Stormwater contaminants in urban streams in the Wellington region

Quality for Life

greater WELLINGTON REGIONAL COUNCIL | Environment

greater WELLINGTON
REGIONAL COUNCIL

Stormwater contaminants in urban streams in the Wellington region

J R Milne and L Watts

Environmental Monitoring and Investigations Department

FOR MORE INFORMATION, CONTACT GREATER WELLINGTON:

Wellington
PO Box 11646

T 04 384 5708
F 04 385 6960
www.gw.govt.nz

GW/EMI-T-08/82

June 2008

www.gw.govt.nz
info@gw.govt.nz

Executive summary

Two investigations have been carried out into stormwater-derived chemical contaminants in selected urban streams across the Wellington region. The first investigation was a screening exercise to assess the level of contamination present in urban stream sediments. The second investigation measured heavy metal contaminants in the wet-weather flow of several urban streams.

The results of the two investigations indicate that significant contamination of urban streams arises as a result of stormwater runoff. Elevated concentrations of one or more contaminants were found in surface sediments of nearly all the streambed sites sampled, and in all stream water samples collected during runoff events.

Zinc and, to a lesser extent, lead were the most common metals present in streambed sediments at concentrations exceeding ANZECC (2000) Interim Sediment Quality Guidelines (ISQG). Concentrations of total high molecular weight polycyclic aromatic hydrocarbons (PAHs) and total PAHs also exceeded guideline values at some sites, and almost all of the 29 sites sampled in 2005 and 24 sites sampled in 2006 recorded concentrations of total DDT above guideline values. Contaminant concentrations in sediment samples from several streams exceeded ISQG–High trigger values, indicating probable adverse effects on benthic biota.

Copper and zinc were the most commonly detected heavy metals in stream waters during both 'base flow' and runoff sampling events. Dissolved concentrations of both metals were consistently above ANZECC (2000) toxicity trigger values in runoff samples, with dissolved concentrations of one or both of these metals also above the toxicity trigger values in 'base flow' samples from Porirua, Kaiwharawhara, Ngauranga and Opahu streams. This suggests that dissolved copper and/or zinc concentrations in these streams frequently exceed chronic toxicity criteria for aquatic life.

Dissolved copper and zinc concentrations also exceeded their respective USEPA (2006) Criteria Maximum Concentrations in around half of the stream water samples collected during runoff events, indicating the likelihood of acute toxicity effects on stream life. Most of the runoff events sampled were not significant from a hydrological perspective, suggesting even greater contaminant concentrations and loads are possible in higher magnitude events, particularly if rainfall is preceded by a prolonged period of fine weather.

The bulk of the contaminant load was found to be associated with suspended sediments, so a further (and possibly greater) risk the contaminants pose to aquatic ecosystems is to the benthic biota in depositional coastal environments. In most cases the streambeds sampled contained little fine sediment (i.e., silts and clays), indicating that much of this material – and its associated contaminant load – is not retained in the streams, but is rapidly flushed through the system and into downstream receiving environments such as Porirua and Wellington harbours.

Recommendations are made relating to the design of any future sediment streambed surveys and wet-weather stream flow contaminant investigations. Also recommended are that monitoring of dissolved heavy metals continues at urban sites in Greater Wellington's Rivers State of Environment Monitoring Programme, and that the existing Porirua and Wellington Harbour subtidal sediment quality monitoring programmes continue.

Contents

1. Introduction

Since 2001, the Greater Wellington Regional Council (Greater Wellington) has been investigating the effects of stormwater discharges from urban areas on aquatic receiving environments (e.g., Cameron 2001, KML 2005, Stephenson & Mills 2006, Stephenson et al. 2008). These investigations have shown that stormwater entering various urban streams and the coastal environment contains a wide range of persistent contaminants, including heavy metals, polycyclic aromatic hydrocarbons and organochlorine pesticides. Some of these contaminants may be having, or through long-term accumulation could eventually have, significant adverse effects on some freshwater and coastal aquatic ecosystems.

This report documents the results of two separate investigations into stormwater-derived chemical contaminants in selected urban streams across the Wellington region. The first investigation, conducted during 2005 and 2006, was a screening exercise that assessed the level of contamination present in urban stream sediments. The second investigation, carried out intermittently from 2005 until 2007, focused on heavy metal contaminants in the wet-weather flow of several urban streams. The primary objectives of these investigations were:

1. to determine if stormwater discharges are causing significant contamination of water and sediments within urban streams in the Wellington region; and

2. to assess if the degree of contamination poses a risk to aquatic ecosystems.

The two investigations are presented and discussed separately in Sections 2 and 3 of this report. Conclusions and recommendations relating to both investigations are presented in Section 4.

2. Contaminants in streambed sediments

2.1 Introduction

Streambed sediments provide a possible 'sink' for stormwater-derived contaminants. In 2005 and 2006 streambed sediment samples were collected from urban streams across the Wellington region to determine the concentrations selected contaminants had reached and if these concentrations were sufficiently high to pose a risk to stream life. Determination of streambed contaminant concentrations also enables an estimation of the contaminant load stored in the system that may be re-mobilised and deposited in the marine environment in the future.

2.2 Sampling sites

Streambed sediments at 29 sites across 22 urban streams were sampled over 17–18 May 2005 (Figure 2.1, Appendix 1). The streams sampled receive stormwater from either industrial or residential sources, or a combination of both. There are either operative or closed landfills in the catchments of several of the streams (e.g., Owhiro, Kaiwharawhara and Mitchell Streams). On 2 June 2006, streambed sediments at 16 of these 29 sites were sampled again, while streambed sediments at a further eight sites on six streams were sampled for the first time (Figure 2.1, Appendix 1).

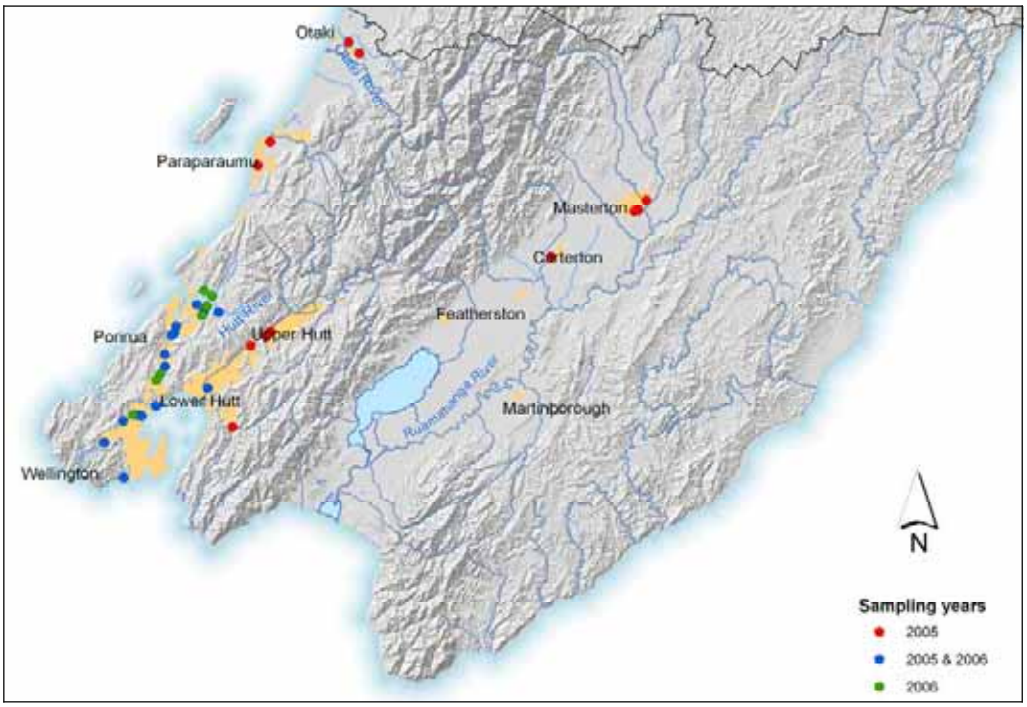

Figure 2.1: Sites where streambed sediments were sampled in May 2005 and/or June 2006

The majority of the new sites sampled in 2006 were located in peri-urban catchments that drain to the Pauatahanui Arm of Porirua Harbour. Samples from these sites were collected primarily to improve our understanding of stream contaminant inputs to this arm, especially DDT, which is present at elevated concentrations in the subtidal sediments (Stephenson & Mills 2006).

Coordinates for all sampling locations were recorded in the field using a global positioning system (GPS). Site photographs were taken for future reference.

2.3 Methods

2.3.1 Sample collection

One composite sample comprising multiple grabs of sediment was collected at each site using a plastic scoop to remove the top 10-20 mm of streambed sediment (Figure 2.2). Approximately one kilogram of sediment was collected, with sampling targeting the finer sediments present at each site because stormwater contaminants are most commonly associated with these sediments (e.g., Ray et al. 2003). The bulk sample was mixed thoroughly and representative sub-samples taken and transferred to appropriate sample bottles for metal or organic analysis. Samples were chilled and dispatched to Hill Laboratories for analysis.

Figure 2.2: Sampling in the Kuripuni Stream, 18 May 2005

2.3.2 Sample analysis

Details of the laboratory analytical methods are provided in Appendix 2. Each sediment sample was analysed for the following[1]:

- Particle size distribution – the relative proportions of gravel (>2 mm), sand (63 μm – 2 mm) and mud (<63 μm);
- Total organic carbon (TOC);
- Total recoverable antimony, arsenic, cadmium, chromium, copper, mercury, nickel, lead, silver and zinc;
- 16 USEPA priority polycyclic aromatic hydrocarbons (PAHs); and
- Organochlorine pesticides (OCPs), including DDT, lindane and dieldrin.

Both particle size and TOC were included in the analyses to assist with characterisation of the streambed and interpretation of the contaminant data. As noted in subsection 2.3.4, the TOC content is also needed when comparing organic contaminant concentrations against sediment quality guidelines.

A Quality Control (QC) report was requested for the two sets of sediment sample analyses. Each report provided data from standard analytical QC checks, including analysis of procedural blanks, duplicates, spiked duplicates, routine repeats and certified reference materials. Surrogate recovery data for PAH and OCP analyses were also included in each report.

2.3.3 Sample limitations

Because the investigation was designed as a 'screening exercise', with only a single composite streambed sediment sample taken from each site, it is not possible to assess within-site spatial variability. For this reason, comparisons between sites and between collection years (i.e., 2005 vs 2006) should be made with caution.

2.3.4 Data analysis

(a) Guidelines

The results of the analyses were compared against the Australian and New Zealand Environment and Conservation Council (ANZECC 2000) Interim Sediment Quality Guidelines (ISQG) to assess the potential ecological effects of contaminants in the streambed sediments. These guidelines are generally considered to be reasonably robust, and conservative (i.e., they err on the side of environmental protection). They are not 'pass' or 'fail' numbers, and the developers of the guidelines emphasise that they are best used as one part of a 'weight of evidence' approach to evaluating potential effects of contaminants on benthic biota.

[1] Analyses were carried out on the sub-2mm sediment fraction – the exception was PAHs where the laboratory analysed the samples on an "as received" basis.

The ANZECC (2000) sediment quality guidelines provide two sets of trigger values (concentrations), low and high (Table 2.1). ANZECC ISQG-Low trigger values are nominally indicative of the contaminant concentrations where the onset of biological effects could possibly occur. These values provide an early warning, enabling management intervention to prevent or minimise adverse environmental effects. ANZECC ISQG-High trigger values are nominally indicative of the contaminant concentrations where significant biological effects are expected. Exceedance of these values therefore indicates that adverse environmental effects are probably already occurring, and management intervention may be required to remediate the problem.

Table 2.1: ANZECC (2000) interim sediment quality guidelines for selected contaminants

Contaminant	ANZECC trigger values	
	ISQG-Low	ISQG-High
Metals (mg/kg dry wt):		
Arsenic[1]	20	70
Cadmium	1.5	10
Chromium	80	370
Copper	65	270
Lead	50	220
Mercury	0.15	1
Nickel	21	52
Zinc	200	410
Polycyclic Aromatic Hydrocarbons (µg/kg dry wt):[2]		
Naphthalene	160	2,100
Acenaphthalene	44	640
Acenaphthene	16	500
Fluorene	19	540
Phenanthrene	240	1500
Anthracene	85	1,100
Low Molecular Weight PAHs[3]	552	3,160
Fluoranthene	600	5,100
Pyrene	665	2,600
Benzo[a]anthracene	261	1,600
Chrysene	384	2,800
Benzo[a]pyrene	430	1,600
Dibenzo[a,h]anthracene	63	260
High Molecular Weight PAHs[4]	1,700	9,600
Total PAHs	4,000	45,000
Organochlorines (µg/kg dry wt):[2]		
Dieldrin	0.02	8
Endrin	0.02	8
4,4'-DDE	2.2	27
2,4'-DDD + 4,4'-DDD	2	20
Total DDT[5]	1.6	46

[1] Arsenic is, strictly speaking, a metalloid (ANZECC 2000).

[2] Normalised to 1% total organic carbon.

[3] Low Molecular Weight PAHs are the sum of the concentrations of naphthalene, 2-methyl-naphthalene, acenaphthalene, acenaphthene, fluorene, phenanthrene and anthracene.

[4] High Molecular Weight PAHs are the sum of the concentrations of fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[a]pyrene and dibenzo[a,h]anthracene.

[5] Total DDT 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.

(b) Data adjustment

For the purpose of calculating Total PAHs, Total Low Molecular Weight (LWM) PAHs, Total High Molecular Weight (HMW) PAHs and Total DDT, any individual compounds reported at a concentration less than the laboratory detection limit were replaced by a value one half of the detection limit (e.g., a value of <2 became 1). The exception was where all individual compounds were below the level of detection; in these instances the total concentration has been reported as being below detection.

For comparison of the sediment concentrations of organic contaminants against the ANZECC (2000) guidelines, the concentrations were normalised to a TOC content of 1%. The exception was where any organic contaminant concentration was below the level of detection; in these instances no comparison with the guidelines was deemed necessary.

2.4 Results

Selected analytical results are summarised in this section. Additional results, including a summary of the QC results, are provided in Appendix 3.

2.4.1 Particle size and total organic carbon

Particle size analysis was limited to three classes: gravel (>2 mm), sand (63 µm–2 mm) and mud (<63 µm). The majority of the streambed sediment samples comprised predominantly gravel and sand (Table 2.1). Mud was only present in significant quantities (>10%) in nine of the 29 samples collected in 2005 and six of the 24 samples collected in 2006. In many streams, the streambed comprised mainly cobbles and fine gravels, making it difficult to find any suitable sediment to sample.

The TOC contents of the streambed sediment samples ranged from 0.22 to 6.88%. Sediments at 20 (69%) of the 29 sites sampled in 2005 and 20 (83%) of the 24 sites sampled in 2006 recorded a TOC content of less than 1%. The median TOC content across all 53 sediment samples was 0.7%. The samples with the highest TOC contents were from the Mawaihakona Stream in Upper Hutt (6.88%), Mangapouri Stream in Otaki (6.52% at Anzac Road and 6.74% at County Lane), Duck Creek in Porirua (5.94% upstream of the Whitby Lakes) and Kuripuni and Opaki streams in Masterton (6.15% and 5.36% respectively). In contrast with the other sites sampled, the samples from these six sites all contained a significant proportion of mud (12.9% to 66%), highlighting that TOC content tends to increase with the proportion of mud present (Figure 2.3).

