

**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.

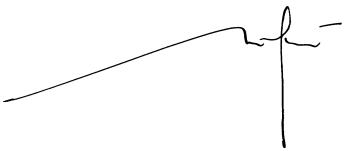
In view of the international concern, the Government decided that we needed better information on the New Zealand situation. The Ministry for the Environment was asked to establish an Organochlorines Programme to carry out research, assess the data, and to consider management issues such as clean up 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 of 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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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.

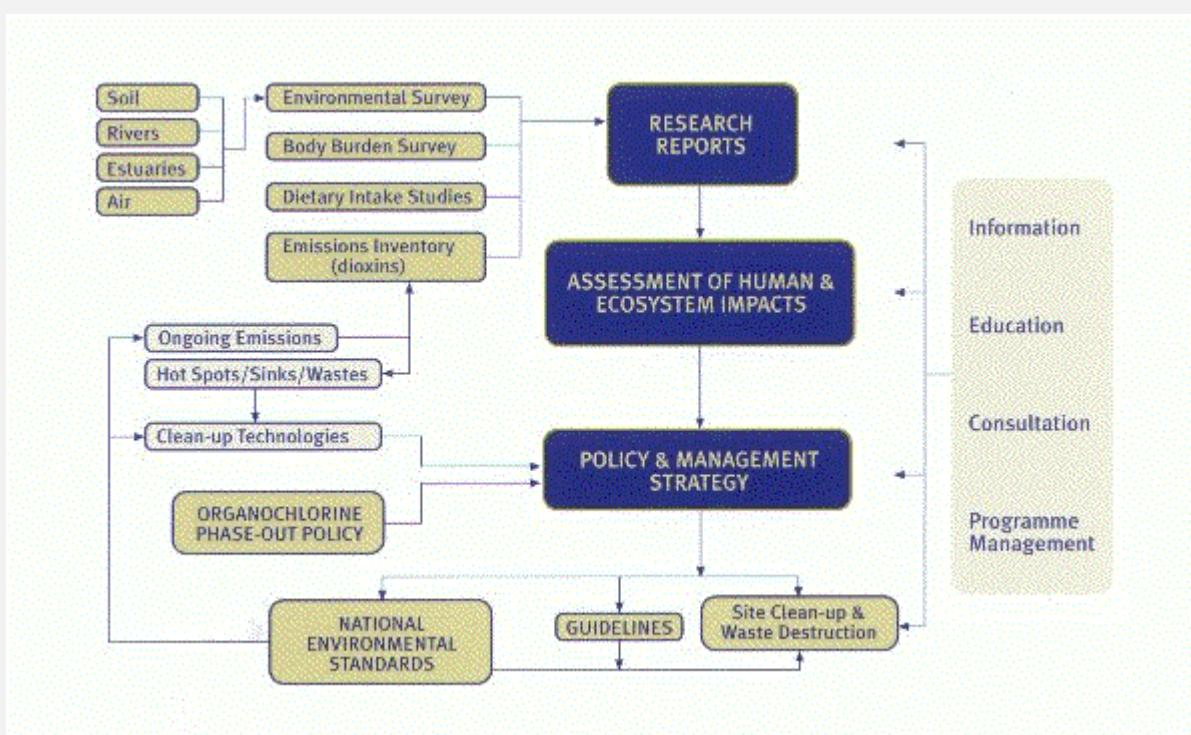


Figure 1.1 Overview of the New Zealand Organochlorines Programme

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.

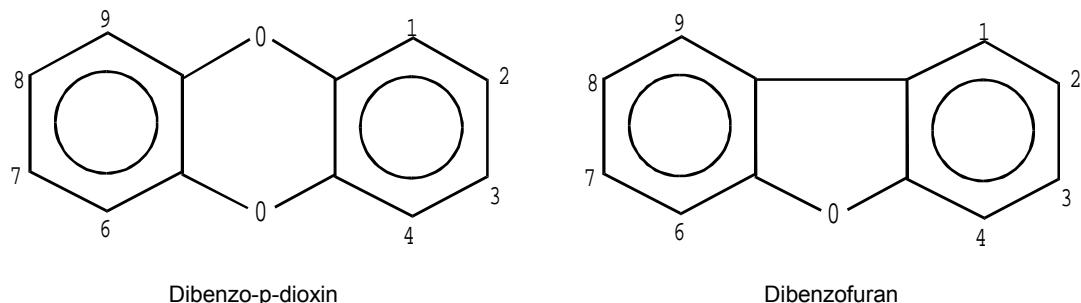


Figure 2.1 Structures of dibenzo-p-dioxin and dibenzofuran

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 |
| HxCDD | 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 |
| HxCDF | 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.

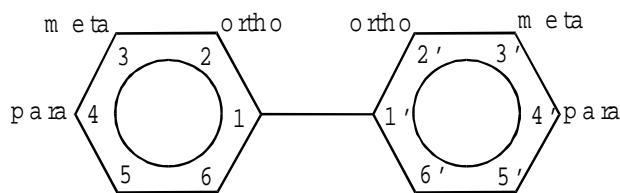


Figure 2.2 Structure of biphenyl

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 | IUPAC No. | Congener Structure | WHO/IPCS TEF (Ahlborg <i>et al.</i> , 1994) | WHO-TEF (humans/mammals) (Van den Berg <i>et al.</i> , 1998) |
|--------------------|-----------|-----------------------|---|--|
| Non- <i>ortho</i> | 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- <i>ortho</i> | 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- <i>ortho</i> | 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.

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.

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 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. 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 Greymouth (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.

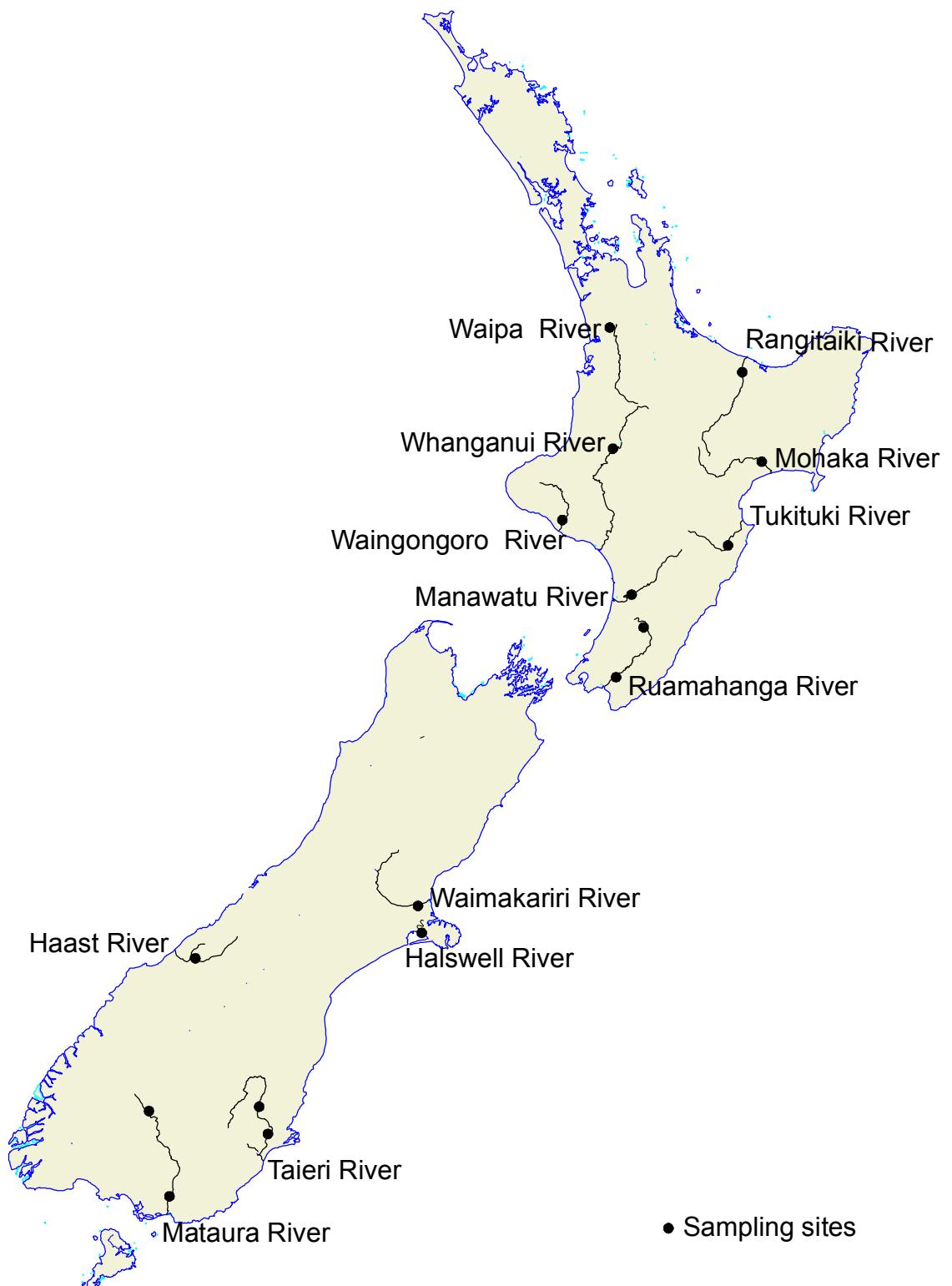


Figure 4.1 Rivers studied and sampling sites

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 ^{13}C isotope dilution using capillary gas chromatography-high resolution mass spectrometry. All data reported are corrected for recovery of the ^{13}C 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).

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 μ g kg⁻¹ in eels and from 0.11 - 8.80 μ 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 μ 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.

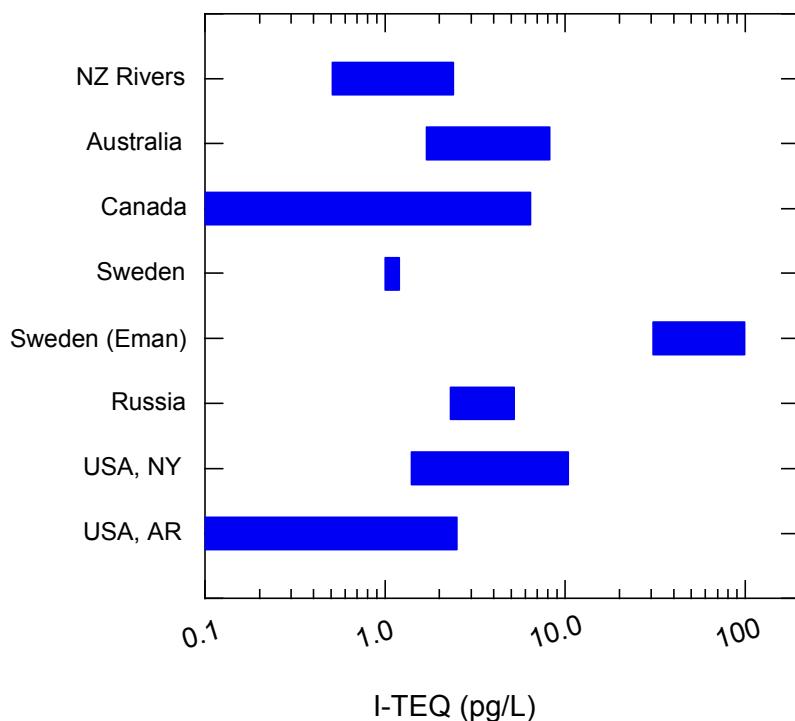


Figure 5.1 Water concentrations of I-TEQ in New Zealand and overseas

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 |
| | PCB #52 | 0.2 |
| Tetrachloro- | PCB #101, #123, #118 | 0.2 |
| | PCB #99, #114, #105 | 0.1 |
| Pentachloro- | PCB #153, #167, #156, #157 | 0.1 |
| | PCB #138 | 0.2 |
| Hexachloro- | PCB #187, #183, #180, #170, #189 | 0.1 |
| | PCB #202, #194 | 0.1 |
| Heptachloro- | PCB #206 | 0.2 |
| Octachloro- | | |
| Nonachloro- | | |

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.

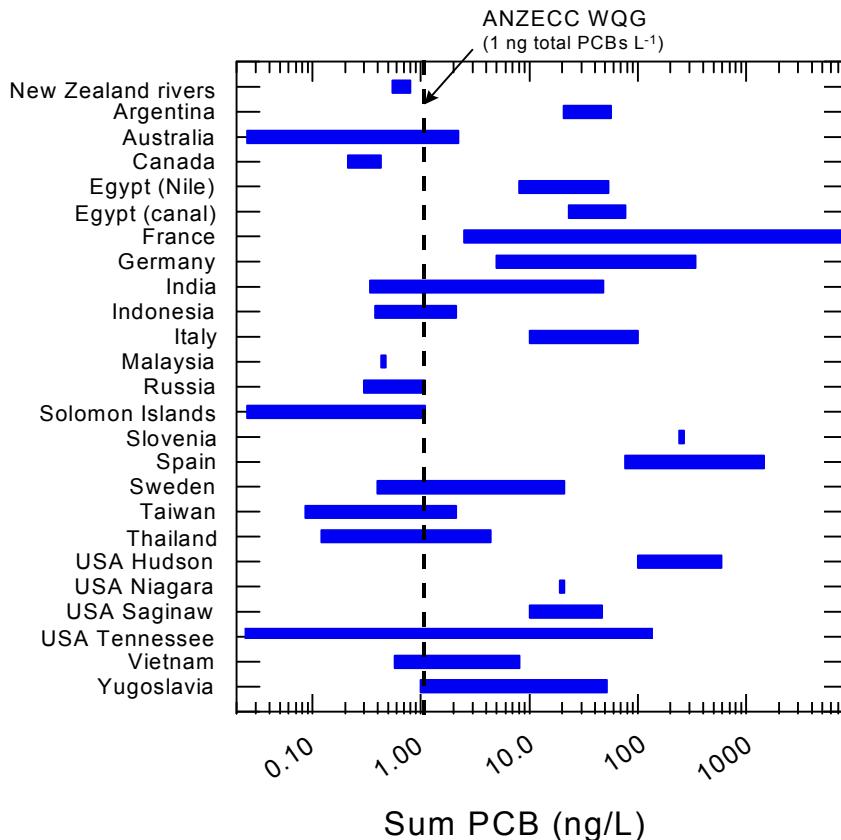


Figure 5.2 Water concentrations of total PCBs in New Zealand and overseas

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).

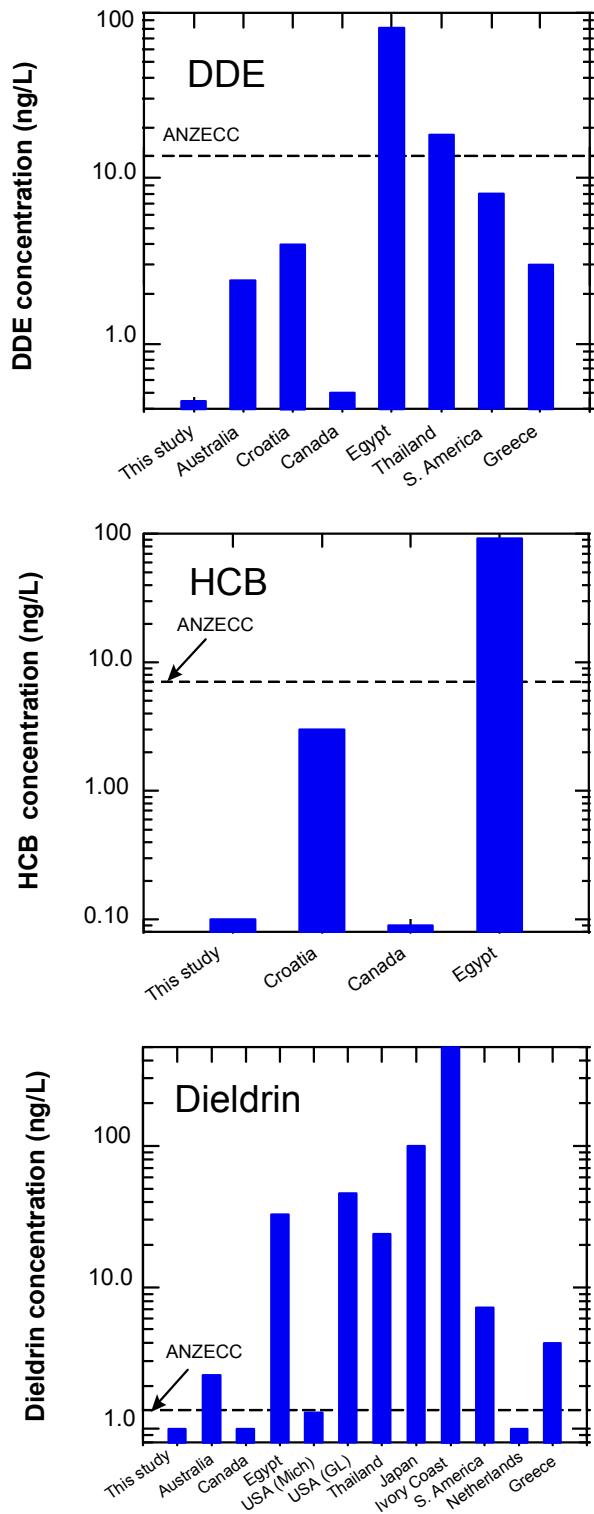


Figure 5.3 Maximum pesticide detection limits in New Zealand river water compared to maximum pesticide concentrations in overseas water

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 (Σ DDTs) | 1 |
| DDE | | 14 |
| Heptachlor and heptachlor epoxide | 10 | 10 (Heptachlor) |
| Σ HCH | 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 $2\text{-}3 \text{ ng L}^{-1}$. 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 $< 10 \text{ ng L}^{-1}$ 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.

