Field Analysis of Chemicals of Emerging Environmental Concern in Auckland's Aquatic Sediments

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Field Analysis of Chemicals of Emerging Environmental Concern in Auckland's Aquatic Sediments

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1 Executive Summary

The Auckland Regional Council (ARC) engaged NIWA to sample, process and co-ordinate the analysis of estuarine sediments, in the greater Auckland region, for metals and emerging chemicals of concern (ECCs). A list of 42 ECCs was established that would serve to cover the major classes reported in a recent ARC review of organic ECCs (ARC Technical Report TR2008/028 Review of Organic Chemicals of Potential Environmental Concern in Use in Auckland, Ahrens 2008), and included surfactants, flame retardants, plasticisers, estrogens, antifoulants and pesticides.

The list of ECCs was further reduced to 35, based on the ability of commercial laboratories to undertake analyses. AsureQuality performed analyses for seven of the nine polybrominated diphenyl ether (PBDE) flame retardants (BDE 203 and BDE 206 could not be analysed) and total dithiocarbamates. Hill Laboratories analysed sediments for a suite of organic biocides. Potential endocrine disrupting chemicals (EDCs) namely, alkylphenols, bisphenol A, triclosan and steroid hormones, were analysed by Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO). For the remaining compounds, further research will be needed to identify possible analytical laboratories.

Sediments were sampled in March 2008 at 13 estuarine locations around Auckland, including sites in both the Waitemata and Manukau Harbours. For metals analysis, sediments were processed as per established ARC protocols and analysed by Hill Laboratories. For all other analyses, sediments were homogenised wet to avoid potential analyte losses by the freeze drying process.

Several ECCs were detectable in Auckland estuarine sediments, including flame retardants (PBDEs), fungicides and herbicides (dithiocarbamates and glyphosate), plasticisers (phthalates), surfactants (alkylphenols) and estrogens.

PBDEs were detected in all sediments, ranging from the limit of detection up to 570 ng/g parts per billion (ppb), with the highest concentrations found at Puketutu Island, adjacent to the Mangere sewage treatment plant. The seemingly ubiquitous detection of PBDEs is due to the extremely low detection limits of the analytical technique, with detection limits in low part per trillion (ppt) levels.

Total dithiocarbamates (a sum of nine dithiocarbamates, including mancozeb and thiram) were detected in sediments from nine sites, at concentrations ranging from 0.02 to 0.11 mg/kg parts per million (ppm).

Sediment concentrations of the estrogenic surfactant breakdown product 4-nonylphenol ranged between 100 ng/g (ppb; Coxs Bay) and 36,000 ppb (Puketutu Island). Another alkylphenol, 4-tert-octylphenol, was detected only in sediment samples from Puketutu Island (two replicates) at concentrations of 100 to 160 ppb. Detectable concentrations of nonylphenol ethoxylates ranged from 100 ppb (Westhaven Marina) to 1800 ppb (Milford Marina).

Bisphenol A was detected primarily in the sediment of Milford Marina (160 ppb), with Hobson Bay (52 ppb) and Halfmoon Bay Marina (50 ppb) being the only other sites at or above the detection limit (50 ppb).

The cosmetic disinfectant triclosan was undetectable in all sediment samples at limits of quantification of 100 ppb.

Concentrations of the estrogenic steroid hormones estrone (E1), 17β-estradiol (E2), 17α-ethynylestradiol (EE2) and estriol (E3) were below limits of detection (5 to 20 ppb) in all sediment samples, when analysed by gas chromatography/mass spectrometry (GC/MS). However, a more sensitive, Enzyme-Linked ImmunoSorbent Assay (ELISA) – specific to E1, E2 and EE2 – returned positive results for around half the sites, with up to 2.8 ppb for E1 and 1.2 ppb for E2.

Independent confirmation of estrogenic activity in sediments was sought by conducting bioassays, using recombinant Yeast Estrogenic Screening (YES) assays. In all but one sample (Puketutu Island) YES activity was undetectable. However, most samples had high-to-medium anti-estrogenic activity, which is likely to have suppressed the sensitivity of the YES assay.

The majority of ECCs in the organic biocide category were below the detection limits. However, detectable concentrations of glyphosate and its degradation product (aminomethyl)phosphonic acid (AMPA) were found for a number of sites at levels up to 1 ppm. The plasticiser, bis(2-ethylhexyl)phthalate (BEP) was detected at three sites (Milford Marina, Hobson Bay and Puketutu Island) at levels up to 12 ppm, while a second, butylbenzylphthalate (BBP), was detected at Milford Marina and Hobson Bay, at concentrations up to 1.7 ppm.

Total extractable metal concentrations (particle size >500 µm) ranged between 68 to 850 ppm for zinc, 9 to 140 ppm for lead and 12 to 160 ppm for copper. Mild acid (2N HCl) extractable concentrations (particle size <63 µm) ranged between 70 to 1000 ppm for zinc, 11 to 240 ppm for lead and 7.4 to 170 ppm for copper. Milford Marina had higher concentrations of zinc compared to the other marinas, Westhaven and Halfmoon Bay.

As a note of warning, the failure to detect many of the ECCs in this study does not take to mean there is no need for concern, as quite often the detection limits were higher than reported environmental values. As such, analytical laboratories should be encouraged to develop their analytical capability further.

It is recommended that any future efforts are focused on a smaller subset of ECCs, for which meaningful analytical or biochemical data can be obtained. By performing replicate sample analyses of PBDEs, 4-nonylphenol and steroid estrogens, good accurate data can at present be achieved, allowing the monitoring of future sediment concentrations. As analytical capabilities are developed and detection limits are reduced, this list could be expanded further to give a wider range of ECCs, including those not currently analysed in this report.

2 Introduction

NIWA was commissioned by the ARC to carry out a pilot study to determine the prevalence of certain emerging chemicals of concern (ECCs) in Auckland's aquatic environment and, if possible, provide a baseline for future comparisons. In addition, samples would also be processed and analyzed for both total metals (on the >500 μm fraction) and bioavailable metals (on the <63 μm fraction) to allow comparisons with data from established monitoring sites.

NIWA undertook sampling and processing of sediment samples, co-ordinated the shipment of sediment samples to various analytical laboratories, implemented suitable QA/QC protocols and summarised results. These findings form the basis of this report.

A list of 42 ECCs (Table 1) was compiled in consultation between ARC and NIWA. The list was designed to cover classes of ECCs which have the highest likelihood of being present in Auckland's aquatic environment, but as this was a pilot study, it was not intended to be exhaustive. This project reports analytical and biochemical results for 35 of the 42 listed ECCs, as well as an expanded suite of pesticides analysed in conjunction with Hill Laboratories.

Also contained in Table 1 is literature data (where available) for reported environmental concentration ranges of these ECCs, to give an indication of levels encountered globally and to allow a rough comparison with results obtained in this study. For some ECCs, many studies have been carried out, with varying environmental concentration ranges. To assist in these cases an overall range is included above the relevant entry (Table 1).

Table 1

List of proposed and analysed target analytes with reported environmental ranges. Numbers in parentheses are comments at the footnote of this table with associated references.

Compound	Type	Analysed in this study (✓)	Reported environmental ranges (dry weight basis)
Tetra-brominated diphenyl ether (BDE 47)	Brominated flame retardant	✓	0.09-2.1 ppb (1) 0.07-0.30 ppb (45)
Penta-brominated diphenyl ether (BDE 99)	Brominated flame retardant	✓	0.07-1.78 ppb (1) 0.14-0.65 ppb (45)
Penta-brominated diphenyl ether (BDE 100)	Brominated flame retardant	✓	0.0-0.5 ppb (1) 0.10-0.17 ppb (45)
Hexa-brominated diphenyl ether (BDE 153)	Brominated flame retardant	✓	0.0-1.8 ppb (1) 0.24-0.51 ppb (45)
Hexa-brominated diphenyl ether (BDE 154)	Brominated flame retardant	✓	0.0-0.2 ppb (1) 0.09-0.28 ppb (45)
Hepta-brominated diphenyl ether (BDE 183)	Brominated flame retardant	✓	0.0-31 ppb (1) 0.40-1.22 ppb (45)
Octa-brominated diphenyl	Brominated flame	-	<0.03-40 ppb (47)

Compound	Type	Analysed in this study (✓)	Reported environmental ranges (dry weight basis)
ether (BDE 203)	retardant		
Nona-brominated diphenyl ether (BDE 206)	Brominated flame retardant	-	0.093-98 ppb (47)
Deca-brominated diphenyl ether (BDE 209)	Brominated flame retardant	✓	Range 0.03-1650 ppb 0.03-35.6 ppb (1) 240-1650 ppb (37) 1-32 ppb (43) ca. 20-80 ppb (44) 2 to 132 ppb (46)
Hexabromocyclododecane (HBCD)	Brominated flame retardant	-	Range 0.4-71 ppb 14-71 ppb (37) 0.8-6.9 ppb (43) ca. 0.4-2.1 ppb (44)
Tris(1-chloro-2-propyl) phosphate (TCPP)	Flame retardant (chlorinated phosphate)	-	No published concentration found
Bis(2-ethylhexyl)phthalate (BEP *or* DEHP)	Phthalate plasticiser	✓	0.04-24 ppm (2)
Di-n-octyl phthalate (DOP *or* DINP)	Phthalate plasticiser	✓	0.09-0.43 ppm (3)
Bisphenol A	Plastic additive	✓	Range 0.6-191 ppb <1.2-22.0 ppb (14) <2.0-118 ppb (28) <1.0-191 ppb (33) 0.6-4.0 ppb (34)
2,4-D	Herbicide (phenoxy)	✓	<10 ppb (19)
Acetochlor	Herbicide (chloroacetamide)	✓	50-188 ppt (7)
Diuron	Herbicide (urea) & anti-foulant	✓	Range <0.07-2440 ppb 250-2440 ppb (6) 59.7-66.4 ppb (10) <0.07-0.58 ppb (14) 0.1-0.2 ppb (15) 0.4-6.2 ppb (16) <100-1400 ppb (18) 0.2-10.1 ppb (19) <0.36-340 ppb (20)
Glyphosate	Herbicide (phosphonyl)	✓	0.5-5.0 ppb (4)
Irgarol 1051	Herbicide & antifoulant (triazine)	✓	Range <0.016-690 ppb 3-690 ppb (8) <1.7-49.3 ppb (10) 3-220 ppb (11) <1-77 ppb (12) <0.016-0.066 ppb (14)

