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Polychlorinated Biphenyls and Organochlorine Pesticides in the Freshwater Mussel *Hyridella menziesi* from the Waikato River, New Zealand

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It is now well established that past human activities have resulted in widespread environmental contamination with persistent chemicals, especially in aquatic ecosystems (Tanabe et al. 1994). The polychlorinated biphenyls (PCBs) and organochlorine pesticides are highly persistent and toxic, and extensive use has led to accumulation of their residues in a number of aquatic environments. This has raised toxicological concerns for both aquatic organisms and man based on historical and ongoing trends in the use of organochlorines (Voldner and Li 1995). While aquatic sediments are an ultimate sink for these anthropogenic compounds, their uptake and accumulation by biota, including shellfish and fish, has resulted in their build-up in the food chain. Marine mammals, particularly cetaceans, are one of the groups receiving high concentrations of persistent organochlorines (Tanabe et al. 1994). Organochlorine pesticides can enter aquatic ecosystems from atmospheric deposition as well as local pollution sources such as agricultural run-off, and industrial and domestic wastes. Similarly, PCBs inputs can occur directly from industrial usage or indirectly via the atmosphere.

Little information exists on the extent of organochlorine chemicals in the New Zealand aquatic ecosystems. Forestry related use of pentachlorophenol (PCP) has resulted in widespread contamination of timber treatment sites which has raised considerable public concern. Receiving water, sediments and biota adjacent to contaminated sites have detectable levels of PCP (Gifford et al. 1995). Chlorinated organics have also been found in sediments downstream of pulp and paper mill operations (Judd et al. 1995). DDT was widely used in New Zealand agriculture until the 1970's (Boul 1995) and has been found together with other organic contaminants in estuarine sediments (Holland et al. 1993) and shellfish (ARWB 1988; ARWB 1990; Hickey et al. 1995a). The extent of organochlorine contamination of New Zealand freshwaters is unknown.

The present study was undertaken to determine the levels of PCBs and organochlorine pesticides in the resident mussel population of the upper Waikato River. The Waikato River is New Zealand's longest and most heavily utilised river. Originating at the oligotrophic Lake Taupo on the central North Island volcanic plateau, it runs 327 km northward to discharge into the Tasman Sea with a mean flow of 400 m^3/s. It has eight hydroelectric dams and power stations and provides cooling water for two thermal and two geothermal power stations. It is

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the source for over 30 communal drinking water supplies and 200 irrigation withdrawals, and receives 20 major industrial discharges (including a large pulp and paper mill) and several sewage treatment plant discharges, as well as diffuse inputs from numerous geothermal fields, and forestry and agricultural activity within the 14,300 km^2 catchment.

The collection and analysis of mussel samples was carried out as part of an assessment of the levels and impacts of organic contaminants in the upper Waikato River system. Resident mussels were collected and analysed for organochlorine pesticide, PCB and dioxin levels. This paper reports the results for the organochlorine and PCB contaminants.

MATERIALS AND METHODS

Sampling of resident mussels was carried out in late October 1990 at eight sites along the Waikato River system, including sites in Lake Taupo, the hydro-electric dam lakes Aratiatia, Ohakuri, Maraetai, Waipapa and Karapiro, and a flowing-water reach of the river at Cobham Bridge, Hamilton. At each site at least 50 mussels were collected by SCUBA divers. On return to the boat, the mussels were placed on ice, and on return to the laboratory were shucked and freeze-dried.

Freeze-dried mussel tissue was Soxhlet extracted with hexane/isopropanol (78:22), the extract diluted with additional hexane and a known volume taken for lipid determination. The remaining extract was washed with potassium carbonate solution and the combined carbonate extract back-extracted with hexane. The aqueous extract was retained for chlorophenol analysis (not reported in this present study). The combined hexane extracts were washed with water, dried (Na_2SO_4) and evaporated. A volume was taken and partitioned with hexane saturated acetonitrile. The combined acetonitrile extracts were evaporated to dryness, the residue dissolved in hexane/ethyl acetate and fractionated by gel permeation chromatography (S-X3 Bio Beads, hexane/ethyl acetate eluant). Following GPC, the extract was evaporated to dryness, the residue redissolved in hexane, and subject to further purification by Florisil chromatography. The column was eluted with hexane (aldrin, α-BHC [hexachlorocyclohexane], cis[α]-chlordane, trans[γ]-chlordane, DDE, *op*'-DDT, *pp*'-DDT & hexachlorobenzene [HCB] fractions) followed by 6 % diethyl ether in hexane (lindane [γ-BHC] & dieldrin fractions). Both fractions were evaporated and made to a final volume in hexane. Extracts were analysed by dual capillary column (DB1 and BP10) GCECD, with external standard quantitation. Subsequent confirmation was by GCMS. Following GCECD, the extracts were concentrated and analysed for PCB residues by GCMS operating in the single ion monitoring mode. Quantitation was again by external standard. Reagent blanks were carried through the method to ensure the absence of interfering substances. Matrix spike data gave recoveries in the range 106-127 %.