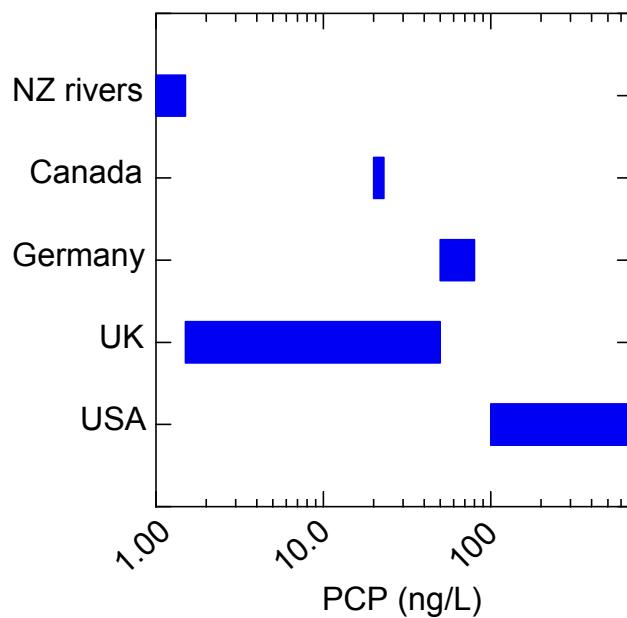


Figure 5.4 Detection limits for PCP in New Zealand river water compared to data for overseas river water
Overseas data from Table K1 (Appendix K).

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 Mataura 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 Mataura 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.

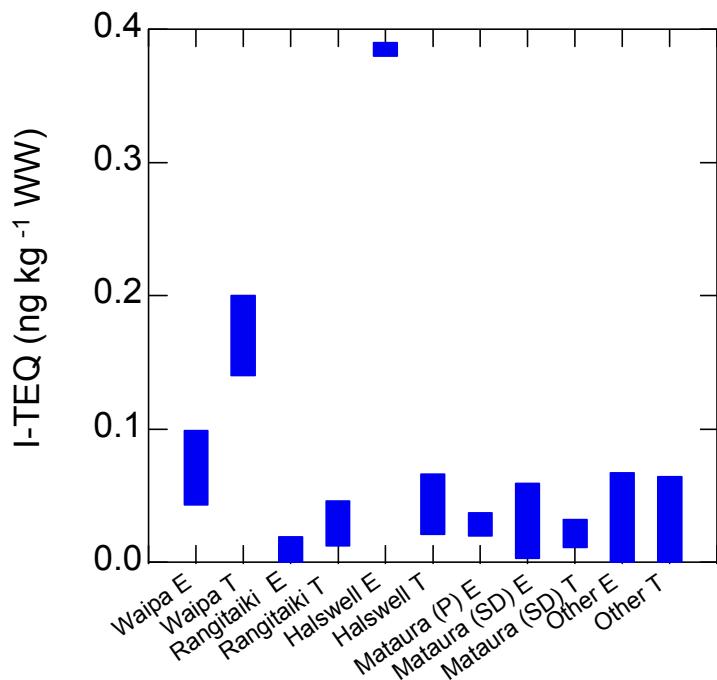


Figure 5.5 Minimum and maximum PCDD and PCDF I-TEQ concentrations in New Zealand fish

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.

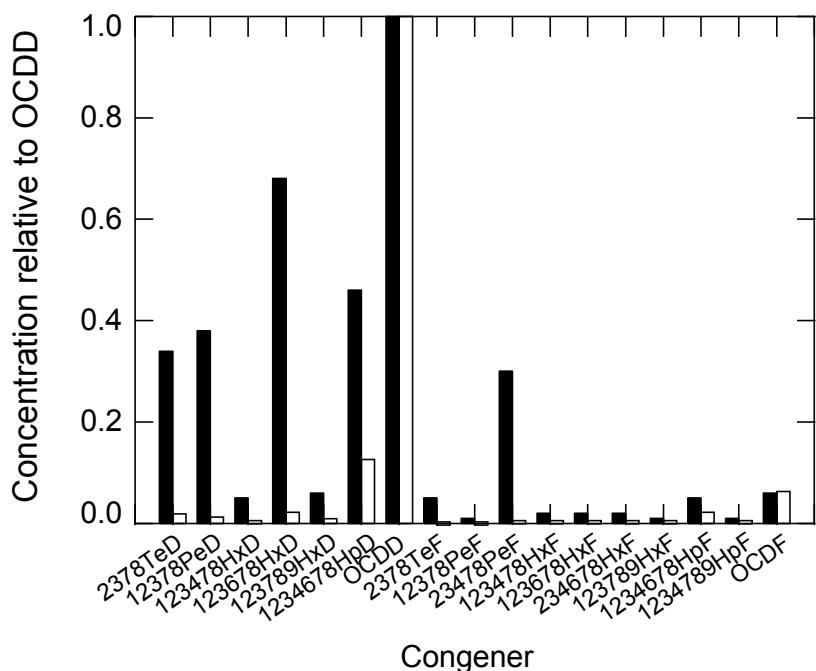


Figure 5.6 PCDD and PCDF congener profile for New Zealand fish flesh

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*, *Carassius 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.

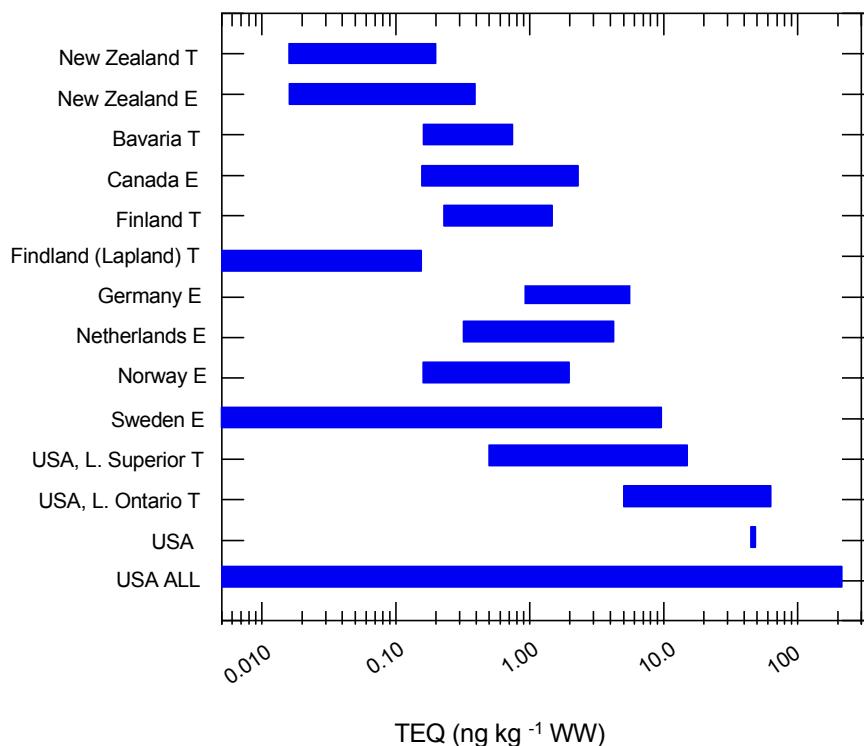


Figure 5.7 PCDD and PCDF TEQ concentrations in New Zealand and overseas fish

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 kg⁻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-HxCDD, 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 ($50 \text{ ng I-TEQ kg}^{-1} \text{ fat}$) and a dietary intake guideline ($1.1 \text{ ng I-TEQ kg}^{-1} \text{ fresh weight}$) 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 $0.11 - 18.5 \mu\text{g kg}^{-1}$. The sum of PCB congeners, were lower in trout, at $0.11 - 8.80 \mu\text{g kg}^{-1}$, than in eel, at $1.29 - 18.5 \mu\text{g kg}^{-1}$.

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.

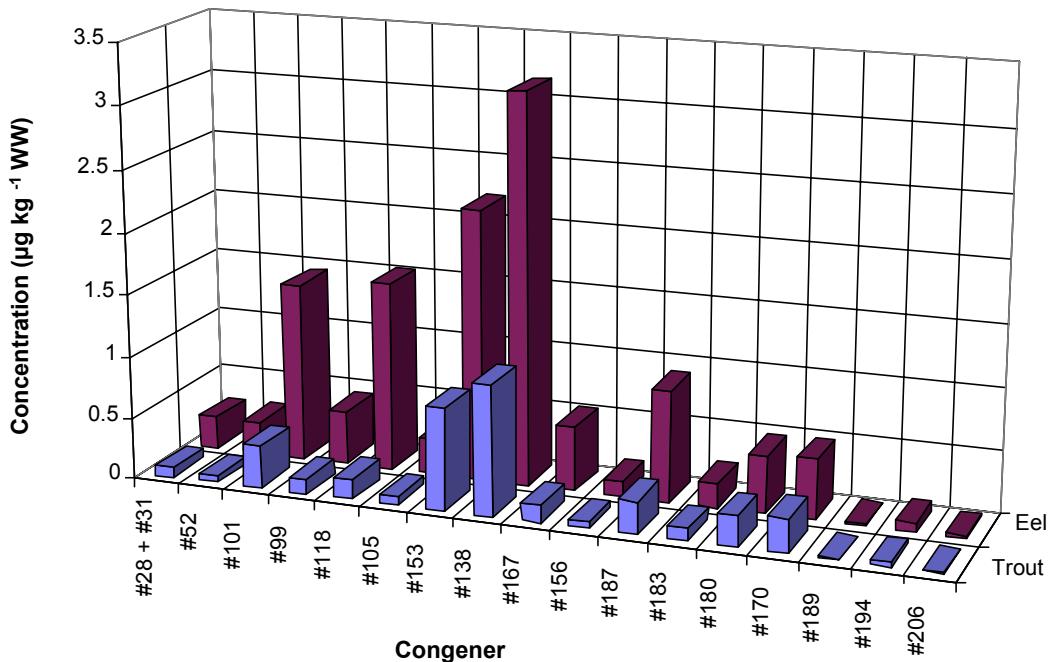


Figure 5.8 PCB congener profile in New Zealand eel and trout

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 $0.069 - 1.39 \text{ ng TEQ kg}^{-1}$ in eel and from $0.065 - 0.32 \text{ ng TEQ kg}^{-1}$ 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 $0.089 - 1.78 \text{ ng TEQ kg}^{-1}$ for eel and $0.085 - 0.52 \text{ ng TEQ kg}^{-1}$ 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 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 | Benoliel 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).

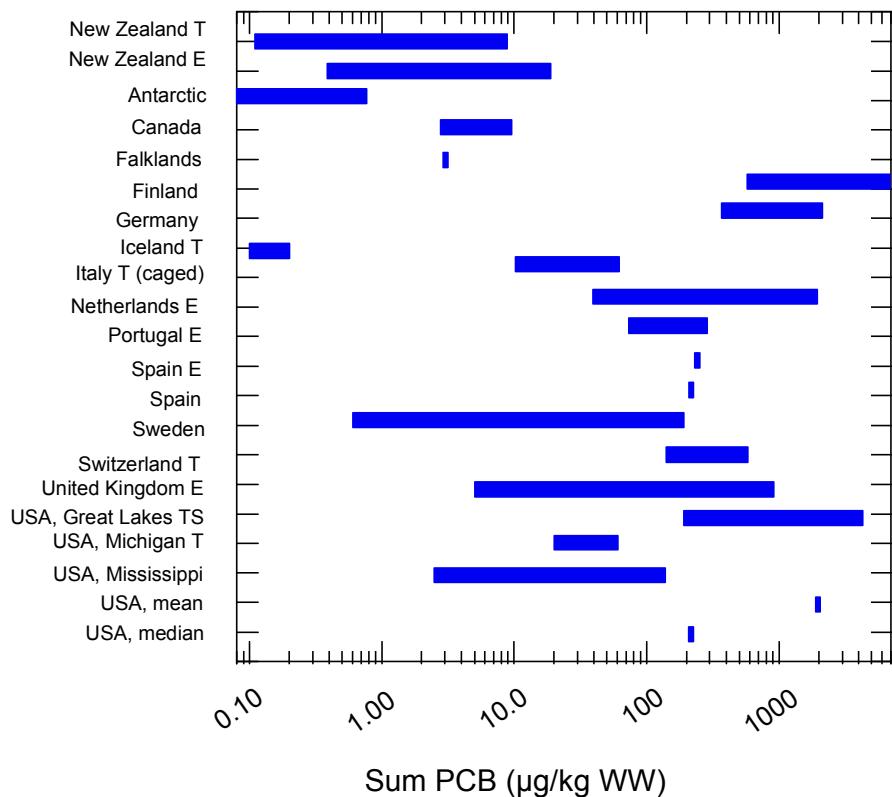


Figure 5.9 Total PCB concentrations in freshwater fish from New Zealand and representative overseas locations

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, $2 - 5 \text{ mg kg}^{-1}$ 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.

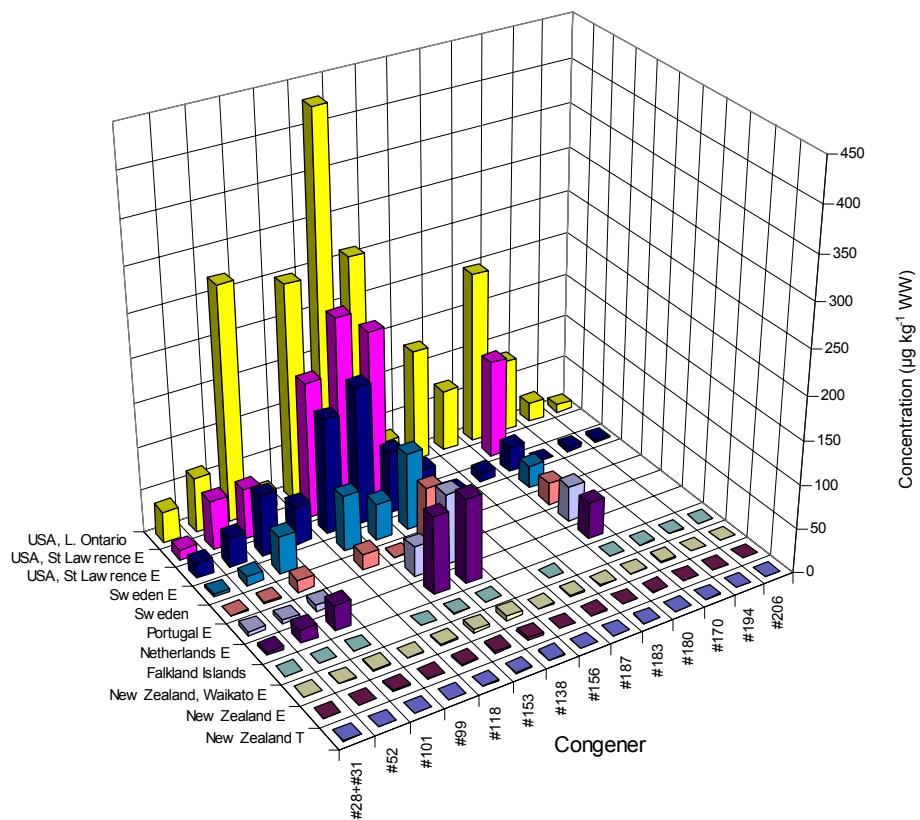


Figure 5.10 PCB congener profile found in New Zealand and overseas fish tissue samples

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).

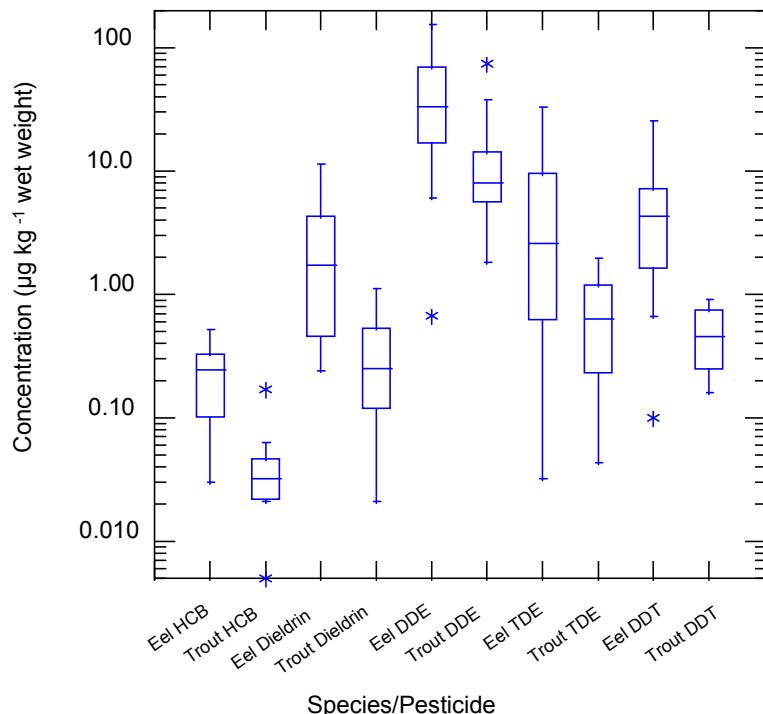


Figure 5.11 Box plot of organochlorine pesticide residues in New Zealand fish

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.