Compound	Type	Analysed in this study (✓)	Reported environmental ranges (dry weight basis)
			0.3-3.5 ppb (16) ca. 5-30 ppb (17) <1-110 ppb (18)
Isoproturon	Herbicide (urea)	✓	No published concentration found
Terbuthylazine	Herbicide (triazine)	✓	0.16-9.36 ppb (6)
Triclopyr	Herbicide (pyridine carboxylic acid)	✓	No published concentration found
Captan	Fungicide (thiophthalimide)	✓	No published concentration found
Chlorothalonil	Fungicide & antifoulant (substituted benzene)	✓	Range <0.12-165 ppb 8-165 ppb (8) <0.12-8.9 ppb (13) ca. 18-42 ppb (17)
Tebuconazole	Fungicide (azole)	✓	No published concentration found
Tolyfluanid	Fungicide & antifoulant (phenylsulfamide)	✓	No published concentration found
Mancozeb	Fungicide & antifoulant (dithiocarbamate)	✓	No value (5)
Thiram	Fungicide & antifoulant (dithiocarbamate)	✓	No value (5)
Carbaryl	Insecticide (carbamate)	✓	<0.5-15 ppb (9) 21-333 ppb (22)
Chlorpyrifos	Insecticide (organophosphorus)	✓	Range <0.02-303.8 ppb 0.0529-0.165 ppb (7) <0.41 ppb (14) <0.02-94 ppb (20) 0.9-303.8 ppb (21)
Diazinon	Insecticide (organophosphorus)	✓	Range 0.5-11,658 ppb 0.5-5.4 ppb (13) <500-6000 ppb (20) 0.9-279 ppb (21) 30-11,658 ppb (22)
Malathion	Insecticide (juvenile hormone mimic)	✓	<0.15-7.2 ppb (13) 2-5.12 ppb (21)
Permethrin	Insecticide (pyrethroid)	✓	cis: 3-5451 ppb (22) trans: 3-567 ppb (22) total: 214-335 ppb (23)
Estradiol (multiple isomers)	Estrogen (natural)	✓	0.22-2.48 ppb (29)
Estrone	Estrogen (natural)	✓	0.16-1.17 ppb (29) <0.05-3.5 ppb (30)
Ethynyl estradiol	Estrogen (synthetic)	✓	<2.0-41 ppb (28) <0.05-0.5 ppb (29)

Compound	Type	Analysed in this study (✓)	Reported environmental ranges (dry weight basis)
Dioctadecyldimethylammonium chloride (DODMAC)	Cationic surfactant		No published concentration found
Nonylphenol (multiple isomers)	Surfactant derivative	✓	Range <0.1-21,000 ppb <0.5-23 ppb (9) 6-69 ppb (22) total: 131-2811 ppb (26) 3.6-299 ppb (27) 47-192 ppb (28) 11.8-21,000 ppb (30) 22-645 ppb (31) total: 1800-11,000 ppb (32) 3.37-1430 ppb (33) 204-664.5 ppb (34) 59-7808 ppb (35) 86 ppb (36) 1222 ppb (37) 3.15-4.46 ppb (39) <0.1-13,700 ppb (40) <0.1-15 ppb (41) total: 150-13,700 ppb (42)
Octylphenol (multiple isomers)	Surfactant derivative	✓	1.12-243 ppb (33) 1-93 ppb (35)
Triclosan	Cosmetic disinfectant	✓	0.27-130.7 ppb (24) Sludge: 420-5400 ppb (25) River: 4.4-35.7 ppb (25)
Copper 2-pyridinethiol-1-oxide	Microbiocide & antifoulant	-	No published concentration found
Zinc 2-pyridinethiol-1-oxide	Microbiocide & antifoulant	-	No published concentration found

(1) Large study on PBDEs from sediments from 46 sites around Australia (Toms et al. 2008).

(2) This is a combined range of sediment concentrations from 10 different studies. Source reference (Lin et al. 2008).

(3) Analysis of Dutch North Sea sediments (Klamer et al. 2005).

(4) Direct comparisons could not be established for glyphosate estuarine sediment levels. A recent study in Argentina around a glyphosate tolerant soybean gave values for water, soil and sediment (Peruzzo et al. 2008).

(5) The method for detection of dithiocarbamates does not differentiate between individual compounds.

(6) Sediments from Sacca di Goro coastal lagoon, Northern Adriatic (Carafa et al. 2007).

(7) Analysis of freshwater sediment from Beijing Guanting reservoir (Xue et al. 2005).

(8) Analysis of 11 Greek port and marina sediments (Albanis et al. 2002).

(9) Analysis of two English river sediments (Daniels et al. 2000).

(10) Analysis of two English marina sediments (Gatidou et al. 2007).

(11) Analysis of 13 German marina sediments (Biselli et al. 2000).

(12) Analysis of UK marina sediment (Bowman et al. 2003).

(13) Analysis of (saline) lake sediment (Sapozhnikova et al. 2004).

(14) River sediments from Okinawa, Japan (Kitada et al. 2008).

(15) Sea grass meadow sediment (McMahon et al. 2005).

(16) Analysis of 10 UK marine sediments (Thomas et al. 2002).

(17) Analysis of UK marina sediments (Voulvoulis et al. 2000).

(18) Analysis of 27 UK sediments (Thomas et al. 2000).

(19) Analysis of intertidal and subtidal tropical Australian sediments (Haynes et al. 2000).

(20) Analysis of 103 sediments from Australian agricultural irrigation channels (Müller et al. 2000).

(21) Sediments in drainage canal of pesticide factory (Abdel-Halim et al. 2006).

(22) Survey of North East England river sediments (Long et al. 1998).

(23) Analysis of contaminated UK river sediment (Bonwick et al. 1995).

(24) Analysis of marine sediments near sewage outfall (Agüera et al. 2003).

(25) Analysis of STP sludge and river sediments (Morales et al. 2005).

(26) Distribution characteristics of nonylphenolic chemicals in Korea (Li et al. 2008).

(27) Distribution characteristics of nonylphenol in China (Fu et al. 2007).

(28) Venice lagoon sediments (Pojana et al. 2007).

(29) Deep ocean sewage outfall (Braga et al. 2005).

(30) Shallow eutrophic lake (Mibu et al. 2004).

(31) Analysis of two Spanish river sediments (Petrovic et al. 2002).

(32) Sediment from Baltimore Harbour, USA (Loyo-Rosales et al. 2007).

(33) Surface sediments from Yeongil Bay, Korea (Koh et al. 2006).

(34) Sediments from Pearl River Estuary, China (Peng et al. 2006).

(35) Pearl River Delta sediments, China (Chen et al. 2006).

(36) North Sea sediments (Jonkers et al. 2005).

(37) Scheldt Estuary sediments (Verslycke et al. 2005).

(38) Occurrence of trace organic contaminants in North China (Hu et al. 2005).

(39) Turkish river sediments (Uguz et al. 2003).

(40) Review of 125 sediment samples from UK, USA, Canada and Japan (Ying et al. 2002).

(41) Survey of UK estuarine sediments (Blackburn et al. 1999).

(42) Venice lagoon sediments (Marcomini et al. 1990).

(43) Analysis of southern North Sea sediments (Klamer et al. 2005).

(44) Analysis of three sediment cores in Japan and South China (Tanabe 2008).

(45) Spanish river and marine sediments (de la Cal et al. 2003).

(46) Determination of decabromodiphenyl ether in sediments using selective pressurized liquid extraction followed by GC–NCI-MS (Eljarrat et al. 2004).

(47) Analysis of PBDEs and PBBS in Australian sewage sludge (Clarke et al. 2008).

3 Methodology

3.1 Sediment sampling

3.1.1 Initial selection of sites

ARC, in consultation with NIWA, selected 13 sites for sampling around the greater Auckland region. These sites were selected to cover a range of land uses and are summarised in Table 2. Seven of these sites (sites 1, 2, 3, 6, 7, 9 and 10) are current ARC monitoring sites (location co-ordinates of ARC sites were provided by ARC) and samples were collected in the vicinity of these sites, without disturbing them. For the three marinas (sites 4, 5 and 8), locations were selected to have the highest likelihood of detecting ECCs, taking into account density of boats and location of sewage outlets. Taihiki river (site 11), with a predominantly rural catchment, was sampled as close as possible to the head of the tidal creek, as requested by ARC. A suitable location at Mahurangi, near Warkworth, was found downstream of the sewage treatment plant (site 12). Puketutu Island (site 13) had only one realistic access point, via the road, and so an appropriate location was determined on site.

Table 2

Sites for collection as specified by ARC.

Site no	Site name	Character*	Comments
1	Coxs Bay	S	ARC RDP site.
2	Meola Inner	S, L	ARC RDP site.
3	Motions	S, L	ARC RDP site.
4	Milford Marina	S, M, I	NIWA to determine best location and report map co-ordinates.
5	Westhaven Marina	S, M	NIWA to determine best location and report map co-ordinates.
6	Hobson Bay, Newmarket	S	ARC RDP site.
7	Shoal Bay, Hillcrest	L, S, I	ARC RDP site.
8	Halfmoon Bay Marina	M	NIWA to determine best location and report map co-ordinates.
9	Pakuranga Upper	M, I	ARC RDP site.
10	Whau Upper	I	ARC RDP site.
11	Taihiki	A	Head of tidal creek. NIWA to determine best location and report map co-ordinates.
12	Mahurangi	A, S	Take sample below sewage treatment plant.
13	Puketutu Island	S	Check modelling undertaken by NIWA for Watercare for contaminant accumulation area to north of Puketutu Island.

* S = Sewage, M = Marina, L = Landfill, I = urban / industrial, A = Agricultural / horticultural

3.1.2 Methods of sampling

To avoid potential contamination with plasticisers, only plastics that do not leach phthalates were used for collection. All plastics were washed with detergent, rinsed with deionised (DI) water and acetone prior to use.

To keep costs to a minimum and remove site spatial variability from the final results, sediments were collected as follows: With the exception of the marinas, each site was marked with a quadrat of 50 x 50 cm and two replicate samples taken randomly within that quadrat. Only the top 3 cm of the sediment (surface sediment) was collected and transferred immediately into clean solvent rinsed glass jars and chilled, on ice. The total wet weight of sediment sampled for each replicate was ca. 2 kg.

Three different protocols of sampling were used:

- where sediment could hold its form without collapsing, cleaned and rinsed polypropylene housings were used to take sediment samples (Protocol A; Figure 1). The top 3 cm was extruded through the corer;
- for sites that had either sediment that was sloppy and would not hold its form, or a high-density of mangroves, a corer was not feasible. In this situation a plastic scoop was used to scrape off the top 3 cm (Protocol B; Figure 2); and
- for sampling subtidal sediments inside marinas a Jenkins corer was used to collect sediment. By using this method (Protocol C; Figure 3) it was possible to sample the top 3 cm of sediment without disturbing the sediment.

Figure 1
Technique for collection of firm sediments: Protocol A.

Figure 2
Technique for collection of sloppy sediments: Protocol B.

Figure 3

Jenkins corer being used in sampling at marinas. Protocol C.

A

B

C

A: Jenkins corer being lowered into the water. B: Jenkins corer after it has been retrieved. C: The core after cleaning and removal from trigger device. The top 3 cm of each core was carefully extruded out of the top of the housing using a plunger.

3.1.3 Selection of sites in the field

The 13 sites were sampled using one of the three protocols described in Section 3.2. GPS co-ordinates were logged at each site and this information as well as sampling protocol are summarised in Table 3.

Where necessary, information on the rationale for choosing the specific location is included in each site subsection.

Table 3

Field site sampling locations.

