



Wellington Harbour marine sediment quality investigation

Supplementary report

Quality for Life





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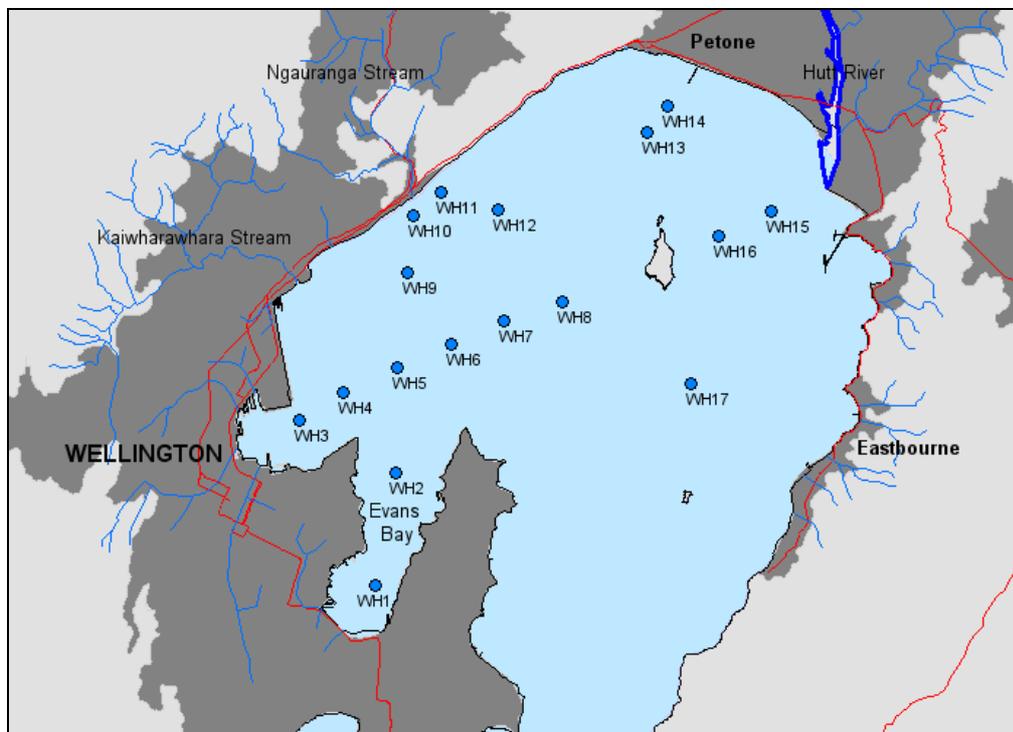
1. Introduction

In late 2006, Greater Wellington Regional Council (Greater Wellington) carried out an investigation of marine sediment quality at 17 subtidal sites in Wellington Harbour (Figure 1.1, Appendix 1). The results of the investigation were documented in detail by Stephenson et al. (2008). This is a supplementary report to the 2006 investigation that presents the results of some additional chemical analyses carried out by NIWA on the sediments collected in 2006, including –

- re-analysis for the 16 USEPA priority pollutant polycyclic aromatic hydrocarbons (PAHs), and re-analysis of a subset of samples for organochlorine pesticides, for quality assurance purposes; and
- analysis for a range of alkylated PAHs and marker compounds to assist with PAH source identification.

Further statistical analysis of the relationships between sediment contaminant concentrations and the benthic fauna also has been carried out (Kelly 2010, reproduced in full in Appendix 2). The rationale for this work and the additional sediment chemistry testing are outlined in Section 1.1.

Only a brief summary and discussion of the sediment chemistry results is presented in this report; the PAH results (Olsen & Guyader 2009) and an evaluation of potential PAH contaminant sources (Depree 2010) are reproduced in full in Appendices 3 and 4 respectively¹.



(Source: Stephenson et al. 2008)

Figure 1.1: Map of Wellington Harbour showing the 17 subtidal locations sampled in 2006 for the Wellington Harbour marine sediment quality investigation

¹ The organochlorine analyses were performed separately and reported by email only (Olsen 2010, Appendix 5).

1.1 Background

Five composite samples derived from the top 30 mm of the sediment at each of the 17 Wellington Harbour sampling locations were analysed for sediment particle size distribution, total organic carbon, a range of total and weak acid-extractable trace metals, organotins, 16 USEPA priority pollutant PAHs and 22 organochlorine pesticides (Stephenson et al. 2008). The sample preparation and analyses were contracted to NIWA, Hamilton, but as a result of problems with key equipment at the NIWA organics laboratory, analyses of the organic compounds were carried out by Hill Laboratories². A range of alkylated PAHs and marker compounds for source identification were to have been included, but these analyses could not be completed prior to publication of the Stephenson et al. report in 2008. Nevertheless, the report included a review and discussion of PAHs with respect to PAH sources using the data that were available, and drawing heavily on interpretation work undertaken for Greater Wellington by Ahrens and Olsen (2008).

In 2009 NIWA subsequently re-analysed all sediment samples for the 16 USEPA priority pollutant PAHs, along with alkylated PAHs and marker compounds (Olsen & Guyader 2009). Re-analysis of the USEPA priority pollutant PAHs was undertaken for quality assurance purposes; NIWA's organics laboratory is specifically designed for undertaking ultra-trace level analysis on a routine basis and can reliably measure very low concentrations of organic contaminants (an essential requirement for long-term monitoring programmes). NIWA also re-analysed some of the composite samples from each of four Wellington Harbour sites (sites WH1–WH4) where sediments contained elevated levels of DDT and its breakdown products (DDD and DDE). This also was undertaken to provide data for comparison with that originally generated by Hill Laboratories and was considered necessary because of difficulties noted in Stephenson et al. (2008) with obtaining consistent analytical results for some isomers of DDT and its breakdown products. This problem also has been observed in other studies of harbours in the Wellington region (e.g., Stephenson & Mills 2006).

Alongside the commissioning of NIWA to assess the alkylated PAHs and marker compound data to assist in PAH source identification (Deprez 2010), in early 2010 Greater Wellington commissioned Coast and Catchment Ltd to undertake some further analysis of the benthic fauna data collected in late 2006. A combination of univariate and standard multivariate statistical techniques used by Stephenson et al. (2008) had not identified any relationship between elevated sediment contaminant concentrations at some sites and indices of species diversity or composition of ecological communities. However, a number of relatively recent studies in the Auckland region have been able to identify relationships between sediment contaminants and benthic community composition through the application of more sophisticated multivariate analyses, including canonical analysis of principal coordinates (Kelly 2010).

² NIWA supervised the delivery of organics results to ultra-trace level (something at the time the harbour investigation was initiated, Hill Laboratories did not offer on a routine basis).

2. Methods

2.1 Polycyclic aromatic hydrocarbons

A portion of the freeze-dried <500 µm fraction of each replicate sediment sample was spiked with nine analytical surrogates (deuterated PAHs) and extracted with solvent. Internal standards were added to all extracts and quantitative analysis of 16 USEPA priority pollutant PAHs, alkylated PAHs and marker compounds carried out by capillary gas chromatography mass spectrometry operated in selected ion mode (GC-MS-SIM) (Olsen & Guyader 2009).

Depree (2010) calculated and compared a variety of diagnostic ratios with those derived from environmental samples taken in Auckland and Christchurch, and numerous source materials (Depree & Ahrens 2007). These ratios were used to determine the relative importance of pyrogenic and petrogenic sources of PAHs to the Wellington Harbour sediments and to assess the likely contribution of specific sources, including bitumen, diesel, coal tar, coal soot, wood soot, diesel soot, engine oil and road runoff particulates.

2.2 Organochlorine pesticides

A portion of the freeze-dried <500 µm fraction of each of three replicates from sites WH1, WH2 and WH4, and of five replicates from site WH3³, was analysed for the organochlorine pesticides gamma BHC (lindane), hexachlorobenzene, dieldrin, heptachlor, heptachlor epoxide, cis-chlordane, trans-chlordane, cis-nonachlor, trans-nonachlor, 2,4'-DDE, 2,4'-DDD, 2,4'-DDT, 4,4'-DDE, 4,4'-DDD and 4,4'-DDT using a procedure involving solvent extraction and GC-MS-SIM.

Olsen (2010) noted that the samples proved difficult to analyse, with interferences observed in the GC chromatograms, particularly for o,p-DDT and p,p'-DDT. Samples were therefore analysed two or three times to ensure reasonable data could be generated.

2.3 Quality assurance

Quality assurance (QA) for PAH and marker compounds comprised monitoring of surrogate recoveries, analysis of six blanks, five duplicate analyses, and analysis of a standard reference material (Olsen & Guyader 2009).

The QA for organochlorine pesticides comprised analysis of a standard reference material.

³ All replicates from site WH3 were analysed because of the elevated levels of DDT observed (Olsen 2010).

3. Results

The results of all the additional PAH (and associated QA) analyses on sediments collected during the Wellington Harbour marine sediment quality investigation in 2006 are presented in full in Olsen and Guyader (2009), Appendix 3. The results are summarised briefly in this section, together with the results of the organochlorine analyses (presented in full in Appendix 5). The reader is referred to Stephenson et al. (2008) for an outline of the ANZECC (2000) Interim Sediment Quality Guidelines (ISQG) and the Auckland Regional Council's (2004) Environmental Response Criteria (ERC) that are used to assess the sediment chemistry results. These guidelines are not "pass or fail" numbers; they are set at the concentrations which experimental and/or field evidence suggests are likely to result in impacts on aquatic life.

3.1 Polycyclic aromatic hydrocarbons

Similar to the results reported in Stephenson et al. (2008), the mean Total PAH and mean Total High Molecular Weight (HMW) PAH concentrations were generally higher in the sediments of sites adjacent to Wellington City than in those of sites elsewhere in Wellington Harbour, with pronounced differences in concentrations between sites WH1 (southern Evans Bay) and WH3 (Lambton Basin entrance) and the remaining sites (Table 3.1). Variability in Total PAH and Total HMW PAH concentrations was low (c.v. 2.2–12.0%).

Total organic carbon (TOC)-normalised mean Total PAH concentrations, which ranged from 170–2,842 µg/kg, were below the ANZECC (2000) and ARC ERC (ARC 2004) sediment quality guidelines in the sediments of all sites. TOC-normalised mean Total HMW PAH concentrations, however, exceeded the ARC ERC amber threshold in the sediments from sites WH1, WH2 (northern Evans Bay), WH3 and WH4 (≈ 0.7 km NW of Pt Jerningham).

TOC-normalised mean concentrations for two individual PAH compounds – acenaphthalene and fluorene – exceeded their respective ANZECC ISQG-Low trigger values in the sediments at site WH1, while the TOC-normalised mean concentration of a third compound – naphthalene – exceeded its trigger value at site WH10 (≈ 0.5 km SSE of Ngauranga stream mouth). The concentrations of the other 13 priority pollutant PAH compounds tested were below sediment quality guidelines at all sites.

Refer to Tables 2.2–2.18 in Appendix 3 (Olsen & Guyader 2009) for the alkylated PAHs and marker results. There are no recommended trigger values for these compounds in the ANZECC (2000) sediment quality guidelines.

Table 3.1: Summary of concentrations and variability (coefficient of variation [cv, %], $n=5$) of total organic carbon (TOC) and selected polycyclic aromatic hydrocarbons (PAHs) in sediments of 17 sites sampled in Wellington Harbour in late 2006. The TOC results are those reported in Stephenson et al. (2008) (generated by Hill Laboratories) and the PAH results represent new data generated by NIWA (Olsen & Guyader 2009). Sediment quality guidelines for comparison are ANZECC (2000) and Auckland Regional Council Environmental Response Criteria (ARC ERC; ARC 2004). Values in amber exceed the ANZECC ISQG-Low or ARC ERC amber threshold.

Analyte	Fraction analysed	ANZECC		ARC ERC		WH1		WH2		WH3		WH4		WH5		WH6	
		ISQG-Low	ISQG-High	amber	red	mean	c.v.	mean	c.v.								
TOC (%)	< 500 μm					1.72	1.7	1.43	2.0	1.78	1.6	1.59	1.0	1.38	0.6	1.38	0.6
<u>PAHs ($\mu\text{g}/\text{kg}$):</u>																	
Naphthalene	< 500 μm					132	4.0	73.0	9.7	111	7.5	66.0	8.3	52.2	5.7	103	6.3
Acenaphthalene	< 500 μm					110	8.1	26.1	7.4	41.2	4.1	20.6	5.7	12.7	4.1	9.5	10.0
Fluorene	< 500 μm					40.2	4.5	16.4	8.3	27.3	3.9	16.0	4.6	9.1	1.4	7.3	6.3
Total PAH ^{1,2}	< 500 μm					4,901	4.5	2,343	8.4	3,603	3.2	2,310	4.6	1,109	2.9	830	4.1
Total HMW PAH ^{1,2}	< 500 μm					2,757	5.3	1,254	9.0	1,990	3.3	1,210	5.4	564	3.5	375	4.9
Naphthalene ³	at 1% TOC	160	2,100			76.5	4.7	51.0	8.8	62.4	6.8	41.4	8.7	37.7	6.3	74.3	6.7
Acenaphthalene ³	at 1% TOC	44	640			64.0	6.9	18.2	6.6	23.2	2.9	13.0	6.5	9.2	4.6	6.9	10.4
Fluorene ³	at 1% TOC	19	540			23.3	3.1	11.5	7.4	15.4	2.7	10.1	5.2	6.5	1.0	5.3	6.7
Total PAH ³	at 1% TOC	4,000	45,000			2,842	3.4	1,638	7.5	2,026	1.9	1,450	5.0	801	2.4	601	4.5
Total HMW PAH ³	at 1% TOC	1,700	9,600	660	1,700	1,598	4.0	876	8.1	1,119	1.9	759	5.7	407	3.0	272	5.1

¹ Polycyclic aromatic hydrocarbons have been summarised as "Total PAH" (all the PAH compounds analysed), and as "Total High Molecular Weight PAH", which is the sum of the concentrations of chrysene, fluoranthene, pyrene, benz[a]anthracene, benzo[a]pyrene, and dibenzo[a,h]anthracene. This is the total used for the ANZECC (2000) sediment quality guidelines and ARC ERC (ARC 2004). All the PAH compounds analysed are listed in Olsen and Guyader (2009, *see* Appendix 3).

² For the purpose of calculating Total PAH and Total HMW PAH, the concentration of any individual compound reported at "less than detection limit" has been replaced by a value one half of the detection limit.

³ This TOC "normalisation" is used in the ANZECC (2000) sediment quality guidelines and ARC (2004) ERC for comparing sediments with different TOC content.

