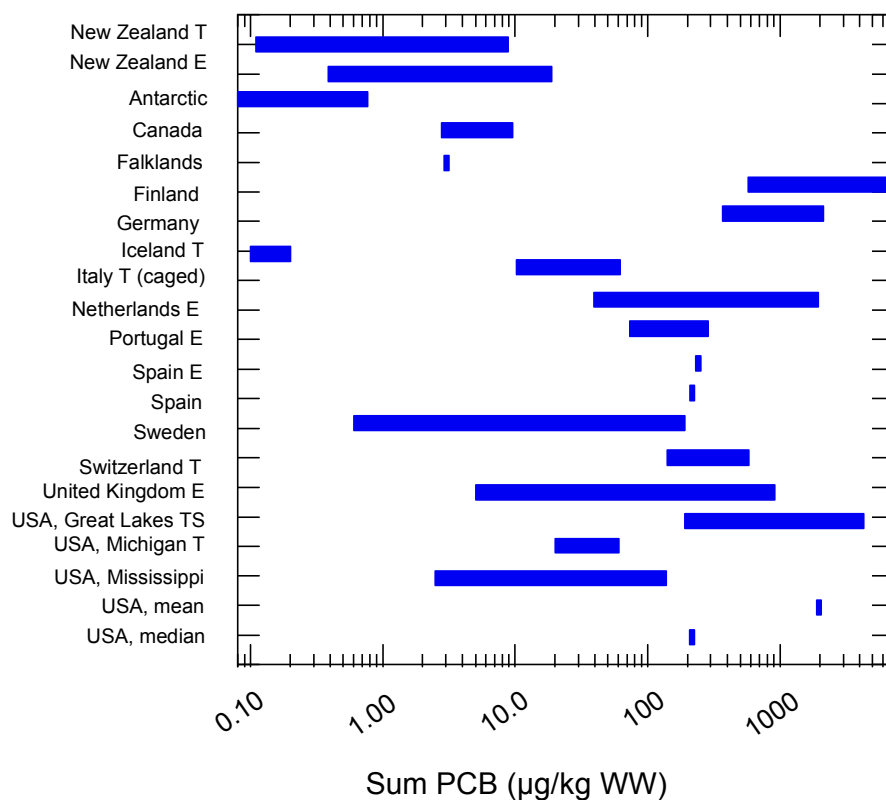


Figure 5.9 Total PCB concentrations in freshwater fish from New Zealand and representative overseas locations

E = eel; T = trout; TS = mixed trout and salmon; Overseas data taken from Table I2 (Appendix I).

The profile of PCB congeners detected in fish from the current study was similar to that measured in other parts of the world. Either PCB #153 or #138 is the predominant congener in all cases, with congeners #101, #187, #180 and #170 also being comparatively abundant (Figure 5.10).

5.2.2.3 Regulatory approaches

Most regulatory criteria for PCBs in fish are aimed at the protection of human health. In North America, including Canada, fish containing greater than 2 mg kg⁻¹ is considered unsuitable for human consumption or inter-state trade. Similarly legal limits for fish and fisheries products for the protection of human health are 1 mg kg⁻¹ in Switzerland, 2 - 5 mg kg⁻¹ in Sweden and 5 mg kg⁻¹ in the Netherlands (reviewed by MacDonald 1994). All the fish samples from the current study are clearly well below these criteria.

Available criteria for the protection of aquatic life based on tissue residue concentrations are lower than those for the protection of human health. Maximum tissue residue concentrations of 0.1, 0.11 and 0.5 mg kg⁻¹ apply in British Columbia, New York and Australia respectively (MacDonald 1994). Again the concentrations quantified in eel and trout from the current study are well below these criteria.

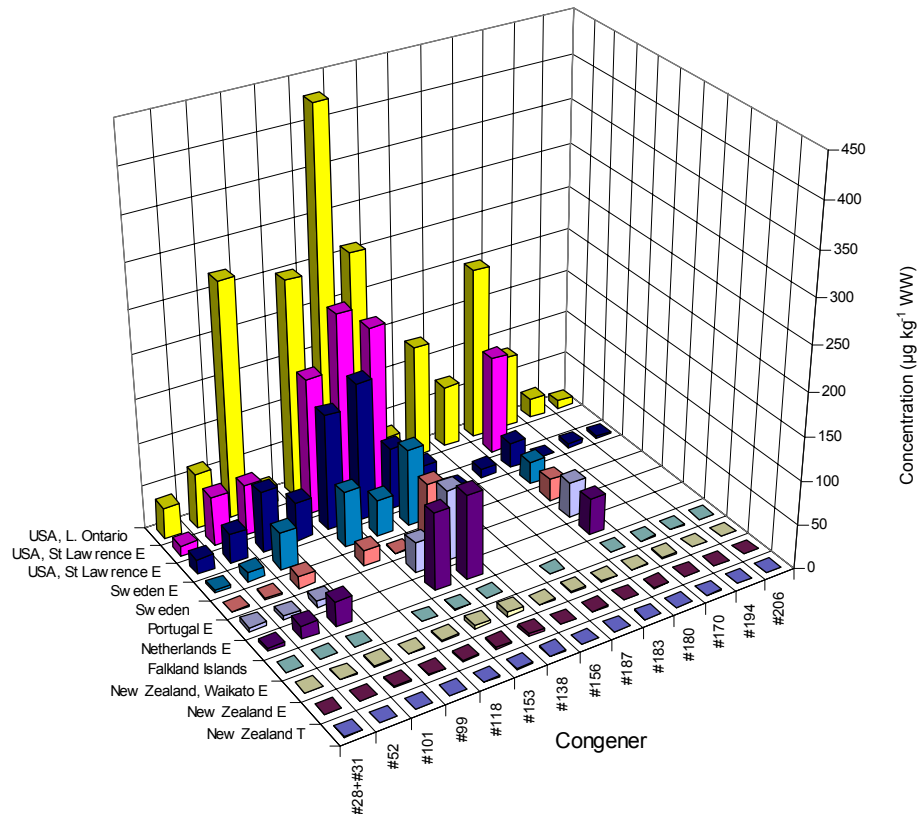


Figure 5.10 PCB congener profile found in New Zealand and overseas fish tissue samples

E =eel; T = trout; New Zealand data are the mean profiles for all samples of the same fish type (see Figure 5.8). Data for the Waikato eels from Jones (1996). Overseas profiles are for those studies listed in Tables I6-I14 (Appendix I).

5.2.3 Organochlorine pesticides

5.2.3.1 New Zealand data

Low levels of a variety of organochlorine pesticides were detected in both eel and trout from the current study. Hexachlorobenzene, dieldrin and DDT residues were the most frequently detected pesticides (including degradation products), and were present at the highest concentrations in the fish samples analysed. The concentration ranges determined for all pesticides are given in Table 5.9. Detailed data for each pesticide in eel and trout from each sampling site is provided in Tables F2 and F3 (Appendix F).

Of the pesticides quantified, contaminant concentrations were consistently higher in eel than in trout, as shown by the median and mean concentrations reported in Table 5.1, and as illustrated for HCB, dieldrin and DDT residues in Figure 5.11.

DDT residues were detected in all 28 fish samples. These residues (measured as the sum of pp'-DDE + pp'-TDE + op'-DDT + pp'-DDT) were less than $1 \mu\text{g kg}^{-1}$ only in eel from the Haast River, this river being one of the three reference sites studied. The highest DDT residues in fish were observed in those caught from the Halswell River. This river has a catchment close to Christchurch, which had the highest DDT loading of soils tested in this study (Buckland *et al.*, 1998a).

Table 5.9 Concentrations of organochlorine pesticides in New Zealand fish

Pesticide	Eel ($\mu\text{g kg}^{-1}$ WW)		Trout ($\mu\text{g kg}^{-1}$ WW)	
	Min.	Max.	Min.	Max.
α -HCH	< 0.01	0.057	< 0.01	< 0.01
β -HCH	< 0.01	0.087	< 0.01	< 0.01
γ -HCH	< 0.01	0.083	< 0.01	0.011
HCB	0.03	0.52	< 0.01	0.17
Aldrin	< 0.01	< 0.02	< 0.01	< 0.01
Dieldrin	0.24	11.4	0.021	1.12
Heptachlor	< 0.01	< 0.02	< 0.01	< 0.01
Heptachlor epoxide	< 0.01	0.26	< 0.01	0.046
α -chlordane	< 0.01	1.24	< 0.01	0.13
γ -chlordane	< 0.01	0.24	< 0.01	0.033
pp'-DDE	0.67	155	1.82	73.9
pp'-TDE	0.032	33.1	0.043	1.97
op'-DDT	< 0.01	0.75	< 0.01	0.29
pp'-DDT	0.1	25.5	0.16	0.91

The range of concentrations of DDT residues (including degradation products) determined in various rivers in this study was broad, presumably reflecting the extent to which the river catchments were originally treated with DDT. However, in all cases the concentrations of these residues were below overseas regulatory limits (see Section 5.2.3.3).

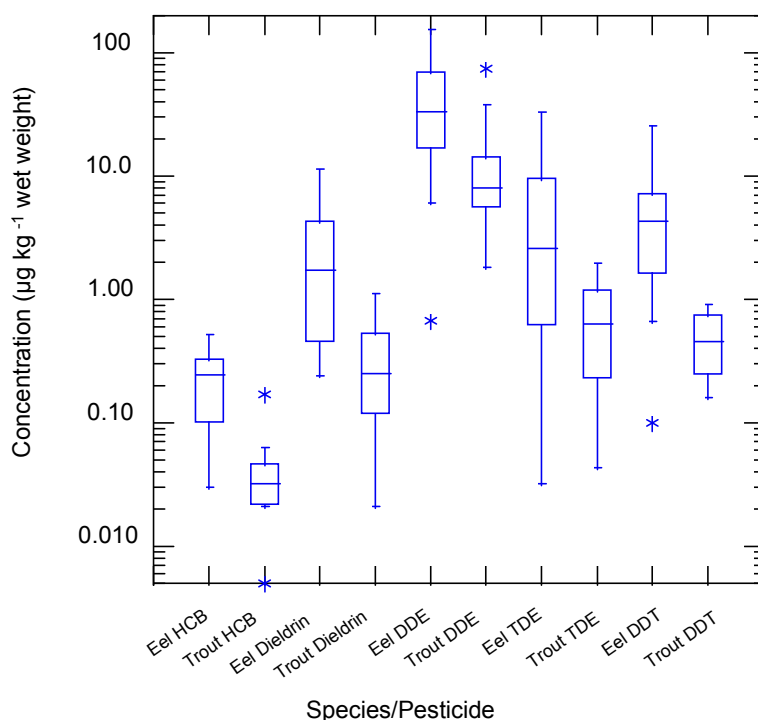


Figure 5.11 Box plot of organochlorine pesticide residues in New Zealand fish

In a box plot, the centre horizontal line represents the *median* of the sample data set. The edges of the box, called *hinges*, mark the first and third quartiles. The median splits the ordered data set in half, and the hinges split the remaining halves in half again, such that the central 50% of the data set falls within the range of the box. The *Hspread* is the absolute value of the difference between the values of the two hinges. The *whiskers* show the range of values that fall within 1.5 Hspreads of the hinges. *Outside values* and *far outside values* are plotted as asterisks and circles respectively.

Of the three HCH compounds analysed, only γ -HCH was detected in the fish samples. γ -HCH was detected in trout from only one of 12 sites at a concentration of $0.011 \mu\text{g kg}^{-1}$ but was detected in eel from 8 of 16 sites. Concentrations in eel ranged from $< 0.01 - 0.083 \mu\text{g kg}^{-1}$. Levels were very low compared to all other studies (Appendix J), and well below regulatory limits (Table 5.11). This result is not unexpected as HCH residues have also been found to be very low in New Zealand soils (Buckland *et al.*, 1998a).

HCB was detected in all eel and all but one trout samples in the current study, but generally at levels only slightly above the LOD (Table 5.9). The levels were well below those detected in eel tissue sampled in 1992 by Karl and Lehmann (1993), but as the source of eels used by these authors is not stated, the significance of this disparity is difficult to ascertain. The sample collection and analysis protocols for the current study were rigorously designed to provide data representative of New Zealand's riverine environments.

Aldrin was not detected in any of the fish samples in the current study. Conversely dieldrin was present in all samples at concentrations ranging from $0.24 - 11.4 \mu\text{g kg}^{-1}$ in eels and from $0.021 - 1.12 \mu\text{g kg}^{-1}$ in trout (Appendix F). The somewhat higher levels of dieldrin detected earlier in New Zealand eel samples by Karl and Lehmann (1993) were more comparable with those prevailing in other countries. It should be remembered, however, that the eels examined in that study had been processed and smoked before analysis. Therefore a comparison between this data and the current study is difficult.

Chlordane application can result in a large family of environmental residues. The present study considered only α - and γ -chlordane, but oxychlordane, various nonachlors, heptachlor epoxide, and other compounds may be included in total chlordane estimates from other studies. Nevertheless, the maximum level recorded in the current study of $1.24 \mu\text{g kg}^{-1}$ for α -chlordane in eels from the Taieri River was very low compared to other studies. Any inclusion of the other chlordane residue species is therefore unlikely to affect this assessment.

Heptachlor was not quantified in any eel or trout samples at a typical LOD of $0.01 \mu\text{g kg}^{-1}$ (Table 5.9). Heptachlor epoxide was quantified in two eel and five trout samples, but appears to be related to chlordane contamination (heptachlor epoxide also being a chlordane degradation product).

Eel and catfish in the Waikato river have also been analysed for organochlorine pesticide residues (Jones, 1996). In agreement with the current study, the investigations by Jones (1996) found that HCB, dieldrin, pp'-DDE and pp'-DDT were the most frequently detected organochlorine pesticides. pp'-DDE was detected at the highest concentration ($24 \mu\text{g kg}^{-1}$ wet weight) in longfinned eels from the lower Waikato River at Rangiriri. Mean concentrations for DDT residues of $14.1 \mu\text{g kg}^{-1}$ wet weight (pp'-DDE + pp'-TDE) and for dieldrin of $3.1 \mu\text{g kg}^{-1}$ wet weight have been reported for trout collected from Lake Rotorua (Gifford *et al.*, 1996). These data are consistent with the current study and reflect the generally low concentrations of organochlorines in the New Zealand environment.

5.2.3.2 Comparative overseas data

The discussion on comparative overseas data focuses on HCB, dieldrin and DDT residues because these were the most frequently detected pesticides (including degradation products), and were present in the highest concentration in the fish samples analysed in the current study. DDT residues in eel were at similar levels to those detected in the multinational study of Karl and Lehmann (1993). Levels in fish were broadly similar to those recorded in most European and Australian studies, and generally lower than those recorded in North America, Asia and Africa (Table 5.10, and Table J2, Appendix J).

There are relatively few reports of aldrin being measured in fish. Concentrations of dieldrin in fish of this study, while ubiquitous were low compared to levels in North America and elsewhere (Table 5.10, and Table J4, Appendix J).

Table 5.10 Representative concentrations of organochlorine pesticide residues in overseas freshwater fish tissue

Country	Species, tissue	pp'-DDE ($\mu\text{g kg}^{-1}$)	Reference
Germany	Eel, edible tissue	33-81	Karl and Lehmann, 1993
Norway	Eel, edible tissue	10-20	Karl and Lehmann, 1993
Poland	Eel, edible tissue	35-164	Karl and Lehmann, 1993
Switzerland	Trout, whole	10-180	Devaux and Monod, 1987
Tanzania	<i>Tilapia</i> (lake)	14	Paasivirta <i>et al.</i> , 1988b
USA, Great Lakes	Trout, eel, fillet	148-166	Newsome and Andrews, 1993
USA, Great Lakes	Trout, fillet	1350	Miller <i>et al.</i> , 1992
USA, CO	Brown trout, whole	6	Tate and Heiny, 1996
USA, NY	Trout	0.45-1.77	Youngs <i>et al.</i> , 1994
USA, Michigan	Various (above dams), whole	10-82	Giesy <i>et al.</i> , 1995
USA, Michigan	Various (below dams), whole	20-200	Giesy <i>et al.</i> , 1995
USA, WA	Various, whole	50-2900	Johnson <i>et al.</i> , 1988

Country	Species, tissue	Dieldrin ($\mu\text{g kg}^{-1}$)	Reference
Germany	Eel, edible tissue	nd-54	Karl and Lehmann, 1993
Norway	Eel, edible tissue	20-43	Karl and Lehmann, 1993
Poland	Eel, edible tissue	23-38	Karl and Lehmann, 1993
USA, Great Lakes	Trout, eel, other fillet	0.24 - 41	Newsome and Andrews, 1993
USA, Great Lakes	Trout, fillet	40 - 1300	Miller <i>et al.</i> , 1993
USA, CO	Brown trout, whole	< 5	Tate and Heiny, 1996

Country	Species, tissue	HCB ($\mu\text{g kg}^{-1}$)	Reference
Finland	Eel	10 max	Tulonen and Vuorinen, 1996
Germany	Eel, edible tissue	8-20	Karl and Lehmann, 1993
Germany	Roach and perch, fillets	nd-230	Schuler <i>et al.</i> , 1985
Italy	Various, muscle	1-21	Galassi <i>et al.</i> , 1994
Norway	Eel, edible tissue	6-12	Karl and Lehmann, 1993
Poland	Eel, edible tissue	8-360	Karl and Lehmann, 1993
USA, Great Lakes	Trout, eel, other fillet	0.22 - 9.3	Newsome and Andrews, 1993

The levels of chlordanes observed were well below levels reported in most studies in North America. Levels were comparable with those reported from parts of Australia (Townsville, Perth and Atherton), but far lower than those found in other areas (Brisbane, Sydney and Hobart)

(Kannan *et al.*, 1994). HCB levels recorded in fish in the current study compare very favourably with those recorded overseas (Table 5.10, and Table J6, Appendix J), which are typically one or two orders of magnitude higher.

5.2.3.3 Regulatory approaches

The regulation of pesticide residues in fish tissues is usually aimed at the protection of human health (Table 5.11). There are currently no New Zealand standards or guidelines for concentrations of pesticide residues in fish for human consumption other than a maximum residue limit for dieldrin and aldrin of 0.1 mg kg⁻¹ wet weight. For both these pesticides, no samples from the current study had residue levels that exceeded this limit.

Similarly, for all organochlorine pesticides studied, the maximum concentrations measured in eel and trout muscle tissue from the current study (Table 5.9) were well below regulatory limits set by other countries for the protection of human health (Table 5.11).

Table 5.11 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

5.2.4 Chlorophenols

5.2.4.1 New Zealand data

In only 3 eel samples were any chlorophenol compounds measured above the LOD: 0.2 - 0.5 $\mu\text{g kg}^{-1}$ for trout muscle and 0.3 - 0.6 $\mu\text{g kg}^{-1}$ for eel muscle. Pentachlorophenol does not tend to accumulate in animal flesh tissue as a consequence of its relatively rapid metabolism to a conjugated chlorophenol derivative and subsequent elimination from the body.

A mean PCP concentration in rainbow trout from Lake Rotorua of 1.6 $\mu\text{g kg}^{-1}$ has been reported by Gifford *et al.* (1995; 1996). This study concluded that the levels of PCP found in fish were similar to data published in the literature for background sites or sites known to have received low inputs of PCP (Gifford *et al.*, 1995; 1996).

5.2.4.2 Comparative overseas data

Only limited overseas data are available on chlorophenols in fish tissue. Only six papers reporting PCP in fish muscle were identified and only one of these provided data for unimpacted fish (Rogers *et al.*, 1988). In general, where comparative data are available, concentrations of chlorinated phenols (as represented by the detection limits) in the background river eel and trout samples collected in the current study are lower than the median levels that have been observed in biota samples collected from both unimpacted and impacted sites overseas (Table K2, Appendix K).

5.3 Miscellaneous

5.3.1 Particulate matter

As previously mentioned, organic compounds tend to adsorb to particulate matter suspended in water. Therefore organochlorines tend to accumulate in sediments as this particulate matter accumulates through the process of sedimentation. Conversely when these sediments are resuspended the organochlorines are also moved into the water column and transported. The effects of catastrophic flood events which can cause the resuspension and redistribution of sediments can have catastrophic effects on wildlife if they result in greatly increased exposure to contaminants (Ludwig *et al.*, 1993).

A consequence of this is that the concentrations of organochlorines in water samples are strongly affected by the amount of suspended matter present in the sample. When highly contaminated sediments are present then PCDD and PCDF concentrations will be relatively high in raw water, but removal of the suspended solids will remove most contamination and leave only trace levels in the soluble phase.

In most cases the particulate contents were relatively low and also uniform. The mean particulate content from the total suspended solids analysis (see Appendix C) of each individual monthly water sample collected from each site is reported in Table 5.12. Data for each individual monthly sample is reported in Table B5 (Appendix B).

Table 5.12 Mean particulate content of 3-month composite river water samples

River and sampling site	Particulate matter (mg L ⁻¹)
Waipa River at Whatawhata	16
Rangitaiki River at Te Teko	7
Waingongoro River at State Highway 45	16
Wanganui River at Te Maire	19
Manawatu River at Opiki Bridge	56
Mohaka River at Raupunga	26
Tukituki River at Tamumu Bridge	< 2
Ruamahanga River at State Highway 2	< 1
Ruamahanga River at Waihenga	4
Haast River at Roaring Billy	5
Waimakariri River at Old H/W Bridge	350
Halswell River at McCartneys Bridge	< 3
Taieri River at Sutton Stream	10
Taieri River at Allanton	16
Mataura River at Parawa	2
Mataura River at Seaward Downs	7

For samples collected from two sites (Manawatu River at Opiki Bridge and Waimakariri River at Old H/W Bridge), the mean particulate content was comparatively high due to flood events shortly before one of the sampling occasions (see Table B5, Appendix B). However, even at these sites, no PCDDs, PCDFs, PCBs, organochlorine pesticides or chlorophenols were detected in the river water collected.

5.3.2 Effects of age and lipid content on organochlorine concentrations in fish

Biometric data for the fish samples are provided in Table 5.6. The data were analysed using Pearson correlation coefficients to determine if any significant relationships existed between the biometric data and organochlorine concentrations. Due to life history differences between eel and trout species these groups were analysed separately but no distinction was made between the different species, longfinned and shortfinned eel, or between brown and rainbow trout.

Not surprisingly there were significant relationships between length and weight for both species (Mann-Whitney U test, $p < 0.001$ for eels and $p < 0.003$ for trout). However, there was no significant relationship ($p > 0.05$) between age and length or weight for either type of fish. This is probably due to differences in growth rates between fish from the different sampling sites spanning the length of the country and also due to the statistical analysis of eel and trout as groups rather than individual species (i.e. longfinned and shortfinned eel; brown and rainbow trout).

There were no significant correlations between organochlorine concentrations and the age or lipid content of eel or trout. This is illustrated for correlations between the sum of PCB congeners and age, the sum of PCB congeners and lipid, and for PCDD and PCDF I-TEQ and age in Figure 5.12. However, any correlation may possibly be masked by the fact that composite samples were analysed rather than individual fish. A lack of correlation between contaminant concentration and age may also reflect the relatively low levels of contamination found in the New Zealand environment in general, as well as the fact that the samples were collected over a wide geographic area. This means that the fish sampled will have experienced a range of contaminant exposures. It may be possible to detect age-related accumulation based on analysis of individual fish collected at

specific sampling sites, but in such a large national survey such as this, any variability due to age is likely masked by the variability between sites.

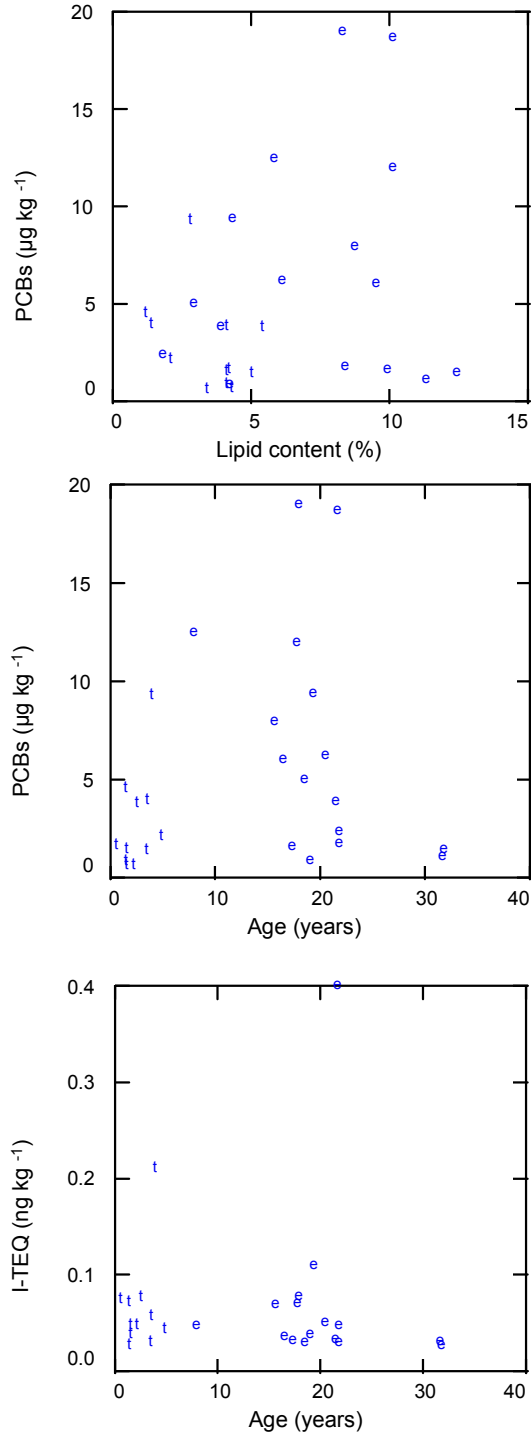


Figure 5.12 Correlation between PCBs or I-TEQ and age or lipid content of New Zealand fish (e = eel; t = trout)

Only two significant correlations were observed between organochlorine concentrations. There was a significant ($p < 0.003$) correlation in eels between the concentrations for pp'-DDE and the sum of PCB congeners. This is probably not surprising given the very persistent nature of these compounds and the relatively long exposure periods for eel as compared to trout, where such a relationship was not seen.

There was also a weakly significant correlation between I-TEQ levels and the sum of PCB congeners for trout ($p < 0.006$) when half LOD values were included for non-detected congeners. However, it should be remembered that the I-TEQ levels were markedly influenced by the inclusion of half LOD values for non-detected PCDDs and PCDFs, and the correlation observed may be pure chance.

5.3.3 Comparison of reference and impacted sites

The original study design selected a variety of New Zealand sites which were either relatively unimpacted 'reference sites' or are impacted by a variety of human activities. Collection of eel at the majority of these sites allows a comparison of contaminant concentrations due to human activities. Trout could only be collected at one of the 'reference sites' and so there are not enough data make a similar comparison for trout.

There were significant differences between the ages of eel collected at the reference and impacted sites (Mann Whitney U, $p < 0.03$), with average ages of 29.3 and 19.1 years at reference and impacted sites respectively. Consequently there were also significant differences in length ($p < 0.3$) and weight ($p < 0.02$) between reference and impacted sites. While lipid content was higher at reference sites (9.6%) compared to impacted sites (7.3%) this difference was not statistically significant. The difference in ages between the two location types can be explained by the life history of the eels. The reference sites were generally either in the upper reaches of the rivers studied or were above any human inputs to the system. Eel tend to move toward upper river locations with increasing age (Beentjes and Chisnall, 1998).

Despite the increased age and lipid content of eels from the reference sites relative to the impacted sites, the PCDD and PCDF I-TEQ level ($p < 0.05$), and concentrations for the sum of PCB congeners ($p < 0.07$) and dieldrin ($p < 0.05$) were all significantly lower in fish from the reference sites (Figure 5.13). In the case of the PCDDs and PCDFs however, as noted earlier, the I-TEQ levels were markedly influenced by the inclusion of half LOD values for non-detected congeners, and as such the correlation observed may be pure chance. Concentrations for the sum of PCDDs and PCDFs, and pp'-DDE were not significantly different between reference and impacted sites.

In summary, levels of human impact on the environment appear to be relatively small in New Zealand, as demonstrated by the generally low levels of organochlorine contaminants found in eel and trout from the current study. There is, however, still some detectable impact for some organochlorines, as indicated by the differences observed between reference and impacted sites for I-TEQ, sum of PCB congeners and dieldrin.