Table 2.1: Percentage of mud, sand and gravel, and TOC contents of streambed sediment samples collected in May 2005 and June 2006

Site No.	Site Name	Particle size classes (%)						TOC (%)	
		2005			2006				
		<63 µm	63µm – 2 mm	>2 mm	<63 µm	63µm – 2 mm	>2 mm	2005	2006
SMS001	Karori S @ Makara Peak	<0.01	36.8	63.2	13.1	46.0	40.9	0.56	0.54
SMS002	Kaiwharawhara S @ Otari Bush	1.0	53.9	45.1	2.62	36.4	61.0	0.59	0.75
SMS003	Kaiwharawhara S @ Ngaio Gorge	5.3	89.8	4.8	9.51	72.5	18.0	0.90	0.75
SMS004	Kaiwharawhara S @ School Rd	0.2	9.4	90.4	29.2	24.6	46.1	0.30	0.72
SMS005	Owhiro S @ Owhiro Bay	0.9	25.9	73.2	2.83	63.0	34.2	0.37	0.34
SMS006	Ngauranga S @ Bottom of Gorge	<0.01	25.8	74.2	1.66	54.4	44.0	0.37	0.53
SMS007	Porirua S @ Redwood Stn	4.1	45.2	50.7	0.62	35.3	64.1	0.33	0.32
SMS008	Porirua S @ Glenside	1.7	31.8	66.5	6.95	79.3	13.8	0.41	0.40
SMS009	Porirua S @ Kenepuru playing field	2.1	41.4	56.5	1.67	40.4	57.9	0.34	0.46
SMS010	Mitchell S d/s of Kenepuru Dr	5.7	72.3	22.0	2.18	36.5	61.4	0.22	0.86
SMS011	Kenepuru S u/s SH 1	<0.01	64.6	35.4	12.9	80.9	6.18	0.42	0.57
SMS012	Pauatahanui S @ SH 58	<0.01	51.4	48.6	1.84	52.4	45.8	0.27	0.31
SMS013	Browns S @ Browns Bay Res.	<0.01	34.5	65.5	3.43	49.8	46.7	1.03	0.74
SMS014	Duck C @ Discovery Dr	<0.01	74.3	25.7	25.4	27.0	47.5	0.29	0.74
SMS015	Duck C @ Observatory Rd	10.2	72.7	17.1	3.47	38.7	57.8	0.60	0.88
SMS020	Black S @ Rowe Rd	<0.01	37.4	62.6	-	-	-	0.83	-
SMS021	Opahu S @ Nikau Gr	<0.01	47.5	52.5	<0.01	35.2	65.6	0.78	1.11
SMS022	Stokes Valley S d/s Eastern Hutt Rd	1.3	32.0	66.7	-	-	-	0.23	-
SMS023	Hulls C @ Field St	22.2	55.9	21.9	-	-	-	1.80	-
SMS024	Mawaihakona S @ Kiwi St	12.9	85.3	1.8	-	-	-	6.88	-
SMS025	Wharemauku S u/s Tui Rd	5.4	94.6	<0.01	-	-	-	0.94	-
SMS026	Tikotu S @ Meredith Way	5.4	94.7	0.1	-	-	-	0.22	-
SMS027	Mangapouri S opp. St Paul's School	15.1	82.2	2.7	-	-	-	1.67	-
SMS028	Mangapouri S d/s Anzac Rd	66.0	33.1	0.9	-	-	-	6.54	-
SMS029	Mangapouri S d/s County Lane	36.7	55.3	8.0	-	-	-	6.74	-
SMS030	Makoura S d/s Makora Rd	8.5	36.2	55.3	-	-	-	0.57	-
SMS031	Opaki S d/s Colombo Rd	25.1	65.5	9.4	-	-	-	5.36	-
SMS032	Kuripuni S d/s Colombo Rd	45.0	54.6	0.4	-	-	-	6.15	-
SMS033	Waikakariki S d/s Lincoln Rd	21.1	74.4	4.5	-	-	-	2.95	-
SMS034	Horokiri S u/s Grays Rd	-	-	-	1.15	37.0	61.8	-	0.26
SMS035	Kakaho S u/s Grays Rd	-	-	-	<0.01	23.9	77.1	-	1.87
SMS037	Duck C u/s Whitby Lakes	-	-	-	46.4	31.6	22.0	-	5.94
SMS038	Kaiwharawhara S @ Trelissick Pk	-	-	-	9.57	74.7	15.8	-	0.97
SMS039	Porirua S @ No. 2 Tunnel	-	-	-	<0.01	66.7	37.2	-	0.41
SMS040	Porirua S @ Wingfield Pl	-	-	-	1.37	34.2	64.4	-	0.70
SMS041	Ration C @ Paekakariki Hill Rd	-	-	-	4.53	26.4	69.1	-	1.41
SMS042	Duck C @ Footbridge	-	-	-	10.7	51.5	37.9	-	0.76

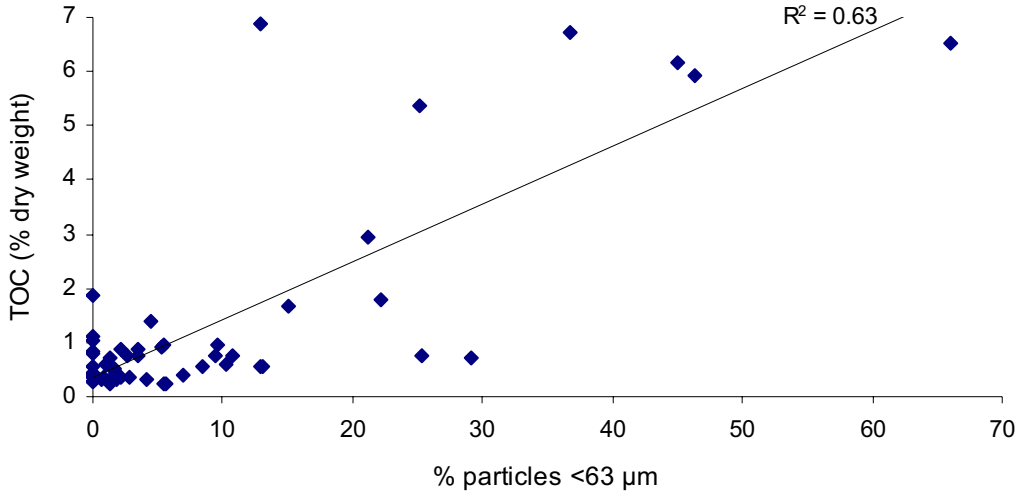

Figure 2.3: Total organic carbon (%) and the percentage of mud present in 53 streambed sediment samples collected in 2005 and 2006

2.4.2 Total recoverable metals

Arsenic, cadmium, chromium, copper, nickel, lead, silver and zinc were detected in all 53 streambed sediment samples collected in 2005 and 2006. Mercury and antimony were detected in all but one and four samples respectively (Table 2.2).

Streambed sediments from 15 (52%) of the sites sampled in 2005 and 12 (50%) of the sites sampled in 2006 exceeded one or more ANZECC (2000) ISQG-Low trigger values for metals (Table 2.2). Samples from three of these sites exceeded at least one ISQG-High trigger value in 2006: Kaiwharawhara Stream at School Road in Wellington City (lead, zinc), Opahu Stream at Nikau Grove in Lower Hutt (zinc), and Porirua Stream at Wingfield Place (zinc).

The most common metals to exceed the ISQG trigger values were zinc and lead; across the 53 streambed sediment samples collected in 2005 and 2006, the trigger values for these metals were exceeded in 12 and 10 samples respectively. No samples exceeded the ISQG trigger values for arsenic, cadmium, chromium or copper. ISQG-Low trigger values for antimony, nickel and silver were exceeded once, each in a different stream. Mercury concentrations exceeded the ISQG-Low trigger value in three samples, two of these from the Mangapouri Stream (Table 2.2).

Streambed sediments at most of the sites sampled in both 2005 and 2006 recorded similar metal concentrations on both occasions. There were two notable exceptions:

- Kaiwharawhara Stream at School Road – recorded markedly higher lead, antimony and zinc concentrations in 2006; and
- Opahu Stream at Nikau Grove – recorded markedly higher silver and mercury concentrations in 2005.

Table 2.2: Total recoverable metal concentrations (mg/kg dry weight) in streambed sediment samples collected in May 2005 and June 2006. Values in amber and red font exceed the ANZECC (2000) ISQG-Low and ISQG-High trigger values respectively.

Site No.	Sample Location	Silver (Ag)		Arsenic (As)		Cadmium (Cd)		Chromium (Cr)		Copper (Cu)		Mercury (Hg)		Nickel (Ni)		Lead (Pb)		Antimony (Sb)		Zinc (Zn)	
		2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006
SMS001	Karori S @ Makara Peak	0.05	0.05	4.9	5.5	0.10	0.14	15.7	14.7	20.5	25.0	0.05	0.06	16.4	17.1	34.8	54.7	0.08	0.14	256	379
SMS002	Kaiwharawhara S @ Otari Bush	0.09	0.04	7.1	7.7	0.17	0.17	18.4	18.3	18.7	20.1	0.06	0.06	14.0	13.1	53.7	58.5	0.18	0.32	259	290
SMS003	Kaiwharawhara S @ Ngaio Gorge	0.12	0.17	5.3	5.1	0.12	0.11	17.6	18.1	19.7	21.6	0.07	0.07	13.1	13.7	45.8	46.6	0.20	0.20	256	284
SMS004	Kaiwharawhara S @ School Rd	0.05	0.17	6.3	5.6	0.22	0.35	25.0	64.2	26.1	31.8	0.07	0.07	21.3	22.5	30.6	337	0.45	2.16	166	540
SMS005	Owhiro S @ Owhiro Bay	0.05	0.03	4.6	3.9	0.13	0.13	13.6	11.9	18.7	27.3	0.04	0.04	11.1	10.1	56.9	38.9	0.55	0.15	237	243
SMS006	Ngauranga S @ Bottom of Gorge	0.04	0.04	5.5	4.9	0.12	0.09	17.8	17.4	24.7	21.4	0.07	0.05	14.4	13.2	38.7	58.2	0.20	0.27	291	292
SMS007	Porirua S @ Redwood Stn	0.03	0.03	4.7	5.1	0.06	0.06	15.4	14.3	13.9	13.5	0.05	0.06	13.0	12.3	23.7	26.3	0.06	0.06	135	160
SMS008	Porirua S @ Glenside	0.04	0.03	5.7	4.7	0.07	0.08	19.1	16.0	17.7	16.2	0.06	0.06	15.6	13.9	26.6	41.4	0.11	0.11	154	158
SMS009	Porirua S @ Kenepuru playing field	0.03	0.04	5.5	5.7	0.06	0.06	16.7	15.3	14.3	14.6	0.06	0.09	12.3	12.7	25.2	26.7	0.08	0.06	140	180
SMS010	Mitchell S d/s of Kenepuru Dr	0.03	0.29	5.1	4.9	0.05	0.09	13.7	15.1	13.2	17.2	0.10	0.11	13.3	15.4	20.9	32.6	0.07	0.10	148	227
SMS011	Kenepuru S u/s SH 1	0.05	0.03	5.7	5.4	0.08	0.06	14.9	14.1	17.9	12.6	0.07	0.06	12.6	11.0	42.5	28.2	0.11	0.12	131	140
SMS012	Pauatahanui S @ SH 58	0.03	0.02	4.6	4.4	0.05	0.05	12.2	9.4	10.1	8.0	0.06	0.04	12.9	9.0	15.3	13.4	0.04	0.04	70.0	60.8
SMS013	Browns S @ Browns Bay Res.	0.04	0.03	12.1	5.9	0.05	0.05	14.3	14.9	16.0	62.2	0.06	0.04	11.6	13.9	39.7	25.6	0.10	0.20	215	217
SMS014	Duck C @ Discovery Dr	0.03	0.02	3.4	3.0	0.04	0.05	14.9	14.6	8.3	9.9	0.05	0.05	12.6	11.8	12.8	15.2	< 0.04	0.07	61.7	107
SMS015	Duck C @ Observatory Rd	0.04	0.03	2.6	3.2	0.04	0.04	14.3	11.9	6.5	6.5	0.09	0.08	10.9	9.1	10.8	12.3	< 0.04	0.11	72.2	82.7
SMS020	Black S @ Rowe Rd	0.04	-	6.2	-	0.09	-	15.8	-	9.4	-	0.04	-	12.7	-	25.6	-	0.25	-	169	-
SMS021	Opahu S @ Nikau Gr	1.01	0.12	3.7	3.9	0.27	0.34	14.3	15.7	38.2	39.6	0.72	0.07	11.4	13.9	53.9	170	0.30	0.32	352	467
SMS022	Stokes Valley S d/s Eastern Hutt Rd	0.03	-	5.3	-	0.05	-	11.7	-	8.9	-	0.04	-	11.0	-	18.1	-	0.09	-	132	-
SMS023	Hulls C @ Field St	0.10	-	7.1	-	0.16	-	13.4	-	27.4	-	0.09	-	10.4	-	43.7	-	0.34	-	249	-
SMS024	Mawaihakona S @ Kiwi St	0.14	-	1.9	-	0.22	-	11.9	-	12.3	-	0.11	-	9.6	-	42.4	-	0.22	-	89.6	-
SMS025	Wharemauku S u/s Tui Rd	0.03	-	4.1	-	0.03	-	7.5	-	6.4	-	0.02	-	6.2	-	5.97	-	< 0.04	-	46.2	-
SMS026	Tikotu S @ Meredith Way	0.04	-	2.0	-	0.03	-	6.0	-	5.3	-	<0.01	-	5.2	-	3.73	-	< 0.04	-	59.4	-
SMS027	Mangapouri S opp. St Paul's School	0.05	-	2.8	-	0.11	-	7.4	-	9.6	-	0.04	-	5.8	-	15.4	-	0.06	-	66.7	-
SMS028	Mangapouri S d/s Anzac Rd	0.39	-	5.9	-	0.38	-	18.4	-	19.5	-	0.25	-	15.0	-	36.9	-	0.14	-	181	-
SMS029	Mangapouri S d/s County Lane	0.24	-	5.4	-	0.44	-	12.5	-	17.1	-	0.19	-	11.0	-	20.4	-	0.18	-	123	-
SMS030	Makoura S d/s Makora Rd	0.08	-	3.9	-	0.16	-	18.9	-	33.2	-	0.07	-	15.4	-	57.7	-	2.10	-	253	-
SMS031	Opaki S d/s Colombo Rd	0.08	-	6.2	-	0.26	-	13.5	-	15.7	-	0.07	-	9.0	-	48.8	-	0.61	-	246	-
SMS032	Kuripuni S d/s Colombo Rd	0.14	-	5.6	-	0.33	-	17.1	-	27.8	-	0.10	-	11.0	-	90.6	-	0.42	-	322	-
SMS033	Waikakariki S d/s Lincoln Rd	0.09	-	11.8	-	0.23	-	32.1	-	18.7	-	0.08	-	10.4	-	50.6	-	0.17	-	180	-
SMS034	Horokiri S u/s Grays Rd	-	0.02	-	3	-	0.04	-	10.5	-	8.2	-	0.04	-	10.4	-	12.2	-	<0.04	-	58.7
SMS035	Kakaho S u/s Grays Rd	-	0.08	-	2.8	-	0.08	-	11.7	-	10.3	-	0.05	-	10.7	-	13.9	-	0.08	-	64.8
SMS037	Duck C u/s Whitby Lakes	-	0.07	-	3.8	-	0.14	-	10.2	-	11.2	-	0.11	-	7.4	-	16.3	-	0.18	-	118
SMS038	Kaiwharawhara S @ Trelissick Pk	-	0.20	-	4.9	-	0.12	-	16.4	-	20.4	-	0.05	-	11.8	-	50.2	-	0.28	-	282
SMS039	Porirua S @ No. 2 Tunnel	-	0.02	-	4.4	-	0.07	-	15.5	-	15.9	-	0.05	-	13.8	-	70.0	-	0.11	-	202
SMS040	Porirua S @ Wingfield Pl	-	0.03	-	6.3	-	0.16	-	16.0	-	24.5	-	0.06	-	14.8	-	62.8	-	0.23	-	406
SMS041	Ration C @ Paekakariki Hill Rd	-	0.03	-	2.5	-	0.07	-	9.8	-	7.6	-	0.04	-	9.5	-	15.7	-	<0.04	-	73.6
SMS042	Duck C @ Footbridge	-	0.07	-	3.6	-	0.03	-	14.5	-	5.7	-	0.06	-	9.6	-	13.7	-	0.04	-	72.1

2.4.3 Polycyclic aromatic hydrocarbons

One or more PAH compounds were detected in all but four streambed sediment samples. Concentrations ranged from "non-detectable" (<2 µg/kg) to 263,000 µg/kg, corresponding to TOC-normalised PAH concentrations of up to 61,500 µg/kg (Table 2.3).

Of the 29 sediment samples collected in 2005, seven exceeded the ANZECC (2000) ISQG-Low trigger value for Total PAHs and two exceeded the ISQG-High trigger value; Makoura Stream at Makora Road (Masterton) and Opaki Stream at Colombo Road (Masterton). In 2006, samples from two sites exceeded the ISQG-Low trigger value for Total PAHs: Kenepuru Stream above SH 1 (Porirua) and Opahu Stream at Nikau Grove (Lower Hutt). Samples from both of these sites also exceeded the ISQG-Low trigger value in 2005 (Table 2.3).

The same samples that exceeded the ANZECC (2000) ISQG trigger values for Total PAHs also exceeded the ISQG trigger values for Total HMW PAHs (Table 2.3). Concentrations of Low Molecular Weight PAHs were low in all samples (Appendix 3).

In the 2005 samples with elevated Total PAH concentrations, the PAH composition was dominated by fluoranthene and pyrene (up to nearly 20%), and often also had high abundances of phenanthrene (see example in Figure 2.4). Although the relative abundances of fluoranthene and pyrene showed little correlation with Total PAH concentrations, both phenanthrene and fluorene correlated positively with Total PAH concentrations (Figure 2.5), meaning that samples with high PAH concentrations were enriched in these two PAH compounds. Overall, all stream sediments showed a pyrogenic character, although those sites with higher PAH concentrations did exhibit a slightly more petrogenic bias[2], primarily because of their high phenanthrene concentrations (Ahrens[3], pers. comm. 2008).

In most cases, PAH concentrations were lower in the 2006 streambed sediment samples, although it should be noted that several Wairarapa streams that recorded very high PAH concentrations in 2005 were not sampled in 2006. The two 2006 sediment samples with elevated Total PAH concentrations (Kenepuru and Opahu streams) were dominated by fluoranthene and pyrene (15–19%), as well as benzo(b)fluoranthene and phenanthrene. The relative abundance of phenanthrene in the Opahu Stream sediment sample was markedly higher in 2006 than in 2005.

In contrast with the samples taken in 2005, major differences in PAH composition were less evident and correlations between individual PAH compounds and Total PAH concentrations were much less pronounced in the samples taken in 2006. In addition, no significant correlation was found between the pyrogenic index (PAHPY) and Total PAH concentrations (Ahrens, pers. comm. 2008).

Overall, most stream sediments across both years showed a pyrogenic character, the PAHPY varying from strongly pyrogenic (PAHPY >0.5) to moderately pyrogenic (PAHPY = 0.15) (Ahrens, pers. comm. 2008).

---

[2] An examination of those sediment samples with elevated PAH concentrations showed a negative correlation (R^2=0.33) between Total PAH concentration and the "pyrogenic index" (PAHPY).

[3] Dr Michael Ahrens, Ecotoxicologist, National Institute of Water and Atmospheric Research Limited.

Table 2.3: Total PAH concentrations (µg/kg dry weight) in streambed sediment samples collected in May 2005 and June 2006. Values in amber and red font exceed the ANZECC (2000) ISQG-Low and ISQG-High trigger values respectively.

