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### Baseline Levels of PCDDs, PCDFs, PCBs and Organochlorine Pesticides in New Zealand Rivers and Estuaries

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#### 1 Abstract

A major study is being undertaken aimed at determining baseline levels of PCDDs, PCDFs, PCBs and other organochlorine contaminants in the New Zealand environment. Levels of PCDDs and PCDFs determined in riverine eel and trout were 0.028 pg/g and 0.018 pg/g I-TEQ respectively. Levels of PCBs were 0.23 pg/g and 0.057 pg/g TEQ. Low levels of PCDDs and PCDFs were also determined in estuarine sediment (0.20 pg/g I-TEQ) and shellfish (0.041 pg/g I-TEQ). The origin of these contaminants is attributed to diffuse background emissions.

#### 2 Introduction

In July 1995 the Ministry for the Environment initiated a major study to characterise and manage the issue of organochlorine substances in the New Zealand environment. The primary focus of this national 'Organochlorines Programme' are the polychlorinated dibenzo-p-dioxins (PCDDs) and the polychlorinated dibenzofurans (PCDFs), substances that are now considered to be ubiquitous environmental contaminants. In addition, issues arising from the historic use of the polychlorinated biphenyls (PCBs), persistent organochlorine pesticides including DDT, aldrin and dieldrin, and pentachlorophenol (PCP) will also be addressed.

As part of this study, a major environmental survey has been undertaken to determine levels of PCDDs, PCDFs, PCBs, organochlorine pesticides and chlorophenols in specific environmental compartments. Details on the background to this environmental survey, and initial data for contaminant levels in river water, have been reported previously<sup>1</sup>. This paper reports further data on the levels of organochlorine contaminants present in New Zealand rivers and presents new information for contaminant concentrations in estuarine ecosystems.

#### 3 Experimental Methods

#### 3.1 Sample Collection

River biota (eel and trout), and estuarine sediment and shellfish (cockles and oysters) were collected according to an internationally peer-reviewed study design <sup>1</sup>). Eel samples were collected from 13 rivers at 16 sampling sites using fine mesh fyke nets. Trout were captured

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from 9 of the 13 rivers (11 of the 16 sampling sites) by a combination of monofilament gill nets and rod and line. Up to eight individual eel or trout were collected from each sampling site. For each sample, all individuals were filleted at the laboratory and composited for analysis.

Sediment and shellfish samples were collected from 12 estuaries around the New Zealand coastline. Within an estuary, sediment cores to a depth of 5 cm were taken from five randomly selected 'sampling stations'. Five sediment cores were taken from each sampling station. The cores from the five sampling stations were composited to provide a single analytical sample. A minimum of two sediment samples were taken from each estuary. After the sediment cores were taken, shellfish samples were collected by excavating the area of each sampling station. Shellfish from the five sampling stations were composited to provide a single analytical sample. A minimum of two shellfish samples were taken from each estuary.

#### 3.2 Analytical Procedures

The biota samples were analysed using freeze-dried material. Typically 25 g (shellfish) or 50 g (eel and trout) of material was taken, spiked with <sup>13</sup>C<sub>12</sub> PCDD, PCDF, PCB and organochlorine pesticide surrogate standards (Cambridge Isotope Laboratories, Massachusetts, USA), and subject to accelerated solvent extraction (ASE). Each extract was split for PCDD/PCDF analysis (40%), PCB/organochlorine pesticide analysis (40%) and reserve (20%). The PCDD and PCDF extract was partitioned with conc. H<sub>2</sub>SO<sub>4</sub>, and then chromatographed sequentially on columns of silica/H<sub>2</sub>SO<sub>4</sub> silica, Al<sub>2</sub>O<sub>3</sub>, and Carbopack C (18 % dispersed on Celite). The PCB and organochlorine pesticide extract was purified by gel permeation (SX-3 bio-beads) and florisil chromatography. For high lipid containing samples, an acetonitrile hexane partition step was also used. Air dried sediment samples (typically 20 g) were spiked with surrogate standards, extracted and purified as above.

Quantitation was carried out by GCMS on a VG70S mass spectrometer operating in the SIM mode. Resolution for PCDDs and PCDFs was 10,000. Extracts were chromatographed on Ultra 2 (all analytes) and SP2331 (PCDDs and PCDFs) capillary columns. Standard quality assurance criteria for <sup>13</sup>C<sub>12</sub> surrogate recoveries, ion ratios (theoretical  $\pm$  10 %), signal to noise (S/N > 3:1), retention times and laboratory blanks were applied.

#### 4 Results and Discussion

The rivers from which biota samples were collected were carefully chosen as being representative of New Zealand's waterways. They ranged from pristine to those which are recipients for a variety of domestic, industrial and agricultural wastes. Two rivers which receive effluent from bleached kraft pulp mills, and which have been extensively studied in other work, were not included in this present survey. PCDDs and PCDFs were detected in only three of the 16 eel samples, and in five of the 11 trout samples collected, Figure 1. The levels quantified were markedly lower than those reported for overseas waterways<sup>21</sup>. PCB contaminants were more frequently detected, and made a greater contribution to the total toxic equivalents than that arising from the PCDDs and PCDFs for samples collected from the same site, Figure 1. Mean PCDD, PCDF and PCB contaminant levels for all sites are reported in Table 1.