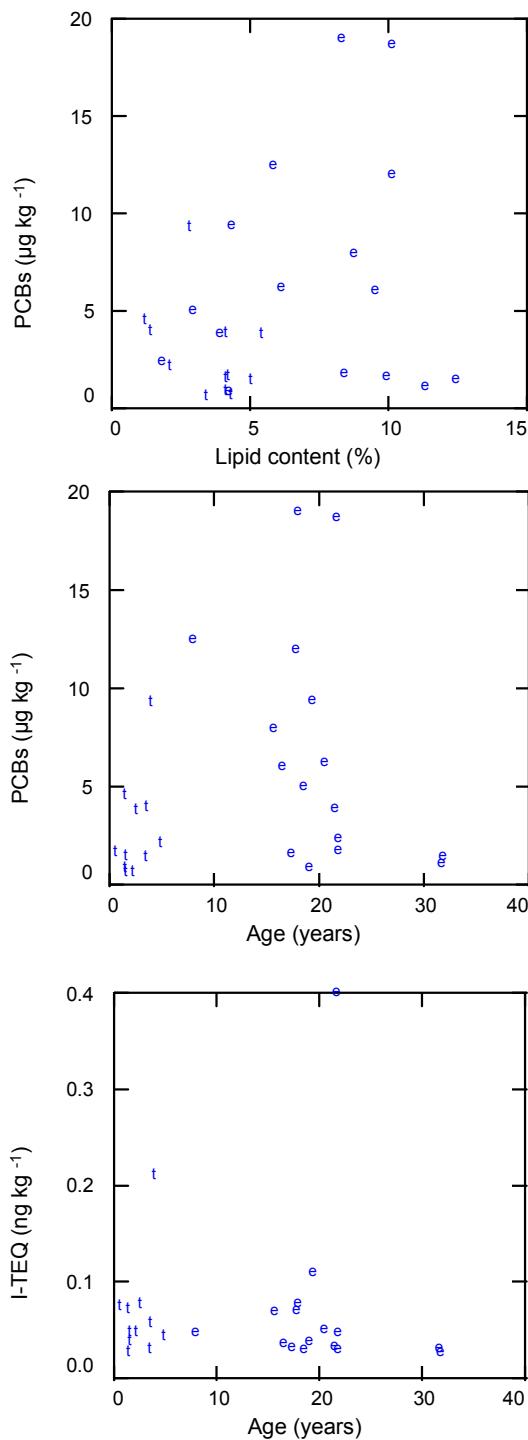


Figure 5.12 Correlation between PCBs or I-TEQ and age or lipid content of New Zealand fish (e = eel; t = trout)

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 to 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.

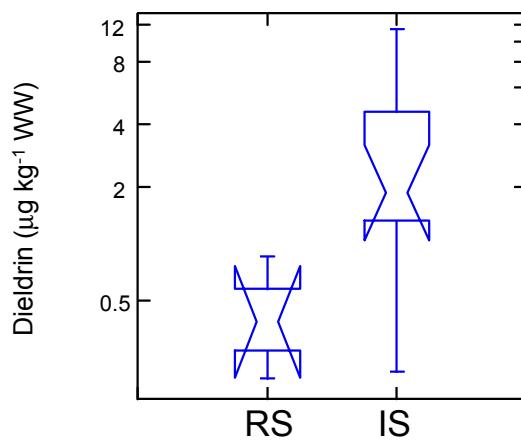
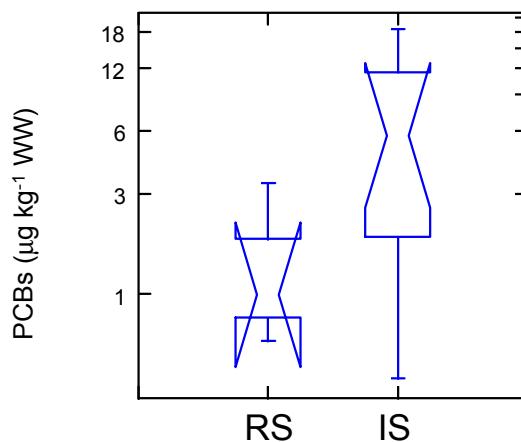
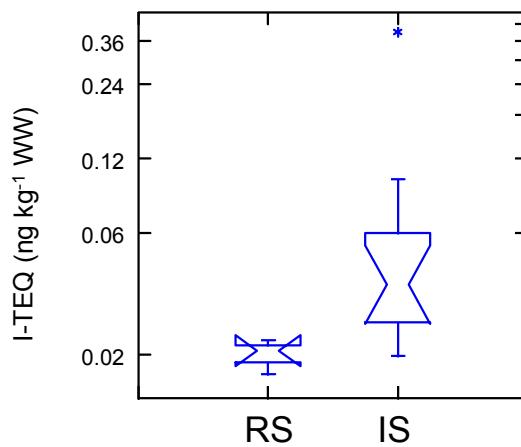


Figure 5.13 Box plot of organochlorines at reference and impacted sites

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.

References

Abrahamsson, K, Xie, TM, 1983. Direct determination of trace amounts of chlorophenols in fresh water, waste water and sea water. *Journal of Chromatography*, 279, 199-208.

Agnihotri, NP, Gajbhiye, VT, Kumar, M, Mohapatra, SP, 1994. Organochlorine insecticide residues in Ganga river water near Farrukhabad, India. *Environmental Monitoring and Assessment*, 30, 105-112.

Ahlborg, UG, Becking, GC, Birnbaum, LS, Brouwer, A, Derkx, HJGM, Feeley, M, Golor, G, Hanberg, A, Larsen, JC, Liem, AKD, Safe, SH, Schlatter, C, Wærn, F, Younes, M, Yrjänheikki, E, 1994. Toxic equivalency factors for dioxin-like PCBs. *Chemosphere*, 28, 1049-1067.

Ahokas, JT, Holdway, DA, Brennan, SE, Goudey, RW, Bibrowska, HB, 1994. MFO activity in carp (*Cyprinus carpio*) exposed to treated pulp and paper mill effluent in Lake Coleman, Victoria, Australia, in relation to AOX, EOX, and muscle PCDD/PCDF. *Environmental Toxicology and Chemistry*, 13, 41-50.

Al Omar, MA, Al Ogaily, NH, Shebil, DA, 1986. Residues of organochlorine insecticides in fish from polluted water. *Bulletin of Environmental Contamination and Toxicology*, 36, 109-113.

Amirova, Z, Kruglov, E, Loshkina, H, Chalilov, R, 1997. PCDD/PCDFs levels in drinking and surface water in Republic Bashkortostan. *Organohalogen Compounds*, 32, 107-111.

Andersson, O, Linder, C, Olsson, M, Reutergardh, L, Uvemo, U, Wideqvist, U, 1988. Spatial differences and temporal trends of organochlorine compounds in biota from the northwestern hemisphere. *Archives of Environmental Contamination and Toxicology*, 17, 755-765.

ANZECC, 1992. *Australian Water Quality Guidelines for Fresh and Marine Waters*. Australian and New Zealand Environment and Conservation Council, Canberra, Australia.

APHA, 1992. *Standard Methods for the Examination of Water and Wastewater*. 18th Ed, Washington, DC.

Arruda, JA, Crangan, MS, Layher, WG, Kersh, G, Bever, C, 1988. Pesticides in fish tissue and water from Tuttle Creek Lake, Kansas. *Bulletin of Environmental Contamination and Toxicology*, 41, 617-624.

Atuma, SS, Linder, C-E, Wicklund-Glynn, A, Andersson, O, Lassson, L, 1996. Survey of consumption fish from Swedish waters for chlorinated pesticides and polychlorinated biphenyls. *Chemosphere*, 33, 791-799.

Badawy, MI, Aly, OA, 1986. PCB levels in surface and waste waters in Egypt. *Environment International*, 12, 577-580.

Bakre, PP, Misra, V, Bhatnagar, P, 1990. Residues of organochlorine insecticides in fish from Mahala water reservoir, Jaipur, India. *Bulletin of Environmental Contamination and Toxicology*, 45, 394-398.

Ballschmiter, K, Zell, M, 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius Zeitschrift für Analytische Chemie*, 302, 20-31.

Beentjes, MP, Chisnall, BL, 1998. Size, age, and species composition of commercial eel catches from market sampling 1996-1997. *NIWA Technical Report* 29. 124 p.

Bengston, S, 1974. DDT and PCB residues in airborne fallout and animals in Iceland. *Ambio*, 3, 84-86.

Benoliel, MJ, Shirley, ML, 1988. PCBs and organochlorine pesticides in eel and flounder in the Tagus estuary. In: *Organic Micropollutants in the Aquatic Environment: Proceedings of the Fifth European Symposium, Rome, Italy, October 20-22 1988*. Kluwer Academic Publishers, Boston, MA 1988, pp. 83-87.

Beurskens, JEM, Mol, GAJ, Barreveld, HL, Van Munster, B, Winkels, HJ, 1993. Geochronology of priority pollutants in a sedimentation area of the Rhine River. *Environmental Toxicology and Chemistry*, 12, 1549-1566.

Braginsky, LP, Komarovskiy, FY, Linnik, PN, Maslova, OV, Shcherban, EP, 1990. Ecotoxicological studies on the Kilian branch and delta of the River Danube. *Water Science and Technology*, 22, 35-38.

Bremle, G, Okla, L, Larsson, P, 1995. Uptake of PCBs in fish in a contaminated river system: Bioconcentration factors measured in the field. *Environmental Science and Technology*, 29, 2010-2015.

Brinkman, GL, Matthews, REF, Earl, WB, 1986. *Possible health effects of manufacture of 2,4,5-T in New Plymouth*. Report of Ministerial Committee of Inquiry to the Minister of Health, Wellington, New Zealand.

Broman, D, Naf, C, Rolff, C, Zebuhr, Y, 1991. Occurrence and dynamics of polychlorinated dibenzo-p-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons in the mixed surface layer of remote coastal and offshore waters of the Baltic. *Environmental Science and Technology*, 25, 1850-1864.

BUA, 1985. (Beratergremium für umweltrelevante Altstoffe). *Pentachlorophenol* BUA Stoffbericht 3, VCH Verlagsgesellschaft, Weinheim, Germany.

Buckland, SJ, Ellis, HK, Salter, RT, 1998. *Organochlorines in New Zealand: Ambient concentrations of selected organochlorines in soils*. Ministry for the Environment, Wellington, New Zealand.

Buckland, SJ, Ellis, HK, Salter, RT, 1999. *Organochlorines in New Zealand: Ambient concentrations of selected organochlorines in air*. Ministry for the Environment, Wellington, New Zealand.

Buckland, SJ, Scobie, S, Heslop, V, 1998c. *Organochlorines in New Zealand: Concentrations of PCDDs, PCDFs, and PCBs in retail foods and an assessment of dietary intake for New Zealanders*. Ministry for the Environment, Wellington, New Zealand.

Buhler, DR, Rasmusson, ME, Nakaaue, HS, 1973. Occurrence of hexachlorophene and pentachlorophenol in sewage and water. *Environmental Science and Technology*, 7, 929-934.

Bush, B, Simpson, KW, Shane, L, Koblitz, RR, 1985. PCB congener analysis of water and caddisfly larvae (Insecta: Trichoptera) in the upper Hudson River by glass capillary chromatography. *Bulletin of Environmental Contamination and Toxicology*, 34, 96-105.

Campbell, D, Ridgway, IM, 1989. The elimination of pentachlorophenol pollution from the Forth catchment. *Journal of the Institution of Water and Environmental Management*, December, 599-603.

Carey, JH, Fox, ME, Hart, JH, 1988. Identity and distribution of chlorophenols in the north arm of the Fraser River estuary. *Water Pollution Research Journal of Canada*, 23, 31-44.

Carey, JH, Hart, JH, 1988. Sources of chlorophenolic compounds to the Fraser River estuary. *Water Pollution Research Journal of Canada*, 23, 55-68.

CCME, 1995. Canadian Council of Ministers of the Environment. *Draft environmental quality guidelines for dioxins (PCDD) and furans (PCDF)*, Winnipeg, Manitoba, Canada.

CCREM, 1991. Canadian Council of Resource and Environment Ministers. *Canadian Water Quality Guidelines*, Water Quality Branch, Environment Canada, Ontario, Canada.

Chevreuil, M, Granier, L, 1991. Seasonal cycle of polychlorinated biphenyls in the waters of the catchment basin of the River Seine (France). *Water, Air, and Soil Pollution*, 59, 217-229.

Clarke, AN, Wilson, DJ, Megehee, MM, Lowe, DL, 1996. A review of 2,3,7,8-tetra chlorinated dibenzodioxins and toxicity equivalences in fish in the United States and international waterways. *Hazardous Waste and Hazardous Materials*, 13, 419-443.

Colombo, JC, Khalil, MF, Arnac, M, Horth, AC, Catoggio, JA, 1990. Distribution of chlorinated pesticides and individual polychlorinated biphenyls in biotic and abiotic compartments of the Rio de La Plata, Argentina. *Environmental Science and Technology*, 24, 498-505.

Coster, AP, Edmonds, AS, Fitzsimons, JM, Goodrich, CG, Howard, JK, Tustin, JR, 1986. *The use of 2,4,5-T in New Zealand*. A report to the Environmental Council, Commission for the Environment, Wellington, New Zealand.

de Boer, J, Stronck, CJN, Traag, WA, van der Meer, J, 1993. Non-*ortho* and mono-*ortho* substituted chlorobiphenyls and chlorinated dibenzo-p-dioxins and dibenzofurans in marine and freshwater fish and shellfish from the Netherlands. *Chemosphere*, 26, 1823-1842.

de Boer, J, Wester, PG, 1991. Chlorobiphenyls and organochlorine pesticides in various sub-Antarctic organisms. *Marine Pollution Bulletin*, 22, 441-447.

De Kock, AC, Boshoff, AF, 1987. PCBs and chlorinated hydrocarbon insecticide residues in birds and fish from the Wilderness Lakes system, South Africa. *Marine Pollution Bulletin*, 18, 413-416.

De Vault, DS, Dunn, WJ, Bergqvist, P, Wieberg, K, Rappe, C, 1989. Polychlorinated dibenzofurans and polychlorinated dibenzo-p-dioxins in Great Lakes fish: A baseline and interlake comparison. *Environmental Toxicology and Chemistry*, 8, 1013-1022.

De Wit, C, Jansson, B, Bergek, S, Hjelt, M, Rappe, C, Olsson, M, Andersson, O, 1992. Polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran levels and patterns in fish and fish-eating wildlife in the Baltic Sea. *Chemosphere* 25, 185-188.

Devaux, A, Monod, G, 1987. PCB and pp'-DDE in Lake Geneva brown trout (*Salmo trutta* L.) and their use as bioenergetic indicators. *Environmental Monitoring and Assessment*, 9, 105-114.

Dikshith, TSS, Raizada, RB, Kumar, SN, Srivastava, MK, Kulshrestha, SK, Adholia, UN, 1990. Residues of DDT and HCH in major sources of drinking water in Bhopal, India. *Bulletin of Environmental Contamination and Toxicology*, 45, 389-393.

Dogheim, SM, Almaz, MM, Kostandi, SN, Hegazy, ME, 1988. Pesticide residues in milk and fish samples collected from Upper Egypt. *Journal of the Association of Official Analytical Chemists*, 71, 872-874.

Dua, VK, Kumari, R, Sharne, VP, 1996. HCH and DDT contamination of rural ponds of India. *Bulletin of Environmental Contamination and Toxicology*, 57, 568-574.

El Dib, MA, Badawy, MI, 1985. Organo-chlorine insecticides and PCBs in River Nile water, Egypt. *Bulletin of Environmental Contamination and Toxicology*, 34, 126-133.

El-Gendy, KS, Abdalla, AA, Aly, HA, Tantawy, El-Sebae, AH, 1991. Residue levels of chlorinated hydrocarbon compounds in water and sediment samples from Nile Branches in The Delta, Egypt. *Journal of Environmental Science and Health*, B26(1), 15-36.

Ellis, HK, 1997. Dioxin contamination in New Zealand from the historical use of pentachlorophenol in the timber industry: Assessment and management options. *Organohalogen Compounds*, 34, 32-37.

El Nabawi, A, Heinzw, B, Kruse, H, Nabawi, AE, 1987. Residue levels of organochlorine chemicals and polychlorinated biphenyls in fish from the Alexandria region, Egypt. *Archives of Environmental Contamination and Toxicology*, 16, 689-696.