Site No.	Sample Location	Total PAH		Total PAH at 1% TOC		Total HMW PAH[1]		Total HMW PAH at 1% TOC	
		2005	2006	2005	2006	2005	2006	2005	2006
SMS001	Karori S @ Makara Peak	3,070	300	5,480	550	1,750	160	3,120	289
SMS002	Kaiwharawhara S @ Otari Bush	9,800	480	16,600	640	6,050	280	10,300	369
SMS003	Kaiwharawhara S @ Ngaio Gorge	5,010	1,650	5,570	2,200	3,140	930	3,490	1,239
SMS004	Kaiwharawhara S @ School Rd	270	1,450	910	2,010	150	830	487	1,149
SMS005	Owhiro S @ Owhiro Bay	330	670	880	1,970	190	390	519	1,132
SMS006	Ngauranga S @ Bottom of Gorge	160	770	420	1,450	70	420	189	783
SMS007	Porirua S @ Redwood Stn	90	60	270	180	50	20	142	72
SMS008	Porirua S @ Glenside	50	60	110	140	20	20	49	58
SMS009	Porirua S @ Kenepuru playing field	90	150	270	330	50	80	135	178
SMS010	Mitchell S d/s of Kenepuru Dr	160	500	710	590	80	280	345	322
SMS011	Kenepuru S u/s SH 1	4,000	10,500	9,530	18,400	2,460	6,770	5,850	11,900
SMS012	Pauatahanui S @ SH 58	110	280	420	900	60	100	211	313
SMS013	Browns S @ Browns Bay Res.	70	60	70	80	40	30	34	34
SMS014	Duck C @ Discovery Dr	<20	40	<70	50	<10	10	<20	19
SMS015	Duck C @ Observatory Rd	<20	30	<30	30	<10	10	<10	9
SMS020	Black S @ Rowe Rd	450	-	540	-	170	-	207	-
SMS021	Opahu S @ Nikau Gr	18,400	23,700	23,600	21,300	10,500	13,500	13,500	12,200
SMS022	Stokes Valley S d/s Eastern Hutt Rd	40	-	180	-	20	-	83	-
SMS023	Hulls C @ Field St	500	-	280	-	270	-	151	-
SMS024	Mawaihakona S @ Kiwi St	1,050	-	150	-	600	-	88	-
SMS025	Wharemauku S u/s Tui Rd	300	-	320	-	180	-	188	-
SMS026	Tikotu S @ Meredith Way	<20	-	<90	-	<10	-	<27	-
SMS027	Mangapouri S opp. St Paul's School	190	-	110	-	100	-	58	-
SMS028	Mangapouri S d/s Anzac Rd	690	-	110	-	410	-	62	-
SMS029	Mangapouri S d/s County Lane	3,310	-	490	-	2,090	-	310	-
SMS030	Makoura S d/s Makora Rd	35,000	-	61,500	-	19,200	-	33,800	-
SMS031	Opaki S d/s Colombo Rd	263,000	-	49,100	-	151,000	-	28,100	-
SMS032	Kuripuni S d/s Colombo Rd	31,100	-	5,050	-	17,500	-	2,850	-
SMS033	Waikakariki S d/s Lincoln Rd	28,200	-	9,560	-	17,000	-	5,760	-
SMS034	Horokiri S u/s Grays Rd	-	180	-	690	-	-	-	-
SMS035	Kakaho S u/s Grays Rd	-	<30	-	<20	-	<110	-	<408
SMS037	Duck C u/s Whitby Lakes	-	100	-	20	-	10	-	5
SMS038	Kaiwharawhara S @ Trelissick Pk	-	890	-	920	-	50	-	8
SMS039	Porirua S @ No. 2 Tunnel	-	1,140	-	2,770	-	480	-	498
SMS040	Porirua S @ Wingfield Pl	-	410	-	590	-	600	-	1,456
SMS041	Ration C @ Paekakariki Hill Rd	-	20	-	10	-	210	-	300
SMS042	Duck C @ Footbridge	-	30	-	40	-	10	-	5

[1] HMW PAHs are the sum of the concentrations of fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[a]pyrene and dibenzo[a,h]anthracene.

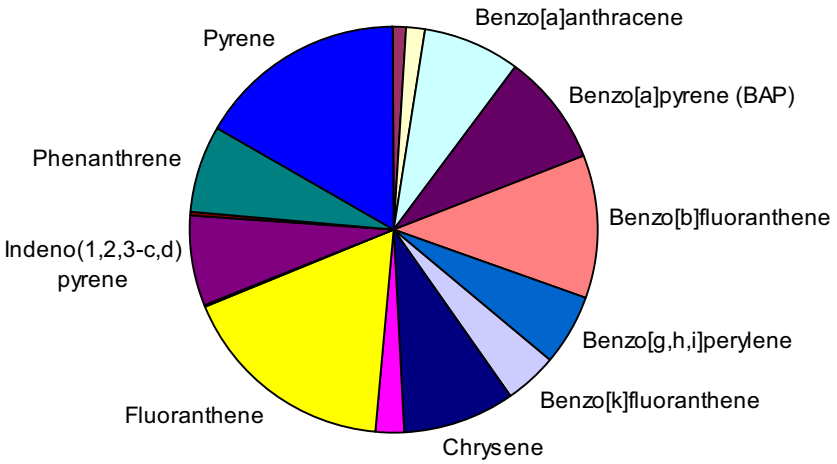

Figure 2.4: PAH composition in surface sediment from the Kenepuru Stream, sampled in May 2005

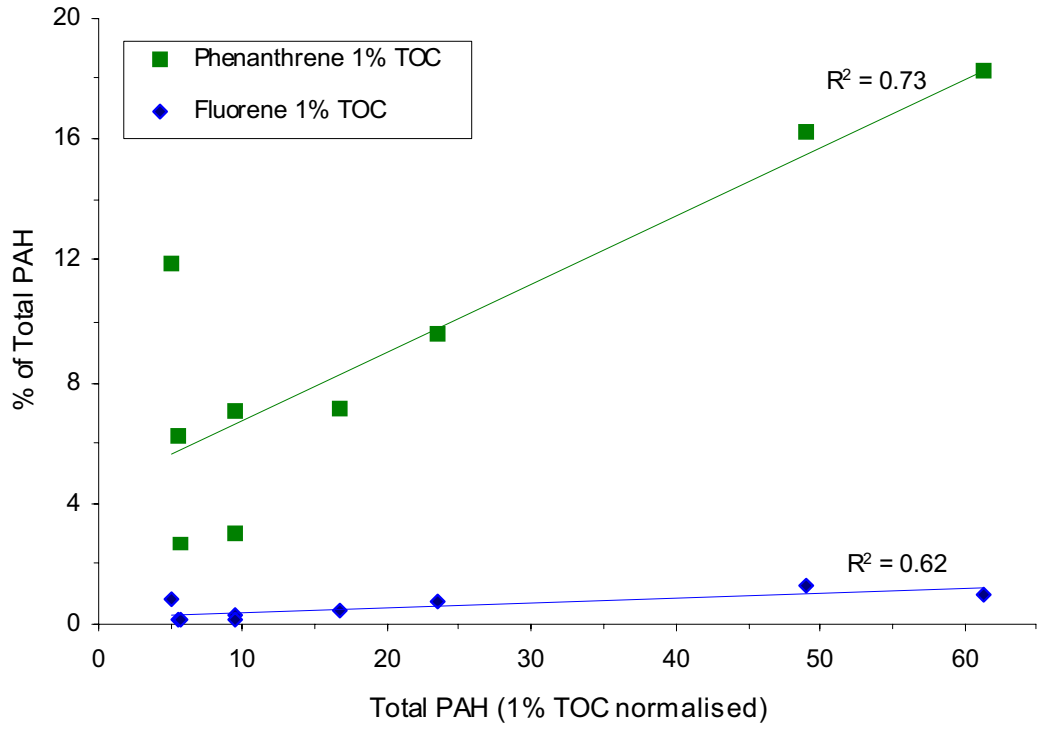

Figure 2.5: Relative abundance of phenanthrene and fluorene compared with Total PAH concentrations in May 2005 streambed sediment samples that recorded Total PAH concentrations above the ANZECC (2000) ISQG-Low trigger value (4,000 µg/kg)

2.4.4 Organochlorine pesticides

Organochlorine pesticides were detected in streambed sediment samples from all but four sites in 2005[4] and one site in 2006. In most cases – 25 (86%) sites sampled in 2005 and 22 (92%) sites sampled in 2006 – the samples exceeded one or more ANZECC (2000) ISQG trigger values.

[4] Lower analytical detection limits were employed in the 2006 sampling round, resulting in the detection of one or more pesticides at all four of these sites in 2006.

The most commonly detected pesticide was DDT; 25 sites in 2005 and 21 sites in 2006 recorded a Total DDT concentration greater than the ISQG-Low trigger value. Four sites in streams entering Porirua Harbour exceeded the ISQG-High trigger value (Table 2.4): Pauatahanui Stream at State Highway 58 (2005), Kenepuru Stream upstream of State Highway 1 (2005), Porirua Stream at Glenside (2006), and Duck Creek at Observatory Road (2006). Most of the DDT present at these sites was in the form of two or more of 4,4'-DDD, 4,4'-DDE and 4,4'-DDT, with the relative abundances of each differing between sites (Figure 2.6, Appendix 3).

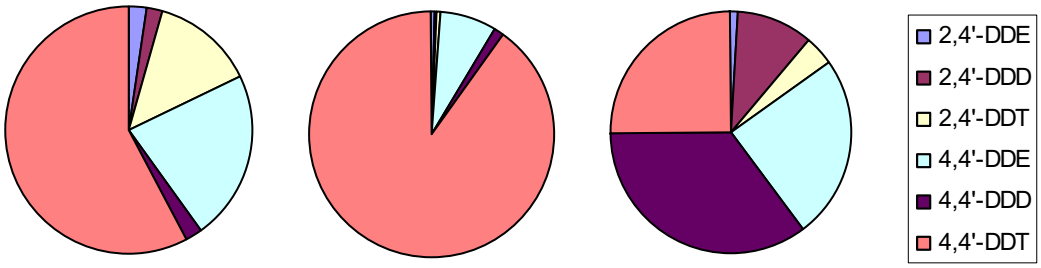

Figure 2.6: DDT composition in streambed sediments from (left to right) the Kenepuru Stream in 2005, Porirua Stream at Glenside in 2006 and Duck Creek at Observatory Road in 2006

Dieldrin and lindane were also detected in samples from a number of sites. Sediment from ten sites sampled in 2005 and eight sites sampled in 2006 exceeded the ISQG-Low trigger value for dieldrin[5] (Table 2.4). Sediment from Owhiro Stream at Owhiro Bay exceeded the ISQG-High trigger value in 2005. Lindane was only detected in samples collected in 2005; samples from three sites recorded concentrations greater than the ISQG-Low trigger value and samples from five sites exceeded the ISQG-High trigger value. The highest lindane concentration (6.8 µg/kg) was found in sediments from the Kaiwharawhara Stream at Otari Bush (Table 2.4).

Other organochlorine pesticides detected – generally at low concentrations – were cis-chlordane (Porirua Stream at Glenside, 2005), endosulfan sulphate and endosulfan II (Opahi Stream in 2005 and 2006), and hexachlorobenzene (Browns Bay Stream, 2006) (Appendix 3). No ISQG trigger values exist for these compounds.

[5] More sites may have exceeded the ISQG-Low trigger value as the laboratory detection limit (<0.5-1 µg/kg) was above the trigger value (0.02 µg/kg). The trigger value is widely regarded as being too low for New Zealand conditions (e.g., Stephenson & Mills 2006).

Table 2.4: Dieldrin and Total DDT concentrations (µg/kg dry weight) present in streambed sediment samples collected in May 2005 and June 2006. Values in amber and red font exceed the ANZECC (2000) ISQG-Low and ISQG-High trigger values respectively.

Site No.	Site Name	Dieldrin		Dieldrin at 1% TOC		Total DDT[1]		Total DDT[1] at 1% TOC	
		2005	2006	2005	2006	2005	2006	2005	2006
SMS001	Karori S @ Makara Peak	<1	0.7	-	1	6	-	10	-
SMS002	Kaiwharawhara S @ Otari Bush	4	2.2	7	3	23	2	38	2
SMS003	Kaiwharawhara S @ Ngaio Gorge	3	1.4	3	2	7	2	7	2
SMS004	Kaiwharawhara S @ School Rd	<1	1.0	-	1	<3	2	-	3
SMS005	Owhiro S @ Owhiro Bay	5	1.4	14	4	15	6	41	18
SMS006	Ngauranga S @ Bottom of Gorge	<1	0.7	-	1	<3	<0.5	-	-
SMS007	Porirua S @ Redwood Stn	<1	<0.5	-	-	<3	2	-	7
SMS008	Porirua S @ Glenside	<1	<0.5	-	-	12	22	29	54
SMS009	Porirua S @ Kenepuru playing field	<1	<0.5	-	-	12	2	34	5
SMS010	Mitchell S d/s of Kenepuru Dr	<1	<0.5	-	-	9	<0.5	39	-
SMS011	Kenepuru S u/s SH 1	<1	<0.5	-	-	23	4	54	6
SMS012	Pauatahanui S @ SH 58	<1	<0.5	-	-	14	4	50	11
SMS013	Browns S @ Browns Bay Res.	<1	<0.5	-	-	16	2	16	3
SMS014	Duck C @ Discovery Dr	<1	<0.5	-	-	7	3	22	4
SMS015	Duck C @ Observatory Rd	<1	<0.5	-	-	7	58	12	66
SMS020	Black S @ Rowe Rd	<1	-	-	-	8	-	10	-
SMS021	Opahu S @ Nikau Gr	4	2.5	5	2	23	9	29	8
SMS022	Stokes Valley S d/s Eastern Hutt Rd	<1	-	-	-	8	-	33	-
SMS023	Hulls C @ Field St	2	-	1	-	24	-	13	-
SMS024	Mawaihakona S @ Kiwi St	<1	-	-	-	39	-	6	-
SMS025	Wharemauku S u/s Tui Rd	<1	-	-	-	14	-	14	-
SMS026	Tikotu S @ Meredith Way	<1	-	-	-	<2	-	-	-
SMS027	Mangapouri S opp. St Paul's School	<1	-	-	-	11	-	7	-
SMS028	Mangapouri S d/s Anzac Rd	<2	-	-	-	80	-	12	-
SMS029	Mangapouri S d/s County Lane	2	-	<1	-	110	-	16	-
SMS030	Makoura S d/s Makora Rd	1	-	2	-	12	-	21	-
SMS031	Opaki S d/s Colombo Rd	13	-	2	-	46	-	8	-
SMS032	Kuripuni S d/s Colombo Rd	6	-	1	-	86	-	14	-
SMS033	Waikakariki S d/s Lincoln Rd	6	-	2	-	25	-	8	-
SMS034	Horokiri S u/s Grays Rd	-	<0.5	-	-	-	2	-	7
SMS035	Kakaho S u/s Grays Rd	-	<0.5	-	-	-	38	-	20
SMS037	Duck C u/s Whitby Lakes	-	<0.5	-	-	-	10	-	2
SMS038	Kaiwharawhara S @ Trelissick Pk	-	2.2	-	2	-	5	-	5
SMS039	Porirua S @ No. 2 Tunnel	-	<0.5	-	-	-	15	-	37
SMS040	Porirua S @ Wingfield Pl	-	<0.5	-	-	-	5	-	8
SMS041	Ration C @ Paekakariki Hill Rd	-	<0.5	-	-	-	9	-	6
SMS042	Duck C @ Footbridge	-	<0.5	-	-	-	7	-	10

[1] Total DDT 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

2.5 Discussion

Elevated concentrations of one or more contaminants were found in streambed sediment samples from almost all of the sites. Of the heavy metals, zinc was the most common to be found in concentrations above ANZECC (2000) ISQG guidelines. This was also observed by Cameron (2001) in a previous study of streambed contaminants in the Porirua Stream catchment and is not overly

surprising; zinc is ubiquitous in urban environments, the primary sources being unpainted galvanized roofs and vehicle tyre wear (Timperley[6], pers. comm. 2008). In the case of lead, which was also present in concentrations above the ISQG-Low trigger value at some sites, it is likely that the sources are primarily historic. Although lead was removed from petrol in New Zealand in 1996, recent stormwater source investigations in Auckland have demonstrated that roadside soils remain contaminated with lead, with the contamination extending more than 100 m from road verges (Kennedy[7], pers. comm. 2008). Soils in some residential areas are also known to be contaminated with lead-based paint residues, despite lead being removed from paint in the mid 1960s.

In addition to lead and zinc, Greater Wellington investigations to characterise stormwater quality in the Wellington region identified significant enrichment of the particulate fraction by copper (KML 2005). Copper-enriched sediments have also been reported at storm drain outlets in Evans Bay and the Lambton Basin in Wellington Harbour (Pilotto 1996). The reason that copper concentrations in Wellington's streambed sediments do not exceed the ISQG-Low trigger value is unclear; like zinc, copper is ubiquitous in urban environments, the primary sources being vehicle brake pad wear and architectural uses such as copper spouting (Timperley, pers. comm. 2008).

Concentrations of Total HMW PAHs and Total PAHs exceeded ISQG trigger values in sediment samples from some sites, notably the lower Kenepuru Stream in Porirua and Opahu Stream in Lower Hutt. There was a high degree of variability in PAH concentrations and composition, suggesting multiple PAH sources. Overall, most stream sediments across both sampling years showed a pyrogenic character, the PAHPY varying from strongly pyrogenic (PAHPY >0.5) to moderately pyrogenic (PAHPY = 0.15) (Ahrens, pers. comm. 2008). Sources of pyrogenic PAHs include soot from coal, diesel, wood or crude oil combustion and creosote/coal tar contamination. High relative percentages of phenanthrene (>10%) were an unusual feature at some sites that recorded the highest PAH concentrations, and point to contamination by unburnt coal or petroleum products (Ahrens, pers. comm. 2008).

Almost all of the 29 sites sampled in 2005 and 24 sites sampled in 2006 recorded concentrations of Total DDT above the ISQG–Low trigger value. The consistent detection of this pesticide, both in this investigation and in previous streambed sediment samples from the Porirua Stream catchment (Cameron 2001) reflects its widespread application to rural and urban land last century. Although the use of DDT in agriculture effectively ceased in the 1970s, and its use in urban areas has been banned since the late 1980s, the present results confirm that substantial sources remain in the environment.