Site no	Site name	GPS co-ordinates	Sampling protocol	Figure
1	Coxs Bay	E 2663973 N 6482258	A	4
2	Meola	E 2662862 N 6481124	B	5
3	Motions	E 2662986 N 6481490	B	6
4	Milford Marina	E 2668052 N 6491185	C	7
5	Westhaven Marina	E 2665869 N 6483431	C	8
6	Hobson Bay, Newmarket	E 2669916 N 6480470	B	9
7	Shoal Bay, Hillcrest	E 2668082 N 6488314	B	10
8	Halfmoon Bay Marina	E 2679816 N 6478521	C	11
9	Pakuranga Upper	E 2678572 N 6473389	B	12
10	Whau Upper	E 2659716 N 6476795	B	13
11	Taihiki	E 2669473 N 6446683	B	14
12	Mahurangi	E 2660722 N 6531876	B	15
13	Puketutu Island	E 2667478 N 6469310	B	16

3.1.3.1 Coxs Bay

Samples were taken at the end of the main channel in the central bay area between sea grass beds (Figure 4). The red marker (left) is the current ARC site and blue marker (right) is the collection site.

Figure 4
Aerial view of Coxs Bay site.

3.1.3.2 Meola Inner

Samples were taken 20 m sea side of the first boat ramp (Figure 5). The red marker (above) is the current ARC site and the blue marker (below) is the collection site.

Figure 5
Aerial view of Meola Inner site.

3.1.3.3 Motions

Samples were taken 30 m beyond the wooden bridge (Figure 6). The red marker (below) is the current ARC site and the blue marker (above) is the collection site.

Figure 6
Aerial view of Motions site.

3.1.3.4 Milford Marina

Samples were taken from the most upstream pier around berths 13, 14, 18 and 19 (blue marker) and at a depth of 0.5 - 1 m (Figure 7).

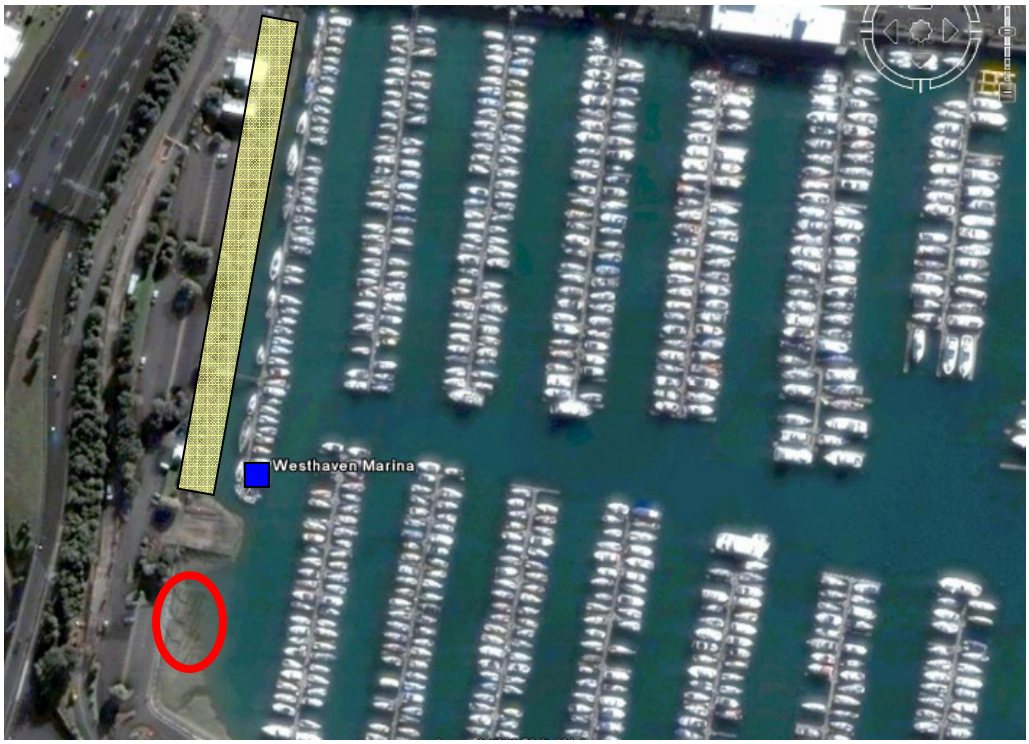
Figure 7
Aerial view of Milford Marina site (Courtesy of Google Earth).

3.1.3.5 Westhaven Marina

Samples were taken at the end of Pier J (Figure 8). This pier was chosen, in consultation with Westhaven Marina, for two reasons. First, Pier J is close to the yacht grids where maintenance is carried out on boats (Figure 8; red circle) and second, stormwater overflow pipes run the length of the shore (Figure 8; yellow box). Samples were taken (blue marker) at a depth of 2 to 3 m.

Figure 8

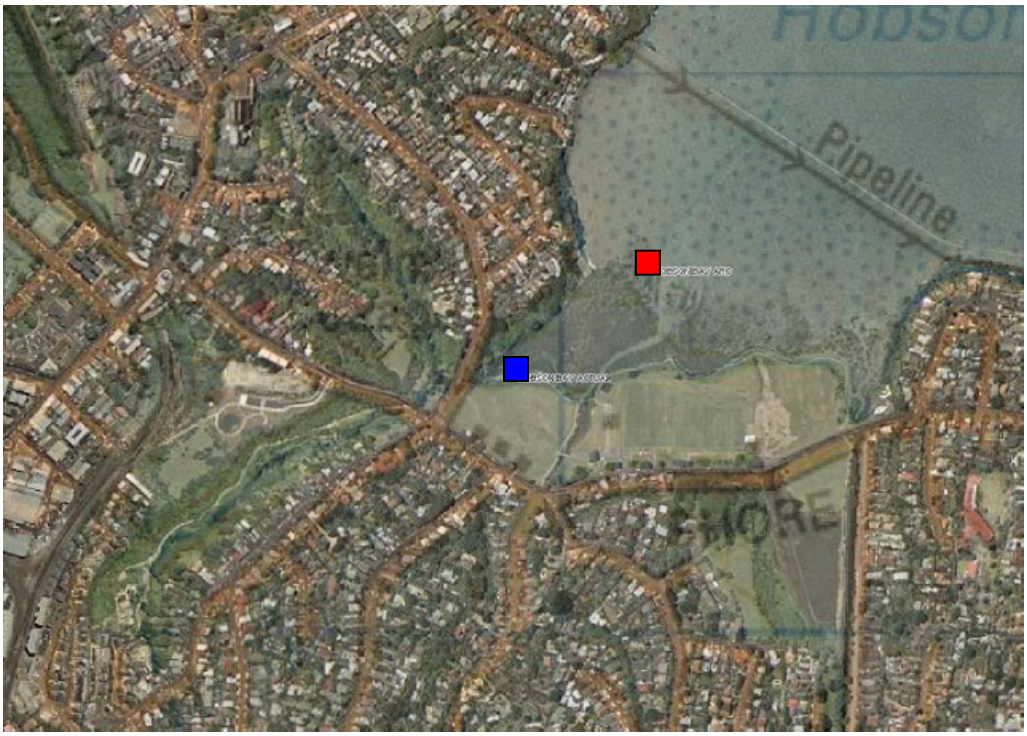
Aerial view of Westhaven Marina site (Courtesy of Google Earth).



3.1.3.6 Hobson Bay Newmarket

Samples were taken from the Northern side of the creek, 20 m from the walkway and 5m from the creek channel (Figure 9). The red marker (right) is the current ARC site and blue marker (left) is the collection site.

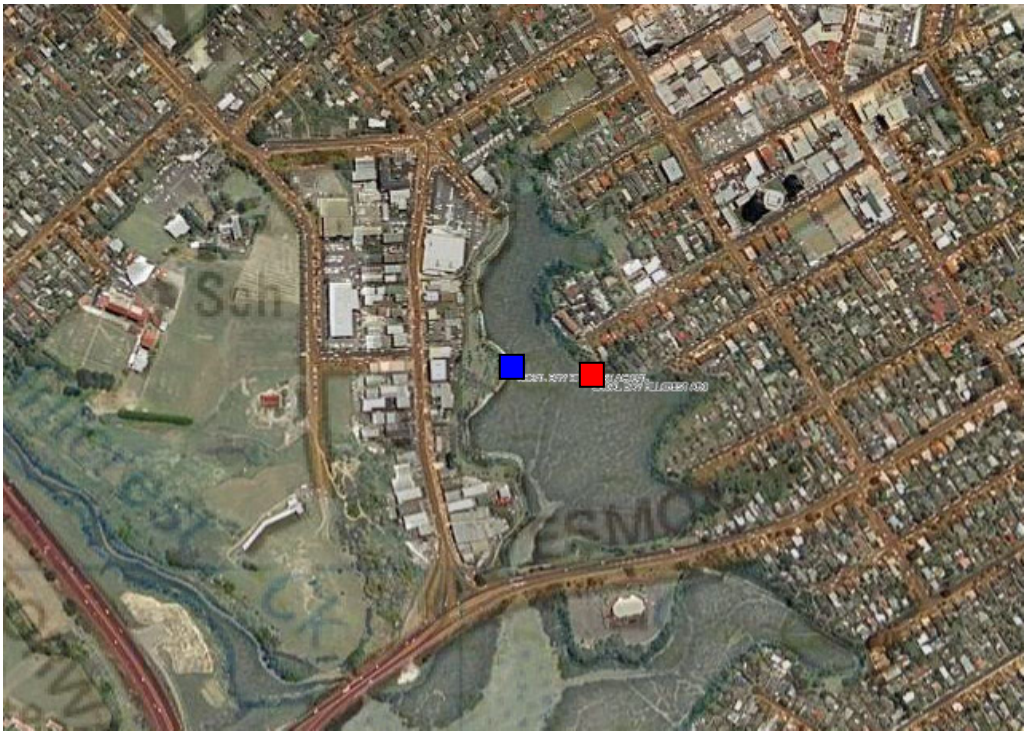
Figure 9
Aerial view of Hobson Bay Newmarket site.



3.1.3.7 Shoal Bay Hillcrest

Samples were taken from the western side of the estuary, 20 m from shore (Figure 10). As can be seen in Figure 10, the western side has a higher concentration of industrial buildings closer to the estuary than the eastern side. The red marker (right) is the current ARC site and blue marker (left) is the collection site.

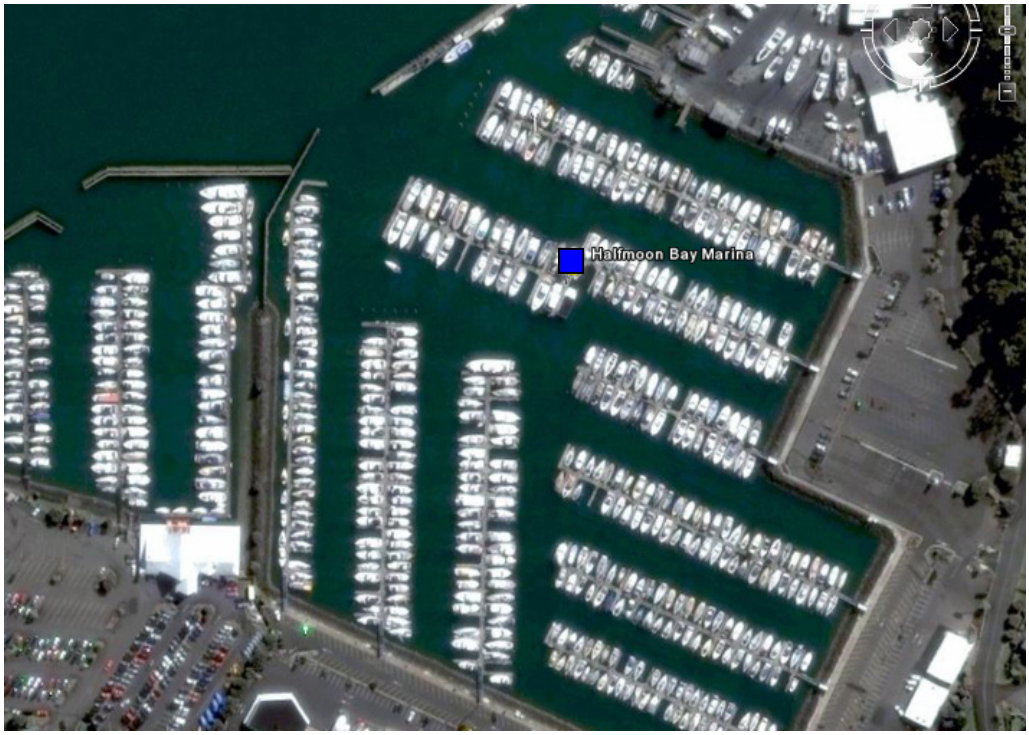
Figure 10
Aerial view of Shoal Bay Hillcrest site.