Fernandez, MA, Hernandez, LM, Gonzalez, MJ, Tabera, MC, 1992. Organochlorinated compounds and selected metals in water and soils from Donana National Park (Spain). *Water, Air, and Soil Pollution*, 65, 293-305.

Fiedler, H, Hutzinger, O, Timms, C, 1990. Dioxins: Sources of environmental load and human exposure. *Toxicology and Environmental Chemistry*, 29, 157-234.

Fingler, S, Drevenkar, V, Tkalcevic, B, Smit, Z, 1992. Levels of polychlorinated biphenyls, organochlorine pesticides, and chlorophenols in the Kupa River water and in drinking waters from different areas in Croatia. *Bulletin of Environmental Contamination and Toxicology*, 49, 805-812.

Fox, ME, Joshi, SR, 1984. The fate of pentachlorophenol in the Bay of Quinte, Lake Ontario. *Journal of Great Lakes Research*, 10, 190-196.

Friege, H, Stock, W, Alberti, J, Poppe, A, Juhnke, I, Knie, J, Schiller, W, 1989. Environmental behaviour of polychlorinated mono-methyl-substituted diphenyl-methanes (Me-PCDMs) in comparison with polychlorinated biphenyls (PCBs). II. Environmental residues and aquatic toxicity. *Chemosphere*, 18, 1367-1378.

Frommberger, R, 1991. Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans in fish from south-west Germany: River Rhine and Neckar. *Chemosphere*, 22, 29-38.

Galassi, S, Guzzella, L, Battegazzore, M, Carrieri, A, 1994. Biomagnification of PCBs, pp'-DDE, and HCB in the River Po ecosystem (northern Italy). *Ecotoxicology and Environmental Safety*, 29, 174-186.

Galassi, S, Provini, A, 1981. Chlorinated pesticides and PCBs contents of the two main tributaries into the Adriatic Sea. *Science of the Total Environment*, 17, 51-57.

Galassi, S, Vigano, L, Sanna, M, 1996. Bioconcentration of organochlorine pesticides in rainbow trout caged in the River Po. *Chemosphere*, 32, 1729-1739.

GEMS website. <http://www.cciw.ca/gems/intro.html>.

Giesy, JP, Bowerman, WW, Mora, MA, Verbrugge, DA, Othoudt, RA, Newsted, JL, Summer, CL, Aulerich, RJ, Bursian, SJ, Ludwig, JP, Dawson, GA, Kubiak, TJ, Best, DA, Tillitt, DE, 1995. Contaminants in fishes from Great Lakes-influenced sections and above dams of three Michigan rivers. III. Implications for health of bald eagles. *Archives of Environmental Contamination and Toxicology*, 29, 309-321.

Giesy, JP, Verbrugge, DA, Othoudt, RA, Bowerman, WW, Mora, MA, Jones, PD, Newsted, JL, Vandervoort, C, Heaton, SN, Aulerich, RJ, Bursian, SJ, Ludwig, JP, Ludwig, ME, Dawson, GA, Kubiak, TJ, Best, DA, Tillitt, DE, 1994. Contaminants in fishes from Great Lakes-influenced sections and above dams of three Michigan rivers. I. Concentrations of organochlorine insecticides, polychlorinated biphenyls, dioxin equivalents, and mercury. *Archives of Environmental Contamination and Toxicology*, 27, 202-212.

Gifford, JS, Judd, MC, McFarlane, PM, Anderson, SM, 1995. Pentachlorophenol (PCP) in the New Zealand environment: Assessment near contaminated sites and remote freshwater lakes. *Toxicological and Environmental Chemistry*, 48, 69-82.

Gifford, JS, Buckland, SJ, Judd, MC, McFarlane, PN, Anderson, SM, 1996. Pentachlorophenol (PCP), PCDD, PCDF and pesticide concentrations in a freshwater lake catchment. *Chemosphere*, 32, 2097-2113.

Gobran, T, Khurana, V, MacPherson, K, Wadell, D, 1995. PCDD/PCDF levels in raw sewage, final effluent, sludge, and ash samples from an Ontario waste water treatment plant. *Organohalogen Compounds*, 24, 75-80.

Gotz, R, Schumacher E, 1990. Polychlorierte Dibenzo-p-dioxine (PCDDs) und polychlorierte Dibenzofurane (PCDFs) in Sedimenten und Fischen aus dem Hamburger Hafen. *Chemosphere*, 20, 51-73.

Granier, L, Chevreuil, M, Carru, A-M, Letolle, R, 1990. Urban runoff pollution by organochlorines (polychlorinated biphenyls and lindane) and heavy metals (lead, zinc and chromium). *Chemosphere*, 21, 1101-1107.

Graynoth, E, 1996. Determination of the age of brown and rainbow trout in a range of New Zealand lakes. *Marine and Freshwater Research*, 47, 749-756.

Grobler, DF, 1994. A note on PCBs and chlorinated hydrocarbon pesticide residues in water, fish and sediment from the Olifants River, Eastern Transvaal, South Africa. *Water South Africa*, 20, 187-194.

Harrod, TR, 1994. Runoff, soil erosion and pesticide pollution in Cornwall. In: *Conserving Soil Resources: European Perspectives*. Selected papers from the First International Congress of the European Society for Soil Conservation (Rickson, RJ, ed.). CAB International, Wallingford UK. Pp. 105-115.

Hassett, AJ, Viljoen, PT, Liebenberg, JJE, 1987. An assessment of chlorinated pesticides in the major surface water resources of the Orange Free State during the period September 1984 to September 1985. *Water South Africa*, 13, 133-136.

Health Council of the Netherlands Committee on Risk Evaluation of Substances/Dioxins, 1996. *Dioxins, polychlorinated dibenzo-p-dioxins, dibenzofurans and dioxin-like polychlorinated biphenyls*. Publication No. 1996/10E, Health Council of the Netherlands, The Hague.

Heath, RGM, 1992. The levels of organochlorine pesticides in indigenous fish from two rivers that flow through the Kruger National Park, South Africa. *Water Supply*, 10, 177-185.

Heida, H, van der Oost, R, 1995. The Volgermeerpolder revisited: Dioxins in sediments, topsoil, and eel. *Organohalogen Compounds*, 24: 281-284.

Herrmann, R, 1987. Temporal variations of some trace organics (HCB, HCH, PCB and PAH) in rainfall, runoff and in lake sediments in remote sites of New Zealand. *Catena*, 14, 233-248.

Hickey, CW, Buckland, SJ, Hannah, DJ, Roper, DS, Stüben, K, 1997. Polychlorinated biphenyls and organochlorine pesticides in the freshwater mussel *Hyridella menziesi* from the Waikato River, New Zealand. *Bulletin of Environmental Contamination and Toxicology*, 59, 106-112.

Himberg, KK, 1993. Coplanar polychlorinated biphenyls in some Finnish food commodities. *Chemosphere*, 27, 1235-1243.

Hodson, PV, Castonguay, M, Couillard, CM, Desjardins, C, Pelletier, E, McLeod, R, 1994. Spatial and temporal variations in chemical contamination of American eels, *Anguilla rostrata*, captured in the estuary of the St Lawrence River. *Canadian Journal of Fisheries and Aquatic Sciences*, 51, 464-477.

Hodson, PV, Desjardins, C, Pelletier, E, Castonguay, M, McLeod, R, Couillard, CM, 1992a. Decrease in chemical contamination of American eels (*Anguilla rostrata*) captured in the estuary of the St Lawrence River. *Canadian Technical Report on Fisheries and Aquatic Sciences*, 1876, 1-57.

Hodson, PV, McWhirter, M, Ralph, K, Gary, B, Thieierge, D, Carey, JH, Van Der Kraak, G, Whittle, DM, Levesque, M-C, 1992b. Effects of bleached kraft mill effluent on fish in the St Maurice River, Quebec. *Environmental Toxicology and Chemistry*, 11, 1635-1651.

Horstmann, M, McLachlan MS, 1995. Concentrations of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in urban runoff and household wastewaters. *Chemosphere*, 31, 2887-2896.

Hu, LC, Todd, PR, 1981. An improved technique for preparing eel otoliths for ageing. *New Zealand Journal of Marine and Freshwater Research*, 15, 446-446.

Ismail, SMM, Reda, LA, Ahmed, MT, 1995. Residues of some organochlorine insecticides from some water bodies, their toxicity to mosquito larvae *Culex pipiens* and influence on mitochondrial ATPase of Bolti fish, *Tilapia niloticus*. *International Journal of Environmental Health Research*, 5, 287-292.

Iwata, H, Tanabe, S, Sakai, N, Nishimura, A, Tatsukawa, R, 1994. Geographical distribution of persistent organochlorines in air, water and sediments from Asia and Oceania, and their implications for global redistribution from lower latitudes. *Environmental Pollution*, 85, 15-33.

Jan, J, Zupancic-Kralj, L, Zigon, D, 1994. Residue profile of PCB, PCB and CBz in fish algae, moss and sediment from the polluted River Krupa (Slovenia). *Toxicological and Environmental Chemistry*, 43, 235-243.

Janiot, LJ, Sericano, JL, Roses, OE, 1994. Chlorinated pesticide occurrence in the Uruguay River (Argentina-Uruguay). *Water, Air, and Soil Pollution*, 76, 323-331.

Jansson, B, Andersson, R, Asplund, L, Litzen, K, Nylund, K, Sellstrom, U, Uvemo, U-B, Wahlberg, C, Wideqvist, U, Odsjo, T, Olsson, M, 1993. Chlorinated and brominated persistent organic compounds in biological samples from the environment. *Environmental Toxicology and Chemistry*, 12, 1163-1174.

Jobb, B, Uza, M, Hunsinger, R, Roberts, K, Tosine, H, Clement, R, Bobbie, B, LeBel, G, Williams, D, Lau, B, 1990. A survey of drinking water supplies in the Province of Ontario for dioxins and furans. *Chemosphere*, 20, 1553-1558.

Johnson, A, Norton, D, Yake, B, 1988. Persistence of DDT in the Yakima River drainage, Washington. *Archives of Environmental Contamination and Toxicology*, 17, 289-297.

Jones, PD, 1996. *Biomarker and contaminant bioaccumulation studies of caged and feral fish in the Waikato River*. A report from the Institute of Environmental Science and Research to Environment Waikato, Hamilton, New Zealand.

Jones, KC, Alcock, RE, 1996. *Dioxin inputs to the environment: A review of temporal trend data and proposals for a monitoring programme to detect past and future changes in the UK*. Report to the Chemicals and Biotechnology Division, Department of the Environment, DoE EPG/1/5/53, Lancaster University, Lancaster, England.

Jones, PD, Hannah, DJ, Buckland, SJ, Power, FM, Gardner, AR, Randall, CJ, 1995. The induction of EROD activity in New Zealand freshwater fish species as an indicator of environmental contamination. *Australasian Journal of Ecotoxicology*, 1, 99-105.

Kannan, K, Tanabe, S, Quynh, HT, Hue, ND, Tatsukawa, R, 1992. Residue pattern and dietary intake of persistent organochlorine compounds in foodstuffs from Vietnam. *Archives of Environmental Contamination and Toxicology*, 22, 3667-374.

Kannan, K, Tanabe, T, Williams, RJ, Tatsukawa, R, 1994. Persistent organochlorine residues in foodstuffs from Australia, Papua New Guinea and the Solomon Islands: Contamination levels and human dietary exposure. *Science of the Total Environment*, 153, 29-49.

Karl, H, Lehmann, I, 1993. Organochlorine residues in the edible part of eels of different origins. *Zeitschrift fur Lebensmittel Untersuchung und Forschung*, 197, 385-388.

Kidwell, JM, Phillips, LJ, Birchard, GF, 1995. Comparative analyses of contaminant levels in bottom feeding and predatory fish using the national contaminant biomonitoring program data. *Bulletin of Environmental Contamination and Toxicology*, 54, 919-923.

Kjeller, L-O, Jones, KC, Johnston, AE, Rappe, C, 1991. Increases in the polychlorinated dibenz-p-dioxin and -furan content of soils and vegetation since the 1840s. *Environmental Science and Technology*, 25, 1619-1627.

Knutzen, J, Oehme M, 1989. Polychlorinated dibenzofuran (PCDF) and dibenzo-p-dioxin (PCDD) levels in organisms and sediments from the Frierfjord, southern Norway. *Chemosphere*, 19, 1897-1909.

Knutzen, J, Schlabach M, 1996. Summary of data on toxicity equivalents from PCDF/PCDD and non-ortho PCB in marine organisms and sediments from Norway. *Organohalogen Compounds*, 28, 219-223.

Koistinen, J, Paasivirta, J, Lahtipera, M, 1993. Bioaccumulation of dioxins, coplanar PCBs, PCDEs, HxCNs, R-PCNs, R-PCPHs and R-PCBBs in fish from a pulp-mill recipient watercourse. *Chemosphere*, 27, 149-156.

Korhonen, M, Verta, M, Vartiainen, T, 1997. Contamination of fish by PCDDs and PCDFs in the Kymijoki River and its estuary. *Organohalogen Compounds*, 32, 305-310.

Kucklick, JR, Bidleman, TF, McConnell, LL, Walla, MD, Ivanov, GP, 1994. Organochlorines in the water and biota of Lake Baikal, Siberia. *Environmental Science and Technology*, 28, 31-37.

Kuehl, DW, Butterworth, B, Marquis, PJ, 1994. A national study of chemical residues in fish. III. Study results. *Chemosphere*, 29, 523-535.

Kuehl, DW, Leonard, EN, Welch, KJ, Veith, GD, 1980. Identification of hazardous organic chemicals in fish from the Ashtabula River, Ohio, and Wabash River, Indiana. *Journal of the Association of Official Analytical Chemists*, 63, 1238-1244.

Kuntz, KW, Warry, ND, 1983. Chlorinated organic contaminants in water and suspended sediments of the lower Niagara River. *Journal of Great Lakes Research*, 9, 241-248.

Kutz, FW, Barnes, DG, Bottimore, DP, Greim, H, Brethauer, EW, 1990. The international toxicity equivalency factor (I-TEF) method of risk assessment for complex mixtures of dioxins and related compounds. *Chemosphere*, 20, 751-757.

Lampi, P, Kimmo, T, Vartiaainen, T, Tuomisto, J, 1992. Chlorophenols in lake bottom sediments: A retrospective study of drinking water contamination. *Chemosphere*, 24, 1805-1824.

Larsson, P, Berglund, O, Backe, C, Bremle, G, Eklov, A, Jarnmark, C, Persson, A, 1995. DDT-fate in tropical and temperate regions. *Naturwissenschaften*, 82, 559-561.

Lebo, JA, Gale, RW, Petty, JD, Tillitt, DE, Huckins, JN, Meadows, JC, Orazio, CE, Echols, KR, Schroeder, DJ, 1995. Use of the semipermeable membrane device as an in situ sampler of waterborne bioavailable PCDD PCDF residues at sub-parts-per-quadrillion concentrations. *Environmental Science and Technology*, 29, 2886-2892.

Leiker, TJ, Rostad, CE, Barnes, CR, Pereira, WE, 1991. A reconnaissance study of halogenated organic compounds in catfish from the lower Mississippi River and its major tributaries. *Chemosphere*, 23, 817-829.

Lockhart, WL, Wagemann, R, Tracey, B, Sutherland, D, Thomas, DJ, 1992. Presence and implications of chemical contaminants in the freshwaters of the Canadian Arctic. *Science of the Total Environment*, 122, 165-243.

Loganathan, BG, Kannan, K, Watanabe, I, Kawano, M, Irvine, K, Kumar, S, Sikka, HC, 1995. Isomer-specific determination and toxic evaluation of polychlorinated biphenyls, polychlorinated/brominated dibenzo-p-dioxins and dibenzofurans, polybrominated biphenyl ethers, and extractable organic halogen in carp from the Buffalo River, New York. *Environmental Science and Technology*, 29, 1832-1838.

Luckas, B, Oehme, M, 1990. Characteristic contamination levels for polychlorinated hydrocarbons, dibenzofurans and dibenzo-p-dioxins in bream (*Abramis brama*) from the River Elbe. *Chemosphere*, 21, 79-89.

Ludwig, JP, Auman, HJ, Kurita, H, Ludwig, ME, Campbell, LM, Giesy, JP, Tillitt, DE, Jones, PD, Yamashita, N, Tanabe, S, Tatsukawa, R 1993. Caspian tern reproduction in the Saginaw Bay ecosystem following a 100-year flood event. *Journal of Great Lakes Research*, 19, 96-108.

Luksemburg, WJ, Mitzel, RS, Zhou, H, Hedin, JM, Silverbush, BB, Wong, AS, 1996. Polychlorinated dioxins and dibenzofurans in environmental samples from China. *Organohalogen Compounds*, 28, 262-266.

Maasdam, R, Smith, DG, 1994. New Zealand's National River Water Quality Network. 2. Relationships between physico-chemical data and environmental factors. *New Zealand Journal of Marine and Freshwater Research*, 28, 37-54.

MacDonald, DD, 1994. *A Review of Environmental Quality Criteria and Guidelines for Priority Substances in the Fraser River Basin*. A report to Environment Canada, Pacific and Yukon Branch, North Vancouver BC, March 1994.

