EAM

ENVIRONMENTAL CONSULTANTS

Napier Inner Harbour: Resurvey of antifoulant and trace metal contamination of sediments.

EAM Client Report: June 2008
EAM Project: HBRC004

EMI 08/14
HBRC Plan Number 4038

CONTENTS

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Project No: HBRC004

Report Status: FINAL

Date: 17/06/2008

1.0 INTRODUCTION

Antifoulant paints have been widely used to prevent the growth of fouling organisms such as barnacles, mussels, calcareous tubeworms and algae on the hulls of vessels and other submerged structures. In response to environmental concerns and the subsequent ban on the sale of TBT, co-biocides (copper plus the addition of a biocide) have largely replaced TBT based antifoulants. The primary active ingredient in co-biocides, copper, is highly toxic to fouling organisms such as barnacles, mussels and tubeworms. However some algal species (i.e. *Enteromorpha)* are tolerant to the effects of copper, and therefore herbicides or algaecides were also required to inhibit the growth of these species (Stewart, 2003).

In June 2005, an investigation was undertaken by Environmental Assessments and Monitoring (EAM) on behalf of the Hawke's Bay Regional Council to elucidate whether substances associated with antifoulant paints and pervasive marine contaminants have accumulated within the inner harbour to levels that may pose a threat to marine health. Sample sites for the initial investigation were chosen to align with boat maintenance and repair facilities, as contamination was considered likely to be associated with these areas. In accordance with Council's Coastal Monitoring Strategy (Madarasz, 2006), sites were resampled to determine whether levels of contaminants of concern are increasing, decreasing or stable.

1.1 Previous results

The results of this study and the initial 2005 study showed concentrations of copper, mercury, lead, zinc, and total TBT and DDT were occurring in the marine sediments adjacent to boat maintenance and repair facilities, at levels equal to, or above, ANZECC interim sediment quality guidelines (2000) (Table 1). At the levels recorded, adverse biological effects could be expected to occur frequently.

Table 1: Contaminant concentrations for 2005 survey and 2007 survey compared to ANZECC Interim Sediment Quality Guidelines (2000). All results expressed as Total recoverable metals mg/kg dry weight.

	Arsenic		Copper		Mercury		Lead		Zinc		Tributyltin (TBT)		Total DDT	
	2005	2007	2005	2007	2005	2007	2005	2007	2005	2007	2005	2007	2005	2007
Site 1	4.7	5.4	435	170	0.11	0.24	40.8	41	227	150	0.534	0.370	<0.0001	<0.0001
Site 2	13.3	11	1070	1600	4.02	3.3	230	490	689	940	1.13	3.50	<0.0001	<0.0001
Site 3	5.1	5.5	301	280	0.12	0.32	70.7	38	129	170	0.276	0.065	<0.0001	<0.0001
Site 4	7	7.3	33	82	0.16	0.10	61.6	28	116	540	0.011	0.010	<0.0001	<0.0001
Site 5	5.9	8.1	31.2	61	0.008	0.16	26.1	190	184	170	<0.005	0.008	<0.0001	<0.0001
ANZECC ISQG-Low	**20**		**65**		**0.15**		**50**		**200**		**0.005**		**0.0016**	
ANZECC ISQG-High	**70**		**270**		**1**		**220**		**410**		**0.07**		**0.046**	

Light orange represents concentrations that exceed ANZECC (2000) Interim Sediment Quality Guidelines-Low (adverse biological effects could be expected to occur occasionally). Dark orange represents concentrations that exceed ANZECC (2000) Interim Sediment Quality Guidelines-High (adverse biological effects could be expected to occur frequently).

As part of the Regional Discharges Project, Auckland Regional Council commissioned the development of Environmental Response Criteria (ERC) for the key marine sediment contaminants copper, lead, zinc and PAH's. These criteria were derived from ANZECC and other recognised guidelines, and were presented in a "traffic light" system corresponding to – green, low; amber, elevated, and red, high contaminant concentrations (ARC, 2003 – Red level generally based on low threshold of effects in order to allow time for appropriate management). When compared to these criteria, Napier Inner Harbour sediment concentrations from both the 2005 and 2007 surveys, copper, lead and zinc concentrations relate to amber and red rankings, as being elevated or high (Table 2). Recent work undertaken by ARC has shown adverse effects in benthic communities associated with amber sediment quality ranks (ARC, 2003).

Table 2: Contaminant concentrations compared to ARC Environmental Response Criteria. All results expressed as Total recoverable metals mg/kg dry weight.