3.1.3.8 Halfmoon Bay Marina

Samples were taken on Pier H (blue marker) in a central part of marina at a depth of 3 to 5 m (Figure 11).

Figure 11
Aerial view of Halfmoon Bay Marina site (Courtesy of Google Earth).



3.1.3.9 Pakuranga Upper

Samples were taken 20 m downstream of the pipeline (Figure 12). The site was chosen as close to the ARC site as possible but was dictated by tide. The red marker (below) is the current ARC site and blue marker (above) is the collection site.

Figure 12
Aerial view of Pakuranga Upper site.

3.1.3.10 Whau Upper

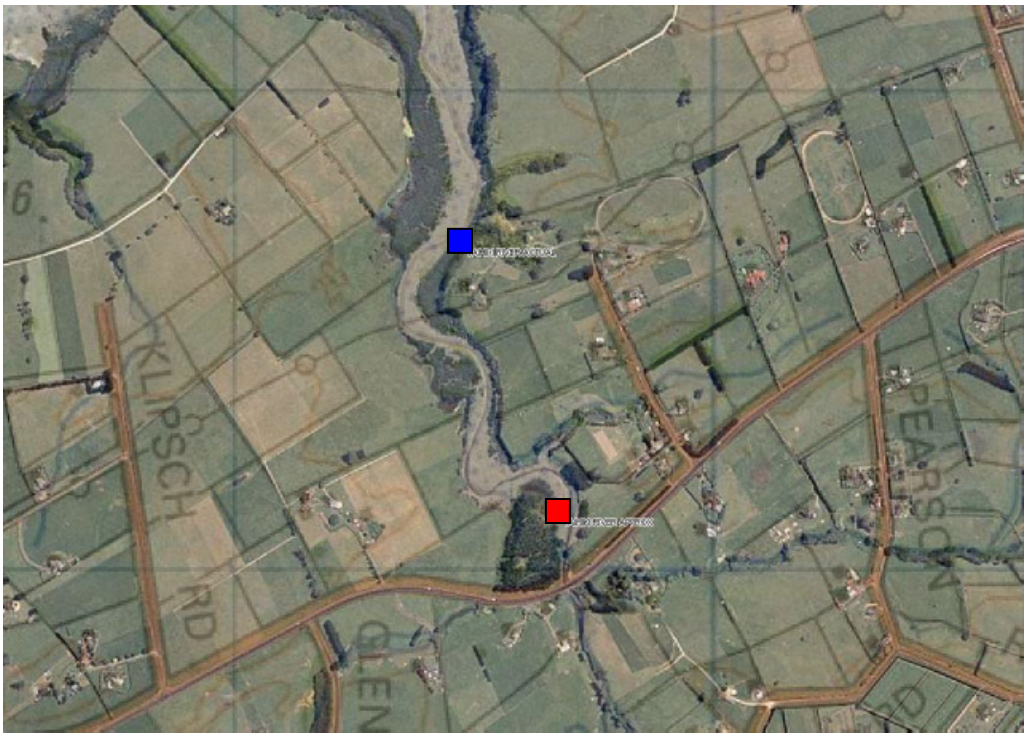
Samples were taken 50 m from the edge of the grass area (Figure 13), near a small water channel. The red marker (above) is the current ARC site and blue marker (below) is the collection site.

Figure 13
Aerial view of Whau Upper site.

3.1.3.11 Taihiki River

After much reconnaissance of the area, the only practical spot for access to the river was through a landowner's property. The landowner was very accommodating and allowed access through their property. It was a 15 m walk through mangroves to the river bank and the site of collection (Figure 14). The red marker (below) was the proposed site and blue marker (above) is the actual collection site.

Figure 14
Aerial view of Taihiki River site.



3.1.3.12 Mahurangi

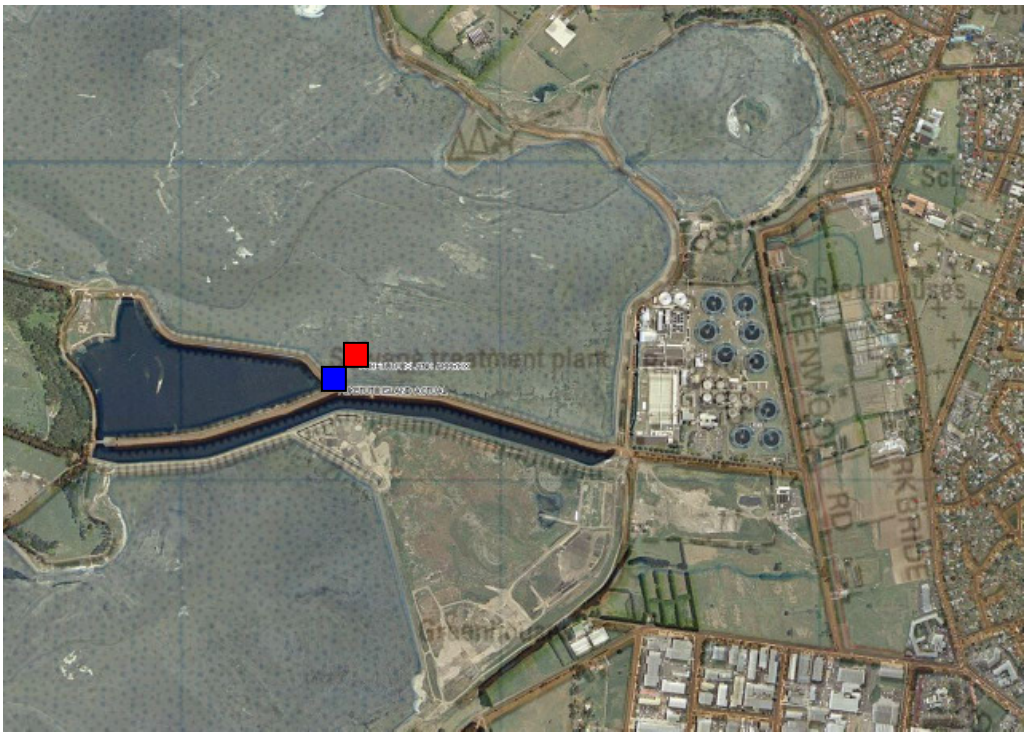
Samples were taken 50 m downstream of the wastewater treatment facility, on a bend in the river, where sediment was built up (Figure 15). The red marker (left) is outflow of the sewage treatment plant and blue marker (right) is the collection site.

Figure 15
Aerial view of Mahurangi site.

3.1.3.13 Puketutu Island

For logistical reasons samples were taken on the northern side of the causeway just before the fork in the road. The red marker (above) is the proposed site and blue marker (below) is the actual collection site (Figure 16).

Figure 16
Aerial view of Puketutu Island site.



3.2 Sediment processing

Sediments were stored at 4°C until processing. For processing, each replicate sample was transferred to a large foil tray and stirred with a stainless steel spoon to form a homogenised mixture. Large debris (stones, shellfish, plant material) were removed at this time by hand. Once a homogenised sample was obtained, sub-sampling was carried out into relevant pre-cleaned labelled vessels.

Samples were apportioned as follows:

- AsureQuality (PBDEs and dithiocarbamates) 100 g
- Hill Laboratories (Organic Biocides) 400 - 500 g
- Hill Laboratories (Total metals) 10 g
- Hill Laboratories (<63 μm metals) 10 g
- CSIRO (EDCs) 2 x 200 g
- Archive Approximately 200 g

Archived samples of whole wet sediment were stored frozen (-20°C) and will be available for future analysis until April 2009. Any remaining freeze dried sediment material will be available for future analysis for a period of up to five years.

Table 4 contains NIWA sample codes for each sample. Sediment samples designated for metal analyses at Hill Laboratories were processed as per established ARC protocols incorporating freeze drying and sieving. Total recoverable metals (<500 μm) were analysed by USEPA method 200.2 with detection limits of 0.20, 0.040 and 0.40 mg/kg (dry weight) for Cu, Pb and Zn, respectively. Bioavailable metals (<63 μm) were analysed using the method described in ARC Technical Publication No. 47, 1994 (ARC 1994), with detection limits of 1.0, 0.20 and 2.0 mg/kg for Cu, Pb and Zn, respectively.

Table 4

NIWA sample codes for sediment analysis.

Sample code	Description
133/1	Coxs Bay replicate 1
133/2	Coxs Bay replicate 2
133/3	Meola replicate 1
133/4	Meola replicate 2
133/5	Motions replicate 1
133/6	Motions replicate 2
133/7	Milford Marina replicate 1
133/8	Milford Marina replicate 2
133/9	Westhaven Marina replicate 1
133/10	Westhaven Marina replicate 2
133/11	Hobson Bay replicate 1
133/12	Hobson Bay replicate 2
133/13	Shoal Bay Hillcrest replicate 1
133/14	Shoal Bay Hillcrest replicate 2
133/15	Halfmoon Bay Marina replicate 1
133/16	Halfmoon Bay Marina replicate 2
133/17	Pakuranga Upper replicate 1
133/18	Pakuranga Upper replicate 2
133/19	Whau Upper replicate 1
133/20	Whau Upper replicate 2
133/21	Taihiki River replicate 1
133/22	Taihiki River replicate 2
133/23	Mahurangi replicate 1
133/24	Mahurangi replicate 2
133/25	Puketutu Island replicate 1
133/26	Puketutu Island replicate 2
133/27	QA1 sample
133/28	QA2 sample

3.3 Analyses

Whole wet homogenized sediment samples were supplied to AsureQuality, Hill Laboratories and CSIRO.