Marien, K, Laflamme, DM, 1995. Determination of a tolerable daily intake of DDT for consumers of DDT contaminated fish from the lower Yakima River, Washington. *Risk Analysis*, 15, 709-717.

Mason, CF, 1993. Organochlorine pesticide residues and PCBs in eels (*Anguilla anguilla*) from some British freshwater reedbeds. *Chemosphere*, 26, 2289-2292.

Mathur, DB, Stephenson, MJ, Wenning, RJ, Paustenbach, DJ, Folwarkow, S, Luksemburg, WJ, 1997. PCDD/PCDFs in storm water outfalls adjacent to urban areas and petroleum refineries in San Francisco Bay, California, USA. *Organohalogen Compounds*, 32, 1-5.

Mayer, R, 1995. PCDD/PCDF levels in rainbow trout and carp from south Germany. *Organohalogen Compounds*, 24, 391-394.

McKenzie Smith, F, Tiller, D, Allen, D, 1994. Organochlorine pesticide residues in water and sediments from the Ovens and King rivers, north-east Victoria, Australia. *Archives of Environmental Contamination and Toxicology*, 26, 483.

Metcalfe, JL, Fox, ME, Carey, JH, 1984. Aquatic leeches (Hirudinea) as bioindicators of organic chemical contaminants in freshwater ecosystems. *Chemosphere*, 13, 143-150.

Meyer, C, O'Keefe, P, Hilker, D, Rafferty, L, Wilson, L, Connor, S, Aldous, K, Markussen, K, Slade, K, 1989. A survey of twenty community water systems in New York State for PCDDs and PCDFs. *Chemosphere*, 19, 21-26.

Miller, MA, Kassulke, NM, Walkowski, MD, 1993. Organochlorine concentrations in Laurentian Great Lakes salmonines: Implications for fisheries management. *Archives of Environmental Contamination and Toxicology*, 25, 212-219.

Miller, MA, Madenjian, CP, Masnado, RG, 1992. Patterns of organochlorine contamination in lake trout from Wisconsin waters of the Great Lakes. *Journal of Great Lakes Research*, 18, 742-754.

Ministry of Agriculture, Fisheries and Food, 1997. Dioxins and polychlorinated biphenyls in foods and human milk. *Food Surveillance Information Sheet*, No. 105, Ministry of Agriculture, Fisheries and Food, London, United Kingdom.

Ministry for the Environment, 1988. *A Strategy for Managing PCBs*. Ministry for the Environment, Wellington, New Zealand.

Ministry for the Environment, 1989. *The herbicide 2,4,5-T: Technical report of an investigation into residues of the herbicide and its dioxin component in sheepmeats*. Ministry for the Environment, Wellington, New Zealand.

Ministry for the Environment, 1992. *Pentachlorophenol Risk Assessment Pilot Study*. Ministry for the Environment, Wellington, New Zealand.

Ministry of Health, 1998. Stirling, F, personal communication.

Ministry of Housing, Spatial Planning and the Environment 1994. *Environmental Quality Objectives for the Netherlands*. Risk Assessment and Environmental Quality Division, Directorate for Chemicals, External Safety and Radiation Protection, Ministry of Housing, Spatial Planning and the Environment, The Hague, The Netherlands.

Miyata, H, Ohta, S, Aozasa, O, 1992. Levels of PCDDs, PCDFs and non-*ortho* coplanar PCBs in drinking water in Japan. *Organohalogen Compounds*, 9, 151-154.

Mosse, PRL, Haynes D, 1993. Dioxin and furan concentrations in uncontaminated waters, sediments and biota of the Ninety Mile Beach, Bass Strait, Australia. *Marine Pollution Bulletin*, 26, 465-468.

Mugachia, JC, Kanja, L, Gitau, F, 1992a. Organochlorine pesticide residues in fish from Lake Naivasha and Tana River, Kenya. *Bulletin of Environmental Contamination and Toxicology*, 49, 207-210.

Mugachia, JC, Kanja, L, Maitho, TE, 1992b. Organochlorine pesticide residues in estuarine fish from the Athi River, Kenya. *Bulletin of Environmental Contamination and Toxicology*, 49, 199-206.

Muir, DCG, Ford, CA, Grift, NP, Metner, DA, Lockhart, WL, 1990. Geographic variation of chlorinated hydrocarbons in burbot (*Lota lota*) from remote lakes and rivers in Canada. *Archives of Environmental Contamination and Toxicology*, 19, 530-542.

Naf, C, Broman, D, Ishaq, R, Zebuhr, Y, 1990. PCDDs and PCDFs in water, sludge and air samples from various levels in a waste water treatment plant with respect to composition changes and total flux. *Chemosphere*, 20, 1503-1510.

Nair, A, Dureja, P, Pillai, MKK, 1991. Levels of aldrin and dieldrin in environmental samples from Delhi, India. *Science of the Total Environment*, 108, 255-259.

Nair, A, Pillai, MKK, 1992. Trends in ambient levels of DDT and HCH residues in humans and the environment of Delhi, India. *Science of the Total Environment*, 121, 145-157.

Napolitano, GE, Richmond, JE, 1995. Enrichment of biogenic lipids, hydrocarbons and PCBs in stream-surface foams. *Environmental Toxicology and Chemistry*, 14, 197-201.

Nayak, AK, Raha, R, Das, AK, 1995. Organochlorine pesticide residues in middle stream of the Ganga River, India. *Bulletin of Environmental Contamination and Toxicology*, 54, 68-75.

NCASI, 1990. *US EPA/Paper industry co-operative dioxin study: The 104 mill study*. Technical Bulletin No. 590.

Nemecek, J, Podlesakova, E, Firyt, P, 1994. Contamination of soils in the north-Bohemian region by organic xenobiotic compounds. *Rostlinna Vyroba*, 40, 113-121.

Newsome, WH, Andrews, P, 1993. Organochlorine pesticides and polychlorinated biphenyl congeners in commercial fish from the Great Lakes. *Journal of the Association of Official Analytical Chemists International*, 76, 707-710.

Niimi, AJ, Oliver, BG, 1989. Assessment of relative toxicity of chlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls in Lake Ontario salmonids to mammalian systems using toxic equivalent factors (TEF). *Chemosphere*, 18, 1413-1423.

OECD, 1987. Control of PCB waste, *Environmental Monographs No. 12*. Organisation for Economic Co-operation and Development.

Oehme, M, Mane, S, Brevik, EM, Knutzen, J, 1989. Determination of polychlorinated dibenzofuran (PCDF) and dibenzo-p-dioxin (PCDD) levels and isomer patterns in fish, Crustacea, mussel and sediment samples from a fjord region polluted by Mg-production. *Fresenius Zeitschrift fur Chemie*, 335, 987-997.

Oliver, BG, Niimi, AJ, 1988. Trophodynamic analysis of polychlorinated biphenyl congeners and other chlorinated hydrocarbons in the Lake Ontario ecosystem. *Environmental Science and Technology*, 22, 388-397.

Orazio, CE, Kapila, S, Puri, RK, Meadows, J, Yanders, AF, 1990. Field and laboratory studies on sources and persistence of chlordane contamination in the Missouri aquatic environment. *Chemosphere*, 20, 1581-1588.

Owens, JW, Swanson, SM, Birkholz, DA, 1994. Environmental monitoring of bleached kraft pulp mill chlorophenolic compounds in a northern Canadian river system. *Chemosphere*, 29, 89-109.

Paasivirta, J, Koistinen, J, Mannila, E, Vuorinen, PJ, Kannan, N, Yamashita, N, Tanabe, S, Tatsukawa, R, 1990. Coplanar PCBs in Finnish wildlife. *Coplanar PCBs*. Ed. Tatsukawa, R, Giesy, JP, Lewis Publishers, Michigan USA.

Paasivirta, J, Palm, H, Paukku, R, Akhabuhaya, J, Lodenius, M, 1988. Chlorinated insecticide residues in Tanzanian environment, Tanzadrin. *Chemosphere*, 17, 2055-2062.

Paasivirta, J, Särkkä, J, Aho, M, Surma-Aho, K, Tarhanen, J, Roos, A, 1981. Recent trends of biocides in pikes of the Lake Päijänne. *Chemosphere*, 4, 405-414.

Paasivirta, J, Särkkä, J, Leskijärvi, T, Roos, A, 1980. Transportation and enrichment of chlorinated phenolic compounds in different aquatic food chains. *Chemosphere*, 9, 441-456.

Parsons, AH, Huntley, SL, Ebert, ES, Algeo, ER, Keenan, RE, 1991. Risk assessment for dioxin in Columbia River fish. *Chemosphere*, 23, 1709-1717.

Paustenbach, DJ, Wenning, RJ, Mathur, D, Luksemburg, W, 1996. PCDD/PCDFs in urban stormwater discharged to San Francisco Bay, California, USA. *Organohalogen Compounds*, 28, 111-116.

Pereira, WE, Domagalski, JL, Hostettler, FD, Brown, LR, Rapp, JB, 1996. Occurrence and accumulation of pesticides and organic contaminants in river sediment, water and clam tissues from the San Joaquin River and tributaries, California. *Environmental Toxicology and Chemistry*, 15, 172-180.

Pham, T, Lum, K, Lemieux, C, 1993. The occurrence, distribution and sources of DDT in the St Lawrence River, Quebec (Canada). *Chemosphere*, 26, 1595-1606.

Power, F, 1994. Organic contaminant inputs/dioxins and organics in foodstuffs. In: Donald, R, 1994. *Environment BOP Tarawera River Regional Plan Technical Investigations: Proceedings of a Toxicity Workshop*, Environment BOP Environmental Report 94/15.

Quemerais, B, Lemieux, C, Lum, KR, 1994. Concentrations and sources of PCBs and organochlorine pesticides in the St Lawrence River (Canada) and its tributaries. *Chemosphere*, 29, 591-610.

Rainer, M, 1996. Dioxin-like PCB in food and breast milk samples. *Organohalogen Compounds*, 28, 271-276.

Rappe, C, Bergqvist, P-A, Kjeller, L-O, 1989a. Levels, trends and patterns of PCDDs, PCDFs in Scandinavian environmental samples. *Chemosphere*, 18, 651-658.

Rappe, C, Kjeller, L-O, Andersson, R, 1989b. Analyses of PCDDs and PCDFs in sludge and water samples. *Chemosphere*, 19, 13-20.

Reed, LW, Hunt, GT, Maisel, BE, Hoyt, M, Keefe, D, Hackney, P, 1990. Baseline assessment of PCDDs/PCDFs in the vicinity of the Elk River, Minnesota, Generating Station. *Chemosphere*, 21, 159-171.

Reiner, EJ, MacPherson, KA, Kolic, TM, Hayton, A, Clement, RE, 1995. Characteristic levels of chlorinated dibenzo-p-dioxins and dibenzofurans in fish from Ontario Great Lakes. *Organohalogen Compounds*, 24, 379-384.

Rico, MC, Hernandez, L, Fernandez, M, Gonzalez, MJ, Montero, M, 1989. Organochlorine contamination in water of the Donana National Park. *Water Research Oxford*, 23, 57-60.

Rinella, JF, Hamilton, PA, McKenzie, SW, 1993. *Persistence of the DDT pesticide in the Yakima River basin, Washington*. United States Printing Office.

Rogers, IH, Servizi, JA, Levings, CD, 1988. Bioconcentration of chlorophenols by juvenile Chinook salmon (*Oncorhynchus tshawytscha*) overwintering in the upper Fraser River: Field and laboratory tests. *Water Pollution Research Journal of Canada*, 23, 100-113.

Rose, CL, McKay, WA, Ambidge, PF, 1994. *Distribution of PCDDs and PCDFs in surface freshwater systems*. R&D Note 242. National Rivers Authority, Bristol, United Kingdom.

Ruelle, R, Keenlyne, KD, 1993. Contaminants in Missouri River pallid sturgeon. *Bulletin of Environmental Contamination and Toxicology*, 50, 898-906.

Ruiz, X, Llorente, GA, 1991. Seasonal variation of DDT and PCB accumulation in muscle of carp (*Cyprinus carpio*) and eels (*Anguilla anguilla*) from the Ebro delta, Spain. *Vie et Milieu*, 41, 133-140.

Ryan, JJ, Lau, PY, Pilon, JC, Lewis, D, 1983a. 2,3,7,8-Tetrachlorinated dibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzofuran residues in Great Lakes commercial and sport fish. In: Choudhary, G, Keith, L, Rappe, C., Eds., 1983. *Chlorinated dioxins and dibenzofurans in the total environment II*. Butterworth Publishers, Boston, MA, 87-97.

Ryan, JJ, Pilon, JC, Conacher, HBS, Firestone, D, 1983b. *Journal Association Official Analytical Chemists*, 66, 700-707.

Safe, SH, 1994. Polychlorinated biphenyls (PCBs): Environmental impact, biochemical and toxic responses, and implications for risk assessment. *Critical Reviews in Toxicology*, 24, 87-149.

Safe, S, Hutzinger, O, Eds., 1987. *Polychlorinated Biphenyls (PCBs): Mammalian and Environmental Toxicology*. Environmental Toxin Series, Volume 1, Springer-Verlag, Berlin, Heidelberg.

Sakurai, T, Kim, J-G, Suzuki, N, Nakanishi, J, 1996. Polychlorinated dibenzo-p-dioxins and dibenzofurans in sediment, soil, fish and shrimp from a Japanese freshwater lake area. *Chemosphere*, 33, 2007-2020.

Schuler, W, Brunn, H, Manz, D, 1985. Pesticides and polychlorinated biphenyls in fish from the Lahn River. *Bulletin of Environmental Contamination and Toxicology*, 34, 608-616.

Scobie, S, Buckland, SJ, Ellis, HK, Salter, RT, 1998. *Organochlorines in New Zealand: Ambient concentrations of selected organochlorines in estuaries*. Ministry for the Environment, Wellington, New Zealand.

Servizi, JA, Gordon, RW, 1988. Bioconcentration of chlorophenols by early life stages of Fraser River Pink and chinook salmon (*Oncorhynchus gorbuscha*, *O. tshawytscha*). *Water Pollution Research Journal of Canada*, 23, 88-98.

Servos, MR, Huestis, SY, Whittle, DM, Van Der Kraak, GJ, Munkittrick, KR, 1994. Survey of receiving water environmental impacts associated with discharges from pulp mills. 3. Polychlorinated dioxins and furans in muscle and liver of white sucker (*Catostomus commersoni*). *Environmental Toxicology and Chemistry*, 13, 1103-1115.

Smit, Z, Drevankar, V, Kodric-Smit, M, 1987. Polychlorinated biphenyls in the Krupa River, Croatia, Yugoslavia. *Chemosphere*, 16, 2351-2358.

Smith, DG, Maasdamp, R, 1994. New Zealand's National River Water Quality Network. 1. Design and physico-chemical characterisation. *New Zealand Journal of Marine and Freshwater Research*, 28, 19-35.

Söderström, M, Wachtmeister, CA, Förlin, L, 1994. Analysis of chlorophenolics from bleach Kraft mill effluents in bile of perch (*Perca fluviatilis*) from the Baltic Sea and development of an analytical procedure also measuring catechols. *Chemosphere*, 28, 1701-1719.

Stortelder, PB, van der Gaag, MA, van der Kooij, LA, 1989. Perspectives for water organisms. An ecological basis for quality objectives for water and sediment. Part 1. Results and calculations. *DBW/RIZA Memorandum N. 89.016a*. (English Version August 1991) Institute for Inland Water Management and Waste Water Treatment, The Netherlands.

Stow, CA, 1995. Factors associated with PCB concentrations in Lake Michigan salmonids. *Environment Science Technology*, 29, 522-527.

Subramanian, BR, Tanabe, S, Hidaka, H, Tatsukawa, R, 1983. DDTs and PCB isomers and congeners in Antarctic fish. *Archives of Environmental Contamination and Toxicology*, 12, 621-626.

Suns, KR, Hitchin, GG, 1992. Species-specific differences in organochlorine accumulation in young-of-the-year spottail shiners, emerald shiners, and yellow perch. *Journal of Great Lakes Research*, 185, 280-285.

Swackhamer, DL, Armstrong, DE, 1987. Distribution and characterization of PCBs in lake Michigan water. *Journal of Great Lakes Research*, 13, 24-36.

Tabucanon, MS, Watanabe, S, Siriwong, C, Boonyatumonond, R, Tanabe, S, Iwata, H, Tatsukawa, R, Ohgaki, S, 1992. Current status of contamination by persistent organochlorines in the lower Chao Phraya River, Thailand. *Water Science and Technology*, 25, 17-24.

Tanabe, S, Hidaka, H, Tatsukawa, R, 1983. PCBs and chlorinated hydrocarbon pesticides in Antarctic atmosphere and hydrosphere. *Chemosphere*, 12, 277-288.

Tate, CM, Heiny, JS, 1996. Organochlorine compounds in bed sediment and fish tissue in the South Platte River Basin, USA, 1992-1993. *Archives of Environmental Contamination and Toxicology*, 30, 62-78.

Terytze, K, Mende, W, 1993. Low volatile chlorinated hydrocarbons in aquatic sediments in Berlin and surrounding areas. *Land Degradation and Rehabilitation*, 4, 361-366.