	Arsenic		Copper		Mercury		Lead		Zinc	
	2005	2007	2005	2007	2005	2007	2005	2007	2005	2007
Site 1	*4.7*	*5.4*	435	170	*0.11*	*0.24*	40.8	41	227	150
Site 2	*13.3*	*11*	1070	1600	*4.02*	*3.3*	230	490	689	940
Site 3	*5.1*	*5.5*	301	280	*0.12*	*0.32*	70.7	38	129	170
Site 4	*7*	*7.3*	33	82	*0.16*	*0.10*	61.6	28	116	540
Site 5	*5.9*	*8.1*	31.2	61	*0.008*	*0.16*	26.1	190	184	170
ARC-Amber			**19-34**				**30-50**		**125-150**	
ARC-Red			**>34**				**>50**		**>150**	

Light orange represents elevated concentrations. Dark orange represents high contaminant concentrations (ARC, 2003). No criteria exist for arsenic and mercury.
Sources of criteria: Zinc – Amber and Green = ISQG-Low (CCME); Red = ERL. Copper– Amber and Green = ISQG-Low (CCME); Red = ERL. Lead– Amber and Green = ISQG-Low (CCME); Red = ISQG – ANZECC.

Although these contaminants are also present in high quantities in urban stormwater which passes through the inner harbour before discharging into Hawke Bay, the levels found adjacent to boat maintenance and repair facilities suggest that these operations are a significant source of contaminants in this area.

Given that the findings of this current survey and the preliminary 2005 investigation have confirmed the presence of contaminants in concentrations likely to affect marine ecosystems, it is recommended that further similar monitoring be undertaken in the future. The aim of this further monitoring is to determine whether or not the contamination is decreasing or increasing i.e. whether or not current boat maintenance practices are continuing to discharge contaminants to the Inner Harbour.

The above brief was formulated and supplied by Hawke's Bay Regional Council Coastal and Marine Scientist Anna Madarasz.

2.0 METHODOLOGY

2.1 Sample Collection

Sample collection was carried out so as to replicate the 2005 survey as follows.

Samples of between 500-1000g of sediment were collected from each site (see Figure 1 for site locations and Appendix 1 for site photos) with each sample being a composite of ten sub-samples. By collecting samples in this manner a greater representation of the study site is obtained and the likelihood of highly variable results due to sampling are reduced. Sediment samples were collected to a maximum depth of 5cm with a Teflon spatula (for sites with exposed intertidal flats - Site 1: Marine Club Slipway, Site 2: Commercial Slipway, and Site 3: Marine Club Slipway) or Ponar® dredge (for sites permanently covered with water – Site 4: Boat Ramp and Site 5: Iron Pot) and placed into acid washed glass containers. Samples were immediately stored in an iced chilly bin to inhibit degradation and couriered the same day to Hill Laboratories Limited in Hamilton.

At each sampling site the following additional information was collected: date and time of sampling, GPS coordinates, sediment texture, and tidal state relative to low tide. A summary of these details is provided in Table 3 below.

Table 3: Location and descriptions of sampling sites in this survey and initial 2005 survey.

Site	Date/time	Tidal state relative to low tide	Location	Sediment description	Distance from hull washing facility
Site 1: Marine Club Slipway	06/11/07 @ 0902	-26 minutes	2844550 E 6184090 N	Mix of sand/gravel and silt. **Paint chips evident in sediment**	5m
Site 2: Commercial Slipway	06/11/07 @ 0926	-02 minutes	2844610 E 6184095 N	Mix of sand/gravel and silt. **Paint chips evident in sediment.**	5m
Site 3: Marine Club Slipway	06/11/07 @ 0952	+24 minutes	2844680 E 6183940 N	Mix of sand/gravel and silt. **Paint chips evident in sediment**	5m
Site 4: Boat Ramp	06/11/07 @ 1036	+68 minutes	2844760 E 6183780 N	Fine mud/silt with anoxic black colouration	300m
Site 5: Iron Pot	06/11/07 @ 1055	+117 minutes	2845155 E 6184140 N	Fine mud/silt with anoxic black colouration	~600m

2.2 Laboratory Methods

Methodologies for sample analyses are attached with Hill Laboratory Reports of Analysis as Appendix 1.

Figure 1: Location of sampling sites in this survey and initial 2005 survey.

Sites sampled in initial 2005 investigation and this survey

Site One: Marine Club Slipway

Site Two: Commercial Slipway

Site Three: Marine Club Slipway and Maintenance Berth

Site Four: Boat ramp

Site Five: Iron Pot

3.0 RESULTS & DISCUSSION

3.1 Antifoulants

Concentrations of antifouling compounds in sediment samples collected for this survey are presented in Table 4. Full reports of analysis from Hill Laboratories are attached as Appendix 2.