Table 3.1 *cont.*: Summary of concentrations and variability (coefficient of variation [cv, %], $n=5$) of total organic carbon (TOC) and selected polycyclic aromatic hydrocarbons (PAHs) in sediments of 17 sites sampled in Wellington Harbour in late 2006. The TOC results are those reported in Stephenson et al. (2008) (generated by Hill Laboratories) and the PAH results represent new data generated by NIWA (Olsen & Guyader 2009). Sediment quality guidelines for comparison are ANZECC (2000) and Auckland Regional Council Environmental Response Criteria (ARC ERC; ARC 2004). Values in amber exceed the ANZECC ISQG-Low or ARC ERC amber threshold.

Analyte	Fraction analysed	ANZECC		ARC ERC		WH7		WH8		WH9		WH10		WH11		WH12	
		ISQG-Low	ISQG-High	amber	red	mean	c.v.	mean	c.v.	mean	c.v.	mean	c.v.	mean	c.v.	mean	c.v.
TOC (%)	< 500 μm					1.31	2.4	1.36	1.9	1.50	1.5	1.67	1.2	1.72	0.5	1.61	0.6
<u>PAHs ($\mu\text{g}/\text{kg}$):</u>																	
Naphthalene	< 500 μm					10.6	5.1	11.4	11.1	50.8	7.6	354	10.3	156	3.9	11.0	9.0
Acenaphthalene	< 500 μm					7.6	8.5	7.9	10.2	11.8	6.8	16.9	7.3	16.6	6.0	9.2	3.4
Fluorene	< 500 μm					6.5	3.6	6.9	11.4	9.2	11.8	11.5	5.9	11.3	4.4	7.7	2.5
Total PAH ^{1,2}	< 500 μm					586	3.3	590	5.2	1,001	4.5	1,608	5.8	1,389	3.5	754	2.2
Total HMW PAH ^{1,2}	< 500 μm					291	3.9	292	5.8	501	5.2	663	5.0	645	3.9	371	2.5
Naphthalene ³	at 1% TOC	160	2,100			8.1	6.2	8.4	10.3	33.8	7.6	211	10.5	90.3	4.0	6.9	8.8
Acenaphthalene ³	at 1% TOC	44	640			5.8	7.6	5.8	9.0	7.8	5.9	10.1	7.5	9.6	6.0	5.7	3.4
Fluorene ³	at 1% TOC	19	540			5.0	4.4	5.1	10.3	6.1	11.2	6.9	5.8	6.6	4.3	4.8	2.8
Total PAH ³	at 1% TOC	4,000	45,000			448	2.3	434	3.4	665	3.6	961	5.8	807	3.4	470	2.2
Total HMW PAH ³	at 1% TOC	1,700	9,600	660	1,700	222	2.7	215	4.0	333	4.2	396	4.7	375	3.8	231	2.4

¹ Polycyclic aromatic hydrocarbons have been summarised as "Total PAH" (all the PAH compounds analysed), and as "Total High Molecular Weight PAH", which is the sum of the concentrations of chrysene, fluoranthene, pyrene, benz[a]anthracene, benzo[a]pyrene, and dibenzo[a,h]anthracene. This is the total used for the ANZECC (2000) sediment quality guidelines and ARC ERC (ARC 2004). All the PAH compounds analysed are listed in Olsen and Guyader (2009, *see* Appendix 3).

² For the purpose of calculating Total PAH and Total HMW PAH, the concentration of any individual compound reported at "less than detection limit" has been replaced by a value one half of the detection limit.

³ This TOC "normalisation" is used in the ANZECC (2000) sediment quality guidelines and ARC (2004) ERC for comparing sediments with different TOC content.

Table 3.1 *cont.*: Summary of concentrations and variability (coefficient of variation [cv, %], $n=5$) of total organic carbon (TOC) and selected polycyclic aromatic hydrocarbons (PAHs) in sediments of 17 sites sampled in Wellington Harbour in late 2006. The TOC results are those reported in Stephenson et al. (2008) (generated by Hill Laboratories) and the PAH results represent new data generated by NIWA (Olsen & Guyader 2009). Sediment quality guidelines for comparison are ANZECC (2000) and Auckland Regional Council Environmental Response Criteria (ARC ERC; ARC 2004). Values in amber exceed the ANZECC ISQG-Low or ARC ERC amber threshold.

Analyte	Fraction analysed	ANZECC		ARC ERC		WH13		WH14		WH15		WH16		WH17	
		ISQG-Low	ISQG-High	amber	red	mean	c.v.								
TOC (%)	< 500 μ m					1.83	0.5	2.16	1.3	2.17	1.2	1.53	1.3	1.21	2.8
<u>PAHs (μg/kg):</u>															
Naphthalene	< 500 μ m					250	10.2	262	6.2	8.0	6.7	9.8	4.6	8.6	6.7
Acenaphthalene	< 500 μ m					8.8	8.7	7.7	5.5	4.3	7.9	7.0	4.2	6.8	13.5
Fluorene	< 500 μ m					8.5	5.4	8.5	7.3	8.0	3.6	7.8	9.2	6.9	20.2
Total PAH ^{1,2}	< 500 μ m					916	2.3	885	3.5	369	9.9	525	3.8	468	6.5
Total HMW PAH ^{1,2}	< 500 μ m					331	3.7	318	5.9	178	12.0	254	4.1	230	8.2
Naphthalene ³	at 1% TOC	160	2,100			137	10.5	121	6.2	3.7	6.9	6.4	4.6	7.1	9.1
Acenaphthalene ³	at 1% TOC	44	640			4.8	8.9	3.5	6.8	2.0	8.6	4.6	4.1	5.6	11.3
Fluorene ³	at 1% TOC	19	540			4.6	5.6	3.9	8.5	3.7	3.9	5.1	8.5	5.6	17.8
Total PAH ³	at 1% TOC	4,000	45,000			501	2.4	410	3.8	170	10.4	343	2.8	386	5.8
Total HMW PAH ³	at 1% TOC	1,700	9,600	660	1,700	181	3.5	147	6.0	82.2	12.6	166	3.1	190	7.6

¹ Polycyclic aromatic hydrocarbons have been summarised as "Total PAH" (all the PAH compounds analysed), and as "Total High Molecular Weight PAH", which is the sum of the concentrations of chrysene, fluoranthene, pyrene, benz[a]anthracene, benzo[a]pyrene, and dibenzo[a,h]anthracene. This is the total used for the ANZECC (2000) sediment quality guidelines and ARC ERC (ARC 2004). All the PAH compounds analysed are listed in Olsen and Guyader (2009, *see* Appendix 3).

² For the purpose of calculating Total PAH and Total HMW PAH, the concentration of any individual compound reported at "less than detection limit" has been replaced by a value one half of the detection limit.

³ This TOC "normalisation" is used in the ANZECC (2000) sediment quality guidelines and ARC (2004) ERC for comparing sediments with different TOC content.

3.2 Organochlorine pesticides

Similar to the results reported in Stephenson et al. (2008), of the 15 organochlorine pesticides analysed, only DDT (principally as 4,4'-DDT but also as 2,4'-DDT at site WH3), DDE (principally as 4,4'-DDE) and DDD were consistently found above detection limits in the sediments of sites WH1–WH4. Mean Total DDT concentrations ranged from 2.4–11.3 µg/kg (including concentrations below detection limit at a value one half of the detection limit, Table 3.2). TOC-normalised mean Total DDT concentrations were above the ARC-ERC red threshold in the sediments from site WH3 (Lambton Basin entrance), and above the ANZECC ISQG-Low trigger value at the other three sites.

Variability in Total DDT concentrations was low at sites WH1, WH2 and WH4 (c.v. 5.4–11.1%), and moderately high at site WH3 (c.v. 53.9%).

Hexachlorobenzene was present in the sediments of site WH3 at a mean concentration of 0.62 µg/kg, but was very close to or below the detection limit (0.1 µg/kg) at the other three sites. There are no recommended trigger values for hexachlorobenzene in the ANZECC (2000) sediment quality guidelines.

3.3 Quality assurance

The PAH-related analytical QA results are provided in full in Olsen & Guyader (2009, Appendix 3) and, in summary, showed:

- Acceptable recoveries, and coefficients of variation of <10%, for all HMW PAH surrogates. Lower recoveries and high variability were observed for naphthalene-d8 and acenaphthene-d10, features which are commonly observed using this method of analysis.
- Good precision for Total PAH (< ±9%) in the within-batch comparisons, covering the entire range of PAH concentrations.
- Quite high differences for some individual PAHs in the Standard Reference Material (SRM) comparison (e.g., anthracene –40%, dibenzo[a,h]anthracene +47%), but good agreement for Total PAH (–0.8%). Difficulties were encountered for the quantitation of selected PAHs during the analysis of the SRM sediment material due to matrix interferences, which were not routinely encountered for the Wellington Harbour sediments, and this may have contributed to the higher variability for these compounds.

In terms of the OCP QA results (Olsen 2010, Appendix 5), there was good agreement of compounds in the SRM sample, indicating that the performance of the analytical method was very good.

Table 3.2: Summary of concentrations and variability (coefficient of variation [cv, %], $n=3-5$) of total organic carbon (TOC) and selected organochlorine pesticide compounds in sediments of four sites sampled in Wellington Harbour in late 2006. The TOC results are those generated by Hill Laboratories and reported in Stephenson et al. (2008) while the OCP results represent new data generated by NIWA (see Olsen & Guyader (2009) in Appendix 3 for all the OCP compounds analysed). Sediment quality guidelines for comparison are ANZECC (2000) and Auckland Regional Council Environmental Response Criteria (ARC ERC; ARC 2004). Values in amber exceed the ANZECC ISQG-Low or ARC ERC amber threshold and values in red exceed the ANZECC ISQG-Low and ARC ERC red threshold.

Analyte	Fraction analysed	ANZECC		ARC ERC		WH1		WH2		WH3		WH4	
		ISQG-Low	ISQG-High	amber	red	mean	c.v.	mean	c.v.	mean	c.v.	mean	c.v.
TOC (%) ¹	< 500 µm					1.73	2.1	1.41	1.8	1.78	1.6	1.59	0.6
<u>Organochlorine pesticides (µg/kg):</u>													
Hexachlorobenzene	< 500 µm					< 0.1	–	< 0.1	–	0.62	60.8	< 0.1	–
Total DDT ^{2,3}	< 500 µm					5.6	5.4	2.4	9.5	11.3	53.9	3.2	11.1
Hexachlorobenzene	at 1% TOC					< 0.1	–	< 0.1	–	0.35	60.8	< 0.1	–
Total DDT ⁴	at 1% TOC	1.6	46		3.9	3.2	4.2	1.7	7.8	6.3	53.7	2.0	11.2

¹ The mean and cv values presented here only relate to the replicates re-analysed by NIWA (i.e., $n=3$ for sites WH1, WH2 and WH4).

² For the purpose of calculating Total DDT, the concentration of any individual compound reported at “less than detection limit” has been replaced by a value one half of the detection limit.

³ DDT and related compounds have been summarised as “Total DDT”, which is the sum of the concentrations of 2,4'-DDE, 2,4'-DDD, 2,4'-DDT, 4,4'-DDE, 4,4'-DDD, and 4,4'-DDT.

⁴ This TOC “normalisation” is used in the ANZECC (2000) sediment quality guidelines and ARC (2004) ERC for comparing sediments with different TOC content.

4. Discussion

This section provides a brief discussion of the differences in PAH and DDT data obtained from Hill Laboratories (reported in Stephenson et al. 2008) and NIWA. A summary of PAH source interpretation drawn from Depree (2010, Appendix 4) is also provided.

4.1 Polycyclic aromatic hydrocarbons

Re-analysis of the 16 USEPA priority pollutant PAHs largely confirms the spatial trends in concentrations described in Stephenson et al. (2008) and, if substituted for the earlier results, leads to only minor changes in relation to compliance with sediment quality guidelines. The TOC-normalised mean Total HMW PAH concentration in sediments at site WH1 would no longer exceed the ANZECC (2000) ISQG-Low threshold but remain above the ARC (2004) ERC amber threshold, while acenaphthalene (site WH1) and naphthalene (site WH10) would replace phenanthrene and benzo[a]anthracene as individual compounds with concentrations exceeding ANZECC (2000) ISQG-Low thresholds.

The 2009 analytical results raise some QA issues which could affect the detection of changes in the concentrations of PAHs over time. Of the 1,360 analyses, comparing concentrations reported by Hill Laboratories and NIWA, 26% showed a variance of more than 30% (the level generally regarded as the cut-off for acceptable variation). Where concentrations were lower (16% of the reported concentrations), this generally involved the Low Molecular Weight PAHs, indicating that earlier results from Hill Laboratories may have underestimated the concentrations of some of these compounds. Conversely, where the concentrations were greater, this generally involved the HMW PAHs, indicating that the earlier results may have over-estimated the concentrations of some of these compounds. The differences between the HMW PAH concentrations are of greater concern because this is the group that will be used for the analysis of temporal trends.

4.1.1 Sources of polycyclic aromatic hydrocarbons (after Depree 2010)

The sediments at sites WH1 (southern Evans Bay) and WH3 (Lambton Basin entrance) are notable for having considerably higher PAH concentrations than the remaining sites. These two sites are relatively distant from major terrigenous (terrestrial-derived) inputs of sediment from sources like the Hutt River, and because the streams discharging to the inner harbour are largely piped, the volume of “clean” natural sediment reaching them is likely to be lower relative to the volume of contaminated anthropogenic particulates than would be the case for sites elsewhere in the harbour. With less dilution of the contaminated particulates, higher sediment concentrations at these inner harbour sites would result. An alternative explanation is that these sites have been impacted by point-source discharges. However, if this were the case, different contaminants in the harbour sediments would be expected to show different source distributions. When the concentrations of some of the trace metals found above sediment quality guidelines in Wellington Harbour sediments are adjusted for background concentrations (Dickinson et al. 1996; KML 2005), their distribution trends across the 17 sites are similar to that of

Total PAH concentrations. This suggests a common source (such as urban runoff) as opposed to point source contamination by PAHs at the inner harbour sites.

Based on several diagnostic PAH ratios, Wellington Harbour sediments contain a relatively pyrogenic composition of PAHs which shows relatively little variation except at site WH15 (\approx 1.1 km SW of Seaview). While absolute PAH concentrations in the sediments at this site are comparatively low, the increased petrogenic nature of the PAHs is supported by other diagnostic ratios, such as that for phenanthrene/anthracene. Additional petrogenic source information could have been derived from testing of additional compounds such as total petroleum hydrocarbons (TPH) and hopanes.

The pyrogenic nature of the PAHs in the sediments indicates that the most likely sources are soot from mobile and/or stationary combustion of fossil fuels, and coal tar from either diffuse pollution (roading) or point sources (discharge of gasworks waste). Of these, coal tar appears to be the most likely source (the likelihood of point sources of pyrogenic PAHs such as a discharge of gasworks waste has already been discounted and the diagnostic ratios, although not specific or conclusive, point towards coal soot and/or coal tar).