3.3.1 AsureQuality

Sediments were analysed for PBDEs by AsureQuality using a method based on USEPA Method 1614 (isotope dilution), with results reported on a dry basis and

corrected for recovery of internal standards. Detection limits were sample specific and are in the full data report (Appendix 1). Dithiocarbamate analyses were performed by AsureQuality using the "Method for Detection of Dithiocarbamates in Foods" (FDT-02), recognised by New Zealand Food Safety Authority (NZFSA). The full data report is in Appendix 2. The method works by treating samples under specific conditions to release carbon disulphide, which is then analysed by gas chromatography/mass spectrometry (GC/MS) with mass selective detection. The minimum detection limit is 0.02 ppm. As two notes of caution, the method is designed for foods not sediments and is specific for the chemical class of dithiocarbamates but not individual dithiocarbamates, with the result being a cumulative measurement for all chemicals in this class. As a consequence, the method used by AsureQuality describes not just mancozeb and thiram but nine such dithiocarbamates: mancozeb (CAS# 8018-01-7); maneb (CAS# 12427-38-2); metam (CAS# 6734-80-1); metham (CAS# 137-42-8); metiram (CAS# 9006-42-2); propineb (CAS# 12071-83-9); thiram (CAS# 137-26-8); zineb (CAS# 12122-67-7); ziram (CAS# 137-30-4).

3.3.2 Hill Laboratories

Sediments were analysed by Hill Laboratories for the suite of organic biocide ECCs using the methods described in Appendix 3. Of particular note, all results are corrected for dry matter content, which reflects a sample dependant variation in detection limits of the reported data. The exception to this is the glyphosate suite of compounds, for which, due to the way the data is processed, has an imposed detection limit which is sample independent.

3.3.3 CSIRO

The analysis of endocrine disrupting chemicals (EDCs) was subcontracted to Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO). Three types of analyses were conducted:

- GC/MS (alkylphenols, bisphenol A, triclosan, estrone (E1), 17β -estradiol (E2), 17α-ethynylestradiol (EE2) and estriol (E3).
- ELISA (E1, E2, EE2).
- YES/YAS (yeast estrogenic screen/yeast androgenic screen).

3.3.3.1 GC/MS

Sediment samples had internal standards added and were freeze dried prior to transport to Australia.

Freeze dried sediments (5 g) were extracted by ultrasonication for 10 min each with 20 + 10 + 10 mL of a solvent mixture containing acetone and methanol (1:1 v/v). After centrifugation at 800 g, supernatant solutions were combined and concentrated to dryness under a gentle stream of nitrogen, followed by reconstitution in methanol. Samples for GC/MS analysis were then cleaned up using solid phase extraction (SPE). An aliquot from this extract was analysed by GC/MS after converting the analytes to

trimethylsilyl esters by derivatisation. Sub-samples of these extracts were also used for ELISA and YES/YAS testing. GC/MS results are reported on a dry weight basis in µg/kg (ppb).

An Agilent 6890 GC, coupled with a 5973 MS, was used for GC/MS analyses. Separation was undertaken with a HP-5MS capillary column (30 m x 0.25 mm ID, film thickness 0.25 µm) and helium was used as the carrier gas (at flow rate of 1 mL min^{-1}). A 2 µL aliquot of sample was injected by splitless injection mode. The oven temperature was programmed as follows: 75°C (1 min) to 150°C (10°Cmin^{-1}) and then to 280°C (15°Cmin^{-1}) and held for 10 min. The injector and interface temperatures were set at 280°C, with the MS quad set at 150°C and the MS source at 230°C. The mass spectrometer was operated in the positive ion electron impact mode with an ionisation voltage of 70 eV using selected ion monitoring (SIM).

3.3.3.2 ELISA

The estrogens E1, E2 and EE2 in the extracts were measured using Enzyme-Linked ImmunoSorbent Assay (ELISA) kits from Japan EnviroChemicals Ltd (Tokyo, Japan). All the assays were conducted according to the instruction manuals supplied with the ELISA kits. The quantification limit for each estrogen was E1 0.58 µg/kg, E2 0.43 µg/kg, EE2 1.8 µg/kg.

3.3.3.3 YES/YAS

The recombinant yeast estrogen and androgen assays were carried out to measure nonspecific estrogenic activity in sample extracts. In the yeast estrogenic assay (YES), the human estrogen receptor (hER) is integrated into the main chromosome of the yeast (*Saccharomyces cerevisiae*). The yeast contains expression plasmids carrying the reporter gene lac-Z (encoding the enzyme β-galactosidase), which is used to measure the receptor's activity. In YES, hER is expressed in a form that is able to bind with estrogen-responsive sequences. Upon binding an active ligand, the estrogen-occupied receptor interacts with transcription factors and other transcriptional components to modulate gene transcription. The reporter gene lac-Z is expressed and β-galactosidase is secreted into the medium, where it metabolises the chromogenic substrate, chlorophenol red-β-D-galactopyranoside (CPRG), which is normally yellow, into a red product that is measured spectrometrically at an absorbance of 540 nm.

The YES results are reported as E2 equivalents (EEQ) and the YAS results are reported as di-hydro-testosterone equivalents (TEQ).

3.4 QA/QC

Due to budget constraints, only single sediment samples were analysed by AsureQuality for PBDEs and dithiocarbamates. Replicate analyses were undertaken by Hill Laboratories for all samples. Five sediment samples were chosen at random for replicate analysis by CSIRO, with the other eight being single analyses.

For organic analyses, an in-house internal laboratory blank was prepared by furnacing acid washed sand at 600°C overnight. In addition, AsureQuality used an in-house internal laboratory blank for PBDE analyses.

QA/QC control for total extractable (<500 μm) metals included a replicate of Mahurangi (133/27) sediment and an archived sediment sample (133/28 = 130/3). QA/QC control for bioavailable (<63 μm) metals included a replicate of Motions sediment (133/27) and an archived sediment sample (133/28 = 130/40).

3.4.1 GC/MS at CSIRO

For samples undergoing GC/MS analysis, Anthracene-d10 was spiked to sediment samples prior to extraction to account for consistency of the extraction procedure. Spiked recoveries of freeze dried sediment samples were analysed to determine extraction efficiency. The average extraction efficiency was 126 per cent; matrix enhancement of the recoveries was evident in the GC/MS analysis.

Samples were analysed in duplicate at a rate of one duplicate for every 10 samples. The average variation between duplicates was less than 10 per cent.

The limit of quantification (LOQ) for the GC/MS method was determined by assessing the background noise level of spiked and unspiked sediment samples. A 10-fold multiplication of the noise level was used to calculate the levels for each compound. The LOQs were determined to be 5 µg/kg for E1 and E2, 20 µg/kg for EE2 and E3, 50 µg/kg for BPA and 100 µg/kg for all others. The LOQs and sample results were determined on a dry weight basis.

The samples were spiked prior to freeze drying at a level of 10 ppb. In retrospect, this level of spiking turned out to be too low given the resultant LOQs for most of the compounds. It is also possible that there were losses of analytes in the freeze drying process, but this could not be determined.

4 Results

4.1 PBDEs and dithiocarbamates

The sediment concentrations of PBDEs and dithiocarbamates (as released carbon disulphide) are summarised in Table 5. The full data reports for PBDEs and dithiocarbamates are reproduced in Appendix 1 and Appendix 2 respectively.

PBDEs were detected in all sediments at concentrations up to 570 ng/g (ppb), recorded for BDE#209 at Puketutu Island. By far the most abundant isomer was BDE#209, whose concentration ranged from 87 and 99 per cent of the total detected PBDEs in the sediments. This is consistent with BDE#209 being the most commonly used brominated flame retardant applied to electronic equipment, constituting approximately 80 per cent of the world market demand for PBDEs (SinoHarvest 2005).

Table 5

Dithiocarbamate and PBDE results.

Site¥	Dithio-carbamates	PBDE analyte concentration (ng/g *or* ppb) on a dry weight basis						
	Carbon disulphide (mg/kg *or* ppm)	BDE# 47	BDE# 99	BDE# 100	BDE# 153	BDE# 154	BDE# 183	BDE# 209
Coxs	0.025	0.033	0.023	**0.0058**	**0.0027**	0.0029	**0.0025**	0.63
Meola	<0.020	0.63	0.70	0.16	0.099	0.085	0.12	12
Motions	0.023	0.20	0.28	0.064	0.049	0.041	**0.054**	9.6
Milford	0.020	1.2	2.2	0.51	0.49	0.33	0.69	95
Westhaven	0.058	0.16	0.17	0.044	0.034	0.037	**0.066**	3.6
Hobson	0.021	1.4	1.8	0.36	0.26	0.19	0.14	30
Shoal Bay	0.11	0.18	0.23	0.044	0.041	0.044	**0.026**	6.9
Halfmoon	0.088	0.14	0.14	0.035	0.022	0.029	0.032	27
Pakuranga	<0.020	0.41	0.58	0.13	0.093	0.11	0.080	140
Whau	<0.020	0.1	0.12	0.030	0.033	0.017	**0.017**	4.7
Taihiki	<0.020	0.022	0.012	0.0032	0.0021	0.0040	ND	7.8
Mahurangi	0.084	0.043	0.024	0.0072	**0.0026**	0.0028	ND	0.47
Puketutu	0.074	0.52	1.5	0.34	0.33	0.36	0.24	570
Sand	<0.020	0.011	0.0033	0.00087	0.00043	ND	ND	ND
Lab blank	-	0.010	0.0039	0.0014	ND	ND	ND	ND

Numbers highlighted bold are Estimated Maximum Possible Concentration (EMPC). ND = Not Detected *recovery outside method guidelines. ¥ Samples were replicate 1 (see Table 4).

The seemingly ubiquitous detection of PBDEs is a result of the extremely low detection limits of the analytical technique, with detection limits in low part per trillion

(ppt) levels. To highlight this, the QA/QC control samples of furnaced acid washed sand and a laboratory blank returned results still above detection limits for the lower molecular weight PBDEs (Table 5). Any sample results below these control values should not be considered reliable.

Dithiocarbamates were detected in sediments from nine out of the 13 sites, at concentrations ranging from 0.02 to 0.11 ppm dry weight (Table 5). As the analytical method detects the released carbon disulphide, this is the total amount of dithiocarbamates in the sample and does not give any information on the individual constituents that are present.

The QA/QC sample of furnaced acid washed sand returned results below detection limits for dithiocarbamate analyses (Table 5).

4.2 Organic biocides and plasticisers

The organic analyses performed by Hill Laboratories consisted of five suites of compounds:

1. Organo-nitrogen and phosphorus (ONP) trace pesticides (90 compounds).
2. Plasticisers (seven compounds).
3. Antifouling co-biocides (irgarol, isoproturon, diuron).
4. Glyphosate (glyphosate, AMPA, glufosinate).
5. Acid herbicides (19 compounds).

In general, the levels of most compounds assessed were less than the detection limits. For ease of interpretation, only selected data has been reproduced in Tables 6 and 7, with the full laboratory reports presented in Appendix 3.

The antifouling co-biocides, irgarol, isoproturon and diuron were not detected in any of the sediment samples, including the 3 marina locations (Milford, Westhaven and Halfmoon Bay). Detection limits were 0.01 ppm.

No detectable concentrations of the 90 ONP pesticides were found in any of the sediment samples, including the two agriculturally-influenced sites (Mahurangi and Taihiki River). The detection limits for this suite of compounds varied with sample and compound, but were in the range of 0.01 to 0.3 ppm, or 10 to 300 ppb. Previously reported environmental levels of most pesticides (Table 1) are in the ppb range, but vary widely.