Table 4: Antifoulant concentrations in sediments (all results expressed on a dry weight basis)

	Site 1: Marine Club Slipway		Site 2: Commercial Slipway		Site 3: Marine Club Slipway		Site 4: Boat Ramp		Site 5: Iron Pot	
Survey Year	**2005**	**2007**	**2005**	**2007**	**2005**	**2007**	**2005**	**2007**	**2005**	**2007**
Irgarol (ng/g)	7	5	90	5.0	5	<5	<5	<5	<5	<5
Diuron (ng/g)	630	20	2350	780	34	40	<5	370	<5	<5
Chlorothalonil (ng/g)	6550	240	19500	1200	920	130	<5	390	<5	14
Monobutyltin (ng/g as Sn)	36	51	90	88	62	18	<3	12	<2	10
Dibutyltin (ng/g as Sn)	139	180	250	600	210	73	5	<10	<5	10
Triphenyltin (ng/g as Sn)	<1	47	70	850	8	38	<1	59	<1	43
Tributyltin (ng/g as Sn)	534	370	1130	3500	276	65	11	10	<5	8
2,4'-DDE (ng/g)*	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
2,4'-DDD (ng/g)*	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
2,4'-DDT (ng/g)*	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
4,4'-DDE (ng/g)*	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
4,4'-DDD (ng/g)*	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
4,4'-DDT (ng/g)*	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Total DDT Isomers (ng/g)*	<0.0001	<0.0001	0.0001	0.0001	0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

DDT and isomers normalised to 1% Organic Carbon

3.1.1 Irgarol and Diuron

Irgarol concentrations in sediment show little difference between the 2005 and 2007 surveys with the exception of Site 2. At this site there is a noticeable decrease in the sediment Irgarol concentration where 90 ng/g was recorded in 2005 compared to 5 ng/g in this survey.

Sediment concentrations of Diuron indicate a decrease at Site 1 (630 ng/g in 2005 and 20 ng/g in 2007) and Site 2 (2350 ng/g in 2005 compared to 780 ng/g in 2007) while an increase from <5 ng/g Diuron in 2005 compared to 370 ng/g in 2007 was recorded for Site 4. Site 3 and Site 5 did not indicate any noticeable differences in sediment Diuron concentrations between surveys.

3.1.3 Chlorothalonil

Sediment concentrations of Chlorothalonil indicate a decrease at Site 1 (6550 ng/g in 2005 and 240 ng/g in 2007) Site 2 (19500 ng/g in 2005 compared to 1200 ng/g in 2007) and Site 3 (920 ng/g Chlorothalonil in 2005 to 130 ng/g in 2007). Site 4 shows an increase in sediment Chlorothalonil concentration from <5 ng/g in 2005 to 390 ng/g in 2007, while Site 5 does not indicate any significant differences (<5 ng/g and 14 ng/g) between surveys.

3.1.4 DDT, DDE and DDD

Results for DDT and its degradation products DDE and DDD in this survey are similar to those recorded in the 2005 survey and show sediment concentrations well below ANZECC guideline values when normalised to 1% total organic carbon (see Table 5). These results suggest that there are no adverse effects to the marine ecosystem occurring from DDT contamination of sediments.

Table 5: Comparison of sediment DDT, DDE and DDD concentrations for sites in this survey and the initial 2005 study and to ANZECC (2000) Sediment Quality Guidelines.

Contaminant	ISQG-Low (ng/g) (Trigger value)	ISQG-High (ng/g)
Total DDT*	1.6	46
p.p'-DDE*	2.2	27
o.p'-+ p.p-DDD*	2	20

DDT and isomers normalised to 1% Organic Carbon

3.2 Trace Metals

Concentrations of trace metals in sediment samples collected for this survey and the initial 2005 study are presented in Table 6 and include ANZECC (2000) interim sediment guideline values and suggested mean sediment trace metal concentrations for comparison. Figures 2 – 6 present this data compared to ANZECC (2000) interim sediment guideline values in the form of graphs. A summary of this data is provided below.

Table 6: Comparison of sediment trace metal concentrations for study sites in this survey and ANZECC (2000) Sediment Quality Guidelines and Mean concentrations for Hawke's Bay Estuaries (Strong, 2005) (all results mg/kg dry wt)

Site		Cu mg/kg		Pb mg/kg		As mg/kg		Hg mg/kg		Zn mg/kg	
Survey Year		2005	2007	2005	2007	2005	2007	2005	2007	2005	2007
Site One: Marine Club Slipway		435	170	40.8	41	4.7	5.4	0.11	0.24	227	150
Site Two: Commercial Slipway		1070	1600	230	490	13.3	11	4.02	3.3	689	940
Site Three: Marine Club Slipway and Maintenance Berth		301	280	70.7	38	5.1	5.5	0.12	0.32	129	170
Site Four: Boat ramp		33	82	61.6	28	7	7.3	0.16	0.10	116	540
Site Five: Iron Pot		31.2	61	26.1	190	5.9	8.1	0.08	0.16	184	170
ANZECC	**ISQG-Low**	**65**		**50**		**20**		**0.15**		**200**	
	ISQG-High	**270**		**220**		**70**		**1**		**410**	