Although largely unknown as a diffuse pollution source, coal tar was widely used throughout New Zealand between the early 1900s and the mid-1970s as a binder for sealing roads, and would have been used in catchments that discharge into Wellington Harbour. Compared to the bitumen binders that are now used exclusively in road construction, coal tar binders are strongly pyrogenic and typically contain about 5,000-10,000 times higher concentrations of PAHs than bitumen (about 150,000 mg/kg compared to 20–30 mg/kg in bitumen). As a result, historic inputs of PAHs from coal-tar impacted catchments are likely to have been much higher than inputs from modern road run-off. This is supported by Mahler et al. (2005) who reported that in Austin, Texas, particles in runoff from parking lots with a coal tar surface had concentrations of PAHs that were about 65 times higher than concentrations in particles washed off asphalt parking lots. Van Metre et al. (2009) showed that the problem of coal tar sealcoats is not limited to Austin, but appears to be a US-wide environmental issue – the analysis of lake sediments in nine US cities showed a strong link between in-catchment usage of coal tar products and higher PAH concentrations in lake sediments.

Further work is required to confirm the likelihood that much of the PAHs in Wellington Harbour sediments could be historic and a result of the once-widespread use of coal tar for sealing roads⁴. If confirmed, this would have important implications for stormwater management and the issuing of resource consents for stormwater discharges. For example, if the Wellington Harbour sediment PAH concentrations reflect historic inputs of urban runoff, and if modern runoff contains considerably lower concentrations of PAHs, then it is

⁴ This does not imply that urban stormwater runoff is not the major source, just that historic inputs may be primarily responsible for the observed concentrations and composition of the PAHs in the harbour floor sediments. As only the top 30 mm of the sediment was sampled, it follows that either the inputs of these legacy contaminants are still occurring (Greater Wellington stormwater investigations clearly suggest this is the case, e.g., KML (2005), Milne & Watts 2008)) and/or bioturbation by benthic fauna has resulted in significant vertical mixing of the sediment.

difficult to make risk assessments or apply protective regulations based on the receiving environment sediment concentrations – simply because there is no link for establishing ‘cause’ (i.e., modern runoff inputs) and ‘effect’ (i.e., sediment concentrations). However, just because coal tar use is historic, it does not necessarily mean the inputs to the receiving environment from this source are exclusively historic. It would be useful to measure runoff particulate PAH concentrations and composition in stormwater drains (or in catchpit sediment and/or street sweepings⁵) discharging into Wellington Harbour, particularly those in Wellington City, to determine if legacy inputs are still occurring or if current runoff contains significantly lower concentrations of particulate PAHs. This in turn would enable an assessment to be made as to whether or not, long-term, PAH concentrations in Wellington Harbour sediments can be expected to increase or decrease with continued discharges of stormwater.

Analysis of one or more sediment cores also would be useful; both to assist in determining the extent of historical contamination and to enable an assessment of the role that bioturbation (mixing of sediments by benthic fauna or flora) may play in maintaining current concentrations of PAHs in the surficial sediments of the inner harbour. In addition, sampling sediments at sites closer to shore would improve spatial information on sediment PAH concentrations. Sites WH1–WH4 (the most impacted sites) are at least 500 m from the shore and, as noted in Stephenson et al. (2008), there is the potential for much higher sediment contaminant concentrations closer to the stormwater discharge outfalls.

4.2 Organochlorine pesticides

Results of the re-analysis of the organochlorine pesticides confirm the elevated levels of DDT and its derivatives at the four inner harbour sites adjacent to Wellington City. In addition, the results raise some QA issues which could affect the detection of changes in the concentrations of these compounds over time. Of the 52 analyses for DDT (and its derivatives) that were available for comparison between the two laboratory data-sets, nearly 70% varied by more than 30%. Overall, of the 14 samples re-analysed by NIWA, 11 have Total DDT values which vary from the earlier results by more than 30% (range -35 to -92%). This suggests that the earlier results may have over-estimated the concentrations of Total DDT. This is difficult to quantify because both laboratories experienced difficulties with the OCP analyses (Stephenson et al. 2008, Olsen 2010).

Irrespective of the variability in DDT concentrations reported by Hill Laboratories and NIWA, the presence of DDT and its derivatives in Wellington Harbour sediments is clear. Total DDT concentrations at sites WH1–WH4 are above the ANZECC (2000) ISQG-Low threshold, with concentrations at site WH3 also above the ARC (2004) ERC red threshold. The levels of DDE and DDD (DDT break-down products) at this site were relatively low, suggesting a more recent addition of DDT to the environment (Olsen 2010). Overall, the widespread presence of DDT highlights the importance of analysing OCPs at all sites sampled in the next harbour sediment survey.

⁵ Analysis of these sources has the benefit of integrating contaminants generated over a greater spatial area (Depree, pers. comm. 2010).

5. Conclusions and recommendations

The pyrogenic nature of the PAH composition in Wellington Harbour sediments collected in late 2006 has limited the usefulness of the data derived from analysis of alkylated PAHs and marker compounds in determining the sources from which the PAH is derived. It appears likely that much of the PAHs in Wellington Harbour sediments could be historic and a result of the once-widespread use of coal tar for sealing roads. Further work is required to confirm this and to assess potential long-term trends in PAH concentrations in Wellington Harbour sediments with continued discharges of stormwater. It is recommended that:

- The analysis of PAHs in future surveys of sediment quality in Wellington Harbour is limited to the 16 USEPA-listed PAHs, TPH, hopanes, retene, and selected deuterated PAHs and marker compounds such as 2,6- and 1,7 1-methylated phenanthrene unless there is evidence of an increase in the petrogenicity of the sediments;
- Sediment samples are collected at sites closer to shore in Evans Bay and Lambton Harbour to improve spatial information on sediment PAH concentrations;
- A core 0.5 m in length is taken at each of sites WH1 and WH3, sub-sampled at depths of 0–30, 150–180 and 300–330 mm, and analysed for the compounds listed above in order to establish historic trends in PAH contamination and permit assessment of the role that bioturbation may play in maintaining current levels of PAHs in the surficial sediments of the inner harbour; and
- Representative samples of particulates (or catchpit sediment and/or street sweepings) are collected from stormwater drains discharging into Wellington Harbour, particularly those in Wellington City, and analysed for the compounds listed above in order to reconcile the source information obtained from the harbour sediments and determine their PAH concentrations relative to PAH concentrations in the harbour sediments.

Re-analysis of both PAHs and organochlorine pesticides (OCPs) in sediments collected during the 2006 survey has revealed inter-laboratory differences which could affect the detection of changes in the concentrations of these compounds over time. The recommendations made by Stephenson et al. (2008) with respect to analytical QA will need to be rigorously applied in future surveys. In addition, it is recommended that:

- Data from the re-analysis are used as the starting point for trend detection, particularly if the NIWA organics laboratory is selected to undertake the PAH and OCP analyses for the next survey; and
- OCPs are analysed at all sites in the next survey and, if the results confirm low levels at all sites other than WH1, WH2, WH3, and WH4, then only these four sites be monitored for OCPs in subsequent surveys.

References

Ahrens, M.; Olsen, G. 2008. *PAH source apportionment in marine sediments from Wellington Harbour*. A report prepared for the Greater Wellington Regional Council. NIWA Client Report: HAM2008-074.

ANZECC 2000. *Australian and New Zealand guidelines for fresh and marine water quality. Volume 1: The guidelines*. Australian and New Zealand Environment and Conservation Council. Agriculture and Resource Management Councils of Australia and New Zealand, Canberra.

ARC 2004. *Blueprint for monitoring urban receiving environments*. Auckland Regional Council, Technical Publication No. 168, revised edition.

Depree, C. 2010. *Potential sources of PAHs in Wellington Harbour sediments*. A report prepared for the Greater Wellington Regional Council. NIWA Client Report: HAM2010-031.

Depree, C.; Ahrens, M. 2007. *Polycyclic aromatic hydrocarbons in Auckland's aquatic environment: Sources, concentrations and potential environmental risks*. A report prepared for the Auckland Regional Council. NIWA Client Report: HAM2006-088.

Dickinson, W.W.; Dunbar, G.B.; McLeod, H. 1996. Heavy metal history from cores in Wellington Harbour, New Zealand. *Environmental Geology* 27: 59–69.

Kelly, S. 2010. *Further statistical analysis of Wellington Harbour sediment contaminant and benthic fauna data*. A report prepared for Greater Wellington Regional Council by Coast & Catchment Limited.

KML 2005. *Assessment of urban stormwater quality in the greater Wellington region*. A report prepared for the Greater Wellington Regional Council by Kingett Mitchell Limited.

Mahler, B.J.; Van Metre, P.C.; Bashara, T.J.; Wilson, J.T.; Johns, D.A. 2005. Parking lot sealcoat: an unrecognized source of urban PAHs. *Environmental Science & Technology* 39: 5,560–5,566.

Milne, J.R.; Watts, L. 2008. *Stormwater contaminants in urban streams in the Wellington region*. Greater Wellington Regional Council, Publication No. GW/EMI-T-08/82.

Olsen, G. 2010. *Wellington Harbour sediment pesticide results*. Email correspondence with Juliet Milne, Greater Wellington Regional Council, 7 May 2010. Greater Wellington document reference #768067.

Olsen, G.; Guyader, G. 2009. *Polycyclic aromatic hydrocarbons and marker compounds in marine sediments from Wellington Harbour*. A report prepared for the Greater Wellington Regional Council. NIWA Client Report: HAM2009-116.

Stephenson, G.; Mills, G.N. 2006. *Porirua Harbour long-term baseline monitoring programme: Sediment chemistry and benthic ecology results from the October 2005 survey*. A report prepared for the Greater Wellington Regional Council by Diffuse Sources Limited and Coastal Marine Ecology Consultants Ltd.

Stephenson, G.; Milne, J.R.; Sorensen, P. 2008. *Wellington Harbour marine sediment quality investigation*. Greater Wellington Regional Council, Publication No. GW/EMI-T-08/83.

Van Metre, P.C.; Mahler, B.J.; Wilson, J.T. 2009. PAHs underfoot. Contaminated dust from coal-tar sealcoated pavement is widespread in the United States. *Environmental Science & Technology* 43: 20–25.

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Dr Judi Hewitt (NIWA) provided initial advice on further statistical analysis of the benthic fauna data and Dr Shane Kelly (Coast and Catchment Ltd) subsequently undertook the analysis and prepared the report presented in Appendix 2.

Appendix 1: Wellington Harbour sampling site details

Site position and collection details for the Wellington Harbour marine sediment quality investigation (Oct/Nov 2006)

Site	Location	Date	NZ Map Grid		Depth (m)
			Easting	Northing	
WH1	Southern Evans Bay	11/10/2006	2661552	5987060	19
WH1B		13/11/2006			
WH2	Northern Evans Bay	11/10/2006	2661732	5989000	19
WH2B		13/11/2006			
WH3	Lambton Basin entrance	03/11/2006	2660078	5990052	18
WH3B		17/11/2006			
WH4	≈ 0.7 km NW of Point Jerningham	03/11/2006	2660785	5990501	20
WH4B		17/11/2006			
WH5	≈ 1.2 km NNE of Point Jerningham	18/10/2006	2661770	5990851	21
WH5B		17/11/2006			
WH6	≈ 1.25 km NW of Point Halswell	18/10/2006	2662687	5991294	22
WH6B		17/11/2006			
WH7	≈ 1.5 km N of Point Halswell	18/10/2006	2663603	5991645	22
WH7B		17/11/2006			
WH8	≈ 1.5 km SW of Matiu/Somes Island	18/10/2006	2664588	5991995	23
WH8B		13/11/2006			
WH9	≈ 1.5 km SSE of Ngauranga Stream mouth	03/11/2006	2661943	5992421	20
WH9B		08/11/2006			
WH10	≈ 0.5 km SSE of Ngauranga Stream mouth	11/10/2006	2662034	5993437	20
WH10B		08/11/2006			
WH11	≈ 0.5 km E of Ngauranga Stream mouth	03/11/2006	2662530	5993797	20
WH11B		08/11/2006			
WH12	≈ 1.5 km E of Ngauranga Stream mouth	03/11/2006	2663502	5993499	21
WH12B		08/11/2006			
WH13	≈ 1.25 km S of Petone Wharf	11/10/2006	2666045	5994834	16
WH13B		08/11/2006			
WH14	≈ 0.65 km S of Petone Wharf	11/10/2006	2666404	5995289	12
WH14B		08/11/2006			
WH15	≈ 1.1 km SW of Seaview (Hutt River mouth)	11/10/2006	2668182	5993492	16
WH15B		13/11/2006			
WH16	≈ 2.1 km SW of Seaview (Hutt River mouth)	18/10/2006	2667265	5993049	19
WH16B		13/11/2006			
WH17	≈ 1.6 km NNW of Makaro/Ward Island	18/10/2006	2666792	5990560	21
WH17B		13/11/2006			

B = Benthic ecology collection area

Appendix 2:

Report on further statistical analysis of Wellington Harbour sediment contaminant and benthic fauna data (Kelly 2010)

FURTHER STATISTICAL ANALYSIS OF WELLINGTON
HARBOUR SEDIMENT CONTAMINANT AND BENTHIC
FAUNA DATA:

A REPORT PREPARED FOR GREATER WELLINGTON REGIONAL COUNCIL



FURTHER STATISTICAL ANALYSIS OF WELLINGTON HARBOUR SEDIMENT CONTAMINANT AND BENTHIC FAUNA DATA:

A REPORT PREPARED FOR GREATER WELLINGTON REGIONAL
COUNCIL

SHANE KELLY

Date: May 2010

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1 EXECUTIVE SUMMARY

Univariate and multivariate analyses of matching benthic ecology and sediment chemistry data from Wellington Harbour indicate that the composition of subtidal macrofaunal communities is influenced by stormwater runoff. In 2006, sediment concentrations of the major stormwater contaminants copper, lead and zinc, declined linearly with offshore distance from the major sources of these metals, while total DDT and total PAH concentrations were elevated at individual sites in Lambton Harbour and Evans Bay. In contrast, no relationship was apparent between the offshore distance from major contaminant sources and sediment mud content.

The number of individuals in ecological samples showed a similar trend to copper lead and zinc concentrations, i.e. declining with distance from major stormwater sources. However, Pielou's evenness increased with distance due to individuals becoming more evenly spread among species (i.e. communities at remote sites were less dominated by one or more species). A strong relationship was also detected between benthic community structure and copper, lead and zinc concentrations. A comparison of sites grouped using K-means partitioning, (based on copper, lead and zinc concentrations), indicated that the ecological differences apparent between "clean" and "contaminated" sites were due to variation in the abundance of multiple species, rather than large changes in the abundance of a single or few species. Other stormwater contaminants such as mercury, PAH and DDT may also affect benthic communities within the harbour, but the effects of these contaminants cannot be separated from those of other environmental variables such as the mud and organic carbon content of sediments.