Relationships between variables were investigated using Spearman-Rank correlations. Plots of linear relationships between variables were inspected and considered to be significant at the 95% level ($P \leq 0.05$).

RESULTS AND DISCUSSION

Results are presented in Table 1 for residue levels of ten persistent organochlorine pesticides and metabolites and in Table 2 for a range of environmentally significant PCB congeners found in *H. menziesi* along the upper Waikato River.

Of the pesticides HCB, α-BHC, aldrin and *op*'-DDT were not detected in any sample, trans-Chlordane was detected in 6 of the 8 samples, with lindane, dieldrin, cis-chlordane, DDE and *pp*'-DDT detected in all samples analysed. The distribution of lindane and dieldrin and was fairly uniform throughout the river system with concentrations ranging 2.6- and 3.7-fold, respectively. This indicates the absence of discrete sources. Indeed, their presence is most consistent with atmospheric transportation and deposition.

Other organochlorines showed some longitudinal pattern in their distribution. Total chlordane (range 6.9-fold) was highest in Taupo and showed a progressive decline with distance downstream, suggesting Lake Taupo as the major contaminant source. A slight increase at Md may indicate chlordane derived from the pulp and paper mill operations upstream. Total DDT ranged 11.3-fold (2.9 to 32.7 ng/g)) with a generally increasing downstream trend and a peak concentration at Ohakuri and Karapiro. Intense agricultural activity is carried out in the catchments of both of these lakes, suggesting that DDT contaminants are derived from diffuse agricultural run-off. *pp*'-DDT was widely used on pastoral land for control of grass grub until the 1970's when such usage was legally restricted. The DDE concentration constitutes the highest percentage of total DDT found in the mussels examined and, as the oxidative dehydrochlorination product of DDT, is consistent with historic DDT application. DDE and *pp*'-DDT concentrations were strongly linearly correlated (r=0.99, n=8, P<0.000l).

Table 1. Organochlorine pesticides in the resident mussel population of the Waikato River[a].

Location	T	A	O	Mu	Md	W	K	H
HCB	<0.8	<0.2	<0.2	<0.1	<0.3	<0.1	<0.6	<0.4
α-BHC	<1	<0.2	<0.3	<0.2	<0.1	<0.1	<0.1	<0.1
lindane	12.2	9.1	11.6	6.5	16.9	8.7	16.0	7.0
aldrin	<0.2	<0.2	<0.3	<0.1	<0.1	<0.2	<0.2	<0.2
dieldrin	0.6	1.8	1.4	0.9	1.8	1.0	1.7	2.2
cis-chlordane	2.0	1.9	2.0	0.7	1.5	0.6	1.2	1.1
trans-chlordane	2.4	1.1	1.3	<0.4	0.50	<0.3	<0.4	<0.4
Sum CHL	**4.4**	**3.0**	**3.3**	**0.7**	**2.0**	**0.6**	**1.2**	**1.1**
DDE	1.9	4.4	11.6	7.4	5.6	10.3	24.8	16.5
op'-DDT	<1	<0.3	<0.5	<0.3	<0.2	<0.4	<1	<0.6
pp'-DDT	1.0	2.7	4.5	3.2	2.1	3.4	7.9	5.4
Total DDT	**2.9**	**7.1**	**16.1**	**10.6**	**7.7**	**13.7**	**32.7**	**21.9**

[a]Results reported in ng/g on a freeze dried weight basis.
Sites are: Lakes Taupo (T), Aratiatia (A), Ohakuri (O) Maraetai (upstream, Mu), Maraetai (downstream, Md), Waipapa (W), Karapiro (K) and the river at Hamilton (H).
Sites proceed downstream towards the right.

Since the 1960's, large quantities of chlordane have been used in New Zealand for treating wood products (e.g. plywoods for export) to prevent insect attack. Interestingly, however, the presence of a plywood mill near the Aratiatia site has not resulted in elevated levels of this contaminant there. The high levels of lindane in Taupo cannot be attributed to known point source discharges suggesting either

diffuse agricultural or atmospheric inputs. Significantly, the most abundant pesticide observed in this study, lindane, is also the most prevalent pesticide detected in a variety of human tissues collected from the New Zealand population (Bates et al. 1994), confirming the ubiquitous nature of this particular contaminant. The lack of significant correlations between total CHL, DDTs and PCBs (n=7, P=0.18-0.42) suggest that these contaminants come from different sources.