Figure 2: Zinc

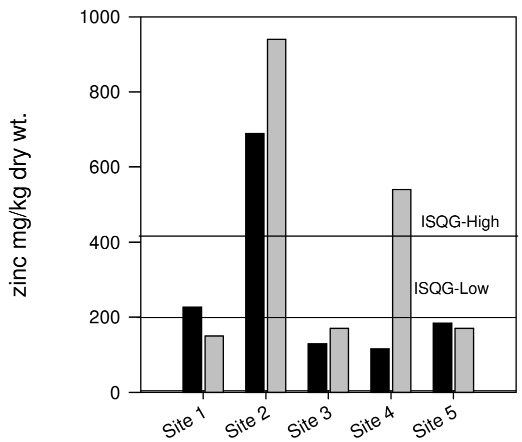


Figure 3: Mercury

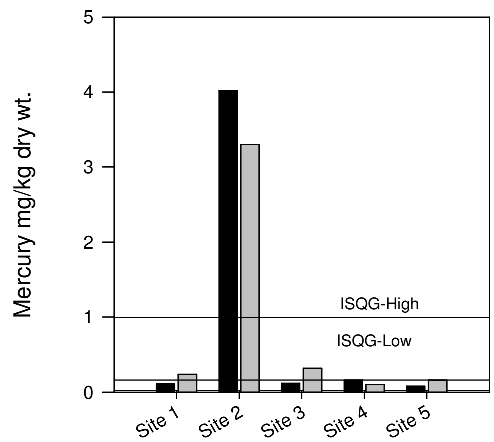


Figure 4: Copper

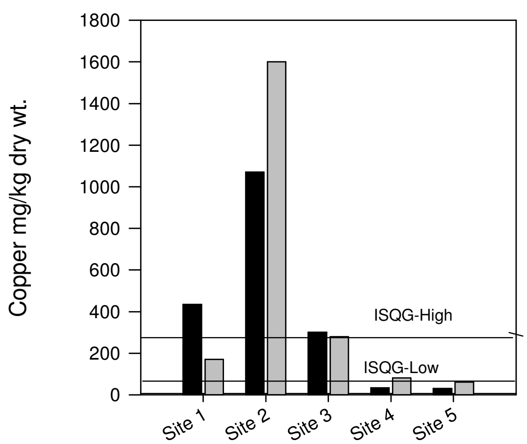


Figure 5: Arsenic

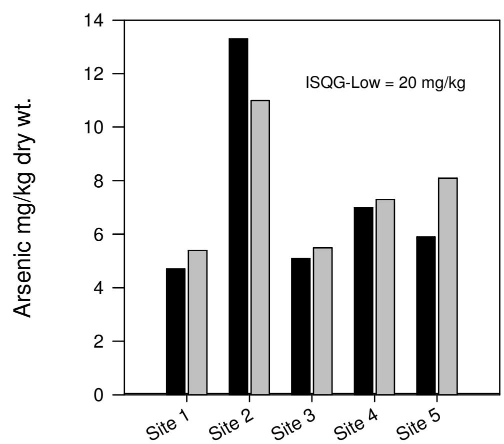
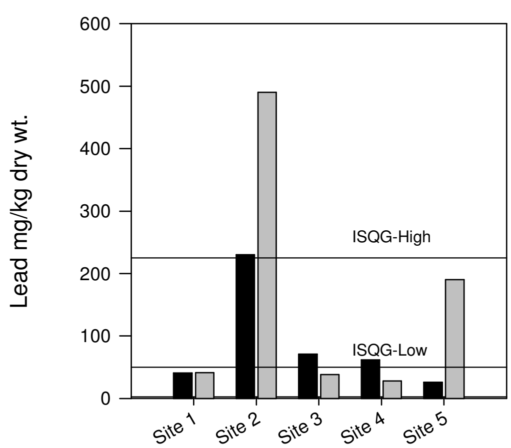
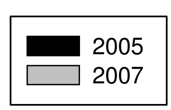


Figure 6: Lead





3.2.1 Summary of Results

Site 1: Sediment trace metal results for this site show a decrease in concentration between surveys for copper (435 mg/kg Cu in 2005 to 170 mg/kg Cu in 2007), and zinc (227 mg/kg Zn in 2005 to 150 mg/kg Zn in 2007). Only mercury shows an appreciable increase in concentration at Site 1 with 0.11 mg/kg Hg recorded in 2005 compared to 0.24 mg/kg Hg in 2007. Compared to ANZECC (2000) Interim Sediment Quality Guidelines, the results for this survey indicate that copper and mercury are above the ISQG-low guideline limit suggesting adverse biological effects could be expected to occur occasionally.

Site 2: This site indicates the greatest contamination with regards to trace metals and shows an increase in concentrations between the initial 2005 survey and the current survey for copper (1070 mg/kg Cu in 2005 to 1600 mg/kg Cu in 2007), lead (230 mg/kg Pb in 2005 to 490 mg/kg Pb in 2007) and zinc (689 mg/kg Pb in 2005 to 940 mg/kg Pb in 2007). Only mercury indicates a noticeable decrease in sediment concentrations with 4.02 mg/kg Hg recorded in 2005 compared to 3.3 mg/kg Hg in this survey. Assessing these results against ANZECC (2000) guidelines the results for this survey indicate exceedances of the ISQG-high limits for Cu, Pb, Hg and Zn and therefore suggest adverse biological effects could be expected to occur frequently.