Theelen, RMC, Liem, AKD, Slob, W, Van Wijnen, JH, 1993. Intake of 2,3,7,8 chlorine substituted dioxins, furans, and planar PCBs from food stuffs in the Netherlands: Median and distribution. *Chemosphere*, 27, 1625-1635.

Thomson, B, Davies, J, 1993. *Interpretation of organochlorine and hydrocarbon contaminants in the Avon and Heathcote river and estuary system*. A report from the Institute of Environmental Health and Forensic Sciences to the Canterbury Regional Council, Christchurch, New Zealand.

Tsipi, D, Hiskia, A, 1996. Organochlorine pesticides and triazines in the drinking water of Athens. *Bulletin of Environmental Contamination and Toxicology*, 57, 250-257.

Tulonen, J, Vuorinen, PJ, 1996. Concentrations of PCBs and other organochlorine compounds in eels (*Anguilla anguilla*, L.) of the Vanajavesi watercourse in southern Finland, 1990-1993. *Science of the Total Environment*, 187, 11-18.

Turkstra, E, Pols, HB, 1989. PCDDs and PCDFs in Dutch inland waters. *Chemosphere*, 18, 539-551.

UNEP, 1997. Governing Council Decision 19/13C.

US EPA, 1987. *The national dioxin study tiers 3, 4, 5 and 7*. EPA 440/4-87-003. Office of Water Regulation and Standards, Washington, DC.

US EPA, 1992. *National Study of Chemical Residues in Fish*. Office of Science and Technology, US Environmental Protection Agency. EPA 823-R-92-008a, Washington DC.

US EPA, 1993. *Interim Report on Data and Methods for Assessment of 2,3,7,8-Tetrachlorodibenzo-p-dioxin: Risks to Aquatic Life and Wildlife*, EPA 600/R-93/055.

US EPA, 1995. *Great Lakes Water Quality Initiative*, Federal Register 40 CFR Parts 122, 123, 131, and 132, March 1995, Vol. 60, No. 56 15366-15423.

US EPA, 1998. *The inventory of sources of dioxin in the United States*. EPA/600/P-98/002Aa. Office of Research and Development, Washington, DC.

Van den Berg, M, Birnbaum, L., Bosveld, ATC, Brunström, B, Cook, P, Feeley, M, Giesy, J, Hanberg, A, Hasegawa, R, Kennedy, SW, Kubiak, T, Larsen, JC, Rolaf van Leeuwen, FX, Liem, AKD, Nolt, C, Peterson, RE, Poellinger, L, Safe, S, Schrenk, D, Tillitt, D, Tysklind, M, Younes, M, Wærn, F, Zacharewski, T, 1998. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environmental Health Perspectives*, 106, 775-792.

van der Oost, R, Heida, H, Opperhuizen, A, 1988. Polychlorinated biphenyl congeners in sediments, plankton, molluscs, crustaceans, and eel in a freshwater lake: Implications of using reference chemicals and indicator organisms in bioaccumulation studies. *Archives of Environmental Contamination and Toxicology*, 17, 721-729.

van der Oost, R, Opperhuizen, A, Satumalay, K, Heida, H, Vermeulen, NPE, 1996. Biomonitoring aquatic pollution with feral eel (*Anguilla anguilla*). I. Bioaccumulation: Biota-sediment ratios of PCBs, OCPs, PCDDs and PCDFs. *Aquatic Toxicology*, 35, 21-46.

Van Oostdam, JC, Ward, JEH, 1995. *Dioxins and Furans in the British Columbia Environment*. BC Environment, Victoria, British Columbia.

Vartiainen, T, Hallikainen A, 1992. Polychlorodibenzo-p-dioxin and polychlorodibenzofuran (PCDD/F) levels in Baltic herring and rainbow trout samples in Finland. *Organohalogen Compounds*, 9, 305-308.

Vartiainen, T, Mannio, K, Strandman, T, 1996. Concentrations of PCDDs, PCDFs and coplanar PCBs in fish from Subarctic lakes in Finland. *Organohalogen Compounds*, 28, 340-343.

Verbrugge, DA, Giesy, JP, Mora, MA, Williams, LL, Rossmann, R, Moll, RA, Tuchman, M, 1995. Concentrations of dissolved and particulate polychlorinated biphenyls in water from the Saginaw River, Michigan. *Journal of Great Lakes Research*, 21, 219-233.

Vigano, L, Galassi, S, Arillo, A, 1994. Bioconcentration of polychlorinated biphenyls (PCBs) in rainbow trout caged in the River Po. *Ecotoxicology and Environmental Safety*, 28, 287-297.

Vojinovic, MB, Pavkov, ST, Buzarov, DD, 1990. Residues of persistent organochlorine compounds in selected aquatic ecosystems of Vojvodina (Yugoslavia). *Water Science and Technology*, 22, 107-111.

Vuorinen, PJ, 1985. Organochlorine compounds in Baltic salmon and trout. I. Chlorinated hydrocarbons and chlorophenols 1982. *Chemosphere*, 14, 1729-1740.

Waid, JS, 1986. *PCBs and the Environment*. CRC Press, Boca Raton, Florida.

Wandan, EN, Zabik, MJ, 1996. Assessment of surface water quality in Cote d'Ivoire. *Bulletin of Environmental Contamination and Toxicology*, 56, 73-79.

Watanabe, I, Kawano, M, Tatsukawa, R, 1995. Polybrominated and mixed polybromo/chlorinated dibenzo-p-dioxins and dibenzofurans in the Japanese environment. *Organohalogen Compounds*, 24, 337-340.

Weber, K, Ernst, W, 1978. Levels and pattern of chlorophenols in water of the Weser estuary and the German Bight. *Chemosphere*, 11, 873-879.

Wegman, RC, Hofstee, WM, 1979. Chlorophenols in surface waters of the Netherlands (1976-1977). *Water Research*, 13, 651-657.

WHO, 1991. Summary report. *Consultation on tolerable daily intake from food of PCDDs and PCDFs*, Bilthoven, Netherlands, 4-7 December, 1990. EUR/ICP/PCS 030(S)0369n, Copenhagen: WHO Regional Office for Europe.

WHO, 1998. *Draft executive summary. Assessment of the health risk of dioxins: re-evaluation of the tolerable daily intake (TDI)*. WHO Consultation Meeting, May 25-29 1998, Geneva, Switzerland.

Wilkinson, L, 1996. *SYSTAT: The system for statistics*. SPSS Inc., Chicago, Illinois.

Williams, LL, Giesy, JP, DeGalan, N, Verbrugge, DA, Tillitt, DE, Ankley, GT, Welch, RL, 1992. Prediction of concentrations of 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents from total concentrations of polychlorinated biphenyls in fish fillets. *Environmental Science and Technology*, 26, 1151-1159.

Youngs, WD, Gutemann, WH, Josephson, DC, Miller, MD, Lisk, DJ, 1994. Residues of pp'-DDE in lake trout in Little Moose Lake in New York State. *Chemosphere*, 29, 405-406.

Zabik, ME, Zabik, MJ, Booren, AM, Daubenmire, S, Pascall, MA, Welch, R, Humphrey, H, 1995. Pesticides and total polychlorinated biphenyls residues in raw and cooked walleye and white bass harvested from the Great Lakes. *Bulletin of Environmental Contamination and Toxicology*, 54, 396-402.

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 "Safe Management of PCBs" was released by the Department of Health. | On application, the Director of the Toxic Substances Act 1979 may exempt companies from the use and storage prohibition on PCBs. However, storage and handling of PCBs must conform at all times with the code of practice "Safe Management of PCBs" in order to qualify for the exemption. |
| 1988 | The Toxic Substances Regulations 1983, Amendment No. 3, Sec. 54A. | The legislation (s.54) provides people who adhere to the code of practice "Safe Management of PCBs" a special defence against conviction under the PCB regulations relating to storage, use, transportation and disposal of PCBs. Transportation of all PCB material must comply with the requirements of NZS: 5433 "Code of Practice for the Transportation of Hazardous Substances on Land". | |

| Year | Legislation/Publication | Regulatory status | Comments |
|------|--|--|--|
| 1993 | The Toxic Substances Regulations 1983, Amendment No. 4 | Use of PCBs is prohibited from 1 January 1994. Storage of PCBs is prohibited effective from 1 August 1994. Disposal and storage of PCBs must comply with the Code of Practice. | The Code of Practice " <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 | Gazette, January 1964 | Application in dust form no longer permitted. | Disposal by spraying of Land and Survey blocks ceased but some special dispensations were allowed. |
| Aldrin, Dieldrin | 1966 | | Agricultural Chemicals Board recommends no further permits for use on agricultural land. By November 1966 no more permits were issued for agricultural use by the Department of Agriculture. | |
| Animal remedies | 1967 | Animal Remedies Act | Establishes Animal Remedies Board. Consolidates and amends the Stock Remedies Act (1934); prohibition on manufacturing, selling, importing, using an animal remedy without a licence; stringent labelling, container, advertising requirements; accuracy of information required. | An animal remedy is defined as any substance used to cure or treat disease, to destroy or prevent parasites, to maintain or improve health in animals. |
| All OC pesticides | 1968 | The Agricultural Chemicals Regulations | General controls on sales, permits, transport, storage; powers given to inspectors. | |
| Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Toxaphene | 1968 | The Agricultural Chemicals Regulations | 14 week withholding period for livestock from pasture treated with these pesticides. | |
| DDT | 1968 | The Agricultural Chemicals Regulations | Restrictions on amount of DDT allowed in packages for home garden use; 12 week withholding period placed on livestock. | |

| Included substances | Year | Legislation/Publication | Regulatory status | Comments |
|---|------------|---|---|---|
| Lindane | 1968 | The Agricultural Chemicals Regulations | 6 week withholding period for livestock from pasture treated with these pesticides. | |
| DDT | 1968 | The Agricultural Chemicals Notice, June 1968 | Further limits placed on DDT formulations including stricter control on permits, pasture types allowed, dry conditions, pellet sizes, abrasion criteria on pellets and acreage allowable. Use on dairy land is prohibited. | Permits were required for use on dairy land but none were issued (an effective prohibition). For other uses a permit was required but few permits were issued. |
| Aldrin, Chlordane, Dieldrin, DDT, Lindane | Up to 1970 | | Non-agricultural uses (timber and industrial pest control) not within the scope of the Agricultural Chemicals Act. | Heavy use of these substances for non-agricultural, industrial purposes during this period, also in timber treatment for borer control (dieldrin, DDT, chlordane). Lindane used as timber preservative. |
| Heptachlor, Endrin, Toxaphene | Up to 1970 | | | Limited use only, from the time of introduction of products containing these substances, up to 1970. |
| DDT, Lindane | 1970 | The Agricultural Chemicals (Pelleted Insecticides Specification) Notice | Specifies sizes, densities, abrasion criteria to be met, and standard testing methods for these. | |
| DDT | 1970 | Revocation of Agricultural Chemical Notice 1968 | All remaining DDT purchase and use subject to Department of Agriculture permit. | Permits then issued only for limited horticulture use where non-organochlorine pesticides were ineffective. |
| Heptachlor | 1971 | <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 | Tamu mu 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. |
| | | | 07/02/96 | 19.1 (at Shag Rock) | PS | < 2 | 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. |
| | | | 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 | Sample ¹ | n ² | Biometric measurement ³ | Min. | Max. | Mean ⁴ |
|-------------|------------------|----------------------|----------------|---|------------------|-------------------|----------------------------------|
| Waipa | Whatawhata | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 440 192 14 | 600 549 26 | 487 296 20 4.7 78.0 |
| Rangitaiki | Te Teko | LFE/SFE ⁵ | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 420 190 18 | 570 440 29 | 495 279 23 2.2 80.1 |
| Waingongoro | State Highway 45 | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 400 176 15 | 520 382 25 | 468 281 19 8.7 76.9 |
| Wanganui | Te Maire | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 430 215 17 | 570 536 26 | 508 380 22 6.5 77.9 |
| Manawatu | Opiki Bridge | SFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 470 236 6 | 600 410 13 | 538 345 9 6.2 78.3 |
| Mohaka | Raupunga | LFE | 4 | length, mm weight, g age, years lipid content, % WW moisture content, % | 390 136 12 | 860 2220 36 | 653 1093 23 4.3 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 weight, g age, years lipid content, % WW moisture content, % | 430 184 14 — — | 785 1780 36 8.8 73.0 | 653 807 23 8.8 73.0 |
| Ruamahanga | State Highway 2 | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 440 201 18 — — | 530 389 23 4.6 78.7 | 475 281 20 4.6 78.7 |
| Ruamahanga | Waihenga | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 350 95 13 — — | 500 408 22 9.9 77.1 | 432 225 18 9.9 77.1 |
| Haast | Roaring Billy | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 435 201 28 — — | 850 2203 37 11.7 77.0 | 593 817 33 11.7 77.0 |
| Waimakariri | Old H/W Bridge | LFE | 8 | length, mm weight, g age, years lipid content, % WW moisture content, % | 355 101 16 — — | 430 206 27 3.3 79.9 | 385 138 20 3.3 79.9 |
| Halswell | McCartney's Bridge | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 405 183 19 — — | 770 1172 32 10.5 75.2 | 506 436 23 10.5 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 weight, g age, years lipid content, % WW moisture content, % | 455 264 16 — — | 620 748 20 — — | 531 456 18 10.3 76.2 |
| Taieri | Allanton | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 460 232 18 — — | 545 442 23 — — | 513 370 20 ⁶ 9.9 74.6 |
| | | LFE BD | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 435 225 14 — — | 690 1003 20 — — | 505 408 18 11.1 75.8 |
| Mataura | Parawa | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 480 352 23 — — | 760 1219 49 — — | 583 672 32 12.8 76.6 |
| Mataura | Seaward Downs | LFE | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 370 130 14 — — | 520 341 20 — — | 430 207 17 10.1 75.3 |
| | | LFE BD | 6 | length, mm weight, g age, years lipid content, % WW moisture content, % | 305 154 13 — — | 510 365 23 — — | 425 235 17 8.2 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 weight, g age, years,months lipid content, % WW moisture content, % | 370 589 3,7 — — | 510 1560 6,7 — — | 453 1024 5,1 3.2 80.4 |
| Rangitaiki | Te Teko | BT | 3 | length, mm weight, g age, years,months lipid content, % WW moisture content, % | 470 1082 3,6 — — | 580 2356 4,7 — — | 510 1530 3,10 1.8 79.9 |
| | | RT | 5 | length, mm weight, g age, years,months lipid content, % WW moisture content, % | 290 272 2,0 — — | 470 1065 3,1 — — | 365 591 2,5 1.6 81.4 |
| Wanganui | Te Maire | RT | 5 | length, mm weight, g age, years,months lipid content, % WW moisture content, % | 230 171 1,1 — — | 410 948 3,1 — — | 304 425 1.9 4.6 78.2 |
| Tukituki | Tamumu Bridge | RT | 5 | length, mm weight, g age, years,months lipid content, % WW moisture content, % | 320 445 2,6 — — | 480 1316 2,6 — — | 368 667 2,6 4.5 76.0 |
| Ruamahanga | Waihenga | BT | 3 | length, mm weight, g age, years,months lipid content, % WW moisture content, % | 350 521 2,6 — — | 450 1007 4,6 — — | 413 832 3,6 5.4 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).

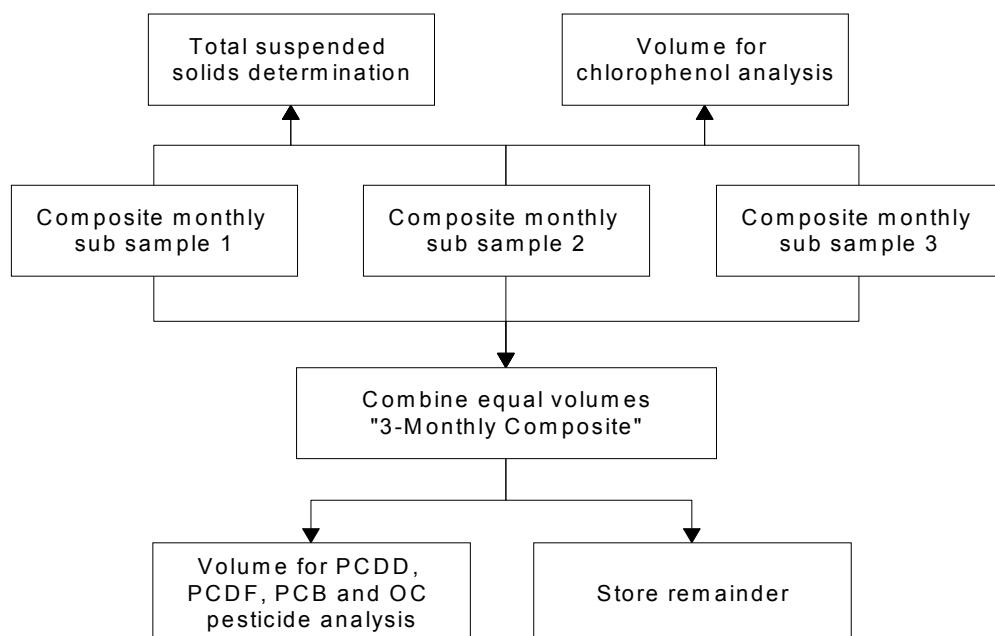


Figure C1 Preparation of composite river water samples

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 1 μ m 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).