As noted previously, the streambed at many of the sites sampled comprised mainly cobbles and fine gravels, making it difficult to find any finer sediment to sample. While this could suggest that there is unlikely to be widespread (spatial) contamination of the streambed habitat at these sites, Suren & Elliott (2004) note that interstitial sediments and sediment trapped in biofilms coating streambed

[6] Dr Mike Timperley, Timperley Associates (former Stormwater Action Team Leader, Auckland Regional Council).

[7] Paul Kennedy, Principal Environmental Scientist, Golder Associates (Auckland).

cobbles – neither of which were sampled in this investigation – can contain high concentrations of heavy metals and PAHs. Moreover, these contaminants have been linked with adverse effects on instream invertebrate communities. For example, Suren (unpublished data, in Suren & Elliott 2004) demonstrated using an *in-situ* cage experiment in three urban streams in Christchurch that metal-contaminated biofilms and sediments, together with high sedimentation levels, were likely to be largely responsible for the absence of sensitive invertebrates such as *Deleatidium* mayflies.

There were only a few streambed sampling locations that comprised predominantly fine sediments and also recorded elevated concentrations of contaminants (e.g., PAHs in Opaki, Kuripuni and Waikakariki streams in 2005). In most of these cases, the TOC content was also high (2.95–6.15% for the above examples). Given organic carbon plays an important role in binding with organic contaminants to reduce their bioavailability, this suggests that exceedance of guidelines at these sites may not necessarily be associated with adverse effects on benthic biota. Indeed, ANZECC (2000) notes that 'relaxation' of guidelines for organic contaminants should be made if the sediment organic carbon content is *"markedly higher than 1%"*.

The lack of silts and clays in sediment samples from many of the sites suggests that these components of any stormwater-derived sediment – and the contaminants attached to them – are not retained in streams for long and instead are rapidly flushed through the system into estuarine and coastal waters. This has important implications for less well flushed receiving environments, notably Porirua Harbour and the Lambton Basin and Evans Bay in Wellington Harbour. Recent sediment quality investigations undertaken in these environments have shown there are already elevated concentrations of contaminants such as copper, lead, zinc, PAHs and DDT in the subtidal sediments (Stephenson & Mills 2006, Stephenson et al. 2008).

3. Heavy metal contaminants in wet weather stream flows

3.1 Introduction

Greater Wellington's urban stormwater study undertaken over the period 2002–2004 (KML 2005) showed that a number of heavy metals can occur in urban stream wet-weather flows (i.e., runoff following rainfall) at concentrations above ANZECC (2000) guidelines, even after reasonable mixing. These results were time-weighted average concentrations (based on a six-unit composite sample) during a runoff event, so the concentrations potentially could be much higher in the early stages of runoff events – the so-called 'first-flush effect'.

Leading on from the 2002–2004 study, the primary objectives of the current investigation were to determine the concentrations of stormwater-derived heavy metal contaminants in the runoff-generated 'first-flush' flow of selected urban streams, and assess whether or not these concentrations pose a risk to stream life. A secondary objective was to obtain further estimates of the total contaminant load associated with individual runoff events; estimates which could be used to calibrate pollution runoff models for urban catchments and hence derive typical annual contaminant loads for sensitive coastal receiving environments such as Porirua and Wellington harbours.

3.2 Sampling sites

Eights sites on five urban streams (Porirua, Owhiro, Kaiwharawhara, Ngauranga and Opahu) within Porirua, Wellington and Lower Hutt cities were included in the investigation (Figure 3.1, Appendix 4). Site locations were limited by a number of factors, including safe and secure access for deployment of the automated sampling equipment. Porirua Stream became the primary focus of the investigation from early 2006, largely because urban development is still occurring in the upper catchment and the stream discharges into the southern end of the Porirua Harbour, where elevated heavy metal concentrations have been recorded in the intertidal and subtidal sediments (e.g., Glasby et al. 1990, Stephenson & Mills 2006).

The streams sampled receive stormwater from a range of sources. The Porirua Stream's catchment comprises rural, residential, commercial and industrial land uses, with an intensive commercial and industrial zone between the 'Glenside' and 'Kenepuru' sampling sites. The Owhiro and Kaiwharawhara stream catchments consist predominantly of residential areas, with some undeveloped land covered by bush, although the Kaiwharawhara Stream passes through a commercial zone shortly before it enters Wellington Harbour. The Ngauranga Stream's catchment comprises a mixture of residential, commercial and industrial use, while Opahu Stream flows through a primarily residential part of Lower Hutt.

There are either operative or closed landfills in the catchments of Porirua, Owhiro, and Kaiwharawhara streams.

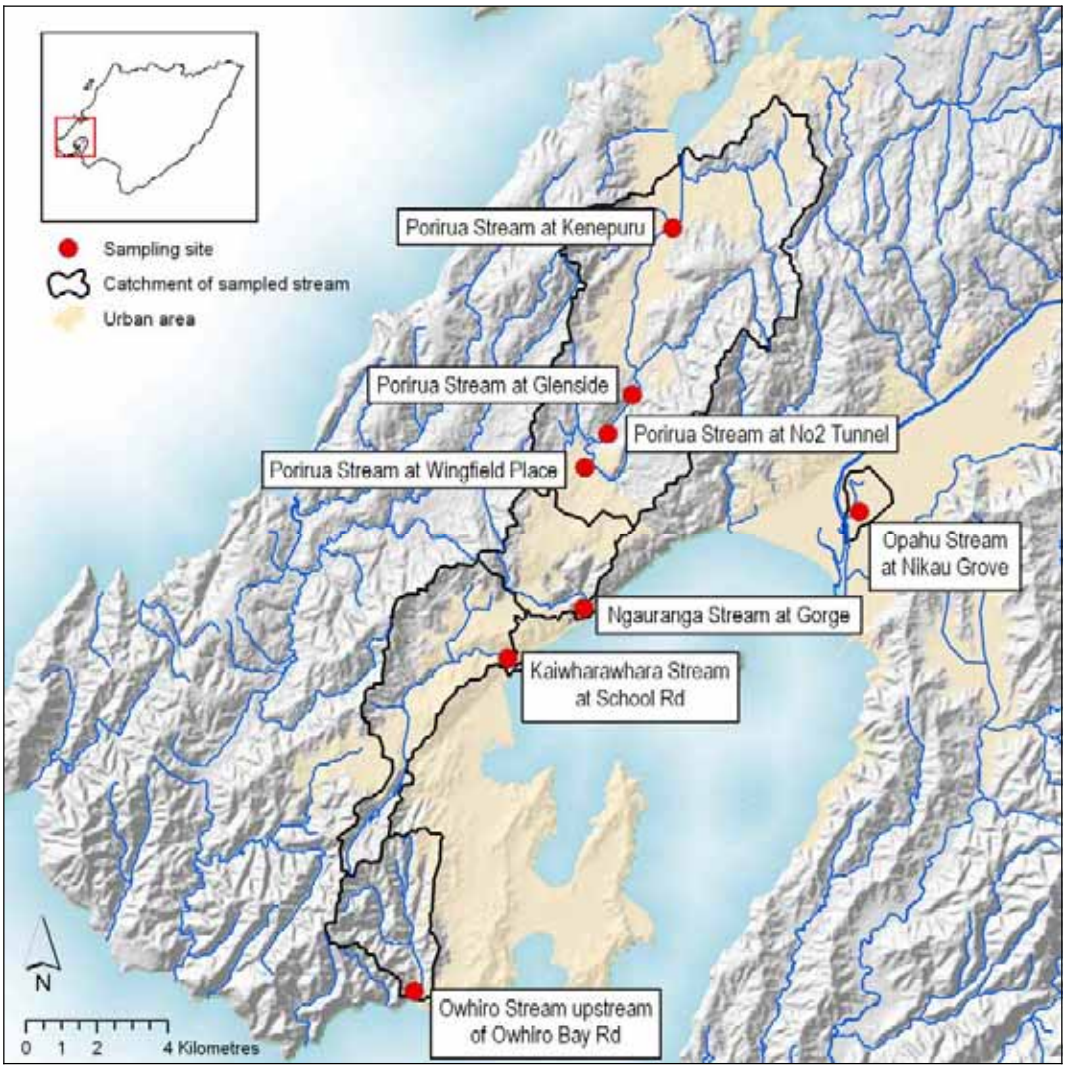

Figure 3.1: Stream sites used for sampling wet-weather flows over the period October 2005 to May 2007

3.3 Methods

3.3.1 Sample collection

An ISCO 6712 automatic sampling device was deployed at each stream site prior to forecast rainfall (Figure 3.2). The sampler incorporates a rainfall or water level trigger that enables multiple flow-proportioned stream water samples to be collected over the course of a runoff event.

The ISCO automatic sampler was triggered when a minimum rate of stream water level rise was detected (35 mm over 15 minutes), with one initial sample taken immediately and followed by two further samples after 5 and 10 minutes. After this 'first flush' sampling period, further time-delayed samples were collected at 20 minute intervals to form a composite 'event' sample (Figure 3.3). Some modifications were made to the sampling regime during the investigation period; for example, from February 2007, the 'first flush' period was reduced to two samples (0 and 5 minutes), with further samples taken at 40 minute intervals over the duration of the runoff event (up to a maximum of nine further samples).

Figure 3.2 Setting up the automatic sampler in the Porirua Stream at No. 2 Tunnel (mid catchment) in December 2005

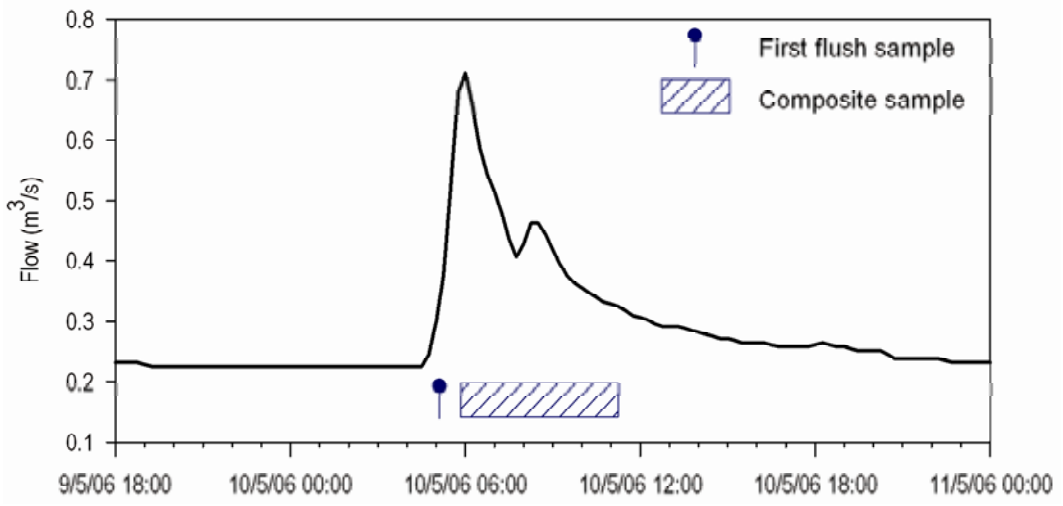

Figure 3.3: Example hydrograph, illustrating 'first flush' and composite sample collection from the Porirua Stream at Kenepuru on 10 May 2006

A bubble flow meter fitted to the automatic sampler recorded stream water level at one minute intervals. These data were collected to enable stream flow to be estimated using Manning's Equation.

During sampling over the period February to May 2007, a sonde was also fitted on the automatic sampler to measure conductivity, turbidity, pH, dissolved oxygen and temperature at one minute intervals.

Over the course of the investigation, which spanned from 19 October 2005 until May 2007, the following sampling was undertaken:

- Ngauranga Stream at bottom of gorge – one runoff event
- Owhiro Stream upstream of Owhiro Bay Road – one runoff event
- Kaiwharawhara Stream at School Road (bottom of Ngaio Gorge) – one runoff event
- Opahu Stream downstream of Nikau Grove – one runoff event
- Porirua Stream at Kenepuru (near hospital) – six runoff events
- Porirua Stream at No. 2 Tunnel (Rowells Rd) – one runoff event
- Porirua Stream at Glenside – one runoff event
- Porirua Stream at Wingfield Place, Johnsonville – six runoff events

In addition to sampling during runoff events, one 'grab' (spot) stream water sample was collected from seven of the sites during near-winter 'base flow' conditions on 9 May 2006. The purpose of the base flow sampling was to provide an indication of background concentrations for comparative purposes.

3.3.2 Sample preparation and analysis

From each runoff event, two stream water samples were prepared for analysis; a 'first flush' sample (a composite of the first two or three 1L samples taken 5 minutes apart) and a single 2-3L composite of the remaining samples. Samples were chilled and dispatched to Hill Laboratories for analysis. In most cases, samples for dissolved metal analysis were filtered prior to sample dispatch.

Details of the laboratory analytical methods are provided in Appendix 2. Each stream sample was analysed for the following:

- Total suspended solids; and
- Dissolved and total[8] arsenic, cadmium, chromium, copper, mercury, nickel, lead and zinc using ICP-MS.

There were a few exceptions:

- Not all stream samples were tested for total suspended solids;
- The 'first flush' and composite samples from the Ngauranga Stream were not analysed for dissolved metals; and
- The 'first flush' and composite samples from the Kaiwharawhara Stream at School Road and Porirua Stream at No. 2 Bridge sites were not analysed for dissolved mercury.

3.3.3 Sampling limitations

A lot of difficulties were experienced during the course of the 18-month investigation. The automatic sampler did not always trigger during runoff events, limiting the number of samples collected. The water level data and resulting stream flow estimates obtained using Manning's Equation appeared to be very

[8] Samples collected from 13 March 2007 onwards were analysed for total recoverable metals.

inaccurate and were unable to be verified through flow gaugings[9], preventing accurate estimation of runoff event contaminant loads. However, one site (Porirua Stream at Kenepuru) was located in close proximity to a Greater Wellington automated flow recorder (Porirua Stream at Town Centre) and so contaminant loads could be estimated for this site. The accuracy of the field measurements made using the sonde is also unclear; the temperature probe broke within a few months of deployment, affecting data collected from 14 April 2007 onwards.

3.3.4 Data analysis

(a) Guidelines

The results of the analyses for dissolved metals were compared against the Australian and New Zealand Environment and Conservation Council (ANZECC 2000) freshwater toxicity trigger values. As noted in subsection 2.3.4, these guidelines are not 'pass' or 'fail' numbers, and the developers of the guidelines emphasise that they are best used as one part of a 'weight of evidence' approach to evaluating potential effects of contaminants on the biota.

The ANZECC (2000) toxicity guidelines provide four sets of protection levels derived as chemical-specific estimates of the concentrations of contaminants that should have no adverse effects on aquatic ecosystems. The 95% protection level is the most commonly applied to aquatic ecosystems that have been modified in some way (Table 3.1) and this is the level used to interpret the stream water sample results in subsection 3.4.

Table 3.1: ANZECC (2000) toxicity trigger values for freshwaters (95% species protection)

Metals & Metalloids	Trigger Value (µg/L)[1]	Comment
Arsenic (AsIII)	26	
Arsenic (AsV)	13	This more conservative TV is used in subsection 3.4 but arsenic speciation was not determined
Cadmium	0.2	
Chromium (CrVI)	1	This conservative TV is used in subsection 3.4 but chromium speciation was not determined
Copper	1.4	
Lead	3.4	
Mercury (organic)	0.6	
Nickel	11	
Zinc	8	

[1] Applicable to soft waters (hardness 0-59 g/m^3 $CaCO_3$)

Because the ANZECC toxicity trigger values for metals are aimed at protection from sustained exposure (i.e., chronic toxicity), and exposure to stormwater-derived contaminants in stream waters is relatively short, the dissolved metal concentrations from the stream water samples were also compared against the United States Environmental Protection Agency (USEPA 2006) Criteria

[9] Stream flow gaugings were attempted in the Porirua Stream at Wingfield Place but it proved very difficult to obtain accurate gaugings during runoff events, due to rapid stream rise (Nick Boyens, Greater Wellington Senior Environmental Monitoring Officer, pers. comm. 2008).

Maximum Concentrations (CMC). A CMC is *"an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect"* (p.20, USEPA 2006). As CMC are set at higher concentrations than the chronic guideline values, only dissolved metal concentrations that exceeded ANZECC (2000) trigger values were compared against the CMC.

(b) Data adjustment

ANZECC (2000) recommends that the toxicity trigger values for hardness-related metals (i.e., cadmium, copper, lead, nickel and zinc) are adjusted to account for local water hardness. This is important because the trigger values for these metals have been derived for a low water hardness (30 g/m^3 $CaCO_3$), corresponding to high toxicity. In this case, no adjustments were deemed necessary; hardness data collected from monitoring sites on the Porirua and Kaiwharawhara streams through Greater Wellington's Rivers State of the Environment (RSoE) Programme indicate that water hardness is low (33-52 g/m^3 $CaCO_3$)[10].

In contrast to the ANZECC (2000) toxicity trigger values, the US EPA (2006) CMC for dissolved metals have been derived for a water hardness of 100 g/m^3 $CaCO_3$. Therefore, the CMC were recalculated based on a median stream water hardness of 42.5 g/m^3 $CaCO_3$ (RSoE data), following the equation provided in the guidelines.

3.4 Results

The results of the total suspended solids and dissolved and total metal analyses in 'base flow' (winter), 'first flush' and composite water samples are presented in Table 3.2.