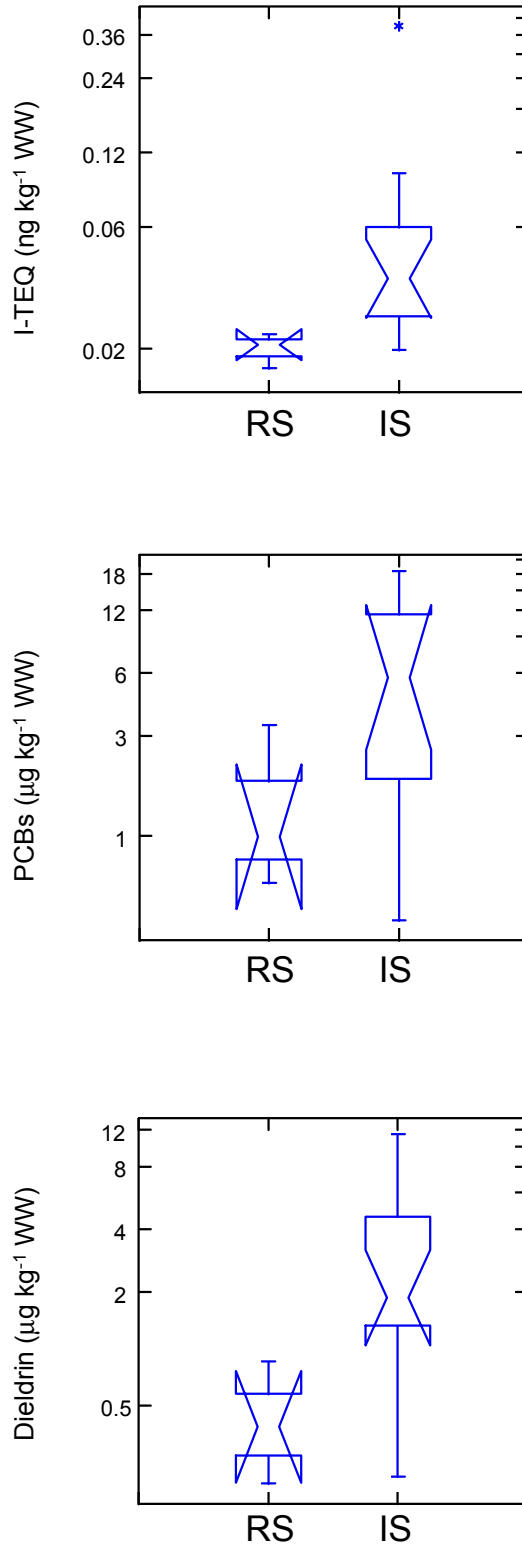


Figure 5.13 Box plot of organochlorines at reference and impacted sites

RS = reference sites; IS = impacted sites. See Figure 5.11 for an explanation of a box plot. In the above plots, the central inflections of the box represents the median of the sample data set. The edges of the box, called *hinges*, mark the first and third quartiles. The addition of a *notch* to a hinge identifies the 95% confidence interval of the median. The medians of two boxes whose notches do not overlap are significantly different at the 95% confidence interval.

5.3.4 Data quality

The organochlorine contaminant concentration data found 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 available from the Ministry's website (<http://www.mfe.govt.nz/issues/waste/organo.htm>).

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, 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 two water samples and four fish 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 present in these samples.

6 References

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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

Table A2 Status of 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 " <i>Safe Management of PCBs</i> " 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 " <i>Safe Management of PCBs</i> " 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 " <i>Safe Management of PCBs</i> " 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 " <i>Code of Practice for the Transportation of Hazardous Substances on Land</i> ".	

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 " <i>Safe management of PCBs</i> " 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	<i>Gazette</i> , 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	<i>Gazette</i> , September 1961	Prohibition of selected substances as active ingredients in stock treatments under the Stock (Insecticides and Oestrogens) Regulations 1961.	
BHC (mixed isomers)	1962	<i>Gazette</i> , 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	<i>Gazette</i> , 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	<i>Gazette</i> , September 1971	Last product withdrawn.	
HCB	1972	<i>Gazette</i> , 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	<i>Gazette</i> , 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	<i>Gazette</i> , September 1985	Last product withdrawn.	
PCP	1988			PCP use ceased voluntarily in the timber treatment industry.
DDT	1989	<i>Gazette</i>	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	<i>Gazette</i>	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	<i>Gazette</i> , December 1990	Last remaining lindane products deregistered and the substance effectively banned.	
PCP	1991	<i>Gazette</i>	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	<i>Gazette</i> , 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 an overview of the riverine sampling programme. It details:

- River and site selection
- River water sample collection
- River water site data
- River biota sample collection
- River biota site and biometric data

B1 River and site selection

A sampling programme was designed for the collection of surface river water and freshwater biota from North Island and South Island rivers. The National River Water Quality Network (NRWQN), operated by the National Institute of Water and Atmospheric Research Ltd (NIWA), was used as a starting point for the preliminary selection of rivers to be included in this study. The NRWQN is a major water quality monitoring study of 77 sites covering 51 rivers throughout New Zealand (Smith and Maasdam, 1994; Maasdam and Smith, 1994). Piggy-backing onto the NRWQN offered the following advantages:

- rivers within this network had already been selected on the basis of their representativeness;
- sampling would be undertaken from rivers for which extensive data on physico-chemical parameters (though not organochlorine concentrations) existed;
- sampling costs could be minimised, as the sampling could be incorporated into the network's own sampling programme.

The criteria used for the selection of rivers from the NRWQN for inclusion in this study were that they should:

- be representative of New Zealand. This should be based on a number of parameters, including: hydrological properties, physico-chemical properties, and invertebrate diversity and mass
- provide a good spatial coverage of New Zealand
- incorporate a large catchment area
- cover a broad range of catchments with respect to physiographical types and land uses
- not be restricted solely to large rivers
- include both reference sites and impacted sites. Reference sites to make up no more than 25% of the total rivers selected. Impacted sites should include sites impacted from: agricultural activity, urban development, and industrial activity
- provide for the collection of eel and trout from all river systems
- ideally have good hydrological records available
- the water quality of the sites should be homogeneous and the rivers not artificially controlled at the point of sampling
- the Waikato and Tarawera Rivers are to be excluded. These rivers are both recipients for bleached kraft pulp mill effluents, and contaminant concentration data already exists for organochlorines in biota from these waterways.

From this process, 18 rivers were provisionally selected for study. A request for information was then sent to Regional Councils. The purpose of this was to confirm the suitability of the rivers selected from the NRWQN. This allowed a check to be made as to how representative each river was for each region. Constraints on the size of the study prevented rivers being selected from all Regional Council regions.

With the information provided by Regional Councils, 13 rivers were confirmed for inclusion in the study (Table B1). Six rivers on the initial provisional list were dropped, and one river not initially selected was included.

Table B1 Rivers selected for study for organochlorine contaminants

Region	River	Sampling site
Waikato	Waipa	Whatawhata
Bay of Plenty	Rangitaiki	Te Teko
Taranaki	Waingongoro	State Highway 45
Manawatu/Wanganui	Wanganui	Te Maire
	Manawatu	Opiki Bridge
Hawke's Bay	Mohaka	Raupunga
	Tukituki	Tamumu Bridge
Wellington	Ruamahanga	State Highway 2
	Ruamahanga	Waihenga
West Coast	Haast	Roaring Billy
Canterbury	Waimakariri	Old H/W Bridge
	Halswell	McCartney's Bridge
Otago	Taieri	Sutton Stream
	Taieri	Allanton
Southland	Mataura	Parawa
	Mataura	Seaward Downs

At the point of sampling (for rivers with more than one sampling site, the downstream site only was considered), these rivers collectively represent 12.7% of the total New Zealand catchment area: 16.1% of the North Island catchment, and 10.1% of the South Island catchment.

For this study, sites that were upstream of any point source discharges or agricultural were taken to be reference sites. Of the 16 sampling sites, three were identified as being reference sites. These were the Mohaka River at Raupunga, the Haast River at Roaring Billy and the Mataura River at Parawa. Sites downstream of any point source discharge, or where the river ran through a highly agricultural area, were considered to be impacted. These included sites that were impacted by agricultural activity, urban development or industrial activity.

Information on each of the rivers selected, including catchment area (at the point of sampling) and known discharges, is provided in Tables B2 and B3. The potential for agricultural runoff was assessed as being 'light', 'moderate' or 'significant' on the basis of information provided by Regional Councils.

B2 River water sample collection

Monthly river water samples were collected in consecutive months during the period January through to March 1996. Each monthly sample was obtained as a series of four individual grab samples taken from across the width of the river in the flowing reaches. This sample consisted of a total of 10 litres of river water, sampled into four amber glass 2.5 litre bottles. All sample collection jars were precleaned (water, acetone, hexane) prior to use, and used with aluminium foil (hexane rinsed) lined lids.

Table B2 North Island rivers: median river flows (Q_{med})¹, catchment areas and discharges

River	Sampling site	Catchment	Discharges ²
Waipa River	Whatawhata	2,826 km ² . Major pasture development. Q_{med} : 62.6 m ³ s ⁻¹ .	Stormwater and sewage from Te Awamutu (Pop. 13,710). Dairy industry, freezing works, timber processing, mining/quarrying, agricultural runoff (light).
Rangitaiki River	Te Teko	2,893 km ² . Region's largest river. Extensive exotic forestry with some dairy pasture. Q_{med} : 63.9 m ³ s ⁻¹ .	Stormwater and sewage from Murupara (Pop. 2,206). Agricultural runoff (light).
Waingongoro River	State Highway 45	201 km ² . Representative of Taranaki ring plain. Q_{med} : 4.84 m ³ s ⁻¹ .	Stormwater and sewage from Eltham (Pop. 2,004). Freezing works, timber processing, mining/quarrying, agricultural runoff (significant).
Wanganui River	Te Maire	2,212 km ² . Pasture/forest development. High recreational values of national importance. Q_{med} : 54.7 m ³ s ⁻¹ .	Stormwater and sewage from Taumarunui (Pop. 5,833).
Manawatu River	Opiki Bridge	4,100 km ² . Major regional river downstream of extensive pasture development. Q_{med} : 63.0 m ³ s ⁻¹ .	Stormwater and sewage from Palmerston North (Pop. 73,095). Dairy industry, freezing works, agricultural runoff (significant), biochemical processing plant.
Mohaka River	Raupunga	2,370 km ² . Low population density. Extensive pastoral agriculture, native and commercial forestry. Q_{med} : 61.1 m ³ s ⁻¹ .	No point source discharges. Reference site.
Tukituki River	Tamumu Bridge	1,900 km ² . Major regional river in Central Hawke's Bay. Is an important recharge to the regions aquifer systems. Q_{med} : 19.7 m ³ s ⁻¹ .	Stormwater and sewage from Waipukurau (Pop. 4,001), Waipawa (Pop. 1,915) and Takapau (Pop. 580). Leachate from landfills, timber processing, agricultural runoff (moderate).
Ruamahanga River	State Highway 2	78 km ² . Low population density. Small exotics/pasture development. Q_{med} : 4.5 m ³ s ⁻¹ .	Agricultural runoff (light).
Ruamahanga River	Waihenga	2,340 km ² . Major regional river. Catchment developed for pastures. Q_{med} : 49.0 m ³ s ⁻¹ .	Stormwater and sewage from Masterton (Pop. 19,688), Carterton (Pop. 6,812) and Greytown (Pop. 1,943). Timber processing, mining/quarrying, agricultural runoff (significant).

¹ Q_{med} = median long term flows. Information from TIDEDA (Smith and Maasdam, 1994) or provided by Regional Council.

² Population data taken from the 1996 Census of Population and Dwellings (Statistics New Zealand).

Table B3 South Island rivers: median river flows (Q_{med})¹, catchment areas and discharges

River	Sampling site	Catchment	Discharges ²
Haast River	Roaring Billy	1,020 km ² . Largest alpine-fed Westland river. Representative of undeveloped catchment. Low population. Q_{med} : 125 m ³ s ⁻¹ .	No point source discharges. Reference site.
Waimakariri River	Old H/W Bridge	3,210 km ² . Major, and representative braided river of the Canterbury Plains. Downstream of pasture/exotic forests/horticulture. Q_{med} : 86.4 m ³ s ⁻¹ .	Freezing works.
Halswell River	McCartney's Bridge	142 km ² . Largely spring fed. Typical regional river draining intensive agricultural catchment.	Agricultural runoff (significant).
Taieri River	Sutton Stream	61 km ² . Tussock catchment typical of region. Largely undeveloped. Typical input into Taieri. Q_{med} : 0.56 m ³ s ⁻¹ .	Stormwater and sewage from Middlemarch (Pop. 202). Agricultural runoff (light).
Taieri River	Allanton	4,889 km ² . Intensive agriculture, dairying and cropping. Low lying, flood prone.	Stormwater and sewage from Mosgiel (Pop. 11,133). Agricultural runoff (significant).
Mataura River	Parawa	766 km ² . Tussock with beech forest catchment, small amount of pasture. Low population. Q_{med} : 13.8 m ³ s ⁻¹ .	No point source discharges. Reference site.
Mataura River	Seaward Downs	5,109 km ² . Downstream of intensive pasture development. Q_{med} : 77.8 m ³ s ⁻¹ .	Stormwater and sewage from Gore (Pop. 13,279). Dairy industry, freezing works, paper mill, agricultural runoff (significant).

¹ Q_{med} = median long term flows. Information from TIDEDA (Smith and Maasdam, 1994) or provided by Regional Council.

² Population data taken from the 1996 Census of Population and Dwellings (Statistics New Zealand).

Each grab sample was obtained, where practical, by field sampling personnel entering the river and moving slowly to a suitable position within the river whilst facing upstream at all times. From this position and holding a sample bottle by the main body of the vessel, and at arm's length, the bottle was immersed in the river, uncapped, filled to the neck, and recapped whilst still under water. For each monthly sample, this procedure was undertaken a total of four times, each time at a different position across the river, and always slightly further upstream to avoid the collection of any disturbed river sediment from earlier movements within the river.

At sites where it was not practical or safe for field personnel to enter the river, samples were collected using the same procedures applied for the collection of samples as part of the NRWQN monitoring programme. This involved collection of samples from a bridge, or by use of a boat. Details of the sampling procedure used at each site were recorded on the field log.

Following collection, each sample was given a unique identification number, and each individual bottle labelled, a custody seal fixed over the screw cap and placed in a polyethylene bag. Each sample was packed in a polystyrene box and sent, along with a chain of custody form, by overnight courier to the primary analytical laboratory.

Simultaneous with the collection of the primary river water samples, a series of quality control samples consisting of field blanks and blind duplicates were also collected (Table B4). Primary and quality control samples were collected in accordance with the study quality assurance project plan (QAPP).

Table B4 River water sampling quality control samples

QC sample	Collected from
Field blanks	Waipa River at Whatawhata Haast River at Roaring Billy
Blind duplicates	Manawatu River at Opiki Halswell River at McCartney's Bridge

River flows were also measured at the time of river water sampling.

B3 River water site data

A field log was completed for each sample collected. This was used to record site data and any deviations from the sampling procedure provided in the QAPP. Site data and other field log information are detailed in Table B5.

Table B5 River water site data

River	Sampling site	Map ref. ¹	Sampling date	Flow (m ³ s ⁻¹)	Samples ²	TSS ³ (mg L ⁻¹)	Comments
Waipa	Whatawhata	S14/997,760	18/01/96	118	PS, FB	29 ⁴	Difficult site access. Unable to wade; boat or bridge sample. All samples taken at one point.
			15/02/96	92.2	PS, FB	15 ⁴	
			14/03/96	56.6	PS, FB	5 ⁴	
Rangitaiki	Te Teko	V15/436,444	17/01/96	93.3	PS	7	River dirty from unseasonal high rainfall.
			15/02/96	70.1	PS	4	River still dirty from unseasonal high rainfall.
			12/03/96	75.5	PS	11	
Waingongoro	State Highway 45	Q21/140,803	16/01/96	5.6	PS	11	Too deep to wade full width of channel.
			20/02/96	2.5	PS	6	River sampled approx. 500 m downstream from January sample due to access being blocked by quarry operations.
			19/03/96	6.7	PS	31	River higher than usual. Sampled at same location as February sample.
Wanganui	Te Maire	S19/998,490	17/01/96	71.5	PS	28	
			21/02/96	56.9	PS	4	
			20/03/96	79.0	PS	25	
Manawatu	Opiki Bridge	S24/195,827	17/01/96	32.4 at P.N. (estimate 34.0 at Opiki)	PS, BD	10 (8) ⁵	The Opiki site does not have a recorder or staff gauge. The heights are from the Manawatu-Wanganui Regional Council recorder in Palmerston North (P.N.). The flows at Opiki are estimated as council flows plus 5%.
			21/02/96	159 P.N. (167 Opiki)	PS, BD	130 (120) ⁵	
			20/03/96	78.5 P.N. (82.4 Opiki)	PS, BD	33 (32) ⁵	
Mohaka	Raupunga	W19/673,283	11/01/96	56.9	PS	64	Difficult to obtain samples directly from the river in anything other than low flow conditions. Not possible to wade across the river, so two samples were taken by wading in towards the centre from the left bank and two by wading in from the right bank. The very centre of the river was not sampled but the four grabs taken were approximately equally spaced across the river.
			13/02/96	71.3	PS	5	As above.
			12/03/96	50.2	PS	9	As above.

Table B5 River water site data (Cont.)

River	Sampling site	Map ref. ¹	Sampling date	Flow (m ³ s ⁻¹)	Samples ²	TSS ³ (mg L ⁻¹)	Comments
Tukituki	Tamumu Bridge	V22/247,318	09/01/96	4.6 (at Shag Rock)	PS	< 1	This site is not a permanent flow measuring station. Flows have been obtained from the Hawke's Bay Regional Council station (Tukituki at Shag Rock) which is located approx. 1 km downstream of the Tamumu Bridge site. Flows will be essentially the same at both sites. The river was in a state of low flow at the time of January sampling. The river was receding from a moderate flood at the time of February sampling. Flows were well above low flow levels but the water was clean.
			07/02/96	19.1 (at Shag Rock)	PS	< 2	
			29/02/96	21.8 (at Shag Rock)	PS	< 2	
Ruamahanga	State Highway 2	T25/309,450	09/01/96	1.3	PS	< 1	River in low flow state.
			07/02/96	1.8	PS	< 1	River in semi-low flow state.
			05/03/96	3.0	PS	< 1	River in low-medium level.
Ruamahanga	Waihenga	S27/146,984	09/01/96	9.8	PS	< 1	River in low flow state.
			07/02/96	16.5	PS	4	River in semi-low flow state.
			05/03/96	50.5	PS	7	River in just below mean flow levels. Two 2.5 L samples collected by grab method, and two 2.5 L samples collected from stainless steel bucket lowered from the bridge.
Haast	Roaring Billy	G37/129,895	17/01/96	167	PS	11	River still slightly coloured from December 1995 floods.
			02/02/96	113	PS, FB	4	River still slightly coloured from December 1995 floods.
			12/03/96	79.4	PS, FB	< 1	
Waimakariri	Old H/W Bridge	M35/745,525	24/01/96	90	PS	36	River flow slightly below mean flow.
			21/02/96	111	PS	15	Samples taken in swift water, mainstream on true R.H.B. Not possible to wade.
			20/03/96	487	PS	1000	River in flood, water swift and dirty. Sampled as on 21/02/96.
Halswell	McCartney's Bridge	M36/718,247	24/01/96	No rating available	PS, BD	< 3 (< 1) ⁵	River clear and at mean or lower flow conditions.
			21/02/96	No rating available	PS, BD	< 2 (< 3) ⁵	River clear but some weed drifting downstream. River too deep to wade.
			20/03/96	No rating available	PS, BD	4 (< 1) ⁵	River 'normal'.

Table B5 River water site data (Cont.)

River	Sampling site	Map ref. ¹	Sampling date	Flow (m ³ s ⁻¹)	Samples ²	TSS ³ (mg L ⁻¹)	Comments
Taieri	Sutton Stream	H43/832,084	11/01/96	3.9	PS	13	
			08/02/96	1.9	PS	14	
			07/03/96	0.58	PS	2	
Taieri	Allanton	I44/971,736	11/01/96	65.4	PS	31 ⁴	
			08/02/96	10.2	PS	2 ⁴	
			07/03/96	9.2	PS	15 ⁴	
Mataura	Parawa	E43/635,073	10/01/96	15.9	PS	5	
			07/02/96	8.7	PS	< 1	
			06/03/96	6.0	PS	< 2	
Mataura	Seaward Downs	F46/866,160	10/01/96	96.5	PS	15	
			07/02/96	35.3	PS	< 1	
			06/03/96	21.7	PS	7	A lot of scum/foam on surface of river.

¹ NZMS 260 Series (1:50,000).

² PS = Primary sample (4 x 2.5 L river water); FB = field blank (4 x 2.5 L bottles uncapped and left exposed on river bank); BD = blind duplicate (4 x 2.5 L river water).

³ TSS = Total suspended solids (see Section C2, Appendix C).

⁴ Mean result of duplicate analyses.

⁵ Value in parenthesis is the TSS result for the blind duplicate sample.

B4 River biota sample collection

The riverine sampling programme included the collection of biota samples in which persistent organochlorine contaminants are likely to bioaccumulate. Longfinned eel (*Anguilla dieffenbachii*) and brown trout (*Salmo trutta*) were the preferred species collected. Both these fish are widely distributed in New Zealand rivers. In addition, eel and trout are commonly consumed by New Zealanders, and dietary intake represents a key pathway for human exposure to organochlorines. At sites where these species could not be caught, shortfinned eel (*Anguilla australis*) or rainbow trout (*Oncorhynchus mykiss*) were collected.

An initial round of biota sampling was undertaken in February 1996 for the South Island rivers and in March 1996 for the North Island rivers. It was proposed that at each sampling point, one composite sample of longfinned eel and one composite sample of brown trout were to be collected. Each composite sample was to consist of six individual fish ideally within the following size ranges:

Longfinned eel:	0.25 - 0.4 m in length
Brown trout:	0.25 - 0.45 m in length

Eel and trout were collected at, or as near as possible to, the sampling point where river water samples were collected. Two types of trap were set overnight in one pool. The traps used were:

- A fine mesh fyke net for the collection of longfinned eel
- A monofilament gill net for the collection of brown trout

The fyke net was set in shallow water on the pool margin near the head or tail of the pool, and staked in place or tied to a tree on the bank. The gill net was set across the pool where water velocities are low, and anchored to trees or stakes. The traps were generally set in the late afternoon/early evening, and retrieved the following morning. Suitable fish were selected from the total capture, and any fish not required were returned to the river. Where netting was unsuccessful, electric fishing and seine netting were attempted. Gear was set away from any dwellings as a precaution against vandalism and theft.

Generally, collection of eel was very successful, with a composite sample being collected from each of the 16 sites at the completion of the initial sampling round. However, collection of trout samples proved more difficult. From the first sampling round, only two sites had each provided a composite brown trout sample consisting of six individual fish.

At sites where a trout sample of the required number of fish was not captured, second and third rounds of sampling were undertaken. In most instances, this was carried out with assistance from the local Fish and Game Council from each region. As a result of the difficulties experienced in collecting trout, the sampling size (initially stipulated as six individual fish for a composite sample) was reduced to a minimum of four fish.

At the completion of all sampling, only seven of the 16 sites had each provided a composite sample of brown trout, and three sites had each provided a composite sample of rainbow trout of four or more individual fish. Two sites provided a sample of brown trout (one from a site where a rainbow trout sample had been successfully captured) of three individual fish. Although this was below the

stipulated number of four fish, it was decided that these two composite samples should be analysed in order to provide as much nationally comparative contaminant concentration data as possible.

From the remaining six sites either none, one or two individual trout were captured. Where one or two trout were captured, these samples were not analysed for contaminant residues.

From each round of sampling, selected fish were killed, wrapped in precleaned aluminium foil, a custody seal affixed and placed in a polyethylene bag. Each sample was given a unique identification number, packed on ice in a polystyrene box and sent, along with a chain of custody form, by overnight courier to the primary analytical laboratory.

Blind duplicate eel samples were collected from the Taieri River at Allanton, and the Mataura River an Seaward Downs. All primary and blind duplicate samples were collected in accordance with the study QAPP.

B5 River biota site and biometric data

Sampling details for each river and site, including information recorded on the field logs, are summarised in Table B6. Summarised biometric data, covering fish lengths, weights, ages, and lipid and moisture contents are provided in Tables B7 (eel) and B8 (trout).

Table B6 River biota site data

Site name	Site name	Map ref. ¹	Sampling date ²	Samples ³	Comments
Waipa	Whatawhata	S14/996,784-963,784	04/03/96	LFE (6) BT (8)	Boat required to set nets in the Waipa River (access limited, banks steep-sided). Fyke and gill nets set night of 04/03/96 and picked up morning of 05/03/96. Six LFE captured, but no trout. Electric fishing and drift netting not possible, water deep and highly turbid. Required trout caught over three separate visits to site on 23/04, 29/04 and 27/05/96. Trout caught by fyke net upstream of Whatawhata Bridge and at Kaniwhaniwha Stream Outlet.
Rangitaiki	Te Teko	V15/444,415-438,437	05/03/96	LFE/SFE (6) ⁴ BT (3) ⁵ RT (5)	Boat required to set nets in the Rangitaiki River (access limited). Fyke and gill nets set night of 05/03/96, and picked up morning of 06/03/96. Mainly a SFE fishery. Five SFE caught, and only one LFE. One BT captured in a fyke net, one BT captured in a gill net. Electric fishing and drift netting not possible, snags present, water deep and fast flowing. Third BT captured 3 km upstream of Te Teko road bridge by angling (13/05/96, grid ref. V15/436,444). Five RT captured by angling on 14/10, 27/10 and 17/11/96 (grid ref. V16/450,388) with assistance from Eastern Fish and Game Council.
Waingongoro	State Highway 45	Q21/142,804	10/03/96	LFE (6)	Fyke and gill nets set night of 10/03/96 and picked up morning of 11/03/96. Sample of LFE successfully captured. Insufficient number of BT captured (1 individual BT) for composite sample. Follow-up sampling with assistance of Taranaki Fish and Game Council also unsuccessful in obtaining BT sample.
Wanganui	Te Maire	S19/998,490-993,492	11/03/96	LFE (6) RT (5)	Fyke and gill nets set night of 11/03/96 and picked up morning of 12/03/96. River large and steep sided at this location. River could not be crossed and riparian cover was so thick that access was not possible to desired site. Bedrock was predominant, preventing the use of standards to attach nets. Sample of LFE successfully captured. One individual RT captured. Further four RT captured 06/11/96 by angling approx. 2 km from Te Maire (grid ref. S18/047,526) with assistance from Auckland/Waikato Fish and Game Council.
Manawatu	Opiki Bridge	S24/205,803-206,828	08/03/96	SFE (6)	Electric fishing machine used to capture SFE. No LFE seen or captured. Fyke nets set overnight but only SFE captured again. Seine netting attempted with the capture of one BT. Gill nets set night of 08/03/96, capturing second BT. Follow-up sampling unsuccessful in capturing further BT for composite sample.
Mohaka	Raupunga	W19/683,277-714,252	06/03/96	LFE (4)	Very little cover, poor eel habitat, limited sites to set fyke nets, limited access to locate further net setting sites. Fyke nets set night of 06/03/96 and picked up morning of 07/03/96. One LFE captured. Further three LFE captured by electric fishing on 07/03/96. Hawke's Bay Fish and Game Council opposed the setting of gill nets. Attempts to organise anglers to capture BT unsuccessful.
Tukituki	Tamumu Bridge	V22/245,317-249,322	07/03/96	SFE (6) RT (5)	No nets set, electric fishing machine used to capture eels. Hawke's Bay Fish and Game Council opposed the setting of gill nets. Five RT caught by angling (30/03/96) with assistance from Fish and Game Council. All were caught within 1 km downstream of Tamumu Bridge (grid ref. V22/247,318).

Table B6 River biota site data (Cont.)

Site name	Site name	Map ref. ¹	Sampling date ²	Samples ³	Comments
Ruamahanga	State Highway 2	T25/306,454	09/03/96	LFE (6)	Electric fishing machine used to capture all LFE. As water visibility was clear, a drift dive was conducted with only two BT observed within a 1-2 km reach. Gill net set overnight of 09/03/96. Only one BT captured. Follow-up sampling unsuccessful in collecting required number of BT required for composite sample. Few BT present within this section of river, as confirmed by drift diving.
Ruamahanga	Waihenga	S27/149,973-149,980	09/03/96	LFE (6) BT (3) ⁵	Mainly a SFE fishery. Few suitable sites to set gill nets away from public interference. Popular location. Fyke and gill nets set night of 09/03/96 and picked up morning of 10/03/96. Three LFE captured in the fyke nets, and three captured by electric fishing. One BT captured in the gill net, and second BT by angling. With assistance from Wellington Fish and Game Council, third BT captured by angling on 24/04/96, approx. 2 km upstream of bridge (grid ref. S27/156,980).
Haast	Roaring Billy	G37/129,895	01/02/96	LFE (6)	Fyke and gill nets set night of 01/02/96 and picked up morning of 02/02/96. Sample of LFE successfully captured. No trout captured except for one 120 mm juvenile trout caught in a fyke net. Second attempt to net trout at a location recommended by locals was conducted over the period 11-13 March 1996, but without success. A local angler also made an attempt to catch trout in the Haast River within 5 km of the true sampling site from the beginning of February to the middle of March 1996, again without success.
Waimakariri	Old H/W Bridge	M35/818,551	29/01/96	LFE (8) BT (4)	Fyke nets set night of 29/01/96 and picked up morning of 30/01/96. Sample of LFE successfully captured. As all fish were small, eight individual fish sent to laboratory for analysis. One individual BT captured in fyke net. No overnight gill netting was conducted as North Canterbury Fish and Game Council required on the hour monitoring of set nets. Seine/drift netting was therefore attempted for capture of further BT, without success. Follow-up sampling (06/11/96, angling) organised with the North Canterbury Fish and Game Council resulted in the capture of further three BT.
Halswell	McCartney's Bridge	M36/706,257	29/01/96	LFE (6) BT (4)	Fyke nets set night of 29/01/96 and picked up morning of 30/01/96. Six LFE successfully captured. Canterbury Regional Council mechanically clearing weed out of the Halswell River, causing continuous weed movement and blockage of nets. No BT captured. Subsequent sampling by electric fishing resulted in the capture of four BT on 26/03/96 (three individual BT) and 01/05/96 (one individual BT) (grid ref. M36/732,272).
Taieri	Sutton Stream	H43/867,116	30/01/96	LFE (6) BT (5)	Fyke and gill nets set night of 30/01/96 and picked up morning of 31/01/96. Six eels successfully captured. Error with sampling site. Sampling occurred at Taieri River at Sutton, not within Sutton Stream itself. River lined with willows. Due to leaf blockage of main gill net, net not effective. No BT captured. Follow-up sampling (19/02/96) by electric fishing only captured small 100-150 mm BT, below the required size range. Seine/drift netting not an option, snags and bedrock outcrops present. Five BT captured by angling on 06/04/96 (one individual BT, grid ref. H43/867,080), 21/11/96 (three individual BT) and 22/11/96 (one individual BT) (grid ref. H43/700,270-707,277) with assistance from Otago Fish and Game Council.