Site 3: Sediment trace metal results for this site show a decrease in concentration between surveys for lead only with 70.7 mg/kg Pb recorded in 2005 compared to 38 mg/kg Pb in 2007. Only mercury shows an appreciable increase in concentration at Site 3 with 0.12 mg/kg Hg recorded in 2005 compared to 0.32 mg/kg Hg in 2007. Compared to ANZECC (2000) Interim Sediment Quality Guidelines, the results for this survey indicate that copper exceeds the ISQG-high value while mercury is above the ISQG-low guideline limit suggesting adverse biological effects could be expected to occur both frequently in the case of copper, and occasionally for mercury.

Site 4: Sediment trace metal results for this site show noticeable decreases in concentration between surveys for lead with 61.6 mg/kg Pb recorded in 2005 compared to 28 mg/kg Pb in 2007 and mercury with 0.16 mg/kg Hg recorded in 2005 compared to 0.10 mg/kg Hg in 2007. Copper (33 mg/kg Cu in 2005 to 82 mg/kg Cu in 2007), and zinc (116 mg/kg Zn in 2005 to 540 mg/kg Zn in 2007) indicate appreciable increases in trace metal concentrations between surveys. Compared to ANZECC (2000) Interim Sediment Quality Guidelines, the results for this survey indicate that copper exceeds the ISQG-low value while zinc is above the ISQG-high guideline limit suggesting adverse biological effects could be expected to occur both occasionally in the case of copper, and frequently for zinc.

Site 5: This site indicates the least overall contamination with regards to trace metals. An increase in concentrations between the initial 2005 survey and the current survey is evident for copper (31.2 mg/kg Cu in 2005 to 61 mg/kg Cu in 2007), lead (26.1 mg/kg Pb in 2005 to 190 mg/kg Pb in 2007) and mercury (0.08 mg/kg Hg in 2005 to 0.16 mg/kg Hg in 2007). Assessing these results against ANZECC (2000) guidelines the results for this survey indicate exceedances of the ISQG-low limits for Cu and Pb and therefore suggest adverse biological effects could be expected to occur occasionally.

4.0 CONCLUSIONS

The conclusions reached as a result of this study are as follows;

- Sediment concentrations of Irgarol are similar for the 2005 and 2007 surveys with the exception of Site 2. At this site there is a noticeable decrease in the sediment Irgarol concentration where 90 ng/g was recorded in 2005 compared to 5 ng/g in this survey.

- Sediment concentrations of Diuron indicate a decrease at Site 1 (630 ng/g in 2005 and 20 ng/g in 2007) and Site 2 (2350 ng/g in 2005 compared to 780 ng/g in 2007). while an increase from <5 ng/g Diuron in 2005 compared to 370 ng/g in 2007 was recorded for Site 4. Site 3 and Site 5 did not indicate any noticeable differences in sediment Diuron concentrations between surveys.

- Chlorothalonil results indicate a significant decrease at Site 1 (6550 ng/g in 2005 and 240 ng/g in 2007), Site 2 (19500 ng/g in 2005 compared to 1200 ng/g in 2007) and Site 3 (920 ng/g Chlorothalonil in 2005 to 130 ng/g in 2007). Site 4 was the only site to show an increase in sediment Chlorothalonil concentration with <5 ng/g in 2005 compared to 390 ng/g in 2007. Site 5 did not indicate any significant differences (<5 ng/g and 14 ng/g) between surveys.

- Results for DDT and its degradation products DDE and DDD in this survey are similar to those recorded in the 2005 survey and show sediment concentrations well below ANZECC guideline values when normalised to 1% total organic carbon.

- Trace metal results suggest similar sediment concentrations for both the 2005 and 2007 surveys. Decreases were noted for copper (Site1), lead (Site 3 and 4), mercury (Site 2 and 4) and zinc (Site 1). Increases in trace metal concentrations were noted for copper (Site 1, 4 and 5), lead (Site 2 and 5), mercury (Site 1, 3 and 5) and Zn (Site 2 and 4).

- Overall, the results from this survey are similar to those in the 2005 survey which suggest that contaminants arising from boat maintenance activities are not being widely distributed. As suggested in the initial 2005 report, contamination of sediments is largely due to discrete paint particles and is likely to be isolated to the immediate areas surrounding these operations.

5.0 REFERENCES

ANZECC. (2000). National water quality management strategy: Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia.

Auckland Regional Council (2003). Regional Discharges Project Marine Receiving Environment Status Report 2003. Technical Publication 203, prepared for ARC by S, Kelly (ARC) and R.B. Williamson (Diffuse Sources Ltd). ISBN 1-877353-04-3.

EAM, (2005). Antifoulant and Trace Metal Contamination of Sediments from the Napier Inner Harbour. Report prepared for Hawke's Bay Regional Council, by Environmental Assessments and Monitoring Ltd. EMI05/11, HBRC Plan Number 3687.

Madarasz, A.L. (2006). Coastal Monitoring Strategy for Hawke's Bay: 2006-2011. EMI 06/07, HBRC Plan Number 3850.