3.4.1 Temperature, electrical conductivity, pH and turbidity

Continuous water temperature, electrical conductivity, pH and turbidity measurements were obtained from several runoff events in the Porirua Stream at Wingfield Place (Johnsonville) during March and April 2007. Turbidity was the only variable to change significantly during this period; monitoring results from 7–13 March 2007 showed a significant increase in turbidity that coincided with a rise in stream water level during the onset of rainfall on the morning of 12 March. This pattern was observed again in the early hours of 13 March when sample collection was triggered by the ISCO sampler. Turbidity measurements fluctuated widely during this second runoff event, peaking at 1,008 NTU. In contrast, turbidity in the days leading up to the runoff events rarely exceeded 3 NTU.

Further field measurements made from 13–16 March 2007 showed another similar increase in turbidity, with values up to 1,001 NTU recorded on the morning of 14 March. The increased turbidity coincided with rainfall in the catchment and a corresponding increase in stream water level.

[10] Since January 2008, routine water samples collected at monthly intervals from RSoE sites on the Porirua and Kaiwharawhara streams have been tested for total suspended solids, anions, cations and heavy metals. This testing is expected to continue for at least 12 months. The results of the first six months of sampling have been considered here.

Table 3.2: Total suspended solid concentrations (g/m^3) and dissolved and total[1] metal concentrations (µg/L) in 'base flow' (winter), 'first flush' and composite water samples collected from urban streams over the period October 2005 to May 2007. Dissolved concentrations shown in bold font and shaded grey exceeded ANZECC (2000) toxicity trigger values (95% protection level) and USEPA (2006) CMC respectively.

Stream and Sample Location	Date	Sample Type	TSS	Arsenic (As)		Cadmium (Cd)		Chromium (Cr)		Copper (Cu)	
				Diss	Total	Diss.	Total	Diss.	Total	Diss.	Total
Ngauranga at bottom of gorge	19/10/2005	First Flush	-	-	5	-	0.27	-	11.8	-	55.3
Ngauranga at bottom of gorge	19/10/2005	Composite	-	-	4	-	0.15	-	9.1	-	39.9
Ngauranga at bottom of gorge	09/05/2006	Base flow	3	<1	<1	<0.05	<0.05	<0.5	<0.5	1.1	1.3
Kaiwharawhara at School Rd	24/11/2005	First Flush	-	<1	<1	<0.05	0.07	<0.5	0.7	**3.7**	10.4
Kaiwharawhara at School Rd	24/11/2005	Composite	6	<1	<1	<0.05	<0.05	<0.5	<0.5	**4.8**	6.5
Kaiwharawhara at School Rd	09/05/2006	Base flow	<3	<1	<1	<0.05	<0.05	<0.5	<0.5	**1.4**	1.3
Owhiro u/s Owhiro Bay Rd	06/12/2005	First Flush	-	<1	7	<0.05	0.29	<0.5	12.8	**3.4**	41.9
Owhiro u/s Owhiro Bay Rd	06/12/2005	Composite	909	<1	7	<0.05	0.37	0.5	15.1	**6**	58.3
Owhiro u/s Owhiro Bay Rd	09/05/2006	Base flow	<3	<1	<1	<0.05	<0.05	<0.5	<0.5	1	1.1
Opahu at Nikau Grove	23/02/2006	First Flush	-	<2	<5	0.4	0.5	<1	<3	**2**	7
Opahu at Nikau Grove	23/02/2006	Composite	21	<5	<5	<0.3	<0.3	<3	<3	**5**	16
Opahu at Nikau Grove	09/05/2006	Base flow	3	<1	<1	<0.05	<0.05	<0.5	<0.5	**2.1**	2.8
Porirua at Wingfield Place	09/05/2006	Base flow	<3	<1	<1	<0.05	<0.05	<0.5	<0.5	**1.5**	1.5
Porirua at Wingfield Place	23/05/2006	First Flush	-	<1	<1	<0.05	<0.05	<0.5	0.9	**6.5**	10
Porirua at Wingfield Place	23/05/2006	Composite	-	<1	1	<0.05	<0.05	0.5	1	**8.1**	14.7
Porirua at Wingfield Place	04/06/2006	First Flush	-	<1	3	<0.05	<0.05	<0.5	2.9	**3.3**	11.8
Porirua at Wingfield Place	04/06/2006	Composite	58	<1	2	<0.05	<0.05	0.6	1.9	**5.7**	14.2
Porirua at Wingfield Place	13/03/2007	First Flush	700	<1	8	<0.05	1.81	**1.5**	18.8	**4.0**	64.7
Porirua at Wingfield Place	13/03/2007	Composite	145	<1	2	<0.05	0.11	**1**	4.4	**4.3**	13.2
Porirua at Wingfield Place	13/04/2007	First Flush	81	<1	2	<0.05	0.08	**27.7**	1.8	**3.6**	10.6
Porirua at Wingfield Place	13/04/2007	Composite	40	<1	1	0.08	0.07	**2.7**	2.6	**5.8**	9.6
Porirua at Wingfield Place	27/04/2007	First Flush	76	<1	2	0.06	0.11	**4.8**	2.1	**5.8**	12.4
Porirua at Wingfield Place	27/04/2007	Composite	22	<1	1	0.08	0.18	**8**	6.3	**6.9**	9
Porirua at Wingfield Place	03/05/2007	First Flush	89	<1	2	<0.05	0.07	**29.4**	29.4	**3.9**	9.9
Porirua at Wingfield Place	03/05/2007	Composite	120	<1	2	<0.05	0.07	**1.0**	13.8	**6.3**	14.6
Porirua at Glenside	14/03/2007	First Flush	848	<1	13	<0.05	0.6	**6.1**	29.8	**3.6**	86
Porirua at Glenside	14/03/2007	Composite	291	<1	5	0.07	0.12	**2.8**	9.6	**8.6**	27.8
Porirua at No. 2 Tunnel	24/01/2006	First Flush	-	<1	1	<0.05	0.05	<0.5	0.9	**5.3**	7
Porirua at No. 2 Tunnel	24/01/2006	Composite	50	<1	1	<0.05	<0.05	<0.5	1.9	**5**	8.9
Porirua at No. 2 Tunnel	09/05/2006	Base flow	<3	<1	<1	<0.05	<0.05	<0.5	<0.5	0.8	0.8
Porirua at Kenepuru	27/03/2006	First Flush	-	<1	1	<0.05	<0.05	**1.5**	1.2	**3.2**	5.9
Porirua at Kenepuru	27/03/2006	Composite	17	<1	1	0.08	0.07	**8.5**	1.4	**9.3**	8.5
Porirua at Kenepuru	07/04/2006	First Flush	-	<1	1	<0.05	<0.05	0.6	1.2	**5.8**	9.4
Porirua at Kenepuru	07/04/2006	Composite	8	<1	<1	<0.05	<0.05	**1.5**	0.8	**4.9**	6.2
Porirua at Kenepuru	08/04/2006	First Flush	-	<1	<1	<0.05	<0.05	**1.2**	0.7	**4.7**	6.3
Porirua at Kenepuru	08/04/2006	Composite	819	<1	8	<0.05	0.24	**1.5**	21.6	**5.6**	40.6
Porirua at Kenepuru	25/04/2006	First Flush	-	<1	2	<0.05	0.09	**1.2**	16.9	**6.1**	20.4
Porirua at Kenepuru	25/04/2006	Composite	119	<1	2	<0.05	0.08	0.9	4.8	**6.9**	18.2
Porirua at Kenepuru	09/05/2006	Base flow	<3	<1	<1	<0.05	<0.05	<0.5	<0.5	**2**	2.2
Porirua at Kenepuru	10/05/2006	First Flush	16	<1	<1	<0.05	<0.05	<0.5	1	**2.1**	4.2
Porirua at Kenepuru	10/05/2006	Composite	19	<1	<1	<0.05	<0.05	<0.5	1.1	**4.2**	6.9
Porirua at Kenepuru	11/05/2006	First Flush	-	<1	1	<0.05	<0.05	**1.4**	3.3	**5.8**	14.5
Porirua at Kenepuru	11/05/2006	Composite	46	<1	1	<0.05	<0.05	0.7	2.5	**8.6**	18.7

[1] Samples collected from 13 March 2007 onwards were analysed for total recoverable metals.

Table 3.2 *cont*: Dissolved and total[1] metal concentrations (µg/L) in 'base flow' (winter), 'first flush' and composite water samples collected from urban streams over the period October 2005 to May 2007. Dissolved concentrations shown in bold font and shaded grey exceeded ANZECC (2000) toxicity trigger values (95% protection level) and USEPA (2006) CMC respectively.

Stream and Sample Location	Date	Sample Type	Mercury (Hg)		Nickel (Ni)		Lead (Pb)		Zinc (Zn)	
			Diss.	Total	Diss.	Total	Diss.	Total	Diss.	Total
Ngauranga at bottom of gorge	19/10/2005	First Flush	-	0.14	-	8.2	-	42.3	-	537
Ngauranga at bottom of gorge	19/10/2005	Composite	-	<0.08	-	5.2	-	35.5	-	378
Ngauranga at bottom of gorge	09/05/2006	Base flow	<0.08	<0.08	<0.5	<0.5	<0.1	0.4	**11**	16
Kaiwharawhara at School Rd	24/11/2005	First Flush	-	<0.08	<0.5	0.8	0.4	11.9	**18**	83
Kaiwharawhara at School Rd	24/11/2005	Composite	-	<0.08	<0.5	<0.5	0.5	3	**16**	34
Kaiwharawhara at School Rd	09/05/2006	Base flow	<0.08	<0.08	<0.5	<0.5	<0.1	<0.1	7	7
Owhiro u/s Owhiro Bay Rd	06/12/2005	First Flush	<0.08	<0.08	<0.5	9.6	0.2	84.4	**9**	436
Owhiro u/s Owhiro Bay Rd	06/12/2005	Composite	<0.08	<0.08	<0.5	11	0.5	104	**11**	418
Owhiro u/s Owhiro Bay Rd	09/05/2006	Base flow	<0.08	<0.08	<0.5	<0.5	<0.1	0.3	2	3
Opahu d/s Nikau Grove	23/02/2006	First Flush	<0.08	<0.08	<1	<3	<0.2	3.9	**68**	106
Opahu d/s Nikau Grove	23/02/2006	Composite	<0.08	<0.08	<3	<3	5	6.6	**83**	150
Opahu d/s Nikau Grove	09/05/2006	Base flow	<0.08	<0.08	<0.5	<0.5	0.3	1	**80**	82
Porirua at Wingfield Place	09/05/2006	Base flow	<0.08	<0.08	<0.5	<0.5	0.1	0.4	**17**	21
Porirua at Wingfield Place	23/05/2006	First Flush	<0.08	<0.08	<0.5	0.6	0.3	2.7	**43**	72
Porirua at Wingfield Place	23/05/2006	Composite	<0.08	<0.08	<0.5	0.7	0.2	4.6	**33**	78
Porirua at Wingfield Place	04/06/2006	First Flush	<0.08	<0.08	<0.5	2.7	0.4	14.9	**31**	145
Porirua at Wingfield Place	04/06/2006	Composite	<0.08	<0.08	<0.5	1.1	0.3	8	**56**	137
Porirua at Wingfield Place	13/03/2007	First Flush	<0.08	0.17	1.3	10.4	0.4	119	**51**	821
Porirua at Wingfield Place	13/03/2007	Composite	<0.08	<0.08	0.5	3.4	0.2	13.6	**17**	110
Porirua at Wingfield Place	13/04/2007	First Flush	<0.08	<0.08	<0.5	1.6	0.8	12.3	**135**	264
Porirua at Wingfield Place	13/04/2007	Composite	<0.08	<0.08	<0.5	1.7	0.3	5.8	**63**	107
Porirua at Wingfield Place	27/04/2007	First Flush	<0.08	<0.08	0.5	1.6	0.3	10.8	**34**	157
Porirua at Wingfield Place	27/04/2007	Composite	<0.08	<0.08	0.5	0.8	0.3	3.1	**22**	48
Porirua at Wingfield Place	03/05/2007	First Flush	<0.08	<0.08	<0.5	1.3	0.6	12	**59**	154
Porirua at Wingfield Place	03/05/2007	Composite	<0.08	<0.08	<0.5	2	0.3	13.8	**28**	122
Porirua at Glenside	14/03/2007	First Flush	<0.08	0.16	0.5	15.6	0.6	168	**40**	1,170
Porirua at Glenside	14/03/2007	Composite	<0.08	<0.08	1.4	7.1	0.3	29.7	**53**	274
Porirua at No. 2 Tunnel	24/01/2006	First Flush	-	<0.08	0.6	1.1	0.4	2.7	**39**	65
Porirua at No. 2 Tunnel	24/01/2006	Composite	-	<0.08	<0.5	1.4	0.3	6.4	**20**	74
Porirua at No. 2 Tunnel	09/05/2006	Base flow	<0.08	<0.08	<0.5	<0.5	<0.1	0.2	7	8
Porirua at Kenepuru	27/03/2006	First Flush	<0.08	<0.08	<0.5	0.8	0.2	3.6	**41**	83
Porirua at Kenepuru	27/03/2006	Composite	<0.08	<0.08	1.8	1.4	1.1	5.5	**46**	47
Porirua at Kenepuru	07/04/2006	First Flush	<0.08	<0.08	0.6	0.8	0.4	3.3	**79**	105
Porirua at Kenepuru	07/04/2006	Composite	<0.08	<0.08	0.5	0.7	0.3	2.3	**33**	54
Porirua at Kenepuru	08/04/2006	First Flush	<0.08	<0.08	<0.5	0.7	0.3	3	**43**	63
Porirua at Kenepuru	08/04/2006	Composite	<0.08	0.18	0.7	16.2	0.4	54.7	**16**	319
Porirua at Kenepuru	25/04/2006	First Flush	<0.08	<0.08	<0.5	2	0.3	16.2	**37**	148
Porirua at Kenepuru	25/04/2006	Composite	<0.08	<0.08	<0.5	2.6	0.2	11.1	**16**	116
Porirua at Kenepuru	09/05/2006	Base flow	<0.08	<0.08	0.6	0.7	0.2	0.6	**43**	48
Porirua at Kenepuru	10/05/2006	First Flush	<0.08	<0.08	<0.5	0.7	0.1	2.9	**29**	59
Porirua at Kenepuru	10/05/2006	Composite	<0.08	<0.08	<0.5	0.9	0.3	2.5	**26**	52
Porirua at Kenepuru	11/05/2006	First Flush	<0.08	<0.08	<0.5	0.9	0.4	8.5	**57**	110
Porirua at Kenepuru	11/05/2006	Composite	<0.08	<0.08	<0.5	1.4	0.2	6.3	**33**	81

[1] Samples collected from 13 March 2007 onwards were analysed for total recoverable metals.

3.4.2 Total suspended solids

Total suspended solid concentrations ranged from below laboratory detection (<3 g/m^3) in the 'base flow' stream samples to 909 g/m^3 in a composite sample from Owhiro Stream (Wellington City) (Figure 3.4). In most cases where 'first flush' and composite stream samples were tested for suspended solids, the 'first flush' sample concentration was significantly greater than the composite sample concentration.

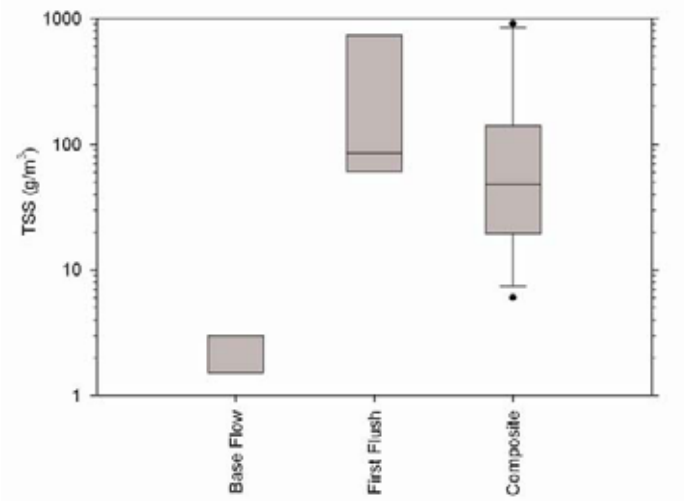

Figure 3.4: Boxplot summarising total suspended solid concentrations recorded in 'base flow' (winter, *n*=7), 'first flush' (*n*=6), and composite (*n*=16) water samples collected from urban streams over the period October 2005 to May 2007. Note the break on the y-axis.

- the lower and upper boundaries of the box represent the lower (25%) and upper (75%) quartiles of the data respectively
- the horizontal line inside the box represents the median value
- the "whiskers" extending below and above the box represent the 5th and 95th percentile values respectively
- the black dots represent outliers

3.4.3 Dissolved and total metals

Copper and zinc were consistently detected in all stream water samples, including the seven 'base flow' samples. In addition, the dissolved concentrations of both metals exceeded their respective ANZECC (2000) 95% toxicity trigger values in all 'first flush' and composite samples, and in three of the seven 'base flow' samples (Table 3.1, Figure 3.5). Dissolved copper concentrations in two 'first flush' and eight composite samples also exceeded the USEPA (2006) hardness-adjusted CMC of 6.0 µg/L. Dissolved zinc concentrations exceeded the USEPA (2006) hardness-adjusted CMC of 56.8 µg/L in nine samples; one 'base flow' sample from Opahu Stream, five 'first flush' samples and three composite samples. During one runoff event in the Porirua Stream at Wingfield Place (Johnsonville), the 'first flush' dissolved zinc concentration exceeded the CMC by an order of magnitude.

Total copper and both dissolved and total zinc concentrations were generally highest in the 'first flush' water samples. In contrast, dissolved copper concentrations tended to be highest in the composite samples (Figure 3.5).