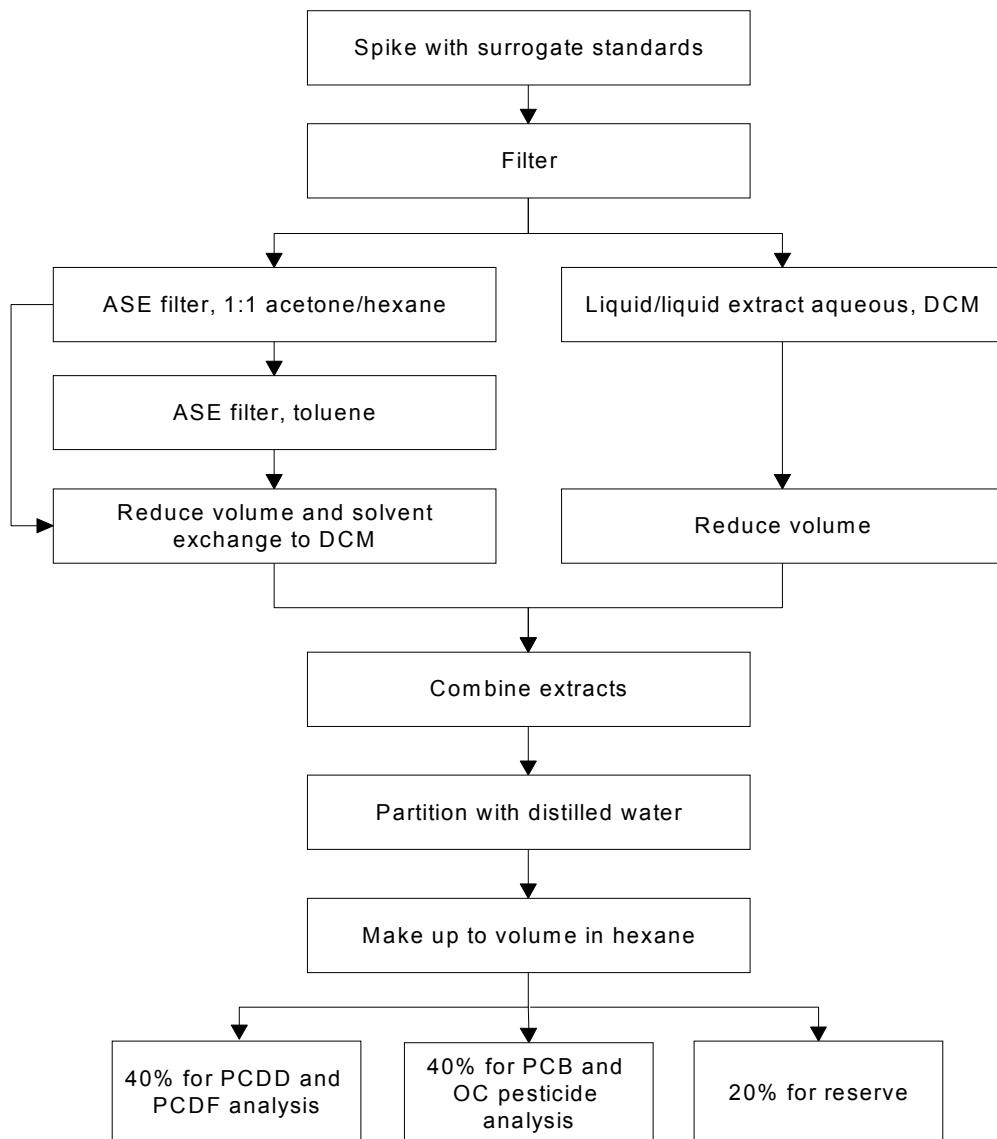


Figure C2 Extraction of river water for PCDD, PCDF, PCB and organochlorine pesticide analysis

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).

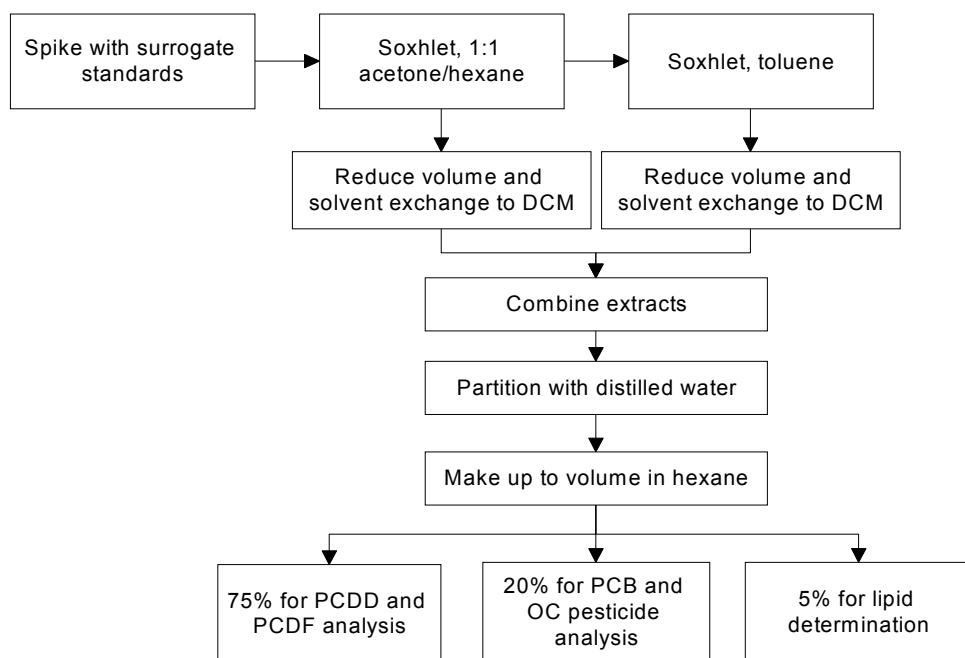


Figure C3 Extraction of river biota for PCDD, PCDF, PCB and organochlorine pesticide analysis

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)
- Carbopack 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)
- Carbopack 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 $\pm 10\%$ 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 $\pm 20\%$ 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 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 ^{13}C surrogate standards. Chlorophenol data is uncorrected for recovery of surrogate standard. For all samples, data for quantified analytes are reported to 2 or 3 significant figures. Limit of detection data for non-quantified analytes are reported to 1 significant figure.

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 (pg L⁻¹)

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

| Congener | Halswell River at McCartneys Bridge (n=2) ^{4,5} | Taieri River at Sutton Stream | Taieri 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 (ng kg⁻¹, wet fillet wt basis)

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 | Taieri River at Sutton Stream ³ | Taieri River at Allanton (n=2) ^{3,6} | Mataura River at Parawa ³ | Mataura River at Seaward Downs (n=2) ^{3,6} | 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 McCarthys Bridge ³ | Taieri River at Sutton Stream ³ | Taieri River at Allanton ³ | Mataura River at Parawa ³ | Mataura River at Seaward Downs ³ | Number of positives | Minimum ⁵ | 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 | < 0.01 | < 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 | 1 | < 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 | < 0.02 | < 0.03 | < 0.01 | < 0.01 | < 0.04 | < 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

4 = Rainbow trout (*Oncorhynchus mykiss*)

2 = Excluding LOD values

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

3 = Brown trout (*Salmo trutta*)

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 | |
|-----------------------------------|--------------------------------|-----------------|--------------------------------|-----------------|-------------------------------------|-----------------|
| | Primary | Blind duplicate | 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 | Taieri River at Allanton | | Taieri River at Allanton | | Mataura River at Seaward Downs | |
|-----------------------------------|--------------------------|-----------------|--------------------------|-----------------|--------------------------------|-----------------|
| | Primary | Blind duplicate | Primary | Blind duplicate | Primary | Blind duplicate |
| 2,3,7,8 TCDD | < 0.04 | < 0.06 | < 0.06 | < 0.06 | < 0.06 | < 0.06 |
| Non 2,3,7,8 TCDD | < 0.03 | < 0.01 | < 0.02 | < 0.02 | < 0.1 | < 0.1 |
| 1,2,3,7,8 PeCDD | < 0.05 | < 0.06 | < 0.04 | < 0.04 | < 0.04 | < 0.04 |
| Non 2,3,7,8 PeCDD | < 0.04 | < 0.02 | < 0.02 | < 0.02 | < 0.02 | < 0.02 |
| 1,2,3,4,7,8 HxCDD | < 0.02 | < 0.01 | < 0.01 | < 0.01 | < 0.02 | < 0.02 |
| 1,2,3,6,7,8 HxCDD | < 0.09 | < 0.07 | < 0.06 | < 0.06 | < 0.08 | < 0.08 |
| 1,2,3,7,8,9 HxCDD | < 0.04 | < 0.02 | < 0.02 | < 0.02 | < 0.03 | < 0.03 |
| Non 2,3,7,8 HxCDD | < 0.04 | < 0.02 | < 0.04 | < 0.04 | < 0.04 | < 0.04 |
| 1,2,3,4,6,7,8 HpCDD | < 0.2 | < 0.1 | 0.30 | < 0.2 | < 0.2 | < 0.2 |
| Non 2,3,7,8 HpCDD | < 0.1 | < 0.1 | 0.20 | < 0.08 | < 0.08 | < 0.08 |
| OCDD | < 0.9 | < 1 | 2.72 | < 0.9 | < 0.9 | < 0.9 |
| 2,3,7,8 TCDF | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| Non 2,3,7,8 TCDF | < 0.02 | < 0.01 | < 0.01 | < 0.01 | < 0.02 | < 0.02 |
| 1,2,3,7,8 PeCDF | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| 2,3,4,7,8 PeCDF | < 0.02 | < 0.05 | < 0.02 | < 0.02 | < 0.02 | < 0.02 |
| Non 2,3,7,8 PeCDF | < 0.02 | < 0.01 | < 0.01 | < 0.01 | < 0.02 | < 0.02 |
| 1,2,3,4,7,8 HxCDF | < 0.01 | < 0.02 | < 0.02 | < 0.02 | < 0.01 | < 0.01 |
| 1,2,3,6,7,8 HxCDF | < 0.01 | < 0.02 | < 0.02 | < 0.02 | < 0.01 | < 0.01 |
| 2,3,4,6,7,8 HxCDF | < 0.02 | < 0.02 | < 0.01 | < 0.01 | < 0.02 | < 0.02 |
| 1,2,3,7,8,9 HxCDF | < 0.02 | < 0.02 | < 0.02 | < 0.02 | < 0.02 | < 0.02 |
| Non 2,3,7,8 HxCDF | < 0.03 | < 0.02 | < 0.07 | < 0.07 | < 0.01 | < 0.01 |
| 1,2,3,4,6,7,8 HpCDF | < 0.04 | < 0.03 | < 0.1 | < 0.1 | < 0.04 | < 0.04 |
| 1,2,3,4,7,8,9 HpCDF | < 0.03 | < 0.01 | < 0.01 | < 0.01 | < 0.03 | < 0.03 |
| Non 2,3,7,8 HpCDF | < 0.04 | < 0.02 | < 0.1 | < 0.1 | < 0.02 | < 0.02 |
| OCDF | < 0.1 | < 0.05 | < 0.1 | < 0.1 | < 0.2 | < 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 | Waingonogoro River at State Highway 45 | | Waingonogoro 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 | Shortfinnel Eel Tukituki River at Tamu mu Bridge | | Shortfinnel Eel Tukituki River at Tamu mu 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 ³ | Split QC ⁴ | Primary | Split QC | Primary | Split QC | Primary | Split QC | Primary | Split QC | Primary | Split QC | Primary | Split QC | Primary | Split QC |
| 2,3,7,8 TCDD | < 0.02 | < 0.09 | < 0.01 | < 0.1 | < 0.09 | < 0.1 | < 0.02 | < 0.05 | < 0.01 | < 0.01 | < 0.02 | < 0.09 | < 0.02 | < 0.05 | < 0.09 | |
| Non 2,3,7,8 TCDD | < 0.05 | < 0.1 | < 0.07 | < 0.1 | < 0.05 | < 0.1 | < 0.01 | < 0.02 | < 0.01 | < 0.02 | < 0.01 | < 0.01 | < 0.05 | < 0.09 | | |
| 1,2,3,7,8 PeCDD | < 0.04 | < 0.1 | < 0.03 | < 0.2 | < 0.11 | < 0.2 | < 0.02 | < 0.02 | < 0.01 | < 0.1 | < 0.01 | < 0.01 | < 0.01 | < 0.1 | | |
| Non 2,3,7,8 PeCDD | < 0.02 | < 0.06 | < 0.01 | < 0.2 | < 0.02 | < 0.2 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.1 | | |
| 1,2,3,4,7,8 HxCDD | < 0.03 | < 0.1 | < 0.01 | < 0.2 | < 0.01 | < 0.2 | < 0.01 | < 0.01 | < 0.01 | < 0.1 | < 0.01 | < 0.01 | < 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 | < 0.04 | < 0.01 | < 0.04 | < 0.01 | < 0.01 | < 0.01 | < 0.02 | | |
| 1,2,3,7,8,9 HxCDD | < 0.05 | < 0.06 | < 0.01 | < 0.05 | < 0.01 | < 0.05 | < 0.01 | < 0.01 | < 0.01 | < 0.04 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | | |
| Non 2,3,7,8 HxCDD | < 0.03 | < 0.1 | < 0.01 | < 0.3 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.01 | < 0.01 | < 0.01 | < 0.2 | | |
| 1,2,3,4,6,7,8 HpCDD | < 0.2 | < 0.2 | < 0.2 | < 0.3 | < 0.08 | < 0.1 | < 0.02 | < 0.08 | < 0.01 | < 0.1 | < 0.2 | < 0.2 | < 0.2 | < 0.2 | | |
| Non 2,3,7,8 HpCDD | < 0.1 | < 0.2 | < 0.05 | < 0.3 | < 0.06 | < 0.1 | < 0.01 | < 0.06 | < 0.01 | < 0.1 | < 0.2 | < 0.2 | < 0.2 | < 0.2 | | |
| OCDD | < 1 | < 0.3 | < 1 | < 0.5 | < 1 | < 0.2 | < 1 | < 0.2 | < 1 | < 0.2 | < 3 | < 0.5 | < 1 | < 0.1 | | |
| 2,3,7,8 TCDF | < 0.01 | < 0.03 | < 0.01 | < 0.05 | 0.82 | 0.56 | < 0.01 | < 0.04 | < 0.01 | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.1 | | |
| Non 2,3,7,8 TCDF | < 0.01 | < 0.1 | < 0.04 | < 0.05 | < 0.01 | < 0.05 | < 0.05 | < 0.05 | < 0.01 | < 0.1 | < 0.01 | < 0.01 | < 0.01 | < 0.05 | | |
| 1,2,3,7,8 PeCDF | < 0.01 | < 0.06 | < 0.01 | < 0.08 | < 0.06 | < 0.06 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.01 | < 0.01 | < 0.01 | < 0.05 | | |
| 2,3,4,7,8 PeCDF | < 0.01 | < 0.03 | < 0.02 | < 0.08 | < 0.06 | < 0.06 | < 0.01 | < 0.1 | < 0.01 | < 0.1 | < 0.01 | < 0.01 | < 0.01 | < 0.05 | | |
| Non 2,3,7,8 PeCDF | < 0.01 | < 0.06 | < 0.01 | < 0.08 | < 0.1 | < 0.1 | < 0.01 | < 0.01 | < 0.01 | < 0.1 | < 0.01 | < 0.01 | < 0.01 | < 0.05 | | |
| 1,2,3,4,7,8 HxCDF | < 0.02 | < 0.06 | < 0.01 | < 0.05 | < 0.03 | < 0.04 | < 0.02 | < 0.08 | < 0.01 | < 0.06 | < 0.01 | < 0.01 | < 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 | < 0.08 | < 0.01 | < 0.06 | < 0.01 | < 0.01 | < 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 | < 0.06 | < 0.01 | < 0.02 | < 0.01 | < 0.01 | < 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 | < 0.01 | < 0.2 | < 0.01 | < 0.01 | < 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 | < 0.01 | < 0.2 | < 0.01 | < 0.01 | < 0.01 | < 0.2 | | |
| 1,2,3,4,6,7,8 HpCDF | < 0.07 | < 0.09 | < 0.04 | < 0.1 | < 0.06 | < 0.08 | < 0.02 | < 0.08 | < 0.01 | < 0.06 | < 0.04 | < 0.04 | < 0.04 | < 0.1 | | |
| 1,2,3,4,7,8,9 HpCDF | < 0.05 | < 0.03 | < 0.01 | < 0.05 | < 0.02 | < 0.02 | < 0.01 | < 0.02 | < 0.01 | < 0.02 | < 0.04 | < 0.04 | < 0.04 | < 0.02 | | |
| Non 2,3,7,8 HpCDF | < 0.07 | < 0.09 | < 0.02 | < 0.1 | < 0.04 | < 0.08 | < 0.01 | < 0.08 | < 0.01 | < 0.08 | < 0.05 | < 0.05 | < 0.05 | < 0.1 | | |
| OCDF | < 0.3 | < 0.06 | < 0.04 | < 0.1 | < 0.09 | < 0.06 | < 0.08 | < 0.06 | < 0.09 | < 0.06 | < 0.08 | < 0.08 | < 0.08 | < 0.1 | | |
| Sum of PCDD/Fs (inc) ¹ | 1.12 | 1.38 | 0.86 | 1.95 | 1.91 | 1.80 | 2.04 | 2.04 | 1.91 | 1.80 | 2.04 | 2.04 | 2.04 | 1.47 | | |
| Sum of PCDD/Fs (exc) ² | 0 | 0 | 0 | 0 | 0.92 | 0.56 | 0.11 | 0.11 | 0.92 | 0.56 | 0.11 | 0.11 | 0.11 | 0 | | |
| Total I-TEQ (inc) ¹ | 0.037 | 0.12 | 0.026 | 0.17 | 0.20 | 0.21 | 0.032 | 0.032 | 0.20 | 0.21 | 0.032 | 0.032 | 0.032 | 0.12 | | |
| Total I-TEQ (exc) ² | 0 | 0 | 0 | 0 | 0.14 | 0.056 | 0.011 | 0.011 | 0.14 | 0.056 | 0.011 | 0.011 | 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