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### Table 1. Mean PCDD, PCDF and PCB Levels<sup>®</sup> in Biota from New Zealand Waterways

|              | PC<br>I-TEQ | CDD/F, pg/g wet wt<br>Total | PC<br>TEQ <sup>©</sup> | B, pg/g wet wt<br>Total |
|--------------|-------------|-----------------------------|------------------------|-------------------------|
| Eel (n=16)   | 0.028       | 0.17                        | 0.23                   | 6,100                   |
| Trout (n=11) | 0.018       | 1.35                        | 0.057                  | 2,130                   |

 $\bigcirc$  = TEQ and totals exclude limit of detection values

@ = PCB TEQ calculated using the WHO/IPCS toxic equivalency factors

③ = Sum of PCB congeners #28, #31, #52, #77, #101, #99, #123, #118, #114, #105, #126,

#153, #138, #167, #156, #157, #169, #187, #183, #180, #170, #189, #202, #194, #206

The PCB congener profile observed was similar for both eel and trout. Figure 2. Significantly, this profile was comparable for samples across all rivers, consistent with general background environmental exposures to these contaminants.



The estuarine ecosystems chosen for this study ranged from pristine to estuarine catchments of urban, industrial and agricultural areas, and represent some of the most major and significant estuaries in the country. Mean levels of PCDDs, PCDFs and PCBs determined in these ecosystems are reported in Table 2. The most commonly detected PCDDs and PCDFs were the higher chlorinated hepta- and octa- congeners. Low parts-per-trillion levels of tetra- and penta-chlorinated congeners were also detected in some samples, but typically these congeners

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contributed less that 40 % of the total toxic equivalents determined. The TCDF and PeCDF congener profiles observed were consistent with that for diffuse background combustion sources.

PCB contaminants were not as frequently detected in the sediments as the PCDDs and PCDFs, and when they were present the toxic equivalent values were consistently lower than for the PCDDs and PCDFs. For those estuaries where PCBs were present, a similar congener profile was observed that was again consistent with general background environmental contamination.

Significantly, for impacted sites, the PCDD, PCDF and PCB concentrations were not markedly elevated above the levels determined for samples collected from sites considered to be pristine environments (Parengarenga Harbour and Whanganui Inlet). For even the most contaminated estuary, the contaminant concentrations determined were noticeably lower than levels that have been reported for estuaries in a number of other countries <sup>3,4</sup>.

|                        |               | Sediment | , ppt dry | wt      | Shellfish, ppt wet wt |         |          |         |
|------------------------|---------------|----------|-----------|---------|-----------------------|---------|----------|---------|
|                        | PCDD/F, I-TEQ |          | PCB, TEQ  |         | PCDD/F, I-TEQ         |         | PCB, TEQ |         |
| Parengarenga Harbour   | 0             | (0.17)   | 0         | (0.065) | 0                     | (0.026) | 0        | (0.065) |
| Whangarei Harbour      | 0.031         | (0.28)   | 0.0047    | (0.18)  | 0.28                  | (0.055) | 0.016    | (0.10)  |
| Manukau Harbour        | 0.26          | (0.56)   | 0.0077    | (0.19)  | 0.0068                | (0.074) | 0.0061   | (0.071) |
| Hellyers Creek         | 1.07          | (2.09)   | 0.18      | (0.40)  | 0.16                  | (0.22)  | 0.035    | (0.49)  |
| Kawhia Harbour         | 0.057         | (0.27)   | 0         | (0.066) | 0                     | (0.032) | 0        | (0.065) |
| Tauranga Harbour       | 0.66          | (0.98)   | 0.49      | (0.25)  | 0.035                 | (0.063) | 0.0011   | (0.066) |
| Wairau Estuary         | 0             | (0.15)   | 0         | (0.13)  | 0.0006                | (0.023) | 0        | (0.065) |
| Whanganui Inlet        | 0             | (0.17)   | 0         | (0.27)  | 0.0007                | (0.026) | 0        | (0.065) |
| Moutere Inlet          | 0.19          | (0.39)   | 0         | (0.093) | 0.0(-35               | (0.025) | 0        | (0.065) |
| Avon Heathcote Estuary | 0.15          | (0.45)   | 0.0075    | (0.10)  | 0.0( 60               | (0.029) | 0.028    | (0.068) |
| Otago Harbour          | 0.0019        | (0.43)   | 0         | (0.065) | 0                     | (0.12)  | 0        | (0.065) |
| New River Estuary      | 0.0055        | (0.11)   | 0         | (0.066) | 0.0()40               | (0.039) | 0.0014   | (0.067) |

## Table 2. PCDD, PCDF and PCB Levels<sup>10</sup> in Estuarine Sediment and Shellfish Samples

① = TEQ calculated excluding non detectable congeners. TEQ calculated using half limit of detection value for non detectable congeners reported in parentheses ().

Only minimal bioaccumulation of PCDDs, PCDFs and PCBs was apparent within the estuaries studied as shown by contaminant concentrations determined in the shellfish samples, Table 2. In contrast, bioaccumulation of a number of organochlorine pesticides into shellfish was more pronounced. The most frequently detected pesticides were dieldrin (11 of 12 estuaries),  $\alpha$ - and  $\gamma$ -chlordane (5 estuaries) and pp'-DDT (6 estuaries), along with its degradation products pp'-DDE and pp'-TDE (11 and 10 estuaries respectively), Figure 3.

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Other pesticides, including hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), aldrin and heptachlor were either less frequently detected or not detected in any estuary.

#### 5 Acknowledgments

The authors wish to acknowledge all agencies participating in this study: The Institute of Environmental Science and Research for undertaking the PCDD, PCDF, PCB and pesticide analytical work; the National Institute of Water and Atmospheric Research with cooperation from Fish and Game Councils for the collection of the river biota samples; and Regional Councils for their assistance with the estuarine sampling.

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