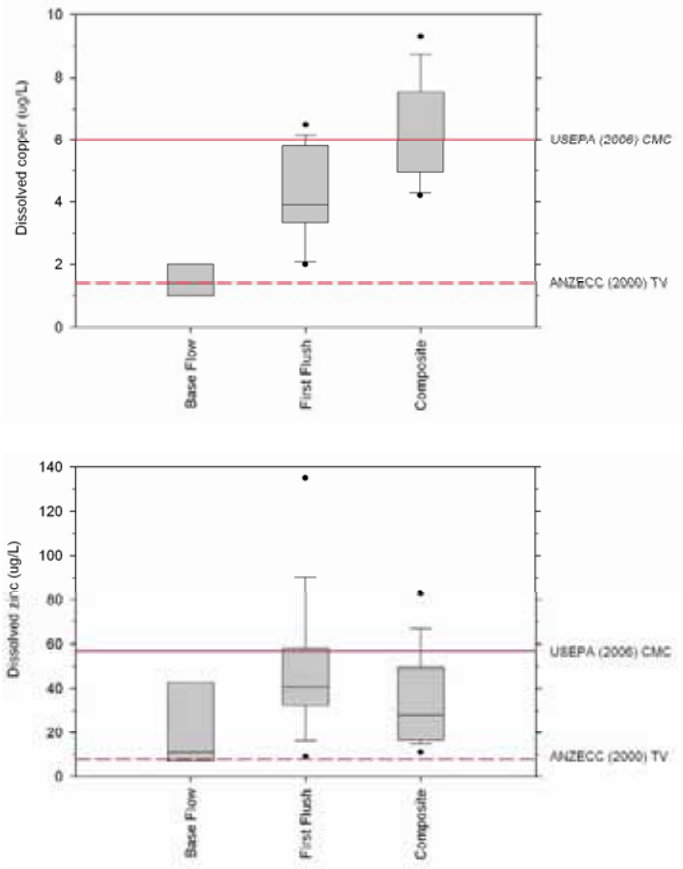

Figure 3.5: Boxplots summarising dissolved copper (top) and zinc concentrations recorded in winter 'base flow' (*n*=7), 'first flush' (*n*=17), and composite (*n*=17) stream samples collected over October 2005 to May 2007

Total and dissolved lead were detected in most stream water samples, the exceptions being in one and four 'base flow' samples respectively, and in the 'first flush' sample from the Opahu Stream. However, no dissolved lead concentrations exceeded the ANZECC (2000) toxicity trigger value (Figure 3.6), nor the USEPA (2006) hardness-adjusted CMC of 25.2 µg/L. Total lead concentrations were generally highest in the 'first flush' samples.

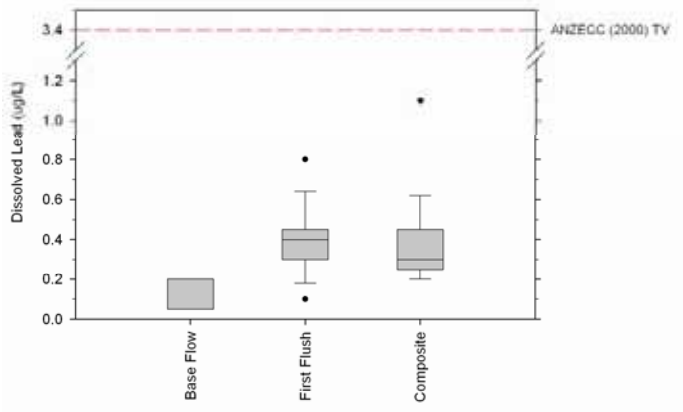

Figure 3.6: Boxplot summarising dissolved lead concentrations recorded in 'base flow' (winter, *n*=7), 'first flush' (*n*=17), and composite (*n*=17) water samples collected from urban streams over the period October 2005 to May 2007. Note the break on the y-axis.

Chromium was detected in almost all 'first flush' and composite water samples. Where detected, dissolved chromium concentrations nearly always exceeded the ANZECC (2000) toxicity trigger value (Figure 3.7), although it should be remembered that this trigger value is conservative as it assumes all of the chromium is present as chromium VI. In two of the 'first flush' samples from Porirua Stream at Wingfield Place the dissolved chromium concentration exceeded the USEPA (2006) chromium VI CMC of 16 µg/L[11].

On seven occasions dissolved chromium concentrations greater than the total chromium concentration were recorded. It is unclear what caused these erroneous results, but in a few cases the differences between the dissolved and total concentrations were deemed to be within acceptable analytical variation.

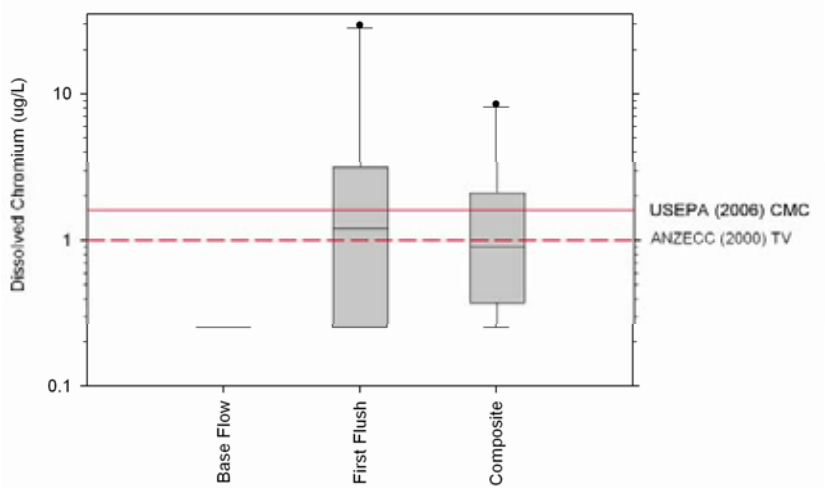

Figure 3.7: Boxplot summarising dissolved chromium concentrations recorded in 'base flow' (winter, *n*=7), 'first flush' (*n*=17), and composite (*n*=17) water samples collected from urban streams over the period October 2005 to May 2007. Note the logarithmic scale on the y-axis.

Nickel was also detected in most of the 'first flush' and composite water samples, with concentrations generally highest in the 'first flush' samples. However, no dissolved nickel concentrations exceeded the ANZECC (2000) toxicity trigger value and, in many cases, dissolved concentrations were below laboratory detection limits (Table 3.2).

Cadmium was detected in eleven 'first flush' and ten composite samples, although rarely in the dissolved form. In all instances the dissolved concentration was below the ANZECC (2000) toxicity trigger value (Table 3.2).

Arsenic was detected in 13 of the 18 'first flush' and composite water samples, but only as total arsenic. The highest concentration (13 µg/L) was recorded in the 'first flush' sample from the Porirua Stream at Glenside (Table 3.2).

Mercury was detected in three 'first flush' water samples and one composite water sample, but only as total mercury (Table 3.2).

[11] One of these two sample results may be a result of analytical error as the total chromium concentration recorded from the same sample was an order of magnitude lower.

3.4.4 Total contaminant loads

With the stream flow estimates (obtained by applying Manning's Equation to the ISCO automatic sampler water level records) deemed unreliable, total contaminant loads for individual runoff events were only able to be calculated for the one site with a Greater Wellington automated flow recorder nearby: Porirua Stream at Kenepuru. Sampling was conducted at this site during six runoff events over the period March to May 2006, with total rainfall ranging from 1.8 mm to 59 mm.

The total contaminant load for each of the six runoff events was conservatively calculated by multiplying the composite water sample contaminant concentration (as an estimate of the average concentrations during the 'fresh') by the estimated volume of runoff for the event. The runoff component was estimated by applying a base flow separation method to remove base flow from the total measured flow (see example in Figure 3.8). The estimated runoff volume and total suspended solids, copper, lead and zinc loads are shown in Table 3.3.

Of the six runoff events, two produced significant instream contaminant loads: the event on 8 April (59 mm of rainfall, generally one or two events of this magnitude per year) and the event on 25 April (32 mm of rainfall; in the order of six events of this magnitude can be expected each year). The remaining events were considered insignificant from a hydrological perspective, with many of this magnitude expected each year.

The dissolved copper, lead and zinc loads during the two larger runoff events are low relative to their respective total metal fractions (0.7% – 38% of the total load), indicating that the majority of the metal load is associated with the particulate fraction.

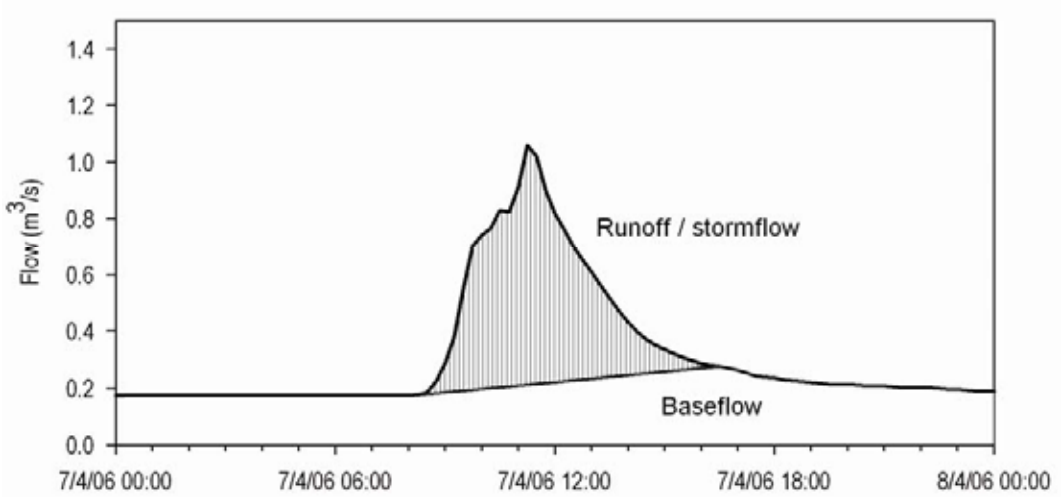

Figure 3.8: Hydrograph for Porirua Stream at Town Centre, showing the separation of baseflow from runoff, for the runoff event on 7 April 2006 (water samples were taken a short distance upstream of the flow recorder at the site Porirua Stream at Kenepuru)

Table 3.3: Calculated loads of total suspended solids (TSS) and selected heavy metals[1] in the Porirua Stream at Kenepuru for six runoff events in the period March to May 2006

Date of event	Estimated runoff volume (m^3)	Total instream contaminant load (kg)						
		TSS	Diss Cu	Total Cu	Diss Pb	Total Pb	Diss Zn	Total Zn
27 March 2006	11,130	189	0.10	0.09	0.01	0.06	0.51	0.52
7 April 2006	9,560	76	0.05	0.06	<0.01	0.02	0.32	0.52
8 April 2006	236,150	193,407	1.32	9.59	0.09	12.92	3.78	75.33
25 April 2006	106,640	12,690	0.74	1.94	0.02	1.18	1.71	12.37
10 May 2006	4,570	87	0.02	0.03	<0.01	0.01	0.12	0.24
11 May 2006	15,370	707	0.13	0.29	<0.01	0.10	0.51	1.24

[1] Metal concentrations below analytical detection limits were assumed to be half the detection limit.

3.5 Discussion

The results confirm the regular occurrence of heavy metal contaminants in the wet-weather flow of the five urban streams included in this investigation. One or more heavy metals were detected in all 18 'first flush' and composite stream water samples at concentrations significantly higher than those recorded in 'base flow' samples. Copper and zinc were the most commonly detected metals, followed by lead, chromium and nickel. Cadmium and arsenic were also detected in some samples, although typically not in the dissolved form. Mercury was only detected in four samples and as total mercury. Concentrations of total suspended solids and most dissolved metals, with the notable exception of copper, tended to be higher in the 'first flush' samples than in the composite samples.

Dissolved concentrations of copper, zinc and to a lesser extent, chromium, were present in the majority of wet weather stream flow samples at concentrations above ANZECC (2000) toxicity trigger values (95% protection level). In addition, dissolved copper and/or zinc concentrations were present above ANZECC trigger values in the 'base flow' samples from the Porirua, Kaiwharawhara, Ngauranga and Opahu streams. Similarly elevated concentrations of these metals have been found in recent RSoE samples from the Porirua and Kaiwharawhara streams (Greater Wellington, unpublished data), suggesting that dissolved copper and/or zinc concentrations in 'base flow' conditions in these streams frequently exceed chronic toxicity or sustained exposure criteria for aquatic life[12].

As well as exceeding ANZECC trigger values on all wet weather sampling occasions, dissolved copper and zinc concentrations also exceeded their respective acute-based USEPA (2006) CMCs in around half of the stream water samples. This suggests high potential for adverse effects on aquatic life during runoff events in the streams studied. Cameron (2001) investigated water quality in the Porirua Stream catchment during two runoff events and came to a similar conclusion; acid-soluble copper and zinc concentrations were found above CMCs in stormwater and stream water samples from several sites.

[12] Note that Fitzpatrick (2008) has suggested the ANZECC toxicity trigger values for zinc may be overly conservative.

The widespread detection of elevated copper and zinc in stream waters during runoff events is not surprising. As noted in subsection 2.5, both metals are reasonably ubiquitous in urban environments, the primary sources in urban stormwater being vehicle brake pad wear and unpainted galvanized roofs respectively. Architectural uses (e.g., copper spouting) and vehicle tyre wear are key secondary sources (Timperley[13], pers. comm. 2008).

Although no specific assessments of aquatic biota were undertaken as part of this investigation, Greater Wellington's RSoE monitoring programme assesses macroinvertebrate community health annually at several sites on streams included in this investigation. RSoE data for the Porirua Stream at Wall Park (Kenepuru) and the Kaiwharawhara Stream at Ngaio Gorge consistently show an impacted invertebrate fauna; the sensitive EPT groups (Ephemeroptera, Plecoptera and Trichoptera) are often poorly represented and macroinvertebrate community index scores indicative of 'moderate pollution' (e.g., Perrie 2007, Perrie 2008). Elevated concentrations of toxicants such as copper and zinc are likely to be a contributing factor to the impacted invertebrate communities at these sites. High stream flows associated with stormwater runoff from impervious surfaces will also be a key factor limiting the biological communities present; high stream flows can wash away invertebrates and also cause extensive substrate movement, reducing habitat stability (Suren & Elliott 2004).

Despite limited data, conservative estimates for the Porirua Stream at Kenepuru indicate that substantial total suspended solids loads can flow through the stream and into the Porirua Harbour during runoff events. The majority of the heavy metal load in the two more significant runoff events measured in this investigation was associated with the particulate fraction, highlighting the importance of sediments in transporting heavy metal contaminants to the harbour. Evidence of rapid transport of the finer sediments downstream during storm events is provided by the findings of the streambed sediment quality investigation; there was a general lack of very fine sediments (i.e., silts and clays) in many streambeds, including that of the Porirua Stream (refer subsection 2.5).

Although significant relative to the other runoff events for which contaminant loads were estimated, the two events with the highest contaminant loads are not overly significant from a hydrological perspective (average recurrence intervals of less than one year). Therefore the potential for even greater instream contaminant concentrations and loads during higher magnitude storms is very high. This will of course depend on a number of factors, including antecedent weather conditions, which are expected to influence 'first flush' stream contaminant concentrations.

[13] Dr Mike Timperley, Timperley Associates (former Stormwater Action Team Leader, Auckland Regional Council).

4. Conclusions and recommendations

The results of the streambed sediment and wet-weather flow investigations have identified that significant contamination of urban streams arises as a result of stormwater runoff. Elevated concentrations of one or more contaminants were found in surface sediments of almost all of the streambed sites sampled, and in all 'first flush' and composite stream water samples taken during runoff events.

Zinc, and to a lesser extent lead, were the most common metals present in streambed sediments at concentrations exceeding ANZECC (2000) ISQG–Low trigger values. Concentrations of Total HMW PAHs and Total PAHs also exceeded ISQG–Low trigger values at some sites, and almost all of the 29 sites sampled in 2005 and 24 sites sampled in 2006 recorded concentrations of Total DDT above the ISQG–Low trigger value. Contaminant concentrations in sediment samples from several stream sites exceeded ISQG–High trigger values, indicating probable adverse effects on benthic biota:

- Duck Creek at Observatory Drive in Pauatahanui (Total DDT – in 2006 only)
- Porirua Stream at Wingfield Place in Johnsonville (zinc) and Glenside (DDT)
- Kenepuru Stream upstream of State Highway 1 in Porirua (Total HMW PAHs – in 2006 only)
- Kaiwharawhara Stream at Otari Bush (Total HMW PAHs – in 2005 only) and School Road in Wellington City (zinc – in 2005 only)
- Opahu Stream in Lower Hutt (zinc – in 2005 only, and Total HMW PAHs)
- Makoura Stream in Masterton (Total HMW PAHs and Total PAHs)
- Opaki Stream in Masterton (Total HMW PAHs and Total PAHs).

Copper and zinc were the most commonly detected heavy metals in stream waters during both 'base flow' and runoff sampling events. In addition to dissolved concentrations of both metals being consistently above ANZECC (2000) toxicity trigger values in runoff samples, dissolved concentrations of one or both of these metals were above the trigger values in 'base flow' samples from Porirua, Kaiwharawhara, Ngauranga and Opahu streams. This suggests that dissolved copper and/or zinc concentrations in these streams frequently exceed chronic toxicity criteria for aquatic life.

The dissolved concentrations of copper and zinc also exceeded their respective USEPA (2006) CMCs in around half of the stream water samples collected during runoff events, indicating the likelihood of acute toxicity effects on stream life. Most of the runoff events sampled were not overly significant from a hydrological perspective, suggesting even greater contaminant concentrations and loads are possible in higher magnitude events, particularly if the rainfall is preceded by a prolonged period of fine weather.

A further (and perhaps greater) risk the contaminants pose to aquatic ecosystems is to the benthic biota in depositional coastal environments. Many of the contaminants are commonly associated with the particulate fraction in stormwater, as evidenced by the contaminant load calculations for the Porirua Stream in the wet-weather flow investigation. However, in most cases the streambeds sampled contained little fine sediment, indicating that much of this material – and its associated contaminant load – is not retained in the streams, but is rapidly flushed

through the system and into downstream receiving environments. Based on available sediment quality data for both Porirua and Wellington harbours, it is evident that harbour sediments are a major 'sink' for the contaminants entering urban streams in stormwater.