All PCBs were below detection in Taupo and coplanar isomers (77, 126 & 129) were not detected at any of the sampling sites. Total PCBs ranged 7.5-fold (2.6 to 23.0 ng/g)) with a peak at Karapiro (Table 2). PCB congener profiles were dominated by penta-, hexa- and hepta-chlorinated compounds (predominantly 118, 138, 153, and 180). These profiles were similar to those found in estuarine shellfish (Hickey et al. 1995a), though the freshwater mussels showed relatively higher levels of 180 and lower levels of 118. The hydro lakes, especially Karapiro, appear to be acting as 'sinks' for PCBs. The extremely low level of PCB measured at Hamilton is somewhat surprising given the higher levels of other organochlorines measured at this site. This suggests that the exposure path may differ between the contaminant classes, possibly being affected by the riverine nature of the Hamilton site with higher sediment sand and lower carbon than Karapiro (86% c.f. 50% sand; 0.9% c.f. 5.1% carbon respectively, (Hickey et al. 1995b)).

Table 2. Polychlorinated biphenyls in the resident mussel population of the Waikato River[a]. See Table 1 for site codes.

Location	T	A	O	Mu	Md	W	K	H
# 77	<0.04	<0.04	<0.04	<0.02	<0.04	<0.04	<0.04	<0.04
# 126	<0.04	<0.05	<0.04	<0.04	<0.05	<0.04	<0.04	<0.04
# 169	<0.08	<0.09	<0.09	<0.09	<0.09	<0.08	<0.09	<0.09
# 28	<0.03	0.61	0.38	0.44	0.78	0.37	0.77	0.04
# 52	<0.08	0.59	0.35	0.43	0.70	0.45	0.80	0.04
# 99	<0.3	0.14	0.08	0.13	0.15	0.18	0.32	<0.07
# 101	<0.1	0.31	0.19	0.22	0.79	1.5	2.0	0.05
# 105	<0.09	0.14	0.06	0.11	0.13	0.11	0.18	<0.03
# 118	<0.05	0.16	0.07	0.14	0.23	0.41	0.52	<0.02
# 138	<0.09	0.87	0.43	0.55	2.8	5.3	5.8	0.09
# 153	<0.09	0.64	0.37	0.44	2.3	4.8	5.9	0.08
# 170	<0.2	0.44	0.22	0.20	0.94	1.4	1.7	<0.06
# 180	<0.1	0.54	0.24	0.22	1.3	2.1	2.7	<0.08
# 183	<0.2	0.14	<0.06	0.093	0.25	0.39	0.42	<0.06
# 187	<0.2	0.37	0.17	0.15	0.78	1.4	1.6	<0.05
Total PCB	**<**	**5.0**	**2.6**	**3.1**	**11.0**	**18.0**	**23.0**	**0.3**
TE[b]	0.0024	0.0031	0.0025	0.0025	0.0032	0.0028	0.0030	0.0025

[a] Results reported in ng/g on a freeze dried weight basis.

[b] TE = Toxic Equivalents calculated according to WHO-ECEH (Ahlborg et al. 1994). Half the limit of detection was taken for non-detectable values.

Although not commonly eaten, freshwater mussels are a traditional food of the indigenous Maori population of New Zealand (Hiroa 1921). Mussel tissue concentrations did not exceed the levels considered safe for human consumption, being maximally less than 1% of the New Zealand Food Regulations (1984) standards for DDT, dieldrin and lindane (5, 0.2, & 2 mg/kg wet weight for “meat

fat in any food" respectively). Toxic Equivalents (TE) for the dioxin-like PCBs were calculated relative to the risk to human consumption (Ahlborg et al. 1994) (Table 2). The TE values were low and similar throughout the river system.

The levels of organochlorine contaminants found in the upper Waikato River mussels were low compared with freshwater mussel data published for known industrially contaminated freshwater sites. The highest concentration of PCBs reported for a 21-d exposure to Detroit River water in mussel caging experiments done in 1982 with *Elliptio complanatus* was 4344 ng/gDW (Kauss and Hamdy 1985), and a mean tissue level of 88.9 ng/g was reported for mussels caged in Lake St. Clair (Pugsley et al. 1985). The Waikato River mussel contaminant concentrations were comparable with or exceeded those found in estuarine shellfish in urbanised or industrialised areas of Auckland. Table 3 compares mussel data with Manukau Harbour oyster monitoring (ARWB 1990) and wedge shell *(Macomona liliana)* and cockle *(Austrovenus stutchburyi)* data (Hickey et al. 1995a) on a lipid weight basis. Surprisingly, the contaminant levels for chlordane, PCBs and PDT were similar while levels of lindane in the Lake Taupo mussels were markedly higher (9-fold) than shellfish from contaminated Auckland estuarine areas.

Table 3. Concentrations of organochlorine contaminants in estuarine and riverine shellfish.