2 INTRODUCTION

Routine and systematic sediment contaminant and ecological monitoring of Wellington Harbour was initiated in October – November 2006. The results of the initial survey showed that concentrations of copper, lead, mercury, zinc, tributyltin, DDT and PAH concentrations exceeded sediment quality guidelines in some parts of the harbour. However, no relationship was identified between elevated contaminant concentrations and indices of species diversity or the composition of ecological communities, using a combination of univariate and standard multivariate techniques of data analysis (Stephenson *et al.* 2008).

The analytical methods used by (Stephenson *et al.* 2008) provide a good representation of the dominant patterns in benthic community structure, and allow the visualisation of relationships between community structure and a range of environmental variables. However, the most abundant species are not necessarily the most sensitive species to environmental change. A number of recent studies have applied more sophisticated multivariate analyses to identify relationships between contaminants and community composition, which would otherwise be masked by the primary drivers of ecological variation (Anderson *et al.* 2006, Thrush *et al.* 2008, Hewitt *et al.* 2009). The use of canonical analysis of principal coordinates (CAP) has proved particularly fruitful. This method underpins the Auckland Regional Council's "benthic health model", which is used to assess the ecological effects of stormwater contaminants on intertidal communities (Anderson *et al.* 2006). The purpose of this study is to re-examine 2006 monitoring data from Wellington Harbour using some of these newer multivariate techniques, to check whether stormwater contaminants are having an underlying effect on subtidal benthic communities in the harbour.

3 METHODS

3.1 SITE LOCATIONS, SAMPLE COLLECTION AND ANALYSIS

Data on sediment quality and texture, and subtidal benthic ecology were collected from 17 subtidal sites in Wellington Harbour during October-November 2006 (Figure 1). Five sediment samples and eight benthic ecological samples were collected per site, using the methods outlined in Stephenson *et al.* (2008). Sediment quality was assessed by determining the concentrations of strong and weak acid extractable metals (antimony, arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver and zinc), total organic carbon, organotins, PAHs, and a range of organochlorine pesticides. Sediment grain size in the sediment quality and ecological core samples was determined using Galai laser particle analysis.

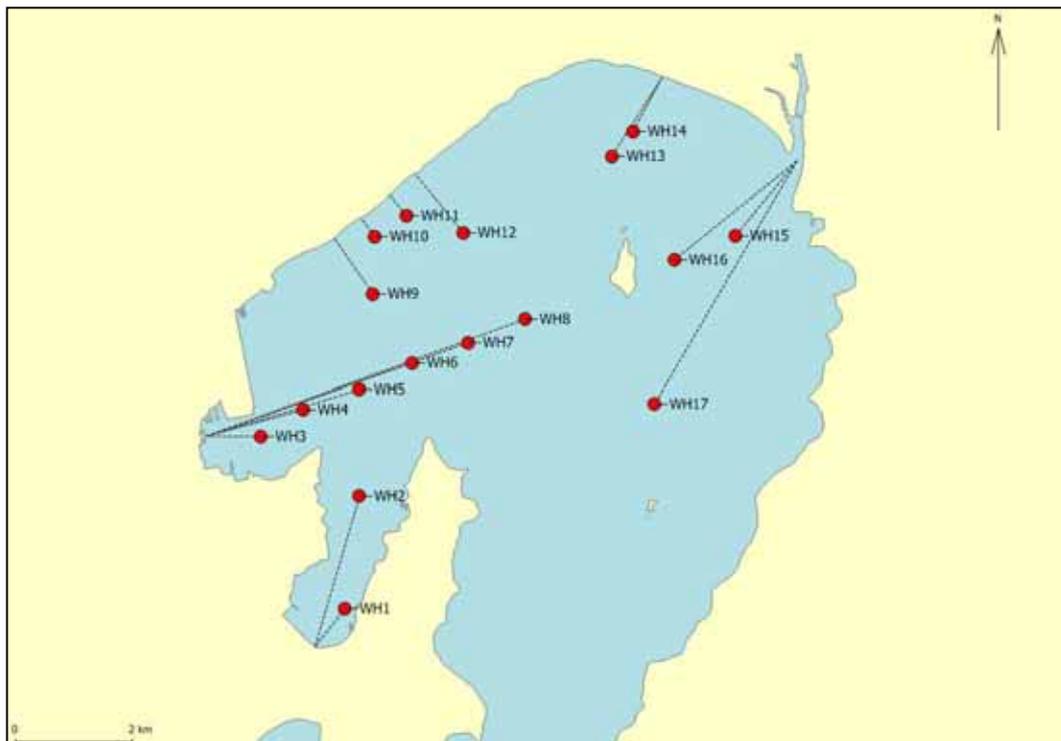
3.2 GENERAL PATTERNS

Least squares regression was used to examine the relationship between proximity to major sources of stormwater contaminants and indices of ecological diversity (number of species, number of individuals, Pielou's evenness and Shannon diversity). The Shannon diversity index is a commonly used measure of diversity that takes into account the number of species present (species richness) and how evenly the number (or biomass) of individuals is spread amongst these species (equitability). The latter consideration is an important feature of the index, as one community may have more species, but lower diversity than another, if one (or a few) species are numerically dominant. Interpretation of Shannon's diversity index is therefore aided by specific information on species richness (i.e. the number of species) and equitability. Pielou's evenness index is a measure of equitability, which indicates how even (i.e., similar) the abundances of individual species are at a site. Low index values indicate that the site is dominated by a single, or a few, species which occur in high abundance(s). The remaining species occur in relatively low abundances. In contrast, high index values indicate that the abundances of all species are fairly similar.

The proximity to major sources of stormwater contaminants was estimated by measuring the distance between each sampling station and the shore location that was expected to contribute most contaminants to that station (Figure 1).

Multi dimensional scaling (MDS) and cluster analysis of square root transformed species count data using Bray Curtis similarity were then used to examine major patterns in the ecological composition of the monitoring stations. Data from individual samples at each site were pooled and the total counts per site were used in these analyses. MDS bubble plots of sediment and total organic carbon contents, and individual contaminant concentrations were then used to provide an initial check for relationships between environmental variables, contaminant concentrations, and community composition.

Figure 1: Ecological sampling stations in Wellington Harbour, together with lines used to measure the nominal distance to the major sources of stormwater contaminants for each station.



3.3 ANALYSIS AND PRE-TREATMENT OF ENVIRONMENTAL VARIABLES

Ecological communities can be affected by a combination of contaminant levels and sediment characteristics (i.e. sediment texture and organic content), which both vary spatially in the coastal environment. Separating the ecological influence of individual stressors is difficult when they are strongly correlated with other environmental variables. For instance, a strong relationship is often observed between the proportion of fine sediment and metal concentrations, because small particles have a high surface area to volume ratio. Consequently, for a given weight (or volume) of sediment, fine sediments are able to bind more metals to their surface than coarse sediments. Initial tests were therefore carried out to examine the relationship between metal and organic contaminant concentrations, and the proportion of mud and organic carbon in sediments. Metal (Cd, Cr, Cu, Hg, Pb, and Zn extracted using strong acid digestion of the < 500 μm sediment fraction) and organic contaminant (total PAH and total DDT) concentrations were reduced to two axes using principal component analysis (PCA), and the relationships between PCA axes and the sediment contents of mud and organic carbon were examined using least squares regression.

Silver, antimony, tributyltin and hexachlorobenzene were excluded from these analyses because most, or all, of the samples had concentrations that were below detection limits. Arsenic concentrations were also excluded because environmental variation in arsenic commonly appears to be unrelated to urban stormwater inputs (e.g. Milne et al 2009).

Principal component analyses (PCA) were initially carried out using raw and normalised¹ metal (Cd, Cr, Cu, Hg, Pb, and Zn concentrations expressed as mg/kg of the <500 μm sediment fraction). An important consequence of normalisation is that it “equalises” the contribution that each variable makes to the multivariate analysis.

¹ Normalisation involves subtracting the variables mean from each data point and dividing by the standard deviation for that variable. This provides a mean of zero and standard deviation of one for each variable. Consequently, the values of all variables become roughly the same.

This may be desirable, because the ecological effects of a small change in the concentration of one contaminant (e.g., cadmium) are likely to be similar to a relatively large change in the concentration of another (e.g., zinc). The disadvantage is that contaminants with environmentally insignificant concentrations are given the same weight as those present in potentially harmful concentrations. Using untransformed concentrations biases the results toward contaminants that occur at higher concentrations. In urban situations, these tend to be the major stormwater contaminants, copper, lead, and zinc, which are also likely to be the contaminants of most ecological concern.

Normalised sediment concentrations² of total PAH and total DDT (expressed as µg/kg from the <500 µm sediment fraction) were used in the PCA analysis of organic contaminants. Raw values were considered inappropriate because only two variables were used in the analysis and PAH concentrations were two orders of magnitude greater than DDT concentrations, although both potentially occurred at ecologically relevant concentrations.

3.4 RELATIONSHIPS BETWEEN ENVIRONMENTAL VARIABLES AND COMMUNITY STRUCTURE

Canonical analysis of principal coordinates (CAP) was used to examine relationships between benthic community structure, and metal (Cu, Pb, and Zn) and organic contaminant concentrations (total PAH and total DDT). Bray Curtis similarities of square root transformed species counts (using total counts for each site) were used for these analyses.

Two variations of CAP were used, whereby species counts were constrained by:

- The quantitative indices of 'environmental quality' obtained from PCAs of environmental variables. Linear regression was then used to examine the relationship between PCA axes and CAP scores of community structure.
- Categorical site groupings obtained from hierarchical agglomerative clustering (using group-averages) and K-means partitioning of contaminant concentrations. The fits obtained from these analyses were checked using "leave-one-out" tests of allocation success (see Anderson *et al.* (2002) and Anderson *et al.* (2006) for a description of this test).

The number of groups identified using K-means partitioning was intentionally limited to three, because contaminant concentrations were relatively uniform over large parts of the harbour and concentration ranges were relatively narrow. Similarly, in order to limit the number of site-groups identified by hierarchical agglomerative clustering, only major breaks on the cluster dendrogram were used. Similarity profile analysis was also used to check that the site-groups identified from the dendrogram came from significant clusters, or combinations of significant clusters.

An important parameter in CAP is the number of principal coordinate analysis (PCO) axes that should be retained in the final model (i.e., the "*m*" value). Ecologically important information may be missed if *m* is too small. Conversely, a misleading canonical plot could be produced if *m* is too large, relative to the number of samples (*N*). The canonical plot can suggest that groups are strongly separated when *m* approaches *N*, even if this is not really the case. The value of *m* must not exceed the number of variables or number of samples, and should be chosen so that the proportion of the variability explained by the *m* PCO axes is more than 60% and less than 100% of the total variability in the original dissimilarity matrix (Anderson and Willis 2003). Within these constraints, Anderson and Willis (2003) recommend that *m* should be chosen in a non-arbitrary manner by minimising either the misclassification error (for analyses with categorical grouping variables) or the residual sum of squares (for analyses with quantitative variables). This approach was adopted here, but alternative *m* values were also used to check the CAP model in cases where *m* exceeded 80% of *N*, and CAP plots appeared to overemphasize the separation of between groups and underemphasize variability within

² Total sediment concentrations were used in these analyses, rather than carbon normalised concentrations.

groups in categorical analyses. Alternative m values were selected by identifying intermediate peaks in allocation success that occurred as PCO axes were added sequentially. In cases where intermediate peaks had several m values with the same allocation success: the minimum value of m that explained more than 60% of the total variability in the original dissimilarity matrix was selected.

When allocation success obtained from the “leave-one-out” analysis confirmed that community composition varied in relation to the environmental variables being examined, species differences between the site-groupings were examined by analysing similarity percentages. Readers are referred to Anderson *et al.* (2002), Anderson and Willis (2003) and Anderson *et al.* (2006) for more detailed descriptions of CAP.

4 RESULTS

4.1 GENERAL PATTERNS

General patterns in community diversity and composition were investigated by examining the relationships between distance from major land-based sources of contaminants and the diversity indices: number of species, number of individuals, Pielou's evenness, and Shannon diversity ($\log e$) (Figure 2). Least squares linear regression indicated that the total number of species and total number of individuals per site tended to decrease with distance from major contaminant sources, while Pielou's evenness and Shannon diversity tended to increase. However, these trends were statistically significant only for the total number of species per site ($p = 0.0231$, $r^2 = 0.3$) and Pielou's evenness ($p = 0.0484$, $r^2 = 0.25$).

Multi dimensional scaling and cluster analysis of square root transformed ecological count data using Bray Curtis similarity also suggested that the ecological composition of sites varied with distance from the shore, with sites in central parts of the harbour generally grouping separately from near-shore sites (Figure 3). Preliminary checks using MDS bubble plots of sediment and total organic carbon contents, and individual contaminant concentrations could not identify the variables responsible for the patterns in the MDS plot and cluster analysis, even though offshore trends were apparent in variables such as zinc, copper and total organic carbon, and localised variation was apparent in total DDT and total PAH concentrations (i.e. high concentrations at sites WH1 and WH3 in Lambton Harbour and Evans Bay (Figure 4). No such relationship was apparent between the offshore distance from contaminant sources and sediment mud content.

More detailed analyses were therefore carried out to identify relationships between ecological and physico-chemical variables using a combination of principal coordinate analysis (PCA), clustering, canonical analysis of principal coordinates (CAP) and univariate statistics.

Figure 2: Relationship between distance (km) from major land based sources of contaminants and the diversity indices: a) total number of species per site; b) total number of individuals per site; c) Pielou's evenness; and, d) Shannon diversity ($\log e$).

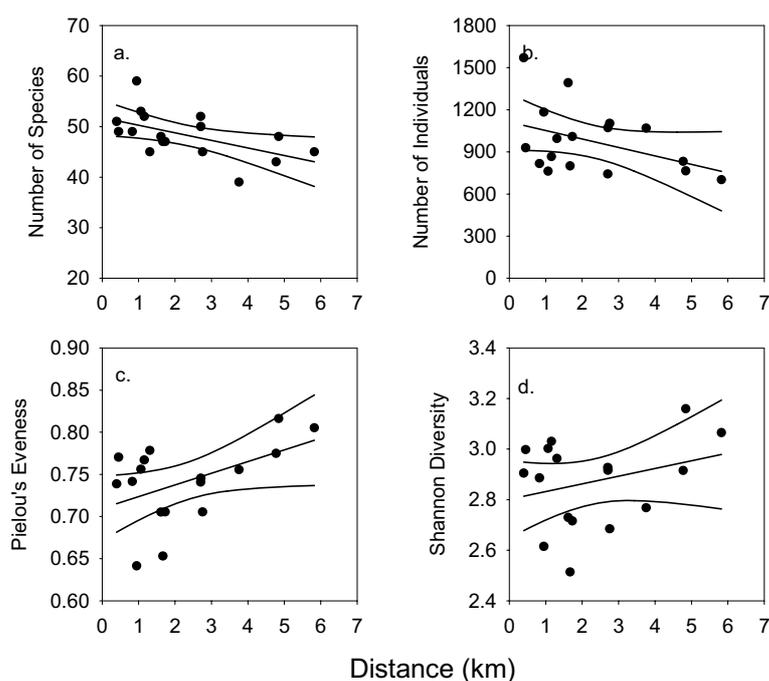


Figure 3: MDS plot (a) and map (b) of groups of sites identified using cluster and similarity profile analysis of square root transformed data using Bray Curtis similarity. Bubble size in the MDS is proportional to the distance from major stormwater contaminant sources and groups are identified by dot colour.