Stewart, C. (2003). Antifouling co-biocides in New Zealand Coastal Waters. Report prepared for the Ministry for the Environment.

APPENDIX 1 LAB REPORT

CAWTHRON

Laboratory Report

Certificate of Analysis: Final

Cawthron Contract Number: 10345

Project Number: P93652

EAM Ltd
PO Box 1154
NAPIER

Attention: Jason Strong

Email Recipients: Jason Strong,Anna Madarasz-Smith

Sample Details

Laboratory ID: P93652-1 **Sample Type:** Sediment
Description: Site 1 **Date Received:** 08/11/2007 08:00

Analysis	Result	Units	Method
Ash Free Dry Weight	2.9	% w/w	APHA 21st Edn 2540 D+ E (Mod)
PGS: Gravel(>2mm)*	36.5	% w/w	In House Method
PGS: Sands (<2mm & >63μm)*	47.7	% w/w	In House Method
PGS: Silt & Clay (<63μm)*	15.8	% w/w	In House Method

Sample Details

Laboratory ID: P93652-2 **Sample Type:** Sediment
Description: Site 2 **Date Received:** 08/11/2007 08:00

Analysis	Result	Units	Method
Ash Free Dry Weight	4.4	% w/w	APHA 21st Edn 2540 D+ E (Mod)
PGS: Gravel(>2mm)*	18.4	% w/w	In House Method
PGS: Sands (<2mm & >63μm)*	59.5	% w/w	In House Method
PGS: Silt & Clay (<63μm)*	22.1	% w/w	In House Method

Sample Details

Laboratory ID: P93652-3 **Sample Type:** Sediment
Description: Site 3 **Date Received:** 08/11/2007 08:00

Analysis	Result	Units	Method
Ash Free Dry Weight	5.1	% w/w	APHA 21st Edn 2540 D+ E (Mod)
PGS: Gravel(>2mm)*	21.4	% w/w	In House Method
PGS: Sands (<2mm & >63μm)*	41.2	% w/w	In House Method
PGS: Silt & Clay (<63μm)*	37.4	% w/w	In House Method

* Indicates an analysis that is not IANZ accredited

Report Number: 210459
Project Number: P93652
V13.16

Sample Details

Laboratory ID: P93652-4 **Sample Type:** Sediment
Description: Site 4 **Date Received:** 08/11/2007 08:00

Analysis	Result	Units	Method
Ash Free Dry Weight	5.7	% w/w	APHA 21st Edn 2540 D+ E (Mod)
PGS: Gravel(>2mm)*	17.0	% w/w	In House Method
PGS: Sands (<2mm & >63µm)*	51.8	% w/w	In House Method
PGS: Silt & Clay (<63µm)*	31.2	% w/w	In House Method

Sample Details

Laboratory ID: P93652-5 **Sample Type:** Sediment
Description: Site 5 **Date Received:** 08/11/2007 08:00

Analysis	Result	Units	Method
Ash Free Dry Weight	5.9	% w/w	APHA 21st Edn 2540 D+ E (Mod)
PGS: Gravel(>2mm)*	13.8	% w/w	In House Method
PGS: Sands (<2mm & >63µm)*	46.7	% w/w	In House Method
PGS: Silt & Clay (<63µm)*	39.5	% w/w	In House Method

Results apply to samples as received

Our routine detection limits for chemical testing relate to samples with a clean matrix.
Reported detection limits may be higher for individual samples if there is insufficient sample or the matrix is complex.

< means less than, > means greater than

Date Generated: 4/12/07

Authorised by: Chelsea Wellington (LAS)

Position: Senior Technician, Environmental Laboratory

Signature:

* Indicates an analysis that is not IANZ accredited

Report Number: 210459
Project Number: P93652
V13.16

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Web www.hill-labs.co.nz

ANALYSIS REPORT

Client:	Hawkes Bay Regional Council	**Lab No:**	618410 SPv1
Contact:	Madarasz-Smith, Anna	**Date Registered:**	09-Nov-2007
	c/o Hawkes Bay Regional Council	**Date Reported:**	10-Dec-2007
	Private Bag 6006	**Quote No:**	
	Napier	**Order No:**	
		Client Reference:	Marine sediments
		Submitted By:	Madarasz-Smith, Anna