Table B6 River biota site data (Cont.)

Site name	Site name	Map ref. ¹	Sampling date ²	Samples ³	Comments
Taieri	Allanton	I44/973,743	30/01/96	LFE (6) LFE BD (6) BT (5)	Nets set night of the 30/01/96 and picked up morning of 31/01/96. One LFE and one BT captured by fyke nets. No BT captured in gill nets. River banks lined with willow, seine/drift netting not possible due to numerous snags. Electric fishing attempted but unsuccessful. River resampled with fyke nets at more suitable location (grid ref. I44/972,747) on night of 18/02/96. Sufficient LFE captured for a blind duplicate sample to be submitted for analysis. Additional four BT captured by angling on 27/11/96 (grid ref. I44/972,747) with assistance from Otago Fish and Game Council.
Mataura	Parawa	E43/635,073	31/01/96	LFE (6) BT (6)	Fyke nets set night of 31/01/96 and picked-up morning of 01/02/96. Only 3 eels captured by fyke nets, with the remaining 3 eels captured by electric fishing machine. Southland Fish and Game Council opposed the setting of gill nets. Fish and Game Council Field Officer caught six BT by angling.
Mataura	Seaward Downs	F46/846,148	31/01/96	LFE (6) LFE BD (6) BT (6)	Fyke and gill nets set night of 31/01/96 and picked up morning of 01/02/96. Captured mixture of LFE and SFE. Sufficient LFE captured for a blind duplicate sample to be submitted for analysis. Gill net full of weed and leaves. No trout caught. Upon inspection of net, morning of 01/02/96 outside true left (TL) end of net found not to be secured. TL securing standard missing. Large hole in net on TL. TL of net must have been struck by some form of large debris (i.e. log) during the night. Wyndham Angling Club captured the six BT over the weekend of 10/02 and 11/02/96.

¹ NZMS 260 Series (1:50,000).

² Sampling date given is date of the initial sampling round. Dates of any follow-up sampling detailed under comments.

³ Only those samples that provided sufficient number of individual fish for subsequent organochlorine contaminant analysis are listed, the number in parenthesis is the number of individual fish collected. LFE = longfinned eel; SFE = shortfinned eel; BT = brown trout; RT = rainbow trout, BD = blind duplicate.

⁴ The site provided both LFE (1 individual fish) and SFE (5) which were combined for organochlorine contaminant analysis.

⁵ Trout sample analysed for organochlorines even though less than the criteria of minimum of four individual trout per composite sample.

Table B7 Biometric data for eel samples

River	Site	Sample¹	n²	Biometric measurement³	Min.	Max.	Mean⁴
Waipa	Whatawhata	LFE	6	length, mm	440	600	487
				weight, g	192	549	296
				age, years	14	26	20
				lipid content, % WW			4.7
				moisture content, %			78.0
Rangitaiki	Te Teko	LFE/SFE ⁵	6	length, mm	420	570	495
				weight, g	190	440	279
				age, years	18	29	23
				lipid content, % WW			2.2
				moisture content, %			80.1
Waingongoro	State Highway 45	LFE	6	length, mm	400	520	468
				weight, g	176	382	281
				age, years	15	25	19
				lipid content, % WW			8.7
				moisture content, %			76.9
Wanganui	Te Maire	LFE	6	length, mm	430	570	508
				weight, g	215	536	380
				age, years	17	26	22
				lipid content, % WW			6.5
				moisture content, %			77.9
Manawatu	Opiki Bridge	SFE	6	length, mm	470	600	538
				weight, g	236	410	345
				age, years	6	13	9
				lipid content, % WW			6.2
				moisture content, %			78.3
Mohaka	Raupunga	LFE	4	length, mm	390	860	653
				weight, g	136	2220	1093
				age, years	12	36	23
				lipid content, % WW			4.3
				moisture content, %			80.5

Table B7 Biometric data for eel samples (Cont.)

River	Site	Sample ¹	n ²	Biometric measurement ³	Min.	Max.	Mean ⁴
Tukituki	Tamumu Bridge	SFE	6	length, mm	430	785	653
				weight, g	184	1780	807
				age, years	14	36	23
				lipid content, % WW			8.8
				moisture content, %			73.0
Ruamahanga	State Highway 2	LFE	6	length, mm	440	530	475
				weight, g	201	389	281
				age, years	18	23	20
				lipid content, % WW			4.6
				moisture content, %			78.7
Ruamahanga	Waihenga	LFE	6	length, mm	350	500	432
				weight, g	95	408	225
				age, years	13	22	18
				lipid content, % WW			9.9
				moisture content, %			77.1
Haast	Roaring Billy	LFE	6	length, mm	435	850	593
				weight, g	201	2203	817
				age, years	28	37	33
				lipid content, % WW			11.7
				moisture content, %			77.0
Waimakariri	Old H/W Bridge	LFE	8	length, mm	355	430	385
				weight, g	101	206	138
				age, years	16	27	20
				lipid content, % WW			3.3
				moisture content, %			79.9
Halswell	McCartney's Bridge	LFE	6	length, mm	405	770	506
				weight, g	183	1172	436
				age, years	19	32	23
				lipid content, % WW			10.5
				moisture content, %			75.2

Table B7 Biometric data for eel samples (Cont.)

River	Site	Sample ¹	n ²	Biometric measurement ³	Min.	Max.	Mean ⁴
Taieri	Sutton Stream	LFE	6	length, mm	455	620	531
				weight, g	264	748	456
				age, years	16	20	18
				lipid content, % WW			10.3
				moisture content, %			76.2
Taieri	Allanton	LFE	6	length, mm	460	545	513
				weight, g	232	442	370
				age, years	18	23	20 ⁶
				lipid content, % WW			9.9
				moisture content, %			74.6
	LFE BD	6	length, mm	435	690	505	
			weight, g	225	1003	408	
			age, years	14	20	18	
			lipid content, % WW			11.1	
			moisture content, %			75.8	
Mataura	Parawa	LFE	6	length, mm	480	760	583
				weight, g	352	1219	672
				age, years	23	49	32
				lipid content, % WW			12.8
				moisture content, %			76.6
Mataura	Seaward Downs	LFE	6	length, mm	370	520	430
				weight, g	130	341	207
				age, years	14	20	17
				lipid content, % WW			10.1
				moisture content, %			75.3
	LFE BD	6	length, mm	305	510	425	
			weight, g	154	365	235	
			age, years	13	23	17	
			lipid content, % WW			8.2	
			moisture content, %			74.0	

1 LFE = Longfinned eel; SFE = shortfinned eel; BD = blind duplicate.

2 Number of individual fish that made up the composite sample.

3 Age was determined from the sagittal otoliths, and recorded as the number of complete dark hyaline (winter) rings after the central sea-life nucleus (refer to Section C2, Appendix C). Eel are aged to the nearest whole year.

4 Lipid content was determined on the composite analytical sample and not on each individual fish.

5 This sample was a mix of one LFE and five SFE.

6 Mean age for 5 of 6 eel; age for one eel not determined.

Table B8 **Biometric data for trout samples**

River	Site	Sample ¹	n ²	Biometric measurement ³	Min.	Max.	Mean ⁴	
Waipa	Whatawhata	BT	8	length, mm	370	510	453	
				weight, g	589	1560	1024	
				age, years,months	3,7	6,7	5,1	
				lipid content, % WW			3.2	
				moisture content, %			80.4	
Rangitaiki	Te Teko	BT	3	length, mm	470	580	510	
				weight, g	1082	2356	1530	
				age, years,months	3,6	4,7	3,10	
				lipid content, % WW			1.8	
				moisture content, %			79.9	
			RT	5	length, mm	290	470	365
					weight, g	272	1065	591
					age, years,months	2,0	3,1	2,5
					lipid content, % WW			1.6
					moisture content, %			81.4
Wanganui	Te Maire	RT	5	length, mm	230	410	304	
				weight, g	171	948	425	
				age, years,months	1,1	3,1	1,9	
				lipid content, % WW			4.6	
				moisture content, %			78.2	
Tukituki	Tamumu Bridge	RT	5	length, mm	320	480	368	
				weight, g	445	1316	667	
				age, years,months	2,6	2,6	2,6	
				lipid content, % WW			4.5	
				moisture content, %			76.0	
Ruamahanga	Waihenga	BT	3	length, mm	350	450	413	
				weight, g	521	1007	832	
				age, years,months	2,6	4,6	3,6	
				lipid content, % WW			5.4	
				moisture content, %			76.5	

Table B8 Biometric data for trout samples (Cont.)

River	Site	Sample ¹	n ²	Biometric measurement ³	Min.	Max.	Mean ⁴
Waimakariri	Old H/W Bridge	BT	4	length, mm weight, g age, years,months lipid content, % WW moisture content, %	430 1012	560 2038	490 1490 nd 4.5 77.0
Halswell	McCartney's Bridge	BT	4	length, mm weight, g age, years,months lipid content, % WW moisture content, %	280 335 2,7	500 1433 5,7	373 816 3,7 5.8 76.9
Taieri	Sutton Stream	BT	5	length, mm weight, g age, years,months lipid content, % WW moisture content, %	260 227 2,1	350 570 3,6	314 405 2,9 3.8 76.9
Taieri	Allanton	BT	5	length, mm weight, g age, years,months lipid content, % WW moisture content, %	240 196 2,1	450 1123 3,1	296 419 2,7 ⁵ 4.5 75.6
Mataura	Parawa	BT	6	length, mm weight, g age, years,months lipid content, % WW moisture content, %	290 275 2,5	520 1395 4,5	408 866 3,3 4.7 76.9
Mataura	Seaward Downs	BT	6	length, mm weight, g age, years,months lipid content, % WW moisture content, %	350 525 3,5	500 1213 7,5	427 825 5,11 2.5 78.8

1 BT = Brown trout; RT = rainbow trout; BD = blind duplicate.

2 Number of individual fish that made up the composite sample.

3 Age was determined from the number of opaque summer bands on the sagittal otoliths. It was assumed that fry emerged from the redds on 1 October (refer to Section C2, Appendix C). Trout are aged to the nearest whole year and months of a year.

4 Lipid content was determined on the composite analytical sample and not on each individual fish.

5 Mean age for 4 of 5 trout; age for one trout not determined.

nd = Age not determined.

Appendix C Analytical methods

This appendix describes the methods of analysis of river water and freshwater biota 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 River water

Samples were stored at 4 °C pending analysis. Each water sample consisted of 3 individual (monthly) samples, with each monthly sample comprising a total of 10 litres of river water collected into 4 amber glass bottles. For each monthly sample, the 4 bottles were shaken thoroughly, and an equal volume of river water was removed from each bottle and combined to provide a 'composite monthly sub-sample'. A '3-monthly composite' analytical sample for PCDD, PCDF, PCB and organochlorine pesticide analysis was prepared by combining equal volumes of river water from each of the 3 'composite monthly sub-samples' (Figure C1).

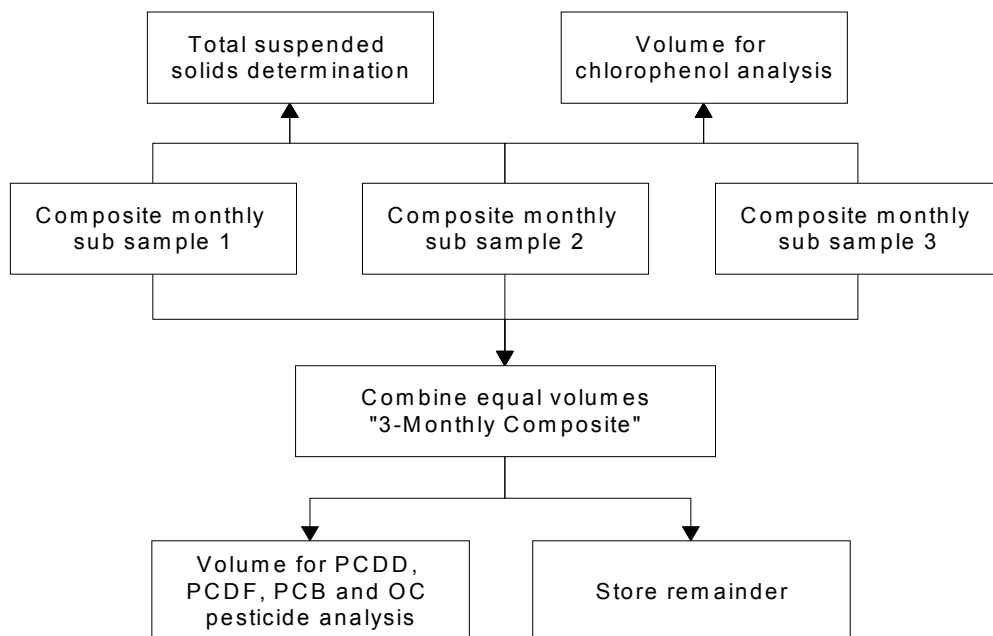


Figure C1 Preparation of composite river water samples

C1.1.2 River biota

Each eel and trout sample consisted of a number of individual fish. The length and weight of each individual fish was recorded. Analytical samples were prepared as follows:

- for eel, approximately equal weights of fillet (including skin) were removed from behind the anus of each fish. The fillets from all the fish for each sample were freeze-dried, the skin was removed, and the freeze-dried muscle tissue was combined and homogenised.
- for trout, approximately equal weights of fillet were removed from the back muscle of each fish and the skin was removed. The fillets from all the fish for each sample were freeze-dried, combined and homogenised.

Moisture content was determined by taking a separate portion of the fillet (less skin) from each individual fish and oven drying to constant weight.

C1.2 Sample extraction

C1.2.1 River water

PCDDs, PCDFs, PCBs and organochlorine pesticides

A volume (4.8 L) of the '3-monthly composite' sample was taken 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 sample was passed through a 1µm Whatman GMF filter and the separated particulate material subject to accelerated solvent extraction (ASE) (Dionex 200) with acetone/hexane (1:1) followed by toluene. The aqueous portion was subjected to liquid/liquid extraction with dichloromethane (DCM). The particulate and aqueous extracts were each reduced by rotary evaporation, and the residues were combined, solvent exchanged into DCM, washed with water, dried (anhydrous Na₂SO₄), 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

The analysis of river water samples for chlorophenols was undertaken on each individual 'composite monthly sub-sample' and not on the '3-monthly composite' sample prepared (Figure C1) for PCDD, PCDF, PCB and organochlorine pesticide analysis.

A volume (200 ml) of each composite monthly sub-sample was taken and spiked with surrogate standard (2,6-dibromo-4-methyl phenol, 50 ng). The pH of the sample was made alkaline and the phenolics were derivatised using phase transfer acetylation in preparation for analysis by gas chromatography using electron capture detection (GC-ECD) (Abrahamsson and Xie, 1983).

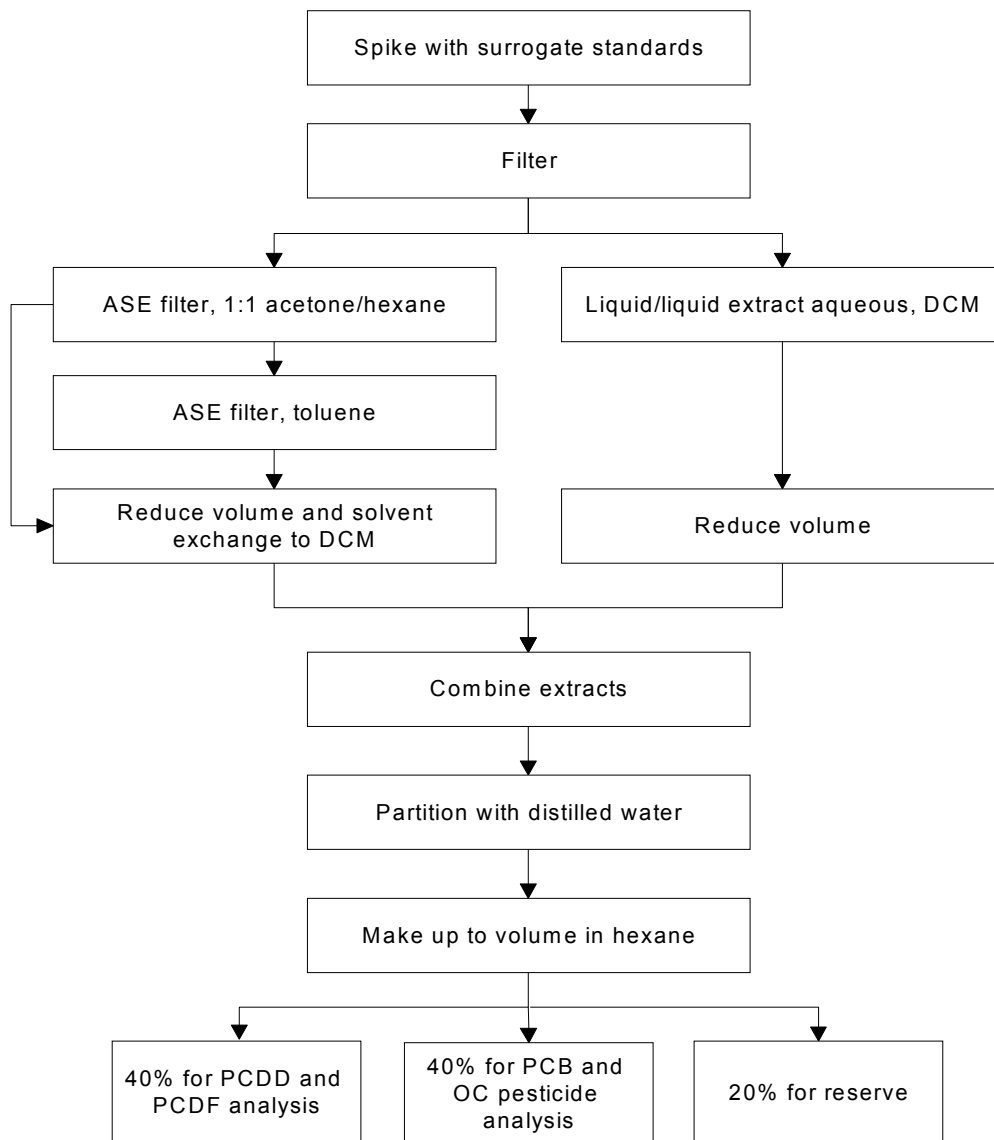


Figure C2 Extraction of river water for PCDD, PCDF, PCB and organochlorine pesticide analysis

C1.2.2 River biota

PCDDs, PCDFs, PCBs and organochlorine pesticides

A weight (50 g) of composite freeze-dried biota 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, and the residues were combined, solvent exchanged into DCM,

washed with water, dried (anhydrous Na_2SO_4), and solvent exchanged into hexane. This extract was then split: 75% for PCDD and PCDF analysis, 20% for PCB and organochlorine pesticide analysis, and 5% for lipid determination (Figure C3).

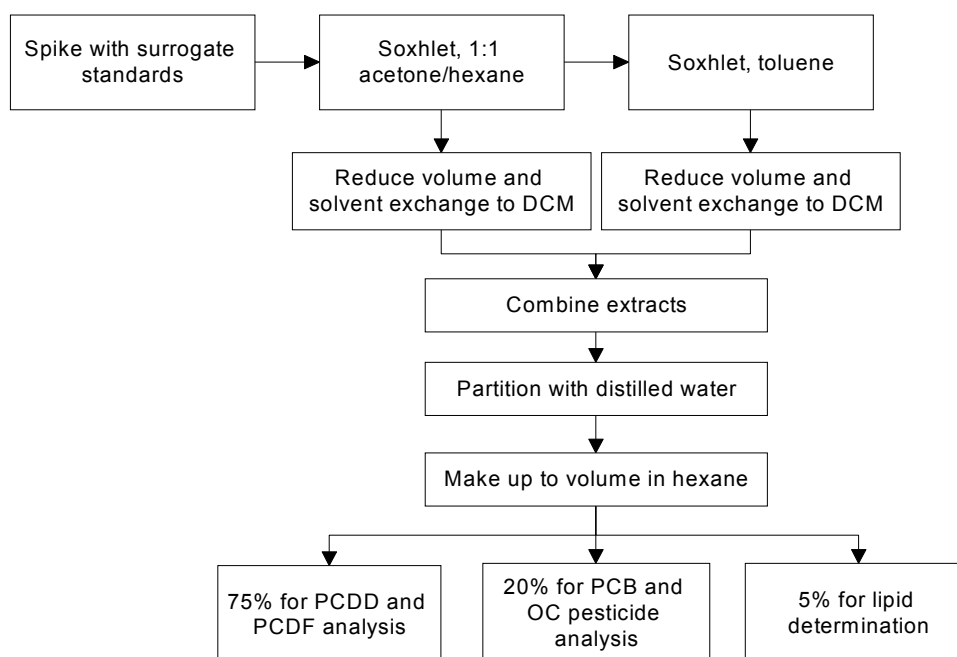


Figure C3 Extraction of river biota for PCDD, PCDF, PCB and organochlorine pesticide analysis

Solvent extractable lipid content was determined gravimetrically by taking 5% of the hexane extract (Figure C3) and drying to constant weight.

Chlorophenols

A weight (2 g) of composite freeze-dried biota 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.

C1.3 Sample purification

C1.3.1 River water

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:

- silica gel, sulphuric acid silica gel (40%), basic alumina (eluent: hexane, 1:1 DCM/hexane)
- Carpack C (18% dispersed on Celite 545) (eluent: hexane, 1:1 DCM/cyclohexane, 15:4:1 DCM/methanol/toluene, toluene)

A volume of $^{13}\text{C}_{12}$ 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 and 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 PCB congeners. Each fraction was reduced by rotary evaporation, then blown down gently under a stream of nitrogen. A volume of $^{13}\text{C}_{12}$ 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.

C1.3.2 River biota

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)
- Carbowack C (18% dispersed on Celite 545) (eluent: hexane, 1:1 DCM/cyclohexane, 15:4:1 DCM/methanol/toluene, toluene)

A volume of $^{13}\text{C}_{12}$ 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 by GCMS.

PCB and organochlorine pesticides

The PCB and organochlorine pesticide split was partitioned with acetonitrile, and the acetonitrile phase was reduced by rotary evaporation. The extract was further purified by gel permeation chromatography (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 PCB congeners. Each fraction was reduced by rotary evaporation, then blown down gently under a stream of nitrogen. A volume of $^{13}\text{C}_{12}$ 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 °C	260 °C
Injection	2 µl splitless	2 µl splitless
Temperature programme	Initial temp 210 °C (hold 4 min), 3 °C min ⁻¹ to 275 °C (11 min).	Initial temp 170 °C (hold 1 min), 10 °C min ⁻¹ to 210 °C (1 min), 3 °C min ⁻¹ to 250 °C (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 °C
Injection	1 µl splitless
Temperature programme	Initial temp 60 °C (hold 0.8 min), 40 °C min ⁻¹ to 170 °C (0.5 min), 5 °C min ⁻¹ to 250 °C (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 the mass spectral ions monitored are detailed in Table C4.

Column	25 m Ultra2
Carrier gas head pressure	100 kPa
Injector temperature	180 °C
Injection	1 µl splitless
Temperature programme	Initial temp 60 °C (hold 0.8 min), 40 °C min ⁻¹ to 170 °C (0.5 min), 5 °C min ⁻¹ to 250 °C (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 °C	240 °C
Injection	1 µl splitless	1 µl splitless
Temperature programme	Initial temp 90 °C (hold 1 min), 20 °C min ⁻¹ to 160 °C (0 min), 5 °C min ⁻¹ to 224 °C (0 min), 50 °C min ⁻¹ to 280 °C (5 min).	Initial temp 85 °C (hold 1 min), 40 °C min ⁻¹ to 150 °C (2 min), 2 °C min ⁻¹ to 220 °C (0 min), 50 °C min ⁻¹ to 300 °C (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 ¹³C₁₂ 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 ¹³C surrogate standard. For congeners with no ¹³C 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 ratio 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 ratio 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.
- Duplicate samples (river water) or a laboratory control sample (river biota) were analysed with each batch of samples 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 (river biota only).
- 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 Data reporting

The bases of reporting for primary and quality control samples are reported in Tables C5 and C6 for river water, and Tables C7 and C8 for river biota.

Concentration data are reported in Appendices D through to G. The data for each river water sample is for the total sample (i.e. particulate plus aqueous phases). PCDD, PCDF, PCB and organochlorine pesticide data are corrected for recovery of ¹³C 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.

The analysis of river water samples for chlorophenols was undertaken on each individual ‘composite monthly sub-sample’ and not on the ‘3-monthly composite’ sample prepared (Figure C1) for PCDD, PCDF, PCB and organochlorine pesticide analysis. The chlorophenol concentration data reported in Table G1 (Appendix G), and the Organochlorines Programme Environmental Survey database, is the average result from the analysis of the three ‘composite monthly sub-samples’ collected from each sampling site.

Table C5 Reporting basis for contaminant concentrations in river water

Contaminant class	Reporting basis
PCDDs and PCDFs	pg L ⁻¹ on an as received basis. Toxic equivalents (TEQs) were calculated using the International Toxic Equivalents Factors (I-TEFs).
PCBs	ng L ⁻¹ on an as received basis. TEQs were calculated using the WHO/IPCS TEFs (Ahlborg <i>et al.</i> , 1994), and reported in pg L ⁻¹ .
OC pesticides	ng L ⁻¹ on an as received basis.
Chlorophenols	ng L ⁻¹ on an as received basis.

Table C6 Reporting basis for river water quality control samples

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

Table C7 Reporting basis for contaminant concentrations in river biota

Contaminant class	Reporting basis
PCDDs and PCDFs	ng kg ⁻¹ on a wet fillet weight basis. TEQs were calculated using the I-TEFs.
PCBs	µg kg ⁻¹ on a wet fillet weight basis. TEQs were calculated using the WHO/IPCS TEFs (Ahlborg <i>et al.</i> , 1994), and reported in ng kg ⁻¹ .
OC pesticides	µg kg ⁻¹ on a wet fillet weight basis.
Chlorophenols	µg kg ⁻¹ on a wet fillet weight basis.

Table C8 Reporting basis for river biota quality control samples

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

C2 Miscellaneous analyses

Total suspended solids

Measurement of total suspended solids in river water was carried out on each individual month composite sub-sample (Figure C1), according to the method described by the American Public Health Association (APHA, 1992). Data are reported in mg L⁻¹ on an as received basis.

Fish ageing

Sagittal otoliths were removed from each eel, air dried and then split with a scalpel across the nucleus. The split otoliths were then toasted at a high heat using a gas burner, and mounted on a microscope slide with clear silicone glue (Hu and Todd, 1981). Otoliths were read using a binocular microscope with a cold light source providing slide illumination. Age was recorded as the number of complete dark hyaline (winter) rings after the central sea-life nucleus. Eel were aged to the nearest whole year.

Sagittal otoliths were removed from each trout and were soaked in a 50% mixture of absolute ethanol and glycerol for several weeks. The otoliths were then removed and examined using a binocular microscope under reflected light against a black background. Fish were aged by counting the number of broad opaque summer bands on the otoliths (Graynoth, 1996). It was assumed that fry emerged from the redds on 1 October and fish were aged from this date. Trout were aged to the nearest whole year and months of a year.