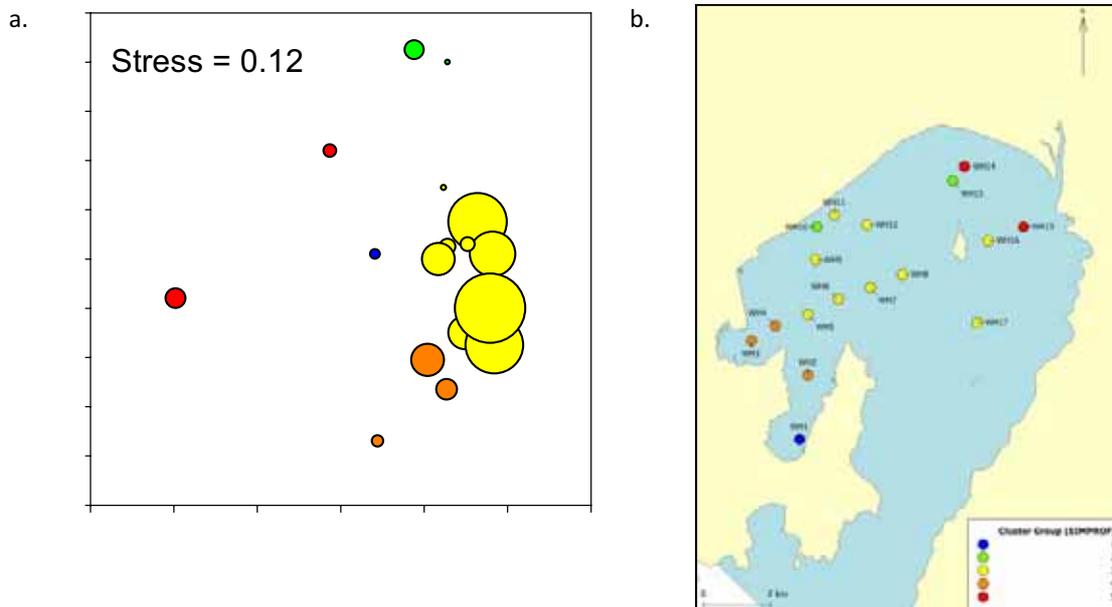
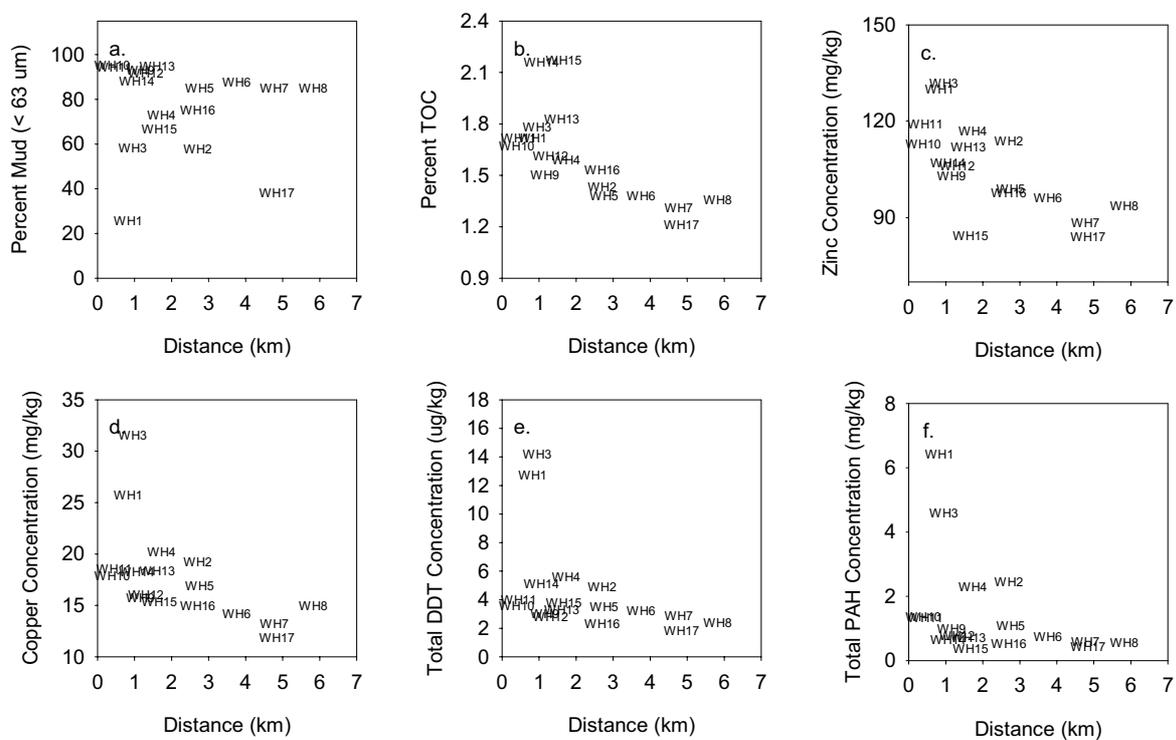


Figure 4: Relationships between the offshore distance from major contaminant sources and sediment concentrations of a) mud (< 63 μm) (%), b) total organic carbon (%), c) zinc (mg/kg), d) copper (mg/kg), e) total DDT, and f) total PAH in Wellington Harbour.



4.2 RELATIONSHIPS BETWEEN CONTAMINANTS AND ECOLOGICAL COMMUNITIES

Principal component analyses were used to examine relationships among contaminant and environmental variables (sediment-mud and TOC contents), and to reduce each contaminant group (i.e. metal and organic contaminants) to single quantitative indices for use in CAP analyses. The primary PCA axis for normalised metal concentrations accounted for 61.4% of the variation in metal concentrations. Eigenvector values indicated that this axis was mainly influenced by concentrations of the major stormwater contaminants copper, lead, mercury and zinc (Figure 5a). In contrast, the secondary PCA axis accounted for 27.1 % of the variation and was mainly influenced by cadmium, chromium and nickel. The influence of copper, lead and zinc was even more apparent when untransformed metals data were used, due to the high concentrations of these metals. The primary PCA axis for untransformed metals accounted for 96.1% of the variation in metal concentrations (Figure 5b). Similarly, the primary PCA axis for normalised DDT and PAH concentrations explained 94.6% of the variation in these contaminants, reflecting the strong correlation between these variables ($r = 0.93$).

No significant relationship was detected between mud or TOC content, and the primary axes of PCAs for normalised or untransformed metal concentrations (Table 4-1, Figure 6). Further testing with least squares regression also confirmed that mud and TOC contents were not significantly related to copper, lead or zinc concentrations (in all cases $p > 0.12$). The lack of a relationship between mud content and, copper and zinc concentrations is likely to be due to sediment-mud content being uniformly high across the harbour (sediments from 15 of the 17 sites had greater than 50% mud). The lack of co-variation in mud or TOC content, and copper lead and zinc enabled an analysis of the relationship between these metals and the composition of benthic communities to be carried out, which was independent of sediment or TOC effects (i.e. the “ecological effects” of copper lead and zinc could be separated from those of sediment-mud and organic carbon contents). The ecological effects of these metals were therefore analysed separately from other environmental variables.

In contrast, significant relationships were detected between sediment mud content and the primary PCA axis for normalised total PAH and total DDT concentrations, and the secondary PCA axis for normalised and untransformed metal concentrations. Similarly, a significant relationship was detected between the secondary PCA axis for normalised metals and TOC content. A significant ($p = 0.024$) negative relationship was also detected between mud content and untransformed mercury concentrations, due to high mercury concentrations and low mud content at stations WH1, WH2 and WH3. However, the presence of these outlying stations meant that the assumption of equally distributed residuals was violated. No significant relationship was detected between mud content and mercury concentrations when these stations were excluded ($p = 0.3091$), or when log transformed mercury concentrations were used ($p = 0.1247$).

The above results indicate that analyses of the ecological effects of DDT, PAH, and metals other than copper, lead and zinc are potentially confounded by the effects of sediment mud and/or TOC content. Subsequent metal analyses were therefore limited to copper, lead and zinc.

Figure 5: Principal component analyses of a) normalised metal concentrations (Cd, Cr, Cu, Hg, Pb, and Zn concentrations expressed as mg/kg of the <500 μm sediment fraction); b) untransformed metal concentrations, and c) total DDT and total PAH concentrations (expressed as $\mu\text{g}/\text{kg}$ from the <500 μm sediment fraction). Point colours indicate site groups identified using k means partitioning.

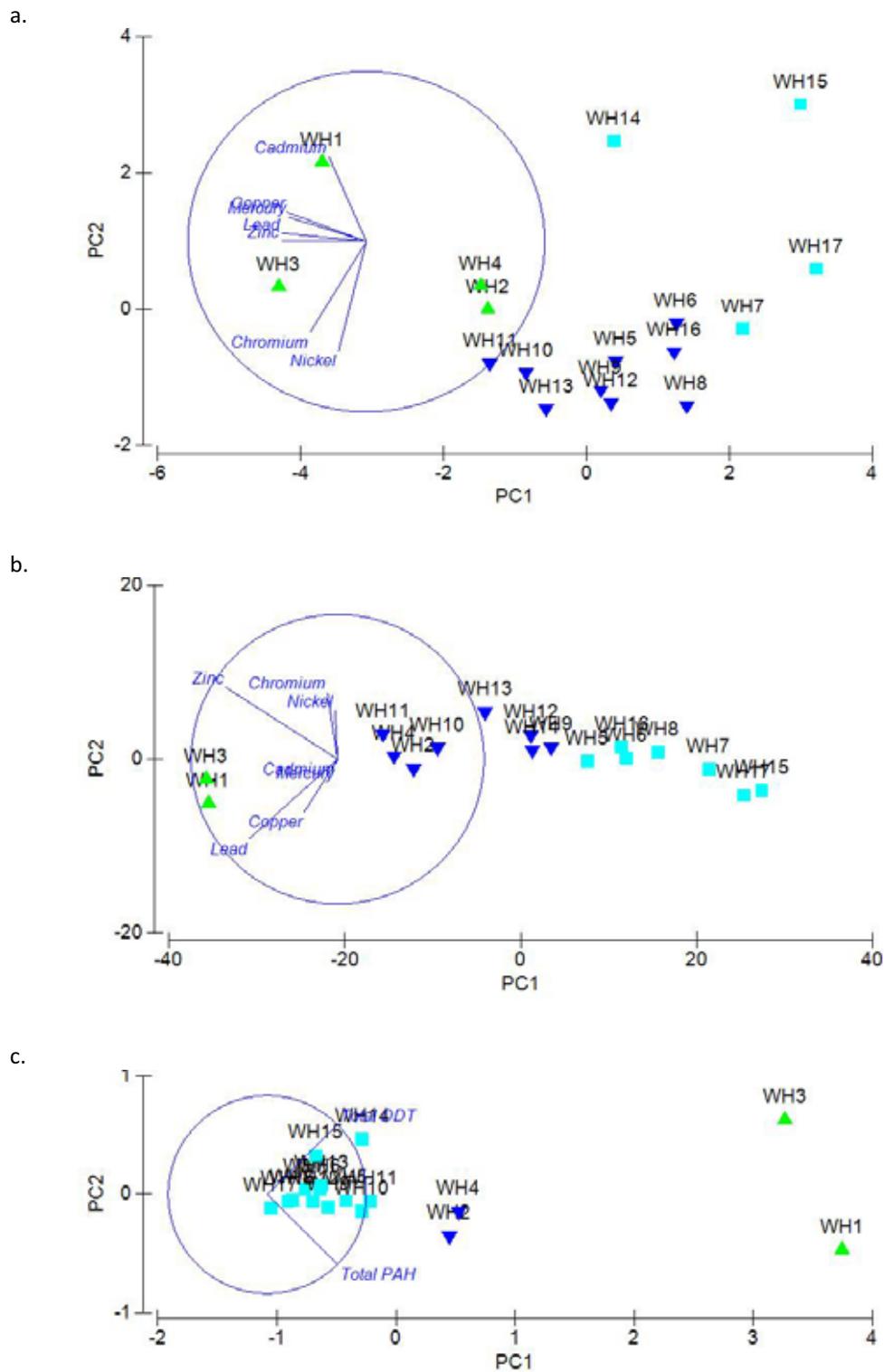


Figure 6: Relationship between mud content and a) copper, b) lead, and c) zinc concentrations, and total organic carbon content and d) copper, e) lead, and f) zinc concentrations.

