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Organochlorine Compounds in Three Species of Shellfish from Waikareao Estuary, Tauranga Harbour, New Zealand

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We have previously reported the levels of some organochlorine compounds (OCCs) in sediments from the Waikareao Estuary (Figure l), a small inlet of Tauranga Harbour, New Zealand (37°39'S, 176°ll'E). The detection of significant levels of OCCs in Waikareao Estuary sediments prompted us to investigate the levels of nine PCB congeners, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, technical chlordane, and dieldrin in three species of shellfish gathered from eleven sites in the estuary.

MATERIALS AND METHODS

Biota species were collected in February 1992 from the Waikareao Estuary, according to availability, from the ten sampling stations (Figure 1) utilised in an earlier the sediment study (Burggraaf et al. 1994). The species examined were: *Macomona liliana* (wedge shell), a surface deposit feeder that resides at depths of up to 10 cm and feeds by means of an inhalant siphon extending to the surface, *Saccostrea glomerata (New* Zealand rock oyster) that feeds by filtering suspended particles from the water column, and *Amphibola crenata* (mud snail) a deposit feeder that feeds on micro-organisms and organic detritus at the sediment surface. In addition *M. liliana, S. glomerata* and sediment were collected from an eleventh site (W5') adjacent to site W5.

The methodology of Wilcock et al. (1993), applied to the analyses of technical chlordane residues in New Zealand biota species, was utilised in this study. After collection biota were depurated for 12 hr in saltwater, before freezing at -20°C. Samples were then thawed, shelled, washed sequentially with tap water and distilled water, and freeze dried. Freeze dried material was ground (mortar and pestle) and extracted in a Soxhlet apparatus with $CHCl_3$. The resulting solution was concentrated to ca 1 mL and transferred to a weighed sample vial. After overnight evaporation at 45°C, the sample vial was reweighed to determine the lipid content. The lipid extracts constituted 11.6% (n = 37, CV = 8.8%), 4.1% (n = 45, CV = 15%) and 5.5 % (n = 16, CV = 12.8%) of the freeze dried *S. glomerata, M. liliana, A. crenata* specimens respectively.

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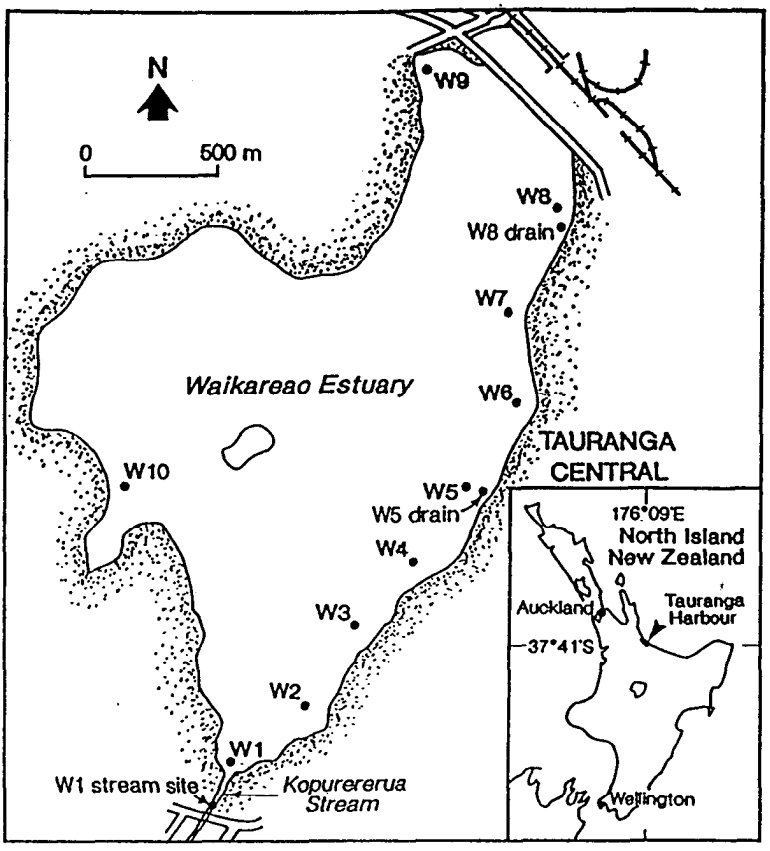

Figure 1. Location of survey sites in the Waikareao Estuary, Tauranga Harbour.