Appendix D Concentrations of PCDDs and PCDFs in New Zealand rivers

This appendix reports the concentrations of PCDDs and PCDFs in river samples 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 in river water
Table D2	Concentrations in eel
Table D3	Concentrations in trout
Table D4	Results of blind duplicate river water sample analyses
Table D5	Results of blind duplicate eel sample analyses
Table D6	Results of split QC river water sample analyses
Table D7	Results of split QC eel and trout sample analyses

Table D1 Concentrations of PCDDs and PCDFs in New Zealand river water (Cont.) (pg L⁻¹)

Congener	Halswell River at McCartneys Bridge (n=2) ^{1,5}	Taiari River at Sutton Stream	Taiari River at Allanton (n=2) ^{3,5}	Mataura River at Parawa	Mataura River at Seaward Downs	Number of positives	Minimum	Maximum	Median	Mean ⁶	Mean of ¹³ C surrogate standard recoveries, %, (n=20)
2,3,7,8 TCDD	< 0.8	< 0.3	< 0.8	< 0.4	< 0.3	0	< 0.3	< 2	< 0.7	-	73
Non 2,3,7,8 TCDD	< 0.8	< 0.5	< 2	< 0.6	< 0.4	0	< 0.3	< 2	< 0.8	-	
1,2,3,7,8 PeCDD	< 1	< 0.5	< 1	< 1	< 0.4	0	< 0.4	< 3	< 1	-	75
Non 2,3,7,8 PeCDD	< 1	< 0.5	< 2	< 1	< 0.4	0	< 0.4	< 3	< 1	-	
1,2,3,4,7,8 HxCDD	< 0.8	< 0.6	< 2	< 0.9	< 0.5	0	< 0.5	< 2	< 0.8	-	65
1,2,3,6,7,8 HxCDD	< 0.6	< 0.8	< 2	< 1	< 0.7	0	< 0.4	< 2	< 0.8	-	71
1,2,3,7,8,9 HxCDD	< 0.7	< 0.7	< 2	< 0.9	< 0.6	0	< 0.4	< 2	< 0.8	-	
Non 2,3,7,8 HxCDD	< 0.8	< 0.6	< 3	< 0.9	< 0.5	0	< 0.5	< 3	< 0.8	-	
1,2,3,4,6,7,8 HpCDD	< 3	< 3	< 5	< 4	< 2	0	< 1	< 5	< 3	-	54
Non 2,3,7,8 HpCDD	< 2	< 3	< 4	< 4	< 2	0	< 1	< 5	< 2	-	
OCDD	< 20	< 20	< 40	< 30	< 20	0	< 10	< 60	< 20	-	42
2,3,7,8 TCDF	< 0.7	< 0.3	< 0.5	< 0.3	< 0.2	0	< 0.2	< 0.9	< 0.4	-	73
Non 2,3,7,8 TCDF	< 0.7	< 0.3	< 1	< 0.4	< 0.3	0	< 0.2	< 1	< 0.5	-	
1,2,3,7,8 PeCDF	< 0.3	< 0.4	< 0.6	< 0.6	< 0.3	0	< 0.2	< 0.6	< 0.4	-	67
2,3,4,7,8 PeCDF	< 0.2	< 0.3	< 0.6	< 0.4	< 0.3	0	< 0.2	< 0.6	< 0.3	-	73
Non 2,3,7,8 PeCDF	< 0.3	< 0.4	< 1	< 0.6	< 0.3	0	< 0.2	< 1	< 0.4	-	
1,2,3,4,7,8 HxCDF	< 0.4	< 0.4	< 0.7	< 0.6	< 0.4	0	< 0.2	< 0.8	< 0.5	-	59
1,2,3,6,7,8 HxCDF	< 0.3	< 0.5	< 0.5	< 0.6	< 0.4	0	< 0.3	< 0.8	< 0.5	-	63
2,3,4,6,7,8 HxCDF	< 0.4	< 0.5	< 1	< 0.7	< 0.4	0	< 0.3	< 0.7	< 0.5	-	58
1,2,3,7,8,9 HxCDF	< 0.5	< 0.6	< 0.7	< 1	< 0.5	0	< 0.4	< 1	< 0.6	-	53
Non 2,3,7,8 HxCDF	< 0.4	< 0.4	< 0.7	< 0.6	< 0.4	0	< 0.2	< 0.7	< 0.5	-	
1,2,3,4,6,7,8 HpCDF	< 0.5	< 1	< 4	< 1	< 1	0	< 0.4	< 4	< 1	-	55
1,2,3,4,7,8,9 HpCDF	< 0.7	< 0.9	< 0.8	< 2	< 1	0	< 0.5	< 2	< 0.9	-	51
Non 2,3,7,8 HpCDF	< 0.5	< 1	< 2	< 1	< 0.7	0	< 0.4	< 2	< 0.9	-	
OCDF	< 1	< 3	< 6	< 4	< 2	0	< 0.9	< 6	< 2	-	
Sum of PCDD/Fs (inc) ¹	16	20	41	29	18		11	44			
Sum of PCDD/Fs (exc) ²	0	0	0	0	0		0	0			
Total I-TEQ (inc) ¹	0.93	0.62	1.3	0.95	0.55		0.51	2.4			
Total I-TEQ (exc) ²	0	0	0	0	0		0	0			

1 = Including half LOD values

2 = Excluding LOD values

3 = Mean of laboratory duplicate analyses

4 = Mean of primary and blind duplicate samples

5 = The congener concentration, Sum of PCDD/Fs and I-TEQ data reported for this sample are the arithmetic means of results obtained from 2 separate analyses, with LOD data rounded to 1 significant figure. Due to rounding errors, summation of the mean congener concentrations, or application of TEFs to the mean concentrations may provide different results for the Sum of PCDD/Fs and Total I-TEQ levels to those reported in this table

6 = Mean value reported only if a PCDD/F congener detected on more than 66% of occasions (minimum of 11 positive determinations)

Table D2 Concentrations of PCDDs and PCDFs in New Zealand longfinned and shortfinned eel (Cont.) (ng kg⁻¹, wet fillet wt basis)

Congener	Halswell River at McCartneys Bridge ³	Taiari River at Sutton Stream ³	Taiari River at Allanton (n=2) ⁶	Mataura River at Parawa ³	Mataura River at Seaward Downs (n=2) ⁶	Number of positives	Minimum	Maximum ⁷	Median	Mean ⁸	Mean of ¹³ C surrogate standard recoveries, %, (n=18)
2,3,7,8 TCDD	0.17	< 0.02	< 0.05	< 0.01	< 0.06	1	< 0.01	0.17	< 0.02	-	86
Non 2,3,7,8 TCDD	< 0.03	< 0.05	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.07	< 0.02	-	
1,2,3,7,8 PeCDD	0.19	< 0.01	< 0.06	< 0.01	< 0.04	2	< 0.01	0.19	< 0.03	-	78
Non 2,3,7,8 PeCDD	< 0.02	< 0.02	< 0.03	< 0.01	< 0.02	0	< 0.01	< 0.05	< 0.02	-	
1,2,3,4,7,8 HxCDD	< 0.05	< 0.01	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.05	< 0.02	-	81
1,2,3,6,7,8 HxCDD	0.34	< 0.02	< 0.08	< 0.01	< 0.07	1	< 0.01	0.34	< 0.05	-	73
1,2,3,7,8,9 HxCDD	< 0.06	< 0.01	< 0.03	< 0.01	< 0.03	0	< 0.01	< 0.06	< 0.02	-	
Non 2,3,7,8 HxCDD	< 0.02	< 0.01	< 0.03	< 0.01	< 0.04	0	< 0.01	< 0.08	< 0.02	-	
1,2,3,4,6,7,8 HpCDD	0.23	< 0.06	< 0.2	< 0.05	0.20	2	< 0.05	0.23	< 0.1	-	62
Non 2,3,7,8 HpCDD	< 0.02	< 0.04	< 0.1	< 0.05	0.12	1	< 0.02	0.12	< 0.08	-	
OCDD	< 1	< 1	< 1	< 0.9	1.59	1	< 0.5	1.59	< 1	-	45
2,3,7,8 TCDF	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.05	< 0.01	-	70
Non 2,3,7,8 TCDF	< 0.08	< 0.01	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.08	< 0.01	-	
1,2,3,7,8 PeCDF	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	63
2,3,4,7,8 PeCDF	< 0.15	< 0.01	< 0.04	< 0.01	< 0.02	1	< 0.01	0.15	< 0.02	-	60
Non 2,3,7,8 PeCDF	< 0.03	< 0.01	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.03	< 0.01	-	
1,2,3,4,7,8 HxCDF	< 0.02	< 0.01	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.05	< 0.01	-	68
1,2,3,6,7,8 HxCDF	< 0.02	< 0.01	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.03	< 0.01	-	64
2,3,4,6,7,8 HxCDF	< 0.02	< 0.01	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.04	< 0.01	-	69
1,2,3,7,8,9 HxCDF	< 0.01	< 0.02	< 0.02	< 0.02	< 0.02	0	< 0.01	< 0.03	< 0.02	-	56
Non 2,3,7,8 HxCDF	< 0.05	< 0.01	< 0.03	< 0.01	< 0.04	0	< 0.01	< 0.05	< 0.02	-	
1,2,3,4,6,7,8 HpCDF	< 0.05	< 0.02	< 0.04	< 0.02	< 0.07	0	< 0.02	< 0.08	< 0.04	-	59
1,2,3,4,7,8,9 HpCDF	< 0.01	< 0.01	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.05	< 0.02	-	59
Non 2,3,7,8 HpCDF	< 0.05	< 0.01	< 0.03	< 0.02	< 0.06	0	< 0.01	< 0.07	< 0.02	-	
OCDF	< 0.06	< 0.05	< 0.08	< 0.05	< 0.2	0	< 0.03	< 0.3	< 0.08	-	
Sum of PCDD/Fs (inc) ¹	1.91	0.73	0.93	0.65	2.31		0.53	2.31	0.87	1.01	
Sum of PCDD/Fs (exc) ²	1.08	0	0	0	1.61		0	1.61	0	0.17	
Total I-TEQ (inc) ¹	0.39	0.021	0.060	0.016	0.059		0.016	0.39	0.033	0.060	
Total I-TEQ (exc) ²	0.38	0	0	0	0.0029		0	0.38	0	0.026	

1 = Including half LOD values

2 = Excluding LOD values

3 = Longfinned eel (*Anguilla dieffenbachii*)

4 = Mix of longfinned and shortfinned eel

5 = Shortfinned eel (*Anguilla australis*)

6 = Mean of primary and blind duplicate samples

7 = Excludes any LOD value which is greater than a maximum measured value

8 = Mean value reported only if a PCDD/F congener detected on more than 66% of occasions (minimum of 11 positive determinations)

Table D3 Concentrations of PCDDs and PCDFs in New Zealand brown and rainbow trout (ng kg⁻¹, wet fillet wt basis)

Congener	Waipa River at Whatawhata ³	Rangitaiki River at Te Teko ³	Rangitaiki River at Te Teko ⁴	Wanganui River at Te Maire ⁴	Tukituki River at Tamumu Bridge ⁴	Ruamahanga River at Waihenga ³	Waimakariri River at Old HW Bridge ³	Halswell River at McCartheys Bridge ³	Taiari River at Sutfon Stream ³	Taiari River at Allantoni ³	Mataura River at Parawa ³	Mataura River at Seaward Downs ³	Number of positives	Minimum	Maximum ⁵	Median	Mean ⁶	Mean of ¹³ C surrogate standard recoveries, % (n=12)
2,3,7,8 TCDD	< 0.09	< 0.03	< 0.04	< 0.04	< 0.01	< 0.01	< 0.04	< 0.05	< 0.02	< 0.04	< 0.01	< 0.02	0	< 0.01	< 0.09	< 0.04	-	98
Non 2,3,7,8 TCDD	< 0.05	< 0.01	< 0.2	< 0.2	< 0.01	< 0.04	< 0.2	< 0.05	< 0.02	< 0.27	< 0.05	< 0.05	1	< 0.01	0.27	< 0.05	-	
1,2,3,7,8 PeCDD	0.11	< 0.03	< 0.05	< 0.1	< 0.01	< 0.01	< 0.1	< 0.03	< 0.02	< 0.02	< 0.01	< 0.01	1	< 0.01	0.11	< 0.03	-	91
Non 2,3,7,8 PeCDD	< 0.02	< 0.02	< 0.2	< 0.5	< 0.01	< 0.01	< 0.5	< 0.01	< 0.03	< 0.05	< 0.01	< 0.01	0	< 0.01	< 0.5	< 0.02	-	
1,2,3,4,7,8 HxCDD	< 0.01	< 0.02	< 0.01	< 0.03	< 0.01	< 0.01	< 0.02	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.03	< 0.01	-	88
1,2,3,6,7,8 HxCDD	< 0.04	< 0.02	< 0.03	< 0.05	< 0.01	< 0.01	< 0.04	< 0.02	< 0.02	< 0.01	< 0.02	< 0.01	0	< 0.01	< 0.05	< 0.02	-	90
1,2,3,7,8,9 HxCDD	< 0.01	< 0.01	< 0.03	< 0.05	< 0.01	< 0.01	< 0.04	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.05	< 0.01	-	
Non 2,3,7,8 HxCDD	< 0.01	< 0.02	0.27	< 0.3	< 0.01	< 0.01	< 0.3	< 0.01	< 0.04	< 0.07	< 0.06	< 0.01	1	< 0.01	0.27	< 0.03	-	
1,2,3,4,6,7,8 HpCDD	< 0.08	< 0.2	0.58	< 0.1	< 0.03	< 0.2	< 0.2	< 0.06	< 0.08	< 0.08	0.67	< 0.2	2	< 0.03	0.67	< 0.2	-	73
Non 2,3,7,8 HpCDD	< 0.06	< 0.2	0.61	< 0.2	< 0.03	< 0.2	< 0.2	< 0.03	< 0.09	< 0.07	0.70	< 0.2	2	< 0.03	0.70	< 0.2	-	
OCDD	< 1	< 2	10.6	< 3	< 0.4	< 3	< 1	< 0.6	< 1	< 1	10.6	< 3	2	< 0.4	10.6	< 2	-	59
2,3,7,8 TCDF	0.82	0.12	< 0.04	< 0.06	< 0.03	< 0.04	< 0.04	0.21	< 0.01	< 0.09	< 0.04	0.11	4	< 0.01	0.82	< 0.05	-	85
Non 2,3,7,8 TCDF	< 0.01	< 0.01	< 0.01	< 0.07	< 0.01	< 0.05	< 0.05	< 0.05	< 0.02	< 0.04	< 0.04	< 0.04	0	< 0.01	< 0.07	< 0.04	-	
1,2,3,7,8 PeCDF	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.05	< 0.01	-	77
2,3,4,7,8 PeCDF	< 0.06	< 0.02	< 0.01	< 0.02	< 0.01	< 0.01	< 0.02	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.06	< 0.01	-	83
Non 2,3,7,8 PeCDF	< 0.1	< 0.02	< 0.03	< 0.1	< 0.01	< 0.01	< 0.05	< 0.04	< 0.02	< 0.03	< 0.01	< 0.01	0	< 0.01	< 0.1	< 0.03	-	
1,2,3,4,7,8 HxCDF	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.03	< 0.01	-	83
1,2,3,6,7,8 HxCDF	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	79
2,3,4,6,7,8 HxCDF	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	84
1,2,3,7,8,9 HxCDF	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	74
Non 2,3,7,8 HxCDF	< 0.1	< 0.03	< 0.05	< 0.05	< 0.01	< 0.04	< 0.04	< 0.01	< 0.02	< 0.01	< 0.09	< 0.01	0	< 0.01	< 0.1	< 0.04	-	
1,2,3,4,6,7,8 HpCDF	< 0.06	< 0.04	0.19	< 0.03	< 0.01	< 0.06	< 0.03	< 0.02	< 0.04	< 0.03	0.26	< 0.04	2	< 0.01	0.26	< 0.04	-	73
1,2,3,4,7,8,9 HpCDF	< 0.02	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.03	< 0.01	< 0.01	< 0.04	0	< 0.01	< 0.04	< 0.02	-	79
Non 2,3,7,8 HpCDF	< 0.04	< 0.05	0.29	< 0.03	< 0.01	< 0.08	< 0.03	< 0.02	< 0.04	< 0.03	0.33	< 0.05	2	< 0.01	0.33	< 0.04	-	
OCDF	< 0.09	< 0.04	0.31	< 0.02	< 0.03	< 0.1	< 0.02	< 0.03	< 0.04	< 0.03	0.65	< 0.08	2	< 0.02	0.65	< 0.04	-	
Sum of PCDD/Fs (inc) ¹	1.91	1.54	13.2	2.51	0.36	1.98	1.49	0.79	0.84	1.12	13.4	2.04		0.36	13.4	1.73	3.43	
Sum of PCDD/Fs (exc) ²	0.92	0.12	12.8	0	0	0	0	0.21	0	0.27	13.2	0.11		0	13.2	0.11	2.30	
Total I-TEQ (inc) ¹	0.20	0.046	0.061	0.064	0.016	0.019	0.061	0.066	0.027	0.037	0.037	0.032		0.016	0.20	0.042	0.056	
Total I-TEQ (exc) ²	0.14	0.012	0.019	0	0	0	0	0.021	0	0	0.020	0.011		0	0.14	0.0055	0.018	

1 = Including half LOD values
 2 = Excluding LOD values
 3 = Brown trout (*Salmo trutta*)

4 = Rainbow trout (*Oncorhynchus mykiss*)
 5 = Excludes any LOD value which is greater than a maximum measured value
 6 = Mean value reported only if a PCDD/F congener detected on more than 66% of occasions (minimum of 8 positive determinations)

Table D4 Comparative PCDD and PCDF concentrations in primary and blind duplicate river water samples (pg L⁻¹)

Congener	Manawatu River at Opiki Bridge	Manawatu River at Opiki Bridge	Halswell River at McCartneys Bridge	Halswell River at McCartneys Bridge
	Primary	Blind duplicate	Primary	Blind duplicate
2,3,7,8 TCDD	< 1	< 0.7	< 0.8	< 0.7
Non 2,3,7,8 TCDD	< 1	< 0.7	< 0.8	< 0.7
1,2,3,7,8 PeCDD	< 2	< 1	< 1	< 1
Non 2,3,7,8 PeCDD	< 2	< 1	< 1	< 1
1,2,3,4,7,8 HxCDD	< 1	< 0.8	< 0.9	< 0.7
1,2,3,6,7,8 HxCDD	< 0.8	< 0.7	< 0.7	< 0.5
1,2,3,7,8,9 HxCDD	< 0.9	< 0.7	< 0.8	< 0.6
Non 2,3,7,8 HxCDD	< 1	< 0.8	< 0.9	< 0.7
1,2,3,4,6,7,8 HpCDD	< 2	< 8	< 3	< 3
Non 2,3,7,8 HpCDD	< 2	< 8	< 2	< 1
OCDD	< 20	< 100	< 20	< 10
2,3,7,8 TCDF	< 0.4	< 0.3	< 0.7	< 0.7
Non 2,3,7,8 TCDF	< 0.4	< 0.3	< 0.7	< 0.7
1,2,3,7,8 PeCDF	< 0.4	< 0.3	< 0.3	< 0.2
2,3,4,7,8 PeCDF	< 0.3	< 0.3	< 0.2	< 0.2
Non 2,3,7,8 PeCDF	< 0.4	< 0.3	< 0.3	< 0.2
1,2,3,4,7,8 HxCDF	< 0.5	< 1	< 0.4	< 0.3
1,2,3,6,7,8 HxCDF	< 0.5	< 1	< 0.3	< 0.3
2,3,4,6,7,8 HxCDF	< 0.5	< 0.4	< 0.4	< 0.3
1,2,3,7,8,9 HxCDF	< 0.7	< 0.5	< 0.4	< 0.5
Non 2,3,7,8 HxCDF	< 0.5	< 0.8	< 0.4	< 0.3
1,2,3,4,6,7,8 HpCDF	< 0.8	< 3	< 0.5	< 0.5
1,2,3,4,7,8,9 HpCDF	< 0.9	< 0.8	< 0.7	< 0.6
Non 2,3,7,8 HpCDF	< 0.8	< 1	< 0.5	< 0.5
OCDF	< 2	< 2	< 1	< 1
Sum of PCDD/Fs (inc) ¹	21	67	19	13
Sum of PCDD/Fs (exc) ²	0	0	0	0
Total I-TEQ (inc) ¹	1.4	1.1	0.97	0.88
Total I-TEQ (exc) ²	0	0	0	0

1 = Including half LOD values
2 = Excluding LOD values

Table D5 Comparative PCDD and PCDF concentrations in primary and blind duplicate eel samples (ng kg⁻¹, wet fillet wt basis)

Congener	Taiari River at Allanton	Taiari River at Allanton	Mataura River at Seaward Downs	Mataura River at Seaward Downs
	Primary	Blind duplicate	Primary	Blind duplicate
2,3,7,8 TCDD	< 0.04	< 0.06	< 0.06	< 0.06
Non 2,3,7,8 TCDD	< 0.03	< 0.01	< 0.02	< 0.1
1,2,3,7,8 PeCDD	< 0.05	< 0.06	< 0.04	< 0.04
Non 2,3,7,8 PeCDD	< 0.04	< 0.02	< 0.02	< 0.02
1,2,3,4,7,8 HxCDD	< 0.02	< 0.01	< 0.01	< 0.02
1,2,3,6,7,8 HxCDD	< 0.09	< 0.07	< 0.06	< 0.08
1,2,3,7,8,9 HxCDD	< 0.04	< 0.02	< 0.02	< 0.03
Non 2,3,7,8 HxCDD	< 0.04	< 0.02	< 0.04	< 0.04
1,2,3,4,6,7,8 HpCDD	< 0.2	< 0.1	0.30	< 0.2
Non 2,3,7,8 HpCDD	< 0.1	< 0.1	0.20	< 0.08
OCDD	< 0.9	< 1	2.72	< 0.9
2,3,7,8 TCDF	< 0.01	< 0.01	< 0.01	< 0.01
Non 2,3,7,8 TCDF	< 0.02	< 0.01	< 0.01	< 0.02
1,2,3,7,8 PeCDF	< 0.01	< 0.01	< 0.01	< 0.01
2,3,4,7,8 PeCDF	< 0.02	< 0.05	< 0.02	< 0.02
Non 2,3,7,8 PeCDF	< 0.02	< 0.01	< 0.01	< 0.02
1,2,3,4,7,8 HxCDF	< 0.01	< 0.02	< 0.02	< 0.01
1,2,3,6,7,8 HxCDF	< 0.01	< 0.02	< 0.02	< 0.01
2,3,4,6,7,8 HxCDF	< 0.02	< 0.02	< 0.01	< 0.02
1,2,3,7,8,9 HxCDF	< 0.02	< 0.02	< 0.02	< 0.02
Non 2,3,7,8 HxCDF	< 0.03	< 0.02	< 0.07	< 0.01
1,2,3,4,6,7,8 HpCDF	< 0.04	< 0.03	< 0.1	< 0.04
1,2,3,4,7,8,9 HpCDF	< 0.03	< 0.01	< 0.01	< 0.03
Non 2,3,7,8 HpCDF	< 0.04	< 0.02	< 0.1	< 0.02
OCDF	< 0.1	< 0.05	< 0.1	< 0.2
Sum of PCDD/Fs (inc) ¹	0.97	0.89	3.61	1.01
Sum of PCDD/Fs (exc) ²	0	0	3.22	0
Total I-TEQ (inc) ¹	0.051	0.068	0.060	0.057
Total I-TEQ (exc) ²	0	0	0.0058	0

1 = Including half LOD values
2 = Excluding LOD values

Table D6 Comparative PCDD and PCDF concentrations in primary and split QC river water samples (pg L⁻¹)

Congener	Waingogoro River at State Highway 45	Waingogoro River at State Highway 45	Mataura River at Seaward Downs	Mataura River at Seaward Downs
	Primary ³	Split QC ⁴	Primary	Split QC
2,3,7,8 TCDD	< 1	< 2	< 0.3	< 2
Non 2,3,7,8 TCDD	< 1	< 2	< 0.4	< 3
1,2,3,7,8 PeCDD	< 2	< 3	< 0.4	< 3
Non 2,3,7,8 PeCDD	< 2	< 3	< 0.4	< 3
1,2,3,4,7,8 HxCDD	< 1	< 2	< 0.5	< 3
1,2,3,6,7,8 HxCDD	< 1	< 1	< 0.7	< 1
1,2,3,7,8,9 HxCDD	< 1	< 1	< 0.6	< 1
Non 2,3,7,8 HxCDD	< 1	< 2	< 0.5	< 3
1,2,3,4,6,7,8 HpCDD	< 3	< 4	< 2	< 3
Non 2,3,7,8 HpCDD	< 2	< 4	< 2	< 3
OCDD	< 30	< 20	< 20	< 6
2,3,7,8 TCDF	< 0.7	< 1	< 0.2	< 1
Non 2,3,7,8 TCDF	< 0.7	< 1	< 0.3	< 1
1,2,3,7,8 PeCDF	< 0.4	< 1	< 0.3	< 1
2,3,4,7,8 PeCDF	< 0.3	< 1	< 0.3	< 1
Non 2,3,7,8 PeCDF	< 0.4	< 2	< 0.3	< 1
1,2,3,4,7,8 HxCDF	< 0.5	< 1	< 0.4	< 1
1,2,3,6,7,8 HxCDF	< 0.5	< 2	< 0.4	< 2
2,3,4,6,7,8 HxCDF	< 0.5	< 2	< 0.4	< 2
1,2,3,7,8,9 HxCDF	< 0.6	< 6	< 0.5	< 6
Non 2,3,7,8 HxCDF	< 0.5	< 6	< 0.4	< 6
1,2,3,4,6,7,8 HpCDF	< 0.8	< 2	< 1	< 2
1,2,3,4,7,8,9 HpCDF	< 0.9	< 1	< 1	< 1
Non 2,3,7,8 HpCDF	< 0.8	< 3	< 0.7	< 2
OCDF	< 2	< 2	< 2	< 2
Sum of PCDD/Fs (inc) ¹	27	38	18	30
Sum of PCDD/Fs (exc) ²	0	0	0	0
Total I-TEQ (inc) ¹	1.4	2.9	0.55	2.9
Total I-TEQ (exc) ²	0	0	0	0

1 = Including half LOD values

2 = Excluding LOD values

3 = Analysed by primary laboratory

4 = Analysed by independent cross-check laboratory

Table D7 Comparative PCDD and PCDF concentrations in primary and split QC eel and trout samples (ng kg⁻¹, wet fillet wt basis)

Congener	Shortfinned Eel Tukituki River at Tamumu Bridge Primary ³	Shortfinned Eel Tukituki River at Tamumu Bridge Split QC ⁴	Longfinned Eel Ruamahanga River at Waihenga Primary	Longfinned Eel Ruamahanga River at Waihenga Split QC	Brown Trout Waipa River at Whatawhata Primary	Brown Trout Waipa River at Whatawhata Split QC	Brown Trout Mataura River at Seaward Downs Primary	Brown Trout Mataura River at Seaward Downs Split QC
2,3,7,8 TCDD	< 0.02	< 0.09	< 0.01	< 0.1	< 0.09	< 0.1	< 0.02	< 0.09
Non 2,3,7,8 TCDD	< 0.05	< 0.1	< 0.07	< 0.1	< 0.05	< 0.1	< 0.05	< 0.09
1,2,3,7,8 PeCDD	< 0.04	< 0.1	< 0.03	< 0.2	< 0.11	< 0.2	< 0.01	< 0.1
Non 2,3,7,8 PeCDD	< 0.02	< 0.06	< 0.01	< 0.2	< 0.02	< 0.2	< 0.01	< 0.1
1,2,3,4,7,8 HxCDD	< 0.03	< 0.1	< 0.01	< 0.2	< 0.01	< 0.1	< 0.01	< 0.1
1,2,3,6,7,8 HxCDD	< 0.05	< 0.06	< 0.05	< 0.1	< 0.04	< 0.08	< 0.01	< 0.02
1,2,3,7,8,9 HxCDD	< 0.05	< 0.06	< 0.01	< 0.05	< 0.01	< 0.04	< 0.01	< 0.01
Non 2,3,7,8 HxCDD	< 0.03	< 0.1	< 0.01	< 0.3	< 0.01	< 0.1	< 0.01	< 0.2
1,2,3,4,6,7,8 HpCDD	< 0.2	< 0.2	< 0.2	< 0.3	< 0.08	< 0.1	< 0.2	< 0.2
Non 2,3,7,8 HpCDD	< 0.1	< 0.2	< 0.05	< 0.3	< 0.06	< 0.1	< 0.2	< 0.2
OCDD	< 1	< 0.3	< 1	< 0.5	< 1	< 0.2	< 3	< 0.5
2,3,7,8 TCDF	< 0.01	< 0.03	< 0.01	< 0.05	0.82	0.56	0.11	< 0.1
Non 2,3,7,8 TCDF	< 0.01	< 0.1	< 0.04	< 0.05	< 0.01	< 0.04	< 0.04	< 0.1
1,2,3,7,8 PeCDF	< 0.01	< 0.06	< 0.01	< 0.08	< 0.05	< 0.1	< 0.01	< 0.05
2,3,4,7,8 PeCDF	< 0.01	< 0.03	< 0.02	< 0.08	< 0.06	< 0.1	< 0.01	< 0.05
Non 2,3,7,8 PeCDF	< 0.01	< 0.06	< 0.01	< 0.08	< 0.1	< 0.1	< 0.01	< 0.05
1,2,3,4,7,8 HxCDF	< 0.02	< 0.06	< 0.01	< 0.05	< 0.03	< 0.04	< 0.01	< 0.09
1,2,3,6,7,8 HxCDF	< 0.02	< 0.09	< 0.01	< 0.1	< 0.02	< 0.08	< 0.01	< 0.09
2,3,4,6,7,8 HxCDF	< 0.02	< 0.09	< 0.01	< 0.1	< 0.01	< 0.06	< 0.01	< 0.07
1,2,3,7,8,9 HxCDF	< 0.03	< 0.3	< 0.01	< 0.3	< 0.01	< 0.2	< 0.01	< 0.2
Non 2,3,7,8 HxCDF	< 0.02	< 0.3	< 0.03	< 0.3	< 0.1	< 0.2	< 0.01	< 0.2
1,2,3,4,6,7,8 HpCDF	< 0.07	< 0.09	< 0.04	< 0.1	< 0.06	< 0.08	< 0.04	< 0.1
1,2,3,4,7,8,9 HpCDF	< 0.05	< 0.03	< 0.01	< 0.05	< 0.02	< 0.02	< 0.04	< 0.02
Non 2,3,7,8 HpCDF	< 0.07	< 0.09	< 0.02	< 0.1	< 0.04	< 0.08	< 0.05	< 0.1
OCDF	< 0.3	< 0.06	< 0.04	< 0.1	< 0.09	< 0.06	< 0.08	< 0.1
Sum of PCDD/Fs (inc) ¹	1.12	1.38	0.86	1.95	1.91	1.80	2.04	1.47
Sum of PCDD/Fs (exc) ²	0	0	0	0	0.92	0.56	0.11	0
Total I-TEQ (inc) ¹	0.037	0.12	0.026	0.17	0.20	0.21	0.032	0.12
Total I-TEQ (exc) ²	0	0	0	0	0.14	0.056	0.011	0

1 = Including half LOD values

2 = Excluding LOD values

3 = Analysed by primary laboratory

4 = Analysed by independent cross-check laboratory

Appendix E Concentrations of PCBs in New Zealand rivers

This appendix reports the concentrations of PCBs in river samples 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 in river water
Table E2	Concentrations in eel
Table E3	Concentrations in trout
Table E4	Results of blind duplicate river water sample analyses
Table E5	Results of blind duplicate eel sample analyses
Table E6	Results of split QC eel and trout sample analyses

Table E1 Concentrations of PCBs in New Zealand river water (ng L⁻¹)¹ (Cont.)