Detectable concentrations of glyphosate and AMPA (but not glufosinate) were found for a number of sites (Meola, Motions, Milford, Hobson, Shoal Bay, Pakuranga, Whau Upper, Mahurangi and Puketutu Island) and are summarised in Table 6, along with total organic carbon (TOC) and dry matter analyses. The maximum glyphosate concentration detected was 1 ppm (Meola), while AMPA had a maximum level of 0.37 ppm (Puketutu Island).

Detectable concentrations of two plasticisers bis(2-ethylhexyl)phthalate (BEP) and butylbenzylphthalate (BBP) were found. BEP was detected at three sites (Milford

Marina, Hobson Bay and Puketutu Island) at levels up to 12 ppm, while BBP was detected at Milford Marina and Hobson Bay, at up to 1.7 ppm (Table 7).

Table 6

Summary of selected organic contaminants, TOC and dry matter for estuarine sediments.

Code	Site	Glyphosate suite in sediment by LCMSMS in Organics, trace level*				
		TOC (g/100g)	Dry matter (g/100g)	AMPA (mg/kg *or* ppm)	Glufosinate (mg/kg *or* ppm)	Glyphosate (mg/kg *or* ppm)
113/1	Coxs	0.56	73	<0.10	< 0.020	<0.040
113/2	Coxs	0.58	70	<0.10	<0.020	<0.040
113/3	Meola	3.4	29	0.18	<0.020	0.89
113/4	Meola	4	28	0.25	<0.020	1.00
113/5	Motions	2.6	40	<0.10	<0.020	0.23
113/6	Motions	2.6	42	<0.10	<0.020	0.24
113/7	Milford	5.1	29	0.1	<0.020	0.12
113/8	Milford	4.3	42	<0.10	<0.020	0.047
113/9	Westhaven	1.7	38	<0.10	<0.020	<0.040
113/10	Westhaven	1.8	35	<0.10	<0.020	<0.040
113/11	Hobson	2.1	65	<0.10	<0.020	0.056
113/12	Hobson	2.5	67	<0.10	<0.020	0.06
113/13	Shoal Bay	7.5	30	<0.10	<0.020	0.14
113/14	Shoal Bay	7.5	30	<0.10	<0.020	0.15
113/15	Halfmoon	1.8	31	<0.10	<0.020	<0.040
113/16	Halfmoon	1.9	31	<0.10	<0.020	<0.040
113/17	Pakuranga	2.3	39	<0.10	<0.020	0.079
113/18	Pakuranga	2.3	40	<0.10	<0.020	0.10
113/19	Whau	1.5	50	<0.10	<0.020	0.31
113/20	Whau	1.6	50	<0.10	<0.020	0.32
113/21	Taihiki	2.1	39	<0.10	<0.020	<0.040
113/22	Taihiki	2.1	37	<0.10	<0.020	<0.040
113/23	Mahurangi	2.3	50	<0.10	<0.020	<0.040
113/24	Mahurangi	2.3	51	<0.10	<0.020	0.045
113/25	Puketutu	1.7	50	0.32	<0.020	0.052
113/26	Puketutu	1.9	52	0.37	<0.020	0.072
113/27	Sand	<0.051	80	<0.10	<0.020	<0.040

* All results reported based on dry weight; Note: For glyphosate suite the detection limit is imposed by the spreadsheet calculation and is independent of dry matter content. TOC = Total Organic Carbon.

Table 7

Summary of plasticisers found in estuarine sediments.

Code	Site	Plasticisers trace in SVOC soil samples by GC-MS* (mg/kg *or* ppm)						
		BEP	BBP	DEA	DEP	DMP	DBP	DOP
113/1	Coxs	<0.59	<0.30	<0.20	<0.30	<0.30	<0.30	<0.30
113/2	Coxs	<0.61	<0.31	<0.20	<0.31	<0.31	<0.31	<0.31
113/3	Meola	2.1	<0.83	<0.42	<0.83	<0.83	<0.83	<0.83
113/4	Meola	<1.7	<0.84	<0.42	<0.84	<0.84	<0.84	<0.84
113/5	Motions	<1.2	<0.60	<0.30	<0.60	<0.60	<0.60	<0.60
113/6	Motions	<1.2	<0.57	<0.29	<0.57	<0.57	<0.57	<0.57
113/7	Milford	12	1.7	<0.41	<0.82	<0.82	<0.82	<0.82
113/8	Milford	11	1.5	<0.29	<0.57	<0.57	<0.57	<0.57
113/9	Westhaven	<1.4	<0.68	<0.34	<0.68	<0.68	<0.68	<0.68
113/10	Westhaven	<1.6	<0.79	<0.40	<0.79	<0.79	<0.79	<0.79
113/11	Hobson	4.8	0.36	<0.20	<0.33	<0.33	<0.33	<0.33
113/12	Hobson	4.8	0.76	<0.20	<0.32	<0.32	<0.32	<0.32
113/13	Shoal Bay	<1.6	<0.78	<0.39	<0.78	<0.78	<0.78	<0.78
113/14	Shoal Bay	<1.7	<0.81	<0.41	<0.81	<0.81	<0.81	<0.81
113/15	Halfmoon	<1.6	<0.78	<0.39	<0.78	<0.78	<0.78	<0.78
113/16	Halfmoon	<1.6	<0.77	<0.39	<0.77	<0.77	<0.77	<0.77
113/17	Pakuranga	<1.2	<0.60	<0.30	<0.60	<0.60	<0.60	<0.60
113/18	Pakuranga	<1.1	<0.54	<0.27	<0.54	<0.54	<0.54	<0.54
113/19	Whau	<0.94	<0.47	<0.24	<0.47	<0.47	<0.47	<0.47
113/20	Whau	<1.1	<0.52	<0.26	<0.52	<0.52	<0.52	<0.52
113/21	Taihiki	<1.2	<0.56	<0.28	<0.56	<0.56	<0.56	<0.56
113/22	Taihiki	<1.3	<0.64	<0.32	<0.64	<0.64	<0.64	<0.64
113/23	Mahurangi	<0.87	<0.44	<0.22	<0.44	<0.44	<0.44	<0.44
113/24	Mahurangi	<0.84	<0.42	<0.21	<0.42	<0.42	<0.42	<0.42
113/25	Puketutu	2.4	<0.48	<0.24	<0.48	<0.48	<0.48	<0.48
113/26	Puketutu	3.9	<0.42	<0.21	<0.42	<0.42	<0.42	<0.42
113/27	Sand	<0.55	<0.28	<0.20	<0.28	<0.28	<0.28	<0.28

All results reported based on dry weight; BEP = Bis(2-ethylhexyl)phthalate; BBP = Butylbenzylphthalate; DEA = Di(2-ethylhexyl)adipate; DEP = Diethylphthalate; DMP = Dimethylphthalate; DBP = Di-n-butylphthalate; DOP = Di-n-octylphthalate.

The QA/QC sample of furnaced acid washed sand returned results below detection limits for all organic biocides and plasticisers (Tables 6 and 7).

4.3 Endocrine disrupting chemicals (EDCs)

Alkylphenols (octylphenol, nonylphenol and derivatives), bisphenol A, triclosan and steroid hormones (estrone, estradiol, ethynylestradiol, estriol) were analysed by GC/MS, with results summarised in Table 8. An ELISA, specific to E1, E2 and EE2, was also performed on all sediment samples, affording the results in Table 9. YES and YAS assays were also undertaken on all sediment samples, with results summarised in Tables 10 and 11, respectively.

The QA/QC sample of furnaced acid washed sand returned results below limits of quantitation for all EDCs analysed by GC/MS and ELISA (Tables 8 and 9). The YES assay also gave no response for this QA/QC sample, however an anti-androgenic response was observed in the YAS assay, suggesting results of this assay are unreliable.

4.3.1 Alkylphenols

Alkylphenols were analysed by GC/MS, with results summarised in Table 8.

- 4-Nonylphenol (4-NP = total 4-nonylphenol branched chain isomers) were detected in all samples except Taihiki River. 4-NP are estrogenic. Sediment concentrations ranged between 100 ppb (Coxs Bay) and 36,000 ppb (Puketutu Island).
- Sediment concentrations of nonylphenol ethoxylates (NPEO12 = Nonylphenol mono and di ethoxylates) ranged from 100 ppb (Westhaven Marina) to 1800 ppb (Milford Marina). NPEO12 was undetectable (<100 ppb) in sediments from Coxs Bay, Halfmoon Bay, Pakuranga Stream, Whau Upper, Taihiki and Mahurangi.
- 4-tert-octylphenol (4-t-OP) was detected only in sediment from Puketutu Island (two replicates) at concentrations of 100 to 160 ppb.
- 4-n-nonylphenol (4-n-NP), a straight isomer of nonylphenol that is weakly estrogenic, was undetectable (<100 ppb) in all sediment samples.

4.3.2 Bisphenol A

Bisphenol A was analysed by GC/MS. Sediment concentrations of Bisphenol A, a starting material of epoxy resin and polycarbonate plastics, ranged between 50 ppb (Halfmoon Bay Marina) and 160 ppb (Milford Marina). It was also detected in Hobson Bay sediments (52 ppb), but was undetectable (<50 ppb) in all other samples.

4.3.3 Triclosan

The cosmetic disinfectant triclosan was undetectable by GC/MS in all sediment samples, with levels of quantification of 100 ppb

Table 8

Concentrations of endocrine disrupting chemicals, analysed by GC/MS (µg/kg or ppb). Abbreviations: 4-t-OP = 4-tert-octylphenol, 4-NP = 4-nonylphenol branched chain isomers, $NPEO_{12}$ = nonylphenol mono and di ethoxylates, 4-n-NP = 4-n-nonylphenol, BPA = bisphenol A, E1 = estrone, E2 = 17β-estradiol, EE2 = 17α-ethynylestradiol, E3 = estriol, TCS = triclosan. Level of Quantification (LOQ) = 5 µg/kg for E1 and E2, 20 µg/kg for EE2 an E3, 50 µg/kg BPA and 100 µg/kg for all other analytes.