Lindane (below detection in all samples) was added as internal standard and the lipid extract (0.25 mL of a ca 0.25 g/mL solution in $CHCl_3$) was cleaned-up on a 0.5 mm x 80 mm mini-column packed with Biobead SX-3, using 1:l light petroleum ether-$CHCl_3$ as eluent. The first 1 mL of eluent consisted predominantly of fatty substances, while OCC species (PCBs, DDTs, chlordanes, etc) were present in the next 4 mL of eluent. This fraction was evaporated and chromatographed on a 10 cm x 1 cm florisil column, prepared by the addition of 2 g of 2% deactivated florisil, capped with a 1 cm layer of Na_2SO_4. Elution with light petroleum ether (30 mL), and 1:19 light petroleum ether-ether (15 mL) afforded fractions A and B respectively. Calibration experiments (Burggraaf et al. 1994) verified that PCB congeners, p,p'-DDT, p,p'-DDD, p,p'-DDE, technical chlordane components and dieldrin were present only in fraction A. The OCC extracts were analysed on a 20 m x 0.22 mm DB-5 capillary column installed in a HP5980 GC fitted with an electron capture detector (ECD). GC conditions and quantification procedures were as reported previously (Burggraaf et al. 1994) for the corresponding sediment samples, other than that the detection limits were 8-10 ng/g lipid weight for PCB

congeners, *p,p* '-DDE, *p,p* '-DDD, chlordane isomers and dieldrin, and 16-20 ng/g for p,p'-DDT. PCB congeners 101, 110, 151, 149, 138, 153 178, 180 and 170 (listed in elution order on the DB-5 column) were identified by comparison with standards available in our laboratory.

The recoverability of OCCs was demonstrated using *M. liliana* extract (10 individuals per experiment), gathered from an uncontaminated site in the Manukau Harbour. Five repetitions of the analysis procedure using spiked lipid extracts revealed the recovery of OCCs to be > 94% with a relative standard derivation of ≤ 7%. Replicate data for five extractions and GC-ECD analyses of S. *glomerata* (four individuals per composite sample) gathered in the vicinity of the W9 site are given in Table 1.

Additional sediment data was obtained from site W5' for PCB congeners 101, 110, 151, 149, 153, 138, 187, 180 and 170 (1.0, 0.7, 0.7, 2.1, 3.2, 2.4, 0.8, 1.5 and 0.9 ng/g respectively), p,p'-DDT (not detected), p,p'-DDD (0.3 ng/g), p,p'-DDE (0.5 ng/g), technical chlordane (trace) and dieldrin (trace) using a previously reported method (Burggraaf et al. 1994).

Table 1. Mean levels (ng/g lipid) and standard deviations of PCB congeners, *p,p'*-DDT, p,p'-DDD, p,p'-DDE, technical chlordane and dieldrin, determined for five replicate extractions of S. *glomerata* from the W9 site.

	mean	σ	CV		mean	σ	CV
PCB 101	91	9	10%	*p,p'*-DDT	206	41	21%
PCB 110	121	18	15%	*p,p'*-DDE	237	48	22%
PCB 151	47	8	18%	*p,p'*-DDD	81	16	20%
PCB 149	198	31	16%	Σ DDTs	523	86	17%
PCB 153	358	58	17%				
PCB 138	225	39	18%	chlordanes[a]	30	7	26%
PCB 187	59	7	13%	dieldrin	15	4	28%
PCB 180	62	12	20%				
PCB 170	33	8	24%				
Σ PCBs	1191	180	15%				

[a] technical chlordane equivalents = 2.33 * *cis*- and *trans*-chlordane levels (43% of technical chlordane).