Congener	Halswell River at McCartneys Bridge (n=2) ⁵	Taiari River at Sutton Stream	Taiari River at Allanton (n=2) ⁴	Mataura River at Parawa	Mataura River at Seaward Downs	Number of positives	Minimum	Maximum	Median	Mean ⁶	Mean of ¹³ C surrogate standard recoveries, %, (n=20)
PCB #77	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	0	< 0.01	< 0.03	< 0.01	-	59
PCB #126	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	54
PCB #169	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	69
PCB #28 + PCB #31	< 0.5	< 0.2	< 0.5	< 0.3	< 0.3	0	< 0.1	< 0.6	< 0.4	-	58
PCB #52	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.2	< 0.1	-	62
PCB #101	< 0.1	< 0.1	< 0.2	< 0.2	< 0.1	0	< 0.1	< 0.2	< 0.1	-	77
PCB #99	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #123	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.2	< 0.1	-	-
PCB #118	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	0	< 0.1	< 0.2	< 0.1	-	-
PCB #114	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #105	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #153	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	70
PCB #138	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	0	< 0.1	< 0.2	< 0.1	-	-
PCB #167	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #156	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #157	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #187	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #183	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #180	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	69
PCB #170	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #189	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #202	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	69
PCB #194	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	-
PCB #206	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0	< 0.1	< 0.2	< 0.1	-	-
Sum of PCBs (inc) ²	1.3	1.1	1.4	1.3	1.2		1.1	1.6			
Sum of PCBs (exc) ³	0	0	0	0	0		0	0			
Total PCB TEQ (inc) ^{1,2}	0.65	0.65	0.66	0.66	0.65		0.65	0.66			
Total PCB TEQ (exc) ^{1,3}	0	0	0	0	0		0	0			

1 = Total PCB TEQ data reported in pg L⁻¹. All other results in ng L⁻¹
 2 = Including half LOD values
 3 = Excluding LOD values

4 = Mean of laboratory duplicate analyses
 5 = Mean of primary and blind duplicate samples
 6 = Mean value reported only if a PCB congener detected on more than 66% of occasions (minimum of 11 positive determinations)

Table E2 Concentrations of PCBs in New Zealand longfinned and shortfinned eel ($\mu\text{g kg}^{-1}$, wet fillet wt basis)¹

Congener	Waipa River at Whatawhata ⁴	Rangitaiki River at Te Teko ⁵	Waingonoro River at State Highway 4 ⁵	Wanganui River at Te Mairé ⁴	Manawatu River at Opiki Bridge ⁶	Mohaka River at Raupunga ⁴	Tukituki River at Tamumu Bridge ⁶	Ruamahanga River at State Highway 2 ⁴	Ruamahanga River at Waihenga ⁴	Haast River at Roaring Billy ⁴	Waimakariri River at Old HW Bridge ⁴
PCB #77	< 0.003	< 0.001	< 0.002	< 0.003	< 0.002	< 0.002	< 0.001	< 0.003	< 0.006	< 0.002	< 0.001
PCB #126	< 0.002	< 0.001	< 0.003	< 0.001	< 0.004	< 0.002	< 0.001	< 0.001	< 0.002	< 0.001	< 0.001
PCB #169	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.002	< 0.001	< 0.001	< 0.002	< 0.001	< 0.001
PCB #28 + PCB #31	0.095	< 0.03	0.28	0.065	0.40	0.063	0.051	0.034	0.069	0.091	0.046
PCB #52	0.12	0.015	0.38	0.081	0.33	0.038	0.038	0.013	0.13	0.019	0.036
PCB #101	0.66	0.10	2.13	0.58	1.72	0.27	0.16	0.037	0.73	0.044	0.30
PCB #99	0.19	0.038	0.78	0.19	0.49	0.085	0.041	< 0.02	0.22	< 0.01	0.075
PCB #123	< 0.04	< 0.008	< 0.2	< 0.03	< 0.06	< 0.02	< 0.02	< 0.01	< 0.06	< 0.01	< 0.03
PCB #118	0.57	0.16	2.75	1.00	1.87	0.38	0.13	0.045	1.01	0.026	0.27
PCB #114	< 0.01	< 0.01	0.036	< 0.01	0.028	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01
PCB #105	0.15	0.028	0.54	0.13	0.32	0.068	0.023	< 0.01	0.17	< 0.01	0.060
PCB #153	1.73	0.39	3.13	0.91	1.63	0.64	0.19	0.064	0.83	0.089	0.90
PCB #138	2.55	0.54	4.31	1.26	3.09	0.92	0.31	0.081	1.17	0.15	1.33
PCB #167	0.21	0.057	1.04	0.29	0.30	0.12	0.021	< 0.01	0.32	< 0.01	0.13
PCB #156	0.094	0.029	0.19	0.078	0.14	0.052	< 0.01	< 0.01	0.067	< 0.01	0.060
PCB #157	< 0.02	< 0.01	0.081	0.029	< 0.03	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01
PCB #187	0.94	0.15	1.23	0.35	0.61	0.23	0.20	0.021	0.27	0.066	0.39
PCB #183	0.23	0.044	0.24	0.10	0.16	0.078	< 0.02	< 0.01	0.079	< 0.01	0.14
PCB #180	0.55	0.12	0.59	0.29	0.32	0.18	0.040	0.017	0.20	0.021	0.32
PCB #170	0.62	0.13	0.57	0.22	0.44	0.19	0.034	0.011	0.18	0.021	0.33
PCB #189	< 0.01	< 0.01	< 0.02	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
PCB #202	< 0.01	< 0.01	< 0.02	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01
PCB #194	0.090	0.016	0.073	0.078	0.058	0.027	< 0.01	< 0.01	0.034	< 0.01	0.078
PCB #206	< 0.02	< 0.01	< 0.02	0.022	< 0.02	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.02
Sum of PCBs (inc) ²	8.86	1.86	18.5	5.71	12.0	3.38	1.29	0.39	5.56	0.59	4.51
Sum of PCBs (exc) ³	8.80	1.82	18.4	5.67	11.9	3.34	1.24	0.32	5.48	0.53	4.47
Total PCB TEQ (inc) ^{1,2}	0.30	0.11	0.72	0.25	0.57	0.21	0.084	0.071	0.30	0.069	0.16
Total PCB TEQ (exc) ^{1,3}	0.19	0.048	0.56	0.19	0.35	0.093	0.019	0.0058	0.17	0.0049	0.10

Table E2 Concentrations of PCBs in New Zealand longfinned and shortfinned eel ($\mu\text{g kg}^{-1}$, wet fillet wt basis)¹ (Cont.)

Congener	Halswell River at McCartneys Bridge ⁴	Taiari River at Sutton Stream ⁴	Taiari River at Allanton (n=2) ^{4,7}	Mataura River at Parawa ⁴	Mataura River at Seaward Downs (n=2) ^{4,7}	Number of positives	Minimum	Maximum	Median	Mean ^{8,9}	Mean of ¹³ C surrogate standard recoveries, %, (n=18)
PCB #77	< 0.002	< 0.001	< 0.002	< 0.003	< 0.002	0	< 0.001	< 0.006	< 0.002	-	60
PCB #126	0.010	< 0.001	< 0.004	< 0.001	< 0.002	1	< 0.001	0.010	< 0.002	-	46
PCB #169	< 0.003	< 0.003	< 0.002	< 0.002	< 0.003	0	< 0.001	< 0.003	< 0.001	-	44
PCB #28 + PCB #31	0.33	0.080	0.31	0.053	0.31	15	< 0.03	0.40	0.075	0.14	75
PCB #52	0.31	0.031	0.34	0.026	0.23	16	0.013	0.38	0.060	0.13	76
PCB #101	1.77	0.10	1.42	0.12	0.87	16	0.037	2.13	0.44	0.69	64
PCB #99	0.43	0.020	0.43	0.025	0.24	14	< 0.01	0.78	0.14	0.20	
PCB #123	< 0.1	< 0.1	< 0.1	< 0.01	< 0.07	0	< 0.008	< 0.2	< 0.04	-	
PCB #118	1.35	0.12	1.55	0.11	1.06	16	0.026	2.75	0.48	0.78	
PCB #114	< 0.02	< 0.01	< 0.03	< 0.01	< 0.02	2	< 0.01	0.036	< 0.01	-	
PCB #105	0.25	0.019	0.34	0.019	0.16	14	< 0.01	0.54	0.099	0.14	
PCB #153	3.84	0.18	1.85	0.15	1.17	16	0.064	3.84	0.87	1.11	46
PCB #138	4.89	0.22	2.82	0.22	1.71	16	0.081	4.89	1.22	1.60	
PCB #167	0.71	0.051	0.40	0.033	0.26	14	< 0.01	1.04	0.17	0.25	
PCB #156	0.15	< 0.02	0.12	< 0.02	0.086	11	< 0.01	0.19	0.064	0.069	
PCB #157	0.052	< 0.01	0.042	< 0.01	0.022	5	< 0.01	0.081	< 0.02	-	
PCB #187	1.57	0.074	0.78	0.12	0.53	16	0.021	1.57	0.31	0.47	
PCB #183	0.38	0.019	0.18	< 0.01	0.14	12	< 0.01	0.38	0.090	0.11	
PCB #180	0.92	0.048	0.37	0.029	0.26	16	0.017	0.92	0.23	0.27	46
PCB #170	0.90	0.044	0.44	0.022	0.32	16	0.011	0.90	0.21	0.28	
PCB #189	< 0.03	< 0.01	< 0.02	< 0.01	< 0.02	0	< 0.01	< 0.03	< 0.01	-	
PCB #202	0.031	< 0.01	< 0.02	< 0.01	< 0.01	1	< 0.01	0.031	< 0.01	-	43
PCB #194	0.15	< 0.01	0.061	< 0.01	0.043	11	< 0.01	0.15	0.038	0.046	
PCB #206	0.038	< 0.01	< 0.02	< 0.01	< 0.02	2	< 0.01	0.038	< 0.02	-	
Sum of PCBs (inc) ²	18.2	1.10	11.5	0.98	7.45		0.39	18.5	5.04	6.37	
Sum of PCBs (exc) ³	18.1	1.01	11.4	0.93	7.38		0.32	18.4	4.98	6.30	
Total PCB TEQ (inc) ^{1,2}	1.39	0.10	0.52	0.087	0.33		0.069	1.39	0.23	0.33	
Total PCB TEQ (exc) ^{1,3}	1.37	0.019	0.32	0.016	0.21		0.0049	1.37	0.14	0.23	

1 = Total PCB TEQ data reported in ng kg^{-1} wet fillet wt. All other results in $\mu\text{g kg}^{-1}$ wet wt
 2 = Including half LOD values
 3 = Excluding LOD values
 4 = Longfinned eel (*Anguilla dieffenbachii*)
 5 = Mix of longfinned and shortfinned eel
 6 = Shortfinned eel (*Anguilla australis*)
 7 = Mean of primary and blind duplicate samples
 8 = Mean value reported only if a PCB congener detected on more than 66% of occasions (minimum of 11 positive determinations)
 9 = For any individual congener, calculation of the mean includes half LOD values

Table E3 Concentrations of PCBs in New Zealand brown and rainbow trout ($\mu\text{g kg}^{-1}$, wet fillet wt basis)¹

Congener	Waipa River at Whatawhata ⁴	Rangitaiki River at Te Teko ⁴	Rangitaiki River at Te Teko ⁵	Wanganui River at Te Mairi ⁵	Tukituki River at Tamumu Bridge ⁵	Ruamahanga River at Waihenga ⁴	Waimakariri River at Old H/W Bridge ⁴	Halswell River at McCartneys Bridge ⁶	Taieri River at Sutton Stream ⁴	Taieri River at Allanton ⁴	Mataura River at Parawa ⁴	Mataura River at Seaward Downs ⁴	Number of positives	Minimum	Maximum ⁶	Median ⁷	Mean ^{8,9}	Mean of ¹³ C surrogate standard recoveries, %, (n=12)
PCB #77	< 0.02	< 0.001	< 0.001	< 0.002	< 0.002	< 0.001	< 0.003	< 0.004	< 0.001	< 0.002	< 0.001	< 0.004	0	< 0.001	< 0.02	< 0.002	-	78
PCB #126	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.002	< 0.004	< 0.001	< 0.001	< 0.001	< 0.002	0	< 0.001	< 0.004	< 0.001	-	71
PCB #169	< 0.002	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.003	< 0.001	< 0.001	< 0.001	< 0.001	0	< 0.001	< 0.003	< 0.001	-	71
PCB #28 + PCB #31	0.22	0.028	< 0.01	0.030	0.041	0.031	0.031	0.048	< 0.02	0.067	0.039	0.087	10	< 0.01	0.22	0.035	0.053	99
PCB #52	0.16	0.034	< 0.01	0.023	0.015	0.022	0.021	0.044	< 0.01	0.028	< 0.01	0.049	9	< 0.01	0.16	0.023	0.034	96
PCB #101	0.89	0.36	0.21	0.12	0.038	0.11	0.27	0.33	< 0.01	0.11	0.011	0.18	11	< 0.01	0.89	0.15	0.22	83
PCB #99	0.28	0.13	0.079	0.047	< 0.02	0.036	0.084	0.081	< 0.01	0.038	< 0.01	0.053	9	< 0.01	0.28	0.050	0.071	
PCB #123	< 0.06	0.021	0.016	< 0.02	< 0.01	< 0.02	0.020	< 0.04	< 0.01	< 0.01	< 0.01	< 0.02	3	< 0.01	0.021	< 0.02	-	
PCB #118	0.96	0.44	0.28	0.18	0.039	0.15	0.29	0.27	< 0.01	0.12	< 0.01	0.22	10	< 0.01	0.96	0.20	0.25	
PCB #114	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	
PCB #105	0.17	0.075	0.051	0.028	< 0.01	0.027	0.058	0.042	< 0.01	0.026	< 0.01	0.041	9	< 0.01	0.17	0.035	0.044	
PCB #153	1.65	0.64	0.95	0.19	0.049	0.15	0.68	0.70	< 0.01	0.17	0.010	0.26	11	< 0.01	1.65	0.23	0.45	70
PCB #138	1.99	0.95	1.17	0.28	0.062	0.21	1.00	0.89	< 0.01	0.24	0.014	0.36	11	< 0.01	1.99	0.32	0.60	
PCB #167	0.36	0.10	0.11	0.037	< 0.01	0.041	0.10	0.12	< 0.01	0.022	< 0.01	0.062	9	< 0.01	0.36	0.052	0.081	
PCB #156	0.11	0.053	0.066	0.015	< 0.01	0.011	0.048	0.030	< 0.01	< 0.01	< 0.01	0.020	8	< 0.01	0.11	0.018	0.031	
PCB #157	0.030	< 0.01	0.011	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	2	< 0.01	0.030	< 0.01	-	
PCB #187	0.54	0.16	0.27	0.041	< 0.02	0.033	0.22	0.25	< 0.01	0.060	< 0.01	0.080	9	< 0.01	0.54	0.070	0.14	
PCB #183	0.21	0.061	0.11	0.015	< 0.01	0.011	0.074	0.068	< 0.01	< 0.02	< 0.01	0.030	8	< 0.01	0.21	0.020	0.050	
PCB #180	0.51	0.16	0.30	0.039	< 0.01	0.031	0.16	0.16	< 0.01	0.030	< 0.01	0.069	9	< 0.01	0.51	0.054	0.12	62
PCB #170	0.57	0.18	0.33	0.043	< 0.01	0.030	0.19	0.18	< 0.01	0.029	< 0.01	0.080	9	< 0.01	0.57	0.062	0.14	
PCB #189	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 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	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.01	< 0.01	-	58
PCB #194	0.079	0.022	0.051	< 0.01	< 0.01	< 0.01	0.022	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	4	< 0.01	0.079	< 0.01	-	
PCB #206	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	
Sum of PCBs (inc) ²	8.80	3.44	4.04	1.13	0.33	0.93	3.30	3.28	0.11	0.99	0.16	1.63		0.11	8.80	1.38	2.35	
Sum of PCBs (exc) ³	8.73	3.41	4.00	1.09	0.24	0.89	3.27	3.21	0	0.94	0.074	1.59		0	8.73	1.34	2.29	
Total PCB TEQ (inc) ^{1,2}	0.32	0.16	0.17	0.10	0.069	0.089	0.19	0.29	0.065	0.082	0.065	0.16		0.065	0.32	0.13	0.15	
Total PCB TEQ (exc) ^{1,3}	0.25	0.10	0.11	0.033	0.0039	0.027	0.082	0.067	0	0.018	0	0.045		0	0.25	0.039	0.061	

1 = Total PCB TEQ data reported in ng kg⁻¹ wet fillet wt. All other results in $\mu\text{g kg}^{-1}$ wet fillet wt
 2 = Including half LOD values
 3 = Excluding LOD values
 4 = Brown trout (*Salmo trutta*)
 5 = Rainbow trout (*Oncorhynchus mykiss*)
 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 PCB congener detected on more than 66% of occasions (minimum of 8 positive determinations)
 9 = For any individual congener, calculation of the mean includes half LOD values

Table E4 Comparative PCB concentrations in primary and blind duplicate river water samples (ng L⁻¹)¹

Congener	Manawatu River at Opiki Bridge	Manawatu River at Opiki Bridge	Halswell River at McCartneys Bridge	Halswell River at McCartneys Bridge
	Primary	Blind duplicate	Primary	Blind duplicate
PCB #77	< 0.01	< 0.03	< 0.01	< 0.01
PCB #126	< 0.01	< 0.01	< 0.01	< 0.01
PCB #169	< 0.01	< 0.01	< 0.01	< 0.01
PCB #28 + PCB #31	< 0.4	< 0.3	< 0.5	< 0.5
PCB #52	< 0.1	< 0.1	< 0.1	< 0.1
PCB #101	< 0.1	< 0.1	< 0.1	< 0.1
PCB #99	< 0.1	< 0.1	< 0.1	< 0.1
PCB #123	< 0.1	< 0.1	< 0.1	< 0.1
PCB #118	< 0.1	< 0.1	< 0.1	< 0.1
PCB #114	< 0.1	< 0.1	< 0.1	< 0.1
PCB #105	< 0.1	< 0.1	< 0.1	< 0.1
PCB #153	< 0.1	< 0.1	< 0.1	< 0.1
PCB #138	< 0.1	< 0.1	< 0.1	< 0.1
PCB #167	< 0.1	< 0.1	< 0.1	< 0.1
PCB #156	< 0.1	< 0.1	< 0.1	< 0.1
PCB #157	< 0.1	< 0.1	< 0.1	< 0.1
PCB #187	< 0.1	< 0.1	< 0.1	< 0.1
PCB #183	< 0.1	< 0.1	< 0.1	< 0.1
PCB #180	< 0.1	< 0.1	< 0.1	< 0.1
PCB #170	< 0.1	< 0.1	< 0.1	< 0.1
PCB #189	< 0.1	< 0.1	< 0.1	< 0.1
PCB #202	< 0.1	< 0.1	< 0.1	< 0.1
PCB #194	< 0.1	< 0.1	< 0.1	< 0.1
PCB #206	< 0.2	< 0.2	< 0.1	< 0.1
Sum of PCBs (inc) ²	1.3	1.2	1.3	1.3
Sum of PCBs (exc) ³	0	0	0	0
Total PCB TEQ (inc) ^{1,2}	0.65	0.66	0.65	0.65
Total PCB TEQ (exc) ^{1,3}	0	0	0	0

1 = Total PCB TEQ data reported in pg L⁻¹. All other results in ng L⁻¹

2 = Including half LOD values

3 = Excluding LOD values

Table E5 Comparative PCB concentrations in primary and blind duplicate eel samples ($\mu\text{g kg}^{-1}$, wet fillet wt basis)¹

Congener	Taiari River at Allanton	Taiari River at Allanton	Mataura River at Seaward Downs	Mataura River at Seaward Downs
	Primary	Blind duplicate	Primary	Blind duplicate
PCB #77	< 0.001	< 0.003	< 0.002	< 0.002
PCB #126	< 0.002	< 0.005	< 0.003	< 0.001
PCB #169	< 0.001	< 0.002	< 0.003	< 0.002
PCB #28 + PCB #31	0.32	0.30	0.39	0.23
PCB #52	0.33	0.35	0.29	0.16
PCB #101	1.15	1.69	1.09	0.65
PCB #99	0.29	0.56	0.31	0.17
PCB #123	< 0.06	< 0.2	< 0.1	< 0.04
PCB #118	1.17	1.93	1.29	0.83
PCB #114	< 0.02	< 0.04	< 0.02	< 0.01
PCB #105	0.26	0.41	0.20	0.12
PCB #153	1.26	2.43	1.43	0.90
PCB #138	2.51	3.13	2.01	1.41
PCB #167	0.24	0.56	0.36	0.15
PCB #156	0.099	0.14	0.10	0.071
PCB #157	0.024	0.060	0.033	< 0.02
PCB #187	0.80	0.76	0.64	0.42
PCB #183	0.13	0.23	0.16	0.11
PCB #180	0.25	0.48	0.30	0.21
PCB #170	0.40	0.47	0.36	0.27
PCB #189	< 0.01	< 0.02	< 0.02	< 0.01
PCB #202	< 0.01	< 0.02	< 0.01	< 0.01
PCB #194	0.046	0.075	0.053	0.032
PCB #206	< 0.01	< 0.02	< 0.02	< 0.01
Sum of PCBs (inc) ²	9.34	13.7	9.11	5.79
Sum of PCBs (exc) ³	9.28	13.6	9.02	5.73
Total PCB TEQ (inc) ^{1,2}	0.36	0.67	0.43	0.23
Total PCB TEQ (exc) ^{1,3}	0.25	0.39	0.26	0.16

1 = Total PCB TEQ data reported in ng kg^{-1} wet fillet wt. All other results in $\mu\text{g kg}^{-1}$ wet fillet wt

2 = Including half LOD values

3 = Excluding LOD values

Table E6 Comparative PCB concentrations in primary and split QC eel and trout samples ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Congener	Shortfinned Eel Tukituki River at Tamumu Bridge	Shortfinned Eel Tukituki River at Tamumu Bridge	Longfinned Eel Ruamahanga River at Waihenga	Longfinned Eel Ruamahanga River at Waihenga	Brown Trout Waipa River at Whatawhata	Brown Trout Waipa River at Whatawhata	Brown Trout Mataura River at Seaward Downs	Brown Trout Mataura River at Seaward Downs
	Primary ¹	Split QC ²	Primary	Split QC	Primary	Split QC	Primary	Split QC
PCB #77	< 0.001	< 0.003	< 0.006	< 0.003	< 0.02	0.016	< 0.004	0.0053
PCB #126	< 0.001	< 0.001	< 0.002	< 0.002	< 0.001	0.0047	< 0.002	< 0.001
PCB #169	< 0.001	< 0.001	< 0.002	< 0.001	< 0.002	< 0.001	< 0.001	< 0.001
PCB #118	0.13	0.12	1.01	0.70	0.96	0.76	0.22	0.17
PCB #105	0.023	0.034	0.17	0.24	0.17	0.25	0.041	0.060

1 = Analysed by primary laboratory

2 = Analysed by independent cross-check laboratory

Appendix F Concentrations of organochlorine pesticides in New Zealand rivers

This appendix reports the concentrations of organochlorine pesticides and pesticide degradation products in river samples 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 in river water
Table F2	Concentrations in eel
Table F3	Concentrations in trout
Table F4	Results of blind duplicate river water sample analyses
Table F5	Results of blind duplicate eel sample analyses
Table F6	Results of split QC river water sample analyses
Table F7	Results of split QC eel and trout sample analyses

Table F1 Concentrations of organochlorine pesticides in New Zealand river water (ng L⁻¹)

Pesticide	Waipa River at Whatawhata (n=2) ¹	Rangitaiki River at Te Teko	Waingonoro River at State Highway 45	Wanganui River at Te Maire	Manawatu River at Opiki Bridge (n=2) ²	Mohaka River at Raupunga	Tukituki River at Tamumu Bridge	Ruamahanga River at State Highway 2	Ruamahanga River at Waihenga	Haast River at Roaring Billy	Waimakariri River at Old H/W Bridge
Alpha-HCH	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Beta-HCH	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Gamma-HCH	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.2	< 0.2	< 0.1	< 0.1	< 0.1	< 0.3
HCB	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Aldrin	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Dieldrin	< 0.5	< 0.8	< 0.7	< 0.6	< 1	< 0.7	< 1	< 1	< 1	< 0.4	< 0.5
Heptachlor	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.2	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1
Heptachlor epoxide	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1
Alpha-chlordane	< 0.3	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2
Gamma-chlordane	< 0.3	< 0.2	< 0.1	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.1	< 0.1	< 0.3
pp-DDE	< 0.2	< 0.1	< 0.3	< 0.1	< 0.2	< 0.1	< 0.2	< 0.1	< 0.2	< 0.1	< 0.2
pp-TDE	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
op-DDT	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
pp-DDT	< 0.1	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	< 0.2	< 0.1	< 0.1	< 0.1	< 0.1

Table F1 Concentrations of organochlorine pesticides in New Zealand river water (ng L⁻¹) (Cont.)