Sample Type: Sediment

Sample Name:		Site 1 Commercial Slipway 06-Nov-2007	Site 2 Marine Club Slipway 06-Nov-2007	Site 3 Maintenance Berth 06-Nov-2007	Site 4 Boat Ramp 06-Nov-2007	Site 5 Iron Pot 06-Nov-2007
Lab Number:		618410.1	618410.2	618410.3	618410.4	618410.5
Heavy metals, trace As,Cd,Cr,Cu,Ni,Pb,Zn,Hg						
Total Recoverable Arsenic	mg/kg dry wt	5.4	11	5.5	7.3	8.1
Total Recoverable Cadmium	mg/kg dry wt	0.069	0.14	0.063	0.19	0.17
Total Recoverable Chromium	mg/kg dry wt	14	43	17	27	28
Total Recoverable Copper	mg/kg dry wt	170	1600	280	82	61
Total Recoverable Lead	mg/kg dry wt	41	490	38	28	190
Total Recoverable Mercury	mg/kg dry wt	0.24	3.3	0.32	0.10	0.16
Total Recoverable Nickel	mg/kg dry wt	11	20	10	13	14
Total Recoverable Zinc	mg/kg dry wt	150	940	170	540	170
Antifouling Co-Biocides in Soil samples by LCMS						
Dry Matter	g/100g as rcvd	74	62	69	60	56
Diuron*	mg/kg dry wt	0.020	0.78	0.040	0.037	< 0.0050
Irgarol*	mg/kg dry wt	0.0050	0.0050	< 0.0050	< 0.0050	< 0.0050
Organochlorine Pesticides Trace in Soil						
Aldrin	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
alpha-BHC	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
beta-BHC	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
delta-BHC	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
gamma-BHC (Lindane)	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
cis-chlordane	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
trans-chlordane	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
2,4'-DDD	mg/kg dry wt	0.021	0.27	< 0.0010	< 0.00072	< 0.0011
4,4'-DDD	mg/kg dry wt	0.049	1.2	0.010	0.0013	< 0.0011
2,4'-DDE	mg/kg dry wt	0.0022	< 0.0011	< 0.0010	< 0.00072	< 0.0011
4,4'-DDE	mg/kg dry wt	0.050	0.13	0.0061	0.0013	< 0.0011
2,4'-DDT	mg/kg dry wt	0.068	0.043	0.0082	0.00081	< 0.0011
4,4'-DDT	mg/kg dry wt	0.33	0.24	0.040	0.0038	< 0.0011
Dieldrin	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Endosulfan I	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Endosulfan II	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Endosulfan sulphate	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Endrin	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Endrin aldehyde	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011

Sample Type: Sediment						
Sample Name:		Site 1 Commercial Slipway 06-Nov-2007	Site 2 Marine Club Slipway 06-Nov-2007	Site 3 Maintenance Berth 06-Nov-2007	Site 4 Boat Ramp 06-Nov-2007	Site 5 Iron Pot 06-Nov-2007
Lab Number:		618410.1	618410.2	618410.3	618410.4	618410.5
Organochlorine Pesticides Trace in Soil						
Endrin Ketone	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Heptachlor	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Heptachlor epoxide	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Hexachlorobenzene	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Methoxychlor	mg/kg dry wt	< 0.00099	< 0.0011	< 0.0010	< 0.00072	< 0.0011
Total Chlordane [(cis+trans)* 100/42]	mg/kg dry wt	< 0.0020	< 0.0020	< 0.0020	< 0.0020	< 0.0020
Organonitro&phosphorus Pesticides Trace in MR Soil by GCMS						
Dry Matter	g/100g as rcvd	74	62	69	60	56
Acetochlor	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Alachlor	mg/kg dry wt	< 0.0060	< 0.0060	< 0.0060	< 0.0063	< 0.0067
Atrazine	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Atrazine-desethyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Atrazine-desisopropyl	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Azaconazole	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Azinphos-methyl	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Benalaxyl	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Bitertanol	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Bromacil	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Bromopropylate	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Butachlor	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Captan	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Carbaryl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Carbofuran	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Chlorfluazuron	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Chlorothalonil	mg/kg dry wt	0.24	1.2	0.13	0.39	< 0.014
Chlorpyrifos	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Chlorpyrifos-methyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Chlortoluron	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Cyanazine	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Cyfluthrin	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Cyhalothrin	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Cypermethrin	mg/kg dry wt	< 0.041	< 0.048	< 0.044	< 0.050	< 0.054
Deltamethrin	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Diazinon	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Dichlofluanid	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Dichloran	mg/kg dry wt	< 0.030	< 0.030	< 0.030	< 0.032	< 0.034
Dichlorvos	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Difenoconazole	mg/kg dry wt	< 0.029	< 0.034	< 0.031	< 0.036	< 0.038
Dimethoate	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Diphenylamine	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Fenpropimorph	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Fluazifop-butyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Fluometuron	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Flusilazole	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Fluvalinate	mg/kg dry wt	< 0.015	< 0.017	< 0.016	< 0.018	< 0.019
Furalaxyl	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Haloxyfop-methyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Hexaconazole	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014