Sample ID	Client site info	EDCs in sediments, by GC/MS (µg/kg *or* ppb)									
		4-t-OP	4-NP	$NPEO_{12}$ (total)	4-n-NP	BPA	E1	E2	EE2	E3	TCS
133/1A	Coxs (rep 1)	<100	100	<100	<100	<50	<5	<5	<20	<20	<100
133/2A	Coxs (rep 2)	<100	190	<100	<100	<50	<5	<5	<20	<20	<100
133/3A	Meola (rep 1)	<100	110	270	<100	<50	<5	<5	<20	<20	<100
133/4A	Meola (rep 2)	<100	240	570	<100	<50	<5	<5	<20	<20	<100
133/5A	Motions	<100	160	120	<100	<50	<5	<5	<20	<20	<100
133/7A	Milford (rep 1)	<100	910	1400	<100	160	<5	<5	<20	<20	<100
133/8A	Milford (rep 2)	<100	1100	1800	<100	130	<5	<5	<20	<20	<100
133/9A	Westhaven	<100	210	100	<100	<50	<5	<5	<20	<20	<100
133/11A	Hobson Bay	<100	430	150	<100	52	<5	<5	<20	<20	<100
133/13A	Shoal Bay	<100	140	153	<100	<50	<5	<5	<20	<20	<100
133/15A	Halfmoon Bay	<100	110	<100	<100	50	<5	<5	<20	<20	<100
133/17A	Pakuranga	<100	120	<100	<100	<50	<5	<5	<20	<20	<100
133/19A	Whau Upper	<100	120	<100	<100	<50	<5	<5	<20	<20	<100
133/21A	Taihiki (rep 1)	<100	<100	<100	<100	<50	<5	<5	<20	<20	<100
133/22A	Taihiki (rep 2)	<100	<100	<100	<100	<50	<5	<5	<20	<20	<100
133/23A	Mahurangi	<100	130	<100	<100	<50	<5	<5	<20	<20	<100
133/25A	Puketutu (rep 1)	110	28000	630	<100	<50	<5	<5	<20	<20	<100
133/26A	Puketutu (rep 2)	160	36000	780	<100	<50	<5	<5	<20	<20	<100
133/27A	Acid washed sand	<100	<100	<100	<100	<50	<5	<5	<20	<20	<100

4.3.4 Steroid hormones

Estrogen hormones were analysed by GC/MS (Table 8) and Enzyme-Linked ImmunoSorbent Assay (ELISA) (Table 9). Concentrations of the estrogenic steroid hormones estrone (E1), 17β-estradiol (E2), 17α-ethynylestradiol (EE2) and estriol (E3) were below limits of detection by GC/MS (5 to 20 ppb) in all sediment samples. The relatively high levels of detection for the GC/MS analyses were a result of strong background noise, as reported by the analytical lab. In order to obtain higher sensitivity, sediments were additionally analysed by ELISA, specific to E1, E2 and EE2. As shown in Table 9, the ELISA method was 10- to 50-fold more sensitive than GC/MS and showed an acceptable reproducibility between the five replicate samples. Estrone (E1) was detected at seven sites: Meola (1.6 to 2.8 ppb), Milford (1.3 to 1.8 ppb), Puketutu (1.3 to 1.5 ppb), Shoal Bay (1.3 ppb), Halfmoon Bay Marina (0.8 ppb), Westhaven Marina (0.75 ppb) and Taihiki (0.64 ppb). Estradiol was detected at seven sites: Milford (0.82 to 1.2 ppb), Puketutu (0.82 to 0.89 ppb), Shoal Bay (0.84 ppb), Westhaven Marina (0.74 ppb), Meola (0.66 ppb), Mahurangi (0.64 ppb) and Hobson (0.47 ppb). Ethynylestradiol was not detected in any samples at the level of quantification of 1.8 ppb.

Table 9

Analysis of steroid estrogens by ELISA. Limits of quantitation: E1 0.58 µg/kg, E2 0.43 µg/kg, EE2 1.8 µg/kg. E1 = estrone, E2 = 17β -estradiol, EE2 = 17α-ethynylestradiol.

Sample ID	Client site info	Results in µg/kg (dry weight basis)		
		E1	E2	EE2
133/1A	Coxs (rep 1)	<LOQ	<LOQ	<LOQ
133/2A	Coxs (rep 2)	<LOQ	<LOQ	<LOQ
133/3A	Meola (rep 1)	1.6	<LOQ	<LOQ
133/4A	Meola (rep 2)	2.8	0.66	<LOQ
133/5A	Motions	<LOQ	<LOQ	<LOQ
133/7A	Milford (rep 1)	1.8	1.2	<LOQ
133/8A	Milford (rep 2)	1.3	0.82	<LOQ
133/9A	Westhaven	0.71	0.74	<LOQ
133/11A	Hobson	<LOQ	0.47	<LOQ
133/13A	Shoal Bay	1.3	0.84	<LOQ
133/15A	Halfmoon Bay	0.80	<LOQ	<LOQ
133/17A	Pakuranga	<LOQ	<LOQ	<LOQ
133/19A	Whau Upper	<LOQ	<LOQ	<LOQ
133/21A	Taihiki (rep 1)	<LOQ	<LOQ	<LOQ
133/22A	Taihiki (rep 2)	0.64	<LOQ	<LOQ
133/23A	Mahurangi	<LOQ	0.64	<LOQ
133/25A	Puketutu (rep 1)	1.5	0.89	<LOQ
133/26A	Puketutu (rep 2)	1.3	0.82	<LOQ
133/27A	Acid washed sand	<LOQ	<LOQ	<LOQ

4.3.5 YES/YAS assay

Total (nonspecific) estrogenic and androgenic "load" were estimated by the YES and YAS assay. Results are summarised in Tables 10 and 11 for YES and YAS, respectively. It should be noted that YES and YAS are screening tools and, therefore, not absolute measurements like analytical tools. In all but one sample (Puketutu Island) YES activity was undetectable (Table 10). However, most samples had high-to-medium anti-estrogenic activity, which is likely to have suppressed the sensitivity of the YES assay. The high anti-estrogenic activity would explain the negative YES results despite E1 and E2 being measurable by ELISA. No androgenic activity was detectable in the YAS assays (Table 11). For the majority of the samples, high-to-medium anti-androgenic activity was observed, limiting the sensitivity of the YAS assay.

Table 10

YES results, expressed as E2 equivalents (EEQ). Limits of quantitation: EEQ 0.44 µg/kg, ND = not detected. Anti-estrogenic ranking: High = 0 to 3.125 per cent extract dilution with Anti-E2 activity, Med= 3.125 to 25 per cent, Low = 25 to 100 per cent.

Sample ID	Client site info	Results		
		Estrogenic Response – E2 Equivalents (EEQ)	Anti-estrogenic response	Anti-estrogenic response ranking
133/1A	Coxes (rep 1)	ND	Yes	Medium
133/2A	Coxes (rep 2)	ND	Yes	High
133/3A	Meola (rep 1)	ND	Yes	High
133/4A	Meola (rep 2)	ND	Yes	High
133/5A	Motions	ND	Yes	High
133/7A	Milford (rep 1)	ND	Yes	High
133/8A	Milford (rep 2)	ND	Yes	High
133/9A	Westhaven	ND	Yes	High
133/11A	Hobson	ND	Yes	High
133/13A	Shoal Bay	ND	Yes	High
133/15A	Halfmoon Bay	ND	Yes	High
133/17A	Pakuranga	ND	Yes	Medium
133/19A	Whau Upper	ND	Yes	Medium
133/21A	Taihiki (rep 1)	ND	Yes	Medium
133/22A	Taihiki (rep 2)	ND	Yes	Medium
133/23A	Mahurangi	ND	Yes	Medium
133/25A	Puketutu (rep 1)	ND	Yes	Low
133/26A	Puketutu (rep 2)	0.81	No	-
133/27A	Acid Washed Sand	ND	No	-

Table 11

YAS results, expressed as testosterone equivalents (TEQ). Limits of quantitation: TEQ 6.34 µg/kg, ND = not detected. Anti-androgenic ranking: High = 0 to 3.125 per cent extract dilution with anti-TEQ activity, Med = 3.125 to 25 per cent, Low = 25 to 100 per cent.

Sample ID	Client site info	Results		
		Androgenic response – testosterone equivalents (TEQ)	Anti-androgenic response	Anti-androgenic response ranking
133/1A	Coxes (rep 1)	ND	Yes	High
133/2A	Coxes (rep 2)	ND	Yes	High
133/3A	Meola (rep 1)	ND	Yes	High
133/4A	Meola (rep 2)	ND	No	-
133/5A	Motions	ND	Yes	Medium
133/7A	Milford (rep 1)	ND	Yes	Medium
133/8A	Milford (rep 2)	ND	Yes	Medium
133/9A	Westhaven	ND	Yes	High
133/11A	Hobson	ND	Yes	High
133/13A	Shoal Bay	ND	No	-
133/15A	Halfmoon Bay	ND	Yes	Medium
133/17A	Pakuranga	ND	Yes	Low
133/19A	Whau Upper	ND	Yes	Low
133/21A	Taihiki (rep 1)	ND	No	-
133/22A	Taihiki (rep 2)	ND	No	-
133/23A	Mahurangi	ND	No	-
133/25A	Puketutu (rep 1)	ND	Yes	Low
133/26A	Puketutu (rep 2)	ND	Yes	Medium
133/27A	Acid Washed Sand	ND	Yes	Medium

4.4 Metals

4.4.1 Total extractable metals (<500 µm)

Analytical results of total extractable metals (zinc, lead and copper) in the <500 µm fraction are summarised in Table 12 and Figure 17. Total extractable metal concentrations (>500 µm) ranged between 68 and 850 ppm for zinc, 9 and 140 ppm for lead and 12 and 160 ppm for copper. Good reproducibility was observed between site replicates. The QA controls of a repeat of Mahurangi (133/27) and an archived sample (133/28) showed good agreement with those data.

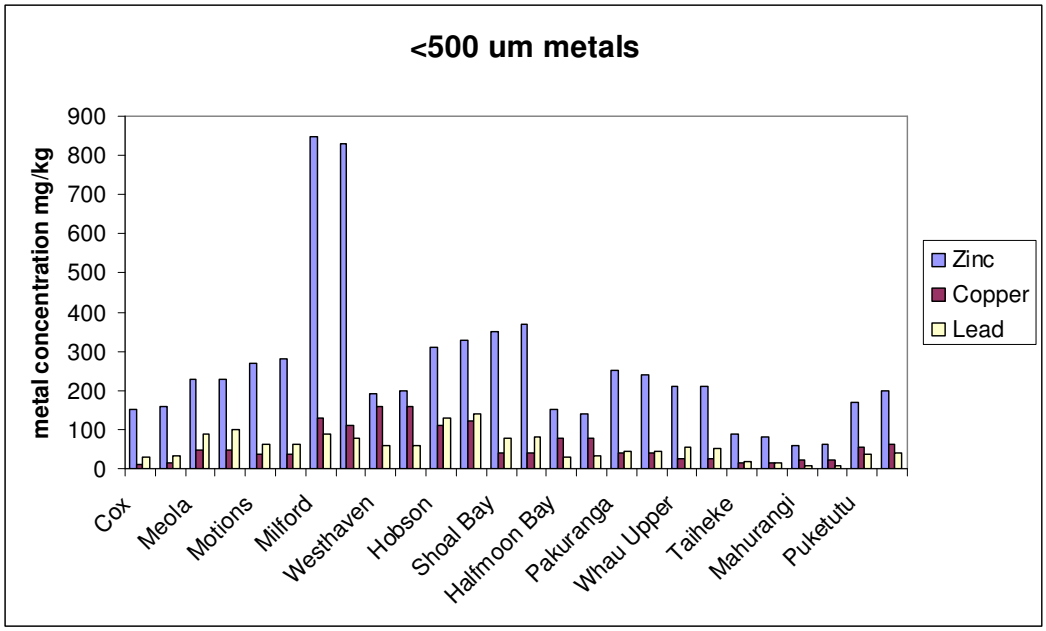
Table 12

Total extractable metals in estuarine sediments.