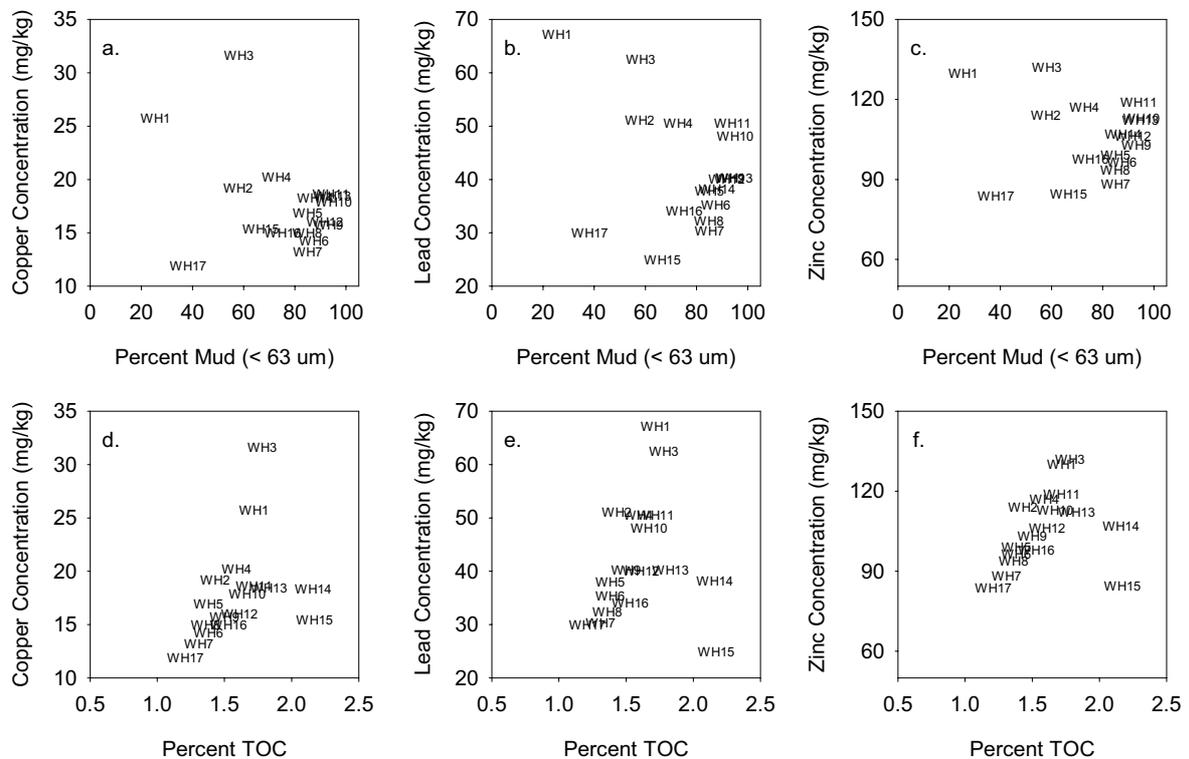


Table 4-1: Summary of results from least squares regression analyses examining the relationships between the mean proportion of mud and total organic carbon (TOC) contents (%), and axes obtained from principal component analyses of mean: normalised metal concentrations; untransformed metal concentrations; and, normalised organic contaminant concentrations. The metals included in the analysis were cadmium, chromium, copper, lead, mercury and zinc, while the organic contaminants were total sediment concentrations of total DDT and total PAH³. Statistically significant ($p < 0.05$) relationships are highlighted in red.

X Axis	Y Axis			r	r ²	p	N
	Transformation	Group	PCA Axis				
Mud	Normalised	Metals	Axis 1	0.228	0.052	0.380	17
Mud	Normalised	Metals	Axis 2	-0.576	0.332	0.016	17
Mud	None	Metals	Axis 1	-0.251	0.063	0.331	17
Mud	None	Metals	Axis 2	0.852	0.725	0.000	17
Mud	Normalised	Organics	Axis 1	0.644	0.415	0.005	17
TOC	Normalised	Metals	Axis 1	-0.231	0.053	0.372	17
TOC	Normalised	Metals	Axis 2	0.577	0.333	0.015	17
TOC	None	Metals	Axis 1	0.254	0.065	0.325	17
TOC	None	Metals	Axis 2	0.077	0.006	0.768	17
TOC	Normalised	Organics	Axis 1	-0.179	0.032	0.491	17

³ Total sediment concentrations were used in these analyses, rather than carbon normalised concentrations.

4.2.1 COPPER, LEAD AND ZINC

K-means partitioning and hierarchical clustering were used to group sites based on copper, lead and zinc concentrations. PCA plots of normalised copper, lead and zinc concentrations indicated that the site-groups identified using K-means partitioning or hierarchical clustering discriminated groups reasonably well (see Figure 7 for PCAs with k-mean groups displayed, and Figure 8 for the spatial distribution of K-means groups). However, the groups identified using K-means partitioning performed better in CAP “leave one out” analyses of allocation success. Consequently, CAP analyses based on PCA and K-means partitioning of normalised copper, lead and zinc concentrations are presented below.

An excellent fit was obtained from a CAP of benthic community data constrained by the primary axis of a PCA of normalised copper, lead and zinc concentrations, with $m = 15$ ($r^2 = 0.99$, Figure 9 a & c). Similarly, the CAP of benthic community data constrained by categorical groupings of sites based on K-means partitioning of normalised copper, lead and zinc concentrations, attained a high allocation success (82%). However, the high m value required to achieve these results suggested that the model might not provide an accurate representation of the relationship between community structure and copper, lead and zinc concentrations. The analyses were therefore checked by re-running the CAPs using $m = 5$ (see the methods section for the criteria used to select this m value). This reduced the proportion of total variance explained from 0.99 to 0.72, and led to decrease in allocation success to 65%⁴ (Figure 9 b & d). However, reasonable separation was still apparent among the site-groups when the CAP was constrained by the categorical groupings. The fit of the CAP constrained by the primary axis of the PCA of normalised copper lead and zinc concentrations was also affected by the reduction in m value, but it still remained reasonably good ($r^2 = 0.75$). Consequently, the checks carried out using a lower m value indicated that CAP provided a reasonable representation of the relationship between copper, lead and zinc concentrations, and benthic community structure.

Species differences between the three site-groups were then examined by running the PRIMER-E similarity percentages routine on the square root transformed total count data from each site, using Bray Curtis similarity. This analysis indicated that the differences between groups were due to variation in the abundance of multiple species, rather than large changes in the abundance of a single or few species. Sixty-one of the 103 species recorded in the survey explained 90% of the difference between the least contaminated and most contaminated groups of sites (as defined by K-means partitioning of normalised copper, lead and zinc concentrations). Plots of the mean abundance of the top 12 species responsible for the differences between groups one (most contaminated) and three (least contaminated), indicated that there was considerable variation in the distribution patterns of individual species (Figure 10). Together, these species explained 39% of the difference between group one and group three sites. A visual assessment of the plots showed that: six of the 12 species displayed declining trends in mean abundance as contamination increased (although individual differences between groups were not necessarily significant); five of the 12 species displayed increasing trends in mean abundance; and one species displayed an intermediate peak in mean abundance. In contrast, indices of species diversity (number of species; number of individuals; Pielou’s evenness and Shannon diversity) were relatively insensitive to the variation in copper, lead and zinc concentrations (Figure 11). Similarly, no significant relationship was detected between the primary PCA axis of normalised copper, lead and zinc concentrations and the number of rare species (Figure 12)⁵.

⁴ Note that this is still substantially better than 33% expected through random allocation.

⁵ In this context, rare species consisted of the 55 species that had total counts of < 10, when data from all 17 sites were pooled.

Figure 7: Principal component analyses of normalised copper, lead and zinc concentrations obtained using strong acid digestion of the <500 µm sediment fraction. Point colours indicate site groups identified using k means partitioning.

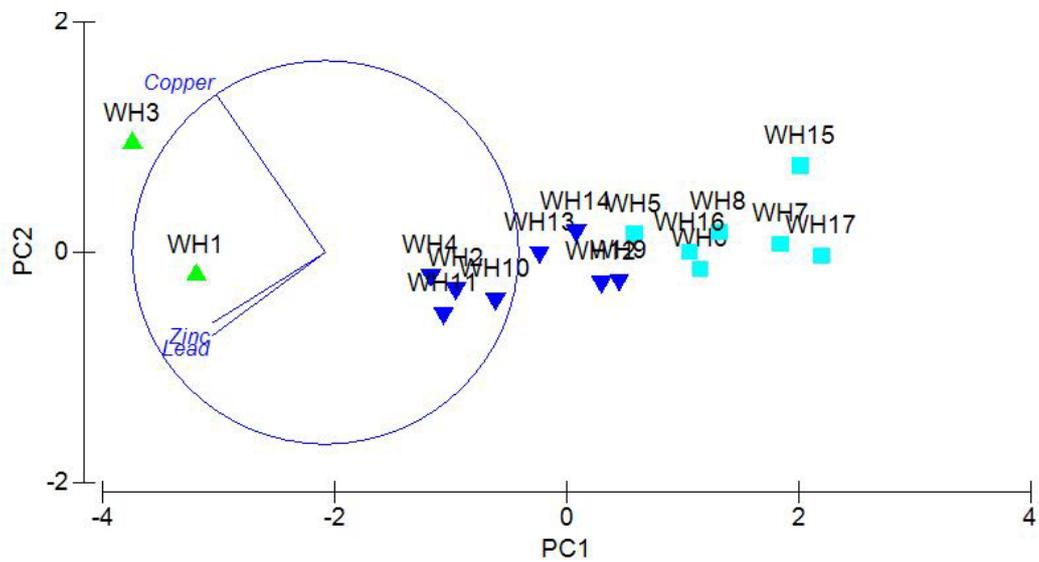


Figure 8: Site groupings identified with K-means partitioning of normalised copper, lead and zinc concentrations.

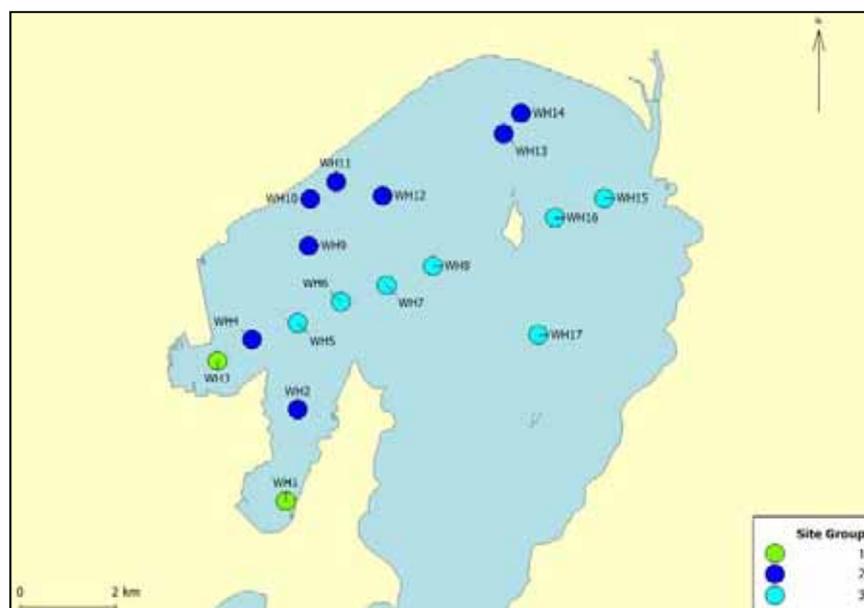


Figure 9: CAP plots with two values of m using benthic ecological data constrained by a) and b) categorical site groupings based on K-means partitioning of normalised copper lead and zinc concentrations, and c) and d) a quantitative index of copper, lead and zinc concentrations derived from the primary axis of a PCA analysis of those metals. Least squares regression ($\pm 95\%$ C.L.) lines are fitted to the latter plots.

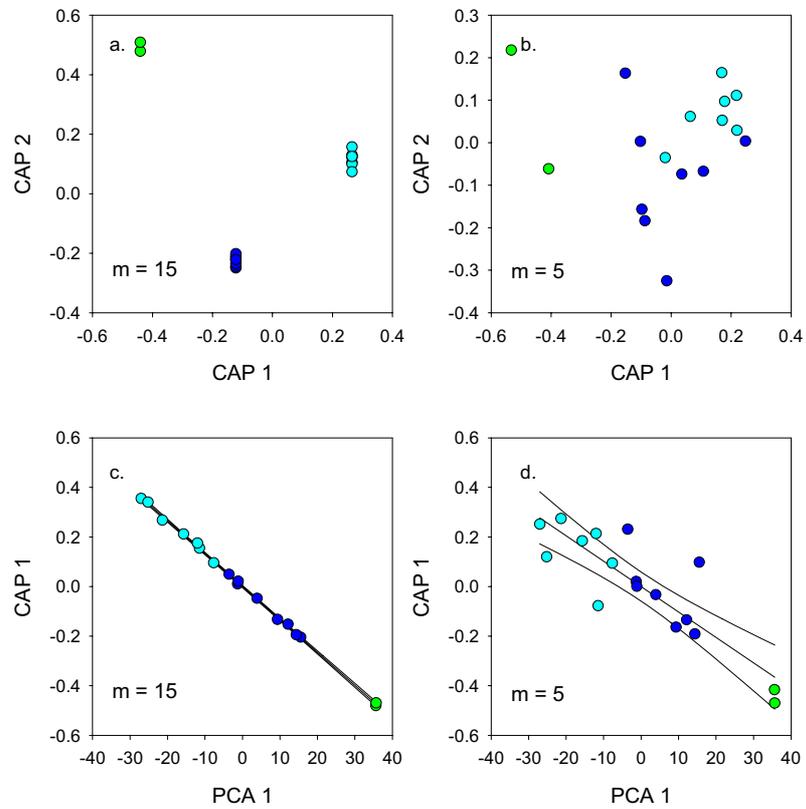


Figure 10: Mean (\pm 95% C.I.) abundance of taxa from sites that have been grouped based on K-means partitioning of normalised copper lead and zinc concentrations into sites with relatively low (L), medium and high (H) levels of contamination. The taxa are: a) Sipunculida sp.#1; b) *Theora lubrica*; c) Cirratulidae sp.#1; d) Paraonidae sp.#1; e) Tanaidacea sp.#1; f) Nematoda spp; g) *Nucula nitidula*; h) *Asychis* sp.#1; i) *Maldane theodori*; j) *Arthritica* sp.#1; k) *Cossura consimilis*; and l) *Nucula hartvigiana*. Site groups are (L) WH5, WH6, WH7, WH8, WH15, WH16, WH17; (M) WH2, WH4, WH9, WH10, WH11, WH12, WH13, WH14; and, (H) WH1, WH3.