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

| Congener | Halswell River at McCartneys Bridge (n=2) ⁵ | Taieri River at Sutton Stream | Taieri 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 | 1.1 | 1.6 | - | - | - |
| Sum of PCBs (exc) ³ | 0 | 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 | 0.65 | 0.66 | - | - | - |
| Total PCB TEQ (exc) ^{1,3} | 0 | 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 | Rangitaki River at Te Teko ⁵ | Waingonogoro River at State Highway 4 ⁵ | Wanganui River at Te Maire 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 H/W 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 | Taieri River at Sutton Stream ⁴ | Taieri 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

6 = Shortfinned eel (*Anguilla australis*)

2 = Including half LOD values

7 = Mean of primary and blind duplicate samples

3 = Excluding LOD values

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

4 = Longfinned eel (*Anguilla dieffenbachii*)

9 = For any individual congener, calculation of the mean includes half LOD values

5 = Mix of longfinned and shortfinned eel

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 Maire ⁵ | Tukituki River at Tamumu Bridge ⁶ | Ruamahanga River at Waihenga ⁴ | Waimakariri River at Old HW Bridge ⁴ | Halswell River at McCartneys Bridge ⁴ | Talieri River at Sutton Stream ⁴ | Talieri 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 | < 0.01 | < 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

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

2 = Including half LOD values

7 = For any individual congener, calculation of the median includes half LOD values

3 = Excluding LOD values

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

4 = Brown trout (*Salmo trutta*)

9 = For any individual congener, calculation of the mean includes half LOD values

5 = Rainbow trout (*Oncorhynchus mykiss*)

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 | |
|------------------------------------|--------------------------------|-----------------|--------------------------------|-----------------|-------------------------------------|-----------------|
| | Primary | Blind duplicate | Primary | Blind duplicate | Primary | Blind duplicate |
| PCB #77 | < 0.01 | < 0.03 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| PCB #126 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| PCB #169 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| PCB #28 + PCB #31 | < 0.4 | < 0.3 | < 0.5 | < 0.5 | < 0.5 | < 0.5 |
| PCB #52 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #101 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #99 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #123 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #118 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #114 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #105 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #153 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #138 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #167 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #156 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #157 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #187 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #183 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #180 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #170 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #189 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #202 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #194 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| PCB #206 | < 0.2 | < 0.2 | < 0.1 | < 0.1 | < 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 | Tairi River at Allanton | | 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 | Primary | Split QC | 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 | Waingonogoro 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 | Taieri River at Sutton Stream | Taieri 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 | Waingonogoro River at State Highway 4 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 ² | Ruamahanga River at Waihenga ¹ | Haast River at Roaring Billy ¹ | Waimakariri River at Old H/W 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 ⁶ | Taieri River at Sutton Stream ¹ | Taieri 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 H/W 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 | 0.047 | 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 | | 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 | Waingonogoro River at State Highway 45 | | Waingonogoro River at State Highway 45 | | Mataura River at Seaward Downs | | Mataura River at Seaward Downs | |
|--------------------|--|-----------------------|--|----------|--------------------------------|----------|--------------------------------|----------|
| | Primary ¹ | Split QC ² | Primary | Split QC | Primary | Split QC | Primary | Split QC |
| Alpha-HCH | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| Beta-HCH | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| Gamma-HCH | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| HCB | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| Aldrin | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| Dieldrin | < 0.7 | < 0.4 | < 0.6 | < 0.4 | < 0.6 | < 0.4 | < 0.6 | < 0.4 |
| Heptachlor | < 0.2 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| Heptachlor epoxide | < 0.2 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| Alpha-chlordane | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| Gamma-chlordane | < 0.1 | < 0.2 | < 0.2 | < 0.2 | < 0.2 | < 0.2 | < 0.2 | < 0.2 |
| pp-DDE | < 0.3 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| pp-TDE | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| op-DDT | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 0.1 | < 0.2 |
| pp-DDT | < 0.1 | < 0.2 | < 0.1 | < 0.2 | < 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 | Shortfinnel Eel Tukituki River at Tamuimu Bridge Primary ¹ | Shortfinnel Eel Tukituki River at Tamuimu Bridge Split QC ² | 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 |
|--------------------|--|---|--|---|--|---|---|--|
| 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)

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

| Chlorophenol | Halswell River at McCartneys Bridge (n=2) ² | Taieri River at Sutton Stream | Taieri 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 Whatawhata¹ | Rangitaiki River at Te Teko² | Wainongoro River at State Highway 45^d | Wanganui River at Te Maire¹ | Manawatu River at Opiki Bridge³ | Mohaka River at Raupunga¹ | Tukituki River at Tamumu Bridge³ | Ruamahanga River at State Highway 2² | Ruamahanga River at Waihenga¹ | Haast River at Roaring Billy¹ | Waimakariri River at Old H/W Bridge¹ |
|---------------------------|--|--|---|---|---|---|--|--|---|---|--|
| 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 Parawa 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} | Rangitaiki River at Te Teko ¹ | Rangitaiki 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 McCartneys 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 | < 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 | < 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 | < 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 | < 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 | < 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 | < 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 | < 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 | < 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 | 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 | Primary | Blind duplicate | Primary | Blind duplicate |
| 2,4,6 Trichlorophenol | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| 2,3,5 Trichlorophenol | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| 2,4,5 Trichlorophenol | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| 2,3,6 Trichlorophenol | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| 2,3,4 Trichlorophenol | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| 2,3,5,6 Tetrachlorophenol | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| 2,3,4,6 Tetrachlorophenol | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| 2,3,4,5 Tetrachlorophenol | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 | < 3 |
| Pentachlorophenol | < 3 | < 2 | < 3 | < 3 | < 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 | Waingonogoro River at State Highway 45 | | Waingonogoro River at State Highway 45 | | Mataura River at Seaward Downs | | Mataura River at Seaward Downs | |
|---------------------------|--|-----------------------|--|----------|--------------------------------|----------|--------------------------------|----------|
| | Primary ¹ | Split QC ² | Primary | Split QC | Primary | Split QC | Primary | Split QC |
| 2,4,6 Trichlorophenol | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 |
| 2,3,5 Trichlorophenol | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 |
| 2,4,5 Trichlorophenol | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 |
| 2,3,4 Trichlorophenol | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 |
| 2,3,5,6 Tetrachlorophenol | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 |
| 2,3,4,6 Tetrachlorophenol | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 |
| 2,3,4,5 Tetrachlorophenol | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 | < 3 | < 5 |
| Pentachlorophenol | < 2 | < 5 | < 2 | < 5 | < 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 | Shortfinnel Eel Tukituki River at Tamumu Bridge | | Shortfinnel 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 | Primary | Split QC | Primary | Split QC | Primary | Split QC | Primary | Split QC |
| 2,4,6 Trichlorophenol | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.2 | < 0.2 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 |
| 2,3,5 Trichlorophenol | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.2 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 |
| 2,4,5 Trichlorophenol | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.2 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 |
| 2,3,4 Trichlorophenol | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.2 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 |
| 2,3,5,6 Tetrachlorophenol | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.2 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 |
| 2,3,4,6 Tetrachlorophenol | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.2 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 |
| 2,3,4,5 Tetrachlorophenol | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.6 | < 0.1 | < 0.2 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 | < 0.5 | < 0.1 |
| Pentachlorophenol | < 0.3 | < 0.1 | < 0.3 | < 0.1 | < 0.3 | < 0.1 | < 0.2 | < 0.2 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 0.5 | < 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 | I-TEQ, ½ LOD | This study |
| New Zealand, Lake Rotorua | Stream waters | 1993 | 5 | nd | I-TEQ, ½ LOD | Gifford <i>et al.</i> , 1996 |
| New Zealand, Lake Rotorua | Lake Rotorua water | 1993 | 4 | nd | I-TEQ, ½ LOD | Gifford <i>et al.</i> , 1996 |
| Treated water | | | | | | |
| Canada, Ontario | Treated water | 1983-87 | 4 | 0.02 | I-TEQ, LOD=0 | Jobb <i>et al.</i> , 1990 |
| Canada, Ontario | Miscellaneous treated water | 1983-89 | 362 | nd | I-TEQ, LOD=0 | Jobb <i>et al.</i> , 1990 |
| Japan, Hirakata, Osaka | Tap water | 1991 | 3 | 0.1 | I-TEQ, ½ LOD | Miyata <i>et al.</i> , 1992 |
| Russia, Bashkortostan | Ufa urban tap water | 1994-97 | 250 | nd | I-TEQ, ½ LOD | Amirova <i>et al.</i> , 1997 |
| Russia, Bashkortostan | Rural tap water | 1996 | 5 | 0.1 | I-TEQ, ½ LOD | Amirova <i>et al.</i> , 1997 |
| Sweden | Outlet treated water | | 2 | 1.0 | I-TEQ, ½ LOD | Rappe <i>et al.</i> , 1989b |
| Sweden, Stockholm | Treated and recipient water | 1989 | 2 | nd | Nordic TEQs | Naf <i>et al.</i> , 1990 |
| USA, Lockport, New York | Drinking water supply | 1986-87 | 19 | 1.4 | I-TEQ, ½ LOD | Meyer <i>et al.</i> , 1989 |
| USA, Lockport, New York | Drinking water | 1986-87 | 4 | 2.9 | I-TEQ, ½ LOD | Meyer <i>et al.</i> , 1989 |
| Raw water | | | | | | |
| Australia, Bass Strait | Woodside beach | 1991-92 | 4 | 1.8 | I-TEQ, ½ LOD | Mosse and Haynes, 1993 |
| Australia, Bass Strait | Seaspray beach | 1991-92 | 4 | 1.7 | I-TEQ, ½ LOD | Mosse and Haynes, 1993 |
| Australia, Bass Strait | Delray beach | 1991-92 | 4 | 2.0 | I-TEQ, ½ LOD | Mosse and Haynes, 1993 |
| Canada, BC | Background runoff | 1990-93 | 9 | nd | I-TEQ, LOD=0 | Van Oostdam and Ward, 1995 |
| Canada, BC | Background water | 1990-93 | 3 | nd | I-TEQ, LOD=0 | Van Oostdam and Ward, 1995 |
| Canada, Ontario | Raw water | 1983-87 | 33 | nd | I-TEQ, LOD=0 | Jobb <i>et al.</i> , 1990 |
| Canada, Ontario | Raw water entering treatment plant | | 1 | 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 |
| Japan, Nagahama, Hiraka | Well water | 1991 | 3 | 0.1 | I-TEQ, ½ LOD | Miyata <i>et al.</i> , 1992 |
| Russia, Bashkortostan | River water | 1996 | 8 | 2.3 | I-TEQ, ½ LOD | Amirova <i>et al.</i> , 1997 |
| Sweden, Eman | Eman River water | | 3 | 30.8 | 99.0 | Rappe <i>et al.</i> , 1989b |
| USA, Bayou Meto Stream, Arkansas | Upstream of beach tributary | 1993 | 1 | 0.0014 | 0.0014 | Lebo <i>et al.</i> , 1995 |
| USA, Bayou Meto Stream, Arkansas | Downstream of beach tributary | 1993 | 1 | 2.5 | I-TEQ, LOD=0 | Lebo <i>et al.</i> , 1995 |
| USA, Lockport, New York | Raw water | 1988 | 1 | 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 |
| China, Anhui | Waste water | 1995 | 2 | 0.1 | 2.6 | I-TEQ |
| China, Jilin | Waste water | 1995 | 3 | nd | 3.4 | I-TEQ |
| Germany, Bayreuth | Urban runoff after rain | 1991 | 4 | 1.0 | 10.0 | I-TEQ, LOD=0 |
| Germany, Bayreuth | Household wastewater | 1992 | 8 | 0.8 | 14.0 | I-TEQ, LOD=0 |
| Germany, Bayreuth | Shower water | 1991 | 5 | 1.8 | 16.2 | I-TEQ, LOD=0 |
| Sweden | Inlet waste water | | 2 | 7.8 | 8.1 | I-TEQ, ½ LOD |
| Sweden, Stockholm | Urban waste water | 1989 | 2 | 2.5 | 3.0 | Nordic TEQs |
| USA, San Francisco Bay | Urban stormwater outfall | 1995-96 | 11 | 0.1 | 65.0 | I-TEQ, LOD=0 |
| USA, San Francisco Bay | Urban stormwater outfall | 1995-96 | 10 | nd | 14.0 | I-TEQ, LOD=0 |
| USA, San Francisco Bay | Urban stormwater | 1995 | 5 | 0.6 | 15.0 | I-TEQ |
| USA, San Francisco Bay | Urban stormwater | 1996 | 6 | 0.14 | 26 | I-TEQ |
| USA, San Francisco Bay | Petroleum plant storm water | 1995 | 5 | 1.0 | 10.0 | I-TEQ |
| USA, San Francisco Bay | Petroleum plant storm water | 1996 | 5 | nd | 3.0 | I-TEQ |

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 Min. Max. | Analysis | Reference |
|------------------------------|--|--------------|-----------------|--|-----------------------------------|--|
| 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, Gorleban, 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 Min. Max. | Analysis | Reference |
|-------------------------|---------------------------------|--------------|-----------------|--|--------------------------------|--|
| 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 Dibenz-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 I1 Concentrations of PCBs in freshwater

| Country | Water type | Date sampled | Concentration (ng L ⁻¹) Min. | Concentration (ng L ⁻¹) Max. | Data type | Reference |
|---------------------|--------------------------|--------------|---|---|---------------------|--------------------------------|
| 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 | Frieger <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/Waipa 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 I3 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/Waipa 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 I4 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/Waipa 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 I5 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/Waipa 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 I6 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/Waipa 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 I7 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/Waipa 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 I8 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/Waipa 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/Waipa 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/Waipa 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/Waipa 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/Waipa 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/Waipa 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/Waipa 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 | | 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 | Bolti 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) Min. | Concentration (ng L ⁻¹) Max. | Reference |
|----------------|---------------------------------------|--------------|---|---|---------------------------------|
| 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 |
| | Fraser River upper reaches impacted | 1987 | 21 | 136 | Rogers <i>et al.</i> , 1988 |
| Finland | 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 Finland | Juvenile salmon, upper Fraser River | 1986-87 | 1.6 | 12.7 | Rogers <i>et al.</i> , 1988 |
| | Pike, <i>L. Vitia</i> (pulp mill) | 1978 | | 8.04 | Passivirta <i>et al.</i> , 1980 |
| | Pike, <i>L. Pajärinne</i> (pulp mill) | 1978 | | 5.72 ¹ | Passivirta <i>et al.</i> , 1980 |
| | Pike, <i>L. Konnevesi</i> (sawmills) | 1978 | | 6.49 ¹ | Passivirta <i>et al.</i> , 1980 |
| | Roach, <i>L. Vitia</i> (pulp mill) | 1978 | | 0.90 ¹ | Passivirta <i>et al.</i> , 1980 |
| | Roach, <i>L. Paijärinne</i> (pulp mill) | 1978 | | 4.84 | Passivirta <i>et al.</i> , 1980 |
| | Roach, <i>L. Konnevesi</i> (sawmills) | 1978 | | 12.8 | Passivirta <i>et al.</i> , 1980 |
| | Pike, <i>L. Paijärinne</i> (pulp mill) | 1980 | 6.4 | 49.6 | Passivirta <i>et al.</i> , 1981 |
| | Pike, <i>L. Paijärinne</i> (pulp mill) | 1980 | 18.0 | 403 | Passivirta <i>et al.</i> , 1981 |
| | Pike, <i>L. Paijärinne</i> | 1980 | 2.7 | 35.7 | Passivirta <i>et al.</i> , 1981 |
| Finland | Trout, Kemi River (Gulf of Bothnia) | 1982 | | 4.2 ¹ | Vuorinen, 1985 |
| | 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.