4.1 Recommendations

1. In any future streambed sediment surveys:
    - utilise a replicated sampling design to assist with differentiating between 'within-site' and 'between-site' variability;
    - include sampling of interstitial sediment and biofilms to improve assessment of the potential exposure risk;
    - obtain a breakdown of particle sizes in the 63–500 μm sediment fraction to improve definition of the sediment present in streambed samples; and
    - include analysis of Standard Reference Materials as part of the quality assurance assessment for organic contaminants.

2. In any future 'first-flush' or wet weather stream flow contaminant investigations:
    - collect at-site flow data;
    - collect both a 'first flush' sample and a flow-proportioned composite sample for the entire runoff event; and
    - sample a range of different magnitude runoff events

    to facilitate calculation of total contaminant loads entering downstream receiving environments.

3. Continue monitoring dissolved heavy metals (in particular, copper, lead and zinc) at Greater Wellington's RSoE stream sites draining urban catchments beyond the current 12-month 'trial' period.

4. Continue the existing Porirua and Wellington Harbour subtidal sediment quality monitoring programmes, ensuring benthic fauna sampling is undertaken in tandem with sediment contaminant sampling, and with sufficient replication to enable early detection of adverse effects on benthic communities.

5. References

ANZECC. 2000. *Australia 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 Council of Australia and New Zealand, Canberra.

Cameron, D. 2001. *Targeted investigation of Porirua Stream water and sediment quality.* A report prepared for Wellington Regional Council by Montgomery Watson New Zealand Limited. v + 15 p. + appendices (13 p.).

Fitzpatrick, M. 2008. A review of the ANZECC 2000 trigger values for zinc. In *Proceedings of the New Zealand Water & Waste Association Stormwater Conference,* Rotorua, 15-16 May 2008. 17 p.

Glasby, P.; Moss, R.L.; Stoffers, P. 1990. Heavy-metal pollution in Porirua Harbour, New Zealand. *New Zealand Journal of Marine and Freshwater Research*, 24:233-237.

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. v + 80 p. + appendices (17 p.).

Perrie, A. 2007. *The state of water quality in selected rivers and streams in the Wellington region, 2003-2006.* Greater Wellington Regional Council, Technical Publication No. GW/EMI-T-07/218. 51 p. + appendices (13 p.).

Perrie, A. 2008. *Annual freshwater quality monitoring report for the Wellington region, 2007/08.* Greater Wellington Regional Council, Technical Publication No. GW/EMI-G-08/161. 17 p. + appendices (27 p.).

Pilotto, P.J. 1996. *Metal pollution in Wellington Harbour.* Unpublished M.Sc. thesis, Victoria University of Wellington. vi + 102 p.

Ray, D.; Timperley, M.; Williamson, B. 2003. *Long term marine sediment monitoring programme for the Wellington and Porirua Harbours*. A report prepared for the Wellington Regional Council. 15 p. [NIWA project no. WRC04201].

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. iv + 108 p.

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. 74 p. + appendices on CD-rom.

Suren, A.; Elliott, S. 2004. Impacts of urbanisation on streams. In Harding, J.; Mosley, P.; Pearson, C. & Sorrell, B. (eds.) *Freshwaters of New Zealand*, pp. 35.1-35.17. Christchurch, New Zealand: New Zealand Hydrological Society Inc. and New Zealand Limnological Society Inc.

USEPA. 2006. *National recommended water quality criteria*. United States Environmental Protection Agency. 21 p. + appendices (3 p.).

Acknowledgements

Bruce Croucher, former Greater Wellington environmental scientist, conducted a significant amount of the fieldwork. Nick Boyens assisted with installing and maintaining the ISCO automatic sampler, and downloading recorded data.

Dr Michael Ahrens (National Institute of Water and Atmospheric Research) provided an assessment of the streambed PAH data.

Gary Stephenson (Coastal Marine Ecology Consultants) provided valuable peer-review comments on a draft version of this report.

Appendix 1: Streambed sediment sampling locations

Site No.	Site Name	City/District	Easting	Northing
SMS001	Karori S @ Makara Peak	Wellington	2654234	5988585
SMS002	Kaiwharawhara S @ Otari Bush	Wellington	2657054	5991834
SMS003	Kaiwharawhara S @ Ngaio Gorge	Wellington	2659215	5992733
SMS004	Kaiwharawhara S @ School Rd	Wellington	2659805	5992637
SMS005	Owhiro S @ Owhiro Bay	Wellington	2657148	5983295
SMS006	Ngauranga S @ Bottom of Gorge	Wellington	2661949	5994056
SMS007	Porirua S @ Redwood Stn	Wellington	2663261	6001897
SMS008	Porirua S @ Glenside	Wellington	2663310	6000077
SMS009	Porirua S @ Kenepuru playing field	Porirua	2664678	6005109
SMS010	Mitchell S d/s of Kenepuru Dr	Porirua	2664304	6004790
SMS011	Kenepuru S u/s SH 1	Porirua	2664982	6006158
SMS012	Pauatahanui S @ SH 58	Porirua	2671283	6008271
SMS013	Browns S @ Browns Bay Res.	Porirua	2668014	6009410
SMS014	Duck Ck @ Discovery Dr	Porirua	2669147	6008408
SMS015	Duck Ck @ Observatory Rd	Porirua	2669522	6009188
SMS020	Black S @ Rowe Rd	Hutt	2673380	5990902
SMS021	Opahu S @ Nikau Gr	Hutt	2669708	5996858
SMS022	Stokes Valley S d/s Eastern Hutt Rd	Hutt	2676136	6003214
SMS023	Hulls Ck @ Field St	Hutt	2678509	6004626
SMS024	Mawaihakona S @ Kiwi St	Hutt	2679090	6005340
SMS025	Wharemauku S u/s Tui Rd	Kapiti	2677176	6030417
SMS026	Tikotu S @ Meredith Way	Kapiti	2679028	6033937
SMS027	Mangapouri S opp. St Paul's School	Kapiti	2690775	6048922
SMS028	Mangapouri S d/s Anzac Rd	Kapiti	2091375	6047953
SMS029	Mangapouri S d/s County Lane	Kapiti	2692368	6047211
SMS030	Makoura S d/s Makora Rd	Masterton	2734118	6023673
SMS031	Opaki S d/s Colombo Rd	Masterton	2733555	6023535
SMS032	Kuripuni S d/s Colombo Rd	Masterton	2735350	6025191
SMS033	Waikakariki S d/s Lincoln Rd	Carterton	2721014	6016676
SMS034	Horokiri S u/s Grays Rd	Porirua	2670336	6010717
SMS035	Kakaho S u/s Grays Rd	Porirua	2669123	6011558
SMS037	Duck Ck u/s Whitby Lakes	Porirua	2668817	6007743
SMS038	Kaiwharawhara S @ Trelissick Pk	Wellington	2658481	5992780
SMS039	Porirua S @ No. 2 Tunnel	Wellington	2662653	5999022
SMS040	Porirua S @ Wingfield Pl	Wellington	2661976	5998050
SMS041	Ration Ck @ Paekakariki Hill Rd	Porirua	2671130	6010407
SMS042	Duck Ck @ Footbridge	Porirua	2669556	6009214

Appendix 2: Analytical methods

Table A2.1: Streambed sediments

Variable	Method	Detection Limit
Sediment Texture (2 mm, 63 µm sieves)	Sieving, gravimetric. All drying 35°C, overnight.	N/A
Total Organic Carbon (TOC)	10% HCl, hotplate 2hrs, acid pretreatment to remove carbonates if present, Elementar Combustion Analyser.	0.05 g/100g dry wt
Total Recoverable Metals	Total Recoverable digest Nitric / hydrochloric acid digestion. US EPA 200.2.	0.01 – 0.4 mg/kg
Polycyclic Aromatic Hydrocarbons (PAHs)	Sonication Extraction, silica gel cleanup, GC-MS selected ion monitoring quantitation. US EPA 3540 & 3630.	N/A
Organochlorine pesticides (OCPs)	Sonication extraction, GPC / Florisil cleanup & GC-ECD/ECD. Chlordane = (cis + trans) x 100/42.	N/A

Table A2.2: Wet-weather stream flow water samples

Variable	Method	Detection Limit
Total Suspended Solids (TSS)	Filtration (GF/C, 1.2 µm), retained residue dried at 103-105 ˚C, Gravimetric. APHA 2540 D 20th ed. 1998.	3 g/m^3
Dissolved Metals (except mercury)	Filtered (0.45 µm) sample. ICP-MS. APHA 3125B 20th ed. 1998.	0.05 – 1 µg/L
Dissolved Mercury	Filtered (0.45 µm) sample. Permanganate / Persulphate digestion. Analysis by FIMS.	0.08 µg/L
Total Recoverable Metals	Nitric acid extraction, 85 ˚C, 2.75 hr, ICP-MS. APHA 3125B 20th ed. 1998.	0.05 – 1 µg/L
Total Metals (except mercury)	Nitric acid extraction (APAHA 3030 E 20th ed. 1998). ICP-MS. APHA 3125B 20th ed. 1998.	0.05 – 1 µg/L
Total Mercury	Permanganate / Persulphate digestion. Analysis by FIMS. US EPA 245.2.	0.08 µg/L

Appendix 3: Streambed sediment analytical results

Results of organic analyses not presented in Section 2.

Table A3.1: Polycyclic aromatic hydrocarbons (µg/kg dry weight), 2005

Site No. & Date	Acenaphthene	Acenaphthylene	Anthracene	Benzo[a]anthracene	Benzo[a]pyrene (BAP)	Benzo[b]fluoranthene	Benzo[g,h,i]perylene	Benzo[k]fluoranthene	Chrysene	Dibenzo[a,h]anthracene
SMS001 17/05/05	<2	74	95	232	287	407	166	140	246	76
SMS002 17/05/05	45	54	203	816	850	1,180	517	426	979	205
SMS003 17/05/05	3	34	66	408	504	620	383	193	398	109
SMS004 17/05/05	<2	3	4	15	25	35	24	12	21	8
SMS005 17/05/05	<2	5	7	23	26	32	19	12	26	7
SMS006 17/05/05	<2	<2	3	7	14	18	21	6	10	8
SMS007 17/05/05	<2	<2	<2	5	8	10	6	4	10	3
SMS008 17/05/05	<2	<2	<2	<2	2	4	4	<2	6	<2
SMS009 17/05/05	<2	<2	<2	5	7	11	6	5	11	2
SMS010 17/05/05	<2	<2	<2	8	12	25	15	9	17	6
SMS011 17/05/05	2	46	56	306	355	460	221	170	347	94
SMS012 18/05/05	<2	<2	<2	7	12	17	9	7	11	4
SMS013 17/05/05	<2	<2	<2	3	4	8	7	2	7	<2
SMS014 17/05/05	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
SMS015 17/05/05	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
SMS020 18/05/05	<2	<2	<2	<2	71	83	61	30	21	27
SMS021 18/05/05	28	179	542	1,140	1,420	2,200	1,220	739	1,770	289
SMS022 18/05/05	<2	<2	<2	2	3	5	3	2	5	<2
SMS023 18/05/05	<5	<5	<5	35	38	70	41	23	49	11
SMS024 18/05/05	<4	7	8	95	111	173	80	52	94	26
SMS025 18/05/05	<2	6	6	26	28	34	17	15	28	6
SMS026 18/05/05	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
SMS027 18/05/05	<2	6	3	11	13	23	20	9	15	4
SMS028 18/05/05	<4	17	11	60	70	88	48	34	65	13
SMS029 18/05/05	10	136	122	287	254	329	137	129	239	36
SMS030 18/05/05	220	280	620	2,040	2,480	3,110	1,800	1,150	2,080	390
SMS031 18/05/05	1,900	1,830	7,950	16,400	19,300	21,700	12,700	7,870	17,400	2,910
SMS032 18/05/05	196	185	614	1,880	2,560	3,280	2,110	1,200	2,280	439
SMS033 18/05/05	30	190	260	2,610	3,590	3,820	2,340	1,350	2,570	520

Table A3.1 *cont.*: Polycyclic aromatic hydrocarbons (µg/kg dry weight), 2005

Site No. & Date	Fluoranthene	Fluorene	Indeno(1,2,3-c,d)pyrene	Naphthalene	Phenanthrene	Pyrene
SMS001 17/05/05	473	4	245	<8	190	431
SMS002 17/05/05	1,550	41	585	9	691	1,650
SMS003 17/05/05	847	6	416	20	134	873
SMS004 17/05/05	38	<2	30	<8	12	39
SMS005 17/05/05	56	<2	25	<8	28	54
SMS006 17/05/05	15	<2	23	<8	7	16
SMS007 17/05/05	10	<2	8	<8	6	11
SMS008 17/05/05	5	<2	3	<8	6	5
SMS009 17/05/05	10	<2	7	<8	9	11
SMS010 17/05/05	16	<2	18	<9	5	17
SMS011 17/05/05	687	13	290	<9	281	668
SMS012 18/05/05	12	<2	14	<9	2	11
SMS013 17/05/05	10	<2	4	<9	6	10
SMS014 17/05/05	<2	<2	<2	<9	<2	<2
SMS015 17/05/05	<2	<2	<2	<10	<2	<2
SMS020 18/05/05	17	<2	91	<9	4	20
SMS021 18/05/05	2,940	139	1,030	40	1,770	2,940
SMS022 18/05/05	4	<2	3	<8	<2	4
SMS023 18/05/05	68	<5	33	<30	32	71
SMS024 18/05/05	139	<4	69	<20	47	139
SMS025 18/05/05	44	<2	17	<10	21	45
SMS026 18/05/05	<2	<2	<2	<9	<2	<2
SMS027 18/05/05	25	<2	12	<10	12	29
SMS028 18/05/05	95	<4	43	<20	25	104
SMS029 18/05/05	697	14	139	<20	190	578
SMS030 18/05/05	6,850	340	1,740	150	6,380	5,400
SMS031 18/05/05	48,700	3,230	11,700	1,100	42,800	45,800
SMS032 18/05/05	5,210	250	1,870	140	3,690	5,160
SMS033 18/05/05	3,710	50	2,110	200	860	4,000

Table A3.2: Polycyclic aromatic hydrocarbons (µg/kg dry weight), 2006

Site No. & Date	Acenaphthene	Acenaphthylene	Anthracene	Benzo[a]anthracene	Benzo[a]pyrene (BAP)	Benzo[b]fluoranthene	Benzo[g,h,i]perylene	Benzo[k]fluoranthene	Chrysene	Dibenzo[a,h]anthracene
SMS001 2/06/06	<2	5	6	21	29	50	28	10	21	5
SMS002 2/06/06	<2	7	8	37	44	75	44	20	36	8
SMS003 2/06/06	2	24	33	133	147	253	128	78	126	27
SMS004 2/06/06	4	20	25	86	118	196	105	62	105	21
SMS005 2/06/06	<2	9	14	48	56	93	50	24	51	10
SMS006 2/06/06	<2	18	22	56	63	106	58	28	54	11
SMS007 2/06/06	<2	<2	<2	3	3	11	6	<2	5	<2
SMS008 2/06/06	<2	<2	<2	3	3	11	6	<2	5	<2
SMS009 2/06/06	<2	2	2	13	13	26	13	3	13	3
SMS010 2/06/06	2	3	7	37	47	88	44	22	42	10
SMS011 2/06/06	5	65	162	1,140	847	1,620	591	525	1,060	150
SMS012 2/06/06	<2	11	4	13	41	61	43	21	11	10
SMS013 2/06/06	<2	<2	<2	2	3	7	8	<2	2	<2
SMS014 2/06/06	<2	<2	<2	<2	2	4	8	<2	2	<2
SMS015 2/06/06	<2	<2	<2	<2	<2	2	4	<2	<2	<2
SMS021 2/06/06	67	471	595	1,350	1,560	2,110	1,210	714	1,420	218
SMS034 2/06/06	<2	<2	3	12	14	20	13	7	11	3
SMS035 2/06/06	<3	<3	<3	<3	<3	<3	<3	<3	<3	<3
SMS037 2/06/06	<4	<4	<4	5	6	11	13	<4	5	<4
SMS038 2/06/06	<2	18	24	58	90	128	78	45	60	20
SMS039 2/06/06	28	4	45	73	90	117	63	43	79	20
SMS040 2/06/06	<2	14	11	30	44	67	37	23	35	11
SMS041 2/06/06	<2	<2	<2	<2	<2	<2	2	<2	<2	<2
SMS042 2/06/06	<2	<2	<2	<2	<2	2	3	<2	<2	<2

Table A3.2 *cont.*: Polycyclic aromatic hydrocarbons (µg/kg dry weight), 2006

Site No. & Date	Fluoranthene	Fluorene	Indeno(1,2,3-c,d)pyrene	Naphthalene	Phenanthrene	Pyrene
SMS001 2/06/06	40	<2	17	<9	18	40
SMS002 2/06/06	76	<2	26	<8	19	76
SMS003 2/06/06	257	5	81	14	100	239
SMS004 2/06/06	262	8	67	<8	132	235
SMS005 2/06/06	112	3	30	<8	58	108
SMS006 2/06/06	113	8	31	<8	76	118
SMS007 2/06/06	5	<2	3	<8	4	6
SMS008 2/06/06	5	<2	3	<9	4	6
SMS009 2/06/06	20	<2	8	<8	9	20
SMS010 2/06/06	72	2	29	<8	26	69
SMS011 2/06/06	1,950	30	381	9	353	1,620
SMS012 2/06/06	10	<2	33	<8	4	12
SMS013 2/06/06	7	<2	2	<8	6	10
SMS014 2/06/06	2	<2	<2	<8	3	6
SMS015 2/06/06	<2	<2	<2	<10	<2	3
SMS021 2/06/06	4,530	287	875	67	3,790	4,430
SMS034 2/06/06	33	<2	9	<8	15	33
SMS035 2/06/06	<3	<3	<3	<20	<3	<3
SMS037 2/06/06	13	<4	4	<20	5	14
SMS038 2/06/06	126	3	57	<9	48	129
SMS039 2/06/06	184	23	51	<9	160	151
SMS040 2/06/06	44	<2	27	<9	14	46
SMS041 2/06/06	<2	<2	<2	<8	<2	2
SMS042 2/06/06	4	<2	<2	<9	2	3