	Estuary			River
Contaminant	*C. gigas*	*M. liliana*	*A. stutchburyi*	*H. menziesi*
Chlordane	0.79, 2.3	0.037, 0.21	0.060, 0.58	0.35, 0.14
PCB[a]	1.6, 3.4	0.12, 0.35	0.12, 0.46	N.D., 2.6
DDT	2.3, 4.5	0.090, 0.56	0.085, 0.66	0.23, 3.7
Lindane	0.20, 0.024	0.11, 0.11	0.11, 0.12	0.98, 1.8
Lipid (%)	8.1, 11.1	3.0, 3.1	5.6, 4.3	8.0, 11.4

N.D.= not detected. All concentrations ng/g lipid weight.

[a] polychlorinated biphenyls.

Manukau Harbour oysters *(Crassostrea gigas)* (ARWB 1990) wedge shells *(Macomona liliana)* and cockles *(Austrovenus stutchburyi)* (Hickey et al. 1995a) from the entrance (Cornwallis Beach for *C. gigas,* Armour Point for *M. liliana* and *A. stutchburyi)* and inner harbour (Grannys Bay) sites respectively.

Waikato River freshwater mussels *(Hyridella menziesi)* from upstream (Lake Taupo) and downstream (Hamilton) sites respectively.

The two indicators of mussel health, lipid content and condition (dry tissue weight/shell weight), showed differing responses between sites. The mussels show a general increase in condition with increasing distance downstream (Table 4). Mussel lipid levels ranged between 4.1 and 11.4%, with similar values for the 3 most upstream sites and the lowest value downstream of the pulp and paper mill effluent discharge (Md) and a maximum at Karapiro. These differences are unlikely to have resulted from spawning occurring at different times down the river, as the sampling occurred in spring (October) and Taupo spawning has been measured by glochidial production in summer (December-March) (authors' unpublished data). Condition measurements showed an inverse relationship with lipid concentration, which was not significant when considering all sites (n=8, r= -0.48, P=0.22), but was highly linear and significant with the exclusion of the two most downstream sites (K & H) (n=6, r=0.96, P=0.002). The relationship between lipid content and condition probably reflects differing mussel diets down the river. The relatively lower lipid levels downstream of the pulp and paper mill discharge (above Md) may reflect a larger bacterial component derived from the

pulp and paper mills biological effluent treatment system, which constitutes about l0-15% of the flow at this site (1% of the fully mixed flow), and a greater proportion of the dissolved and particulate organic carbon.

Generally, lipid content or condition were not significantly correlated ($P \leq 0.05$) with levels of total CHL, DDTs or PCBs. However, CHL did show a strong inverse relationship with condition (n=8, r=-0.91, P<0.002). The decreasing concentration of CHL in mussels downstream of the oligotrophic Lake Taupo is associated with eutrophication indicated by a 7-fold increase in chlorophyll a concentrations (Huser and Wilson 1995) and subsequent increase in mussel condition (Roper and Hickey 1994), which results in the observed inverse relationship. Interestingly, unlike an earlier reported study (Galindo-Beet and Flores-Baez 1991), there was only a weak relationship between the percentage lipid content of the mussels (Table 4) and total DDT levels (n=8 r=0.64, P=0.09).

Table 4. Percentage extractable lipid and condition index of resident mussels from the Waikato River. See Table 1 for site codes.

Location	T	A	O	Mu	Md	W	K	H
% Lipid	8.0	8.4	8.6	4.1	5.8	5.6	11.4	9.1
Condition index[a]	91	107	96	158	135	147	120	155

[a] mg DW/shell weight, from Roper and Hickey (1994)

The relationship between lipid and condition measurements showed contrasting responses between sites for *H. menziesi* in this study. The highest body burdens of organochlorine contaminants, which occurred in the Karapiro mussels, were not reflected in reduced lipid levels which were maximal at this site. However, condition was reduced here relative to both the upstream and downstream sites suggesting that some physiological stress may be occurring. Contrasting lipid and condition responses to differing contaminant exposures have also been observed for two estuarine shellfish species (Hickey et al. 1995a). Although marked reductions in shellfish lipid content have been reported for high contaminant exposures (Bender et al. 1988), our results suggest that for low contaminant levels, lipid content may be a relatively poor indicator of shellfish health, being markedly influenced by other environmental factors such as food availability.

These results have shown multiple sources of persistent organochlorine contaminants to the Waikato River, with the highest DDT levels associated with known inputs of agricultural run off. The surprisingly high levels of lindane and chlordane detected in mussels from the oligotropic Lake Taupo cannot be attributed to known point source discharges. Overall, organochlorine levels were low, indicating widespread contamination but at levels where mussels are considered safe for consumption and where condition was unaffected.

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