RESULTS & DISCUSSION

The levels (ng/g lipid) of nine PCB congeners, *p,p'-DDT, p,p'-DDD, p,p'-DDE,* chlordanes (expressed as technical chlordane equivalents) and dieldrin identified in Waikareao Estuary biota species are given in Table 2. Concentrations of Σ PCB (sum of nine congeners), Σ DDT (sum of p,p'-DDT, p,p'-DDD and p,p'-DDE), total chlordane and dieldrin in biota (lipid and dry weight basis) are given in Table 3, and are compared with sediment values from the same sites (Burggraaf et al. 1994) (Figure 1). The relative abundances of OCCs in biota and sediment from the same site were similar (Figure 2), as might be expected.

Table 2. Concentrations (ng/g lipid) of selected PCB congeners, p,p'-DDT, p,p'-DDE, p,p'-DDD, technical chlordane (chl) and dieldrin (diel) detected in biota from Waikareao Estuary, Tauranga Harbour, New Zealand.

		PCB congener													
site	species	101	110	151	149	153	138	187	180	170	DDT	DDE	DDD	chl[a]	diel
W1	*A. crenata*	62	437	76	427	437	440	82	180	114	324	2216	768	52	127
W2	*S. glomerata*	171	173	80	359	729	355	138	111	26	258	485	237	34	32
W3	*M. liliana*	93	61	27	47	152	105	18	15	10	nd	106	30	37	33
W4	*M. liliana*	91	58	25	59	200	134	24	nd	12	nd	80	33	tr	30
W5	*S. glomerata*	161	349	83	326	610	354	110	113	43	234	425	100	38	20
W5'	*S. glomerata*	160	141	93	330	829	394	137	126	38	232	305	152	36	36
W5'	*M. liliana*	110	64	52	220	436	331	69	54	20	nd	195	132	30	27
W6	*M. liliana*	118	37	28	137	165	93	19	nd	nd	nd	62	24	tr	27
W7	*M. liliana*	50	27	12	55	75	42	9.3	nd	nd	nd	38	18	nd	tr
W8	*S. glomerata*	188	275	100	396	658	427	115	124	44	500	721	289	44	15
W9	*S. glomerata*	103	96	46	166	316	167	55	54	17	216	263	50	39	12
W10	*A. crenata*	40	30	13	54	73	49	19	18	10	40	96	38	tr	19

[a]technical chlordane equivalents = 2.33 * *cis* and *trans*-chlordane levels, tr = trace (< 8-20 ng/lipid weight of biota, or < 0.1 ng/g dry weight of sediment); nd = not detected.

Table 3. Σ PCBs, Σ DDTs, technical chlordane and dieldrin concentrations determined for sediments (ng/g) and biota (expressed as ng/g lipid, and as ng/g dry weight) from the Waikareao Estuary, Tauranga Harbour, New Zealand.

		Σ PCB[a]			Σ DDT[b]			tech. chlordane[c]			dieldrin		
site	species	lipid[d]	dry[e]	sed[f]	lipid	dry	sed	lipid	dry	sed	lipid	dry	sed
W1	*A. crenata*	2256	124	5.3	3308	182	2.4	52	2.8	tr	127	7.0	0.1
W2	*S. glomerata*	2142	250	2.9	979	114	1.0	34	4.0	tr	32	3.8	tr
W3	*M. liliana*	528	21	1.6	136	5.4	tr	37	1.5	tr	33	1.3	tr
W4	*M. liliana*	604	24	1.8	113	4.5	0.1	tr	nc	nd	30	1.2	tr
W5	*S. glomerata*	2149	251	16	759	89	2.8	38	4.4	tr	20	2.3	tr
W5'	*S. glomerata*	2250	261	13	689	80	0.8	36	3.9	tr	36	4.1	tr
W5'	*M. liliana*	1354	54	13	327	13	0.8	30	1.2	tr	27	1.1	tr
W6	*M. liliana*	598	24	0.1	86	3.4	nd	tr	nc	tr	27	1.1	tr
W7	*M. liliana*	271	11	tr	57	2.2	tr	nd	nc	nd	tr	nc	nd
W8	*S. glomerata*	2326	272	9.9	1510	176	5.4	44	5.1	tr	15	1.8	tr
W9	*S. glomerata*	1020	119	0.5	529	62	tr	39	4.6	tr	12	1.4	tr
W10	*A. crenata*	302	17	tr	180	9.9	tr	tr	nc	nd	19	1.4	nd