Pesticide	Halswell River at McCartneys Bridge (n=2) ²	Tairi River at Sutton Stream	Tairi River at Allanton (n=2) ¹	Mataura River at Parawa	Mataura River at Seaward Downs	Number of positives	Minimum	Maximum	Median	Mean ³	Mean of ¹³ C surrogate standard recoveries, %, (n=20)
Alpha-HCH	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.2	< 0.1	-	
Beta-HCH	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.2	< 0.1	-	
Gamma-HCH	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0	< 0.1	< 0.3	< 0.1	-	52
HCB	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	39
Aldrin	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	
Dieldrin	< 0.7	< 0.5	< 2	< 2	< 0.6	0	< 0.4	< 2	< 0.7	-	36
Heptachlor	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.2	< 0.1	-	
Heptachlor epoxide	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.2	< 0.1	-	
Alpha-chlordane	< 0.1	< 0.1	< 0.2	< 0.1	< 0.1	0	< 0.1	< 0.3	< 0.1	-	
Gamma-chlordane	< 0.3	< 0.2	< 0.2	< 0.2	< 0.2	0	< 0.1	< 0.3	< 0.2	-	
pp-DDE	< 0.4	< 0.1	< 0.2	< 0.9	< 0.1	0	< 0.1	< 0.9	< 0.2	-	73
pp-TDE	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	
op-DDT	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0	< 0.1	< 0.1	< 0.1	-	
pp-DDT	< 0.1	< 0.1	< 0.1	< 0.2	< 0.1	0	< 0.1	< 0.2	< 0.1	-	79

1 = Mean of laboratory duplicate analyses

2 = Mean of primary and blind duplicate samples

3 = Mean value reported only if a pesticide detected on more than 66% of occasions (minimum of 11 positive determinations)

Table F2 Concentrations of organochlorine pesticides in New Zealand longfinned and shortfinned eel ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Pesticide	Waipa River at Whatawhata ¹	Rangitaiki River at Te Teko ²	Waingonoro River at State Highway 45 ⁵	Wanganui River at Te Maire ¹	Manawatu River at Opiki Bridge ³	Mohaka River at Raupunga ¹	Tukituki River at Tamumu Bridge ³	Ruamahanga River at State Highway 2 ¹	Ruamahanga River at Waihenga ¹	Haast River at Roaring Billy ¹	Waimakariri River at Old HW Bridge ¹
Alpha-HCH	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	0.022	< 0.01	< 0.02	< 0.02	< 0.01
Beta-HCH	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	0.087	< 0.01	< 0.01	< 0.01	< 0.01
Gamma-HCH	< 0.02	< 0.01	< 0.03	< 0.02	0.083	< 0.02	0.027	< 0.01	0.053	< 0.01	0.023
HCB	0.080	0.030	0.26	0.18	0.14	0.13	0.27	0.050	0.23	0.27	0.066
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01
Dieldrin	1.76	0.26	1.38	1.88	3.97	0.45	11.4	0.42	2.97	0.24	0.46
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	0.026	< 0.01	< 0.01	< 0.01	< 0.01	0.044	< 0.01
Alpha-chlordane	0.038	< 0.01	0.022	0.034	0.15	0.050	0.033	< 0.02	0.030	0.041	0.026
Gamma-chlordane	< 0.01	< 0.01	< 0.01	< 0.01	0.025	< 0.02	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01
pp-DDE	20.9	8.37	153	22.4	40.5	27.2	13.7	6.03	80.4	0.67	52.4
pp-TDE	3.55	0.37	10.5	5.34	8.74	1.27	0.69	0.38	3.78	0.032	0.57
op-DDT	0.058	0.019	0.25	0.30	0.39	0.031	0.15	0.041	0.31	< 0.01	0.10
pp-DDT	1.88	0.93	7.90	5.11	4.31	4.29	1.45	0.66	6.63	0.10	2.39

Table F2 Concentrations of organochlorine pesticides in New Zealand longfinned and shortfinned eel ($\mu\text{g kg}^{-1}$, wet fillet wt basis) (Cont.)

Pesticide	Halswell River at McCartneys Bridge ¹	Taiari River at Sutton Stream ¹	Taiari River at Allanton (n=2) ^{1,4}	Mataura River at Parawa ¹	Mataura River at Seaward Downs (n=2) ^{1,4}	Number of positives	Minimum	Maximum	Median ⁵	Mean ⁶	Mean of ¹³ C surrogate standard recoveries, %, (n=18)
Alpha-HCH	< 0.01	0.057	0.035	< 0.02	0.054	4	< 0.01	0.057	< 0.02	-	
Beta-HCH	< 0.02	0.038	0.070	< 0.01	0.048	4	< 0.01	0.087	< 0.01	-	
Gamma-HCH	0.030	< 0.02	0.039	< 0.02	0.032	7	< 0.01	0.083	0.017	-	55
HCB	0.37	0.29	0.52	0.43	0.39	16	0.030	0.52	0.25	0.23	35
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	
Dieldrin	7.43	1.70	4.98	0.93	4.60	16	0.24	11.4	1.73	2.80	46
Heptachlor	< 0.01	< 0.01	< 0.02	< 0.01	< 0.01	0	< 0.01	< 0.02	< 0.01	-	
Heptachlor epoxide	0.26	< 0.01	0.13	< 0.01	0.031	5	< 0.01	0.26	< 0.01	-	
Alpha-chlordane	0.58	0.021	1.24	0.062	0.16	14	< 0.01	1.24	0.036	0.16	
Gamma-chlordane	0.10	< 0.01	0.24	< 0.01	0.026	4	< 0.01	0.24	< 0.01	-	
pp-DDE	155	55.9	67.5	24.2	72.3	16	0.67	155	33.9	50.0	108
pp-TDE	33.1	1.90	20.7	0.94	13.3	16	0.032	33.1	2.73	6.57	
op-DDT	0.75	0.24	0.47	0.17	0.36	15	< 0.01	0.75	0.21	0.23	
pp-DDT	25.5	4.56	12.1	2.79	8.94	16	0.10	25.5	4.30	5.60	68

1 = Longfinned eel (*Anguilla dieffenbachii*)

2 = Mix of longfinned and shortfinned eel

3 = Shortfinned eel (*Anguilla australis*)

4 = Mean of primary and blind duplicate samples

5 = For any pesticide, calculation of the median includes half LOD value

6 = Mean value reported only if a pesticide detected on more than 66% of occasions (minimum of 11 positive determinations)

Table F3 Concentrations of organochlorine pesticides in New Zealand brown and rainbow trout ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Pesticide	Waipa River at Whatawhata ¹	Rangitaiki River at Te Teko ¹	Rangitaiki River at Te Teko ²	Wanganui River at Te Maire ²	Tukituki River at Tamumu Bridge ²	Ruamahanga River at Waihenga ¹	Waimakariri River at Old HW Bridge ¹	Halswell River at McCartneys Bridge ¹	Taieri River at Sutton Stream ¹	Taieri River at Allanton ¹	Mataura River at Parawa ¹	Mataura River at Seaward Downs ¹	Number of positives	Minimum	Maximum ³	Median	Mean ⁴	Mean of ¹³ C surrogate standard recoveries, %, (n=12)
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	< 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	< 0.01	< 0.01	< 0.01	-	
Gamma-HCH	< 0.02	< 0.01	< 0.01	< 0.01	< 0.02	0.011	< 0.01	< 0.02	< 0.01	< 0.01	< 0.01	< 0.02	1	< 0.01	0.011	< 0.01	-	62
HCB	0.032	0.022	< 0.01	0.021	0.022	0.028	0.032	0.040	0.043	0.17	0.063	0.050	11	< 0.01	0.17	0.032	0.044	45
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	< 0.01	< 0.01	< 0.01	-	
Dieldrin	0.37	0.047	0.021	0.17	0.13	0.38	0.55	1.12	0.11	0.56	0.15	0.51	12	0.021	1.12	0.27	0.34	60
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	< 0.01	< 0.01	< 0.01	-	
Heptachlor epoxide	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.018	< 0.01	0.046	< 0.01	< 0.01	2	< 0.01	0.046	< 0.01	-	
Alpha-chlordane	< 0.04	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.04	< 0.01	0.13	< 0.04	< 0.02	1	< 0.01	0.13	< 0.02	-	
Gamma-chlordane	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.01	0.033	< 0.01	< 0.01	1	< 0.01	0.033	< 0.01	-	
pp-DDE	12.2	8.80	37.6	6.89	3.86	7.36	15.7	73.9	4.58	7.20	1.82	13.1	12	1.82	73.9	8.08	16.1	103
pp-TDE	1.11	0.63	1.27	0.63	0.22	0.24	0.59	1.62	0.72	1.97	0.043	0.091	12	0.043	1.97	0.63	0.76	
op-DDT	0.062	0.013	< 0.01	0.053	0.023	0.034	0.064	0.29	0.020	0.12	0.019	0.042	11	< 0.01	0.29	0.038	0.062	
pp-DDT	0.91	0.34	0.16	0.69	0.43	0.39	0.66	0.81	0.18	0.82	0.17	0.48	12	0.16	0.91	0.46	0.50	74

1 = Brown trout (*Salmo trutta*)

2 = Rainbow trout (*Oncorhynchus mykiss*)

3 = Excludes any LOD value which is greater than a maximum measured value

4 = Mean value reported only if a pesticide detected on more than 66% of occasions (minimum of 8 positive determinations)

Table F4 Comparative organochlorine pesticide concentrations in primary and blind duplicate river water samples (ng L⁻¹)

Pesticide	Manawatu River at Opiki Bridge	Manawatu River at Opiki Bridge	Halswell River at McCartneys Bridge	Halswell River at McCartneys Bridge
	Primary	Blind duplicate	Primary	Blind duplicate
Alpha-HCH	< 0.1	< 0.1	< 0.1	< 0.1
Beta-HCH	< 0.1	< 0.1	< 0.1	< 0.1
Gamma-HCH	< 0.2	< 0.2	< 0.1	< 0.1
HCB	< 0.1	< 0.1	< 0.1	< 0.1
Aldrin	< 0.1	< 0.1	< 0.1	< 0.1
Dieldrin	< 1	< 1	< 0.7	< 0.7
Heptachlor	< 0.1	< 0.1	< 0.1	< 0.1
Heptachlor epoxide	< 0.1	< 0.1	< 0.1	< 0.1
Alpha-chlordane	< 0.1	< 0.1	< 0.1	< 0.1
Gamma-chlordane	< 0.2	< 0.2	< 0.3	< 0.3
pp-DDE	< 0.2	< 0.2	< 0.2	< 0.5
pp-TDE	< 0.1	< 0.1	< 0.1	< 0.1
op-DDT	< 0.1	< 0.1	< 0.1	< 0.1
pp-DDT	< 0.2	< 0.2	< 0.1	< 0.1

Table F5 Comparative organochlorine pesticide concentrations in primary and blind duplicate eel samples ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Pesticide	Taieri River at Allanton		Mataura River at Seaward Downs	
	Primary	Blind duplicate	Primary	Blind duplicate
Alpha-HCH	0.043	0.026	0.050	0.058
Beta-HCH	0.065	0.075	0.037	0.058
Gamma-HCH	0.041	0.037	0.039	0.025
HCB	0.46	0.58	0.38	0.39
Aldrin	< 0.01	< 0.01	< 0.01	< 0.01
Dieldrin	5.50	4.46	4.03	5.17
Heptachlor	< 0.02	< 0.01	< 0.01	< 0.01
Heptachlor epoxide	0.098	0.17	0.024	0.038
Alpha-chlordane	1.58	0.89	0.16	0.15
Gamma-chlordane	0.27	0.20	0.030	0.022
pp-DDE	64.4	70.6	62.1	82.5
pp-TDE	12.1	29.2	9.28	17.3
op-DDT	0.40	0.54	0.36	0.36
pp-DDT	12.2	11.9	9.66	8.21

Table F6 Comparative organochlorine pesticide concentrations in primary and split QC river water samples (ng L⁻¹)

Pesticide	Waingonoro River at State Highway 45	Waingonoro River at State Highway 45	Mataura River at Seaward Downs	Mataura River at Seaward Downs
	Primary ¹	Split QC ²	Primary	Split QC
Alpha-HCH	< 0.1	< 0.2	< 0.1	< 0.2
Beta-HCH	< 0.1	< 0.2	< 0.1	< 0.2
Gamma-HCH	< 0.1	< 0.2	< 0.1	< 0.2
HCB	< 0.1	< 0.2	< 0.1	< 0.2
Aldrin	< 0.1	< 0.2	< 0.1	< 0.2
Dieldrin	< 0.7	< 0.4	< 0.6	< 0.4
Heptachlor	< 0.2	< 0.2	< 0.1	< 0.2
Heptachlor epoxide	< 0.2	< 0.2	< 0.1	< 0.2
Alpha-chlordane	< 0.1	< 0.2	< 0.1	< 0.2
Gamma-chlordane	< 0.1	< 0.2	< 0.2	< 0.2
pp-DDE	< 0.3	< 0.2	< 0.1	< 0.2
pp-TDE	< 0.1	< 0.2	< 0.1	< 0.2
op-DDT	< 0.1	< 0.2	< 0.1	< 0.2
pp-DDT	< 0.1	< 0.2	< 0.1	< 0.2

1 = Analysed by primary laboratory

2 = Analysed by independent cross-check laboratory

Table F7 Comparative organochlorine pesticide concentrations in primary and split QC eel and trout samples ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Pesticide	Shortfinned Eel Tukituki River at Tamumu Bridge	Shortfinned Eel Tukituki River at Tamumu Bridge	Longfinned Eel Ruamahanga River at Waihenga	Longfinned Eel Ruamahanga River at Waihenga	Brown Trout Waipa River at Whatawhata	Brown Trout Waipa River at Whatawhata	Brown Trout Mataura River at Seaward Downs	Brown Trout Mataura River at Seaward Downs
	Primary ¹	Split QC ²	Primary	Split QC	Primary	Split QC	Primary	Split QC
Alpha-HCH	0.022	< 0.05	< 0.02	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
Beta-HCH	0.087	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
Gamma-HCH	0.027	< 0.05	0.053	< 0.05	< 0.02	< 0.05	< 0.02	< 0.05
HCB	0.27	< 0.05	0.23	< 0.05	0.032	< 0.05	0.050	< 0.05
Aldrin	< 0.02	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
Dieldrin	11.4	12	2.97	1.5	0.37	0.35	0.51	0.28
Heptachlor	< 0.01	< 0.07	< 0.01	< 0.07	< 0.01	< 0.07	< 0.01	< 0.07
Heptachlor epoxide	< 0.01	< 0.05	< 0.01	< 0.05	< 0.02	< 0.05	< 0.01	< 0.05
Alpha-chlordane	0.033	< 0.05	0.030	< 0.05	< 0.04	< 0.05	< 0.02	< 0.05
Gamma-chlordane	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05	< 0.01	< 0.05
pp-DDE	13.7	14	80.4	47	12.2	12	13.1	12
pp-TDE	0.69	1.1	3.78	2.1	1.11	1.0	0.091	0.45
op-DDT	0.15	0.05	0.31	0.17	0.062	0.11	0.042	< 0.05
pp-DDT	1.45	1.2	6.63	4.4	0.91	0.88	0.48	0.39

1 = Analysed by primary laboratory

2 = Analysed by independent cross-check laboratory

Appendix G Concentrations of chlorophenols in New Zealand rivers

This appendix reports the concentrations of chlorophenols in river samples 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 in river water
Table G2	Concentrations in eel
Table G3	Concentrations in trout
Table G4	Results of blind duplicate river water sample analyses
Table G5	Results of blind duplicate eel sample analyses
Table G6	Results of split QC river water sample analyses
Table G7	Results of split QC eel and trout sample analyses

Table G1 Concentrations of chlorophenols in New Zealand river water¹ (ng L⁻¹)

Chlorophenol	Waipa River at Whatawhata	Rangitaiki River at Te Teko	Waingonoro River at State Highway 45	Wanganui River at Te Maire	Manawatu River at Opiki Bridge (n=2)	Mohaka River at Raupunga	Tukituki River at Tamumu Bridge	Ruamahanga River at State Highway 2	Ruamahanga River at Waihenga	Haast River at Roaring Billy	Waimakariri River at Old H/W Bridge
2,4,6 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
2,3,5 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
2,4,5 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
2,3,6 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
2,3,4 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
2,3,5,6 Tetrachlorophenol	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
2,3,4,6 Tetrachlorophenol	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
2,3,4,5 Tetrachlorophenol	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3	< 3
Pentachlorophenol	< 2	< 3	< 2	< 2	< 3	< 2	< 3	< 2	< 2	< 2	< 2

Table G1 Concentrations of chlorophenols in New Zealand river water (ng L⁻¹) (Cont.)¹

Chlorophenol	Halswell River at McCartneys Bridge (n=2) ²	Taiari River at Sutton Stream	Taiari River at Allanton	Mataura River at Parawa	Mataura River at Seaward Downs	Number of positives	Minimum	Maximum	Median	Mean ³
2,4,6 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	0	< 3	< 3	< 3	-
2,3,5 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	0	< 3	< 3	< 3	-
2,4,5 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	0	< 3	< 3	< 3	-
2,3,6 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	0	< 3	< 3	< 3	-
2,3,4 Trichlorophenol	< 3	< 3	< 3	< 3	< 3	0	< 3	< 3	< 3	-
2,3,5,6 Tetrachlorophenol	< 3	< 3	< 3	< 3	< 3	0	< 3	< 3	< 3	-
2,3,4,6 Tetrachlorophenol	< 3	< 3	< 3	< 3	< 3	0	< 3	< 3	< 3	-
2,3,4,5 Tetrachlorophenol	< 3	< 3	< 3	< 3	< 3	0	< 3	< 3	< 3	-
Pentachlorophenol	< 3	< 3	< 2	< 3	< 2	0	< 2	< 3	< 2	-

1 = For each chlorophenol, the result reported from each sampling site is the average concentration of the 3 individual monthly river water samples analysed

2 = Mean of primary and blind duplicate samples

3 = Mean value reported only if a chlorophenol detected on more than 66% of occasions (minimum of 11 positive determinations)

Table G2 Concentrations of chlorophenols in New Zealand longfinned and shortfinned eel ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Chlorophenol	Waipa River at Whatawhata ¹	Rangitaiki River at Te Teko ²	Waingonoro River at State Highway 45 ⁵	Wanganui River at Te Maitre ¹	Manawatu River at Opiki Bridge ³	Mohaka River at Raupunga ¹	Tukituki River at Tamumu Bridge ⁶	Ruamahanga River at State Highway 2 ²	Ruamahanga River at Waihenga ¹	Haast River at Roaring Billy ⁷	Waimakariri River at Old H/W Bridge ¹
2,4,6 Trichlorophenol	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6	< 0.5	< 0.6	< 0.5	< 0.6	< 0.5	< 0.5
2,3,5 Trichlorophenol	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6	< 0.5	< 0.6	< 0.5	< 0.6	< 0.5	< 0.5
2,4,5 Trichlorophenol	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6	< 0.5	< 0.6	< 0.5	< 0.6	< 0.5	< 0.5
2,3,6 Trichlorophenol	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6	< 0.5	< 0.6	< 0.5	< 0.6	< 0.5	< 0.5
2,3,4 Trichlorophenol	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6	< 0.5	< 0.6	< 0.5	< 0.6	< 0.5	< 0.5
2,3,5,6 Tetrachlorophenol	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6	< 0.5	< 0.6	< 0.5	< 0.6	< 0.5	< 0.5
2,3,4,6 Tetrachlorophenol	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6	< 0.5	< 0.6	< 0.5	< 0.6	< 0.5	< 0.5
2,3,4,5 Tetrachlorophenol	< 0.5	< 0.5	< 0.5	< 0.6	< 0.6	< 0.5	< 0.6	< 0.5	< 0.6	< 0.5	< 0.5
Pentachlorophenol	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.32	< 0.3	< 0.3	< 0.3

Table G2 Concentrations of chlorophenols in New Zealand longfinned and shortfinned eel ($\mu\text{g kg}^{-1}$, wet fillet wt basis) (Cont.)

Chlorophenol	Halswell River at McCartneys Bridge ¹	Taieri River at Sutton Stream ¹	Taieri River at Allanton (n=2) ^{1,4}	Mataura River at Parawā ¹	Mataura River at Seaward Downs (n=2) ^{1,4}	Number of positives	Minimum	Maximum	Median	Mean ⁵
2,4,6 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	0	< 0.5	< 0.6	< 0.6	-
2,3,5 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	0	< 0.5	< 0.6	< 0.6	-
2,4,5 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	0	< 0.5	< 0.6	< 0.6	-
2,3,6 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	0	< 0.5	< 0.6	< 0.6	-
2,3,4 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	0	< 0.5	< 0.6	< 0.6	-
2,3,5,6 Tetrachlorophenol	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	0	< 0.5	< 0.6	< 0.6	-
2,3,4,6 Tetrachlorophenol	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	0	< 0.5	< 0.6	< 0.6	-
2,3,4,5 Tetrachlorophenol	< 0.6	< 0.6	< 0.6	< 0.6	< 0.6	0	< 0.5	< 0.6	< 0.6	-
Pentachlorophenol	< 0.3	0.45	< 0.3	< 0.3	< 0.3	2	< 0.3	0.45	< 0.3	-

1 = Longfinned eel (*Anguilla dieffenbachii*)

2 = Mix of longfinned and shortfinned eel

3 = Shortfinned eel (*Anguilla australis*)

4 = Mean of primary and blind duplicate samples

5 = Mean value reported only if a chlorophenol detected on more than 66% of occasions (minimum of 11 positive determinations)

Table G3 Concentrations of chlorophenols in New Zealand brown and rainbow trout ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Chlorophenol	Waipa River at Whatawhata (n=2) ^{1,2}	Rangitai River at Te Teko ¹	Rangitai River at Te Teko ³	Wanganui River at Te Maire ³	Tukituki River at Tamumu Bridge ³	Ruamahanga River at Waihenga ¹	Waimakariri River at Old H/W Bridge ¹	Halswell River at McCarneys Bridge ¹	Taieri River at Sutton Stream ¹	Taieri River at Allanton ¹	Mataura River at Parawa ¹	Mataura River at Seaward Downs (n=2) ^{1,2}	Number of positives	Minimum	Maximum	Median	Mean ⁴
2,4,6 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	< 0.5	< 0.5	0	< 0.2	< 0.5	< 0.2	-
2,3,5 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	< 0.5	< 0.5	0	< 0.2	< 0.5	< 0.2	-
2,4,5 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	< 0.5	< 0.5	0	< 0.2	< 0.5	< 0.2	-
2,3,6 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	< 0.5	< 0.5	0	< 0.2	< 0.5	< 0.2	-
2,3,4 Trichlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	< 0.5	< 0.5	0	< 0.2	< 0.5	< 0.2	-
2,3,5,6 Tetrachlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	< 0.5	< 0.5	0	< 0.2	< 0.5	< 0.2	-
2,3,4,6 Tetrachlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	< 0.5	< 0.5	0	< 0.2	< 0.5	< 0.2	-
2,3,4,5 Tetrachlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	< 0.5	< 0.5	0	< 0.2	< 0.5	< 0.2	-
Pentachlorophenol	< 0.2	< 0.2	< 0.2	< 0.2	< 0.5	< 0.3	< 0.2	< 0.2	< 0.2	< 0.3	0.8	< 0.5	1	< 0.2	0.8	< 0.2	-

1 = Brown trout (*Salmo trutta*)

2 = Mean of laboratory duplicate analyses

3 = Rainbow trout (*Oncorhynchus mykiss*)

4 = Mean value reported only if a chlorophenol detected on more than 66% of occasions (minimum of 8 positive determinations)

Table G4 Comparative chlorophenol concentrations in primary and blind duplicate river water samples (ng L⁻¹)

Chlorophenol	Manawatu River at Opiki Bridge	Manawatu River at Opiki Bridge	Halswell River at McCartneys Bridge	Halswell River at McCartneys Bridge
	Primary	Blind duplicate	Primary	Blind duplicate
2,4,6 Trichlorophenol	< 3	< 3	< 3	< 3
2,3,5 Trichlorophenol	< 3	< 3	< 3	< 3
2,4,5 Trichlorophenol	< 3	< 3	< 3	< 3
2,3,6 Trichlorophenol	< 3	< 3	< 3	< 3
2,3,4 Trichlorophenol	< 3	< 3	< 3	< 3
2,3,5,6 Tetrachlorophenol	< 3	< 3	< 3	< 3
2,3,4,6 Tetrachlorophenol	< 3	< 3	< 3	< 3
2,3,4,5 Tetrachlorophenol	< 3	< 3	< 3	< 3
Pentachlorophenol	< 3	< 2	< 3	< 2

Table G5 Comparative chlorophenol concentrations in primary and blind duplicate eel samples ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Chlorophenol	Taieri River at Allanton	Taieri River at Allanton	Mataura River at Seaward Downs	Mataura River at Seaward Downs
	Primary	Blind duplicate	Primary	Blind duplicate
2,4,6 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6
2,3,5 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6
2,4,5 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6
2,3,6 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6
2,3,4 Trichlorophenol	< 0.6	< 0.6	< 0.6	< 0.6
2,3,5,6 Tetrachlorophenol	< 0.6	< 0.6	< 0.6	< 0.6
2,3,4,6 Tetrachlorophenol	< 0.6	< 0.6	< 0.6	< 0.6
2,3,4,5 Tetrachlorophenol	< 0.6	< 0.6	< 0.6	< 0.6
Pentachlorophenol	< 0.3	< 0.3	< 0.3	< 0.3

Table G6 Comparative chlorophenol concentrations in primary and split QC river water samples (ng L⁻¹)

Chlorophenol	Waingonoro River at State Highway 45	Waingonoro River at State Highway 45	Mataura River at Seaward Downs	Mataura River at Seaward Downs
	Primary ¹	Split QC ²	Primary	Split QC
2,4,6 Trichlorophenol	< 3	< 5	< 3	< 5
2,3,5 Trichlorophenol	< 3	< 5	< 3	< 5
2,4,5 Trichlorophenol	< 3	< 5	< 3	< 5
2,3,4 Trichlorophenol	< 3	< 5	< 3	< 5
2,3,5,6 Tetrachlorophenol	< 3	< 5	< 3	< 5
2,3,4,6 Tetrachlorophenol	< 3	< 5	< 3	< 5
2,3,4,5 Tetrachlorophenol	< 3	< 5	< 3	< 5
Pentachlorophenol	< 2	< 5	< 2	< 5

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

Table G7 Comparative chlorophenol concentrations in primary and split QC eel and trout samples ($\mu\text{g kg}^{-1}$, wet fillet wt basis)

Chlorophenol	Shortfinned Eel Tukituki River at Tamumu Bridge	Shortfinned Eel Tukituki River at Tamumu Bridge	Longfinned Eel Ruamahanga River at Waihenga	Longfinned Eel Ruamahanga River at Waihenga	Brown Trout Waipa River at Whatawhata	Brown Trout Waipa River at Whatawhata	Brown Trout Mataura River at Seaward Downs	Brown Trout Mataura River at Seaward Downs
	Primary ¹	Split QC ²	Primary	Split QC	Primary	Split QC	Primary	Split QC
2,4,6 Trichlorophenol	< 0.6	< 0.1	< 0.6	< 0.1	< 0.2	< 0.2	< 0.5	< 0.1
2,3,5 Trichlorophenol	< 0.6	< 0.1	< 0.6	< 0.1	< 0.2	< 0.1	< 0.5	< 0.1
2,4,5 Trichlorophenol	< 0.6	< 0.1	< 0.6	< 0.1	< 0.2	< 0.1	< 0.5	< 0.1
2,3,4 Trichlorophenol	< 0.6	< 0.1	< 0.6	< 0.1	< 0.2	< 0.1	< 0.5	< 0.1
2,3,5,6 Tetrachlorophenol	< 0.6	< 0.1	< 0.6	< 0.1	< 0.2	< 0.1	< 0.5	< 0.1
2,3,4,6 Tetrachlorophenol	< 0.6	< 0.1	< 0.6	< 0.1	< 0.2	< 0.1	< 0.5	< 0.1
2,3,4,5 Tetrachlorophenol	< 0.6	< 0.1	< 0.6	< 0.1	< 0.2	< 0.1	< 0.5	< 0.1
Pentachlorophenol	< 0.3	< 0.1	< 0.3	< 0.1	< 0.2	< 0.2	< 0.5	< 0.5

1 = Analysed by primary laboratory

2 = Analysed by independent cross-check laboratory

Appendix H New Zealand and overseas PCDD and PCDF water and biota data

This appendix provides a summary of the New Zealand Organochlorines Programme PCDD and PCDF contaminant level data (as reported in full in Appendix D), and details comparative data for PCDD and PCDF concentrations in river and ocean water and in freshwater and saltwater fish as reported in the published literature.