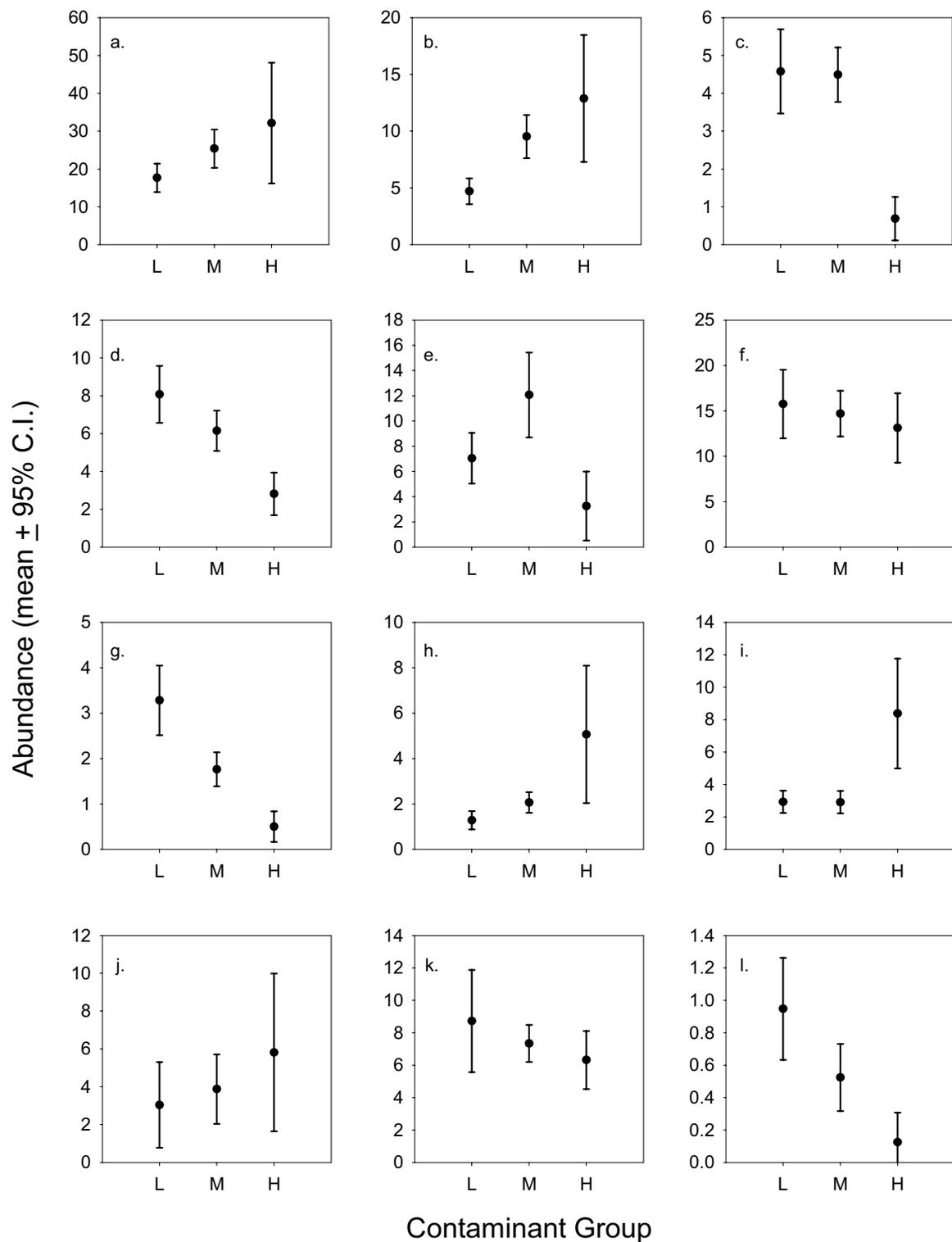


Figure 11: Mean (\pm 95% C.I.) a) number of species; b) number of individuals; c) Pielou's evenness values; and, d) Shannon diversity values for sites that have been grouped based on K-means partitioning of normalised copper, lead and zinc concentrations. Contaminant concentrations increase from groups 1 to 3.

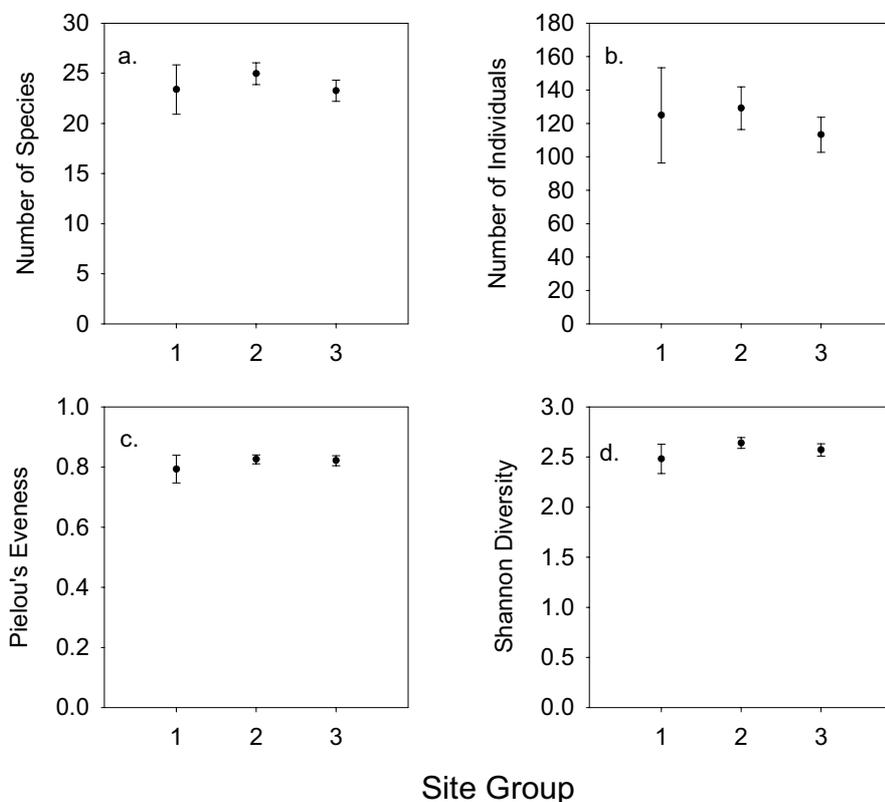
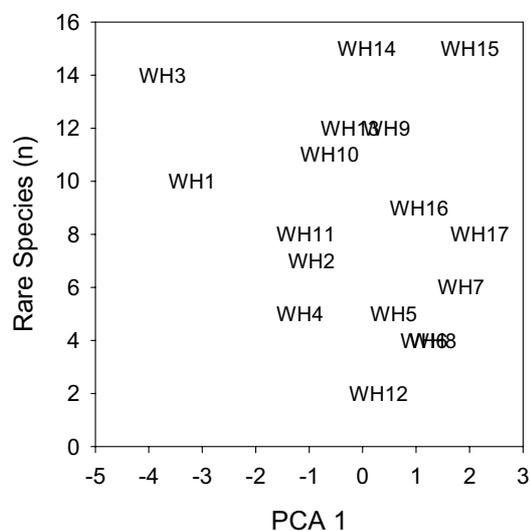


Figure 12: Relationship between the primary PCA axis of normalised copper, lead and zinc concentrations and the number of rare species. In this context, rare species consisted of 55 species that had total counts of < 10, when data from all 17 sites were pooled.



4.2.2 DDT AND PAH

The grouping of sites by K-means clustering of normalised total DDT and total PAH concentrations mirrored trends in the concentrations of these contaminants running from inner Lambton Harbour and Evans Bay to the central harbour (Figure 5c and Figure 13). Group one contained two sites (one in the inner part of Lambton Harbour and one in the inner part of Evans Bay); group two contained two sites (one in the outer part of Lambton Harbour and one in the outer part of Evans Bay); and, group three contained 13 sites that were all located in the central harbour. Total PAH and total DDT concentrations graded from moderately elevated in the upper reaches of Lambton Harbour and Evans Bay, to uniformly low in the central harbour (except for sites WH11 off Ngauranga and site WH14 off Petone, where total DDT levels were slightly elevated). Clear differences in the benthic communities were apparent in a CAP constrained by the three site groupings, with the overall model providing an 82% allocation success and explaining 72% of the overall variability with an m value of 5 (Figure 14 a). However, the relatively high allocation success was somewhat misleading, as it was heavily weighted toward sites in the central harbour, which constituted the bulk of stations. Neither of the two sites in the upper reaches of Lambton Harbour and Evans Bay was successfully allocated to group one, but both of the intermediate sites were successfully allocated to group two.

An excellent fit was obtained when the CAP was constrained by the primary axis of a PCA of normalised total DDT and total PAH concentrations based on the methods recommended for the non-arbitrary selection of m (Anderson and Willis 2003). However, the high m value obtained using this method ($m = 15$) meant that the model might not provide an accurate representation of the relationship between community structure, and total DDT and total PAH concentrations (Figure 14 b). The CAP was therefore checked by re-running the analysis using an m value of 5 (Figure 14 c). The fit of the revised model remained excellent ($r^2 = 0.83$), confirming that the data representation provided by CAP was relatively good.

Species differences between the three site-groups were then examined by running the PRIMER-E similarity percentages routine on the square root transformed total count data from each site, using Bray Curtis similarity. This analysis indicated that the differences between groups were due to variation in the abundance of multiple species, rather than large changes in the abundance of a single or few species. A variety of species responses were apparent in plots of the mean abundance of the 12 species that were most influential in producing the differences between groups one and three (Figure 15). A visual assessment of the plots indicated that:

- The mean abundance of four species decreased between groups one and three in a “linear” or “non-linear” fashion (*Sipunculida* sp.#1, *Theora lubrica*, *Maldane theodori*, *Asychis* sp.#1.);
- The mean abundance of four species increased from groups one to three in a “linear” or “non-linear” fashion (*Tanaidacea* sp.#1, *Paraonidae* sp.#1, *Cirratulidae* sp.#1, *Nucula nitidula*); and,
- Two species displayed a peak (*Nematoda* spp.) or a dip (*Cossura consimilis*) in mean abundance in the group 2 sites; and,
- Two species showed little discernable response (*Phoxocephalidae* sp.#1, *Arthritica* sp.#1).

(Note that: differences between groups were not necessarily significant; and, while it is useful to describe trends in species abundance as “linear” or “non-linear”, the site-groups are categorical variables so this description is not a statistically valid one).

As with metals, indices of species diversity (number of species; number of individuals; Pielou’s evenness and Shannon diversity) were relatively insensitive to the variation in total DDT and total PAH concentrations among the site-groups (Figure 16).

Figure 13: Site groupings identified with K-means partitioning of total DDT and total PAH concentrations. Dot colour indicates site group, while dot size varies in relation to total PAH concentrations. Contaminant concentrations increase from groups 1 to 3.



Figure 14: CAP plots with the models constrained by: a) categorical site groupings based on K-means partitioning of normalised total DDT and total PAH concentrations; and, the primary axis of a PCA analysis of normalised total DDT and total PAH concentrations with CAP "m" values of b) 15 and c) 5. Least squares regression ($\pm 95\%$ C.L.) lines are fitted to the latter plots.

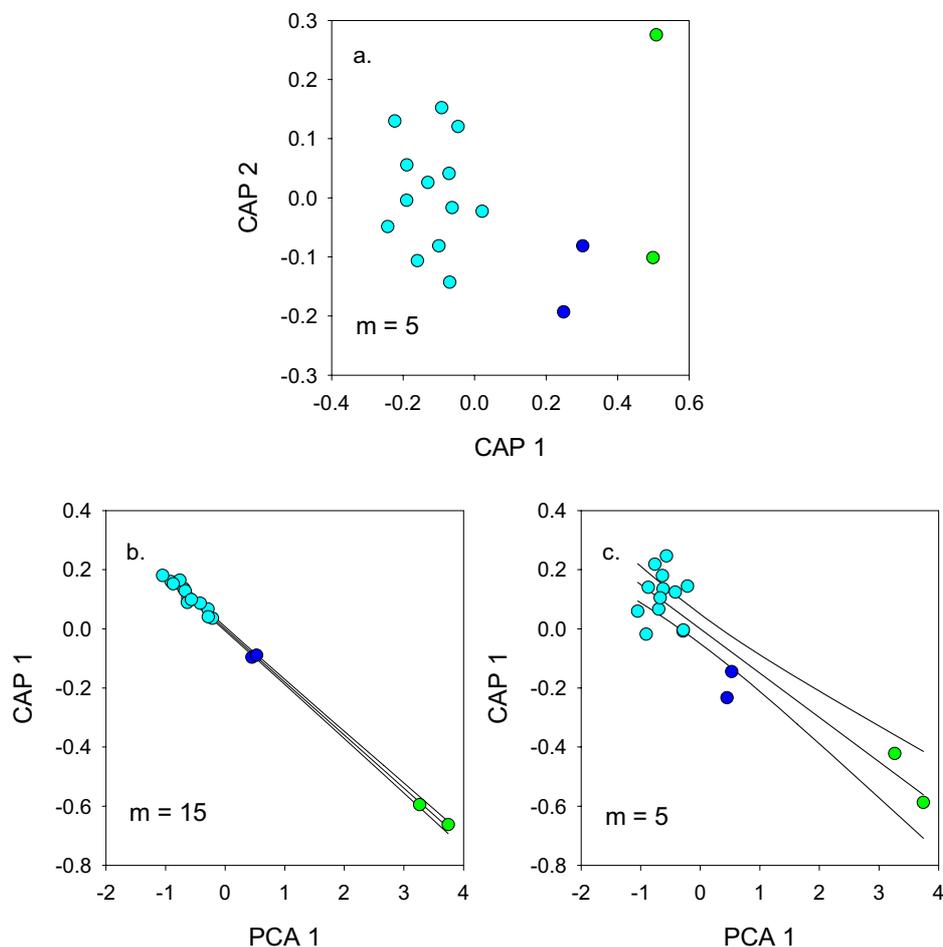


Figure 15: Mean (\pm 95% C.I.) abundance of taxa from sites that have been grouped based on K-means partitioning of normalised total DDT and total PAH concentrations into sites with relatively low (L), medium and high (H) levels of contamination. The taxa are: a) Sipunculida sp.#1; b) Tanaidacea sp.#1; c) Cirratulidae sp.#1; d) Maldane theodori; e) Theora lubrica; f) Paraonidae sp.#1; g) Arthritica sp.#1; h) Nematoda spp.; i) Asychis sp.#1; j) Nucula nitidula; k) Cossura consimilis; l) Phoxocephalidae. Site groups are (L) WH5, WH6, WH7, WH8, WH9, WH10, WH11, WH12, WH13, WH14; WH15, WH16, and WH17, (M) WH2, WH4; and, (H) WH1, WH3.