Table A3.3: Organochlorine pesticides (µg/kg dry weight), 2005

Site No. & Date	Hexachlorobenzene	Alpha-BHC	Beta-BHC	Gamma-BHC (Lindane)	Delta-BHC	Heptachlor	Heptachlor epoxide	Aldrin	Dieldrin	Endrin	Endrin Aldehyde	Endosulfan I
SMS001 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS002 17/05/05	<1	<1	<1	4	<1	<1	<1	<1	4	<1	<1	<1
SMS003 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	3	<1	<1	<1
SMS004 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS005 17/05/05	<1	<1	<1	1	<1	<1	<1	<1	5	<1	<1	<1
SMS006 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS007 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS008 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS009 17/05/05	<1	<1	<1	2	<1	<1	<1	<1	<1	<1	<1	<1
SMS010 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS011 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS012 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS013 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS014 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS015 17/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS020 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS021 18/05/05	<1	<1	<1	2	<1	<1	<1	<1	4	<1	<1	<1
SMS022 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS023 18/05/05	<1	<1	<1	3	<1	<1	<1	<1	2	<1	<1	<1
SMS024 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS025 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS026 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
SMS027 18/05/05	<1	<1	<1	1	<1	<1	<1	<1	<1	<1	<1	<1
SMS028 18/05/05	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
SMS029 18/05/05	<1	<1	<1	3	<1	<1	<1	<1	2	<1	<1	<1
SMS030 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	1	<1	<1	<1
SMS031 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	13	<1	<1	<1
SMS032 18/05/05	<2	<2	<2	4	<2	<2	<2	<2	6	<2	<2	<2
SMS033 18/05/05	<1	<1	<1	<1	<1	<1	<1	<1	6	<1	<1	<1

Table A3.3 *cont.*: Organochlorine pesticides (µg/kg dry weight), 2005

Site No. & Date	Endosulfan II	Endosulfan sulphate	2,4'-DDE	2,4'-DDD	2,4'-DDT	4,4'-DDE	4,4'-DDD	4,4'-DDT	Total Chlordane ((cis+trans)*100/42)	cis-Chlordane	trans-Chlordane	Methoxychlor
SMS001 17/05/05	<1	<1	<1	<1	2	<1	<1	<3	<5	<1	<1	<1
SMS002 17/05/05	<1	<1	<1	<1	8	2	<1	11	<5	<1	<1	<1
SMS003 17/05/05	<1	<1	<1	<1	<1	<1	<1	4	<5	<1	<1	<1
SMS004 17/05/05	<1	<1	<1	<1	<1	<1	<1	<3	<5	<1	<1	<1
SMS005 17/05/05	<1	<1	<1	<1	3	<1	<1	10	<5	<1	<1	<1
SMS006 17/05/05	<1	<1	<1	<1	<1	<1	<1	<3	<5	<1	<1	<1
SMS007 17/05/05	<1	<1	<1	<1	<1	<1	<1	<3	<5	<1	<1	<1
SMS008 17/05/05	<1	<1	<1	<1	2	2	1	6	<5	1	<1	<1
SMS009 17/05/05	<1	<1	<1	<1	3	1	<1	6	<5	<1	<1	<1
SMS010 17/05/05	<1	<1	<1	<1	1	1	<1	5	<5	<1	<1	<1
SMS011 17/05/05	<1	<1	<1	<1	3	5	<1	13	<5	<1	<1	<1
SMS012 18/05/05	<1	<1	<1	<1	2	3	<1	7	<5	<1	<1	<1
SMS013 17/05/05	<1	<1	<1	2	<1	2	6	5	<5	<1	<1	<1
SMS014 17/05/05	<1	<1	<1	<1	<1	3	<1	<3	<5	<1	<1	<1
SMS015 17/05/05	<1	<1	<1	<1	<1	2	<1	3	<5	<1	<1	<1
SMS020 18/05/05	<1	<1	<1	<1	<1	2	<1	4	<5	<1	<1	<1
SMS021 18/05/05	<1	2	<1	<1	4	5	3	10	<5	<1	<1	<1
SMS022 18/05/05	<1	<1	<1	<1	<1	<1	<1	5	<5	<1	<1	<1
SMS023 18/05/05	<1	<1	<1	<1	4	5	2	12	<5	<1	<1	<1
SMS024 18/05/05	<1	<1	<1	3	1	16	11	7	<5	<1	<1	<1
SMS025 18/05/05	<1	<1	<1	<1	1	1	<1	10	<5	<1	<1	<1
SMS026 18/05/05	<1	<1	<1	<1	<1	<1	<1	<2	<5	<1	<1	<1
SMS027 18/05/05	<1	<1	<1	<1	2	4	1	3	<5	<1	<1	<1
SMS028 18/05/05	<2	<2	<2	3	7	31	9	29	<9	<2	<2	<2
SMS029 18/05/05	<1	<1	<1	10	6	40	29	24	<6	<1	<1	<1
SMS030 18/05/05	<1	<1	<1	<1	<1	4	<1	6	<5	<1	<1	<1
SMS031 18/05/05	<1	<1	<1	<1	<1	12	13	19	<5	<1	<1	<1
SMS032 18/05/05	<2	<2	<2	<2	13	17	11	43	<9	<2	<2	<2
SMS033 18/05/05	<1	<1	<1	<1	3	5	1	15	<5	<1	<1	<1

Table A3.4: Organochlorine pesticides (µg/kg dry weight), 2006

Site No.	Hexachlorobenzene	Alpha-BHC	Beta-BHC	Gamma-BHC (Lindane)	Delta-BHC	Heptachlor	Heptachlor epoxide	Aldrin	Dieldrin	Endrin	Endrin Aldehyde	Endosulfan I
SMS001 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.7	<0.5	<0.5	<0.5
SMS002 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	2.2	<0.5	<0.5	<0.5
SMS003 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.4	<0.5	<0.5	<0.5
SMS004 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.0	<0.5	<0.5	<0.5
SMS005 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1.4	<0.5	<0.5	<0.5
SMS006 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.7	<0.5	<0.5	<0.5
SMS007 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS008 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS009 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS010 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS011 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS012 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS013 2/06/06	1.2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS014 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS015 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS021 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	2.5	<0.5	<0.5	<0.5
SMS034 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS035 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS037 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS038 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	2.2	<0.5	<0.5	<0.5
SMS039 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS040 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS041 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
SMS042 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

Table A3.4 *cont.*: Organochlorine pesticides (µg/kg dry weight), 2006

Site No.	Endosulfan II	Endosulfan sulphate	2,4'-DDE	2,4'-DDD	2,4'-DDT	4,4'-DDE	4,4'-DDD	4,4'-DDT	Total Chlordane ((cis+trans)*100/42)	cis-Chlordane	trans-Chlordane	Methoxychlor
SMS001 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<2	<0.5	<0.5	<0.5
SMS002 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	<2	<0.5	<0.5	<0.5
SMS003 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.5	<0.5	<2	<0.5	<0.5	<0.5
SMS004 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	<2	<0.5	<0.5	<0.5
SMS005 2/06/06	<0.5	<0.5	<0.5	<0.5	0.7	1.5	0.6	2.9	<2	<0.5	<0.5	<0.5
SMS006 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<2	<0.5	<0.5	<0.5
SMS007 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	0.7	<0.5	0.6	<2	<0.5	<0.5	<0.5
SMS008 2/06/06	<0.5	<0.5	<0.5	2.2	0.9	5.3	7.6	5.5	<2	<0.5	<0.5	<0.5
SMS009 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	<0.5	0.8	<2	<0.5	<0.5	<0.5
SMS010 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<2	<0.5	<0.5	<0.5
SMS011 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	1.1	<0.5	1.6	<2	<0.5	<0.5	<0.5
SMS012 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	1.6	<0.5	0.9	<2	<0.5	<0.5	<0.5
SMS013 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	1.0	<0.5	<0.5	<2	<0.5	<0.5	<0.5
SMS014 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	1.7	<0.5	<0.5	<2	<0.5	<0.5	<0.5
SMS015 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	4.4	0.6	52	<2	<0.5	<0.5	<0.5
SMS021 2/06/06	1.2	1.3	<0.5	<0.5	1.3	2.5	2	2.4	<2	<0.5	<0.5	<0.5
SMS034 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	<0.5	<0.5	<2	<0.5	<0.5	<0.5
SMS035 2/06/06	<0.5	<0.5	<0.5	0.8	2.1	20.8	2.1	11.9	<2	<0.5	<0.5	<0.5
SMS037 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	7.6	0.9	<0.5	<2	<0.5	<0.5	<0.5
SMS038 2/06/06	<0.5	<0.5	<0.5	<0.5	<0.5	1.2	<0.5	2.5	<2	<0.5	<0.5	<0.5
SMS039 2/06/06	<0.5	<0.5	<0.5	<0.5	1.3	1.4	<0.5	11.7	<2	<0.5	<0.5	<0.5
SMS040 2/06/06	<0.5	<0.5	<0.5	<0.5	0.5	0.7	<0.5	3.3	<2	<0.5	<0.5	<0.5
SMS041 2/06/06	<0.5	<0.55	<0.5	<0.5	<0.5	5.5	0.9	1.5	<2	<0.5	<0.5	<0.5
SMS042 2/06/06	<0.5	<0.5	<0.5	<0.5	0.7	4.1	<0.5	1.8	<2	<0.5	<0.5	<0.5

Quality Control (QC) results

The QC results of the within-batch (duplicate) and certified reference material comparisons carried out are presented in Tables A3.5–A3.9. For Tables A3.5–A3.6 and Tables A3.8–A3.9, any difference (%) between the new result (denoted with a "2") and the original result (denoted with a "1") is expressed as 100 x (new result – original result)/mean of the two results. Note that not all of the QC data presented in Table A3.6 relate to Greater Wellington's streambed sediment samples; other sediment samples were analysed by the laboratory in the same batch as Greater Wellington's samples and one of these was randomly selected for duplicate heavy metal analysis in 2006.

In summary, the analytical QC results indicate:

- Good precision for TOC in the within-batch comparison (Table A3.5).
- Good precision for total recoverable metals in the within-batch comparisons except for silver in 2006 (Table A3.6).
- A very good level of agreement with the laboratory's in-house limits for total recoverable metal concentrations in certified reference material AGAL 10, but varying levels of agreement with the "certified" range – in some cases because the digestion method used to obtain the certified values also releases interstitially bound metals (Table A3.7).
- Variable precision for PAHs, with differences in the within-batch comparison ranging from 0–67% (Table A3.8). Some of this variability is due to many of the detected compounds being close to analytical detection limits.
- No measure of precision is possible for most organochlorine pesticides as a result of the within-batch comparison (Table A3.9). Only 4,4'-DDT was detected, and only in the original analysis.

Table A3.5: Within-batch comparison for total organic carbon in 2006, <2 mm fraction (no duplicate analyses were performed in 2005)

Site	SMS042 (2006)		
Result Number	1	2	Diff (%)
Total Organic Carbon (%)	0.746	0.776	3.9

[1] Note that the average value of these two duplicate analyses was reported as the result for site SMS042.

Table A3.6: Within-batch comparisons for total recoverable metals, <2 mm fraction. Concentrations in mg/kg dry weight.

Site	SMS033 (2005)[1]			Non-GWRC sample (2006)		
Result Number	1	2	Diff (%)	1	2	Diff (%)
Antimony	0.15	0.20	28.6	-	-	-
Arsenic	10.0	13.7	31.2	7.5	7.6	1.3
Cadmium	0.21	0.26	21.3	0.334	0.349	4.4
Chromium	29.1	35.0	18.4	25.6	23.8	-7.3
Copper	17.0	20.4	18.2	169	171	1.2
Lead	49.19	51.84	5.3	130.5	136.7	4.6
Mercury	0.08	0.09	11.8	0.098	0.084	-15.4
Nickel	10.3	10.5	1.9	12.0	11.7	-2.5
Silver	0.09	0.10	10.5	0.23	0.16	-35.9
Zinc	174.6	185.3	6.0	689	694	0.7

[1] Note that the average value of these two duplicate analyses was reported as the result for site SMS033.

Table A3.7: Certified Reference Material (CRM) comparisons for total recoverable metal concentrations. Concentrations in mg/kg dry weight.

	2005			2006		
	Result	Certified Range	In House Limits	Result	Certified Range	In House Limits
Antimony	3.89	6.4 ± 3.2	2.36 – 9.06	6.82	6.4 ± 3.2	0.35 – 16.73
Arsenic	18.3	17.2 ± 3.0	15.8 – 22.6	18.8	17.2 ± 3.0	16.1 – 22.9
Cadmium	8.809	9.33 ± 0.64	7.71 – 10.47	9.28	9.33 ± 0.64	7.75 – 10.75
Chromium	53.32	82 ± 11	38.6 – 72.6[1]	50.63	82 ± 11	22.5 – 58.7[1]
Copper	20.82	23.2 ± 1.9	15.8 – 28.4	22.57	23.2 ± 1.9	19.0 – 25.4
Lead	36.59	40.4 ± 2.7	32.56 – 42.96	39.34	40.4 ± 2.7	32.35 – 45.67
Mercury	10.40	11.6 ± 1.1	9.36 – 12.24	12.263	11.6 ± 1.1	9.60 – 12.68
Nickel	11.08	17.8 ± 2.7	9.7 – 13.3[1]	11.45	17.8 ± 2.7	8.7 – 12.9[1]
Silver	50.37	N/A[2]	38.01 – 58.45[2]	0.08	0.07 ± 0.002	0.02 – 0.18
Zinc	50.36	57 ± 4.2	45.5 – 57.1	52.48	57 ± 4.2	44.0 – 57.2

[1] The In House Limits for chromium and nickel are lower than the values in the Certified Range because the digestion method used to obtain the In House results is not as strong as that used to obtain the certified values.

[2] AGAL-10 CRM unsuitable for Silver – In-house QC4 used in its place.

Table A3.8: Within-batch comparison for PAHs in 2005 (only a spiked sample was re-tested in 2006). Concentrations in µg/kg dry weight.

Site	SMS022 (2005)		
Result Number	1	2	Difference (%)
Acenaphthene	<2	<2	-
Acenaphthylene	<2	<2	-
Anthracene	<2	<2	-
Benzo[a]anthracene	2	3	40
Benzo[a]pyrene [BAP]	3	3	0
Benzo[b]fluoranthene	5	5	0
Benzo[g,h,i]perylene	3	4	29
Benzo[k]fluoranthene	2	2	0
Chrysene	5	3	-50
Dibenzo[a,h]anthracene	<2	<2	-
Fluoranthene	4	5	22
Fluorene	<2	<2	-
Indeno(1,2,3-c,d)pyrene	3	2	-40
Naphthalene	<8	<8	-
Phenanthrene	<2	2	67[1]
Pyrene	4	6	40

[1] Calculated assuming Result 1 is equal to half the detection limit (i.e., 1 µg/kg).

Table A3.9: Within-batch comparison for organochlorine pesticides in 2005 (only a spiked sample was re-tested in 2006). Concentrations in µg/kg dry weight.

Site	SMS022 (2005)		
Result Number	1	2	Difference (%)
Hexachlorobenzene	<1	<1	
Alpha-BHC	<1	<1	
Beta-BHC	<1	<1	
Gamma-BHC (Lindane)	<1	<1	
Delta-BHC	<1	<1	
Heptachlor	<1	<1	
Heptachlor epoxide	<1	<1	
Aldrin	<1	<1	
Dieldrin	<1	<1	
Endrin	<1	<1	
Endrin Aldehyde	<1	<1	
Endosulfan I	<1	<1	
Endosulfan II	<1	<1	
Endosulfan sulphate	<1	<1	
2,4'-DDE	<1	<1	
2,4'-DDD	<1	<1	
2,4'-DDT	<1	<1	
4,4'-DDE	<1	<1	
4,4'-DDD	<1	<1	
4,4'-DDT	5	<3	-108[1]
Total Chlordane ((cis+trans)*100/42)	<5	<5	
cis-Chlordane	<1	<1	
trans-Chlordane	<1	<1	
Methoxychlor	<1	<1	

[1] Calculated assuming Result 2 is equal to half the detection limit (i.e., 1.5 µg/kg).

Appendix 4: Stream wet-weather flow sampling locations

Site Name	City	Easting	Northing
Porirua S @ Kenepuru	Porirua	2664446	6004802
Porirua S @ Glenside	Wellington	2663310	6000077
Porirua S @ No. 2 Tunnel	Wellington	2662653	5999022
Porirua S @ Wingfield Pl	Wellington	2661976	5998050
Owhiro S upstream of Owhiro Bay Rd	Wellington	2657148	5983295
Kaiwharawhara S @ School Rd	Wellington	2659805	5992637
Ngauranga S @ Bottom of Gorge	Wellington	2661949	5994056
Opahu S downstream of Nikau Grove	Lower Hutt	2669708	5996858

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

For more information, contact Greater Wellington:

Wellington office
PO Box 11646
Manners Street
Wellington 6142
T 04 384 5708
F 04 385 6960

Masterton office
PO Box 41
Masterton 5840
T 06 378 2484
F 06 378 2146

Photo Credit
Installing an automatic sampler in the Porirua Stream

GW/EMI-T-08/82
Date June 2008

www.gw.govt.nz