Table H1 Concentrations of PCDDs and PCDFs in water

Table H2 Concentrations of PCDDs and PCDFs in fish

Table H3 Concentrations of PCDDs and PCDFs eel

Table H1 Concentrations of PCDDs and PCDFs in water

Country	Water type	Date sampled	No. of sites	Concentration (pg L ⁻¹) ¹		Analysis	Reference
				Min.	Max.		
New Zealand	River water	1996	16	0.51 ²	2.4 ²	I-TEQ, ½ LOD	This study
New Zealand, Lake Rotorua	Stream waters	1993	5	nd	5.4	I TEQ, ½ LOD	Gifford <i>et al.</i> , 1996
New Zealand, Lake Rotorua	Lake Rotorua water	1993	4	nd	1.6	I TEQ, ½ LOD	Gifford <i>et al.</i> , 1996
Treated water							
Canada, Ontario	Treated water	1983-87	4	0.02	0.05	I-TEQ, LOD=0	Jobb <i>et al.</i> , 1990
Canada, Ontario	Miscellaneous treated water	1983-89	362	nd	0.00	I-TEQ, LOD=0	Jobb <i>et al.</i> , 1990
Japan, Hirakata, Osaka	Tap water	1991	3	0.1	0.3	I-TEQ, ½ LOD	Miyata <i>et al.</i> , 1992
Russia, Bashkortostan	Ufa urban tap water	1994-97	250	nd	1.0	I-TEQ, ½ LOD	Amirova <i>et al.</i> , 1997
Russia, Bashkortostan	Rural tap water	1996	5	0.1	0.1	I-TEQ, ½ LOD	Amirova <i>et al.</i> , 1997
Sweden	Outlet treated water		2	1.0	1.2	I-TEQ, ½ LOD	Rappe <i>et al.</i> , 1989b
Sweden, Stockholm	Treated and recipient water	1989	2	nd	0.1	Nordic TEQs	Naf <i>et al.</i> , 1990
USA, Lockport, New York	Drinking water supply	1986-87	19	1.4	10.4	I-TEQ, ½ LOD	Meyer <i>et al.</i> , 1989
USA, Lockport, New York	Drinking water	1986-87	4	2.9	27.5	I-TEQ, ½ LOD	Meyer <i>et al.</i> , 1989
Raw water							
Australia, Bass Strait	Woodside beach	1991-92	4	1.8	4.8	I TEQ, ½LOD	Mosse and Haynes, 1993
Australia, Bass Strait	Seaspray beach	1991-92	4	1.7	8.2	I TEQ, ½ LOD	Mosse and Haynes, 1993
Australia, Bass Strait	Delray beach	1991-92	4	2.0	4.9	I TEQ, ½ LOD	Mosse and Haynes, 1993
Canada, BC	Background runoff	1990-93	9	nd	6.4	I-TEQ, LOD=0	Van Oostdam and Ward, 1995
Canada, BC	Background water	1990-93	3	nd	4.3	I-TEQ, LOD=0	Van Oostdam and Ward, 1995
Canada, Ontario	Raw water	1983-87	33	nd	0.18	I-TEQ, LOD=0	Jobb <i>et al.</i> , 1990
Canada, Ontario	Raw water entering treatment plant		1	1.6	1.6	I-TEQ, LOD=0	Gobran <i>et al.</i> , 1995
Finland and Sweden, Baltic Sea	Offshore and coastal water	1988	5	0.0015	0.0028	Nordic TEQ	Broman <i>et al.</i> , 1991
Japan, Nagahama, Hiraka	Well water	1991	3	0.1	0.1	I-TEQ, ½ LOD	Miyata <i>et al.</i> , 1992
Russia, Bashkortostan	River water	1996	8	2.3	5.2	I-TEQ, ½ LOD	Amirova <i>et al.</i> , 1997
Sweden, Eman	Eman River water		3	30.8	99.0	I-TEQ, ½ LOD	Rappe <i>et al.</i> , 1989b
USA, Bayou Meto Stream, Arkansas	Upstream of beach tributary	1993	1	0.0014	0.0014	I TEQ, LOD=0	Lebo <i>et al.</i> , 1995
USA, Bayou Meto Stream, Arkansas	Downstream of beach tributary	1993	1	2.5	2.5	I TEQ, LOD=0	Lebo <i>et al.</i> , 1995
USA, Lockport, New York	Raw water	1988	1	10.4	10.4	I-TEQ, ½ LOD	Meyer <i>et al.</i> , 1989

Table H1 Concentrations of PCDDs and PCDFs in water (Cont.)

Country	Water type	Date sampled	No. of sites	Concentration (pg L ⁻¹) ¹		Analysis	Reference
				Min.	Max.		
Waste water							
Canada, BC	Water, secondary source	1990-93	13	nd	204	I-TEQ, LOD=0	Van Oostdam and Ward, 1995
China, Anhui	Waste water	1995	2	0.1	2.6	I-TEQ	Luksemburg <i>et al.</i> , 1996
China, Jilin	Waste water	1995	3	nd	3.4	I-TEQ	Luksemburg <i>et al.</i> , 1996
Germany, Bayreuth	Urban runoff after rain	1991	4	1.0	10.0	I TEQ, LOD=0	Horstmann and McLachlan, 1995
Germany, Bayreuth	Household wastewater	1992	8	0.8	14.0	I TEQ, LOD=0	Horstmann and McLachlan, 1995
Germany, Bayreuth	Shower water	1991	5	1.8	16.2	I TEQ, LOD=0	Horstmann and McLachlan, 1995
Sweden	Inlet waste water		2	7.8	8.1	I-TEQ, ½ LOD	Rappe <i>et al.</i> , 1989b
Sweden, Stockholm	Urban waste water	1989	2	2.5	3.0	Nordic TEQs	Naf <i>et al.</i> , 1990
USA, San Fransisco Bay	Urban stormwater outfall	1995-96	11	0.1	65.0	I-TEQ, LOD=0	Paustenbach <i>et al.</i> , 1996
USA, San Fransisco Bay	Urban stormwater outfall	1995-96	10	nd	14.0	I-TEQ, LOD=0	Paustenbach <i>et al.</i> , 1996
USA, San Fransisco Bay	Urban stormwater	1995	5	0.6	15.0	I-TEQ	Mathur <i>et al.</i> , 1997
USA, San Fransisco Bay	Urban stormwater	1996	6	0.14	26	I-TEQ	Mathur <i>et al.</i> , 1997
USA, San Fransisco Bay	Petroleum plant storm water	1995	5	1.0	10.0	I-TEQ	Mathur <i>et al.</i> , 1997
USA, San Fransisco Bay	Petroleum plant storm water	1996	5	nd	3.0	I-TEQ	Mathur <i>et al.</i> , 1997

¹ In some instances, TEQ levels have been calculated using the congener data reported in the original reference.

² New Zealand I-TEQ levels from the current study derived solely from inclusion of half LOD values for non-detected PCDD and PCDF congeners. If LOD values are excluded from the calculation, both the minimum and maximum I-TEQ levels = 0 pg L⁻¹
 nd = Not detected.

Table H2 Concentrations of PCDDs and PCDFs in fish

Country	Species	Date sampled	Number of sites	Concentration (ng kg ⁻¹ WW) ¹		Analysis	Reference
				Min.	Max.		
New Zealand	Trout, fillet	1996	11	0.016	0.20	I-TEQ, ½ LOD	This study
	Eel, fillet	1996	16	0.016	0.39	I-TEQ, ½ LOD	This study
New Zealand, Lake Rotorua	Trout muscle	1993	1	0.082	0.74	I-TEQ, ½ LOD	Gifford <i>et al.</i> , 1996
Australia, Lake Coleman	Carp muscle fillets, composite	1990	1	0.48	4.0	I-TEQ, ½ LOD	Ahokas <i>et al.</i> , 1994
Bavaria	Carp, farmed		1	0.11	1.58	I-TEQ	Mayer, 1995
Bavaria	Trout, free		1	0.16	0.74	I-TEQ	Mayer, 1995
Bavaria	Carp, free		1	0.03	5.26	I-TEQ	Mayer, 1995
Canada, BC	Fish, background waters	1990-93	1	0.12	0.12	I-TEQ, LOD=0	Van Oostdam and Ward, 1995
Canada, BC	Fish, secondary source pollution	1990-93	4	nd	0.19	I-TEQ, LOD=0	Van Oostdam and Ward, 1995
Canada, Lake Erie	Carp, walleye, salmon, catfish	1990-93	4	0.5	9	I-TEQ, ½ LOD	Reiner <i>et al.</i> , 1995
Canada, Lake Huron	Trout, whitefish, salmon, catfish	1990-94	12	0.5	13	I-TEQ, ½ LOD	Reiner <i>et al.</i> , 1995
Canada, Lake Ontario	Trout and salmon, muscle		4	9.7	13.4	COM-TEQ	Niimi and Oliver, 1989
Canada, Lake Ontario	Trout and salmon	1991-94	21	5.0	63	I-TEQ, ½ LOD	Reiner <i>et al.</i> , 1995
Canada, Lake Superior	Trout and whitefish, various bays and harbours	1989-93	8	0.5	15	I-TEQ, ½ LOD	Reiner <i>et al.</i> , 1995
Canada, Ontario bays/rivers	Reference sites	1991	3	1.23	3.14	I TEQs, ½ LOD	Servos <i>et al.</i> , 1994
Canada, St Maurice River	White sucker, upstream of mill	1989	1	0.78	23.8	³ TEQ of Walker, ½ LOD	Hodson <i>et al.</i> , 1992b
Canada, St Maurice River	White sucker, downstream of mill	1989	3	2.08	46.0	³ TEQ of Walker, ½ LOD	Hodson <i>et al.</i> , 1992b
Canada, St Maurice River	Pike, walleye, bass, general sites	1989	5	1.26	36.5	³ TEQ of Walker, ½ LOD	Hodson <i>et al.</i> , 1992b
Canada, St Maurice River	Pike, walleye, sucker, fallfish, industrial waters	1989	6	11.2	82.9	³ TEQ of Walker, ½ LOD	Hodson <i>et al.</i> , 1992b
Finland	Rainbow trout		1	0.23	1.47	Nordic TEQ, ½ LOD	Vartiainen and Hallikainen, 1992
Finland, Ahvenkoskenlhti Bay	Burbot and bream, muscle tissue	1996	1	0.4	84.2	I-TEQ	Korhonen <i>et al.</i> , 1997
Finland, Kymijoki River	Pike, perch, bream near outfall		6	0.1	0.9	Nordic TEQ, LOD=0	Koistinen <i>et al.</i> , 1993
Finland, Kymijoki River	Burbot, pike, perch, bream, in river	1996	8	0.70	122	I-TEQ	Korhonen <i>et al.</i> , 1997
Finland, Kymijoki River	Burbot, pike, perch, bream, in estuary	1996	11	0.30	82.4	I-TEQ	Korhonen <i>et al.</i> , 1997
Finland, Kymijoki River	Pike and perch, near outfall		2	0.2	4.3	Nordic TEQ, LOD=0	Koistinen <i>et al.</i> , 1993
Finland, Subarctic lakes	Trout muscle, lake at NE Lapland	1993-94	4	0.005	0.16	I-TEQ, ½ LOD	Vartiainen <i>et al.</i> , 1996
Germany, Elbe River	Bream, Gorleben, upstream	1986	2	7.3	9.5	Nordic TEQs	Luckas and Oehme, 1990
Germany, Elbe River	Bream, Muhlenberger	1986	3	4.1	23.8	Nordic TEQs	Luckas and Oehme, 1990
Germany, Hamburg	Bream	1984	1	1.4	94.4	US EPA, LOD=0	² Gotz and Schumacher, 1990
Germany, Hamburg	Perch	1984	1	1.8	8.1	US EPA, LOD=0	² Gotz and Schumacher, 1990
Germany, Neckar	Trout, grayling, carp, barbel, chub	1988	4	0.40	2.9	I-TEQ	Frommberger, 1991

Table H2 Concentrations of PCDDs and PCDFs in fish (Cont.)

Country	Species	Date sampled	Number of sites	Concentration (ng kg ⁻¹ WW) ¹		Analysis	Reference
				Min.	Max.		
Japan, Lake Kasumigaura	Various	1994	1	0.4	2.64	I-TEQ, LOD=0	Sakurai <i>et al.</i> , 1996
Sweden, Baltic Sea	Arctic char, Lake Vattern		5	14.25	59.3	I TEQ, ½ LOD	Rappe <i>et al.</i> , 1989a
USA	Fish tissue, pristine sites	1986-89	34	nd	3.02	US EPA, ½ LOD, no Octas	US EPA, 1992
USA	Fish tissue, all data	1986-89	388	nd	213	US EPA, ½ LOD, no Octas	US EPA, 1992
USA	Fish tissue, agricultural sites	1986-89	17	nd	4.44	US EPA, ½ LOD, no Octas	US EPA, 1992
USA	Various US watersheds	1986-89	400	nd	334	EPA QA, ½ LOD	Kuehl <i>et al.</i> , 1994
USA	Fish tissue, urban-industrial	1986-89	105	nd	61.0	US EPA, ½ LOD, no Octas	US EPA, 1992
USA, Buffalo River, NY	Carp muscle	1991	2	0.1	1.8	I TEQs	Loganathan <i>et al.</i> , 1995
USA, Great Lakes	Trout, walleye, L. Superior	1984	8	5.3	67.0	I-TEQ, ½ LOD	De Vault <i>et al.</i> , 1989
USA, Great Lakes	Lake Michigan fish	1984	10	15.6	54.2	I-TEQ, ½ LOD	De Vault <i>et al.</i> , 1989
USA	Rainbow and lake trout		2	45	47.7	I-TEQ, LOD=0	Ryan <i>et al.</i> , 1983b
USA, Minnesota	Fillet, Lake Orono fish	1988-90	3	0.17	1.51	I TEQ, LOD=0	Reed <i>et al.</i> , 1990
USA, Mississippi River	Fillet, Mississippi River fish	1988-90	3	3.07	10.6	I TEQ, LOD=0	Reed <i>et al.</i> , 1990
World wide, various	Fish, various, summary of data		2482	nd	1430	⁴ US EPA TEQ, LOD=0	² Clarke <i>et al.</i> , 1996

¹ In some instances, TEQ levels have been calculated using the congener data reported in the original reference.

² Secondary reference (data taken from a citation rather than original paper).

³ TEQs from: Walker, M.K. and Peterson, R.E., 1992, *Aquat. Toxicol.*, 21, 219-238.

⁴ These TEQs were estimated using US EPA TEFs from: US EPA, 1989, Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs and CDFs) and 1989 Update, EPA/625/3-89/016.

nd = Not detected.

Table H3 Concentrations of PCDDs and PCDFs in eel (freshwater and saltwater)¹

Country	Species, location ¹	Date sampled	Number of sites	Concentration (ng kg ⁻¹ WW) ^{2,3}		Analysis	Reference
				Min.	Max.		
New Zealand	Eel, fillet	1996	16	0.016	0.39	I-TEQ, ½ LOD	This study
Canada, Lake Ontario	American eel, East Lake Ontario	1994	1	13.0	13.0	I-TEQ, ½ LOD	Reiner <i>et al.</i> , 1995
Canada, Quebec	Silver eels, Riviere aux Pins	1990	1	0.80	0.80	I-TEQ, ½ LOD	Hodson <i>et al.</i> , 1994
Canada, Quebec	Silver eels, Kamouraska	1990	7	0.16	2.30	I-TEQ, ½ LOD	Hodson <i>et al.</i> , 1994
Germany, Rhine	Eel fillet	1987	2	2.9	5.4	I-TEQ	Frommberger, 1991
Germany, Neckar	Eel fillet	1987	4	0.94	3.6	I-TEQ	Frommberger, 1991
Germany, Rhine	Eel edible tissue	1995	3	1.35	7.79	I-TEQ	Rainer, 1996
Netherlands	Eel at market	1987-88	6	28	28 (lipid wt)	Dutch TEQ	Theelen <i>et al.</i> , 1993
Netherlands	Yellow eel, freshwater	1991	6	0.32	4.2	I-TEQ	de Boer <i>et al.</i> , 1993
Netherlands, Amsterdam	Eel, Volgermeerpolder	1991	1	2	52 (lipid wt)	Dutch or NATO TEQ	van der Oost <i>et al.</i> , 1996
Netherlands, Amsterdam	Eel, Volgermeerpolder	1994	1	6.56	194 (lipid wt)	I-TEQ, LOD=0	Heida and van der Oost, 1995
Netherlands, Amsterdam	Eel, Diemerzeedijk	1991	1	nd	38.7 (lipid wt)	Dutch or NATO TEQ	van der Oost <i>et al.</i> , 1996
Netherlands, Dutch waters	Eel flesh, various locations	1989	3	2.0	5.0	Dutch TEQ	Turkstra and Pols, 1989
Netherlands, Dutch waters	Eel flesh, industrial sites	1989	2	6.0	8.0	Dutch TEQ	Turkstra and Pols, 1989
Norway	Eel, various locations	1988-94	50	0.16	1.98	Nordic TEQ	Knutzen and Schlabach, 1996
Norway, Frierfjord	Eel fillet, coast and Bays, saltwater	1987-88	3	6.3	20	Nordic TEQ	Knutzen and Oehme, 1989
Norway, Frierfjord	Eel, fillet, saltwater	1988-94	50	6.38	42.6	Nordic TEQ	Knutzen and Schlabach, 1996
Norway, Frierfjord	Eel fillet, Bay near outfall, saltwater	1987-88	1	22	22	Nordic TEQ	Knutzen and Oehme, 1989
Sweden	Eel fillets	1987-88	1	nd	9.6	US EPA, ½ LOD	⁴ Oehme <i>et al.</i> , 1989
United Kingdom	Eel samples	1992	24	2.6	15 (lipid wt)	I-TEQs	Ministry of Agriculture, Fisheries and Food, 1997
World wide	Eel, muscle	1996	5	6.7	65.9	⁵ US EPA TEQ, LOD=0	⁴ Clarke <i>et al.</i> , 1996

¹ Locations are mainly freshwater sites unless otherwise indicated.

² In some instances, TEQ levels have been calculated using the congener data reported in the original reference.

³ TEQs reported on a wet weight or whole weight basis unless otherwise specified.

⁴ Secondary reference (data taken from a citation rather than original paper).

⁵ These TEQs were estimated using US EPA TEFs from: US EPA, 1989, Interim Procedures for Estimating Risks Associated with Exposures to Mixtures of Chlorinated Dibenzo-p-dioxins and Dibenzofurans (CDDs and CDFs) and 1989 Update, EPA/625/3-89/016.

nd = Not detected.

Appendix I New Zealand and overseas PCB water and biota data

This appendix provides a summary of the New Zealand Organochlorines Programme PCB contaminant level data (as reported in full in Appendix E), and details comparative data for PCB concentrations in river water and in freshwater and salt water fish as reported in the published literature.

Table I1	Concentrations of PCBs in freshwater
Table I2	Concentrations of PCBs in fish
Table I3	Concentrations of PCB #77 in freshwater fish
Table I4	Concentrations of PCB #126 in freshwater fish
Table I5	Concentrations of PCB #169 in freshwater fish
Table I6	Concentrations of PCB #28 + #31 in freshwater fish
Table I7	Concentrations of PCB #52 in freshwater fish
Table I8	Concentrations of PCB #101 in freshwater fish
Table I9	Concentrations of PCB #118 in freshwater fish
Table I10	Concentrations of PCB #105 in freshwater fish
Table I11	Concentrations of PCB #153 in freshwater fish
Table I12	Concentrations of PCB #138 in freshwater fish
Table I13	Concentrations of PCB #156 in freshwater fish
Table I14	Concentrations of PCB #180 in freshwater fish

Table 11 Concentrations of PCBs in freshwater

Country	Water type	Date sampled	Concentration (ng L ⁻¹)		Data type	Reference
			Min.	Max.		
New Zealand	River water	1996	1.1 ¹	1.6 ¹	Sum of 25 congeners	This study
Antarctic	Lake water	1980-82	0.048	0.048	Total PCBs	Tanabe <i>et al.</i> , 1983
Argentina	Rio de La Plata	1986	20.5	56.5	Sum of 10 congeners	Colombo <i>et al.</i> , 1990
Australia	Various ²	1990	< 0.05	2.2	Total PCBs	Iwata <i>et al.</i> , 1994
Canada	North Ontario	1984	0.21	0.43	Total PCBs	Lockhart <i>et al.</i> , 1992
	North Quebec	1987	< 9	< 9	Total PCBs	Lockhart <i>et al.</i> , 1992
Egypt	River Nile	1982-83	8	54	Total PCBs	Badawy and Aly, 1986
	Ismalia and El-Mahmodia	1982-83	23	77	Total PCBs	Badawy and Aly, 1986
	Nile Delta		8.3	653	Total PCBs	El-Gendy <i>et al.</i> , 1991
France	Urban runoff	1989	36	2600	Sum of 7 congeners	Granier <i>et al.</i> , 1990
	River Marne	1985-90	< 5	7800	Total PCBs	Chevreuil and Granier, 1991
Germany	River Lippe	1987	< 10	340	Sum of 6 congeners	Friege <i>et al.</i> , 1989
Great Lakes	Niagara River	1979-81		19.9 ³	Total PCBs	Kuntz and Warry, 1983
	Saginaw River	1991	10	46	Total PCBs	Verbrugge <i>et al.</i> , 1995
India	Various ²	1989	0.34	48	Total PCBs	Iwata <i>et al.</i> , 1994
Indonesia	Various ²	1991	0.38	2.1	Total PCBs	Iwata <i>et al.</i> , 1994
Italy	River Po	1977-78	< 20	100	Total PCBs	Galassi and Provini, 1981
	River Adige	1977-78	< 20	100	Total PCBs	Galassi and Provini, 1981
Malaysia	Rural	1991	0.45	0.45	Total PCBs	Iwata <i>et al.</i> , 1994
Russia	Lake Baikal	1991	0.3	1.1	Total PCBs	Kucklick <i>et al.</i> , 1994
Slovenia	River Krupa	1987		251 ³	Total PCBs	Jan <i>et al.</i> , 1994
Solomon Islands	Various ²	1990	< 0.05	1.1	Total PCBs	Iwata <i>et al.</i> , 1994
Spain	Doñana		76	1450	Total PCBs	Fernandez <i>et al.</i> , 1992
Sweden	River Emån	1991	0.4	20.8	Total PCBs	Bremle <i>et al.</i> , 1995
Taiwan	Various ²	1990	0.085	2.1	Total PCBs	Iwata <i>et al.</i> , 1994
Thailand	Various ²	1990	< 0.24	4.4	Total PCBs	Iwata <i>et al.</i> , 1994
USA	Hudson River	1983	100	586	Total PCBs	Bush <i>et al.</i> , 1985
USA (Lake Michigan)	Open water and Green Bay	1980	0.36	121	Total PCBs	Swackhamer and Armstrong, 1987
USA (Tennessee)	Oak Ridge reserve	1993	nd	124	Total PCBs	Napolitano and Richmond, 1995
Vietnam	Various ²	1990	0.57	8	Total PCBs	Iwata <i>et al.</i> , 1994
Yugoslavia	River Krupa	1985-86	1	52	Total PCBs	Smit <i>et al.</i> , 1987

¹ New Zealand PCB concentration data from the current study derived solely from inclusion of half LOD values for non-detected congeners. If LOD values are excluded from the calculation, both the minimum and maximum sum of PCB congener concentrations = 0 ng L⁻¹

² Samples included a range of urban and rural waters and also some industrial and sewage samples. A small proportion of the samples were seawater.

³ Mean concentration.

nd = Not detected.

Table I2 Concentrations of PCBs in fish

Country	Species	Date sampled	Concentration ($\mu\text{g kg}^{-1}$ WW)		Data type	Reference
			Min.	Max.		
New Zealand	Trout, fillet	1996	0.11	8.80	Sum of 25 congeners	This study
	Eel, fillet	1996	0.39	18.5	Sum of 25 congeners	This study
New Zealand	Waikato/Waipā catchment	1996	1.04	21.1	Sum of 24 congeners	Jones, 1996
Antarctic	Marine fish	1981	0.08	0.77	Total PCBs	Subramanian <i>et al.</i> , 1983
Canada	Lake whitefish/north	1986	2.8	9.61	Sum of homologues	Lockhart <i>et al.</i> , 1992
	Eels, St Lawrence River	1990	612	2130	Total PCBs	Hodson <i>et al.</i> , 1994
Falklands	Marine fish	1988	2.9	3.1	Sum of 27 congeners	de Boer and Wester, 1991
Finland	Salmon muscle	1983-89	572	6850	Total PCBs	Paasivirta <i>et al.</i> , 1990
Germany	Bream, River Elbe	1986	365	2100	Total PCBs	Luckas and Oehme, 1990
Iceland	Brown trout liver	1972	0.13	0.13	Total PCBs	Bengston, 1974
Italy	RBT, River Po caged 30 days		10.2	62	Total PCBs	Vigano <i>et al.</i> , 1994
Netherlands	Eel, Amsterdam		393	877	Total PCBs	van der Oost <i>et al.</i> , 1996
Netherlands	Eel, various rivers	1991	39.1	1930	Sum of 7 congeners	de Boer <i>et al.</i> , 1993
Portugal	Tagus estuary		73	286	Sum of 13 congeners	Benoliel and Shirley, 1988
South Africa	Wilderness Lakes system	1983	< 1	< 1	Total PCBs	De Kock and Boshoff, 1987
Spain	Eel, Ebro delta	1985	235	235		Ruiz and Llorente, 1991
	Carp, Ebro delta	1985	210	210		Ruiz and Llorente, 1991
Sweden	Lake salmonids		0.6	41	Total PCBs	Andersson <i>et al.</i> , 1988
Sweden	Arctic char and whitefish	1986-87	3.8	191	Sum of 7 congeners	Jansson <i>et al.</i> , 1993
	Eel	1992-93	101	347	Sum of 7 congeners	Atuma <i>et al.</i> , 1996
Switzerland	Brown trout, Lake Geneva	1984	140	575	Total PCBs	Devaux and Monod, 1987
USA	Various, 3 Michigan rivers	1990	20	6000	Total PCBs	Giesy <i>et al.</i> , 1994
USA	Catfish, Mississippi	1987	< 5	138	Total PCBs	Leiker <i>et al.</i> , 1991
USA	All species, all sites ¹	1985-90	< 15	124000	Total PCBs	US EPA, 1992
United Kingdom	Eel, reedbeds	1991	< 10	910		Mason, 1993
Vietnam	Food fish, marine and fresh			10	Total PCBs	Kannan <i>et al.</i> , 1992

¹ 314 locations, most samples of 14 species of fish although a total of 119 species were collected.

Table 13 Concentrations of PCB #77 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.001	< 0.002	This study
	Eel, fillet	< 0.001	< 0.006	This study
New Zealand	Eel, Waikato/Waipā catchment	< 0.001	< 0.008	Jones, 1996
Finland	Rainbow trout	0.008	0.150	Himberg, 1993
Finland	Salmon	1.5	18.5	Paasivirta <i>et al.</i> , 1990
Netherlands	Eel, various rivers and lakes	0.0075	0.4	de Boer <i>et al.</i> , 1993
Sweden	Char, whitefish	0.017	0.95	Jansson <i>et al.</i> , 1993
USA	Lake Michigan chinook salmon	0.46	5.34	Williams <i>et al.</i> , 1992

Table 14 Concentrations of PCB #126 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.001	< 0.002	This study
	Eel, fillet	< 0.001	0.01	This study
New Zealand	Eel, Waikato/Waipā catchment	< 0.001	< 0.005	Jones, 1996
Finland	Rainbow trout	0.005	0.035	Himberg, 1993
Finland	Salmon	0.18	1.97	Paasivirta <i>et al.</i> , 1990
Netherlands	Eel, various rivers and lakes	0.018	0.58	de Boer <i>et al.</i> , 1993
Sweden	Char, whitefish	0.0032	0.37	Jansson <i>et al.</i> , 1993
USA	Lake Michigan chinook salmon	< 0.08	1.35	Williams <i>et al.</i> , 1992

Table 15 Concentrations of PCB #169 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.001	< 0.002	This study
	Eel, fillet	< 0.001	< 0.003	This study
New Zealand	Eel, Waikato/Waipā catchment	< 0.001	< 0.001	Jones, 1996
Finland	Rainbow trout	< 0.05	0.0074	Himberg, 1993
Finland	Salmon	< 0.1	0.63	Paasivirta <i>et al.</i> , 1990
Netherlands	Eel, various rivers and lakes	0.003	0.24	de Boer <i>et al.</i> , 1993
Sweden	Char, whitefish	0.0018	0.064	Jansson <i>et al.</i> , 1993
USA	Lake Michigan chinook salmon	< 0.08	< 0.08	Williams <i>et al.</i> , 1992

Table 16 Concentrations of PCB #28 + #31 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	0.041	0.22	This study
	Eel, fillet	0.034	0.40	This study
New Zealand	Eel, Waikato/Waipā catchment	< 0.02	0.93	Jones, 1996
Falkland Islands	Marine fish	0.05	0.06	de Boer and Wester 1991
Netherlands	Eel, clean lake		3.98 ¹	van der Oost <i>et al.</i> , 1988
Portugal	Eel	0.41	4.9	Benoliel and Shirley, 1990
Sweden	Char, whitefish	< 0.007	0.74	Jansson <i>et al.</i> , 1993
Sweden	Eel	0.04	3.2	Atuma <i>et al.</i> , 1996
USA	Lake Ontario salmonids	36	36	Oliver and Niimi, 1988
	Eel, St Lawrence River	2	12	Hodson <i>et al.</i> , 1994
	Eel, St Lawrence River	1.29	17.31	Hodson <i>et al.</i> , 1992a

¹ Mean concentration.

Table 17 Concentrations of PCB #52 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	0.015	0.16	This study
	Eel, fillet	0.019	0.38	This study
New Zealand	Eel, Waikato/Waipā catchment	0.014	0.49	Jones, 1996
Falkland Islands	Marine fish	0.06	0.1	de Boer and Wester, 1991
Netherlands	Eel, clean lake		14.7 ¹	van der Oost <i>et al.</i> , 1988
Portugal	Eel	0.4	3.4	Benoliel and Shirley, 1990
Sweden	Char, whitefish	< 0.007	2.5	Jansson <i>et al.</i> , 1993
Sweden	Eel	2.9	10	Atuma <i>et al.</i> , 1996
USA	Lake Ontario salmonids	62	62	Oliver and Niimi, 1988
	Eel, St Lawrence River	23	56	Hodson <i>et al.</i> , 1994
	Eel, St Lawrence River	2.46	33.5	Hodson <i>et al.</i> , 1992b

¹ Mean concentration.

Table 18 Concentrations of PCB #101 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.01	0.89	This study
	Eel, fillet	0.037	2.13	This study
New Zealand	Eel Waikato/Waipā catchment	0.096	1.82	Jones, 1996
Falkland Islands	Marine fish	0.09	0.1	de Boer and Wester, 1991
Germany	River Elbe bream	19	32	Luckas and Oehme, 1990
Netherlands	Eel, clean lake		28.4 ¹	van der Oost <i>et al.</i> , 1988
Portugal	Eel	1.9	7.5	Benoliel and Shirley, 1990
Sweden	Char, whitefish	0.36	13.8	Jansson <i>et al.</i> , 1993
Sweden	Eel	5.3	43	Atuma <i>et al.</i> , 1996
USA	Lake Ontario salmonids	270	270	Oliver and Niimi, 1988
	Eel, St Lawrence River	22	57	Hodson <i>et al.</i> , 1994
	Eel, St Lawrence River (#90 + #101)	4.28	68.9	Hodson <i>et al.</i> , 1992a

¹ Mean concentration.