Code	Site	Total extractable metals <500 m mg/kg (ppm) (dry weight)		
		Copper	Lead	Zinc
133/1	Coxs	12	31	150
133/2	Coxs	13	34	160
133/3	Meola	49	90	230
133/4	Meola	47	98	230
133/5	Motions	37	63	270
133/6	Motions	37	64	280
133/7	Milford	130	87	850
133/8	Milford	110	78	830
133/9	Westhaven	160	58	190
133/10	Westhaven	160	59	200
133/11	Hobson	110	130	310
133/12	Hobson	120	140	330
133/13	Shoal Bay	39	78	350
133/14	Shoal Bay	41	80	370
133/15	Halfmoon Bay	76	31	150
133/16	Halfmoon Bay	76	32	140
133/17	Pakuranga	42	45	250
133/18	Pakuranga	41	44	240
133/19	Whau	27	54	210
133/20	Whau	27	51	210
133/21	Taihiki	15	17	88
133/22	Taihiki	13	16	82
133/23	Mahurangi	21	8.5	60
133/24	Mahurangi	21	8.6	62
133/25	Puketutu	56	36	170
133/26	Puketutu	64	41	200
133/27	QA1: repeat Mahurangi	22	9	64
133/28	QA2: archived sample (130/3)	14	21	85
130/3	Original data	15	21	85

Figure 17

Total extractable metal concentrations (zinc, copper, lead) in <500 μm surface sediments (0 to 3 cm).



4.4.2 Bioavailable metals (<63 μm)

Analytical results of mild acid (2N HCl) extractable metals (zinc, lead and copper) in the <63 μm fraction are summarised in Table 13 and Figure 18. Mild acid (2N HCl) extractable concentrations ranged between 70 and 1000 ppm for zinc, 11 and 240 ppm for lead and 7.4 and 170 ppm for copper.

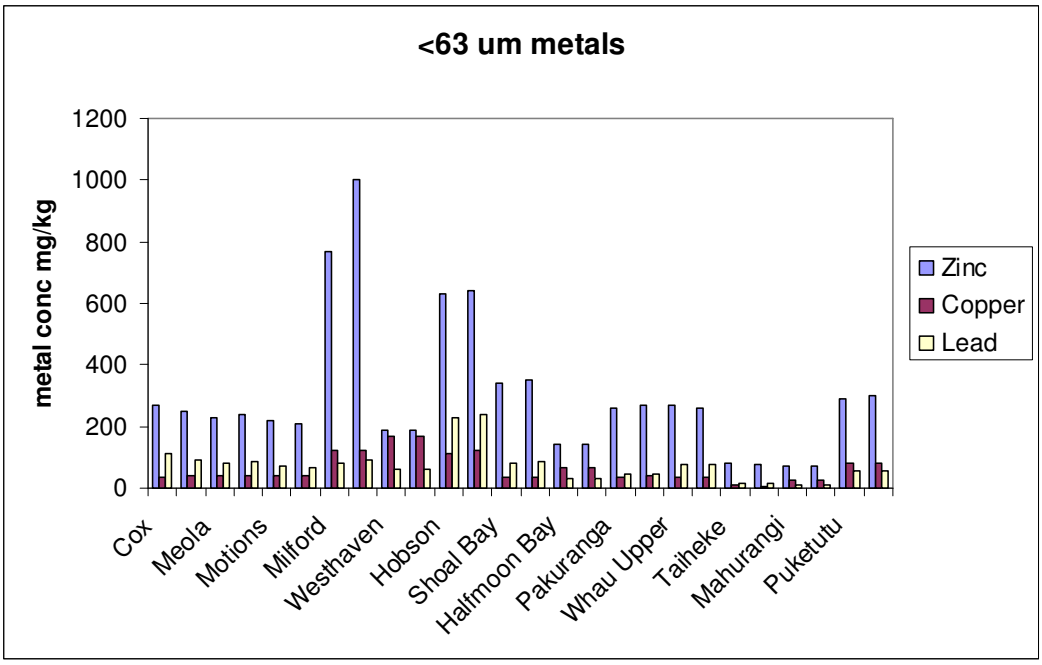
Good reproducibility was observed between site replicates. The QA/QC controls for bioavailable (<63 μm) metals, a repeat of Motions (133/27) and an archived sample (133/28), showed good agreement with these data.

Table 13

Bioavailable metals in estuarine sediments.

Code	Site	Extractable metals <63 m mg/kg (ppm) (dry weight)		
		Copper	Lead	Zinc
133/1	Coxs	38	110	270
133/2	Coxs	39	94	250
133/3	Meola	39	82	230
133/4	Meola	40	84	240
133/5	Motions	39	69	220
133/6	Motions	39	68	210
133/7	Milford	120	82	770
133/8	Milford	120	92	1000
133/9	Westhaven	170	62	190
133/10	Westhaven	170	63	190
133/11	Hobson	110	230	630
133/12	Hobson	120	240	640
133/13	Shoal Bay	36	83	340
133/14	Shoal Bay	37	84	350
133/15	Halfmoon Bay	67	31	140
133/16	Halfmoon Bay	64	32	140
133/17	Pakuranga	37	46	260
133/18	Pakuranga	39	47	270
133/19	Whau	36	77	270
133/20	Whau	35	76	260
133/21	Taihiki	7.7	17	81
133/22	Taihiki	7.4	17	78
133/23	Mahurangi	24	11	70
133/24	Mahurangi	25	11	70
133/25	Puketutu	80	57	290
133/26	Puketutu	80	58	300
133/27	QA1: repeat mot	39	68	210
133/28	QA2: archived sample (130/40)	16	28	88
130/3	Original data	19	32	100

Figure 18
Mild (2N HCl) extractable metal concentrations (zinc, copper, lead) in <63 m surface sediments (0 to 3 cm).



4.5 Overseas laboratories

Seven ECCs in Table 1 could not be analysed by the laboratories contracted in this report. Two of these (BDE 203 and BDE 206) are scheduled to become available in the near future as part of the suite of PBDEs analysed by AsureQuality. For the remaining five, further research was necessary to find suitable overseas labs that can analyse for these. Among the criteria for selecting laboratories was their ability to undertake the analyses routinely, reasonable turn-around times and an indication of the stability of each analyte on storage, so that analyses may be undertaken at a future date.

4.5.1 DODMAC (surfactant)

Dimethyldioctadecylammonium chloride (DODMAC) is the principal active component of di(hydrogenated tallow alkyl)dimethylammonium chloride (DHTDMAC), a cationic surfactant formerly used in laundry fabric softeners. DODMAC was discontinued in the EU in 2002 (high partitioning to sediment, slow biodegradation and potential effects on microbial processes during sewage treatment).

A very recent European study on DODMAC bioaccumulation and toxicity using High Performance Liquid Chromatography (HPLC) with fluorescence detection performed spiking experiments of sediment with DODMAC between 150 and 5000 ppm. They discovered that DODMAC was stable in sediment for up to 28 days (Comber et al. 2008). If future analyses are required, then suggested options would be for either

NIWA to develop capabilities for this analysis in-house, or to co-ordinate these analyses with this group.

4.5.2 TCPP and HBCD (flame retardants)

Tris-(2-chloroisopropyl) phosphate (TCPP) is an organophosphate ester flame retardant. A recent Austrian study at the Department of Organic Analysis, Austrian Federal Environment Agency, in Vienna, used Liquid Chromatography with Tandem Mass Spectrometry (LC/MS/MS) to determine nine priority organophosphate esters (including TCPP) in sediments and waste and surface water (Martínez-Carballo et al. 2007).

Hexabromocyclododecane (HBCD) is a flame retardant with known EDC activity. The analysis is complicated as there are 16 possible stereoisomers produced in the commercial production of HBCD. However, the three major stereoisomers of HBCD (α,β,γ-HBCD) account for virtually all of commercial HBCD, with minor stereoisomers found in trace levels. GC/MS does not resolve these isomers and thermally induced rearrangements and degradation occur at elevated temperatures.(Morris et al. 2006) There is a recent drive to use LC/MS with either ElectroSpray Ionisation (ESI) (Morris et al. 2006) or Atmospheric Pressure Chemical Ionisation (APCI) (Heeb et al. 2005) probes as suitable methods for quantifying HBCD stereoisomers. Clean up is very similar to PBDEs with Soxhlet extraction, gel permeation chromatography, silica chromatography and final treatment with concentrated sulphuric acid. AsureQuality are currently in the process of developing analytical methods for the analysis of HBCD in New Zealand which should be available in 2009.

4.5.3 Zinc and copper omadine/pyrithione (antifouling biocides)

Two distinct routes to the aquatic environment exist for zinc pyrithione (ZnPT; zinc omadine), either as the active ingredient in personal care products or leaching from antifouling paints. ZnPT is difficult to analyse due to problematic chromatography and unwanted metal chelation and is usually converted to the more stable copper pyrithione (CuPT) (Bones et al. 2006). A study of ZnPT (as CuPT) in a British marina by LC/APCI/MS gave limits of detection (LOD) of 20 ng/L, however nothing was detected above this LOD (Thomas 1999). A revised method using LC/APCI/MS with online clean up and pre-concentration has recently been devised (Bones et al. 2006) with comparable LOD but 10 per cent volume work-up.

4.6 Summary and recommendations

This was always intended as a pilot study to try and obtain a "snapshot" of which ECCs were present in Auckland's aquatic environment and at what concentrations. This was a first of its kind study in New Zealand and so many challenges were encountered, especially in sourcing analytical laboratories which were capable of delivering reliable results at the extremely low (typically parts per billion) concentrations of ECCs present.

However, this was achieved for some classes of ECCs, namely PBDEs, alkylphenols and steroid hormones, largely due to the very low limits of quantitation these methods returned. However, due to the high cost of these analyses, they were mostly run on single replicate samples. For PBDEs all 13 sites were single replicate analyses, while for alkylphenols and steroid hormones eight out of 13 sites were single replicate analyses. A result of this is that a gauge of analytical reliability could not be accurately ascertained.

The plasticiser and glyphosate suite of analytes gave some reliable results in the parts per million range, with good reproducibility between replicates.

Other analytical methods were typically not sensitive enough (in the case of organic biocides, triclosan and bisphenol A) or were not necessarily suitable for marine sediments (ie dithiocarbamates in foods).

The recommendations that can be made from this study are to focus any future efforts on a smaller subset of ECCs, for which meaningful analytical or biochemical data can be obtained. By performing replicate sample analyses of PBDEs, 4-nonylphenol and steroid estrogens, good accurate data can at present be achieved, allowing the monitoring of future sediment concentrations. As analytical capabilities are developed and detection limits are reduced, this list could be expanded further to give a wider range of ECCs, including those not currently analysed in this report.

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6 Appendix 1

Analysis of polybrominated diphenyl ethers (PBDPEs) found in sediment, based on USEPA Method 1614 (isotope dilution).

Sample identification:	Reference:
Certificate of Analysis – AsureQuality Limited.	
133/1	38176-1
133/3	38176-2
133/5	38176-3
133/7	38176-4
133/9	38176-5
133/11	38176-6
133/13	38176-7
133/15	38176-8
133/17	38176-9
133/19	38176-10
133/21	38176-11
133/23	38176-12
133/25	38176-13
133/27	38176-14
Blank	38176 BLANK

7 Appendix 2

Analysis of dithiocarbamates in food (method: FDT-02).

Sample identification:	Reference:
133/1	41579-1
133/3	41579-2
133/5	41579-3
133/7	41579-4
133/9	41579-5
133/11	41579-6
133/13	41579-7
133/15	41579-8
133/17	41579-9
133/19	41579-10
133/21	41579-11
133/23	41579-12
133/25	41579-13
133/27	41579-14

8 Appendix 3

Analysis report of sediments.