Sample Type: Sediment						
	Sample Name:	Site 1 Commercial Slipway 06-Nov-2007	Site 2 Marine Club Slipway 06-Nov-2007	Site 3 Maintenance Berth 06-Nov-2007	Site 4 Boat Ramp 06-Nov-2007	Site 5 Iron Pot 06-Nov-2007
	Lab Number:	618410.1	618410.2	618410.3	618410.4	618410.5
Organonitro&phosphorus Pesticides Trace in MR Soil by GCMS						
Hexazinone	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
IPBC (3-Iodo-2-propynyl-n-butylcarbamate)	mg/kg dry wt	< 0.051	< 0.060	< 0.055	< 0.063	< 0.067
Iprodione	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Kresoxim-methyl	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Linuron	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Malathion	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Metalaxyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Methamidophos	mg/kg dry wt	< 0.051	< 0.060	< 0.055	< 0.063	< 0.067
Metolachlor	mg/kg dry wt	< 0.0060	< 0.0060	< 0.0060	< 0.0063	< 0.0067
Metribuzin	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Molinate	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Myclobutanil	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Naled	mg/kg dry wt	< 0.051	< 0.060	< 0.055	< 0.063	< 0.067
Norflurazon	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Oxadiazon	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Oxyfluorfen	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Paclobutrazol	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Parathion-ethyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Parathion-methyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Pendimethalin	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Permethrin	mg/kg dry wt	< 0.0072	< 0.0085	< 0.0077	< 0.0089	< 0.0095
Pirimicarb	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Pirimiphos-methyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Prochloraz	mg/kg dry wt	< 0.051	< 0.060	< 0.055	< 0.063	< 0.067
Procymidone	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Prometryn	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Propachlor	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Propanil	mg/kg dry wt	< 0.030	< 0.030	< 0.030	< 0.030	< 0.030
Propazine	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Propiconazole	mg/kg dry wt	< 0.015	< 0.017	< 0.016	< 0.018	< 0.019
Pyriproxyfen	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Quizalofop-ethyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Simazine	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Simetryn	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Sulfentrazone	mg/kg dry wt	< 0.051	< 0.060	< 0.055	< 0.063	< 0.067
TCMTB [2-(thiocyanomethylthio) benzothiazole,Busan]	mg/kg dry wt	< 0.021	< 0.024	< 0.022	< 0.025	< 0.027
Tebuconazole	mg/kg dry wt	< 0.051	< 0.060	< 0.055	< 0.063	< 0.067
Terbacil	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Terbufos	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Terbumeton	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Terbuthylazine	mg/kg dry wt	< 0.0051	< 0.0060	< 0.0055	< 0.0063	< 0.0067
Terbuthylazine-desethyl	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Terbutryn	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Thiabendazole	mg/kg dry wt	< 0.051	< 0.060	< 0.055	< 0.063	< 0.067
Thiobencarb	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Tolylfluanid	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Triazophos	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014

Sample Type: Sediment						
Sample Name:		Site 1 Commercial Slipway 06-Nov-2007	Site 2 Marine Club Slipway 06-Nov-2007	Site 3 Maintenance Berth 06-Nov-2007	Site 4 Boat Ramp 06-Nov-2007	Site 5 Iron Pot 06-Nov-2007
Lab Number:		618410.1	618410.2	618410.3	618410.4	618410.5
Organonitro&phosphorus Pesticides Trace in MR Soil by GCMS						
Trifluralin	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Vinclozolin	mg/kg dry wt	< 0.011	< 0.012	< 0.011	< 0.013	< 0.014
Tributyl Tin Trace in Soil samples by GCMS						
Dry Matter	g/100g as rcvd	74	62	69	60	56
Dibutyltin (as Sn)	mg/kg dry wt	0.18	0.60	0.073	< 0.010	< 0.010
Monobutyltin (as Sn)	mg/kg dry wt	0.051	0.088	0.018	0.012	0.010
Tributyltin (as Sn)	mg/kg dry wt	0.37	3.5	0.065	0.010	0.0080
Triphenyltin (as Sn)	mg/kg dry wt	0.047	0.85	0.038	0.059	0.043

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Sediment			
Test	**Method Description**	**Default Detection Limit**	**Samples**
Environmental Solids Sample Preparation*	Air dried at 35°C and sieved, <2mm fraction.	-	1-5
Heavy metals, trace As,Cd,Cr,Cu,Ni,Pb,Zn,Hg*	Dried sample, <2mm fraction. Nitric/Hydrochloric acid digestion, ICP-MS, trace level.	-	1-5
Antifouling Co-Biocides in Soil samples by LCMS*	Ethylacetate extraction, SPE cleanup, determination by LC-MS.	-	1-5
Organochlorine Pesticides Trace in Soil*	Sonication extraction, SPE cleanup, GPC cleanup (if required), dual column GC-ECD analysis	-	1-5
Organonitro&phosphorus Pesticides Trace in MR Soil by GCMS*	Sonication extraction, GPC cleanup, GC-MS analysis	-	1-5
Tributyl Tin Trace in Soil samples by GCMS*	Solvent extraction, ethylation, SPE cleanup, GC-MS SIM analysis	-	1-5
Dry Matter (Org)	Dried at 103°C (removes 3-5% more water than air dry), gravimetry.	0.10 g/100g as rcvd	1-5
Total Recoverable digestion	Nitric / hydrochloric acid digestion. US EPA 200.2	-	1-5

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Graham Corban MSc Tech (Hons)
Client Services Manager - Environmental Division