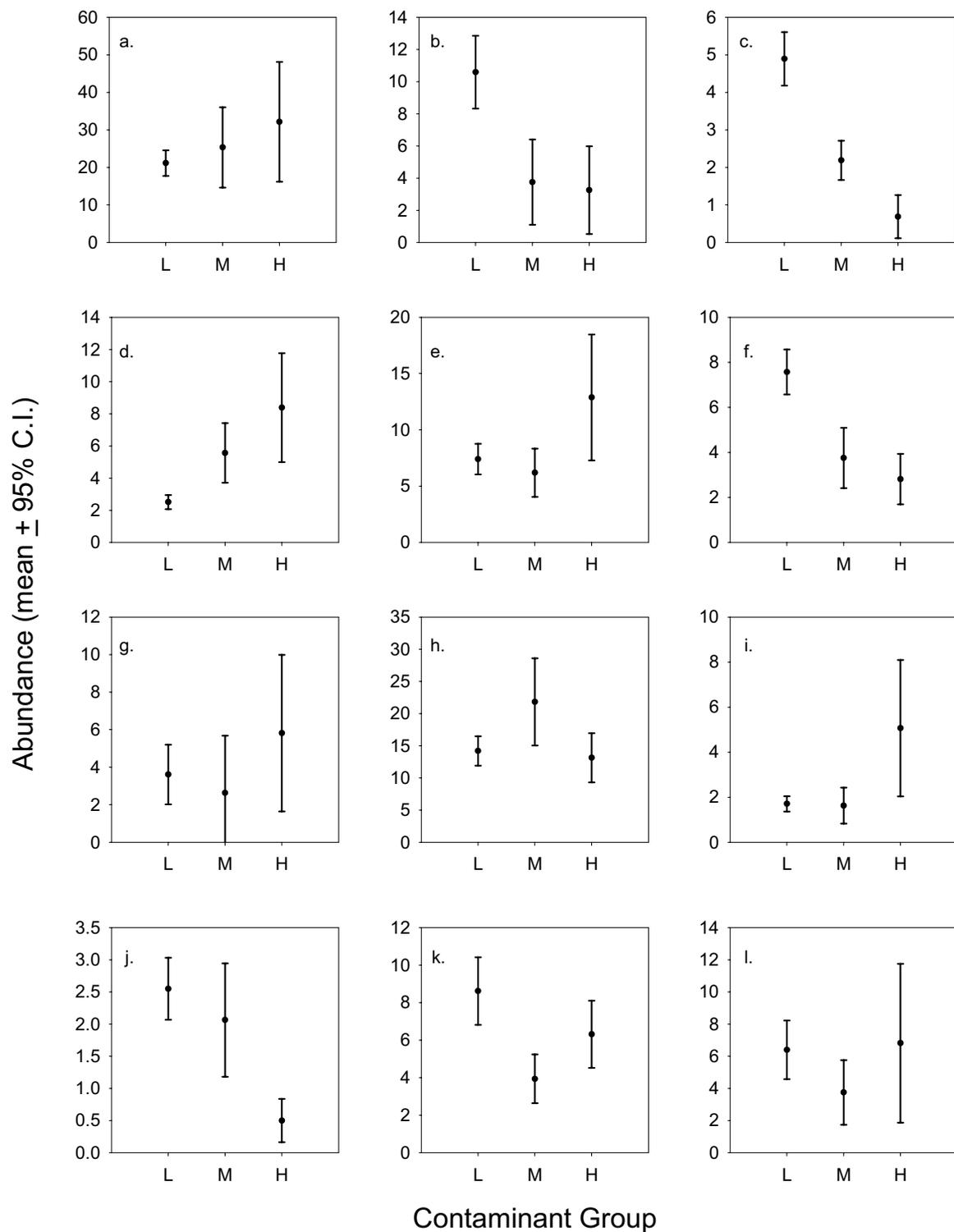
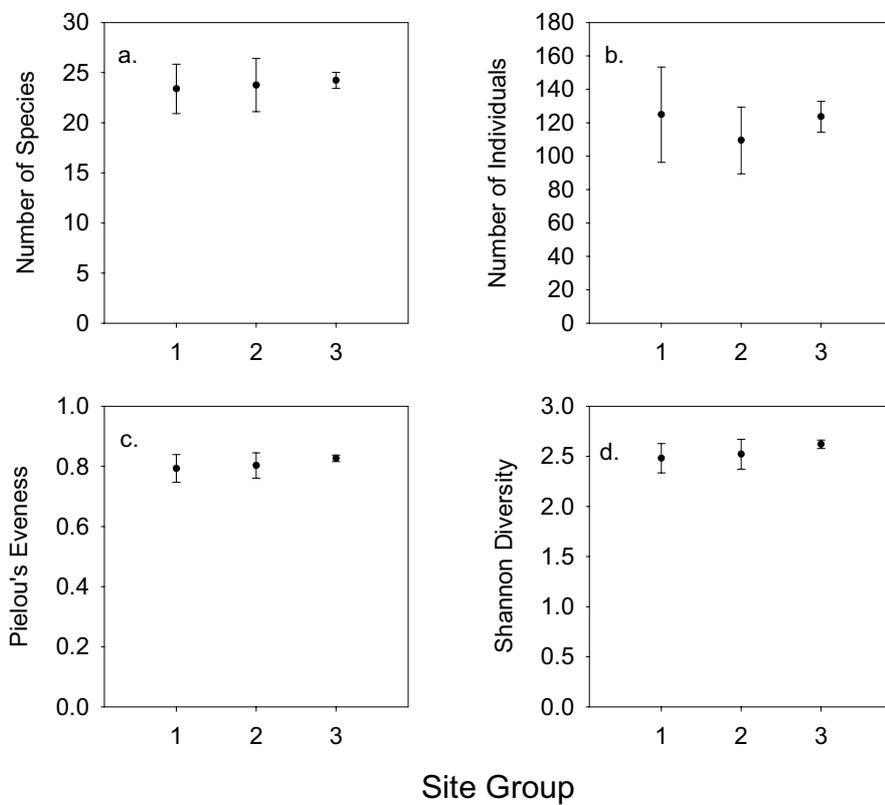


Figure 16: Mean (\pm 95% C.I.) a) number of species; b) number of individuals; c) Pielou's evenness values; and, d) Shannon diversity values for sites that have been grouped based on K-means partitioning of normalised sediment concentrations of total DDT and total PAH.



5 DISCUSSION

Matching ecological and contaminant monitoring data from Wellington Harbour suggests that in 2006, stormwater contamination was affecting benthic communities in the harbour. Sediment concentrations of copper, lead and zinc, declined with offshore distance from the major stormwater sources, while total DDT and total PAH concentrations were elevated at individual sites in Lambton Harbour and Evans Bay. The number of individuals in ecological samples showed a similar trend to copper lead and zinc concentrations, i.e. declining with distance from major stormwater sources. Conversely, Pielou's evenness increased with distance, due to individuals becoming more evenly spread among species (i.e. communities at remote sites were less dominated by one or more species).

Significant trends of higher abundance and lower evenness (i.e. greater dominance by one or more species) at sites closer to metal contaminant sources in Wellington Harbour are consistent with an intermediately disturbed system according to the model of faunal succession developed by Pearson and Rosenberg (1978). This model suggests that highly disturbed systems are generally dominated by small species that occur in low numbers. As the magnitude of disturbance decreases, or distance from the disturbance increases, the number of organisms will increase to a peak, and the benthic assemblage will become dominated by a few, highly abundant, opportunistic (r-selected) species. Further reductions in the level of disturbance, or increasing distance from the disturbance leads to an increase in both the number of species present within the community (species richness) and the relative abundance of individuals among species (evenness). At the same time there is a decline in the overall faunal abundance. Ultimately, mature benthic communities in undisturbed systems are theoretically dominated by low numbers of large, deep-dwelling, equilibrium (K-selected) species that have a long lifespan and low fecundity.

The composition of benthic communities in Wellington Harbour also varied in relation to sediment concentrations of copper, lead, zinc, DDT and PAH. However, the relationship between community structure and DDT and PAH concentrations was potentially confounded by co-variation in sediment-mud content. Elevated mercury concentrations may have also affected benthic communities, but the influence of this metal was also confounded by co-variation in sediment-mud content. In contrast, spatial variation in copper, lead and zinc was not related to sediment-mud or organic carbon contents. This allowed the effects of copper, lead and zinc to be analysed independently of mud and organic carbon. Community level responses to copper, lead and zinc concentrations at subtidal sites in Wellington Harbour were generally consistent with those reported for intertidal benthic communities in Auckland (Hewitt et al. 2009), except that the number of rare species did not decrease as contamination increased. Responses varied from species to species, with some species increasing in abundance along the contaminant gradient (e.g. Sipunculida sp.#1 and *Theora lubrica*) and others declining (e.g. Cirratulidae sp.#1 and Paraonidae sp.#1) or displaying peaks at intermediate levels of contamination.

Hewitt *et al.* (2009) found that the onset of ecological effects in intertidal communities occurred at relatively low copper, lead and zinc concentrations. They went on to derive alternative sediment quality guidelines for copper, lead and zinc using species-sensitivity distributions. These guidelines were based on the concentrations where statistical modelling predicted that a 50 % decrease in abundance of 5 % of the taxa occurred. Guideline values ranged from 6.5 - 9.3 mg/kg for copper, 18.8 - 19.4 mg/kg for lead, and 114 - 118 mg/kg for zinc. The derived copper and lead values were notable because they were between 35 - 50%, and 61 - 64% of their respective threshold effects levels (TEL) (MacDonald *et al.* 1996). In Wellington Harbour, the 2006 concentrations of mercury exceeded TEL sediment quality guideline values at all 17 monitoring sites, lead exceeded TEL values at 13 sites, copper at four sites and zinc at two sites (copper and zinc exceedances were in Lambton Harbour and Evans Bay). In contrast, all sites exceeded the copper and lead guideline values of Hewitt et al (2009) and two to five sites exceeded the zinc guideline values (depending on which value was used).

The effects of metal and organic contaminants can be modified by other environmental stressors. Thrush *et al.* (2008) used regression models to examine interactions between copper, lead and zinc concentrations, and mud and organic content on intertidal macrofauna⁶. They found that changes in the abundance of most taxa were predicted by two or three stressors. Taxa responding to metals generally displayed a stronger correlation to one particular metal, with copper tending to be more influential than lead or zinc. However, in some cases more than one metal was important. The effects of copper, lead and zinc tended to be stronger at sites with higher levels of mud or organic carbon. Only one taxon showed a different response. The effect of copper on the abundance of Nereidae was lower at sites with low mud content, indicating that for Nereids, low mud concentrations are a stressor. The results of Thrush *et al.* (2008) therefore suggest that the effects of metal contamination in Wellington Harbour could be exacerbated by the high mud content of sediments in the harbour.

5.1 CONCLUSIONS

The analysis of matching benthic ecology and sediment chemistry data from Wellington Harbour suggests that the composition of subtidal macrofaunal communities is influenced by elevated concentrations of the stormwater contaminants copper, lead and zinc. Other stormwater contaminants such as mercury, PAH and DDT may also affect benthic communities within the harbour, but the effects of these contaminants were not separated from those of other environmental variables such as the mud and organic carbon content of sediments.

⁶An additive effect was one where the effects of two or more stressors added together to produce a larger total effect. A multiplicative effect is one where the effects of two or more stressors multiply to produce a much larger total effect. Effects were further interpreted as being synergistic or antagonistic based on whether they increased or decreased the effect of the main contaminant.

6 REFERENCES

- Anderson M.J., Hewitt J., Thrush S. (2002) The development of criteria for assessing community health of urban intertidal flats. ARC Technical Publication TP184, Auckland Regional Council, Auckland
- Anderson M.J., Hewitt J.E., Ford R.B., Thrush S.F. (2006) Regional models of benthic ecosystem health: predicting pollution gradients from biological data TP317, Auckland Regional Council, Auckland
- Anderson M.J., Willis T.J. (2003) Canonical analysis of principal coordinates: a useful method of constrained ordination for ecology. *Ecology* 84:511-525
- Hewitt J.E., Anderson M.J., Hickey C.W., Kelly S., Thrush S.F. (2009) Enhancing the ecological significance of sediment contamination guidelines through integration with community analysis. *Environmental Science and Technology* 43:2118-2123
- MacDonald D.D., Carr R.S., Calder F.D., Long E.R., Ingersoll C.G. (1996) Development and evaluation of sediment quality guidelines for Florida coastal waters. *Ecotoxicology* 5:253-278
- Pearson T.H., Rosenberg R. (1978) Macrobenthic succession in relation to organic enrichment and pollution of the marine environment. *Oceanography and Marine Biology Annual Review* 16:229-311
- Stephenson G., Milne J.R., Sorensen P. (2008) Wellington Harbour marine sediment quality investigation, Greater Wellington Regional Council, Wellington
- Thrush S.F., Hewitt J.E., Hickey C.W., Kelly S. (2008) Seeking generality in the response of species abundances to multiple stressors. *Journal of Experimental Marine Biology and Ecology* 366:160-168

Appendix 3:

Report on PAHs and marker compounds in marine sediments from Wellington Harbour (Olsen & Guyader 2009)

Appendix 4:

Report on potential sources of PAHs in Wellington Harbour sediments (Deprea 2010)

Appendix 5: Tabulated organochlorine pesticide data for sites WH1–WH4

Organochlorine pesticide concentrations ($\mu\text{g}/\text{kg}$ dry weight) in replicate composite sediment samples collected at sites WH1–WH4 in late 2006 and analysed by NIWA in 2009 (Olsen 2010). Concentrations determined through analysis of Standard Reference Material (SRM) are also included.

NIWA Lab Code	OA123/1	OA123/2	OA123/3	OA123/6	OA123/7	OA123/8	OA123/11	OA123/12	OA123/13	OA123/14	OA123/15	OA123/16	OA123/17	OA123/18	SRM1941a	SRM1941a
GWRC Site/Replicate Code	WH1/1	WH1/2	WH1/3	WH2/1	WH2/2	WH2/3	WH3/1	WH3/2	WH3/3	WH3/4	WH3/5	WH4/1	WH4/2	WH4/3	Cert	2009
DDTs																
2,4'-DDE	0.1	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.7	0.7
4,4'-DDE	2.1	2.1	2.6	0.8	0.9	0.8	1.1	1.2	1.2	1.1	1.1	1.0	0.9	0.9	6.6	6.6
2,4'-DDD	0.3	0.5	0.5	< 0.2	< 0.2	0.2	0.4	0.7	0.7	0.6	0.6	0.2	< 0.2	< 0.2	< 0.1	
4,4'-DDD	1.8	2.2	1.8	1.3	0.9	0.9	2.5	3.4	3.6	2.1	2.0	1.3	1.3	1.2	5.1	5.1
2,4'-DDT	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.3	0.3	0.4	0.2	0.2	< 0.1	< 0.1	< 0.1	< 0.1	
4,4'-DDT	0.9	0.6	0.8	0.4	0.3	0.3	7.2	13.6	9.2	1.5	1.2	1.0	0.7	0.6	1.2	1.3
Total DDT (< D.L. = 0)	5.2	5.5	5.8	2.5	2.1	2.2	11	19	15	5.4	5.1	3.5	2.8	2.7	13.5	13.6
Total DDT (< D.L. = 0.5 x D.L.)	5.3	5.6	5.9	2.7	2.3	2.3	11.6	19.3	15.2	5.6	5.2	3.6	3.0	2.9		
Chlordanes																
Heptachlor	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	
Heptachlor epox	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
trans-chlordane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	3.1	
cis-chlordane	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	2.2	2.3
trans-nonachlor	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	1.1	1.3
cis-nonachlor	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	1.2	
Other OCPs																
Hexachlorobenzene	0.11	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.65	1.21	0.29	0.66	0.29	< 0.1	< 0.1	< 0.1	68.4	70.0
Lindane	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.1
Dieldrin	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	1.6	1.3

Water, air, earth and energy – elements in Greater Wellington's logo that combine to create and sustain life. Greater Wellington promotes **Quality for Life** by ensuring our environment is protected while meeting the economic, cultural and social needs of the community

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