Table I9 Concentrations of PCB #118 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.01	0.29	This study
	Eel, fillet	0.026	2.75	This study
New Zealand	Eel, Waikato/Waipua catchment	0.073	1.82	Jones, 1996
Falkland Islands	Marine fish	0.11	0.14	de Boer and Wester, 1991
Finland	Salmon	190	340	Paasivirta <i>et al.</i> , 1990
Netherlands	Eel, various rivers and lakes	7.9	340	de Boer <i>et al.</i> , 1993
Sweden	Char, whitefish	0.30	17.0	Jansson <i>et al.</i> , 1993
Sweden	Eel	15	64	Atuma <i>et al.</i> , 1996
USA	Lake Michigan chinook salmon	14.8	120	Williams <i>et al.</i> , 1992
	Lake Ontario salmonids	250	250	Oliver and Niimi, 1988
	Eel, St Lawrence River	52	156	Hodson <i>et al.</i> , 1994
	Eel, St Lawrence River	9.16	133	Hodson <i>et al.</i> , 1992a

Table I10 Concentrations of PCB #105 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.01	0.17	This study
	Eel, fillet	< 0.01	0.54	This study
New Zealand	Eel, Waikato/Waipua catchment	0.014	0.41	Jones, 1996
Falkland Islands	Marine fish	0.04	0.04	de Boer and Wester, 1991
Finland	Rainbow trout	0.41	2.1	Himberg, 1993
Finland	Salmon	0.35	170	Paasivirta <i>et al.</i> , 1990
Netherlands	Eel, various rivers and lakes	1.9	110	de Boer <i>et al.</i> , 1993
USA	Lake Michigan chinook salmon	5.5	51.2	Williams <i>et al.</i> , 1992
	Lake Ontario salmonids	110	110	Oliver and Niimi, 1988

Table I11 Concentrations of PCB #153 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.01	1.65	This study
	Eel, fillet	0.064	3.84	This study
New Zealand	Eel, Waikato/Waipua catchment	0.34	3.91	Jones, 1996
Falkland Islands	Marine fish	0.28	0.45	de Boer and Wester, 1991
Germany	River Elbe bream	43	67	Luckas and Oehme, 1990
Netherlands	Eel, various rivers and lakes	28	1460	de Boer <i>et al.</i> , 1993
Netherlands	Eel, clean lake		89.0 ¹	van der Oost <i>et al.</i> , 1988
Portugal	Eel	34	123	Benoliel and Shirley, 1990
Sweden	Char, whitefish	1.32	63.6	Jansson <i>et al.</i> , 1993
Sweden	Eel	43	112	Atuma <i>et al.</i> , 1996
USA	Lake Ontario salmonids	430	430	Oliver and Niimi, 1988
	Eel, St Lawrence River	76	219	Hodson <i>et al.</i> , 1994
	Eel, St Lawrence River (#132 + #153 + #105)	10.4	158	Hodson <i>et al.</i> , 1992a

¹ Mean concentration.

Table I12 Concentrations of PCB #138 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.01	1.99	This study
	Eel, fillet	0.15	4.89	This study
New Zealand	Eel, Waikato/Waipua catchment	0.46	5.81	Jones, 1996
Falkland Islands	Marine fish (#138 + #163)	0.26	0.31	de Boer and Wester, 1991
Germany	River Elbe bream	35	61	Luckas and Oehme, 1990
Netherlands	Eel, clean lake		97.3 ¹	van der Oost <i>et al.</i> , 1988
Portugal	Eel	28	82	Benoliel and Shirley, 1990
Sweden	Char, whitefish	1.29	68.9	Jansson <i>et al.</i> , 1993
Sweden	Eel	25	89	Atuma <i>et al.</i> , 1996
USA	Lake Ontario salmonids	260	260	Oliver and Niimi, 1988
	Eel, St Lawrence River	63	192	Hodson <i>et al.</i> , 1994
	Eel, St Lawrence River	0.62	70.9	Hodson <i>et al.</i> , 1992a

¹ Mean concentration.

Table I13 Concentrations of PCB #156 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.01	0.066	This study
	Eel, fillet	< 0.01	0.19	This study
New Zealand	Eel, Waikato/Waipua catchment	0.017	0.24	Jones, 1996
Finland	Salmon	29	39	Paasivirta, <i>et al.</i> , 1990
Netherlands	Eel, various rivers and lakes	1.3	57	de Boer <i>et al.</i> , 1993
USA	Lake Michigan chinook salmon	3.2	34.2	Williams <i>et al.</i> , 1992
	Lake Ontario salmonids	34	34	Oliver and Niimi, 1988
	Eel, St Lawrence River (#202 + #171 + #156)	2.00	37.3	Hodson <i>et al.</i> , 1992a

Table I14 Concentrations of PCB #180 in freshwater fish

Country	Species	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
		Min.	Max.	
New Zealand	Trout, fillet	< 0.01	0.51	This study
	Eel, fillet	0.32	0.92	This study
New Zealand	Eel, Waikato/Waipua catchment	0.10	0.94	Jones, 1996
Falkland Islands	Marine fish	0.15	0.16	de Boer and Wester, 1991
Germany	River Elbe bream	13	28	Luckas and Oehme, 1990
Netherlands	Eel, clean lake		40.9 ¹	van der Oost <i>et al.</i> , 1988
Portugal	Eel	nd	41	Benoliel and Shirley, 1990
Sweden	Char, whitefish	0.59	24.9	Jansson <i>et al.</i> , 1993
Sweden	Eel	9.3	26	Atuma <i>et al.</i> , 1996
USA	Lake Ontario salmonids	200	200	Oliver and Niimi, 1988
	Eel, St Lawrence River	37	113	Hodson <i>et al.</i> , 1994
	Eel, St Lawrence River	1.85	29.3	Hodson <i>et al.</i> , 1992a

¹ Mean concentration.

Appendix J New Zealand and overseas organochlorine pesticide freshwater and freshwater fish data

This appendix provides a summary of the New Zealand Organochlorines Programme pesticide contaminant level data (as reported in full in Appendix F), and details comparative data for pesticide concentrations in freshwater and freshwater fish as reported in the published literature.

Table J1	Concentrations of DDT residues in freshwater
Table J2	Concentrations of DDT residues in freshwater fish
Table J3	Concentrations of aldrin and dieldrin residues in freshwater
Table J4	Concentrations of aldrin and dieldrin residues in freshwater fish
Table J5	Concentrations of HCB residues in freshwater
Table J6	Concentrations of HCB residues in freshwater fish

Table J1 Concentrations of DDT residues in freshwater

Country	Water type	Date sampled	Number of sites	Concentration range (ng L ⁻¹)			Reference	
				Sum DDT	pp'-DDT	pp'-DDE		pp'-TDE
New Zealand	River water	1996	16		< 0.1-< 0.2	< 0.1-< 0.9	< 0.1	This study
Argentina/Uruguay	River	1988-89			nd -18	nd-8	nd	Janiot <i>et al.</i> , 1994
Australia	Various	1989-91	20	0.001-1.1	< 0.001-0.13	0.001-0.17	< 0.001-0.75	Iwata <i>et al.</i> , 1994
Australia	River	1990			nd-340	nd-2.4	nd-2.9	McKenzie Smith <i>et al.</i> , 1994
Canada	Filtered	1990-91	14	nd-1.0	nd-0.27	nd-0.30	nd-0.005	Pham <i>et al.</i> , 1993
Canada	Unfiltered	1990-91	14	0.26-2.7	nd-1.5	nd-0.56	nd-0.23	Pham <i>et al.</i> , 1993
China		1988-90	4	40-264				GEMS website
Croatia	River unfiltered	1988-89	2		nd-6	nd-4	nd-4	Fingler <i>et al.</i> , 1992
Danube-Ukraine	River	1978-85		3-590				Braginsky <i>et al.</i> , 1990
Egypt	Irrigation canals				nd-3	nd-10.4	nd-4	Ismail <i>et al.</i> , 1995
Egypt	River unfiltered		8	0.27-100	nd-41	0.25-81	nd-69	El Gendy <i>et al.</i> , 1991
Egypt	River unfiltered	1982	5		0.1-24	0.2-13	2.3-29	El Dib and Badawy, 1985
Germany	River/lake/canal	1987	10	11-230				Terytze and Mende, 1993
Greece	Filtered	1992-93	3		nd	1-3	nd-2	Tsipi and Hiskia, 1996
India	Various	1989-91	8	0.87-120	0.044-25	0.083-1.8	0.047-89	Iwata <i>et al.</i> , 1994
India	Drinking water ponds			3.7-35	nd-6	nd-0.2	1.2-27	Dikshith <i>et al.</i> , 1990
India	River	1992		100-143000	nd-80000	nd-14000		Nemecek <i>et al.</i> , 1994
India	River (site means)	1988-89		nd-24000	nd-800	nd-500	nd-500	Nair and Pillai, 1992
India	Pond filtered	1992	22	nd-15000	nd-9500	nd-3200		Dua <i>et al.</i> , 1996
India	Unfiltered	1992	34	100-143000	nd-80000	nd-18000		Nayak <i>et al.</i> , 1995
India		1991-92			nd-331	nd-532		Agnihotri <i>et al.</i> , 1994
Indonesia	Various	1989-91	3	0.19-0.27	0.016-0.087	3.1-22	0.038-0.087	Iwata <i>et al.</i> , 1994
Ivory Coast	Unfiltered		5		nd-400	nd		Wandan and Zabik, 1996
Japan		1988-90	7	< 7-100				GEMS website
Malaysia	Various	1989-91	1	1.7	0.21	0.25	1.2	Iwata <i>et al.</i> , 1994
Serbia	River	1988	2	86-110	19-23	67-87		Vojinovic <i>et al.</i> , 1990
Solomon Islands	Various	1989-91	5	0.062-21	0.039-16	0.009-2	0.004-0.14	Iwata <i>et al.</i> , 1994
South Africa	Unfiltered	1984-85	15		nd-800			Hassett <i>et al.</i> , 1987
Spain		1982-86	10		9-350	10-350	nd-40	Rico <i>et al.</i> , 1989
Taiwan	Various	1989-91	3	0.01-0.19	< 0.002-0.013	0.007-0.13	0.002-0.037	Iwata <i>et al.</i> , 1994
Thailand	River	1988-91	32		nd-29	nd-18	nd-18	Tabucanon <i>et al.</i> , 1992
Thailand	Various	1989-91	4	0.23-2.5	0.031-1.2	0.038-0.15	0.12-0.93	Iwata <i>et al.</i> , 1994
United Kingdom		1988-90	8	< 1-60				GEMS website
USA, CA	River	1992	4	nd-24	nd-2	nd-19	nd-3.5	Pereira <i>et al.</i> , 1996
USA, WA	Unfiltered	1985	8	nd-60	nd-40	nd-30	nd-10	Johnson <i>et al.</i> , 1988
Vietnam	Various	1989-91	7	0.29-25	0.031-9	0.015-3.2	0.23-11	Iwata <i>et al.</i> , 1994

nd = Not detected.

Table J2 Concentrations of DDT residues in freshwater fish

Country	Species	Date sampled	Number of sites	Concentration range ($\mu\text{g kg}^{-1}$ WW)			Reference	
				Sum DDT	pp'-DDT	pp'-DDE		pp'-TDE
New Zealand	Trout, fillet	1996	12		0.16-0.91	1.82-73.9	0.043-1.97	This study
New Zealand	Eel, fillet	1996	16		0.1-25.5	0.67-155	0.032-33.1	This study
Australia	Various (river and coastal)	1990-92	6	0.1-230				Kannan <i>et al.</i> , 1994
Canada	Various, whole	1981-87	8	tr-190				Suns and Hitchin, 1992
Danube-Ukraine	Various	1978-85		nd - 5700				Braginsky <i>et al.</i> , 1990
Egypt	Bolti fish, edible parts	1985	1	340	nd	120	440	Dogheim <i>et al.</i> , 1988
Egypt	Catfish, edible parts	1985	1	904	60	490	460	Dogheim <i>et al.</i> , 1988
Egypt	<i>Tilapia</i> spp., fillet	1985	2	20-41	5-17	11-17	3-12	El Nabawi <i>et al.</i> , 1987
Finland	Eel	1990-93		56-176				Tulonen and Vuorinen, 1996
Germany	Roach and perch, fillet	1980-81	22			nd-180		Schuler <i>et al.</i> , 1985
Germany	Eel, edible tissue	1992			nd-29	33-81	12-43	Karl and Lehmann, 1993
India	Various, muscle	1986-87	1		nd-320	60-1400	140-1100	Bakre <i>et al.</i> , 1990
India	Various	1988-89		2-1380	60-230avs	130-170avs	30-140avs	Nair and Pillai, 1992
India	Various	1992	22	190-23000	nd-17000	3-4700		Dua <i>et al.</i> , 1996
Iraq	Various, muscle	1983-84	30	3800-27000				Al Omar <i>et al.</i> , 1986
Italy	Trout (caged), muscle	1991	2		0.05-0.06	0.17-0.18	0.09-0.13	Galassi <i>et al.</i> , 1996
Kenya	Various, fillet	1988-89	3	nd-1200	nd-1100	nd-54		Mugachia <i>et al.</i> , 1992a; Mugachia <i>et al.</i> , 1992b
Norway	Eel, edible tissue	1992			nd-7	10-20	4-8	Karl and Lehmann, 1993
Poland	Eel, edible tissue	1992			6-24	35-164	24-160	Karl and Lehmann, 1993
Serbia	Various	1988	1	39 - 150	6.3 - 33	26 - 110		Vojinovic <i>et al.</i> , 1990
South Africa	Various muscle	1987-91	4	8.4 -205	nd - 176	< 10 - 198	nd - 13	Heath, 1992, Grobler, 1994
Sweden	Pike (lake)	1993		490-3890				Larsson <i>et al.</i> , 1995
Switzerland	Trout, whole	1984-85	1			10-180		Devaux and Monod, 1987
Tanzania	<i>Tilapia</i> (lake)	1986			6	14	4	Paasivirta <i>et al.</i> , 1988
USA, Great Lakes	Eel and trout, fillet				50-90	148-166	nd-6.9	Newsome and Andrews, 1993
USA, Great Lakes	Trout, fillet	1990			260	1350	140	Miller <i>et al.</i> , 1992
USA, CO	Brown trout, whole	1992-93	2		< 5	6	< 5	Tate and Heiny, 1996
USA, IN/OH	Various, whole		2	130-310				Kuehl <i>et al.</i> , 1980
USA, KA	Various	1985	2			62 - 70	8	Arruda <i>et al.</i> , 1988
USA, Michigan	Bass and walleye, fillet	1991	3	78 - 139				Zabik <i>et al.</i> , 1995
USA, MO	Various	1987	1		< 5 - 180	11 - 270	< 5 - 370	Orazio <i>et al.</i> , 1990
USA, NY	Trout	1993				0.45-1.77		Youngs <i>et al.</i> , 1994
USA, WA	Various, whole	1985	4	50-3000	nd-120	50-2900	nd-140	Johnson <i>et al.</i> , 1988
USA, WA	Largescale sucker	1989-90		1300				Rinella <i>et al.</i> , 1993
USA, WA	Mountain whitefish, whole	1989-90	7	100-1700				Marien and Laflamme, 1995
USA, WA	Largescale sucker, whole	1989-90	13	50-4400				Marien and Laflamme, 1995
USA	Pallid sturgeon, muscle	1983-88	2		150-260	3600-3700	300-1200	Ruelle and Keenlyne, 1993
USA	Catfish, whole	1987	17		nd-180	20-270	nd-370	Leiker <i>et al.</i> , 1991
Zimbabwe	Tigerfish (lake)	1994		150-4770				Larsson <i>et al.</i> , 1995

nd = Not detected.

Table J3 Concentrations of aldrin and dieldrin residues in freshwater

Country	Water type	Date sampled	Number of sites	Concentration range (ng L ⁻¹)		Reference
				Dieldrin	Aldrin	
New Zealand	River water	1996	16	< 0.4-< 2	< 0.1	This study
Argentina/Uruguay	River	1988-89		nd-7.2	nd-6.3	Janiot <i>et al.</i> , 1994
Australia	River	1990		nd-2.4		McKenzie Smith <i>et al.</i> , 1994
Belgium		1988-90	9	< 1-3020	< 1-88	GEMS website
Canada		1988-90	4	< 2	< 1	GEMS website
Colombia		1988-90	1	11	9	GEMS website
Egypt	Irrigation canals			1-32.5	1.8-27	Ismail <i>et al.</i> , 1995
Greece	Filtered	1992-93	3	2-4	1	Tsipi and Hiskia, 1996
India	River	1988-89		100-100000	500-50000	Nair <i>et al.</i> , 1991
India		1991-92		nd-49	nd-99	Agnihotri <i>et al.</i> , 1994
Ivory Coast	Unfiltered		5	100-500	nd	Wandan and Zabik, 1996
Japan		1988-90	7	< 1-100	< 1-10	GEMS website
Malaysia		1988-90	2	nd	nd	GEMS website
Netherlands		1988-90	3	< 1-1	< 1-4	GEMS website
Senegal		1988-90	1	10	10	GEMS website
Thailand	River	1988-91	32	nd-24	nd-22	Tabucanon <i>et al.</i> , 1992
United Kingdom		1989-90	8	nd-50	nd-50	GEMS website
United Kingdom	Drain	1989-90		8-890	1-960	Harrod, 1994
USA, CA	River	1992	4	nd		Pereira <i>et al.</i> , 1996
USA, Michigan	Above dams	1989-90	3	0.35-1.3		Giesy <i>et al.</i> , 1995
USA, Michigan	Below dams	1989-90	3	8.8-46		Giesy <i>et al.</i> , 1995

nd = Not detected.

Table J4 Concentrations of aldrin and dieldrin residues in freshwater fish

Country	Species	Date sampled	Number of sites	Concentration range ($\mu\text{g kg}^{-1}$ WW)		Reference
				Dieldrin	Aldrin	
New Zealand	Trout, fillet	1996	12	0.021-1.12	< 0.01	This study
New Zealand	Eel, fillet	1996	16	0.24-11.4	< 0.01-< 0.02	This study
Canada	Burbot, liver	1985-86	8	7.1-71		Muir <i>et al.</i> , 1990
Egypt	<i>Tilapia</i> spp., fillet	1985	2	0.74-10	1.1-13	El Nabawi <i>et al.</i> , 1987
Egypt	Boliti fish, edible parts	1985	1	590	nd	Dogheim <i>et al.</i> , 1988
Egypt	Catfish, edible parts	1985	1	70	10	Dogheim <i>et al.</i> , 1988
Germany	Eel, edible tissue	1992		nd-54		Karl and Lehmann, 1993
India	Unknown	1988-89		0.1-200	0.1-30	Nair <i>et al.</i> , 1991
India	Various, muscle	1986-87	1		70-1800	Bakre <i>et al.</i> , 1990
Norway	Eel, edible tissue	1992		20-43		Karl and Lehmann, 1993
Poland	Eel, edible tissue	1992		23-38		Karl and Lehmann, 1993
South Africa	Various, muscle (species means)	1987-91	1	< 10-28		Heath, 1992
South Africa	Various, muscle	1990	3	nd		Grobler, 1994
Tanzania	<i>Tilapia</i> (lake)	1986		10		Paasivirta <i>et al.</i> , 1988
USA, Great Lakes	Trout, fillet			41		Newsome and Andrews, 1993
USA, Great Lakes	Eel, fillet			31		Newsome and Andrews, 1993
USA, Great Lakes	Other, fillet			0.24-40		Newsome and Andrews, 1993
USA, Great Lakes	Trout, fillet	1985		40-210		Miller <i>et al.</i> , 1993
USA, Great Lakes	Lake trout, fillet	1990	15	130		Miller <i>et al.</i> , 1992
USA, Great Lakes	Trout, fillet	1990		60-1300		Miller <i>et al.</i> , 1993
USA, CO	Brown trout, whole	1992-93	2	< 5		Tate and Heiny, 1996
USA, KA	Carp (lake), whole	1985	2	69		Arruda <i>et al.</i> , 1988
USA, KA	White bass (lake), fillet	1985	2	58		Arruda <i>et al.</i> , 1988
USA, Michigan	Walleye (lake), fillet	1991	3	6-9		Zabik <i>et al.</i> , 1995
USA, Michigan	White bass (lake), fillet	1991	2	11		Zabik <i>et al.</i> , 1995
USA, MO	Carp, fillet	1987	1	41	< 2	Orazio <i>et al.</i> , 1990
USA, MO	Channel catfish, fillet	1987	1	85	< 2	Orazio <i>et al.</i> , 1990
USA, MO	River carpsucker, fillet	1987	1	14	< 2	Orazio <i>et al.</i> , 1990
USA, MO	Shovelnose sturgeon, fillet	1987	1	100	< 2	Orazio <i>et al.</i> , 1990
USA	Catfish, whole	1987	17	nd-60		Leiker <i>et al.</i> , 1991)
USA	Bottom feeders	1984-85	112	50		Kidwell <i>et al.</i> , 1995
USA	Predators	1984-85	112	40		Kidwell <i>et al.</i> , 1995
USA	Pallid sturgeon, muscle	1983-88	2	50-140	< 10	Ruelle and Keenlyne, 1993

nd = Not detected.

Table J5 Concentrations of HCB residues in freshwater

Country	Water type	Date sampled	Number of sites	Concentration range HCB (ng L ⁻¹)	Reference
New Zealand	River water	1996	16	< 0.1	This study
New Zealand	River/lake	1985	3	0.5-20	Herrmann, 1987
Canada	Filtered	1991	9	nd-0.006	Quemerais <i>et al.</i> , 1994
Canada	Unfiltered	1991	9	nd-0.09	Quemerais <i>et al.</i> , 1994
Croatia	River unfiltered	1988-89	2	nd-3	Fingler <i>et al.</i> , 1992
Egypt	River unfiltered		8	nd-92	El Gendy <i>et al.</i> , 1991

nd = Not detected.

Table J6 Concentrations of HCB residues in freshwater fish

Country	Species	Date sampled	Number of sites	Concentration range HCB (µg kg ⁻¹ WW)	Reference
New Zealand	Trout, fillet	1996	12	< 0.01-0.17	This study
New Zealand	Eel, fillet	1996	16	0.03-0.52	This study
Canada	Burbot, liver	1985-86	8	22-66	Muir <i>et al.</i> , 1990
Canada	Various, whole	1981-86	8	nd-270	Suns and Hitchin, 1992
Egypt	<i>Tilapia</i> spp., fillet	1985	2	1.7-9.1	El Nabawi <i>et al.</i> , 1987
Finland	Eel	1990-93		10 max	Tulonen and Vuorinen, 1996
Germany	Roach and perch, fillet	1980-81	22	nd-230	Schuler <i>et al.</i> , 1985
Germany	Eel, edible tissue	1992		8-20	Karl and Lehmann, 1993
Italy	Various, muscle	1990	1	1-21	Galassi <i>et al.</i> , 1994
Italy	Trout (caged), muscle	1991	2	0.04-0.06	Galassi <i>et al.</i> , 1996
Norway	Eel, edible tissue	1992		6-12	Karl and Lehmann, 1993
Poland	Eel, edible tissue	1992		8-360	Karl and Lehmann, 1993
USA, Great Lakes	Trout, fillet			9.1	Newsome and Andrews, 1993
USA, Great Lakes	Eel, fillet			9	Newsome and Andrews, 1993
USA, Great Lakes	Other, fillet			0.22-9.3	Newsome and Andrews, 1993
USA, general	Bottom feeders	1984-85	112	0	Kidwell <i>et al.</i> , 1995
USA, general	Predators	1984-85	112	10	Kidwell <i>et al.</i> , 1995
USA, IN/OH	Various, whole		2	30-3140	Kuehl <i>et al.</i> , 1980
USA	Pallid sturgeon, muscle	1983-88	2	< 10	Ruelle and Keenlyne, 1993
USA	Catfish, whole	1987	17	nd-11	Leiker <i>et al.</i> , 1991

nd = Not detected.

Appendix K New Zealand and overseas pentachlorophenol water and fish data

This appendix provides a summary of the New Zealand Organochlorines Programme data for pentachlorophenol (as reported in full in Appendix G), and details comparative data for pentachlorophenol concentrations in water and biota as reported in the published literature.

Table K1 Concentrations of pentachlorophenol in river water

Table K2 Concentrations of pentachlorophenol in river biota

Table K1 Concentrations of pentachlorophenol in river water

Country	Water type	Date sampled	Concentration (ng L ⁻¹)		Reference
			Min.	Max.	
New Zealand	River water	1996	< 2	< 3	This study
Canada	Lake Ontario reference site	1978	10	14	Fox and Joshi, 1984
	Small stream, sewage/chemical dump	1980-81	4	75	Metcalfe <i>et al.</i> , 1984
	River impacted by pulp mill	1990-91	< 50	< 50	Owens <i>et al.</i> , 1994
	Fraser River estuary, various impacts	1986	6.9	47	Carey and Hart, 1988
	Fraser River estuary, various impacts	1984	2	56	Carey <i>et al.</i> , 1988
	Fraser River upper reaches unimpacted	1987	20	23	Rogers <i>et al.</i> , 1988
Finland	Fraser River upper reaches impacted	1987	21	136	Rogers <i>et al.</i> , 1988
	Stream impacted by groundwater	1988-89	40	5260	Lampi <i>et al.</i> , 1992
Germany	Weser River	1977	17.3	409	Weber and Ernst, 1978
	River Rhine	1980	100	300	BUA, 1985
	River Rhine	1983		100 ¹	BUA, 1985
	River Rhine	1984	50	80	BUA, 1985
Netherlands	River Rhine	1976-77		11000	Wegman and Hofstee, 1979
	River Boven Merwede	1976-77		9600	Wegman and Hofstee, 1979
	River Ijssel	1976-77		10000	Wegman and Hofstee, 1979
	River Meuse	1976-77	8900	10000	Wegman and Hofstee, 1979
Sweden	Baltic Sea impacted by pulp mill	1987	60	200	Söderström <i>et al.</i> , 1994
United Kingdom	Tributary rivers of the Forth	1988-89	< 3	50	Campbell and Ridgway, 1989
United States	Willamette River	1969	100	700	Buhler <i>et al.</i> , 1973

¹ Mean concentration.

Table K2 Concentrations of pentachlorophenol in river biota

Country	Species	Date sampled	Concentration ($\mu\text{g kg}^{-1}$ WW)		Reference
			Min.	Max.	
New Zealand	Trout, fillet	1996	< 0.2	0.8	This study
	Eel, fillet	1996	< 0.3	< 0.45	This study
Canada	Whitefish, Wapiti/Smokey River	1991	< 0.5	4.0	Owens <i>et al.</i> , 1994
	Flounder, Fraser River	1984	2.7	29.9	Carey <i>et al.</i> , 1988
	Pink salmon fry, Sweltzer Creek	1986		0.8 ¹	Servizi and Gordon, 1988
	Pink salmon fry, Jones Creek	1986		2.4	Servizi and Gordon, 1988
	Juvenile salmon, Fraser River	1986	1.0	2.7	Rogers <i>et al.</i> , 1988
	Juvenile salmon, Fraser River	1986		1.9 ¹	Rogers <i>et al.</i> , 1988
Canada	Juvenile salmon, upper Fraser River	1986-87	1.6	12.7	Rogers <i>et al.</i> , 1988
Finland	Pike, L. Vitia (pulp mill)	1978		8.04	Passivirta <i>et al.</i> , 1980
	Pike, L. Pajänne (pulp mill)	1978		5.72 ¹	Passivirta <i>et al.</i> , 1980
	Pike, L. Konnevesi (sawmills)	1978		6.49 ¹	Passivirta <i>et al.</i> , 1980
	Roach, L. Vitia (pulp mill)	1978		0.90 ¹	Passivirta <i>et al.</i> , 1980
	Roach, L. Pajänne (pulp mill)	1978		4.84	Passivirta <i>et al.</i> , 1980
	Roach, L. Konnevesi (sawmills)	1978		12.8	Passivirta <i>et al.</i> , 1980
	Pike, L. Pajänne (pulp mill)	1980	6.4	49.6	Passivirta <i>et al.</i> , 1981
	Pike, L. Pajänne (pulp mill)	1980	18.0	403	Passivirta <i>et al.</i> , 1981
	Pike, L. Pajänne	1980	2.7	35.7	Passivirta <i>et al.</i> , 1981
	Finland	Trout, Kemi River (Gulf of Bothnia)	1982		4.2 ¹
	Salmon, Kemi River (Gulf of Bothnia)	1982		1.8 ¹	Vuorinen, 1985
	Salmon, Kymi River (Gulf of Finland)	1982		3.0 ¹	Vuorinen, 1985

¹ Mean concentration.