[a]sum of nine PCB congener levels given in Table 1;[b]sum of p,p'-DDT, p,p'-DDD and p,p'-DDE levels, [c]technical chlordane equivalents = 2.33 * *cis* and *trans*-chlordane levels; [d]ng/g lipid weight of biota; [e]ng/g dry weight of biota; [f]ng/g dry weight of sediment, levels are from Burggraaf et al. (1994) except for Σ PCB levels = 0.64 * the reported Aroclor 1260 level; tr = trace (< 8-20 ng/lipid weight of biota, or < 0.1 ng/g dry weight of sediment); nd = not detected; nc = not calculated.

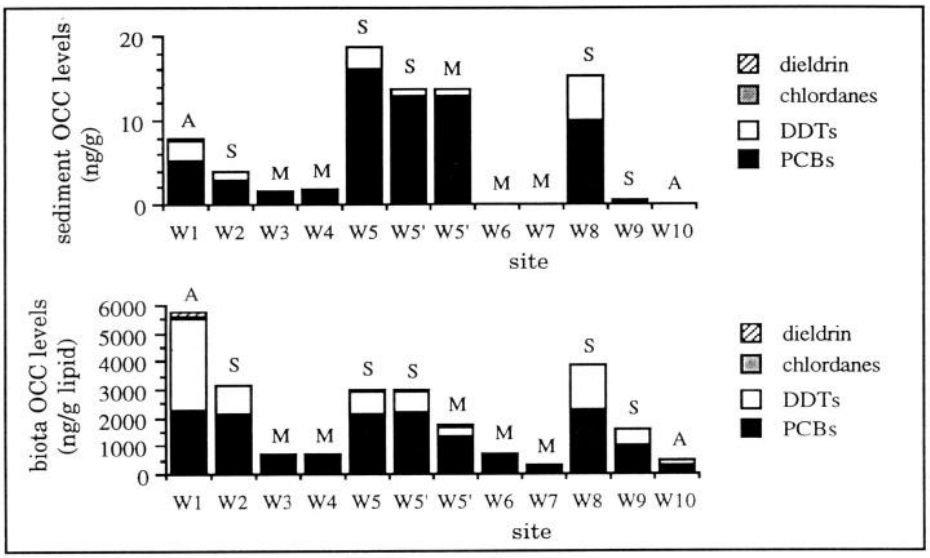

Figure 2. Sediment and biota levels determined for Waikareao Estuary samples. A = *A. crenata,* S = *S. glomerata,* M = *M. liliana.*

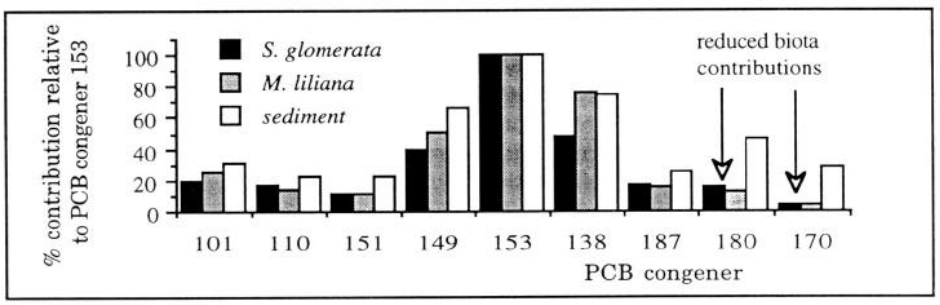

Figure 3. % Contribution of PCB congeners, relative to PCB congener 153 levels in biota and sediment from site W5'.

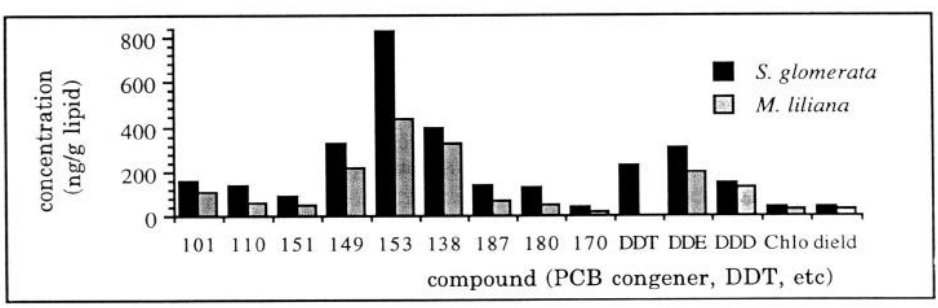

Figure 4. Concentrations (ng/g lipid) of OCCs in biota from the W5' site.

A notable feature was that the GC-ECD PCB congener profiles of the biota extracts, in comparison to those determined for the W1-W10 sediment extracts in our earlier study (Burggraaf et al. 1994), and the W5' sediment sample in this investigation (Figure 3), were deficient in higher PCB congeners (especially the hepta-chlorinated PCB congeners 180 and 170). Although highly chlorinated congeners are strongly lipophilic (for example octachloro-PCB congener 169 has log K_{ow} = 7.73, de Bruijn 1989), they have low sediment to biota concentration factors (CF's). This is generally attributed to the unfavourable stereochemistry of PCBs with seven or more chlorine atoms, which can influence their transport across cellular membranes (Colombo et al. 1990).

It is also apparent (at least at the W5' site) that PCB and DDT residues are more strongly accumulated (up to ca 2 fold) by *S. glomerata* than by *M. liliana* (Figure 4). This result contrasts with observations from a previous study (Wilcock et al. 1993) in which it was shown that lipid-normalised chlordane concentrations accumulated more rapidly in a surface deposit feeding shellfish *(M. liliana)* than in a filter feeder *(A. stutchburyi),* but tended to have similar equilibrium values.

Elevated levels of OCCs were found in biota collected from the W1, W2, W5, W5', W8 and W9 sites. These sites are adjacent to the mouth of the Kopurererua stream (W1 and W2 sites), and two stormwater drains which discharge adjacent to the W5/W5' and W8/W9 sites respectively (Figure 2). It is clear that the Kopurererua stream and the two stormwater drains are the dominant sources of the OCCs entering the Waikareao estuary, but that the effects are localised to within a few hundred metres of each source. For example, total OCC concentrations in *M. liliana* from sites W3, W4, W6 and W7 were similar to those from W10, a comparatively unimpacted area of the estuary. The Σ PCB, Σ DDT, technical chlordane equivalent and dieldrin levels (51, 32, 4.0 and 2.2 ng/g dry weight respectively) determined in an early study (MAFTECH 1991) for *S. glomerata* gathered at the mouth of the Waikareao Estuary are similar to values found at inner estuary sites (Table 3).

The dry weight OCC levels identified in the Waikareao Estuary biota specimens are comparable to those reported in mussels from inner Californian Harbours and San Francisco Bay, and in oysters from some sites in the Gulf of Mexico and the Mangere inlet, Manukau Harbour, New Zealand (Draper & Koszdin 1990, Phillips & Spies 1988, Sericano et al. 1990, ARWB 1990). The levels determined for Waikareao estuary biota (eg max. levels of 176 and 272 ng/g dry weight for Σ DDT and Σ PCB respectively at the W8 site) are substantially lower than the USEPA recommended safe levels of 1000, 1000, 1000 and 2000 ng/g dry weight for DDT, DDD, DDE and total PCBs respectively in shellfish for human consumption. Similarly the technical chlordane and dieldrin levels in shellfish (Table 3) are substantially lower than the Australian water quality criteria (Nicholson, 1984) for human consumption for technical chlordane and dieldrin of 200 and 50 ng/g dry weight respectively.

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